Supplementary Information

Photoluminescence of Copper(I) 4,7-Dichloroquinoline Complexes: A Combined Experimental and Theoretical Perspective

Kaíque A. D'Oliveira,[a] Linus P. F. Peixoto,[b] Débora F. M. da Silva,[c] Douglas H. Pereira,[c] Adilson D. da Silva[b] and Alexandre Cuin*[,a]

[a]Laboratório de Química Bioinorgânica, Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora (UFJF), 36036-900 Juiz de Fora-MG, Brazil

[b]Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora (UFJF), 36036-900 Juiz de Fora-MG, Brazil

[c]Instituto Tecnológico de Aeronáutica (ITA), 12228-900 São José dos Campos-SP, Brazil

*e-mail: alexandre.cuin@ufjf.edu.br, alexandre_cuin@yahoo.com

ORCID ID list:
Kaíque A. D'Oliveira: https://orcid.org/0000-0002-2057-0057
Linus P. F. Peixoto: https://orcid.org/0000-0003-2989-1372
Débora F. M. da Silva: https://orcid.org/0009-0008-8630-9848
Douglas H. Pereira: https://orcid.org/0000-0002-7700-4769
Alexandre Cuin: https://orcid.org/0000-0002-5444-5027

ATR-FTIR spectra

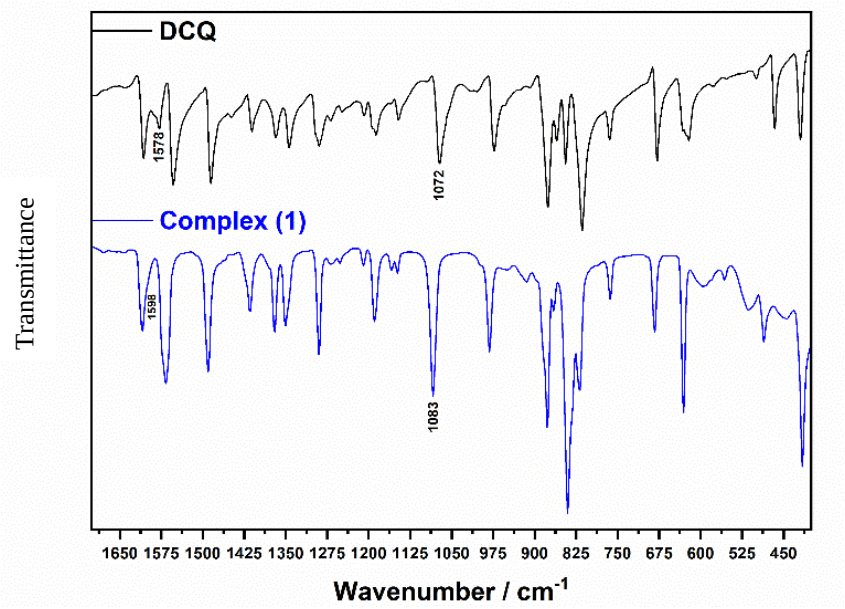


Figure S1. Experimental FTIR (ATR) spectra for complex (**1**) and 4,7-dichloroquinoline (DCQ) ligand, range 1700-400 cm^{-1}.

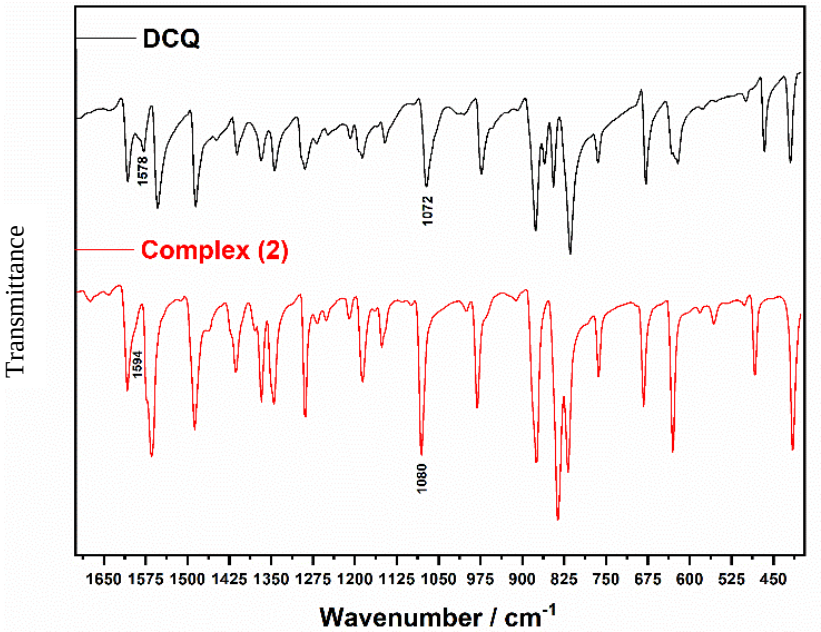


Figure S2. Experimental FTIR (ATR) spectra for complex (**2**) and DCQ ligand, range 1700-400 cm^{-1}.

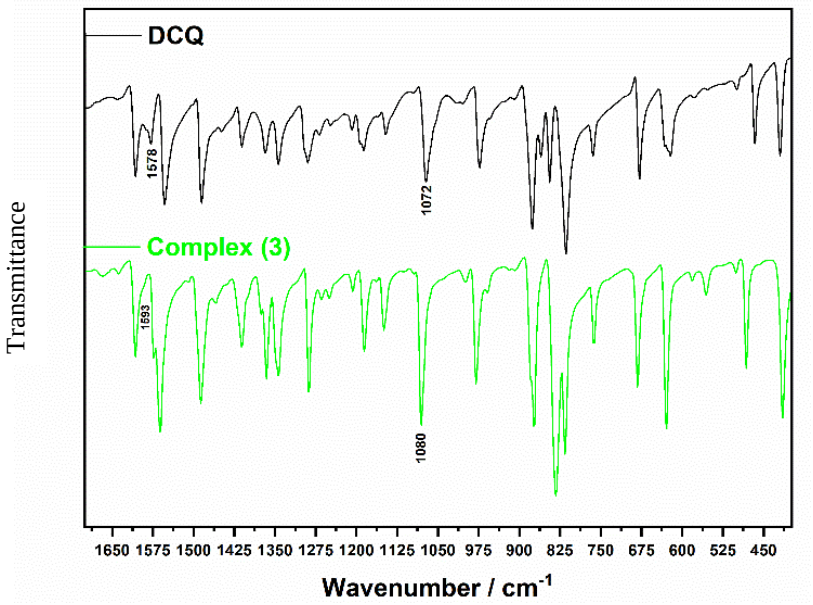


Figure S3. Experimental FTIR (ATR) spectra for complex **3** and DCQ ligand, range 1700-400 cm^{-1}.

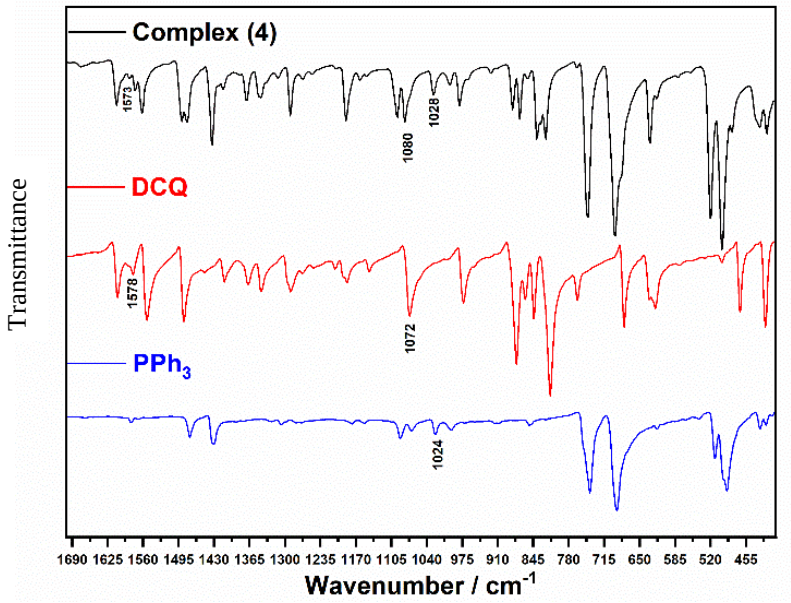


Figure S4. Experimental FTIR (ATR) spectra for complex **4** and DCQ/PPh_3 ligands range 1700-400 cm^{-1}.

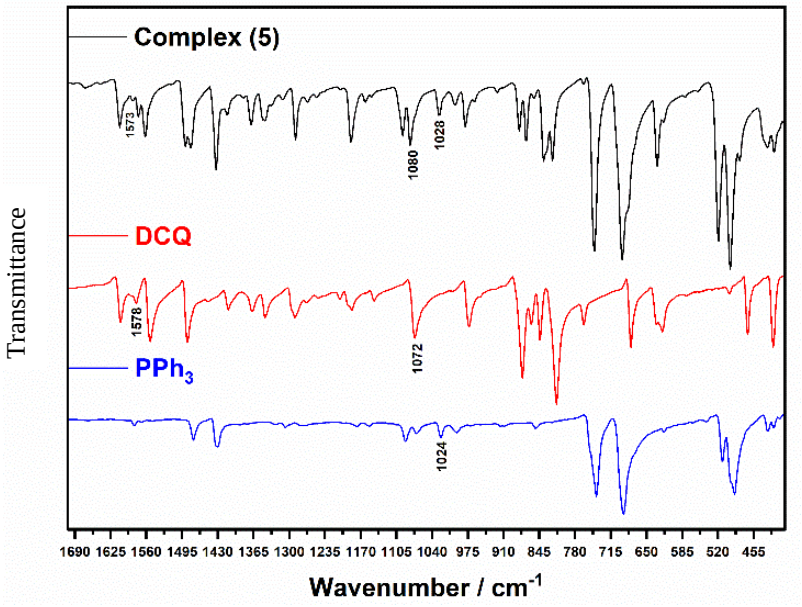


Figure S5. Experimental FTIR (ATR) spectra for complex **5** and DCQ/PPh_3 ligands, range 1700-400 cm^{-1}.

FT-Raman spectra

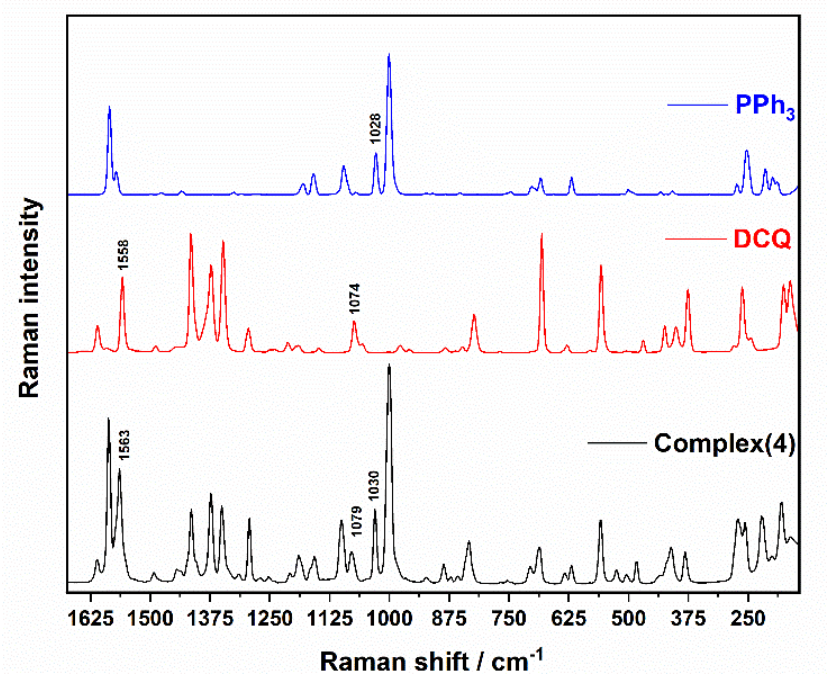


Figure S6. Experimental FT Raman spectra for complex (**4)** and DCQ/PPh_3 ligands, range 1675-145 cm^{-1}.

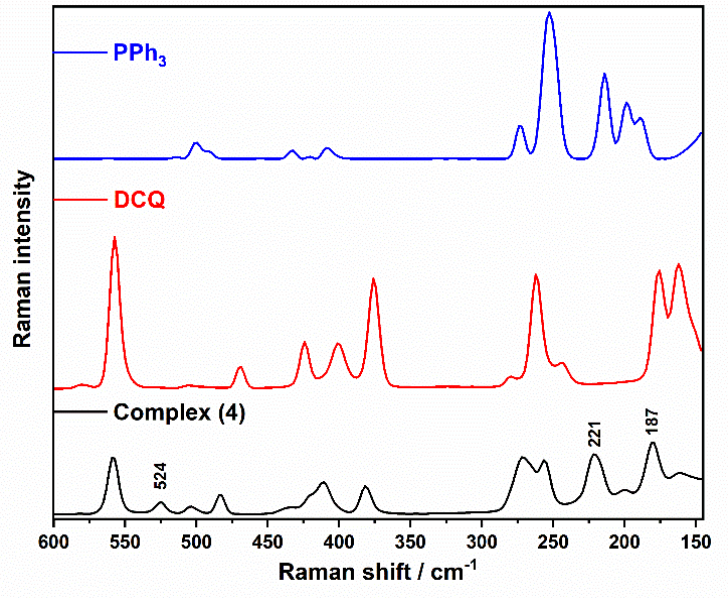


Figure S7. Exp. FT Raman spectra for complex (**4**) and DCQ/PPh_3 ligands range 600-145 cm^{-1}.

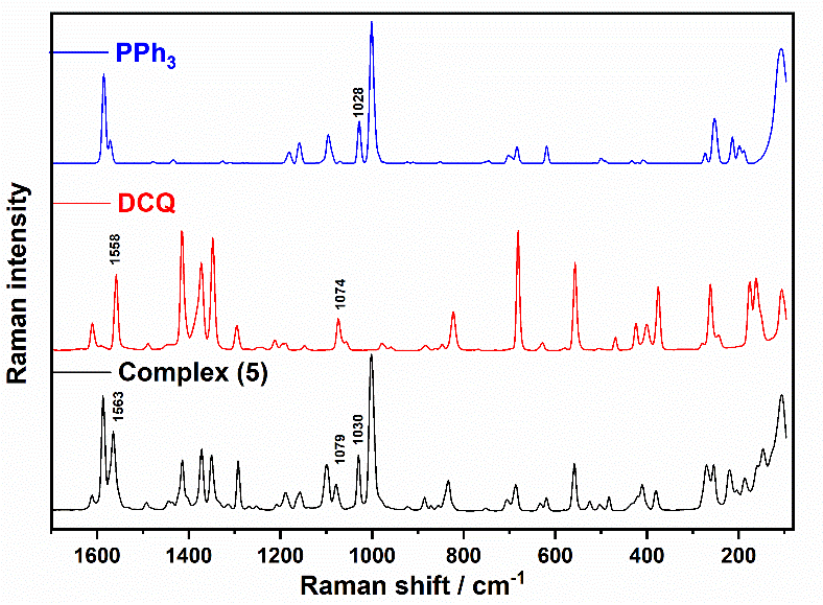


Figure S8. Exp. FT Raman spectra for complex (**5**) and DCQ/PPh_3 ligands, range 1675-145 cm^{-1}.

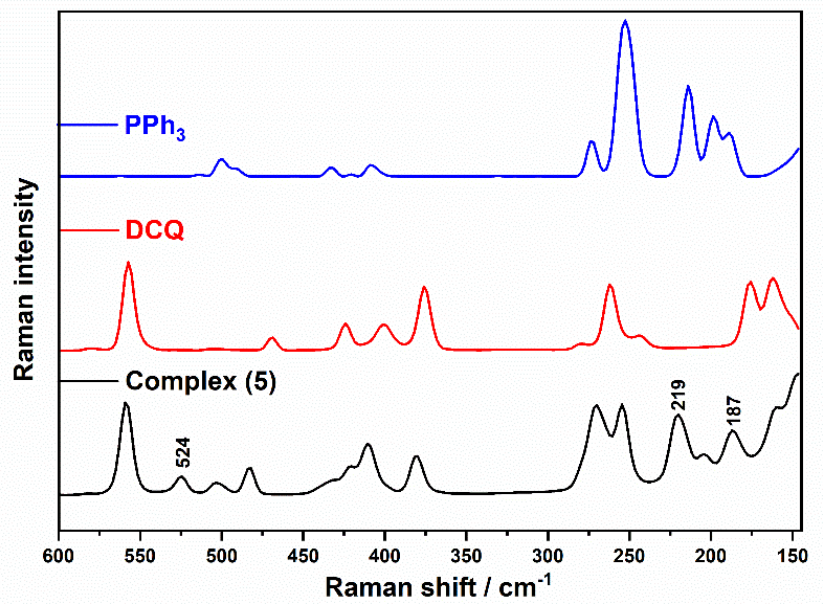


Figure S9. Exp. FT Raman spectra for complex (**5**) and DCQ/PPh_3 ligands range 600-145 cm^{-1}.

Table S1. The main bands observed in the ATR-FTIR and FT Raman spectra and its assignments for DCQ, PPh_3 and complexes (**1-5**)

Compound	ATR-FTIR / cm^{-1}		FT Raman / cm^{-1}				
	$\nu_{(CC+CN)}$	$\tau_{(PPh3)}$	$\nu_{(CC+CN)}$	$\tau_{(PPh3)}$	$\nu_{(CuN)}$	$\nu_{(CuX)}$	$\nu_{(CuP)}$
DCQ	1578	–	1558	–	–	–	–
PPh_3	–	1024	–	1028	–	–	–
1	1598	–	–	–	–	–	–
2	1594	–	–	–	–	–	–
3	1593	–	–	–	–	–	–
4	1573	1028	1563	1030	524	221	187
5	1573	1028	1563	1030	524	219	187

X = Cl for (**4**) and Br for (**5**). ν: stretching and τ: torsion; FTIR: Fourier-transform infrared; ATR: attenuated total reflectance; DCQ: 4,7-dichloroquinoline.

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR (spectra and data)

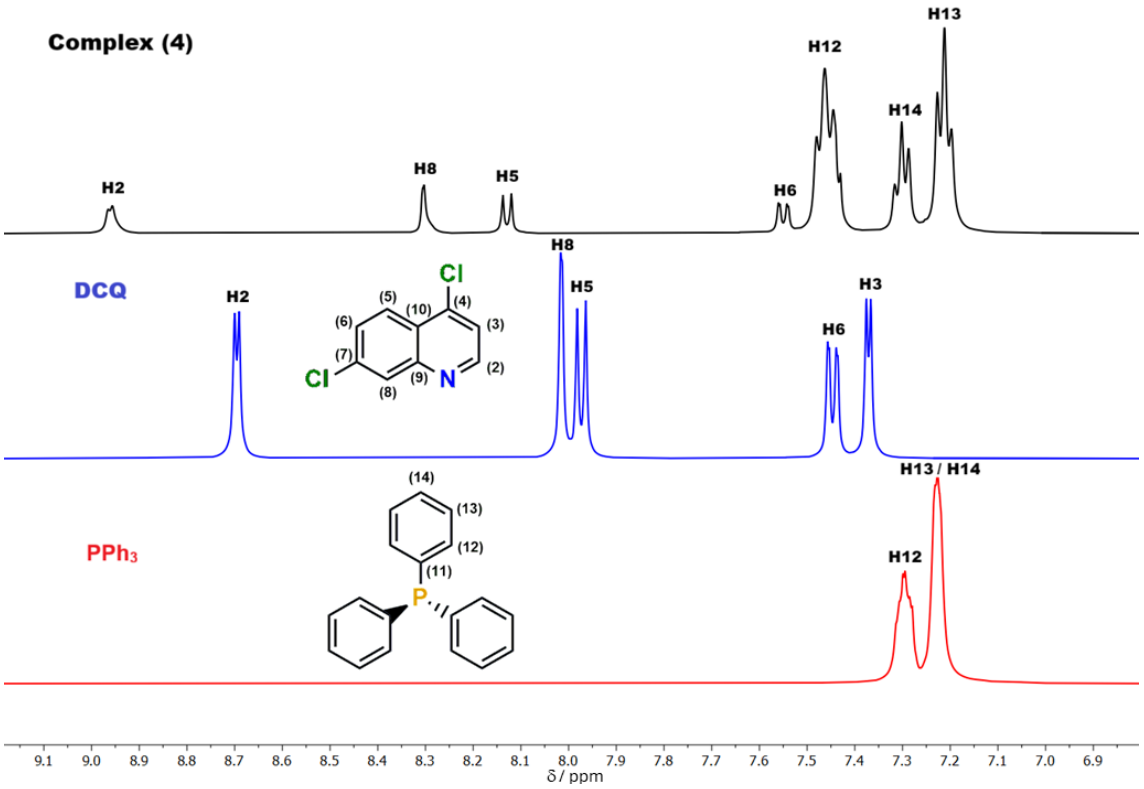


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) for free ligands and complex (**4**).

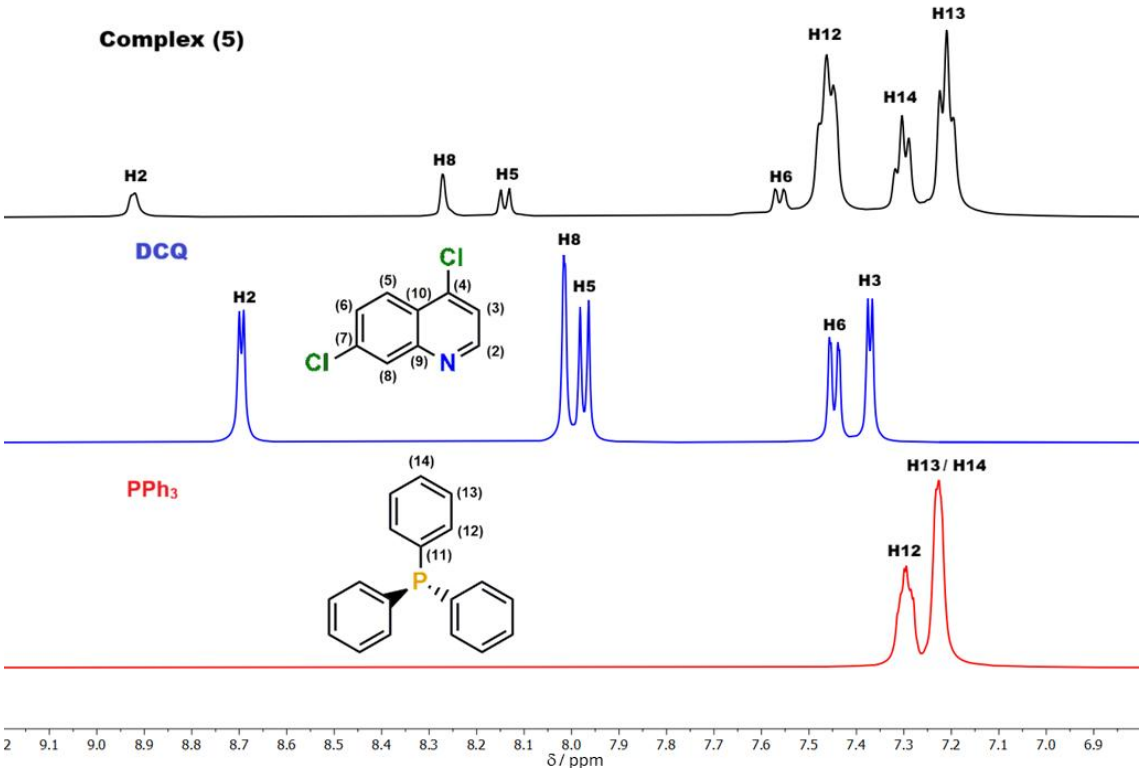


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) for free ligands and complex (**5**).

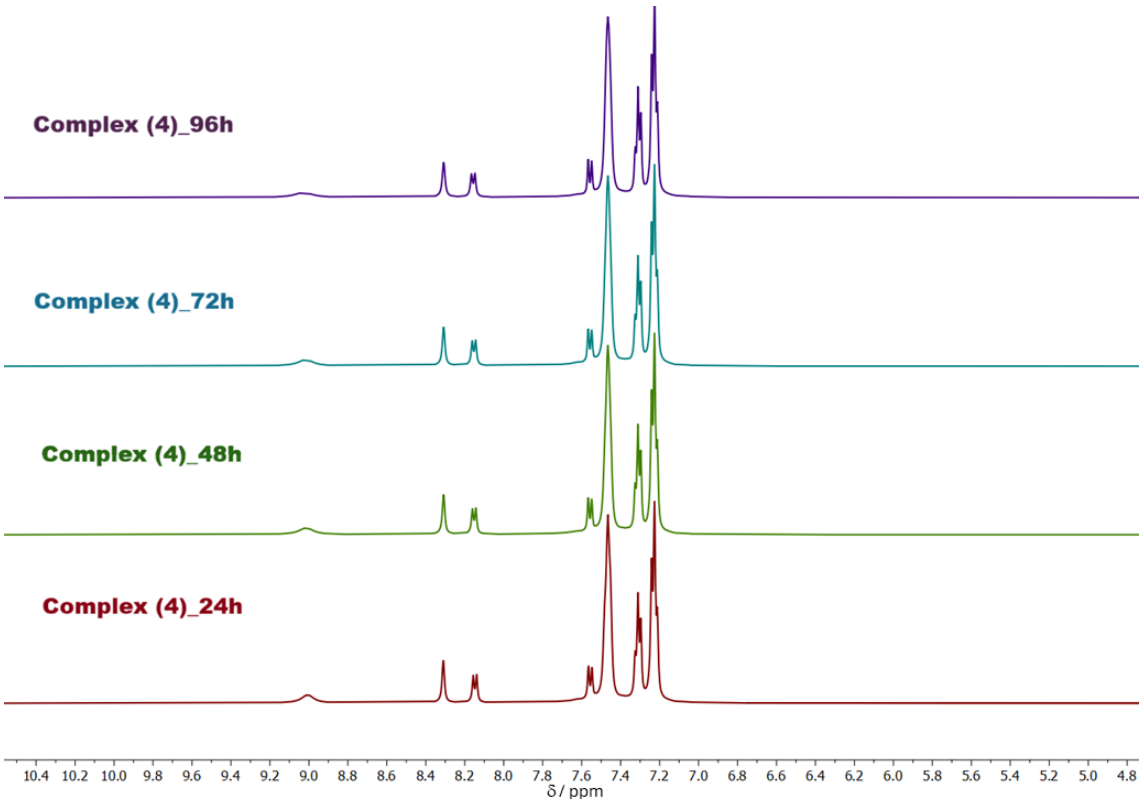


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) over time of complex (**4**).

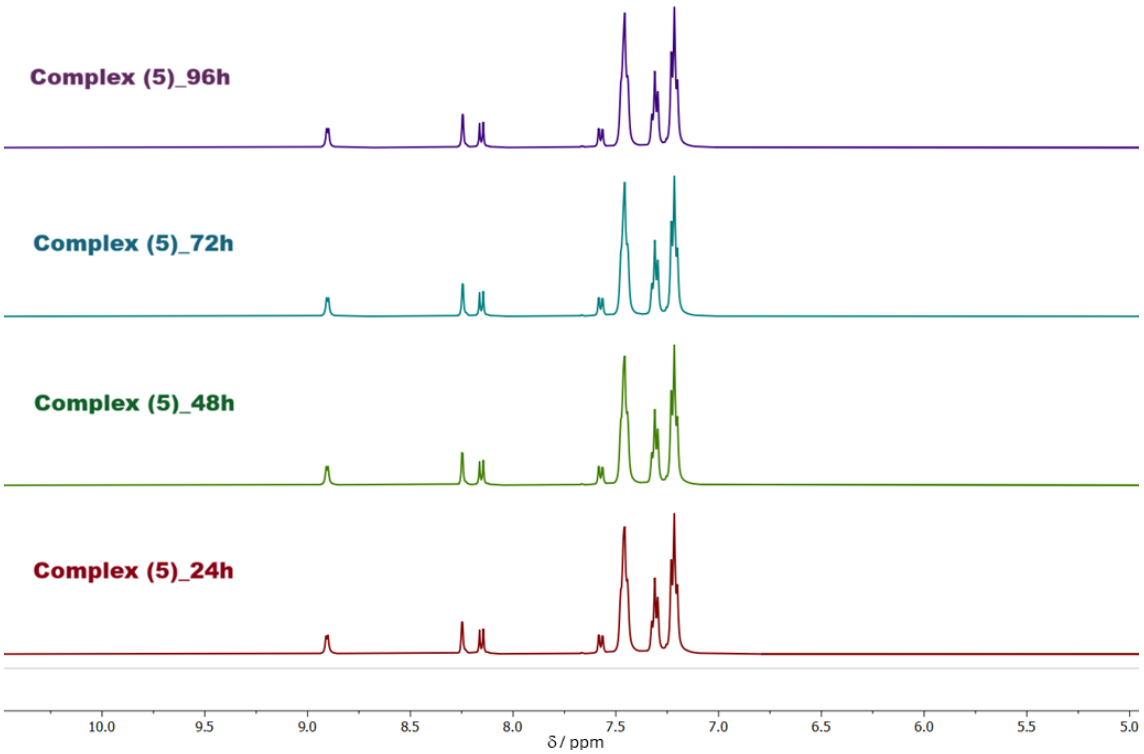


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) over time of complex (**5**).

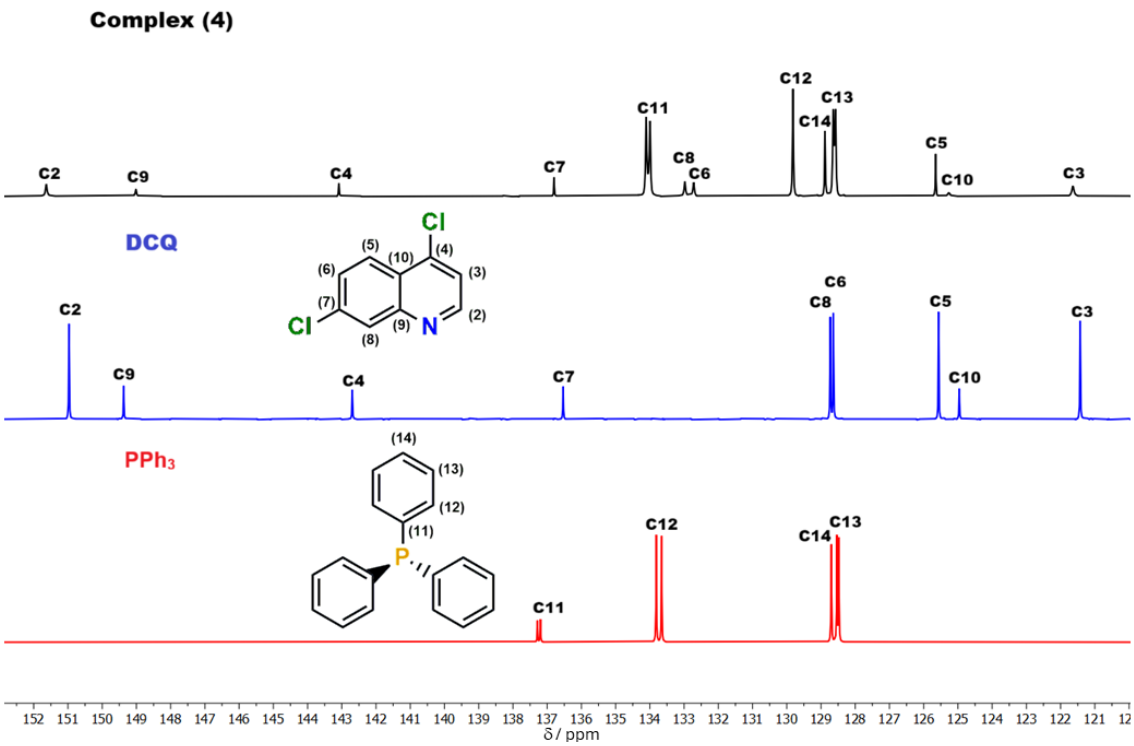


Figure S14. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) for free ligands and their complex (**4**).

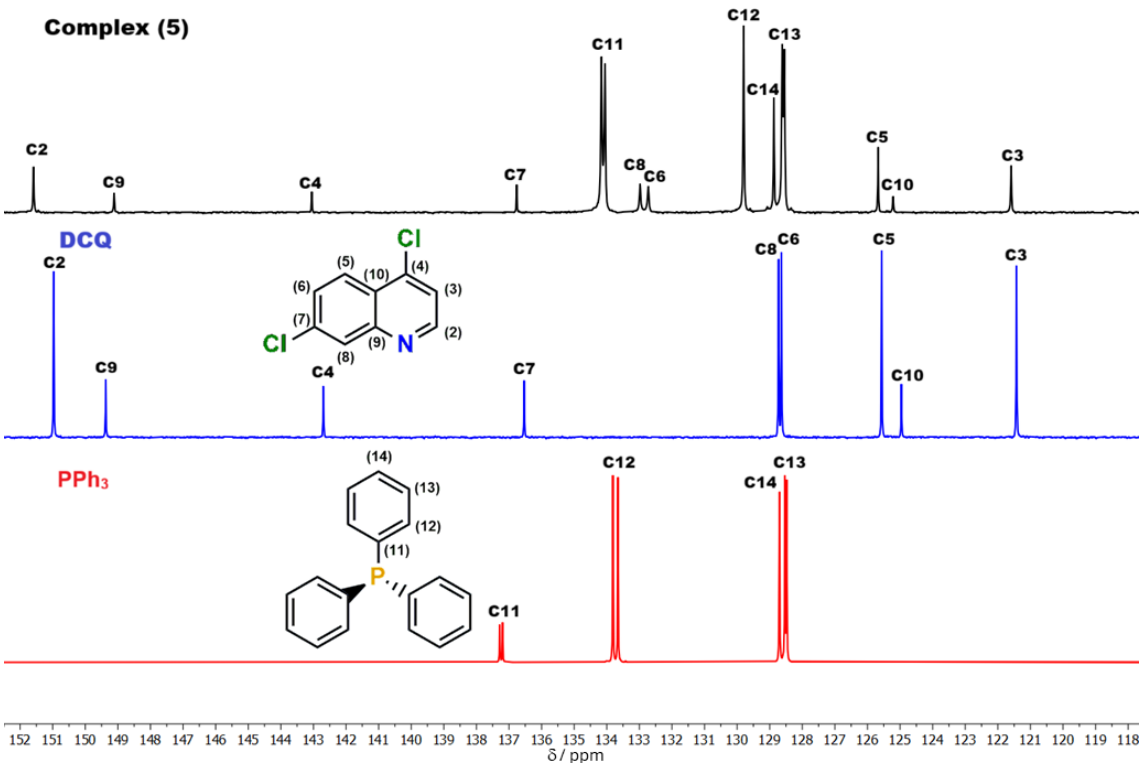


Figure S15. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) for free ligands and their complex (**5**).

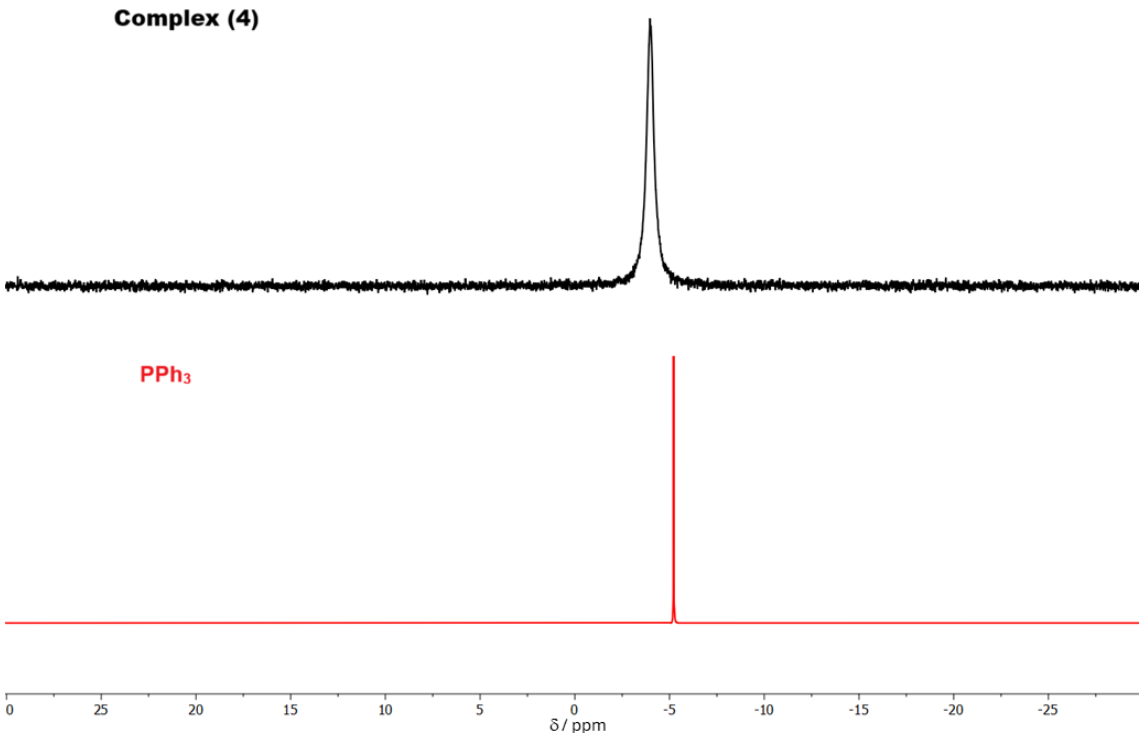


Figure S16. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) for free PPh_3 and complex (**4**).

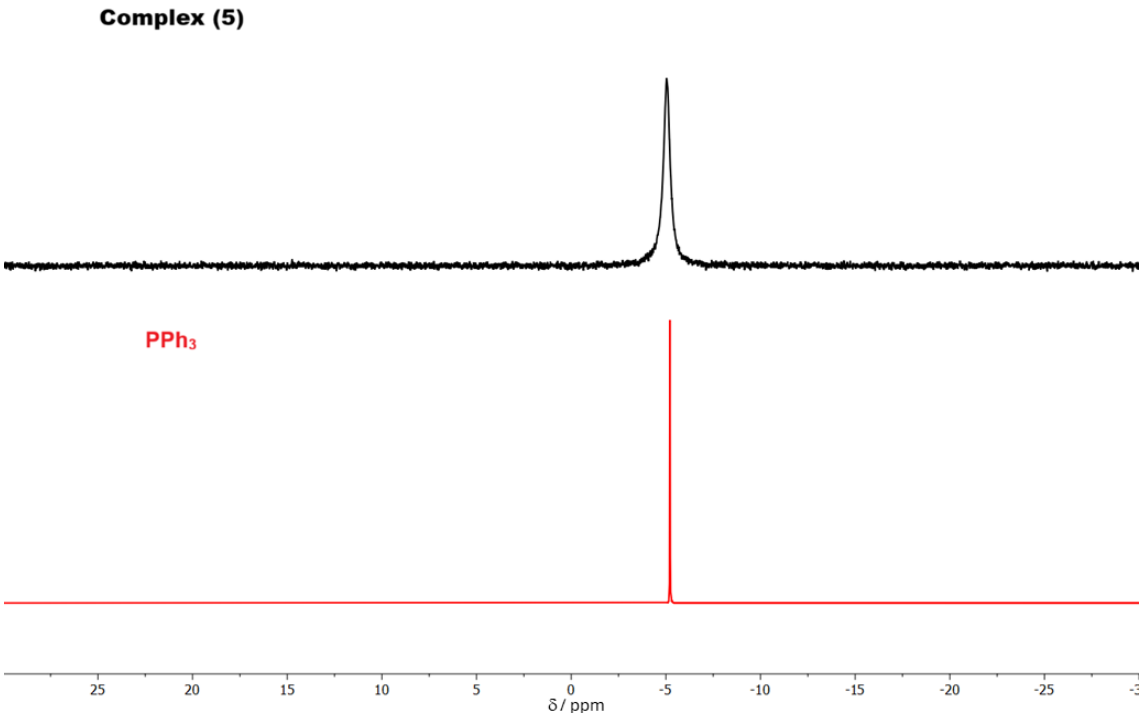


Figure S17. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) for free PPh_3 and complex (**5**).

