Supporting Information for

Transition-Metal-Free Synthesis of Conjugated Microporous Polymers via Amine-Catalyzed Suzuki-Miyaura Coupling Reaction

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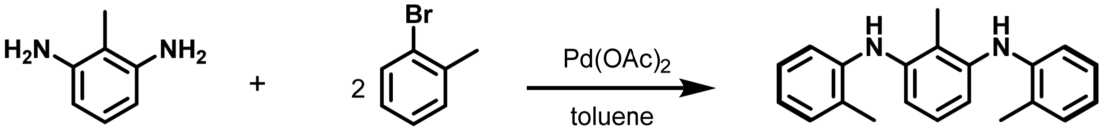
Contents

1. Experimental Section

Materials: 1, 3, 6, 8-tetrabromopyrene, 1, 4-benzene diboronic acid, benzene-1, 3, 5-triyltriboronic acid, tris-(4-bromophenyl) amine, 2, 4, 6-tris-(*p*-bromophenyl)-1, 3, 5-triazine, tetrakis-(*p*-bromophenyl) methane were obtained from Sigma-Aldrich. 2-methylbenzene-1, 3-diamine, 1-bromo-2-methylbenzene, 1, 3, 5-triethynylbenzene, *N*-bromosuccinimide (NBS), Pd(OAc)$_2$, tricyclohexylphosphane and KOH were purchased from Sinopharm Chemical Reagent Co. Ltd. All the other solvents mentioned were purchased from Adamas-beta Reagent and used without further purification.

Synthesis of 2-methyl-N^1, N^3-di-*o*-tolylbenzene-1, 3-diamine.[1]



2-methylbenzene-1, 3-diamine (0.224 g, 2.0 mmol, 1.0 equiv), 1-bromo-2-methylbenzene (1.360 g, 8.0 mmol, 4.0 equiv), Pd(OAc)$_2$ (0.014 g, 0.06 mmol, 0.03 equiv), and tricyclohexylphosphane (0.056 g, 0.2 mmol, 0.1 equiv), KOH (0.448 g, 8.0 mmol, 4.0 equiv) were placed in a 100 mL three-neck round bottom flask equipped with a stirring bar. The toluene (10 mL) was added under N$_2$ flow. The reaction mixture was stirred at 110 °C for 24 h. The reaction mixture was cooled to room temperature, filtered by silica gel, the filter cake was washed with ethyl acetate. The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 30 : 1) (0.382 g, 63.0 %). (No Pd can be detected by ICP analysis in product.)

^{1}H NMR (600 MHz, *d*-CDCl$_3$) δ 7.18 (d, 2H), 7.12 (t, 2H), 7.04 (t, 1H), 6.90 (dd, 4H), 6.74 (d, 2H), 5.19 (s, 2H), 2.28 (s, 6H), 2.13 (s, 3H).

^{13}C NMR (600 MHz, *d*-CDCl$_3$) δ 142.60, 130.70, 126.72, 126.23, 126.51, 120.85, 120.15, 117.27, 114.36, 17.90, 11.87. HRMS *m/z* 303.20 (M+1).

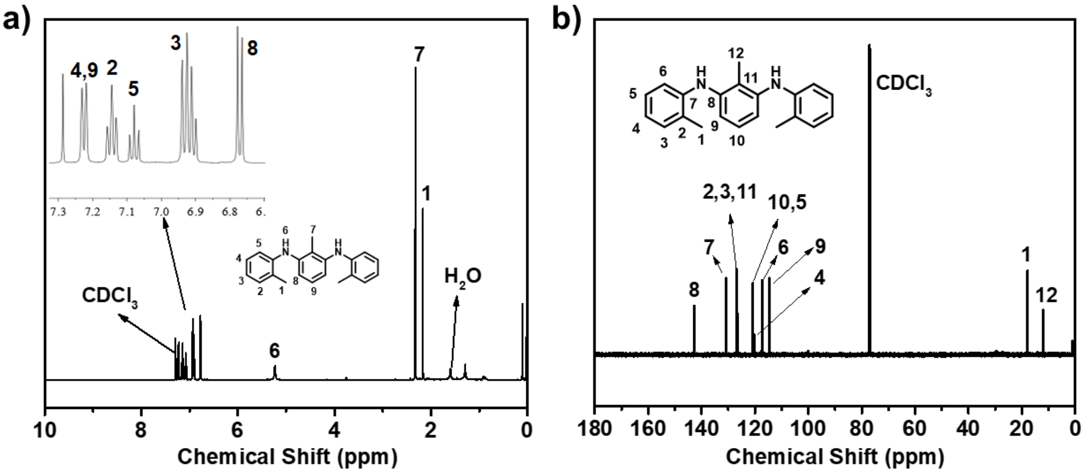


Fig. S1 The ^{1}H NMR and ^{13}C NMR spectrum of organic amine catalyst.

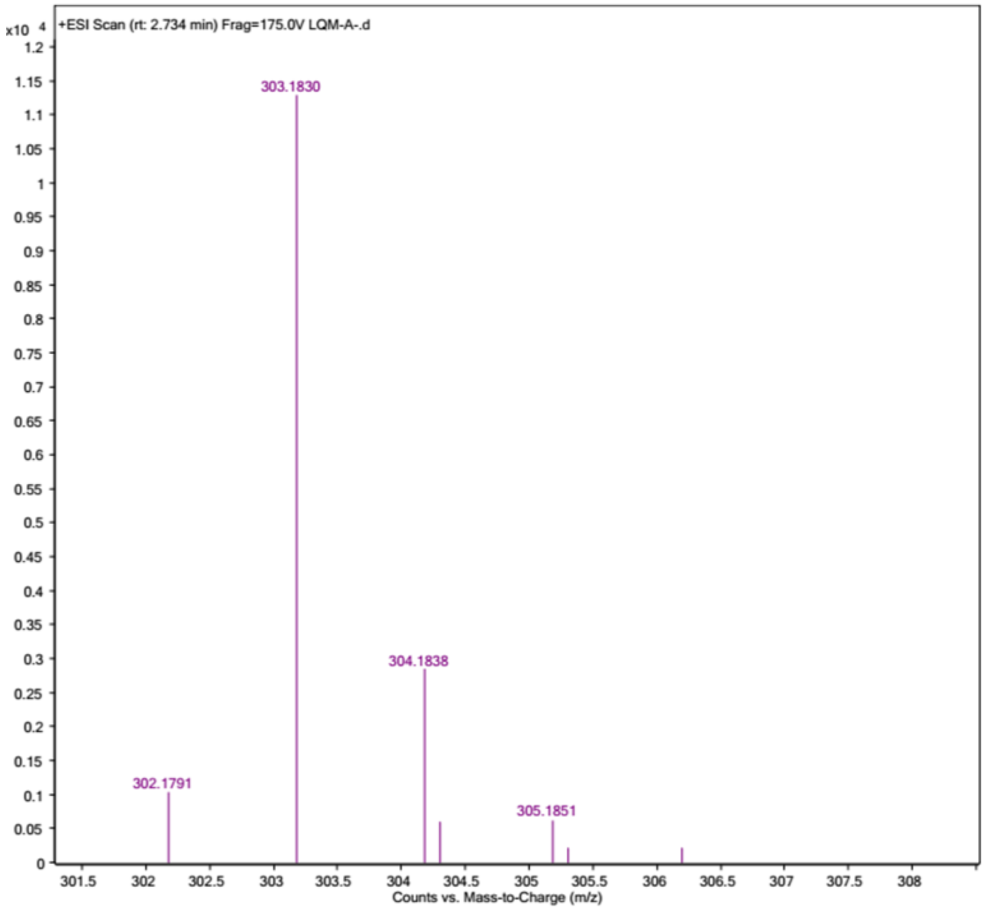
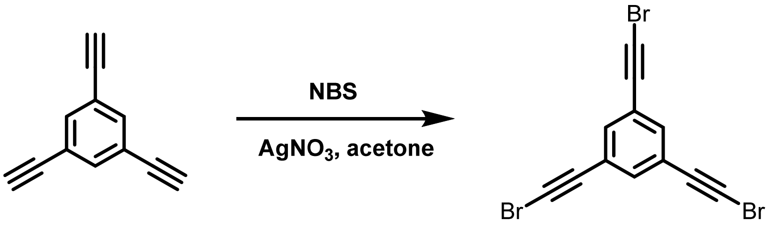


Fig. S2 The HRMS spectrum of organic amine catalyst.

