

Electronic Supplementary Information

Transition-Metal-Free Radical Homocoupling Polymerization to Conjugated Poly(Phenylene butadiynylene) Polymers

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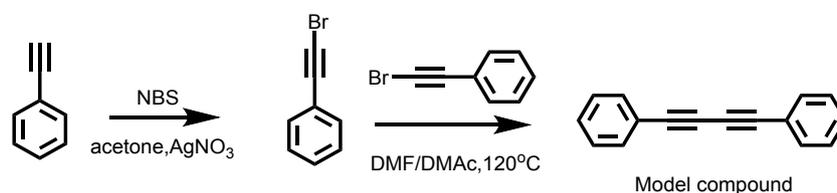
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A. General Information

Materials. 1, 3, 5-triethynylbenzene, 2, 4, 6-(4-bromophenyl)-1, 3, 5-triazine, Tetrakis(p-bromophenyl)Methane, trimethylsilylacetylene, *N*-Bromosuccinimide, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), potassium carbonate, potassium iodide, copper iodide, tetrakis(triphenylphosphine)palladium, acetone, palladium(II)bis(triphenylphosphine) dichloride, diisopropylamine, triethylamine, methanol and absolute ethanol were purchased from Aladdin Chemicals of China and they were used without further purification. The residual element content was determined by inductively coupled plasma mass spectrometry (ICP-MS) 730 equipment produced Agilent.

B. Synthesis of Model Compound and Monomers



Scheme S1. The general synthetic routes of model product.

Synthesis of model compound.¹ A mixture of phenylacetylene (1.00 g, 9.80 mmol), *N*-bromosuccinimide (2.62 g, 14.70 mmol) and silver nitrate (0.01 g, 0.06 mmol) dispersed in acetone (25 mL) was stirred for 2 hours at room temperature under black conditions. Removal of the solvent

and purification by column (silica, petroleum ether as eluent) gave 1-bromo-2-phenylacetylene (1.57 g, 88.5%) as yellow oil. ^1H NMR (400 MHz, $d\text{-CDCl}_3$) δ = 7.53 (Ar-H), 7.43 (Ar-H), 7.53 (Ar-H) ppm. ^{13}C NMR (400 MHz, $d\text{-CDCl}_3$) δ = 132.09 (Ar-C), 128.44 (Ar-C), 122.65 (Ar-C), 80 (Ar-C \equiv -Br), 49.97 ($=\text{C}$ -Br) ppm.

1-bromo-2-phenylacetylene (0.18 g, 1.00 mmol) and KI (1.00 g, 6.00 mmol) in DMF (2.0 mL) were reacted under stirring at 120 °C for 12 h in a 50 mL round bottom flask. 5 mL water was added and the aqueous solution was extracted with diethyl ether (15 mL), and the combined organic solvent was dried with anhydrous MgSO_4 . The solvent was removed and the crude product was separated by column chromatography to give a yellow sample (0.098 g, 96.6 %). ^1H NMR (400 MHz, $d\text{-CDCl}_3$) δ = 7.46 (Ar-H), 7.29 (Ar-H), 7.19 (Ar-H) ppm. ^{13}C NMR (400 MHz, $d\text{-CDCl}_3$) δ = 131.49 (Ar-C), 128.28 (Ar-C), 127.36 (Ar-C), 120.84 (Ar-C), 80.53 (Ar-C \equiv -), 72.86 ($=\text{C}$ -) ppm.

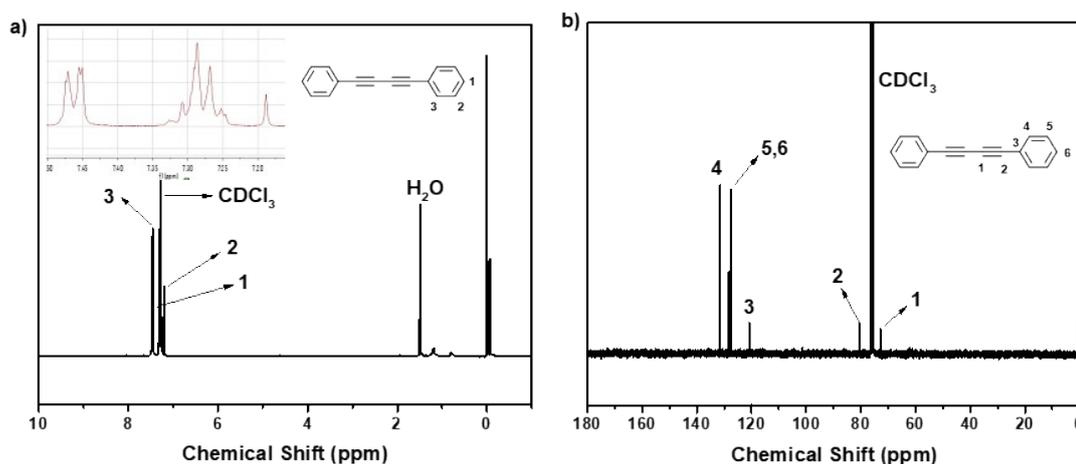
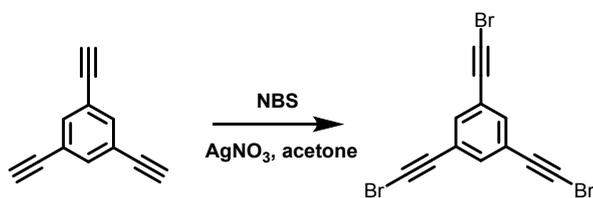


Figure S1. a) ^1H NMR and b) ^{13}C NMR spectrum of model compound.



Scheme S2. The synthetic routes of 1, 3, 5-tribromoethynylbenzene.

