# A new class of thermo- and solvatochromic metal-organic frameworks based on 4-(pyridin-4-yl)benzoic acid

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## Supplementary material

**Table S1** Crystallographic data for compounds **1** – **3**.

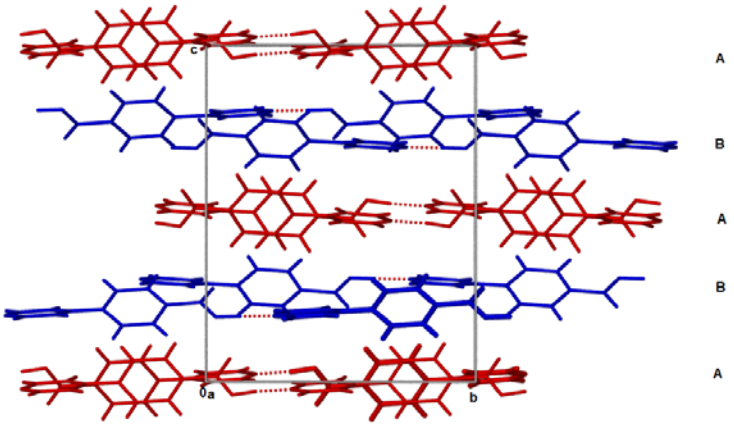
| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{12}$ $H_9$ N $O_2$ | $[Co_4(C_{12}H_8NO_2)_8]_n$ . $(C_3H_7NO)_{3.25}$ .$(C_2H_6O)_{0.25}$ . $(H_2O)_{4.25}$ | $[Ni_4(C_{12}H_8NO_2)_8]_n$ . $(C_3H_7NO)_{3.6}$ .$(C_2H_6O)$ . $(H_2O)_{1.25}$ |
| $M_r$ | 199.20 | 2146.92 | 2152.13 |
| Temperature (K) | 173 | 173 | 173 |
| Crystal size ($mm^3$) | 0.13 x 0.08 x 0.03 | 0.26 x 0.26 x 0.25 | 0.30 x 0.26 x 0.25 |
| Crystal system | Orthorhombic | Tetragonal | Tetragonal |
| Space group (No.) | $P2_12_12_1$ | $I4$ | $I4$ |
| *a* (Å) | 10.7482(12) | 31.9819(12) | 31.8199(19) |
| *b* (Å) | 11.7997(13) | 31.9819(12) | 31.8199(19) |
| *c* (Å) | 14.7279(15) | 25.3323(11) | 25.1149(15) |
| V ($Å^3$) | 1867.9(3) | 25910.9(18) | 25429(3) |
| *Z* | 8 | 8 | 8 |
| ρ(calcd) ($Mgm^{-3}$) | 1.417 | 1.101 | 1.124 |
| μ(Mo-$K_\alpha$) ($mm^{-1}$) | 0.098 | 0.565 | 0.646 |
| Theta range for data collection (deg) | 2.21-27.17 | 1.64 – 27.34 | 1.64 – 28.29 |
| Reflections collected | 6844 | 47724 | 90225 |
| No. unique data [R(int)] | 4121 [0.0344] | 21374 [0.0455] | 31528 [0.0556] |
| No. data with $I > 2\sigma(I)$ | 2564 | 11366 | 17448 |
| final *R* ( $I > 2\sigma(I)$) | 0.0547 | 0.0764 | 0.1397 |
| final *wR2* (all data) | 0.1177 | 0.2718 | 0.4313 |
| Max, min e density (e $A^{-3}$) | 0.197, -0.204 | 0.756, -1.013 | 2.067, -1.942 |

**Table S2** Hydrogen bonding interactions in **1**.

**Compound 1**

| D-H...A (°) | **symmetry operator** | | **D-H (Å)** | **D...A (Å)** |
|---|---|---|---|---|
| O(15A)--H(15A)...N(1A) | [ x, y-1, z] | 1.07(4) | 2.619(3) | 168(4) |
| O(15B)--H(15B)...N(1B) | [ x, y+1, z] | 1.07(4) | 2.611(3) | 173(3) |
| C(2A) --H(2A)...O(14A) | [ 1/2+x,3/2-y,-z] | 0.95 | 3.189(4) | 135 |
| C(9A) --H(9A)...O(14B) | [ 1-x,-1/2+y,1/2-z] | 0.95 | 3.510(4) | 165 |
| C(12B)--H(12B)...O(14A) | [1/2-x,1-y,1/2+z] | 0.95 | 3.192(4) | 148 |

