Supplementary Information

Construction of Metallo-Helicoids with High Antimicrobial Activity via Intermolecular Coordination

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1. General Information

The chemicals, including 4-acetyl-4'-bromobiphenyl, triisopropylsilylacetylene, 4-nitrobenzaldehyde, 4-tert-butylbenzaldehyde and 2-acetylpyridine, were purchased from Sigma-Aldrich or Fisher, and were used without further purification. Column chromatography was conducted using basic Al_2O_3 (Acros Organics, activated, 60 Å) or SiO_2 (SiliCycle, 40-63 μm, 60 Å). The thin-layer chromatography (TLC) was monitored by UV light (254 nm). NMR spectra were recorded on a 600 MHz Bruker NMR spectrometer or a 500 MHz JEOL JNM-ECZ500R NMR spectrometer in $CDCl_3$ or d_6-DMSO with TMS as reference.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). MALDI-TOF MS was performed on a Bruker UltrafleXtreme TOF/TOF mass spectrometer (Bruker Daltonics GmbH & Co. KG, Bremen, Germany Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd: YAG laser (355 nm). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, purchased from TCI) was applied as the matrix, and poly(methylmethacrylate) (PMMA, M_n = 1.0, 3.0, 5.0 kDa) were used as standards for calibration. DCTB and the ligands were dissolved in $CHCl_3$ at concentration of 20 mg/mL and 5 mg/mL, respectively. Each sample was prepared by depositing 0.5 μL of matrix on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of the sample on a spot of dry matrix, and adding another 0.5 μL of matrix on top of the dry sample. The plate was inserted into the MALDI source after drying. The sample was conducted in reflection mode. And the data analysis was conducted with Bruker FlexAnalysis software.

Electrospray ionization-mass spectrometry (ESI-MS). ESI-MS spectra were collected on a Waters Synapt G2 tandem mass spectrometer (Waters Corp., MA, USA), using solutions of 0.1 mg sample in 1 mL of $CHCl_3$/MeOH (v/v, 4:1).

Transmission Electron Microscopy (TEM). The sample solutions were drop-casted onto a carbon-coated Cu grid (400 mesh, SPI supplies), and the extra solution was absorbed by filter paper. The TEM images were taken on the FEI Morgagni or HITACH HT7700 Transmission Electron Microscope.

Atomic Force Microscopy (AFM). AFM imaging was carried out on a Digital Instrument Nanoscope Dimension 3100 system. The sample solutions were dropped on freshly cleaved highly

oriented pyrolytic graphite (HOPG), incubated for 3 minutes and then washed with methanol and acetone, and dried in the fume hood overnight. Silicon cantilever tip (Nanoandmore Tap300-G) with resonant frequency of 300 kHz and force constant of 40 N/m was used for the experiments.

Molecular modeling. The structural optimization and energy calculation of the metallo-helicoids **H1** and **H2** were carried out in Materials Studio version 7.0, using the Geometry Optimization and Energy tasks in the Forcite module (Accelrys Software, Inc.). The initial structural model was built up with all counterions omitted for clarity. The Geometry Optimization was performed by using Universal Force Field (UFF) with atom-based summation and cubic spline truncation for both the electrostatic and Van der Waals parameters. The smart algorithm was used within ultrafine calculation quality (2.0×10^{-5} kcal/mol energy, 0.001 kcal/mol/Å Force, 1.0×10^{-5} Å displacement as the convergence tolerance). The energy calculation of the optimized structure was then carried out by using the same parameters.The calculation results were summarized below in Table S1.

Table S1. The calculated energies of **H1** and **H2**.[a.]

	Bond	Angle	Torsion	Inversion	Van der Waals	Energy
H1	305.369	3980.087	438.460	3.769	1711.155	6438.839902
H2	293.675	4022.479	590.079	6.738	1512.041	6425.012288

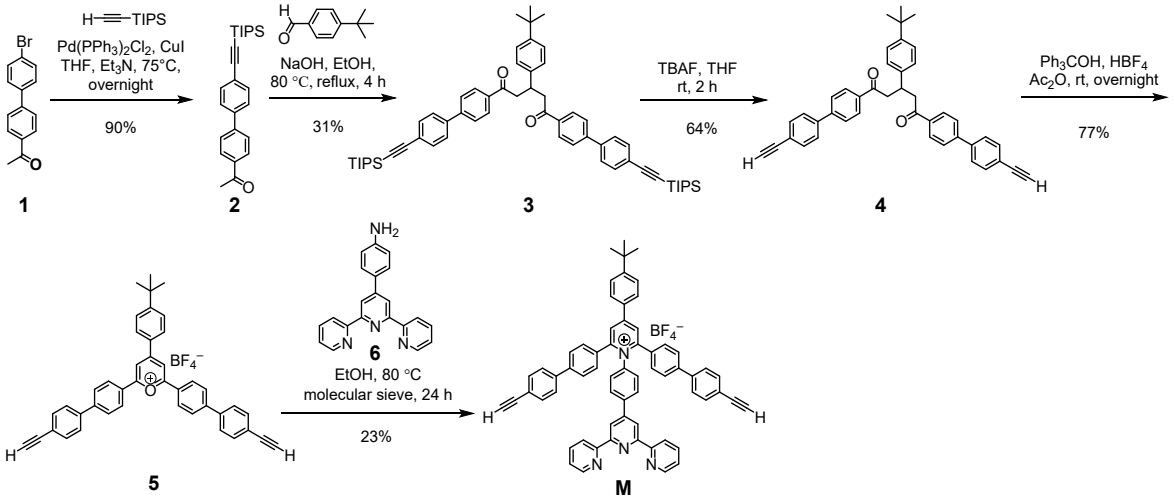
[a.] All the energies are reported in kcal/mol.

Half-maximal inhibitory concentration (IC_{50}) against MRSA and *E. Coli.* [1] The antimicrobial activity of the compounds is tested against Methicillin-resistant *S. aureus* (MRSA, ATCC 33591) and *E. coli*, respectively. Briefly, a single colony of MRSA bacterium was inoculated in 3 mL TBS medium and allowed to grow overnight at 37 °C. The bacteria culture was then diluted at 1:100 and the bacteria were able to re-grow to mid-logarithmic phase in 6-8 h. Next, 50 μL compounds in 2-fold serially diluted solution with the concentrations of 0.1-100 μg/mL were added the 96-well plate containing 50 μL of bacteria suspension (1×10^6 CFU/mL) in each well. Following that, the plate was incubated at 37 °C for 16 h, and the absorption of those wells at 600 nm wavelength was read on a Biotek Synergy H1 microtiter plate reader. The IC_{50}s were determined as the concentrations of compounds that inhibit half of the growth of MRSA or *E. coli.* The experiments were repeated at least three times with duplicates each time.

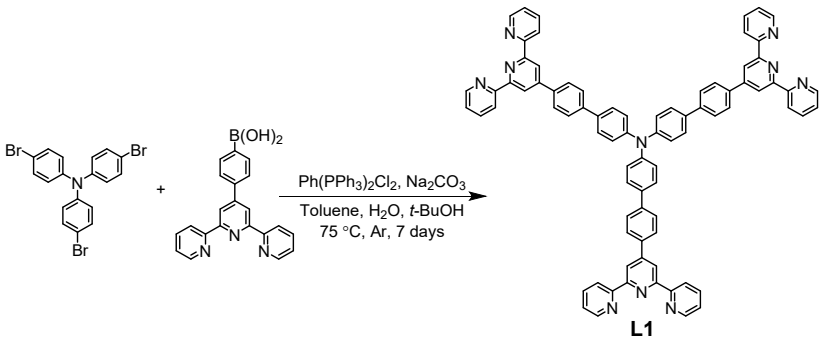
Hemolytic assay. [1] The freshly drawn human red blood cells (hRBCs) were washed with 1× PBS buffer multiple times and centrifuged at 3500 rpm for 10 min, until the supernatant became clear.

Next, the supernatant was removed, and the RBCs were diluted into 5% v/v suspension. The aliquots of suspension (50 μL) were then incubated with compounds at various concentrations in 2-fold serially diluted solution (50 μL) at 37 °C for 1 h. The mixture was centrifuged at 3500 rpm for 10 min and the supernatant was collected. Following that, 100 μL PBS was added to 30 μL of the supernatant, and the absorbance of the solution at 540 nm was read on a Biotek Synergy H1 plate reader. 2% Triton X-100 was used as the positive control and 1× PBS was used the negative control. The hemolysis activity was calculated by the formula % hemolysis = (Abs_{sample} − Abs_{PBS})/(Abs_{Triton} − Abs_{PBS})×100%. The experiment was repeated at least three times with duplicates each time.

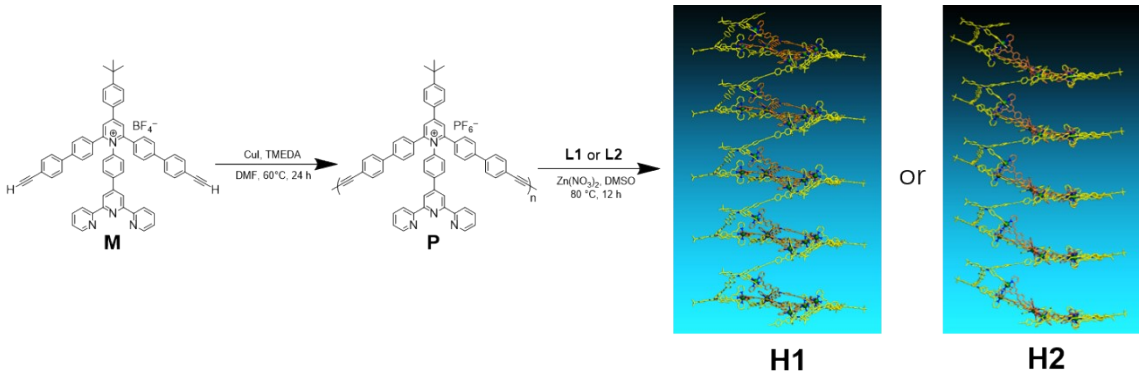
2. Synthesis of monomer M, polymer P and helicoid H



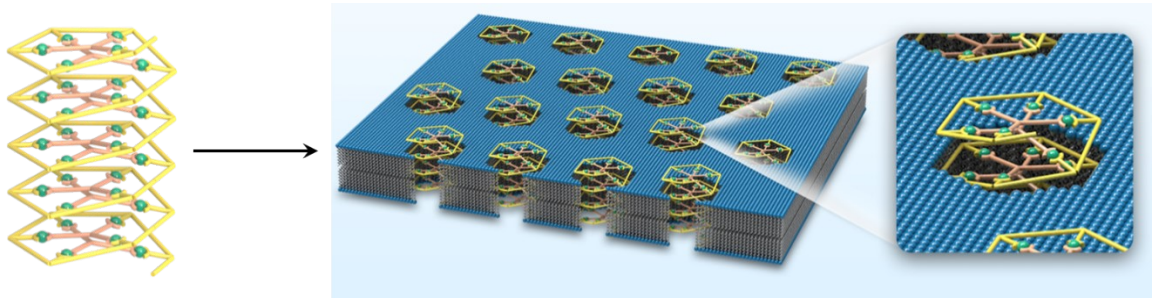
Scheme S1. Synthesis of compound **M**.



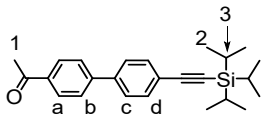
Scheme S2. Synthesis of compound **L1**.



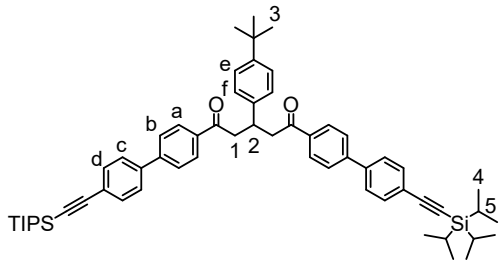
Scheme S3. Synthesis of polymer **P**, helicoid **H1**, and helicoid **H2**.



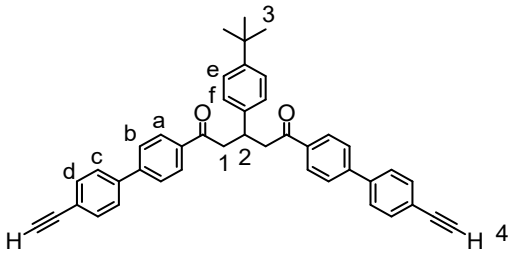
Scheme S4. Schematic illustration of the formation of transmembrane channels via the incubation of **H1** with MRSA or *E. coli*.



Compound **2**: Under N_2 atmosphere, anhydrous THF (30 mL) and Et_3N (15 mL) were added to the mixture of compound **1** (5.00 g, 18.17 mmol), $Pd(PPh_3)_2Cl_2$ (0.64 g, 0.91 mmol) and CuI (0.17 g, 0.91 mmol). Then triisopropylsilylacetylene (6.50 g, 35.6 mmol) was added with syringe. The mixture was stirred at 75 °C overnight. After cooling down to room temperature, the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel with *n*-hexane/dichloromethane (DCM) (v/v, 4:1) as eluent to afford the compound **2** as an orange solid (6.23 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 12.6 Hz, 2H, Ph-H^a), 7.67 (d, J = 12.6 Hz, 2H, Ph-H^b), 7.57 (s, 4H, Ph-H^c and Ph-H^d), 2.64 (s, 3H, H^1), 1.15 (s, 21H, H^2 and H^3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.66, 144.92, 139.61, 136.10, 132.63, 129.00, 127.14, 127.04, 123.55, 106.64, 92.19, 26.69, 18.69, 17.69, 11.34. ESI-MS (*m/z*): $[M+H^+]^+$ 377.2316 (calcd. *m/z*: 377.2300).

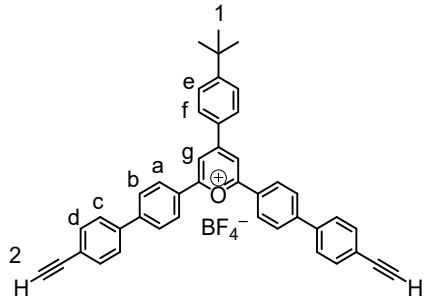


Compound **3**: To a 100 mL Schlenk flask, compound **2** (5.00 g, 13.28 mmol), 4-tert-butylbenzaldehyde (0.90 g, 5.55 mmol), NaOH (0.66 g, 16.5 mmol) were added. Then ethanol (30 mL) was added. The reaction mixture was refluxed at 80 °C for 4 h. After cooling down to room temperature, the mixture was extracted with DCM, washed with water and brine, and dried over Na_2SO_4. After removing the solvent with rotary evaporator, the crude product was purified by column chromatography on silica gel with *n*-hexane/DCM (v/v, 3:1) as eluent to afford the compound **3** as orange solid (1.52 g, 31%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 4H, Ph-H^a), 7.65 (d, J = 8.5 Hz, 4H, Ph-H^b), 7.56 (s, 8H, Ph-H^c and Ph-H^d), 7.30 (d, J = 8.3 Hz, 2H, Ph-H^e), 7.24 (d, J = 8.3 Hz, 2H, Ph-H^f), 4.08 (p, J = 6.8 Hz, 1H, H^2), 3.51 (m, 2H, H^1), 3.39 (m, 2H, H^1), 1.28 (m, 9H, H^3), 1.14 (d, 42H, H^4 and H^5). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.31, 149.45, 144.84, 140.73, 139.64, 135.92, 132.62, 128.87, 127.19, 127.13, 127.07, 127.03, 125.58, 125.51, 106.67, 92.15, 45.05, 36.83, 34.40, 31.36, 18.70, 11.35. ESI-MS (*m/z*): $[M+H^+]^+$ 897.5434, (calcd. *m/z*: 897.5462).

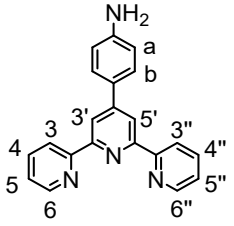


Compound **4**: Under N_2 atmosphere, tetra-*n*-butylammonium fluoride (TBAF) (1M in THF, 6.79 mmol) was added dropwise to a THF solution (25 mL) containing compound **3** (1.52 g, 1.69 mmol) at 0 °C. After that, the mixture was stirred at room temperature for 2 h. Then the mixture was extracted with DCM, washed with water and brine, and tried over Na_2SO_4. After removing the solvent with rotary evaporator, the crude product was purified by column chromatography on silica gel with *n*-hexane/DCM (v/v, 3:1~2:1) as eluent to afford the compound **4** as a white powder (0.58 g, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 4H, Ph-H^a), 7.66 (d, J = 8.5 Hz, 4H, Ph-

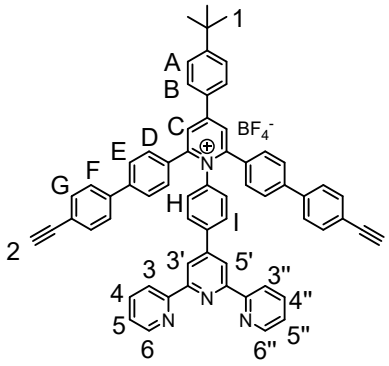
H^b), 7.58 (s, 8H, Ph-H^c and Ph-H^d), 7.30 (d, J = 8.4 Hz, 2H, Ph-H^e), 7.24 (d, J = 8.4 Hz, 2H, Ph-H^f), 4.08 (p, J = 6.9 Hz, 1H, H^2), 3.52 (m, 2H, H^1), 3.39 (m, 2H, H^1), 3.16 (s, 2H, H^4), 1.28 (s, 9H, H^3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.31, 149.48, 144.65, 140.73, 140.19, 136.02, 132.73, 128.89, 127.17, 127.07, 125.59, 122.04, 83.29, 78.41, 45.05, 36.79, 34.41, 31.36. ESI-MS (*m/z*): $[M+H^+]^+$ 585.2833, (calcd. *m/z*: 585.2793).



