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Supporting information

Novel covalent organic frameworks: preparation, characterization and application

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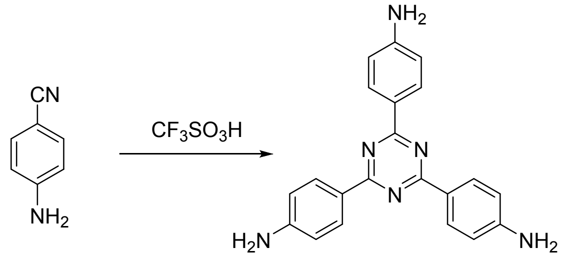
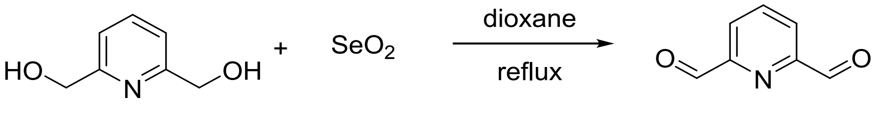
Synthesis of materials

1. Synthesis of 1,3,5-tris-(4-aminophenyl) triazine (TAPT)



1,3,5-Tris-(4-aminophenyl) triazine was prepared based on the reported procedure[1]. In a typical synthesis, 4-aminobenzonitrile (0.772 g, 6.538 mmol) was added in a round bottom flask at 0 ºC. Then trifluoromethanesulfonic acid (2.0 mL, 22.2 mmol) was added dropwise in 20 min. maintaining the temperature at 0 ºC. The resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, distilled water (20 mL) was added to the mixture and it was neutralized by 2 M NaOH solution to pH= 7.0. The precipitate was filtered and washed with water to give pale yellow powder, then dried in vacuum at 100 ºC for 12h to afford TAPT. Yield: 62.2%. ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm} = 8.39 (d, J = 4 Hz, 6H), 6.73 (d, J = 4 Hz, 6H), 5.93 (s, 6H).

2. Synthesis of 2,6-diformylpyridine (DAP)



2,6-Bis(hydroxymethyl) pyridine (695.8 mg, 5 mmol), 1,4-dioxane (25 mL) and SeO_2 (554.8 mg, 5 mmol) were added to a 100 mL round-bottom flask. The reaction mixture was stirred under reflux until the disappearance of 2,6-bis(hydroxymethyl) pyridine (about 6h, monitoring by TLC). The reaction mixture was immediately filtrated, and the filtrate was concentrated by evaporation. The obtained crude product was purified by silica gel column chromatography using dichloromethane-ethyl acetate (2:1) as an eluent.[2] Yield: 80.5%. ^{1}H NMR (400MHz, $CDCl_3$)

δ_{ppm} = 8.13-8.21 (m, 3H), 10.19 (s, 2H).

3. Synthesis of the amorphous component corresponding to TaDAP (TaDAP-A)

1,3,5-Tris-(4-aminophenyl) triazine (566.4 mg, 1.6 mmol), 2,6-diformylpyridine (325.0 mg, 2.4 mmol), N, N'-dimethylformamide (20 mL) were added to a 250 mL round bottom flask. The reaction mixture was stirred under reflux at N_2 atmosphere for 24h to yield a yellow precipitate, which was collected by centrifugation. After being washed with acetone and dichloromethane three times and dried in vacuum at 120 ^oC for 12h, the final product named TaDAP-A was obtained.

4. Synthesis of the amorphous component corresponding to TaDA (TaDA-A)

1,3,5-Tris-(4-aminophenyl) triazine (283.2 mg, 0.8 mmol), 1,3-benzenedialdehyde (161.0 mg, 1.2 mmol), N, N'-dimethylformamide (10 mL) were added to a 100 mL round bottom flask. The reaction mixture was stirred under reflux at N_2 atmosphere for 24h to yield a yellow precipitate, which was collected by centrifugation. After being washed with acetone and dichloromethane three times and dried in vacuum at 120 ^oC for 12h, the final product named TaDA-A was obtained.

5. Process of adsorbing Cr^{3+} and Al^{3+}

TaDA (9 mg) was added to the solution of Cr^{3+} and Al^{3+} (1 mL, 1M), respectively. The mixture was sonicated for 1 h and then stood still for 4 h. After being filtered under reduced pressure and dried in vacuum, their PXRD were conducted.