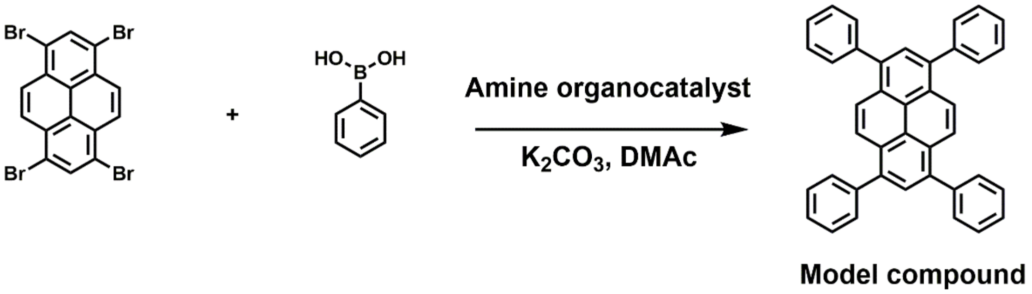
Synthesis of 1, 3, 5-tribromoethynylbenzene.[2]



A mixture of 1, 3, 5-triethynylbenzene (0.20 g, 1.33 mmol), *N*-bromosuccinimde (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 %).

^{1}H NMR (400 MHz, d-$CDCl_3$) δ = 7.48 (3H, Ar-H). ^{13}C NMR (400 MHz, d-$CDCl_3$) δ = 51.5 (-≡C-Br), 79.7.0 (Ar-C≡-Br), 121.9 (Ar-C), 135.8 (Ar-C).

Synthesis of model compound.[1]



1,3,6,8-tetrabromopyrene (0.1 g, 0.19 mmol), phenylboronic acid (0.09 g, 0.77 mmol), 2-methyl-N^1,N^3-di-o-tolylbenzene-1,3-diamine (6 mg, 0.019 mmol) and K_2CO_3 (0.32 g, 2.31 mmol) were placed in a 50 mL three neck round flask equipped with a stirring bar, and 10 mL DMAc was added, and the reaction was conducted at 120 °C under nitrogen atmosphere for 24 h. The reaction mixture was cooled to room temperature, then quenched with water. The reaction mixture was extracted with dichloromethane (30 mL). The obtained organic extracts were dried with anhydrous Na_2SO_4 and filtered, and the final filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (PE:Dichloromethane=1:4 as eluent) to provide yellow powder (yield:

91.3 %). ^{1}H NMR (600 MHz, d-$CDCl_3$) δ = 8.50 (s, 2H, Ar-H), 7.79 (m, 8H, Ar-H), 7.70 (d, 4H, Ar-H), 7.41-7.48 (m, 12H, Ar-H). ^{13}C NMR (600 MHz, d-$CDCl_3$) δ =141.04, 137.22, 130.61, 129.50, 128.31, 128.10, 127.26, 125.91, 125.28; HRMS *m/z* 507.37 (M+1).

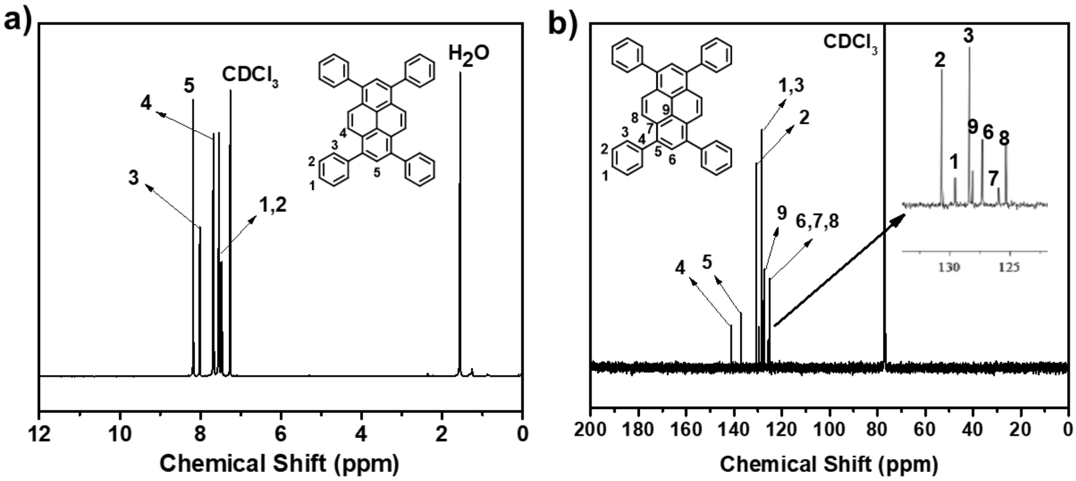


Figure S3 The a) ^{1}H NMR and b) ^{13}C NMR spectrum of model compound.

General procedure for the synthesis of MF-CMPs: A new glass tube equipped with a stirrer bar was charged with the monomers, *N*, *N*-dimethylacetamide, K_2CO_3, and 2-methyl-N^1, N^3-di-*o*-tolylbenzene-1, 3-diamine as catalyst. The glass tube was frozen in a liquid nitrogen bath, evacuated and flame sealed. The mixture was heated to 120 °C for 72 hours. The tube was cooled to room temperature, after broken the reaction suspensions were poured into water. The precipitate was collected by filtration and washed with hot H_2O, methanol, THF and DMF. Further purification of the polymers was carried out by Soxhlet extraction with CH_2Cl_2 and THF for 48 h, respectively, and the final product was dried under freeze drying for 24 h.

MF-CMP-1: 1, 3, 6, 8-tetrabromopyrene (0.10 g, 0.19 mmol), 1, 4-benzene diboronic acid (0.064 g, 0.38 mmol), K_2CO_3 (0.32 g, 2.32 mmol) and 2-methyl-*N*^{1}, *N*^{3}-di-*o*-tolylbenzene-1, 3-diamine (0.012 g, 0.04 mmol) in *N*, *N*-dimethylacetamide (4.0 mL) were used in this polymerization. After work-up and Soxhlet extraction, 0.060 g product was obtained as a dark yellow powder, yield: 88.2 %.

