SUPPORTING INFORMATION

Dibenzochrysene Enables Tightly Controlled Docking and Stabilizes Photoexcited States in Dual-Pore Covalent Organic Frameworks

Niklas Keller,^{a+} Torben Sick, ^{a+} Nicolai N. Bach,^a Andreas Koszalkowski,^a Julian M. Rotter,^a Dana D. Medina^{a*} and Thomas Bein^{a*}

^a Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU), Butenandtstraße 5-13, 81377 Munich, Germany

TABLE OF CONTENTS

1	Materials and Methods2
2	Synthetic Procedures
3	SEM6
4	TEM6
5	X-Ray Diffraction Analysis7
6	Sorption9
7	Structural Simulations of DBC-COFs11
8	Crystallographic Data17
9	IR Spectroscopy18
10	UV-Vis Spectroscopy20
11	Photoluminescence Spectroscopy21
12	Time-Correlated Single Photon Counting22
13	Thermogravimetric Analysis
14	Elemental Analysis
15	NMR
16	References

1 Materials and Methods

All reagents and solvents were obtained from in house supply or commercial suppliers and used as received. Acetic acid (in house supply), benzyl alcohol (BnOH, anhydrous, Sigma-Aldrich), 4,4'biphenyldicarboxaldehyde (Biph, >98%, TCI), 1,4-dioxane (anhydrous, Sigma Aldrich), dibenzo[*g*,*p*]chrysene (DBC, >98%, TCI), ethanol (anhydrous, Sigma Aldrich), hydrazine monohydrate (Sigma Aldrich), mesitylene (anhydrous, Sigma-Aldrich), nitrobenzene (anhydrous, Sigma Aldrich), Raney-Nickel slurry (Sigma Aldrich), terephthalaldehyde (TA, 99%, Sigma-Aldrich), tetrahydrofuran (THF, extra dry, stabilized, Acros Organics). Thieno[3,2-*b*]thiophene-2,5dicarboxaldehyde (TT, >93%, TCI) was recrystallized from N,N-dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich).

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 and AV 400 TR spectrometers. Proton chemical shifts are expressed in parts per million (δ scale) and are calibrated using residual non-deuterated solvent peaks as internal reference (e.g. DMSO- d_6 : 2.50 ppm).

Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum BX II FT-IR system and a Thermo Scientific Nicolet[™] 6700 FT-IR spectrometer in transmission mode. IR data are reported in wavenumbers (cm⁻¹).

UV-Vis spectra were recorded using a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere. **Diffuse reflectance spectra** were collected with a Praying Mantis (Harrick) accessory and were referenced to barium sulfate powder as white standard.

Nitrogen sorption isotherms were recorded on a Quantachrome Autosorb 1 at 77 K within a pressure range of $p/p^0 = 0.001$ to 0.98. Prior to the measurement of the sorption isotherms the samples were heated for 24 h at 120 °C under turbo-pumped vacuum. For the evaluation of the surface area the BET model was applied between 0.05 and 0.3 p/p^0 . Pore size distributions were calculated using the QSDFT equilibrium model (desorption branch) with a carbon kernel for cylindrical pores. Connolly surfaces were generated using an N₂-sized probe (r = 0.184 nm) at a 0.025 nm grid interval.

Thermogravimetric analysis (TGA) measurements were performed on a Netzsch Jupiter ST 449 C instrument equipped with a Netzsch TASC 414/4 controller. The samples were heated from room temperature to 900 °C under a synthetic air flow (25 mL min⁻¹) at a heating rate of 10 K min⁻¹.

Powder X-ray diffraction (PXRD) measurements were performed using a Bruker D8 Discover with Ni-filtered Cu-K α radiation and a LynxEye position-sensitive detector (scan speed of 4 s per 0.01 °2 θ). Experimental XRD data were used for Pawley refinement to optimize the hypothetical structure.

