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Supporting Information

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A Belt-Shaped, Blue Luminescent and Semiconductive
Covalent Organic Framework

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Section 1. Materials and Methods

THF was distilled over benzophenone ketyl under Ar before use. Cyclohexane was

distilled under Ar before use. Pyrene, bispinacolatodiboron, anhydrous 1,4-dioxane (99.8%) and anhydrous acetone (99.8%) were purchased from Wako Chemicals. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and mesitylene (98%) were purchased from TCI. 4,4'-Di-*tert*-butyl-2,2'-bipyridine was purchased from Aldrich. Sodium periodate and hydrochloric acid were purchased from Kanto Co. Ltd. Methoxy(cyclooctadiene)iridium(I) dimer was purchased from Alfa Aesar Chemicals. Silica gel Wakogel C–300HG was used for column chromatography. Deuterated solvents for NMR measurements were obtained from Cambridge Isotope Laboratories, Inc. Pyrene-2,7-diboronic ester was prepared according to reported methods[1].

^{1}H and ^{13}C NMR spectra were recorded on JEOL models JNM–LA400 or JNM–LA500 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. UV-Vis-IR diffuse reflectance spectrum (Kubelka-Munk spectrum) was recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. 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 using 9–nitroanthracene or dithranol as matrix. Field emission scanning electron microscopy (FE SEM) was performed on a JEOL model JSM–6700 FE–SEM operating at an accelerating voltage of 1.5 or 5.0 kV. The sample was prepared by drop–casting an acetone suspension onto mica substrate and then coated with gold. Transmission Electron Microscope (TEM) images were obtained on a JEOL model JEM–3200 microscope. The sample was prepared by drop–casting an acetone suspension of TP-COF onto a copper grid. Powder X–ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to $60°$ with $0.02°$ increment, equipped with temperature-variable sample holder.

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 200 °C for more than 6h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using density functional theory (DFT) model, the pore

volume was derived from the sorption curve.

Electrical measurements were carried out at 25 °C in air on TP-COF or I_2-doped TP-COF between 10-μm width Pt electrodes by a two-probe method using a Keithley model 2635 sourcemeter. TP-COF was homogenously dispersed in acetone and casted onto the electrode to give a film. For I_2 doping, the TP-COF electrode was put into an I_2 atmosphere for 1h before measurement.

Geometry optimization of the unit pore structure was performed at PM3 level by using the Gaussian 03 program package (Revision C.02)[2] to give the pore size of 3.26 nm in diameter. Geometry optimization of the repeating unit was performed at B3LYP/6-31G(d) level by using the Gaussian 03 program package in order to make unit cell structure. The final molecular structure in a hexagonal unit cell was prepared by using geometrical parameters from the optimized structure. Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from PXRD pattern, implemented in MS modeling ver 4.2 (Accelrys Inc.)[3]. Unit cell dimension was first manually determined from the observed PXRD peak positions by using hexagonal arrangement. We performed Pawley refinement to optimize the lattice parameters iteratively until the R_{WP} value converges. The refinement indicates a hexagonal crystal system with a unit cell of $a = b = 37.5412$ Å and $c = 3.3784$ 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 8.50 and 5.63%, respectively. Simulated PXRD patterns were calculated from the refined unit cell and compared with the experimentally observed patterns. This structure could have two distinct arrangements: (1) a staggered AB type arrangement with graphite-like packing, where three-connected vertices lie over the center of the six-membered rings of neighboring layers; (2) an eclipsed AA type arrangement, where all atoms in an each layer of the framework lie exactly over one another. The AA type arrangement was constructed in space group $P6/mmm$ symmetry (space group number 191) and the AB type arrangement was constructed in space group $P6_3/mmc$ symmetry (space group number 194). The atoms are placed on the special position to form the 2D framework where all bond lengths and angles are taken from the optimized geometrical parameters calculated at B3LYP/6-31G(d) to maintain reasonable values. After comparing each simulated

pattern with experimentally observed pattern, only the simulated pattern from the eclipsed AA type arrangement shows good agreement with the observed PXRD pattern.

