Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Section A. Materials and Methods

All chemicals and solvents were purchased from commercial suppliers including Energy Chemical Co., Ltd., J&K Chemical Co., Ltd., TCI (Shanghai) Development Co., Ltd. and Beijing Chemical Reagent Company, and used without further purification.

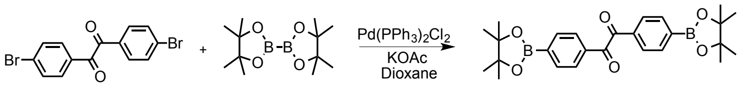
^{1}H NMR spectra were recorded on a Bruker ARX-400 spectrometer. The solid-state ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed on Agilent DD2 NMR 400 MHz NMR Spectrometer with one NMR probe. Electron ionization mass spectrometry (EI-MS) spectra were recorded on Agilent 6120 instrument. Powder X-ray diffraction (PXRD) patterns of the samples were measured with a Cu-Kα X-ray radiation source (λ = 0.154056 nm) incident radiation by a Rigaku MiniFlEX 600 instrument operating at 40 kV voltage and 50 mA current. The Fourier transform infrared attenuated total reflection (FT-ATR) spectra were recorded in the range 400-4000 cm^{-1} on Bruker ALPHA spectrometer. The measurement of Brunauer-Emmett-Teller (BET) surface area and pore size were performed at 77 K on a Quantachrome Instrument ASiQMVH002-5 after pretreatment (samples were degassed at 120 °C for 12 h). Elemental analyses including C, H were measured by VARIO EL-III Elemental Analyzer. Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) under N_2 atmosphere at a heating rate of 10 ^{o}C min^{-1} within a temperature range of 20-900 °C. Prior to the field-emission scanning electron microscopy (FE-SEM), the acetone suspension of COF and POP were dropped onto the Si/SiO_2, and then naturally dried. FE-SEM images were acquired from a JEOL model S-4800 scanning electron microscope.

The UV-Vis absorption spectra were recorded on a Shimadzu 2600 UV- Vis-NIR spectrophotometer. The photoluminescent (PL) spectra were recorded using a NanoLog fluorescence spectrometer (Nanolog FL3-2iHR, HORIBA JOBIN YVON). Time-resolved phosphorescence decay by delay was measured using an UltraFast lifetime Spectrofluorometer (Horiba Jobinyvon IBH Inc.).

We using the Pawley method ultrafine convergence quality mode in the Reflux module in Material Studio 7.0 software package to refine the experimental PXRD pattern. We chose the Pseudo-Voigt function and Berar-Baldinozzi asymmetry correction in the whole refinement procedure.

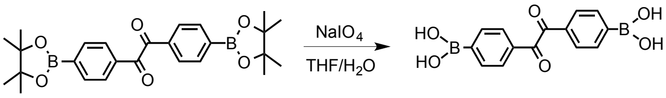
Section B. Synthetic Procedures

4,4’- benzildiboronic acid pinacol ester



4,4'-Dibromobenzil (0.198 g, 0.543 mmol, 1.0 equiv.), bis(pinacolato)diboron (0.303 g, 1.19 mmol, 2.2 equiv.), potassium acetate (0.319 g, 3.258 mmol, 6 equiv.), and $Pd(PPh_3)_2Cl_2$ (0.038 g, 0.0543 mmol, 10 mol %) were charged in an oven-dried 3-neck round bottomed flask, the solid mixture was pumped vacuum and then charged with N_2 for three cycles. The 1,4-dioxane (50 mL) was degassed with bubbling nitrogen for 20 minutes, then added to the solid mixture. The suspension was heated to reflux overnight. After the reaction was finished, the mixture was filtered and the filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography using dichloromethane/petroleum ether (1:2) as eluent. 4,4’-benzildiboronic acid pinacol ester was obtained as light green solid, (0.22 g, 0.47 mmol, 88 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 8H, Ar-H), 1.35 (s, 24H, CH_3). EI-MS (m/z): calcd. 462.24 for $C_{26}H_{32}B_2O_6$, found 231.12, 462.24.

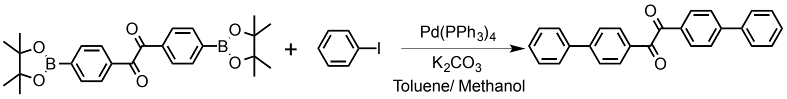
4,4’- benzildiboronic acid



4,4’-Benzildiboronic acid pinacol ester (0.15g, 0.325 mmol, 1.0 equiv.) and sodium periodate (0.42 g, 1.95 mmol, 6.0 equiv.) were stirred in 50 mL of a 4:1 mixture of THF and H_2O for 30 min, at which time aqueous hydrochloric acid (1N, 0.52 mL) was added to the suspension. The mixture was stirred at ambient temperature for 12 hours. After the reaction finished, the mixture was filtered, and concentrated to dryness by rotary evaporation. The crude product was washed with water, hexane and chloroform. 4,4’- benzildiboronic acid was obtained as light green solid, (0.09 g, 0.3

