Sulfonamide-imines as selective fluorescent chemosensors for the fluoride anion

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Electronic Supporting information (ESI)

Crystallographic data for H_3L^b

Empirical formula	$C_{31}\ H_{32}\ N_4\ O_5\ S_2$	
Formula weight	604.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 1 2 1	
Unit cell dimensions	a = 26.510(2) Å	α= 90°
	b = 8.1629(4) Å	β= 90.200(2)°
	c = 27.3038(15) Å	γ = 90°
Volume	5908.6(6) $Å^3$	
Z	8	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.228 mm^{-1}	
F(000)	2544	
Crystal size	0.18 × 0.08 × 0.05 mm^3	
Theta range for data collection	1.49 to 26.40°.	
Index ranges	$-33 \le h \le 33, -10 \le k \le 10, 0 \le l \le 34$	
Reflections collected	42208	
Independent reflections	11944 [R(int) = 0.0751]	
Completeness to theta = 26.40°	99. 8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.991 and 0.894	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11937 / 9 / 779	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 =0.01045	
R indices (all data)	R1 = 0.0905, wR2 = 0.1147	
Absolute structure parameter	-0.11(6)	
Largest diff. peak and hole	0.707 and -0.375 e.$Å^{-3}$	

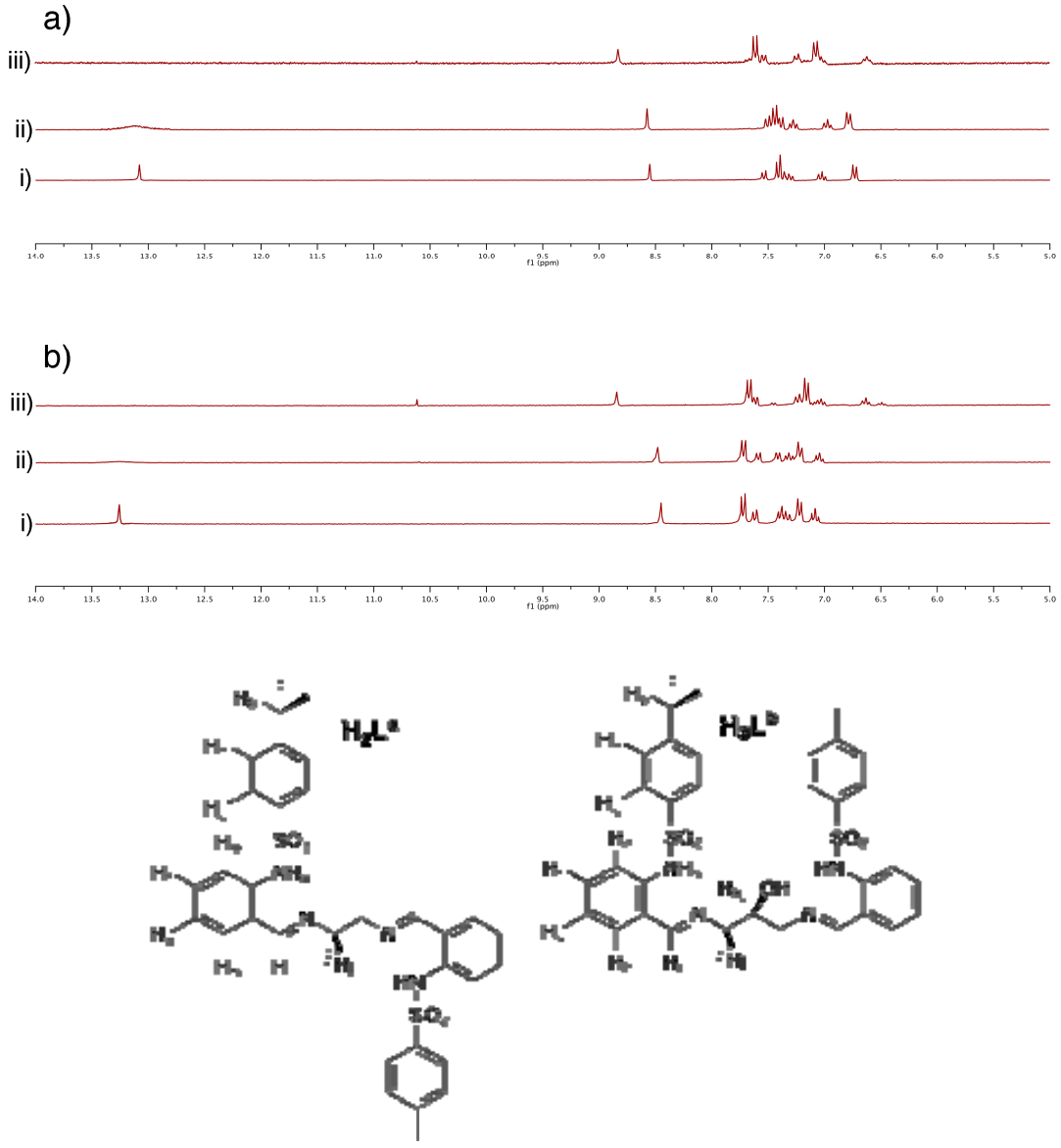
Selected bond distances for H_3L^b

C(56)–N(8)	1. 373(5)
N(7)–C(50)	1. 290(5)
N(8)–S(4)	1. 591(3)
N(6)–C(47)	1. 460(5)
N(5)–C(40)	1. 422(5)
S(3)–N(5)	1. 616(3)
C(8) –N(1)	1.379(5)
N(1) –S(1)	1.594(3)
C14–N(2)	1.283(5)
N(4)- S(2)	1.626(3)
C(24) –N(4)	1.418(4)
C(18) –N(3)	1.266(4)

