

IR, UV-Vis data for rehydration procedure of **1** – **5**.

**[Co( $\mu$ -TBG)( $\mu$ -H<sub>2</sub>O)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (**1**)** IR (KBr),  $\nu/\text{cm}^{-1}$  : 3503 (m), 3323 (w), 2965 (w), 1643 (s), 1607 (s), 1559 (s), 1497 (m), 1436 (m), 1396 (s), 1318 (s), 1272 (m), 1175 (w), 1123 (w), 1002 (w), 709 (m). Electronic spectrum (DRS, BaSO<sub>4</sub>) (nm): 522, 482 (sh), 450(sh). Dehydrated **1** IR (KBr),  $\nu/\text{cm}^{-1}$  3399 (m), 2931 (w), 1656 (s), 1626 (s), 1559 (s), 1495 (m), 1441 (m), 1401 (s), 1389 (m), 1308 (s), 1176 (w), 1063 (w), 1001 (m), 933 (w), 864 (m), 746 (m). Electronic spectrum (DRS, BaSO<sub>4</sub>) (nm): 570, 524(sh), 491(sh). Rehydrated **1** I.R. (KBr),  $\nu/\text{cm}^{-1}$  3503 (m), 3323 (w), 2965 (w), 1643 (s), 1607 (s), 1559 (s), 1497 (m), 1436 (m), 1396 (s), 1318 (s), 1272 (m), 1175 (w), 1123 (w), 1002 (w), 709 (m). Electronic spectrum (DRS, BaSO<sub>4</sub>) (nm): 522, 482 (sh), 450(sh).

**[Cu( $\mu$ -TBG)( $\mu$ -H<sub>2</sub>O)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (**2**).** IR (KBr),  $\nu/\text{cm}^{-1}$  3503 (m), 3338 (w), 2965 (w), 1642 (s), 1608 (s), 1559 (s), 1498 (m), 1432 (m), 1396 (s), 1310 (s), 1267 (m), 1175 (w), 1121 (w), 1001 (w), 867 (m), 788 (m). Electronic spectrum (DRS, BaSO<sub>4</sub>) (nm): 775. Dehydrated **2** IR (KBr),  $\nu/\text{cm}^{-1}$  3377 (m), 3325(m), 2985 (w), 1656 (s), 1627 (s), 1559 (s), 1495 (m), 1441 (m), 1401 (s), 1389 (m), 1308 (s), 1176 (w), 1063 (w), 1001 (m), 933 (w), 864 (m), 746 (m). Electronic spectrum (DRS, BaSO<sub>4</sub>) (nm): 870 – 500. Rehydrated **2** IR (KBr/pellet),  $\nu/\text{cm}^{-1}$  3503 (m), 3338 (w), 2965 (w), 1642 (s), 1608 (s), 1559 (s), 1498 (m), 1432 (m), 1396 (s), 1310 (s), 1267 (m), 1175 (w), 1121 (w), 1001 (w), 867 (m), 788 (m). Electronic spectrum (DRS, BaSO<sub>4</sub>) (nm): 775.

**[Mn( $\mu$ -TBG)(H<sub>2</sub>O)<sub>4</sub>] $\cdot$ 2H<sub>2</sub>O (**3**)** IR (KBr),  $\nu/\text{cm}^{-1}$  3421 (s), 3366 (w), 2934 (w), 1648 (s), 1632 (s), 1560 (s), 1499 (m), 1430 (m), 1396 (s), 1299 (s), 1172 (w), 1119 (w), 1003 (w), 734 (m), 593 (m). (**3**, heated) (KBr),  $\nu/\text{cm}^{-1}$ : 3324 (s), 1628 (s), 1584 (s), 1547 (s), 1498 (m), 1433 (m), 1389 (s), 1309 (s), 1170 (w), 1071 (w), 1001 (m), 926 (w), 861 (m), 739 (m), 665 (m), 572 (m). (**3** rehydrated) (KBr),  $\nu/\text{cm}^{-1}$  3325 (s), 2949 (w), 1637 (s), 1586 (s), 1546 (s), 1498 (m), 1432 (s), 1389 (s), 1309 (s), 1171 (w), 1118 (w), 1071 (w), 1001 (m), 925 (w), 861 (m),

739 (m), 665 (w), 572 (m). Far – IR ( $\text{cm}^{-1}$ ): 452 (w), 391 (w), 272 (w), 224 (w), 178 (m), 151 (s), 122 (m). Electronic spectrum (DRS,  $\text{BaSO}_4$  solution) (nm): 294, 265.

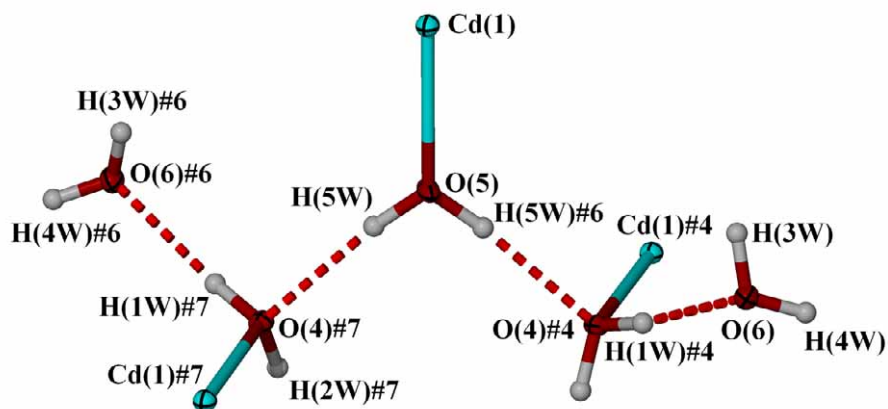
**[Cd( $\mu$ -TBG)( $\text{H}_2\text{O}$ ) $_3$ ] $\cdot$ 2 $\text{H}_2\text{O}$  (4)** IR ( $\text{cm}^{-1}$ ): 3407 (s), 3370 (s), 2928 (w), 1628 (s), 1592 (s), 1552 (s), 1497 (m), 1433 (m), 1387 (s), 1302 (s), 1174 (w), 1121 (w), 1002 (w), 928 (w), 865 (m), 736 (m), 634 (m). Far – IR ( $\text{cm}^{-1}$ ): 425 (w), 320 (w), 292 (w), 255 (m, br), 180 (s), 150 (s), 142 (s). Electronic spectrum (DRS,  $\text{BaSO}_4$  solution) (nm): 294, 265. (**4**, heated) IR ( $\text{cm}^{-1}$ ): 3243 (s), 3082 (m), 1643 (s), 1568 (s), 1552 (s), 1498 (m), 1440 (m), 1403 (s), 1313 (s), 1176 (w), 1114 (w), 1001 (w), 863 (m), 732 (m), 687 (m), 554(m). (**4**, rehydrated) IR ( $\text{cm}^{-1}$ ): 3497(s), 3372 (s), 2930 (w), 1623 (s), 1593 (s), 1554 (s), 1498 (m), 1435 (m), 1390 (s), 1304 (s), 1175 (w), 1121 (w), 1002 (w), 929 (w), 867 (m), 733 (m), 635 (m).

