Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Structural insights into the functional origin of conjugated microporous polymers: geometry management of porosity and electronic properties

Yanhong Xu and Donglin Jiang*

Corresponding Author:

Professor Donglin Jiang

Department of Materials Molecular Science, Institute for Molecular Science, National Institutes of Natural Sciences, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan.

Tel./Fax: +81-564-59-5520.

E-mail: jiang@ims.ac.jp

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Section A. Materials and methods

Bis(1,5-cyclooctadiene)nickel(0) and anhydrous *N*, *N*-dimethylformamide (DMF, 99.0%), 1,2,4,5-tetrabromobenzene, 1,2,4-tribromobenzene, and 1,3,5-tribromobenzene were purchased from Aldrich Chemicals. 1,5-Cyclooctadiene and 2,2′-bipyridyl were purchased from TCI. Concentrated HCl, methanol, tetrahydrofunan, and acetone were purchased from Wako Chemicals. Chloroform and Calcium hydride were purchased from Kanto Co.

UV-Vis-IR diffuse reflectance spectra (Kubelka-Munk spectrum) were recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Photoluminescence spectra were recorded on a JASCO model FP-6600 spectrofluorometer. The absolute quantum yield was determined by standard procedure with an integral sphere JASCO model ILF-533 mounted on the FP-6600 spectrofluorometer. Time-resolved fluorescence spectroscopy of CMP samples in the solid state and dispersed in solvents were recorded on Hamamatsu compact fluorescence lifetime spectrometer Quantaurus–Tau model C11367-11. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting a THF suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. The sample was prepared by drop-casting a THF suspension of the CMP samples onto a copper grid. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment.

Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size and pore size distribution.

Carbon dioxdie sorption isotherms were measured at 298 K and 273K with a Bel Japan Inc. model BELSORP-mini II analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

Section B. Synthetic procedures

PP-CMP@*mmm*. 1,5-Cyclooctadiene (cod, 0.28 mL, 2.304 mmol, dried over CaH_2) was added to a solution of bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)$_2$], 0.63 g, 2.304 mmol) and 2,2′-bipyridyl (0.36 g, 2.304 mmol) in dehydrated DMF (10 mL), and the mixture was heated at 80 °C for 1 h. To the resulting purple solution was added the solution of 1,3,5-tribromobenzene (201.5 mg, 0.64 mmol) in dehydrated DMF (22 mL) and the mixture was stirred at 80 °C for 24 or 72 h, respectively. After cooling to room temperature, the mixture was added with concentrated HCl (24 mL) and stirred for 10 h at room temperature. After filtration, the residue was washed with H_2O (5 × 30 mL), $CHCl_3$ (5 × 30 mL), and THF (5 × 30 mL), respectively, extracted by Soxhlet with H_2O, $CHCl_3$, methanol, acetone and THF for 1 day respectively and dried at 150 °C under vacuum for 24 h, to give PP-CMP@*mmm*-24h and PP-CMP@*mmm*, respectively, as white powders. Elemental analysis calcd (%) for $(C_6H_3)_n$ (theoretical formula for an infinite PP-CMP@*mmm*): C 96, H 4; found: C 94.05, H 5.02 (PP-CMP@*mmm*-24h), and C 93.90, H 4.84 (PP-CMP@*mmm*). The absolute luminescence quantum yields at 25 °C for PP-CMP@*mmm* in solid state and THF are 2.9% and 2.1%, respectively.

