Supplementary Material (ESI) for Energy & Environmental Science


Supporting Information for:

# Hydrogen Storage in Water-Stable Metal-Organic Frameworks Incorporating 1,3- and 1,4-Benzenedipyrazolate

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*Energy & Environmental Science*

***Table S1***. Crystallographic Data for Co(1,3-BDP)·DEF·0.5$H_2O$.

| Identification | Co(BDP)·DEF·0.5$H_2O$ |
|---|---|
| Formula | $CoC_{17}H_{20}N_5O_{1.5}$ |
| FW | 377.31 |
| $T$, K | 150(2) |
| Wavelength, Å | 0.77490 |
| Crystal system, space group | Tetragonal, I4(1)/amd |
| Z | 16 |
| $a$, Å | 22.847(15) |
| $c$, Å | 12.458(16) |
| $V$, Å$^3$ | 6503(10) |
| $d_{calc}$, g/cm$^3$ | 1.542 |
| Adsorption coefficient, mm$^{-1}$ | 1.074 |
| $F$(000) | 2674 |
| Crystal size, mm$^3$ | 0.015 × 0.015 × 0.04 |
| Theta range for data collection | 2.75-19.14° |
| Index range | $-19 \le h \le 19$, $-19 \le k \le 19$, $-10 \le l \le 10$ |
| Reflections collected | 10681 |
| Independent reflections | 559 [$R$(int) = 0.1042] |
| Data/restrains/parameters | 559 / 6 / 81 |
| GOF on $F^2$ | 1.341 |
| Largest diff. peak and hole, e·Å$^{-3}$ | 0.346 and -0.271 |
| $R_1$ ($wR_2$)[a], [I>2sigma(I)] | 0.0635 (0.1642) |
| $R_1$ ($wR_2$)[a], all data | 0.0794 (0.1748) |

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

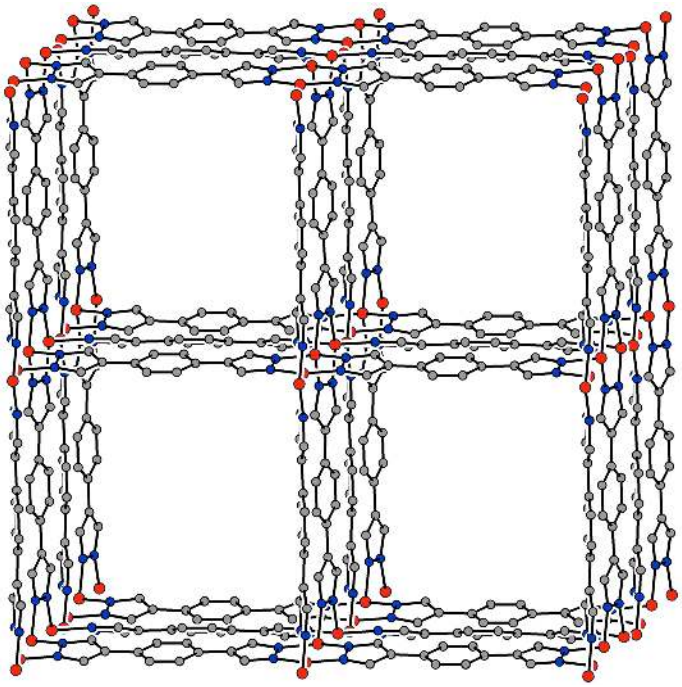

**Fig. S1** A portion of the crystal structure of **1**, which is isostructural to Co(1,4-BDP).[1] Red, blue, and grey spheres represent Zn, N, and C atoms, respectively.

[1]H. J. Choi, M. Dinca, J. R. Long, *J. Am. Chem. Soc.* 2008, **130**, 7848.