**[Pb( $\mu$ -TBG)( $\text{H}_2\text{O}$ ) $_2$ ] $\cdot$ 3 $\text{H}_2\text{O}$  (5).** IR (KBr),  $\nu/\text{cm}^{-1}$  3531 (m), 3459 (m), 3297 (s), 1650 (s), 1630 (s), 1554 (s), 1504 (m), 1434 (m), 1394 (s), 1312 (m), 1268 (m), 734 (m). (**5**, heated) IR ( $\text{cm}^{-1}$ ): 3243 (s), 3082 (m), 1647 (s), 1562 (s), 1552 (s), 1498 (m), 1442 (m), 1401 (s), 1318 (s), 1177 (w), 1112 (w), 1000 (w), 864 (m), 731 (m), 684 (m), 554(m). (**5**, Rehydrated) I.R. (KBr),  $\nu/\text{cm}^{-1}$  3503 (m), 3323 (w), 2965 (w), 1645 (s), 1607 (s), 1557 (s), 1497 (m), 1436 (m), 1398 (s), 1321 (s), 1272 (m), 1175 (w), 1123 (w), 1002 (w), 709 (m).

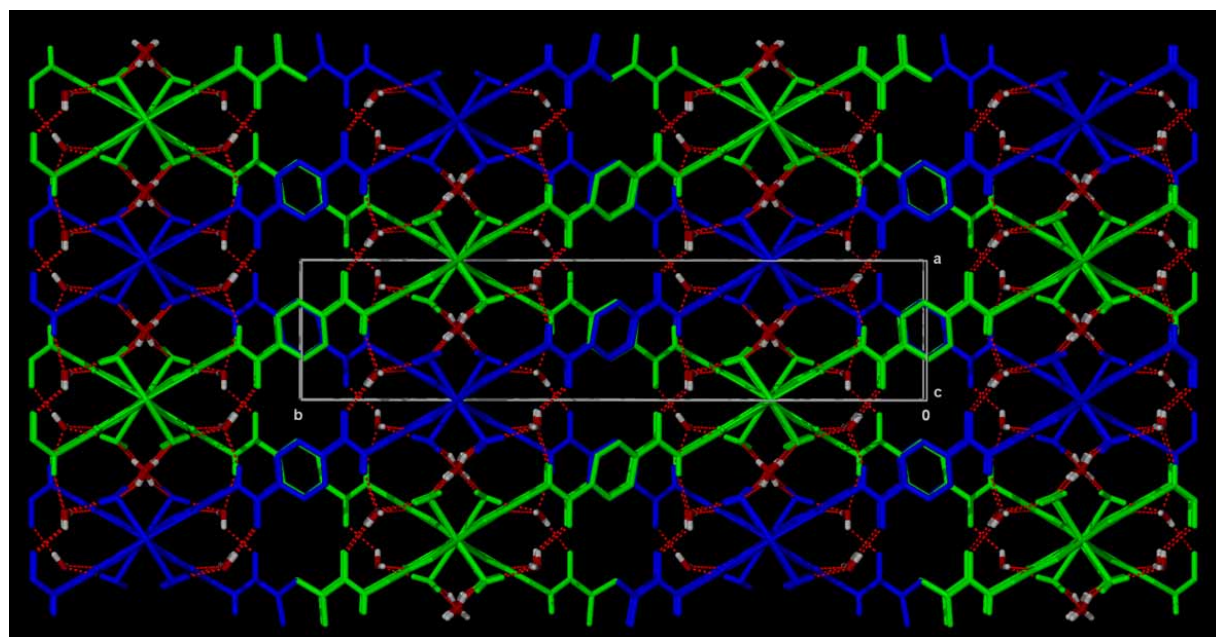
#### Twining and pseudosymmetry for compound 5 :

The structure has been refined in space group  $\text{P2}_1/\text{c}$ . The  $\beta$  angle is close to  $90^\circ$  and the assumption that the crystal was a pseudo-merohedral twin with twin law  $1\ 0\ 0 / 0\ -1\ 0 / 0\ 0\ -1$  and refined BASF = 0.348(3) reduced R from 0.08 to its final value of 0.055. The resulting structure has Pb and O(5W) nearly at  $y = \frac{1}{4}$  which defines a pseudosymmetric diad axis operation  $-x, \frac{1}{2}-y, z$ . The refinement was not without its problems. Uij of four C atoms were constrained to near isotropic values to prevent them going non-positive definite. Other Uij are physically unreasonable and it is clear that correction for absorption is only partly successful. The alternative hypothesis that the structure is really orthorhombic, space group

Pccb, gives  $R$  (all data) = 0.11. Refinement is unstable and fails to converge satisfactorily. Also the experimental  $\beta$  value of  $90.331(4)^\circ$  rules out orthorhombic metric symmetry. Both O(2W) and one O(3W) hydrogen atoms were not observed in difference maps and were placed to give plausible hydrogen bond arrangements.

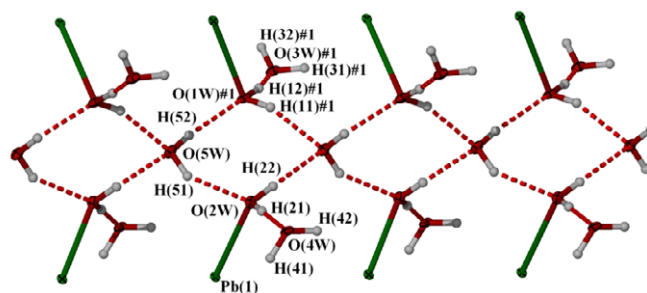


**Figure S1.** The D5 water pentamer formed in **4**. Symmetry operations to generate equivalent atoms: #4,  $x-1/2, y-1/2, z$ ; #6,  $-x+1, y, -z+1/2$ ; #7,  $-x+3/2, y-1/2, -z+1/2$ .



**Figure S2.** A packing diagram of **5** showing the lattice water molecules connecting the two pts interpenetrating nets.