Supplementary Figures

1. Thermogravimetric Analysis

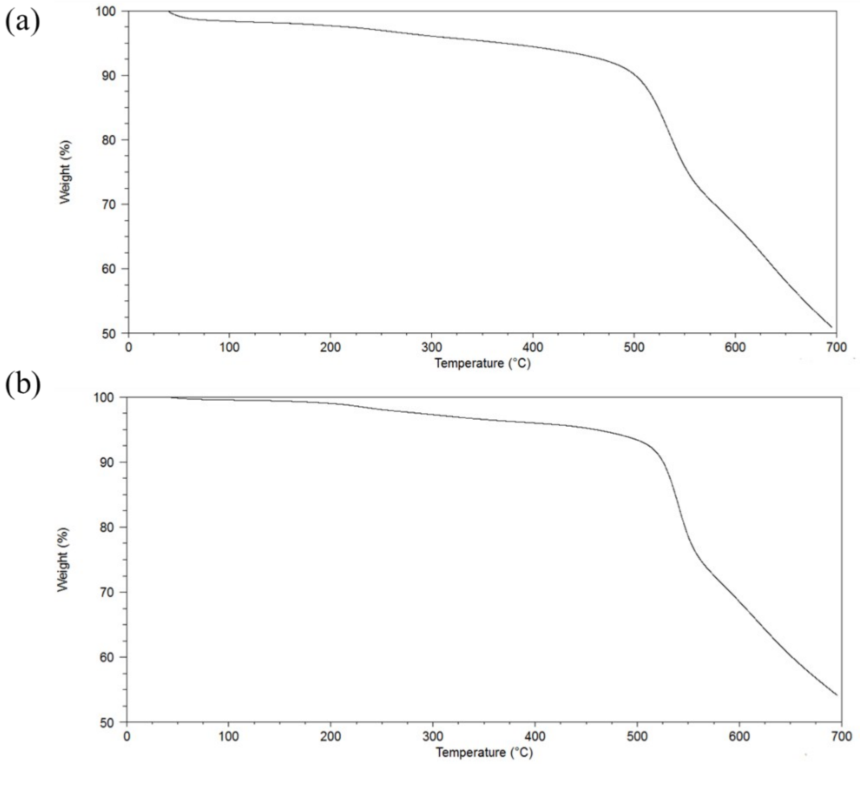


Fig. S1 TGA data of TaDAP(a) and TaDA(b)

2. Structural simulation and refinement

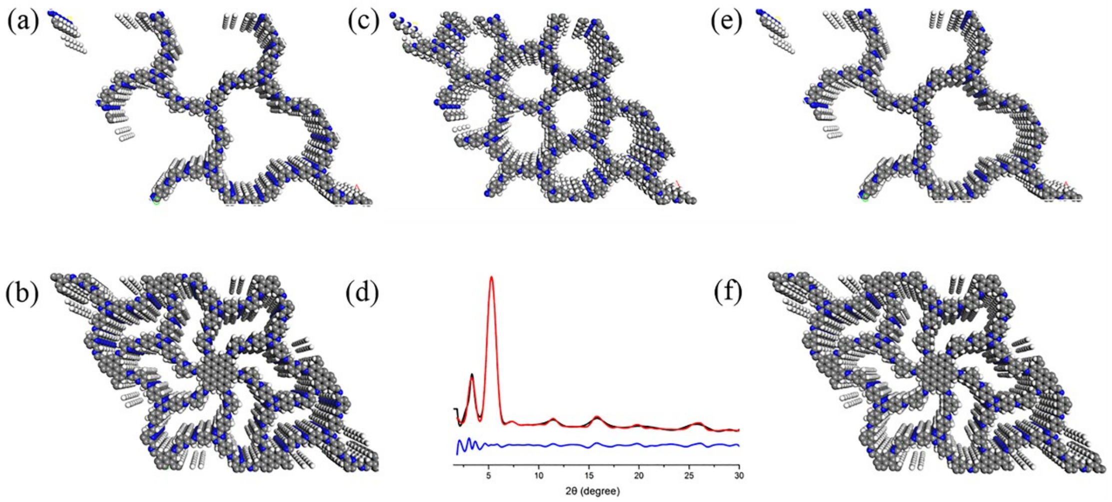


Fig. S2 (a) Simulated AA-stacking mode and (b) AB-stacking one of TaDAP; (c) Optimal simulated mode of TaDA; (d) Observed PXRD pattern (red, the major reflections are assigned) and refined modeling profile (black) of TaDA; (e) Simulated AA-stacking mode and (f) AB-stacking one of TaDA (gray, carbon; white, hydrogen; blue, nitrogen)

