Electronic Supporting Information

Deuterium Substitution Effects on the Structural and Magnetic Phase Transitions of a Hydrogen-Bonded Coordination Polymer, Bis(glycolato)copper(II)

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1. Crystal Parameters.

Table S1. Crystal parameters of **1-3**.

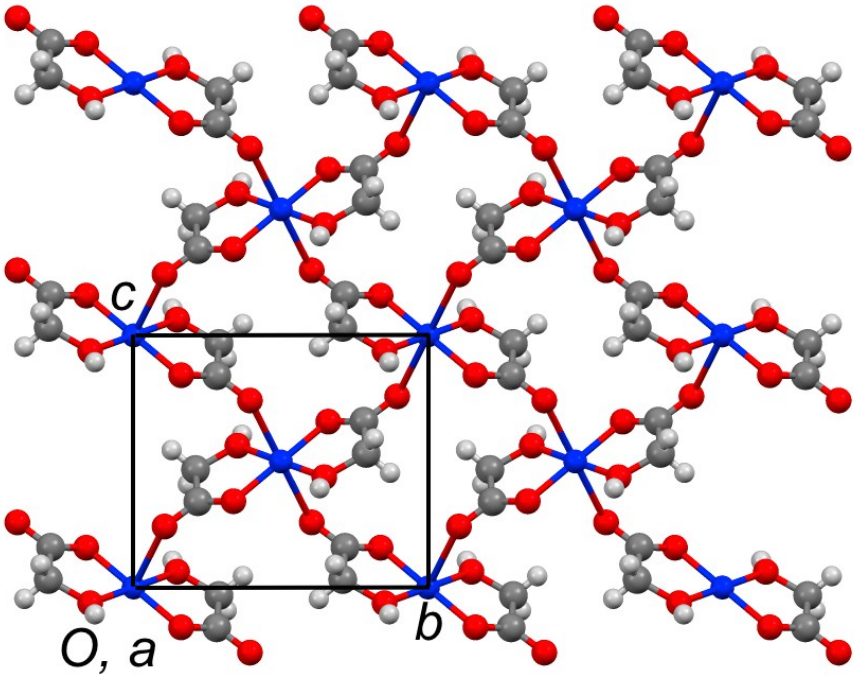
	1[a]	**1**[a]	**2**	□**2**	**3**	**3**
Phase	LT	HT	LT	HT	LT	HT
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	5.178(4)	5.0908(8)	5.1849(14)	5.0794(5)	5.201(4)	5.113(4)
b / Å	7.208(5)	8.6939(12)	7.2517(16)	8.6924(8)	7.356(5)	8.672(6)
c / Å	8.889(7)	7.7300(14)	8.875(3)	7.7046(8)	8.839(6)	7.753(5)
β / °	100.840(9)	107.141(8)	100.857(5)	107.338(3)	101.169(7)	106.996(10)
V / Å^3	325.8(5)	326.93(10)	327.72(16)	324.72(6)	331.8(4)	328.8(4)
Z	2	2	2	2	2	2
$R_1(I > 2\sigma)$	0.0457	0.0255	0.0213	0.0228	0.0268	0.0293
wR_2(All data)	0.1166	0.0640	0.0596	0.0667	0.0694	0.0724
T / K	150	250	230	230	290	290
CCDC Number	950567	950568	1493335	1493336	1493337	1493338

a) S. Yoneyama, T. Kodama, K. Kikuchi, Y. Kawabata, K. Kikuchi, T. Ono, Y. Hosokoshi, and W. Fujita, *CrystEngComm* 2013, **15**, 10193.

Table S2. Crystal parameters of the HT phases in the partially deuterated samples.

