Supporting Information

Incorporating Cuprous-halide Clusters and Lanthanide Clusters to Construct Heterometallic Cluster Organic Frameworks with Luminescent and Gas Adsorption Properties

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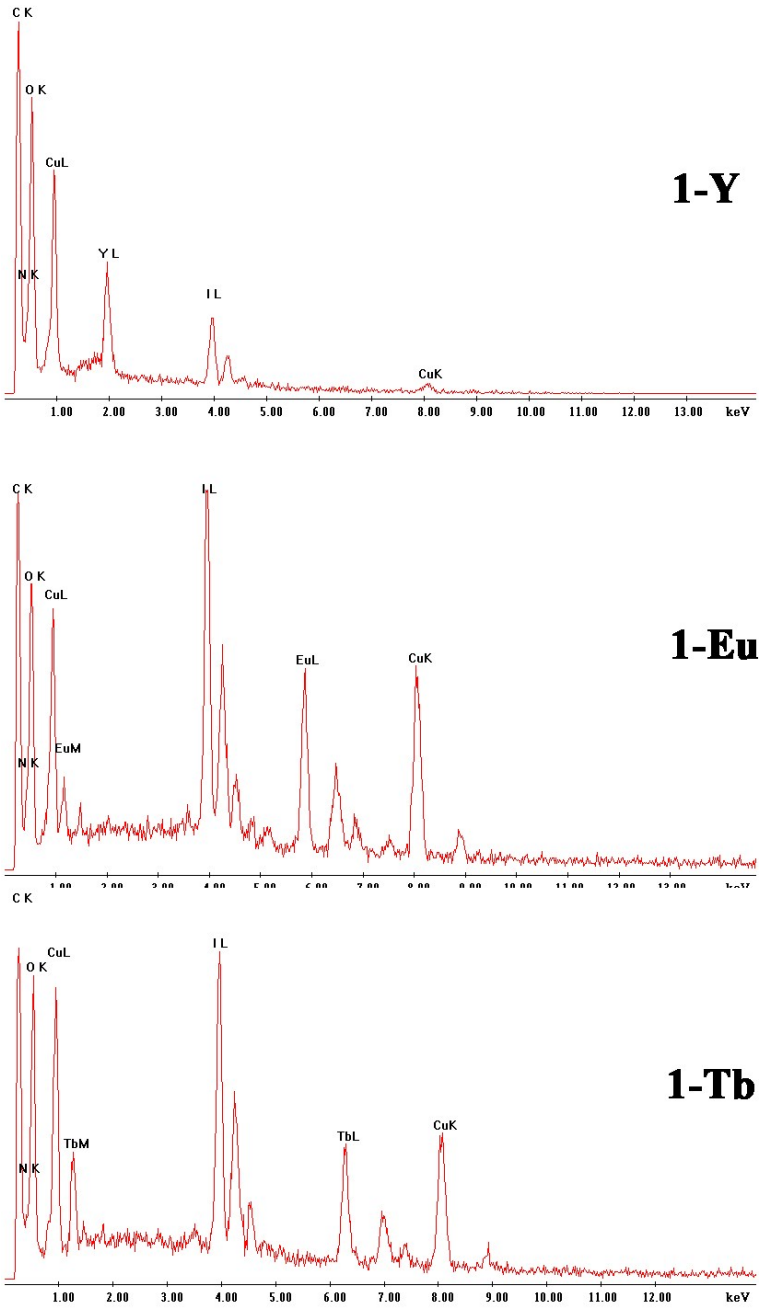

Figure S1 Energy-dispersive X-ray spectroscopy of **1-Ln**.

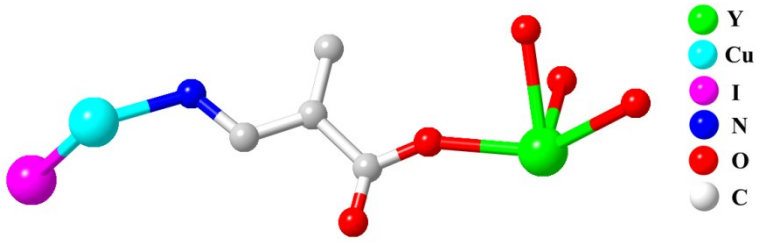

Figure S2 The asymmetric unit of **1-Y**.

