Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Pore Wall Fluorescence Labeling of Covalent Organic Frameworks

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Section 1: Materials and Methods

All materials (if not otherwise noted) were purchased from Aldrich or Fluka in the common purities purum and puriss. All materials were used without further purification.

Powder Xray diffraction (PXRD) measurements were carried out in reflection mode on a Bruker D8 Discover diffractometer with Nifiltered Kαradiation (λ = 1.54060 Å) and a position-sensitive detector (LynxEye). For visualizing the crystallinity of the resulting COF material, high resolution measurements had to be carried out. For this purpose the material was placed on a silicon wafer and measurements were performed by applying a low scan speed.

The **IRSpectra** were recorded on a *Perkin Elmer Spectrum BX FTIR* device in combination with an attenuated total reflection (ATR) accessory comprising an ATR diamond crystal. All samples were measured at room temperature without further preparation.

Scanning electron microscopy (SEM) was performed on an FEI Helios G3 UC instrument at 2 kV. For this purpose the samples were put on an adhesive graphite film and sputtered with carbon with a BALTEC MED 020 Coating Sytem.

Transmission electron microscopy (TEM) data were obtained with a Tecnai G2 20 STwin at an acceleration voltage of 200 kV.

^{1}H/^{13}C NMR solution spectra were recorded on a Bruker Avance III-400 MHz and a Bruker Avance III-270 MHz spectrometer. Therefore, 4 mg of material and an access of pinacol were put together in DMSO-d6 to cleave the boronate ester bonds. Proton chemical shifts are expressed in parts per million (δ scale) and are calibrated using residual undeuterated solvent peaks as an internal reference (^{1}H NMR DMSO-d6: 2.50).

^{11}B and ^{13}C MASNMR spectra were recorded on a Bruker DSX Avance 500 with a magnetic field of 11.2 Tesla. A 4 mm MAS rotor in a tripleresonance sample head was used. The frequency of the rotors was 10 kHz.

Thermogravimetric (TG) measurements were performed in a stream of synthetic air (25 ml / min) on a Netzsch STA 440 C TG/DSC instrument. The measurements were carried out with a heating rate of 10 °C / min, and a temperature range from 30 °C to 900 °C was covered.

Nitrogen sorption was measured using a Quantachrome AUTOSORB1 station at 77.3 K after degassing the sample for at least 12 h under vacuum at 120 °C. The Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption branch in the range of $p/p_0 = 0.05–0.17$. Pore sizes were calculated with a QSDFT adsorption model of N_2 on carbon (cylindrical, adsorption branch) and a NLDFT adsorption model (slit pore, equilibrium).

Based on the symmetry of the applied building blocks, the final 2D COF structure can be approximately predicted and then confirmed with experimental powder X-ray diffraction (PXRD) data. The **simulation** was carried out with the visualization environment of Materials Studio software 4.4, and the geometry of the twodimensional layers was optimized with calculations using forcite methods. Based on the geometry of the precursor molecules, the repeating unit was constructed into a unit cell by directly applying the symmetry operators of the P6 space group. To this end, the repeating fragments were placed in the bare hexagonal unit cell and connected to each other, resulting in the complete unit cell. The geometry of the T-COF-OH layer was optimized in the unit cell using the Dreiding forcefield and the QEq correction for weak interactions. The simulated pattern shows very good agreement with our experimental PXRD data.

The postsynthetically modified fluorescent COFs were imaged using spinning disc **microscopy** (Zeiss Cell Observer SD utilizing a Yokogawa spinning disk unit CSUX1). The objective was a 1.40 NA 63x Plan apochromat oil immersion objective (Zeiss). FITC was imaged with 488 nm laser excitation. Images were acquired using an electron multiplier charge coupled device (EMCCD) camera (Photometrics Evolve^{TM}).

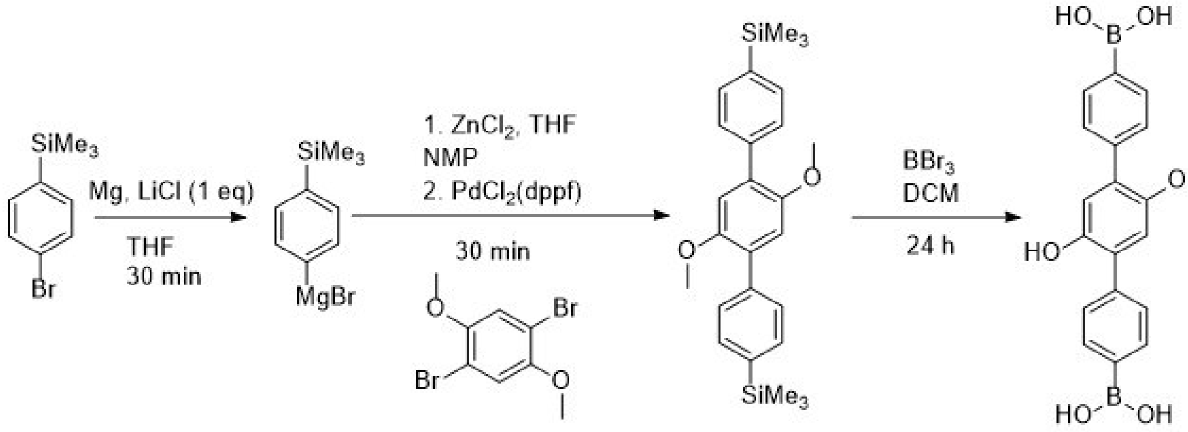
Elementary analysis was performed on a Vario micro cube CHNS analyzer detecting carbon, nitrogen, hydrogen and sulfur. The dried powder of the COF was pyrolized at 1150 °C in an oxygen-enriched He-atmosphere. The resulting gases were detected by thermal conductivity measurements.

