Supporting Information for

Donor and Acceptor Engineering for BINOL based AIEgens with Enhanced Fluorescence Performance

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Contents

1. Experimental Section

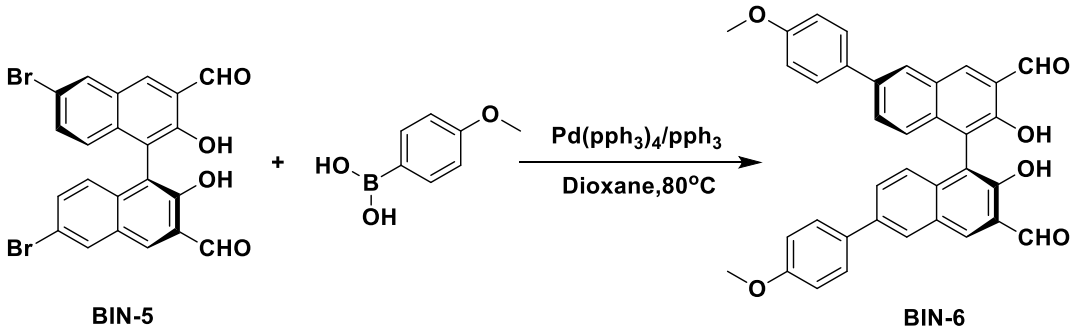
1.1 General information

All chemicals and solvents were commercially available and were used without further purification. All commercially available reagents were used as received unless otherwise stated. ^{1}H NMR, ^{13}C NMR spectra were measured on a Agilent AV-400 NMR spectrometer. Proton Chemical shifts of NMR spectra were given in ppm relative to internals reference TMS (1H, 0.00 ppm). ESI-HRMS spectral data were recorded on a Finnigan LCQDECA mass spectrometer. Fluorescence emission spectra were obtained using Hitachi F-7000 spectrometer at 298 K. Absorption spectra were recorded on a Hitachi PharmaSpec UV-1900 UV-Visible Spectrophotometer. The absolute fluorescence quantum yield was measured using a Hamamatsu quantum yield spectrometer C11347 Quantaurus_QY. The fluorescence lifetime was measured using a Hamamatsu Compact Fluorescence Lifetime Spectrometer C11367. The particle size was measured using a MAL-DLS Zetasizer Nano-ZS90. Single crystals were grown from isopropanol/ dichloroethane via solute solution diffusion method. Single crystal X-ray diffraction intensity data of **2b** were collected on Agilent Technologies (Gemini), and the data of **1c** were collected on Broker D8 venture with METAUET D2 X-ray source 153K, and the data of **2c** were collected Bruker apex II DUO with microfocus Mo X-ray Source 153K. The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP hybrid functional at the basis set level of 6-31G (d,p). All the calculations were performed using Gaussian 09 package. MTS method was used for testing the cell viability and described in the experimental section. HepG 2 cells were obtained from Shanghai Institute of Biochemistry and Cell Bioc emistry and Cell Biology, Chinese Academy of Science. Confocal lasing scanning microscopic (CLSM) images of single-photo were obtained using LSM 780 (Zeiss). Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were dried according to the standard methods prior to use. All of the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies.

1.2 Reaction procedures

Synthesis of BIN-5, BIN-COM and BIN-COP

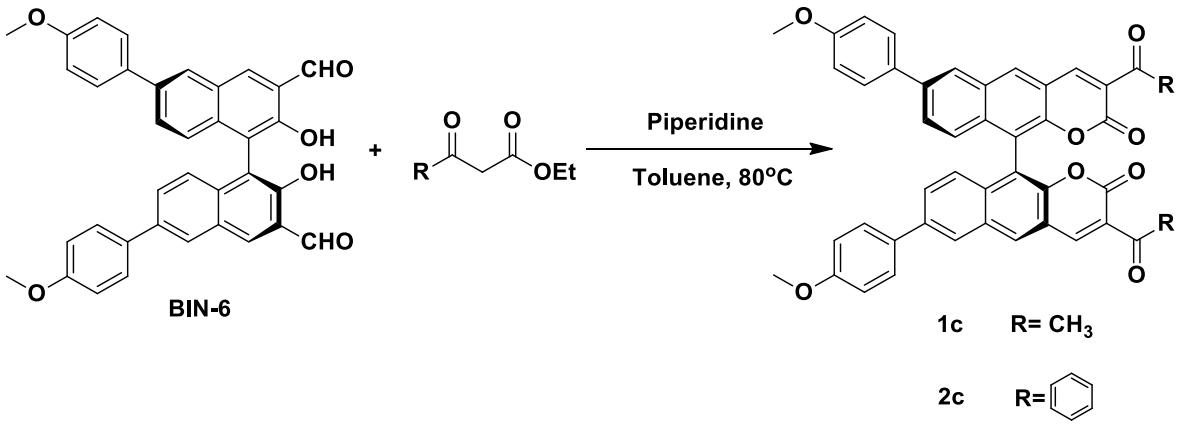
The synthesis methods of BIN-COM and BIN-COP can be found in our previous work.[1] The synthesis methods of BIN-5 can be found in reference.[2] All of them have been characterized by NMR and HRMS which are same as reference.



Scheme S1. Synthesis of **BIN-6**

Synthesis of BIN-6

Added 20 mL dioxane and 10 mL K_2CO_3 (2 M) in a flask. After solution was purged with argon, **BIN-5** (499.9 mg, 1 mmol), 4-methoxyphenylboronic acid (456 mg, 3 mmol), Pd $(PPh_3)_4$ (227 mg, 0.2 mmol), and PPh_3(104.8 mg, 0.4 mmol) were added. The gas phase mutually was displaced for 3 times. Then the mixture was heated at 80°C for about 8 h. After cooling down to room temperature, filter the solid residue, collect the filtrate, added an equal volume of water, part the organic phase. The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with hexane/ ethyl acetate (5:1). **BIN-6** was obtained as orange solids in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 10.62 (s, 2H), 10.22 (s, 2H), 8.40 (s, 2H), 8.14 (d, *J* = 1.6 Hz, 2H), 7.67 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 4H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 4H), 3.87 (s, 6H).



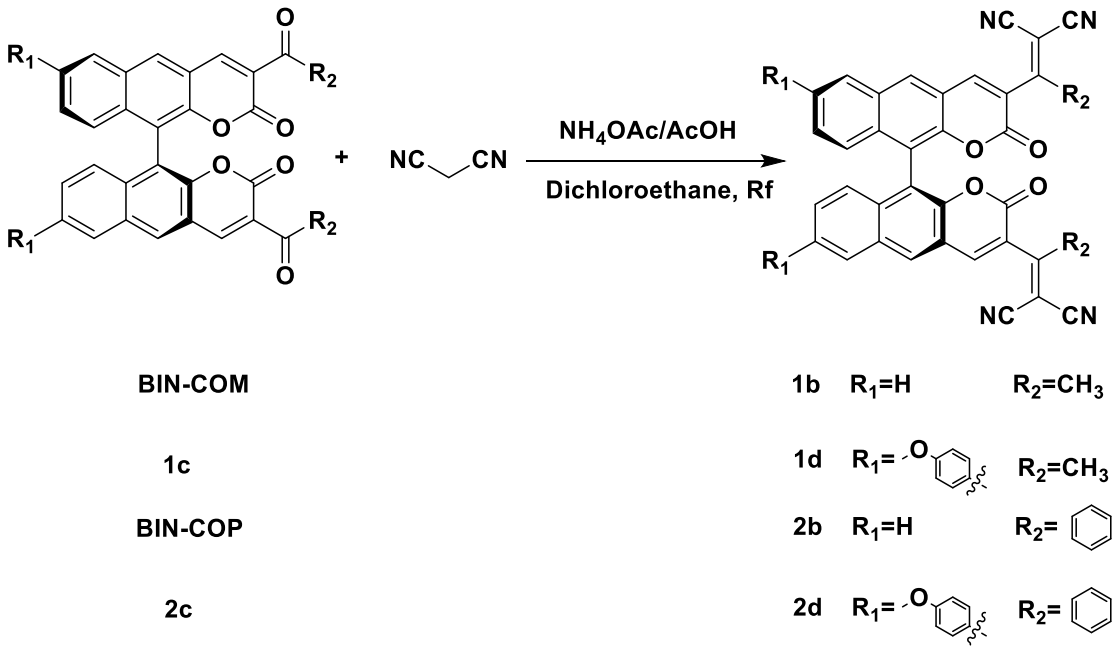
Scheme S2. Synthesis of **1c** and **2c**

Synthesis of 1c

After compound **BIN-6** (555 mg, 1 mmol) and ethyl acetoacetate (286.3 mg, 2.2 mmol) were added in toluene (10 mL), two drops piperidine were dropped to the stirred solution. Then the mixture was heated at reflux for about 4 h. After cooling down to room temperature, filter the solid residue, and the solid was washed with EtOH (5 mL× 3). The product was purified by recrystallized with methanol. **1c** was obtained as yellow solid in 77.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 8.77 (s, 2H), 8.47 (s, 2H), 8.23 (s, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 4H), 7.28 (s, 2H), 7.04 (d, *J* = 7.9 Hz, 4H), 3.89 (s, 6H), 2.70 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ(TMS, ppm) 195.4, 159.6, 158.8, 148.5, 147.6, 138.7, 134.1, 132.9, 132.1, 130.8, 129.8, 128.3, 126.1, 126.0, 125.1, 118.6, 116.3, 114.5, 55.4, 30.6.

Synthesis of 2c

The synthesis steps are the same as **1c**. **2c** was obtained as orange-red solid in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 8.33 (d, J = 18.2 Hz, 4H), 8.19 (s, 2H), 7.96 (d, J = 7.6 Hz, 4H), 7.69 (d, J = 9.3 Hz, 2H), 7.62 (d, J = 7.6 Hz, 6H), 7.48 (t, J = 7.4 Hz, 4H), 7.30 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 8.4 Hz, 4H), 3.86 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (TMS, ppm) 191.6, 159.6, 158.1, 148.4, 145.4, 138.7, 136.1, 133.9, 133.8, 132.2, 131.4, 130.9, 129.8, 129.5, 128.6, 128.3, 127.6, 126.1, 125.9, 118.5, 116.7, 114.4, 55.3.



Scheme S3. Synthesis of **1b**, **1d**, **2b** and **2d**.

Synthesis of 1b

BIN-COM (230 mg, 0.4 mmol) and malononitrile (158.4 mg, 2.4 mmol) was added in a round-bottomed flask. Add as little dichloroethane as possible to dissolve it. Then NH_4AcO (186 mg, 2.4 mmol) and AcOH (0.3 mL) was added. The mixture was heated at reflux for about 0.5 h. After cooling down to room temperature, added 20 mL DCM and 20 mL water, part the organic phase. The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with DCM. **1b** was obtained as yellow solid in 87% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ(TMS, ppm) 8.81 (d, *J* = 5.2 Hz, 4H), 8.35 (d, *J* = 8.3 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 2.59 (s, 6H). ^{13}C NMR (101 MHz, d_6-DMSO) δ(TMS, ppm) δ 176.8, 161.7, 152.7, 150.5, 139.3, 137.4, 135.4,135.2, 135.0, 131.7, 130.3, 129.5, 123.0, 120.8 117.5, 117.4, 92.6, 28.2.

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Synthesis of 1d

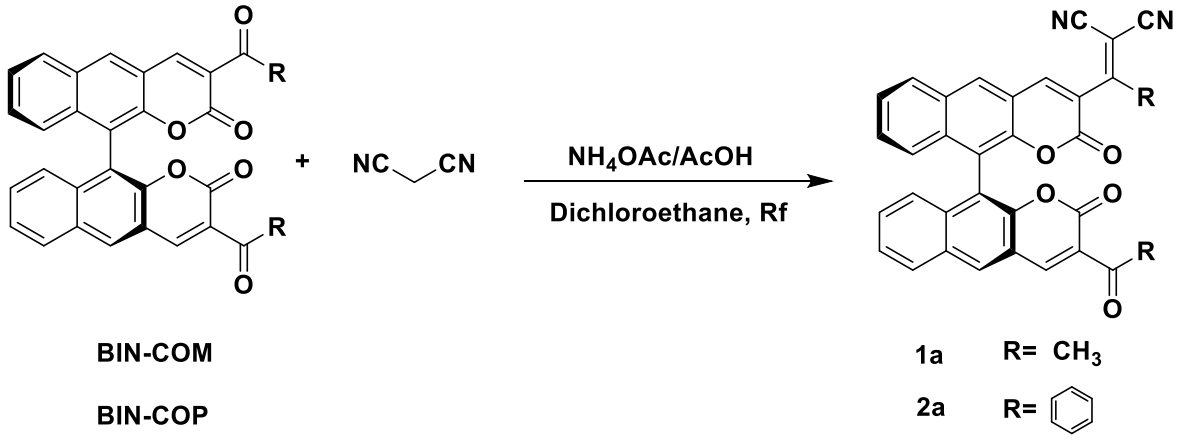
The synthesis steps of **1d** were the same as **1b**. **1d** was obtained as a red solid in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 8.42 (s, 2H), 8.23 (s, 4H), 7.74 (dd, *J* = 8.9, 1.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 4H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 4H), 3.87 (s, 6H), 2.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ(TMS, ppm) 171.5, 159.7, 157.0, 147.7, 144.5, 139.2, 133.9, 131.9, 130.9, 130.2, 128.4, 126.2, 126.1, 124.5, 117.6, 116.6, 114.5, 111.7, 111.5, 88.6, 55.4, 22.8.

Synthesis of 2b

The synthesis steps of **2b** were the same as **1b**. **2b** was obtained an orange solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm) 8.37 (s, 2H), 8.21 (s, 2H), 8.09 (d, *J* = 8.6 Hz, 2H), 7.62 (dd, *J* = 4.8, 3.8 Hz, 4H), 7.60 – 7.54 (m, 4H), 7.50 (d, *J* = 7.9 Hz, 6H), 7.27 (s, 1H), 7.25 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (TMS, ppm) 168.0, 156.8, 148.1, 147.1, 135.2, 134.0, 133.1, 132.2, 130.6, 130.4, 129.6, 129.3, 129.3, 126.8, 125.7, 124.55 117.5, 116.7, 115.2, 112.9, 112.8, 85.6.

Synthesis of 2d

The synthesis steps of **2d** were the same as **1b**. **2d** was obtained as red solid in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ(TMS, ppm) 8.39 (s, 2H), 8.21 (d, *J* = 6.5 Hz, 4H), 7.75 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.65 – 7.62 (m, 8H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.35 (d, *J* = 8.9 Hz, 2H), 7.05 – 7.02 (m, 4H), 3.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ(TMS, ppm) 168.1, 159.7, 156.9, 147.9, 147.0, 139.2, 134.1, 134.0, 133.1, 132.1, 132.0, 130.8, 130.4, 129.3, 129.3, 128.4, 126.2, 126.1, 124.5, 117.8, 114.5, 112.8, 112.8, 85.6, 55.4.



Scheme S4. Synthesis of **1a** and **2a**.

Synthesis of 1a

BIN-COM (230 mg, 0.4 mmol) and malononitrile (52.8 mg, 0.8 mmol) was added in a round-bottomed flask. Add as little dichloroethane as possible to dissolve it. Then NH_4AcO (62 mg, 0.8 mmol) and AcOH (0.1 mL) was added. The mixture was heated at reflux for about 0.5 h. After cooling down to room temperature, added 20 mL DCM and 20mLwater, part the organic phase. The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with DCM. **1a** was obtained as orange-red solid in 41% yield and **1b** was obtained as yellow solid in 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) of **1a**. δ(TMS, ppm) 8.74 (s, 1H), 8.41 (d, *J* = 16.9 Hz, 2H), 8.22 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.57 (dd, *J* = 13.4, 6.7 Hz, 2H), 7.44 (dt, *J* = 16.1, 7.4 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 2.67 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (TMS, ppm) 195.2, 171.6, 158.8, 157.0, 148.6, 147.8, 147.6, 144.4, 135.2, 133.1, 131.9, 130.4, 130.3, 130.3, 130.3, 129.6, 129.5, 126.7, 126.4, 125.6, 125.5, 125.1, 124.4, 121.3, 118.1, 117.3, 117.1, 115.9, 111.7, 111.5, 88.5, 30.6, 22.8.

Synthesis of 2a

The synthesis steps of **2a** were the same as **1a**. **2a** was obtained as orange solid in 39% yield and **2b** was obtained as orange solid in 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) of **2a**. δ(TMS, ppm) 8.38 (s, 1H), 8.34 (s, 1H), 8.27 (s, 1H), 8.22 (s, 1H), 8.11 – 8.05 (m, 2H), 7.95 – 7.91 (m, 2H), 7.66 – 7.45 (m, 12H), 7.25 – 7.21 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (TMS, ppm) 191.4, 168.1, 158.0, 156.9, 148.4, 148.1, 147.1, 145.3, 136.0, 135.4, 134.8, 134.0, 133.9, 133.1, 132.1, 131.5, 130.4, 130.4, 130.3, 130.0, 129.8, 129.6, 129.3, 129.3, 129.3, 128.6, 127.5, 126.7, 126.4, 125.6, 125.6, 124.5, 118.0, 117.6, 117.2, 116.3, 112.9, 112.8, 85.8.

1.3 Cell culture and imaging

HepG 2 cells were cultured in Dulbecco's modified Eagle medium (DMEM) containing 10% fetal bovine serum and 1% Antibiotic–antimycotic at 37℃ in a 5% CO_2/95% air incubator. For fluorescence imaging, cells (4×10^3/well) were passed on a 6-well plate and incubated for 24 h. For fluorescence imaging, cells (4×10^3/well) were passed on a 6-well plate and incubated for 24 h. Before the staining experiment, cells were washed twice with physiological saline, incubated with 5 μM probe and 2 ul oleic acid for different times at 37℃. Then washed 3-6 times with physiological saline. The confocal fluorescent images were captured with an excitation light at 405 nm. For co-localization experiment, cells were incubated with 5 μM probe and 2ul oleic acid for 6h, then washed 3-6 times with physiological saline, then incubated with 1μm BODIPY 493/503 for 15 min. The excitation light of BODIPY 493/503 is 488 nm.

1.4 Cytotoxicity study

Toxicity toward HepG 2 cells was determined by MTS (3-(4, 5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazoliu m reduction assay following literature procedures. About 10000 cells per well were seeded in 96-well plates and cultured overnight for 70-80% cell confluence. The medium was replaced with 100 μL of fresh medium with different concentration of probes, to which 100 μL complexes at 200 μL. 24 hours later, 100 μL of 20% MTS solution in PBS was replaced with the old medium in each well for additional 0.5h incubation. The metabolic activity of the probes treated cells was expressed as a relative to untreated cell controls taken as 100% metabolic activity.