The initial **structure models of the COFs** were built using the Forcite module of the Accelrys Materials Studio software package. We applied the space group with the highest possible symmetry, i.e. *P*6, considering the propeller-like conformation of the central building blocks. Using this coarse model, we determined the unit cell parameters via Pawley refinement of our PXRD data.

Transmission electron microscopy (TEM) was performed on an FEI Titan Themis equipped with a field emission gun operated at 300 kV.

Scanning electron microscopy (SEM) images were recorded with a JEOL 6500F and an FEI Helios NanoLab G3 UC scanning electron microscope equipped with a field emission gun operated at 3-5 kV.

Photoluminescence (PL) and **time-correlated single photon counting (TCSPC)** data were processed with a FluoTime 300 from PicoQuant GmbH. The samples were photo-excited using lasers with suitable wavelengths according to the sample absorption, i.e. 378 nm, 403 nm or 507 nm wavelength (LDH-P-C-375, LDH-P-C-405, and LDH-P-C-510, respectively, all from PicoQuant GmbH) pulsed at 500 kHz, with a pulse duration of ~100 ps and fluence of ~ 300 nJcm⁻²/pulse. The samples were exposed to the pulsed light source set at 3 μ Jcm⁻²/pulse fluence for ~10 minutes prior to measurement to ensure stable sample emission. The PL was collected using a high-resolution monochromator and photomultiplier detector assembly (PMA-C 192-N-M, PicoQuant GmbH).

2 Synthetic Procedures

Tetranitro-DBC



DBC (1.0 g, 3.0 mmol) was slowly added with stirring at 0 °C to a mixture of 10 mL nitric acid (\geq 99%) and 10 mL glacial acetic acid. After 10 min at 0 °C the solution was stirred at 100 °C for 2 h. The solution was poured into an ice-water mixture. The resulting precipitate was filtered, washed with 1,4-dioxane and recrystallized from nitrobenzene. After filtration and extensive washing with ethanol, 1.1 g of a yellow solid of tetranitro-DBC with 69% yield were obtained. MS-EI: calculated (m/z): 508.066, measured (m/z): 508.065.

Tetraamino-DBC (DBCTA, adapted from Lu et al.¹)



Under argon, tetranitro-DBC (500 mg, 0.98 mmol) was dissolved in 80 mL of anhydrous THF in a flame-dried 500 mL flask. Approximately 2.3 g of Raney-nickel catalyst slurry was added to the mixture with stirring. Hydrazine monohydrate (0.67 mL, 8.8 mmol) was added dropwise to the stirred mixture. The resulting solution was heated to reflux for two hours. The solution was allowed to cool to room temperature and filtered. The filtrate was dried under reduced pressure, giving 320 mg of a yellowish-greenish solid with 84% yield. ¹H NMR (400 MHz, DMSO- d_6) δ (ppm):

8.15 (d, *J* = 8.8 Hz, 4H, CH), 7.56 (d, *J* = 2.3 Hz, 4H, CH), 6.90 (dd, *J* = 8.8, 2.3 Hz, 4H, CH), 5.39 (s, 8H, NH₂). MS-EI: calculated (m/z): 388.169, measured (m/z): 388.168.

Synthesis of TA DBC-COF

In a 6 mL culture tube, terephthalaldehyde (4.02 mg, 30.0 μ mol) and DBCTA (5.83 mg, 15.0 μ mol) were suspended in a mixture of BnOH and mesitylene (500 μ L, v:v 9:1). After adding 50 μ L of acetic acid (aqueous, 6 M) the tube was sealed and heated at 120 °C for 72 h. The resulting precipitate was filtered and rinsed with anhydrous THF before Soxhlet extraction with anhydrous THF for 12 h. The final product was vacuum-dried, to yield 5.07 mg (58%) as a light brown powder.

Synthesis of Biph DBC-COF

In a 6 mL culture tube, 4,4'-biphenyldicarboxaldehyde (6.31 mg, 30.0 μ mol) and DBCTA (5.83 mg, 15.0 μ mol) were suspended in a mixture of BnOH and mesitylene (500 μ L, v:v 1:1). After adding 50 μ L of acetic acid (aqueous, 6 M) the culture tube was sealed and heated at 120 °C for 72 h. The resulting precipitate was filtered and rinsed with anhydrous THF before Soxhlet extraction with anhydrous THF for 12 h. The final product was vacuum-dried, to yield 5.47 mg (50%) as a brown powder.