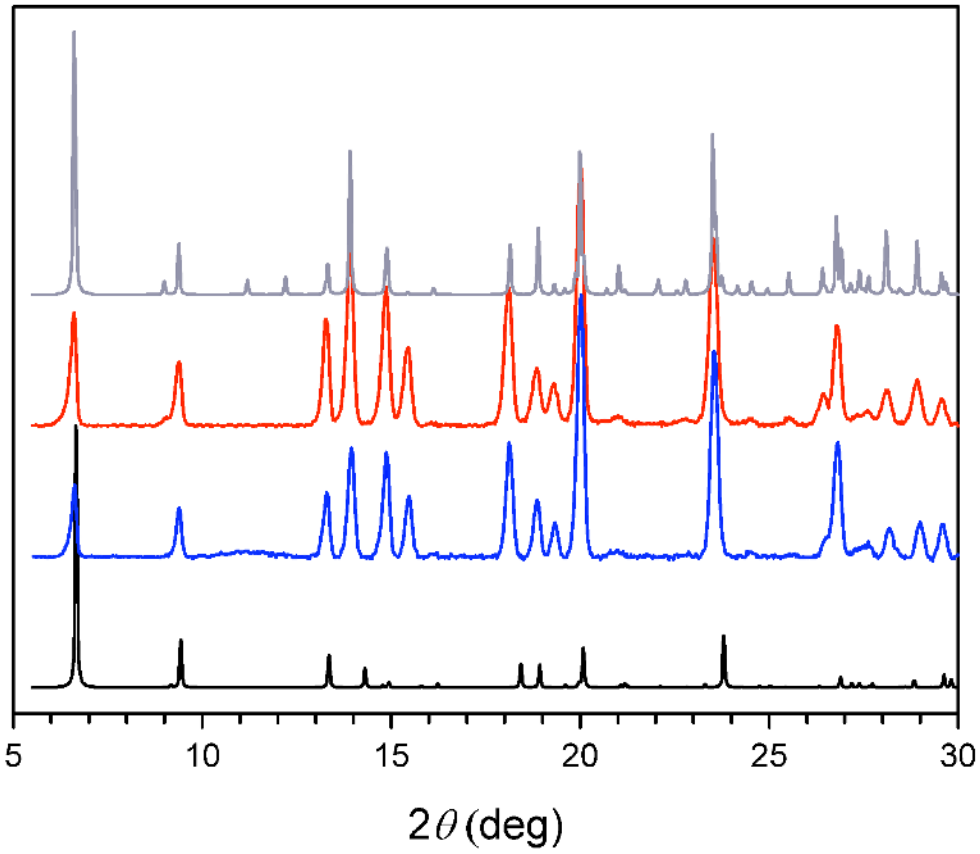


**Fig. S2** Powder X-ray diffraction patterns for the crystallographic simulation for Co(1,4-BDP)·2DEF·$H_2O$ (black) and its pulverized crystals (blue), and Zn(1,4-BDP)·2DEF·$H_2O$ (**1**) (red) and its simulation pattern based on the unit cell refinement (grey).

