

Electronic Supplementary Information

for

Ladder-Type Boron-Containing π -Systems with Enhanced Open-Shell Characters and Photothermal Conversion Properties

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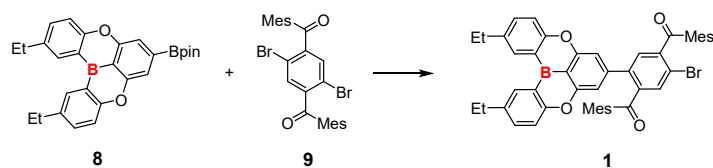
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1. Experimental details

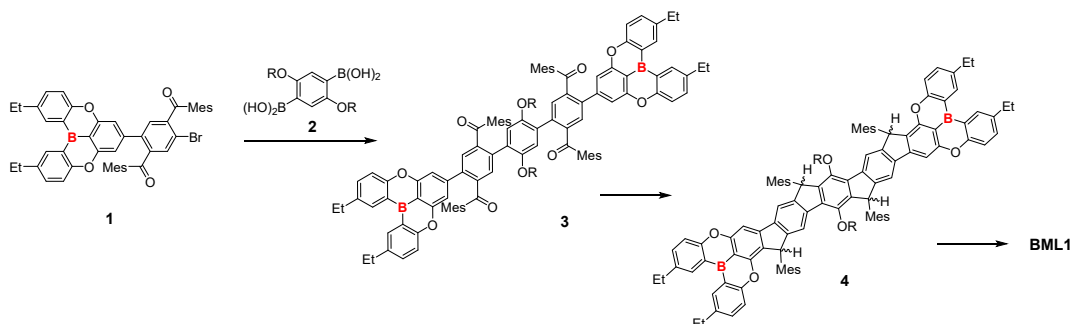
General. ^1H and ^{13}C NMR spectra were obtained using Zhongke Niujin AS400 (400 MHz for ^1H NMR and 101 MHz for ^{13}C NMR) spectrometer in CDCl_3 at 25 °C. Variable-temperature ^1H NMR spectra were measured with a Bruker AV III HD-500 spectrometer in CD_2Cl_2 or $\text{THF-}d_8$. Chemical shifts are reported in δ ppm using CHCl_3 (7.26 ppm), CH_2Cl_2 (5.32 ppm) and THF (3.58 ppm) for ^1H NMR and CDCl_3 (77.16 ppm) for ^{13}C NMR as internal standard. High resolution mass spectra were measured with a Bruker Autoflex speed TOF spectrometer. Electron paramagnetic resonance (EPR) measurements were performed on the solids using a Bruker ELEXSYS-II E500 CW-EPR spectrometer. UV/Vis absorption spectra were measured using Hitachi U-2900 spectrometer. Cyclic voltammetry (CV) was performed on a CHI660e electrochemical workstation using $n\text{Bu}_4\text{NPF}_6$ (0.1 M) as electrolyte at a scan rate of 100 mV s^{-1} . The CV cell has a glassy carbon electrode, a Pt wire counter electrode, and an Ag/Ag^+ reference electrode. The measurement was carried out under an argon atmosphere in CH_2Cl_2 for oxidation and in *o*-dichlorobenzene for reduction (1.0 mM). The redox potentials were internally calibrated using the ferrocene/ferrocenium couple. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated based on the equations: $E_{\text{LUMO}}/E_{\text{HOMO}} = -(4.80 + E_{\text{onset}}^{\text{red}}/E_{\text{onset}}^{\text{ox}})$ eV.

Materials and reagents. All reactions were performed under an argon atmosphere, unless stated otherwise. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. 1,2-Distearoyl-sn-glycero-3-phosphoethanolamine-poly(ethylene glycol)_{2K} (DSPE-PEG) was purchased from Ponsure Biotechnology Co., Ltd.. Dry toluene and THF were distilled via the standard method. Compounds **2**, **5**, **8** and **9** were prepared according to the literature methods.^[1,2,3,4]

2. Syntheses and characterizations



Compound 1: In a Schlenk tube, **8** (500.0 mg, 1.10 mmol), **9** (702.6 mg, 1.33 mmol), Pd(PPh₃)₄ (70.3 mg, 0.061 mmol), Na₂CO₃ (216.8 mg, 2.04 mmol) were added into toluene (20 mL), ethanol (8 mL) and water (4 mL) under argon. The reaction mixture was stirred at 60 °C for 12 h. After cooling down to room temperature, water and toluene were added. The organic layer was collected and aqueous layer was extracted with toluene (40 mL). The combined organic phase was dried over anhydrous Na₂SO₄. After removing the solvents under reduced pressure, the obtained solid was purified by silica gel column chromatography with CH₂Cl₂/hexane (1/1) as eluent to afford compound **1** (641.6 mg, 75%) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ (ppm) 8.47 (s, 2H), 8.06 (s, 1H), 7.56 (d, *J* = 12.0 Hz, 2H), 7.45 (s, 1H), 7.42 (d, *J* = 4.0 Hz, 2H), 6.84 (d, *J* = 12.0 Hz, 4H), 6.47 (s, 2H), 2.89–2.83 (m, 4H), 2.27 (s, 3H), 2.19 (s, 6H), 2.04 (s, 6H), 1.85 (s, 3H), 1.40 (t, *J* = 4.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ (ppm) 198.83, 198.55, 158.93, 156.76, 145.09, 142.42, 141.19, 140.43, 140.16, 138.48, 136.27, 136.02, 135.79, 135.63, 133.87, 133.25, 133.15, 129.40, 129.02, 122.20, 121.04, 118.30, 113.94, 108.58, 28.65, 21.36, 20.89, 20.80, 20.41, 15.97. HR-MALDI-TOF MS (*m/z*): [M] calcd. for C₄₈H₄₂BBro₄, 774.2355; found: 774.2386.

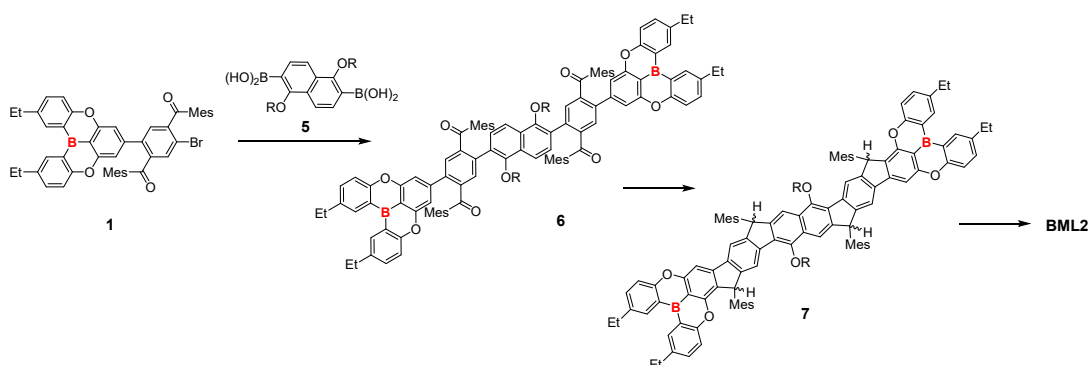


Compound 3: In a Schlenk tube, **1** (230.0 mg, 0.30 mmol), **2** (43.6 mg, 0.12 mmol), Pd(PPh₃)₄ (6.8 mg, 0.0059 mmol) and K₂CO₃ (98.7 mg, 0.71 mmol) were added into THF (15 mL) and H₂O (9 mL) under argon. The reaction

mixture was stirred at 60 °C for 5 h. After cooling down to room temperature, water and chloroform were added. The organic layer was collected and aqueous layer was extracted with CH₂Cl₂ (20 mL). The combined organic phase was dried over anhydrous Na₂SO₄. After removing the solvents under reduced pressure, the obtained solid was purified by silica gel column chromatography with CH₂Cl₂/hexane (2/1) as eluent to afford compound **3** (87.1 mg, 44%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ (ppm) 8.51 (s, 4H), 7.87 (s, 2H), 7.58 (d, *J* = 12.0 Hz, 4H), 7.49 (s, 2H), 7.46 (d, *J* = 4.0 Hz, 4H), 7.14 (s, 4H), 6.71 (s, 4H), 6.31 (s, 4H), 6.05 (s, 2H), 3.54 (s, 2H), 3.34 (s, 2H), 2.91–2.85 (m, 8H), 2.22 (s, 12H), 2.05 (s, 12H), 1.90 (s, 12H), 1.54 (s, 4H), 1.41 (t, *J* = 8.0 Hz, 12H), 1.34–1.29 (m, 12H), 0.93 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ (ppm) 200.64, 199.68, 159.11, 157.05, 147.94, 147.07, 143.60, 141.53, 139.94, 139.28, 138.66, 138.34, 136.69, 136.62, 135.76, 135.40, 133.75, 133.20, 132.51, 129.24, 128.49, 118.39, 108.96, 68.07, 31.76, 29.35, 28.69, 25.71, 22.72, 21.13, 21.06, 20.92, 20.82, 16.02, 14.24. HR-MALDI-TOF MS (*m/z*): [M–OC₆H₁₃] calcd. for C₁₀₈H₉₉B₂O₉, 1561.7503; found: 1561.7594.

Compound 4: In a dry Schlenk tube, lithium aluminum hydride (182.5 mg, 4.81 mmol) was dissolved in dry THF (15 mL) under argon, and then a solution of **3** (80.0 mg, 0.048 mmol) in dry THF (5 mL) was added slowly at room temperature. The reaction mixture was stirred for 12 h and quenched with anhydrous Na₂SO₄. The mixture was filtered to remove all solids, which were washed with ethyl acetate. The solvents were removed under reduced pressure. The obtained solid was transferred to a dry Schlenk tube and then dry CH₂Cl₂ (20 mL) was added under argon. A solution of BF₃·Et₂O (0.19 mL, 1.54 mmol) was added dropwise at room temperature. The mixture was stirred for 25 minutes and quenched by slow addition of methanol. All volatiles were removed under reduced pressure, providing an isomeric mixture of intermediate **4** (56.2 mg, 73% in two steps) as yellowish green solid. Compound **4** was directly used in next step without further purification.

Compound BML1: In a dry Schlenk tube, compound **4** (50.0 mg, 0.031 mmol) was dissolved in toluene (10 mL) under argon. After heating the solution to 80 °C, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (14.2 mg, 0.062 mmol) in toluene (2 mL) was added dropwise and the mixture was stirred for 50 minutes at 80 °C. After cooling down to room temperature, the reaction mixture was filtered through a neutral aluminum oxide column chromatography with toluene as eluent. All volatiles were removed under reduced pressure, and the obtained solid was purified by silica gel column chromatography with CH₂Cl₂/CS₂ (1/20) as eluent to yield compound **BML1** (21.0 mg, 42%). ¹H NMR (400 MHz, THF-*d*₈, 0 °C): δ (ppm) 8.44 (d, *J* = 20.0 Hz, 4H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 2H), 7.41 (s, 1H), 7.40 (s, 2H), 7.38 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 4H), 7.00 (d, *J* = 12.0 Hz, 8H), 6.50 (d, *J* = 4.0 Hz, 2H), 3.34 (t, *J* = 4.0 Hz, 4H), 2.83–2.73 (m, 8H), 2.24 (s, 6H), 2.38 (s, 6H), 2.24 (s, 12H), 2.18 (s, 12H), 1.32 (t, *J* = 8.0 Hz, 8H), 1.29–1.23 (m, 20H), 0.97 (t, *J* = 8.0 Hz, 6H). HR-MALDI-TOF MS (*m/z*): [M–C₆H₁₃+H]⁺ calcd. for C₁₀₈H₉₆B₂O₆, 1510.7421; found: 1510.7400.



Compound 6: In a Schlenk tube, **1** (200.0 mg, 0.26 mmol), **5** (49.1 mg, 0.12 mmol), Pd(PPh₃)₄ (6.8 mg, 0.0059 mmol), K₂CO₃ (97.4 mg, 0.71 mmol) were added into THF (15 mL) and H₂O (9 mL) under argon. The reaction mixture was stirred at 60 °C for 4 h. After cooling down to room temperature, water and chloroform were added. The organic layer was collected and aqueous layer was extracted with chloroform (20 mL) two times. The combined organic phase was dried over Na₂SO₄. After removing the solvents under reduced pressure, the obtained solid was purified by silica gel column chromatography with CH₂Cl₂/hexane (2/1) as eluent to afford compound **6**

(173.9 mg, 86%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ (ppm) 8.51 (s, 4H), 7.87 (s, 2H), 7.82 (s, 2H), 7.67 (s, 2H), 7.58 (d, $J = 12.0$ Hz, 4H), 7.48 (d, $J = 8.0$ Hz, 4H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.03 (s, 4H), 6.65 (s, 2H), 6.52 (s, 4H), 6.46 (s, 2H), 3.70 (s, 2H), 3.57 (s, 2H), 2.91–2.85 (m, 8H), 2.13 (s, 26H), 1.95 (s, 4H), 1.89 (s, 6H), 1.61–1.56 (m, 4H), 1.42 (t, $J = 4.0$ Hz, 12H), 1.36–1.30 (m, 12H), 0.94 (t, $J = 8.0$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): δ (ppm) 199.98, 199.04, 159.05, 156.86, 152.40, 146.47, 141.61, 141.39, 139.84, 139.41, 138.39, 136.47, 135.47, 133.80, 133.19, 129.01, 122.31, 120.26, 118.36, 118.02, 108.91, 74.52, 31.82, 30.36, 28.69, 25.83, 22.83, 21.03, 20.93, 20.77, 16.02, 14.29. HR-MALDI-TOF MS (m/z): $[\text{M}-\text{OC}_6\text{H}_{13}]$ calcd. for $\text{C}_{112}\text{H}_{101}\text{B}_2\text{O}_9$, 1611.7660; found: 1611.7685.