Refine special details

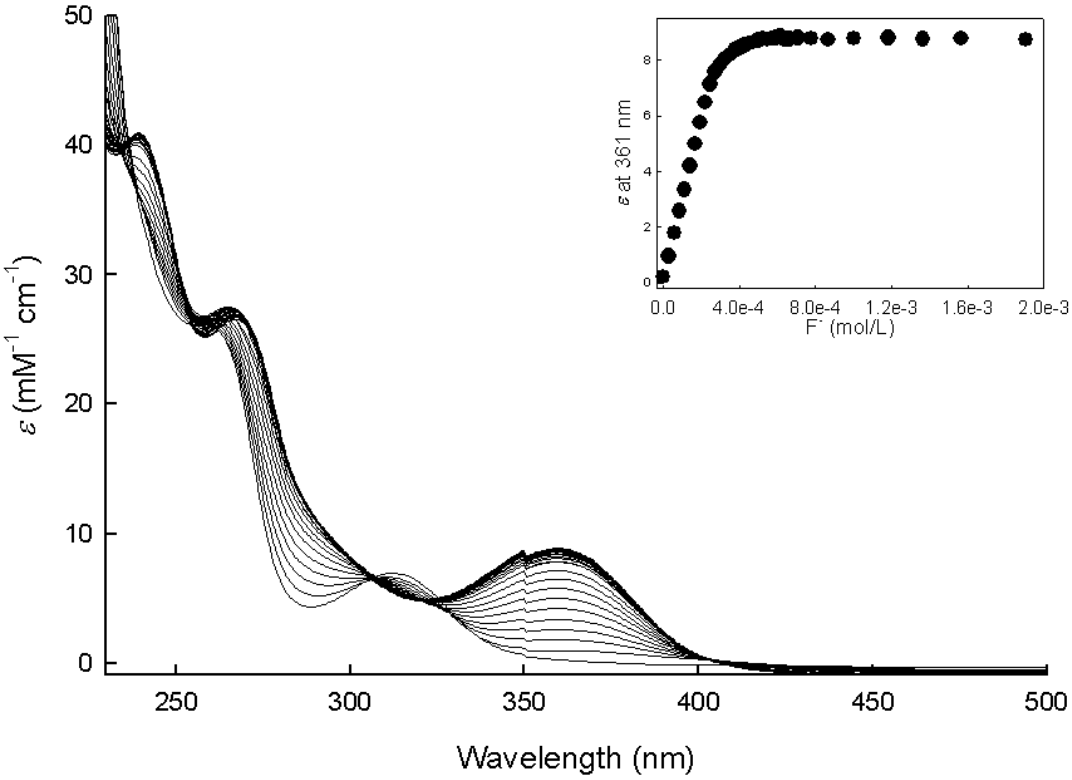
Structure refinement was performed with 9 restrains: DFIX for the distances between the hydrogens H(1N) H(8N) H(50) and H(10O) and their corresponding heteroatoms, which if left unrestricted resulted in too short bond distances (0.7 Amstrongs), and DELU restrain for nitrogen N(2) and its neighbor atoms because the components of the anisotropic displacement parameters along chemical bonds present large deviations (high Hirshfeld Test values).

^{1}H NMR titration of H_2L^a and H_3L^b with fluoride ions



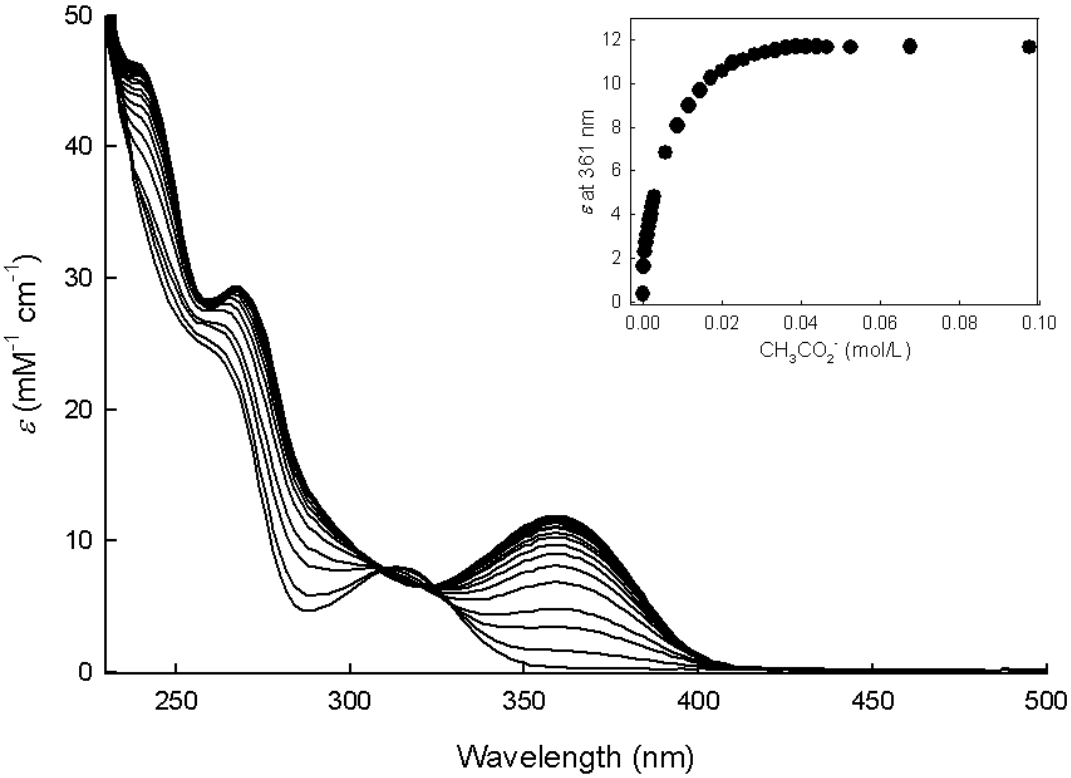
Top: Partial ^{1}H NMR (250 MHz) spectra of a) **H_2L^a** and b) **H_3L^b** (1.0 mM) in CD_3CN in the absence (i) and the presence of 1.0 (ii) and 10.0 (iii) equivalents of $[N(Bu)_4]F$. Bottom: Schematic representation of the receptors **H_2L^a** and **H_3L^b** including the corresponding labelling schemes for the ^{1}H NMR studies. ^{1}H NMR data for **H_2L^a** (250 MHz, CD_3CN, 25 ºC, ppm): 13.11 (H_a, s, 2H); 8.55 (H_i, s, 2H); 7.54 (H_e, d, 2H); 7.41 (H_d, d, 4H); 7.31 (H_f+H_h, m, 4H); 7.02 (H_g, t, 2H); 6.73 (H_c, d, 4H); 4.10 (s, 4H); 2.23 (s, 6H). ^{1}H NMR data for **H_3L^b** (250 MHz, CD_3CN, 25 ºC, ppm): 13.25 (H_a, s, 2H); 8.45 (H_i, s, 2H); 7.72 (H_d, d, 4H); 7.62 (H_e, d, 2H); 7.41–7.31 (H_f+H_h, m, 4H); 7.22 (H_c, d, 4H); 7.08 (H_g, t, 2H); 4.27 (H_k, m, 1H); 4.00–3.79 (H_j, m, 4H); 3.31 (H_l, m, 1H); 2.29 (H_b, s, 6H).

