Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Copolymerisation at work: first example of a highly porous MOF comprising a triarylborane based linker

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S1. Syntheses of *(S)*-2-(4-Benzyl-2oxazolidin-3-yl)terephthalic acid & 4,4’,4’’-boranetriyltris(3,5-dimethylbenzoic acid)

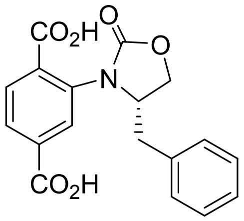
S1.1 Materials and methods

Tetrakis(triphenylphosphine)palladium(0) and *n*-BuLi solution were purchased from Acros. $BF_3 \cdot Et_2O$ was purchased from Merck. 5-Bromo-1,3-dimethyl-2-iodobenzene was purchased from Apollo Scientific. Methanol was purchased from Roth and was stored over molecular sieve. Toluene and diethyl ether were purified by distillation over CaH_2 and sodium respectively, prior to use. Triethylamine was distilled over CaH_2 and was transferred under argon. The solvents used for column chromatography were purified by distillation. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with shortwave UV light. Flash chromatography was performed on Merck silica gel (40-63 mesh) using standard techniques eluting with solvents as indicated.

NMR spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm and $(CD_3)_2SO$: δ_H =2.50 ppm, δ_C = 39.5 ppm). Coupling constants (*J*) are quoted in Hz. ESI mass spectra were recorded on a Bruker Daltonics MicroTof spectrometer. Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur or on a Shimadzu FTIR 8400S spectrometer. The wave numbers (ν) of recorded IR signals are quoted in cm^{-1}.

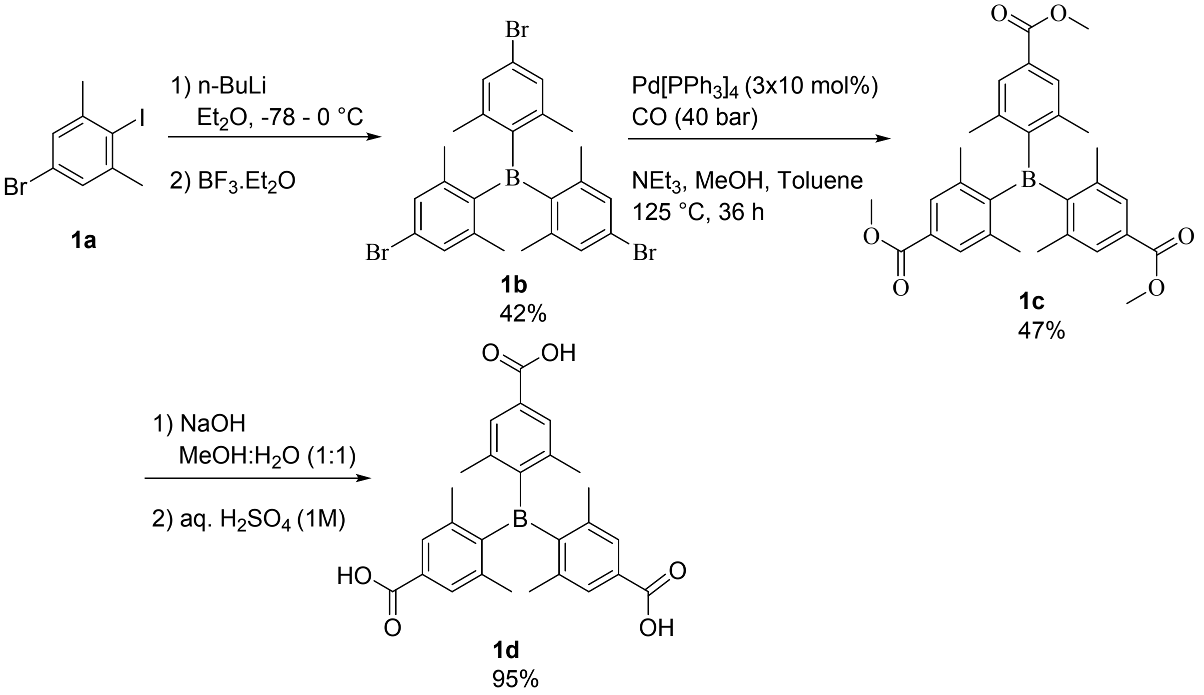
S1.2 Synthesis of *(S)*-2-(4-benzyl-2oxazolidin-3-yl)terephthalic acid:

(S)-2-(4-Benzyl-2oxazolidin-3-yl)terephthalic acid has been synthesized following our previously reported procedure.[1]



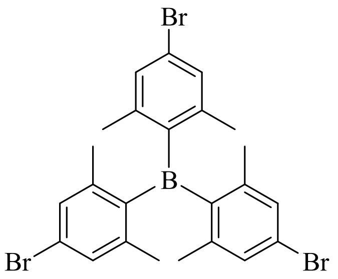
(S)-2-(4-Benzyl-2oxazolidin-3-yl)terephthalic acid

S1.3 Synthesis of 4,4',4"-boranetriyltris(3,5-dimethylbenzoic acid):



Scheme 1: Synthesis of 4,4',4"-boranetriyltris(3,5-dimethylbenzoic acid) (**1d**).

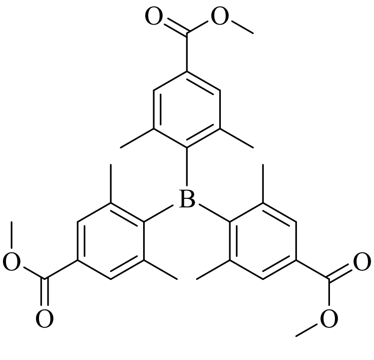
Tris(4-bromo-2,6-dimethylphenyl)borane (1b):



