Supplementary material

A post-synthetic modification strategy for the synthesis of pyrene-fused azaacene covalent organic frameworks

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1. Materials and Methods

Commercial reagents and solvents were obtained from diverse suppliers and used as received, with exception of pyrene, which was recrystallized prior to use from a mixture of CH_2Cl_2/hexane. Reactions' progress were monitored by analytical thin-layer chromatography (TLC) on ALUGRAM® Xtra SIL G/UV_{254} aluminium sheets from Macherey Nagel. TLC plates were rendered visible by exposure to ultraviolet light. All purifications were carried out under flash-chromatographic conditions on silica gel (60 Å, 40–63 μm, 230–400 mesh).

Infrared (IR) spectra were recorded on a Bruker VERTEX 80v FT-IR spectrometer in ATR mode. IR data is background corrected and reported in frequency of adsorption (cm^{-1}).

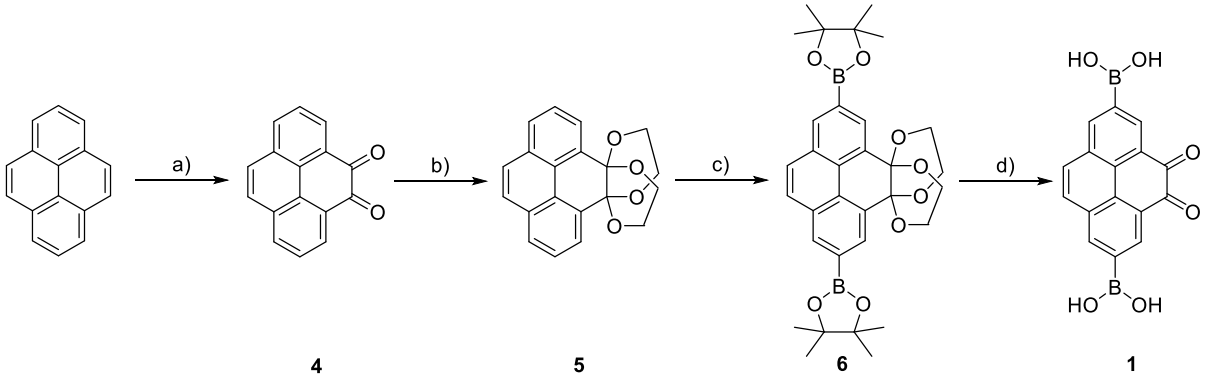
Thermogravimetric analysis (TGA) were performed on a TGA/DSC 1 $STAR^e$ system (Mettler-Toledo). The samples were heated from 303.15 to 1173.15 K at 283.15 K min^{-1} under a continuous flow of argon of 20 mL min^{-1}.

Scanning electron microscopy (SEM) studies were performed using a Quanta 650 field-emission scanning electron microscope operating at 3 kV and employing an Everhardt-Thornley secondary electrons detector, with a working distance of ca. 10 mm. The samples were prepared by adhesion of the sample powder directly on a conductive double-sided copper tape attached to SEM pin stub.

2. Synthetic Procedures

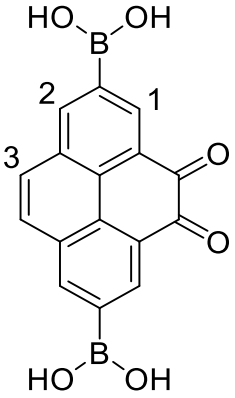
2.1. Synthesis of boronic acid-bearing pyrene-4,5-dione building block **1**

Starting point of synthetic route of boronic acid-bearing pyrene-4,5-dione building block **1** is the selective ruthenium-catalyzed oxidation of pyrene in its 4- and 5-positions, to afford pyrene-4,5-dione (**4**).[1] The following protection of ketone groups using ethylene glycol gave **5** in 43% yield. Up next, iridium-catalyzed C–H borylation takes place at the 2,7-positions to afford **6** in 49% yield.[2] Finally, deprotection of both protecting groups at room temperature with $NaIO_4$ under acidic conditions[2] gave boronic acid-bearing pyrene-4,5-dione building block **1** in 88% yield.[3]



Scheme S1. Synthetic route of boronic acid-bearing pyrene-4,5-dione building block **1**. a) CH_2Cl_2, THF, $RuCl_3$•$2H_2O$, *N*-methylimidazole, H_2O, $NaIO_4$, 2.5 h, 50%; b) ethylene glycol, PTSA, toluene, 125 °C, 20 h, 43%; c) bis(pinacolato)diboron, $[Ir(OMe)COD]_2$, 4,4'-di-*tert*-butyl-2,2'-bipyridine, MTBE, 80 °C, 20 h, 49%; d) $NaIO_4$, TFA, THF, H_2O, air, RT, 3 d, 88%.

(7-Borono-4,5-dioxo-pyren-2-yl)boronic acid (boronic acid-bearing pyrene-4,5-dione)[3] **(1)**

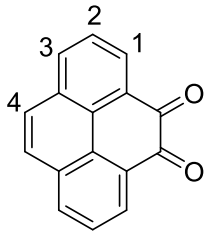


The procedure was adapted from literature procedures.[2,3] In a round-bottom flask, **6** (522 mg, 0.91 mmol, 1 equiv) was dissolved in a mixture of THF/H_2O (41/12 mL). $NaIO_4$ (1.65 g, 7.71 mmol, 8.5 equiv) was added, and the mixture was stirred at room temperature for 30 min. Then, TFA (85 mL) was added dropwise and the reaction mixture was stirred for 3 days at room temperature while bubbling air through the solution. An orange solid precipitated and the suspension was diluted with CH_2Cl_2 and H_2O. Aqueous phase was extracted with CH_2Cl_2, and

the organic phase was filtered. Collected solid was combined with aqueous phase and centrifuged (15 min, 4400 rpm). Orange solid was suspended in water and centrifugation repeated. This last wash step was repeated four times in total. The solid was dried under high vacuum to give boronic acid-bearing pyrene-4,5-dione building block **1** (255 mg, 88%) as an orange solid.

^{1}H NMR (400 MHz, DMSO-d_6+D_2O): δ = 8.72 (d, *J* = 1.3 Hz, 2H; H–C(1)), 8.68 (d, *J* = 1.3 Hz, 2H; H–C(2)), 8.01 (s, 2H; H–C(3)).

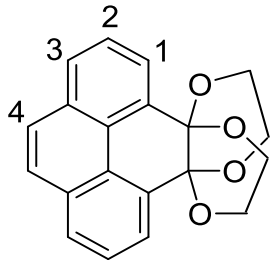
Pyrene-4,5-dione[1] **(4)**



In a round-bottom flask, pyrene crystals (9.7 g, 47.9 mmol, 1 equiv) were dissolved in a mixture of CH_2Cl_2 and THF (240/240 mL). To the yellow solution were added $RuCl_3$•$2H_2O$ (0.99 g, 4.79 mmol, 0.1 equiv), *N*-methylimidazole (190.5 μL, 2.39 mmol, 0.05 equiv) and water (240 mL). Then, over a period of 20 min, sodium periodate (46.1 g, 215.4 mmol, 4.5 equiv) was added in small portions, and the mixture was stirred at RT for 2.5 h. Organic solvents were removed under reduced pressure, and the aqueous phase was extracted with CH_2Cl_2. Collected organic phase was washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to afford a dark-orange solid. Purification by column chromatography (SiO_2; CH_2Cl_2) gave **4** (5.5 g, 23.7 mmol, 50%) as a bright-orange solid.

R_f = 0.3 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 7.4 Hz, *J* = 1.3 Hz, 2H, H–C(1) or H–C(3)), 8.13 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 2H, H–C(1) or H–C(3)), 7.80 (s, 2H, H–C(4)), 7.72 (dd, *J* = 7.9 Hz, *J* = 7.5 Hz, 2H, H–C(2)).

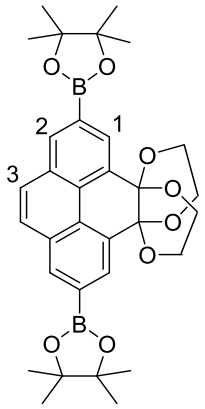
Pyrene-4,5-di(ethyleneglycol)ketal[2] **(5)**



To a suspension of pyrene-4,5-dione (**4**) (2.99 g, 12.9 mmol, 1 equiv) in toluene (150 mL) were added ethylene glycol (90 mL, 1.61 mol, 125 equiv) and *p*-toluenesulfonic acid (1.11 g, 5.81 mmol, 0.45 equiv). The obtained orange reaction mixture was refluxed at 125 ºC for 20 h. Reaction mixture was cooled down and toluene was removed under reduced pressure. Then, 200 mL of water was added and a light brown solid precipitated, which was collected by filtration and washed with water. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate 9:1) gave **5** (1.80 g, 5.54 mmol, 43%) as white solid.

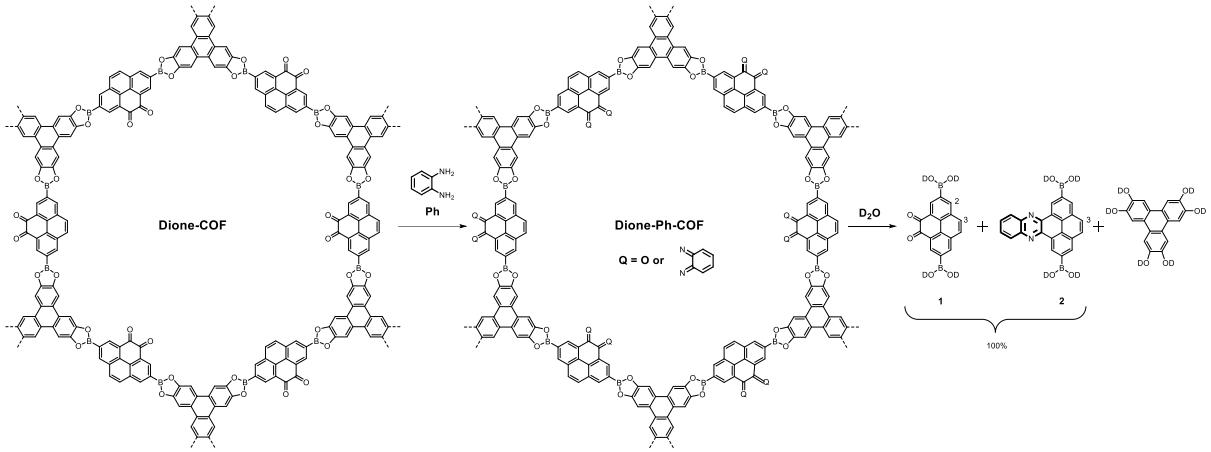
R_f = 0.29 (cyhex/EtOAc 9:1); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.94 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 4H; H–C(1) or H–C(3)), 7.80 (s, 2H; H–C(4)), 7.70 (t, *J* = 7.6 Hz, 2H; H–C(2)), 4.27 (br, 4H), 3.73 (br, 4H).

