Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Facile Construction of Butadiynylene Based Conjugated Porous Polymers by Cost-effective Glaser Coupling

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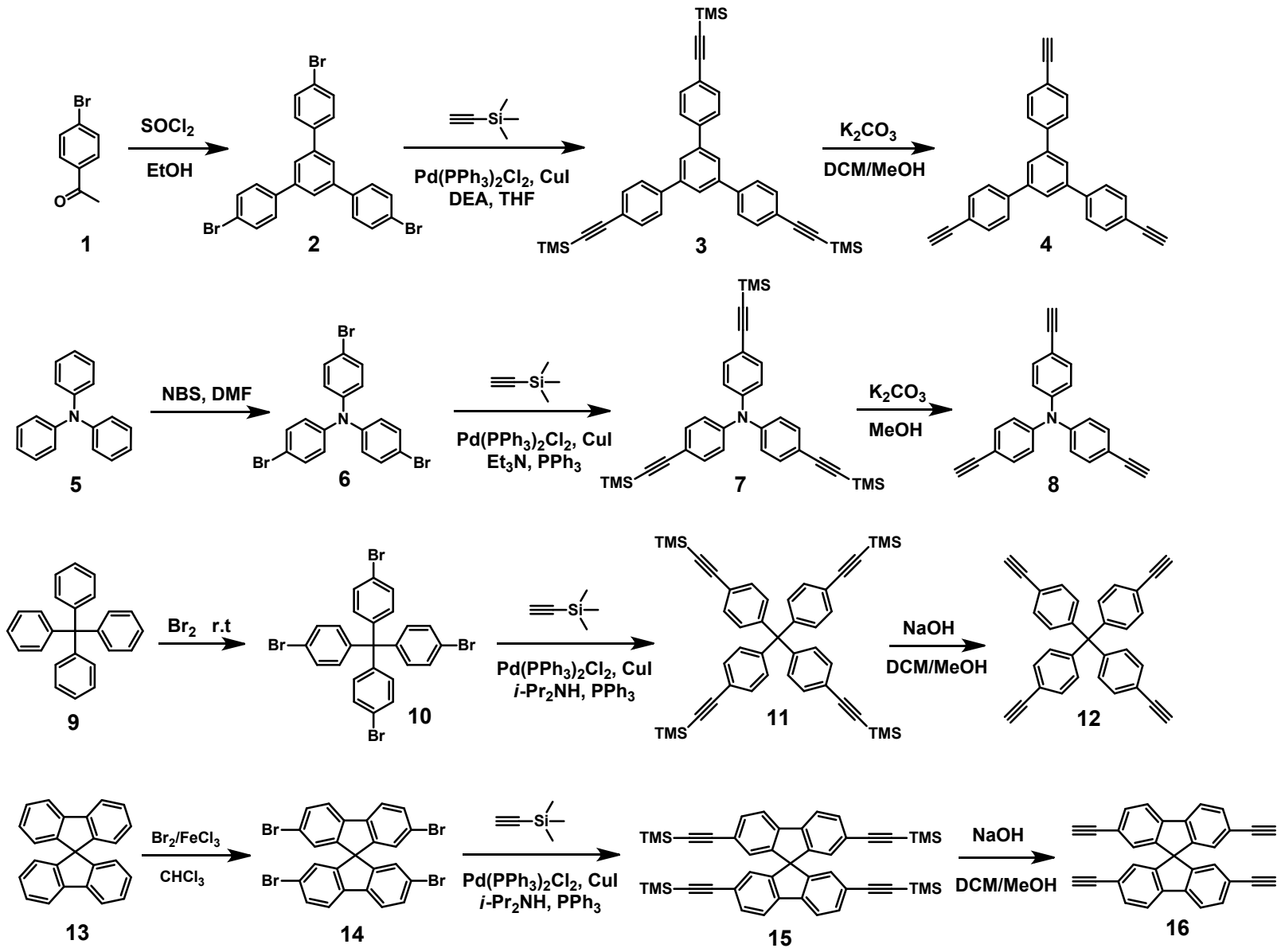
Section 1. Materials and Methods

Trimethylsilylacetylene and *p*-bromoacetophenone were purchased from Acros. Tetraphenylmethane was purchased from Alfa Aesar. Triphenylamine was obtained from Sigma Aldrich in 97% purity. $PdCl_2(PPh_3)_2$ was purchased from Creasyn Finechem(Tianjin) Co., Ltd . All the commercial chemicals were directly used without further purification. Solvents were purified according to standard procedures. All the alkynyl monomers were synthesized according to the literature *via* modified procedures.

FT-IR spectra were collected in transmission on a Bruker Alpha spectrometer using KBr pellets with a scan range of 400-4000 cm^{-1}. The UV-vis diffuse reflectance spectra were obtained from PerkinElmer Lambda 750 spectrophotometer equipped with integration sphere with standard procedure. The ^{1}H NMR spectra of all organic compounds were recorded on a Bruker AVANCE III-400 NMR spectrometer. Solid-state NMR experiments were performed on a Bruker WB AVANCE II 400 MHz NMR spectrometer. The ^{13}C cross-polarization magic angle spinning (CP/MAS) spectra were recorded with a 4 mm double-resonance MAS probe and at a MAS rate of 10.0 kHz with a contact time of 2 ms (ramp 100) and a pulse delay of 3 s. The residual Cu content was determined by ICP-MS techniques using Agilent 7700X ICP-MS model. The samples were prepared by nitrohydrochloric acid digestion before measurement. The thermal properties of all the CMPs were evaluated using a thermogravimetric analysis (TGA) with a differential thermal analysis instrument (NETZSCH STA 409PC analyzer) over the temperature range from 30^{o}C to 700^{o}C under air atmosphere with a heating rate of 15 ^{o}C/min. Powder X-ray diffraction measurement was carried out on X-ray diffractometer model Flex 600 diffractometer (Japan) at 40 kV, 15 mA with a Cu-target tube and a graphite monochromator. Field emission scanning electron microscopies (FE-SEM) were performed on a Hitachi Limited model S-4800 microscope operating at an accelerating voltage of 3.0 kV. High resolution transmission electron microscopies (TEM) were performed on a JEOL model JEM-2100F microscope. The nitrogen and carbon dioxide adsorption and desorption isotherms were measured at 77 K and 273 K using a Bel Japan Inc. model BELSOPR-mini II analyser, respectively. The CH_4 adsorption/desorption isotherms were recorded at 273 K using Micromeritics ASAP 2020M gas adsorption analyzer. The samples were degassed at 150^{o}C for 3 h under vacuum (10^{-5} bar) before analysis. Surface areas were calculated from the nitrogen adsorption data. The pore size distributions were calculated from the nitrogen adsorption branch with the nonlocal density functional theory (NLDFT).

Section 2. Synthetic procedures



Scheme S1. Synthetic routes of four terminal alkyne monomers **4, 8, 12, 16** with different aromatic cores.

1,3,5-Tris(4-bromophenyl)benzene 2

To a solution of *p*-bromoacetophenone (**1**) (11.65 g, 58.53 mmol) in methanol (300 ml) was added $SOCl_2$ (70 ml) dropwise at -30 °C until the mixture became red. Then the mixture was stirred at reflux for 1.5 h and lots of light yellow precipitate was generated. The reaction mixture was cooled to -30 °C again, the precipitate was collected by filtration and washed with methanol, dried in vacuum, to afford compound **2** as a yellow solid (4.45 g, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (s, 3H), 7.61 (d, 6H), 7.54 (d, 6H).

1,3,5-tris-(4-trimethylsilylethynylphenyl)benzene 3

A mixture of 1,3,5-Tris(4-bromophenyl)benzene (**2**) (2.0 g, 3.68 mmol), $PdCl_2(PPh_3)_2$ (200 mg, 0.285 mmol), PPh_3 (160 mg, 0.61 mmol) and CuI (20 mg, 0.11 mmol) in diethylamine (120 mL) and trimethylsilylacetylene (TMSA) (120 mL) was stirred at 55℃for 42 hours under nitrogen. The precipitate was purified by silica gel column chromatography (petroleum ether) to obtain a yellowish solid and recrystallized with dichloromethane/ethanol to afford compound **3** as a white solid (1.13g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (s, 3H), 7.63 (d, 6H), 7.57 (d, 6H), 0.28 (s, 27H).

