Supplementary Data

Porphyrin and Pyrene-Based Conjugated Microporous Polymer for Efficient Sequestration of CO_2, Iodine and Photosensitization for Singlet Oxygen Generation.

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Section 1. Materials and Methods

Materials and instruments

1,3,6,8-Tetrabromopyrne(97%), Copper(Ⅰ) iodide (99.999% trace metals basis), N,N-Dimethylformamide (99.8%, anhydrous), Triethylamine (99.5%), 1,3-diphenylisobenzofuran, iodine was purchased from Aldrich chemicals and used as received. Tetrakis(triphenylphosphine)palladium(0) was purchased G-OLED and used as received. Tetrahydrofuran (99.5%), Chloroform (99.5%), N-Hexane (96%), Dichloromethane (99.5%), Methanol (99.5%) was purchased Daejung and used as received. 5,10,15,20-Tetrakis(4-(ethynylphenyl)porphyrin) was synthesized according to a published procedure.

Powder X-ray diffraction measurements were carried out on a Rigaku smartlab with Cu Kα radiation over a range of 5°<2θ<40° in 0.02 steps with a 1 s counting time per step. SEM images were obtained using a field emission scanning electron microscope (JEOL, JSM-7001F) operated at an acceleration voltage of 15.0kV. Samples were coated with a layer of Pt (~3 nm thickness) prior to imaging.

N_2 adsorption/desorption isotherms were measured volumetrically at 77K in the range of 7.0 x $10^{-6} < P/P_0 < 1.00$ with an Autosorb-iQ outfitted with the micropore option from Quantachrome Instruments (Boynton Beach, Florida USA) using the Autosorb-iQ Win software package. The samples were activated at 120°C for 15 h using the outgas port of the Autosorb-iQ instrument. The specific surface areas for N_2 were calculated using the Brunauer-Emmett-Teller (BET) model in the linear range, as determined using the consistency criteria. Pore size distribution was calculated by NLDFT method in the Autosorb-iQ Win software package. Microporous and mesoporous surface areas were calculated by t-plot method in the range of $0.2 < P/P_0 < 0.5$.

The CO_2 adsorption isotherms were obtained using Quantachrome Instruments (Boynton Beach, Florida USA) using the Autosorb-iQ Win software package. The samples were activated at 120°C for 15 h using the outgas port of the Autosorb-iQ instrument. Fourier transform infrared (FTIR) spectrum was recorded on Bruker VERTEX 80V spectrometer. The spectral resolution is 2 cm^{-1}. Solid-state NMR experiments were performed on a Bruker Avance Ⅱ 500 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm MAS BB-1H probe and with a sample spinning rate of 5 kHz; a contact time of 2 ms and pulse delay of 5 s were applied. Thermogravimetric analysis (TGA) was performed on a TGA N-1000 by measuring the weight loss while heating at a rate of 3 °C min^{-1} from 25 to 950 °C under nitrogen.

Synthesis of Por-Py-CMP

5,10,15,20-Tetrakis(4-(ethynylphenyl)porphyrin) (120 mg, 0.169 mmol), 1,3,6,8-tetrabromopyrene (58.3 mg, 0.113 mmol), $Pd(PPh_3)_4$ (39.4 mg), and CuI (6.4mg) were added a 100 mL two-neck round bottom flask. Then 16.3 mL of DMF and 0.33 mL of TEA was added to dissolve all the solid and N_2 bubbling for 10 min. The solution was heated to 100°C for 42 h and then cooled to room temperature. After vaccum filtration and washing with $CHCl_3$ and MeOH, solid was collected. After Soxhlet extraction with $CHCl_3$, THF, and MeOH and drying under vaccum at 100°C overnight.

Capture of iodine with Por-Py-CMP

The sample of Por-Py-CMP powder was placed in a pre-weighted glass vial. The vial and excess solid iodine were put together in a closed system at 350K and ambient pressure. Then, the system was cooled and weighted. The iodine uptake was calculated as $(m_2 - m_1)/m_1$ x 100 wt%, where m_1 and m_2 are the mass of the CMP sample before and after iodine uptake.

Singlet oxygen generation

Visible irradiation was provided using a fiber optic coupled halogen lamp (150W, SCHOTT, KL 1500 compact) combined with a 500 nm long pass filter (semrock). Irradiation of solution of 1,3-diphenylisobenzofuran(37μM) in DMF (3ml) with light in the presence of Por-Py-CMP (2mg) causes a steady generation of singlet oxygen.

