

Electronic Supplementary Information for
Insights on the Low Surface Area of Conjugated Microporous Polymers
and Methodological Suggestion for the Enhancement of Porosity

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Experimental Sections

SEM images were obtained by using a FE-SEM (JSM6700F). The N₂ adsorption-desorption isotherm curves at 77 K were measured by using a BELSORP II-mini system. The pore size distribution diagrams were obtained by the DFT method. PXRD patterns were obtained by using a Rigaku MAX-2200 operating with filtered Cu-Kα radiation. Infrared absorption spectra were obtained by using a Bruker VERTEX 70 FT-IR spectrometer. The solid phase ¹³C-NMR spectra were recorded on a Bruker 400 MHz Solid State DSX NMR spectrometer at the Korea Basic Science Institute. Combustion elemental analysis was performed by using a CE EA1110 elemental analyzer.

Synthetic procedure for microporous Zn-porphyrin networks in Table 1

The 5,10,15,20-tetra(4-ethynylphenyl) Zn(II) porphyrin building block was prepared by the synthetic procedure in the literature. (Refs. 8-9 in text) For the preparation of microporous Zn-porphyrin materials, PdCl₂(PhCN)₂ (2.5 mg, 0.0065 mmol) and phosphine or phosphite (0.013 mmol) were added to THF (10 mL) in flame-dried Schlenk flask under argon. The solution was stirred for 5 minutes at room temperature. 5,10,15,20-Tetra(4-ethynylphenyl) Zn(II) porphyrin building block (50 mg, 0.065 mmol), 1,4-diiodobenzene (42 mg, 0.13 mmol), and CuI (2.5 mg, 0.013 mmol) were added under argon. After diisopropylamine (5 mL) was added to solution, the reaction mixture was heated at 90 °C with stirring for 24 hours under argon. After the reaction mixture was cooled to room temperature, the precipitates were separated by centrifugation, washed with THF and methanol, and dried under vacuum.

Synthetic procedure for microporous Zn-porphyrin networks via homo-coupling (Fig. S13 in the ESI)

PdCl₂(PhCN)₂ (2.5 mg, 0.0065 mmol) and triphenyl phosphine or tri(o-tolyl)phosphine (0.013 mmol) were added to THF (10 mL). The solution was stirred for 5 minutes at room temperature. 5,10,15,20-Tetra(4-ethynylphenyl) Zn(II) porphyrin building block (50 mg, 0.065 mmol) and CuI (2.5 mg, 0.013 mmol) were added. After diisopropylamine (5 mL) was added to solution, the reaction mixture was bubbled by O₂ gas for 30 seconds then, heated at 90 °C with stirring for 24 hours. After the reaction mixture was cooled to room temperature, the precipitates were separated by centrifugation, washed with THF and methanol, and dried under vacuum. Without treatment of oxygen bubbling, no precipitates were formed.

Synthetic procedure for CMP and MP materials in Table 2

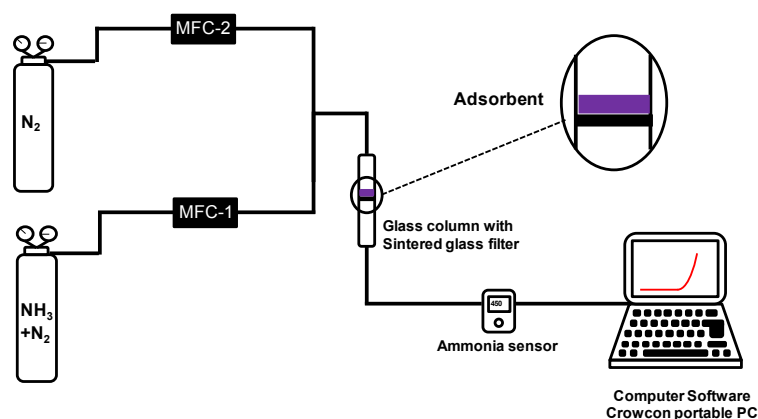
2,5-Diiodothiophene, 3,6-diiodo-9H-carbazole, and 2,5-dimethoxy-1,4-diiodobenzene were prepared by the synthetic procedures in the literatures (T. Cardolaccia *et al.* *J. Phys. Chem. B* 2007, **111**, 10871; Z. -H. Zhao *et al.*

Macromolecule 2011, **44**, 1405; A. Wild *et al. Chem. Commun.* 2012, **48**, 964, respectively). For the preparation of CMP materials in table 2, PdCl₂(PhCN)₂ (7.5 mg, 0.0195 mmol) and PPh₃ or P(*o*-tolyl)₃ (0.039 mmol) were added to THF (30 ml) in a flame-dried 50 mL Schlenk flask under argon. The reaction mixture was stirred for 5 minutes at room temperature under argon. 1,3,5-triethynylbenzene (39 mg, 0.26 mmol) or tetrakis(4-ethynylphenyl)methane (81 mg, 0.195 mmol), halide building block (0.39 mmol), and CuI (7.5 mg, 0.039 mmol) were added. After diisopropylamine (15 ml) was added, the reaction mixture was heated at 90 °C with stirring for 24 hours under argon. After the reaction mixture was cooled to room temperature, the precipitates were retrieved by centrifugation, washed with THF and methanol, and dried under vacuum. For the preparation of P12~13 and P18~19 materials in Table 2, 75 mL of diisopropylamine and 150 mL of THF were used due to the low solubility of 4,4'-diiodo-*p*-terphenyl building block, instead of 15 mL of diisopropylamine and 30 mL of THF.

Comparison of reaction rates of the Sonogashira coupling with (PPh₃)₂PdCl₂ and [(P(*o*-tolyl)₃]₂PdCl₂ (Fig. S11)

PdCl₂(PhCN)₂ (2.5 mg, 0.0065 mmol) and triphenylphosphine or tri(*o*-tolyl)phosphine (0.013 mmol) were added to THF (10 mL) under argon. The reaction mixture was stirred for 5 minutes at room temperature. Phenylacetylene (0.50 ml, 4.6 mmol), 1,4-diodobenzene (751 mg, 2.3 mmol), and CuI (2.5 mg, 0.039 mmol) were added. After diisopropylamine (5 ml) was added, the reaction mixture was heated 90 °C with stirring for 30 minutes under argon. After the reaction mixture was cooled to room temperature, the solvent was evaporated. The coupled products were isolated to get isolated yields by column chromatography using a 1:7 mixture of CH₂Cl₂ and hexane as an eluent.

Ammonia breakthrough adsorption studies for breakthrough capacities in Fig. S12 in the ESI

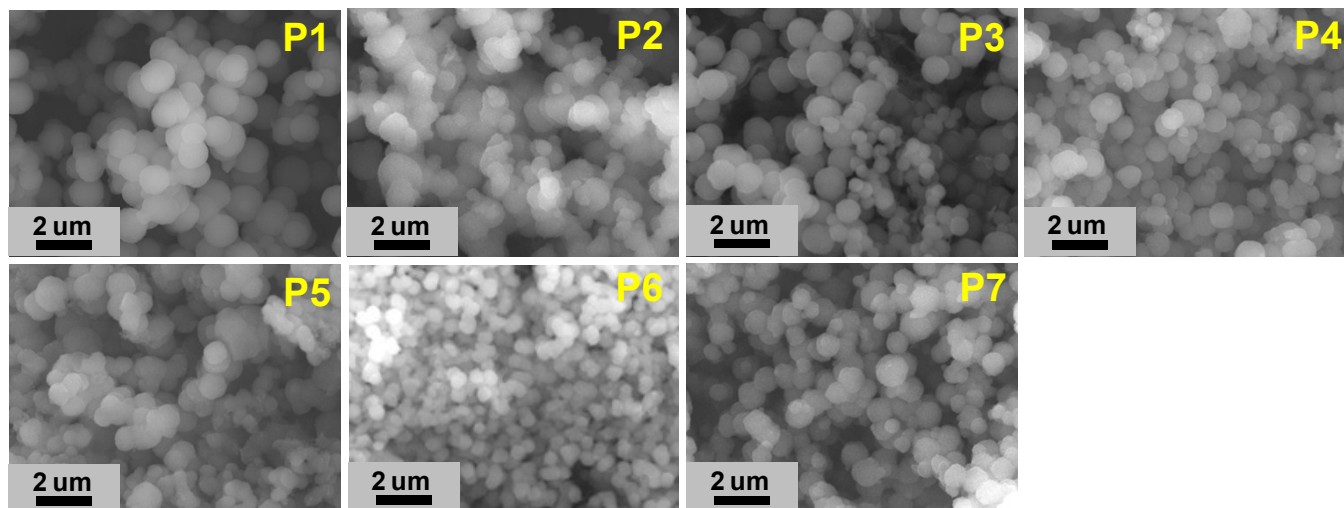


Ammonia adsorption studies were conducted at 20°C using the set-up shown in the Figure above. The CMP materials (40 mg) were loaded on a sintered glass filter (G3 pore size, 0.8 cm diameter) in a glass column (30 cm × 1 cm). Through a mass flow controller (MFC), NH₃ in N₂ was passed with a 3.4 sccm flow rate for all the tests. N₂ was passed with a 40 sccm flow rate. The inlet concentration of ammonia for adsorbents was 4500 ppm. The outlet NH₃ concentration was measured by using Gasman-NH₃ sensor (Crowcon Co.). The upper detection limit of the ammonia sensor was 1000 ppm. Thus, we stopped measurement at 1000 ppm. The breakthrough time was

