Supporting Information

A feasible strategy to obtain air-stable triphenylamine radicals in solid state by introducing conjugated donor-acceptor module

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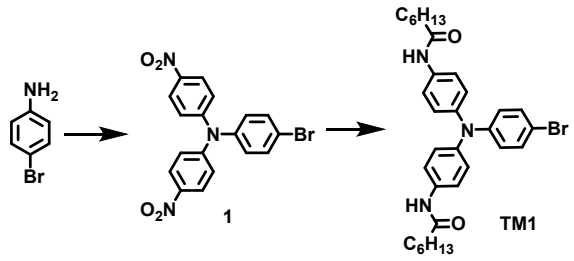
Experimental

1. Note

Unless stated otherwise, all commercially available chemicals and solvents were used directly without further purification. The dichloromethane (DCM) was dried via distillation from P_2O_5.

2. Synthetic Procedure



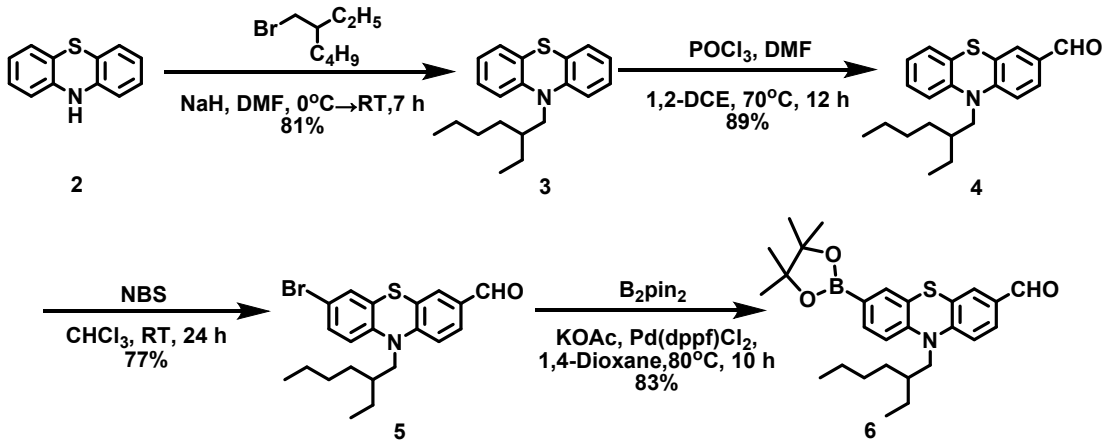
***4-bromo-N,N-bis(4-nitrophenyl)aniline* (1)**[1]

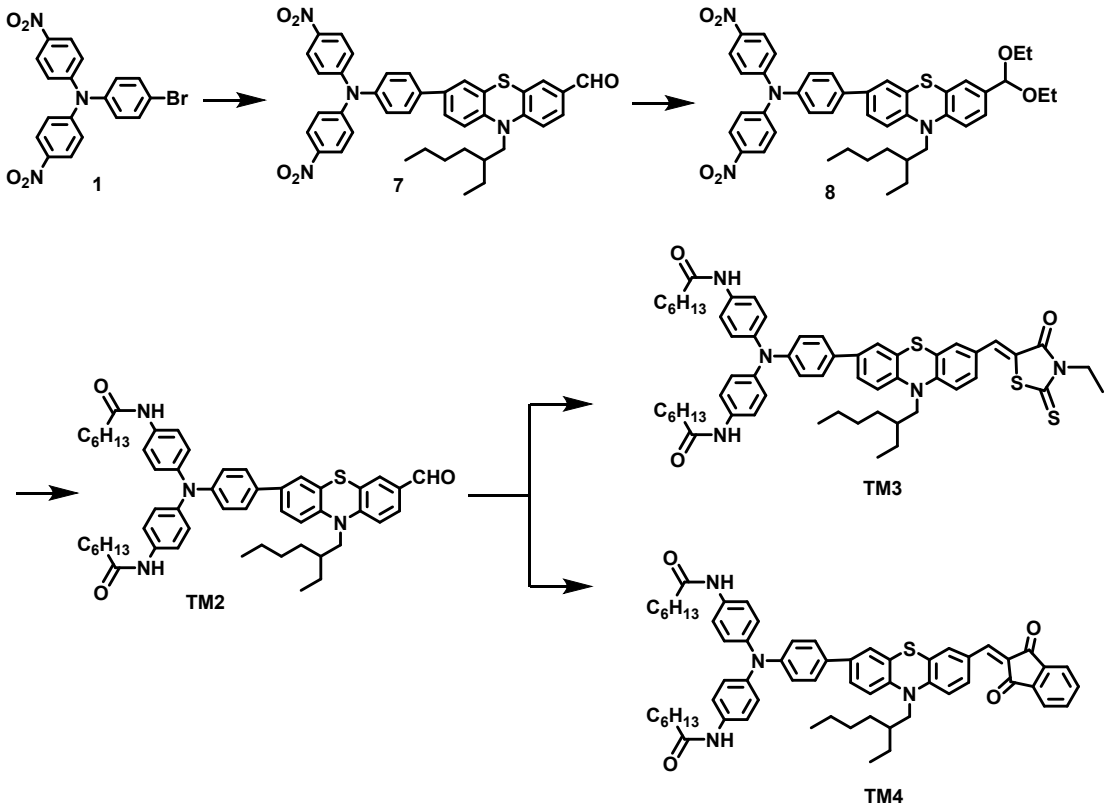
4-bromoaniline (2.0 g, 11.63 mmol), CsF (3.52 g, 23.17mmol), 1-fluoro-4-nitrobenzene (4.08 g, 28.92 mmol) and DMSO (70 mL) were added into a 250 mL 3-neck round-bottom flask and reacted for 10 h at 120°C under argon. After pouring into 50 mL of cold saturated salt water, yellow precipitates were collected and recrystallization by ethanol. The purified product was light yellow needle type crystals with a yield of 66%.

***N,N'-(((4-bromophenyl)azanediyl)bis(4,1-phenylene)) diheptanamide* (TM1)**

Compound **1** (0.91 g, 2.21 mmol), 10% Pd/C (0.05 g), hydrazine monohydrate (10.0 mL) and ethanol (20 mL) were placed in 3-neck round-bottom flask, heated at reflux for 8 h under argon, the reaction process was detected by TLC. After the end of the reaction, Pd/C was removed by thermal filtration. After the filtrate was cooled, the target diamine was separated out with water and filtrated to obtain a white solid 0.56 g, which was unstable and directly transferred to the next step without further purification. The above diamine intermediates (0.56 g), trethylamine (0.44 g, 4.4 mmol), dried dichloromethane (40 mL) were added to a 100 mL round-bottom flask, and the reaction

mixture was cooled to 0°C in an ice bath. Heptanoyl chloride (0.49 g, 3.3 mmol) solution was slowly added to the reaction system, and stirred overnight at room temperature. The reaction mixture was extracted by DCM (25 mL×3), and the organic phase was decompressed to remove the solvent and recrystallized with methanol. The compound **TM1** was white solid 350 mg with a yield of 27%.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ：9.85 (s,2H, NH), 7.53 (d, *J* = 8.8 Hz, 4H, ArH), 7.35 (d, *J* = 8.8 Hz, 2H, ArH), 6.97 (d, *J*=8.8 Hz, 4H, ArH), 6.78 (d, *J* = 8.8 Hz, 2H, ArH), 2.27 (t, *J* = 7.2 Hz, 4H, CH_2), 1.59-1.1.55 (m, 4H, CH_2), 1.28 (m, 12H, CH_2), 0.88-0.85 (m, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-*d6*, ppm) δ: 171.5, 147.6, 142.7, 142.1, 135.9, 135.3, 132.4, 129.7, 125.6, 125.1, 123.1, 122.1, 120.9, 112.7, 36.8, 31.5, 28.8, 25.6, 22.5, 14.4. HRMS(ESI)$^{+}$ m/z: $[M+H]^{+}$ calcd. $C_{32}H_{40}BrN_3O_2$, 578.2377 and 580.2377; found, 578.2377 and 580.2360 (Isotopic peak intensity ratio of bromine =1:1)





