Electronic Supporting Information (ESI)

Room-temperature synthesis of crystalline one-dimensional covalent organic frameworks

Xin Jiang, Menghao Lin, Can Deng, Xiao Xue, Chenyang Lu, Luxi Tan, Lichun Dong* and Cailong Zhou*

School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China

* Corresponding authors: lcdong72@cqu.edu.cn (L. Dong); cezcl@cqu.edu.cn (C. Zhou)

Experimental section

Materials

Tetrakis(4-aminophenyl)ethene (ETTA) was purchased from Beijing InnoChem Science & Technology Co., Ltd. 1,1-Diphenyl-2,2-di(4-formylphenyl)ethylene (TPEDH) was purchased from Shanghai Titan Scientific Co., Ltd. 4,4"-*m*-Terphenyldicarboxaldehyde and 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetraaniline were purchased from Shanghai Bide Pharmatech Co., Ltd. Acetic acid (AcOH) was purchased from Shanghai J&Z Biochemical Co., Ltd. Ethanol, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), *n*-hexane, methanol, dichloromethane (DCM), Span 80 and cyclohexane were purchased from Chengdu Cologne Chemical Co., Ltd. Isooctane and *n*-butanol were purchased from Shanghai Macklin Biochemical Co., Ltd. Xylenes was purchased from Beijing Merida Technology Co., Ltd. Mesitylene was purchased from Shanghai Meiruier Chemical Technology Co., Ltd. Karl Fischer reagent was purchased from Tianjin Comio Chemical Reagent Co., Ltd.

Preparation of 1D COFs

The synthetic condition of the COFs could be seen in Table S1. Taking ETTA-TPE as an example, 8.8 mg of ETTA (0.0225 mmol) and 12.9 mg of TPE (0.045 mmol) were added to a 10 mL glass vial. Then 0.75 mL of a mixture of *n*-butanol, acetic acid, and water was added into the vial. The vial was sealed and stirred at a speed of 200 r/min for 48 hours at room temperature (about 20-25 ^{o}C). After the reaction, the mixture was filtered through a nylon membrane with the pore size of 0.45 μm. The obtained precipitate was washed with ethanol, DMF, and THF until the filtrate becomes clear. After that, the resulting powder was dried under vacuum at 60 °C for 12 hours. Depending on the reaction time, the products were designated as ETTA-TPE-24/48/72h.

Table S1. The synthetic condition of the COFs.

COF	*n*-Butanol (mL)	H_2O (mL)	AcOH (mL)	Aldehyde monomer (mg)	Amine monomer (mg)	Reaction time (h)
ETTA-TPE	0.503	0.075	0.172	12.9	8.8	24/48/72
ETTA-TPEDH				17.5	8.8	24/48/72
PyTTA-TPE				12.9	12.8	24/48/72

Oil-water separation

The oil-water separation capability of ETTA-TPEDH was investigated through absorption measurements and separation tests. In the absorption measurements, a predetermined amount of COFs was used to adsorb oil. The oil absorption capacity was defined as the weight of oil adsorbed per unit weight of COFs, expressed as g g^{-1} for ETTA-TPEDH. In each adsorption-desorption cycle, the COFs were washed three times with methanol.

The separation test was conducted by filtering a water-in-oil emulsion. The emulsion was prepared by mixing 1 mL of deionized water, 99 mL of oil, and 0.8 g/L Span 80, followed by magnetic stirring and ultrasonication for 20 minutes. A self-made simple setup was used for the emulsion separation: the COF powder was packed into the tip of a syringe with cotton as a support. The emulsified water-in-oil mixture was then poured into the syringe and gently pressed from the top side of the emulsion at a constant pressure using a nylon filter plunger. After separation, the separation efficiency (η) of the emulsified oil was calculated according to Eq. S1:

$$\eta = (1 - \frac{A \cdot F}{W}) \times 100\% \quad \text{(S1)}$$

Where A is the volume (mL) of Karl Fischer reagent consumed by the filtrate; $F = x/y$, x and y denote the weight (mg) of water and the volume (mL) of Karl Fischer reagent consumed for the water titration, respectively; and W is the weight of the collected filtrate.