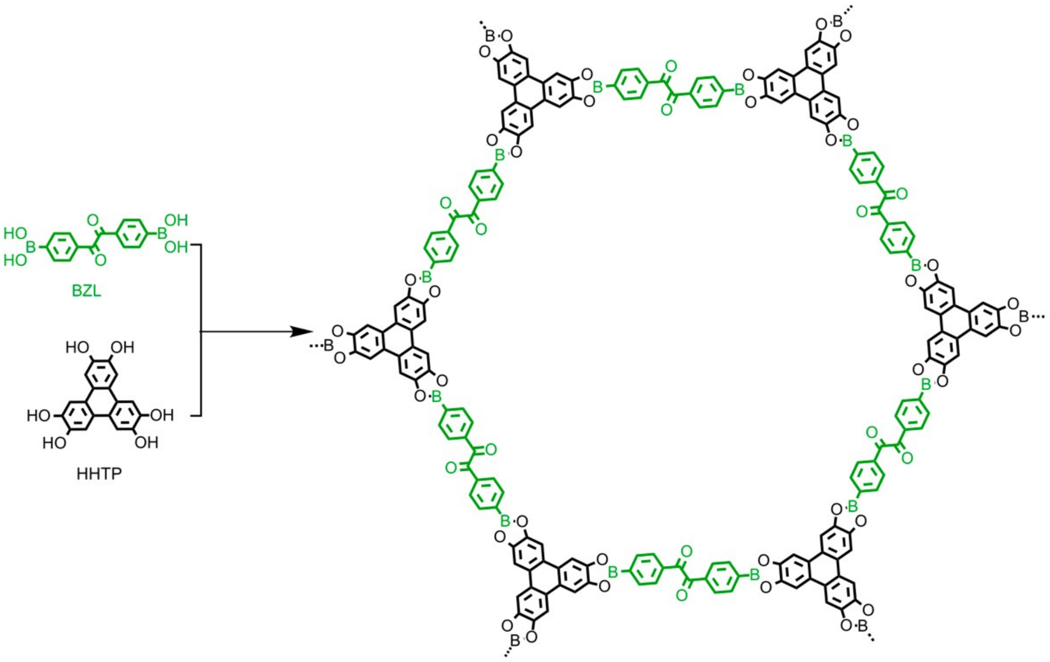
mmol, 93 % yield). ^{1}H NMR (400 MHz, DMSO) δ = 8.40 (s, 4H, OH), 7.98 (d, J = 7.2 Hz, 4H, Ar-H), 7.88 (d, J = 7.3 Hz, 4H, Ar-H).

4,4'- diphenylbenzil



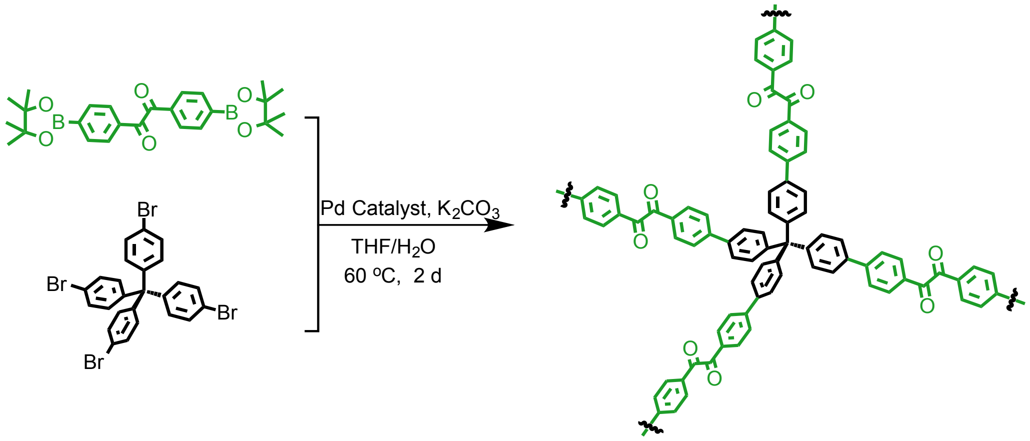
4,4'-Benzildiboronic acid pinacol ester (0.232g, 0.5 mmol, 1.0 equiv.), Iodobenzene (0.306g, 1.5 mmol, 3.0 equiv.), potassium carbonate (0.552g, 2.0 mmol, 4.0 equiv.) and $Pd(PPh_3)_4$ (0.028 g, 0.025 mmol, 5 mol %) were were charged in an oven-dried 3-neck round bottomed flask. the solid mixture was pumped vacuum and then charged with N_2 for three cycles. The toluene (90 mL) and methanol (30 mL) were degassed with bubbling nitrogen for 20 minutes, then added to the solid mixture. The suspension was heated to 85 °C for 10 hours. After the reaction was finished, the product was extracted with $CHCl_3$ and washed with brine. The organic layer was combined and dried with $MgSO_4$. The crude product was purified by flash column chromatography using dichloromethane/petroleum ether (1:1) as eluent. 4,4'-diphenylbenzil was obtained as light green solid, (0.115 g, 0.32 mmol, 63 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8 Hz, 4H, Ar-H), 7.76 (d, J = 8 Hz, 4H, Ar-H), 7.65 (d, J = 8 Hz, 4H, Ar-H), 7.50 (m, 6H, Ar-H). EI-MS (m/z): calcd. 362.13 for $C_{26}H_{18}O_2$, found 181.05, 362.13.

