Electronic Supplementary Material (ESI) for Polymer Chemistry.

Hierarchically Porous Π-Conjugated PolyHIPE as Heterogeneous Photoinitiator for Free Radical Polymerization under Visible Light

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1. Experimental Methods

Materials

Benzoxadiazole, 2,7-dibromo-9H-carbazole (CB), tetrakis(triphenylphosphine) palladium(0) (99%), potassium carbonate (K_2CO_3), Span® 80 nonionic surfactant, chloroform-d ($CDCl_3$, 99.8%), dimethylaminopyridine (DMAP) and all other solvents were purchased from Aldrich. 1,3,5-Tribromobenzene and di-*tert*-butyl dicarbonate (di-BOC) were obtained from Alfa Aesar and 1,3,5-Phenyltriboronic acid (PB) (98%) was purchased from Combi-Blocks Inc. Dibromobenxadiazole (BO) was synthesized according to literature.[1] All chemicals and solvents were used as received unless otherwise specified.

Synthesis of Boc-CB

0.991 g CB (3.06 mmol), 1.334 g di-BOC (6.11 mmol) and 0.373 g DMAP (3.05 mmol) were dissolved in 50 mL dried THF. The reaction mixture was stirred at room temperature under nitrogen for 12 h. After completion, the reaction mixture was poured into 500 mL of Milli-Q water. The precipitate was then washed with cold methanol and dried under vacuum, yielding 1.18 g (91%) product.

1H NMR (Figure S3): 8.37 (d, 2H), 7.64 (d, 2H), 7.37 (d, 2H), 1.69 (s, 9H)

13C NMR (Figure S4): 150.3, 139.1, 126.5, 123.8, 121.0, 120.5, 119.6, 85.2, 28.3

Synthesis of B-(Boc-CB)$_2$-BO

To 100 mg (0.22 mmol) of PB, 94 mg (0.22 mmol) of BOC-CB, 32 mg (0.11 mmol) of BO, 13 mg (0.011 mmol) of tetrakis(triphenylphosphine) palladium(0) and 100 mg of Span® 80 were dissolved in 1 mL of toluene. 182 mg (1.32 mmol) of K_2CO_3 was dissolved in 9 mL of Milli-Q water. Then, the aqueous phase was slowly added to the organic phase under vigorous stirring using an Ultra Turrax® IKA T18 mechanical stirrer at 14000 RPM. After 30 min, the homogeneous mixture became viscous and was heated to 80 ^oC for 12 h. The resulted poly(HIPE) was then rinsed with Milli-Q water several times and extracted with 50/50 dichloromethane and methanol solution in a soxhlet for 24 h. Drying of the poly(HIPE) was then performed using supercritical CO_2 (CPD 300 critical point dryer).

Photopolymerization of MMA with B-$(BOC\text{-}CB)_2$-BO

Typical polymerization procedure: In a glass vial, a mixture of MMA (1 mL, 9,39 mmol), B-$(BOC\text{-}CB)_2$-BO (25 mg) and Et_3N (20 mg) were added. The mixture was purged with N_2 for 5 min and the vial was sealed from air. The mixture was then irradiated with a 23 W household energy saving lamp (Osram) for 24 h. After the irradiation, the mixture was dissolved in more THF, the PolyHIPE was filtered off and the product precipitated in methanol. The polymers were collected by filtration and dried under vacuum at 40 ^{o}C overnight. The conversions were determined by comparing the integrated peaks corresponding to the vinyl protons (δ = 6.09 and 5.55 ppm) of MMA to the methoxy and methyl group (δ = 3.75 and 1.95) corresponding to the monomers and polymers.

Characterization

UV-vis absorption and emission spectra were recorded at room temperature on a Perkin Elmer Lambda 100 spectrophotometer and J&M TIDAS spectrofluorometer, respectively. NMR measurements were recorded on Bruker AVANCE 300 or Bruker AVANCE 500. FT-IR sepctra were recorded on a Varian 1000 FT-IR spectrometer. Solid State NMR measurements were carried out using Bruker Avance II solid state NMR spectrometer operating at 300 MHz Larmor frequency equipped with a standard 4mm magic angle spinning (MAS) double resonance probe head. Scanning electron microscope (SEM) images were acquired on a LEO Gemini 1530 (Carl Zeiss AG, Germany) using an in lens SE detector. Polymer surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using Quadrasorb SI (Quantachrome Instruments). Data was evaluated using QuadraWin software from Quantachrome Instruments. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using Quenched Solid Density Functional Theory (QSDFT, N_2, assuming carbon adsorbent with slit pores). Samples were degassed at 100 ^{o}C for 24 h under high vacuum before analysis.

