Electronic Supplementary Information (ESI)

For

A Dual State Emission Luminogen based on 1,3,3-trimethylindoline and chroman-2,4-dione Conjugate for Highly Selective Dual Channel Detection of Cyanide Ion

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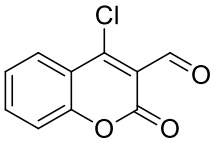

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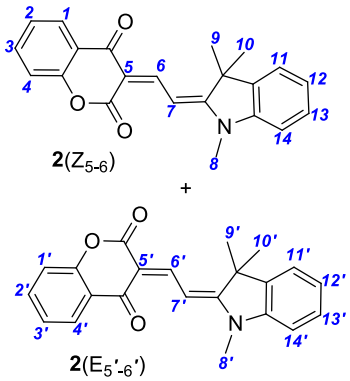

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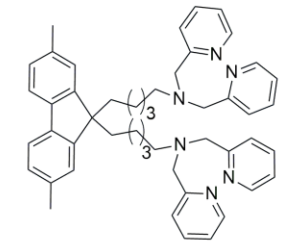

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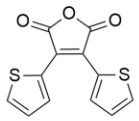
ACS Appl. Mater. Interfaces 2016



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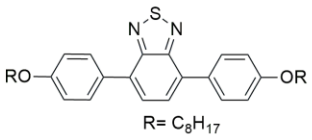

L. Meng et al.
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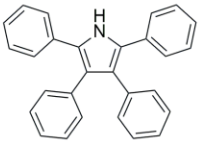

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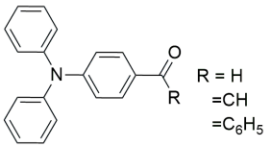

Z. Qian et al
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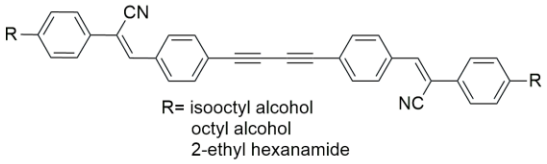

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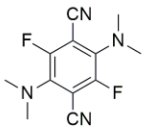

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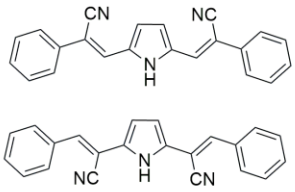

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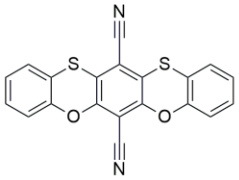

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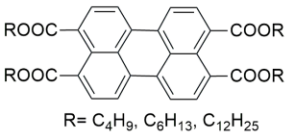

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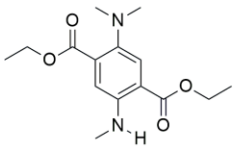

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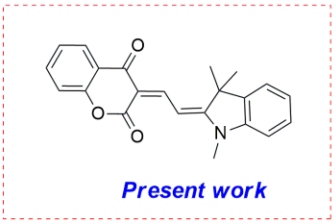


Present work

Chart S1: Chemical structures of reported dual state emission luminogen (DSEgen).

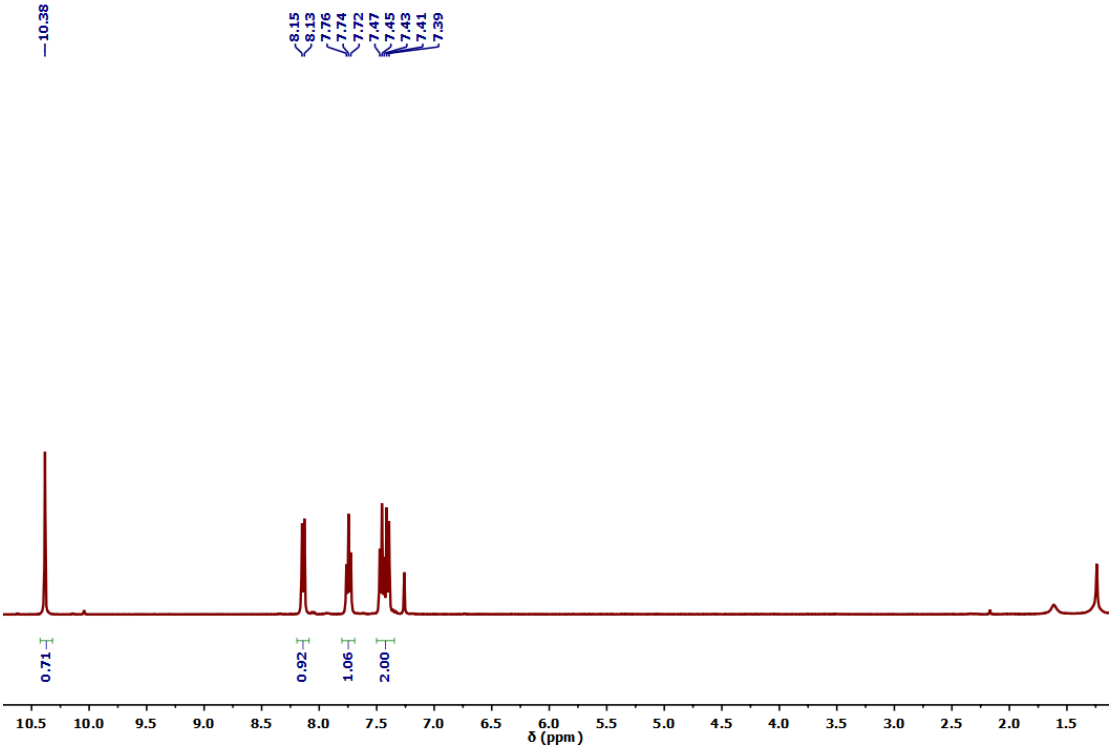


Figure S1. ^{1}H-NMR spectrum of **1** in $CDCl_3$.

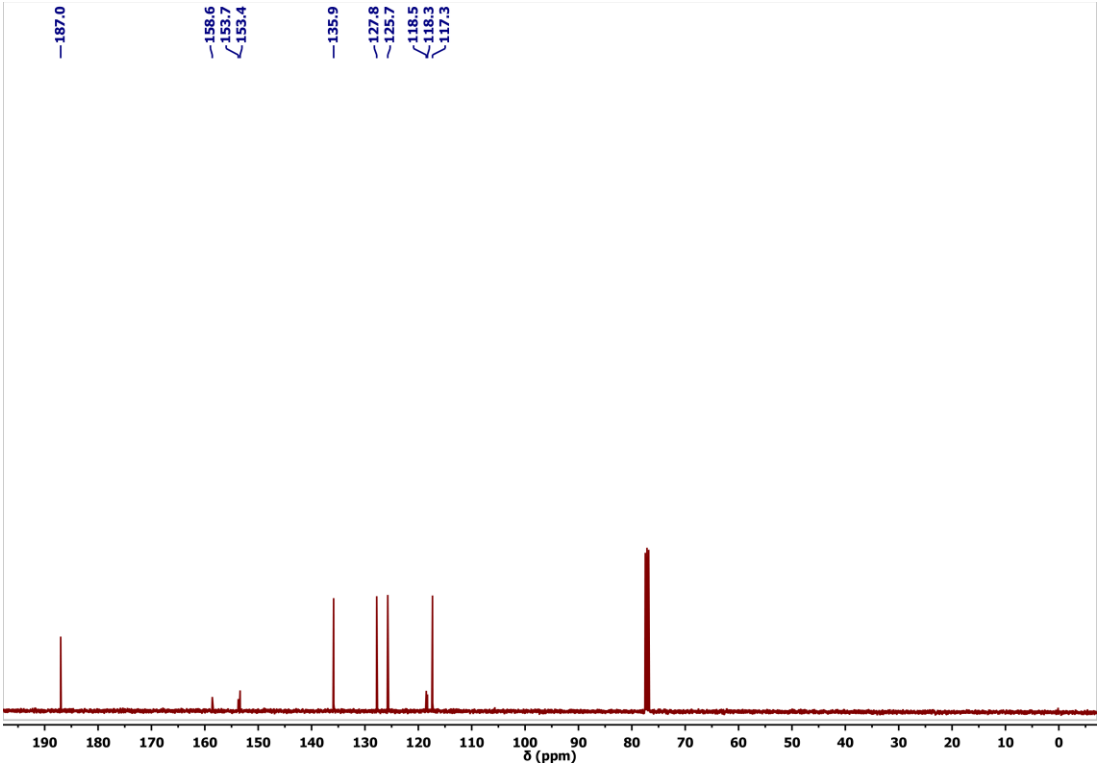


Figure S2. ^{13}C-NMR spectrum of **1** in $CDCl_3$.

