Supporting Information for

# Synthesis of Fulvene-Containing Boron Complexes with Aggregation-Induced Emission and Mechanochromic Luminescence

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## EXPERIMENTAL SCETION

### Instruments and Characterizations

$^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a BrukerBiospinAvance-III 400 NMR spectrometer at ambient temperature for $^{1}H$ and 75.5 MHz for $^{13}C$. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak ($CDCl_3$, $^{1}H$ = 7.26 ppm, $^{13}C$ = 77.16 ppm, DMSO, $^{1}H$ = 2.54 ppm, $^{13}C$ = 40.45 ppm). Coupling constants (J) are given in hertz (Hz) and are quoted to the nearest 0.5 Hz. Peak multiplicities are described in the following way: s, singlet; d, doublet; t, triplet; m, multiplet. High-resolution mass spectra (HRMS) were obtained by using a Bruker microTOF II focus spectrometer (ESI). Absorption spectra and photoluminescence (PL) spectra were recorded on a Shimadzu UV-2700 and an Edinburgh Instrument FLS920. Absolute PL quantum yields were measured on a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics). Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a platinum disk working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium–ferrocene ($Fc^{+}$/Fc) as standard. The electrochemical experiments were carried out in $CH_3CN$ for oxidation and reduction potentials with $Bu_4NPF_6$ (0.1 M) as a supporting electrolyte. Powder X-Ray diffraction patterns of **BL2** in solid state were collected using a Bruker D8 ADVANCE diffractometer (Cu K$\alpha$ radiation, $\lambda$ = 1.540598 Å) with an operating power of 40 KV and fixed divergence slit of 0.76 mm. The data were collected in the range of $2\theta$ = 5-50°. X-Ray diffraction of thin films were collected in the reflection mode by using a Bruker D8 ADVANCE diffractometer (Cu K$\alpha$ radiation, $\lambda$ = 1.540598 Å) with an operating power of 40 KV. Aggregation-induced fluorescence (AIE) experiments was conducted in the condition of THF/$H_2O$ mixed solution with specific ration and the concentration of $1*10^{-3}$ M. The films were fabricated by preparing saturated stock solutions (50 mg in 1 mL 1, 2-dichloroethane) and applying 20 drops to the coverslips rotating at 2000 rpm. The films were dried in air for 12 h before measurements or thermal annealing. Annealing temperatures were determined experimentally by heating spin-cast films for 10 min at temperatures ranging from 60 to 100 °C in 10 °C increments before PL emission measurements. Annealed films were gently smeared with a weighing paper. The sample morphologies of spin-cast films were characterized by atomic force microscopy (AFM) (Digital Image, DI 3000) in tapping mode, and the resulting images were processed using Gwyddion software version 2.31. The MCF-7 (human breast adenocarcinoma cell line) was provided by Stem Cell Bank, Chinese Academy of Sciences (Shanghai, P. R. China), and cultured in DMEM supplemented with FBS (10%), Normocin (50 μg/mL), penicillin (100 U/mL) and streptomycin (100 μg/mL) in an atmosphere of $CO_2$ (5 vol%) and air (95 vol%) at 37°C.

### Materials and Reagents

All reagents were used as received from commercial sources without further purification. Air and/or water-sensitive reactions were conducted under nitrogen in dry, freshly distilled

solvents. 6, 6'-dimethylfulvene were prepared was obtained via methods according to the literature. [1-4]

**Synthesis of L1.**

A solution of *p*-methoxybenzoyl chloride (3.24 g, 19 mmol) in anhydrous ether (40 mL) was added dropwise for 3 hours to a solution of tert-butylcyclopentadienyl anions (28.5 mmol) in anhydrous ether at 0 °C, which derived from 6, 6-dimethylfulvene (28.5 mmol) and 1.3 M methyl lithium/ether solution (22 mL) in anhydrous ether (50mL). The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Petroleum ether was added before yellow precipitate was obtained. The precipitate was washed with hexane several times and stirred in HCl (5%, 40 mL) for 12 hours. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/petroleum ether = 1:4) to afford the product as yellow solid. (1.97 g, 53%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.8 Hz, 4H), 7.13 (s, 2H), 7.02 (d, J = 8.8 Hz, 4H), 3.91 (s, 6H), 1.23 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 183.6, 162.3, 148.7, 136.4, 131.6, 130.2, 123.2, 113.4, 55.5, 31.8, 31.2; HRMS (ESI): m/z calcd for 390.1831; Found: 391.1878 $[M+H]^+$.

**Synthesis of BL1.**

Under $N_2$ protection, $BF_3{\cdot}Et_2O$ (1.0ml, 7.9 mmol) was added in the solution of L1 (0.5 g, 1.5 mmol) in anhydrous DCM (50 ml). The reaction mixture was stirred at 45 °C overnight. After the reaction mixture was cooled to room temperature, 50 ml of water was added. The layers were separated. The aqueous phase was extracted with DCM (3 × 25 mL), and the combined organic phases were dried over sodium sulfate, filtered, and then the solvent was removed. The crude product was purified by multi-precipitation of $CH_2Cl_2$/Hexane to afford the product as red solid (0.40 g, 70%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.8 Hz, 4H), 7.37 (s, 2H), 7.05 (d, J = 8.9 Hz, 4H), 3.94 (s, 6H), 1.28 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 179.0, 164.4, 152.8, 143.1, 134. 7, 128.6, 123.4, 114.0, 77.3, 55.7, 32.0, 31.1; HRMS (ESI): m/z calcd for 438.1814; Found: 439.1819 $[M+H]^+$.

**Synthesis of L2.**

A solution of 2-naphthoyl chloride (3.6 g, 19 mmol) in anhydrous ether (40 mL) was added dropwise for 3 hours to a solution of tert-butylcyclopentadienyl anions (28.5 mmol) in anhydrous ether at 0 ºC, which derived from 6, 6-dimethylfulvene (28.5 mmol) and 1.3 M methyl lithium/ether solution (22 mL) in anhydrous ether (50mL). The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Petroleum ether was added before yellow precipitate was obtained. The precipitate was washed with hexane several times and stirred in HCl (5%, 40 mL) for 12 hours. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/petroleum ether = 1:2) to afford the product as yellow solid. (2.72 g, 67.3%). $^1$H NMR (400 MHz, DMSO): δ = 8.43 (s, 2H), 8.13 (d, J = 8.6 Hz, 4H), 8.07 (d, J = 7.9 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.68 (s, 2H), 7.24 (s, 2H), 1.18 (s, 9H). $^{13}$C NMR (101 MHz,

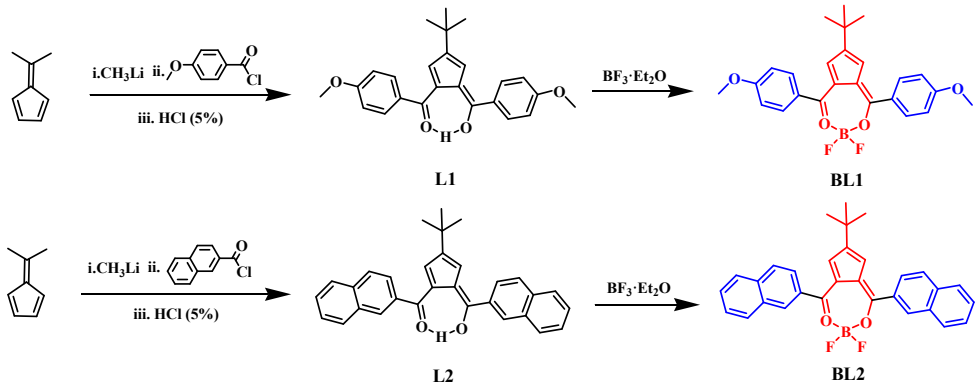
DMSO): δ = 183.5, 149.9, 138.1, 134.3, 132.0, 130.4, 129.2, 128.2, 127.7, 127.1, 125.9, 123.8, 31.6, 30.8. HRMS (ESI): m/z calcd for 430.1933; Found: 430.1945 $[M]^+$.