PP-CMP@*omp*. 1,5-Cyclooctadiene (cod, 0.28 mL, 2.304 mmol, dried over CaH_2) was added to a solution of bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)$_2$], 0.63 g, 2.304 mmol) and 2,2′-bipyridyl (0.36 g, 2.304 mmol) in dehydrated DMF (10 mL), and the mixture was heated at 80 °C for 1 h. To the resulting purple solution was added the solution of 1,2,4-tribromobenzene (201.5 mg, 0.64 mmol) in dehydrated DMF (22 mL) and the mixture was stirred at 80 °C for 24 or 72 h to give deep purple suspensions, respectively. After cooling to room temperature, the mixture was added with concentrated HCl (24 mL) and stirred for 10 h at room temperature. After filtration, the residue was washed with H_2O (5 × 30 mL), $CHCl_3$ (5 × 30 mL), and THF (5 × 30 mL), respectively, extracted by Soxhlet with H_2O, $CHCl_3$, methanol, acetone and THF for 1 day respectively and dried at 150 °C under vacuum for 24 h, to give PP-CMP@*omp*-24h and PP-CMP@*omp*, respectively, as light-yellow powders. Elemental analysis calcd (%) for $(C_6H_3)_n$ (theoretical formula for an infinite PP-CMP@*omp*): C 96, H 4; found: C 84.99, H 5.02 (PP-CMP@*omp*-24h), and C 85.44, H 4.38 (PP-CMP@*omp*). The absolute luminescence quantum yields at 25 °C for PP-CMP@*omp* in solid state and THF are 2.8% and 1.5%, respectively.

PP-CMP@*omom*-12h, PP-CMP@*omom*-24h, PP-CMP@*omom*-36h and PP-CMP@*omom*. 1,5-Cyclooctadiene (cod, 0.37 mL, 3.07 mmol, dried over CaH_2) was added to a solution of bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)$_2$], 0.84 g, 3.07 mmol) and 2,2′-bipyridyl (0.48 g, 3.07 mmol) in dehydrated DMF (10 mL) and the mixture was heated at 80 °C for 1 h. To the

resulting purple solution was added the solution of 1,2,4,5-tetrabromobenzene (250 mg, 0.64 mmol) in dehydrated DMF (22 mL), and the mixture was stirred at 80 °C for 12, 24, 36, or 72 h, respectively. After cooling to room temperature, the mixture was added with concentrated HCl (24 mL) and stirred for 10 h at room temperature. After filtration, the residue was washed with H_2O (5 × 30 mL), $CHCl_3$ (5 × 30 mL) and THF (5 × 30 mL), respectively, extracted by Soxhlet with H_2O, $CHCl_3$, methanol, acetone and THF for 1 day respectively and dried at 150 °C under vacuum for 24 h, to give PP-CMP@*omom*-12h, PP-CMP@*omom*-24h, PP-CMP@*omom*-36h and PP-CMP@*omom*, respectively, as yellow powders. Elemental analysis calcd (%) for $(C_6H_2)_n$ (theoretical formula for an infinite PP-CMP@*omom*): C 97.3, H 2.7; found: C 85.13, H 4.89 (CMP@*omom*-12h), C 84.50, H 5.14 (PP-CMP@*omom*-24h), C 86.14, H 5.01 (PP-CMP@*omom*-36h), and C 84.69, H 4.83 (PP-CMP@*omom*). The absolute luminescence quantum yields at 25 °C for PP-CMP@*omom* in solid state and THF are 3.2% and 2.1%, respectively.

Section C. Supporting figures

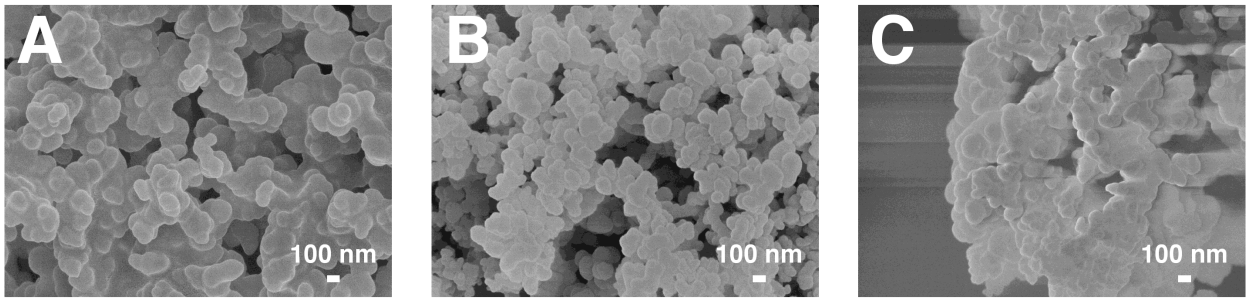

Figure S1. FE-SEM images of (A) PP-CMP@*mmm*, (B) PP-CMP@*omp* and (C) PP-CMP@*omom*.