Synthesis of 1, 3, 5-tribromoethynylbenzene. A mixture of 1, 3, 5-triethynylbenzene (0.20 g, 1.33 mmol), *N*-bromosuccinimide (0.95 g, 5.34 mmol) and silver nitrate (0.02 g, 0.12 mmol) dispersed in 60 mL acetone was reacted for 24 h at room temperature under black conditions. Removal of the

organic solvent under reduced pressure, purification by column (silica, petroleum ether as eluent) and further dried in vacuum oven at 50 °C for 24 h to yield the target compound as yellow solid (0.49 g, 95.3 %). ^1H NMR (400 MHz, $d\text{-CDCl}_3$) δ = 7.48 (3H, Ar-H). ^{13}C NMR (400 MHz, $d\text{-CDCl}_3$) δ = 51.5 (--C--Br), 79.7.0 ($\text{Ar--C}\equiv\text{Br}$), 121.9 (Ar-C), 135.8 (Ar-C).

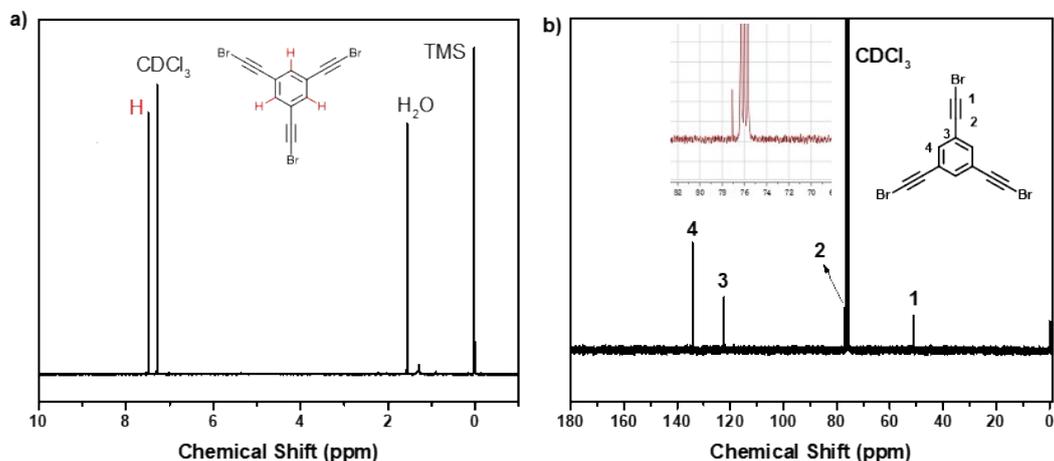
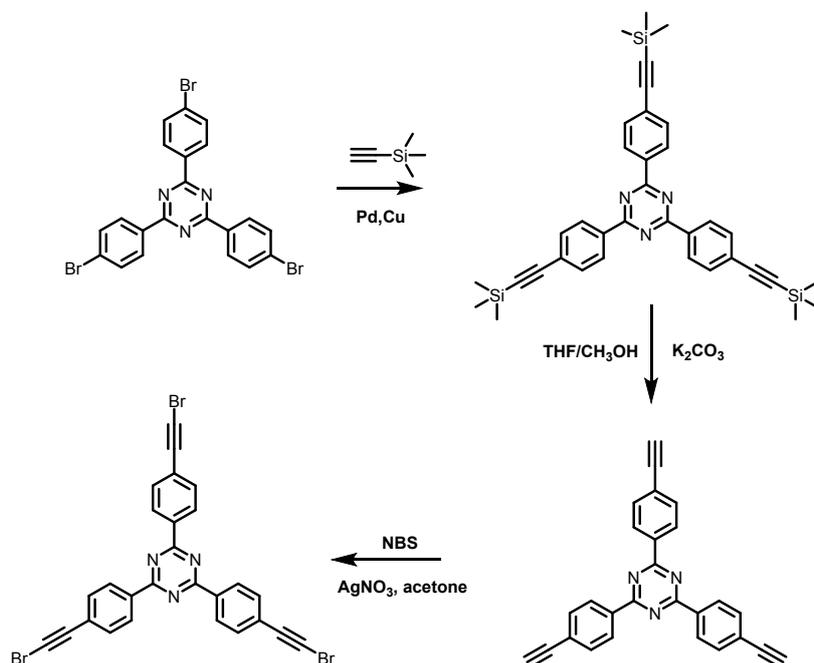


Figure S2. a) ^1H NMR and b) ^{13}C NMR of 1, 3, 5-tribromoethynylbenzene.



Scheme S3. The general synthetic route for 2, 4, 6-tris(4-bromoacetylenophenyl)-1, 3, 5-triazine.

Synthesis of 2, 4, 6-tris(4-[(trimethylsilyl)ethynyl]phenyl)-1, 3, 5-triazine. Under nitrogen atmosphere, trimethylsilylacetylene (0.60 mL, 4.25 mmol) was added to a mixture of 2, 4, 6-tris(4-bromophenyl)-1, 3, 5-triazine (0.20 g, 0.41 mmol) dissolved in triethylamine (100 mL). After the addition of tetrakis(triphenylphosphine)-palladium(0) (0.05 g, 0.043 mmol), copper(I) iodide (0.02

g, 0.11 mmol), and the mixture was reacted for 24 h at 80 °C under N₂ atmosphere. The product was extracted with ethyl acetate (3×100 mL) and dried with magnesium sulfate. The organic phase was removed by reduced pressure. The obtained solid was purified by a column (petroleum ether: ethyl acetate, 100:1/V:V), and the product was further recrystallized from CH₂Cl₂, yielding a colorless solid (0.23 g, 92.0 %). ¹H NMR (400 MHz, *d*-CDCl₃): δ = 8.77 (6 H, Ar-H), 7.64 (6 H, Ar-H), 0.30 (27 H, Si(CH₃)₃) ppm. ¹³C NMR (400 MHz, *d*-CDCl₃): δ = 171.02 (triazine-C), 135.73 (Ar-C), 132.22 (Ar-C), 128.75 (Ar-C), 127.43 (Ar-C), 104.76 (Ar-C≡C), 97.50 (Ar-C≡C), 0.00 (Si(CH₃)₃) ppm.

