

Supporting Information

Highly Stable Crystalline Catalysts Based on a Microporous Metal-Organic Framework and Polyoxometalates

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Table S1. Crystal data and structure refinements for NENU-*n* (*n* = 1-6).

	1	2	3	4	5	6
formula	C ₇₆ H ₃₆ NCu ₁₂ Si	C ₇₆ H ₃₆ NCu ₁₂ Ge	C ₁₄₈ H ₄₈ N ₂ Cu ₂₄ P ₂	C ₃₀₄ N ₄ Cu ₄₈ Si ₄ M	C ₁₄₈ H ₄₈ NCu ₂₄ P ₂	C ₁₄₈ H ₄₈ NCu ₂₄ As
fw	5752.07	5795.86	11402.62	18854.16	9313.57	9209.47
crystal system	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
space group	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>Fm-3m</i>
<i>a</i> (Å)	26.3044(10)	26.3189(12)	26.3141 (14)	26.3034 (9)	26.3348(8)	26.3239(6)
<i>V</i> (Å ³)	18200.6(10)	18229.0(10)	18220.7(14)	18198.5 (11)	18263.8(10)	18241.1(7)
<i>Z</i>	4	4	2	1	2	2
<i>D_c</i> (mg/m ³)	2.099	2.098	2.078	1.720	1.681	1.684
abs coeff, mm ⁻¹	9.016	9.152	9.010	2.266	2.248	2.428
reflns collected	24577	23342	28325	24556	25649	24509
independent	924	874	1189	921	975	929
θ range (deg)	1.34–25.67	1.34–25.06	1.34–28.30	1.34–25.55	2.19–26.17	2.19–25.65
GOF on <i>F</i> ²	1.089	1.295	1.275	1.042	1.139	1.102
<i>R</i> _{int}	0.0464	0.0489	0.433	0.0513	0.0488	0.0306
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0313	0.0448	0.0411	0.0580	0.0513	0.0496
<i>wR</i> ₂ (all data) ^b	0.1005	0.1608	0.1393	0.1958	0.1656	0.1561

^a $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$. ^b $wR2 = [\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2]^{1/2}$

Table S2. Selected bond distances (Å) of NENU-n (n = 1-6).

1		2		3		4		5		6	
W–O1	1.888(3)	W–O5	1.893(5)	W–O1	1.892(3)	Mo–O3	1.882(4)	Mo–O2	1.889(3)	Mo–O2	1.901(3)
W–O2	1.675(4)	W–O4	1.668(12)	W–O3	1.681(9)	Mo–O2	1.620(17)	Mo–O3	1.641(8)	Mo–O3	1.644(8)
W–O3	2.382(9)	W–O3	2.341(13)	W–O5	2.460(9)	Mo–O1	2.390(9)	Mo–O1	2.449(8)	Mo–O1	2.394(7)
Si–O3	1.643(17)	Ge–O3	1.740(3)	P–O5	1.553(16)	Si–O1	1.62(17)	P–O1	1.553(14)	As–O1	1.677(14)
Cu–O4	1.952(3)	Cu–O2	1.954(5)	Cu–O2	1.955(4)	Cu–O5	1.948(4)	Cu–O5	1.961(3)	Cu–O5	1.955(3)
Cu–O5	2.195(10)	Cu–O1	2.183(13)	Cu–O4	2.228(11)	Cu–O4	2.204(10)	Cu–O4	2.171(9)	Cu–O4	2.194(8)
C1–C3	1.490(9)	C1–C3	1.404(6)	C3–C4	1.492(5)	C1–C3	1.486(10)	C1–C2	1.489(8)	C1–C2	1.485(8)
C2–C3	1.398(5)	C2–C3	1.473(13)	C4–C5	1.400(5)	C2–C3	1.389(5)	C2–C3	1.394(4)	C2–C3	1.394(4)
C1–O4	1.261(5)	C2–O2	1.267(7)	C3–O2	1.262(5)	C1–O1	1.266(5)	C1–O5	1.258(4)	C1–O5	1.260(4)

Table S3. Selected bond angles (°) of NENU-n (n = 1-6).