2. Views of the molecular stacking structures in single crystals

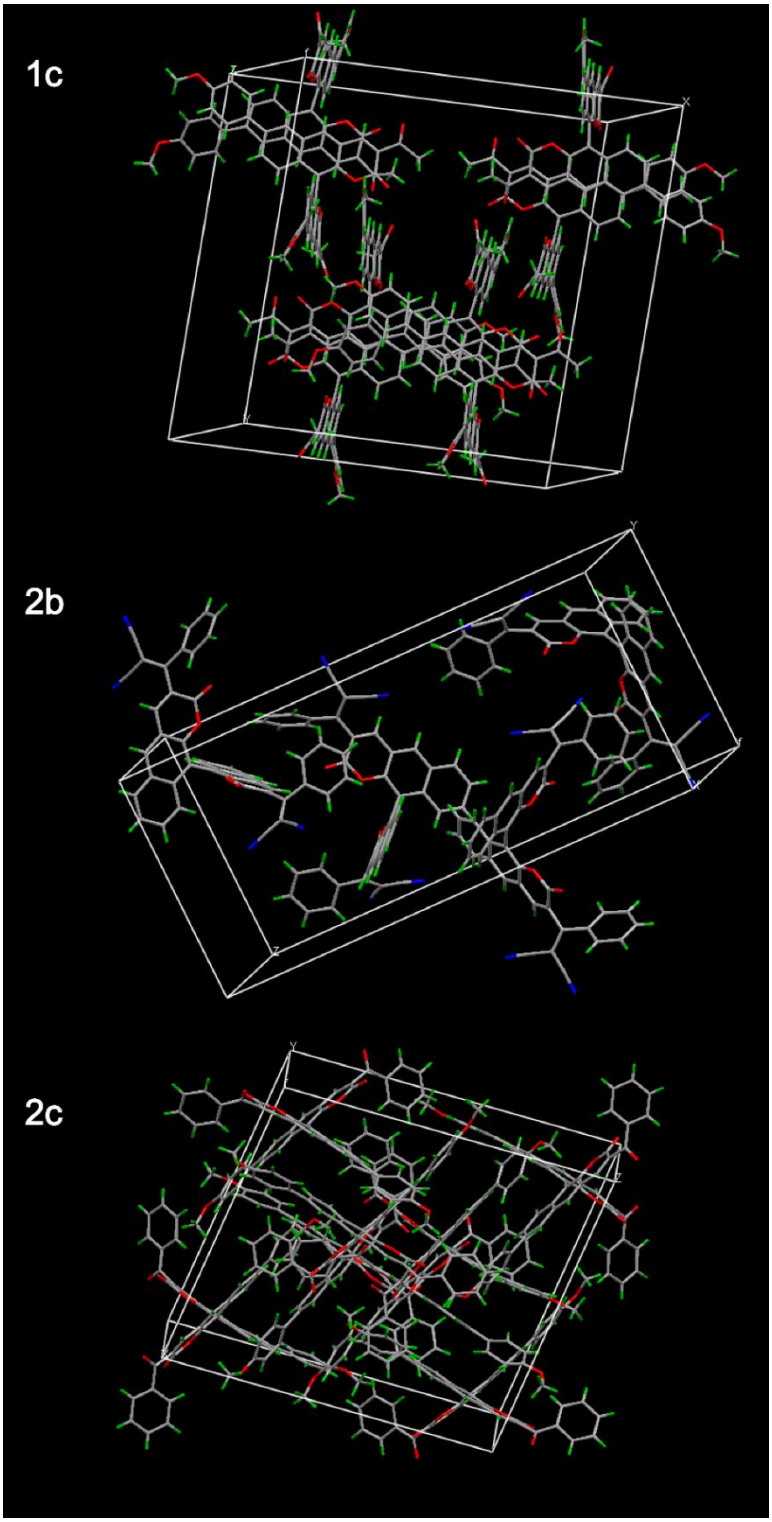


Figure S1. Views of crystal packing mode of **1c**, **2b** and **2c**. Carbon, hydrogen, oxygen and nitrogen atoms are shown in gray, green, red and blue, respectively. The single-crestal data can be found on CCDC, the deposition number of 2b, 1c and 2c are 1907970, 1907963 and 1907968, respectively.

Table S1. The dihedral angle and the distance data of **1c**, **2b**, and **2c**.

Compounds	$Ø_{P\text{-}D}$[a]	$Ø_{P\text{-}A}$[a]	$Ø_{P\text{-}P}$[b]	$d_{D\text{-}D}$[b]	$d_{A\text{-}A}$[b]	$d_{A\text{-}P}$[b]	$d_{P\text{-}P}$[b]	$d_{P\text{-}P}$[c]
1c	17.62	34.63	65.52	4.847	4.755	-	3.851 ~4.271	3.944
2b	-	67.32	102.04	-	-	4.207	-	-
2c	33.10	78.80	109.96	4.884	9.844	-	4.013 4.823	4.156

[a]The dihedral angle of purine core and donor group ($Ø_{P\text{-}D}$) or acceptor group ($Ø_{P\text{-}A}$). [b]The distance of adjacent molecule's purine core (P), donor group (D), and acceptor group (A). [c]The vertical distance of adjacent molecule's purine core (P).

3. Crystallographic data of 1c, 2b, and 2c

Crystal data and structure refinements of 1c:

Deposition number of CCDC：1907963

Identification code	1c	
Chemical formula	$C_{44}H_{30}O_8$	
Formula weight	686.68 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.200 x 0.200 mm	
Crystal system	monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 25.64(2) Å	α = 90°
	b = 23.425(18) Å	β = 125.282(13)°
	c = 18.464(15) Å	γ = 90°
Volume	9053.(12) $Å^3$	
Z	8	

Density (calculated)	1.008 g/cm^3
Absorption coefficient	0.069 mm^{-1}
F(000)	2864
Theta range for data collection	1.42 to 25.23°
Reflections collected	8290
Independent reflections	8290 [R(int) = 0.0797]
Coverage of independent reflections	98.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9860 and 0.9860
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8290 / 718 / 945
Goodness-of-fit on F^2	1.050
Δ/σ_{max}	0.025
Final R indices	5060data; I>2σ(I) $R_1 = 0.0928$, $wR_2 = 0.2271$
	all data $R_1 = 0.1310$, $wR_2 = 0.2419$
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0800P)^2+35.0000P]$
	where $P = (F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.6(19)
Largest diff. peak and hole	0.338 and -0.305 eÅ^{-3}
R.M.S. deviation from mean	0.068 eÅ^{-3}

Crystal data and structure refinements of 2b:

Deposition number of CCDC：1907970

Identification code	2b	
Chemical formula	$C_{46}H_{22}N_4O_4$	
Formula weight	694.67 g/mol	
Temperature	291.16(10) K	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.6696(3) Å	α = 90°
	b = 13.5192(3) Å	β = 90°
	c = 30.1865(8) Å	γ = 90°
Volume	3946.13(17) $Å^3$	
Z	4	
Density (calculated)	1.169 g/cm^3	
Absorption coefficient	0.614 mm^{-1}	
F(000)	1432.0	
Crystal size/mm^3	0.7 × 0.4 × 0.2	
Radiation	CuKα (λ = 1.54184)	
Theta range for data collection	8.782 to 145.394°	
Reflections collected	8290	
Independent reflections	7042 [R_{int} = 0.0276, R_{sigma} = 0.0355]	
Data/restraints/parameters	7042/84/527	
Goodness-of-fit on F^2	1.039	
Final R indexes [I>=2σ (I)]	R_1 = 0.0553, wR_2 = 0.1545	

Final R indexes [all data]	R_1 = 0.0594, wR_2 = 0.1603
Largest diff. peak/hole / e Å^{-3}	0.38/-0.32
Flack parameter	0.87(14)

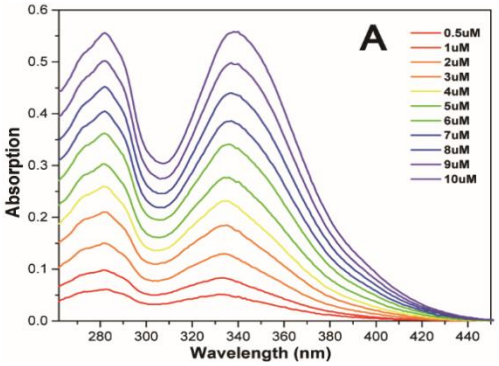
Crystal data and structure refinements of 2c:

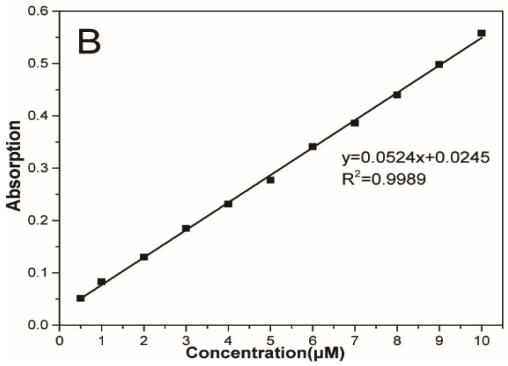
Deposition number of CCDC：1907968

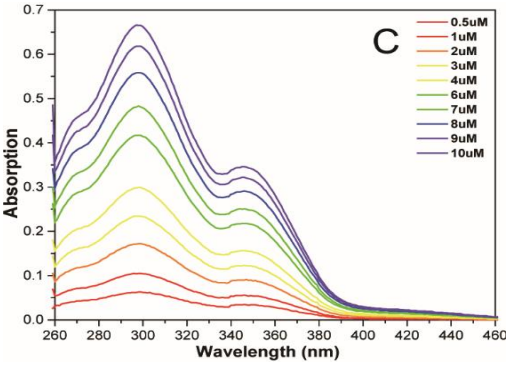
Identification code	2c	
Chemical formula	$C_{54}H_{34}O_8$	
Formula weight	810.81 g/mol	
Temperature	193(2) K	
Wavelength	1.34139 Å	
Crystal size	0.100 x 0.100 x 0.100 mm	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 18.690(4) Å	α = 90°
	b = 23.158(6) Å	β = 98.343(12)°
	c = 21.551(5) Å	γ = 90°
Volume	9229.(4) Å^3	
Z	8	
Density (calculated)	0.403 mm^{-1}	
Absorption coefficient	0.069 mm^{-1}	
F(000)	3376	
Theta range for data collection	1.80 to 51.60°	
Index ranges	-21<=h<=18, -26<=k<=25, -25<=l<=24	
Reflections collected	46510	

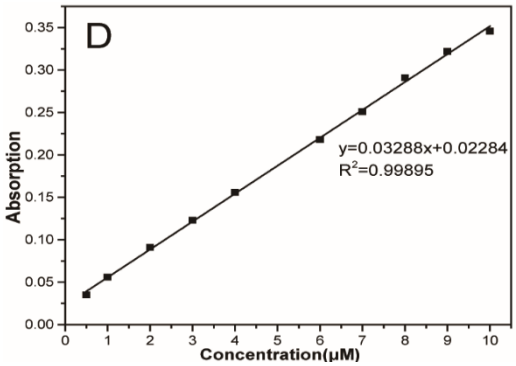
Independent reflections	25262 [R(int) = 0.1185]	
Coverage of independent reflections	96.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9610 and 0.9610	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	25262 / 1705 / 2096	
Goodness-of-fit on F^2	0.967	
Δ/σ_{max}	0.012	
Final R indices	8764 data; I>2σ(I)	$R_1 = 0.0928$, $wR_2 = 0.2271$
	all data	$R_1 = 0.1310$, $wR_2 = 0.2419$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0800P)^2+10.0000P]$	
	where $P = (F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.1(6)	
Extinction coefficient	0.0012(1)	
Largest diff. peak and hole	0.270 and -0.257 eÅ^{-3}	
R.M.S. deviation from mean	0.056 eÅ^{-3}	

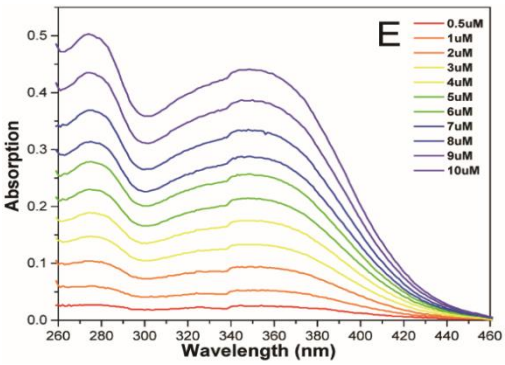
4. Molar Extinction Coefficient of all compounds

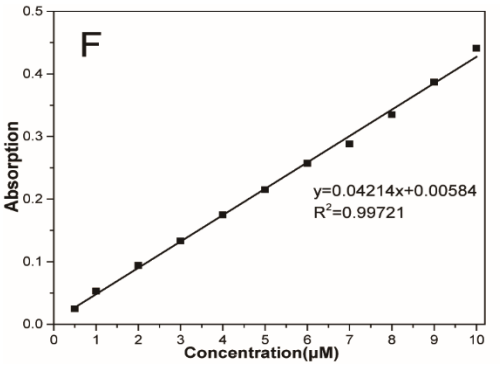


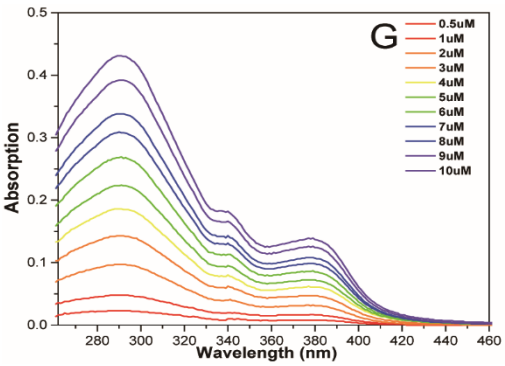


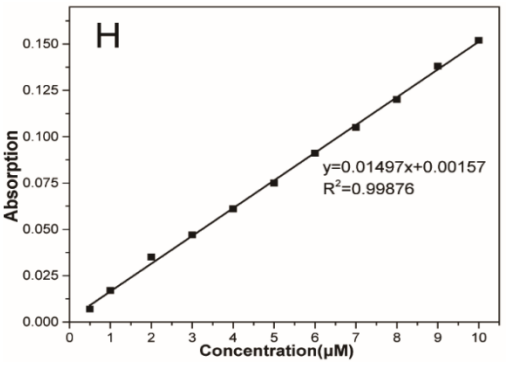












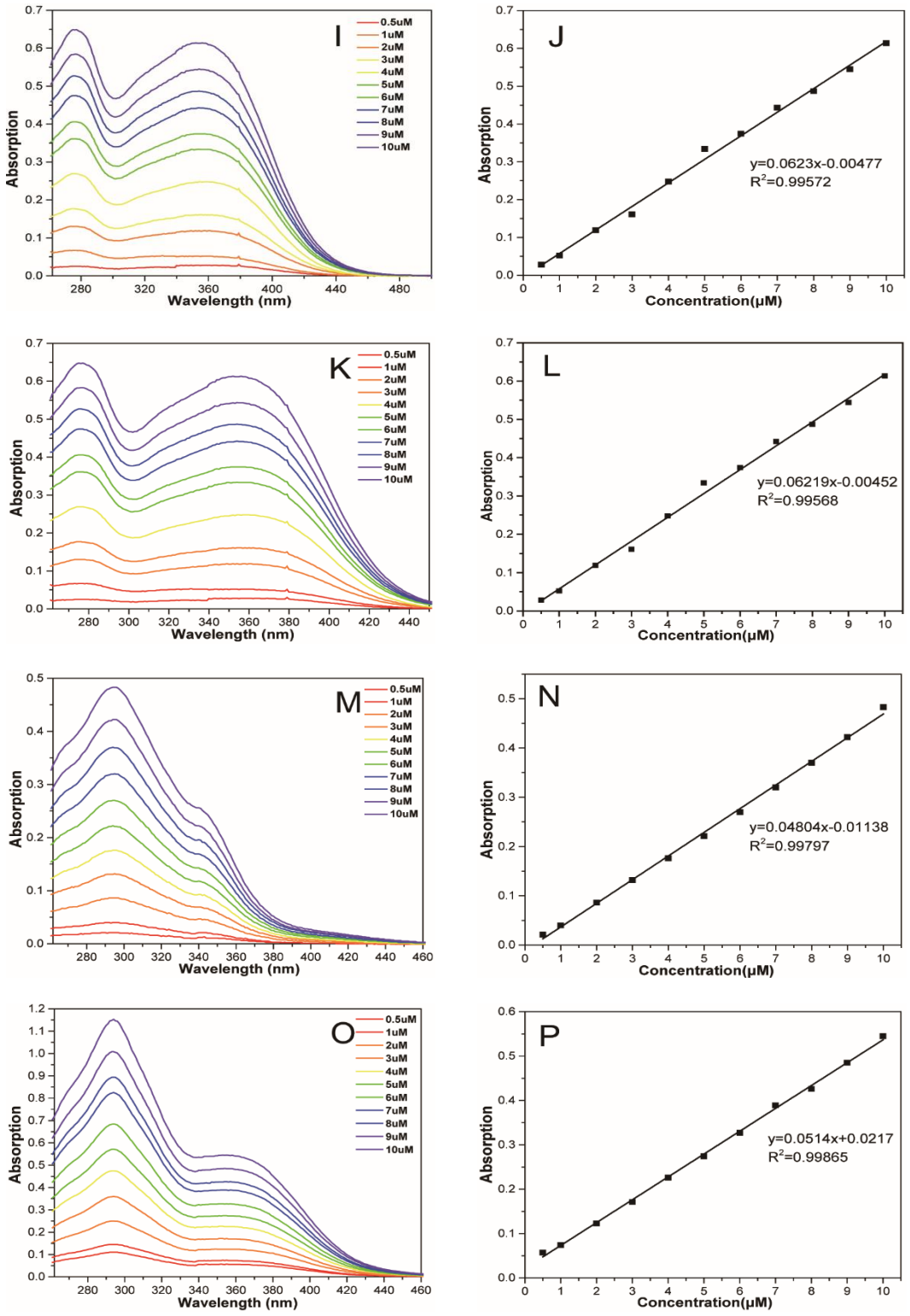
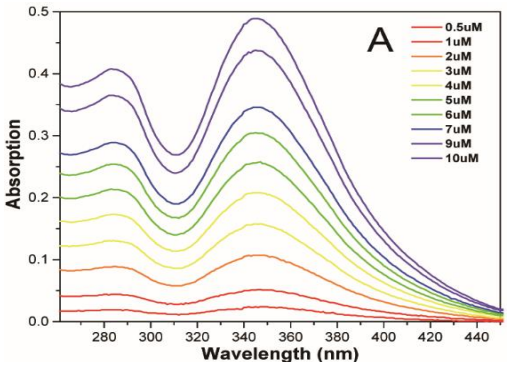
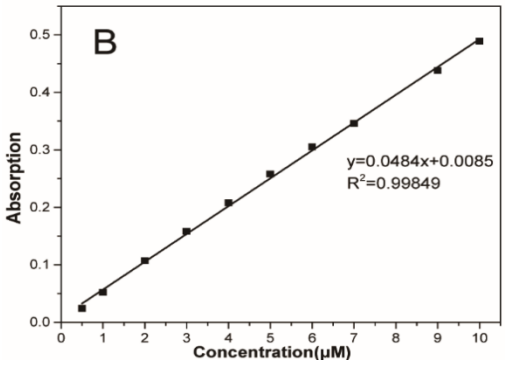
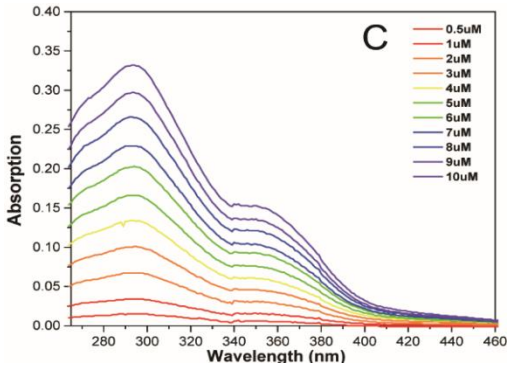
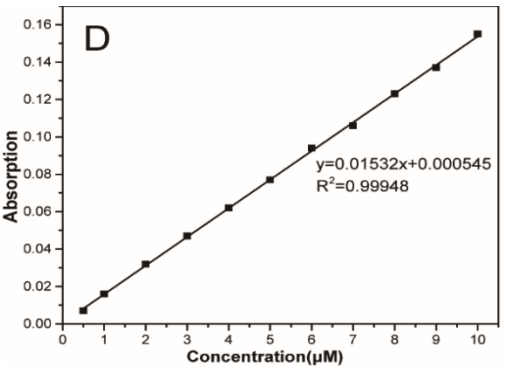


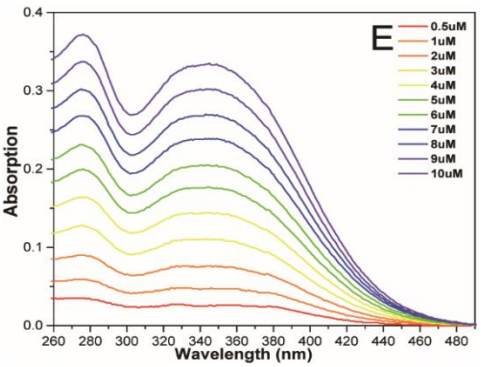
Figure S2. UV spectra and absorption-concentration curve of fluorophores **1a-2d** at different concentrations (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 μM) in DMSO. **1a**: (A) and (B); **1b**: (C) and (D); **1c**: (E) and (F); **1d**: (G) and (H); **2a**: (I) and (J); **2b**: (K) and (L); **2c**: (M) and (N); **2d**: (O) and (P).