2. Monomer Characterizations

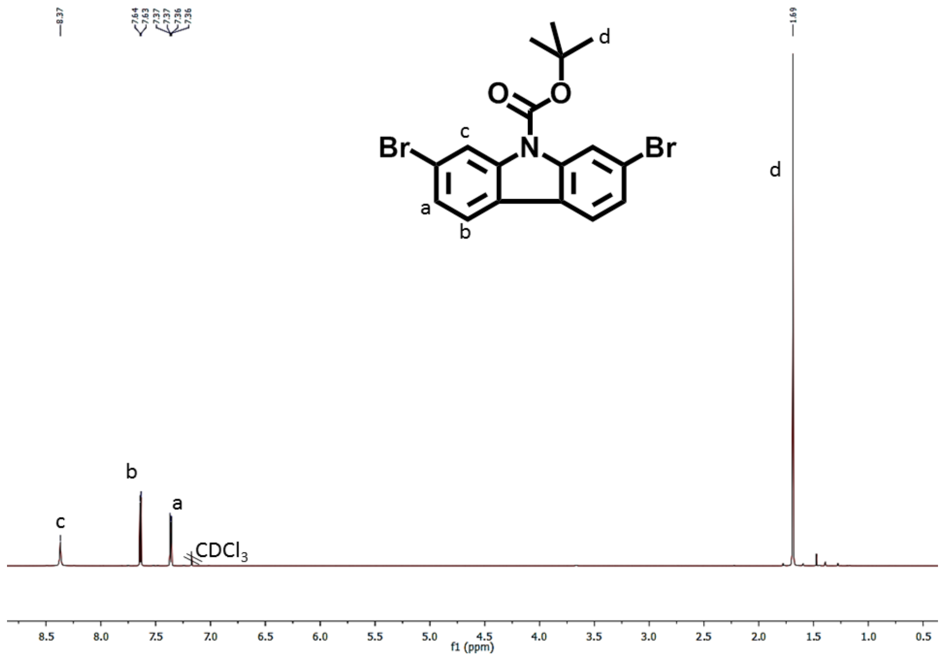

Figure S1. ^{1}H NMR spectrum of BOC-CB.

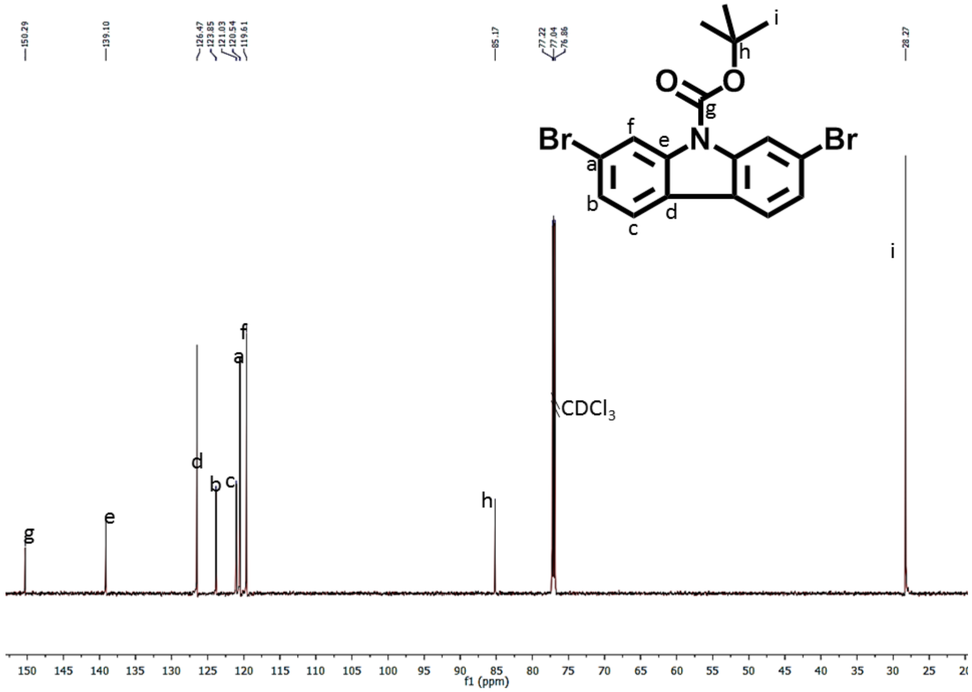

Figure S2. ^{13}C NMR spectrum of BOC-CB.

