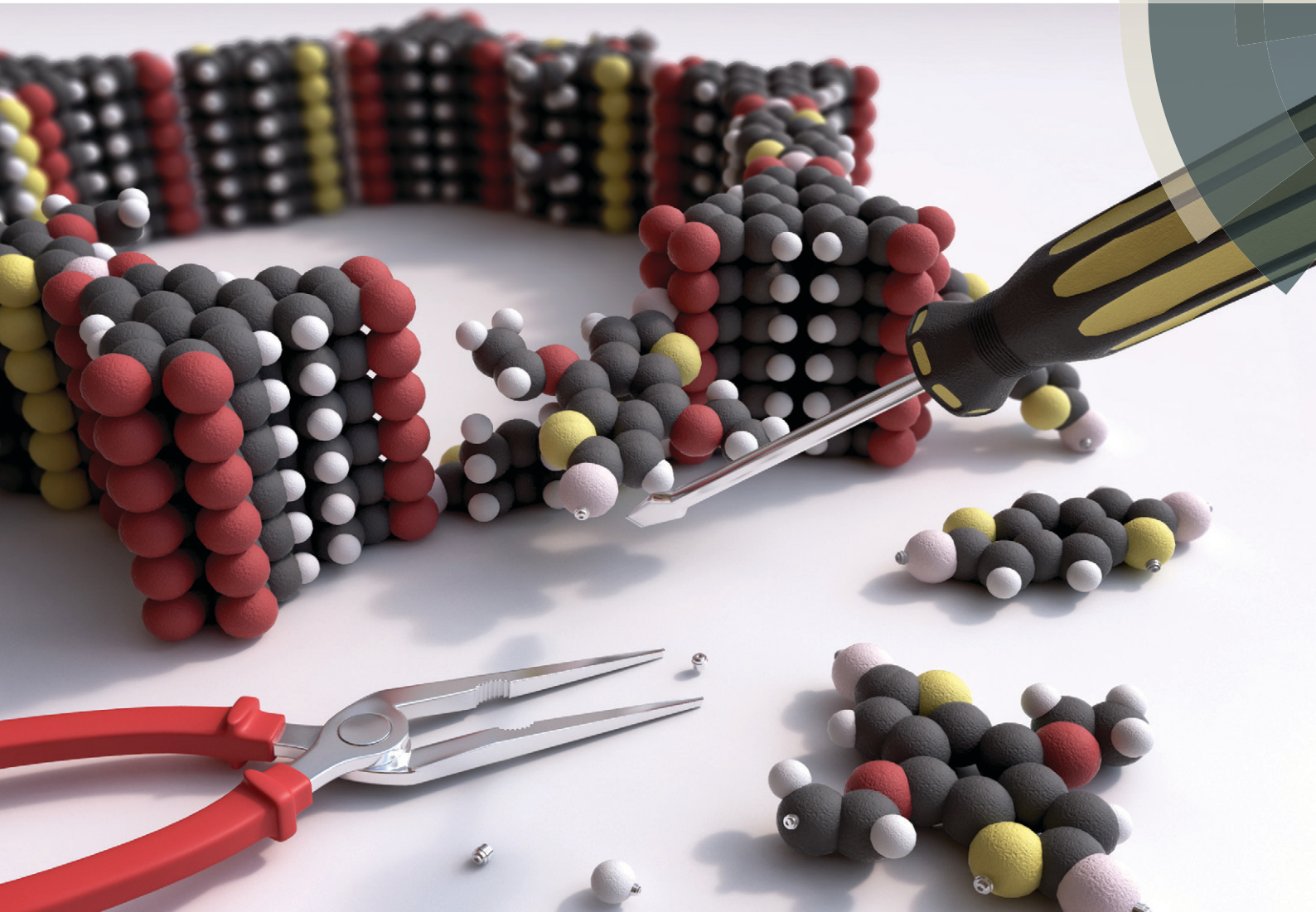


CrystEngComm

www.rsc.org/crystengcomm



Themed issue: 2016 New talent: crystal engineering at its biggest and strongest



PAPER

Thomas Bein, Dana D. Medina *et al.*
From benzodithiophene to diethoxy-benzodithiophene covalent organic frameworks – structural investigations

175 YEARS



Cite this: *CrystEngComm*, 2016, 18, 4295

From benzodithiophene to diethoxy-benzodithiophene covalent organic frameworks – structural investigations†

Maria S. Lohse,^{‡a} Julian M. Rotter,^{‡a} Johannes T. Margraf,^b Veronika Werner,^a Matthias Becker,^a Simon Herbert,^a Paul Knochel,^a Timothy Clark,^b Thomas Bein^{*a} and Dana D. Medina^{*a}