1,3,5-tris-(4-ethynylphenyl)benzene 4 [S1]

A mixture of 1,3,5-tris-(4-trimethylsilylethynylphenyl)benzene (**3**) (1.0 g, 1.68 mmol) and K_2CO_3 (1.02 g, 7.38 mmol) in dichloromethane (22 mL) and methanol (22 mL) was stirred at room temperature for 22 hours. The reaction

mixture was added water (40 ml) and then extracted with dichloromethane for three times. The organic phase was then concentrated in vacuum and recrystallized with dichloromethane/ethanol to afford compound **4** as a white solid (0.55 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76 (s, 3H), 7.65 (d, 6H), 7.61 (d, 6H), 3.16 (s, 3H).

Tri(4-bromophenyl)amine 6

To a solution of triphenylamine (**5**) (4.9 g, 10.97 mmol) in DMF (50 mL) was added dropwise with a solution of NBS (10.4 g, 58.43 mmol) in DMF (20 mL). Then the mixture was stirred at room temperature for 14 h, subsequently poured into 50 ml water and lots of white solid was generated. The precipitate was collected by filtration and washed with ethanol, dried in vacuum, to afford the compound **6** as a white solid (8.82 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35 (d, 6H), 6.92 (d, 6H).

tris(4-((trimethylsilyl)ethynyl)phenyl)amine 7 [S2]

A mixture of tri(4-bromophenyl)amine (**6**) (4.0 g, 8.28 mmol), $PdCl_2(PPh_3)_2$ (332 mg, 0.48 mmol), PPh_3 (64 mg, 0.24 mmol) and CuI (44 mg, 0.23 mmol) in Et_3N (160 mL) and trimethylsilylacetylene (TMSA) (5.2 mL, 37.3 mmol) was refluxed overnight under nitrogen. After cooling down to room temperature, the reaction mixture was evaporated to dryness and the residue was purified by silica gel column chromatography (PE as eluent) to afford compound **7** as a yellow solid (3.93 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34 (d, 6H), 6.95 (d, 6H), 0.24 (s, 27H).

tri(4-ethynylphenyl)amine 8 [S3]

A mixture of tris(4-((trimethylsilyl)ethynyl)phenyl)amine (**7**) (3.93 g, 7.36 mmol) and K_2CO_3 (2.35 g, 17.0 mmol) in methanol (300 mL) was stirred at room temperature for 22 h. The reaction mixture was evaporated, and diethyl ether and water was added sequentially into the residue. The organic layer was dried over $MgSO_4$ and rotary evaporated. The residue was purified by silica gel column chromatography with PE:EA = 10:1 as eluent to afford compound **8** as a brown solid (2.06 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, 6H), 7.01 (d, 6H), 3.06 (s, 3H).

tetrakis(4-bromophenyl)methane 10[S4]

Tetraphenylmethane (**9**) (0.9g, 2.8 mmol) was placed in a two-necked round bottom flask and liquid bromine (2.5 mL, 98 mmol) was added slowly in the flask. The mixture was stirred at room temperature for 5 h. The reaction mixture was added ethanol at -78^{o}C, the resulted precipitate was collected by filtration and washed with aqueous $Na_2S_2O_3$. The crude product was purified by silica gel column chromatography with petroleum ether (PE) as eluent to afford compound **10** as a white solid (510 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35 (d, 8H), 6.92 (d, 8H).

Tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane 11[S5]

A mixture of tetrakis(4-bromophenyl)methane (**10**) (0.8 g, 1.27 mmol), $PdCl_2(PPh_3)_2$ (108 mg, 0.156 mmol), PPh_3 (80 mg, 0.3 mmol) and CuI (24.6 mg, 0.13 mmol) in *i*-Pr_2NH (30 mL) and trimethylsilylacetylene (TMSA) (0.86 mL, 6.0 mmol) was refluxed for 42 h under nitrogen. After cooling down to room temperature, the precipitate was first filtered via a pad of celite and then vacuum concentrated. The residue was purified by silica gel column

chromatography wtih PE:DCM = 20:1 as eluent to afford compound **11** as a pale white solid (0.6 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (d, 8H), 7.04 (d, 8H), 0.23 (s, 36H).

Tetrakis(4-ethynylphenyl)methane 12 [S5]

A mixture of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (**11**) (0.6 g, 0.85 mmol) and NaOH (0.33 g, 0.83 mmol) in CH_3OH (10 mL) and CH_2Cl_2 (40 mL) was stirred at room temperature for 40 h. The reaction mixture was washed with water and then extracted with CH_2Cl_2 for three times. The organic phases were then washed with brine and dried over anhydrous Na_2SO_4. The solvent was concentrated on reduced pressure, ethanol was added to the residue and then the precipitate was collected by filtration, dried, to afford compound **12** as a pale solid (258 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, 8H), 7.12 (d. 8H), 3.07 (s, 4H).

2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] 14[S6]

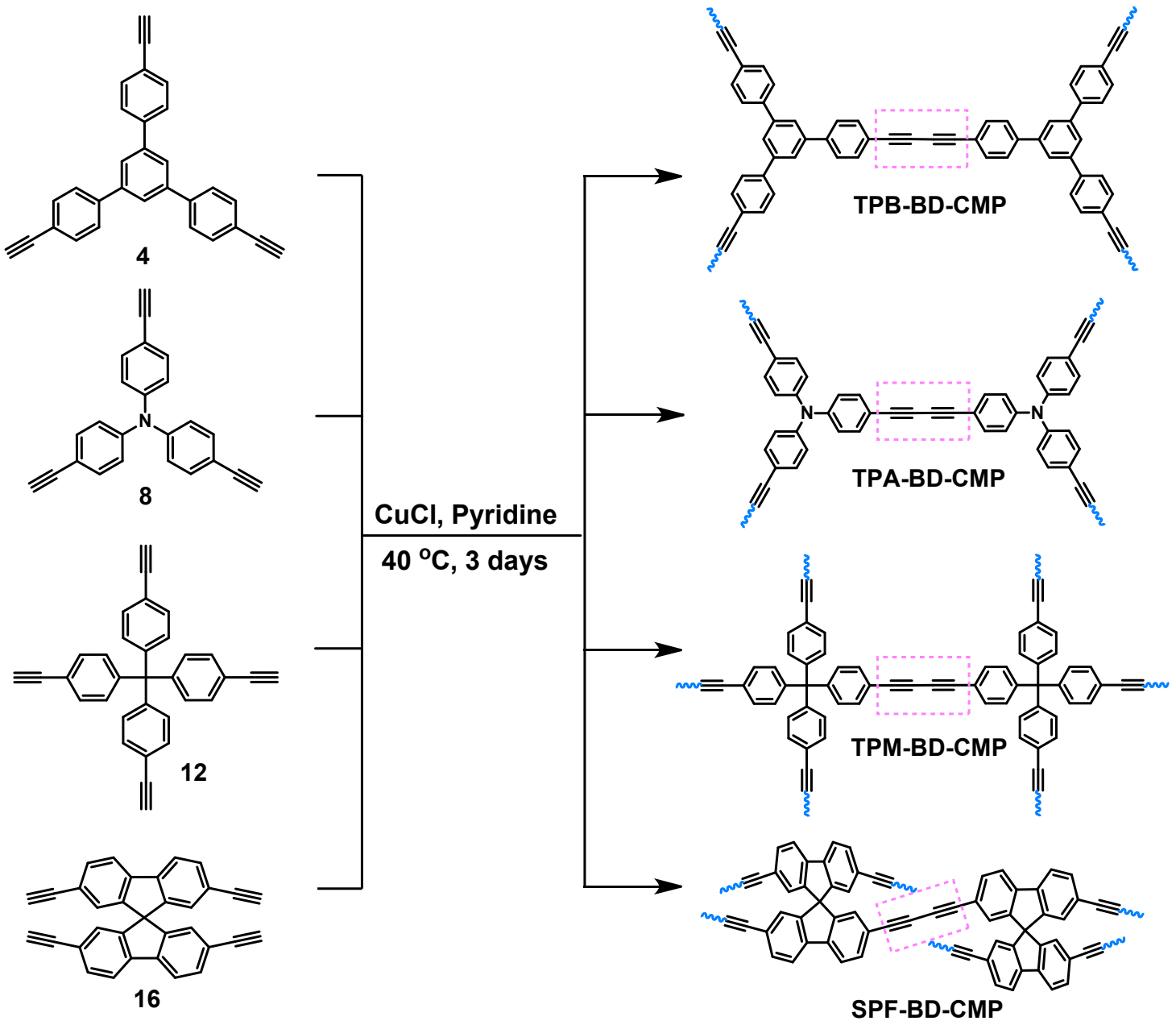
To a solution of 9,9'-spirobi[fluorene] **(13)** (0.632 g, 2 mmol) in chloroform (3 mL) at 0^{o}C was added ferric chloride (16 mg, 0.1 mmol) and bromine (0.8 mL, 8.2 mmol). Then the mixture was warm to room temperature and stirred for 3 h. The resulting slurry was washed with water and saturated sodium thiosulfate until the filtrate was colorless. Then the mixture was extracted with dichloromethane for three times, dried over $MgSO_4$ and vacuum concentrated to afford compound **14** as a white solid (0.811 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, 4H), 7.54 (dd, 4H), 6.93 (s, 4H).