Compound 7: Lithium aluminum hydride (221.2 mg, 5.83 mmol) was dissolved in dry THF (20 mL) in a dry Schlenk tube under argon. A solution of **6** (100 mg, 0.0583 mmol) in dry THF (8 mL) was injected slowly at room temperature. The reaction mixture was stirred for 12 h and quenched with anhydrous Na_2SO_4 . The mixture was filtered to remove all solids and washed with EtOAc. The solvent was removed under reduced pressure. The obtained solid was transferred to a dry Schlenk flask and then dry CH_2Cl_2 (30 mL) was then added under argon. A solution of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.23 mL, 1.87 mmol) was added dropwise at room temperature. The mixture was stirred for 30 minutes and quenched by slow addition of methanol. All volatiles were removed under reduced pressure, providing an isomeric mixture of intermediate **7** (74.1 mg, 77% in two steps). Compound **7** was directly used for the next step without further purification.

Compound BML2: Compounds **6** and **7** were synthesized according to the syntheses of **3** and **4**. In a dry Schlenk tube, compound **7** (60.0 mg, 0.036 mmol) was dissolved in toluene (12 mL) under argon. After heating the solution to 80 °C, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (16.5 mg, 0.073 mmol) in toluene (2 mL) was added dropwise and the mixture was stirred for 50 minutes at 80 °C. After cooling down to room temperature, the reaction mixture was filtered through a neutral aluminum oxide column chromatography with toluene as eluent. All volatiles were removed under reduced pressure, and the obtained solid was purified

by silica gel column chromatography with $\text{CH}_2\text{Cl}_2/\text{CS}_2$ (1/15) as eluent to yield compound **BML2** (31.8 mg, 53%). ^1H NMR (400 MHz, CD_2Cl_2 , $-20\text{ }^\circ\text{C}$): δ (ppm) 8.41 (d, $J = 16.0$ Hz, 4H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.35 (s, 2H), 7.26 (s, 2H), 7.13 (s, 4H), 7.07 (s, 8H), 6.58 (d, $J = 8.0$ Hz, 2H), 3.90 (s, 4H), 2.82–2.76 (m, 8H), 2.45 (s, 6H), 2.41 (s, 6H), 2.21 (s, 12H), 2.17 (s, 12H), 1.32 (t, $J = 4.0$ Hz, 4H), 1.29–1.24 (m, 12H), 1.21 (s, 12H), 0.93 (t, $J = 4.0$ Hz, 6H). HR-MALDI-TOF MS (m/z): $[\text{M}]$ calcd. for $\text{C}_{118}\text{H}_{110}\text{B}_2\text{O}_6$, 1645.8542; found: 1645.8561.

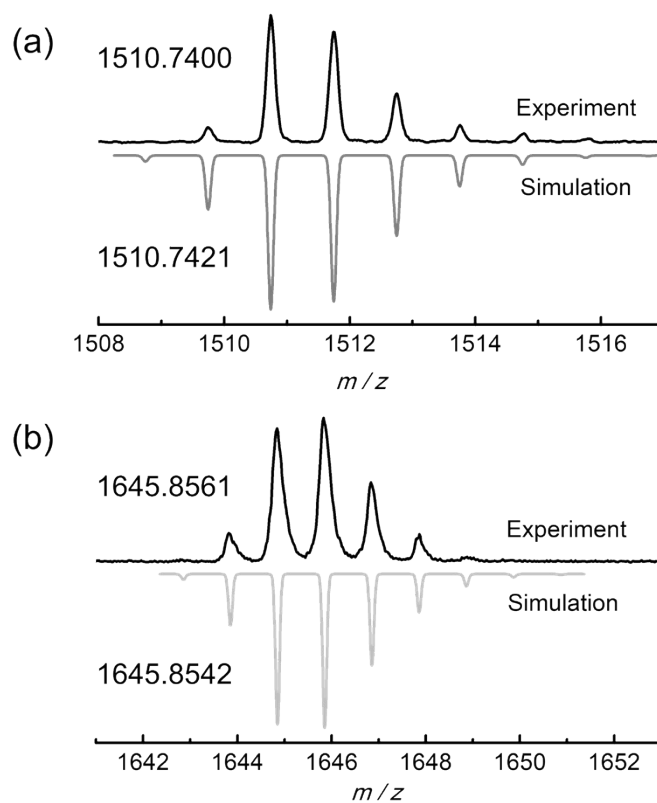


Fig. S1. High-resolution mass spectra of a) **BML1** and b) **BML2**.

3. X-ray crystallographic analysis

Single crystal X-ray diffraction (XRD) measurements were performed on a Rigaku RAXIS-PRID diffractometer with graphite monochromator Mo·K α radiation. The structure was solved using the SHELXTL-97 and refined by the full-matrix least-squares on F^2 (SHELXL-97). CCDC 2225204 (**BML1**) and 2225206 (**BML2**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.

X-ray crystallographic analysis of BML1. The single crystals of **BML1** suitable for XRD analysis were grown by the diffusion of *n*-heptane into its CS₂ solution. The crystal data of **BML1** are as follows: C₁₂₁H₁₂₄B₂O₆; FW = 1695.81, triclinic, space group $P\bar{1}$, $a = 9.2180(4)$ Å, $b = 13.5824(6)$ Å, $c = 18.8248(9)$ Å, $\alpha = 82.478(2)^\circ$, $\beta = 87.674(2)^\circ$, $\gamma = 87.686(2)^\circ$, $V = 2333.24(18)$ Å³, $Z = 1$, $D_{\text{calcd}} = 1.207$ g cm⁻³, $R_1 = 0.0653$ ($I > 2\sigma(I)$), $wR_2 = 0.1905$ (all data), GOF = 1.028.

X-ray crystallographic analysis of BML2. The single crystals of **BML2** suitable for XRD analysis were grown by the diffusion of *n*-heptane into its CS₂ solution. The crystal data of **BML2** are as follows: C₂₄₃H₂₃₄B₄O₁₂; FW = 3389.53, monoclinic, space group $P2/c$, $a = 22.316(3)$ Å, $b = 11.7617(14)$ Å, $c = 35.062(4)$ Å, $\alpha = 90^\circ$, $\beta = 96.717(4)^\circ$, $\gamma = 90^\circ$, $V = 9139.7(19)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.232$ g cm⁻³, $R_1 = 0.1391$ ($I > 2\sigma(I)$), $wR_2 = 0.3934$ (all data), GOF = 1.076.

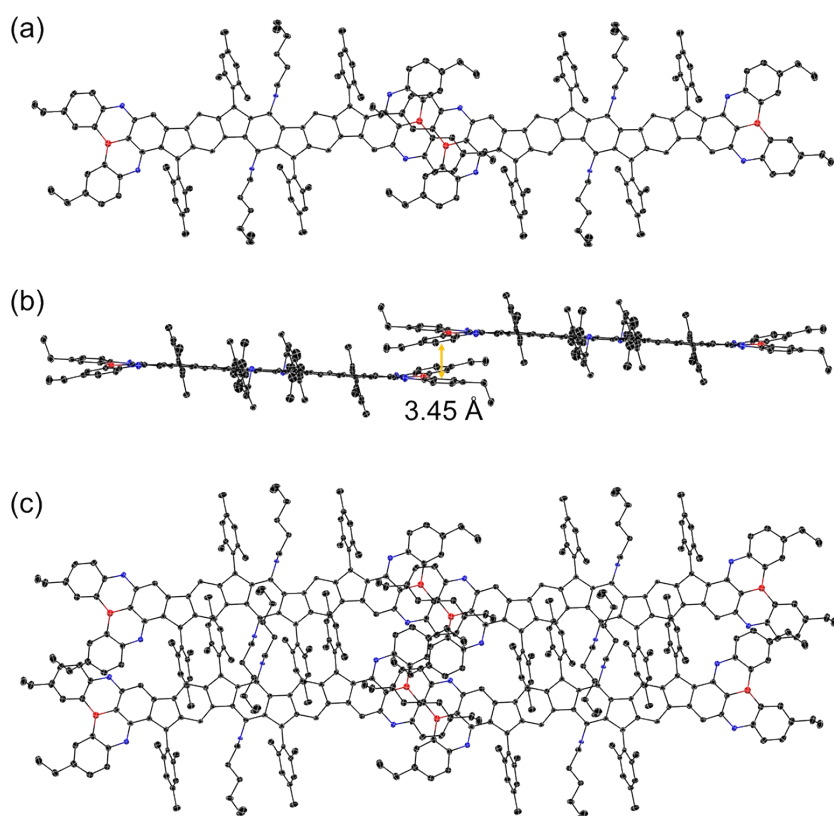


Fig. S2. a,b) Packing dimer with π - π stacking distance and c) packing structure in the crystalline state of **BML1**. Hydrogen atoms are omitted for clarity.

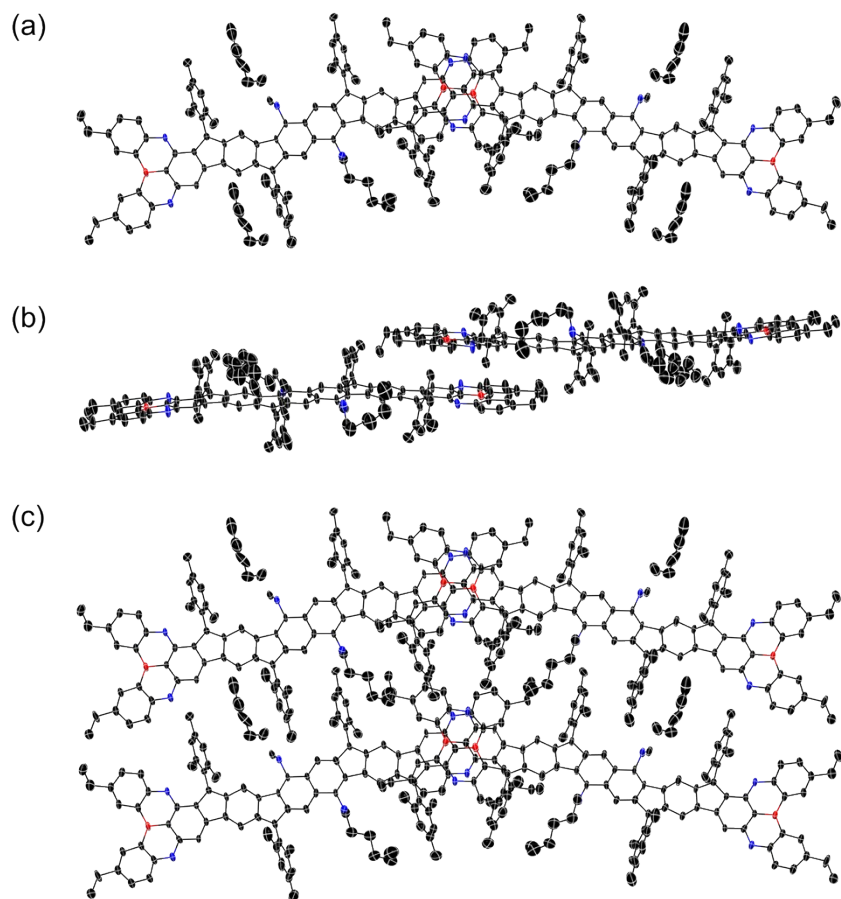


Fig. S3. a,b) Packing dimer and c) packing structure in the crystalline state of **BML2**. Hydrogen atoms are omitted for clarity.

4. Variable-temperature ^1H -NMR and EPR measurements

The variable-temperature (VT) ^1H NMR and VT EPR measurements were performed to reveal the radical nature. The VT ^1H NMR spectra of **BML1** and **BML2** and their Lewis acid-base complexes were recorded using a Bruker AV III HD-500 spectrometer with a temperature modulation device. The VT EPR measurements were conducted on the solids of **BML1** and **BML2** using a Bruker ELEXSYS-II E500 CW-EPR spectrometer with a temperature-control heater. The fitting of $I \cdot T$ versus T using the modified Bleaney–Bowers equation gives a ρ of 1.00 and 0.99, respectively.^[5]

$$IT = \frac{2\rho N_A g^2 \beta^2}{k_b} \frac{1}{3 + \exp(-2J/k_b T)} + \frac{(1 - \rho) N_A g^2 \beta^2}{2k_b}$$

where I is intensity of EPR curves, N_A is Avogadro constant, g is the g-factor, β is Bohr magneton, k_b is Boltzmann constant and ρ is the paramagnetic purity.