Fig S1: Packing diagram for **1**



## Thermal Analysis

Fig S2: TGA and DSC for **1**

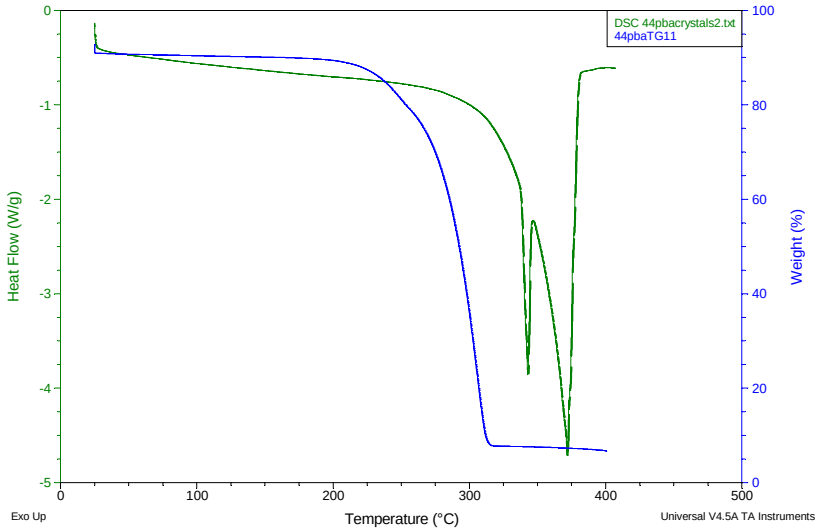



Fig S3: TGA and DSC for **2**

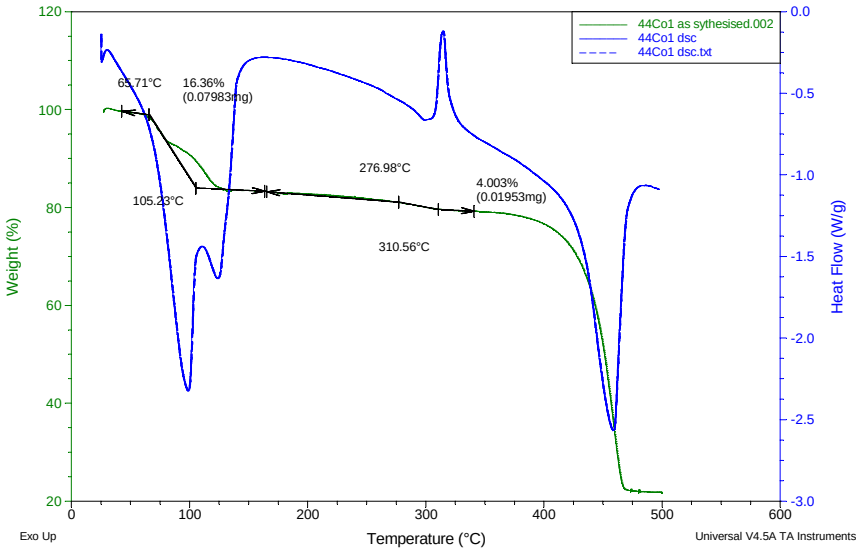



Fig S4: TGA for **2d-w** (**2** which has been dried, then exposed to water)