10-(2-ethylhexyl)-10H-phenothiazine (**2**), *10-(2-ethylhexyl)-10H-phenothiazine-3-carbaldhyde* (**3**), *7-bromo-10-(2-ethylhexyl)-10H-phenothiazine-3-carbaldehyde* (**4**) and *10-(2-ethylh-exyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine-3-carbaldehyde* (**5**) were prepared according to literature procedures.[2]

7-(4-(bis(4-nitrophenyl)amino)phenyl)-10-(2-ethylhexyl)-10H-phenothiazine-3-cabal-dehyde (**7**)[3]

Compound **1** (5.92 g, 13.5 mmol), compound **6** (6.29 g, 13.5 mmol) and K_2CO_3 (11.2 g, 81 mmol) were added to THF/H_2O (70 mL/25 mL). After this, the solution was degassed with Ar for 30 minutes. Under protection of Ar flow, $Pd(PPh_3)_4$ (780 mg, 0.675 mmol) was added. The mixture was refluxed under Ar for 12 hours. Then, the mixture was extracted with ethyl acetate, and washed with water and brine. The obtained organic phase was dried by anhydrous Na_2SO_4, concentrated and purified on a silica column with Hexane: Dichloromethane (10 : 1) as eluent to yield a yellow solid (5.44g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.83 (s,1H, CHO), 8.17 (d, J = 9.2 Hz, 4H, ArH), 7.68 (d, J = 8.4 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 7.58 (d, J = 8.8 Hz, 2H, ArH), 7.41 (d, J = 8.4 Hz, 1H, ArH), 7.39 (s, 1H, ArH), 7.22-7.18 (m, 6H, ArH),

7.00-6.97 (m, 2H, ArH), 3.84 (d, J = 7.2 Hz, 2H, CH_2), 2.00-1.93 (m, 1H, CH), 1.50-1.26 (m, 8H, CH_2), 0.92-0.86 (m, 6H, CH_3).

HRMS(ESI)$^+$ m/z: $[M+H]^+$ calcd. $C_{39}H_{37}N_4O_5S$, 673.2479; found, 673.2470.

4-(7-(diethoxymethyl)-10-(2-ethylhexyl)-10H-phenothiazin-3-yl)-N,N-bis(4-nitrophenyl)aniline (**8**)

Compound **7** (0.5 g, 0.74mmol), triethyl orthoformate (0.33g, 2.2 mmol) was dissolved in 10 mL toluene solution, heated at reflux for 2 h, and the reaction process was detected by TLC. After the end of the reaction, the solution was washed with saturated sodium bicarbonate aqueous solution twice, and saturated salt water was washed twice, the organic phase was decompressed to remove the solvent to obtain the orange solid 450 mg, and the product was unstable and directly transported to the next step without further purification

N,N'-(((4-(10-(2-ethylhexyl)-7-formyl-10H-phenothiazin-3-yl)phnyl)azanediyl)bis-(4,1-phenylene))diheptanamide (**TM2**)

Compound 8 (0.45 g, 0.675 mmol),10% Pd/C (0.02 g), hydrazine monohydrate (10.0 mL), ethanol (15 mL) and THF (1 mL) were placed in a three-necked flask and heated at reflux for 8 h under the protection of Ar. The reaction process was detected by TLC. After the reaction, Pd/C was removed by thermal filtration After the filtrate was cooled, the target diamine was separated out with water, and the yellow solid 275 mg was obtained by extraction and filtration. The product was unstable, and was directly transferred to the next step without further purification.

The above diamine intermediate (260 mg), triethylamine (0.42 mL, 3.04 mmol), and dried methylene chloride (15 mL) were added to a 50 mL round-bottom flask, and the reaction mixture was cooled to 0℃ in an ice bath. The solution of heptanoyl chloride (60.6 mg, 0.4080 mmol) dissolved in dried dichloromethane (5 mL) was slowly added to the reaction system and stirred overnight at room temperature. The reaction mixture was extracted with DCM (25 mL × 3) and the organic phase was decompressed to remove the solvent. Compound **TM2** was purified by silica gel column chromatography with a yellow solid of 200 mg and a yield of 32%. ^{1}H NMR (400 MHz, DMSO-d_6,

ppm) δ: 9.85 (s, 2H, NH), 9.80 (s, 1H, CHO), 7.74 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.64 (d, J = 2.0 Hz, 1H, ArH), 7.54 (d, J = 8.8 Hz, 4H, ArH), 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.48 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.43 (d, J = 2.4 Hz, 1H, ArH), 7.23 (d, J = 8.8 Hz, 1H, ArH), 7.16 (d, J = 8.8 Hz, 1H, ArH), 6.99 (d, J = 8.8 Hz, 4H, ArH), 6.91 (d, J = 8.8 Hz, 2H, ArH), 3.95-3.85 (m, 2H, CH_2), 2.28 (t, J = 7.2 Hz, 4H, CH_2), 1.87-1.81 (m, 1H, CH), 1.62-1.54 (m, 4H, CH_2), 1.43-1.16 (m, 20H, CH_2), 0.89-0.78 (m, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-*d6*, ppm) δ: 191.0, 171.5, 152.1, 147.5, 143.3, 142.0, 135.7, 135.6, 131.7, 131.3, 130.1, 128.5, 127.4, 126.4, 125.4, 124.6, 121.8, 118.4, 118.0, 116.2, 114.8, 37.2, 35.6, 31.5, 30.1, 28.8, 28.2, 25.6, 24.0, 22.9, 22.5, 14.4, 14.2, 10.3.

HRMS(ESI)$^+$ m/z: $[M+H]^+$ calcd. $C_{53}H_{65}N_4O_3S$, 837.4772; found, 837.4776.

N,N'-(((4-(7-((3-ethyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)-10-(2-ethylhexyl)-10H-phenothiazin-3- yl)phenyl)azanediyl)bis(4,1phenylene))diheptanamide (**TM3**)

Compound **TM2** (200 mg, 0.24 mmol) and 3-Ethylrhodanine (112 mg, 0.7 mmol) were dissolved in dry chloroform (35 mL). Then, three drops of piperidine were added and the resulting solution was stirred overnight at 70℃ under argon. The reaction mixture was extracted with dichloromethane and water. The collected organic layer was dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude product was separated by column chromatography using hexane: ethyl acetate (3 : 1) as eluent to afford a purple-red solid (0.14 g, 60%).

^{1}H NMR (400 MHz, DMSO-*d6*, ppm) δ: 9.84 (s, 2H, NH), 7.71 (s, 1H, CH), 7.75-7.53 (m, 6H, ArH), 7.47 (d, J = 8.4 Hz 2H, ArH), 7.43 (s, 2H, ArH), 7.20 (d, J = 8.8 Hz, 1H, ArH), 7.15 (d, J = 8.8 Hz, 1H, ArH), 6.98 (d, J = 8.8 Hz, 4H, ArH), 6.90 (d, J = 8.4 Hz, 2H, ArH), 4.09-3.4.03 (m, 2H, CH_2), 3.93-3.82 (m, 2H, CH_2), 2.28 (t, J = 7.6 Hz, 4H, CH_2), 1.85-1.84 (m, 1H, CH), 1.59-1.56 (m, 4H, CH_2), 1.43-1.17 (m, 24H, CH_2), 0.89-0.78 (m, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-*d6*, ppm) δ: 171.5, 167.1, 161.3, 153.7, 148.0, 147.5, 143.3, 142.4, 135.7, 135.6, 132.7, 131.7, 131.1, 130.1, 127.6, 127.3, 125.8, 125.4, 125.1, 124.3, 121.8, 120.8, 119.7, 117.7, 117.1, 36.8, 36.1, 31.5,

30.1, 28.8, 28.2, 25.6, 23.6, 22.9, 22.5, 14.4, 14.3, 12.4, 10.7.

