Electronic supplementary information (ESI)

Synthesis and stabilization of a hypothetical porous framework based on a classic flexible metal carboxylate cluster

Yong-Sheng Wei, Pei-Qin Liao, Jian-Qiang Shen, Wei Xue, Jie-Peng Zhang, and Xiao-Ming Chen*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

*To whom correspondence should be addressed.

E-mail: zhangjp7@mail.sysu.edu.cn (J.-P. Zhang)

Table S1. Crystallographic Data and Structural Refinements.

Complex	**1**	**2**	**3**
Formula	$C_{84}H_{50}N_{12}Ni_6O_{26}$	$C_{84}H_{51.5}N_6Ni_9O_{41}$	$C_{84}H_{51.5}Fe_{7.5}N_6O_{39.5}$
Formula weight	1995.62	2329.20	2191.62
Temperature (K)	150	213	213
Crystal system	Cubic	Cubic	Cubic
Space group	*Fm*-3*m*	*Fm*-3*m*	*Fm*-3*m*
a/Å	41.5216(3)	41.286(2)	41.258(3)
V/Å^3	71585.0(16)	70375(12)	70230(15)
Z	16	16	16
ρ_{calc} (g cm^{-3})	0.741	0.879	0.829
μ (mm^{-1})	1.031	1.453	1.273
$R_1{}^a$ ($I > 2\sigma$)	0.0656	0.0628	0.1120
$wR_2{}^b$ (all data)	0.2421	0.2235	0.3774
GOOF	1.036	1.001	1.065

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

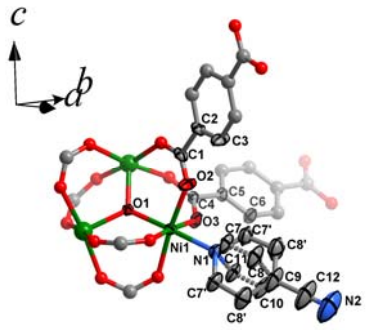

Figure S1(a). Perspective views of the coordination environments in **1**. Hydrogen atoms are omitted for clarity (Thermal ellipsoids are drawn for the asymmetric units with probability 30%). Dashed bonds represent another part of the 2-fold disordered pyridyl group.

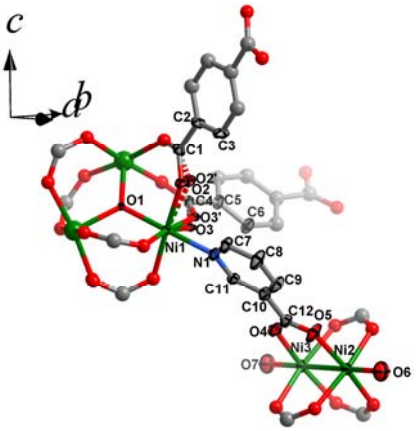

Fig. S1(b). Perspective views of the coordination environments in **2**. Hydrogen atoms are omitted for clarity (Thermal ellipsoids are drawn for the asymmetric units with probability 30%). Dashed bonds represent another part of the 2-fold disordered carboxylate groups.

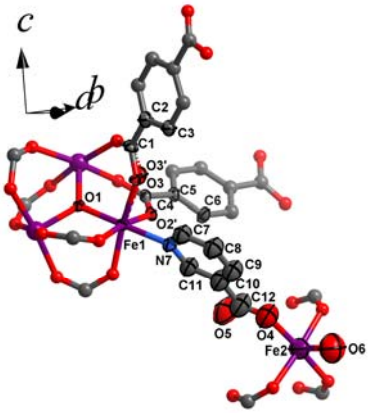

Fig. S1(c). Perspective views of the coordination environments in **3**. Hydrogen atoms are omitted for clarity (Thermal ellipsoids are drawn for the asymmetric units with probability 20%). Dashed bonds represent another part of the 2-fold disordered carboxyl groups.