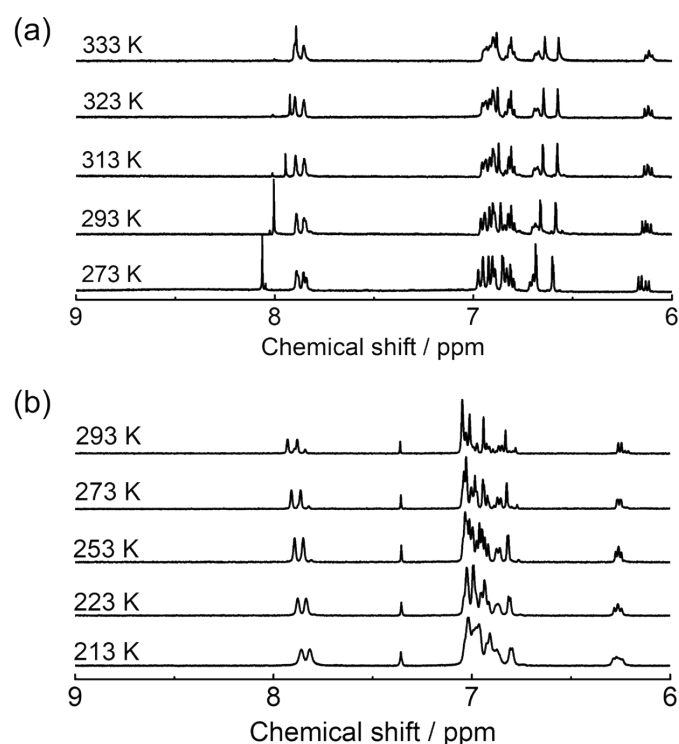


Fig. S4. Variable-temperature ^1H NMR spectra of a) **BML1**·(TABF)₂ in THF-*d*₈ and b) **BML2**·(TABF)₂ in CD₂Cl₂.

5. Geometry optimizations, radical character and (anti)aromaticity

All calculations were carried out using the Gaussian 09 program.^[5] The calculations of **BML1'**, **BML2'**, **BML1'·(F⁻)₂** and **BML2'·(F⁻)₂** were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-311G(d) basis set for all atoms. The initial geometry optimization was performed with the restricted B3LYP level of theory. The resulting DFT solution (closed-shell) was further tested for its stability with the STABLE=OPT keyword. A spin symmetry broken DFT solution was found with lower energy. Then the Guess=Read keyword was used to perform the optimization at the UB3LYP level (open-shell structure). The geometries were fully optimized in gas phase using the default convergence criteria without any constraints. The Cartesian coordinates of **BML1'** and **BML2'** are also shown.

The open-shell characters of **BML1'**, **BML2'**, **BML1'·(F⁻)₂** and **BML2'·(F⁻)₂** are characterized with the unrestricted hartree-fock (UHF) method. Within the UHF method, the radical character y is expressed as the following equation:

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}$$

where T_i ($i = 0, 1$) indicates the orbital overlap between the corresponding orbital pair (HONO $-i$, LUNO $+i$). Using the occupation numbers of UHF natural orbitals (UNO), the overlap T_i is calculated as follows:

$$T_i = \frac{n_{HONO-i} - n_{LUNO+i}}{2}$$

Nucleus-independent chemical shift (NICS)-XY scan was employed to study the (anti)aromaticity. The (NICS)-XY calculations were performed with the nmr=GIAO key word based on the UB3LYP/6-311+G(d) level of theory. The NICS values are taken 1.7 Å on top the molecular plane and employ the σ -only model^[6] to consider only the π contributions. For improving the calculation efficiency, calculations were performed on the molecular skeletons that omit the C₂H₅ and OC₆H₁₃ chains.

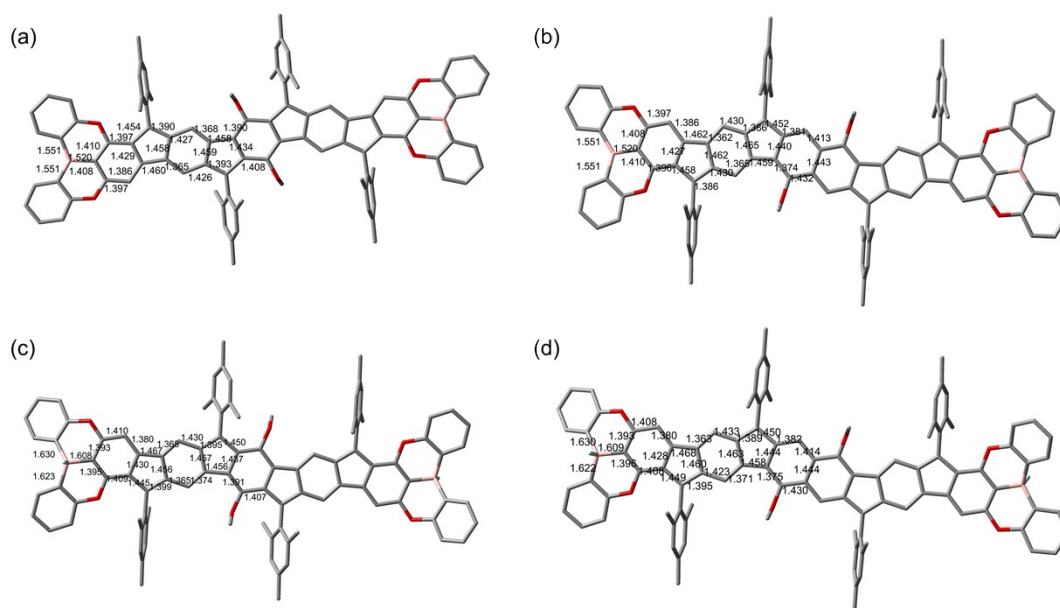


Fig. S5. Optimized geometries and selected bond lengths of a) **BML1'**, b) **BML2'**, c) **BML1'·(F⁻)₂** and d) **BML2'·(F⁻)₂** based on the UB3LYP/6-311G(d) level of theory.

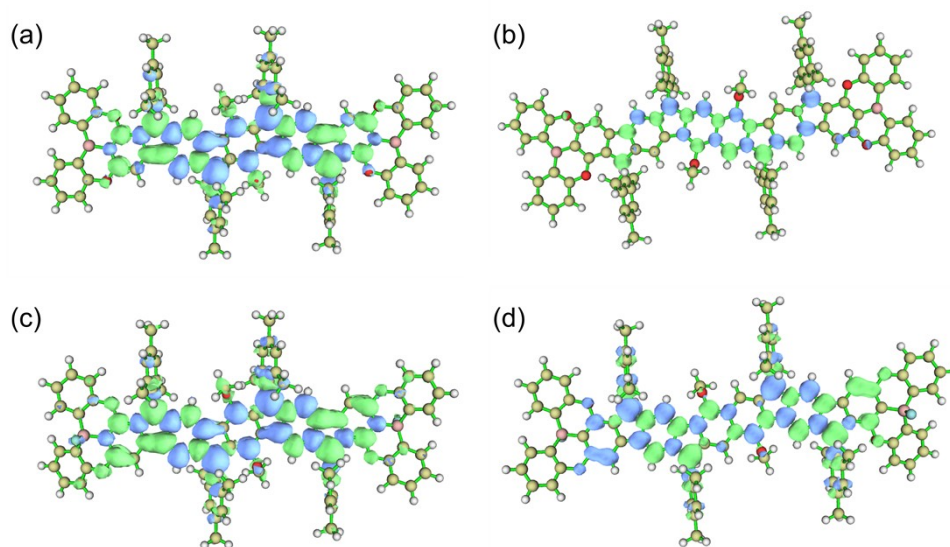


Fig. S6. Calculated spin-density distributions of a) **BML1'**, b) **BML2'**, c) **BML1'·(F⁻)₂** and d) **BML2'·(F⁻)₂** based on the UB3LYP/6-311G(d) level of theory.

Table S1. Coordinates of the optimized structure for **BML1'** at the UB3LYP/6-311G(d) level.

| Atom | x | y | z |
|------|-----------|----------|-----------|
| O | 3.488590 | 6.633269 | 5.886827 |
| O | -0.301002 | 5.700652 | 8.679332 |
| O | 2.353660 | 1.453517 | -0.497584 |
| C | 5.486300 | 9.295235 | 8.361761 |
| C | 4.199909 | 8.890893 | 8.710427 |
| H | 3.738658 | 9.335145 | 9.587314 |
| C | 3.454126 | 7.965642 | 7.959684 |
| C | 1.549754 | 6.323026 | 7.278794 |
| C | 2.301762 | 6.013832 | 6.145248 |
| C | 1.871046 | 5.046910 | 5.214838 |
| C | 2.433130 | 4.552237 | 3.979200 |
| C | 1.577988 | 3.570318 | 3.466446 |
| C | 1.664429 | 2.804664 | 2.272312 |
| H | 2.509708 | 2.927427 | 1.605270 |
| C | 0.667391 | 1.900913 | 1.995107 |
| C | 0.451919 | 0.979013 | 0.888419 |
| C | -0.749525 | 0.242340 | 1.171455 |
| C | 1.185552 | 0.746786 | -0.270584 |
| C | 4.084579 | 7.500343 | 6.796975 |
| C | 5.374530 | 7.884885 | 6.417584 |
| H | 5.793798 | 7.476250 | 5.503945 |
| C | 6.080382 | 8.781697 | 7.207902 |
| H | 7.083771 | 9.083858 | 6.919236 |
| C | 1.380359 | 7.105467 | 12.199939 |
| C | 1.962180 | 7.462769 | 10.984020 |
| H | 2.859502 | 8.072801 | 11.003127 |
| C | 1.438647 | 7.073062 | 9.741780 |
| C | 0.304938 | 6.246051 | 9.806131 |
| C | -0.309440 | 5.881968 | 11.005989 |
| H | -1.188023 | 5.245112 | 10.972417 |
| C | 0.226761 | 6.321800 | 12.210265 |
| H | -0.243361 | 6.038872 | 13.148608 |
| C | 0.411373 | 5.556041 | 7.518872 |
| C | -0.075769 | 4.581873 | 6.625186 |
| H | -0.979151 | 4.033304 | 6.870527 |
| C | 0.650347 | 4.348429 | 5.475587 |
| C | 0.447626 | 3.406347 | 4.369056 |
| C | 3.695754 | 4.988168 | 3.328072 |

| | | | |
|---|-----------|-----------|----------|
| C | 4.851400 | 4.190152 | 3.426935 |
| C | 6.021628 | 4.604323 | 2.785948 |
| H | 6.912724 | 3.986578 | 2.873286 |
| C | 6.079255 | 5.783263 | 2.044634 |
| C | 7.343466 | 6.191741 | 1.326050 |
| H | 7.346906 | 5.836975 | 0.288599 |
| H | 8.232116 | 5.779045 | 1.811229 |
| H | 7.454968 | 7.279273 | 1.295187 |
| C | 4.925278 | 6.563451 | 1.966509 |
| H | 4.949014 | 7.493517 | 1.402615 |
| C | 3.737612 | 6.191859 | 2.597604 |
| C | 2.525638 | 7.086394 | 2.509978 |
| H | 1.630965 | 6.529783 | 2.219289 |
| H | 2.680325 | 7.887550 | 1.783041 |
| H | 2.312940 | 7.548213 | 3.478064 |
| C | 4.851257 | 2.914449 | 4.236576 |
| H | 4.211372 | 2.148862 | 3.789333 |
| H | 4.476184 | 3.086820 | 5.248884 |
| H | 5.860542 | 2.503066 | 4.315022 |
| C | -0.444980 | 1.709690 | 2.917106 |
| C | -1.290415 | 0.710743 | 2.432826 |
| C | -2.510919 | 0.234385 | 3.134188 |
| C | -2.394723 | -0.508872 | 4.327149 |
| C | -3.553076 | -0.920639 | 4.995101 |
| H | -3.451104 | -1.500493 | 5.909865 |
| C | -4.825905 | -0.612855 | 4.522796 |
| C | -4.922546 | 0.122199 | 3.339738 |
| H | -5.906829 | 0.373568 | 2.949894 |
| C | -3.795719 | 0.546956 | 2.637412 |
| C | -3.965697 | 1.325821 | 1.356906 |
| H | -3.750797 | 0.691282 | 0.493224 |
| H | -3.284590 | 2.178656 | 1.309533 |
| H | -4.988628 | 1.697710 | 1.256988 |
| C | -6.066401 | -1.040869 | 5.270505 |
| H | -6.812278 | -1.476064 | 4.598154 |
| H | -6.544128 | -0.191818 | 5.772715 |
| H | -5.835548 | -1.784780 | 6.037184 |
| C | -1.045755 | -0.887039 | 4.897083 |
| H | -0.348449 | -1.201913 | 4.117548 |
| H | -1.144918 | -1.702464 | 5.618260 |
| H | -0.571285 | -0.046890 | 5.412867 |
| C | -0.539515 | 2.501946 | 4.104004 |

