Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers

Solvent-Driven Selective π-Cation Templating in Dynamic Assembly of Interlocked Molecules

Andrew B. Pun,[1] Kevin J. Gagnon,[3] Liana Klivansky,[1] Simon J. Teat,[3] Zhan-Ting Li,[2*] Yi Liu[1*]

1. The Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Rd, MS 67R6110, Berkeley, CA, USA 94720

2. Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, China, 200433

3. Advanced Light Source, Lawrence Berkeley National Laboratory, One Cyclotron Rd, MS 67R6110, Berkeley, CA, USA 94720

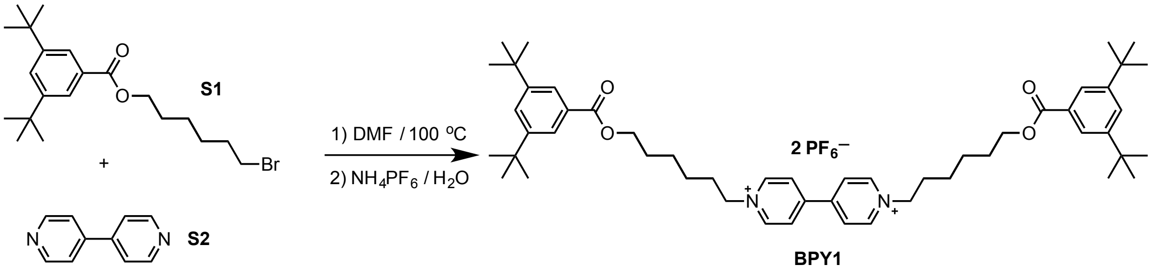
Email: yliu@lbl.gov, ztli@fudan.edu.cn

Electronic Supplementary Information

Experimental Section

General Methods: Reagents were purchased from Aldrich or synthesized as described. Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV-light. Melting points were determined on an Electrothermal MEL-TEMP 3.0 apparatus and are uncorrected. Proton and carbon nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) spectra were recorded on a Bruker Avance500 II, using the deuterated solvent as lock and the residual solvent as internal standard. All chemical shifts are quoted using the δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Electrospray mass spectra (ESI-MS) were measured on a Q-Tof Premier mass spectrometer from Micromass Technologies (now Waters Corporation). Cyclic voltammetry was performed using a 273A potentiostat (Princeton Applied Research), wherein glassy carbon, platinum and a silver wire act as the working electrode, the counter electrode and the reference electrode, respectively. Samples were prepared in CH_3CN solution with tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte at a scan rate of 100 mV s^{-1}, using ferrocene/ferronium (F_c/F_c^+) redox couple as an internal standard. Trisaldehyde **1**,[s1] bromide **S1**,[s2] **TPY1**[s2] and **TPY2**[s2] were synthesized according to literature procedures.

Scheme S1. Synthesis of **BPY1**.



Synthesis of **BPY1**. Bispyridine **S2** (156 mg, 1.00 mmol), bromide **S1** (1.19 g, 3.00 mmol) and DMF (5 mL) were mixed in a round bottom flask and heated at 100 ºC for 24 hrs. The flask was cooled to room temperature and H_2O (2 mL) was added. NH_4PF_6 was added to the mixture until there was no more precipitate formed. The precipitate was collected by filtration, washed with H_2O, and further purified by column chromatography (SiO_2, Acetone, followed by 0.3 wt/v% NH_4PF_6 in Acetone) to give the product as a white solid (0.812 g, 75%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.80 (d, *J* = 6.7 Hz, 4 H), 8.24 (d, *J* = 6.7 Hz, 4 H), 7.85 (d, *J* = 1.9 Hz, 4 H), 7.61 (t, *J* = 1.9 Hz, 2 H), 4.61 (t, *J* = 7.3 Hz, 4 H), 4.27 (t, *J* = 6.7 Hz, 4 H), 2.04 (m, 4 H), 1.76 (m, 4 H), 1.47 (m, 8 H), 1.33 (s, 36 H). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 167.5, 151.0, 150.4, 145.0, 129.7, 127.2, 127.1, 123.7, 64.6, 62.4, 34.9, 33.9, 31.4, 28.3, 25.5, 25.2. M.P.: >300 ºC (dec). HRMS for $C_{52}H_{74}F_{12}N_2O_4P_2$ (ESI): $[M - PF_6]^+$: calcd 935.5285, found 935.5322; $[M - 2PF_6]^{2+}$: calcd 395.2819, found 395.2825.

