Supplementary Information

Porphyrin-based two-dimensional covalent organic frameworks: Synchronized synthetic control of macroscopic structures and pore parameters

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Contents

Section A. Materials and Methods

p-(1,3,2-dioxaborinan-2-yl)benzaldehyde, anhydrous 1,4-dioxane (99.8%) and anhydrous acetone (99.8%) were purchased from Wako Chemicals. Boron trifluoride ethyl ether complex and mesitylene (98%) were purchased from TCI. 2,5-didydroxy-1,4-benzoquinone, pyrrole and tetrachloro-1,4-benzoquinone were purchased from Aldrich. Hydrochloric acid and other common solvents were purchased from Kanto Co. Ltd. Silica gel Wakogel C-200HG was used for column chromatography. Deuterated solvents for NMR measurements were obtained from Cambridge Isotope Laboratories, Inc. 1,2,4,5-Tetrahydroxybenzene (THB) was prepared according to the method reported.[S1]

^{1}H and ^{13}C NMR spectra were recorded on JEOL models JNM-LA400 NMR spectrometers, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Infrared (IR) spectra were recorded on a JASCO model FT IR-6100 Fourier transform infrared spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF-MS) spectra were recorded on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode. Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-6700 FE-SEM operating at an accelerating voltage of 5.0 kV. The sample was prepared by drop-casting a dioxane suspension onto mica substrate and then coated with gold. X-ray Powder diffraction (XRPD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 2θ = 1.5° up to 60° with 0.02° increment. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the nonlinear density functional theory (NLDFT) model, the pore volume and pore width distribution were derived from the sorption curves.

Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from XRPD pattern, implemented in MS modeling ver 4.4 (Accelrys Inc.) [S2]. Unit cell dimension was first manually determined from the observed XRPD peak positions using the coordinates. We performed Pawley refinement to optimize the lattice parameters iteratively until the RWP value converges. The refinement indicates a tetragonal

crystal system with a unit cell of $a = b = 24.4340$ Å and $c = 3.8298$ Å. The pseudo-Voigt profile function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The final R_{WP} and R_P values were 18.36% and 8.59%, respectively. Simulated XRPD patterns were calculated for (1) an AA-stacking arrangement of $P4$ space group and (2) a staggered AB-stacking of $I4$ space group. After comparing each simulated pattern with experimentally observed pattern, the pattern from $P4$ shows good agreement with the observed XRPD pattern.

Section B. Synthetic Procedures

Preparation of 5,10,15,20-tetrakis[4-(1,3,2-dioxaborinan-2-yl)phenyl]-*21H,23H*-porphine.
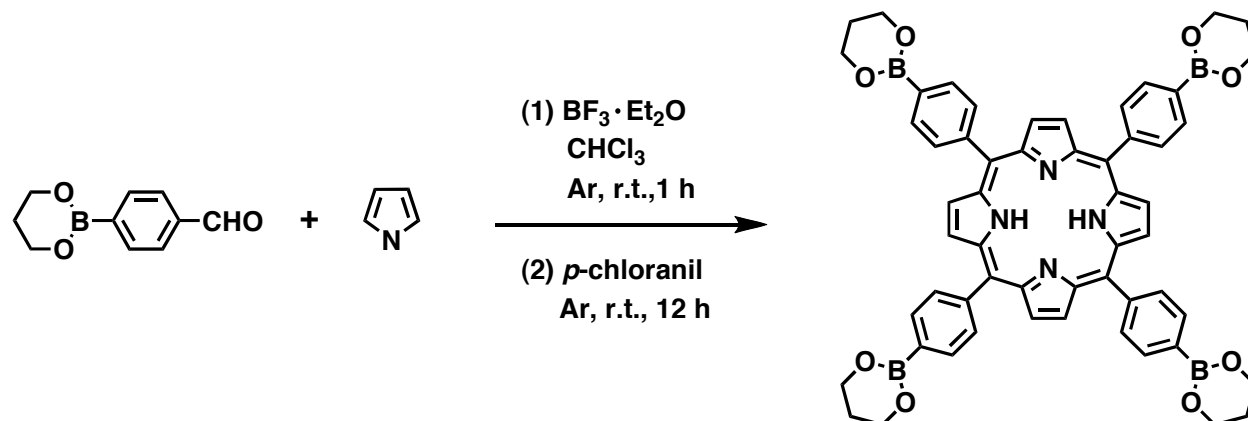