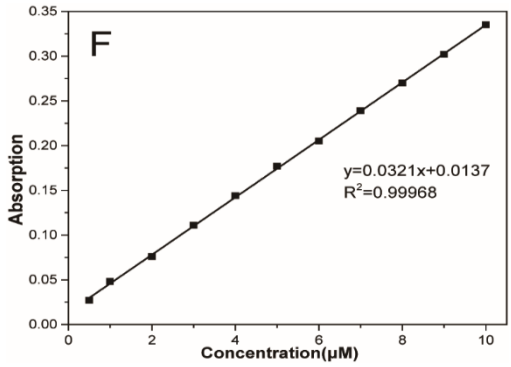

A
0.5uM
1uM
2uM
3uM
4uM
5uM
6uM
7uM
9uM
10uM
Absorption
Wavelength (nm)

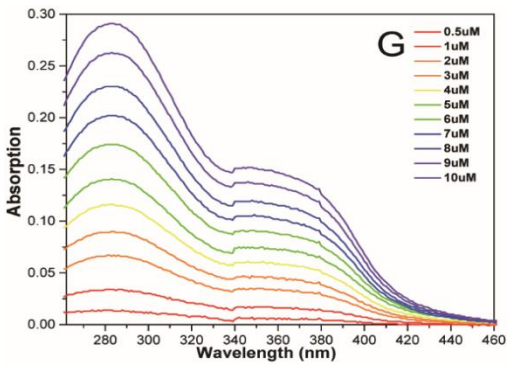

B
y=0.0484x+0.0085
R²=0.99849
Absorption
Concentration(μM)

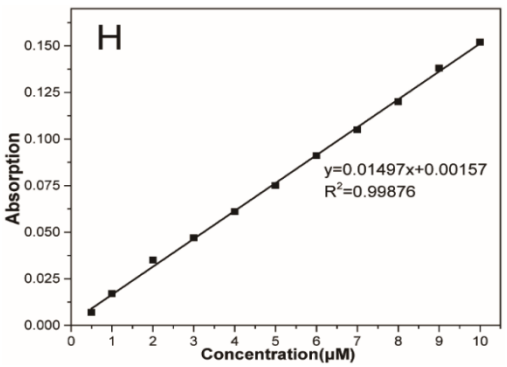

C
0.5uM
1uM
2uM
3uM
4uM
5uM
6uM
7uM
8uM
9uM
10uM
Absorption
Wavelength (nm)


D
y=0.01532x+0.000545
R²=0.99948
Absorption
Concentration(μM)


E
0.5uM
1uM
2uM
3uM
4uM
5uM
6uM
7uM
8uM
9uM
10uM
Absorption
Wavelength (nm)


F
y=0.0321x+0.0137
R²=0.99968
Absorption
Concentration(μM)


G
0.5uM
1uM
2uM
3uM
4uM
5uM
6uM
7uM
8uM
9uM
10uM
Absorption
Wavelength (nm)


H
y=0.01497x+0.00157
R²=0.99876
Absorption
Concentration(μM)

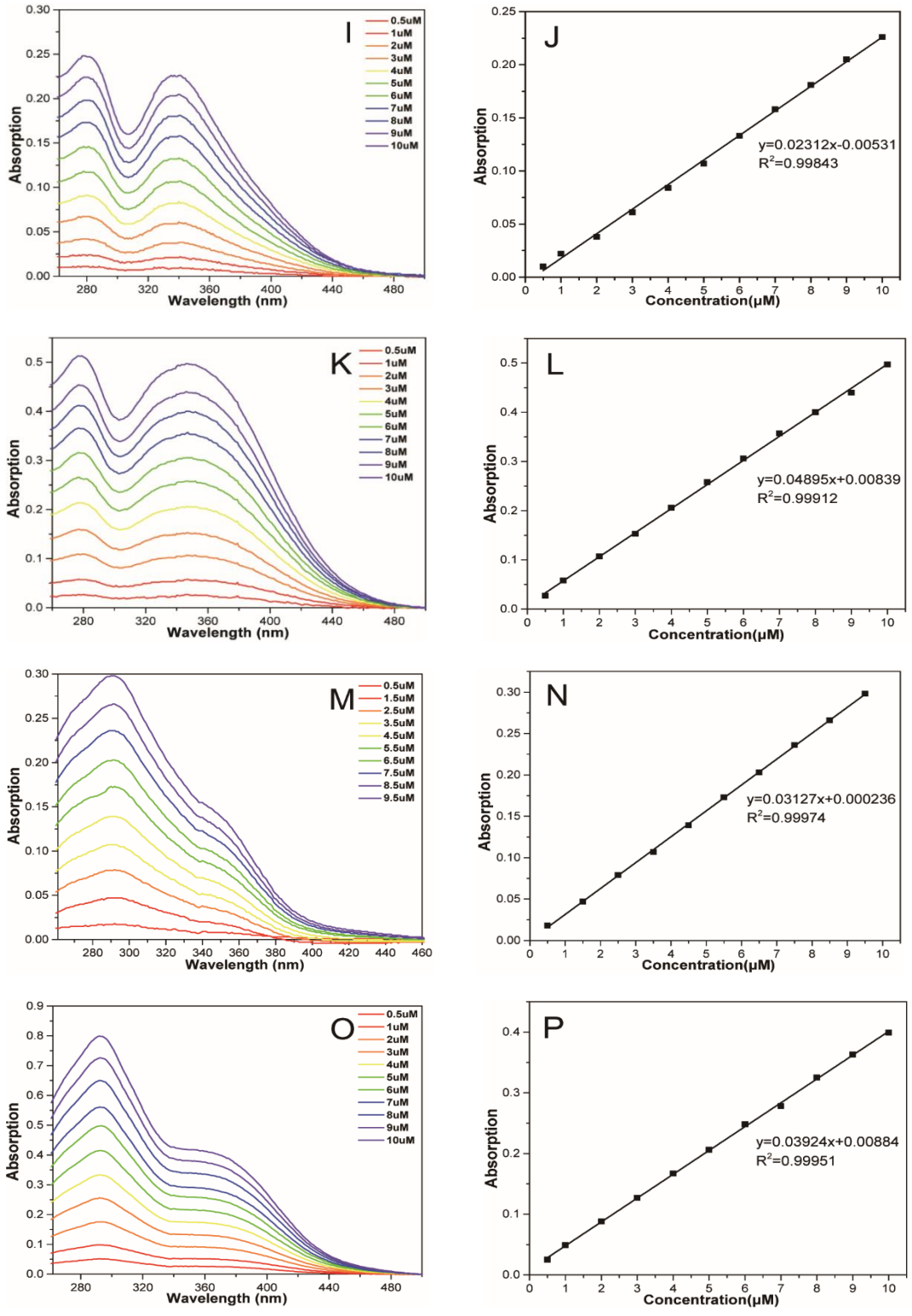
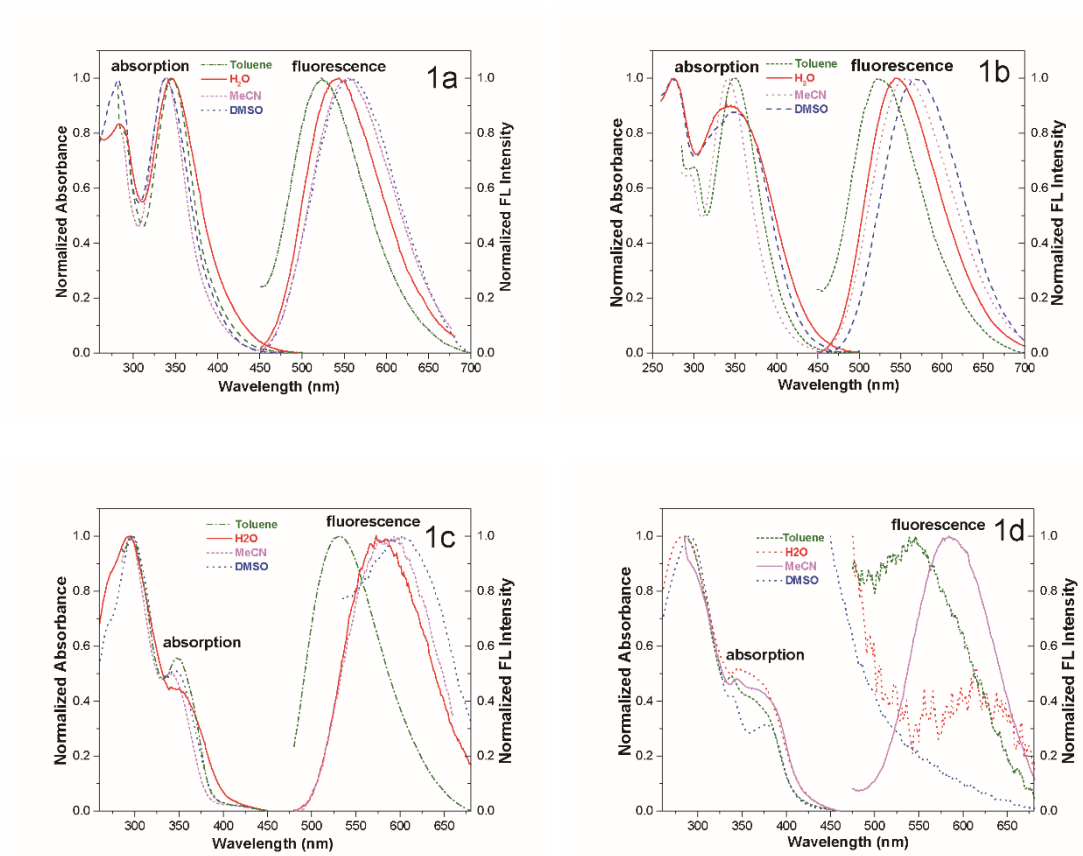


Figure S3. UV spectra and absorption-concentration curve of fluorophores **1a-2d** at different concentrations (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 μM) in water. **1a**: (A) and (B); **1b**: (C) and (D); **1c**: (E) and (F); **1d**: (G) and (H); **2a**: (I) and (J); **2b**: (K) and (L); **2c**: (M) and (N); **2d**: (O) and (P).

Table S2. Summary of all the compounds' molar extinction coefficient

Compounds	DMSO		Water	
	λ_{Abs} (nm)	ε (M^{-1} cm^{-1})	λ_{Abs} (nm)	ε (M^{-1} cm^{-1})
1a	340	5.24×10^4	346	4.84×10^4
1b	346	4.21×10^4	350	3.21×10^4
1c	349	3.29×10^4	339	1.53×10^4
1d	379	1.35×10^4	347	1.50×10^4
2a	354	6.20×10^4	337	2.31×10^4
2b	354	6.22×10^4	346	4.90×10^4
2c	340	4.80×10^4	340	3.13×10^4
2d	353	5.14×10^4	357	3.92×10^4

5. Solvent effect of all compounds



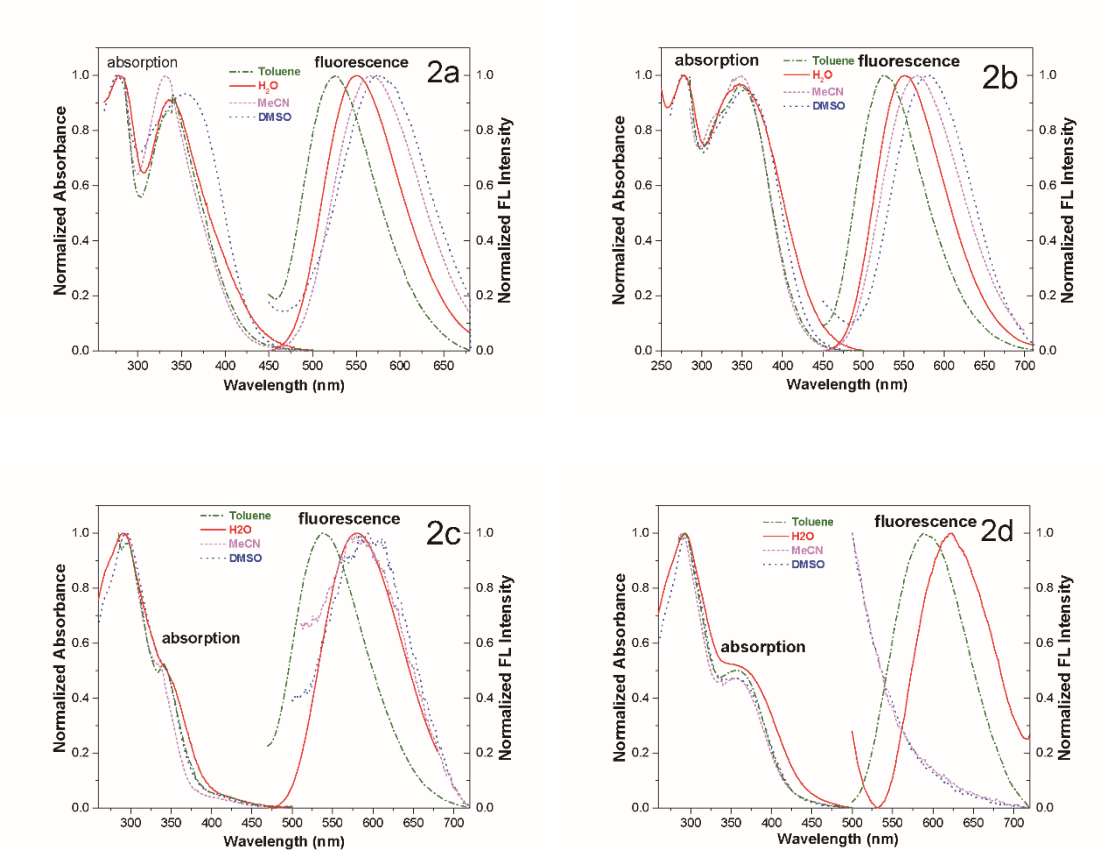
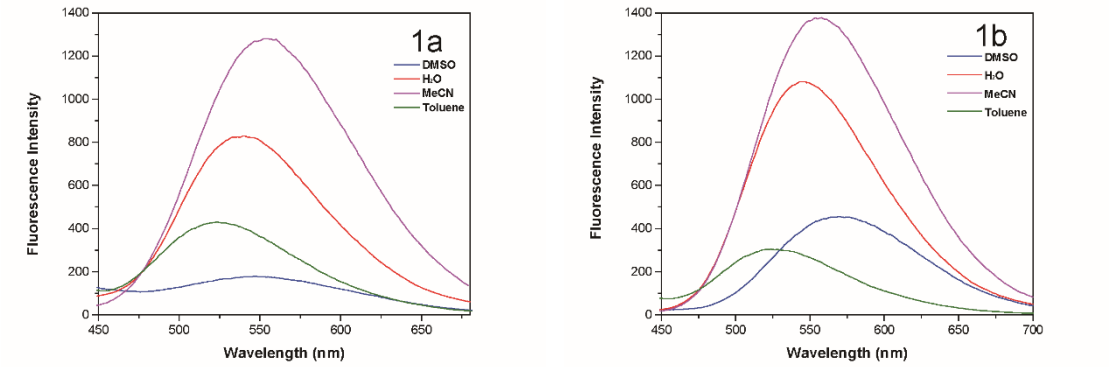


Figure S4. Normalized absorption and fluorescence spectra of fluorophores in different solvents (Toluene, H_2O, MeCN, DMSO).