The incorporation of side groups into a covalent organic framework (COF) backbone can be of significant importance for developing new frameworks with enhanced properties. Here we present a novel π -stacked thiophene-based COF containing a benzodithiophene building unit modified with ethoxy side chains. The resulting BDT-OEt COF is a crystalline mesoporous material featuring high surface area and accessible hexagonal pores. We further synthesized a series of COFs containing both BDT and BDT-OEt building units at different ratios. The impact of the gradual incorporation of the BDT-OEt building units into the COF backbone on the crystallinity and porosity was investigated. Furthermore, molecular dynamic simulations shed light on the possible processes governing the COF assembly from molecular building blocks.

Received 24th January 2016,
Accepted 9th March 2016

DOI: 10.1039/c6ce00193a

www.rsc.org/crystengcomm

Introduction

The self-organization of π -stacked organic layers into highly ordered three-dimensional porous structures endows covalent organic frameworks (2D COFs) with interesting properties for diverse applications, including chemical separations, catalysis and optoelectronics.^{1–7} The extended organic layers constituting a 2D COF are generally obtained by the copolymerization of rigid building units having complimentary geometries through the formation of strong yet reversible covalent bonds. Boroxines and boronic esters, obtained by condensation reactions of boronic acids and diols, are commonly utilized as integral COF assembly motifs and thereby enable the growth of planar two-dimensional layers.⁸ Along with the condensation reactions, stacking of the formed organic layers takes place through dispersive forces.⁹ Therefore, 2D COFs connected through boronate esters feature an assembly of organic building units (or linkers) in a columnar fashion. This permits the formation of supramolecular structures having

long-range order, one-dimensional channels and high surface areas.^{10–15}

Tuning the structural and physical properties of a COF while maintaining its key features, namely porosity and crystallinity, can pose significant synthetic challenges. For example, incorporating building units having a large conjugated π -system into a framework can be highly desirable for enhanced light absorption properties.^{11,16} However, such attractive building units tend to exhibit poor solubility under the reaction conditions, often leading to poor crystallinity of the resulting COF.¹⁷ To overcome solubility limitations, a modification of the building units with solubilizing agents such as alkyl side chains can be considered. In the final COF structure the solubilizing side chains are oriented orthogonally to the COF pore walls and therefore need to be compatible with the stacking of the COF layers. In addition, these groups can play an important role in defining the electronic properties of the COF. Electron donating or electron withdrawing side groups can have a strong impact on the COF optical bandgap, and they can affect the fine balance between the Coulomb repulsion and the weak attractive London dispersion interactions holding the COF layers together.

In an early study, Lavigne and co-workers reported the synthesis of a boronate ester-linked COF-18 series where the catechol building units were modified with linear alkyl side chains ranging from methyl to propyl groups. The impact of the integrated alkyl side chains on guest molecule uptake was investigated.¹⁸ In a later study, enhanced stability towards humidity of the propyl modified COF structure was shown within the COF-18 series.¹⁹ However, the overall

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

E-mail: bein@lmu.de, dana.medina@cup.uni-muenchen.de

^b Computer-Chemie-Centrum, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Nügelbachstraße 25, 91052 Erlangen, Germany

† Electronic supplementary information (ESI) available: BDT-OEt structure simulations, MD simulations, nitrogen sorption isotherms and pore size distribution calculations; SEM and TEM images; TGA traces; FT-IR spectra; ¹¹B and ¹³C solid-state NMR spectra of BDT-OEt; ¹H NMR spectra of dissolved COFs. See DOI: 10.1039/c6ce00193a

‡ These authors contributed equally to this work.

