

Supplementary Information

Chromogenic Chemosensors Based on Phenolic Imines for the Detection of Alkylamines and Lidocaine in Water and in the Vapor Phase

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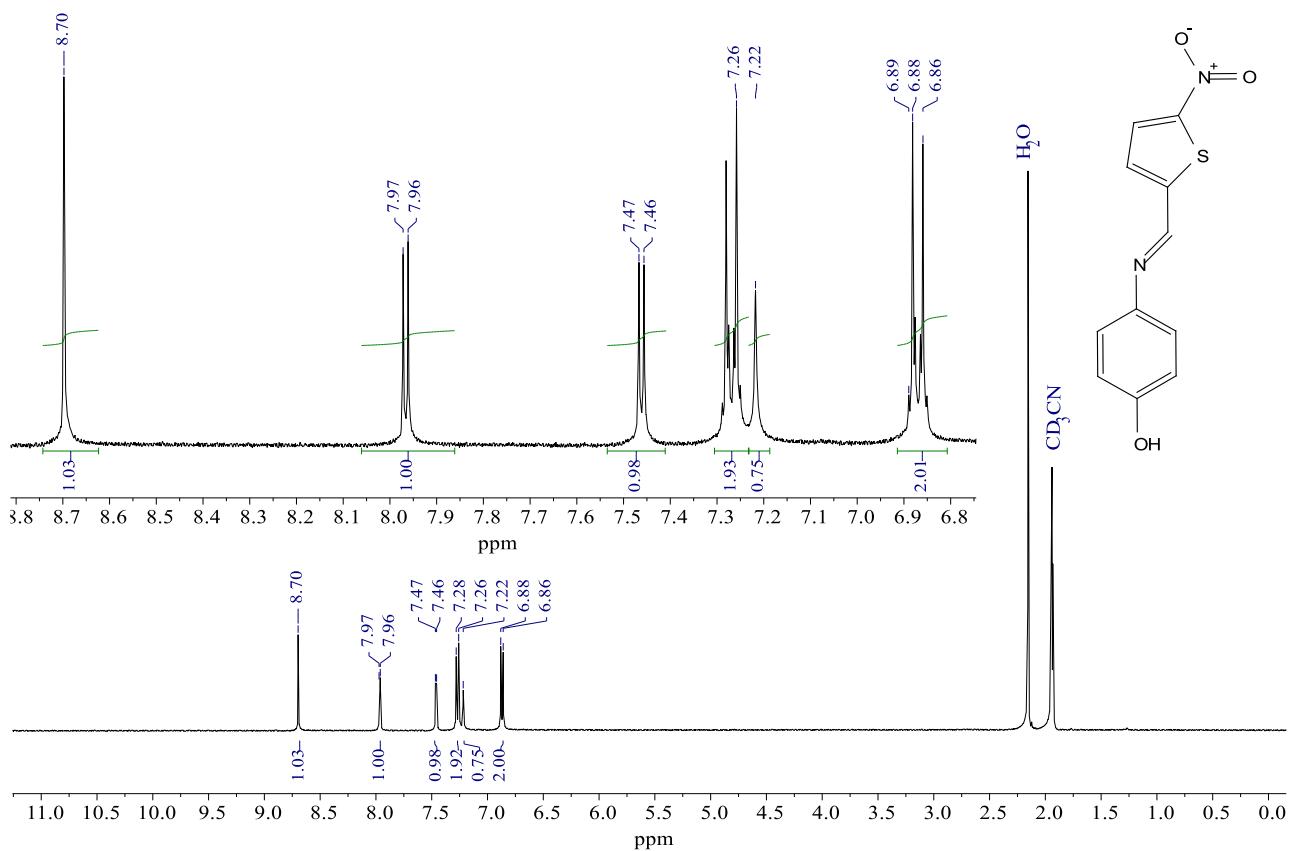


Figure S1. ^1H NMR spectrum (400 MHz, CD_3CN) of compound **3a**.

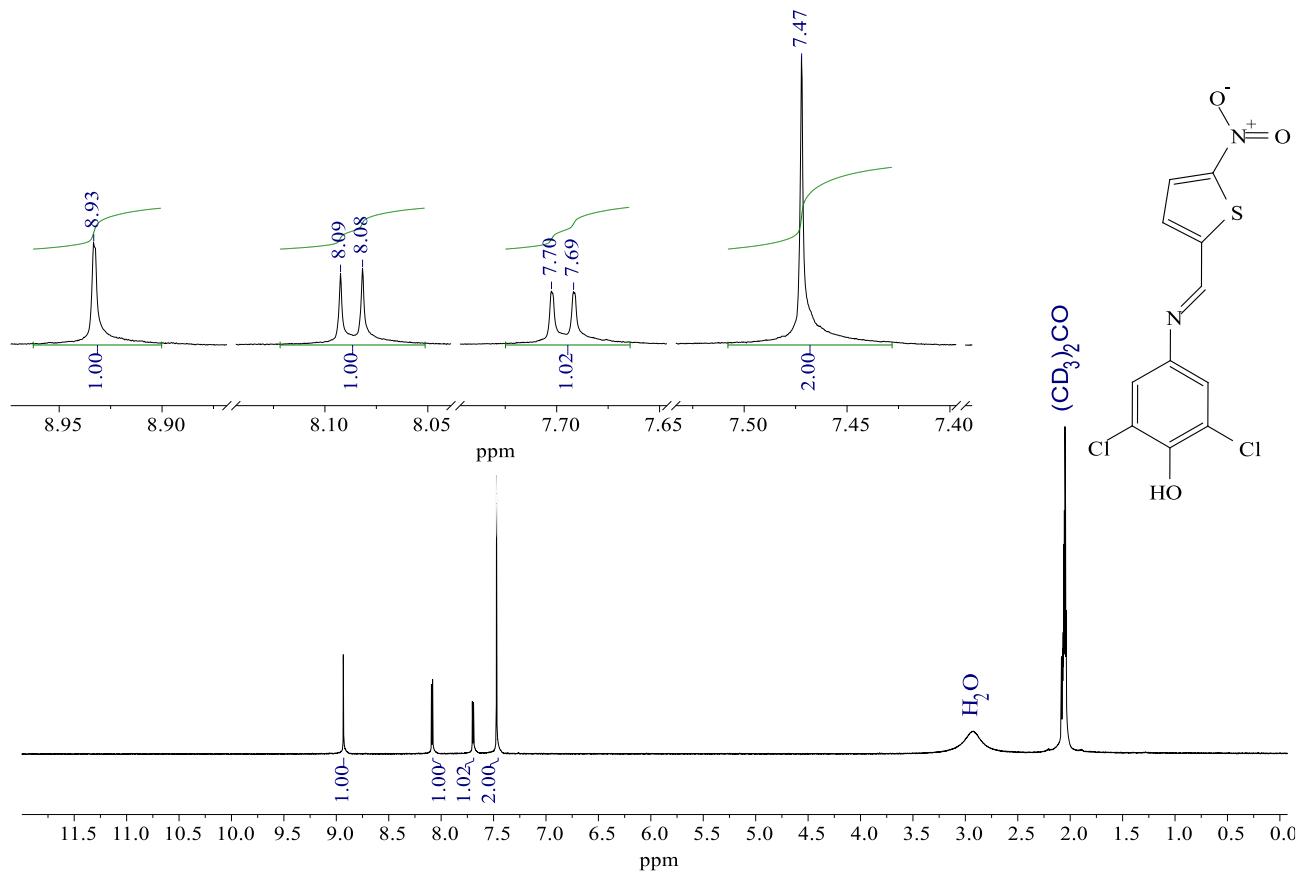


Figure S2. ^1H NMR spectrum (400 MHz, acetone- d_6) of compound **4a**.

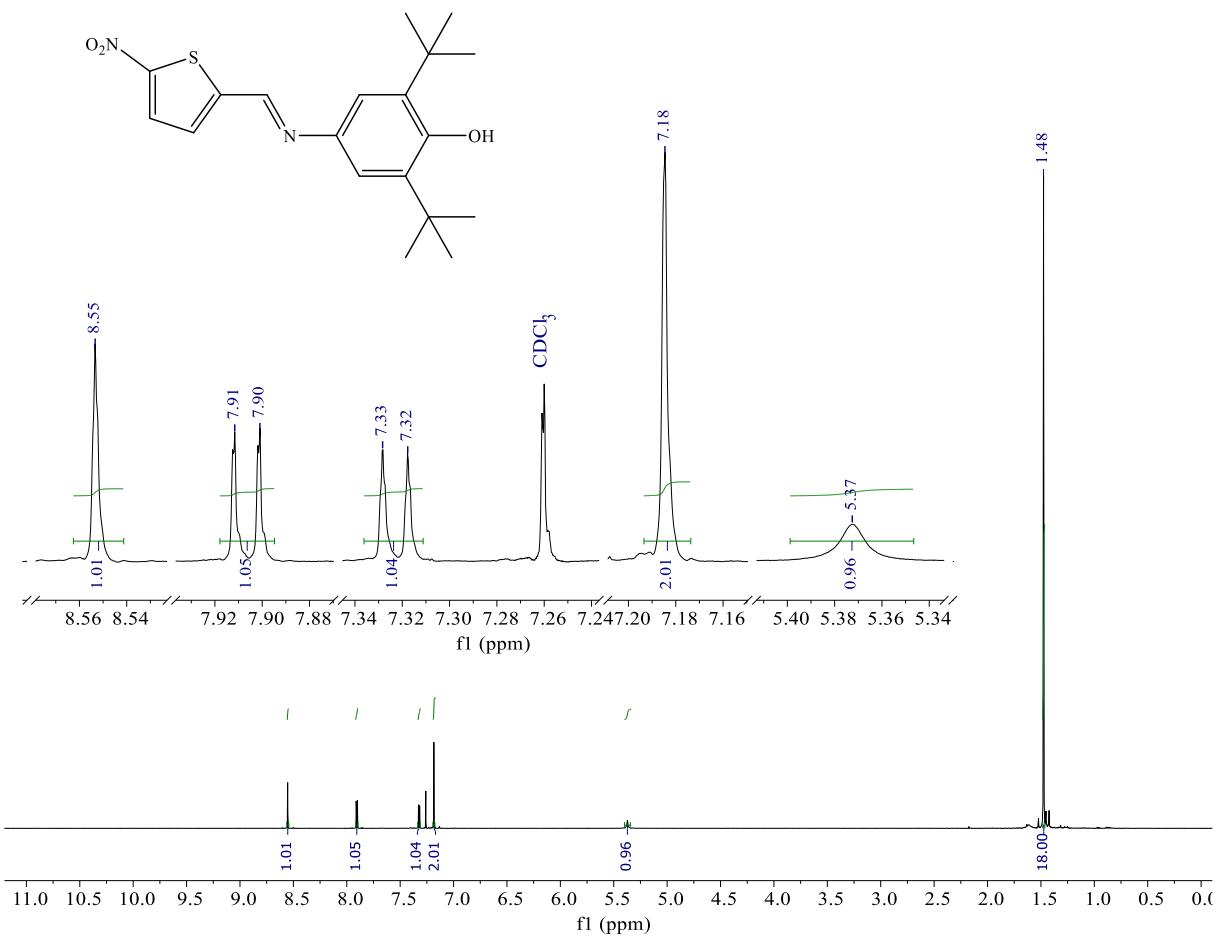


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 5a.

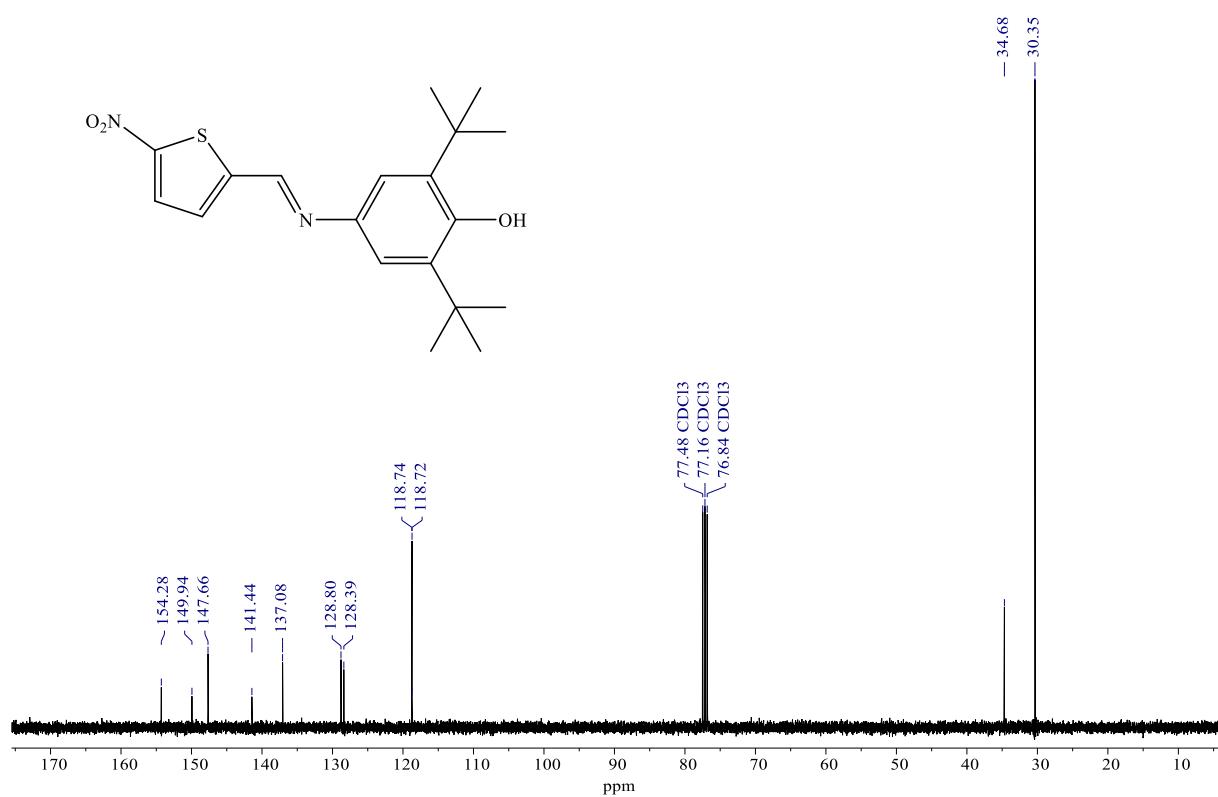


Figure S4. ¹³C NMR spectrum (100 MHz, CDCl₃) compound of **5a**.