2,7-Bis(Bpin)-4,5-di(ethyleneglycol)ketal-pyrene[2] **(6)**



In an nitrogen-filled 100 mL pressure tube (ACE glass, bushing type back seal, 17.8 cm x 38.1 mm) were added pyrene-4,5-di(ethyleneglycol)ketal (**5**) (0.89 g, 2.76 mmol, 1 equiv), bis(pinacolato)diboron (1.41 g, 5.52 mmol, 2 equiv), $[Ir(OMe)COD]_2$ (0.09 g, 0.14 mmol, 0.05 equiv), 4,4'-di-*tert*-butyl-2,2'-bipyridine (0.07 g, 0.28 mmol, 0.1 equiv), and *tert*-butyl methyl ether (18 mL). Reaction mixture was stirred at 80 ºC for 20 h, cooled down and passed through a pad of silica using toluene as the eluent. The solvent was removed under reduced pressure and the product was purified by flash chromatography (SiO_2; cyclohexane/ethyl acetate 9:1 → 8:2 → 7:3), as off-white solid (0.77 g, 0.95 mmol, 49%).

R_f = 0.2 (cyhex/EtOAc 9:1); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.36 (d, *J* = 1.2 Hz, 2H; H–C(1) or H–C(2)), 8.24 (d, *J* = 1.2 Hz, 2H; H–C(1) or H–C(2)), 7.81 (s, 2H; H–C(3)), 4.28 (br, 4H), 3.71 (br, 4H), 1.37 (s, 24H).



Scheme S2. Hydrolysis of Dione-Ph-COF by D_2O to the respective building blocks for the determination of the yield of the PSM. The yield was calculated by ^1H NMR spectroscopy by comparison of the signal intensities between the proton H–3 of the cleaved pyrene-fused pyrazaacene **2** and proton H–2 of pyrene-4,5-dione building block **1**. The yield of the reaction was calculated by dividing the integrated intensity of the pyrazaacene proton signal with the sum of the intensities of the pyrazaacene proton signal and that of the pyrene-4,5-dione building block **1**.

The yield for Dione-Naph-COF was calculated in a similar manner but using the proton H–3 of pyrene-4,5-dione building block **1** due to signal overlap.

3. NMR Spectra

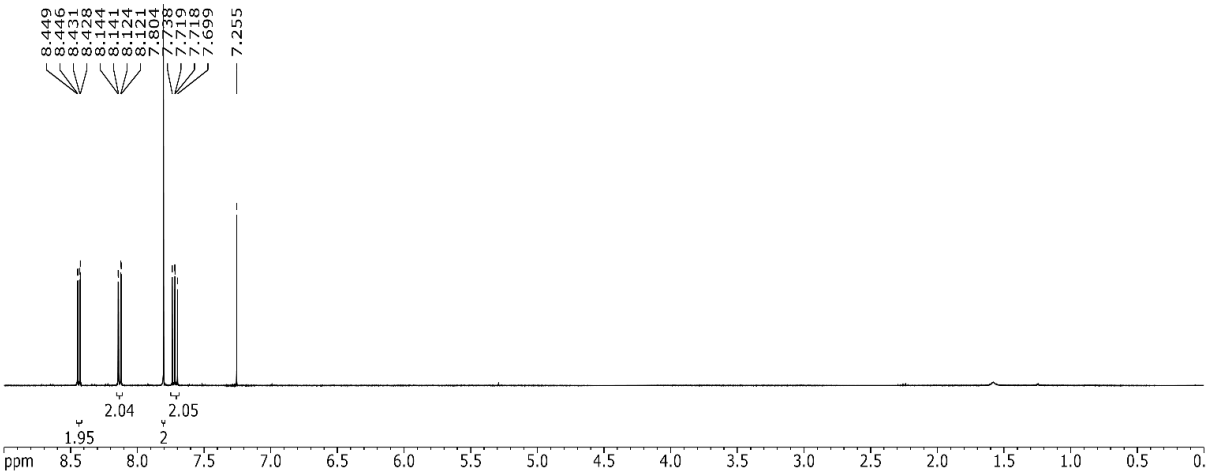


Figure S1. ^{1}H NMR spectrum of pyrene-4,5-dione (**4**) measured at 400 MHz in $CDCl_3$.

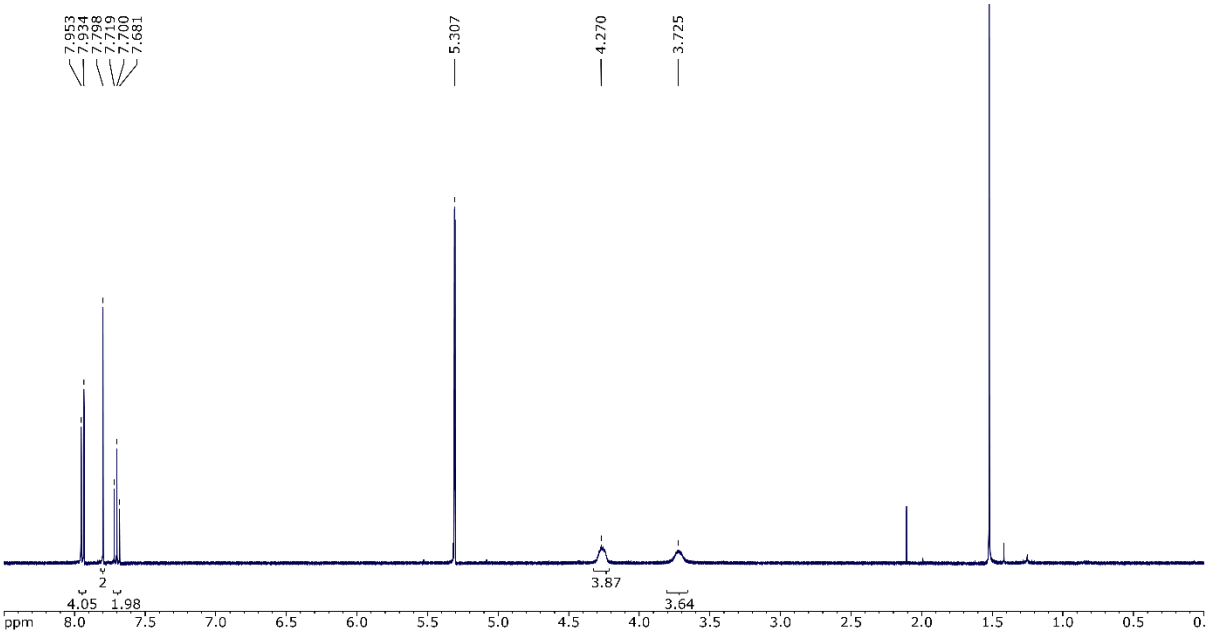


Figure S2. ^{1}H NMR spectrum of pyrene-4,5-di(ethyleneglycol)ketal (**5**) measured at 400 MHz in CD_2Cl_2.

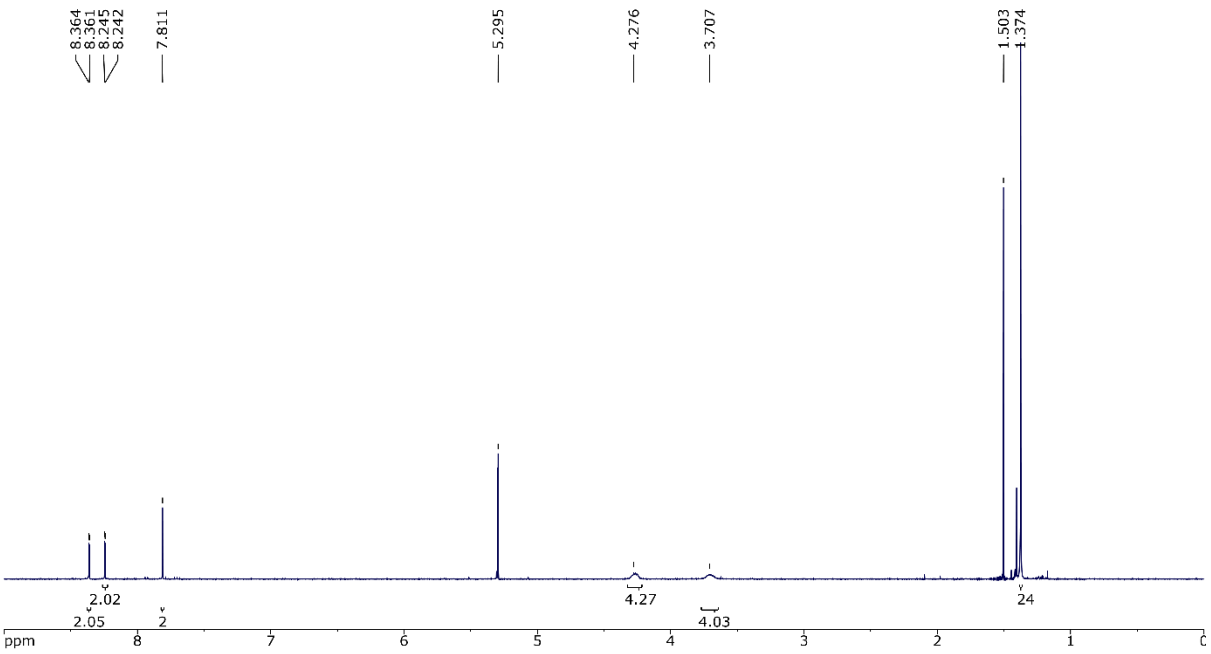


Figure S3. ^{1}H NMR spectrum of 2,7-bis(Bpin)-4,5-di(ethyleneglycol)ketal-pyrene (**6**) measured at 400 MHz in CD_2Cl_2.

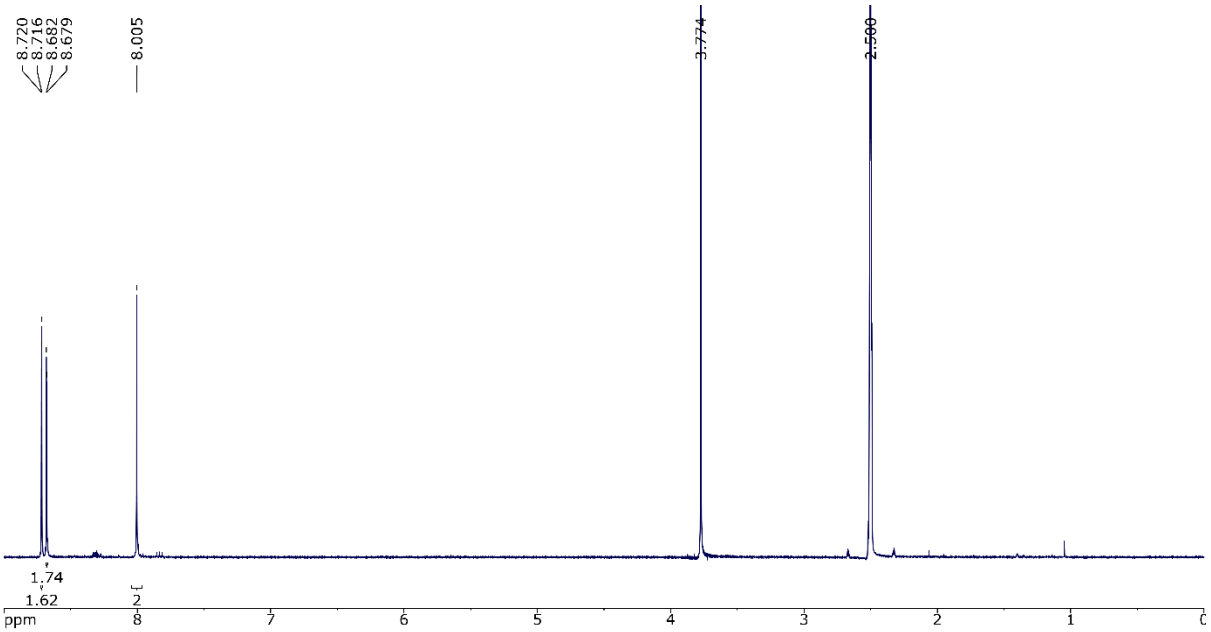


Figure S4. ^{1}H NMR spectrum of (7-borono-4,5-dioxo-pyren-2-yl)boronic acid (pyrene-4,5-dione building block **1**) measured at 400 MHz in $(CD_3)_2SO+D_2O$.