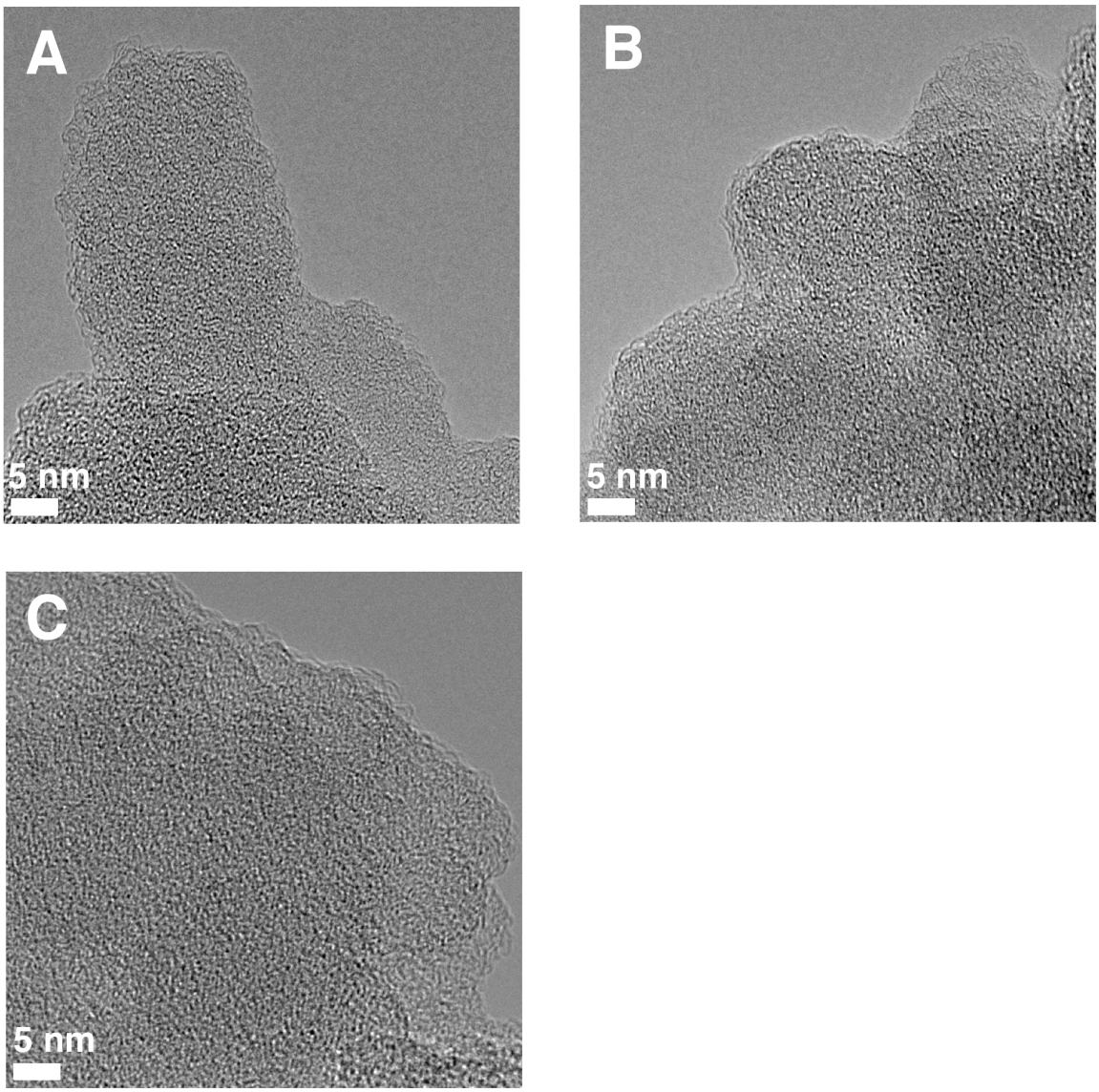

Figure S2. HR-TEM images of (A) PP-CMP@*mmm*, (B) PP-CMP@*omp* and (C) PP-CMP@*omom*.

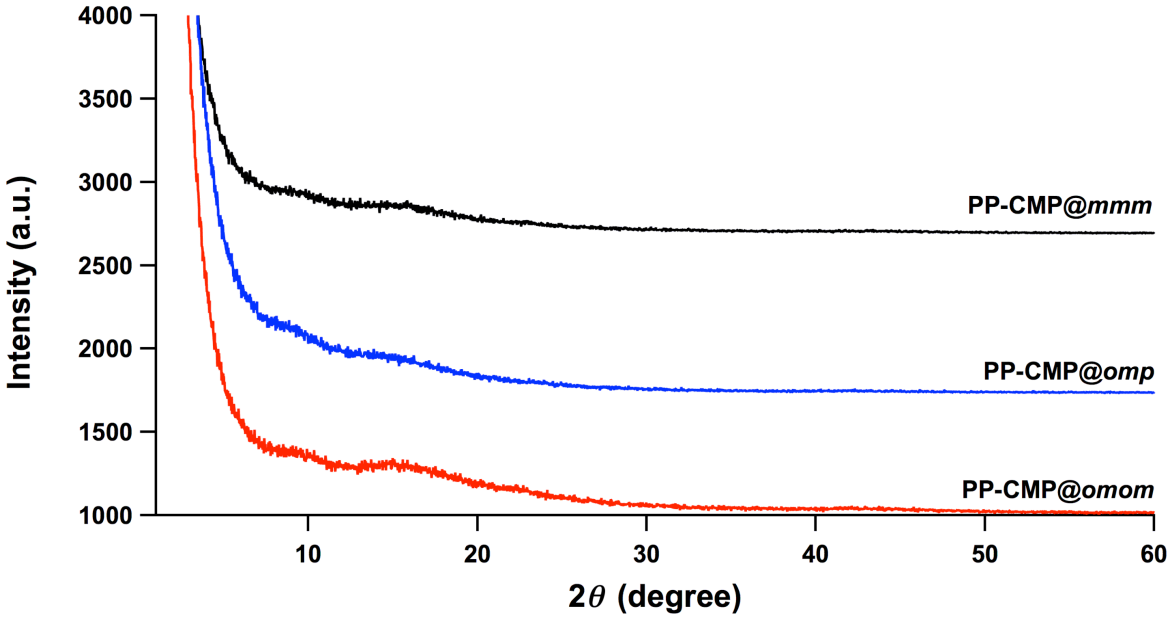

Figure S3. Powder X-ray diffraction profiles of PP-CMP@*mmm*, PP-CMP@*omp* and PP-CMP@*omom*. These CMPs exhibited very weak halo peaks, indicating their amorphous structure.

