Supporting Information

BODIPY-Based Conjugated Porous Polymers for Efficient Volatile Iodine Captures

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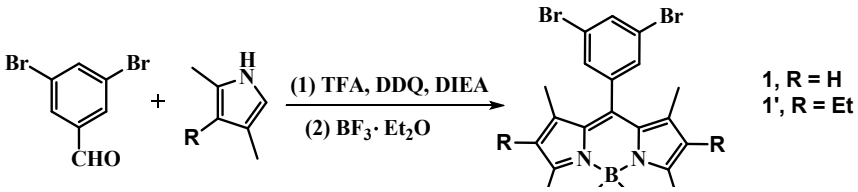
Synthesis of some compounds

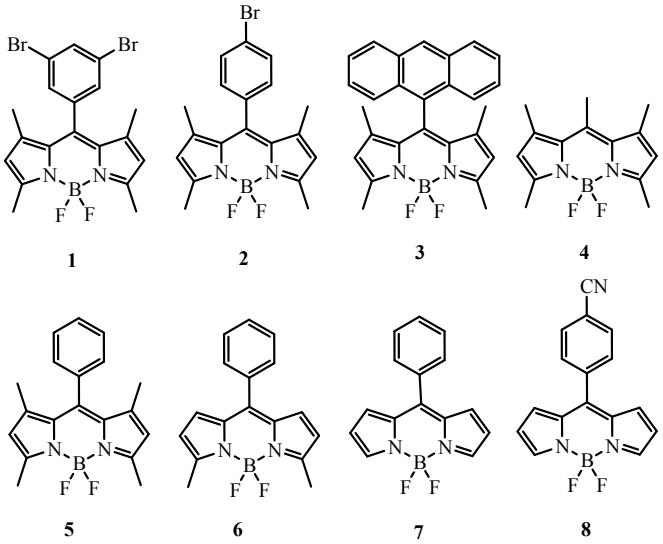
Monomer **1** and **2** was prepared according to literature [s1].



Scheme S1. Synthetic route for monomer **1** and **1'**.

*Monomer **1***: **1** was isolated as golden yellow crystal (115 mg, 24%). ^{1}H NMR ($CDCl_3$): δ = 7.81 (t, *J* = 1.76 Hz, 1H), 7.44 (d, *J* =1.80 Hz, 6H), 6.01 (s, 2H), 2.55 (s, 6H), 1.49 (s, 6H).

*Monomer **1'***: **1'** was isolated as red crystal (419 mg, 26%). ^{1}H NMR ($CDCl_3$): δ = 7.86 (t, J = 1.76 Hz, 1H), 7.41 (d, J = 1.72 Hz, 2H), 2.52 (s, 6H), 2.31(m, J = 7.60 Hz, 4H), 1.38 (s, 6H), 1.00 (t, J = 7.60 Hz, 6H).



*Monomer **2***: ^{1}H NMR ($CDCl_3$): δ = 7.65 (d, *J* = 8.40 Hz, 2H), 7.18 (d, *J* =8.40 Hz, 2H), 5.99 (s, 2H), 2.55 (s, 6H), 1.41 (s, 6H).

*Monomer **3***: ^{1}H NMR ($CDCl_3$): δ = 8.57 (s, 1H), 8.04 (d, *J* =8.44 Hz, 2H), 7.91 (d, *J* =8.76 Hz, 2H), 7.49 (t, *J* =14.94 Hz, 2H), 7.43 (t, *J* =15.22 Hz, 2H), 2.63 (s, 6H), 0.65 (s, 6H).

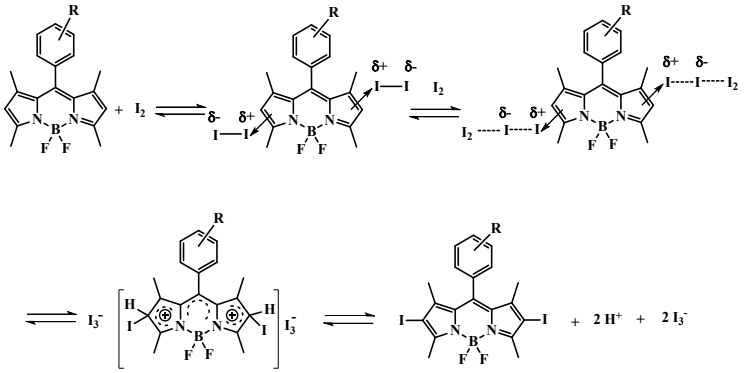
*Monomer **4***: ^{1}H NMR ($CDCl_3$): δ = 6.05(s, 2H), 2.58 (s, 3H), 2.52 (s, 6H), 2.41 (s, 6H).

*Monomer **5***: ^{1}H NMR ($CDCl_3$): δ = 7.48 (m, 3H), 7.28 (m, 2H), 5.98 (s, 2H), 2.56 (s, 6H), 1.37 (s, 6H).

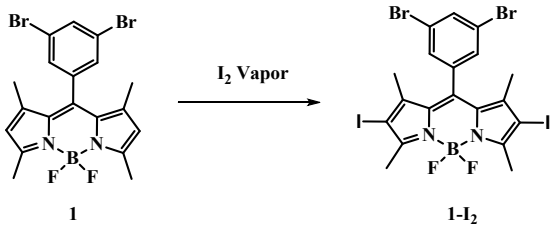
*Monomer **6***: ^{1}H NMR ($CDCl_3$): δ = 7.49 (m,5H), 6.71 (d, *J* = 4.12 Hz, 2H), 6.27 (d, *J* = 4.12 Hz, 2H), 2.65 (s, 6H).

*Monomer **7***: ^{1}H NMR ($CDCl_3$): δ = 7.95 (s,2H), 7.57 (m, 5H), 6.94 (d, *J* = 4.16 Hz, 2H), 6.55 (d, *J* = 3.76 Hz, 2H).

*Monomer **8***: ^{1}H NMR ($CDCl_3$): δ = 7.99 (s, 2H), 7.85 (d, *J* = 8.30 Hz, 2H), 7.69 (d, *J* = 8.35 Hz, 2H), 6.84 (d, *J* = 4.20 Hz, 2H), 6.58 (d, *J* = 4.05 Hz, 2H).



Scheme S2. A mechanistic proposal for this iodination reaction.



Scheme S3. Synthetic route for compound **1-I_2**.

*Compound **1-I_2***: Monomer **1**（10 mg，0.02 mmol）was dissolved in anhydrous CH_2Cl_2 (15 mL) and then followed by spraying on a big silica gel plate (5 × 20 cm). The air dry plate was placed in wild-mouth bottle filled with iodine at the bottom. After staining by iodine vapor for 16 hrs at room temperature, the red silica gel was scraped from plate and the organic compound was extracted by DCM. The solvent was evaporated and the residue was chromatographed on silica gel using PE/DCM = 5:1 to afford **1-I_2** as a red crystal (15 mg, 100%). ^{1}H NMR ($CDCl_3$): δ = 7.86 (t, *J* = 1.76 Hz, 1H), 7.41 (d, *J* = 1.72 Hz, 2H), 2.64 (s, 6H), 1.51 (s, 6H). ^{13}C NMR ($CDCl_3$): δ = 157.9, 145.0, 138.2, 137.0, 135.4, 130.9, 130.0, 124.1, 86.4, 17.7, 16.3. HRMS (ESI): *m/z* calculated for $C_{19}H_{16}BBr_2F_2I_2N_2$:732.7831 $[M+H]^+$; found, 732.8387.

*The Compound **n-I_2*** (n=2,3,4,5,6,7,8) were obtained by the method as the *Compound **1-I_2***.

*Compound **2-I_2***: ^{1}H NMR ($CDCl_3$): δ = 7.68 (d, *J* = 8.40 Hz, 2H), 7.15 (d, *J* =8.40 Hz, 2H), 2.64 (s, 6H), 1.43 (s, 6H).

*Compound **3-I_2***: ^{1}H NMR ($CDCl_3$): δ = 8.63 (s, 1H), 8.06 (d, *J* =8.45 Hz, 2H), 7.82 (d, *J* =8.55 Hz, 2H), 7.51 (t, *J* =14.40 Hz, 2H), 7.44 (t, *J* =14.30 Hz, 2H), 2.72 (s, 6H), 0.67 (s, 6H).

*Compound **4-I_2***: ^{1}H NMR ($CDCl_3$): δ = 2.64 (s, 3H), 2.61 (s, 6H), 2.47 (s, 6H).

*Compound **5-I_2***: ^{1}H NMR (DMSO-d): δ = 7.59 (t, *J* =3.20 Hz,3H), 7.39 (m, 2H), 3.37 (s, 6H), 1.33 (s, 6H).