A chloroform solution (250 mL) containing pyrrole (0.14 mL, 2 mmol) and 4-(1,3,2-dioxaborinan-2-yl)-benzaldehyde (0.38 g, 2 mmol) was degassed with a stream of Ar for 30 min. To a solution was added with boron trifluoride ethyl ether complex (BF$_3$·Et$_2$O, 30 μL). After the reaction mixture was stirred at r. t. for 1 h under Ar, p-chloranil (0.74 g, 3 mmol) was added to the mixture, and the mixture was further stirred for 12 h. The solvent was evaporated and then the residue was purified by column chromatography (silica gel, CHCl$_3$/CH$_3$OH = 9.5/0.5 in vol.), yield 25.4%. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.81$ (s, 8H, CH of pyrrole), 8.13-8.20 (dd, $J = 12.0$ Hz, 16H, ArH), 4.30-4.33 (t, $J = 6.0$ Hz, 16H, CH$_2$), 2.17-2.21 (m, 8H, CH$_2$), -2.80 (s, 2H, NH of Pyrrole) ppm; ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 144.6, 134.2, 132.1, 120.4, 62.36, 27.75$ ppm; MALDI-TOF MS: m/z calcd 950.40 for C$_{56}$H$_{50}$B$_4$N$_4$O$_8$, found 950.07.

Preparation of 5, 10, 15, 20-tetrakis[4-(dihydroxyboryl)phenyl]-*21H,23H*-porphine.
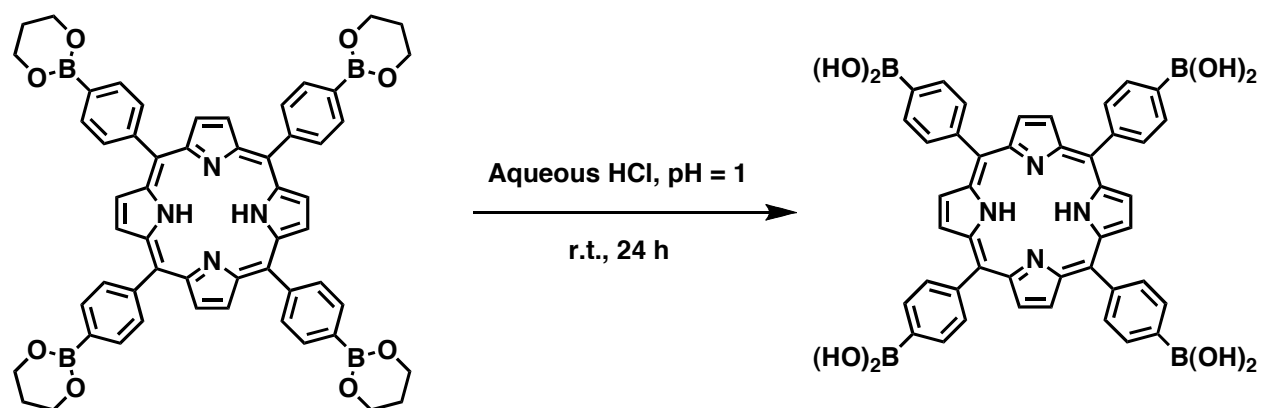
5,10,15,20-Tetrakis[4-(1,3,2-dioxaborinan-2-yl)phenyl]-*21H,23H*-porphine (95 mg, 0.1 mmol) was dissolved in THF (100 mL), an aqueous solution of HCl (pH = 1.0, 100 mL) was added to the mixture slowly. The mixture was stirred at room temperature for 24 h. CH_2Cl_2 (100 mL) was added to the mixture, and the organic layer was washed with aqueous solution of $NaHCO_3$ (100 mL × 3; 5% in wt) and water (100 mL × 3), and dried over anhydrous Na_2SO_4. The solution was concentrated under vacuum and poured into hexane (100 mL). The purple precipitate was collected by centrifugation, yield 80%. ^{1}H NMR (400 MHz, *d*[8]-THF): δ = 8.83 (s, 8H, CH of pyrrole), 8.18-8.23 (dd, *J* = 4.0 Hz ,16H, ArH), 7.47 (s, 8H, OH), -2.78 (m, 2H, NH of Pyrrole) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 145.0, 134.7, 133.5, 121.4 ppm; MALDI-TOF MS: *m/z* calcd 790.27 for $C_{44}H_{34}B_4N_4O_8$, found 790.01.