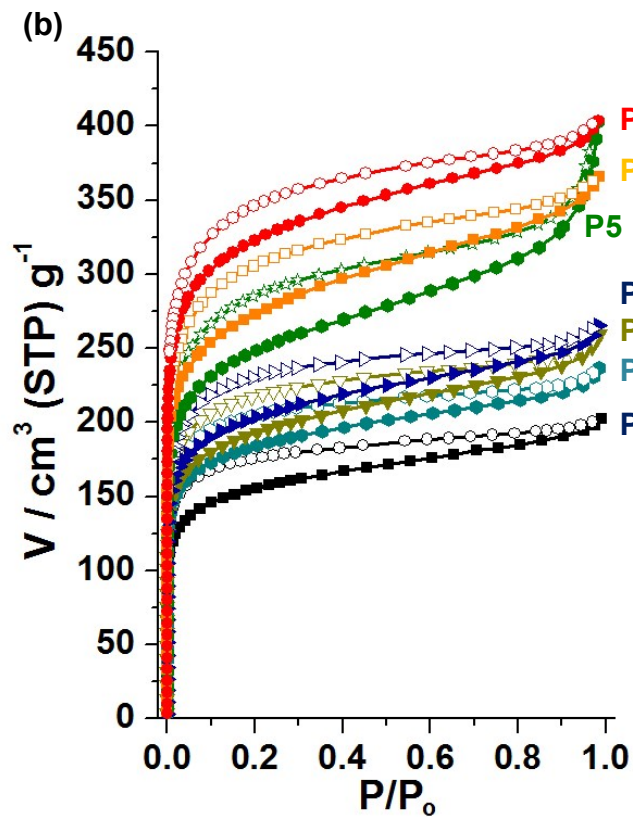
measured at 450 ppm of NH_3 outlet concentration. The breakthrough capacities ($\text{mg NH}_3/\text{g}$) were calculated using breakthrough times, inlet concentration, flow rate values, and mass of the loaded CMP adsorbents.

Fig. S1 Characterization data of microporous Zn-porphyrin materials (P1~P7) in Table 1. (a) SEM images, (b) N_2 adsorption-desorption isotherm curves at 77K, and (c) pore size distribution based on the DFT method.

(a)



(b)



(c)

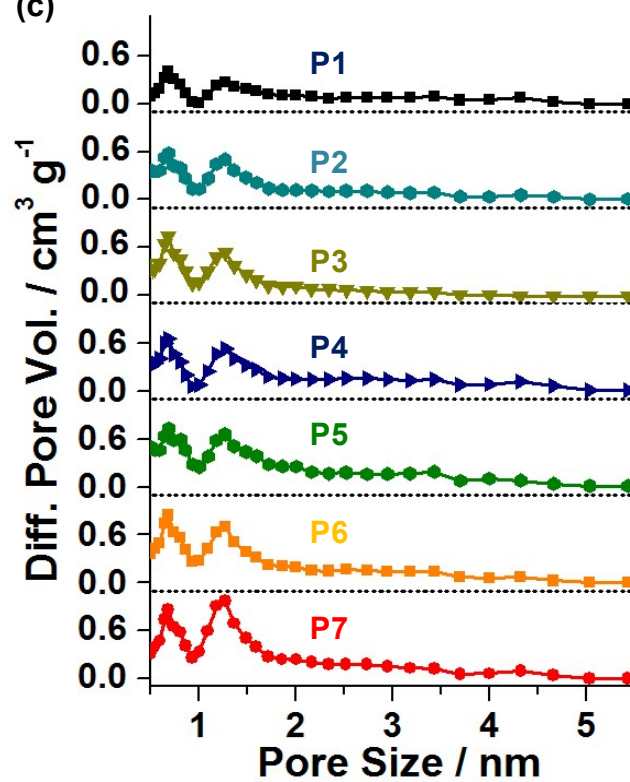


Fig. S2 Characterization data of microporous Zn-porphyrin materials (P1~P7) in Table 1. (a) PXRD patterns, and (b) solid phase ^{13}C NMR spectra.

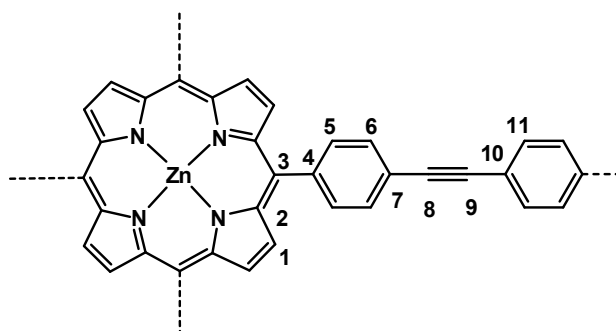
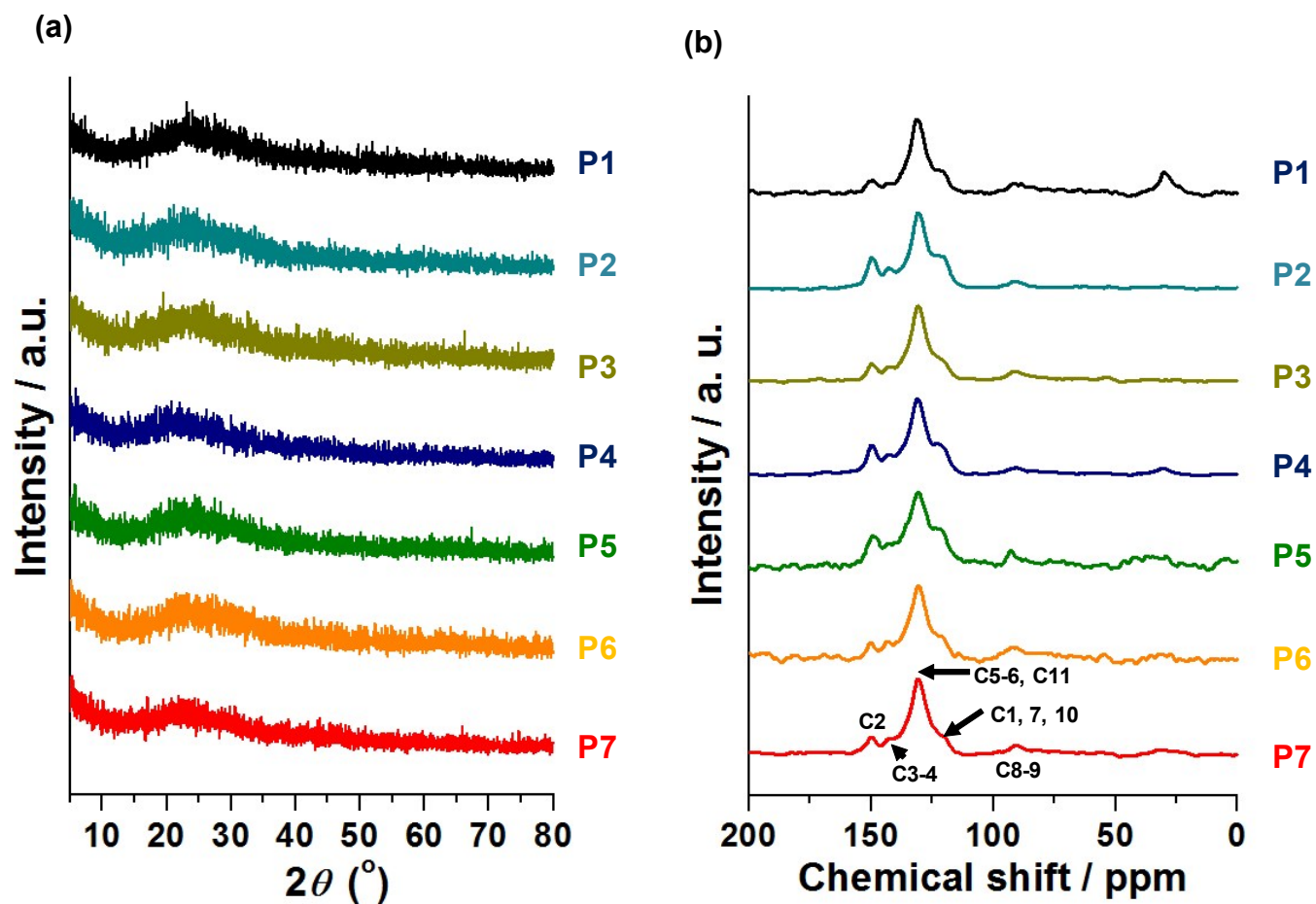


Fig. S3 IR absorption spectra of microporous Zn-porphyrin materials (P1~P7) in Table 1. The intensity of the vibration peaks of terminal alkynes increases from P1 to P7.

