Supporting Information for

A novel chemodosimeter for fluoride ion based on depr otonation of the C-H group followed by autoxidative decyanation process

Jinju Chen, Chuanxiang Liu*, Jiali Zhang, Min Zhou and Fanhong Wu*

School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 201418 Shanghai, China

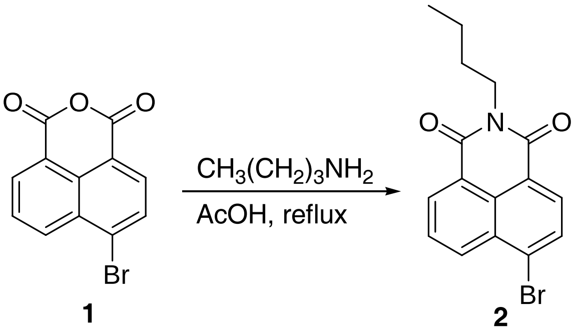
E-mail: cxliu@sit.edu.cn, wfh@sit.edu.cn

Contents of Supporting Information

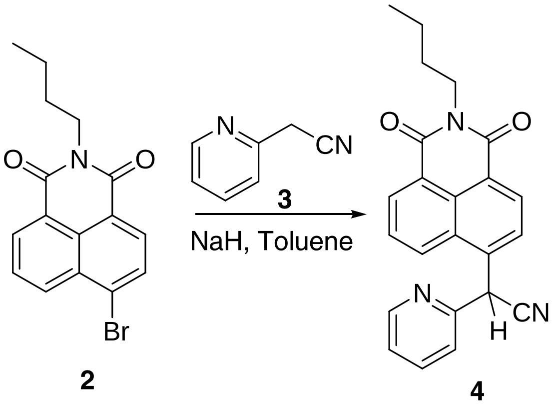
1. General methods.

All chemicals were obtained from commercial suppliers and used without further purification. Toluene were distilled from CaH_2 prior to use. Melting points were determined using melting point apparatus (WRS-2A) and uncorrected. Flash chromatography was carried out on silica gel (200 – 300 mesh). Analytical TLC was performed on Haiyang ready-to-use plates with silica gel 60 (F_{254}). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500 MHz (operating at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) in $CDCl_3$ with tetramethylsilane as internal standard. HRMS were recorded on solanX 70 FT-MS spectrometer with methanol and water (v/v=1:1) as solvent. IR were recorded on NICOLET 6700 FT-IR .UV-visible absorption spectra were determined on a SHIMADZU UV-1800 spectrophotometer. Fluorescence spectra were determined on a VARIAN CARY Eclipse Fluorescence spectrophotometer. Multiplicities of signals are described as follows: s --- singlet, br. s --- broad singlet, d --- doublet, t --- triplet, m --- multiplet. Coupling constants (*J*) are given in Hz.

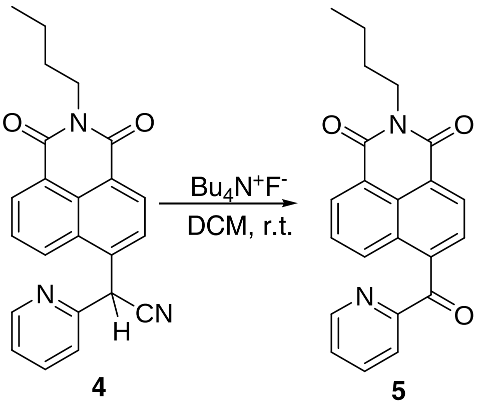
2. Synthesis and characterization of compounds 2, 4 and 5



4-Bromo-N-butyl-1,8-naphthalimide (2) was synthesized according to the literature reported procedure[1].



Synthesis of 2-(N-butyl-1,8-naphthalimide)-2-(pyridin-2-yl)acetonitrile (4)[2]: Sodium hydride (60 w% in oil, 0.65 g, 16.30 mmol) was added to a solution of 2-cyanomethylpyridine (**3**, 0.50 g, 4.20 mmol) under N_2 in toluene (30 mL), and the mixture was stirred at room temperature for 1h. After adding compound **2** (1.00g, 3.00 mmol), the mixture was refluxed under N_2 for 3 h . After cooling at room temperature, the reaction mixture was added with 15% hydrochloric acid until PH = 2~3 , then extraction with ethyl acetate (20 ml × 3), then the organic layer was washed with brine , dried with Na_2SO_4 and filtered. After concentration of solvent, the residue was purified via chromatography with silica gel (PE : EA = 15 : 1) to afford the target **4** (0.45 g, 66%) as a red-violet solid. mp 140.7-140.8 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.5, 1H), 8.54 (d, *J* = 6.5 Hz, 2H), 8.39 (d, *J* = 8.5 Hz, 1H), 7.98(d, *J* = 7.5 Hz, 1H), 7.70 (dd, *J* = 8.5,7.5, Hz, 1H), 7.62 (td, *J* = 8.0 ,1.5Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 7.5, 5.5 Hz, 1H), 6.01 (s, 1H), 4.10 (t, *J* = 7.5 Hz, 2H), 1.63 (m, 2H), 1.37 (m, 2H), 0.90 (t, *J* = 7.0Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.81, 163.50, 154.25, 150.15, 137.80, 136.99, 131.38, 130.86, 129.62, 129.01, 128.90, 127.81, 127.52, 123.72, 123.62, 123.58, 122.30, 118.13, 43.43, 40.36, 30.17, 20.35, 13.79; IR (neat): ν_{max} = 2961, 2933, 2874, 2245 (-C≡N), 1760, 1692, 1651, 1615, 1585, 1473, 1438, 1388, 1370, 1350, 1233, 1084, 953, 863, 784, 767, 760, 749, 695 cm^{-1}; HRMS-ESI (m/z): $[M + H]^+$ Calcd. for ($C_{23}H_{19}N_3O_2$), 370.15555, Found:370.15634.



Synthesis of N-butyl-1,8-naphthalimide-1-yl(pyridin-2-yl)methanone (5): The mixture of compound **4** (0.04 g, 0.18 mmol) and tetrabutylammonium fluoride (2.00 g, 7.70 mmol) in dichloromethane was stirred at room temperature. After the completion of reaction, the reaction liquid was evaporated to dryness under reduced pressure. The residue was purified by chromatography with silica gel (PE : EA = 10 : 1) to afford the target **5** (0.035 g , 90 %). mp 116.6-116.8℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (m, 3H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.93 (td, *J* = 8.0, 2.0 Hz, 1H), 7.85 (t, *J* = 7.5, Hz, 1H), 7.68 (dd, *J* =8.5,7.5 Hz, 1H), 7.48 (ddd, *J* = 6.0, 4.5, 1.0 Hz, 1H), 4.14 (t, *J* = 7.5 Hz, 2H), 1.66 (m, 2H), 1.39 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.66, 164.02, 163.67, 154.13, 149.34, 140.84, 137.31, 131.86, 131.40, 129.64, 129.57, 128.89, 128.50, 127.81, 127.41, 124.71, 124.36, 122.95, 40.37, 30.20, 20.37, 13.83; IR (neat): ν_{max} = 2955, 2924, 2853, 1697, 1678, 1657, 1616, 1593, 1578, 1439, 1438, 1407, 1370, 1355, 1329, 1233, 1086, 859, 781, 760, 749, 712, 689 cm^{-1}; HRMS-ESI (m/z): $[M + H]^+$ Calcd. for ($C_{22}H_{18}N_2O_3$), 359.13957, Found:359.14028.

Reference:

(1) L. Song, Y. Yang, Q. Zhang, H. Tian and W. Zhu, *J. Phys. Chem. B*, 2011, **115**, 14648.

(2) (a) Y. Kubota, T. Tsuzuki, K. Funabiki, M. Ebihara and M. Matsui, *Org. Lett.* 2010, **12**, 4010; (b) G. R. Newkome, Y. J. Joo, D. W. Evans, S. Pappalardo and F. R. Fronczek, *J. Org. Chem.* 1988, **53**, 786.

