

## A facile route by using FeCl<sub>3</sub> to prepare dimeric BODIPY based porous organic polymers

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## **1. Materials and methods**

### **1.1 Materials.**

All chemical reagents were commercially available and used as received unless otherwise stated. Dichloromethane was dried by standard methods using CaCl<sub>2</sub> before distillation using distilling apparatus. All reactions were performed under an inert atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed using TLC plates pre-coated with silica gel (TLC: 10-40  $\mu\text{m}$ , 0.2 $\pm$ 0.03 mm). Flash column chromatography was performed using 40-63  $\mu\text{m}$  (230-400 mesh) silica gels as the stationary phase.

### **1.2 Structure Characterization and Analysis.**

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained from a Bruker Avance spectrometer at 500 and 125 MHz respectively. All chemical shifts were reported in  $\delta$  units relative to tetramethylsilane (TMS). A Hitachi U-5100 was used to measure UV-vis absorption spectra. A Hitachi F-2700 was used to perform fluorescence measurements. A high resolution mass spectrum was obtained by using a Tsq quantum access max from Thermo. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 6700 and reported in terms of the frequency of absorption (cm<sup>-1</sup>). Samples were prepared by dispersing in anhydrous KBr. Solid-state cross-polarization magic angle spinning (CP/MAS) NMR spectra were recorded from a AVANCE III 400 MHz produced by Bruker. Thermogravimetric analyses were conducted in an N<sub>2</sub> stream with an SDT Q600 V8.0 Build 95 analyzer. The samples were heated from room

temperature to 800 °C with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) measurements of POPs were made in a FEI SIRION200 microscopy with an accelerating voltage of 10 and 20 kV respectively. All the samples were coated with gold before test. High-resolution transmission electron microscopy (HR-TEM) images of BDPs were performed on a JEOL JEM-2100F microscopy with an accelerating voltage of 200 kV. Prior to TEM measurements, samples were ultrasonically dispersed in ethanol and dropped to a copper grid with a diameter of 3 mm and coated with carbon film. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 sorption analyzer. According to the absorption-desorption isotherms, BET (Brunauer-Emmett-Teller) specific surface area, pore size distribution and pore volume could be evaluated. Before each measurement, the samples were degassed at 120 °C for 6 h.

## 2. Synthesis

### 2.1 Synthesis of BDP-0

**BDP-0** was prepared according to the literature.<sup>[1]</sup> Crush product was purified via chromatography silica gel column with an eluting solvent petroleum ether (PE- DCM (v/v = 2:1) and afford the product **BDP-0** as red powder (50 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 6.02 (s, 4H, pyrrole-H), 2.57 (s, 12H, CH<sub>3</sub>), 1.90 (s, 12H, CH<sub>3</sub>).

### 2.2 Synthesis of BDP-1

**BDP-1** was prepared according to the literature.<sup>[2]</sup> Crush product was purified by chromatography silica gel column with an eluting solvent PE-DCM (v/v = 1:1) and afford the product **BDP-1** as red power (180 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.52 (s, 4H, Ar-H), 6.01 (s, 4H, pyrrole-H), 2.57 (s, 12H, CH<sub>3</sub>), 1.52 (s, 12H, CH<sub>3</sub>).

### 2.3 Synthesis of BDP-2

4,4'-Biphenyldicarboxaldehyde (631 mg, 3 mmol) was dissolved in dry DCM (100 ml), followed by dropwise addition of 2,4-dimethylpyrrole (1142 mg, 12 mmol). After that, catalytic amount of TFA was added to the mixture. The reaction system was degassed for 2 minutes and protected by a N<sub>2</sub> atmosphere. After oxidation by 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1430 mg, 6.3 mmol), the product was complexed with boron trifluoride etherate (BF<sub>3</sub>·OEt<sub>2</sub>) without further purification. After a 16 h, the solvent was evaporated under vacuum and the dark residue was purified by chromatography silica gel column with an eluting solvent PE-DCM (v/v = 1:1) and afforded product **BDP-2** as a red power (181 mg). Due to the bad solubility, no satisfied <sup>13</sup>C NMR spectrum of **BDP-2** could be obtained. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.82 (d, 4H, Ar-H), 7.41 (d, 4H, Ar-H), 6.01 (s, 4H, pyrrole-H) 2.57 (s, 12H, CH<sub>3</sub>), 1.48 (s, 12H, CH<sub>3</sub>). HRMS-EI calcd for C<sub>38</sub>H<sub>37</sub>B<sub>2</sub>F<sub>4</sub>N<sub>4</sub> 646.3062, found [M+H]<sup>+</sup> 647.2916; [M+Na]<sup>+</sup> 669.2738; [M+K]<sup>+</sup> 685.4121.