**Preparation of zinc(II) 5, 10, 15, 20-tetrakis[4-(dihydroxyboryl)phenyl]porphine (TDHB-ZnP).**
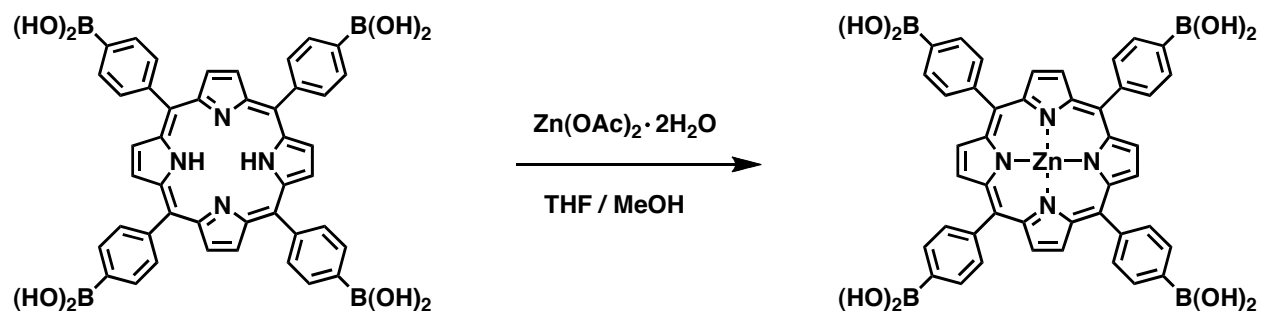
5,10,15,20-tetrakis[4-(dihydroxyboryl)phenyl]-*21H,23H*-porphine (159 mg, 0.2 mmol) was dissolved in THF (100 mL), and then a 100 mL solution of $Zn(OAc)_2 \cdot 2H_2O$ (88 mg, 0.4 mmol) in methanol was added. The mixture was stirred at room temperature for 12h. Water (100 mL) and CH_2Cl_2 (100 mL) was added to the reaction mixture to extract the compound, the organic layer was collected and then dried over Na_2SO_4. The solution was concentrated and then poured into hexane. The purple precipitate was collected by centrifugation, yield 85%. ^{1}H NMR (400 MHz, *d*[8]-THF): $\delta = 8.84$ (s, 8H, CH of pyrrole), 8.18 (s, 16H, ArH), 7.44 (s, 8H, OH) ppm; ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 151.1, 146.5, 134.9, 133.2, 132.4, 121.9$ ppm; MALDI-TOF MS: *m/z* calcd 852.19 for $C_{44}H_{32}B_4N_4O_8Zn$, found 851.76.

Synthesis of ZnP-COF

Typical Procedure: A mixture of TDHB-ZnP (17.1 mg, 0.02 mmol) and 1,2,4,5-tetrahydroxybenzene (THB; 5.7 mg, 0.04 mmol) in 1,4-dioxane/mesitylene (2 mL, 9/1 in vol.) in a 10 mL Pyrex tube was degassed through three freeze-pump-thaw cycles. The tube was sealed and heated at 120 °C for 6 days. The resulting precipitate was collected by centrifugation, washed with anhydrous acetone, and dried at 150 °C under vacuum to give ZnP-COF (17.3 mg) in 90% isolated yield as purple solid.

Condensation reactions of TDHB-ZnP with THB in mesitylene and mixtures of mesitylene and dioxane at different ratios were carried out according to the typical procedure under otherwise identical reaction conditions. Condensation reactions to prepare ZnP-COF samples at different reaction times were carried out according to the typical procedures under otherwise identical reaction conditions.

