

Supporting information for

Hierarchically Porous Covalent Organic Frameworks Assembled in Ionic Liquids for Highly Effective Catalysis of C-C Coupling Reactions

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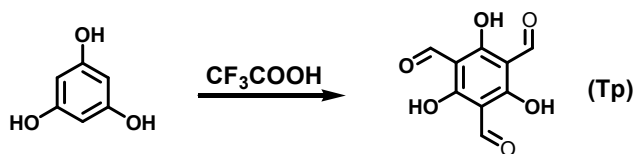
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Table of Contents

1. Experimental Procedures
2. Figures S1-28
3. Tables S1-2
- 4. References**

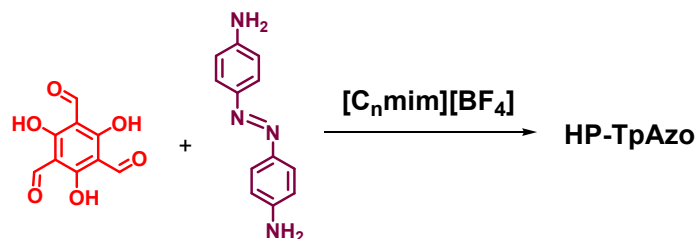
1. Experimental Procedures

General procedure for the synthesis of triformylphloroglucinol (Tp)



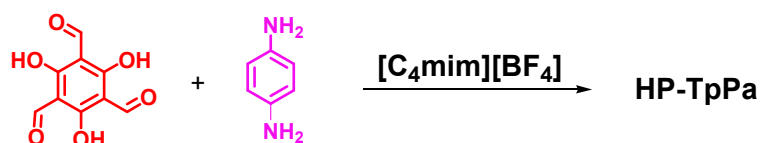
A mixture of hexamethylenetetraamine (5.0 g, 36 mmol), phloroglucinol (2.0 g, 16 mmol) and trifluoroacetic acid (30 mL) was placed in a dry 100 mL round bottom flask and heated at 100 °C for 2.5 h under N_2 . Then 40 mL of 3 M HCl was added and the solution was heated at 100 °C for 1 h. After the reaction was completed, the solution was filtered and extracted with dichloromethane. The solvent was evaporated and an off-white powder (0.5 g) was obtained.

Synthetic Procedure of HP-TpAzo in ILs



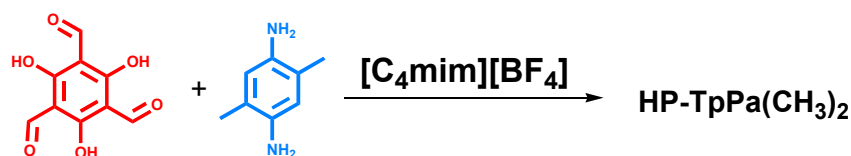
For the preparation of HP-TpAzo, 0.1125 mmol of p-Azoaniline was dissolved in an IL (200 μl) under vigorous stirring. Then, 0.075 mmol (15.7 mg) of 1,3,5-triformylphloroglucinol was added in the mixture and stirred at 50 °C for 12 h. After the reaction was finished, the mixture was soaked in ethanol, and the precipitate was isolated by filtration. The IL could be recovered from the filtrate by removing ethanol under reduced pressure. Then, the precipitate was washed with THF and DMF three times to remove the small polymer molecules. At the end, the collected powder was activated using Soxhlet extraction in methanol for 3 times and then dried at 120 °C under vacuum for 12 h to give a red colored powder with up to 90-92% isolated yield (92% in $[\text{C}_4\text{mim}][\text{BF}_4]$, 92% in $[\text{C}_6\text{mim}][\text{BF}_4]$, and 90% in $[\text{C}_{10}\text{mim}][\text{BF}_4]$, respectively).

Synthetic Procedure of HP-TpPa in $[\text{C}_4\text{mim}][\text{BF}_4]$



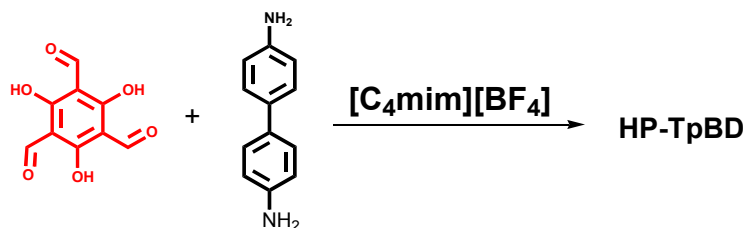
For the preparation of MP-TpPa, 0.1125 mmol of p-phenylenediamine was dissolved in [C₄mim][BF₄] (200 ul) under vigorous stirring. Then, 0.075 mmol of 1,3,5-triformylphloroglucinol was added in the mixture and stirred at °C for 12 h. After the reaction was finished, the mixture was soaked in ethanol, and the precipitate was isolated by filtration. The IL could be recovered from the filtrate by removing ethanol under reduced pressure. Then, the precipitate was washed with THF and DMF three times to remove the small polymer molecules. At the end, the collected powder was activated using Soxhlet extraction in methanol for 3 times and then dried at 120 °C under vacuum for 12 h to give a colored powder with up to 87% isolated yield.