**Synthesis of BL2.**

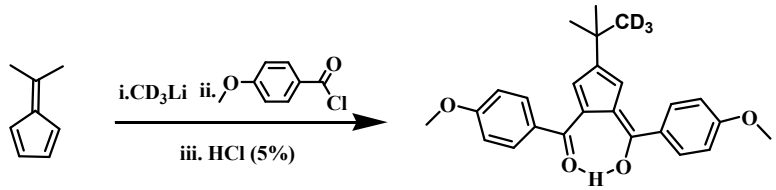
Under $N_2$ protection, $BF_3{\cdot}Et_2O$ (1.0ml, 7.9 mmol) was added in the solution of L2 (0.5 g, 1.5 mmol) in anhydrous DCM (50 ml). The reaction mixture was stirred at 45 °C overnight. After the reaction mixture was cooled to room temperature, 50 ml of water was added. The layers were separated. The aqueous phase was extracted with DCM (3 × 25 mL), and the combined organic phases were dried over sodium sulfate, filtered, and then the solvent was removed. The crude product was purified by multi-precipitation of $CH_2Cl_2$/Hexane to afford the product as red solid (0.58 g, 82%).$^1$H NMR (400 MHz, $CDCl_3$):δ = 8.42 (s, 2H), 8.00 (s, 8H), 7.65 (s, 4H), 7.52 (s, 2H),1.27 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 180.4, 154.4, 145.7, 135.9, 134.8, 133.6, 132.5, 129.8, 129.3, 128.6, 128.1,127.5,124.6, 32.3, 31.2; HRMS (ESI): m/z calcd for 478.1916; Found: 478.1917 $[M]^+$.

**Synthesis of L3.**

Under $N_2$ protection, $^t$BuLi (9 mmol, 6.9 mL) was added dropwise to $CD_3I$ solution (10 mmol in 15 mL dry $Et_2O$) in -78 °C, which was stirred for 40 min and then warmed to 0 °C. 6, 6-dimethylfulvene (9 mmol,0.954 g) in $Et_2O$ (15 mL) was added to the reaction mixture and stirred for one hour at 0 °C to produce tert-butylcyclopentadienyl anion, which was added dropwise by the solution of p-methoxybenzoyl chloride (6 mmol,1.024 g) and $Et_2O$ (20 mL) in one hour. The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Petroleum ether was added before yellow precipitate was obtained. The precipitate was washed with hexane several times and stirred in HCl (5%, 40 mL) for 12 hours. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/petroleum ether = 1:4) to afford the product as yellow solid.(0.56 g, 48%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.8 Hz, 4H), 7.13 (s, 2H), 7.02 (d, J = 8.8 Hz, 4H), 3.91 (s, 6H), 1.23 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 183.4, 162.3, 148.8, 136.5, 131.9, 130.4, 123.8, 113.6, 55.5, 31.6, 31.2; HRMS (ESI): m/z calcd for 393.2019; Found: 394.2098 $[M+H]^+$.




**Scheme S1** Schematic representation of the synthesis of **BL1** and **BL2**.




**L3**

**Scheme S2** Schematic representation of the synthesis of **L3**.

**Single Crystal Data Collection and Refinement.**

Suitable single crystals were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 100.01 K on an Agilent SuperNova CCD-based diffractometer (Cu K$\alpha$ radiation, $\lambda$ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[5] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[5] None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against $F^2$ by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2 Ueq of the attached atom. Crystallographic processing parameter for **L2**, **BL1** and **BL2** are listed in Tables S1, respectively. Crystallographic data for **L2**, **BL1** and **BL2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1914741-1914743.

**Table S1** Crystallographic data for **L2**, **BL1**, **BL2**.

| | **L2** | **BL1** | **BL2** |
|---|---|---|---|
| Formula | $C_{31}H_{26}O_2$ | $C_{25}H_{25}BF_2O_4$ | $C_{31}H_{25}BF_2O_2$ |
| Molecule Weight | 430.52 | 438.26 | 478.32 |
| Crystal System | triclinic | triclinic | monoclinic |
| Space group | *P-1* | *P-1* | *C2/c* |
| a [Å] | 9.6358(7) | 7.8130(6) | 24.275(11) |
| b [Å] | 10.2626(6) | 9.3837(6) | 12.1694(17) |
| c [Å] | 12.5875(8) | 16.3462(11) | 21.588(10) |
| α [º] | 75.480(5) | 101.355(6) | 90.00 |
| β [º] | 73.810(6) | 97.002(6) | 123.726(11) |
| γ [º] | 83.749(6) | 104.391(6) | 90.00 |
| V [Å3] | 1156.20(13) | 1119.52(13) | 5134.1(6) |
| Z | 2 | 2 | 8 |
| $\rho_{calcd}$ [g $cm^{-3}$] | 1.237 | 1.300 | 1.238 |
| Temp. [K] | 293 | 293 | 293 |
| No. of Reflns. | 7623 | 7135 | 16290 |
| R1 | 0.0498 | 0.0403 | 0.0745 |
| wR2 [I>2.00σ (I) ] | 0.1294 | 0.1002 | 0.2210 |

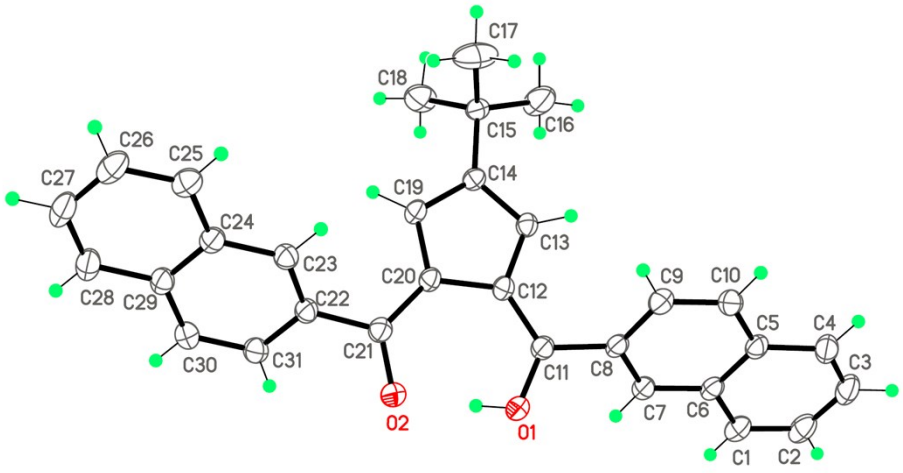



**Fig. S1** ORTEP figure of L2 (30% probability displacement ellipsoids).

**Table S2.** Hydrogen-bond and C—H···π geometry (Å, °) for **L2**.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O(1)—H(1)···O(2) | 0.82 | 1.6542(13) | 2.4675(19) | 171.457(102) |

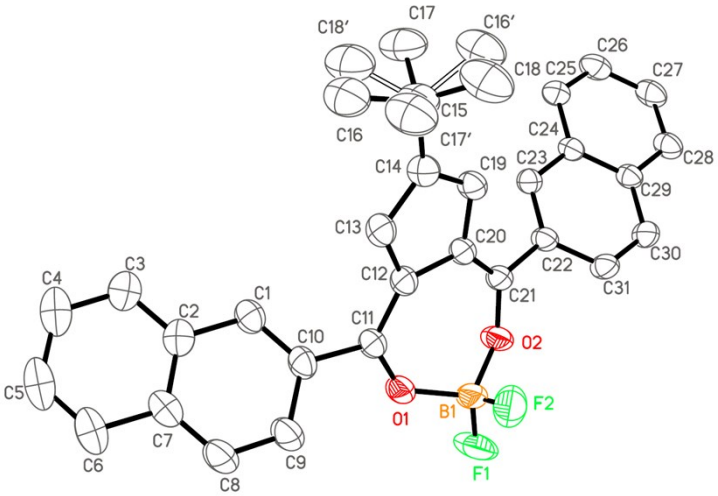



**Fig. S2** ORTEP figure of **BL2** (30% probability displacement ellipsoids).

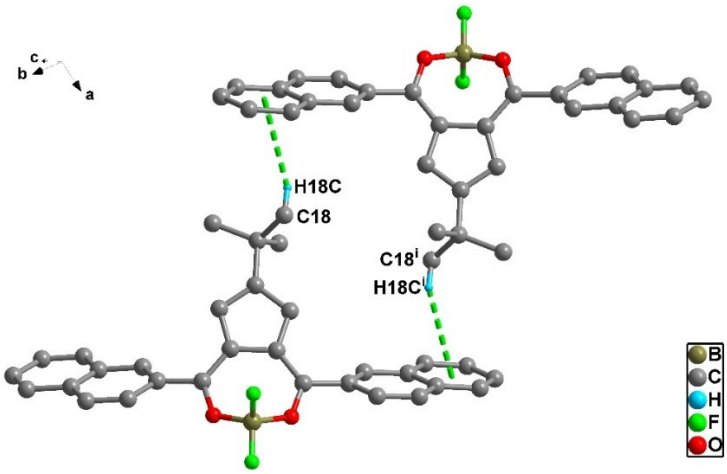



**Fig. S3** Schematic representation of C-H···F interactions.

**Table S2.** C—H···π and C—H···F geometry (Å, °) for B**L2**.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C(18)—H(18C)···*Cg*(1)[a] | 0.82 | 3.0992(5) | 3.7927(6) | 130.419(8) |
| C(26)—H(26)···F(1) | 0.93 | 2.7099(1) | 3.2163(1) | 115.079(3) |
| C(27)—H(27)···F(1) | 0.93 | 2.5598(1) | 3.1407(1) | 120.927(3) |
| C(4)—H(4)···F(2) | 0.93 | 2.7152(3) | 3.1716(3) | 111.148(4) |

[a] *Cg*(1) represents the centroid of the C12-C13-C14-C19-C20 ring (Cp ring).