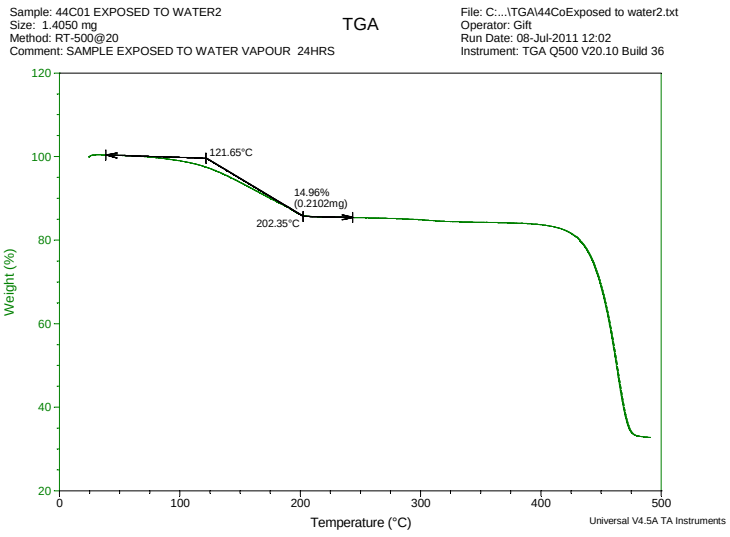


Fig S5: TGA and DSC for **3**

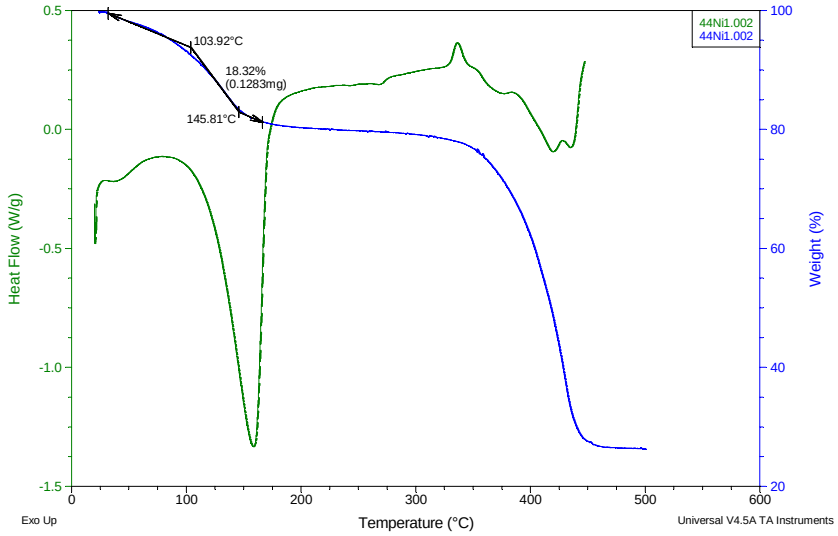
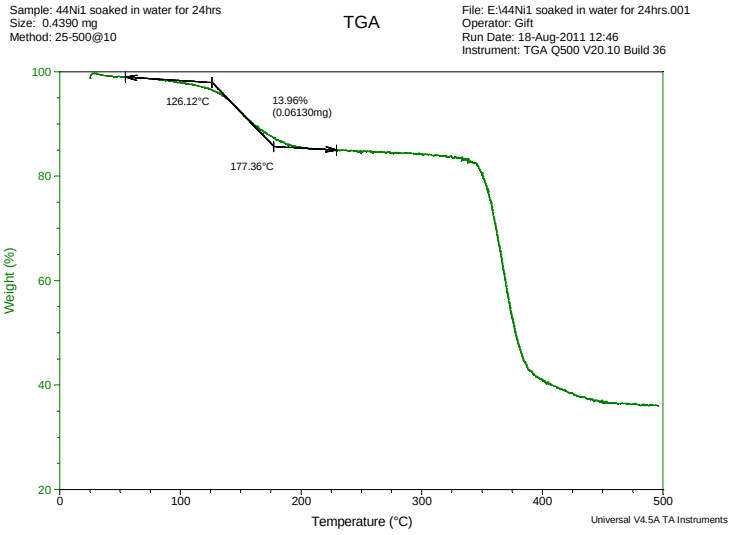



Fig S6: TGA for **3d-w** (**3** which has been dried, then exposed to water)



**XRPD**

Fig S7:

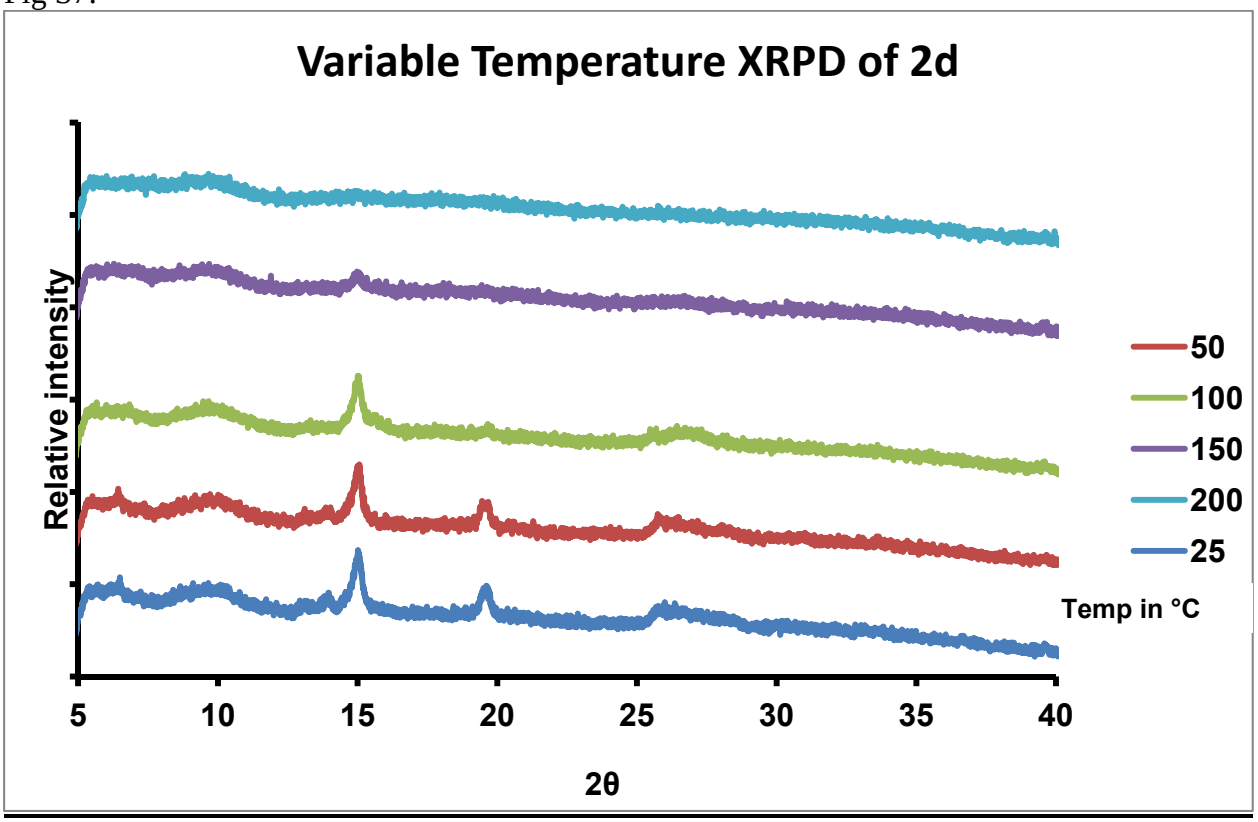
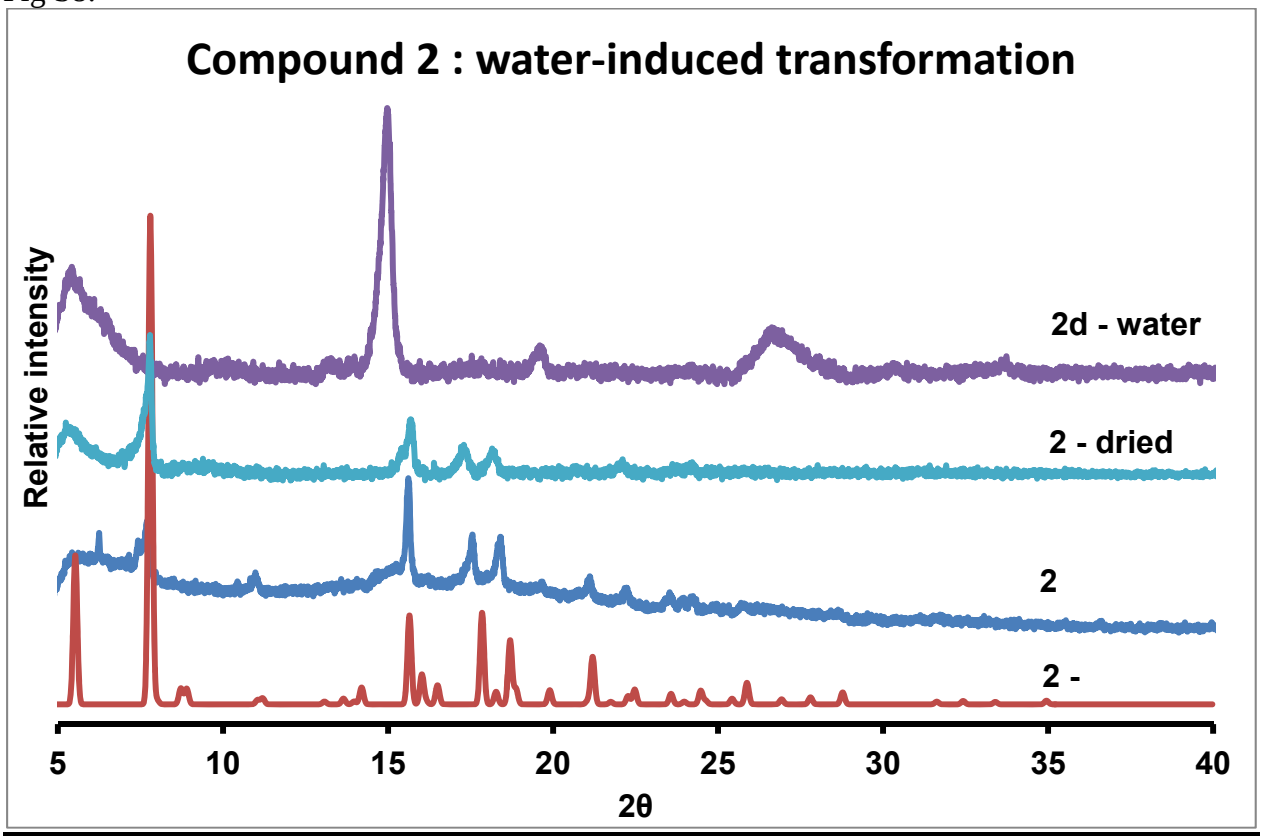