| | | | |
|---|-----------|-----------|------------|
| H | -1.389676 | 2.377525 | 4.769027 |
| C | 2.183807 | 2.662285 | -1.238598 |
| H | 1.470283 | 3.329328 | -0.744448 |
| H | 1.846715 | 2.453202 | -2.257502 |
| O | -3.488590 | -6.633269 | -5.886827 |
| O | 0.301002 | -5.700652 | -8.679332 |
| O | -2.353660 | -1.453517 | 0.497584 |
| C | -5.486300 | -9.295235 | -8.361761 |
| C | -4.199909 | -8.890893 | -8.710427 |
| H | -3.738658 | -9.335145 | -9.587314 |
| C | -3.454126 | -7.965642 | -7.959684 |
| C | -1.549754 | -6.323026 | -7.278794 |
| C | -2.301762 | -6.013832 | -6.145248 |
| C | -1.871046 | -5.046910 | -5.214838 |
| C | -2.433130 | -4.552237 | -3.979200 |
| C | -1.577988 | -3.570318 | -3.466446 |
| C | -1.664429 | -2.804664 | -2.272312 |
| H | -2.509708 | -2.927427 | -1.605270 |
| C | -0.667391 | -1.900913 | -1.995107 |
| C | -0.451919 | -0.979013 | -0.888419 |
| C | 0.749525 | -0.242340 | -1.171455 |
| C | -1.185552 | -0.746786 | 0.270584 |
| C | -4.084579 | -7.500343 | -6.796975 |
| C | -5.374530 | -7.884885 | -6.417584 |
| H | -5.793798 | -7.476250 | -5.503945 |
| C | -6.080382 | -8.781697 | -7.207902 |
| H | -7.083771 | -9.083858 | -6.919236 |
| C | -1.380359 | -7.105467 | -12.199939 |
| C | -1.962180 | -7.462769 | -10.984020 |
| H | -2.859502 | -8.072801 | -11.003127 |
| C | -1.438647 | -7.073062 | -9.741780 |
| C | -0.304938 | -6.246051 | -9.806131 |
| C | 0.309440 | -5.881968 | -11.005989 |
| H | 1.188023 | -5.245112 | -10.972417 |
| C | -0.226761 | -6.321800 | -12.210265 |
| H | 0.243361 | -6.038872 | -13.148608 |
| C | -0.411373 | -5.556041 | -7.518872 |
| C | 0.075769 | -4.581873 | -6.625186 |
| H | 0.979151 | -4.033304 | -6.870527 |
| C | -0.650347 | -4.348429 | -5.475587 |
| C | -0.447626 | -3.406347 | -4.369056 |
| C | -3.695754 | -4.988168 | -3.328072 |

| | | | |
|---|-----------|-----------|-----------|
| C | -4.851400 | -4.190152 | -3.426935 |
| C | -6.021628 | -4.604323 | -2.785948 |
| H | -6.912724 | -3.986578 | -2.873286 |
| C | -6.079255 | -5.783263 | -2.044634 |
| C | -7.343466 | -6.191741 | -1.326050 |
| H | -7.346906 | -5.836975 | -0.288599 |
| H | -8.232116 | -5.779045 | -1.811229 |
| H | -7.454968 | -7.279273 | -1.295187 |
| C | -4.925278 | -6.563451 | -1.966509 |
| H | -4.949014 | -7.493517 | -1.402615 |
| C | -3.737612 | -6.191859 | -2.597604 |
| C | -2.525638 | -7.086394 | -2.509978 |
| H | -1.630965 | -6.529783 | -2.219289 |
| H | -2.680325 | -7.887550 | -1.783041 |
| H | -2.312940 | -7.548213 | -3.478064 |
| C | -4.851257 | -2.914449 | -4.236576 |
| H | -4.211372 | -2.148862 | -3.789333 |
| H | -4.476184 | -3.086820 | -5.248884 |
| H | -5.860542 | -2.503066 | -4.315022 |
| C | 0.444980 | -1.709690 | -2.917106 |
| C | 1.290415 | -0.710743 | -2.432826 |
| C | 2.510919 | -0.234385 | -3.134188 |
| C | 2.394723 | 0.508872 | -4.327149 |
| C | 3.553076 | 0.920639 | -4.995101 |
| H | 3.451104 | 1.500493 | -5.909865 |
| C | 4.825905 | 0.612855 | -4.522796 |
| C | 4.922546 | -0.122199 | -3.339738 |
| H | 5.906829 | -0.373568 | -2.949894 |
| C | 3.795719 | -0.546956 | -2.637412 |
| C | 3.965697 | -1.325821 | -1.356906 |
| H | 3.750797 | -0.691282 | -0.493224 |
| H | 3.284590 | -2.178656 | -1.309533 |
| H | 4.988628 | -1.697710 | -1.256988 |
| C | 6.066401 | 1.040869 | -5.270505 |
| H | 6.812278 | 1.476064 | -4.598154 |
| H | 6.544128 | 0.191818 | -5.772715 |
| H | 5.835548 | 1.784780 | -6.037184 |
| C | 1.045755 | 0.887039 | -4.897083 |
| H | 0.348449 | 1.201913 | -4.117548 |
| H | 1.144918 | 1.702464 | -5.618260 |
| H | 0.571285 | 0.046890 | -5.412867 |
| C | 0.539515 | -2.501946 | -4.104004 |

| | | | |
|---|-----------|------------|------------|
| H | 1.389676 | -2.377525 | -4.769027 |
| C | -2.183807 | -2.662285 | 1.238598 |
| H | -1.470283 | -3.329328 | 0.744448 |
| H | -1.846715 | -2.453202 | 2.257502 |
| B | 1.914542 | 7.547430 | 8.256132 |
| B | -1.914542 | -7.547430 | -8.256132 |
| H | -6.019614 | -10.014649 | -8.978469 |
| H | 1.821027 | 7.442228 | 13.135278 |
| H | -1.821027 | -7.442228 | -13.135278 |
| H | 3.162767 | 3.140179 | -1.276846 |
| H | -3.162767 | -3.140179 | 1.276846 |
| H | 6.019614 | 10.014649 | 8.978469 |
| F | 1.074490 | 8.698574 | 7.902079 |
| F | -1.074490 | -8.698574 | -7.902079 |

Table S2. Coordinates of the optimized structure for **BML2'** at the UB3LYP/6-311G(d) level.

| Atom | x | y | z |
|------|-----------|-----------|-----------|
| C | 12.563590 | 2.951216 | 0.173043 |
| C | 5.708636 | 2.011216 | 0.140462 |
| C | 6.671494 | 1.047544 | 0.170224 |
| C | 13.272337 | 1.747761 | 0.307282 |
| C | -5.718557 | -2.036466 | -0.128366 |
| C | 1.646011 | -0.929504 | -0.069018 |
| C | 2.534241 | 0.118701 | -0.013493 |
| C | -2.047290 | -1.501741 | -0.095896 |
| C | -6.681512 | -1.072186 | -0.135136 |
| C | 14.575009 | 4.254386 | -0.077714 |
| C | -0.240305 | 0.668903 | -0.092237 |
| C | -2.539966 | -0.144773 | -0.125092 |
| H | -8.218667 | 7.331300 | -0.866301 |
| H | 0.312741 | 2.756038 | -0.026544 |
| C | 10.379884 | 1.939844 | 0.291801 |
| H | 5.958869 | 3.068054 | 0.176174 |
| H | 15.272392 | 0.982465 | 0.432558 |
| H | -3.501037 | -4.619417 | -3.423299 |
| C | 12.799354 | -1.007284 | -0.153749 |
| C | 3.091589 | 3.857012 | 0.076946 |
| C | 0.235251 | -0.695042 | -0.085006 |

| | | | |
|---|------------|-----------|-----------|
| C | -0.690111 | -1.764398 | -0.085999 |
| H | -8.660690 | -3.252280 | -0.053389 |
| C | 2.040283 | 1.475464 | 0.001174 |
| C | -10.923879 | -0.673579 | -0.204780 |
| C | -10.029631 | 0.397952 | -0.166298 |
| C | -2.281918 | 2.733441 | -1.483334 |
| H | -2.656363 | 3.750449 | -1.364542 |
| C | -10.390186 | -1.957021 | -0.113865 |
| C | -6.334257 | 0.345574 | -0.127505 |
| H | 4.706552 | -1.830946 | 0.105039 |
| C | -8.636906 | 0.194198 | -0.156627 |
| H | -7.165978 | 5.223086 | 1.987398 |
| C | -9.007639 | -2.225741 | -0.109318 |
| C | -4.343121 | -1.633836 | -0.125392 |
| C | 14.013334 | -1.413444 | -0.728272 |
| C | 14.210428 | -2.686378 | -1.262716 |
| C | 13.169444 | -3.614147 | -1.241732 |
| B | 12.471485 | 0.376834 | 0.641248 |
| H | 12.572502 | 5.074432 | -0.121692 |
| C | -13.038008 | -4.075840 | 1.018524 |
| H | 15.065128 | 5.212415 | -0.230833 |
| H | 16.411165 | 3.128103 | 0.058012 |
| C | -3.995987 | -0.212333 | -0.132229 |
| C | 13.189701 | 4.186749 | -0.023546 |
| H | -6.535729 | 7.299954 | -0.344486 |
| H | -7.825202 | 7.326708 | 0.855877 |
| C | 6.326175 | -0.370627 | 0.141404 |
| C | 7.498733 | -1.125493 | 0.185869 |
| C | 11.770242 | -1.960820 | -0.199686 |
| C | 10.908864 | 0.656854 | 0.384473 |
| C | 10.016217 | -0.415621 | 0.302369 |
| H | 8.648012 | 3.229425 | 0.177220 |
| H | -7.992935 | 5.232625 | -2.211872 |
| C | -14.147872 | 1.614155 | -0.002205 |
| C | 8.625958 | -0.217634 | 0.257567 |
| C | 8.995472 | 2.202910 | 0.231415 |
| C | 11.936422 | -3.246969 | -0.714755 |
| C | -14.312364 | -4.052993 | 1.572394 |
| C | -12.852418 | 1.074808 | -0.084749 |
| H | -3.827354 | -8.648517 | 0.227865 |
| H | -2.130332 | -8.572894 | 0.694852 |
| B | -12.507262 | -0.476555 | -0.410486 |

| | | | |
|---|------------|-----------|-----------|
| C | 4.335033 | 1.608125 | 0.072437 |
| O | 11.180674 | 3.047871 | 0.244805 |
| C | -15.029549 | -2.857003 | 1.590048 |
| C | -14.473586 | -1.709462 | 1.025641 |
| C | -13.206306 | -1.690592 | 0.423321 |
| O | -11.205640 | -3.051907 | -0.002675 |
| H | 14.838389 | -0.708737 | -0.757550 |
| H | 15.174062 | -2.955623 | -1.688688 |
| H | 13.308284 | -4.612275 | -1.649010 |
| O | 2.102268 | -2.236531 | -0.085769 |
| C | -8.147399 | -1.147413 | -0.147170 |
| O | -2.104465 | 2.211164 | -0.165581 |
| C | -3.185448 | -2.400737 | -0.100403 |
| C | 2.325136 | -2.755379 | -1.397507 |
| H | 2.712613 | -3.766219 | -1.268451 |
| H | 3.058479 | -2.151436 | -1.941207 |
| H | -3.009527 | 2.141918 | -2.047689 |
| C | -11.813515 | 2.013131 | -0.009100 |
| O | 10.477705 | -1.700966 | 0.255713 |
| H | 11.092324 | -3.928922 | -0.707325 |
| C | 7.545482 | -2.610237 | 0.161757 |
| O | -10.466252 | 1.689431 | -0.137794 |
| C | 3.177159 | 2.374613 | 0.052412 |
| C | -1.650338 | 0.903624 | -0.136284 |
| C | 3.989473 | 0.186482 | 0.041412 |
| C | 4.962936 | -0.777580 | 0.089083 |
| H | -0.320177 | -2.782420 | -0.052350 |
| C | 14.671736 | 1.872604 | 0.271199 |
| C | 0.684066 | 1.738190 | -0.047832 |
| C | 15.324860 | 3.087470 | 0.077230 |
| C | 8.136003 | 1.124333 | 0.237792 |
| C | -12.504437 | -2.906358 | 0.473453 |
| H | -2.577186 | -8.616092 | -1.013688 |
| H | -4.524580 | -3.439511 | -2.598297 |
| C | -4.970174 | 0.752047 | -0.124792 |
| H | -4.714504 | 1.805466 | -0.103156 |
| H | -5.970523 | -3.093474 | -0.121109 |
| C | -14.397977 | 2.971810 | 0.182107 |
| C | -13.327464 | 3.862088 | 0.278795 |
| C | -12.028789 | 3.382379 | 0.176337 |
| H | -14.994187 | 0.943927 | -0.118746 |
| H | -15.420561 | 3.336864 | 0.239291 |