*Compound **6-I_2***: ^{1}H NMR ($CDCl_3$): δ = 7.93 (s, 2H), 7.87 (d, *J* = 8.52Hz, 2H), 7.66 (d, *J* = 8.48 Hz, 2H), 7.01 (s, 2H).

*Compound **7-I_2***: ^{1}H NMR ($CDCl_3$): δ = 7.51 (m,5H), 6.94 (s, 2H), 2.66 (s, 6H).

*Compound **8-I_2***: ^{1}H NMR ($CDCl_3$): δ = 7.53 (m,5H), 7.36 (s, 2H), 7.12 (t, *J* = 2.45Hz, 2H).

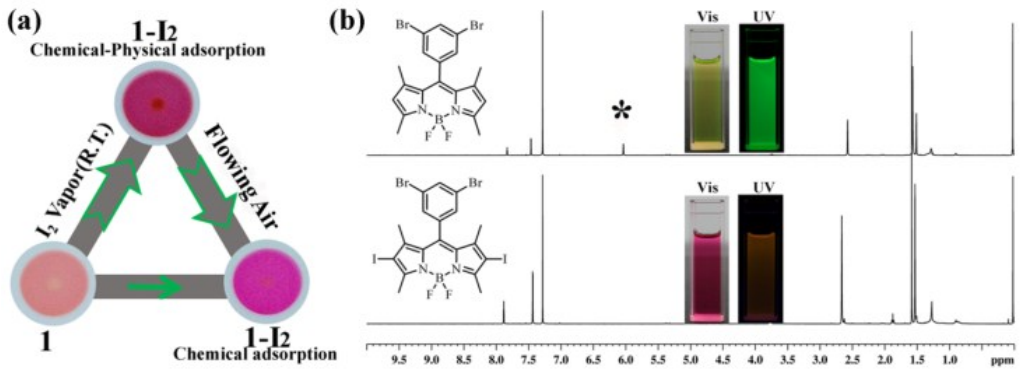


Fig. S1 (a) TLC spot diagram of the iodine staining process; (b) ^{1}H NMR spectra of monomer **1** and corresponding iodine stain product **1-I$_2$**. The insets are their corresponding photographs of DCM solution of **1** and **1-I$_2$** under visible light (left) and UV lamp (right).

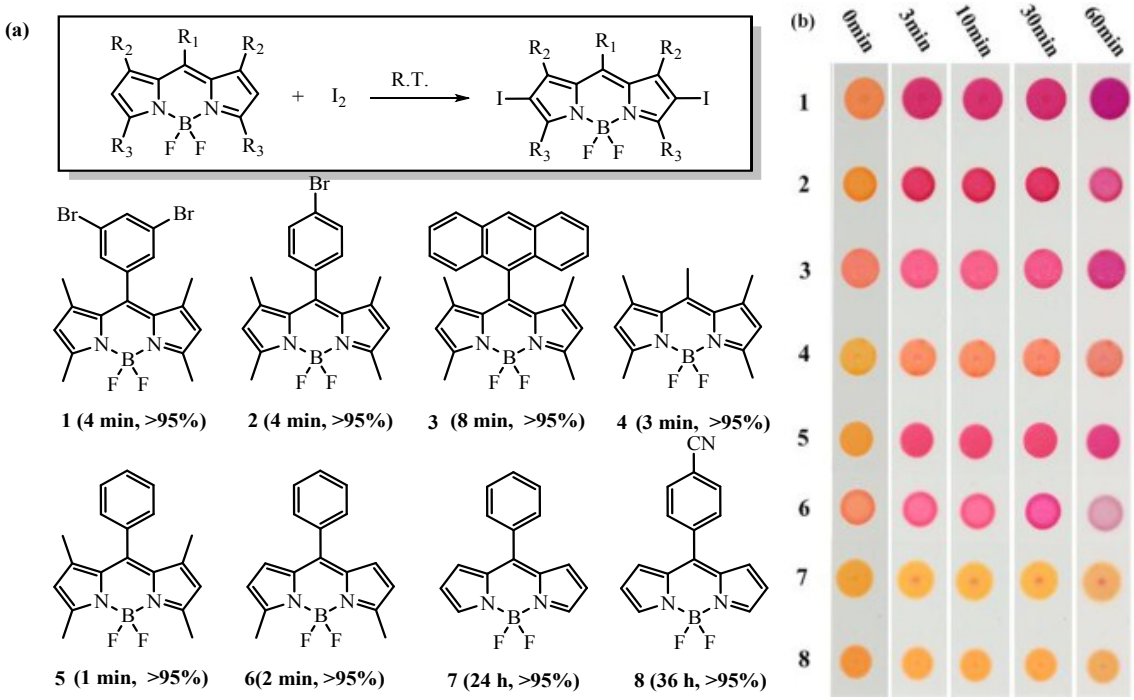
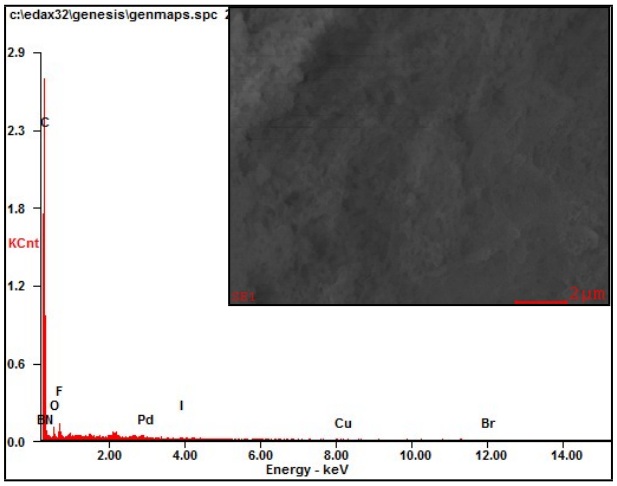
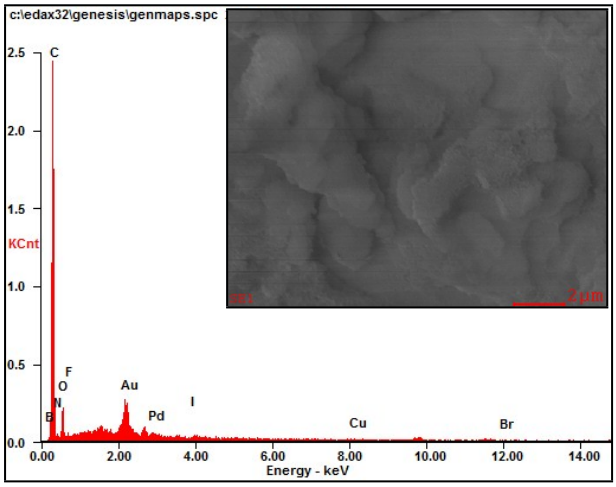


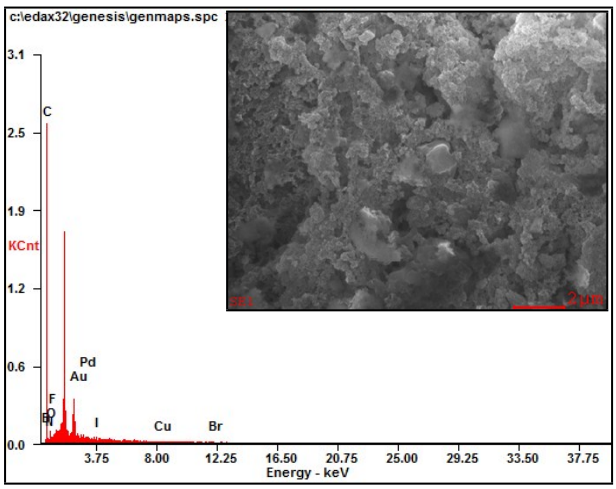
Fig. S2 (a) BODIPY iodination reaction with volatile iodine and the effect of BODIPY on this reaction, time for iodination is determined by TLC, followed by the confirmation of a full conversion (>95%) by ^{1}H NMR; (b) TLC images for the BODIPY derivatives under iodine vapor with different time at room temperature.



Element	Wt%	At%
BK	03.62	04.21
CK	83.91	87.67
NK	05.32	04.77
FK	04.59	03.03
PdL	01.47	00.18
IL	00.72	00.07
CuK	00.37	00.07
Matrix	Correction	ZAF



Element	Wt%	At%
BK	03.61	04.10
CK	89.62	91.36
NK	04.38	03.83
FK	00.76	00.48
PdL	00.52	00.06
IL	00.52	00.06
CuK	00.58	00.11
Matrix	Correction	ZAF



Element	Wt%	At%
BK	03.41	03.85
CK	92.61	94.15
NK	01.79	01.56
FK	00.26	00.17
PdL	00.62	00.07
IL	00.66	00.06
CuK	00.65	00.14
Matrix	Correction	ZAF

Fig. S3 The element content data of BDP-CPP-1,BDP-CPP-2 and NBDP-CPP (from up todown) by EDS analysis.