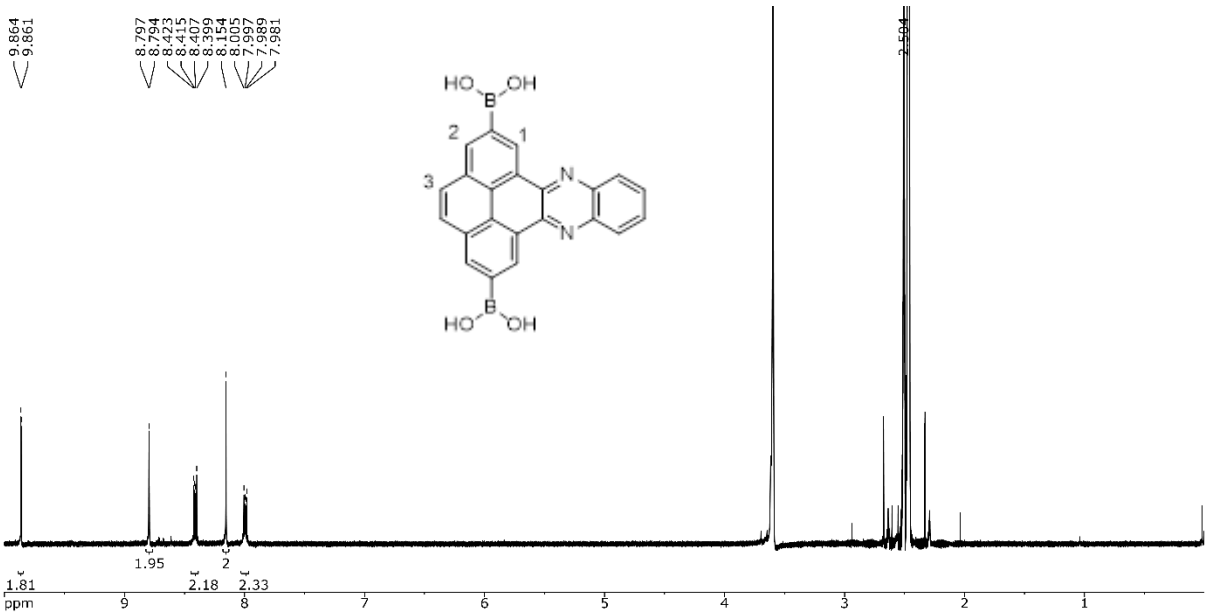


Figure S5. ^{1}H NMR spectrum of model compound **2** measured at 400 MHz in $(CD_3)_2SO+D_2O$.

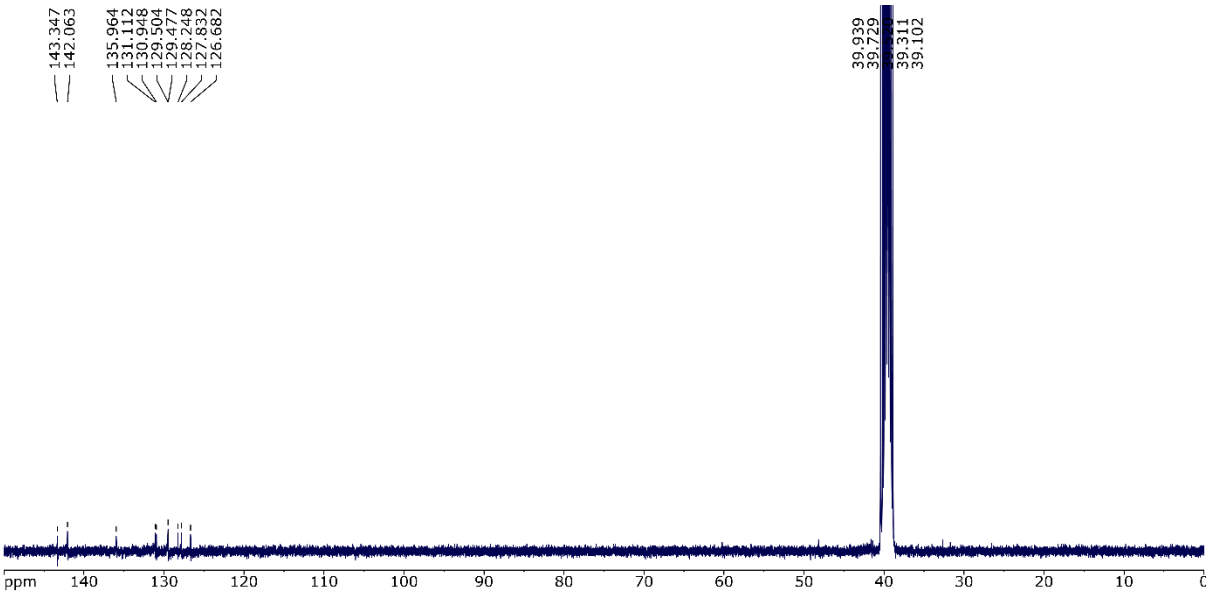


Figure S6. ^{13}C NMR spectrum of model compound **2** measured at 100 MHz in $(CD_3)_2SO+D_2O$.

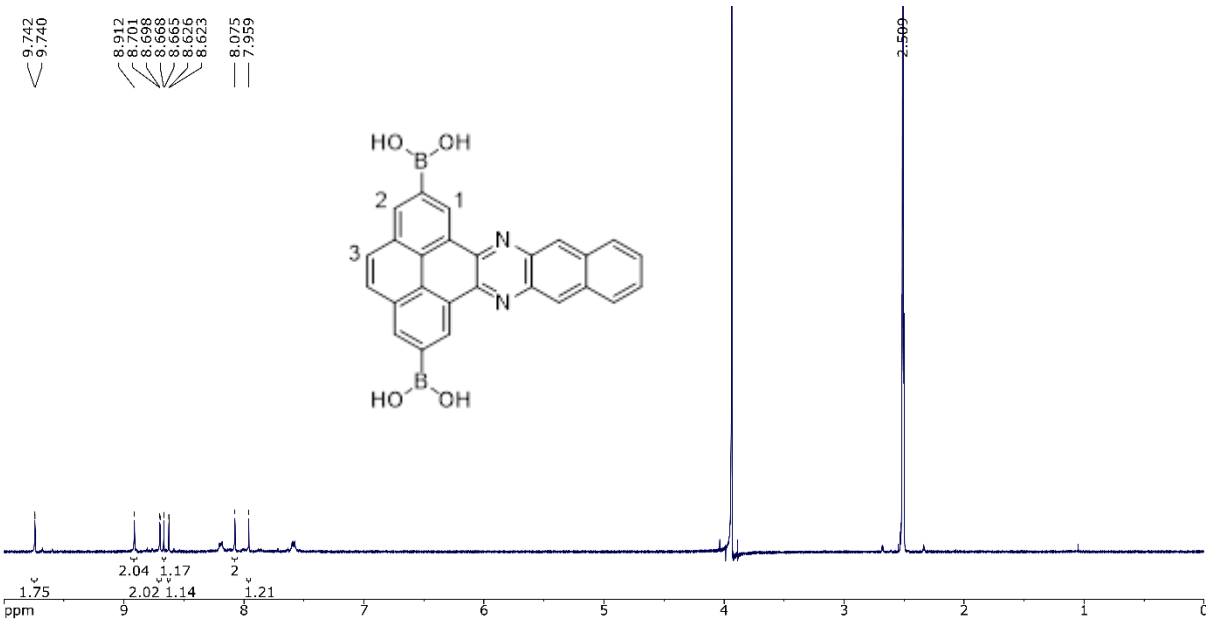


Figure S7. ^{1}H NMR spectrum of model compound **3** measured at 400 MHz in $(CD_3)_2SO+D_2O$.

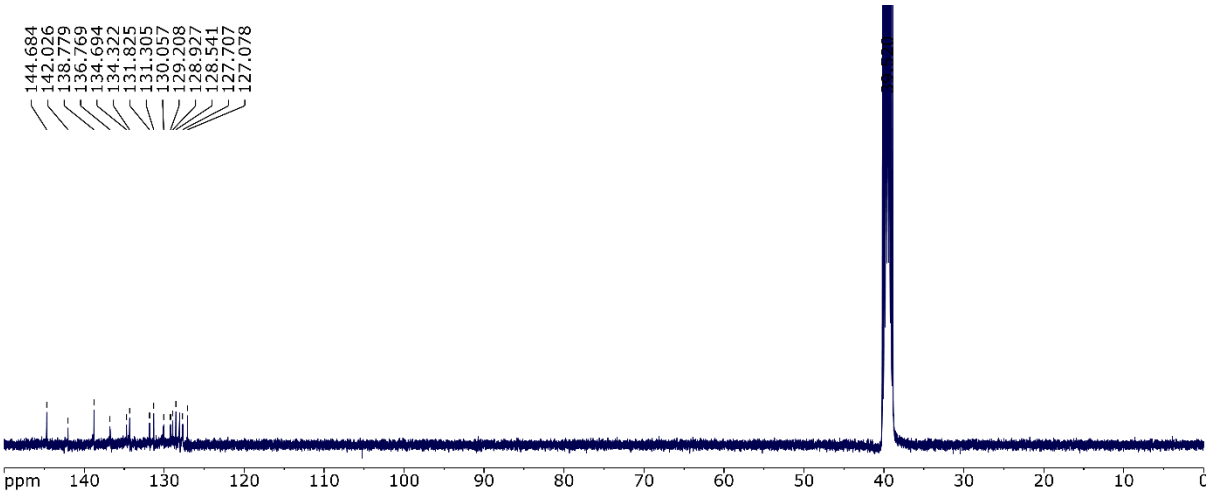


Figure S8. ^{13}C NMR spectrum of model compound **3** measured at 100 MHz in $(CD_3)_2SO+D_2O$.