Display Report

Analysis Info

Analysis Name D:\Data\LabSelen 07.11\161017-A1000001.d
Method testeinicinal APPI_Elis.m
Sample Name 161017-A1
Comment

Acquisition Date 11/7/2017 12:59:57 PM

Operator tofq
Instrument micrOTOF-Q 228888.10243

Acquisition Parameter

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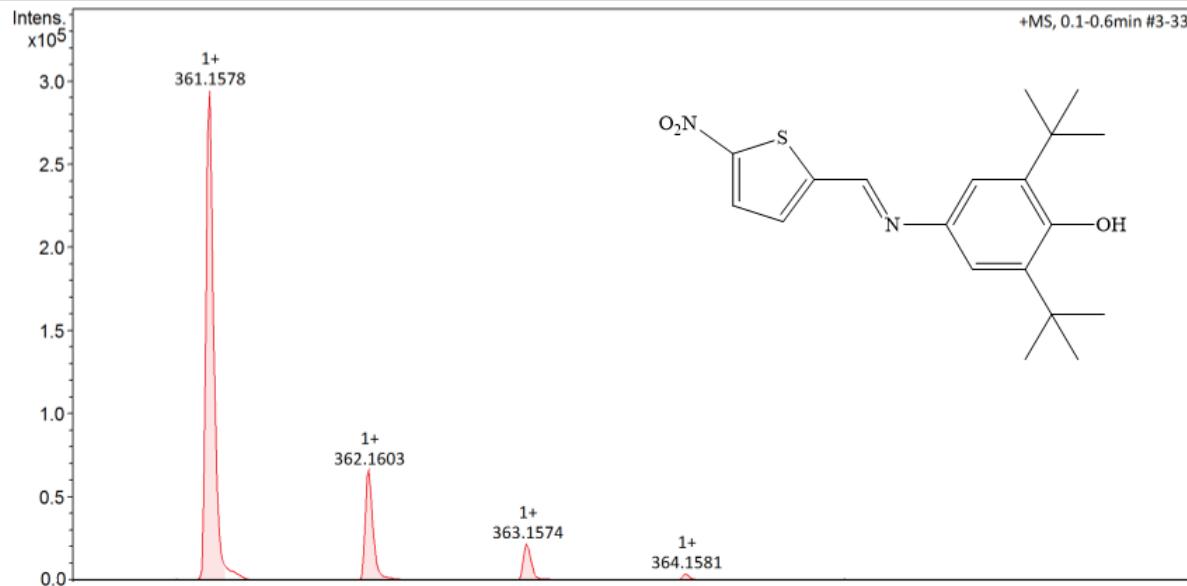


Figure S5. HRMS spectrum of compound 5a.

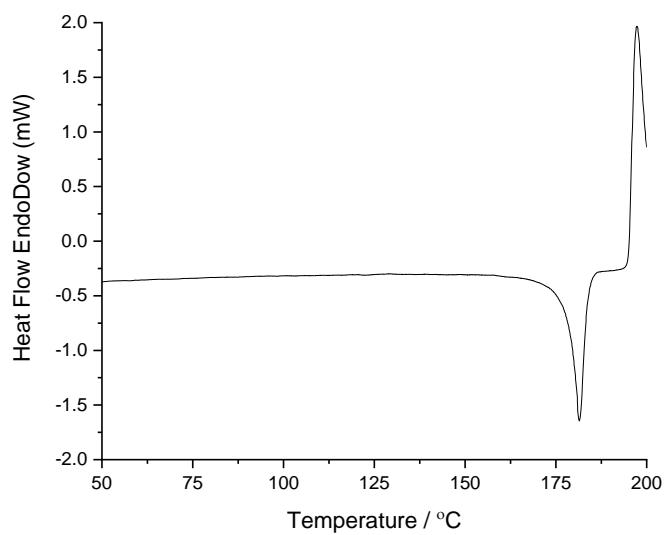


Figure S6. DSC analysis for compound **5a**. Melting temperature 181.46 °C; melting enthalpy $\Delta H_f = -82.35 \text{ J g}^{-1}$.

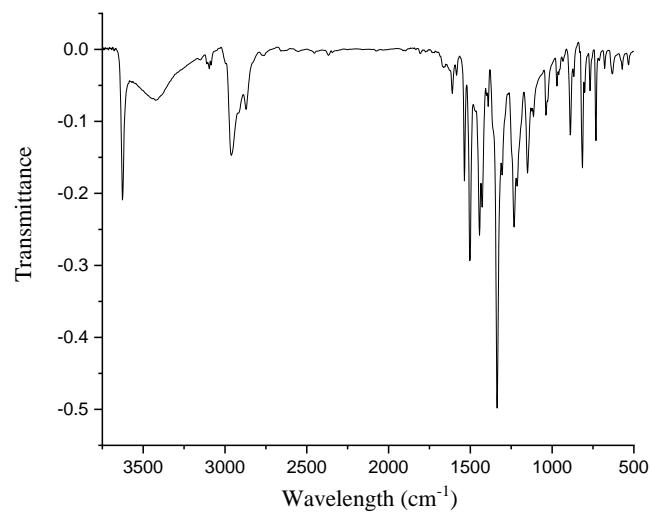


Figure S7. FTIR spectrum of **5a** (KBr pellet).

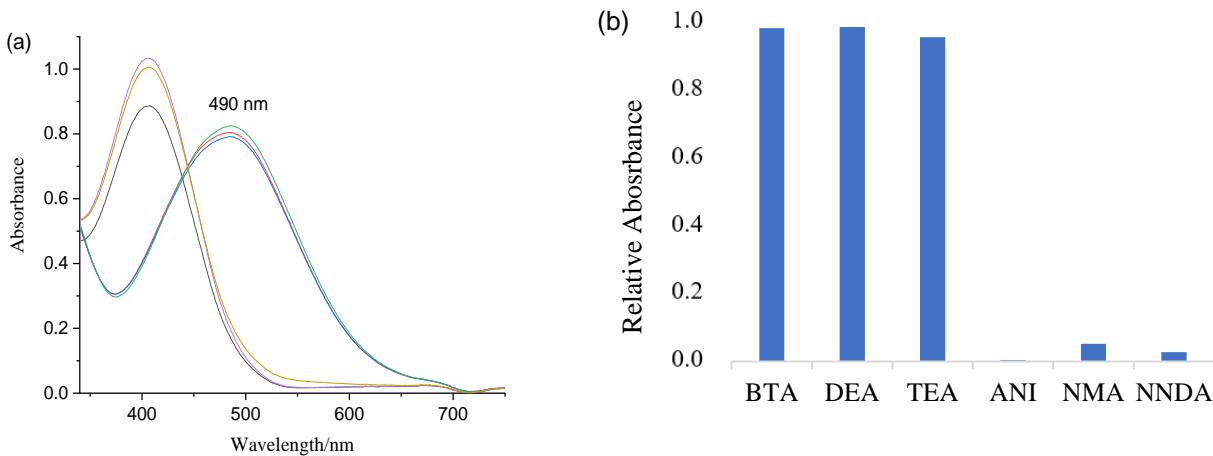


Figure S8. (a) UV-Vis spectra of the solutions of **3a** in water in the absence and after addition of BTA, DEA, TEA, ANI, NMA, and NNDA at 25.0 °C. (b) Corresponding relative absorbances. c (amine) = 2.0×10^{-4} mol L⁻¹.

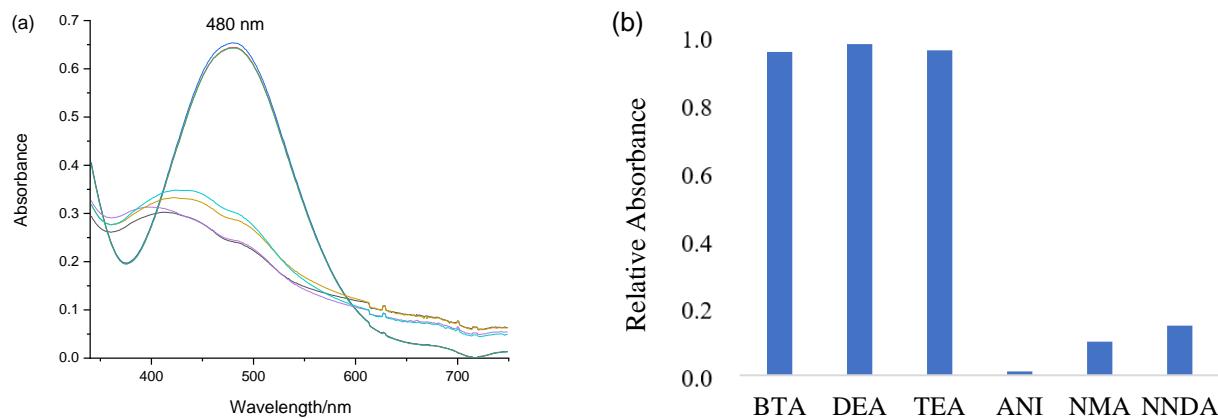


Figure S9. (a) UV-Vis spectra of the solutions of **4a** in water in the absence and after addition of BTA, DEA, TEA, ANI, NMA, and NNDA at 25.0 °C. (b) Corresponding relative absorbances. c (amine) = 2.0×10^{-4} mol L⁻¹.

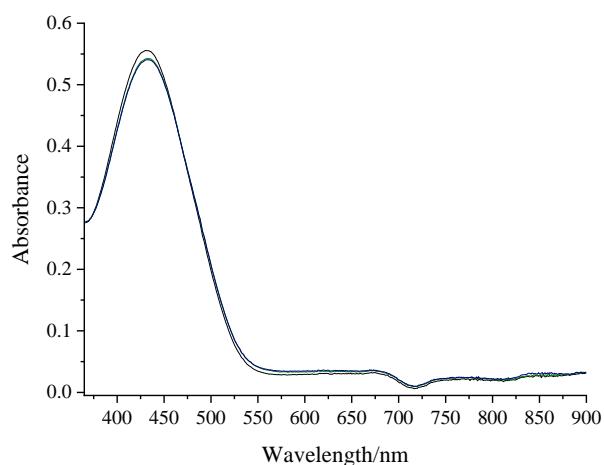


Figure S10. UV-Vis spectra of the solutions of **5a** in water in the absence and after addition of BTA, DEA, TEA, ANI, NMA, and NNDA at 25.0 °C. c (amine) = 2.0×10^{-4} mol L⁻¹.

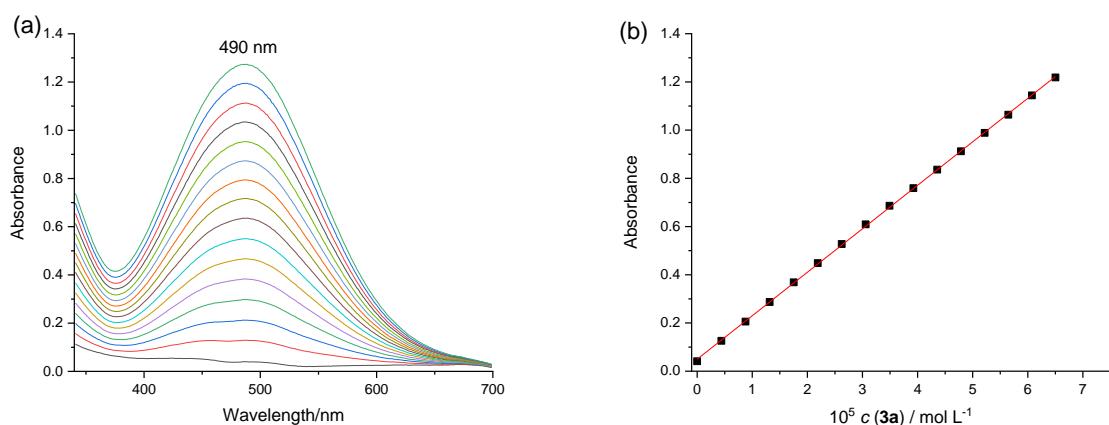


Figure S11. (a) UV-Vis spectra and (b) absorbances at 490 nm for increasing amounts of **3b** in water at 25.0 °C. Compound **3a** was deprotonated using c (BTA) = 1.0×10^{-3} mol L⁻¹. Data were fitted through a linear equation (—), providing $\epsilon_{\text{max}} = (1.804 \pm 0.006) \times 10^4$ L mol⁻¹ cm⁻¹ ($r^2 = 0.999$).

