

Supplementary Information

Semiconducting Three-Dimensional Polymeric Frameworks with Full sp/sp²-Carbon Skeletons for Efficient Photocatalysis

Sidra Mushtaq, Fancheng Meng, Zixing Zhang, Shuai Bi * and Fan Zhang *

School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 200240 Shanghai, P. R. China

Email: bishuai-kiven@sjtu.edu.cn; fan-zhang@sjtu.edu.cn

Table of Contents

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

1. Experimental Section

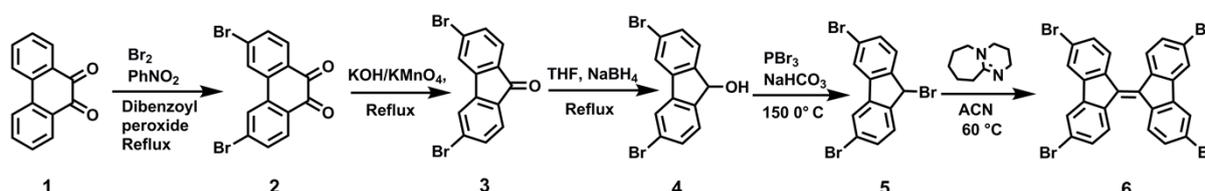
Materials

The chemicals phenanthren-9,10-quinone, phosphorous tribromide (PBr_3), diazabicycloundecene (DBU), 1,4-diethynylbenzene and 1,3,5-triethynylbenzene were purchased from Aldrich. The solvents such as toluene, dimethylformamide, acetonitrile and tetrahydrofuran were dried before use. The air-sensitive reactions were performed by applying the Schlenk vacuum-line technique in a nitrogen atmosphere. All intermediates and products were purified using column chromatography, while thin-layer chromatography was employed to track the reaction progress. Removal of palladium catalyst from the polymer network was done by suspending the polymer powder (100 mg) in chloroform (25 mL) following the addition of 300 mg of thiourea and stirring for 24 hours, then filtration and subsequent Soxhlet extraction were done to thoroughly remove the impurity, and the obtained polymer was dried in a vacuum oven at 60 °C.

Characterization

The liquid nuclear magnetic resonance (NMR) spectra of intermediates and monomers were obtained by Mercury plus 400 (400 MHz for proton, 100 MHz for carbon) spectrometer using CDCl_3 as a solvent with tetramethylsilane as the internal reference. ^{13}C cross-polarization solid state NMR experiments were performed on a Bruker AVANCE-III 400 operating at 100.62 MHz. Fourier transformed infrared (FT-IR) analysis was performed in transmission mode on a Perkin Elmer (Spectrum-100) spectrometer, with a scan range of 400–4000 cm^{-1} . The diffuse reflectance spectrometer (DRS) and ultraviolet-visible spectrometer (UV-Vis) were used to obtain UV-Vis absorption and diffuse reflectance spectra at room temperature, respectively, using the HITACHI (U-4100) Spectrophotometer and standard protocols. Thermal stability of materials was tested using a Perkin-Elmer (TGA-7) thermogravimetric analyzer in a nitrogen environment at a rate of 10 °C min^{-1} from 45 °C to 800 °C. Powder X-ray diffraction patterns were carried out by using a RIGAKU D/MAX-2500 diffractometer with $\text{Cu-K}\alpha_1$ radiation. The nitrogen physisorption analyses were carried out at 77 K using Auto-sorb-iQA3200-4 (Quanta tech Co., USA) equipment. Prior to analysis, the samples were degassed at 120 °C for 12 hours under vacuum. The SEM images were taken using an FEI Sirion-200 field emission scanning electron microscope, and TEM images were taken with a JEM-2100 (JEOL Ltd., Japan) for morphological analysis. Cyclic voltametric experiments were carried out using a Chenhua 650D electrochemical analyzer. The cyclic voltammograms were obtained at room temperature by using Ag/AgCl as a reference electrode and the potentials are transferred to versus standard hydrogen electrode. A glassy carbon working electrode and a platinum wire counter electrode were employed in a three-electrode arrangement with standard procedure. All electrochemical experiments were performed in a nitrogen environment. To get an average result, each CV measurement was tested three times.

