SUPPORTING INFORMATION

Pyridine-Hydrazone-Controlled Cyanide Detection in Aqueous Media and Solid-State: Tuning the Excited-State Intramolecular Proton Transfer (ESIPT) Fluorescence Modulated by Intramolecular NH···Br Hydrogen Bonding

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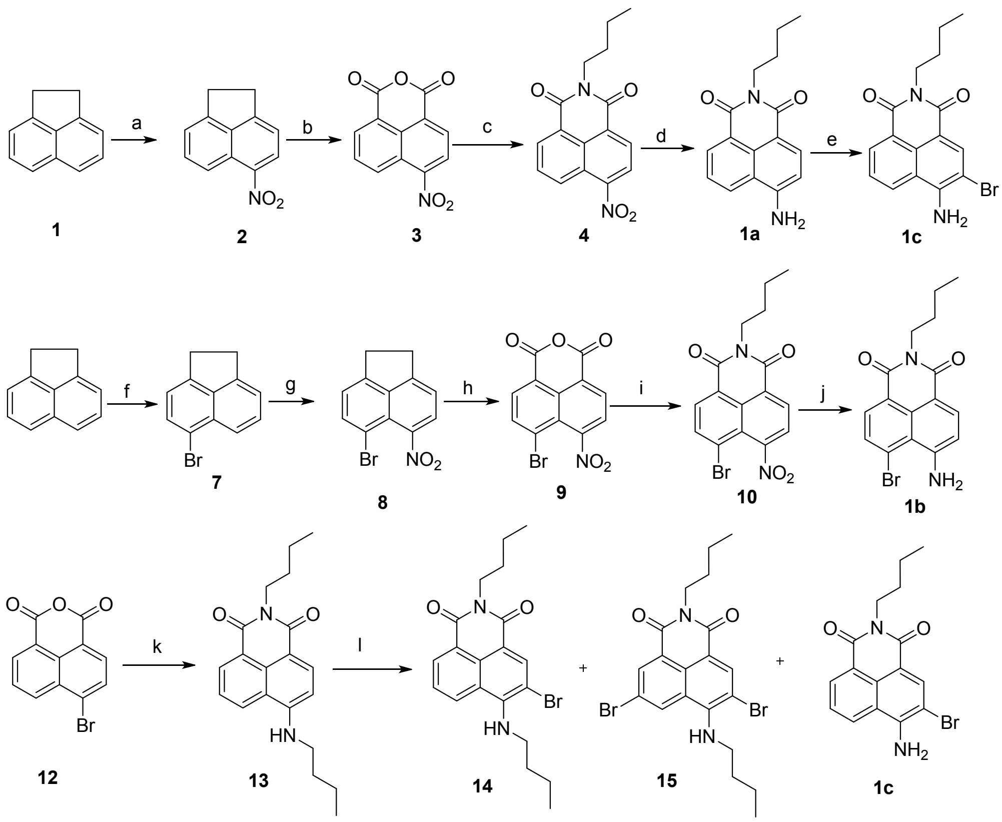
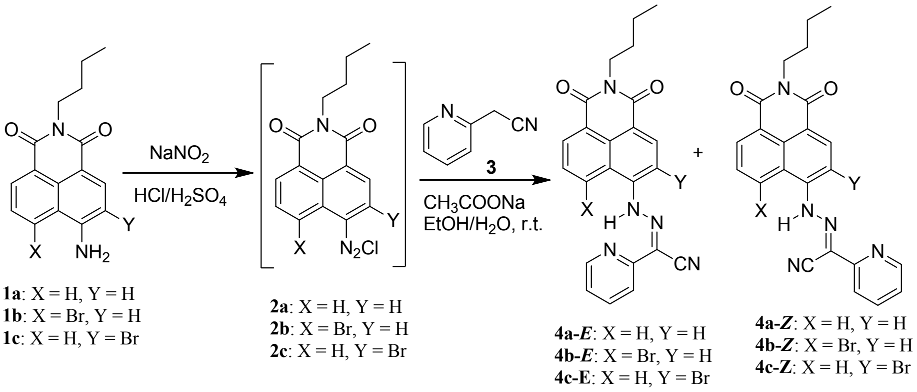
General methods

Unless otherwise noted, solvents and reagents were analytical grade and used without further purification. THF were distilled from Na prior to use. Flash chromatography was carried out on silica gel (200–300 mesh). UV-visible absorption spectra were obtained on a SHIMADZU UV-1800 spectrophotometer. Fluorescence emission spectra were obtained on a Edinburgh Instruments FS5 Fluorescence spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for ^{1}H-NMR) and ^{13}C-NMR spectra were recorded on Bruker AVANCE III 500 MHz (125 MHz for ^{13}C-NMR), and chemical shifts were reported in parts per million (ppm, δ) downfield from internal standard Me_4Si (TMS). Multiplicities of signals are described as follows: s --- singlet, d --- doublet, dd --- doublet d, t --- triplet, m --- multiplet. HRMS were recorded on solanX 70 FT-MS spectrometer with methanol and water (v/v = 1:1) as solvent.

Synthesis of compounds



Synthesis of the intermediates: (a) DCM/HNO_3, rt, 90.1%; (b) $K_2Cr_2O_7$/AcOH, reflux, 66.3%; (c) $C_4H_9NH_2$ /AcOH, reflux, 67.1%; (d) Pa/C, H_2, r.t, 95.2%; (e) Br_2, ice bath, 90.5%; (f) NBS, DMF, r.t, 80.3%; (g) fuming HNO_3/AcOH, ice bath, 53.1%; (h) $K_2Cr_2O_7$/AcOH, reflux, 58.8% (i) $C_4H_9NH_2$ /AcOH, reflux, 77.6%; (j) $SnCl_2$/AcOH, r.t, 94.1%; (k) $C_4H_9NH_2$ /EtOH, reflux, 79.6%; (l) Br_2, ice bath, **14** (50.1%), **15** (29.6), **1c** (8.6%).



Scheme S1 Synthesis of the probe **4**

Synthetic procedures

6-amino-2-butyl-1H-benzo[*de*]isoquinoline-1,3(2H)-dione (1a) was synthesized according to the literature reported procedure

6-amino-7-bromo-2-butyl-1H-benzo[*de*]isoquinoline-1,3(2H)-dione (1b) was synthesized according to the literature reported procedure

Synthesis of **4a-*E***, **4a-*Z*** and **4b-*E*** is according to the literature reported procedure

General procedure: The compound **1 (1a** and **1b)** was added to a mixture of 2 mL HCl (or H_2SO_4) and 3 mL of ice cold water. The solution was stirred at 0 ºC for 30 min. Sodium nitrite (1.0 equiv.) was dissolved in 1 mL of water maintaining a similar cold temperature. The sodium nitrite solution was then slowly added to the solution of **1** over a period of 1 hour. In a separate round bottomed flask compound 2-cyanomethylpyridine (1.1 equiv.) and sodium acetate (6.0 equiv.) was stirred in ethanol/water (9 ml/3 ml) solution for 1 hour at 0 ºC. The diazotized solution was then added drop-wise to the cooled (0 ºC) solution containing the 2-cyanomethylpyridine salt. After the addition was completed, the resulting reaction mixture was stirred at room temperature 3h. The precipitated product was collected by filtration and thoroughly washed with cold water. The crude product was purified by column chromatography (DCM/PE) to give the hydrazone **4** (**4a-*E***, **4a-*Z***, **4b-*E*** and **4c-*Z***) as a yellow solid.

(*E*)-N'-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[*de*]isoquinolin-6-yl)picolinohydrazonoyl cyanide (**4a-*E***)

This compound was prepared from coupling of **1a** with 2-cyanomethylpyridine.

Yield (42.05%).^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm]: 16.16 (s, 1H), 8.87 (d, J = 4.5 Hz, 1H), 8.64 (d, J = 7.0 Hz, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.5 Hz, 1H), 8.06 (td, J_1 = 1 Hz, J_2 = 7.5 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.53 (m, 1H), 4.18 (t, J = 8.0 Hz, 2H), 1.73 (m, 2H), 1.46 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 164.19, 163.74, 151.50, 147.68, 142.92, 138.65, 133.07, 133.00, 131.38, 129.35, 126.69, 125.94, 124.42, 123.58, 120.46, 117.25, 116.67, 116.36, 110.30, 40.35, 30.38, 20.55, 13.98. HRMS (ESI): $[M + H]^+$ calcd for $C_{23}H_{19}N_5O_2$: 398.1617; found 398.1627.

(*Z*)-N'-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[*de*]isoquinolin-6-yl)picolinohydrazonoyl cyanide (**4a-*Z***)

This compound was prepared from coupling of **1a** with 2-cyanomethylpyridine.

Yield (45.95%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm]: 9.75 (s, 1H), 8.73 (d, J = 4.5 Hz, 1H), 8.69 (d, J = 7.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.84 (m, 2H), 7.38 (m, 1H), 4.18 (t, J = 8.0 Hz, 2H), 1.73 (m, 2H), 1.46 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ [ppm]: 164.07, 163.72, 150.40, 149.97, 141.36, 137.06, 132.75, 131.75, 129.35, 126.99, 124.92, 124.65, 123.71, 122.89, 122.11, 119.71, 117.35, 110.96, 110.68, 40.39, 30.35, 20.53, 13.97. HRMS (ESI): $[M + H]^+$ calcd for $C_{23}H_{19}N_5O_2$: 398.1617; found 398.1645.

(*E*)-N'-(7-bromo-2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[*de*]isoquinolin-6-yl)picolinohydr-azonoyl cyanide (**4b-*E***)

This compound was prepared from coupling of **1b** with 2-cyanomethylpyridine.

Yield (69.92%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm]: 15.94 (s, 1H), 8.69 (d, J = 4.5 Hz, 1H), 8.64 (d, J = 8.5 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.99 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.47 (m, 1H), 4.15 (t, J = 7.5 Hz, 2H), 1.72 (m, 2H), 1.45 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 163.74, 163.30, 150.41, 147.84, 143.95, 138.42, 133.62, 133.34, 131.68, 131.37, 124.51, 123.40, 122.97, 119.95, 117.84, 117.63, 116.55, 115.02, 40.48, 30.25, 20.51, 13.94. HRMS (ESI): $[M + H]^+$ calcd for $C_{23}H_{18}BrN_5O_2$: 478.0702; found 478.0704.

(*Z*)-N'-(5-bromo-2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)picolinohydraz-onoyl cyanide

This compound was prepared from coupling of **1c** with 2-cyanomethylpyridine.

Yield (78.28%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm]: 10.03 (s, 1H), 9.23 (d, J = 8.5 Hz, 1H), 8.75 (d, J = 4.0 Hz, 1H), 8.682 (d, J = 7.0 Hz, 1H), 8.61 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.84 (m, 2H), 7.39 (m, 1H), 4.18 (t, J = 7.5 Hz, 1H), 1.72 (m, 2H), 1.46 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.76, 162.62, 150.30, 150.16, 137.69, 137.20, 132.18, 131.92, 130.82, 128.75, 127.60, 124.69, 123.29, 123.24, 122.61, 119.46, 118.86, 110.09, 40.53, 30.26, 20.48, 13.96, 0.12. HRMS (ESI): $[M + H]^+$ calcd for $C_{23}H_{18}BrN_5O_2$: 476.0722; found 476.0715.

The theoretical DFT calculations of compounds **4a-4c**

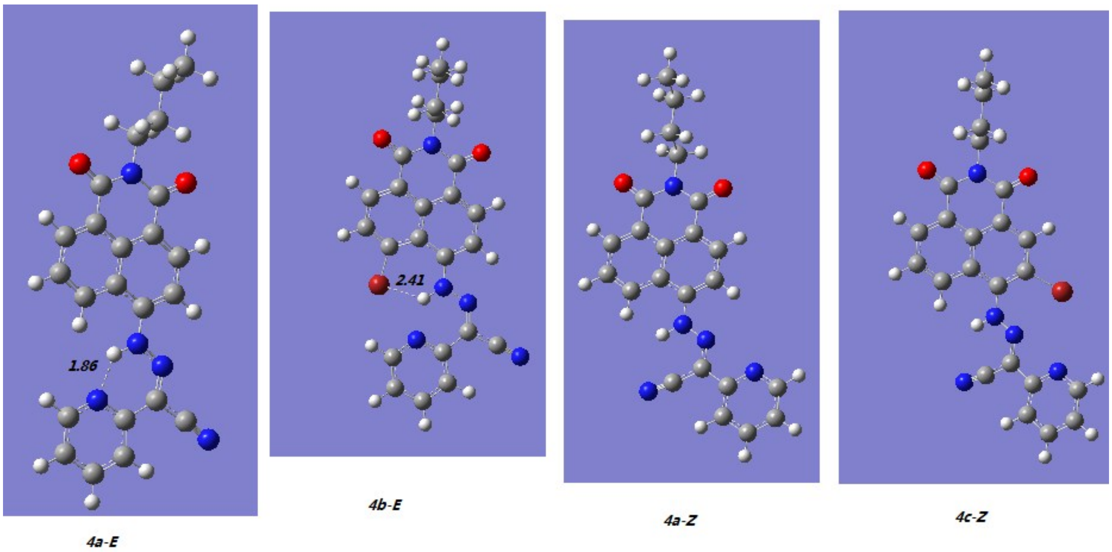


Fig. S1 the theoretical DFT calculations of compounds **4a-4c**

NMR and HRMS spectra of compound **4a-c**

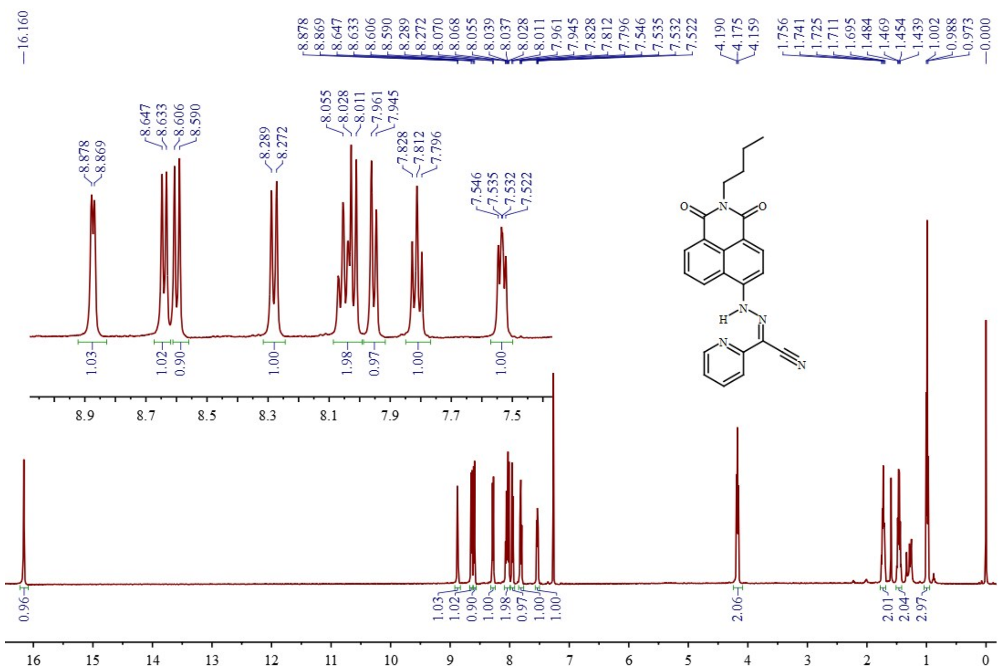


Fig. S2 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **4a-*E***

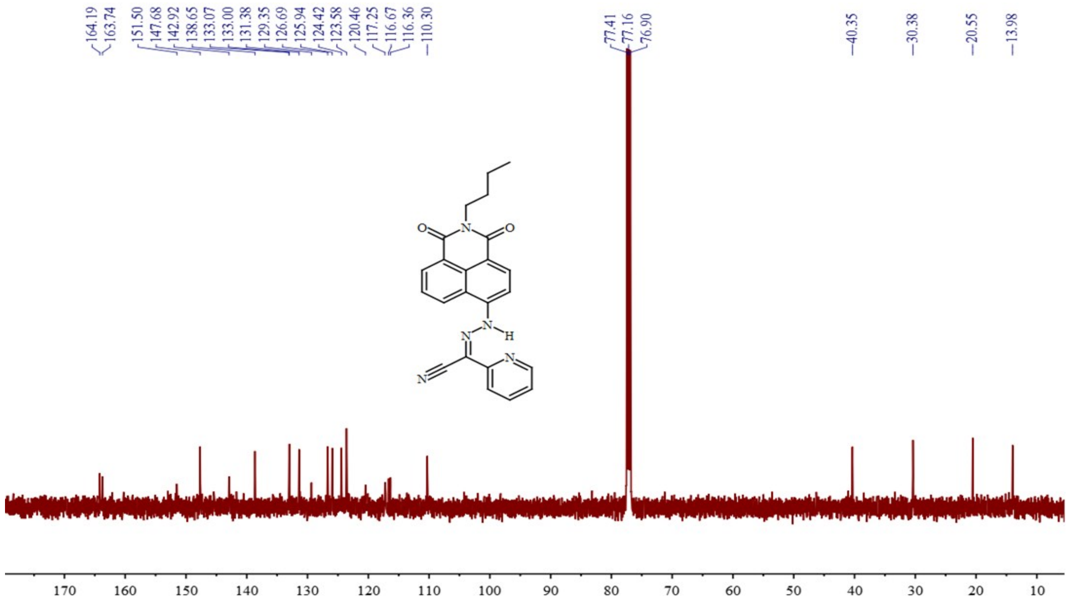


Fig. S3 ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound **4a-*E***

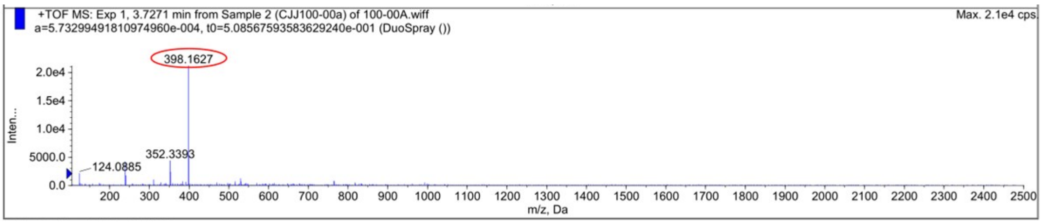


Fig. S4 HRMS-ESI mass spectra of compound **4a-*E***

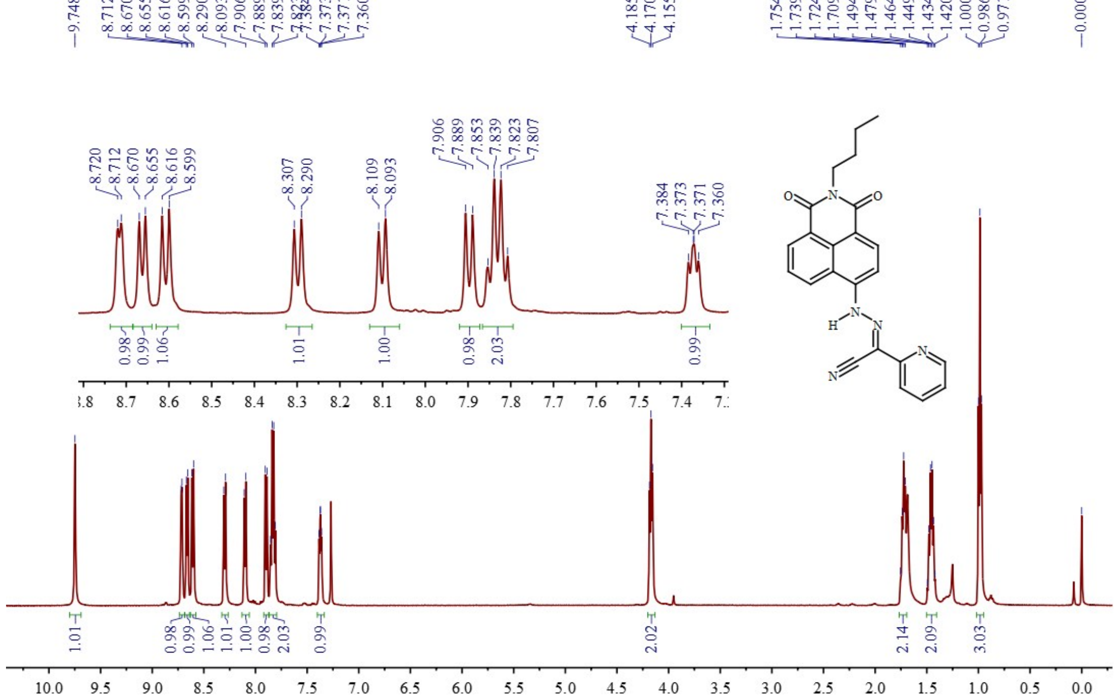


Fig. S5 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **4a-*Z***.