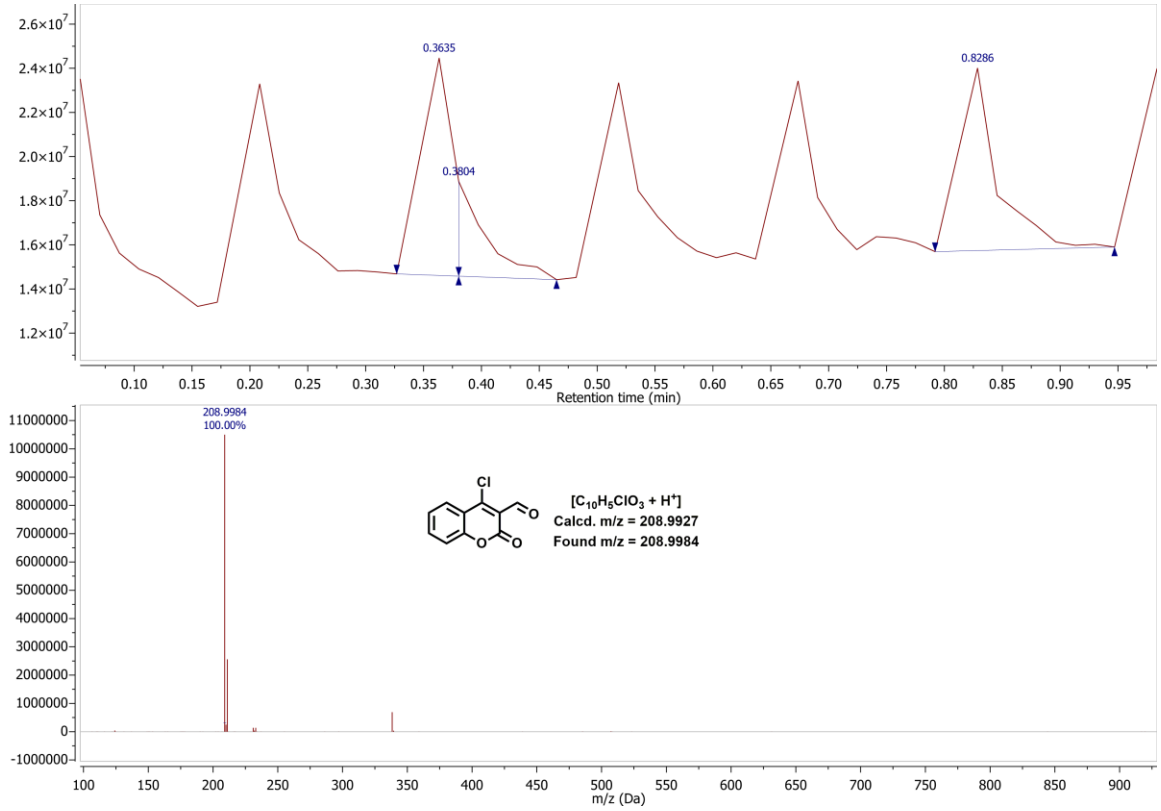


Figure S3. ESI-HRMS of **1** in CH_3CN.

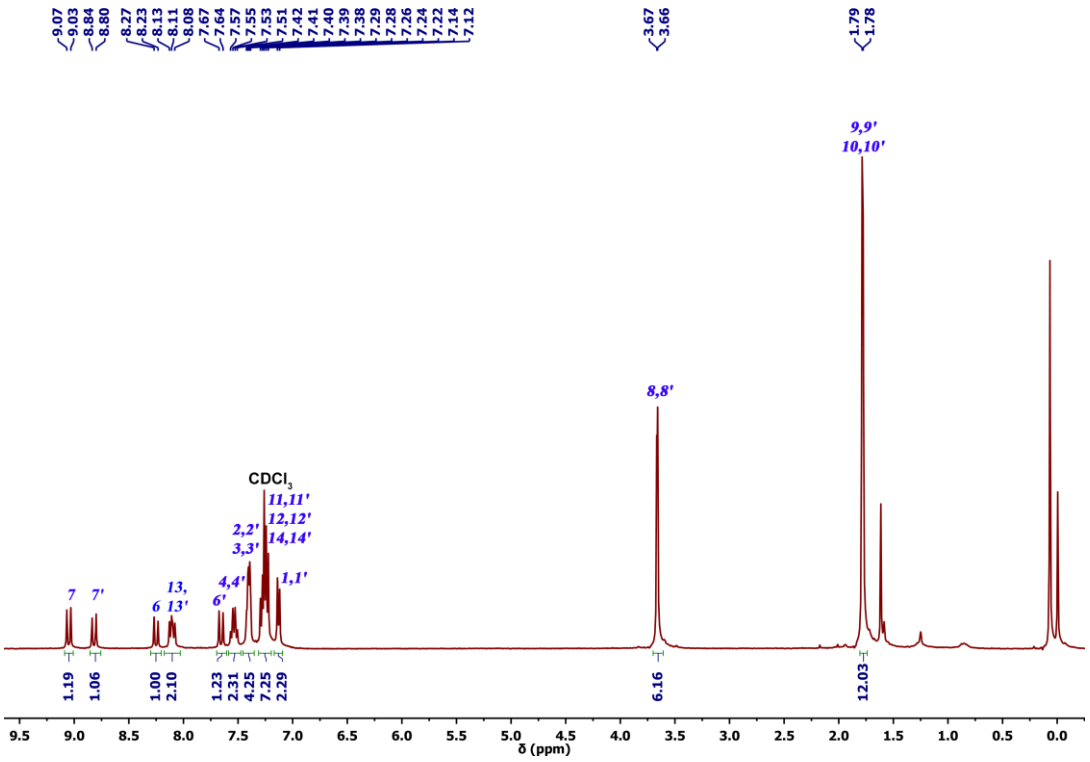


Figure S4. ^{1}H-NMR spectrum of **2** in $CDCl_3$.

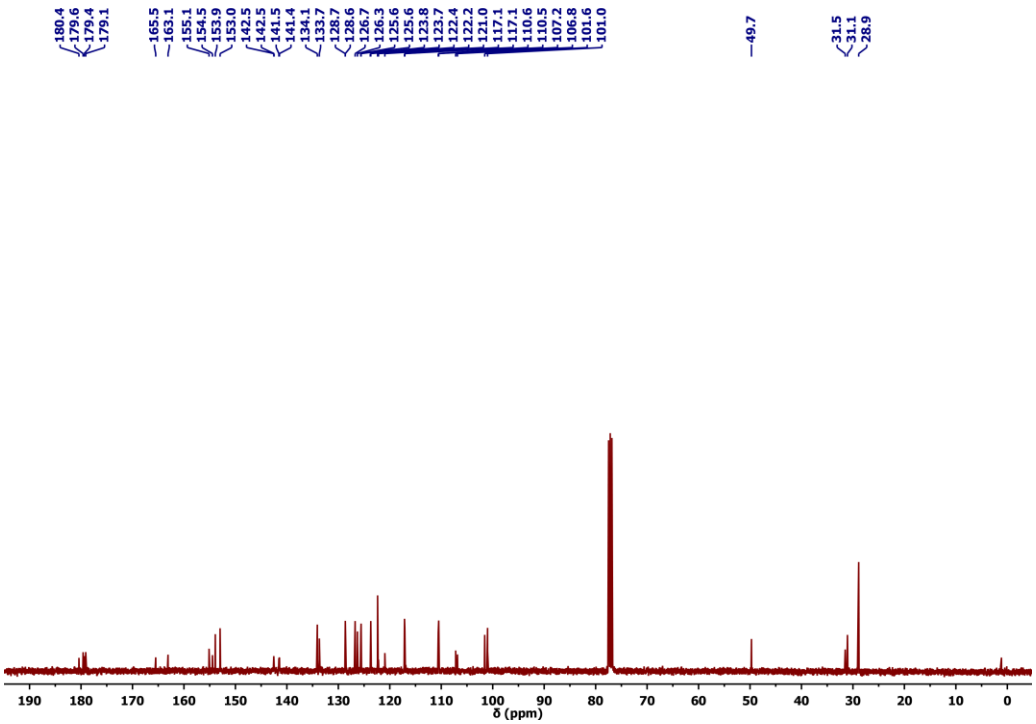


Figure S5. ^{13}C-NMR spectrum of **2** in $CDCl_3$.