### 2.4 General synthetic procedure for the BDP-POPs

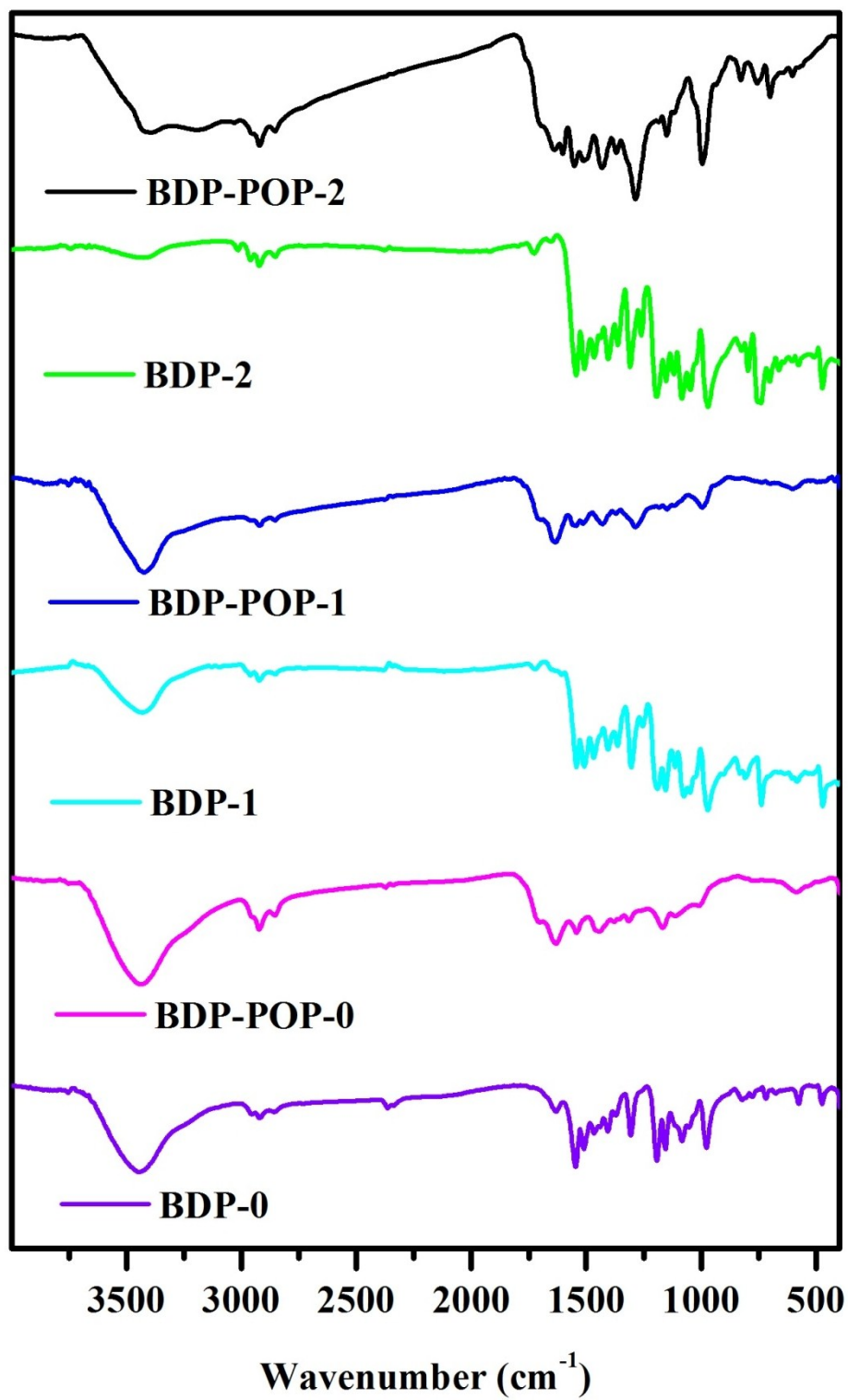
The preparation and treatment of **BDP-POP-n** (n = 0, 1 and 2) were in a similar way.