Following a modified procedure by Zhang and Zhang et al.[2], a flame dried Schlenk tube was charged with 5-bromo-2-iodo-1,3-dimethyl benzene (**1a**, 1.0 g, 3.216 mmol) in a glovebox. Dry diethyl ether (20 ml) was added to the flask and the mixture was cooled to -78 °C. To the reaction mixture at -78 °C, a solution of *n*-BuLi (1.6M, 2 ml, 3.216 mmol) in hexane was added dropwise. The reaction mixture was allowed to warm up to 0 °C and stirred for 30 min. The reaction mixture was again cooled down to -78 °C and $BF_3.Et_2O$ (0.1 ml, 0.8 mmol) was added dropwise. The whole reaction mixture was slowly allowed to warm up to room temperature (rt) and stirred overnight. Water was added to quench the reaction and the mixture was extracted with diethyl ether. The organic layers were washed with brine, dried over anhydrous $MgSO_4$ and the solvents were removed under reduced pressure. The crude reaction mixture was purified by column chromatography (eluent: pentane) to give tris(4-bromo-2,6-dimethylphenyl)borane (**1b**) as a white solid (189.2 mg, 42%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.11 (s, 6H), 1.97 (s, 18H); **^{13}C NMR (75.5 MHz, $CDCl_3$):** δ (ppm): 144.7, 142.6, 130.9, 124.5, 22.9; **R_f (pentane):** 0.36; **HR-MS (ESI):** *m/z* calculated for $[C_{24}H_{24}B_1Br_3HCOO]^-$ ($[M+HCOO]^-$): 604.9504, measured: 604.9491; **IR (ATR):** ν (cm^{-1}): 2966, 2923, 1565, 1437, 1240, 1201, 1118, 1030, 938, 881, 850, 712, 662.

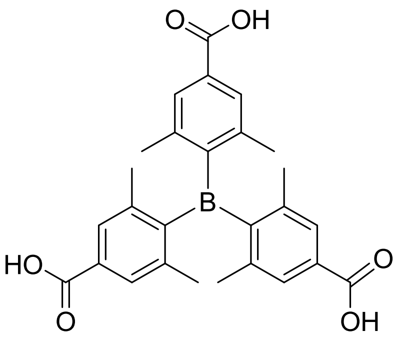
Trimethyl 4,4',4''-boranetriyltris(3,5-dimethylbenzoate) (1c):



Tris(4-bromo-2,6-dimethylphenyl)borane (**1b**, 100 mg, 0.178 mmol) and tetrakis(triphenylphosphine)palladium(0) (62.4 mg, 0.054 mmol) were added to an oven-dried screw-capped 3 ml glass vial equipped with a magnetic stirring bar under argon. Dry toluene (0.6 ml), distilled triethylamine (0.3 ml) and dry methanol (0.6 ml) were added to the vial. The vial was placed in a 150 ml stainless-steel reactor (*Note: four vials were placed in a reactor at a time*). The autoclave was carefully purged with carbon monoxide gas three times before the pressure was adjusted 40 bar. The reaction mixture was stirred at 125 °C for 36 h. Then the mixture was allowed to cool down to rt and the autoclave was carefully depressurized. The crude mixture was filtered through a plug of celite using ethyl acetate as eluent and the solvents were removed under reduced pressure. The residue was purified by column chromatography (eluent: pentane: ethyl acetate = 10:1) to give trimethyl 4,4',4''-boranetriyltris(3,5-dimethylbenzoate)(**1c**) as a light brown foamy solid (41.9 mg, 47%).

^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.61 (s, 6H), 3.90 (s, 9H), 2.05 (s, 18H); **^{13}C NMR (75.5 MHz, CDCl$_3$):** δ (ppm): 167.3, 150.6, 140.8, 131.4, 128.9, 52.2, 23.0; **R$_f$ (pentane:ethyl acetate 10:1):** 0.15; **HR-MS (ESI):** *m/z* calculated for $[C_{30}H_{33}B_1O_6Na]^+$ ($[M+Na]^+$): 523.2262, measured: 523.2263; **IR (ATR):** ν (cm^{-1}): 2953, 2360, 1719, 1553, 1435, 1410, 1301, 1208, 1142, 1115, 1016, 984, 898, 837, 768, 746, 711, 666.

4,4',4''-boranetriyltris(3,5-dimethylbenzoic acid) (1d):