The grafting yield of the post-synthetic modification reaction was determined by **fluorescence measurements**. For this purpose, a calibration curve with diverse concentrations of FITC in water was recorded. The two different COF materials were dissolved with excess of pinacol in water and measured under the same conditions. Fluorescence investigations were recorded on a PTI fluorescence system featuring a PTI 814 photomultiplier detector and a PTI A1010B Xenon arc lamp driven by a PTI LPS-220B lamp power supply. Fluorescein was excited with 495 nm and emission was detected at 516 nm (excitation slit 2.0 mm, emission slit 2.0 mm).

Section 2: Syntheses and Characterizations

1. Synthesis

Synthesis of 2',5'dihydroxy[1,1';4',1'']terphenyl4,4''diboronic acid



A 500 ml roundbottom flask equipped with a magnetic stirring bar was charged with magnesium turnings (0.645 g, 26.5 mmol, 1.4 eq) and lithium chloride (0.9 g, 21.3 mmol, 90 %, 1.0 eq). The reactants were dried under vacuum at 250 °C for 20 min. After cooling to room temperature under nitrogen atmosphere, 15 ml of anhydrous tetrahydrofuran (THF) was added. The reaction solution was stirred for 30 minutes. Afterwards 1bromo4(trimethylsilyl)benzene (4.5 g, 18.7 mmol, 1.0 eq) was added dropwise. After 5 minutes, an exothermic reaction set in. The solution was stirred for another hour and added dropwise to an ice bath-cooled solution of zinc (II) chloride (1.28 g, 32 mmol, 0.5 eq) and 0.96 ml (10 %) *N*-methyl-2-pyrrolidone (NMP) in 9.6 ml THF. The mixture was stirred for additional 30 min.

In a 100 ml round-bottom flask, bis(di-tert-butyl)4-dimethylaminophenyl)-phosphine)-dichloropalladium (II) (13.31 mg, 0.019 mmol, 1 mol%) and 1,4dibromo-2,5dimethoxybenzene (2.22 g, 7.4 mmol, 0.4 eq) were dissolved in THF (6 ml). The mixture was added dropwise to the already produced zinc (II) chloride solution and the whole mixture was stirred overnight. The suspension was quenched with 100 ml of a saturated ammonium chloride solution. The amount of 60 ml diethyl ether was added and the mixture was extracted with diethyl ether (4 x 60 ml). Subsequently, the solution was dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation. Recrystallization in n-heptane yielded the product as a grey powder (102.34 mg, 0.23 mmol).

2',5'Dihydroxy[1,1';4',1'']terphenyl4,4''ditrimethylsilane (102.34 mg, 0.23 mmol, 1 eq) was dissolved in 1 ml dichloromethane (DCM). Boron tribromide (0.15 ml, 1.56 mmol, 6.8 eq) was added dropwise and the reaction mixture was stirred at room temperature for 24 h. The amount of 50 g ice was added carefully to the grey reaction suspension and it was stirred until the ice was completely molten. DCM was removed on the rotary evaporator and the product was filtered. The crude product was dissolved in acetone (1.3 ml), and subsequently reduced to half volume by rotary evaporation. Then 1,4dioxane (0.5 ml) was added and the volume was again reduced to half by rotary evaporation. Recrystallization from nheptane yielded a grey powder (101.83 mg, 0.29 mmol).

IR: 3347 (s), 1606 (m), 1556 (w), 1537 (w), 1423 (m), 1395 (m), 1376 (m), 1338 (s), 1290 (w), 1271 (w), 1256 (w), 1202 (w), 1154 (m), 1094 (m), 1024 (m), 1001 (m), 813 (m), 794 (m), 737 (m), 643 (w), 627 (m).

^{13}C-CP-MAS NMR (10 kHz): δ = 146.5 (CO), 139.6 (Cq), 133.2 (CH), 129.0 (Cq), 127.2 (CH), 115.7 (CH) ppm

^{11}B-NMR (10 kHz): δ = 17.44 ppm.

^{1}H-NMR (270 MHz, Methanol-D4, 27 °C, TMS): δ = 7.78 (d, *J* = 7.7 Hz, 1H), 7.69 – 7.53 (m, 5H), 6.95 (s, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.86 (s, 1H), 3.65 (s, 2H).

^{13}C NMR (400 MHz, Methanol-D4, 27 °C, TMS): *δ = 133.0 (CH), 133.2 (CH), 128.2 (CC), 128.1 (CH), 117.5 (CH) ppm.*

Synthesis of T-COF-OH

A 10 ml Schott Duran glass was charged with 2',5'-dihydroxy-[1,1';4',1'']terphenyl-4,4''-diboronic acid (9.17 mg, 0.075 mmol, 2.1 eq) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP; 10.8 mg, 0.036 mmol, 1.0 eq). The amount of 0.5 ml of a 9 : 1 v : v mixture of toluene : methanol was added. The reaction mixture was heated at 120 °C for 72 h. The brown solid was isolated by filtration and washed with dry acetone (5 x 1 ml). After washing, T-COF-OH was obtained as brownish powder (69%).

IR: 3307 (w), 1609 (m), 1526 (m), 1491 (m), 1440 (m), 1392 (m), 1353 (s), 1278 (m), 1243 (s), 1164 (m), 1111 (w), 1070 (m), 1039 (w), 1015 (m), 999 (w), 854 (m), 838 (m), 804 (w), 768 (w), 748 (w), 727 (w), 705 (w), 679 (w), 653 (w), 613 (w).

^{13}C NMR (400 MHz, DMSO-d6, 27 °C, TMS): δ = 151.7 (CO), 133.9 (CC), 133.5 (CC), 133.1 (CC), 145.8 (CC), 128.2 (CH), 127.9 (CH), 122.1 (CC), 116.8 (CH), 108.1 (CC), 62.5 (Cq), 26.0 (pinacol) ppm.

