Supporting Information

# Structurally well-characterized new multinuclear Cu(II) and Zn(II) clusters: X-ray crystallography, theoretical studies, and applications in catalysis

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**Table S1**. Crystal data with refinement parameters for **1** and **2**.

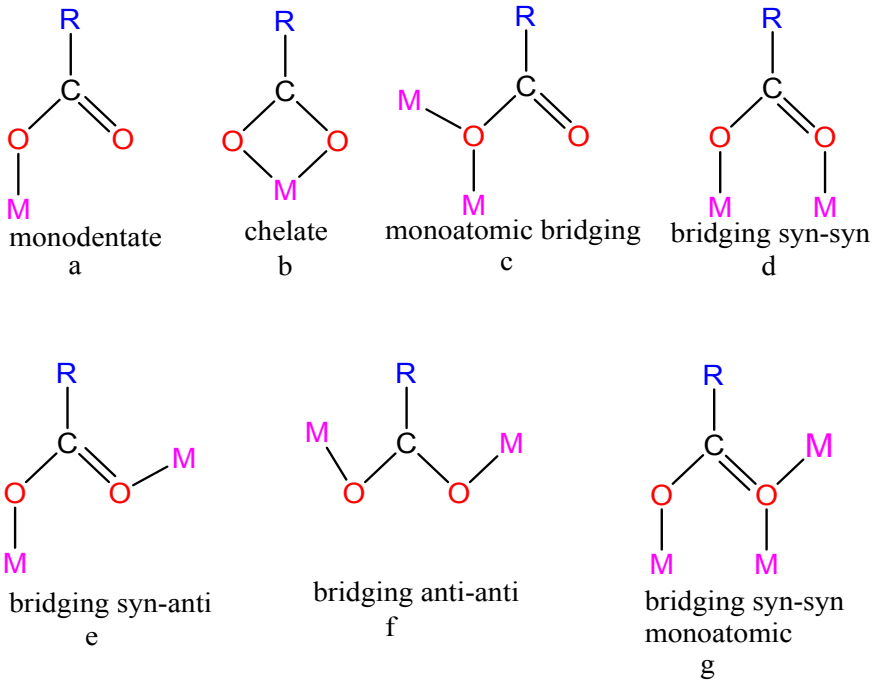
| Parameters | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{26}H_{38}Cu_3N_4O_{16}$ | $C_{27}H_{31}Zn_2NO_{10}$ |
| Formula weight | 853.22 | 660.27 |
| Temp (K) | 296(2) | 296(2) |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P $2_1$/c | P $2_1$/n |
| Unit cell dimensions | | |
| a (Å) | 8.1872(6) | 14.49(4) |
| b (Å) | 16.9482(13) | 11.44(3) |
| c (Å) | 11.7093(9) | 18.17(5) |
| α (°) | 90 | 90 |
| β(°) | 101.284(4) | 109.49(5) |
| γ (°) | 90 | 90 |
| V (Å$^3$) | 1593.4(2) | 2839(14) |
| Z | 2 | 4 |
| ρ (calc) (g cm$^{-3}$) | 1.778 | 1.545 |
| F (000) | 874 | 1360 |
| Index ranges | -9≤ h ≤ 9 | -17≤ h ≤ 17 |
| | -20≤ k ≤ 19 | -13≤ k ≤ 13 |
| | -14 ≤ l ≤ 14 | -21 ≤ l ≤ 21 |
| No of reflections collected | 17858 | 34548 |
| No. of independent reflection | 2404 | 3220 |
| GOF | 1.035 | 1.039 |
| Final R indices [ I > 2σ(I) ] | $R_1$ = 0.0310 | 0.0407 |
| | $wR_2$ = 0.0791 | 0.0785 |
| R indices all data | $R_2$ = 0.0417 | 0.0791 |
| | $wR_2$ = 0.0843 | 0.0898 |

**Table S2**. Selected bond lengths (Å) and bond angles (°) of **1** and **2.**

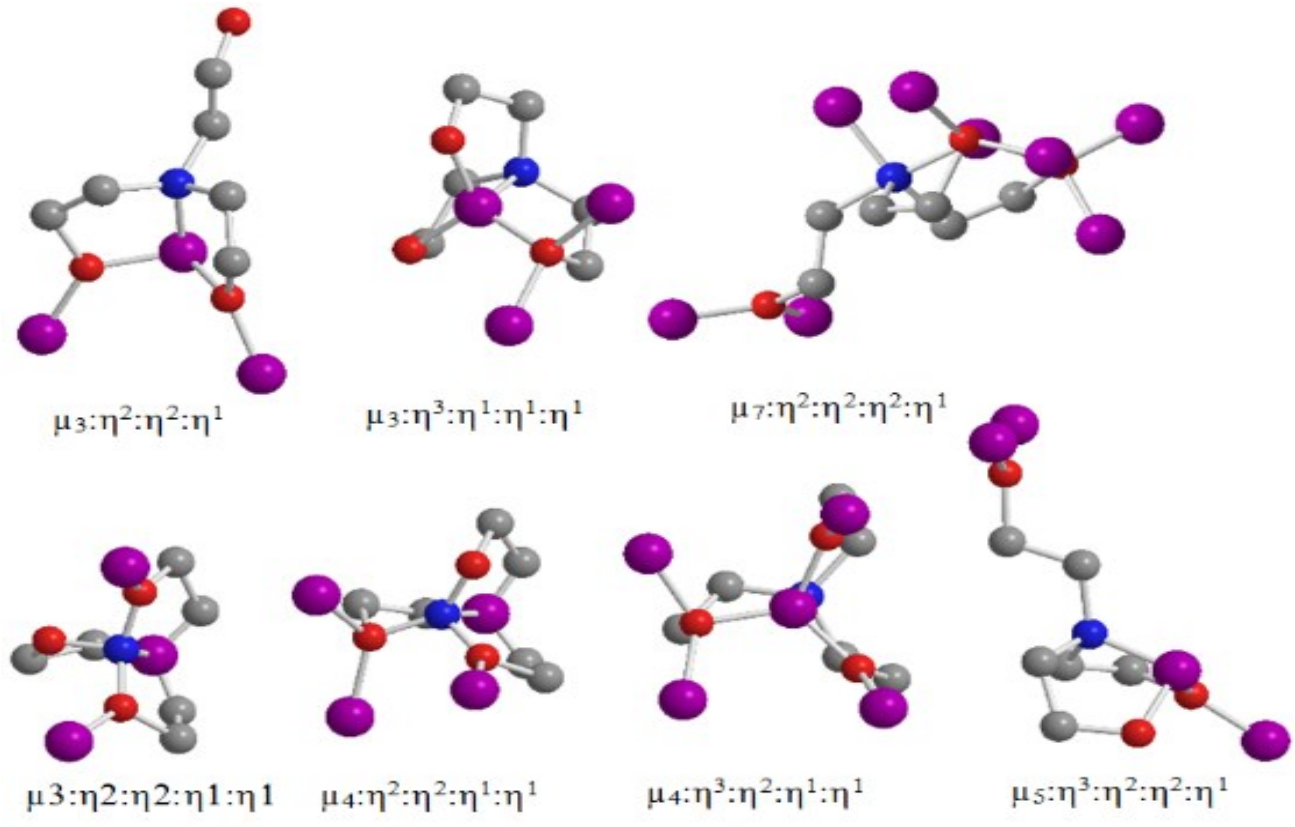
| **1** | | **2** | |
|---|---|---|---|
| Bond lengths | | | |
| Cu1−O1 | 1.911(2) | Zn1−O3 | 2.124(5) |
| Cu1−O4 | 1.959(2) | Zn1−O5 | 1.988(5) |
| Cu1−N1 | 2.019(2) | Zn1−N1 | 2.140(5) |
| Cu1−O3 | 2.067(2) | Zn1−O8 | 2.078(4) |
| Cu1−O5 | 2.239(3) | Zn1−O7 | 2.172(6) |
| Cu2−O4 | 1.938(2) | Zn2−O8 | 1.941(5) |
| Cu2−O2 | 1.994(2) | Zn2−O1 | 1.926(5) |
| Cu2−O2 | 1.9933(19) | Zn2 −O4 | 1.960(4) |
| Cu1−O1 | 1.9099(19) | Zn2−O6 | 1.959(6) |
| Bond angles | | | |
| O1−Cu1−O4 | 97.42(9) | O5−Zn1−O3 | 97.11(11) |
| O1−Cu1−N1 | 173.90(10) | N1−Zn1−O3 | 97.10(12) |
| O4−Cu1−N1 | 88.63(9) | N1−Zn1−O5 | 165.68(12) |
| O1−Cu1−O3 | 90.53(10) | O8−Zn1−O3 | 92.65(10) |
| O4−Cu1−O3 | 157.57(10) | O8−Zn1−O5 | 95.60(10) |
| N1−Cu1−O3 | 83.57(9) | O8 −Zn1−N1 | 82.02(11) |
| O1−Cu1−O5 | 99.17(11) | O7−Zn1−O3 | 81.56(11) |
| O4−Cu1−O5 | 99.77(10) | O7−Zn1−O5 | 102.80(11) |
| N1−Cu1−O5 | 80.38(10) | O7−Zn1−N1 | 81.02(12) |
| O3−Cu1−O5 | 99.61(11) | O7−Zn1−O8 | 161.24(11) |
| O4−Cu2−O4 | 180.00(5) | O9−Zn1−O3 | 167.84(12) |
| O4−Cu2−O2 | 91.82(9) | O9−Zn1−O5 | 88.36(13) |
| O4−Cu2−O2 | 88.18(9) | O9−Zn1−N1 | 78.02(14) |
| O4−Cu2−O2 | 88.18(9) | O9−Zn1−O8 | 97.63(12) |
| O4−Cu2−O2 | 91.82(9) | O9−Zn1−O7 | 86.65(13) |
| O2−Cu2−O2 | 180.0 | O4−Zn2−O1 | 99.85(11) |
| C1−O1−Cu1 | 127.3(2) | O6−Zn2−O1 | 112.45(13) |
| N1−C12−C13 | 112.8(2) | O6−Zn2−O4 | 111.85(12) |
| N1−C10−C11 | 109.7(2) | O8−Zn2−O1 | 120.92(11) |
| N1−C8−C9 | 109.4(2) | O8−Zn2−O4 | 107.99(11) |
| Cu1−Cu2−Cu1 | 180.0 | O8−Zn2−O6 | 103.83(12) |

