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Supplementary Information

Fully unsaturated all-carbon bifuorenylidene-based polymeric frameworks: synthesis and efficient photocatalysis

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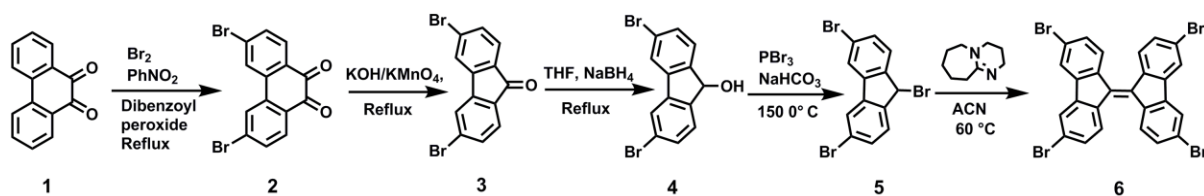
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Table of Contents

1. Experimental Section	2
2. Elemental analysis	3
3. Powder X-Ray diffraction profiles	4
4. Nitrogen physisorption analysis and pore size distribution	4
5. UV-Vis spectroscopy and DRS UV-Vis absorption spectra	7
6. Electron paramagnetic resonance spectroscopy	7
7. Electrochemical data	8
8. Scanning electron microscopic spectroscopy	9
9. Transmission electron microscopic spectroscopy	10
10. Photocatalytic degradation experiments	10
11. Recyclability tests	11
12. TGA analysis	13
13. FTIR analysis	13
13. NMR spectra and Maldi-TOF Mass spectra of intermediates and key monomer	14
14. References	19

1. Experimental Section

Experimental Procedures for key Dimer:



Scheme S1 Synthetic route for the key dimer (6)

Procedure for the synthesis of (2)¹

10 g (48.02 mmol) of phenanthrene-9, 10-quinone, 0.93 g (3.84 mmol) of dibenzoyl peroxide as initiator, and 1 mL (3.10 g, 19.40 mmol) of bromine were mixed with 60 mL nitrobenzene in a 200 mL schlenk flask and was heated to 120 °C. With the evolution of HBr gas (initiation of reaction), an additional 4 mL (12.40 g, 77.59 mmol) of bromine was added slowly dropwise. Then the resulting mixture was stirred for 1.5 h at 120 °C and the mixture was allowed to cool down to room temperature then 60 mL of hexane was added to precipitate out the product. The yellow product was obtained after filtration, washing with hexanes, and drying in a vacuum. Yield: 73 %. ¹H NMR (400 MHz, CDCl₃): δ(ppm) = 7.66 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H).

Procedure for the synthesis of (3)²

1.35g (3.7 mmol) of 3,6-dibromophenanthrenequinone (2), and 2 g of KOH in 15 mL H₂O/dioxane (1:1) were stirred for 18 hours under reflux. After that KMnO₄ was added to the refluxing reaction mixture three-time (each time 0.75 g) with 8h periods between the additions. After 24 hours reaction mixture was cooled to room temperature, filtered, and the dark blackish and brownish solid material was extracted with toluene by Soxhlet extractor for 3 days and the yellow crystalline pure compound was obtained. Yield: 83%.

Procedure for the synthesis of (4)³

0.24 g (6.34mmol) of NaBH₄ were added to suspension of 0.6 g (1.77mmol) of 3, 6-dibromofluorenone (3) in 15 mL THF in 50 mL flask and refluxed for 2 hrs. Then 15 mL of water were added to the reaction mixture after 2 hours. The precipitated white solid was filtered out as

product and air-dried. Yield: 83 %. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 1.89 (d, J = 10.1 Hz, 1H), 5.47 (d, J = 10.0 Hz, 1H), 7.49 (dd, J = 8.0, 1.6 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 1.5 Hz, 2H).

Procedure for the synthesis of (5)

The compound (4) (272.0 mg, 0.8 mmol) and an excess of PBr_3 (2.2 mg, 10 eq, 0.008 mmol) were heated at 150°C for 40 minutes. After that mixture was allowed to cool down to room temperature and water was added dropwise and neutralized with NaHCO_3 followed by extraction with DCM (3 x 20 mL). Then MgSO_4 was added to the yellow organic layer to dry it and was filtered, concentrated by a rotary evaporator under reduced pressure and the desired product was obtained. Yield: 59%. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) = 7.77 (d, J = 1.2 Hz, 2H), 7.49 (dd, J = 8.1 Hz, J = 1.6 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 5.88 (s, 1H). ^{13}C -NMR (400 MHz, CDCl_3): δ (ppm) = 44.2, 123.4, 124.5, 128.0, 131.6, 140.9, 143.7.

Procedure for the synthesis of key Dimer (6)⁴

Under an inert atmosphere, to a suspension of (200 mg, 0.49 mmol) in acetonitrile (50 mL) was added 1,5-diazabicyclo[5.4.0]undec-5-ene, DBU (90 mg, 152.24 mmol) in 100 mL flask in the dark at 60°C . After 2 h the mixture was allowed to cool, filtered, and washed with acetonitrile to give the desired orange dimer with a 50 % yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.36 (dd, J = 8.4, 1.9 Hz, 1H), 7.80 (d, J = 1.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H). ^{13}C NMR characterization was not done due to the limited solubility of this monomer. FT-IR (cm^{-1}) = 3432 (C-H_{arom}), 1587 (C=C_{arom}), 1421, 1061 (C-C), 810, 510 (C-Br).

2. Elemental Analysis

Table S1 Elemental analysis of the as-synthesized porous polymers.

Polymers	CMP-P1 (Expt./Calc.)	CMP-P2 (Expt./Calc.)
C (wt. %)	86.54/93.71	89.60/94.15
H (wt. %)	5.80/6.29	5.30/5.85
O (wt. %)	6.3/0	3.2/0

3. Powder X-Ray diffraction profiles

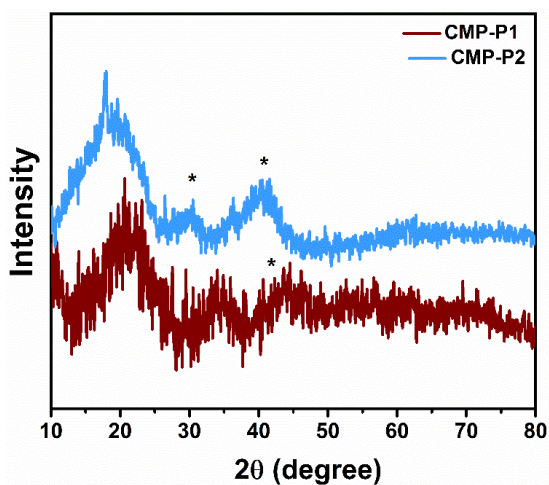


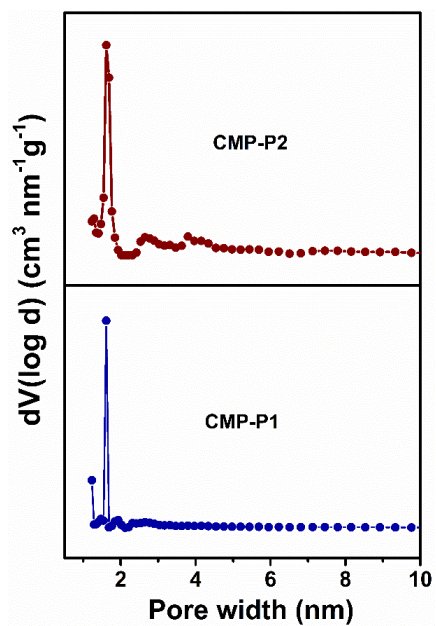
Figure S1 PXRD patterns of polymers.