1		2		3	
O2–W1–O3	156.5(3)	O4–W1–O3	154.6(63)	O3–W2–O5	158.6(3)
O2–W1–O1	101.2(3)	O4–W1–O5	101.5(4)	O3–W2–O1	102.4(3)
O1–W1–O3	63.0(3)	O5–W1–O3	96.5(6)	O1–W2–O5	63.2(3)
Si–O3–W1	121.3(3)	Ge–O3–W1	119.3(6)	P–O5–W2	123.4(3)
C1–O4–Cu 1	122.4(4)	C2–O2–Cu 1	123.0(5)	C3–O2–Cu 1	122.3(4)
O4–Cu1–O5	95.41(11)	O2–Cu1–O1	95.47(15)	O2–Cu1–O4	95.50(12)
O4–C1–C3	117.0(3)	O24–C2–C3	117.5(5)	O2–C3–C4	116.8(3)
C2–C3–C1	120.2(4)	C1–C3–C2	120.0(5)	C5–C4–C3	119.9(4)
4		5		6	
O2–Mo2–O1	157.0(4)	O3–Mo1–O1	158.5(3)	O3–Mo1–O1	156.2(3)
O2–Mo2–O3	101.9(4)	O3–Mo2–O2	101.9(3)	O3–Mo1–O2	101.3(3)
O3–Mo2–O1	94.3(5)	O2–Mo1–O1	63.5(3)	O2–Mo1–O1	62.5(3)
Si–O1–Mo2	121.7(3)	P–O1–Mo1	123.3(3)	As–O1–Mo1	123.1(3)
C1–O5–Cu 1	123.5(4)	C1–O5–Cu 1	122.7(3)	C1–O5–Cu 2	122.7(3)
O5–Cu1–O4	95.59(11)	O5–Cu1–O4	95.50(10)	O5–Cu2–O4	95.54(9)
O5–C1–C3	117.9(3)	O5–C1–C2	117.3(3)	O5–C1–C2	117.6(3)
C2–C3–C1	119.8(4)	C3–C2–C1	119.8(3)	C3–C2–C1	119.9(3)

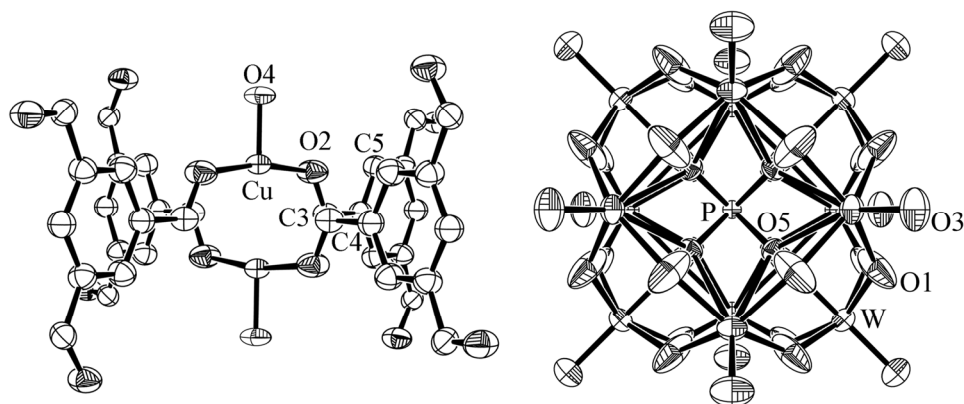


Figure S1. ORTEP view of the Cu₂-BTC building block and the disordering anion [PW₁₂O₄₀]³⁻ in NENU-3 with thermal ellipsoids at 50% level, the hydrogen atoms are omitted for clarity. The disordering polyanion is formed as a result of superimposition of one Keggin anions (with T_d symmetry) and another anion which is 90°-rotated about a S₄ axis. The resulting molecule has pseudo O_h symmetry with a specific structural feature: seven-coordinate for W, cubic eight-coordinate for P, and radially elongated displacement ellipsoids for the bridging oxygen.