Table S1: elemental analysis of T-COF-OH.

N	**C**	**H**	**S**
0	62.35	3.94	0

Fig. S1: SEM image of T-COF-OH powder.

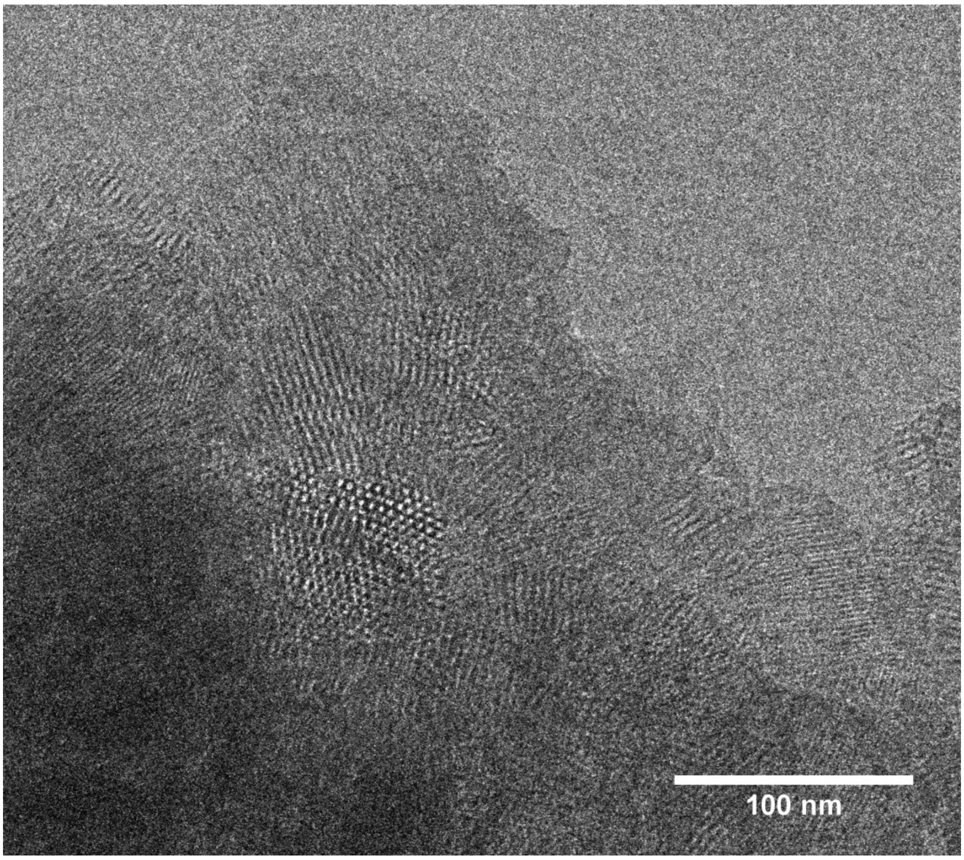
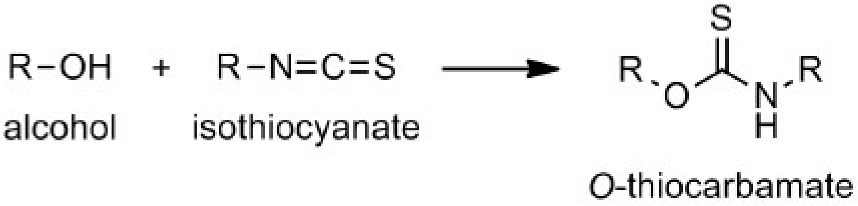


Fig. S2: TEM micrograph of T-COF-OH powder showing the polycrystalline sample, projection along the caxis showing the hexagonal structure.

Post-synthethic modification of T-COF-OH with fluorescein isothiocyanate (FITC)



A stock solution of fluorescein isothiocyanate (FITC) (20 mg in 10 ml acetone) was prepared. In a small Eppendorf tube (2 ml size), T-COF-OH (1 mg) and the prepared stock solution (1 ml) of FITC were added together. The reaction suspension was sonicated for ca. 1 min and then left on a shaking plate (600 rpm) at room temperature for seven days. At the end of the reaction, the supernatant was removed by centrifugation (4 min, 14000 rpm). Subsequently, the obtained modified COF material was washed with dry acetone (10 x 1 ml) until the supernatant did not show any fluorescence. Fluorescent T-COF-OH, named T-COF-OFITC, was obtained as brownish powder (0.91 µg FITC/ 1 mg COF; 0.091 wt%).

IR: 3346 (s), 2921 (w), 2351 (w), 1642 (w), 1608 (m), 1519 (w), 1492 (w), 1434 (w), 1399 (w), 1345 (s), 1244 (w), 1159 (w), 1070 (w), 992 (w), 911 (w), 841 (w), 799 (w), 736 (w).