Section 2. Synthesis

All reactions were performed under argon using Schlenk line technique.

PDBA: A THF/water mixture (60 mL, 4/1 in vol.) of pyrene-2,7-diboronic ester (1g, 2.21 mmol) and sodium periodate (2.84 g, 13.25 mmol) was stirred for 30 min and was added with aqueous hydrochloric acid (1N, 3.1 ml, 3.1 mmol). The reaction mixture was stirred at room temperature overnight, diluted with water (30 ml) and extracted with ethyl acetate (3 × 50 ml). The combined extracts were washed with water (3 × 30 ml) and brine (30 ml), dried over sodium sulfate, filtered, and concentrated to dryness. The solid residue after rinsed with small portions of hexane gave **PDBA** as brown solid in 98% yield (638 mg)[4].

^{1}H NMR (400 MHz, DMSO-d^6): δ ppm 8.68 (4H, s, 1,3,6,7-H-pyrene), 8.44 (4H, s, 4,5,9,10-H-pyrene), 8.16 (4H, s, BO–H).

^{13}C NMR (100 MHz, DMSO-d^6): δ ppm 130.80, 130.03, 127.44, 124.95.

MALDI–TOF MS for $C_{16}H_{12}B_2O_4$ (Cacld. 290.0922), m/z = 290.2092 ([M + H]$^+$).
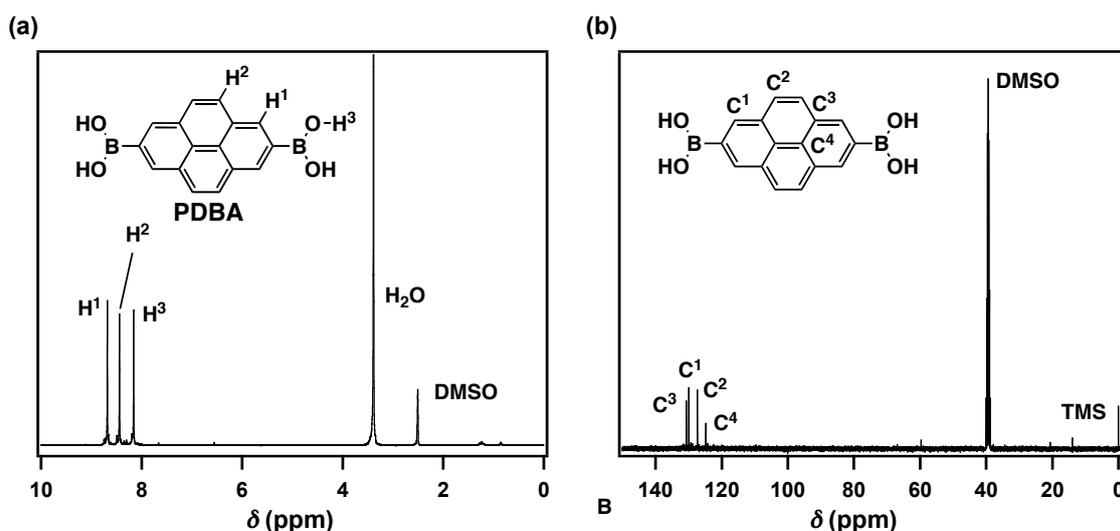
Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of PDBA in DMSO-d^6.

TP-COF: A 1,4-dioxane/mesitylene mixture (20 mL, 1/1 in vol.) of PDBA (100 mg, 0.345 mmol) and HHTP (74.58 mg, 0.23 mmol) was stirred at 85 °C for 3 days under Ar. The precipitate was collected by centrifugation, washed with anhydrous acetone and dried at 150 °C under vacuum to give **TP-COF** (123 mg) as a pale yellow powder in 90% yield.