2,2',7,7'-tetrakis((trimethylsilyl)ethynyl)-9,9'-spirobi[fluorene] 15[S7]

The solvent of *i*-Pr_2NH (24 mL) was placed in a two-necked round bottom flask and degassed by three free-pump-thaw cycles and then added into the mixture of 2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] **(14)** (450 mg, 0.712 mmol), $PdCl_2(PPh_3)_2$ (39 mg, 0.056 mmol), PPh_3 (36 mg, 0.14 mmol) and CuI (11 mg, 0.058 mmol). The mixture was degassed by free-pump-thaw cycles again, then trimethylsilylacetylene (TMSA) (0.75 ml, 5.3 mmol) was added, and the mixture was stirred at 90℃ for 22 h. Then the reaction mixture was vacuum concentrated to dryness and the residue was purified by silica gel column chromatography with PE:DCM = 20:1 as eluent to afford compound **15** as a white solid (0.456 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, 4H), 7.49 (dd, 4H), 6.77 (s, 4H), 0.16 (s, 36H).

2,2',7,7'-tetraethynyl-9,9'-spirobi[fluorene] 16 [S7]

A solution of NaOH (0.286 g, 7.1 mmol) in CH_3OH (5 mL) was added into the solution of 2,2',7,7'-tetra(trimethylsilylacetyl)-9,9'-spirodifluorene (**15**) (0.5 g, 0.71 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with water and the aqueous phase was thoroughly extracted with CH_2Cl_2. The organic phases were then washed with brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated on reduced pressure, ethanol was added to the residue and the resulted precipitate was collected by filtration, dried, to afford compound **16** as a light yellow solid (0.226 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78 (d, 4H), 7.53 (dd, 4H), 6.83 (s, 4H), 3.01 (s, 4H).



Scheme S2. Synthesis of **TPB-BD-CMP**, **TPA-BD-CMP**, **TPM-BD-CMP** and **SPF-BD-CMP.**

TPB-BD-CMP[S8]

A mixture of 1,3,5-tris-(4-ethynylphenyl)benzene (**4**) (189 mg, 0.5 mmol) and CuCl (20 mg, 0.2 mmol) in pyridine (20 mL) was kept unstirred at 40 °C for 3 days. The reaction mixture started gelation after ca. 2 days. The product was thoroughly washed with various organic solvents (e.g. CH_2Cl_2, THF, MeOH) and aqueous ethylenediaminetetraacetic acid disodium sequentially to replace the residual monomers, oligomers and metal species if any. The in situ formed gel was exchanged with water several times and then freeze-dried by lyophilizer at -20°C to afford a brown xerogel (180 mg, 96%), the Cu residual content was determined to be 0.12% by ICP-MS techniques using Agilent 7700X ICP-MS model.

TPA-BD-CMP [S8]

A mixture of tri(4-ethynylphenyl)amine (**8**) (190 mg, 0.6 mmol) and CuCl (20 mg, 0.2 mmol) in pyridine (24 mL) was kept unstirred at 40 °C for 3 days. The reaction mixture started gelation after ca. 2 days. The product was thoroughly washed with various organic solvents (e.g. CH_2Cl_2, THF, MeOH) and aqueous ethylenediaminetetraacetic acid disodium sequentially to replace the residual monomers, oligomers and metal species if any. The in situ formed gel was exchanged with water several times and then freeze-dried by lyophilizer at -20°C to afford a dark brownish xerogel (184 mg, 98%), the Cu residual content was determined to be 0.21% by ICP-MS techniques using Agilent 7700X ICP-MS model.

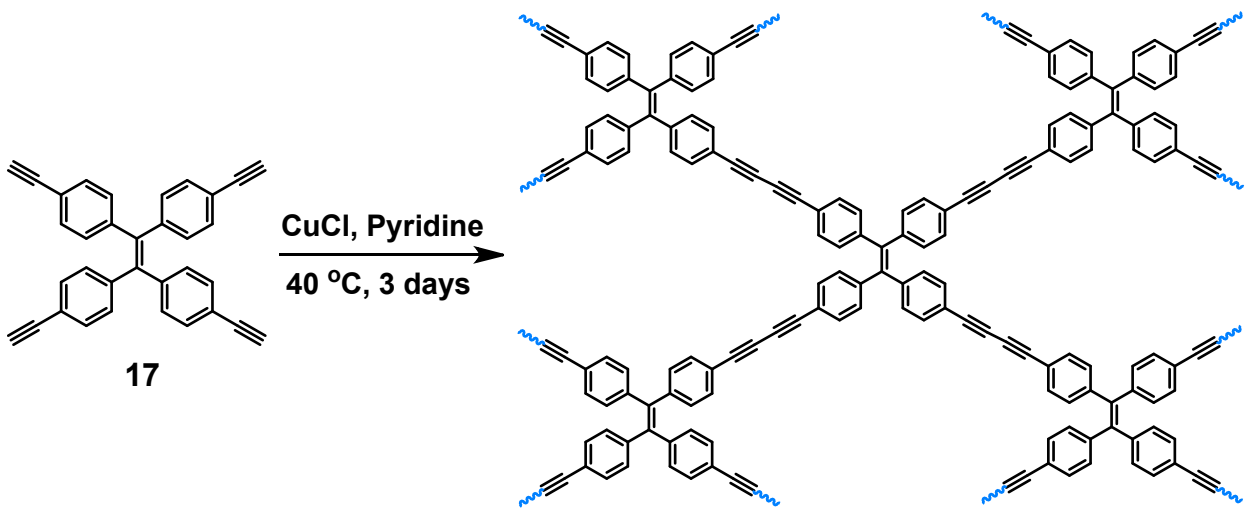
TPM-BD-CMP [S8]

A mixture of tetrakis(4-ethynylphenyl)methane (**12**) (208 mg, 0.5 mmol) and CuCl (30 mg, 0.3 mmol) in pyridine (40 mL) was kept unstirred at 40 °C for 3 days. The reaction mixture started gelation after ca. 2 days. The product was thoroughly washed with various organic solvents (e.g. CH_2Cl_2, THF, MeOH) and aqueous ethylenediaminetetraacetic acid disodium sequentially to replace the residual monomers, oligomers and metal species if any. The in situ formed gel was exchanged with water several times and then freeze-dried by lyophilizer at -20°C to afford a dark brownish xerogel (186 mg, 90%), the Cu residual content was determined to be 0.10% by ICP-MS techniques using Agilent 7700X ICP-MS model.