**Table S3.** Characterization data for catalysts (**1** and **2**) recovered after catalytic reactions.

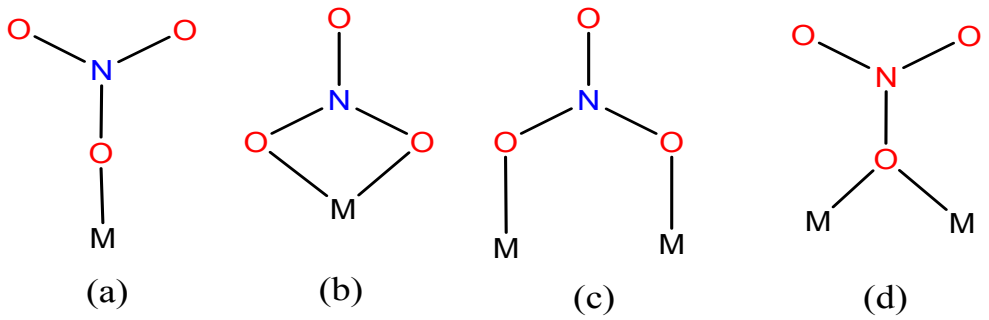
| catalyst | Analytical data | FTIR spectra |
|---|---|---|
| (**1**) | Elemental analysis for $C_{26}H_{34}Cu_3N_4O_{16}$ (M = 795): C, 36.74; N, 6.59; H, 4.00%. Found: C, 36.88; N, 6.71; H, 4.16%. Molar conductance, $\Lambda_m$ ($10^{-3}$ M, methanol): 39.0 $\Omega^{-1}cm^2mol^{-1}$. | 1567/1382s $\nu_{as}/\nu_s(COO^-)$, 3410 (O–H), 942s (Cu–O–Cu). |
| (**2**) | Elemental analysis for $C_{27}H_{31}NO_{10}Zn_2$ (M = 660): C, 49.10; N, 2.12; H, 4.69%. Found: C, 49.74; N, 2.31; H, 4.49%. Molar conductance, $\Lambda_m$ ($10^{-3}$ M, methanol): 48.0 $\Omega^{-1}cm^2mol^{-1}$. | 1555/1380s $\nu_{as}/\nu_s(COO^-)$, 3435w (O–H), 936s (Zn–O–Zn). |



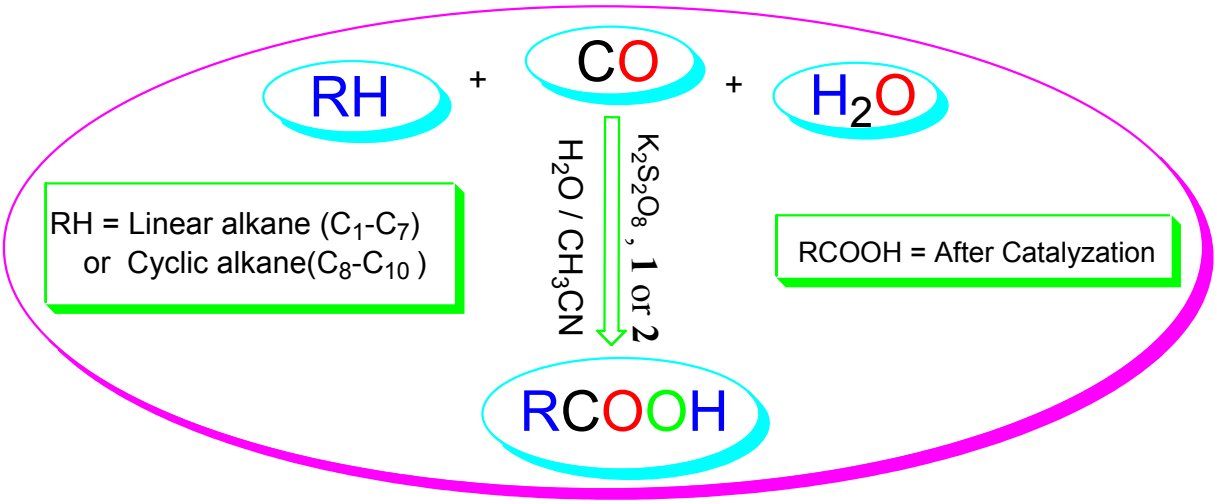

**Scheme S1**.Selected coordination modes of carboxylate ($COO^-$) group.




**Scheme S2**. Coordination modes of the ligand triethanolamine ($H_3$tea). Metals ions are purple, oxygen atoms red, nitrogen atom blue and carbon atoms grey. (H atoms are not shown for clarity).