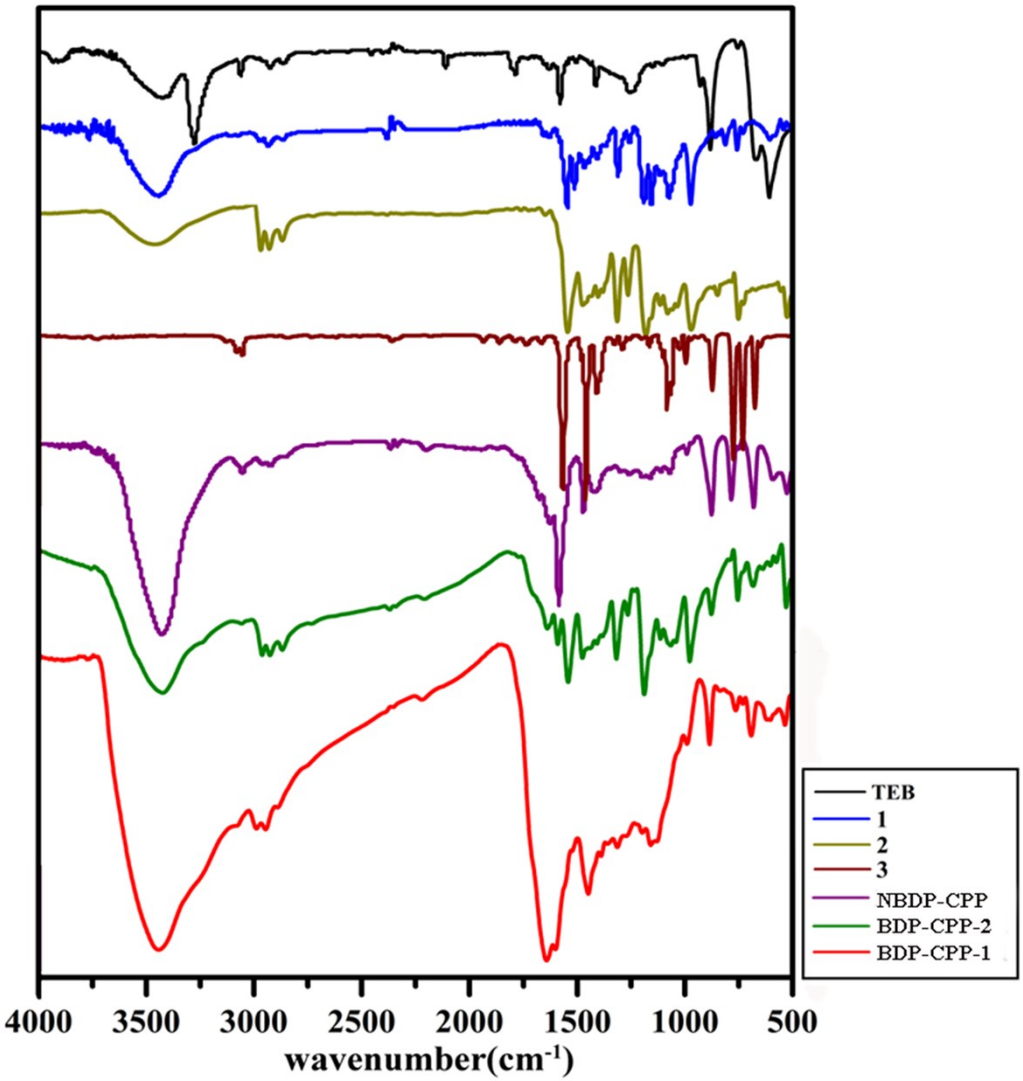


Fig. S4 IR spectra of monomers and CPPs.

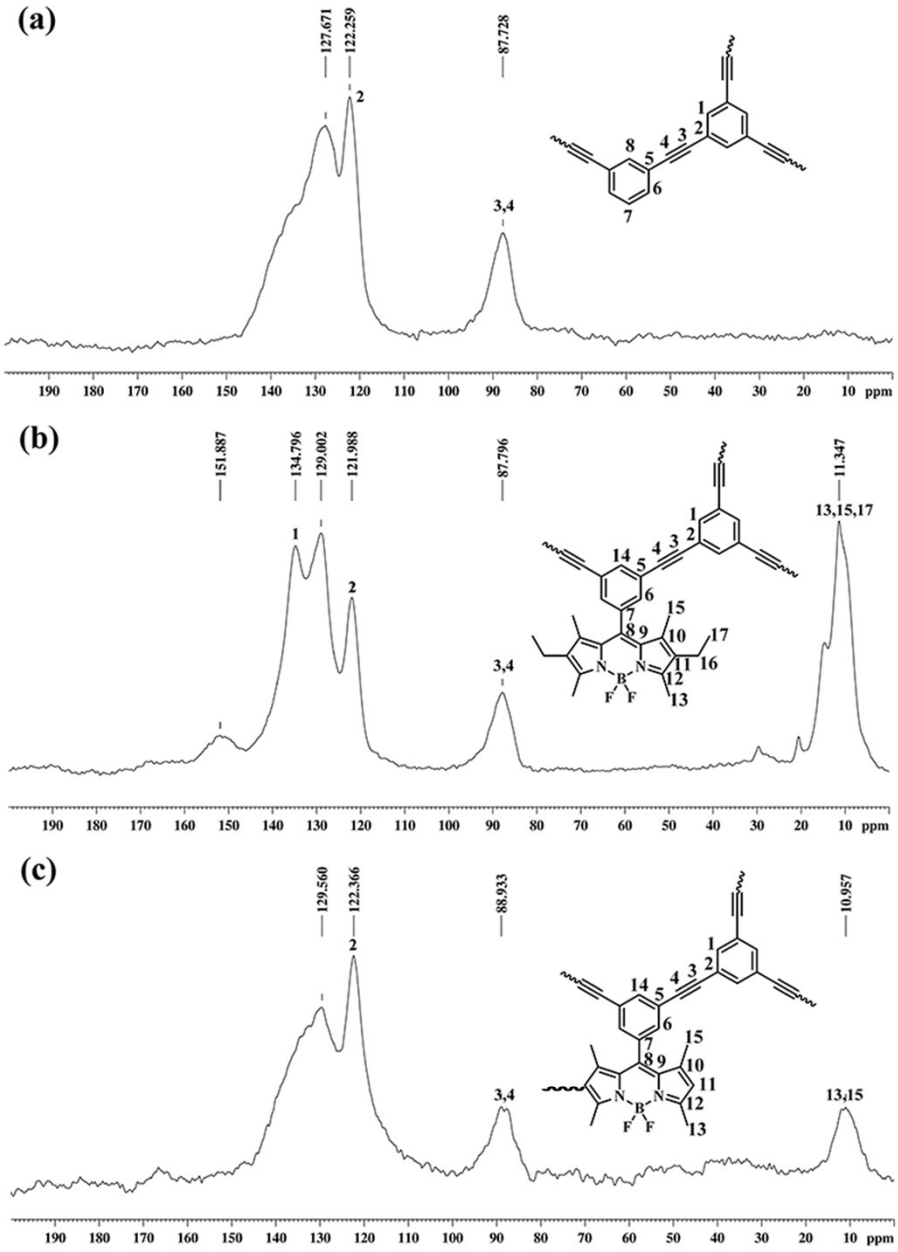


Fig. S5 Solid state NMR spectra for **BDP-CPP-1**, **BDP-CPP-2** and **NBDP-CPP**.