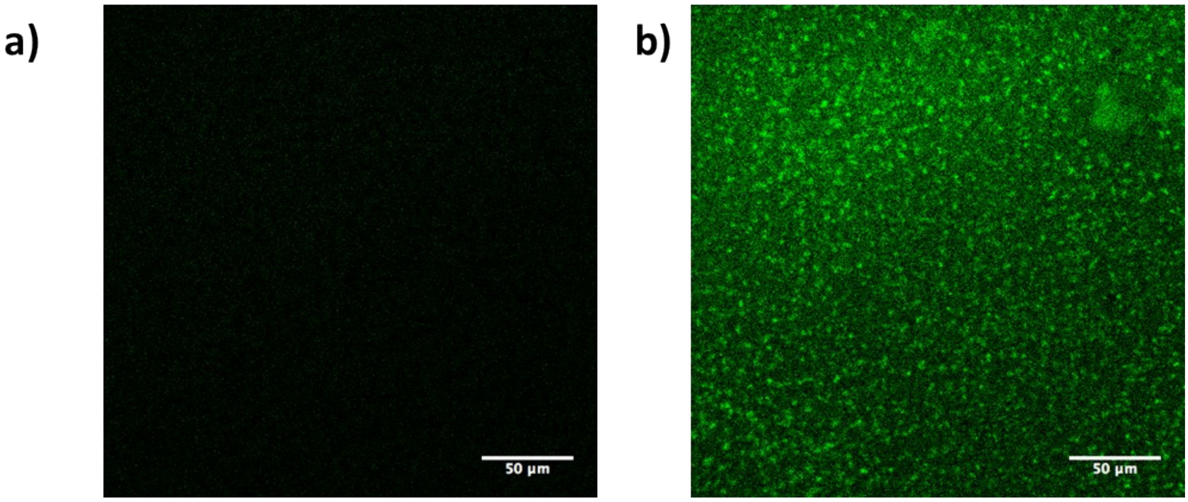


Fig. S3: a) Fluorescence microscopy image of T-COF-OH illustrating the non-fluorescent behavior of T-COF-OH without covalently bound FITC, and b) Fluorescence microscopy image of T-COF-OFITC illustrating the successful post-synthetic modification reaction with FITC.

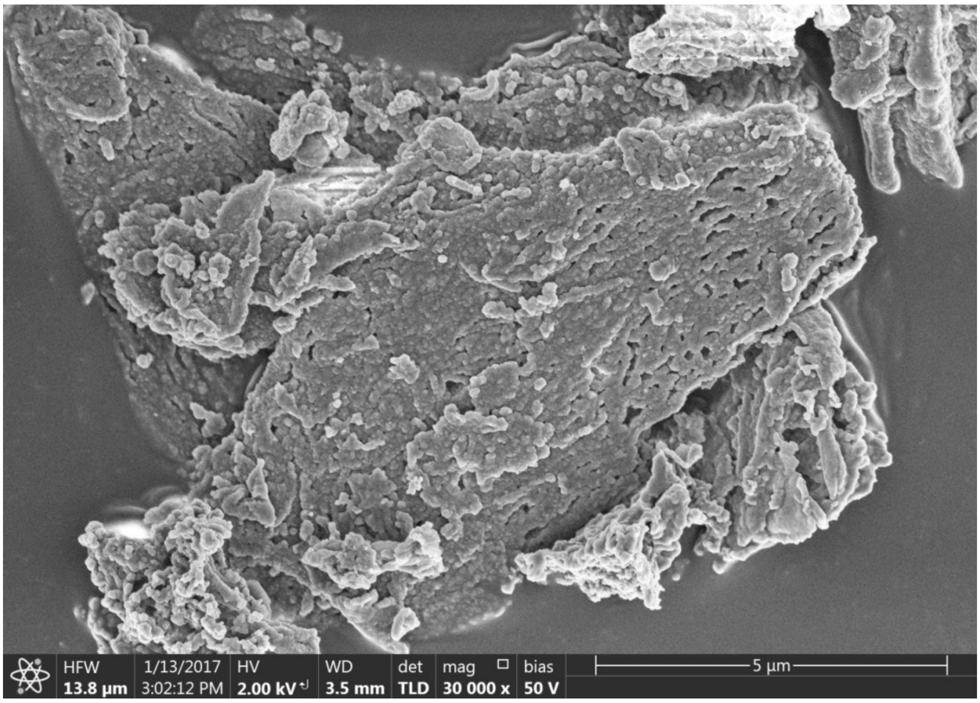


Fig. S4: SEM image of T-COF-OFITC powder.

Post-synthetic modification of COF-5 with fluorescein isothiocyanate (FITC)

COF-5 was also post-synthetically modified with fluorescein isothiocyanate (FITC). In this case, COF-5 is expected to exhibit available OH-groups belonging to terminating HHTP linker molecules located at the surface of the COF crystals. A stock solution with a large excess of fluorescein isothiocyanate (FITC) (20 mg in 10 ml acetone) was prepared to obtain a virtually constant concentration of the reaction solution as in the reaction procedure for T-COF-OH. In a small Eppendorf tube (2 ml size) COF5 (1 mg) and the prepared stock solution of FITC (1 ml) were added together. The reaction suspension was sonicated for ca. 1 min and later left on a shaking plate (600 rpm) at room temperature for seven days. Subsequently, the supernatant was removed by centrifugation (4 min, 14000 rpm). Thereafter, the obtained modified COF material was washed with dry acetone (10 x 1 ml) until the supernatant did not show any fluorescence. Fluorescent COF-5, named COF-5-FITC, was obtained as brownish powder (0.73 µg FITC/ 1 mg COF; 0.073 wt%).

IR: 3381 (w), 2954 (w), 2905 (w), 1662 (w), 1616 (w), 1515 (m), 1507 (w), 1337 (s), 1240 (m), 1159 (m), 1054 (m), 1004 (m), 829, (m), 741 (m).