Interestingly, an  $T4(1)^{18}$  infinite water tape is observed in **5**. The individual tetrameric clusters are bridged along the  $c$  axis by two water molecules O1W and O2W that lie in a plane perpendicular to that containing the four water molecules forming the tetramer. The data presented in Table S5 suggest that the hydrogen-bonding interaction of O1W is equal to O2W. Water molecule O(5W) forms four hydrogen bonds with four terminal waters from four different lead centres, while O1W and O2W are involved in forming two hydrogen bonds, each one, with two different O5W molecules and one hydrogen bond with the other lattice water molecules O3W and O4W, respectively, since they belong to lead's environment. The O  $\cdots$  O distances are measured to be  $O(2W)\cdots O(5W) = 2.767 \text{ \AA}$ ,  $O(2W)\cdots O(5W) = 2.799 \text{ \AA}$ ,  $O(1W)\cdots O(5W) = 2.804 \text{ \AA}$  and  $O(1W)\cdots O(5W) = 2.818 \text{ \AA}$ . The average O  $\cdots$  O distance is  $2.797(5) \text{ \AA}$  within the "bridged tetramer" is significantly shorter than those observed previously  $2.833 \text{ \AA}^{21h}$ ,  $2.874 \text{ \AA}^{21c}$ ,  $2.887 \text{ \AA}^{21b}$  and  $3.004 \text{ \AA}^{21a}$  and comparable to those  $2.790^{21f}$ ,  $2.794^{21d}$  and  $2.803^{21e}$  and among the average of those in other known cases ( $2.768\text{--}2.834$ ).<sup>21g,22c-g</sup> The oxygen atoms involved in the formation of the cyclic tetramer lie in a plane, with nonbonding distances  $O(1W)\cdots O(2W) = 3.823 \text{ \AA}$  and  $O(5W)\cdots O(5W) = 4.084 \text{ \AA}$  and an  $O(1W)\text{--}O(5W)\text{--}O(2W)$  angle of  $86.4^\circ$ . As it may appear from Figure 9 that chain is formed by "corner-sharing tetramers", where the following tetrameric units lie in two perpendicular planes and not as "bridged tetramers", since the distance between O5W atoms forming the tetramers is always equal to  $4.084 \text{ \AA}$ .