| | | | |
|---|------------|-----------|-----------|
| H | -13.501667 | 4.925065 | 0.424006 |
| H | -11.170205 | 4.043875 | 0.228562 |
| C | -7.507006 | 1.101127 | -0.134732 |
| H | -12.435310 | -4.978811 | 1.013383 |
| H | -14.732816 | -4.958303 | 2.002655 |
| H | -16.020540 | -2.820272 | 2.036085 |
| H | -15.051455 | -0.791296 | 1.052715 |
| H | -8.106255 | 3.258104 | -3.450934 |
| H | -7.346541 | 1.793339 | -2.808671 |
| H | -9.063388 | 2.070688 | -2.558282 |
| H | -6.140821 | 2.012750 | 2.372926 |
| H | -7.070771 | 3.255828 | 3.215796 |
| H | -7.875413 | 1.822719 | 2.561882 |
| H | -2.809894 | -3.123745 | -2.775176 |
| H | -3.514135 | -3.165842 | 2.620417 |
| H | -2.537313 | -4.498025 | 3.255867 |
| H | -2.547839 | -6.480125 | 2.043406 |
| H | -3.305723 | -6.567876 | -2.167330 |
| C | -7.538013 | 6.918107 | -0.116767 |
| C | -7.088535 | 2.558245 | 2.374986 |
| C | -8.090452 | 2.567688 | -2.604022 |
| C | -7.799975 | 3.296405 | -1.315069 |
| C | -7.798977 | 4.691618 | -1.288188 |
| C | -7.565627 | 5.407937 | -0.114058 |
| C | -7.335358 | 4.686629 | 1.056392 |
| C | -7.319617 | 3.289872 | 1.073345 |
| C | -7.548080 | 2.586655 | -0.124913 |
| C | -2.857576 | -8.211613 | -0.037545 |
| C | -3.539936 | -3.915606 | -2.588304 |
| C | -2.656131 | -3.811426 | 2.414385 |
| C | -2.835718 | -4.567462 | 1.119224 |
| C | -2.751194 | -5.960907 | 1.109388 |
| C | -2.921661 | -6.702813 | -0.059580 |
| C | -3.178174 | -6.010385 | -1.241981 |
| C | -3.271069 | -4.616778 | -1.277103 |
| C | -3.100797 | -3.883342 | -0.085566 |
| C | 3.317487 | 4.601589 | -1.098187 |
| C | 3.223627 | 5.994971 | -1.054245 |
| C | 2.912460 | 6.676325 | 0.121342 |
| C | 2.687317 | 5.923430 | 1.274016 |
| C | 2.770797 | 4.529976 | 1.274620 |
| C | 2.530957 | 3.761908 | 2.552808 |

| | | | |
|---|------------|-----------|-----------|
| C | 3.646488 | 3.912756 | -2.402232 |
| C | 2.847437 | 8.184871 | 0.155224 |
| C | 7.789398 | -3.332733 | 1.346751 |
| C | 7.791524 | -4.726936 | 1.304115 |
| C | 7.572019 | -5.431556 | 0.120043 |
| C | 7.353173 | -4.698557 | -1.044894 |
| C | 7.333594 | -3.301209 | -1.046441 |
| C | 7.125130 | -2.557645 | -2.345609 |
| C | 8.068601 | -2.618613 | 2.646044 |
| C | 7.551318 | -6.941713 | 0.109168 |
| H | 3.394299 | 6.561101 | -1.967323 |
| H | 2.441008 | 6.433964 | 2.202478 |
| H | 2.375490 | 4.440658 | 3.394682 |
| H | 3.377248 | 3.112132 | 2.791364 |
| H | 3.648355 | 4.624935 | -3.231043 |
| H | 2.924328 | 3.124723 | -2.631238 |
| H | 4.629449 | 3.434132 | -2.370544 |
| H | 3.797563 | 8.618040 | 0.488991 |
| H | 2.632103 | 8.599936 | -0.832878 |
| H | 2.073490 | 8.539067 | 0.841883 |
| H | 7.976506 | -5.277456 | 2.223962 |
| H | 7.198479 | -5.225424 | -1.983974 |
| H | 7.108150 | -3.249408 | -3.191406 |
| H | 6.185928 | -1.997629 | -2.350498 |
| H | 7.923877 | -1.831689 | -2.519448 |
| H | 8.054764 | -3.315464 | 3.487606 |
| H | 9.052386 | -2.141576 | 2.621531 |
| H | 7.335374 | -1.832404 | 2.842653 |
| H | 8.309420 | -7.359140 | 0.778129 |
| H | 6.581018 | -7.331148 | 0.439074 |
| H | 7.736241 | -7.338322 | -0.892620 |
| H | 1.653180 | 3.114493 | 2.475727 |
| H | -1.332605 | 2.755702 | -2.028838 |
| H | 1.392474 | -2.792366 | -1.970347 |
| H | -1.777420 | -3.161437 | 2.383651 |
| F | -12.827857 | -0.707723 | -1.824551 |
| F | 12.666874 | 0.091228 | 2.068125 |

6. Photophysical properties

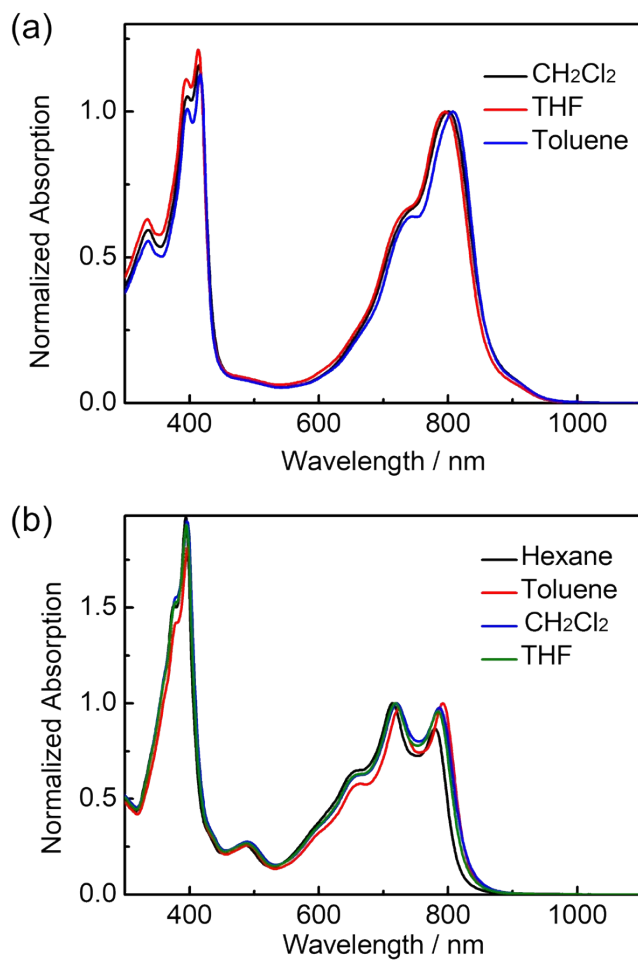


Fig. S7. UV/Vis absorption spectra of a) **BML1** and b) **BML2** in various solvents, respectively.

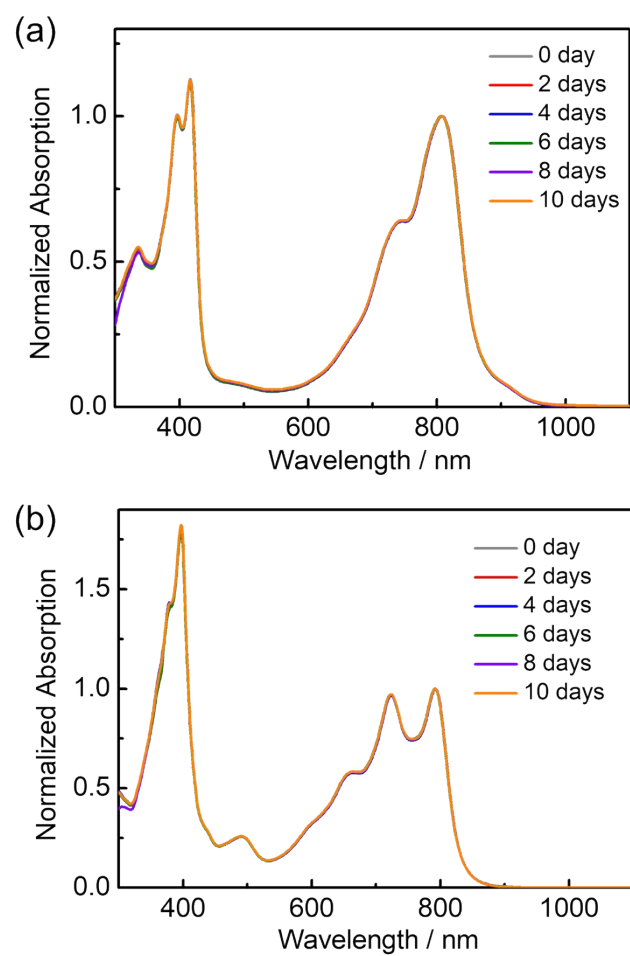


Fig. S8. UV/Vis absorption spectra of a) **BML1** and b) **BML2** in toluene left at ambient condition for ten days.

7. Time-dependent DFT calculations

To assign the UV/Vis absorption spectra of **BML1** and **BML2**, time-dependent DFT calculations were performed on **BML1'** and **BML2'** at the UB3LYP/6-311G(d) level.

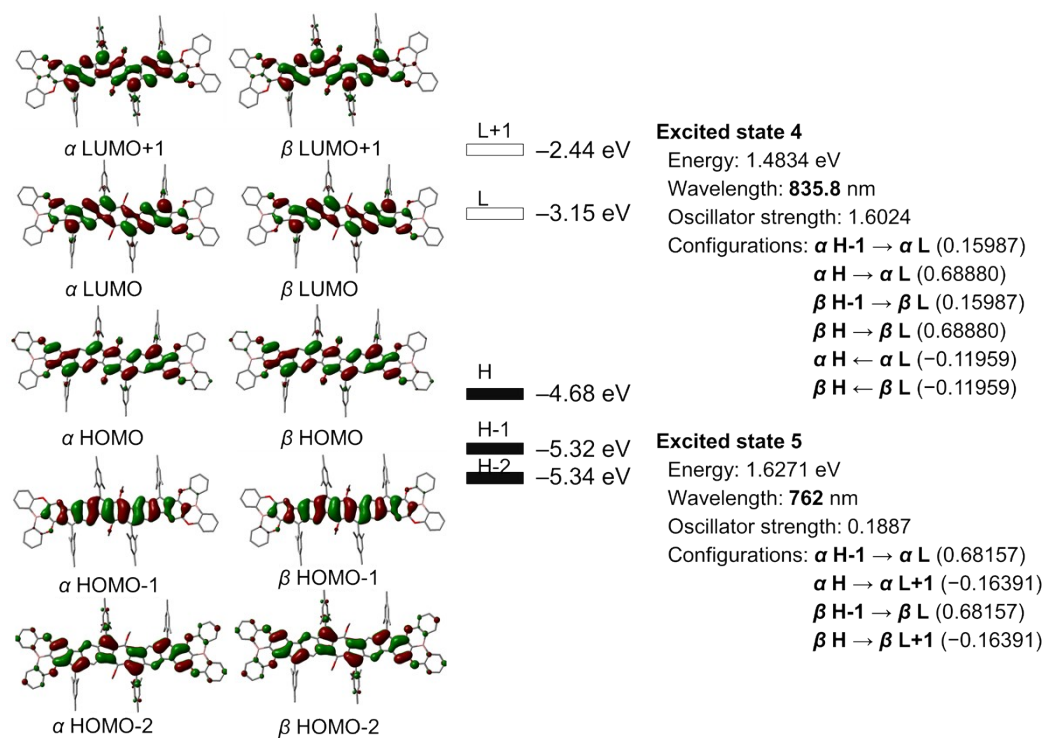


Fig. S9. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **BML1'**.