SPF-BD-CMP [S8]

A mixture of 2,2',7,7'-tetraethynyl-9,9'-spirobi[fluorene] (**16**) (230 mg, 0.558 mmol) and CuCl (29 mg, 0.29 mmol) in pyridine (20 ml) was kept unstirred at 40 °C for 3 days. The reaction mixture started gelation after ca. 2 days. The product was thoroughly washed with various organic solvents (e.g. CH_2Cl_2, THF, MeOH) and aqueous ethylenediaminetetraacetic acid disodium sequentially to replace the residual monomers, oligomers and metal species if any. The in situ formed gel was exchanged with water several times and then freeze-dried by lyophilizer at -20°C to afford a brownish xerogel (218 mg, 95%), the Cu residual content was determined to be 0.24% by ICP-MS techniques using Agilent 7700X ICP-MS model.

To expand the monomers further, 1,1,2,2-tetrakis(4-ethynylphenyl)ethene was introduced as new building blocks for this kind of CMPs:



Scheme S3. Synthesis of **TPE-BD-CMP**,

TPE-BD-CMP

A mixture of 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (**17**)[S9] (148 mg, 0.345 mmol) and CuCl (20 mg, 0.29 mmol) in pyridine (14 ml) was kept unstirred at 40 °C for 3 days. The reaction mixture started gelation after ca. 2 days. The product was thoroughly washed with various organic solvents (e.g. CH_2Cl_2, THF, MeOH) and aqueous ethylenediaminetetraacetic acid disodium sequentially to replace the residual monomers, oligomers and metal species if any. The in situ formed gel was exchanged with water several times and then freeze-dried by lyophilizer at -20°C to afford a dark brown xerogel (136 mg, 93%), the Cu residual content was determined to be 0.02% by ICP-MS techniques using Agilent 7700X ICP-MS model.

Section 3. FT-IR Spectroscopy

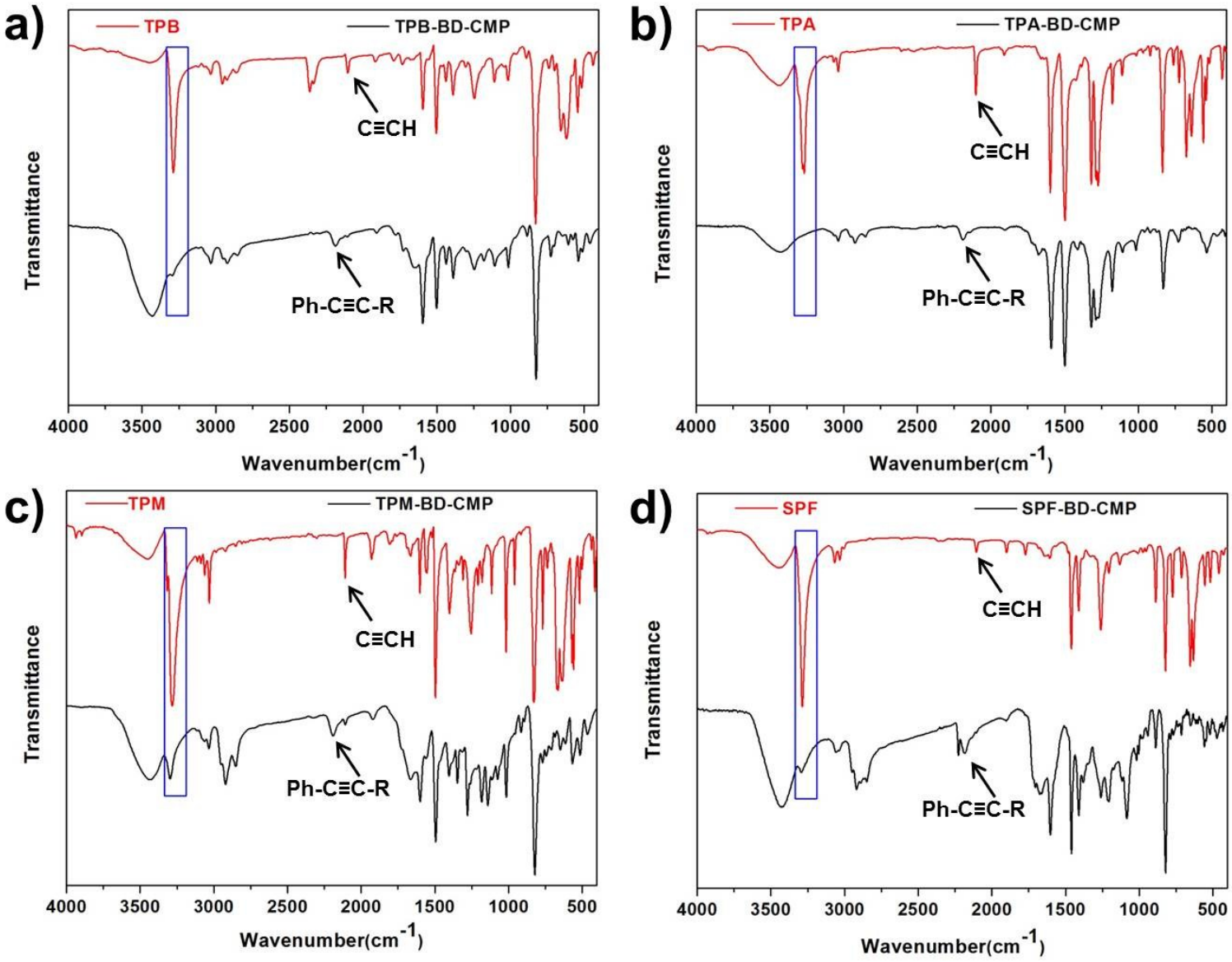


Fig. S1 FT-IR spectra of terminal alkynes (red line) and the CMPs (black lines). The comparison between the stretching vibration of C-H in terminal alkyne monomers and that of CMPs was highlighted in the blue rectangle.