**Fig. S3** The  $T4(1)$  water chain. Symmetry operation to generate equivalent atom :#1,  $x+1$ ,  $y$ ,  $z$ .

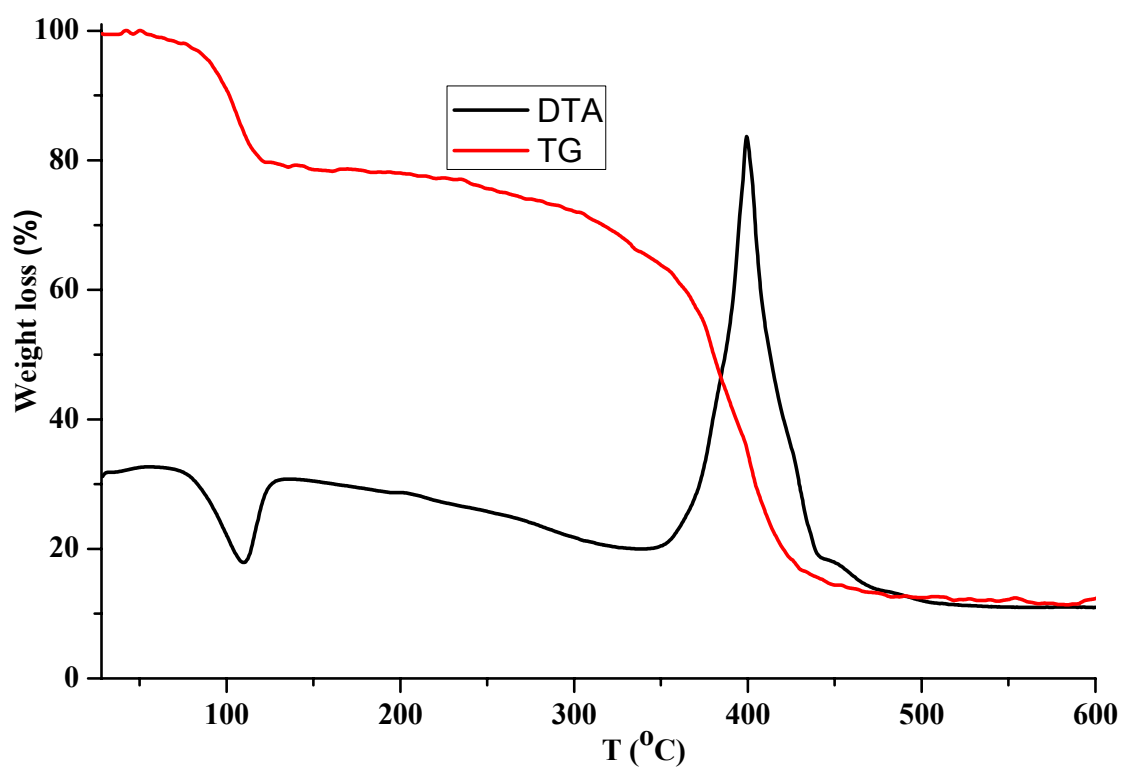


Figure S4 TGA-DTA graphs of compound 1

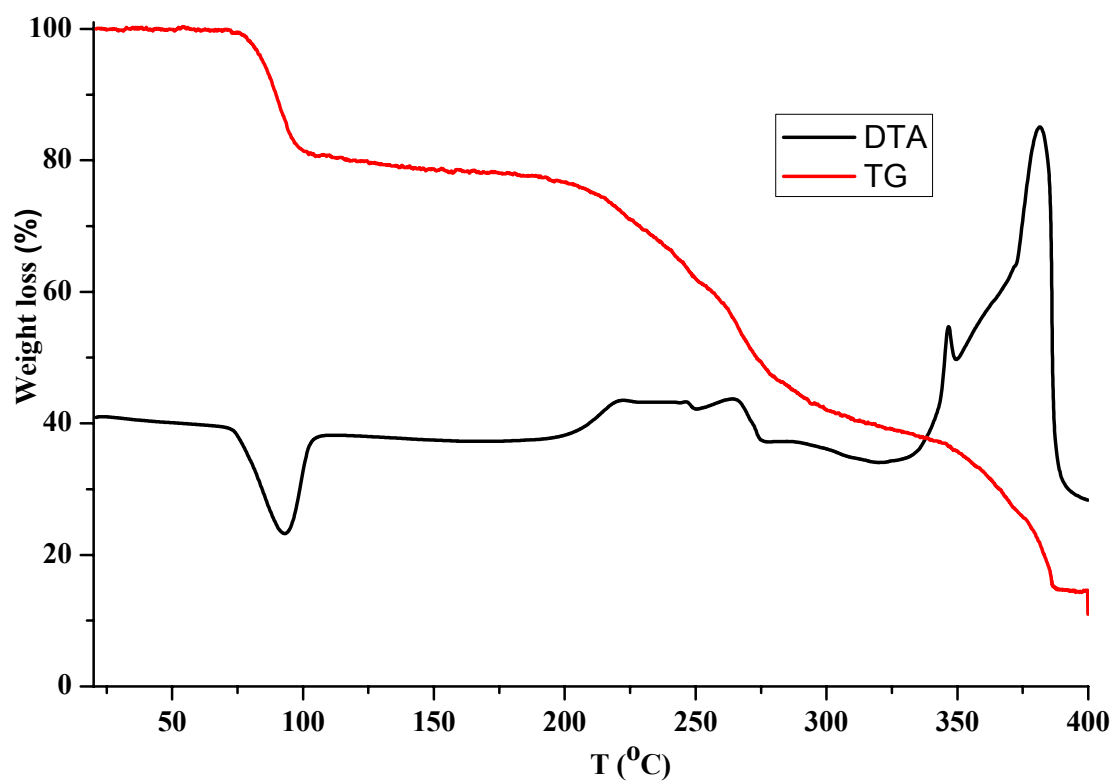


Figure S5 TGA-DTA graphs of compound 2