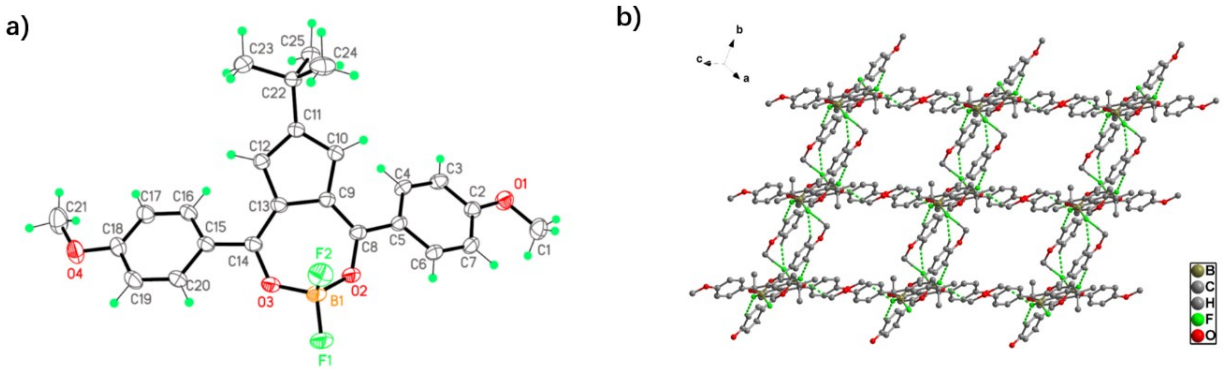



**Fig. S4** a) ORTEP figure of **BL1** (30% probability displacement ellipsoids); b) two-dimensional (2D) networks view along [*211*] axis.

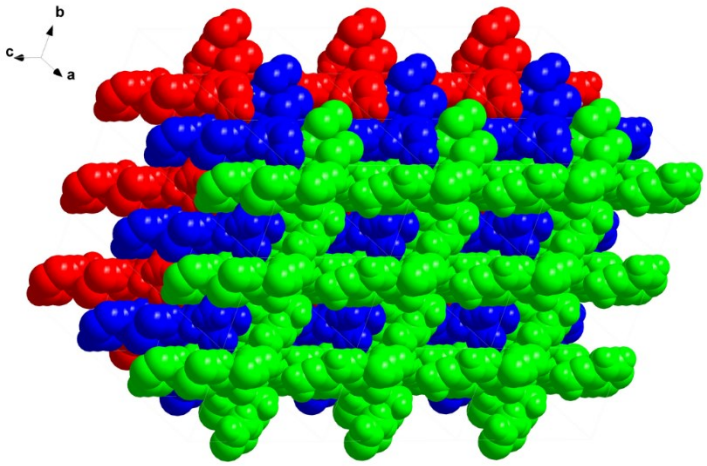



**Fig. S5** 3D packing pattern view along [*211*] axis in **BL1**.

**Table S4** C—H···F bond geometry (Å, °) for **BL1**.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C(17)—H(17)···F(2) | 0.93 | 2.5476(2) | 3.3921(2) | 151.170(9) |
| C(19)—H(19)···F(1) | 0.93 | 2.6381(2) | 3.3635(3) | 135.316(7) |
| C(1)—H(1B)···F(1) | 0.93 | 2.7611(2) | 3.3374(2) | 119.363(2) |
| C(21)—H(21C)···F(1) | 0.93 | 2.7974(2) | 3.5555(3) | 136.479(6) |

**Computational Data.**

All calculations were carried out using the Gaussian 09 program package. The geometries of **BL1** and **BL2** in the ground state were optimized via DFT calculations at the B3LYP/6-31G* level.[6]

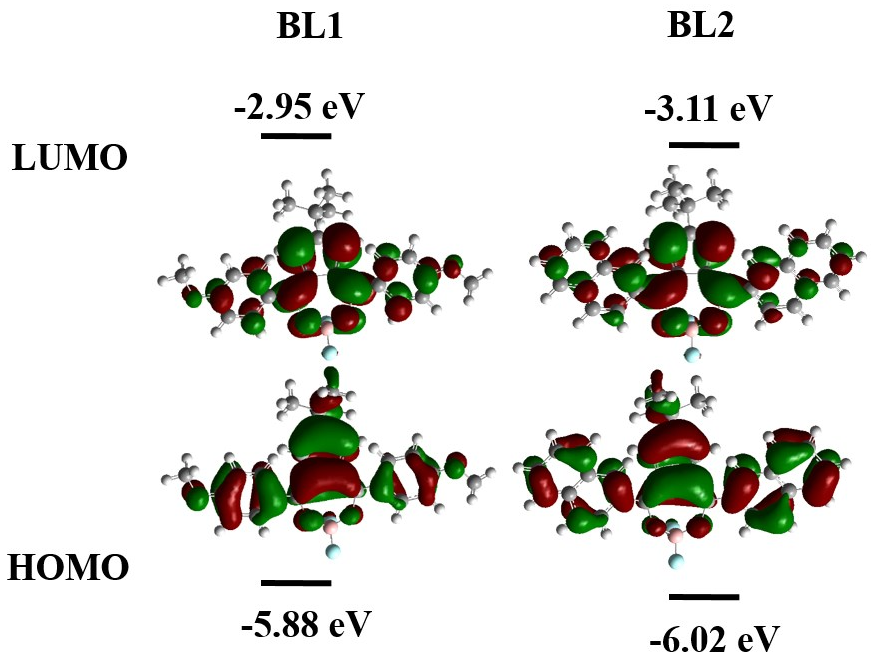



**Fig. S6** Molecular-orbital distribution and calculated energies of the HOMO and LUMO for **BL1** and **BL2**.

**Electrochemical data**

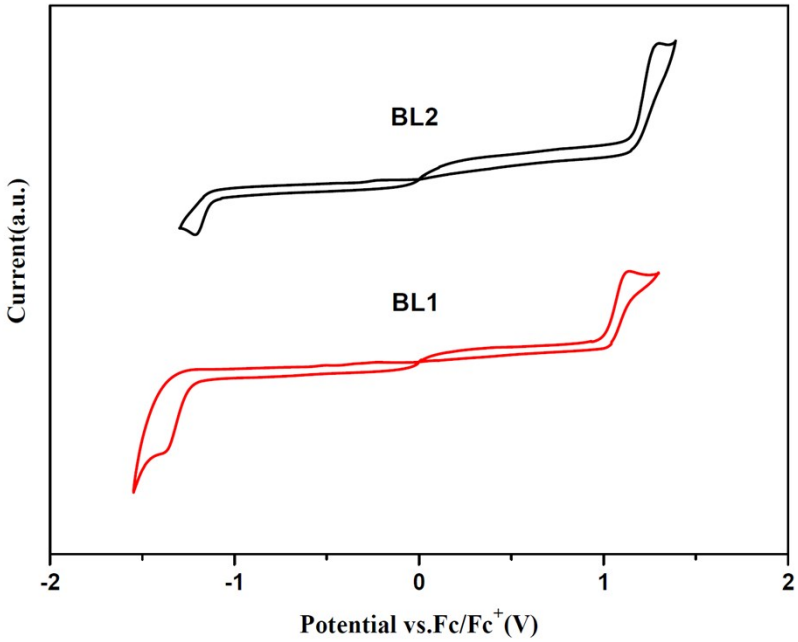



**Fig. S7** Cyclic voltammograms of **BL1** and **BL2**. (The oxidation and reduction potentials *vs.* $Fc^+/Fc$ were recorded in $CH_3CN$ with concentration of 0.001 M).