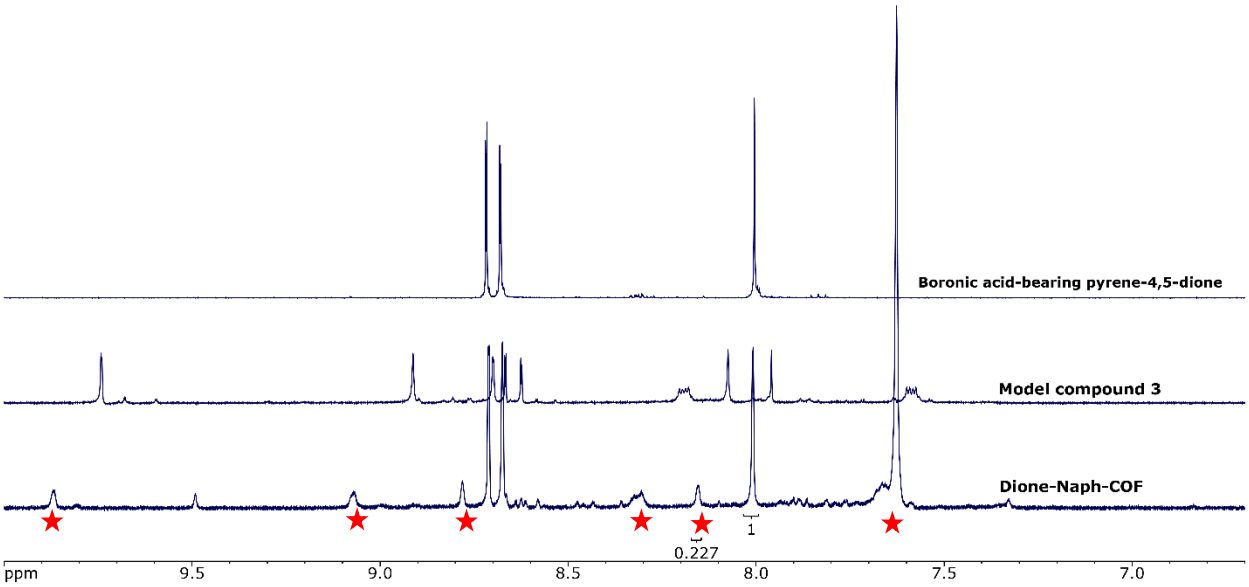


Figure S9. ^{1}H NMR spectrum of Dione-Naph-COF overlaid with boronic acid-bearing pyrene-4,5-dione building block **1** and model compound **3** measured at 400 MHz in $(CD_3)_2SO+D_2O$.

4. Crystal Structure Simulation

The simulated unit cell of Dione-Ph-COF and Dione-Naph-COF were constructed with the visualization environment of Materials Studio and the geometry optimized using force field methods. The simulated diffraction pattern corresponds well with the experimental powder X-ray diffraction (PXRD) data.

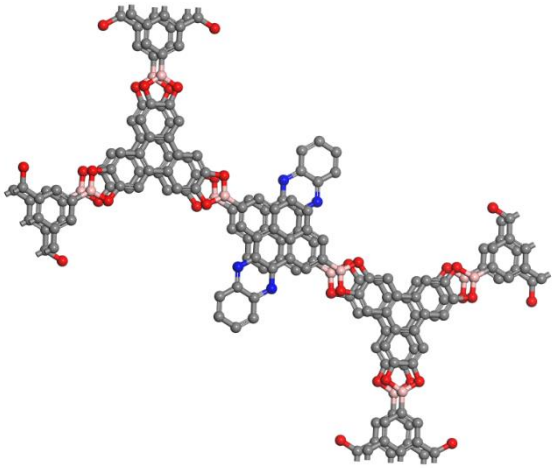


Figure S10. Simulation of the crystal unit cell of Dione-Ph-COF. View on ab-plane.

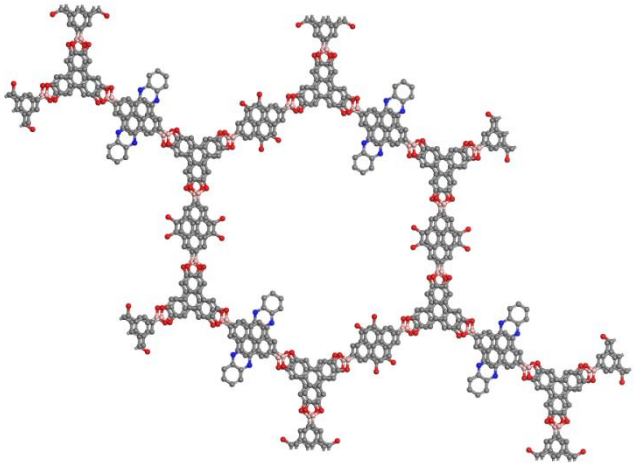


Figure S11. View of four unit cells constructing the Dione-Ph-COF pore.

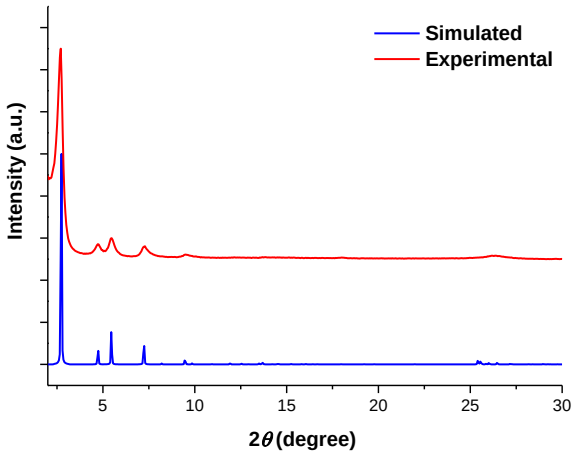


Figure S12. Experimentally obtained PXRD pattern (red) of Dione-Ph-COF and its simulated PXRD pattern (blue) obtained in Material Studio.

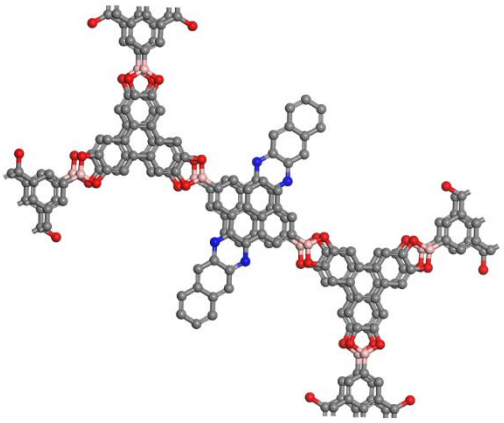


Figure S13. Simulation of the crystal unit cell of Dione-Naph-COF. View on ab-plane.

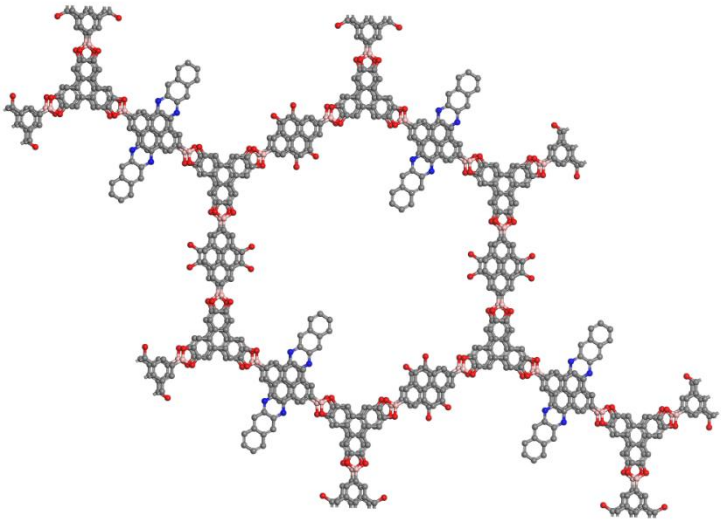


Figure S14. View of four unit cells constructing the Dione-Naph-COF pore.

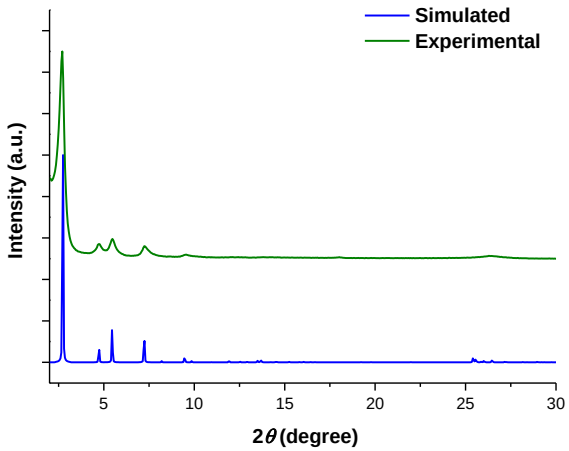


Figure S15. Experimentally obtained PXRD pattern (green) of Dione-Naph-COF and its simulated PXRD pattern (blue) obtained in Material Studio.

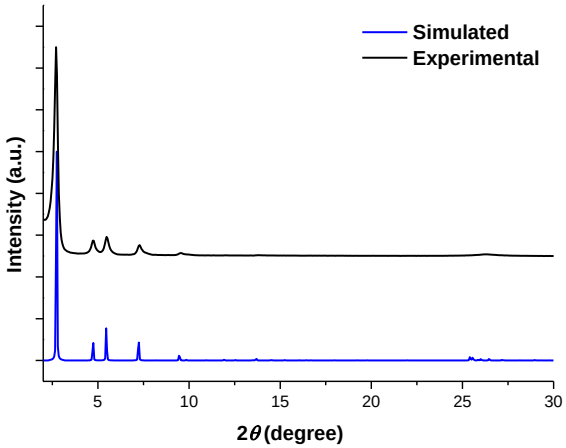


Figure S16. Experimentally obtained PXRD pattern (black) of Dione-COF and its simulated PXRD pattern (blue) obtained in Material Studio.