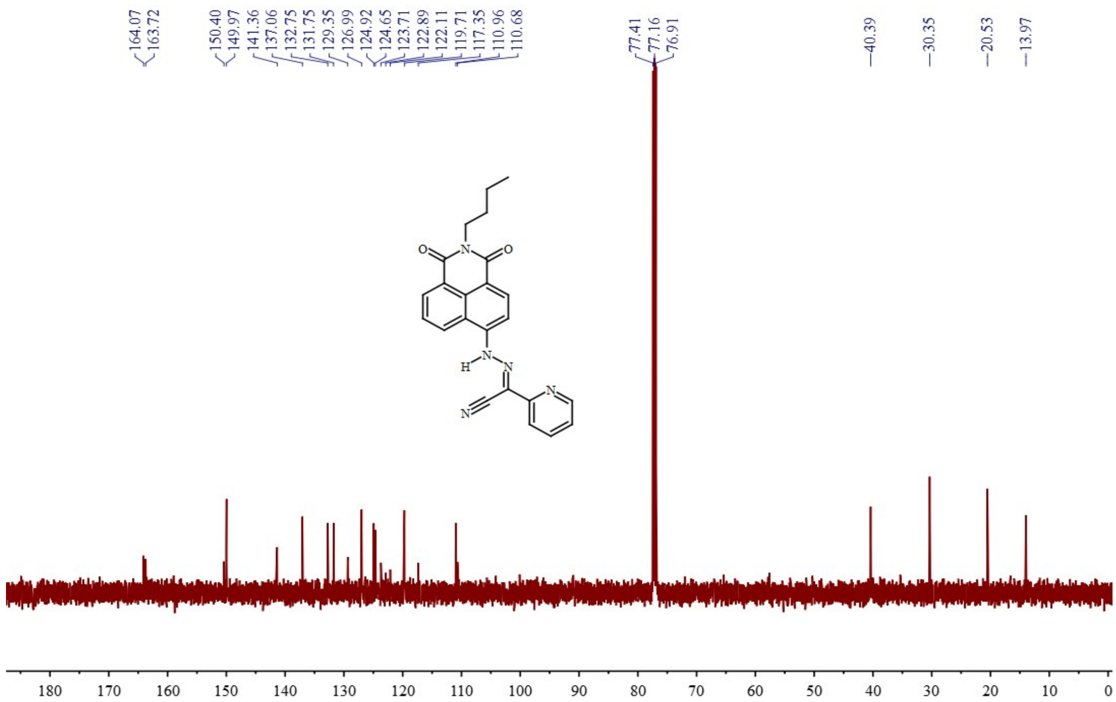


Fig. S6 ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound **4a-*Z***.

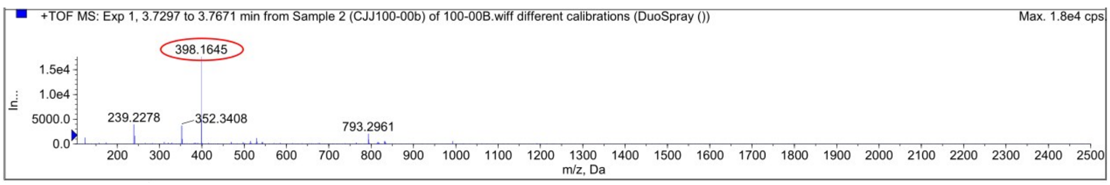


Fig. S7 HRMS-ESI mass spectra of compound **4a-*Z***.

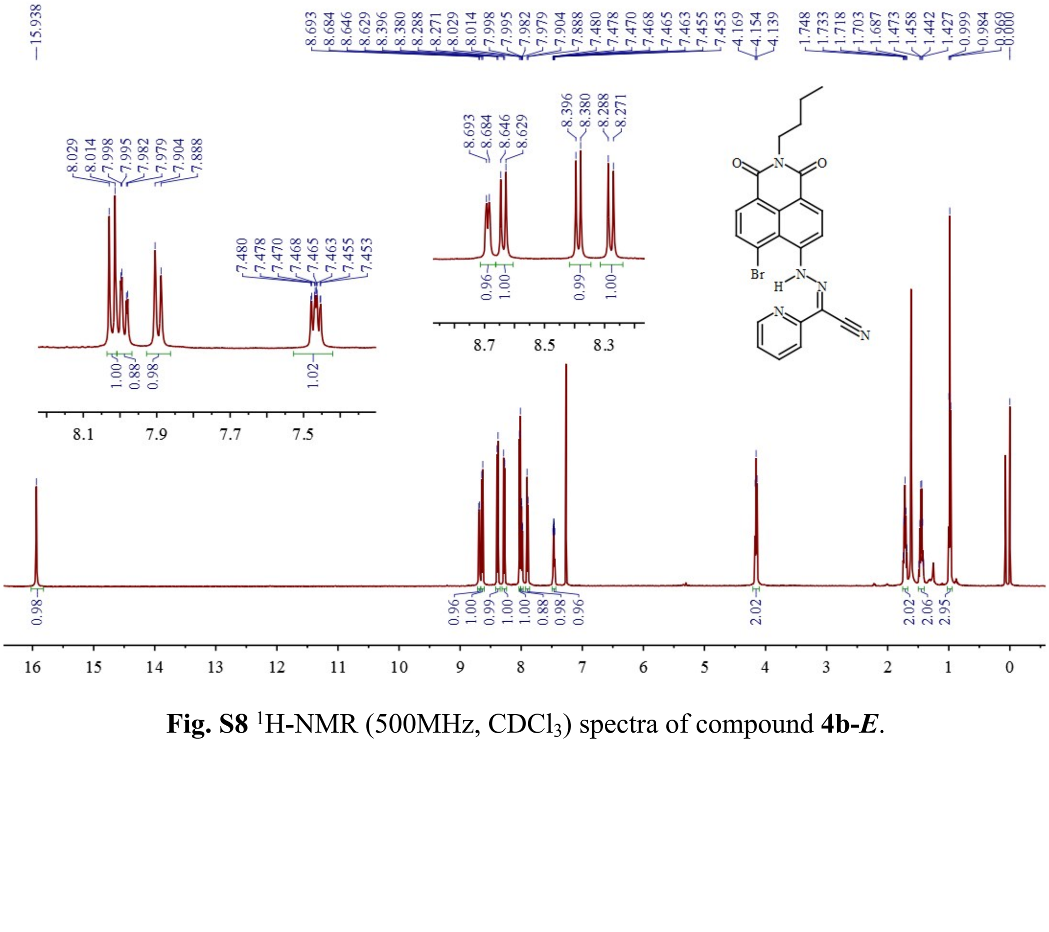


Fig. S8 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **4b-*E***.

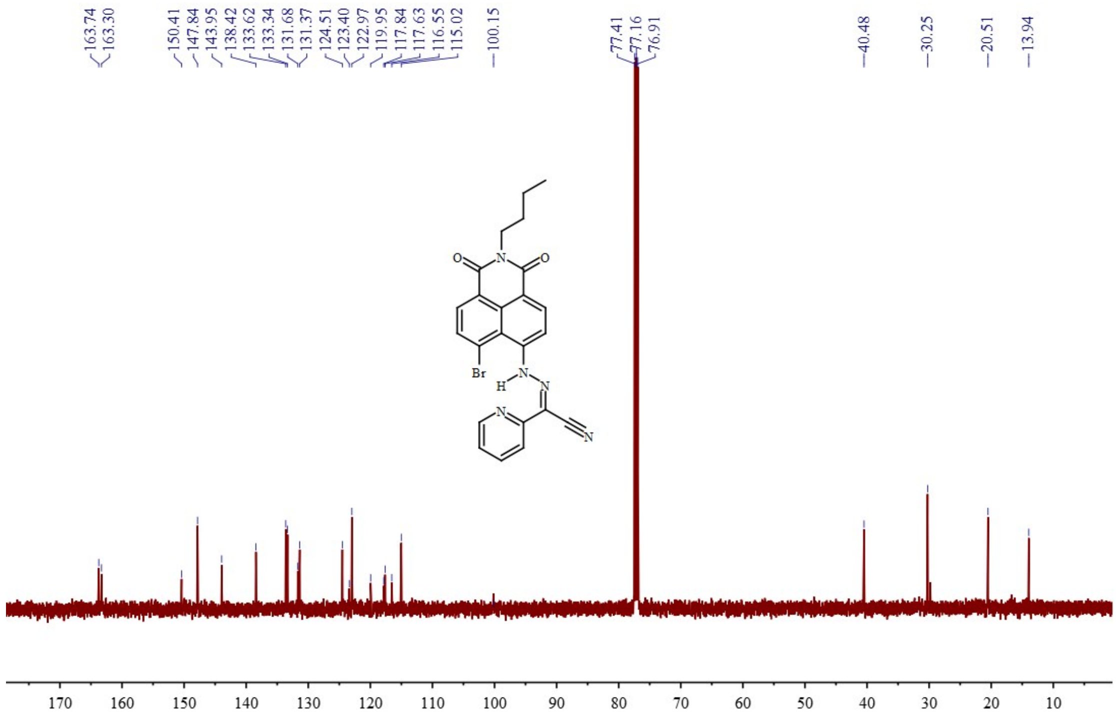


Fig. S9 ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound **4b-*E***.

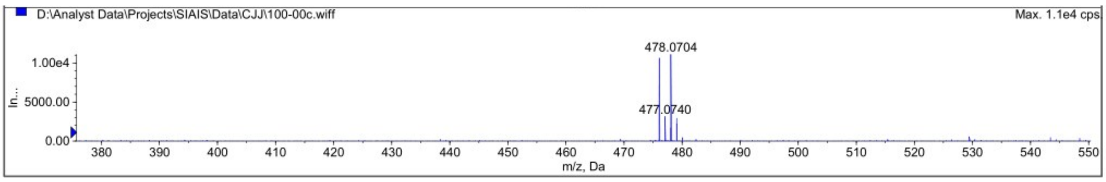


Fig. S10 HRMS-ESI mass spectra of compound **4b-*E***.

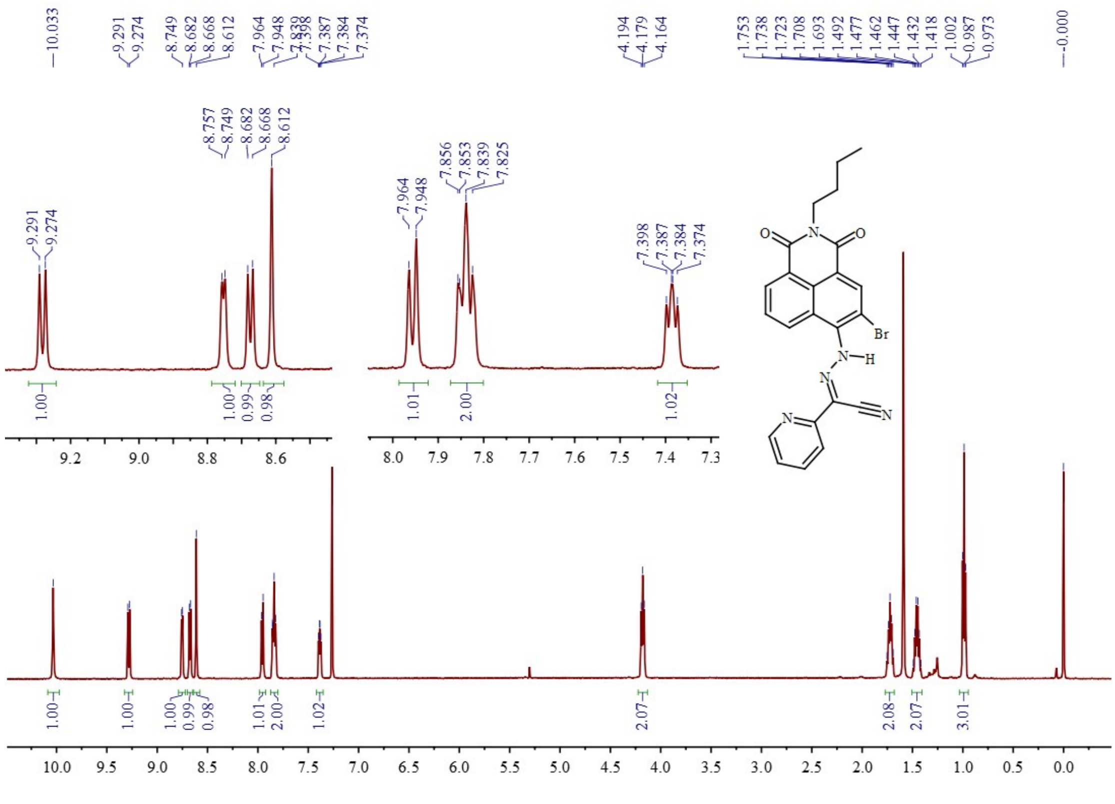


Fig. S11 [1]H-NMR (500MHz, $CDCl_3$) spectra of compound **4c-*Z***.

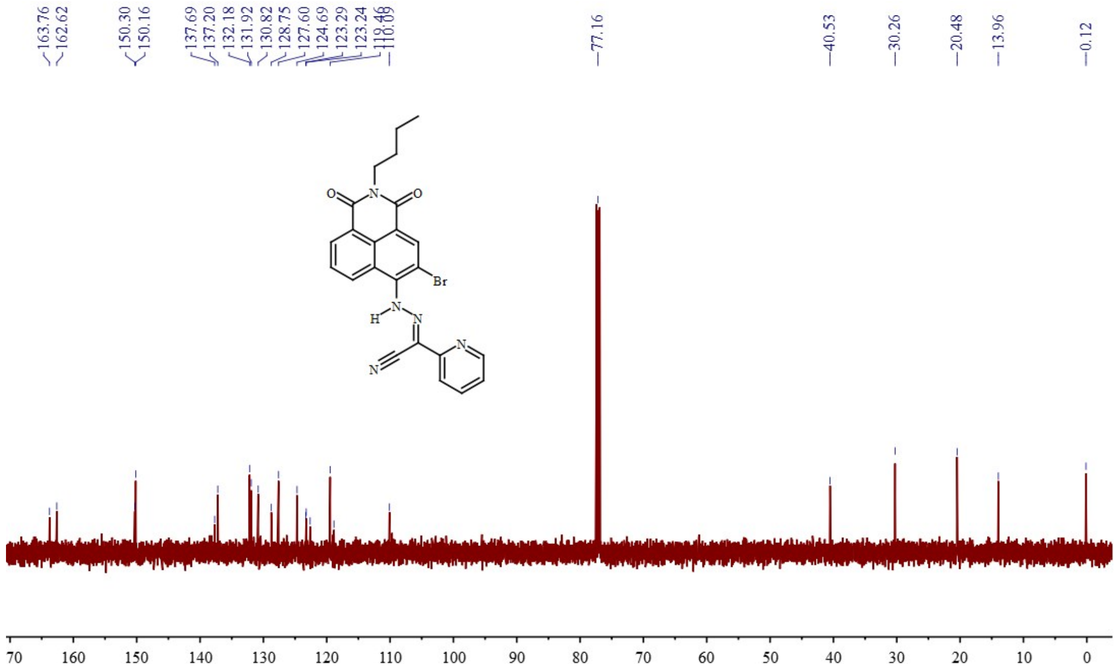


Fig. S12 [13]C-NMR (125 MHz, $CDCl_3$) spectra of compound **4c-*Z***.