Experimental Procedures for monomer 9,9'-BF-4Br (6):

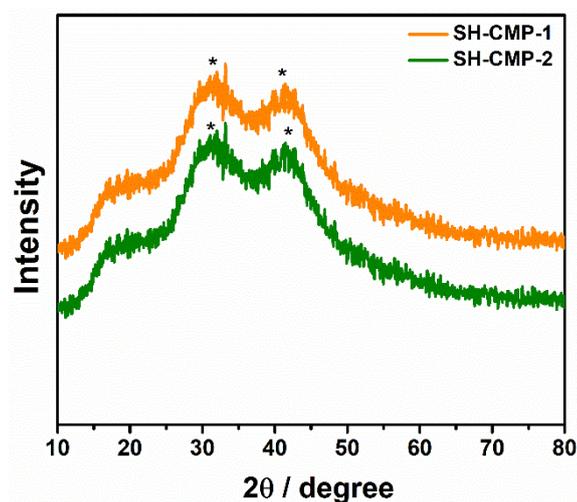


Scheme S1. Synthetic routes to intermediates and 9,9'-BF-4Br.

The monomer was synthesized from commercially available starting materials according to the modified procedures.^{1,2} The mass analysis data and NMR spectra were in accordance with the previous literature.

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

Polymers	SH-CMP-1 (Expt./Calc.)	SH-CMP-2 (Expt./Calc.)
C (wt. %)	93.78/95.42	92.67/95.32
H (wt. %)	5.22/4.58	6.32/4.68

3. Powder X-Ray diffraction profiles**Figure S1.** PXRD patterns of SH-CMP-1 and SH-CMP-2, Asterisks are the background peaks.

4. Nitrogen physisorption analysis

Table S2. Nitrogen physisorption data of polymers.

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]
SH-CMP-1	587	742	325	4.495	0.155	6.604
SH-CMP-2	615	776	393	3.424	0.185	5.271

[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 $P/P_0 = 0.99$.

5. Pore size distribution profiles

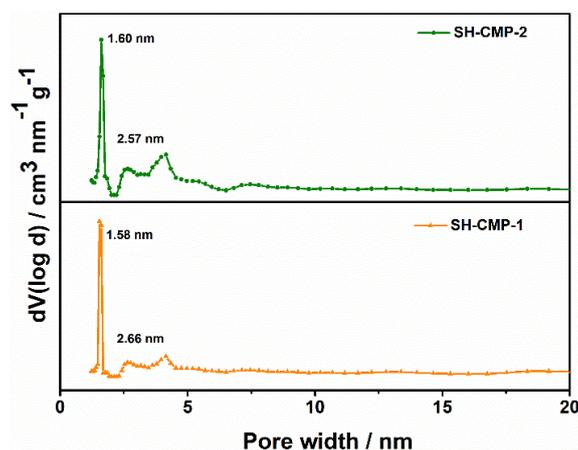


Figure S2. Pore size distribution profiles calculated after fitting DFT model to N₂ adsorption data of polymers.

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

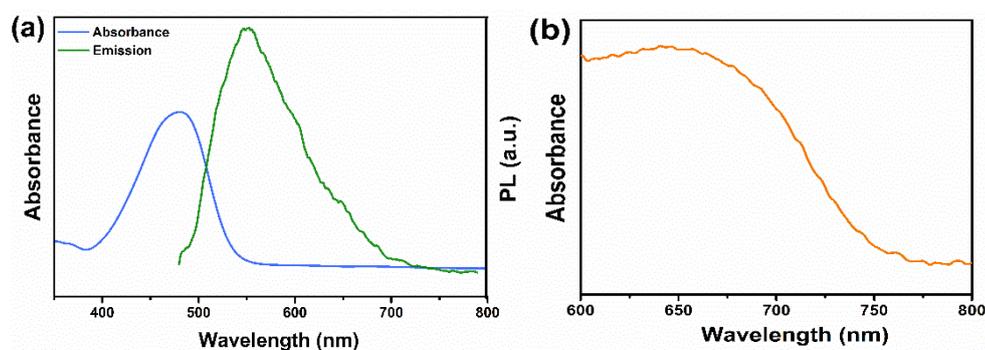


Figure S3. a) UV-Vis absorption spectra and fluorescence spectra of 9,9'-BF-4Br in chloroform, b) UV-Vis DRS reflectance spectra of 9,9'-BF-4Br in the solid-state.

