Electronic Supplementary Information

Hierarchical self-assembly of helical coordination polymers and formation of a lamellar structure *via* the cooperativity of two-step Ag (I) coordination and π-π interactions

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1. General information

N, N-dimethylformamide (DMF), triethylamine (TEA) and dichloromethane (DCM) were dried by distillation after stirring with CaH_2 at room temperature for 3 days. Distilled water was polished by ion exchange and filtration. Tetrahydrofuran (THF) was dried by distillation from sodium–benzophenone prior to use. Other organic reagents were purchased from commercial vendors and used without further purification. Characterization instruments: proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on AVANCE III HD 400MHz. Chemical shifts were reported in ppm relative to the residual solvent peak ($CDCl_3$ = δ 7.26 ppm, DMSO = δ 2.50 ppm for ^{1}H NMR spectrum; $CDCl_3$ = δ 77.16 ppm, DMSO = δ 39.52 ppm for ^{13}C NMR spectrum). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad singlet). ESI-MS AmaZon SL from Bruker, Circular Dichroism (CD) PMS450 from Biologic Company, Ultraviolet-Visible (UV-Vis) Absorption Spectrometry UH4150 and Fluorescence Spectrometers F7000 from Hitachi Company, Scanning Probe Microscopy DimensionIcon and X-ray Single Crystal Diffractometer (XRD) D8 VENTURE and Wide Angle X-ray Powder Diffractometer (WAXRD) D8 Advance from Bruker.

AFM measurement

The sample was prepared by mixing **TEG-DPP** and $AgBF_4$ at the molar ratio of 1:1.5 with the concentration of 5.0 x 10^{-5} mol·L^{-1} in CH_3OH/H_2O for 2 h and 12 h. Then the sample was spin-coated on the surface of the silicon wafer for AFM measurements of helical polymer and lamellar structure, respectively.

2. Figures mentioned in manuscript.

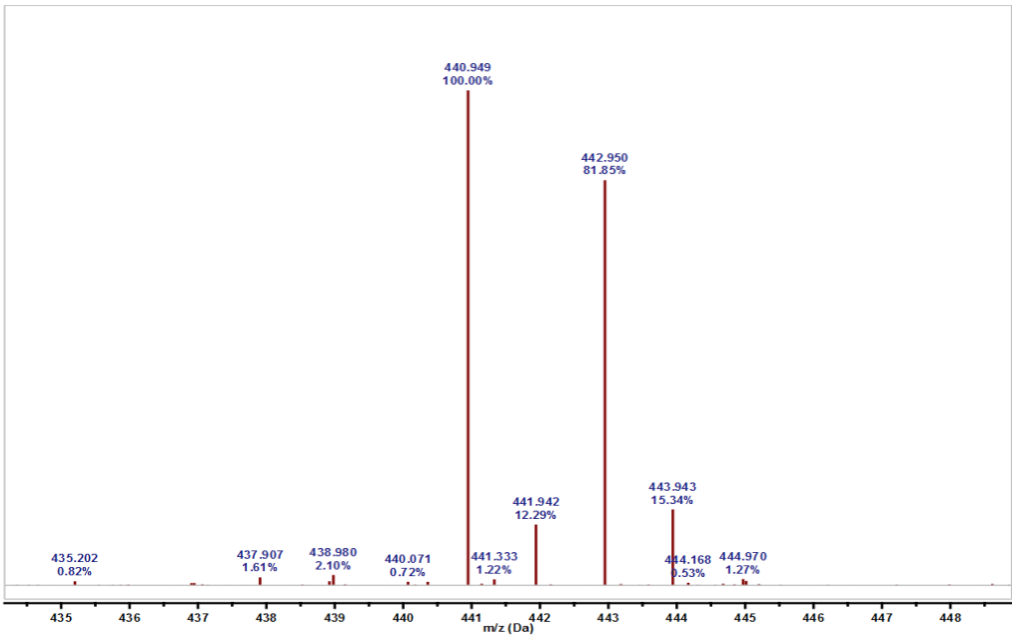


Fig. S1 HR-MS (ESI) spectrum of **DPP** with $AgBF_4$ at the molar ratios of 1:1.

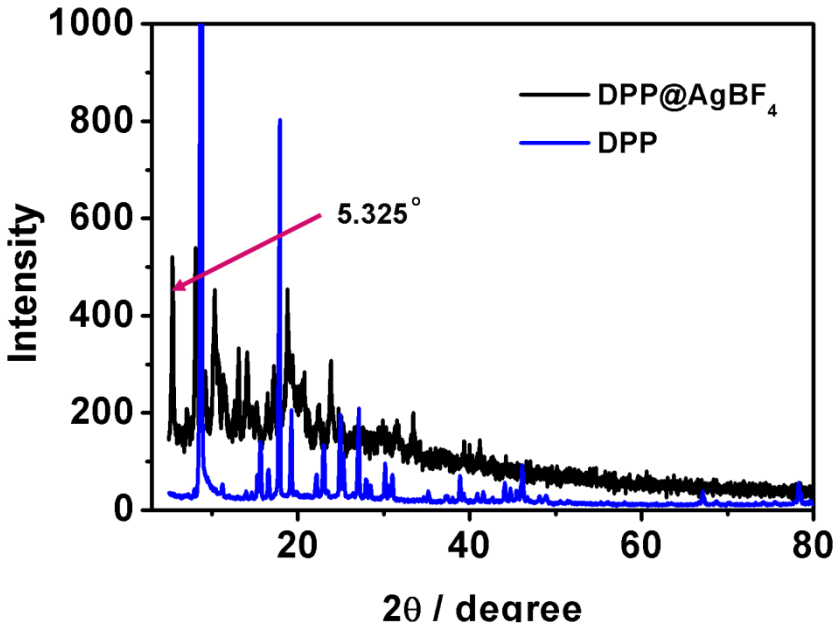


Fig. S2 WAXRD patterns of **DPP** and **DPP** with $AgBF_4$ (1:1.5). The d spacing of 1.66 nm corresponding to the peak of 5.325° was calculated by Bragg equation $2d\sin\theta = n\lambda$ (λ = 0.15418 nm).

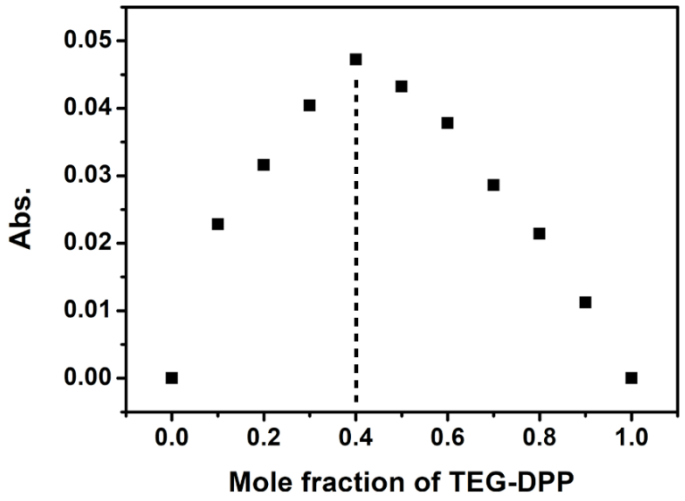


Fig. S3 Job's plot of **TEG-DPP** with Ag^+ from UV-Vis titration experiments.

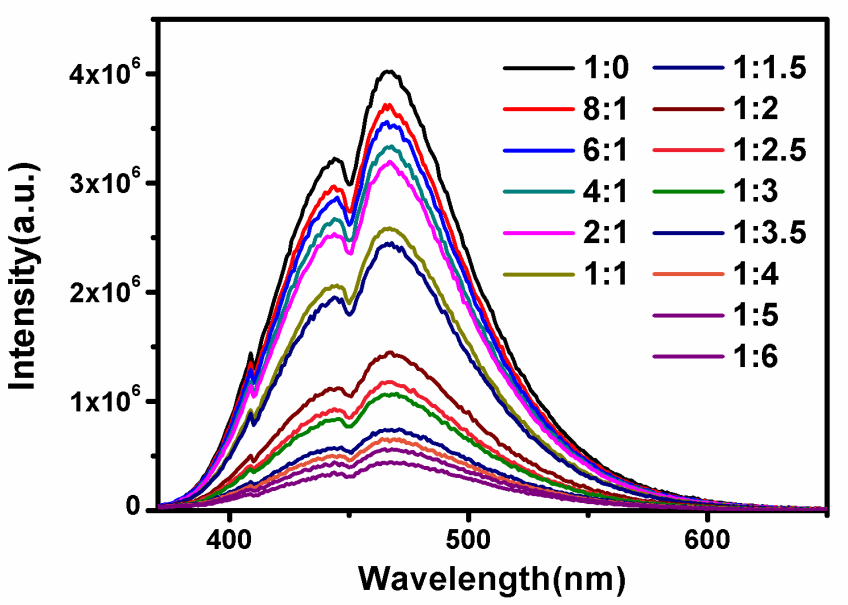


Fig. S4 Fluorescence spectra of **TEG-DPP** with Ag^+ at different ratios from 1:0 to 1:5 in CH_3CN.