A typically procedure for preparation of **BDP-POP-1** was given as follows: **BDP-1** (100 mg, 0.175 mmol) was dissolved in anhydrous 1,2-dichloroethane (8 mL). The mixture was degassed by three freeze-pump-thaw cycles and then FeCl<sub>3</sub> (234 mg, 1.44 mmol) was added into the mixture under N<sub>2</sub> atmosphere. After that, the mixture was degassed by three freeze-pump-thaw cycles and then kept at room temperature with stirring for 48 h. The precipitate was obtained by filtration washed by vast quantities of dichloromethane, tetrahydrofuran and chloroform. To guarantee a total removal of impurities, the precipitate was further purified by Soxhlet extraction with tetrahydrofuran, acetone, chloroform, methanol and water for 24 hours, respectively. Finally, the solid was freeze-dried for 3 days to afford black powders **BDP-POP-1** (70 mg, 70 %). **BDP-POP-0** and **BDP-POP-2** were synthesized by the similar route with yield 65% and 80%, respectively.

#### References

- [1] L. Wang, J. Cao, J. Wang, Q. Chen, A. Cui and M. He, *RSC Adv.*, 2014, **45**, 14786-14790.
- [2] J. Y. Liu, Y. Huang, R. Menting, B. Röder, E. A. Ermilov and D. K. P. Ng, *Chem. Commun.*, 2013, **49**, 2998-3000.