	25 %	50 %	75 %
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	5.103(3)	5.1096(19)	5.111(6)
b / Å	8.678(5)	8.680(3)	8.6823(10)
c / Å	7.752(5)	7.757(3)	7.748(9)
β / °	106.870(8)	160.817(4)	106.767(16)
V / Å^3	328.5(4)	329.3(2)	329.2(6)
Z	2	2	2
$R_1(I > 2\sigma)$	0.0280	0.0266	0.0261
wR_2(All data)	0.0695	0.0669	0.0643
T / K	290	290	290
CCDC Number	1507357	1507358	1507359

(a)



(b)

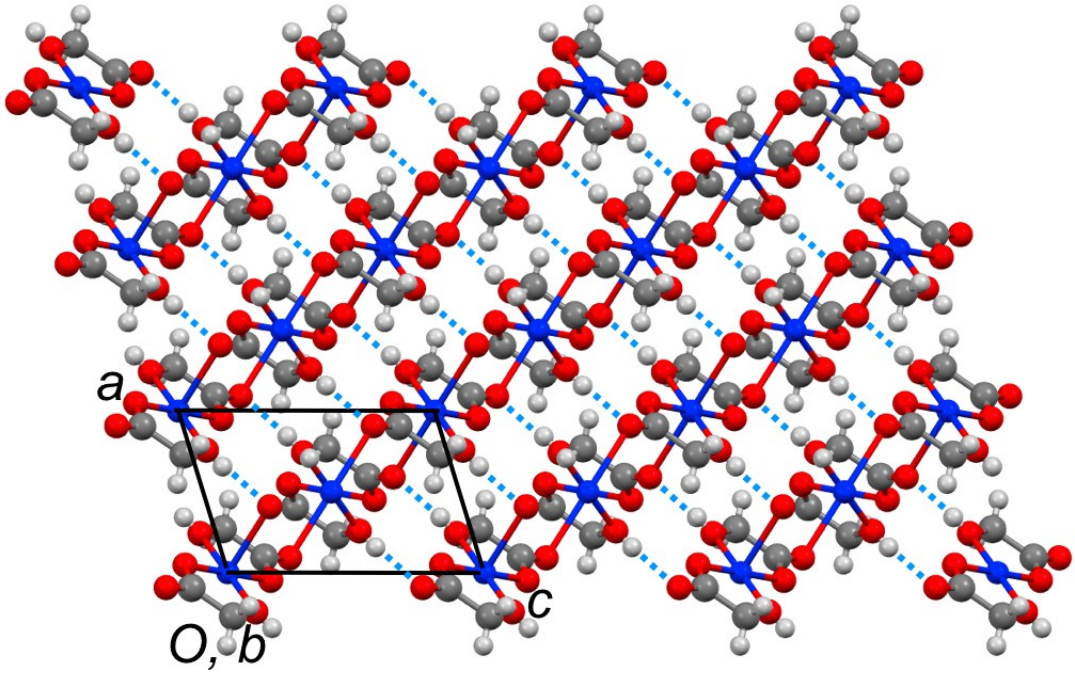
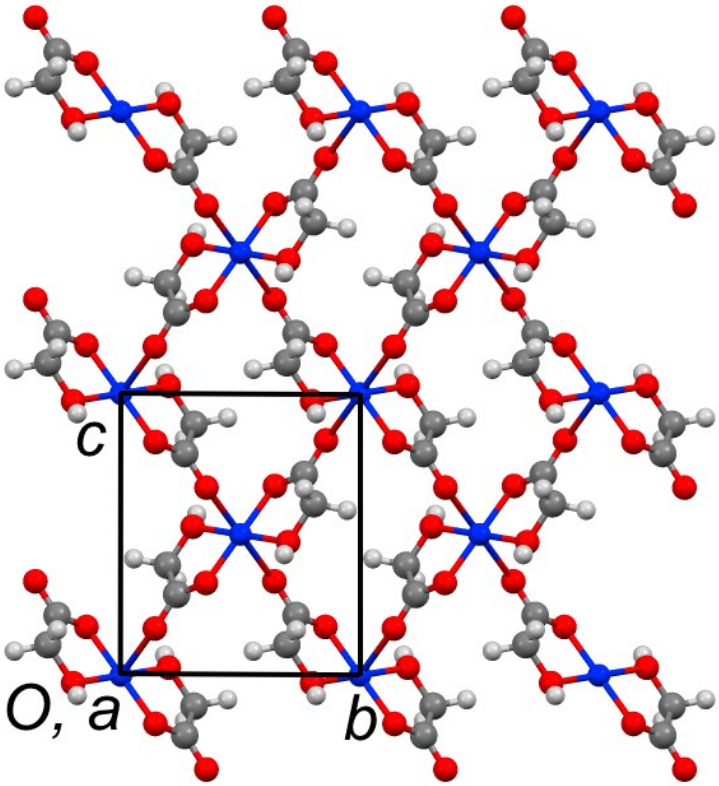