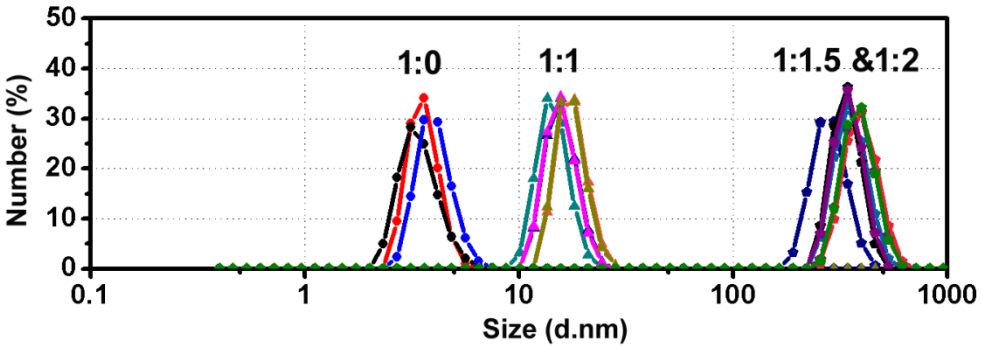


Fig. S5 Dynamic light scattering (DLS) profiles of **TEG-DPP** with 0, 1.0, 1.5, 2.0 equiv. of Ag^+ in CH_3CN at 25℃.

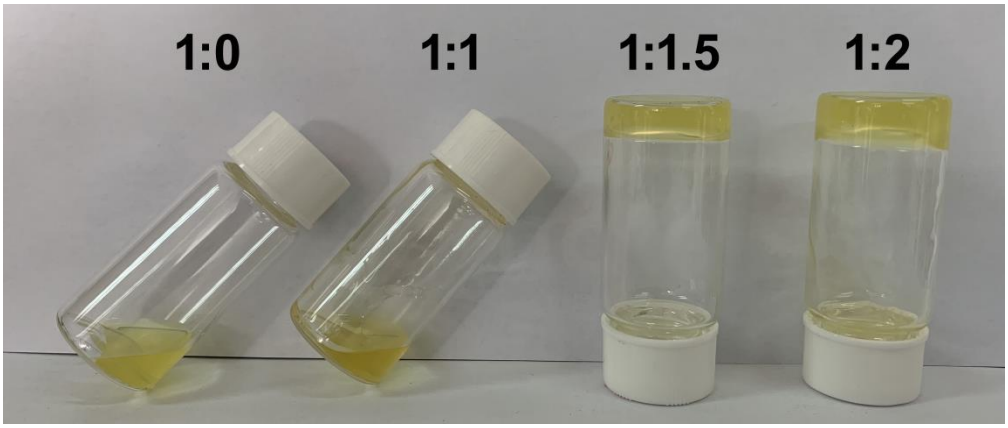


Fig. S6 The solution states of **TEG-DPP** with 0, 1.0, 1.5, 2.0 equiv. of Ag^+ in CH_3CN at 25℃.

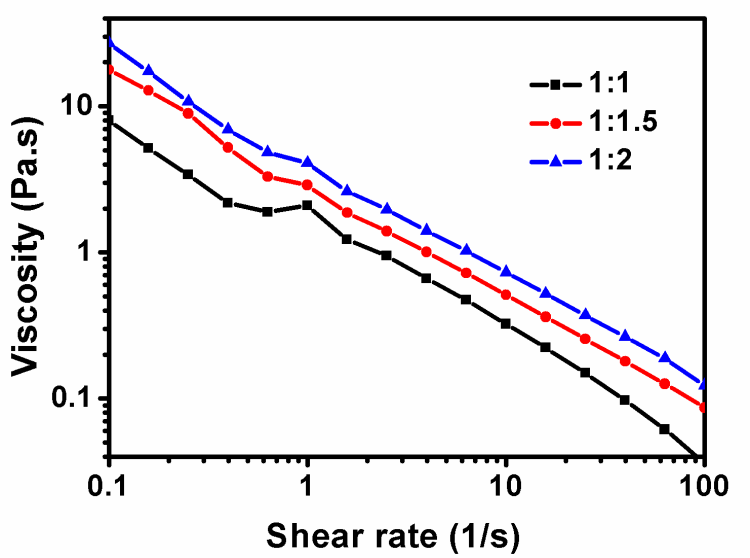


Fig. S7 Viscosities of **TEG-DPP** with 1.0, 1.5, 2.0 equiv. of Ag^+ in CH_3CN at 25℃.

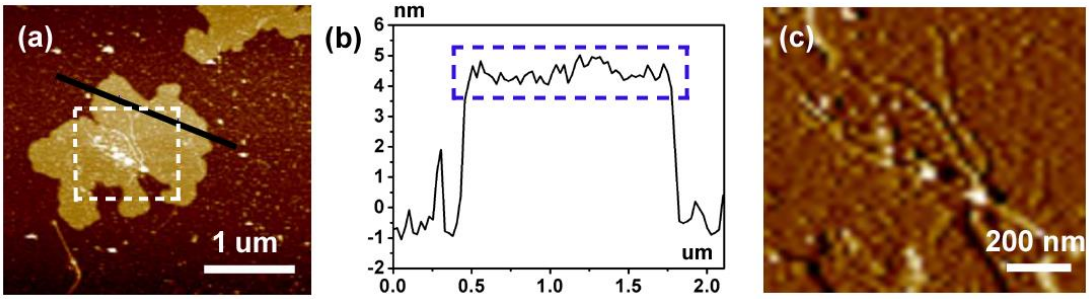


Fig. S8 (a) AFM image of lamellar assemblies formed by helical coordination polymers. (b) The height profile along the black line in a. (c) Partial enlarged AFM phase image from the white dashed block in a.

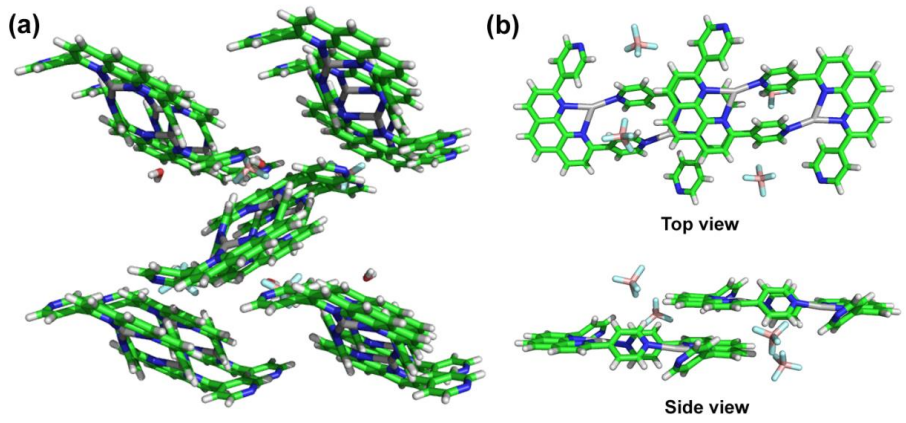


Fig. S9 (a) Packing model of the crystal structure of $[Ag_2(\mathbf{DPP})_2(BF_4)_2]$. The antiparallel arrangement of $[Ag_2(\mathbf{DPP})_2(BF_4)_2]$ in pairs based on the π-π interaction. (b) Top view and side view of the coupled $[Ag_2(\mathbf{DPP})_2(BF_4)_2]$ with a vertical distance of about 0.35 nm in a.