Unit cell parameters (*P*-1) and atomic coordinates for Dione-Ph-COF

a = b = 37.3, c = 7.0 Å

α = β = 90°, ɣ = 120°

Atom	**a/x**	**b/y**	**c/z**
C1	0.62880	0.29532	0.24348
C2	0.66715	0.29562	0.24348
C3	0.59137	0.25721	0.24348
C4	0.59266	0.22067	0.24348
C5	0.62952	0.22090	0.24348
C6	0.66708	0.25777	0.24348
O7	0.55864	0.18124	0.24348
B8	0.57934	0.15673	0.24348
O9	0.62455	0.18158	0.24348
C10	0.55521	0.10874	0.24348
C11	0.51208	0.08777	0.24348
C12	0.48943	0.04455	0.24348
C13	0.51044	0.02188	0.24349
C14	0.55420	0.04339	0.24348
C15	0.57624	0.08658	0.24348
C16	0.44385	0.02269	0.24348
C17	0.57555	0.02158	0.24348
O18	0.42116	0.04538	0.24348
C19	0.30771	0.35309	0.74348
C20	0.30771	0.28502	0.74348
C21	0.70468	0.33348	0.24348
C22	0.70438	0.37153	0.24348
C23	0.74279	0.33416	0.24348
C24	0.77933	0.37199	0.24348
C25	0.77910	0.40862	0.24348

C26	0.74223	0.40931	0.24348
O27	0.81876	0.37740	0.24348
B28	0.84327	0.42261	0.24348
O29	0.81842	0.44297	0.24348
C30	0.89126	0.44647	0.24348
C31	0.91223	0.42431	0.24348
C32	0.95545	0.44488	0.24348
C33	0.97812	0.48856	0.24349
C34	0.95661	0.51081	0.24348
C35	0.91342	0.48966	0.24348
C36	0.97731	0.42116	0.24348
C37	0.97842	0.55397	0.24348
O38	0.95462	0.37578	0.24348
C39	0.66652	0.37120	0.24348
C40	0.62847	0.33285	0.24348
C41	0.66584	0.40863	0.24348
C42	0.62801	0.40734	0.24348
C43	0.59138	0.37048	0.24348
C44	0.59069	0.33292	0.24348
O45	0.62260	0.44136	0.24348
B46	0.57739	0.42066	0.24348
O47	0.55703	0.37545	0.24348
C48	0.55353	0.44479	0.24348
C49	0.57569	0.48792	0.24348
C50	0.55512	0.51057	0.24348
C51	0.51144	0.48956	0.24349
C52	0.48919	0.44580	0.24348
C53	0.51034	0.42376	0.24348
C54	0.57884	0.55615	0.24348

C55	0.44603	0.42445	0.24348
N56	0.62422	0.57884	0.24348
C57	0.64691	0.62422	0.24348
C58	0.37120	0.70468	0.74348
C59	0.33285	0.70438	0.74348
C60	0.40863	0.74279	0.74348
C61	0.40734	0.77933	0.74348
C62	0.37048	0.77910	0.74348
C63	0.33292	0.74223	0.74348
O64	0.44136	0.81876	0.74348
B65	0.42066	0.84327	0.74348
O66	0.37545	0.81842	0.74348
C67	0.44479	0.89126	0.74348
C68	0.48792	0.91223	0.74348
C69	0.51057	0.95545	0.74348
C70	0.48956	0.97812	0.74349
C71	0.44580	0.95661	0.74348
C72	0.42376	0.91342	0.74348
C73	0.55615	0.97731	0.74348
C74	0.42445	0.97842	0.74348
O75	0.57884	0.95462	0.74348
C76	0.69229	0.64691	0.24348
C77	0.69229	0.71498	0.24348
C78	0.29532	0.66652	0.74348
C79	0.29562	0.62847	0.74348
C80	0.25721	0.66584	0.74348
C81	0.22067	0.62801	0.74348
C82	0.22090	0.59138	0.74348
C83	0.25777	0.59069	0.74348

O84	0.18124	0.62260	0.74348
B85	0.15673	0.57739	0.74348
O86	0.18158	0.55703	0.74348
C87	0.10874	0.55353	0.74348
C88	0.08777	0.57569	0.74348
C89	0.04455	0.55512	0.74348
C90	0.02188	0.51144	0.74349
C91	0.04339	0.48919	0.74348
C92	0.08658	0.51034	0.74348
C93	0.02269	0.57884	0.74348
C94	0.02158	0.44603	0.74348
O95	0.04538	0.62422	0.74348
C96	0.33348	0.62880	0.74348
C97	0.37153	0.66715	0.74348
C98	0.33416	0.59137	0.74348
C99	0.37199	0.59266	0.74348
C100	0.40862	0.62952	0.74348
C101	0.40931	0.66708	0.74348
O102	0.37740	0.55864	0.74348
B103	0.42261	0.57934	0.74348
O104	0.44297	0.62455	0.74348
C105	0.44647	0.55521	0.74348
C106	0.42431	0.51208	0.74348
C107	0.44488	0.48943	0.74348
C108	0.48856	0.51044	0.74349
C109	0.51081	0.55420	0.74348
C110	0.48966	0.57624	0.74348
C111	0.42116	0.44385	0.74348
C112	0.55397	0.57555	0.74348

N113	0.37578	0.42116	0.74348
C114	0.35309	0.37578	0.74348
C115	0.70468	0.37120	0.74348
C116	0.70438	0.33285	0.74348
C117	0.74279	0.40863	0.74348
C118	0.77933	0.40734	0.74348
C119	0.77910	0.37048	0.74348
C120	0.74223	0.33292	0.74348
O121	0.81876	0.44136	0.74348
B122	0.84327	0.42066	0.74348
O123	0.81842	0.37545	0.74348
C124	0.89126	0.44479	0.74348
C125	0.91223	0.48792	0.74348
C126	0.95545	0.51057	0.74348
C127	0.97812	0.48956	0.74349
C128	0.95661	0.44580	0.74348
C129	0.91342	0.42376	0.74348
C130	0.97731	0.55615	0.74348
C131	0.97842	0.42445	0.74348
O132	0.95462	0.57884	0.74348
C133	0.64691	0.69229	0.24348
C134	0.71498	0.69229	0.24348
C135	0.66652	0.29532	0.74348
C136	0.62847	0.29562	0.74348
C137	0.66584	0.25721	0.74348
C138	0.62801	0.22067	0.74348
C139	0.59138	0.22090	0.74348
C140	0.59069	0.25777	0.74348
O141	0.62260	0.18124	0.74348

B142	0.57739	0.15673	0.74348
O143	0.55703	0.18158	0.74348
C144	0.55353	0.10874	0.74348
C145	0.57569	0.08777	0.74348
C146	0.55512	0.04455	0.74348
C147	0.51144	0.02188	0.74349
C148	0.48919	0.04339	0.74348
C149	0.51034	0.08658	0.74348
C150	0.57884	0.02269	0.74348
C151	0.44603	0.02158	0.74348
O152	0.62422	0.04538	0.74348
C153	0.62880	0.33348	0.74348
C154	0.66715	0.37153	0.74348
C155	0.59137	0.33416	0.74348
C156	0.59266	0.37199	0.74348
C157	0.62952	0.40862	0.74348
C158	0.66708	0.40931	0.74348
O159	0.55864	0.37740	0.74348
B160	0.57934	0.42261	0.74348
O161	0.62455	0.44297	0.74348
C162	0.55521	0.44647	0.74348
C163	0.51208	0.42431	0.74348
C164	0.48943	0.44488	0.74348
C165	0.51044	0.48856	0.74349
C166	0.55420	0.51081	0.74348
C167	0.57624	0.48966	0.74348
C168	0.44385	0.42116	0.74348
C169	0.57555	0.55397	0.74348
N170	0.42116	0.37578	0.74348

C171	0.37578	0.35309	0.74348
C172	0.29532	0.62880	0.24348
C173	0.29562	0.66715	0.24348
C174	0.25721	0.59137	0.24348
C175	0.22067	0.59266	0.24348
C176	0.22090	0.62952	0.24348
C177	0.25777	0.66708	0.24348
O178	0.18124	0.55864	0.24348
B179	0.15673	0.57934	0.24348
O180	0.18158	0.62455	0.24348
C181	0.10874	0.55521	0.24348
C182	0.08777	0.51208	0.24348
C183	0.04455	0.48943	0.24348
C184	0.02188	0.51044	0.24349
C185	0.04339	0.55420	0.24348
C186	0.08658	0.57624	0.24348
C187	0.02269	0.44385	0.24348
C188	0.02158	0.57555	0.24348
O189	0.04538	0.42116	0.24348
C190	0.35309	0.30771	0.74348
C191	0.28502	0.30771	0.74348
C192	0.33348	0.70468	0.24348
C193	0.37153	0.70438	0.24348
C194	0.33416	0.74279	0.24348
C195	0.37199	0.77933	0.24348
C196	0.40862	0.77910	0.24348
C197	0.40931	0.74223	0.24348
O198	0.37740	0.81876	0.24348
B199	0.42261	0.84327	0.24348

O200	0.44297	0.81842	0.24348
C201	0.44647	0.89126	0.24348
C202	0.42431	0.91223	0.24348
C203	0.44488	0.95545	0.24348
C204	0.48856	0.97812	0.24349
C205	0.51081	0.95661	0.24348
C206	0.48966	0.91342	0.24348
C207	0.42116	0.97731	0.24348
C208	0.55397	0.97842	0.24348
O209	0.37578	0.95462	0.24348
C210	0.37120	0.66652	0.24348
C211	0.33285	0.62847	0.24348
C212	0.40863	0.66584	0.24348
C213	0.40734	0.62801	0.24348
C214	0.37048	0.59138	0.24348
C215	0.33292	0.59069	0.24348
O216	0.44136	0.62260	0.24348
B217	0.42066	0.57739	0.24348
O218	0.37545	0.55703	0.24348
C219	0.44479	0.55353	0.24348
C220	0.48792	0.57569	0.24348
C221	0.51057	0.55512	0.24348
C222	0.48956	0.51144	0.24349
C223	0.44580	0.48919	0.24348
C224	0.42376	0.51034	0.24348
C225	0.55615	0.57884	0.24348
C226	0.42445	0.44603	0.24348
N227	0.57884	0.62422	0.24348
C228	0.62422	0.64691	0.24348

Unit cell parameters (*P*-1) and atomic coordinates for Dione-Naph-COF

a = b = 37.3, c = 7.0 Å

α = β = 90°, ɣ = 120°

Atom	a/x	b/y	c/z
C1	0.62880	0.29532	0.24348
C2	0.66715	0.29562	0.24348
C3	0.59137	0.25721	0.24348
C4	0.59266	0.22067	0.24348
C5	0.62952	0.22090	0.24348
C6	0.66708	0.25777	0.24348
O7	0.55864	0.18124	0.24348
B8	0.57934	0.15673	0.24348
O9	0.62455	0.18158	0.24348
C10	0.55521	0.10874	0.24348
C11	0.51208	0.08777	0.24348
C12	0.48943	0.04455	0.24348
C13	0.51044	0.02188	0.24349
C14	0.55420	0.04339	0.24348
C15	0.57624	0.08658	0.24348
C16	0.44385	0.02269	0.24348
C17	0.57555	0.02158	0.24348
O18	0.42116	0.04538	0.24348
C19	0.30771	0.35309	0.74348
C20	0.30771	0.28502	0.74348
C21	0.70468	0.33348	0.24348
C22	0.70438	0.37153	0.24348
C23	0.74279	0.33416	0.24348
C24	0.77933	0.37199	0.24348
C25	0.77910	0.40862	0.24348

C26	0.74223	0.40931	0.24348
O27	0.81876	0.37740	0.24348
B28	0.84327	0.42261	0.24348
O29	0.81842	0.44297	0.24348
C30	0.89126	0.44647	0.24348
C31	0.91223	0.42431	0.24348
C32	0.95545	0.44488	0.24348
C33	0.97812	0.48856	0.24349
C34	0.95661	0.51081	0.24348
C35	0.91342	0.48966	0.24348
C36	0.97731	0.42116	0.24348
C37	0.97842	0.55397	0.24348
O38	0.95462	0.37578	0.24348
C39	0.66652	0.37120	0.24348
C40	0.62847	0.33285	0.24348
C41	0.66584	0.40863	0.24348
C42	0.62801	0.40734	0.24348
C43	0.59138	0.37048	0.24348
C44	0.59069	0.33292	0.24348
O45	0.62260	0.44136	0.24348
B46	0.57739	0.42066	0.24348
O47	0.55703	0.37545	0.24348
C48	0.55353	0.44479	0.24348
C49	0.57569	0.48792	0.24348
C50	0.55512	0.51057	0.24348
C51	0.51144	0.48956	0.24349
C52	0.48919	0.44580	0.24348
C53	0.51034	0.42376	0.24348
C54	0.57884	0.55615	0.24348