Figure S1. Crystal structure of the HT phase in **3** at 290 K. (a) Projection of the coordination network toward the *a* axis. (b) Stacking fashion of the coordination sheets toward the *b* axis. There are hydrogen bonds between the coordination sheets (blue broken lines). The O•••O distance was 2.593(4) Å.

(a)



(b)

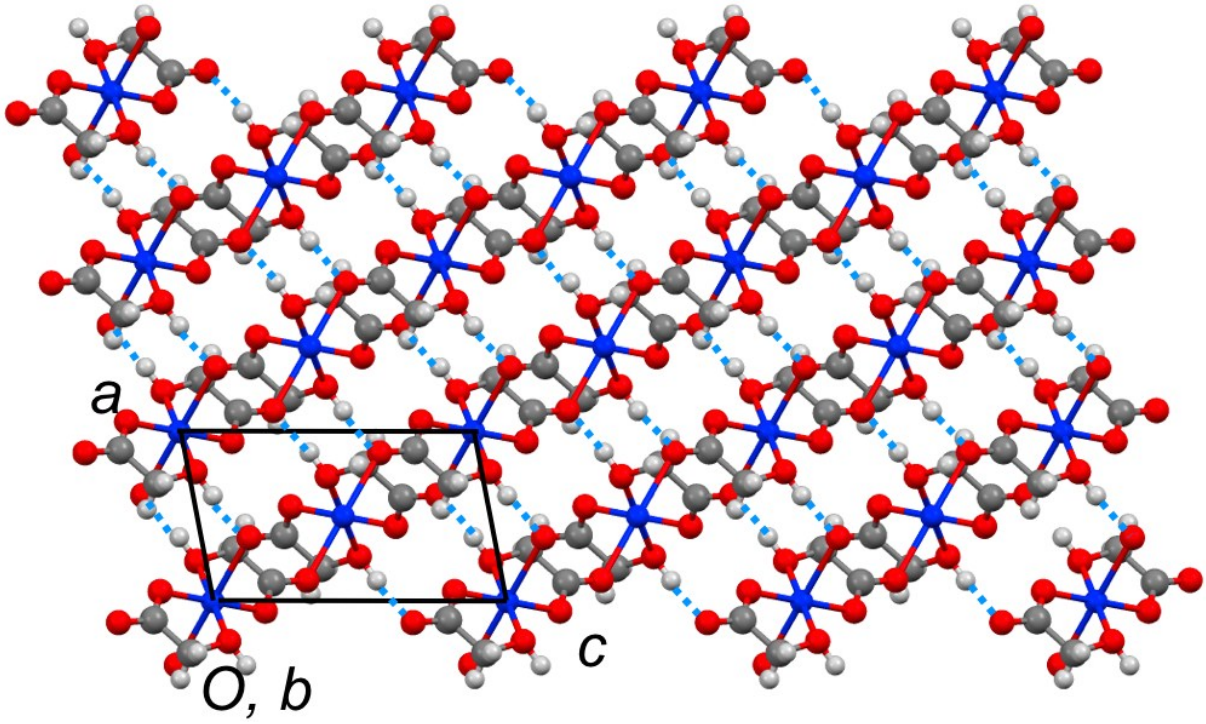


Figure S2. Crystal structure of the LT phase in **3** at 290 K. (a) Projection of the coordination network toward the *a* axis. (b) Stacking fashion of the coordination sheets toward the *b* axis. There are hydrogen bonds between the coordination sheets (blue broken lines). The O•••O distance was 2.597(3) Å.