Fig S8:



## Kinetics of water sorption

Fig S9: **Rate plots for water adsorption by compound 2d**

**a: 20, b: 25, c: 26, d: 27, e: 30 °C**

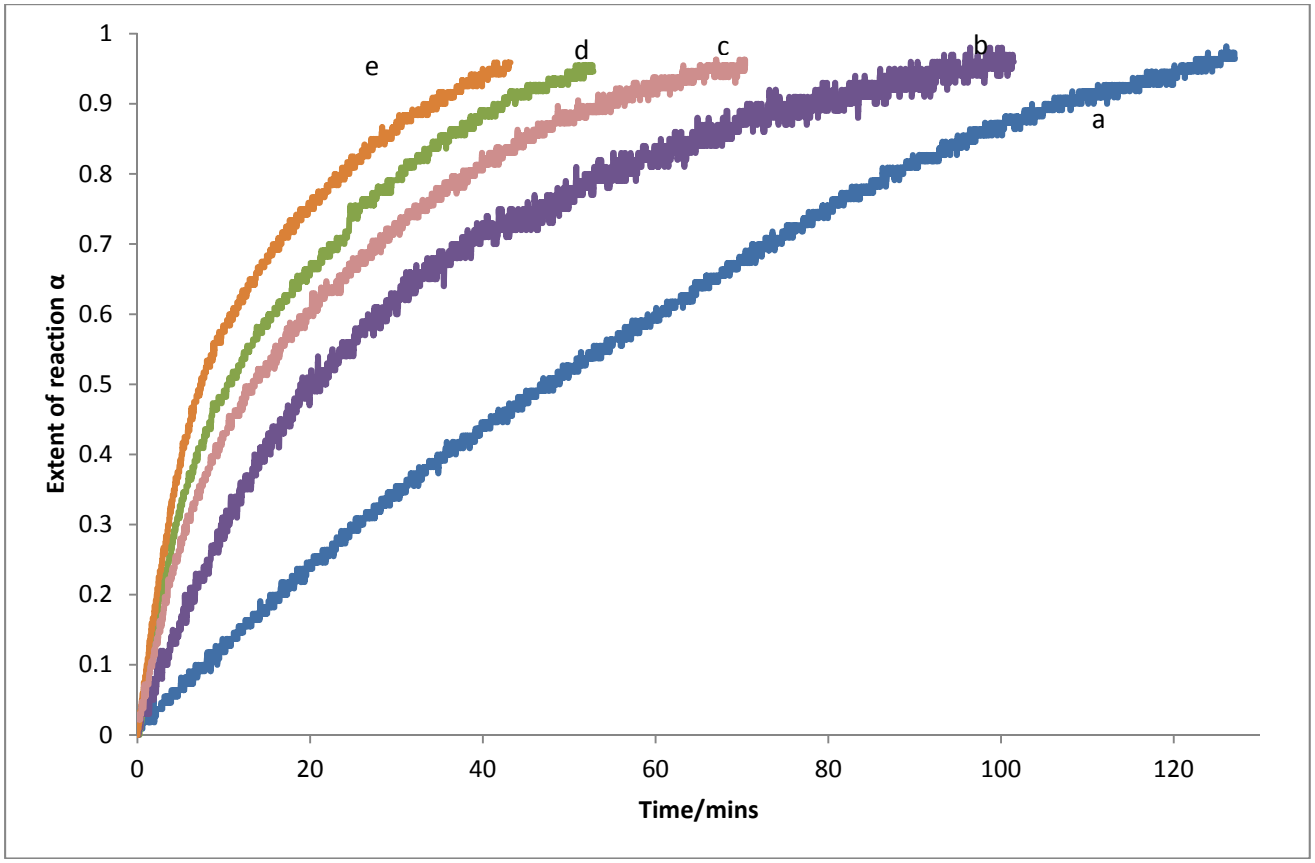
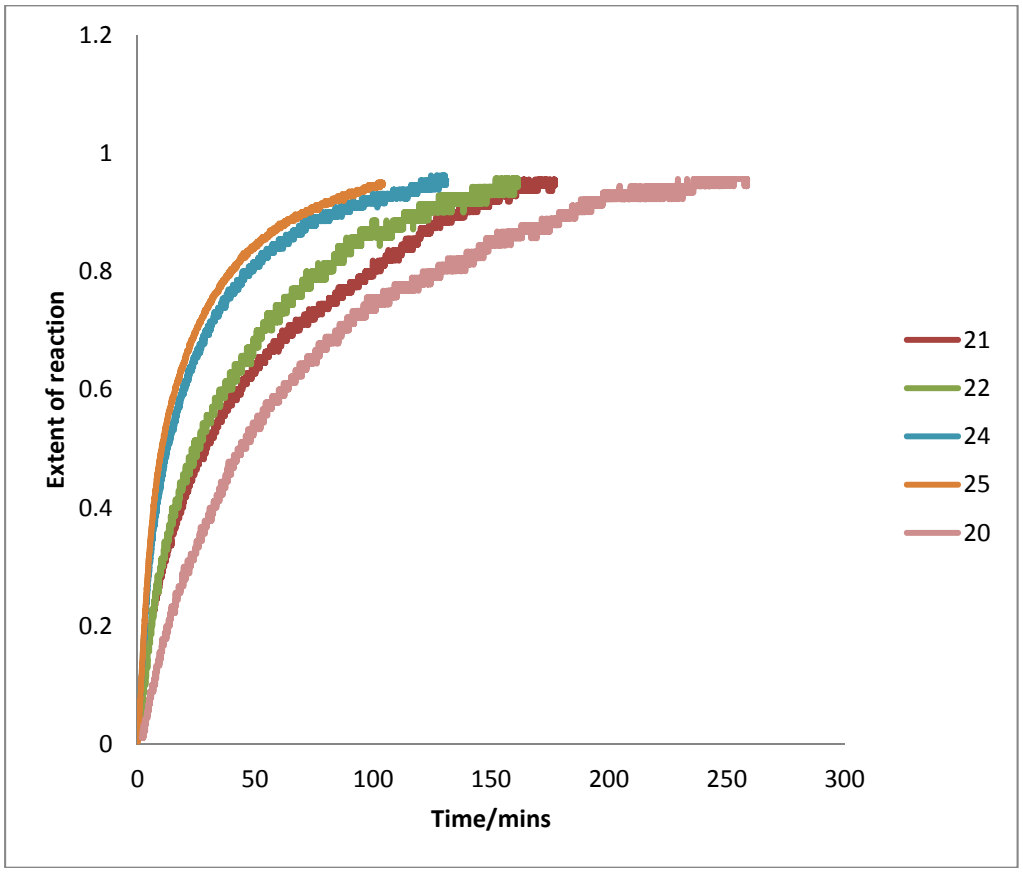
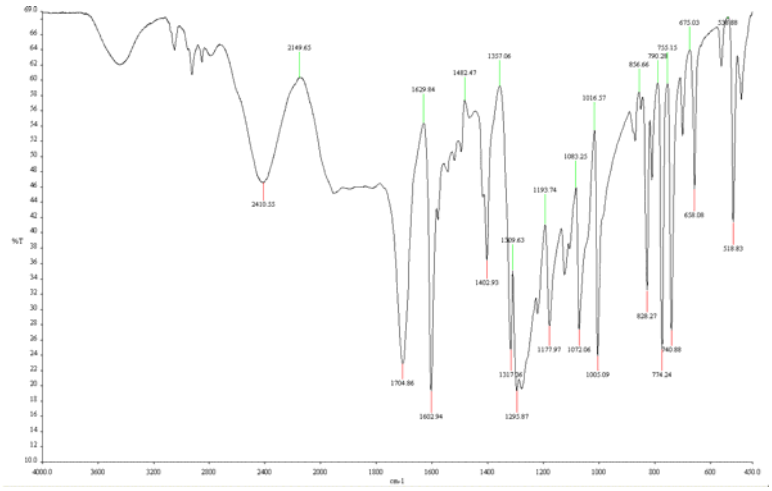