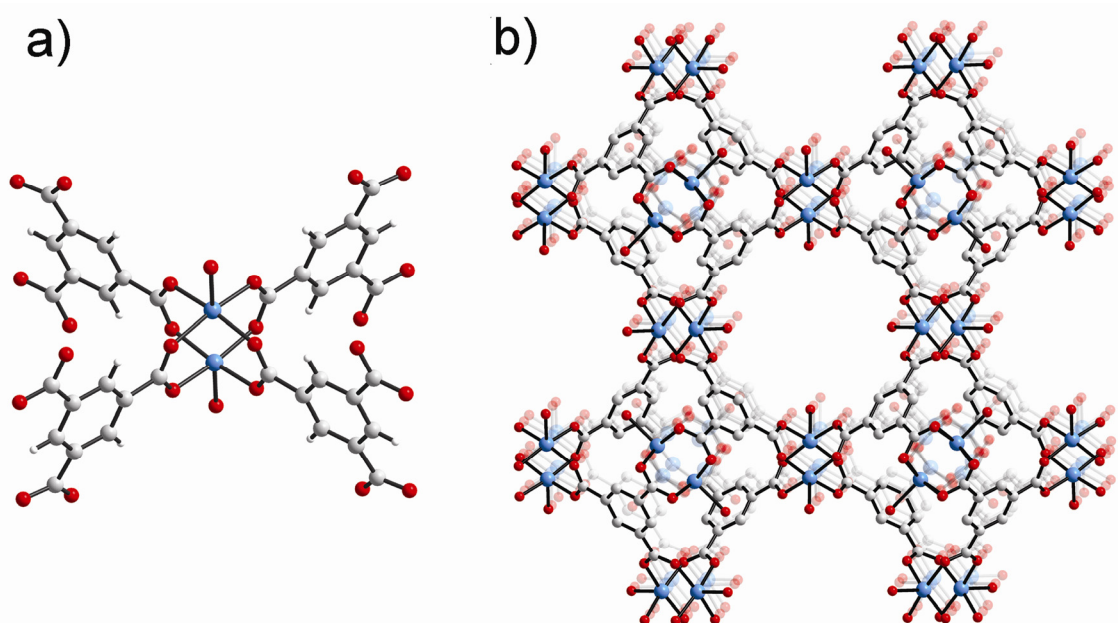


Figure S2. Perspective view of a) the paddle-wheel Cu₂ unit and b) the (3, 4)-connected framework of NENU-*n* (*n*=1-6). Blue, red, gray, and white spheres represent Cu, O, C and H atoms, respectively. Hydrogen atoms are not shown in b) for clarity.