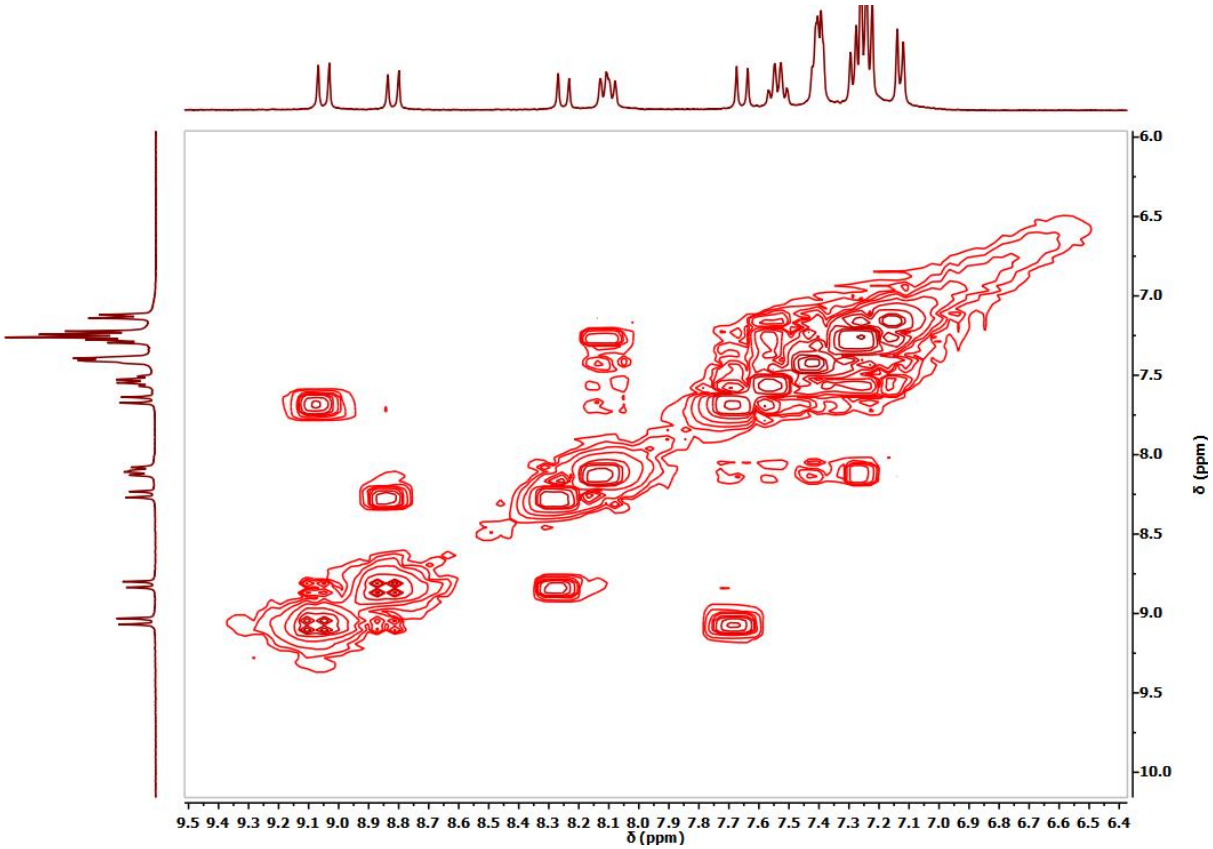


Figure S6. ^{1}H -^{1}H COSY NMR spectrum of compound **2** in $CDCl_3$.

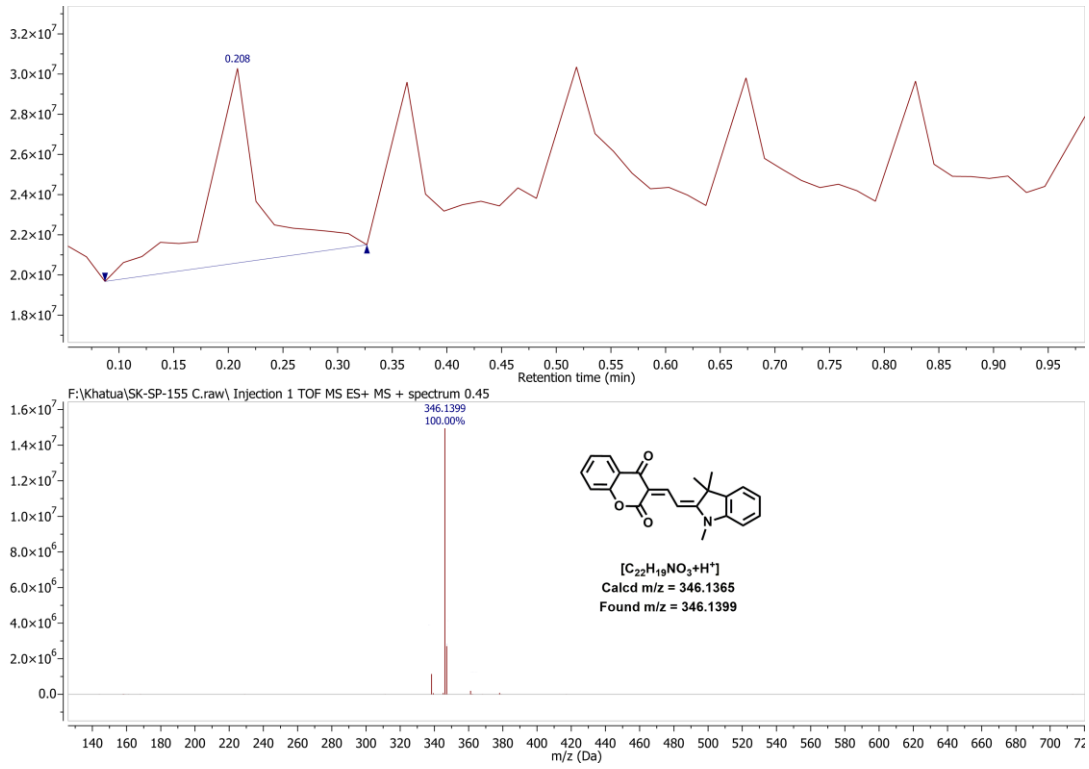


Figure S7. ESI-HRMS of **2** in CH_3CN.