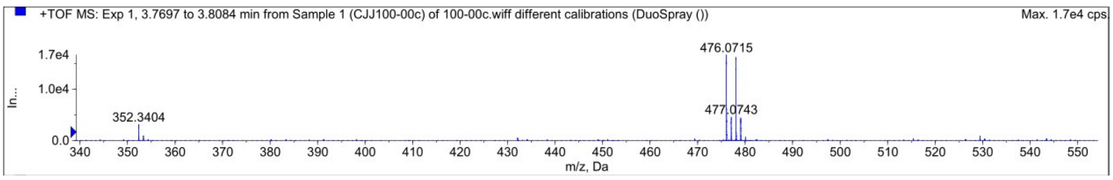


Fig. S13 HRMS-ESI mass spectra of compound **4c-*Z*.**

Solvent effect of probe **4a-*E***

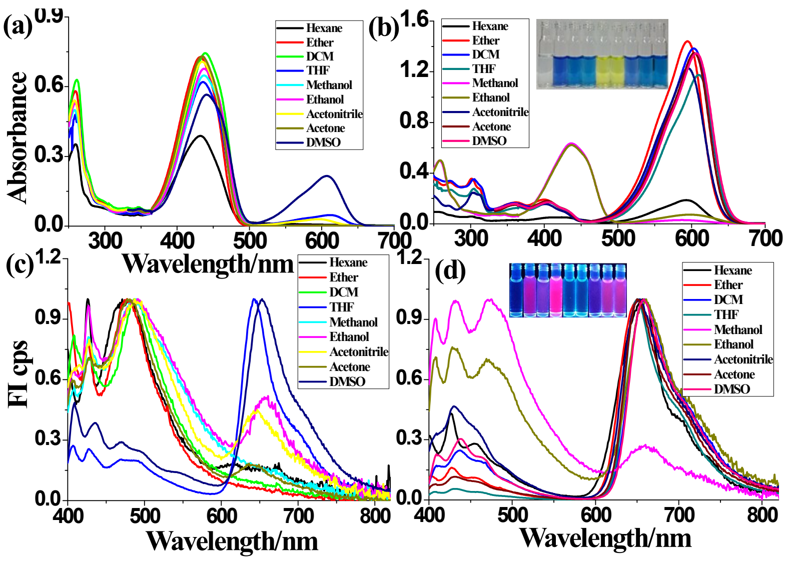


Fig. S14. Normalized absorbance and emission responses with the solvent effect: (a) UV–visible responses of **4a-*E*** (20 μM) in various solvents (Hexane, Ether, Dichloromethane, Tetrahydrofuran, Methanol, Ethanol, Acetonitrile, Acetone, Dimethyl Sulfoxide). (b) The system (a) + CN^- (2.0 equiv.). (c) Fluorescence emission of **4a-*E*** (20 μM) in various solvents (Hexane, Ether, Dichloromethane, Tetrahydrofuran, Methanol, Ethanol, Acetonitrile, Acetone, Dimethyl Sulfoxide). (d) The system (c) + CN^- (2.0 equiv.).

Interference experiments and titration spectra of the control probes

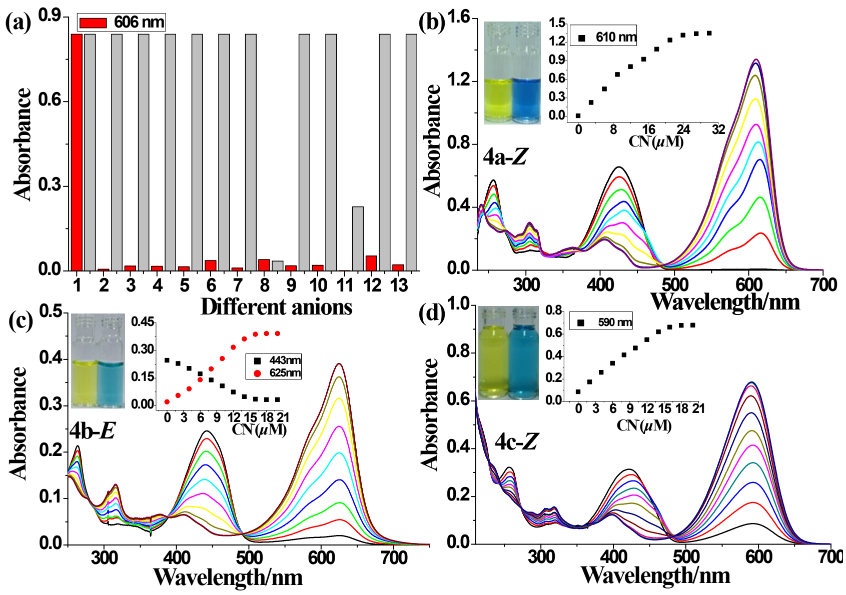


Fig. S15 (a) Interference experiments of **4a-*E*** (20 μM) in THF/water mixtures with 50% of water fractions for CN^- in the presence of other anions. The red bars represent the absorbance at 594 nm of **4a-*E*** in the presence of 30 equiv. of the anion of interest (from left to right: CN^-, F^-, Cl^-, Br^-, I^-, NO_3^-, AcO^-, HSO_4^-, BF_4^-, ClO_4^-, $H_2PO_4^-$, S^-, SCN^-). The gray bars indicate the change that occurs upon subsequent addition of 30 equiv. of CN^- to the solution containing **4a-*E*** and the anion of interest. (b) UV-visible titration spectra of **4a-*Z*** (20 μM) with TBACN (0 to 1.0 equiv.) in THF solution. The inset shows the absorbance at 610 nm as a function of CN^-. (c) UV-visible titration spectra of **4b-*E*** (20 μM) with TBACN (0 to 1.2 equiv.) in THF solution. The inset shows the absorbance at 610 nm as a function of CN^-. (d) UV-visible titration spectra of **4c-*Z*** (20 μM) with TBACN (0 to 1.0 equiv.) in THF solution. The inset shows the absorbance at 610 nm as a function of CN^-.

Job plot diagram

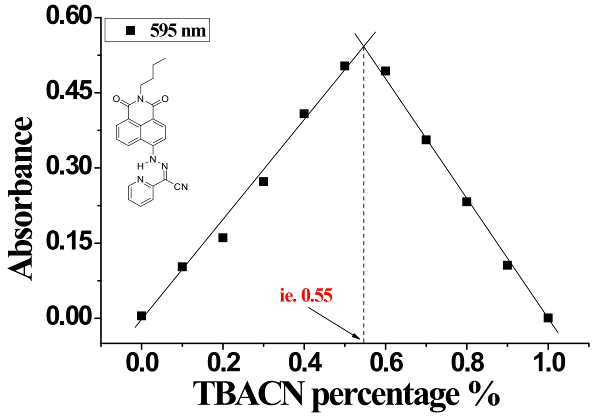


Fig. S16 Job plot diagram for binding interaction between probe **4a-*E*** and **TBACN** in THF.

Influence of pH on the absorbance of the probe **4a**

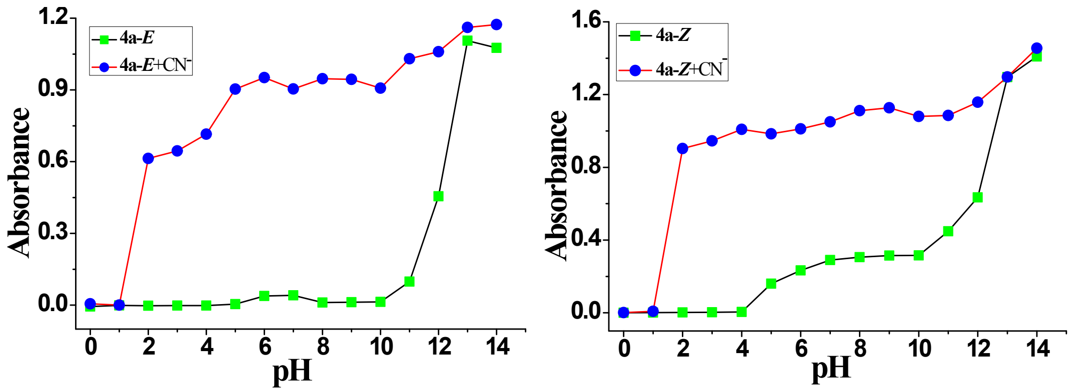


Fig. S17 (a) Influence of pH on the absorbance at 595 nm of **4a-*E*** (20 μM) and **4a-*E***+CN⁻ in CH_3CN/H_2O (9:1, v/v). (b) Influence of pH on the absorbance at 603 nm of **4a-*Z*** (20 μM) and **4a-*Z***+CN⁻ in CH_3CN/H_2O (9:1, v/v).

pKa of NH group

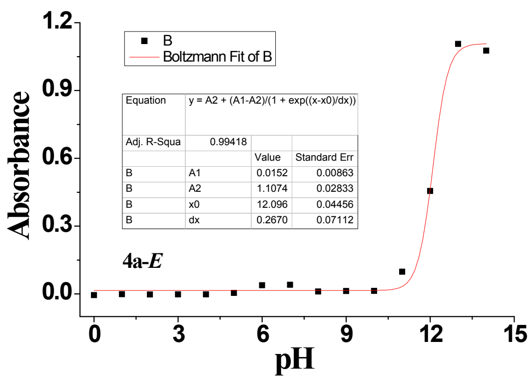


Fig. S18 Non-linear fitting curve of probe **4a-*E*** with TBACN by Boltzmann equation and the pKa of the proton in the NH group is 12.10.

Emission response of **4a** and control probe **4b-*E***

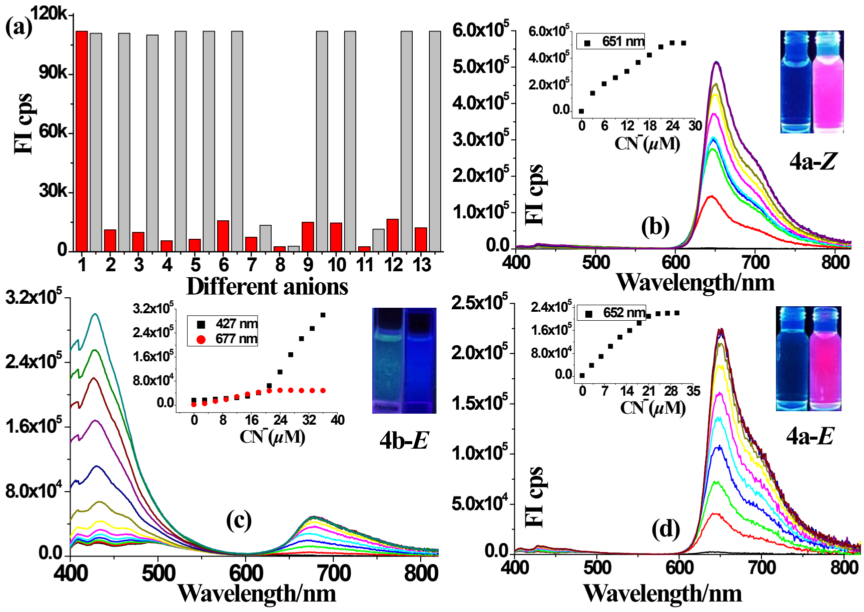


Fig. S19 (a) Interference experiments of **4a-*E*** (20 μM) in THF/water mixtures with 50% of water fractions for CN^- in the presence of other anions. The red bars represent the emission intensity at 661 nm of **4a-*E*** in the presence of 30 equiv. of the anion of interest (from left to right: CN^-, F^-, Cl^-, Br^-, I^-, NO_3^-, AcO^-, HSO_4^-, BF_4^-, ClO_4^-, $H_2PO_4^-$, S^-, SCN^-). The gray bars indicate the change that occurs upon subsequent addition of 30 equiv. of CN^- to the solution containing **4a-*E*** and the anion of interest. (b) Emission titration spectra of **4a-*Z*** (20 μM) with TBACN (0 to 1.2 equiv.) in THF. The inset shows the emission at 651 nm as a function of CN^-. (c) Emission titration spectra of **4b-*E*** (20 μM) with TBACN (0 to 1.8 equiv.) in THF. The inset shows the emission at 427 nm and 677 nm as a function of CN^-. (d) Emission titration spectra of **4a-*E*** (20 μM) with TBACN (0 to 1.5 equiv.) in THF. The inset shows the emission at 652 nm as a function of CN^-.

Solid state fluorescence

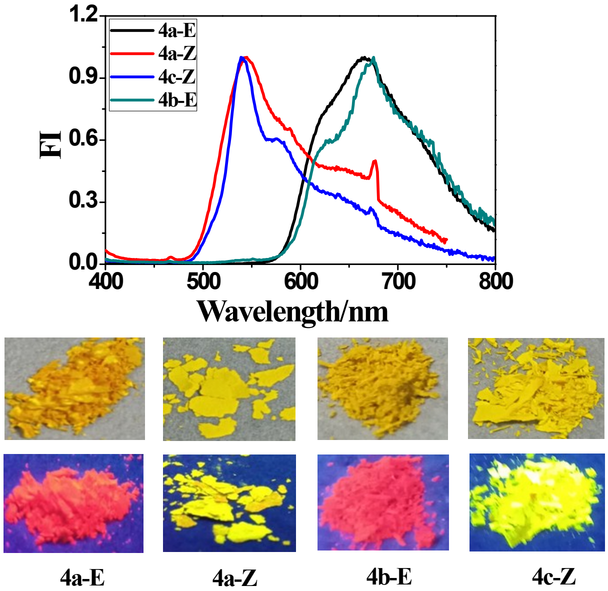


Fig. S20 Solid state fluorescence of the four compounds **4a-*E***, **4a-*Z***, **4b-*E*** and **4c-*Z***.

Reversibility and reusability in solution

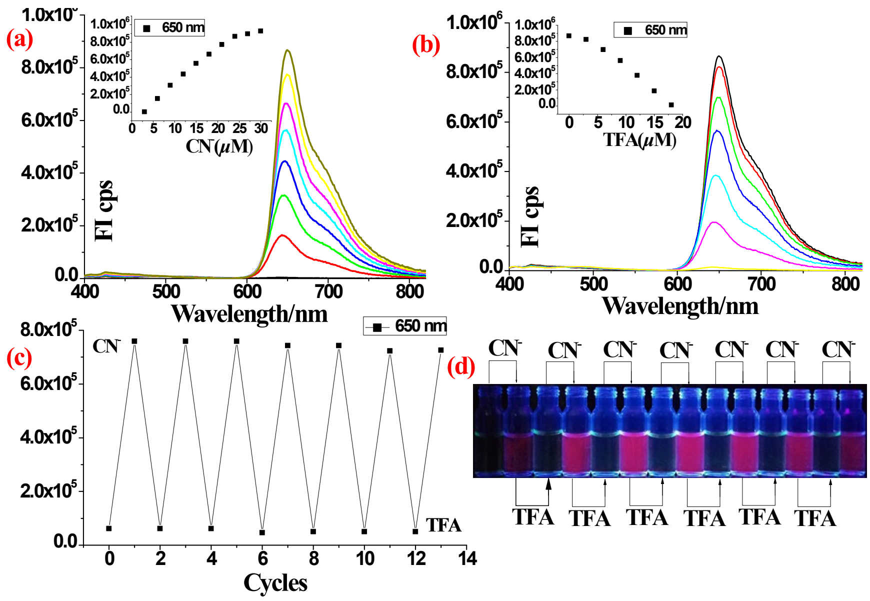


Fig. S21 (a) Emission titration spectra of **4a-*E*** (20 μM) with TBACN (0 to 1.4 equiv.) in THF. The inset shows the emission intensity at 650 nm as a function of CN^-. (b) Emission titration spectra of **4a-*E***+CN^- (20 μM) with TFA (0 to 1.0 equiv.) in THF. The inset shows the emission intensity at 650 nm as a function of TFA. (c) Relative fluorescence emission during the titration of **4a-*E*** with CN^- and H^+ (TFA) in THF. (d) Visual fluorescence colour after each sequential addition of CN^- and H^+ (TFA) in THF.

Colorimetric assays in the paper test strip

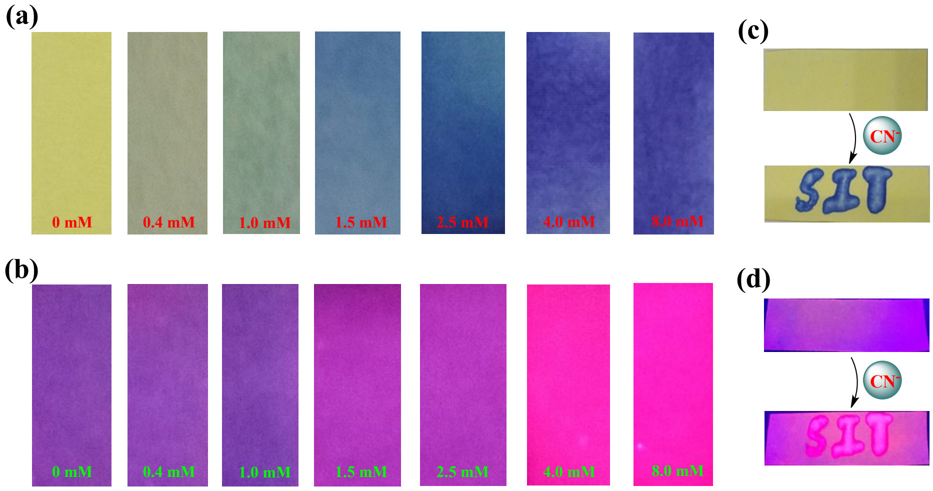
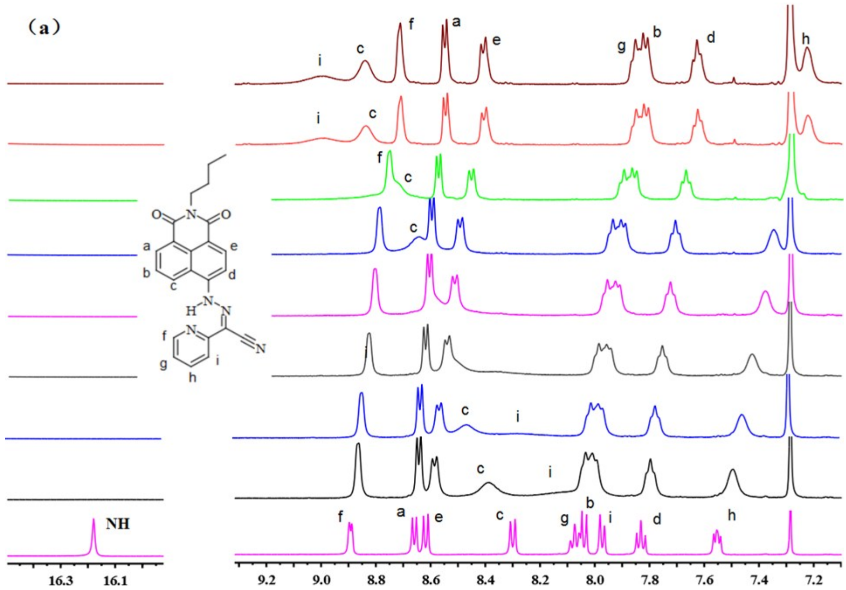
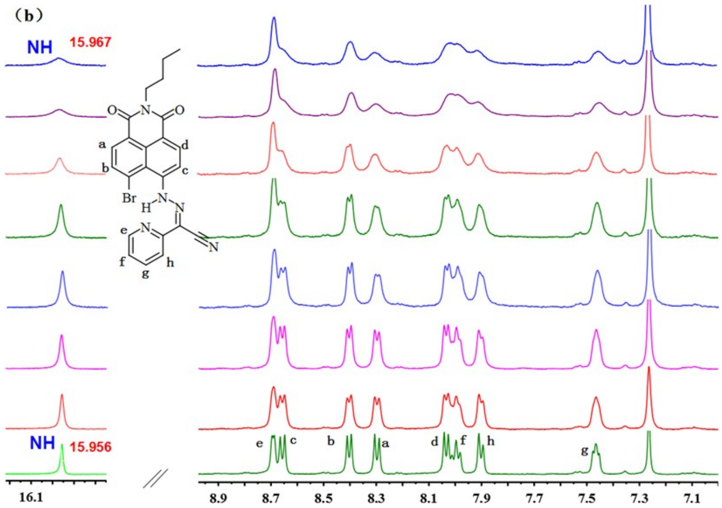


Fig. S22 Photographs of test strips of **4a-*E***. (a) The naked eye photo of absorbance of **4a-*E*** treated with CN^- of different concentrations (from 0 to 8.0 mM) (b) The fluorescence emission photo under UV light (365 nm) of **4a-*E*** treated with CN^- of different concentrations (from 0 to 8.0 mM). (c - d) Demonstration of **4a-*E*** as a writable platform: the white strips coated with **4a-*E*** (soaked in 1 mM THF solution) to give the sensor-loaded trips, then writing word ‘‘SIT’’ with a small Chinese brush stained with the TBACN (5.0 mM) solution. Blue word ‘‘SIT’’ in a naked eye photo (d) and red word ‘‘SIT’’ under UV light (365 nm).