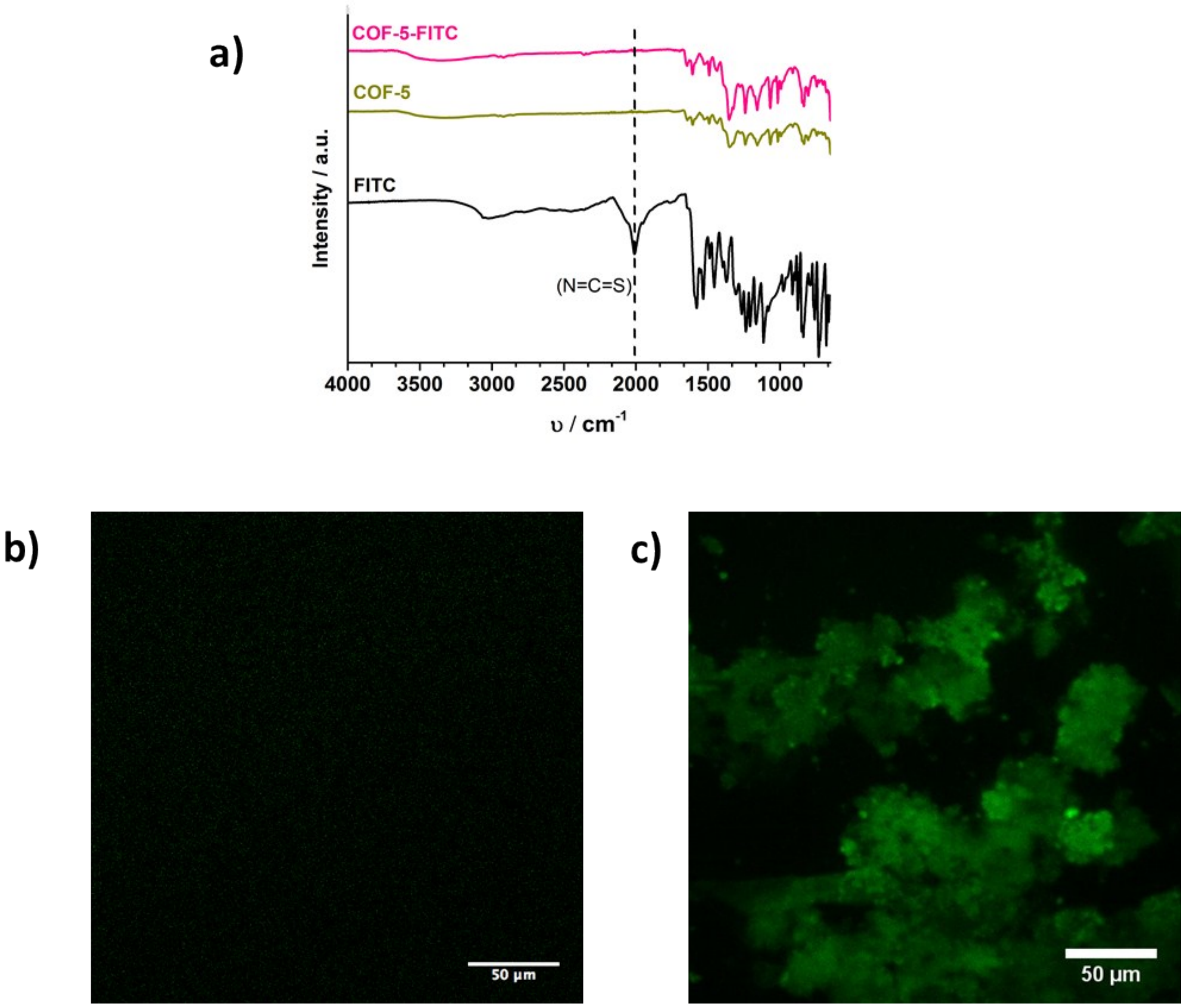


Fig. S5: a) IR spectra of COF-5 (pink), modified COF-5 with FITC (green) and free FITC (black) showing the removal of the isocyanate vibration, b) fluorescence microscopy image of COF-5 illustrating the non-fluorescent behavior of COF-5 without covalently bound FITC, and c) Fluorescence microscopy image of COF-5-FITC illustrating the successful post-synthetic modification reaction with FITC.

Post-synthetic modification of T-COF-OH with n-octylisothiocyanate (octyl)

To show the generality of the above PSM reaction, the concept was transferred to noctylisothiocarbamate exhibiting the same functional group as FITC bound to an octyl alkyl chain. Hence, a stock solution with large excess of noctylisocyanate (octyl) (1.65 mL in 3 ml acetone) was prepared to obtain a virtually constant concentration of the reaction solution as in the reaction procedure for T-COF-OH with FITC. In a small glass vial (10 ml) covered with an aluminum cap, T–COFOH (40 mg) and the prepared stock solution (3 mL) of octyl were added together. The reaction suspension was sonicated and then shaked at room temperature (600 rpm) for seven days. After the reaction time, the supernatant was removed by centrifugation (4 min, 14000 rpm). Subsequently, the obtained modified COF material was washed with dry acetone (10 x 1 ml). T-COF-OH functionalized with an octyl alkyl chain, named T-COF-Ooctyl, was obtained as brownish powder.

IR: 3363 (vs), 1693 (s), 1617 (m), 1514 (vw), 1491 (vw), 1426 (m), 1400 (vw), 1354 (m), 1239 (s), 1152 (s), 1064 (m), 846 (m).