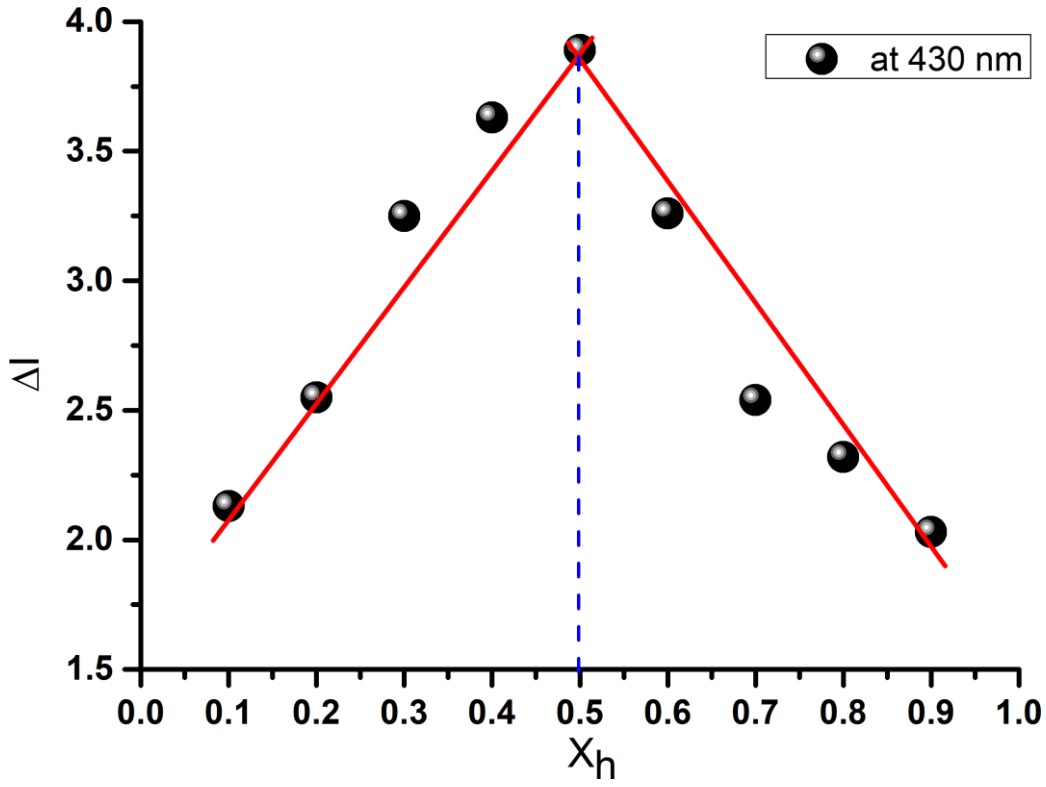


Figure S8. Job plot analysis between probe **2** and CN^- at a total concentration of 5 μM in CH_3CN (λ_{em} = 430 nm).

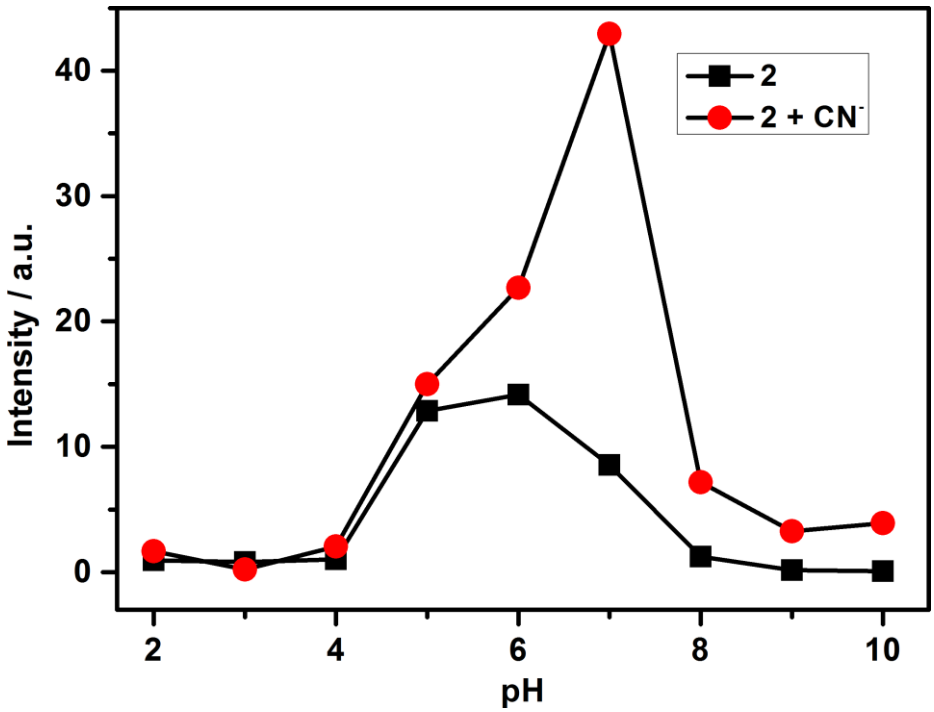


Figure S9. pH-dependent fluorescence response of **2** (10 μM) upon addition of CN^- (8 equiv.) at 430 nm.

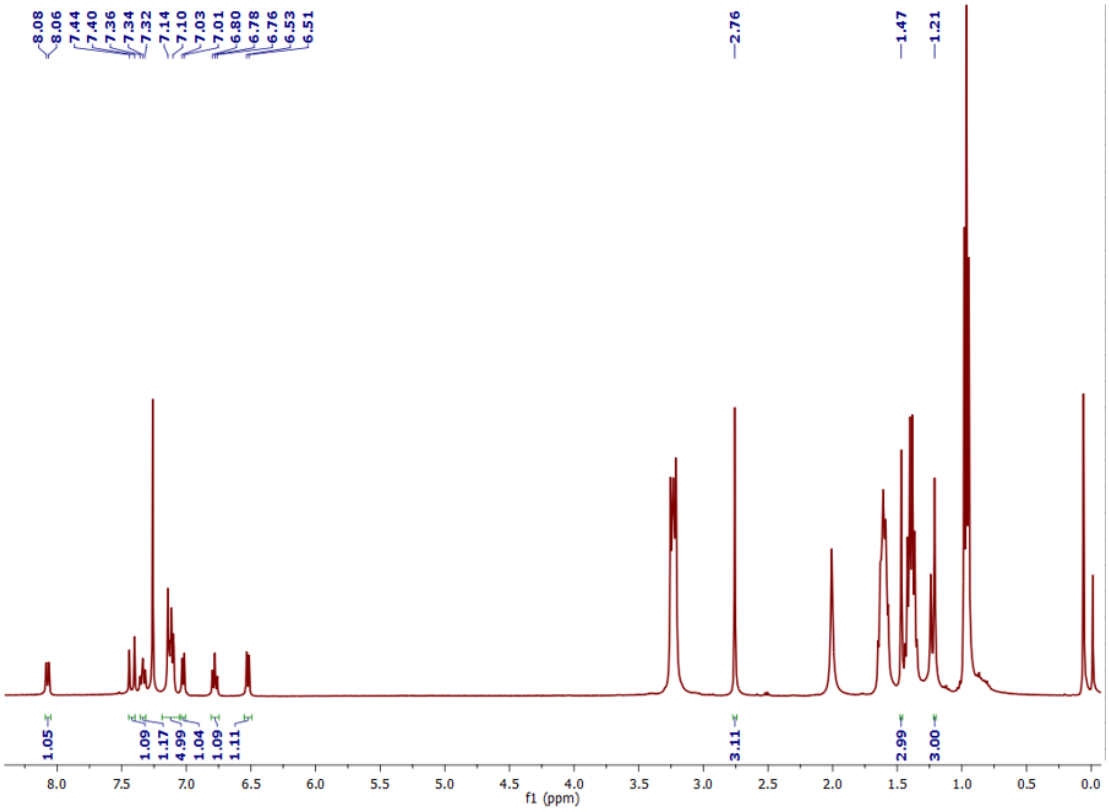


Figure S10. ^{1}H-NMR spectrum of **2-CN** (compound **2** + 1.25 equiv. TBACN) in $CDCl_3$.