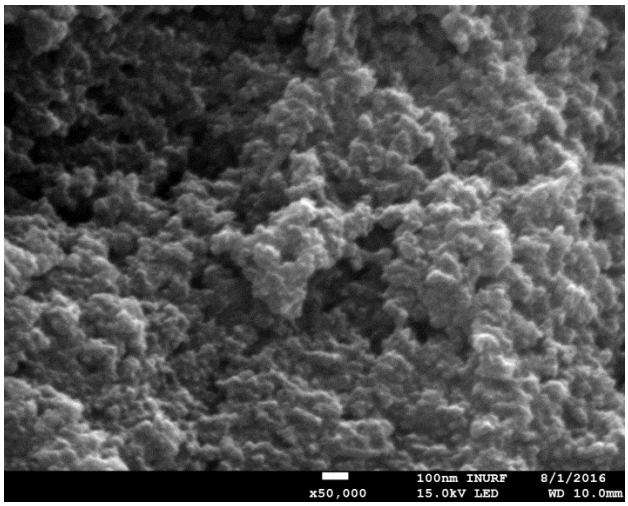

Figure S1. SEM image of Por-Py-CMP.

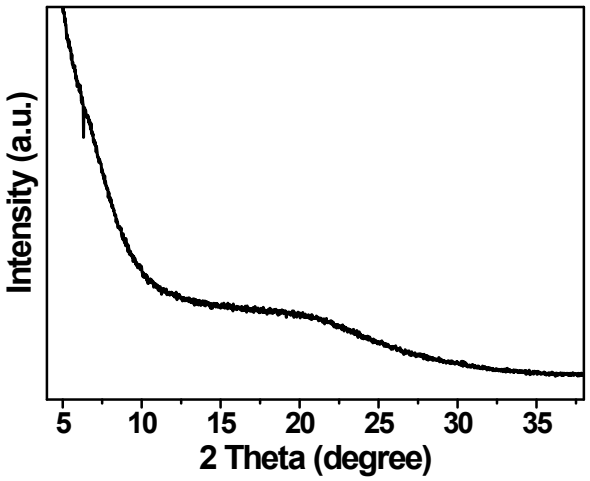

Figure S2. Powder X-ray diffraction pattern of Por-Py-CMP.

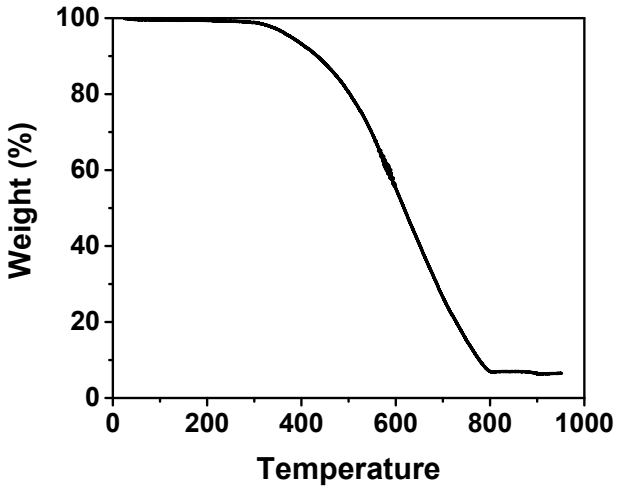

Figure S3. TGA data of Por-Py-CMP.