Synthetic Procedure of HP-TpPa(CH₃)₂ in [C₄mim][BF₄]



For the preparation of HP-TpPa(CH₃)₂, 0.1125 mmol of 2,5-dimethylbenzene-1,4-diamine was dissolved in [C₄mim][BF₄] (200 ul) under vigorous stirring. Then, 0.075 mmol of 1,3,5-triformylphloroglucinol was added in the mixture and stirred at 50 °C for 12 h. After the reaction was finished, the mixture was soaked in ethanol, and the precipitate was isolated by filtration. The IL could be recovered from the filtrate by removing ethanol at reduced pressure. Then, the precipitate was washed with THF and DMF three times to remove the small polymer molecules. At the end, the collected powder was activated using Soxhlet extraction in methanol for 3 times and then dried at 120 °C under vacuum for 12 h to give a colored powder with up to 80% isolated yield.

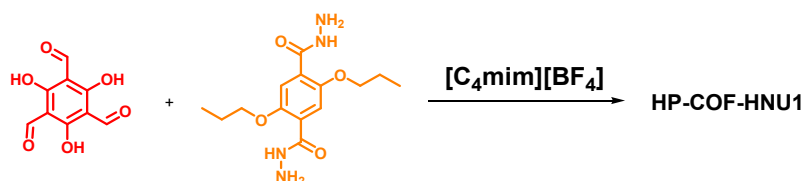
Synthetic Procedure of HP-TpBD in [C₄mim][BF₄]



For the preparation of HP-TpBD, 0.1125 mmol of hydrazine was dissolved in [C₄mim][BF₄] (200 ul) under vigorous stirring. Then, 0.075 mmol of 1,3,5-triformylphloroglucinol was added in the mixture and stirred at 50 °C for 12 h. After the reaction was finished, the mixture was soaked in ethanol,

and the precipitate was isolated by filtration. The IL could be recovered from the filtrate by removing ethanol at reduced pressure. Then, the precipitate was washed with THF and DMF three times to remove the small polymer molecules. At the end, the collected powder was activated using Soxhlet extraction in methanol for 3 times and then dried at 120 °C under vacuum for 12 h to give a colored powder with up to 83% isolated yield.

Synthetic Procedure of HP- COF-HNU1 in [C₄mim][BF₄]



For the preparation of HP-COF-HNU1, 0.1125 mmol of 2,5-dipropoxybenzene-1,4-dihydrazide was dissolved in [C₄mim][BF₄] (200 μ l) with vigorous stirring. Then, 0.075 mmol of 1,3,5-triformylphloroglucinol was added in the mixture and stirred at 50 °C for 12 h. After the reaction was finished, the mixture was soaked in ethanol, and the precipitate was isolated by filtration. The IL could be recovered from the filtrate by removing ethanol under reduced pressure. Then, the precipitate was washed with THF and DMF three times to remove the small polymer molecules. At the end, the collected powder was activated using Soxhlet extraction in methanol for 3 times and then dried at 120 °C under vacuum for 12 h to give a colored powder with up to 78% isolated yield.

Synthesis of TpAzo@Pd

In a 25 mL stand-up bottle, palladium acetate (20 mg) and TpAzo (50 mg) were added in 20 mL of CH₂Cl₂. Then the mixture was stirred at room temperature for 36 h. The TpAzo@Pd was obtained by isolation and washing with methanol. The Pd loading amount was decided to be 6.1 wt% by ICP.

Synthetic Procedures of COF@Ag

Taking the preparation of HP-TpAzo@Ag as an example, the HP-TpAzo (100 mg) and acetonitrile (5 mL) were added in a 20 mL round-bottom flask, and then the mixture was sonicated at room temperature for 2 hours. After that, AgNO₃ (10.0 mg) was directly added in the mixture, and continuously stirred for 8 hours at room temperature. The resulting solid was isolated and washed with acetonitrile three times. Finally, the obtained solid was mixed with a solution of NaBH₄ (20 mg) in ethanol (5 mL), and the mixture was stirred for 4 hours. The precipitate was isolated by filtration and

washed with ethanol (30 mL). The HP-TpAzo@Ag was obtained after drying at 60 °C under vacuum for 12 hours.

