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Synthesis, preparation and characterization of pyridine-containing organic crystals with different substitute position using solvothermal method

Synthesis of TBOP

A mixture of 2-vinylpyridine (20.0 mmol, 2.2 mL), 2,8-dibromo-6*H*,12*H*-5,11-methanodibenzo [*b*,*f*] [1,5] diazocine (5.0 mmol, 1.9 g)， K_2CO_3 (20.0 mmol, 2.8 g), palladium acetate (0.001 mmol, 0.0023 g) and tris(2-methylphenyl) phosphine (0.001 mmol, 0.003 g) in NMP (10 mL) was stirred at 130 °C for 10 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 for three times. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2/Ethanol = 50/1 in the ratio of volume) to afford **TBOP** (0.84 g, 1.96 mmol) in 39% yield as a light yellow solid. ^1H NMR (400 MHz, DMSO-d_6), δ ppm: 8.53 (d, J = 3.9 Hz, 2H), 7.72-7.77 (m, 2H), 7.54 (d, J = 16.2 Hz, 2H), 7.45 (d, J = 7.8 Hz, 4H), 7.17- 7.26 (m, 6H), 7.13 (d, J = 7.2 Hz, 2H), 4.67 (d, J = 16.5 Hz, 2H), 4.27 (s, 2H), 4.18 (d, J = 16.8 Hz, 2H). ^{13}C NMR (75.47 MHz, DMSO-d_6), δ ppm 155.56, 149.88, 148.95, 137.19, 132.15, 132.08, 128.84, 127.21, 126.29, 126.09, 125.53, 122.59, 122.55, 66.66, 58.62. HRMS (ESI-TOF)) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{24}N_4$ 429.20737; Found 429.20694.

Synthesis of TBMP

First, 3-vinylpyridine was synthesized according to literature. A mixture of 3-vinylpyridine (20.0 mmol, 2.2 mL), 2,8-dibromo-6*H*,12*H*-5,11-methanodibenzo [*b*,*f*] [1,5] diazocine (5.0 mmol, 1.9 g)， K_2CO_3 (20.0 mmol, 2.8 g), palladium acetate (0.001 mmol, 0.0023 g) and tris(2-methylphenyl) phosphine (0.001 mmol, 0.003 g) in NMP (10 mL) was stirred at 130 °C for 10 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 for three times. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2/Ethanol = 50/1 in the ratio of volume) to afford **TBMP** (0.84 g, 1.96 mmol) in 39.4% yield as a light yellow solid. ^1H NMR (400 MHz, DMSO-d_6), δ ppm 8.69 (s, 2H), 8.41 (d, J = 4 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 9.6 Hz, 2H), 7.36 (d, 2H, J = 8 Hz, 2H), 7.25 (d, J = 16.5 Hz, 2H), 7.21 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 16.5 Hz, 2H), 4.67 (d, J = 16.7 Hz, 2H), 4.26 (s, 2H), 4.18 (d, J = 16.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6), δ ppm 148.24, 148.14, 148.07, 132.95, 132.51, 132.02, 130.07, 128.38, 125.54, 125.19, 125.07, 123.81, 123.57, 66.26, 58.21. HRMS (ESI-TOF)) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{24}N_4$ 429.20737; Found 429.20697.

General organic chemical synthesis of PHZOP

A solution of **TBOP** (0.193 g, 0.45 mmol) in a mixture of trifluoroacetic anhydride (0.5 mL, 3.6 mmol) and dichloromethane (1 mL) was stirred under a nitrogen atmosphere at room temperature for 1 h. The reaction was quenched with water and basified with saturated sodium hydrogen carbonate solution. The reaction mixture was extracted with dichloromethane (3 x 50 mL) and the organic layers were combined and washed with brine, dried over anhydrous sodium sulfate and distilled under reduced pressure to give a red solid. The red solid was dissolved in alkaline ethanol solution (100 mg sodium hydroxide dissolved in 5 mL ethanol) and stirred at room temperature until completion (TLC). The reaction mixture dissolved in a mixture of water and dichloromethane. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Then, the residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2/Ethanol = 100/1 in the ratio of volume) to afford brown-red solid **PHZOP** (0.059 g, 31.5%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.49 (d, J = 4.0 Hz, 2H), 7.73-7.68 (m, 2H), 7.48 (d, J = 16.0 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.25-7.23 (m, 4H), 7.16-7.13 (m, 2H), 6.95 (d, J = 16.0 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 6.40 (t, 2H), 4.50 (s, br, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.83, 149.35, 136.61, 132.29, 131.45, 126.88, 124.87, 124.54, 122.95, 121.46, 121.35, 117.12, 48.33. HRMS (ESI-TOF)) *m/z*: [M+H]$^+$ Calcd for $C_{28}H_{24}N_4$ 417.20737; Found 417.20673.

General organic chemical synthesis of PHZMP

A solution of **TBMP** (0.193 g, 0.45 mmol) in a mixture of trifluoroacetic anhydride (0.5 mL, 3.6 mmol) and dichloromethane (1 mL) was stirred under a nitrogen atmosphere at room temperature for 1 h. The reaction was quenched with water and basified with saturated sodium hydrogen carbonate solution. The reaction mixture was extracted with dichloromethane (3 x 50 mL) and the organic layers were combined and washed with brine, dried over anhydrous sodium sulfate and distilled under reduced pressure to give a red solid. The red solid was dissolved in alkaline ethanol solution (100 mg sodium hydroxide dissolved in 5 mL ethanol) and stirred at room temperature until completion (TLC). The reaction mixture dissolved in a mixture of water and CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Then, the residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2/Ethanol = 100/1 in the ratio of volume) to afford brown-red solid **PHZMP** (0.063 g, 3%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (t, J = 10.9 Hz, 2H), 8.36 (d, J = 4.1 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 6.4 Hz, 4H), 7.14 (m, 4H), 6.89 (m, 2H), 6.66 (m, 2H), 6.34 (s, 1H), 5.22 (s, 1H), 4.40 (s, br, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.14, 147.72, 133.59, 131.94, 131.05, 128.89, 126.43, 125.35, 124.61, 123.76, 119.63, 117.18, 48.47. HRMS (ESI-TOF)) *m/z*: [M+H]$^+$ Calcd for $C_{28}H_{24}N_4$ 417.20737; Found 417.20676.