C55	0.44603	0.42445	0.24348
N56	0.62422	0.57884	0.24348
C57	0.64691	0.62422	0.24348
C58	0.37120	0.70468	0.74348
C59	0.33285	0.70438	0.74348
C60	0.40863	0.74279	0.74348
C61	0.40734	0.77933	0.74348
C62	0.37048	0.77910	0.74348
C63	0.33292	0.74223	0.74348
O64	0.44136	0.81876	0.74348
B65	0.42066	0.84327	0.74348
O66	0.37545	0.81842	0.74348
C67	0.44479	0.89126	0.74348
C68	0.48792	0.91223	0.74348
C69	0.51057	0.95545	0.74348
C70	0.48956	0.97812	0.74349
C71	0.44580	0.95661	0.74348
C72	0.42376	0.91342	0.74348
C73	0.55615	0.97731	0.74348
C74	0.42445	0.97842	0.74348
O75	0.57884	0.95462	0.74348
C76	0.69229	0.64691	0.24348
C77	0.69229	0.71498	0.24348
C78	0.29532	0.66652	0.74348
C79	0.29562	0.62847	0.74348
C80	0.25721	0.66584	0.74348
C81	0.22067	0.62801	0.74348
C82	0.22090	0.59138	0.74348
C83	0.25777	0.59069	0.74348

O84	0.18124	0.62260	0.74348
B85	0.15673	0.57739	0.74348
O86	0.18158	0.55703	0.74348
C87	0.10874	0.55353	0.74348
C88	0.08777	0.57569	0.74348
C89	0.04455	0.55512	0.74348
C90	0.02188	0.51144	0.74349
C91	0.04339	0.48919	0.74348
C92	0.08658	0.51034	0.74348
C93	0.02269	0.57884	0.74348
C94	0.02158	0.44603	0.74348
O95	0.04538	0.62422	0.74348
C96	0.33348	0.62880	0.74348
C97	0.37153	0.66715	0.74348
C98	0.33416	0.59137	0.74348
C99	0.37199	0.59266	0.74348
C100	0.40862	0.62952	0.74348
C101	0.40931	0.66708	0.74348
O102	0.37740	0.55864	0.74348
B103	0.42261	0.57934	0.74348
O104	0.44297	0.62455	0.74348
C105	0.44647	0.55521	0.74348
C106	0.42431	0.51208	0.74348
C107	0.44488	0.48943	0.74348
C108	0.48856	0.51044	0.74349
C109	0.51081	0.55420	0.74348
C110	0.48966	0.57624	0.74348
C111	0.42116	0.44385	0.74348
C112	0.55397	0.57555	0.74348

N113	0.37578	0.42116	0.74348
C114	0.35309	0.37578	0.74348
C115	0.70468	0.37120	0.74348
C116	0.70438	0.33285	0.74348
C117	0.74279	0.40863	0.74348
C118	0.77933	0.40734	0.74348
C119	0.77910	0.37048	0.74348
C120	0.74223	0.33292	0.74348
O121	0.81876	0.44136	0.74348
B122	0.84327	0.42066	0.74348
O123	0.81842	0.37545	0.74348
C124	0.89126	0.44479	0.74348
C125	0.91223	0.48792	0.74348
C126	0.95545	0.51057	0.74348
C127	0.97812	0.48956	0.74349
C128	0.95661	0.44580	0.74348
C129	0.91342	0.42376	0.74348
C130	0.97731	0.55615	0.74348
C131	0.97842	0.42445	0.74348
O132	0.95462	0.57884	0.74348
C133	0.64691	0.69229	0.24348
C134	0.71498	0.69229	0.24348
C135	0.66652	0.29532	0.74348
C136	0.62847	0.29562	0.74348
C137	0.66584	0.25721	0.74348
C138	0.62801	0.22067	0.74348
C139	0.59138	0.22090	0.74348
C140	0.59069	0.25777	0.74348
O141	0.62260	0.18124	0.74348

B142	0.57739	0.15673	0.74348
O143	0.55703	0.18158	0.74348
C144	0.55353	0.10874	0.74348
C145	0.57569	0.08777	0.74348
C146	0.55512	0.04455	0.74348
C147	0.51144	0.02188	0.74349
C148	0.48919	0.04339	0.74348
C149	0.51034	0.08658	0.74348
C150	0.57884	0.02269	0.74348
C151	0.44603	0.02158	0.74348
O152	0.62422	0.04538	0.74348
C153	0.62880	0.33348	0.74348
C154	0.66715	0.37153	0.74348
C155	0.59137	0.33416	0.74348
C156	0.59266	0.37199	0.74348
C157	0.62952	0.40862	0.74348
C158	0.66708	0.40931	0.74348
O159	0.55864	0.37740	0.74348
B160	0.57934	0.42261	0.74348
O161	0.62455	0.44297	0.74348
C162	0.55521	0.44647	0.74348
C163	0.51208	0.42431	0.74348
C164	0.48943	0.44488	0.74348
C165	0.51044	0.48856	0.74349
C166	0.55420	0.51081	0.74348
C167	0.57624	0.48966	0.74348
C168	0.44385	0.42116	0.74348
C169	0.57555	0.55397	0.74348
N170	0.42116	0.37578	0.74348

C171	0.37578	0.35309	0.74348
C172	0.29532	0.62880	0.24348
C173	0.29562	0.66715	0.24348
C174	0.25721	0.59137	0.24348
C175	0.22067	0.59266	0.24348
C176	0.22090	0.62952	0.24348
C177	0.25777	0.66708	0.24348
O178	0.18124	0.55864	0.24348
B179	0.15673	0.57934	0.24348
O180	0.18158	0.62455	0.24348
C181	0.10874	0.55521	0.24348
C182	0.08777	0.51208	0.24348
C183	0.04455	0.48943	0.24348
C184	0.02188	0.51044	0.24349
C185	0.04339	0.55420	0.24348
C186	0.08658	0.57624	0.24348
C187	0.02269	0.44385	0.24348
C188	0.02158	0.57555	0.24348
O189	0.04538	0.42116	0.24348
C190	0.35309	0.30771	0.74348
C191	0.28502	0.30771	0.74348
C192	0.33348	0.70468	0.24348
C193	0.37153	0.70438	0.24348
C194	0.33416	0.74279	0.24348
C195	0.37199	0.77933	0.24348
C196	0.40862	0.77910	0.24348
C197	0.40931	0.74223	0.24348
O198	0.37740	0.81876	0.24348
B199	0.42261	0.84327	0.24348

O200	0.44297	0.81842	0.24348
C201	0.44647	0.89126	0.24348
C202	0.42431	0.91223	0.24348
C203	0.44488	0.95545	0.24348
C204	0.48856	0.97812	0.24349
C205	0.51081	0.95661	0.24348
C206	0.48966	0.91342	0.24348
C207	0.42116	0.97731	0.24348
C208	0.55397	0.97842	0.24348
O209	0.37578	0.95462	0.24348
C210	0.37120	0.66652	0.24348
C211	0.33285	0.62847	0.24348
C212	0.40863	0.66584	0.24348
C213	0.40734	0.62801	0.24348
C214	0.37048	0.59138	0.24348
C215	0.33292	0.59069	0.24348
O216	0.44136	0.62260	0.24348
B217	0.42066	0.57739	0.24348
O218	0.37545	0.55703	0.24348
C219	0.44479	0.55353	0.24348
C220	0.48792	0.57569	0.24348
C221	0.51057	0.55512	0.24348
C222	0.48956	0.51144	0.24349
C223	0.44580	0.48919	0.24348
C224	0.42376	0.51034	0.24348
C225	0.55615	0.57884	0.24348
C226	0.42445	0.44603	0.24348
N227	0.57884	0.62422	0.24348
C228	0.62422	0.64691	0.24348

C229	0.71498	0.76036	0.24348
C230	0.76036	0.78305	0.24348
C231	0.78305	0.76036	0.24348
C232	0.76036	0.71498	0.24348
C233	0.28502	0.23964	0.74348
C234	0.23964	0.21695	0.74348
C235	0.21695	0.23964	0.74348
C236	0.23964	0.28502	0.74348

5. N_2 Physisorption

Dione-COF

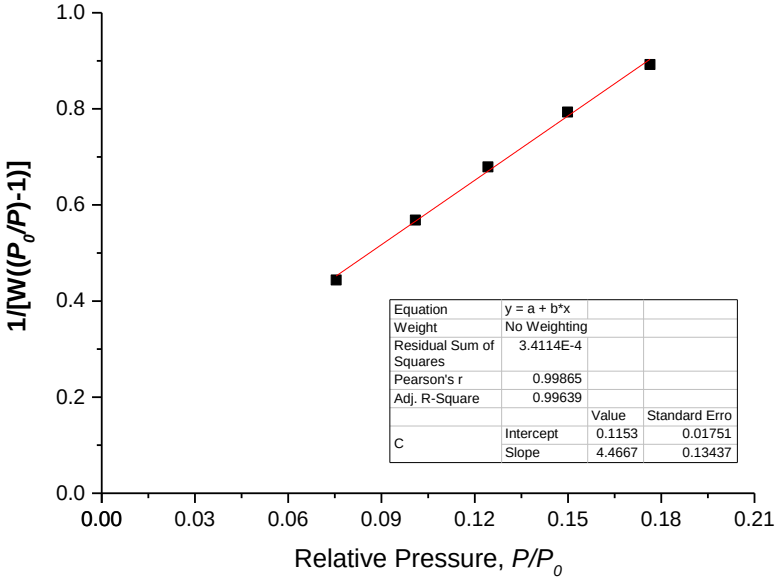


Figure S17. Multi-point BET plot and linear fit.

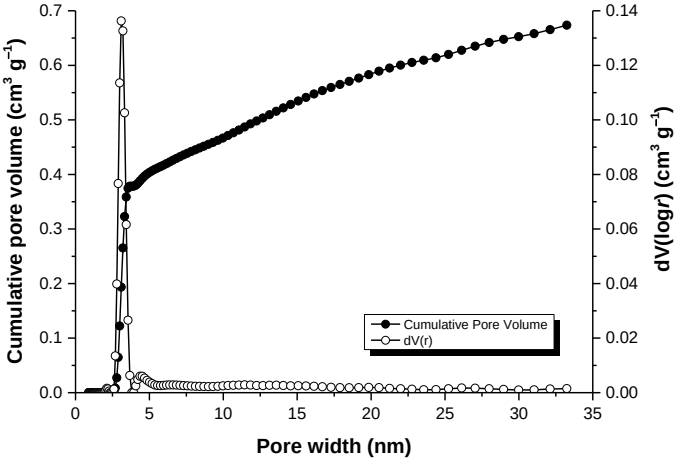


Figure S18. Pore size distribution (hollow spheres) and cumulative pore volume (filled spheres) profiles.