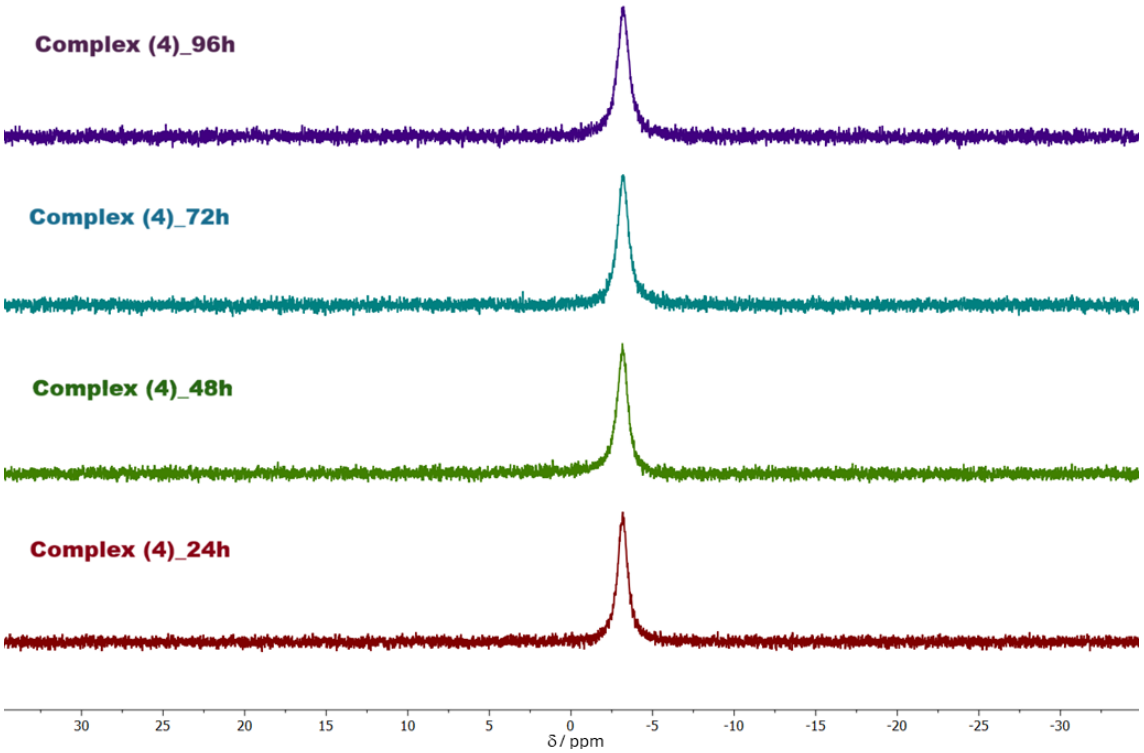


Figure S18. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) over time of complex (**4**).

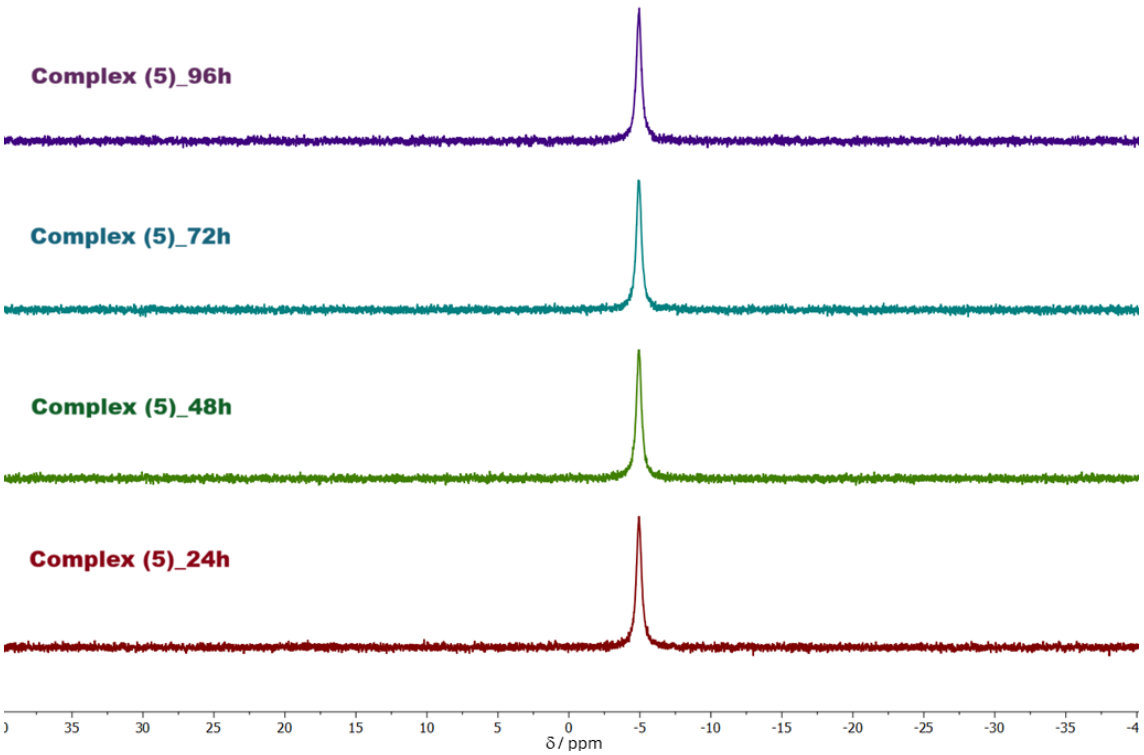


Figure S19. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) over time of complex (**5**).

Table S2. δ values and comparison between shifts and assignments for ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR signals observed in (**4**), DCQ and PPh_3 spectra

δ / ppm					Assignment
(**4**)	DCQ	Δ1	PPh_3	Δ2	
8.96	8.70	0.26	–	–	H(2)
[a]	7.37	–	–	–	H(3)
8.13	7.97	0.16	–	–	H(5)
7.55	7.45	0.10	–	–	H(6)
8.30	8.02	0.28	–	–	H(8)
7.46	–	–	7.30	0.16	H(12)
7.30	–	–	7.23	0.07	H(13)
7.21	–	–	7.23	–0.02	H(14)
151.63	150.97	0.66	–	–	C(2)
121.64	121.43	0.21	–	–	C(3)
143.09	142.69	0.40	–	–	C(4)
125.65	125.56	0.09	–	–	C(5)
128.88	128.64	0.24	–	–	C(6)
136.80	136.53	0.27	–	–	C(7)
128.88	128.73	0.15	–	–	C(8)
149.01	149.37	–0.36	–	–	C(9)
125.27	124.96	0.31	–	–	C(10)
132.85	–	–	137.24	–4.39	C(11)
134.05	–	–	133.73	0.32	C(12)
128.61	–	–	128.51	0.10	C(13)
129.82	–	–	128.70	1.12	C(14)
–3.98	–	–	–5.22	1.24	P

[a]Signal superimposed by the H(12) signal; δ: chemical shift; ppm: parts *per* million; Δ1: difference between the chemical shift (complex) and the chemical shift (DCQ); Δ2: difference between the chemical shift (complex) and the chemical shift (PPh_3).

Table S3. δ values and comparison between shifts and assignments for ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR signals observed in (**5**), DCQ and PPh_3 spectra

δ / ppm					Assignment
(**5**)	DCQ	Δ1	PPh_3	Δ2	
8.92	8.70	0.22	–	–	H(2)
[a]	7.37	–	–	–	H(3)
8.14	7.97	0.17	–	–	H(5)
7.56	7.45	0.11	–	–	H(6)
8.27	8.02	0.25	–	–	H(8)
7.46	–	–	7.30	0.16	H(12)
7.30	–	–	7.23	0.07	H(13)
7.21	–	–	7.23	–0.02	H(14)
151.59	150.97	0.62	–	–	C(2)
121.59	121.43	0.16	–	–	C(3)
143.05	142.69	0.36	–	–	C(4)
125.67	125.56	0.11	–	–	C(5)
128.87	128.64	0.23	–	–	C(6)
136.73	136.53	0.20	–	–	C(7)
128.87	128.73	0.14	–	–	C(8)
149.11	149.37	–0.26	–	–	C(9)
125.21	124.96	0.25	–	–	C(10)
132.83	–	–	137.24	–4.41	C(11)
134.11	–	–	133.73	–0.38	C(12)
128.58	–	–	128.51	0.07	C(13)
129.80	–	–	128.70	1.10	C(14)
–5.05	–	–	–5.22	0.17	P

[a]Signal superimposed by the H12 signal; δ: chemical shift; ppm: parts *per* million; Δ1: difference between the chemical shift (complex) and the chemical shift (DCQ); Δ2: difference between the chemical shift (complex) and the chemical shift (PPh_3).

UV-Vis (spectra and data)

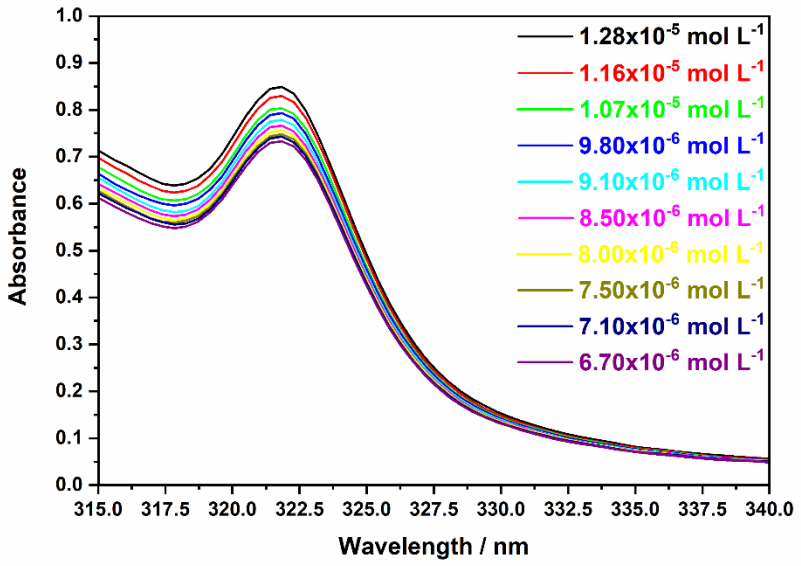


Figure S20. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**4**) in CH_3CN solution.

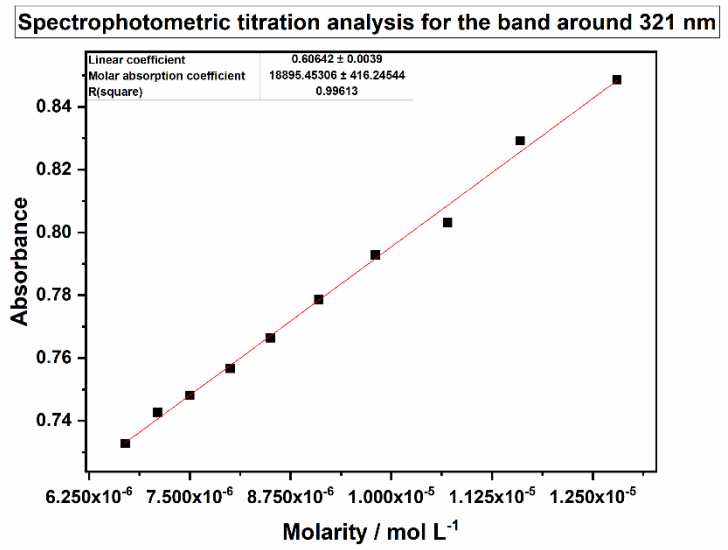


Figure S21. Spectrophotometric titrations analysis for complex (**4**) in CH_3CN solution.

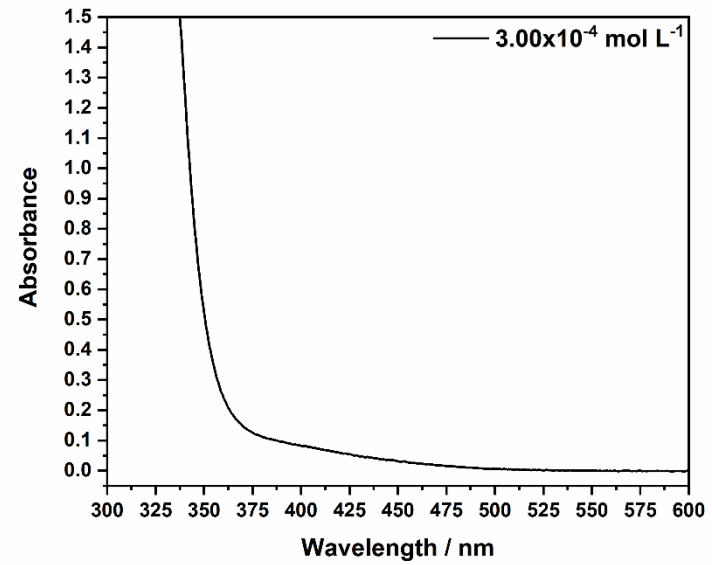


Figure S22. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**4**) in CH_3CN solution.

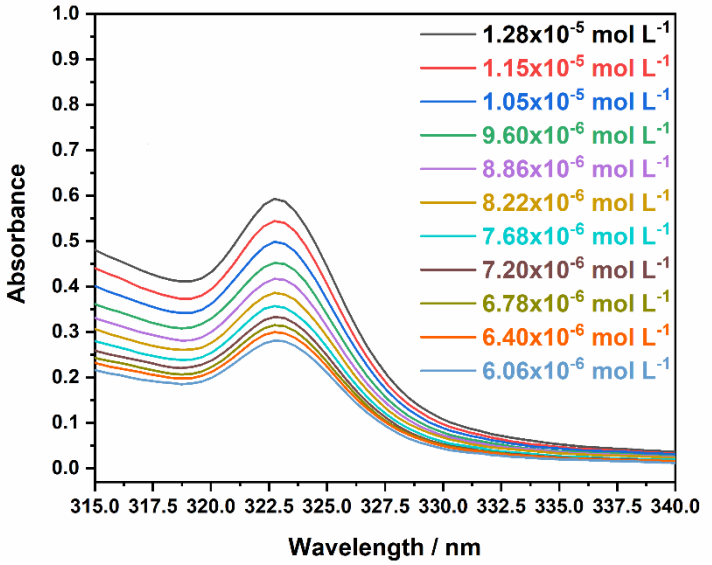


Figure S23. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**4**) in CH_2Cl_2 solution.

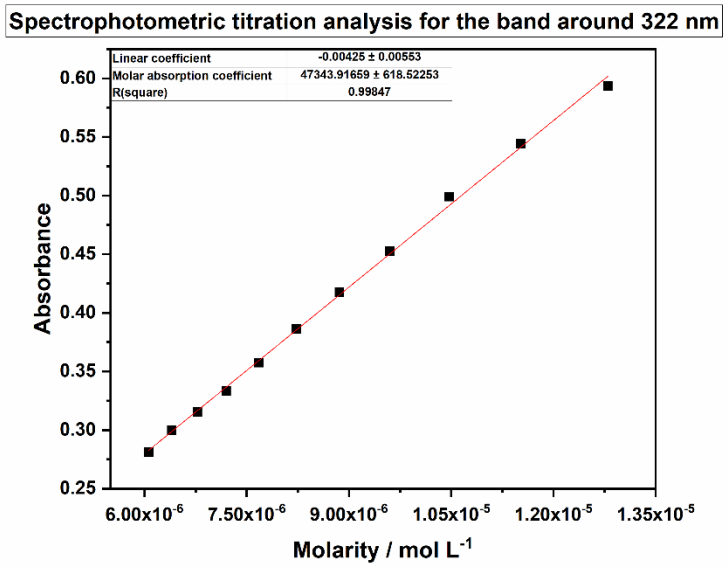


Figure S24. Spectrophotometric titrations analysis for complex **(4)** in CH_2Cl_2 solution.

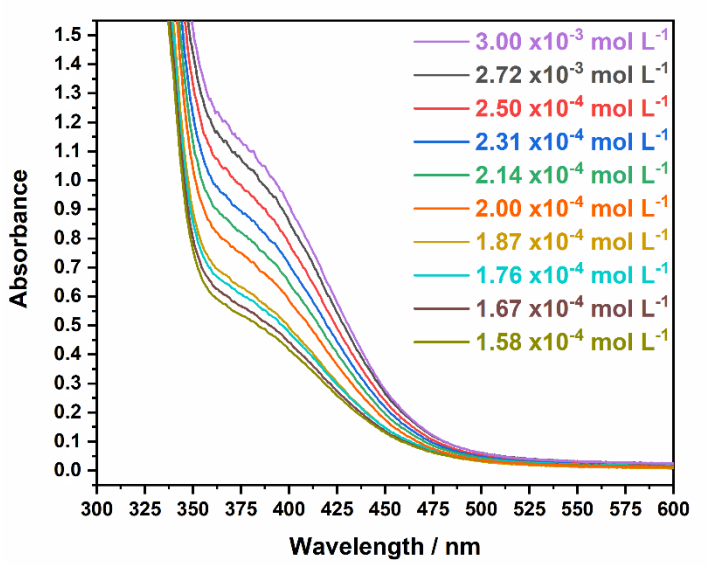


Figure S25. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**4**) in CH_2Cl_2 solution.

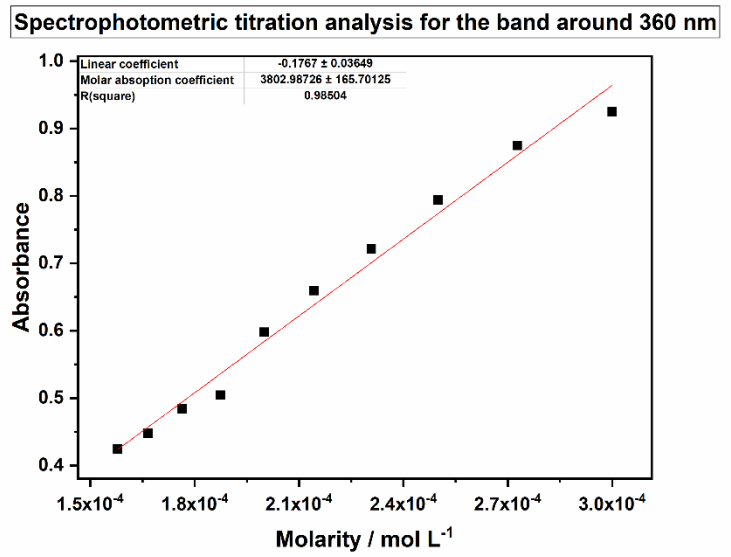


Figure S26. Spectrophotometric titrations analysis for complex (**4**) in CH_2Cl_2 solution.

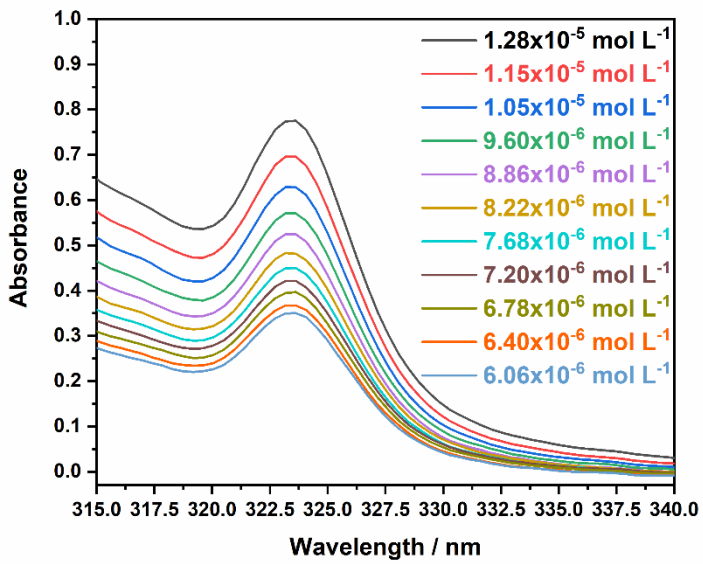


Figure S27. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**4**) in $CHCl_3$ solution.

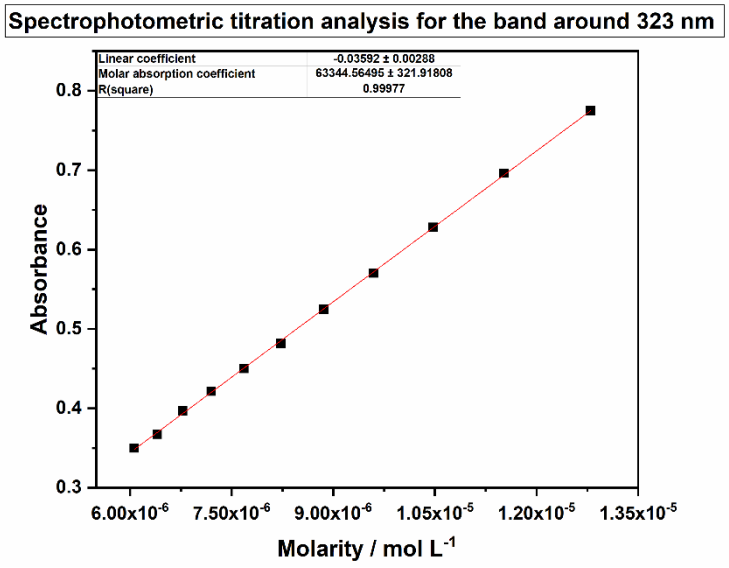


Figure S28. Spectrophotometric titrations analysis for complex **(4)** in $CHCl_3$ solution.

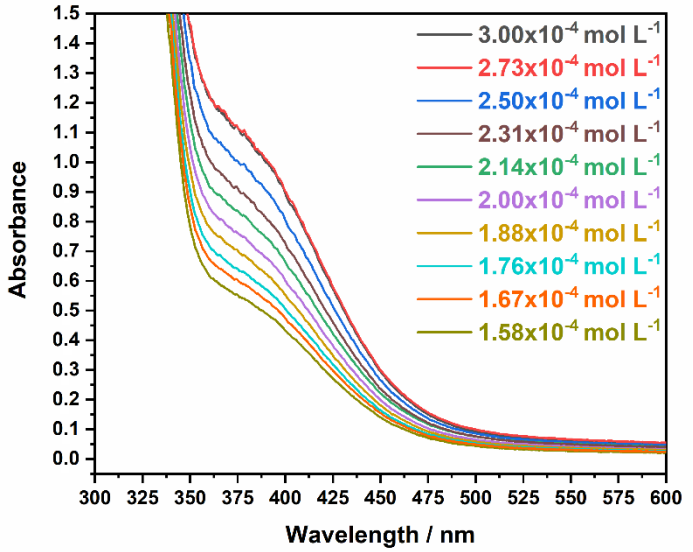


Figure S29. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**4**) in $CHCl_3$ solution.

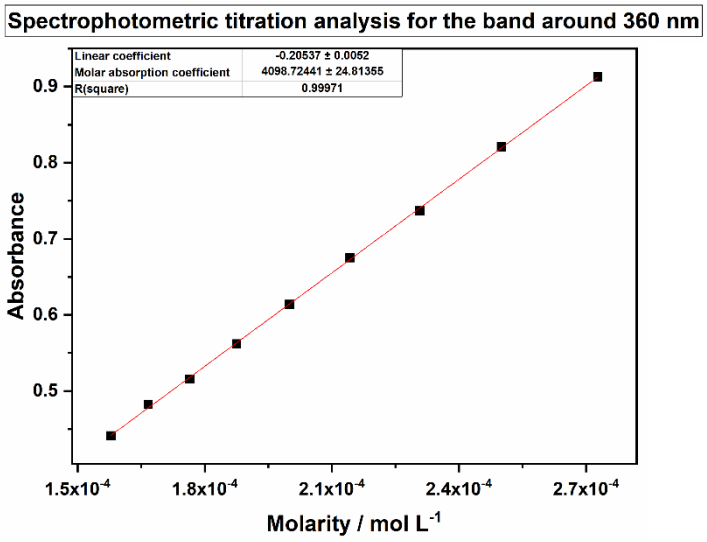


Figure S30. Spectrophotometric titrations analysis for complex (**4**) in $CHCl_3$ solution.

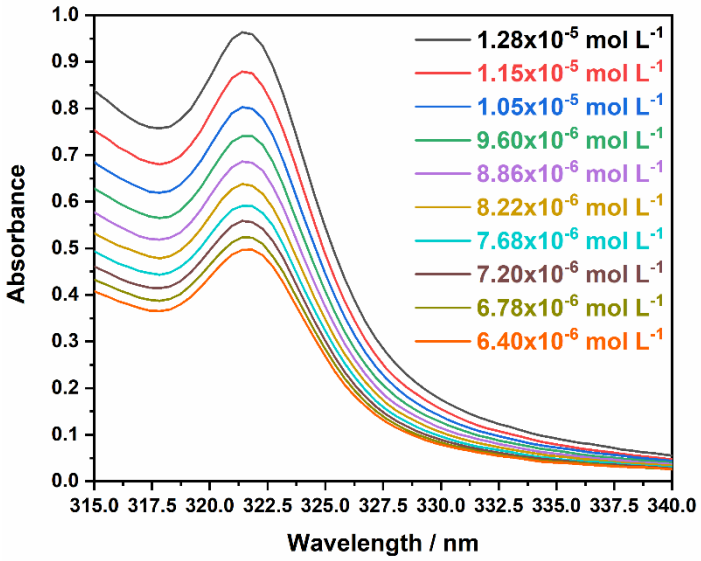


Figure S31. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**5**) in CH_3CN.

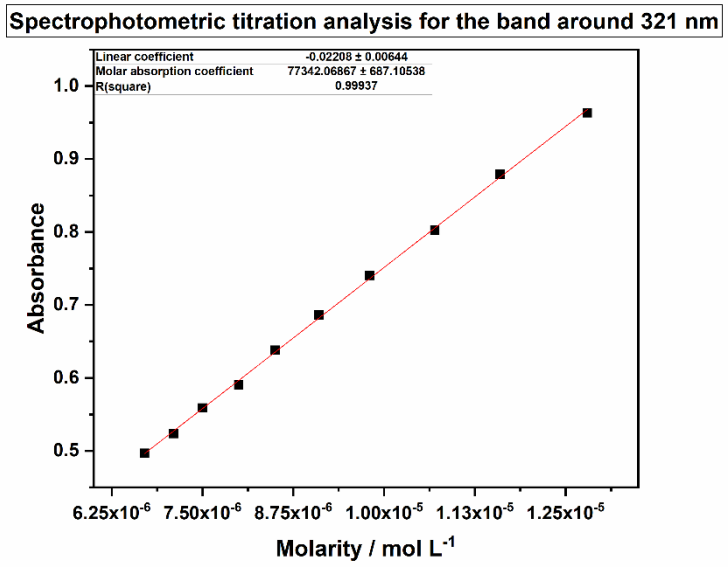


Figure S32. Spectrophotometric titrations analysis for complex (**5**) in CH_3CN solution.

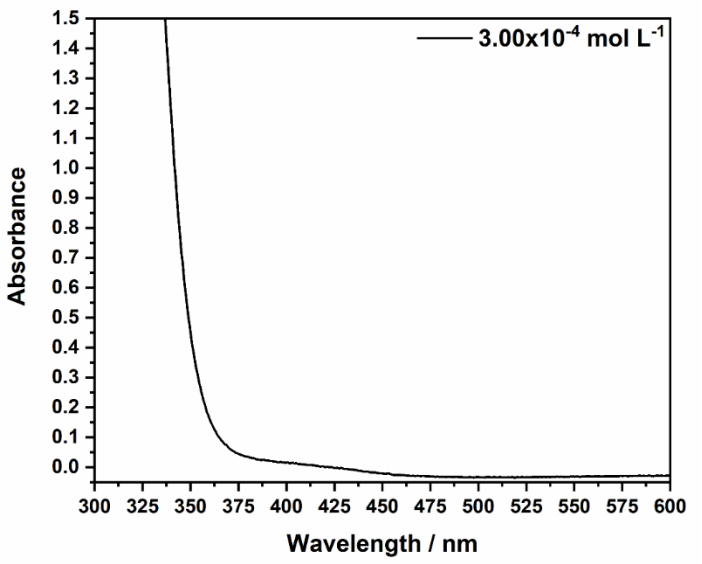


Figure S33. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**5**) in CH_3CN.

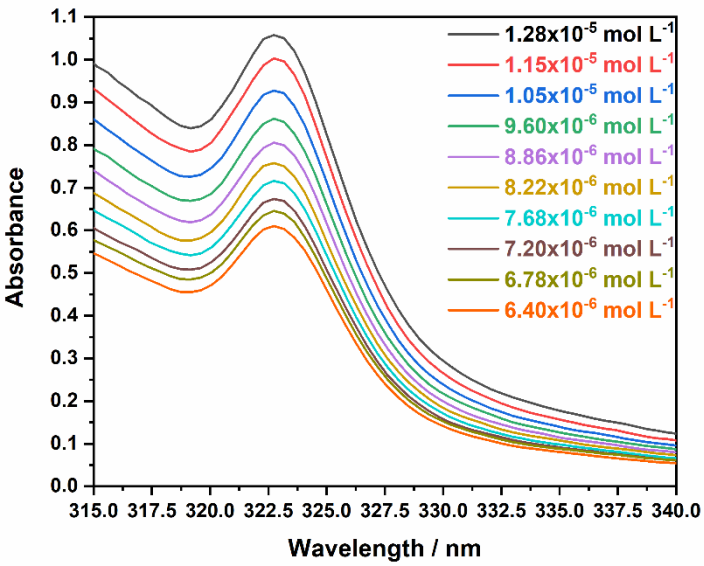


Figure S34. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**5**) in CH_2Cl_2 solution.

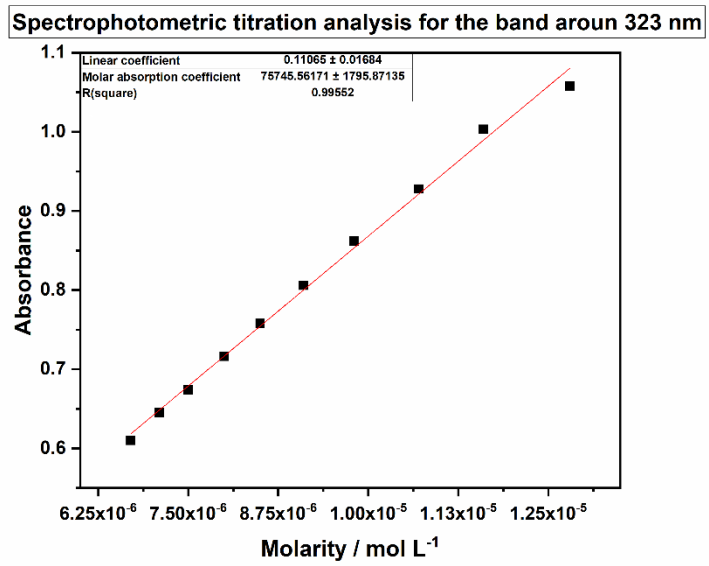


Figure S35. Spectrophotometric titrations analysis for complex (**5**) in CH_2Cl_2 solution.

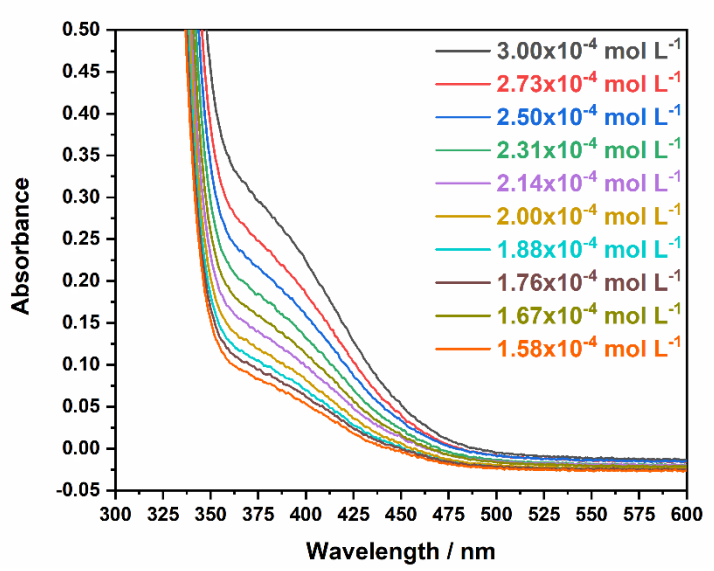


Figure S36. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**5**) in CH_2Cl_2 solution.

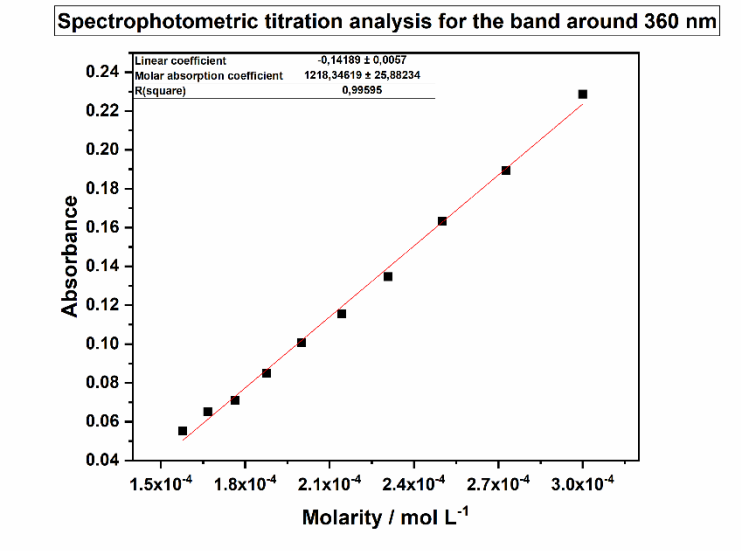


Figure S37. Spectrophotometric titrations analysis for complex (**5**) in CH_2Cl_2 solution.

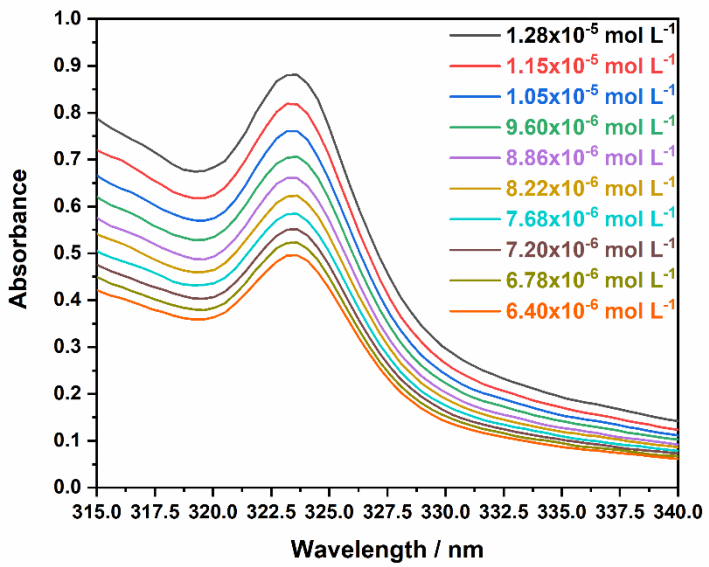


Figure S38. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**5**) in $CHCl_3$ solution.

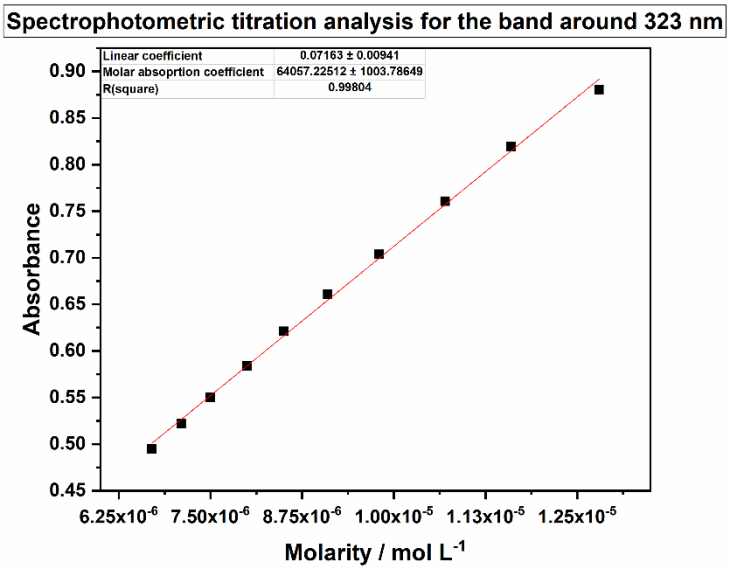


Figure S39. Spectrophotometric titrations analysis for complex (**5**) in $CHCl_3$ solution.

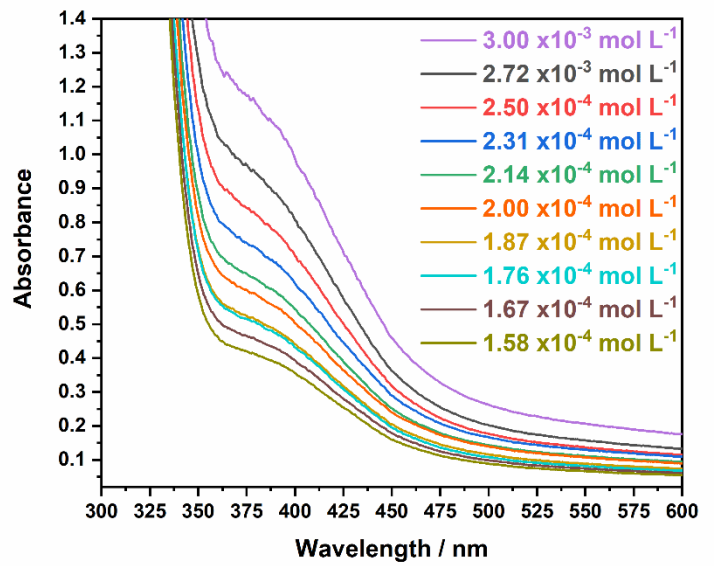


Figure S40. Spectrophotometric titrations and experimental UV-Vis spectra for complex (**5**) in $CHCl_3$ solution.

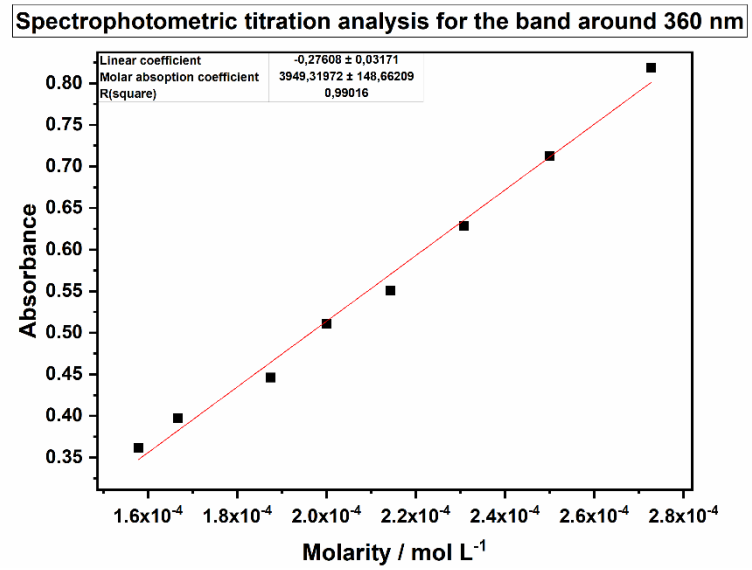


Figure S41. Spectrophotometric titrations analysis for complex (**5**) in $CHCl_3$ solution.