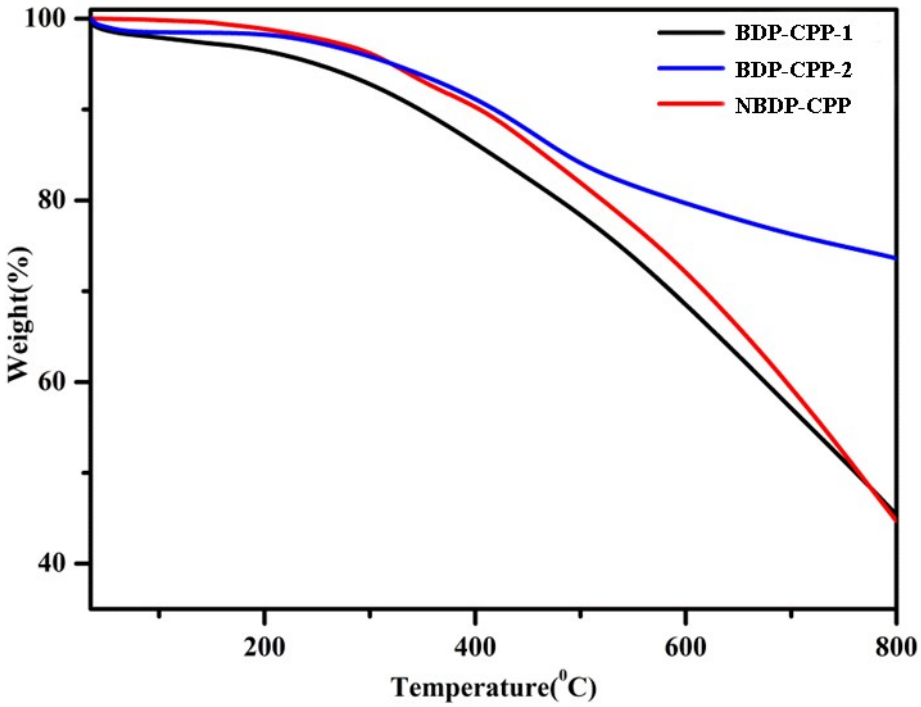


Fig. S6 TGA of **BDP-CPP-1**, **BDP-CPP-2** and **NBDP-CPP**.

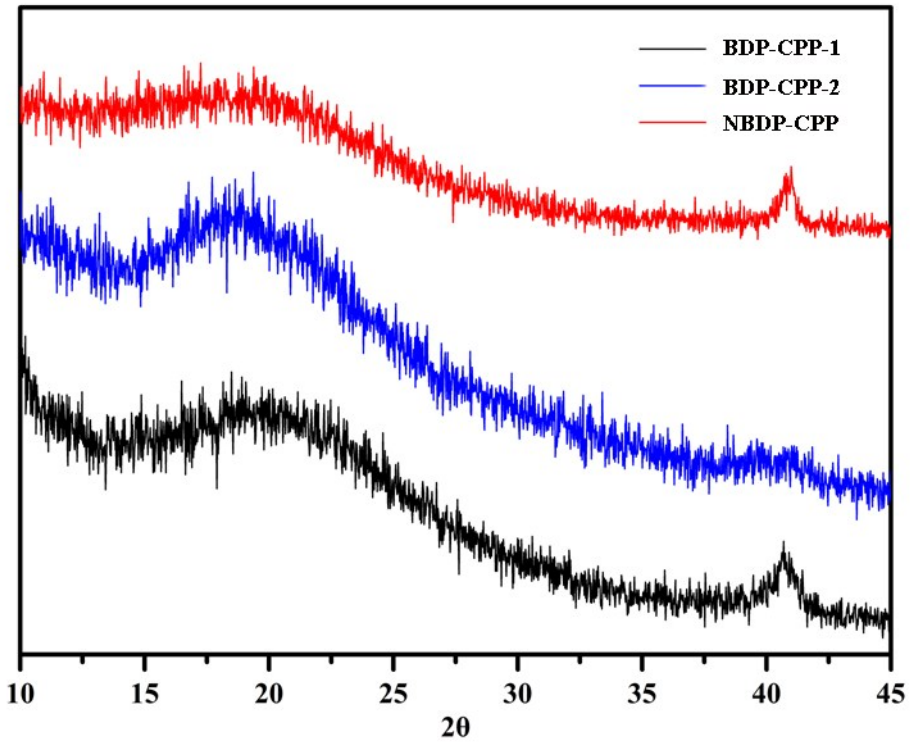


Fig. S7 XRD spectra of **BDP-CPP-1**, **BDP-CPP-2** and **NBDP-CPP**.

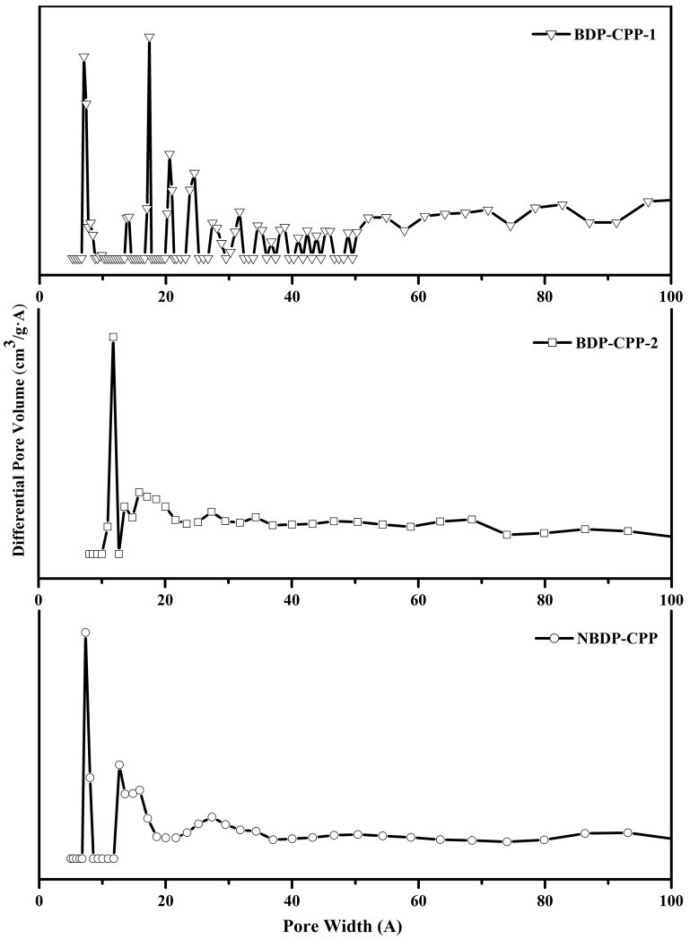


Fig. S8 Pore size distribution for **BDP-CPP-1**, **BDP-CPP-2** and **NBDP-CPP** calculated by DFT.

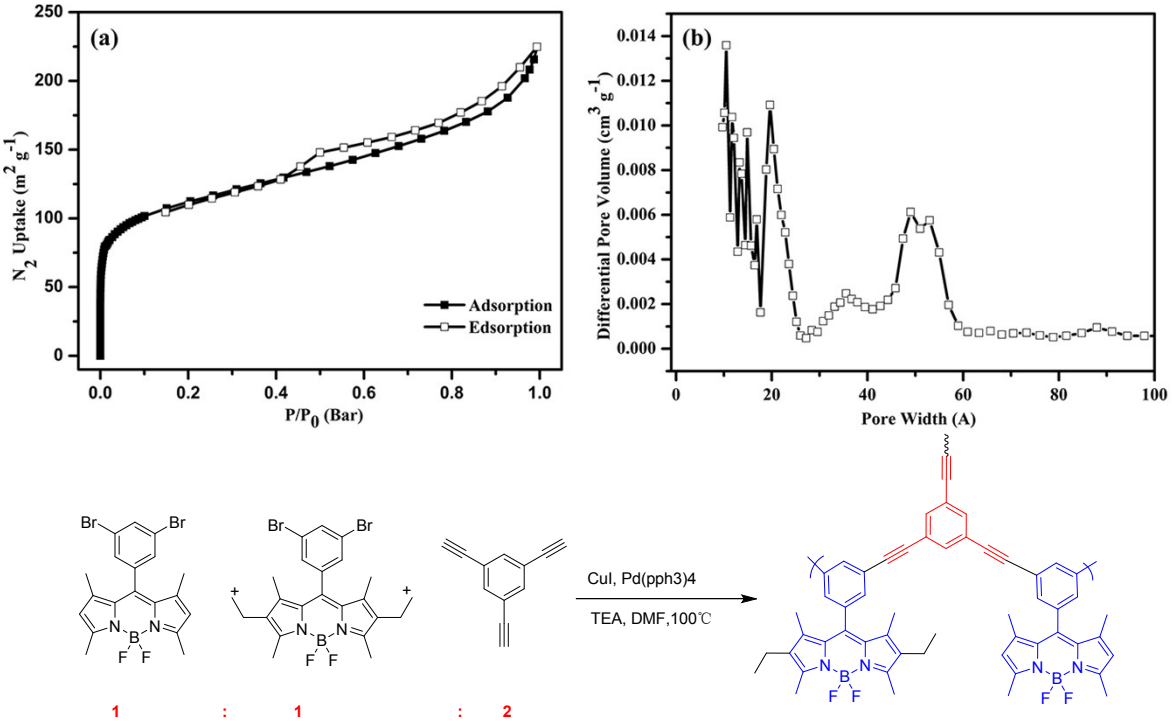


Fig. S9 Nitrogen adsorption-desorption isotherms of **BDP-CPP-3** measured at 77 K (a), Pore size distribution for **BDP-CPP-3** calculated by DFT (b) and the route of **BDP-CPP-3** (c).