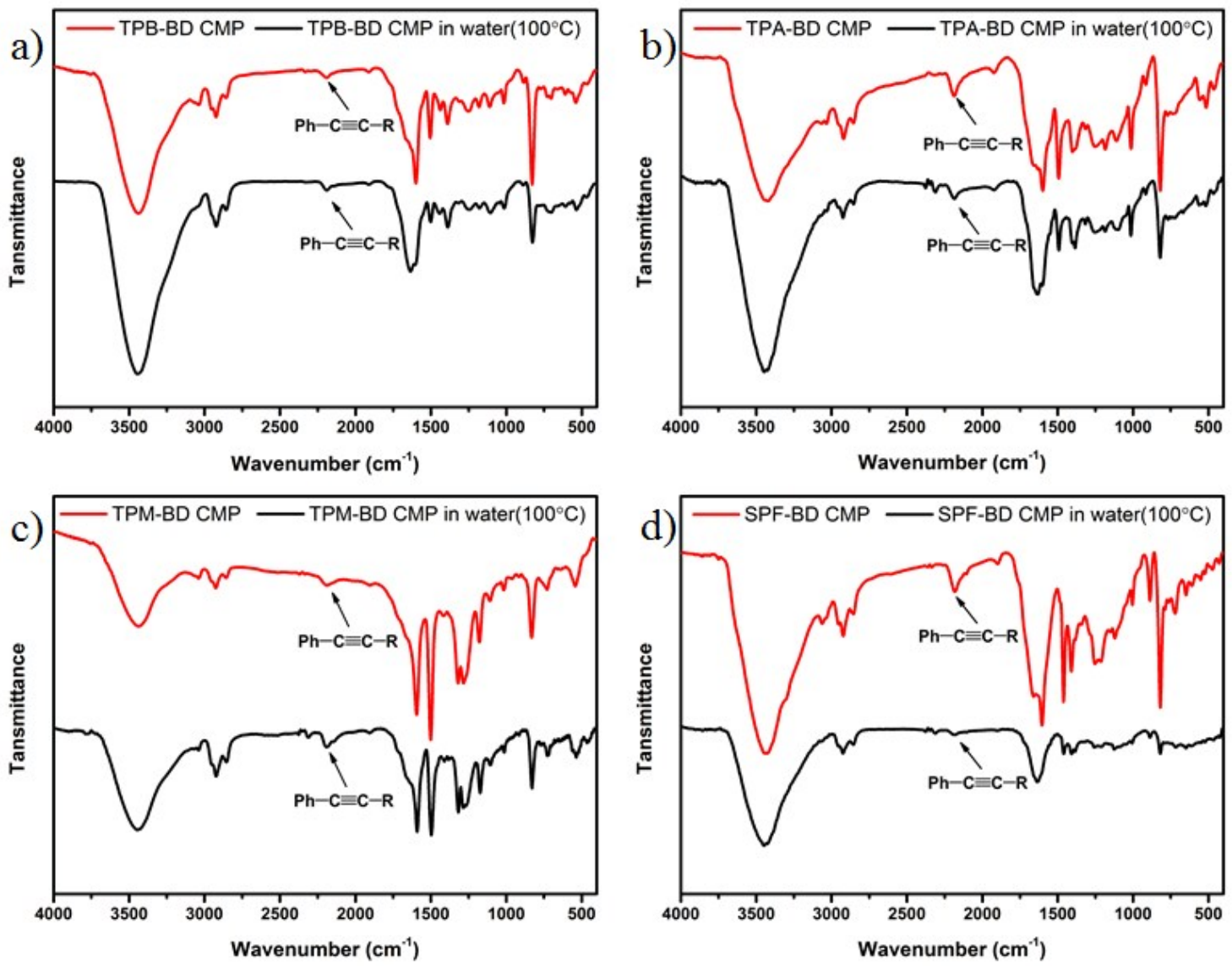


Fig. S2 FT-IR spectra comparison of four CMPs before (red line) and after (black lines) treatment with boiling water (100℃) for 1 day: a) TPB-BD-CMP, b) TPA-BD-CMP, c) TPM-BD-CMP, and d) SPF-BD-CMP. These results indicated all the four BD-CMPs exhibited good hydrothermal stailities.

Section 4. Thermogravimetric Analysis

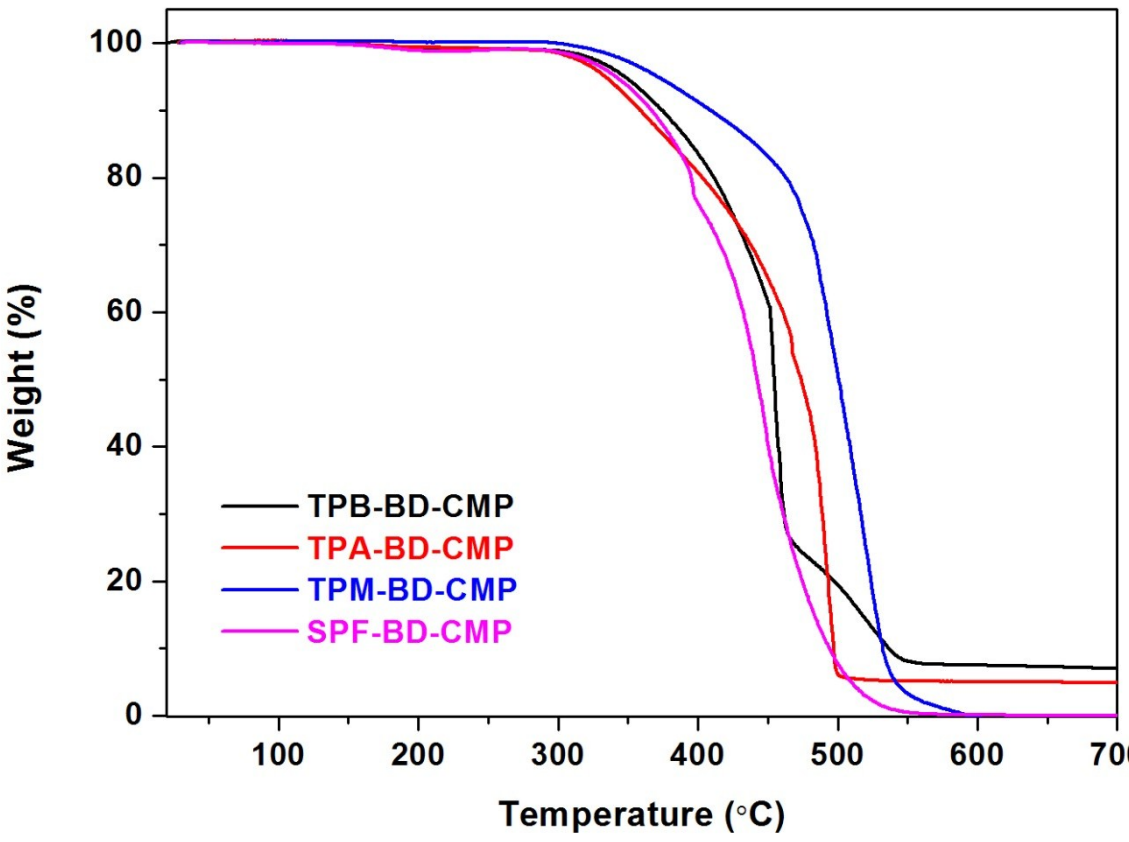


Fig. S3 TGA curves of **TPB-DB-CMP** (black line), **TPA-DB-CMP** (red line), **TPM-BD-CMP** (blue line), and **SPF-DB-CMP** (pink line). The weight loss of 5% for **TPB-BD-CMP**, **TPA-BD-CMP**, **TPM-BD-CMP** and **SPF-BD-CMP** was determined to be 348°C, 334°C, 372°C and 342°C, respectively.

.Section 5. PXRD profiles

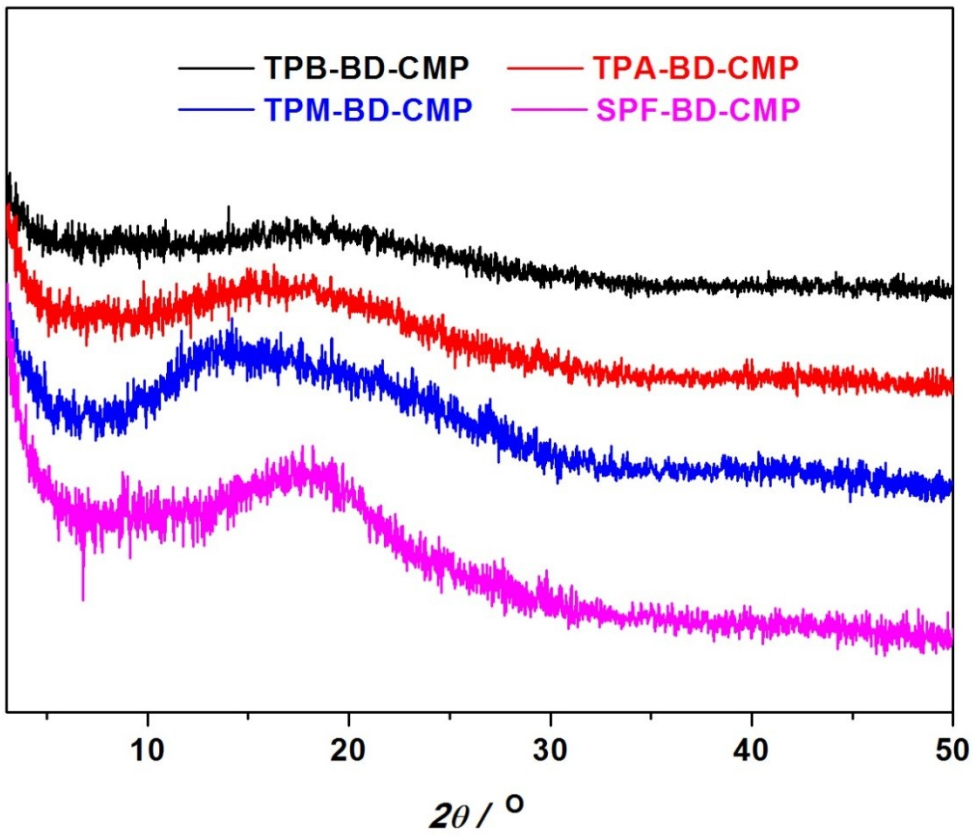


Fig. S4 Powder X-ray diffraction patterns of **TPB-BD-CMP** (black line), **TPA-BD-CMP** (red line), **TPM-BD-CMP** (blue line), and **SPF-BD-CMP** (pink line).