Typical procedures for the Knoevenagel condensation reaction

In a 10 mL Schlenk flask, 4-biphenylcarboxaldehyde (1.0 mmol), malononitrile (2.0 mmol) and the corresponding catalyst (20mg) were added, and then the mixture was stirred at 25 °C for a certain time. Conversion of 4-biphenylcarboxaldehyde was calculated by ¹H NMR spectroscopy (CDCl₃, 600MHz) using anisole as an internal standard.

Typical procedures for the Suzuki-Miyaura coupling reactions

In a 10 mL Schlenk flask, phenylboronic acid (1.5 mmol), aryl bromide (1.0 mmol), K₂CO₃ (2.0 mmol) and the HP-TpAzo@Pd (10 mg) were added to 5mL of xylene. The mixture was stirred at 100 °C for 24 hours. After the reaction was finished, the mixture was centrifuged, and the product was purified by column chromatography over silica gel.

Molecular Dynamics Simulations

AMBER force fields of [C_nmim][BF₄] (n=4, 6, 10)¹ were used in our simulations. All simulations were performed with MDynaMix 5.2 package.² The double time-step algorithm³ was adopted with long and short time steps of 2 and 0.5 fs, respectively. Ewald summation method⁴ was used to treat the long-range electrostatic interaction, in which the long-range parts were cut off at 15 Å. The simulations were performed by using 200 ion pairs of IL ([C₄mim][BF₄], [C₆mim][BF₄], and [C₁₀mim][BF₄]) at 298 K. The initial configuration was prepared by PACKMOL68 in a square box, typically larger than the “real” size to make the packing easier.

A starting simulation was carried out at 700 K in NVE ensemble. After a relaxation for a few MD steps to reduce the possible overlapping in the initial configuration, the Nose-Hoover NPT ensemble simulation⁵ was performed. Descending from 700 K to the sampling temperature of 298 K, a series of NPT simulations were carried out under the standard atmospheric conditions. At the sampling temperature point, the system was equilibrated for at least 5 ns, and then the production phase was lasted for 4 ns. The conformations in trajectories were dumped with an interval of 20 fs for further analysis.

2. Figures S1-28

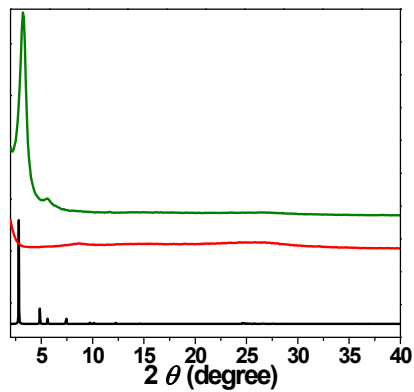


Figure S1. PXRD patterns of TpAzo prepared in neat organic solvent DMSO alone (red line), and in DMSO in the presence of catalytic amounts of $[\text{C}_4\text{mim}][\text{BF}_4]$ (12 mol% based on Tp) (green line).

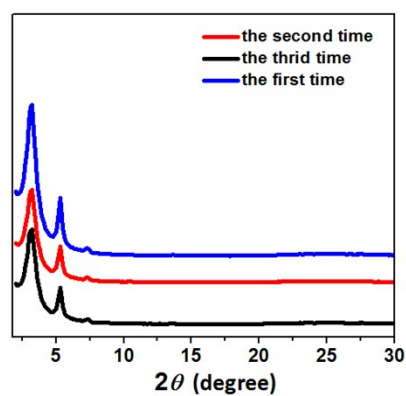


Figure S2. PXRD patterns of HP-TpAzo synthesized in the fresh and recovered IL.

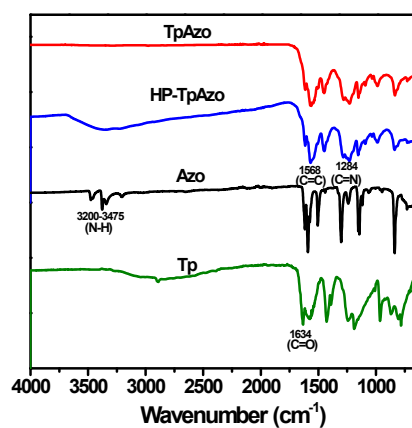


Figure S3. Comparison of FTIR spectra of the starting materials Tp and Azo with HP-TpAzo and uni-pore TpAzo shows the absence of the starting materials in the COF matrix.