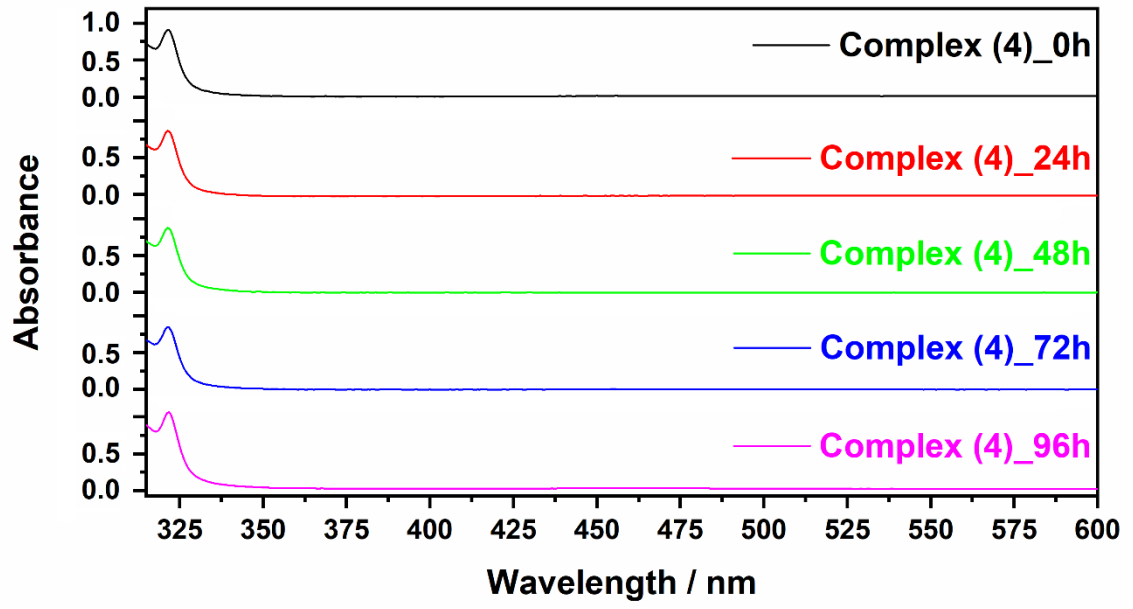


Figure S42. Experimental UV-Vis spectra over time for complex (**4**) in CH_3CN solution.

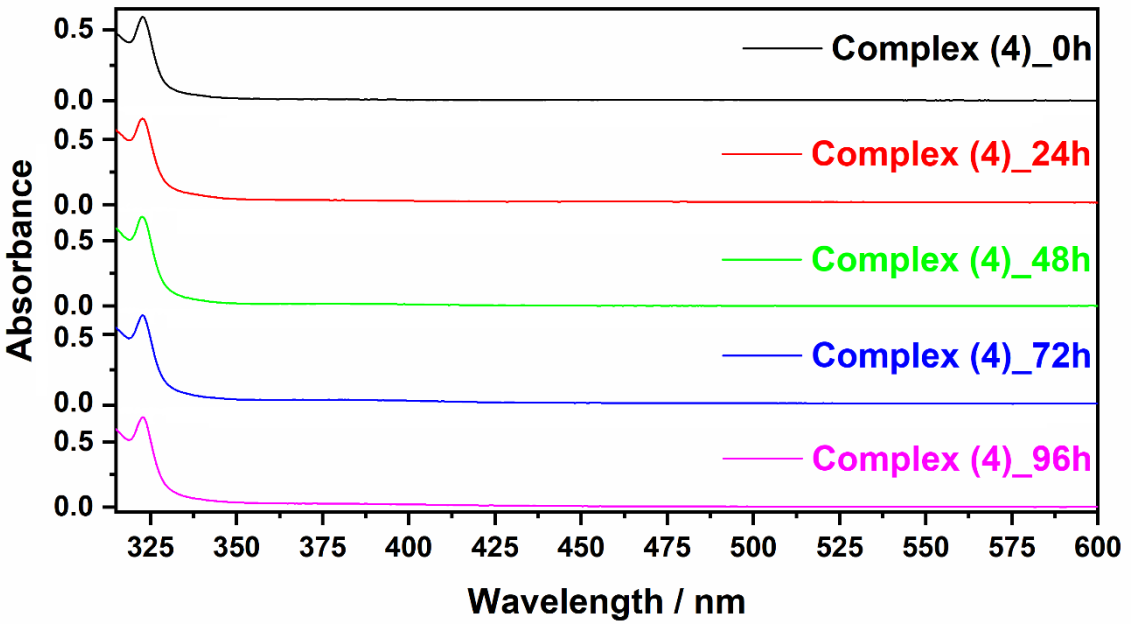


Figure S43. Experimental UV-Vis spectra over time for complex (**4**) in CH_2Cl_2 solution.

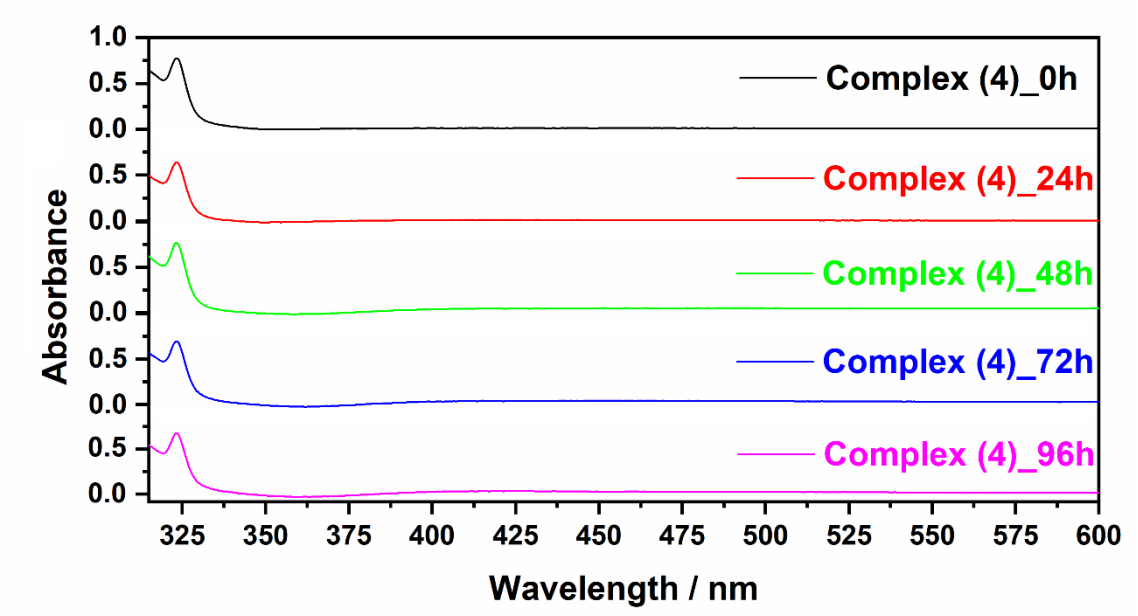


Figure S44. Experimental UV-Vis spectra over time for complex (**4**) in $CHCl_3$ solution.

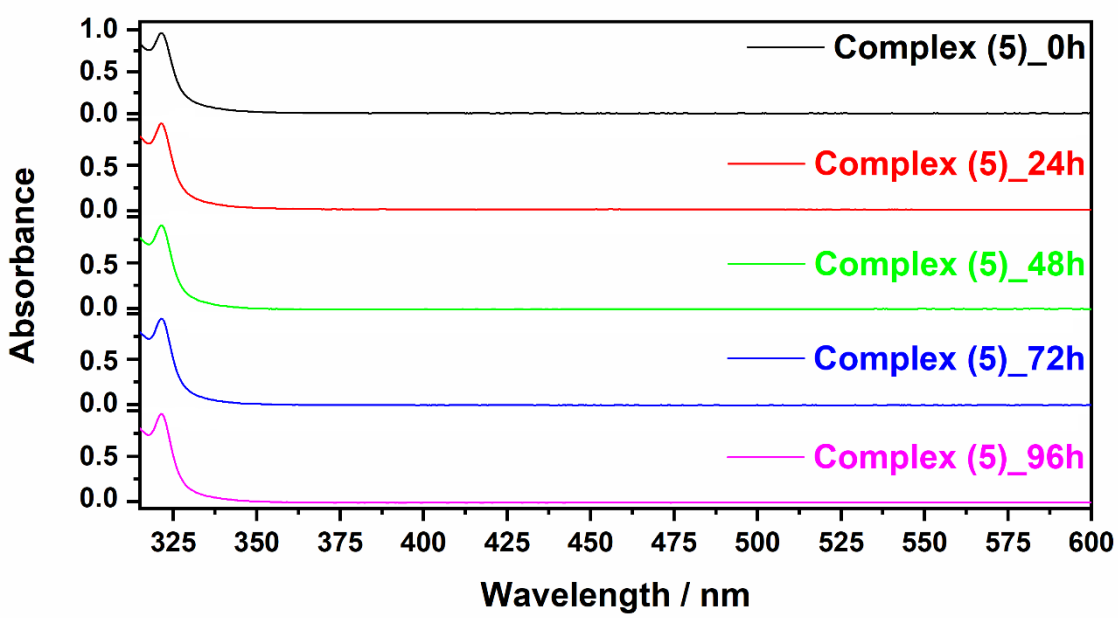


Figure S45. Experimental UV-Vis spectra over time for complex (**5**) in CH_3CN solution.

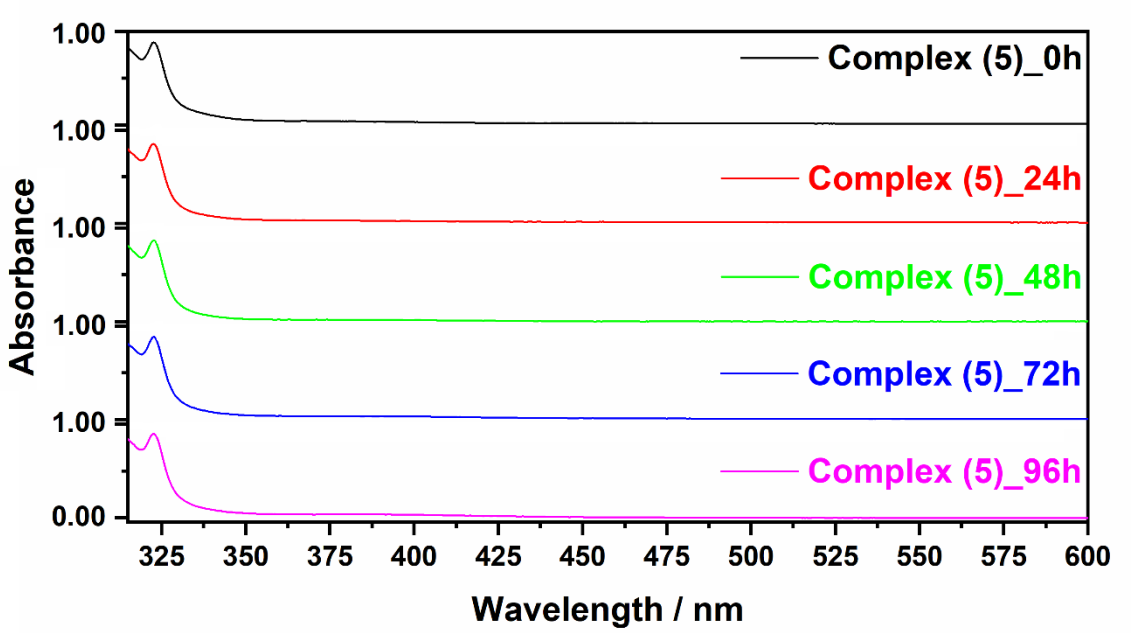


Figure S46. Experimental UV-Vis spectra over time for complex (**5**) in CH_2Cl_2 solution.

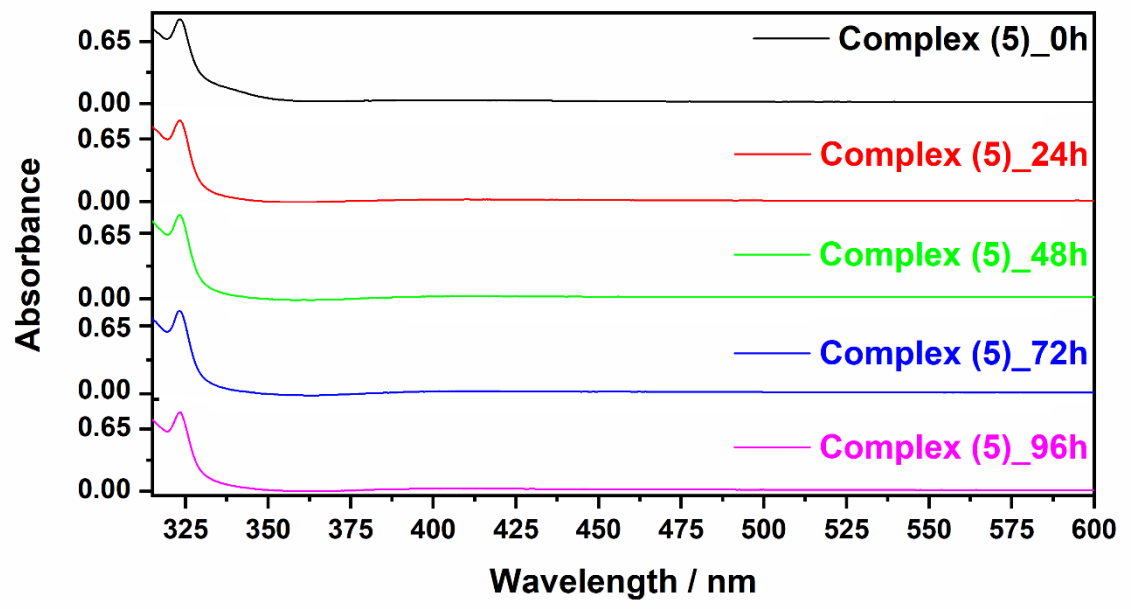


Figure S47. Experimental UV-Vis spectra over time for complex (**5**) in $CHCl_3$ solution.

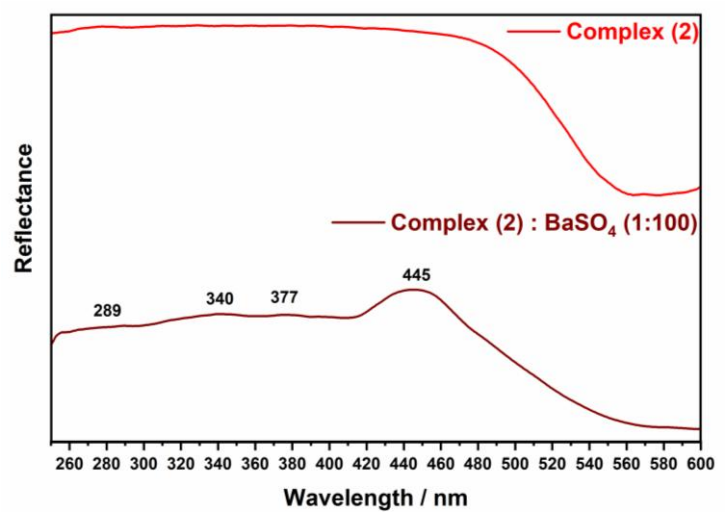


Figure S48. Experimental diffuse reflectance UV-Vis spectra for complex (**2**).

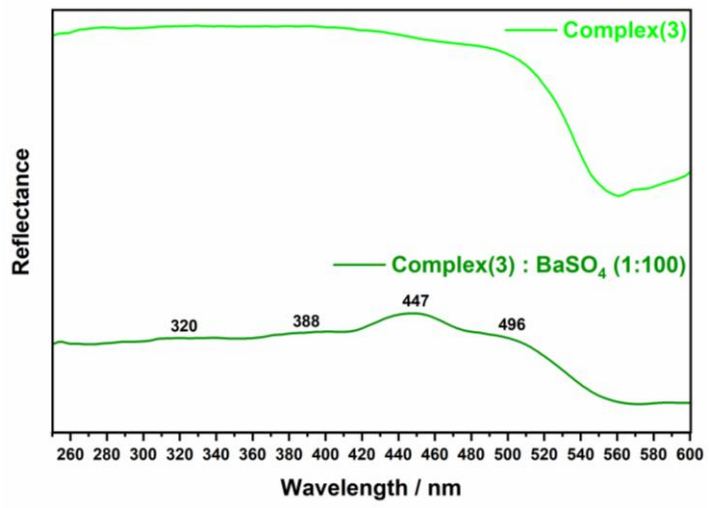


Figure S49. Experimental diffuse reflectance UV-Vis spectra for complex (**3**).

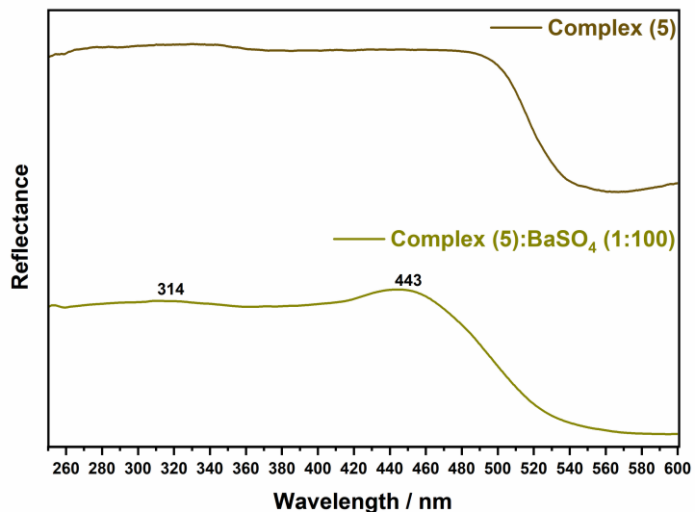


Figure S50. Experimental diffuse reflectance UV-Vis spectra for complex (**5**).

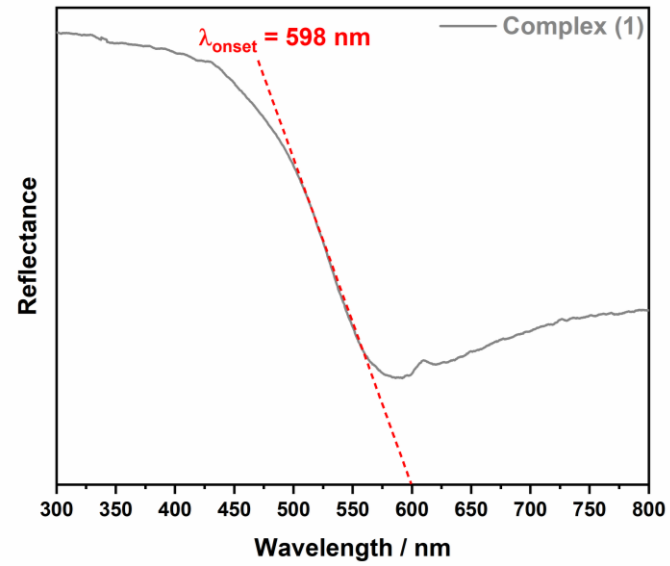


Figure S51. Diffuse reflectance UV-Vis spectrum of complex (**1**).

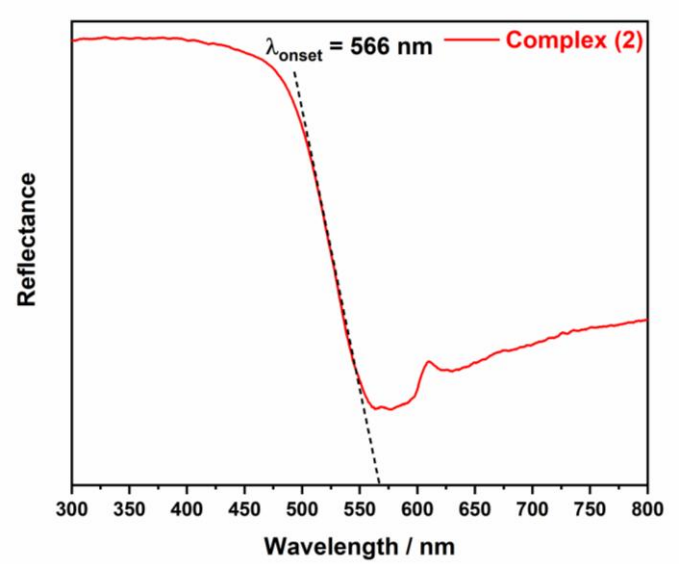


Figure S52. Diffuse reflectance UV-Vis spectrum of complex (**2**).

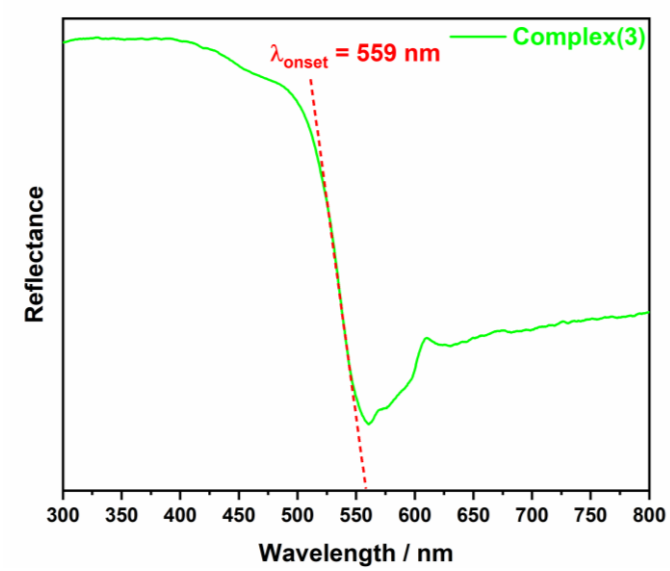


Figure S53. Diffuse reflectance UV-Vis spectrum of complex (**3**).

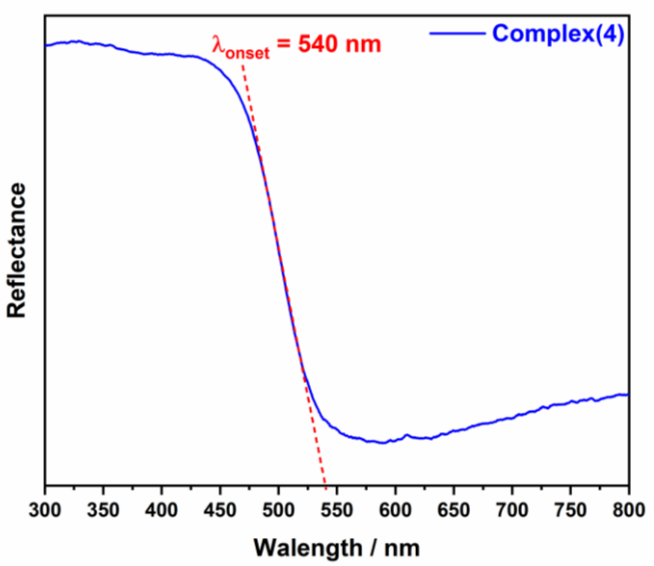


Figure S54. Diffuse reflectance UV-Vis spectrum of complex (**4**).

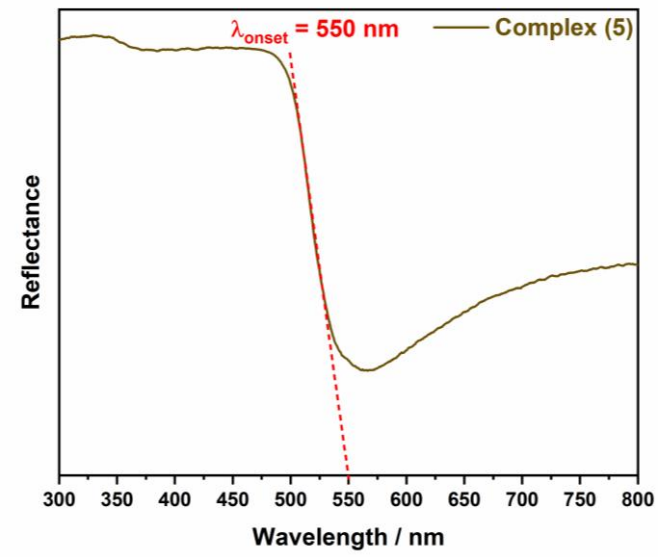


Figure S55. Diffuse reflectance UV-Vis spectrum of complex (**5**).

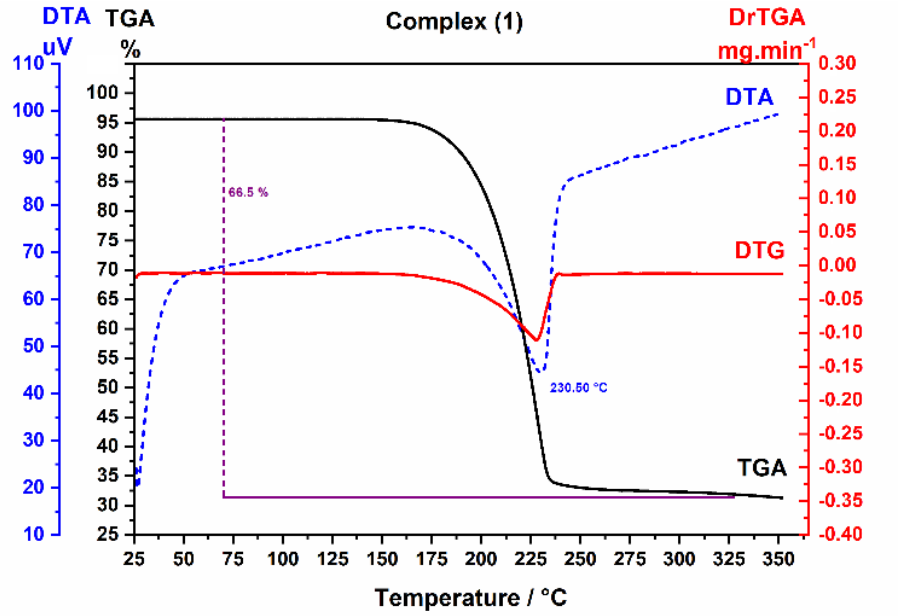


Figure S56. TGA, DTG and DTA curves for the complex (**1**).

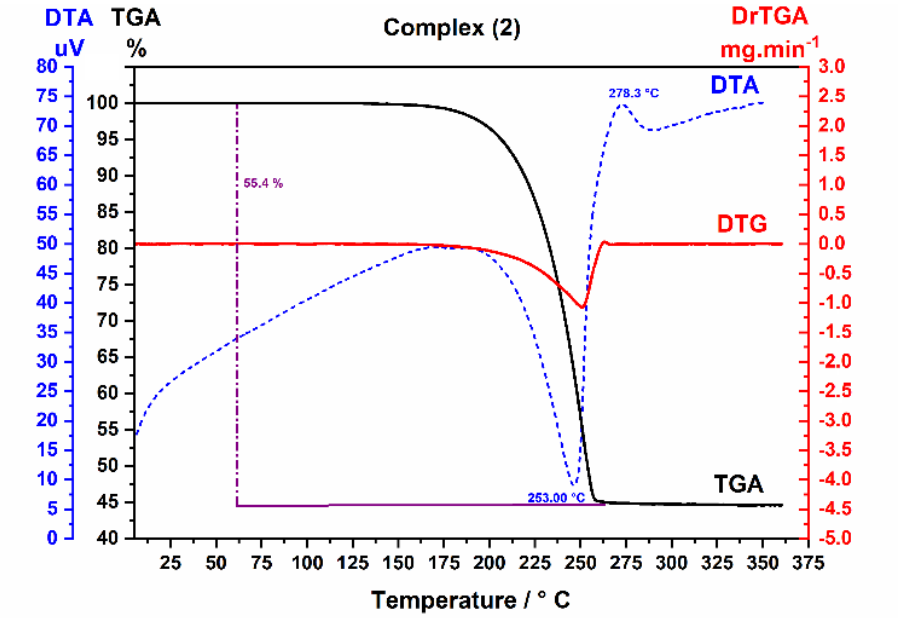


Figure S57. TGA, DTG and DTA curves for the complex (**2**).

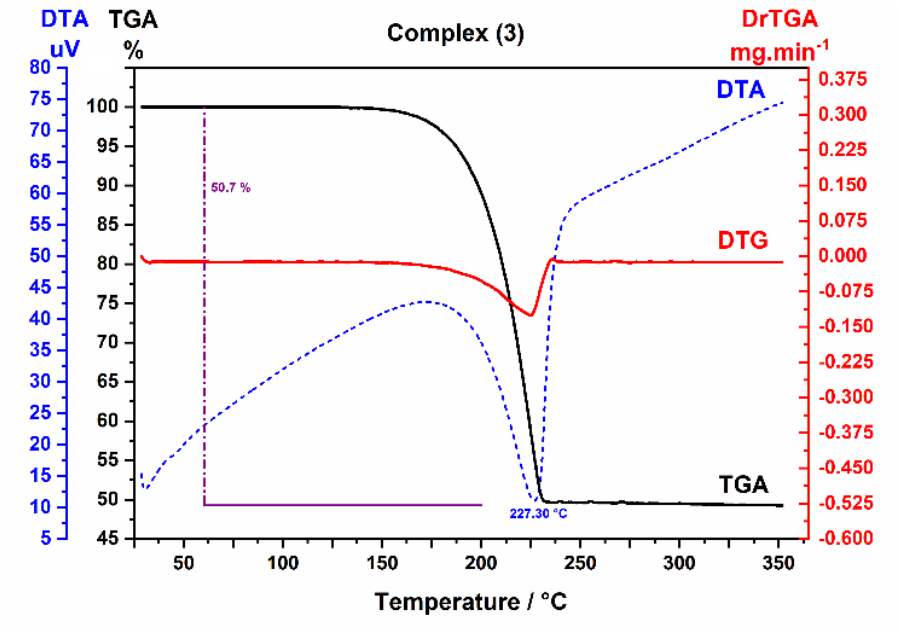


Figure S58. TGA, DTG and DTA curves for the complex (**3**).

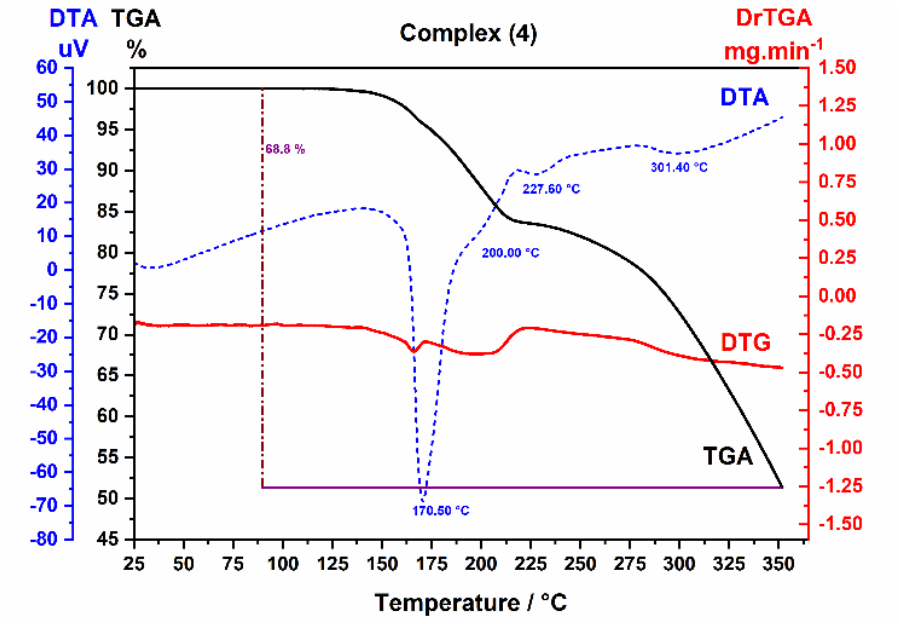


Figure S59. TGA, DTG and DTA curves for the complex (**4**).

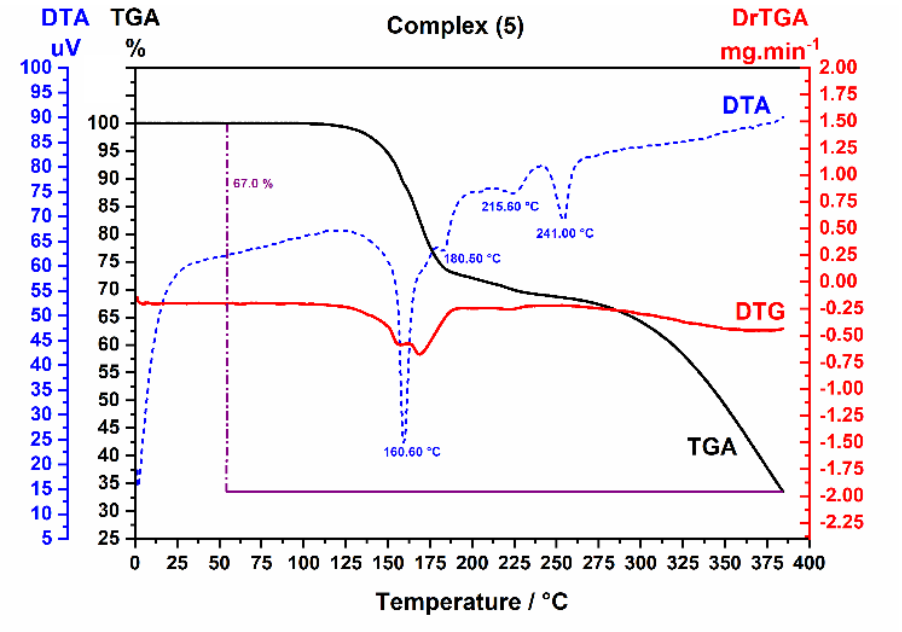


Figure S60. TGA, DTG and DTA curves for the complex (**5**).

Conductometry data

Table S4. Conductivity evolution in solution over time for complexes (**1-5**) dissolved in CH_3CN

Complex	0 h	2 h	4 h	6 h	24 h	48 h	72 h	96 h
	$\mu S\ cm^2\ mol^{-1} \pm SD$							
1	65.5 ± 0.3	66.6 ± 0.1	65.26 ± 0.04	70.7 ± 0.1	80.8 ± 0.2	95.75 ± 0.1	78.8 ± 0.7	78.0 ± 0.2
2	58.4 ± 0.2	59.6 ± 0.2	61.6 ± 0.3	64.21 ± 0.03	77 ± 1	92.94 ± 0.4	88 ± 2	78.5 ± 0.5
3	63 ± 1	63.3 ± 0.1	67.6 ± 0.2	67.6 ± 0.3	82.2 ± 0.5	94 ± 6	88.2 ± 0.1	79.8 ± 0.1
4	80.6 ± 0.7	84 ± 1	86.14 ± 0.04	90 ± 1	115.2 ± 0.3	117.2 ± 0.8	114 ± 1	103.3 ± 0.4
5	78.2 ± 0.5	78.8 ± 0.3	92 ± 1	91 ± 1	88.5 ± 0.5	100.7 ± 0.1	98.5 ± 0.6	97.1 ± 0.1

SD: standard deviation.

Table S5. Conductivity evolution in solution over time for complexes (**4**) and (**5**) dissolved in aprotic solvents

Complex (**4**)	0 h	2 h	4 h	6 h	24 h	48 h	72 h	96 h
	$\mu S\ cm^2\ mol^{-1} \pm SD$							
CH_3CN	80.6 ± 0.7	84 ± 1	86.14 ± 0.04	90 ± 1	115.2 ± 0.3	117.2 ± 0.8	114 ± 1	103.3 ± 0.4
DMSO	55.6 ± 0.1	55.5 ±0.3	57.3 ± 0.2	58.55 ± 0.8	59.1 ± 0.6	61.1 ± 0.1	58.0 ± 0.2	55.7 ± 0.1
CH_2Cl_2	0.15 ± 0.03	0.11 ± 0.02	0.18 ± 0.01	0.12 ± 0.02	0.2 ± 0.05	0.16 ± 0.04	0.11 ± 0.01	0.25 ± 0.09
$CHCl_3$	0.20 ± 0.02	0.19 ± 0.02	0.13 ± 0.03	0.17 ± 0.09	0.18 ± 0.02	0.19 ± 0.05	0.14 ± 0.01	0.20 ± 0.02
Complex **5**	0 h	2 h	4 h	6 h	24 h	48 h	72 h	96 h
	$\mu S\ cm^2\ mol^{-1} \pm SD$							
CH_3CN	78.2 ± 0.5	78.8 ± 0.3	92 ± 1	91 ± 1	88.5 ± 0.5	100.7 ± 0.1	98.5 ± 0.6	97.1 ± 0.1
DMSO	58.1 ± 0.3	52.8 ±0.8	61.8 ± 0.6	60.3 ± 0.8	61.4 ± 0.9	54.1 ± 0.4	59.4 ± 0.4	58.2 ± 0.1
CH_2Cl_2	0.16 ± 0.01	0.13 ± 0.05	0.14 ± 0.07	0.17 ± 0.03	0.15 ± 0.03	0.24 ± 0.02	0.22 ± 0.08	0.21 ± 0.02
$CHCl_3$	0.17 ± 0.09	0.20 ± 0.03	0.15 ± 0.03	0.16 ± 0.07	0.19 ± 0.08	0.19 ± 0.02	0.13 ± 0.09	0.16 ± 0.05

SD: standard deviation.

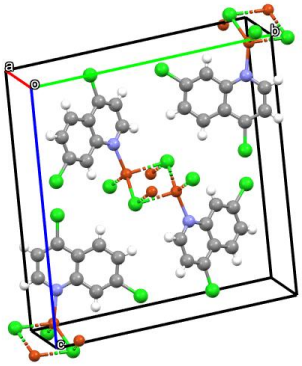


Figure S61. Unit cell for species (**1**).

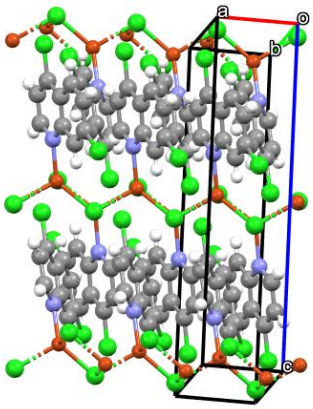


Figure S62. Supramolecular structures viewed down a axe for species (**1**).

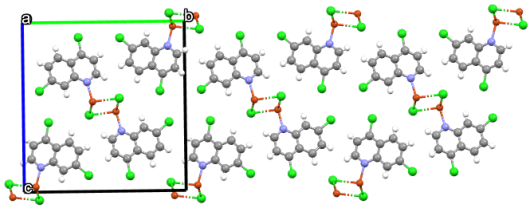


Figure S63. Supramolecular structures viewed down b axe for species (**1**).

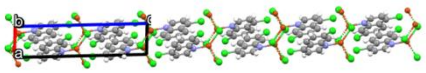


Figure S64. Supramolecular structures viewed down c axe for species (**1**).

Table S6. Table of hydrogen bonds of species (**1**)

D-H···A	H···A / Å	D···A / Å	D-H···A / degree
C5-H5···Cl^{i}	2.94121(2)	3.59607(7)	128.62704(4)
π···π^{ii}	–	3.80(6)	–

Symmetry codes: i (−x,–1/2+y, 1/2−z) ii (1−x, y, z).

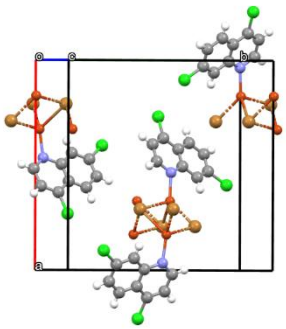


Figure S65. Unit cell for species (**2**).

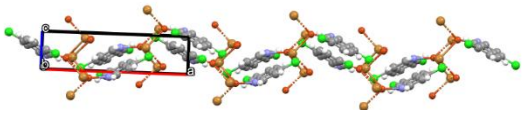


Figure S66. Supramolecular structures viewed down a axe for species (**2**).