3. FTIR Spectroscopy

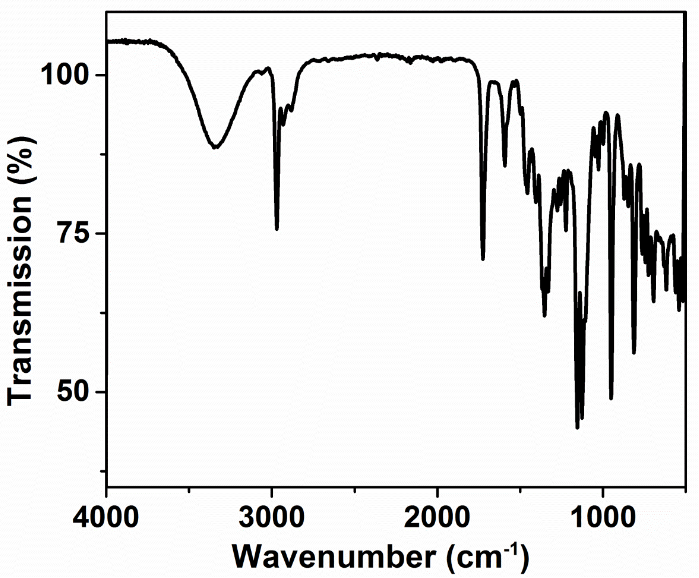

Figure S3. FTIR spectrum of conjugated poly(HIPE) B-(Boc-CB)$_2$-BO.

4. Thermogravimetric Analysis (TGA)

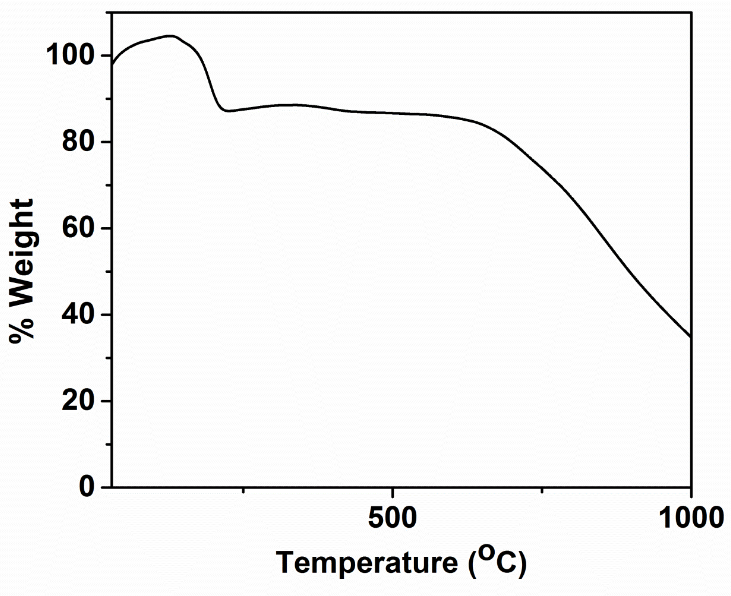

Figure S4. Thermogravimetry analysis (TGA) of B(BOC-CB)$_2$BO.