### 3. FTIR spectra



**Fig S1.** FT-IR spectra of BODIPY-based monomers and POPs.

#### 4. Solid-state NMR spectra

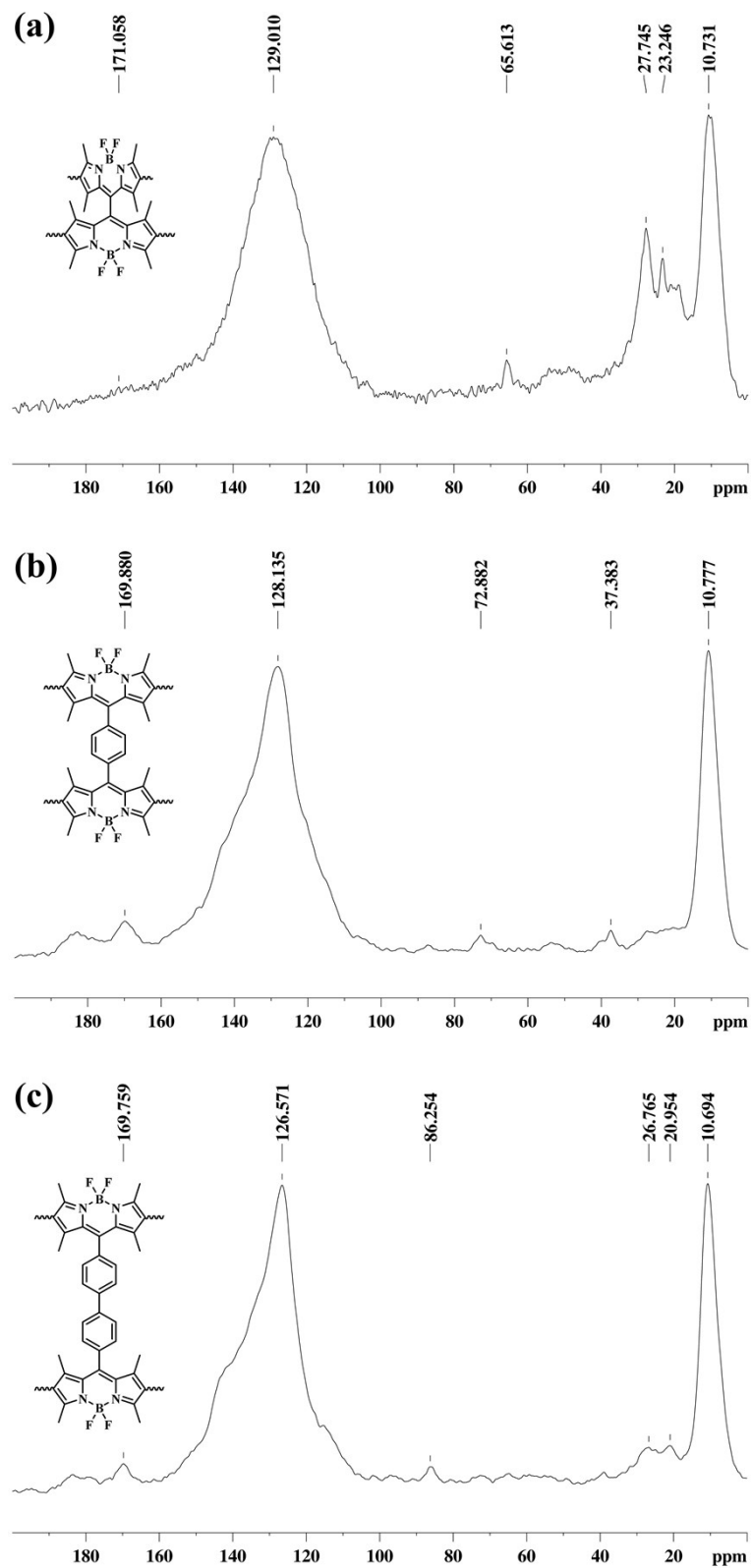


Fig S2.  $^{13}\text{C}$  CP-MAS solid-state NMR spectra of **BDP-POP-n** ( $n = 0, 1$  and  $2$ ).

## 5. TGA analysis

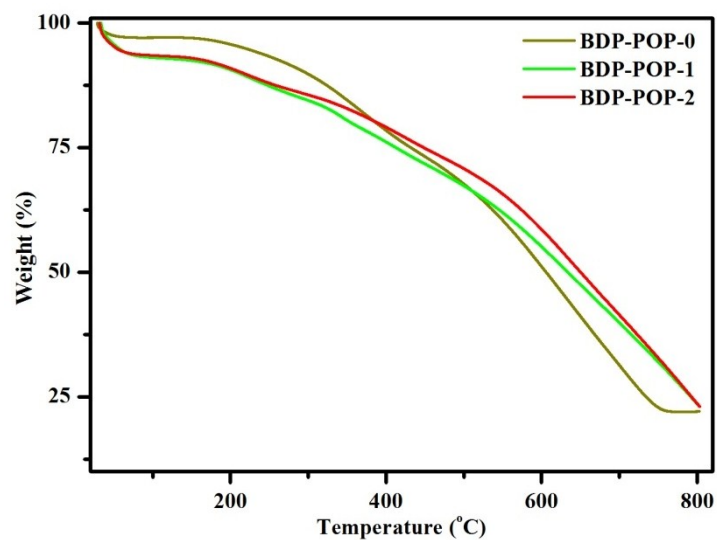
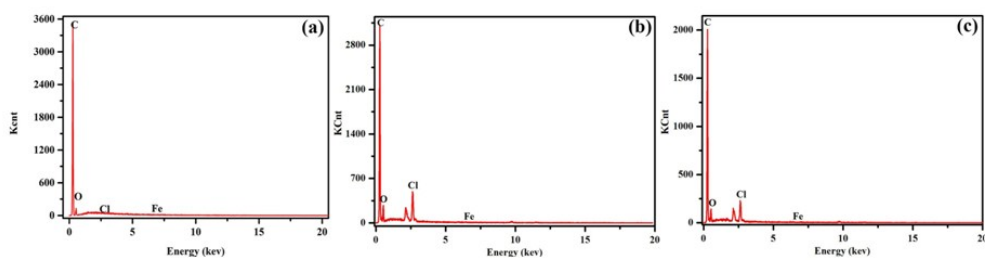


Fig S3. TGA curves of BDP-POP-n (n = 0, 1, 2).

## 6. EDS analysis results



Element	Wt%	At%
BK	03.70	04.17
CK	89.56	90.78
FK	00.06	00.04
ClK	00.07	00.02
FeK	00.09	00.02
Matrix	Correction	ZAF

Element	Wt%	At%
BK	02.51	02.98
CK	81.72	87.26
FK	00.21	00.14
ClK	05.60	02.02
FeK	00.67	00.15
Matrix	Correction	ZAF

Element	Wt%	At%
BK	02.08	02.61
CK	73.26	82.74
FK	00.36	00.25
ClK	03.85	01.47
FeK	00.50	00.12
Matrix	Correction	ZAF

Fig S4. EDS results of (a) BDP-POP-0, (b) BDP-POP-1 and (c) BDP-POP-2.