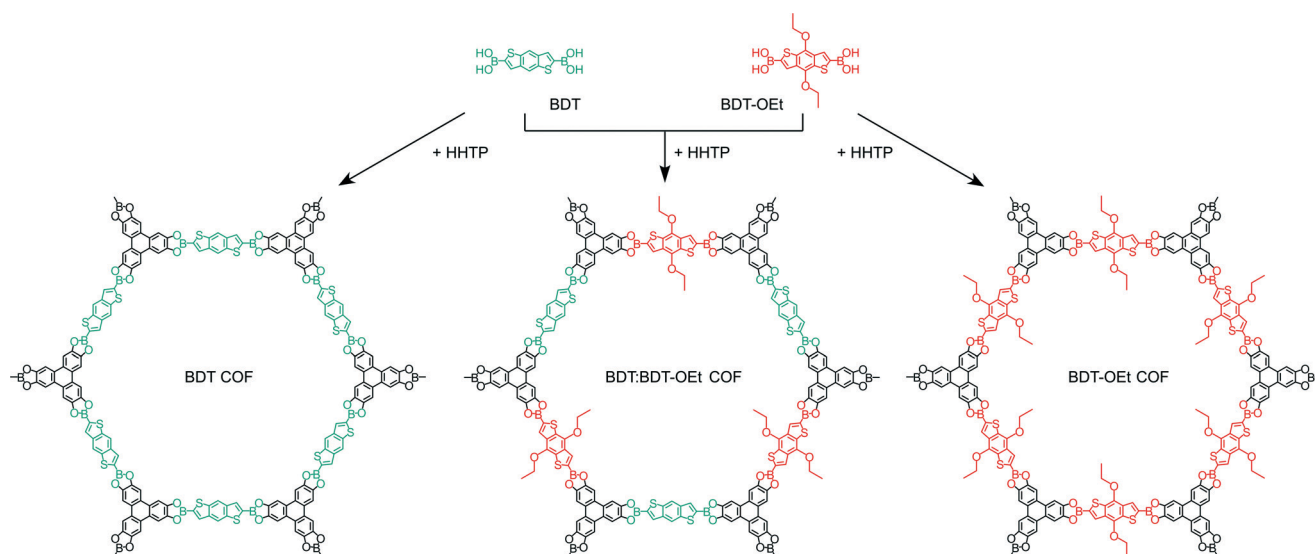


Herein, we describe the synthesis of a highly porous boronate ester linked BDT-OEt COF containing (4,8-diethoxybenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)diboric acid. The BDT core is modified with electron-donating ethoxy side chains thereby expanding the family of thiophene-based COFs.^{7,22,24,25} We synthesized a series of COFs consisting of BDT and BDT-OEt building unit mixtures and studied their structural properties (Scheme 1). The impact of the gradual layer perturbation imposed by the increased fraction of incorporated BDT-OEt building units into the COF backbone on the crystallinity and porosity was investigated. Furthermore, molecular dynamic simulations shed light on the possible processes governing the COF assembly from molecular building units.

Materials

Synthesis of 4,8-diethoxybenzo[1,2-*b*:4,5-*b'*]dithiophene (1). The reaction was performed based on a literature procedure.²⁶ A mixture of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (1.10 g, 4.99 mmol, 1.0 equiv.), zinc dust (0.981 g, 15.0 mmol, 3.0 equiv.), NaOH (10 mL) and EtOH (10 mL) was stirred at 95 °C for 2 h. Ethyl *p*-toluenesulfonate (3.00 g, 15.0 mmol, 3.0 equiv.) was added and the resulting solution was stirred at 95 °C for additional 3 h. The reaction mixture was allowed to cool down to room temperature and was diluted with dichloromethane (DCM) (70 mL). The aqueous layer was extracted with DCM (4 × 100 mL) and the combined organic fractions were dried over Na₂SO₄. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography (silica, isohexane/DCM = 3 : 1) to afford **1** as a colorless solid (0.675 g, 49%). Mp: 96.9–102.6 °C. ¹H NMR (400 MHz, CDCl₃) δ/ppm = 7.46 (d, *J* = 5.5 Hz, 2H), 7.35 (d, *J* = 5.5 Hz, 2H), 4.35 (q, *J* = 7.0 Hz, 4H), 1.47 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm = 144.3, 131.8, 130.4, 126.0, 120.3, 69.4, 16.1. IR (cm⁻¹): $\tilde{\nu}$ = 3100, 2980, 2873, 1892, 1515, 1477, 1436, 1372, 1347, 1199, 1106, 1085, 1029, 977, 873, 810, 752, 736, 695, 661. MS (70 eV, EI) *m/z* (%) = 278 (27, M⁺), 223 (11), 222 (13), 221 (100), 111 (37), 44 (31), 43 (80). HRMS for C₁₄H₁₄O₂S₂ (278.0435) found: 278.0428.

Synthesis of 2,6-dibromo-4,8-diethoxybenzo[1,2-*b*:4,5-*b'*]-dithiophene (2). In a dry argon flushed Schlenk-flask, equipped with a magnetic stirring bar and septum, **1** (1.39 g, 5.0 mmol,



Scheme 1 Schematic representation of the synthesis of BDT COF (left), BDT:BDT-OEt 1:1 COF (middle), and BDT-OEt COF (right).