Characterization

Fourier transform infrared (FTIR) spectra were collected on a Nicolet iS50 Spectrometer. X-ray diffraction (XRD) patterns were collected at the 2θ range of 2°-40° using a Malvern Panalytical Empyrean X-ray diffractometer. Water contact angles (WCA) were obtained from a Defnuo ZR-SDJ-QH contact angle analyzer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA 2 instrument by heating samples from 30 to 800 ℃ under nitrogen atmosphere with a heating rate of 10 ℃ min^{-1}. N_2 adsorption-desorption test was performed on an automatic volumetric adsorption apparatus (Micrometrics ASAP 2460). The ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) spectra were performed on JNM-ECZL600G solid state spectrometer with a 3.2-mm double-resonance MAS NMR probe and at a sample spinning rate of 18.0 kHz. High-resolution transmission electron microscopy (HRTEM) images of COFs were gotten in a FEI Talos F200X

equipment operated at 200 kV. Scanning electron microscopy (SEM) was performed on a JEOL JSM-7800F. The moisture content in water-in-oil emulsion filtrate was measured by an Anting ZSD-2 moisture meter through the Karl-Fischer method.

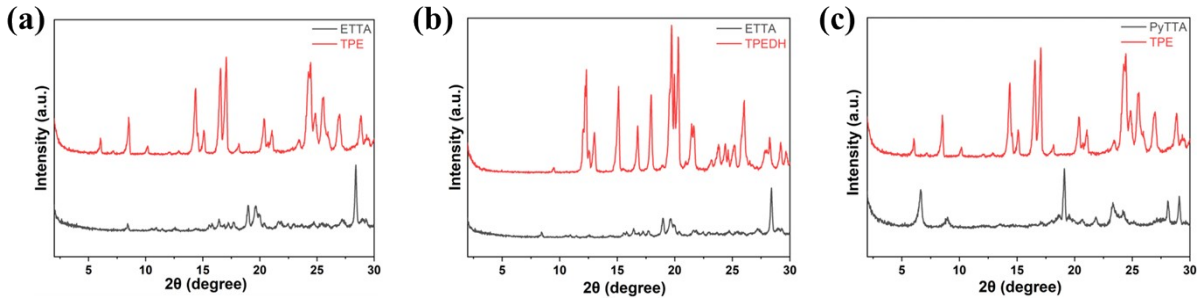

Fig. S1. PXRD patterns of the monomers: (a) ETTA and TPE, (b) ETTA and TPEDH, (c) PyTTA and TPE.

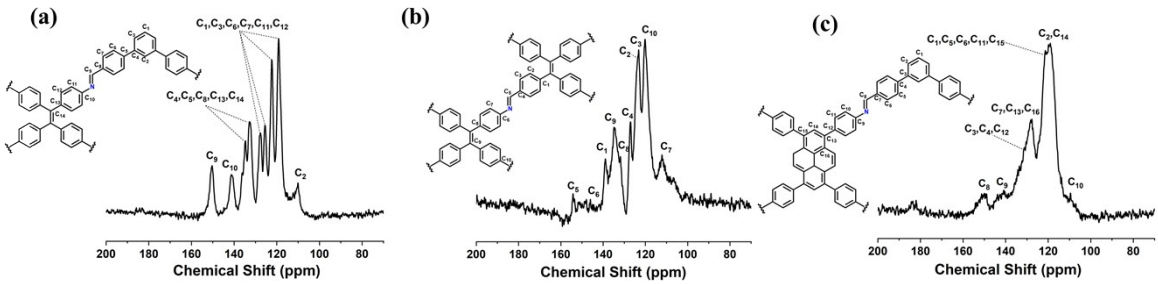

Fig. S2. Solid-state 13C CP-MAS NMR spectrum: (a) ETTA-TPE, (b) ETTA-TPEDH, (c) PyTTA-TPE.