3. ^{1}H-NMR spectrum of the compound 2.

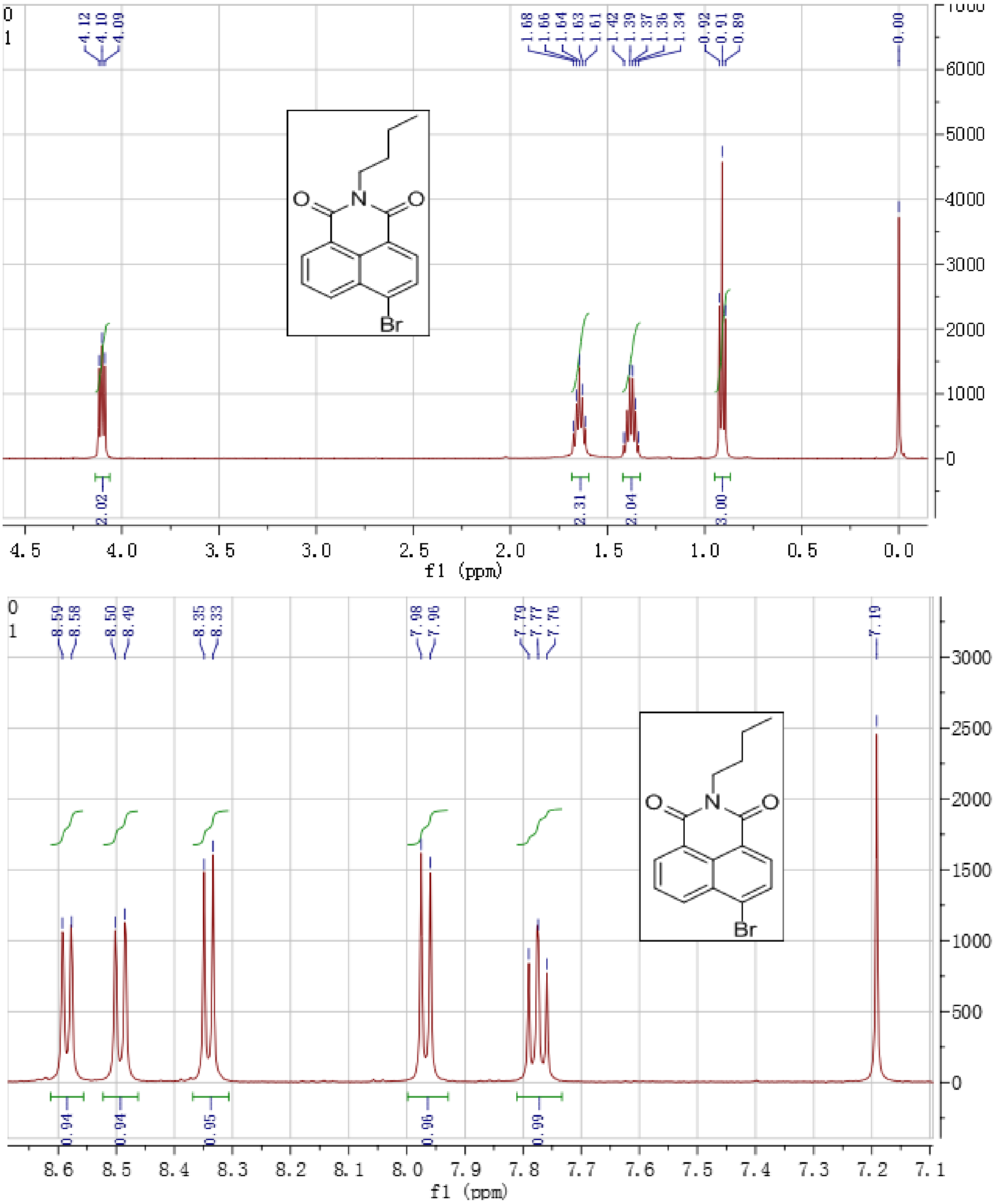


Figure S1. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of compound **2**

4. ^{1}H-NMR, ^{13}C-NMR, IR and HRMS-ESI spectrum of the compound 4.