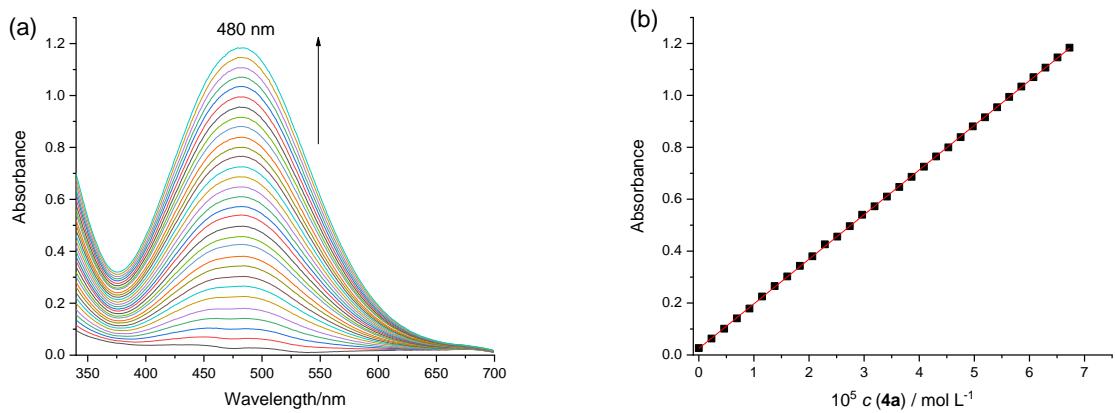


Figure S12. (a) UV-Vis spectra and (b) absorbances at 480 nm for increasing amounts of **4b** in water at 25.0 °C. Compound **4a** was deprotonated using c (BTA) = 1.0×10^{-3} mol L⁻¹. Data were fitted through a linear equation (—), providing $\epsilon_{\text{max}} = (1.719 \pm 0.003) \times 10^4$ L mol⁻¹ cm⁻¹ ($r^2 = 0.999$).

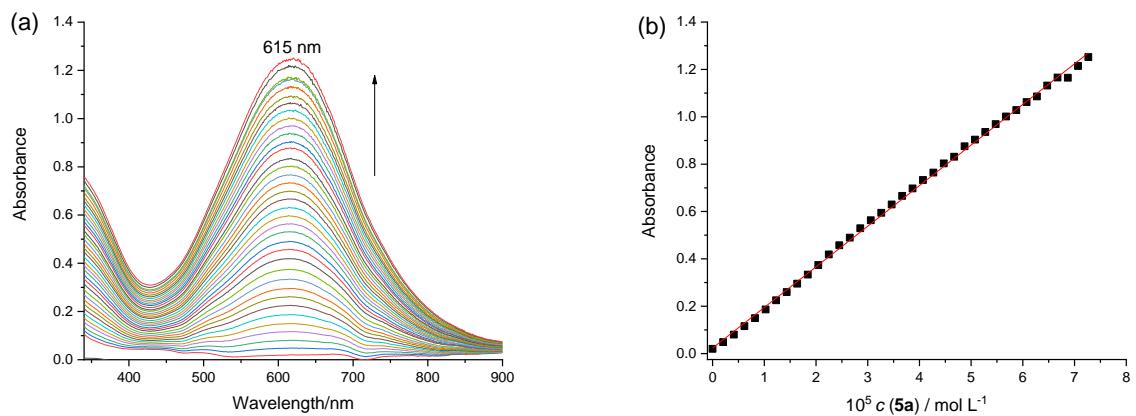


Figure S13. (a) UV-Vis spectra and (b) absorbances at 615 nm for increasing amounts of **5b** in water at 25.0 °C. Compound **5a** was deprotonated using c (NaOH) = 1.0 mol L⁻¹. Data were fitted through a linear equation (—), providing $\epsilon_{\text{max}} = (1.715 \pm 0.010) \times 10^4$ L mol⁻¹ cm⁻¹ ($r^2 = 0.999$).

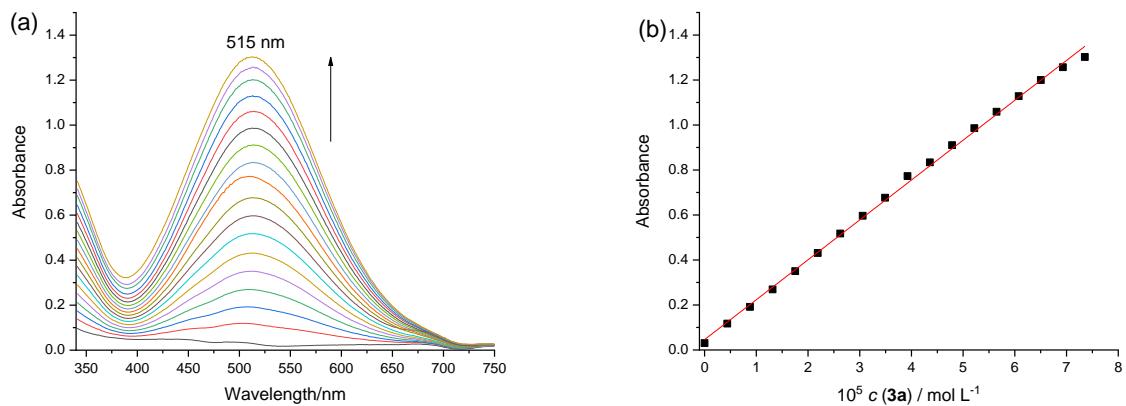


Figure S14. (a) UV-Vis spectra and (b) absorbances at 515 nm for increasing amounts of **3b** in water containing CTAB (1.0×10^{-3} mol L⁻¹) at 25.0 °C. Compound **3a** was deprotonated using c (BTA) = 1.0×10^{-3} mol L⁻¹. Data were fitted through a linear equation (—), providing $\epsilon_{\text{max}} = (1.773 \pm 0.019) \times 10^4$ L mol⁻¹ cm⁻¹ ($r^2 = 0.998$).

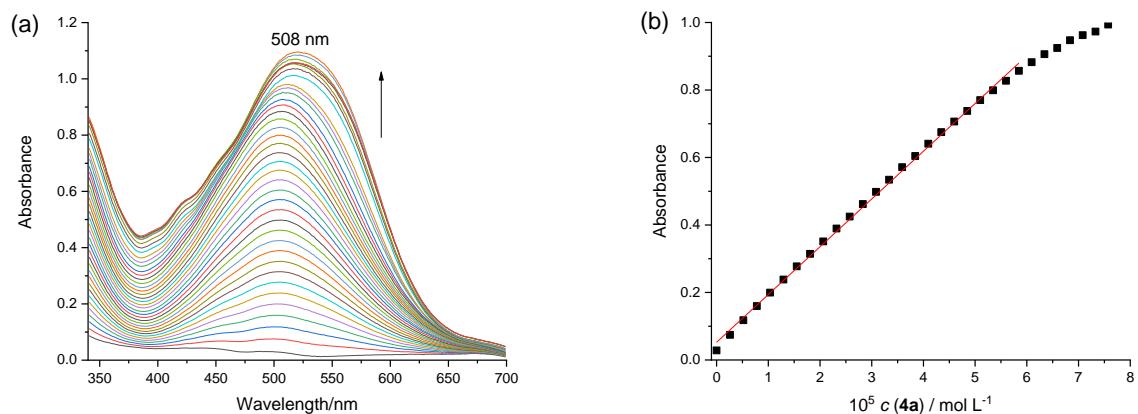


Figure S15. (a) UV-Vis spectra and (b) absorbances at 508 nm for increasing amounts of **4b** in water containing CTAB (1.0×10^{-3} mol L⁻¹) at 25.0 °C. Compound **4a** was deprotonated using c (BTA) = 1.0×10^{-3} mol L⁻¹. Data were fitted through a linear equation (—), providing $\epsilon_{\text{max}} = (1.415 \pm 0.013) \times 10^4$ L mol⁻¹ cm⁻¹ ($r^2 = 0.998$).

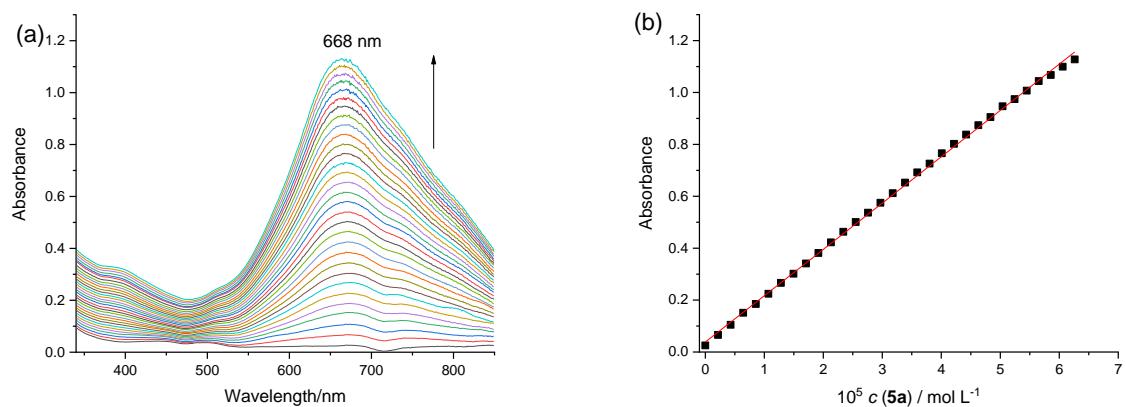


Figure S16. (a) UV-vis spectra and (b) absorbances at 668 nm for increasing amounts of **5b** in water containing CTAB ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) at 25.0°C . Compound **5a** was deprotonated using $c(\text{BTA}) = 1.0 \times 10^{-3} \text{ mol L}^{-1}$. Data were fitted through a linear equation (—), providing $\varepsilon_{\max} = (1.785 \pm 0.010) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ($r^2 = 0.999$).

Table S1. Values of pK_a for the protonated form of the amines utilized in this paper

Protonated amine	pK_a
BTA	10.59 ^a
DEA	10.98 ^a
TEA	10.65 ^a
ANI	4.58 ^b
NMA	4.85 ^b
NNDA	5.06 ^b

^aFrom Juranić;¹ ^bfrom Gohar and Habeeb.² BTA: *n*-butylamine; DEA: diethylamine; TEA: triethylamine; ANI: aniline; NMA: *N*-methylaniline; NNDA: *N,N*-dimethylaniline.

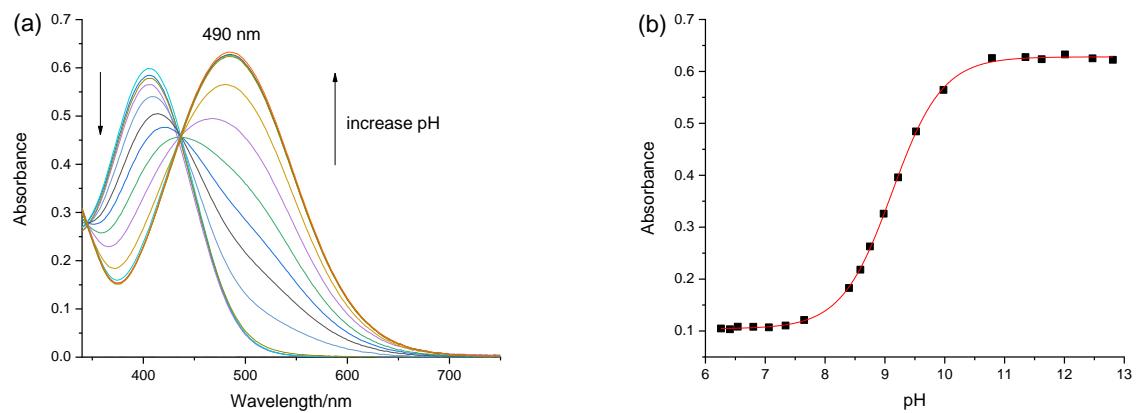


Figure S17. (a) UV-Vis spectra and (b) absorbance values for **3a** at 490 nm as a function of pH in water. Data were fitted using a sigmoidal equation, providing $pK_a = 9.11 \pm 0.01$ ($r^2 = 0.999$).

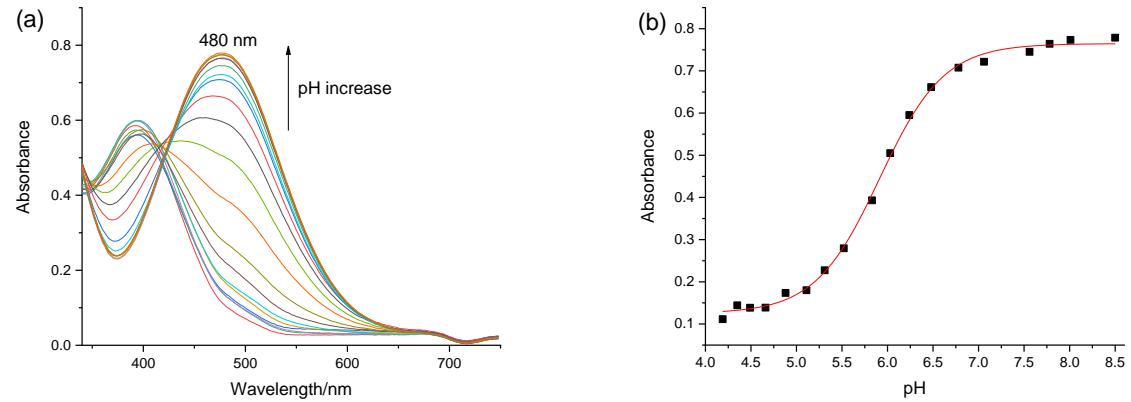


Figure S18. (a) UV-Vis spectra and (b) absorbance values for **4a** at 480 nm as a function of pH in water. Data were fitted using a sigmoidal equation, providing $pK_a = 5.91 \pm 0.01$ ($r^2 = 0.997$).

