Electronic Supplementary Material (ESI) for ChemComm.

Fluorescent and cooperative ion pair receptor based on tolan for Na^+ (or Li^+) and HSO_4^- : logic AND gate

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Contents

1. General experimental and synthetic details

General experimental

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields of synthesized compounds were measured after chromatographic purification. UV-vis spectra were recorded on a UV 1800 (Shimadzu) spectrophotometer. Proton and ^{13}C-NMR spectra were measured at 25 ºC using Jeol 400 instruments.

Synthetic Details

2,2'-(phenylazanediyl)bis(ethan-1-ol) (1)

In a round-bottom flask fitted with a reflux condenser, 2-iodoaniline (1 g, 2.56 mmol), $CaCO_3$ (0.9 g, 5.12 mmol), KI (90 mg, 0.26 mmol), and water (6 mL) were charged. The resulting solution was then stirred at reflux for 12 h. After cooling to room temperature, the mixture was filtered and then the solution was extracted with water and EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and then filtered; the filtrate was concentrated under reduced pressure to obtain the residue. The residue was purified over silica gel to afford **1** (250 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 9.4 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.28 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.92 (ddd, *J* = 8.0, 7.2, 1.7 Hz, 1H), 3.59 (m, 4H), 3.19 (m, *J* = 9.5 Hz, 4H), 2.47 (s, 2H), ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 151.71, 139.69, 129.87, 127.92, 126.23, 102.86, 60.02, 57.94, HRMS–EI: m/z $[M]^+$ calcd for $C_{10}H_{14}NO_2I$: 307.0069; found:307.0070.

13-(2-iodophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (2)

In a round-bottom flask fitted with a reflux condenser, compound **1** (0.5 g, 1.63 mmol) and di-tosylate (0.60 g, 1.30 mmol) were dissolved in THF (40 mL). NaH (0.31 g, 13.04 mmol) was slowly added to the mixture, which was then stirred at reflux for 3 days. After cooling to room temperature, the solution was concentrated under reduced pressure to afford a residue. The residue was extracted with water and EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and then filtered; the filtrate was concentrated under reduced pressure to obtain the residue. The residue was purified over silica gel to afford **2** (137 mg, 20%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.33 – 7.25 (m, 2H), 6.77 (ddd, *J* = 7.9, 6.7, 2.1 Hz, 1H), 3.69 (s, 4H), 3.68 – 3.58 (m, 12H), 3.38 (t, *J* = 6.2 Hz, 4H), ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 152.92, 139.99, 128.91, 125.85, 125.40, 100.83, 70.95, 70.73, 70.57, 70.45, 54.47, HRMS–EI: m/z $[M]^+$ calcd for $C_{16}H_{24}NO_4I$: 421.0750; found:421.0751.

1-(2-((2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)phenyl)ethynyl)phenyl)-3-hexylurea (4)

3a (160 mg, 0.712 ,mmol) and tributyltin methoxide (0.056 mL, 2.13 mmol) were charged in a pressure bottle. The solution was stirred at 120 ºC for 4 h. The resulting solution of **3b** was used without purification. To a well stirred solution of **2** (200 mg, 0.475 mmol) in DMF (4 mL), $Pd(PPh_3)_4$ (37 mg, 0.0475 mmol) and the solution of **3b** was added and then flushed with argon for 5-10 min. The soultion was stirred at 70 ºC for 5h. After cooling to room temperature, the solution was concentrated under reduced pressure to afford a residue. The residue was extracted with water and EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and then filtered; the filtrate was concentrated under reduced pressure to obtain the residue. The residue was purified over silica gel to afford **4** (66 mg, 26%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.24 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.69 (s, 1H), 7.44 (ddd, *J* = 7.7, 1.6, 0.5 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.08 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.93 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (td, *J* = 7.4, 1.1 Hz, 1H), 6.41 (s, 1H), 3.78 – 3.63 (m, 8H), 3.60 – 3.49 (m, 12H), 3.19 (td, *J* = 7.0, 5.7 Hz, 2H), 1.57 – 1.42 (m, 2H), 1.38 – 1.21 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H), ^{13}C NMR (101 MHz, ACETONE-D_6) δ 155.73, 153.11, 142.23, 136.10, 132.76, 130.45, 129.89, 122.08, 120.62, 119.97, 119.67, 114.67, 112.73, 96.15, 90.26, 71.76, 71.11, 70.75, 54.07, 40.62, 40.50, 32.44, 31.03, 27.46, 23.39, 14.42, HRMS–EI: m/z $[M]^+$ calcd for $C_{31}H_{43}N_3O_5$: 537.3203; found: 537.3201.

2. Spectroscopic titrations

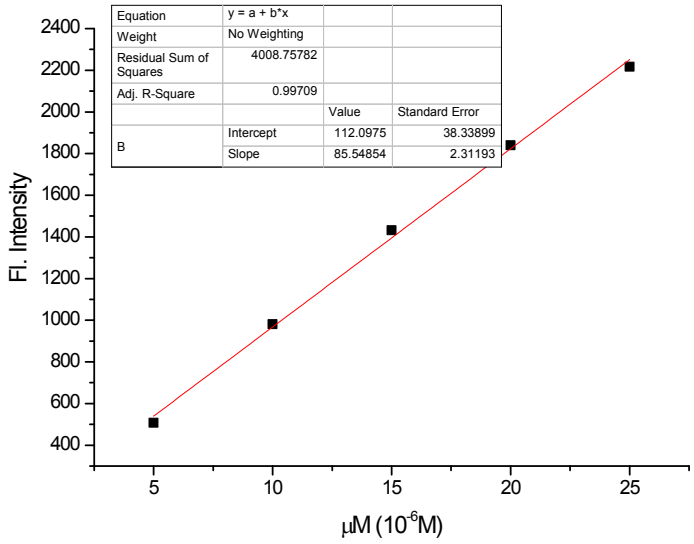
Stock solutions of all of the compounds studied were made up in CH_3CN with the final concentrations being between 2.0×10^{-5} M. ACS grade solvents were purchased and used without purification. The stock solutions were appropriately diluted with the solvents for the ensuing studies.

Binding Constants by UV-vis titrations

Upon addition of incremental amounts of anions to the solution of receptor **4**, absorbance change of **4** (2.0×10^{-5} M of **4** was used, unless otherwiswe stated) were recorded in CH_3CN. Equilibrium constants of complexes were calculated using the equation, $y = (b \times x)/(1 + x \times K)$, where $x = [G]$, $y = A - A_o$ (A is the absorbance of the solution of **4** at a certain concentration of anions and A_o is the absorbance of the solution of 4 without anions).

Binding constants by fluorescent titrations

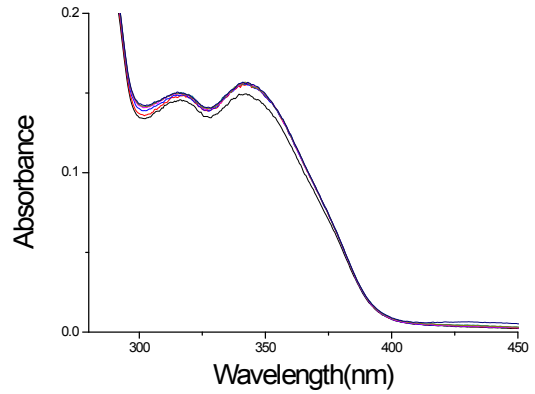
Upon addition of incremental amounts of anion to the solution of receptor **4**, fluorescence change of each chemosensor (2.0×10^{-5} M) were recorded in CH_3CN by irradiating the solution at $\lambda_{ex} = 340$ nm. Equilibrium constants of complexes were calculated using the equation below.
$y = (1 + b \times x \times K)/(1 + x \times K)$, where $x = [G]$, $y = F/F_o$ (F intensity at a certain concentration of anions/F_o intensity without anions).
The observed fluorescent intensities were shown below at a various concentrations of **4** in CH_3CN at 420nm.



Binding Constants by ^{1}H NMR titrations

Upon addition of incremental amounts of anions to the solution of receptor **4**, chemical shift change of **4** (4 mM of **4** was used, unless otherwise stated) were recorded in CD_3CN. Equilibrium constants of complexes were calculated using the equation, $y = (b \times x)/(1 + x \times K)$, where $x = [G]$, $y = \delta - \delta_o$ (δ is a chemical shift of **4** at a certain concentration of anions and δ_o is a chemical shift of **4** without anions).

F^-


Absorbance
Wavelength(nm)
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0.1
0.2
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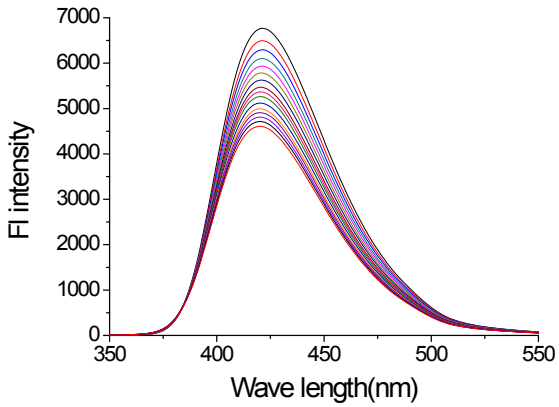
350
400
450


FI intensity
Wave length(nm)
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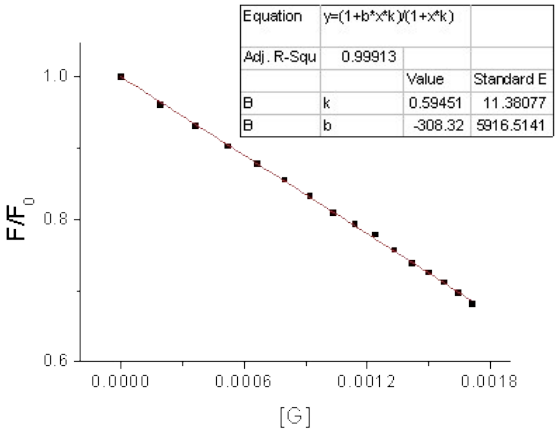
2000
3000
4000
5000
6000
7000
350
400
450
500
550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Value Standard E
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F/F0
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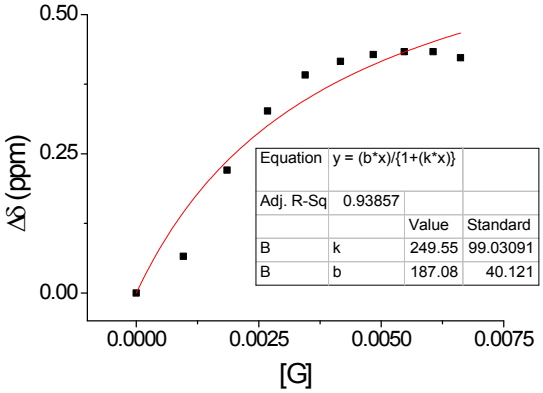
0.0012
0.0018


Δδ (ppm)
[G]
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0.25
0.50
0.0000
0.0025
0.0050
0.0075
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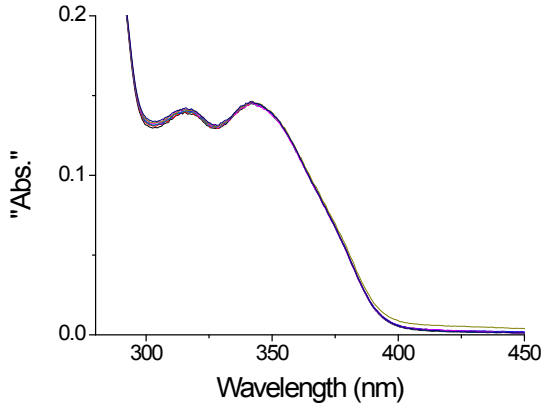
B b 187.08 40.121