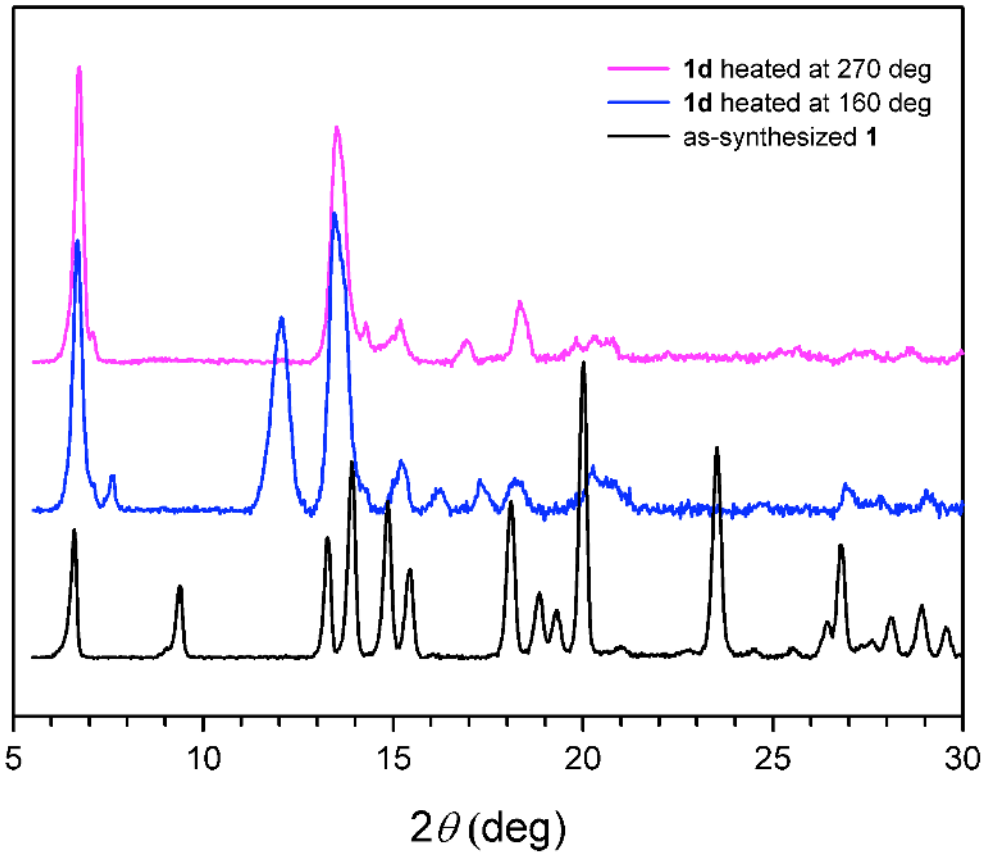


**Fig. S3** Powder X-ray diffraction patterns for the as-synthesized solid **1** (black), and its desolvated form **1d** heated at 160 °C (blue) and 270 °C (pink).