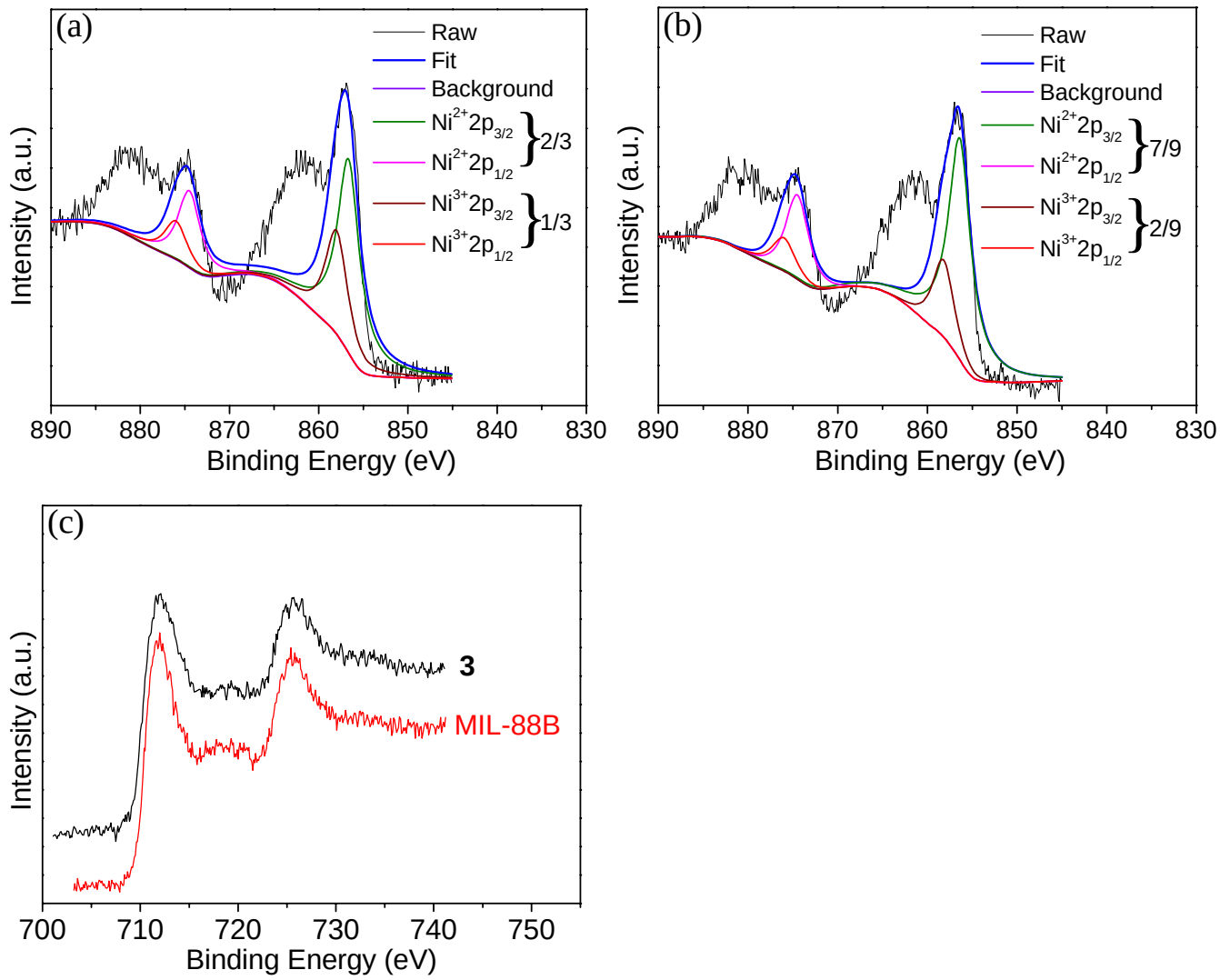

Fig. S2. XPS spectra of (a) **1**, (b) **2** and (c) **3**.

Table S2. Results of the fitting of the Ni 2p X-ray Photoelectron Spectra.

Compound		Ni(II)		Ni(III)	
	Spectral line	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$
1	Binding Energy (eV)	856.6	874.5	858.0	876.0
	Area (%)	2/3		1/3	
2	Binding Energy (eV)	856.4	874.5	858.2	876.0
	Area (%)	7/9		2/9	