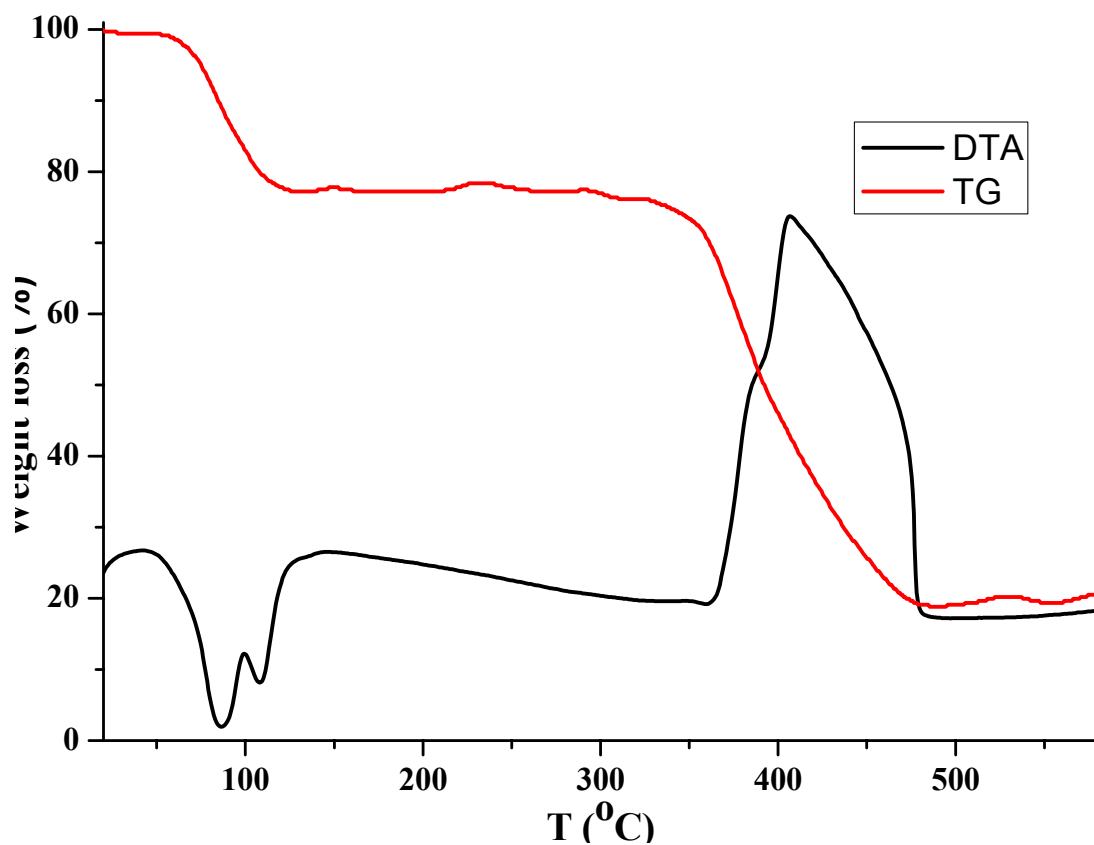


Figure S6 TGA-DTA graphs of compound 3

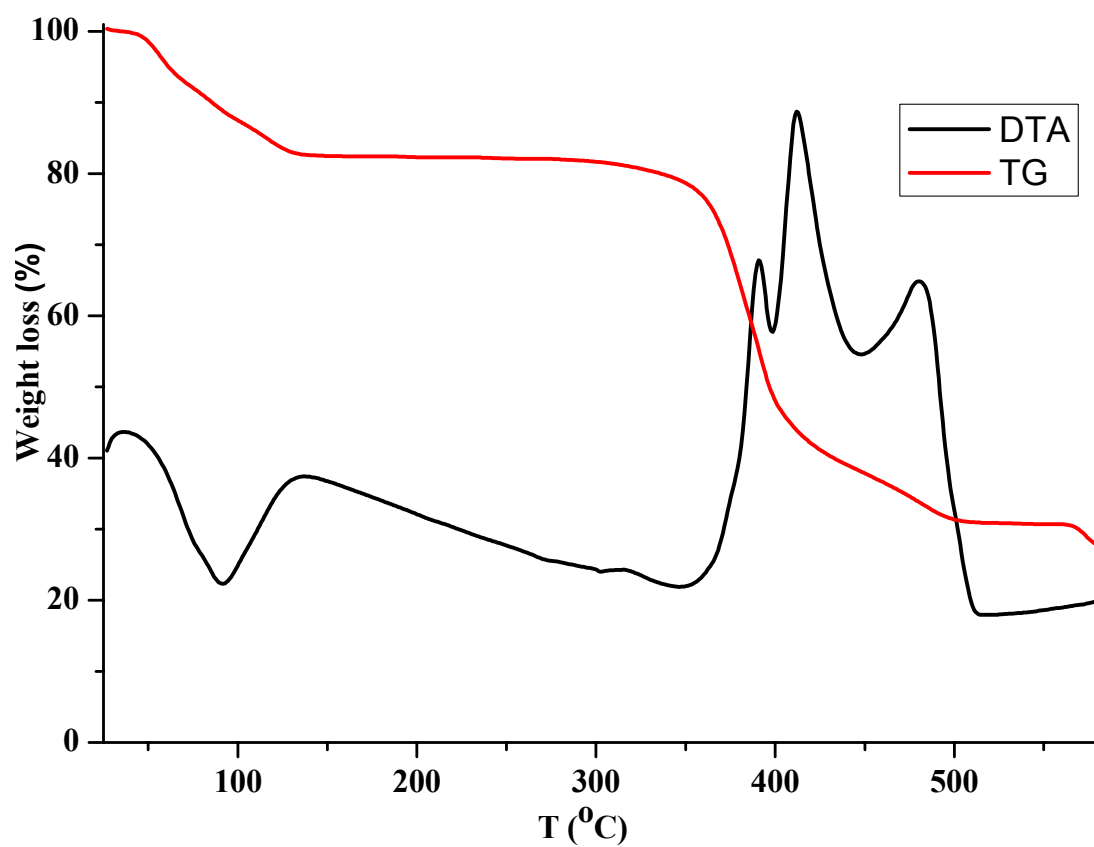


Figure S7 TGA-DTA graphs of compound 4

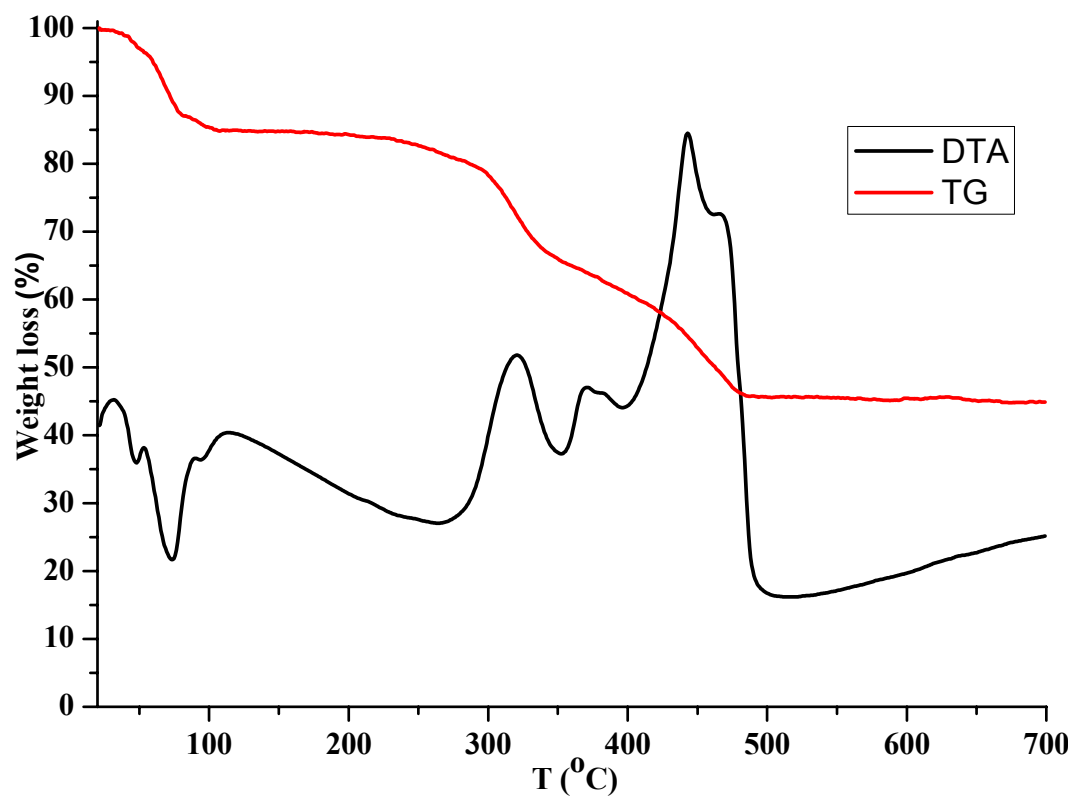


Figure S8 TGA-DTA graphs of compound 5.