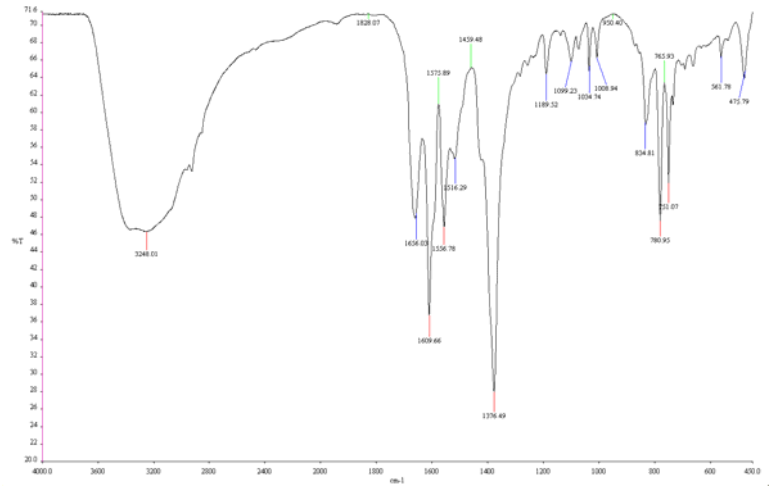

Fig S10: **Rate plots for water adsorption by compound 3d**



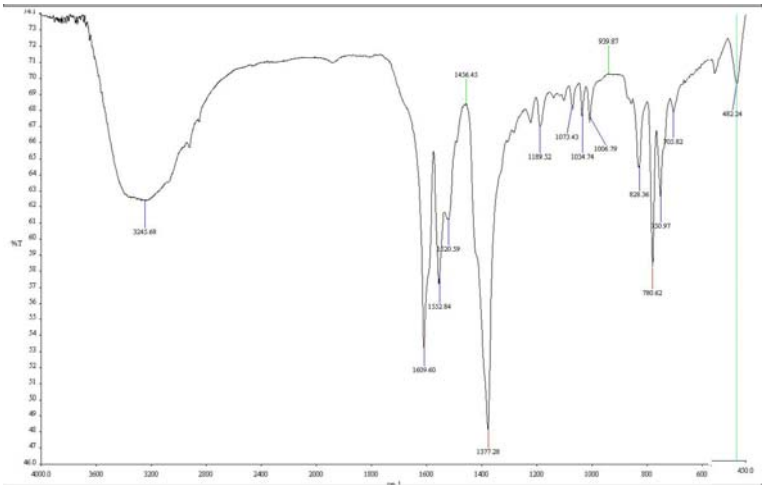
## Infrared spectra (KBr)