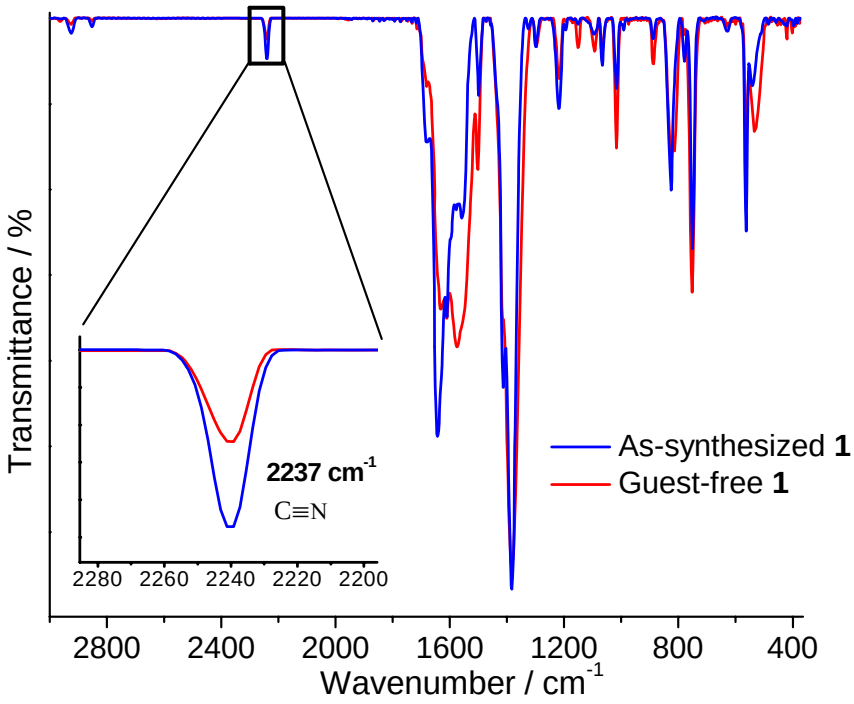

Fig. S3. IR spectrum of as-synthesized and guest-free **1**. The characteristic carbonitrile stretching bands of the 4-pyCN at 2237 cm^{-1} are highlighted, which indicate that this terminal ligand tend to leave the coordination framework during activation.