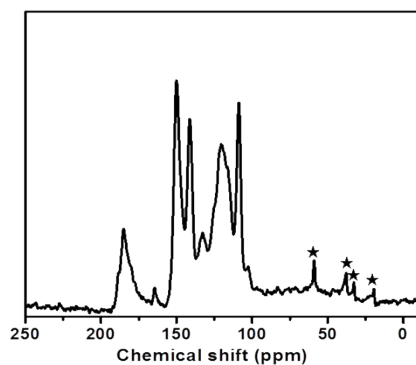


Figure S4. Solid state ^{13}C CP/MAS NMR spectrum of HP-TpAzo. Asterisks denote spinning side bands.

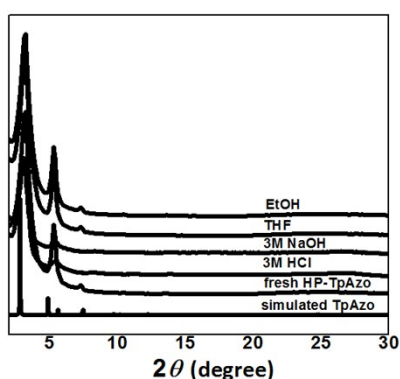


Figure S5. PXRD patterns of the HP-TpAzo after soaking in different solvents for 72 hours.

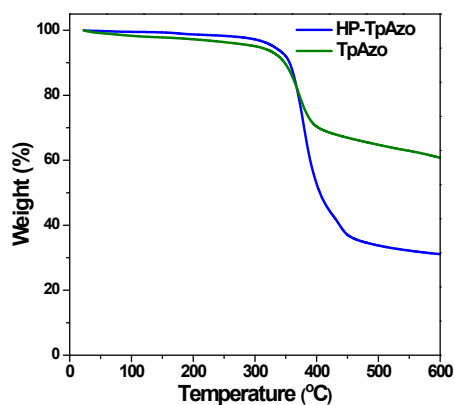


Figure S6. TGA curves of HP-TpAzo (blue) and uni-pore TpAzo (green) under N_2 atmosphere. The continuous weight loss of the HP-TpAzo over the range of 350-450 $^{\circ}\text{C}$ may be ascribed to the generation of numerous defects in the structures of HP-COFs. The structure defects thus introduce more polar groups such as $-\text{CHO}$ and $-\text{NH}_2$ in HP-COFs. The ability of the nitrogen and oxygen atoms to inductively withdraw electrons weakens the neighboring carbon-carbon bonds, causing thermal breakdown of HP-COF compared with their parent COF at higher temperatures range, thereby leading to a continuous weight loss as observed ⁶.

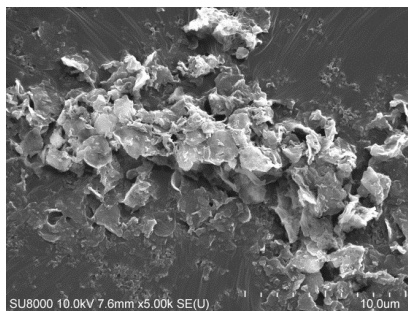


Figure S7. SEM images of HP-TpAzo.

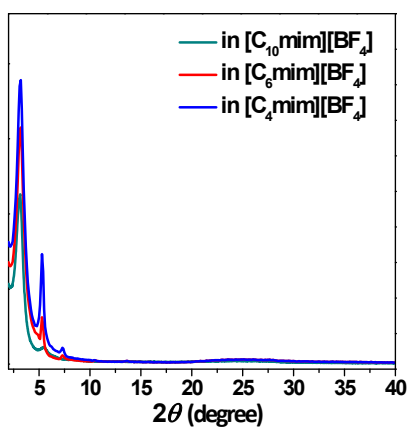


Figure S8. PXR D patterns of the HP-TpAzo synthesized in $[C_6mim][BF_4]$ and $[C_{10}mim][BF_4]$, respectively.

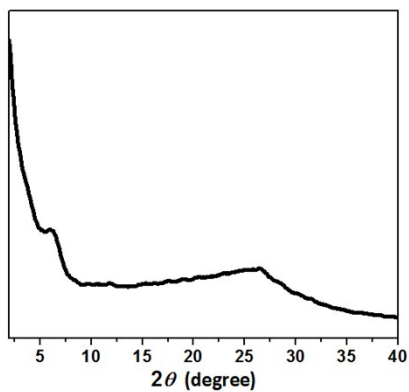


Figure S9. PXR D patterns of the HP-TpTpAzo synthesized in $[C_{12}mim][BF_4]$.