Synthesis of 2, 4, 6-tris(4-ethynylphenyl)-1, 3, 5-triazine. A mixture of 2,4,6-tris{4-[(trimethylsilyl)ethynyl]-phenyl}-1,3,5-triazine (0.50 g, 0.84 mmol) and 0.25 g K₂CO₃ dispersed in THF (50 mL) and methanol (5 mL) was reacted for 24 h at room temperature. The solvent was removed, and obtained solid was extracted with dichloromethane (3×25 mL) and dried with magnesium sulfate. The crude product was purified by a silica column (petroleum ether: ethyl acetate, 100:1/V:V), and further recrystallized from a CH₂Cl₂, yielding a white solid (0.29 g, 90.0 %). ¹H NMR (400 MHz, *d*-CDCl₃): δ = 8.64 (6 H, Ar-H), 7.64 (6 H, Ar-H), 3.22 (3 H, -C≡CH) ppm. ¹³C NMR (400MHz, *d*-CDCl₃): δ = 170.03 (triazine-C), 134.95 (Ar-C), 131.36 (Ar-C), 127.81 (Ar-C), 125.31 (Ar-C), 82.44 (-C≡H), 78.93 (-≡CH) ppm.

Synthesis of 2, 4, 6-tris(4-bromoacetylenophenyl)-1, 3, 5-triazine. A mixture of 2, 4, 6-tris(4-ethynylphenyl)-1, 3, 5-triazine (0.30 g, 0.79 mmol), *N*-bromosuccinimide (0.70 g, 3.93 mmol) and silver nitrate (0.01 g, 0.06 mmol) dispersed in 60 mL acetone was reacted for 24 h at room temperature under black conditions. The solvent was removed under reduced pressure and the solid was purified by a CC, PE: CH₂Cl₂ (1:1/V:V) as eluent. The obtained solid was recrystallized from acetone to give the target product as yellowish solid (0.36 g, 73.0%). ¹H NMR (400 MHz, *d*-CDCl₃) δ = 8.75 (6H, Ar-H), 7.74 (6H, Ar-H) ppm. ¹³C NMR (400 MHz, *d*-CDCl₃) δ = 171.7 (triazine-C), 122.7-134 (Ar-C), 80.0 (Ar-C≡Br), 49.5 (-≡C-Br) ppm.

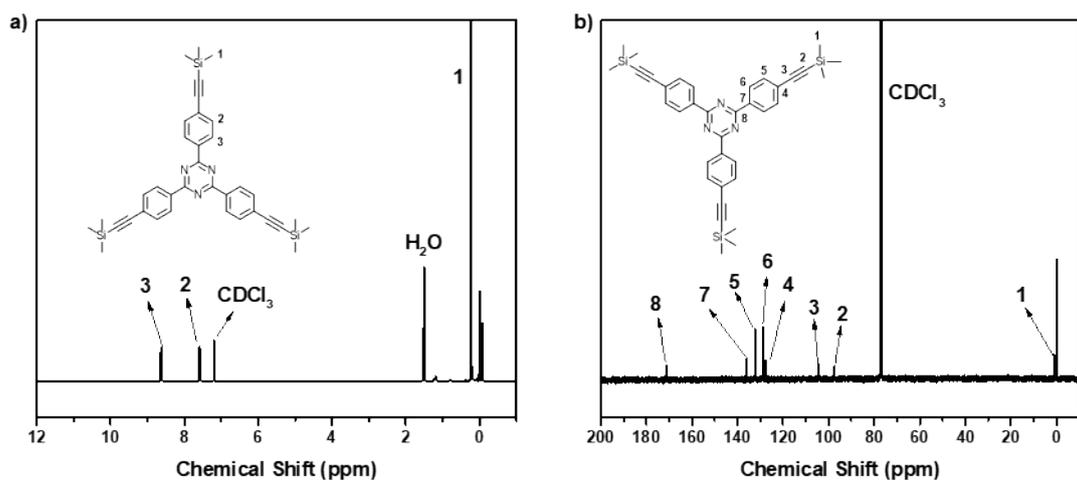


Figure S3. a) ^1H NMR and b) ^{13}C NMR of 2, 4, 6-tris(4-[(trimethylsilyl)ethynyl]phenyl)-1, 3, 5-triazine.

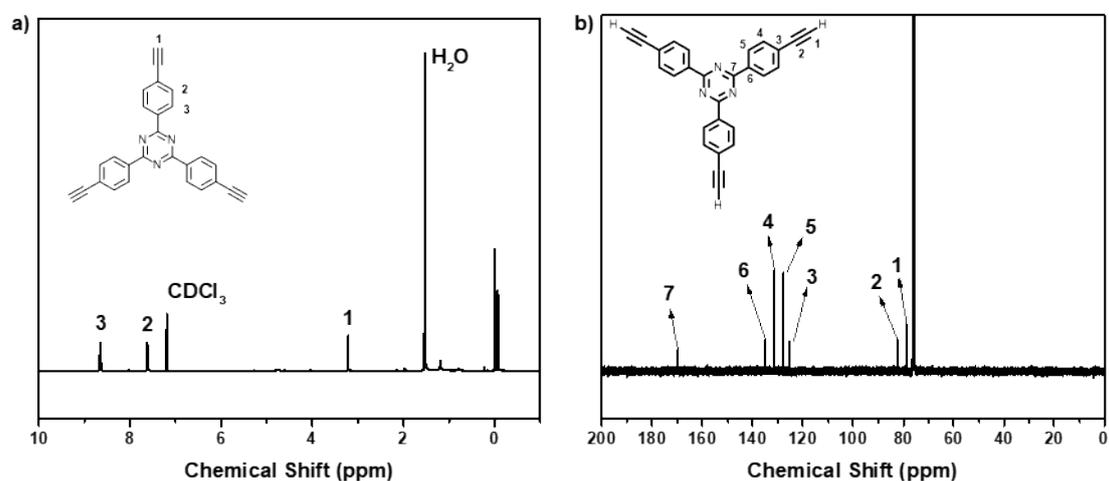


Figure S4. a) ^1H NMR and b) ^{13}C NMR of 2, 4, 6-tris(4-ethynylphenyl)-1, 3, 5-triazine.