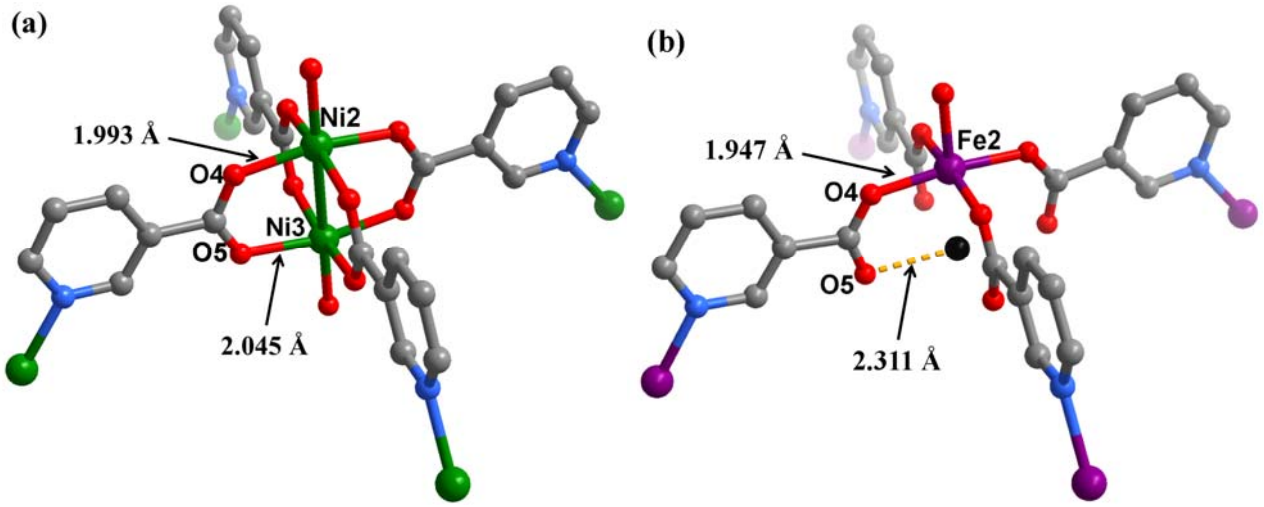

Fig. S4. Local coordination structures of (a) $\{Ni_2(na)_4(H_2O)_2\}$ in **2** and (b) $\{Fe(na)_4(H_2O)\}^-$ in **3**. Note that because the pyridyl ends of the na^- ligands in these metalloligands are fixed by coordination with the metal ions in the $M_3(\mu_3\text{-O/OH})(bdc)_3$ networks, the four carboxylate ends cannot adopt the ideal D_{4d} symmetry of the $M_2(RCOO)_4$ paddle wheel structure, which can be judged by the unequal bonding distances of Ni2-O4 and Ni3-O5. Because the high-valence cation Fe(III) has a smaller radius than Ni(II), the Fe2-O4 bonds in $\{Fe(na)_4(H_2O)\}^-$ (1.947 Å) are shorter than the Ni2-O4 bonds in $\{Ni_2(na)_4(H_2O)_2\}$ (1.993 Å). To approach the position for binding Fe(III), the na^- ligands need to bend toward the 4-fold symmetry axis, which push O5 away from the 4-fold symmetry axis. The shortest bonding distance will be 2.311 Å if four O5 atoms coordinate with a metal ion (the black sphere at the centre of the square defined by four O5 atoms), which is not suitable for an Fe(III) ion.

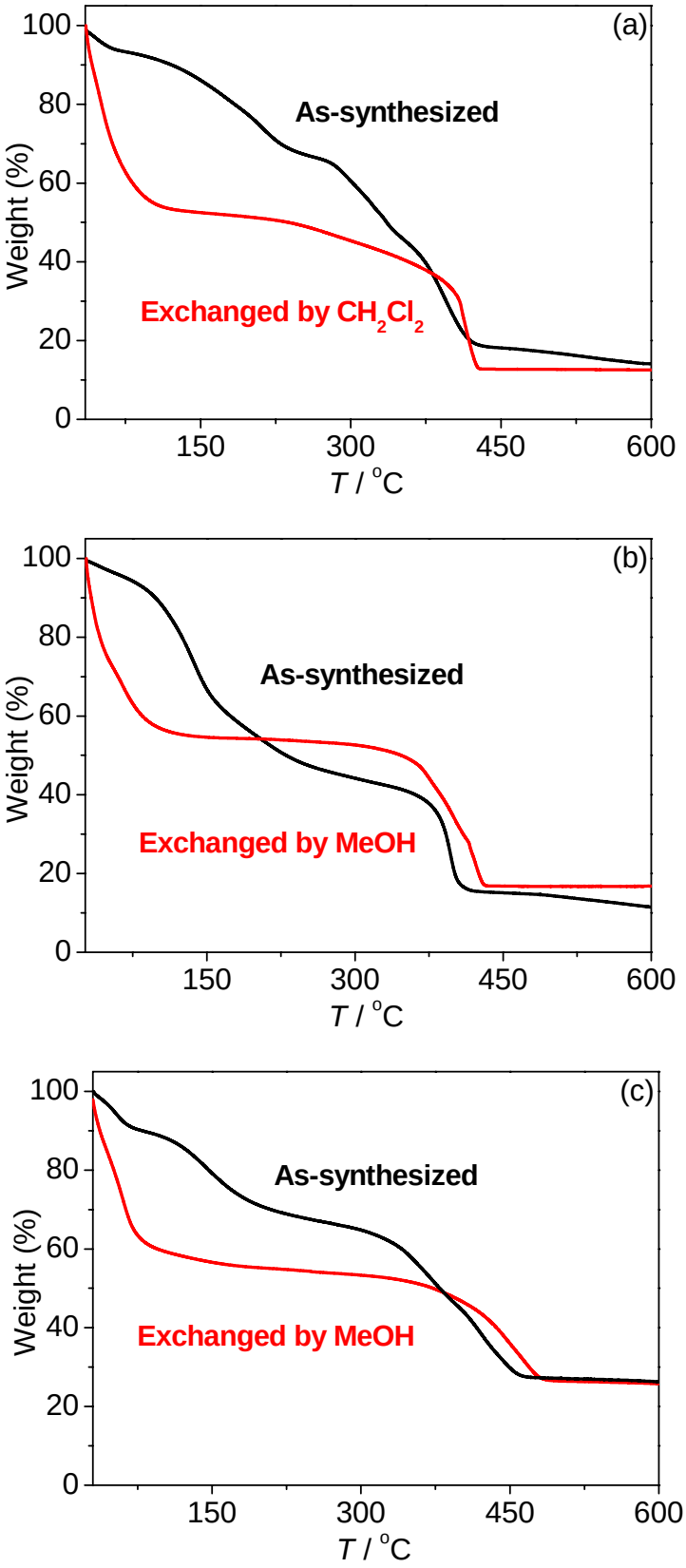

Fig. S5. TGA curves of (a) **1**, (b) **2** and (c) **3**.