Compound **5**: Triphenylmethanol (0.43 g, 1.64 mmol) was dissolved in acetic anhydride (10 mL) by heating to 65 °C. After cooling down to room temperature, HBF_4 (250 μL, 50 wt. % in water) was added dropwise. Then compound **4** (0.80 g, 1.37 mmol) in acetic anhydride (13 mL) was added. The reaction mixture was stirred at room temperature overnight. After the reaction was complete, the solvent was removed under vacuum. The crude product was dissolved again in acetone (2 mL). Then the mixture was poured into diethyl ether (50 mL) to form precipitate. The precipitate was collected by filtration, repeatedly washed with fresh diethyl ether, and dried under vacuum. A red solid was obtained (0.60 g, 77%), and directly used for the next step without further purification. ^{1}H NMR (600 MHz, d_6-DMSO) δ 9.14 (s, 2H, Py-H^g), 8.65 (d, J = 8.6 Hz, 4H, Ph-H^d), 8.56 (d, J = 8.5 Hz, 2H, Ph-H^f), 8.11 (d, J = 8.5 Hz, 4H, Ph-H^c), 7.92 (d, J = 8.4 Hz, 4H, Ph-H^b), 7.78 (d, J = 8.7 Hz, 2H, Ph-H^e), 7.66 (d, J = 8.3 Hz, 4H, Ph-H^a), 4.38 (s, 2H, H^2), 1.40 (s, 9H, H^1). ^{13}C NMR (150 MHz, d_6-DMSO) δ 169.50, 164.76, 159.63, 145.38, 144.26, 138.81, 133.00, 130.66, 130.34, 129.90, 129.52, 129.10, 128.97, 128.83, 128.32, 128.10, 128.04, 127.91, 127.27, 126.73, 122.90, 115.11, 83.62, 83.02, 56.25, 35.77, 31.42, 31.14. ESI-MS(*m/z*): $[M-BF_4^-]^+$ 565.2517, (calcd *m/z*: 565.2526).

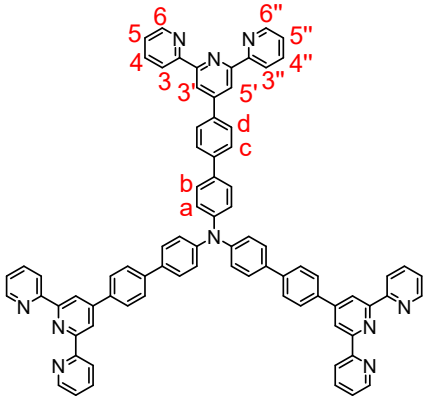


Compound **6**: 4'-(4-nitrophenyl)-2,2':6',2''-terpyridine[1] (2.00 g, 5.64 mmol), $SnCl_2$ (9.63 g, 50.80 mmol), and HCl were added to a round-bottom flask. The mixture was stirred at 100 ℃ overnight. After cooling down to room temperature, the solution of NaOH was added to make the system basic (pH>10). Then the mixture was extracted with DCM, and washed with fresh water, and dried over Na_2SO_4. After removing the solvent with rotary evaporator, compound **6** was obtained as a white solid (1.10 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, J = 3.8 Hz, 2H, Tpy-$H^{6, 6''}$), 8.69 (s, 2H, Tpy-$H^{3', 5'}$), 8.67 (d, J = 8.0 Hz, 2H, Tpy-$H^{3, 3''}$), 7.87 (td, J = 7.7, 1.8 Hz, 2H, Tpy-$H^{4, 4''}$), 7.79 (d, J = 8.5 Hz, 2H, Ph-H^{b}), 7.35 (m, 2H, Tpy-$H^{5, 5''}$), 6.80 (d, J = 8.4 Hz, 2H, Ph-H^{a}), 1.71 (s, 2H, H^{c}). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.50, 155.69, 150.06, 149.06, 147.59, 136.89, 128.42, 128.20, 123.72, 121.40, 117.83, 115.25. ESI-MS (*m/z*): $[M+H^+]^+$ 325.1464, (calcd *m/z*: 325.1453).

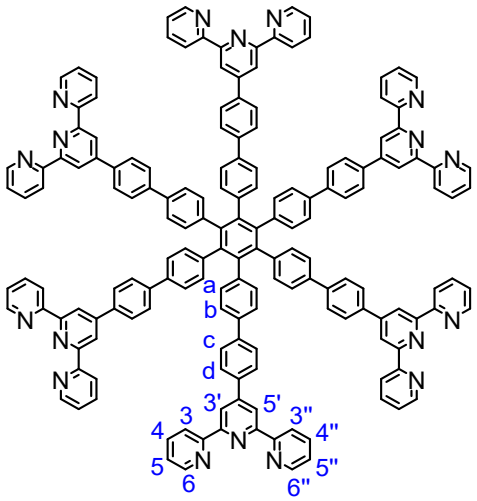


Compound **M**: Under N_2 atmosphere, compound **5** (530 mg, 0.81 mmol), compound **6** (264 mg, 0.81 mmol), 4Å molecular sieve (53 mg) and EtOH (30 mL) were added into a 100 mL Schlenk flask. The reaction mixture was stirred at 80 °C for 24 h. After cooling down to room temperature, the mixture was extracted with DCM, washed with fresh water and brine, and dried over Na_2SO_4. After removing the solvent with rotary evaporator, the crude product was purified by column chromatography on Al_2O_3 with DCM/MeOH (v/v, 100:0~100:0.4) as eluent to afford the compound **M** as a yellow solid (180 mg, 23%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, J = 3.4 Hz, 2H, Tpy-$H^{6, 6''}$), 8.59 (d, J = 7.9 Hz, 2H, Tpy-$H^{3, 3''}$), 8.50 (s, 2H, Tpy-$H^{3', 5'}$), 8.21 (s, 2H, Py-H^{C}), 7.93 (t, J = 8.9 Hz, 4H, Ph-H^{D}), 7.85 (td, J = 7.6, 1.7 Hz, 2H, Tpy-$H^{4, 4''}$), 7.77 (d, J = 8.3 Hz, 4H, Ph-H^{G}), 7.68 (d, J = 8.2 Hz, 2H, Ph-H^{E}), 7.59(d, J = 8.7 Hz, 2H, Ph-H^{E}), 7.56 (d, J = 8.3 Hz, 4H, Ph-H^{F}), 7.50-7.47 (m, 8H, Ph-$H^{A,B,H,I}$), 7.35-7.33 (m, 2H, Tpy-$H^{5, 5''}$), 3.10 (s, 2H, H^{2}), 1.36 (s, 9H, H^{1}) ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.81, 156.63, 156.54, 148.73, 147.93, 141.97, 139.77, 139.59, 132.62, 132.21, 131.13, 130.61, 129.52, 128.37, 127.97, 127.10, 127.07, 126.89, 125.93,

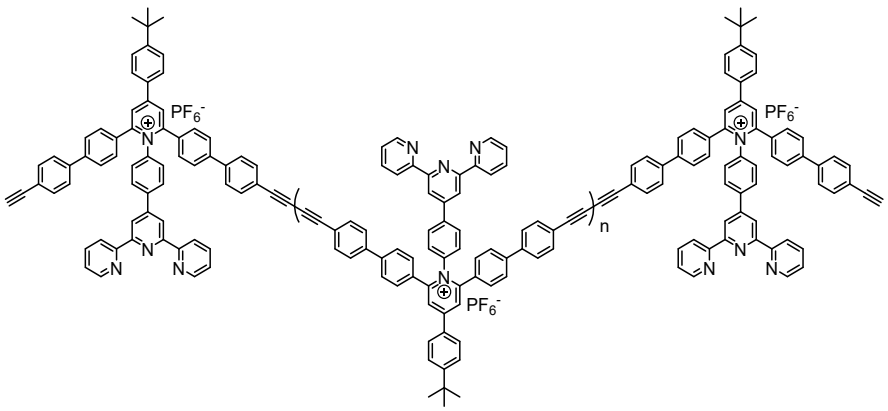
124.26, 121.86, 121.73, 118.95, 83.30, 78.28, 35.16, 31.07, 29.71. MALDI-TOF MS (*m/z*): 871.39, $[M-BF_4^-]^+$ (calcd *m/z*: 871.38).



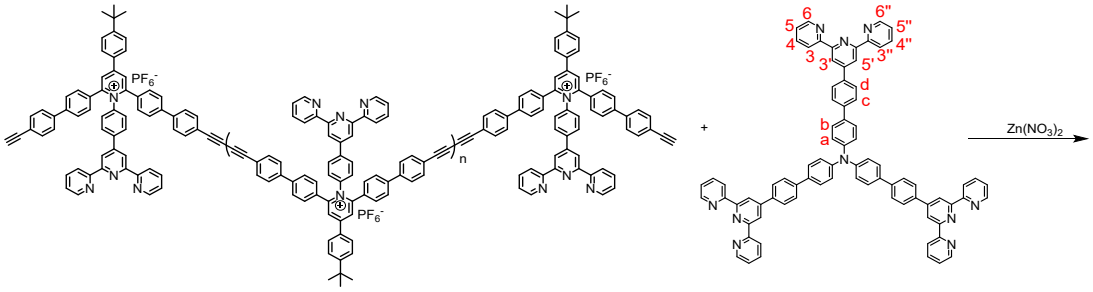
Compound **L1**: Under N_2 atmosphere, tris(4-bromophenyl) amine (964 mg, 2.00 mmol), [4-(2,2':6',2"-terpyridin-4'-yl)phenyl]boronic acid (2.83 g, 8.00 mmol), $Pd(PPh_3)_2Cl_2$ (211 mg, 0.30 mmol), Na_2CO_3 (2.54 g, 24.0 mmol), toluene (80 mL), H_2O (30 mL), and *t*-BuOH (10 mL) were added into a 200 mL Schlenk flask. Then the mixture was stirred at 75 °C for 3 days. After cooling down to room temperature, the mixture was extracted with DCM, washed with water and brine, and dried over Na_2SO_4. After removing the solvent with rotary evaporator, the crude product was purified by column chromatography on silica gel with DCM/MeOH (v/v, 100:0~100:1) as eluent to afford the compound **L1** as a yellow solid (668 mg, 28%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (s, 6H, Tpy-$H^{3',5'}$), 8.75 (d, 6H, J = 4.0 Hz, Tpy-$H^{6,6''}$), 8.69 (d, J = 7.9 Hz, 6H, Tpy-$H^{3,3''}$), 8.02 (d, J = 8.4 Hz, 6H, Ph-H^b), 7.90 (td, J = 7.6, 1.8 Hz, 6H, Tpy-$H^{4,4''}$), 7.78 (d, J = 8.4 Hz, 6H, Ph-H^a), 7.65 (d, J = 8.6 Hz, 6H, Ph-H^d), 7.38-7.36 (m, 6H, Tpy-$H^{5,5''}$), 7.32 (d, J = 8.6 Hz, 6H, Ph-H^c). ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD) δ 160.18, 159.86, 153.93, 152.96, 151.06, 145.35, 141.30, 140.57, 138.81, 131.95, 131.63, 131.23, 128.54, 128.05, 125.76, 122.70. MALDI-TOF MS (*m/z*): 1166.43, $[M]^•$ (calcd *m/z*: 1166.46).

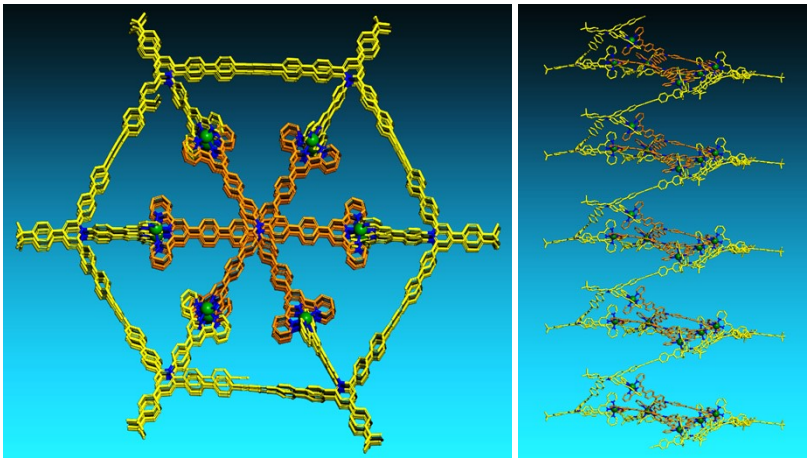


Compound **L2**[2]: Under N_2 atmosphere, 1,2,3,4,5,6-hexakis (4-bromophenyl)benzene (202 mg, 0.20 mmol), [4-(2,2':6',2"-terpyridin-4'-yl)phenyl]boronic acid (580 mg, 8.00 mmol), $Pd(PPh_3)_2Cl_2$ (425.5 mg, 0.06 mmol), Na_2CO_3 (640 mg, 6.00 mmol), toluene (20 mL), H_2O (10 mL), and *t*-BuOH (3 mL) were added into a 100 mL Schlenk flask. Then the mixture was stirred at 75 °C for 7 days. After cooling down to room temperature, the mixture was extracted with DCM, washed with water and brine, and dried over Na_2SO_4. After removing the solvent with rotary evaporator, the crude product was purified by column chromatography on silica gel with DCM/MeOH (v/v, 100:0~100:2) as eluent to afford the compound **L2** as a white solid (194 mg, 41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 12H, Tpy-$H^{3', 5'}$), 8.68 (d, J = 5.6 Hz, 12H, Tpy-$H^{6, 6''}$), 8.63 (d, J = 12.0 Hz, 12H, Tpy-$H^{3, 3''}$), 7.92 (td, J = 12.6 Hz, 12H, Ph-H^{a}), 7.84 (td, J = 11.6, 2.7 Hz, 12H, Tpy-$H^{4, 4''}$), 7.63 (d, J = 12.6 Hz, 12H, Ph-H^{b}), 7.35-7.29 (m, 24H, Ph-H^{c}, Tpy-$H^{5, 5''}$), 7.10 (d, J = 12.2 Hz, 12H, Ph-H^{d}). MALDI-TOF MS (*m/z*): 2377.93, $[M+H^+]^+$ (calcd *m/z*: 2377.91).

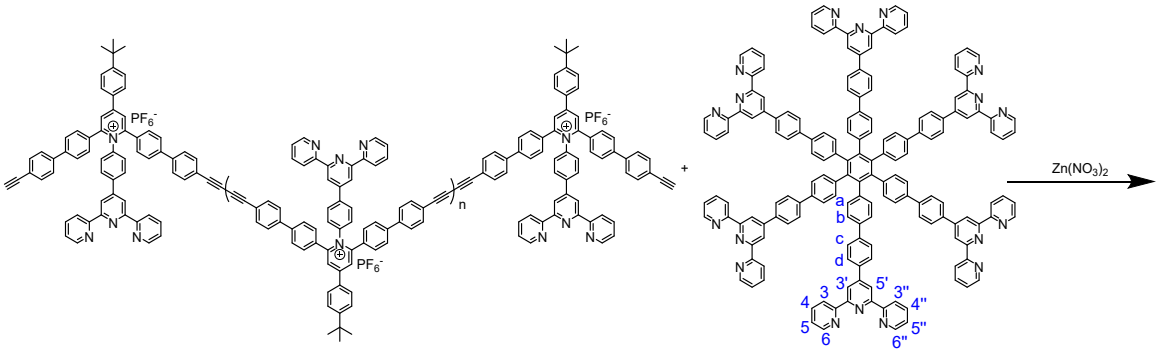


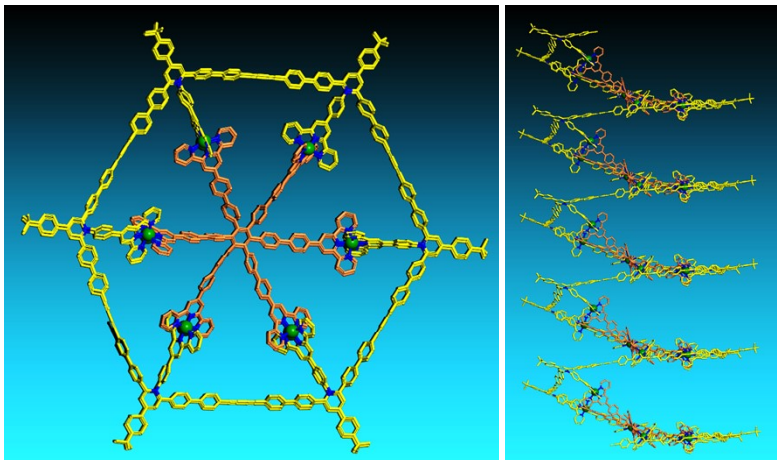
Compound **P**: To a solution of monomer **M** (5.0 mg, 5.2 μmol) in $CHCl_3$ (500 μL), a solution of $FeCl_2$ (0.37 mg, 2.9 μmol) in MeOH (185 μL) was added, after 1 mL more MeOH was added in, the mixture was then kept at 60 ºC for 15 h. After cooling to room temperature, the mixture was added into 7 mL saturated solution of NH_4PF_6, and purple precipitate was observed. The yielded supramolecular dimer was then washed with methanol and applied for following polymerization. Then the yielded supramolecular dimer was mixed with copper(I) iodide (2.0 mg, 10 μmol), tetramethylethylenediamine (1.2 mg, 10 μmol) and dissolved with 620 μL of anhydrous DMF. The reaction mixture was heated to 60 °C and stirred for 24 h, in an oxygen-rich atmosphere. After that, 1.5 mL of saturated Na_2H_2EDTA aqueous solution was added into the mixture and the mixture was stirred at 60 °C and for another 12 hours, to completely remove all the metal ions from the resulting polymer. The precipitated product was then collected by centrifugation and washed with water and ethanol. The final product was dried in vacuum, yielding a yellow solid (4 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (br, 6H, Tpy-$H^{6, 6''}$, Tpy-$H^{3, 3''}$ and Tpy-$H^{3', 5'}$), 8.23 (s, 2H, Py-H^{A}), 7.94 (d, 2H, Tpy-$H^{4, 4''}$), 7.63 (m, 16H, Ph-H^{B}, Ph-H^{C}, Ph-H^{D} and Ph-H^{E}), 7.48 (d, 2H, Ph-H^{G}), 7.42(d, 2H, Ph-H^{F}), 7.36 (d, 2H, Tpy-$H^{5, 5''}$). P was also characterized by MALDI-TOF-MS (Figure S37).