Fourier-transform infrared spectra were measured with a Bruker Equinox 55 equipped with a PIKE MIRacle ATR-unit at room temperature in the scan range 650–4000 cm⁻¹. Nitrogen sorption was measured with 20–25 mg sample using a Quantachrome AUTOSORB-1 station at 77.3 K after degassing the sample for at least 12 h under vacuum at 150 °C. The Brunauer–Emmett–Teller (BET) surface areas were calculated from the adsorption branch in the range of $p/p_0 = 0.05$ – 0.13 . Pore sizes were calculated with a QSDFT adsorption model of N₂ on carbon (cylindrical, adsorption branch). Powder X-ray diffraction (PXRD) measurements were carried out in reflection mode on a Bruker D8 Discover diffractometer with Ni-filtered K α -radiation ($\lambda = 1.54060$ Å) and a position-sensitive detector (LynxEye). Molecular geometry optimization was performed with Accelrys MS Modeling 4.4 using the universal and Dreiding forcefield method. The final hexagonal unit cell was calculated with the geometric parameters from the optimized structure. For the Pawley refinement and simulation of the PXRD patterns the Reflex module was used (a software package implemented in MS Modeling 4.4). Scanning electron microscopy (SEM) was performed on a JEOL 6500F instrument at an acceleration voltage of 2–5 kV. The samples were coated with a thin carbon layer by carbon fiber flash evaporation at high vacuum. Transmission electron microscopy (TEM) data were obtained with a FEI Titan Themis 60–300 microscope at an acceleration voltage of 300 kV. Cross-polarized ¹¹B and ¹³C solid-state NMR (ssNMR) measurements were

Synthesis of 4,8-diethoxybenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diylidiboronic acid (3). In a dry argon flushed Schlenk-flask, equipped with a magnetic stirring bar and septum, **2** (434 mg, 1.00 mmol, 1.0 equiv.) was dissolved in tetrahydrofuran (THF) (8 mL) and cooled down to -40 °C. *n*-BuLi (1.06 mL, 2.5 mmol, 2.5 equiv., 2.35 M in hexane) was added and the resulting solution was stirred for 1.5 h and cooled down to -85 °C. Then, triisopropyl borate (0.69 mL, 3.0 mmol, 3.0 equiv.) was added and the reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was diluted with half-concentrated aq NH₄Cl solution (25 mL). The alkaline solution was acidified to pH 6 (with 2.0 M HCl) and extracted with a 3 : 1 THF : diethyl ether mixture (3 × 150 mL). The combined organic layers were dried over Na₂SO₄. After filtration, the solvents were evaporated *in vacuo*. The crude product was suspended in isohexane (70 mL) and the mixture was stirred at room temperature for 5 h. The precipitate was filtered off and dried *in vacuo*. **3** was obtained as green solid (184 mg, 50%) and was used without further purification. Mp: 271.9–274.3 °C. ¹H NMR (400 MHz, acetone-*d*₆) δ/ppm = 8.14 (s, 2H), 4.39 (q, *J* = 7.2 Hz, 4H), 1.47 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (75 MHz, acetone-*d*₆) δ/ppm = 145.5, 135.1, 134.5, 130.3, 70.4, 16.8. IR (cm⁻¹): $\tilde{\nu}$ = 3209, 2978, 1532, 1445, 1373, 1344, 1320, 1161, 1084, 1046, 989, 959, 850, 788, 700. HRMS for C₁₄H₁₅O₆B₂S₂ (365.0496) found: 365.0501.

COF synthesis

A 25 mL Schott Duran glass bottle with a Teflon sealed polybutylene terephthalate cap was equipped with 2,3,6,7,10,11-hexahydroxytriphenylene, HHTP (11 mg, 0.034 mmol) and a total of 0.051 mmol of BDT:BDT-OEt linkers in molar ratios of 1:0, 3:1, 1:1, 1:3, and 0:1. The reaction mixture was suspended in 1.5 mL of a 1:1 (v/v) solution of mesitylene/dioxane and heated for 72 h at 100 °C. Afterwards, the green

performed on a Bruker Avance III-500 spectrometer in a 4 mm ZrO_2 rotor with a spinning rate of 10 kHz. Thermogravimetric analyses (TGA) were recorded on a Netzsch STA 440 C TG/DSC. The measurements proceeded at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ up to $900\text{ }^\circ\text{C}$, in a stream of synthetic air of about 25 mL min^{-1} . Hydrolyzed COF ^1H NMR solution spectra were recorded on a Bruker Avance III-400 MHz spectrometer. 5 mg of COF powder was dissolved in $\text{DMSO-}d_6$ containing 5% D_2O in every case. A relaxation delay of 8 s was employed to increase the precision of aromatic signal integration.

