

Supplementary Information

N-Containing Boronic Esters as Self-Complementary Building Blocks for the Assembly of 2D and 3D Molecular Networks

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Available Information:

1. Experimental details and spectroscopic characterization of compounds **1** and **2**
2. Additional data and figures
3. References

1. Experimental Details

Materials: 5-Isoquinolineboronic acid, 4-pyridineboronic acid and pentaerythritol were commercially available from SIGMA-ALDRICH. Absolute EtOH (purity > 99.2 %) was acquired from ALTA PUREZA and reagent-grade Toluene from MERCK. All starting materials and solvents and have been used as received without further purification. All preparative methods were carried out under air without using inert atmosphere.

Instrumentation: Elemental analyses have been carried out on Perkin Elmer Series II 2400 and Elementar Vario ELIII instruments. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer and measured in the range of 4000-400 cm^{-1} using the KBr pellet technique. Differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were accomplished with a TA SDT Q600 instrument. Approximately 3 mg of each solid sample were placed in alumina crucibles and analyzed in the temperature range of 30-600 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$, using a current of 50 mL/min of nitrogen as inert gas purge.

Preparation of compounds 1 and 2

{[5-iqba]₂[C₅H₈]}·EtOH (1)

A solution of 5-isoquinolineboronic acid (0.050 g, 0.288 mmol) and pentaerythritol (0.019 g, 0.139 mmol) in 8 mL of a 3:1 solvent mixture of toluene and absolute ethanol was heated to 120 $^{\circ}\text{C}$ for 50 h in a Pyrex pressure tube. After cooling to room temperature colorless crystals had formed, which were separated by filtration. Yield: 0.023 g, 36 %. M.p. 218-220 $^{\circ}\text{C}$ (dec.). IR (KBr): $\tilde{\nu}$ = 3433 (br, m, OH), 2956 (w), 2902 (w), 2829 (w), 1627 (m), 1565 (w), 1470 (w), 1422 (w), 1376 (w), 1316 (m), 1265 (m), 1238 (m), 1176 (s), 1114 (s), 1062 (s), 952 (w), 845 (m), 802 (w), 761 (w), 706 (m), 664 (w), 620 (w), 556 (w), 517 (w) cm^{-1} . Anal. calcd. (%) for $\text{C}_{23}\text{H}_{20}\text{B}_2\text{N}_2\text{O}_4\cdot\text{EtOH}$ (456.11 g mol^{-1}): C, 65.83; H, 5.75; N, 6.14. Found: C, 66.09; H, 5.52; N, 6.23.

Alternative synthetic methods for the preparation of 1

Reflux method

5-Isoquinolineboronic acid (0.100 g, 0.577 mmol) and pentaerythritol (0.039 g, 0.288 mmol) were located in a boiling flask equipped with a condenser and dissolved in 30 mL of

a 2:1 solvent mixture of toluene and absolute ethanol. Then the solution was heated to reflux for 36 h in the presence of a Dean Stark trap. After cooling to room temperature a precipitate had formed, which was separated by filtration. Yield: 0.056 g, 43 %.

Microwave-assisted synthesis

5-Isoquinolineboronic acid (0.050 g, 0.288 mmol) and pentaerythritol (0.019 g, 0.139 mmol) in 8 mL of a 3:1 solvent mixture of toluene and absolute ethanol were located in the vessel of a *CEM Discover* microwave oven, which after reaching the programmed reaction conditions (120 °C, 15 psi) was operated at 100 W for 20 Min. After cooling to room temperature colorless crystals had formed, which were separated by filtration. Yield: 0.016 g, 25 %.

Liquid-assisted grinding

5-Isoquinolineboronic acid (0.050 g, 0.288 mmol) and pentaerythritol (0.019 g, 0.139 mmol) were placed into stainless steel grinding jars (1.5 mL) and two drops of absolute ethanol were added before grinding the mixture mechanically in a Retsch MM400 mixer mill (60 min. at 25 Hz).

Thermal stability measurements

In order to examine the thermal stability of compound **1**, 50 mg of the compound were heated under normal air/pressure conditions for 2h at 140 °C in a convection oven.

DSC-TG measurements (Fig. S3a-b) and elemental analysis confirmed the absence of solvent in the sample. Anal. calcd. (%) for C₂₃H₂₀B₂N₂O₄ (410.04 g mol⁻¹): C, 67.37; H, 4.92; N, 6.83. Found: C, 67.49; H, 5.16; N, 7.06.