Compound **H1:** To a solution of **P** (3.0 mg, 2.9 μmol) in d_6-DMSO (600 μL), a solution of **L1** (1.2 mg, 1.0 μmol) in d_6-DMSO (230 μL), and a solution of $Zn(NO_3)_2$•$6H_2O$ (0.9 mg, 2.95 μmol) in 400 μL d_6-DMSO were added. Then the mixture was stirred at 80 °C for 12 hours, the resultant **H1** solution was subjected to characterization directly. ^{1}H NMR (600 MHz, d_6-DMSO) 9.19 (s, 1H, Tpy-$H^{3',5'}$ and Tpy^{L1}-$H^{3',5'}$), 9.02 (s, 1H, Tpy-$H^{6,6''}$ and Tpy^{L1}-$H^{6,6''}$), 8.86-8.70 (m, 13H, Tpy-$H^{3,3''}$, Tpy^{L1}-$H^{3,3''}$, Ph-$H^{H,I,G}$ and Tpy-$H^{4,4''}$), 8.64-8.63 (d, J = 7.9 Hz, 1H, Tpy^{L1}-$H^{4,4''}$), 8.53 (s, 1H, Py-H^{C}), 8.37 (s, 6H, Tpy-$H^{5,5''}$), 8.10-7.96 (m, 12H, Ph-$H^{F,b,D}$), 7.90-7.79 (m, 15H, Ph-$H^{E,F,a}$), 7.71-7.53 (m, 15H, Ph-$H^{d,A}$, Tpy^{L1}-$H^{5,5''}$ and Ph-H^{c}), 7.19 (s, 1H, Ph-H^{B}), 1.38 (s, 9H, H^{1}). It should be note that the sample for the UV, FL, TEM, AFM and antimicrobial studies were prepared in non-deuterated DMSO solution.





Compound **H2:** To a solution of **P** (3.0 mg, 2.9 μmol) in $CDCl_3$/d_6-DMSO (600 μL, v/v, 1:2), a solution of **L2** (1.2 mg, 1.0 μmol) in d_6-DMSO (230 μL), and a solution of $Zn(NO_3)_2$•$6H_2O$ (0.9 mg, 2.95 μmol) in 400 μL d_6-DMSO were added. Then the mixture was stirred at 80 °C for 12 hours, the resultant **H2** solution was subjected to characterization directly. ^{1}H NMR (500 MHz, $CDCl_3$/d_6-DMSO) 9.33-8.86 (m, 3H, Tpy-$H^{3',5'}$, Tpy^{L2}-$H^{3',5'}$, Tpy-$H^{6,6''}$, Tpy^{L2}-$H^{6,6''}$, Tpy-$H^{3,3''}$, and

Tpy^{L2}-$H^{3,3''}$), 9.10-8.91 (s, 7H,), 8.59 (s, 1H, Py-H^{C}), 8.27-8.18 (m, 3H, Ph-$H^{D,d,G}$), 8.97-7.57 (m, 17H, Ph-H^{I}, Tpy-$H^{5,5''}$, Tpy^{L2}-$H^{4,4''}$, and Ph-$H^{H,b,F}$), 8.37 (s, 6H, Tpy-$H^{5,5''}$), 7.41-6.77 (m, 12H, Ph-$H^{E,a}$, Tpy^{L2}-$H^{5,5''}$, and Ph-$H^{A,c,B}$), 1.36 (s, 3H, H^{1}). It should be note that the sample for the UV, FL, TEM, AFM and antimicrobial studies were prepared in non-deuterated DMSO solution.

3. ^{1}H NMR, ^{13}C NMR, and 2D COSY NMR

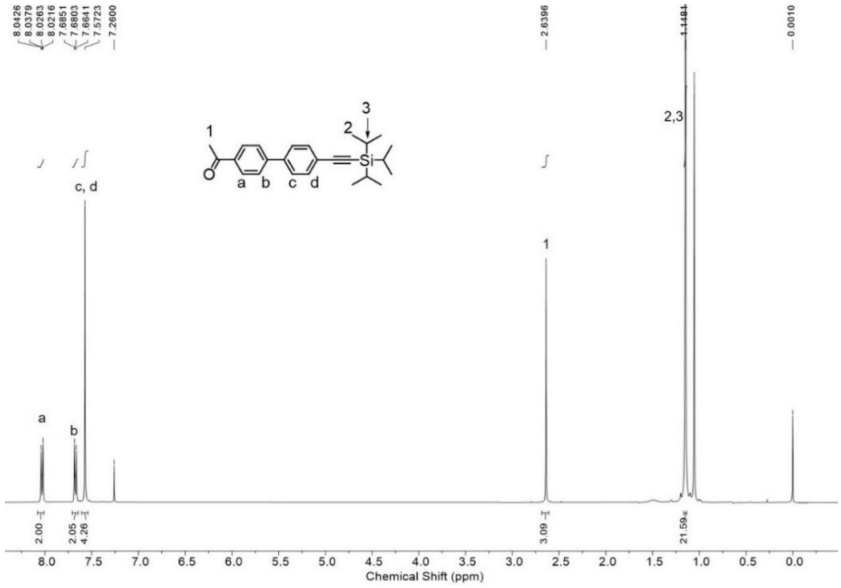


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **2.**

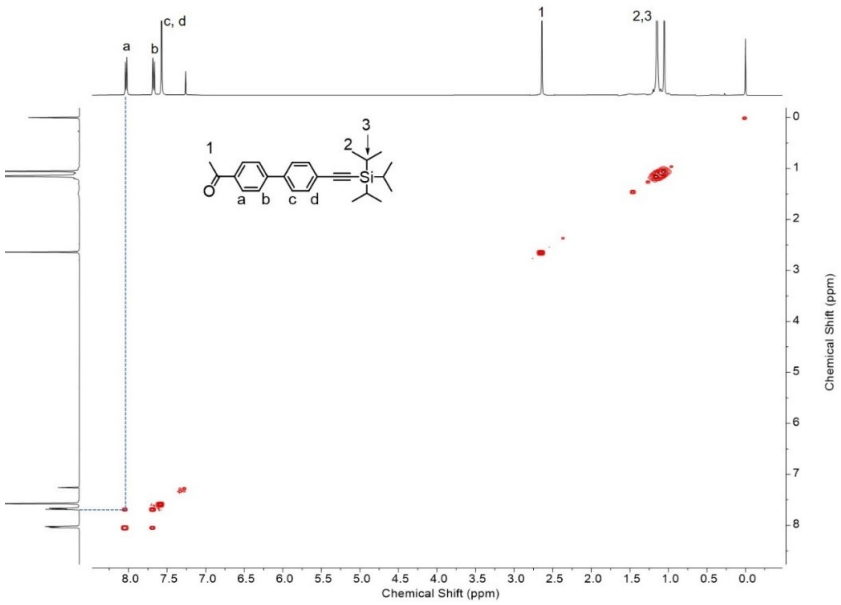


Figure S2. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **2**.

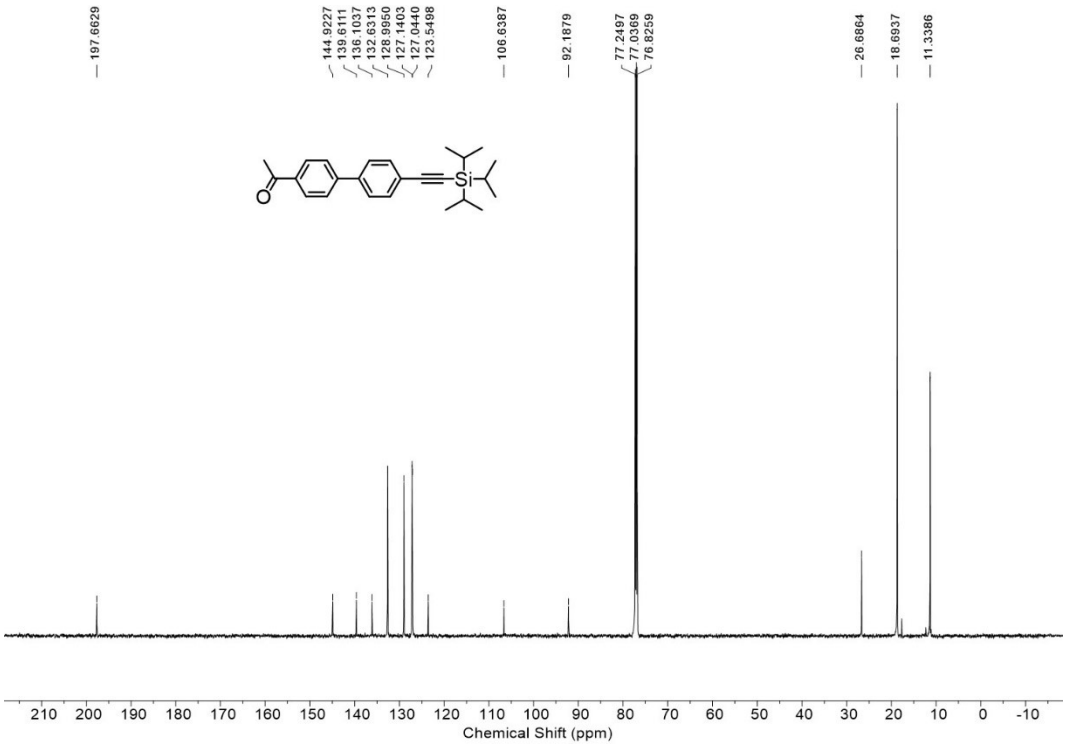


Figure S3. ^{13}C NMR (150 MHz, $CDCl_3$, 300 K) spectrum of compound **2**.

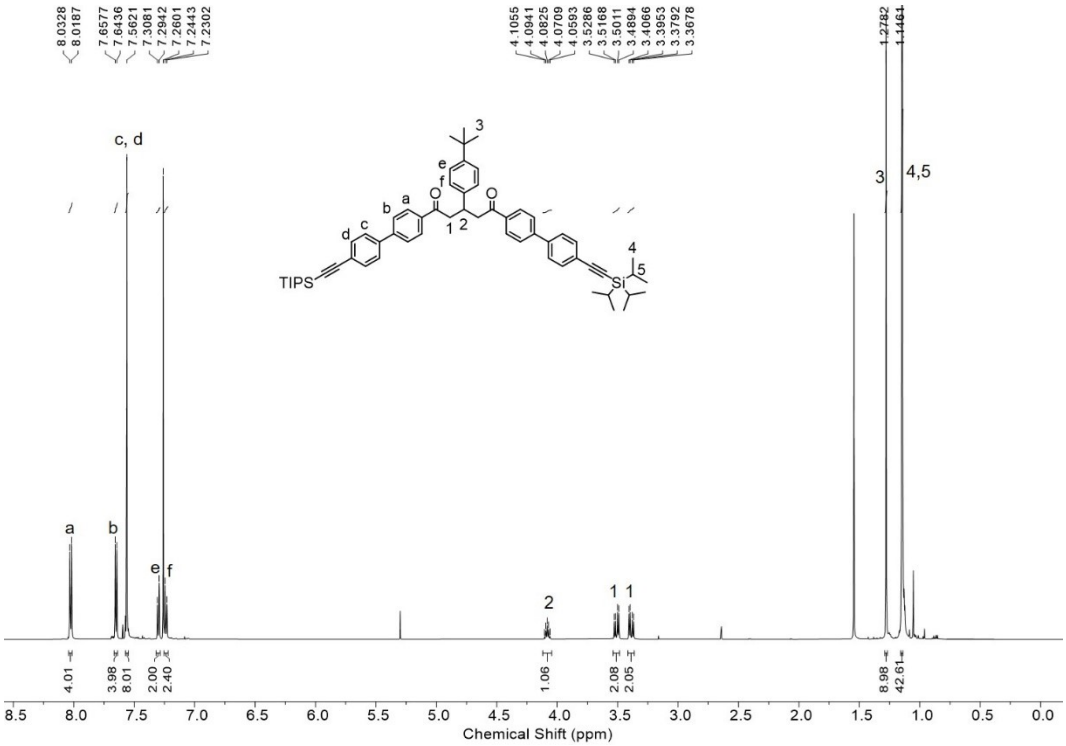


Figure S4. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **3.**

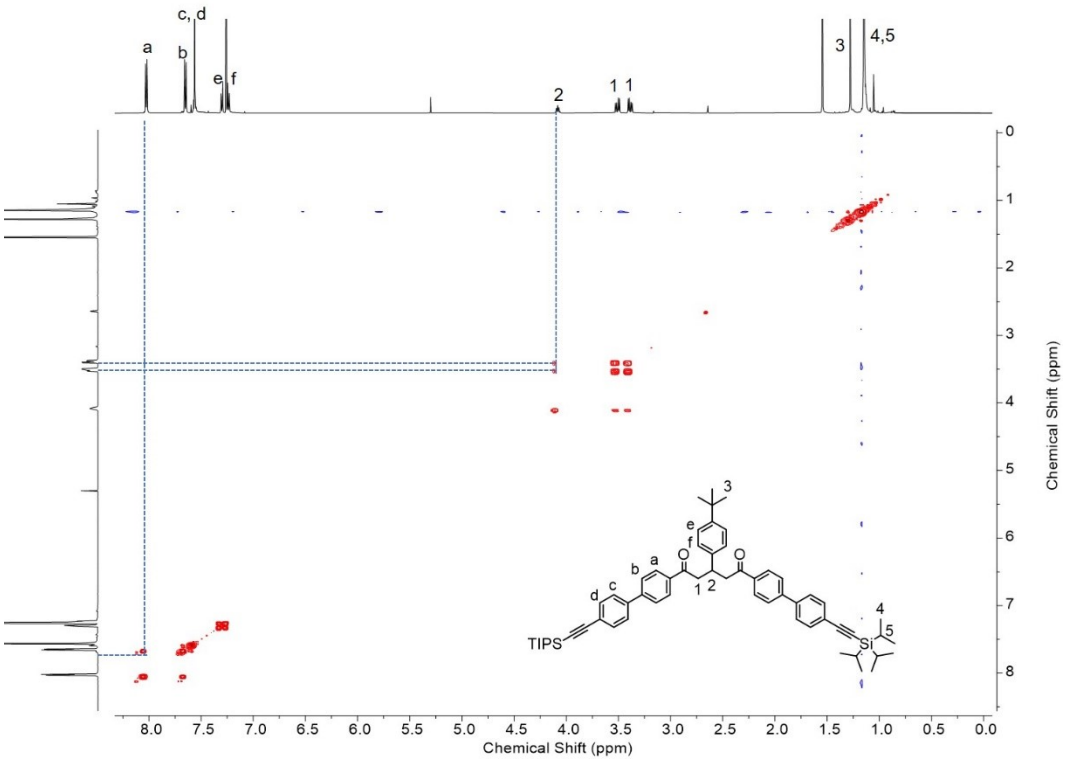


Figure S5. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **3**.

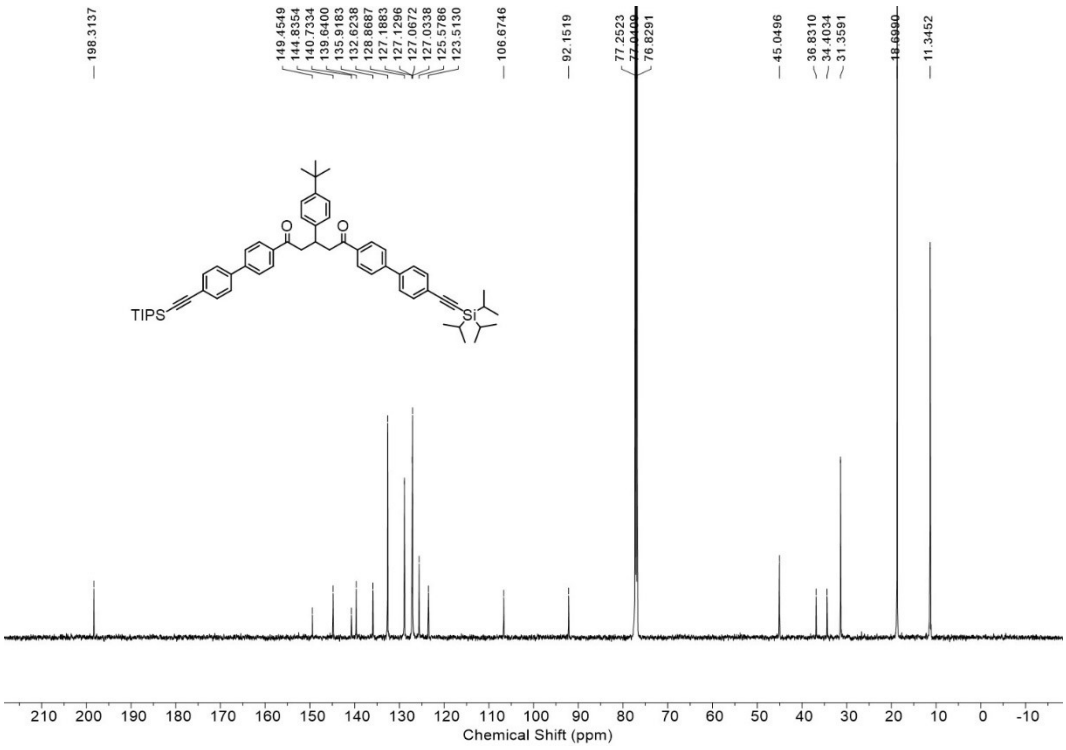


Figure S6. ^{13}C NMR (150 MHz, $CDCl_3$, 300 K) spectrum of compound **3**.