Synthesis of BZL -COF



A 10mL Pyrex tube was charged with BZLBA (23 mg, 0.075 mmol), HHTP (16mg, 0.05 mmol), 0.5 mL dioxane and 0.5 mL methylene. Then the resulting suspension was sonicated for 30 seconds at room temperature. After being degassed by freeze-pump-thaw technique for three times and then sealed under vacuum, the tube was placed in an oven at 100 °C for 72 h. The resulting precipitate was filtered, washed with anhydrous dioxane and acetone. The solid was dried at 120 °C under vacuum for 12 h to afford green powder (22 mg, 67.27 % yield). Elemental analysis for the calculated $C_{13}H_6O_3B$: C, 70.58%; H, 2.71%. Found: C, 72.08%; H, 3.88%.

Synthesis of BZL-POP



In an oven-dried 3-neck round bottomed flask was charged with a 4,4’-benzildiboronic acid pinacol ester (0.485g, 1.05 mmol, 2.1 equiv), tetrakis-(4-bromophenyl)methane (0.32g, 0.5 mmol, 1.0 equiv), and chloro(2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]-palladium(II) (0.70-1.1 mol% relative to -Br functional groups) and was pumped vacuum and then charged with N_2 for three cycles. Degassed THF (12 mL) and degassed aqueous potassium carbonate (2 M, 1.5 mL) were added, and the solution was heated to 60 °C for 48 h. The resulting powder was washed with hot hydrochloric acid (3 N, 5 washes with triple THF volume), hot water (5 washes with triple THF volume), hot ethanol (5 washes with triple THF volume), and hot $CHCl_3$ (5 washes with triple THF volume). The resulting powder was then further purified by Soxhlet extraction with THF (24 h). The polymer was activated at the appropriate temperature under vacuum to deliver the desired material (0.35 g, 95.11% yield). Elemental analysis for the calculated $C_{53}H_{32}O$: C, 86.89%; H, 4.37%%. Found: C, 83.44%; H, 4.04%.

Section C. Supplementary Figures and Tables

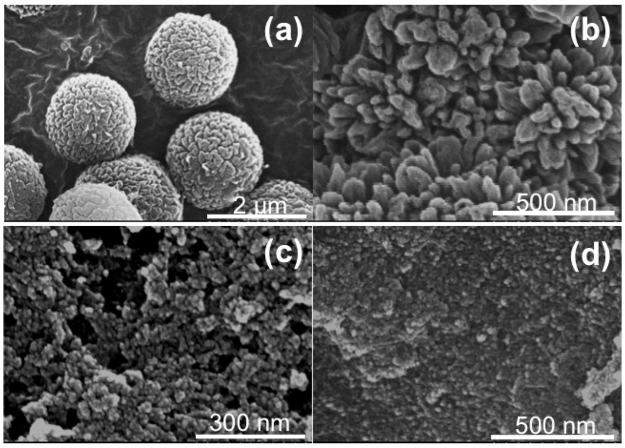


Figure S1. SEM images of a-b) BZL-COF and c-d) BZL-POP.

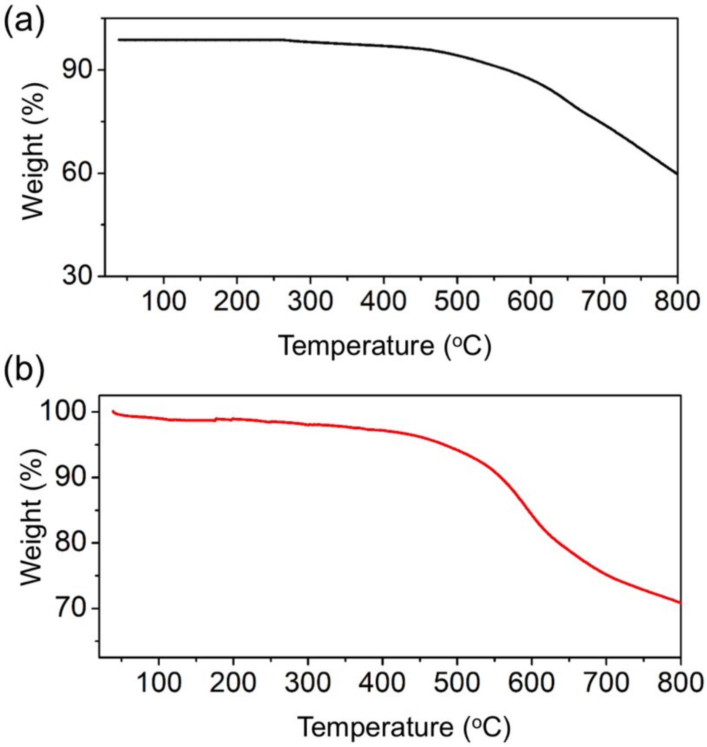


Figure S2. TGA profiles of a) BZL-COF and b) BZL-POP after activation.

Table S1. Elemental analysis results of BZL-COF and BZL-POP.