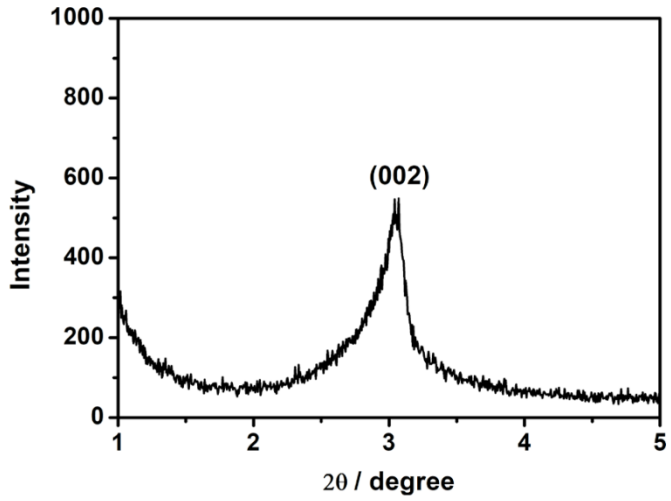


Fig. S10 SAXRD pattern of **TEG-DPP** with $AgBF_4$ (1:1.5). The d spacing of 5.80 nm corresponding to the peak of 3.04 ° was calculated by Bragg equation 2dsinθ= nλ (λ = 0.15418 nm).

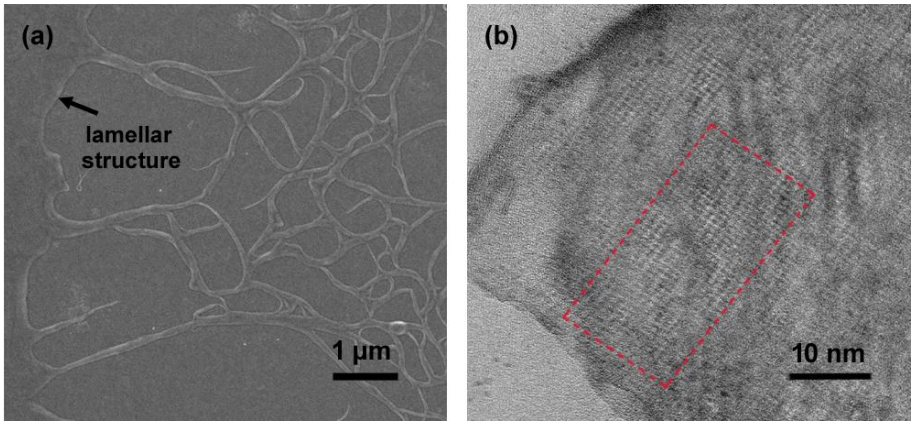
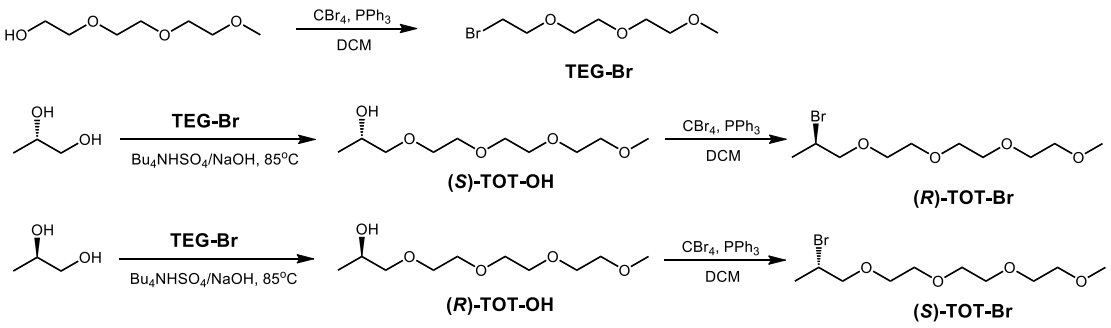


Fig. S11 SEM (a) and HR-TEM (b) images of the assemblies involving helical coordination polymers and lamellar structures.

3. Synthesis and characterization of target molecules

Scheme S1. Synthetic procedures of side chains.



Synthesis of 1-(2-(2-methoxyethoxy)ethoxy)-2-bromoethane (TEG-Br)

TEG-Br was prepared according to the Apple reaction.[S1] Under the protection of an anhydrous nitrogen atmosphere, 4.92 g triethylene glycol monomethyl ether (30 mmol) and 12 g carbon tetrabromide (36 mmol) were added to 150 mL dry CH_2Cl_2 in a well dried two-neck flask equipped with a dropping funnel containing a solution of 11.7 g (45 mmol) triphenyl phosphine in 30 mL dry CH_2Cl_2. The reaction mixture was cooled to 0 °C and stirred for 30 min. Then, the solution of triphenyl phosphine was slowly added to the reaction mixture keeping the temperature of the mixture at 0 °C. After stirring for 5 h at room temperature, the solvent was evaporated out. 200 mL diethyl ether was added to the residue and sonicated at room temperature for 15 minutes, kept for 5 min and filtered. The same process (addition of diethyl ether to filter cake and filtration) was repeated until without product residues in filter cake. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuum. The pure **TEG-Br** was then obtained by flash chromatography (SiO_2) eluting with Petroleum ether/ethyl acetate (2:1, vol/vol) in 82.3% yield. The spectral data for **TEG-Br** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (t, *J* = 6.3 Hz, 2H), 3.75-3.62 (m, 6H), 3.56 (dd, *J* = 5.4, 3.3 Hz, 2H), 3.48 (t, *J* = 6.3 Hz, 2H), 3.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 71.88 (s), 71.15 (s), 70.54 (s), 70.52 (s), 70.48 (s), 58.91 (s), 30.18 (s). MS (ESI): Calculated for $C_7H_{15}BrO_3$ $[M+Na]^+$:249.01, Found:$[M+Na]^+$:249.02.

Synthesis of (*R*)-TOT-OH and (*S*)-TOT-OH[S2]

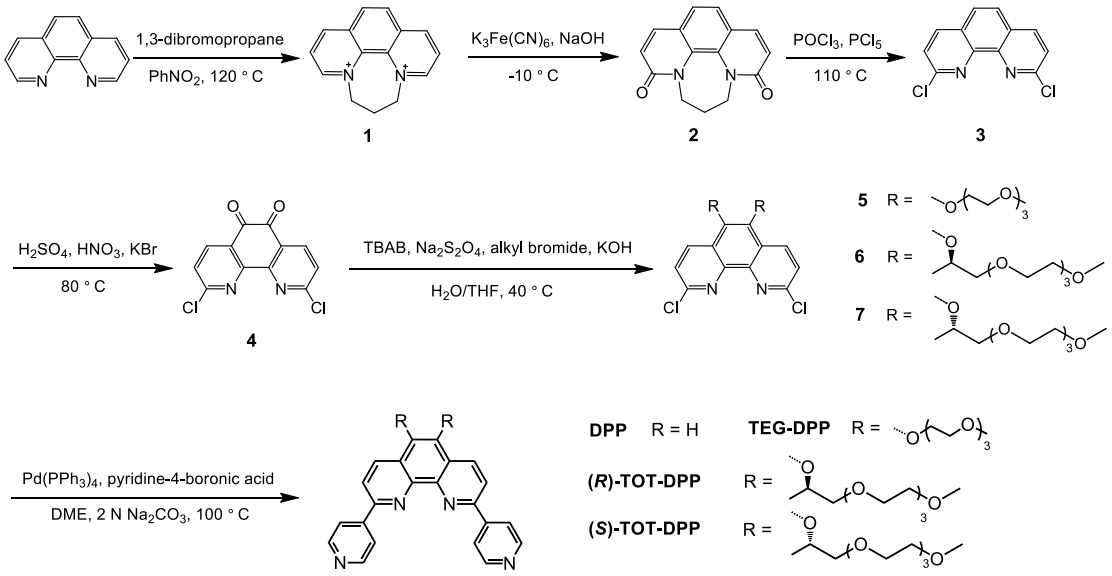
A mixture of 0.5 mol (*S* or *R*)-propane-1,2-diol, 0.1 mol **TEG-Br**, 150 mL 50% aqueous (aq.) NaOH, and 0.01 mol tetrabutylammonium hydrogensulfate was stirred and heated for 3 h at 85 ^{O}C. After cooling, 100 mL hexane and 500 mL water was added. The layers have been separated, the organic layer has been washed three times with 20 mL water and dried with anhydrous $MgSO_4$. The product has been distilled and 1-butoxy-2-propanol was obtained in 80% yield. The oil was used without further purification. The spectral data for (*R* or *S*)-**TOT-OH** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ

4.25-4.11 (m, 1H), 3.73-3.52 (m, 14H), 3.38 (s, 3H), 1.69 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 77.04 (s), 74.63 (d, *J* = 20.6 Hz), 71.75 (s), 70.75-69.88 (m), 68.25 (s), 65.42 (s), 58.51 (s), 20.75 (s), 17.61 (s). MS (ESI): Calculated for $C_{10}H_{22}O_5$ $[M+H]^+$: 223.15, $[M+Na]^+$: 245.14, Found: $[M+H]^+$:222.91, $[M+Na]^+$:244.91.