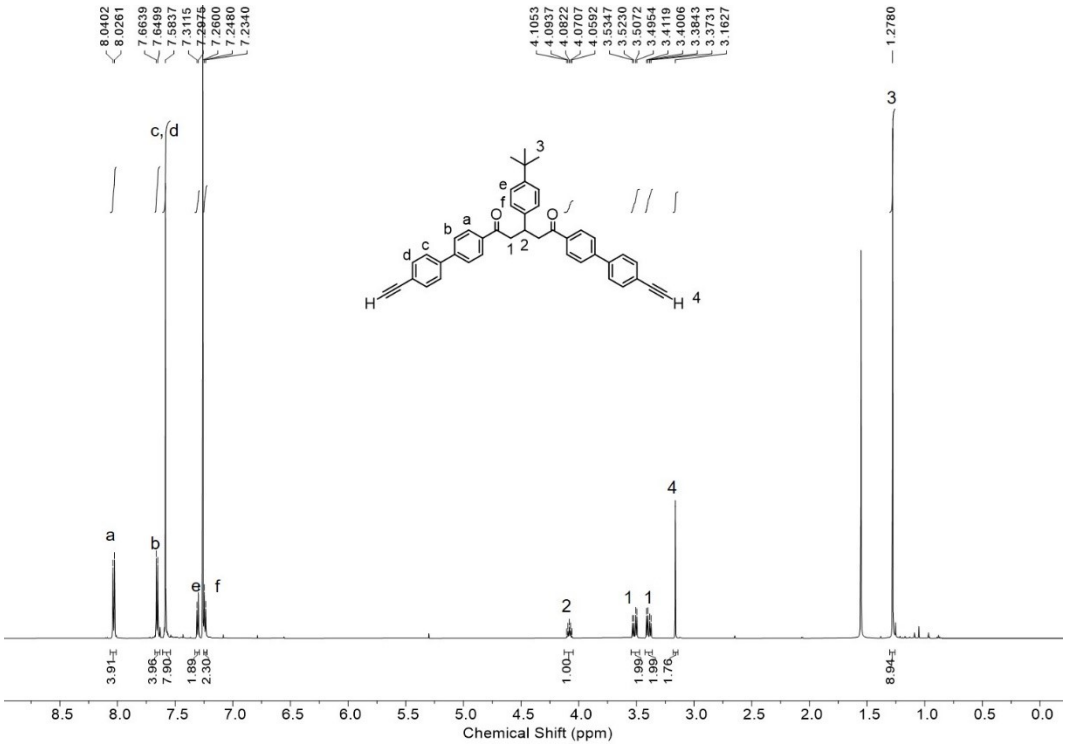


Figure S7. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **4**.

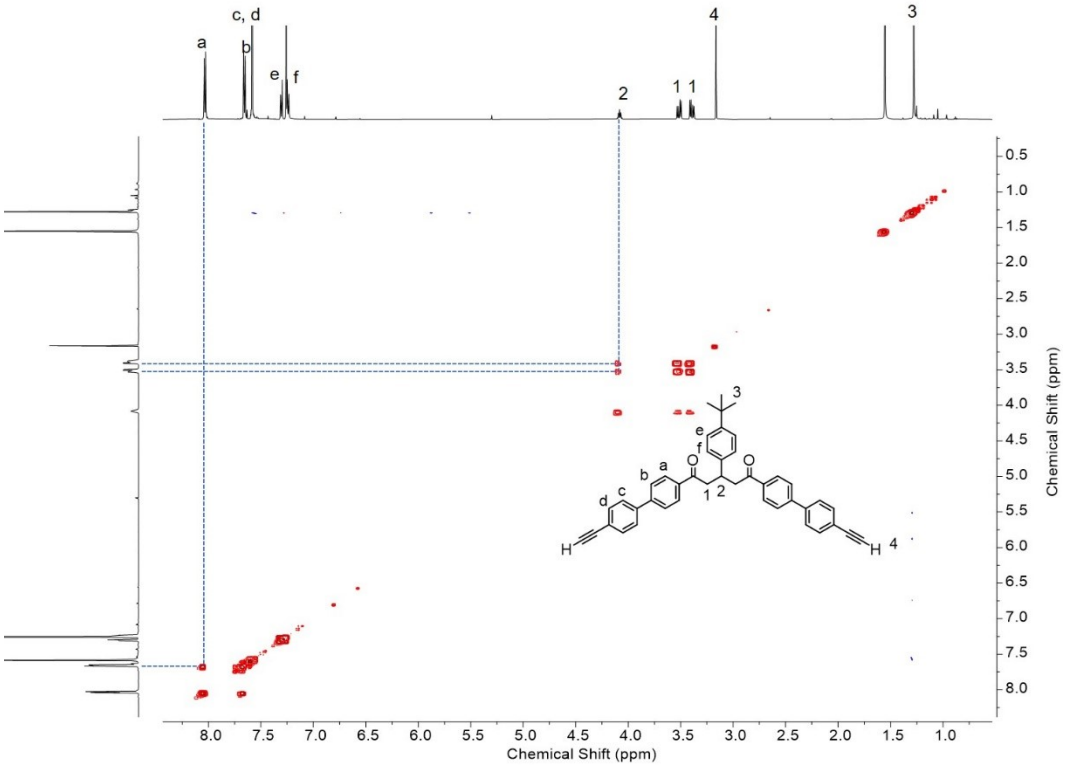


Figure S8. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **4**.

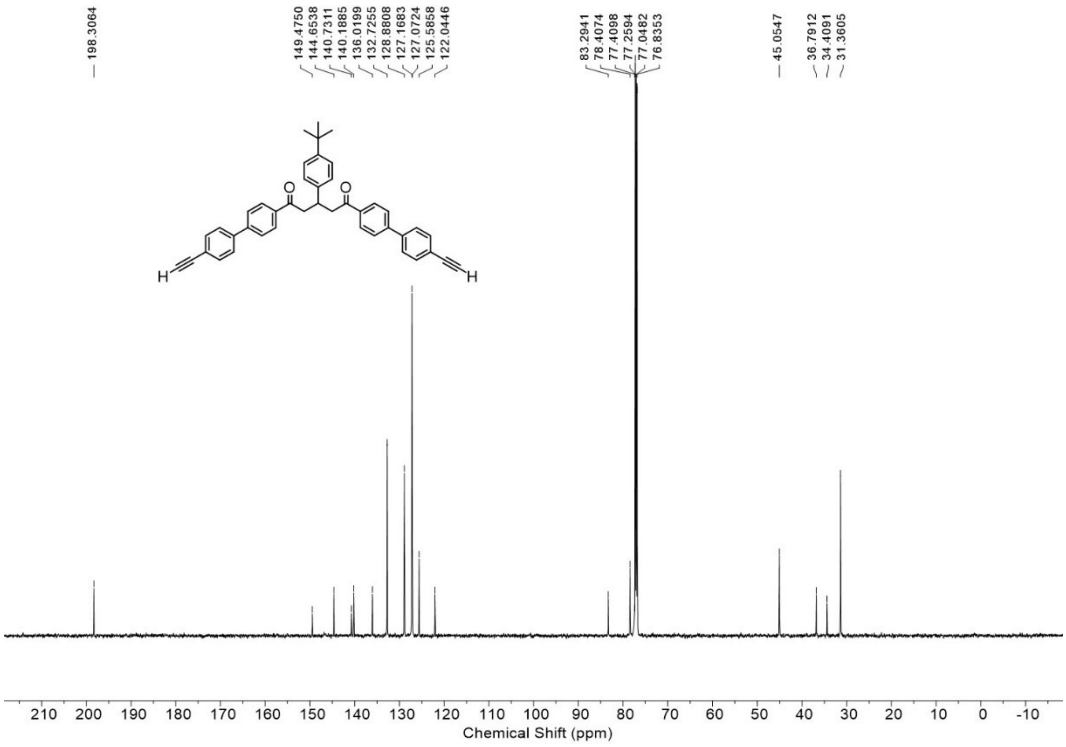


Figure S9. ^{13}C NMR (150 MHz, $CDCl_3$, 300 K) spectrum of compound **4**.

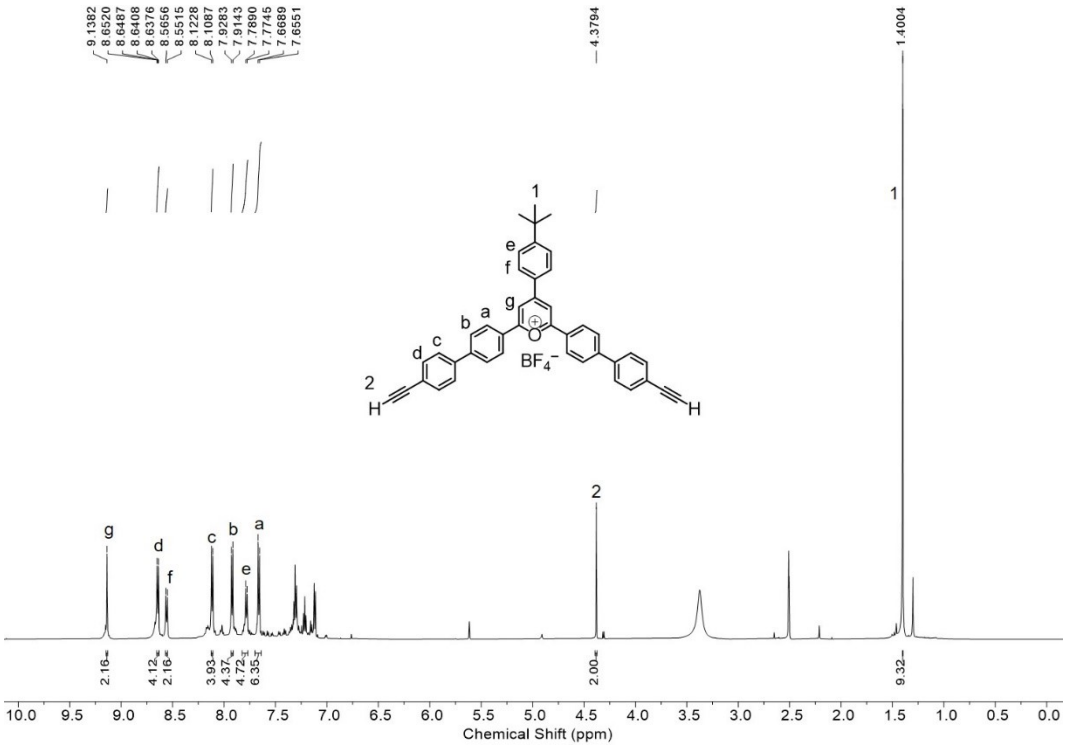


Figure S10. ^{1}H NMR (600 MHz, d_6-DMSO, 300 K) spectrum of compound **5**.

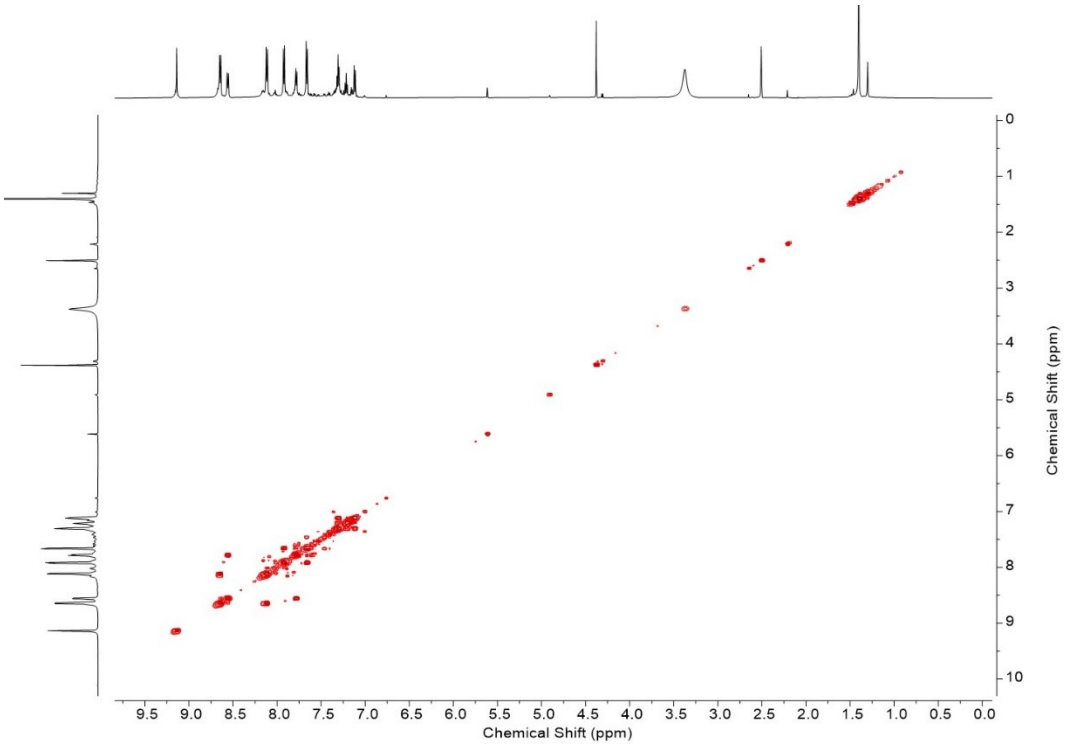


Figure S11. 2D COSY NMR (600 MHz, d_6-DMSO, 300 K) spectrum of compound **5**.

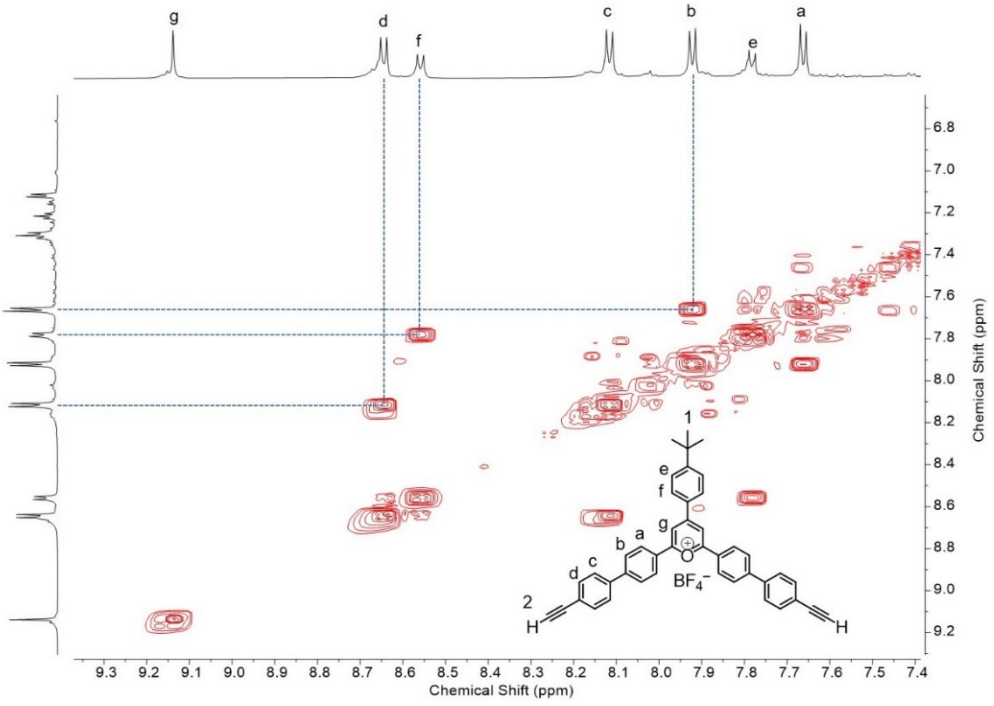


Figure S12. 2D COSY NMR (600 MHz, d_6-DMSO, 300 K) spectrum of compound **5** (aromatic region).

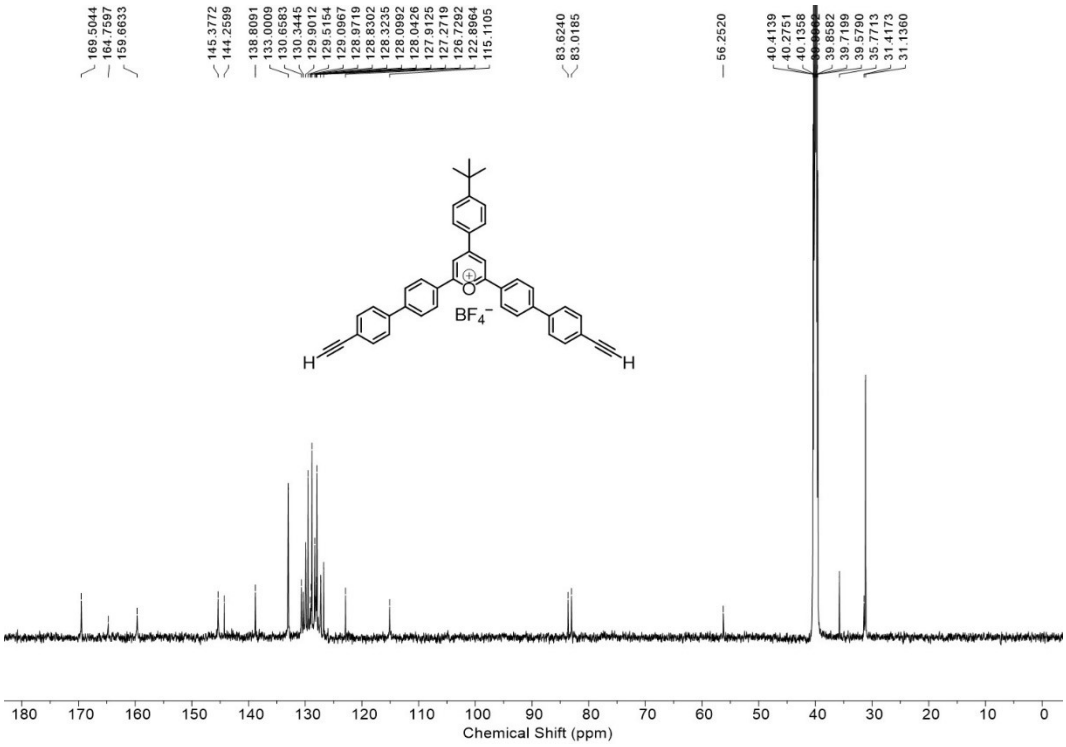


Figure S13. ^{13}C NMR (150 MHz, d_6-DMSO, 300 K) spectrum of compound **5**.