References:

s1. N. Kaur, J-G. Delcros, J. Imran, A. Khaled, M. Chehtane, N. Tschammer, B. Martin, O. Phanstiel, *J. Med. Chem.* 2008, **51**, 1393-1401.

s2. A. Pun, D. A. Hanifi, G. Kiel, E. O'Brien and Y. Liu, *Angew. Chem. Int. Ed.*, 2012, **51**, 13119-13122.

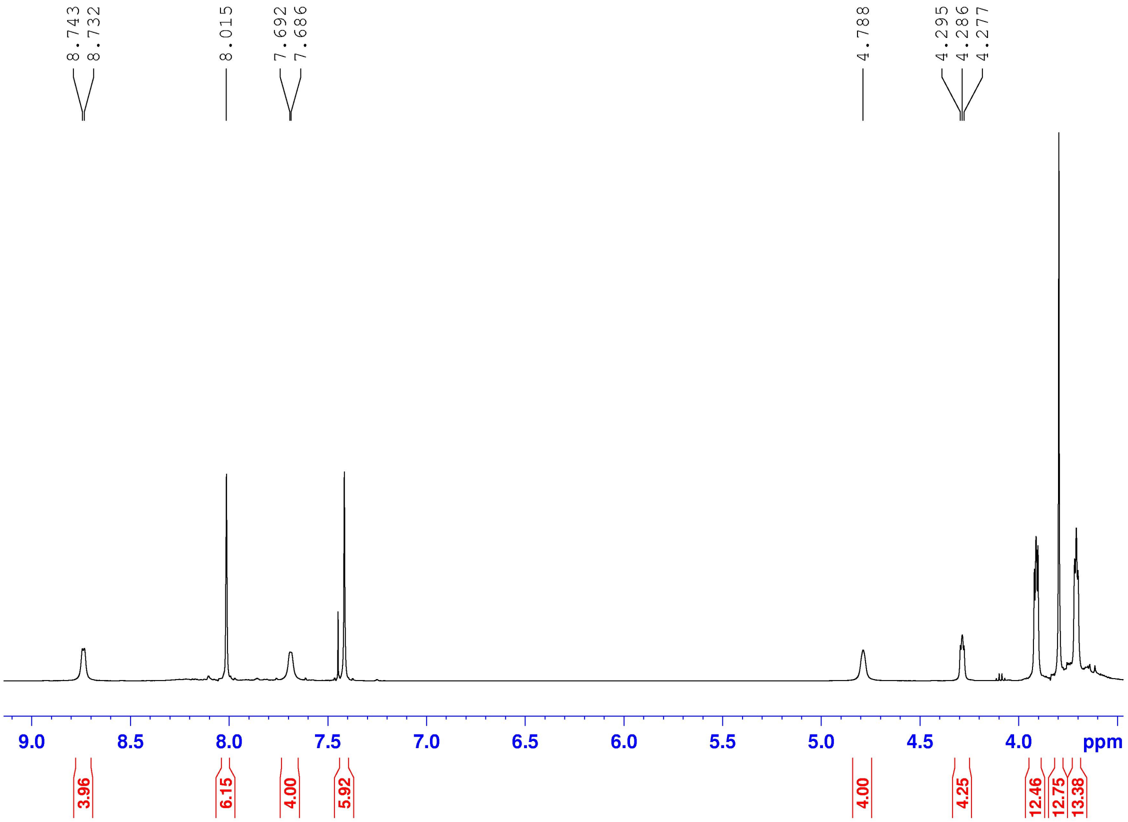


Figure S1. ^{1}H NMR spectrum of **LR2** from clipping reaction (in $CDCl_3/CD_3CN$, v/v 1:0.4). Due to fast equilibrium, the resonances are averaged to give a higher symmetry spectrum as opposed to that of **LR1**.