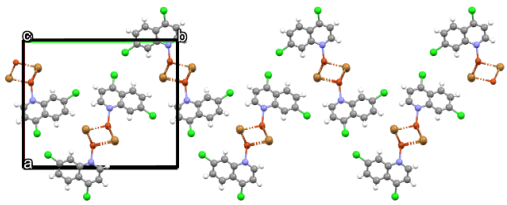


Figure S67. Supramolecular structures viewed down b axe for species (**2**).

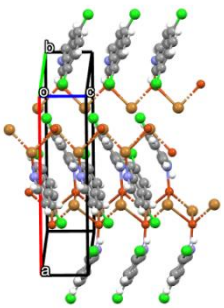


Figure S68. Supramolecular structures viewed down c axe for species (**2**).

Table S7. Table of hydrogen bonds of species (**2**)

D-H···A	H···A / Å	D···A / Å	D-H···A / degree
C3-H3···Cl1^{i}	2.36026(8)	3.93199(2)	148.24666(2)
C2-H2···Cl2^{ii}	2.76946(9)	4.23391(9)	131.34465(4)
C3-H3···Cl2^{iii}	2.89229(9)	4.23391(9)	131.34465(4)
C6-H6···Br^{iv}	2.98781(4)	3.8205(8)	147.10879(7)
π···π^{v}	–	3.7(60)	–

Symmetry codes: i (3/2–x, −y, −1/2+z) ii (1–x, 1/2+y, –1/2–z), iii (1–x, –1/2+y, 1/2–z) iv (1/2+x, 1/2–y, 1–z) v (x, y, 1+z).

Table S8. Fractional atomic coordinates for structure (**2**)

Atom	$u \times 10^4$	$v \times 10^4$	$w \times 10^4$
Cu	0.8929	0.6927	0.5798
Br	0.9295	0.3409	0.7261
N1	0.8951	0.1853	0.5595
C2	0.8948	0.1849	0.5575
C3	0.8942	0.1850	0.5529
C4	0.8940	0.1854	0.5501
C5	0.8944	0.1857	0.5520
C6	0.8949	0.1857	0.5567
C7	0.8953	0.1860	0.5586
C8	0.8951	0.1864	0.5558
C9	0.8945	0.1864	0.5512
C10	0.8942	0.1861	0.5493
H2	0.8949	0.1847	0.5594
H3	0.8940	0.1848	0.5516
H7	0.8957	0.1860	0.5618
H9	0.8944	0.1867	0.5493
H10	0.8938	0.1861	0.5461
Cl1	0.8933	0.1854	0.5443
Cl2	0.8955	0.1868	0.5582

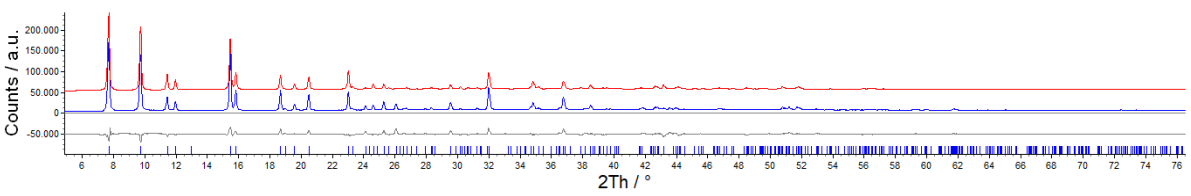


Figure S69. Final Rietveld refinement plot for complex (**2**), experimental, blue, calculated, red, with difference plot and peak markers at the bottom.

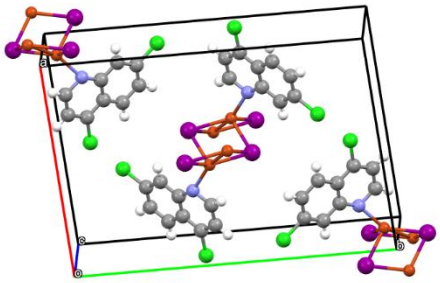


Figure S70. Unit cell for species (**3**).

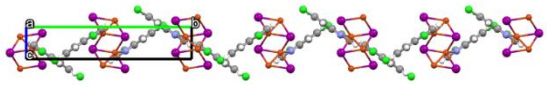


Figure S71. Supramolecular structures viewed down a axe for species (**3**).

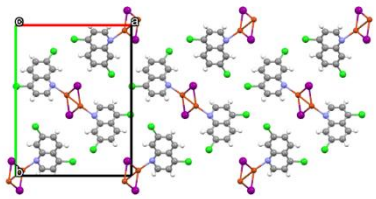


Figure S72. Supramolecular structures viewed down b axe for species (**3**).

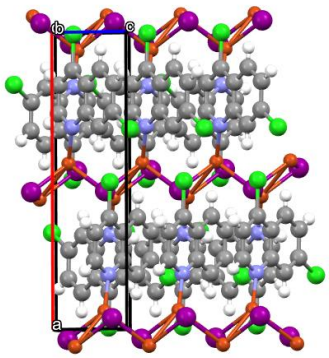


Figure S73. Supramolecular structures viewed down c axe for species (**3**).

Table S9. Table of hydrogen bonds of species (**3**)

D-H···A	H···A / Å	D···A / Å	D-H···A / degree
C3-H3···Cl^{i}	2.09214(4)	2.94967(2)	149.38518(2)
C3-H3···Cl2^{ii}	2.79253(3)	3.50681(5)	132.68251(4)
C6-H6···I^{iii}	2.60368(3)	3.42047(9)	144.29840(3)
π···π^{iv}	–	3.59(1)	–

Symmetry codes: i (−x, 1−y, 1−z) ii (1/2–x, 1/2+y, 1/2−z), iii (1/2–x, –1/2+y, 1/2−z) iv (x, y, 1+z).

Table S10. Fractional atomic coordinates for structure (**3**)

Atom	$u \times 10^4$	$v \times 10^4$	$w \times 10^4$
Cu	0.0125	0.7054	0.9665
I	0.3781	0.2443	0.2565
N1	0.3116	0.6578	0.1406
C2	0.3151	0.6547	0.1133
C3	0.3208	0.6552	0.0637
C4	0.3230	0.6587	0.0415
C5	0.3195	0.6619	0.0689
C6	0.3138	0.6614	0.1184
C7	0.3103	0.6645	0.1458
C8	0.3125	0.6681	0.1235
C9	0.3182	0.6686	0.0740
C10	0.3217	0.6654	0.0466
H2	0.3136	0.6523	0.1286
H3	0.3232	0.6530	0.0449
H7	0.3063	0.6642	0.1799
H9	0.3197	0.6710	0.0587
H10	0.3256	0.6657	0.0125
Cl1	0.3302	0.6593	0.9790
Cl2	0.3080	0.6721	0.1580

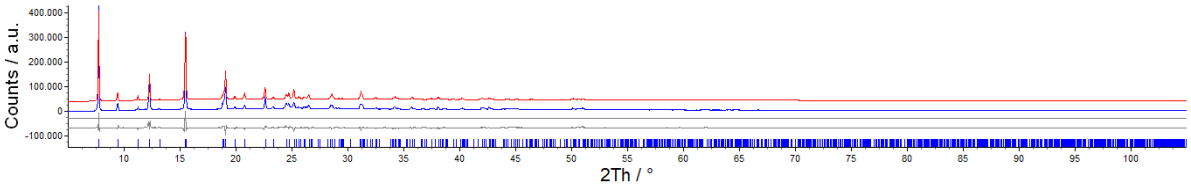


Figure S74. Final Rietveld refinement plot for complex (**3**), experimental, blue, calculated, red, with difference plot and peak markers at the bottom.

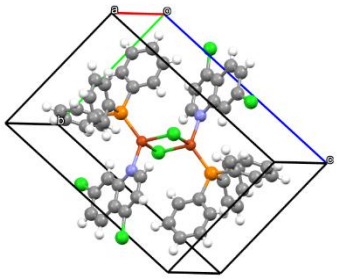


Figure S75. Unit cell for species (**4**).

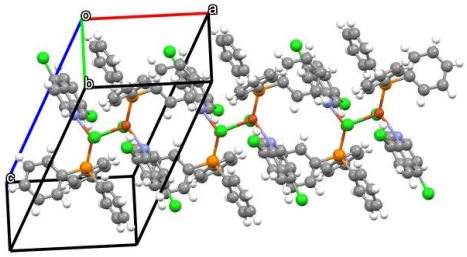


Figure S76. Supramolecular structures viewed down a axe for species (**4**).

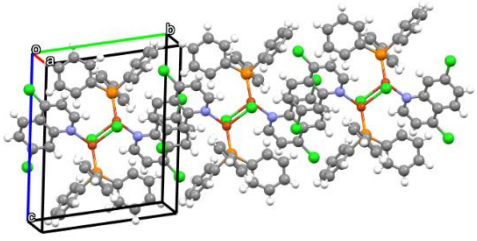


Figure S77. Supramolecular structures viewed down b axe for species (**4**).

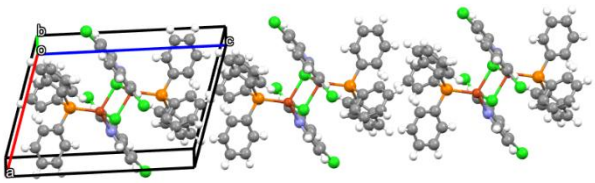


Figure S78. Supramolecular structures viewed down c axe for species (**4**).

Table S11. Table of hydrogen bonds of species (**4**)

D-H···A	H···A / Å	D···A / Å	D-H···A / degree
C6-H6···Cl^{i}	2.96076(4)	3.80988(9)	152.41226(7)
C27-H27···Cl^{ii}	2.99208(2)	3.75535(1)	140.34432(2)
C21-H21···Cl2^{iii}	2.9679(9)	3.48052(4)	116.22298(6)
C22-H22···Cl2^{iii}	2.95060(9)	3.46393(5)	116.29222(7)
π···π^{iv}	–	3.97(3)	–

Symmetry codes: i (1−x,−y, 1−z) ii (1+x, y, z) iii (x, 1+y, z) iv (−x,1− y, 1−z).

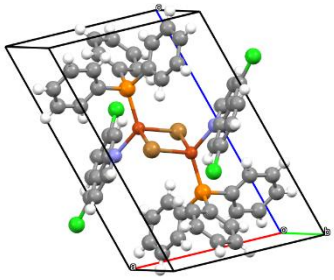


Figure S79. Unit cell for species (**5**).

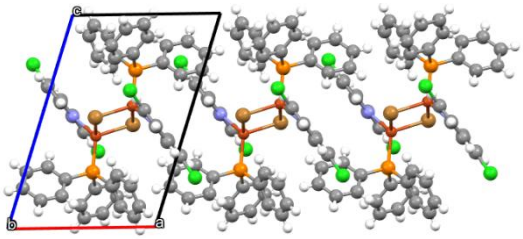


Figure S80. Supramolecular structures viewed down a axe for species (**5**).

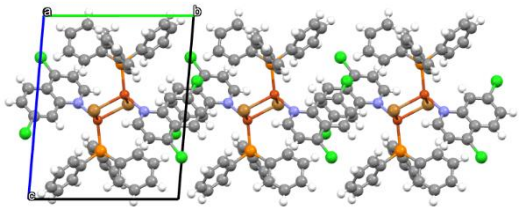


Figure S81. Supramolecular structures viewed down b axe for species (**5**).

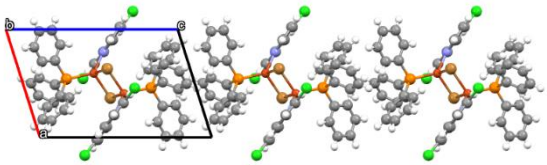


Figure S82. Supramolecular structures viewed down c axe for species (**5**).

Table S12. Table of hydrogen bonds of species (**5**)

D-H···A	H···A / Å	D···A / Å	D-H···A / degree
C6-H6^{i}···Br	2.9814(5)	3.83843(5)	153.94783(3)
C27-H27···Br^{ii}	3.05532(3)	3.78766(3)	136.87601(4)
C12-H12···Cl2^{iii}	3.01803(8)	3.56466(2)	119.15311(3)
C13-H13···Cl2^{iii}	3.05410(3)	3.5770(9)	117.36086(5)
π···π^{iv}	–	3.99(1)	–

Symmetry codes: i (1−x,−y, 1−z) ii (−1+x, y, z) iii (x, 1+y, z) iv (2−x, −y, 1−z).

Optical properties

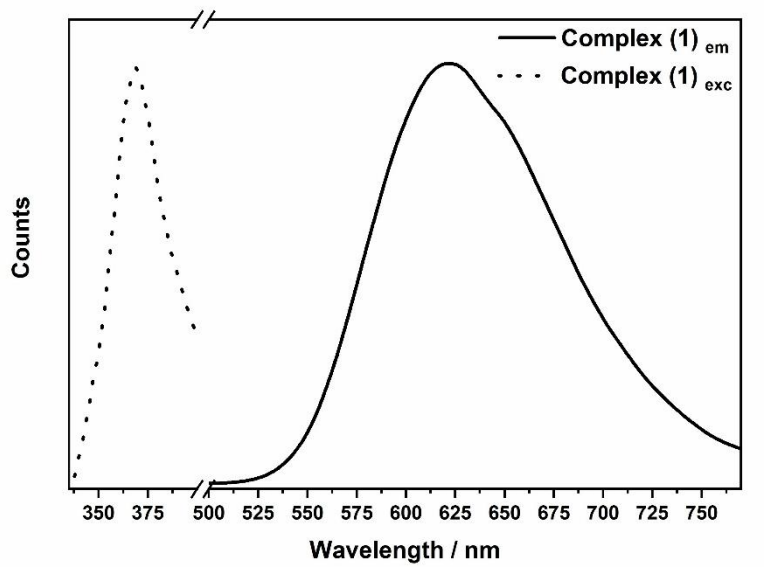


Figure S83. Room-temperature emission and excitation spectra of the complex (**1**) (λ_{exc} = 370 nm).

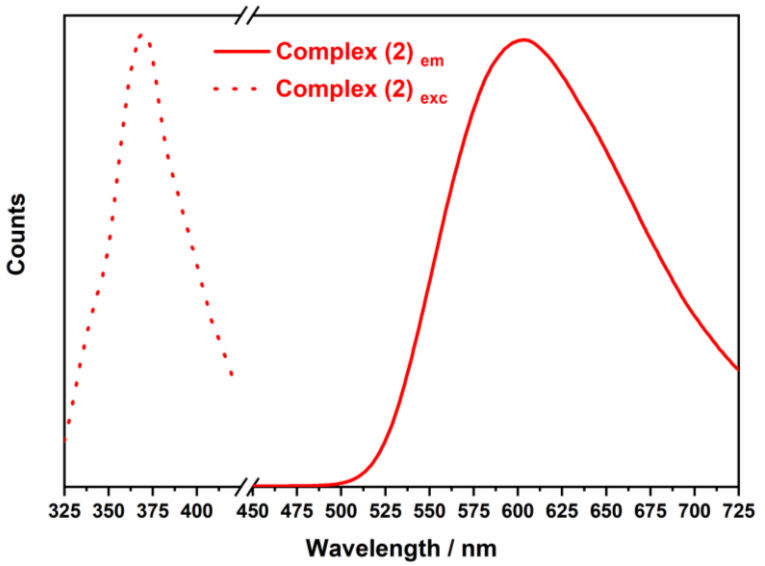


Figure S84. Room-temperature emission and excitation spectra of the complex (**2**) (λ_{exc} = 370 nm).

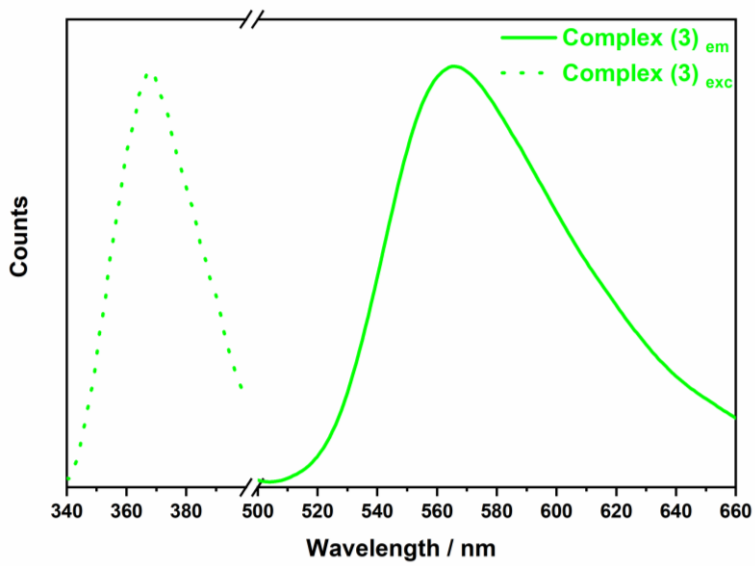


Figure S85. Room-temperature emission and excitation spectra of the complex (**3**) (λ_{exc} = 370 nm).

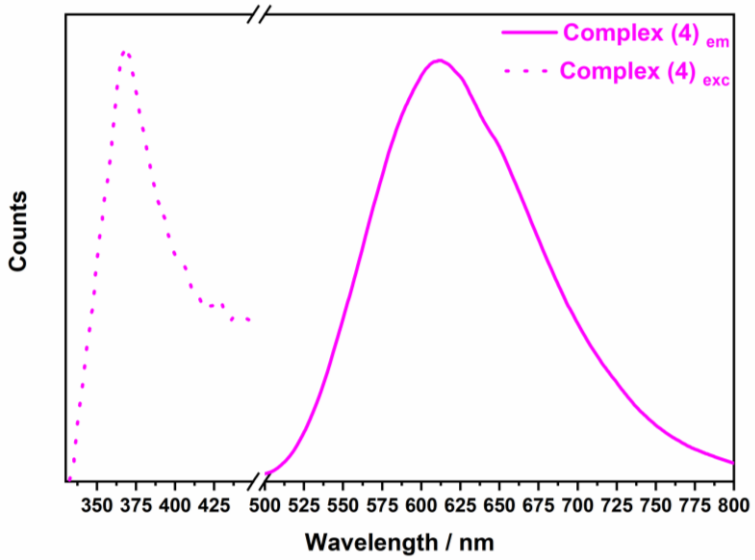


Figure S86. Room-temperature emission and excitation spectra of the complex (**4**) (λ_{exc} = 370 nm).

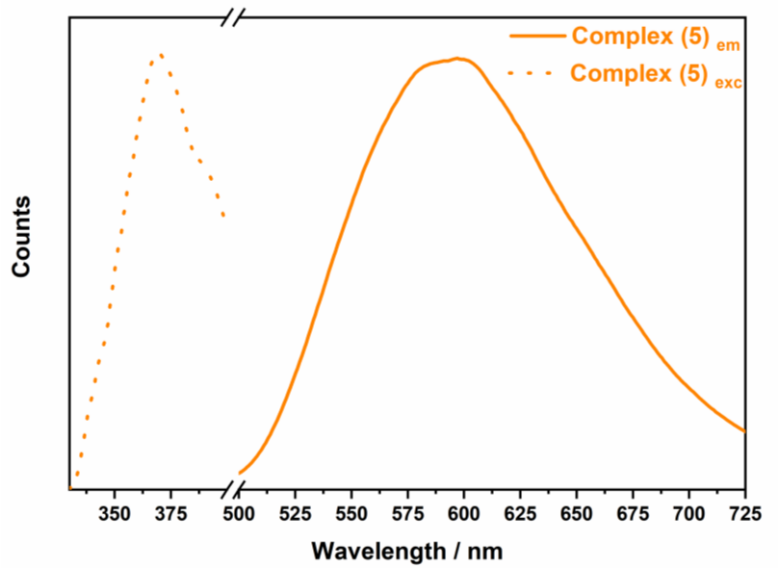


Figure S87. Room-temperature emission and excitation spectra of the complex (**5**) (λ_{exc} = 370 nm).

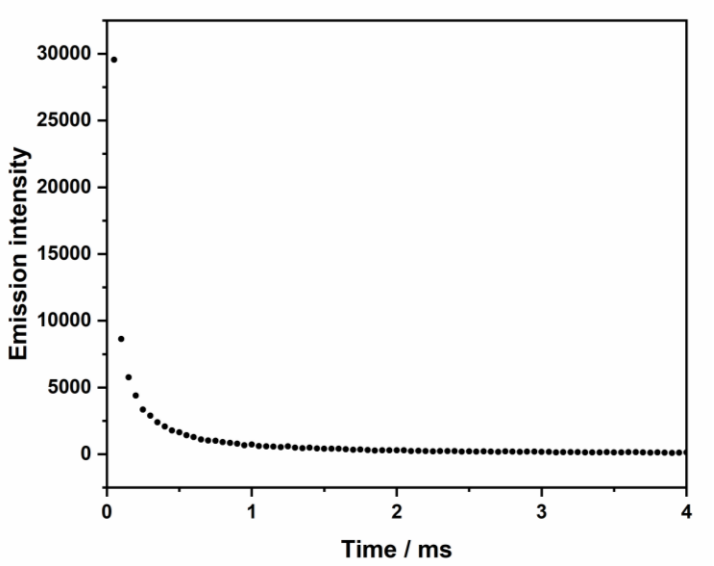


Figure S88. The photoluminescence decay curve for complex (**1**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 547 nm).

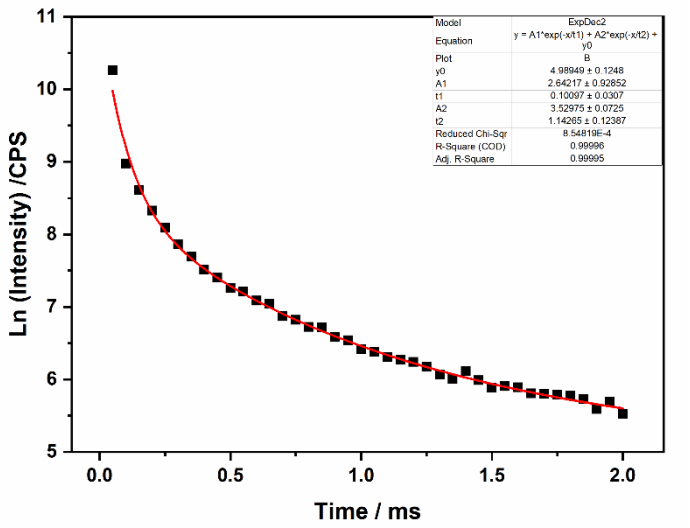


Figure S89. Exponential fit of photoluminescence decay curve for complex (**1**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 547 nm).

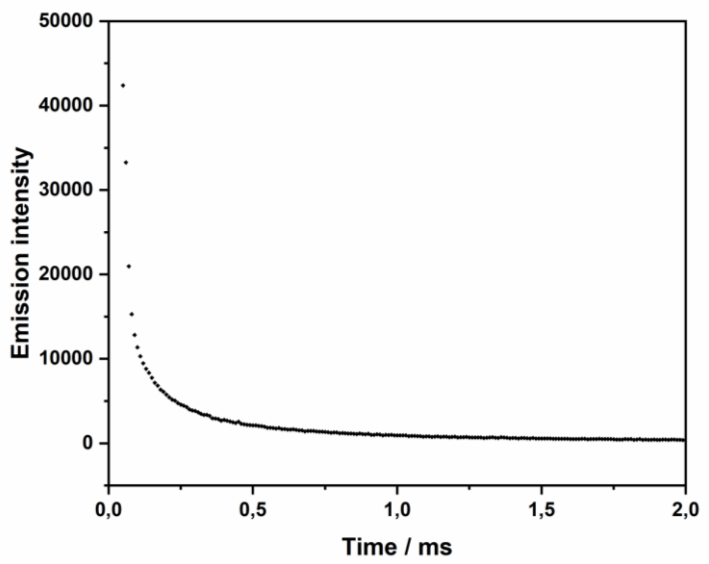


Figure S90. The photoluminescence decay curve for complex (**2**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 600 nm).

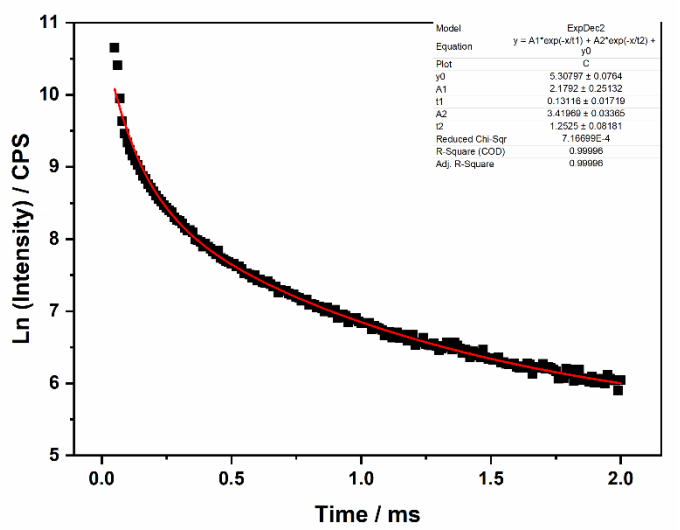


Figure S91. Exponential fit of photoluminescence decay curve for complex (**2**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 600 nm).

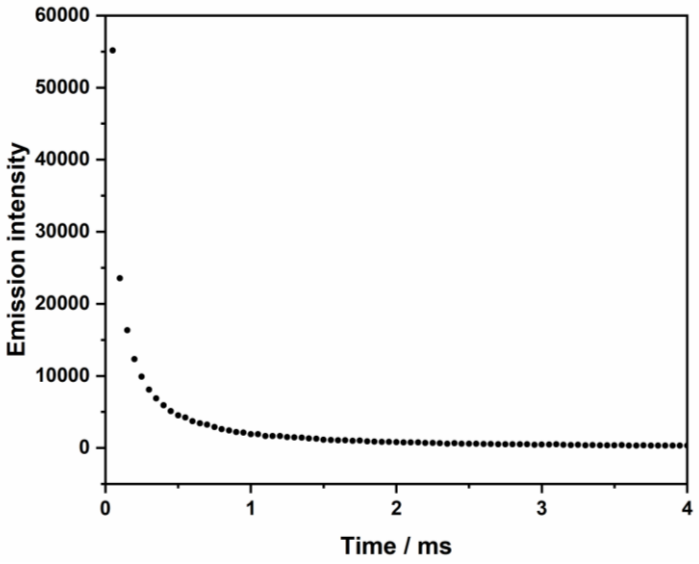


Figure S92. The photoluminescence decay curve for complex (**3**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 574 nm).

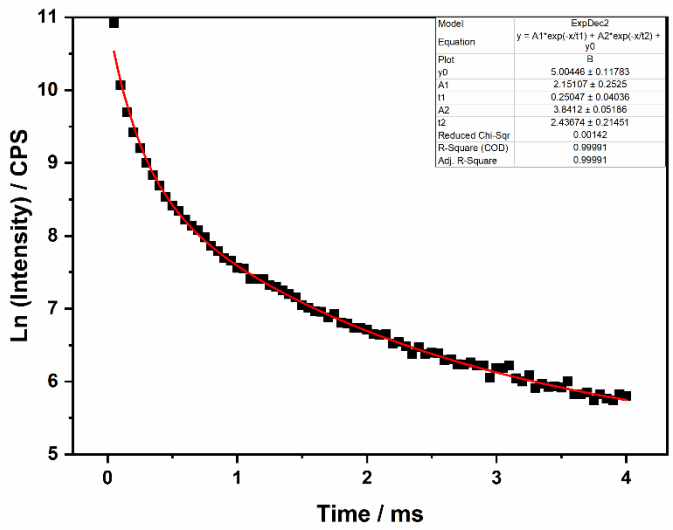


Figure S93. Exponential fit of photoluminescence decay curve for complex (**3**) at 298 K in the solid state ((λ_{ex} = 370 nm, λ_{em} = 574 nm).

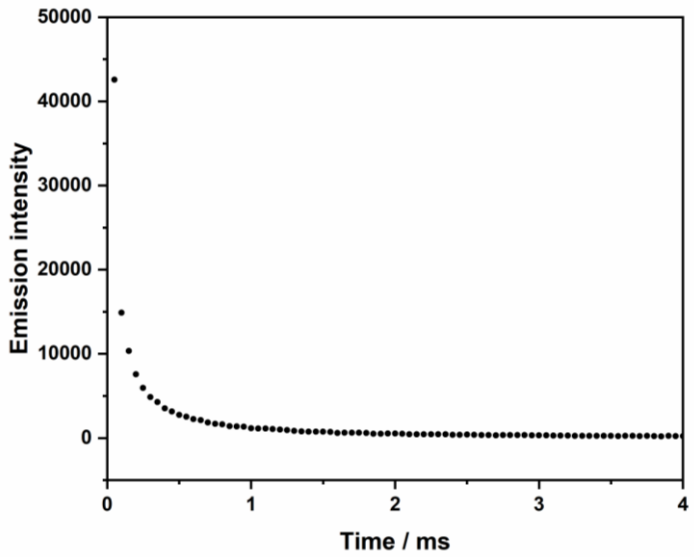


Figure S94. The photoluminescence decay curve for complex (**4**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 647 nm).

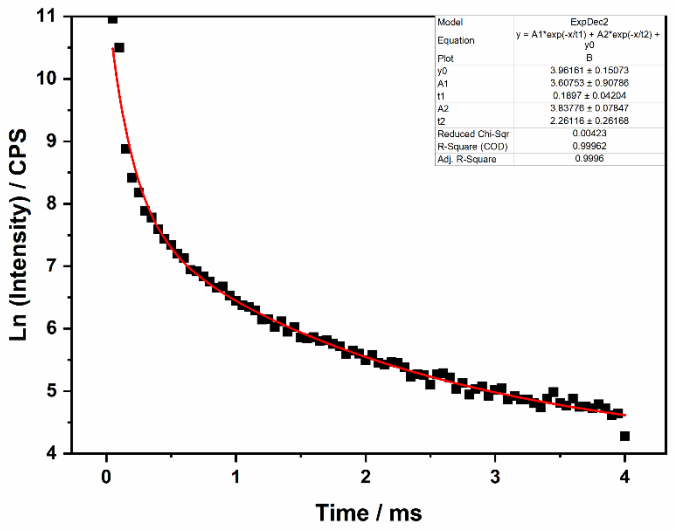


Figure S95. Exponential fit of photoluminescence decay curve for complex (**4**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 647 nm).

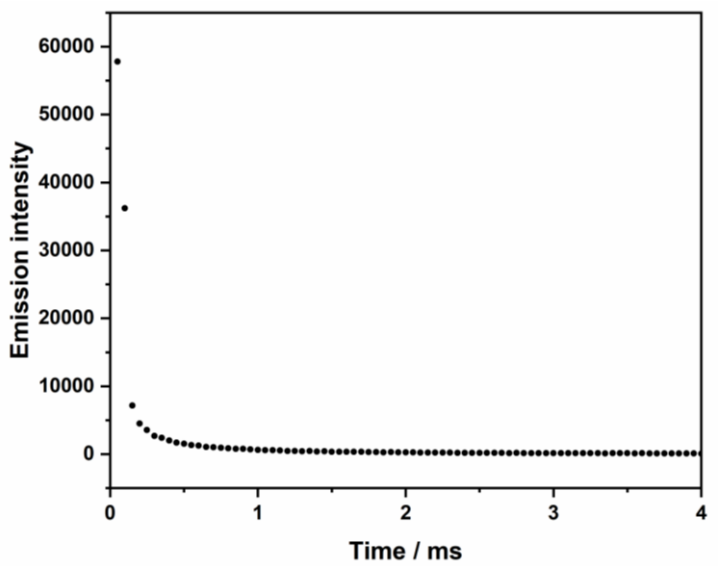


Figure S96. The photoluminescence decay curve for complex (**5**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 621 nm).

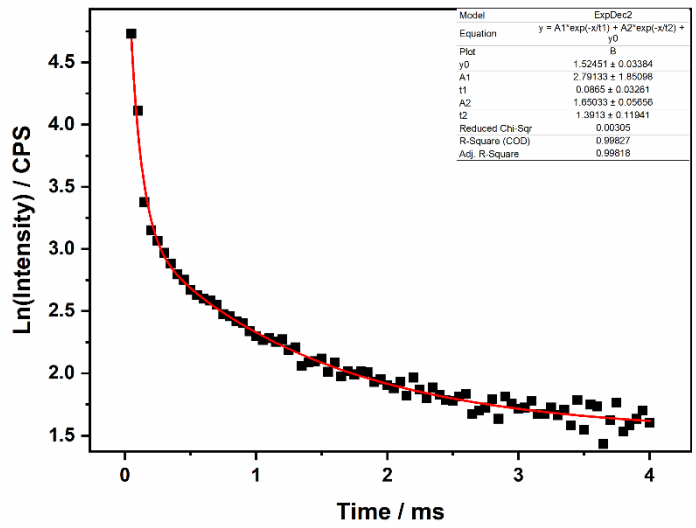


Figure S97. Exponential fit of photoluminescence decay curve for complex (**5**) at 298 K in the solid state (λ_{ex} = 370 nm, λ_{em} = 621 nm).

Equation S1 defines the optical band gap (E_{gap}^{opt}) [1] estimated from the onset of the absorption band (λ_{onset}).

$$E_{gap}^{opt} = \frac{1240}{\lambda_{onset}} \text{(S1)}$$

Equation S2 corresponds to the photoluminescence energy (E_{PL}) [1] calculated from the emission maximum.

$$E_{PL} = \frac{1240}{\lambda_{em}} \text{(S2)}$$

Equation S3 provides the Stokes shift (ΔE), [1] representing the energy difference between absorption and emission processes.

$$\Delta E = E_{gap}^{opt} - E_{PL} \text{(S3)}$$

Equation S4[2] The emission decays of complexes were analyzed using multi exponential, i.e., $I = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2} + \ldots + A_i e^{-t/\tau i}$, where τ_i denote the lifetimes, and A_i are the pre-exponential factors. Therefore, for the determination of radiative and nonradiative rate constants, the emission average lifetimes $<\tau>$ were estimated using the following equation:

$$<\tau> = \frac{\sum_{i=1}^{n} A_i \tau_i^2}{\sum_{i=1}^{n} A_i \tau_i} \text{(S4)}$$

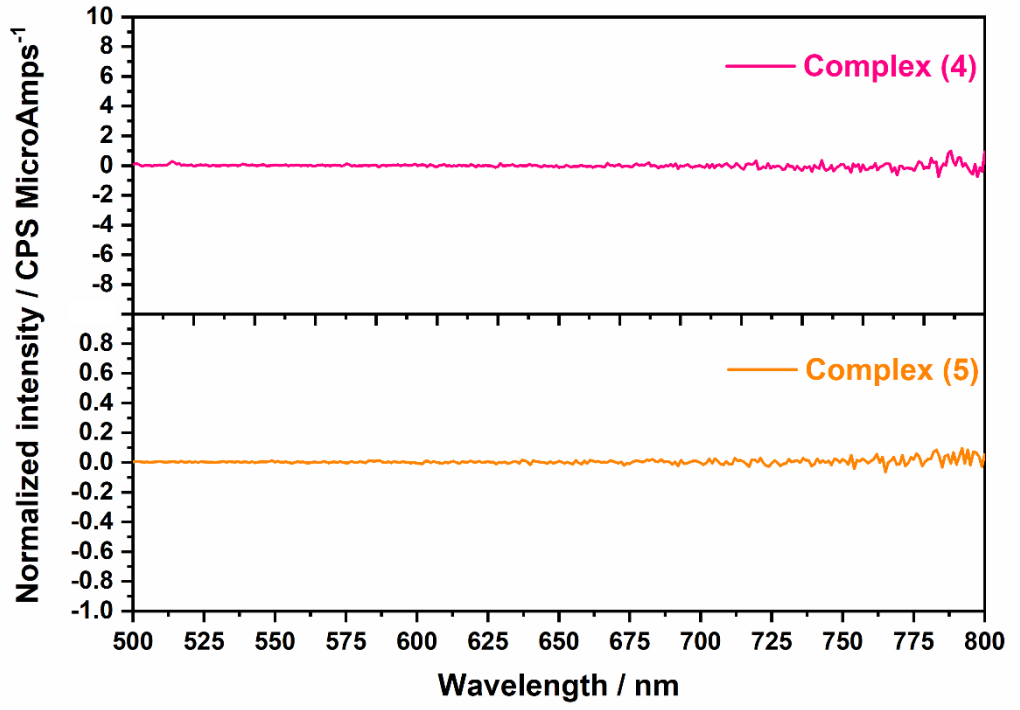


Figure S98. Comparison of the emission spectra in CH_3CN solution, normalized intensities, of the complexes (**4**) and (**5**). (λ_{ex} = 370 nm)

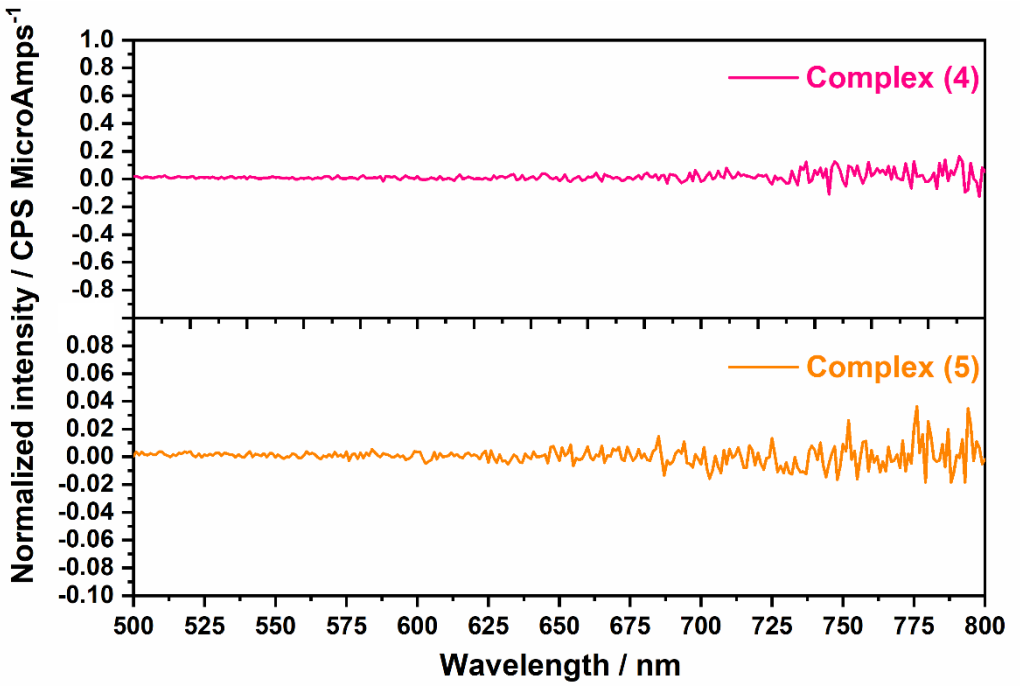


Figure S99. Comparison of the emission spectra in CH_2Cl_2 solution, normalized intensities, of the complexes (**4**) and (**5**). (λ_{ex} = 370 nm)

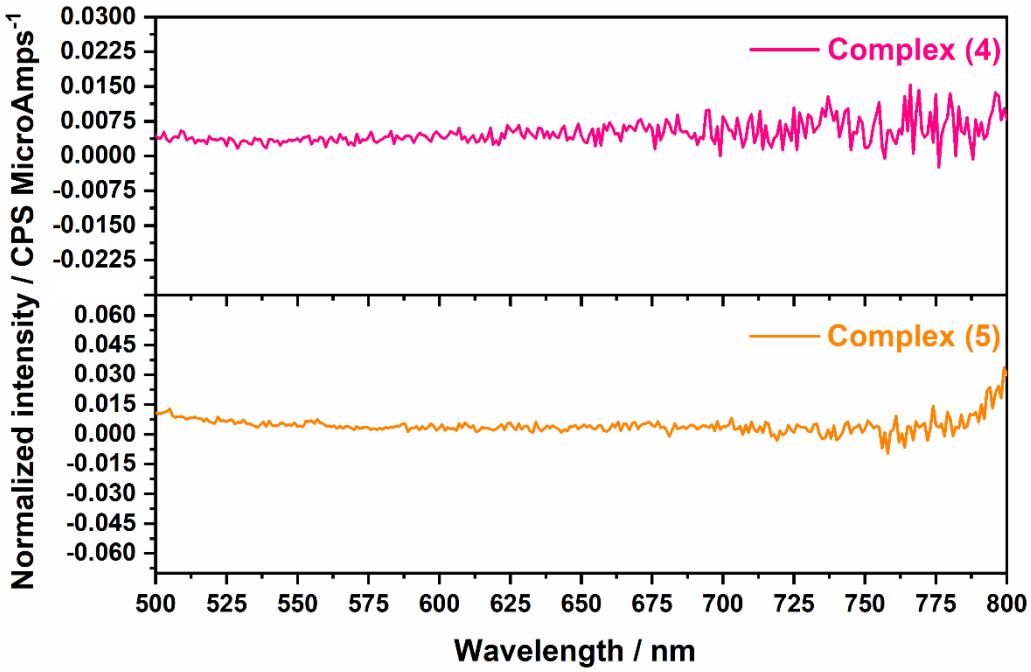


Figure S100. Comparison of the emission spectra in $CHCl_3$ solution, normalized intensities, of the complexes (**4**) and (**5**). (λ_{ex} = 370 nm)

Table S13. Experimental conditions for excitation and emission measurements of complexes (**1**-**5**) in the solid state and in solution

Compound	Physical state	λ_{exc} / nm	Excitation range / nm	λ_{em} / nm	Emission range / nm	Slit / nm	Slit (τ)/ nm
1	solid	370	300-450	547	500-800	2.00	10.0
2	solid	370	200-420	600	450-750	0.50	2.0
3	solid	370	300-400	574	500-800	1.00	7.0
4	solid	370	300-450	647	500-800	1.00	10.0
4	solution (CH_3CN)	370	300-450	–	500-800	1.00	–
4	solution (CH_2Cl_2)	370	300-450	–	500-800	1.00	–
4	solution ($CHCl_3$)	370	300-450	–	500-800	1.00	–
5	solid	370	300-400	621	500-800	1.00	5.0
5	solution (CH_3CN)	370	300-400	–	500-800	1.00	–
5	solution (CH_2Cl_2)	370	300-400	–	500-800	1.00	–
5	solution ($CHCl_3$)	370	300-400	–	500-800	1.00	–

Integration time: 0.1 s (solid); 0.5 s (solution); $Grating_{exc}$: 1200 (Density) /330 (Blaze); $Grating_{em}$: 1200 (Density) /500 (Blaze); λ_{exc} : maximum excitation wavelength for decay by delay experiments; λ_{em} : maximum emission wavelength for decay by delay experiments; Slit = monochromator bandwidths (excitation range/emission range); Slit (τ) = emission monochromator bandwidths (decay by delay).