Sample		C%	H%
BZL-COF	Anal. Calcd.	70.58	2.71
	Found.	72.08	3.88
BZL-POP	Anal. Calcd.	86.89	4.37
	Found.	83.44	4.04

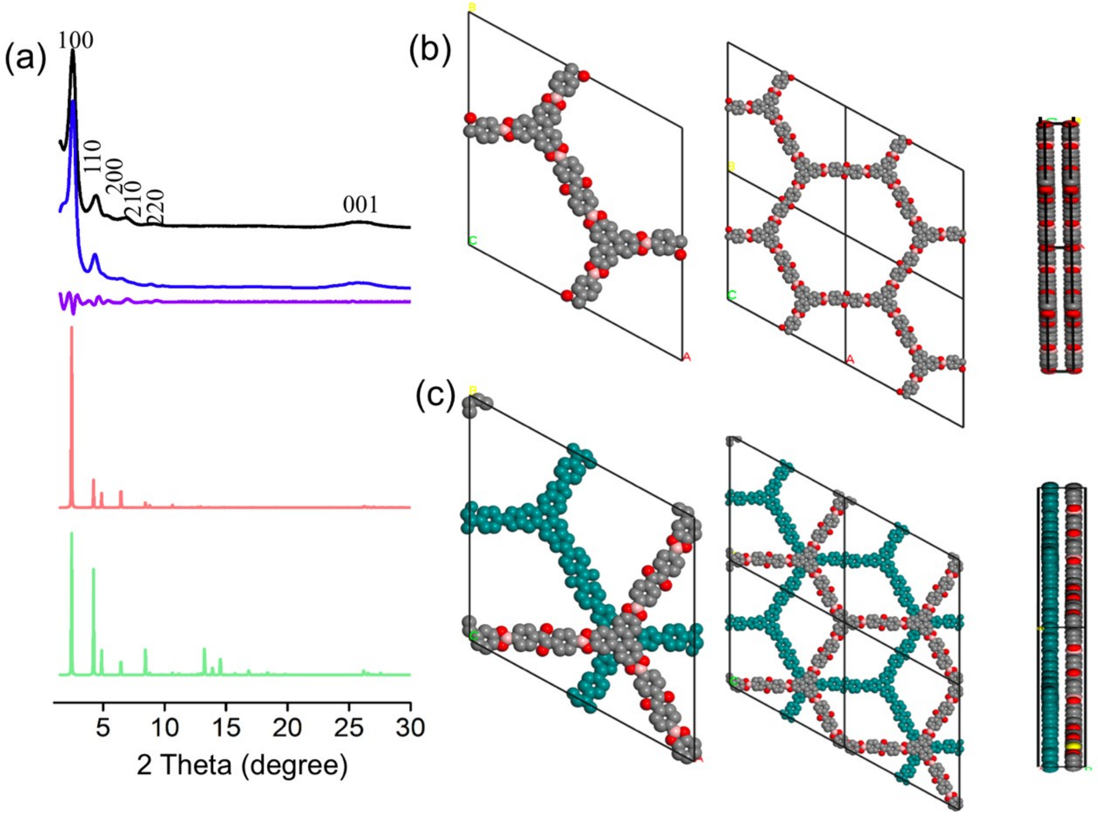


Figure S3. a) Experimental PXRD pattern of BZL-COF (black curve), Pawley refined pattern (blue curve), their difference (purple curve), and simulated PXRD patterns using the eclipsed AA stacking (red curve) and staggered AB stacking models (green curve). b) The structures of BZL-COF derived using the AA stacking models. c) The structures of BZL-COF derived using the AB stacking models.

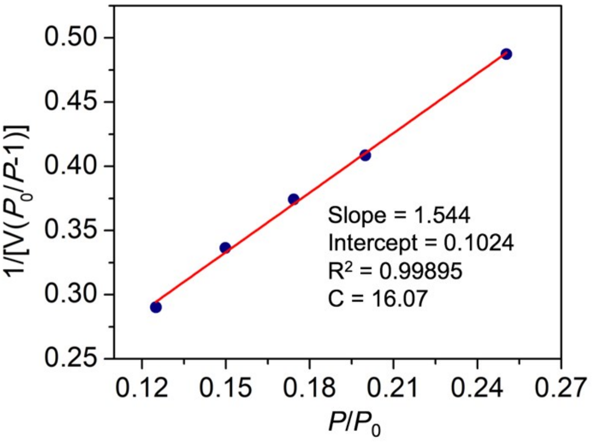


Figure S4. Selected BET Plots of BZL-COF for BET surface area calculated based on nitrogen adsorption isotherm at 77 K.