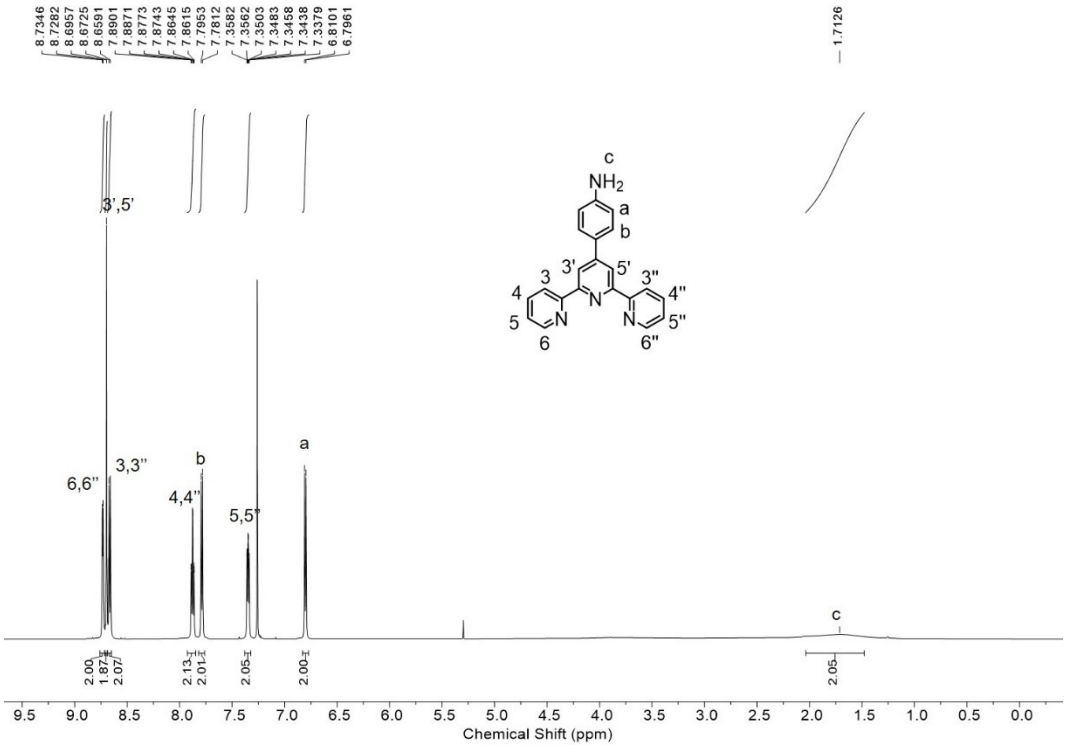


Figure S14. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of compound **6**.

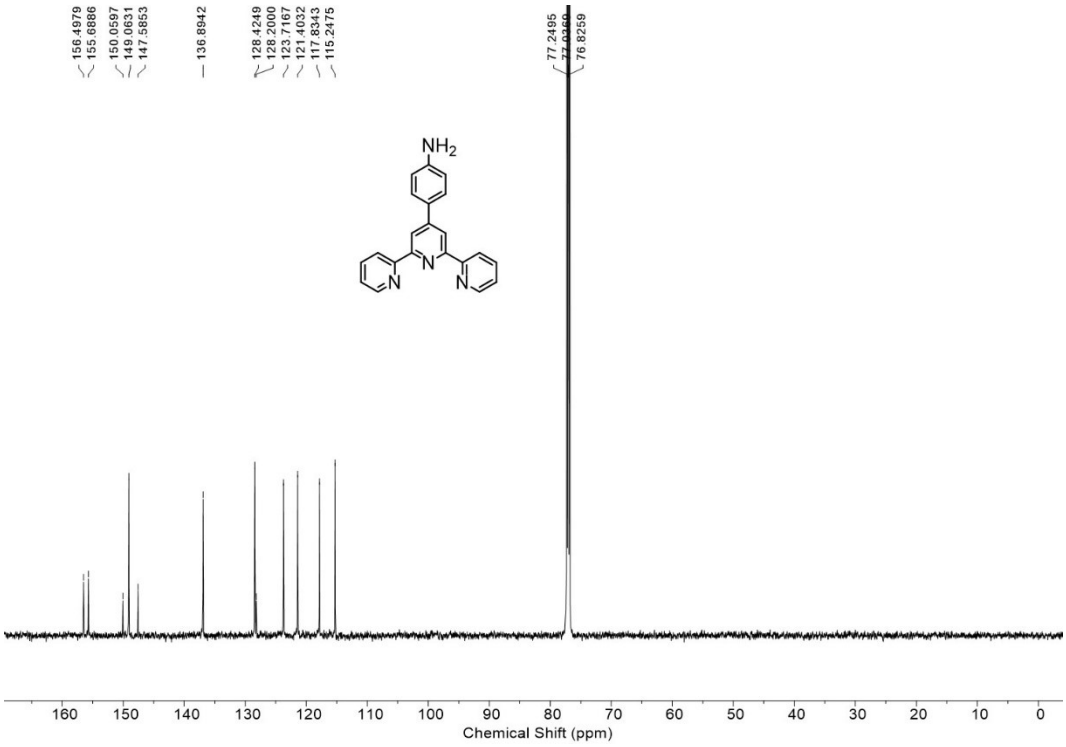


Figure S15. ^{13}C NMR (150 MHz, $CDCl_3$, 300 K) spectrum of compound **6**.

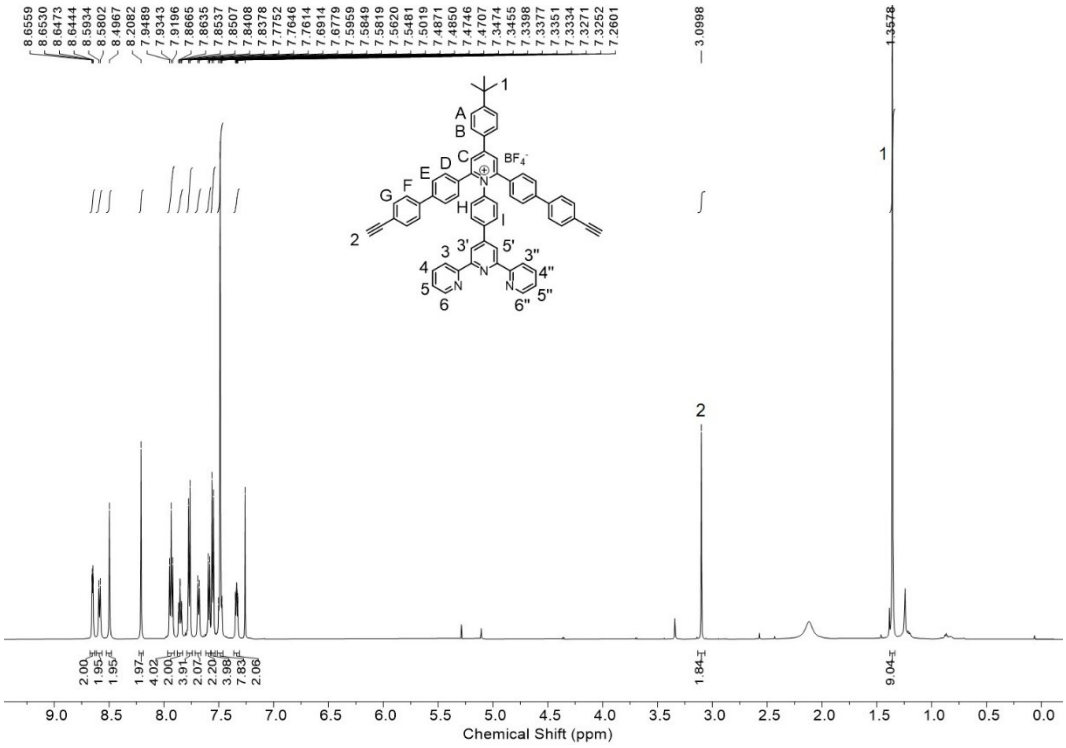


Figure S16. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of monomer **M**.

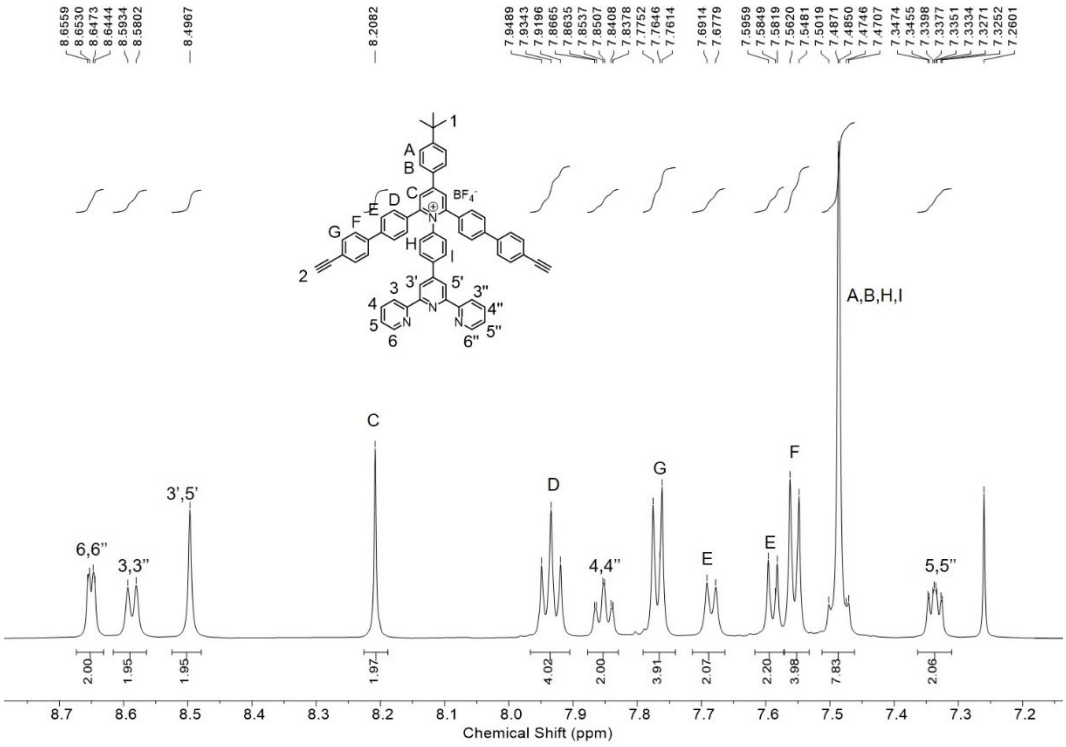


Figure S17. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of monomer **M** (aromatic region).

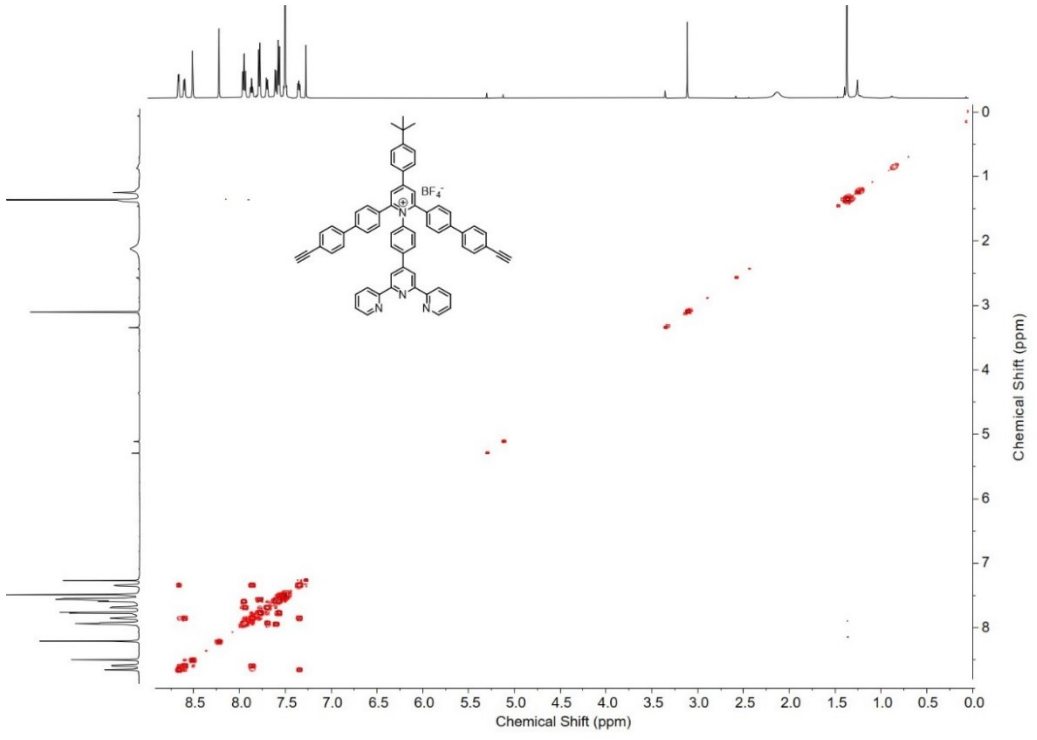


Figure S18. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of monomer **M**.

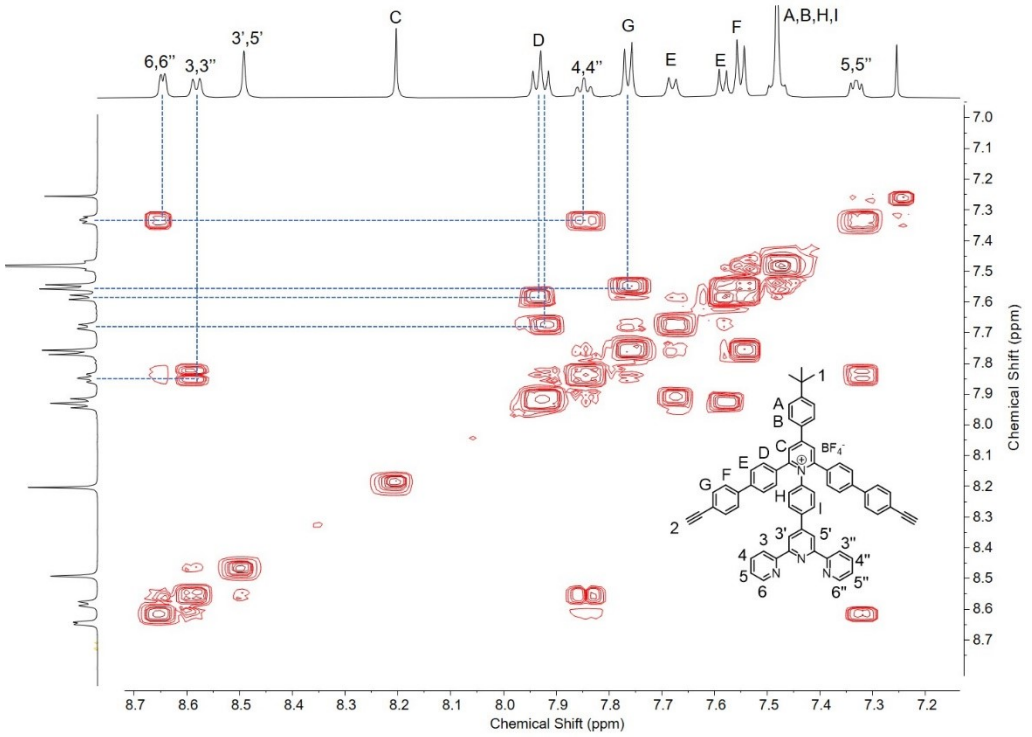


Figure S19. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of monomer **M** (aromatic region).