**Scheme S3.** Selected coordination modes of nitrate ($NO_3^-$) group.




**Scheme S4.** Hydrocarboxylation of alkanes to carboxylic acids catalyzed by **1** and **2**.

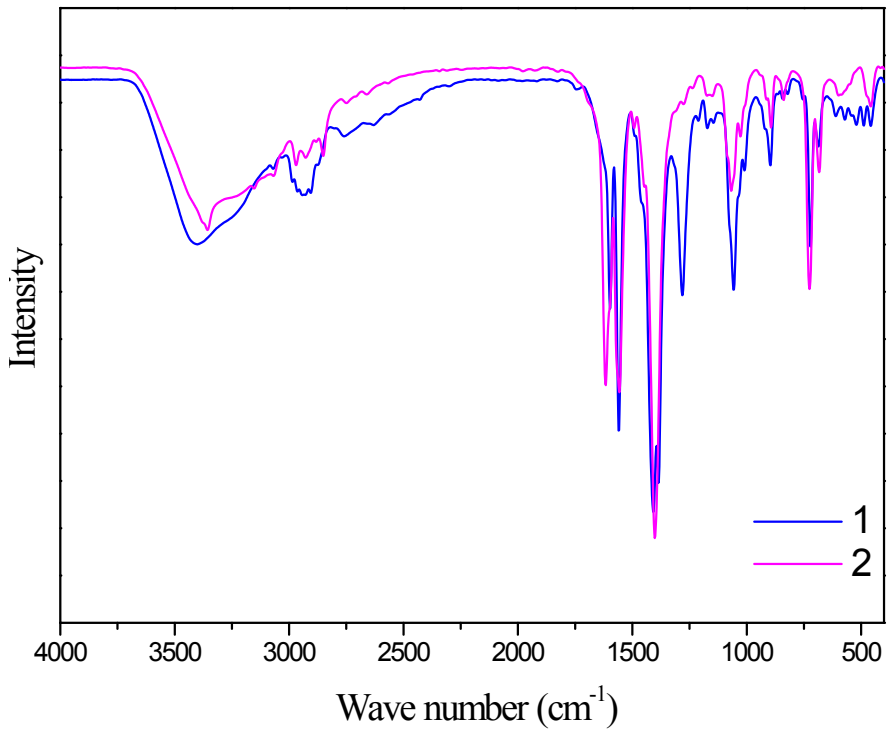



**Fig. S1** FTIR spectra for the complexes (**1** and**2**).

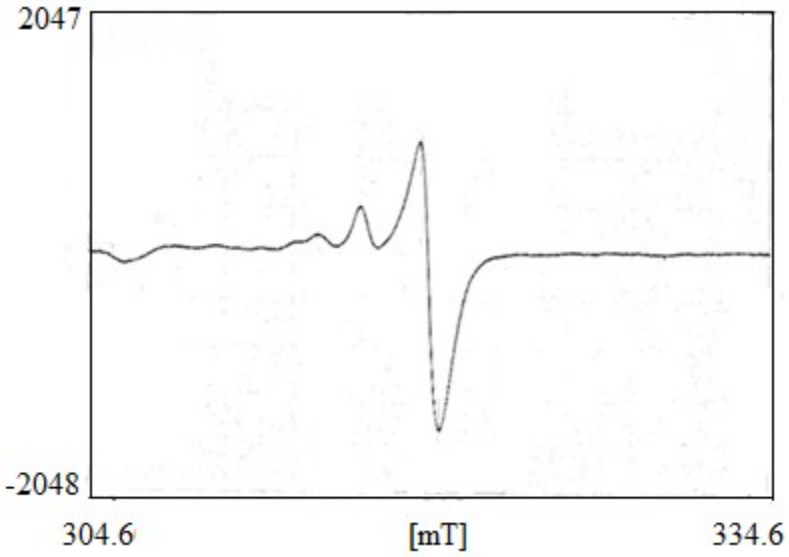



**Fig. S2:** EPR spectrum of **1**.

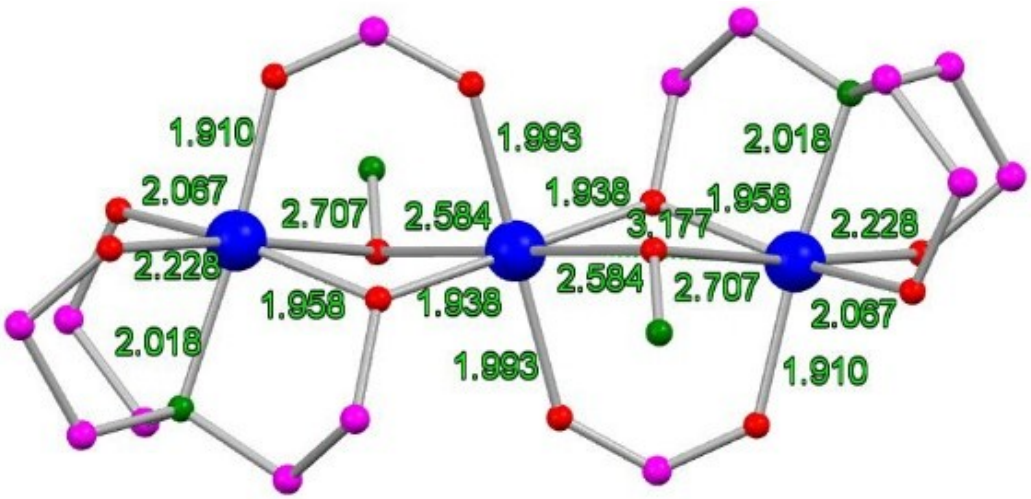



**Fig. S3 (a):** Molecular core of **1** with bond lengths.

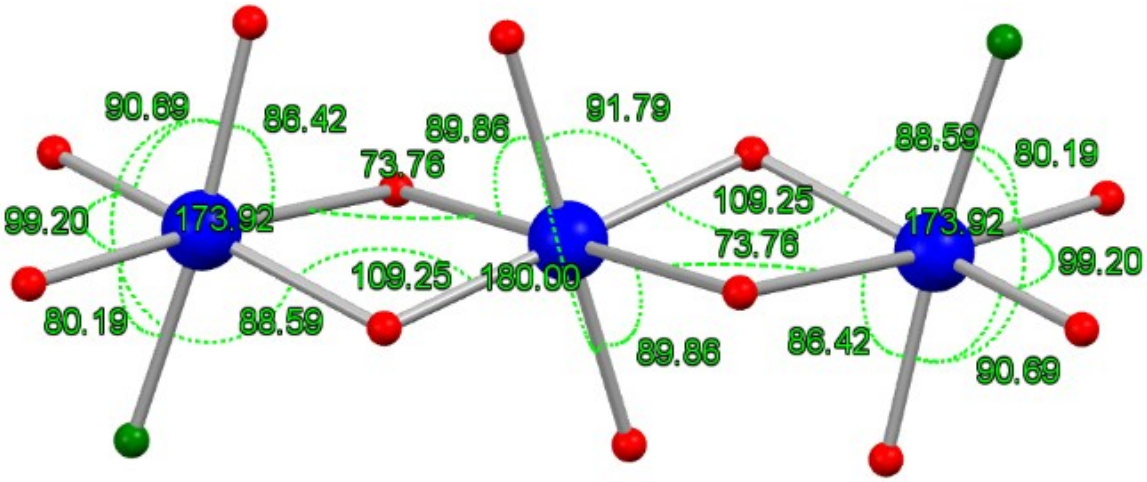