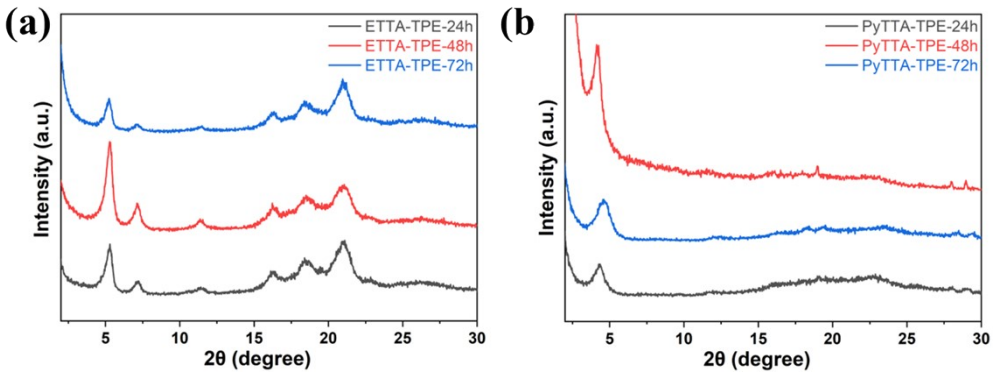

Fig. S3. PXRD patterns of the COFs obtained with different reaction time: (a) ETTA-TPE, (b) PyTTA-TPE.

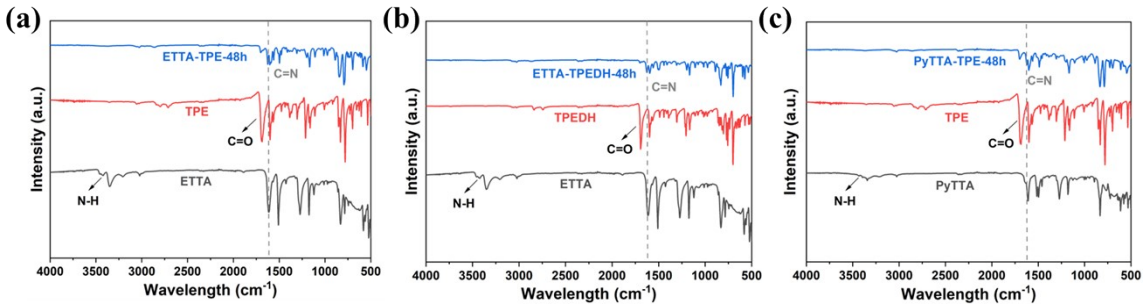

Fig. S4. FTIR spectra of the monomers and the COFs: (a) ETTA, TPE and ETTA-TPE. (b) ETTA, TPEDH and ETTA-TPEDH. (c) PyTTA, TPE and PyTTA-TPE.