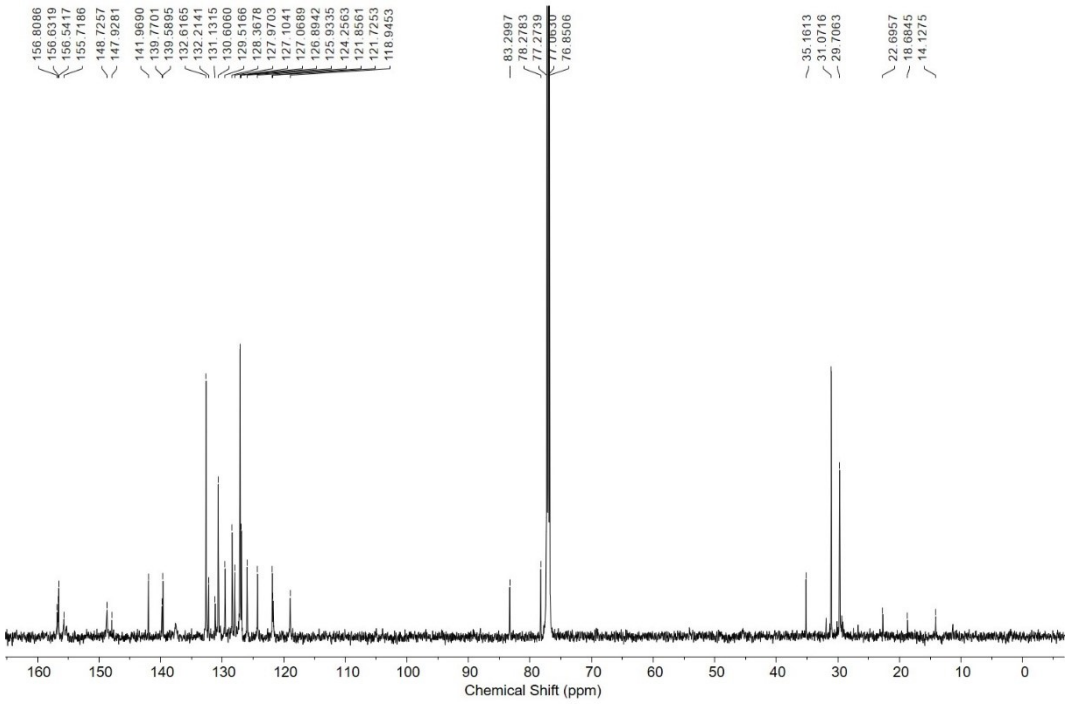


Figure S20. ^{13}C NMR (150 MHz, $CDCl_3$, 300 K) spectrum of monomer **M**.

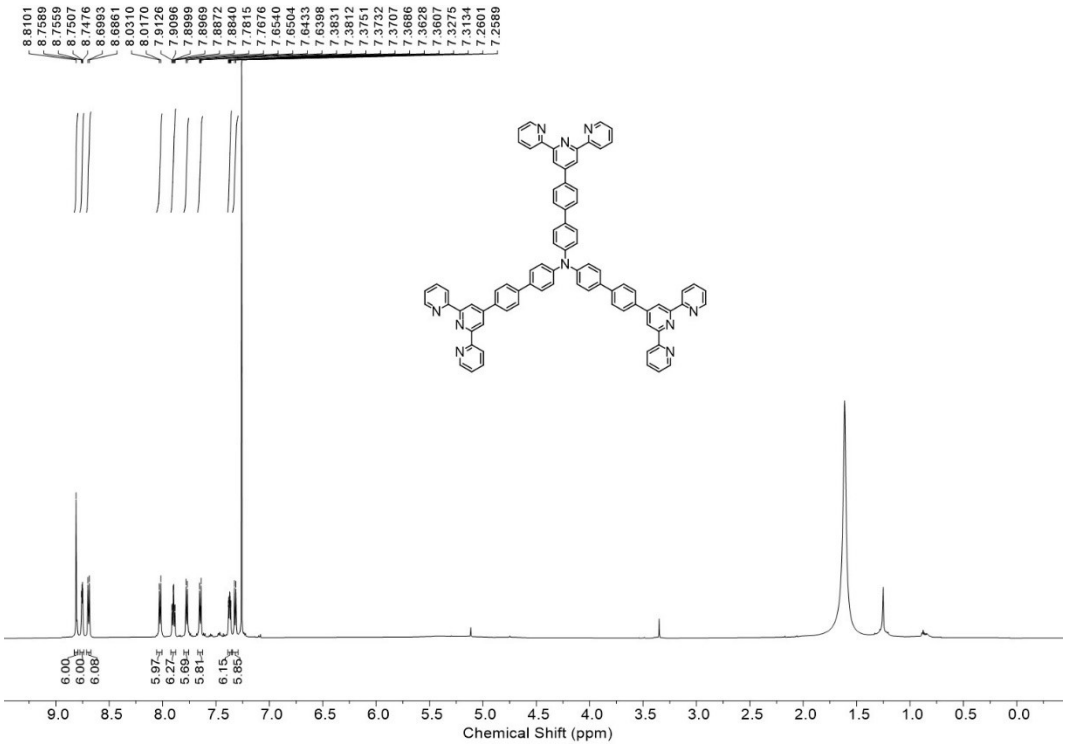


Figure S21. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of ligand **L1**.

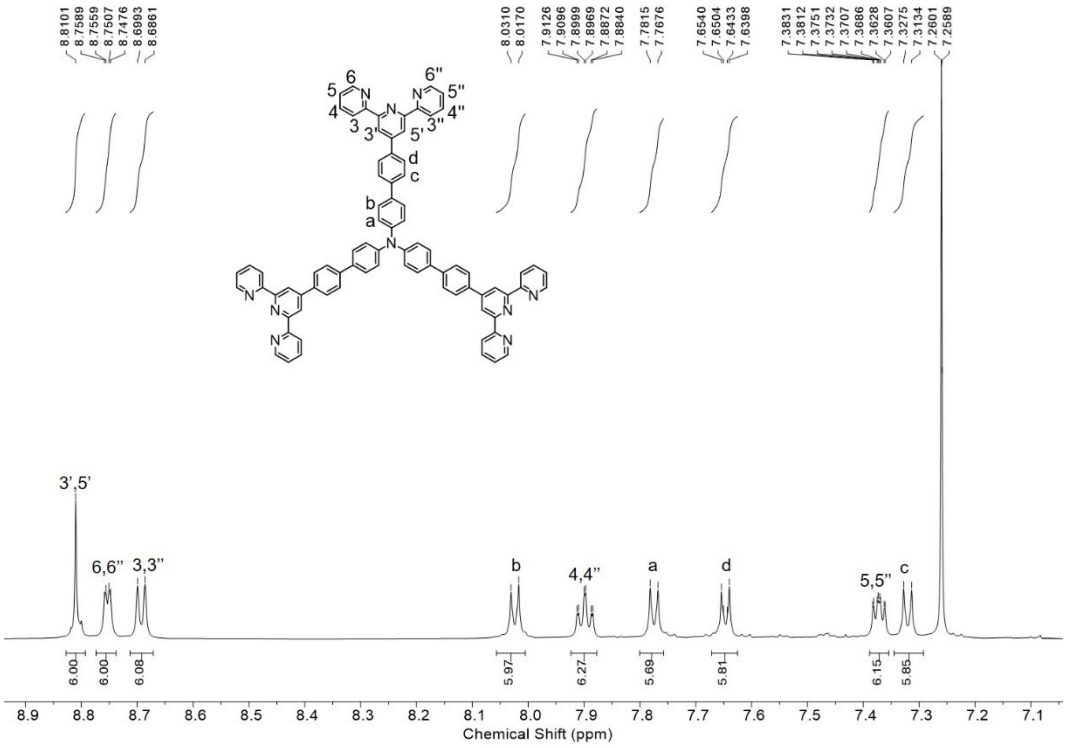


Figure S22. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of ligand **L1** (aromatic region).

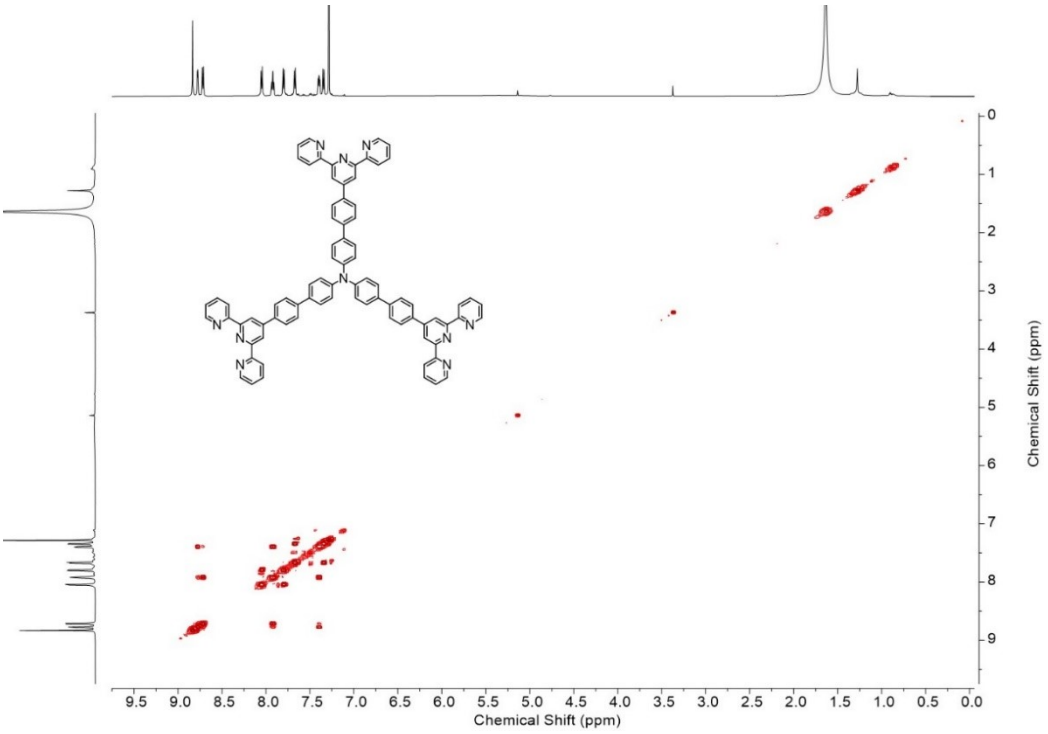


Figure S23. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of ligand **L1**.

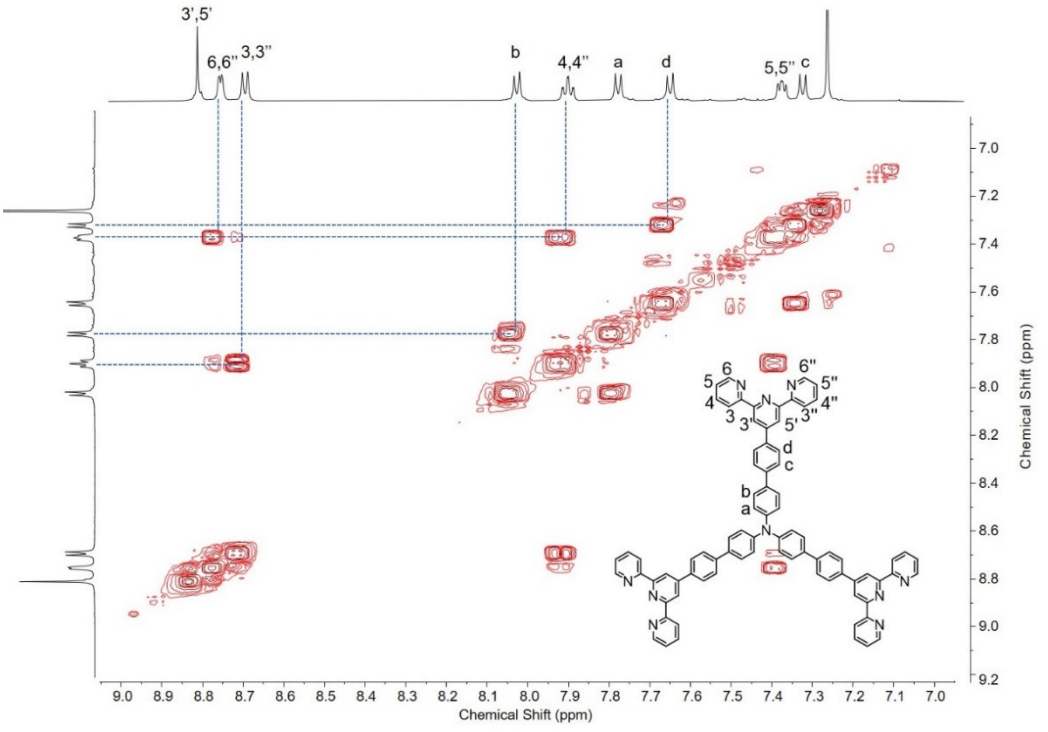


Figure S24. 2D COSY NMR (600 MHz, $CDCl_3$, 300 K) spectrum of ligand **L1** (aromatic region).

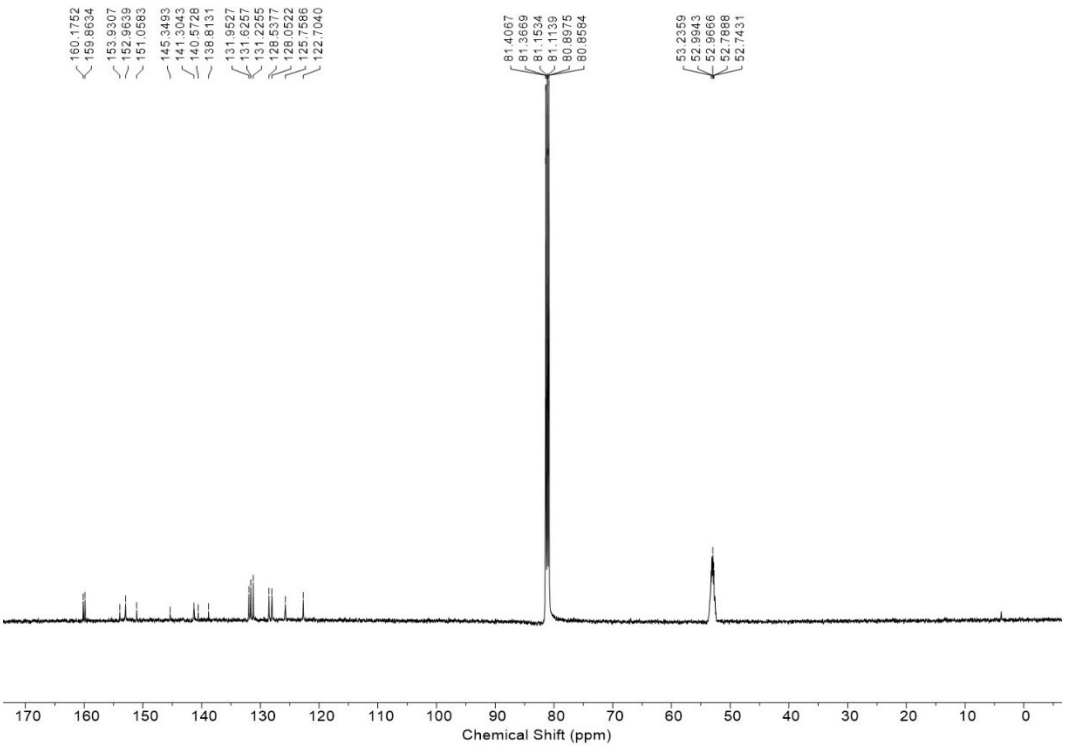


Figure S25. ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$, 300 K) spectrum of monomer **L1**.

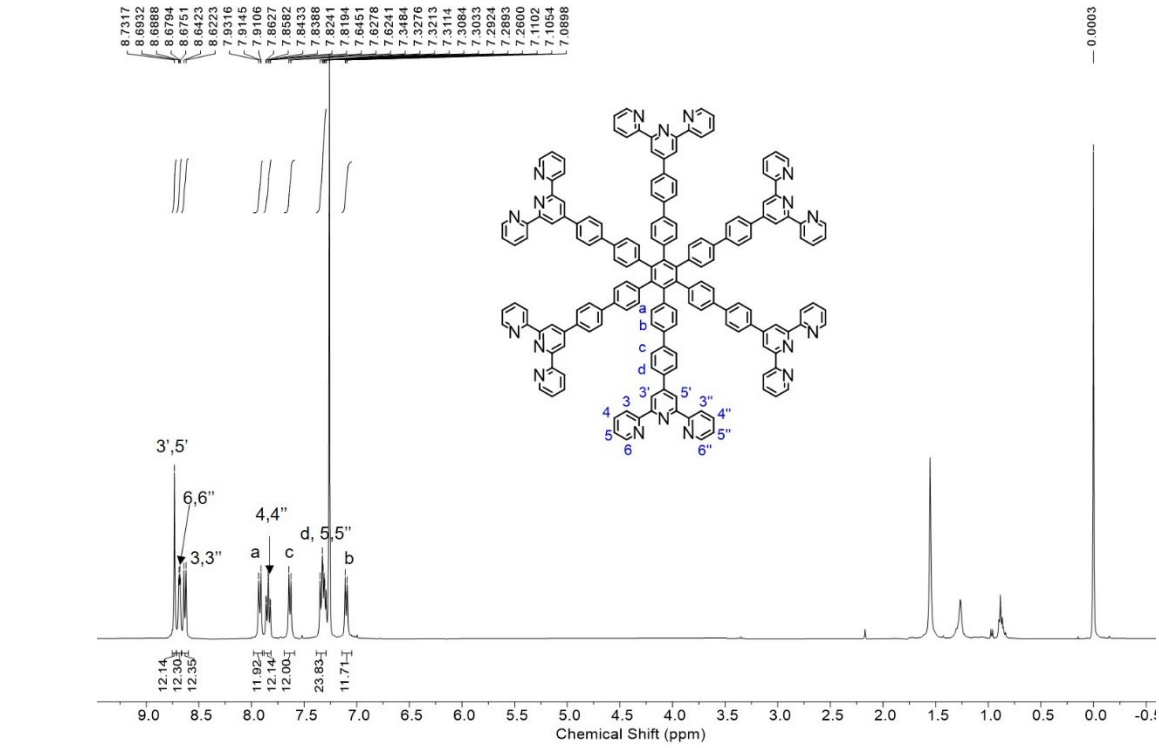


Figure S26. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of ligand **L2**.