Synthesis of (*R*)-TOT-Br and (*S*)-TOT-Br

This compound was prepared analogously to **TEG-Br** from (*R* or *S*)-**TOT-OH**. The spectral data for (*R* or *S*)-**TOT-Br** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.18 (dd, *J* = 13.2, 6.4 Hz, 1H), 3.77-3.51 (m, 14H), 3.39 (s, 3H), 1.69 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 76.31 (s), 71.76 (s), 70.31 (s), 70.26 (s), 70.07 (s), 58.38 (d, *J* = 35.4 Hz), 49.17 (s), 22.84 (s). MS (ESI): Calculated for $C_{10}H_{21}BrO_4$ $[M+Na]^+$: 308.16, Found: $[M+Na]^+$: 308.82.

Scheme S2. Synthetic procedures of **DPP**, **TEG-DPP**, **(*R*)-TOT-DPP** and **(*S*)-TOT-DPP**.



Synthesis of compound 1, 2, 3 and 4.

The compounds **1**, **2**, **3** and **4** were synthesized according to the previously reported methods. [S3]

Synthesis of compound 5

Add 1.00 g compound **4** (3.62mmol), 0.76 g tetra-n-butylammonium bromide (2.34 mmol) and 3.78 g sodium dithionite (21.66 mmol) to a mixed solvent of 20 mL water and 20 mL THF at room temperature. Then, 2.73 g (12.00 mmol) **TEG-Br** was slowly added to the mixture. Subsequently, after a solution of 3.00 g (54.14 mmol) of potassium hydroxide in 20.0 ml water was added, the reaction mixture gradually turned black. The reaction mixture was stirred for 72 hour at 40 °C. After dilution with water, the reaction mixture was extracted with ethyl acetate. The crude product was purified by

column chromatographyeluting with DCM/ethyl acetate (50:1, vol/vol) to yield 1.19 g (2.07 mmol) of compound **9** in 57 % as a white powder.The spectral data for compound **5** are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.6 Hz, 2H), 7.58 (dd, *J* = 8.6, 4.3 Hz, 2H), 4.40-4.35 (m, 4H), 3.77-3.71 (m, 4H), 3.61-3.55 (m, 12H), 3.48 (dd, *J* = 5.7, 3.5 Hz, 4H), 3.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.94 (s), 142.58 (s), 142.23 (s), 134.26 (s), 125.59 (s), 124.65 (s), 72.85 (s), 71.93 (s), 70.67 (s), 70.62 (s), 70.57 (s), 70.14 (s), 59.00 (s). MS (ESI): Calculated for $C_{26}H_{34}Cl_2N_2O_8$ $[M+H]^+$: 573.16, $[M+Na]^+$: 596.16, Found: $[M+H]^+$: 573.35, $[M+Na]^+$:596.36.

Synthesis of compound 6 and 7

These two compounds were prepared analogously to compound **5** from (*R*)-**TOT-Br** and (*S*)-**TOT-Br**, respectively. The spectral data for **6 or 7** are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.66 (m, 2H), 7.68-7.56 (m, 2H), 4.83 (dd, *J* = 9.5, 5.5 Hz, 2H), 3.69-3.48 (m, 28H), 3.37 (d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 6.4 Hz, 4H), 1.36-1.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.87 (s), 142.69 (s), 141.50 (s), 134.68 (s), 126.42 (s), 124.53 (s), 78.18 (s), 74.21 (s), 71.93 (s), 70.74 (s), 70.63 (s), 70.52 (s), 59.04 (s), 17.28 (s). MS (ESI): Calculated for $C_{32}H_{46}Cl_2N_2O_{10}$ $[M+H]^+$: 689.26, $[M+Na]^+$: 711.24, $[M+K]^+$: 727.22, Found: $[M+H]^+$: 689.22, $[M+Na]^+$: 711.20, $[M+K]^+$: 727.19.

Synthesis of DPP

A Schlenck flask was charged with compound **3** (1.00g, 4 mmol), pyridine-4-boronic acid (1.08 g, 8.8 mmol), $Pd(PPh_3)_4$ (464 mg, 0.4 mmol). The mixture was degassed by four vacuum-pure nitrogen cycles and a mixed solvent of 20 mL freshly distilled and degassed dimethoxyethane and 20 mL degassed aqueous solution of 2 mol L^{-1} $Na_2CO_3$was added. The mixture was heated at reflux for 12 h. The solvents were evaporated under reduced pressure and the crude product was dispersed in CH_2Cl_2 and washed with water (3x 50 mL). The combined organic layer was dried over Na_2SO_4 and then dried under vacuum. The resulting material was purified by flash column chromatograhy on silica eluted with CH_2Cl_2/MeOH (50:1, vol/vol) to yield 1.12g of **DPP** in 84% as a white solid. The spectral data for **DPP** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, *J* = 5.9 Hz, 2H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 6.0 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.19 (s), 150.57 (s), 146.29 (s), 146.15 (s), 137.37 (s), 128.91 (s), 126.91 (s), 121.58 (s), 120.17 (s). MS (ESI): Calculated for $C_{22}H_{14}N_4$ $[M+H]^+$: 335.12, Found:$[M+H]^+$: 334.93

Synthesis of TEG-DPP

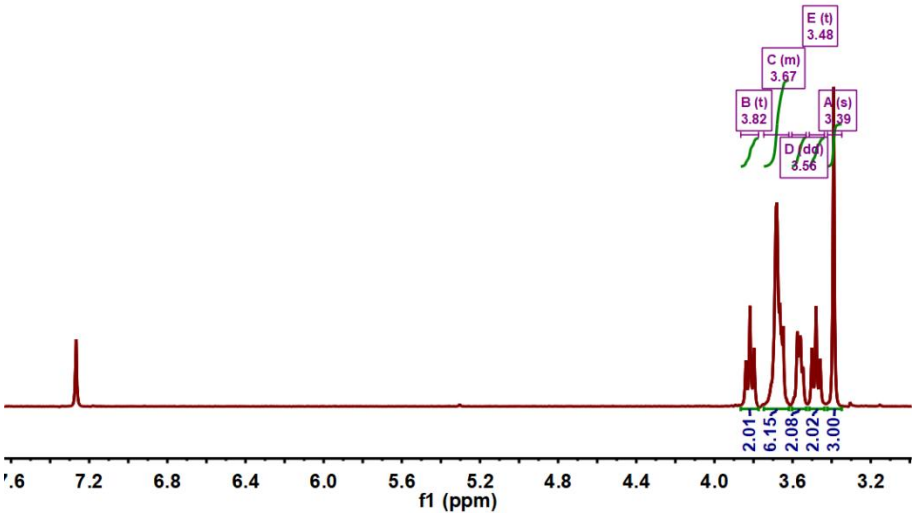
This compound was prepared analogously to compound **DPP** from compound **5**. The spectral data for **TEG-DPP** are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (t, *J* = 6.8 Hz, 2H), 8.79 (dd, *J* = 4.6, 1.5 Hz, 4H), 8.26 (dd, *J* = 4.6, 1.5 Hz, 4H),

8.17 (d, *J* = 8.6 Hz, 2H), 4.49-4.42 (m, 4H), 3.83-3.78 (m, 4H), 3.65-3.59 (m, 12H), 3.50 (dd, *J* = 5.7, 3.6 Hz, 4H), 3.32-3.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.19 (s), 150.42 (s), 146.45 (s), 144.20 (s), 142.54 (s), 132.55 (s), 126.72 (s), 121.57 (s), 120.24 (s), 72.80 (s), 71.94 (s), 70.67 (s), 70.60 (s), 70.57 (s), 70.25 (s), 58.98 (s). MS (ESI): Calculated for $C_{36}H_{42}N_4O_8$ $[M+H]^+$: 659.30, $[M+Na]^+$: 681.29, Found:$[M+H]^+$: 659.50, $[M+Na]^+$: 681.47.