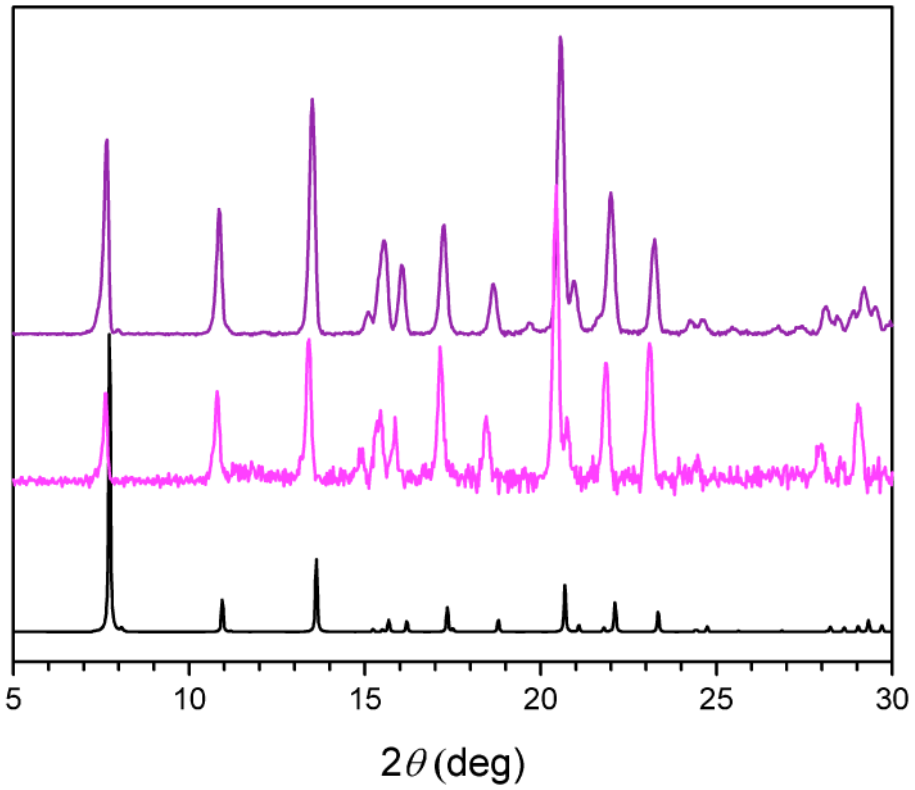


**Fig. S4** Powder X-ray diffraction patterns for the crystallographic simulation for Co(1,3-BDP)·DEF·0.5$H_2O$ (**2**) (black), pulverized crystals of **2** (pink) and Zn(1,3-BDP)·0.7DMF·0.5$H_2O$ (**3**) (dark pink).

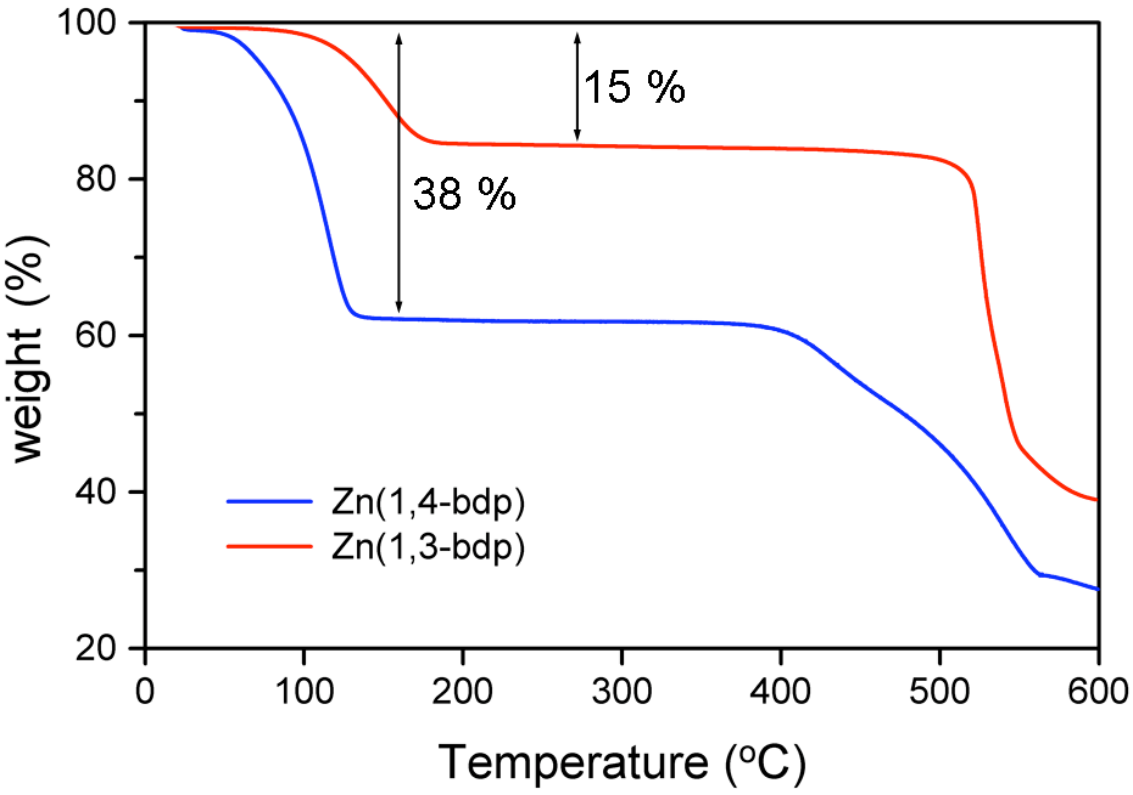


**Fig. S5** Thermogravimetric analysis data for Zn(1,4-BDP)·2DEF·$H_2O$ (**1**) (blue) and Zn(1,3-BDP)·0.7DMF·0.5$H_2O$ (**3**) (red) measured using a ramp rate of 1.0 °C/min.