**Table S5** Electrochemical data, HOMO and LUMO energy levels of **BL1** and **BL2**.

| Ligands | $E_{ox}$[a] (V) | $E_{re}$[a] (V) | HOMO (eV) | LUMO (eV) |
|---|---|---|---|---|
| **BL1** | 1.01 | -1.25 | -6.01 | -3.29 |
| **BL2** | 1.15 | -1.15 | -6.21 | -3.41 |

[a] The oxidation and reduction potentials *vs.* $Fc^+/Fc$ were recorded as the onset of redox curves in $CH_3CN$-$Bu_4NPF_6$ (0.1 M). [b] HOMO and LUMO level were calculated from $E_{ox}$ and $E_{red}$ according to the equation of $-1.4\ E_{ox} - 4.6$ for the HOMO and $-1.19\ E_{red} - 4.78$ for the LUMO provided by the literature.[1]

**Photophysical properties**

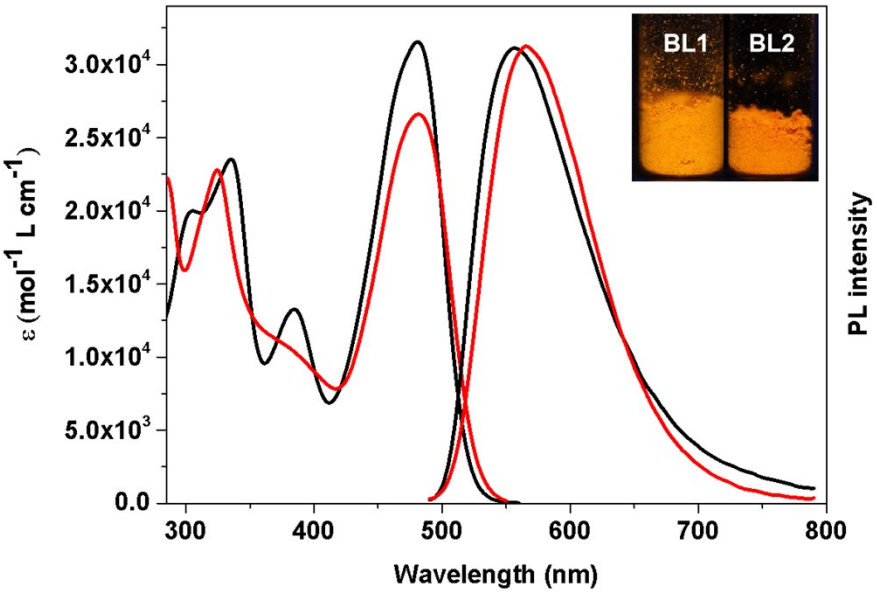



**Fig. S8** Absorption and PL emission spectra (in toluene) of **BL1** (black line) and **BL2** (red line). Inset: photos of **BL1** and **BL2** in solid state under the excitation of UV lamp.

**Table S6.** Photophysical properties of **BL1** and **BL2** in toluene.

| Complexes | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | τ (ns) | PLQY (%) |
|---|---|---|---|---|
| **BL1** | 481 | 556 | 0.8 | < 1 |
| **BL2** | 482 | 566 | 1.0 | < 1 |

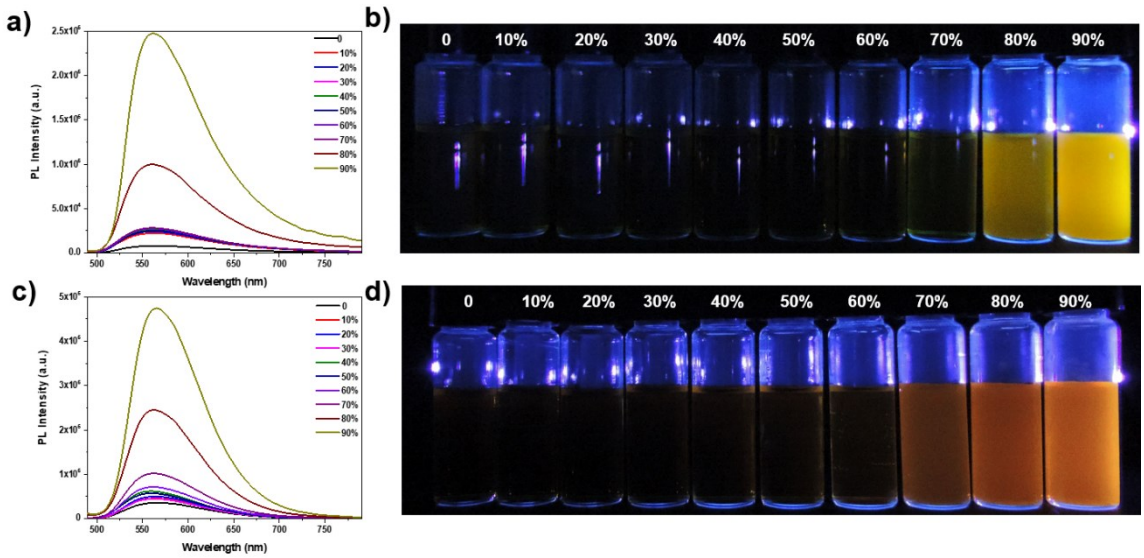



**Fig. S9** a) Emission spectra of THF/water solution containing **BL1** (a), **BL2** (c) and the photographs of **BL1** (b), **BL2** (d) in the THF/water solution taken under the UV irradiation.

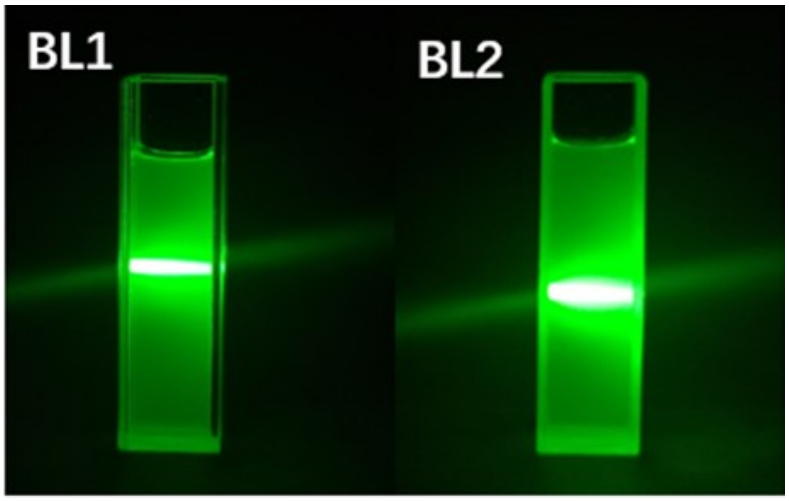



**Fig. S10** Photographs of **BL1** and **BL2** in THF/water solution (90% water in volume) taken in the dark with the UV light beam irradiation.

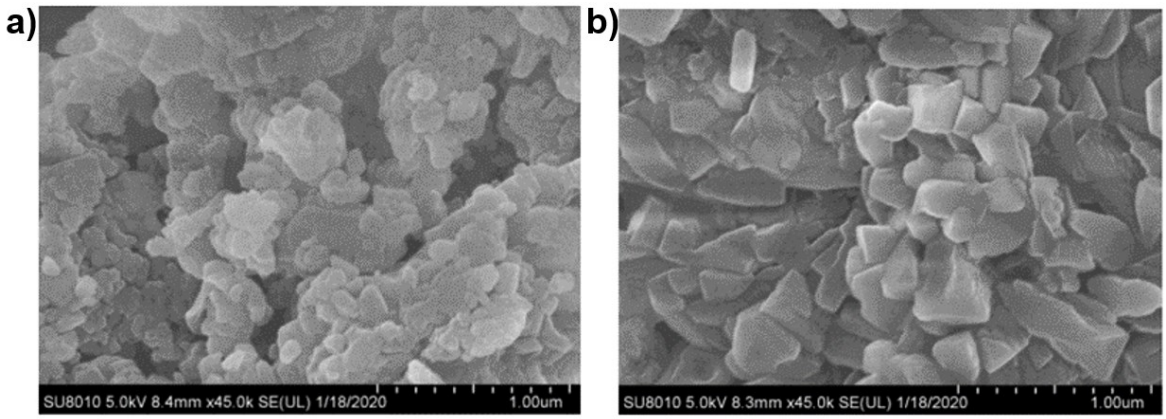



**Fig. S11** Scanning electron microscope (SEM) images of **BL1** (a) and **BL2** (b) obtained from the THF/water solution (90% water in volume).