Results

A novel BDT-OEt COF featuring a BDT core decorated with ethoxy side chains was synthesized through the co-condensation of (4,8-diethoxybenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)diboronic acid and HHTP (2,3,6,7,10,11-hexahydroxytriphenylene) under solvothermal conditions (for more details see Experimental section).

Powder X-ray diffraction data of the newly synthesized BDT-OEt COF clearly indicate the formation of a crystalline framework. The diffraction pattern reveals an intensive reflection at 2.78° corresponding to the (100) plane. Additional reflections observed at 4.85° , 5.58° and 7.38° , 9.71° and $\sim 25.7^\circ$ (broad) are attributed to the (110), (200), (120), (220) and (001) planes, respectively (Fig. 1a). The obtained *d*-values correspond to lattice parameters of $a = b = 3.66\text{ nm}$ for an ideal hexagonal BDT-OEt COF structure. Effective crystallite domain sizes of 21 nm in diameter for BDT-OEt COF were calculated using the Scherrer equation for reflection broadening. Molecular mechanics simulations for the possible COF layer arrangements were carried out using Materials Studio software and the Forcite module. Assuming a hexagonal symmetry, the BDT-OEt COF unit cell was constructed in the $P6$ space group corresponding to an ideal eclipsed AA COF layer arrangement, and featuring a completely open pore system (Fig. S1†). To obtain the final unit cell parameters and the crystallite domain sizes, Pawley refinement was employed. For this purpose, the geometry optimized BDT-OEt COF unit cell was refined against the experimental powder X-ray diffraction pattern. Lattice parameters of $a = b = 3.65\text{ nm}$, $c = 0.365\text{ nm}$ and crystallite sizes of 20 nm in diameter were obtained. The simulated powder diffraction pattern corrected for reflection broadening is in very good agreement with the experimentally observed pattern with regard to reflection positions and relative intensities (Fig. 1a). Additionally, we simulated the BDT-OEt COF unit cell in the triclinic $P1$ space group where no symmetry constraints are imposed. After geometry optimization and Pawley refinement, the refined unit cell reveals an eclipsed configuration with tilted COF layers.³⁶ This layer configuration produced a nearly identical simulated diffraction pattern, and therefore the exact eclipsed layer arrangement cannot be determined based on the experimental diffraction pattern (see Fig. S5†). To confirm the eclipsed layer arrangement for the BDT-OEt COF, we also simulated the X-ray diffraction pattern for an alternative hex-

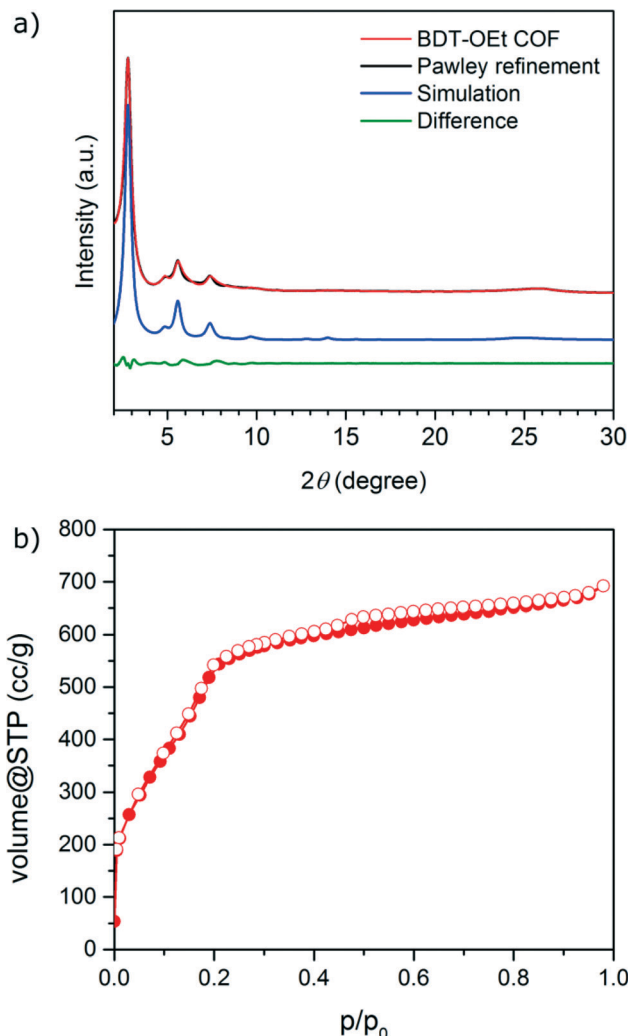


Fig. 1 (a) XRD patterns of BDT-OEt COF: experimental (red), Pawley refinement (black), simulated pattern (blue), and difference plot (green). (b) Nitrogen sorption isotherm of BDT-OEt COF. Full symbols: adsorption, empty symbols: desorption.