Examination of solvent reabsorption for solvent-free **1**

In order to test if solvent-free **1** is able to reabsorb the solvent (EtOH), 50 mg of **1** were heated under normal air/pressure conditions for 2h at 140 °C in a convection oven followed by immersion in absolute ethanol for 24 h under stirring. Thermogravimetric (found weight loss: 3.62 %) and elemental analysis indicated that 33% of the initial solvent content had

been reabsorbed (Fig. S3d). Anal. calcd. (%) for $C_{23}H_{20}B_2N_2O_4 \cdot 1/3EtOH$ (425.38 gmol^{-1}): C, 66.83; H, 5.21. Found: C, 66.34; H, 4.94.

{[4-pyba]₂[C₅H₈]}·4EtOH·H₂O·Toluene (2)

A solution of 4-pyridineboronic acid (0.050 g, 0.406 mmol) and pentaerythritol (0.028 g, 0.203 mmol) in 7 mL of a 1:2 solvent mixture of absolute ethanol and toluene was heated to 120 °C for 50 h in a Pyrex pressure tube. After cooling to room temperature colorless crystals had formed, which were separated by filtration. Yield: 0.029 g, 24 %. M.p. 264-265 °C (dec.). IR (KBr): $\tilde{\nu} = 3411$ (br, m, OH), 2961 (w), 2919 (w), 2850 (w), 1625 (m), 1472 (w), 1417 (m), 1313 (w), 1202 (s), 1050 (s), 953 (w), 773 (m), 732 (m), 683 (m), 642 (m), 600 (m) cm^{-1} . Anal. calcd. (%) for $C_{15}H_{16}B_2N_2O_4 \cdot 4EtOH \cdot H_2O \cdot Toluene$ (604.35 gmol^{-1}): C, 59.62; H, 8.34; N, 4.64. Found: C, 59.97; H, 8.68; N, 4.73.

X-ray Diffraction Analysis: X-ray powder diffraction (XRPD) analyses were carried out in the transmission mode on a BRUKER D8-ADVANCE diffractometer equipped with a LynxEye detector ($\lambda_{Cu-K\alpha 1} = 1.5406 \text{ \AA}$, monochromator: germanium). The equipment was operated at 40 kV and 40 mA and data were collected at room temperature in the range of $2\theta = 5\text{-}50^\circ$. X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073 \text{ \AA}$, monochromator: graphite). Frames were collected at $T = 100 \text{ K}$ via ω/ϕ -rotation at 10 s per frame (Bruker-SMART).^{1a} The measured intensities were reduced to F^2 and corrected for absorption with SADABS (Bruker-SMART).^{1b} Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the Bruker-SHELXTL-NT program package.^{1c-1d} Non hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. Simulated PXRD patterns were calculated with MERCURY.² Figures were created with DIAMOND.³

The crystal structure of compound **1** contains EtOH solvent molecules, which are disordered over two sites (occ. 0.50). DFIX, SIMU, DELU and ISOR instructions have been used during the refinement in order to model the EtOH geometry and thermal motion. In the case of the solvent-free sample the quality of the single crystals was diminished when compared to the ethanol solvate **1**, giving R_{int} values above 0.1. Although relatively

large crystals could be grown for compound **2**, they diffracted only weakly. This can be attributed to the presence of large amounts of disordered solvent (64 % of the total unit cell volume) in the crystal lattice. The electron density was too diffuse to be meaningfully modeled and its scattering contributions were removed using the SQUEEZE routine in PLATON, which improved the R values significantly.⁴ The low resolution of the data affects the reliability of the bond lengths and angles, and the refinement of the anisotropic thermal parameters.