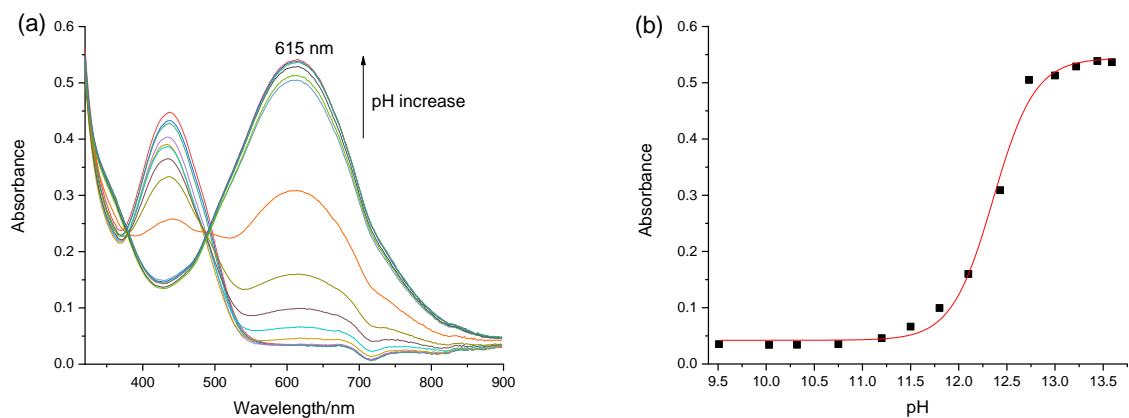


Figure S19. (a) UV-Vis spectra and (b) absorbance values for **5a** at 615 nm as a function of pH in water. Data were fitted using a sigmoidal equation, providing $pK_a = 12.35 \pm 0.02$ ($r^2 = 0.994$).

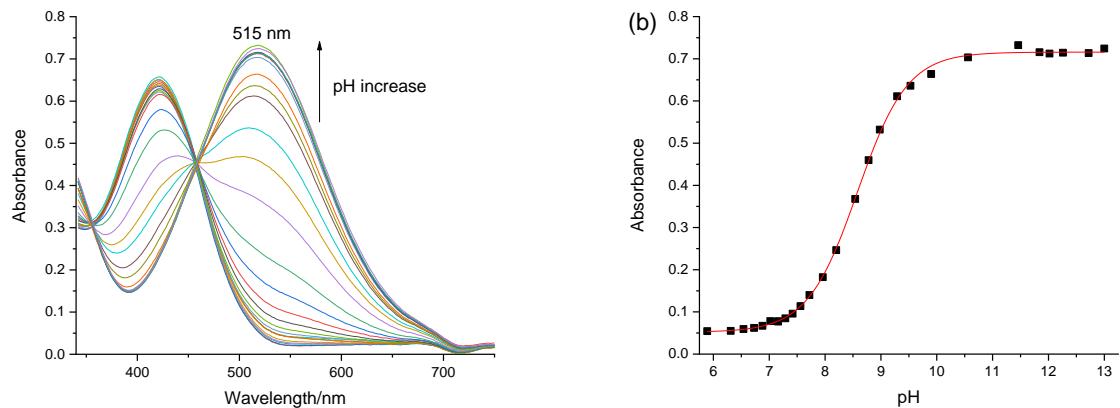


Figure S20. (a) UV-Vis spectra and (b) absorbance values for **3a** at 515 nm as a function of pH in water containing CTAB (1.0×10^{-3} mol L⁻¹). Data were fitted using a sigmoidal equation, providing $pK_a = 8.57 \pm 0.01$ ($r^2 = 0.999$).

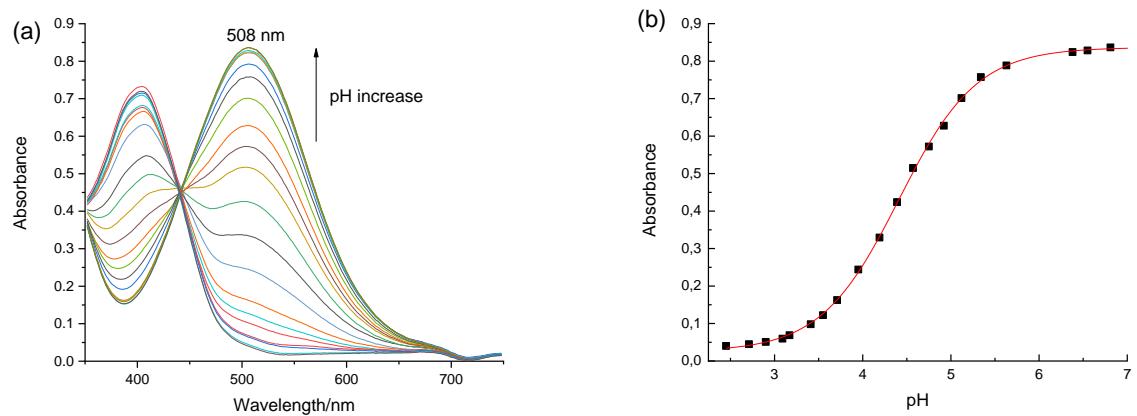


Figure S21. (a) UV-Vis spectra and (b) absorbance values for **4a** at 508 nm as a function of pH in water containing CTAB (1.0×10^{-3} mol L⁻¹). Data were fitted using a sigmoidal equation, providing $pK_a = 4.40 \pm 0.01$ ($r^2 = 0.999$).

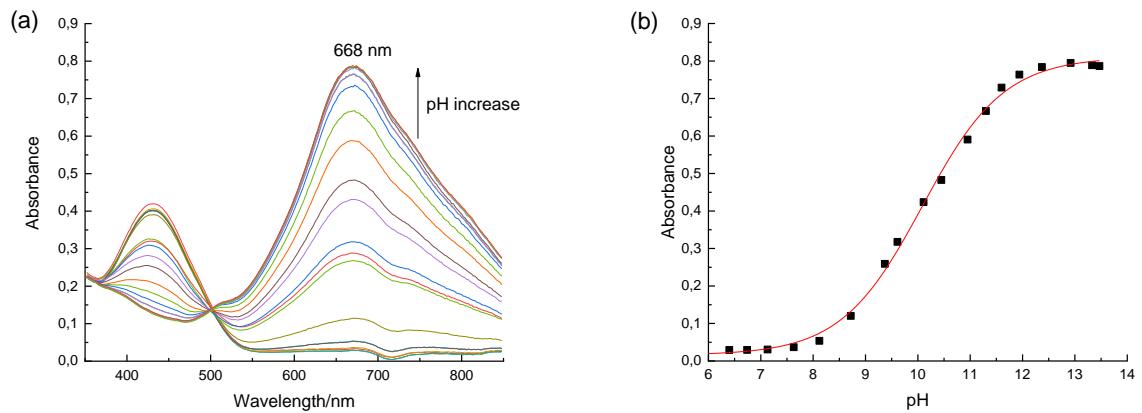


Figure S22. (a) UV-Vis spectra and (b) absorbance values for **5a** at 668 nm as a function of pH in water containing CTAB (1.0×10^{-3} mol L⁻¹). Data were fitted using a sigmoidal equation, providing $pK_a = 10.08 \pm 0.02$ ($r^2 = 0.999$).

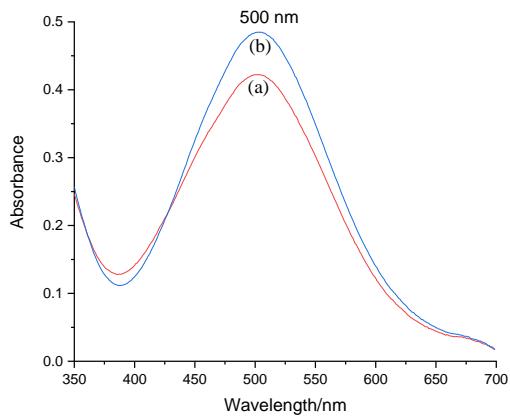


Figure S23. UV-Vis spectra of the solutions of **4a** in water in the absence (a) and after addition of BTA (b) at 25.0 °C. c (amine) = 2.0×10^{-4} mol L $^{-1}$.

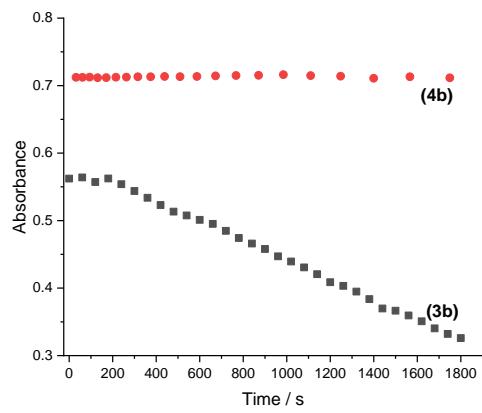


Figure S24. Stability assays of **3b** and **4b** (4.0×10^{-5} mol L $^{-1}$) in aqueous medium at 25.0 °C. The absorbance values were collected at λ_{max} at 486 and 480 nm for **3a** and **4a**, respectively (pH = 7.0 and c (BTA) = 2.0×10^{-3} mol L $^{-1}$).

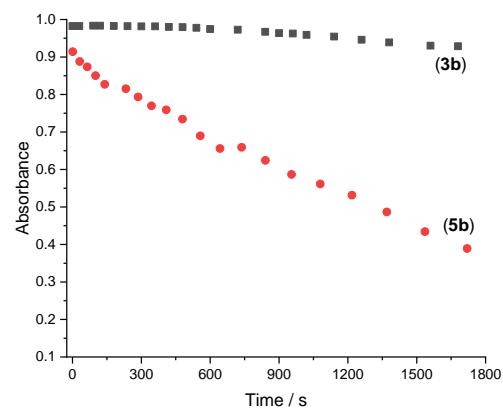


Figure S25. Stability assays of **3a** (5.0×10^{-5} mol L $^{-1}$) and **5a** (4.8×10^{-5} mol L $^{-1}$) in aqueous medium containing CTAB (1.0×10^{-3} mol L $^{-1}$) at 25.0 °C. The absorbance values were collected at λ_{max} at 515 and 668 nm for **3a** and **5a**, respectively (pH = 7.0 and c (BTA) = 2.0×10^{-3} mol L $^{-1}$).

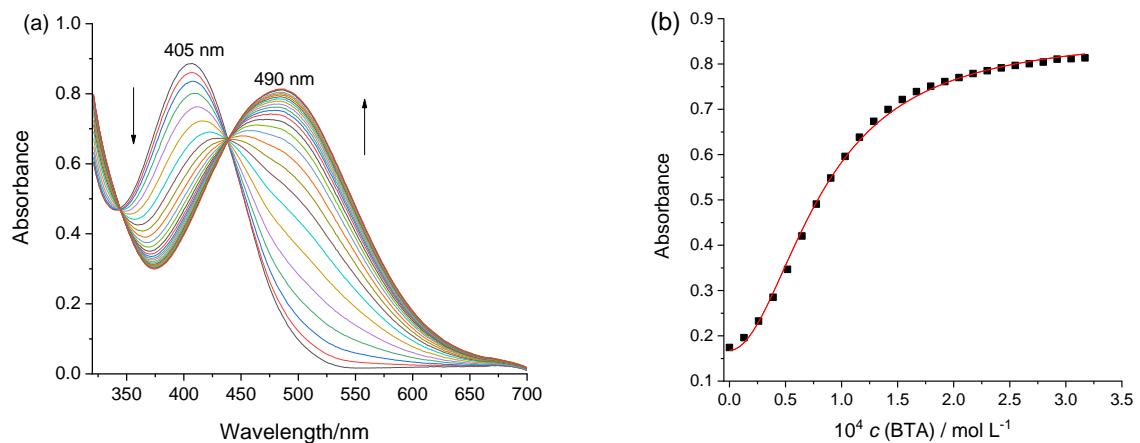


Figure S26. (a) UV-Vis spectra for titration of compound **3a** (4.0×10^{-5} mol L $^{-1}$) with BTA in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 490 nm. $K_{12} = (1.463 \pm 0.048) \times 10^8$ L 2 mol $^{-2}$ ($r^2 = 0.998$; SD = 5.02×10^{-3}).

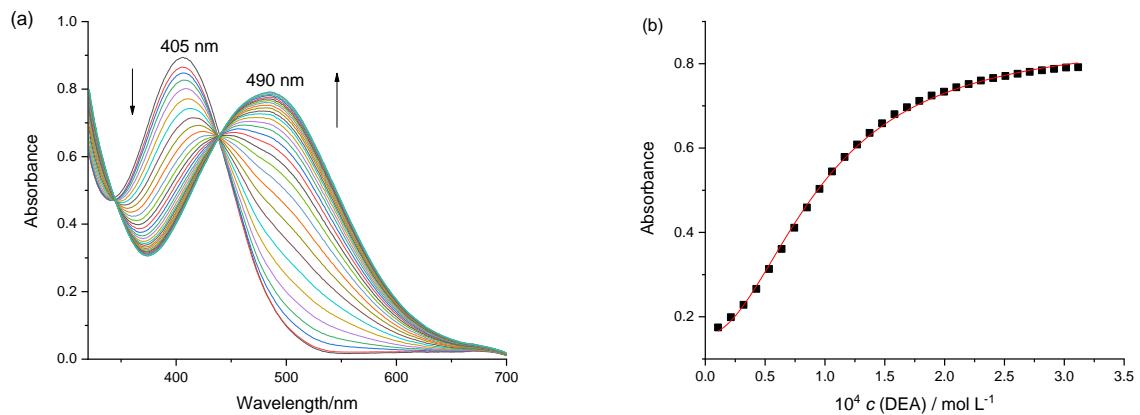


Figure S27. (a) UV-Vis spectra for titration of compound **3a** (4.0×10^{-5} mol L⁻¹) with DEA in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 490 nm. $K_{12} = (1.070 \pm 0.028) \times 10^8$ L² mol⁻² ($r^2 = 0.999$; SD = 4.05×10^{-3}).