**Fig. S3 (b):** Molecular core of **1** with bond angles.

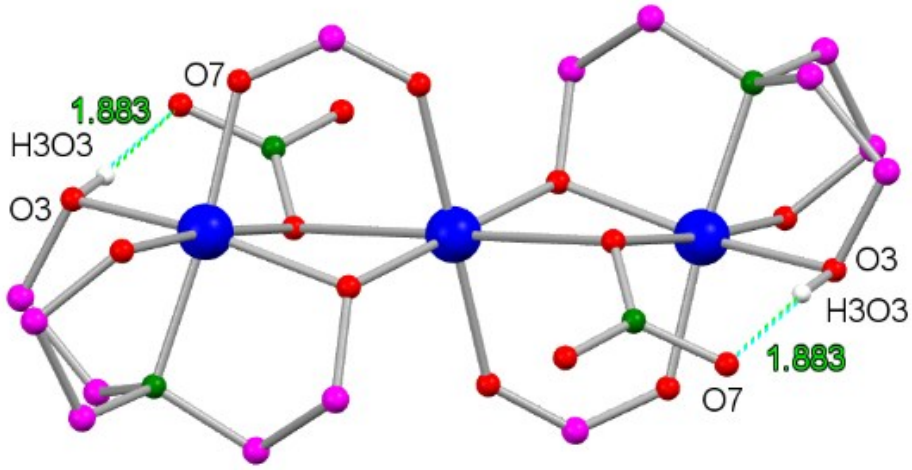



**Fig. S4**. Intramolecular O−H···O interactions in **1**.

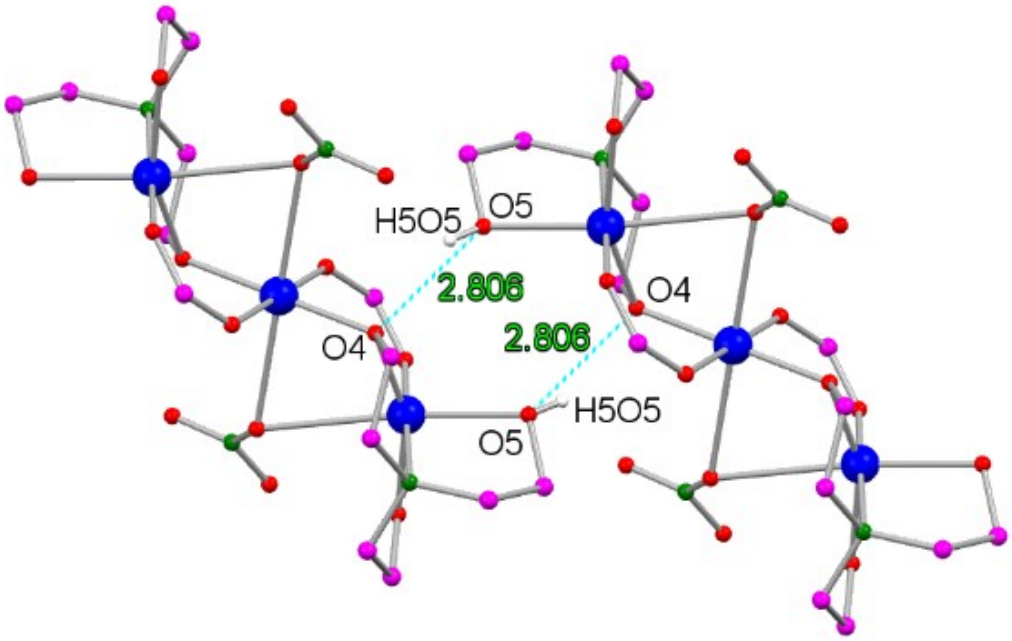



**Fig. S5**. Intermolecular O−H···O interactions in **1**.

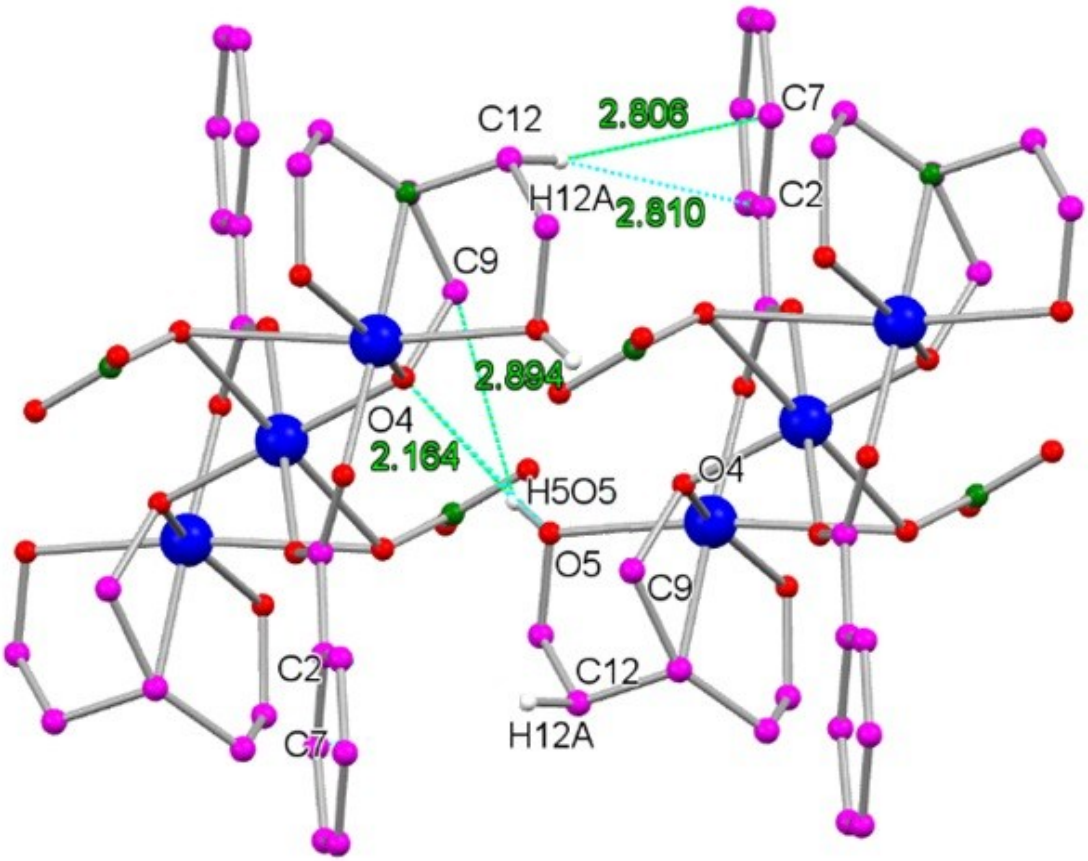



**Fig. S6**. C−H···π and O−H···O interactions in **1**.

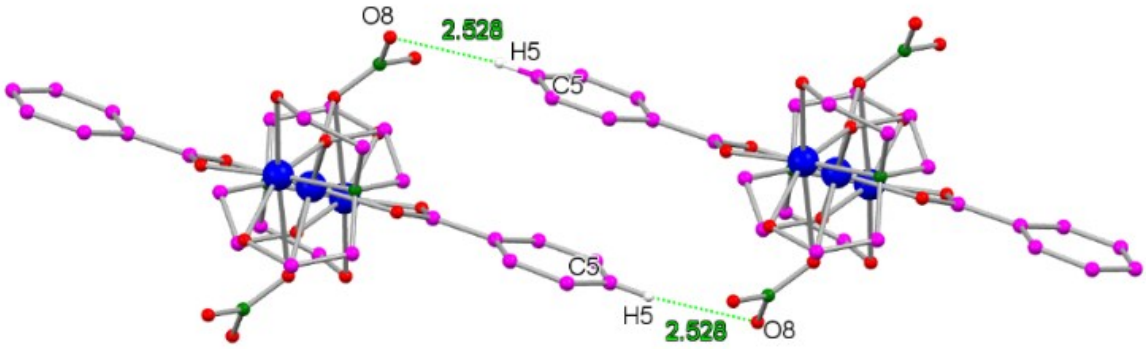