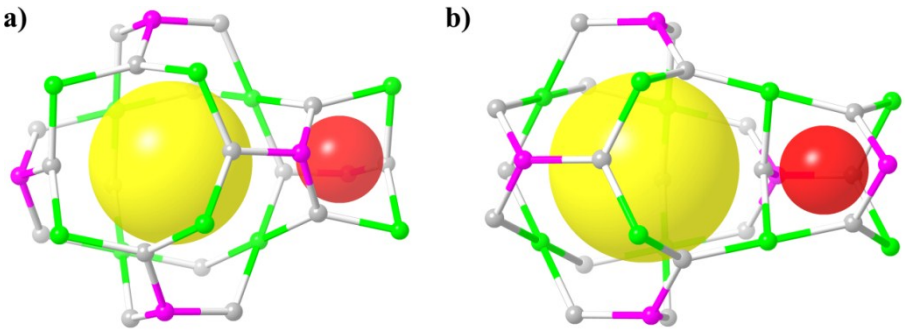

Figure S3 The simplified representation of two types of heterometallic coordination cages with different sizes.

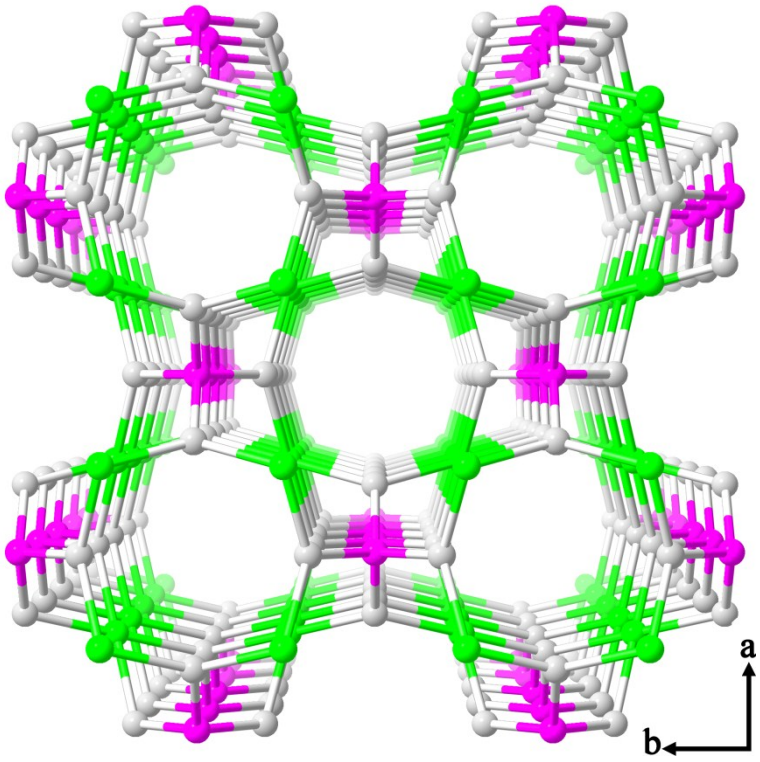

Figure S4 The 3-D 3, 4, 4-connected topology of **1-Y**.

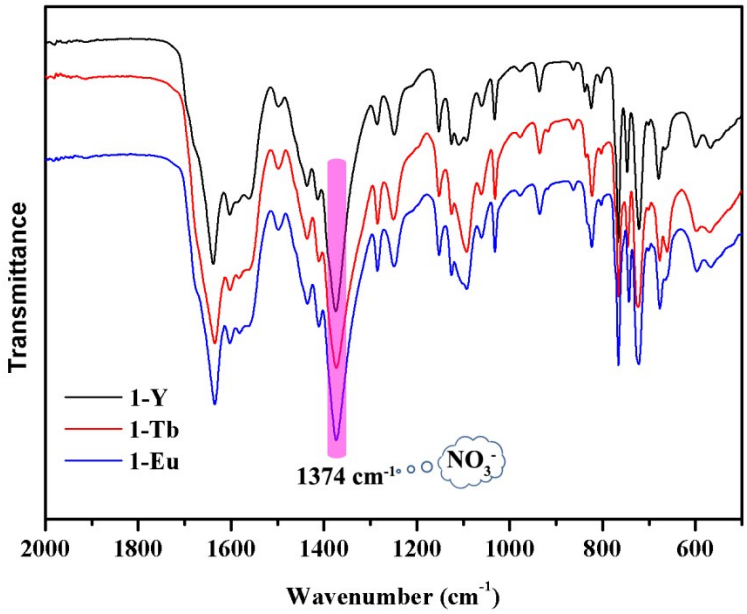

Figure S5 The IR spectra of compounds **1-Ln**.