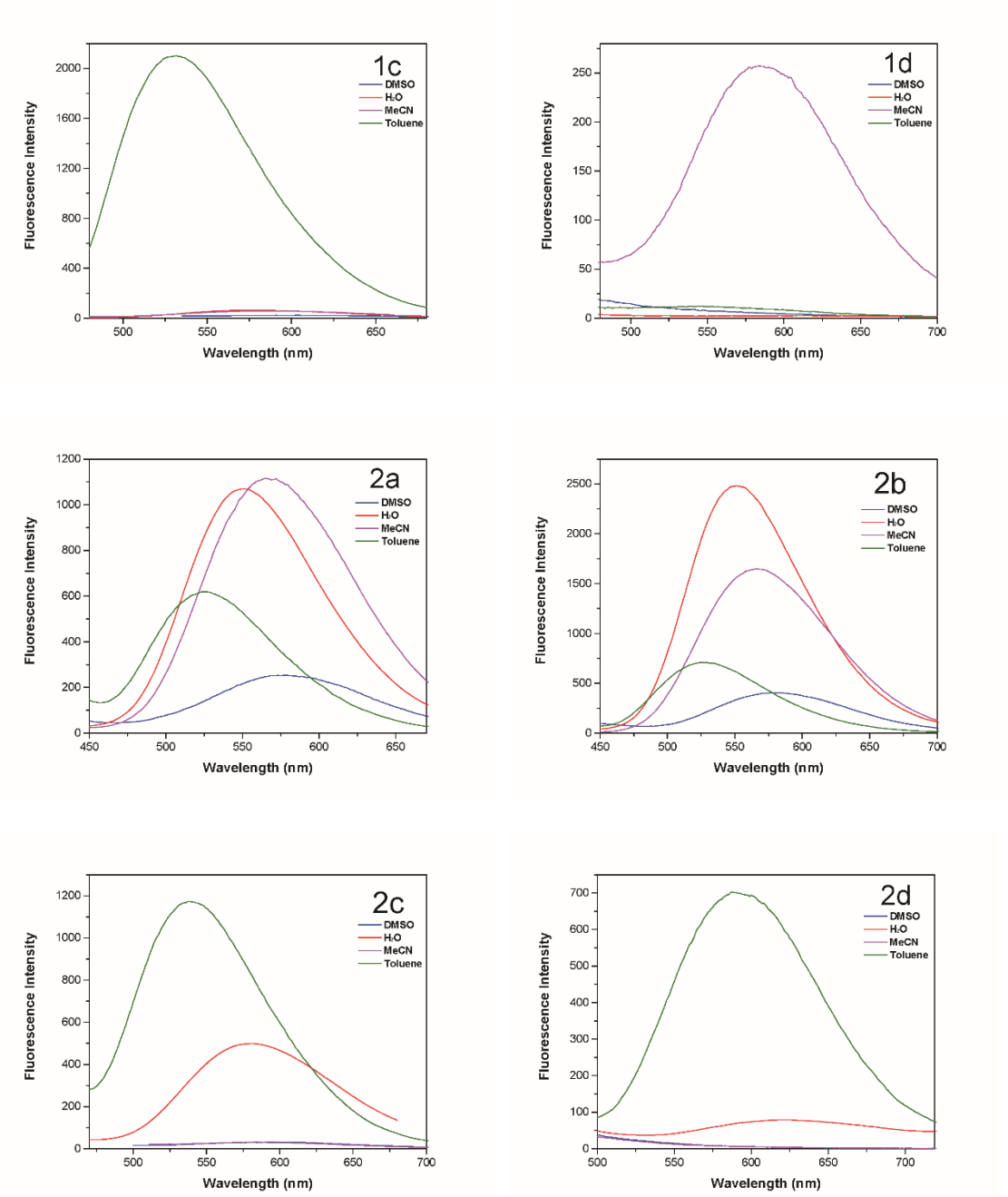


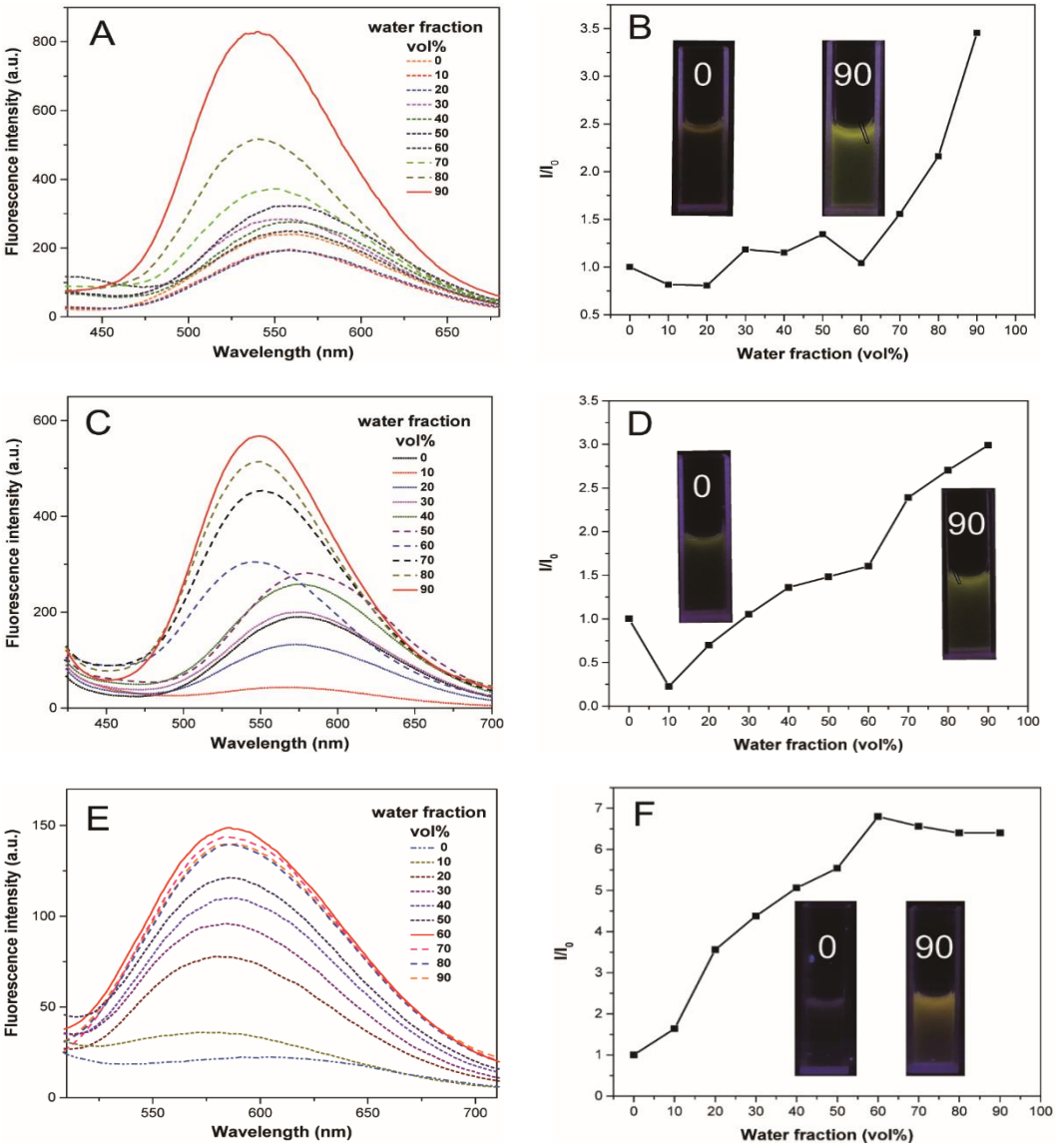
Figure S5. Fluorescence emssion spectra of **1a**-**2d** in different solvents (Toluene, H_2O, MeCN, DMSO). Concentration: 5 μM

Table S3. Optical transitions of all the compounds in different solvents, $\Delta\lambda = \lambda_{em}-\lambda_{abs}$.

	toluene			water			acetonitrile			DMSO		
	λ_{abs}	λ_{em}	Δλ	λ_{abs}	λ_{em}	Δλ	λ_{abs}	λ_{em}	Δλ	λ_{abs}	λ_{em}	Δλ
1a	345	523	178	346	544	198	340	555	215	340	562	222
1b	349	524	175	339	546	211	340	558	218	349	574	225
1c	349	532	183	350	588	238	339	593	254	346	605	259

1d	344	542	202	347	623	268	338	584	246	379	-	-
2a	340	527	187	337	551	214	332	566	234	354	579	225
2b	349	525	176	346	551	205	348	565	217	354	582	228
2c	340	537	197	340	580	241	340	579	239	340	608	268
2d	358	587	229	357	624	267	355	-	-	353	-	-

6. Fluorescence spectra of all compounds in DMSO/PBS mixtures



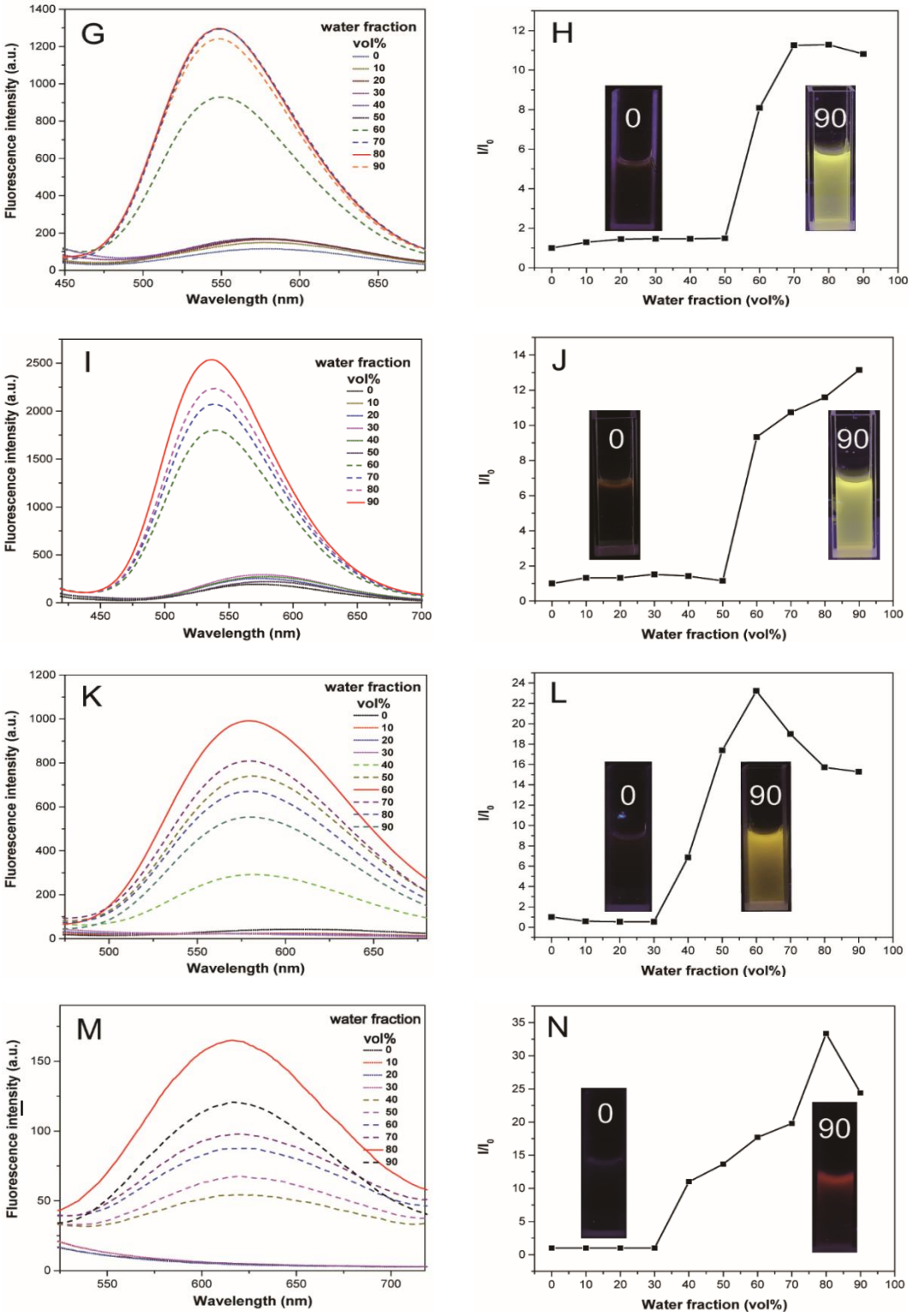


Figure S6. Fluorescence spectra of all the compounds in DMSO/H_2O mixtures and dependence of the I/I_0 ratios of all the compounds on the solvent composition of the DMSO/H_2O mixture. **1a**: (A) and (B), Ex = 353 nm; **1b**: (C) and (D) Ex = 366 nm; **1c**: (E) and (F) Ex = 370 nm; **2a**: (G) and (H) Ex = 350 nm; **2b**: (I) and (J) Ex = 372 nm; **2c**: (K) and (L) Ex = 350 nm; **2d**: (M) and (N) Ex = 372 nm, concentration: 5 μM. Insert: photographs of each compound in DMSO/H_2O mixtures with f_P values of 0 and 90% under irradiation with 365 nm UV light.

7. Particle size of all compounds in aggregation state

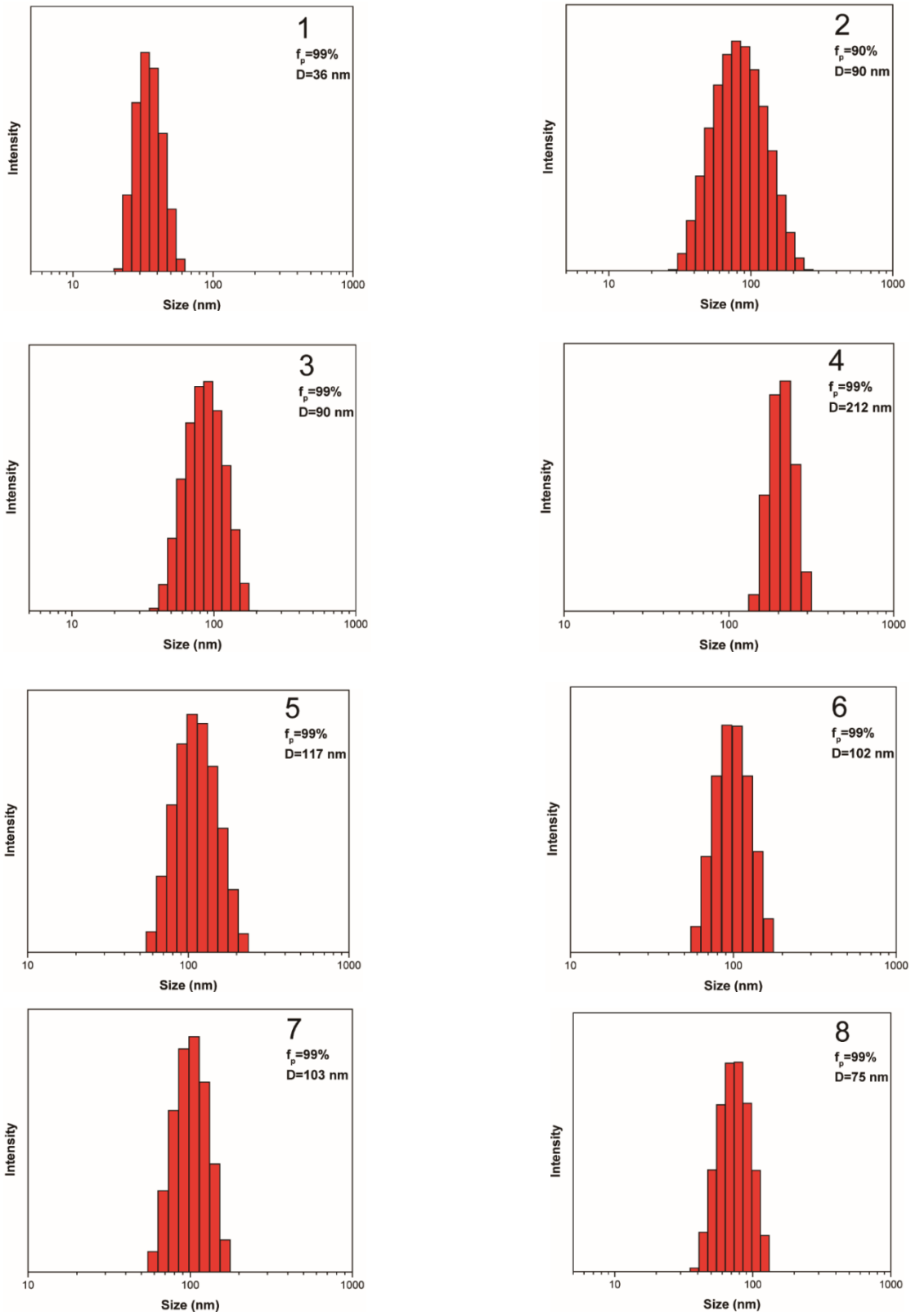


Figure S7. Particle size distribution of compounds **1a**-**1d**: 1-4; **2a**-**2d**: 5-8 in DMSO/H_2O mixture with an f_P value of 99%. Concentration: 10 μM

8. Wavelength of solid fluorescence and their CIE diagram

Table S4. Coordinates of compounds 1a-1d and 2a-2d on CIE diagram.

Compound	λ_{em}(nm)	Coordinate (X)	Coordinate (Y)
1a	534	0.352	0.5753
1b	538	0.3536	0.563
1c	570	0.4753	0.5168
1d	601	0.5298	0.4621
2a	538	0.3676	0.5808
2b	541	0.3619	0.581
2c	560	0.4304	0.538
2d	609	0.5743	0.4236

9. Fluorescent lifetime and quantum yield of all compounds in solution, aggregation and solid state

Table S5. Fluorescent lifetime of all compounds in DMSO, water and solid state.