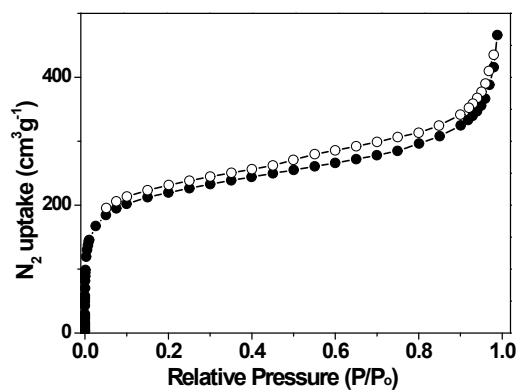


Figure S10. N₂ sorption isotherms of HP-TpAzo prepared in [C₆mim][BF₄].

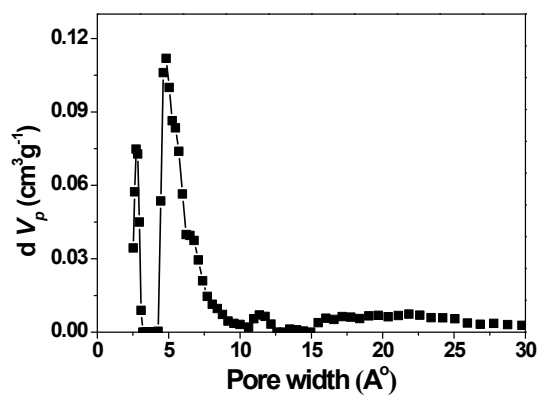


Figure S11. DFT pore size distribution of HP-TpAzo prepared in [C₆mim][BF₄].

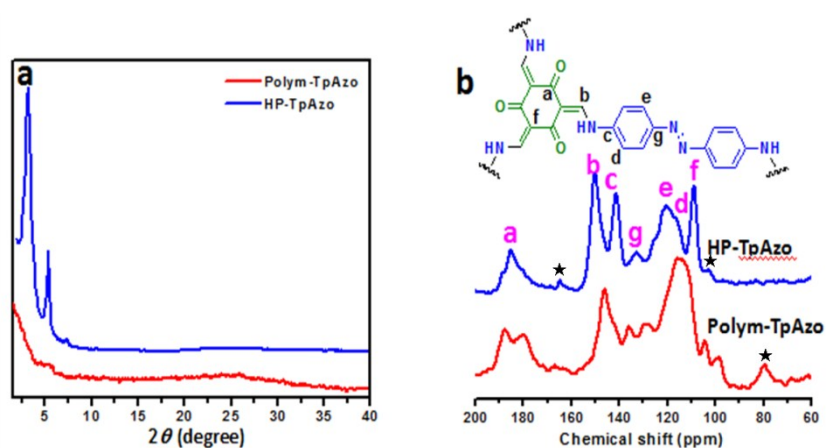


Figure S12. PXRD patterns of Polym-TpAzo and HP-TpAzo (a); Solid state ¹³C CP/MAS NMR spectrum of Polym-TpAzo and HP-TpAzo (b). Asterisks denote spinning side bands.

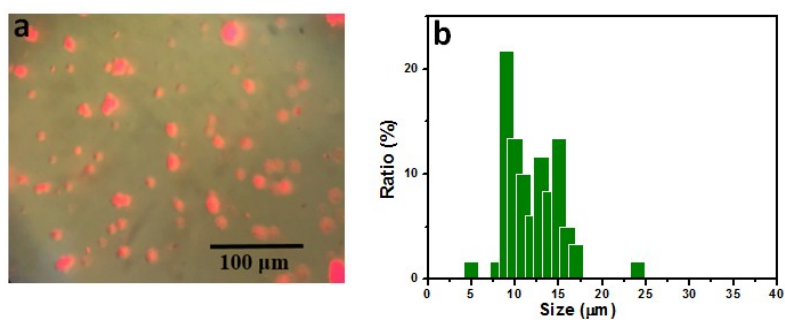


Figure S13. The image (a) and size distribution (b) of HP-TpAzo particles.

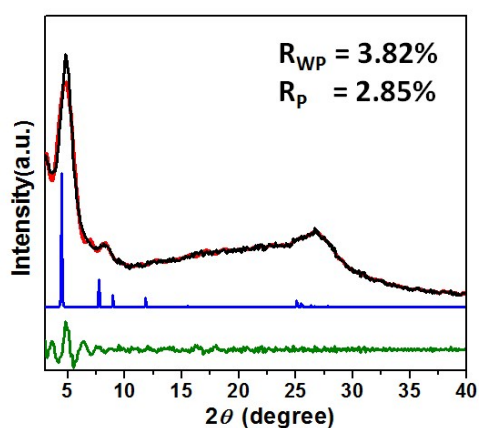


Figure S14. Experimental PXRD pattern of HP-TpPa (black), Pawley-refined (red), and simulated PXRD pattern of TpPa (blue) using the eclipsed AA-stacking. The difference plot between experimental and Pawley-refined patterns is presented in green.