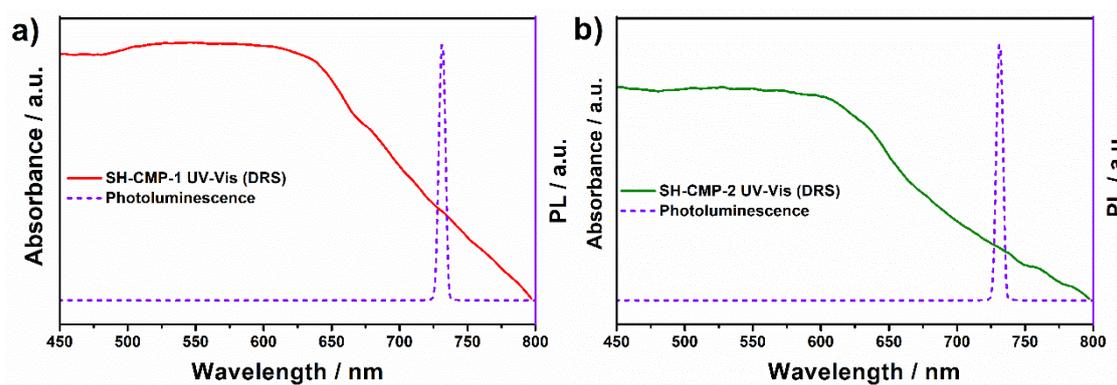


Figure S4. The UV/vis diffuse reflectance spectra (DRS and photoluminescence spectra of as-synthesized polymers.

7. Electron paramagnetic resonance spectroscopy

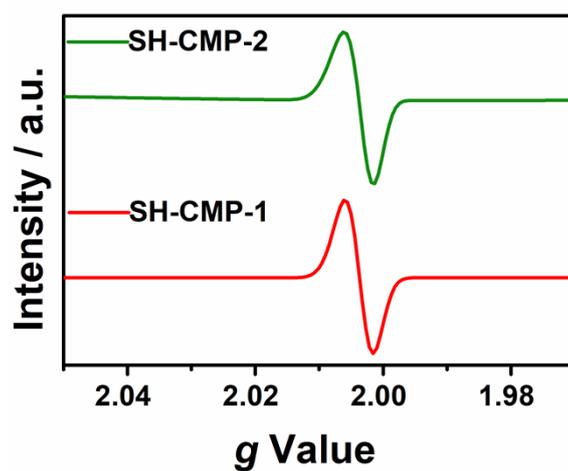


Figure S5. EPR spectra of polymers.

8. Electrochemical data

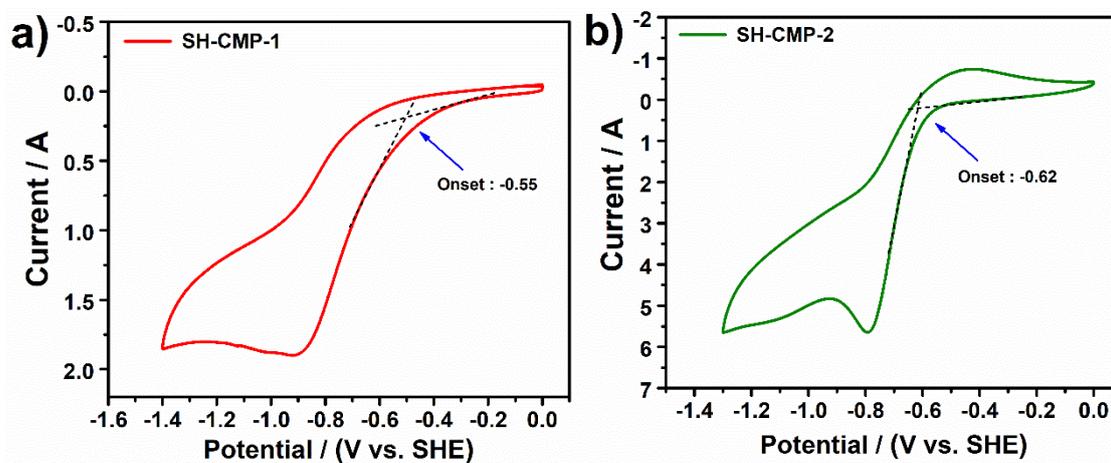


Figure S6. Cyclic voltammetric measurements of SH-CMP-1 and SH-CMP-2.