Compd	Lifetie in soluetion (s)	Lifetime in aggregation (s)	Lifetime in solid state (s)
1a	τ_1=2.69×10^{-09}(17%) τ_2=7.15×10^{-10}(82%) τ_3=1.16×10^{-08}(1%) τ_{avg}=1.18×10^{-09}	τ_1=1.23×10^{-09}(83%) τ_2=4.61×10^{-09}(17%) τ_{avg}=1.81×10^{-09}	τ_1=5.35×10^{-09} (10%) τ_2=1.58×10^{-07} (1%) τ_3=9.52×10^{-10} (89%) τ_{avg}=1.66×10^{-09}
1b	τ_1=7.61×10^{-10}(98%) τ_2=5.57×10^{-09}(2%) τ_{avg}=8.52×10^{-10}	τ_1=1.34×10^{-09}(82%) τ_2=4.72×10^{-09}(18%) τ_{avg}=1.96×10^{-09}	τ_1=5.33×10^{-9}(3%) τ_2=8.04×10^{-10}(97%) τ_{avg}=1.10×10^{-9}
1c	τ_1=4.78×10^{-10}(99%) τ_2=5.95×10^{-09}(1%) τ_{avg}=5.19×10^{-10}	τ_1=1.14×10^{-09}(81%) τ_2=4.78×10^{-09}(19%) τ_{avg}=1.83×10^{-09}	τ_1=8.62×10^{-9}(~40%) τ_2=1.90×10^{-7}(1%) τ_3=1.76×10^{-09}(59%) τ_{avg}=5.21×10^{-9}

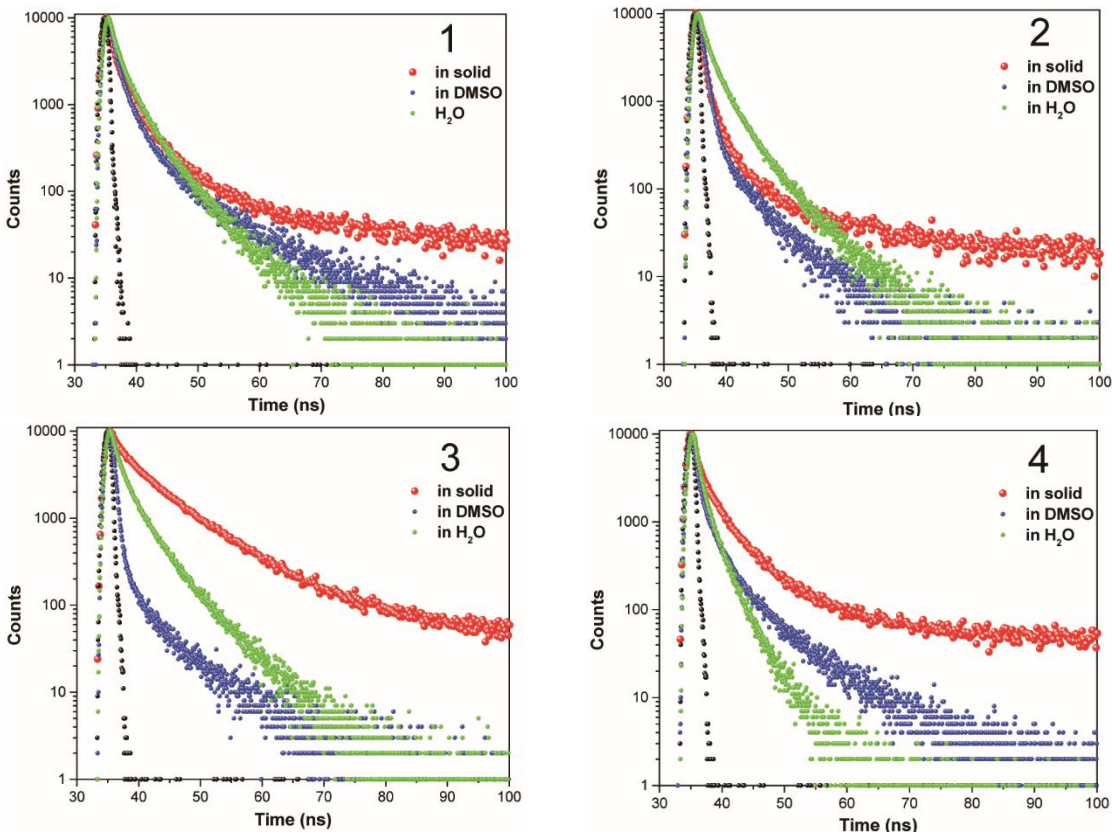
1d	τ_1=1.93×10^{-09}(9%) τ_2=2.90×10^{-10}(90%) τ_3=7.78×10^{-09}(1%) τ_{avg}=5.0×10^{-10}	τ_1=6.99×10^{-10}(86%) τ_2=2.69×10^{-09}(14%) τ_{avg}=9.74×10^{-10}	τ_1=6.28×10^{-10}(86%) τ_2=4.75×10^{-9}(14%) τ_{avg}=1.54×10^{-9}
2a	τ_1=6.25×10^{-10}(83%) τ_2=1.89×10^{-09}(16%) τ_3=6.28×10^{-09}(1%) τ_{avg}=8.65×10^{-10}	τ_1=1.56×10^{-09}(83%) τ_2=5.54×10^{-09}(17%) τ_{avg}=2.23×10^{-09}	τ_1=4.68×10^{-9}(16%) τ_2=1.93×10^{-9}(84%) τ_{avg}=2.49×10^{-9}
2b	τ_1=6.60×10^{-10}(99%) τ_2=5.15×10^{-09}(1%) τ_{avg}=6.95×10^{-10}	τ_1=2.53×10^{-09}(76%) τ_2=7.27×10^{-09}(24%) τ_{avg}=3.67×10^{-09}	τ_1=5.98×10^{-9}(24%) τ_2=1.38×10^{-9}(76%) τ_{avg}=2.82×10^{-9}
2c	τ_1=5.60×10^{-10}(97%) τ_2=5.65×10^{-09}(3%) τ_{avg}=7.22×10^{-10}	τ_1=1.72×10^{-09}(73%) τ_2=6.89×10^{-09}(27%) τ_{avg}=3.10×10^{-09}	τ_1=7.87×10^{-09}(19%) τ_2=7.26×10^{-10}(81%) τ_{avg}=2.52×10^{-9}
2d	τ_1=2.95×10^{-09}(13%) τ_2=4.73×10^{-10}(85%) τ_3=9.34×10^{-09}(2%) τ_{avg}=9.64×10^{-10}	τ_1=7.77×10^{-10}(83%) τ_2=3.86×10^{-09}(17%) τ_{avg}=1.31×10^{-9}	τ_1=5.61×10^{-10}(87%) τ_2=5.17×10^{-9}(13%) τ_{avg}=1.42×10^{-9}

Table S6. Quantum yield of all compounds in DMSO, water and solid state.

Compd.	Quantum yield in solution (%)	Quantum yield in aggregation (%)	Quantum yield in solid state (%)
1a	~0.1	0.58	3.1
1b	~0.1	3.23	2.55
1c	0	0.3	2.93
1d	0	~0.1	0.16
2a	~0.1	3.58	4.43
2b	~0.1	5.41	6.3
2c	0	3.46	6.3
2d	0	~0.1	0.15

Table S7. The rate constants for radiative (k_r) and non-radiative decay (k_{nr}) were calculated from the Φ and τ values according to the formulae $k_r = \Phi_F/\tau$ and $k_{nr} = (1-\Phi_F)/\tau$.

Compound	Solution		aggregation		Solid state	
	K_r (s^{-1})	K_{nr} (s^{-1})	K_r (s^{-1})	K_{nr} (s^{-1})	K_r (s^{-1})	K_{nr} (s^{-1})
1a	$8.47x10^5$	$8.47 x10^8$	$3.20 x10^6$	$5.49 x10^8$	$4.78 x10^7$	$8.14 x10^8$
1b	$1.17 x10^6$	$1.17 x10^9$	$1.65 x10^7$	$4.94 x10^8$	$2.32 x10^7$	$8.86 x10^8$
1c	0	$1.93 x10^9$	$1.64 x10^6$	$5.45 x10^8$	$5.62 x10^6$	$1.86 x10^8$
1d	0	$2.00 x10^9$	$1.03 x10^6$	$1.03 x10^9$	$1.04 x10^6$	$6.48 x10^8$
2a	$1.16 x10^6$	$1.15 x10^9$	$1.61 x10^7$	$4.32 x10^8$	0.00E+00	$3.55 x10^8$
2b	$1.44 x10^6$	$1.44 x10^9$	$1.47 x10^7$	$2.58 x10^8$	$2.53 x10^7$	$3.76 x10^8$
2c	0	$1.39 x10^9$	$1.12 x10^7$	$3.11 x10^8$	$2.50 x10^7$	$3.72 x10^8$
2d	0	$1.04 x10^9$	$7.63 x10^5$	$7.63 x10^8$	$8.45 x10^5$	$7.03 x10^8$



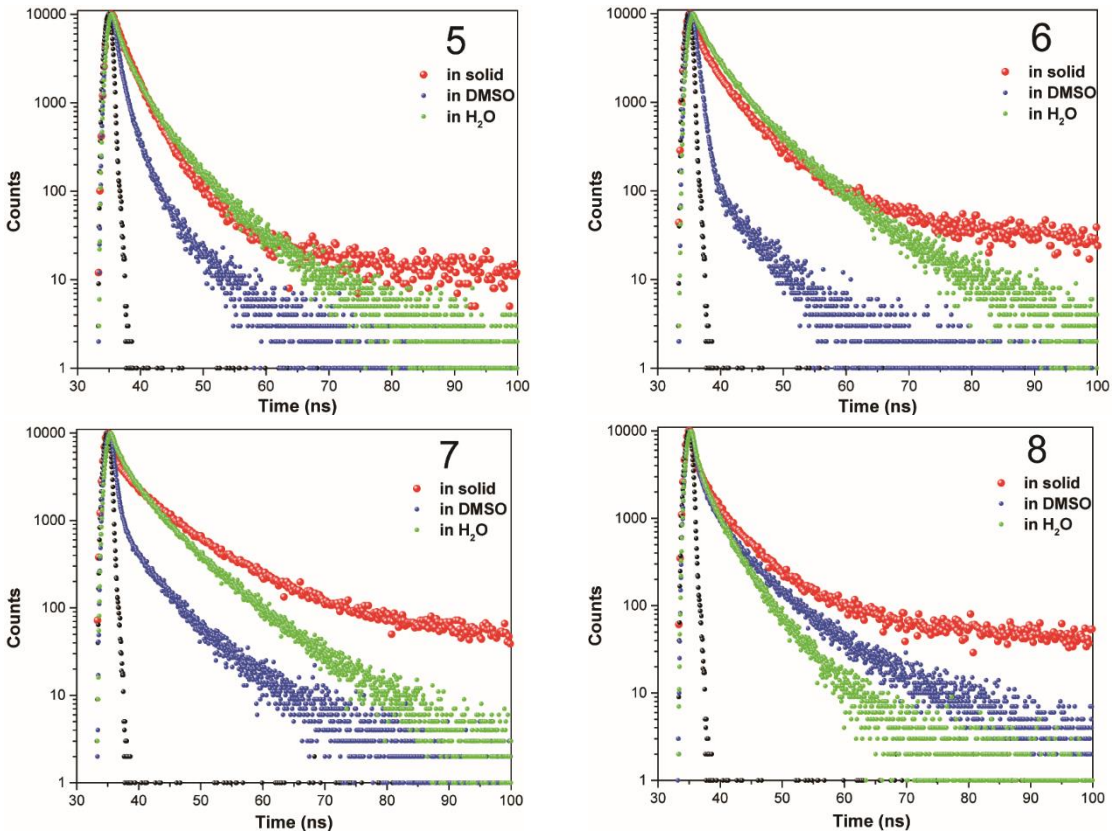


Figure S8. Emission decay of compounds **1a**-**1d**: 1-4; **2a**-**2d**: 5-8 in DMSO, H_2O, and solid.

10. Particle size and fluorescence study of oleic acid, 2b and OA-2b in PBS

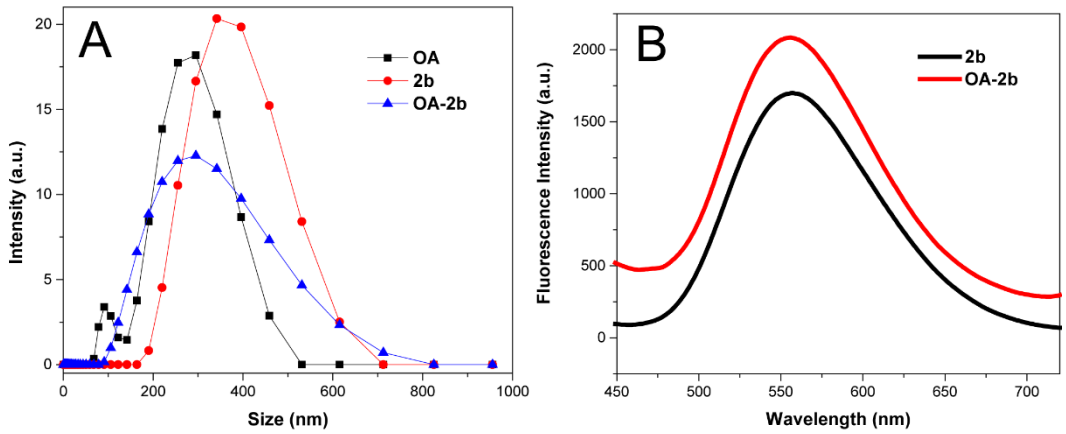


Figure S9. (A) Particle size distribution of oleic acid (OA), **2b** and **OA-2b** in PBS, concentration: 10 µM; **(B)** Fluorescence spectra of **2b** and **OA-2b** in PBS, Ex = 372 nm. concentration: 5 µM.

11. Single-photo CLSM images of HepG 2 incubated with OA-2b

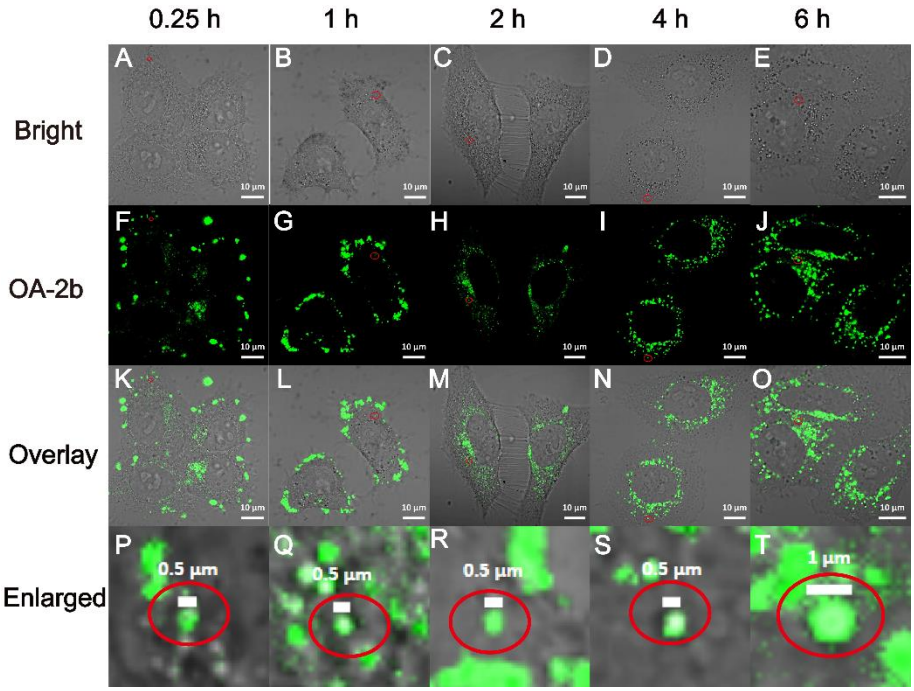


Figure S10. Live HepG 2 cells incubated with **OA-2b** for different times and the process of expanding LDs: (P-T) enlarged LDs imaging of inset (the area of ellipse red line).

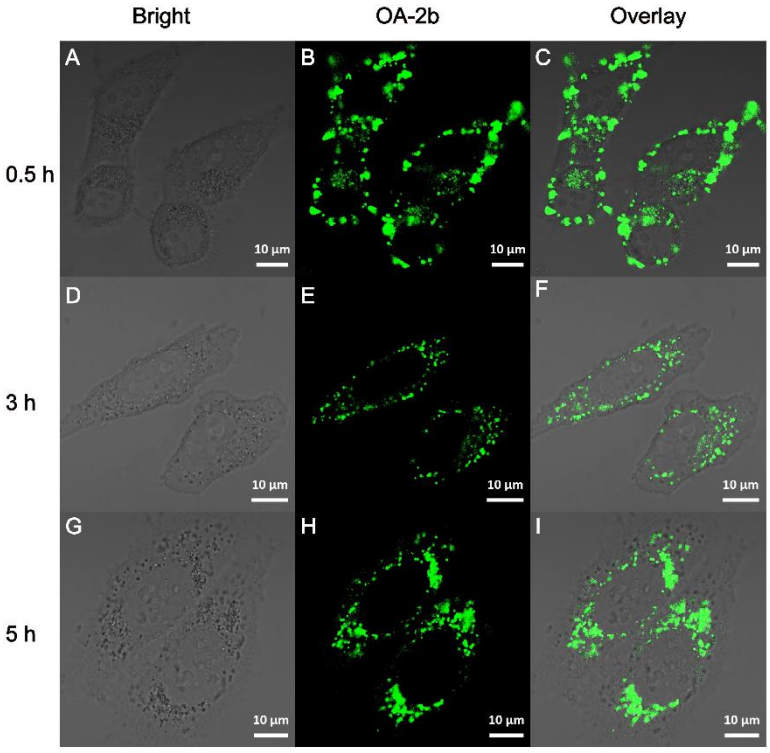


Figure S11. Live HepG 2 cells incubated with **OA-2b** for 0.5 h, 3 h and 5 h.

12. Cytotoxicity of 2b in HepG 2 cells evaluated by MTS assay

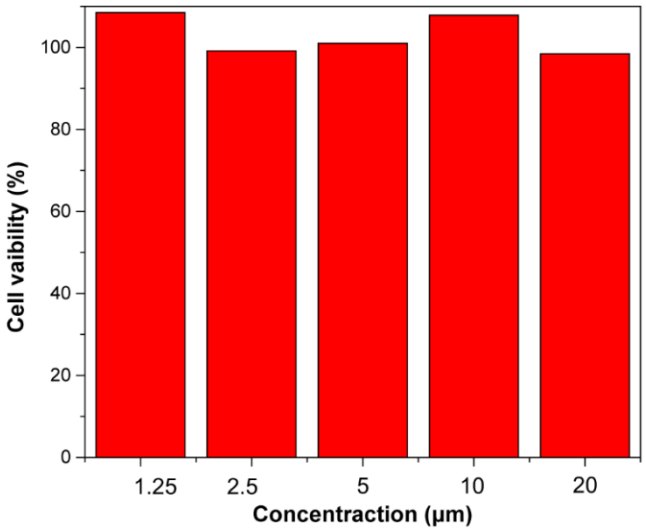


Figure S12. Cell viabilities of HepG 2 cells after incubation with different concentrations of compound **2b** (1.25, 2.5, 5, 10, 20 μM) for 24 h.