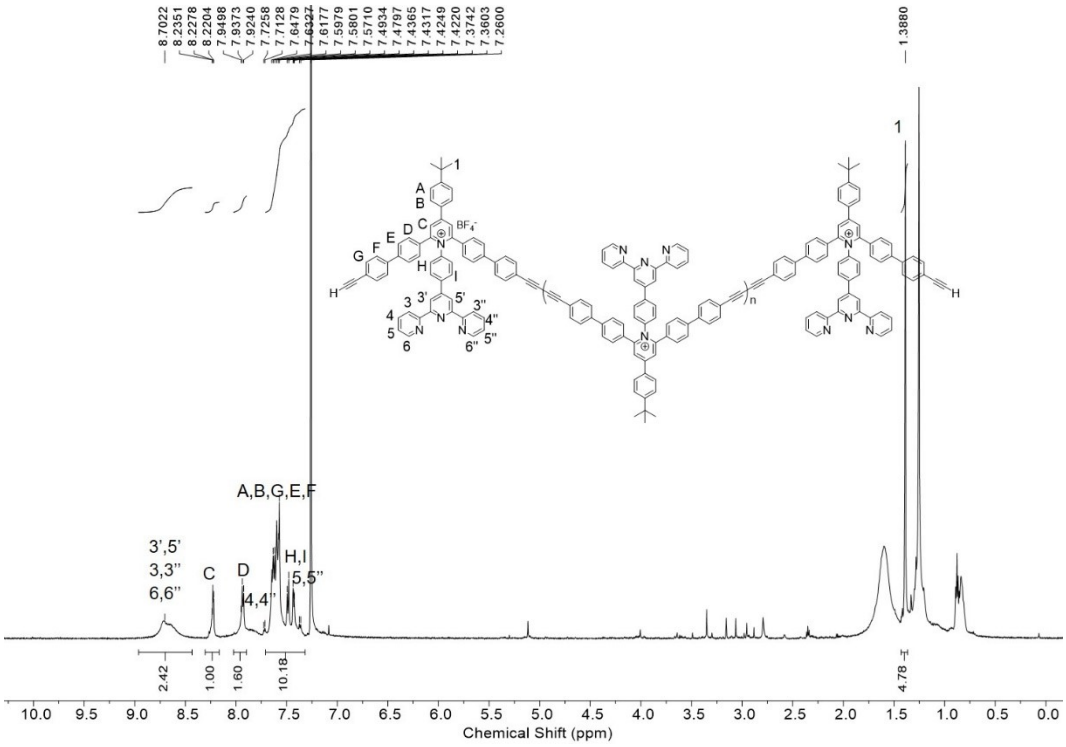


Figure S27. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of polymer **P**.

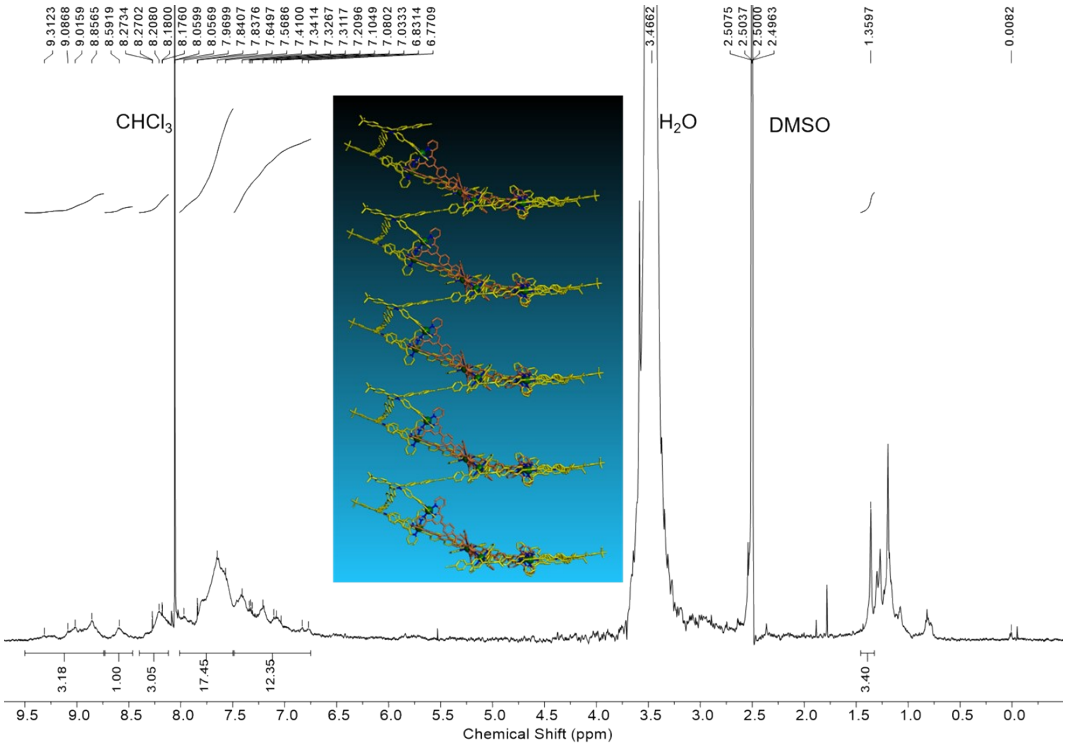


Figure S28. ^{1}H NMR (600 MHz, DMSO-d_6, 300 K) spectrum of **H1**.

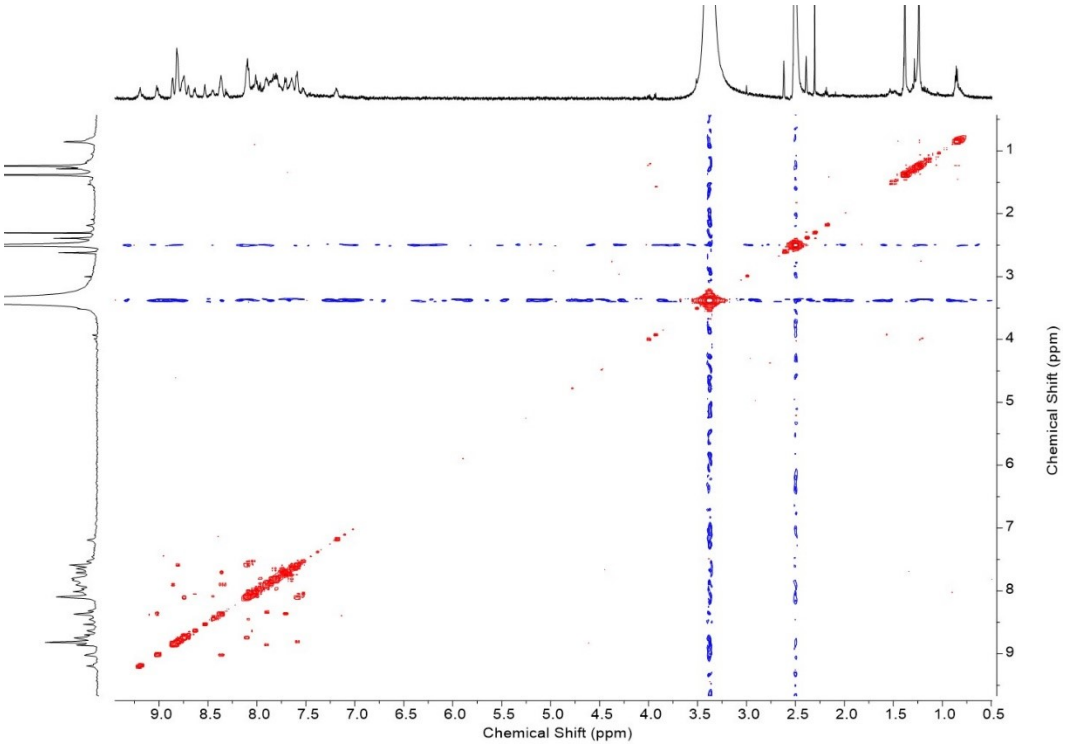


Figure S29. 2D COSY NMR (600 MHz, DMSO-d_6, 300 K) spectrum of **H1**.

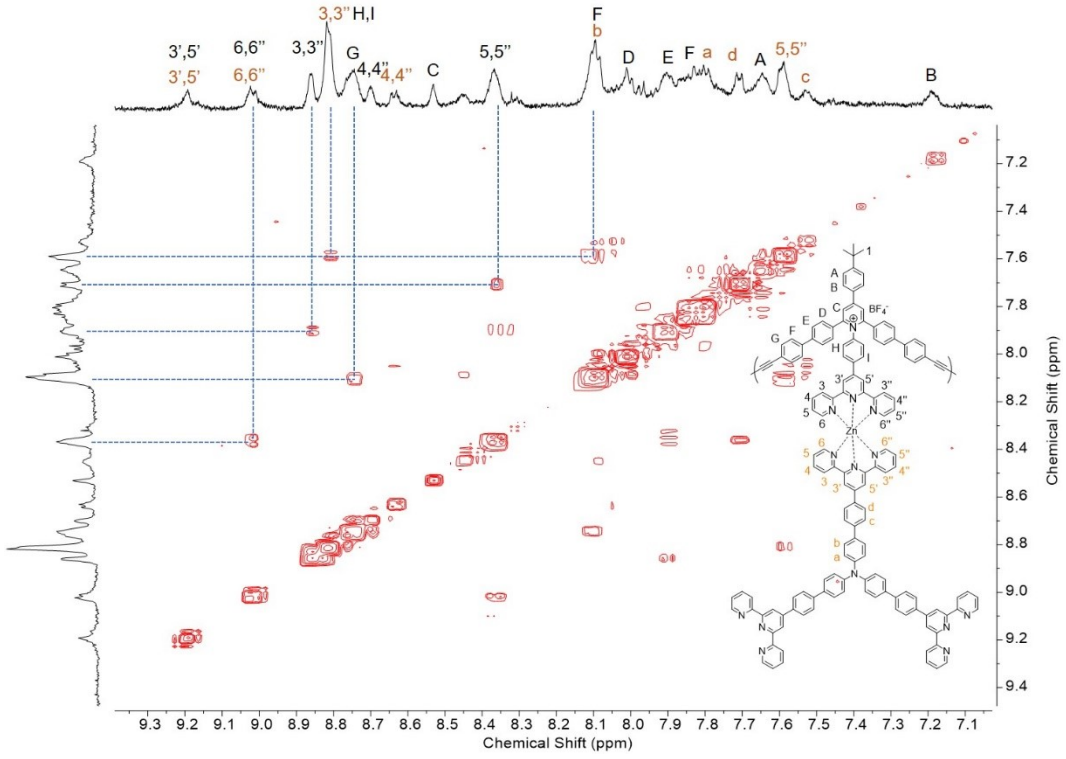


Figure S30. 2D COSY NMR (600 MHz, DMSO-d_6, 300 K) spectrum of **H1** (aromatic region).

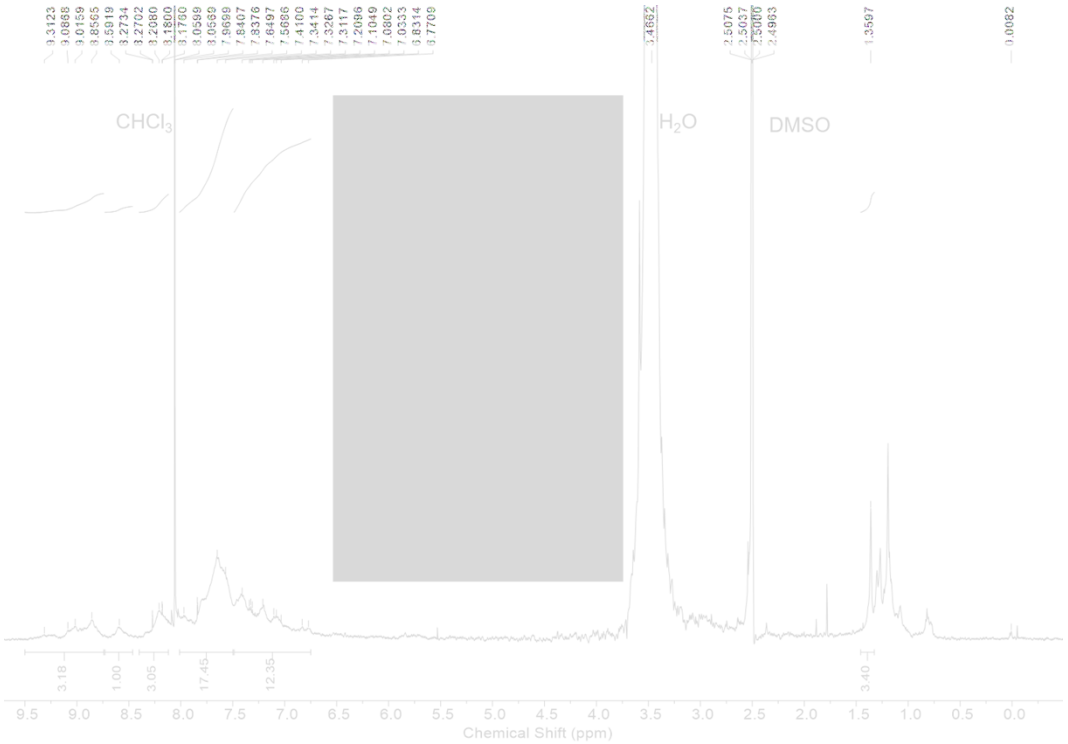


Figure S31. ^{1}H NMR (600 MHz, $CDCl_3$/ DMSO-d_6, 300 K) spectrum of **H2**.

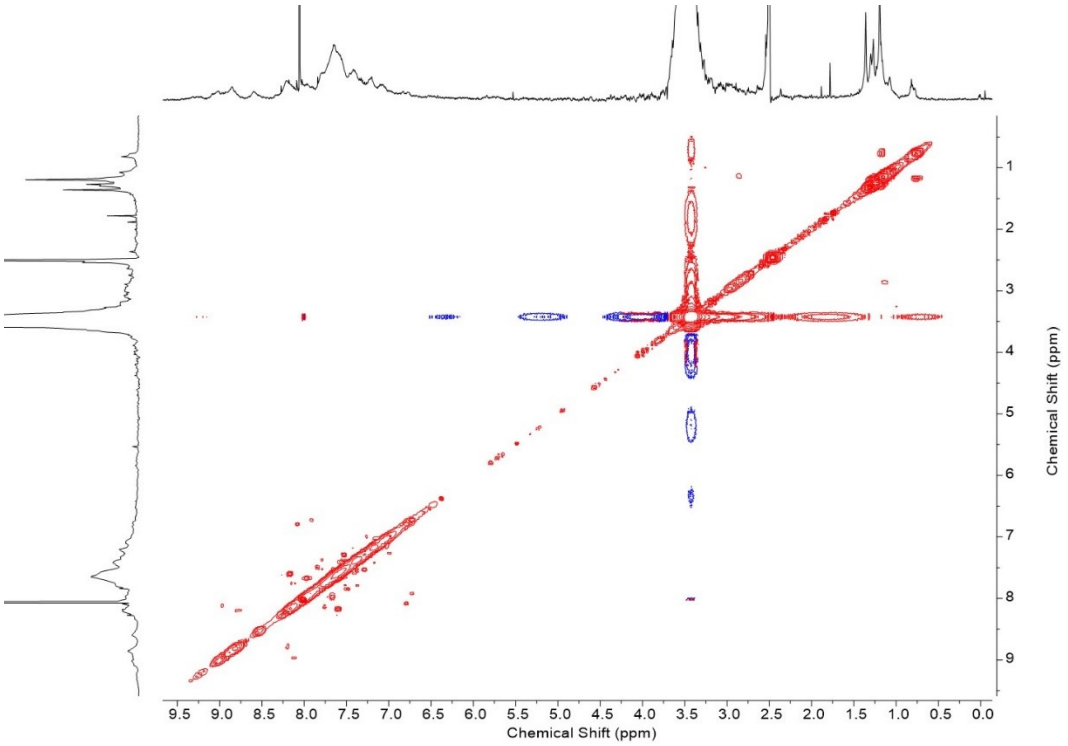


Figure S32. 2D COSY NMR (500 MHz, $CDCl_3$/ DMSO-d_6, 300 K) spectrum of **H2**.

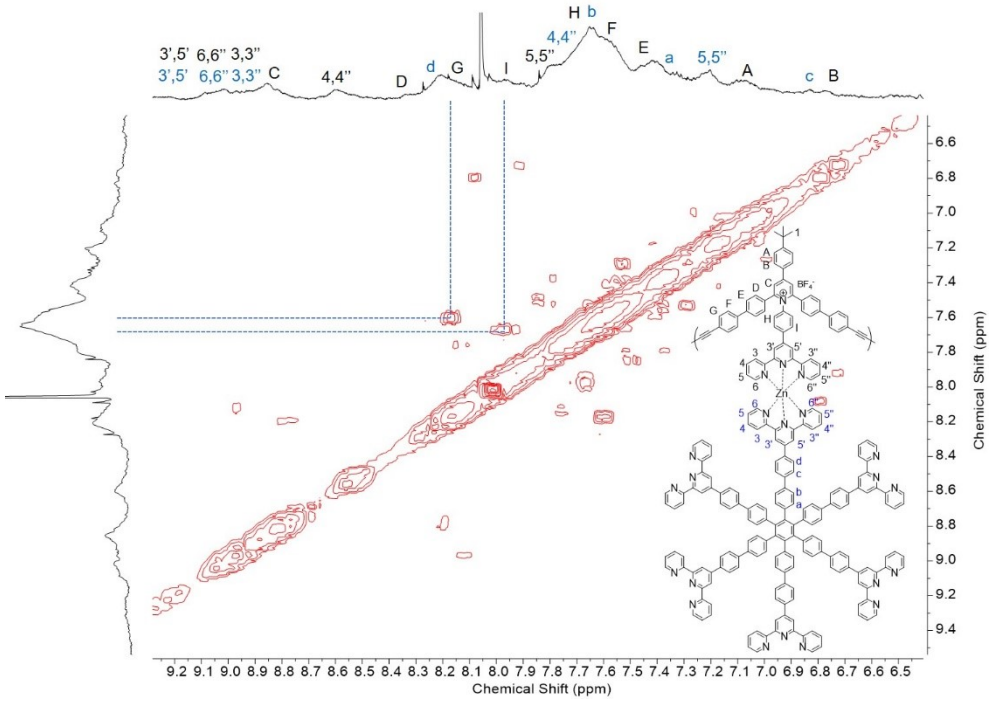


Figure S33. 2D COSY NMR (500 MHz, $CDCl_3$/ DMSO-d_6, 300 K) spectrum of **H2** (aromatic region).