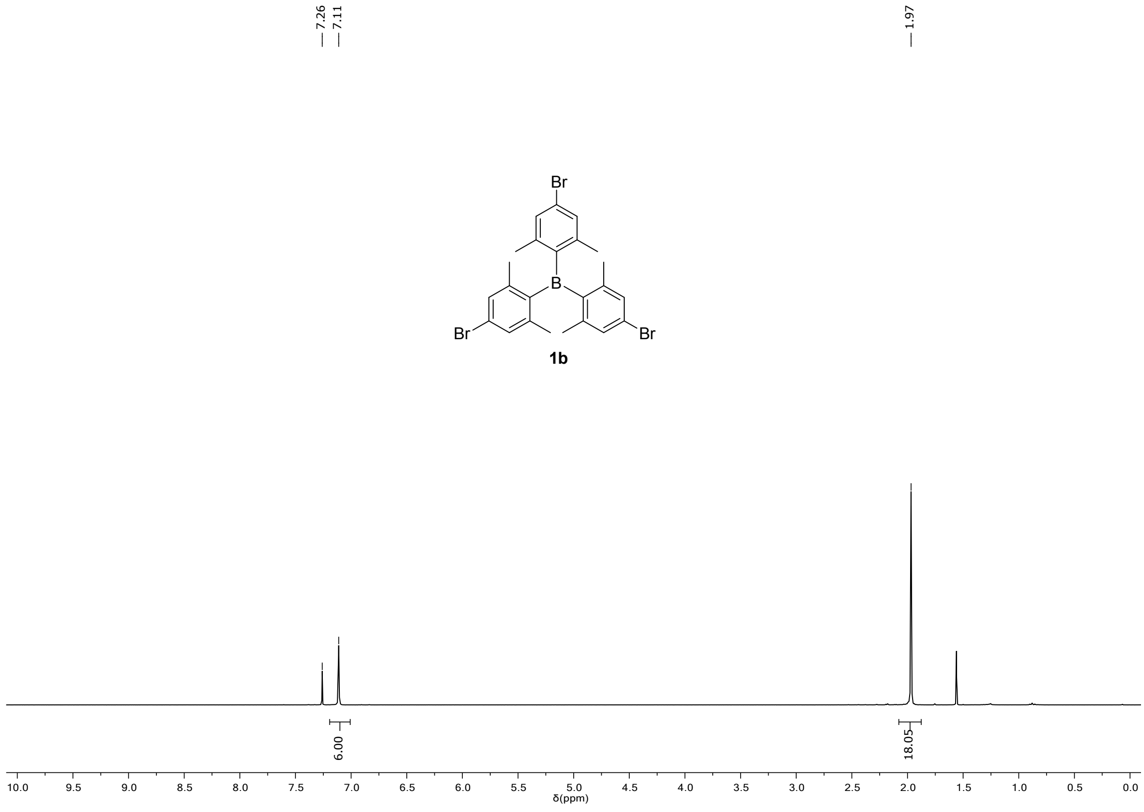


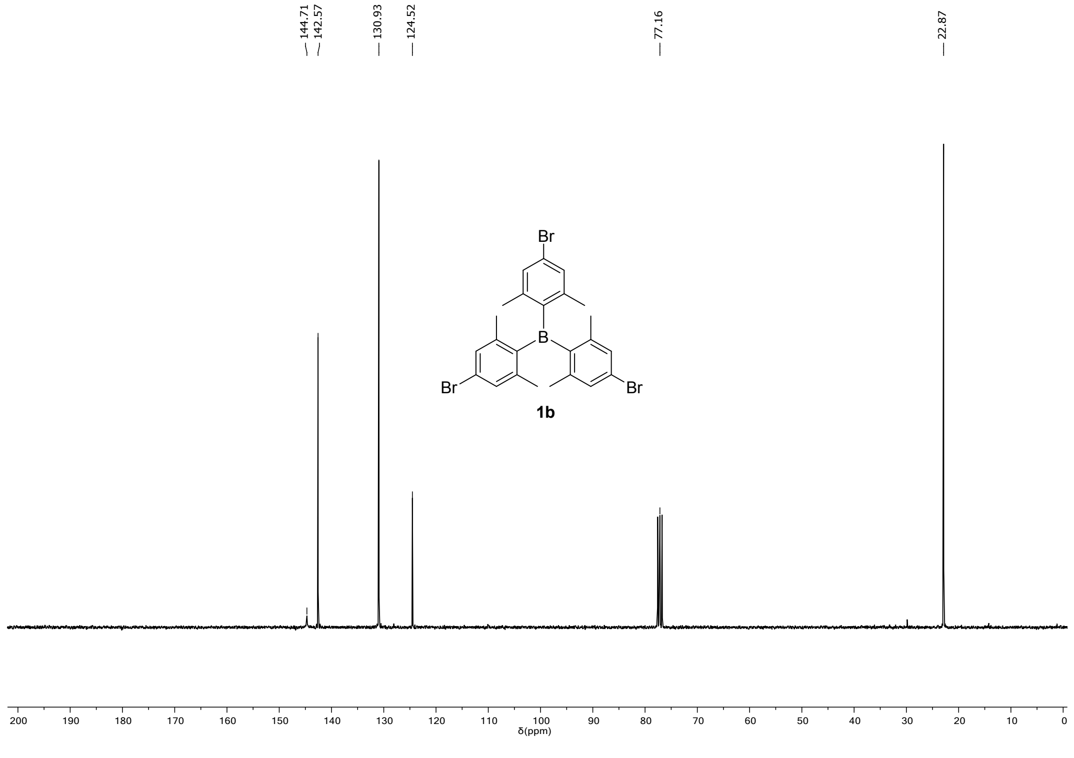
In a 250 ml round bottom flask, trimethyl 4,4',4''-boranetriyltris(3,5-dimethylbenzoate) (**1c**, 694 mg, 1.387 mmol) was dissolved in 28 ml methanol. To this methanol solution, sodium hydroxide (277.4 mg, 6.935 mmol) in 28 ml water was added and the reaction mixture was refluxed at 70 °C for 15 h (turbid reaction mixture turned to clear solution). After cooling the reaction mixture down to rt, it was diluted with water and filtered through Buchner funnel equipped with a sinter disc. The filtrate was acidified with aq. H_2SO_4 solution (1M) at pH 5-6 to precipitate out the product. The precipitate was filtered and dried under vacuum to give 4,4',4''-boranetriyltris(3,5-dimethylbenzoic acid) (**1d**) as a white solid (604 mg, 95%).

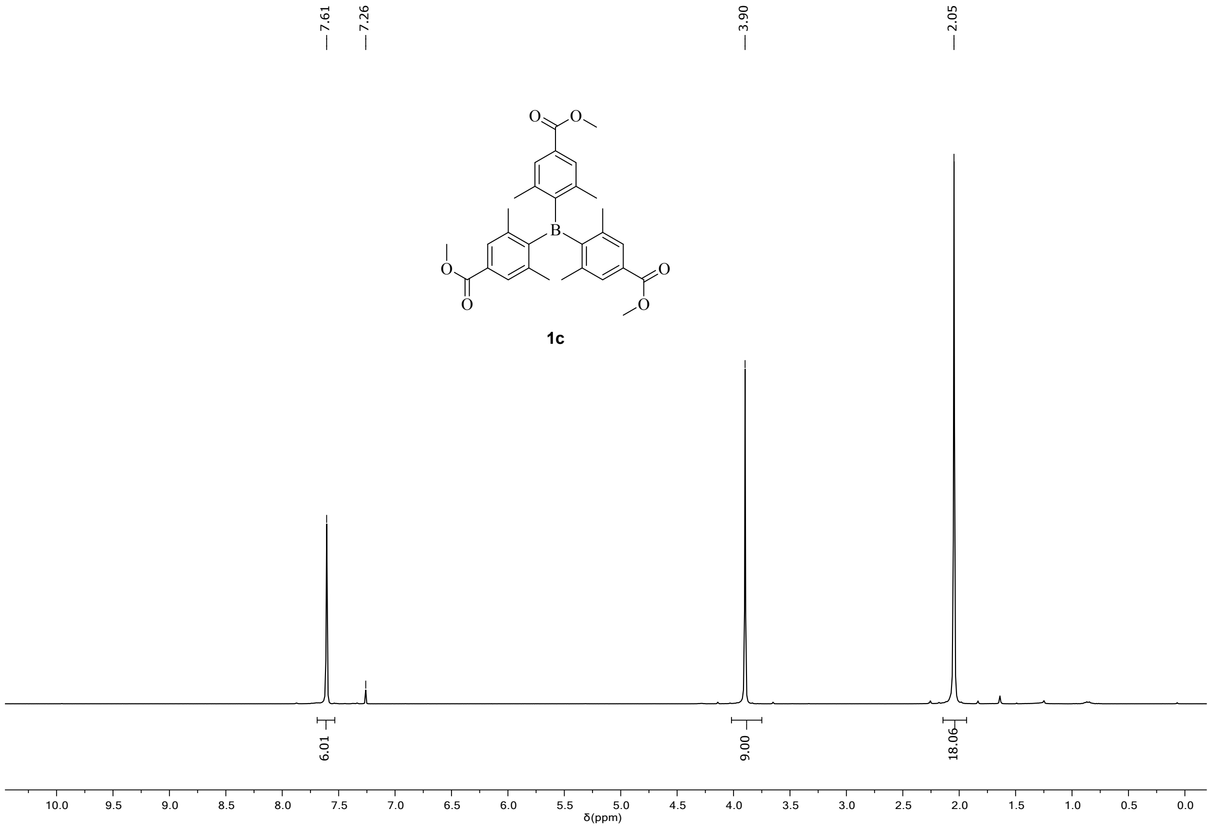
^{1}H NMR (300 MHz, DMSO-d$_6$): δ (ppm): 12.96 (broad signal, 3H), 7.55 (s, 6H), 2.02 (s, 18H); **^{13}C NMR (75.5 MHz, DMSO-d$_6$):** δ (ppm): 167.2, 149.7, 140.2, 131.9, 128.4, 22.2;