13. NMR Data

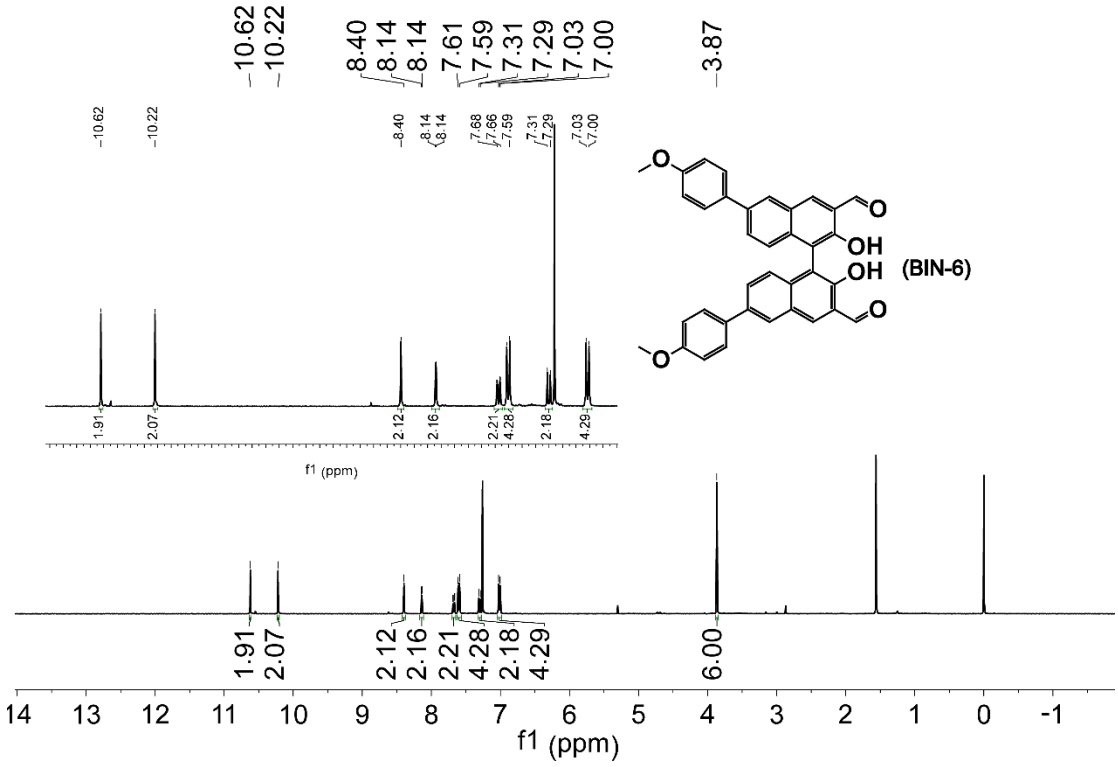


Figure S13. ^{1}H NMR of Compound **BIN-6** in $CDCl_3$

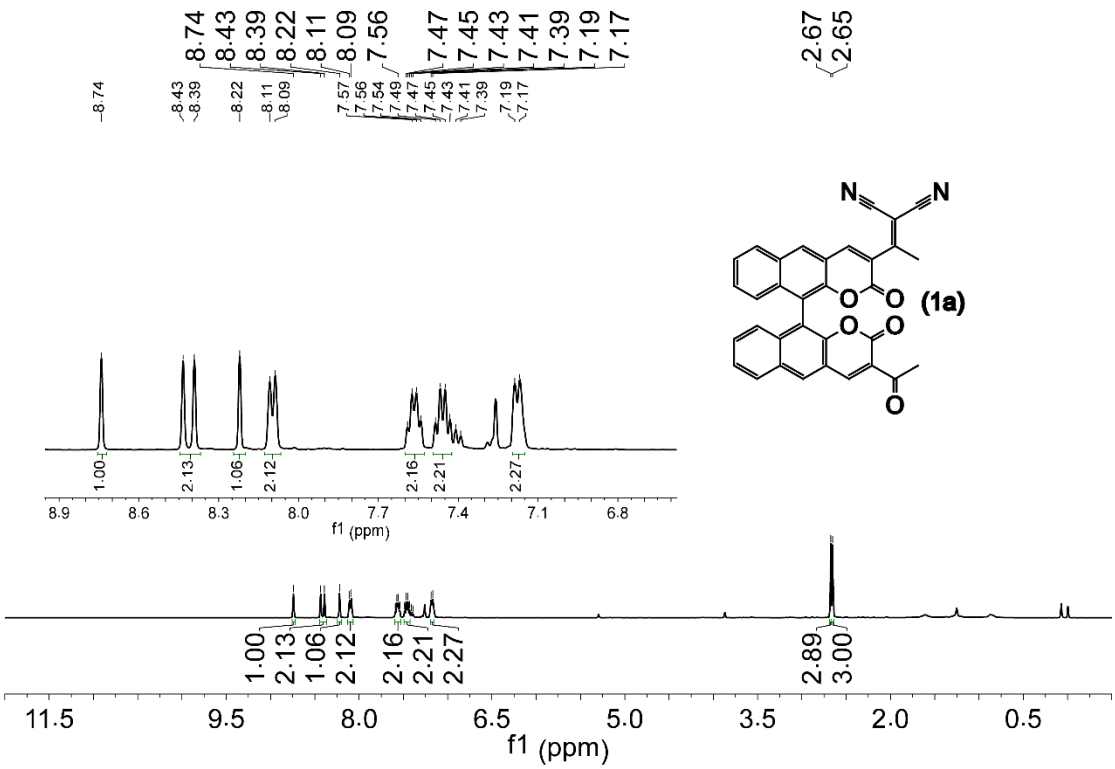


Figure S14. ^{1}H NMR of Compound **1a** in $CDCl_3$

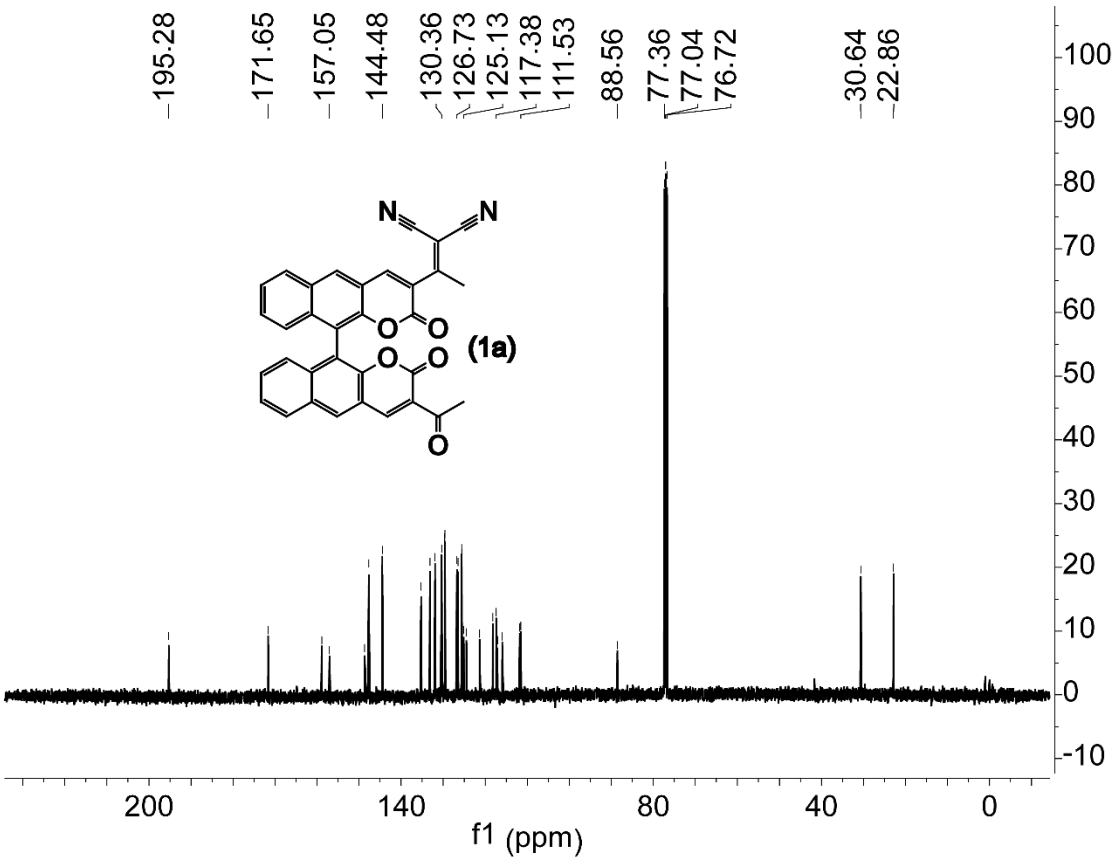


Figure S15. ^{13}C NMR of Compound **1a** in $CDCl_3$

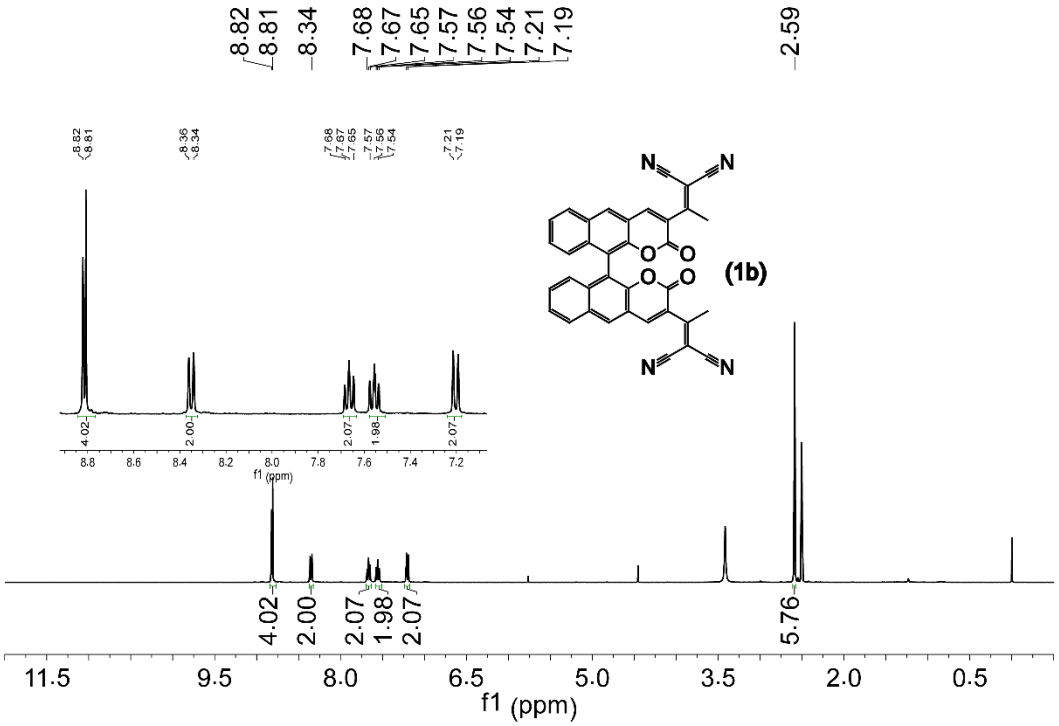


Figure S16. ^{1}H NMR of Compound **1b** in d_6-DMSO

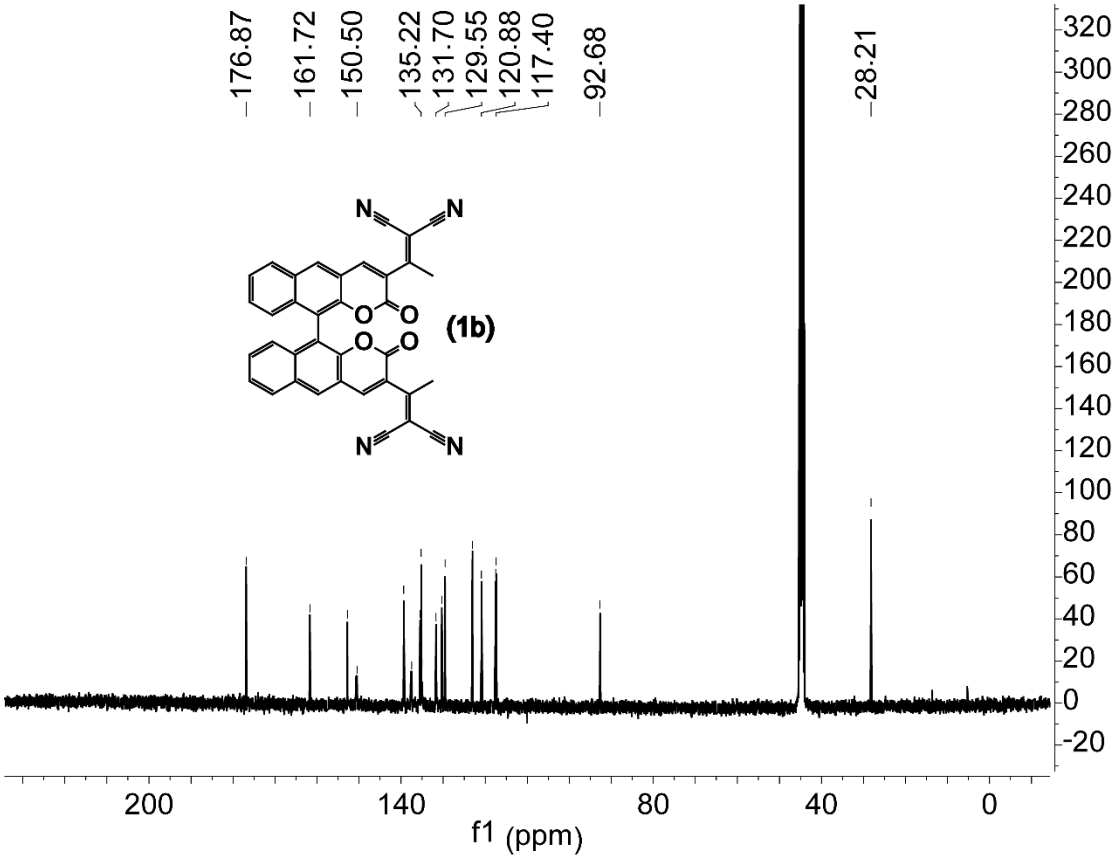


Figure S17. ^{13}C NMR of Compound **1b** in d_6-DMSO

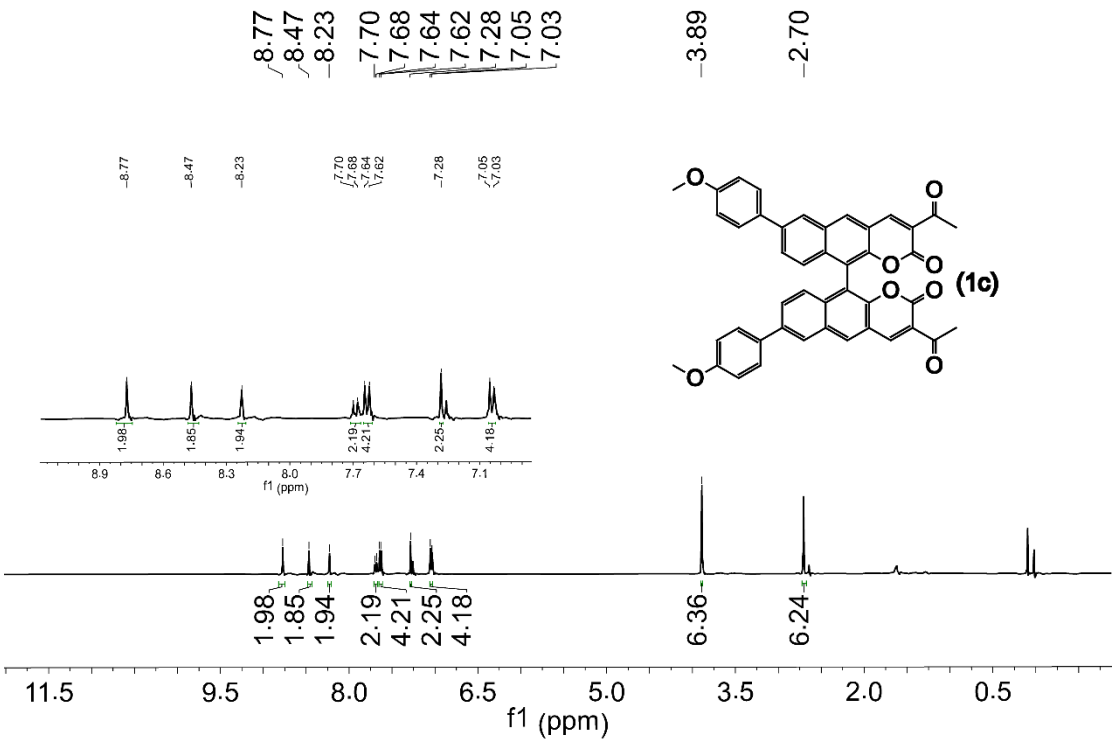


Figure S18. ^{1}H NMR of Compound **1c** in $CDCl_3$

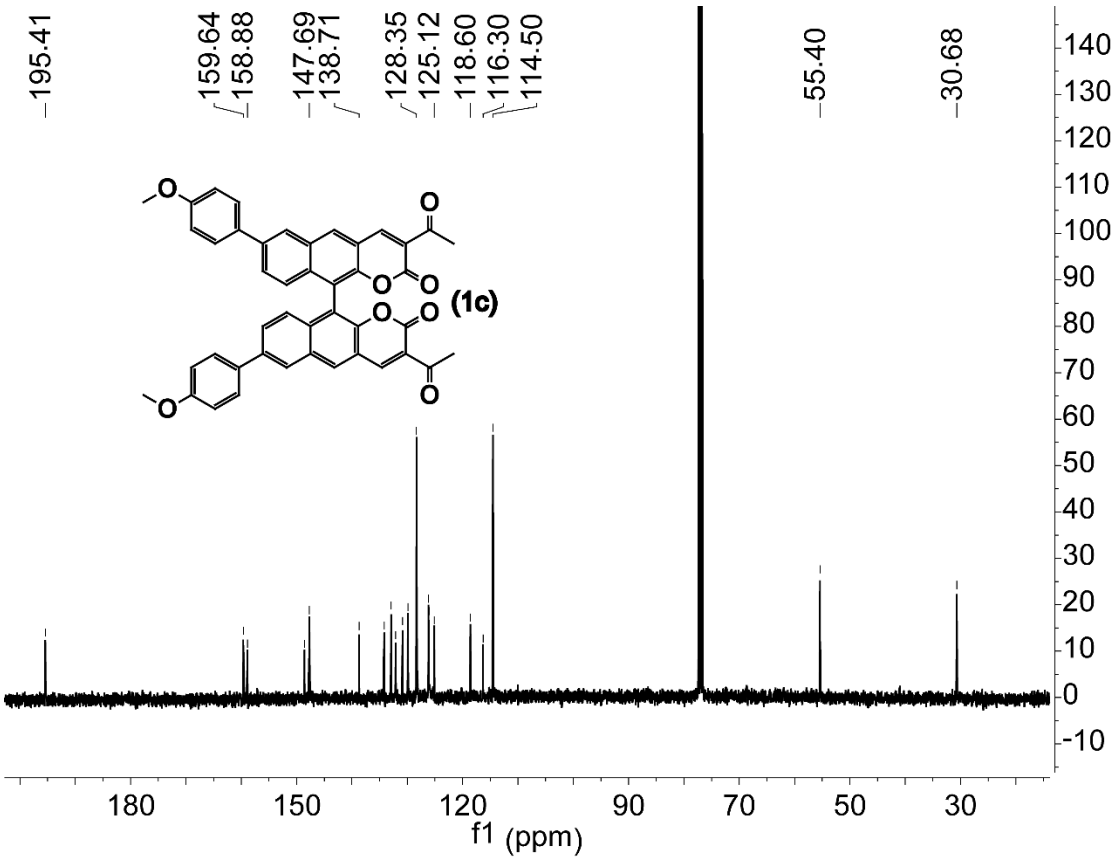


Figure S19. ^{13}C NMR of Compound **1c** in $CDCl_3$

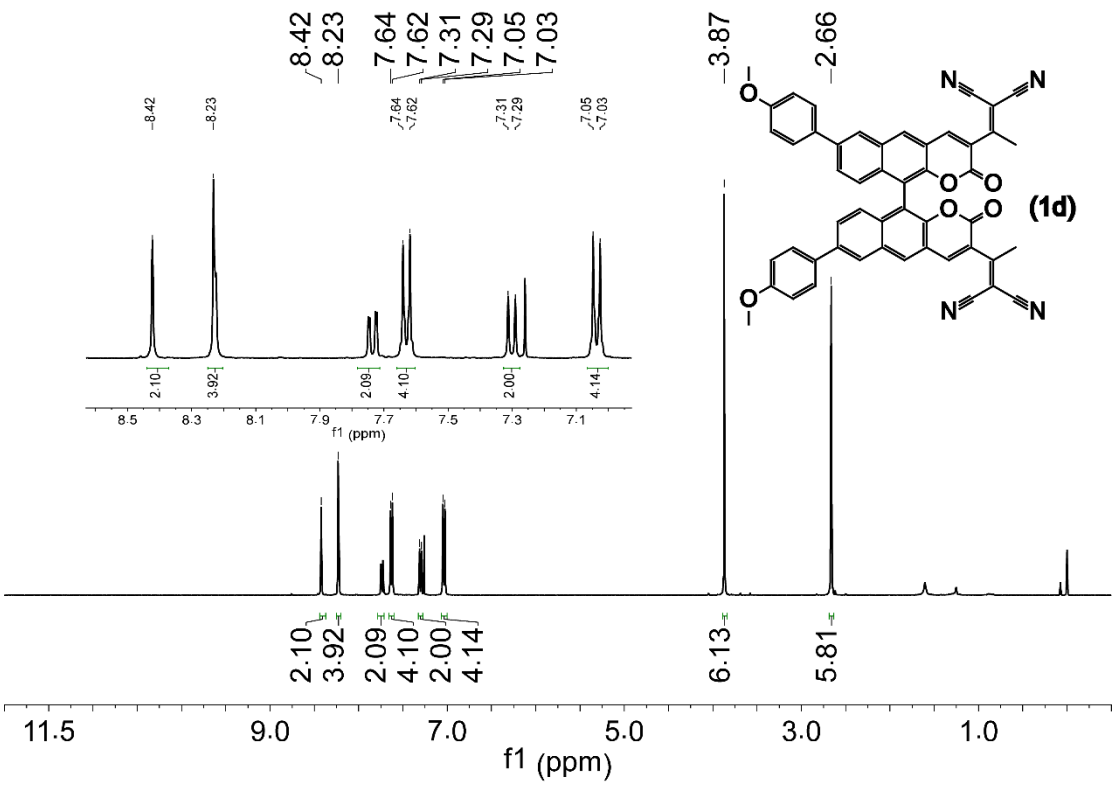