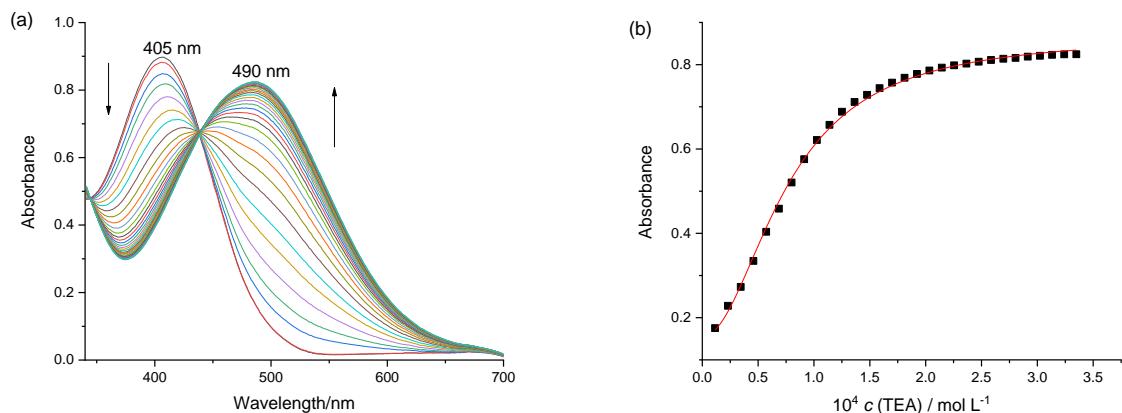


Figure S28. (a) UV-Vis spectra for titration of compound **3a** (4.0×10^{-5} mol L⁻¹) with TEA in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 486 nm. $K_{12} = (1.729 \pm 0.055) \times 10^8$ L² mol⁻² ($r^2 = 0.998$; SD = 5.92×10^{-3}).

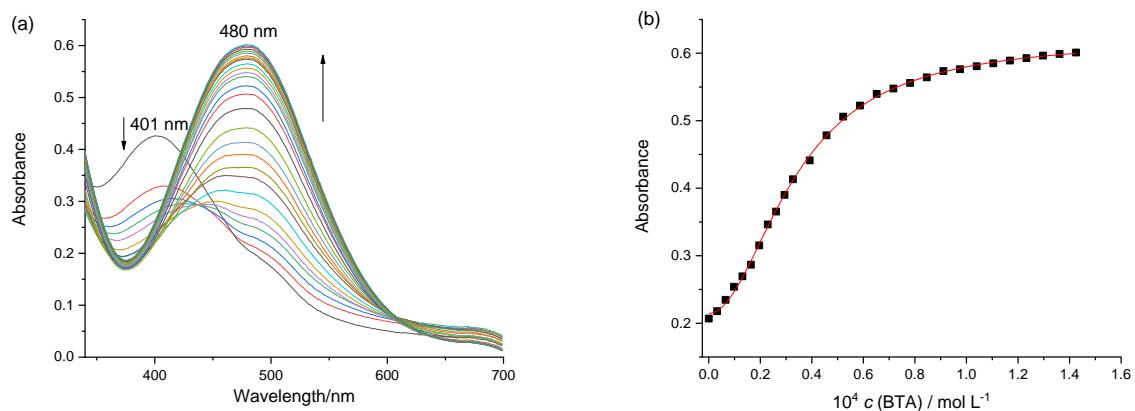


Figure S29. (a) UV-Vis spectra for titration of compound **4a** (4.0×10^{-5} mol L⁻¹) with BTA in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 480 nm. $K_{12} = (8.797 \pm 0.191) \times 10^8$ L² mol⁻² ($r^2 = 0.999$; SD = 1.78×10^{-3}).

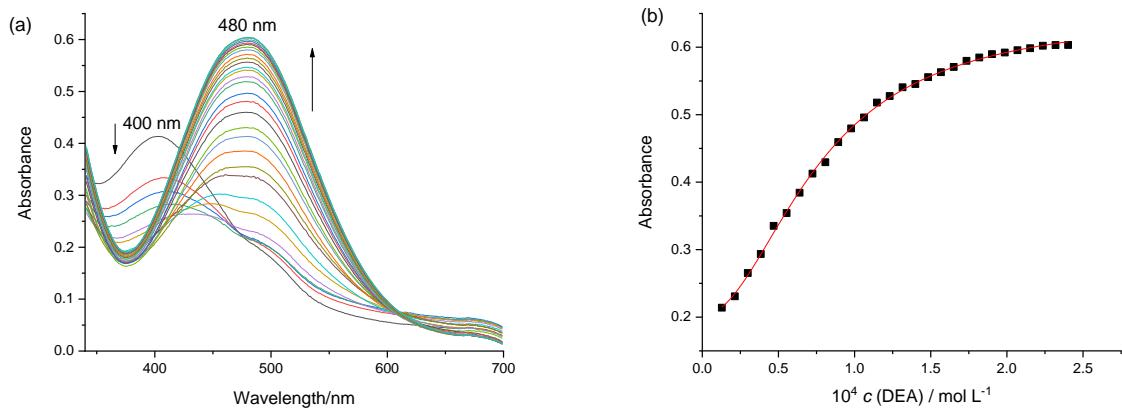


Figure S30. (a) UV-Vis spectra for titration of compound **4a** (4.0×10^{-5} mol L⁻¹) with DEA in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 480 nm. $K_{12} = (1.721 \pm 0.044) \times 10^8$ L² mol⁻² ($r^2 = 0.999$; SD = 2.62×10^{-3}).

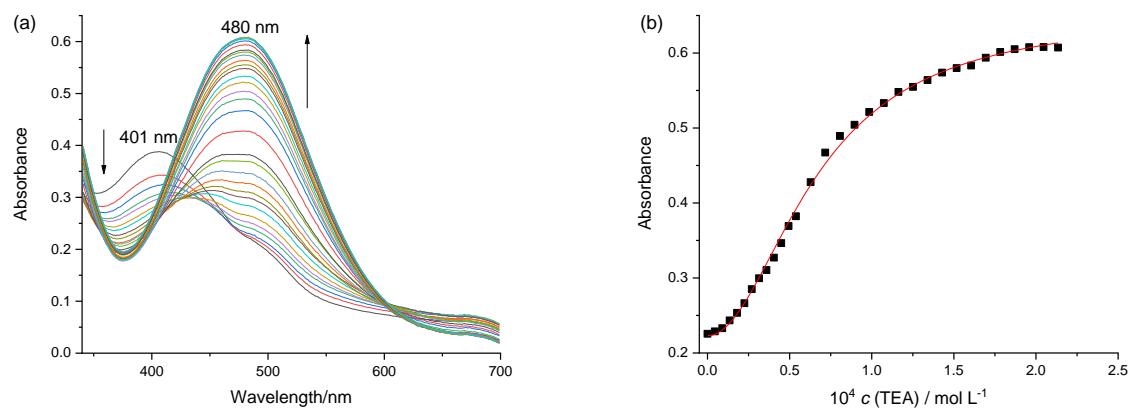


Figure S31. (a) UV-Vis spectra for titration of compound **4a** (4.0×10^{-5} mol L⁻¹) with TEA in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 480 nm. $K_{12} = (2.237 \pm 0.080) \times 10^8$ L² mol⁻² ($r^2 = 0.998$; SD = 2.61×10^{-3}).

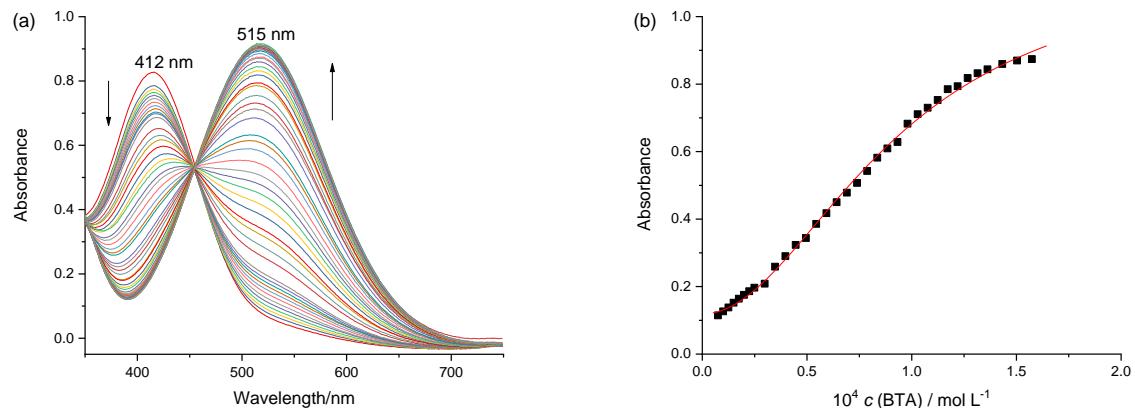


Figure S32. (a) UV-Vis spectra for titration of compound **3a** (4.0×10^{-5} mol L⁻¹) with BTA in aqueous medium containing CTAB (1.0×10^{-3} mol L⁻¹) at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 515 nm. $K_{12} = (1.162 \pm 0.050) \times 10^8$ L² mol⁻² ($r^2 = 0.997$; S.D. = 4.63×10^{-3}).

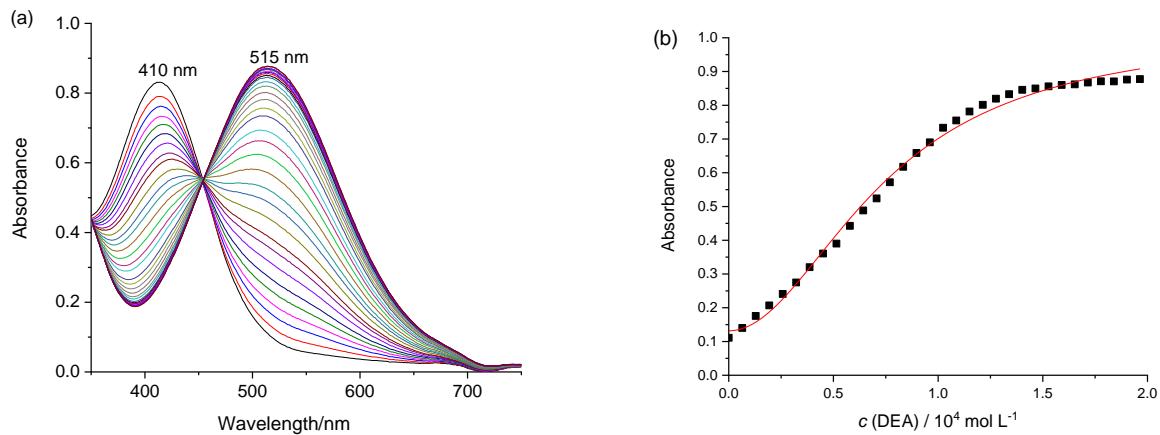


Figure S33. (a) UV-Vis spectra for titration of compound **3a** ($4.0 \times 10^{-5} \text{ mol L}^{-1}$) with DEA in aqueous medium containing CTAB ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) at $25.0 \text{ }^\circ\text{C}$. (b) Corresponding titration curve, with absorbances collected at 515 nm. $K_{12} = (1.173 \pm 0.049) \times 10^8 \text{ L}^2 \text{ mol}^{-2}$ ($r^2 = 0.995$; SD = 3.29×10^{-3}).

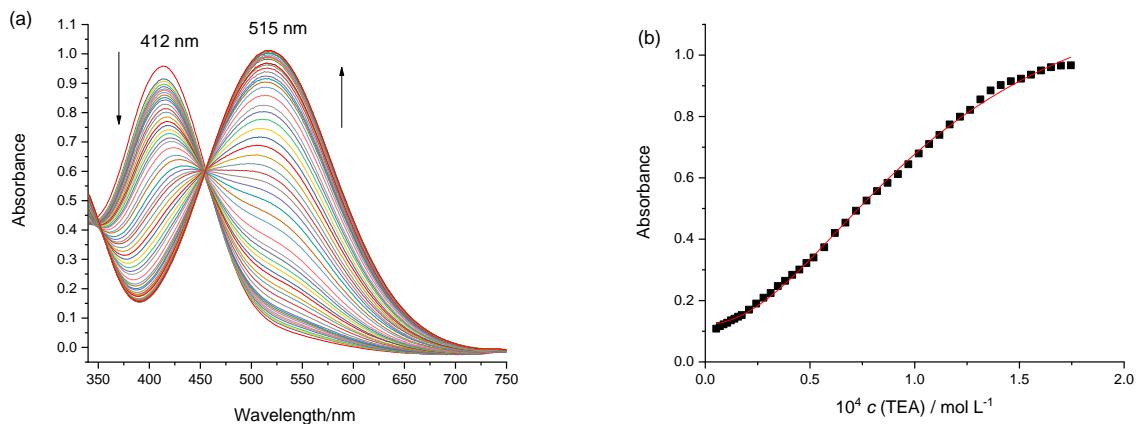


Figure S34. (a) UV-Vis spectra for titration of compound **3a** ($4.0 \times 10^{-5} \text{ mol L}^{-1}$) with TEA in aqueous medium containing CTAB ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) at $25.0 \text{ }^\circ\text{C}$. (b) Corresponding titration curve, with absorbances collected at 515 nm. $K_{12} = (8.511 \pm 0.262) \times 10^7 \text{ L}^2 \text{ mol}^{-2}$ ($r^2 = 0.995$; SD = 3.29×10^{-3}).