2. IR Spectra

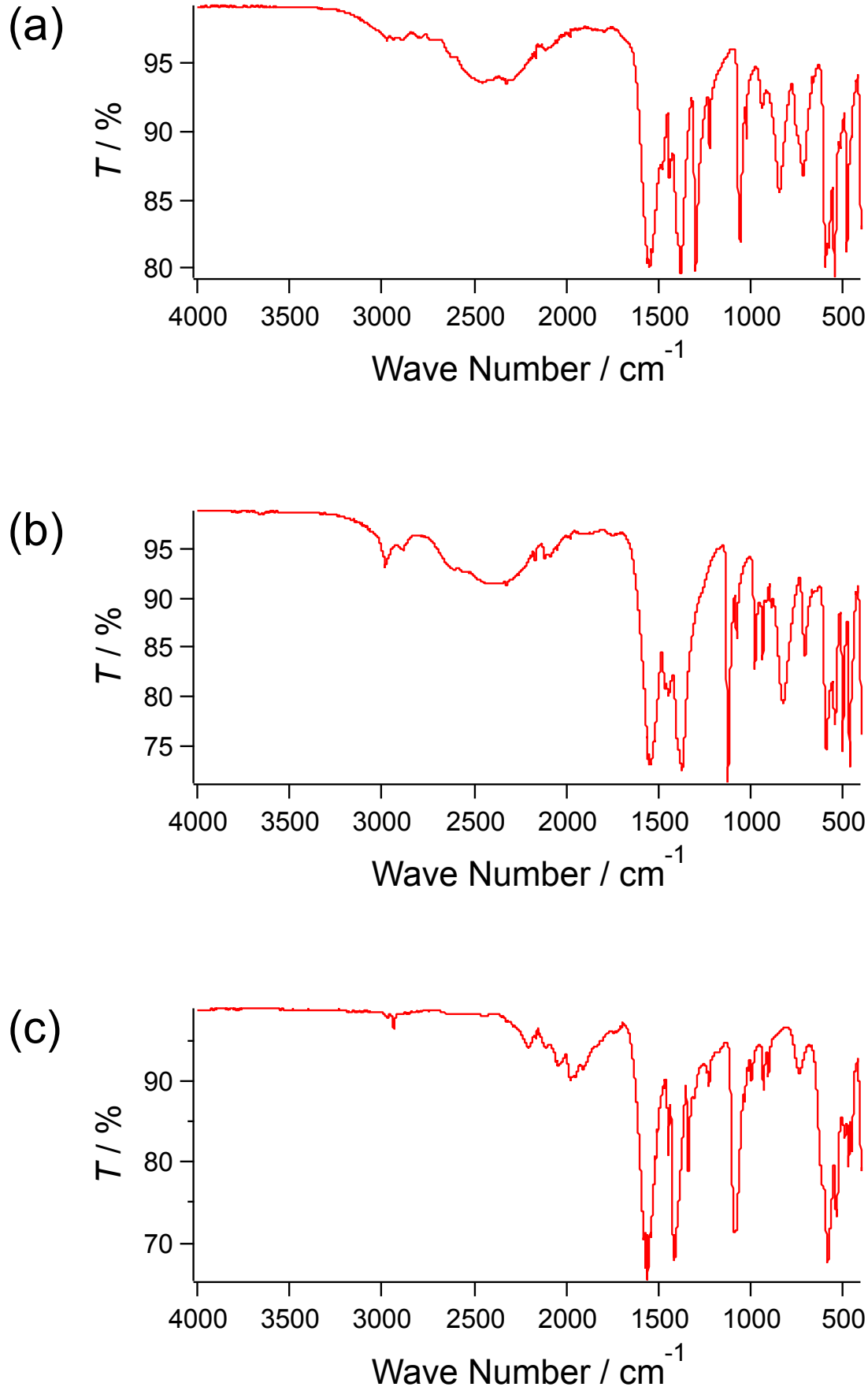


Figure S3. IR spectra of the HT phase in for **1**, (b) **2**, and (c) **3** at 290 K.