2. Additional figures and data

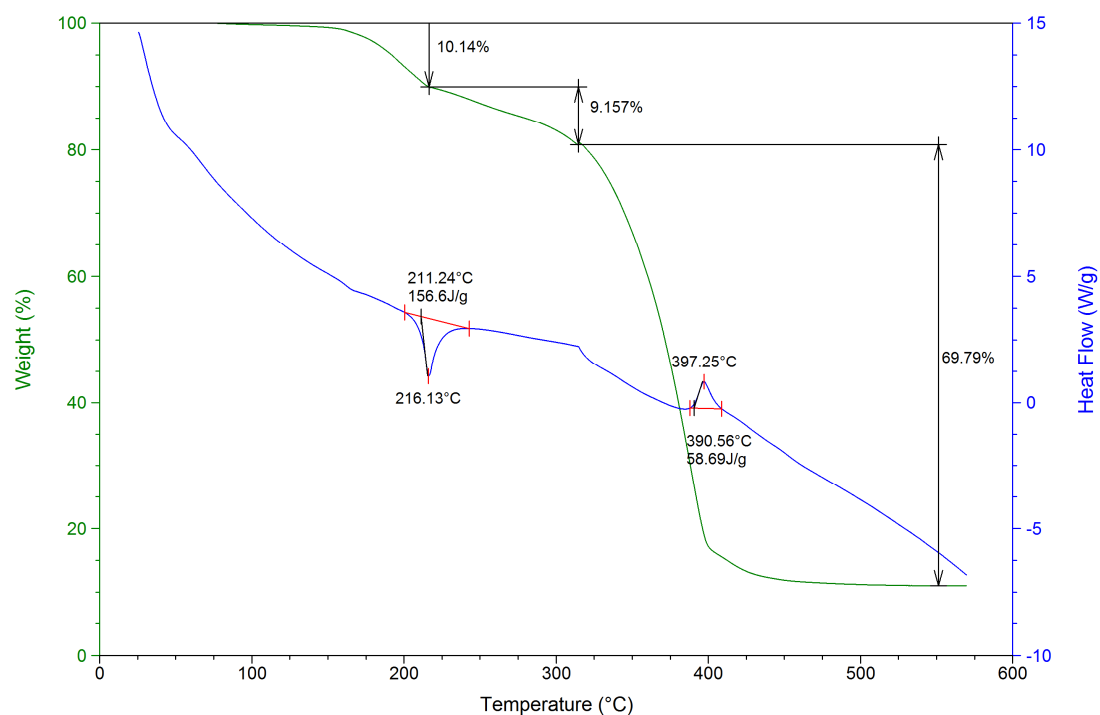


Figure S1. TG-DSC curve of compound $\{[5\text{-iqba}]_2[\text{C}_5\text{H}_8]\} \cdot \text{EtOH}$ (1)