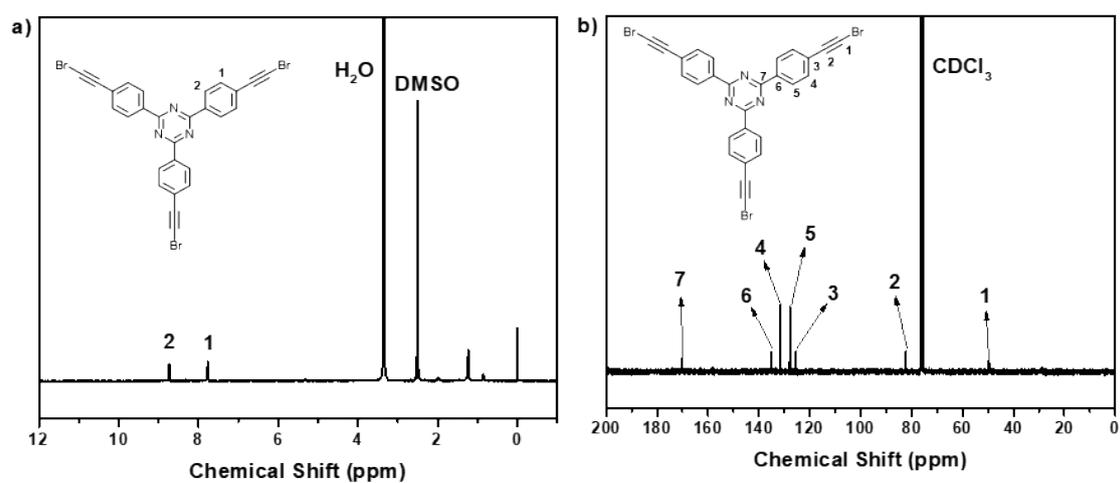
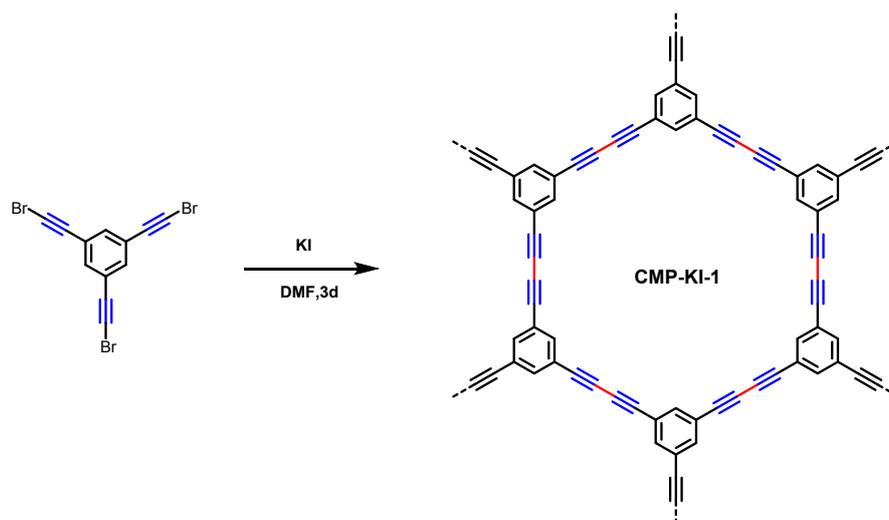


Figure S5. a) ^1H NMR and b) ^{13}C NMR of 2, 4, 6-tris(4-bromoacetylenophenyl)-1, 3, 5-triazine.

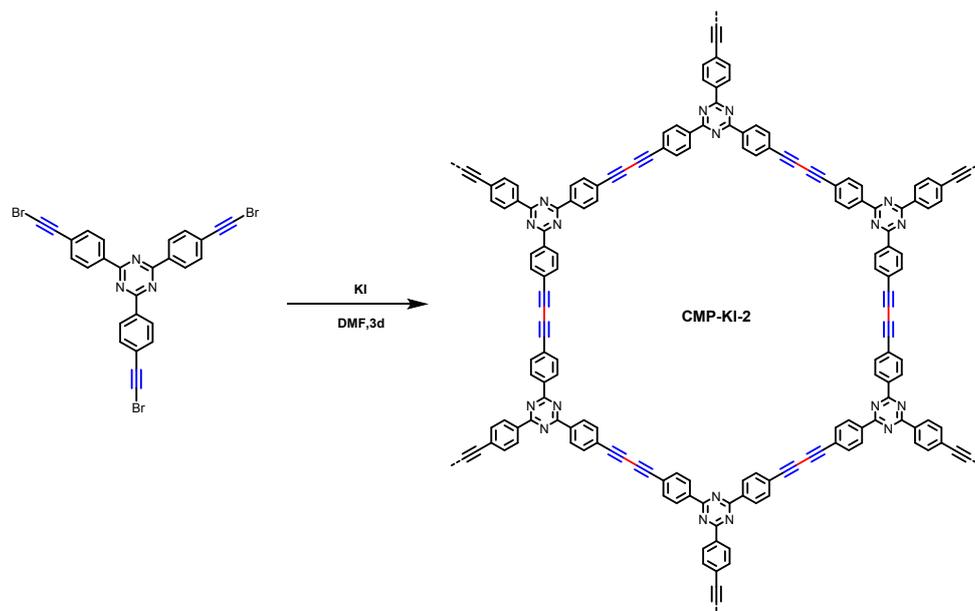
C. Synthesis of CMP-KI-1



Synthesis of O-CMP-KI-1 in the open flask system. 1, 3, 5-tribromoethynylbenzene (0.10 g, 0.26 mmol) and KI (5 g) dissolved in DMAc (2 mL) were reacted at 120 °C for 48 h under ambient condition. After cooling to room temperature, the polymer powder was collected by filtration and washed with water, methanol, DMF, respectively, and further purification by Soxhlet extractor method with THF, methanol, chloroform for 24, respectively. The obtained deep brown solid was dried under vacuum oven at 60 °C for 48 h to give the solid product (0.035 g, 93.1 %).

Synthesis of S-CMP-KI-1 under solvothermal in the sealed flask. 1,3,5-tribromoethynylbenzene (0.10g, 0.26 mmol) was added into an 18 cm lass tube, then 0.5 mL DMF was added above-mentioned tube, and sonication for 5 min. 3 g KI was suspended in the mixture. After ultrasonication 10 min, the mixture was degassed by at least three freeze-pump-thaw cycles. The tube was frozen at 77 K (liquid nitrogen bath) and evacuated to high vacuum and flame-sealed. After 150 °C for 72 h, the reaction mixture gave a black solid. After cooled to RT, the tube was broken, and the solid product was filtrated and washed with DMF, CH₃OH and water, subsequently. The product was further purified by Soxhlet extractor with THF and CH₃OH as solvents. The final product was dried in vacuum at 60 °C for more than 48 h (0.037 g, 98.4%).