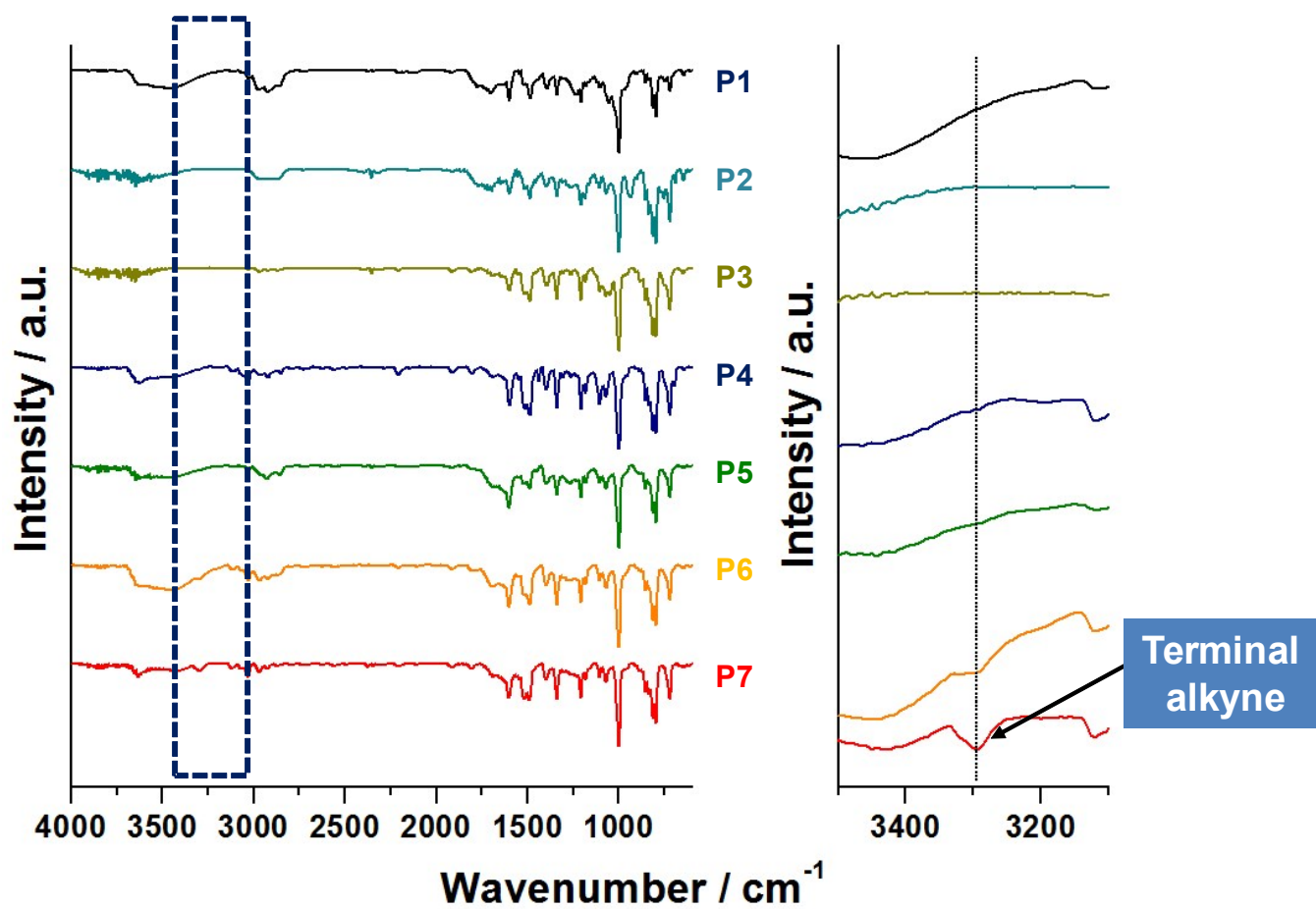


Fig. S4 Characterization data of CMP materials in Table 2 (P8~P13). (a) SEM images, (b) N₂ adsorption-desorption isotherm curves at 77K, and (c) pore size distribution diagrams based on the DFT method.

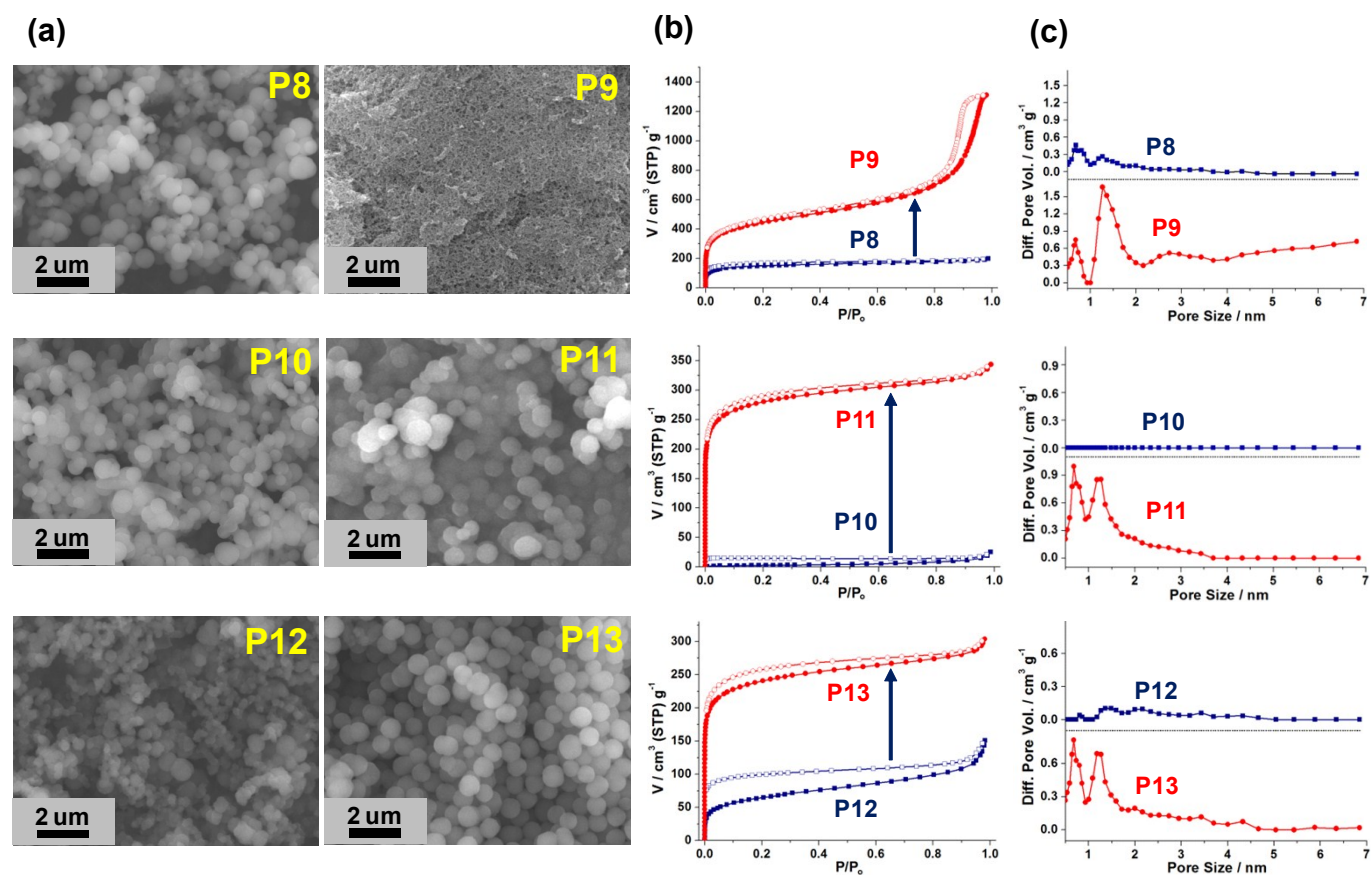


Fig. S5 Characterization data of CMP materials in Table 2 (P8~P13). (a) Solid phase ^{13}C NMR spectra and (b) IR absorption spectra.