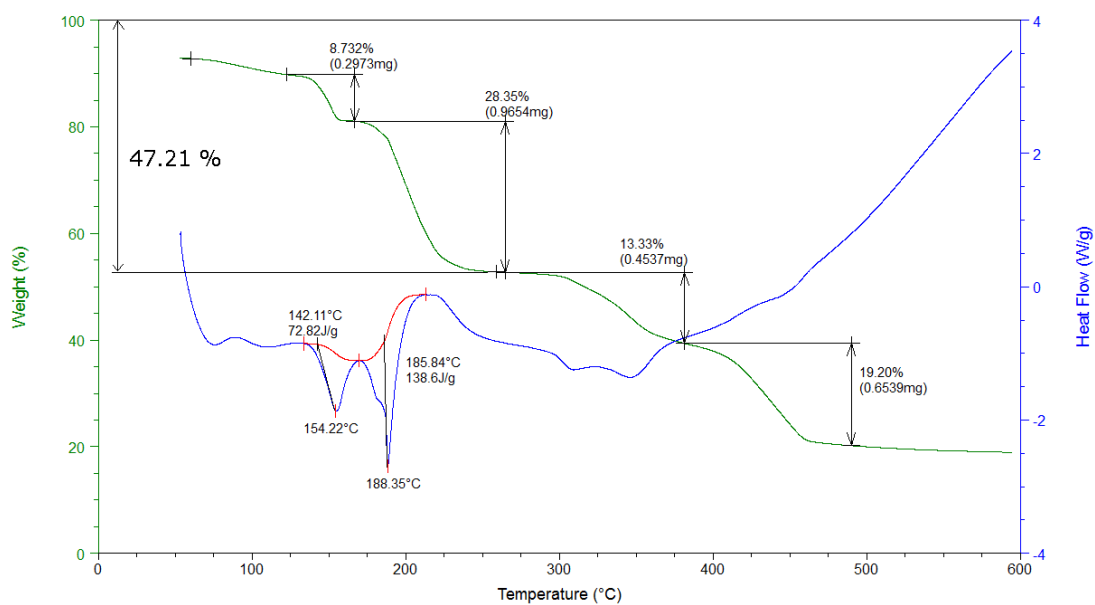
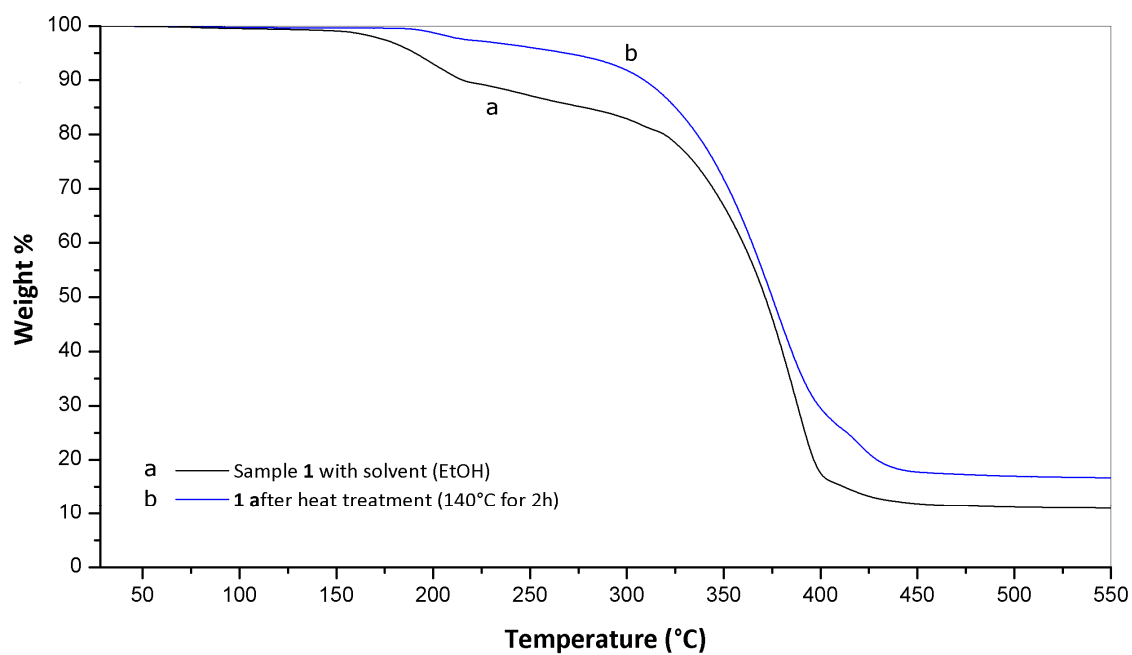
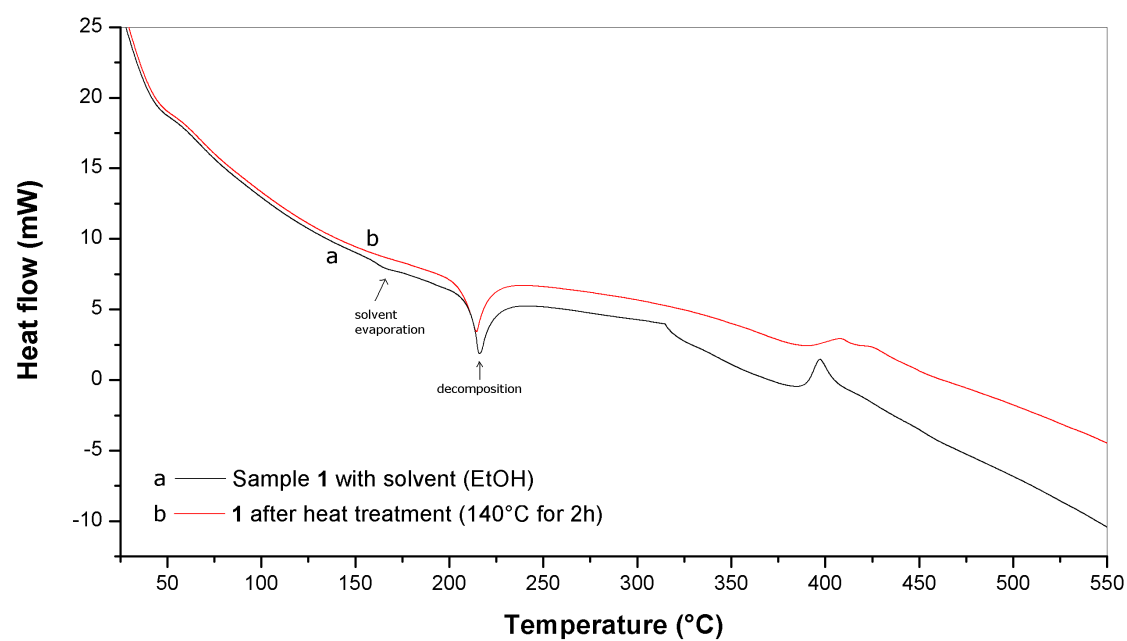


Figure S2. TG-DSC curve of compound 2 (prepared by the reflux method). Calculated weight loss for the evaporation of the solvent molecules from $\{[4\text{-pyba}]_2[\text{C}_5\text{H}_8]\} \cdot 4\text{EtOH} \cdot \text{H}_2\text{O} \cdot \text{Toluene}$: 48.7% (exp.: 47.21%). Note: The initial weight loss of the sample can be attributed to solvent evaporation during the calibration process that precedes the measurement.