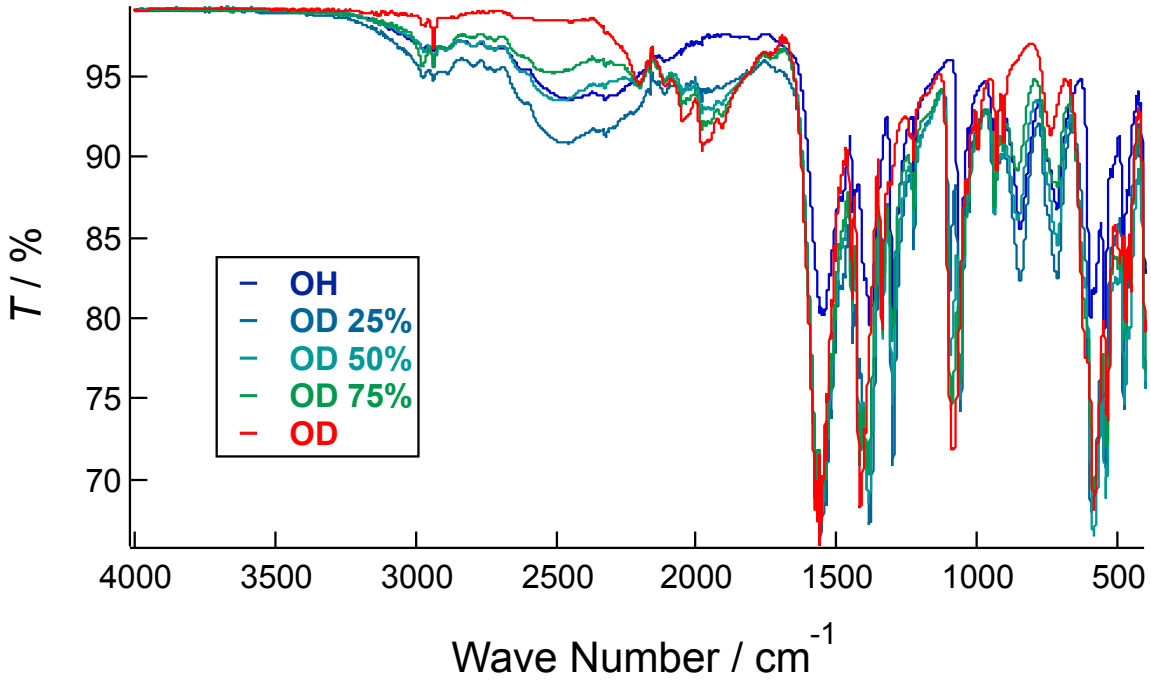


Figure S4. IR spectra of the HT phase for **1**, 25 %, 50 %, 75 % deuterated derivatives, and **3** at 290 K.