Section 3. FT IR Spectral Profiles
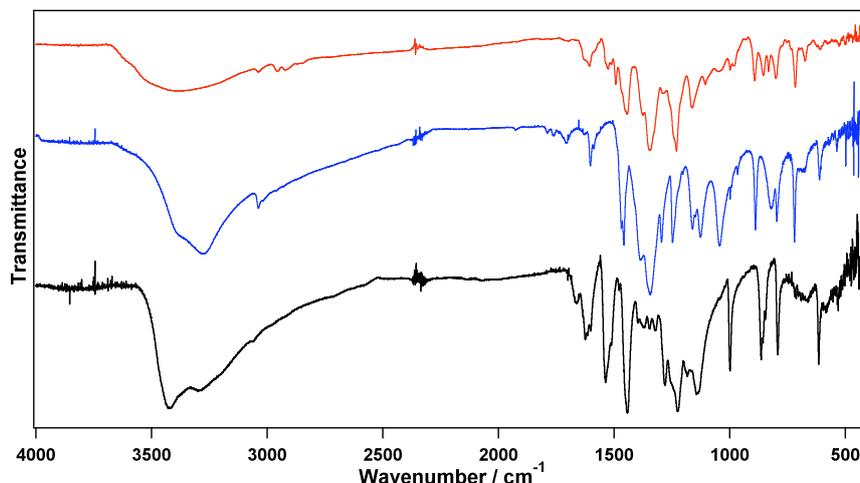
Figure S2. FT IR spectra of PDBA, HHTP and TP-COF. The red, blue and black curves are IR spectra of TP-COF, PDBA and HHTP, respectively.

Table S1: Peak assignments for FT-IR spectrum of TP-COF.

Peak (cm^{-1})	Assignment and Notes
3395.07 (m)	O–H stretch from the end B(OH)$_2$ or OH groups
3037.34 (w)	Aromatic C–H stretch from pyrene units
2955.38 (w)	
2922.11 (w)	C–H stretching from triphenylene building blocks
2871.01 (w)	
1630.3 (w)	C=C stretch for fused aromatics. Also observed in HHTP
1525.9 (m)	C=C vibrational mode of phenyl ring. Characteristic band
1492.63 (m)	C=C vibrational modes for triphenylene building blocks,
1443.94 (m)	Characteristic bands for triphenylene
1344.62 (s)	B–O stretch, characteristic band for boroxoles
1328.23 (s)	B–O stretch
1245.79 (s)	C–O stretch, characteristic for boroxoles
1163.8 (m)	
1105.98 (m)	C–H in-plane bending modes
1049.09 (m)	B–C stretch
855.28 (m)	
832.62 (m)	C–H out-of-plane bending modes for *p*-substituted aromatic rings
800.80 (m)	
716.91 (m)	
675.45 (m)	C–H out-of-plane bending modes
609.88 (w)	