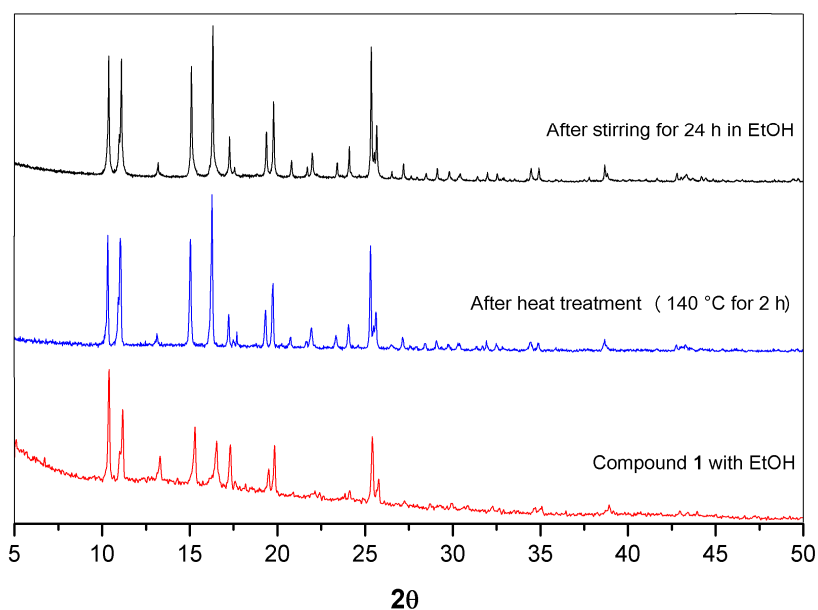
a)



b)



c)



d)

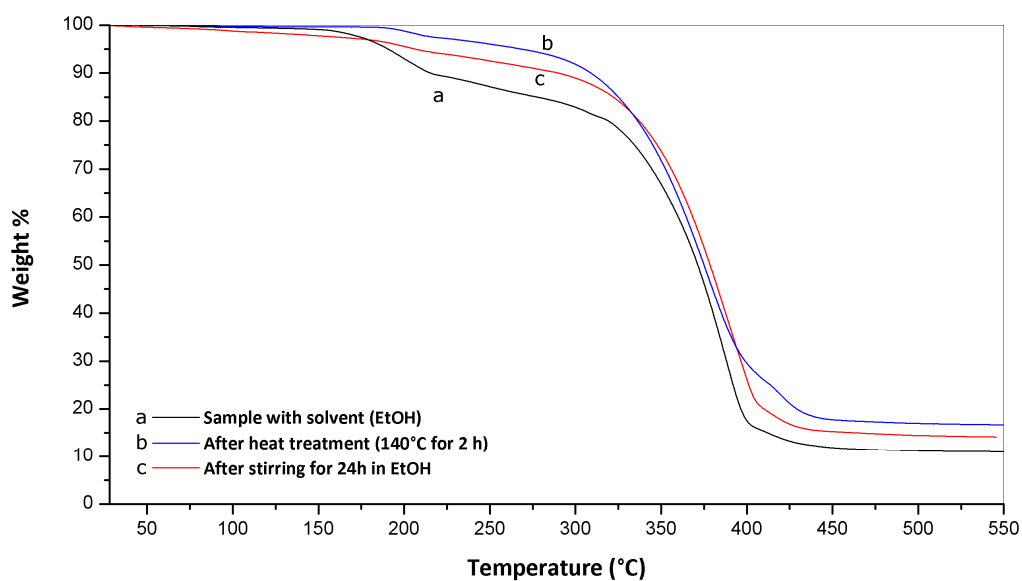
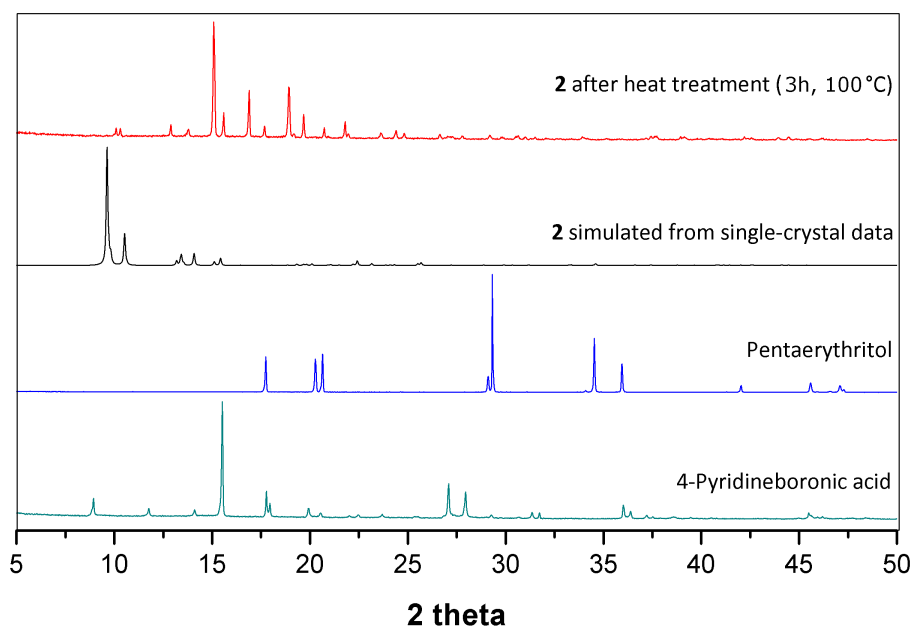