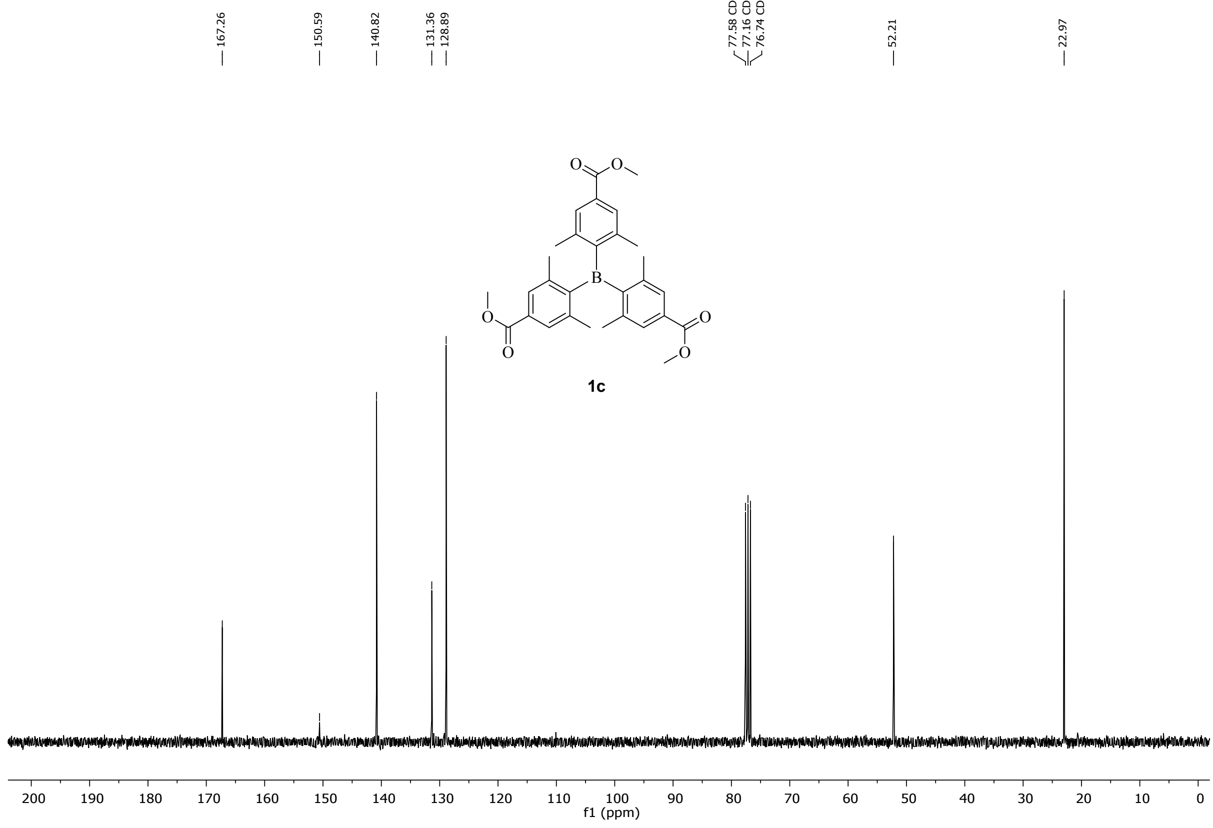
HR-MS (ESI): *m/z* calculated for $[C_{27}H_{26}B_1O_6]^-$ ($[M-H]^-$): 457.1828, measured: 457.1812; **IR (ATR):** ν (cm^{-1}): 2963, 2925, 1686, 1549, 1418, 1295, 1228, 1199, 1119, 1031, 899, 834, 771, 719, 665.

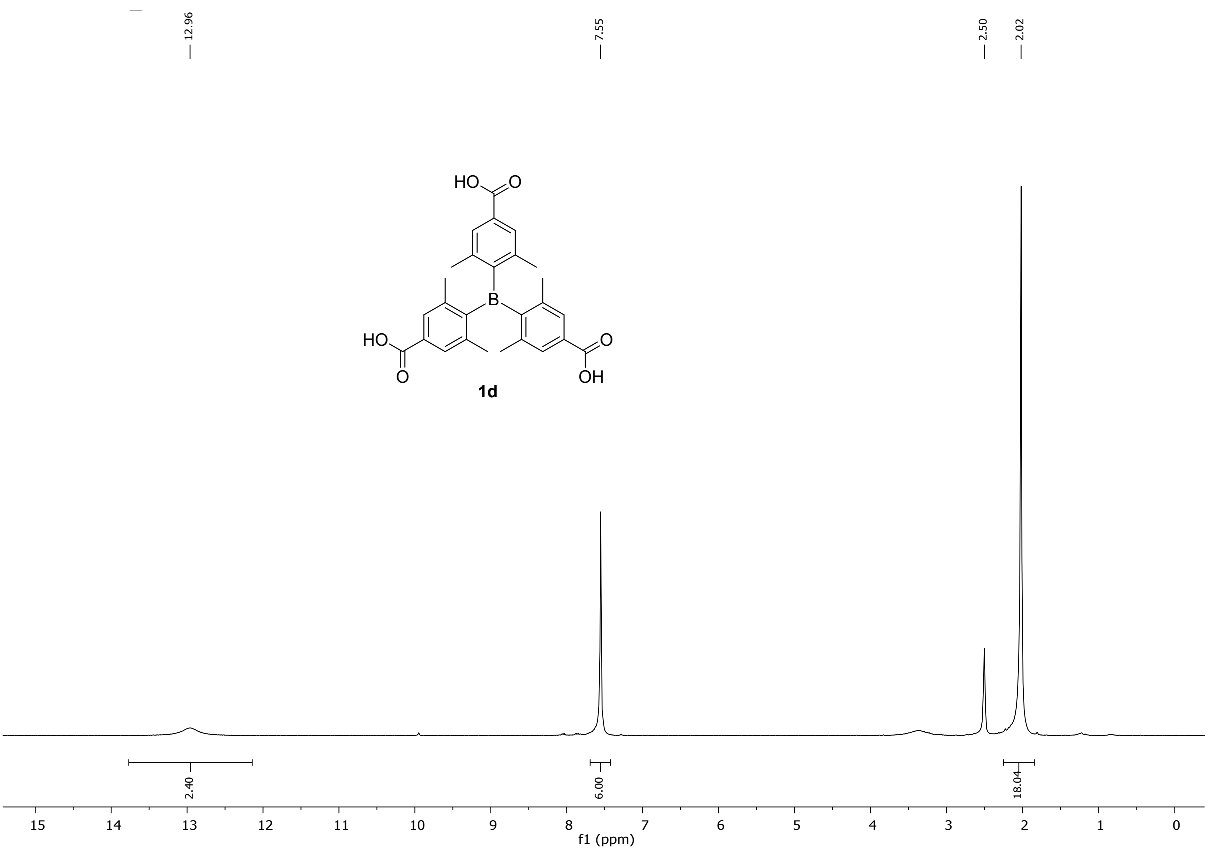
S1.4 NMR Spectra:

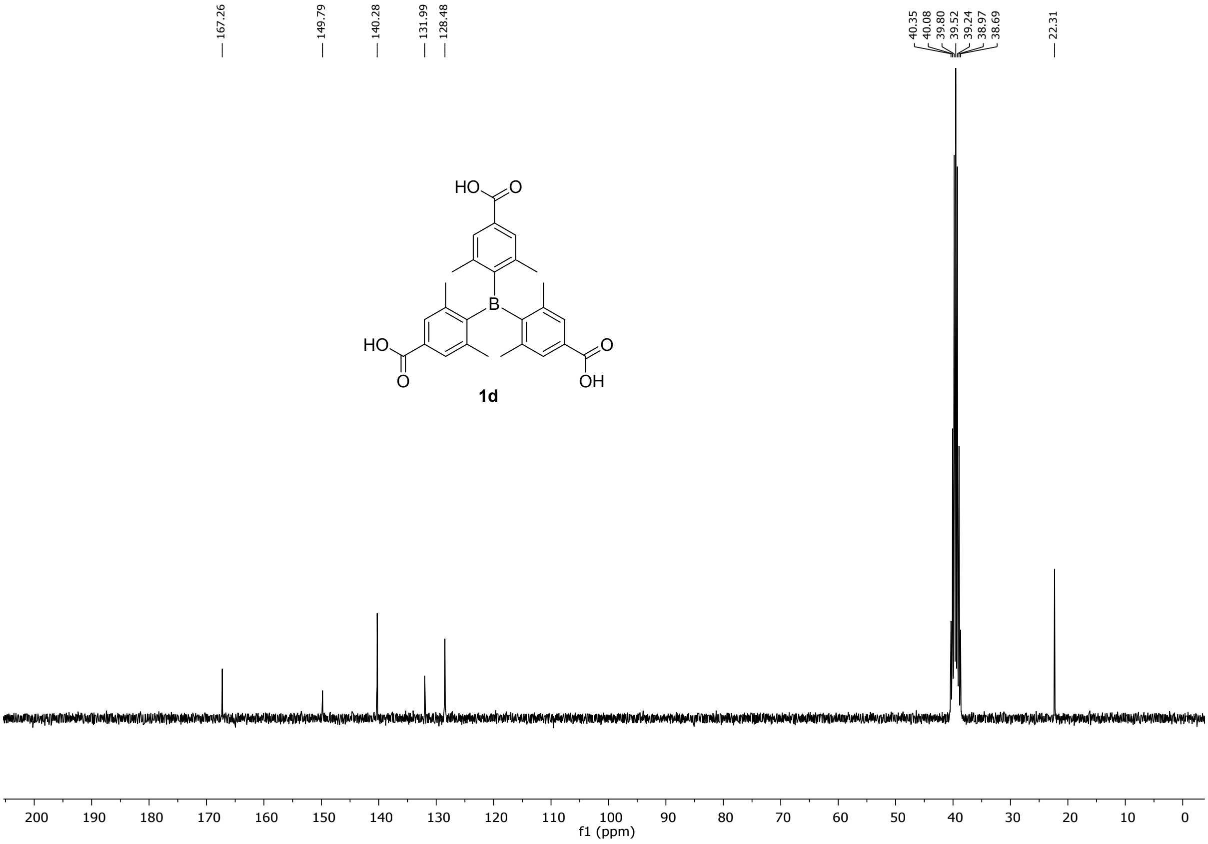





7.61
7.26
3.90
2.05
1c
6.01
9.00
18.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ(ppm)


167.26
150.59
140.82
131.36
128.89
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
52.21
22.97
1c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.96
7.55
2.50
2.02
HO
O
B
HO
O
O
OH
1d
2.40
6.00
18.04
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


167.26
149.79
140.28
131.99
128.48
40.35
40.08
39.80
39.52
39.24
38.97
38.69
22.31
HO
O
B
HO
O
O
OH
1d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2. Determination of BET area

Rouquerol and Llewellyn suggested three consistency criteria when using the BET method to determine the surface area of metal-organic frameworks.[3] We chose the area of the adsorption branch for BET area determination accordingly.

The first criterion states that the analysis should be limited to the range in which the term $n\left(1-\frac{p}{p_0}\right)$ increases continuously as a function of the relative pressure which can be well seen in (Fig. S1) depicting this function with the chosen pressure range of $7.7 * 10^{-4} \leq p/p_0 \leq 9.8 * 10^{-2}$.

The second criterion states that the BET constant resulting from the linear fit should be positive and have a minimum value of C = 10 which is also met as the resulting BET constant is C = 343.12.

According to the third consistency criterion, the relative pressure that corresponds to the calculated BET monolayer capacity applying equation $\left(\frac{p}{p_0}\right)_{n_m} = \frac{1}{\sqrt{C}+1}$ should be located in the chosen pressure range. Inserting the determined BET constant into this equation gives $\left(\frac{p}{p_0}\right)_{n_m} = 0.05122$ which is located in the abovementioned chosen pressure range and therefore all three consistency criteria are met.