Energy and structural data (DFT)

Table S14. Non-optimized crystal fragments used in DFT and TD-DFT studies

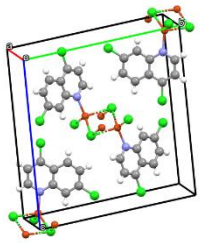
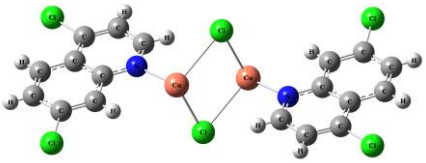
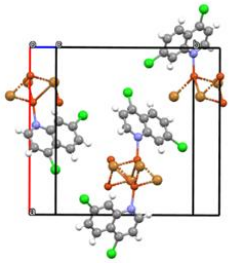
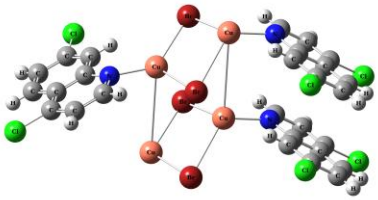
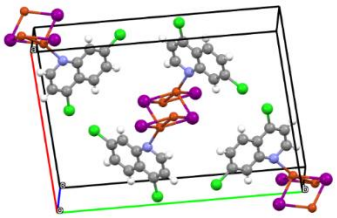
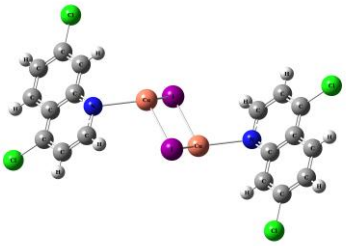
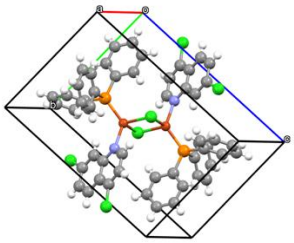
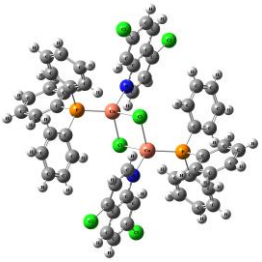
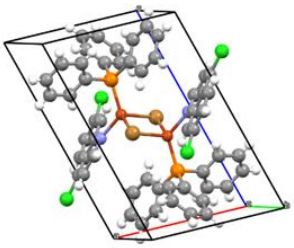
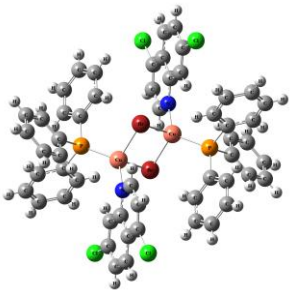
	Unit cell	Crystal fragment
Complex (**1**)		
Complex (**2**)		
Complex (**3**)		
Complex (**4**)		
Complex (**5**)		

Table S15. Selected distances and angles bonds for the five copper(I) complexes

Complex	Length / Å		Complex	Length / Å	
1	Cu-N1	2.008(3)	**2**	Cu-N1	2.0425(99)
	Cu-Cl	2.6426(10)		Cu-Br	2.8466(75)
	Cu-Cl[1]	2.3709(10)		Cu-Br[1]	2.5864(65)
	Cu-Cl[2]	2.2903(10)		Cu-Br[2]	2.6393(41)
	Cu···Cu[1]	3.0111(1)		Cu···Cu[1]	3.4624(9)
	[1] 1–x,–y,1–z			[1] x,y,–1+z	
	[2] –x,–y,1–z			[2] 1/2–x,–y,–1/2+z	
3	Cu-N1	2.43656(6)	**4**	Cu-N1	2.0959(19)
	Cu-I	2.75483(5)		Cu-P	2.2003(6)
	Cu-I[1]	2.33832(8)		Cu-Cl	2.3871(6)
	Cu-I[2]	2.51921(9)		Cu-Cl[1]	2.4128(6)
	Cu···Cu[1]	2.6541(4)		Cu···Cu[1]	3.1068(6)
	[1] 1–x,1–y,1–z				
	[2] 1–x,1–y,–z			[1] 1–x,1–y,1–z	
5	Cu-N1	2.092(2)			
	Cu-P	2.2128(7)			
	Cu-Br	2.5130(4)			
	Cu-Br[1]	2.5270(4)			
	Cu···Cu[1]	3.1673(7)			
	[1] 1–x,1–y,1–z				

Table S16. Energy and model specification for the TD-DFT single-point calculations

Complex	Model (geometry source)	Stoichiometry	Degrees of freedom	Point group	Charge	Multiplicy	E_{total} / (kcal mol^{-1})	ΔE_{rel} / (kcal mol^{-1})
1	crystal fragment (XRD) no optimization	$C_{18}H_{10}Cl_6Cu_2N_2$	108	C1	0	1	−2481599.60	0.00
2	crystal fragment (XRD) no optimization	$C_{27}H_{15}Br_4Cl_6Cu_4N_3$	171	C1	0	1	−9440608.89	0.00
3	crystal fragment (XRD) No optimization	$C_{18}H_{10}Cl_4Cu_2I_2N_2$	108	C1	0	1	−10588467.00	0.00
4	crystal fragment (XRD) no optimization	$C_{27}H_{20}Cl_3CuNP$	156	CI	0	1	−3781540.08	0.00
5	crystal fragment (XRD) no optimization	$C_{27}H_{20}BrCl_2CuNP$	156	CI	0	1	−6434677.58	0.00

XRD = X-ray diffraction; E_{total} = denotes single-point electronic energies obtained at the stated level of theory using crystallographic fragment geometries (no optimization); ΔE_{rel} = computed relative to the lowest E_{total} among the models compared at the same level of theory. If only one model is reported, ΔE_{rel} can be set to 0.00 (reference).

Table S17. Cartesian coordinates of the crystallographic fragment used for the calculations (no geometry optimization) for species **1**

	Atomic coordinates		
	X/ Å	Y / Å	Z / Å
Cl	0.1296	14.65432	–7.93063
H	–0.58759	15.44383	–6.176
Cu	–0.44241	13.86319	–4.31837
Cl	–0.58245	13.65492	–3.4227
N	–1.41595	16.14652	–4.02644
C	0.11676	12.94102	–5.14963
C	–1.75668	17.34976	–4.57072
C	–2.16141	18.00982	–4.05509
H	–1.4822	17.56293	–5.91821
C	0.93304	12.01238	–7.55466
C	0.37618	12.11153	–4.81709
H	–2.27378	19.5259	–9.62249
C	–1.07705	20.83763	–15.89384
C	–1.91291	20.03389	–11.5314
C	–2.00399	21.56652	–13.43059
H	–2.79536	22.23605	–11.21226
C	–2.9456	22.0497	–10.31362
Cl	–2.22841	21.26019	–12.06826
H	–2.37359	22.84083	–13.92588
Cu	–2.23355	23.0491	–14.82156
Cl	–1.40005	20.5575	–14.21781
N	–1.05932	19.35426	–13.67353
C	–0.65459	18.6942	–14.18916
C	–1.3338	19.14109	–12.32604
H	–0.32133	19.86193	–8.32003
C	–1.71951	18.38378	–6.28668
C	–2.93276	23.763	–13.09462
H	–3.20219	24.6002	–13.39865
C	–3.1174	23.4614	–11.73724
C	–3.68611	24.70845	–10.67355
H	0.1296	14.65432	–7.93063
C	–0.58759	15.44383	–6.176
Cl	–0.44241	13.86319	–4.31837
H	–0.58245	13.65492	–3.4227
C	–1.41595	16.14652	–4.02644
H	0.11676	12.94102	–5.14963
C	–1.75668	17.34976	–4.57072
Cl	–2.16141	18.00982	–4.05509

Table S18. Cartesian atomic coordinates from the Standard orientation section of the Gaussian output for the fragment model used in the TD-DFT calculations for species (**1**)

Center number	Atomic number	Atomic type	Coordinates (standard orientation)		
			X / Å	Y / Å	Z / Å
1	17	0	–2.494667	16.842091	–9.924226
2	1	0	–1.096490	18.320245	–11.957571
3	29	0	–0.542223	17.178115	–8.621763
4	17	0	–1.738950	15.866390	–2.350412
5	7	0	–0.903094	16.670132	–6.712847
6	6	0	0.301404	13.242624	–6.507013
7	6	0	–0.812007	15.137496	–4.813662
8	6	0	–0.020638	14.467975	–7.031989
9	1	0	0.129598	14.654320	–7.930634
10	6	0	–0.587589	15.443834	–6.175995
11	6	0	–0.442414	13.863195	–4.318373
12	1	0	–0.582452	13.654917	–3.422697
13	6	0	–1.415954	16.146515	–4.026445
14	6	0	0.116756	12.941024	–5.149627
15	6	0	–1.756681	17.349759	–4.570718
16	1	0	–2.161407	18.009822	–4.055093
17	6	0	–1.482201	17.562932	–5.918208
18	17	0	0.933035	12.012378	–7.554657
19	1	0	0.376178	12.111528	–4.817093
20	29	0	–2.273777	19.525905	–9.622489
21	17	0	–1.077050	20.837630	–15.893840
22	7	0	–1.912906	20.033888	–11.531405
23	6	0	–2.003993	21.566524	–13.430590
24	6	0	–2.795362	22.236045	–11.212263
25	1	0	–2.945598	22.049700	–10.313618
26	6	0	–2.228411	21.260186	–12.068257
27	6	0	–2.373586	22.840825	–13.925879
28	1	0	–2.233548	23.049103	–14.821555
29	6	0	–1.400046	20.557504	–14.217807
30	6	0	–1.059319	19.354261	–13.673534
31	1	0	–0.654593	18.694198	–14.189159
32	6	0	–1.333799	19.141088	–12.326044
33	17	0	–0.321333	19.861929	–8.320026
34	1	0	–1.719510	18.383775	–6.286681
35	6	0	–2.932756	23.762996	–13.094625
36	1	0	–3.202188	24.600203	–13.398653
37	6	0	–3.117404	23.461396	–11.737239
38	17	0	–3.686109	24.708451	–10.673545

Table S19. Cartesian coordinates of the crystallographic fragment used for the calculations (no geometry optimization) for species (**2**)

	Atomic coordinates		
	X/ Å	Y / Å	X/ Å
C	35.85902	–13.18816	–4.29776
C	36.49667	–14.18401	–3.58707
C	37.64871	–13.89959	–2.88308
C	38.16323	–12.61921	–2.88969
C	39.83001	–11.05444	–2.19226
C	39.31549	–12.33481	–2.18565
H	40.62315	–10.85859	–1.7076
H	39.75442	–13.02039	–1.6964
Cl	38.44534	–15.14388	–1.99524
Cu	35.07715	–10.35863	–4.67944
Br	34.28621	–8.66977	–2.52872
N	36.32776	–11.9348	–4.32793
C	37.52572	–11.62326	–3.60034
C	38.04025	–10.34288	–3.60695
C	39.19236	–10.05858	–2.90295
H	31.86325	–6.62518	–2.79421
H	37.60131	–9.6573	–4.0962
Cl	39.83526	–8.45882	–2.91119
H	36.14247	–15.06543	–3.58252
Cu	31.96285	–9.59466	–3.37307
Br	32.66897	–11.32615	–5.15997
N	30.60544	–8.07216	–3.26653
C	30.94919	–6.88163	–2.76058
C	29.22771	–8.47406	–3.22305
C	28.83394	–9.69375	–3.73437
H	35.0658	–13.38388	–4.78243
H	29.47686	–10.27681	–4.12003
Cl	27.01427	–11.59021	–4.32433
C	35.01079	–13.61445	–0.65958
C	35.64844	–14.61031	0.05111
C	36.80047	–14.32588	0.7551
C	37.315	–13.04551	0.74849
C	38.98178	–11.48073	1.44592
C	38.46726	–12.76111	1.45253
H	39.77492	–11.28489	1.93058
H	38.90619	–13.44669	1.94178
Cl	37.5971	–15.57017	1.64294
Cu	34.22892	–10.78493	–1.04126

Br	33.43797	–9.09606	1.10947
N	35.47953	–12.3611	–0.68975
C	36.67749	–12.04955	0.03785
C	37.19201	–10.76917	0.03123
C	38.34413	–10.48487	0.73523
H	30.28631	–5.19504	–1.84839
H	36.75308	–10.08359	–0.45801
Cl	38.98702	–8.88511	0.72699
H	35.29424	–15.49173	0.05566
Cu	31.11462	–10.02095	0.26511
Br	31.82074	–11.75245	–1.52179
C	30.01524	–6.03468	–2.20038
C	28.68767	–6.40732	–2.15149
C	28.2939	–7.62701	–2.6628
C	27.50629	–10.06626	–3.68548
C	26.57234	–9.21932	–3.12528
C	26.96611	–7.99963	–2.61396
H	34.21757	–13.81017	–1.14424
H	25.65836	–9.47589	–3.09164
H	26.32319	–7.41657	–2.2283
Cl	27.52087	–5.34907	–1.45162

Table S20. Cartesian atomic coordinates from the Standard orientation section of the Gaussian output for the fragment model used in the TD-DFT calculations for species (**2**)

Center number	Atomic number	Atomic type	Coordinates (standard orientation)		
			X / Å	Y / Å	Z / Å
1	6	0	2.325564	–3.239786	–0.603483
2	6	0	3.393814	–3.297740	0.267662
3	6	0	4.462784	–2.440447	0.106293
4	6	0	4.463609	–1.525060	–0.926280
5	6	0	5.533628	0.247670	–2.120260
6	6	0	5.532804	–0.667717	–1.087687
7	1	0	6.269569	0.837893	–2.231387
8	1	0	6.268176	–0.707632	–0.487957
9	17	0	5.797419	–2.512974	1.194696
10	29	0	0.509428	–1.737759	–2.394784
11	35	0	–0.469456	0.862795	–1.776417
12	7	0	2.290413	–2.365693	–1.616520
13	6	0	3.395463	–1.466989	–1.797514
14	6	0	3.396287	–0.551602	–2.830086
15	6	0	4.465378	0.305624	–2.991404
16	1	0	–3.480221	1.712329	–2.355331
17	1	0	2.660914	–0.511686	–3.429816
18	17	0	4.466435	1.449374	–4.281539
19	1	0	3.393246	–3.927900	0.978489
20	29	0	–2.399437	–0.677605	–0.844386
21	35	0	–1.421096	–3.050521	–1.163493
22	7	0	–4.181105	0.236926	–1.245882
23	6	0	–4.217055	1.446466	–1.817929
24	6	0	–5.287303	–0.179323	–0.430636
25	6	0	–5.287356	–1.418775	0.175910
26	1	0	1.589502	–3.829942	–0.492406
27	1	0	–4.550680	–2.006114	0.055979
28	17	0	–6.357661	–3.353554	1.714388
29	6	0	2.320144	–0.963406	2.389119
30	6	0	3.388394	–1.021360	3.260263
31	6	0	4.457364	–0.164067	3.098895
32	6	0	4.458189	0.751320	2.066322
33	6	0	5.528208	2.524050	0.872342
34	6	0	5.527384	1.608663	1.904915
35	1	0	6.264149	3.114273	0.761214
36	1	0	6.262756	1.568748	2.504644
37	17	0	5.791999	–0.236594	4.187297
38	29	0	0.504008	0.538621	0.597818

39	35	0	–0.474876	3.139175	1.216185
40	7	0	2.284993	–0.089313	1.376082
41	6	0	3.390042	0.809392	1.195088
42	6	0	3.390867	1.724779	0.162515
43	6	0	4.459958	2.582004	0.001198
44	1	0	–5.287161	3.152850	–2.061250
45	1	0	2.655494	1.764694	–0.437215
46	17	0	4.461015	3.725754	–1.288938
47	1	0	3.387826	–1.651520	3.971091
48	29	0	–2.404858	1.598775	2.148215
49	35	0	–1.426516	–0.774141	1.829109
50	6	0	–5.287198	2.299605	–1.643698
51	6	0	–6.357290	1.913387	–0.863040
52	6	0	–6.357343	0.673934	–0.256494
53	6	0	–6.357569	–1.804927	0.956517
54	6	0	–7.427712	–0.951788	1.130748
55	6	0	–7.427659	0.287664	0.524202
56	1	0	1.584082	–1.553562	2.500195
57	1	0	–8.164425	–1.217717	1.668202
58	1	0	–8.164335	0.875003	0.644133
59	17	0	–7.694290	2.979325	–0.645472

Table S21. Cartesian coordinates of the crystallographic fragment used for the calculations (no geometry optimization) for species (**3**)

	Atomic coordinates		
	X / Å	Y / Å	Z / Å
Cu	6.45603	8.56494	0.71823
I	6.60875	11.27561	1.18508
N	10.16437	10.52665	3.47131
C	10.90787	9.41885	3.1187
C	12.12062	9.57679	2.47951
C	12.59001	10.84252	2.1929
C	11.84636	11.95031	2.54552
C	10.63361	11.79238	3.18474
C	9.89011	12.90017	3.53735
C	10.35936	14.1659	3.25078
C	11.57211	14.32384	2.61156
C	12.31561	13.21604	2.25894
H	10.58486	8.54749	3.316
H	12.63246	8.81423	2.23675
H	11.89526	15.1952	2.41429
H	13.1506	13.32466	1.81892
Cl	14.1191	11.04168	1.38697
Cu	7.86807	10.25911	2.87292
I	7.71536	7.54844	2.40607
N	4.15971	8.2974	0.11985
C	3.41621	9.40519	0.47247
C	2.20346	9.24726	1.11166
C	1.73407	7.98153	1.39826
C	2.47771	6.87373	1.04565
C	3.69046	7.03167	0.40643
C	4.43397	5.92387	0.05381
C	3.96472	4.65814	0.34038
C	2.75197	4.50021	0.97961
C	2.00847	5.608	1.33222
H	3.73921	10.27656	0.27517
H	1.69161	10.00982	1.35442
H	2.42882	3.62884	1.17687
H	1.17347	5.49939	1.77225
Cl	0.20498	7.78237	2.20419
Cl	4.90219	3.2614	–0.1042
H	5.26896	6.03268	–0.38621
Cl	9.42189	15.56265	3.69537
H	9.05518	12.79138	3.97735

Table S22. Cartesian atomic coordinates from the Standard orientation section of the Gaussian output for the fragment model used in the TD-DFT calculations for species (**3**)

Center number	Atomic number	Atomic type	Coordinates (standard orientation)		
			X / Å	Y / Å	Z / Å
1	29	0	6.456034	8.564943	0.718230
2	53	0	6.608751	11.275606	1.185079
3	7	0	10.164366	10.526649	3.471314
4	6	0	10.907869	9.418854	3.118699
5	6	0	12.120619	9.576788	2.479510
6	6	0	12.590010	10.842517	2.192900
7	6	0	11.846363	11.950312	2.545515
8	6	0	10.633613	11.792378	3.184740
9	6	0	9.890110	12.900174	3.537355
10	6	0	10.359357	14.165903	3.250781
11	6	0	11.572107	14.323837	2.611557
12	6	0	12.315610	13.216041	2.258942
13	1	0	10.584863	8.547489	3.315996
14	1	0	12.632463	8.814225	2.236748
15	1	0	11.895256	15.195202	2.414295
16	1	0	13.150603	13.324656	1.818918
17	17	0	14.119098	11.041675	1.386975
18	29	0	7.868074	10.259107	2.872919
19	53	0	7.715357	7.548444	2.406070
20	7	0	4.159711	8.297397	0.119852
21	6	0	3.416209	9.405192	0.472466
22	6	0	2.203459	9.247258	1.111655
23	6	0	1.734068	7.981529	1.398265
24	6	0	2.477714	6.873734	1.045650
25	6	0	3.690465	7.031668	0.406425
26	6	0	4.433967	5.923872	0.053810
27	6	0	3.964721	4.658143	0.340384
28	6	0	2.751970	4.500209	0.979609
29	6	0	2.008467	5.608005	1.332223
30	1	0	3.739214	10.276557	0.275169
31	1	0	1.691614	10.009821	1.354417
32	1	0	2.428822	3.628844	1.176870
33	1	0	1.173474	5.499390	1.772247
34	17	0	0.204980	7.782371	2.204190

35	17	0	4.902186	3.261399	–0.104200
36	1	0	5.268960	6.032675	–0.386213
37	17	0	9.421891	15.562647	3.695365
38	1	0	9.055179	12.791379	3.977346

Table S23. Cartesian coordinates of the crystallographic fragment used for the calculations (no geometry optimization) for **species (4)**

	Atomic coordinates		
	X / Å	Y / Å	Z / Å
Cl	20.73348	–18.84365	–7.70043
H	17.86433	–14.31753	0.03479
H	18.61617	–15.57579	–1.74207
C	21.05365	–16.5669	–6.3454
H	20.42296	–16.20178	–6.92392
C	21.40015	–17.87004	–6.43507
Cl	25.04315	–20.05065	–2.36424
C	22.69456	–19.78894	–5.50329
H	22.37081	–20.36484	–6.1577
C	24.00649	–19.40106	–3.58776
C	23.5199	–20.26267	–4.57022
H	23.76891	–21.15917	–4.57356
Cu	23.57186	–14.85266	–3.28692
Cl	25.85303	–15.08675	–3.95007
P	23.25507	–14.69866	–1.11499
N	22.53745	–16.22069	–4.49121
C	24.03161	–13.29629	–0.22766
C	21.48824	–14.52224	–0.68146
C	23.80746	–16.1335	–0.12239
C	22.83487	–17.56142	–4.53929
C	24.5398	–13.4026	1.0576
H	24.51141	–14.22098	1.49834
C	24.0957	–12.07565	–0.86781
H	23.77977	–11.99355	–1.73788
C	21.01926	–13.7604	0.37676
H	21.6217	–13.29863	0.91429
C	23.06116	–16.7255	0.88138
H	22.20366	–16.41462	1.06429
C	22.30098	–18.43055	–5.52019
C	20.56654	–15.18439	–1.476
H	20.86358	–15.68308	–2.2028
C	25.07368	–16.6328	–0.39348

H	25.57644	–16.26322	–1.08324
C	19.66713	–13.68066	0.63966
H	19.36099	–13.16528	1.35042
C	25.08763	–12.30496	1.68969
C	23.69396	–18.08411	–3.56697
H	24.04963	–17.529	–2.91104
C	18.77463	–14.36336	–0.14916
C	25.13441	–11.09821	1.05162
H	25.50767	–10.36085	1.47789
C	19.22303	–15.11563	–1.20829
C	21.66658	–15.77574	–5.36424
H	21.43964	–14.87493	–5.32993
C	24.62716	–10.97508	–0.22194
H	24.64246	–10.14909	–0.64953
C	23.58291	–17.77467	1.61432
H	23.07345	–18.16984	2.28438
C	25.59265	–17.67229	0.34856
H	26.44748	–17.9913	0.16808
C	24.84763	–18.23627	1.35701
H	25.20147	–18.93143	1.86433
Cu	25.32557	–13.02338	–5.08419
Cl	23.0444	–12.78929	–4.42103
P	25.64237	–13.17738	–7.25612
Cl	28.16395	–9.03239	–0.67067
Cl	23.85428	–7.82539	–6.00687
N	26.35999	–11.65535	–3.8799
C	24.86583	–14.57975	–8.14345
C	27.4092	–13.3538	–7.68965
C	25.08997	–11.74254	–8.24871
C	26.06256	–10.31462	–3.83182
C	24.35763	–14.47344	–9.4287
H	24.38603	–13.65506	–9.86944
C	24.80174	–15.80039	–7.50329
H	25.11766	–15.88249	–6.63322
C	27.87818	–14.11564	–8.74787
H	27.27573	–14.57741	–9.2854
C	25.83628	–11.15054	–9.25248
H	26.69378	–11.46142	–9.43539
C	26.59645	–9.44549	–2.85092
C	28.3309	–12.69165	–6.89511
H	28.03386	–12.19296	–6.16831
C	23.82376	–11.24324	–7.97763

H	23.321	–11.61282	–7.28787
C	29.2303	–14.19538	–9.01077
H	29.53644	–14.71076	–9.72153
C	23.80981	–15.57108	–10.0608
C	25.20348	–9.79193	–4.80414
H	24.84781	–10.34704	–5.46007
C	30.12281	–13.51268	–8.22194
H	31.03311	–13.55851	–8.40589
C	23.76303	–16.77783	–9.42272
H	23.38976	–17.51519	–9.849
C	29.67441	–12.76041	–7.16281
H	30.28126	–12.30025	–6.62904
C	26.20287	–8.0871	–2.86781
H	26.52662	–7.5112	–2.2134
C	27.23086	–12.1003	–3.00686
H	27.4578	–13.00111	–3.04117
C	24.27028	–16.90096	–8.14917
H	24.25497	–17.72695	–7.72158
C	25.31453	–10.10137	–9.98543
H	25.82399	–9.7062	–10.65548
C	23.30478	–10.20375	–8.71967
H	22.44996	–9.88474	–8.53919
C	27.84379	–11.30914	–2.02571
H	28.47447	–11.67426	–1.44719
C	27.49729	–10.006	–1.93604
C	24.89094	–8.47498	–4.78334
C	25.37753	–7.61337	–3.80089
H	25.12852	–6.71687	–3.79755
C	24.0498	–9.63977	–9.72812
H	23.69597	–8.94461	–10.23543
H	23.47062	–15.48867	–10.9223
H	25.42681	–12.38737	2.5512

Table S24. Cartesian atomic coordinates from the Standard orientation section of the Gaussian output for the fragment model used in the TD-DFT calculations for **species (4)**

			Coordinates (Standard orientation)		
Center Number	Atomic Number	Atomic Type	X / Å	Y / Å	Z / Å
1	17	0	–3.715234	–4.905635	–3.514882
2	1	0	–6.584388	–0.379513	4.220340
3	1	0	–5.832547	–1.637769	2.443484
4	6	0	–3.395070	–2.628878	–2.159845

5	1	0	–4.025753	–2.263764	–2.738364
6	6	0	–3.048572	–3.932017	–2.249514
7	17	0	0.594433	–6.112627	1.821314
8	6	0	–1.754154	–5.850920	–1.317740
9	1	0	–2.077907	–6.426821	–1.972152
10	6	0	–0.442227	–5.463035	0.597791
11	6	0	–0.928814	–6.324649	–0.384666
12	1	0	–0.679807	–7.221148	–0.388005
13	29	0	–0.876855	–0.914636	0.898636
14	17	0	1.404314	–1.148728	0.235478
15	15	0	–1.193651	–0.760639	3.070567
16	7	0	–1.911268	–2.282670	–0.305653
17	6	0	–0.417111	0.641730	3.957897
18	6	0	–2.960481	–0.584218	3.504095
19	6	0	–0.641255	–2.195485	4.063160
20	6	0	–1.613845	–3.623401	–0.353736
21	6	0	0.091084	0.535419	5.243148
22	1	0	0.062689	–0.282960	5.683889
23	6	0	–0.353022	1.862374	3.317741
24	1	0	–0.668944	1.944468	2.447669
25	6	0	–3.429458	0.177620	4.562316
26	1	0	–2.827016	0.639393	5.099847
27	6	0	–1.387559	–2.787477	5.066929
28	1	0	–2.245060	–2.476605	5.249840
29	6	0	–2.147733	–4.492535	–1.334634
30	6	0	–3.882181	–1.246373	2.709553
31	1	0	–3.585140	–1.745063	1.982756
32	6	0	0.624962	–2.694778	3.792075
33	1	0	1.127721	–2.325197	3.102315
34	6	0	–4.781585	0.257362	4.825214
35	1	0	–5.087725	0.772739	5.535974
36	6	0	0.638912	1.633057	5.875247
37	6	0	–0.754762	–4.146092	0.618584
38	1	0	–0.399090	–3.590980	1.274517
39	6	0	–5.674088	–0.425342	4.036389
40	6	0	0.685691	2.839812	5.237170
41	1	0	1.058954	3.577173	5.663447
42	6	0	–5.225689	–1.177615	2.977260
43	6	0	–2.782139	–1.837722	–1.178688
44	1	0	–3.009081	–0.936910	–1.144380
45	6	0	0.178442	2.962940	3.963615
46	1	0	0.193747	3.788929	3.536025

47	6	0	–0.865808	–3.836650	5.799873
48	1	0	–1.375270	–4.231822	6.469932
49	6	0	1.143937	–3.734265	4.534116
50	1	0	1.998758	–4.053276	4.353635
51	6	0	0.398916	–4.298252	5.542563
52	1	0	0.752748	–4.993413	6.049880
53	29	0	0.876855	0.914636	–0.898636
54	17	0	–1.404314	1.148728	–0.235478
55	15	0	1.193651	0.760639	–3.070567
56	17	0	3.715234	4.905635	3.514882
57	17	0	–0.594433	6.112627	–1.821314
58	7	0	1.911268	2.282670	0.305653
59	6	0	0.417111	–0.641730	–3.957897
60	6	0	2.960481	0.584218	–3.504095
61	6	0	0.641255	2.195485	–4.063160
62	6	0	1.613845	3.623401	0.353736
63	6	0	–0.091084	–0.535419	–5.243148
64	1	0	–0.062689	0.282960	–5.683889
65	6	0	0.353022	–1.862374	–3.317741
66	1	0	0.668944	–1.944468	–2.447669
67	6	0	3.429458	–0.177620	–4.562316
68	1	0	2.827016	–0.639393	–5.099847
69	6	0	1.387559	2.787477	–5.066929
70	1	0	2.245060	2.476605	–5.249840
71	6	0	2.147733	4.492535	1.334634
72	6	0	3.882181	1.246373	–2.709553
73	1	0	3.585140	1.745063	–1.982756
74	6	0	–0.624962	2.694778	–3.792075
75	1	0	–1.127721	2.325197	–3.102315
76	6	0	4.781585	–0.257362	–4.825214
77	1	0	5.087725	–0.772739	–5.535974
78	6	0	–0.638912	–1.633057	–5.875247
79	6	0	0.754762	4.146092	–0.618584
80	1	0	0.399090	3.590980	–1.274517
81	6	0	5.674088	0.425342	–4.036389
82	1	0	6.584388	0.379513	–4.220340
83	6	0	–0.685691	–2.839812	–5.237170
84	1	0	–1.058954	–3.577173	–5.663447
85	6	0	5.225689	1.177615	–2.977260
86	1	0	5.832547	1.637769	–2.443484
87	6	0	1.754154	5.850920	1.317740
88	1	0	2.077907	6.426821	1.972152

89	6	0	2.782139	1.837722	1.178688
90	1	0	3.009081	0.936910	1.144380
91	6	0	–0.178442	–2.962940	–3.963615
92	1	0	–0.193747	–3.788929	–3.536025
93	6	0	0.865808	3.836650	–5.799873
94	1	0	1.375270	4.231822	–6.469932
95	6	0	–1.143937	3.734265	–4.534116
96	1	0	–1.998758	4.053276	–4.353635
97	6	0	3.395070	2.628878	2.159845
98	1	0	4.025753	2.263764	2.738364
99	6	0	3.048572	3.932017	2.249514
100	6	0	0.442227	5.463035	–0.597791
101	6	0	0.928814	6.324649	0.384666
102	1	0	0.679807	7.221148	0.388005
103	6	0	–0.398916	4.298252	–5.542563
104	1	0	–0.752748	4.993413	–6.049880
105	1	0	–0.978096	–1.550647	–6.736751
106	1	0	0.978096	1.550647	6.736751

Table S25. Cartesian coordinates of the crystallographic fragment used for the calculations (no geometry optimization) for **species (5)**

	Atomic coordinates		
	X / Å	Y / Å	Z / Å
Cl	42.43711	–6.42717	8.993
H	39.489	–11.05844	1.26374
H	40.25806	–9.70271	2.94259
C	43.06967	–7.41844	7.71622
C	42.68357	–8.71226	7.63157
H	42.04807	–9.06014	8.21472
Cl	45.35706	–17.52984	7.31339
C	46.4055	–16.90799	6.09271
C	46.86676	–17.77935	5.10669
H	46.59881	–18.66976	5.1059
C	47.69959	–17.32532	4.15953
H	47.99881	–17.90804	3.49954
Br	44.53223	–12.64547	5.7005
Cu	46.93854	–12.37928	6.37349
P	47.22458	–12.18126	8.55907
Cl	49.66356	–16.42651	1.95114
N	47.95515	–13.76441	5.18054
C	48.98786	–12.00416	8.98756

C	46.45266	–10.76181	9.429
C	46.669	–13.60125	9.56648
C	47.62339	–15.09362	5.13649
C	49.46833	–11.19112	9.99535
H	48.87335	–10.69291	10.50778
C	45.40916	–14.10816	9.31123
H	44.90033	–13.74948	8.62081
C	47.43572	–14.18285	10.57323
H	48.29327	–13.8681	10.74765
C	46.46053	–9.52964	8.8059
H	46.82022	–9.44532	7.95287
C	45.88836	–10.86921	10.68726
H	45.87119	–11.69429	11.11643
C	49.9041	–12.72568	8.2332
H	49.60484	–13.26583	7.53718
C	46.7595	–15.5979	6.11085
H	46.42672	–15.03616	6.77299
C	50.81149	–11.10805	10.24801
H	51.12294	–10.55247	10.92531
C	48.13241	–15.9771	4.14269
C	51.70048	–11.84527	9.50299
H	52.61167	–11.79524	9.68041
C	45.34765	–9.7574	11.31178
C	45.37277	–8.54495	10.69503
H	45.00862	–7.802	11.11884
C	48.83253	–13.34271	4.30076
H	49.08312	–12.44778	4.33617
C	44.89595	–15.14193	10.0705
H	44.039	–15.46222	9.90508
C	46.91438	–15.23107	11.31437
C	51.24112	–12.64947	8.50401
H	51.84261	–13.15097	8.00156
C	45.65847	–15.69763	11.07337
H	45.31405	–16.3931	11.58666
C	49.031	–15.43524	3.22793
C	45.93479	–8.415	9.44727
H	45.96241	–7.58283	9.03265
C	49.4171	–14.14143	3.31258
H	50.05261	–13.79354	2.72943
Br	47.56844	–10.20821	5.24364
Cu	45.16214	–10.4744	4.57066
P	44.8761	–10.67242	2.38507

Cl	46.74362	–5.32385	3.63076
N	44.14553	–9.08927	5.76361
C	43.11281	–10.84952	1.95659
C	45.64801	–12.09188	1.51514
C	45.43168	–9.25243	1.37767
C	44.47728	–7.76006	5.80766
C	42.63235	–11.66257	0.94879
H	43.22732	–12.16077	0.43637
C	46.69152	–8.74552	1.63292
H	47.20034	–9.10421	2.32333
C	44.66495	–8.67083	0.37091
H	43.80741	–8.98558	0.1965
C	45.64014	–13.32404	2.13824
H	45.28046	–13.40836	2.99128
C	46.21231	–11.98448	0.25689
H	46.22949	–11.15939	–0.17228
C	42.19657	–10.128	2.71094
H	42.49583	–9.58785	3.40696
C	45.34117	–7.25578	4.83329
H	45.67395	–7.81752	4.17115
C	41.28918	–11.74563	0.69613
H	40.97774	–12.30121	0.01883
C	43.96826	–6.87658	6.80146
C	40.40019	–11.00841	1.44116
C	46.75302	–13.09628	–0.36764
C	46.7279	–14.30873	0.24912
H	47.09205	–15.05169	–0.17469
C	43.26815	–9.51098	6.64338
H	43.01755	–10.4059	6.60797
C	47.20472	–7.71175	0.87364
H	48.06167	–7.39146	1.03906
C	45.69518	–5.94569	4.85143
C	45.1863	–7.62261	0.37023
C	40.85955	–10.20421	2.44014
C	46.4422	–7.15605	0.12923
H	46.78662	–6.46059	–0.64252
C	45.23392	–5.07433	5.83746
H	45.50186	–4.18392	5.83825
C	46.16588	–14.43869	1.49687
H	46.13827	–15.27085	1.9115
C	44.40108	–5.52837	6.78462
H	44.10186	–4.94564	7.4446

H	47.13494	–13.01357	–1.21173
H	44.96573	–9.84011	12.15587
H	47.42893	–15.62131	11.98456
H	44.67175	–7.23237	–1.04041

Table S26. Cartesian atomic coordinates from the Standard orientation section of the Gaussian output for the fragment model used in the TD-DFT calculations for **species (5)**