Table S1 Solution systems and products from solvothermal experiments.

DMF/ H_2O	**Product**	**MeOH/ H_2O**	**Product**	**EtOH/ H_2O**	**Product**
1:0	Amor. **TBOP/**Amor. **TBMP**	1:0	Amor. **TBOP/**Amor. **TBMP**	1:0	Amor. **TBOP/**Amor. **TBMP**
2:8	Amor. **TBOP/**Amor. **TBMP**	2:8	Amor. **TBOP**+Cyrs. **TBOP**/ Amor. **TBMP**+Cyrs. **TBMP**	2:8	Amor. **TBOP**+Cyrs. **TBOP**/ Amor. **TBMP**+Cyrs. **TBMP**
3:7	Crys. **PHZOP**/Crys. **PHZMP**	3:7	Crys. **TBOP**/Amor. **TBMP**	3:7	Crys. **TBOP**/Amor. **TBMP**
4:6	Crys. **PHZOP**/Crys. **PHZMP**	4:6	Crys. **TBOP**/Cyrs. **TBMP**	4:6	Crys. **TBOP**/Cyrs. **TBMP**
5:5	Amor. **TBOP/**Amor. **TBMP**	5:5	Crys. **TBOP**/Cyrs. **TBMP**	5:5	Crys. **TBOP**/Cyrs. **TBMP**
6:4	Amor. **TBOP/**Amor. **TBMP**	6:4	Crys. **TBOP**/Cyrs. **TBMP**	6:4	Crys. **TBOP**/Cyrs. **TBMP**
7:3	Amor. **TBOP/**Amor. **TBMP**	7:3	Crys. **TBOP**/Amor. **TBMP**	7:3	Crys. **TBOP**/Amor. **TBMP**
2:8	Amor. **TBOP/**Amor. **TBMP**	2:8	Amor. **TBOP**+Cyrs. **TBOP**/ Amor. **TBMP**+Cyrs. **TBMP**	2:8	Amor. **TBOP**+Cyrs. **TBOP**/ Amor. **TBMP**+Cyrs. **TBMP**
0:1	Amor. **TBOP** / Amor. **TBMP**				

Amor. is the abbreviation of amorphous; Crys. is the abbreviation of crystalline.

Table S2 $\pi\cdots\pi$ interactions in **PHZMP** crystals.

D-H···Cg	H···Cg / Å	X-H···Cg / °	X-H, Cg / °	X···Cg / Å
C5-H5···Cg4	2.62	131	47	3.307
C10-H10···Cg2	2.86	136	56	3.5894
C14-H14A···Cg4	2.78	115	37	3.308
C14-H14B···Cg4	2.91	105	34	3.308
C18-H18···Cg1	2.88	124	49	3.489
C25-H25···Cg3	2.98	132	54	3.672
C27-H27···Cg3	2.63	142	51	3.412
C27-H27···Cg1	3.039	130	67	3.711

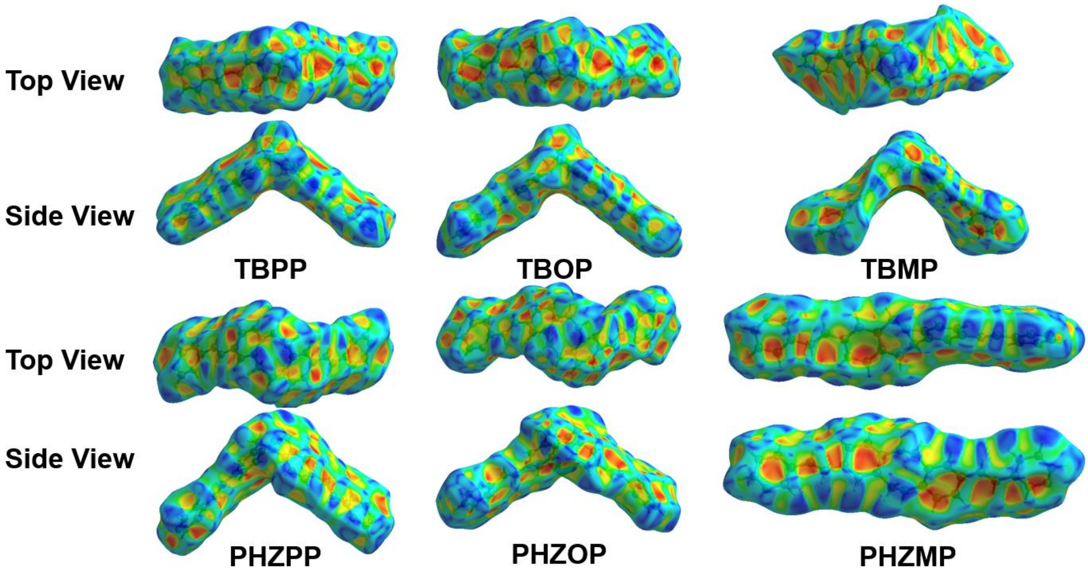

Fig. S1 Hirshfeld surface of **TBPP**, **TBOP**, **TBMP**, **PHZPP**, **PHZOP**, and **PHZMP** mapped with d_{norm}.