Figure S3. Thermal treatment of compound **1** at 140 °C for 2h under normal air/pressure conditions in a convection oven provides a solvent-free crystalline sample without decomposition of the underlying molecular network as indicated by the TG-DSC curves (a and b), and a comparison of the PXR D diffractograms (c). After immersing crystals of the solvent-free sample in EtOH for 24h, the sample had reabsorbed EtOH only partially (33 %) (c and d).

a)



b)

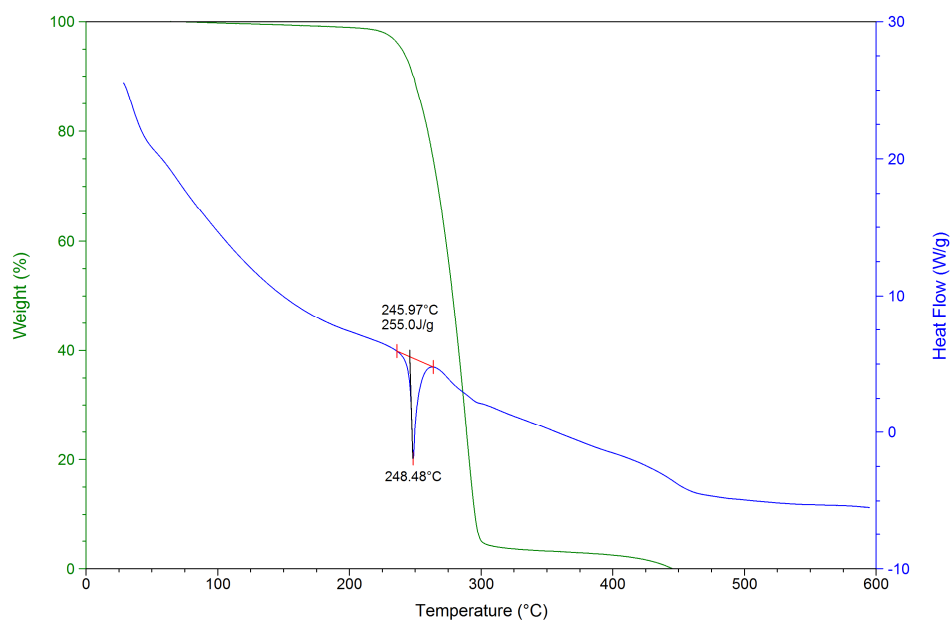
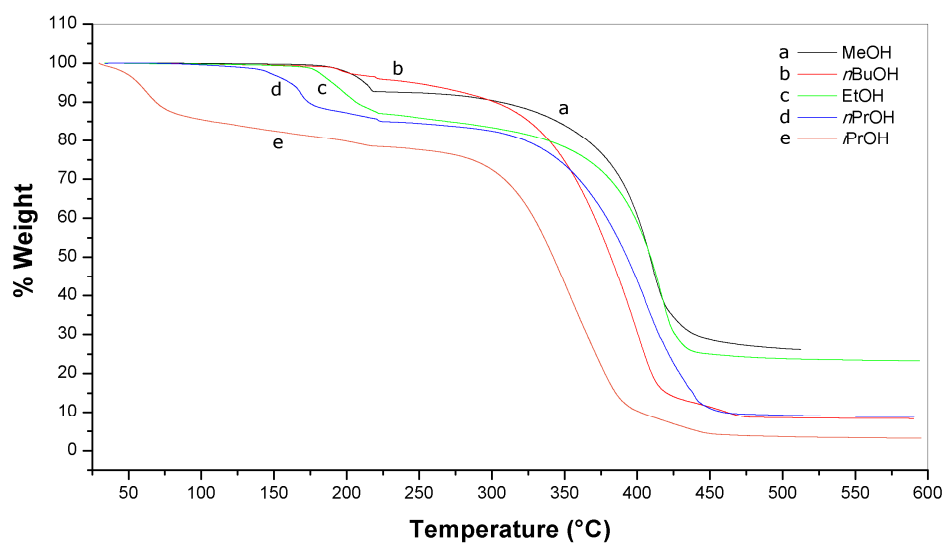
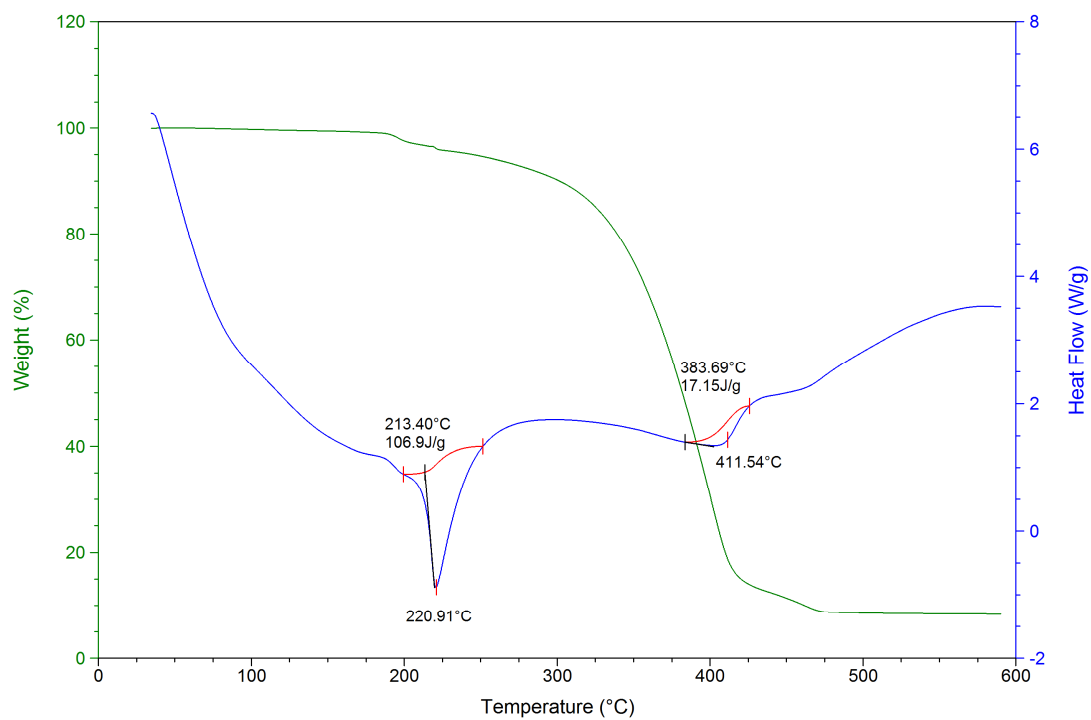