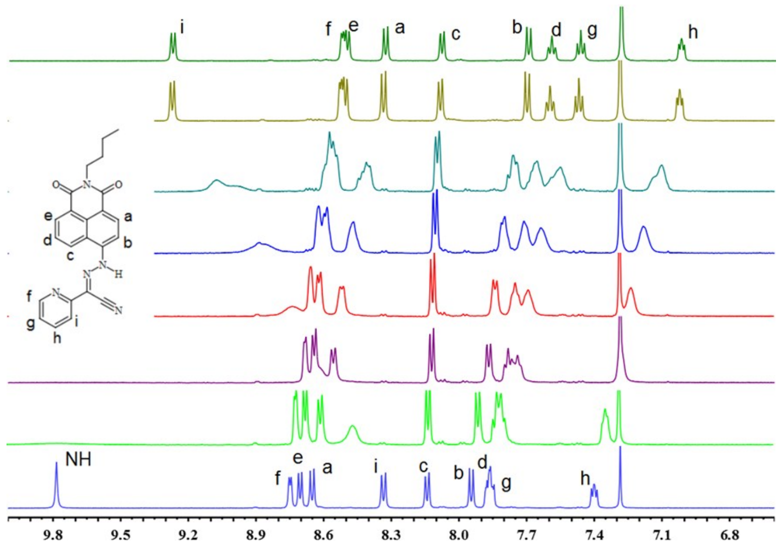
^{1}H-NMR titration spectra of probe **4a-*E*** and control probes



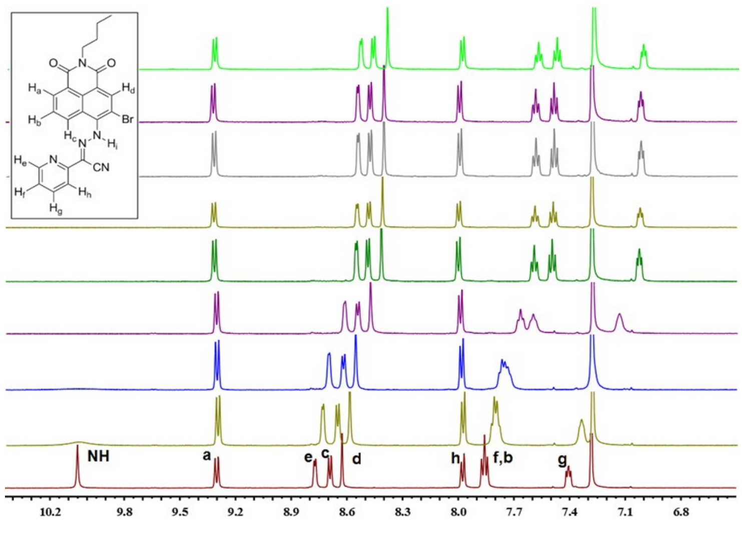
(a) ^{1}H-NMR titration spectra of probe **4a-*E***



(b) ^{1}H-NMR titration spectra of probe **4b-*E***



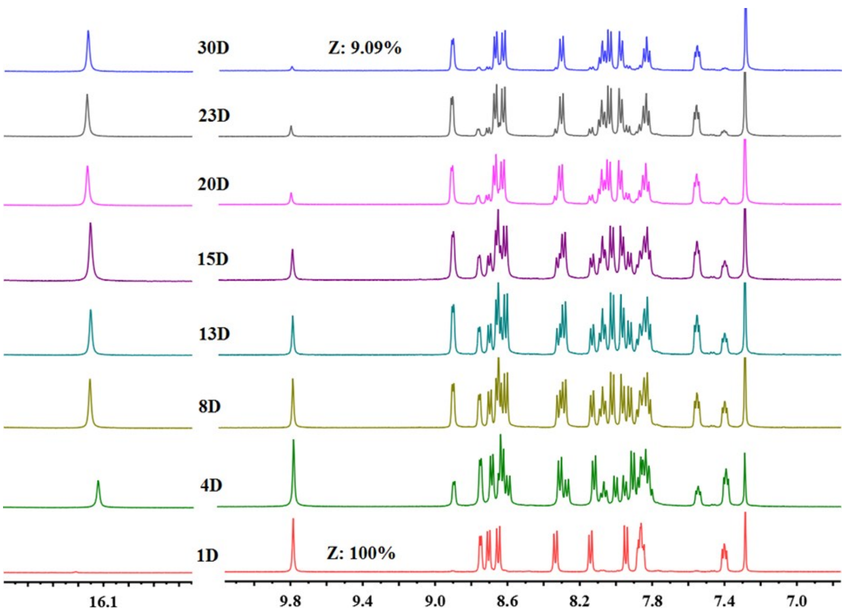
(c) ^{1}H-NMR titration spectra of probe **4a-*Z***



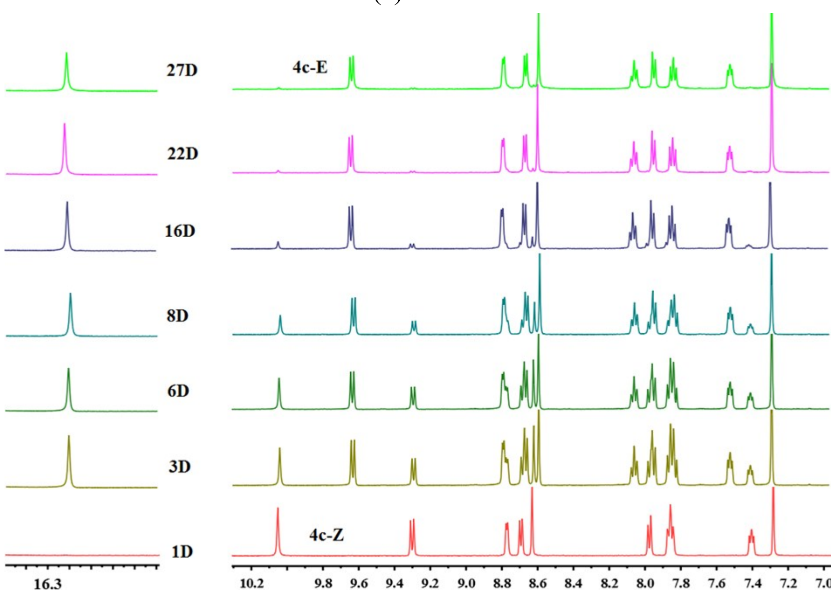
(d) ^{1}H-NMR titration spectra of probe **4c-*Z***

Fig. S23 (a) ^{1}H-NMR titration spectra of probe **4a-*E*** (2.0 x 10 $^{-2}$ mol/L) in $CDCl_3$ upon addition of CN^- ions (as alts in $CDCl_3$) at 298 K. From the bottom to top: **4a-*E*** only, 0.2, 0.4, 0.6, 1.0, 1.5, 2.0, 2.5, 3.5 equiv. (b) ^{1}H-NMR titration spectra of probe **4b-*E*** (2.0 x 10 $^{-2}$ mol/L) in $CDCl_3$ upon addition of CN^- ions (as alts in $CDCl_3$) at 298 K. From the bottom to top: **4b-*E*** only, 0.2, 0.4, 0.6, 1.0, 1.5, 2.0, 2.5 equiv.(c) ^{1}H-NMR titration spectra of probe **4a-*Z*** (2.0x10^{-2} mol/L) in $CDCl_3$ upon addition of CN^- ions (as alts in $CDCl_3$) at 298 K. From the bottom to top: **4a-*Z*** only, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.5 equiv. (d) ^{1}H-NMR titration spectra of probe **4c-*Z*** (2.0x10^{-2} mol/L) in $CDCl_3$ upon addition of CN^- ions (as alts in $CDCl_3$) at 298 K. From the bottom to top: **4c-*Z*** only, 0.2, 0.5, 0.6, 1.0, 1.5, 2.0, 2.5, 3.5 equiv.

^{1}H-NMR spectra time-dependent response



(a) **4a-*Z***



(b) **4c-*Z***

Fig. S24 Time-dependent ^{1}H-NMR spectra of probe **4a-*Z*** and **4c-*Z*** (2.0 x 10^{-2} mol/L) in $CDCl_3$ at 298 K. From the bottom to top: 0 day to 30 days.

Solvent effect and pertinent photophysical data

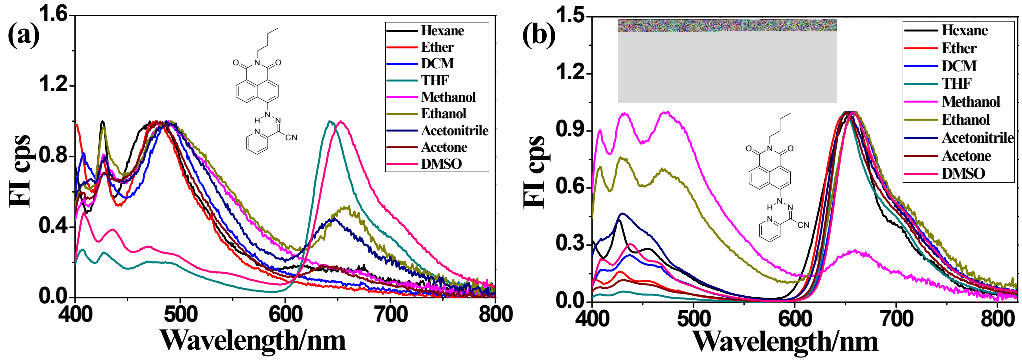


Fig. S25 (a) Normalized emission responses of **4a-*E*** (20 μM) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO). (b) Normalized emission responses of **4a-*E*** (20 μM) with TBACN (2.0 equiv.) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO). (λ_{ex}: 378 nm)

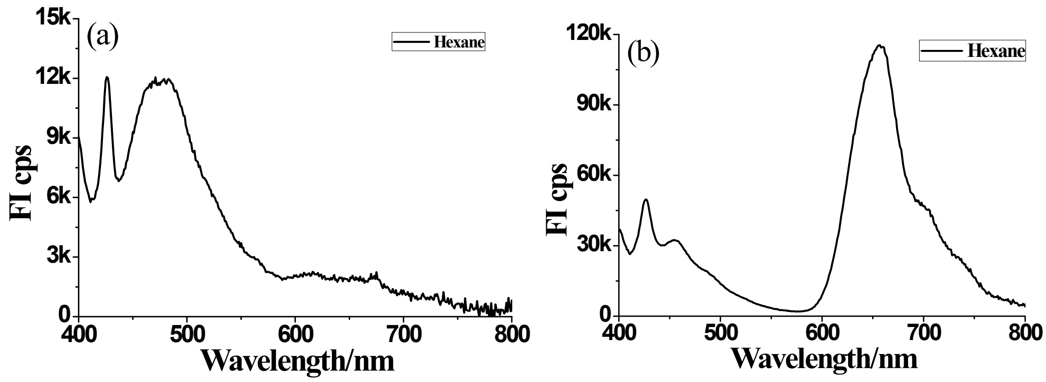


Fig. S26 Normalized emission spectra of **4a-*E*** (20 μM) in Hexane: (a) probe (b) probe+CN$^-$

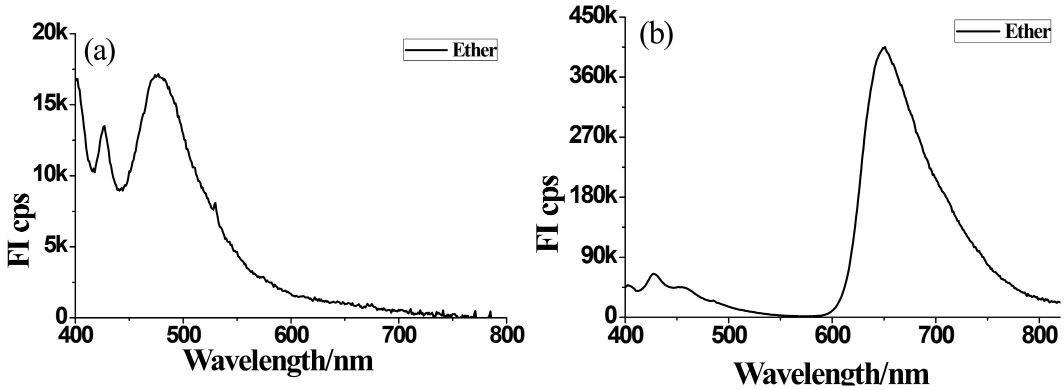


Fig. S27 Normalized emission spectra of **4a-*E*** (20 μM) in Ether: (a) probe (b) probe+CN$^-$

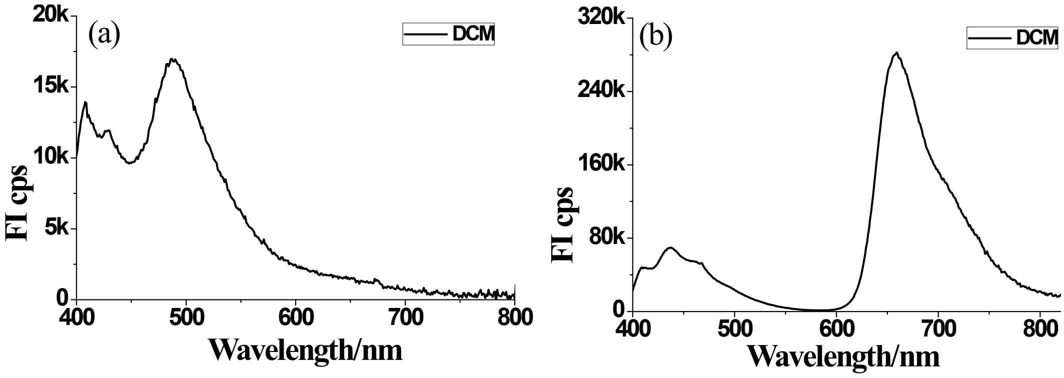


Fig. S28 Normalized emission spectra of **4a-*E*** (20 μM) in DCM: (a) probe (b) probe+CN^-

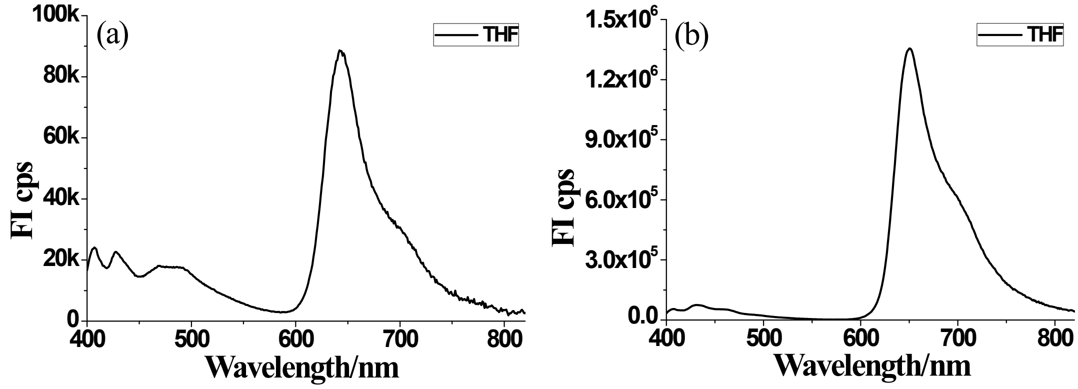


Fig. S29 Normalized emission spectra of **4a-*E*** (20 μM) in THF: (a) probe (b) probe+CN^-

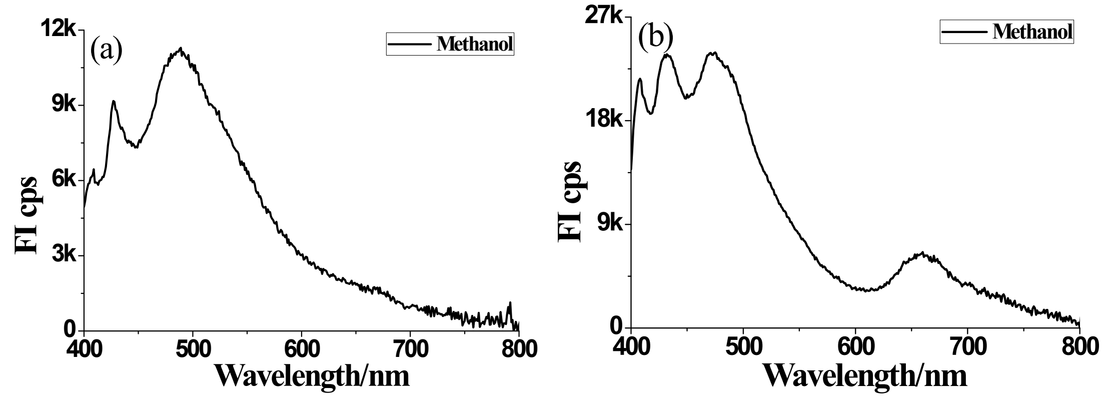


Fig. S30 Normalized emission spectra of **4a-*E*** (20 μM) in Methanol: (a) probe (b) probe+CN^-

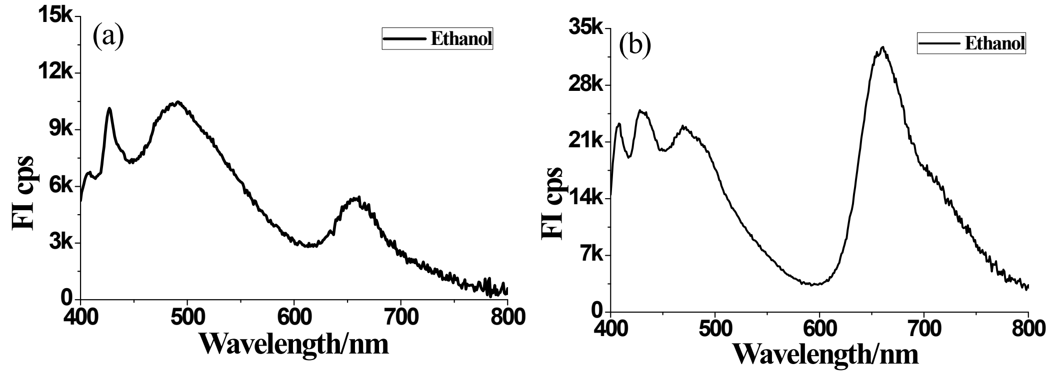


Fig. S31 Normalized emission spectra of **4a-*E*** (20 μM) in Eethanol: (a) probe (b) probe+CN^-