D. Synthesis of CMP-KI-2



Synthesis of O-CMP-KI-2 in the open flask system. 2, 4, 6-Tris(4-bromoacetylenophenyl)-1, 3, 5-triazine (0.1 g, 0.16 mmol) and KI (5 g) dissolved in DMAc (2 mL) was reacted at 120 °C for 72 h. After the system was cooled to room temperature, the polymer sample was collected by filtration and washed with water, methanol, DMF, respectively. The product was further purified by Soxhlet extractor method with THF, methanol, chloroform for 24, respectively. The resulting brown powder was dried under vacuum oven at 60 °C for 48 h to give deep brown solid product (0.055 g, 89.28 %).

Synthesis of S-CMP-KI-2 under solvothermal method. The S-CMP-HUST-2 was synthesized according to S-CMP-HUST-1 synthetic process, with 2, 4, 6-Tris(4-bromoacetylenophenyl)-1,3,5-triazine instead of 1,3,5-tribromoethynylbenzene (0.059 g, 95.8 %).

E. Synthesis conditions optimization of CMP-KI-1 in the open flask system

Table S1 Synthesis of the O-CMP-KI-1 under variable conditions.

Solvent	KI (g)	Time (h)	Temp (°C)	S_{BET} (m^2/g)	MPV (cm^3/g)	PV (cm^3/g)
DMF	0.8	48	120	680	0.16	0.39
DMF	3.0	48	120	754	0.13	0.50
DMF	5.0	48	120	903	0.12	0.54
DMAc	0.8	48	120	751	0.18	0.41
DMAc	5.0	48	120	988	0.22	0.62
DMAc	10	48	120	712	0.13	0.42

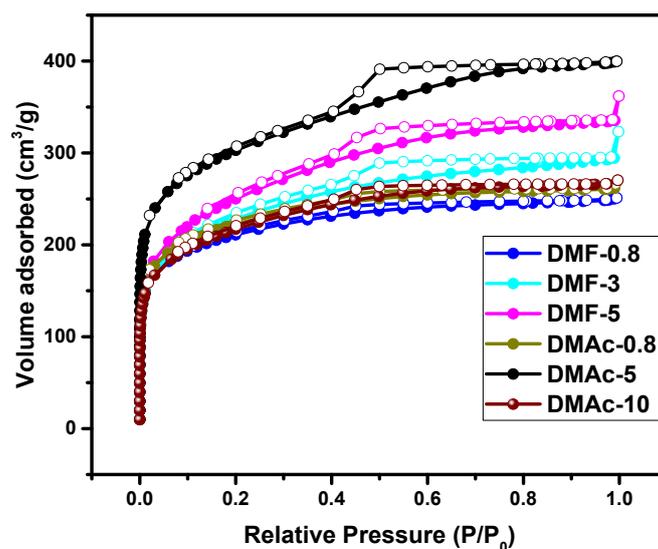


Figure S6. Nitrogen adsorption and desorption isotherms under the different reaction conditions for the CMP-KIs open system method (the number indicates the mass of KI used).

F. Synthesis conditions optimization of CMP-KI-1 under solvothermal conditions

Table S2 Synthesis of the S-CMP-KI-1 under variable conditions.

Solvent	KI (g)	Time (h)	Temp (°C)	S_{BET} (m ² g ⁻¹)	MPV (cm ³ g ⁻¹)	PV (cm ³ g ⁻¹)
DMF/THF	0.8	72	150	1068	0.91	1.28
DMF/o-DCB	0.8	72	150	1103	0.98	1.05
NMP/mesitylene	0.8	72	150	1076	0.86	0.98
CH ₃ OH/THF	0.8	72	150	142	0.05	--
DMF	0.3	72	150	952	0.72	0.83
DMF	0.8	72	150	1346	0.017	1.41
DMF	1.2	72	150	1469	1.02	1.12
DMAc	1.2	72	150	1170	0.70	0.78
DMF	1.8	72	150	1151	0.78	0.90
DMF	3.0	72	150	1477	1.00	1.08
DMF	4.0	72	150	1161	0.88	1.04

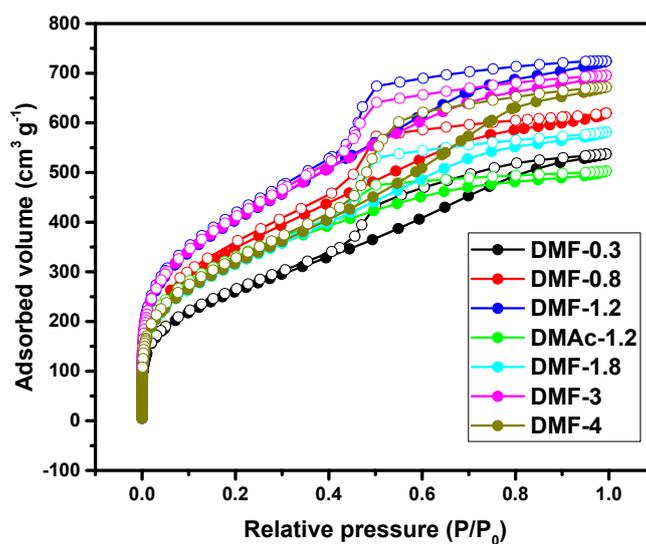


Figure S7. Nitrogen adsorption and desorption isotherms under the different reaction conditions for the CMP-KIs under solvothermal method (the number is the mass of KI used).