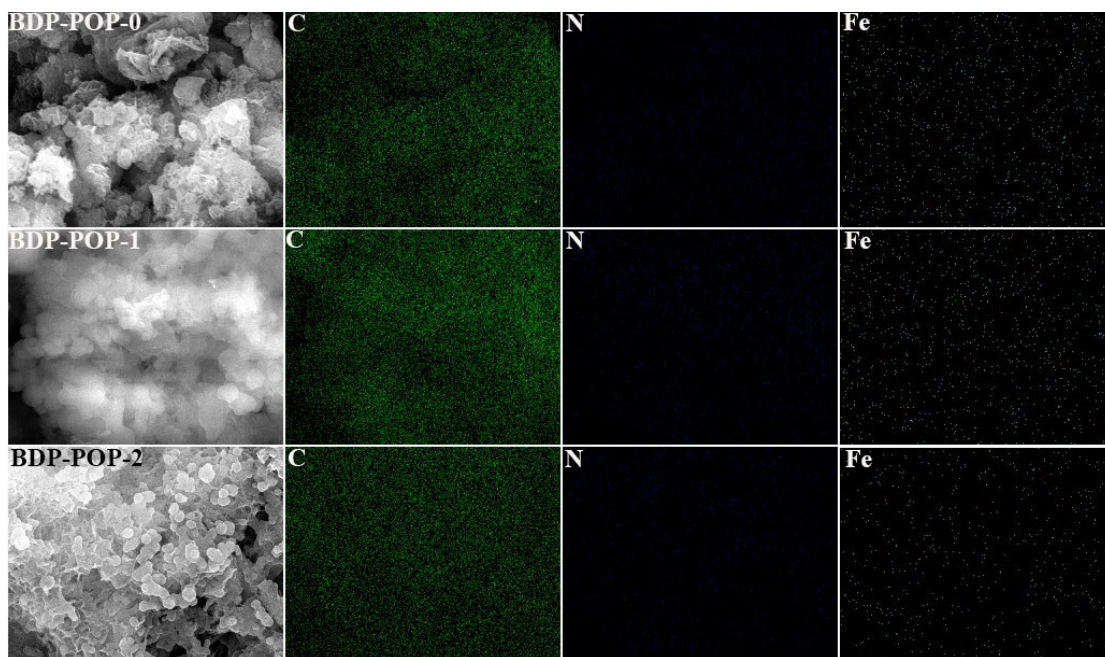


Fig S5. EDS mapping results of (a) **BDP-POP-0**, (b) **BDP-POP-1** and (c) **BDP-POP-2**.