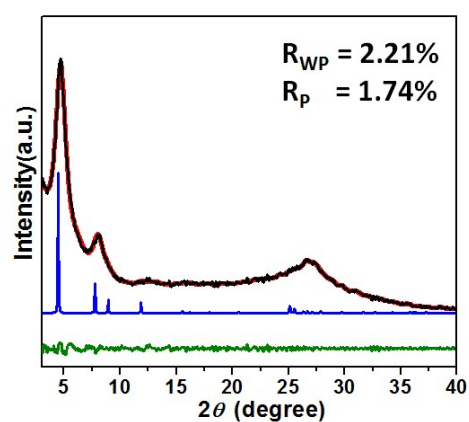


Figure S15. Experimental PXRD pattern of HP-TpPa(CH₃)₂ (black), Pawley-refined (red), and simulated PXRD pattern of TpPa(CH₃)₂ (blue) using the eclipsed AA-stacking. The difference plot between experimental and Pawley-refined patterns is presented in green.

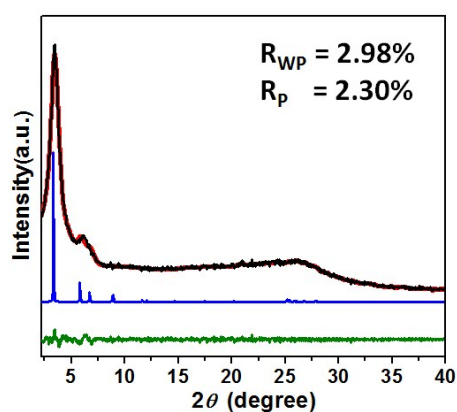


Figure S16. Experimental PXRD pattern of HP-TpBD(black), Pawley-refined (red), and simulated PXRD pattern of TpBD (blue) using the eclipsed AA-stacking. The difference plot between experimental and Pawley-refined patterns is presented in green.

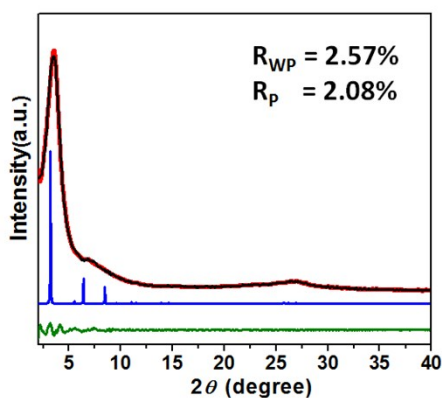


Figure S17. Experimental PXRD pattern of HP-COF-HNU1, Pawley-refined (red), and simulated PXRD pattern of COF-HNU1 (blue) using the eclipsed AA-stacking. The difference plot between experimental and Pawley-refined patterns is presented in green.

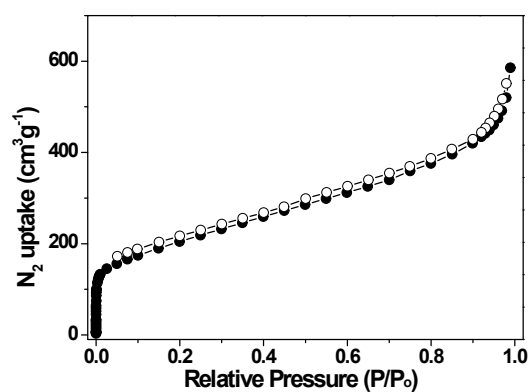


Figure S18. N_2 adsorption-desorption isotherms for HP-TpPa.

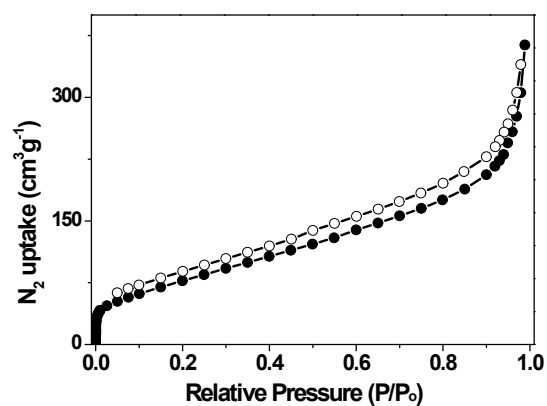


Figure S19. N₂ adsorption-desorption isotherms for HP-TpPa(CH₃)₂.