**Fig. S7**. C−H···C interactions in **1**.

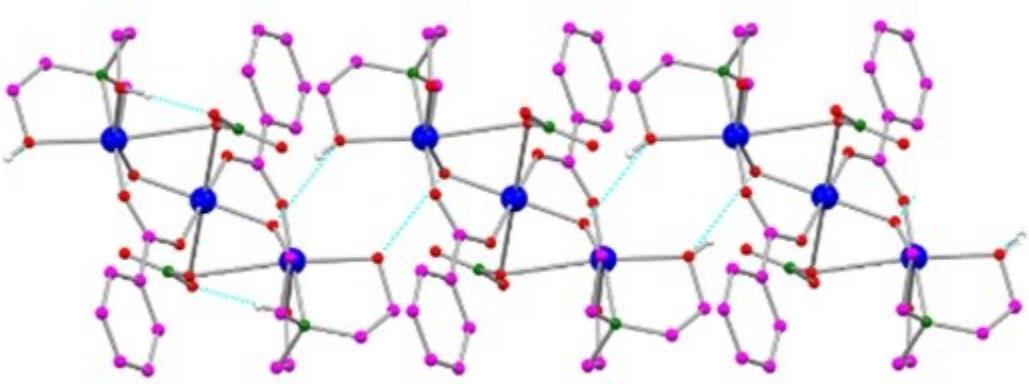


**Fig. S8**.1 D polymer chain formed by non-covalent interactions in **1**.

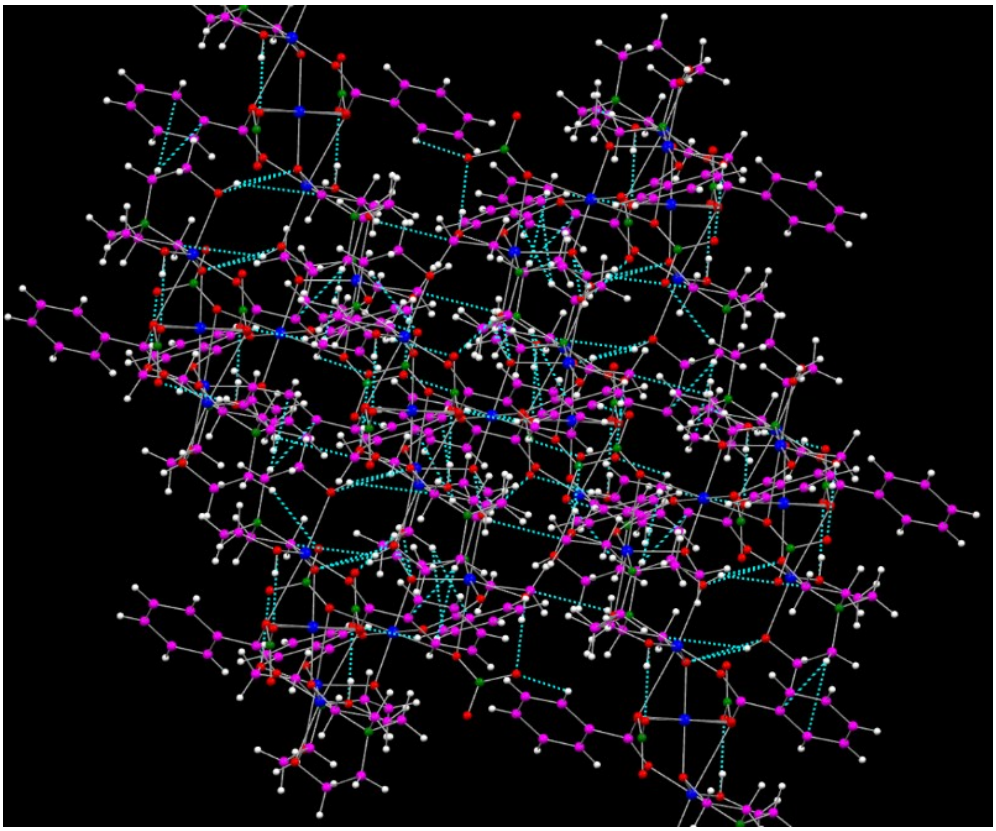


**Fig. S9**. 3 D supra molecular network of **1**.

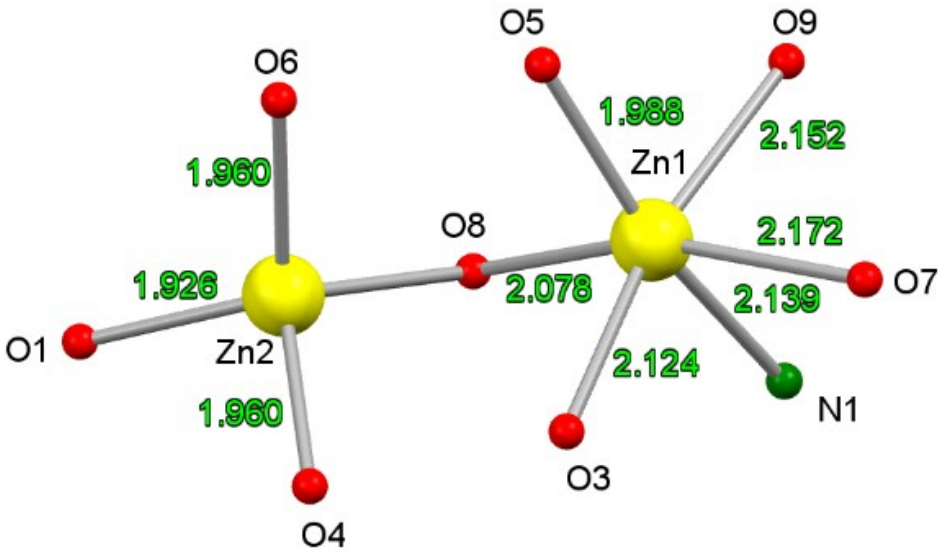



**Fig. S10 (a):** Molecular core of **2** with bond lengths.

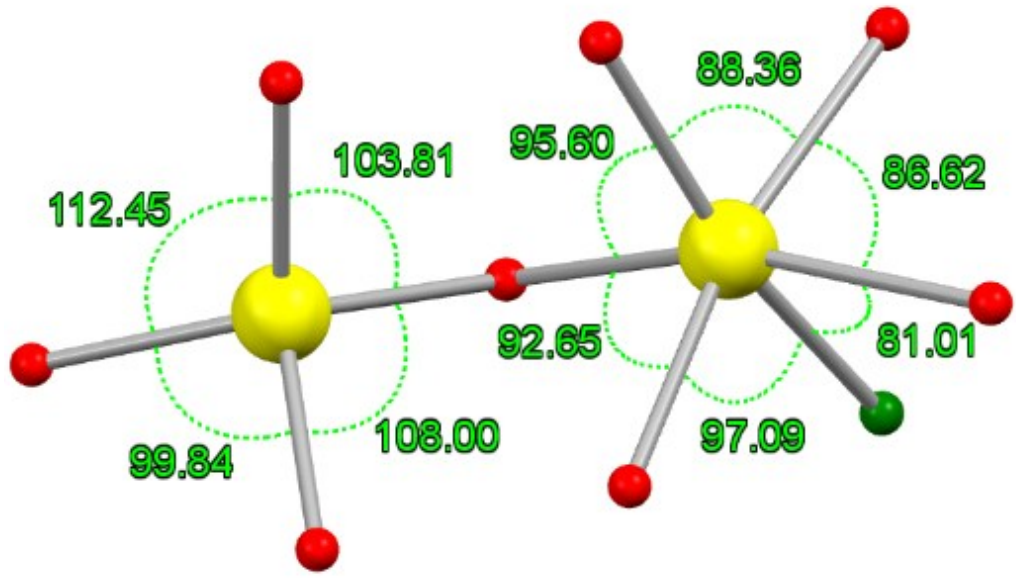



**Fig. S10(b):** Molecular core of **2** with bond angles.

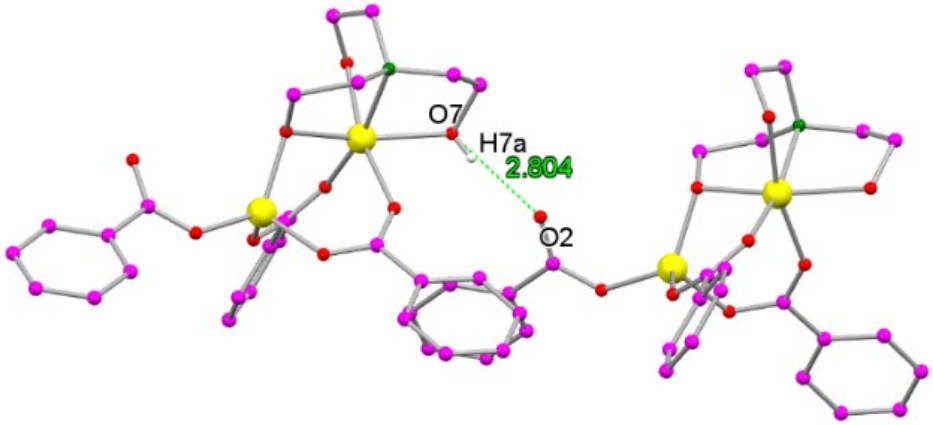