Section 4. Temperature-Variable PXRD Patterns
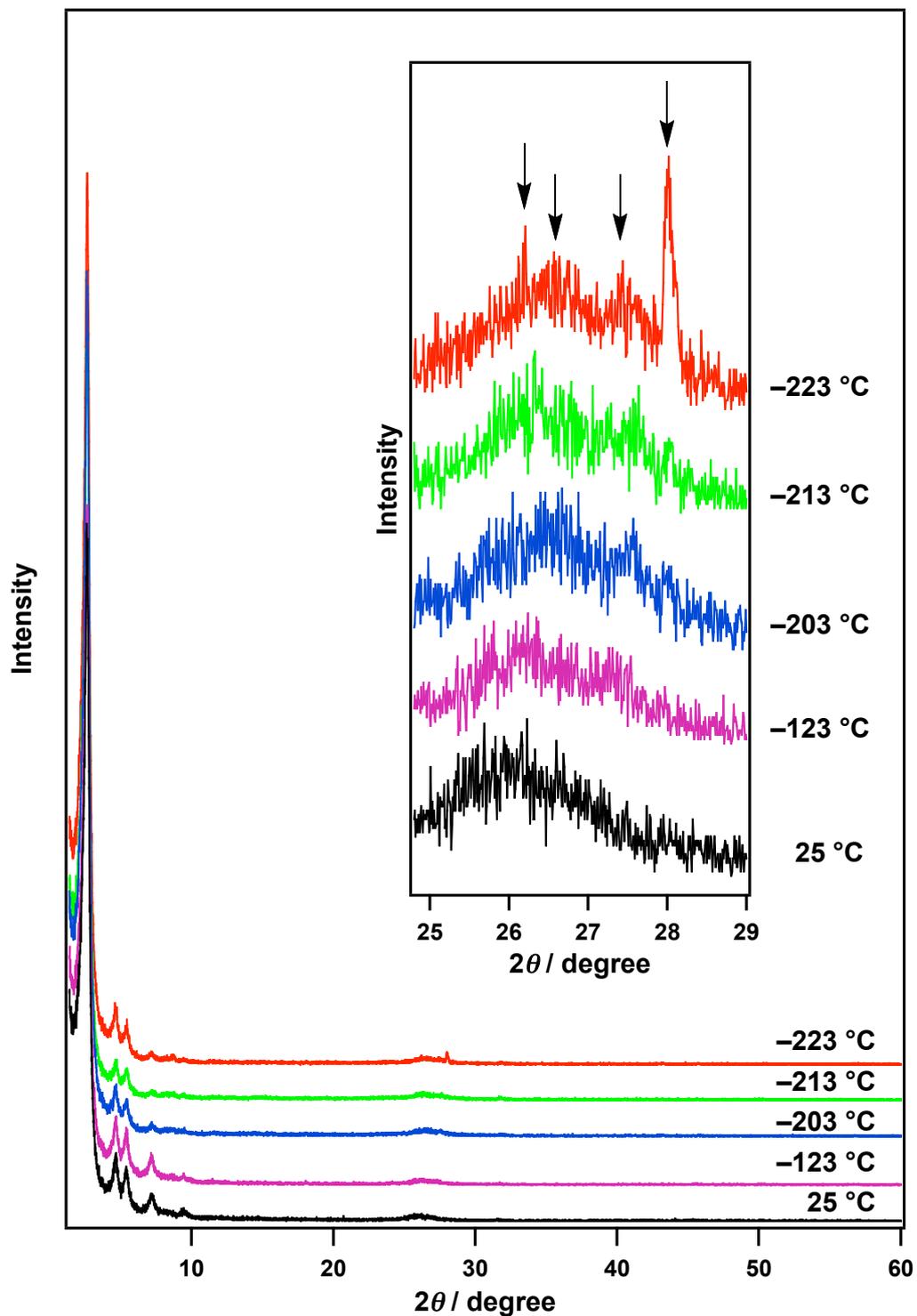
Figure S3. (a) Temperature variable PXRD patters of TP-COF. Inset: Enlarged PXRD patterns around 2θ = 26 degree. At decreased temperature, the PXRD peak around 2θ = 26 degree becomes resolved into four sets.

Section 5. Simulation and Calculation of Crystal Lattice Packing

Table S2. Refined crystal data

Formula	$C_{84}O_{12}B_6$
Formula weight	1265.78
Crystal system	Hexagonal
Space group	$P6/mmm$ (No.191)
Unit cell dimensions	$a = b = 37.5412$ Å
	$c = 3.3784$ Å
Cell volume	4123.42 Å^3
Density calculated	0.510 g/cm^3

Table S3. Fractional atomic coordinate

Atom	Wyck.	x	y	z
C1	12q	0.29457	0.62814	0.50000
C2	12q	0.33388	0.59643	0.50000
C3	12q	0.37097	0.59167	0.50000
O4	12q	0.37899	0.55964	0.50000
C7	12q	0.42428	0.51126	0.50000
C8	12q	0.44513	0.48902	0.50000
C10	12q	0.42390	0.44477	0.50000
B5	6m	0.42181	0.57819	0.50000
C6	6m	0.44552	0.55448	0.50000
C9	6m	0.48905	0.51095	0.50000