Cl^-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Wavelength (nm)
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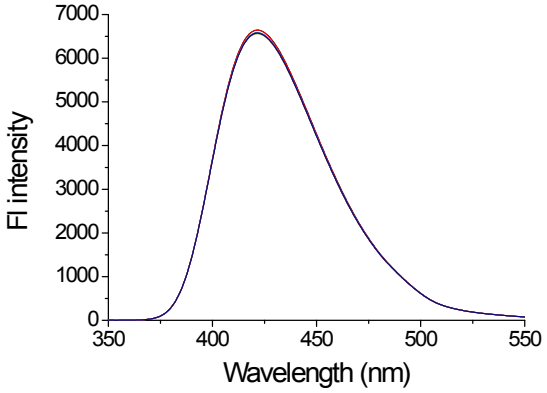
450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5000
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7000
350
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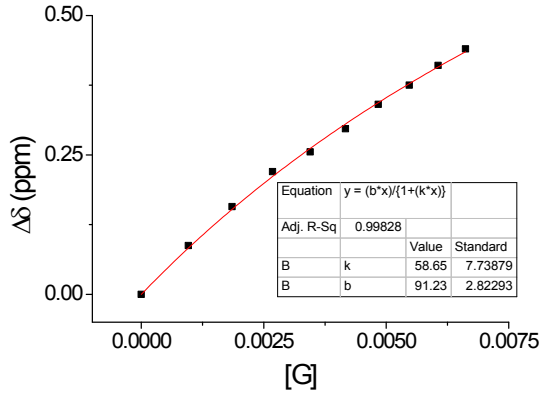
450
500
550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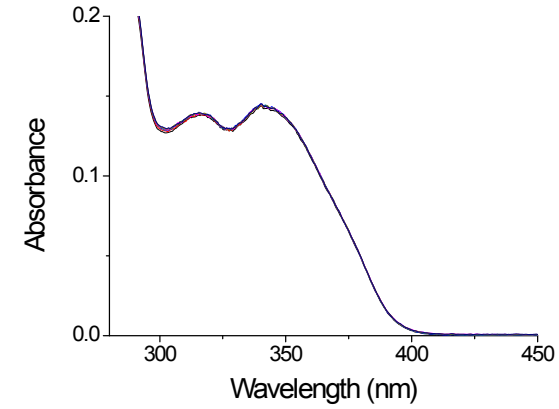
B b 91.23 2.82293

Br^-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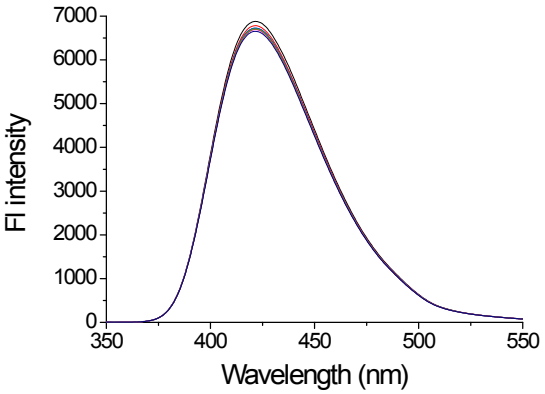
350
400
450
Wavelength (nm)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5000
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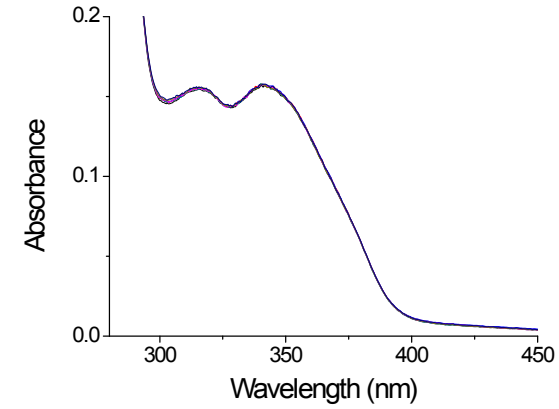
3000
2000
1000
0
350
400
450
500
550
Wavelength (nm)

I^-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0.1
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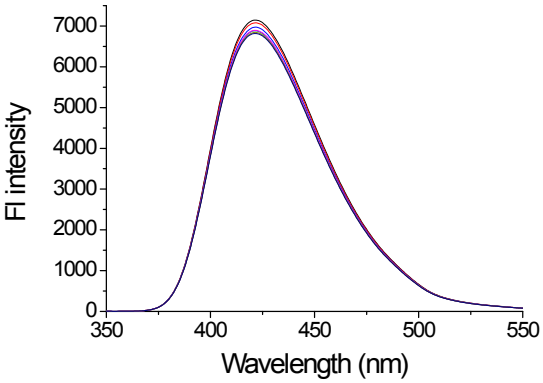
300
350
400
450
Wavelength (nm)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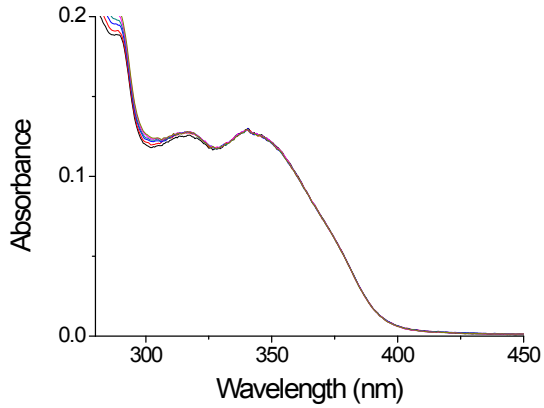
3000
2000
1000
0
Fl intensity
350
400
450
500
550
Wavelength (nm)

BzO^-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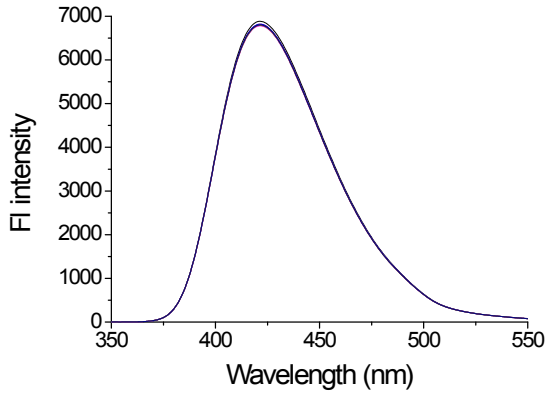
0.1
0.0
Absorbance
300
350
400
450
Wavelength (nm)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450
500
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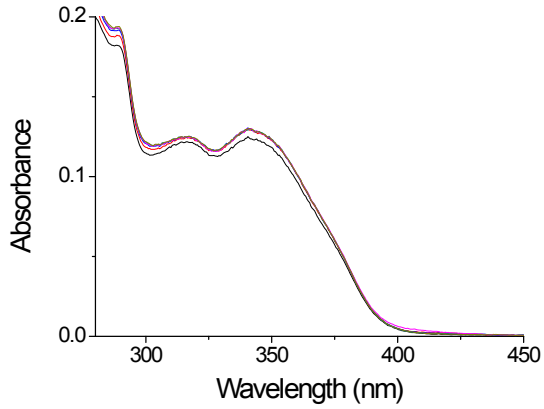
Wavelength (nm)

$H_2PO_4^-$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Absorbance
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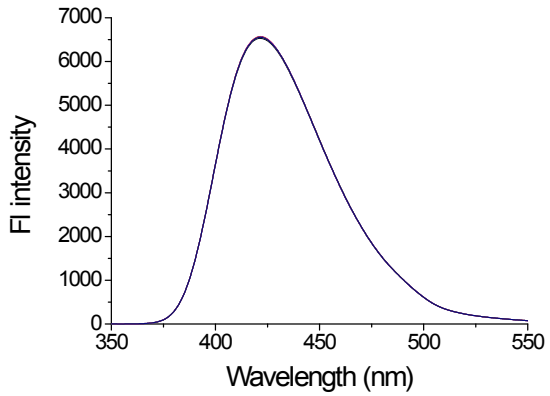
Wavelength (nm)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1000
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FI intensity
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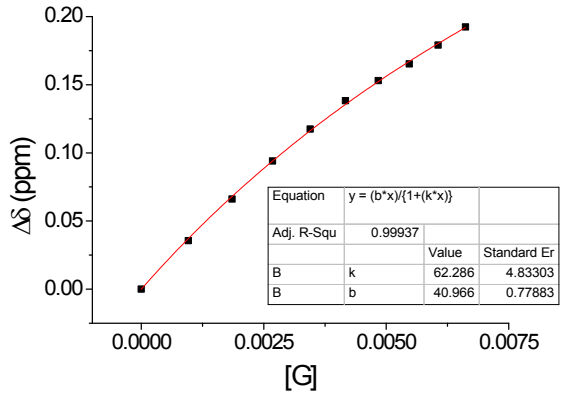
400
450
500
550
Wavelength (nm)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0.10
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0.00
Δδ (ppm)
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0.0025
0.0050
0.0075
[G]
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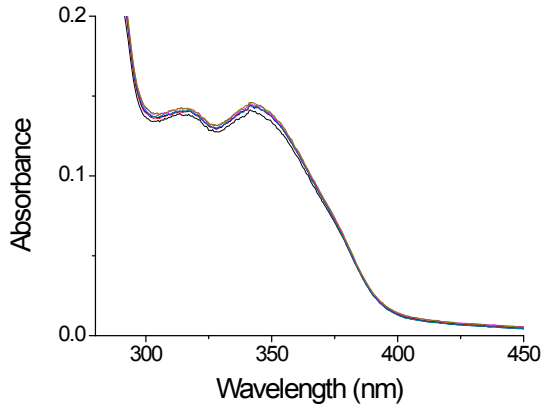
B b 40.966 0.77883

HSO_4^-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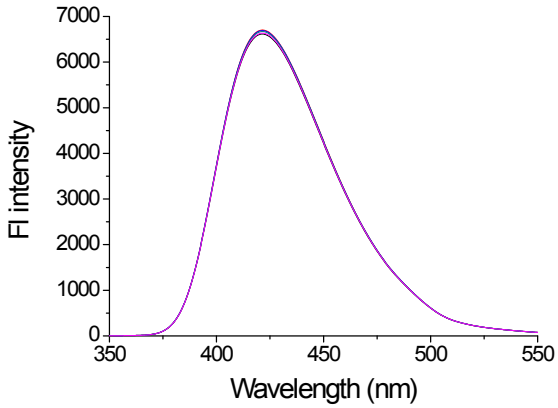
0.0
Absorbance
300
350
400
450
Wavelength (nm)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FI intensity
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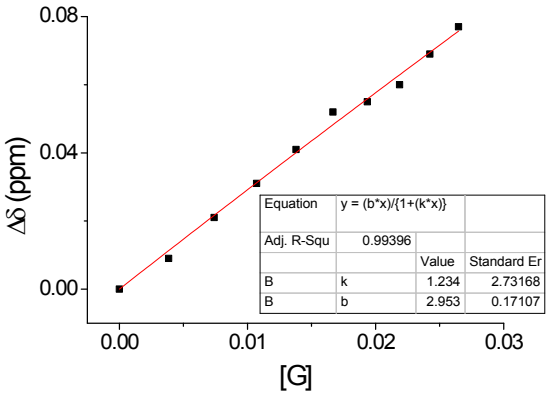
400
450
500
550
Wavelength (nm)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[G]
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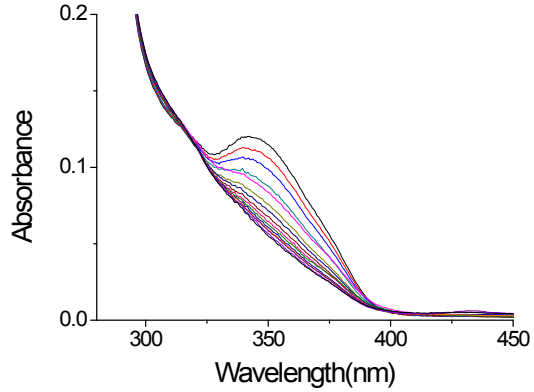
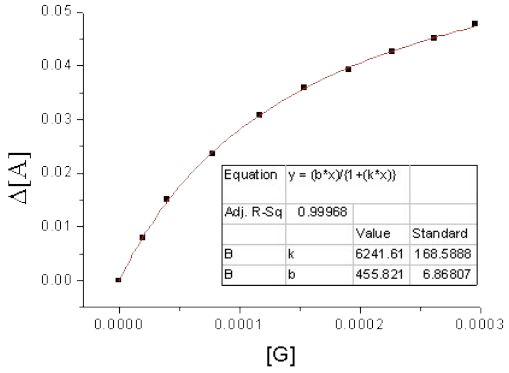
B b 2.953 0.17107