9. Photocatalytic degradation experiments

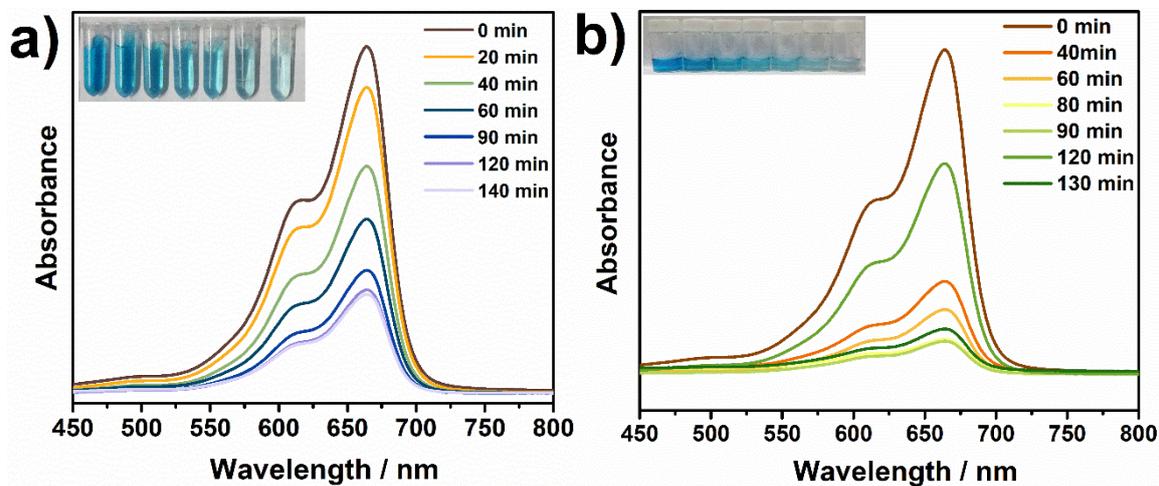


Figure S7. Time-dependant UV-vis absorption spectra of MB degradation catalyzed with a) SH-CMP-1 and b) SH-CMP-2. (Inset) Digital photographs of methylene blue (MB) dye before and after degradation.

10. Recyclability tests

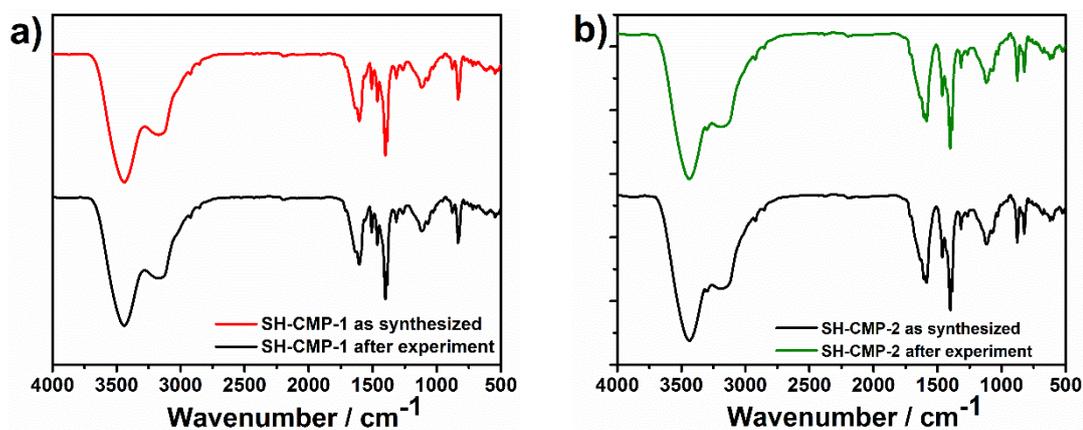


Figure S8. Transmission FT-IR spectra of polymers SH-CMP-1 and SH-CMP-2 before and after experiments.