			Coordinates (Standard orientation)		
Center Number	Atomic Number	Atomic Type	X / Å	Y / Å	Z / Å
1	17	0	–3.613224	4.999666	3.520928
2	1	0	–6.561337	0.368400	–4.208335
3	1	0	–5.792278	1.724129	–2.529487
4	6	0	–2.980669	4.008401	2.244148
5	6	0	–3.366766	2.714585	2.159496
6	1	0	–4.002270	2.366698	2.742642
7	17	0	–0.693281	–6.102995	1.841316
8	6	0	0.355159	–5.481152	0.620639
9	6	0	0.816420	–6.352508	–0.365387
10	1	0	0.548471	–7.242918	–0.366177
11	6	0	1.649254	–5.898474	–1.312542
12	1	0	1.948472	–6.481197	–1.972531
13	35	0	–1.518106	–1.218627	0.228431
14	29	0	0.888200	–0.952443	0.901417
15	15	0	1.174240	–0.754420	3.086999
16	17	0	3.613224	–4.999666	–3.520928
17	7	0	1.904810	–2.337567	–0.291532
18	6	0	2.937523	–0.577319	3.515487
19	6	0	0.402327	0.665035	3.956931
20	6	0	0.618661	–2.174409	4.094404
21	6	0	1.573057	–3.666780	–0.335586
22	6	0	3.417990	0.235725	4.523280
23	1	0	2.823013	0.733927	5.035703
24	6	0	–0.641179	–2.681324	3.839152
25	1	0	–1.150002	–2.322635	3.148739
26	6	0	1.385389	–2.756011	5.101161
27	1	0	2.242930	–2.441257	5.275575
28	6	0	0.410196	1.897197	3.333830
29	1	0	0.769880	1.981519	2.480794
30	6	0	–0.161976	0.557635	5.215183
31	1	0	–0.179150	–0.267453	5.644356
32	6	0	3.853768	–1.298839	2.761131

33	1	0	3.554507	–1.838987	2.065109
34	6	0	0.709168	–4.171060	0.638779
35	1	0	0.376388	–3.609317	1.300919
36	6	0	4.761155	0.318792	4.775941
37	1	0	5.072599	0.874373	5.453241
38	6	0	2.082074	–4.550264	–1.329386
39	6	0	5.650142	–0.418434	4.030915
40	1	0	6.561337	–0.368400	4.208335
41	6	0	–0.702681	1.669443	5.839709
42	6	0	–0.677567	2.881890	5.222957
43	1	0	–1.041712	3.624845	5.646766
44	6	0	2.782190	–1.915865	–1.171311
45	1	0	3.032782	–1.020943	–1.135899
46	6	0	–1.154382	–3.715092	4.598431
47	1	0	–2.011336	–4.035379	4.433009
48	6	0	0.864041	–3.804229	5.842300
49	6	0	5.190782	–1.222633	3.031932
50	1	0	5.792278	–1.724129	2.529487
51	6	0	–0.391868	–4.270793	5.601300
52	1	0	–0.736285	–4.966255	6.114591
53	6	0	2.980669	–4.008401	–2.244148
54	6	0	–0.115546	3.011844	3.975200
55	1	0	–0.087929	3.844014	3.560577
56	6	0	3.366766	–2.714585	–2.159496
57	1	0	4.002270	–2.366698	–2.742642
58	35	0	1.518106	1.218627	–0.228431
59	29	0	–0.888200	0.952443	–0.901417
60	15	0	–1.174240	0.754420	–3.086999
61	17	0	0.693281	6.102995	–1.841316
62	7	0	–1.904810	2.337567	0.291532
63	6	0	–2.937523	0.577319	–3.515487
64	6	0	–0.402327	–0.665035	–3.956931
65	6	0	–0.618661	2.174409	–4.094404
66	6	0	–1.573057	3.666780	0.335586
67	6	0	–3.417990	–0.235725	–4.523280
68	1	0	–2.823013	–0.733927	–5.035703
69	6	0	0.641179	2.681324	–3.839152
70	1	0	1.150002	2.322635	–3.148739
71	6	0	–1.385389	2.756011	–5.101161
72	1	0	–2.242930	2.441257	–5.275575
73	6	0	–0.410196	–1.897197	–3.333830
74	1	0	–0.769880	–1.981519	–2.480794

75	6	0	0.161976	–0.557635	–5.215183
76	1	0	0.179150	0.267453	–5.644356
77	6	0	–3.853768	1.298839	–2.761131
78	1	0	–3.554507	1.838987	–2.065109
79	6	0	–0.709168	4.171060	–0.638779
80	1	0	–0.376388	3.609317	–1.300919
81	6	0	–4.761155	–0.318792	–4.775941
82	1	0	–5.072599	–0.874373	–5.453241
83	6	0	–2.082074	4.550264	1.329386
84	6	0	–5.650142	0.418434	–4.030915
85	6	0	0.702681	–1.669443	–5.839709
86	6	0	0.677567	–2.881890	–5.222957
87	1	0	1.041712	–3.624845	–5.646766
88	6	0	–2.782190	1.915865	1.171311
89	1	0	–3.032782	1.020943	1.135899
90	6	0	1.154382	3.715092	–4.598431
91	1	0	2.011336	4.035379	–4.433009
92	6	0	–0.355159	5.481152	–0.620639
93	6	0	–0.864041	3.804229	–5.842300
94	6	0	–5.190782	1.222633	–3.031932
95	6	0	0.391868	4.270793	–5.601300
96	1	0	0.736285	4.966255	–6.114591
97	6	0	–0.816420	6.352508	0.365387
98	1	0	–0.548471	7.242918	0.366177
99	6	0	0.115546	–3.011844	–3.975200
100	1	0	0.087929	–3.844014	–3.560577
101	6	0	–1.649254	5.898474	1.312542
102	1	0	–1.948472	6.481197	1.972531
103	1	0	1.084604	–1.586730	–6.683801
104	1	0	–1.084604	1.586730	6.683801
105	1	0	1.378590	–4.194473	6.512487
106	1	0	–1.378590	4.194473	–6.512487

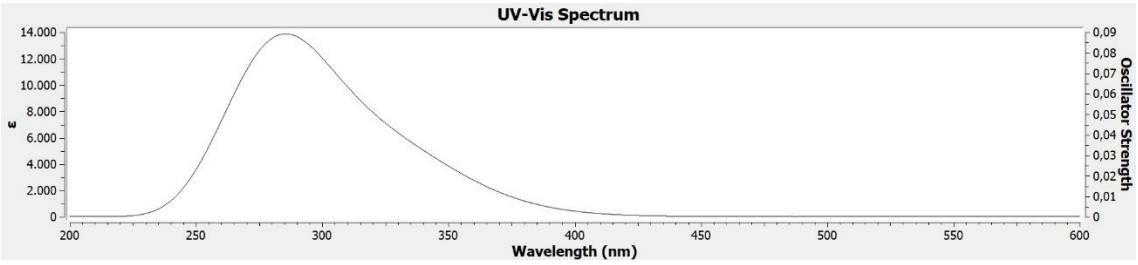


Figure S101. TD-DFT absorption spectrum simulated for the fragment of **(1)**.

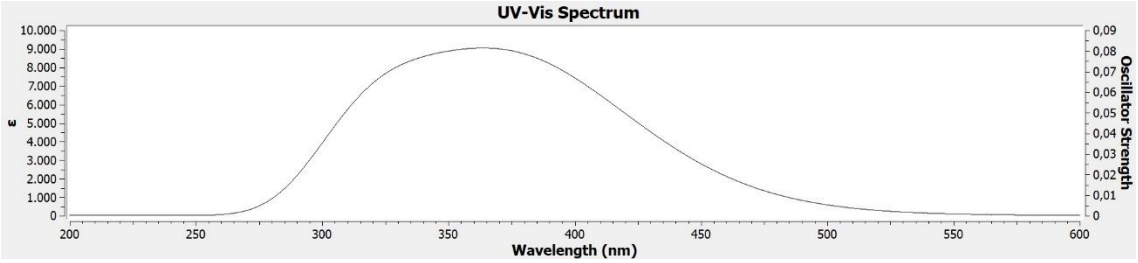


Figure S102. TD-DFT absorption spectrum simulated for the fragment of **(2)**.

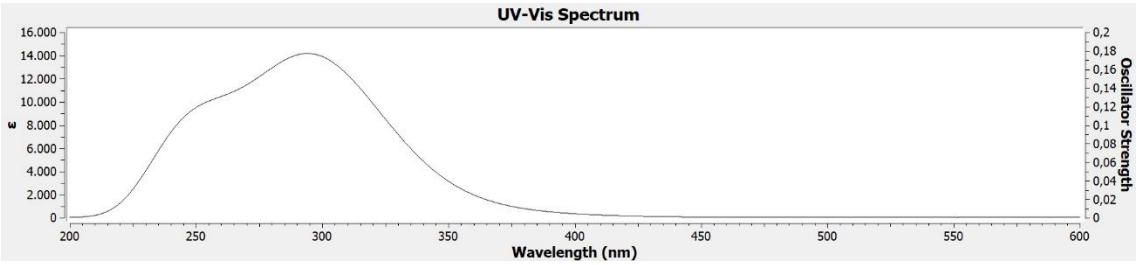


Figure S103. TD-DFT absorption spectrum simulated for the fragment of **(3)**.

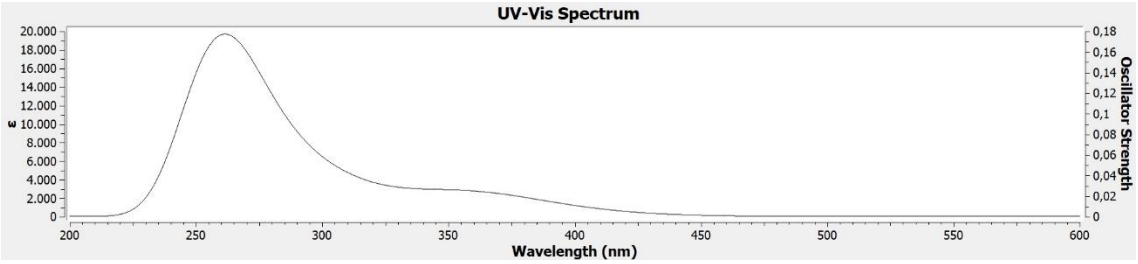


Figure S104. TD-DFT absorption spectrum simulated for the complex **(4)**.

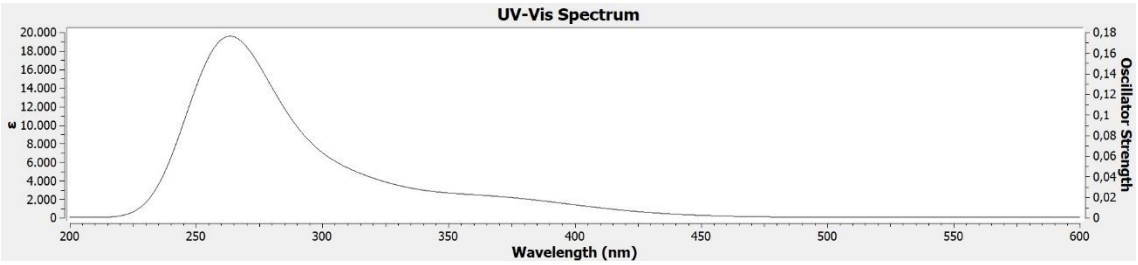


Figure S105. TD-DFT absorption spectrum simulated for the complex **(5)**.

Table S27. UV-Vis spectral details for complex **(1)**. Results obtained at the TD-DFT/CAM-B3LYP/6-311G (d,p) theory level

Wavelength / nm	Energy / eV	Osc. Strength	Symmetry	Major contribs	Minor contribs
487.5	2.5431	0.0	Triplet-A	H–7→LUMO (11%), H–6→LUMO (11%)	H–13→LUMO (2%), H–11→LUMO (2%), H–9→LUMO (3%), H–9→L+1 (2%), H–8→LUMO (3%), H–8→L+1 (2%), H–7→L+1 (8%), H–6→L+1 (7%), H–4→LUMO (3%), H–4→L+1 (2%), H–3→LUMO (7%), H–3→L+1 (5%), H–1→LUMO (3%)
486.8	2.5470	0.0	Triplet-A	H–7→L+1 (11%), H–6→L+1 (10%)	H–13→L+1 (2%), H–11→L+1 (3%), H–9→LUMO (2%), H–9→L+1 (3%), H–8→LUMO (2%), H–8→L+1 (3%), H–7→LUMO (8%), H–6→LUMO (7%), H–4→LUMO (2%), H–4→L+1 (3%), H–3→LUMO (5%), H–3→L+1 (6%), H–1→L+1 (3%)
383.9	3.2297	0.0	Triplet-A	H–2→L+1 (10%), H–2→L+5 (14%), HOMO→LUMO (25%), HOMO→L+4 (27%)	HOMO→L+2 (6%)
379.2	3.2696	0.0	Triplet-A	H–2→LUMO (19%), H–2→L+4 (19%), HOMO→L+1 (23%), HOMO→L+5 (15%)	H–2→L+2 (4%)
362.1	3.4244	0.0	Triplet-A	H–2→L+1 (19%), HOMO→LUMO (28%), HOMO→L+4 (17%)	H–2→L+5 (7%), H–2→L+7 (3%), HOMO→L+6 (4%)
361.3	3.4313	0.0	Triplet-A	H–2→LUMO (10%), H–2→L+4 (19%), HOMO→L+1 (30%), HOMO→L+5 (11%)	H–2→L+2 (2%), H–2→L+6 (3%), HOMO→L+7 (4%)
358.7	3.4564	0.003	Singlet-A	H–2→L+1 (23%), HOMO→LUMO (54%)	H–2→L+5 (3%), HOMO→L+2 (3%), HOMO→L+4 (8%)
356.2	3.4808	0.0	Singlet-A	H–2→LUMO (31%), HOMO→L+1 (54%)	HOMO→L+5 (2%)

352.5	3.5173	0.0	Triplet-A	H–1→LUMO (11%), H–1→L+4 (41%)	H–5→L+5 (7%), H–3→L+5 (5%), H–1→L+2 (8%)
340.5	3.6412	0.0	Triplet-A	H–1→L+1 (17%), H–1→L+5 (17%)	H–13→L+1 (3%), H–12→LUMO (5%), H–11→L+1 (4%), H–9→LUMO (3%), H–7→LUMO (2%), H–5→LUMO (2%), H–5→L+4 (6%), H–3→LUMO (4%), H–3→L+2 (2%), H–3→L+4 (8%)
337.6	3.6728	0.0335	Singlet-A	H–2→L+5 (12%), HOMO→L+4 (42%)	H–2→L+1 (9%), H–2→L+7 (2%), H–1→LUMO (3%), HOMO→LUMO (6%), HOMO→L+2 (6%), HOMO→L+6 (3%)
334.9	3.7022	0.0	Triplet-A	H–13→LUMO (15%), H–12→L+1 (19%), H–1→LUMO (12%)	H–11→LUMO (9%), H–9→L+1 (4%), H–8→LUMO (2%), H–7→L+1 (3%), H–3→L+1 (3%), H–1→L+4 (6%), H–1→L+6 (2%)
332.9	3.7246	0.0	Triplet-A	H–13→L+1 (11%), H–12→LUMO (15%), H–1→L+5 (15%)	H–11→L+1 (5%), H–5→L+4 (8%), H–3→L+4 (6%), H–1→L+1 (5%), H–1→L+7 (3%)
331.3	3.7418	0.0584	Singlet-A	H–1→LUMO (45%), H–1→L+4 (22%)	H–5→L+1 (3%), H–5→L+5 (2%), H–3→L+1 (4%), H–3→L+5 (3%), H–1→L+2 (5%), HOMO→L+4 (3%)
330.2	3.7548	0.0	Singlet-A	H–2→L+4 (35%), HOMO→L+5 (28%)	H–2→L+2 (6%), HOMO→L+1 (5%), HOMO→L+7 (3%)
323.7	3.8304	0.0	Singlet-A	H–1→L+1 (54%), H–1→L+5 (10%)	H–5→LUMO (5%), H–3→LUMO (9%), H–3→L+4 (6%)
323.6	3.8313	0.0	Triplet-A	H–13→L+1 (17%), H–12→LUMO (15%), H–1→L+1 (24%)	H–20→L+1 (2%), H–19→LUMO (3%), H–15→LUMO (5%), H–13→LUMO (3%), H–10→LUMO (3%), H–3→LUMO (3%), H–1→LUMO (4%)
323.3	3.8351	0.0	Triplet-A	H–13→LUMO (16%), H–12→L+1 (14%), H–1→LUMO (22%)	H–20→LUMO (3%), H–19→L+1 (3%), H–15→L+1 (5%), H–13→L+1 (3%), H–10→L+1 (3%), H–3→L+1 (4%), H–1→L+1 (4%)
320.1	3.8737	0.0	Triplet-A	H–10→L+5 (12%), H–4→L+4 (35%)	H–14→L+4 (4%), H–4→LUMO (3%), H–4→L+2 (6%), H–3→L+5 (6%), H–2→L+5 (4%), HOMO→L+4 (2%)
319.0	3.8864	0.0	Triplet-A	H–5→L+4 (10%), H–4→L+5 (13%), H–3→L+4 (20%)	H–15→L+4 (6%), H–14→L+5 (2%), H–11→L+5 (5%), H–10→L+4 (4%), H–6→L+5 (4%), H–3→L+2 (3%), H–1→L+1 (3%)

313.4	3.9560	0.0	Triplet-A	H–6→L+4 (24%), H–3→L+5 (10%)	H–15→L+5 (3%), H–11→L+4 (8%), H–10→L+5 (3%), H–8→L+4 (4%), H–6→LUMO (3%), H–6→L+2 (4%), H–5→L+5 (8%), H–1→LUMO (4%)
311.0	3.9872	0.0	Triplet-A	H–10→L+4 (27%), H–6→L+5 (11%)	H–11→L+5 (4%), H–10→L+2 (4%), H–5→L+4 (6%), H–4→L+5 (9%), HOMO→L+5 (6%)
310.2	3.9965	0.0244	Singlet-A	H–1→LUMO (30%), H–1→L+4 (31%)	H–17→L+4 (2%), H–10→L+5 (3%), H–5→L+1 (3%), H–5→L+5 (3%), H–3→L+1 (4%), H–3→L+5 (2%), H–1→L+2 (4%), H–1→L+6 (3%)
309.8	4.0018	0.0011	Singlet-A	H–3→L+4 (17%), H–1→L+1 (25%), H–1→L+5 (22%)	H–10→L+4 (3%), H–5→L+4 (3%), H–3→L+2 (3%), H–1→L+7 (3%)
303.2	4.0897	0.0	Triplet-A	H–9→L+4 (20%), H–8→L+5 (11%), H–7→L+4 (12%)	H–20→L+1 (2%), H–11→L+5 (7%), H–9→L+2 (4%), H–9→L+6 (2%), H–8→L+7 (2%), H–1→L+1 (3%)
302.5	4.0983	0.0	Triplet-A	H–11→L+4 (16%), H–9→L+5 (14%), H–8→L+4 (21%)	H–14→L+4 (2%), H–11→L+2 (3%), H–8→LUMO (2%), H–8→L+2 (4%), H–7→L+5 (8%)
301.7	4.1090	0.0	Triplet-A	H–1→L+1 (16%)	H–20→L+1 (7%), H–19→LUMO (7%), H–9→L+4 (5%), H–8→L+5 (5%), H–7→L+6 (5%), H–6→L+1 (2%), H–6→L+7 (4%), H–4→L+1 (2%), H–3→LUMO (3%), H–1→LUMO (5%)
301.5	4.1120	0.0	Triplet-A	H–1→LUMO (19%)	H–20→LUMO (8%), H–20→L+1 (2%), H–19→L+1 (7%), H–7→L+7 (4%), H–6→LUMO (3%), H–6→L+6 (4%), H–5→L+1 (3%), H–3→L+1 (4%), H–1→L+1 (5%)
299.3	4.1428	0.0	Singlet-A	H–5→L+4 (10%), H–3→LUMO (12%)	H–15→L+4 (3%), H–11→L+5 (4%), H–10→L+4 (5%), H–4→L+1 (6%), H–4→L+5 (6%), H–3→L+4 (8%), H–2→LUMO (6%), H–1→L+5 (7%)
298.0	4.1607	0.0242	Singlet-A	H–4→LUMO (17%), H–4→L+4 (13%), H–2→L+1 (11%)	H–11→L+4 (3%), H–10→L+1 (2%), H–10→L+5 (2%), H–8→LUMO (2%), H–8→L+4 (3%), H–4→L+2 (3%), H–3→L+1 (8%), H–3→L+5 (5%), H–2→L+5 (5%), H–1→LUMO (3%), HOMO→LUMO (5%)
292.5	4.2395	0.0621	Singlet-A	H–6→LUMO (11%), H–6→L+4 (14%)	H–11→L+4 (3%), H–8→L+4 (3%), H–6→L+1 (3%), H–6→L+2 (3%), H–6→L+5 (2%), H–5→L+1 (2%), H–5→L+4 (2%), H–5→L+5 (6%), H–3→L+1 (4%), H–3→L+5 (4%), H–2→LUMO (4%), H–2→L+1 (2%), HOMO→LUMO (2%), HOMO→L+1 (4%)

292.4	4.2398	0.021	Singlet-A	H–2→LUMO (15%), HOMO→L+1 (10%)	H–10→LUMO (3%), H–6→LUMO (5%), H–6→L+1 (4%), H–6→L+4 (5%), H–6→L+5 (6%), H–5→LUMO (3%), H–5→L+4 (6%), H–5→L+5 (2%), H–4→L+1 (4%), H–3→L+4 (3%)
291.8	4.2488	0.0	Triplet-A	H–4→L+1 (10%), H–2→LUMO (28%), HOMO→L+1 (20%)	H–10→LUMO (4%), H–6→L+1 (5%), H–4→LUMO (2%), H–3→LUMO (3%), H–2→L+1 (3%), HOMO→LUMO (5%)
291.6	4.2519	0.0	Triplet-A	H–2→L+1 (29%), HOMO→LUMO (20%)	H–10→L+1 (4%), H–6→LUMO (4%), H–4→LUMO (9%), H–4→L+1 (2%), H–3→L+1 (4%), H–2→LUMO (2%), HOMO→L+1 (5%)
287.8	4.3084	0.0811	Singlet-A	H–4→L+4 (13%), H–3→L+1 (10%), H–2→L+1 (17%)	H–11→L+4 (4%), H–8→L+4 (6%), H–4→LUMO (6%), H–3→L+5 (4%), H–2→L+5 (2%), HOMO→LUMO (9%)
286.3	4.3302	0.0001	Singlet-A	H–9→L+4 (10%), H–4→L+1 (14%), H–3→LUMO (16%)	H–11→L+5 (4%), H–8→L+5 (7%), H–7→LUMO (9%), H–7→L+4 (4%), H–6→L+1 (8%), H–3→L+4 (3%), H–2→L+4 (3%)
283.6	4.3722	0.0368	Singlet-A	H–6→LUMO (12%), H–6→L+4 (10%), H–3→L+1 (10%)	H–11→L+4 (6%), H–10→L+5 (3%), H–7→L+1 (6%), H–5→L+1 (3%), H–5→L+5 (5%), H–4→LUMO (2%), H–2→L+1 (9%), HOMO→LUMO (9%)
283.2	4.3783	0.001	Singlet-A	H–6→L+1 (10%), H–2→LUMO (12%), HOMO→L+1 (10%)	H–10→L+4 (8%), H–9→L+4 (3%), H–8→L+5 (4%), H–6→L+5 (8%), H–5→L+4 (7%), H–4→L+5 (3%), H–3→LUMO (4%), H–2→L+4 (2%)
280.6	4.4186	0.0203	Singlet-A	H–8→L+4 (11%)	H–14→L+4 (4%), H–11→LUMO (4%), H–11→L+4 (4%), H–10→L+1 (3%), H–10→L+5 (3%), H–9→L+1 (4%), H–9→L+5 (9%), H–8→LUMO (5%), H–8→L+2 (3%), H–7→L+5 (5%), H–6→LUMO (4%), H–5→L+1 (5%), H–4→LUMO (5%), H–4→L+4 (8%), H–3→L+1 (6%)
279.4	4.4372	0.0	Singlet-A		H–14→L+5 (3%), H–10→LUMO (4%), H–10→L+4 (9%), H–9→LUMO (8%), H–9→L+2 (2%), H–9→L+4 (7%), H–8→L+1 (5%), H–8→L+5 (3%), H–7→L+4 (6%), H–6→L+1 (4%), H–5→LUMO (4%), H–4→L+5 (9%), H–3→LUMO (9%), H–3→L+4 (3%)
279.0	4.4435	0.0	Triplet-A	H–5→L+1 (11%), H–3→L+1 (15%)	H–20→LUMO (3%), H–19→L+1 (3%), H–11→LUMO (3%), H–11→L+2 (2%), H–7→L+3 (5%), H–6→LUMO (5%), H–6→L+2 (4%), H–6→L+4 (2%), H–5→LUMO (3%), H–3→LUMO (4%), H–3→L+3 (4%)

278.8	4.4464	0.0	Triplet-A	H–5→LUMO (10%), H–3→LUMO (15%)	H–20→L+1 (3%), H–19→LUMO (2%), H–11→L+1 (3%), H–11→L+3 (3%), H–8→L+3 (2%), H–7→L+2 (4%), H–6→L+1 (5%), H–6→L+3 (6%), H–5→L+1 (3%), H–3→L+1 (4%), H–3→L+2 (2%)
276.7	4.4813	0.0	Triplet-A		H–13→L+2 (5%), H–13→L+3 (2%), H–12→L+2 (4%), H–12→L+3 (6%), H–11→LUMO (4%), H–11→L+1 (2%), H–11→L+2 (5%), H–11→L+3 (2%), H–9→L+3 (2%), H–8→L+2 (3%), H–7→LUMO (3%), H–7→L+1 (3%), H–7→L+2 (4%), H–7→L+3 (5%), H–6→L+2 (5%), H–5→LUMO (4%), H–5→L+1 (4%), H–3→LUMO (3%), H–3→L+1 (3%)
276.4	4.4854	0.0	Triplet-A		H–13→L+2 (2%), H–13→L+3 (5%), H–12→L+2 (5%), H–12→L+3 (5%), H–11→L+1 (5%), H–11→L+2 (2%), H–11→L+3 (5%), H–9→L+2 (2%), H–9→L+3 (2%), H–8→L+3 (3%), H–7→LUMO (3%), H–7→L+1 (2%), H–7→L+2 (4%), H–7→L+3 (5%), H–6→L+2 (2%), H–6→L+3 (4%), H–5→LUMO (4%), H–5→L+1 (3%), H–3→LUMO (3%), H–3→L+1 (2%)
274.1	4.5235	0.0079	Singlet-A	H–13→L+1 (14%), H–12→LUMO (18%)	H–13→LUMO (3%), H–11→L+1 (6%), H–10→LUMO (3%), H–7→LUMO (2%), H–7→L+2 (5%), H–6→L+3 (4%), H–4→L+1 (5%), H–3→LUMO (3%), H–3→L+2 (4%), H–2→LUMO (2%)
273.8	4.5276	0.057	Singlet-A	H–13→LUMO (15%), H–12→L+1 (18%)	H–13→L+1 (3%), H–11→LUMO (6%), H–10→L+1 (4%), H–7→L+3 (5%), H–6→L+2 (4%), H–4→LUMO (4%), H–3→L+1 (4%), H–3→L+3 (4%), H–2→L+1 (2%)
272.3	4.5526	0.0	Triplet-A	H–13→L+2 (10%)	H–15→L+2 (3%), H–15→L+3 (2%), H–13→L+3 (8%), H–12→L+2 (7%), H–12→L+3 (7%), H–7→L+2 (3%), H–7→L+3 (2%), H–6→L+2 (3%), H–4→LUMO (6%), H–4→L+1 (4%), H–2→LUMO (2%)
272.2	4.5556	0.0	Triplet-A	H–13→L+3 (11%)	H–15→L+2 (2%), H–15→L+3 (3%), H–13→L+2 (7%), H–12→L+2 (5%), H–12→L+3 (8%), H–7→L+2 (2%), H–7→L+3 (3%), H–6→L+3 (3%), H–4→LUMO (4%), H–4→L+1 (6%), H–3→L+3 (2%), H–2→L+1 (2%)
271.2	4.5709	0.0	Triplet-A	H–9→LUMO (10%), H–4→L+1 (13%)	H–14→L+1 (2%), H–13→L+3 (6%), H–12→LUMO (3%), H–12→L+2 (5%), H–10→LUMO (5%), H–8→LUMO (3%), H–8→L+1 (7%), H–4→LUMO (5%), H–2→LUMO (5%)
271.1	4.5733	0.0	Triplet-A	H–9→L+1 (11%), H–4→LUMO (13%)	H–14→LUMO (2%), H–13→L+2 (4%), H–13→L+3 (2%), H–12→L+1 (3%), H–12→L+3 (5%), H–10→L+1 (5%), H–

					8→LUMO (7%), H–8→L+1 (3%), H–4→L+1 (5%), H–2→L+1 (4%)
270.7	4.5794	0.0011	Singlet-A	H–11→L+1 (13%), H–7→LUMO (10%), H–5→LUMO (16%), H–4→L+1 (15%)	H–10→LUMO (3%), H–10→L+4 (2%), H–9→L+4 (3%), H–7→L+4 (2%), H–2→LUMO (8%)
270.4	4.5857	0.0213	Singlet-A	H–11→LUMO (11%), H–7→L+1 (12%), H–5→L+1 (18%), H–4→LUMO (12%)	H–11→L+4 (2%), H–10→L+1 (3%), H–9→L+5 (2%), H–4→L+4 (3%), H–2→L+1 (8%)
265.1	4.6770	0.0002	Singlet-A	H–9→L+1 (15%), H–8→LUMO (18%), H–7→L+1 (12%)	H–8→L+4 (2%), H–6→LUMO (5%), H–5→L+1 (7%), H–3→L+1 (6%), H–2→L+1 (7%), H–1→LUMO (3%), HOMO→LUMO (4%)
264.8	4.6824	0.0	Singlet-A	H–9→LUMO (11%), H–8→L+1 (17%), H–7→LUMO (12%)	H–11→L+1 (2%), H–9→L+4 (3%), H–6→L+1 (7%), H–5→LUMO (8%), H–3→LUMO (5%), H–2→LUMO (7%), H–1→L+1 (4%), HOMO→L+1 (4%)
262.1	4.7310	0.0014	Singlet-A	H–9→LUMO (14%), H–8→L+1 (12%)	H–15→LUMO (5%), H–14→L+1 (4%), H–13→L+1 (7%), H–12→LUMO (6%), H–7→LUMO (9%), H–6→L+1 (9%), H–4→L+1 (4%), H–3→LUMO (4%)
261.6	4.7388	0.0444	Singlet-A	H–9→L+1 (14%), H–8→LUMO (11%)	H–15→L+1 (4%), H–14→LUMO (4%), H–13→LUMO (7%), H–12→L+1 (6%), H–10→L+1 (3%), H–7→L+1 (8%), H–6→LUMO (9%), H–4→LUMO (4%), H–3→L+1 (6%)
256.2	4.8395	0.0003	Singlet-A	H–5→LUMO (23%), H–4→L+1 (11%), H–3→LUMO (16%)	H–11→L+1 (2%), H–10→LUMO (3%), H–9→LUMO (8%), H–4→LUMO (3%), H–2→L+2 (3%), H–1→L+1 (6%), HOMO→L+3 (5%)
256.1	4.8411	0.002	Singlet-A	H–5→L+1 (25%), H–4→LUMO (14%), H–3→L+1 (16%)	H–11→LUMO (2%), H–10→L+1 (3%), H–9→L+1 (8%), H–4→L+1 (2%), H–1→LUMO (7%)
254.3	4.8757	0.0018	Singlet-A	H–2→L+2 (17%), HOMO→L+2 (22%), HOMO→L+3 (32%)	H–5→LUMO (2%), H–2→L+3 (8%)
254.2	4.8775	0.0038	Singlet-A	H–2→L+3 (21%), HOMO→L+2 (30%), HOMO→L+3 (23%)	H–2→L+2 (6%), HOMO→L+4 (3%)

eV: electron-volt; Singlet-A: singlet state of A symmetry; Triplet-A: Triplet state of A symmetry; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

Table S28. UV-Vis spectral details for complex (**2**). Results obtained at the TD-DFT/CAM-B3LYP/6-311G (d,p) theory level

Wavelength / nm	Energy / eV	Osc. Strength	Symmetry	Major contribs	Minor contribs
565.0	2.1945	0.0	Triplet-A	H–16→L+1 (12%), H–1→L+1 (14%)	H–18→LUMO (2%), H–18→L+1 (6%), H–16→LUMO (4%), H–15→LUMO (3%), H–15→L+1 (5%), H–11→L+1 (4%), H–10→L+1 (2%), H–9→L+1 (3%), H–1→LUMO (8%)
550.4	2.2525	0.0	Triplet-A	H–17→L+2 (11%), H–15→L+2 (24%), H–11→L+2 (12%), HOMO→L+2 (13%)	H–38→L+10 (2%), H–25→L+2 (2%), H–16→L+2 (2%), H–13→L+2 (3%), H–10→L+2 (2%), H–8→L+2 (5%), H–2→L+2 (9%)
538.0	2.3045	0.0	Triplet-A	H–22→LUMO (10%), H–17→LUMO (14%), H–12→LUMO (12%)	H–40→L+8 (2%), H–28→LUMO (3%), H–22→L+1 (3%), H–17→L+1 (5%), H–16→LUMO (7%), H–15→LUMO (3%), H–14→LUMO (7%), H–12→L+1 (4%), H–7→LUMO (2%)
490.2	2.5290	0.0	Triplet-A	H–7→L+3 (11%), H–3→L+3 (22%), H–2→L+3 (11%)	H–31→L+3 (6%), H–30→L+3 (3%), H–29→L+3 (4%), H–10→L+3 (3%), H–9→L+3 (7%), H–8→L+3 (3%), H–6→L+3 (7%), H–1→L+3 (3%), HOMO→L+3 (8%)
433.5	2.8602	0.0	Triplet-A	H–5→LUMO (10%), H–5→L+1 (16%)	H–10→LUMO (3%), H–10→L+1 (5%), H–6→L+1 (3%), H–3→L+1 (3%), H–2→LUMO (8%), H–2→L+1 (9%), H–1→LUMO (5%), H–1→L+1 (5%), HOMO→LUMO (6%), HOMO→L+1 (5%)
422.6	2.9337	0.0	Triplet-A	H–4→L+2 (15%), H–1→L+2 (15%), HOMO→L+2 (30%)	H–15→L+2 (3%), H–10→L+2 (3%), H–9→L+2 (3%), H–7→L+2 (6%), H–3→L+2 (6%)
422.2	2.9367	0.0	Triplet-A	H–24→L+3 (15%), H–18→L+3 (14%), H–1→L+3 (13%)	H–23→L+3 (3%), H–20→L+3 (4%), H–19→L+3 (2%), H–16→L+3 (5%), H–15→L+3 (2%), H–11→L+3 (4%), H–9→L+3 (7%), H–8→L+3 (3%), H–5→L+3 (4%)
419.0	2.9588	0.0034	Singlet-A	H–3→L+3 (15%), H–2→L+3 (11%)	H–31→L+3 (5%), H–30→L+3 (2%), H–29→L+3 (3%), H–9→L+3 (3%), H–7→L+3 (5%), H–6→L+3 (4%), H–5→L+1 (3%), H–2→LUMO (3%), H–2→L+1 (4%), H–1→LUMO (2%), H–1→L+3 (4%), HOMO→LUMO (2%), HOMO→L+3 (9%)
417.4	2.9707	0.0208	Singlet-A	H–5→L+1 (11%), H–1→LUMO (11%)	H–5→LUMO (7%), H–3→LUMO (2%), H–3→L+1 (3%), H–3→L+3 (5%), H–2→LUMO (7%), H–2→L+1 (7%), H–2→L+3 (4%), H–1→L+1 (8%), HOMO→LUMO (5%), HOMO→L+1 (2%), HOMO→L+3 (3%)

409.1	3.0310	0.0	Triplet-A	H–26→L+3 (23%), H–25→L+3 (15%), H–5→L+3 (13%)	H–27→L+3 (4%), H–21→L+3 (4%), H–6→L+3 (9%), H–3→L+3 (8%), H–2→L+3 (4%)
406.2	3.0525	0.0316	Singlet-A	H–1→L+2 (18%), HOMO→L+2 (48%)	H–10→L+2 (3%), H–9→L+2 (2%), H–7→L+2 (5%), H–4→L+2 (9%), H–3→L+2 (5%)
404.7	3.0637	0.0	Triplet-A	H–3→LUMO (11%), HOMO→LUMO (33%)	H–17→LUMO (4%), H–16→L+1 (2%), H–7→LUMO (5%), H–7→L+1 (3%), H–5→LUMO (4%), H–3→L+1 (3%), H–2→LUMO (3%), H–1→L+1 (9%)
400.9	3.0926	0.0	Triplet-A	H–1→LUMO (27%), HOMO→L+1 (15%)	H–18→LUMO (3%), H–18→L+1 (4%), H–16→LUMO (2%), H–7→LUMO (4%), H–3→LUMO (5%), H–2→L+1 (5%), H–1→L+1 (7%)
399.8	3.1008	0.0397	Singlet-A	H–1→LUMO (25%), H–1→L+1 (19%), HOMO→LUMO (29%)	H–3→LUMO (2%), H–2→LUMO (3%), H–2→L+1 (3%), HOMO→L+1 (6%)
395.1	3.1381	0.0	Triplet-A	H–21→L+3 (39%), H–20→L+3 (11%)	H–29→L+3 (6%), H–26→L+3 (9%), H–24→L+3 (3%), H–23→L+3 (3%), H–5→L+3 (2%), H–2→L+3 (5%), HOMO→L+3 (3%)
394.6	3.1424	0.0	Triplet-A	H–24→L+3 (10%), H–20→L+3 (46%)	H–31→L+3 (2%), H–30→L+3 (3%), H–26→L+3 (2%), H–23→L+3 (6%), H–21→L+3 (6%), H–14→L+3 (3%)
392.6	3.1578	0.0003	Singlet-A	H–3→LUMO (15%), H–1→LUMO (13%), HOMO→LUMO (17%), HOMO→L+1 (14%)	H–8→LUMO (3%), H–7→LUMO (8%), H–7→L+1 (3%), H–5→LUMO (6%), H–3→L+1 (2%), H–2→L+1 (3%)
380.4	3.2595	0.0009	Singlet-A	H–26→L+3 (13%), H–25→L+3 (11%), H–21→L+3 (11%), H–6→L+3 (10%), H–5→L+3 (12%), H–3→L+3 (10%)	H–27→L+3 (3%), H–4→L+3 (2%), H–2→L+3 (8%)
378.8	3.2727	0.0	Triplet-A	H–5→L+1 (15%), H–2→LUMO (10%)	H–9→LUMO (2%), H–9→L+1 (3%), H–7→LUMO (3%), H–7→L+1 (2%), H–6→LUMO (2%), H–6→L+1 (2%), H–5→LUMO (8%), H–4→LUMO (5%), H–3→LUMO (8%), H–3→L+1 (3%), H–2→L+1 (8%), H–1→LUMO (5%)