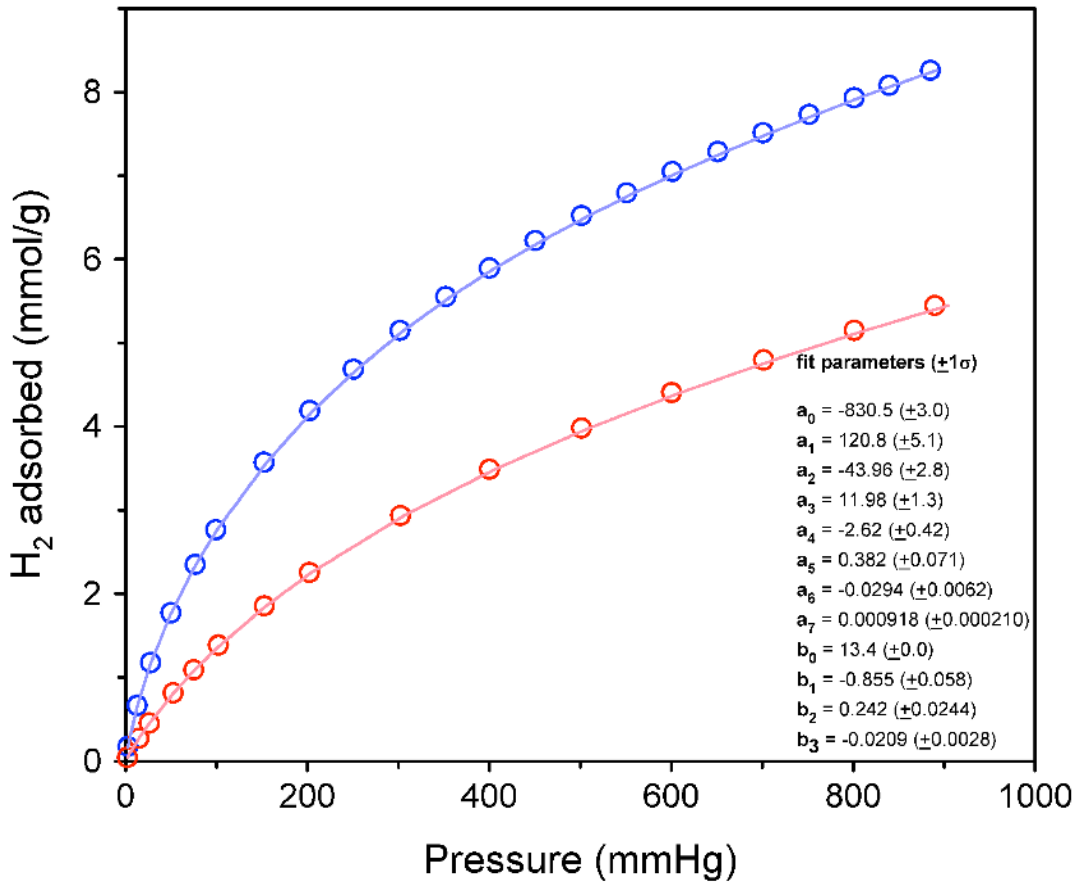


**Fig. S6** $H_2$ adsorption isotherms for **1d** at 77 K (blue) and 87 K (red), and the respective virial fits (solid lines).