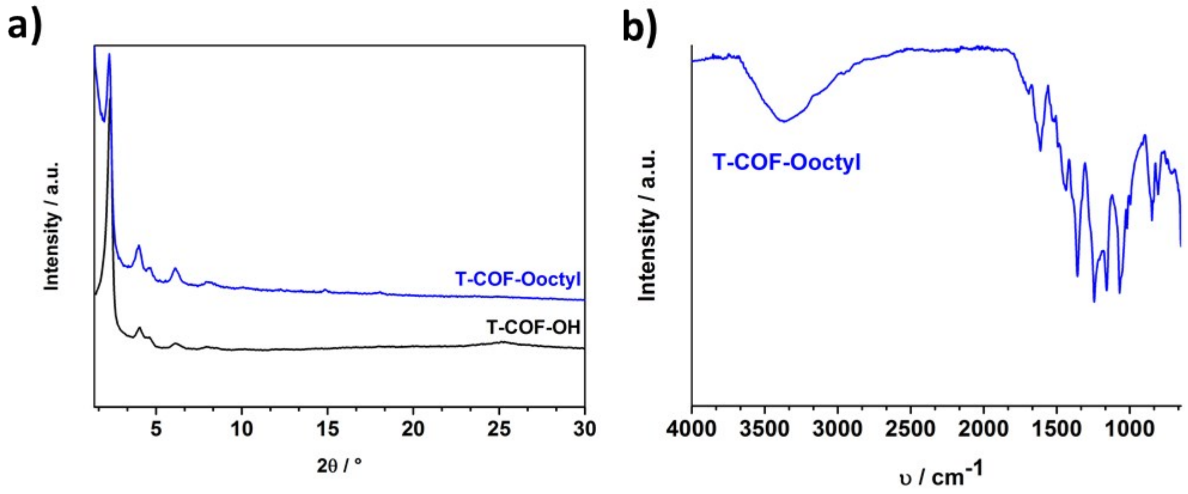


Fig. S6: a) Comparison of PXRD patterns of T-COF-Ooctyl (blue) and T-COF-OH (black) showing that crystallinity is maintained after the postsynthetic modification reaction, b) ATR-IR spectra of T-COF-Ooctyl. The absence of the isothiocyanate vibration band at 2011 cm^{-1} indicates that no free noctylisocyanate molecules are present in the COF sample.

2. Structural Characterization

Table S2: Refined crystal data

	T-COF-OH
Chemical formula	$C_{90}H_{48}O_{15}B_6$
Formula weight	1434.23 g/mol
Crystal system	hexagonal
Space group	P 6 (168)
Unit cell dimension	a=b=45.02 Å c=3.71 Å α=β=90° γ=120°
Cell volume	6528.84 $Å^3$

Table S3: Atomic parameters for T-COF-OH.

Atom	Atom label	x/a	y/b	z/c
C1	C	-0.01636	-0.47082	-0.26932
C2	C	-0.03846	-0.50847	-0.05036
C3	C	-0.02373	-0.52746	0.15710
C4	C	-0.07662	-0.52784	-0.04127
C5	C	-0.09518	-0.51025	-0.03734
C6	C	-0.13087	-0.52807	-0.03899
C7	C	-0.14863	-0.56379	-0.04416
C8	C	-0.13046	-0.58173	-0.04121
C9	C	-0.09479	-0.56394	-0.03908
O10	O	-0.02670	-0.45565	-0.44154
H11	H	-0.04106	-0.55808	0.33398
H12	H	-0.08085	-0.48122	-0.03278
H13	H	-0.14563	-0.51353	-0.03612
H14	H	-0.14478	-0.61095	-0.04054
H15	H	-0.08017	-0.57869	-0.03553
C16	C	-0.73618	-0.39002	0.09108
C17	C	-0.70509	-0.35971	0.11824
C18	C	-0.70497	-0.32718	0.09772
C19	C	-0.73614	-0.32678	0.05597
C20	C	-0.76553	-0.35720	0.03479
C21	C	-0.76553	-0.38791	0.05099
C22	C	-0.67409	-0.29623	0.11742
C23	C	-0.64274	-0.29710	0.14239
C24	C	-0.64234	-0.32845	0.13838
C25	C	-0.67417	-0.36070	0.15057
C26	C	-0.67369	-0.39296	0.18757
C27	C	-0.64237	-0.39174	0.17832
C28	C	-0.61158	-0.36010	0.13214
C29	C	-0.61069	-0.32850	0.11503
C30	C	-0.61259	-0.26634	0.17671
C31	C	-0.61345	-0.23584	0.16882
C32	C	-0.64283	-0.23450	0.13268
C33	C	-0.67325	-0.26390	0.11081
O34	O	-0.63859	-0.20157	0.12343
O35	O	-0.58587	-0.20421	0.19454
O36	O	-0.58271	-0.36343	0.10250
O37	O	-0.63820	-0.42054	0.19166
B38	B	-0.60230	-0.18272	0.16616
C39	C	-0.58186	-0.14201	0.14807
C40	C	-0.54743	-0.12579	0.20074
C41	C	-0.52869	-0.08901	0.16908
C42	C	-0.54397	-0.06769	0.08166
C43	C	-0.57883	-0.08445	0.03777
C44	C	-0.59760	-0.12126	0.07123