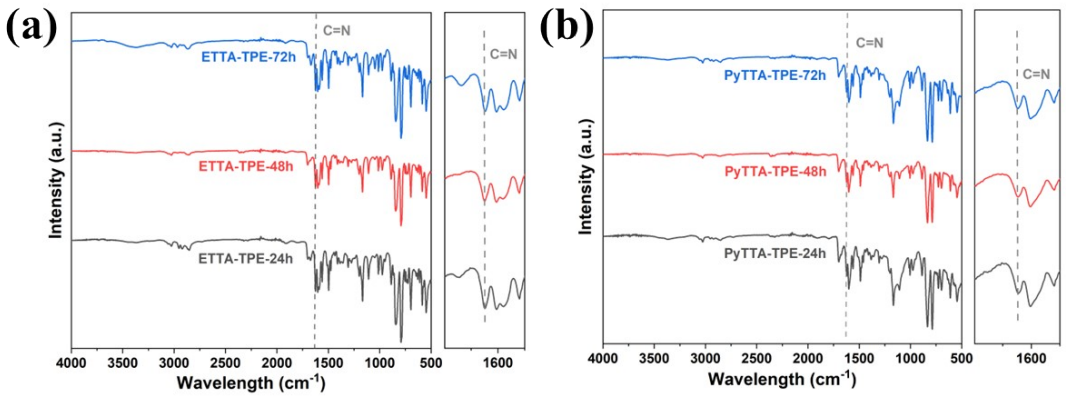

Fig. S5. FTIR spectra of the COFs obtained with different reaction time: (a) ETTA-TPE, (b) PyTTA-TPE.

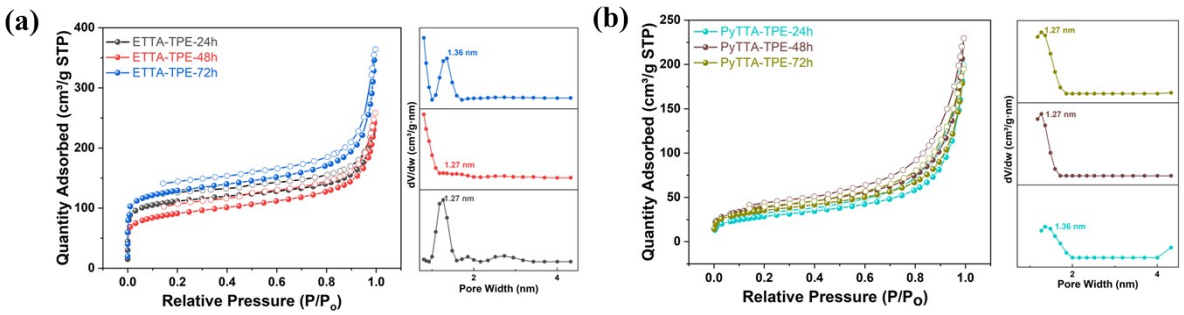

Fig. S6. N_2 sorption isotherms of (a) ETTA-TPE and (b) PyTTA-TPE under different reaction time (left). Pore size distribution of (a) ETTA-TPE and (b) PyTTA-TPE under different reaction time (right).

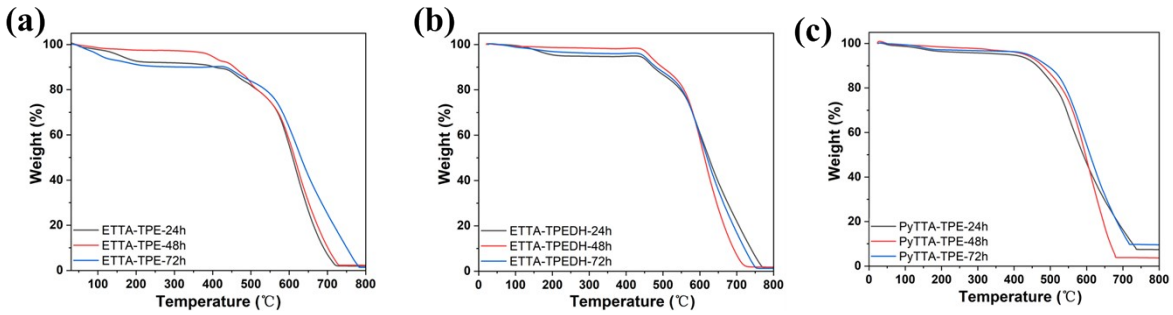

Fig. S7. TGA trace for samples of the COFs under N_2 atmosphere: (a) ETTA-TPE, (b) ETTA-TPEDH, and (c) PyTTA-TPE. The initial mass loss could be attributed to evaporation of water or tetrahydrofuran absorbed by the COFs.