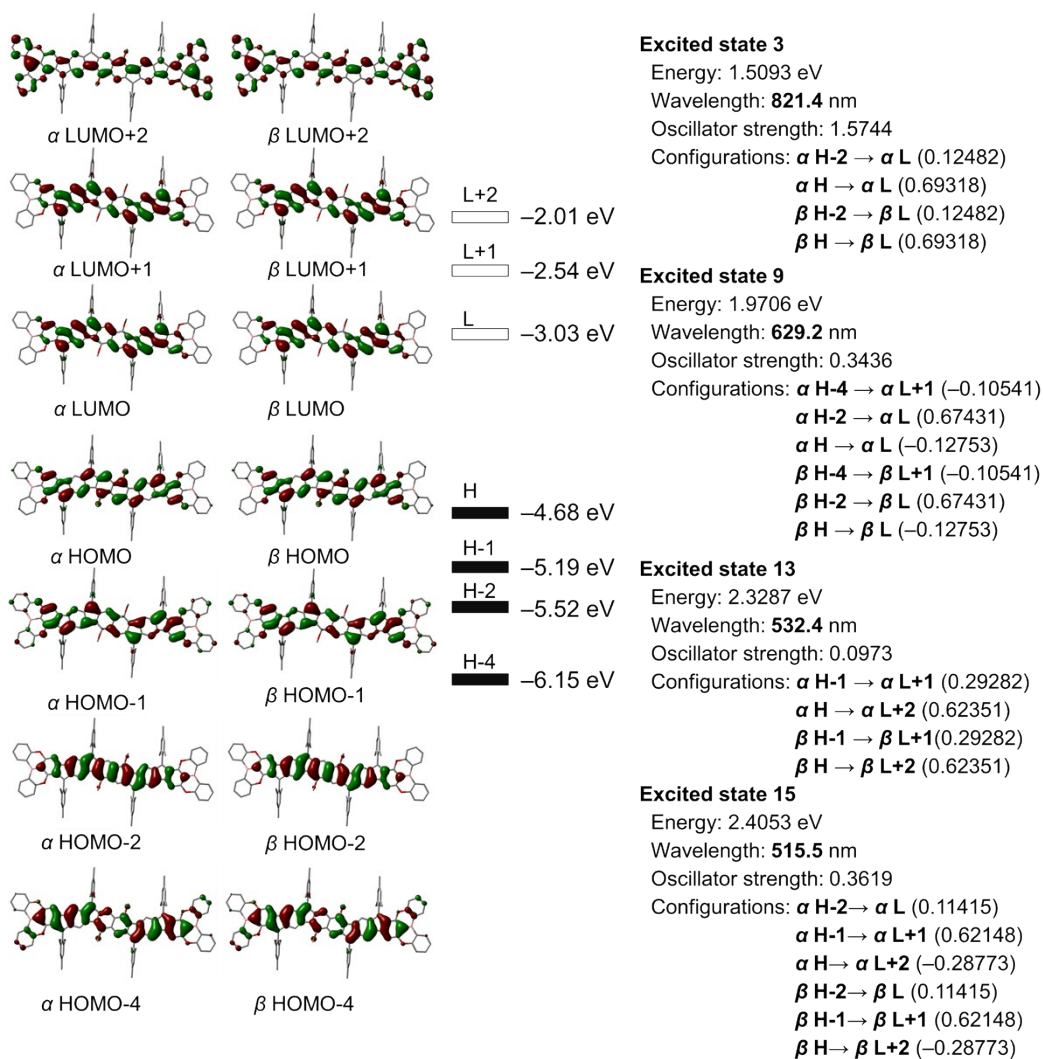


Fig. S10. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **BML2'**.

8. Titration experiment and Lewis acidity

To estimate the Lewis acidity of **BML1** and **BML2**, the titration experiment was performed by adding Lewis base TBAF to the solution (2.0×10^{-5} M, 3 mL) of **BML1** and **BML2** in THF with a micro syringe, and UV/Vis absorption spectra were recorded using Hitachi U-2900 spectrometer. The binding constant K was determined with the online tools at <http://supramolecular.org>.^[7]

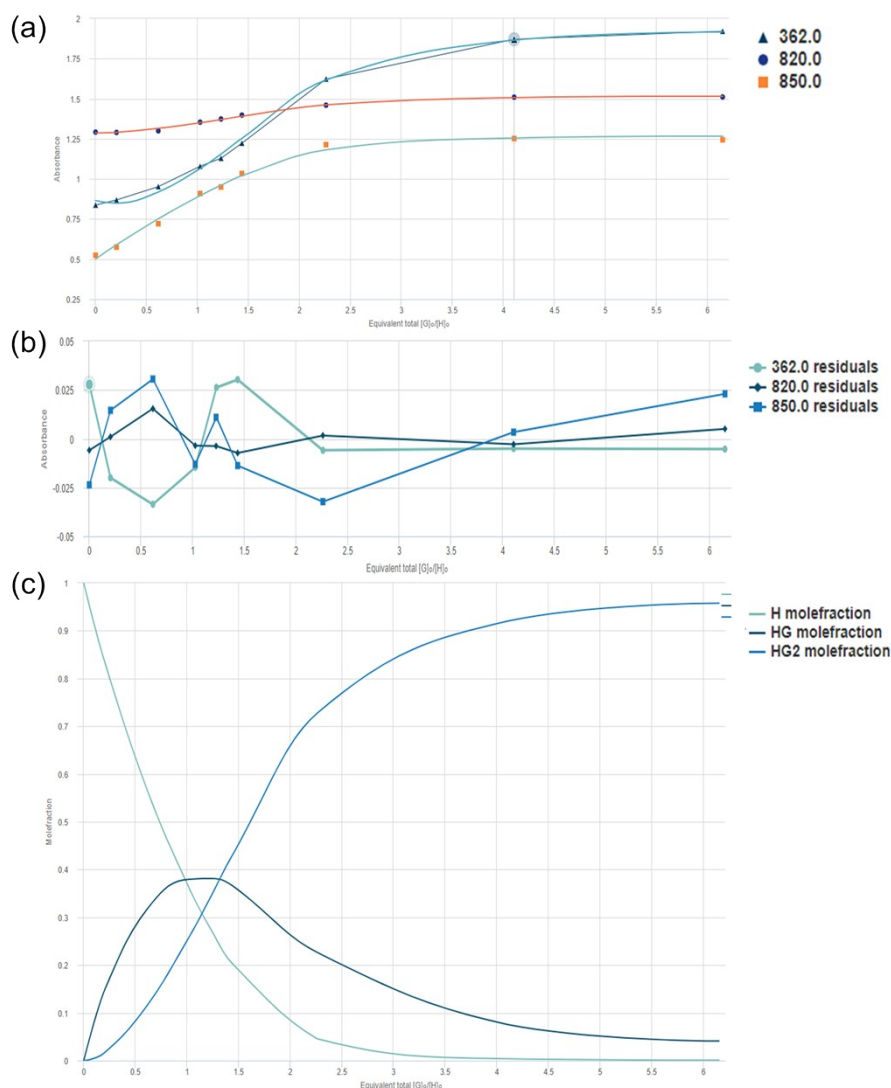


Fig. S11. a–c) Fitting curves for the binding constants of **BML1** toward TBAF.

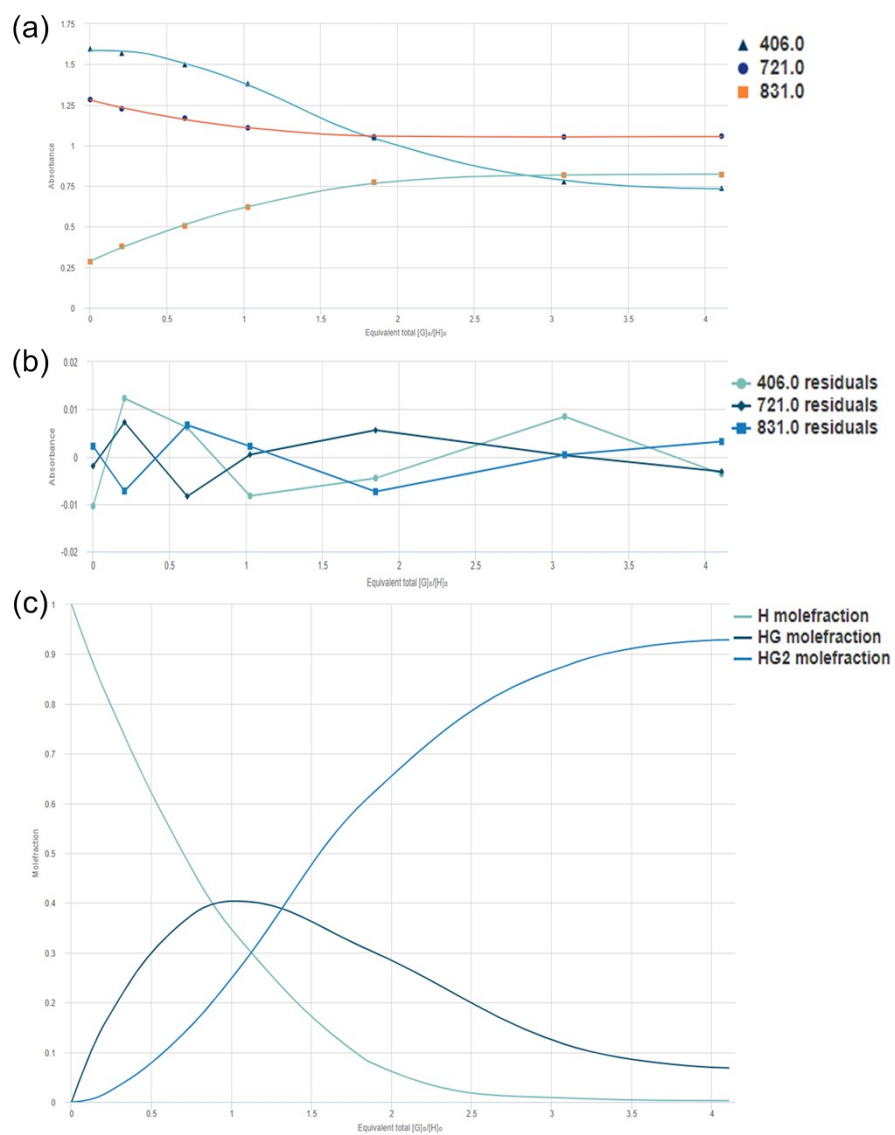


Fig. S12. a–c) Fitting curves for the binding constants of **BML2** toward TBAF.

9. Photothermal Conversion Properties

BML1 (or **BML2**) and DSPE-PEG at a weight ratio of 1:3 were dissolved in THF (4 mL). Then, the solution was added dropwise to deionized water (10 mL) under stirring. After THF was fully evaporated, the mixture was dialyzed for 24 h.

BML1-NPs and **BML2**-NPs at various concentrations (0–10 μM) were subjected to 808 nm laser irradiation (0.8 W cm^{-2}) for 10 min. The photothermal conversion efficiencies of **BML1**-NPs and **BML2**-NPs were measured by recording the photothermal response of nanoparticles under 808 nm laser irradiation (0.8 W cm^{-2}) and the temperature during the cooling period. The photostability of **BML1**-NPs and **BML2**-NPs upon 808 nm laser irradiation was investigated by measuring the temperature variations of nanoparticles in water over 5 cycles of heating and natural cooling.