378.5	3.2755	0.0	Triplet-A	H–4→L+2 (13%), H–2→L+2 (22%), HOMO→L+2 (19%)	H–19→L+2 (3%), H–17→L+2 (8%), H–15→L+2 (7%), H–3→L+2 (7%)
374.5	3.3109	0.0053	Singlet-A	H–5→LUMO (10%), H–5→L+1 (17%)	H–10→LUMO (2%), H–10→L+1 (2%), H–9→LUMO (2%), H–9→L+1 (3%), H–7→LUMO (4%), H–7→L+1 (2%), H–6→LUMO (2%), H–6→L+1 (2%), H–4→LUMO (5%), H–3→LUMO (7%), H–3→L+1 (2%), H–2→LUMO (9%), H–2→L+1 (6%), H–1→LUMO (3%)
373.4	3.3200	0.0033	Singlet-A	H–24→L+3 (10%), H–2→L+2 (14%), H–1→L+3 (11%)	H–18→L+3 (6%), H–16→L+3 (3%), H–9→L+3 (3%), H–4→L+2 (9%), H–3→L+2 (4%), HOMO→L+2 (8%)
371.3	3.3388	0.0841	Singlet-A	H–4→L+2 (11%), H–2→L+2 (17%), H–1→L+3 (10%), HOMO→L+2 (14%)	H–24→L+3 (8%), H–18→L+3 (5%), H–16→L+3 (2%), H–9→L+3 (3%), H–3→L+2 (4%)
370.6	3.3454	0.0	Triplet-A	H–4→LUMO (12%), H–2→LUMO (12%), HOMO→LUMO (32%)	H–17→LUMO (2%), H–9→LUMO (3%), H–1→LUMO (6%), H–1→L+1 (9%), HOMO→L+1 (5%)
367.5	3.3735	0.0	Triplet-A	H–1→LUMO (33%), H–1→L+1 (26%)	H–16→LUMO (2%), H–5→LUMO (4%), H–4→L+1 (3%), H–3→LUMO (3%), H–3→L+1 (6%), H–2→L+1 (3%), HOMO→LUMO (5%)
366.3	3.3844	0.0058	Singlet-A	H–1→LUMO (29%), H–1→L+1 (44%)	H–5→LUMO (4%), H–3→L+1 (5%), H–2→L+1 (4%)
364.5	3.4016	0.0101	Singlet-A	H–4→LUMO (16%), H–2→LUMO (13%), HOMO→LUMO (27%)	H–12→LUMO (4%), H–9→LUMO (2%), H–7→LUMO (4%), H–4→L+1 (4%), H–3→LUMO (6%), H–3→L+1 (3%), HOMO→L+1 (4%)
359.4	3.4497	0.0	Triplet-A	H–8→L+2 (11%), H–4→L+2 (36%), H–2→L+2 (12%), H–1→L+2 (12%)	H–11→L+2 (3%), H–10→L+2 (9%), H–5→L+2 (4%)
358.6	3.4572	0.009	Singlet-A	H–26→L+3 (16%), H–21→L+3 (34%), H–5→L+3 (10%)	H–29→L+3 (4%), H–25→L+3 (2%), H–23→L+3 (3%), H–15→L+3 (3%), H–2→L+3 (4%), HOMO→L+3 (6%)

357.5	3.4685	0.0	Triplet-A	H–7→L+7 (16%), H–3→L+7 (16%), HOMO→L+7 (10%)	H–30→L+7 (2%), H–29→L+7 (2%), H–17→L+7 (3%), H–12→L+7 (3%), H–10→L+7 (3%), H–9→L+7 (2%), H–8→L+7 (4%), H–5→L+7 (5%)
354.8	3.4940	0.0006	Singlet-A	H–20→L+3 (37%), H–4→L+2 (14%)	H–24→L+3 (4%), H–23→L+3 (3%), H–11→L+3 (2%), H–10→L+2 (3%), H–8→L+2 (4%), H–2→L+2 (5%), H–1→L+2 (4%)
354.4	3.4985	0.0076	Singlet-A	H–20→L+3 (21%), H–4→L+2 (24%)	H–24→L+3 (2%), H–10→L+2 (5%), H–8→L+2 (6%), H–5→L+2 (3%), H–2→L+2 (9%), H–1→L+2 (8%)
353.7	3.5053	0.0	Triplet-A	H–4→LUMO (21%), H–3→LUMO (11%), HOMO→LUMO (10%)	H–22→LUMO (2%), H–13→LUMO (2%), H–11→L+1 (2%), H–10→L+1 (3%), H–8→LUMO (2%), H–6→LUMO (3%), H–5→L+1 (5%), H–4→L+1 (3%), H–2→L+1 (4%)
350.3	3.5391	0.0	Triplet-A	H–2→LUMO (11%), HOMO→L+1 (37%)	H–13→LUMO (4%), H–13→L+1 (5%), H–11→LUMO (3%), H–11→L+1 (3%), H–6→L+1 (4%), H–5→LUMO (7%), H–3→LUMO (3%), H–1→LUMO (2%)
349.7	3.5458	0.0011	Singlet-A	H–4→LUMO (17%), H–3→LUMO (12%), HOMO→L+1 (11%)	H–8→LUMO (3%), H–6→LUMO (4%), H–6→L+1 (3%), H–5→LUMO (6%), H–5→L+1 (5%), H–4→L+1 (4%), H–3→L+1 (2%), H–2→LUMO (7%), H–2→L+1 (6%), H–1→LUMO (2%), H–1→L+1 (2%), HOMO→LUMO (7%)
347.5	3.5683	0.0008	Singlet-A	H–4→LUMO (13%), H–2→LUMO (21%), HOMO→L+1 (20%)	H–13→LUMO (6%), H–13→L+1 (4%), H–11→LUMO (4%), H–11→L+1 (3%), H–8→L+1 (4%), H–6→L+1 (3%), H–5→LUMO (3%), H–5→L+1 (2%), H–4→L+1 (2%), H–1→L+1 (2%)
344.8	3.5961	0.0	Triplet-A	H–6→LUMO (11%), H–2→LUMO (32%), H–2→L+1 (18%)	H–22→LUMO (4%), H–13→LUMO (2%), H–11→L+1 (2%), H–4→LUMO (4%)
341.3	3.6323	0.0121	Singlet-A	H–6→LUMO (12%), H–2→LUMO (16%), H–2→L+1 (20%)	H–13→LUMO (4%), H–13→L+1 (5%), H–11→L+1 (3%), H–9→LUMO (2%), H–9→L+1 (2%), H–8→LUMO (2%), H–4→LUMO (9%), H–3→LUMO (3%), H–1→L+1 (5%), HOMO→L+1 (6%)

339.5	3.6524	0.0	Triplet-A	HOMO→L+3 (31%)	H–26→L+3 (2%), H–25→L+3 (2%), H–24→L+3 (4%), H–9→L+3 (3%), H–7→L+3 (5%), H–6→L+3 (2%), H–2→L+3 (6%), H–1→L+2 (5%), H–1→L+3 (9%), HOMO→L+2 (3%)
338.2	3.6663	0.0	Triplet-A	H–9→L+1 (10%)	H–16→LUMO (4%), H–16→L+1 (5%), H–13→LUMO (3%), H–13→L+1 (3%), H–11→LUMO (5%), H–11→L+1 (7%), H–10→LUMO (3%), H–10→L+1 (3%), H–9→LUMO (7%), H–8→LUMO (5%), H–8→L+1 (9%), H–5→L+1 (2%), H–1→L+1 (2%)
337.5	3.6736	0.0	Triplet-A	H–1→L+2 (15%)	H–38→L+2 (3%), H–15→L+2 (5%), H–12→L+2 (8%), H–11→L+2 (6%), H–9→L+2 (5%), H–8→L+2 (2%), H–7→L+2 (4%), H–5→L+2 (2%), H–1→L+3 (2%), HOMO→L+2 (7%), HOMO→L+3 (9%)
336.2	3.6882	0.0	Triplet-A	H–32→LUMO (12%)	H–33→LUMO (3%), H–33→L+1 (2%), H–32→L+1 (6%), H–31→LUMO (5%), H–28→LUMO (4%), H–27→LUMO (7%), H–23→LUMO (8%), H–22→LUMO (8%), H–19→LUMO (5%), H–18→LUMO (4%), H–4→LUMO (4%)
333.8	3.7148	0.0	Triplet-A	H–14→L+2 (17%), H–7→L+2 (25%), H–6→L+2 (14%), H–2→L+2 (10%)	H–38→L+2 (2%), H–10→L+2 (8%), H–1→L+2 (3%), HOMO→L+2 (3%)
333.5	3.7181	0.0127	Singlet-A	H–2→L+2 (20%), H–1→L+2 (23%), HOMO→L+2 (10%)	H–14→L+2 (5%), H–12→L+2 (6%), H–11→L+2 (9%), H–10→L+2 (3%), H–7→L+2 (2%), H–6→L+2 (9%)
332.2	3.7323	0.012	Singlet-A	H–11→LUMO (10%), H–11→L+1 (14%), H–9→LUMO (10%), H–9→L+1 (12%)	H–16→L+1 (2%), H–14→LUMO (3%), H–14→L+1 (3%), H–10→LUMO (6%), H–10→L+1 (5%), H–8→LUMO (5%), H–8→L+1 (7%)
330.2	3.7551	0.0	Triplet-A	H–13→L+7 (10%), H–12→L+7 (12%), H–4→L+7 (18%)	H–30→L+7 (5%), H–17→L+7 (4%), H–9→L+7 (2%), H–8→L+7 (8%), H–6→L+7 (3%), HOMO→L+7 (8%)
328.6	3.7735	0.0	Triplet-A	H–28→L+1 (14%), H–27→L+1 (10%)	H–39→L+1 (2%), H–33→LUMO (3%), H–32→LUMO (6%), H–32→L+1 (3%), H–28→LUMO (6%), H–27→LUMO (3%), H–22→L+1 (5%), H–19→L+1 (4%), H–18→L+1 (2%), H–5→LUMO (2%)
326.2	3.8004	0.0284	Singlet-A	H–7→L+2 (18%), HOMO→L+3 (27%)	H–14→L+2 (7%), H–10→L+2 (4%), H–9→L+2 (3%), H–7→L+3 (3%), H–6→L+2 (4%), H–6→L+3 (3%), H–2→L+3 (2%)

325.5	3.8092	0.0	Triplet-A	H–6→LUMO (11%), H–5→LUMO (18%), H–3→LUMO (14%)	H–7→LUMO (3%), H–7→L+1 (3%), H–6→L+1 (8%), H–5→L+1 (8%), H–4→LUMO (4%), H–2→LUMO (3%), H–2→L+1 (6%)
325.0	3.8145	0.0006	Singlet-A	H–6→LUMO (10%), H–5→LUMO (22%), H–5→L+1 (12%), H–3→LUMO (11%)	H–7→LUMO (3%), H–7→L+1 (3%), H–6→L+1 (8%), H–4→L+1 (2%), H–2→LUMO (4%), H–2→L+1 (6%)
324.7	3.8188	0.0258	Singlet-A	H–7→L+2 (19%), HOMO→L+3 (19%)	H–14→L+2 (6%), H–11→L+2 (2%), H–10→L+2 (3%), H–9→L+2 (5%), H–7→L+3 (3%), H–6→L+2 (3%), H–6→L+3 (2%), H–2→L+3 (2%), H–1→L+2 (2%)
324.3	3.8227	0.0	Triplet-A	H–40→LUMO (14%)	H–40→L+1 (4%), H–32→LUMO (5%), H–22→LUMO (4%), H–22→L+8 (2%), H–17→L+8 (3%), H–5→LUMO (5%), H–5→L+1 (5%), H–4→LUMO (6%), H–3→L+1 (2%), H–2→LUMO (2%), H–2→L+1 (2%)
321.1	3.8608	0.0015	Singlet-A	H–6→LUMO (16%), H–4→L+1 (10%), H–3→LUMO (12%), H–3→L+1 (22%), HOMO→L+1 (10%)	H–7→LUMO (4%), H–6→L+1 (4%), HOMO→LUMO (3%)
319.8	3.8767	0.0303	Singlet-A	H–7→L+7 (11%), H–3→L+7 (13%)	H–17→LUMO (2%), H–16→LUMO (2%), H–12→LUMO (4%), H–8→L+7 (2%), H–5→L+7 (4%), H–4→LUMO (5%), H–3→L+1 (2%), H–1→L+7 (2%), HOMO→L+7 (8%)
314.7	3.9392	0.0013	Singlet-A	H–7→LUMO (11%), H–3→LUMO (11%), H–2→L+1 (11%)	H–8→LUMO (2%), H–6→LUMO (7%), H–6→L+1 (3%), H–5→LUMO (5%), H–4→LUMO (4%), H–3→L+1 (5%), H–1→LUMO (3%), H–1→L+3 (5%), HOMO→L+1 (6%)
313.4	3.9559	0.0053	Singlet-A	H–1→L+3 (46%)	H–26→L+3 (3%), H–25→L+3 (3%), H–24→L+3 (4%), H–7→L+3 (2%), H–5→L+3 (4%), HOMO→L+3 (8%)
310.8	3.9891	0.0029	Singlet-A		H–17→LUMO (4%), H–13→L+1 (8%), H–11→LUMO (4%), H–11→L+1 (2%), H–10→L+1 (2%), H–8→LUMO (8%), H–7→L+1 (3%), H–6→LUMO (2%), H–6→L+1 (5%), H–5→LUMO (5%), H–3→L+1 (6%), H–2→L+1 (4%), H–2→L+3 (5%), HOMO→LUMO (3%), HOMO→L+1 (4%), HOMO→L+7 (2%)

310.2	3.9965	0.0216	Singlet-A	H–12→LUMO (10%), H–6→LUMO (11%)	H–14→LUMO (2%), H–13→L+1 (3%), H–8→LUMO (8%), H–6→L+1 (2%), H–5→LUMO (9%), H–5→L+1 (2%), H–4→LUMO (4%), H–3→L+1 (9%), H–2→L+3 (2%), HOMO→L+7 (3%)
309.0	4.0129	0.0017	Singlet-A	H–6→L+2 (18%), H–1→L+2 (12%)	H–13→L+2 (2%), H–12→L+2 (9%), H–11→L+2 (3%), H–8→L+2 (3%), H–5→L+2 (7%), H–4→L+2 (2%), H–3→L+2 (4%), H–2→L+2 (9%), H–2→L+3 (3%), HOMO→L+2 (8%)
308.1	4.0237	0.0035	Singlet-A	H–2→L+3 (25%)	H–21→L+3 (3%), H–17→LUMO (3%), H–13→LUMO (5%), H–5→L+1 (3%), H–5→L+3 (3%), H–4→LUMO (2%), H–4→L+1 (3%), H–1→L+3 (3%), HOMO→L+3 (7%)

eV: electron-volt; Singlet-A: singlet state of A symmetry; Triplet-A: Triplet state of A symmetry; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

Table S29. UV-Vis spectral details for complex **(3)**. Results obtained at the TD-DFT/CAM-B3LYP/6-311G (d,p) theory level

Wavelength / nm	Energy / eV	Osc. strength	Symmetry	Major contribs	Minor contribs
551.4	2.2485	0.0	Triplet-A	H–6→LUMO (37%), H–5→L+1 (31%)	H–4→L+1 (9%), H–2→LUMO (5%)
551.4	2.2487	0.0	Triplet-A	H–6→L+1 (37%), H–5→LUMO (31%)	H–10→L+2 (2%), H–4→LUMO (9%), H–2→L+1 (5%)
377.6	3.2838	0.0	Triplet-A	HOMO→LUMO (83%)	H–8→L+1 (2%)
374.3	3.3123	0.0	Triplet-A	HOMO→L+1 (82%)	H–8→LUMO (2%)
371.7	3.3358	0.0	Singlet-A	HOMO→LUMO (92%)	H–4→L+1 (2%)
368.5	3.3647	0.0086	Singlet-A	HOMO→L+1 (92%)	H–4→LUMO (2%)
338.1	3.6669	0.0	Triplet-A	H–10→L+1 (25%), H–9→LUMO (21%), H–2→LUMO (10%)	H–13→LUMO (4%), H–11→LUMO (6%), H–7→L+1 (9%), H–6→LUMO (3%), H–6→L+5 (3%), H–5→L+7 (2%)
337.8	3.6700	0.0	Triplet-A	H–10→LUMO (27%), H–9→L+1 (23%)	H–13→L+1 (5%), H–11→L+1 (6%), H–7→LUMO (9%), H–6→L+1 (3%), H–6→L+7 (2%), H–5→L+5 (2%), H–2→L+1 (6%)
332.7	3.7263	0.0	Triplet-A	H–2→LUMO (37%), H–1→L+1 (13%)	H–22→LUMO (3%), H–19→L+1 (3%), H–14→LUMO (2%), H–11→LUMO (2%), H–10→L+1 (5%), H–9→LUMO (5%), H–8→L+1 (6%), H–5→L+1 (2%), H–4→L+1 (3%), HOMO→LUMO (2%)
332.1	3.7332	0.0	Triplet-A	H–2→L+1 (36%), H–1→LUMO (16%)	H–22→L+1 (3%), H–19→LUMO (3%), H–14→L+1 (2%), H–10→LUMO (3%), H–9→L+1 (3%), H–8→LUMO (6%), H–5→LUMO (2%), H–4→LUMO (4%), HOMO→L+1 (3%)
319.3	3.8833	0.1056	Singlet-A	H–2→L+1 (44%), H–1→LUMO (39%)	H–8→LUMO (2%), H–5→LUMO (5%)
318.7	3.8907	0.0	Singlet-A	H–2→LUMO (59%), H–1→L+1 (25%)	H–8→L+1 (3%), H–5→L+1 (5%)

314.9	3.9373	0.0	Triplet-A	H–20→LUMO (10%), H–18→L+1 (12%), H–17→LUMO (10%), H–6→L+5 (10%)	H–19→L+1 (7%), H–11→LUMO (4%), H–10→L+1 (4%), H–5→L+7 (7%), H–4→L+7 (2%), H–1→L+1 (5%), HOMO→LUMO (4%)
314.9	3.9374	0.0	Triplet-A	H–18→LUMO (11%), H–1→LUMO (10%)	H–20→L+1 (9%), H–19→LUMO (7%), H–17→L+1 (9%), H–11→L+1 (4%), H–10→LUMO (4%), H–6→L+7 (9%), H–5→L+5 (6%), H–4→L+5 (3%), HOMO→L+1 (4%)
310.4	3.9943	0.0	Triplet-A	H–1→LUMO (22%), HOMO→L+4 (51%)	H–2→L+1 (3%)
308.1	4.0246	0.0	Triplet-A	H–2→L+1 (10%), H–1→LUMO (43%), HOMO→L+4 (22%)	H–18→LUMO (2%), H–3→L+1 (3%)
307.4	4.0339	0.0095	Singlet-A	H–2→L+1 (32%), H–1→LUMO (55%)	H–5→LUMO (4%), H–3→L+1 (3%)
307.3	4.0342	0.0	Triplet-A	H–2→LUMO (10%), H–1→L+1 (73%)	H–3→LUMO (5%)
306.6	4.0445	0.0	Singlet-A	H–2→LUMO (21%), H–1→L+1 (69%)	H–3→LUMO (3%)
297.0	4.1746	0.197	Singlet-A	H–6→L+1 (35%), H–5→LUMO (19%), H–4→LUMO (24%)	H–3→L+1 (8%), HOMO→L+4 (3%)
295.6	4.1939	0.0	Singlet-A	H–6→LUMO (37%), H–5→L+1 (21%), H–4→L+1 (23%), H–3→LUMO (10%)	H–12→L+4 (3%), H–8→L+4 (3%), HOMO→LUMO (2%)
292.0	4.2456	0.0	Triplet-A	H–4→L+4 (10%), HOMO→L+5 (17%), HOMO→L+6 (35%), HOMO→L+12 (10%)	H–6→L+1 (2%), H–5→LUMO (2%)
287.5	4.3125	0.0088	Singlet-A	HOMO→L+4 (77%)	H–10→L+1 (6%), H–9→LUMO (5%), H–7→L+1 (3%), H–6→LUMO (8%), H–6→L+2 (4%), H–5→L+1 (7%), H–5→L+3 (3%), H–4→L+1 (6%), H–2→LUMO (3%)
280.8	4.4156	0.0	Singlet-A	H–3→LUMO (42%)	H–14→LUMO (2%), H–8→L+1 (4%), H–4→L+1 (9%), H–1→L+1 (2%)

280.7	4.4170	0.0	Triplet-A	H–3→LUMO (63%)	H–11→L+1 (2%), H–10→LUMO (8%), H–9→L+1 (6%), H–7→LUMO (4%), H–6→L+1 (6%), H–6→L+3 (4%), H–5→LUMO (6%), H–5→L+2 (4%), H–2→L+1 (4%)
280.1	4.4265	0.0652	Singlet-A	H–4→LUMO (10%), H–3→L+1 (33%)	H–14→L+1 (3%), H–8→LUMO (5%), H–3→L+4 (3%), H–2→L+4 (2%)
279.9	4.4301	0.0	Triplet-A	H–4→LUMO (18%), H–3→L+1 (46%)	H–4→L+1 (3%), H–4→L+3 (8%), H–3→LUMO (3%), H–2→LUMO (3%), H–2→L+2 (3%)
276.1	4.4902	0.0	Triplet-A	H–6→L+2 (28%), H–5→L+3 (23%)	H–7→L+2 (2%), H–4→L+2 (8%), H–2→L+1 (3%), H–2→L+3 (4%), H–2→L+4 (3%), HOMO→L+3 (2%)
275.9	4.4936	0.0	Triplet-A	H–6→L+3 (27%), H–5→L+2 (22%), H–3→L+1 (12%)	H–6→L+3 (7%), H–5→L+2 (4%), H–4→L+2 (2%), H–3→L+1 (6%), H–1→L+6 (2%)
273.9	4.5261	0.0	Triplet-A	H–2→L+4 (44%)	H–11→LUMO (6%), H–8→L+1 (3%), H–6→L+2 (5%), H–5→L+3 (4%), H–4→L+1 (3%), HOMO→L+5 (4%), HOMO→L+6 (9%)
273.7	4.5302	0.0	Singlet-A	H–10→L+1 (14%), H–9→LUMO (11%), H–3→LUMO (23%)	H–25→L+1 (2%), H–22→LUMO (3%), H–19→L+1 (4%), H–14→LUMO (3%), H–8→L+1 (4%), H–5→L+3 (7%), H–4→L+1 (9%), H–4→L+3 (3%), H–2→LUMO (7%), H–2→L+6 (4%)
273.0	4.5417	0.0	Triplet-A	H–6→L+2 (10%), H–1→L+4 (11%)	H–11→L+1 (6%), H–8→LUMO (5%), H–6→L+3 (6%), H–5→L+2 (5%), H–4→LUMO (2%)
272.8	4.5449	0.0388	Singlet-A	H–10→LUMO (15%), H–9→L+1 (13%), H–3→L+1 (36%)	H–12→L+4 (4%), H–10→L+1 (3%), H–9→LUMO (3%), H–4→L+4 (4%), H–3→LUMO (6%), H–1→L+4 (3%), HOMO→L+12 (7%)
272.5	4.5503	0.0	Singlet-A	HOMO→L+5 (15%), HOMO→L+6 (35%)	H–25→LUMO (2%), H–22→L+1 (4%), H–19→LUMO (4%), H–14→L+1 (4%), H–8→LUMO (4%), H–6→L+3 (3%), H–5→L+2 (3%),

					H–3→L+1 (7%), H–2→L+4 (9%), HOMO→L+1 (2%)
271.4	4.5677	0.0	Triplet-A	H–4→LUMO (17%), H–2→L+1 (16%)	H–15→L+4 (3%), H–4→L+1 (5%), H–3→LUMO (5%), H–2→LUMO (7%), H–2→L+5 (4%), H–2→L+6 (5%)
270.4	4.5849	0.0	Triplet-A	H–1→L+4 (38%)	H–17→L+1 (2%), H–14→L+1 (3%), H–10→LUMO (3%), H–9→L+1 (3%), H–8→LUMO (6%), H–5→LUMO (8%), HOMO→L+1 (3%)
266.4	4.6536	0.0131	Singlet-A	H–4→LUMO (46%), H–3→L+1 (11%)	H–17→LUMO (2%), H–14→LUMO (3%), H–10→L+1 (2%), H–9→LUMO (3%), H–8→L+1 (7%), H–5→L+1 (8%), H–3→LUMO (7%), HOMO→LUMO (3%)
265.7	4.6658	0.0	Singlet-A	H–4→L+1 (48%)	H–22→L+1 (2%), H–13→L+1 (2%), H–12→LUMO (2%), H–11→L+1 (3%), H–10→LUMO (2%), H–8→LUMO (5%), H–5→LUMO (4%), H–3→L+1 (3%), H–3→L+4 (8%), H–2→L+1 (9%)
264.7	4.6837	0.0	Triplet-A	H–4→LUMO (31%)	H–12→L+4 (2%), H–11→LUMO (3%), H–10→L+3 (3%), H–8→L+1 (3%), H–5→L+1 (4%), H–3→LUMO (3%), H–3→L+6 (2%), H–2→LUMO (5%)
264.6	4.6853	0.0	Triplet-A	H–4→L+1 (39%)	H–14→L+4 (4%), H–4→LUMO (4%), H–3→L+1 (8%), H–1→L+5 (6%), H–1→L+12 (4%)
262.9	4.7164	0.0	Triplet-A	H–3→L+4 (30%), H–1→L+6 (12%)	H–13→L+2 (4%), H–11→LUMO (2%), H–11→L+2 (9%), H–7→L+3 (4%), H–6→LUMO (2%), H–5→L+1 (3%), H–4→L+1 (2%), HOMO→L+2 (8%)
262.5	4.7236	0.0	Triplet-A	H–10→L+3 (27%), H–9→L+2 (18%)	H–13→L+3 (4%), H–11→L+3 (9%), H–7→L+2 (4%), H–6→L+1 (2%), H–5→LUMO (2%), HOMO→L+3 (8%)
262.4	4.7245	0.0	Triplet-A	H–10→L+2 (28%), H–9→L+3 (19%)	H–12→L+4 (4%), H–8→L+1 (2%), H–8→L+4 (5%), H–5→L+4 (5%),

					H–4→L+1 (3%), H–4→L+4 (5%), H–3→LUMO (4%), H–3→L+5 (3%), H–3→L+6 (6%), H–3→L+12 (2%), H–2→LUMO (5%), H–2→L+5 (5%), H–2→L+12 (3%), H–1→L+4 (7%), HOMO→L+6 (2%)
260.6	4.7585	0.0	Triplet-A	H–2→L+6 (11%)	H–21→L+4 (2%), H–8→L+6 (2%), H–2→L+1 (3%), H–1→L+5 (2%), H–1→L+6 (3%)
260.4	4.7622	0.06	Singlet-A	H–2→L+4 (59%)	H–15→L+4 (3%), H–2→L+5 (4%), H–2→L+6 (6%)
259.5	4.7783	0.0	Singlet-A	H–1→L+4 (60%)	H–11→L+4 (6%), H–9→L+1 (7%), H–9→L+4 (4%), H–7→L+5 (4%), H–7→L+6 (2%), H–4→LUMO (3%), H–2→L+1 (2%)
256.4	4.8359	0.0	Triplet-A	H–11→L+1 (11%), H–7→LUMO (27%), H–5→LUMO (11%)	H–9→LUMO (8%), H–9→L+5 (2%), H–7→L+4 (9%), H–4→L+1 (4%), H–4→L+4 (2%)
256.0	4.8440	0.0	Triplet-A	H–11→LUMO (13%), H–7→L+1 (23%), H–5→L+1 (10%)	H–22→L+1 (4%), H–18→LUMO (7%), H–14→L+1 (7%), H–13→L+1 (4%), H–11→L+1 (8%), H–10→LUMO (4%), H–9→L+1 (5%), H–7→LUMO (4%), H–5→LUMO (6%), H–4→LUMO (4%), H–2→L+1 (8%), H–2→L+4 (3%)
255.6	4.8509	0.0087	Singlet-A	H–8→LUMO (19%)	H–22→LUMO (4%), H–18→L+1 (7%), H–14→LUMO (7%), H–13→LUMO (5%), H–10→L+1 (5%), H–9→LUMO (5%), H–7→L+1 (5%), H–5→L+1 (6%), H–4→L+1 (5%), H–2→LUMO (8%)
255.5	4.8525	0.0	Singlet-A	H–11→LUMO (10%), H–8→L+1 (18%)	H–14→L+1 (3%), H–9→L+1 (8%), H–8→LUMO (3%), H–2→L+1 (4%)
252.0	4.9202	0.0051	Singlet-A	H–11→L+1 (14%), H–7→LUMO (41%), H–5→LUMO (10%)	H–14→LUMO (3%), H–9→LUMO (8%), H–8→L+1 (3%), H–2→LUMO (4%)
251.6	4.9288	0.0	Singlet-A	H–11→LUMO (12%), H–7→L+1 (34%), H–5→L+1 (10%), HOMO→L+2 (12%)	H–11→LUMO (5%), H–7→L+1 (4%)

249.7	4.9650	0.0	Singlet-A	HOMO→L+2 (76%)	H–11→L+1 (2%)
249.3	4.9728	0.0607	Singlet-A	HOMO→L+3 (88%)	H–16→L+4 (3%), H–5→L+4 (7%), H–4→L+4 (6%), H–3→L+6 (2%), H–2→L+5 (8%), H–2→L+12 (4%), H–1→L+4 (7%), HOMO→L+2 (3%)
246.8	5.0238	0.0	Singlet-A	H–8→L+4 (12%), H–2→L+6 (22%)	H–15→L+6 (3%), H–14→L+4 (3%), H–13→L+4 (9%), H–1→L+12 (6%)
244.5	5.0715	0.0533	Singlet-A	H–3→L+4 (23%), H–1→L+5 (12%), H–1→L+6 (19%)	H–25→LUMO (2%), H–22→L+1 (4%), H–18→LUMO (3%), H–17→L+1 (3%), H–13→L+4 (2%), H–12→LUMO (8%), H–8→LUMO (7%), H–3→L+1 (3%)
238.0	5.2087	0.0284	Singlet-A	H–15→LUMO (12%), H–13→L+1 (19%), H–3→L+4 (11%)	H–25→L+1 (2%), H–22→LUMO (4%), H–18→L+1 (3%), H–17→LUMO (3%), H–12→L+1 (8%), H–11→LUMO (3%), H–8→L+1 (8%), H–4→L+4 (2%), H–3→LUMO (2%)
237.3	5.2246	0.0	Singlet-A	H–15→L+1 (14%), H–13→LUMO (28%)	H–11→L+5 (3%), H–11→L+6 (8%), H–11→L+12 (2%), H–10→L+4 (2%), H–9→L+6 (3%), H–7→L+1 (3%), H–5→L+4 (4%), H–3→L+5 (2%), H–3→L+6 (5%)
233.6	5.3072	0.0	Singlet-A	H–7→L+4 (22%), H–4→L+4 (12%)	H–15→LUMO (3%), H–13→L+1 (7%), H–13→L+4 (6%), H–11→L+1 (2%), H–8→LUMO (5%), H–8→L+6 (2%), H–7→L+6 (4%), H–2→L+4 (2%), H–1→L+5 (3%), H–1→L+6 (8%)
233.2	5.3163	0.0188	Singlet-A	H–11→L+4 (13%), H–3→L+4 (12%)	H–4→L+1 (9%), H–2→LUMO (5%)

eV: electron-volt; Singlet-A: singlet state of A symmetry; Triplet-A: Triplet state of A symmetry; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

Table S30. UV-Vis spectral details for complex **(4)**. Results obtained at the TD-DFT/CAM-B3LYP/6-311G (d,p) theory level

Wavelength / nm	Energy / eV	Osc. Strength	Symmetry	Major contribs	Minor contribs
459.2	2.6998	0.0	Triplet-AG	H–9→LUMO (18%), H–7→L+1 (18%)	H–25→LUMO (4%), H–25→L+3 (2%), H–24→L+1 (4%), H–24→L+2 (3%), H–16→L+1 (2%), H–15→LUMO (6%), H–12→L+1 (6%), H–8→L+1 (3%), H–2→LUMO (9%), HOMO→L+1 (6%)
459.2	2.6998	0.0	Triplet-AU	H–9→L+1 (18%), H–7→LUMO (18%)	H–25→L+1 (4%), H–25→L+2 (2%), H–24→LUMO (4%), H–24→L+3 (3%), H–16→LUMO (2%), H–15→L+1 (6%), H–12→LUMO (6%), H–8→LUMO (3%), H–2→L+1 (9%), HOMO→LUMO (6%)
363.4	3.4122	0.0	Triplet-AG	HOMO→L+1 (70%)	H–15→LUMO (3%), H–9→LUMO (3%), H–7→L+1 (2%), H–2→LUMO (9%)
363.2	3.4132	0.0	Triplet-AU	HOMO→LUMO (70%)	H–15→L+1 (3%), H–9→L+1 (3%), H–7→LUMO (2%), H–2→L+1 (9%)
361.1	3.4332	0.0	Singlet-AG	H–2→LUMO (12%), HOMO→L+1 (83%)	
361.0	3.4349	0.0575	Singlet-AU	H–2→L+1 (12%), HOMO→LUMO (83%)	
355.0	3.4929	0.0	Triplet-AU	H–4→L+1 (24%), H–3→LUMO (54%)	H–5→L+1 (2%), H–2→L+1 (4%)
355.0	3.4930	0.0	Triplet-AG	H–4→LUMO (24%), H–3→L+1 (54%)	H–5→LUMO (2%), H–2→LUMO (4%)
344.8	3.5958	0.0	Triplet-AU		H–23→L+5 (5%), H–22→L+7 (3%), H–21→L+7 (2%), H–19→L+14 (2%), H–18→L+15 (4%), H–13→L+8 (2%), H–12→L+9 (3%), H–11→L+8 (3%), H–11→L+14 (3%), H–10→L+9 (3%), H–8→L+5 (4%), H–2→L+7 (6%), HOMO→L+5 (6%)
344.8	3.5961	0.0	Triplet-AG		H–23→L+7 (4%), H–22→L+5 (4%), H–19→L+15 (3%), H–18→L+14 (3%), H–14→L+8 (2%), H–13→L+9 (2%), H–12→L+8 (3%), H–11→L+9 (4%), H–11→L+15 (3%), H–10→L+8 (2%), H–8→L+7 (4%), H–2→L+5 (6%), HOMO→L+7 (5%)
342.7	3.6175	0.0	Triplet-AG		H–23→L+11 (3%), H–22→L+10 (2%), H–21→L+5 (4%), H–21→L+6 (2%), H–20→L+4 (7%), H–18→L+14 (3%), H–13→L+9 (3%),

					H–13→L+15 (4%), H–12→L+14 (2%), H–8→L+4 (6%), H–2→L+6 (5%), HOMO→L+4 (5%)
342.7	3.6177	0.0	Triplet-AU		H–23→L+10 (3%), H–22→L+11 (3%), H–21→L+4 (6%), H–20→L+5 (5%), H–20→L+6 (2%), H–19→L+4 (3%), H–18→L+15 (2%), H–18→L+17 (2%), H–13→L+8 (2%), H–13→L+14 (3%), H–12→L+15 (2%), H–9→L+4 (3%), H–8→L+6 (6%), H–2→L+4 (6%), HOMO→L+6 (4%)
340.2	3.6443	0.0	Triplet-AU		H–23→L+6 (4%), H–22→L+7 (2%), H–22→L+8 (2%), H–21→L+4 (3%), H–20→L+5 (2%), H–19→L+7 (3%), H–19→L+11 (2%), H–18→L+6 (2%), H–18→L+9 (3%), H–11→L+4 (2%), H–11→L+16 (5%), H–10→L+17 (7%), H–8→L+10 (5%), H–2→L+11 (3%), HOMO→L+10 (2%)
340.2	3.6447	0.0	Triplet-AG		H–23→L+7 (2%), H–22→L+6 (4%), H–20→L+4 (3%), H–19→L+10 (3%), H–18→L+7 (2%), H–13→L+17 (2%), H–11→L+6 (3%), H–11→L+17 (5%), H–10→L+4 (2%), H–10→L+16 (8%), H–8→L+8 (2%), H–8→L+11 (4%), H–2→L+10 (3%)
338.3	3.6650	0.0	Singlet-AG	H–4→LUMO (22%), H–3→L+1 (58%)	H–2→LUMO (6%), H–1→L+1 (4%)
338.2	3.6659	0.0031	Singlet-AU	H–4→L+1 (22%), H–3→LUMO (58%)	H–2→L+1 (6%), H–1→LUMO (4%)
331.9	3.7360	0.0	Triplet-AG	H–1→L+1 (80%)	H–6→LUMO (8%), H–5→LUMO (3%)
331.8	3.7363	0.0	Triplet-AU	H–1→LUMO (80%)	H–6→L+1 (8%), H–5→L+1 (3%)
329.9	3.7583	0.0	Singlet-AG	H–1→L+1 (82%)	H–6→LUMO (7%), H–5→LUMO (4%), H–3→L+1 (3%)
329.7	3.7610	0.0074	Singlet-AU	H–1→LUMO (82%)	H–6→L+1 (7%), H–5→L+1 (4%), H–3→LUMO (3%)
319.9	3.8760	0.0	Triplet-AG	H–25→LUMO (24%), H–24→L+1 (28%)	H–22→LUMO (2%), H–16→L+1 (3%), H–15→LUMO (8%), H–14→L+1 (3%), H–12→L+1 (2%), H–9→LUMO (2%), H–2→LUMO (4%), H–1→L+1 (2%), HOMO→L+1 (6%)
319.9	3.8761	0.0	Triplet-AU	H–25→L+1 (24%), H–24→LUMO (28%)	H–22→L+1 (2%), H–16→LUMO (3%), H–15→L+1 (8%), H–14→LUMO (3%), H–

					12→LUMO (2%), H–9→L+1 (2%), H–2→L+1 (4%), H–1→LUMO (2%), HOMO→LUMO (6%)
303.6	4.0844	0.0	Triplet-AU	H–2→L+1 (32%), HOMO→LUMO (11%)	H–33→L+1 (3%), H–32→LUMO (5%), H–31→L+1 (3%), H–27→LUMO (3%), H–25→L+1 (8%), H–24→LUMO (4%), H–9→L+13 (2%), H–7→LUMO (4%), H–7→L+12 (2%), H–4→L+1 (3%)
303.5	4.0846	0.0	Triplet-AG	H–2→LUMO (32%), HOMO→L+1 (11%)	H–33→LUMO (3%), H–32→L+1 (5%), H–31→LUMO (3%), H–27→L+1 (3%), H–25→LUMO (8%), H–24→L+1 (4%), H–9→L+12 (2%), H–7→L+1 (4%), H–7→L+13 (2%), H–4→LUMO (3%)
300.3	4.1290	0.0797	Singlet-AU	H–2→L+1 (67%), HOMO→LUMO (12%)	H–7→LUMO (8%), H–4→L+1 (5%)
300.2	4.1303	0.0	Singlet-AG	H–2→LUMO (68%), HOMO→L+1 (12%)	H–7→L+1 (8%), H–4→LUMO (5%)
286.0	4.3346	0.0	Triplet-AU	H–2→L+1 (32%)	H–33→L+1 (8%), H–32→LUMO (9%), H–31→L+1 (4%), H–30→LUMO (4%), H–9→L+13 (4%), H–7→L+12 (3%), H–3→LUMO (2%)
286.0	4.3355	0.0	Triplet-AG	H–2→LUMO (32%)	H–33→LUMO (8%), H–32→L+1 (9%), H–31→LUMO (4%), H–30→L+1 (4%), H–9→L+12 (4%), H–7→L+13 (3%), H–3→L+1 (2%)
282.2	4.3930	0.0	Triplet-AU	H–5→L+1 (43%), H–4→L+1 (26%)	H–16→LUMO (6%), H–14→LUMO (3%), H–6→L+1 (3%), H–3→LUMO (5%)
282.2	4.3934	0.0	Triplet-AG	H–5→LUMO (43%), H–4→LUMO (26%)	H–16→L+1 (6%), H–14→L+1 (3%), H–6→LUMO (3%), H–3→L+1 (5%)
281.5	4.4039	0.0022	Singlet-AU	H–5→L+1 (47%), H–4→L+1 (26%)	H–16→LUMO (7%), H–6→L+1 (3%), H–3→LUMO (3%)
281.5	4.4049	0.0	Singlet-AG	H–5→LUMO (49%), H–4→LUMO (25%)	H–16→L+1 (7%), H–14→L+1 (2%), H–6→LUMO (3%), H–3→L+1 (3%)
280.6	4.4181	0.0	Triplet-AG	H–9→L+3 (15%), H–7→L+2 (12%), H–2→L+3 (10%), HOMO→L+2 (20%)	H–16→L+2 (3%), H–15→L+3 (8%), H–14→L+2 (3%), H–12→L+2 (6%), H–8→L+2 (2%)
280.5	4.4195	0.0	Triplet-AU	H–9→L+2 (15%), H–7→L+3 (12%), H–2→L+2 (10%), HOMO→L+3 (18%)	H–16→L+3 (3%), H–15→L+2 (8%), H–14→L+3 (3%), H–12→L+3 (6%), H–8→L+3 (2%)