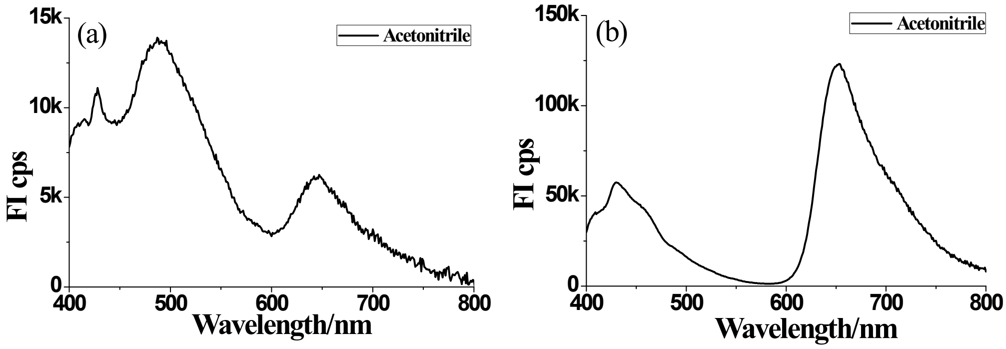


Fig. S32 Normalized emission spectra of **4a-*E*** (20 μM) in Acetonitrile: (a) probe (b) probe+CN^-

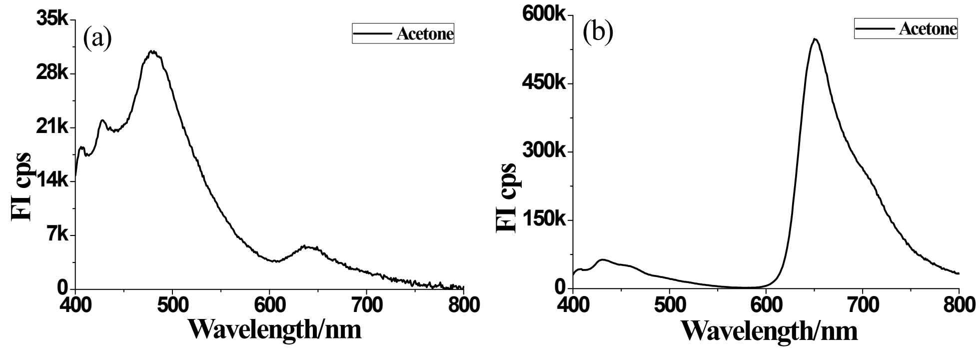


Fig. S33 Normalized emission spectra of **4a-*E*** (20 μM) in Acetone: (a) probe (b) probe+CN^-

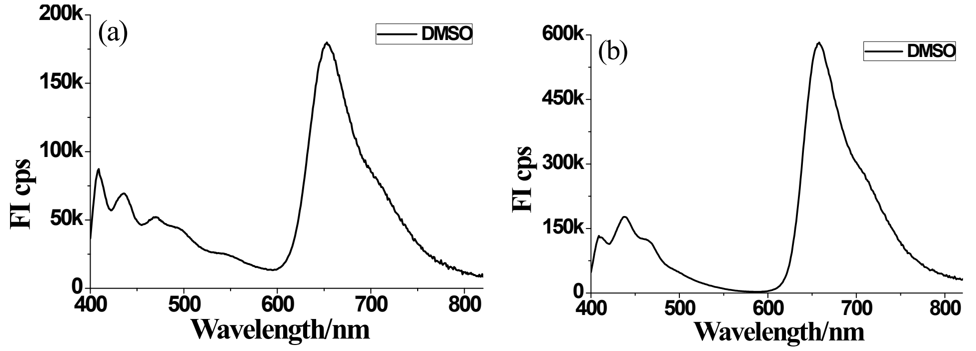


Fig. S34 Normalized emission spectra of **4a-*E*** (20 μM) in DMSO: (a) probe (b) probe+CN^-

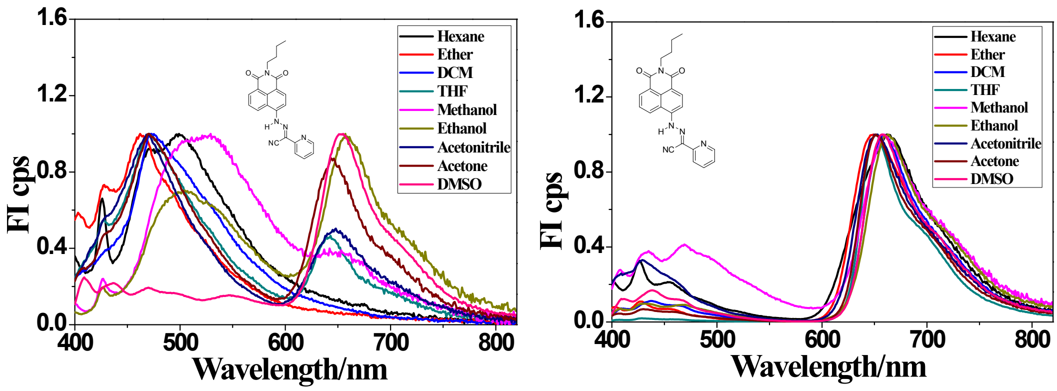


Fig. S35 (a) Normalized emission responses of **4a-*Z*** (20 μM) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO). (b) Normalized emission responses of **4a-*Z*** (20 μM) with TBACN (2.0 equiv.) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO)

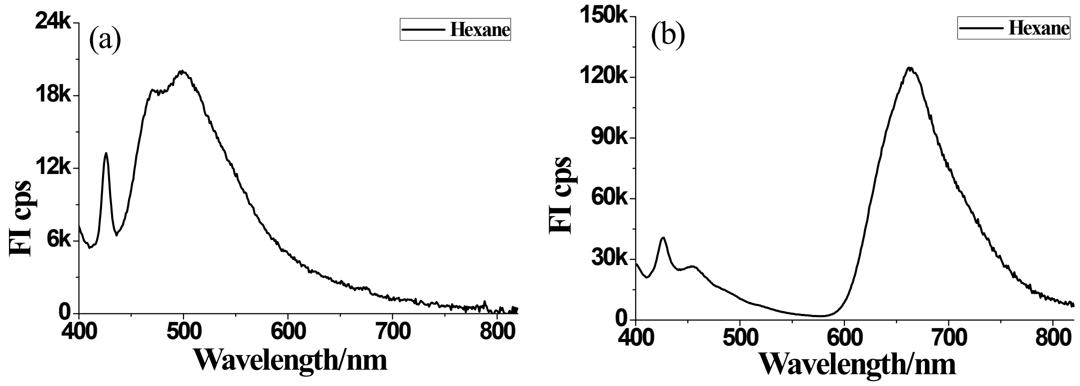


Fig. S36 Normalized emission spectra of **4a-*Z*** (20 μM) in Hexane: (a) probe (b) probe+CN^{-}

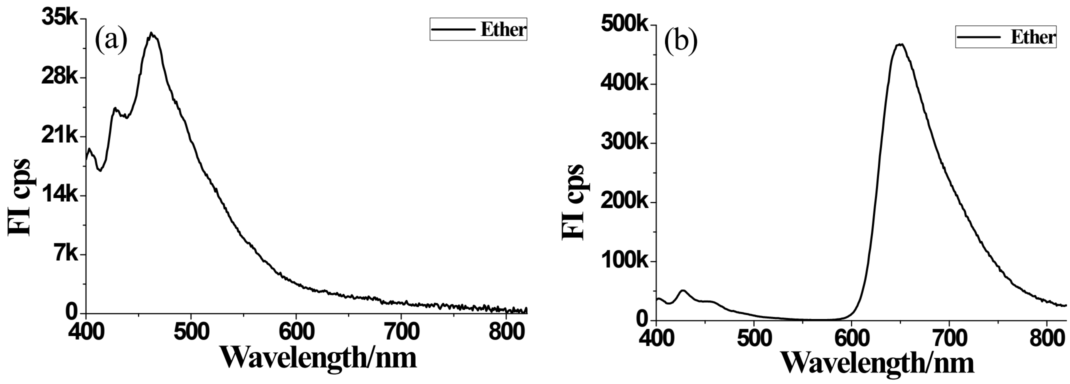


Fig. S37 Normalized emission spectra of **4a-*Z*** (20 μM) in Ether: (a) probe (b) probe+CN^{-}

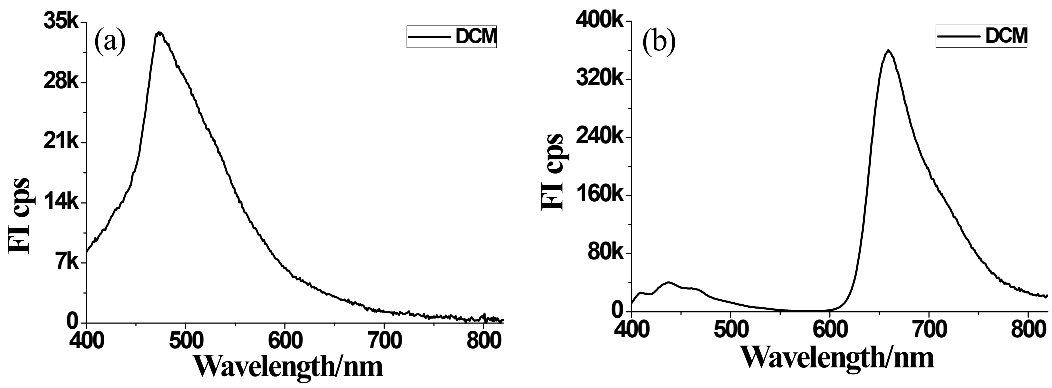


Fig. S38 Normalized emission spectra of **4a-*Z*** (20 μM) in DCM: (a) probe (b) probe+CN^{-}

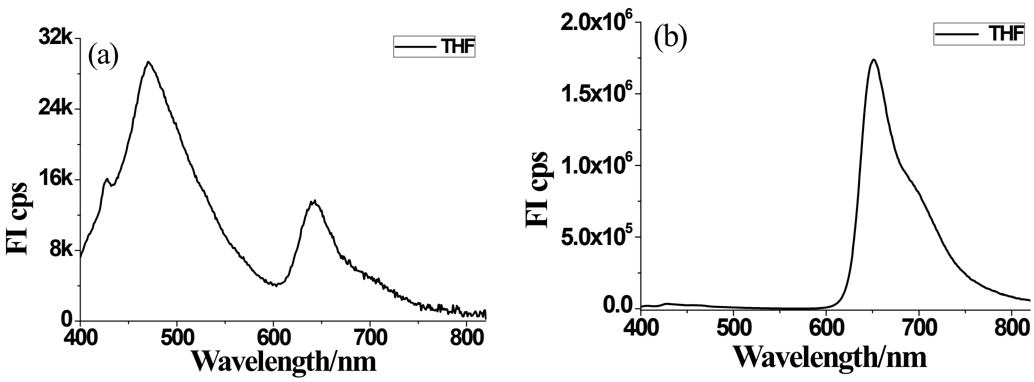


Fig. S39 Normalized emission spectra of **4a-*Z*** (20 μM) in THF: (a) probe (b) probe+CN^{-}

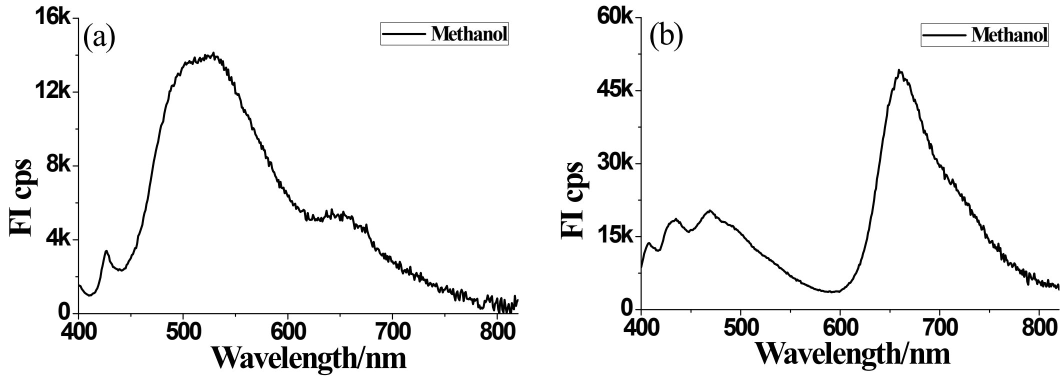


Fig. S40 Normalized emission spectra of **4a-*Z*** (20 μM) in Methanol: (a) probe (b) probe+CN^{-}

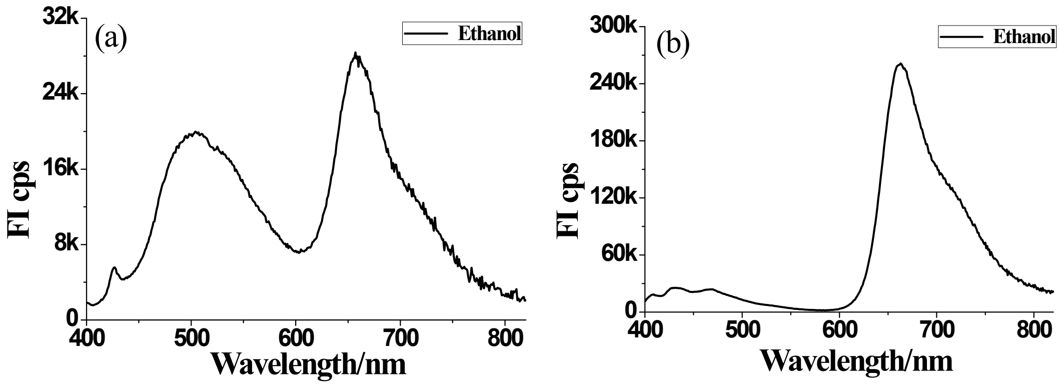


Fig. S41 Normalized emission spectra of **4a-*Z*** (20 μM) in Eethanol: (a) probe (b) probe+CN^{-}

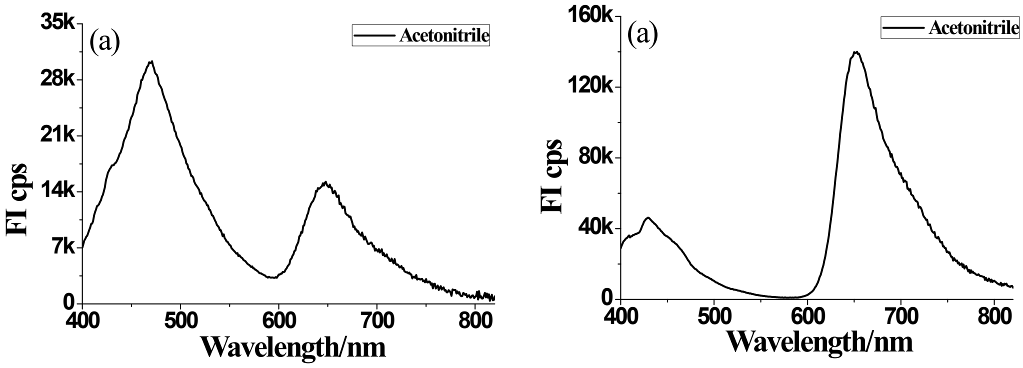


Fig. S42 Normalized emission spectra of **4a-*Z*** (20 μM) in Acetonitrile: (a) probe (b) probe+CN^{-}

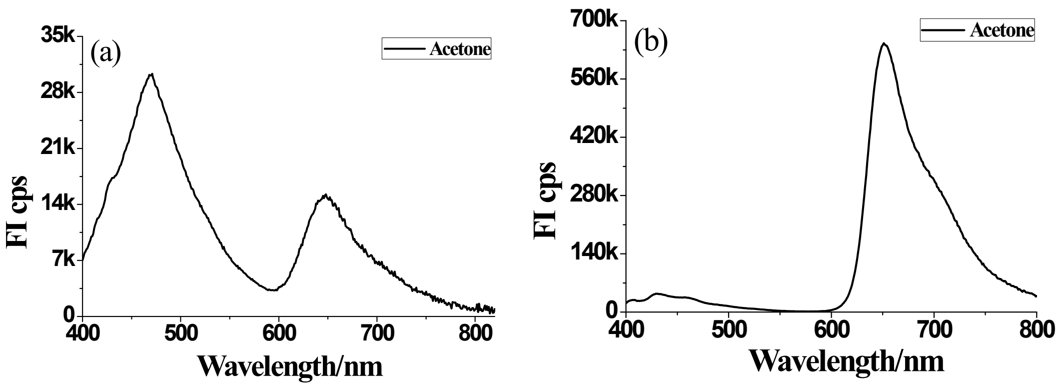


Fig. S43 Normalized emission spectra of **4a-*Z*** (20 μM) in Acetone: (a) probe (b) probe+CN^{-}

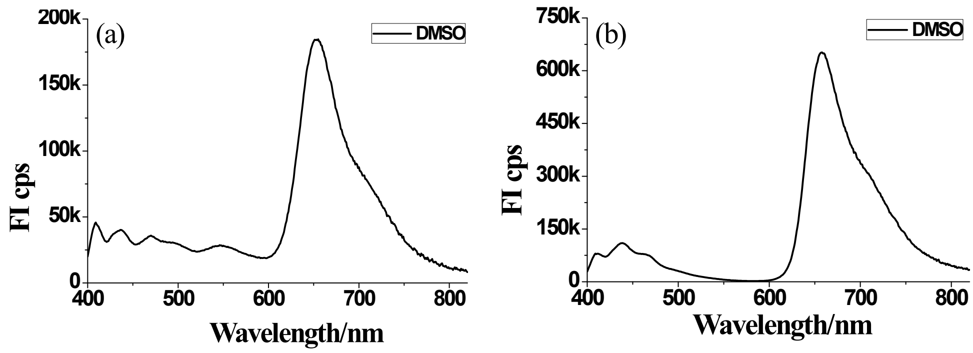


Fig. S44 Normalized emission spectra of **4a-*Z*** (20 μM) in DMSO: (a) probe (b) probe+CN^-

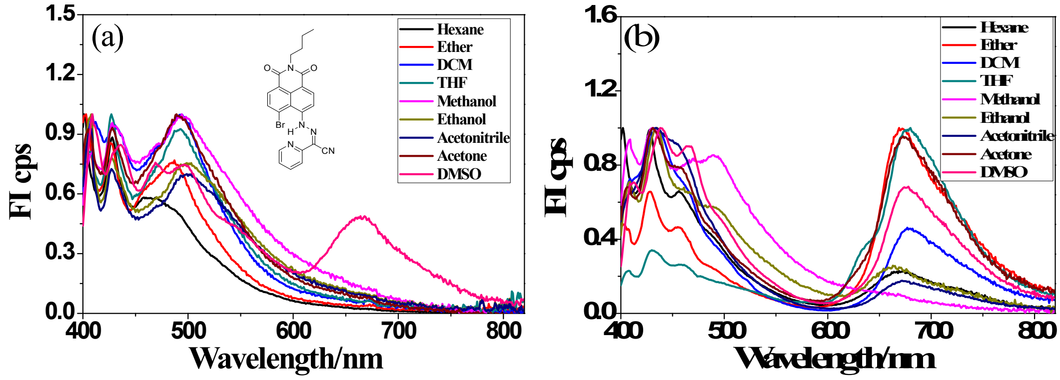


Fig. S45 (a) Normalized emission responses of **4b-*E*** (20 μM) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO). (b) Normalized emission responses of **4b-*E*** (20 μM) with TBACN (2.0 equiv.) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO).