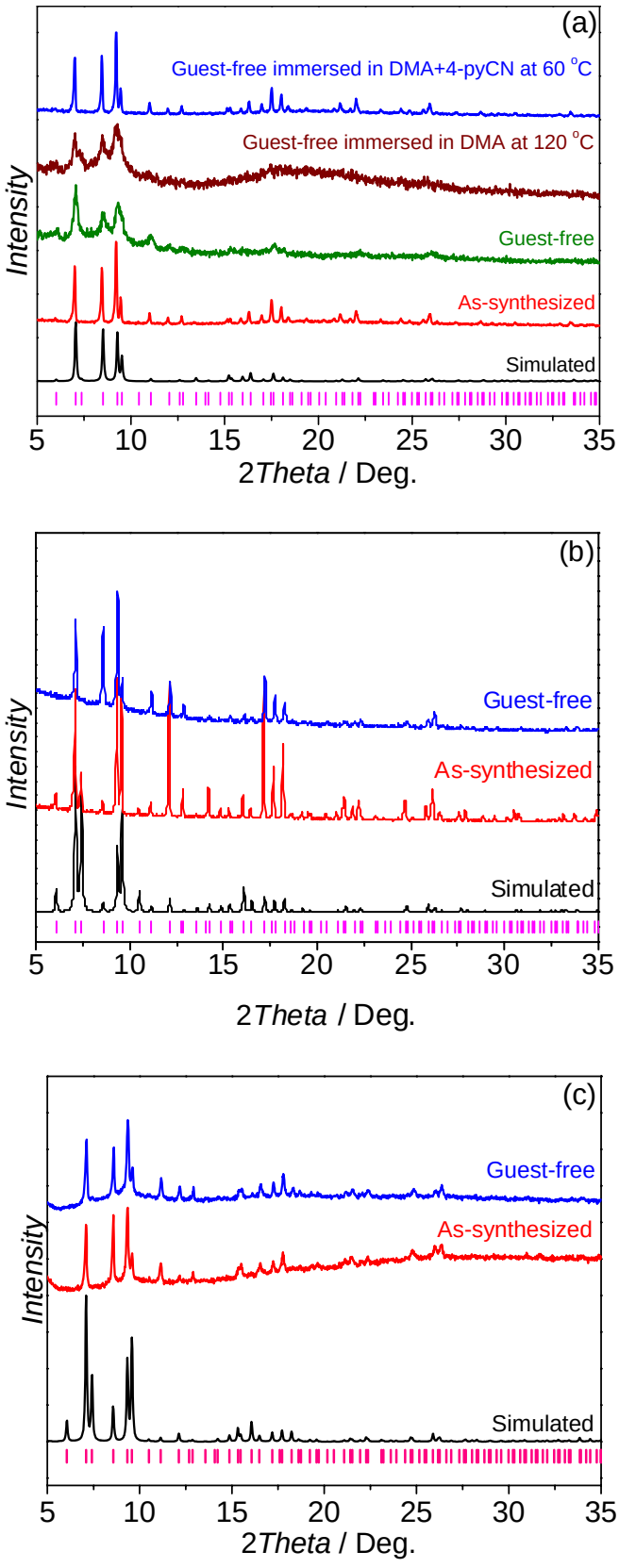

Fig. S6. Room-temperature PXRD patterns of (a) **1**, (b) **2** and (c) **3**.