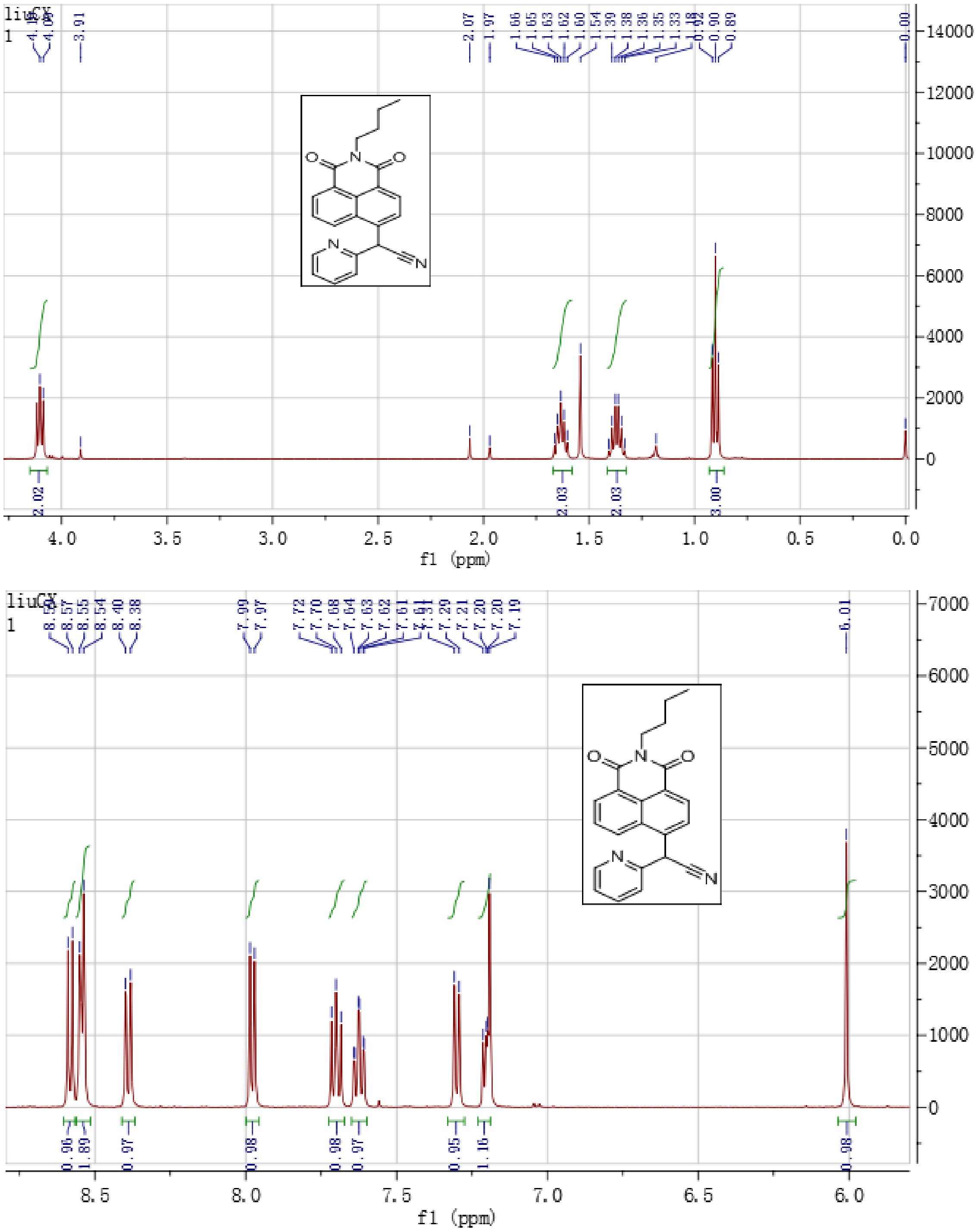


Figure S2. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of compound **4**

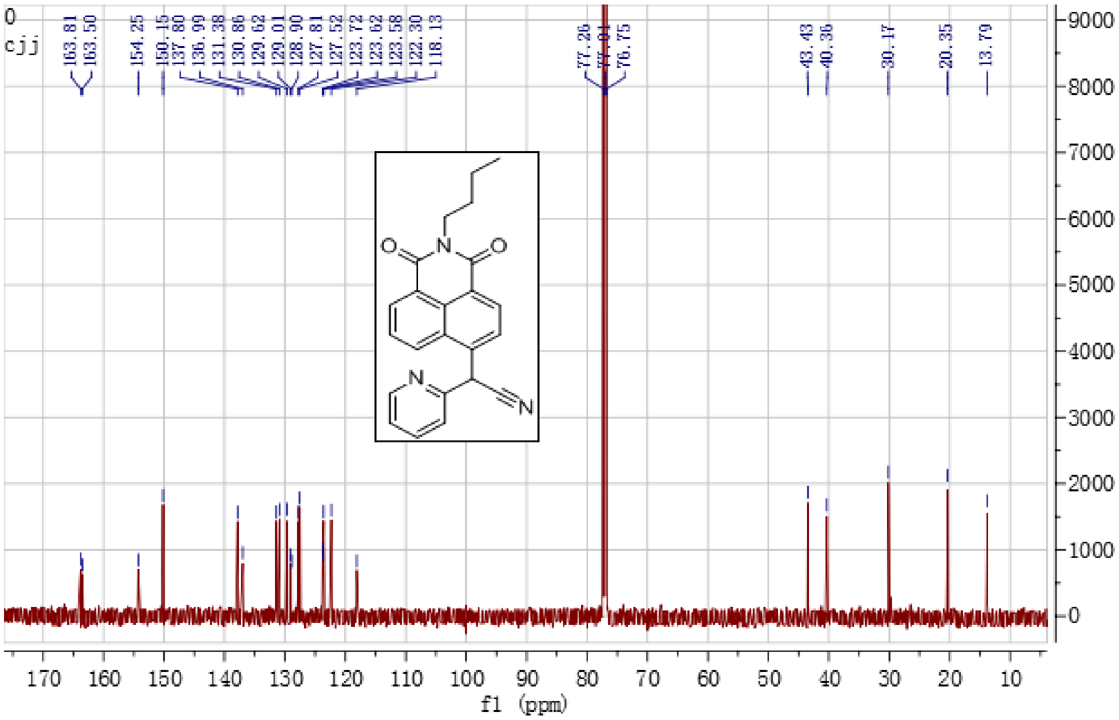


Figure S3. ^{13}C-NMR (CDCl$_3$, 125 MHz) spectrum of compound **4**

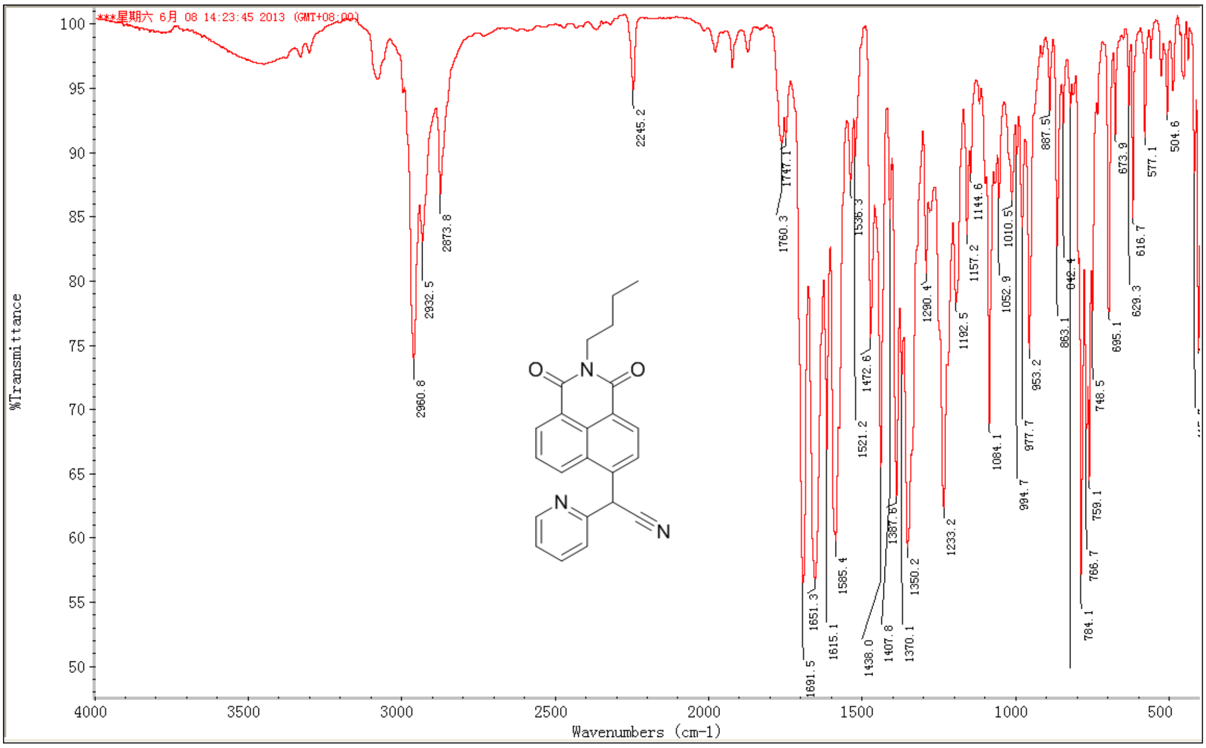
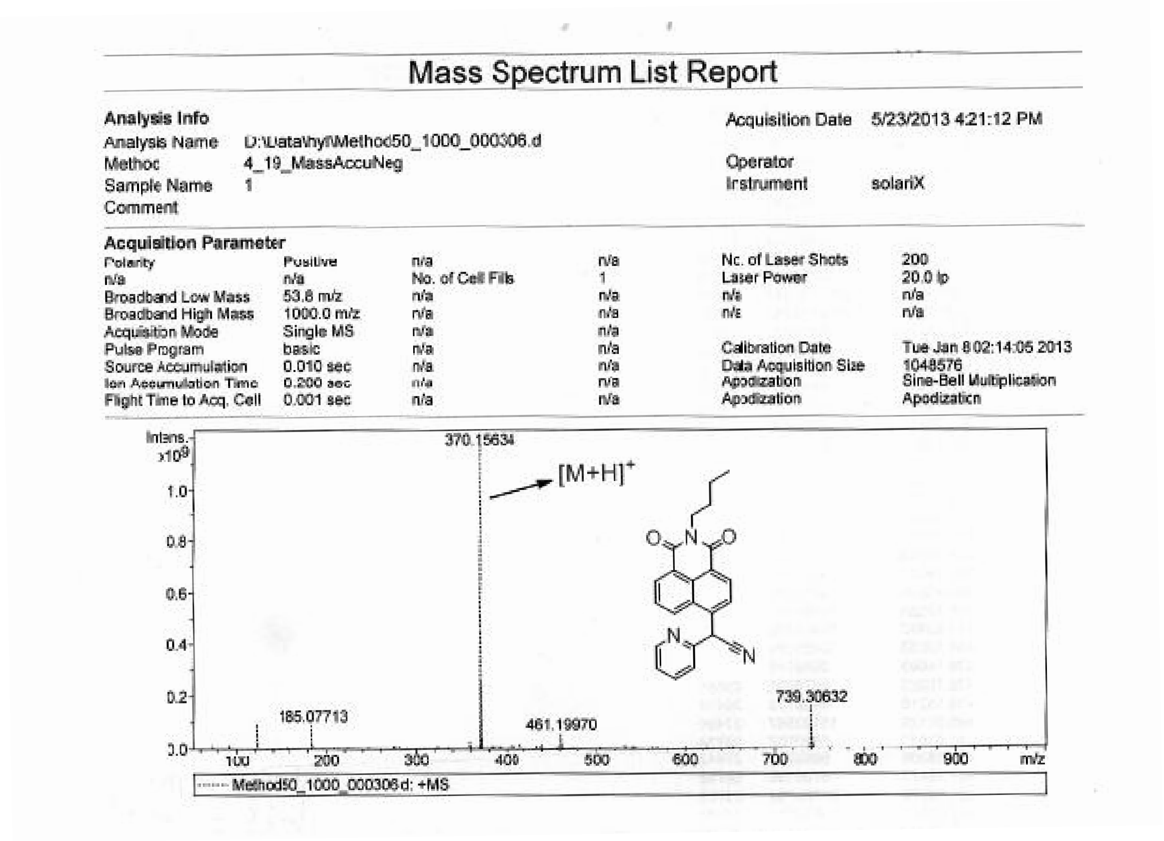