5. Brunauer-Emmett-Teller (BET) Surface Area Measurements

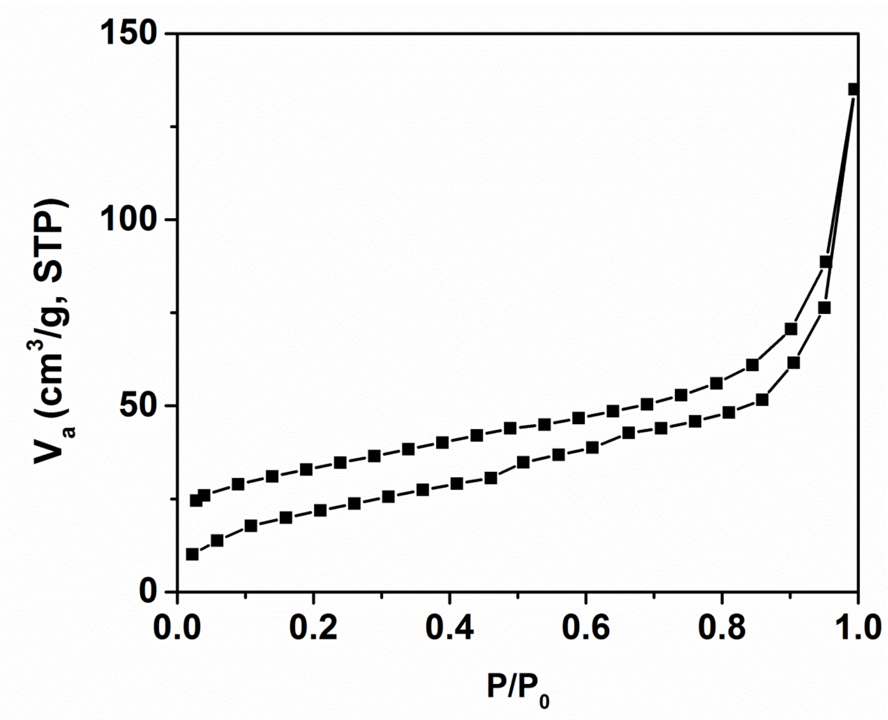

Figure S5. N_2 sorption isotherms of BET surface area measurement.

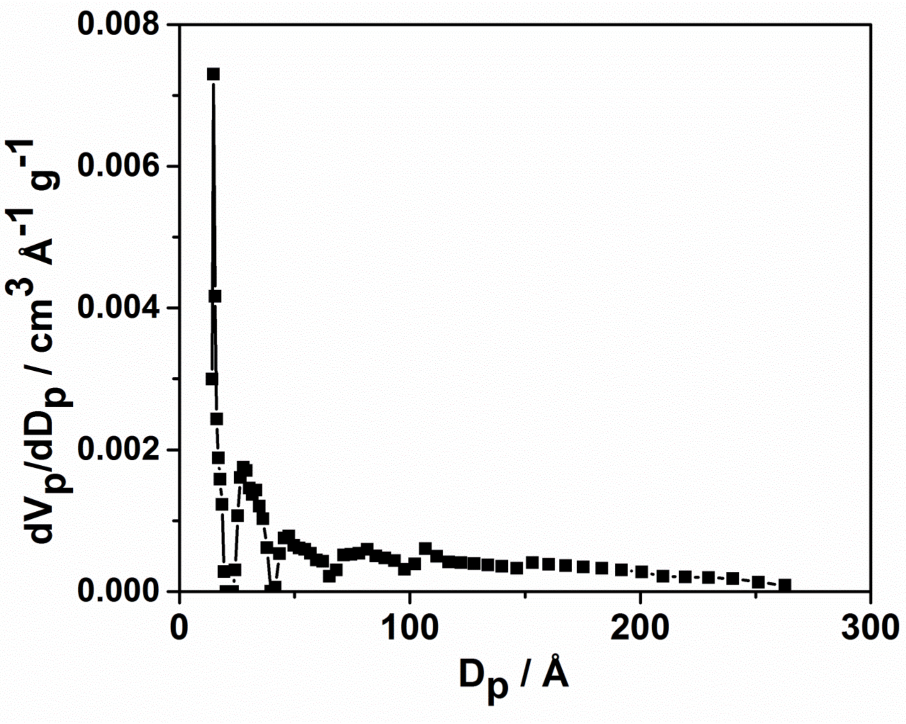

Figure S6. Pore size distribution of BET measurement.