4. Nitrogen physisorption analysis

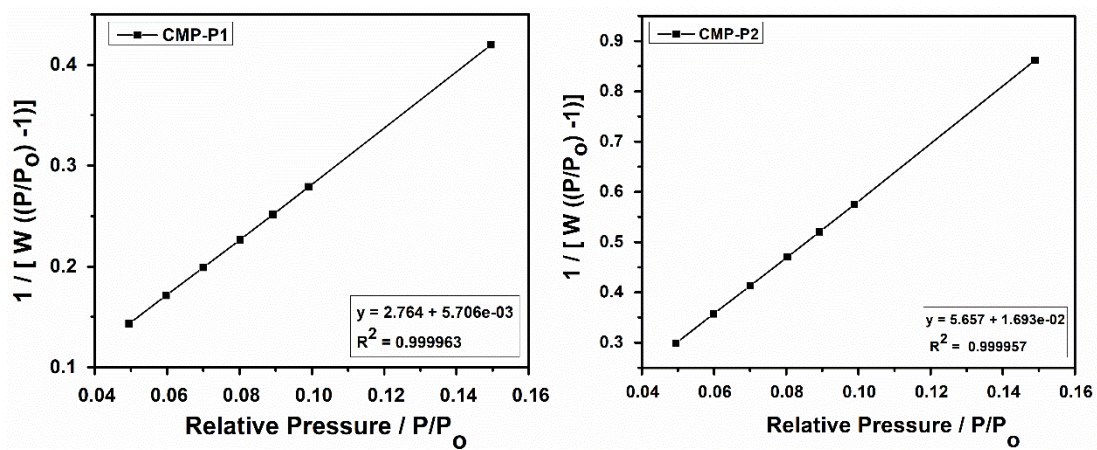
Table S2 Nitrogen physisorption data of the optimized CMP-P1 and CMP-P2.

Sample	(S_{BET}) ^a [m ² g ⁻¹]	(S_{lang}) ^b [m ² g ⁻¹]	(S_{micro}) ^c [m ² g ⁻¹]	(D_{av}) ^d [nm]	(V_{micro}) ^e [cm ³ g ⁻¹]	(V_{tot}) ^f [cm ³ g ⁻¹]
CMP-P1	1257	1582	852	0.99	0.392	8.955
CMP-P2	613	773	386	3.34	0.181	9.509

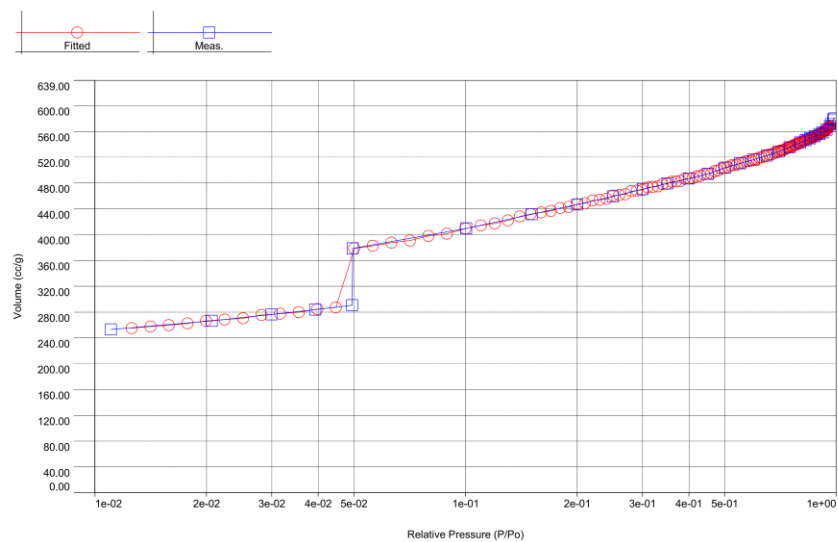
[a] Surface area (S_{BET}) calculated from N₂ adsorption isotherm using BET [b] Langmuir surface area (S_{lang}) by Langmuir theory [c] Micropore surface area [d] Average pore size diameter [e] Micropore volume [f] Total pore volume at $P/P_0 = 0.99$



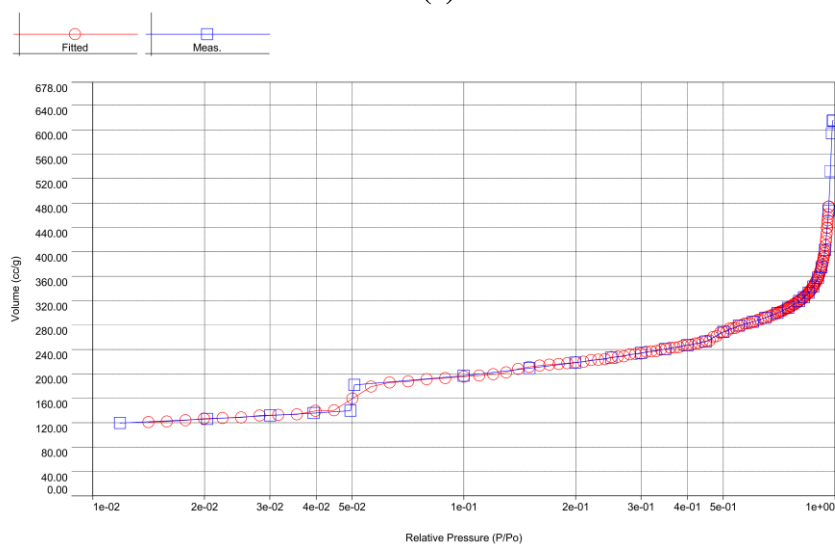
(a)



(b)



(c)



(d)

Figure S2 (a) Pore size distribution profiles calculated after fitting DFT model to N₂ adsorption data of polymers **CMP-P1** and **CMP-P2**. (b) BET plot from N₂ isotherms at 77 K of **CMP-P1** and **CMP-P2**. The goodness of fit and comparison isotherms of (c) **CMP-P1** and (d) **CMP-P2**.