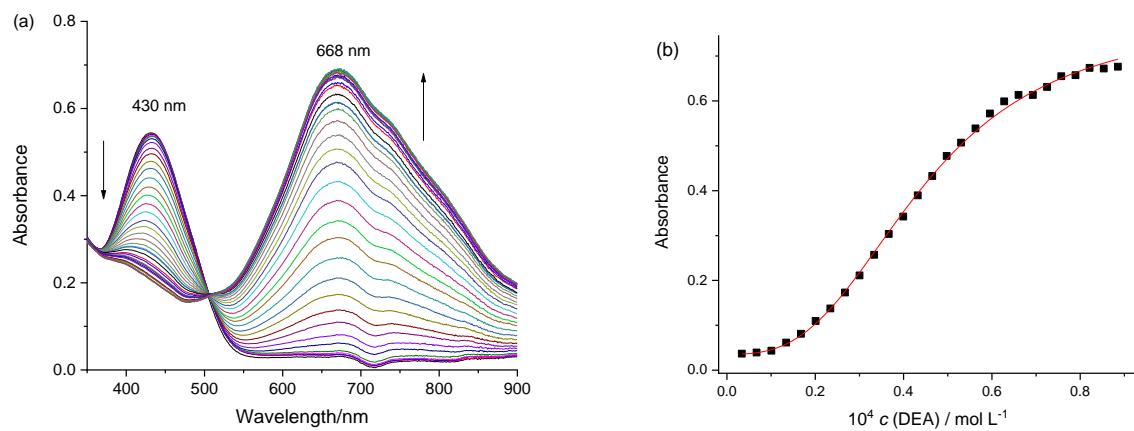


Figure S35. (a) UV-Vis spectra for titration of compound **5a** (4.0 × 10⁻⁵ mol L⁻¹) with DEA in aqueous medium containing CTAB (1.0 × 10⁻³ mol L⁻¹) at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 670 nm. $K_{12} = (1.240 \pm 0.279) \times 10^8 \text{ L}^2 \text{ mol}^{-2}$ and $K_{13} = (7.160 \pm 0.182) \times 10^4 \text{ L}^3 \text{ mol}^{-3}$ ($r^2 = 0.997$; SD = 6.17×10^{-3}).

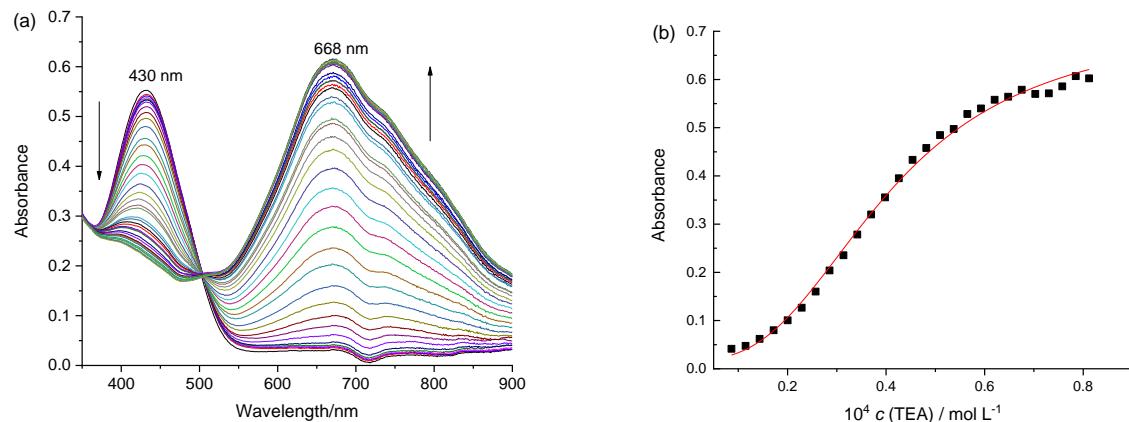


Figure S36. (a) UV-Vis spectra for titration of compound **5a** (4.0 × 10⁻⁵ mol L⁻¹) with TEA in aqueous medium containing CTAB (1.0 × 10⁻³ mol L⁻¹) at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 668 nm. $K_{12} = (1.844 \pm 0.325) \times 10^8 \text{ L}^2 \text{ mol}^{-2}$ and $K_{13} = (7.780 \pm 1.099) \times 10^4 \text{ L}^3 \text{ mol}^{-3}$ ($r^2 = 0.998$; SD = 5.44×10^{-3}).

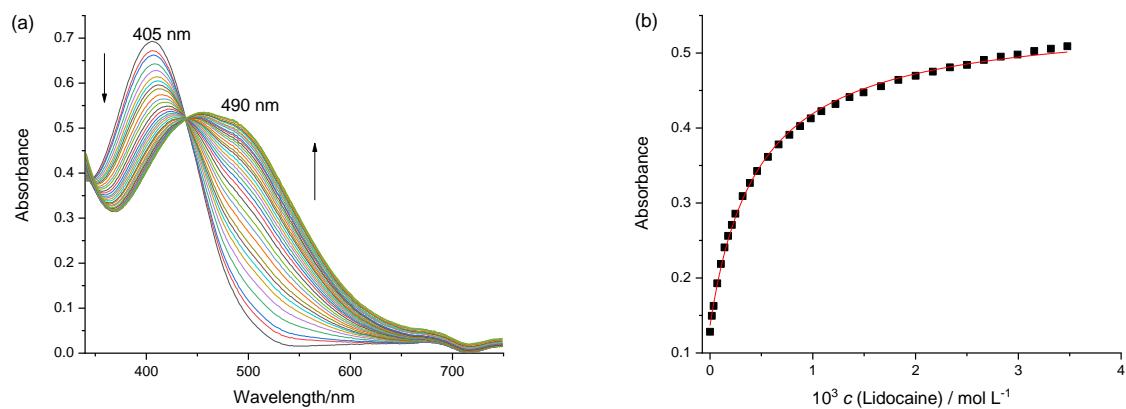


Figure S37. (a) UV-Vis spectra for titration of compound **3a** (5.0 × 10⁻⁵ mol L⁻¹) with lidocaine in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 490 nm. $K_{11} = (2.164 \pm 0.006 \times 10^3 \text{ L mol}^{-1}$ ($r^2 = 0.998$; SD = 2.53×10^{-3}).

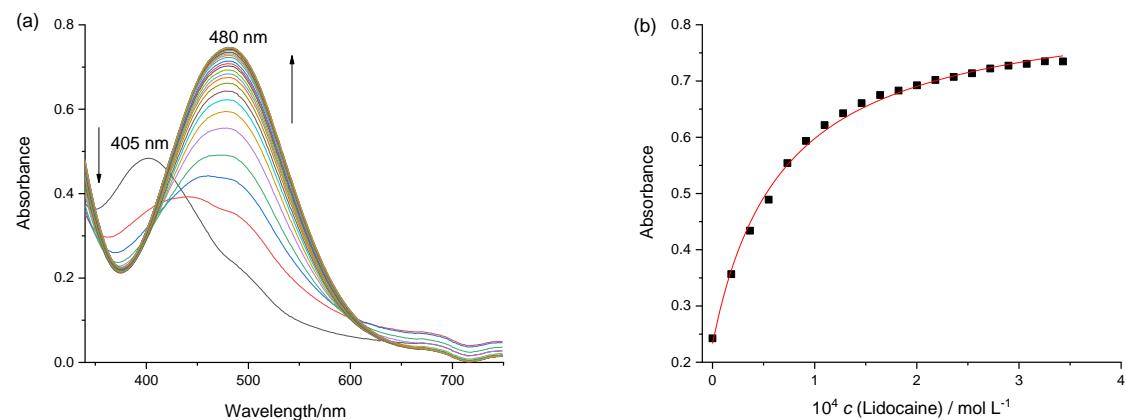


Figure S38. (a) UV-Vis spectra for titration of compound **4a** (5.0 × 10⁻⁵ mol L⁻¹) with lidocaine in aqueous medium at 25.0 °C. (b) Corresponding titration curve, with absorbances collected at 480 nm. $K_{11} = (1.493 \pm 0.088 \times 10^4 \text{ L mol}^{-1}$ ($r^2 = 0.995$; SD = 7.91×10^{-3}).

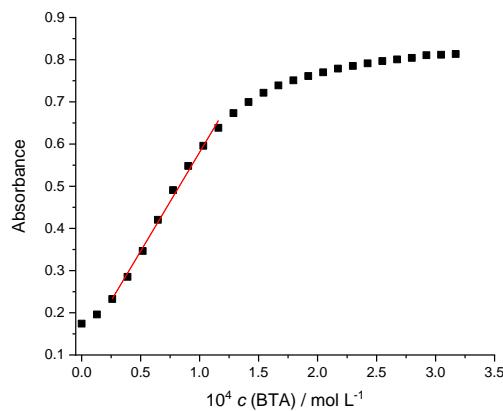


Figure S39. Curve for the titration of **3a** with BTA in aqueous medium, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 2.36×10^{-6} mol L⁻¹, and LOQ = 7.88×10^{-6} mol L⁻¹ ($r^2 = 0.993$; SD = 1.11×10^{-2}).

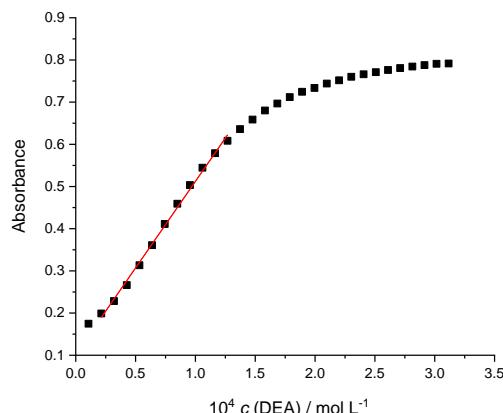


Figure S40. Curve for the titration of **3a** with DEA in aqueous medium, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 1.61×10^{-6} mol L⁻¹, and LOQ = 5.36×10^{-6} mol L⁻¹ ($r^2 = 0.996$; SD = 6.61×10^{-3}).

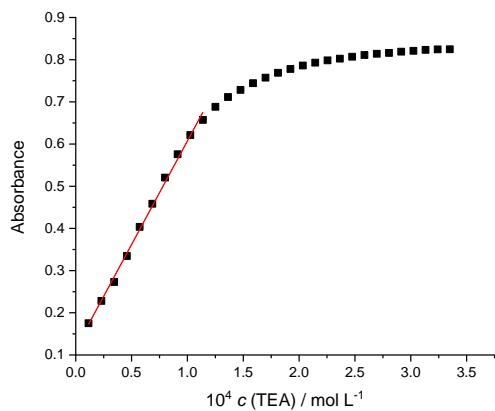


Figure S41. Curve for the titration of **3a** with TEA in aqueous medium, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 1.45×10^{-6} mol L⁻¹, and LOQ = 4.18×10^{-6} mol L⁻¹ ($r^2 = 0.996$; SD = 7.09×10^{-3}).

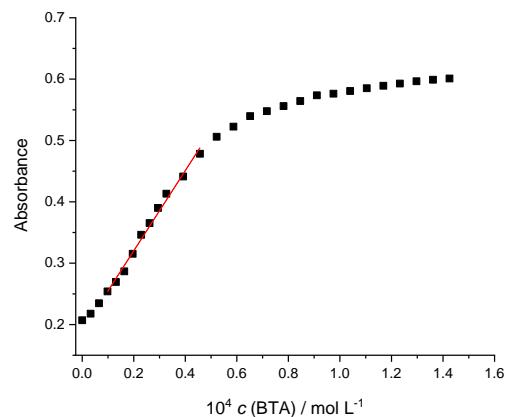


Figure S42. Curve for the titration of **4a** with BTA in aqueous medium, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 9.71×10^{-7} mol L⁻¹, and LOQ = 3.23×10^{-6} mol L⁻¹ ($r^2 = 0.989$; SD = 3.35×10^{-3}).

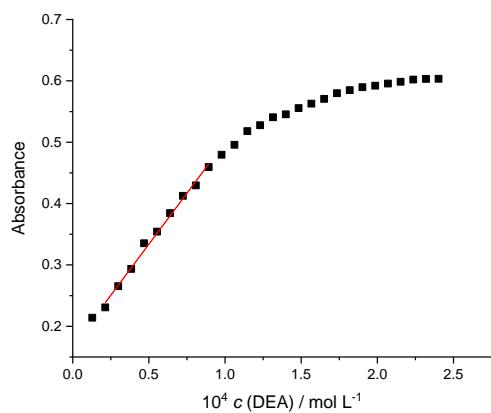


Figure S43. Curve for the titration of **4a** with DEA in aqueous medium, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 1.84×10^{-6} mol L⁻¹, and LOQ = 6.54×10^{-6} mol L⁻¹ ($r^2 = 0.989$; SD = 6.14×10^{-3}).

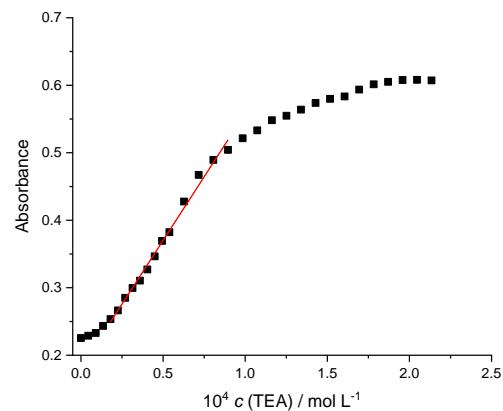


Figure S44. Curve for the titration of **4a** with TEA in aqueous medium, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 1.42×10^{-6} mol L⁻¹, and LOQ = 4.75×10^{-6} mol L⁻¹ ($r^2 = 0.991$; SD = 5.38×10^{-3}).

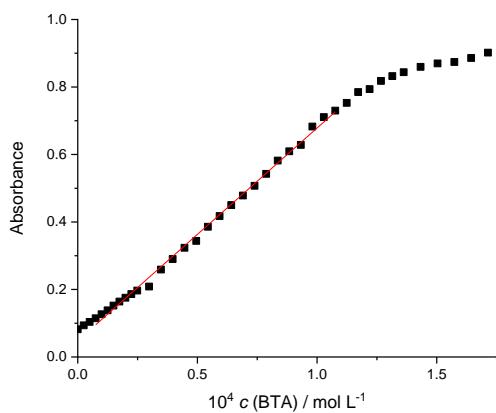


Figure S45. Curve for the titration of **3a** with BTA in water containing CTAB (1.0×10^{-3} mol L $^{-1}$), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 6.89×10^{-7} mol L $^{-1}$, and LOQ = 2.29×10^{-6} mol L $^{-1}$ ($r^2 = 0.997$; SD = 4.43×10^{-3}).