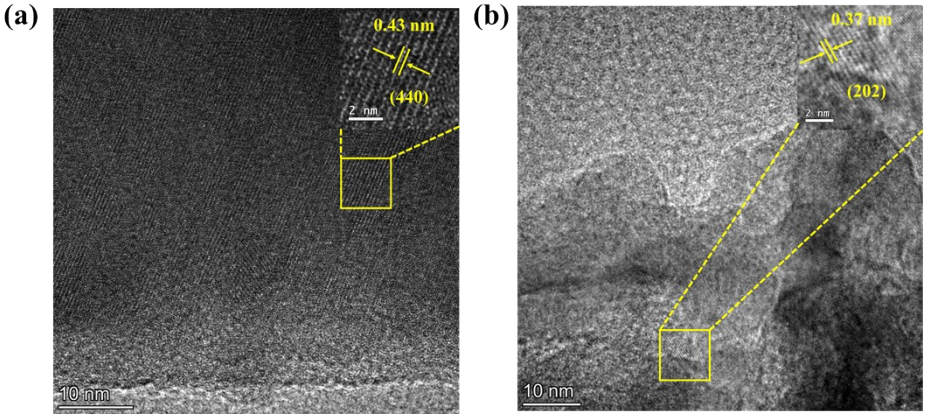

Fig. S8. HRTEM images of the 48-hour COFs: (a) ETTA-TPE, (b) PyTTA-TPE.

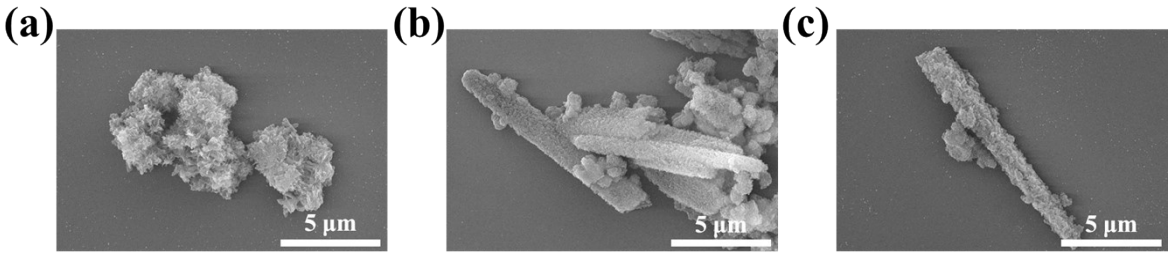

Fig. S9. SEM images of the 48-hour COFs: (a) ETTA-TPE, (b) ETTA-TPEDH, and (c) PyTTA-TPE.

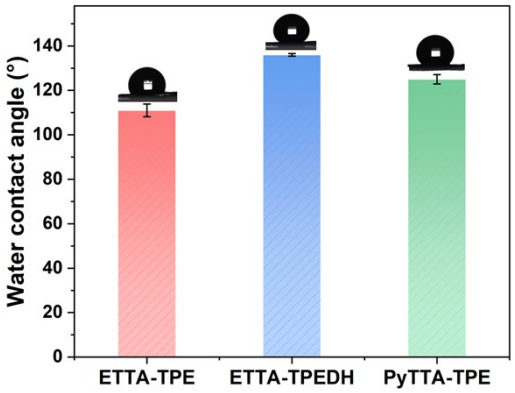

Fig. S10. Water contact angles of the 48-hour COFs.

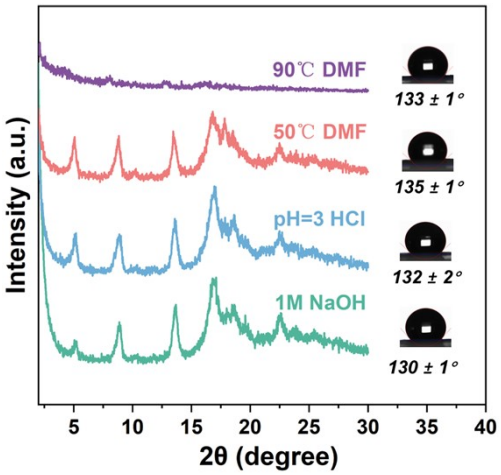

Fig. S11. PXRD patterns and WCAs showing the chemical stability

Table S2. Atomic coordinates and initial unit cell parameters of ETTA-TPE.