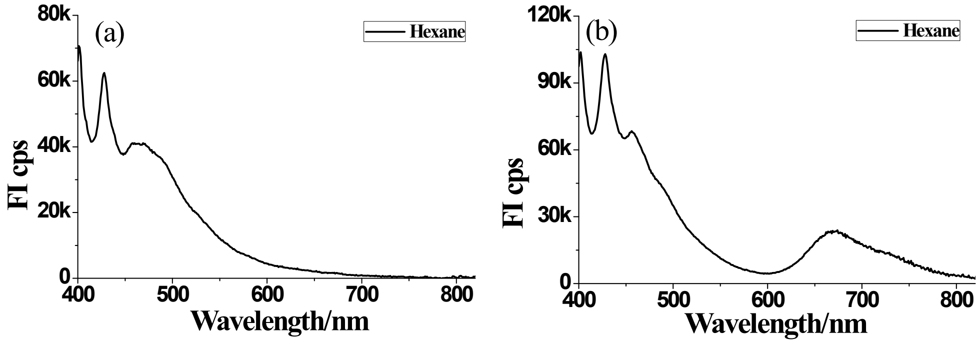


Fig. S46 Normalized emission spectra of **4b-*E*** (20 μM) in Hexane: (a) probe (b) probe+CN^-

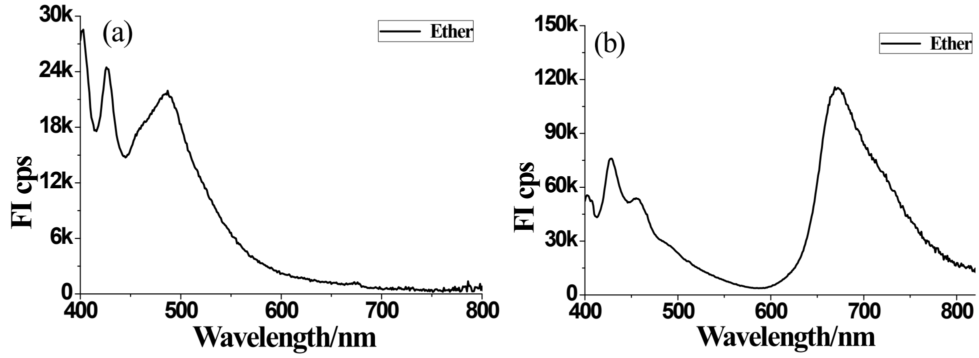


Fig. S47 Normalized emission spectra of **4b-*E*** (20 μM) in Ether: (a) probe (b) probe+CN^-

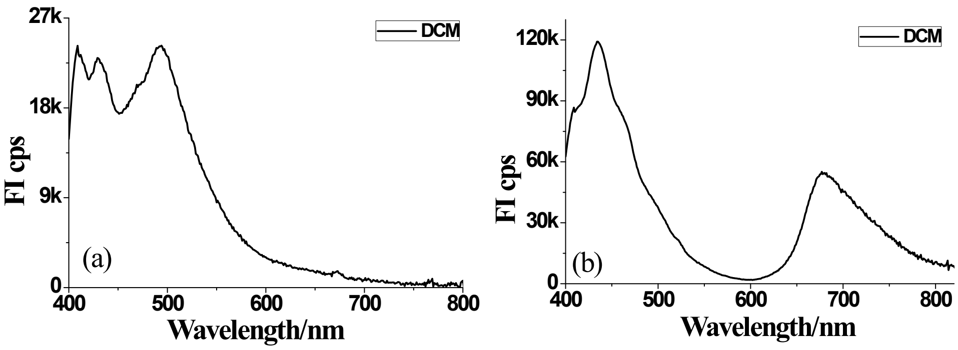


Fig. S48 Normalized emission spectra of **4b-*E*** (20 μM) in DCM: (a) probe (b) probe+CN^-

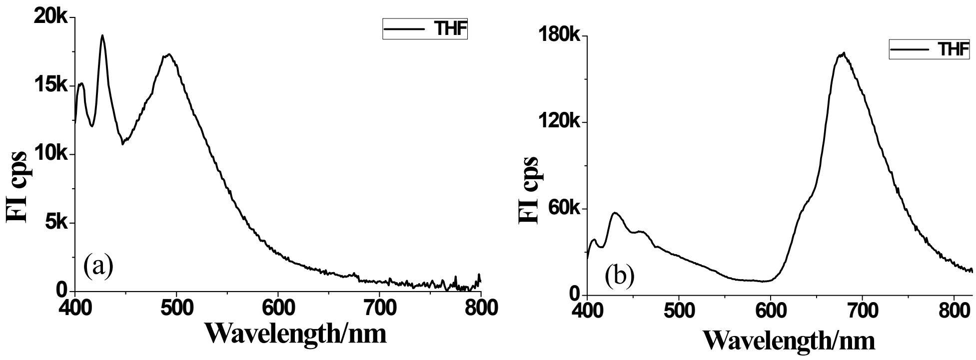


Fig. S49 Normalized emission spectra of **4b-*E*** (20 μM) in THF: (a) probe (b) probe+CN^-

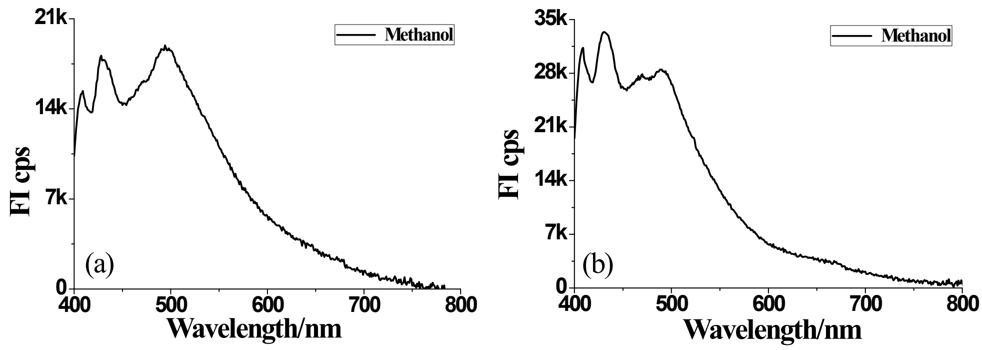


Fig. S50 Normalized emission spectra of **4b-*E*** (20 μM) in Methanol: (a) probe (b) probe+CN^-

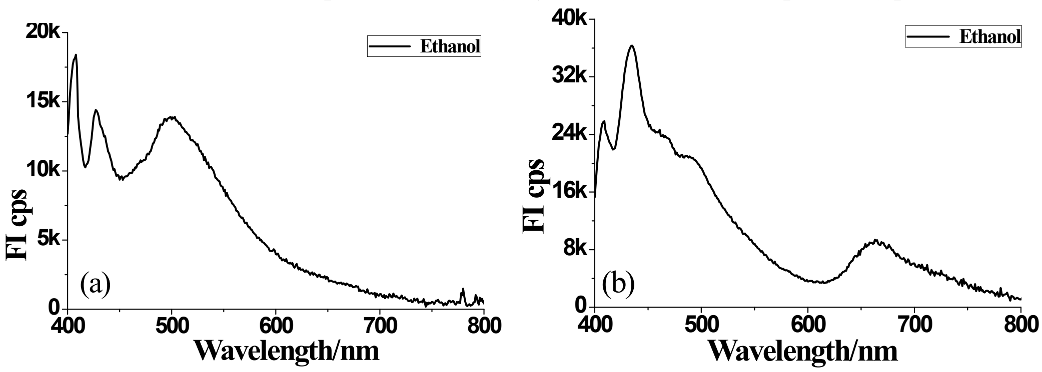


Fig. S51 Normalized emission spectra of **4b-*E*** (20 μM) in Eethanol: (a) probe (b) probe+CN^-

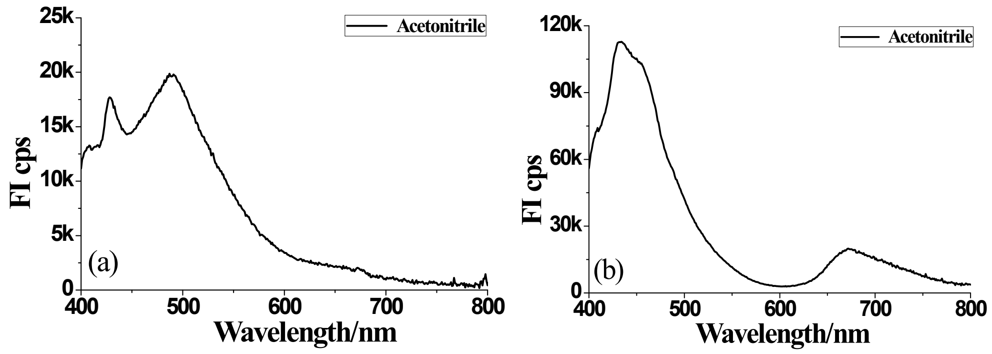


Fig. S52 Normalized emission spectra of **4b-*E*** (20 μM) in Acetonitrile: (a) probe (b) probe+CN^{-}

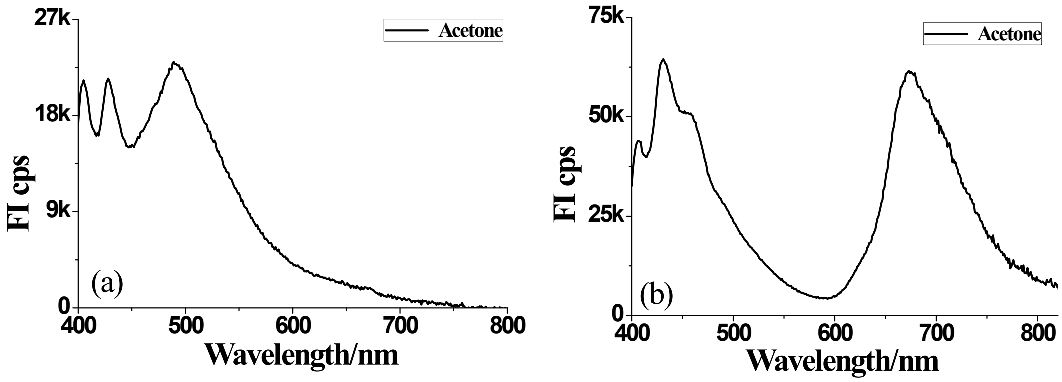


Fig. S53 Normalized emission spectra of **4b-*E*** (20 μM) in Acetone: (a) probe (b) probe+CN^{-}

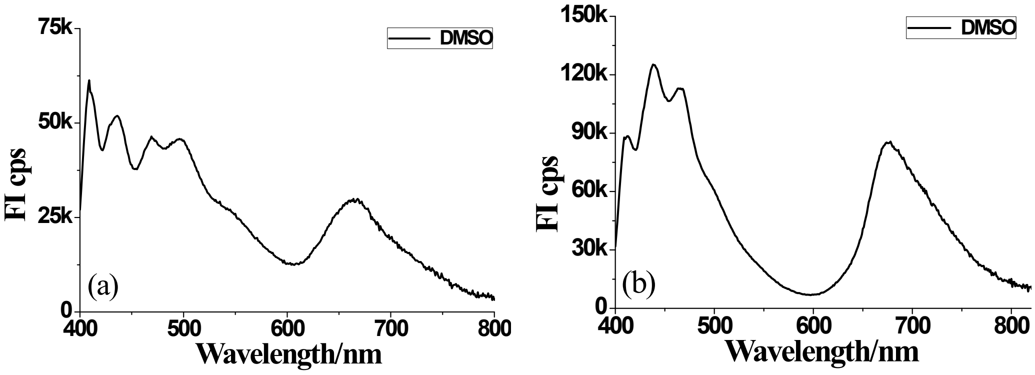


Fig. S54 Normalized emission spectra of **4b-*E*** (20 μM) in DMSO: (a) probe (b) probe+CN^{-}

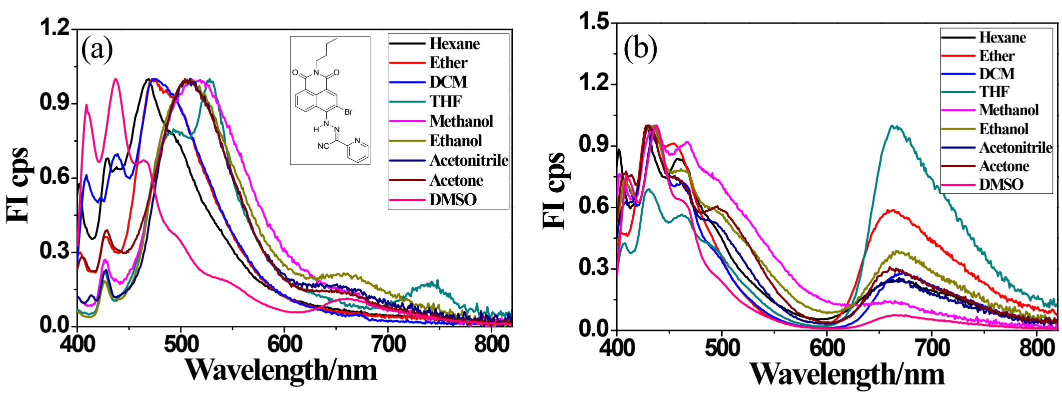


Fig. S55 (a) Normalized emission responses of **4c-*Z*** (20 μM) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO). (b) Normalized emission responses of **4c-*Z*** (20 μM) with TBACN (2.0 equiv.) in various solvents (Hexane, Ether, DCM, THF, Methanol, Ethanol, Acetonitrile, Acetone, DMSO).

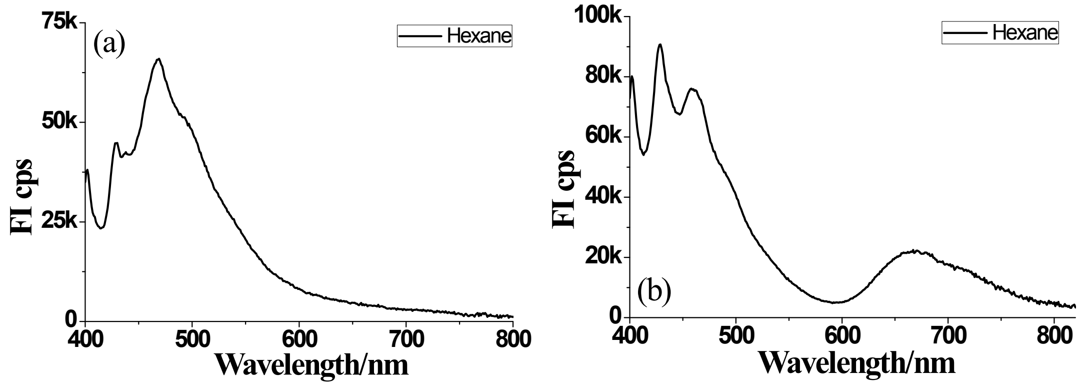


Fig. S56 Normalized emission spectra of **4c-*Z*** (20 μM) in Hexane: (a) probe (b) probe+CN^-

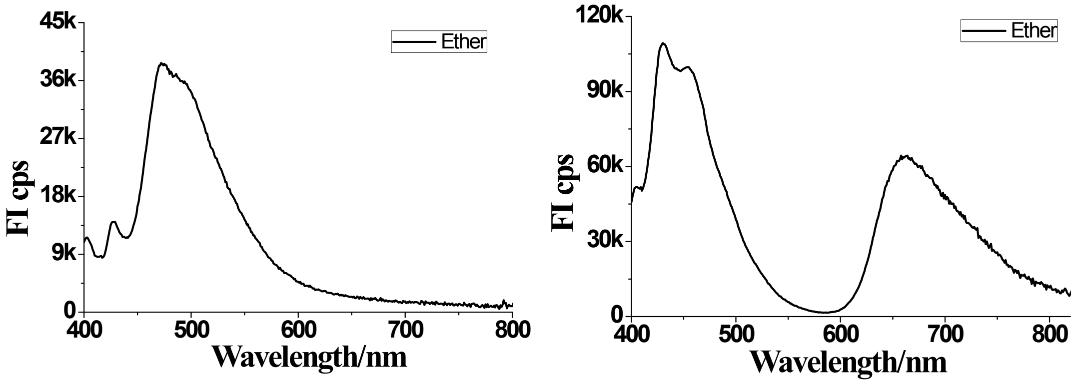


Fig. S57 Normalized emission spectra of **4c-*Z*** (20 μM) in Ether: (a) probe (b) probe+CN^-

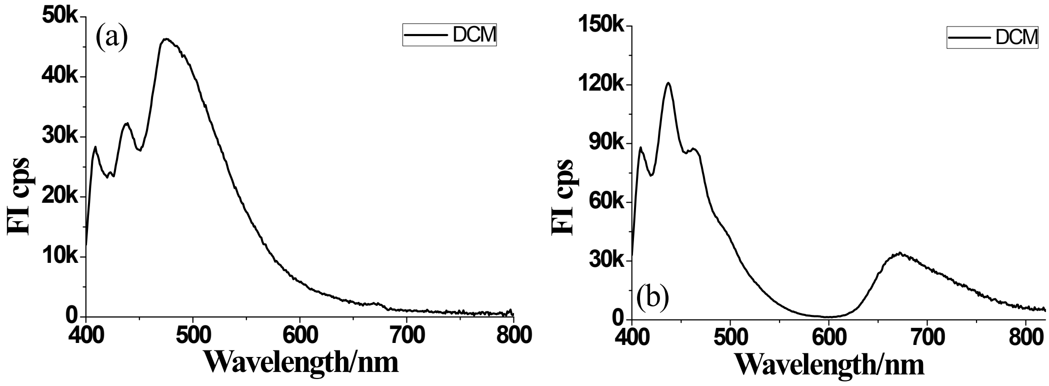


Fig. S58 Normalized emission spectra of **4c-*Z*** (20 μM) in DCM: (a) probe (b) probe+CN^-