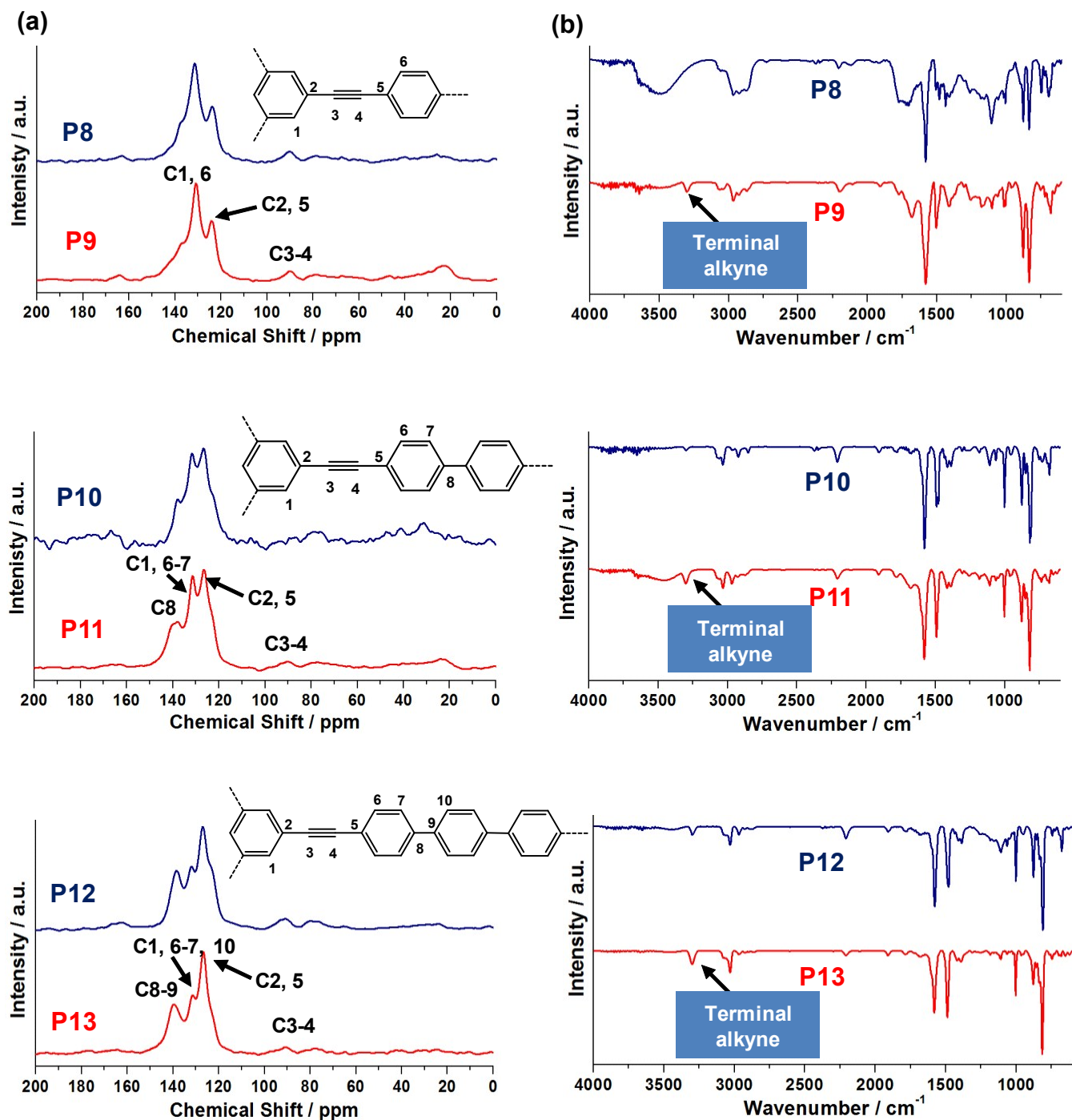


Fig. S6 Characterization data of MP materials in Table 2 (P14~P19). (a) SEM images, (b) N_2 adsorption-desorption isotherm curves at 77K, and (c) pore size distribution diagrams based on the DFT method.

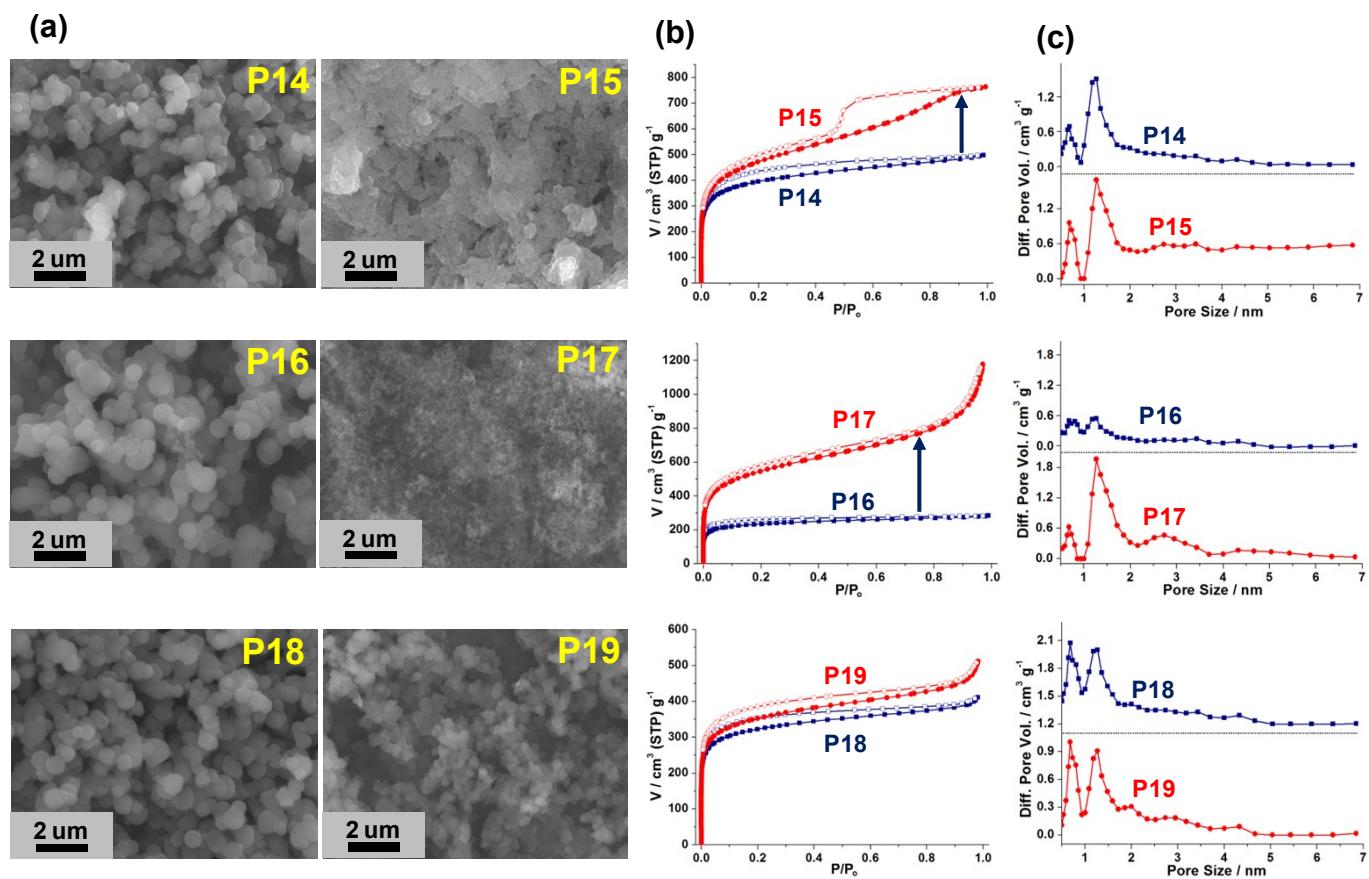


Fig. S7 Characterization data of MP materials in Table 2 (P8~P13). (a) Solid phase ^{13}C NMR spectra and (b) IR absorption spectra.