Figure S20. ^{1}H NMR of Compound **1d** in $CDCl_3$

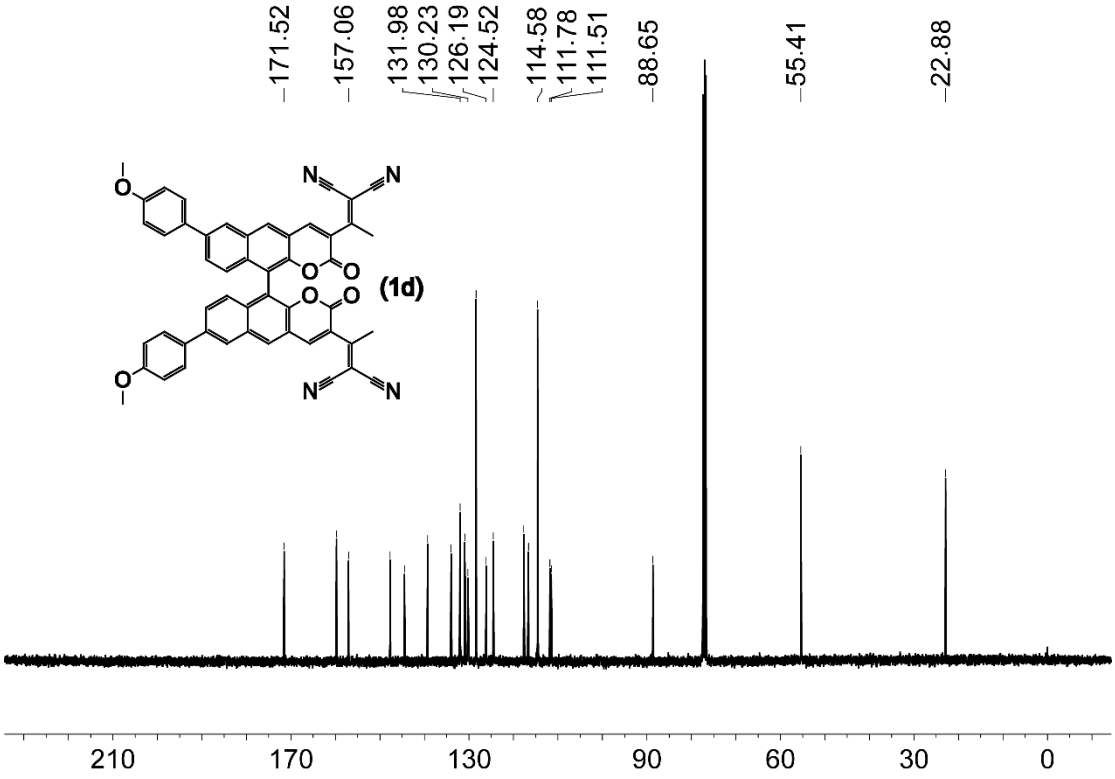


Figure S21. ^{13}C NMR of Compound **1d** in $CDCl_3$

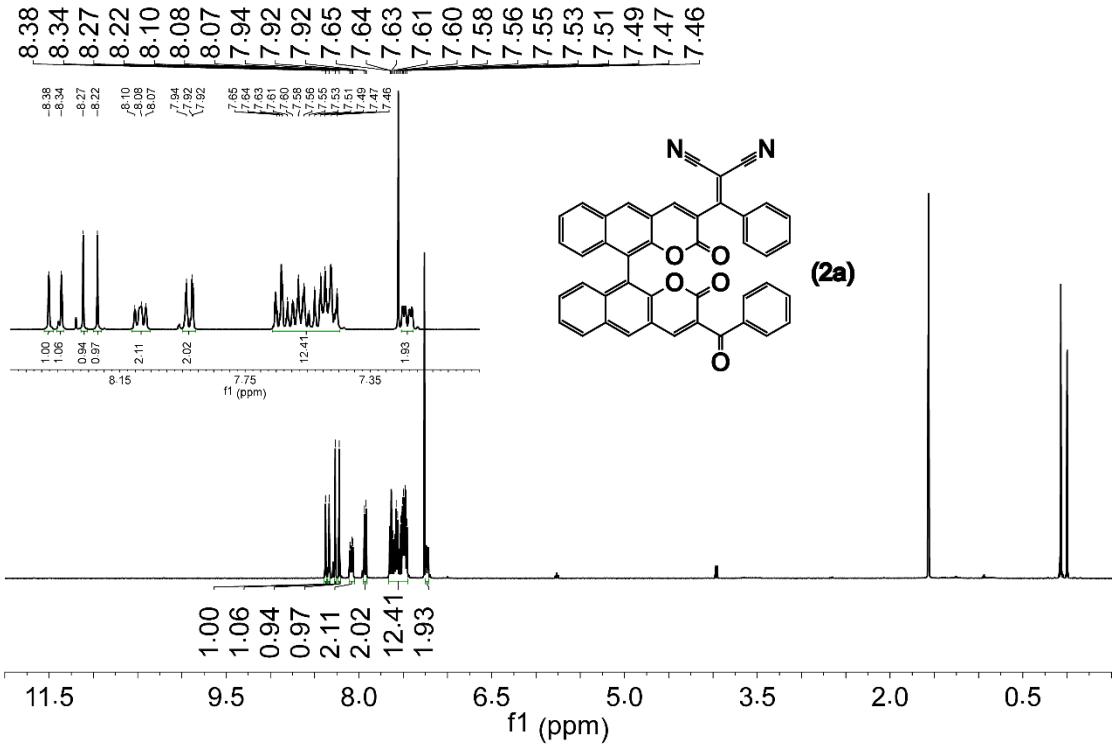


Figure S22. ^{1}H NMR of Compound **2a** in $CDCl_3$

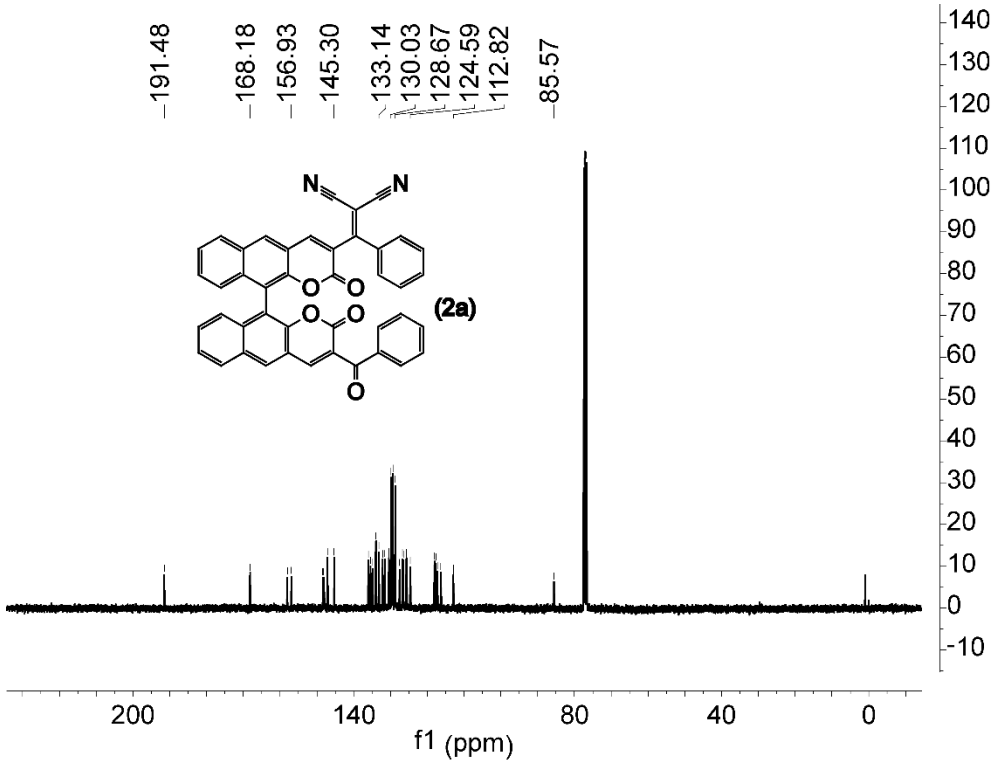


Figure S23. ^{13}C NMR of Compound **2a** in $CDCl_3$

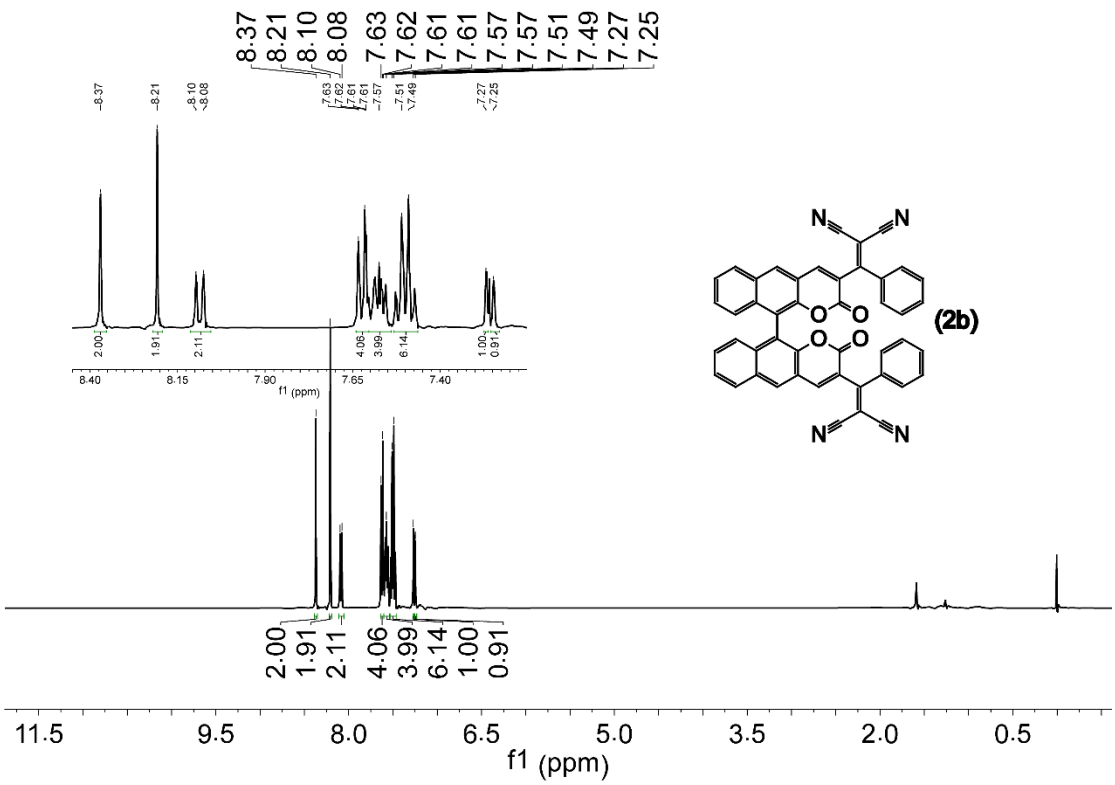


Figure S24. ^{1}H NMR of Compound **2b** in $CDCl_3$

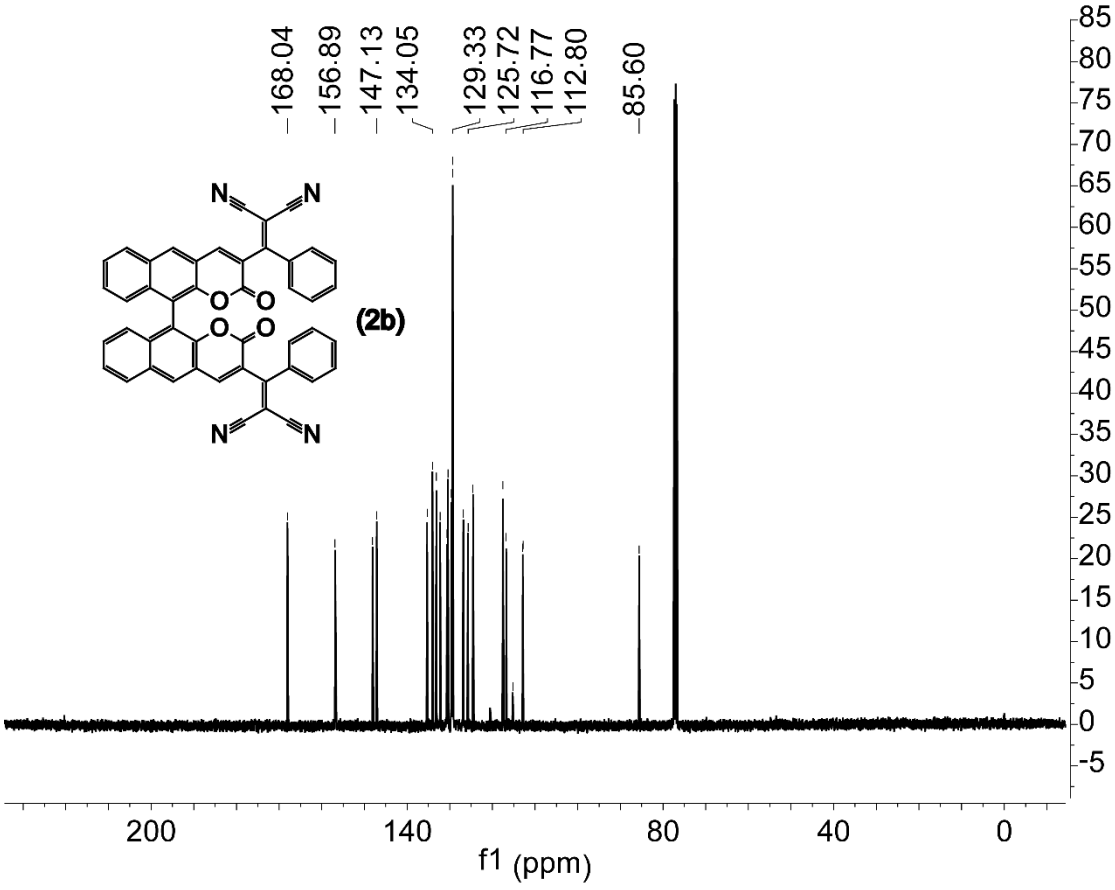


Figure S25. ^{13}C NMR of Compound **2b** in $CDCl_3$

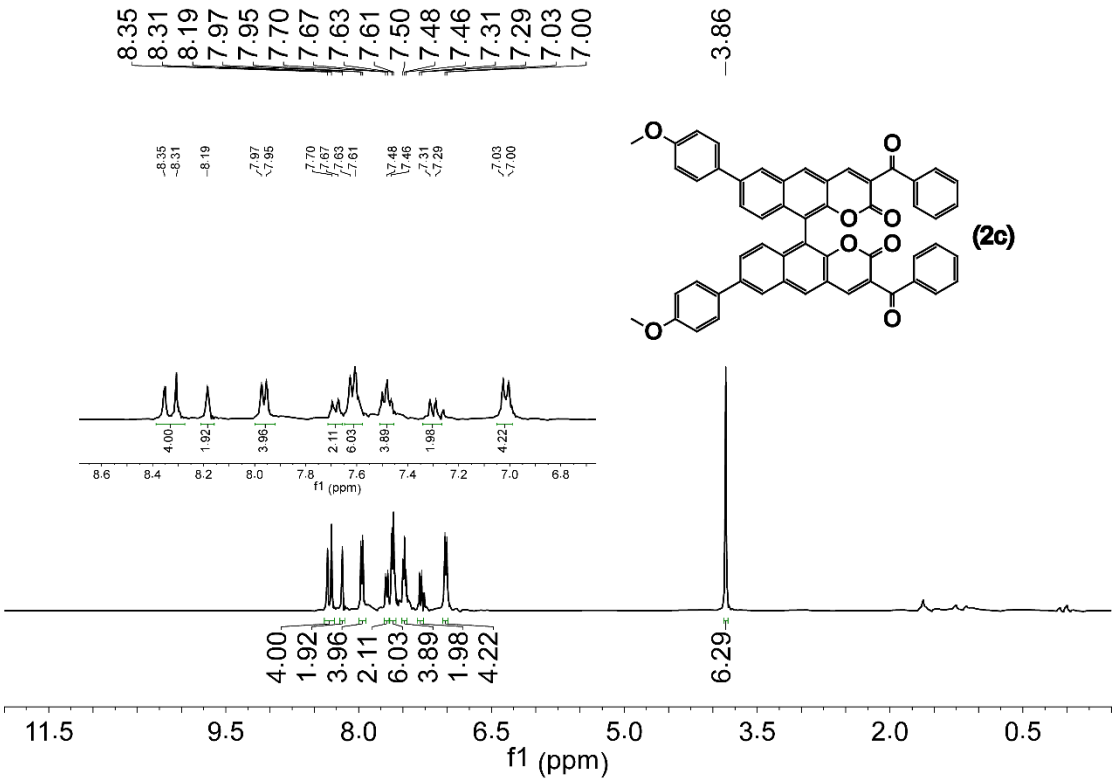


Figure S26. ^{1}H NMR of Compound **2c** in $CDCl_3$

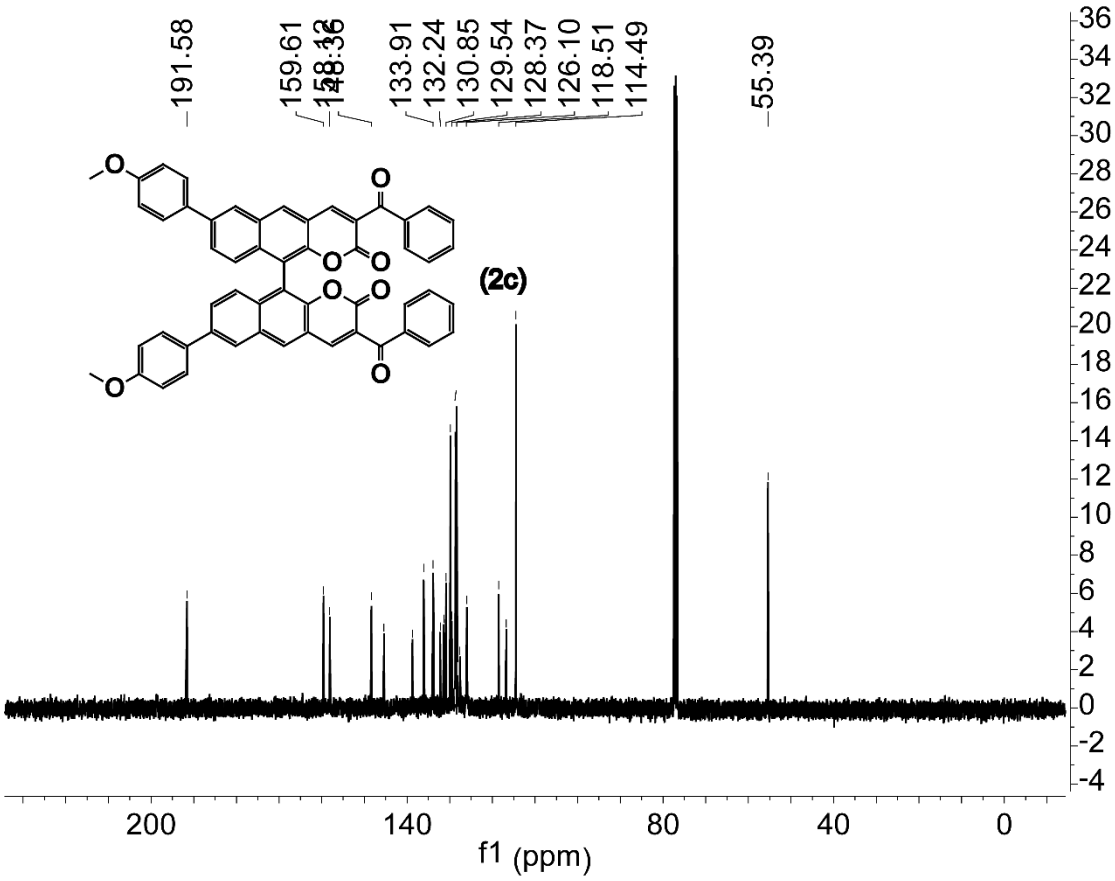


Figure S27. ^{13}C NMR of Compound **2c** in $CDCl_3$