$Li^{+}ClO_4^{-}$


0.2
0.1
0.0
Absorbance
300
350
400
450
Wavelength(nm)


0.05
0.04
0.03
0.02
0.01
0.00
Δ[A]
0.0000
0.0001
0.0002
0.0003
[G]
Equation y = (b*x)/{1+(k*x)}
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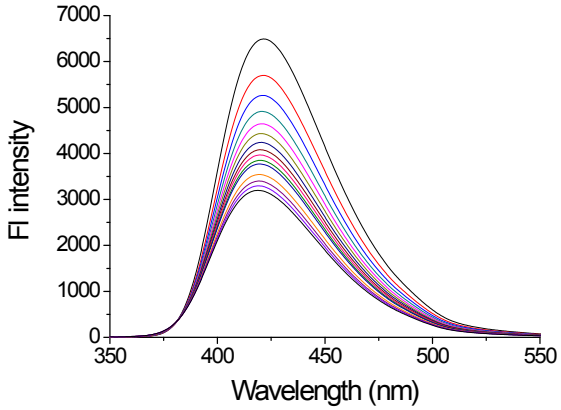
B b 455.821 6.86807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6000
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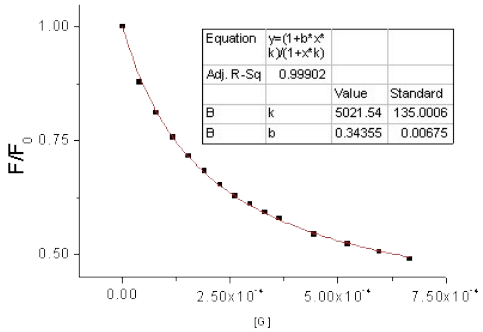
2000
1000
0
FI intensity
350
400
450
500
550
Wavelength (nm)


1.00
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F/F0
0.00
2.50x10-4
5.00x10-4
7.50x10-4
[G]
Equation y=(1+b*x*k)/(1+x*k)
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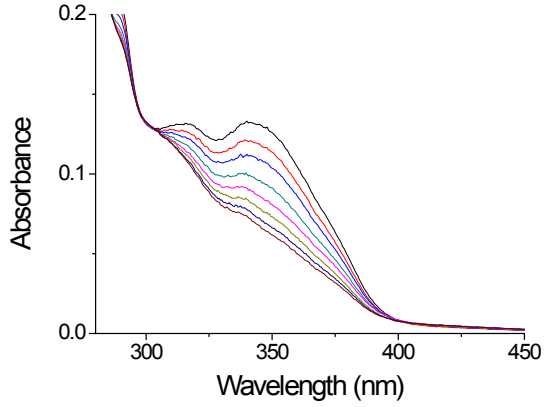
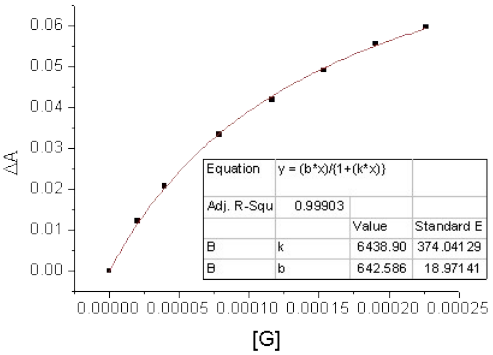
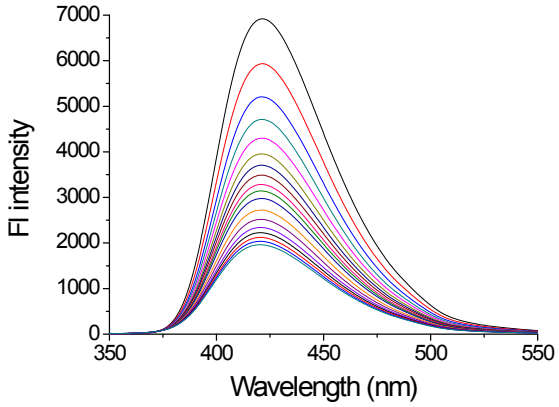
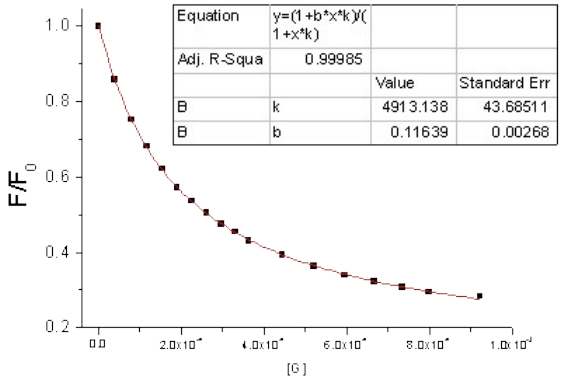
$Na^+(BPh_4)^-$

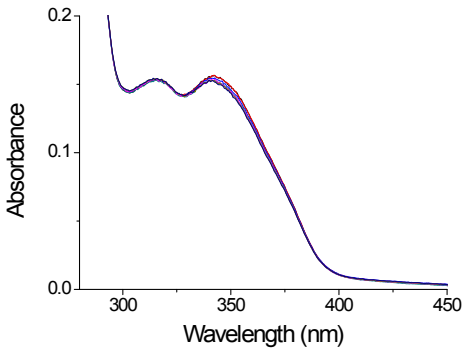


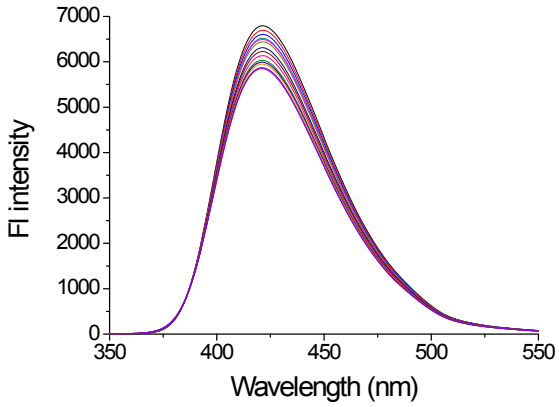


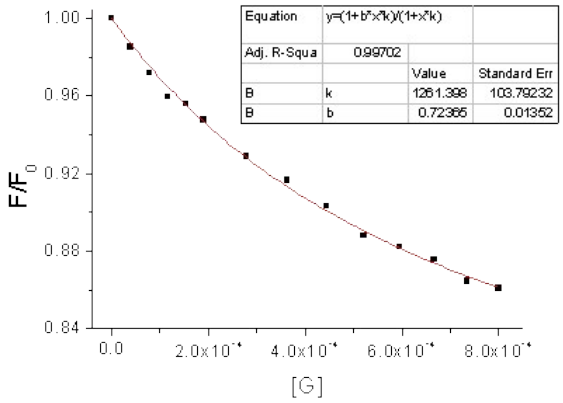




$K^+(BPh_4)^-$




Fl intensity
Wavelength (nm)


Equation y=(1+b*x^k)/(1+x^k)
Adj. R-Squa 0.99702
Value Standard Err
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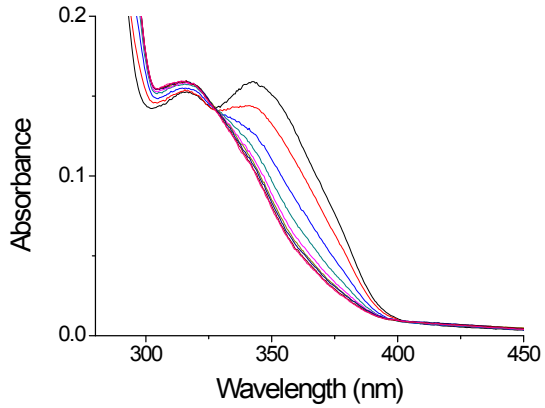
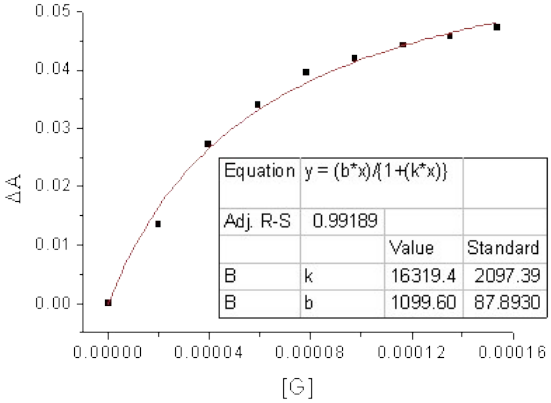
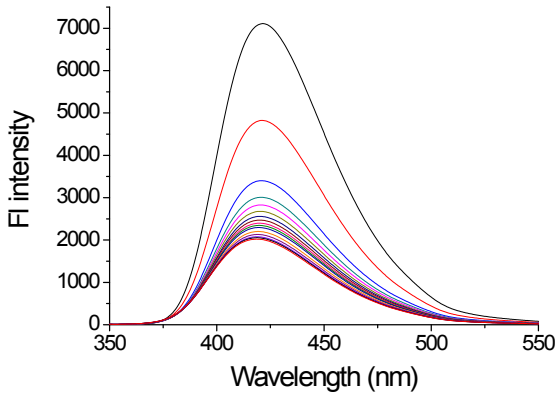
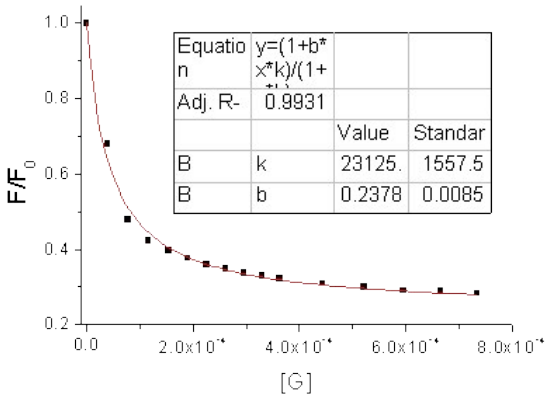
B b 0.72365 0.01352
F/F0
[G]

$LiHSO_4$

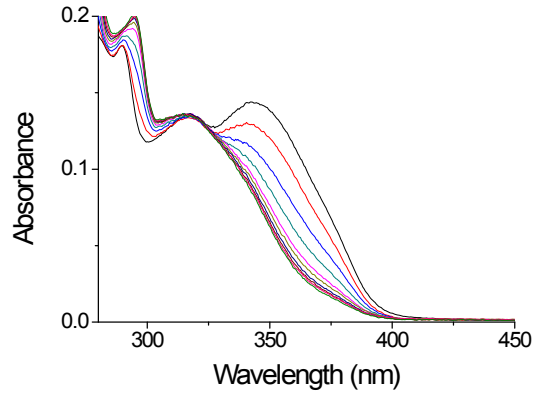

Absorbance
Wavelength (nm)


Equation y = (b*x)/(1+(k*x))
Adj. R-S 0.99189
Value Standard
B k 16319.4 2097.39
B b 1099.60 87.8930
ΔA
[G]


Fl intensity
7000
6000
5000
4000
3000
2000
1000
0
350
400
450
500
550
Wavelength (nm)


F/F0
1.0
0.8
0.6
0.4
0.2
0.0
2.0x10-4
4.0x10-4
6.0x10-4
8.0x10-4
[G]
Equation y=(1+b*x*k)/(1+
Adj. R- 0.9931
Value Standar
B k 23125. 1557.5
B b 0.2378 0.0085