6. Solid State ^{13}C NMR Spectroscopy

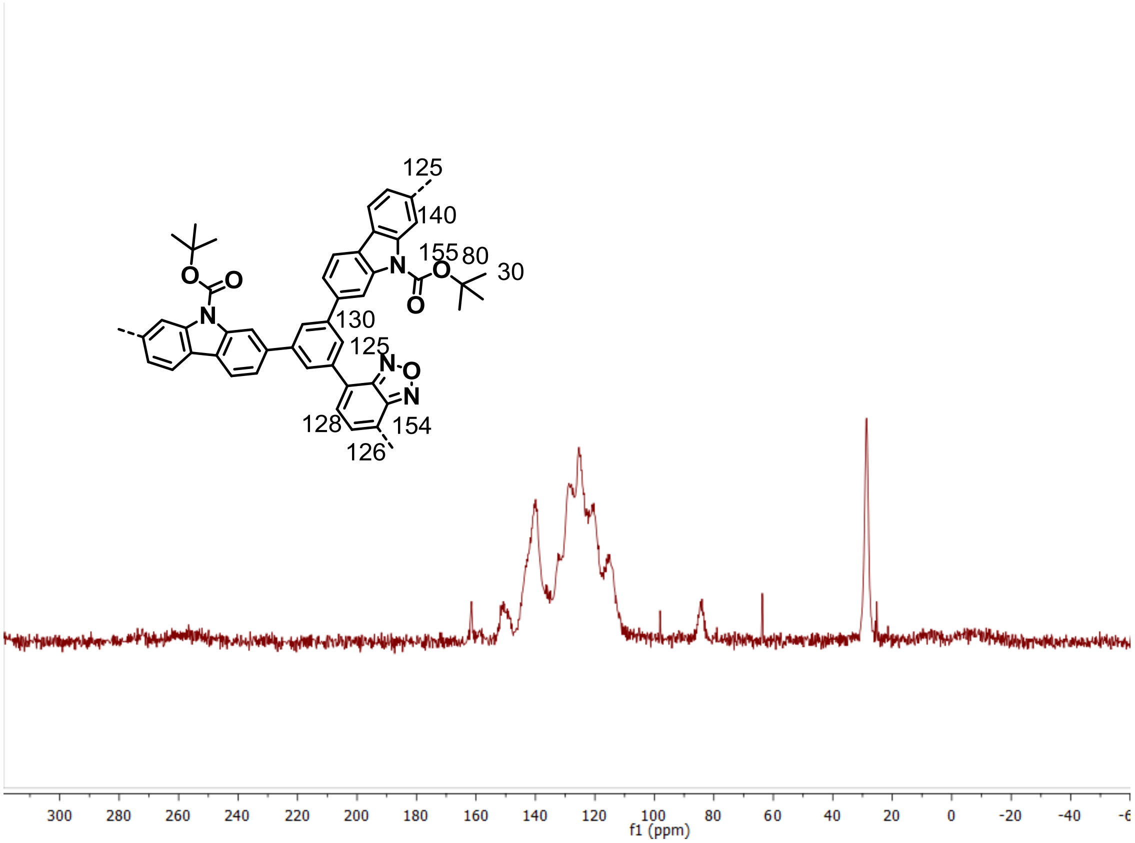

Figure S7. Solid state ^{13}C NMR of B-(BOC-CB)$_2$-BO.

7. Photopolymerization of MMA.

Figure S8. A simple photoinitiation set-up using a 23 W household energy saving light bulb.