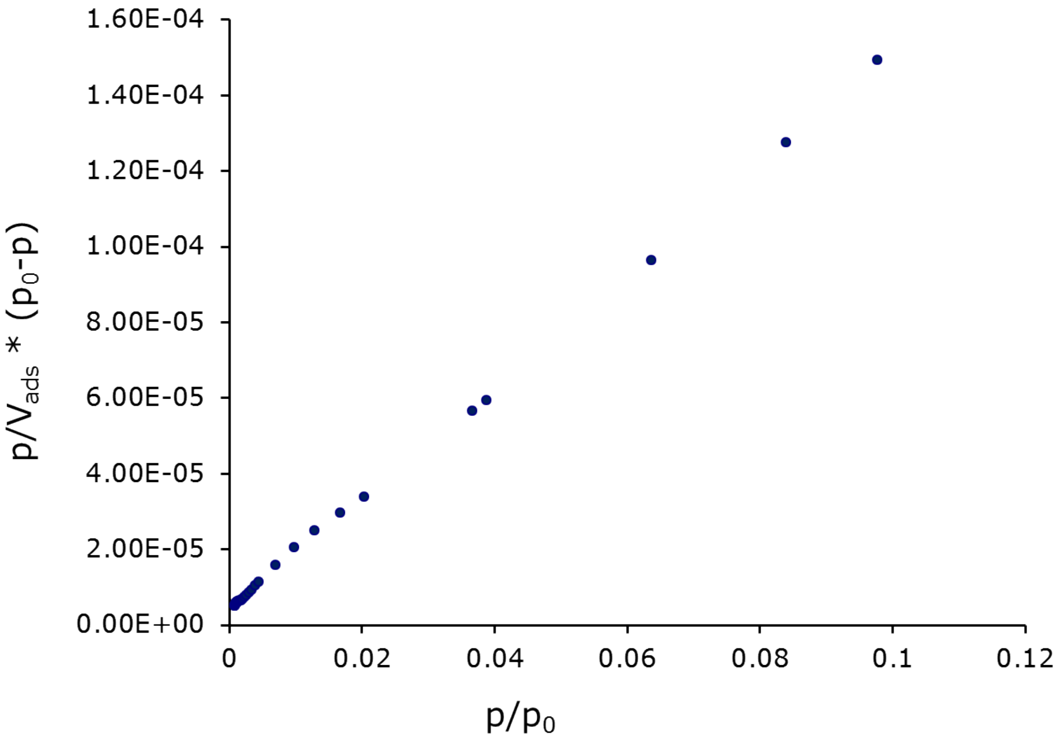


Fig. S1. BET plot of the p/p_0 range chosen for the determination of the BET surface area.

S3. Thermogravimetric analysis

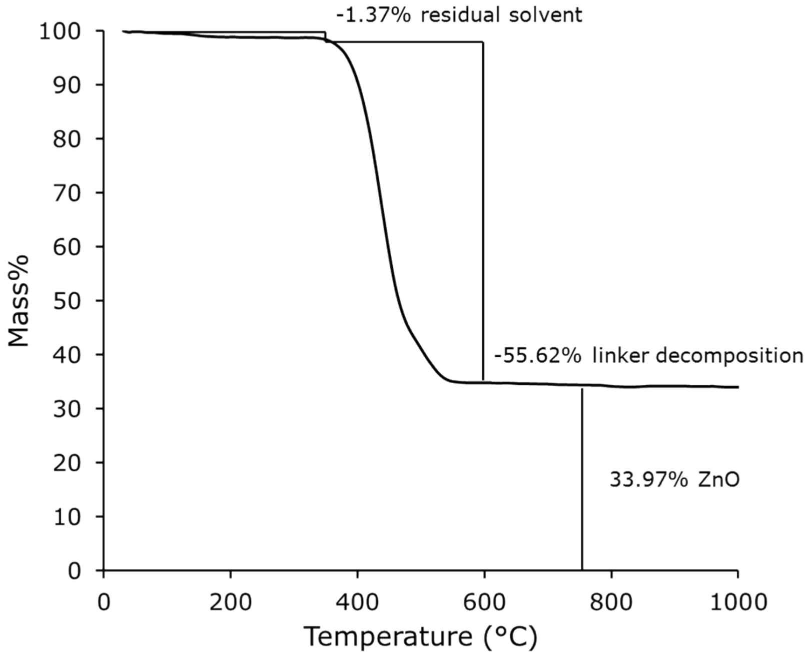


Fig. S2. Thermogravimetric analysis of **1.**

Thermogravimetric analysis of **1** was performed with synthetic air as carrier gas to afford complete oxidation of the residue to ZnO in order to gain information about the framework composition. Linker decomposition sets on at 368 °C according to DTA analysis. The residual mass of ZnO of 33.97% is in satisfactory accordance with the calculated value of 31.05%.

S4. Dye adsorption experiments

The solvent within the pores of the compounds was exchanged to ethanol. The crystals were then suspended in a 1mM solution of the respective dye in ethanol for 24 hours. After that, the crystals were briefly washed with fresh ethanol and investigated under an optic microscope.

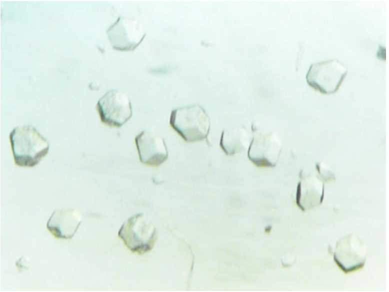


Fig. S3. Crystals of **1** in DEF.