agonal unit cell with $P6_3$ space group corresponding to a staggered, AB layer arrangement (Fig. S8†). Based on the comparison of the simulated AA and AB patterns with the experimentally obtained pattern, we conclude that BDT-OEt crystallizes with an eclipsed layer arrangement allowing for an open pore system.

In previous reports, the side groups decorating the pore walls were considered as an amorphous contribution to the X-ray scattering data, having no preferred orientation in the pore due to their free rotation.^{18,20,37} To investigate the preferred orientation of the ethoxy groups in the pores, several separate molecular dynamics simulations were carried out (Fig. S10†). Independent of the initial orientation of the groups, which can either face the adjacent hydrogen or sulfur atom of the BDT core or alternate between these two cases, nearly all ethoxy-groups rotated to face the sulfur atom within less than 1 ns. The ethoxy groups retained their position, indicating that the groups can in principle rotate at room temperature, and that the sulfur-facing position is



Powder X-ray diffraction patterns of the obtained BDT:BDT-OEt COFs confirmed the formation of a series of crystalline frameworks (Fig. 3). Upon the incorporation of ethoxy side chains into the BDT COF backbone, gradual changes in the BDT:BDT-OEt COF diffraction patterns were observed. The relative intensities of the (110) and (200) planes change with the increased fraction of BDT-OEt building units. This is

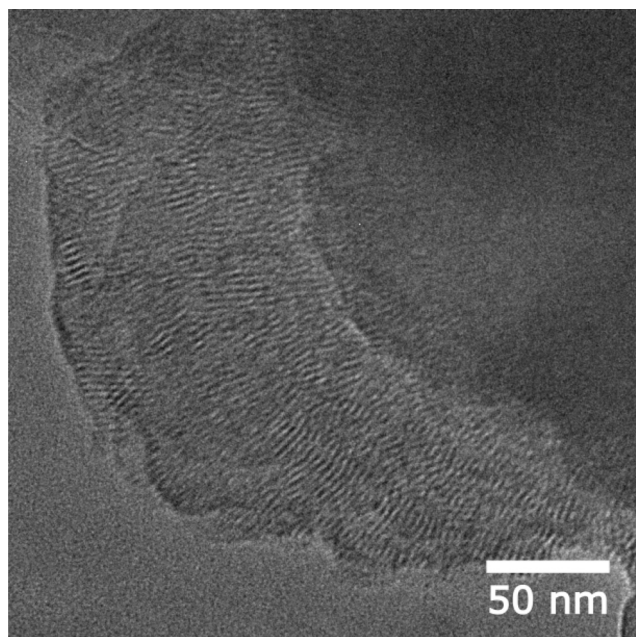


Fig. 3 PXRD patterns of BDT COF, BDT:BDT-OEt COFs, and BDT-OEt COF.

The impact of the gradual incorporation of the ethoxy side chains on the pore accessibility of the frameworks was investigated by nitrogen sorption. The BDT:BDT-OEt COF series retained the typical type IV isotherms for mesoporous materials. The relative partial pressure of the slope of the nitrogen uptake is shifted to lower values as expected for the gradually increasing pore occupancy with ethoxy side chains. Pore size distribution evaluation revealed a gradual decrease of the pore size upon the incorporation of ethoxy side chains. In all the BDT:BDT-OEt COF structures only one type of pore is present, indicating a random integration of the ethoxy groups into the frameworks, as opposed to the formation of phase-separated domains. High surface areas were calculated for the BDT:BDT-OEt COF series. This clearly illustrates that incorporation of BDT-OEt building units into the framework does not affect the accessible surface areas and pores of the BDT:BDT-OEt COF (Fig. 4, S12[†]).

These analyses confirm that with BDT and BDT-OEt building units, COFs can be formed from freely selected ratios of the respective boronic acids. While mixing these building units in a COF leads to structural changes in the framework, a highly porous, crystalline and thermally stable framework is generated in all cases.