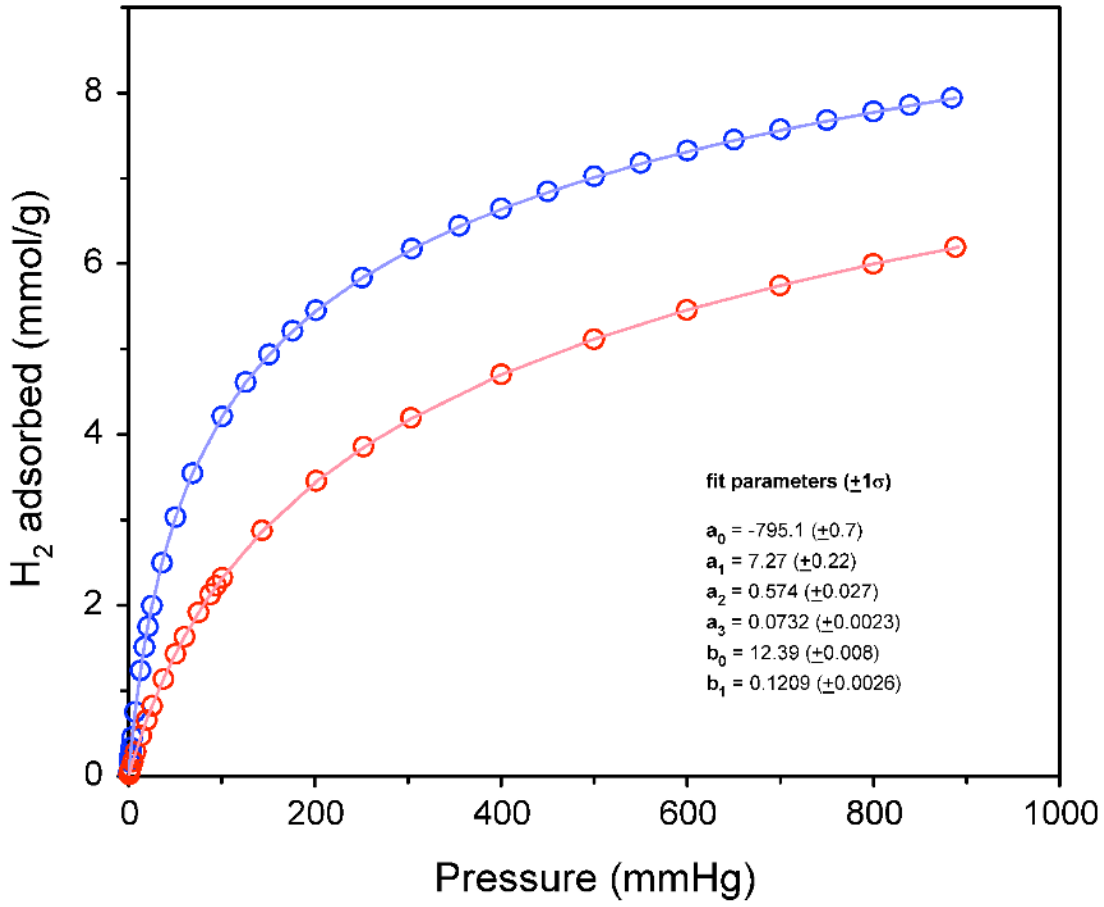


**Fig. S7** $H_2$ adsorption isotherms for **3d** at 77 K (blue) and 87 K (red), and the respective virial fits (solid lines).