Section C. FT IR Spectral Profile
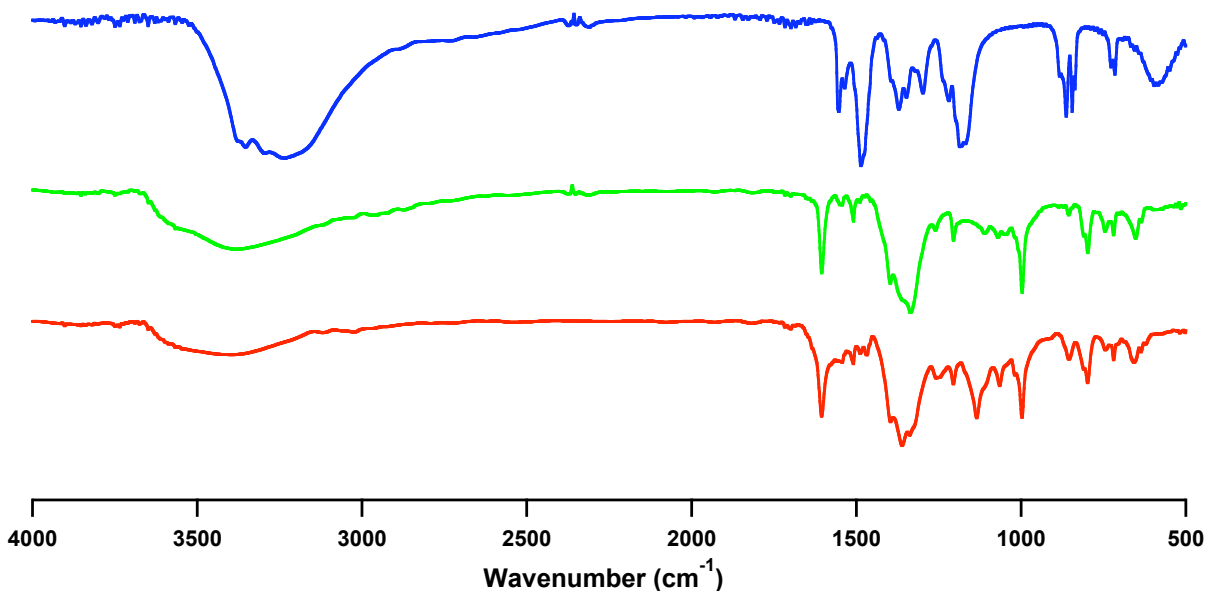
Fig. S1 IR spectra of THB (blue curve), TDHB-ZnP (green curve) and ZnP-COF (red curve).

**Table S1** Peak assignments for IR spectrum of ZnP-COF

Peak (cm^{-1})	Assignment and Notes
3400.85 (w)	O–H stretch of the end-groups B(OH)$_2$ or OH
1605.45 (s)	C=C stretch for phenyl ring
1542.77 (w) 1509.03 (w) 1487.81 (w) 1467.56 (w)	Skeletal vibration of porphyrin ring
1396.21 (m)	C=C vibration of phenyl ring
1361.50 (s)	B–O stretch (boronic ester)
1257.36 (w)	C–B stretch
1205.29 (w)	C–H in plane deformation
1134.90 (s)	C–O stretch (characteristic band for boronic ester)
997.98 (s)	C–B stretch
855.28 (w)	C–H out of plane deformation of *p*-substituted benzene
797.42 (m) 744.39 (w) 735.32 (w) 656.64 (w)	C–H out of plane deformation