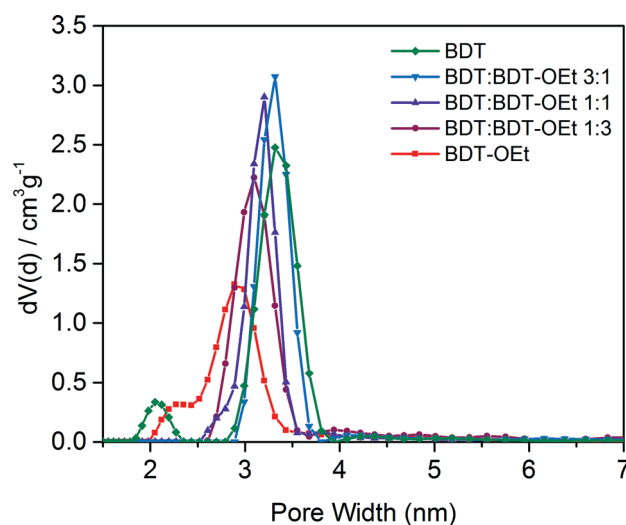


Fig. 4 Detail of the pore size distributions of BDT COF, mixed BDT:BDT-OEt COFs and BDT-OEt COF showing the decrease of the main pore diameter upon the incorporation of ethoxy side chains into the COF structure.

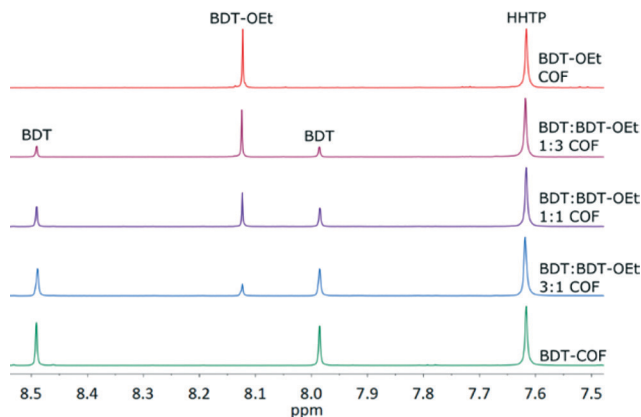


Fig. 5 ^1H -NMR spectra of the hydrolyzed COFs showing the stoichiometric incorporation of BDT and BDT-OEt linkers into the respective frameworks.

Conclusions

In conclusion, a novel ethoxy-functionalized benzo-dithiophene based COF, namely BDT-OEt COF, was synthesized under solvothermal conditions. BDT-OEt COF features crystallinity, mesoporosity and high surface area. A series of COFs consisting of both BDT and BDT-OEt building units in different ratios was synthesized. Highly crystalline, mesoporous frameworks were obtained for all BDT:BDT-OEt COFs. A nearly linear evolution from BDT to BDT-OEt COF was observed with regard to pore size and crystallite domain size upon the gradual incorporation of BDT-OEt building units into the COF backbone. Furthermore, we show that the final building unit ratios in the framework can be predetermined prior to the COF synthesis. Therefore, the COF backbones and chemical pore environment can be finely tuned towards desired properties while an eclipsed layer arrangement is retained. Molecular dynamics simulations and DFT calculations shed light on the preferred orientation of the ethoxy groups in the pores. Furthermore, the simulations illustrate that the incorporation of ethoxy chains facilitates a subtle lateral displacement of the BDT COF layers relative to each other.

Acknowledgements

The authors are grateful for funding from the German Science Foundation (DFG; Excellence Cluster NIM) and the Free State of Bavaria (Research Network SolTech). The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ERC Grant Agreement no. 321339. We thank Christian Minke and Thomas Bräuniger for ssNMR, Markus Döblinger for TEM, and Steffen Schmidt and Erika Mühlbauer for SEM measurements.

Notes and references

- 1 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.