Spectrophotometric titration of H_3L^b with F^-



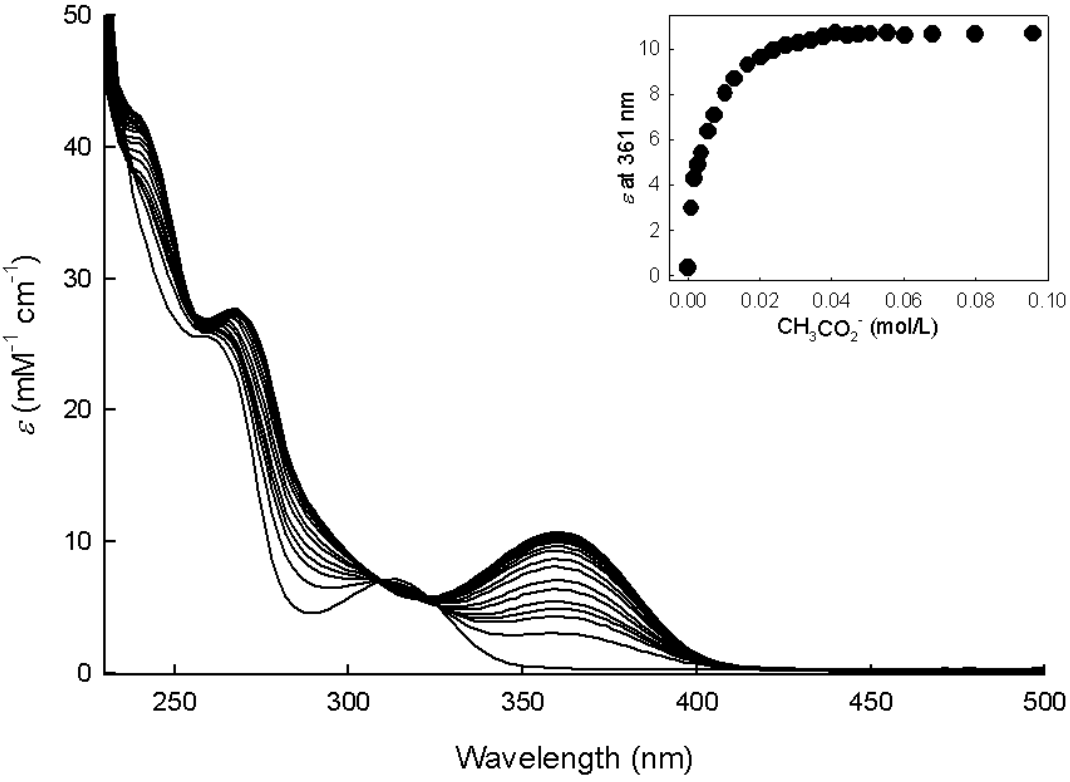
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_3L^b}$ with a standard solution of fluoride ions. Inset: absorbance at 361 nm *vs.* concentration of fluoride ions.

Spectrophotometric titration of H_2L^a with $CH_3CO_2^-$



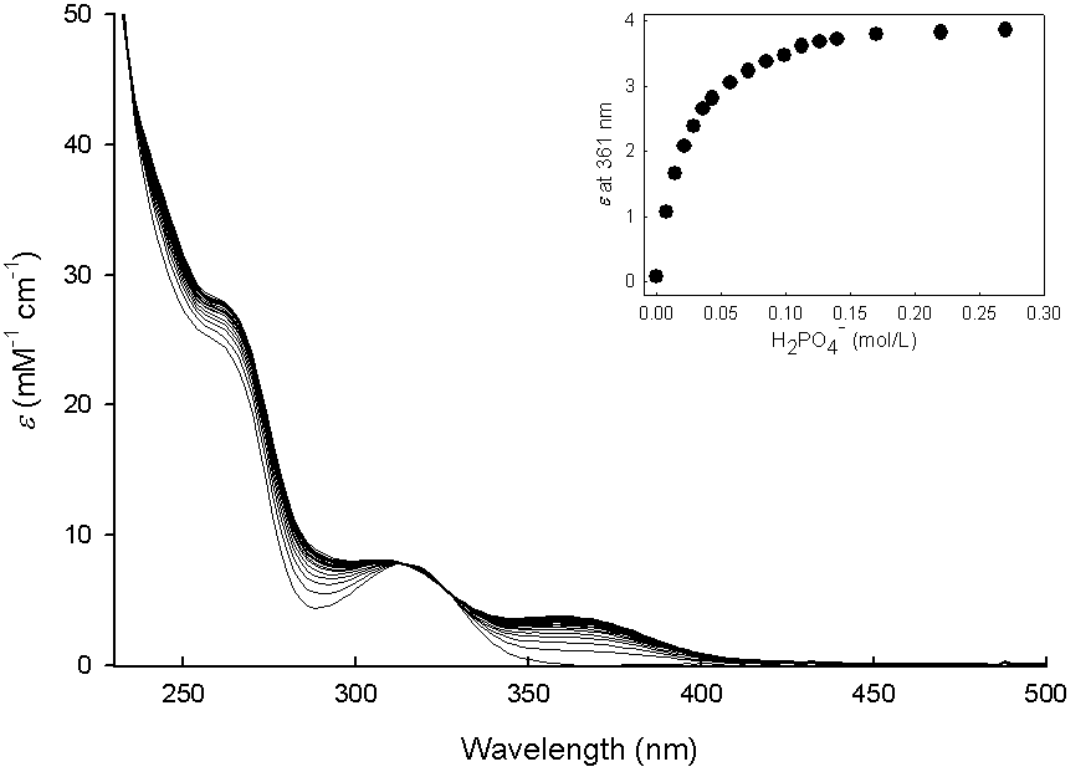
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_2L^a}$ with a standard solution of acetate ions. Inset: absorbance at 361 nm *vs.* concentration of acetate ions.