HRMS(ESI)$^+$ m/z: [M+H]$^+$ calcd. $C_{59}H_{70}N_5O_3S_3$, 980.4635; found, 980.4616

N,N'-(((4-(7-((1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)methyl)-10-(2-ethylhexyl)-10H-phenothiazin-3-yl)phenyl)azanediyl)bis(4,1-phenylene))diheptanamide (**TM4**)

Compound **TM2** (400 mg, 0.48 mmol) and 1,3-Indanedione (140 mg, 0.96 mmol) were dissolved in dry chloroform (40 mL). Then, three drops of piperidine were added and the resulting solution was stirred overnight at 70℃ under argon. The reaction mixture was extracted with dichloromethane and water. The collected organic layer was dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude product was separated by column chromatography using hexane: ethyl acetate (3 : 1) as eluent to afford a purple-red solid (0.22 g, 56%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ: 9.85 (s, 2H, NH), 8.59 (s, 1H, ArH), 8.36 (d, J = 8.8 Hz, 1H, ArH), 7.97-7.01 (m, 4H, ArH), 7.72 (s, 1H, ArH), 7.56-7.52 (m, 6H, ArH), 7.48 (d, J = 8.4 Hz, 1H, ArH), 7.46 (s, 1H, ArH), 7.21 (d, J = 8.8 Hz, 1H, ArH), 7.18 (d, J = 8.8 Hz, 1H, ArH), 6.99 (d, J = 8.8 Hz, 4H, ArH), 6.91 (d, J = 8.8 Hz, 2H, ArH), 3.99-3.89 (m, 2H, CH_2), 2.28 (t, J = 7.6 Hz, 4H, CH_2), 1.91-1.81 (m, 1H, CH), 1.62-1.55 (m, 4H, CH_2), 1.43-1.18 (m, 20H, CH_2), 0.89-0.79 (m, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 189.7, 188.9, 170.9, 149.9, 147.0, 144.4, 141.8, 141.7, 141.6, 139.3, 135.3, 135.1, 132.4, 132.1, 131.0, 127.3, 126.8, 126.1, 124.9, 124.5, 123.8, 123.2, 122.7, 122.7, 121.2, 120.3, 117.4, 115.8, 36.3, 31.0, 29.5, 28.2, 27.6, 25.1, 23.0, 22.4, 21.9, 13.8, 13.7, 10.2.

HRMS(ESI)$^+$ m/z: [M+H]$^+$ calcd. $C_{62}H_{69}N_4O_4S$, 965.5034; found, 965.5033.

3. Electrochemical data

Cyclic voltammetry was performed by using a cell equipped with a glassy carbon electrode as working electrode, a platinum wire as counter electrodes, and $Ag/AgNO_3$ as a referential electrode with scan rate 50 mV s^{-1} in CH_2Cl_2. All potentials are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple, used as a standard.

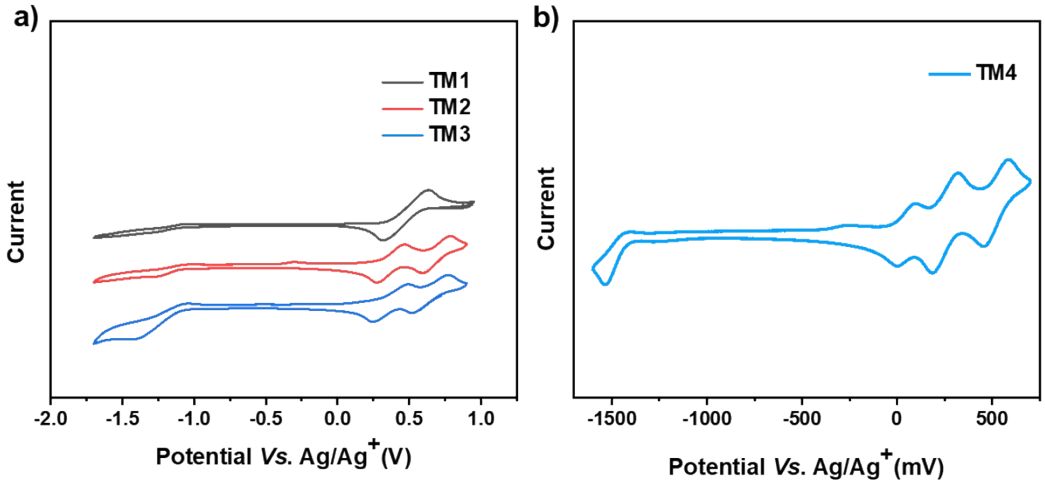
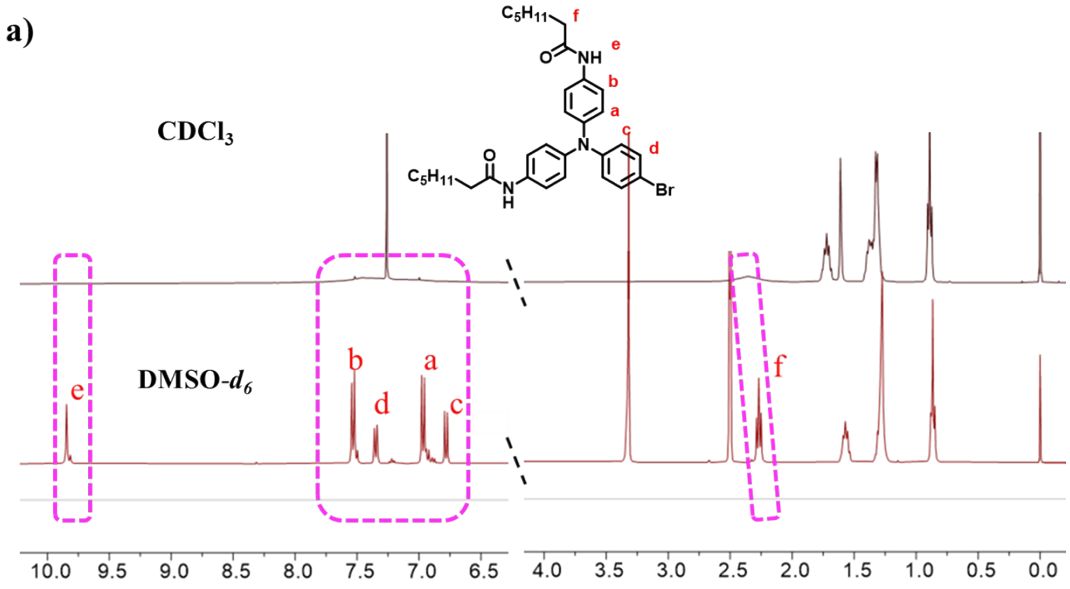


Figure S1. Cyclic voltammograms of **TM1-4** at scan rate 50 mV s^{-1} in CH_2Cl_2 at 298 K

4. ^{1}H NMR spectra

^{1}H NMR spectra were recorded on a Bruker Avance AVII at 400 MHz and ^{13}C spectra at 100 MHz in DMSO-*d6* at 25°C.



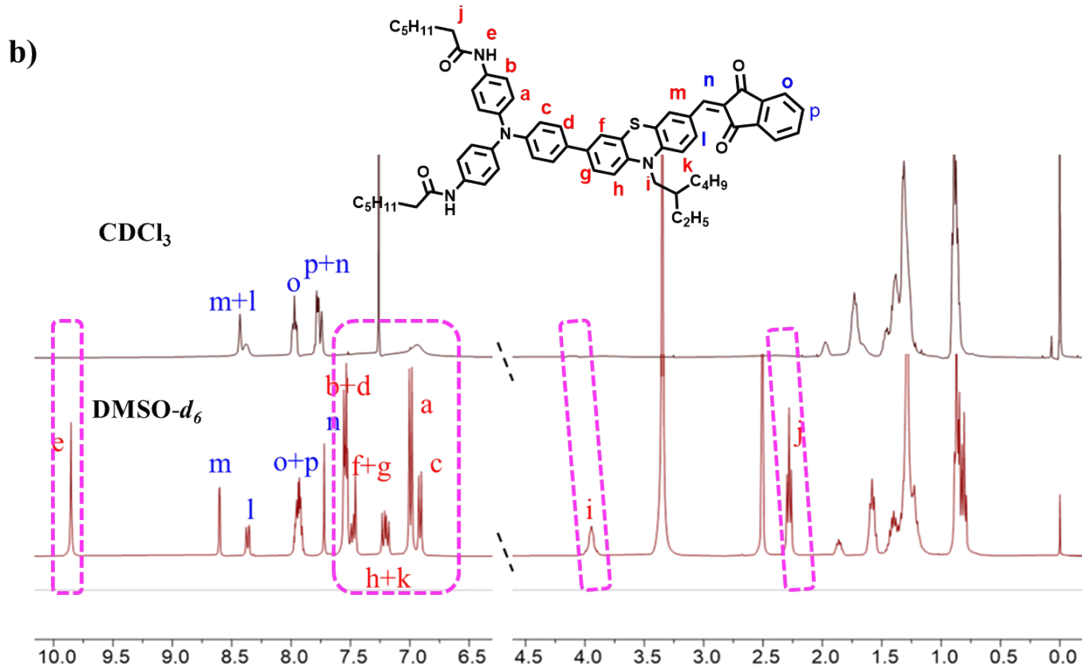


Figure S2. Spectral change after photoirradiation. ^{1}H NMR spectra of (a) **TM1** and (b) **TM4** in $CDCl_3$ after irradiation with visible light, and in DMSO-*d6* after $CDCl_3$ volatilization by heat.