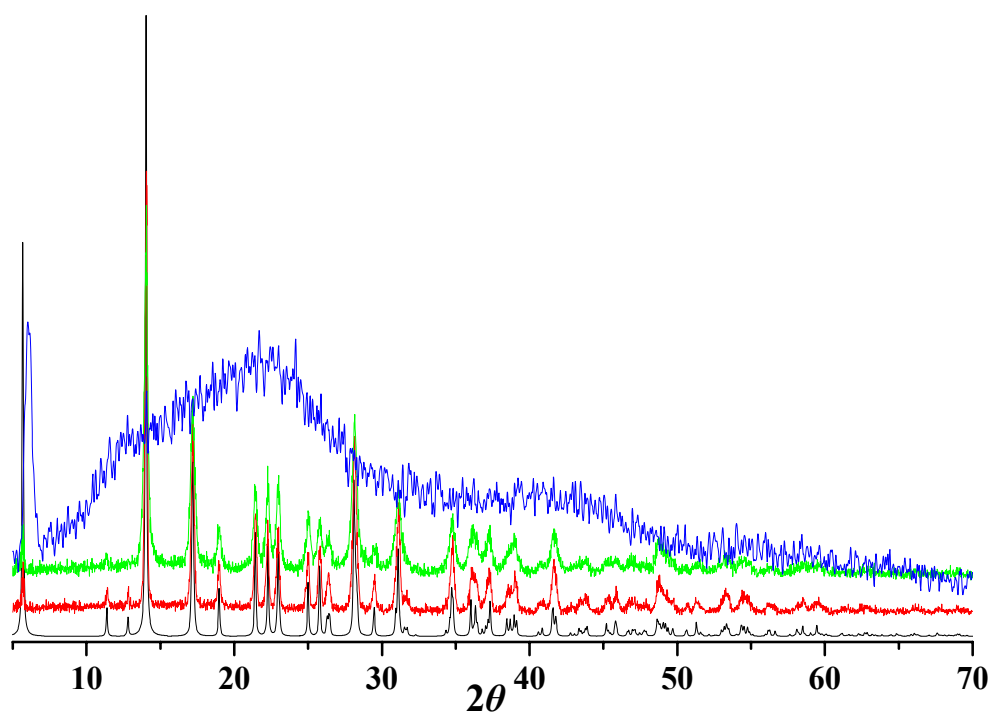
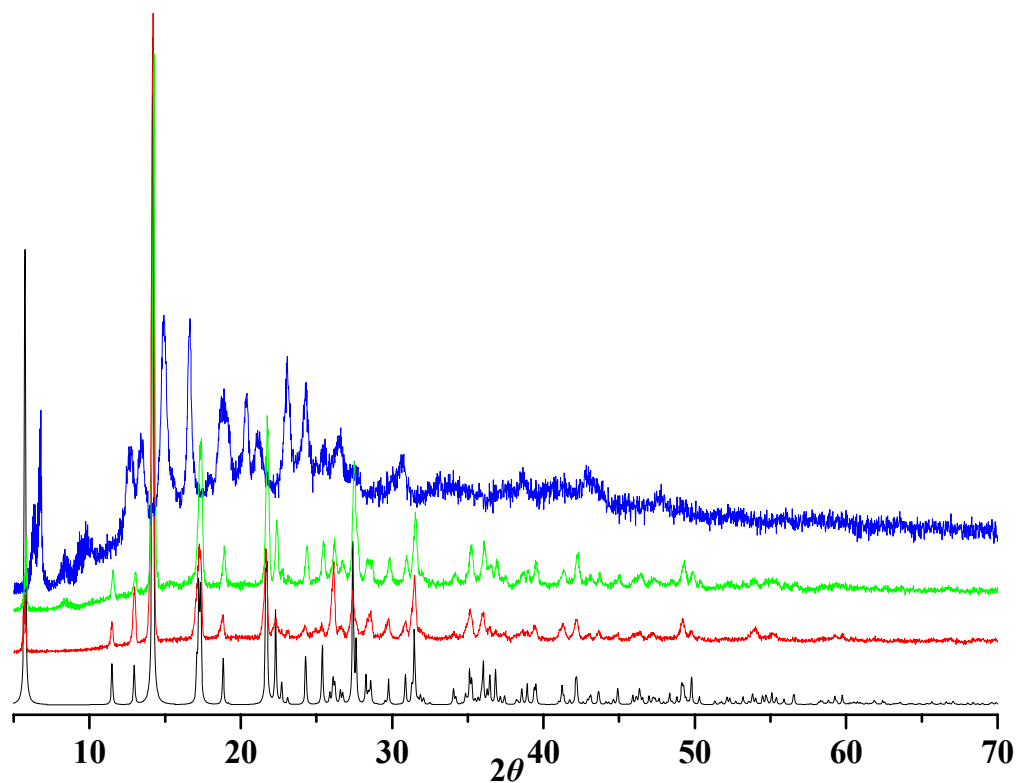
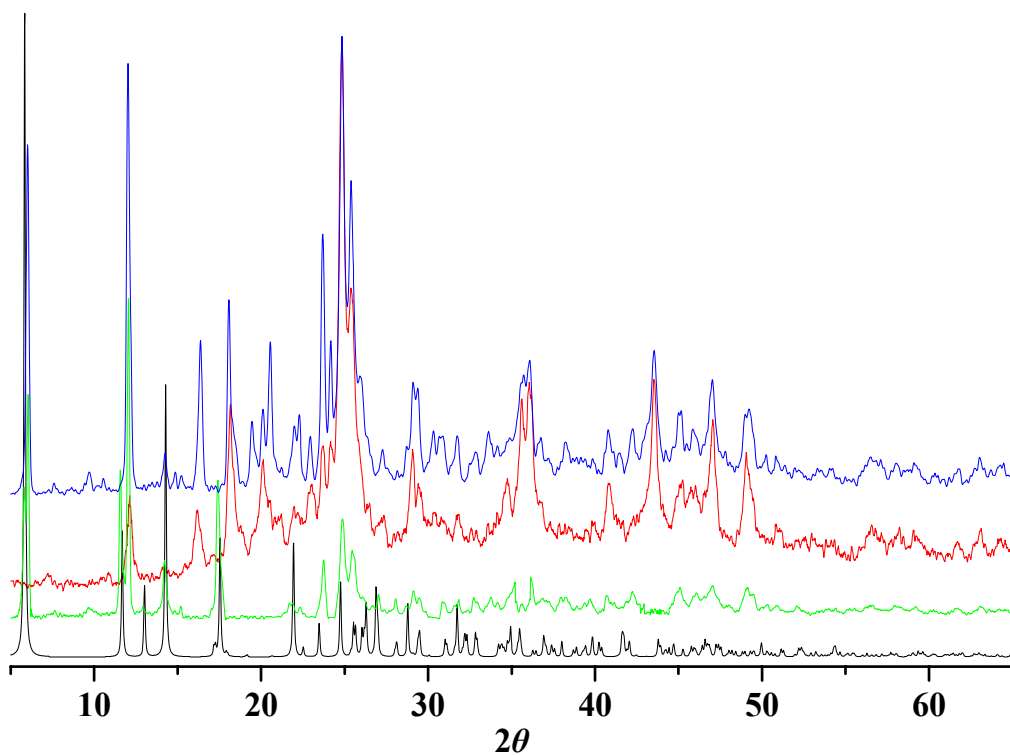


Figure S9 Powder XRD graphs of compound 1 (Black: Simulated from the crystal structure;  
Red: Original Sample; Blue: Dehydrated sample; Green: Rehydrated dry sample)



**Figure S10** Powder XRD graphs of compound **2** (Black: Simulated from the crystal structure; Red: Original Sample; Blue: Dehydrated sample; Green: Rehydrated dry sample)



**Figure S11** Powder XRD graphs of compound **5**. (Black: Simulated from the crystal structure; Green: Original Sample; Red: Dehydrated sample; Blue: Rehydrated dry sample)



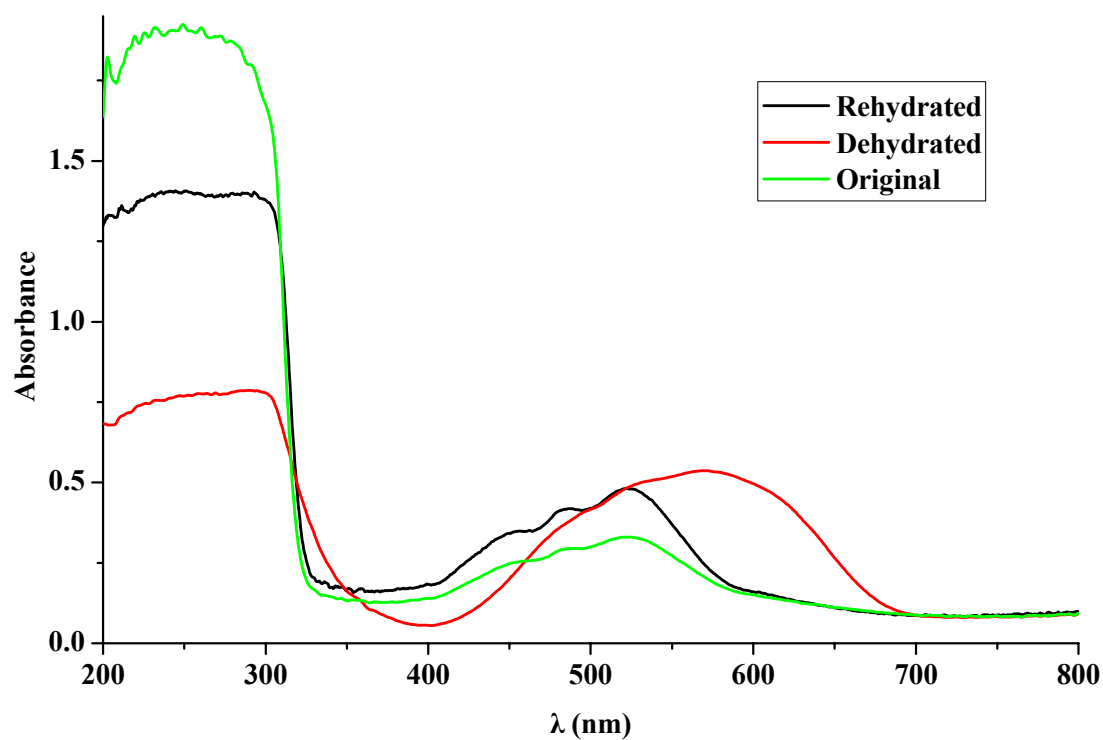


Figure S12 UV - Vis spectra of compounds 1.