3. Compared PXRD between experimental and simulated

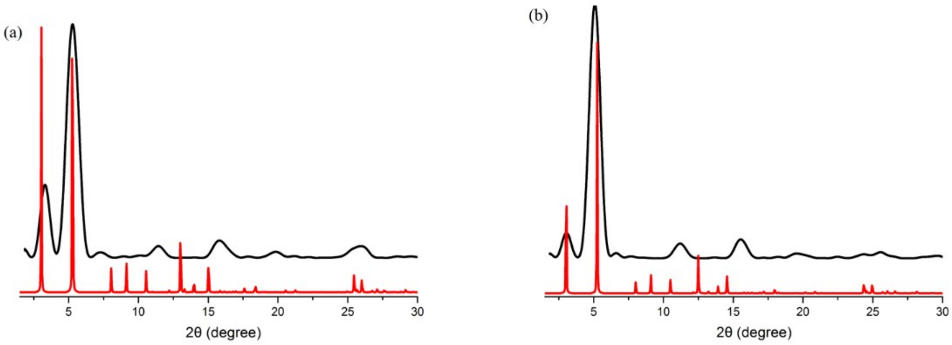


Fig. S3 (a) PXRD of TaDAP (black) and its optimal simulation (red); (b) PXRD of TaDA (black) and its optimal simulation (black)

4. Fluorescence spectra TaDAP-C and TaDAP-A

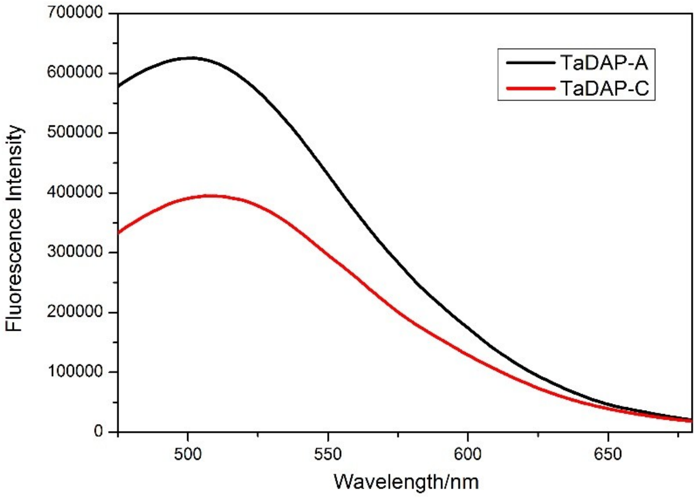


Fig. S4 Fluorescence spectra of TaDAP (TaDAP-C) and its corresponding amorphous component (TaDAP-A)

5. Fluorescence spectra of TaDA-C and TaDA-A

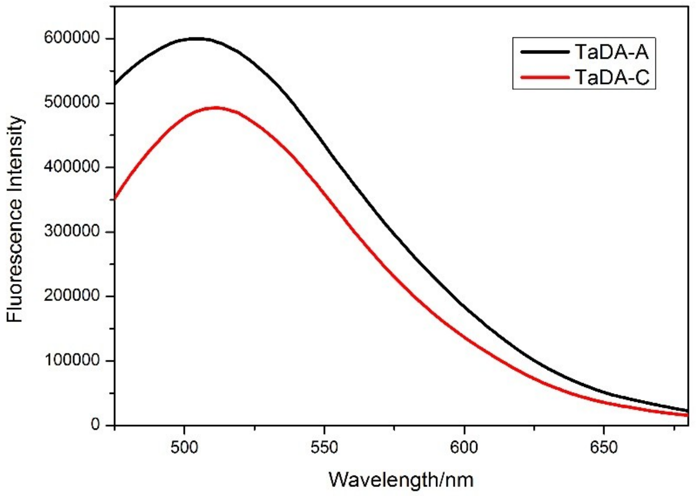


Fig. S5 Fluorescence spectra of TaDA (TaDA-C) and its corresponding amorphous component (TaDA-A)

6. PXRD patterns of TaDAP-A and TaDA-A

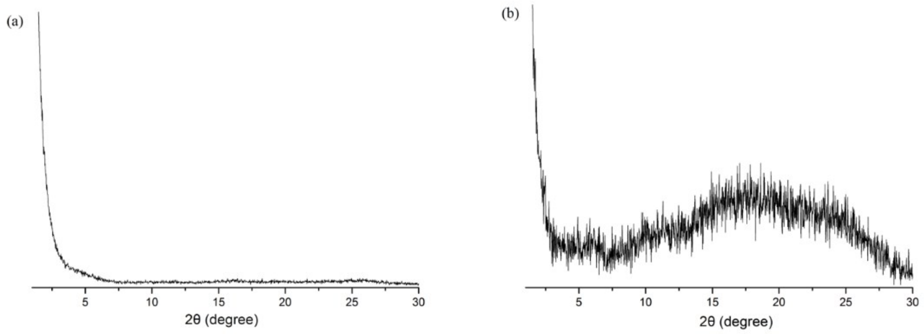


Fig. S6 PXRD patterns of TaDAP-A (a) and TaDA-A (b)