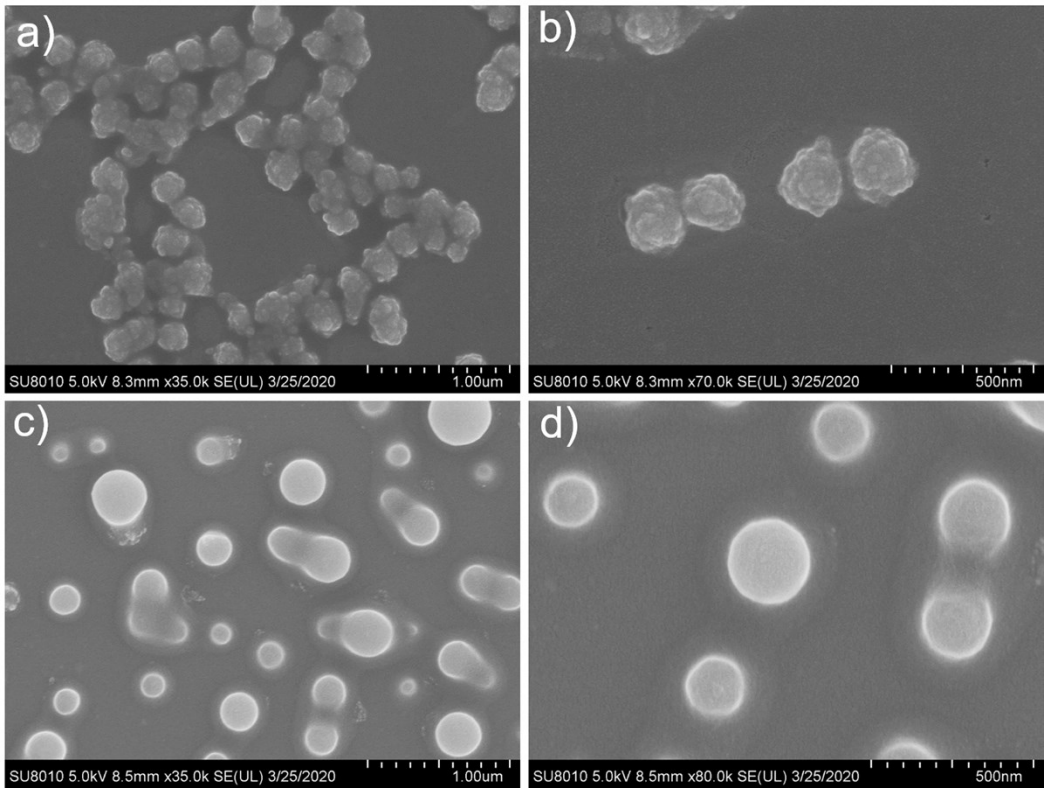



**Fig. S12** Scanning electron microscope (SEM) images of nanospheres of **BL1** (a, b) and **BL2** (c, d).

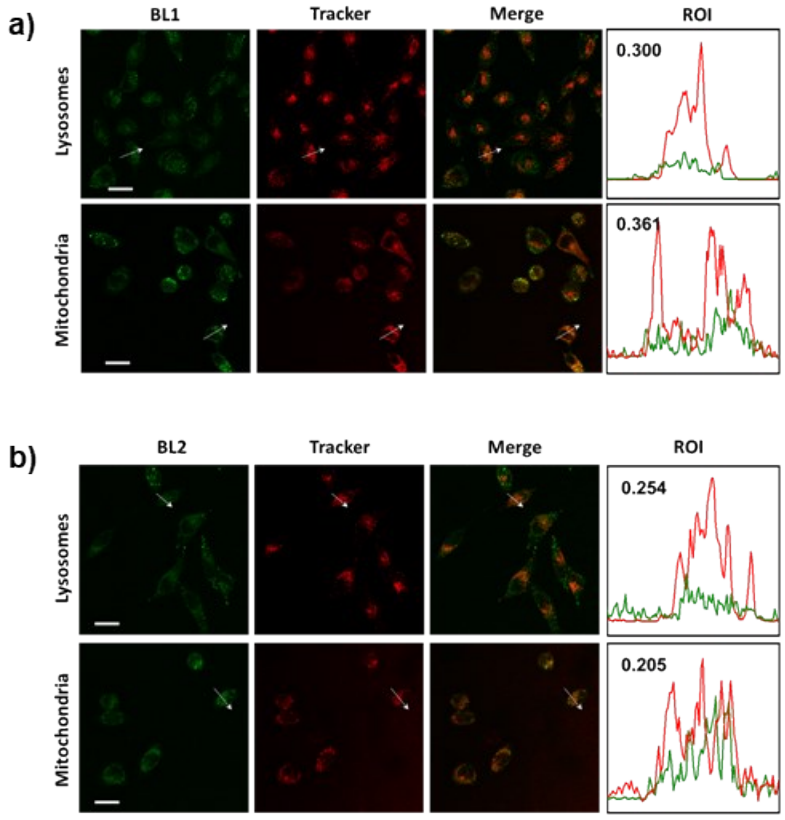



**Fig. S13** Subcellular localization of **BL1** and **BL2** in MCF-7 cancer cells (Scale bar: 25 μm). The confocal laser scanning microscope (CLSM) images of live MCF-7 cancer cells pretreated with **BL1**/**BL2** (200 μL, 10 μg/mL, 60 min), subsequently coincubated with Mito/LysoTracker (200 μL, 10 nM, 10 min). Green images of **BL1**/**BL2** excited by 405 nm light, with emission collected at 500-550 nm. Red images of tracker for mitochondria excited by 633 nm light, with emission collected at 650-690 nm, for lysosomes excited by 561 nm light, with emission collected at 580-610 nm. Merged images of the green and red channel images, intensity profiles along the line segment in merged images. Green and red lines represent the intensities of BL1/BL2 and Tracker, respectively. Pearson correlation coe□cients: R = 0.361 for mitochondria (**BL1**), R = 0.300 for lysosomes (**BL1**), R = 0.205 for mitochondria (**BL2**), R = 0.254 for lysosomes (**BL2**).

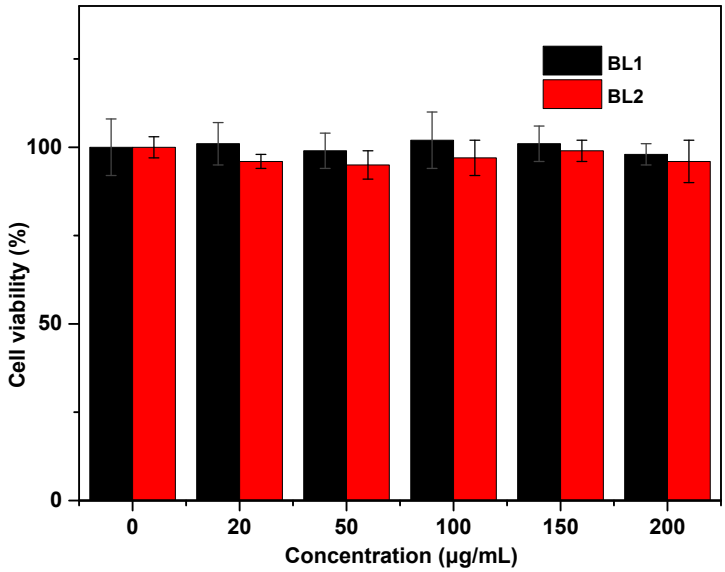



**Fig. S14** In vitro cytotoxicity of **BL1** and **BL2** against MCF- 7 cells. The MCF-7 cells were treated with increasing concentrations of **BL1** and **BL2** (200 μL/well) as a treatment group, treated with free DMEM as a control group for 24 h at 37 °C under a 5% $CO_2$ atmosphere, and incubated for 1 h.