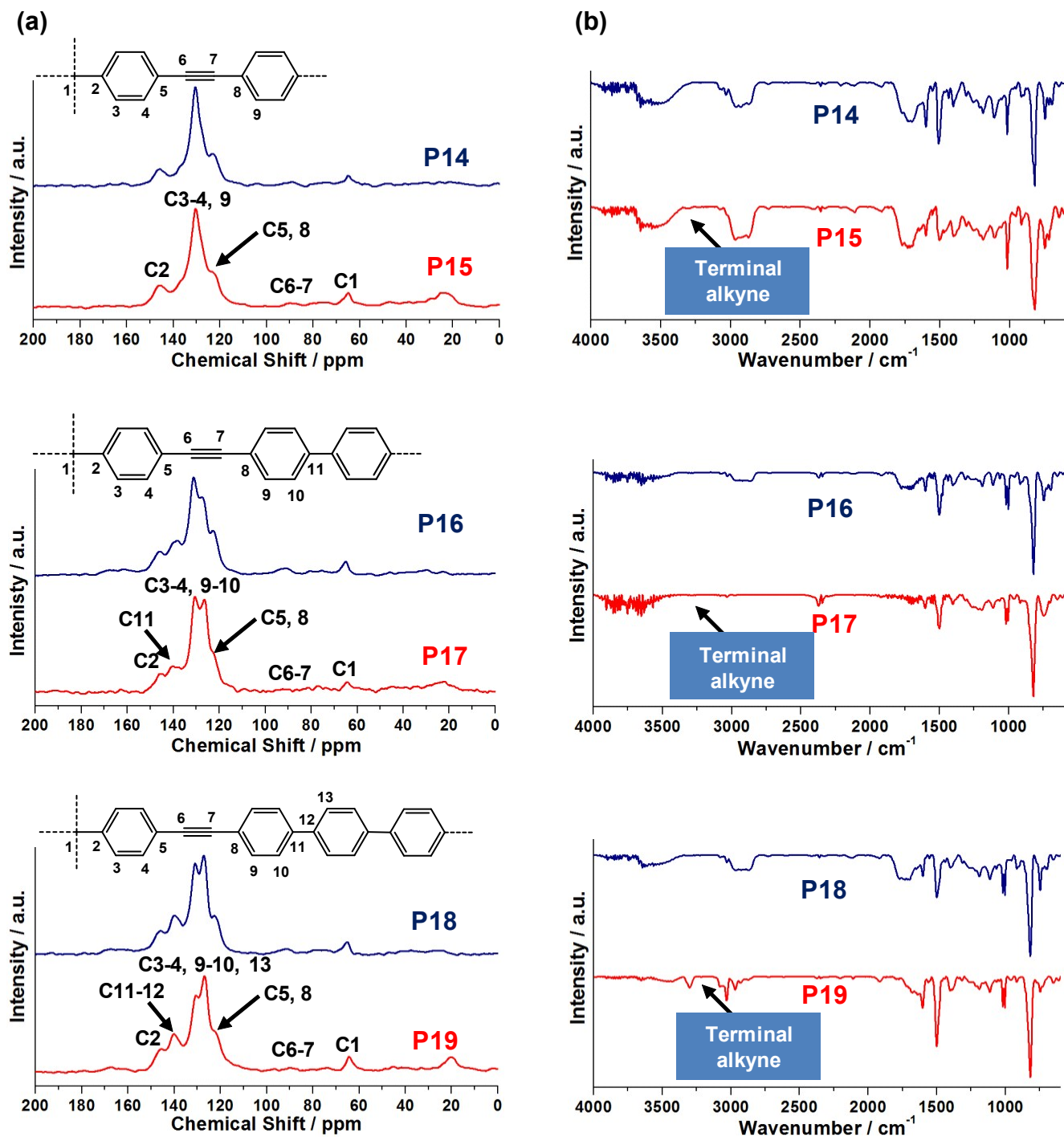


Fig. S8 Characterization data of CMP materials in Table 2 (P20~P25). (a) SEM images, (b) N₂ adsorption-desorption isotherm curves at 77K, and (c) pore size distribution diagrams based on the DFT method.

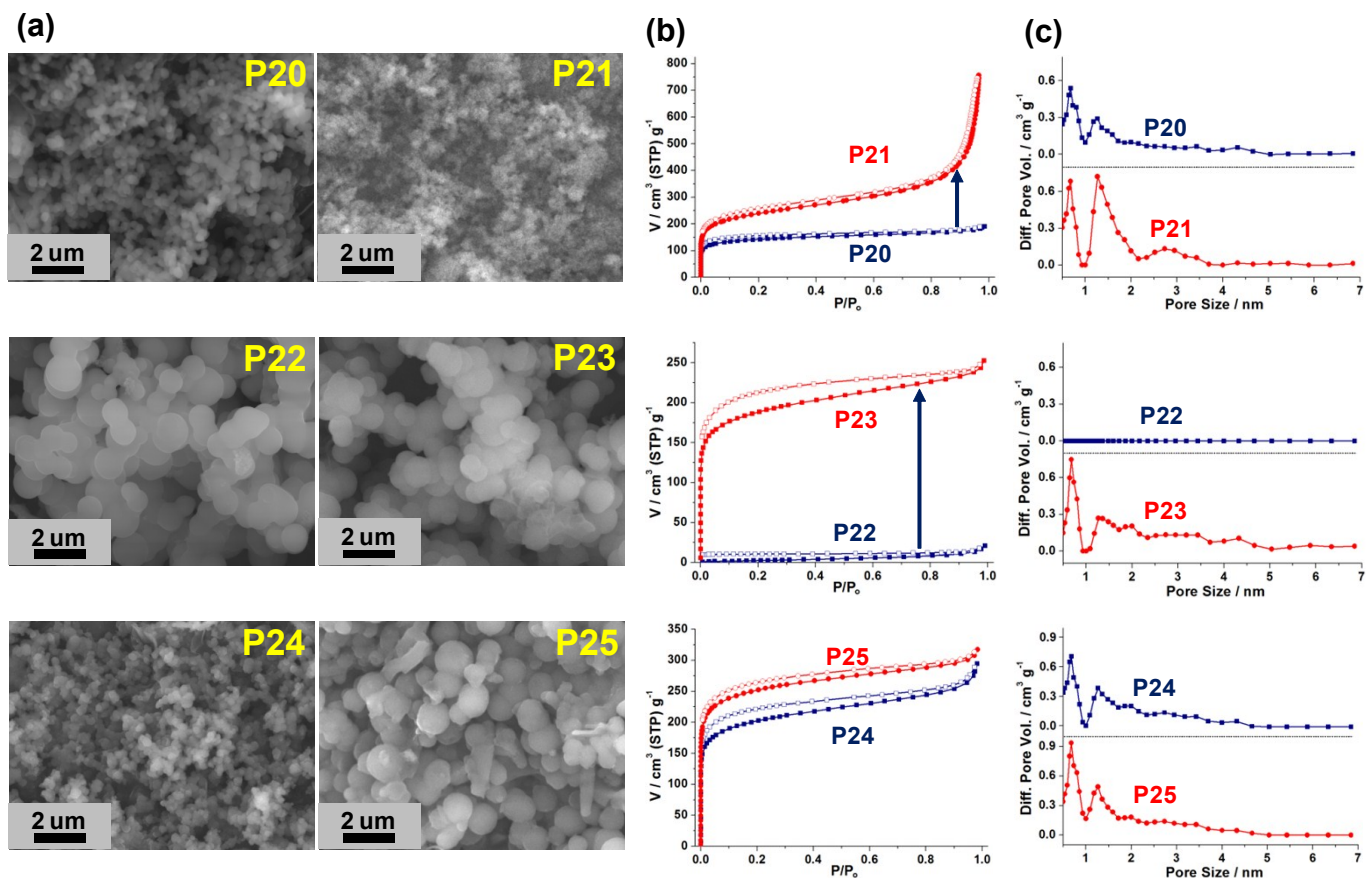


Fig. S9 Characterization data of CMP materials in Table 2 (P20~P25). (a) Solid phase ^{13}C NMR spectra and (b) IR absorption spectra.

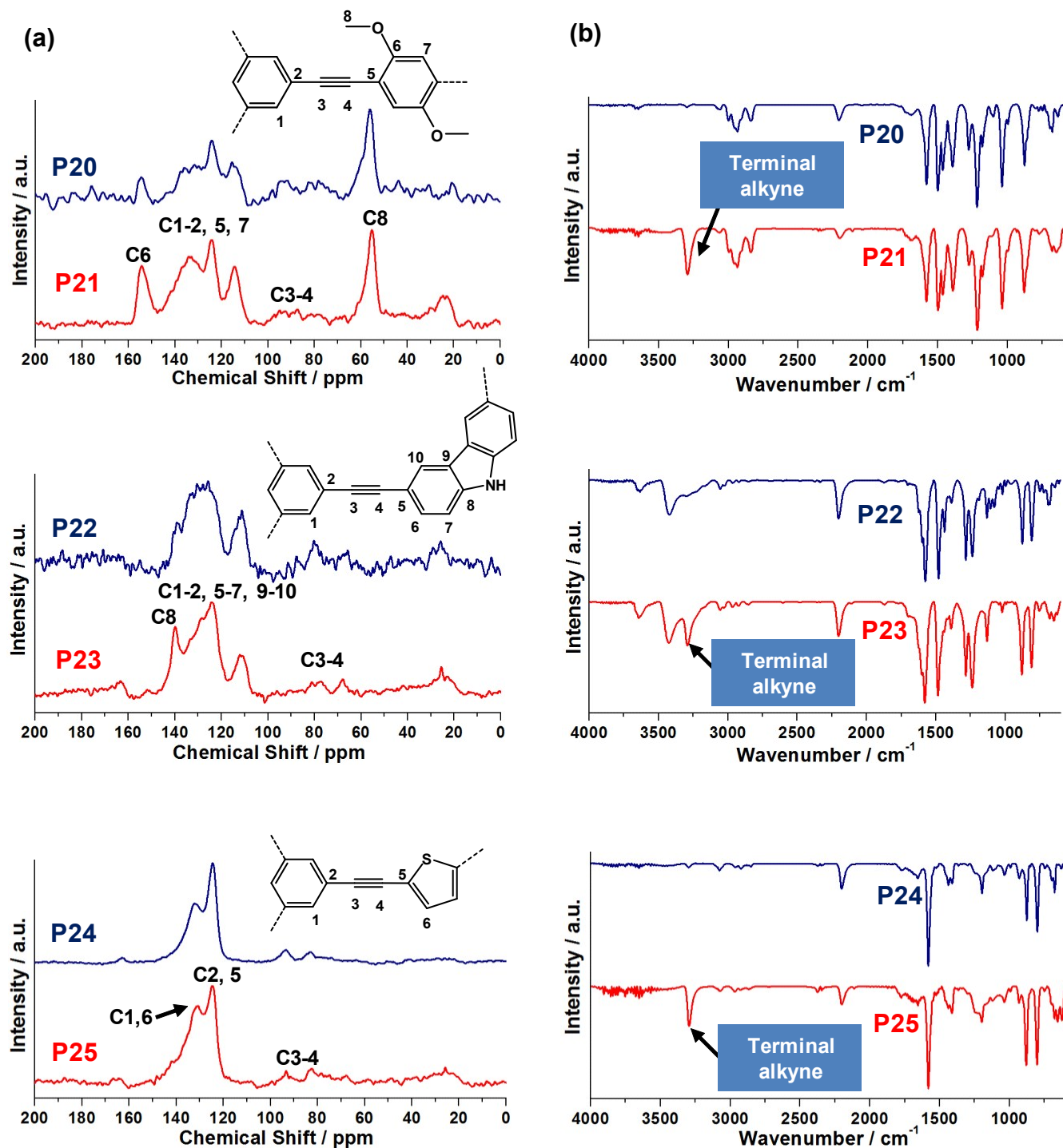


Fig. S10 PXRD patterns of CMP and MP materials in Table 2 (P8~P25).