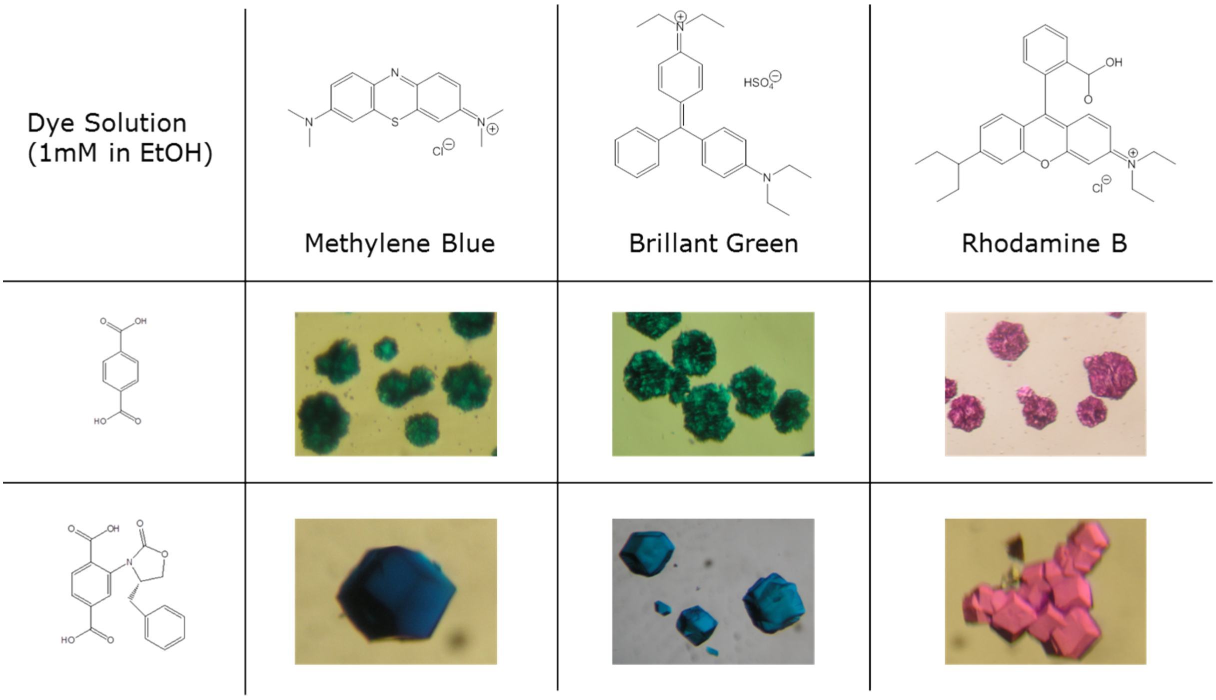


Fig. S4. Crystals of **1** (top) and **2** (bottom) coloured by organic dyes.

S5. CO_2 physisorption isotherms for DUT-6

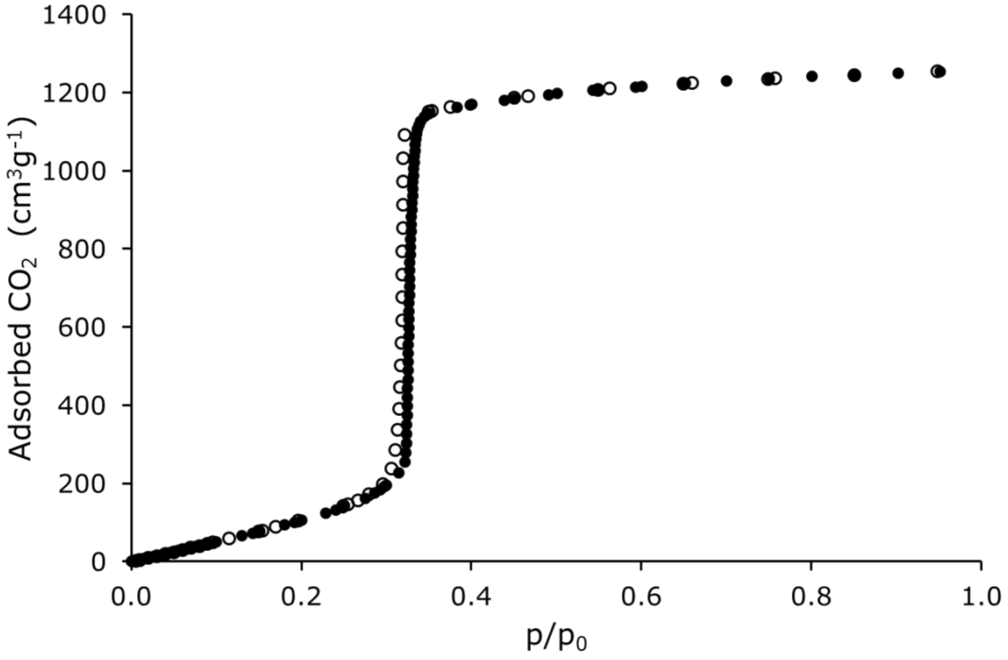


Fig. S5: CO_2 physisorption isotherm at 194 K of DUT-6; solid symbols represent adsorption, empty symbols represent desorption

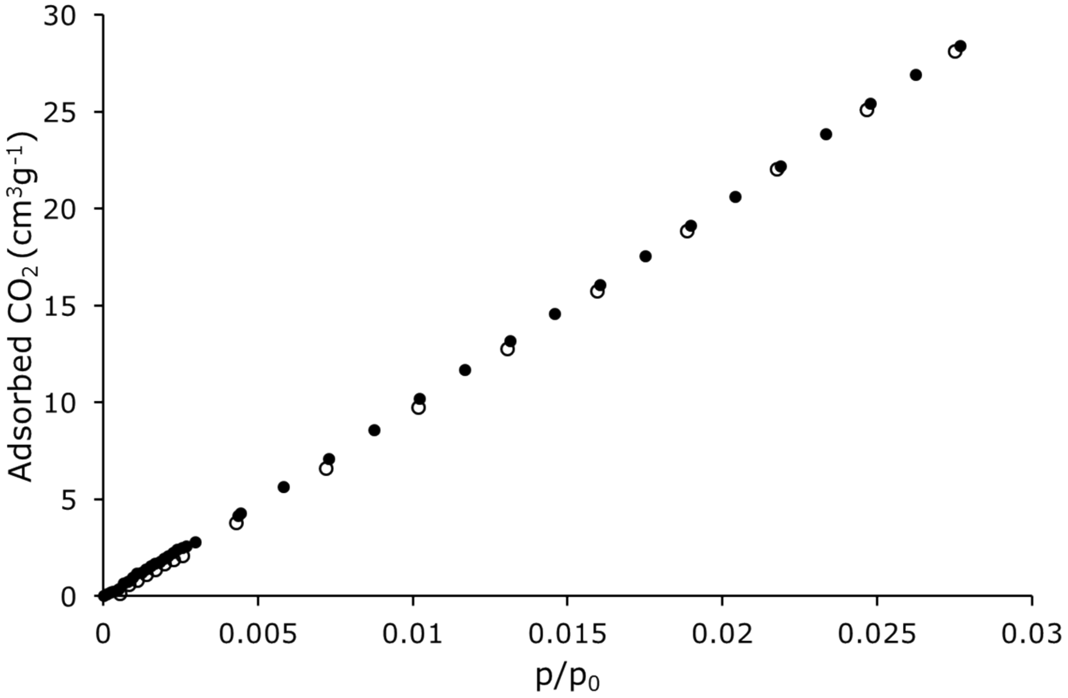


Fig. S6: CO_2 physisorption isotherm at 273 K of DUT-6 (solid symbols represent adsorption, empty symbols represent desorption).