C45	C	-0.52345	-0.02805	0.03044
C46	C	-0.48734	-0.00634	-0.13752
C47	C	-0.53978	-0.01140	0.14296
B48	B	-0.60010	-0.40197	0.13919
O49	O	-0.79694	-0.41514	0.01477
B50	B	-0.81666	-0.39687	-0.02566
O51	O	-0.79707	-0.35998	-0.01002
C52	C	-0.33365	-0.71695	-0.15100
C53	C	-0.33291	-0.68512	-0.13984
C54	C	-0.36471	-0.68489	-0.13824
C55	C	-0.39525	-0.71570	-0.16593
C56	C	-0.39426	-0.74568	-0.17719
C57	C	-0.36440	-0.74645	-0.16543
C58	C	-0.36521	-0.65413	-0.11432
C59	C	-0.33316	-0.62171	-0.13415
C60	C	-0.30167	-0.62194	-0.13227
C61	C	-0.30165	-0.65403	-0.12897
C62	C	-0.26996	-0.65385	-0.11300
C63	C	-0.24013	-0.62323	-0.10156
C64	C	-0.24018	-0.59283	-0.10416
C65	C	-0.27004	-0.59133	-0.11823
C66	C	-0.33405	-0.59014	-0.14622
C67	C	-0.36573	-0.59217	-0.10820
C68	C	-0.39655	-0.62400	-0.05610
C69	C	-0.39718	-0.65493	-0.06153
O70	O	-0.42570	-0.62156	0.00258
O71	O	-0.37018	-0.56409	-0.09698
O72	O	-0.20834	-0.56543	-0.07838
O73	O	-0.20815	-0.62003	-0.07752
B74	B	-0.40846	-0.58335	-0.02193
C75	C	-0.42904	-0.56430	0.01591
C76	C	-0.41142	-0.52594	-0.11119
C77	C	-0.42989	-0.50880	-0.08986
C78	C	-0.46625	-0.52974	0.06802
C79	C	-0.48355	-0.56830	0.20421
C80	C	-0.46519	-0.58541	0.17443
C81	C	-0.48606	-0.51141	0.08256
C82	C	-0.47018	-0.47738	0.13269
C83	C	-0.48849	-0.45978	0.13572
C84	C	-0.52320	-0.47562	0.08754
C85	C	-0.53912	-0.50971	0.03874
C86	C	-0.52082	-0.52732	0.03589
C87	C	-0.54280	-0.45694	0.09422
C88	C	-0.52518	-0.41834	-0.04501
C89	C	-0.54339	-0.40086	-0.02714
C90	C	-0.57970	-0.42158	0.12106
C91	C	-0.59760	-0.45998	0.25237

C92	C	-0.57929	-0.47751	0.24360
B93	B	-0.18832	-0.58324	-0.05979
O94	O	-0.36856	-0.77892	-0.17206
B95	B	-0.40536	-0.79816	-0.19620
O96	O	-0.42215	-0.77730	-0.19912
H97	H	-0.73682	-0.41598	0.10246
H98	H	-0.73678	-0.30137	0.04013
H99	H	-0.69903	-0.41970	0.22471
H100	H	-0.58468	-0.30257	0.08233
H101	H	-0.58778	-0.26688	0.21063
H102	H	-0.69763	-0.26230	0.08754
H103	H	-0.53470	-0.14271	0.26963
H104	H	-0.50075	-0.07600	0.21417
H105	H	-0.59202	-0.06797	-0.02573
H106	H	-0.62585	-0.13455	0.03600
H107	H	-0.47348	-0.01908	-0.23385
O108	O	-0.56738	-0.02733	0.27891
H109	H	-0.30889	-0.71804	-0.14800
H110	H	-0.42045	-0.71559	-0.17876
H111	H	-0.26923	-0.67894	-0.10968
H112	H	-0.26940	-0.56563	-0.11860
H113	H	-0.30870	-0.56327	-0.18716
H114	H	-0.42322	-0.68102	-0.02385
H115	H	-0.38189	-0.50869	-0.23240
H116	H	-0.41554	-0.47756	-0.20090
H117	H	-0.51283	-0.58592	0.34043
H118	H	-0.47963	-0.61664	0.27932
O119	O	-0.44388	-0.46478	0.18151
H120	H	-0.47530	-0.43225	0.17758
O121	O	-0.56535	-0.52227	-0.01138
H122	H	-0.53405	-0.55491	-0.00459
H123	H	-0.49577	-0.40132	-0.17324
H124	H	-0.52870	-0.36961	-0.13340
H125	H	-0.62723	-0.47708	0.36699
H126	H	-0.59387	-0.50877	0.35811
C127	C	-0.46803	-0.96910	-0.18860
C128	C	-0.48433	-0.95245	-0.07498
C129	C	-0.52044	-0.97419	0.09332
C130	C	-0.46380	-0.91286	-0.12400
C131	C	-0.42877	-0.89606	-0.08524
C132	C	-0.40997	-0.85932	-0.11569
C133	C	-0.42586	-0.83873	-0.18280
C134	C	-0.46047	-0.85496	-0.23018
C135	C	-0.47920	-0.89162	-0.20301
O136	O	-0.44050	-0.95318	-0.32623
H137	H	-0.53428	-0.96150	0.19118
H138	H	-0.41577	-0.91274	-0.02846

H139	H	-0.38156	-0.84599	-0.08590
H140	H	-0.47345	-0.83827	-0.29113
H141	H	-0.50724	-0.90461	-0.24495
C142	C	-0.98788	-0.50916	0.14926
C143	C	-0.96579	-0.47148	-0.06905
C144	C	-0.98050	-0.45253	-0.27762
C145	C	-0.92770	-0.45204	-0.07352
C146	C	-0.90910	-0.46971	-0.06792
C147	C	-0.87360	-0.45195	-0.05745
C148	C	-0.85604	-0.41617	-0.05391
C149	C	-0.87419	-0.39808	-0.06824
C150	C	-0.90969	-0.41584	-0.07812
O151	O	-0.97761	-0.52434	0.32262
H152	H	-0.96315	-0.42194	-0.45579
H153	H	-0.92323	-0.49876	-0.07198
H154	H	-0.85882	-0.46657	-0.05176
H155	H	-0.85999	-0.36876	-0.07188
H156	H	-0.92433	-0.40100	-0.09002
H157	H	-0.01326	-0.42751	-0.43359
H158	H	-0.57284	-0.01351	0.45244
H159	H	-0.44073	-0.44688	0.34768
H160	H	-0.58026	-0.51303	0.12106
H161	H	-0.42698	-0.92842	-0.24667
H162	H	-0.95717	-0.50658	0.44899