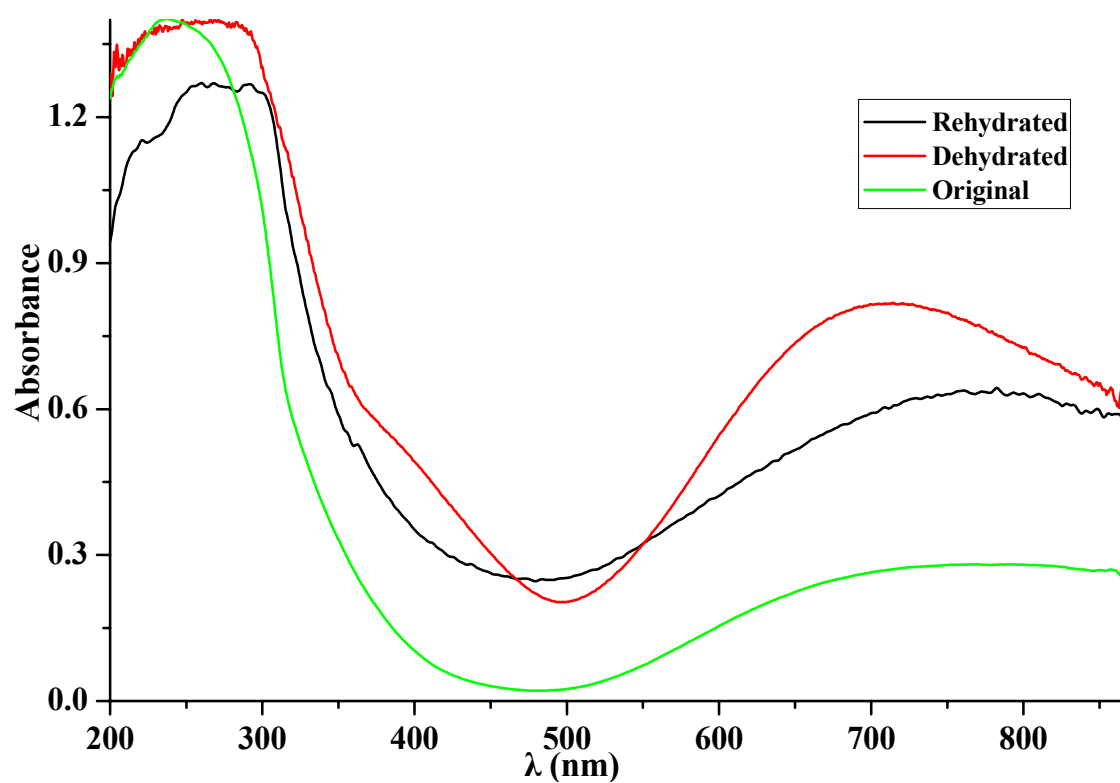
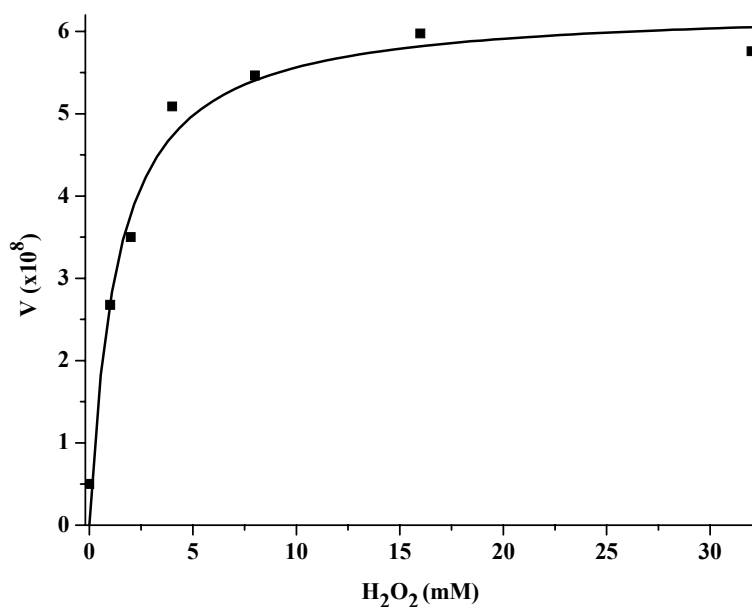
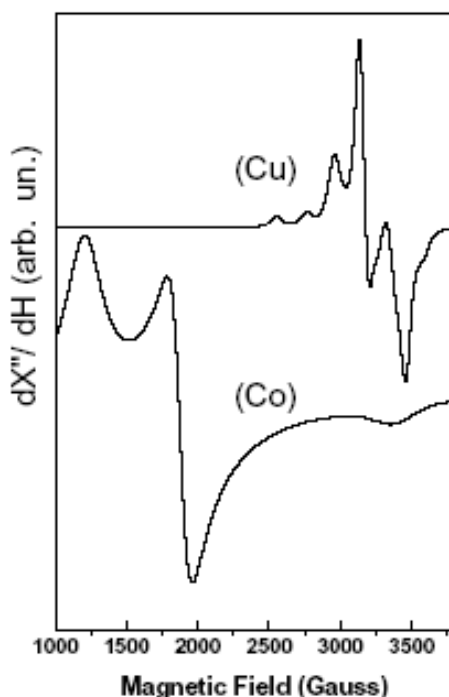


Figure S13 UV - Vis spectra of compounds 2.



**Figure S14** Dependence of the reaction rates in the second phase of DTBQ formation on the concentration of hydrogen peroxide.



**Figure S15** Powder EPR spectrum of **1** (bottom) and **2** (top). Experimental conditions: Temperature 4.3K, microwave frequency, 9.45 GHz, Mod. Ampl. 12.5 Gpp, microwave power 32mW, mod. Frequency 100KHz.