$NaHSO_4$


Absorbance
Wavelength (nm)
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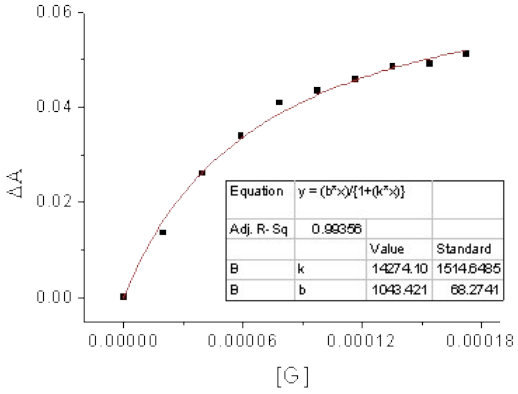
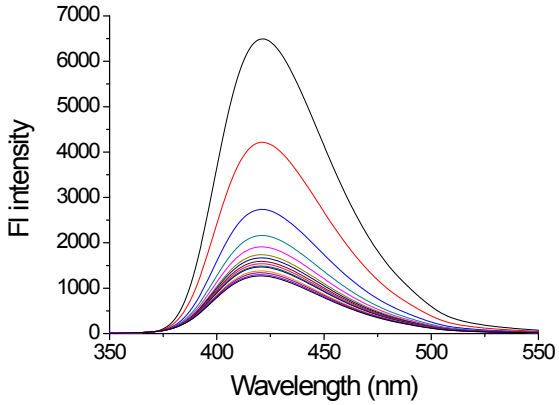
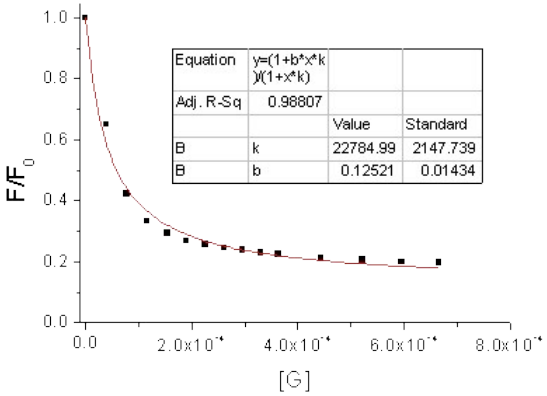
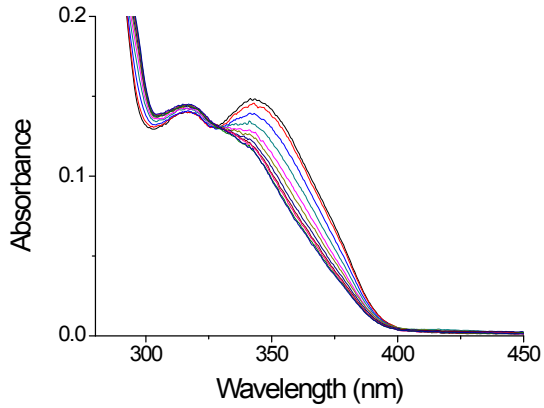
0.1
0.2
300
350
400
450

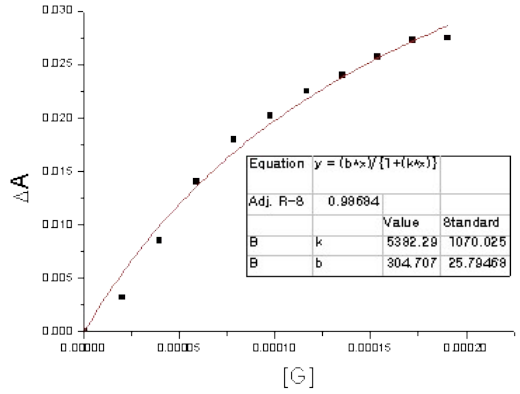

ΔA
[G]
0.00
0.02
0.04
0.06
0.00000
0.00006
0.00012
0.00018
Equation y = (b*x)/(1+(k*x))
Adj. R-Sq 0.99356
Value Standard
B k 14274.10 1514.6485
B b 1043.421 68.2741

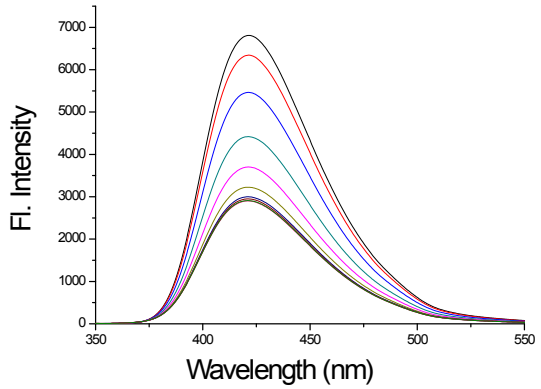

FI intensity
Wavelength (nm)
0
1000
2000
3000
4000
5000
6000
7000
350
400
450
500
550

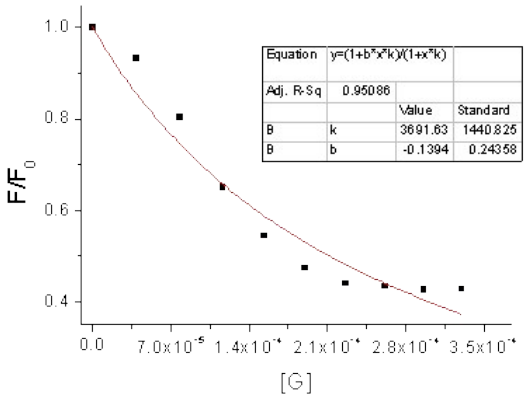

F/F0
[G]
0.0
0.2
0.4
0.6
0.8
1.0
0.0
2.0x10-4
4.0x10-4
6.0x10-4
8.0x10-4
Equation y=(1+b*x*k)/(1+x*k)
Adj. R-Sq 0.98807
Value Standard
B k 22784.99 2147.739
B b 0.12521 0.01434

$KHSO_4$


Absorbance
Wavelength (nm)
0.2
0.1
0.0
300
350
400
450


△A
[G]
Equation y = (b*x)/(1+(k*x))
Adj. R-S 0.98684
Value Standard
B k 5382.29 1070.025
B b 304.707 25.79468


Fl. Intensity
Wavelength (nm)
7000
6000
5000
4000
3000
2000
1000
0
350
400
450
500
550


F/F0
[G]
Equation y=(1+b*x*k)/(1+x*k)
Adj. R-Sq 0.95086
Value Standard
B k 3691.63 1440.825
B b -0.1394 0.24358
1.0
0.8
0.6
0.4
0.0
7.0x10-5
1.4x10-4
2.1x10-4
2.8x10-4
3.5x10-4

Job Plot for 4·$M^+HSO_4^-$

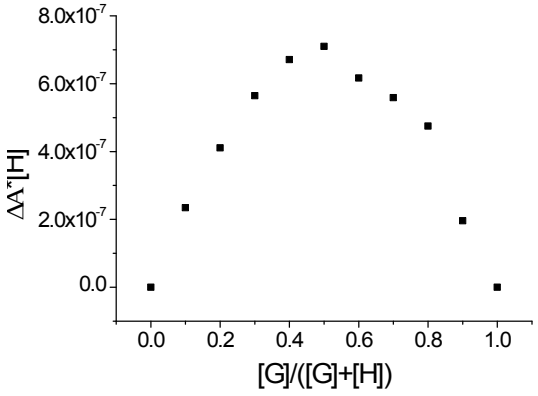


Figure S1. Job plots for $LiHSO_4$ obtained by UV-vis titrations

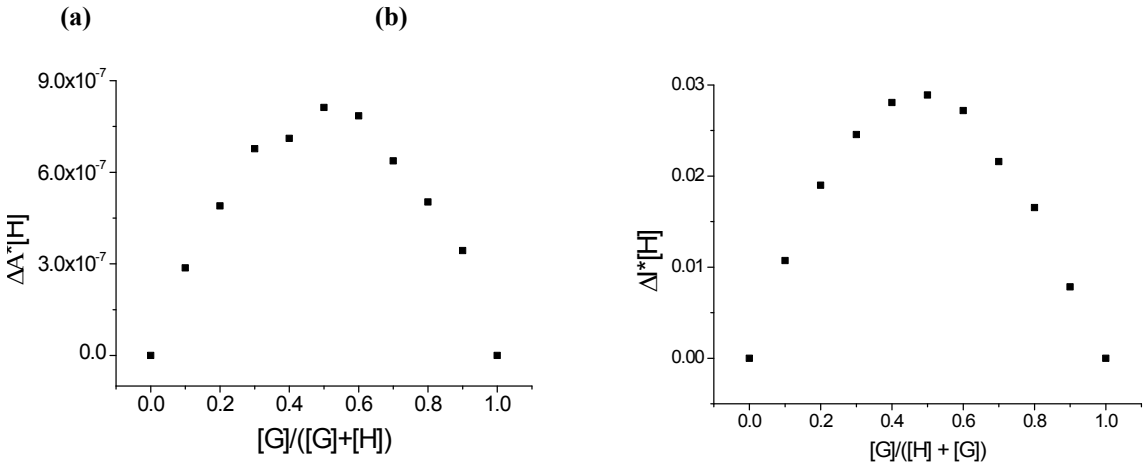


Figure S2. Job plots for $NaHSO_4$ obtained by a) UV-vis titrations b) fluorescent titrations

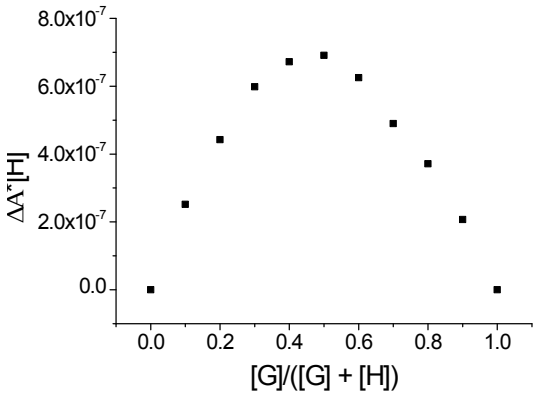


Figure S3. Job plots for $KHSO_4$ obtained by UV-vis titrations

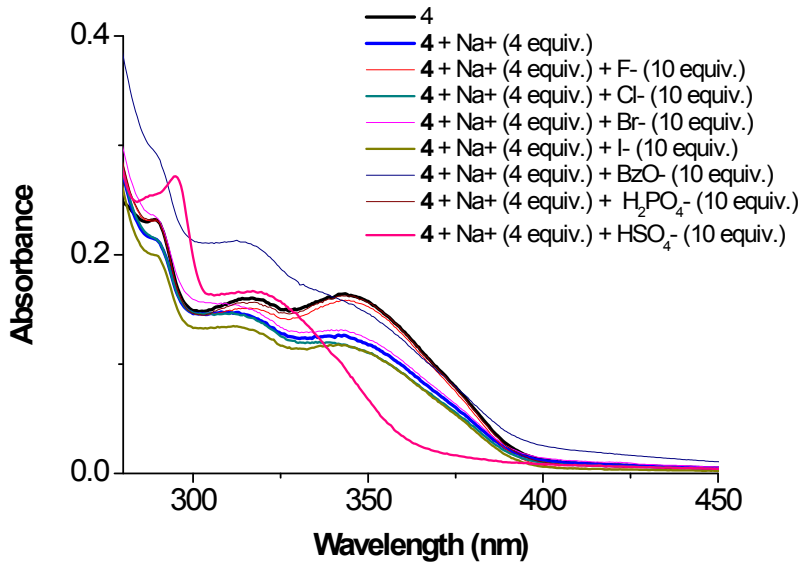


Figure S4. UV-vis spectra changes of **4** (20 μM in CH_3CN) were recorded upon the addition of various anions (10 equiv.) in the presence of Na^+ (4equiv.) at 25 °C.

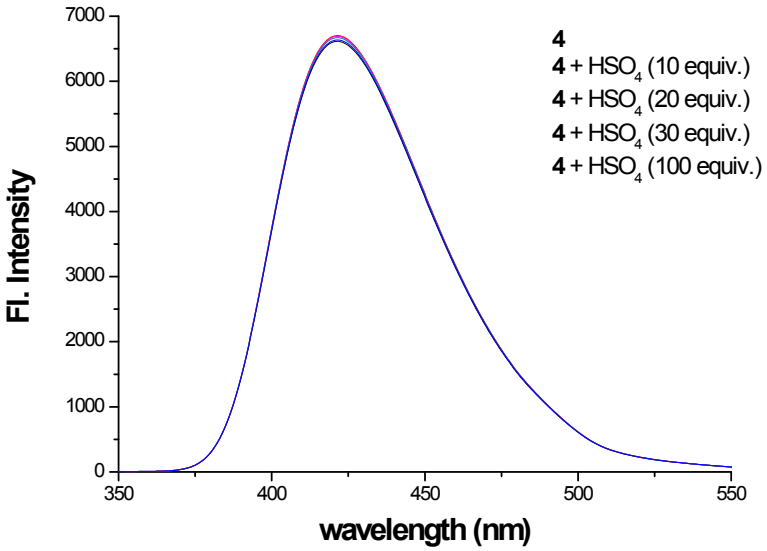


Figure S5. Fluorescent changes of **4** (20 μM in CH_3CN) Upon the addition of various amount of HSO_4^- at 25 °C.