Spectrophotometric titration of H_3L^b with $CH_3CO_2^-$



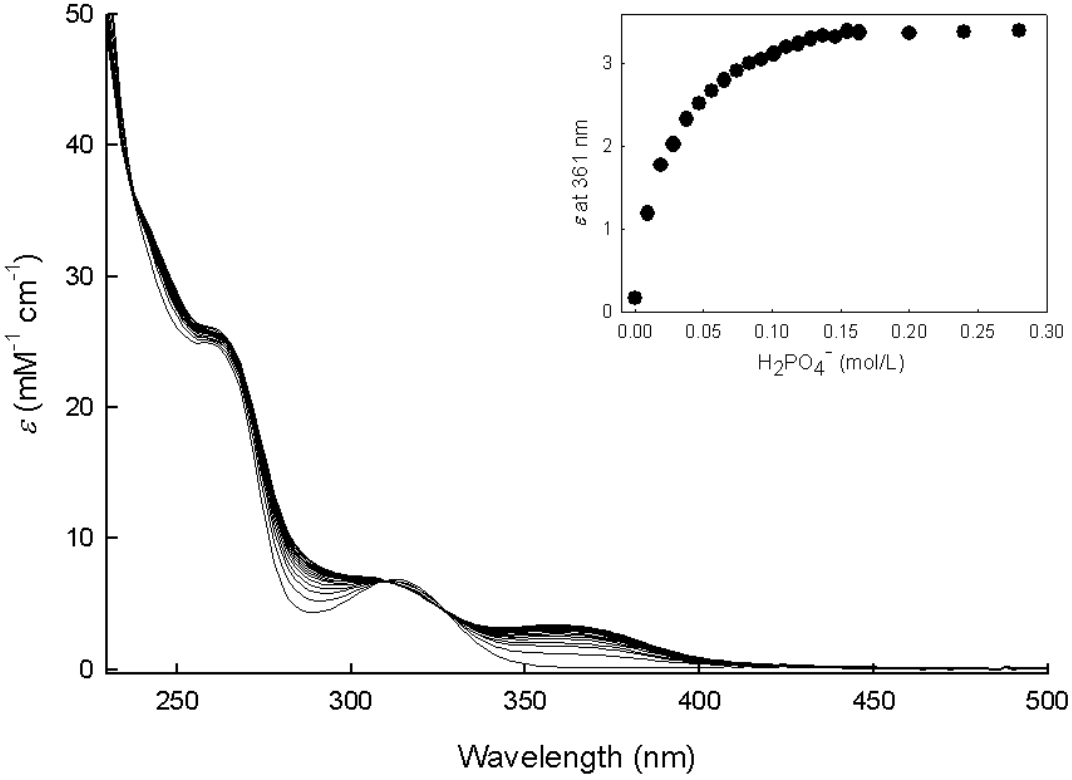
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_3L^b}$ with a standard solution of acetate ions. Inset: absorbance at 361 nm *vs.* concentration of acetate ions.

Spectrophotometric titration of H_2L^a with $H_2PO_4^-$



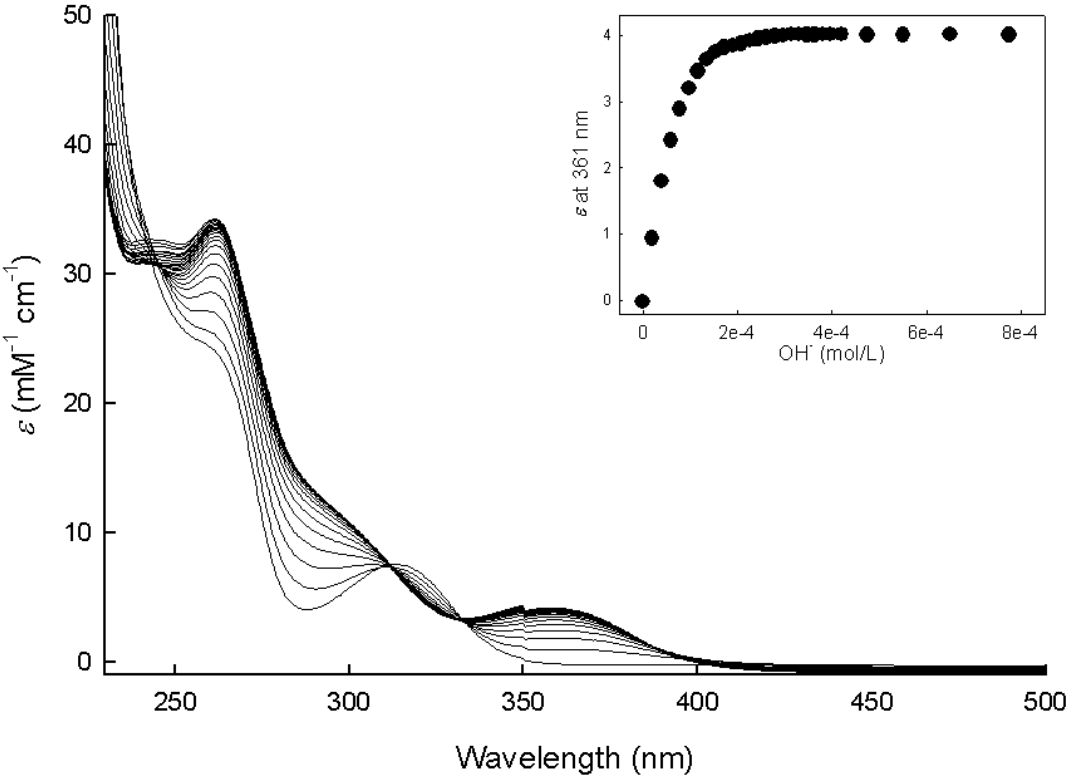
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_2L^a}$ with a standard solution of phosphate ions. Inset: absorbance at 361 nm *vs.* concentration of phosphate ions.