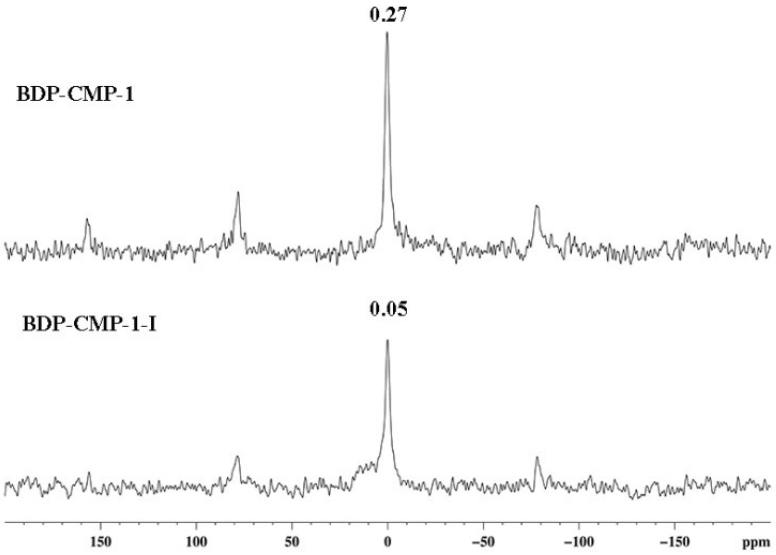


Fig. S10 Solid-state ^{11}B MAS NMR spectra of **BDP-CPP-1** before and after iodine capture.

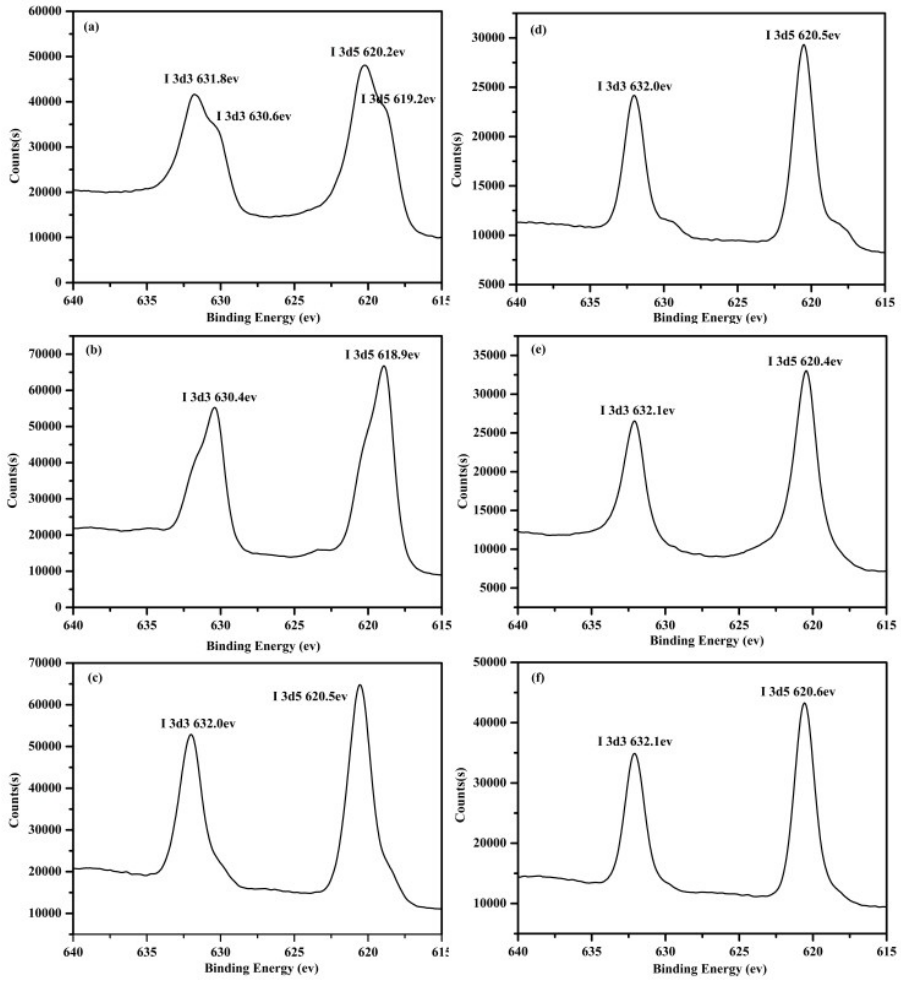


Fig. S11 XPS spectra of (a) **BDP-CPP-1**, (b) **BDP-CPP-2** and (c) **NBDP-CPP** after iodine uptaking, respectively. Iodine loaded (d) **BDP-CPP-1**, (e) **BDP-CPP-2** and (f) **NBDP-CPP** after washing by ethanol solvents for three days.

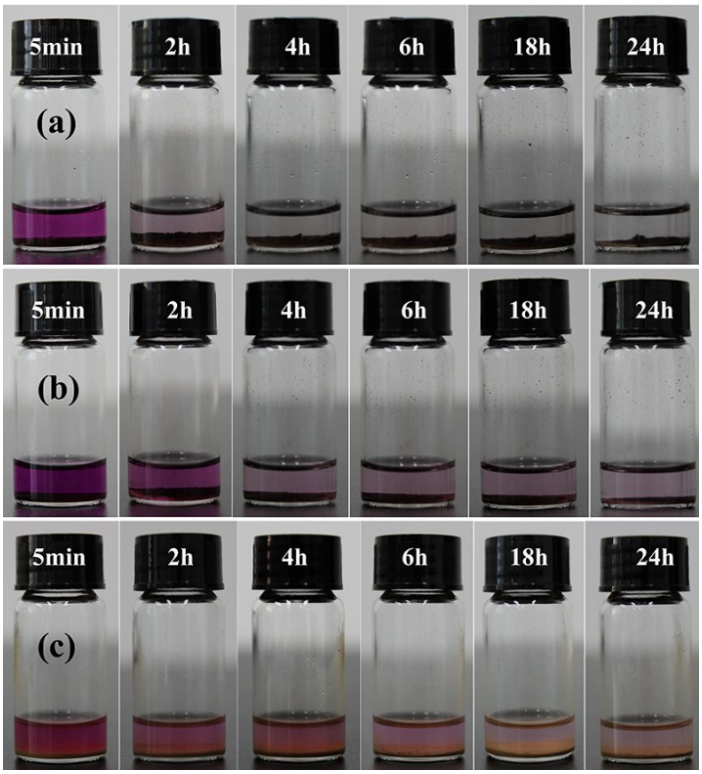


Fig. S12 Photographs of (a) **BDP-CPP-1**, (b) **BDP-CPP-2**, and (c) **NBDP-CPP** absorption capacity of iodine in hexane solution from 5 min to 24 hrs. The same weight CPPs (16 mg) were immersed in the iodine solution (c = 8 mM, 2 mL) at 25 ^{o}C.