277.4	4.4690	0.0702	Singlet-AU	H–7→LUMO (16%), H–5→L+1 (17%), H–4→L+1 (12%), H–3→LUMO (15%)	H–24→LUMO (2%), H–9→L+1 (7%), H–6→L+1 (4%), H–2→L+1 (7%), HOMO→L+3 (3%)
277.1	4.4742	0.0	Singlet-AG	H–7→L+1 (16%), H–5→LUMO (16%), H–4→LUMO (13%), H–3→L+1 (15%)	H–24→L+1 (3%), H–9→LUMO (7%), H–6→LUMO (3%), H–2→LUMO (6%), HOMO→L+2 (4%)
275.7	4.4968	0.0	Triplet-AU	H–5→L+1 (16%), H–4→L+1 (17%), H–3→LUMO (21%)	H–25→L+2 (2%), H–24→L+3 (2%), H–7→LUMO (4%), H–6→L+1 (4%), HOMO→L+3 (5%), HOMO→L+5 (2%)
275.6	4.4985	0.0	Triplet-AG	H–5→LUMO (17%), H–4→LUMO (18%), H–3→L+1 (22%)	H–25→L+3 (2%), H–24→L+2 (2%), H–7→L+1 (4%), H–6→LUMO (4%), HOMO→L+2 (4%)
274.6	4.5144	0.0	Triplet-AU	H–2→L+7 (10%), HOMO→L+5 (28%)	H–18→L+15 (3%), H–12→L+9 (2%), H–11→L+8 (3%), H–5→L+1 (3%), H–3→LUMO (3%), H–2→L+4 (5%), HOMO→L+6 (2%)
274.5	4.5169	0.0	Triplet-AG	H–2→L+5 (16%), HOMO→L+4 (15%), HOMO→L+7 (15%)	H–19→L+15 (2%), H–18→L+14 (3%), H–13→L+9 (2%), H–12→L+8 (2%), H–11→L+9 (2%), H–5→LUMO (2%)
274.4	4.5182	0.0	Singlet-AG	H–4→LUMO (10%), HOMO→L+2 (33%)	H–25→LUMO (5%), H–24→L+1 (4%), H–15→LUMO (4%), H–14→L+1 (3%), H–12→L+1 (2%), H–9→L+3 (2%), H–7→L+2 (2%), H–5→LUMO (3%), H–3→L+1 (8%), H–2→L+3 (9%)
274.3	4.5208	0.0107	Singlet-AU	H–4→L+1 (10%), H–2→L+2 (10%), HOMO→L+3 (32%)	H–25→L+1 (5%), H–24→LUMO (5%), H–15→L+1 (4%), H–14→LUMO (3%), H–12→LUMO (2%), H–9→L+2 (2%), H–7→L+3 (2%), H–5→L+1 (3%), H–3→LUMO (7%)
272.8	4.5456	0.0	Triplet-AG	H–25→L+3 (12%), H–24→L+2 (13%), HOMO→L+2 (15%), HOMO→L+4 (11%)	H–25→LUMO (2%), H–24→L+1 (2%), H–15→L+3 (2%), H–2→L+3 (4%), H–2→L+6 (3%)
272.4	4.5511	0.0	Triplet-AU	H–25→L+2 (15%), H–24→L+3 (16%), HOMO→L+3 (18%)	H–25→L+1 (3%), H–24→LUMO (3%), H–15→L+2 (2%), H–5→L+1 (2%), H–2→L+2 (5%), H–2→L+4 (3%), HOMO→L+5 (4%)
265.6	4.6689	0.0	Singlet-AG	HOMO→L+2 (37%)	H–16→L+1 (3%), H–15→LUMO (8%), H–14→L+1 (3%), H–12→L+1 (5%), H–9→LUMO (9%), H–7→L+1 (4%), H–6→LUMO (5%), H–5→LUMO (6%), H–

					4→LUMO (3%), H–3→L+1 (3%), H–2→L+3 (2%)
265.3	4.6733	0.0555	Singlet-AU	H–6→L+1 (18%), HOMO→L+3 (28%)	H–16→LUMO (3%), H–15→L+1 (6%), H–14→LUMO (3%), H–12→LUMO (4%), H–9→L+1 (7%), H–7→LUMO (3%), H–5→L+1 (8%), H–4→L+1 (4%), H–3→LUMO (3%), H–2→L+2 (2%), H–1→LUMO (3%)
264.8	4.6819	0.0	Singlet-AG	H–6→LUMO (70%), H–1→L+1 (10%)	H–5→LUMO (4%), HOMO→L+2 (6%)
264.7	4.6839	0.0134	Singlet-AU	H–6→L+1 (56%), HOMO→L+3 (16%)	H–9→L+1 (3%), H–5→L+1 (2%), H–1→LUMO (8%)
260.6	4.7571	0.0	Singlet-AG	H–2→L+5 (23%), HOMO→L+4 (55%)	H–2→L+6 (2%), HOMO→L+7 (8%)
259.9	4.7710	0.1692	Singlet-AU	H–2→L+4 (10%), H–2→L+7 (13%), HOMO→L+5 (54%)	H–25→L+1 (2%), HOMO→L+6 (2%)
257.9	4.8072	0.0	Singlet-AG	H–2→L+6 (13%), HOMO→L+7 (24%)	H–25→LUMO (9%), H–24→L+1 (8%), H–9→LUMO (5%), H–7→L+1 (4%), HOMO→L+4 (9%), HOMO→L+8 (3%)
256.7	4.8293	0.1367	Singlet-AU	H–2→L+4 (13%), HOMO→L+6 (26%)	H–25→L+1 (9%), H–24→LUMO (8%), H–9→L+1 (5%), H–9→L+2 (2%), H–7→LUMO (3%), H–7→L+3 (2%), HOMO→L+3 (3%), HOMO→L+5 (7%)
255.9	4.8453	0.0553	Singlet-AU	HOMO→L+6 (35%)	H–25→L+1 (9%), H–24→LUMO (8%), H–9→L+1 (4%), H–7→LUMO (3%), H–2→L+4 (5%), H–2→L+7 (7%), HOMO→L+3 (6%)
255.7	4.8497	0.0	Singlet-AG	H–25→LUMO (10%), HOMO→L+7 (22%)	H–24→L+1 (9%), H–9→LUMO (5%), H–9→L+3 (2%), H–7→L+1 (3%), H–7→L+2 (2%), H–2→L+5 (3%), H–2→L+6 (8%), HOMO→L+2 (7%), HOMO→L+8 (3%)
253.1	4.8980	0.0	Singlet-AG	H–4→L+3 (20%), H–3→L+2 (57%)	H–2→L+3 (5%), H–1→L+2 (4%)
252.9	4.9022	0.0039	Singlet-AU	H–4→L+2 (21%), H–3→L+3 (57%)	H–2→L+2 (6%), H–1→L+3 (4%)
249.8	4.9642	0.0	Singlet-AG	H–17→LUMO (13%), H–15→LUMO (11%), H–7→L+1 (18%), H–4→LUMO (10%)	H–14→L+1 (7%), H–12→L+1 (6%), H–9→LUMO (2%), H–8→L+1 (3%), H–3→L+1 (4%), H–1→L+2 (5%)
249.8	4.9643	0.0025	Singlet-AU	H–17→L+1 (14%), H–15→L+1 (12%), H–7→LUMO (20%), H–4→L+1 (11%)	H–14→LUMO (8%), H–12→LUMO (7%), H–9→L+1 (2%), H–8→LUMO (3%), H–3→LUMO (5%)

249.2	4.9758	0.0	Singlet-AG	H–1→L+2 (78%)	H–6→L+3 (5%), H–5→L+3 (2%), H–3→L+2 (5%)
248.7	4.9849	0.004	Singlet-AU	H–1→L+3 (82%)	H–6→L+2 (5%), H–5→L+2 (2%), H–3→L+3 (4%)

eV: electron-volt; Singlet-AG: Low-lying singlet excited states of A_g symmetry; Singlet-AU: Low-lying singlet excited states of A_u symmetry; Triplet-AG: Low-lying triplet excited states of A_g symmetry; Triplet-AU: Low-lying triplet excited states of A_u symmetry; HOMO: Highest Occupied Molecular Orbital; LUMO: Lowest Unoccupied Molecular Orbital.

Table S31. UV-Vis spectral details for complex (**5**). Results obtained at the TD-DFT/CAM-B3LYP/6-311G (d,p) theory level

Wavelength / nm	Energy / eV	Osc. Strength	Symmetry	Major contribs	Minor contribs
466.8	2.6559	0.0	Triplet-AG	H–9→L+1 (18%), H–8→LUMO (11%), H–7→LUMO (12%), H–2→L+1 (10%)	H–25→L+1 (3%), H–25→L+3 (2%), H–15→L+1 (3%), H–14→LUMO (4%), H–12→LUMO (3%), H–11→L+1 (4%), HOMO→LUMO (5%)
466.8	2.6559	0.0	Triplet-AU	H–9→LUMO (18%), H–8→L+1 (11%), H–7→L+1 (12%), H–2→LUMO (10%)	H–26→L+1 (2%), H–25→LUMO (3%), H–25→L+2 (2%), H–15→LUMO (3%), H–14→L+1 (3%), H–12→L+1 (3%), H–11→LUMO (4%), HOMO→L+1 (5%)
375.3	3.3040	0.0	Triplet-AG	HOMO→LUMO (76%)	H–9→L+1 (3%), H–3→LUMO (2%), H–2→L+1 (5%)
375.1	3.3053	0.0	Triplet-AU	HOMO→L+1 (76%)	H–9→LUMO (3%), H–3→L+1 (2%), H–2→LUMO (5%)
373.1	3.3229	0.0	Singlet-AG	HOMO→LUMO (87%)	H–2→L+1 (9%)
372.9	3.3253	0.043	Singlet-AU	HOMO→L+1 (87%)	H–2→LUMO (9%)
354.3	3.4997	0.0	Triplet-AG	H–5→L+1 (20%), H–3→LUMO (57%)	H–6→L+1 (4%), H–2→L+1 (3%)
354.3	3.4999	0.0	Triplet-AU	H–5→LUMO (20%), H–3→L+1 (57%)	H–6→LUMO (4%), H–2→LUMO (3%)
345.4	3.5893	0.0	Triplet-AU		H–23→L+5 (3%), H–23→L+6 (2%), H–19→L+7 (5%), H–18→L+14 (3%), H–17→L+15 (3%), H–13→L+8 (2%), H–13→L+11 (2%), H–13→L+14 (2%), H–12→L+9 (2%), H–12→L+15 (2%), H–11→L+8 (4%), H–11→L+14 (2%), H–10→L+9 (4%), H–2→L+7 (6%), HOMO→L+5 (3%), HOMO→L+6 (3%)
345.4	3.5897	0.0	Triplet-AG		H–23→L+7 (4%), H–19→L+6 (3%), H–18→L+15 (3%), H–17→L+14 (3%), H–13→L+15 (2%), H–12→L+8 (3%), H–12→L+14 (2%), H–11→L+9 (4%), H–11→L+15 (2%), H–10→L+8 (3%), H–7→L+7 (2%), H–2→L+5 (4%), H–2→L+6 (3%), HOMO→L+7 (5%)
341.6	3.6290	0.0	Triplet-AU		H–22→L+7 (2%), H–22→L+11 (2%), H–20→L+4 (2%), H–18→L+16 (2%), H–17→L+17 (2%), H–13→L+8 (4%), H–12→L+9 (2%), H–11→L+14 (3%), H–10→L+15 (4%), H–8→L+6

					(3%), H–8→L+9 (2%), H–2→L+4 (3%)
341.6	3.6291	0.0	Triplet-AG		H–22→L+6 (2%), H–22→L+10 (2%), H–21→L+4 (2%), H–18→L+17 (2%), H–13→L+9 (4%), H–12→L+8 (2%), H–11→L+15 (3%), H–10→L+14 (5%), H–8→L+8 (3%), H–2→L+5 (2%), H–2→L+6 (2%), HOMO→L+4 (3%)
340.7	3.6395	0.0	Triplet-AG	H–1→LUMO (86%)	H–6→L+1 (5%)
340.6	3.6405	0.0	Triplet-AU	H–1→L+1 (86%)	H–6→LUMO (5%)
339.9	3.6476	0.0	Singlet-AG	H–3→LUMO (33%), H–1→LUMO (44%)	H–6→L+1 (7%), H–5→L+1 (5%), H–2→L+1 (2%)
339.7	3.6496	0.0109	Singlet-AU	H–3→L+1 (38%), H–1→L+1 (38%)	H–6→LUMO (7%), H–5→LUMO (6%), H–2→LUMO (3%)
339.4	3.6534	0.0	Triplet-AG		H–22→L+9 (2%), H–21→L+4 (4%), H–21→L+8 (2%), H–20→L+5 (2%), H–20→L+10 (2%), H–19→L+5 (5%), H–18→L+9 (2%), H–17→L+4 (4%), H–13→L+17 (5%), H–12→L+16 (4%), H–9→L+5 (3%), H–8→L+11 (3%), H–2→L+5 (2%), H–2→L+10 (3%)
339.4	3.6535	0.0	Triplet-AU		H–22→L+8 (3%), H–21→L+5 (4%), H–21→L+9 (2%), H–19→L+4 (5%), H–17→L+5 (2%), H–17→L+6 (3%), H–13→L+16 (4%), H–12→L+17 (4%), H–9→L+4 (3%), H–8→L+10 (2%), H–2→L+4 (3%), H–2→L+11 (3%)
338.6	3.6617	0.0	Singlet-AG	H–5→L+1 (14%), H–3→LUMO (33%), H–1→LUMO (46%)	
338.2	3.6659	0.0038	Singlet-AU	H–5→LUMO (13%), H–3→L+1 (29%), H–1→L+1 (52%)	
324.5	3.8212	0.0	Triplet-AG	H–25→L+1 (18%), H–24→LUMO (18%)	H–27→L+1 (4%), H–26→LUMO (8%), H–22→L+1 (3%), H–16→LUMO (3%), H–15→L+1 (8%), H–14→LUMO (5%), H–9→L+1 (2%), H–2→L+1 (8%), HOMO→LUMO (5%)
324.5	3.8213	0.0	Triplet-AU	H–25→LUMO (18%), H–24→L+1 (18%)	H–27→LUMO (4%), H–26→L+1 (8%), H–22→LUMO (3%), H–16→L+1 (3%), H–15→LUMO (8%), H–14→L+1 (5%), H–9→LUMO (2%), H–2→LUMO (8%), HOMO→L+1 (5%)
308.1	4.0238	0.0	Triplet-AU	H–2→LUMO (41%)	H–33→LUMO (4%), H–32→L+1 (4%), H–26→L+1 (7%), H–25→LUMO (9%), H–24→L+1 (3%), H–4→LUMO (3%), HOMO→L+1 (8%)

308.1	4.0244	0.0	Triplet-AG	H–2→L+1 (41%)	H–33→L+1 (4%), H–32→LUMO (4%), H–26→LUMO (7%), H–25→L+1 (9%), H–24→LUMO (3%), H–4→L+1 (3%), HOMO→LUMO (8%)
307.8	4.0285	0.0843	Singlet-AU	H–2→LUMO (75%), HOMO→L+1 (10%)	H–7→L+1 (5%), H–5→LUMO (2%)
307.5	4.0321	0.0	Singlet-AG	H–2→L+1 (75%)	H–7→LUMO (5%), H–5→L+1 (2%), HOMO→LUMO (9%)
292.7	4.2355	0.0	Triplet-AU	H–4→LUMO (81%)	H–25→LUMO (2%), H–16→L+1 (2%), H–2→LUMO (3%)
292.6	4.2367	0.0	Triplet-AG	H–4→L+1 (81%)	H–25→L+1 (2%), H–16→LUMO (2%), H–2→L+1 (3%)
292.6	4.2374	0.001	Singlet-AU	H–4→LUMO (88%)	H–16→L+1 (3%)
292.5	4.2384	0.0	Singlet-AG	H–4→L+1 (88%)	H–16→LUMO (3%)
287.8	4.3079	0.0	Triplet-AU	H–33→LUMO (14%), H–32→L+1 (14%), H–2→LUMO (20%)	H–9→L+13 (5%), H–8→L+12 (2%), H–7→L+12 (3%), H–6→LUMO (5%), H–4→LUMO (2%)
287.8	4.3085	0.0	Triplet-AG	H–33→L+1 (14%), H–32→LUMO (14%), H–2→L+1 (20%)	H–9→L+12 (5%), H–8→L+13 (3%), H–7→L+13 (3%), H–6→L+1 (5%), H–4→L+1 (2%)
283.2	4.3785	0.0	Triplet-AG	H–9→L+3 (11%), H–2→L+3 (12%), HOMO→L+2 (34%)	H–15→L+3 (4%), H–14→L+2 (3%), H–12→L+2 (2%), H–11→L+3 (3%), H–8→L+2 (8%), H–7→L+2 (7%)
283.0	4.3812	0.0	Triplet-AU	H–9→L+2 (12%), H–2→L+2 (12%), HOMO→L+3 (32%)	H–15→L+2 (4%), H–14→L+3 (4%), H–12→L+3 (2%), H–11→L+2 (4%), H–8→L+3 (8%), H–7→L+3 (7%)
279.3	4.4392	0.0538	Singlet-AU	HOMO→L+3 (29%)	H–25→LUMO (3%), H–24→L+1 (5%), H–15→LUMO (3%), H–9→LUMO (5%), H–8→L+1 (5%), H–7→L+1 (5%), H–6→LUMO (5%), H–5→LUMO (8%), H–3→L+1 (5%), H–2→LUMO (3%), H–2→L+2 (7%)
279.2	4.4406	0.0	Singlet-AG	HOMO→L+2 (41%)	H–25→L+1 (3%), H–24→LUMO (5%), H–15→L+1 (3%), H–9→L+1 (4%), H–8→LUMO (4%), H–7→LUMO (3%), H–6→L+1 (2%), H–5→L+1 (3%), H–2→L+3 (9%)
279.1	4.4428	0.0	Triplet-AU	H–5→LUMO (37%), H–3→L+1 (28%)	H–14→L+1 (4%), H–6→LUMO (7%), HOMO→L+3 (3%)
279.0	4.4439	0.0	Triplet-AG	H–5→L+1 (38%), H–3→LUMO (29%)	H–14→LUMO (4%), H–6→L+1 (7%), HOMO→L+2 (2%)
277.6	4.4667	0.0133	Singlet-AU	H–5→LUMO (31%), H–3→L+1 (16%), HOMO→L+3 (24%)	H–26→L+1 (2%), H–14→L+1 (3%), H–7→L+1 (2%), H–6→LUMO (7%), H–2→L+2 (4%)
277.5	4.4687	0.0	Singlet-AG	H–5→L+1 (37%), H–3→LUMO (20%), HOMO→L+2 (14%)	H–8→LUMO (3%), H–7→LUMO (4%), H–6→L+1 (8%), H–2→L+1 (2%)

276.9	4.4783	0.0	Triplet-AU	H–2→L+7 (12%), HOMO→L+5 (21%), HOMO→L+6 (15%)	H–12→L+9 (2%), H–11→L+8 (3%), H–10→L+9 (2%), H–2→L+4 (4%), HOMO→L+33 (2%)
276.6	4.4818	0.0	Triplet-AG	HOMO→L+4 (10%), HOMO→L+7 (18%)	H–25→L+3 (2%), H–24→L+2 (2%), H–2→L+5 (9%), H–2→L+6 (5%), HOMO→L+2 (5%)
275.2	4.5058	0.0	Triplet-AU	H–25→L+2 (11%), H–24→L+3 (10%), HOMO→L+3 (22%)	H–27→L+2 (2%), H–26→L+3 (6%), H–25→LUMO (2%), H–15→L+2 (4%), H–14→L+3 (3%), H–9→L+2 (2%), H–5→LUMO (4%), H–3→L+1 (2%), H–2→L+2 (3%), HOMO→L+5 (3%)
275.2	4.5060	0.0	Triplet-AG	HOMO→L+2 (17%)	H–26→L+2 (5%), H–25→L+3 (9%), H–24→L+2 (8%), H–15→L+3 (3%), H–14→L+2 (2%), H–5→L+1 (3%), H–2→L+3 (2%), H–2→L+5 (4%), HOMO→L+4 (8%), HOMO→L+7 (3%)
270.6	4.5814	0.0	Singlet-AG	H–6→L+1 (54%)	H–25→L+1 (3%), H–9→L+1 (3%), H–5→L+1 (5%), H–1→LUMO (6%), HOMO→L+2 (9%)
270.6	4.5825	0.0022	Singlet-AU	H–6→LUMO (66%), H–5→LUMO (15%)	H–1→L+1 (7%)
270.1	4.5896	0.0	Singlet-AG	H–6→L+1 (14%), H–5→L+1 (17%), HOMO→L+2 (21%)	H–15→L+1 (5%), H–14→LUMO (5%), H–11→L+1 (3%), H–9→L+1 (8%), H–8→LUMO (3%), H–7→LUMO (4%), H–3→LUMO (3%)
269.9	4.5936	0.0803	Singlet-AU	H–9→LUMO (10%), HOMO→L+3 (31%)	H–16→L+1 (2%), H–15→LUMO (6%), H–14→L+1 (7%), H–12→L+1 (2%), H–11→LUMO (3%), H–8→L+1 (3%), H–7→L+1 (4%), H–5→LUMO (9%), H–3→L+1 (3%)
263.5	4.7056	0.0	Singlet-AG	H–2→L+5 (22%), HOMO→L+4 (54%)	HOMO→L+7 (9%)
262.5	4.7241	0.1605	Singlet-AU	H–2→L+4 (10%), H–2→L+7 (11%), HOMO→L+5 (47%), HOMO→L+6 (13%)	
260.4	4.7617	0.0	Singlet-AG	H–25→L+1 (13%), H–9→L+1 (10%)	H–26→LUMO (5%), H–24→LUMO (8%), H–9→L+3 (3%), H–8→LUMO (3%), H–7→LUMO (7%), H–6→L+1 (4%), H–2→L+6 (4%), H–1→L+2 (2%), HOMO→L+2 (2%), HOMO→L+4 (5%), HOMO→L+7 (7%), HOMO→L+8 (3%)
259.7	4.7735	0.0642	Singlet-AU	H–25→LUMO (15%), H–9→LUMO (11%)	H–26→L+1 (6%), H–24→L+1 (9%), H–9→L+2 (3%), H–8→L+1 (4%), H–7→L+1 (7%), H–7→L+3 (2%), H–6→LUMO (5%), H–1→L+3 (3%), HOMO→L+3 (4%), HOMO→L+5 (6%)
258.1	4.8033	0.0	Singlet-AG	H–2→L+6 (16%), HOMO→L+7 (41%)	H–25→L+1 (2%), H–9→L+1 (2%), HOMO→L+4 (3%), HOMO→L+8 (9%)

257.6	4.8124	0.1294	Singlet-AU	H–2→L+4 (11%), HOMO→L+5 (10%), HOMO→L+6 (52%)	H–2→L+7 (7%), H–2→L+8 (4%), HOMO→L+9 (5%)
254.9	4.8631	0.0	Singlet-AG	H–1→L+2 (86%)	H–6→L+3 (5%)
254.5	4.8718	0.007	Singlet-AU	H–1→L+3 (84%)	H–6→L+2 (5%), H–3→L+3 (3%)
254.0	4.8804	0.0	Singlet-AG	H–5→L+3 (16%), H–3→L+2 (67%)	H–2→L+3 (2%)
253.7	4.8866	0.0025	Singlet-AU	H–5→L+2 (17%), H–3→L+3 (64%)	H–2→L+2 (3%), H–1→L+3 (5%)
249.1	4.9773	0.0109	Singlet-AU	H–20→LUMO (10%), H–15→LUMO (10%), H–14→L+1 (12%), H–7→L+1 (19%), HOMO→L+9 (11%)	H–26→L+1 (3%), H–18→LUMO (3%), H–16→L+1 (2%), H–5→LUMO (3%), H–2→L+8 (3%)
249.0	4.9794	0.0	Singlet-AG	H–20→L+1 (11%), H–15→L+1 (12%), H–14→LUMO (15%), H–7→LUMO (22%)	H–26→LUMO (4%), H–18→L+1 (4%), H–16→LUMO (3%), H–12→LUMO (2%), H–5→L+1 (4%), H–3→LUMO (2%)

eV: electron-volt; Singlet-AG: Low-lying singlet excited states of A_g symmetry; Singlet-AU: Low-lying singlet excited states of A_u symmetry; Triplet-AG: Low-lying triplet excited states of A_g symmetry; Triplet-AU: Low-lying triplet excited states of A_u symmetry; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) dcq_b_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: dcq_b_auto

```
Bond precision:   C-C = 0.0047 A          Wavelength=1.54184

Cell:             a=3.80609(19)     b=15.7906(7)      c=16.5048(7)
                  alpha=90          beta=92.154(4)    gamma=90
Temperature:      292 K
```

	Calculated	Reported
Volume	991.25(8)	991.25(8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C9 H5 Cl3 Cu N	C9 H5 Cl3 Cu N
Sum formula	C9 H5 Cl3 Cu N	C9 H5 Cl3 Cu N
Mr	297.04	297.03
Dx,g cm-3	1.990	1.990
Z	4	4
Mu (mm-1)	10.159	10.159
F000	584.0	584.0
F000'	581.29	
h,k,lmax	4,19,20	4,19,20
Nref	1967	1947
Tmin,Tmax	0.499,0.596	0.102,1.000
Tmin'	0.009	

```
Correction method= # Reported T Limits: Tmin=0.102 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.990          Theta(max)= 72.162

R(reflections)= 0.0546( 1740)                wR2(reflections)=
                                             0.1590( 1947)
S = 1.055                 Npar= 127
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.128
```

Alert level G

```
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          1 Info
PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 .....        0.128 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large      0.11 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu1      --Cl4      .      32.8 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu1      --Cl4_a    .      19.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu1      --Cl4_b    .      35.2 s.u.
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        20 Note
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value .....        2.631 Note
             Predicted wR2: Based on SigI**2  6.04 or SHELX Weight 15.08
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

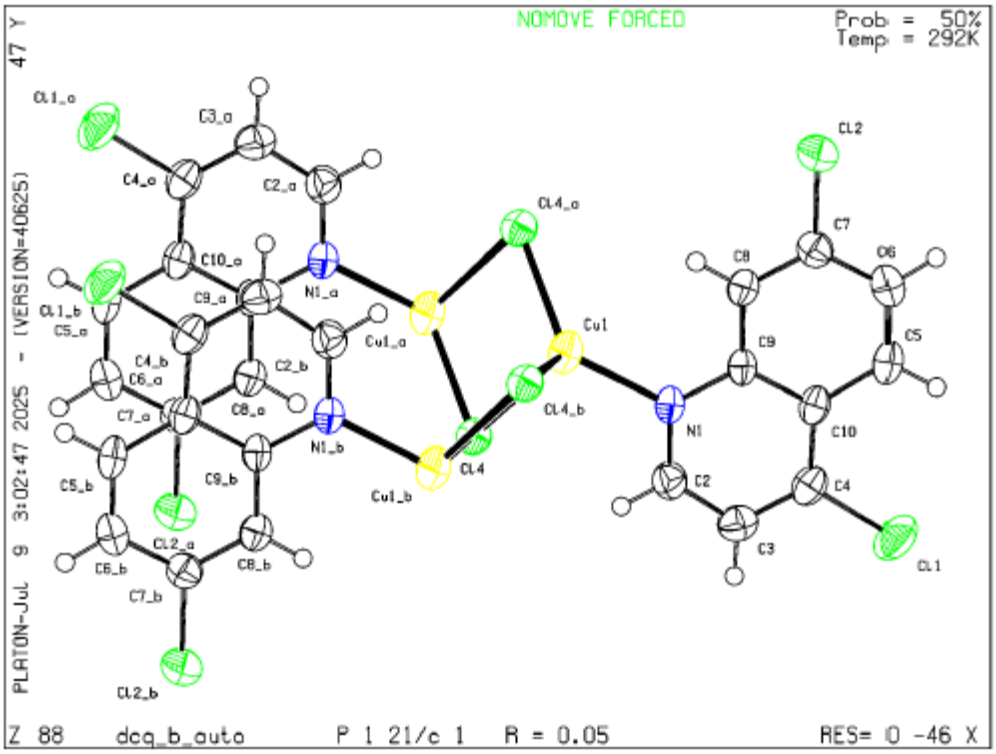
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 04/06/2025; check.def file version of 30/05/2025

Datablock dcq_b_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cuclpph3_abs

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cuclpph3_abs

```
Bond precision:   C-C = 0.0040 A          Wavelength=0.71073

Cell:          a=9.1960(2)       b=10.8845(3)      c=13.6493(4)
               alpha=90.711(2)   beta=107.013(2)   gamma=104.575(2)
Temperature:   292 K
```

	Calculated	Reported
Volume	1258.91(6)	1258.91(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C54 H40 Cl6 Cu2 N2 P2	C54 H40 Cl6 Cu2 N2 P2
Sum formula	C54 H40 Cl6 Cu2 N2 P2	C54 H40 Cl6 Cu2 N2 P2
Mr	1118.62	1118.60
Dx,g cm-3	1.475	1.475
Z	1	1
Mu (mm-1)	1.266	1.266
F000	568.0	568.0
F000'	569.86	
h,k,lmax	11,13,16	11,13,16
Nref	4534	4524
Tmin,Tmax	0.583,0.711	0.531,0.753
Tmin'	0.364	

```
Correction method= # Reported T Limits: Tmin=0.531 Tmax=0.753
AbsCorr = ANALYTICAL

Data completeness= 0.998          Theta(max)= 25.217

R(reflections)= 0.0326( 4018)                    wR2(reflections)=
                                                 0.0845( 4524)
S = 1.080                 Npar= 298
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X)  Cu1      --P1       .        7.3 s.u.
PLAT910_ALERT_3_C Missing FCF Reflection(s) Below Theta(Min)[Deg]=       3.32 Note
                1  0  0,  -1  1  0,   0  1  0,   0 -1  1,  -1  0  1,   0  0  1,
                1  0  1,  -1  1  1,   0  1  1,   0  0  2,
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or U(i,j)  Restrained non-H-Atoms          2 Report
PLAT063_ALERT_4_G Crystal Size Possibly too Large for Beam Size ..       0.79 mm
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.002 Degree
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu1      --Cl3      .       20.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu1      --Cl3_a    .       20.7 s.u.
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        72% Note
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      3.336 Note
              Predicted wR2: Based on SigI**2  2.53 or SHELX Weight  7.82
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

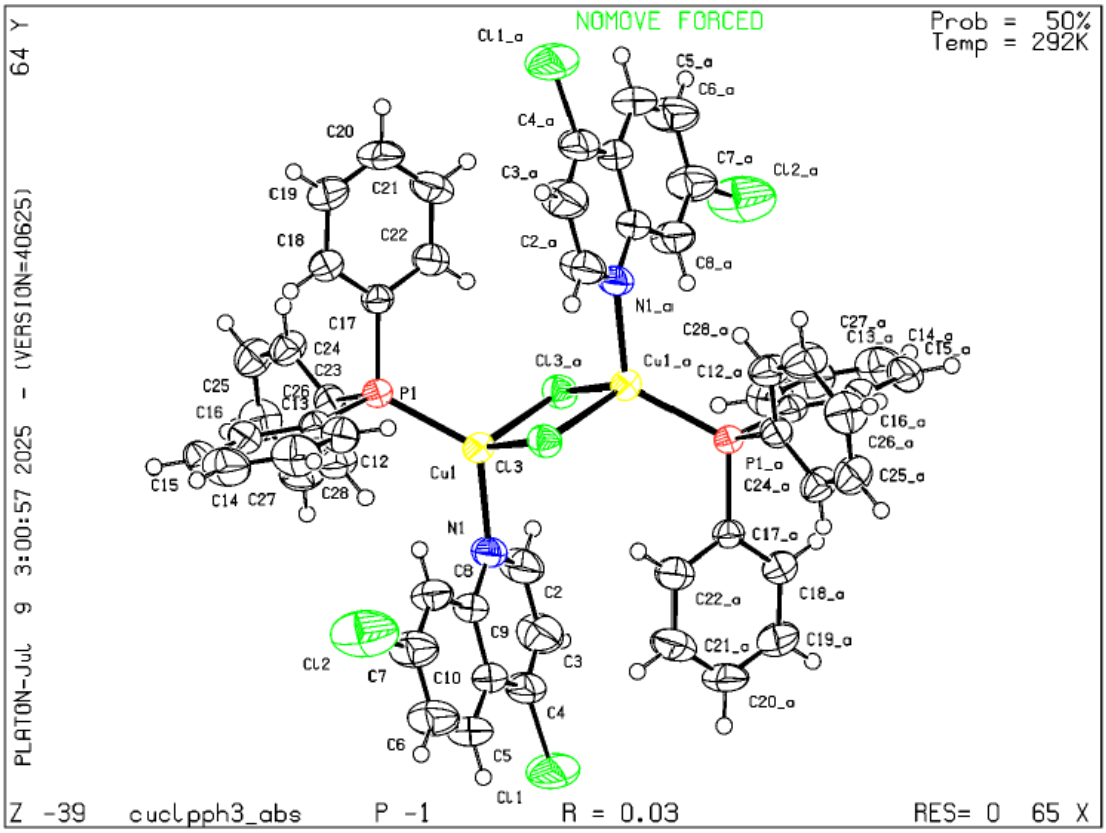
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 04/06/2025; check.def file version of 30/05/2025

Datablock cuclpph3_abs - ellipsoid plot



No syntax errors found.
Please wait while processing ....

CIF dictionary
Interpreting this report

Datablock: cubrpph3_b

Bond precision: C-C = 0.0045 A Wavelength=0.71073
Cell: a=9.2590(3) b=11.0640(3) c=13.5883(4)
alpha=89.960(2) beta=73.119(3) gamma=74.366(3)
Temperature: 291 K

	Calculated	Reported
Volume	1278.19(7)	1278.19(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C54 H40 Br2 Cl4 Cu2 N2 P2	C54 H40 Br2 Cl4 Cu2 N2 P2
Sum formula	C54 H40 Br2 Cl4 Cu2 N2 P2	C54 H40 Br2 Cl4 Cu2 N2 P2
Mr	1207.52	1207.52
Dx,g cm-3	1.569	1.569
Z	1	1
Mu (mm-1)	2.705	2.705
F000	604.0	604.0
F000'	605.01	
h,k,lmax	12,15,18	12,15,18
Nref	7266	6395
Tmin,Tmax	0.540,0.645	0.544,1.000
Tmin'	0.501	

Correction method= # Reported T Limits: Tmin=0.544 Tmax=1.000
AbsCorr = GAUSSIAN
Data completeness= 0.880 Theta(max)= 29.716
R(reflections)= 0.0377(4705) wR2(reflections)= 0.0839(6395)
S = 1.027 Npar= 298

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT910_ALERT_3_B Missing FCF Reflection(s) Below Theta(Min)[Deg]= 3.33 Note
1 0 0, 0 1 0, 1 1 0, -1 -1 1, 0 -1 1, -1 0 1,
0 0 1, 1 0 1, 0 1 1, 1 1 1, 0 0 2,

Alert level C

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.530 Check

Alert level G

PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 = 3 Note
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br01 --Cu1 . 25.0 s.u.
And 2 other PLAT232 Alerts
More ...
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 48 Note

Br01	P003	Cl04	Cl05	C00A	C00B	H00B	C00C
H00C	C00D	H00D	C00E	H00E	C00F	H00F	C00G
H00G	C00H	H00H	C00I	H00I	C00J	C00K	H00K
C00L	H00L	C00M	H00M	C00N	C00O	H00O	C00P
H00P	C00Q	C00R	H00R	C00S	H00S	C00T	H00T
C00U	H00U	C00V	H00V	C00W	H00W	C00X	H00X

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 860 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 3.9 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ..... 2.786 Note
Predicted wR2: Based on SigI**2 3.01 or SHELX Weight 8.17
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 7 Info

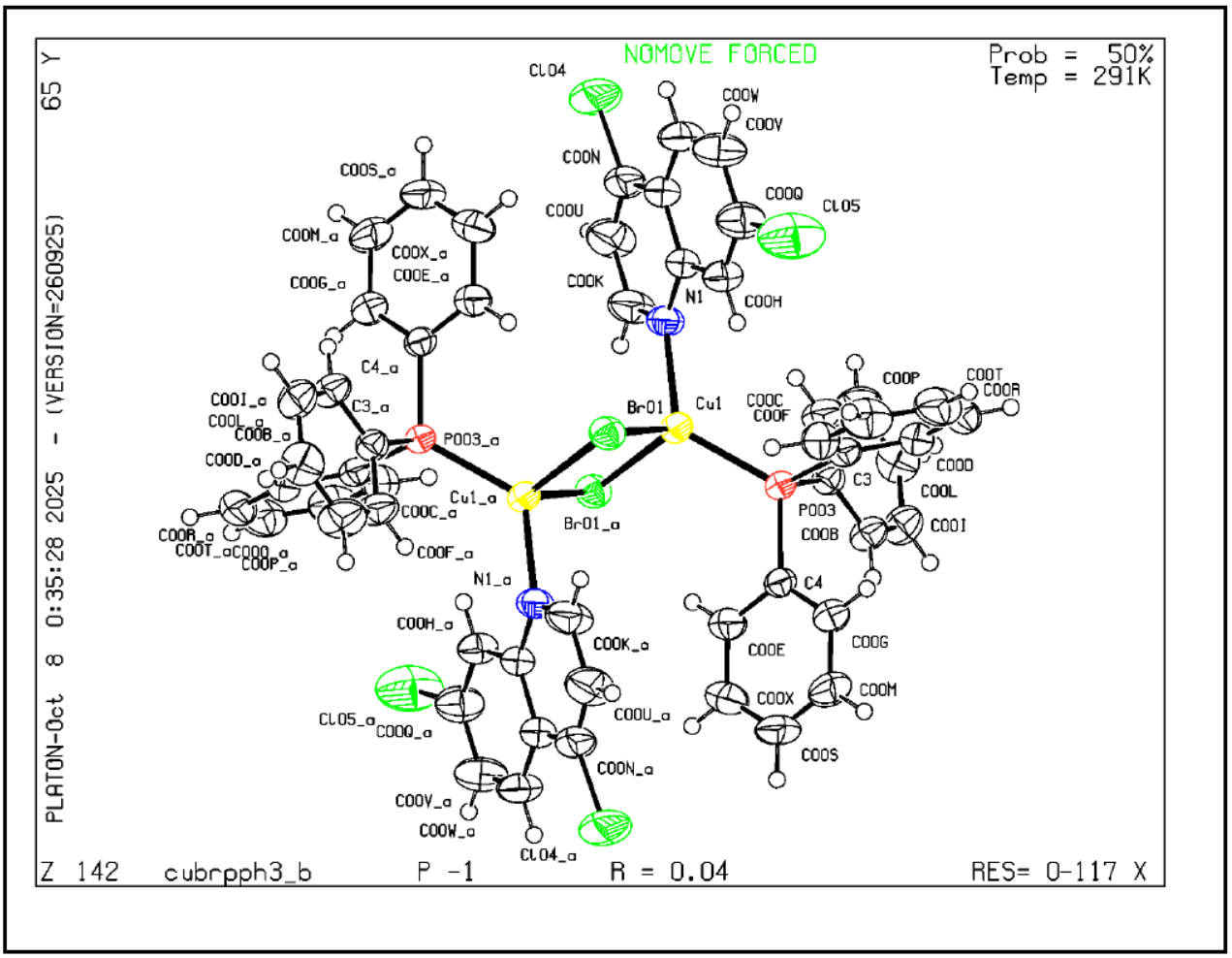
0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
9 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

PLATON version of 26/09/2025; check.def file version of 20/09/2025

Datablock cubrpph3_b - ellipsoid plot



References

1. Lakowicz, J. R.; *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: Boston, MA, 2006.
2. Kobayashi, F.; Takatsu, Y.; Saito, D.; Yoshida, M.; Kato, M.; Tadokoro, M.; *Inorg. Chem*. **2024**, *63*, 15323. [Crossref]