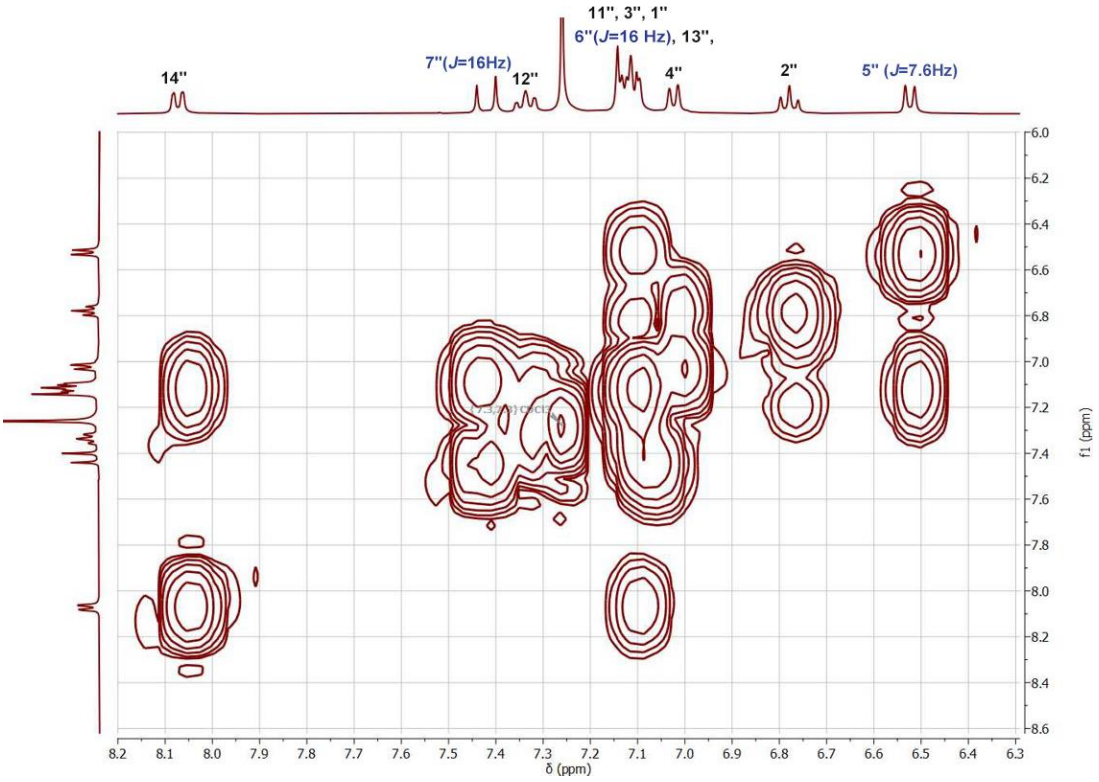


Figure S11. ^{1}H -^{1}H COSY NMR spectrum of compound **2-CN** (compound **2** + 1.25 equiv. TBACN) in $CDCl_3$.

Calculation of Limit of Detection (LOD)

The detection limit was calculated based on PL titration data. The standard deviation of the blank solution was calculated with ten replicate data of 2 without the addition of CN^- in PL spectroscopy. Finally, the detection limit (DL) of 2 for cyanide was determined from the following equation.

$$DL = 3\sigma/K$$

Where σ is the standard deviation of the blank solution, and K is the slope obtained from the plot of the calibration curve.

Calculation of Excited States Lifetimes

The fluorescence lifetimes of probe **2** (5 μM) and in the presence of cyanide in acetonitrile were measured using a time-correlated single-photon counting (TCSPC) picosecond spectrophotometer (LifeSpec-II, Edinburgh Instruments, U.K.) at excitation wavelength of 340 nm. In addition, the luminescence lifetime of probe **2** (5 μM) with 95% PEG in the CH_3CN/PEG mixture was also collected at excitation wavelength of 485 nm. The fluorescence decays were monitored at the corresponding emission maxima as observed in the steady-state fluorescence measurement. The EzTime decay analysis software was used to fit the data. Fluorescence decays were fitted with a biexponential function with χ^2 ~1, which indicates the good fitting. Experimental lifetimes were calculated using the following multiexponential decay equation

$$<\tau> = \sum a_i \tau_i$$

Whereas, ai is the amplitude of the ith decay component (ai = αi/Σαi) and τ_i is the excited state luminescence lifetime of the i^{th} component.

Electrochemical Studies

A three electrodes cell system was taken for electrochemical analysis. The setup contains a Pt working electrode, a Pt wire auxiliary electrode, and an Ag wire as a pseudo-reference electrode. Experiments were performed on 1.0 mM dry and degassed acetonitrile solution of probe **2** in the presence of supporting electrolyte tetra-*n*-butylammonium perchlorate (0.1 M). The electrochemical potential window was calibrated using ferrocene (as internal standard) after each experiment. The standard redox potential of the ferrocene/ferrocenium (Fc/Fc^+) couple was taken as +0.400 V vs. Ag wire electrode. A scan rate of 100 mV s^{-1} was fixed for all the measurements.

Preparation of test paper strips with probe 2 and solid-state CN^- detection

Probe **2**-coated paper strips were prepared with Whatman filter paper. Evenly sliced Whatman papers were immersed in the acetonitrile solution of probe **2** (100 μM) and dried in air for 15 min. To demonstrate its application in a paper-based fluorescence sensing of cyanide, different concentration of cyanide solution in acetonitrile (1 μM–50 μM) were added dropwise on the test paper strips using a micropipette. After drying the strips under vacuum, the strips were observed under a 365 nm UV light, and the photos were taken by a Nikon D90 DSLR camera with a Nikon AF-S DX Nikkor 35 mm f/1.8 G Prime Lens.

Calculation of Quantum Yield

The quantum yield of **2** and **2-CN** were determined in acetonitrile using Quinine sulphate (Φ_R = 0.6 in 5N H_2SO_4) respectively. The quantum yields were calculated according to the following equation:

$$\Phi_S = \Phi_R \times \frac{1 - 10^{-A_R}}{1 - 10^{-A_S}} \times \frac{I_S}{I_R} \times \frac{{\eta_S}^2}{{\eta_R}^2}$$

Where, Φ_S and Φ_R are the quantum yields of the sample and reference, respectively. A_S and A_R are the absorbance at the excitation wavelength of sample and reference, respectively. The area under the emission spectra of the sample and the reference are denoted as I_S and I_R respectively. The η_S and η_R are represented as the refractive index of the respective solvents used in this study at 25°C (here, acetonitrile).

X-ray Crystallography

Single crystals of compounds **1** and **2** suitable for X-ray diffraction were obtained by slow evaporation of acetone and methanol/chloroform mixture(1:1) after four (for **1)** and three days (for **2**), respectively. The X-ray data of **1** was collected at 293 K with Agilent Xcalibur (Eos, Gemini) diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data was collected, reduced, and cell refinement was done in CrysAlis PRO (Agilent, 2013) software.[1] The absorption of the compounds was corrected by SCALE3 ABSPACK multi-scan method in CrysAlisPro. The X-ray data of **2 (Z)** and **2 (E)** was collected in a Bruker D8 single-crystal X-ray diffractometer using graphite monochromatized Mo(Kα) (λ = 0.71073 Å) radiation. The data was collected using the Bruker APEX II program suite[2] and the data integration and reduction were processed with SAINT[3] software. Empirical absorption correction was applied to the collected reflections with SADABS.[4] The structures of **1** and **2** were solved by direct methods using the program SHELXS-97[5] and refined by full-matrix least-squares calculations (F^2) by using the SHELXL-2018/3[6] within the WinGX[7]. The crystal data quality of compound **2 (*E*)** was not good. It contains highly disorder solvent water molecule and the PLATON SQUEEZE program[8] was applied to calculate the contribution of electron density in the region to the structure factors in the form of FAB file which was used in subsequent refinement cycle. Molecular and packing diagrams were generated using Mercury. Geometrical calculations were performed using PLATON[8] and ORTEP figures were prepared using ORTEP-3.[9] Crystal data collection and refinement details, for compounds **1** and **2 (*Z*)** and 2 **(*E*)** are given in Table S1 and selected bond lengths and angles are given in Table S2 , Table S3 and Table S4 respectively. The cif file was deposited with the Cambridge Crystallographic Data Centre, and the following code was allocated: CCDC-2085904 and CCDC-2085905 and 2373472 for compounds **1** and **2Z** and **2E** respectively. This data can be obtained free of charge via the Internet: www.ccdc.cam.ac.uk/ data_request/cif

Table S1. Crystal data and structure refinement details of **1** and **2**.