ETTA-TPE with eclipsed (AA) stacking mode **Space group symmetry: PMA2(28)** **a=26.2544 Å, b=21.7883 Å, c=5.0222 Å** **α=β=γ=90°**			
Atom	**x/a**	**y/b**	**z/c**
C1	1.35253	-0.09311	0.05694
C2	1.32858	-0.11339	-0.13166
C3	1.30504	-0.16598	-0.12678
C4	1.3017	-0.19707	0.06987
C5	1.3246	-0.17671	0.25987
C6	1.35008	-0.12485	0.25377
C7	1.27438	-0.25126	0.07587
C8	1.30257	-0.30477	0.06668
C9	1.30726	-0.33947	0.25394
C10	1.33344	-0.39041	0.24339
C11	1.35768	-0.40563	0.05021
C12	1.35462	-0.36957	-0.13667
C13	1.32677	-0.31968	-0.12777
N14	1.38484	-0.45794	0.05288
C15	1.41207	-0.47704	-0.10602
C16	1.43501	-0.53382	-0.09184
C17	1.43209	-0.56687	0.10123
C18	1.4536	-0.62079	0.11039
C19	1.47793	-0.64294	-0.07251
C20	1.48176	-0.60983	-0.26534
C21	1.45994	-0.55571	-0.27513
C22	1.50378	-0.69745	-0.04513
C23	1.4825	-0.75017	-0.10384
C24	1.50328	-0.80237	-0.03332
C25	1.54592	-0.80044	0.08997
C26	1.567	-0.7483	0.14629
C27	1.54555	-0.69713	0.08311
C28	1.47821	-0.85829	-0.06364
C29	1.45578	-0.87237	-0.26438
C30	1.42944	-0.92346	-0.28403
C31	1.4243	-0.96062	-0.10272
C32	1.44964	-0.94879	0.09243
C33	1.47629	-0.89799	0.11177
C34	1.39135	-1.01028	-0.11906
N35	1.38314	-0.04354	0.05053
H36	1.32793	-0.08936	-0.28393
H37	1.2892	-0.18253	-0.27646
H38	1.32427	-0.20256	0.4085
H39	1.37044	-0.11118	0.39833

H40	1.29004	-0.32723	0.40696
H41	1.33466	-0.41894	0.38502
H42	1.37447	-0.37811	-0.28728
H43	1.32501	-0.29183	-0.27121
H44	1.41747	-0.45297	-0.25604
H45	1.41366	-0.55081	0.2469
H46	1.4526	-0.64495	0.26354
H47	1.50348	-0.62443	-0.40338
H48	1.46313	-0.53051	-0.42472
H49	1.44755	-0.75031	-0.18338
H50	1.56183	-0.83942	0.15265
H51	1.59837	-0.74767	0.25143
H52	1.55982	-0.65711	0.14639
H53	1.45829	-0.84327	-0.40434
H54	1.41211	-0.93371	-0.43966
H55	1.44856	-0.97908	0.22939
H56	1.49526	-0.88953	0.26538
H57	1.37324	-1.01653	-0.27557

Table S3. Atomic coordinates and initial unit cell parameters of ETTA-TPEDH.