Spectrophotometric titration of H_3L^b with $H_2PO_4^-$



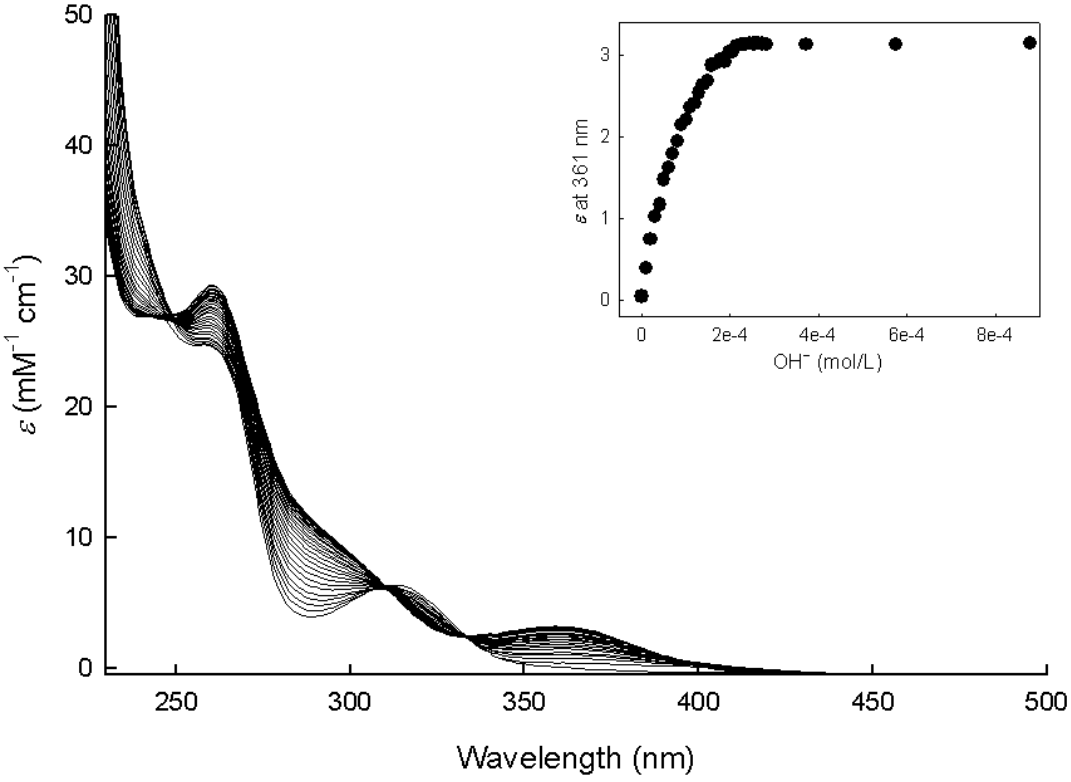
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_3L^b}$ with a standard solution of phosphate ions. Inset: absorbance at 361 nm *vs.* concentration of phosphate ions.

Spectrophotometric titration of H_2L^a with OH^-



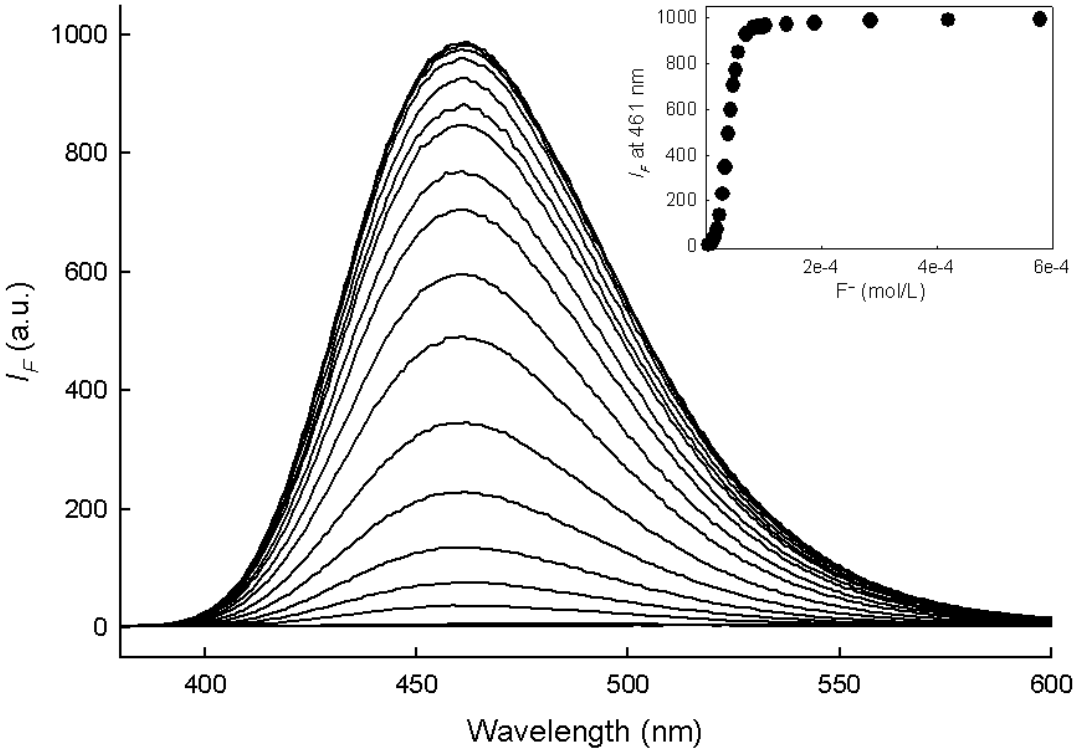
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_2L^a}$ with a standard solution of OH^-. Inset: absorbance at 361 nm *vs.* concentration of OH^-.