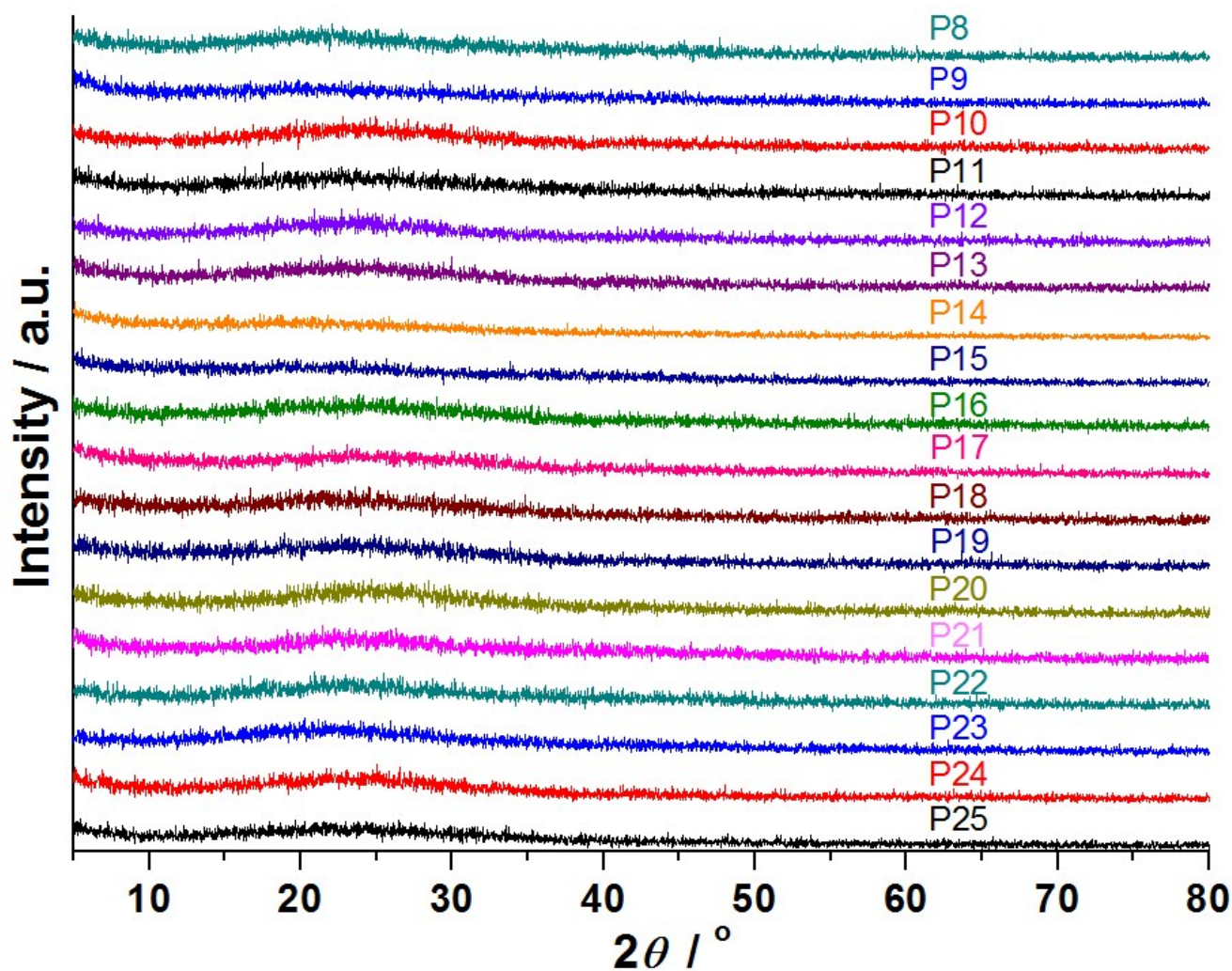


Table S1. Elemental analysis of CMP and MP materials (P1~P25) in this work.

| Materials | C / % | H / % | N / % | S / % | O / % |
|------------|-------|-------|-------|-------|-------|
| P1 | 70.50 | 3.71 | 4.76 | - | - |
| P2 | 72.23 | 3.39 | 5.04 | - | - |
| P3 | 70.88 | 3.16 | 5.07 | - | - |
| P4 | 72.38 | 3.38 | 5.12 | - | - |
| P5 | 72.60 | 3.82 | 5.62 | - | - |
| P6 | 71.90 | 3.20 | 5.34 | - | - |
| P7 | 72.56 | 3.60 | 5.40 | - | - |
| P8 | 69.98 | 3.12 | - | - | - |
| P9 | 77.54 | 3.59 | - | - | - |
| P10 | 76.26 | 3.33 | - | - | - |
| P11 | 80.40 | 3.84 | - | - | - |
| P12 | 77.55 | 3.49 | - | - | - |
| P13 | 84.28 | 4.05 | - | - | - |
| P14 | 79.77 | 4.09 | - | - | - |
| P15 | 79.74 | 4.42 | - | - | - |
| P16 | 80.26 | 4.04 | - | - | - |
| P17 | 83.84 | 4.56 | - | - | - |
| P18 | 82.67 | 4.14 | - | - | - |
| P19 | 82.13 | 4.62 | - | - | - |
| P20 | 70.58 | 3.52 | - | - | 10.15 |
| P21 | 70.01 | 3.85 | - | - | 10.42 |
| P22 | 68.33 | 3.02 | 3.15 | - | - |
| P23 | 73.59 | 3.35 | 3.99 | - | - |
| P24 | 72.40 | 2.41 | - | 14.28 | - |
| P25 | 73.29 | 2.61 | - | 14.52 | - |

Fig. S11 Model studies and isolated yields: The Sonogashira coupling of 1,4-diiodobenzene and phenylacetylene with $(\text{PPh}_3)_2\text{PdCl}_2$ and $[\text{P}(o\text{-tolyl})_3]_2\text{PdCl}_2$ at 90 °C for 30 mins. Refer to Experimental procedure in the ESI for detail information.