5. DFT Calculation

DFT calculation were performed with Gaussian 09. The alkyl chain groups of TM compounds were replaced by ethyl groups to simplify calculations. The ground-state(S_0) was optimized at the DFT level based on B3LYP/6-311G(d). The T_1 geometry of TM was optimized via spin-unrestricted SCF calculations based on optimized S_0 geometry.

The spin density distributions (SDDs) of TM were obtained in UB3LYP/6-311G* level with $CHCl_3$ polarizable continuum solvation model, and the SDDs of radical cation based on optimized geometry was obtained using the same functional theory level and basis. The visualizations of the frontier molecular orbital and SDDs analyses were using VMD and Multiwfn.[4]

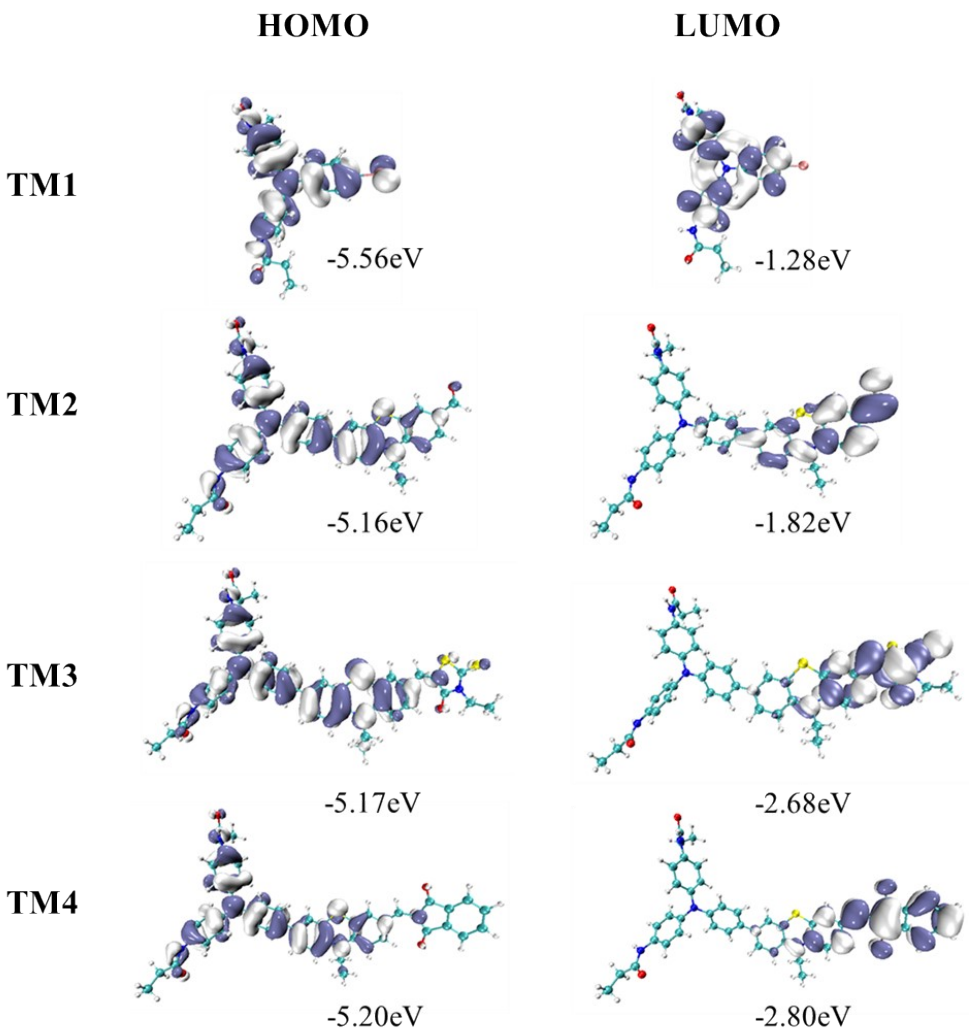


Figure S3. Frontier orbital distribution and energy levels of **TM1-TM4**

6. UV-vis Absorption Spectroscopy

The UV-Vis absorption spectrum was recorded by HITACHI U2910. The initial chloroform solution was prepared in a dark environment, and 365nm LED lamp with a light intensity of 5mW cm^{-2} was used to irradiate the solution (0.1 mM), and the relationship between each irradiation time and absorbance was recorded at room temperature.

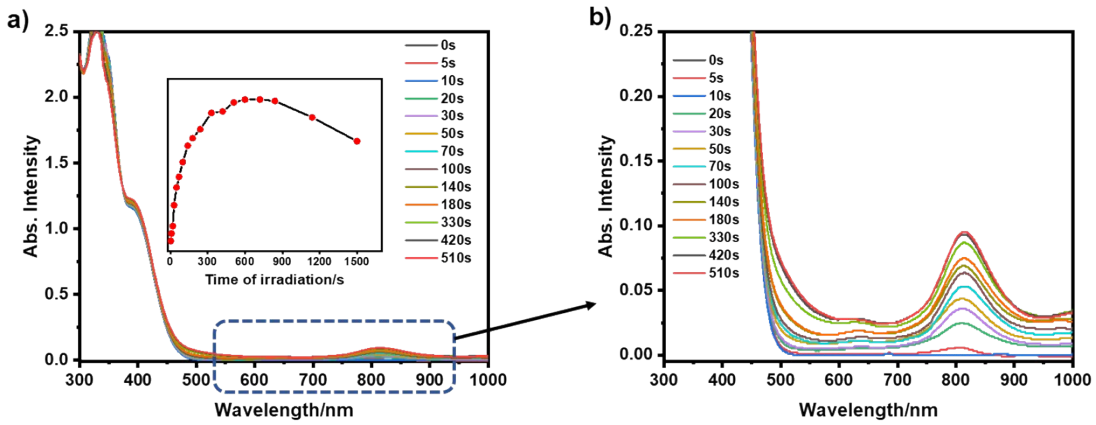


Figure S4. UV−vis spectra obtained as a function of time on irradiation of (a) **TM2** in chloroform solution with 0.1 mM concentration. Inset: the curve of the absorption intensity of **TM2**$^{\bullet+}$ at 815 nm as a function of illumination time.

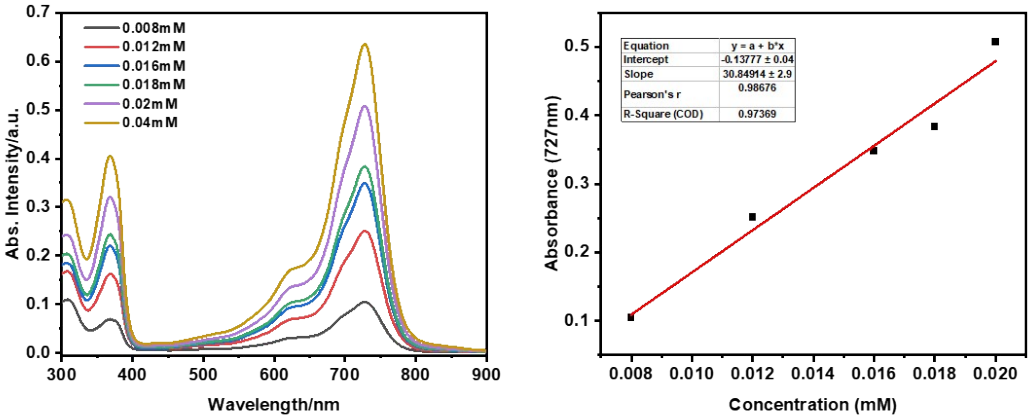


Figure S5. UV-vis spectra of Magic Blue in different concentrations and UV-vis calibration curve of Magic Blue.