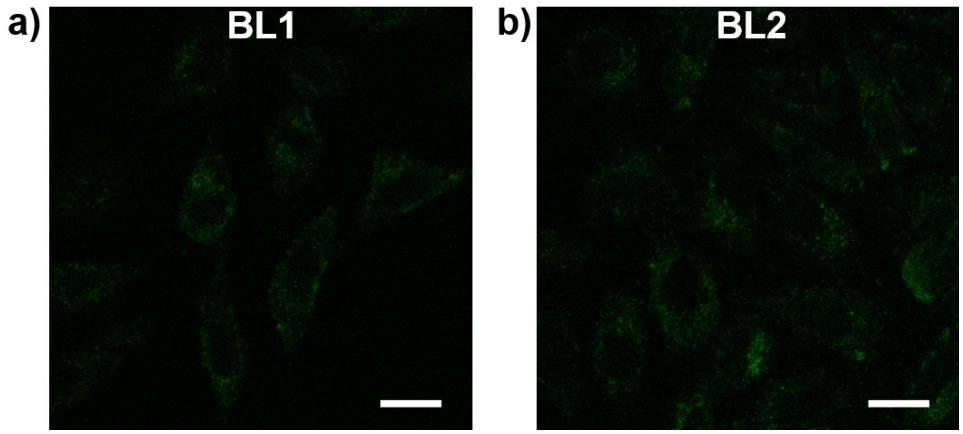



**Fig. S15.** The CLSM imaging of the cell tracing aspects (Scale bar: 25 μm). The CLSM images of live MCF-7 cancer cells pretreated with **BL1**/**BL2** (200 μL, 10 μg/mL, 60 min), subsequently coincubated with DMEM (200 μL, 24 h).