Simulation of PXRD Pattern and Crystal Packing
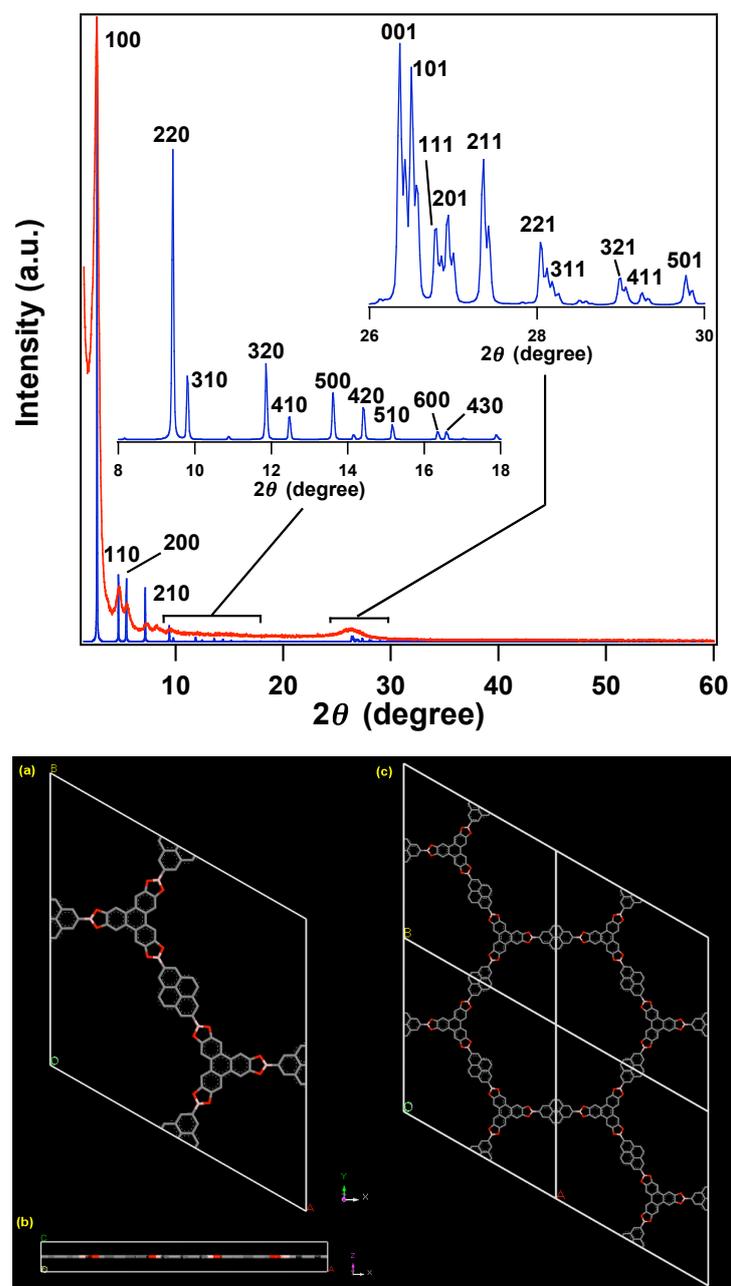
Figure S4. PXRD pattern of TP-COF and simulation of crystal lattice packing in the eclipsed form. In the upper figure, the red curve represents the experimental PXRD pattern and the blue pattern is calculated from the eclipsed crystal packing (Crystal space group $P6$/mmm; No. 191). The calculated pattern simulates the experimental data well. The insets show the assignment of PXRD signals. The lower figure shows the eclipsed crystal lattice packing of TP-COF. The pore size is 3.26 nm in diameter in the defined structure.