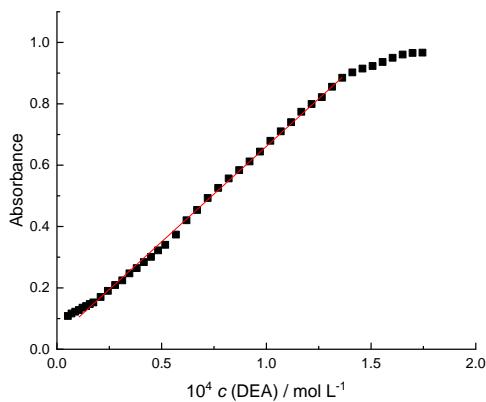


Figure S46. Curve for the titration of **3a** with DEA in water containing CTAB (1.0×10^{-3} mol L $^{-1}$), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 5.29×10^{-7} mol L $^{-1}$, and LOQ = 1.76×10^{-6} mol L $^{-1}$ ($r^2 = 0.998$; SD = 6.72×10^{-3}).

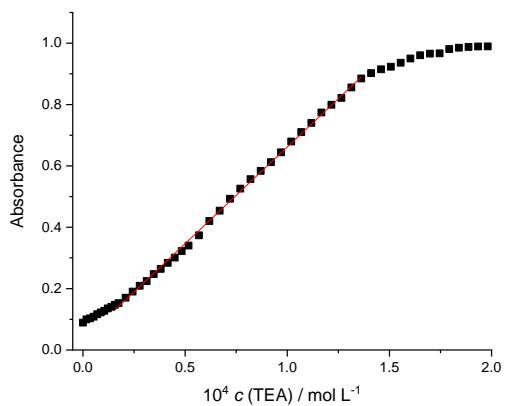


Figure S47. Curve for the titration of **3a** with TEA in water containing CTAB (1.0×10^{-3} mol L $^{-1}$), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 6.27×10^{-7} mol L $^{-1}$, and LOQ = 2.09×10^{-6} mol L $^{-1}$ ($r^2 = 0.998$; SD = 3.98×10^{-3}).

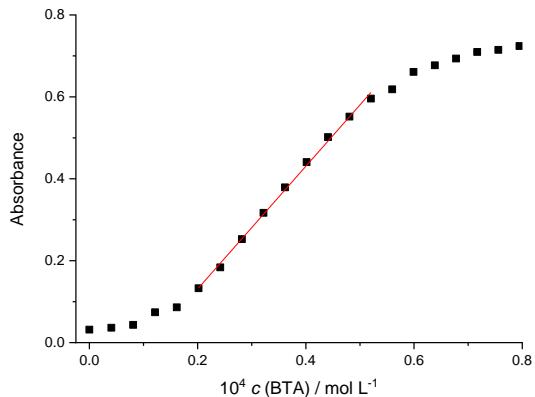


Figure S48. Curve for the titration of **5a** with BTA in water containing CTAB (1.0×10^{-3} mol L $^{-1}$), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 7.00×10^{-7} mol L $^{-1}$, and LOQ = 2.33×10^{-6} mol L $^{-1}$ ($r^2 = 0.997$; SD = 1.05×10^{-2}).

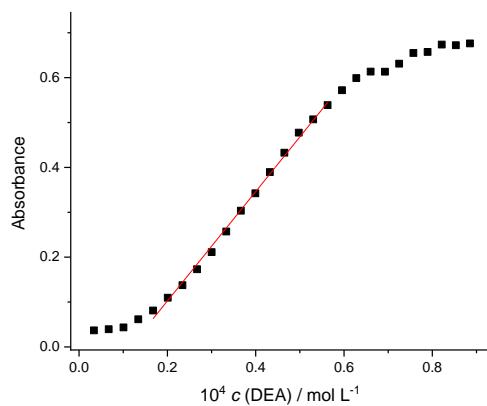


Figure S49. Curve for the titration of **5a** with DEA in water containing CTAB (1.0×10^{-3} mol L $^{-1}$), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 6.99×10^{-7} mol L $^{-1}$, and LOQ = 2.33×10^{-6} mol L $^{-1}$ ($r^2 = 0.996$; SD = 8.53×10^{-3}).

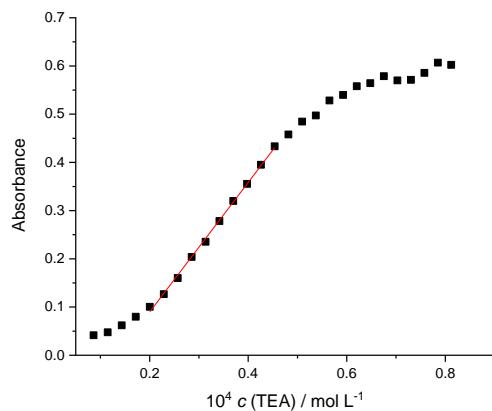


Figure S50. Curve for the titration of **5a** with TEA in water containing CTAB (1.0×10^{-3} mol L $^{-1}$), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 5.08×10^{-7} mol L $^{-1}$, and LOQ = 1.69×10^{-6} mol L $^{-1}$ ($r^2 = 0.997$; SD = 7.59×10^{-3}).

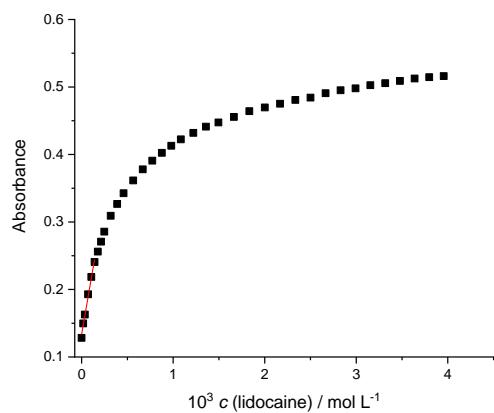


Figure S51. Curve for the titration of **3a** with lidocaine in water, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 5.72×10^{-6} mol L $^{-1}$, and LOQ = 1.75×10^{-5} mol L $^{-1}$ ($r^2 = 0.998$; SD = 3.81×10^{-3}).

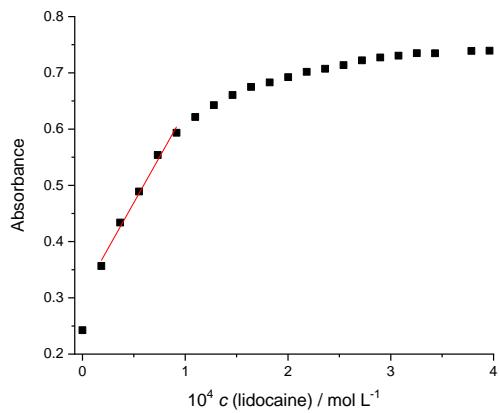


Figure S52. Curve for the titration of **4a** with lidocaine in water, utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 3.57×10^{-6} mol L $^{-1}$, and LOQ = 1.19×10^{-5} mol L $^{-1}$ ($r^2 = 0.989$; SD = 1.16×10^{-2}).

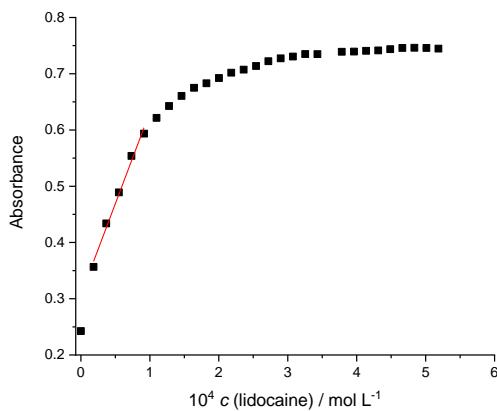


Figure S53. Curve for the titration of **3a** with lidocaine in water containing CTAB (1.0×10^{-3} mol L⁻¹), utilized to estimate values of LOD and LOQ. Fitting of experimental data (—), LOD = 5.35×10^{-6} mol L⁻¹, and LOQ = 1.78×10^{-6} mol L⁻¹ ($r^2 = 0.994$; SD = 1.58×10^{-2}).

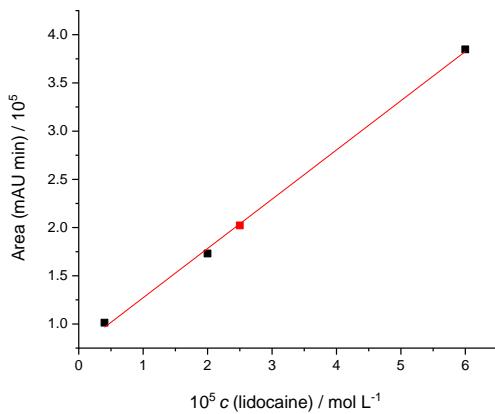


Figure S54. Calibration curve for standard (■) and commercial (■) lidocaine using LC-MS technique. A Phenomenex C18 column (particle size = 5 μ m; internal diameter = 4.6 mm; length = 150 mm) was utilized. The experiments were performed in acetonitrile, the volume injection was of 10 μ L and the flow rate was 0.2 mL min⁻¹.

Datafile Name:AM05_Solvente.lcd
Sample Name:AM05_Lidocaina_Commercial
Sample ID:Alberton

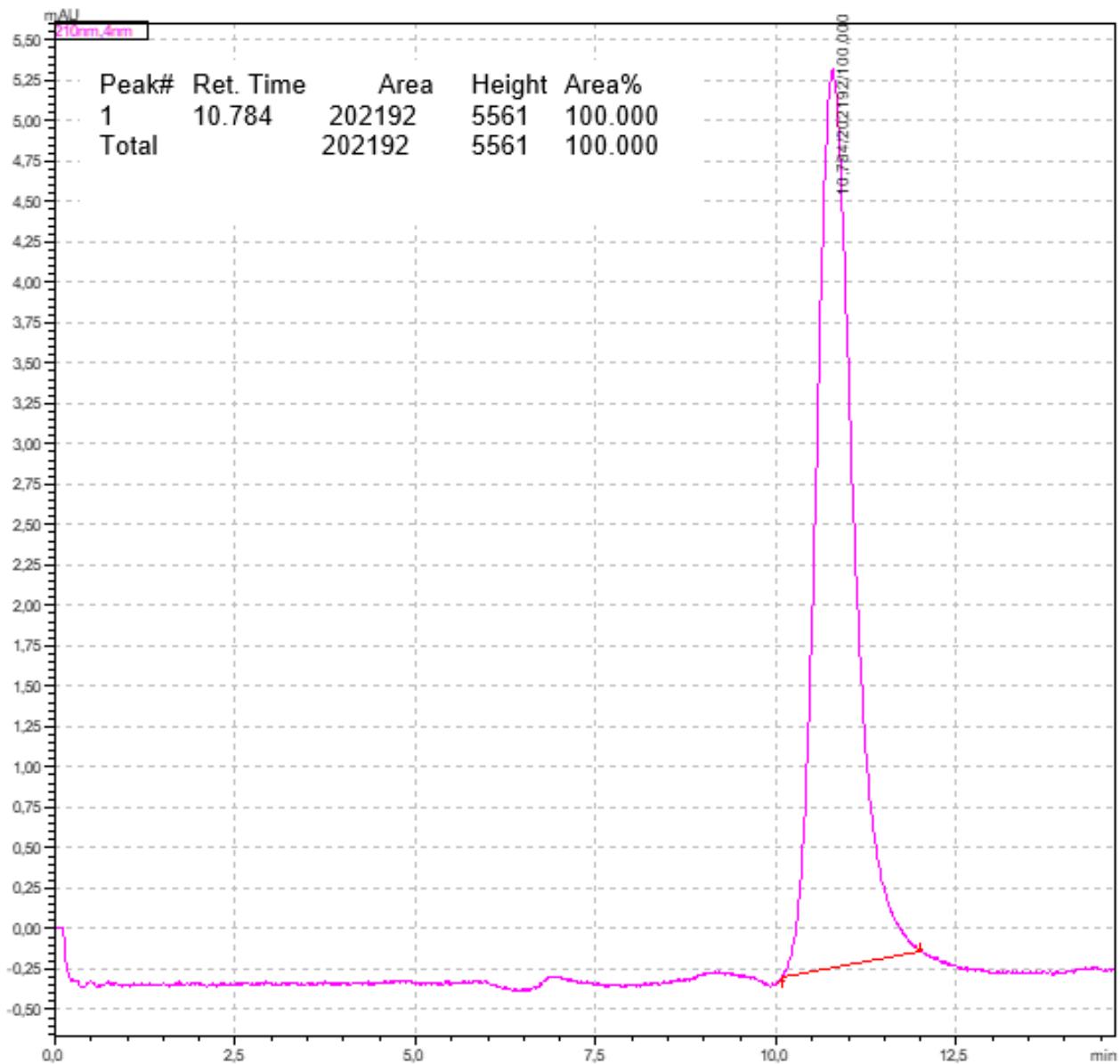


Figure S55. Chromatogram of the commercial lidocaine (c (lidocaine) = 2.5×10^{-5} mol L $^{-1}$).