**Fig. S11**. Intramolecular O−H···O interactions in **2**.

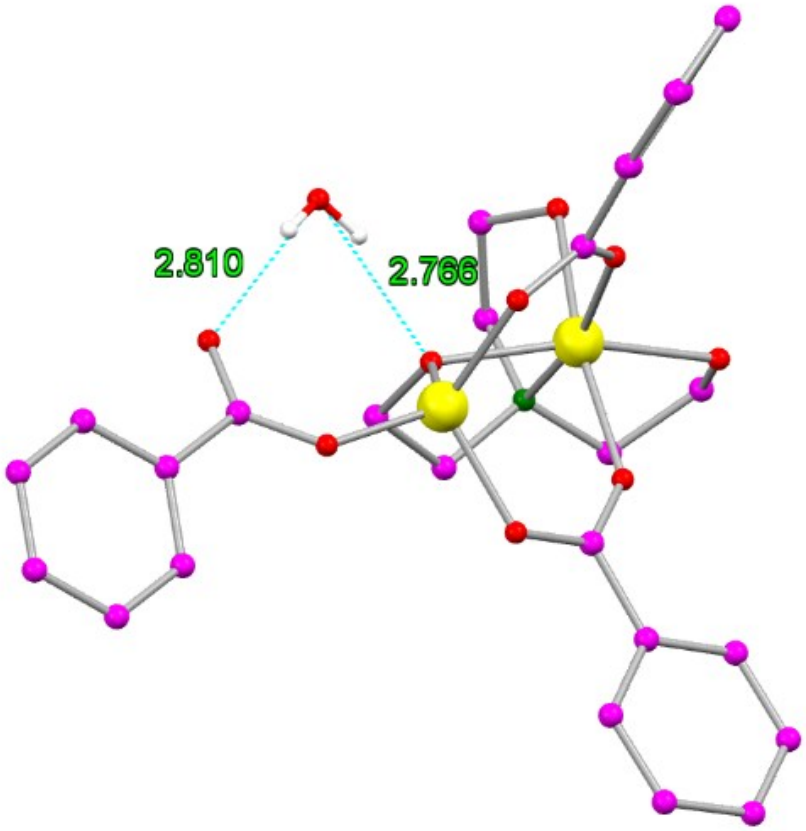



**Fig. S12**. Intermolecular O−H···O interactions in **2**.

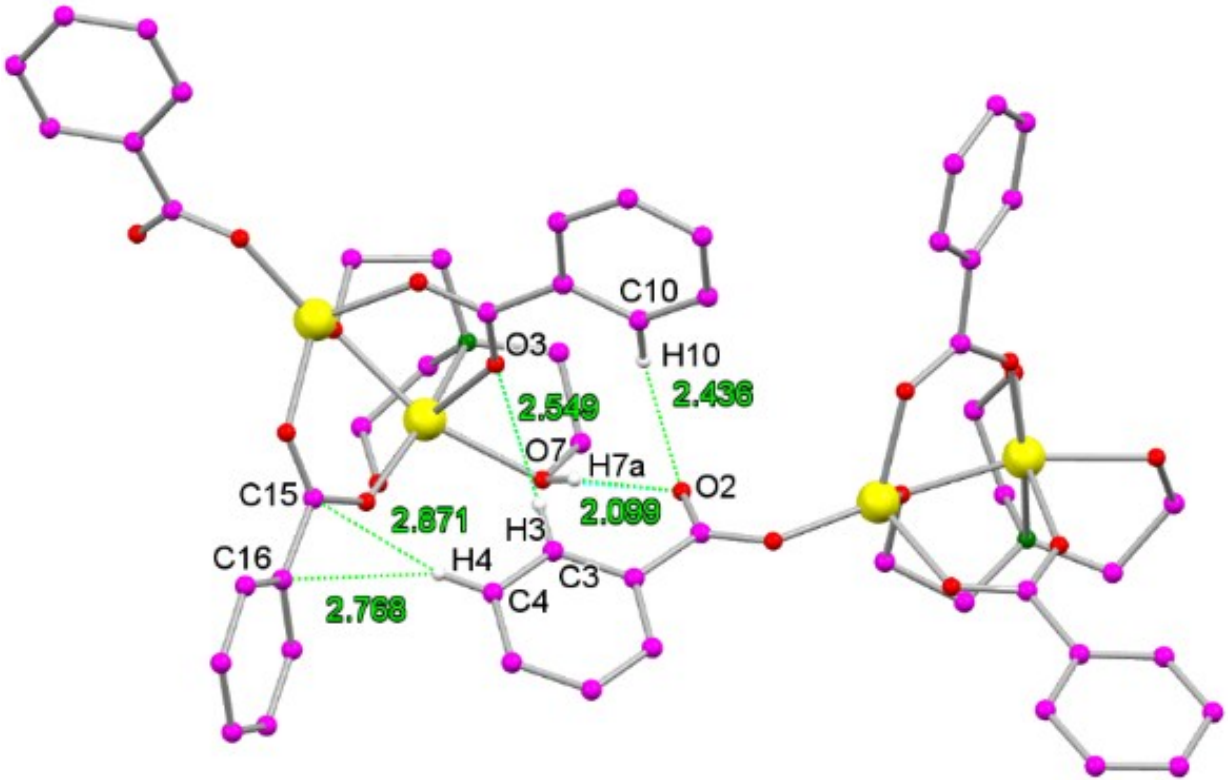



**Fig. S13**. C−H···C interactions in **2**.

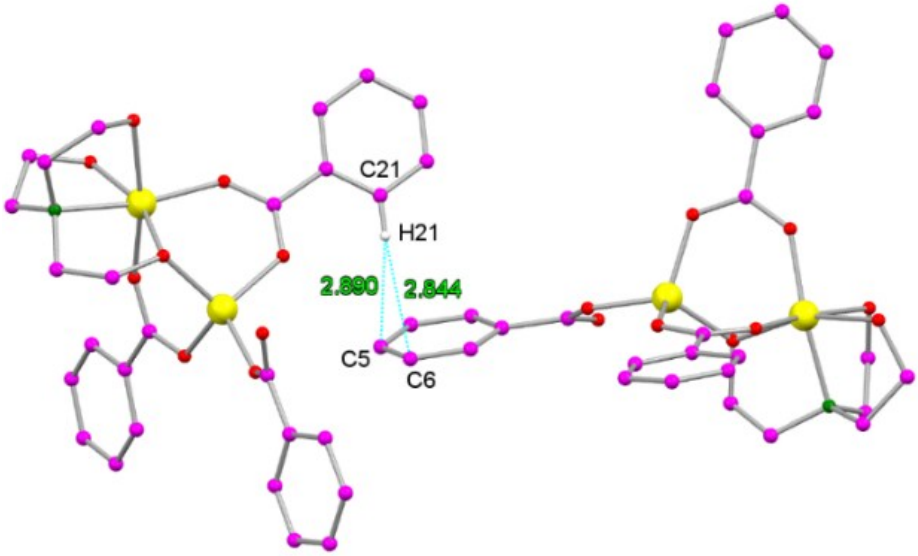



**Fig. S14**. C−H···π interactions in **2**.

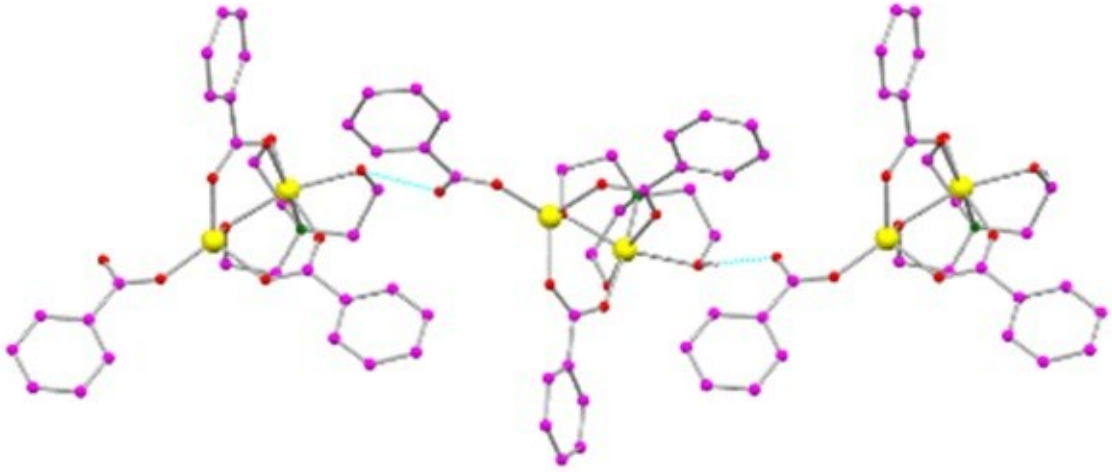