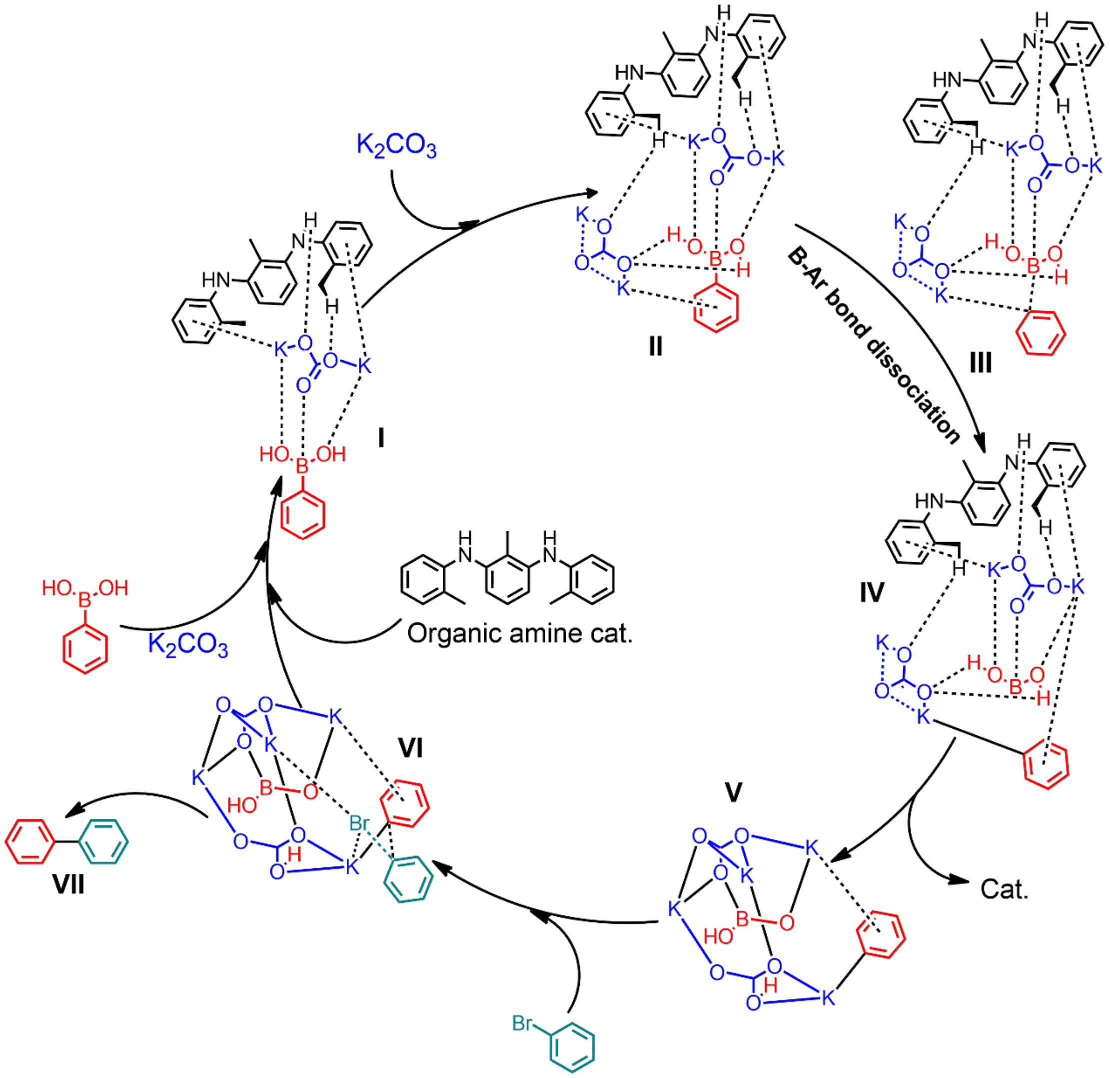
MF-CMP-2: Tris-(4-bromophenyl) amine (0.10 g, 0.21 mmol), 1, 4-benzene diboronic acid (0.052 g, 0.31 mmol), K_2CO_3 (0.26 g, 1.88 mmol) and 2-methyl-*N*^{1}, *N*^{3}-di-*o*-tolylbenzene-1, 3-diamine (0.010 g, 0.03 mmol) in *N*, *N*- dimethylacetamide (4.0 mL) were used in this polymerization. After work-up and Soxhlet extraction, 0.056 g product was obtained as a light yellow powder, yield: 75.7 %.

MF-CMP-3: 2, 4, 6-tris-(*p*-bromophenyl)-1, 3, 5-triazine (0.10 g, 0.18 mmol), 1, 4-benzene diboronic acid (0.045 g, 0.27 mmol), K_2CO_3 (0.23 g, 1.66 mmol) and 2-methyl-*N*^{1}, *N*^{3}-di-*o*-tolylbenzene-1, 3-diamine (0.008 g, 0.026 mmol) in *N*, *N*- dimethylacetamide (4.0 mL) were used in this polymerization. After work-up and Soxhlet extraction, 0.046 g product was obtained as a pale yellow powder, yield: 88.5 %.

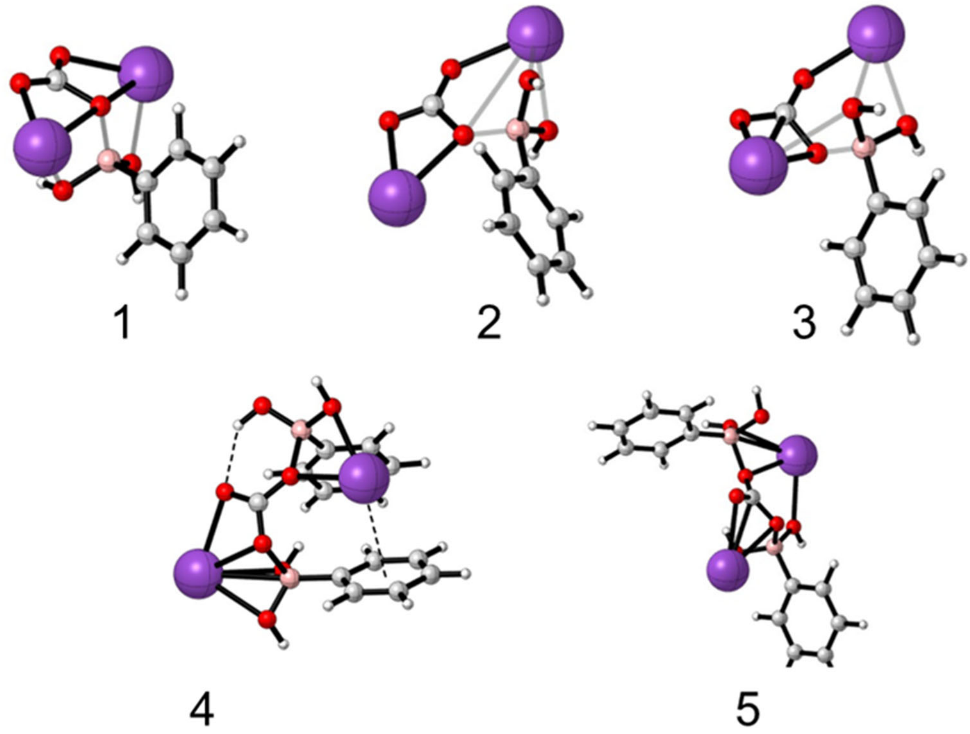
MF-CMP-4: Tetrakis-(*p*-bromophenyl) methane (0.10 g, 0.16 mmol), 1, 4-benzene diboronic acid (0.052 g, 0.31 mmol), K_2CO_3 (0.30 g, 2.17 mmol) and 2-methyl-N^1, N^3-di-*o*-tolylbenzene-1, 3-diamine (0.010 g, 0.03 mmol) in *N*, *N*- dimethylacetamide (4.0 mL) were used in this polymerization. After work-up and Soxhlet extraction, 0.055 g product was obtained as a white powder, yield: 74.3 %.

General procedure for the synthesis of MF-CMP-A1: A new glass tube equipped with a bran-new stirrer bar was charged with the monomers, *N*, *N*- dimethylacetamide, K_2CO_3, and 2-methyl-N^1, N^3-di-*o*-tolylbenzene-1, 3-diamine as catalyst. The glass tube was flash frozen in a liquid nitrogen bath, evacuated and flame sealed. The mixture was heated to 120 °C for 72 hours. The tube was cooled to room temperature, after broken the reaction suspensions were poured into water. The precipitate was collected by filtration and washed with hot H_2O, methanol, THF and DMF. Further purification of the polymers was carried out by Soxhlet extraction with CH_2Cl_2 and THF for 48 h, respectively, and the final product was dried under freeze drying for 24 h.