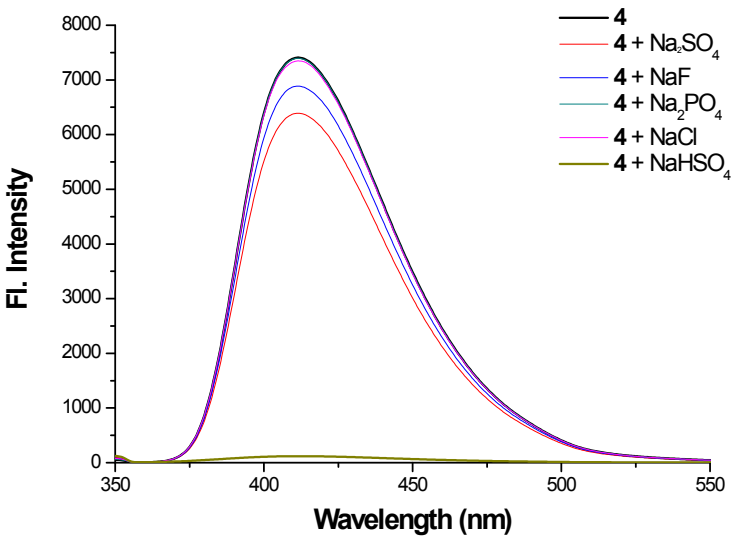


Figure S6. Fluorescent changes of **4** (20 μM in CH_2Cl_2) after the extraction of various inorganic salts (excess amount of solid salts) with the solution at 25 °C.

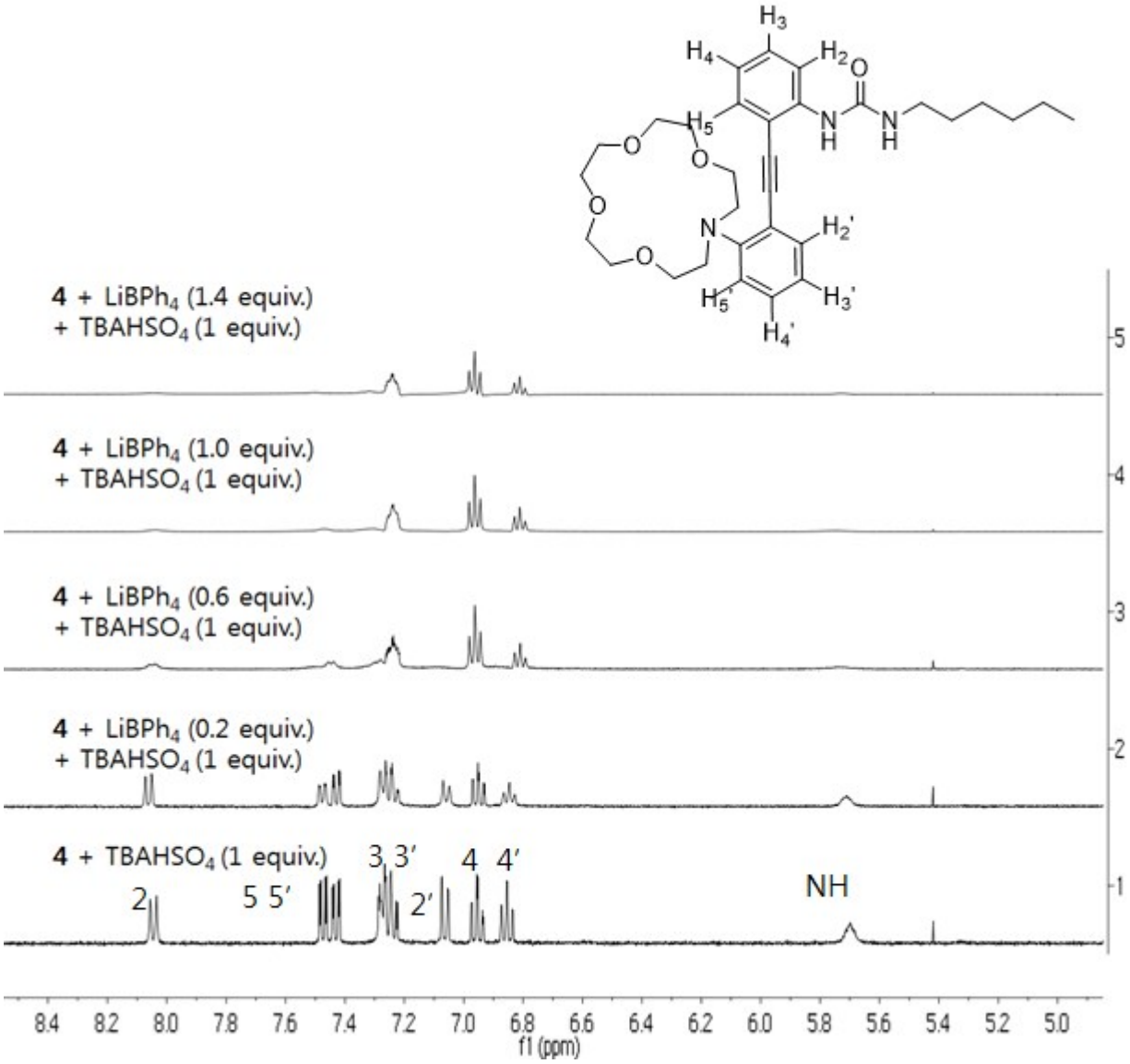


Figure S7. Partial ^{1}H-NMR spectra recorded during the titration of **4** ([H] = 4.0×10^{-3} M in CD_3CN) with $LiBPh_4$ in the presence of 1 equiv. of $TBA{\cdot}HSO_4$

(a) **(b)**

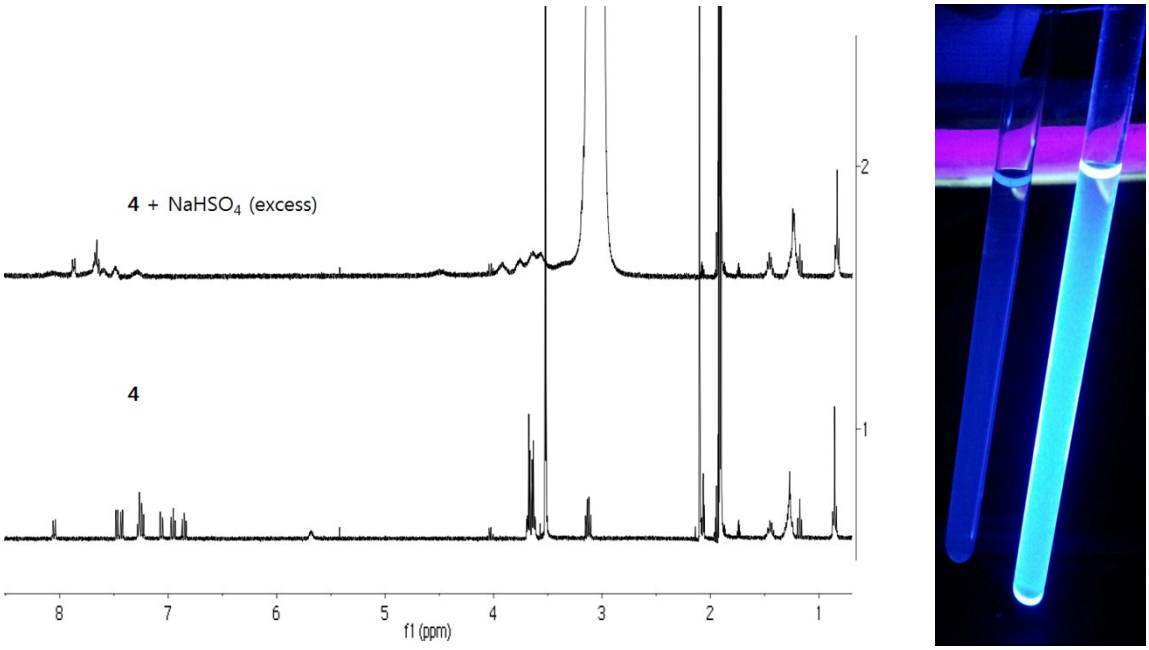


Figure S8. (a) ^{1}H-NMR spectra of **4** and **4** containing $NaHSO_4$ after the extraction of solid $NaHSO_4$ with **4** (4 mM in CD_3CN) (b) left (**4** + $NaHSO_4$) and right (only **4**) under a laboratory hand-held UV light.

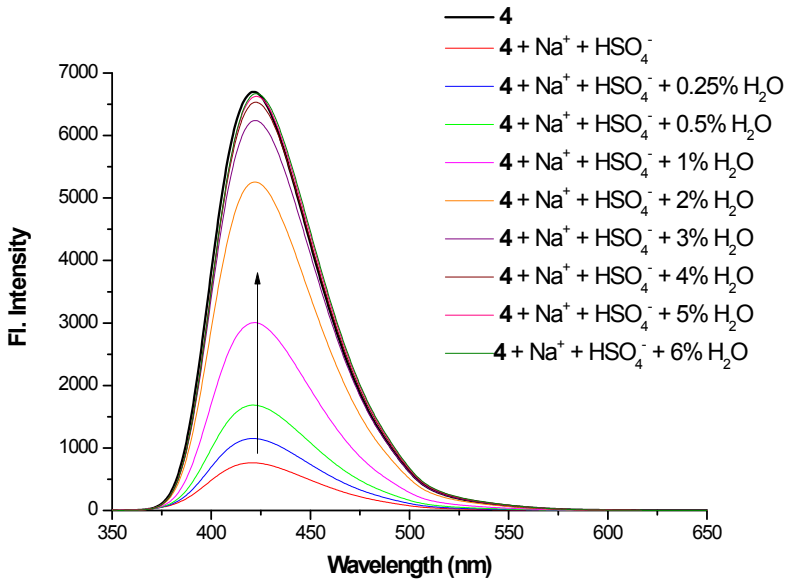
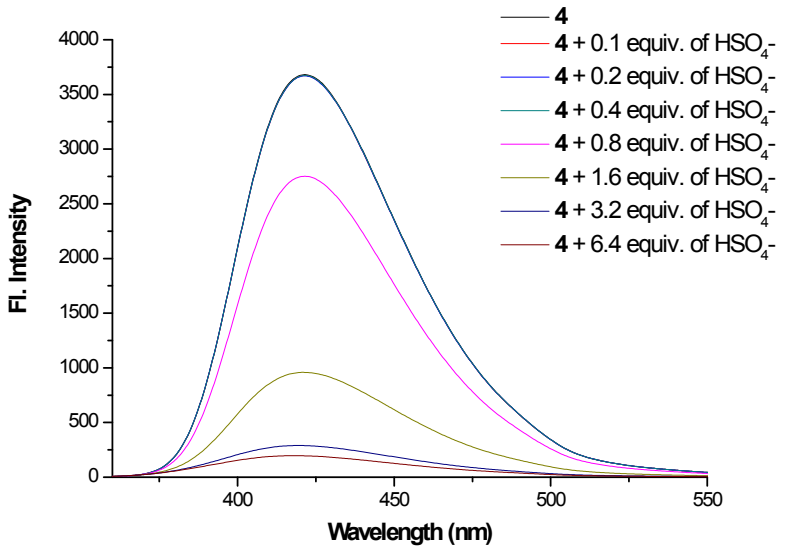


Figure S9. Evolution of the fluorescent spectrum of **4** (2.0×10^{-5} M in CH_3CN containing 4 equiv. of Na^+ and HSO_4^- during the titration with water (from 0 – 6%)

(a)



(b)

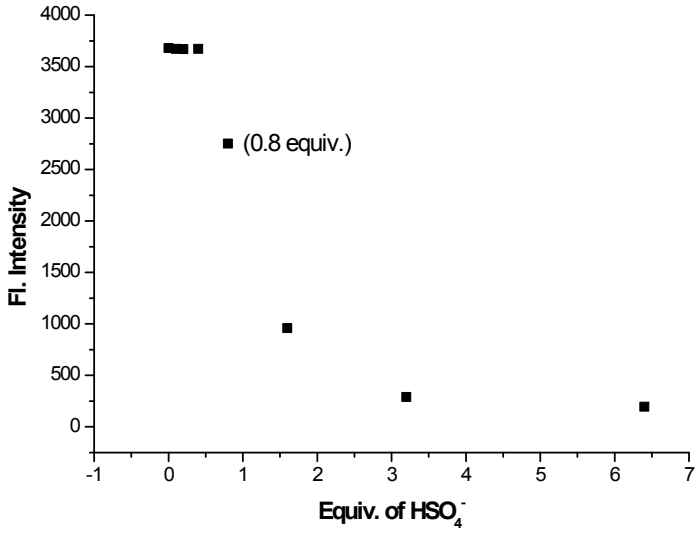


Figure S10. (a) Evolution of the fluorescent spectrum of **4** (2.0×10^{-5} M in CH_3CN containing 1% water and 32 equiv. of Na^+) during the titration with tetrabutylammonium HSO_4^- ($TBA{\cdot}HSO_4$; 0 – 6.4 equiv.) (b) The fluorescent intensities of **4** at 422 nm *vs* equiv. of HSO_4^- obtained from Figure S10a.