## 7. Time dependent absorption spectra of DPBF in dimethylformamide (DMF) upon irradiation.

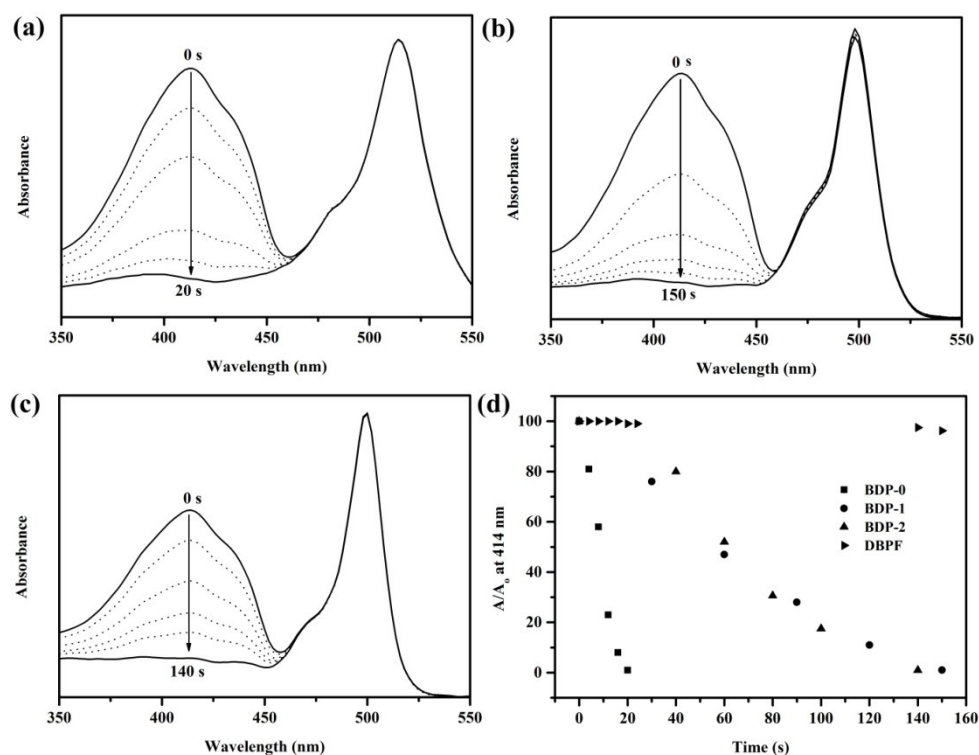


Fig S6. Time dependent absorption spectra of DPBF in dimethylformamide (DMF) upon irradiation with a low power green LED lamp: (a) **BDP-0**, (b) **BDP-1**, (c) **BDP-2**. (d) decay kinetics of DPBF with different BDPs. Test conditions: DPBF ( $4 \times 10^{-5}$  M) in DMF (2.5 mL) solution with BDP ( $6.4 \times 10^{-6}$  M) for (a), (b) and (c), respectively.

## 8. Solid emission spectra of POPs researched in this work.

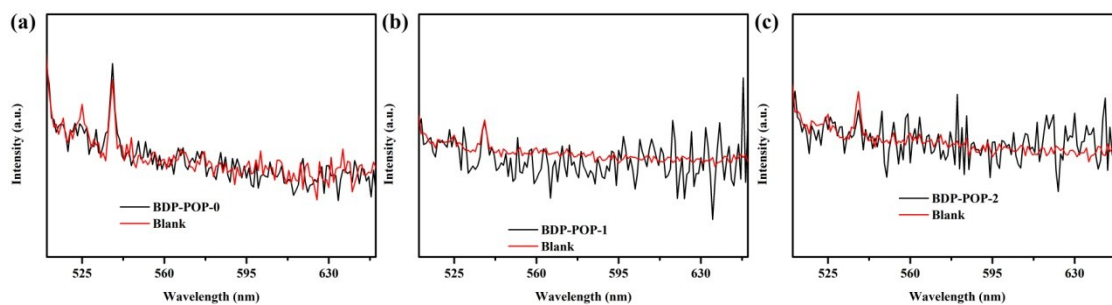


Fig. S7 Solid emission spectra of (a) BDP-POP-0, (b) BDP-POP-1 and (c) BDP-POP-2.

## 9. Porous properties comparison of BDP-POP-1 synthesized in $\text{CHCl}_3$ and $\text{CH}_2\text{ClCH}_2\text{Cl}$ .

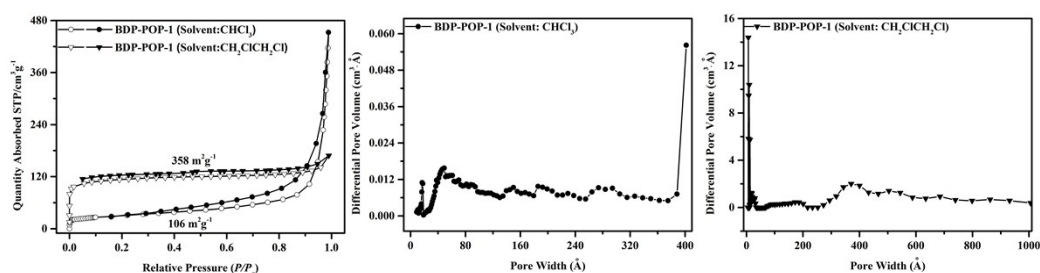


Fig. S8 (a) Nitrogen adsorption-desorption isotherms, (b) pore size distribution for BDP-POP-1 synthesized in  $\text{CHCl}_3$ , (c) pore size distribution for BDP-POP-1 synthesized in  $\text{CH}_2\text{ClCH}_2\text{Cl}$  calculated by NLDFT measured at 77 K.