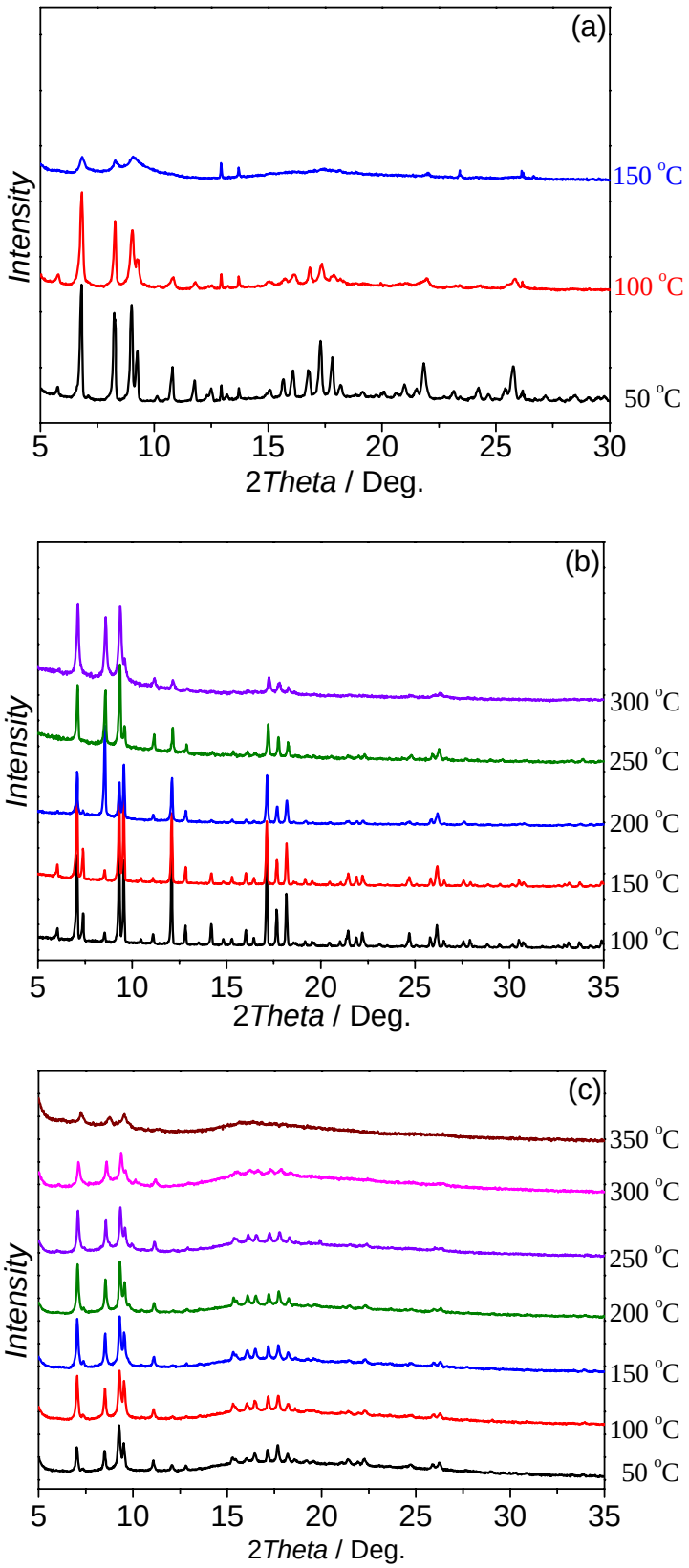

Fig. S7. PXRD patterns of (a) **1**, (b) **2**, and (c) **3** after heated at different temperatures under N_2 for 30 min.

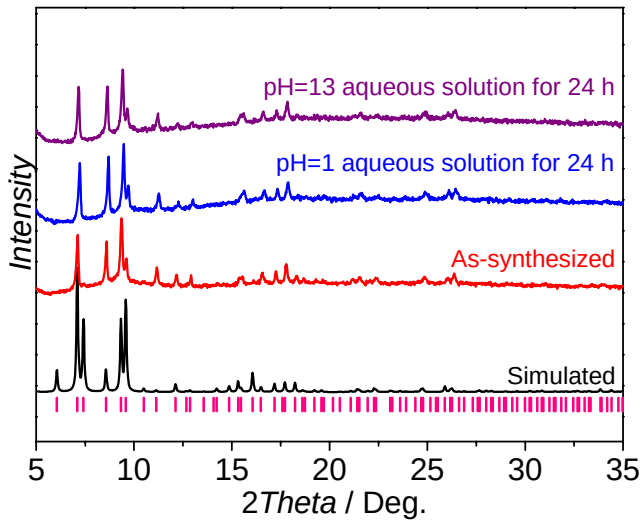

Fig. S8. Room-temperature PXRD patterns of **3** after different treatments.