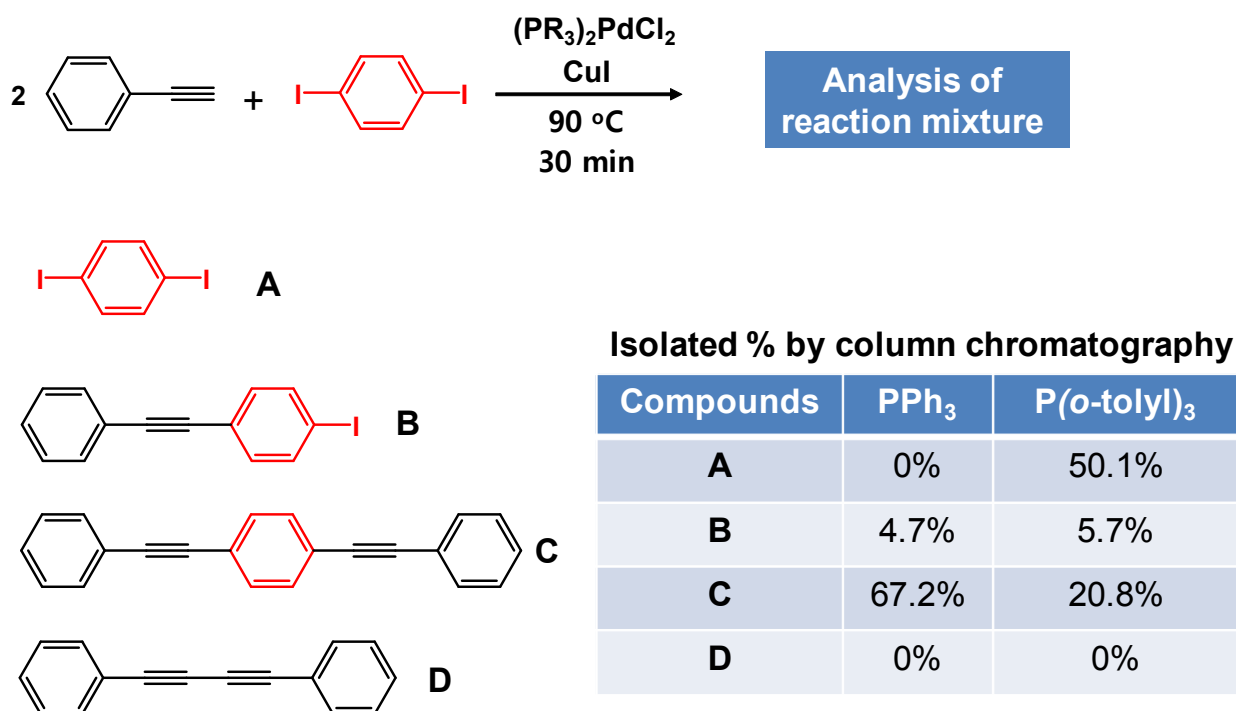
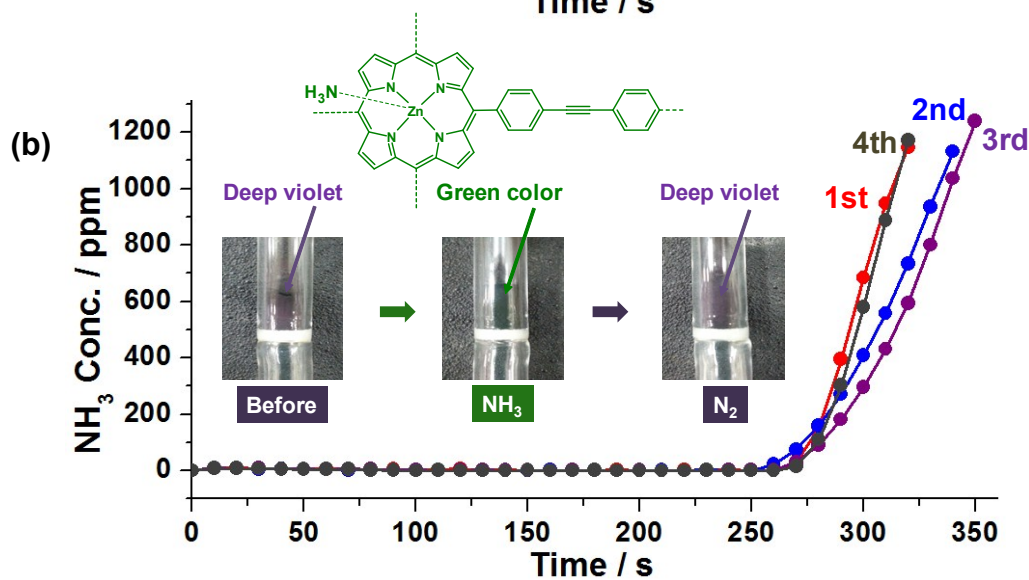
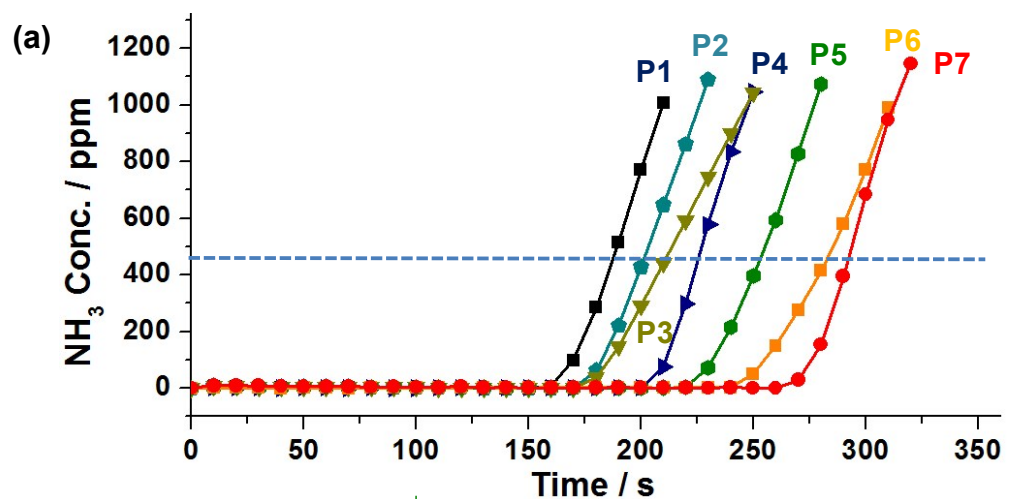


Fig. S12 (a) Ammonia adsorption breakthrough curves, (b) re-adsorption tests, and (c) breakthrough capacities of microporous Zn-porphyrin materials (P1~P7). Refer to Experimental procedure in the ESI for detail information.



(c)

| Materials | Breakthrough time/ s | Breakthrough capacity/ mg g ⁻¹ |
|-----------|----------------------|---|
| P1 | 187 | 10.8 |
| P2 | 201 | 11.6 |
| P3 | 211 | 12.1 |
| P4 | 225 | 13.0 |
| P5 | 253 | 14.5 |
| P6 | 282 | 16.2 |
| P7-1 | 292 | 16.8 |
| P7-2 | 303 | 17.4 |
| P7-3 | 311 | 17.9 |

Fig. S13 Characterization data of CMP-PPh₃ and CMP-P(*o*-tolyl)₃ materials prepared using an 1:1 ratio of 1,3,5-triethynylbenzene (0.39 mmol) and 4,4'-diiodobiphenyl (0.39 mmol) under the same synthetic conditions for P10 and P11, respectively. (a) SEM images, (b) N₂ adsorption-desorption isotherm curves at 77K, and (c) IR absorption spectra.

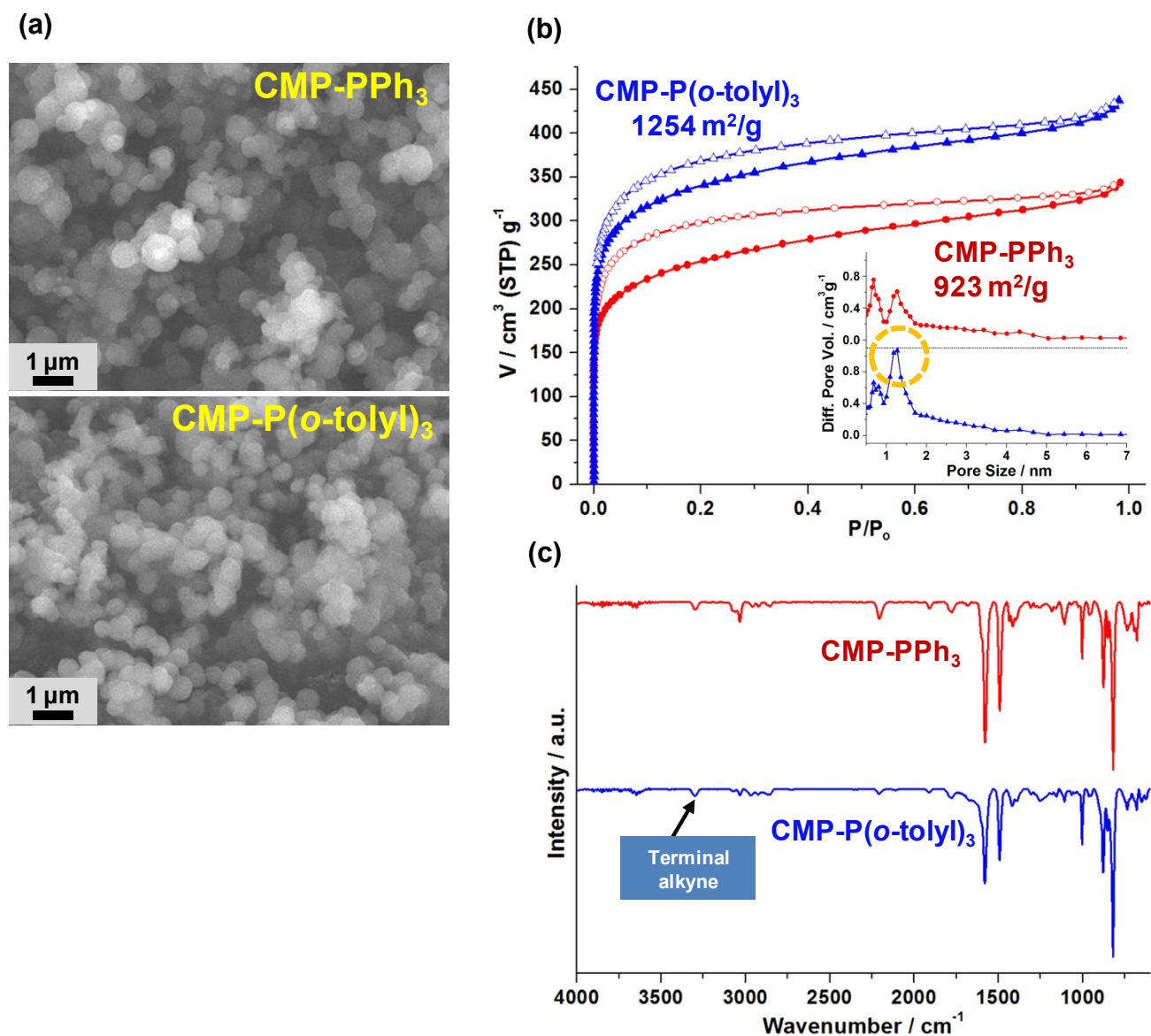


Fig. S14 Characterization data of CMP-PPh₃ and CMP-P(*o*-tolyl)₃ materials prepared using a 2:3 ratio of 1,3,5-triethynylbenzene and 4,4'-diiodobiphenyl under the same synthetic conditions for P10 and P11 except using DMF instead of THF, respectively. (a) SEM images, (b) N₂ adsorption-desorption isotherm curves at 77K, and (c) IR absorption spectra.