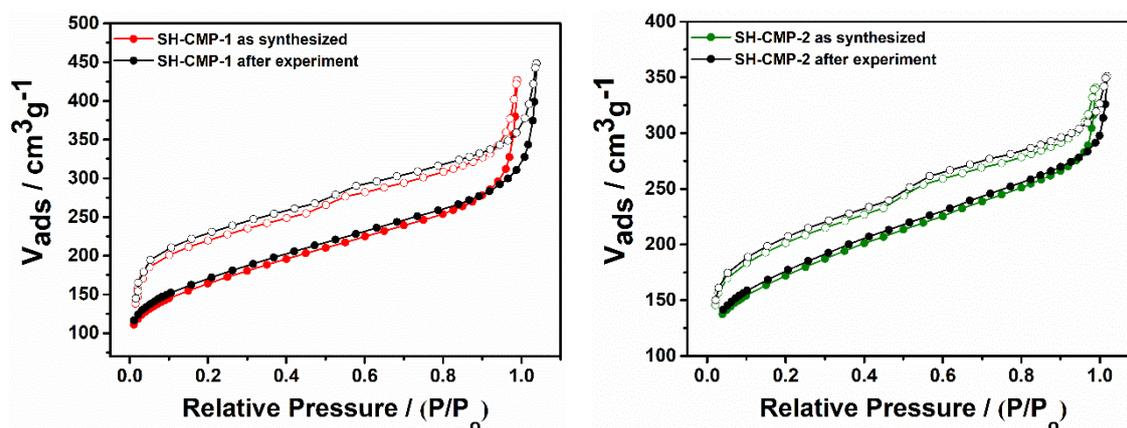


Figure S9. Nitrogen sorption isotherms for as-synthesized and after photodegradation experiments of SH-CMP-1 and SH-CMP-2.

11. Thermogravimetric analysis

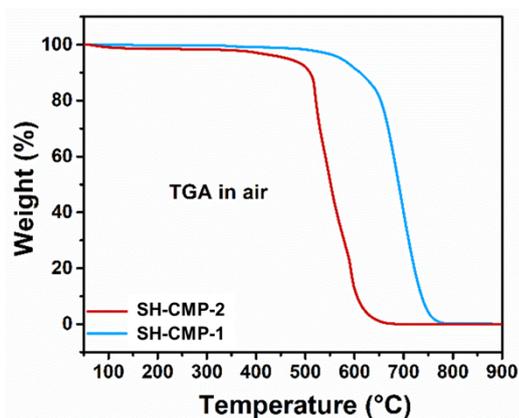


Figure S10. TG analysis in air atmosphere for SH-CMP-1 and SH-CMP-2 polymer for detection of residual metals after thiourea treatment

Table S3. Photocatalytic activities of synthesized polymers compared with reported polymer-based catalysts for degradation of dyes.

Organic material	Surface area (BET) (m ² g ⁻¹)	Bandgap (eV)	Dye	Efficiency in 1 h (%)	Reference
SH-CMP-1	587	1.76	MB	75	This work
			RhB	67	
			MB+RhB	56/39	
SH-CMP-2	615	1.83	MB	97	
			RhB	80	
			MB+RhB	84/47	
COP-NT	48	2.02	MB	38	Ref ³
			RhB	12	
POP-1	639	2.87	MB	>99	Ref ⁴
			RhB	93.5	
POP-2	281	2.77	MB	87.5	
			RhB	79	
			MO	<1	
PDA-COP-1	260	2.1	MO	45	Ref ⁵
P-FL-BT-3	-	2.11	MB	81.5	Ref ⁶
			RhB	88	
B-FL3-a	18	3.04	RhB	11	Ref ⁷
B-BT3-a	93	1.96		52.5	
B-BPh3-b	512	2.36		39.5	
Py-BF-CMP	1306	1.55	RhB	98	Ref ⁸
TPE-BF-CMP	777	1.98		77	
TPA-BF-CMP	590	1.89		77	
Ph-BF-PC	116	2.22		>99	Ref ⁹
				67	
			MB	7	
BPh-BF-PC	80	2.20		80	
				>99	
				11	
COF _{A+B}	-	2.49	MO	29.6	Ref ¹⁰
COF _{A+C}	-	2.56		>99	
PCN-1	58	-	RhB	<90	Ref ¹¹
PCN-2	558	-		>90	