Section 6. N_2 Adsorption/Desorption Isotherms

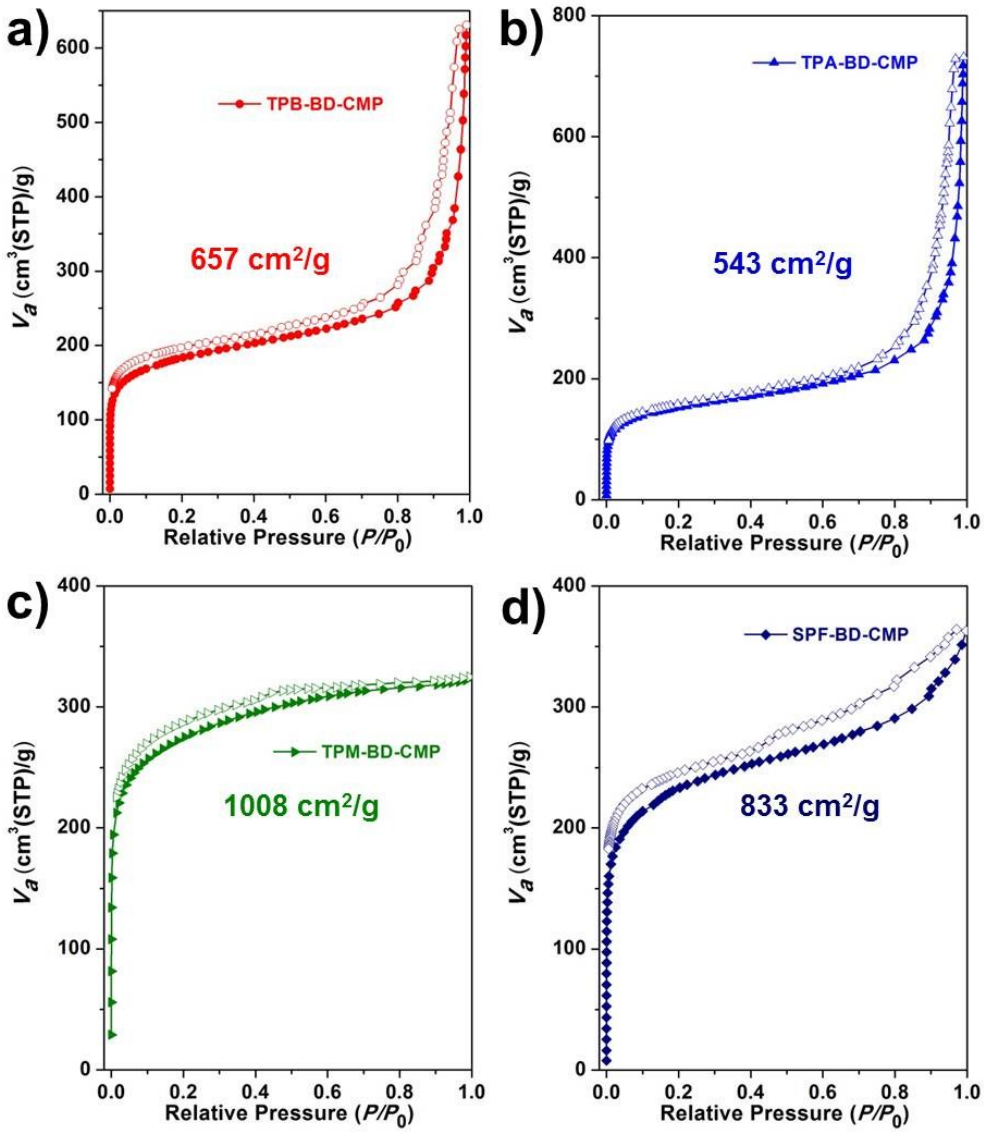


Fig. S5 Nitrogen adsorption/desorption isotherms of four BD-CMPs prepared in typical conditions at 77 K: a) **TPB-BD-CMP**; b) **TPA-BD-CMP**; c) **TPM-BD-CMP**; and d) **SPF-BD-CMP** (The adsorption branches are labeled with filled symbols, and the desorption branches are labeled with empty symbols).

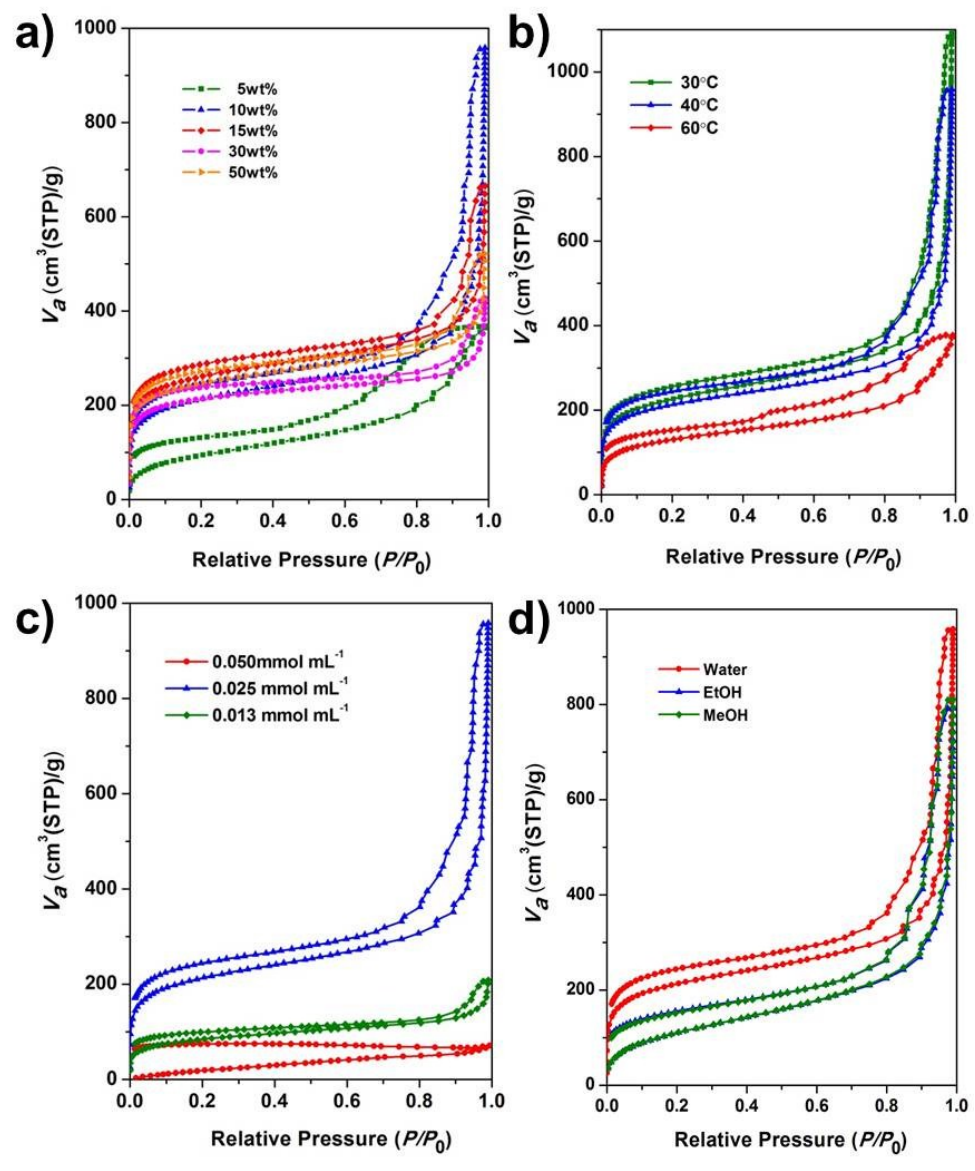


Fig. S6 Nitrogen adsorption/desorption isotherms of **TPB-BD-CMP**s prepared by different conditions at 77 K. a) The influence of variation of CuCl catalyst content on the porosity of **TPB-BD-CMP**; b) The influence of variation reaction temperature on the porosity of **TPB-BD-CMP**; c) The influence of variation of monomer's concentration on the porosity of **TPB-BD-CMP**; d) The influence of variation of lyophilizing solvents on the porosity of **TPB-BD-CMP**.