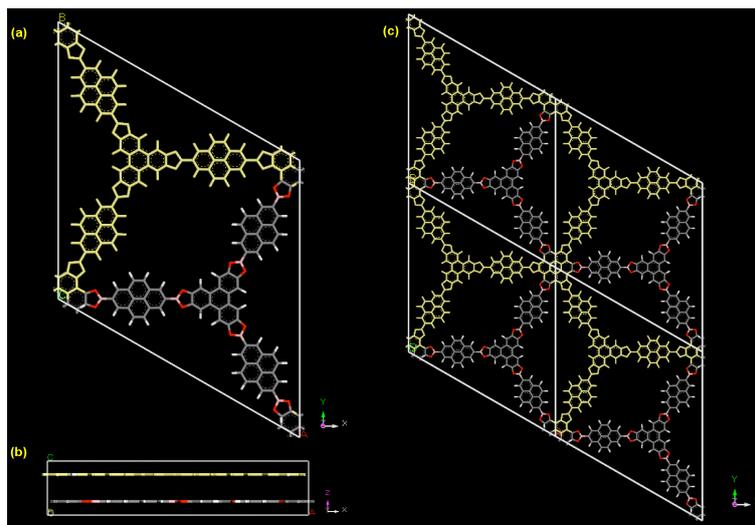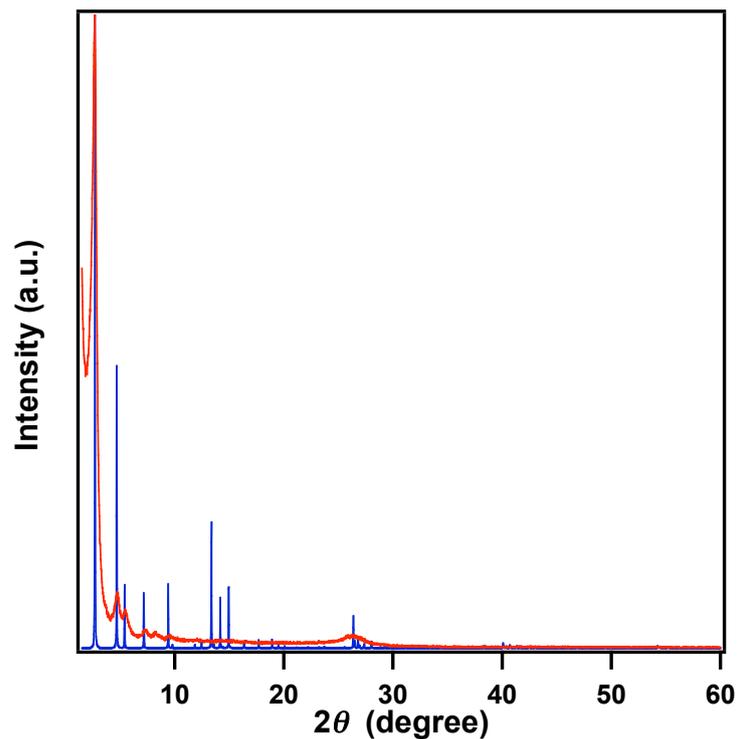
Figure S5. PXRD pattern of TP-COF and simulation of crystal lattice packing in the staggered form. In the upper figure, the red curve represents the experimental PXRD pattern and the blue pattern is calculated from the staggered crystal packing (Crystal space group *P*63/mmc; No. 194). The simulated pattern does not fit the experimental data at all. The lower figure shows the staggered crystal lattice packing. In this case, the pore is covered and the pore size is significantly smaller than the experimental one.