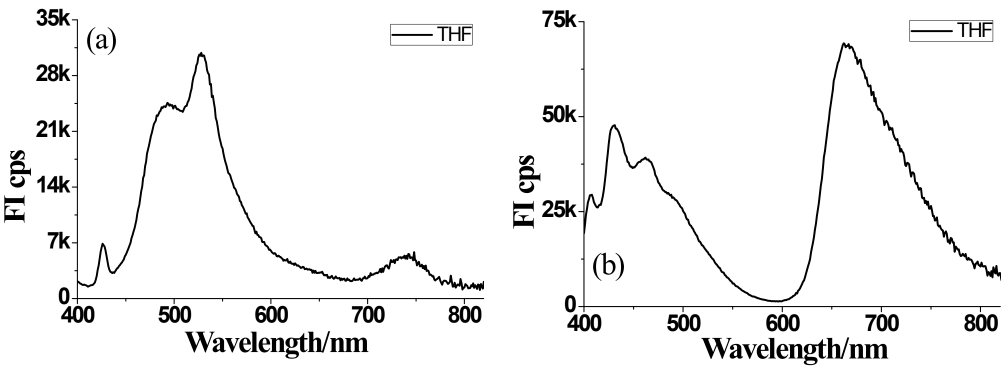


Fig. S59 Normalized emission spectra of **4c-*Z*** (20 μM) in THF: (a) probe (b) probe+CN^-

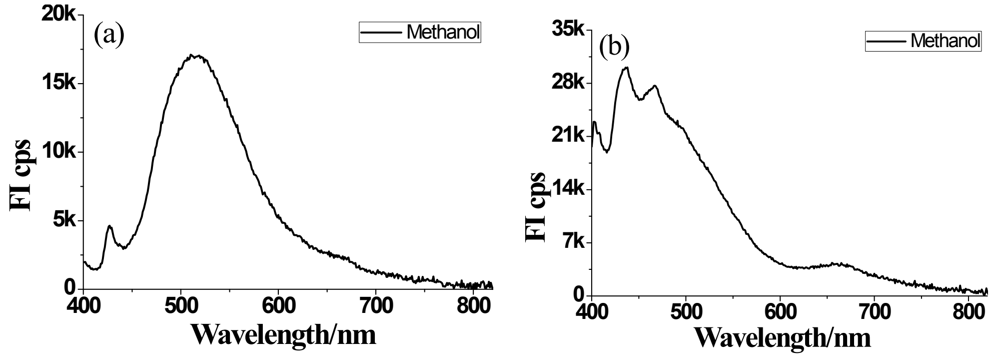


Fig. S60 Normalized emission spectra of **4c-*Z*** (20 μM) in MeOH: (a) probe (b) probe+CN^-

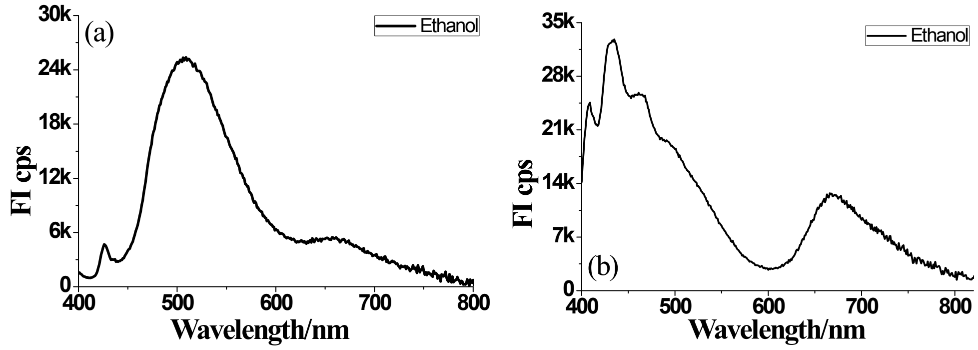


Fig. S61 Normalized emission spectra of **4c-*Z*** (20 μM) in EtOH: (a) probe (b) probe+CN^-

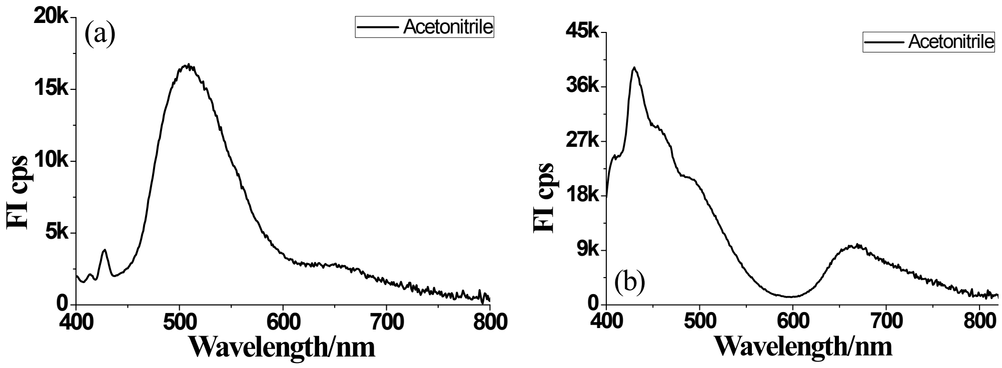


Fig. S62 Normalized emission spectra of **4c-*Z*** (20 μM) in Acetonitrile: (a) probe (b) probe+CN^-

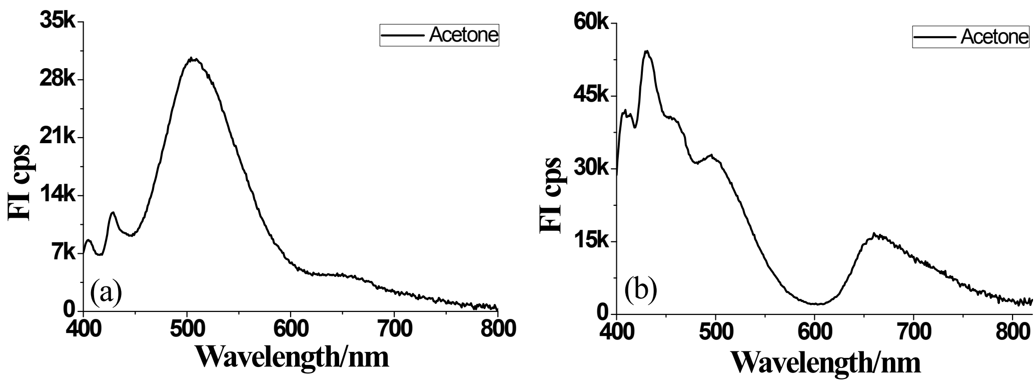


Fig. S63 Normalized emission spectra of **4c-*Z*** (20 μM) in Acetonitrile: (a) probe (b) probe+CN^-

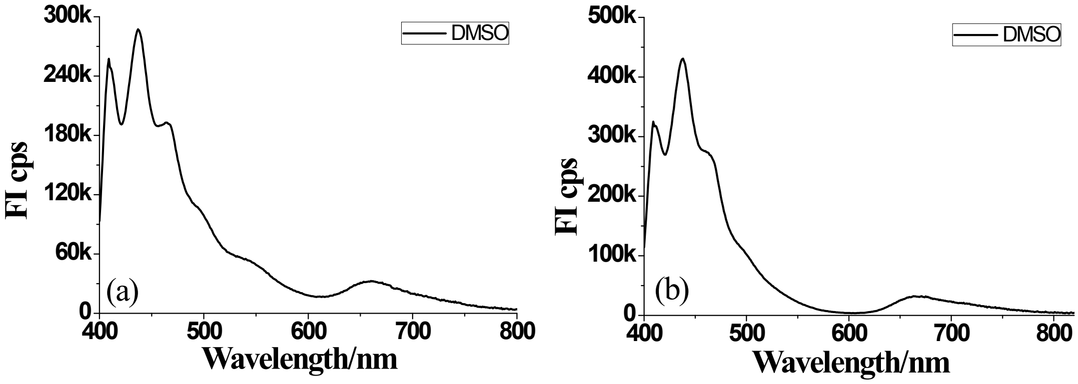


Fig. S64 Normalized emission spectra of **4c-*Z*** (20 μM) in DMSO: (a) probe (b) probe+CN^-

Table S1: optical data of **4a-c** measured at room temperature

Dye	λ_{abs}/nm		λ_{em}/nm		$\triangle_{ss}{}^{a}$/nm	Probe	Probe+CN^-	solvent
	Probe	Probe+CN^-	Probe	Probe+CN^-		$\varepsilon/M^{-1}cm^{-1}$	$\varepsilon/M^{-1}cm^{-1}$	
4a-E	432	593	476	426 657	225	19400	9365	Hexane
4a-E	431	595	475	427 649	218	36335	72035	Ether
4a-E	438	603	488	436 658	220	37190	69200	DCM
4a-E	435 615	609	479 643	485 650	215	30985 2355	58690	THF
4a-E	437	589	487	430 659	222	32415	1490	MeOH
4a-E	437	596	488 658	429 660	223	33855	3625	EtOH
4a-E	435 596	595	489 645	430 652	217	35355 1495	61370	MeCN
4a-E	435	604	479 640	430 651	216	36510	67365	Acetone
4a-E	441 606	606	469 653	438 657	216	28275 10780	67235	DMSO
4a-Z	415	592	498	426 664	249	16095	5150	Hexane
4a-Z	418 598	594	462	427 649	231	34780 1705	68240	Ether
4a-Z	425	604	473	659	234	34585	76055	DCM
4a-Z	425	609	470 642	651	226	31505	78825	THF
4a-Z	427	432 587	529 654	469 661	234	34095	32130/89 30	MeOH
4a-Z	436	435	504	663	227	33850	34400/95	EtOH

	595	598	658			2135	30	
4a-Z	422	596	469	429	230	31915	66575	MeCN
	596		648	652		7300		
4a-Z	422	604	470	651	229	30195	81955	Acetone
	606		645			1795		
4a-Z	434	606	653	438	224	22850	72700	DMSO
	607			658				
4b-E	440	623	470	427	230	28850	6900	Hexane
				670				
4b-E	433	626	488	428	238	30310	46495	Ether
				671				
4b-E	448	632	493	435	231	33095	27960	DCM
				679				
4b-E	444	641	492	431	234	30290	44895	THF
				678				
4b-E	444	446	495	490	44	33970	32265	MeOH
		606					780	
4b-E	444	443	499	434	221	49495	26475	EtOH
		635		665			2675	
4b-E	442	624	489	434	231	29380	22910	MeCN
	619			673		855		
4b-E	441	634	491	430	233	32170	36510	Acetone
				674				
4b-E	447	633	497	438	228	25230	42455	DMSO
	635		663	675				
4c-Z	414	586	468	429	255	22415	8895	Hexane
				669				
4c-Z	413	591	473	430	248	18505	61245	Ether
				661				
4c-Z	424	601	476	437	247	20475	38795	DCM
				671				
4c-Z	416	609	528	430	249	15120	36685	THF
			742	665				
4c-Z	416	586	515	437	247	14825	9630	MeOH
				663				
4c-Z	418	596	508	434	252	17705	29705	EtOH
	601			670		1725		
4c-Z	420	591	507	430	244	16385	37520	MeCN
	594			664		2310		
4c-Z	418	600	506	431	243	18635	43835	Acetone
	601			661		2830		
4c-Z	405	604	437	438	259	7095	38615	DMSO
	604		661	664		29465		

[a] Stokes' shift.

Optical data of **4a-c** in various solvents (Hexane, Ether, Dichloromethane, Tetrahydrofuran, Methanol, Ethanol, Acetonitrile, Acetone, Dimethyl sulfoxide).

Table S2: Recovery data for CN^- detection in spiked water samples

Samples	Spiked (μM)	Found (μM)	Recovery (%)	SD (%), n>5
Tap water	80	97.81	122.26	4.25
	150	120.97	80.64	3.36
	300	259.23	86.41	6.25
Drinking water	35	33.92	86.41	0.42
	80	73.15	91.44	4.15
	150	129.89	86.6	5.93
River water	80	39.34	49.18	6.99
	150	63.94	42.63	1.27
	300	196.08	65.36	15.98
Mineral water	60	40.07	66.78	3.113
	150	50.76	33.84	6.548
	300	108.28	36.09	10.45

Recovery data of probe **4a-*E*** for CN^- detection in spiked water samples (Tap water, Drinking water, River water and Mineral water).

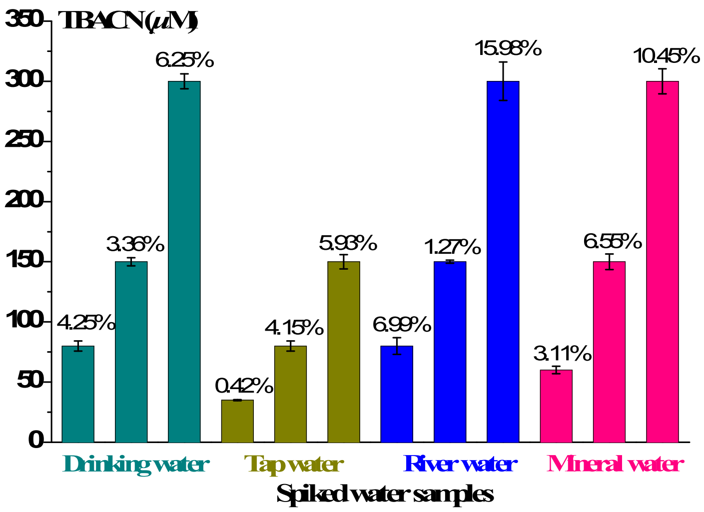


Fig. S65 Error bars for cyanides detection in real-world water samples.