Section 7. SEM & TEM images

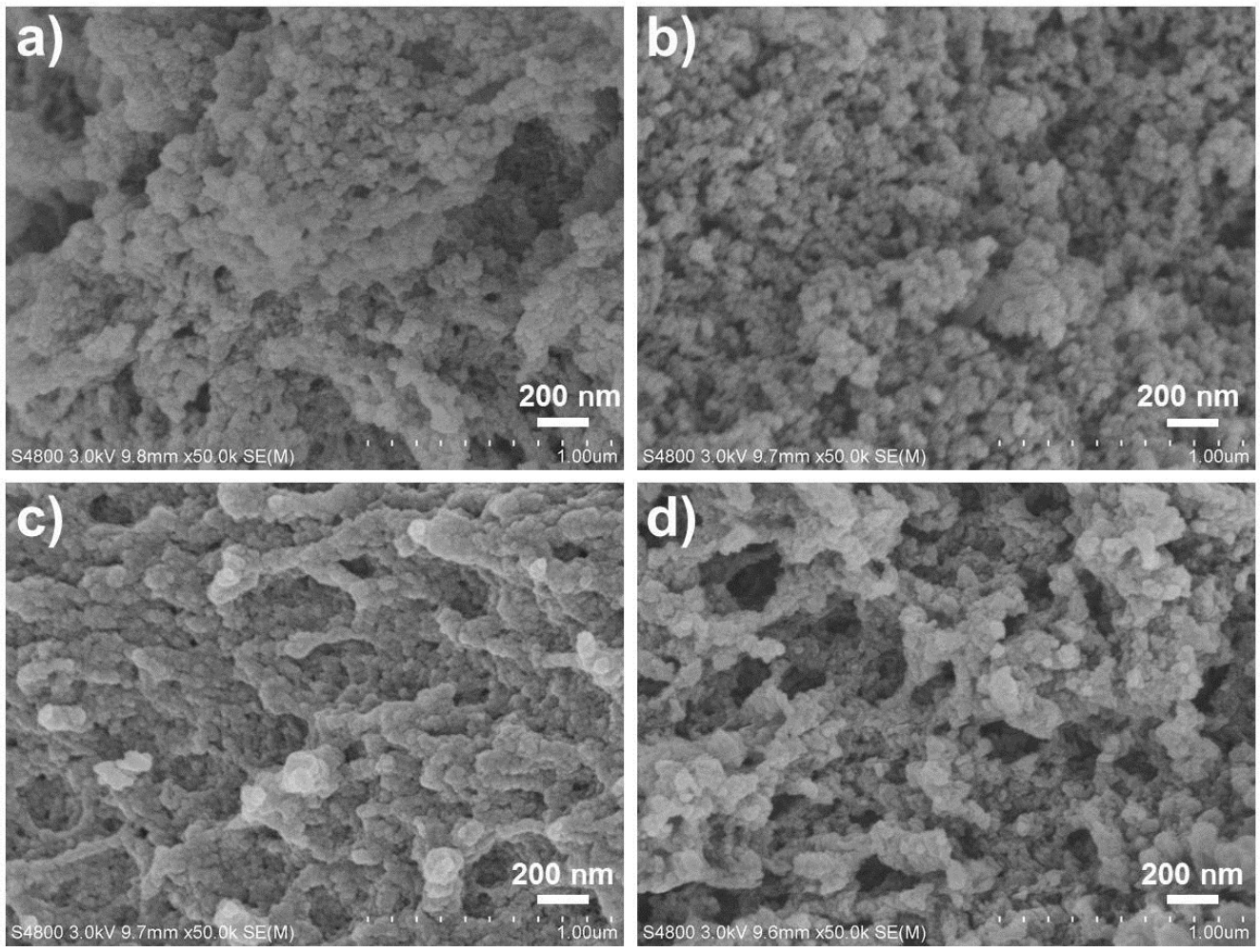


Fig. S7 SEM images of a) **TPB-BD-CMP**, b) **TPA-BD-CMP**, c) **TPM-BD-CMP** and d) **SPF-BD-CMP** (all the scale bars are 200 nm).

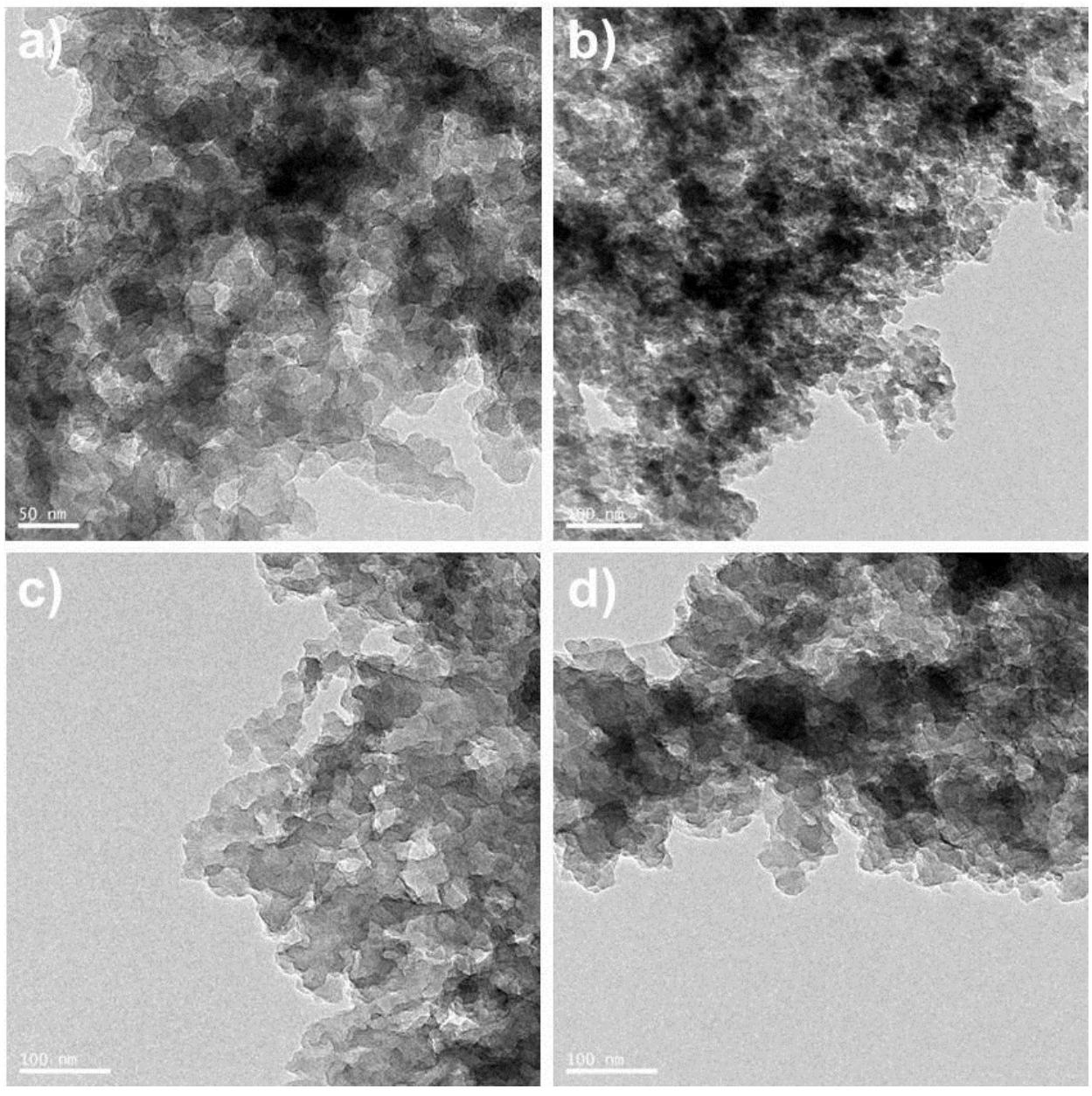


Fig. S8 TEM images of a) **TPB-BD-CMP**, scale bar: 50 nm; b) **TPA-BD-CMP**, c) **TPM-BD-CMP** and d) **SPF-BD-CMP** (the scale bars are 100 nm for images b,c,d).