G. FT-IR and ^{13}C NMR of corresponding monomer or model molecular and CMP-KIs

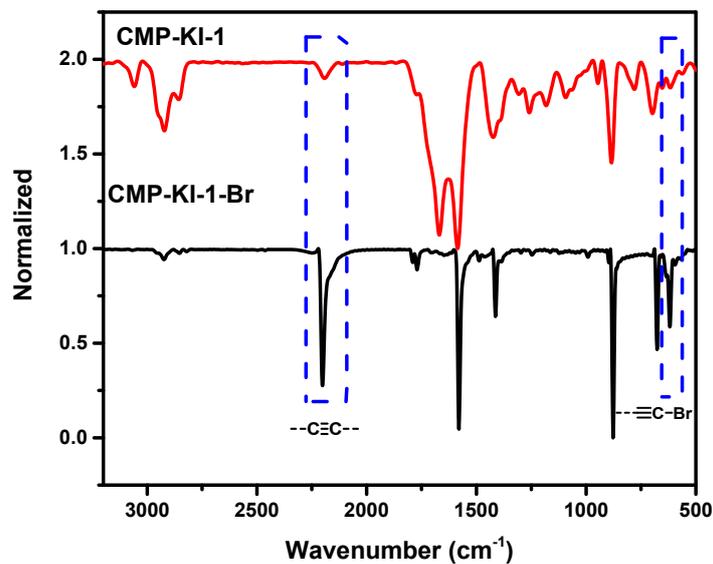


Figure S8. FT-IR spectrum of CMP-KI-1 (red) and corresponding monomer (black).

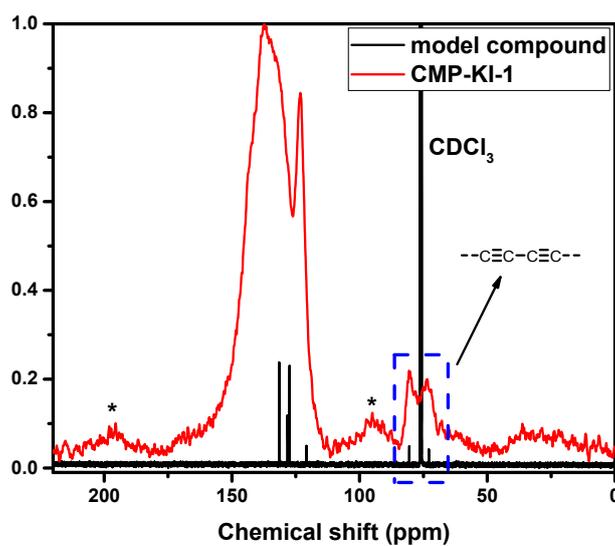


Figure S9. ^{13}C NMR spectrum of CMP-KI-1 (red) in the solid state and model compound in CDCl₃ (black).

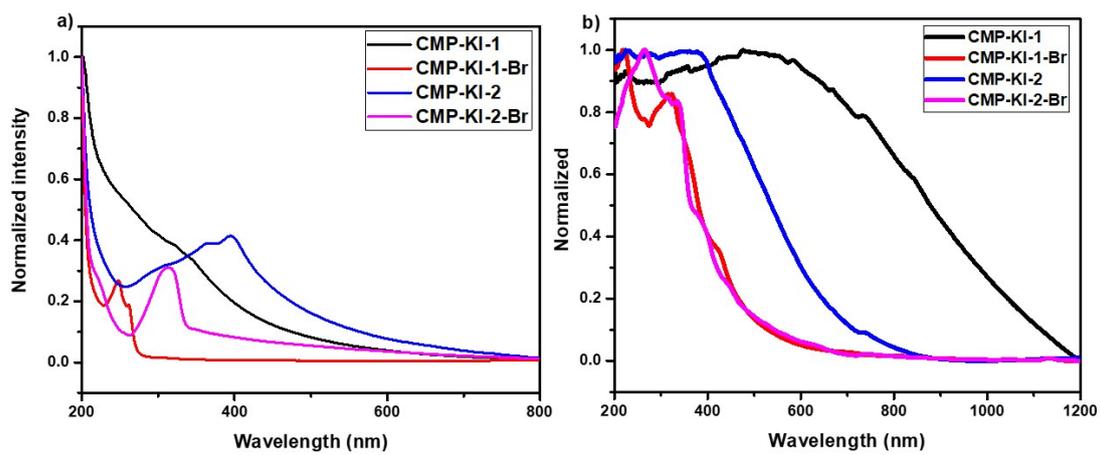


Figure S10. UV-vis adsorption spectrum of CMP-KIs and corresponding monomers a) solution in ethanol, b) UV-Visible diffuse reflectance spectrum.

G. XPS spectra

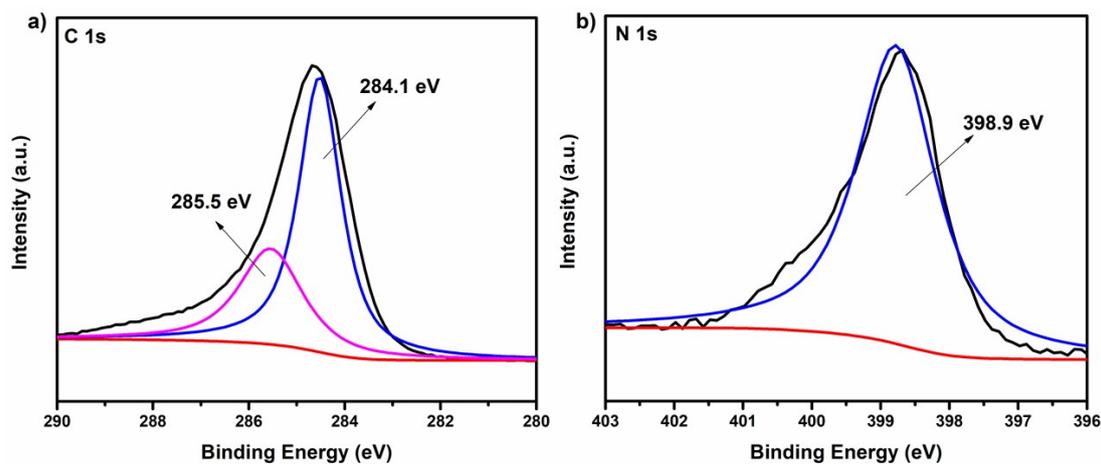


Figure S11. X-ray photoelectronic spectroscopy of a) C1s of CMP-KI-1, b) N1s of CMP-KI-2.