Spectrophotometric titration of H_3L^b with OH^-



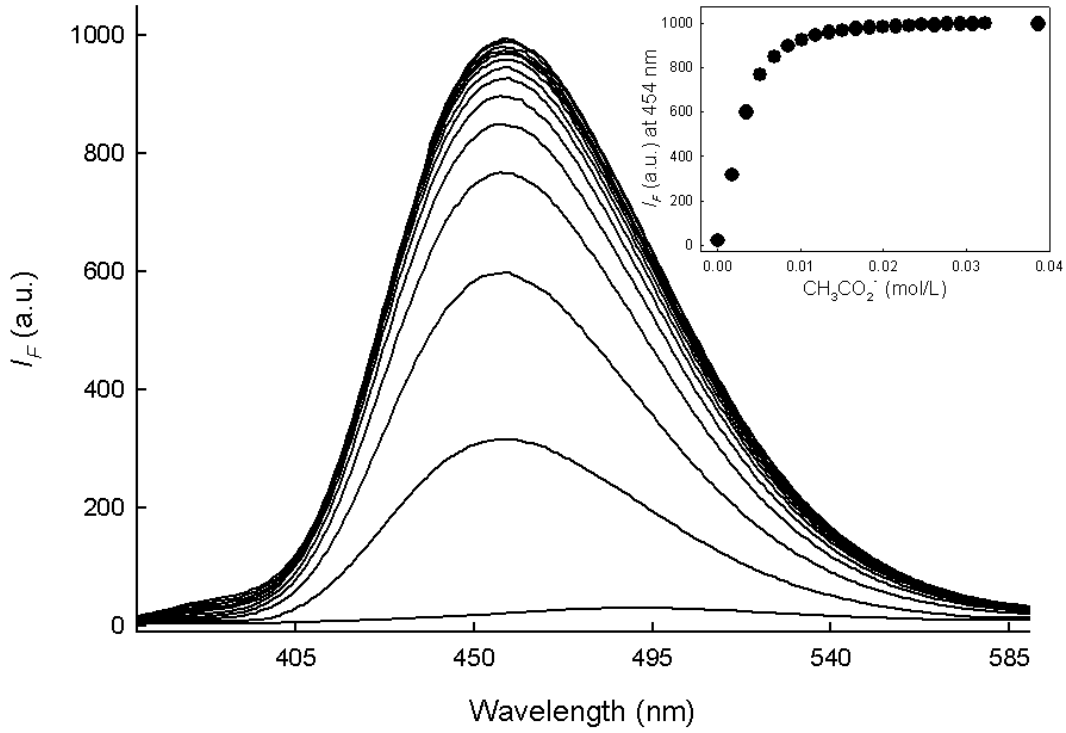
Spectrophotometric titration of a CH_3CN solution 40 μM in $\mathbf{H_3L^b}$ with a standard solution of OH^-. Inset: absorbance at 361 nm *vs.* concentration of OH^-.

Spectrofluorimetric titration of H_3L^b with F^-



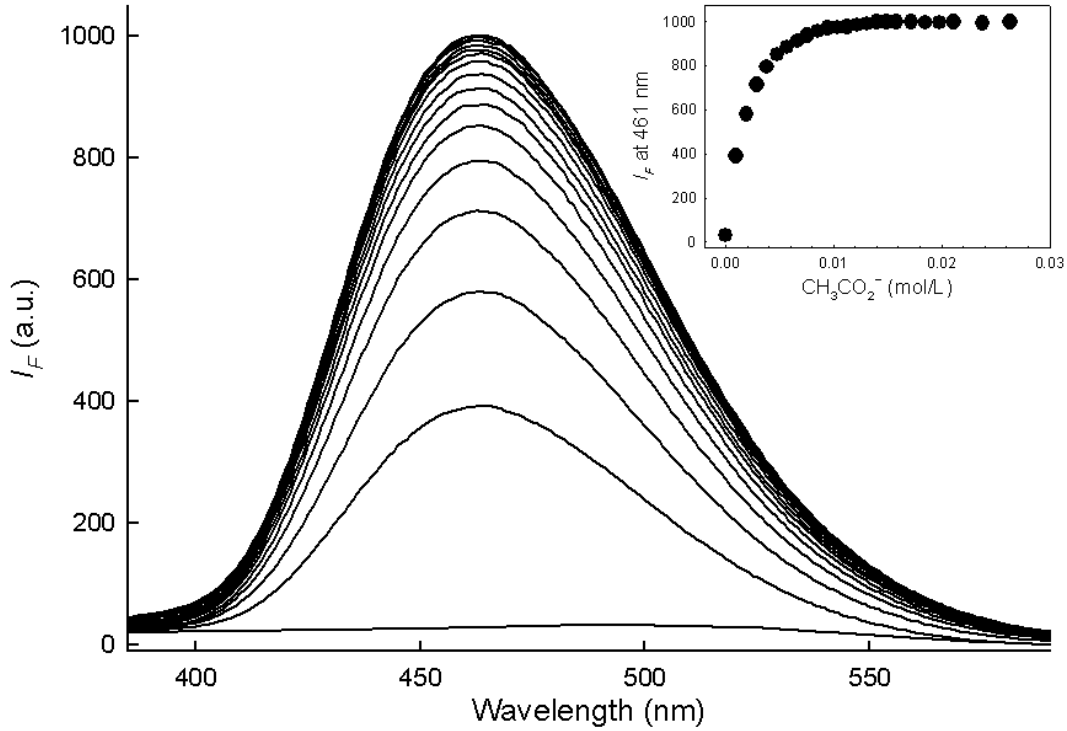
Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_3L^b}$ with a standard solution of fluoride ions. Inset: fluorescence intensity at 461 nm *vs.* equivalents of fluoride ions.