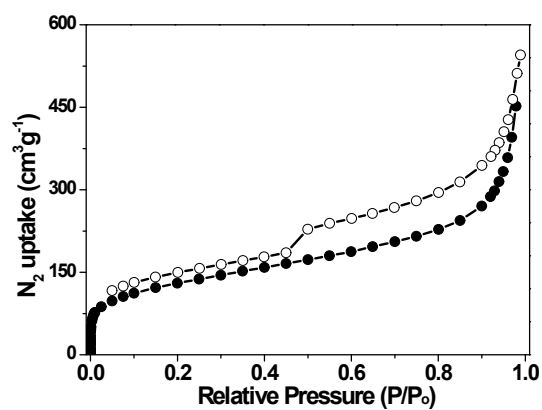


Figure S20. N₂ adsorption-desorption isotherms for HP-BD.

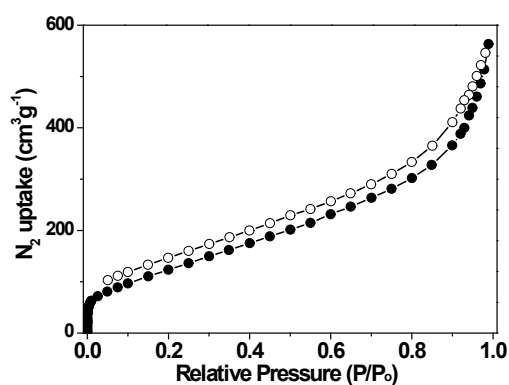


Figure S21. N₂ adsorption-desorption isotherms for HP-COF-HNU1.

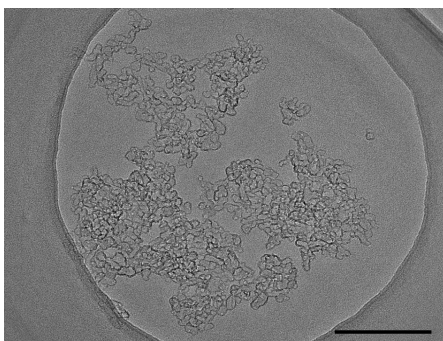


Figure S22. TEM image of HP-TpPa.

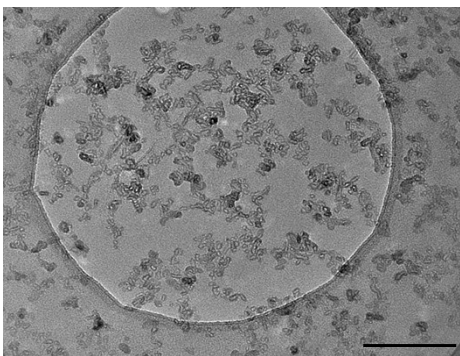


Figure S23. TEM image of HP-TpPa(CH₃)₂.

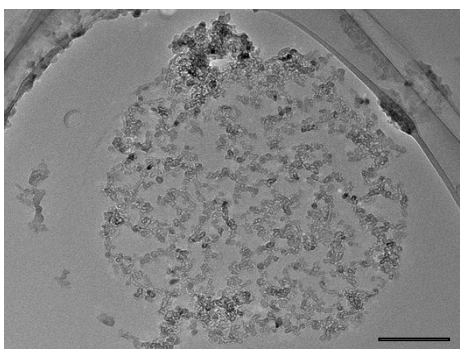


Figure S24. TEM image of HP-TpBD.

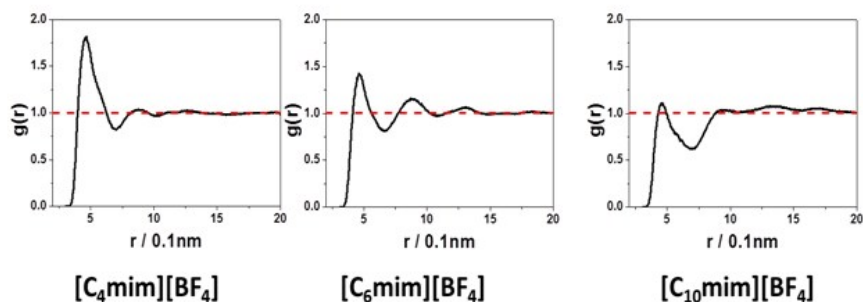


Figure S25. RDFs of B atom of $[\text{BF}_4]^-$ around terminal C atom of the tail in $[\text{C}_n\text{mim}]^+$ cation. When the value of $g(r)$ is close to 1, the local density that stands for the microheterogeneity of the ILs is equal to the overall average density of the system.