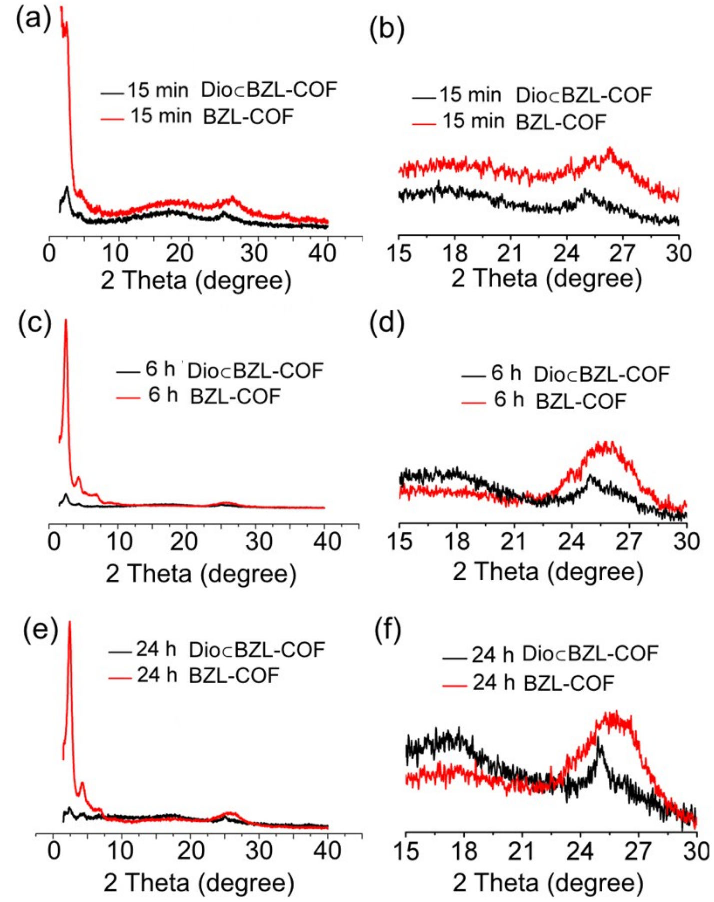


Figure S5. Experimental PXRD patterns of Dio⊂BZL-COF (black curve) and BZL-COF (red curve) at different reaction time a-b) 15 min, c-d) 6 h and e-f) 24 h.

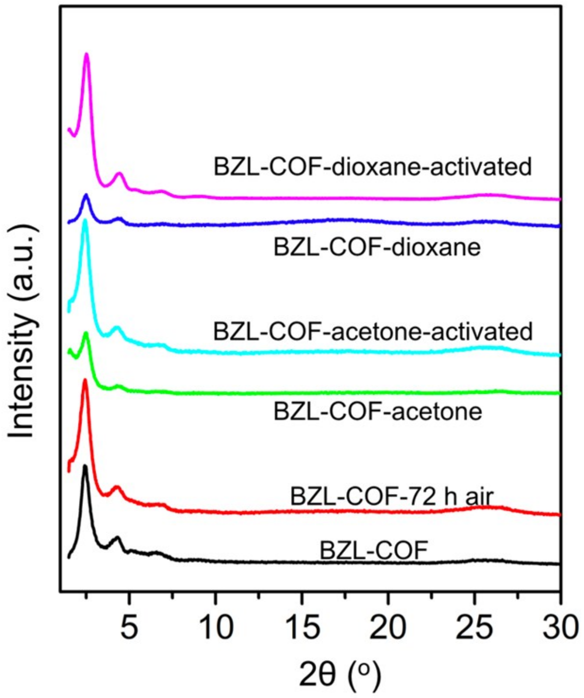


Figure S6. PXRD patterns of the BZL-COF samples before and after treatment with different solvents for 24 h and stored in air for 72 h. After treatment with different solvents for 24 h, the intensities of (100), (110) facets are decreased owing to the existence of disordered solvents in the COF channels, and the intensities of which can be recovered after reactivation.

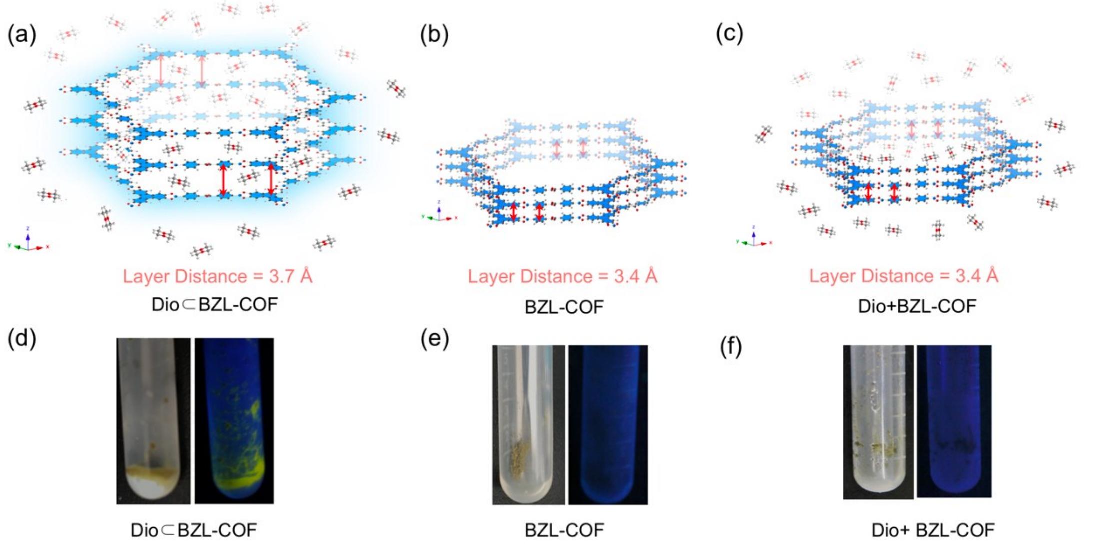


Figure S7. a-c) General scheme for the layer distance of Dio⊂BZL-COF, BZL-COF and Dio+BZL-COF. e-f) Photograph of Dio⊂BZL-COF, BZL-COF and Dio+BZL-COF irradiated under normal light and 365 nm in cryogenic temperature.