8. SEM image of B-(Boc-CB)$_2$-BO after the repeating photopolymerization of MMA

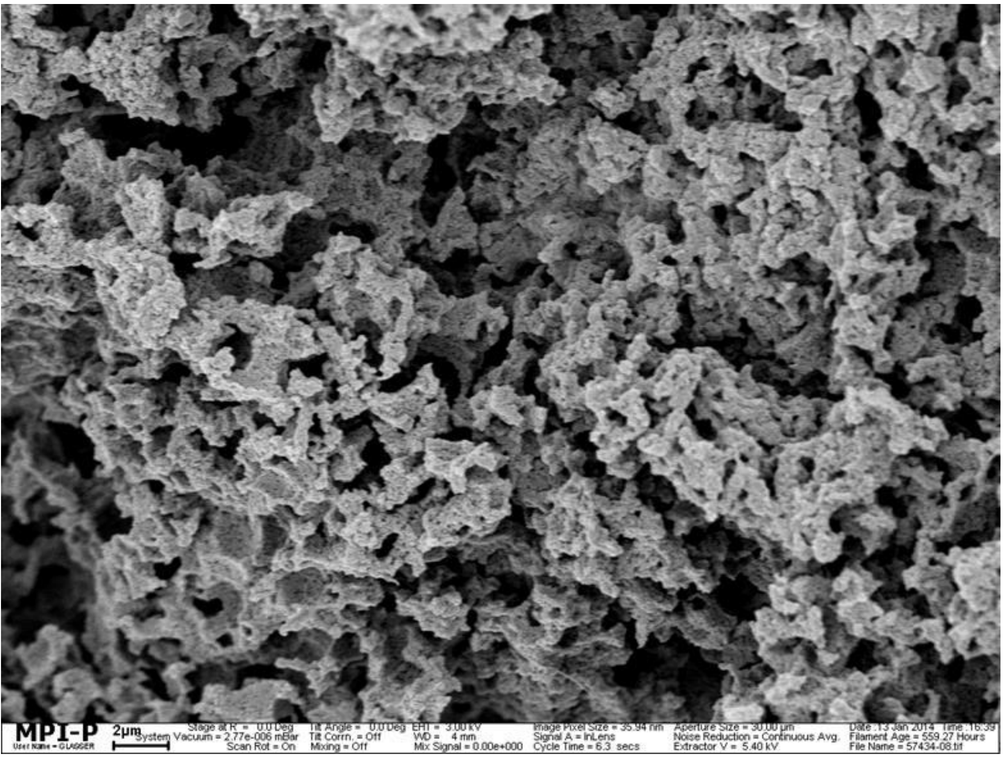

Figure S9. SEM image of B-(Boc-CB)$_2$-BO after the photoinitiation under visible light.

9. Additional SEM Images of B-(Boc-CB)$_2$-BO

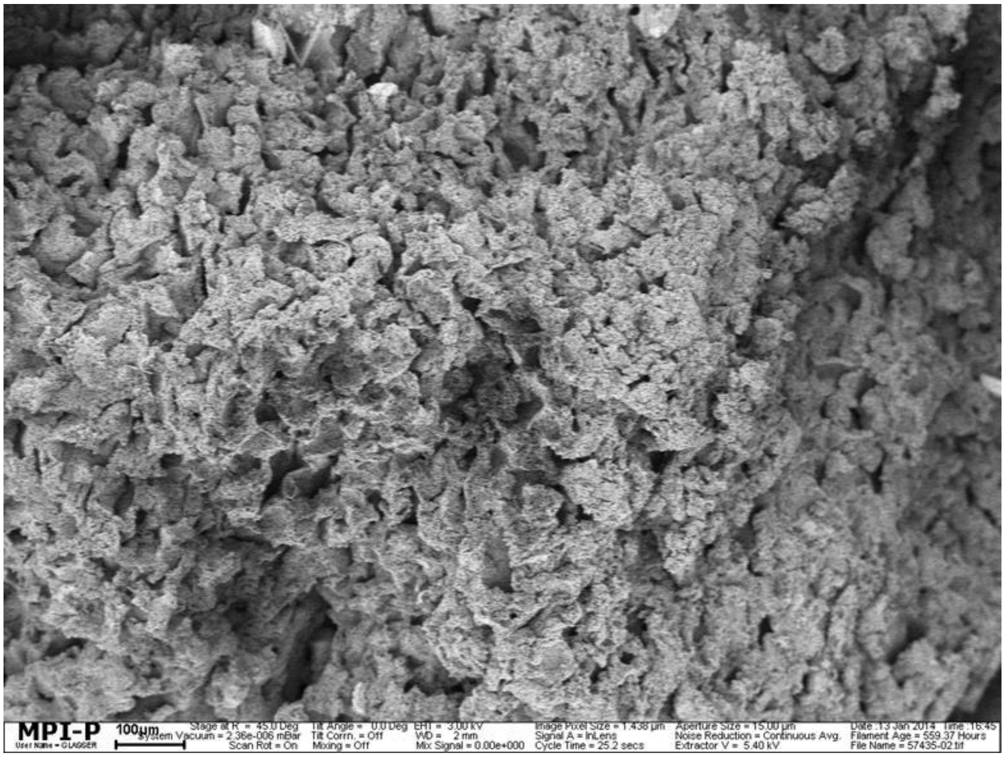

Figure S10. SEM image of B-(Boc-CB)$_2$BO.