Figure S4. IR spectrum of compound **4**



Mass Spectrum List Report

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Comment		Irstrument	solariX

Acquisition Parameter

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n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
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Broadband High Mass	1000.0 m/z	n/a	n/a	n/a	n/a
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Pulse Program	basic	n/a	n/a	Calibration Date	Tue Jan 8 02:14:05 2013
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Flight Time to Acq. Cell	0.001 sec	n/a	n/a	Apodization	Apodization

Figure S5. HRMS-ESI mass spectrum of compound **4**

5. ^{1}H-NMR, ^{13}C-NMR, IR and HRMS-ESI spectrum of the compound 5.

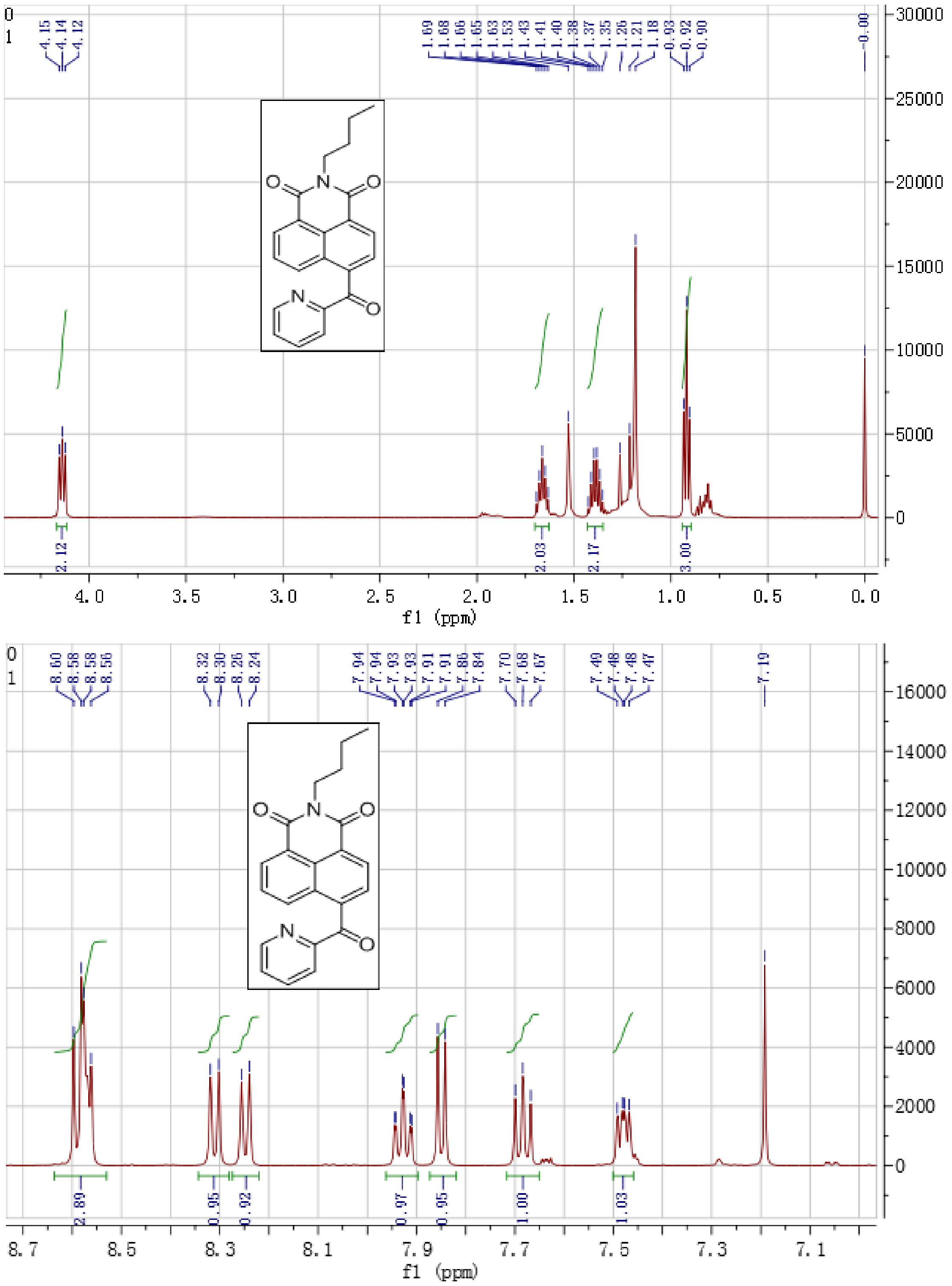


Figure S6. ^{1}H-NMR(CDCl$_3$, 500 MHz) spectrum of compound **5**

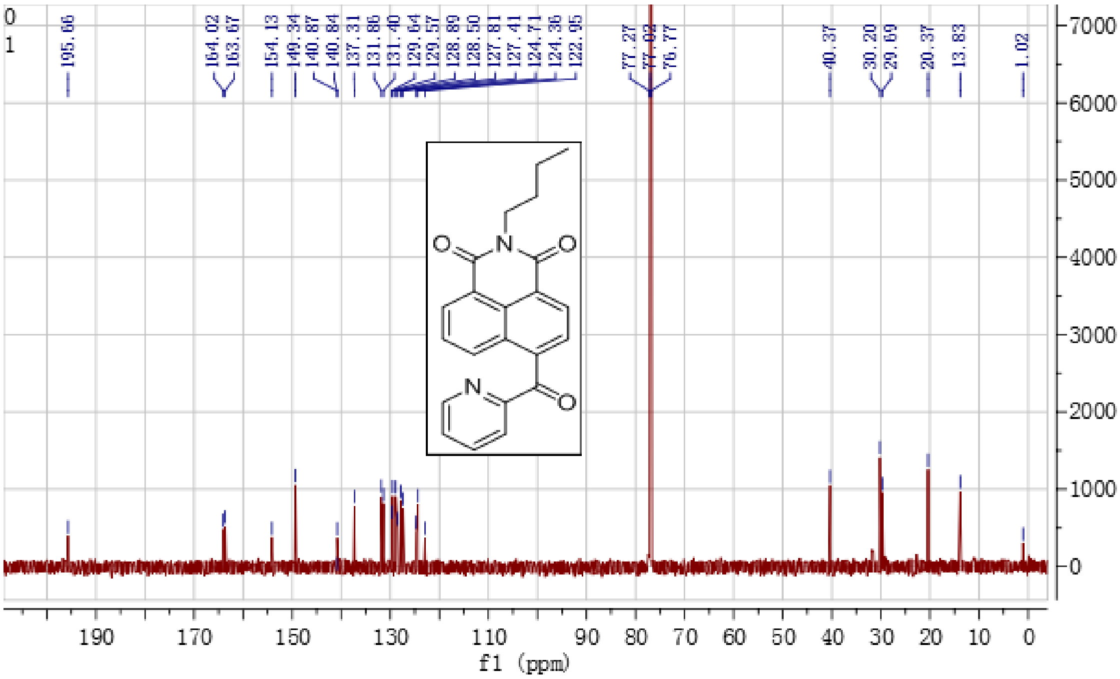


Figure S7. ^{13}C-NMR (CDCl$_3$, 125 MHz) spectrum of compound **5**

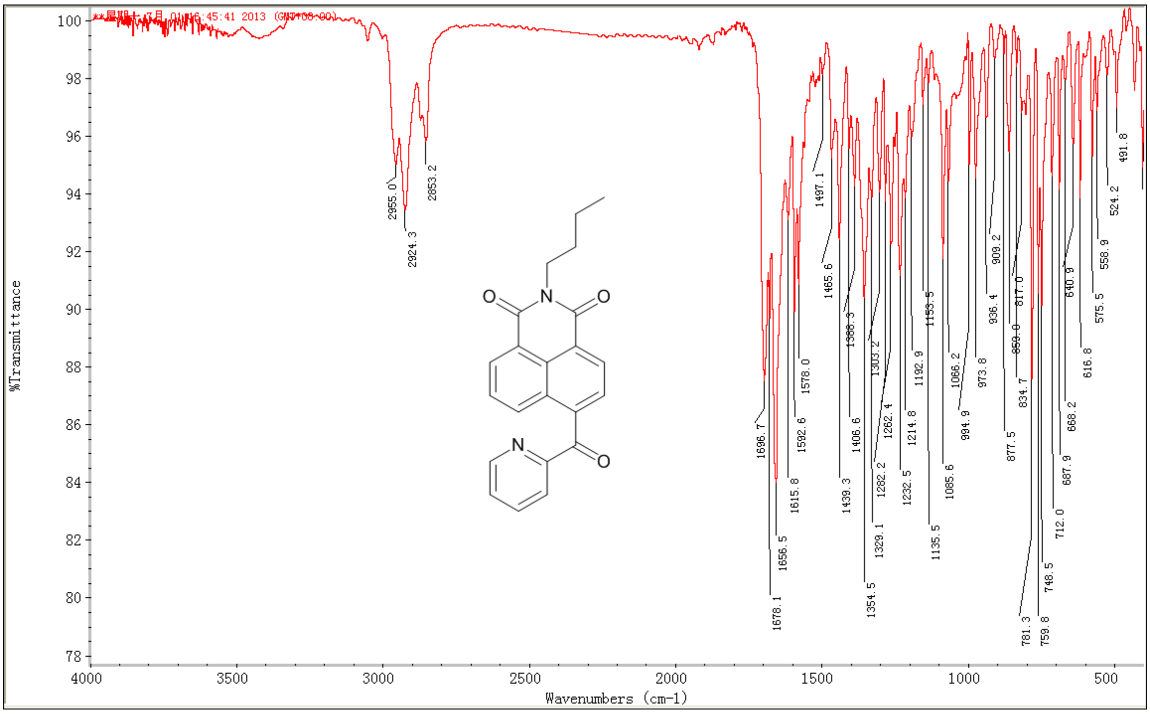