Synthesis of TT DBC-COF

In a 6 mL culture tube, thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde (5.89 mg, 30.0 μ mol) and DBCTA (5.83 mg, 15.0 μ mol) were suspended in a mixture of BnOH and mesitylene (500 μ L, v:v 9:1). After adding 50 μ L of acetic acid (aqueous, 6 M) the tube was sealed and heated at 120 °C for 72 h. The resulting precipitate was filtered and rinsed with anhydrous THF before Soxhlet extraction with anhydrous THF for 12 h. The final product was vacuum-dried, to yield 5.87 mg (55%) as a red powder.

Synthesis of analogue 4PE COFs

The ETTA-based COFs, 4PE-1P, 4PE-2P and 4PE-TT, are well-studied COF systems. Their synthesis here was carried out under the reported conditions previously reported in the literature.²

3 SEM



Figure S1: SEM images of TA DBC-COF (a), Biph DBC-COF (b) and TT DBC-COF (c). A hexagonal morphology is visible for many of the crystallites.

4 TEM



Figure S2: TEM images of TA DBC-COF (a), Biph DBC-COF (b) and TT DBC-COF (c). The long-range order of the hexagonal crystallites is apparent from the large domains of about 50 to 100 nm.

5 X-Ray Diffraction Analysis



Figure S3: Pawley refinement of TA DBC-COF. Experimental (black), Pawley refined simulation (red), difference (navy) and Bragg positions (olive) show good agreement of experimental and simulated PXRD patterns.



Figure S4: Pawley refinement of Biph DBC-COF. Experimental (red), Pawley refined simulation (black), difference (navy) and Bragg positions (olive) show good agreement of experimental and simulated PXRD patterns.



Figure S5: Pawley refinement of TT DBC-COF. Experimental (blue), Pawley refined simulation (black), difference (navy) and Bragg positions (olive) show good agreement of experimental and simulated PXRD patterns.

6 Sorption



Figure S6: Nitrogen physisorption isotherm of TA DBC-COF (a) and the corresponding PSD with a QSDFT carbon equilibrium kernel for cylindrical pores reveal the dual-pore COF-structure (b).



Figure S7: Nitrogen physisorption isotherm of Biph DBC-COF (a) and the corresponding PSD with a QSDFT carbon equilibrium kernel for cylindrical pores reveal the dual-pore COF-structure (b).



Figure S8: Nitrogen physisorption isotherm of TT DBC-COF (a) and the corresponding PSD with a QSDFT carbon kernel for cylindrical pores reveal the dual-pore COF-structure (b).

The first steep uptakes at very low p/p^0 in Figures S6 – S8 indicate the micropore filling, while the second one ($p/p^0 = 0.15$ to 0.35) represents the capillary condensation within the mesopores, respectively. Due to the comparably small size of the mesopores (≤ 4 nm), a type IVb physisorption isotherm without a hysteresis loop is obtained.³ The pore size distribution was calculated from the equilibrium branch (desorption) with QSDFT with a carbon kernel for cylindrical pore geometry.

7 Structural Simulations of DBC-COFs

Space group: P6 with an AA-hexagonal eclipsed stacking (AA-H).

Table S1: Fractional atomic coordinates for the unit cell of AA-H calculated with Materials Studio v7.0 modeling program for TA DBC-COF.