7. UV-Vis absorption spectra

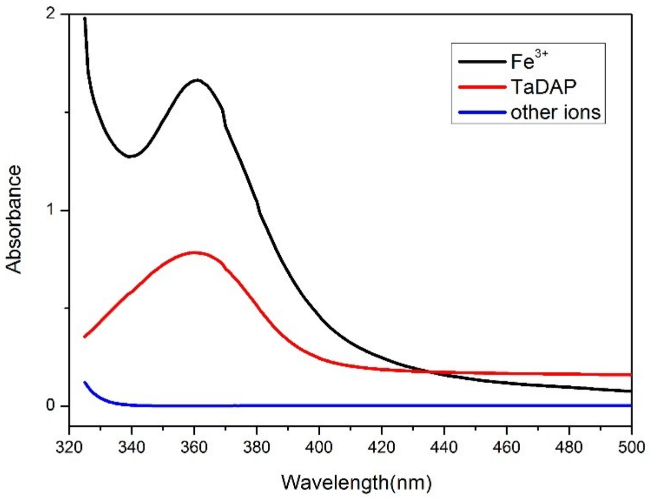


Fig. S7 UV-Vis absorption spectra of Fe^{3+}, TaDAP and other metal ions (Na^{+}, Ag^{+}, K^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Mg^{2+}, Cr^{3+}, Al^{3+})

8. Comparative PXRD patterns of TaDA before and after adsorbing Al^{3+} and Cr^{3+}

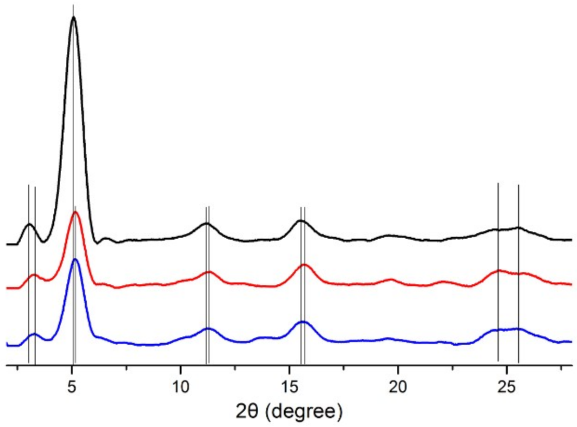


Fig. S8 PXRD of original TaDA (black) and after adsorbing Al^{3+} (red) and Cr^{3+} (blue)

Supplementary Tables

Table S1. Comparison of catalytic property of monomers and two COFs[a]

Catalyst	TAPT	DAP	DA	TaDAP	TaDA
Conversion[b]/ %	80.3	-	-	56.8	68.9

[a] Reaction conditions: benzaldehyde (2 mmol), malononitrile (2 mmol), toluene (2 mL), 90 °C, 8h.

[b] Conversion was determined by GC and based on benzaldehyde.

Table S2. Measured size of referred molecules and pore size of two COFs

	benzaldehyde	malononitrile	benzylidenemalononitrile	TaDAP	TaDA
Size/ Å	6.1	4.3	8.8	15.4	13.0

Table S3. Comparison of catalytic performance of TaDA and other materials

Entry	Catalyst	Ratio	Amount	Solvent	T[°C]	t [h]	Yield [%]	Ref.
1	TaDA	1:1	20 mg	toluene	100	8	>99	this work
2	$\{[Pb_4(\mu_8\text{-MTB})_2]\}_n$	1:1.5	50 mg	*p*-xylene	100	6	67	3
3	$\{[Eu(TATMA)(H_2O)_2 \cdot H_2O\}_n$	1:1.2	100 mg	toluene	80	3	98	4
4	PAF_{Ad}-NProRh	1:0.84	2 mol %	toluene	90	12	80	5
5	$\{[Co_{24}(BDPO)_{12}(H_2O)_{12}] \cdot 18DMF \cdot 40H_2O\}_n$	1:1.1	100 mg	toluene	80	3	97	6
6	NH_2-MONNs	1:4	5 mg	toluene	80	0.75	>99	7
7	LZU-301	1:3	0.04 mmol	MeCN	60	6	72	8
8	LZU-101	1:3	0.04 mmol	MeCN	60	6	21	8
9	COF-320	1:3	0.04 mmol	MeCN	60	6	42	8
10	MPU	1:1.1	18 mg	THF	50	14	98	9
11	MOF-NH_2	1:1	013 mmol	DMF	80	4.5	51	10
12	$\{[Ni_4(\mu_6\text{-MTB})_2(\mu_2\text{-}H_2O)_4(H_2O)_4] \cdot 10DMF \cdot 11H2O\}_n$	1:1.5	50 mg	*p*-xylene	130	6	78	11
13	Fe(BTC)	1:1.5	200 mg	xylene	80	5	33	12
14	BF-COF-1	1:1	5 mol%	benzene	25	10	96	13

Reference

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