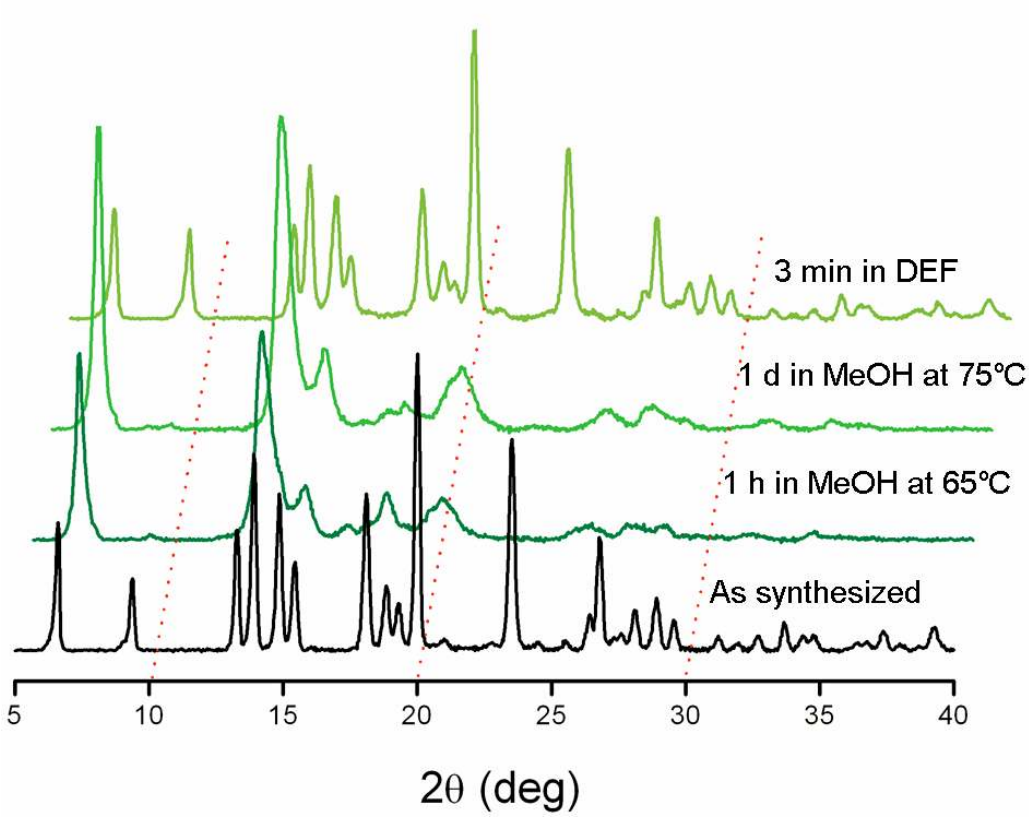


**Fig. S8** Powder X-ray diffraction patterns for **3** treated under various conditions, showing its high thermal stability as well as chemical stability.