MF-CMP-A-1: 1, 3, 5-tribromoethynylbenzene (0.10 g, 0.26 mmol), 1, 4-benzene diboronic acid (0.064 g, 0.38 mmol), K_2CO_3 (0.35 g, 2.53 mmol) and 2-methyl-*N*[1], *N*[3]-di-o-tolylbenzene-1, 3-diamine (0.012 g, 0.04 mmol) in *N*, *N*- dimethylacetamide (4.0 mL) were used in this polymerization. After work-up and Soxhlet extraction, 0.065 g product was obtained as a brown powder, yield: 96.3 %.



Scheme S1 A plausible reaction mechanism for MF-CMPs synthesis.



Scheme S2 Different binding modes of K_2CO_3 and Ph-B(OH)$_2$ in the absence of the catalyst.

2. Characterization

Polymer surface areas, N_2 adsorption and desorption isotherm (77.3 K), pore size distributions, H_2 uptake volumetric analysis (up to 1.1 bar, 77.3 K) were measured using Micromeritics ASAP 2020 M surface area and porosity analyzer. Before analysis, the samples were degassed at 100 °C for 12 h under vacuum (10^{-5} bar). FT-IR spectra were recorded under ambient conditions in the wavenumber range of 4000-400 cm^{-1} using a Bruker VERTEX 70 FT-IR Spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and pulse delay of 3 s. X-ray photoelectron spectroscopy (XPS) analysis were conducted on an Axis Ultra DLD 600 W instrument (Shimadzu, Japan). Elemental analyses (EA) was performed on a Vario Micro cube Elemental Analyzer (Elementar, Germany). Thermogravimetric analysis (TGA) measurements were performed on a PerkinElmer Instruments Pyris1 TGA, thermobalance at a heating rate of 10 °C/min under nitrogen. Optical absorption and emission properties of MF-CMPs were measured on a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu Japan) and fluorescence spectrophotometer (RF-6000, Shimadzu Japan). Polymer morphologies were investigated with a FEI Sirion 200 field emission scanning electron microscope (FE-SEM). Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert Pro diffractometer operated at 40 kV and 40 mA with Cu Kα radiation (step size of 0.017° and step time of 7.11 s).

3. Nitrogen sorption isotherm curves and ^{13}C CP-MAS solid state NMR spectra

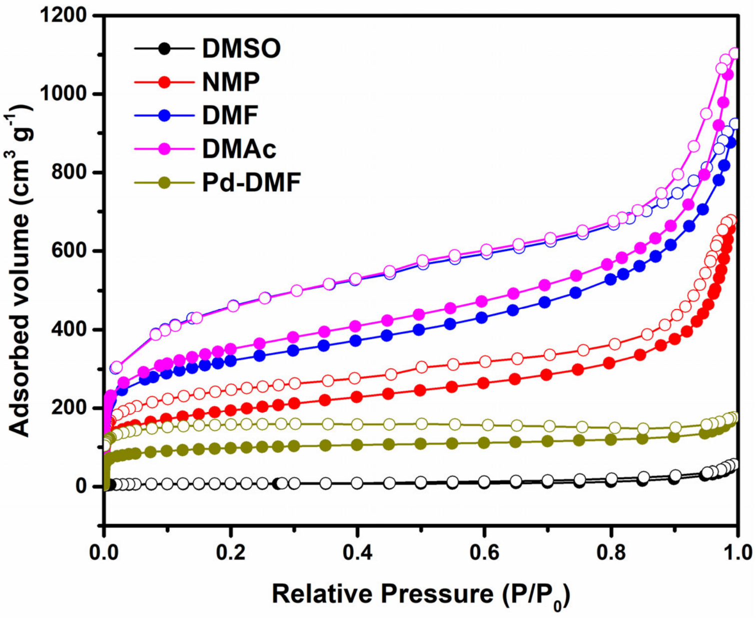


Fig. S4. Nitrogen sorption isotherm curves of MF-CMP-1 synthesized in different solvent.

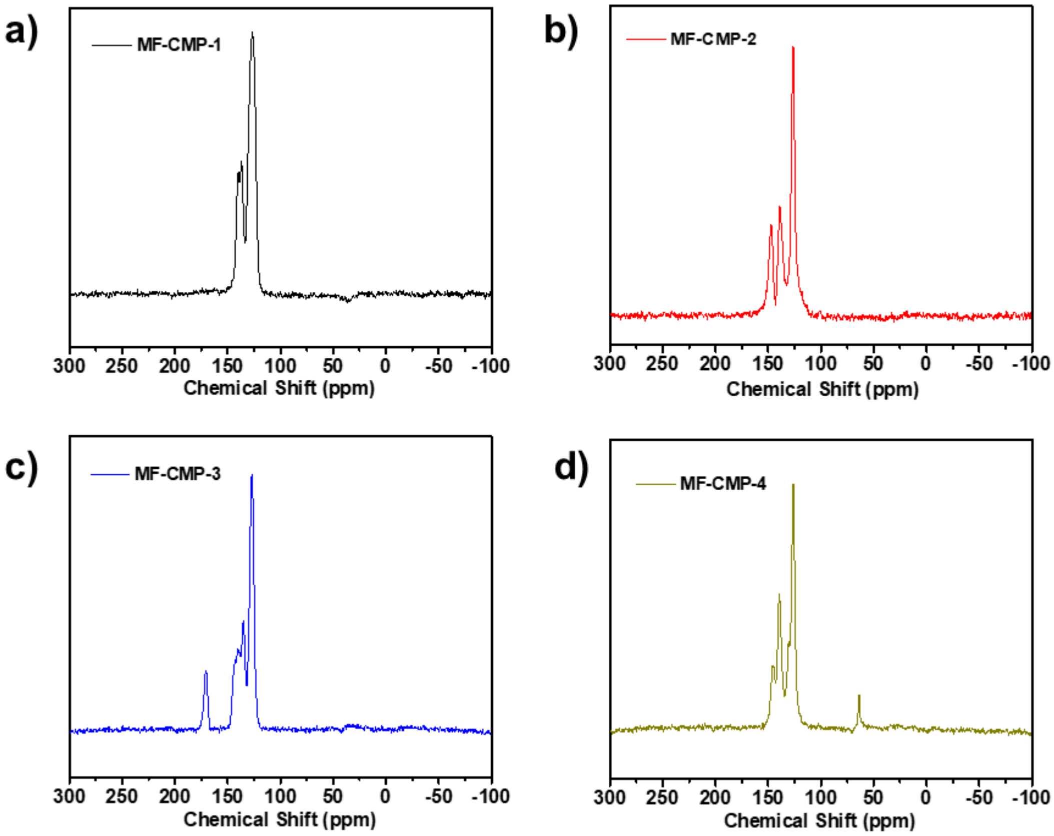


Fig. S5. ^{13}C CP-MAS solid state NMR spectra of MF-CMP-1 (a), MF-CMP-2 (b), MF-CMP-3 (c), MF-CMP-4 (d).