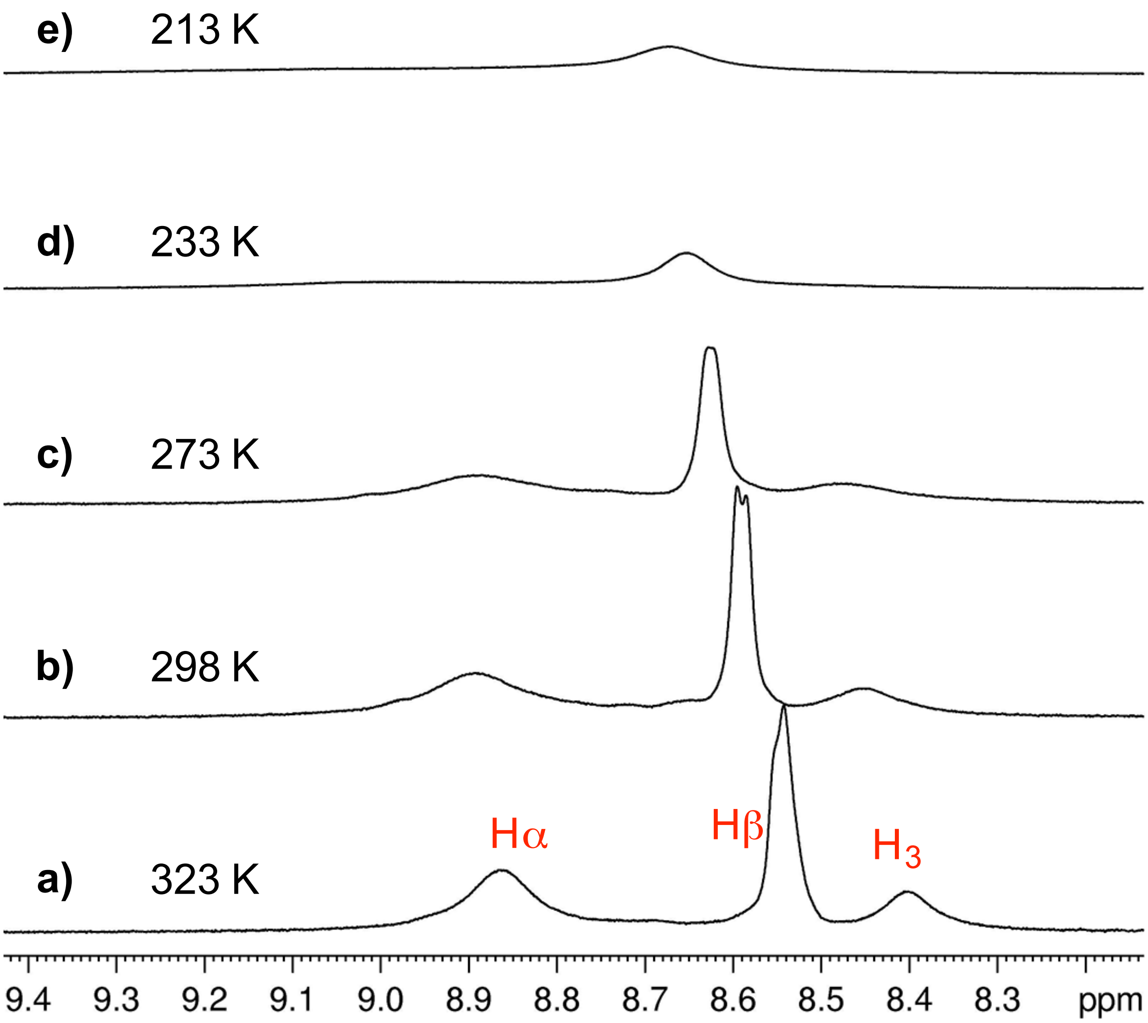
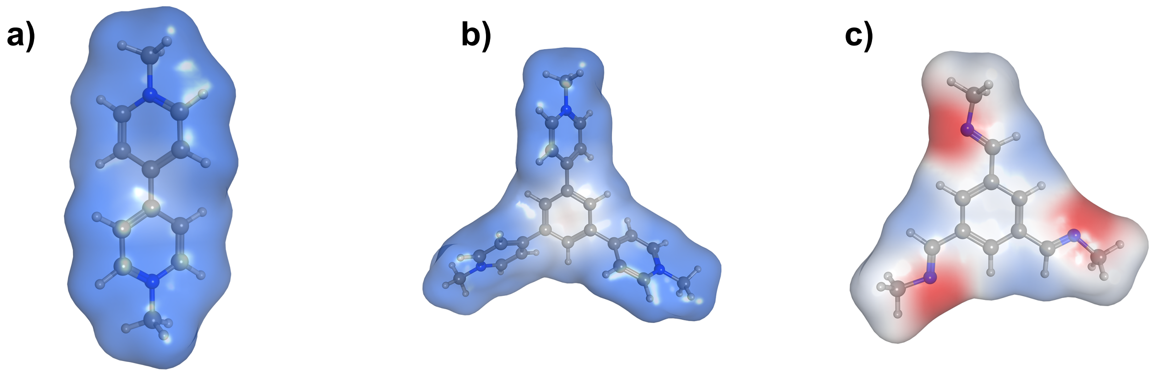