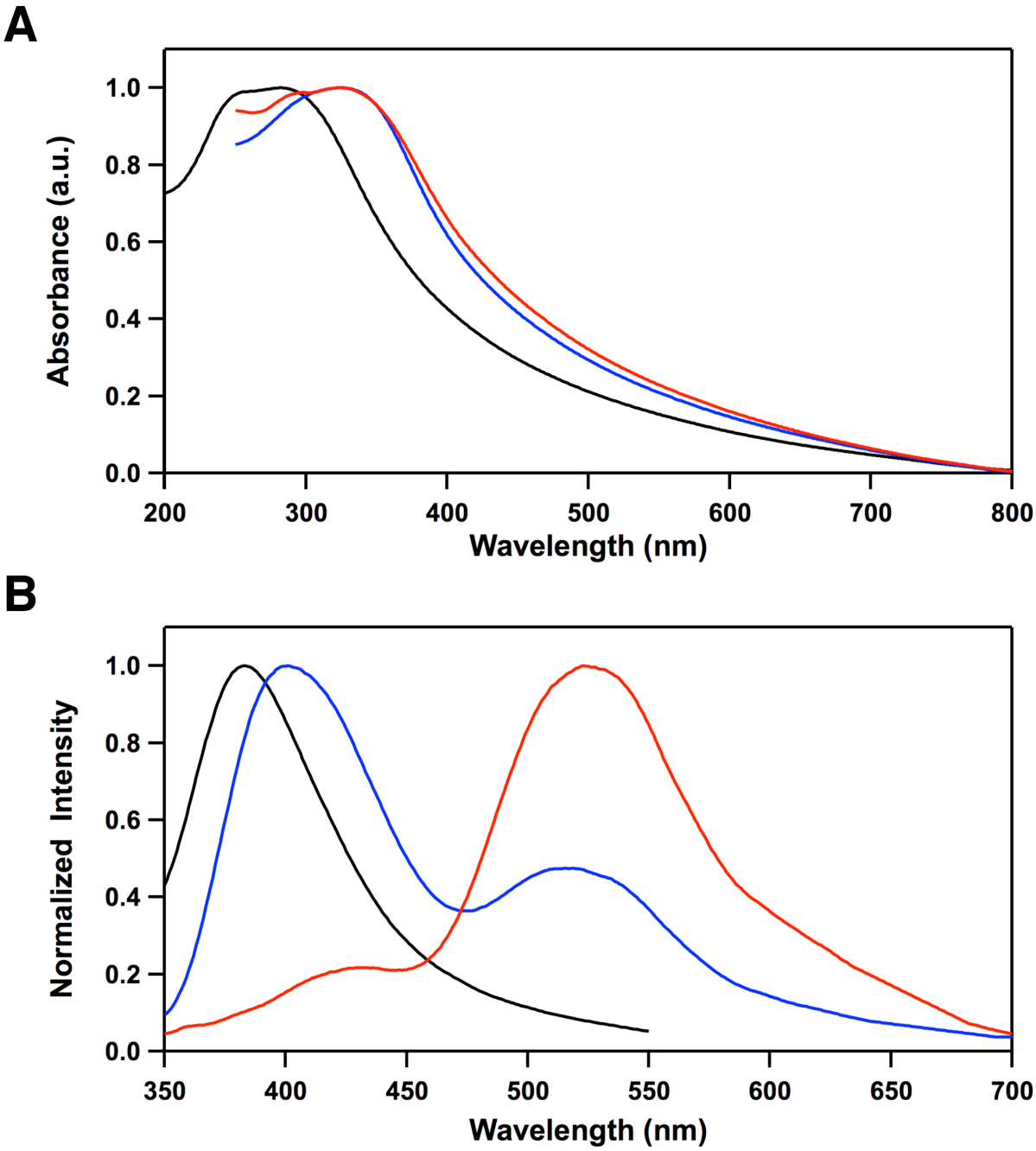

Figure S4. (A) Electronic absorption spectra and (B) fluorescence spectra of PP-CMP@*mmm* (black), PP-CMP@*omp* (blue) and PP-CMP@*omom* (red) dispersed in THF at 25 °C.