3. DFT calculation

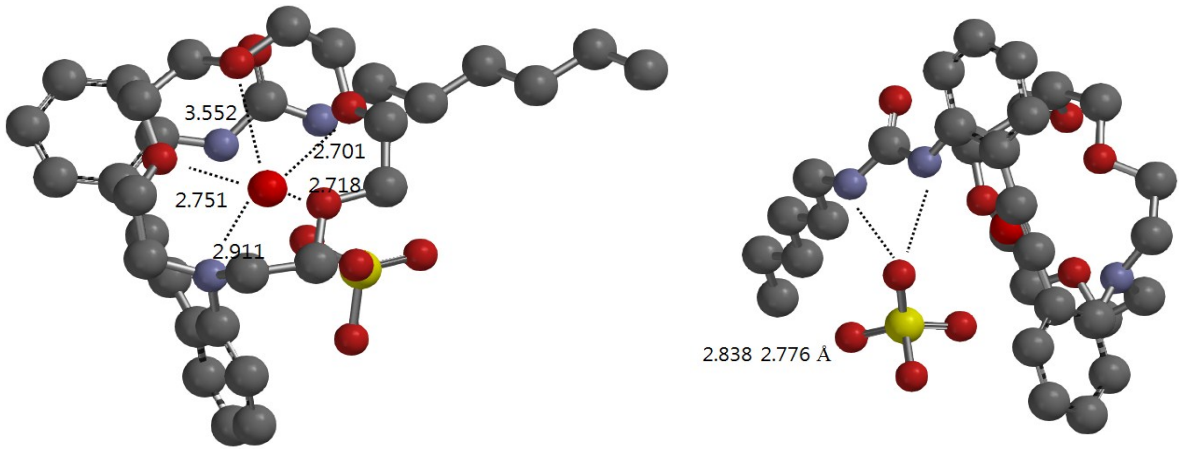


Figure S11. Optimized structures of **4**·$KHSO_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

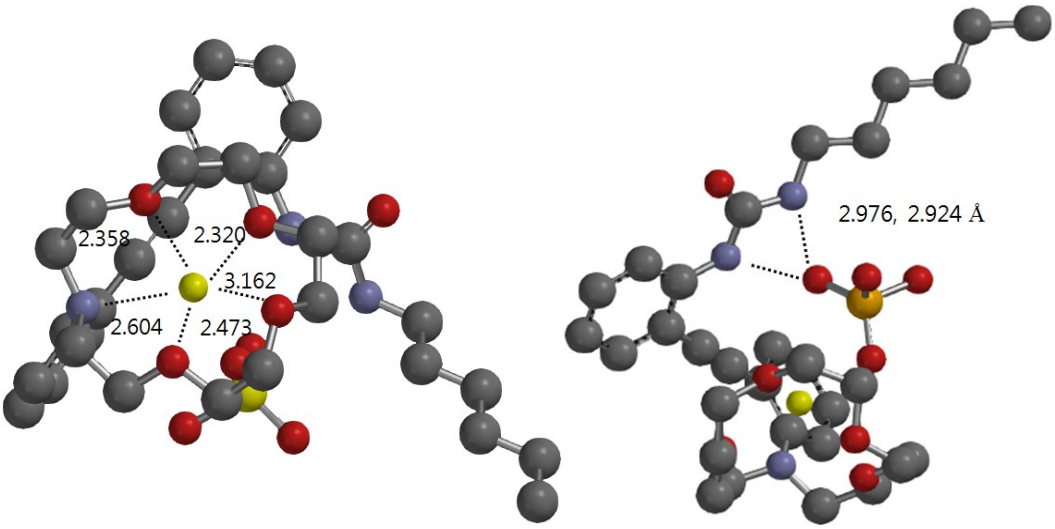


Figure S12. Optimized structures of **4**·$NaHSO_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity

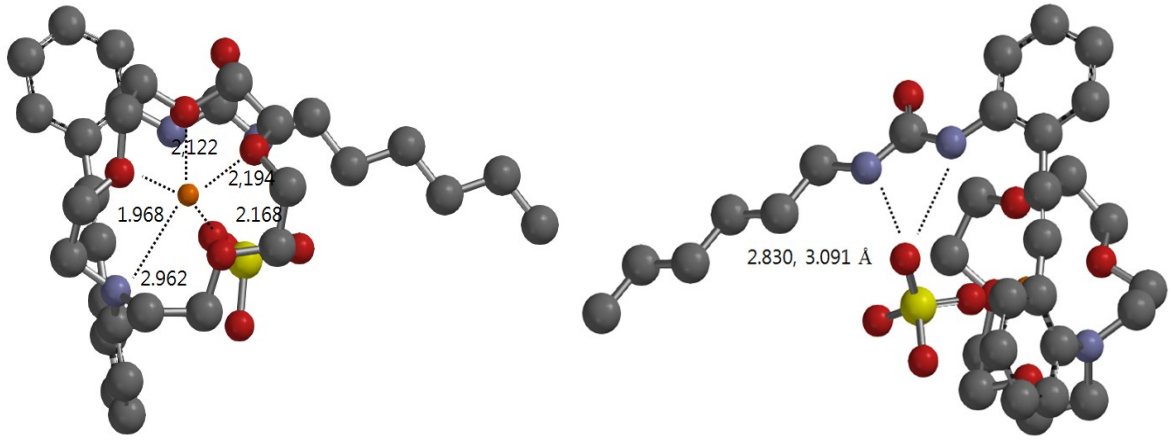


Figure S13. Optimized structures of **4**·$LiHSO_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

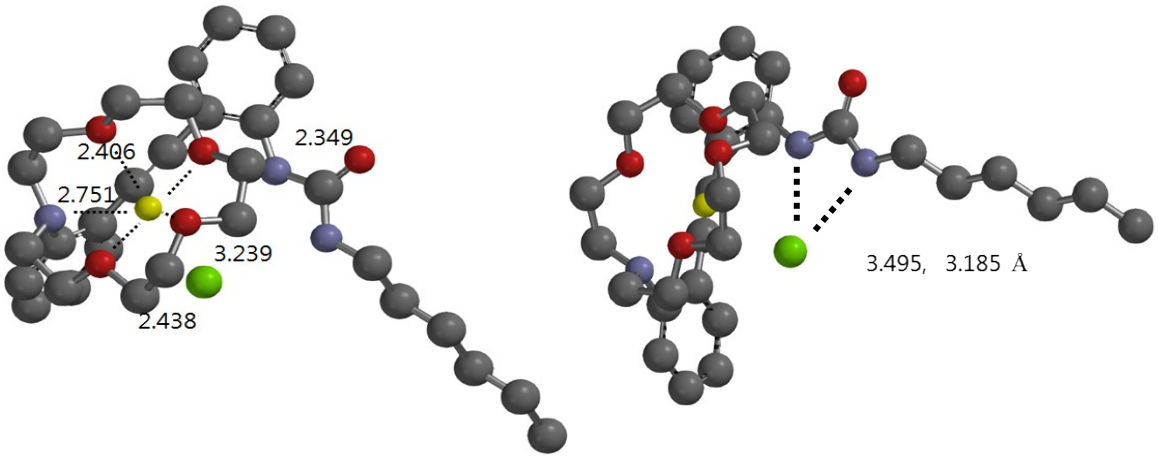


Figure S14. Optimized structures of **4**·NaCl based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

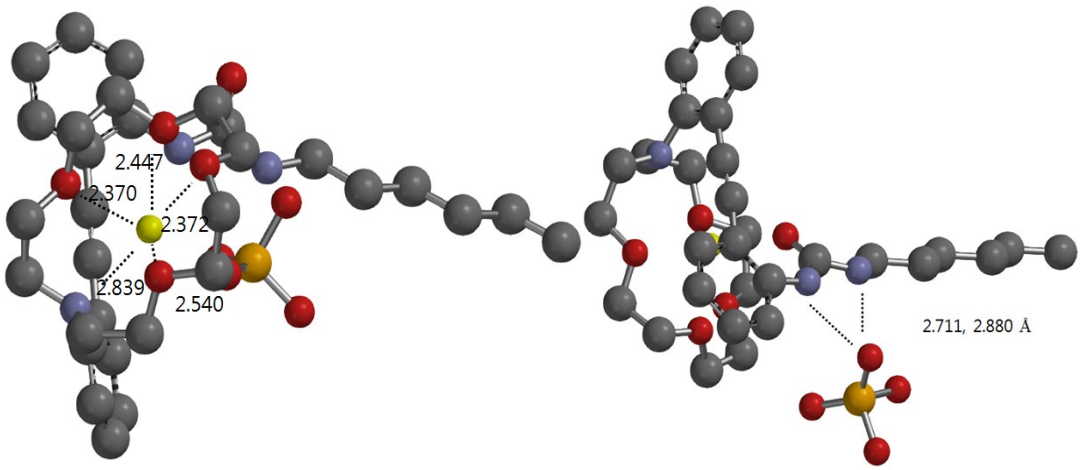


Figure S15. Optimized structures of **4**·H_2PO_4 based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

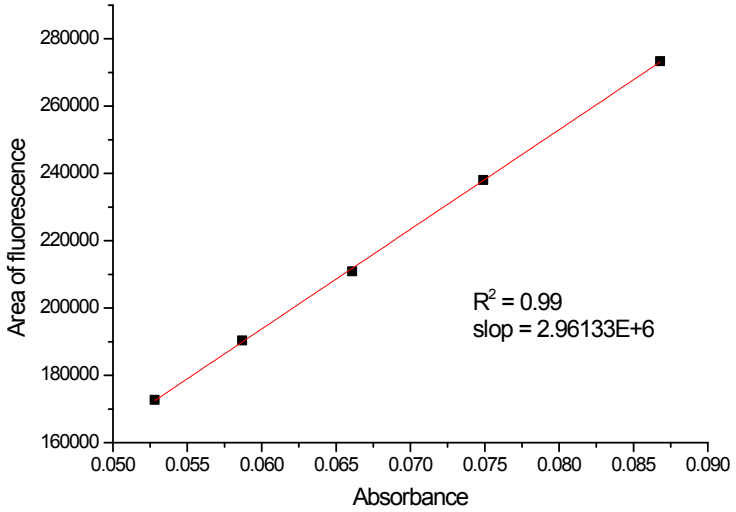
4. Quantum Yields

Table S1. Summarized slops and the relative quantum yields of **4** from those of coumarin 120.