P <i>6</i> (168) – hexagonal					
a = t	o = 347762(9)	nm, c = 0.361	L1(6) nm		
	α = β =	90°, γ = 120°			
Atom x/a y/b z/c					
C1	0.48191	0.48325	0.48052		
C2	0.55441	0.51297	0.42694		
C3	0.52066	0.55641	0.54156		
C4	0.59020	0.54403	0.29244		
C5	0.62475	0.54203	0.29230		
C6	0.62425	0.50820	0.42101		
C7	0.58821	0.47561	0.51286		
C8	0.55272	0.47667	0.48965		
C9	0.44374	0.40906	0.63294		
C10	0.44115	0.37230	0.64931		
C11	0.47408	0.36870	0.58695		
C12	0.51035	0.40275	0.52521		
C13	0.51377	0.44046	0.52582		
N14	0.65911	0.50510	0.45965		
N15	0.46921	0.32992	0.56729		
C16	0.49663	0.32108	0.62398		
C17	0.69535	0.53248	0.40083		

Atom	x/a	y/b	z/c
H18	0.59210	0.57034	0.18775
H19	0.65141	0.56709	0.19352
H20	0.58881	0.44988	0.60748
H21	0.41715	0.40928	0.69160
H22	0.41317	0.34619	0.70662
H23	0.53515	0.39927	0.45855
H24	0.70243	0.56149	0.31031
C25	0.72818	0.52481	0.46130
C26	0.76693	0.55452	0.38691
C27	0.79842	0.54785	0.44169
C28	0.79169	0.51129	0.57228
C29	0.75295	0.48161	0.64787
C30	0.72145	0.48829	0.59315
H31	0.77280	0.58279	0.28273
H32	0.82803	0.57105	0.37785
H33	0.74708	0.45329	0.75074
H34	0.69183	0.46504	0.65574
H35	0.47430	0.65667	0.71292

Table S2: Fractional atomic coordinates for the unit cell of AA-H calculated with Materials Studio v7.0 modeling program for Biph DBC-COF.

P <i>6</i> (168) – hexagonal				
a = b = 4.6299(9) nm, c = 0.4017(6) nm				
α = β = 90°, γ = 120°				
Atom x/a y/b z/c				

C1	0.48657	0.48523	0.40595
C2	0.54747	0.51934	0.47987
C3	0.51209	0.54571	0.33928
C4	0.57621	0.54952	0.58548
C5	0.60724	0.55217	0.64763
C6	0.61072	0.52399	0.61072
C7	0.58252	0.49341	0.52786
C8	0.55050	0.48998	0.47046
C9	0.46428	0.42667	0.20464
C10	0.46592	0.39731	0.18524
C11	0.49474	0.39752	0.29305
C12	0.52262	0.42804	0.38814
C13	0 52182	0.45850	0 39736
	0.52102	0.45050	0.33730
N14	0.63973	0.52397	0.64491
N14 Atom	0.63973 x/a	0.52397 y/b	0.64491 z/c
N14 Atom N15	0.63973 x/a 0.49293	0.52397 y/b 0.36755	0.64491 z/c 0.31443
N14 Atom N15 C16	0.63973 x/a 0.49293 0.51695	0.52397 y/b 0.36755 0.35928	0.64491 z/c 0.31443 0.35322
N14 Atom N15 C16 C17	0.63973 x/a 0.49293 0.51695 0.67165	0.52397 y/b 0.36755 0.35928 0.54914	0.64491 z/c 0.31443 0.35322 0.67079
N14 Atom N15 C16 C17 C18	0.63973 x/a 0.49293 0.51695 0.67165 0.69733	0.52397 y/b 0.36755 0.35928 0.54914 0.54129	0.64491 z/c 0.31443 0.35322 0.67079 0.67394
N14 Atom N15 C16 C17 C18 C19	0.63973 x/a 0.49293 0.51695 0.67165 0.69733 0.72920	0.52397 y/b 0.36755 0.35928 0.54914 0.54129 0.56440	0.64491 z/c 0.31443 0.35322 0.67079 0.67394 0.54611
N14 Atom N15 C16 C17 C18 C19 C20	0.63973 x/a 0.49293 0.51695 0.67165 0.69733 0.72920 0.75392	0.52397 y/b 0.36755 0.35928 0.54914 0.54129 0.56440 0.55532	0.64491 z/c 0.31443 0.35322 0.67079 0.67394 0.54611 0.51221
N14 Atom N15 C16 C17 C18 C19 C20 C21	0.63973 x/a 0.49293 0.51695 0.67165 0.69733 0.72920 0.75392 0.74763	0.52397 y/b 0.36755 0.35928 0.54914 0.54129 0.56440 0.55532 0.52321	0.64491 z/c 0.31443 0.35322 0.67079 0.67394 0.54611 0.51221 0.61062
N14 Atom N15 C16 C17 C18 C19 C20 C21 C22	0.63973 x/a 0.49293 0.51695 0.67165 0.69733 0.72920 0.75392 0.74763 0.71632	0.52397 y/b 0.36755 0.35928 0.54914 0.54129 0.56440 0.55532 0.52321 0.50088	0.64491 z/c 0.31443 0.35322 0.67079 0.67394 0.54611 0.51221 0.61062 0.75625
N14 Atom N15 C16 C17 C18 C19 C20 C21 C22 C23	0.63973 x/a 0.49293 0.51695 0.67165 0.69733 0.72920 0.75392 0.74763 0.71632 0.69152	0.52397 y/b 0.36755 0.35928 0.54914 0.54129 0.56440 0.55532 0.52321 0.50088 0.50981	0.64491 z/c 0.31443 0.35322 0.67079 0.67394 0.54611 0.51221 0.61062 0.75625 0.78764