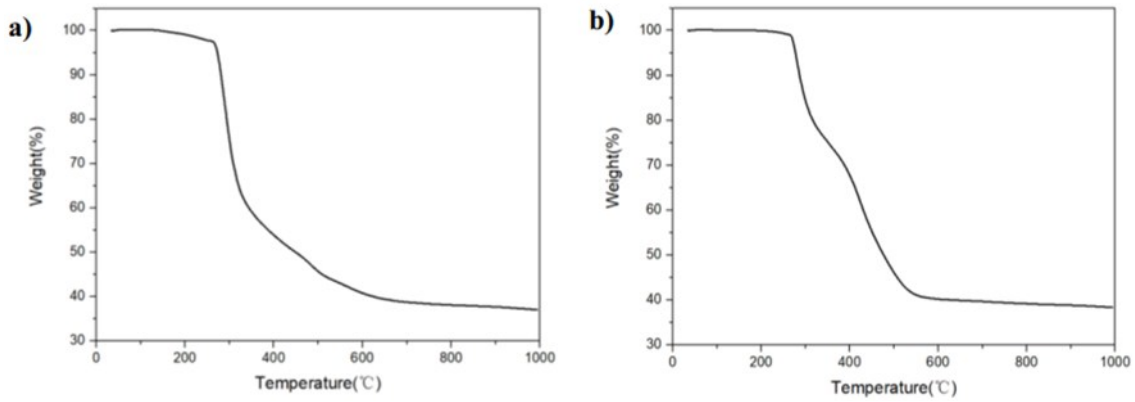



**Fig. S16** TGA traces of **BL1** (a) and **BL2** (b).

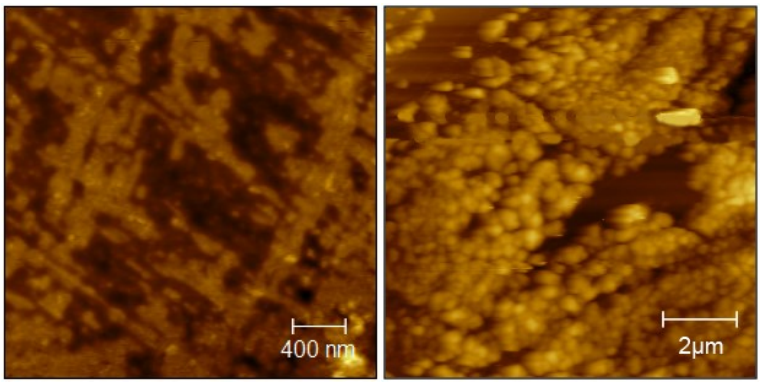



**Fig. S17** AFM image of **BL2** thin film in AS (left) and TA (right) states.

**NMR Spectra**

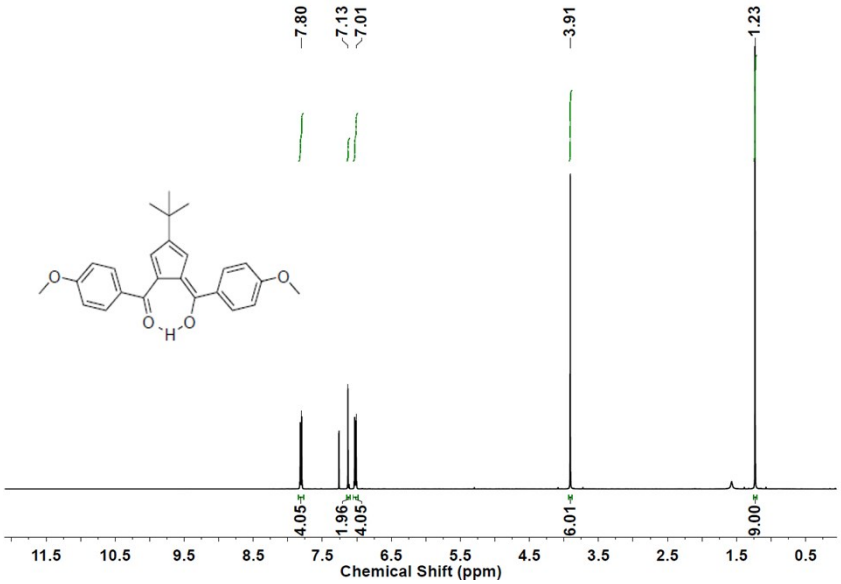



**Fig. S18** $^{1}$H NMR spectrum of **L1.**

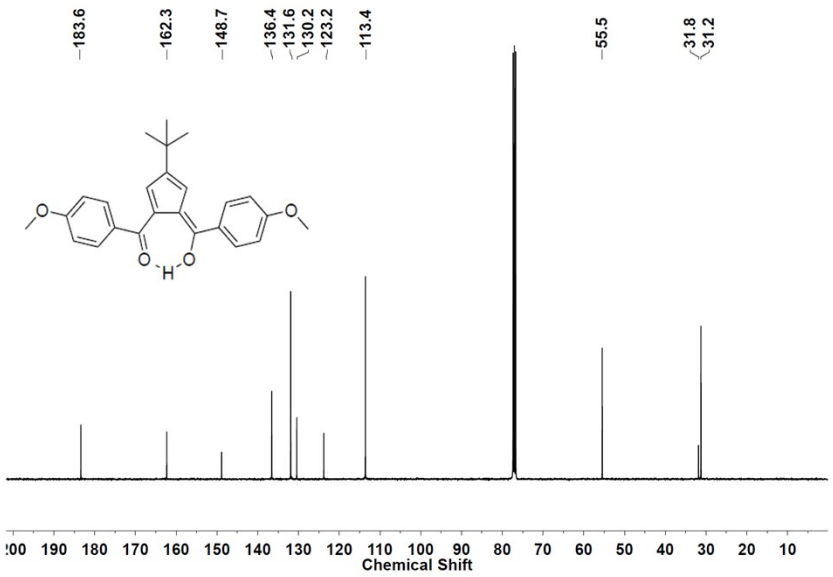



**Fig. S19** $^{13}$C NMR spectrum of **L1.**

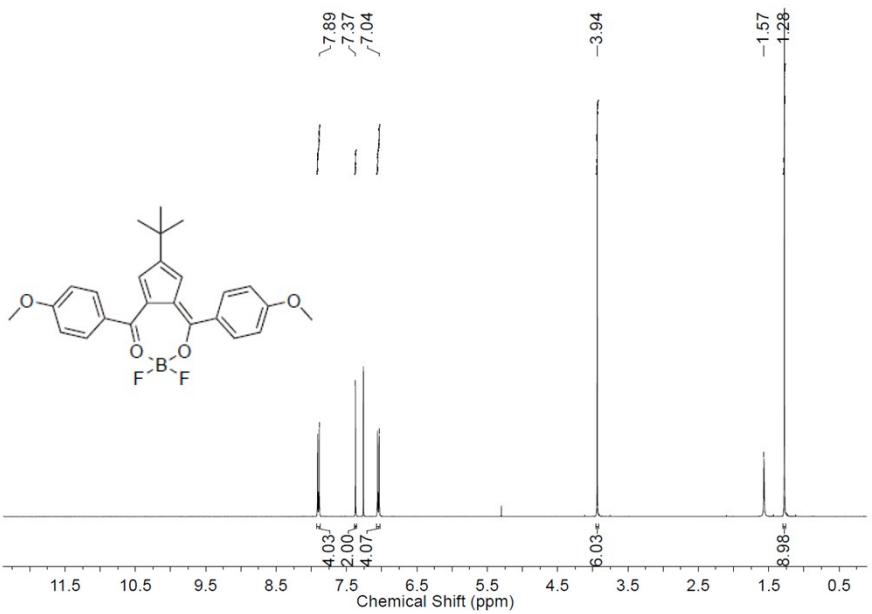



**Fig. S20** $^{1}$H NMR spectrum of **BL1.**

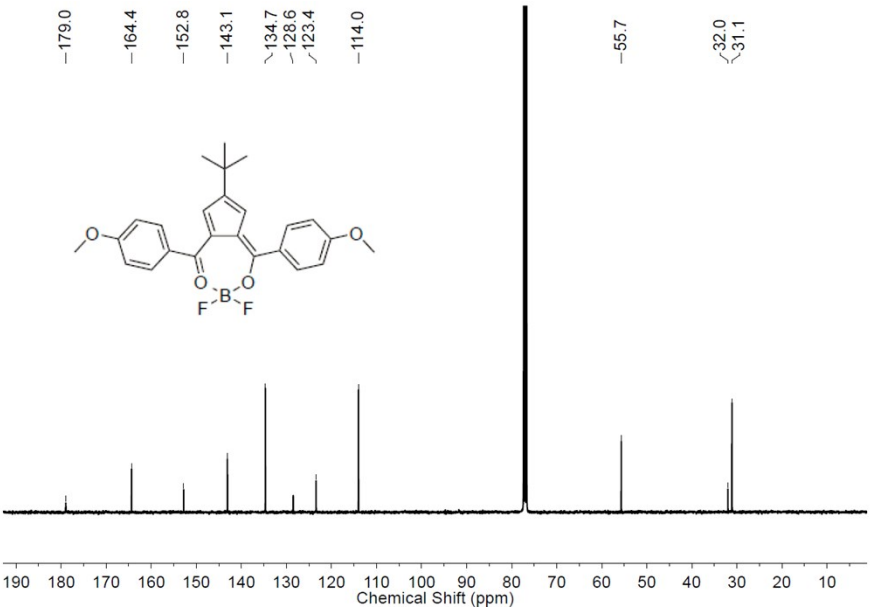