ETTA-TPEDH with eclipsed (AA) stacking mode **Space group symmetry: PMA2(28)** **a=34.1000 Å, b=19.4700 Å, c=4.7600 Å** **α=β=γ=90°**			
Atom	**x/a**	**y/b**	**z/c**
C1	-1.72955	-4.24063	0.26663
N2	-1.64918	-4.49554	0.13191
N3	-1.65609	-3.97683	0.29482
C4	-1.63168	-3.95244	0.46228
C5	-1.60908	-4.57626	-0.10422
C6	-1.58035	-4.58148	0.10349
C7	-1.55514	-4.63677	0.10686
C8	-1.55607	-4.68515	-0.10787
C9	-1.58374	-4.67827	-0.32384
C10	-1.61092	-4.62493	-0.31818
C11	-1.53419	-4.74955	-0.0668
C12	-1.5583	-4.8033	0.07653
C13	-1.4951	-4.75344	-0.13401
C14	-1.59759	-4.81306	-0.00819
C15	-1.62251	-4.85596	0.13625
C16	-1.60832	-4.89534	0.35783
C17	-1.56931	-4.88848	0.44083
C18	-1.54497	-4.83966	0.31317
C19	-1.47512	-4.69416	-0.27682
C20	-1.46939	-4.8158	-0.08858
C21	-1.45212	-4.70825	-0.51308
C22	-1.42654	-4.65928	-0.62062
C23	-1.4262	-4.59344	-0.51098
C24	-1.44988	-4.57704	-0.28373
C25	-1.4728	-4.62774	-0.15978
C26	-1.48327	-4.8838	-0.09134
C27	-1.45817	-4.93892	-0.03786
C28	-1.41887	-4.92735	-0.01447
C29	-1.40407	-4.8611	0.00356
C30	-1.42859	-4.80655	-0.05507
C31	-1.63545	-4.5181	-0.10374
C32	0.29446	0.69546	0.25111
C33	0.29388	0.82422	0.25838
C34	0.3233	0.68852	0.04483
C35	0.3415	0.62558	-0.00134
C36	0.33144	0.56874	0.16425
C37	0.30696	0.57831	0.39452
C38	0.29168	0.64298	0.44893
C39	0.29047	0.87059	0.03836

C40	0.30242	0.93819	0.06852
C41	0.32542	0.95623	0.2968
C42	0.33848	0.90427	0.47729
C43	0.32342	0.83791	0.45295

Table S4. Atomic coordinates and initial unit cell parameters of PyTTA-TPE.

PyTTA-TPE with eclipsed (AA) stacking mode **Space group symmetry: C2/M(12)** **a=38.4767 Å, b=25.1457 Å, c=3.9825 Å** **α=γ=90°, β=87°**			
Atom	**x/a**	**y/b**	**z/c**
C1	0.2501	0.5482	0.2472
C2	0.2158	0.5478	0.141
C3	0.2682	0.401	0.3036
C4	0.3019	0.3922	0.1619
C5	0.2517	0.3611	0.4983
C6	0.3185	0.3437	0.2081
C7	0.2687	0.3132	0.5529
C8	0.302	0.3037	0.4028
C9	0.3189	0.2519	0.4507
N10	0.3469	0.2391	0.2717
C11	0.3542	0.1462	0.472
C12	0.4178	0.1407	0.1026
C13	0.3745	0.1002	0.4812
C14	0.4071	0.0974	0.303
C15	0.3978	0.8131	0.0977
C16	0.3661	0.8097	0.2842
C17	-0.0712	0.4515	0.3241
C18	-0.0356	0.4513	0.4087
C19	-0.0173	0.5959	0.4586
H20	0.2024	0.5844	0.0924
H21	0.3148	0.4222	0.0067
H22	0.226	0.3675	0.615
H23	0.3442	0.3371	0.0896
H24	0.3072	0.2252	0.6363
H25	0.3299	0.1472	0.6188
H26	0.4707	0.1342	0.4373
H27	0.3654	0.0674	0.6371
H28	0.4067	0.7799	-0.0549
H29	0.256	0.2838	0.7139
H30	0.4419	0.139	-0.048
C31	0.2673	0.5	0.298
C32	0.1988	0.5	0.0866
C33	-0.0879	0.5	0.2781
C34	-0.0178	0.5	0.4525
H35	0.2936	0.5	0.3853
H36	0.1726	0.5	-0.0017
H37	-0.1148	0.5	0.2084