C25	0.76261	0.48184	0.41627
C26	0.78678	0.47255	0.35085
C27	0.82080	0.49480	0.42288
C28	0.82988	0.52607	0.57053
C29	0.80569	0.53521	0.63833
H30	0.57550	0.57078	0.62568
H31	0.62702	0.57457	0.71974
H32	0.58659	0.47382	0.50670
H33	0.44290	0.42517	0.12112
H34	0.44592	0.37570	0.09814
H35	0.54311	0.42699	0.45890
H36	0.67735	0.57358	0.66739
H37	0.73437	0.58762	0.46757
H38	0.77636	0.57219	0.40737
H39	0.71121	0.47784	0.83934
H40	0.66899	0.49303	0.89182
H41	0.73825	0.46540	0.35523
H42	0.77938	0.44963	0.24633
H43	0.85426	0.54239	0.63296
H44	0.81311	0.55787	0.74889
H45	0.83795	0.46094	0.33347

Table S3: Fractional atomic coordinates for the unit cell of AA-H calculated with Materials Studio v7.0 modeling program for TT DBC-COF.

$\alpha = \beta = 90^\circ, \gamma = 120^\circ$				
Atom	x/a	y/b	z/c	
C1	0.0338	0.48331	0.55114	
C2	0.03593	0.45208	0.66021	
C3	0.06869	0.45123	0.67445	
C4	0.10173	0.48243	0.58930	
C5	0.10105	0.51468	0.51320	
C6	0.06812	0.51646	0.51685	
N7	0.13190	0.47895	0.58251	
C8	0.16786	0.50433	0.56654	
C9	0.19472	0.49415	0.53650	
S10	0.18458	0.44890	0.46926	
C11	0.23115	0.46555	0.45473	
C12	0.25258	0.50249	0.50360	
C13	0.23222	0.51956	0.55076	
C14	0.25154	0.44857	0.40208	
C15	0.28904	0.47401	0.41620	
S16	0.29915	0.51912	0.49306	
C17	0.31599	0.46407	0.37540	
C18	0.48282	0.48310	0.49344	
N19	0.44993	0.48486	0.43522	
C20	0.44981	0.51846	0.47705	
C21	0.41555	0.51758	0.48434	
C22	0.38229	0.48620	0.40126	
C23	0.38319	0.45469	0.30274	

C24	0.41632	0.45455	0.31703
N25	0.35176	0.48897	0.42046
H26	0.06849	0.42769	0.74564
Atom	x/a	y/b	z/c
H27	0.12536	0.53671	0.44594
H28	0.17600	0.53155	0.57639
H29	0.24348	0.54707	0.58927
H30	0.24031	0.42112	0.35984
H31	0.30814	0.43753	0.31501
H32	0.41364	0.53983	0.55603
H33	0.35995	0.43173	0.22183
H34	0.41493	0.43116	0.23370
H35	0.01350	0.42866	0.73592