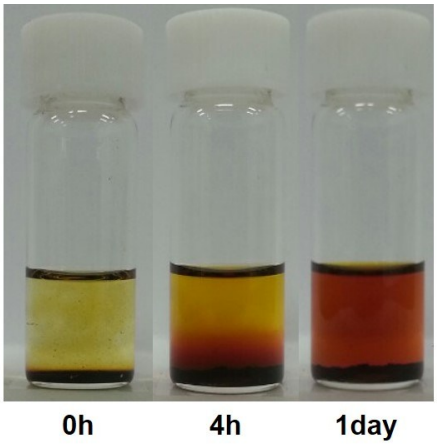

Figure S4. Iodine release from the I_2@Por-Py-CMP in ethanol solution

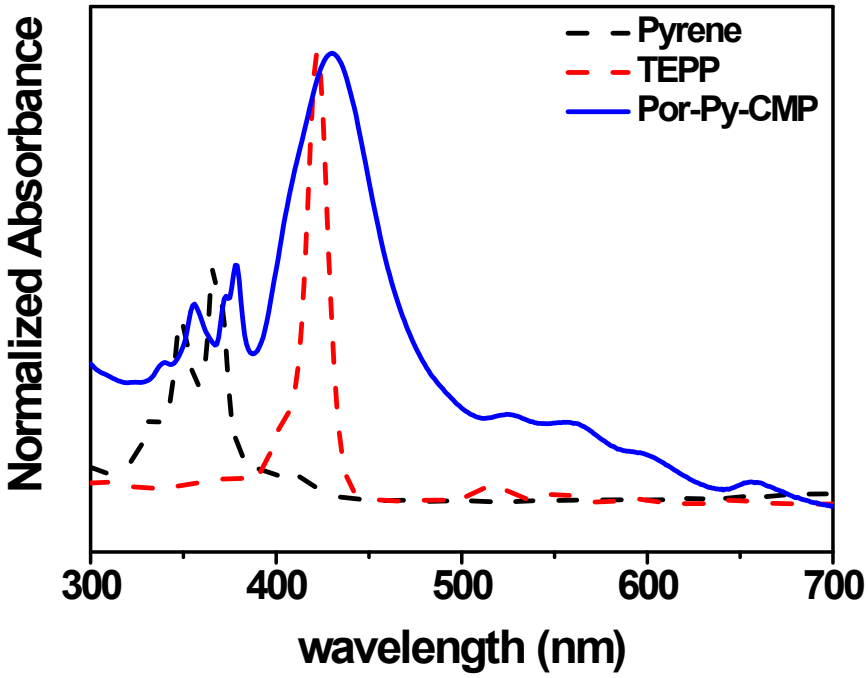

Figure S5. UV-Vis spectra of pyrene, TEPP, and Por-Py-CMP dispersed in DMF.

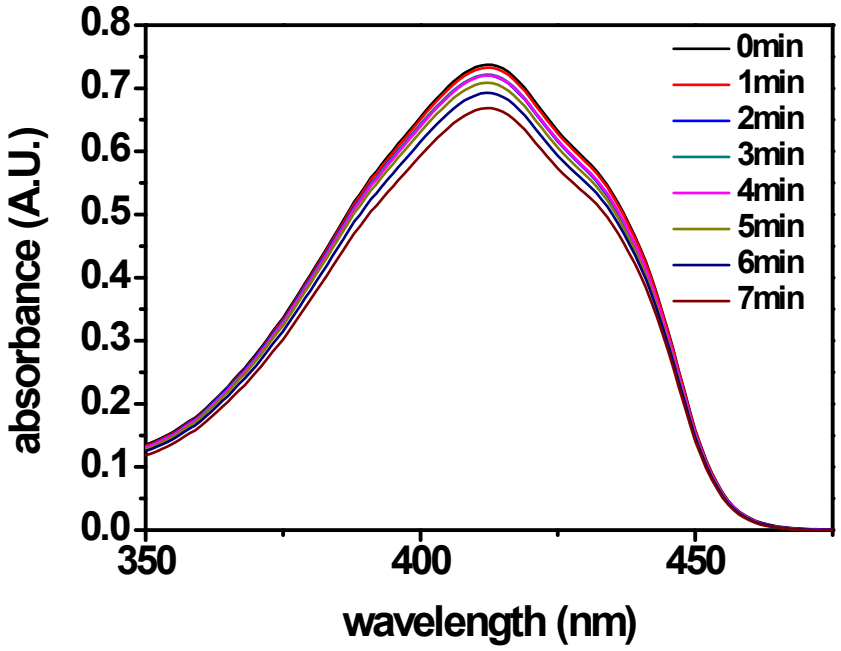

Figure S6. Time-dependent absorption spectra of DPBF upon irradiation without Por-Py-CMP

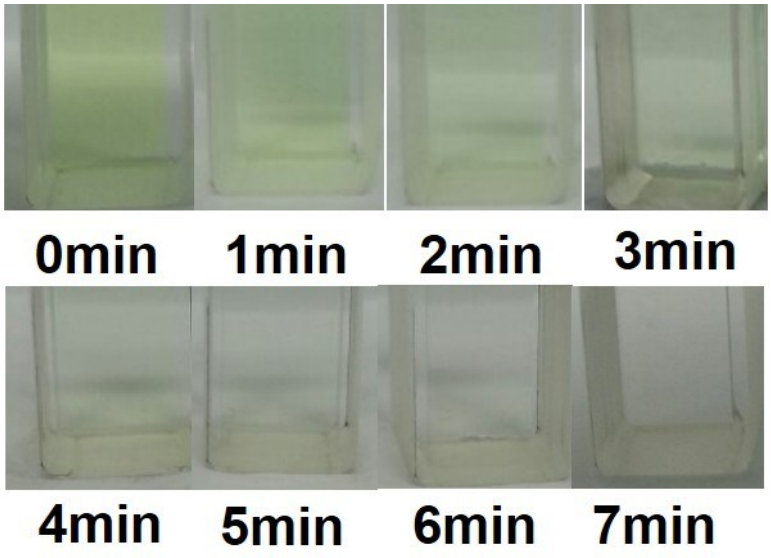

Figure S7. Photograph images of DPBF solution in the presence of Por-Py-CMP during the irradiation.