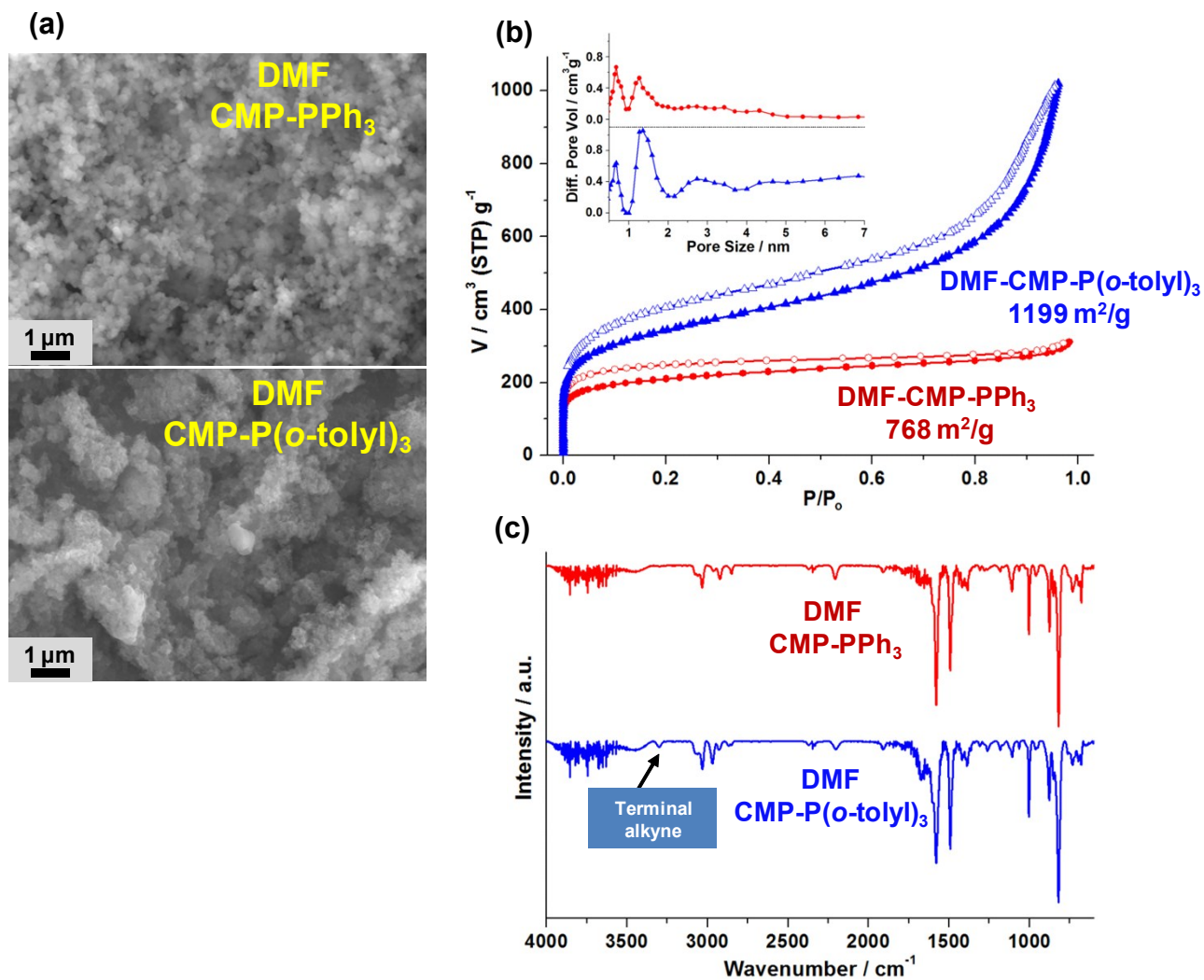


Fig. S15 Characterization data of CMP-P(*o*-tolyl)₃, **P11** obtained by prolonged reaction times (1 day, 2 days, and 5 days). (a) SEM images, (b) N₂ adsorption-desorption isotherm curves at 77K, and (c) IR absorption spectra.

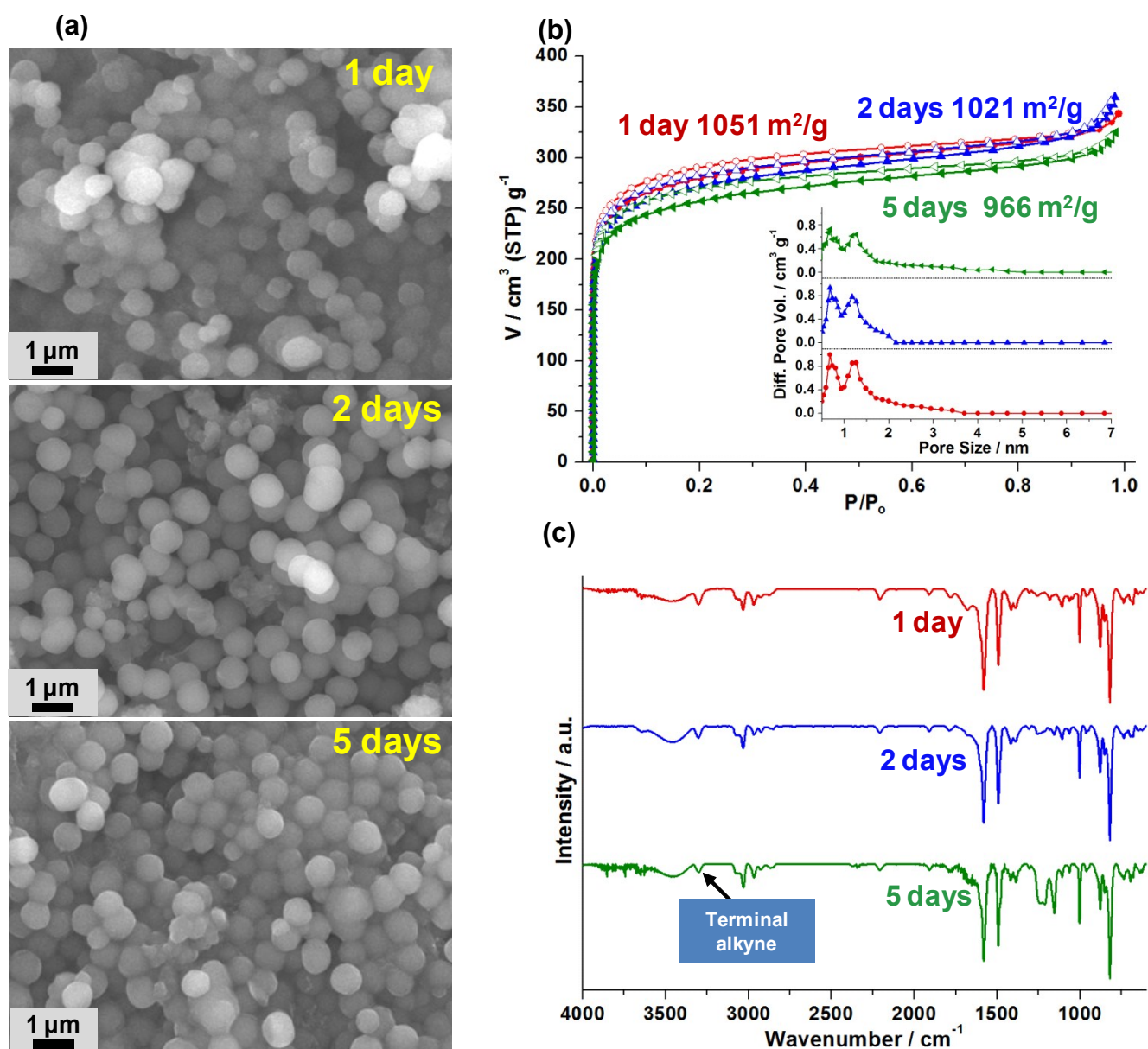


Fig. S16 Model studies: Characterization data of the CMP materials prepared by homo-coupling of 5,10,15,20-tetra(4-ethylphenyl) Zn(II) porphyrin building block using $(\text{PPh}_3)_2\text{PdCl}_2$ (denoted as HOMO-PPh₃) or $[\text{P}(o\text{-tolyl})_3]_2\text{PdCl}_2$ (denoted as HOMO-P(o-tolyl)₃). (a) SEM images, (b) PXRD patterns, (c) N₂ sorption isotherm curves at 77K, (d) pore size distribution based on the DFT method, (e) solid phase ¹³C NMR spectra, and (f) IR absorption spectra of HOMO-PPh₃ and HOMO-P(o-tolyl)₃. Refer to Experimental procedure in the ESI for detail information.

(a)

(b)