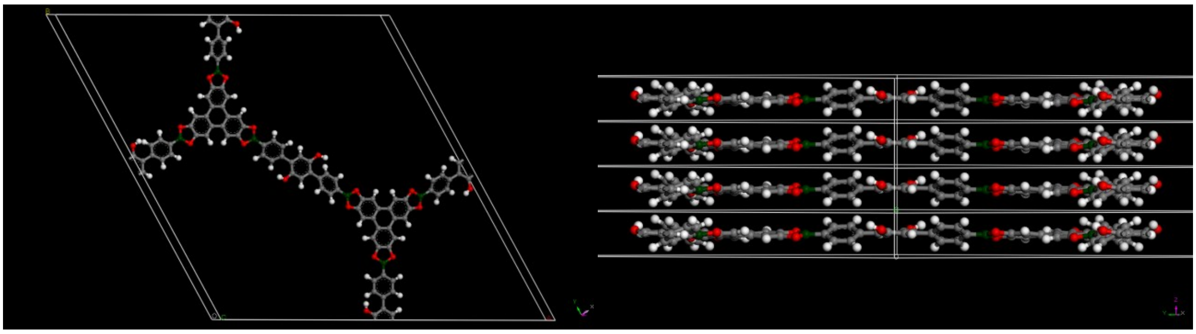


Fig. S7: Simulation of crystal lattice of the unit cell calculated in an eclipsed arrangement for T-COF-OH (left); side view at the c-axis of 4 unit cells stacked on top of each other with slightly tilted hexagonal layers due to phenyl rings and hydroxyl groups of T-COF-OH rotating out of plane (right).

3. Sorption

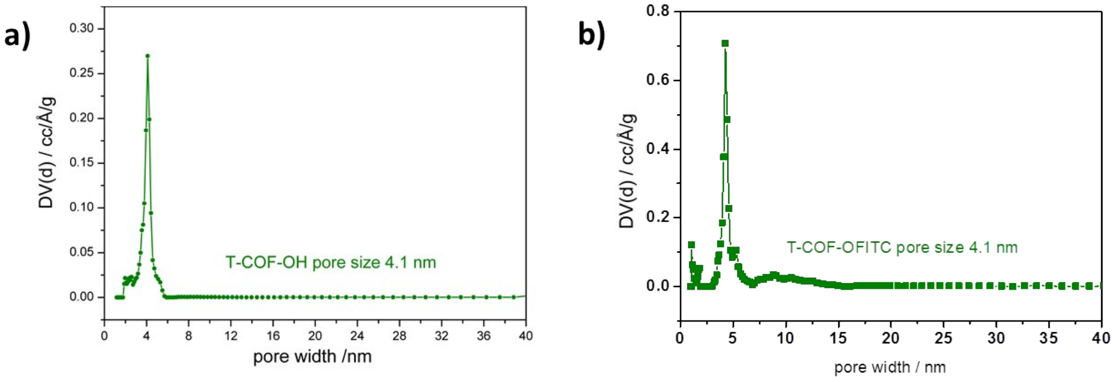


Fig. S8: a) pore size distribution of **T-COF-OH**, b) pore size distribution of **T-COF-OFITC**; porosity could have been maintained after pore modification with main pore size of 4.1 nm.

4. TGA

The TGA analysis of T-COF-OH indicates complete removal of volatile guest molecules at about 150 °C. Degradation of the T-COF-OH starts at 450 °C and the remaining amount of 10 wt % corresponds to approximately 3 mol B_2O_3, related to the sample weight.

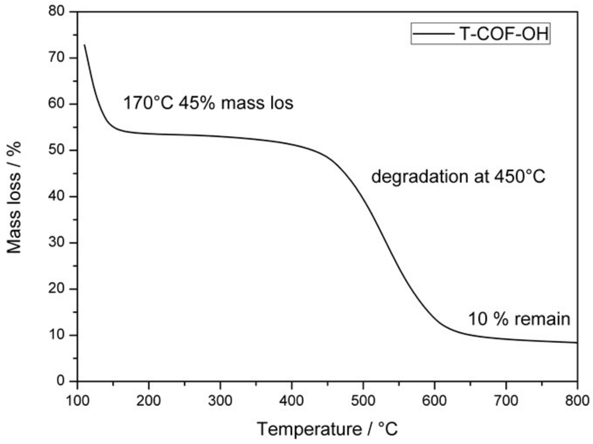


Fig. S9: TGA data of T-COF-OH.

5. Solid state MASNMR

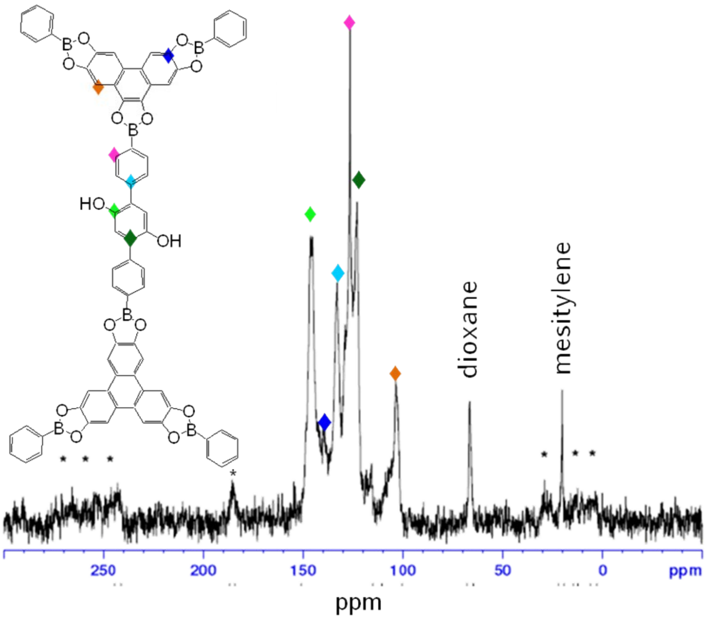


Fig. S10: ^{13}C NMR spectrum of T-COF-OH with assigned signals for carbon atoms present. Asterisks (*) indicate peaks arising from spinning side bands.