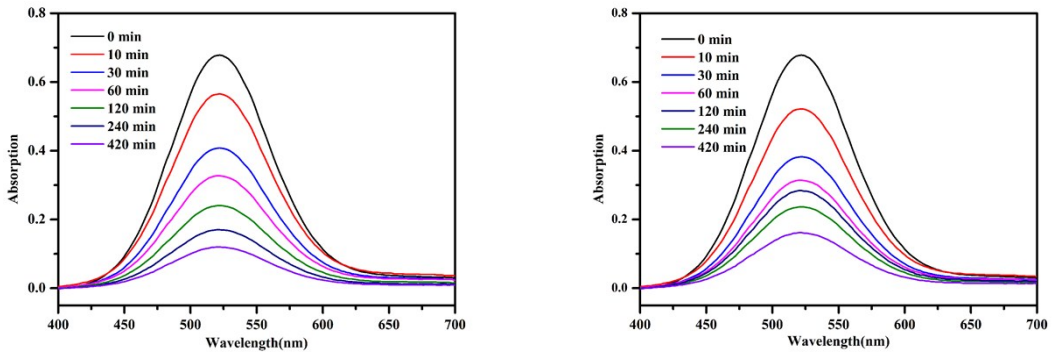


Fig. S13 UV-vis absorption spectra for **BDP-CPP-2 and NBDP-CPP** (16 mg) and iodine (212.0 mg/L) containing in hexane solution at different time. (left: **BDP-CPP-2**, right: **NBDP-CPP**)

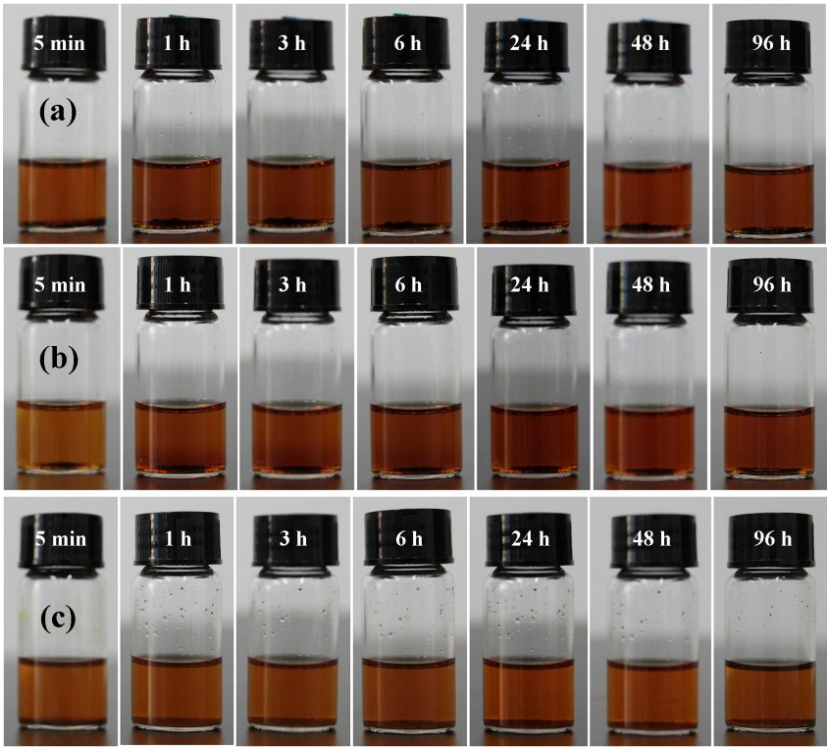


Fig. S14 Photographs of (a) **BDP-CPP-1**, (b) **BDP-CPP-2**, and (c) **NBDP-CPP** desorption iodine in ethanol solution from 5 min to 96 hrs. The same weight iodine loaded CPPs (10 mg) were immersed in ethanol (4 mL) at 25 °C.

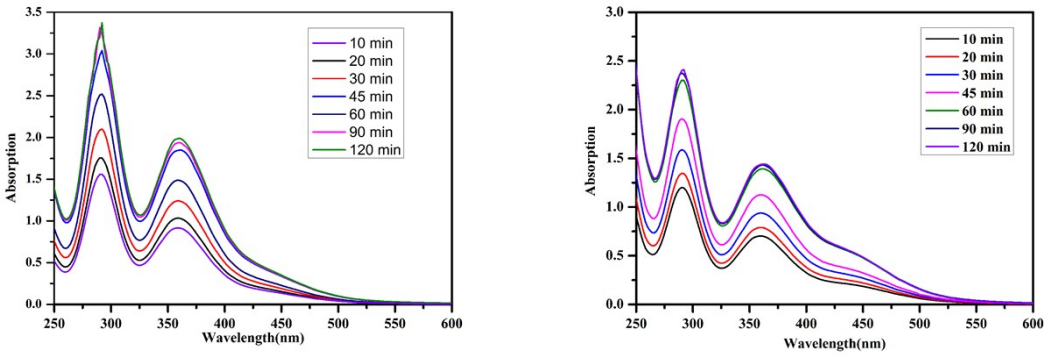


Fig. S15 UV-vis spectra of iodine released from **BDP-CPP-2@I_2** and **NBDP-CPP@I_2** (12 mg) in 4 mL ethanol (left: **BDP-CPP-2@I_2**, right: **NBDP-CPP@I_2**).

NMR and MASS spectra

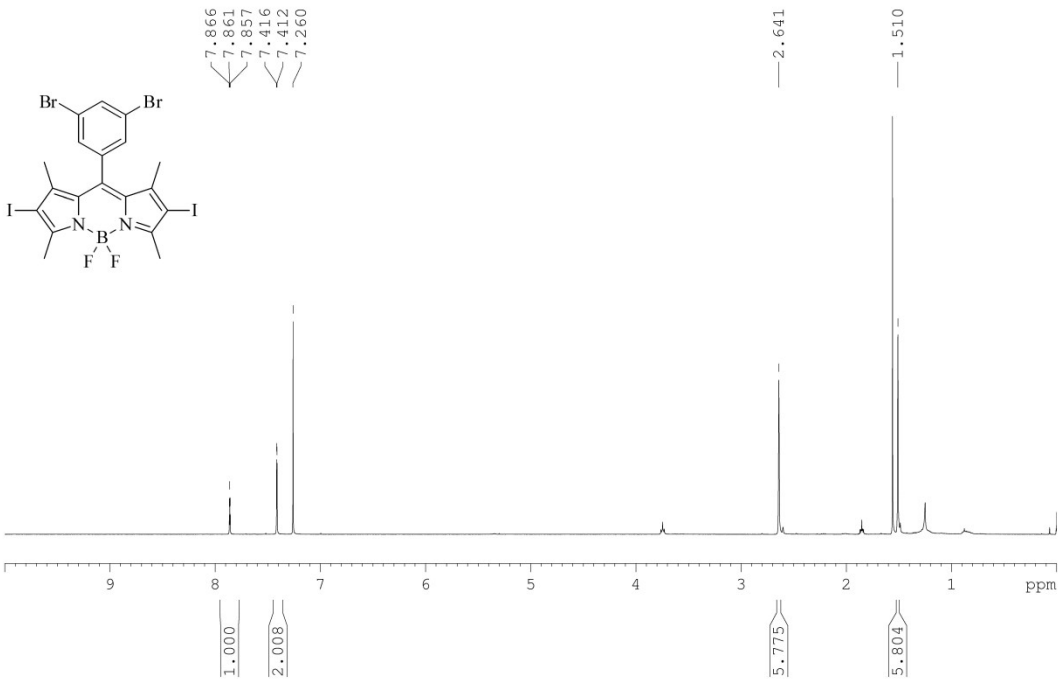


Fig. S16 ^{1}H NMR spectrum of **1- I_2.**

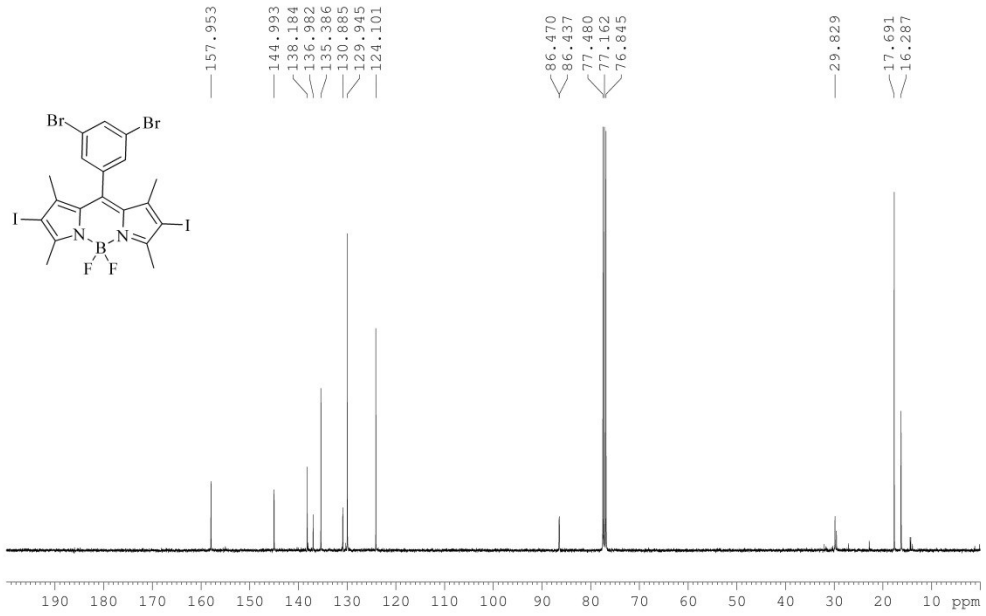


Fig. S17 ^{13}C NMR spectrum of **1-I_2**.