Spectrofluorimetric titration of H_2L^a with $CH_3CO_2^-$



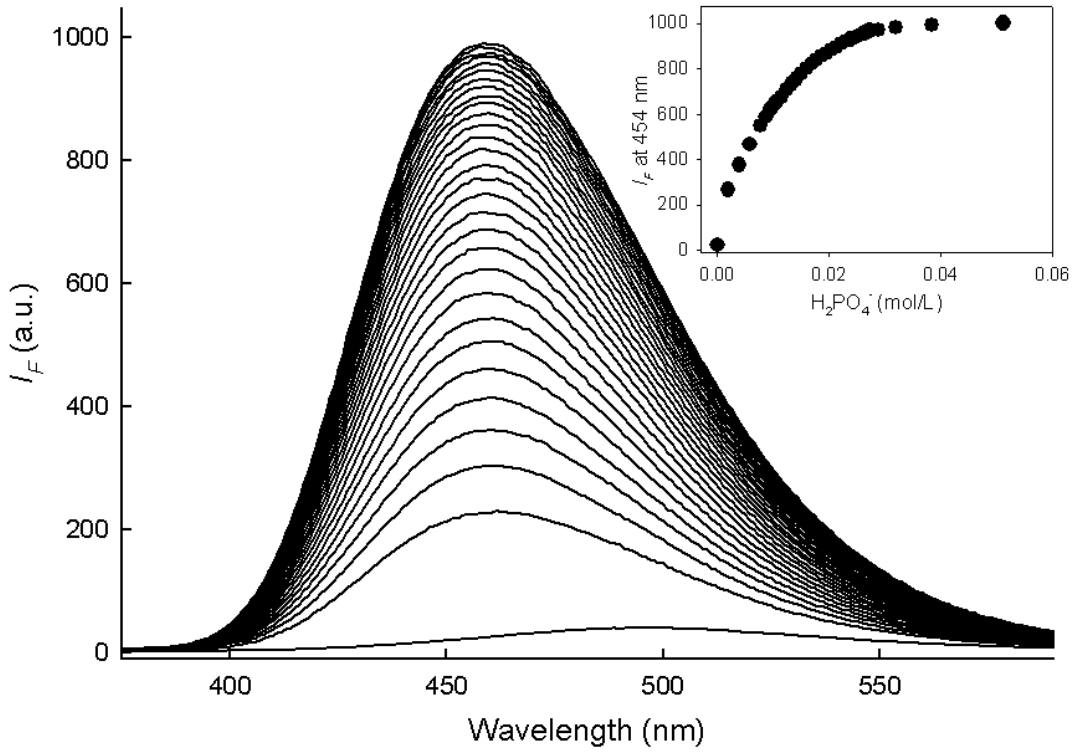
Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_2L^a}$ with a standard solution of acetate ions. Inset: fluorescence intensity at 454 nm *vs.* equivalents of acetate ions.

Spectrofluorimetric titration of H_3L^b with $CH_3CO_2^-$



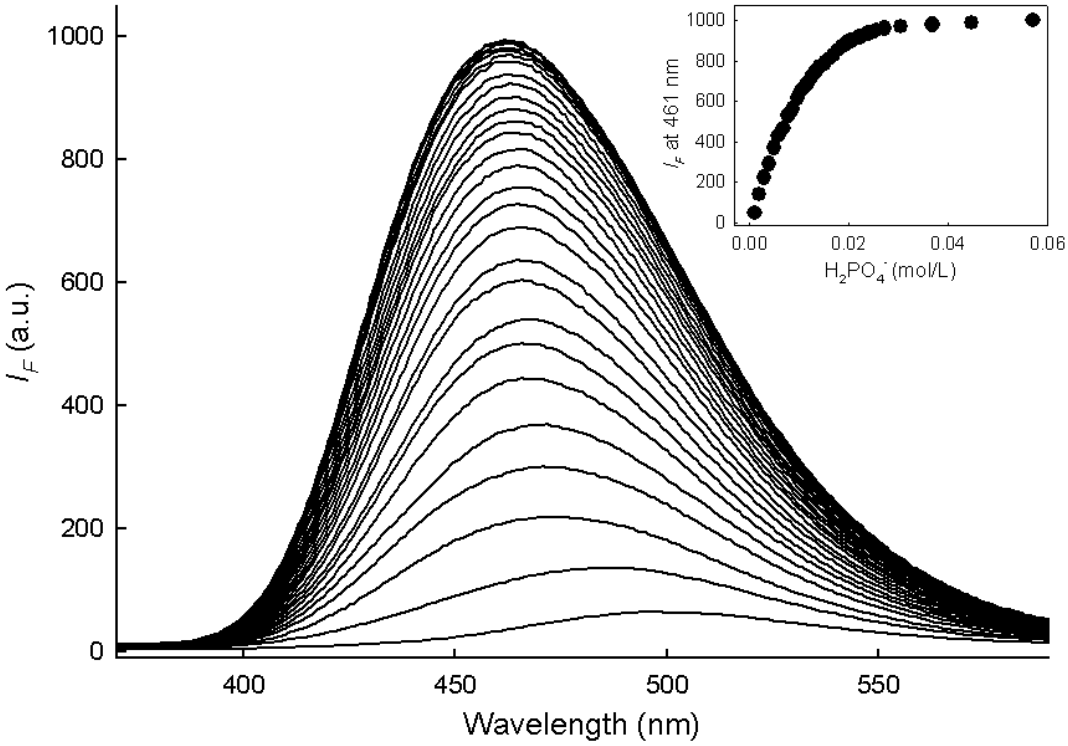
Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_3L^b}$ with a standard solution of acetate ions. Inset: fluorescence intensity at 461 nm *vs.* equivalents of acetate ions.