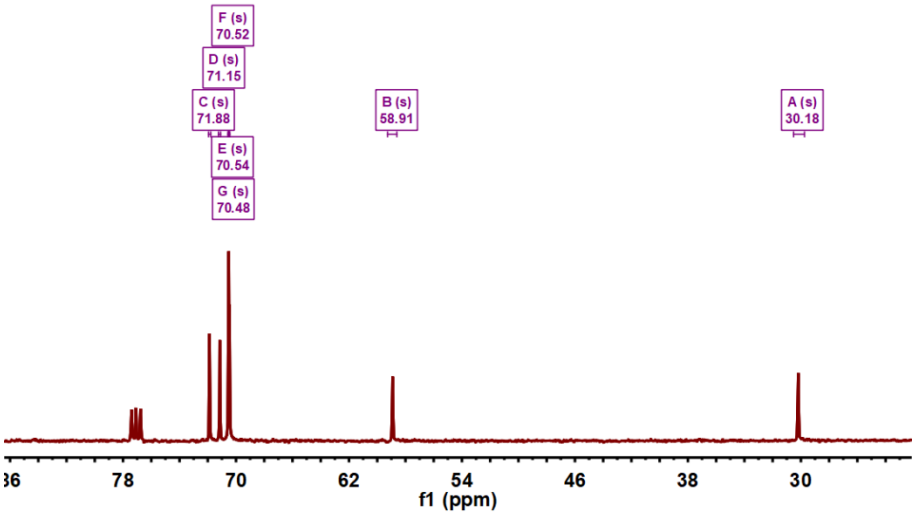
Synthesis of compound (*R or S*)-TOT-DPP

This compound was prepared analogously to **DPP** from compound **6**. The spectral data for (*R or S*)-**TOT-DPP** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.6 Hz, 2H), 8.87 (d, *J* = 6.0 Hz, 4H), 8.33 (d, *J* = 6.1 Hz, 4H), 8.22 (d, *J* = 8.6 Hz, 2H), 4.94 (dd, *J* = 9.8, 5.2 Hz, 2H), 3.66-3.49 (m, 28H), 3.34 (s, 6H), 1.48-1.36 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.03 (s), 149.56 (s), 145.37 (s), 143.14 (s), 140.72 (s), 131.91 (s), 126.57 (s), 120.52 (s), 119.02 (s), 76.94 (s), 73.41 (s), 70.89 (s), 69.77 (s), 69.59 (s), 69.54 (s), 69.48 (s), 57.99 (s), 16.30 (s). Calculated for $C_{42}H_{54}N_4O_{10}$ $[M+H]^+$: 775.39, $[M+Na]^+$: 797.37, $[M+K]^+$: 813.35, Found: $[M+H]^+$: 775.36, $[M+Na]^+$: 797.36, $[M+K]^+$: 813.34.

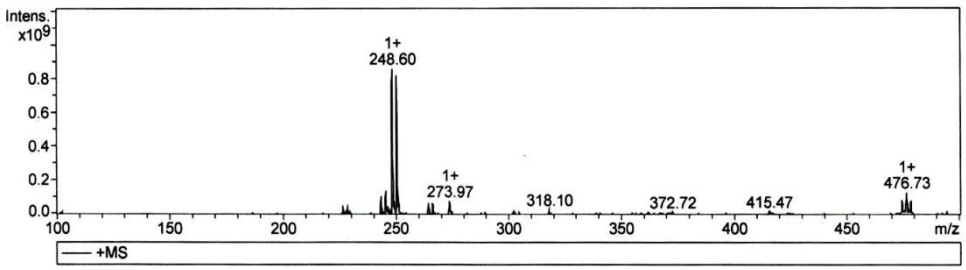
4. ^{1}H NMR, ^{13}C NMR and HR-MS (ESI) spectra of synthetic compounds



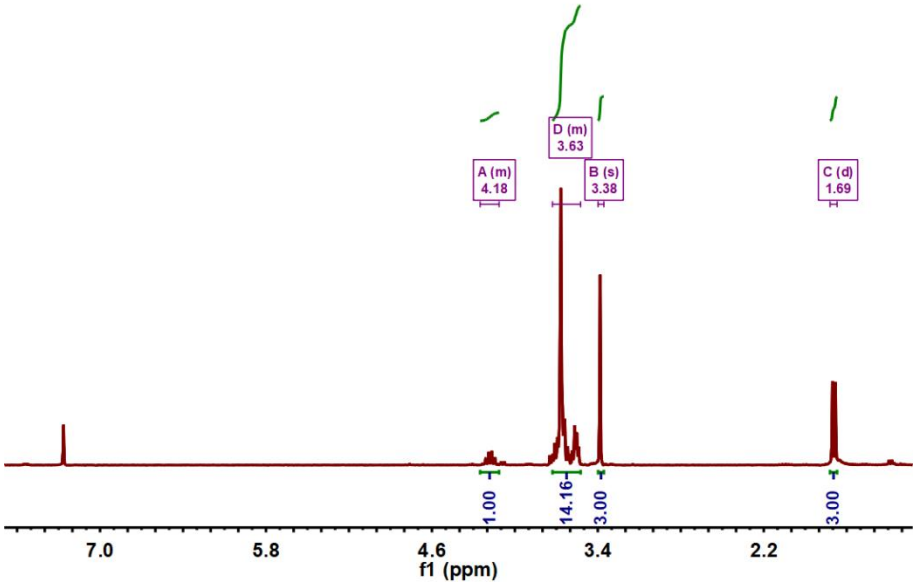
^{1}H NMR spectrum of **TEG-Br** in $CDCl_3$.



^{13}C NMR spectrum of **TEG-Br** in $CDCl_3$.



MS spectrum of **TEG-Br**.



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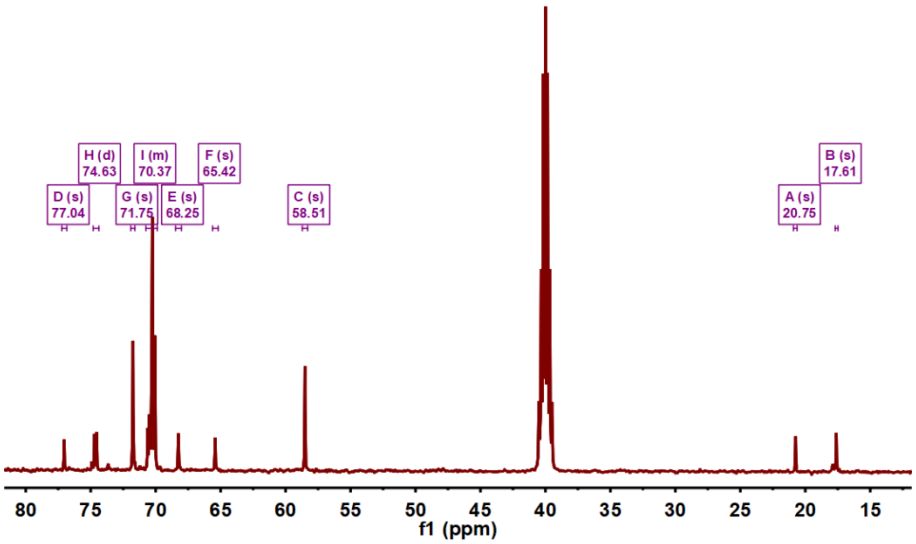
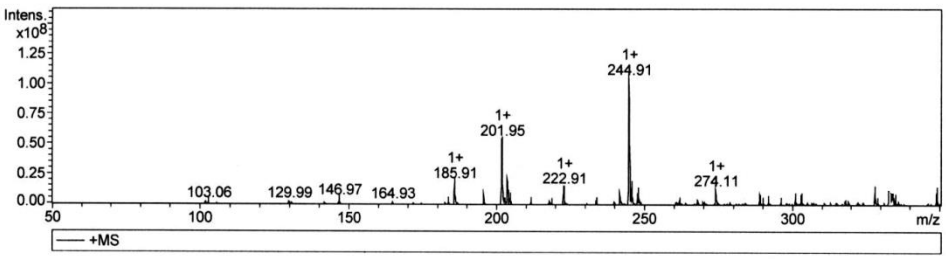
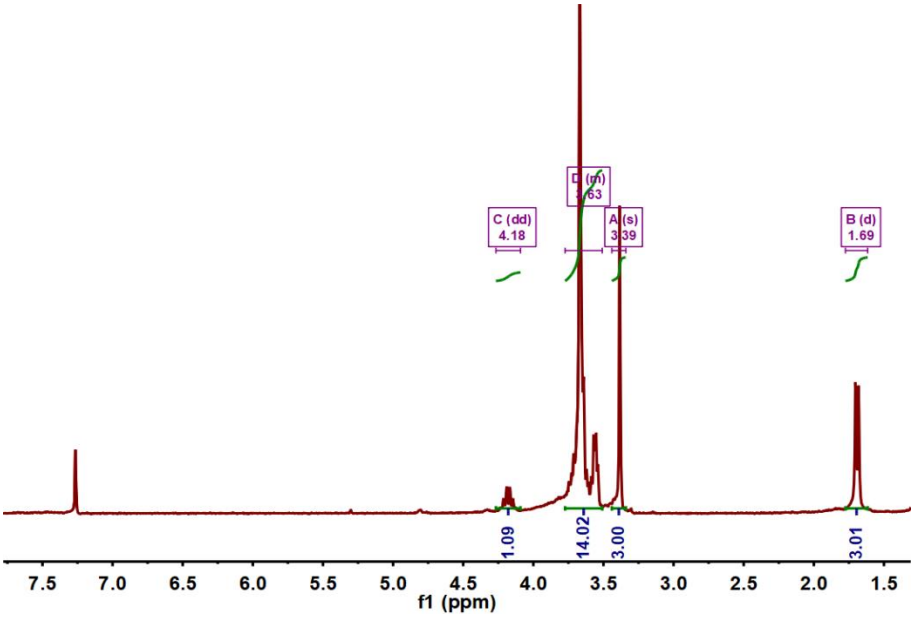


^{13}C NMR spectrum of (*R* and *S*)-**TOT-OH** in DMSO.