## 10. Singlet oxygen generation comparison of BDP-POP-1 synthesized in $\text{CHCl}_3$ and $\text{CH}_2\text{ClCH}_2\text{Cl}$ .

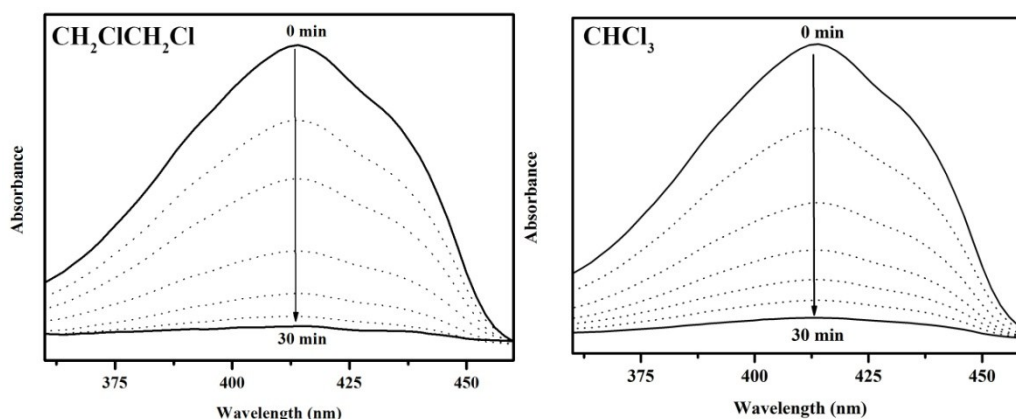
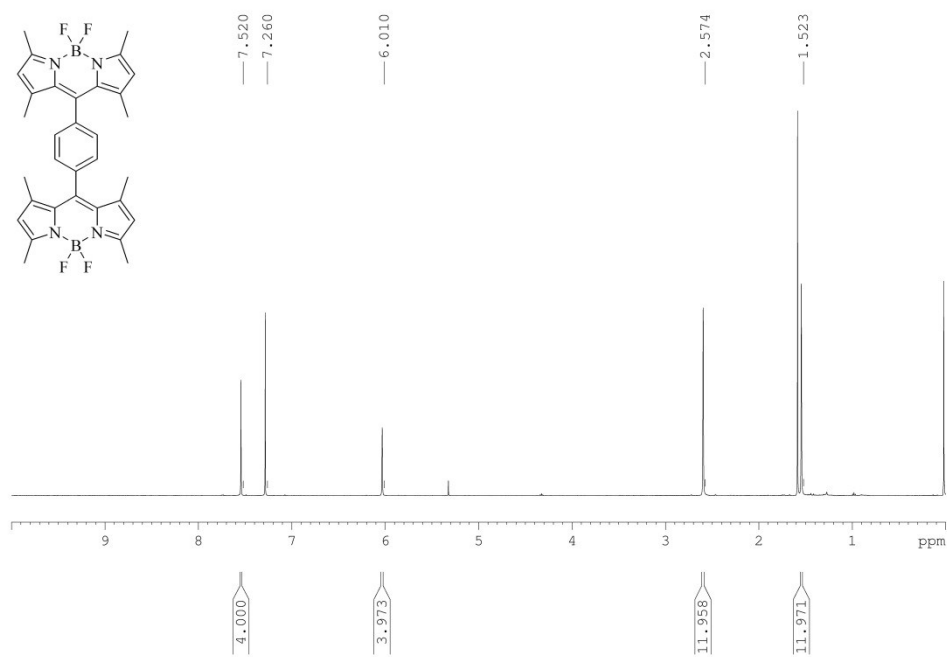
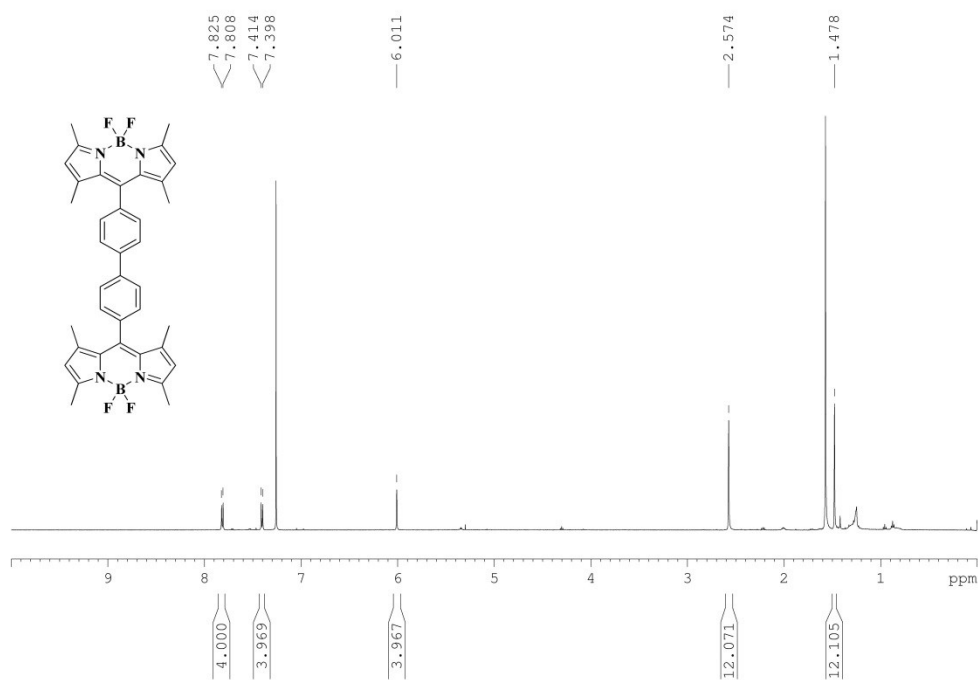