Spectrofluometric titration of H_2L^a with $H_2PO_4^-$



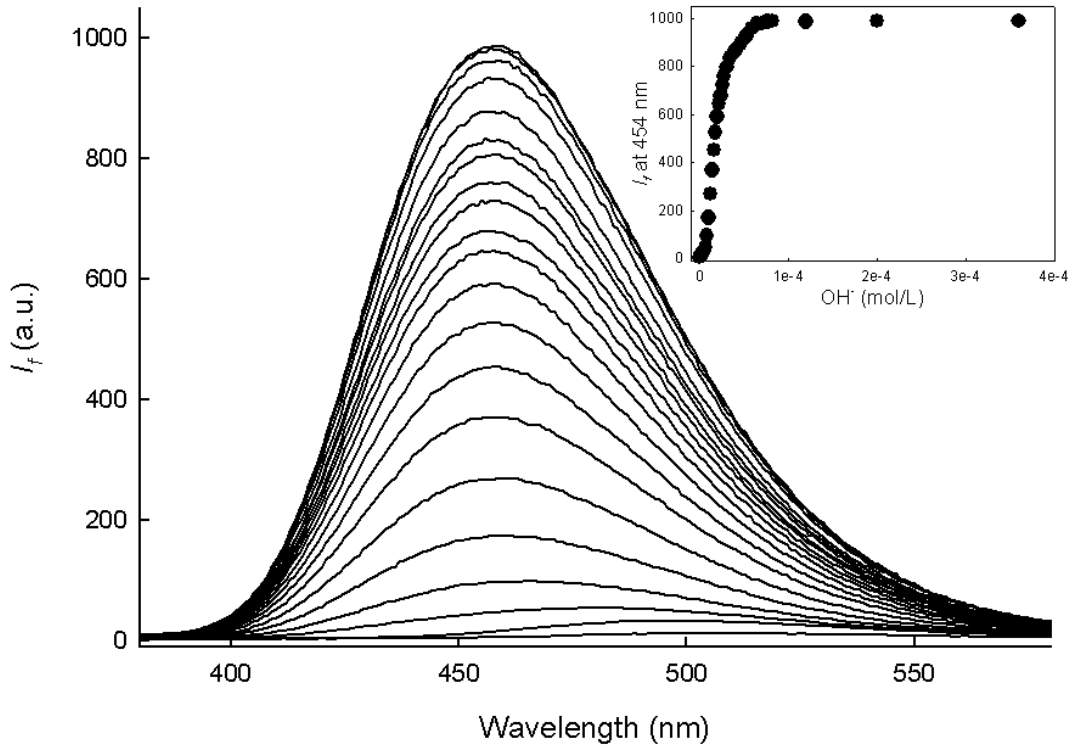
Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_3L^b}$ with a standard solution of phosphate ions. Inset: fluorescence intensity at 454 nm *vs.* equivalents of phosphate ions.

Spectrofluometric titration of H_3L^b with $H_2PO_4^-$



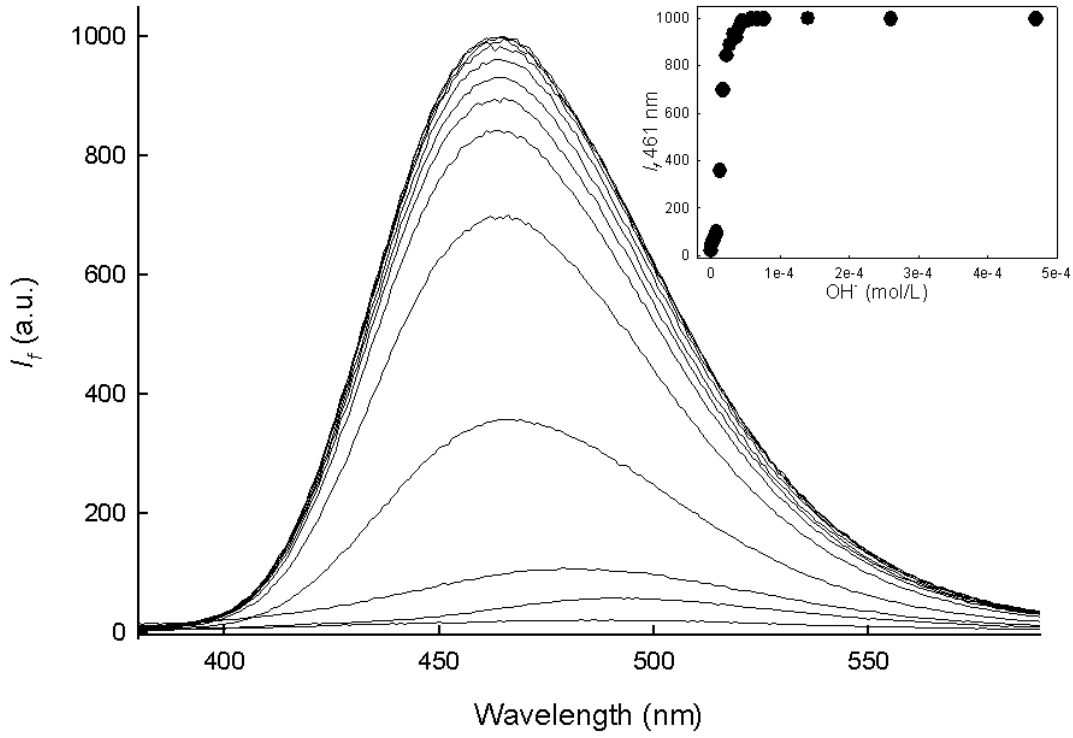
Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_3L^b}$ with a standard solution of phosphate ions. Inset: fluorescence intensity at 461 nm *vs.* concentration of phosphate ions.

Spectrofluorimetric titration of H_2L^a with OH^-



Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_2L^a}$ with a standard solution of OH^- ions. Inset: fluorescence intensity at 454 nm *vs.* concentration of OH^- ions.

Spectrofluorimetric titration of H_3L^b with OH^-



Spectrofluorimetric titration of a CH_3CN solution 10 μM in $\mathbf{H_3L^b}$ with a standard solution of OH^- ions. Inset: fluorescence intensity at 461 nm *vs.* concentration of OH^- ions.