**Table S1.** Hydrogen bonding parameters (Å) for **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H41 $\cdots$ O2 <sup>i</sup>	0.89(5)	1.80(5)	2.652(5)	160(7)
O5—H51 $\cdots$ O6 <sup>ii</sup>	0.85(5)	1.93(5)	2.781(6)	172(7)
O5—H52 $\cdots$ O1 <sup>iii</sup>	0.92(5)	1.82(5)	2.727(5)	169(6)
O6—H61 $\cdots$ O3	0.89(7)	1.88(8)	2.723(6)	157(8)
O6—H62 $\cdots$ O2 <sup>iii</sup>	0.89(7)	2.19(8)	2.916(7)	138(8)
N1—H1 $\cdots$ O6 <sup>iv</sup>	0.92(7)	2.07(7)	2.896(7)	149(6)

Symmetry codes: (i)  $x-1/2, -y, z$ ; (ii)  $-x+2, -y, -z+2$ ; (iii)  $-x+3/2, y, -z+2$ ; (iv)  $x, y+1, z$

**Table S2.** Hydrogen bonding parameters (Å) for **2**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H41 $\cdots$ O2 <sup>i</sup>	0.81(5)	1.92(5)	2.675(3)	153(5)
O5—H51 $\cdots$ O6 <sup>ii</sup>	0.82(5)	1.96(5)	2.790(4)	175(4)
O5—H52 $\cdots$ O1 <sup>iii</sup>	0.80(5)	1.92(5)	2.719(4)	170(x4)
O6—H61 $\cdots$ O3	0.78(5)	1.94(5)	2.719(4)	169(5)
O6—H62 $\cdots$ O2 <sup>iii</sup>	0.71(5)	2.25(5)	2.896(4)	150(5)
N1—H1 $\cdots$ O6 <sup>iv</sup>	0.78(3)	2.15(3)	2.888(5)	156(3)

Symmetry codes: (i)  $x-1/2, -y, z$ ; (ii)  $-x+2, -y, -z+2$ ; (iii)  $-x+3/2, y, -z+2$ ; (iv)  $x, y+1, z$

**Table S3** Hydrogen bonding parameters (Å) for **3**

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ OW5	0.82(4)	2.18(4)	2.873(4)	142(4)
N2—H2N $\cdots$ OW6	0.87(4)	2.19(4)	2.920(4)	142(4)
OW1—H1W $\cdots$ O1 <sup>iii</sup>	0.86(4)	1.90(4)	2.738(3)	166(4)
OW1—H2W $\cdots$ OW2 <sup>iv</sup>	0.72(4)	2.26(5)	2.975(4)	167(5)
OW2—H3W $\cdots$ OW6 <sup>v</sup>	0.86(5)	1.90(5)	2.758(4)	171(4)
OW2—H4W $\cdots$ OW3 <sup>iii</sup>	0.69(4)	2.16(4)	2.827(3)	161(5)
OW3—H5W $\cdots$ O2 <sup>vi</sup>	0.82(4)	2.04(4)	2.849(3)	167(5)
OW3—H6W $\cdots$ O6 <sup>vi</sup>	0.87(4)	1.93(4)	2.713(4)	149(4)
OW3—H6W $\cdots$ OW1 <sup>vi</sup>	0.87(4)	2.41(4)	2.875(3)	114(3)
OW4—H7W $\cdots$ O5 <sup>iii</sup>	0.86(4)	2.03(4)	2.865(3)	163(4)
OW4—H8W $\cdots$ OW5 <sup>v</sup>	0.80(4)	1.94(4)	2.730(4)	167(5)
OW5—H9W $\cdots$ O6 <sup>vii</sup>	0.88(4)	1.99(5)	2.784(4)	149(4)
OW5—H10W $\cdots$ O3 <sup>viii</sup>	0.80(4)	1.96(5)	2.735(4)	163(5)
OW6—H11W $\cdots$ O4 <sup>viii</sup>	0.74(4)	2.02(5)	2.759(4)	176(5)
OW6—H12W $\cdots$ O2 <sup>vii</sup>	0.73(4)	2.12(5)	2.781(4)	150(5)

Symmetry codes: (iii)  $x+1/2, -y+1/2, z+1/2$ ; (iv)  $x-1/2, -y+1/2, z+1/2$ ; (v)  $x+1, y, z$ ;  
 (vi)  $x+1/2, -y+1/2, z-1/2$ ; (vii)  $x-1/2, -y+1/2, z-1/2$ ; (viii)  $x-1, y, z$ .

**Table S4** Hydrogen bonding parameters (Å) for **4**

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H1W $\cdots$ O6 <sup>iii</sup>	0.82(3)	1.92(3)	2.736(2)	172(2)
O4—H2W $\cdots$ O1 <sup>iv</sup>	0.81(3)	1.84(3)	2.645(3)	168(3)
O6—H3W $\cdots$ O2	0.78(3)	2.12(3)	2.842(3)	154(3)
O6—H4W $\cdots$ O3 <sup>v</sup>	0.75(3)	2.02(3)	2.774(2)	175(3)
O5—H5W $\cdots$ O4 <sup>vi</sup>	0.82(3)	1.88(3)	2.690(2)	173(3)
N1—H1N $\cdots$ O6 <sup>vii</sup>	0.83(3)	2.16(3)	2.908(3)	150(2)

Symmetry codes: (iii)  $x+1/2, y+1/2, z$ ; (iv)  $x+1/2, y-1/2, z$ ; (v)  $x-1/2, y-1/2, z$ ; (vi)  $-x+3/2, y-1/2, -z+1/2$ ; (vii)  $x-1/2, y+1/2, z$ .

**Table S5** Hydrogen bonding parameters (Å) for **5**

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O4W <sup>v</sup>	0.88	2.06	2.875(7)	153
N2—H2 $\cdots$ O3W <sup>vi</sup>	0.88	2.05	2.875(7)	155
O1W—H11 $\cdots$ O5W <sup>vii</sup>	0.84	2.01	2.818(6)	162
O1W—H12 $\cdots$ O3W	0.84	1.95	2.755(7)	162
O2W—H21 $\cdots$ O4W	0.84	1.92	2.763(6)	180
O2W—H22 $\cdots$ O5W <sup>ii</sup>	0.84	1.93	2.768(6)	180
O3W—H31 $\cdots$ O2 <sup>ii</sup>	0.84	2.06	2.757(7)	140
O3W—H32 $\cdots$ O6	0.84	1.93	2.768(7)	180
O4W—H41 $\cdots$ O3	0.84	2.09	2.727(6)	132
O4W—H42 $\cdots$ O5 <sup>ii</sup>	0.84	1.96	2.767(7)	160
O5W—H51 $\cdots$ O2W	0.84	2.04	2.800(6)	150
O5W—H52 $\cdots$ O1W <sup>vi</sup>	0.84	1.98	2.804(6)	168

Symmetry codes: (v)  $x-1, y, z$ ; (vi)  $x+1, y, z$ ; (vii)  $x-1, -y+1/2, z-1/2$ ; (ii)  $x, -y+1/2, z-1/2$ .