NMR spectra of intermediate compounds

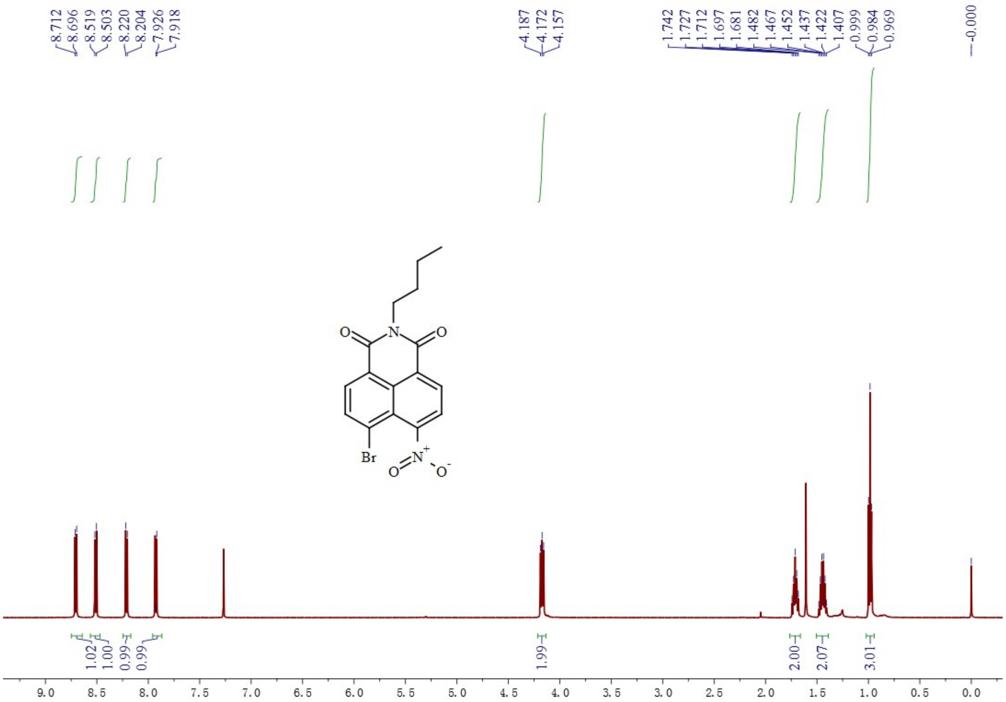


Fig. S66 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **10**

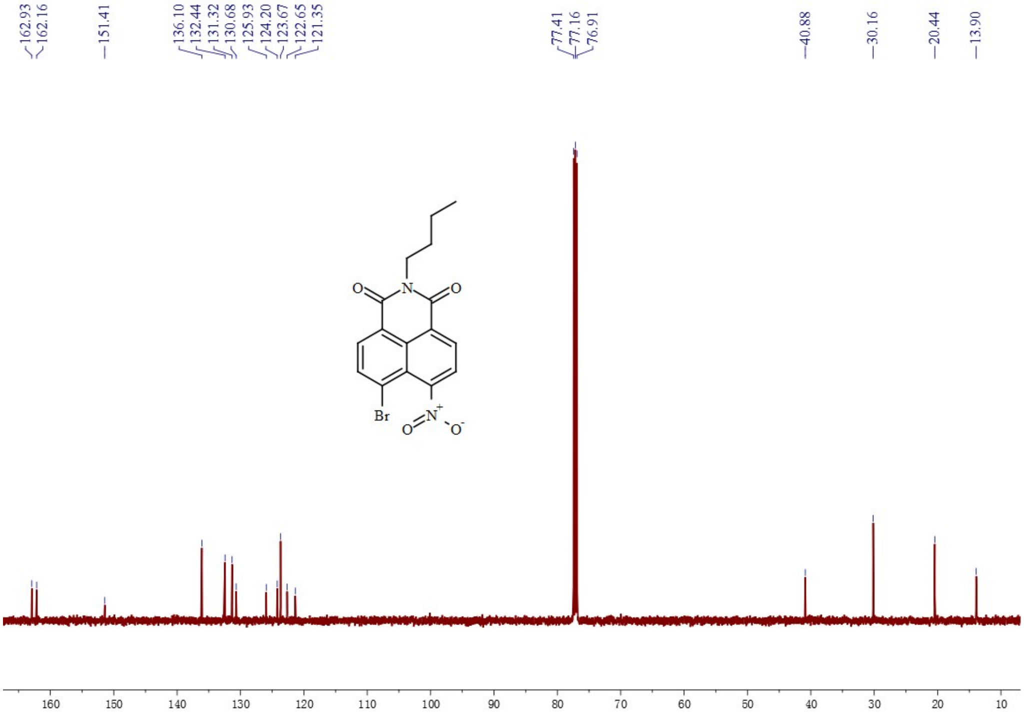


Fig. S67 ^{13}C-NMR (125 MHz, $CDCl_3$) spectra of compound **10**

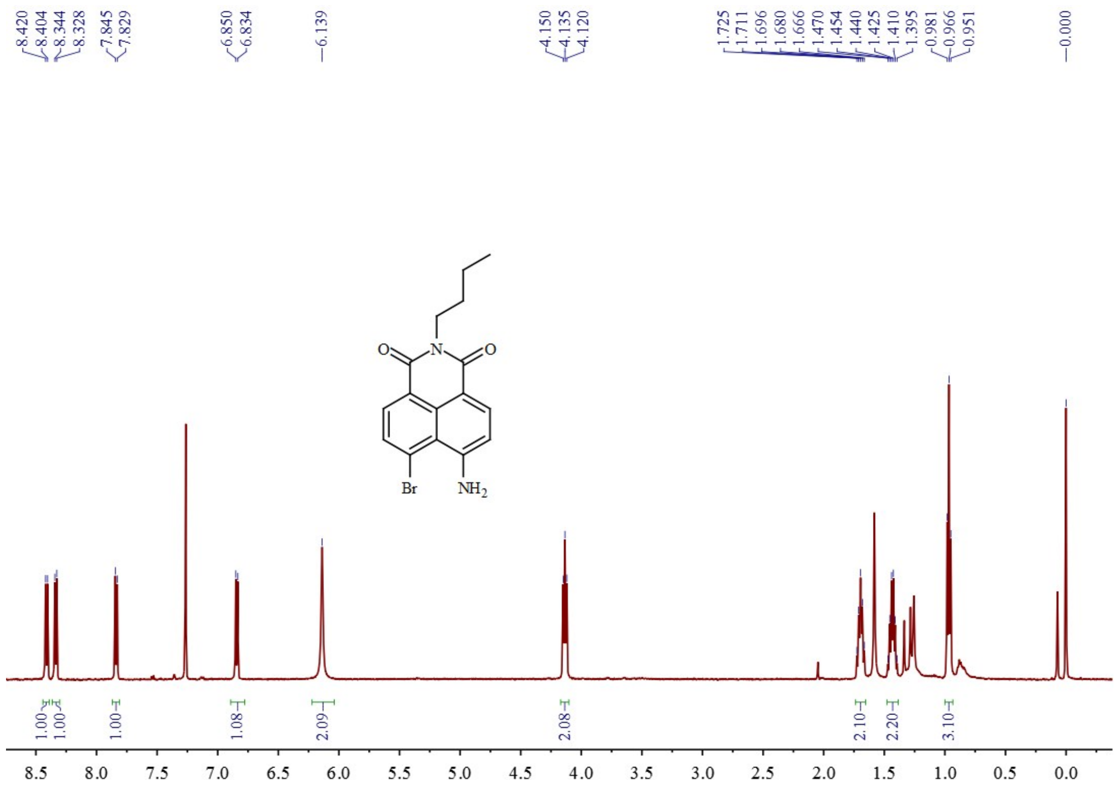


Fig. S68 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **1b**

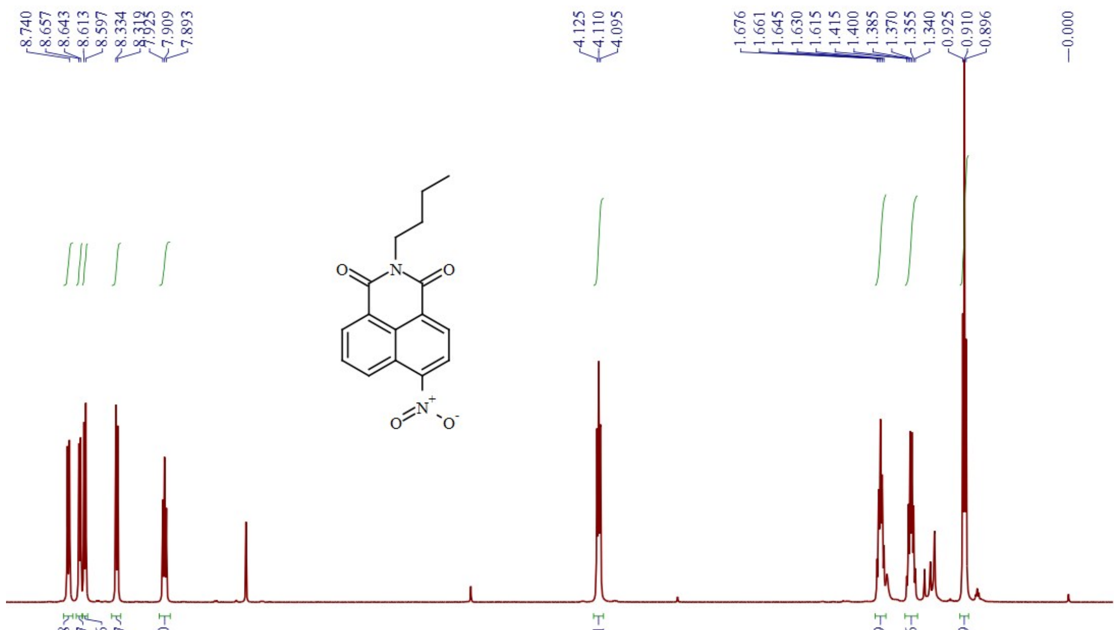


Fig. S69 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **4**

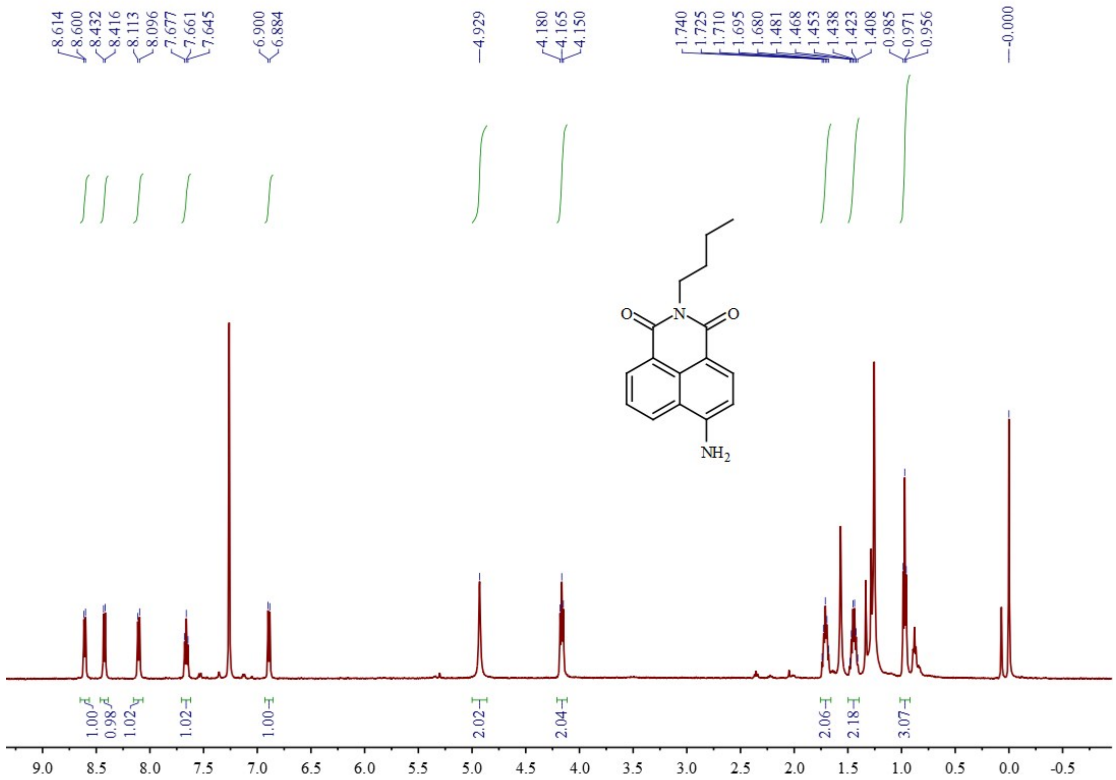


Fig. S70 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **1a**

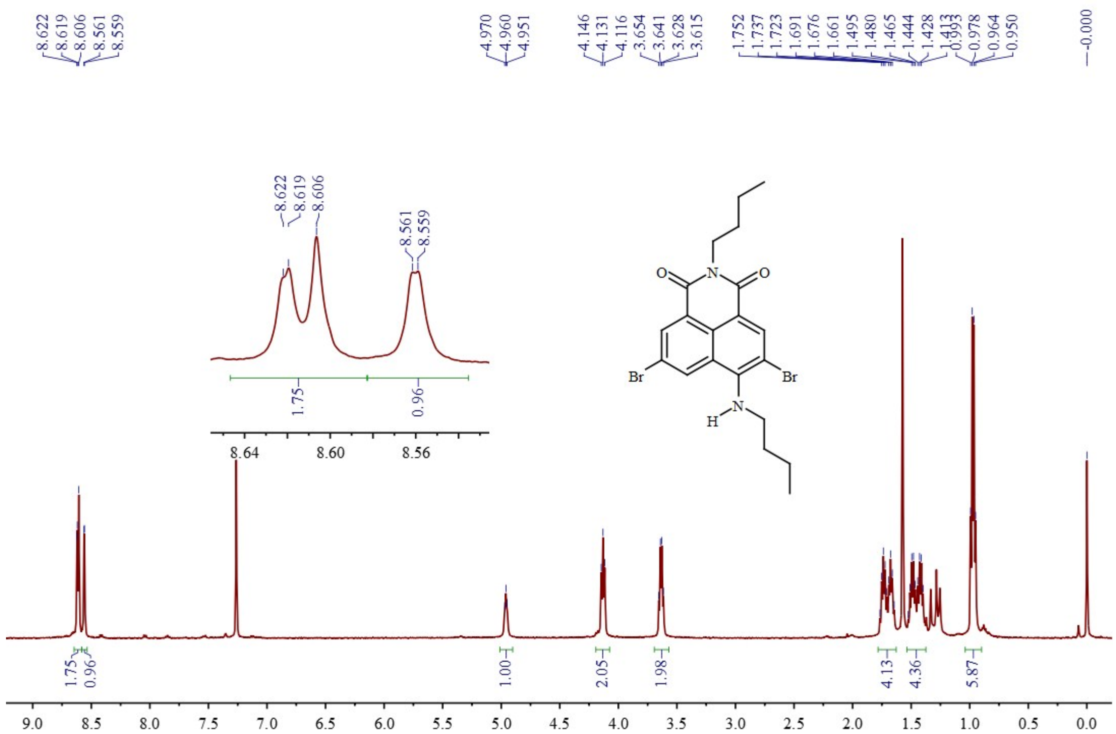


Fig. S71 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **15**

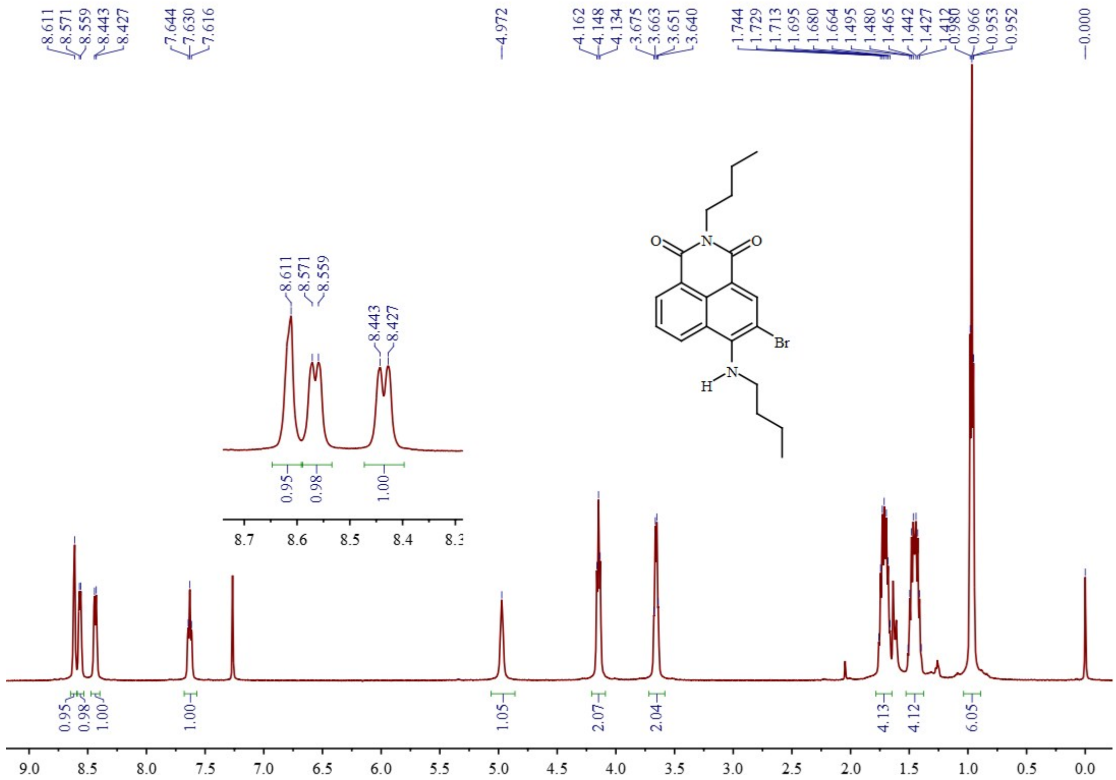


Fig. S72 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **14**

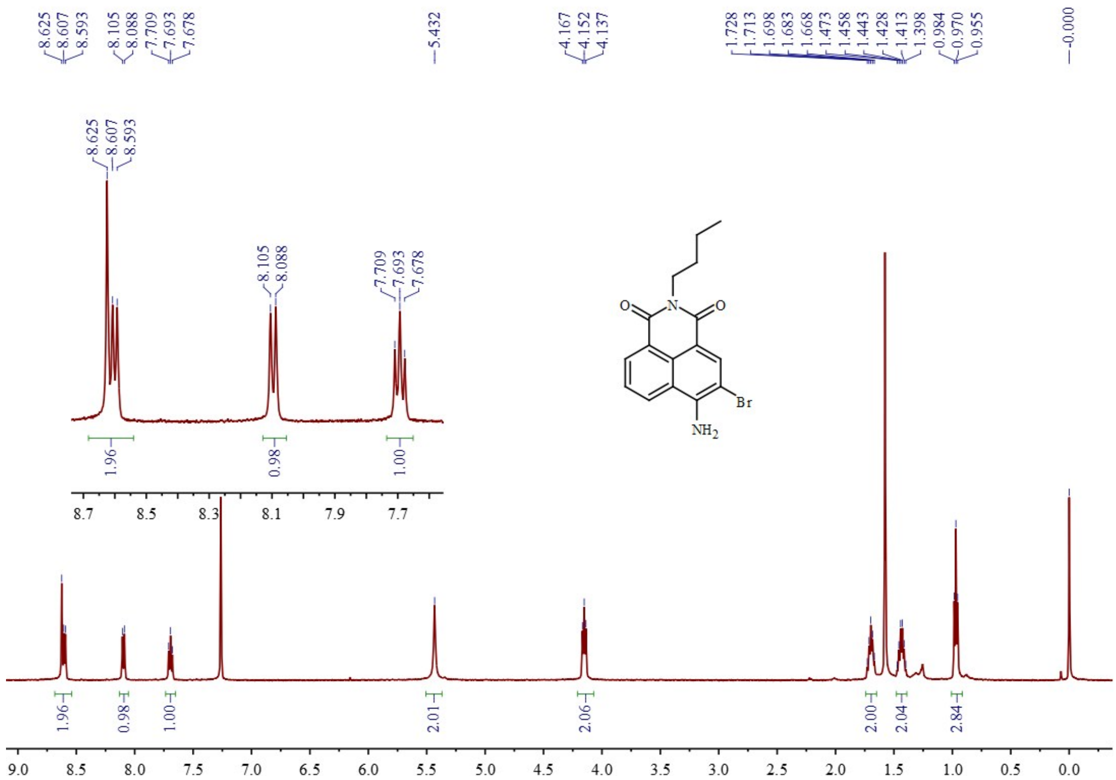


Fig. S73 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **1c**

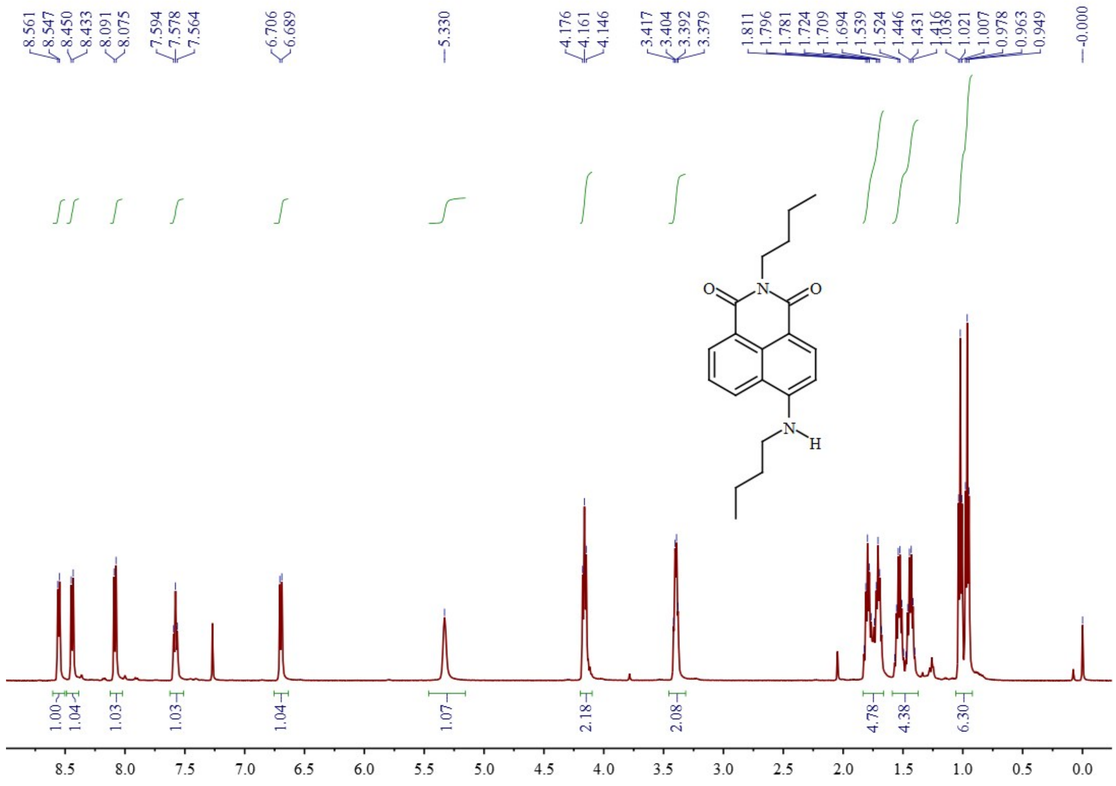


Fig. S74 ^{1}H-NMR (500MHz, $CDCl_3$) spectra of compound **13**