4. MALDI-TOF MS spectra

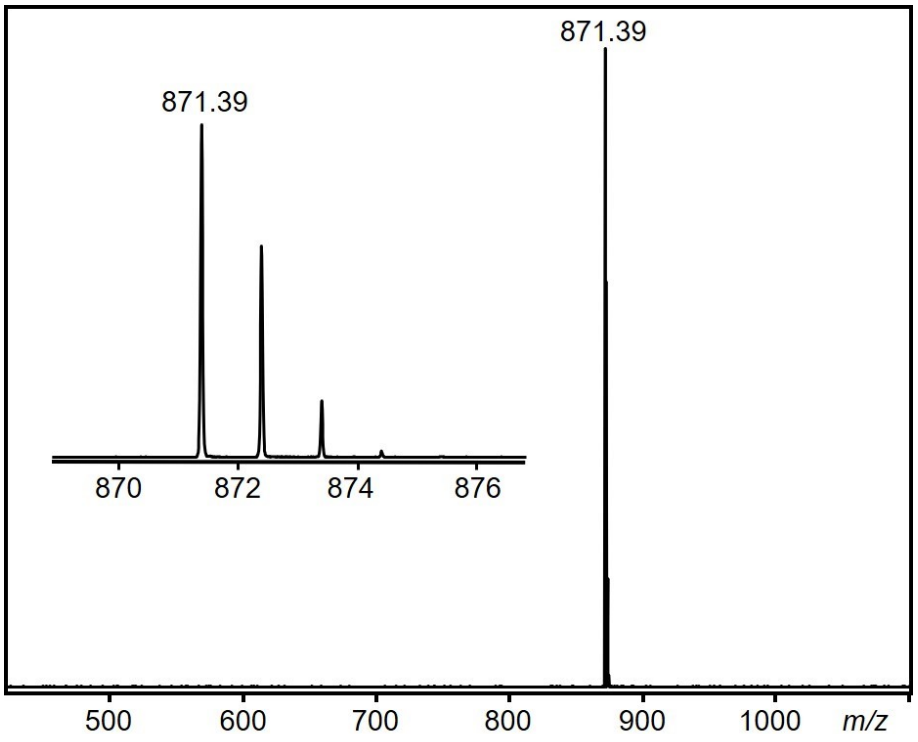


Figure S34. MALDI-TOF MS of monomer **M**.

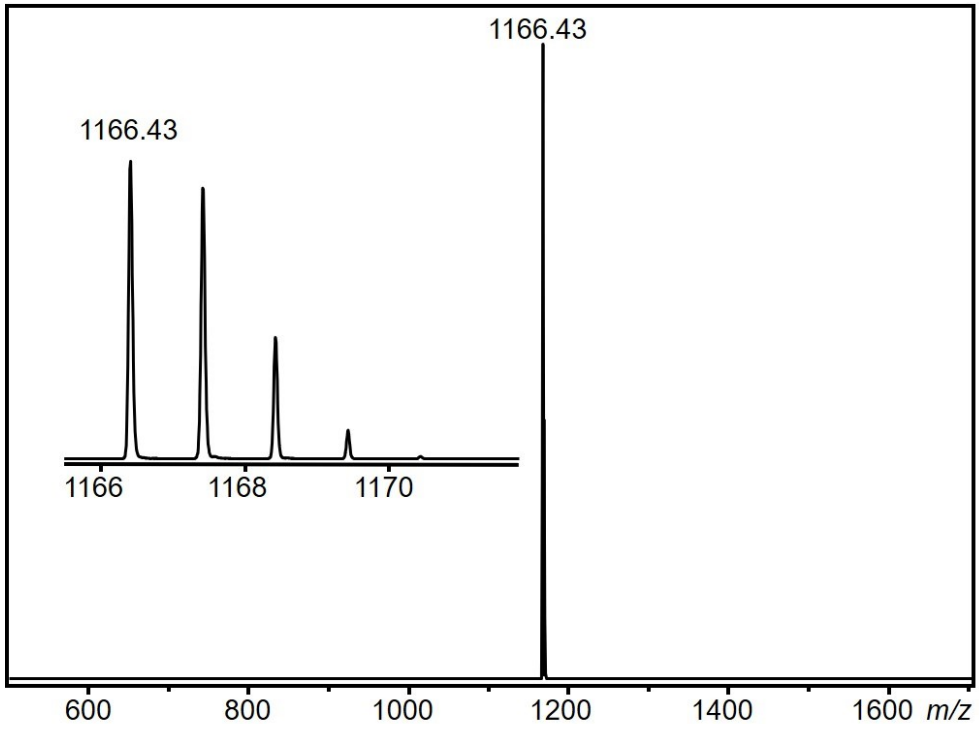


Figure S35. MALDI-TOF MS of ligand **L1**.

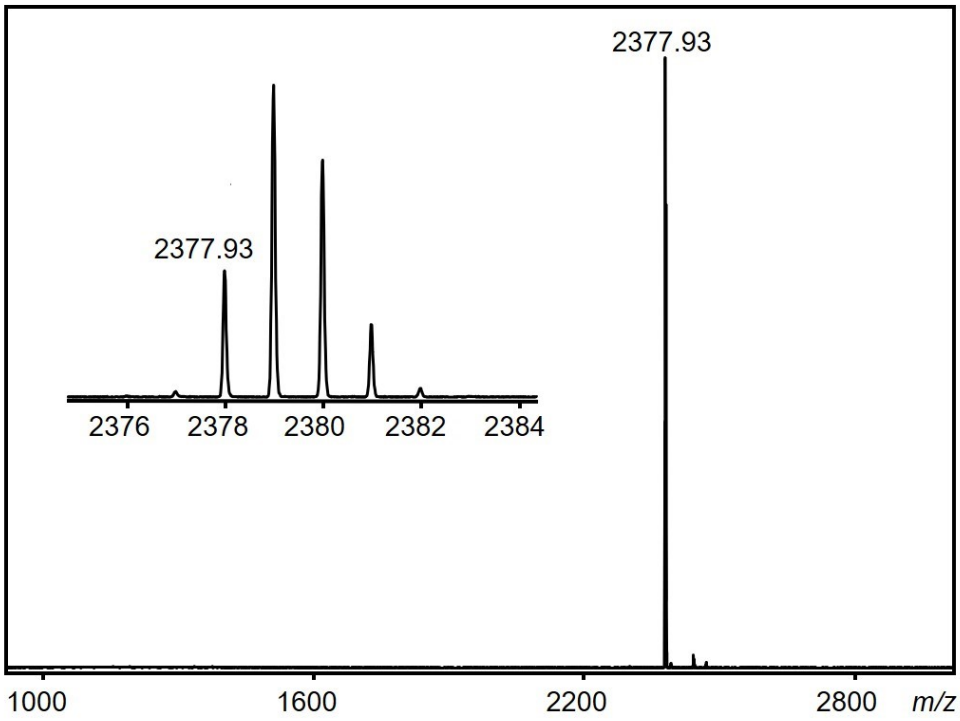


Figure S36. MALDI-TOF MS of ligand **L2**.

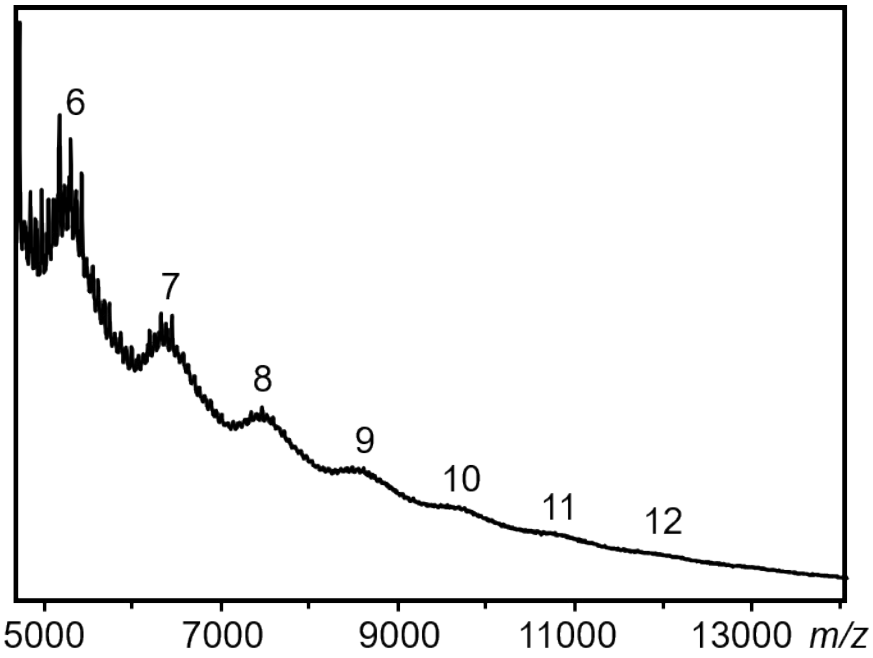


Figure S37. MALDI-TOF MS of polymer **P**.

5. TEM and AFM images

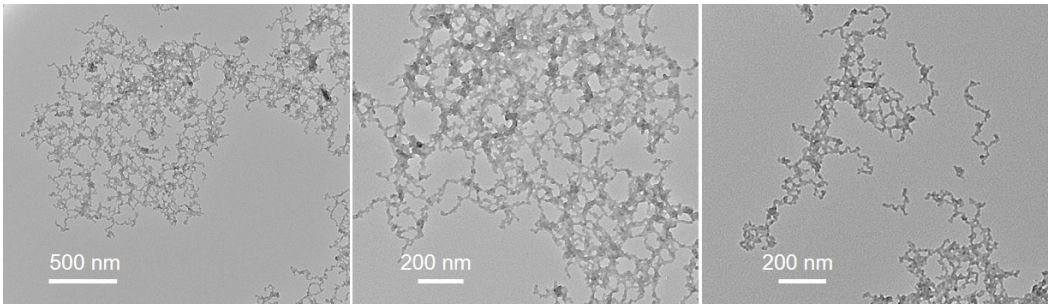


Figure S38. TEM images of polymer **P**.

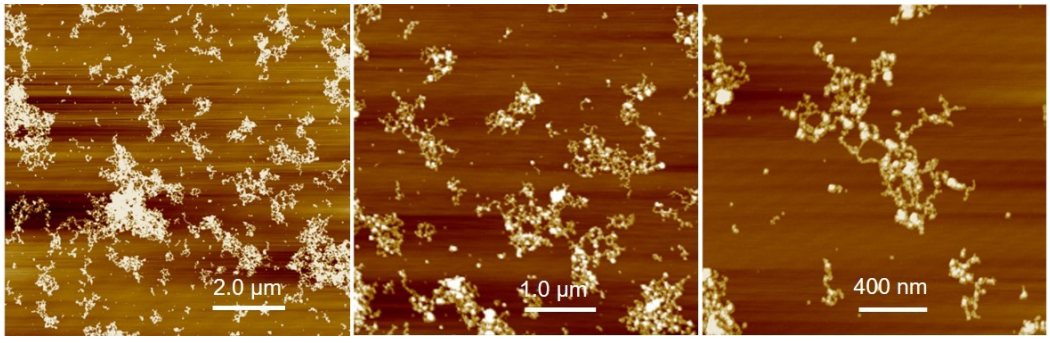


Figure S39. AFM images of polymer **P**.

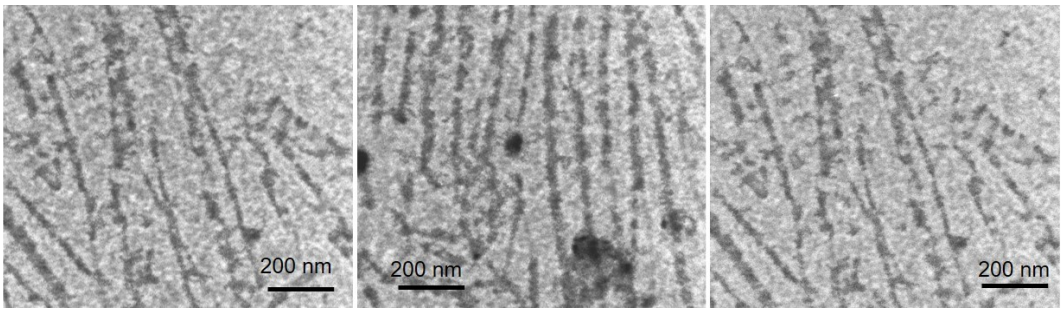


Figure S40. TEM images of helicoid **H2**.

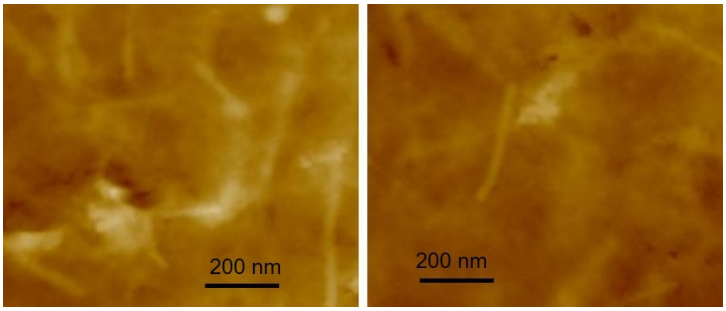


Figure S41. AFM images of helicoid **H2**.

6. UV-Vis and fluorescence spectra

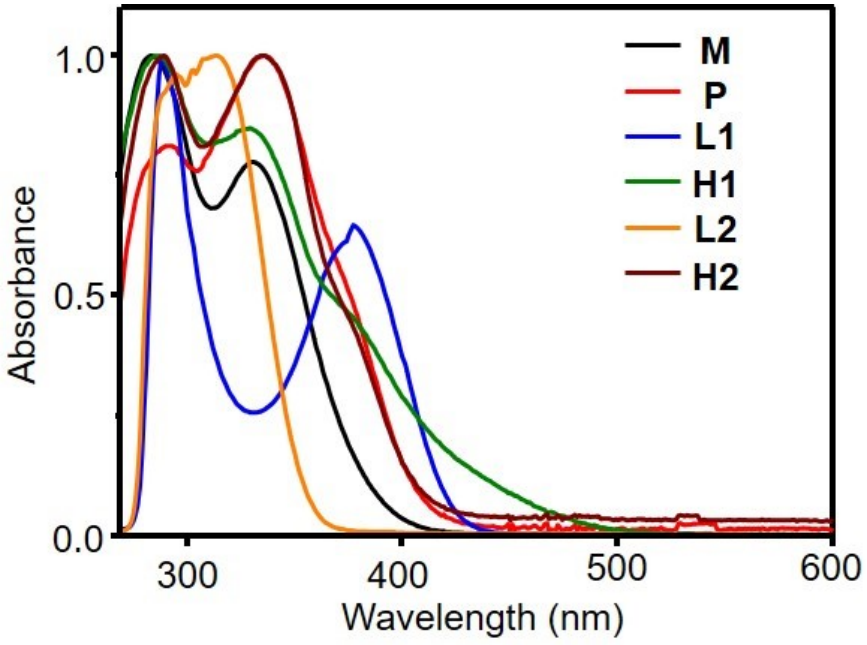


Figure S42. Normalized UV absorbance spectra of monomer **M**, ligand **L1**, ligand **L2**, polymer **P**, helicoid **H1**, and helicoid **H2**.

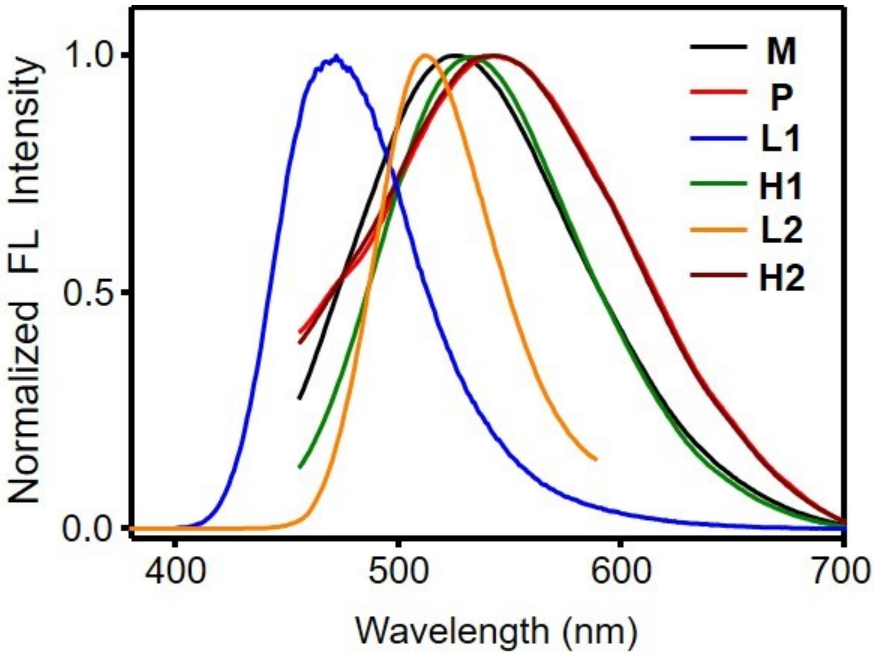


Figure S43. Normalized fluorescence spectra of monomer **M**, ligand **L1**, ligand **L2**, polymer **P**, helicoid **H1**, and helicoid **H2**.

7. References

1. Y. Li, H. Wu, P. Teng, G. Bai, X. Lin, X. Zuo, C. Cao, and J. Cai, *J. Med. Chem.*, 2015, **58**, 4802-4811.

2. T. Bauer, A. D. Schlüter, and J. Sakamoto, *Synlett*, 2010, **6**, 877-880.