7. Circular dichroism spectroscopy

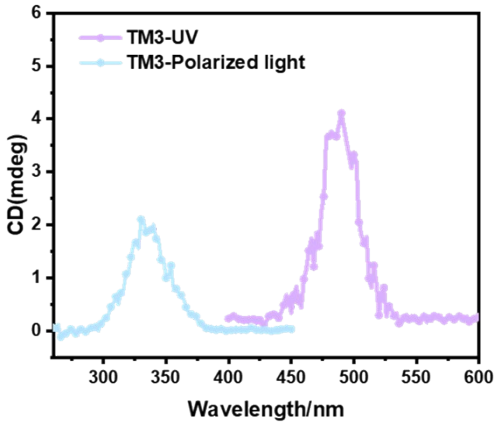


Figure S6. Circular dichroism spectroscopy of **TM3** in $CHCl_3$ solution (1.0 mM) after irradiation with PL and UV.

8. EPR Measurements

EPR measurements were carried out on a Bruker EMX plus equipped with a Bruker X-band microwave bridgehead. All spectra were recorded at room temperature. The 365 nm LEDs is a point source and light intensity is 5mW cm^{-2}. The EPR signal were doubly integrated to obtain the area under the curve. In this calibration, the area of the EPR spectra for varying concentrations of 100 μL Magic Blue solutions in dichloromethane were recorded. Each Magic Blue molecule is considered to have one radical per molecule. This allows for a line of best fit to approximate the number of radicals in a given sample.The chloroform solutions of **TM1-4** were prepared in 1mM and irradiated for 0.5 min, 10 min, 10 min and 6 min, respectively by 365 nm LEDs and tested immediately.

Preparation of film samples: weigh 4.1 mmol **TM1-4** into quartz EPR tube, add 200 microliter chloroform, and control the UV illumination time consistent with the above solution samples. Then, place the EPR tube in a decompression environment, slowly and carefully volatilize the chloroform, and maintain the vacuum state for 30 minutes.

Preparation of powder samples: after the film samples were obtained from other quartz containers, the film was pulverized and the same molar amount of powder was weighed for the EPR tests. All operations above are performed in an air environment.

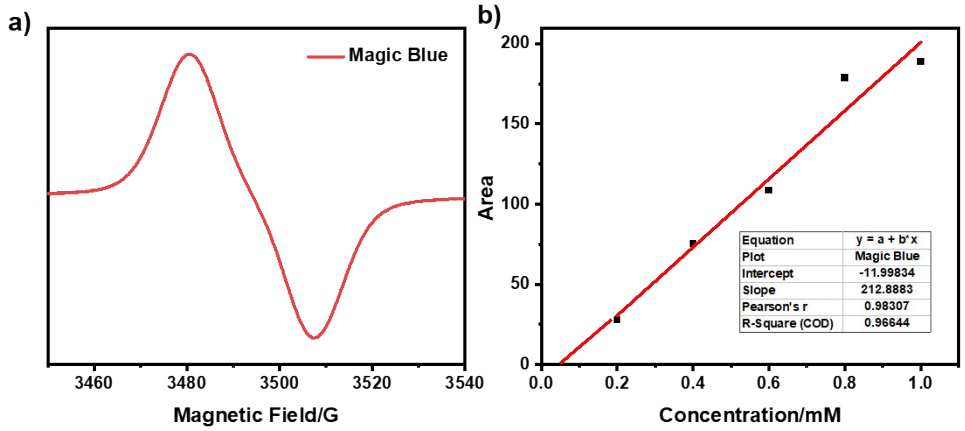


Figure S7. EPR data and radical concentration determination for Magic Blue. (a) EPR spectra for Magic Blue as a 1 mM solution in degassed dichloromethane. (b) Calibration curve for radical concentration determination.

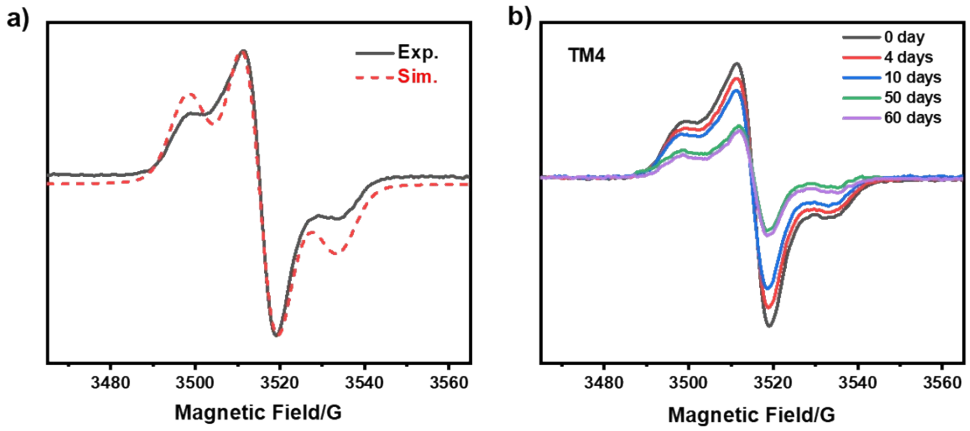


Figure S8. a) EPR spectra and the simulations via EPR simulation programs of **TM4** in film. b) The decay spectrum for **TM4** in the film.

9. Atomic force microscopy (AFM)

Tapping-mode AFM (Bruker INNOVA) was carried out with commercially available tapping mode tips. Sample preparation: all the samples were divided into two groups. Natural light control group: compound **TM1-4** was prepared into 10^{-5} M chloroform solution, which was stirred at room temperature for 2 h to ensure complete dissolution. Then take 50 microliter solution and drop cast on the quartz substrate, naturally volatilized into film; UV light group: the solution of the same concentration

is prepared as above in dark and irradiated by LED point source at illumination intensity of 5mW cm^{-2} with different time (**TM1**: 5 s, **TM2**: 10 min, **TM3**: 10 min, **TM4**: 6 min). Then take 50 microliter solution and drop cast on the quartz substrate, naturally volatilized into film. All the films were fresh prepared and stocked in the dark.

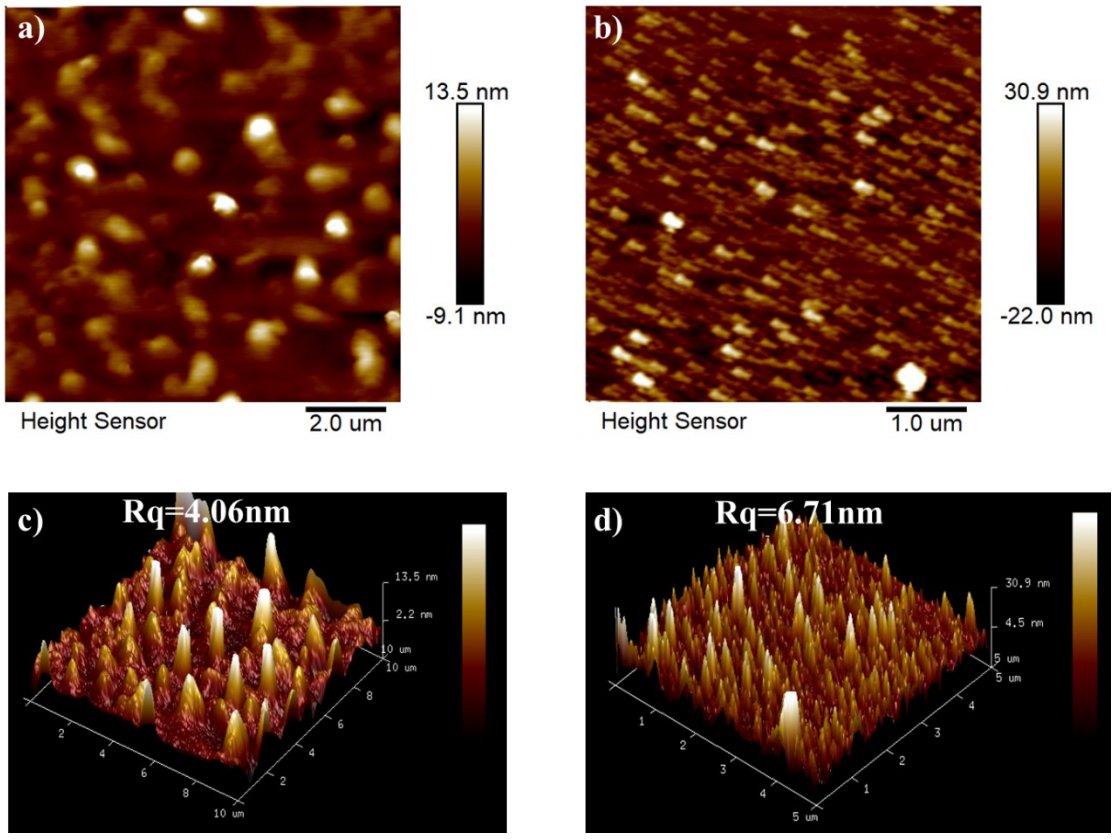


Figure S9. AFM height images and corresponding 3D images of drop-cast films from 10^{-5} M $CHCl_3$ solutions of a, c) **TM3** and b, d) **TM4** after UV irradiation.