Figure S2. Partial ^{1}H NMR (500 MHz) spectra of **TPY1** in $CDCl_3$ at a) 323 K, b) 298 K, c) 273 K, d) 233 K, and e) 213 K.



BPY-Me **TPY-Me** **TIP-Me**

Figure S3. Electrostatic potential surfaces of three model compounds with methyl substituents. a) **BPY-Me**, b) **TPY-Me**, and c) **TIP-Me**. Blue represents positive electrostatic potential and red stands for negative electrostatic potential. The surfaces were optimized with the MMFF94x force field.

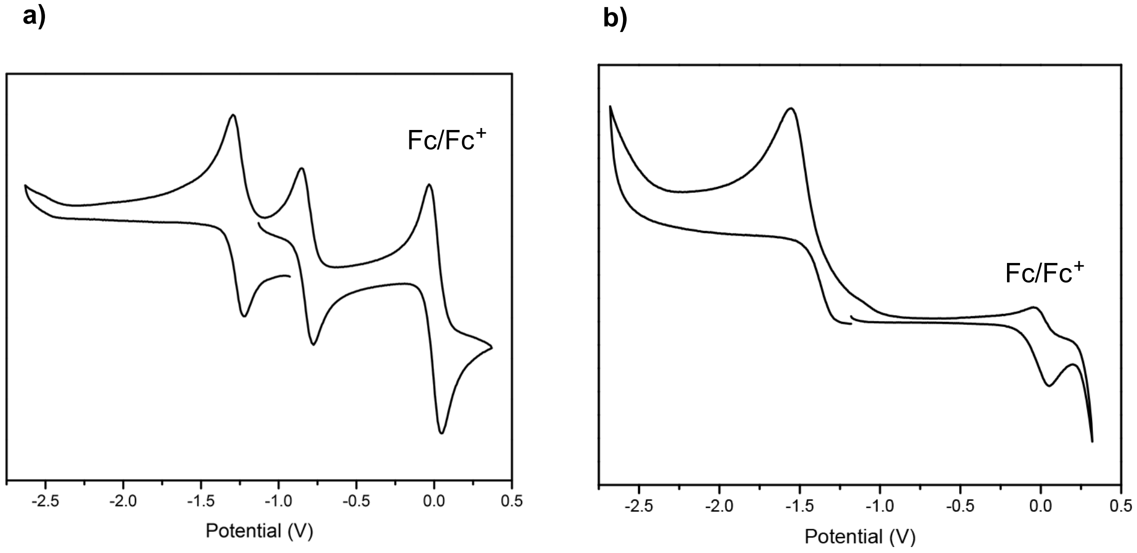


Figure S4. CV of a) **BPY1**, and b) **TPY1** in MeCN, using tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte, using ferrocene/ferronium (F_c/F_c^+) redox couple as an internal standard. The graphs were calibrated with respect to F_c.