5. UV-Vis spectroscopy, photoluminescence spectroscopy, and Diffused Reflectance UV-Vis absorption spectra (DRS)

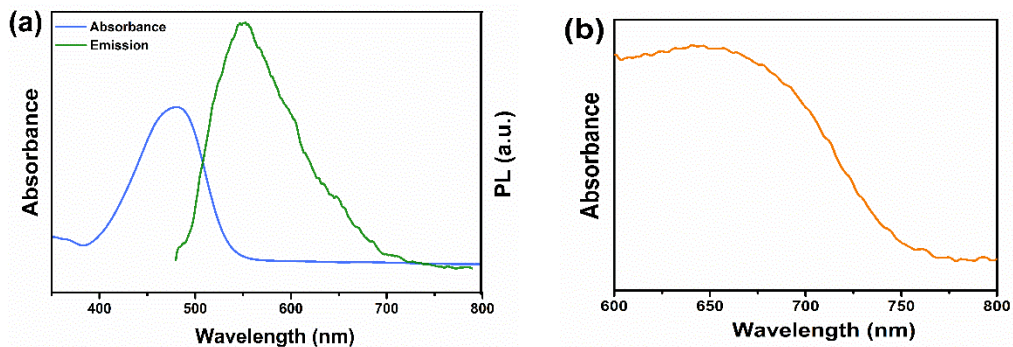


Figure S3 a) UV-Vis absorption spectra and fluorescence spectra of dimer in chloroform, b) DRS UV-Vis reflectance spectra of dimer in the solid-state.

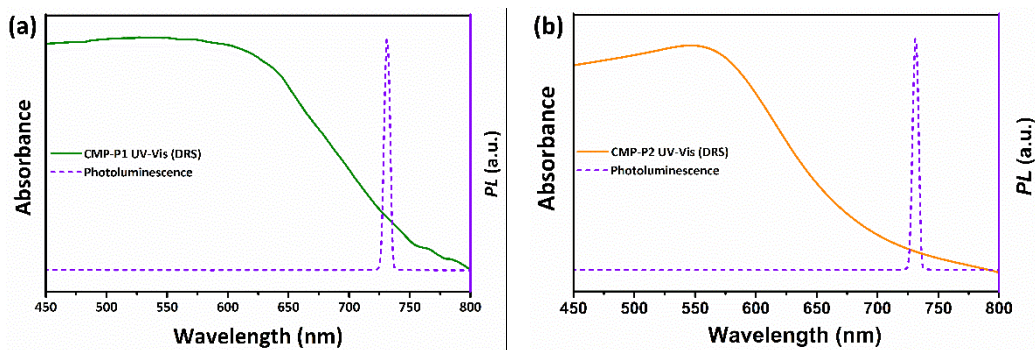


Figure S4 The UV/vis diffuse reflectance spectra (DRS and photoluminescence spectra of as-synthesized polymers.

6. Electron paramagnetic resonance spectroscopy

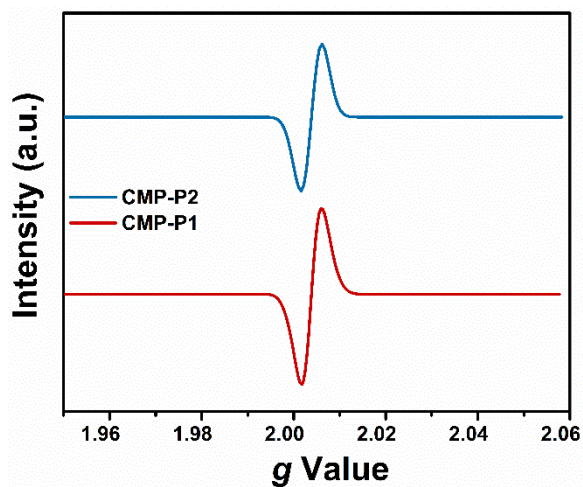


Figure S5 EPR spectra of as-synthesized CMP-P1 and CMP-P2.

7. Electrochemical data

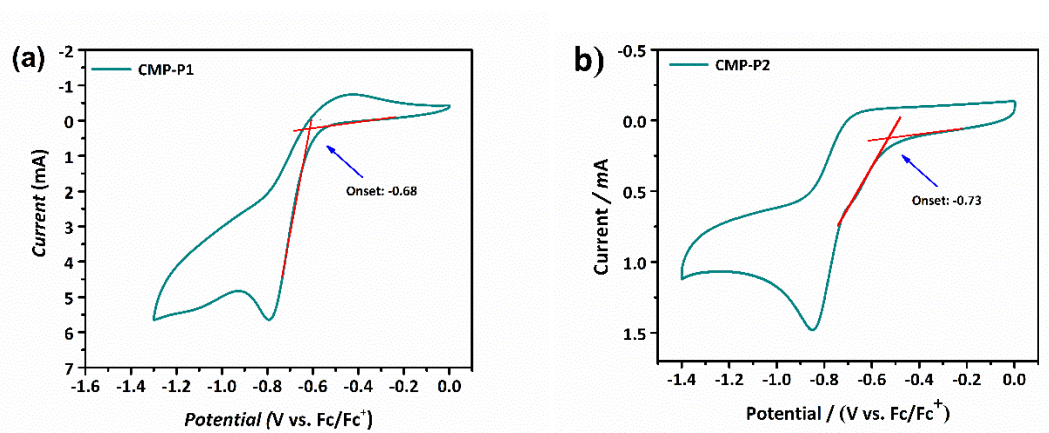


Figure S6 Cyclic voltammetric measurements of polymer CMP-P1 and CMP-P2.

8. Scanning Electron Microscopy

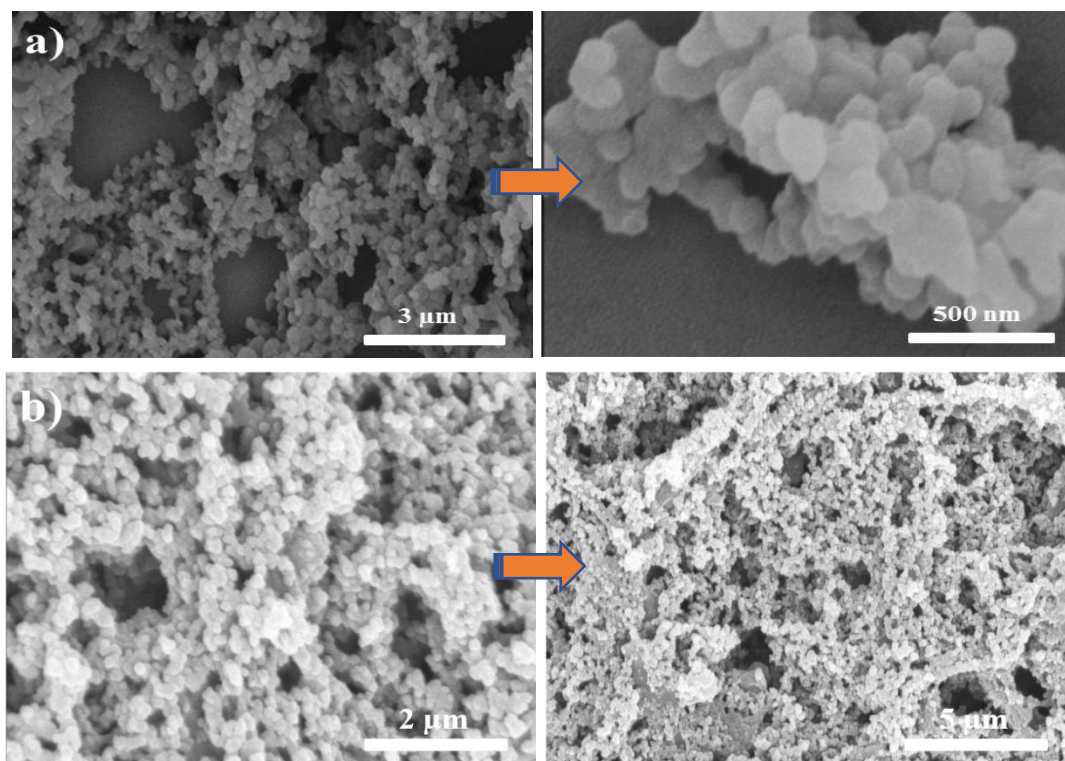


Figure S7 Scanning electron microscopic images of a) **CMP-P1** and b) **CMP-P2**.