10. NMR

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AVII (400 MHz).

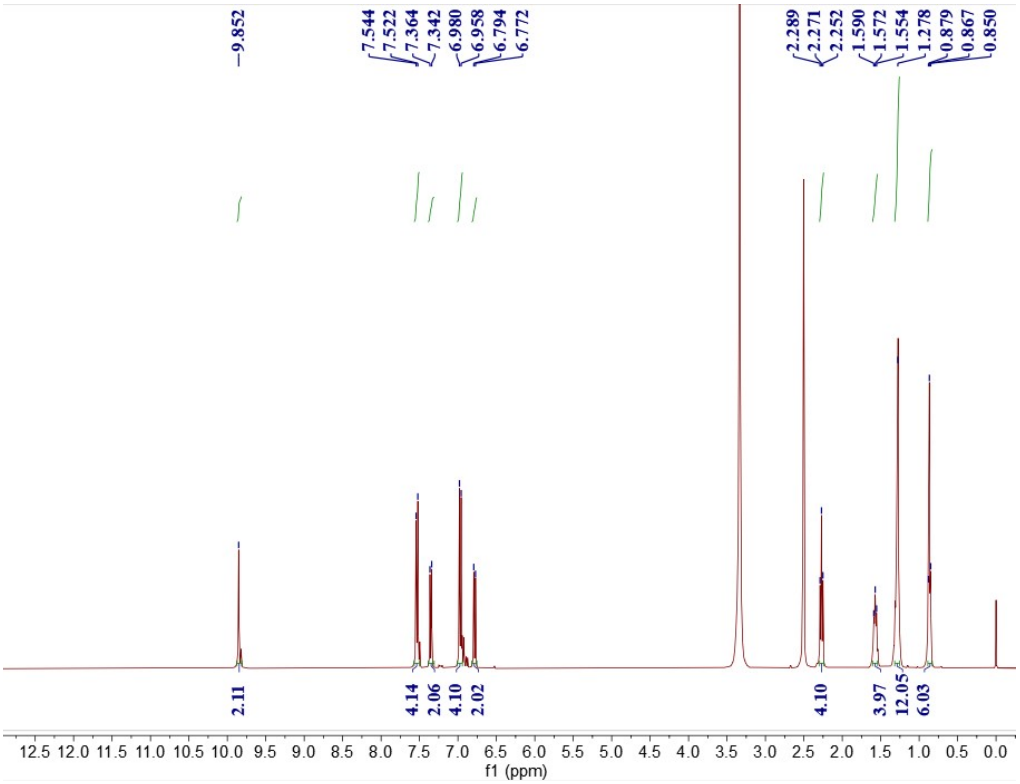


Figure S10. ^{1}H NMR spectrum of **TM1**

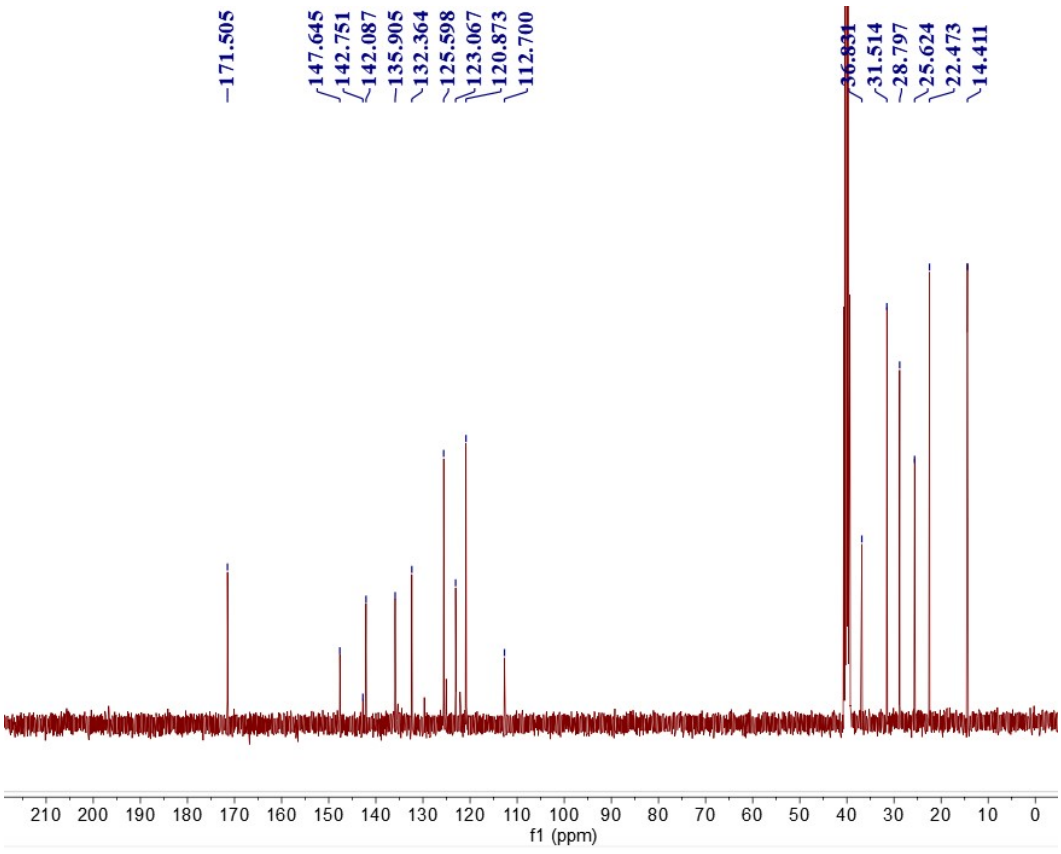


Figure S11. ^{13}C NMR spectrum of **TM1**

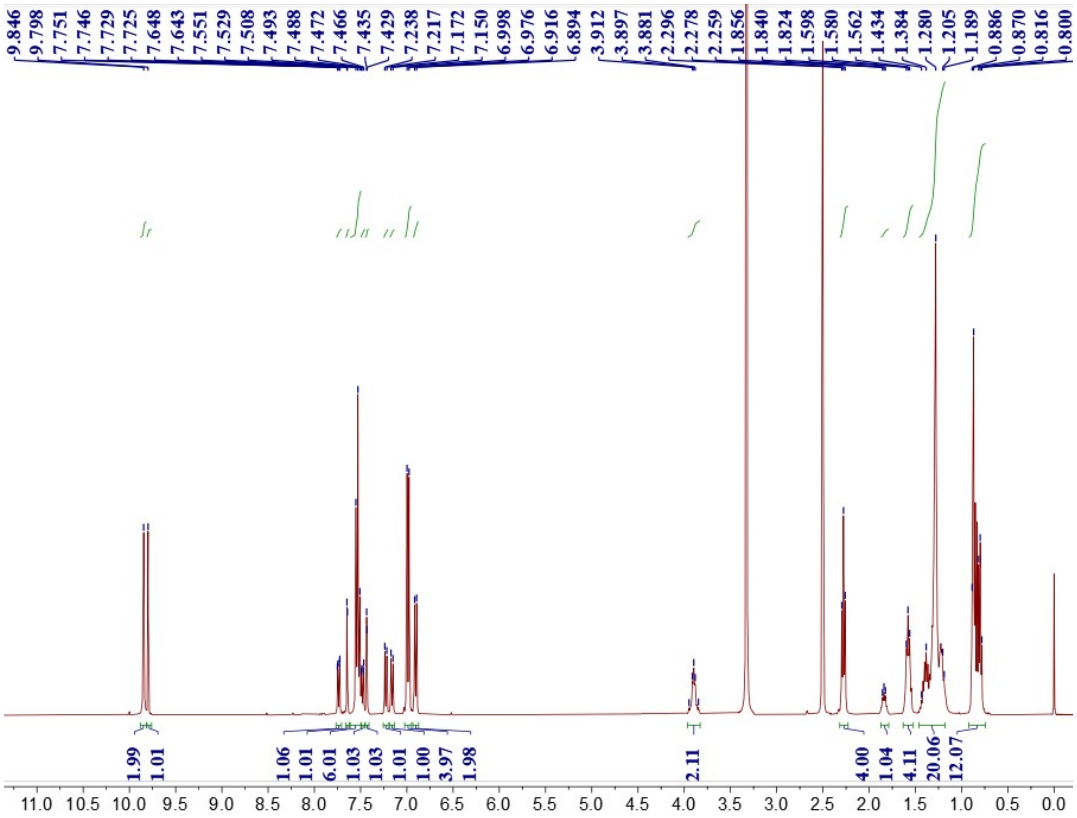