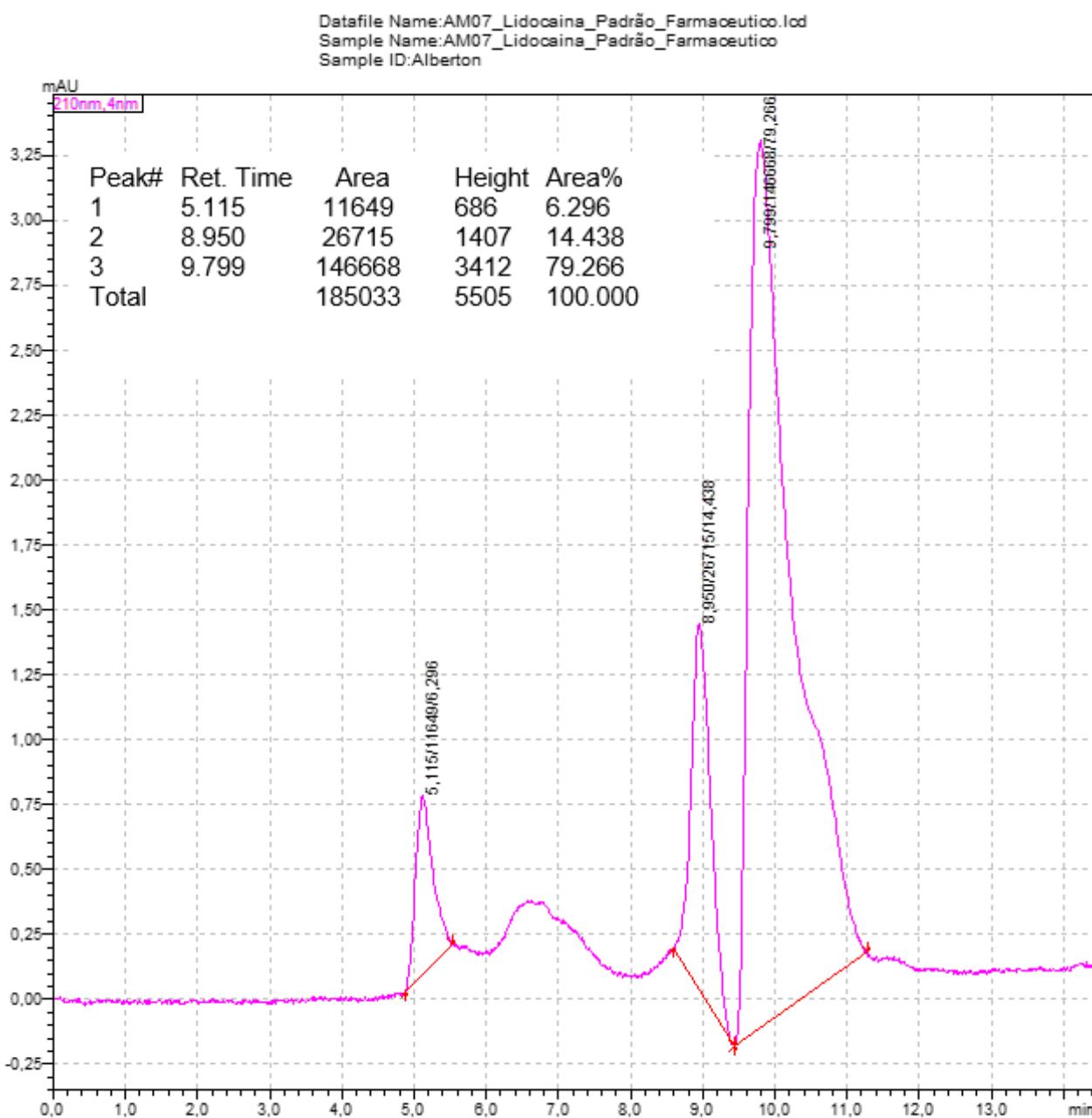


Figure S56. Chromatogram of the standard lidocaine (c (lidocaine) = 3.9×10^{-6} mol L $^{-1}$).

Datafile Name:AM09_Lidocaina_Padrão_Farmaceutico.lcd
Sample Name:AM09_Lidocaina_Padrão_Farmaceutico
Sample ID:Alberton

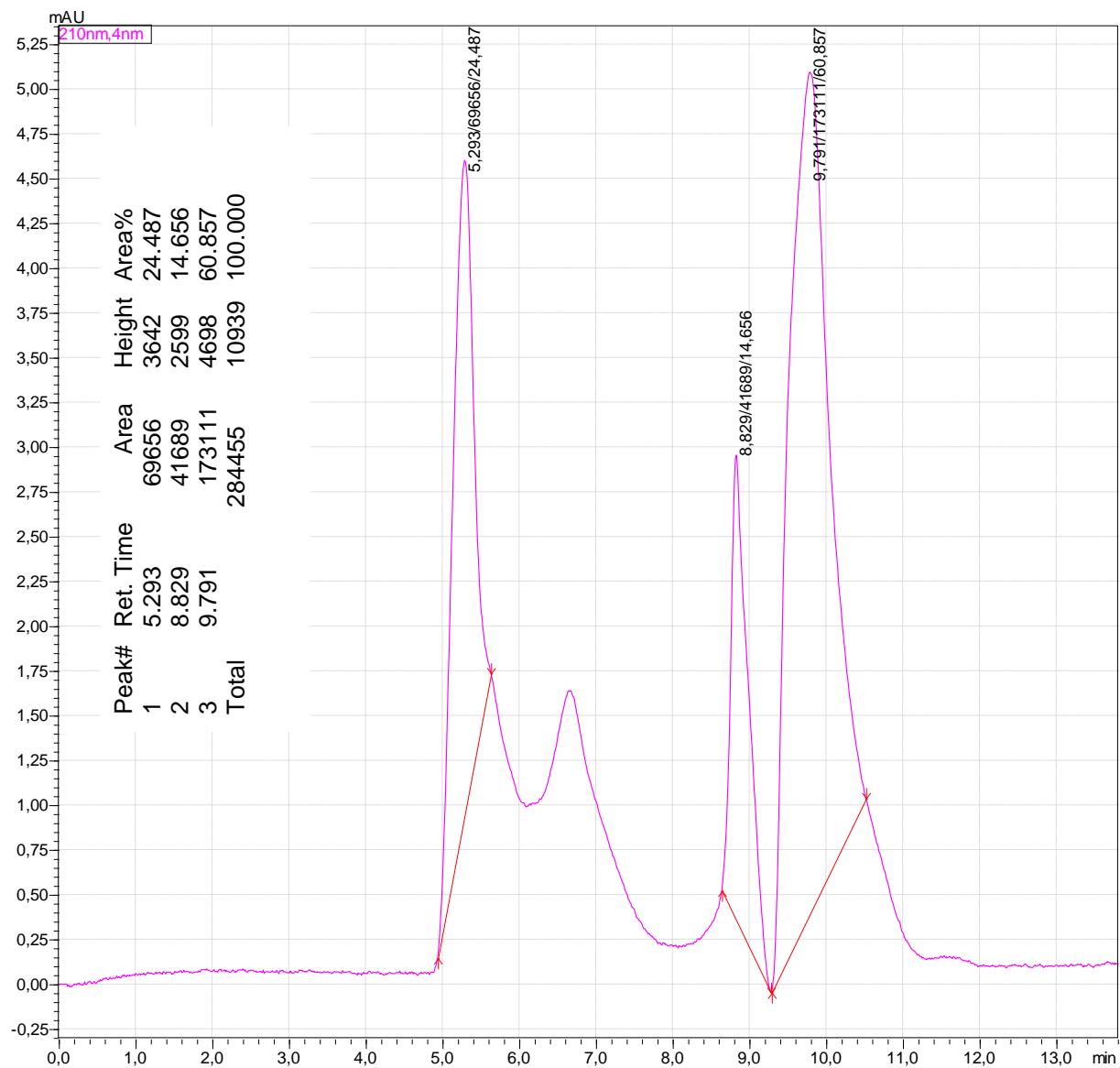


Figure S57. Chromatogram of the standard lidocaine (c (lidocaine) = 1.9×10^{-5} mol L $^{-1}$).

Datafile Name:AM010_Lidocaina_Padrão_Farmacêutico.lcd
Sample Name:AM010_Lidocaina_Padrão_Farmacêutico
Sample ID:Alberton

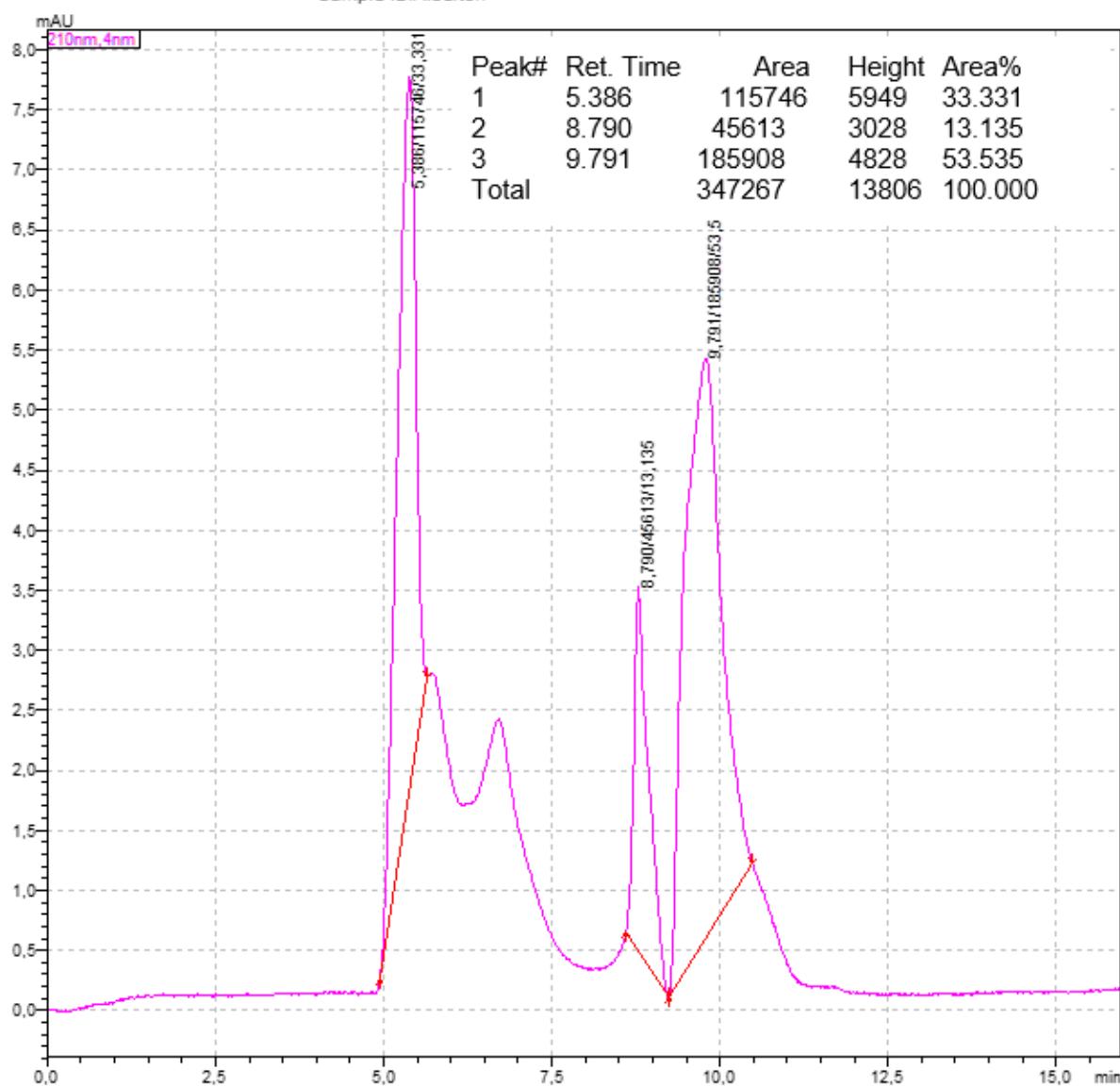


Figure S58. Chromatogram of the standard lidocaine (c (lidocaine) = 6.0×10^{-5} mol L $^{-1}$).

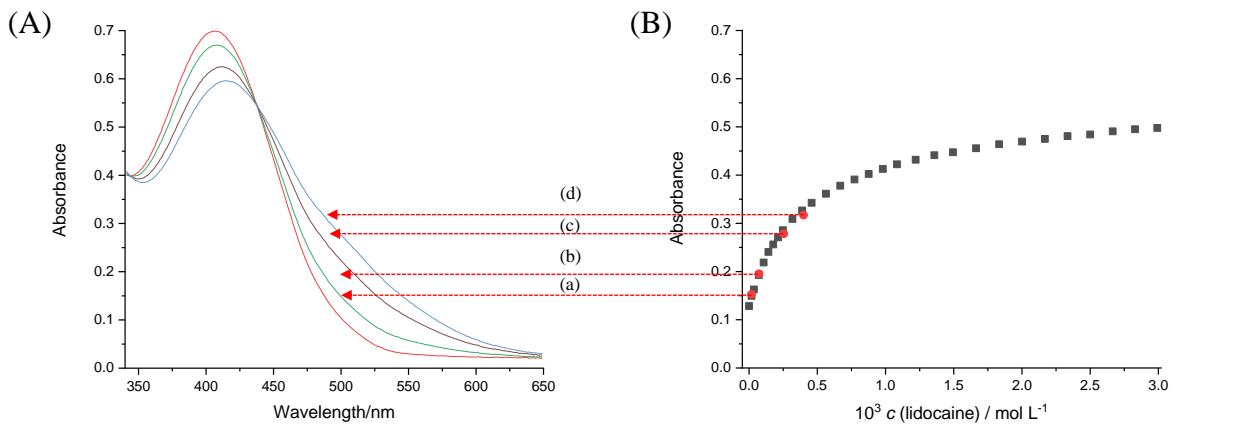


Figure S59. (A) UV-Vis spectra of **3a** in water without amine (a) and with (b) 1.45×10^{-4} , 2.54×10^{-4} (c), and (d) 3.99×10^{-4} mol L⁻¹ of a commercial sample of lidocaine. (B) Curve at 490 nm for the titration of compound (4.0×10^{-5} mol L⁻¹) with increasing amounts of a standard pharmaceutical lidocaine in 490 nm. The red circles correspond to the commercial samples of lidocaine.

References

1. Juranić, I.; *Croat. Chem. Acta* **2014**, *87*, 343.
2. Gohar, G. A.; Habeeb, M. M.; *Spectrosc. Int. J.* **2000**, *14*, 99.



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