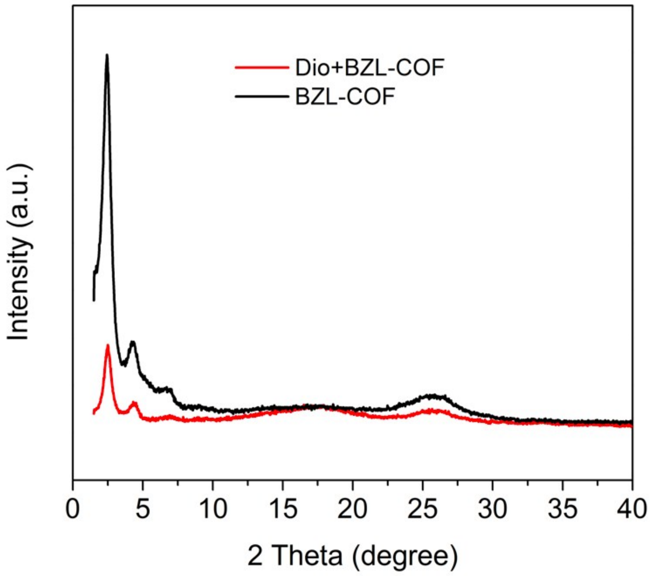


Figure S8. Experimental PXRD patterns of Dio+BZL-COF and BZL-COF.

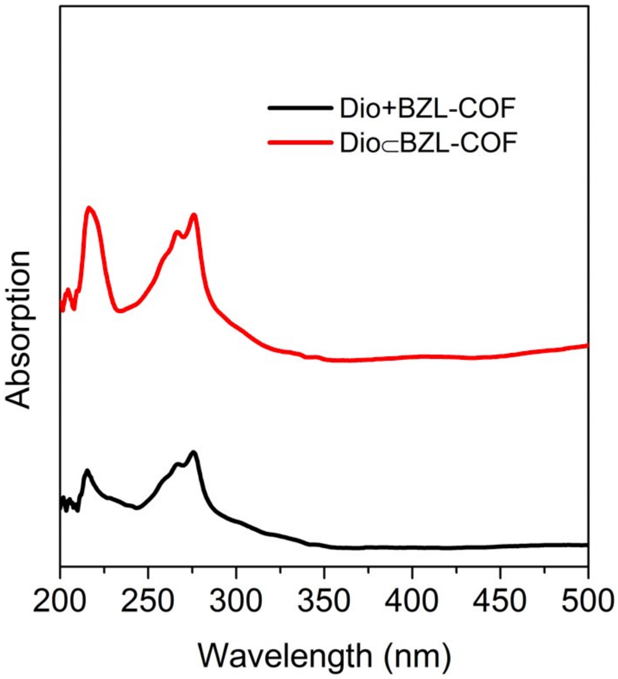


Figure S9. UV−Vis spectra of Dio+BZL-COF and Dio⊂BZL-COF.

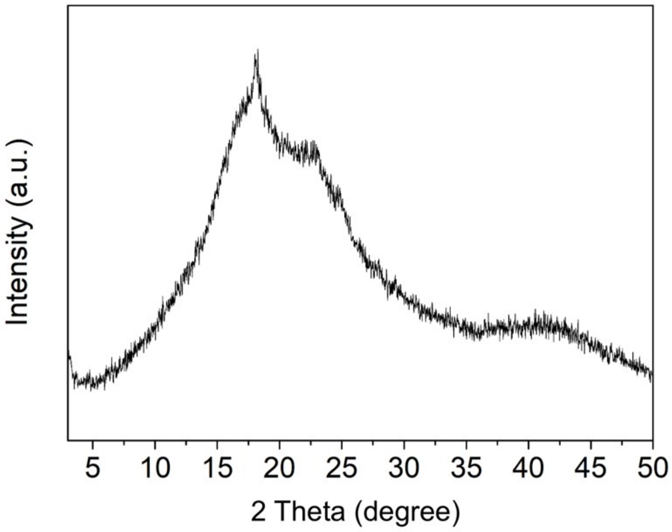


Figure S10. Experimental PXRD pattern of BZL-POP.