Figure S12. ^{1}H NMR spectrum of **TM2**

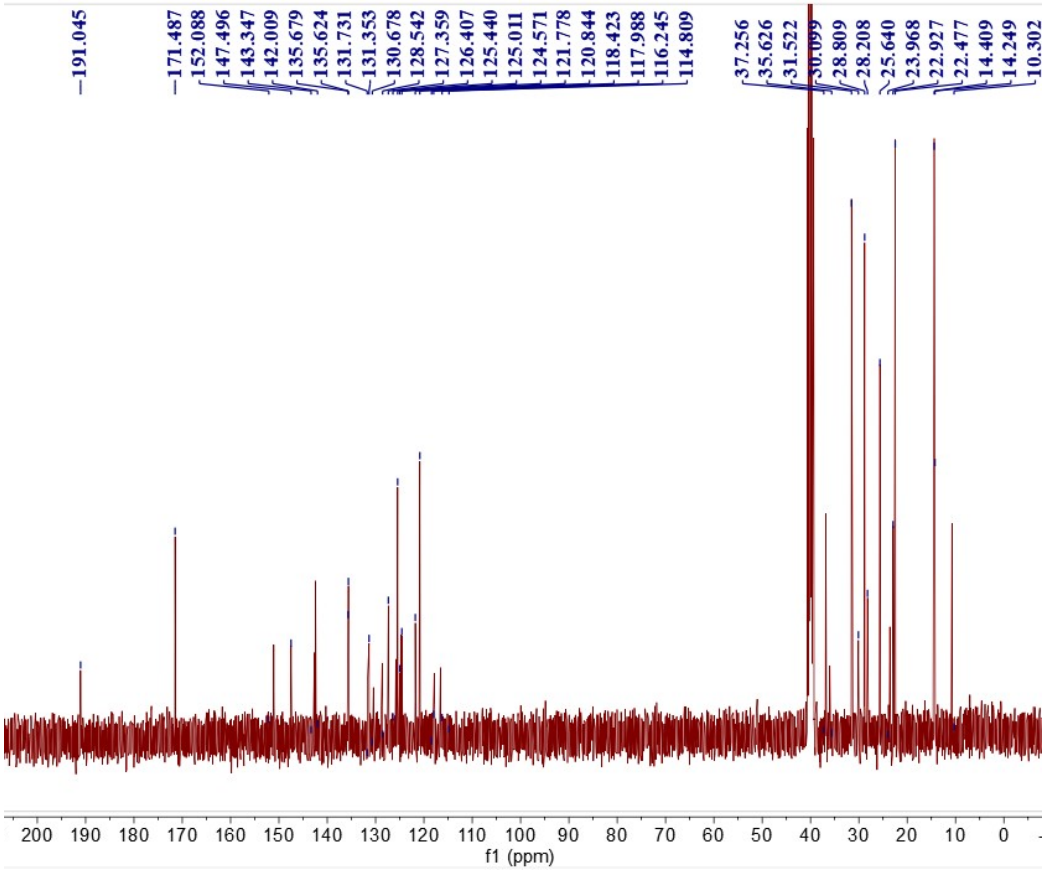


Figure S13. ^{13}C NMR spectrum of **TM2**

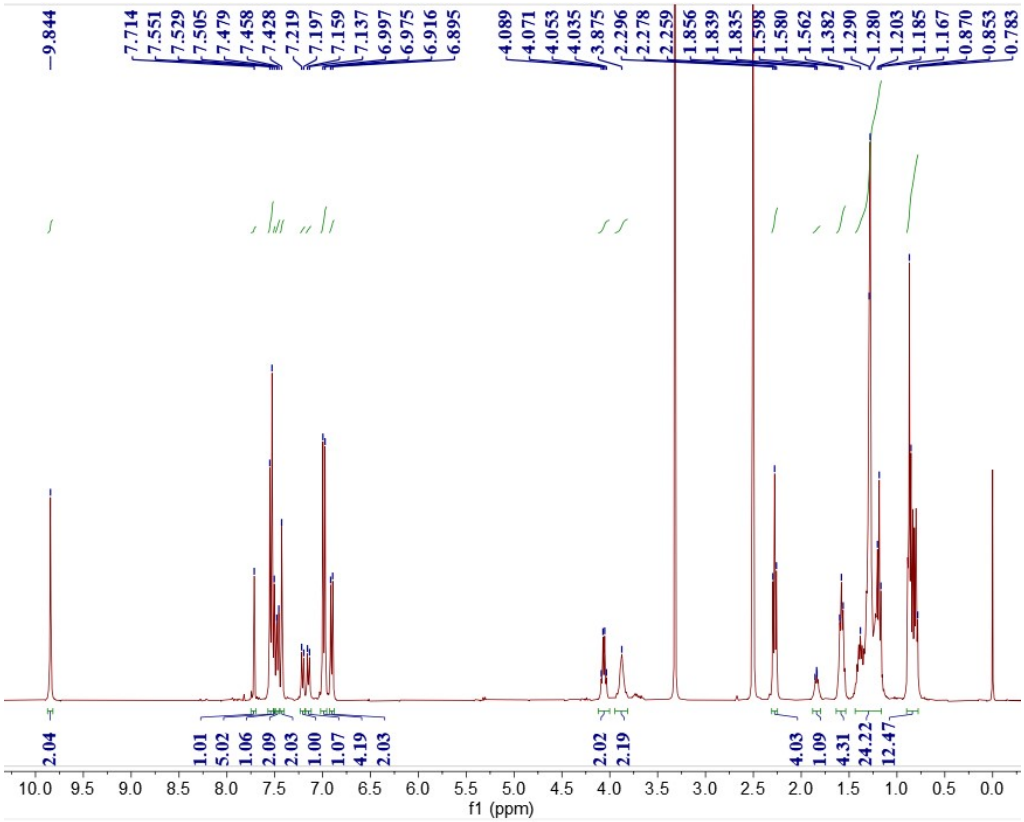


Figure S14. ^{1}H NMR spectrum of **TM3**

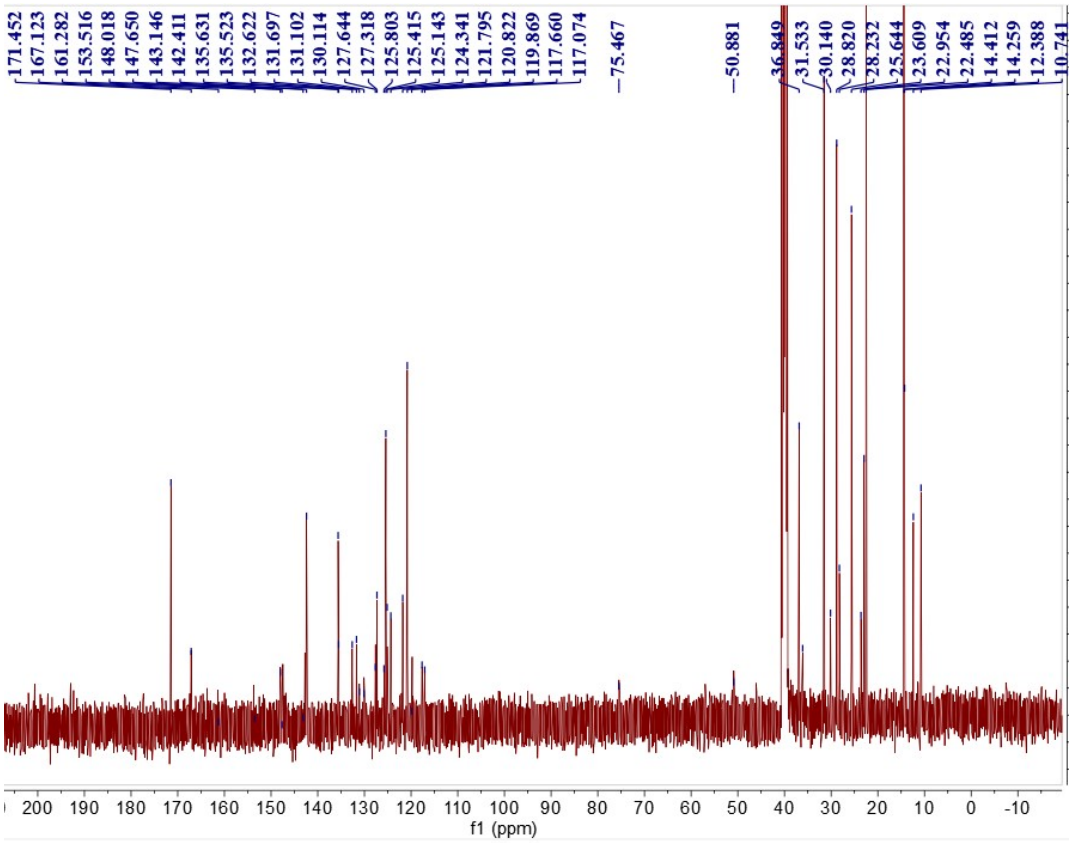