	1	**2 (*Z*)**	**2 (*E*)**
Empirical formula	$C_{20}H_{10}Cl_2O_6$	$C_{22}H_{19}NO_3$	$C_{22}H_{19}NO_3$
Formula weight	417.18	345.38	345.38
Temperature	293(2) K	293(2) K	302(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	*C 2/m*
Unit cell dimensions	*a* = 7.3370(11) Å	*a* = 8.3545(4) Å	*a* = 15.848(10) Å
	b = 9.4146(15) Å	*b* = 10.5110(6) Å	*b* = 6.963(4) Å
	c = 13.7164(19) Å	*c* = 11.3187(6) Å	*c* = 17.373(11) Å
	α= 80.661(12)°.	α = 103.653(2)°.	α= 90°.
	β= 77.547(12)°.	β =95.545(2)°.	β= 104.891(18)°.
	γ = 71.660(14)°.	γ = 111.128(2)°.	γ = 90°.
Volume, Z	873.6(2) $Å^3$, 2	882.64(8) $Å^3$, 2	1853(2) $Å^3$, 4
Density (calcd.)	1.300 Mg/m^3	1.300 Mg/m^3	1.238 Mg/m^3
Absorption coefficient	0.409 mm^{-1}	0.087 mm^{-1}	0.082 mm^{-1}
F (000)	424	364	728
Θ range for data collection	3.182 to 26.371°.	2.428 to 30.551°.	2.426 to 18.640°.
Reflections collected	6352	31067	2371
Independent reflections	3549 [R(*int*) = 0.0460]	5351 [R(*int*) = 0.0216]	780 [R(int) = 0.0740]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Data / restraints / parameters	3549 / 0 / 253	5351 / 0 / 300	780 / 0 / 157
Goodness-of-fit on F^2	1.086	1.067	1.116
Final *R* indices [$I>2\sigma(I)$][a]	*R1* = 0.0929, *wR2* = 0.2316	*R1* = 0.0482, *wR2* = 0.1367	*R1* = 0.0983, *wR2* = 0.2183
R indices (all data) [a]	*R1* = 0.1266, *wR2* = 0.2592	*R1* = 0.0576, *wR2* = 0.1461	*R1* = 0.1495, *wR2* = 0.2881

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

Table S2. Bond lengths [Å] and angles [°] for **1**

Bond lengths (Å)			
C(1)-O(2)	1.192(6)	C(1)-O(1)	1.373(5)
C(1)-C(2)	1.450(7)	C(2)-C(4)	1.358(6)
C(2)-C(3)	1.477(6)	C(3)-O(3)	1.178(7)
C(4)-C(10)	1.446(6)	C(4)-Cl(1)	1.701(5)
C(5)-C(6)	1.376(8)	C(5)-C(10)	1.398(6)
C(6)-C(7)	1.384(9)	C(7)-C(8)	1.353(8)
C(8)-C(9)	1.402(6)	C(9)-O(1)	1.358(6)
C(9)-C(10)	1.387(7)	C(11)-O(5)	1.180(6)
C(11)-O(4)	1.358(6)	C(11)-C(12)	1.471(6)
C(12)-C(14)	1.338(7)	C(12)-C(13)	1.486(7)
C(13)-O(6)	1.151(7)	C(14)-C(19)	1.439(7)
C(14)-Cl(2)	1.704(4)	C(15)-C(16)	1.345(8)
C(15)-C(19)	1.405(7)	C(16)-C(17)	1.415(10)
C(17)-C(18)	1.356(9)	C(18)-C(20)	1.371(7)
C(19)-C(20)	1.388(7)	C(20)-O(4)	1.373(6)
Bond angles (°)			
O(2)-C(1)-O(1)	116.5(4)	O(2)-C(1)-C(2)	125.1(5)
O(1)-C(1)-C(2)	118.3(4)	C(4)-C(2)-C(1)	119.8(4)
C(4)-C(2)-C(3)	125.4(5)	C(1)-C(2)-C(3)	114.8(4)
O(3)-C(3)-C(2)	126.6(5)	C(2)-C(4)-C(10)	121.0(4)
C(2)-C(4)-Cl(1)	122.2(4)	C(10)-C(4)-Cl(1)	116.8(4)
C(6)-C(5)-C(10)	119.9(6)	C(5)-C(6)-C(7)	120.4(5)
C(8)-C(7)-C(6)	121.5(5)	C(7)-C(8)-C(9)	118.2(5)
O(1)-C(9)-C(10)	122.9(4)	O(1)-C(9)-C(8)	115.3(5)
C(10)-C(9)-C(8)	121.8(5)	C(9)-C(10)-C(5)	118.2(4)
C(9)-C(10)-C(4)	116.7(4)	C(5)-C(10)-C(4)	125.1(5)
O(5)-C(11)-O(4)	117.8(5)	O(5)-C(11)-C(12)	124.9(5)
O(4)-C(11)-C(12)	117.3(4)	C(14)-C(12)-C(11)	120.3(4)
C(14)-C(12)-C(13)	126.6(4)	C(11)-C(12)-C(13)	113.1(5)
O(6)-C(13)-C(12)	128.3(6)	C(12)-C(14)-C(19)	121.1(4)
C(12)-C(14)-Cl(2)	121.5(4)	C(19)-C(14)-Cl(2)	117.4(4)

C(16)-C(15)-C(19)	122.0(6)	C(15)-C(16)-C(17)	119.3(6)
C(18)-C(17)-C(16)	119.8(5)	C(17)-C(18)-C(20)	120.4(6)
C(20)-C(19)-C(15)	117.2(5)	C(20)-C(19)-C(14)	117.3(4)
C(15)-C(19)-C(14)	125.5(5)	C(18)-C(20)-O(4)	116.9(5)
C(18)-C(20)-C(19)	121.4(5)	O(4)-C(20)-C(19)	121.6(4)
C(9)-O(1)-C(1)	121.3(4)	C(11)-O(4)-C(20)	122.2(4)

Table S3. Bond lengths [Å] and angles [°] for **2 (*Z*)**

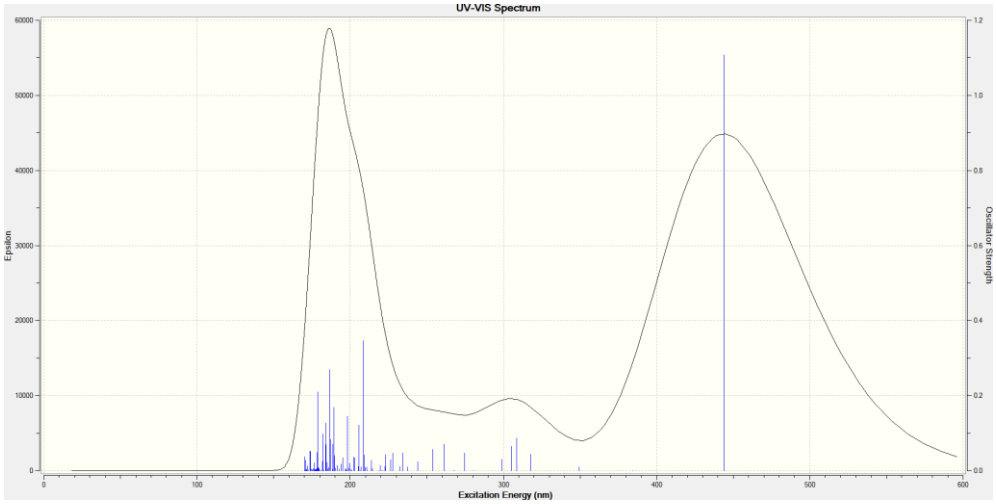
Bond lengths (Å)			
O(1)-C(9)	1.2038(15)	O(2)-C(1)	1.3694(15)
O(2)-C(9)	1.3885(14)	O(3)-C(7)	1.2356(14)
N(1)-C(12)	1.3435(12)	N(1)-C(19)	1.4035(13)
N(1)-C(20)	1.4514(13)	C(1)-C(6)	1.3824(17)
C(1)-C(2)	1.3919(17)	C(2)-C(3)	1.372(2)
C(3)-C(4)	1.382(3)	C(16)-C(17)	1.376(2)
C(4)-C(5)	1.375(2)	C(7)-C(8)	1.4430(15)
C(5)-C(6)	1.3961(17)	C(8)-C(9)	1.4446(16)
C(6)-C(7)	1.4695(15)	C(10)-C(11)	1.3781(15)
C(8)-C(10)	1.3950(15)	C(11)-C(12)	1.3947(15)
C(12)-C(13)	1.5332(14)	C(13)-C(14)	1.5093(15)
C(13)-C(21)	1.5371(17)	C(13)-C(22)	1.5384(16)
C(14)-C(15)	1.3762(16)	C(15)-C(16)	1.392(2)
C(14)-C(19)	1.3846(14)		
Bond angles (°)			
C(1)-O(2)-C(9)	121.96(9)	C(12)-N(1)-C(19)	111.89(8)
C(12)-N(1)-C(20)	125.68(9)	C(19)-N(1)-C(20)	122.40(9)
O(2)-C(1)-C(6)	122.66(10)	O(2)-C(1)-C(2)	116.28(12)
C(6)-C(1)-C(2)	121.06(13)	C(3)-C(2)-C(1)	118.88(15)
C(2)-C(3)-C(4)	121.08(14)	C(4)-C(5)-C(6)	120.37(15)
C(5)-C(4)-C(3)	119.78(14)	C(1)-C(6)-C(5)	118.82(12)