4. XPS spectrum

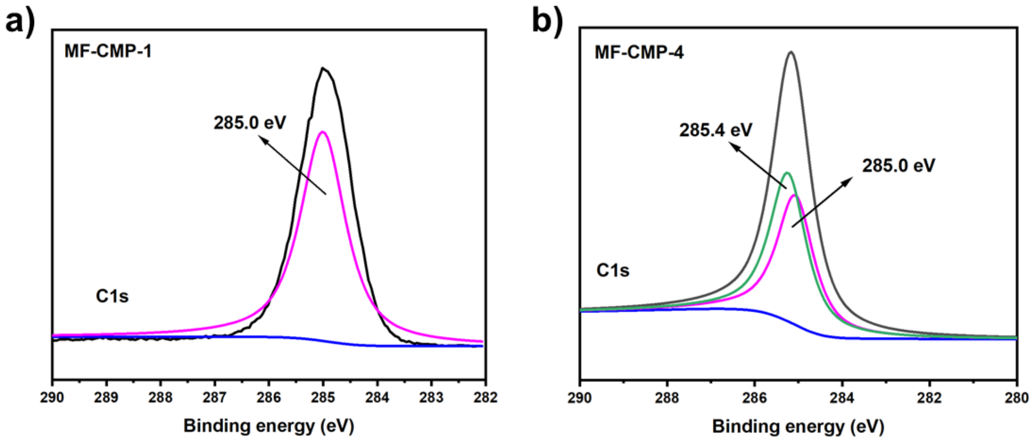


Fig. S6. XPS spectra of C1s of a) MF-CMP-1, b) MF-CMP-4.

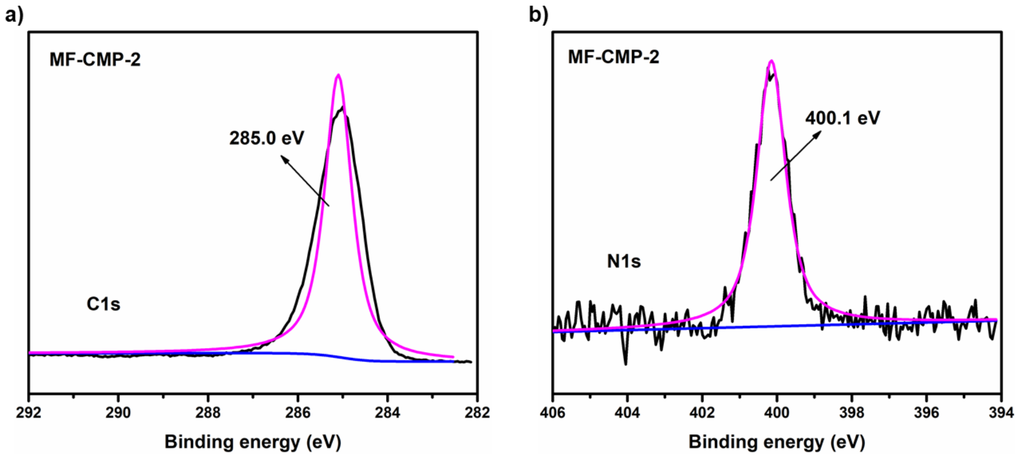


Fig. S7. XPS spectra of MF-CMP-2 a) C1s, b) N1s.

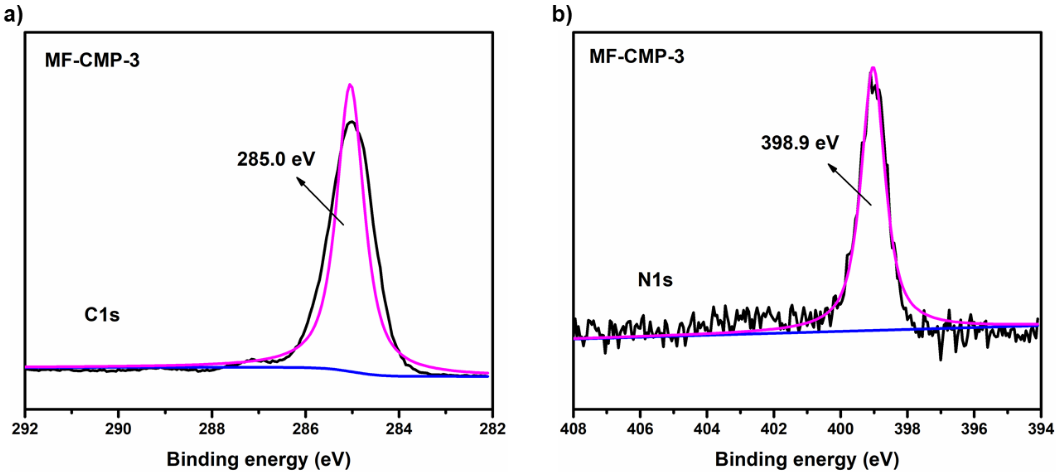


Fig. S8. XPS spectra of MF-CMP-3 a) C1s, b) N1s.

5. SEM, PXRD and TGA

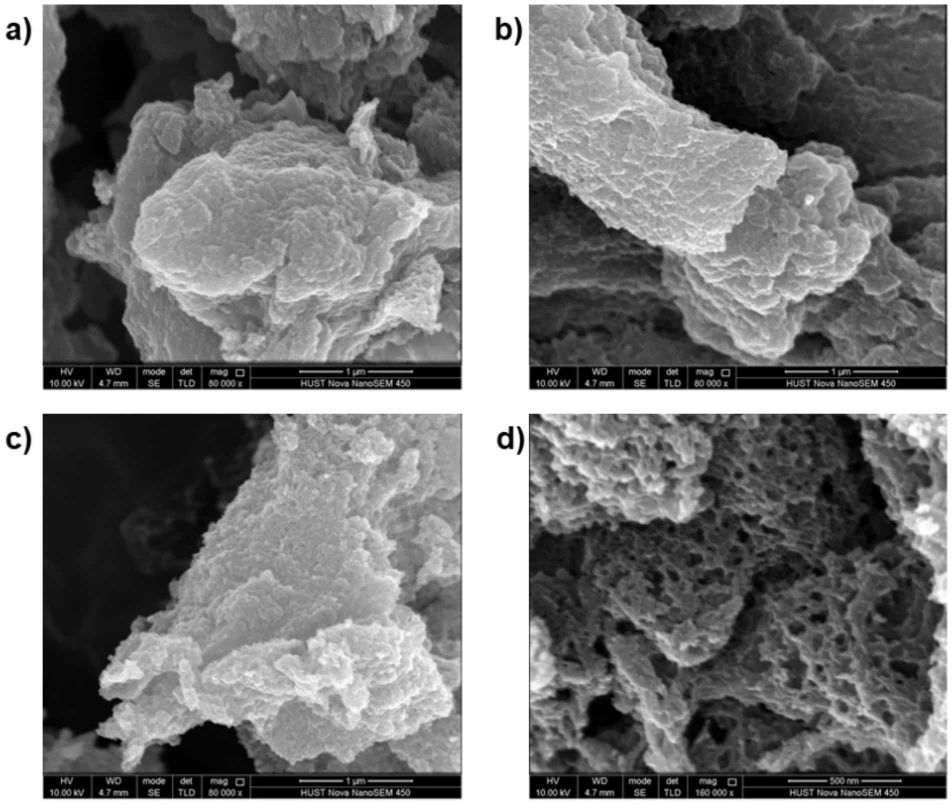


Fig. S9. SEM images of (a) MF-CMP-1, (b) MF-CMP-2, (c) MF-CMP-3 and (d) MF-CMP-4.