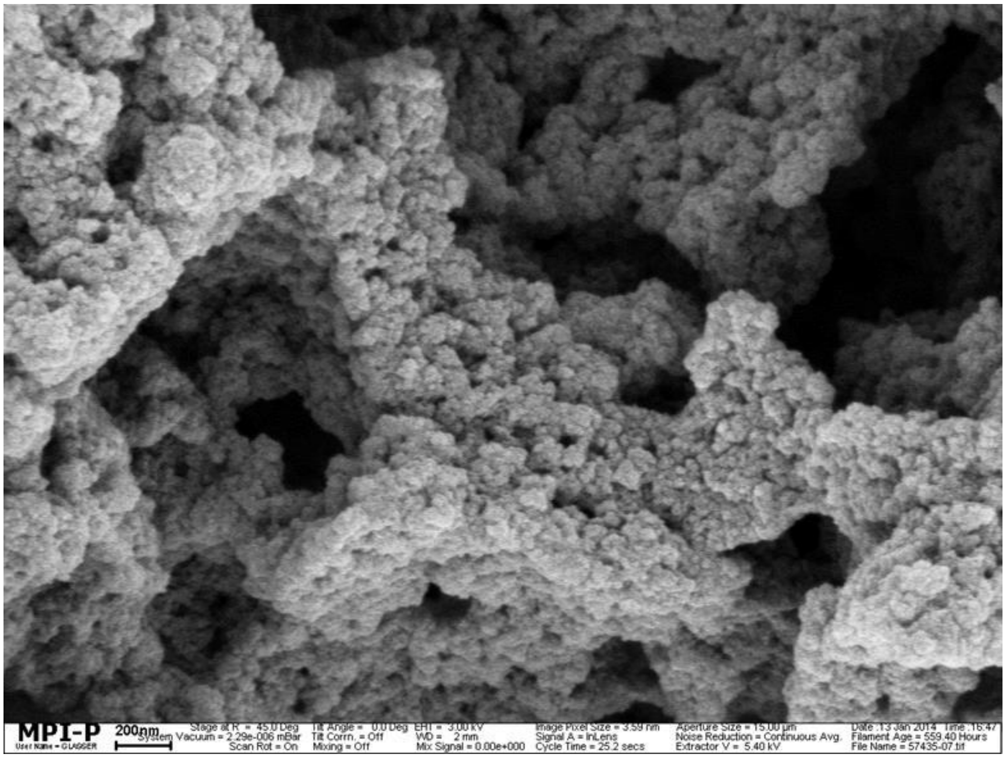

Figure S11. SEM image of B-(Boc-CB)$_2$-BO.

10. Repeating Experiments

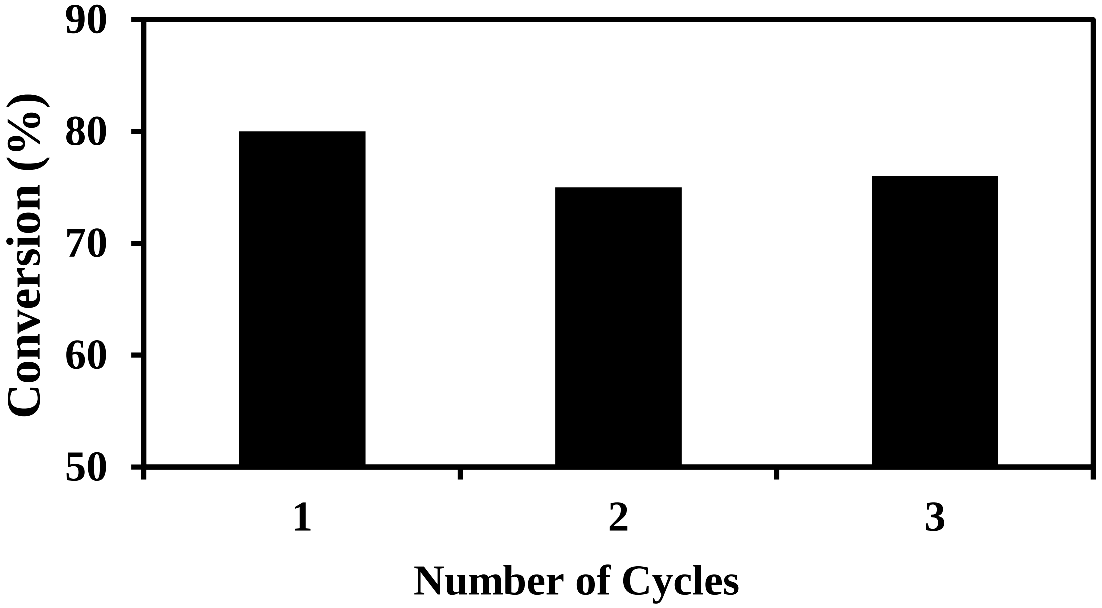

Figure S12. Additional repeating experiments of the photopolymerization of methyl methacrylate in 50 wt% THF solution in the presence of Et_3N at room temperature with visible light.

11. Supporting Reference

(1) Bijleveld, J. C.; Shahid, M.; Gilot, J.; Wienk, M. M.; Janssen, R. A. J. *Adv Funct Mater* **2009**, *19*, 3262-3270.