Table S4. Bond lengths [Å] and angles [°] for **2 (*E*)**

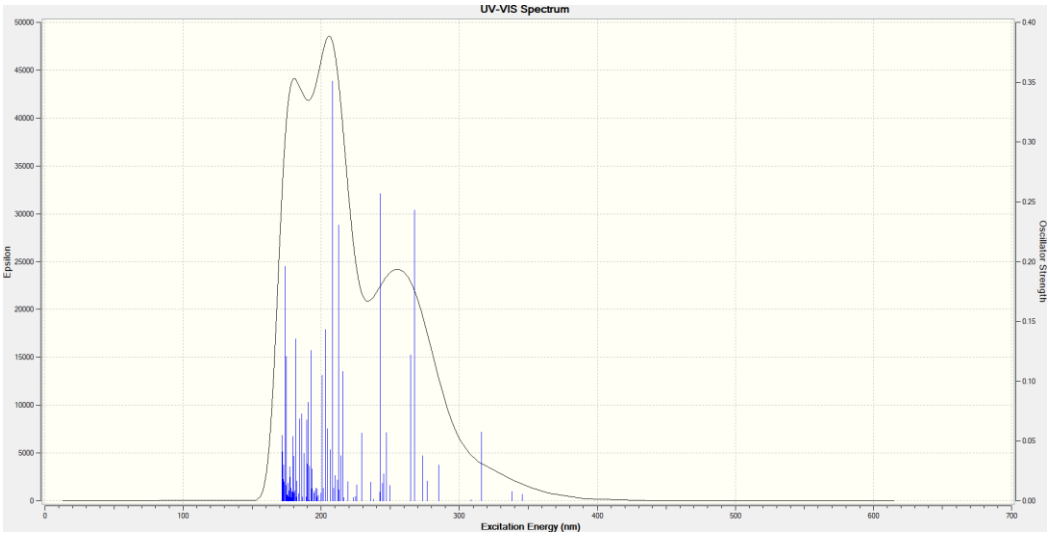
Bond lengths (Å)			
O(1)-C(9)	1.398(12)	O(1)-C(1)	1.402(12)
O(2)-C(9)	1.213(12)	N(1)-C(12)	1.332(13)
N(1)-C(19)	1.423(13)	N(1)-C(20)	1.475(12)
O(3)-C(7)	1.263(13)	C(11)-C(12)	1.391(14)
C(11)-C(10)	1.417(15)	C(12)-C(13)	1.505(14)
C(13)-C(14)	1.522(14)	C(13)-C(21)	1.567(9)
C(13)-C(21)#1	1.567(9)	C(9)-C(8)	1.431(15)
C(14)-C(15)	1.361(14)	C(14)-C(19)	1.370(13)
C(16)-C(17)	1.385(14)	C(16)-C(15)	1.430(14)
C(10)-C(8)	1.380(14)	C(6)-C(5)	1.364(15)
C(6)-C(1)	1.377(14)	C(6)-C(7)	1.503(15)
C(19)-C(18)	1.372(14)	C(1)-C(2)	1.367(15)
C(8)-C(7)	1.412(15)	C(17)-C(18)	1.386(14)
C(5)-C(4)	1.372(16)	C(2)-C(3)	1.340(16)
C(4)-C(3)	1.379(17)		
Bond angles (°)			
C(9)-O(1)-C(1)	120.3(9)	C(12)-N(1)-C(19)	110.5(9)
C(12)-N(1)-C(20)	125.3(9)	C(19)-N(1)-C(20)	124.2(10)
C(12)-C(11)-C(10)	125.1(11)	N(1)-C(12)-C(11)	121.0(10)
N(1)-C(12)-C(13)	110.0(10)	C(11)-C(12)-C(13)	129.0(12)
C(12)-C(13)-C(14)	101.6(9)	C(12)-C(13)-C(21)	113.4(6)
O(2)-C(9)-O(1)	113.2(11)	O(2)-C(9)-C(8)	126.7(12)
O(1)-C(9)-C(8)	120.1(10)	C(15)-C(14)-C(19)	120.5(11)
C(15)-C(14)-C(13)	131.2(11)	C(19)-C(14)-C(13)	108.4(10)
C(17)-C(16)-C(15)	119.1(11)	C(8)-C(10)-C(11)	129.2(11)
C(5)-C(6)-C(1)	118.2(12)	C(5)-C(6)-C(7)	123.4(13)
C(1)-C(6)-C(7)	118.3(13)	C(14)-C(19)-C(18)	123.7(11)
C(14)-C(19)-N(1)	109.5(11)	C(18)-C(19)-N(1)	126.8(13)
C(2)-C(1)-C(6)	120.6(11)	C(2)-C(1)-O(1)	116.8(14)
C(6)-C(1)-O(1)	122.6(12)	C(10)-C(8)-C(7)	123.7(10)
C(10)-C(8)-C(9)	115.7(11)	C(7)-C(8)-C(9)	120.6(12)

Computational studies

The geometry optimization of Probe **2** (singlet) and **2-CN** was performed with the Gaussian 09 and Gaussian 16 program packages, using density functional theory (DFT). The B3LYP/6-31G+(d)[10] basis set was used for C, H, N, O. Time-dependent density functional theory (TD-DFT) calculations at the ground-state geometry in acetonitrile were performed in conjunction with the conductor like polarizable continuum model (CPCM)[11] for acetonitrile with a spin-restricted formalism to examine low-energy excitations at the same level of calculation, which employed for geometry optimizations with 50 number states.



(a)



(b)

Figure S9. Theoretical UV-vis spectrum of (a) probe **2** and (b) **2-CN.**

Table S4. Selected bond lengths and angles in the optimized structure of **2**

Bond lengths (Å)			
O(1)-C(1)	1.3715	C(14) -C(19)	1.3992
O(1) -C(9)	1.3902	C(15) -C(16)	1.4020
O(2) -C(9)	1.2156	C(16) -C(17)	1.3953
O(3-C(7)	1.2352	C(17) -C(18)	1.3998
N(1) -C(12)	1.3693	C(18) -C(19)	1.3925
N(1) -C(19)	1.4079	N(1) -C(20)	1.4543
C(1) -C(2)	1.3977	C(1) -C(6)	1.3993
C(2) -C(3)	1.3907	C(3) -C(4)	1.4029
C(4) -C(5)	1.3871	C(5) -C(6)	1.4030
C(6) -C(7)	1.4777	C(7) -C(8)	1.4752
C(8) -C(9)	1.4627	C(8) -C(10)	1.3877
C(10) -C(11)	1.4065	C(11) -C(12)	1.3830
C(12) -C(13)	1.5401	C(13) -C(14)	1.5224
C(13) -C(21)	1.5481	C(13) -C(22)	1.5481
Bond Angles (°)			
C(1) -O(1) -C(9)	122.73	C(12) -C(13) -C(14)	101.33
C(12) -N(1) -C(19)	111.77	C(12) -C(13) -C(21)	111.77
C(12) -N(1) -C(20)	123.52	C(12) -C(13) -C(22)	111.77
C(19) -N(1) -C(20)	124.71	C(14) -C(13) -C(21)	110.29
O(1) -C(1) -C(2)	116.42	C(14) -C(13) -C(22)	110.29
O(1) -C(1) -C(6)	122.64	C(21) -C(13) -C(22)	111.02
C(2) -C(1) -C(6)	120.94	C(13) -C(14) -C(15)	130.56
C(1) -C(2) -C(3)	119.16	C(13) -C(14) -C(19)	109.48
C(2) -C(3) -C(4)	120.70	C(15) -C(14) -C(19)	119.97
C(3) -C(4) -C(5)	119.56	C(14) -C(15) -C(16)	119.09
C(4) -C(5) -C(6)	120.67	C(15) -C(16) -C(17)	120.30
C(1) -C(6) -C(5)	118.95	C(16) -C(17) -C(18)	121.18
C(1) -C(6) -C(7)	119.88	C(17) -C(18) -C19)	117.58
C(5) -C(6) -C(7)	121.16	N(1) -C(19) -C(14)	108.86
O(3) -C(7) -C(6)	121.55	N(1) -C(19) -C(18)	129.26