Section D. Solid State ^{13}C CP/MAS NMR Spectroscopy
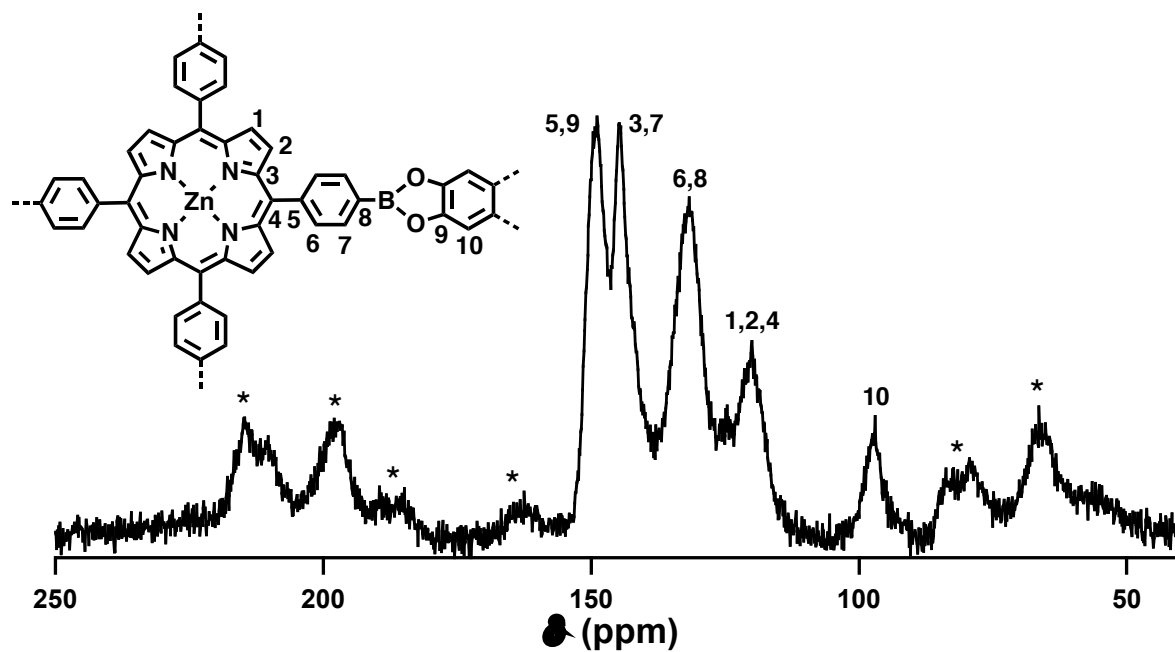
Fig. S2 Solid state ^{1}H-^{13}C CP/MAS NMR spectra of ZnP-COF (a CP contact time of 5ms), recorded at a MAS rate of 15 kHz. Signals with * are side bands.