MS spectrum of (*R* and *S*)-**TOT-OH**.



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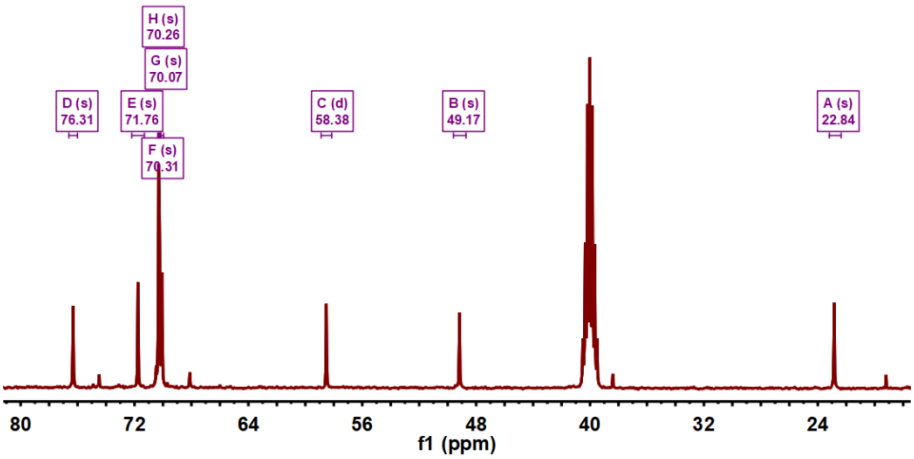

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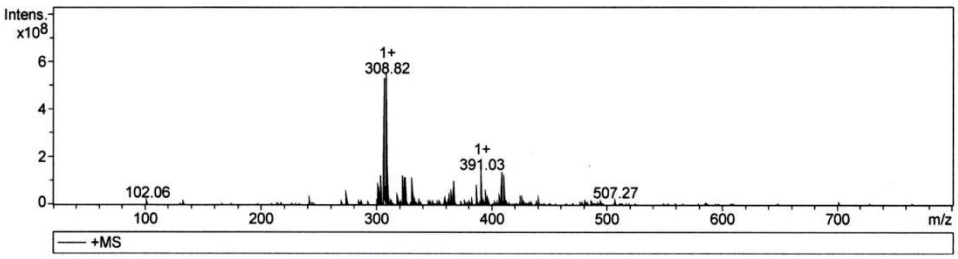
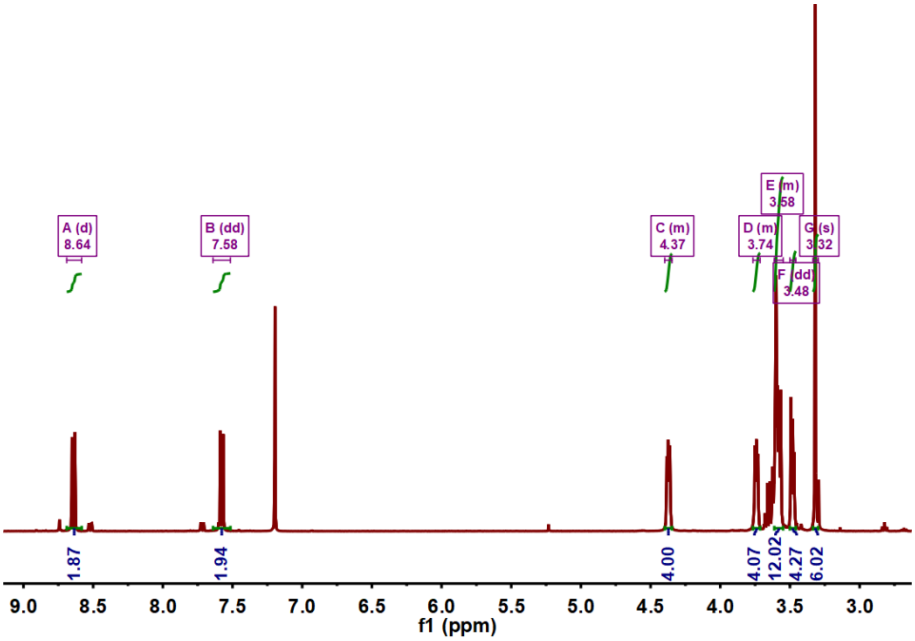
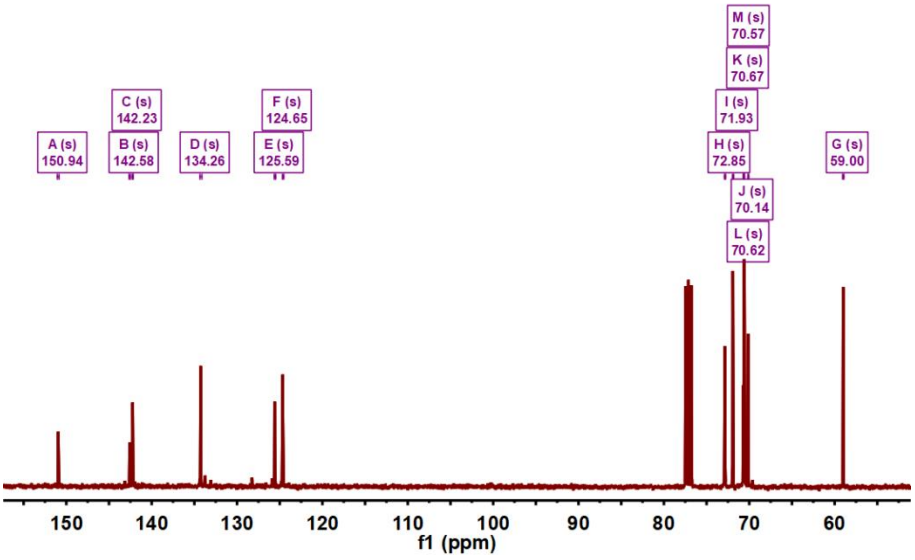


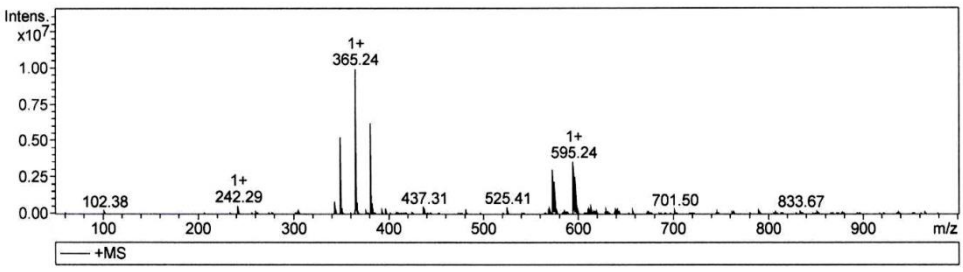
MS spectrum of (*R* and *S*)-**TOT-Br**.