9. Transmission Electron Microscopy

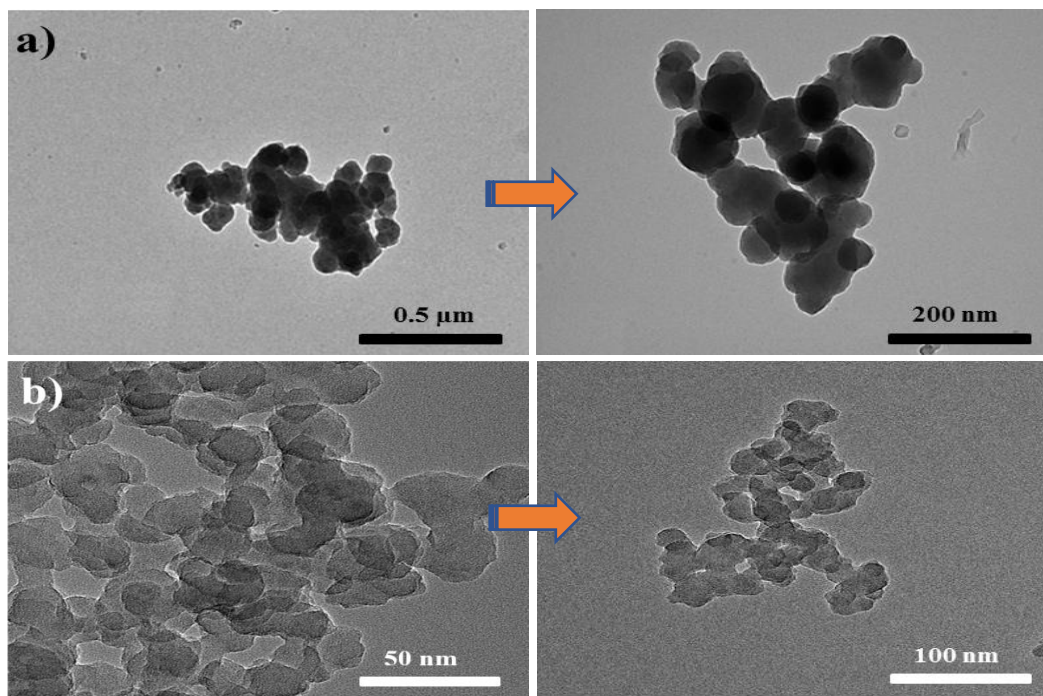


Figure S8 Transmission Electron Microscopic Images of a) **CMP-P1** and b) **CMP-P2**.

10. Photocatalytic degradation experiments

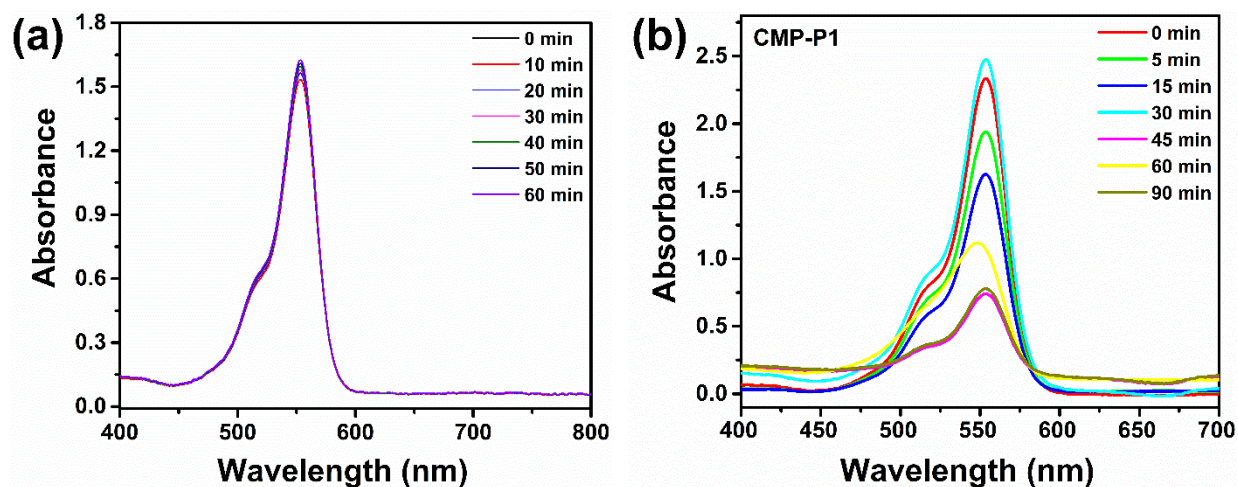


Figure S9 UV-Vis spectra of the control experiments: a) UV-vis spectra of RhB (75 mg L^{-1}) upon visible light irradiation without a catalyst; (b) UV-Vis spectra of RhB (75 mg L^{-1}) with **CMP-P1** kept in dark for 90 min.