Section E. FE-SEM Images

a

b

c

d
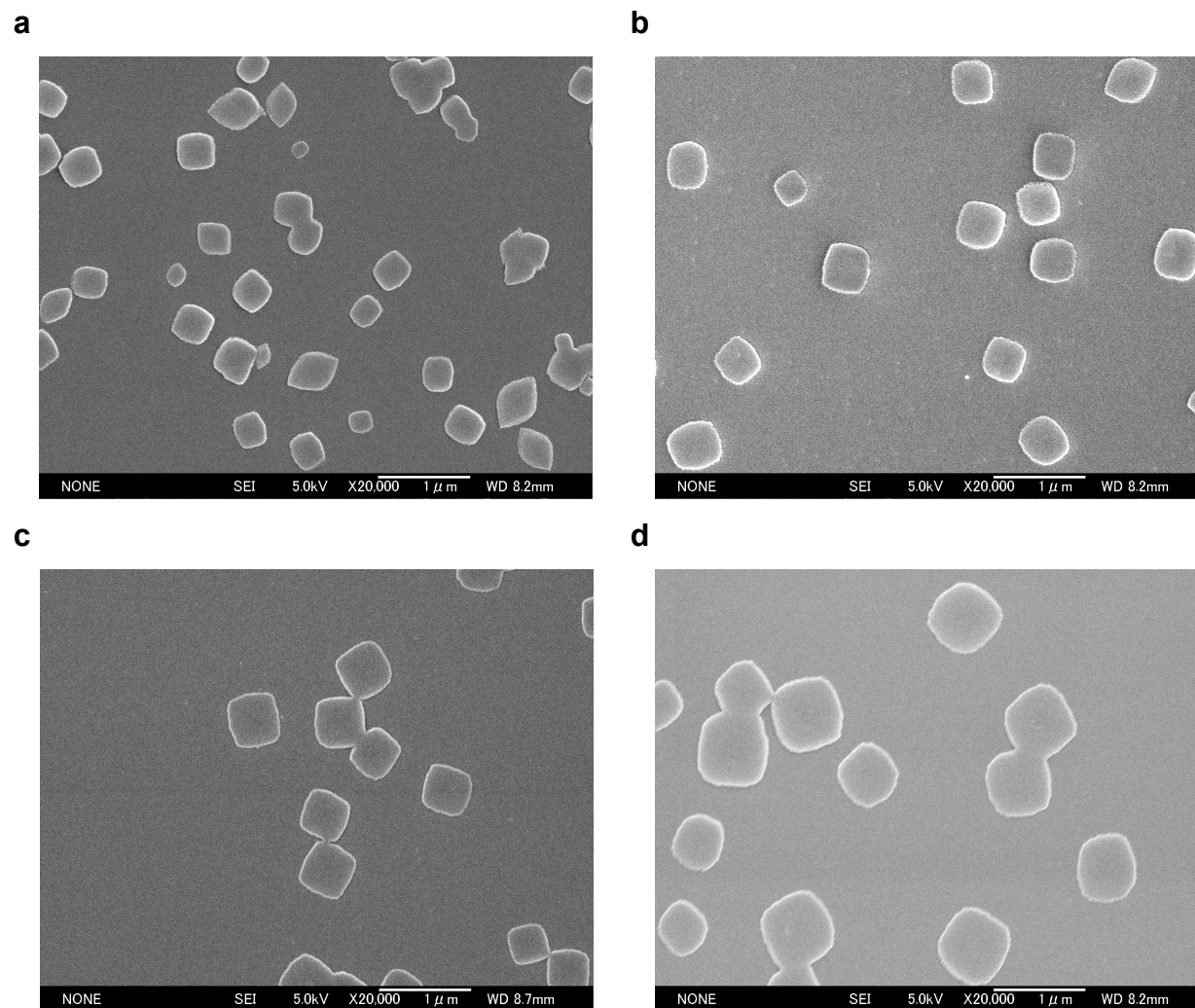
Fig. S3 FE-SEM images of ZnP-COF prepared after (a) 1, (b) 2, (c) 6 and (d) 15 day reactions.
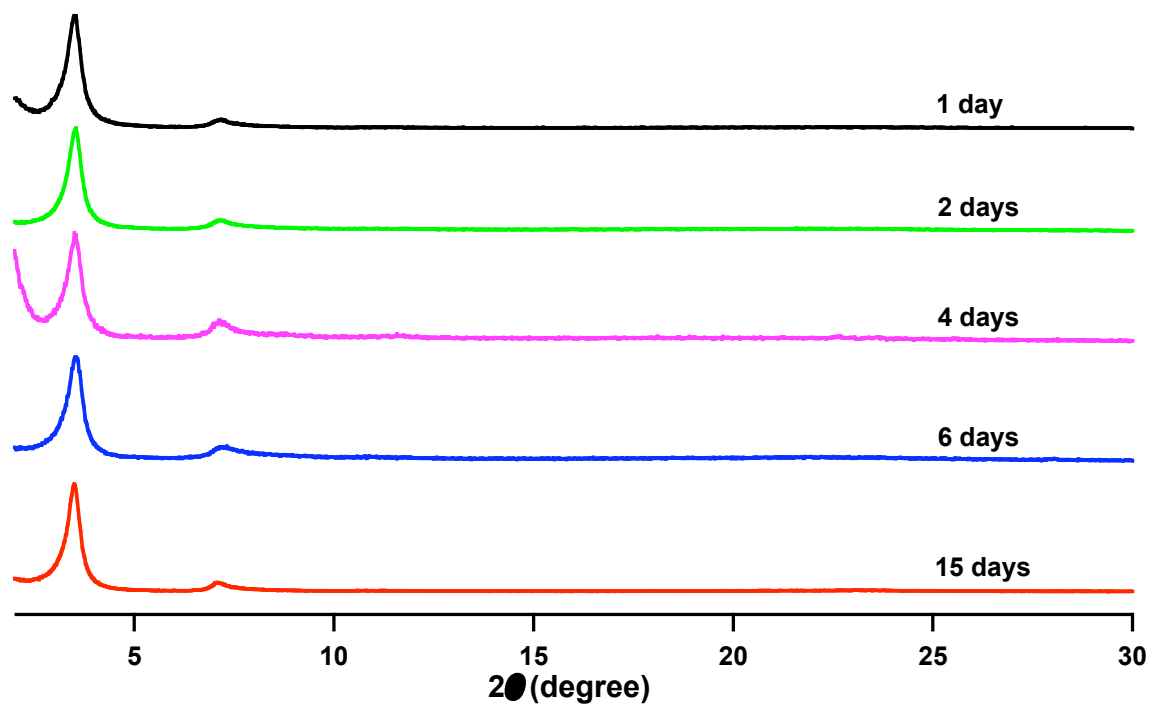
Section F. PXRD Patterns of ZnP-COF