2. Magnetic Analyses

The analytical expression for the paramagnetic susceptibility of the isolated two-dimensional square lattice model is given as

$$\chi_{2D} = \frac{C}{T}[1 + \sum_{n \geq 1}(\alpha_n / 2^n n!) y^n] \qquad (1),$$

where C is the Curie constant, $y = J/(k_B T)$, J is half of the intermolecular exchange coupling constant, n is a positive integer number, and the coefficients a_n are as follows: $a_1 = 4$, $a_2 = 16$, $a_3 = 64$, $a_4 = 416$, $a_5 = 4544$, $a_6 = 23488$, $a_7 = -207616$, $a_8 = 4205056$, $a_9 = 198295552$, and $a_{10} = -2574439424$.[1] On the basis of Eq. (1), the magnetic parameters, $g = 2.17$ and $2J/k_B = +1.2$ K for **2**, and $g = 2.08$ and $2J/k_B = +1.3$ K for **3**, respectively, were estimated by curve fitting, as shown by the solid curves in Figs. 2(a) and (b).

3. DSC data

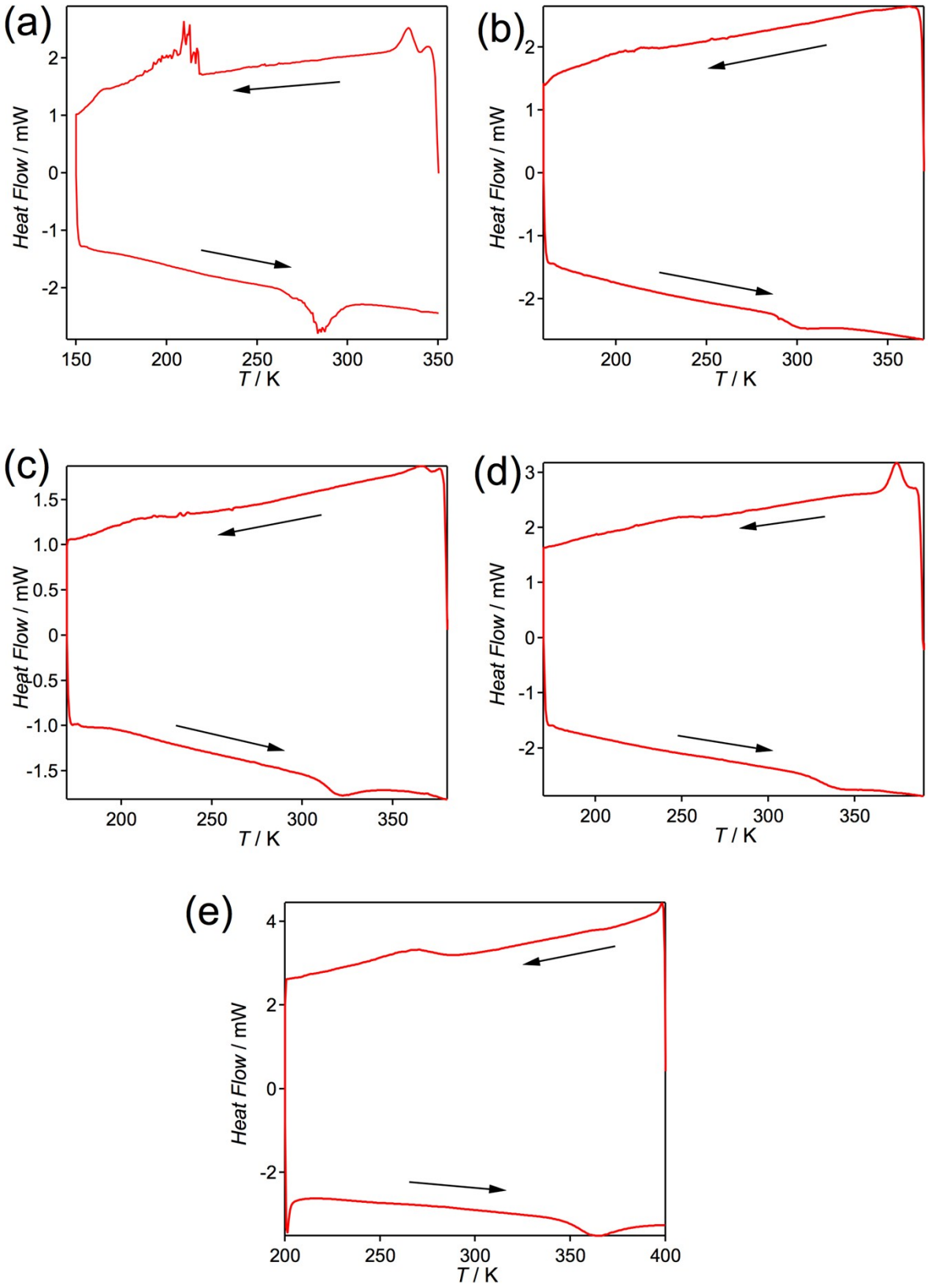


Figure S5. DSC curves for (a) **1**, (b) 25 % deuterated, (c) 50 % deuterated, (d) 75 % deuterated samples, and (e) **3**.