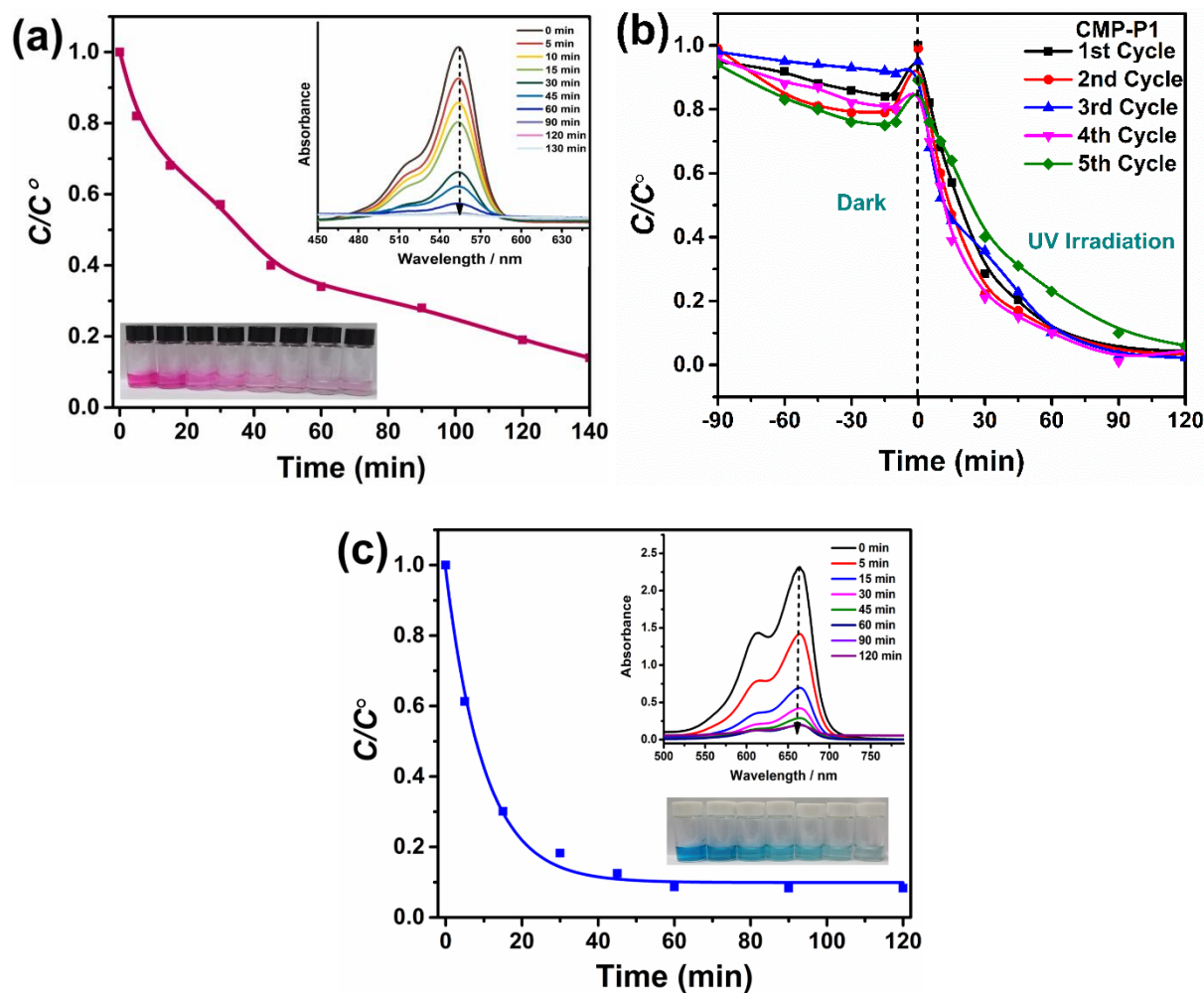


Figure S10 a) The fate of RhB in the presence of **CMP-P1** under UV light irradiation showing Photocatalytic degradation rate, inset: Time dependant UV-vis absorption spectra of RhB aqueous solution at different illumination time intervals with **CMP-P1** (the initial concentration of MB is 75 mg L^{-1}). b) The photocatalytic degradation rate of RhB with **CMP-P1** before and after UV light exposure after five cycles. c) The fate of MB in the presence of **CMP-P1** under UV light irradiation showing Photocatalytic degradation rate, inset: showing UV-vis absorption spectra of MB aqueous solution at different illumination time intervals with **CMP-P1** (the initial concentration of MB is 55 mg L^{-1}).

11. Recyclibility tests and characterization

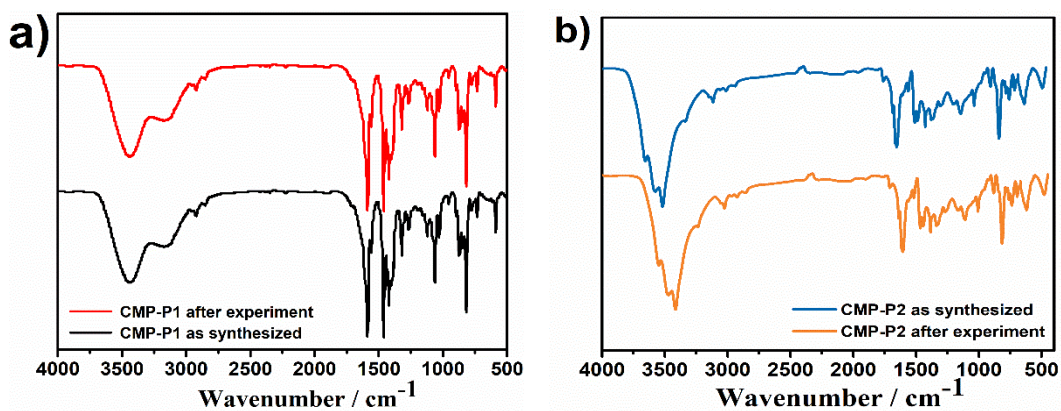


Figure S11 Transmission FT-IR spectra of polymers a) **CMP-P1** and b) **CMP-P2** before and after experiments.

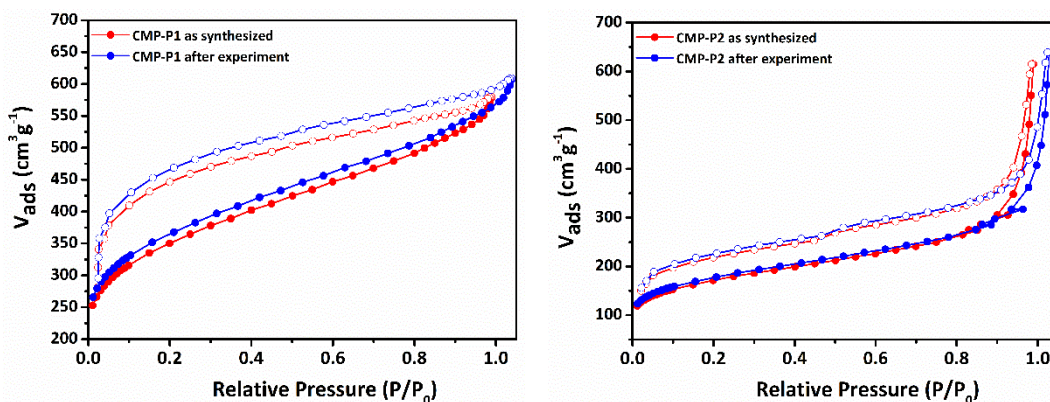


Figure S12 Nitrogen sorption isotherms for as-synthesized and after photodegradation experiments of **CMP-P1** and **CMP-P2**.