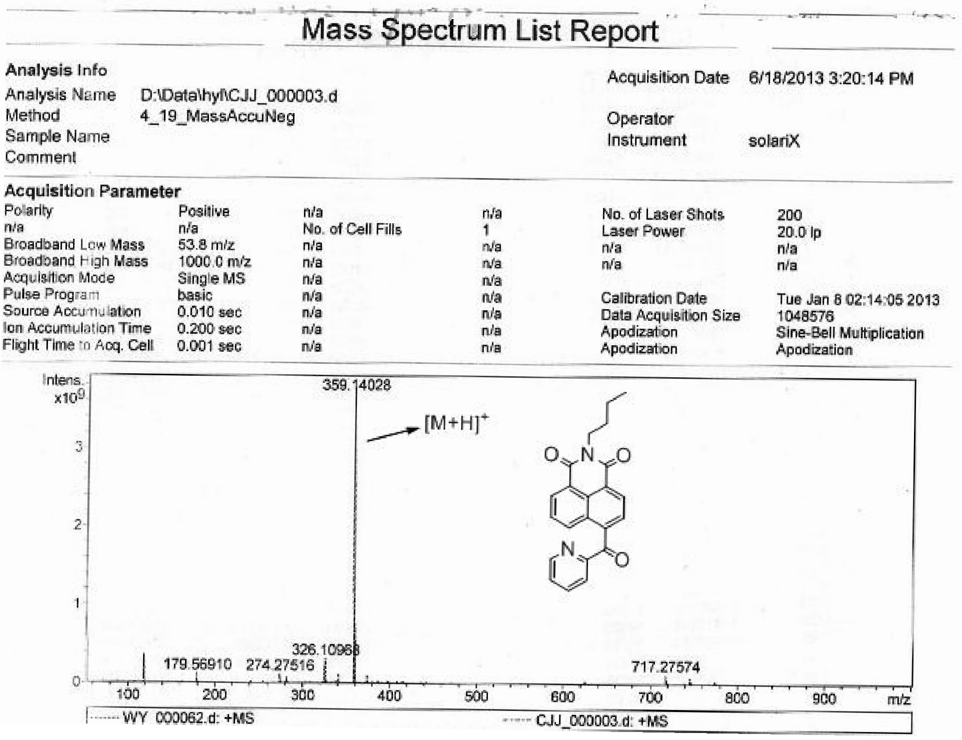


Figure S8. IR spectrum of compound **5**



Mass Spectrum List Report

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Sample Name
Comment

Acquisition Date 6/18/2013 3:20:14 PM

Operator
Instrument solariX

Acquisition Parameter

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n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	53.8 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1000.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Tue Jan 8 02:14:05 2013
Source Accumulation	0.010 sec	n/a	n/a	Data Acquisition Size	1048576
Ion Accumulation Time	0.200 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec	n/a	n/a	Apodization	Apodization

Figure S9. HRMS-ESI mass spectrum of compound **5**

6.UV-visible titration of compound 4 with AcO$^-$ in CH_3CN.

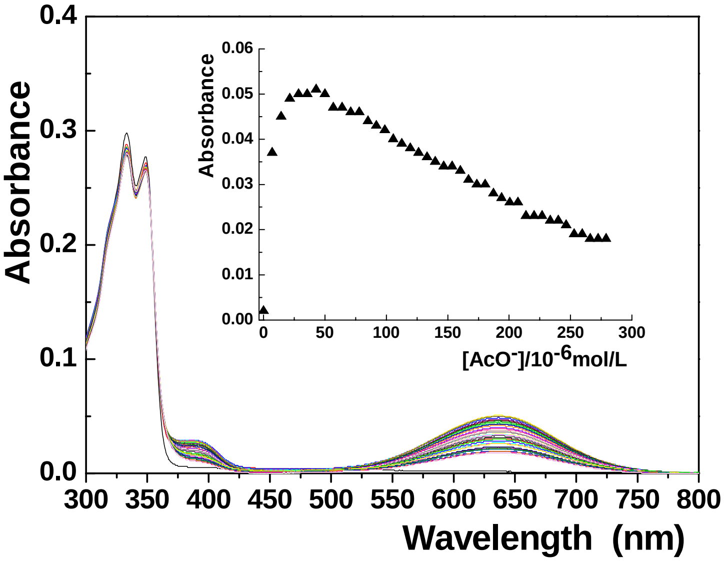


Figure S10. UV-visible titration of **4** (20 μM) with $Bu_4N^+AcO^-$ in CH_3CN. The inset shows the absorbance at 637 nm as a function of [AcO$^-$].