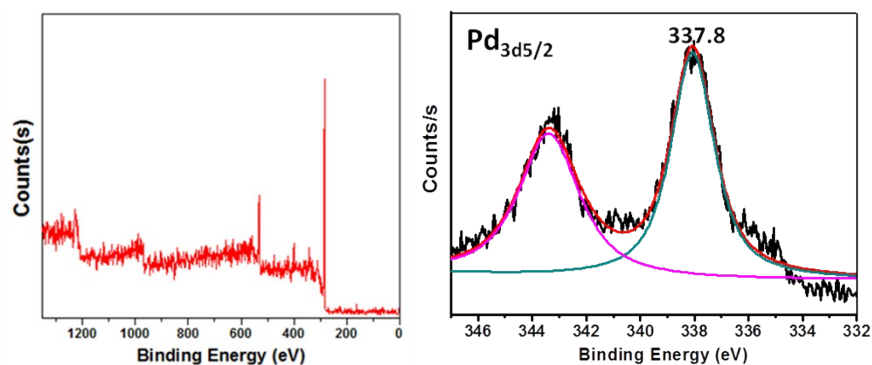


Figure S26. X-ray photoelectronic spectrum of HP-TpAzo@Pd. It was noteworthy that the binding energy (BE) of 337.8 eV for Pd(II) species in the HP-TpAzo@Pd shifted negatively by 0.6 eV in comparison with that of 338.4 eV for free $\text{Pd}(\text{OAc})_2$ ^[7]. This negative shift indicates the strong coordination of $\text{Pd}(\text{OAc})_2$ with β -ketoenamine groups of the HP-TpAzo. Wang et.al^[7] have demonstrated that the XPS spectrum of the coordination complex Pd/1,10-phenanthroline (with the BE of 337.8 eV for the Pd(II) species) also shows a negative shift of 0.6 eV in comparison with that of free $\text{Pd}(\text{OAc})_2$. Therefore, $\text{Pd}(\text{OAc})_2$ is most probably located in between the adjacent layers of HP-TpAzo and efficiently coordinated with the nitrogen atoms from different layers.

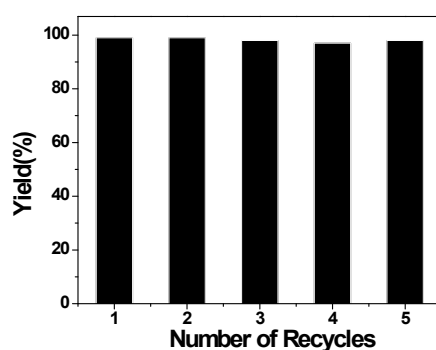


Figure S27. Recycle test of HP-TpAzo@Pd in the Suzuki C-C coupling Reaction of bromobenzene and Phenylboronic Acid.

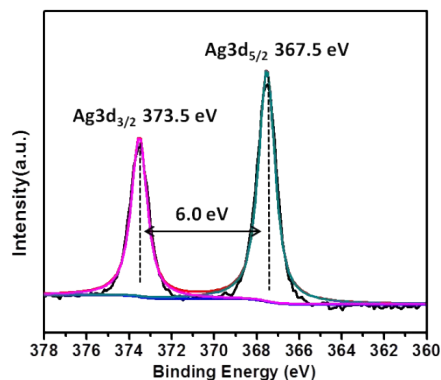


Figure S28. High-resolution XPS spectrum of Ag 3d of the HP-TpAzo@Ag. The binding energies of Ag 3d_{3/2} and Ag 3d_{5/2} appear at 373.5 and 367.5 eV, respectively, and the splitting of the 3d doublet is 6.0 eV, confirming that Ag exists as a metallic state on the HP-TpAzo.⁸

3. Tables S1-2

Table S1 Surface area and pore size distribution of HP-COFs

COF	S_{BET} [m ² g ⁻¹] ^[a]	D_{Meso} [nm] ^[b]
HP-TpPa	727	3-13
HP-TpPa(CH ₃) ₂	298	3-15
HP-TpBD	467	3-30
HP-COF-HTU1	475	3-15

^[a]BET specific surface area. ^[b]The mesopore size distribution determined by the DFT method from the adsorption branch of the N₂ isotherm at 77K.

Table S2 Reaction of CO₂ with alkynes catalyzed by HP-TpAzo@Ag^a

Entry	Alkyne	Product	Yield
1			94 [†] 82 [‡]
2			93 [†] 79 [‡]
3			92 [†] 47 [‡]

[a] Reaction conditions: alkyne (1.0 mmol), catal. (60 mg), Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 80°C, DMF (5 mL), 18 h.
‡ Yield using the HP-TpAzo@Ag.
‡ Yield using the TpAzo@Ag.

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