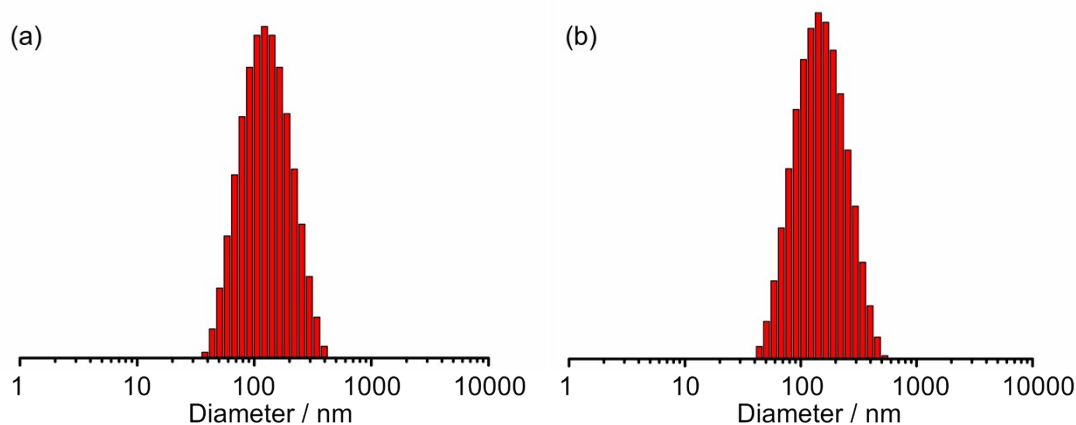


Fig. S13. Dynamic light scattering results of a) **BML1**-NPs and b) **BML2**-NPs

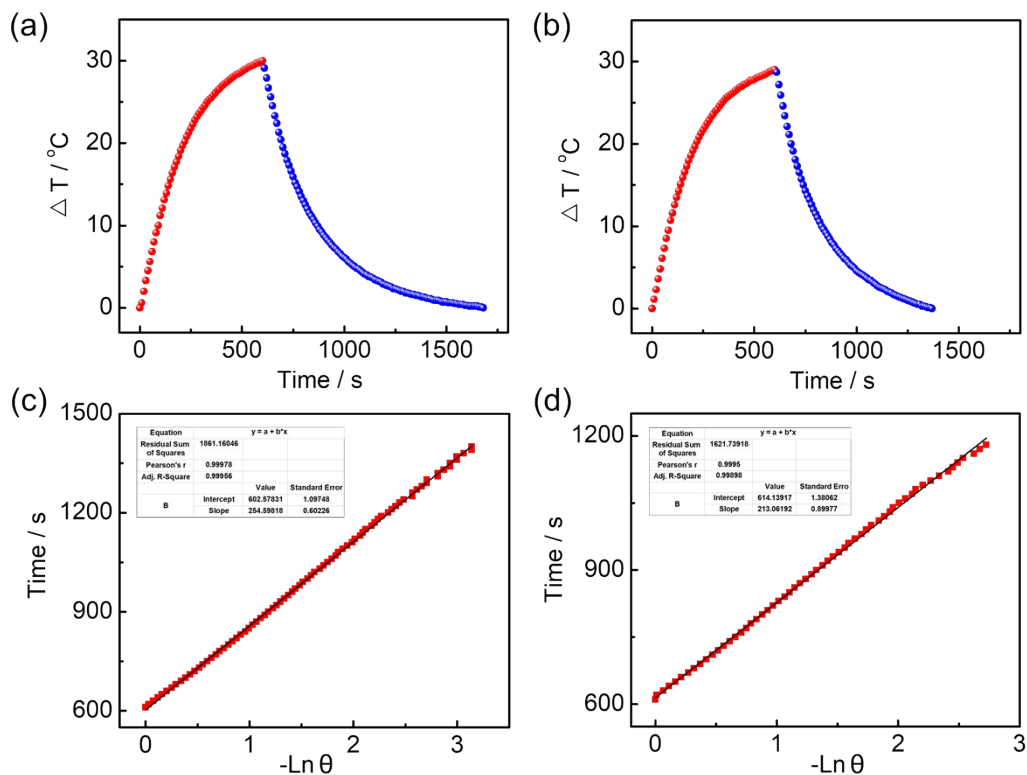


Fig. S14. Temperature changes of a) **BML1-NPs** and b) **BML2-NPs** (10 μM) under laser irradiation (0.8 W cm^{-2}) for 10 min followed by removal of laser. Linear plots of the cooling time versus $-\text{Ln}\theta$ calculated from the cooling stage for c) **BML1-NPs** and d) **BML2-NPs**.

10. ^1H NMR and ^{13}C NMR spectra

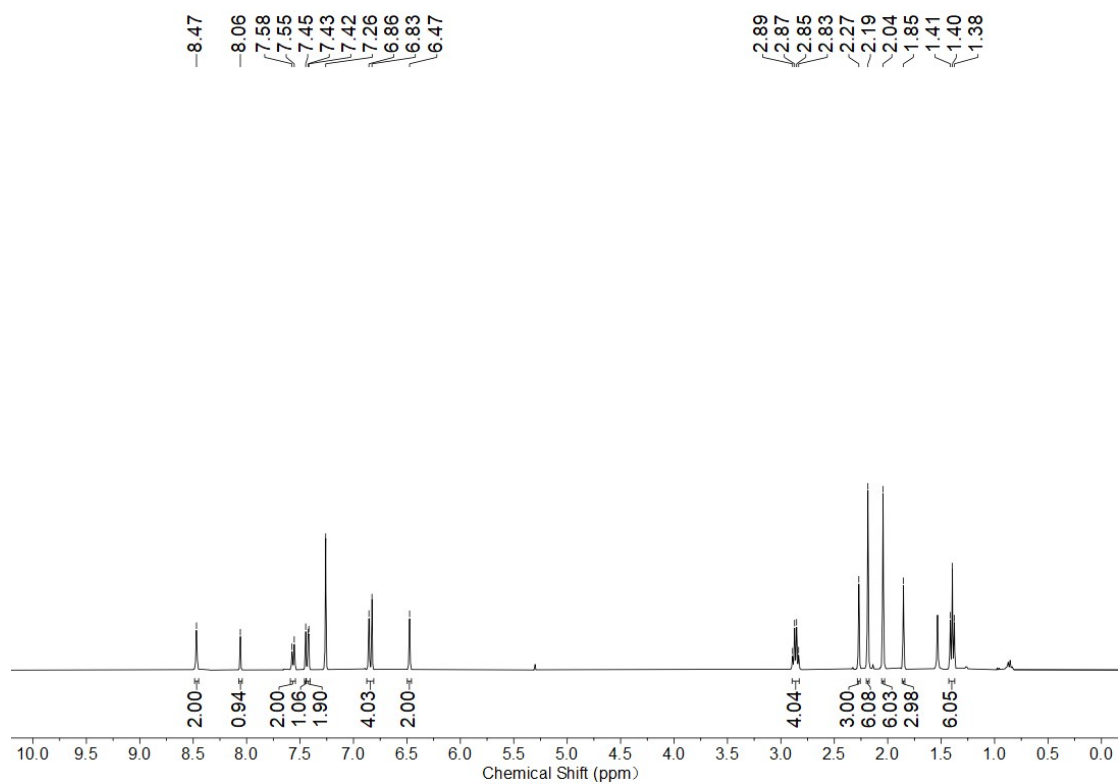


Fig. S15. ^1H NMR spectrum of **1** in CDCl_3 .

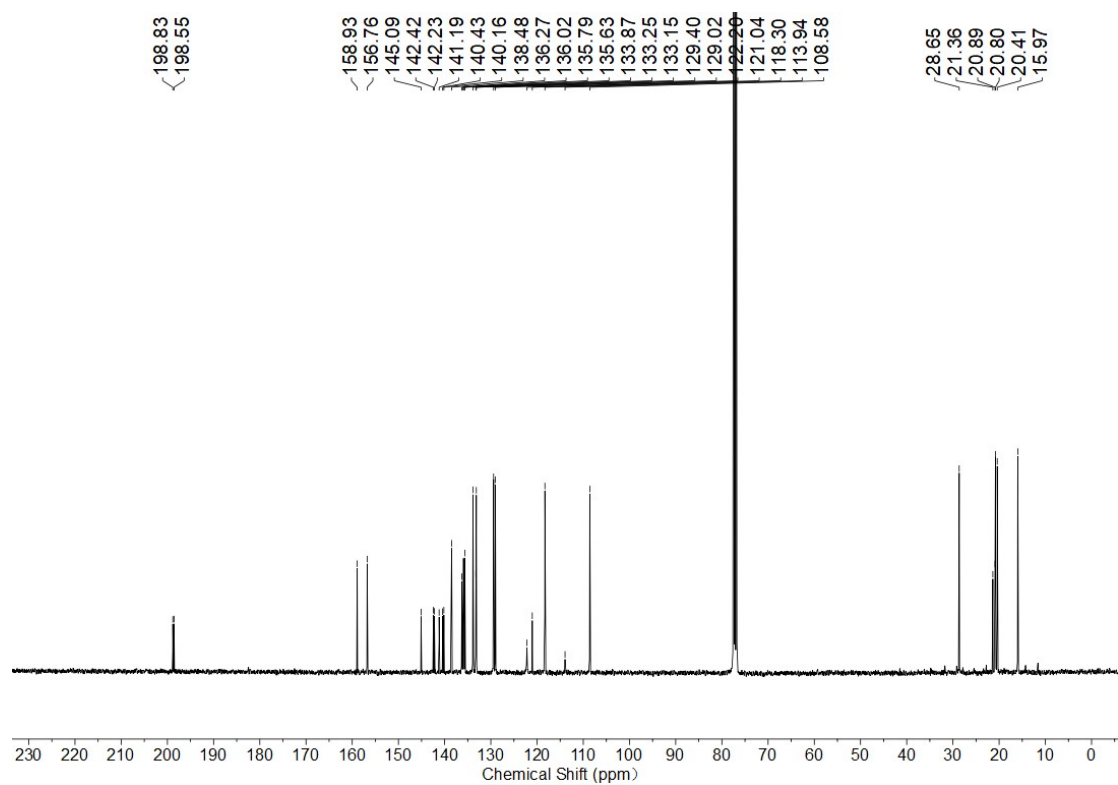


Fig. S16. ^{13}C NMR spectrum of **1** in CDCl_3 .

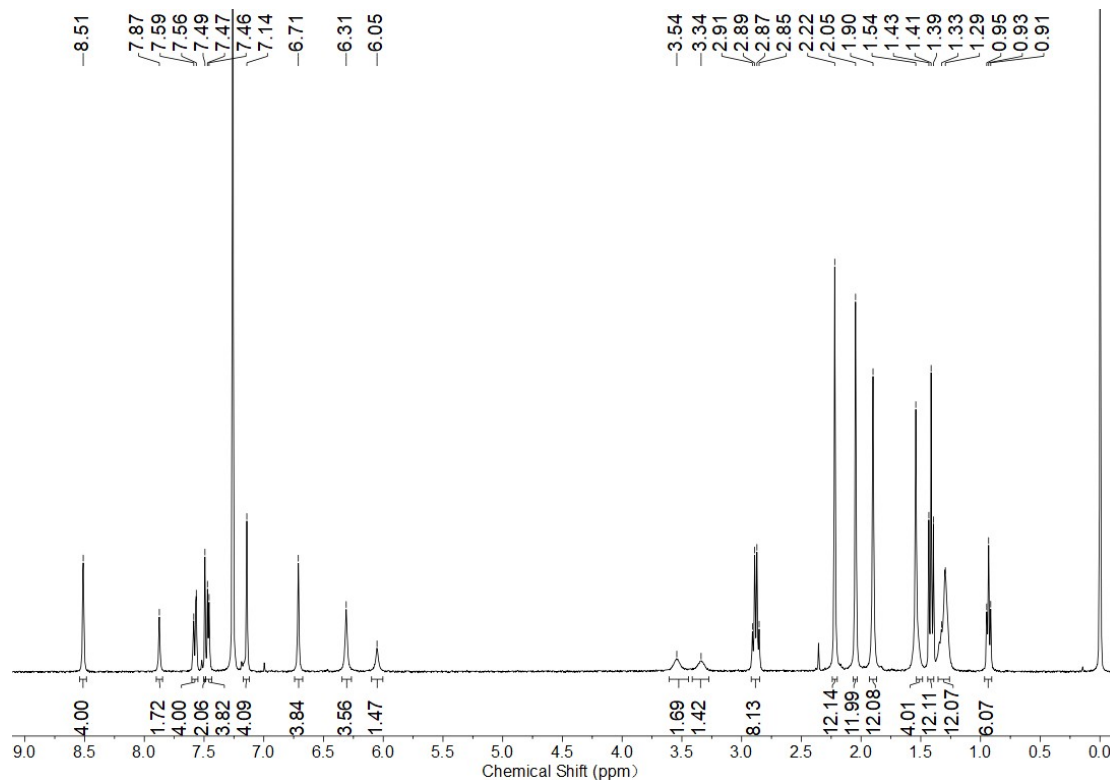


Fig. S17. ^1H NMR spectrum of **3** in CDCl_3 .

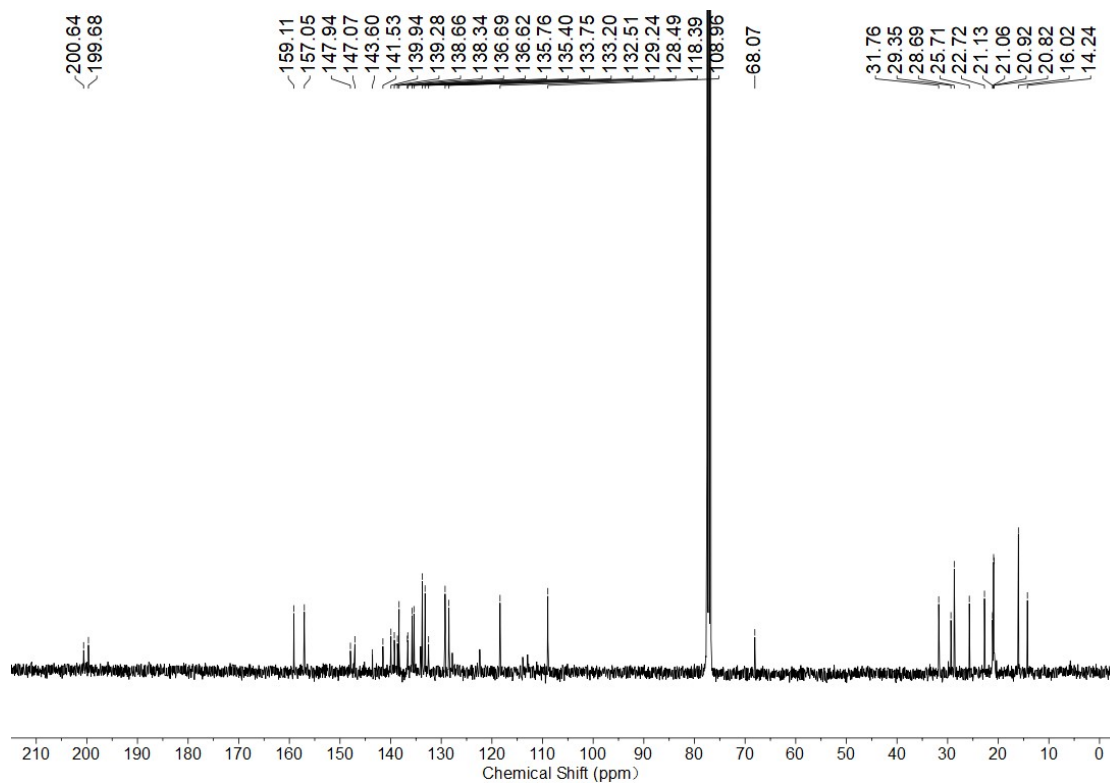


Fig. S18. ^{13}C NMR spectrum of **3** in CDCl_3 .