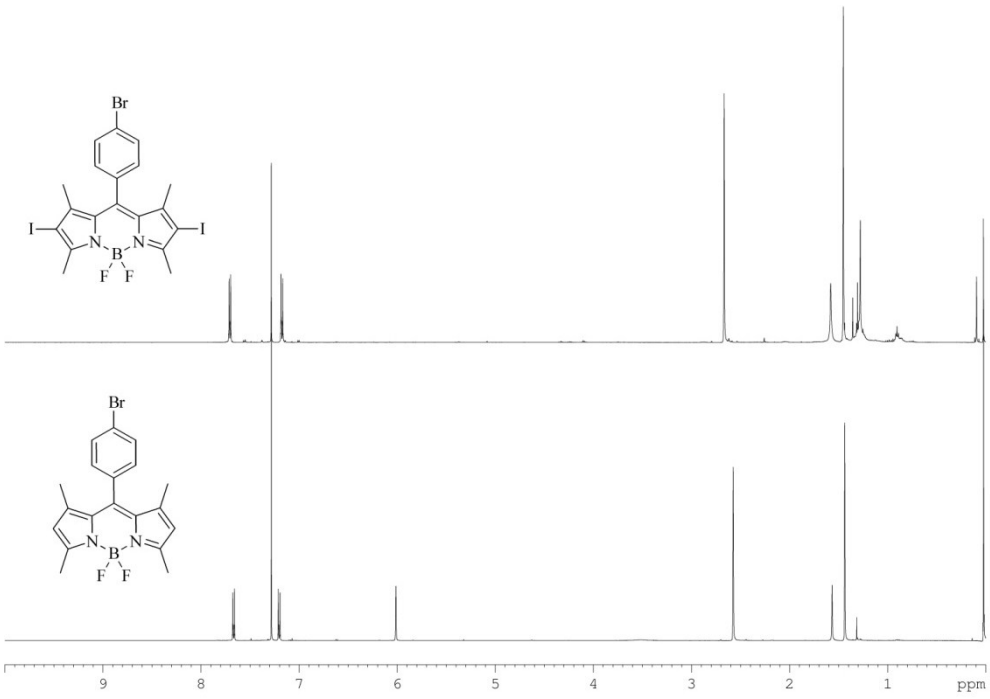


Fig. S18 ^{1}H NMR spectrum of **2-I$_2$** and **2**.

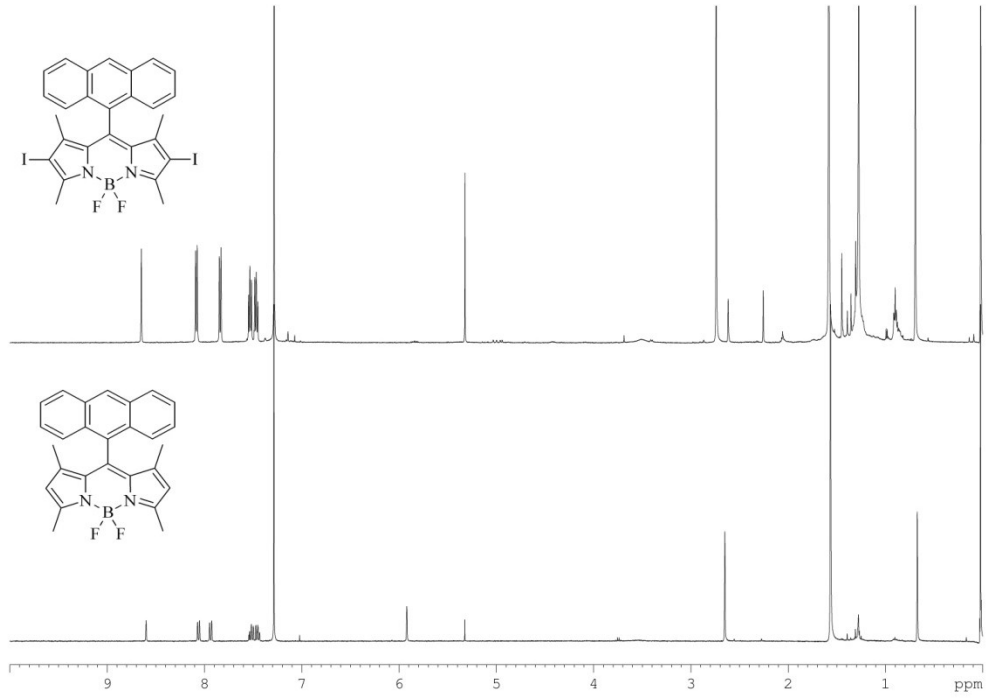


Fig. S19 ^{1}H NMR spectrum of **3-I$_2$** and **3**.

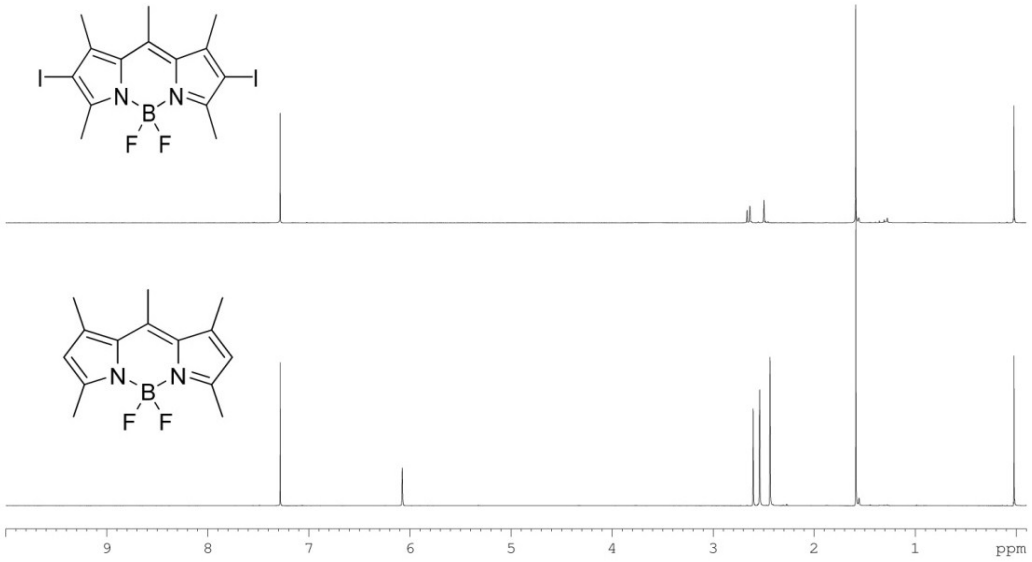


Fig. S20 ^{1}H NMR spectrum of **4-I$_2$** and **4**.

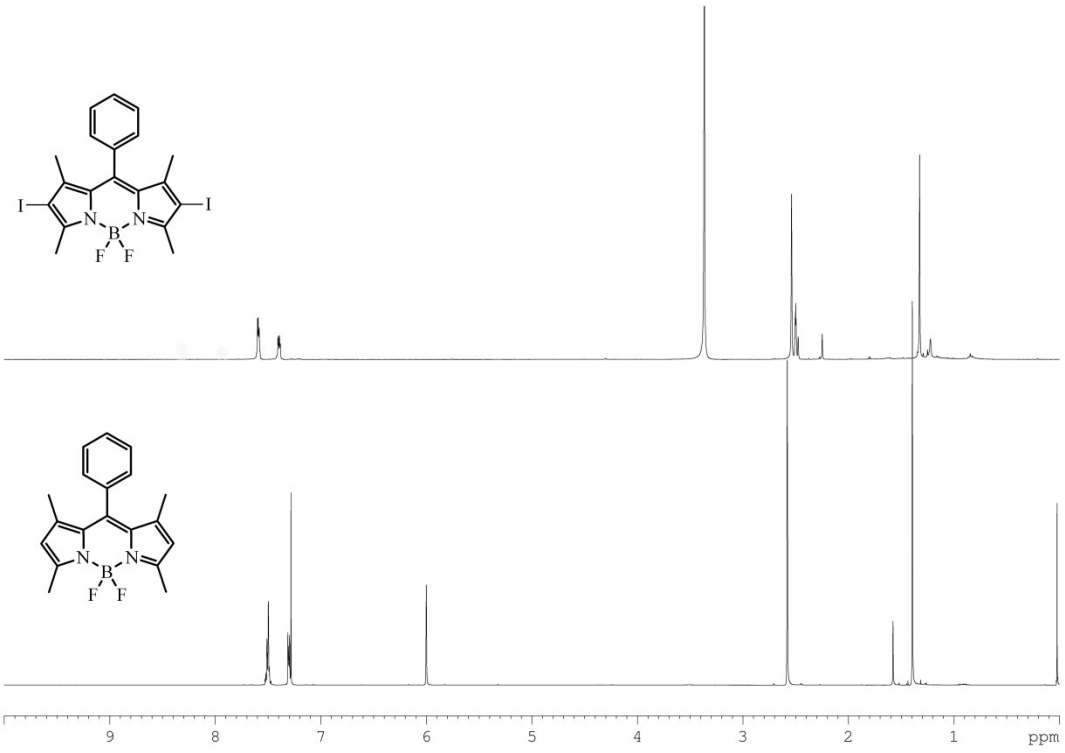


Fig. S21 ^{1}H NMR spectrum of **5-I$_2$** and **5**.