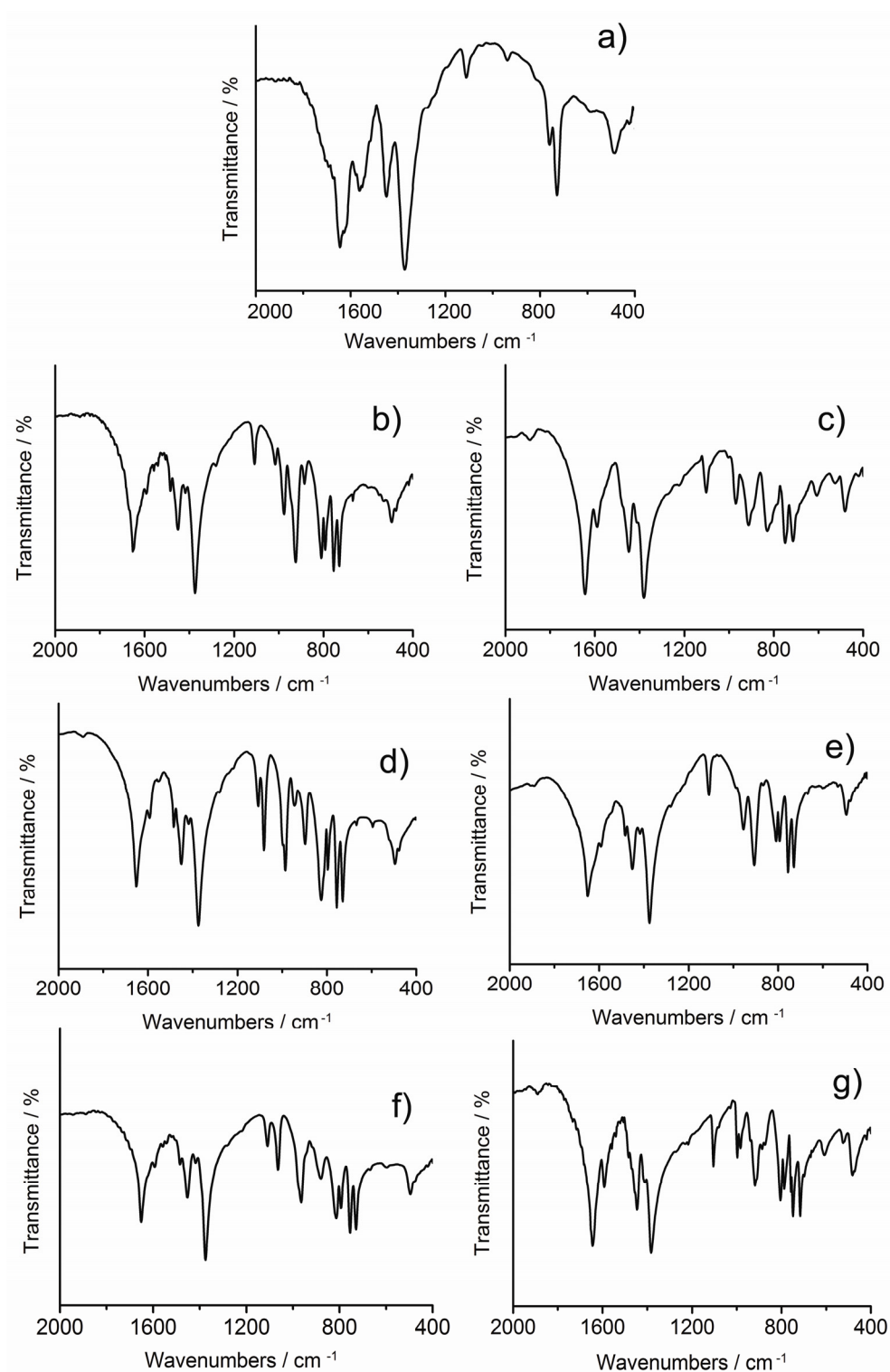


Figure S3. IR spectra of (a) the parent material in absence of Keggin polyanions (HKUST-1); (b) NENU-1; (c) NENU-2; (d) NENU-3; (e) NENU-4; (f) NENU-5; (g) NENU-6.

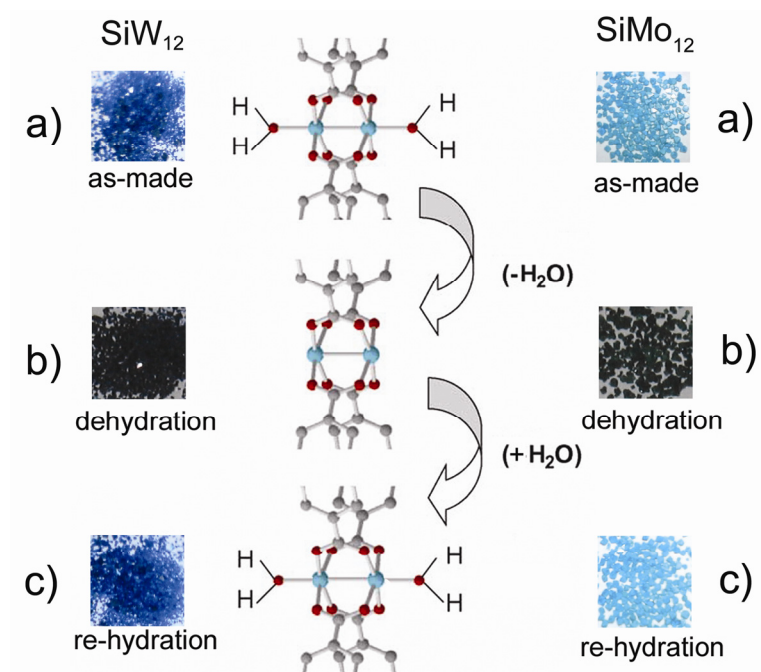


Figure S4. Digital photographs of compounds **NENU-1** (left) and **NENU-4** (right): (a) as-synthesized; (b) dehydration under 180 °C for 3 h; (c) rehydration under atmosphere for 30 min.