**Fig. S15**. 1 D polymeric chain formed by non-covalent interactions in **2**.

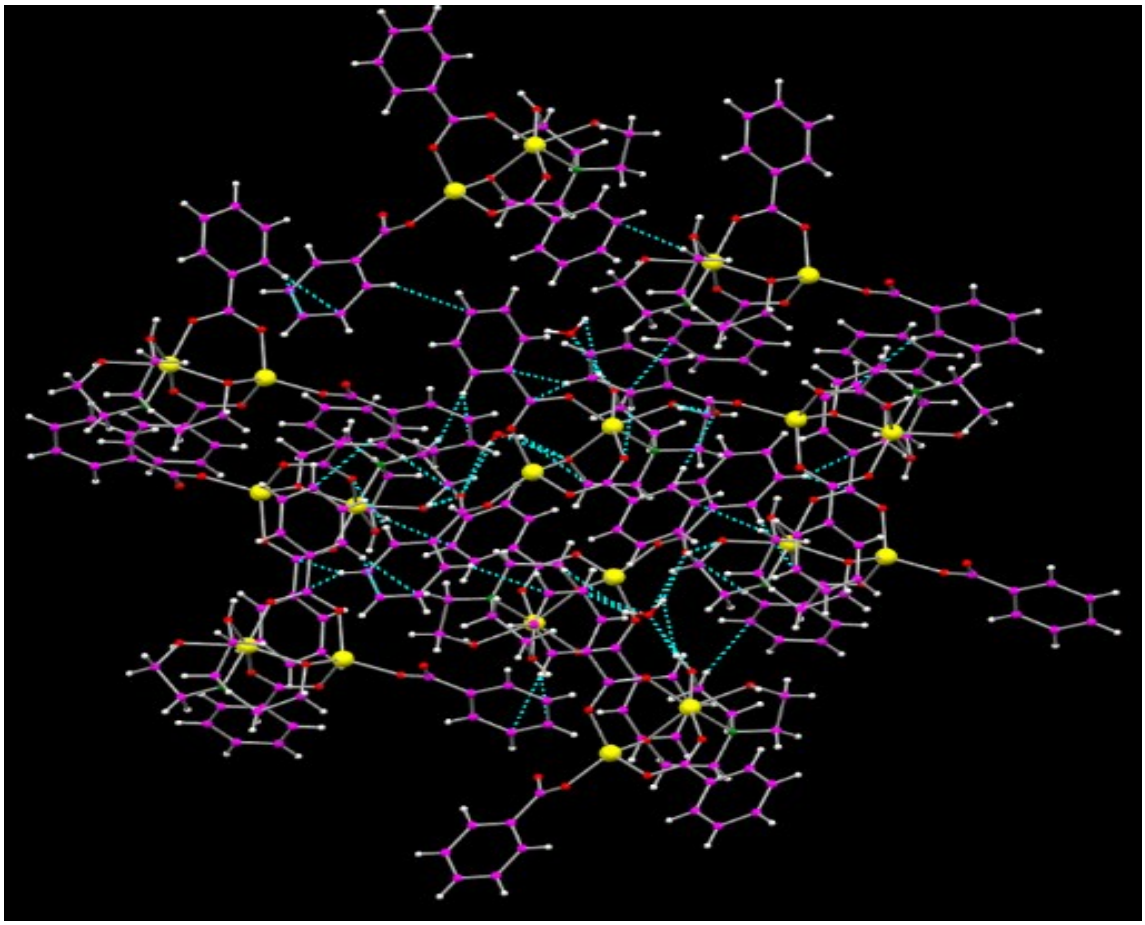


**Fig. S16**. 3 D supramolecular network of **2**.

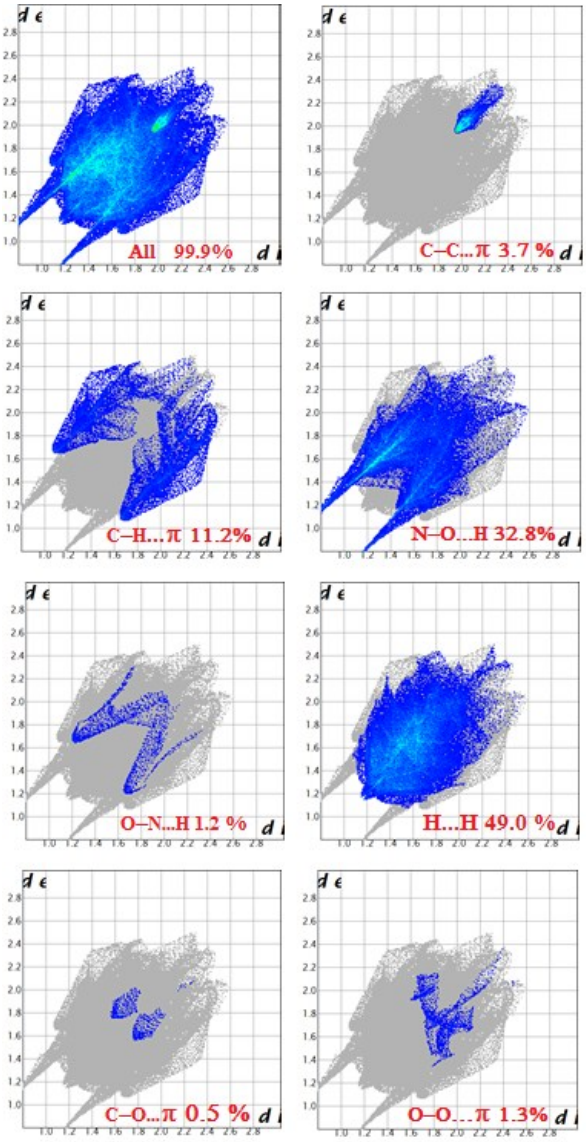



**Fig. S17(a)**. 2D-fingerprint plots of **1** showing different interactions**.**

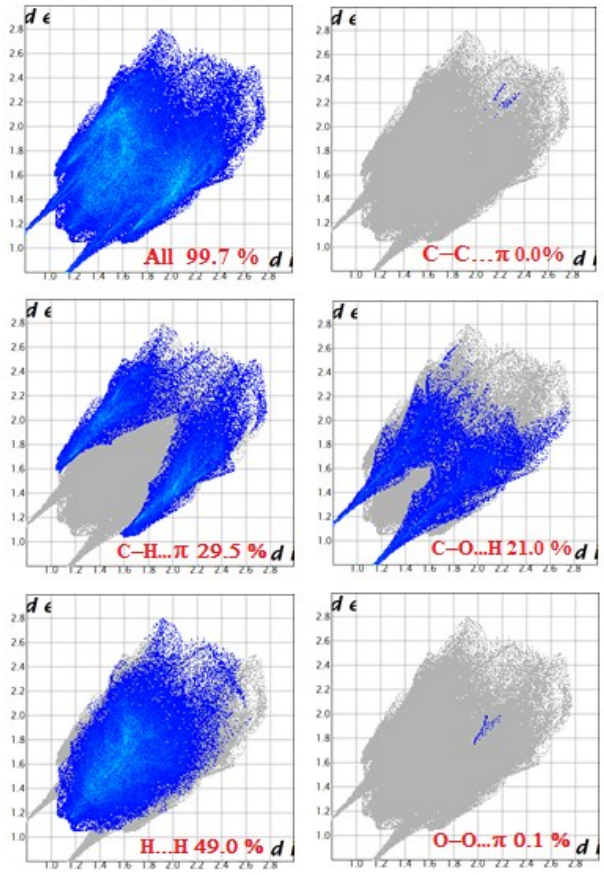



**Fig. S17(b)**. 2D-fingerprint plots of **2** showing different interactions.

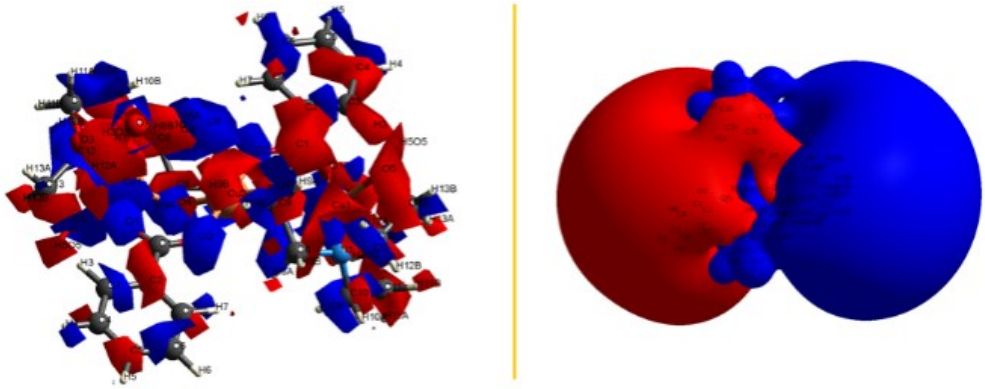