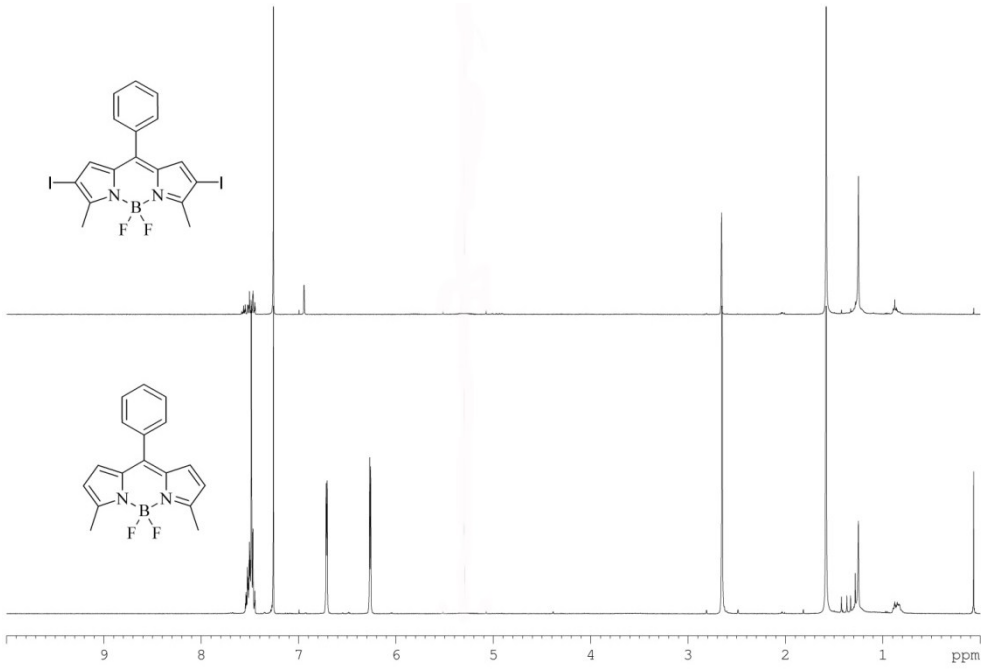


Fig. S22 ^{1}H NMR spectrum of **6-I$_2$** and **6**.

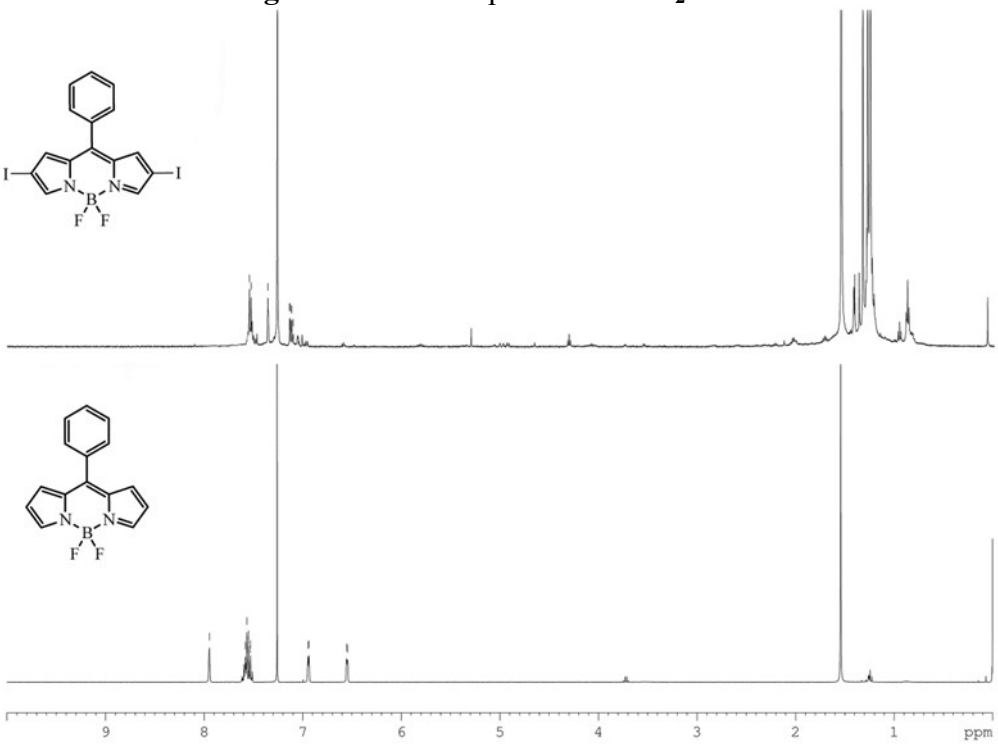


Fig. S23 ^{1}H NMR spectrum of **7-I$_2$** and **7**.

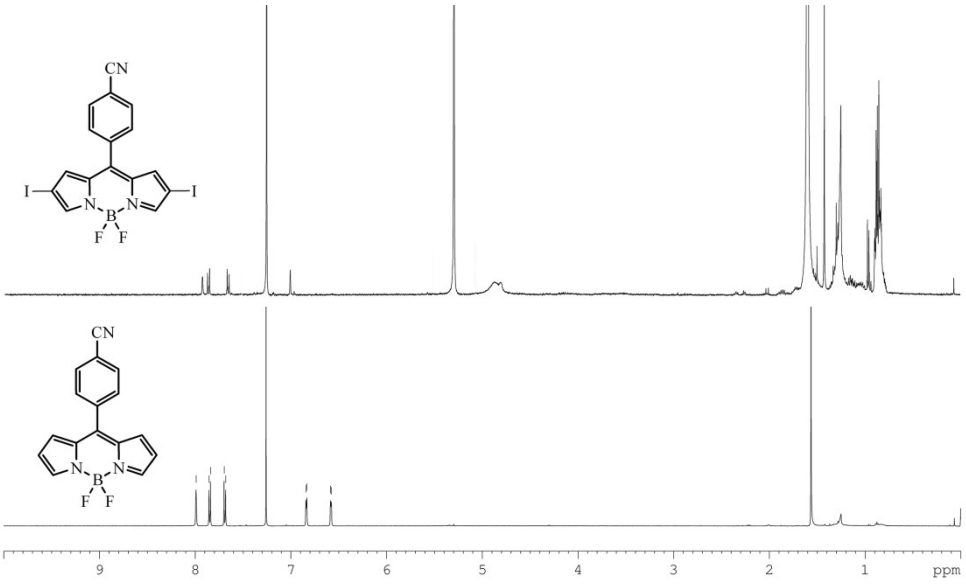


Fig. S24 ^{1}H NMR spectrum of **8-I$_2$** and **8**.

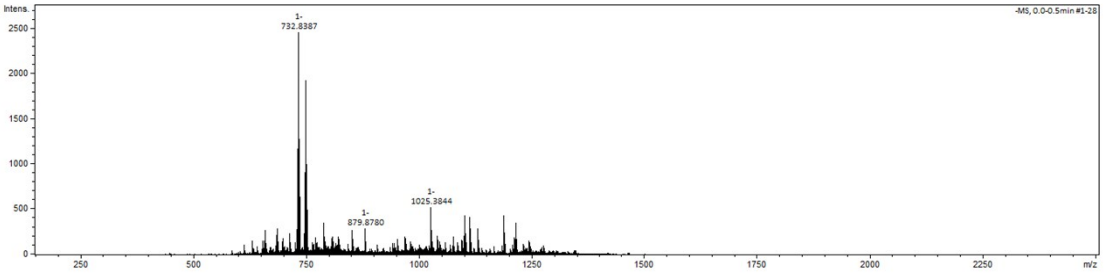


Fig. S25 Mass spectrum of **1-I$_2$**.

[s1] M. Benstead, G. A. Rosser, A. Beeby, G. H. Mehl and R. W. Boyle, *New J. Chem*., 2011, **35**, 1410-1417.