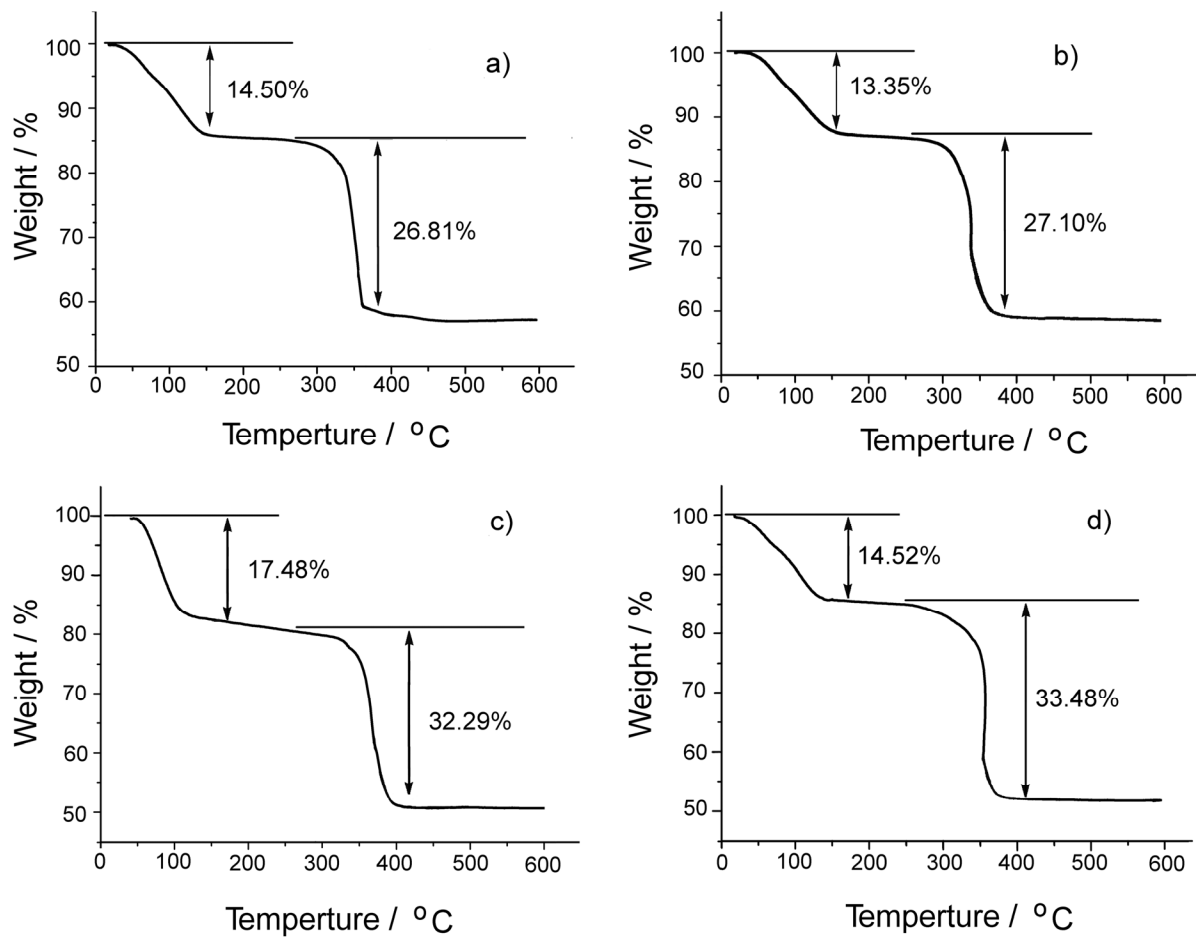


Figure S5. The thermogravimetric (TG) analysis curves of (a) NENU-1; (b) NENU-3; (c) NENU-4; (d) NENU-5.

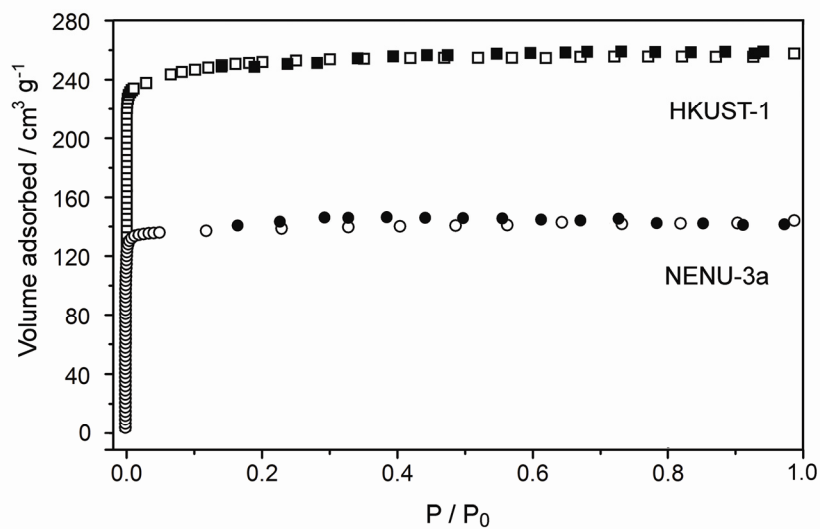


Figure S6. N_2 gas sorption isotherms of HKUST-1 (squares) and NENU-3a (circles) measured at 77K. Open symbols, adsorption; filled symbols, desorption.