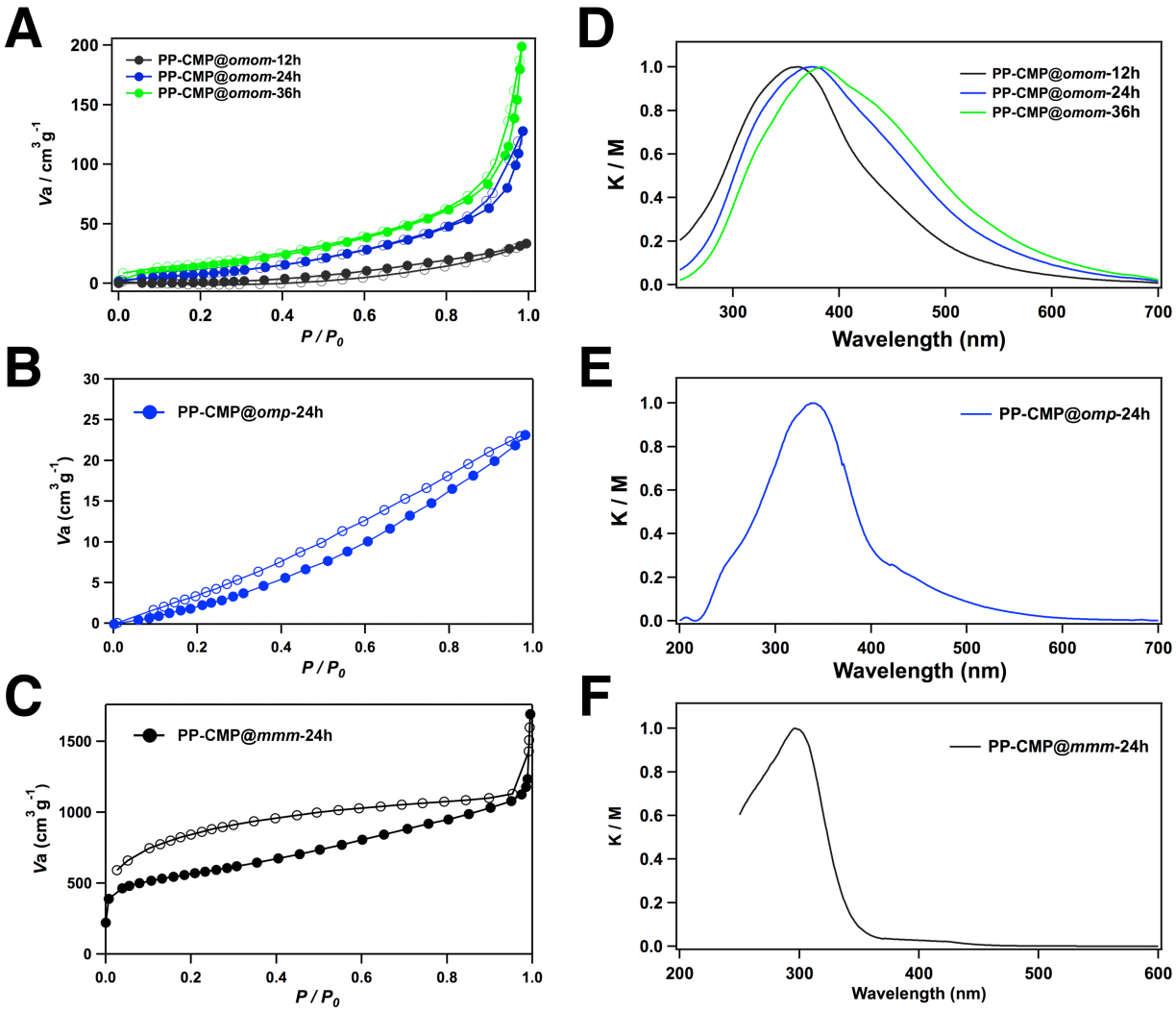

Figure S5. Nitrogen sorption isotherm profiles of (A) PP-CMP@*omom*-12h, PP-CMP@*omom*-24h and PP-CMP@*omom*-36h, (B) PP-CMP@*omp*-24h and (C) PP-CMP@*mmm*-24h. Electronic absorption spectra of (D) PP-CMP@*omom*-12h, PP-CMP@*omom*-24h and PP-CMP@*omom*-36h, (E) PP-CMP@*omp*-24h and (F) PP-CMP@*mmm*-24h.