8 Crystallographic Data



Figure S9: The calculated dihedral angle (green) for (a) ETTA and (b) DBC cores building blocks. The molecular models are based on reported crystallographic data for the respective compounds, ETTA⁴ and DBC⁵. It is evident that the dihedral angle of ETTA is much larger (47.3°) due to steric crowding caused by the phenyl-substituted ethylene moiety. In the case of DBC, the aromatic rings fused to the naphthalene core force the system to stay more planar (dihedral angle of 24.7°).

9 IR Spectroscopy



Figure S10: IR spectra of tetranitro- (a) and tetraamino-DBC (DBCTA) (b).



Figure S11: IR spectra of TA (a), Biph (b) and TT (c) precursors.



Figure S12: IR spectra of the synthesized DBC-COFs, namely TA DBC-COF (a), Biph DBC-COF (b) and TT DBC-COF (c).

10 UV-vis Spectroscopy

Absorption spectra of the DBC-COFs were collected from solid samples in diffuse reflectance mode and transferred into absorption spectra by applying the Kubelka Munk equation.



Figure S13: Optical absorption spectra of the DBC-COFs (a), and the corresponding analogous 4PE COFs (b) measured as diffuse reflectance spectra of the solids and converted with the Kubelka Munk equation.



Figure S14: Tauc plots of the DBC-based COFs with a linear fit illustrated in orange.

11 Photoluminescence Spectroscopy



Figure S15: (a) Normalized PL spectra of the solid precursors tetraamino-DBC, TT, Biph and TA obtained with 378 nm excitation. (b) Normalized PL spectrum of DBC measured as solution in 1,4-dioxane (50 μ M) and excited by a 378 nm laser. A strong emission could be detected at 480 nm.



Figure S16: PL spectra of TA, Biph and TT DBC-COFs (a) and of 4PE-1P, -2P and -TT COFs (b). All compounds were measured as solids.



12 Time-Correlated Single Photon Counting

Figure S17: (a) PL decay of TA DBC-COF excited at 378 nm and measured at the maximum of the PL emission at 718 nm. (b) PL decay of 4PE-1P COF excited at 378 nm and measured at the maximum of the PL emission at 597 nm. Experimental decay: black (TA DBC-COF), grey (4PE-1P COF) dots, tri-exponential fit of the decay: cyan line.



Figure S18: (a) PL decay of Biph DBC-COF excited at 378 nm and measured at the maximum of the PL emission at 724 nm. (b) PL decay of 4PE-2P COF excited at 378 nm and measured at the maximum of the PL emission at 643 nm. Experimental decay: red (Biph DBC-COF), wine-red (4PE-2P COF) dots, tri-exponential fit of the decay: cyan line.



Figure S19: (a) PL decay of TT DBC-COF excited at 378 nm and measured at the maximum of the PL emission at 758 nm. (b) PL decay of 4PE-TT COF excited at 378 nm and measured at the maximum of the PL emission at 683 nm. Experimental decay: blue (TA DBC-COF), green (4PE-TT COF) dots, tri-exponential fit of the decay: cyan line.

Table S4: PL decay times of TA DBC-COF shown above	e. The given errors are uncertainties from
the fit and hence do not reflect the real time-resolution	n of the setup. The latter is limited by the
laser pulse duration of around 100 ps.	