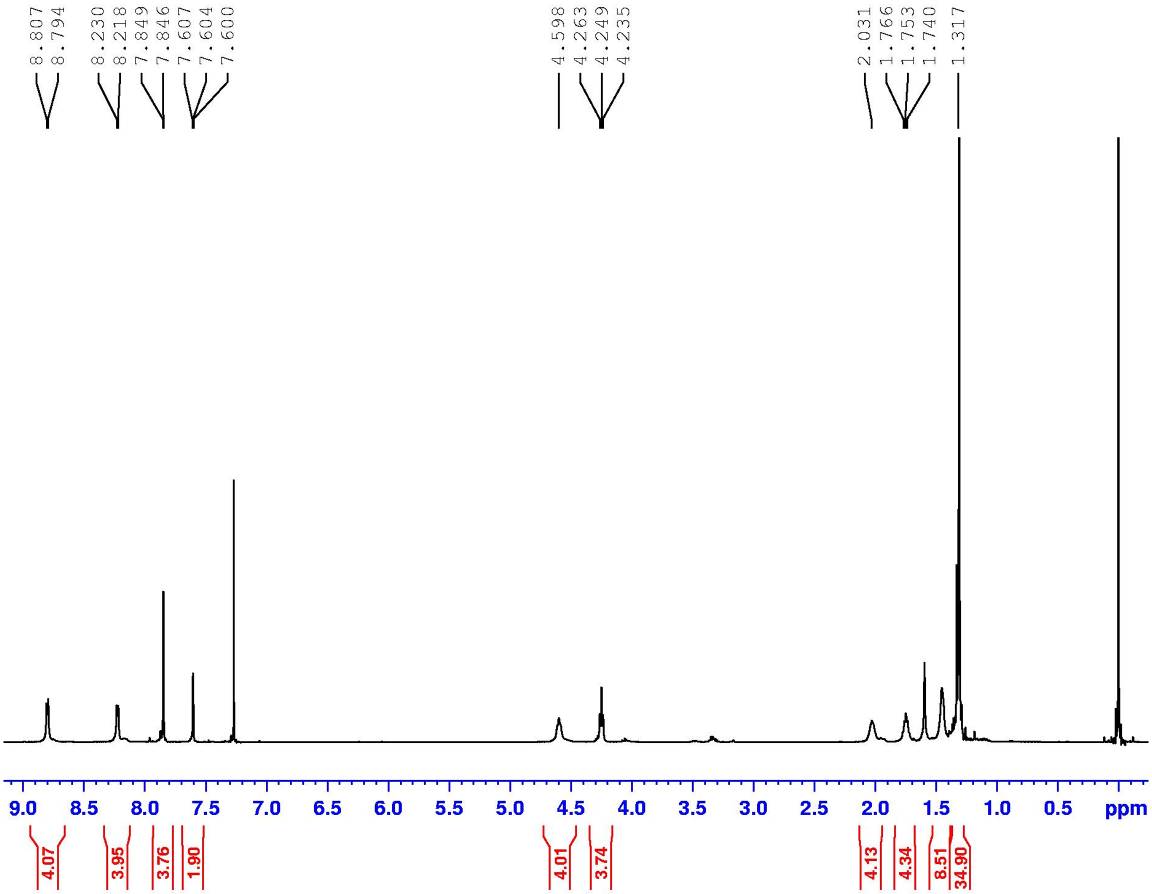


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 500 MHz) of **BPY1**.