12. TGA analysis

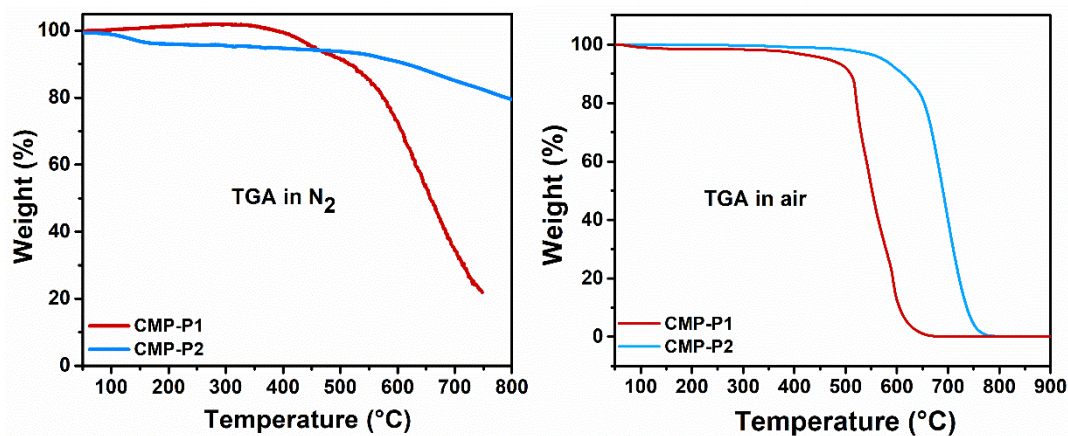


Figure S13 TG analysis in nitrogen and in air atmosphere for CMP-P1 and CMP-P2 polymer for detection of residual metals after thiourea treatment.

13. FTIR analysis

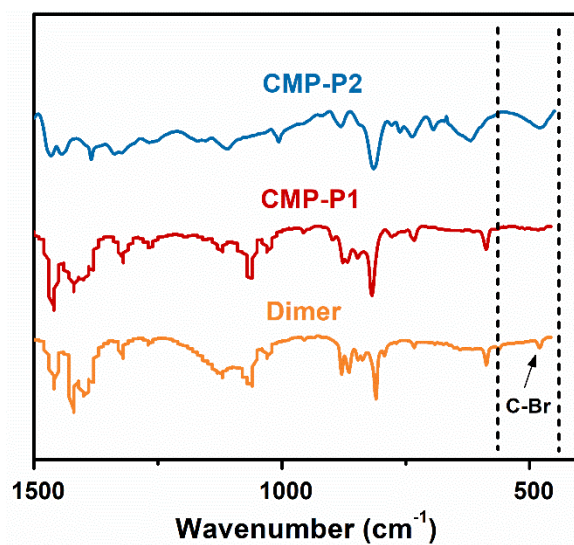
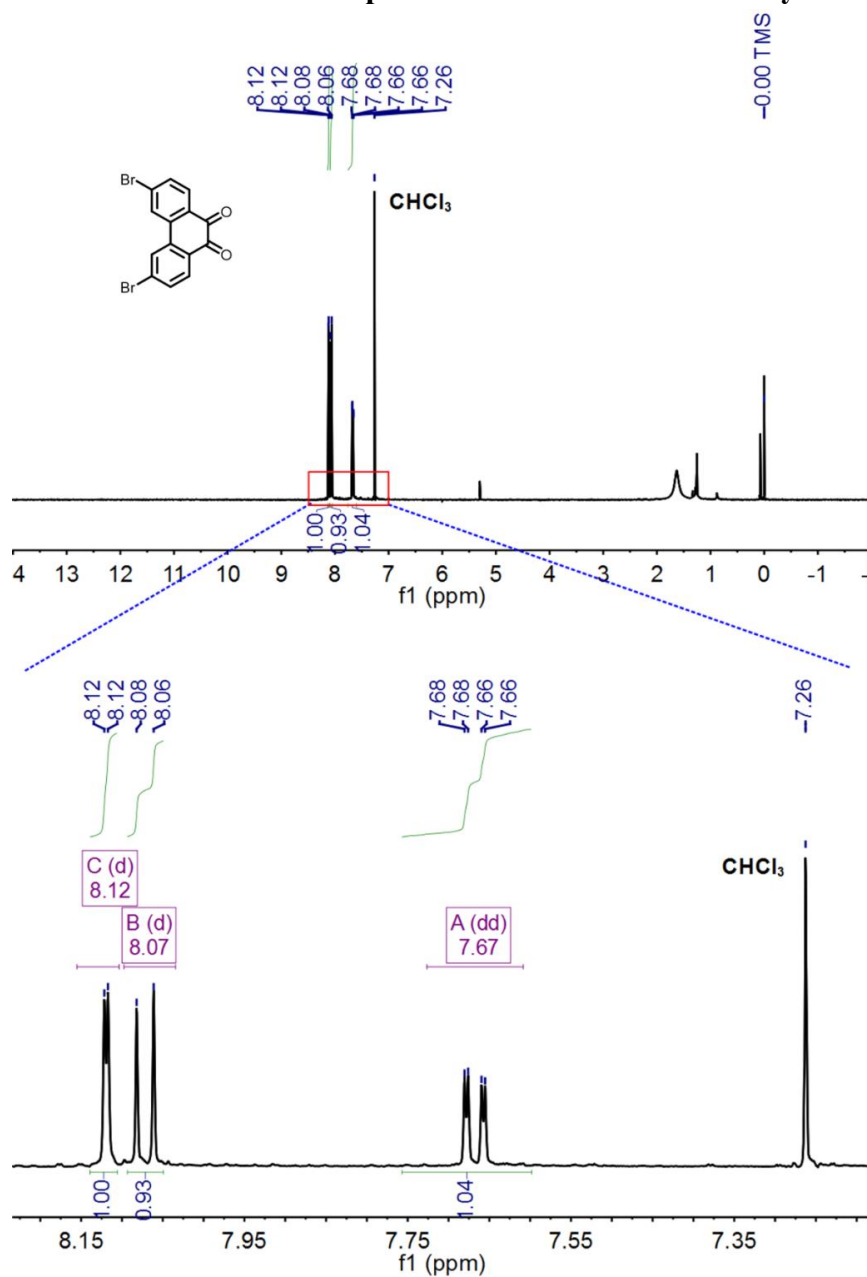


Figure S14 Enlarged FT-IR spectra of polymers and dimer.