4. Difference Fourier Maps.

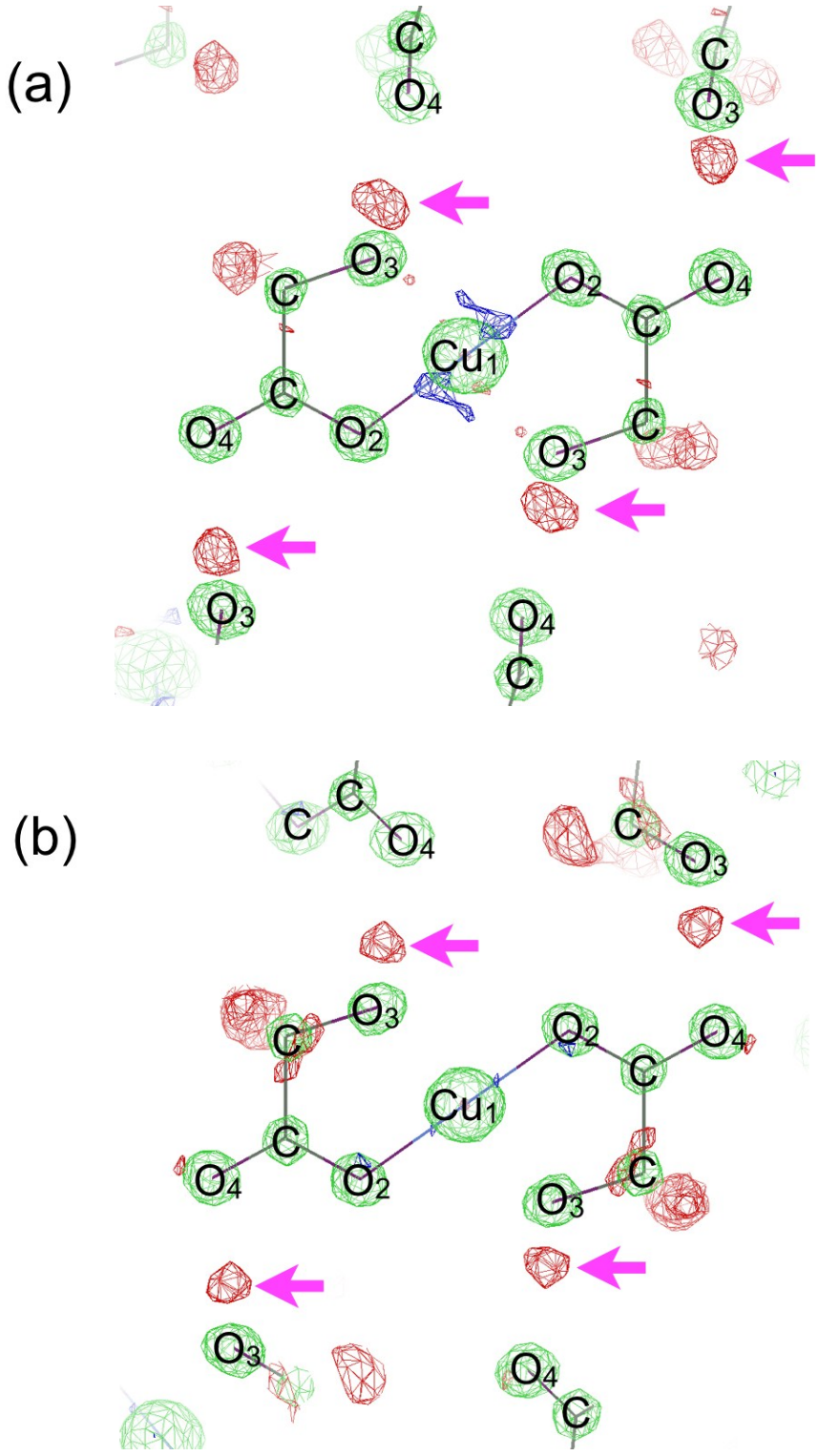


Figure S6. Fourier electron density maps of **3** in (a) the LT and (b) the HT phases. Structure models without hydrogen and deuterium atoms were used in the Fourier synthesis. The green mesh shows the F_o map (F_o: observed structure factor). The red and blue meshes show the positive and negative