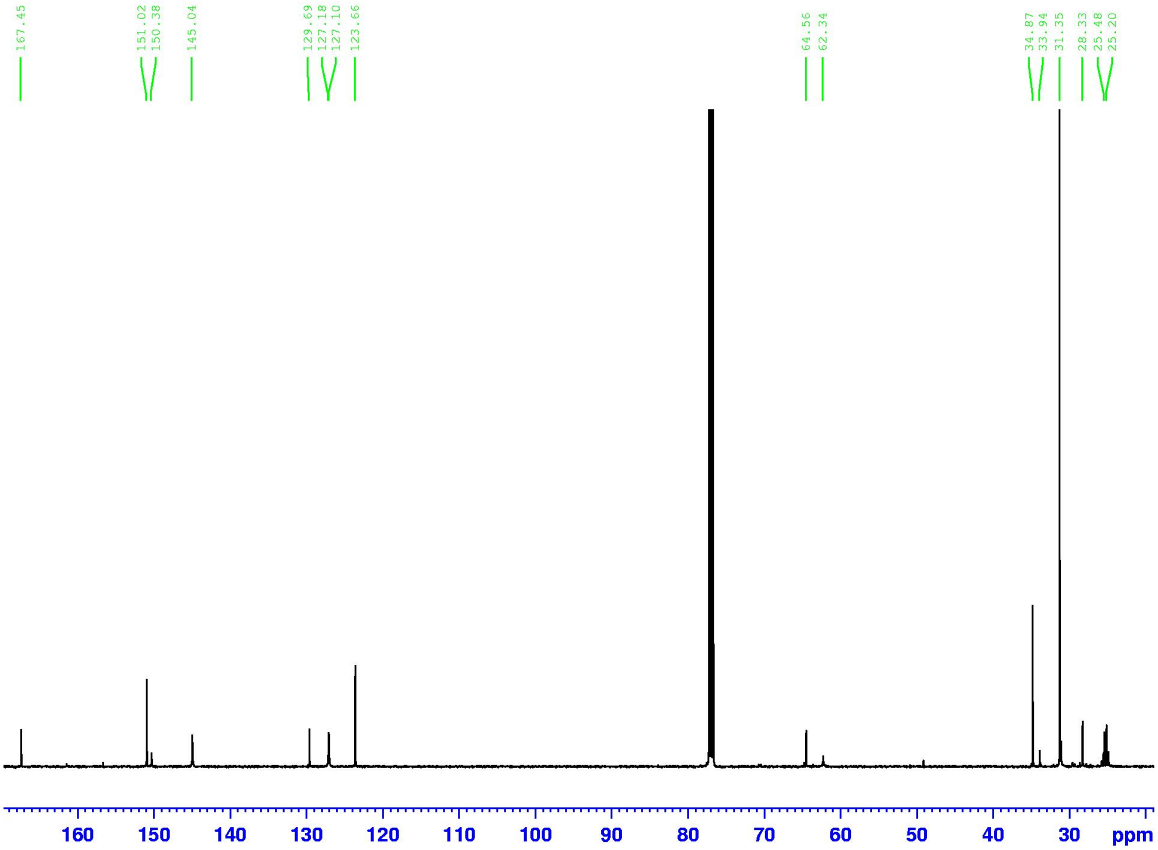


Figure S6. ^{13}C NMR spectrum (CDCl$_3$, 298 K, 125 MHz) of **BPY1**.