Figure S4. The PXRD patterns (a) and TG curves (b) of compound **2** and a sample treated for 3 h at 100 °C under normal air/pressure conditions indicate that a phase transformation occurs upon elimination of the solvent molecules from the crystal lattice.

a)



b)



c)

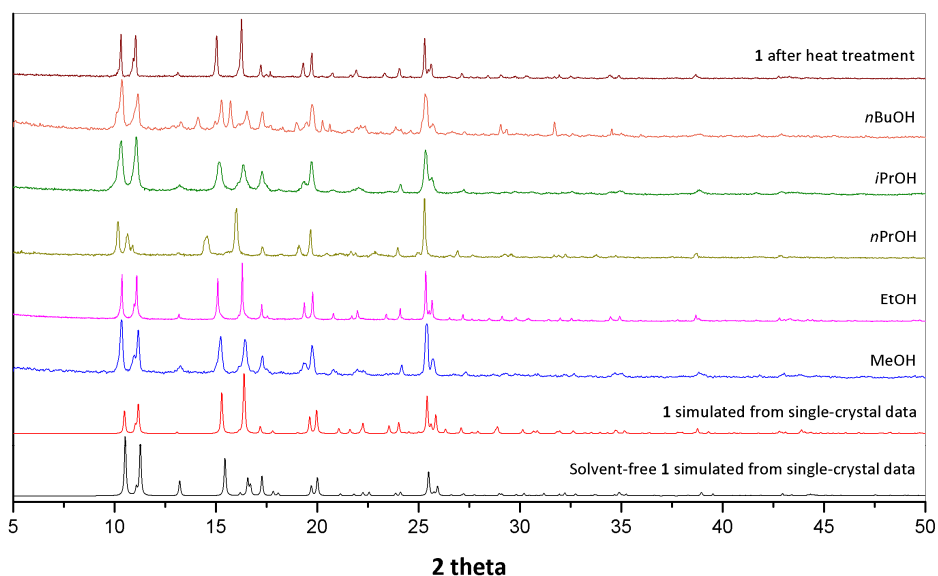


Figure S5. a) TG curves for the resulting molecular network of compound **1** when using different aliphatic alcohols (MeOH, EtOH, *n*PrOH, *i*PrOH and *n*BuOH) for the preparation. The results show that solvates of varying thermal stability are formed for the C₁-C₃ members of the series, but not for *n*BuOH. b) A comparison of the TG-DSC curves for the samples prepared from EtOH (Fig. S1) and *n*BuOH (Figure S5b) shows that the weight loss initiating at approximately 180 °C corresponds to a decomposition process. c) Comparison of the XRPD pattern of {[5-*iqba*]₂[C₅H₈]}·EtOH (**1**) with samples prepared in the presence of other aliphatic alcohols (MeOH, *n*PrOH, *i*PrOH and *n*BuOH). For comparison, the XRPD patterns of the solvent-free form of **1** obtained by thermal treatment and the simulated patterns from the single-crystal diffraction analyses of {[5-*iqba*]₂[C₅H₈]}·EtOH and the corresponding solvent-free form are included.

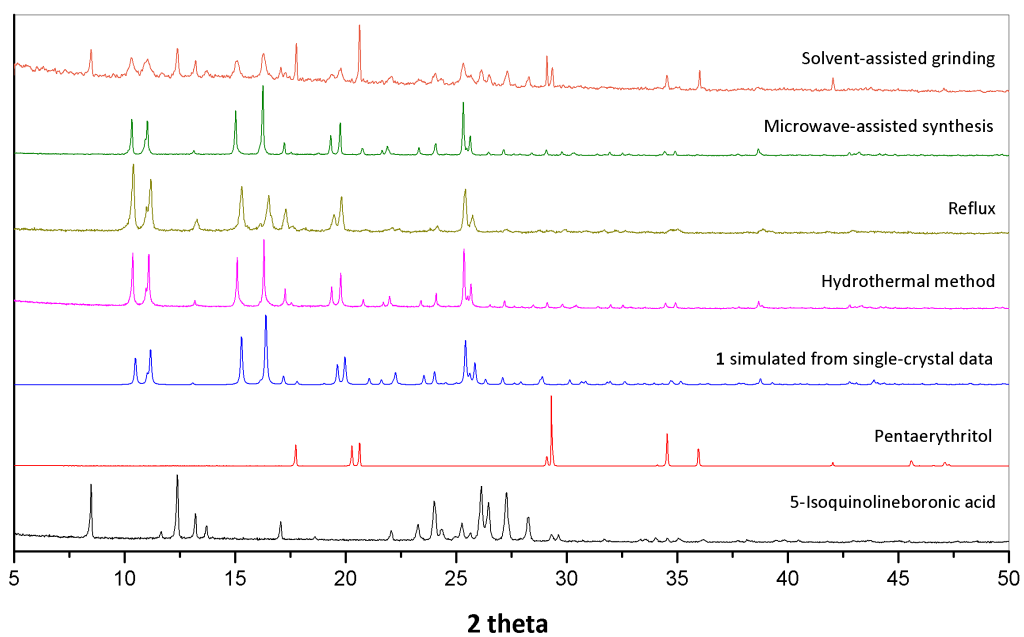


Figure S6. PXRD patterns for samples of compound **1**, which have been prepared by different synthetic methods. For comparison, the PXRD patterns of the starting materials and the simulated pattern from the single-crystal diffraction analysis are included.

3. References

- 1 (a) Bruker Analytical X-ray Systems. *SMART: Bruker Molecular Analysis Research Tool, Versions 5.057 and 5.618*, Bruker AXS Inc, Madison, Wisconsin, USA, 1997 and 2000. (b) Bruker Analytical X-ray Systems. *SAINTE + NT, Versions 6.01 and 6.04*, Bruker AXS Inc, Madison, Wisconsin, USA, 1999 and 2001. (c) G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122. (d) Bruker Analytical X-ray Systems. *SHELXTL-NT Versions 5.10 and 6.10*, Bruker AXS Inc, Madison, Wisconsin, USA, 1999 and 2000.
- 2 Cambridge Crystallographic Data Center, *Mercury, Version 2.2*, Cambridge, United Kingdom, 2008.
- 3 Brandenburg, K. *Diamond, version 3.1c*, Crystal Impact GbR, Bonn, Germany, 1997.
- 4 (a) A. L. Spek, *Acta Cryst. Sect. A*, 1990, **46**, C-34; (b) A. L. Spek, *PLATON – A multipurpose crystallographic tool*, Utrecht University, Utrecht, the Netherlands, 2003.