F_o-F_c maps, respectively (F_c: calculated structure factor). The arrows show residual electron density peaks on hydrogen bonds between O3 and O4.

5. H-bonded Magnets.

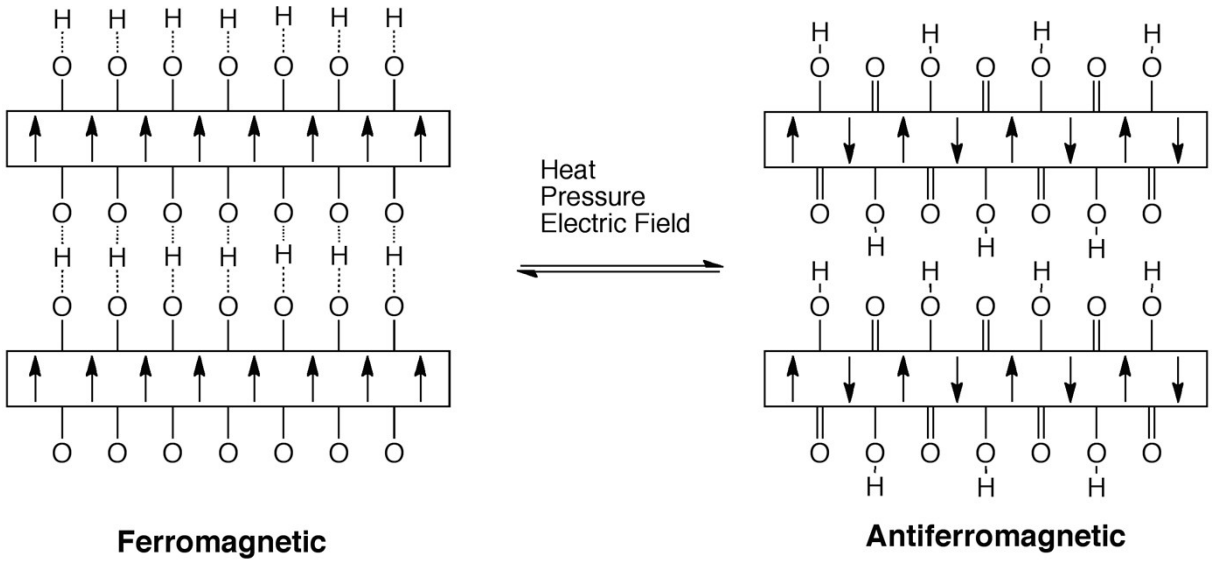


Figure S7. Schematic presentation of H-bonded Magnets.

6. References

1. G. A. Baker, H. E. Gilbert, J. Eve, G. S. Rushbrooke, *Phys. Lett. A* 1967, **25**, 207.