14. NMR spectra and Maldi-TOF Mass spectra of intermediates and key monomer



15.
Figure S15 ^1H NMR spectra of (2).

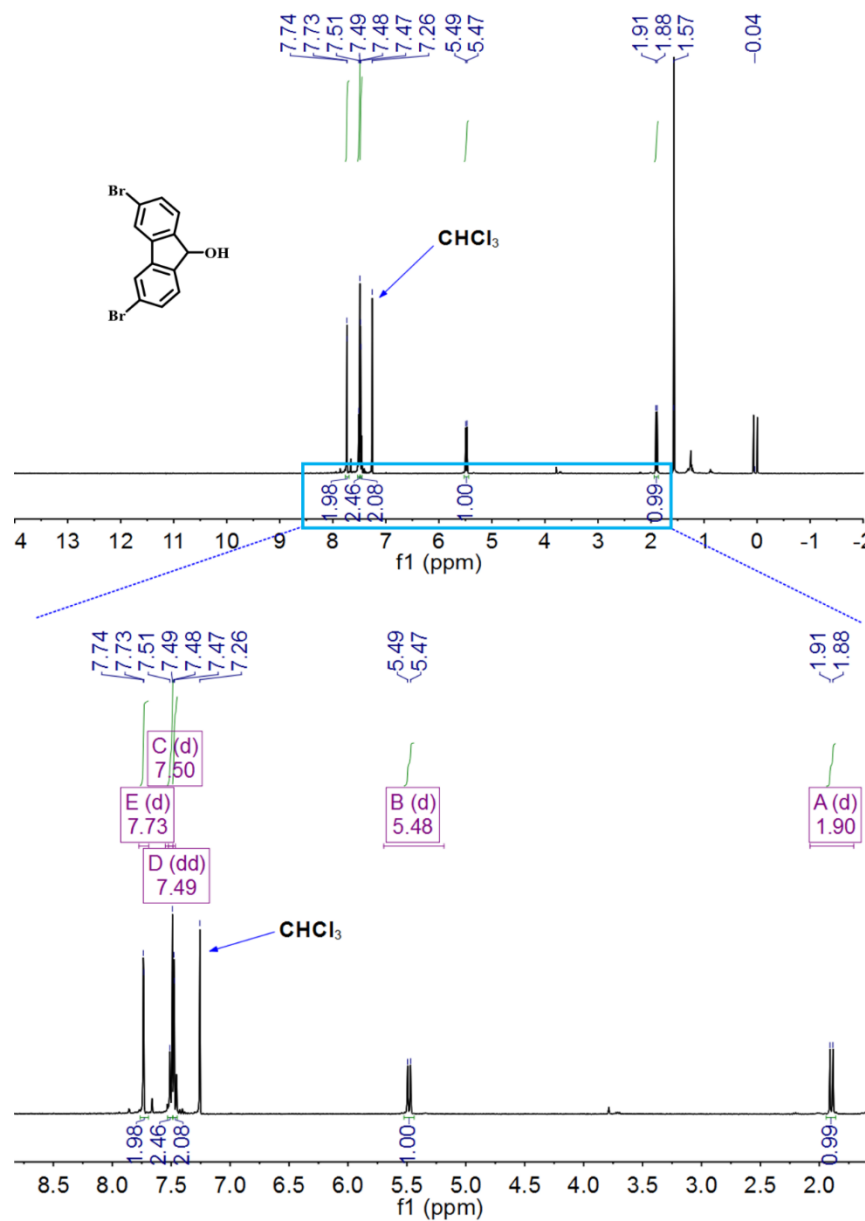


Figure S16 ^1H NMR spectra of (4).

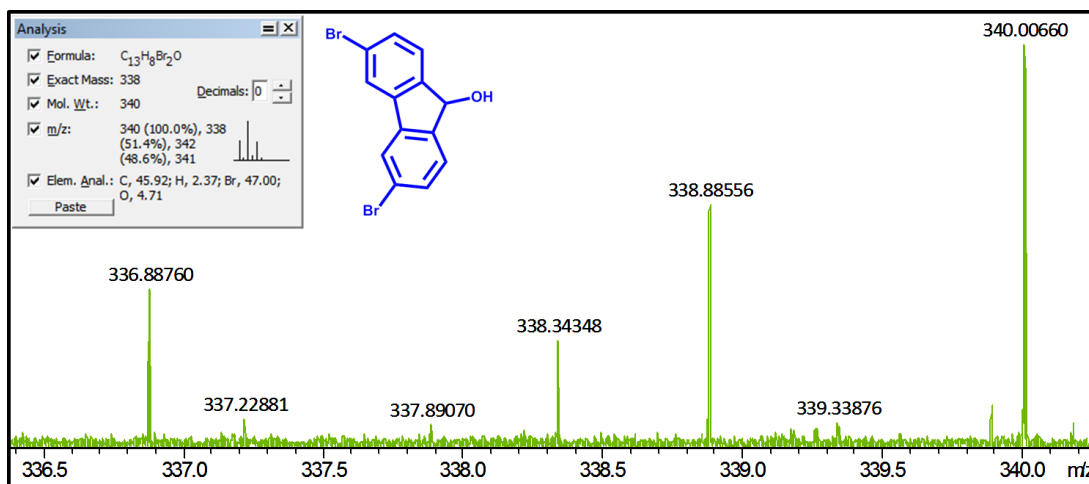


Figure S17 MALDI-TOF spectrum of (4).

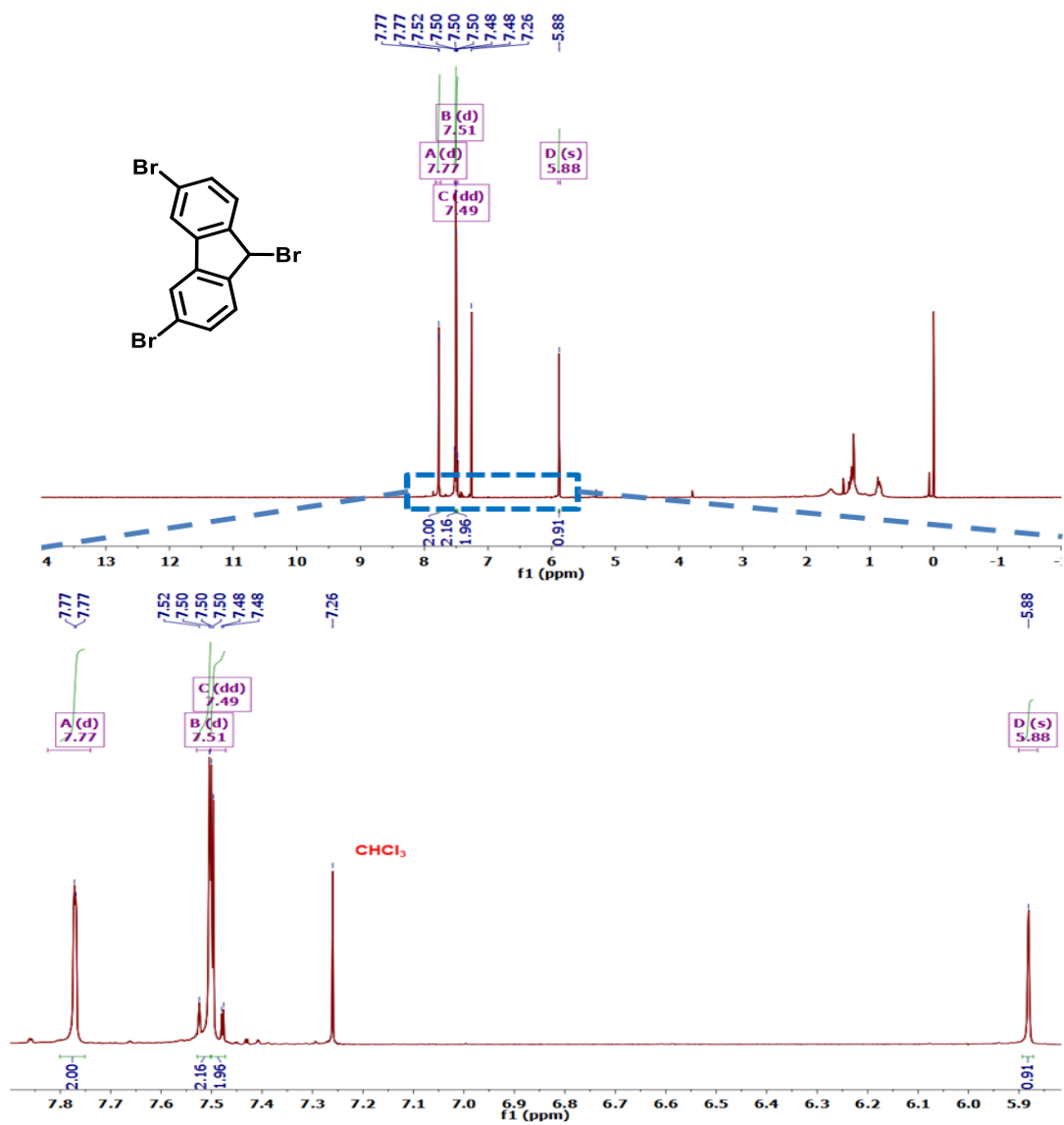


Figure S18 ¹H NMR spectra of (5).