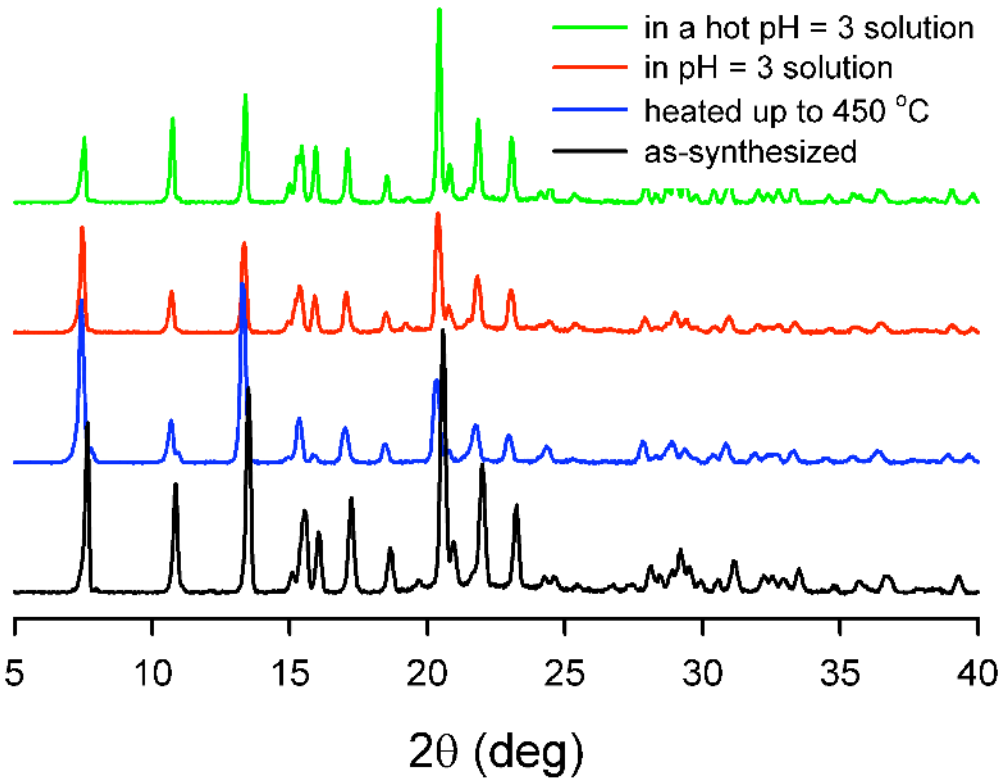


**Fig. S9** Powder X-ray diffraction patterns for **3** treated under various conditions, showing its high thermal stability as well as chemical stability.

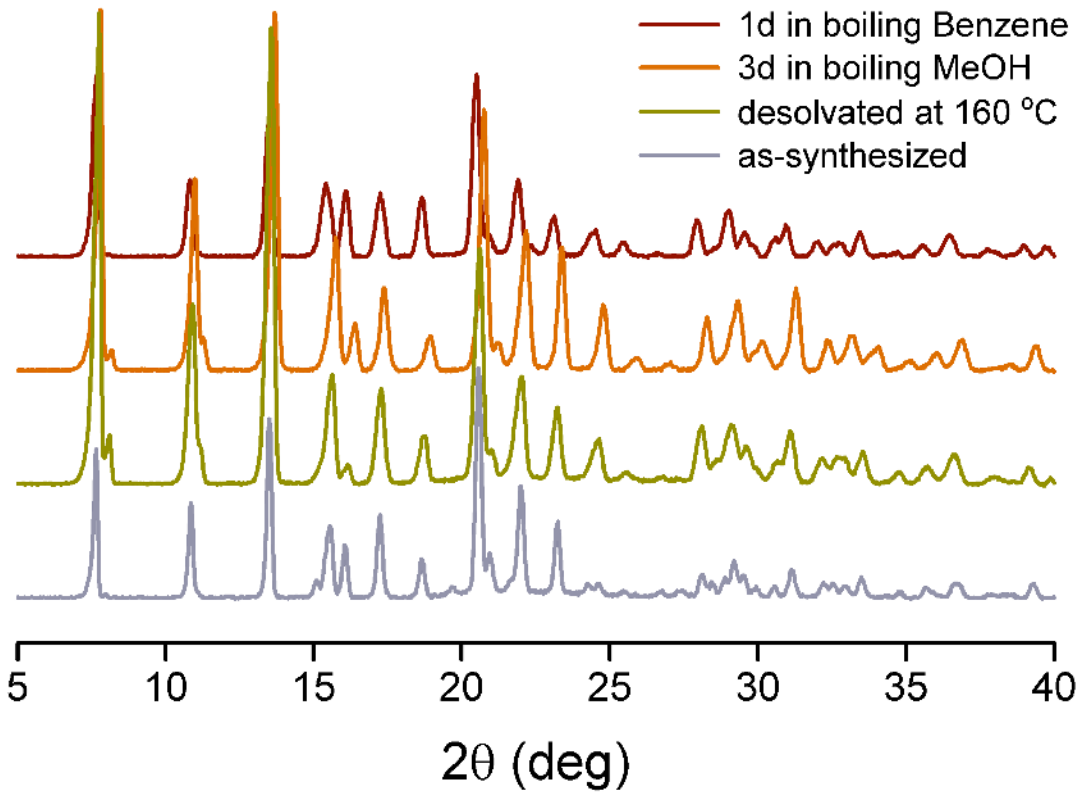


**Fig. S10** Powder X-ray diffraction patterns for **3** treated under various conditions (1d = 1 day, 3d = 3 days), showing its high thermal stability as well as chemical stability.