K. TGA and DSC curves of CMP-KIs

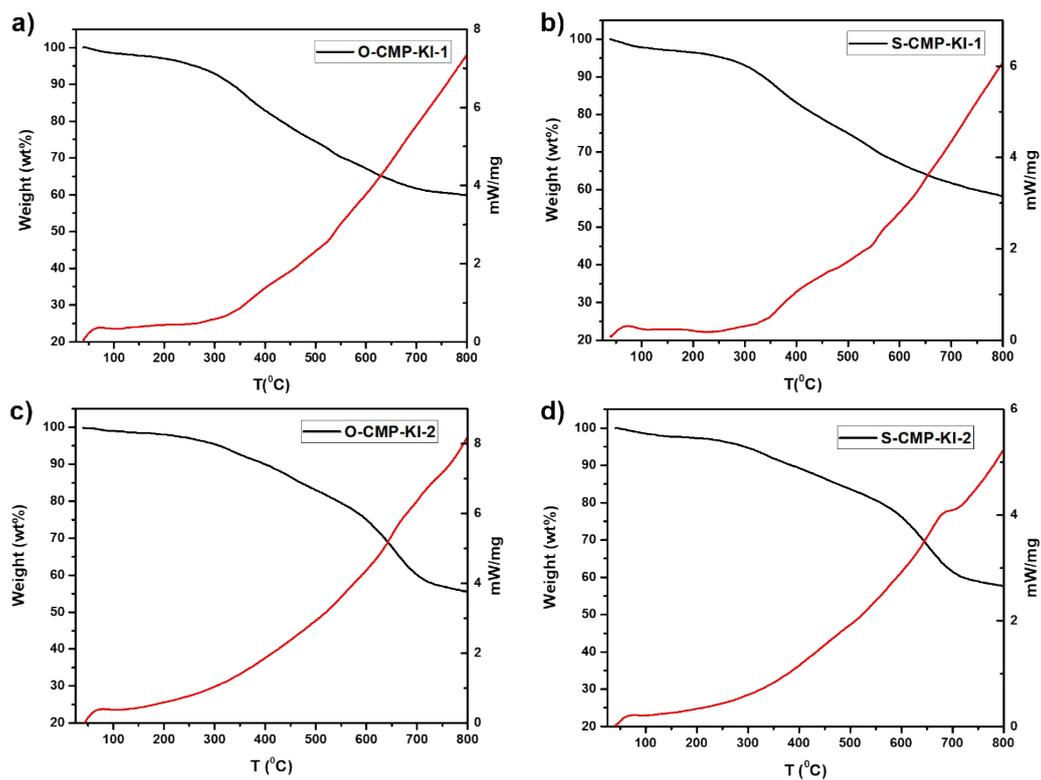


Figure S12. TGA (black) and DSC (red) curves of CMP-KIs.

L. SEM images and PXRD patterns

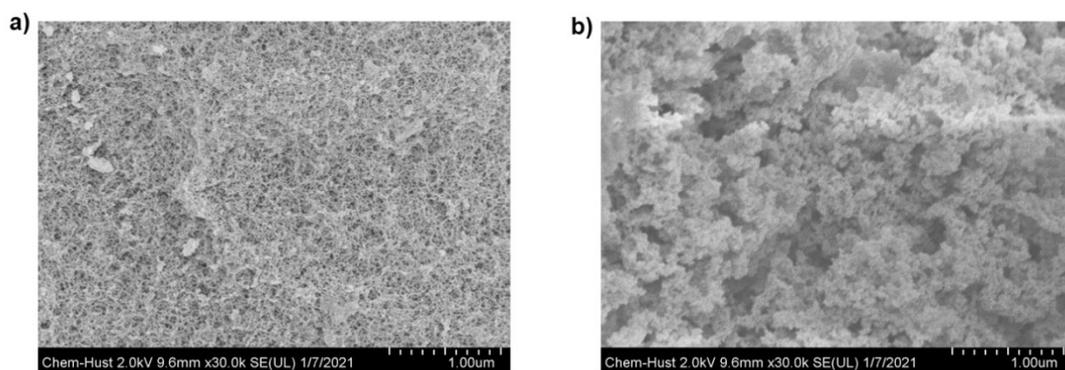


Figure S13. SEM images for CMP-KI-1 (a) and CMP-KI-2 (b).

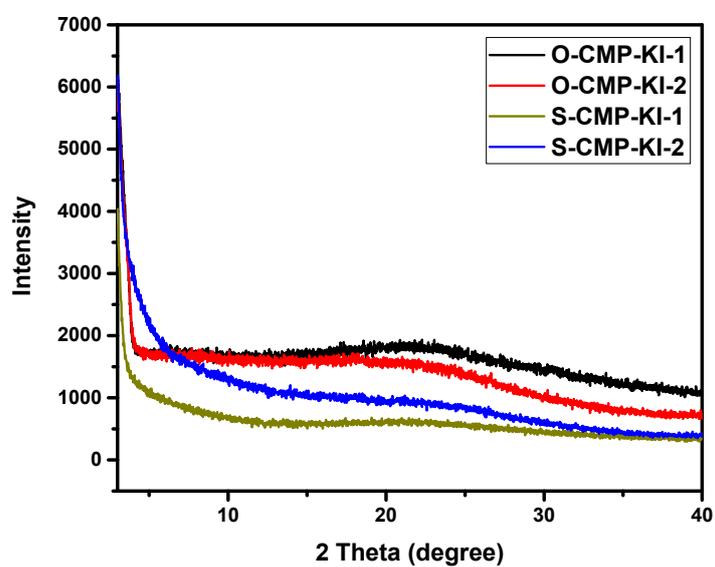


Figure S14. PXRD patterns of O-CMP-KI-1 (black), O-CMP-KI-2 (red), S-CMP-KI-1 (dark yellow) and S-CMP-KI-2 (blue).