Figure S15. ^{13}C NMR spectrum of **TM3**

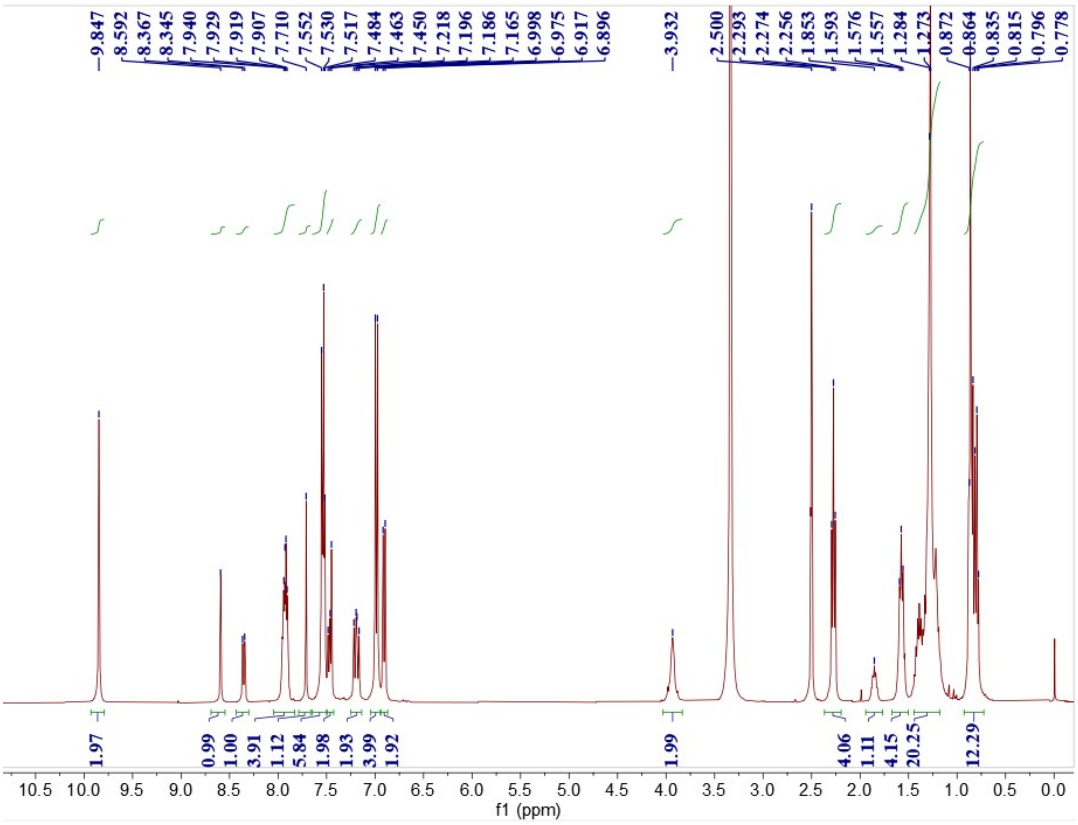


Figure S16. ^{1}H NMR spectrum of **TM4**

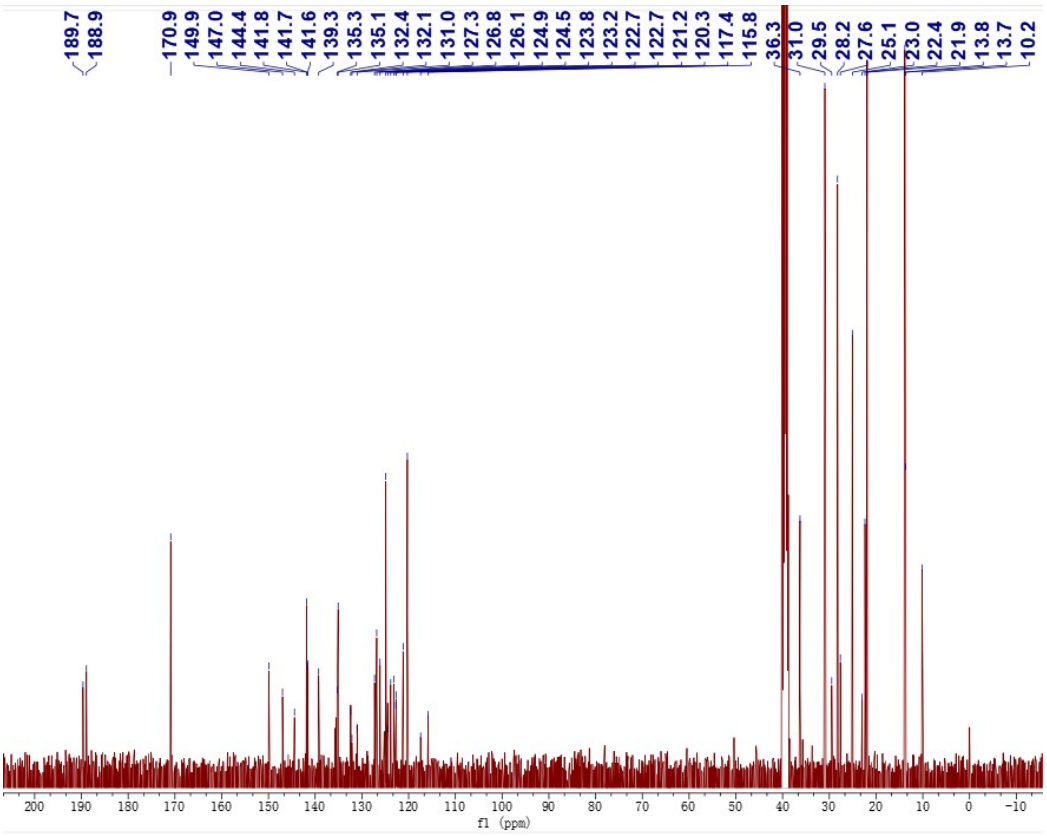


Figure S17. ^{13}C NMR spectrum of **TM4**

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