7. UV-visible titration of compound 4 with $H_2PO_4^-$ in CH_3CN

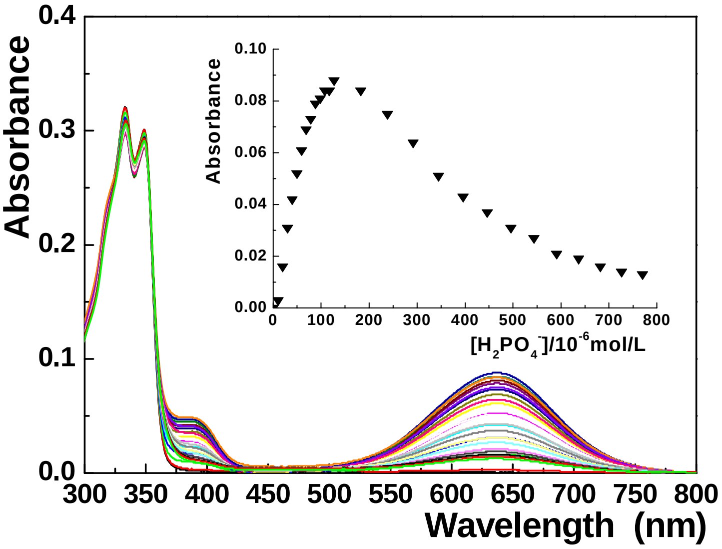


Figure S11. UV-visible titration of **4** (20 μM) with $Bu_4N^+H_2PO_4^-$ in CH_3CN. The inset shows the absorbance at 637 nm as a function of $[H_2PO_4^-]$.

8.The absorbance detection limit of the 4 with F^- in CH_3CN.

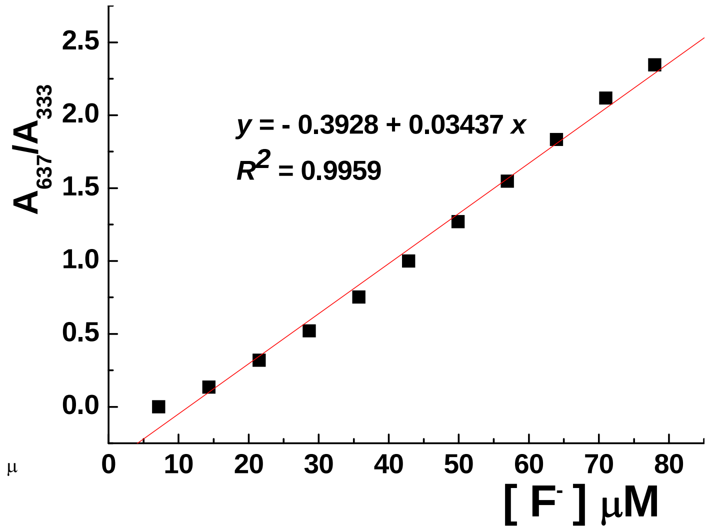


Figure S12. Absorbance intensity ratio (A637/A333) of dosimeter **4** (20 μM) as a function of F^- concentration from 0- 80 *μ*M (0 – 4.0 equivalents),

Equation	Y = A + B * X	
Parameter	Value	Error
A	- 0.3928	0.05011
B	0.03437	0.00104
R	SD	N
0.99591	0.07712	11

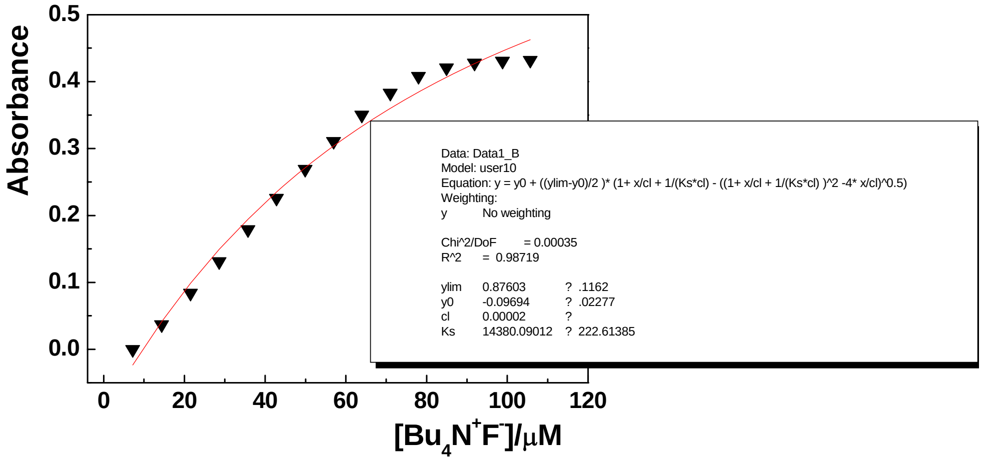
The result of the analysis as follows:

Linear Equation: Y = - 0.3928 + 0.03437 * X, R = 0.9959

S= 3.437 * 10^4 , K = 3, δ = 0.07712

LOD = K *δ / S = 6.73 μM

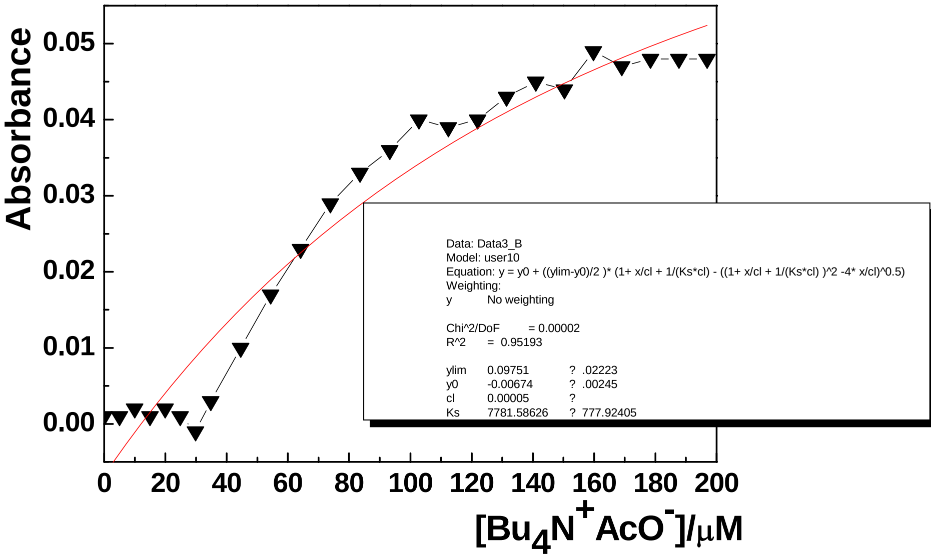
9. The standard 1:1 curve-fitting procedures for binding constants of F^- , AcO^- and $H_2PO_4^-$



```
Data: Data1_B
Model: user10
Equation: y = y0 + ((ylim-y0)/2 )* (1+ x/cl + 1/(Ks*cl) - ((1+ x/cl + 1/(Ks*cl) )^2 -4* x/cl)^0.5)
Weighting:
y          No weighting

Chi^2/DoF       = 0.00035
R^2      =  0.98719

ylim     0.87603          ?  .1162
y0       -0.09694         ?  .02277
cl       0.00002          ?
Ks       14380.09012   ?  222.61385
```



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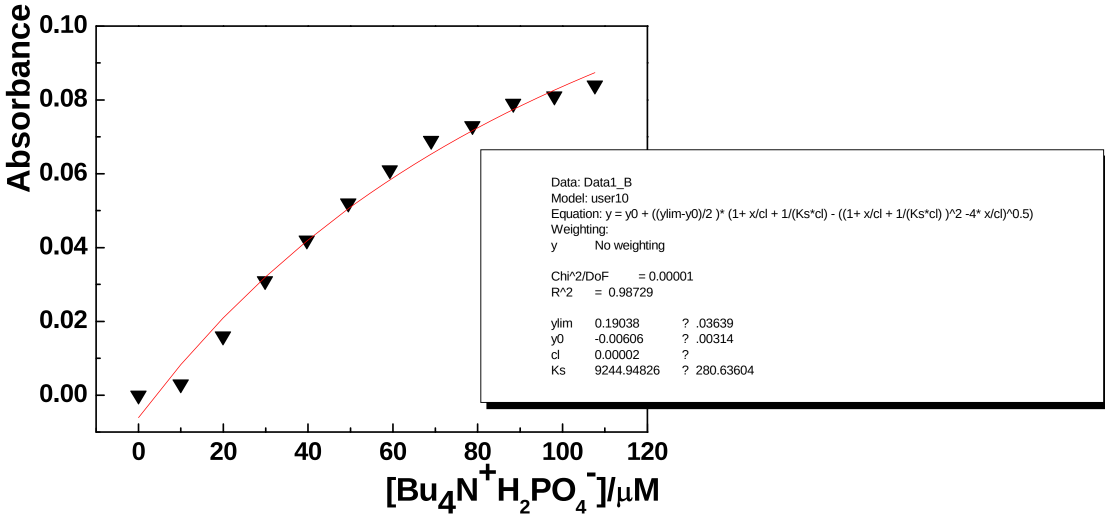
Data: Data3_B
Model: user10
Equation: y = y0 + ((ylim-y0)/2 )* (1+ x/cl + 1/(Ks*cl) - ((1+ x/cl + 1/(Ks*cl) )^2 -4* x/cl)^0.5)
Weighting:
y          No weighting