Dione-Ph-COF

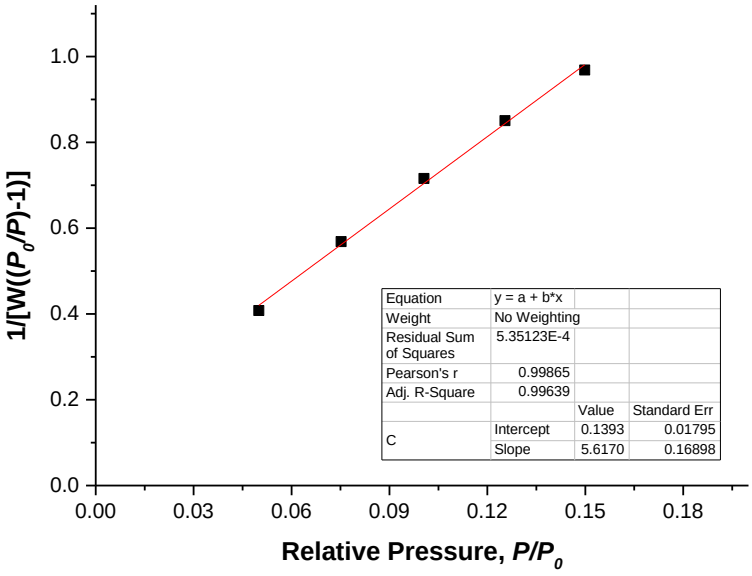


Figure S19. Multi-point BET plot and linear fit.

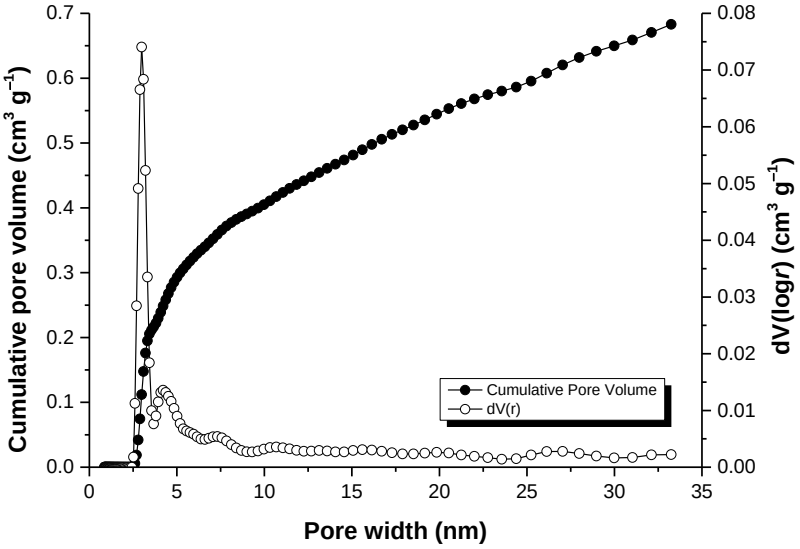


Figure S20. Pore size distribution (hollow spheres) and cumulative pore volume (filled spheres) profiles.

Dione-Naph-COF

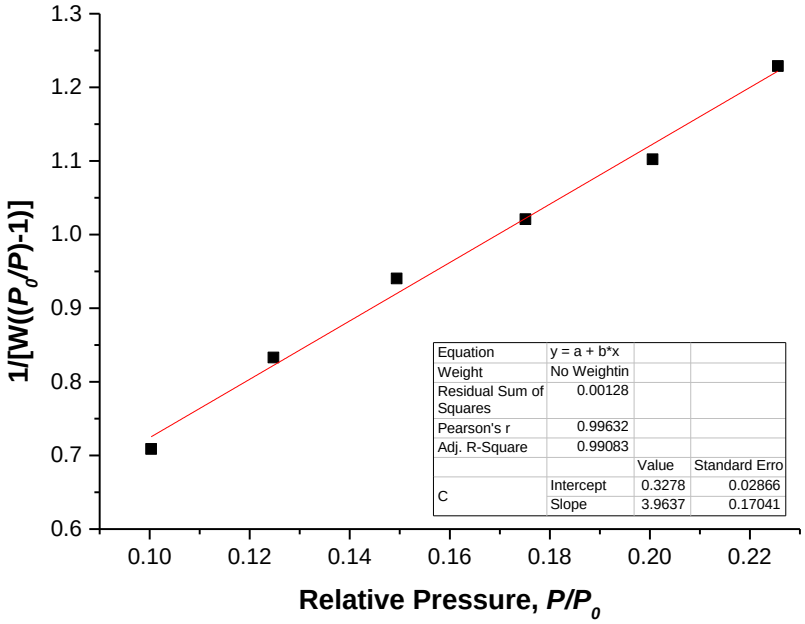


Figure S21. Multi-point BET plot and linear fit.

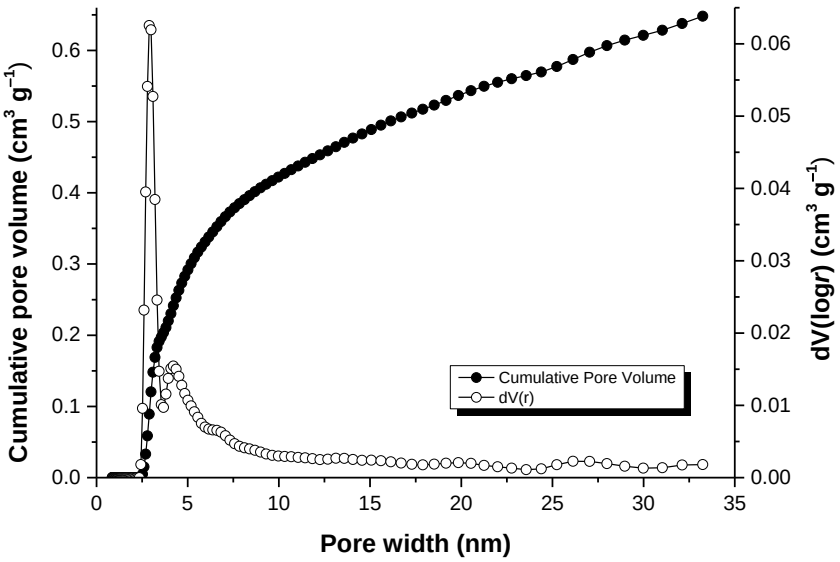


Figure S22. Pore size distribution (hollow spheres) and cumulative pore volume (filled spheres) profiles.

6. Fourier-transform infrared (FTIR) Spectra

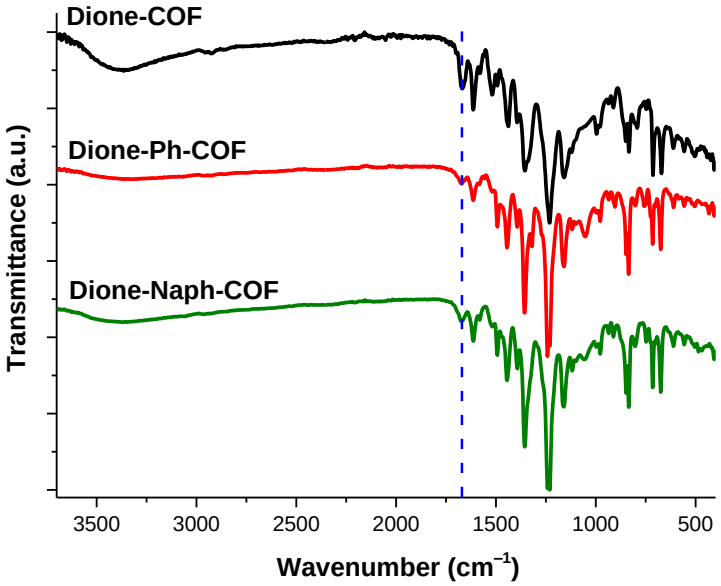


Figure S23. FTIR spectrum of Dione-COF, Dione-Ph-COF, and Dione-Naph-COF.

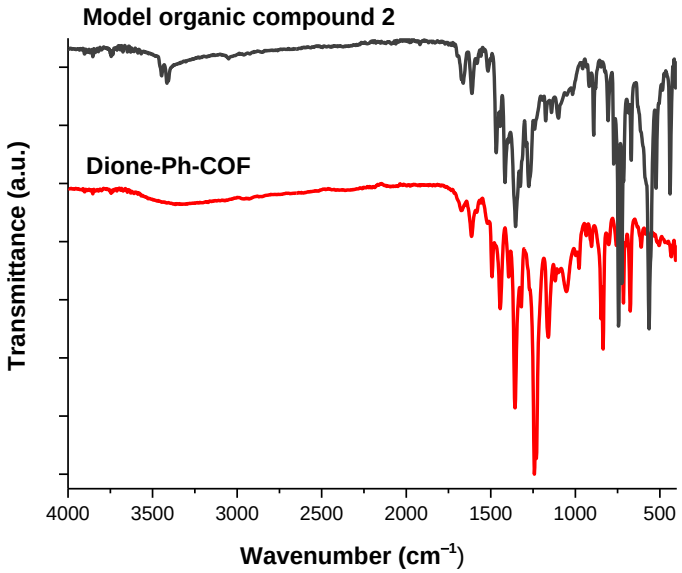


Figure S24. FTIR spectrum of model organic compound **2** and Dione-Ph-COF.

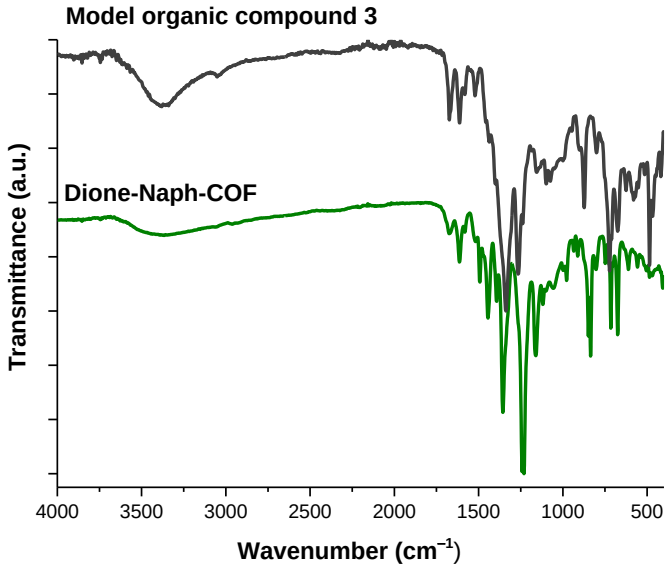


Figure S25. FTIR spectrum of model organic compound **3** and Dione-Naph-COF.

7. Thermogravimetric Analysis (TGA)

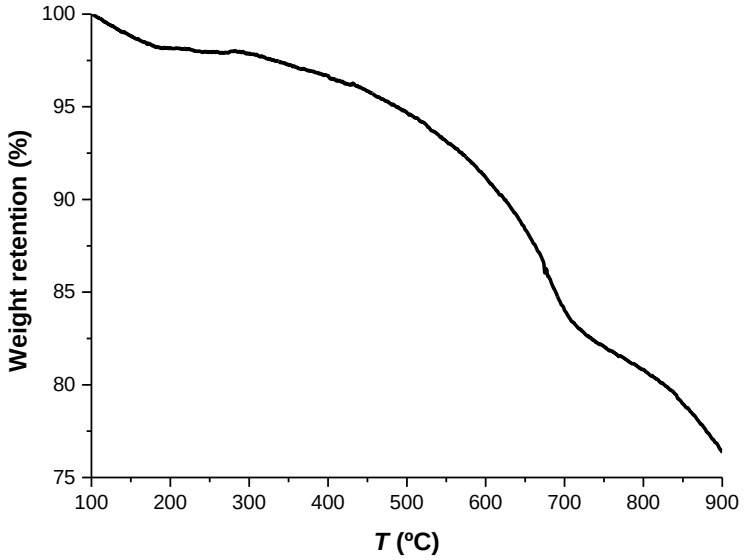


Figure S26. TGA profile of Dione-COF.