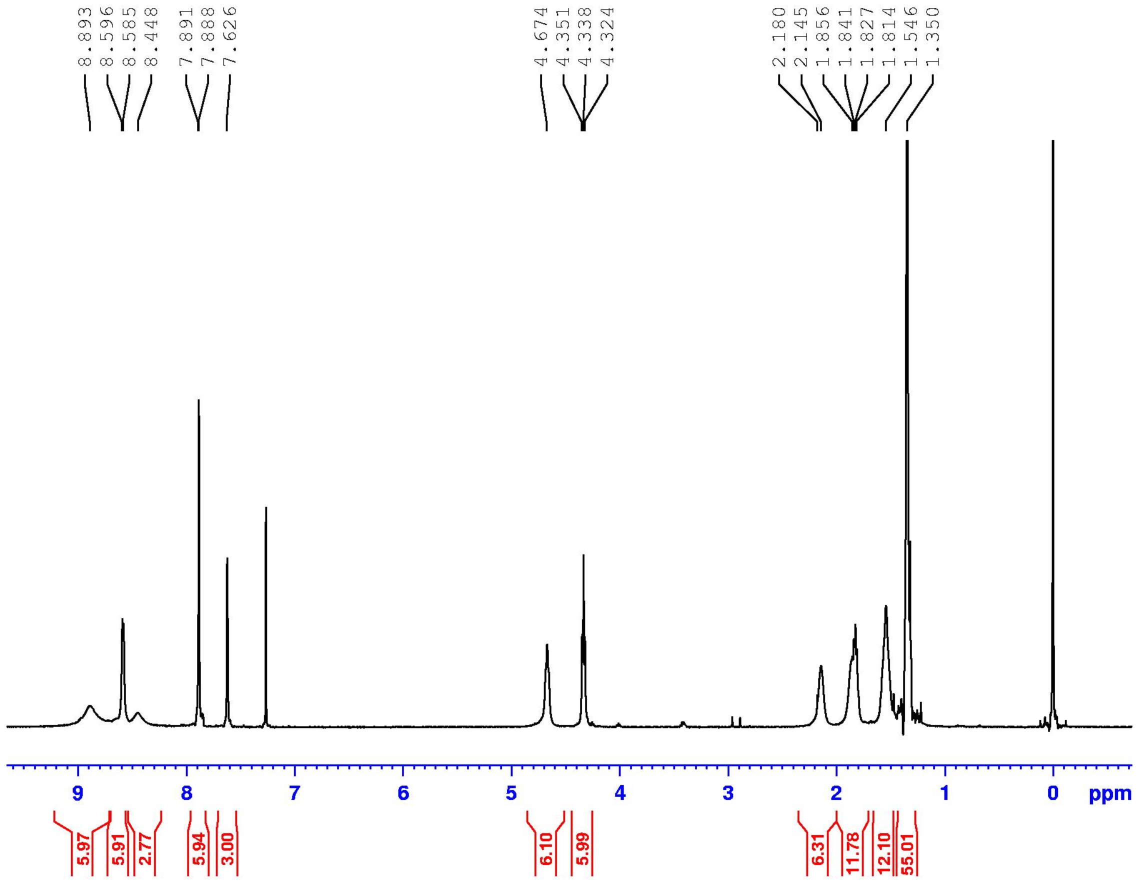


Figure S7. ^{1}H NMR spectrum (CDCl$_3$, 298 K, 500 MHz) of **TPY1**.

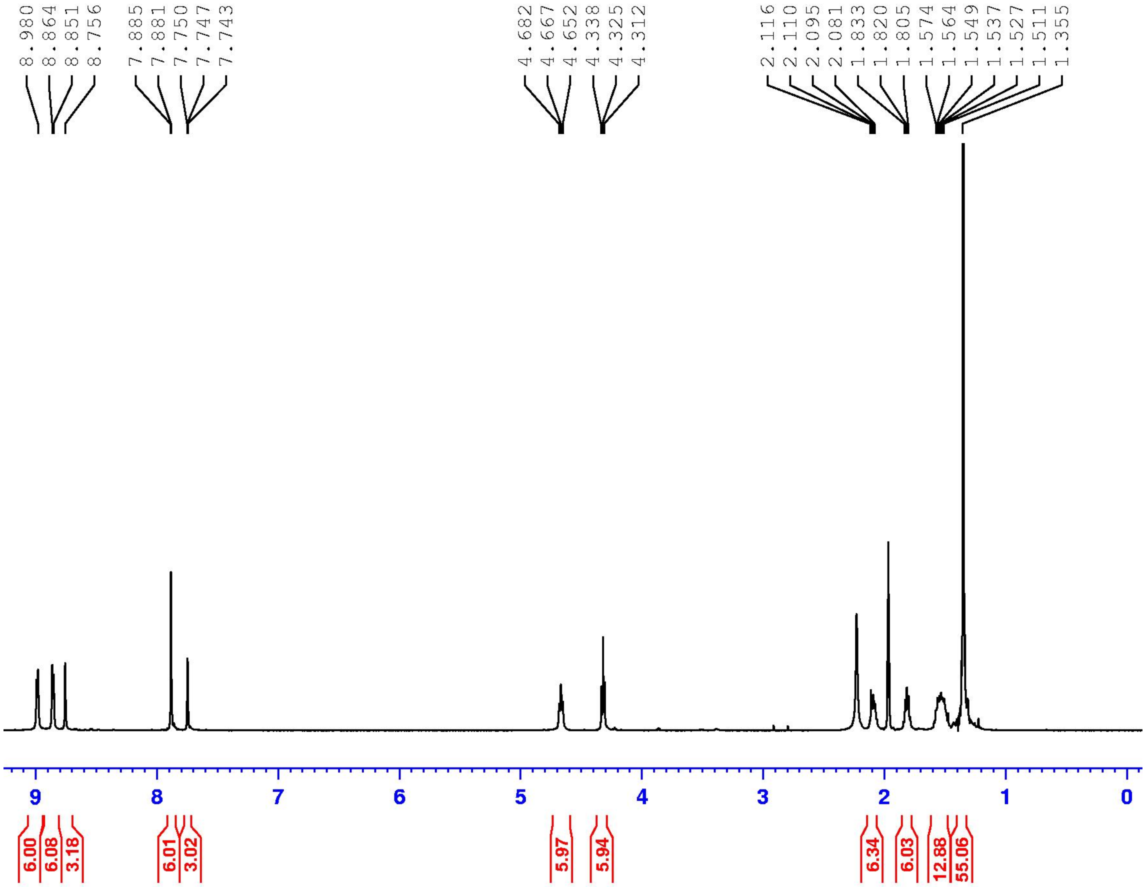


Figure S8. ^{1}H NMR spectrum (CD_3CN, 298 K, 500 MHz) of **TPY1**.