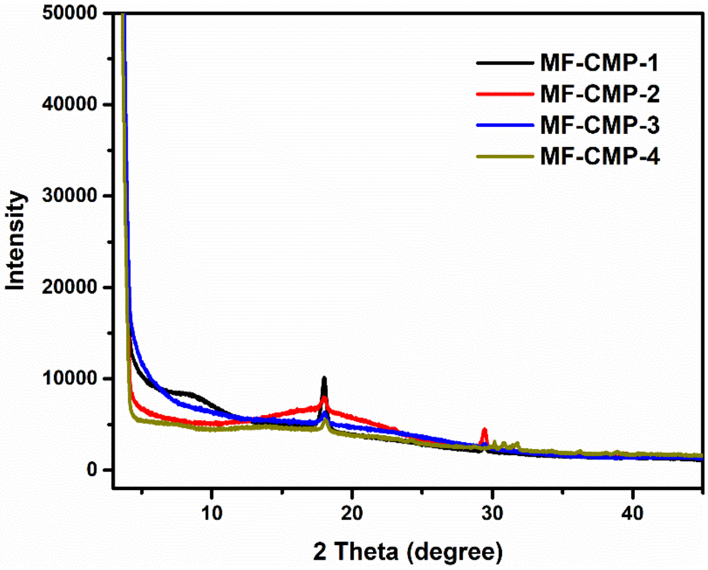


Fig. S10. PXRD curves of MF-CMP-1 (black), MF-CMP-2 (red), MF-

CMP-3 (blue), MF-CMP-4 (dark yellow).

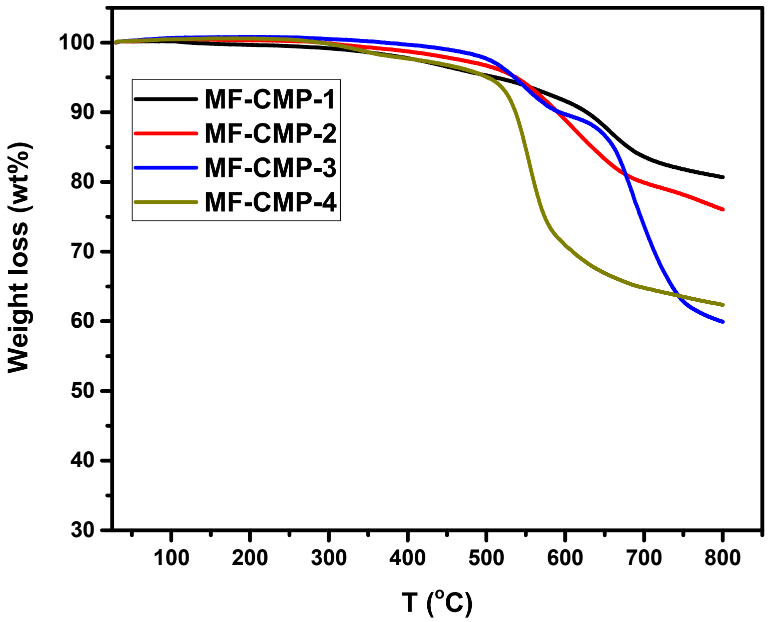


Fig. S11. TGA curves of MF-CMP-1 (black), MF-CMP-2 (red), MF-CMP-3 (blue), MF-CMP-4 (dark yellow).

6. Fluorescence spectrum of MF-CMPs in DMF solution

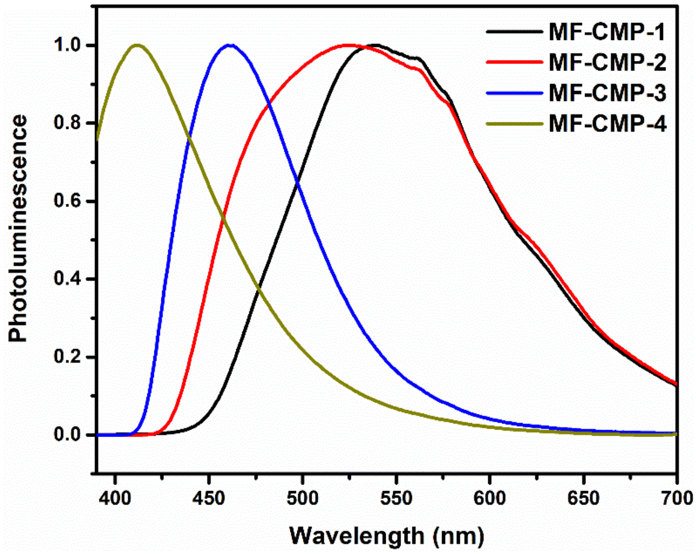


Fig. S12. Photoluminescence spectra of the MF-CMPs measured in the DMF solution ($\lambda_{ex} = 360$ nm).

7. Electrochemical testing and hydrogen evolution

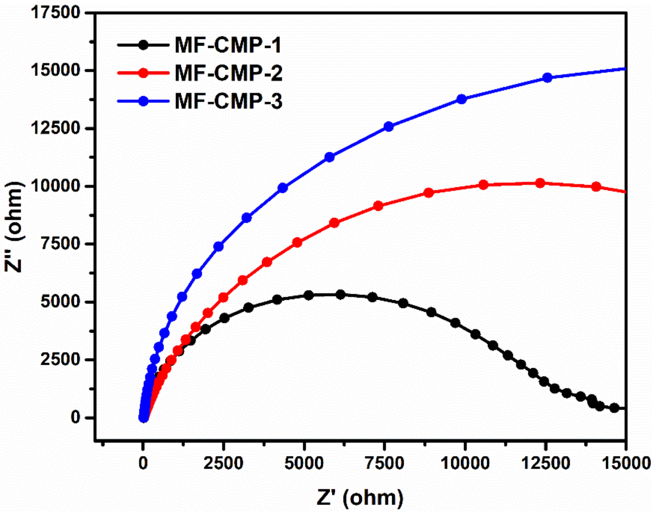


Fig. S13. EIS Nyquist plots of the MF-CMP-1, MF-CMP-2 and MF-CMP-3.

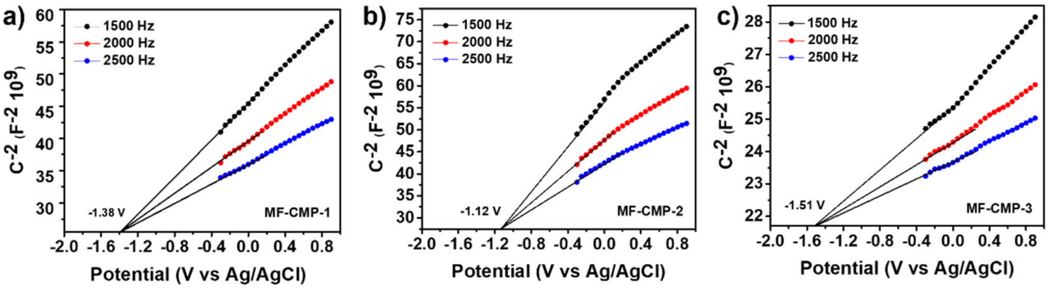


Fig. S14. Mott–Schottky plots of MF-CMP-1 (a), MF-CMP-2 (b) and MF-CMP-3 (c).

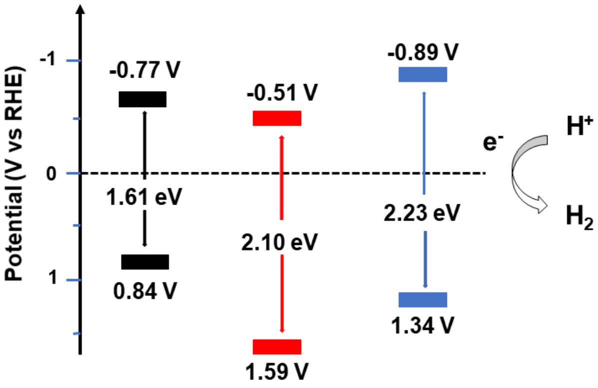


Fig. S15. The energy level diagrams of MF-CMP-1 (black), MF-CMP-2 (red) and MF-CMP-3 (blue).