Section 8. CO_2 and CH_4 Adsorption Isotherms

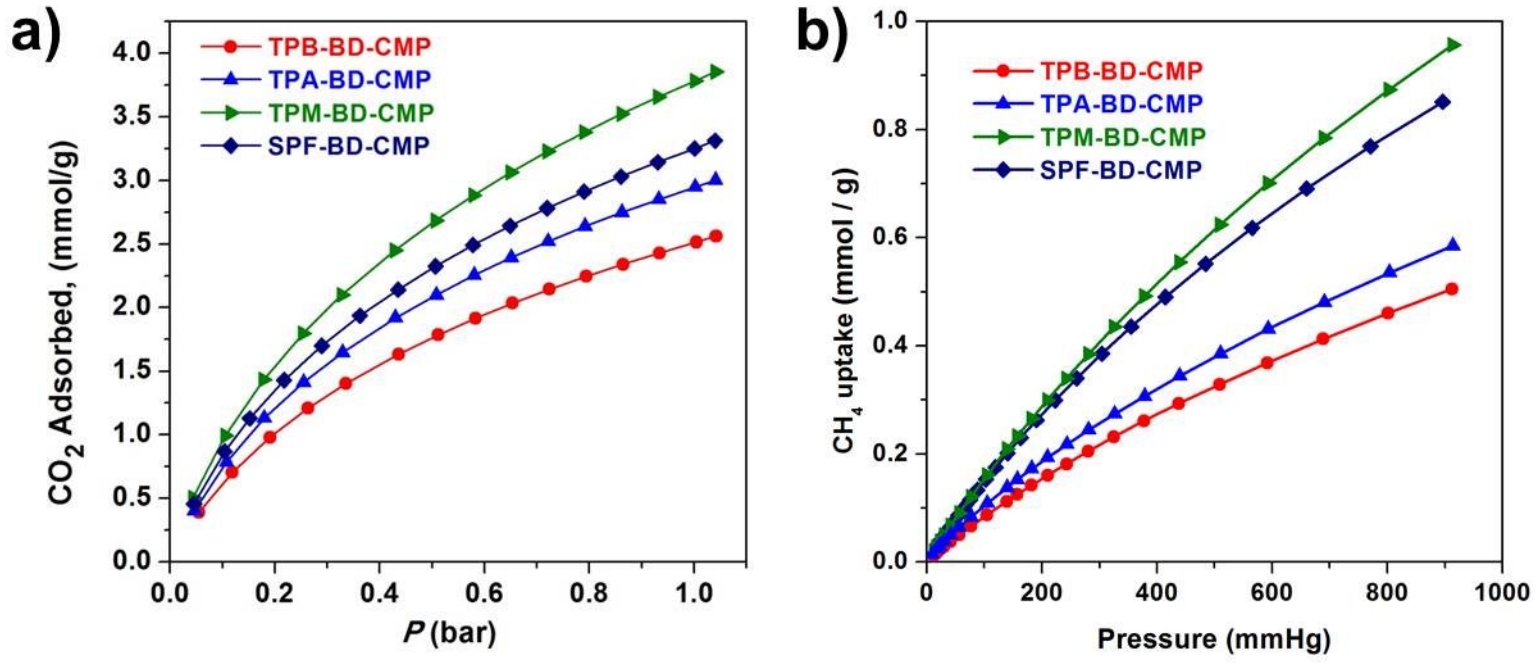


Fig. S9 a) CO_2 adsorption isotherm curves of **TPB-BD-CMP** (red line), **TPA-BD-CMP** (blue line), **TPM-BD-CMP** (green line), and **SPF-BD-CMP** (navy line). The CO_2 uptake capacities were 2.51 mmol/g for **TPB-BD-CMP**, 2.94 mmol/g for **TPA-BD-CMP**, 3.78 mmol/g for **TPM-BD-CMP**, and 3.25 mmol/g for **SPF-BD-CMP**, respectively; b) CH_4 adsorption/desorption isotherm of the BD-CMPs xerogel at 273K. The CH_4 uptake capacities were 0.51 mmol/g for **TPB-BD-CMP**, 0.59 mmol/g for **TPA-BD-CMP**, 0.95 mmol/g for **TPM-BD-CMP**, and 0.85 mmol/g for **SPF-BD-CMP**, respectively.

Table S1. Summary of CO_2 adsorption data of various reported materials.

Materials	BET surface area / $m^2\ g^{-1}$	CO_2 adsorption / mmol g^{-1}	CH_4 adsorption / mmol g^{-1}	Pore volume /$cm^3\ g^{-1}$	Reference
MFCMP-1	843	3.69 [a]	--	0.521 [c]	1
PTEB aerogel	1085~1701	Up to 3.47[a]	Up to 0.913[a]	Up to 0.6608 [b]	2
CMP-0	1018	2.10 [a]	--	0.38[b]	3
TNCMP-2	995	2.62 [a]	--	0.40[b]	3
CMP-1, CMP-1-$(CH_3)_2$, CMP-1-(COOH), CMP-1-(NH2), CMP-1-(OH)	522~1043	1.60~2.05 [a]	--	0.45~0.7 [c]	4
$[HO_2C]_{100\%}$-H_2P-COF	364	4.1[a]	--	0.43	5
Zn@AB-COF	1120	4.68[a]	--	/	6
COF-10, COF-102	1760~3620	1.34~1.79[a]	0.36~0.67 [a]	1.44~1.55[d]	7
PECONF	449~851	1.86~3.49[a]	0.83~1.07 [a]	0.29~0.43[d]	8
BD-CMPs	**543~1008**	**2.51~3.78**[a]	**0.51~0.95** [a]	**0.50~1.11**[c]	**Our work**

[a] CO_2 adsorption capacity collected at 273 K, 1 bar; [b] Pore volume derived at p/p_0=0.1; [c] Pore volume derived at p/p_0=0.99; [d] Pore volume derived at p/p_0=0.95.

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Table S2. Summary of porosity and nitrogen adsorption data of TPB-BD CMPs derived from different reaction conditions.

Entry	V_{total} [a] / $cm^3\ g^{-1}$	S_{BET} [b] / $m^2\ g^{-1}$	Method
1	0.56	349	Typical conditions[c] except with 5 wt% CuCl
2	1.03	968	Typical conditions except with 15 wt% CuCl
3	0.66	809	Typical conditions except with 25 wt% CuCl
4	0.80	917	Typical conditions except with 50 wt% CuCl
5	0.58	471	Typical conditions except conducting at 25 ^oC
6	1.68	830	Typical conditions except conducting at 60 ^oC
7	0.11	97	Typical conditions except with 0.013 mmol ml^{-1} monomer
8	0.32	313	Typical conditions except with 0.05 mmol ml^{-1} monomer
9	1.21	417	Typical conditions except with ethanol as lyophilizing solvent
10	1.24	416	Typical conditions except with methanol as lyophilizing solvent
9	1.48	769	Typical conditions[c]

[a] Pore volume derived at p/p_0=0.99.
[b] BET surface area was calculated in the partial pressure (p/p_0) range of 0.01–0.1 to give the best linearity.
[c] Typical condition: With initial monomer concentration c_0=0.025 mmol ml^{-1},catalysts (CuCl) amount of 10 wt%, reaction temperature of 40 ^oC, freeze-dried with water.

Section 9. Supporting references

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