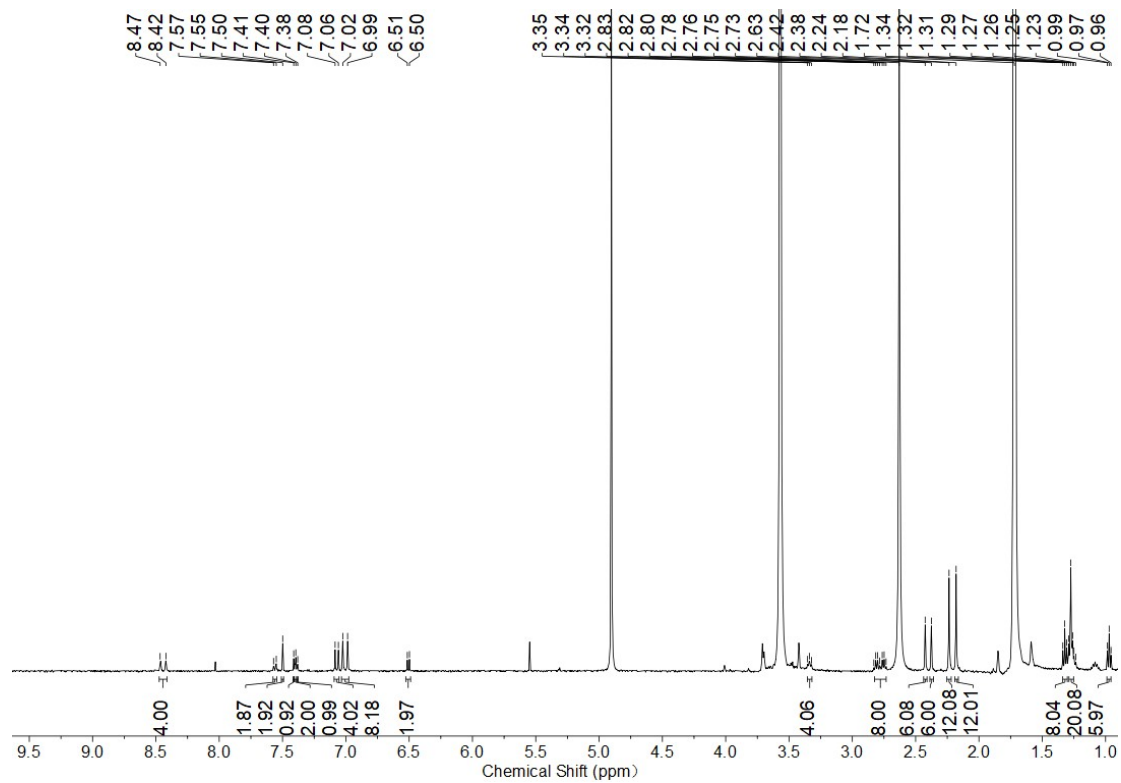


Fig. S19. ^1H NMR spectrum of **BML1** in $\text{THF-}d_8$ at 273 K.

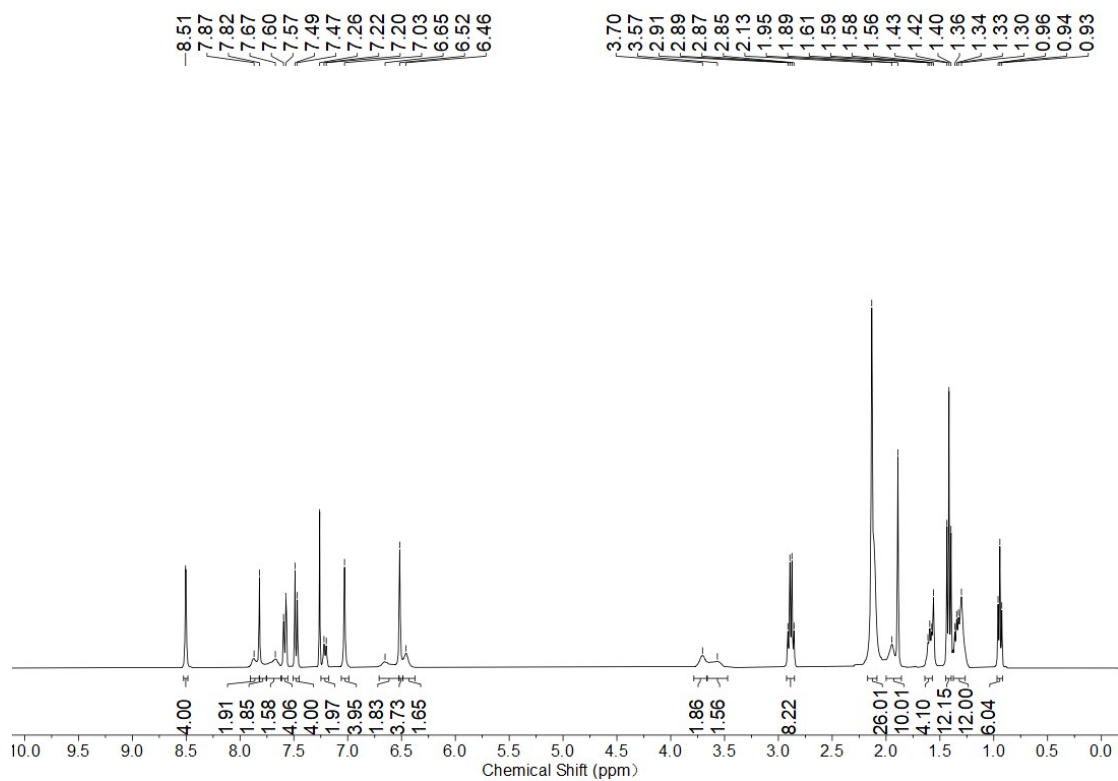


Fig. S20. ^1H NMR spectrum of **6** in CDCl_3 .

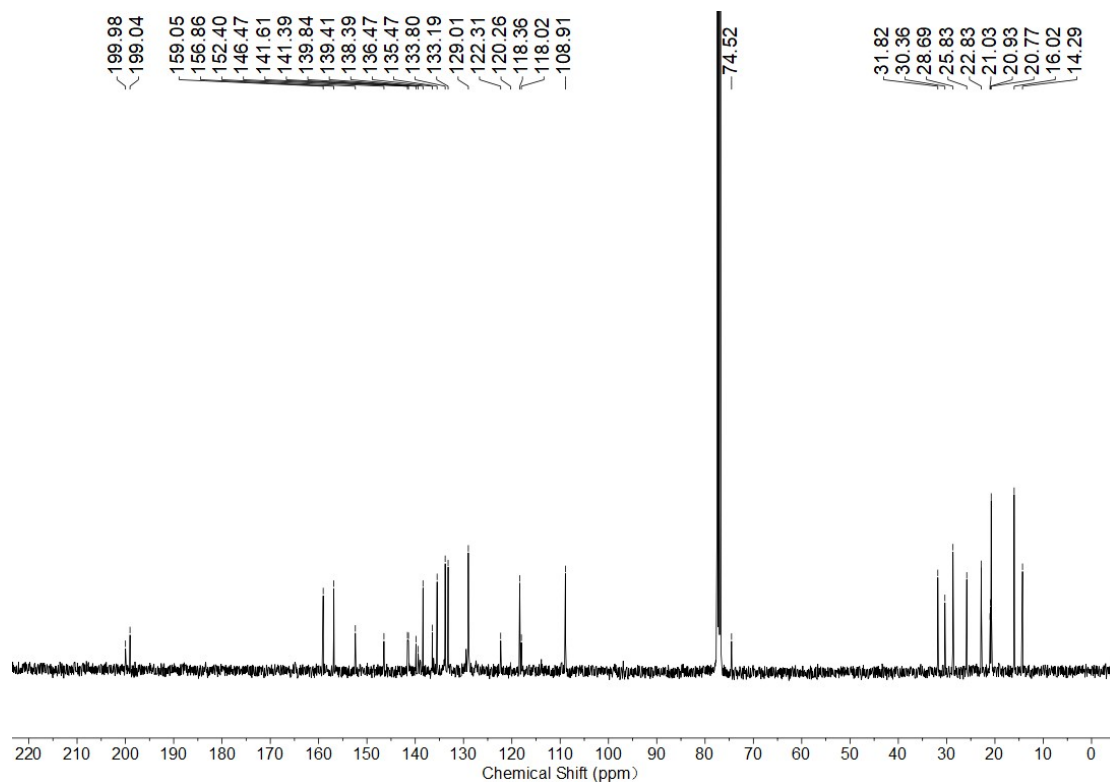


Fig. S21. ^{13}C NMR spectrum of **6** in CDCl_3 .

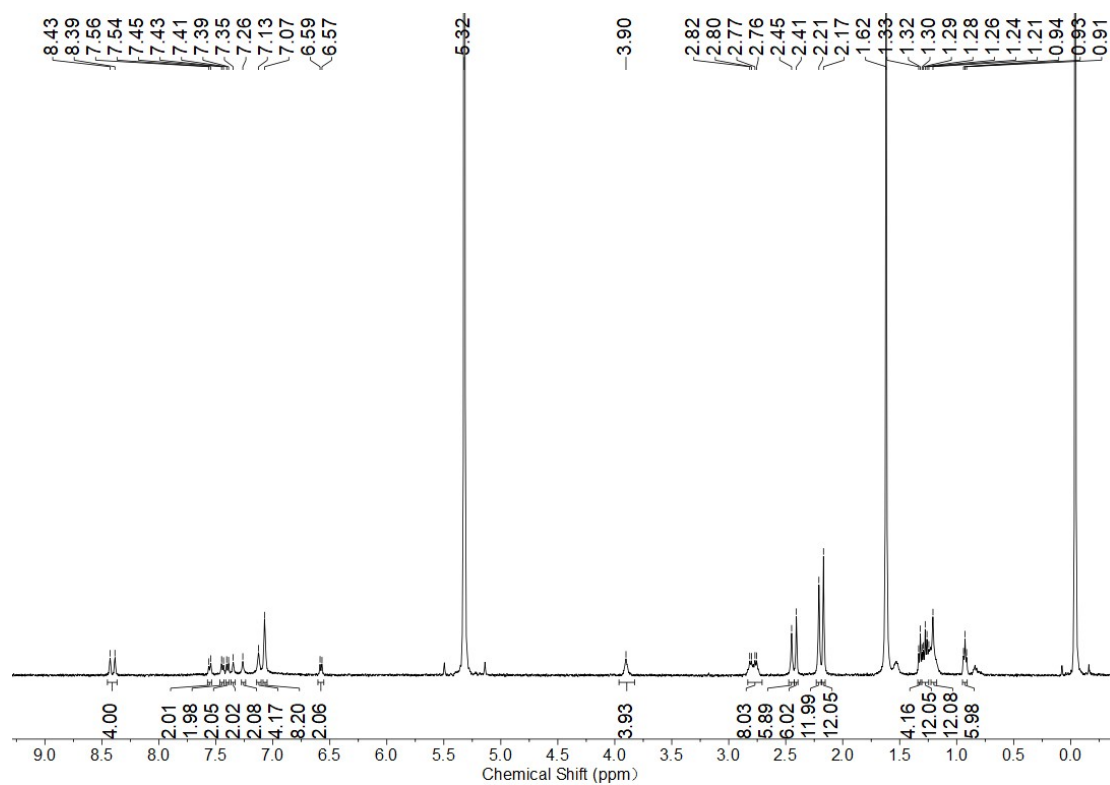


Fig. S22. ^1H NMR spectrum of **BML2** in CD_2Cl_2 at 253 K.

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