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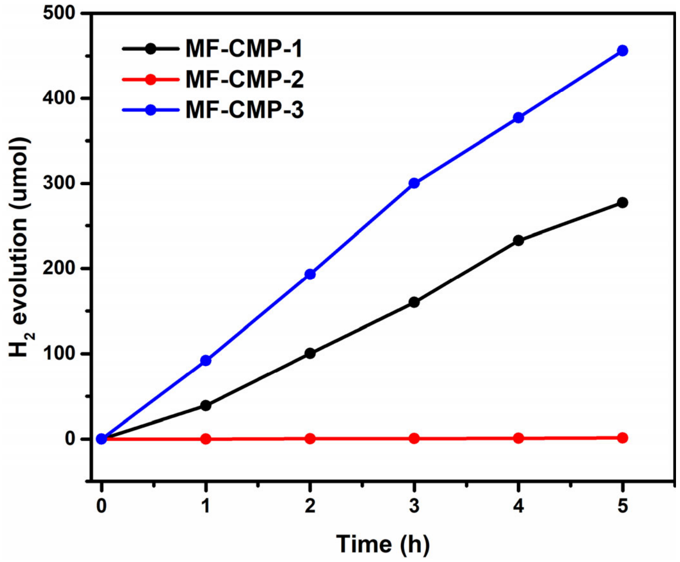


Fig. S16. Time course of H_2 evolution of MF-CMP-1, MF-CMP-2 and MF-CMP-3. Photocatalytic hydrogen production condition: 50 mg catalyst, 3wt%Pt, TEOA as sacrificial agent (V_{TEOA}/V_{water}=90/10), light> 420 nm.

8. Structural characterization of MF-CMP-A-1

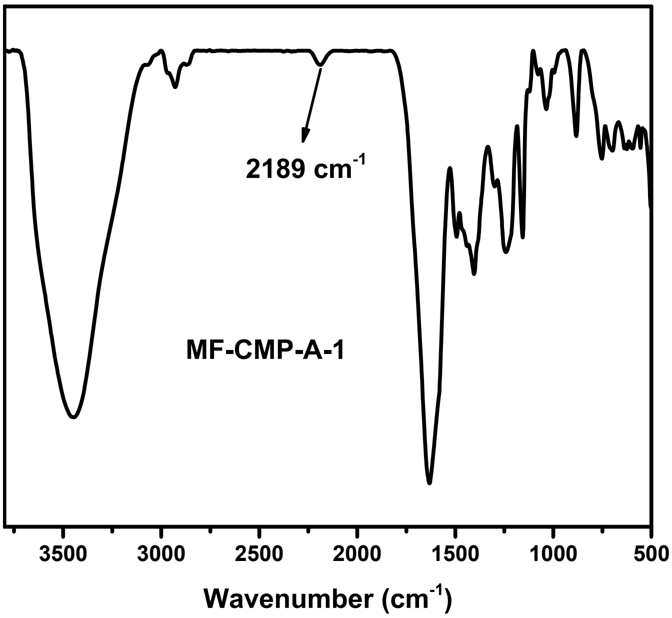


Fig. S17. FT-IR spectra of the as-prepared MF-CMP-A-1. The peak at

2189 cm^{-1} can be ascribed to -C≡C- group.

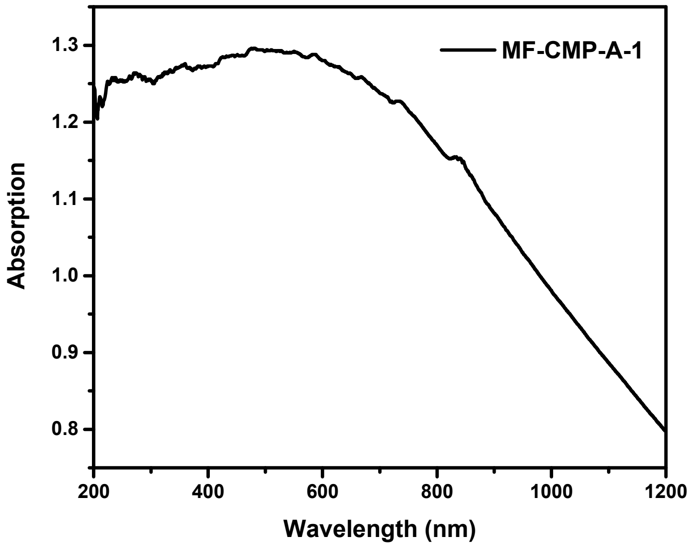


Fig. S18. UV-Vis spectra of the as-prepared MF-CMP-A-1. The absorption edge is larger than 1000 nm.

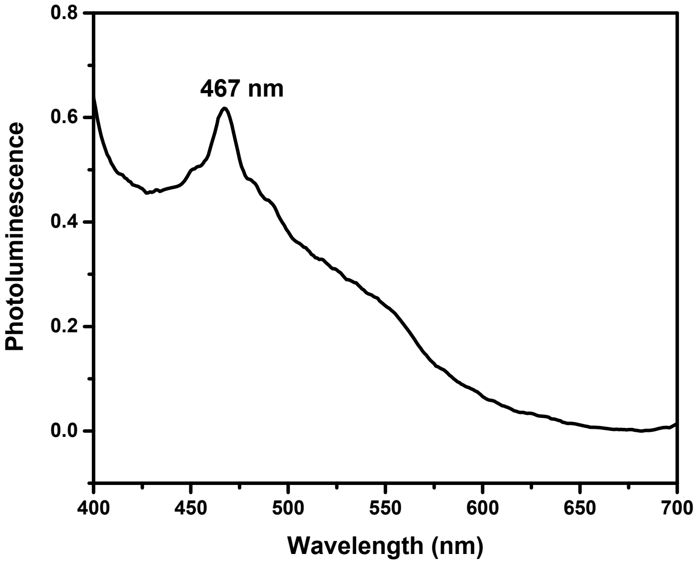


Fig. S19. Photoluminescence spectra of the MF-CMP-A-1, measured in the solid state (λ_{ex} = 360 nm).

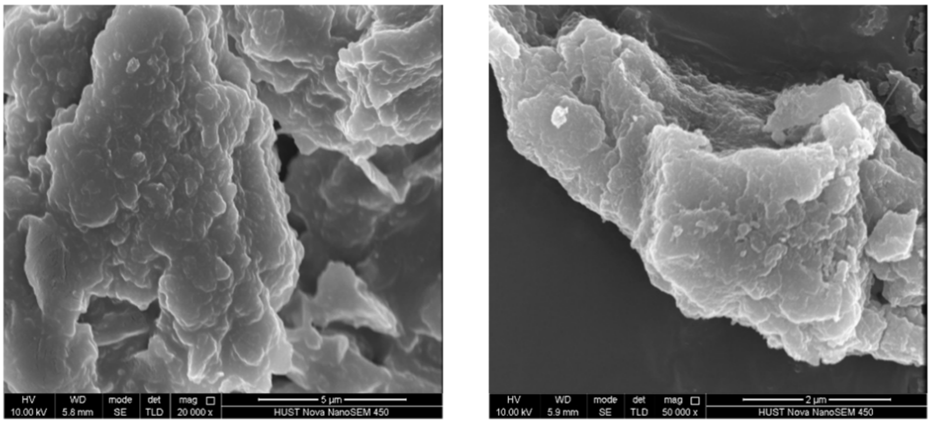


Fig. S20. SEM images of MF-CMP-A-1.