Fig S9. Time dependent absorption spectra of DPBF in dimethylformamide (DMF) upon irradiation with a low power green LED lamp: (a) BDP-POP-1 synthesized in  $\text{CH}_2\text{ClCH}_2\text{Cl}$ , (b) BDP-POP-1 synthesized in  $\text{CH}_3\text{Cl}$ . Test conditions: DPBF ( $4 \times 10^{-5}$  M) in DMF (2.5 mL) solution with BDP-POP (0.1 mg), respectively.

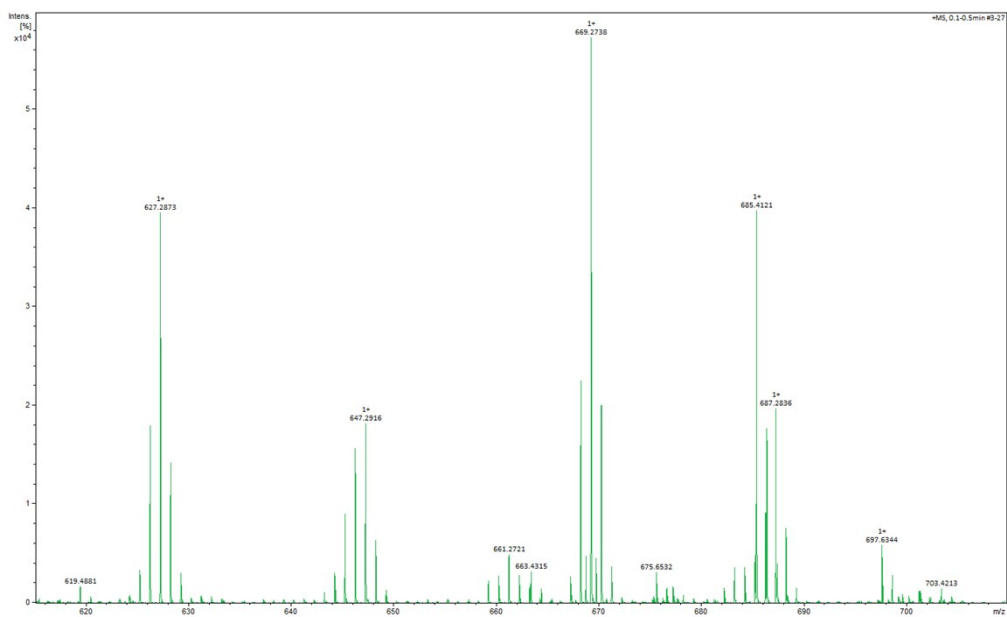




**Fig S12.**  $^1\text{H}$  NMR spectrum of **BDP-1**.



**Fig S13.**  $^1\text{H}$  NMR spectrum of **BDP-2**.



**Fig S14.** HRMS-EI spectrum of **BDP-2**.