12. NMR spectra and Maldi-TOF Mass spectra of key monomer

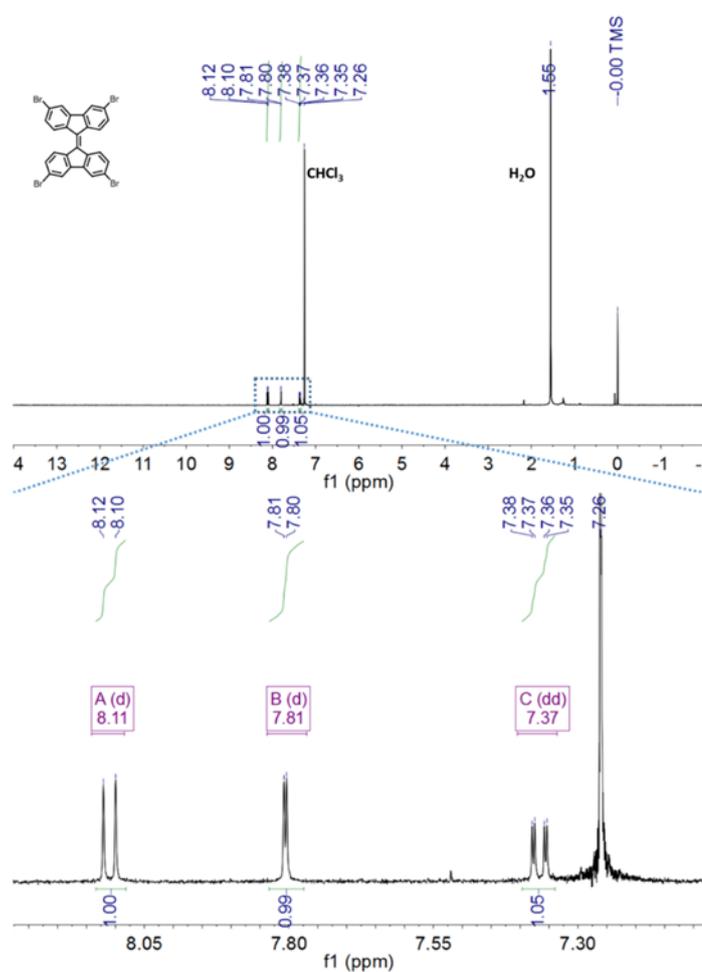


Figure S11. $^1\text{H-NMR}$ spectra of monomer 9,9'-BF-4Br

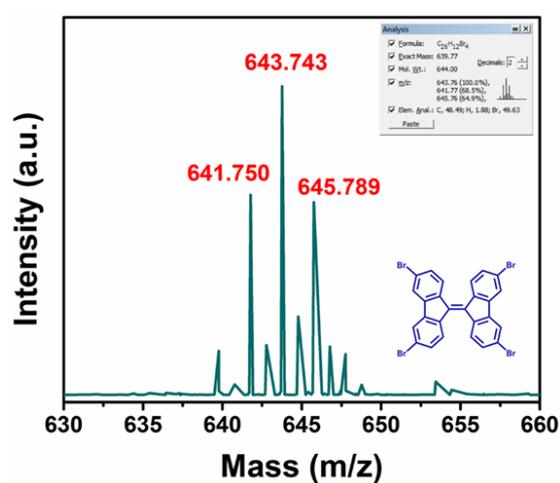


Figure S12. Maldi-TOF MS spectra of 9,9'-BF-4Br

References

1. R. Francke; R.D, Little. *J. Am. Chem. Soc.* 2013, **136**, 427-435.
2. F.G, Brunetti; X, Gong; M, Tong; A, Heeger; F, Wudl. *Angew. Chem. Int. Ed.* 2010, **49**, 532-536.
3. N. Xu, R.-L. Wang, D.-P. Li, X. Meng, J.-L. Mu, Z.-Y. Zhou and Z.-M. Su, *Dalton Trans.*, 2018, **47**, 4191-4197.
4. I. Nath, J. Chakraborty, P. M. Heynderickx and F. Verpoort, *Appl. Catal. B: Environ.*, 2018, **227**, 102-113.
5. S. Bhowmik, R. G. Jadhav and A. K. Das, *J. Phys. Chem. C*, 2018, **122**, 274-284.
6. S. Ghasimi, S. Prescher, Z. J. Wang, K. Landfester, J. Yuan and K. A. Zhang, *Angew. Chem. Int. Ed*, 2015, **54**, 14549-14553.
7. Y-L. Wong, J. Tobin, Z. Xu and F. Vilela, *J. Mater. Chem. A*, 2016, **4**, 18677-18686
8. B. Wang, Z. Xie, Y. Li, Z. Yang and L. Chen, *Macromolecules*, 2018, **51**, 3443-3449.
9. W. Ming, S. Bi, Y. Zhang, K. Yu, C. Lu, X. Fu, F. Qiu, P. Liu, Y. Su and F. Zhang, *Adv. Funct. Mater.*, 2019, **29**, 1808423.
10. S. He, B. Yin, H. Niu and Y. Cai, *Appl. Catal. B: Environ.*, 2018, **239**, 147-153.
11. J. Pan, L. Guo, S. Zhang, N. Wang, S. Jin and B. Tan, *Asian. J. Chem.*, 2018, **13**, 1674-1677.