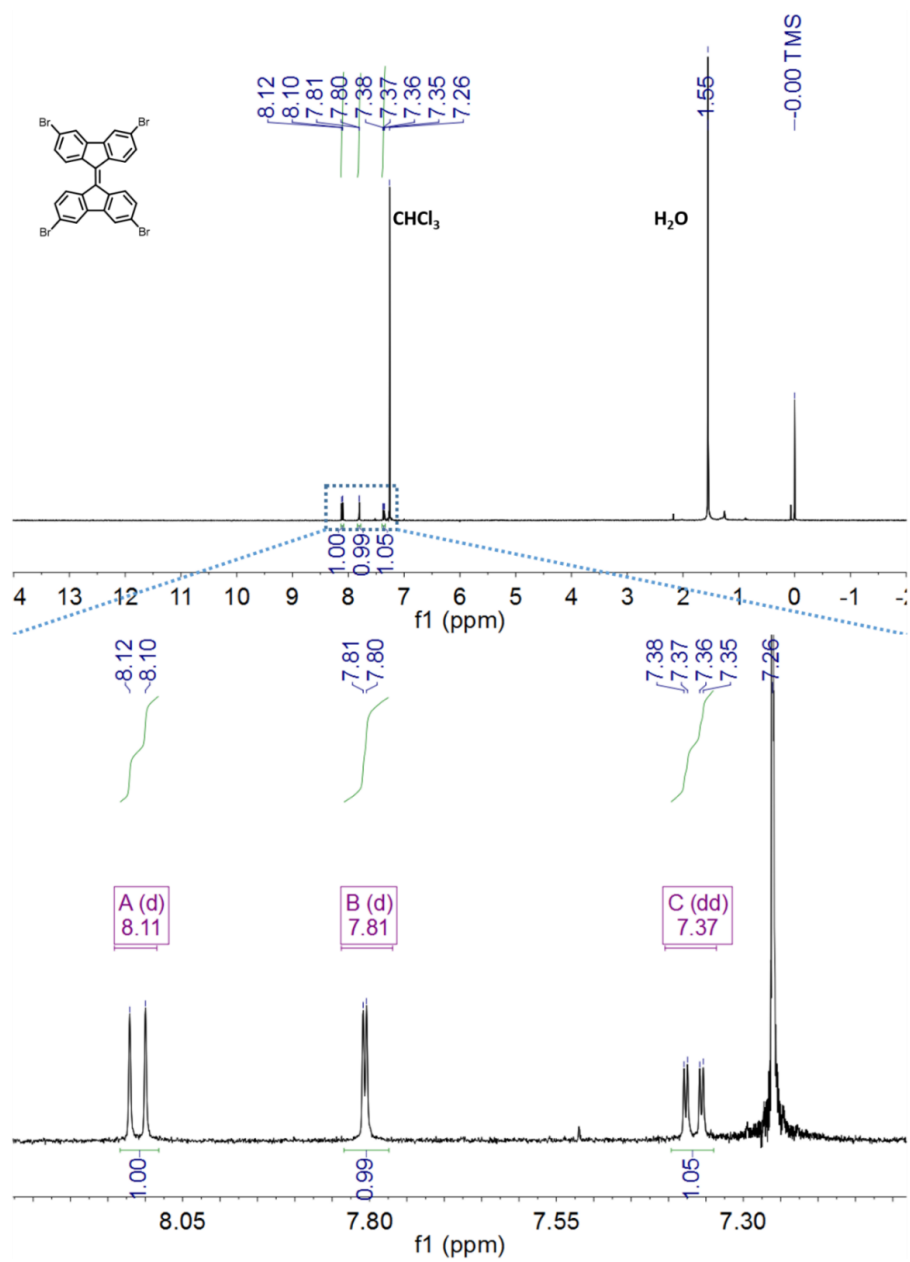


Figure S19 ^1H NMR spectrum of 3, 3', 6, 6'-tetrabromo-9, 9'-bifluorenylidene.

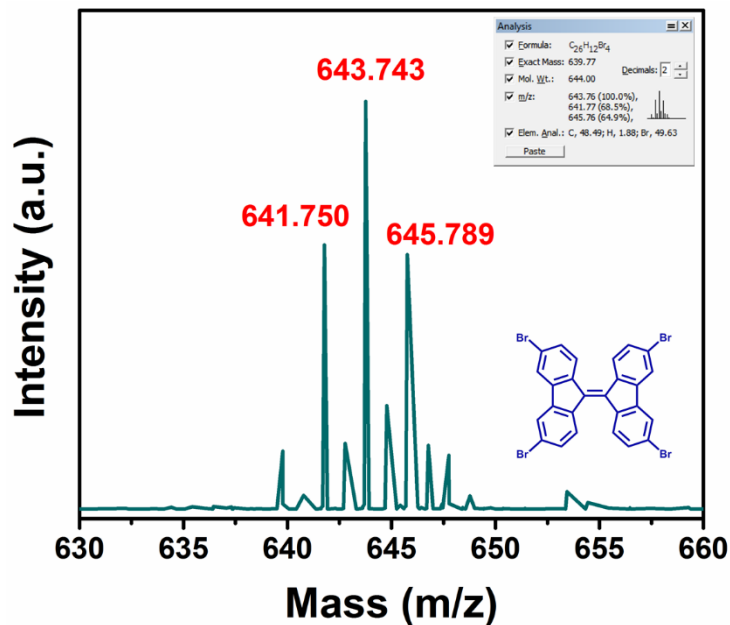


Figure S20 MALDI-TOF spectrum of 3, 3', 6, 6'-tetrabromo-9, 9'-bifluorenylidene.

References

1. R. Francke and R. D. Little, *Journal of the American Chemical Society*, 2013, **136**, 427-435.
2. L. A. Estrada and D. C. Neckers, *The Journal of organic chemistry*, 2009, **74**, 8484-8487.
3. N. Fomina and T. E. Hogen-Esch, *Macromolecules*, 2008, **41**, 3765-3768.
4. F. G. Brunetti, X. Gong, M. Tong, A. Heeger and F. Wudl, *Angewandte Chemie International Edition*, 2010, **49**, 532-536.