S6. Photophysical properties of $Zn_4O(TPB)_{4/3}(BDC)$ and H_3TPB

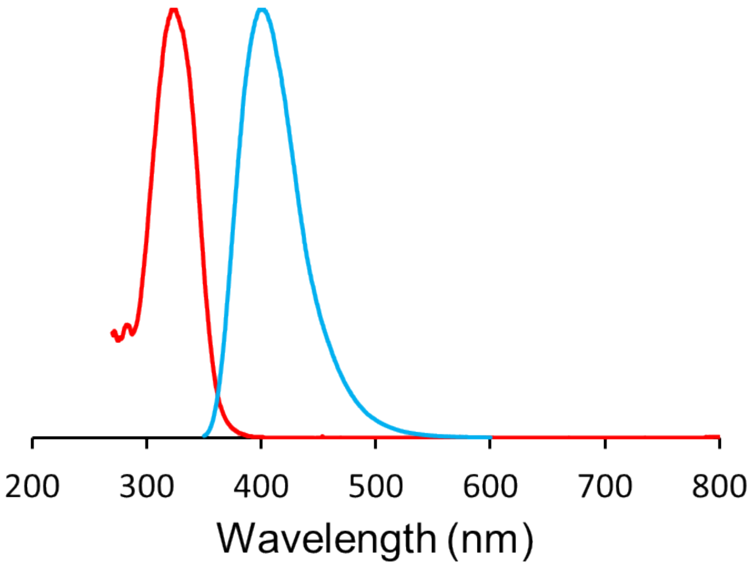


Fig. S7: Red: normalized absorption spectrum of H_3TPB in DMF (λ_{max} = 324 nm); blue: normalized emission spectrum of H_3TPB in DMF (λ_{ex} = 324 nm; λ_{max} = 402 nm).

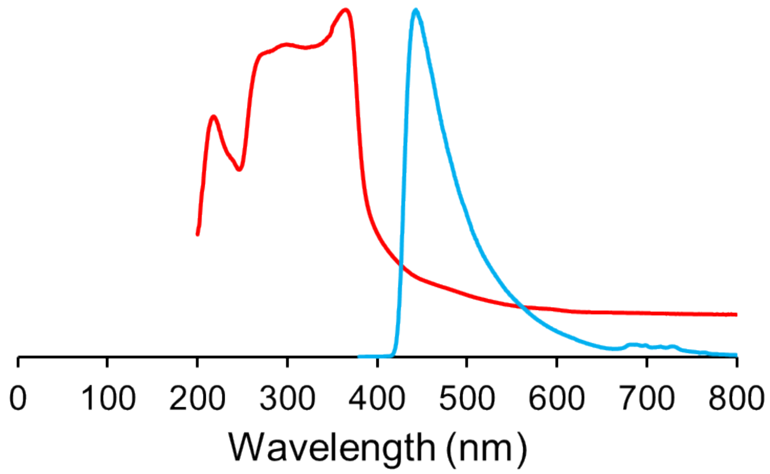


Fig. S8: Red: normalized solid state absorption spectrum of $Zn_4O(TPB)_{4/3}(BDC)$ (λ_{max} = 364 nm); Blue: normalized solid state emission spectrum of $Zn_4O(TPB)_{4/3}(BDC)$ (λ_{ex} = 364 nm, λ_{max} = 443 nm).

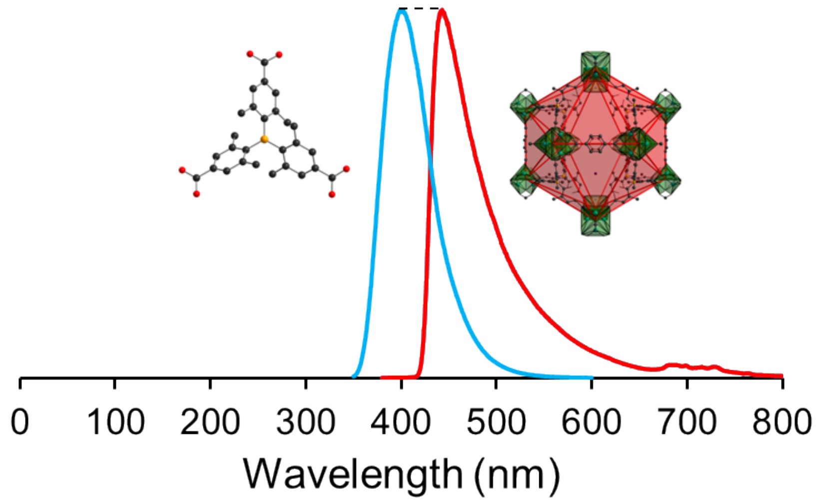


Fig. S9: Comparison of normalized emission spectra of H_3TPB (blue) and $Zn_4O(TPB)_{4/3}(BDC)$ (red) depicting bathochromic shift in emission wavelength.

References

1. M. Padmanaban, P. Müller, C. Lieder, K. Gedrich, R. Grünker, V. Bon, I. Senkovska, S. Baumgärtner, S. Opelt, S. Paasch, E. Brunner, F. Glorius, E. Klemm, and S. Kaskel, *Chem. Commun.*, 2011, **47**, 12089-12091.
2. J. Li, G. Zhang, D. Zhang, R. Zheng, Q. Shi, and D. Zhu, *J. Org. Chem.*, 2010, **75**, 5330-5333.

3. J. Rouquerol, P. Llewellyn, and F. Rouquerol, in *Characterization of Porous Solids VII Proceedings of the 7th International Symposium on the Characterization of Porous Solids (COPS-VII), Aix-en-Provence, France, 26-28 May 2005*, eds. J. R. P.L. Llewellyn F. Rodriquez-Reinoso and N. Seaton, Elsevier, 2007, vol. **160**, pp. 49–56.