	Slop in CH_2Cl_2	Slop in CH_3CN	Q* in CH_2Cl_2	Q* in CH_3CN
4	2.96133E+6	3.00872E+6	0.558 (56%)	0.392 (39%)
Coumarin 120	4.35014E+6	4.68023E+6	0.82 (82%)	0.61 (61%)

Q* denotes quantum yields.

a)



b)

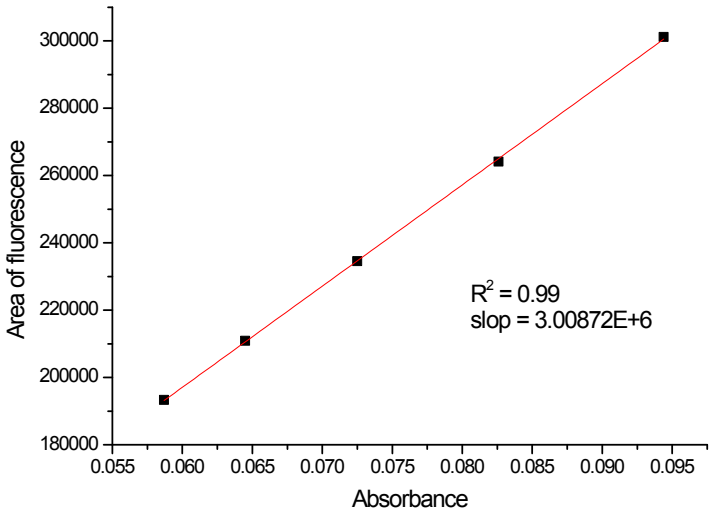
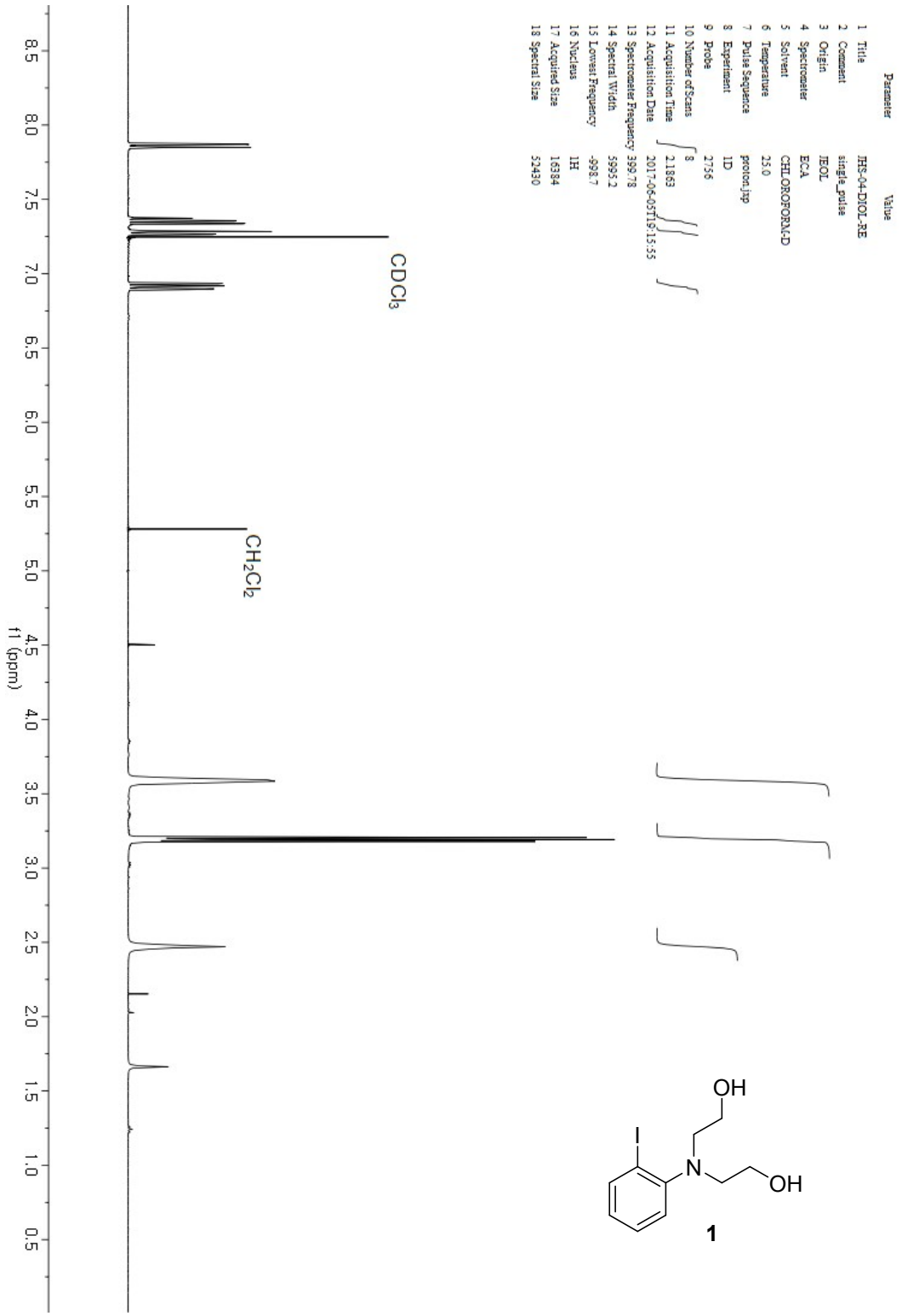
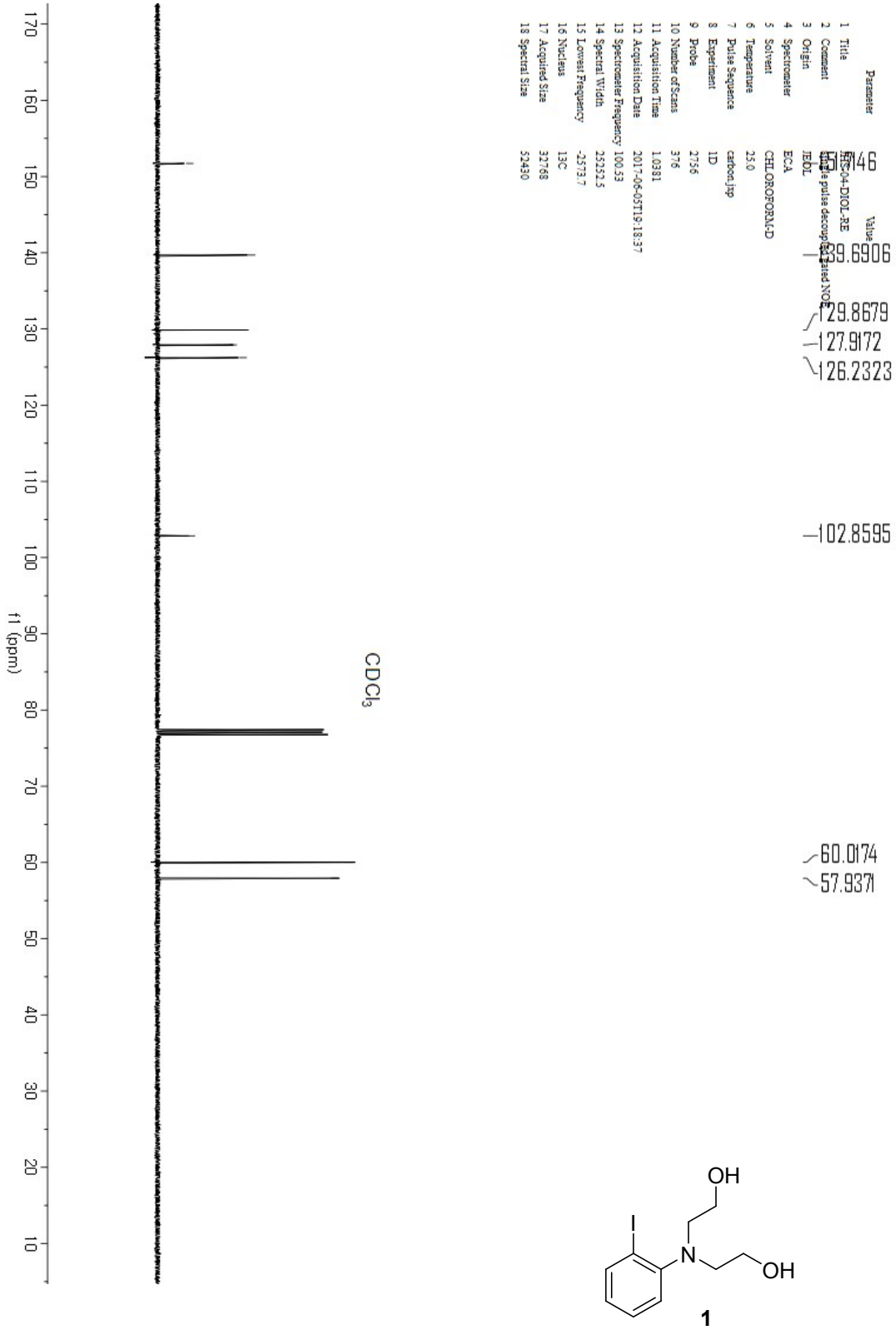


Figure S16. Plots of absorbance against the area under the fluorescence curve of **4**. a) In CH_2Cl_2. b) In CH_3CN.