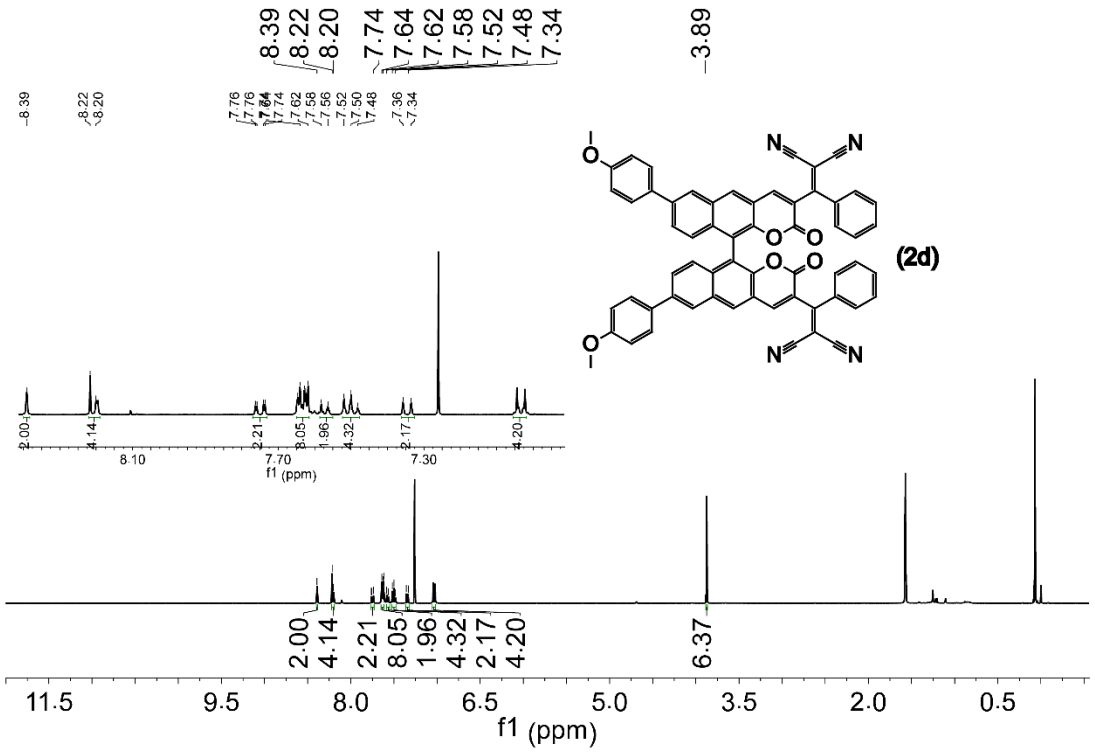


Figure S28. ^{1}H NMR of Compound **2d** in $CDCl_3$

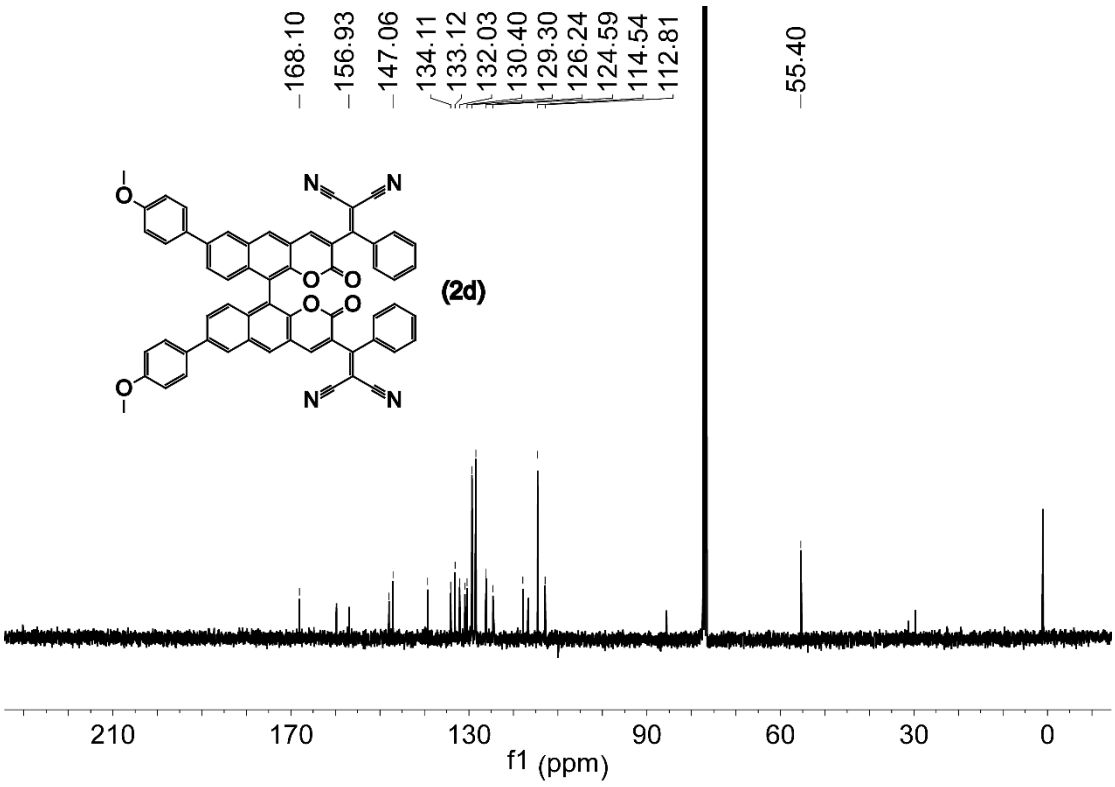
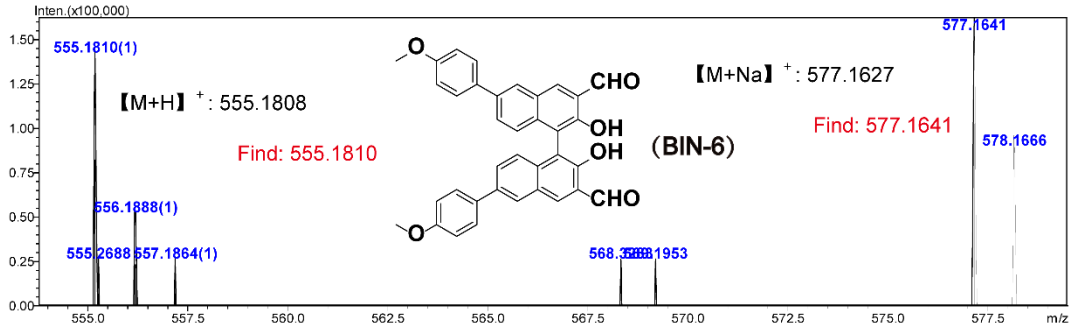
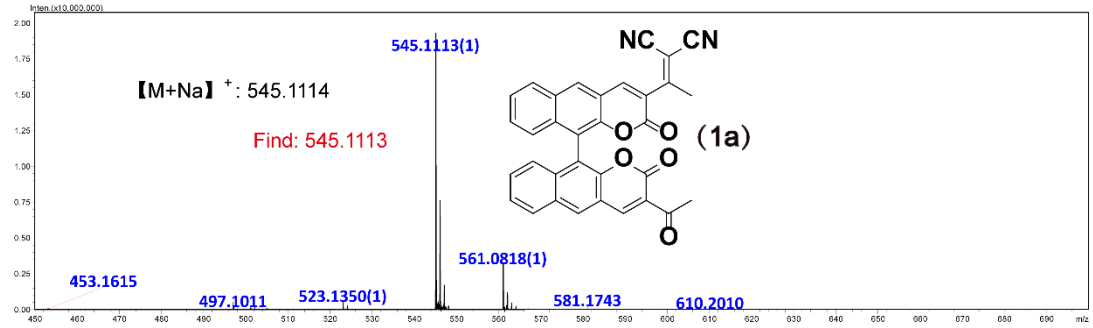
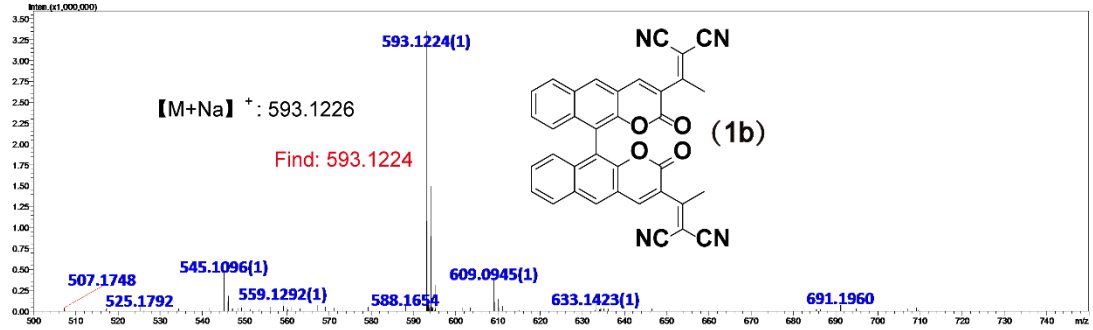


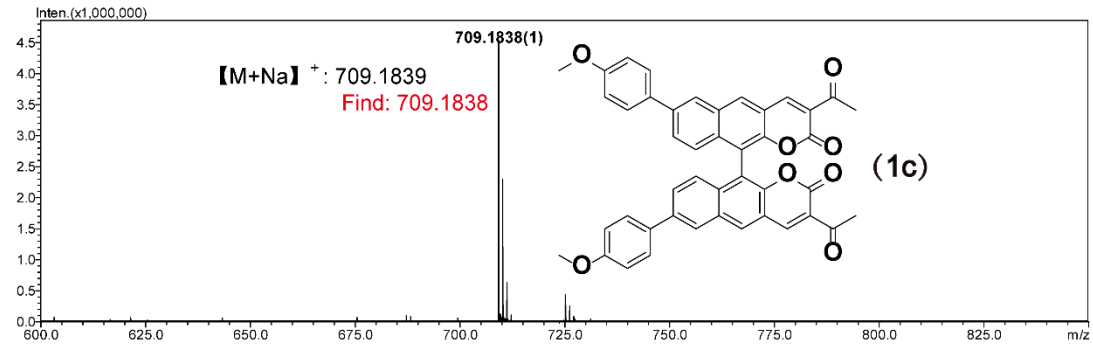
Figure S29. ^{13}C NMR of Compound **2d** in $CDCl_3$

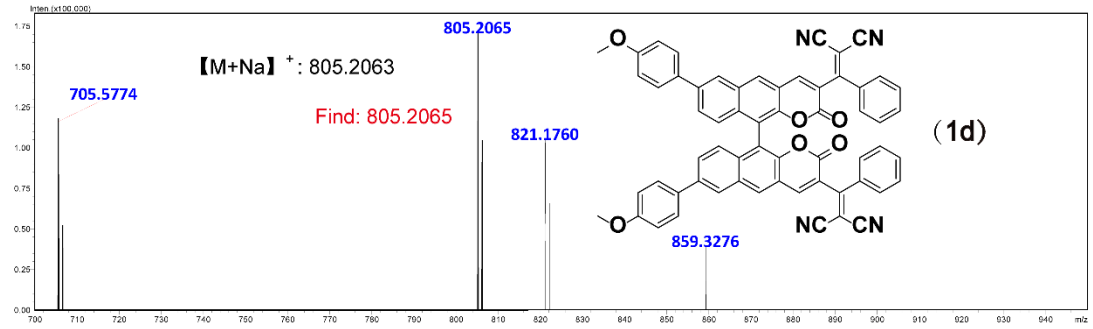
14. ESI-MS Data











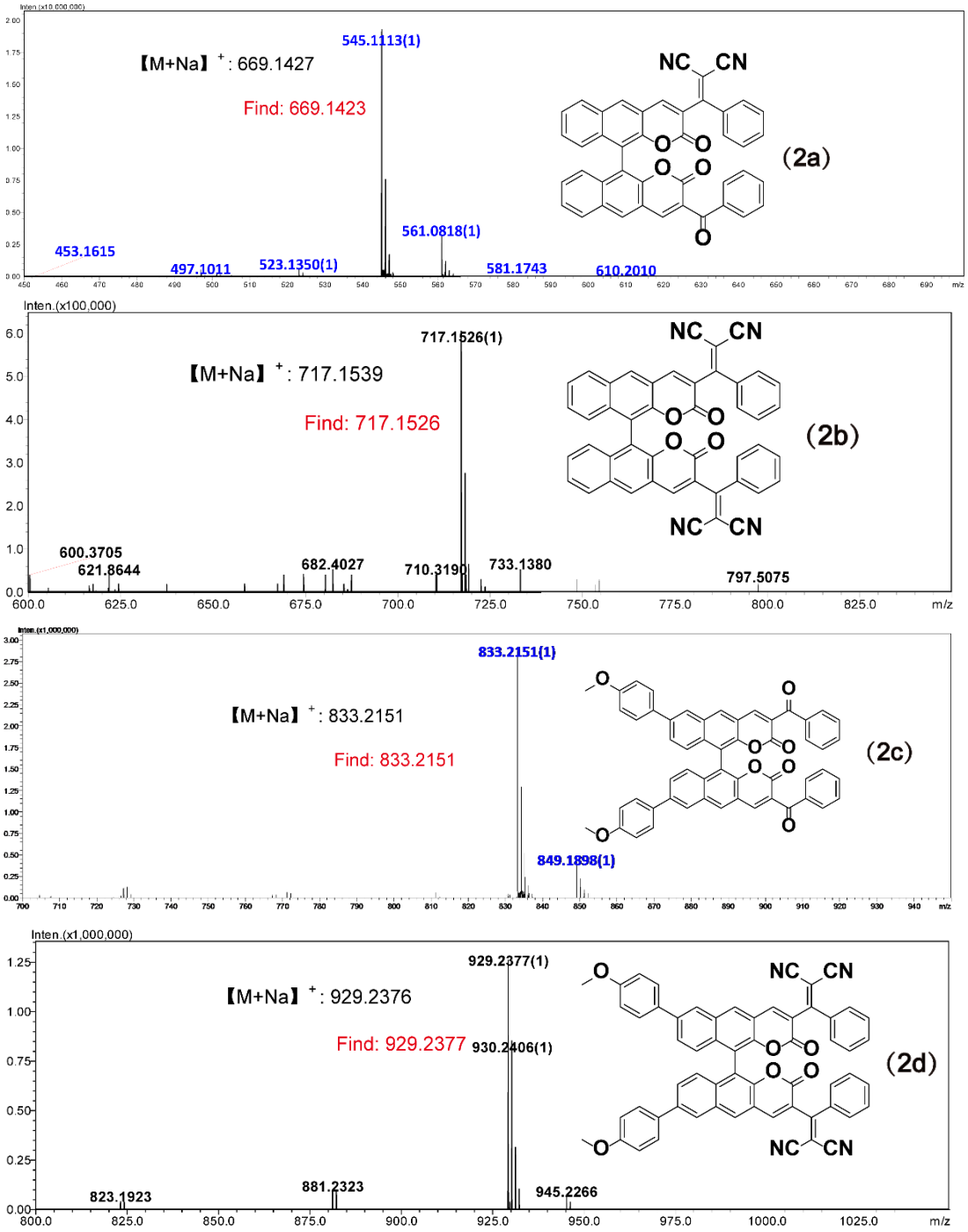


Figure S30. MS spectra of 1a-1d and 2a-2d.

15. References

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2 M. Sako, T. Aoki, N. Zumbrägel, L. Schober, H. Gröger, S. Takizawa and H. Sasai, Chiral. *J. Org.Chem.* **2019,** *84*, 1580.