Fig. S4 XRPD patterns of ZnP-COF prepared at different reaction times.
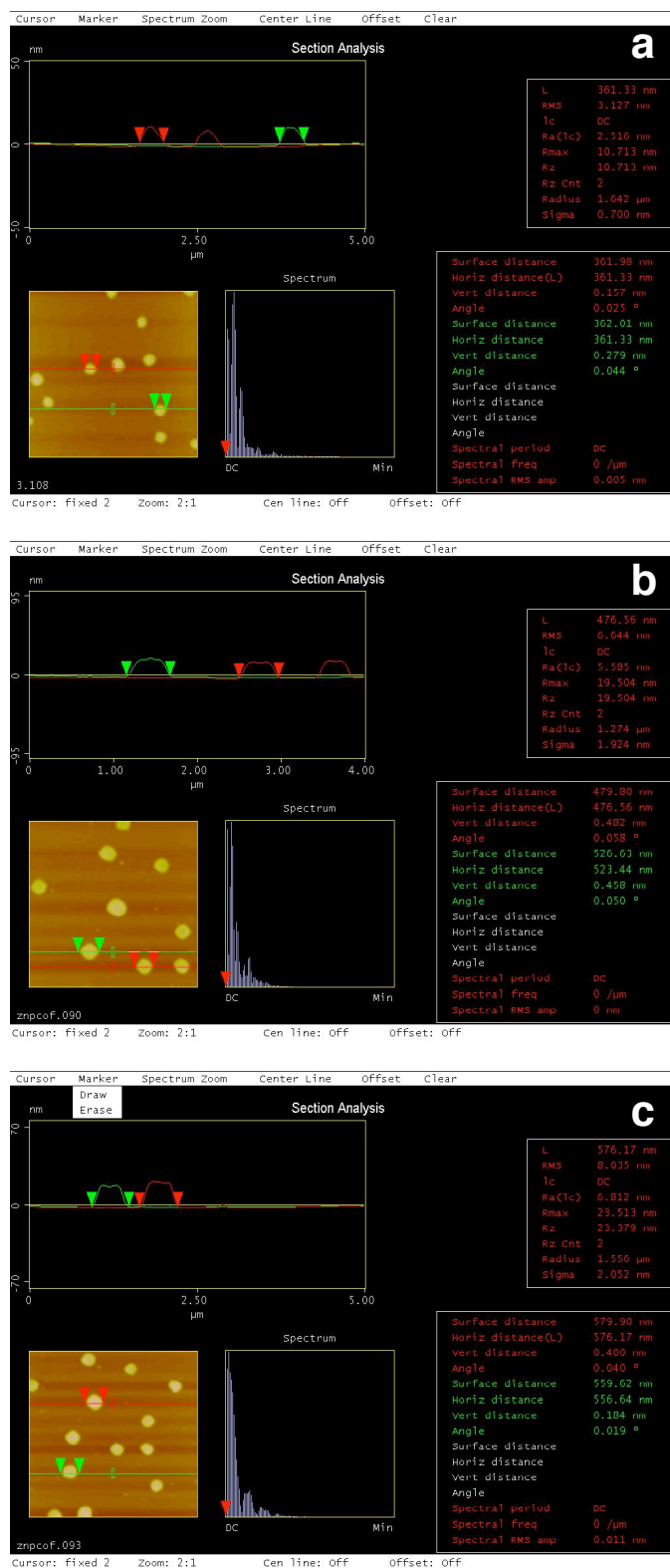
Section G. AFM Images

Fig. S5 AFM images of ZnP-COF prepared after (a) 1, (b) 4 and (c) 6 day reactions.

Section H. Supporting References

S1. P.R., Weider, L. S. Hegedus, H. Asada and S. V. Dandreq, *J. Org. Chem.*, 1985, **50**, 4276.

S2. Accelrys, Material Studio Release Notes, Release 4.4, Accelrys Software, San Diego 2009.