- 2 N. Huang, X. Chen, R. Krishna and D. Jiang, *Angew. Chem., Int. Ed.*, 2015, **54**, 2986–2990.
- 3 H. Xu, J. Gao and D. Jiang, *Nat. Chem.*, 2015, **7**, 905–912.
- 4 S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi and C. J. Chang, *Science*, 2015, **349**, 1208–1213.
- 5 C. R. DeBlase, K. E. Silberstein, T.-T. Truong, H. D. Abruña and W. R. Dichtel, *J. Am. Chem. Soc.*, 2013, **135**, 16821–16824.
- 6 M. S. Lohse, T. Stassin, G. Naudin, S. Wuttke, R. Ameloot, D. De Vos, D. D. Medina and T. Bein, *Chem. Mater.*, 2016, **28**, 626–631.
- 7 M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, *Angew. Chem., Int. Ed.*, 2013, **52**, 2920–2924.
- 8 J. W. Colson and W. R. Dichtel, *Nat. Chem.*, 2013, **5**, 453–465.
- 9 B. J. Smith and W. R. Dichtel, *J. Am. Chem. Soc.*, 2014, **136**, 8783–8789.
- 10 L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong and D. Jiang, *J. Am. Chem. Soc.*, 2014, **136**, 9806–9809.
- 11 S. Jin, X. Ding, X. Feng, M. Supur, K. Furukawa, S. Takahashi, M. Addicoat, M. E. El-Khouly, T. Nakamura, S. Irle, S. Fukuzumi, A. Nagai and D. Jiang, *Angew. Chem., Int. Ed.*, 2013, **52**, 2017–2021.
- 12 S. Jin, K. Furukawa, M. Addicoat, L. Chen, S. Takahashi, S. Irle, T. Nakamura and D. Jiang, *Chem. Sci.*, 2013, **4**, 4505–4511.
- 13 J. Guo, Y. Xu, S. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang, *Nat. Commun.*, 2013, **4**, 2736.
- 14 E. L. Spitler, J. W. Colson, F. J. Uribe-Romo, A. R. Woll, M. R. Giovino, A. Saldivar and W. R. Dichtel, *Angew. Chem., Int. Ed.*, 2012, **51**, 2623–2627.
- 15 H. Yang, Y. Du, S. Wan, G. D. Trahan, Y. Jin and W. Zhang, *Chem. Sci.*, 2015, **6**, 4049–4053.
- 16 M. Calik, F. Auras, L. M. Salonen, K. Bader, I. Grill, M. Handloser, D. D. Medina, M. Dogru, F. Löbermann, D. Trauner, A. Hartschuh and T. Bein, *J. Am. Chem. Soc.*, 2014, **136**, 17802–17807.
- 17 S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle and D. Jiang, *J. Am. Chem. Soc.*, 2015, **137**, 7817–7827.
- 18 R. W. Tilford, S. J. Mugavero, P. J. Pellechia and J. J. Lavigne, *Adv. Mater.*, 2008, **20**, 2741–2746.
- 19 L. M. Lanni, R. W. Tilford, M. Bharathy and J. J. Lavigne, *J. Am. Chem. Soc.*, 2011, **133**, 13975–13983.
- 20 A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding and D. Jiang, *Nat. Commun.*, 2011, **2**, 536.
- 21 B. J. Smith, N. Hwang, A. D. Chavez, J. L. Novotney and W. R. Dichtel, *Chem. Commun.*, 2015, **51**, 7532–7535.
- 22 D. D. Medina, V. Werner, F. Auras, R. Tautz, M. Dogru, J. Schuster, S. Linke, M. Döblinger, J. Feldmann, P. Knochel and T. Bein, *ACS Nano*, 2014, **8**, 4042–4052.
- 23 D. D. Medina, J. M. Rotter, Y. Hu, M. Dogru, V. Werner, F. Auras, J. T. Markiewicz, P. Knochel and T. Bein, *J. Am. Chem. Soc.*, 2015, **137**, 1016–1019.



- 24 G. H. V. Bertrand, V. K. Michaelis, T.-C. Ong, R. G. Griffin and M. Dincă, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 4923–4928.
- 25 S. Duhović and M. Dincă, *Chem. Mater.*, 2015, **27**, 5487–5490.
- 26 D. W. Slocum and P. L. Gierer, *J. Org. Chem.*, 1976, **41**, 3668–3673.
- 27 S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.*, 1990, **94**, 8897–8909.
- 28 O. Alexiadis and V. G. Mavrantzas, *Macromolecules*, 2013, **46**, 2450–2467.
- 29 A. K. Rappe and W. A. Goddard, *J. Phys. Chem.*, 1991, **95**, 3358–3363.
- 30 J. Clark Stewart, D. Segall Matthew, J. Pickard Chris, J. Hasnip Phil, I. J. Probert Matt, K. Refson and C. Payne Mike, *Z. Kristallogr.*, 2005, **220**, 567.
- 31 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 32 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
- 33 E. R. McNellis, J. Meyer and K. Reuter, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 205414.
- 34 D. Vanderbilt, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1990, **41**, 7892–7895.
- 35 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1976, **13**, 5188–5192.
- 36 E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.*, 2011, **133**, 19416–19421.
- 37 H. Xu, X. Chen, J. Gao, J. Lin, M. Addicoat, S. Irle and D. Jiang, *Chem. Commun.*, 2014, **50**, 1292–1294.