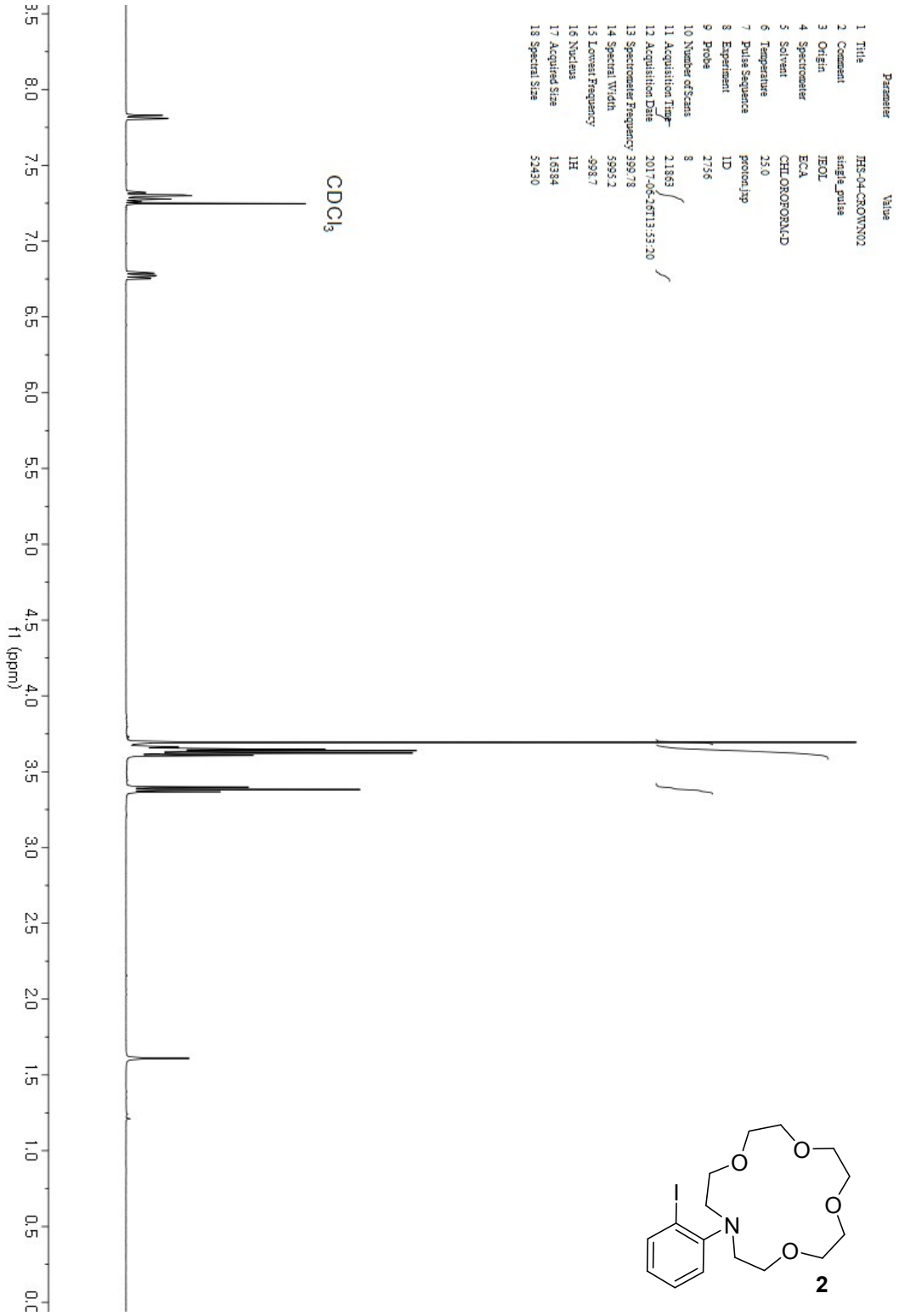
5. NMR Spectra



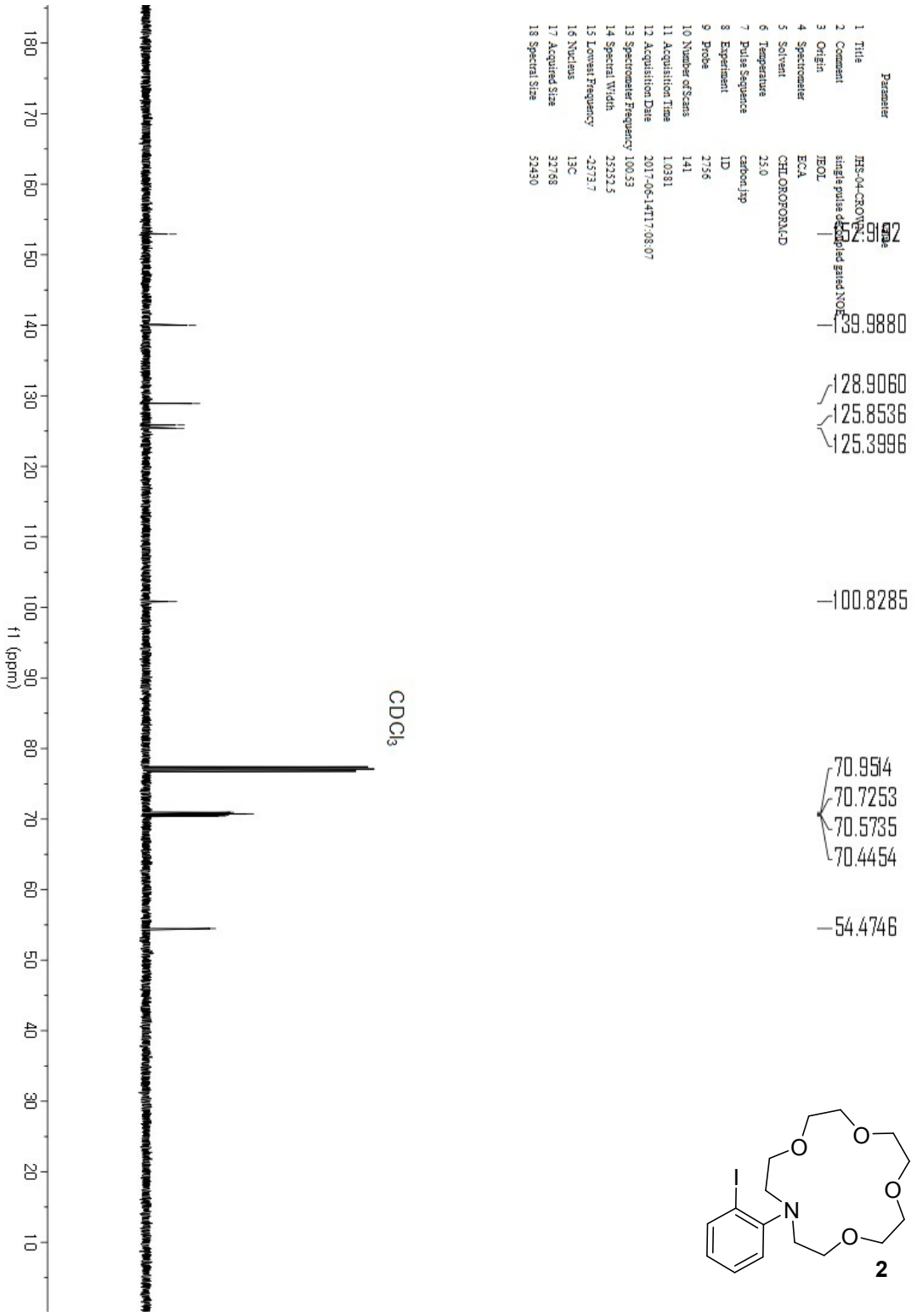
^{1}H NMR spectrum of **1** recorded in $CDCl_3$



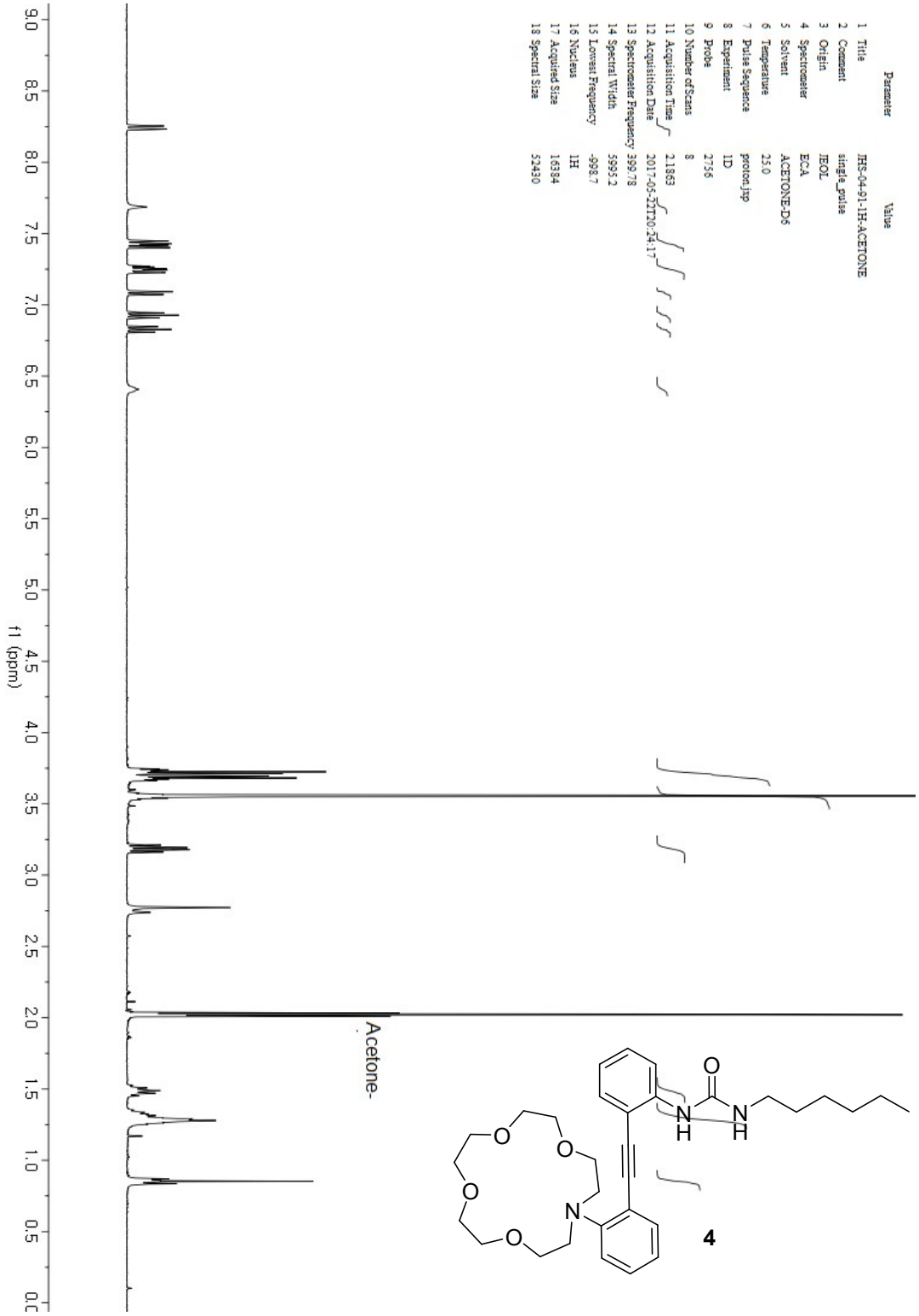
^{13}C NMR spectrum of **1** recorded in $CDCl_3$



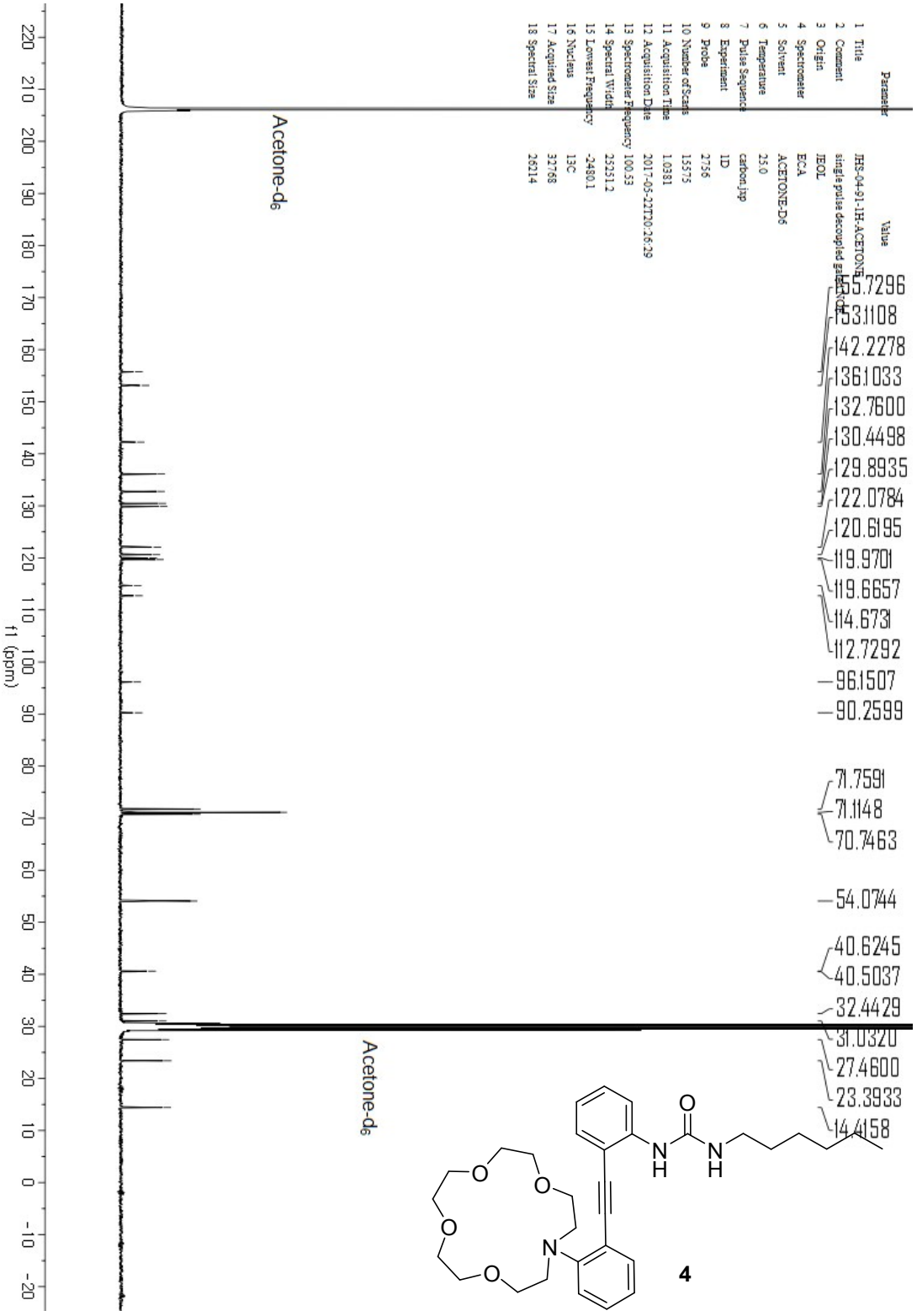
^{1}H NMR spectrum of **2** recorded in $CDCl_3$



^{13}C NMR spectrum of **2** recorded in $CDCl_3$



^{1}H NMR spectrum of **4** recorded in Acetone-d_6



^{13}C NMR spectrum of **4** recorded in Acetone-d_6