M. CO₂ uptake and heat of adsorption

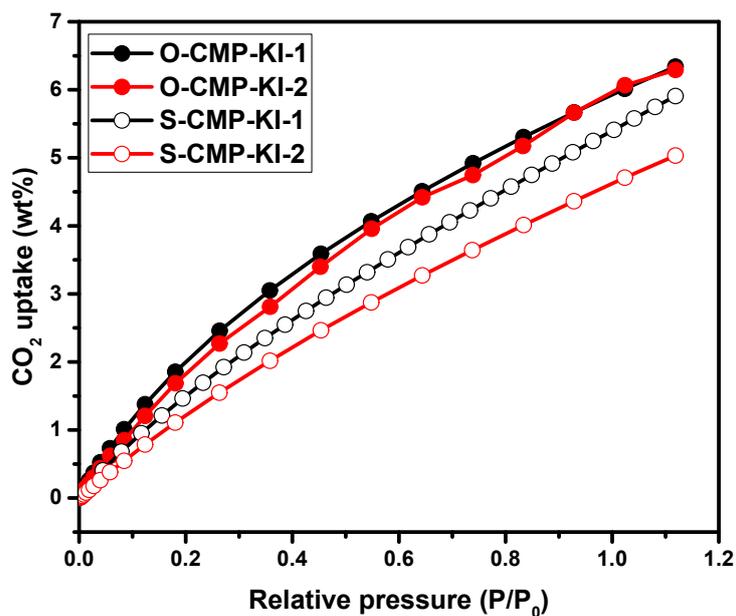


Figure S15. The CO₂ adsorption curves of CMP-KIs at 298 K.

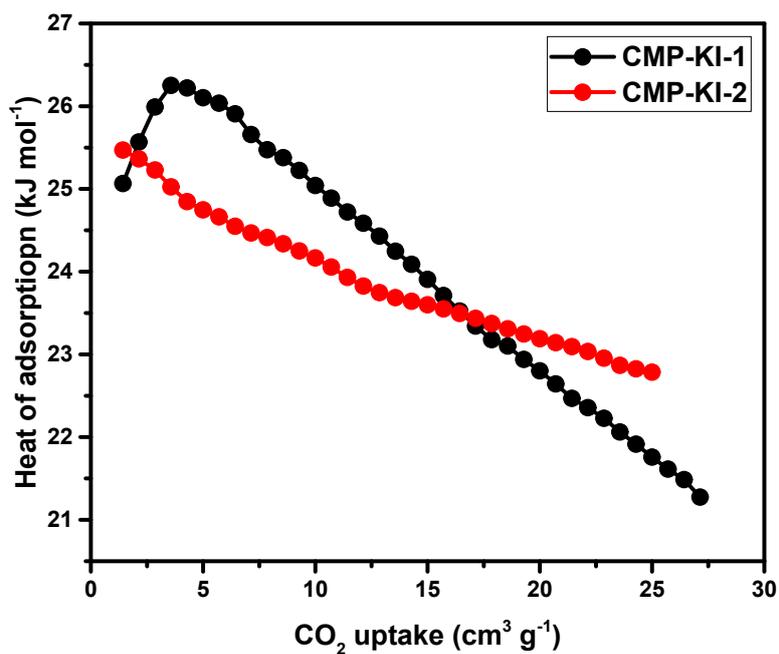


Figure S16. The adsorption heat of CO₂ for CMP-KIs.

N. Comparing between this work and reported literatures

Table S3 Summary of BET surface areas for some reported CMPs and CMP-KIs in this work.

CMPs	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	Ref.
CMP-3	522	350	[2]
HCMP-1	842	177	[3]
HCMP-2	827	324	[3]
NCMP-4	546	327	[4]
P5	520	--	[5]
PPV	761	--	[6]
HPOP-2	742	328	[7]
E2	488	430	[8]
CMP_60	660	--	[9]
1DPC-M3	753	594	[10]
FeP-CMP	1270	--	[11]
P6	1152	--	[12]
P5-CMP-1	400	198	[13]
O-CMP-KI-1	988	411	<i>This work</i>
O-CMP-KI-2	774	319	<i>This work</i>
S-CMP-KI-1	1477	1439	<i>This work</i>
S-CMP-KI-2	1388	813	<i>This work</i>

Table S4. Summary of the CO₂ uptake capacity of some reported porous materials and this work.

Polymer	S _{BET} (m ² g ⁻¹)	CO ₂ uptake ^a (wt%)	Ref.
Polymer 1B	897	9.0	[14]
Polymer 4	826	9.5	[14]
InCz-HCP1	750	9.9	[15]
BDPCMP-2	582	9.9	[16]
COF-102	3620	6.9	[17]
PAF-1	5460	9.2	[18]
Azo-1	571	9.42	[19]
CMP-1-(CH ₃) ₂	899	4.1	[20]
CMP-1-COOH	522	7.0	[20]
HAT-CTF-400	17	11.8	[21]
P1M	4	4.1	[12]
CMP-1-COOH	522	7.22	[22]
O-CMP-KI-1	988	11.03	<i>This work</i>
O-CMP-KI-2	774	10.54	<i>This work</i>
S-CMP-KI-1	1477	10.45	<i>This work</i>
S-CMP-KI-2	1388	9.07	<i>This work</i>

^a Data obtained at 1.13 bar and 273 K.

Table S5. Summary of the H₂ uptake capacity of some reported porous materials and this work.

Polymer	S _{BET} (m ² g ⁻¹)	H ₂ uptake ^a (wt%)	Ref.
Polymer 5	438	0.64	[14]
ILCOF-1	2723	1.3	[23]
CTV-COF-2	1170	0.65	[24]
MM3	1884	1.43	[25]
BLP-1(Br)	503	0.68	[26]
PSN-2	1042	1.00	[27]
O-CMP-KI-1	988	0.81	<i>This work</i>
O-CMP-KI-2	774	0.96	<i>This work</i>
S-CMP-KI-1	1477	0.92	<i>This work</i>
S-CMP-KI-2	1388	1.30	<i>This work</i>

^a H₂ uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1 bar and 77 K.

O. Elemental analysis

Table S6. Elemental analysis of CMP-KIs.

EA (wt%)	CMP-KI-1		CMP-KI-2	
	Exp.	Cal.	Exp.	Cal.
C	73.5	77.3	68.7	77.3
H	3.3	3.2	3.9	2.9
N	0	0	11.0	15.0

P. References

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