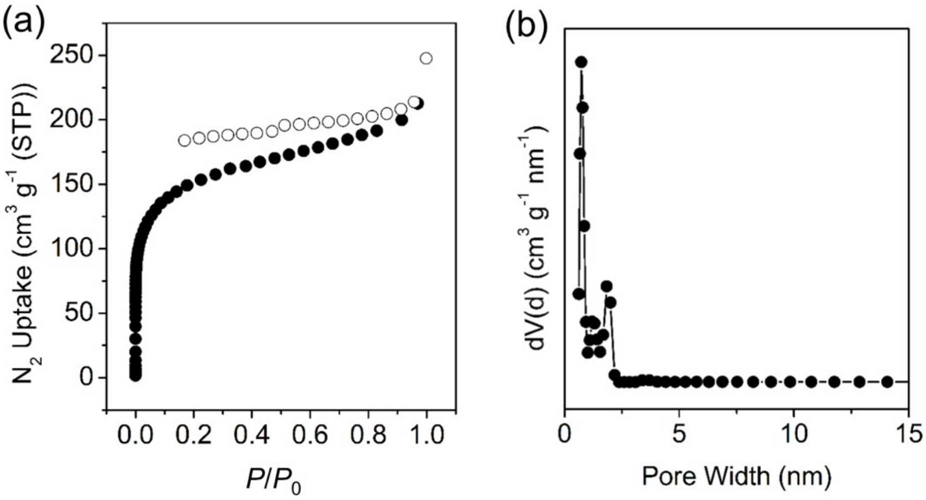


Figure S11. Nitrogen a) adsorption-desorption isotherms and b) pore size distribution curves of the BZL-POP.

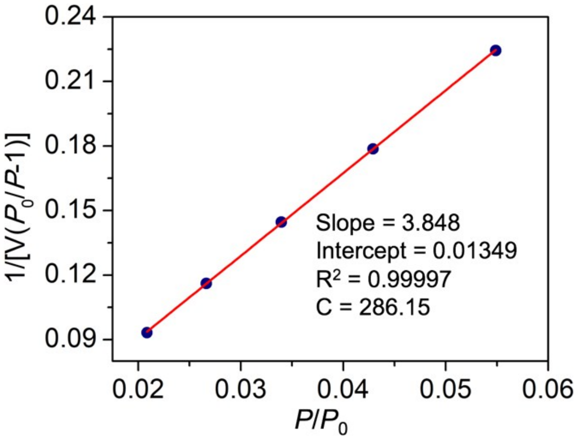


Figure S12. Selected BET Plots of BZL-POP for BET surface area calculated based on nitrogen adsorption isotherm at 77 K.

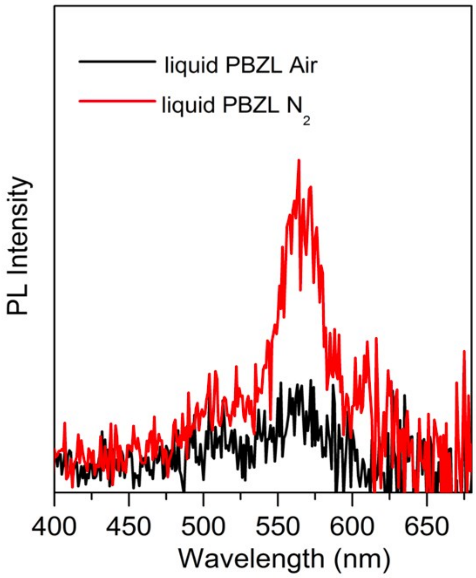


Figure S13. PL spectra of the liquid PBZL samples in air and N_2 at 77 K.

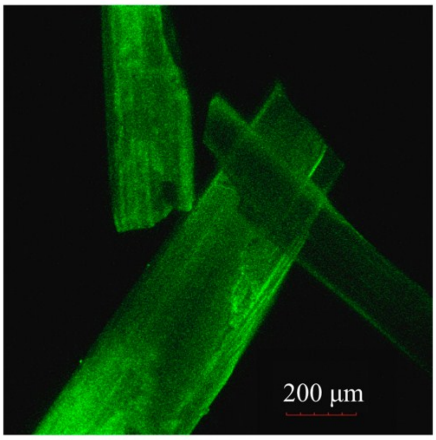


Figure S14. The confocal microscopy image of PBZL crystal at room temperature, λ_{ex} = 405 nm.

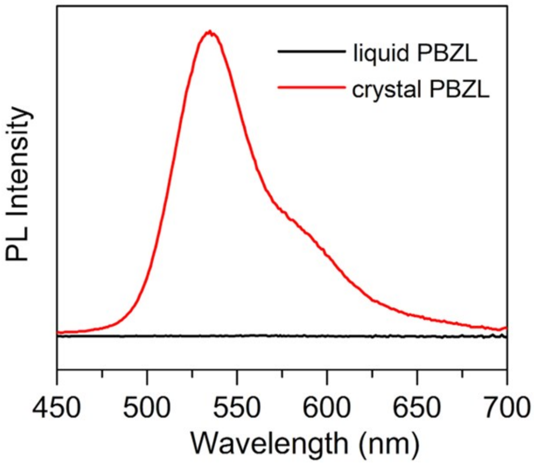


Figure S15. The PL spectra of the liquid and crystal PBZL samples in N_2 at 298 K, λ_{ex} = 345 nm.