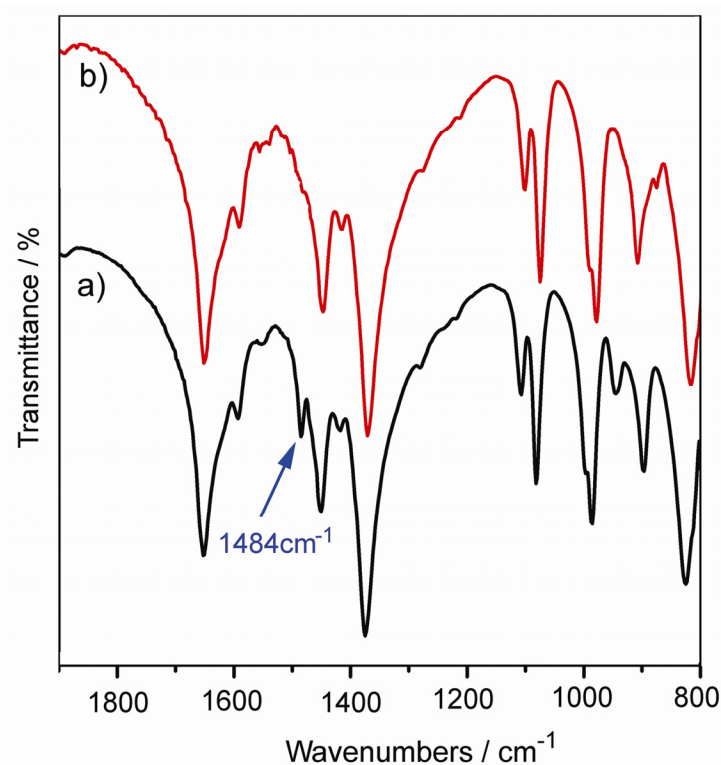


Figure S7. IR spectra of (a) NENU-3 and (b) NENU-3a. Arrow indicates the C-H (of $[(CH_3)_4N]^+$) stretching frequencies at 1484 cm^{-1} in NENU-3, it disappeared in NENU-3a.

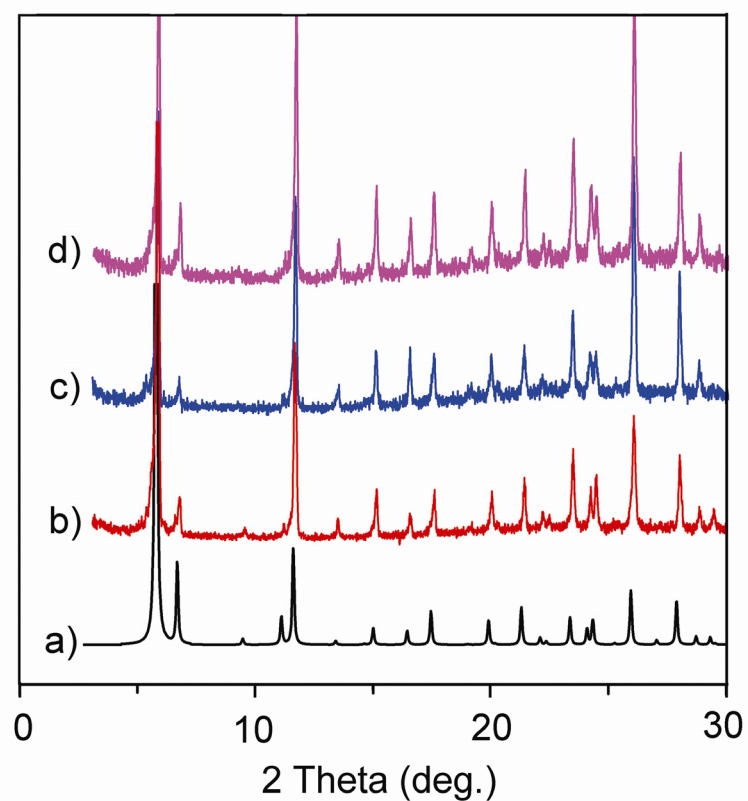


Figure S8. Powder X-ray diffraction patterns of NENU-3: (a) simulated from the X-ray crystal structure; (b) for as-synthesized NENU-3; (c) for NENU-3a before the hydrolysis reaction; (d) for NENU-3a after the hydrolysis reaction.