	τ / ns	error / ns	fractional intensity / %
τ ₁	6.3	±0.2	15
τ ₂	1.1	±0.02	65
τ ₃	0.25	±0.01	20

Table S5: PL decay times of Biph DBC-COF shown above. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

	τ / ns	error / ns	fractional intensity / %
τ ₁	14.1	±0.6	12
τ ₂	2.8	±0.06	50
τ ₃	0.71	±0.02	38

Table S6: PL decay times of TT DBC-COF shown above. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

	τ / ns	error / ns	fractional intensity / %
τ ₁	5.0	±0.1	25
τ ₂	1.0	±0.02	60
τ ₃	0.20	±0.01	15

Table S7: PL decay times of 4PE-1P COF shown above. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

	τ / ns	error / ns	fractional intensity / %
τ ₁	3.2	±0.2	8

τ ₂	0.66	±0.01	54
τ_3	0.12	±0.004	38

Table S8: PL decay times of 4PE-2P COF shown above. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

	τ / ns	error / ns	fractional intensity / %
τ ₁	3.6	±0.1	11
τ ₂	0.80	±0.01	50
τ ₃	0.14	±0.003	39

Table S9: PL decay times of 4PE-TT COF shown above. The given errors are uncertainties from the fit and hence do not reflect the real time-resolution of the setup. The latter is limited by the laser pulse duration of around 100 ps.

	τ / ns	error / ns	fractional intensity / %
τ ₁	4.5	±0.4	5
τ ₂	0.65	±0.01	41
τ ₃	0.14	±0.003	54

13 Thermogravimetric Analysis



Figure S20: Thermogravimetric analysis of DBC COFs. TA DBC-COF (black), Biph DBC-COF (red) and TT DBC-COF (blue) are stable up to about 350 °C under a heating rate of 10 °C/min and under synthetic air (N_2/O_2 V/V 79.5/20.5, 25 mL min⁻¹).

14 Elemental Analysis

Table S10: Elemental analysis of TA DBC-COF bulk material compared with the calculated mass percentages.

	TA DBC-COF		
Element	Theoretical percentage	Measured percentage	
Ν	9.58	8.49	
С	86.28	77.68	
н	4.14	4.70	

Table S11: Elemental analysis of Biph DBC-COF bulk material compared with the calculated mass percentages.

Biph DBC-COF

Element	Theoretical percentage	Measured percentage
N	7.60	7.63
С	88.02	83.35
н	4.38	4.59

Table S12: Elemental analysis of TT DBC-COF bulk material compared with the calculated mass percentages.

TT DBC-COF

Element		
	Theoretical percentage	Measured percentage
Ν	7.90	7.01
С	71.16	65.73
н	2.84	3.19
S	18.09	16.64

The differences between theoretical and measured atomic percentages are tentatively attributed to COF structures having a certain number of defects (missing building blocks).

15 NMR





Figure S21: ¹H NMR spectrum of DBCTA: ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.15 (d, *J* = 8.8 Hz, 4H, C(1)H), 7.55 (d, *J* = 2.3 Hz, 4H, C(2)H), 6.9 (dd, *J* = 8.8, 2.3 Hz, 4H, C(3)H), 5.39 (s, 8H, NH₂).

Tetraamino-DBC

¹³C, 100 MHz, DMSO-*d*₆



Figure S22: ¹³C NMR spectrum of DBCTA. ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 146.3, 130.7, 128.9, 122.1, 120.3, 115.3, 105.5.

16 References

- 1 J. Lu and J. Zhang, J. Mater. Chem. A, 2014, 2, 13831-13834.
- 2 L. Ascherl, T. Sick, J. T. Margraf, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M. Döblinger, T. Clark, K. W. Chapman, F. Auras and T. Bein, *Nat. Chem.*, 2016, **8**, 310-316.
- 3 M. Thommes, K. Kaneko, V. Neimark Alexander, P. Olivier James, F. Rodriguez-Reinoso, J. Rouquerol and S. W. Sing Kenneth, *Journal*, 2015, **87**, 1051.
- 4 G.-F. Zhang, Z.-Q. Chen, M. P. Aldred, Z. Hu, T. Chen, Z. Huang, X. Meng and M.-Q. Zhu, *Chem. Commun.*, 2014, **50**, 12058-12060.
- 5 T. Hatakeyama, S. Hashimoto, S. Seki and M. Nakamura, J. Am. Chem. Soc., 2011, 133, 18614-18617.