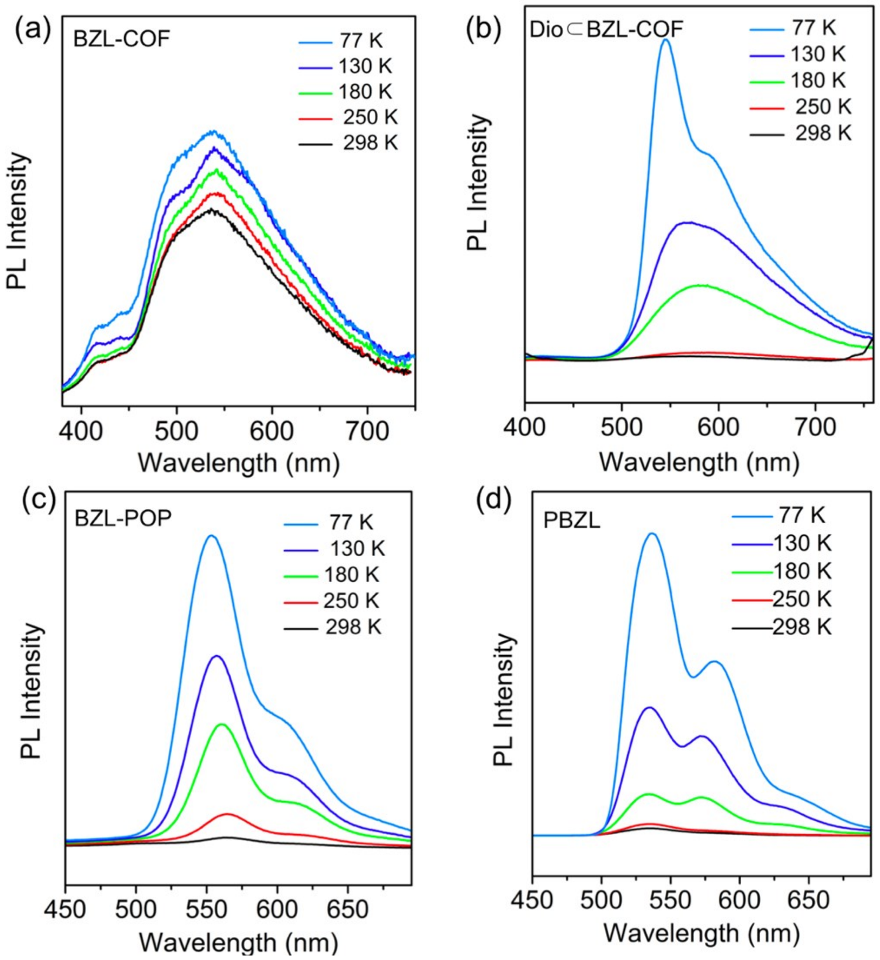


Figure S16. PL spectra of a) Dio⊂BZL-COF, b) BZL-COF, c) BZL-POP and d) PBZL measured at different temperatures from 77 K to 298 K.

Table S2. Photophysical parameters of varying samples at 77 K and 298 K.

	77 K (ex 345 nm)		298 K (ex 345 nm)				
Sample	τ (ms)	λ_{em} (nm)	τ (ms)	λ_{em} (nm)	Φ (%)	k_r (s^{-1})	$k_{nr}+k_q$ (s^{-1})
BZL-COF	τ_1 =0.24(34.2%) τ_2 =1.42 (65.8%) τ(average)=1.02	540	τ_1=0.1(16.73%) τ_2=0.82(83.27%) τ(average)=0.69	540	0.08	1.14	1.44×10^3
Dio⊂BZL-COF	@545 nm τ_1 =0.69 (35.7%), τ_2 =2.23(64.3%) τ(average)=1.29 @590 nm τ_1 =0.67(62%) τ_2 =2.25 (38%) τ(average)=1.27	545, 590(sh)	τ_1=0.05(35.13%) τ_2=0.34(64.87%) τ(average)=0.23	565	0.13	5.56	4.34×10^3
BZL-POP	@557 nm τ_1=0.54(35.75%) τ_2=1.98(64.25%) τ(average)=1.01 @605 nm τ_1=0.50(34.69%) τ_2=1.88(65.31%) τ(average)=0.96	557, 605(sh)	@564 nm τ_1 =4.33 μs (22.2%) τ_2=0.028 (30.2%) τ_3=0.42 (47.6%) τ(average)=0.02	564	0.32	1.6×10^2	4.98×10^4
PBZL	@537 nm τ=2.30 @582 nm τ=2.42	537， 582(sh	@537 nm τ_1=0.035(45.5%) τ_2 =0.21 (54.5%) τ(average)=0.13 @589 nm τ_1=0.034(46.98%) τ_2=0.28(53.02%) τ(average)=0.16	537, 589(sh)	3.42	2.6×10^2	5.06×10^3

$k_r = \Phi / < \tau >$; $k_{nr}+k_q = (1-\Phi)/<\tau>$

Table S3. Structural data of PBZL.

Formula	$C_{26}H_{18}O_2$
Space group	*C2/c*
Z	4
a (Å)	22.874(3)
b (Å)	4.0616(6)
c (Å)	22.609(3)
α (°)	90.00
β (°)	118.113
γ (°)	90.00
R_1, wR_2 (all)	0.0581, 0.1130
CCDC	No. 1832662