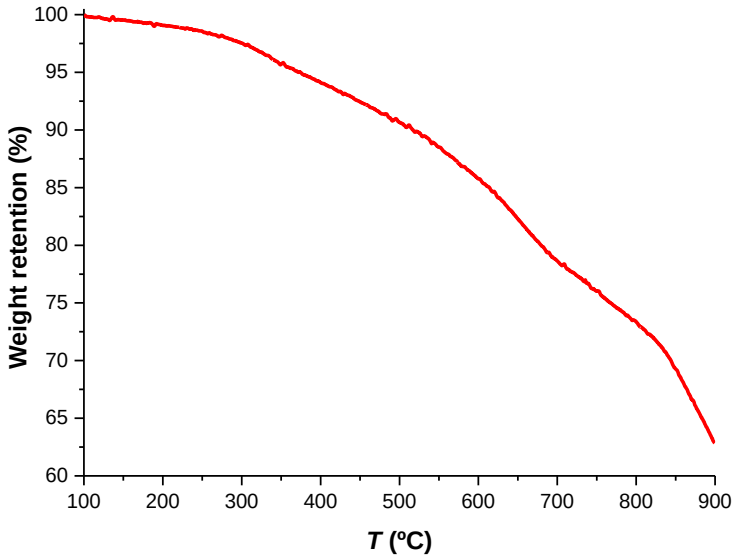


Figure S27. TGA profile of Dione-Ph-COF.

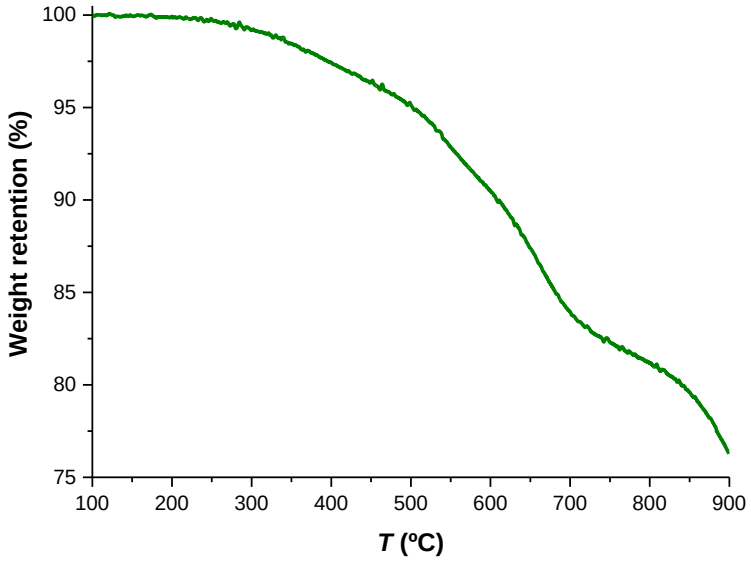


Figure S28. TGA profile of Dione-Naph-COF.

8. Scanning electron microscopy (SEM)

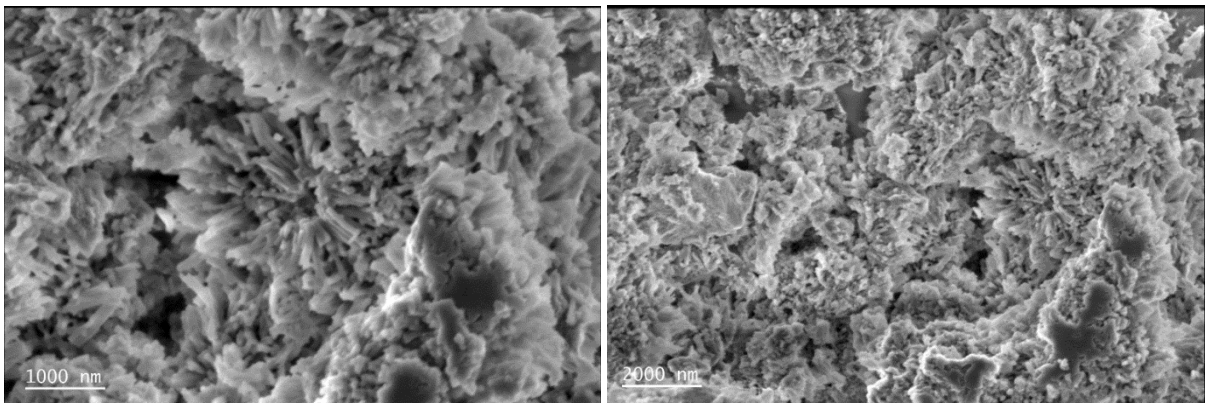


Figure S29. SEM image of Dione-Ph-COF.

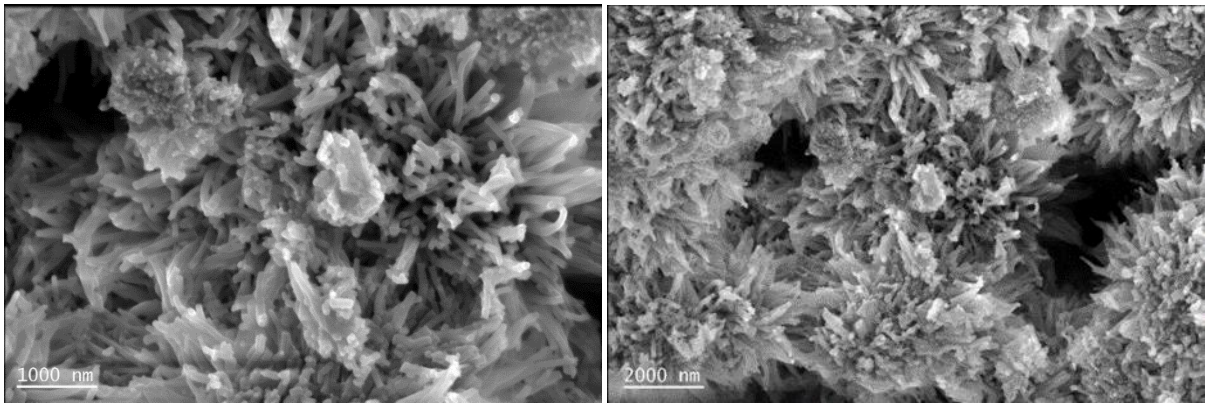


Figure S30. SEM image of Dione-Naph-COF.

9. Optical Properties of the Dione Building Block

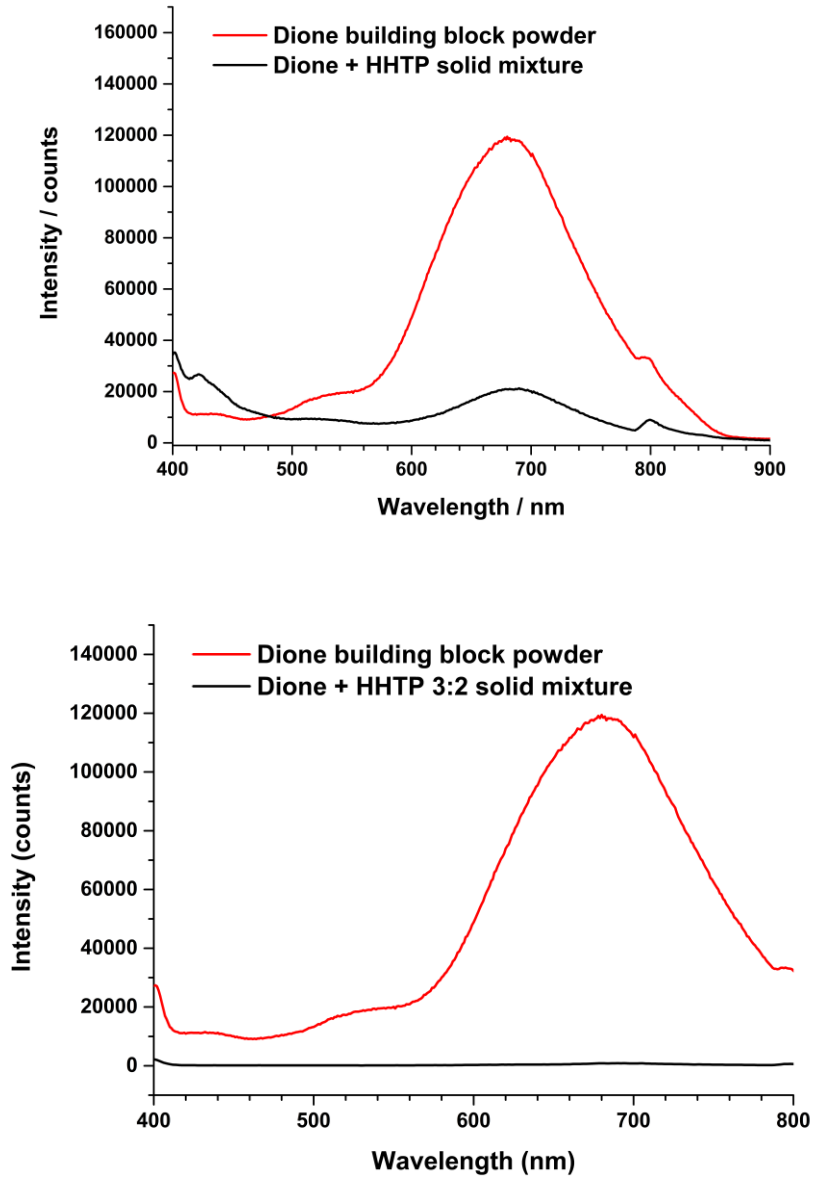


Figure S31. Top: PL spectra of dione building block **1** as powder (red), and a physical mixture of **1** and HHTP as powder (black). Bottom: PL spectra of dione building block **1** as powder (red), and a dropcasted mixture of **1** and HHTP as 2:3 slurry (black).

10. References

[1] K. M. Williams, D. Lungerich, G. J. Bodwell, *Eur. J. Org. Chem.* **2016**, 5933–5936.

[2] J. Merz, M. Dietz, Y. Vonhausen, F. Wçber, A. Friedrich, D. Sieh, I. Krummenacher, H. Braunschweig, M. Moos, M. Holzapfel, C. Lambert, T. B. Marder, *Chem. Eur. J.* **2020**, *26*, 438–453.

[3] L. M. Salonen, D. D. Medina, E. Carbó-Argibay, M. G. Goesten, L. Mafra, N. Guldris, J. M. Rotter, D. G. Stroppa, C. Rodríguez-Abreu, *Chem. Commun.* **2016**, *52*, 7986–7989.