O(3) -C(7) -C(8)	122.81	C(14) -C(19) -C(18)	121.88
C(6) -C(7) -C(8)	115.64	C(7) -C(8) -C(9)	121.40
C(7) -C(8) -C(10)	116.51	C(9) -C(8) -C(10)	122.10
O(1) -C(9) -O(2)	115.66	O(1) -C(9) -C(8)	117.72

Table S5. Selected bond lengths and angles in the optimized structure of **2-CN**

Bond lengths (Å)			
O(1) -C(4)	1.3573	C(14) -C(15)	1.5217
O(1) -C(7)	1.3953	C(15) -C(21)	1.5337
O(2) -C(9)	1.3527	C(15) -C(22)	1.5434
O(3) -C(7)	1.2094	C(16) -C(17)	1.4009
N(1) -C(12)	1.4766	C(17) -C(18)	1.3941
N(1) -C(13)	1.4065	C(18) -C(19)	1.4023
N(1) -C(20)	1.4595	N(2) -C(23)	1.1622
O(2) -H(5)	0.9700	C(1) -C(2)	1.4023
C(1) -C(6)	1.3870	C(2) -C(3)	1.3888
C(3) -C(4)	1.3958	C(4) -C(5)	1.4065
C(5) -C(9)	1.4497	C(5) -C(6)	1.4094
C(7) -C(8)	1.4700	C(8) -C(10)	1.4620
C(8) -C(9)	1.3757	C(10) -C(11)	1.3440
C(11) -C(12)	1.5163	C(12) -C(15)	1.6069

Bond Angles (°)			
C(4) -O(1) -C(7)	122.80	C(11) -C(12) -C(15)	113.93
C(12) -N(1) -C(13)	107.48	C(11) -C(12) -C(23)	106.85
C(12) -N(1) -C(20)	118.85	C(15) -C(12) -C(23)	109.63
C(13) -N(1) -C(20)	118.62	N(1) -C(12) -C(15)	102.94
C(9) -O(2) -H(5)	111.00	N(1) -C(13) -C(14)	111.02
C(2) -C(1) -C(6)	119.86	N(1) -C(13) -C(16)	128.01
C(1) -C(2) -C(3)	120.38	C(14) -C(13) -C(16)	120.97
C(2) -C(3) -C(4)	119.41	C(13) -C(14) -C(19)	120.39
O(1) -C(4) -C(5)	121.51	C(15) -C(14)-C(19)	130.21
C(3) -C(4) -C(5)	121.40	C(13) -C(14) -C(15)	109.29

O(1) -C(4) -C(3)	117.09	C(12) -C(15) -C(14)	99.83
C(4) -C(5) -C(9)	117.36	C(12) -C(15) -C(22)	110.43
C(6) -C(5) -C(9)	124.67	C(14) -C(15)-C(21)	114.49
C(4) -C(5) -C(6)	117.97	C(12) -C(15) -C(21)	113.19
C(1) -C(6) -C(5)	120.97	C(21) -C(15)-C(22)	109.70
O(1) -C(7) -C(8)	117.72	C(14) -C(15) -C(22)	108.80
O(3) -C(7) -C(8)	125.69	C(13) -C(16) -C(17)	118.12
O(1) -C(7) -O(3)	116.59	C(16) -C(17) -C(18)	121.25
C(7) -C(8) -C(10)	114.34	C(17) -C(18) -C(19)	119.98
C(9) -C(8) -C(10)	126.70	C(14) -C(19) -C(18)	119.29
C(7) -C(8) -C(9)	118.96	N(2) -C(23) -C(12)	176.63
O(2) -C(9) -C(8)	118.71	C(5) -C(9) -C(8)	121.64

Table S6: The x,y,z Cartesian coordinates of the compound **2** calculated using Gaussian 09 at [B3LYP/6-31G+ (d)] level.

Probe 2					
C	4.59489	0.68719	0.00055	H	-5.03059 -2.65119 0.00112
C	5.94974	1.03041	0.00095	C	-6.43812 -1.00947 0.00124
H	6.2257	2.07922	0.00144	H	-7.31052 -1.6549 0.00176
C	6.90482	0.01939	0.00066	C	-6.59865 0.37715 0.00103
H	7.95848	0.28298	0.00098	H	-7.59705 0.80366 0.00144
C	6.52035	-1.32953	-0.00003	C	-5.49319 1.23535 0.00039
H	7.27419	-2.11042	-0.00025	H	-5.63595 2.31032 0.00045
C	5.17175	-1.65736	-0.00042	C	-4.22738 0.65497 -0.00013
H	4.83052	-2.68729	-0.00096	C	-2.74606 2.71327 -0.00179
C	4.19176	-0.65303	-0.00013	H	-2.18721 3.01863 0.88826
C	2.75298	-0.98932	-0.00048	H	-3.70667 3.22492 -0.00701
C	1.82858	0.16134	-0.00018	H	-2.17932 3.01596 -0.88768
C	2.32489	1.53687	0.00028	C	-2.18438 -1.84595 -1.27582
C	0.4734	-0.13426	-0.00042	H	-2.7372 -2.7901 -1.29784
H	0.28927	-1.20413	-0.00085	H	-1.11776 -2.07761 -1.30723
C	-0.62075	0.74993	-0.00022	H	-2.44106 -1.28236 -2.17692
H	-0.38987	1.80684	0.00021	C	-2.1837 -1.84567 1.2755

C	-1.94659 0.35735 -0.0005	H	-2.43961 -1.28175 2.17662
C	-2.56247 -1.0547 -0.00015	H	-1.11713 -2.07759 1.30625
C	-4.04993 -0.73285 0.00022	H	-2.73674 -2.78968 1.29819
C	-5.15416 -1.5718 0.00086	N	-2.96309 1.2753 -0.00102
O	2.3626 -2.16057 -0.00112	O	3.70238 1.72789 0.00085

Table S7: The x,y,z Cartesian coordinates of the compound **2-CN** calculated using Gaussian 09 at [B3LYP/6-31G+ (d)] level.

2-CN			
C	-6.50215 -1.2486 -0.11679	H	-2.98129 -2.52012 0.47695
C	-6.94431 0.06809 -0.30836	H	0.02762 1.33643 0.08266
C	-6.03241 1.11431 -0.36257	H	-0.05919 -1.69859 0.51148
C	-4.66961 0.84415 -0.21995	H	4.54705 2.50931 1.21528
C	-4.20001 -0.46604 -0.01678	H	6.71686 2.28446 0.04288
C	-5.14718 -1.5088 0.02466	H	7.09933 0.45167 -1.57904
O	-3.81951 1.89997 -0.28903	H	5.2873 -1.18805 -2.05718
C	-2.43566 1.76503 -0.17387	H	2.7582 0.96283 2.83615
C	-1.89681 0.41573 0.05073	H	1.08114 1.23358 2.29981
C	-2.76855 -0.64546 0.13121	H	2.31371 2.44541 1.94773
O	-2.26776 -1.88263 0.34585	H	3.35055 -2.82097 -1.87749
O	-1.78443 2.77969 -0.26009	H	1.87337 -3.1101 -0.95883
C	-0.44225 0.36332 0.18425	H	3.42846 -2.96855 -0.11512
C	0.34815 -0.70168 0.40286	H	2.48458 -0.7228 -2.97381
C	1.85931 -0.61929 0.49846	H	1.63937 0.50547 -2.02007
N	2.38689 0.73833 0.7433	C	2.83234 -2.58068 -0.94376
C	3.69141 0.78531 0.21772	C	1.86062 -0.56216 -2.08933
C	3.90386 -0.25915 -0.69357	C	2.27229 -1.5073 1.63021
C	2.62212 -1.06479 -0.84383	N	2.5763 -2.14628 2.55165
C	4.697 1.70966 0.49821	H	-7.21593 -2.06467 -0.08235
C	5.92157 1.5752 -0.16776	H	-8.00419 0.27366 -0.41905
C	6.13936 0.54389 -1.08094	H	-6.34421 2.14147 -0.51489
C	5.11926 -0.38039 -1.3497	H	-4.83394 -2.54216 0.15711
C	2.129 1.37152 2.032	H	0.91845 -1.10001 -2.22943

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