Chi^2/DoF       = 0.00002
R^2      =  0.95193

ylim     0.09751          ?  .02223
y0       -0.00674         ?  .00245
cl       0.00005          ?
Ks       7781.58626     ?  777.92405
```



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Data: Data1_B
Model: user10
Equation: y = y0 + ((ylim-y0)/2 )* (1+ x/cl + 1/(Ks*cl) - ((1+ x/cl + 1/(Ks*cl) )^2 -4* x/cl)^0.5)
Weighting:
y          No weighting

Chi^2/DoF       = 0.00001
R^2      =  0.98729

ylim     0.19038          ?  .03639
y0       -0.00606         ?  .00314
cl       0.00002          ?
Ks       9244.94826     ?  280.63604
```

Figure S13. The binding constants for F^- (top), AcO^- (middle) and $H_2PO_4^-$ (bottom) using the standard 1:1 curve-fitting procedures

10. Time-dependence UV-visible spectra of compound 4 with F^-

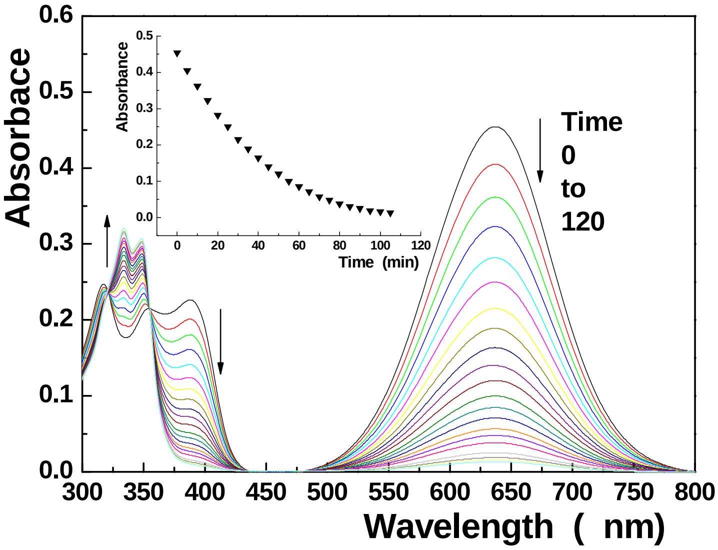


Figure S14. Time-dependence UV-visible spectra of **4** (20 μM) with F^- (5.4 equiv.) Inset: plot of A_{637} vs time.

11. UV-visible titration of compound 4 with F$^-$ in CH_3CN

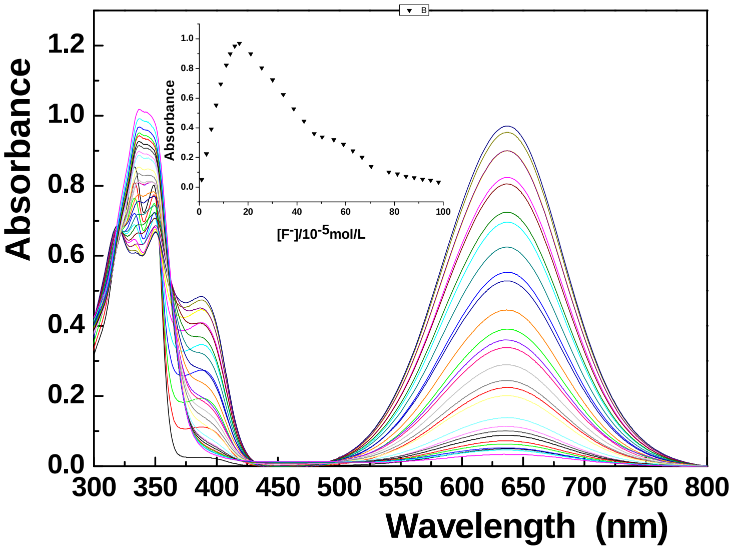


Figure S15. UV-visible titration of **4** (50 μM) with $Bu_4N^+F^-$ in CH_3CN. The inset shows the absorbance at 637 nm as a function of [F$^-$].

12. The final state of compound 4 with F$^-$ and the UV-visible spectrum of compound 5

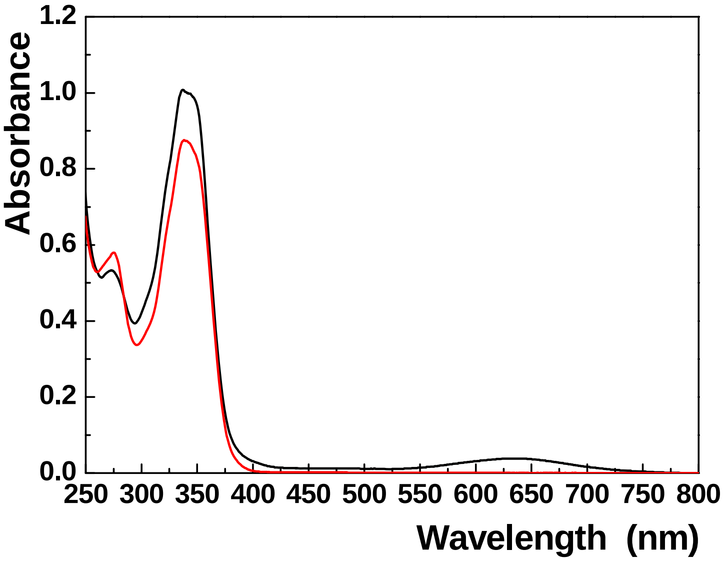


Figure S16 . The final state of **4** (50 μM, black) with $Bu_4N^+F^-$ (20 equiv.) and the UV-visible spectrum of **5**（50 μM , red）

13. UV-vis titration of compound 4 with OH^- in CH_3CN

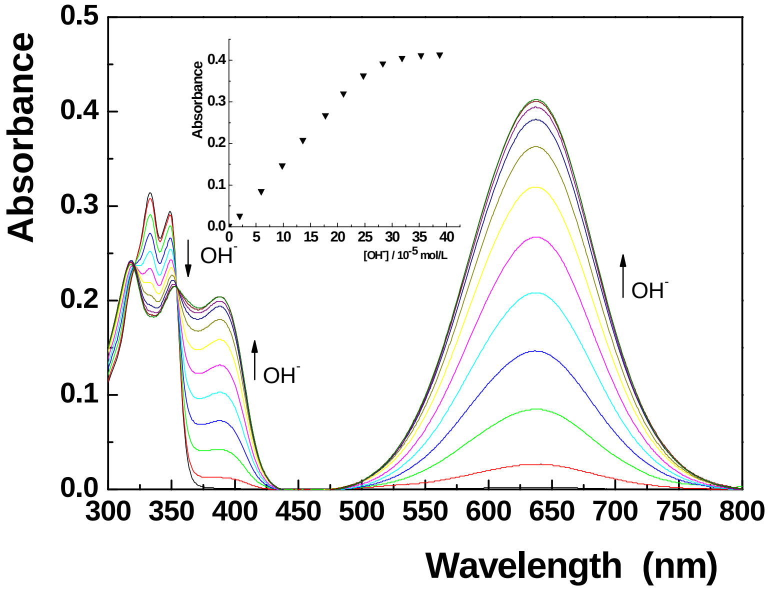


Figure S17. UV-visible titration of **4** (20 μM) with $Bu_4N^+OH^-$ (25% aq.) in CH_3CN. Arrows show changes due to increasing concentration of OH^-(500 μM). The inset shows the absorbance at 637 nm as a function of $[OH^-]$.