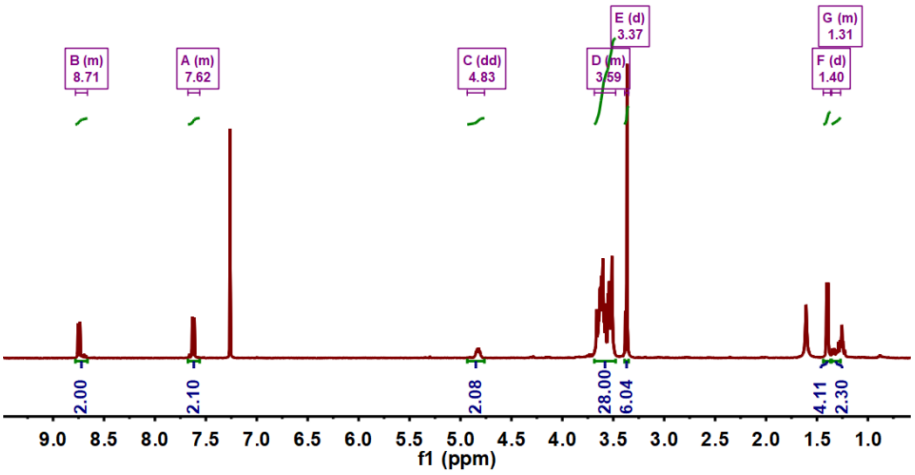
^{1}H NMR spectrum of compound **5** in $CDCl_3$.



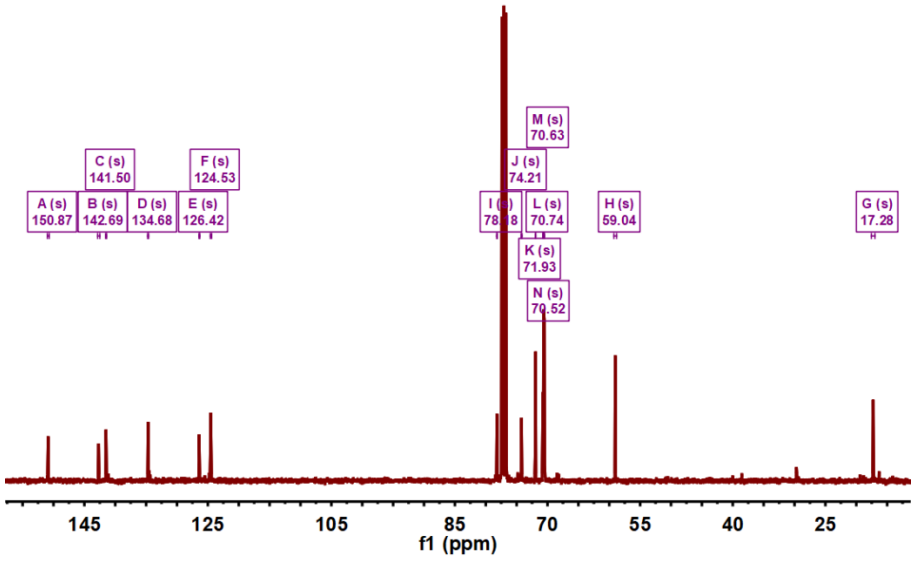
^{13}C NMR spectrum of compound **5** in $CDCl_3$.



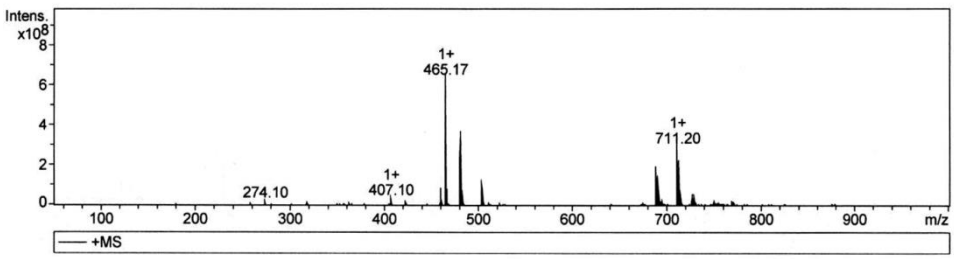
MS spectrum of compound **5**.



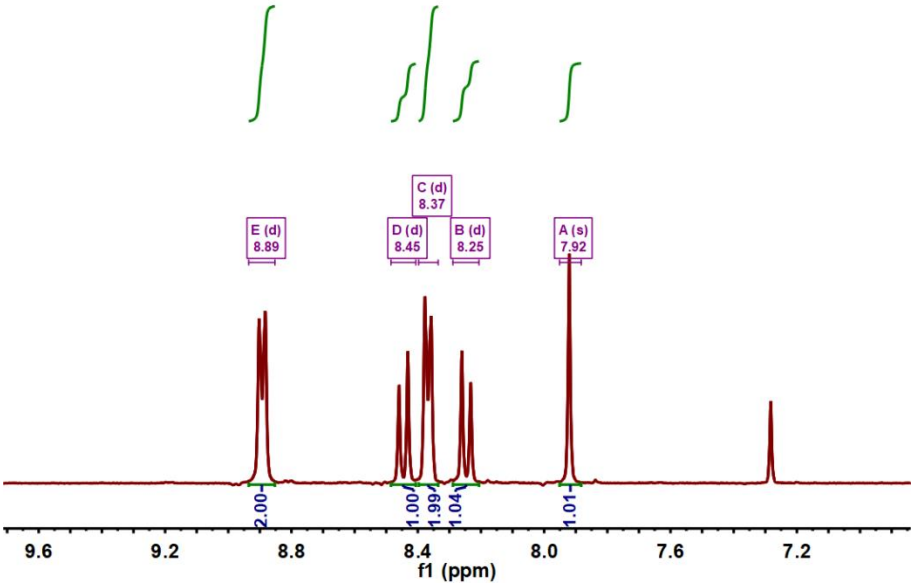
^{1}H NMR spectrum of compound **6** and **7** in $CDCl_3$.



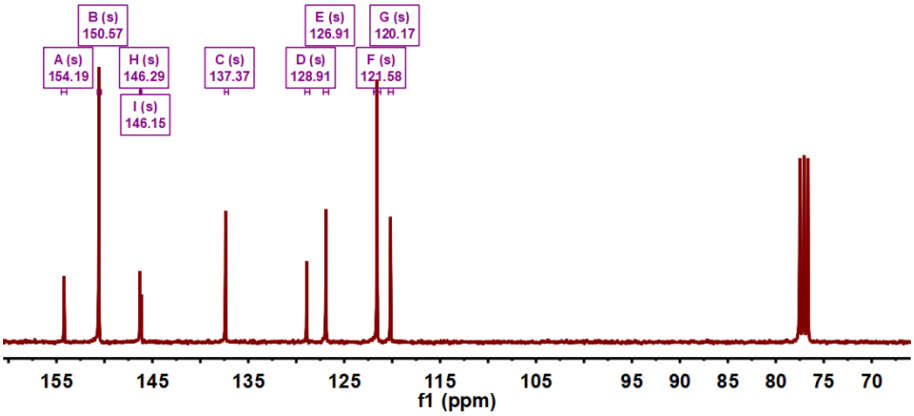
^{13}C NMR spectrum of compound **6** and **7** in $CDCl_3$.



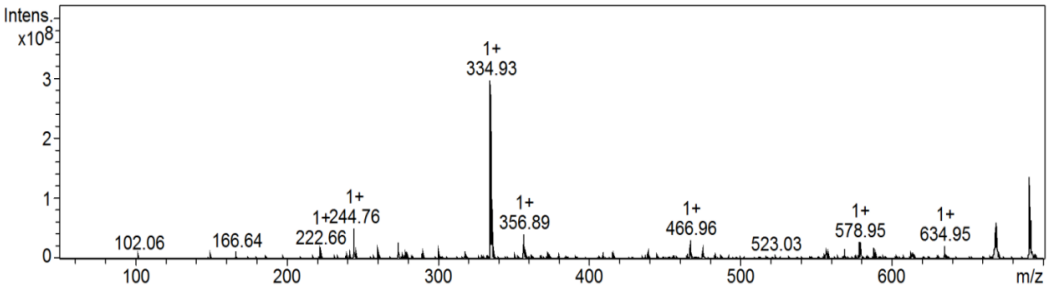
MS spectrum of compound **6** and **7**.