**Fig. S21** $^{13}$C NMR spectrum of **BL1.**

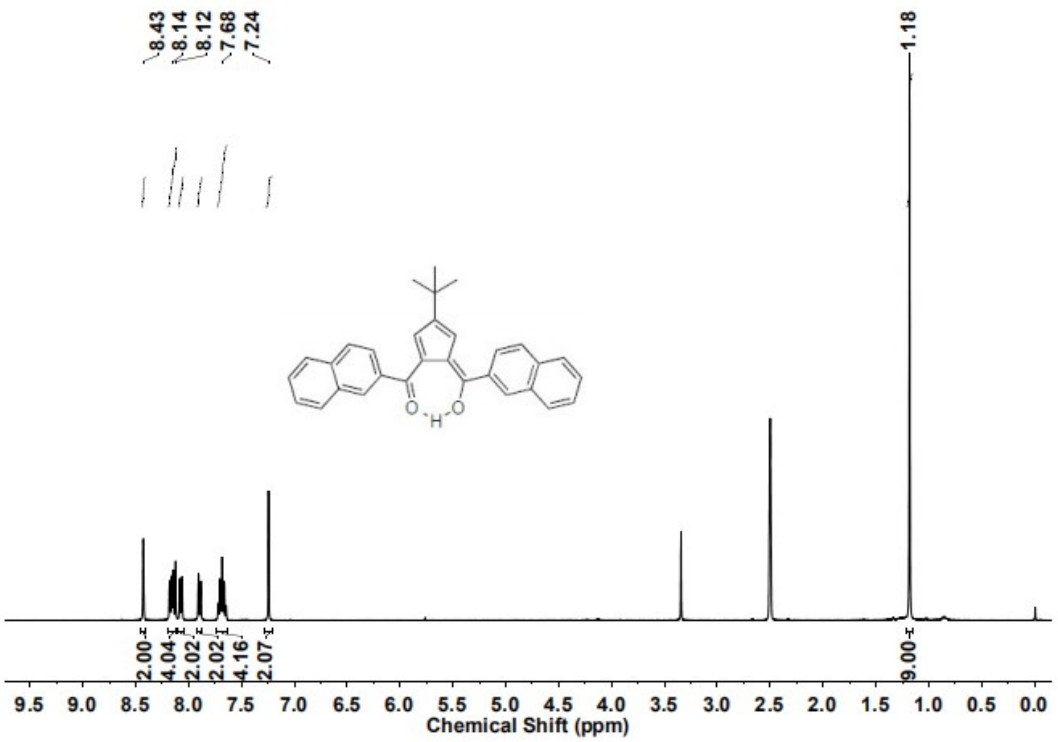



**Fig. S22** [1]H NMR spectrum of **L2**.

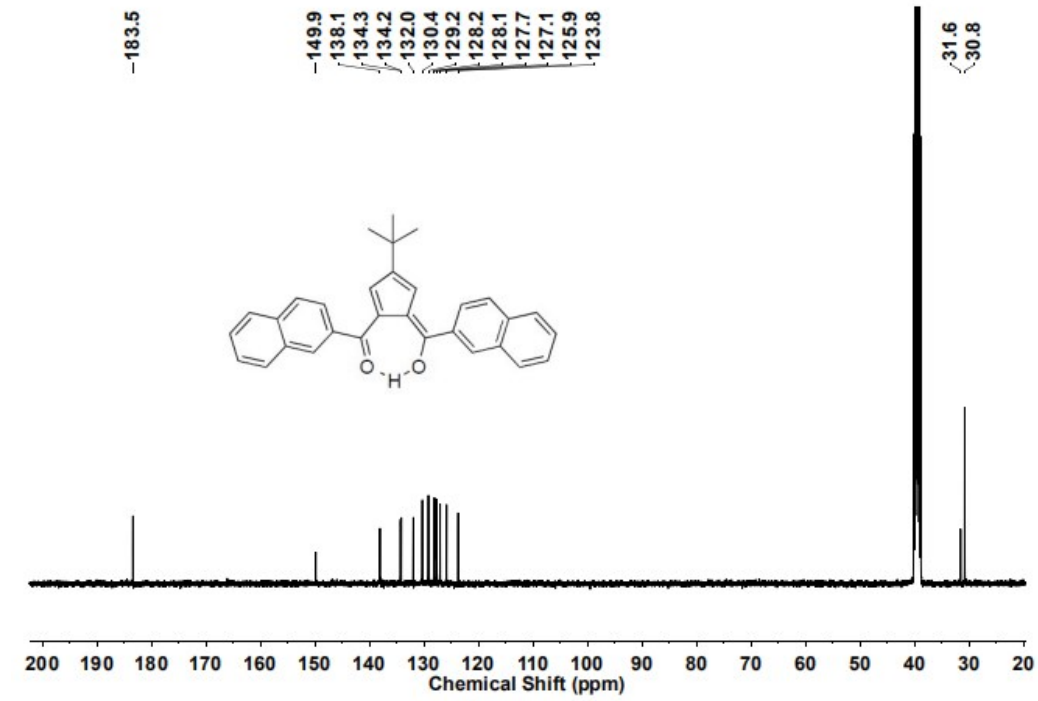



**Fig. S23** [13]C NMR spectrum of **L2**.

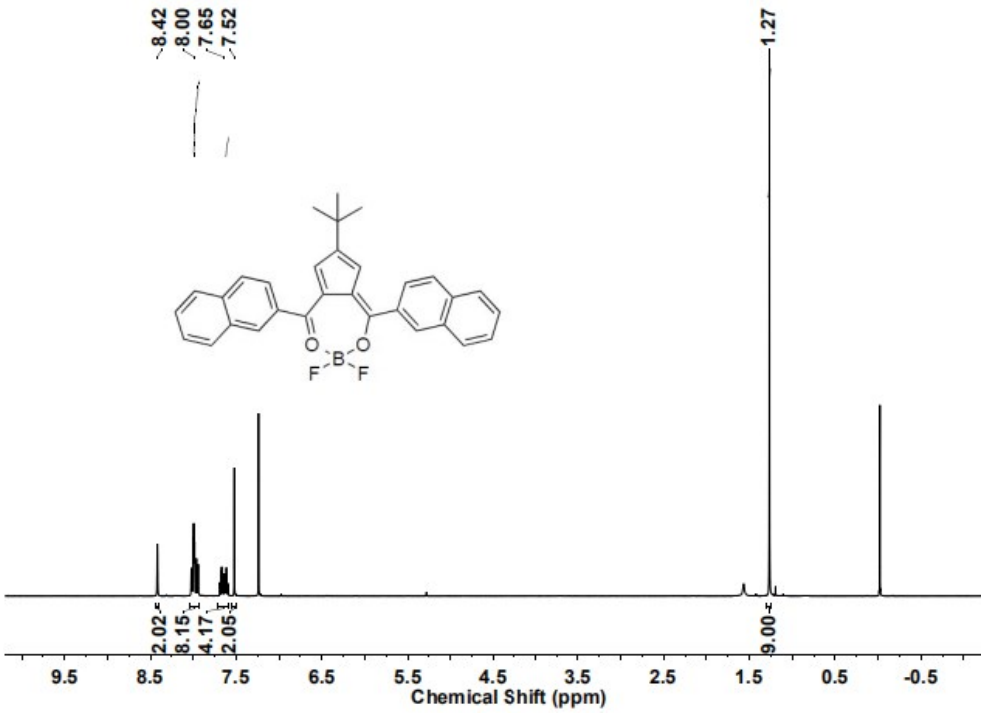



**Fig. S24** [1]H NMR spectrum of **BL2.**

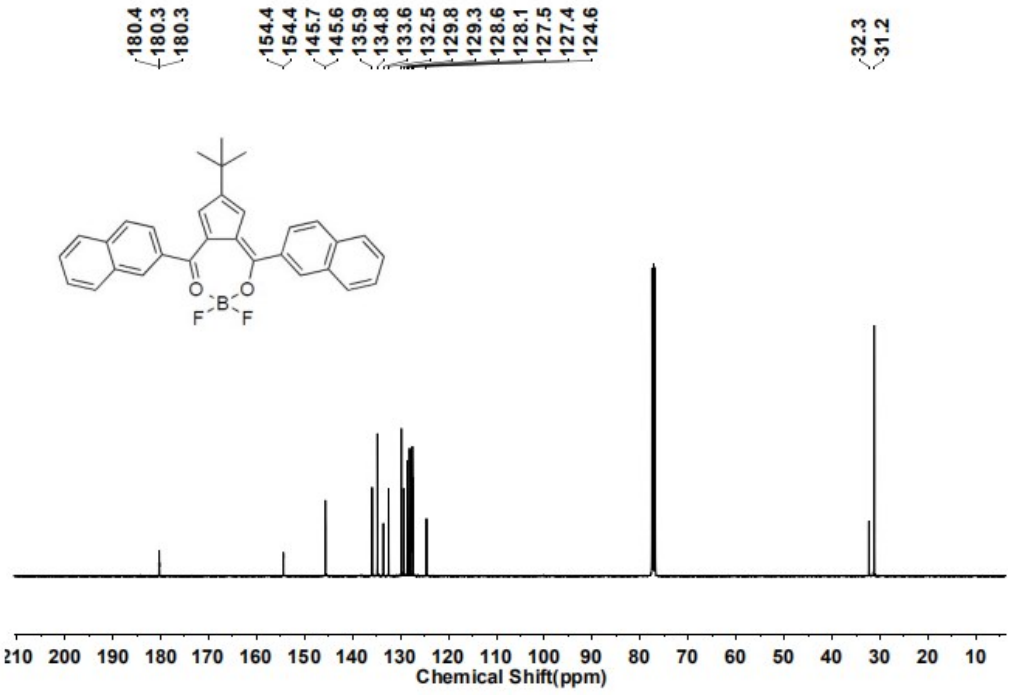



**Fig. S25** [13]C NMR spectrum of **BL2.**

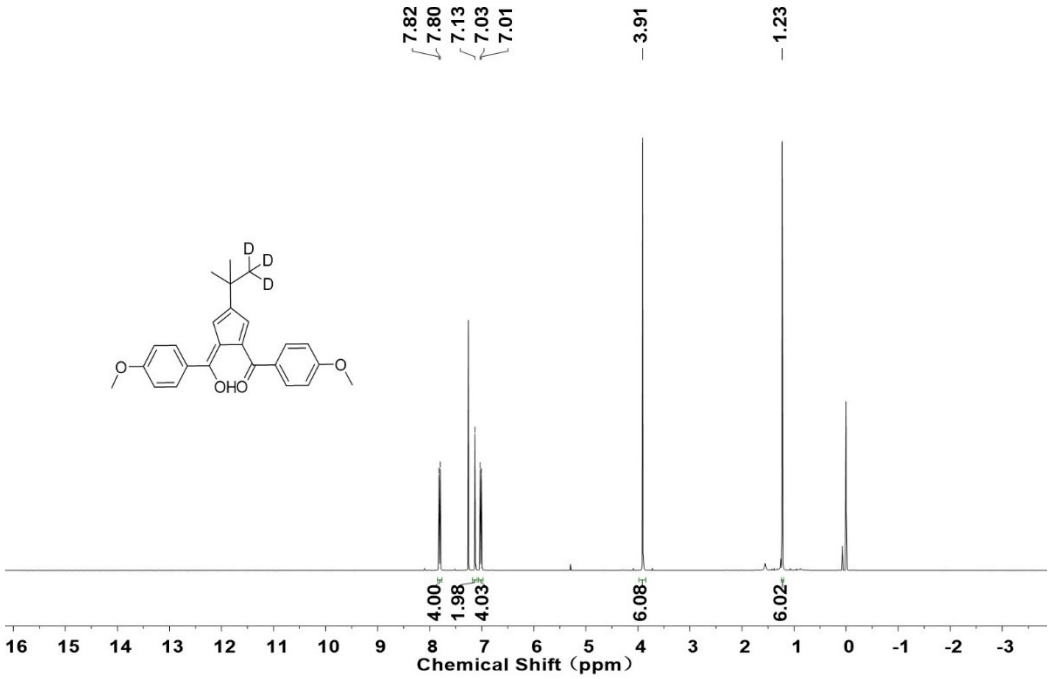



**Fig. S26** $^{1}$H NMR spectrum of **L3.**

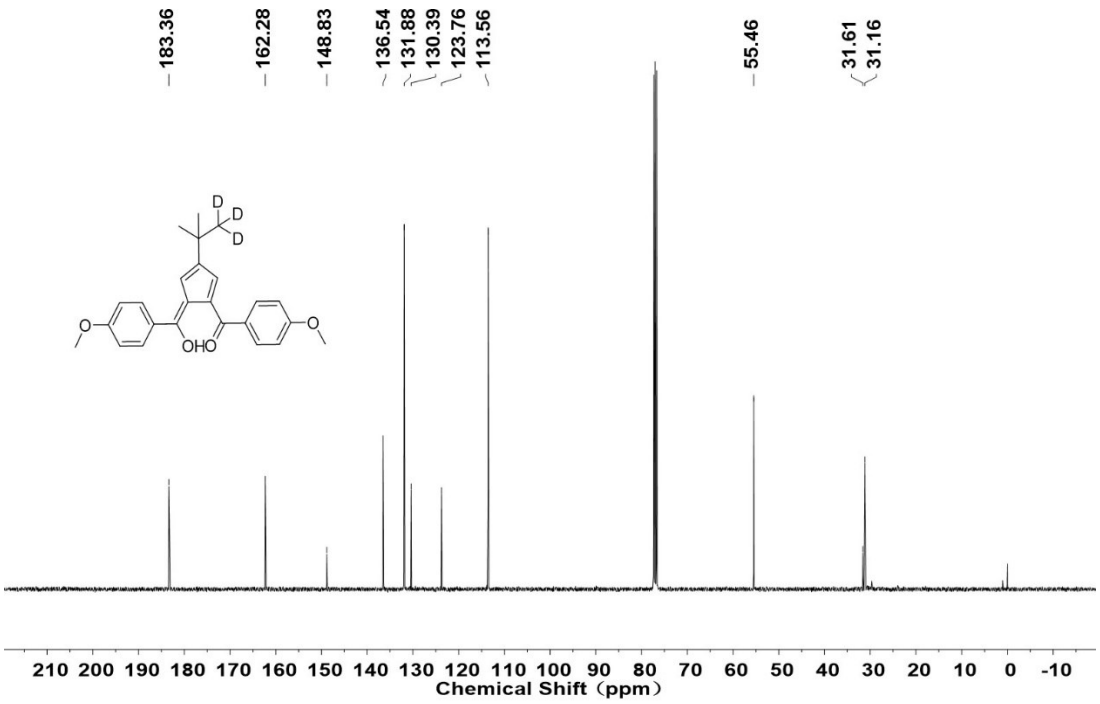



**Fig. S27** $^{13}$C NMR spectrum of **L3.**

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