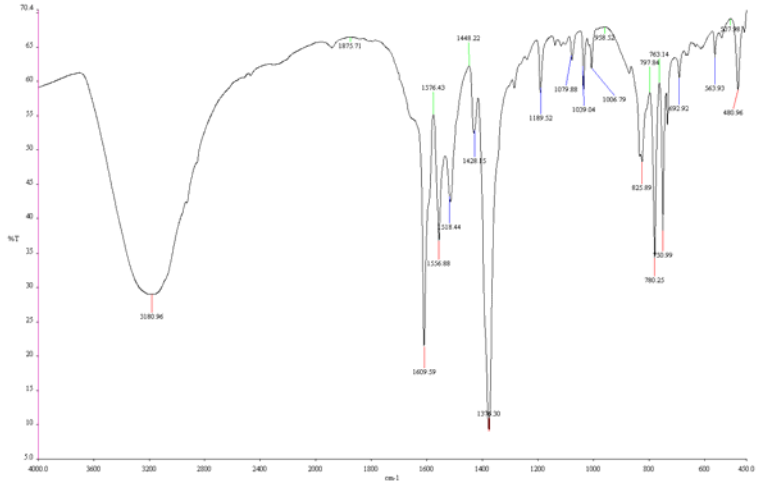
**1**



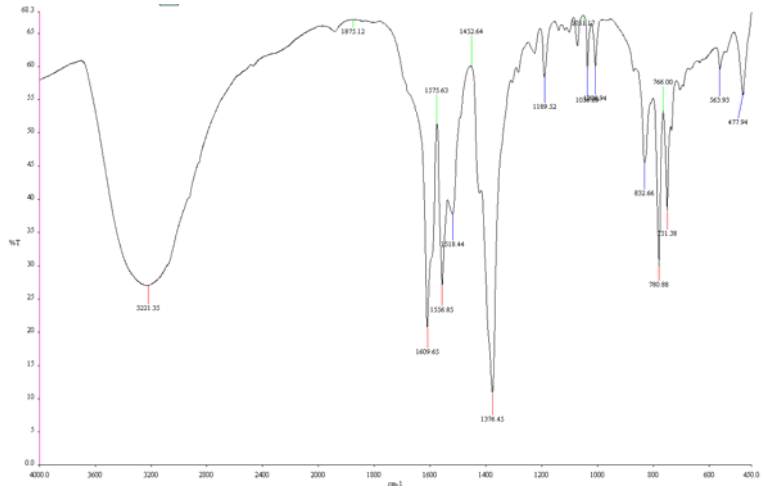
**2** (as made)



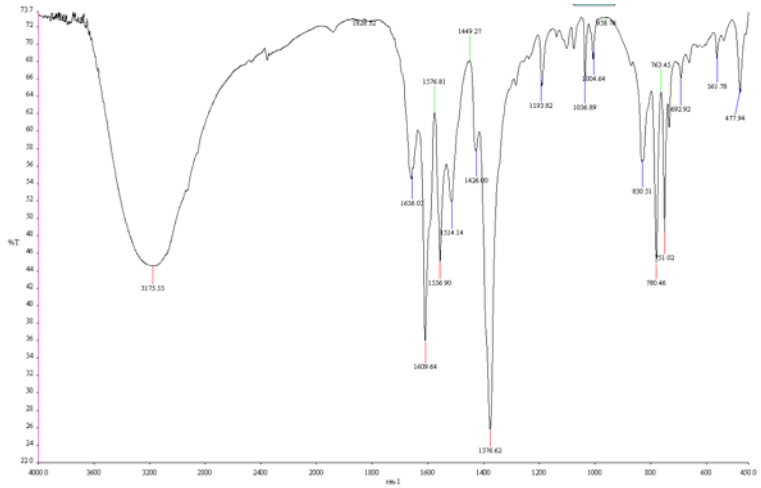
**2d**



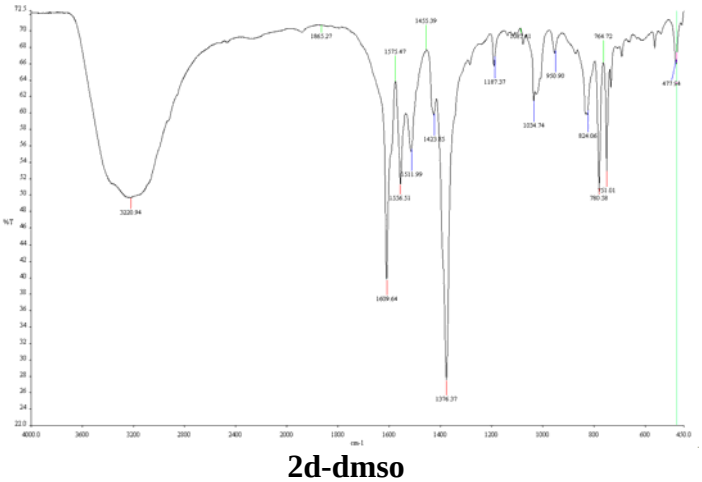
**2d-water**



**2d-methanol**



**2d-dmf**



**2d-dmso**