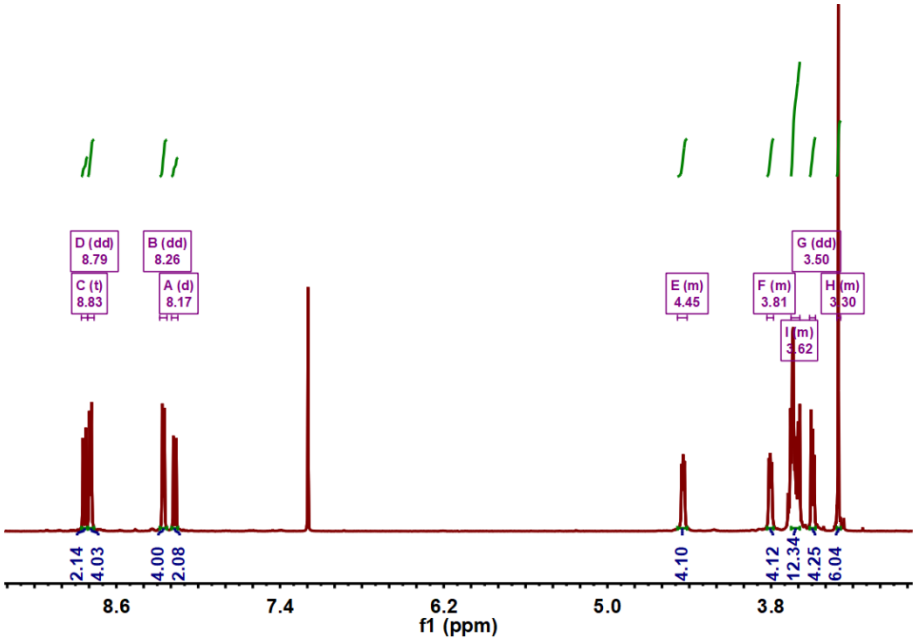
^{1}H NMR spectrum of **DPP** in $CDCl_3$.



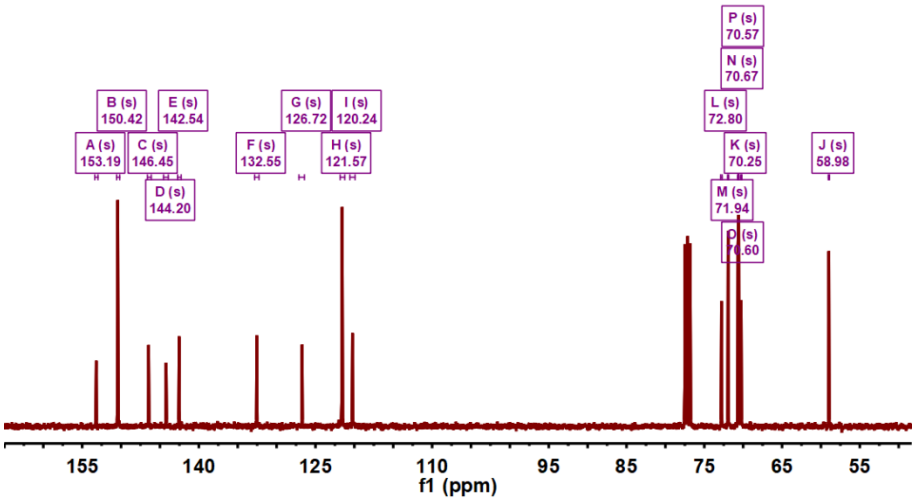
^{13}C NMR spectrum of **DPP** in $CDCl_3$.



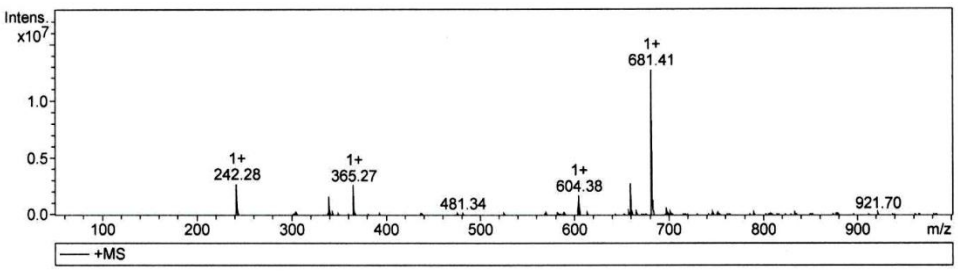
MS spectrum of **DPP**.



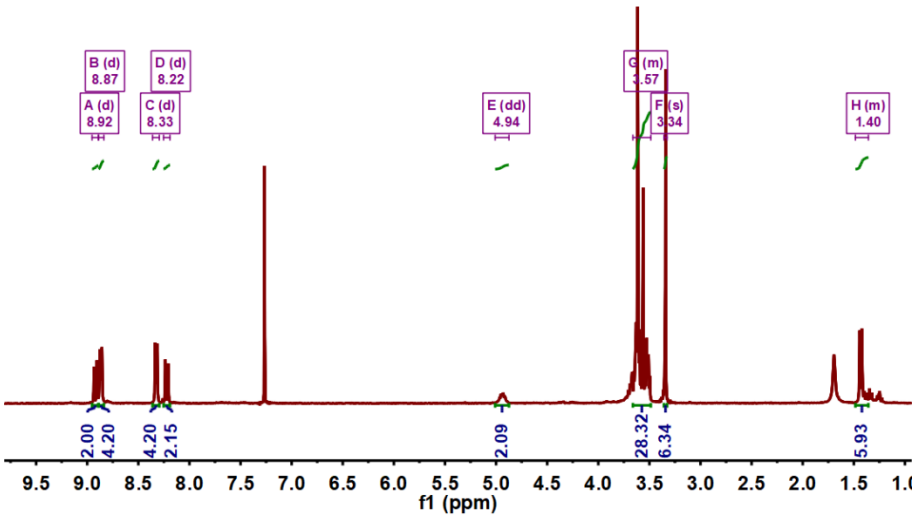
^{1}H NMR spectrum of **TEG-DPP** in $CDCl_3$.



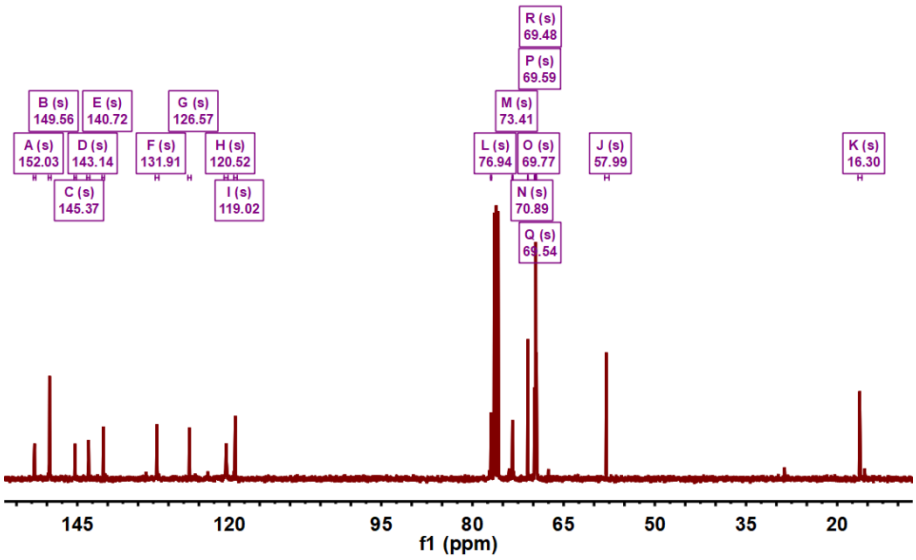
^{13}C NMR spectrum of **TEG-DPP** in $CDCl_3$.



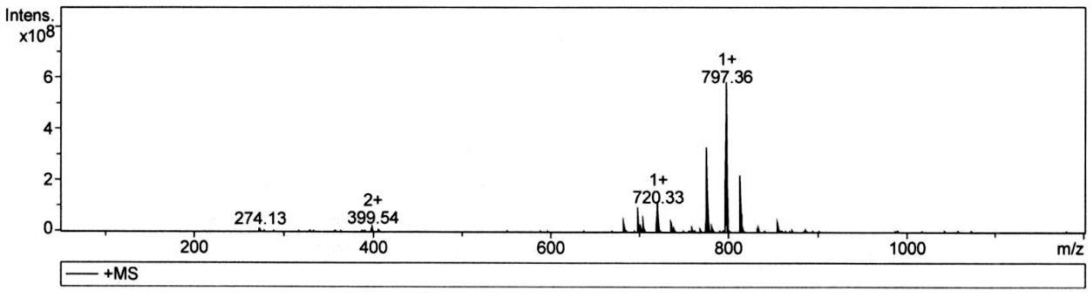
MS spectrum of **TEG-DPP**.



^{1}H NMR spectrum of (*R* and *S*)-**TOT-DPP** in $CDCl_3$.



^{13}C NMR spectrum of (*R* and *S*)-**TOT-DPP** in $CDCl_3$.



MS spectrum of (*R* and *S*)-**TOT-DPP**.

5. Reference

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