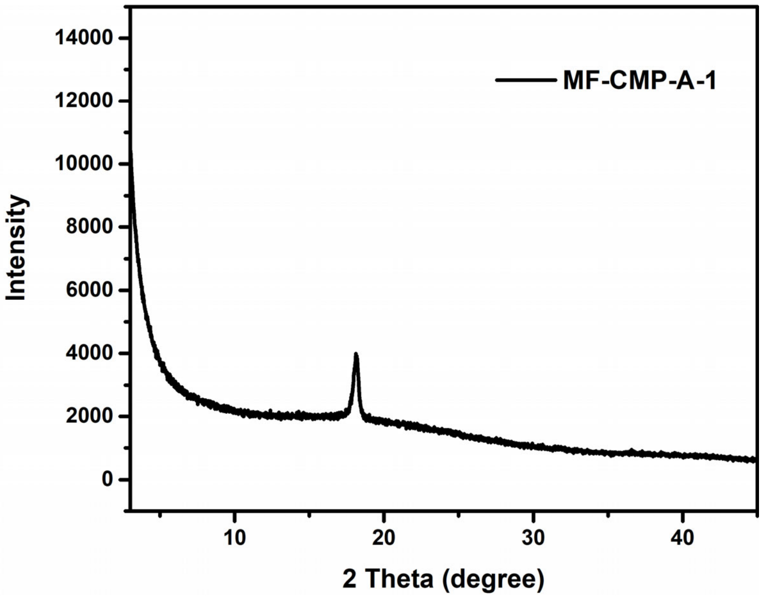


Fig. S21. PXRD of MF-CMP-A-1. The sample is amorphous, and the peak at 18° is ascribed to the in-plane antiparallel arrangement.

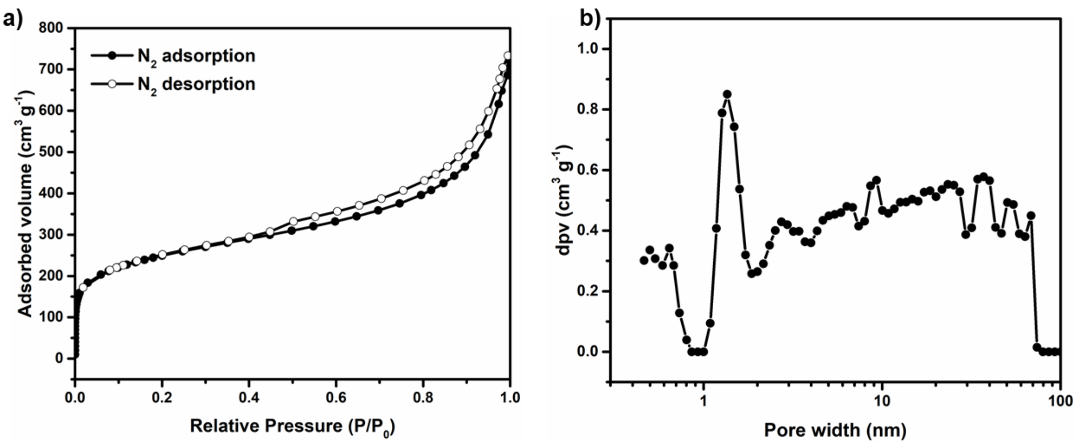


Fig. S22. Nitrogen adsorption-desorption isotherms (a) and the pore size distribution (b) of MF-CMP-A-1.

9. Hydrogen storage performance

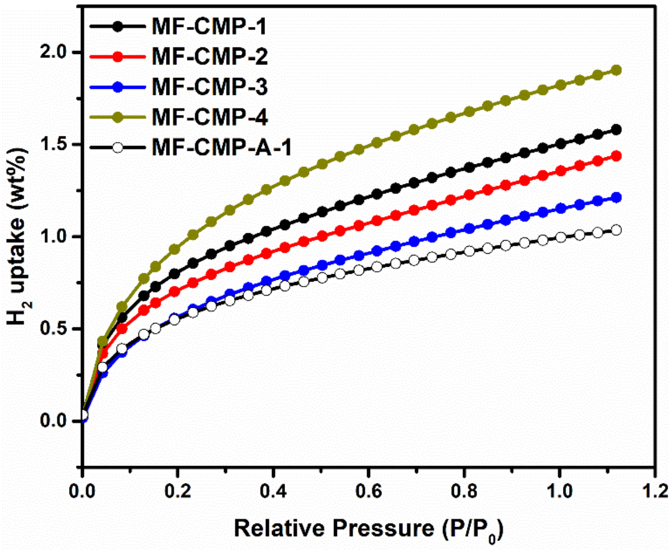


Fig. S23. H_2 uptake properties of MF-CMPs and MF-CMP-A-1.

10. Supporting Tables

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

Solvent	Temperature	Reaction time	Yield	S_{BET}

	(°C)	(h)	(%)	(m^2 g^{-1})
Xylene	120	72	N.R	--
Toluene	120	72	N.R	--
Dioxane	120	72	N.R	--
Toluene/dioxane	120	72	N.R	--
DMSO	120	72	Trace	25
NMP	120	72	73.5	700
DMF	120	72	88.2	1152
DMAc	120	72	93.0	1269
[a]DMF	120	72	90.3	353

[a] Tetrakis(triphenylphosphine)-palladium was used as catalyst.[3]

Table S2. Optimization of the amine catalyst

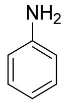
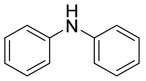
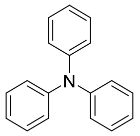
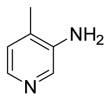
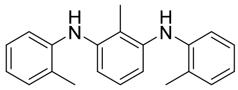
Entry	Amine catalyst	Yield (%)
1		0
2		0
3		0
4		0
5		88.2 %

Table S3 Hydrogen storage with reported CMPs and this work

CMPs	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	H_2 uptake (wt%)	Ref.
CMP-4	744	0.39	--	4
P1	450	--	--	5
P2	210	--	--	5
P3	510	--	--	5
YSN	1275	0.99	--	6
YBN	1255	0.97	--	6
PTPA-3	450	0.36	--	7
PPV	761	0.63	--	8
HCMP-1	842	1.16	0.95	9
HCMP-2	827	1.35	1.16	9
CMP-0	1018	0.56	1.40	10
CMP-1	834	0.47	1.15	10
CMP-2	634	0.53	0.91	10
CMP-3	522	0.26	0.71	10
CMP-5	512	0.47	0.64	10
CP-CMP10	995	--	--	3
PP-CMP	1083	--	--	11
YDPPy	303			12
TPE-CMP@2h	753	--	--	13
HPOP-1	1148	1.28	1.50	14
HPOP-2	742	0.45	1.08	14
POFs	1063	1.13	1.50	15
BILP-10	787	0.45	1.60	16
TPOP-2	673	0.46	0.91	17
TPOP-5	810	0.48	1.07	17
Li@COP-1	573	0.37	1.67	18
BLP-2 (Cl)	1174	0.65	1.30	19

Network 1–22	136–880	0.20–0.33	0.74–1.14	20
CPs-B	409	--	--	21
Cat-1	7	--	--	22
Cat-3	475	--	--	22
PPS1	150	0.22	0.21	23
PPS2	767	0.45	0.65	23
PON-2	700	0.33	--	24
PPAF-I	565	0.88	--	25
MF-CMP-1	1269	0.20	1.60	This work
MF-CMP-2	841	0.28	1.44	This work
MF-CMP-3	806	0.30	1.21	This work
MF-CMP-4	1249	0.38	1.90	This work

Table S4 Elemental analysis of MF-CMPs

Sample	C %		H %		N %	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
MF-CMP-1	91.07	95.84	4.97	4.16	0	0
MF-CMP-2	88.63	91.72	5.04	3.85	5.51	4.43
MF-CMP-3	82.82	85.19	4.64	4.07	11.41	10.74
MF-CMP-4	92.68	96.09	5.32	3.91	0	0

Table S5 Br and B content of MF-CMPs

Sample	Br wt%	B wt%
MF-CMP-1	0.073	0.059
MF-CMP-2	0.160	0.082
MF-CMP-3	0.063	0.051
MF-CMP-4	0.046	0.022

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