Section 6. Fluorescence Excitation and Diffuse Reflectance UV-VIS-NIR
Spectral Profiles

(a)
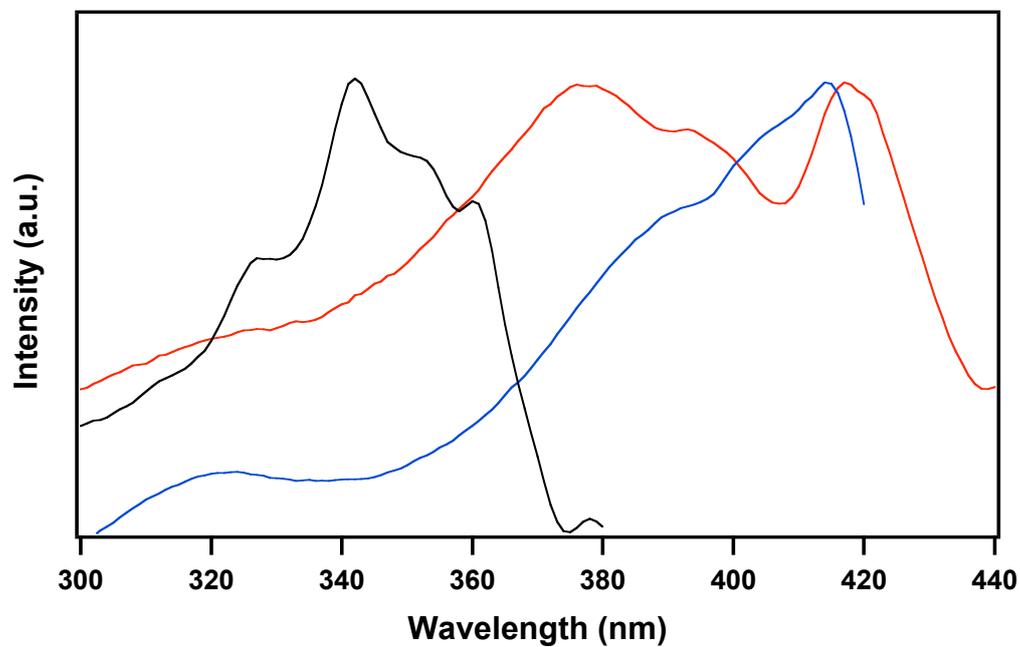
(b)
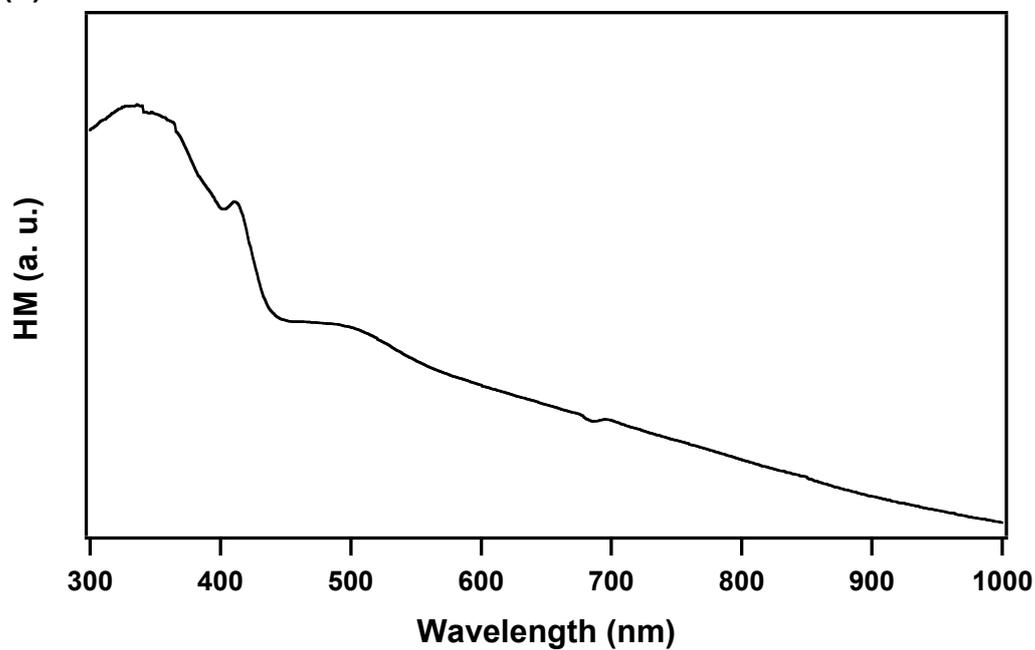
Figure S6. (a) Normalized fluorescence excitation spectra of PDBA (blue curve), HHTP
(black curve) and TP-COF (red curve). (b) Diffuse reflectance UV-VIS-NIR spectrum of
TP-COF.

Section 7. Supporting References

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