**Fig. S18**. 3D-deformation density map for **1** (left) and **2** (right) showing the presence of CD regions (in red) and CC regions (in blue), mapped using Crystal Explorer 3.1. The iso surfaces are drawn at 0.008 $eau^{-3}$.

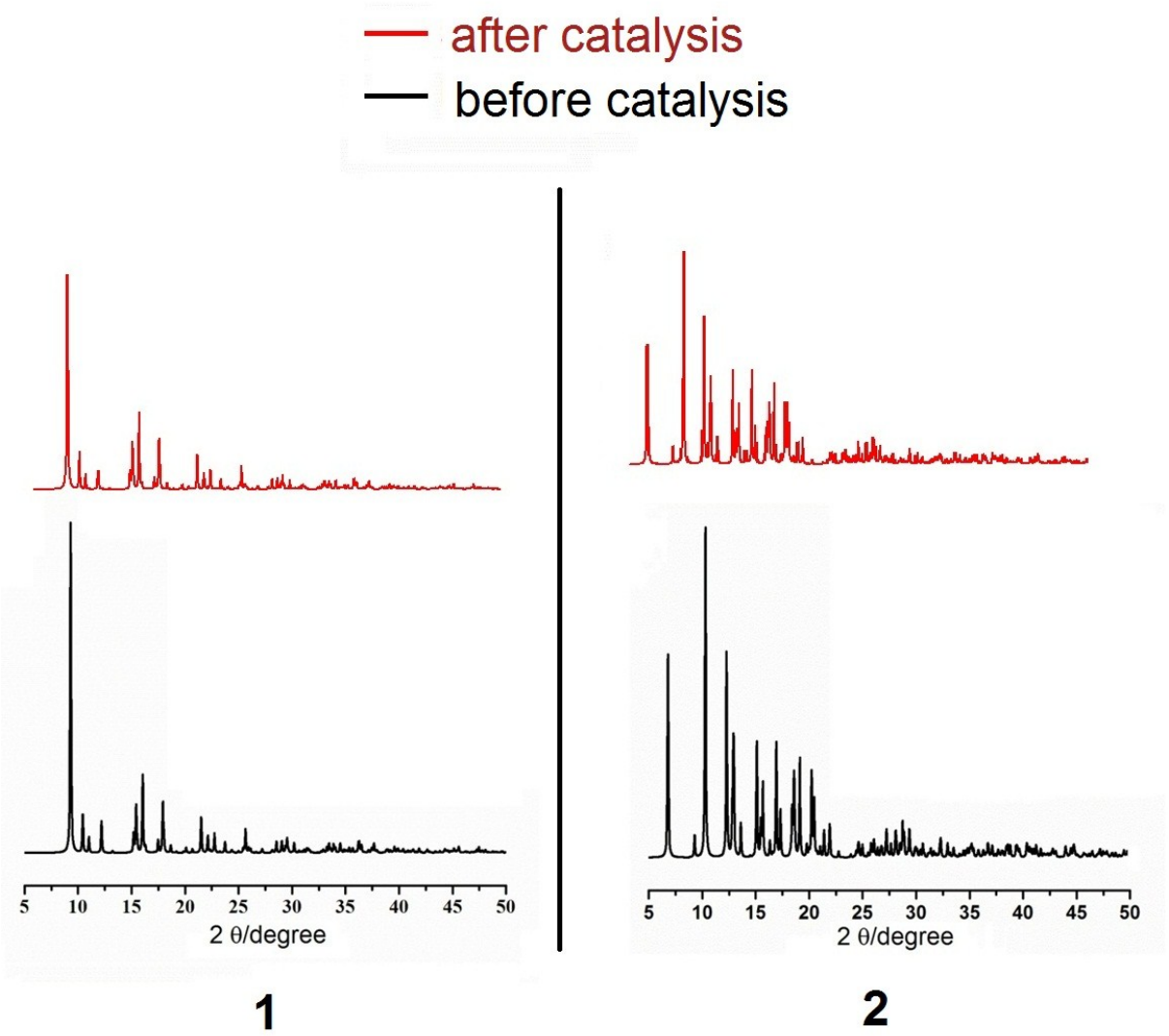



**Fig. S19.** PXRD patterns of **1** and **2** before and after catalytic cycle (The pattern remains the same before and after the catalysis indicating that the composition of the catalysts does not change after the catalytic reactions).