14. UV-visible titration of compound 4 with F⁻ in mixture of solvent

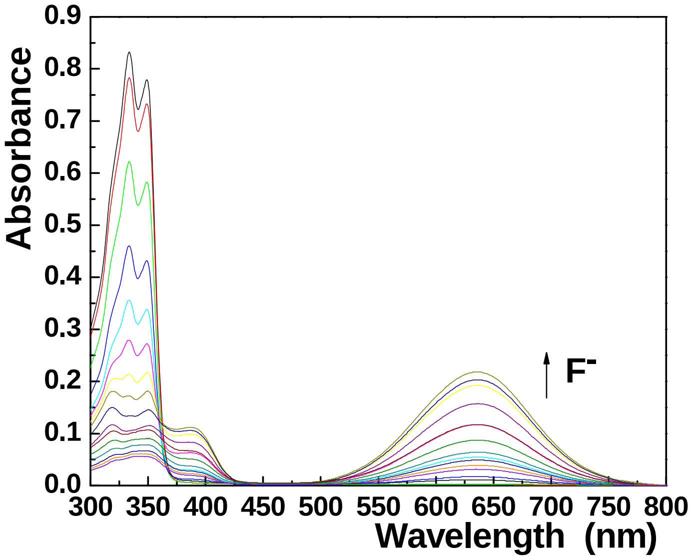
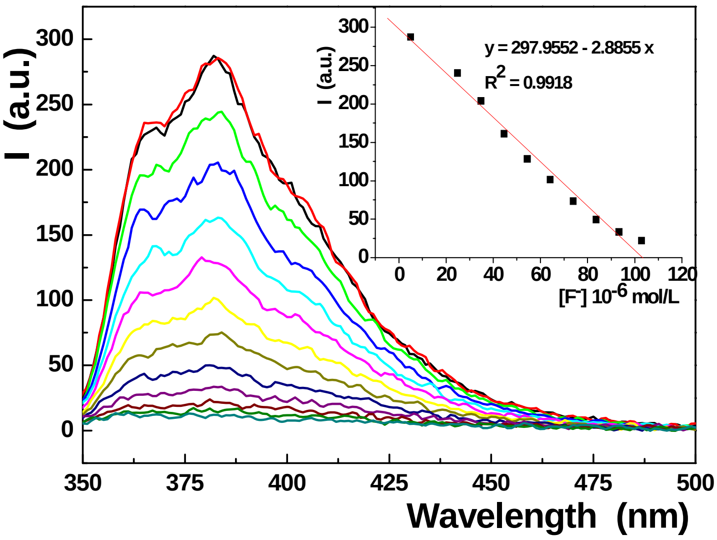


Figure S18. UV-visible titration of **4** (50 μM) with $Bu_4N^+F^-$ in mixture of solvent (CH_3CN: Water = 95: 5). Arrows show changes due to increasing concentration of F^- (0-108 equiv).

15. Fluorescence titrations of compound 4 with with F$^-$ in CH$_3$CN



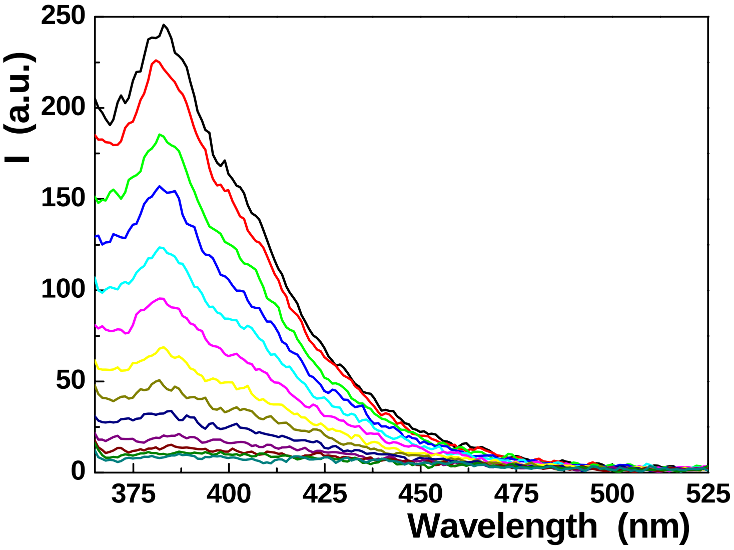
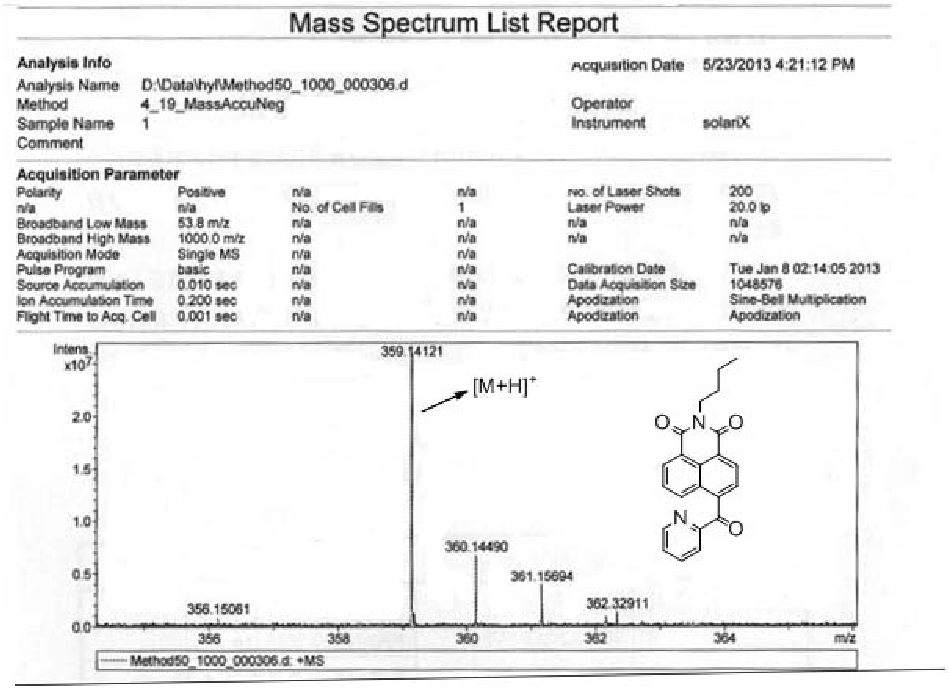


Figure S19. Emission spectra of **4** (20 μM, λ_{ex} = 322 nm (top), λ_{ex} = 353 nm (bottom), in CH$_3$CN) upon addition of increasing concentrations of F$^-$ (as its TBA salt, 0 to 5.0 equiv). Inset: Plot of emission intensity (λ_{em} = 382 nm) versus TBAF concentration.

16. HRMS-ESI mass spectrum after the ^{1}H-NMR titration of compound 4 with F^- in $CDCl_3$



Mass Spectrum List Report

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Comment

Acquisition Date 5/23/2013 4:21:12 PM
Operator
Instrument solariX

Acquisition Parameter

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n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
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Broadband High Mass	1000.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Tue Jan 8 02:14:05 2013
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Ion Accumulation Time	0.200 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec	n/a	n/a	Apodization	Apodization

Figure S20. HRMS-ESI mass spectrum after the ^{1}H-NMR titration of compound **4** with 2.75 equiv. of F^- (as its TBA salt) in $CDCl_3$.