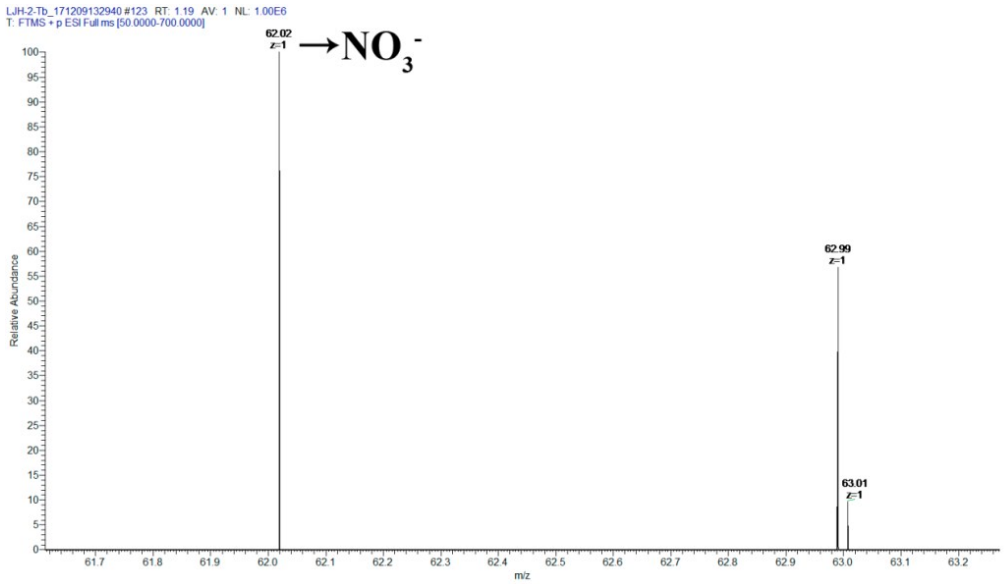

Figure S6 Electrospray-ionization mass spectrometry (ESI-MS) of **1-Ln**

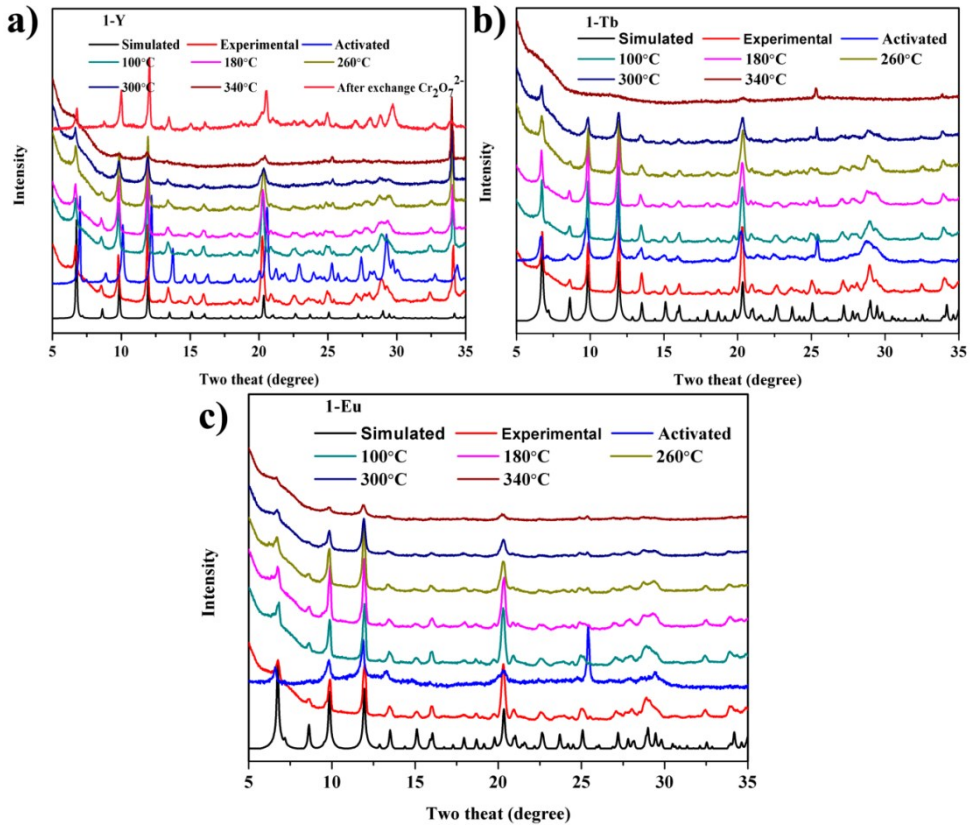

Figure S7 The simulated and temperature dependent PXRD patterns of **1-Ln** from room temperature to 340 ºC.

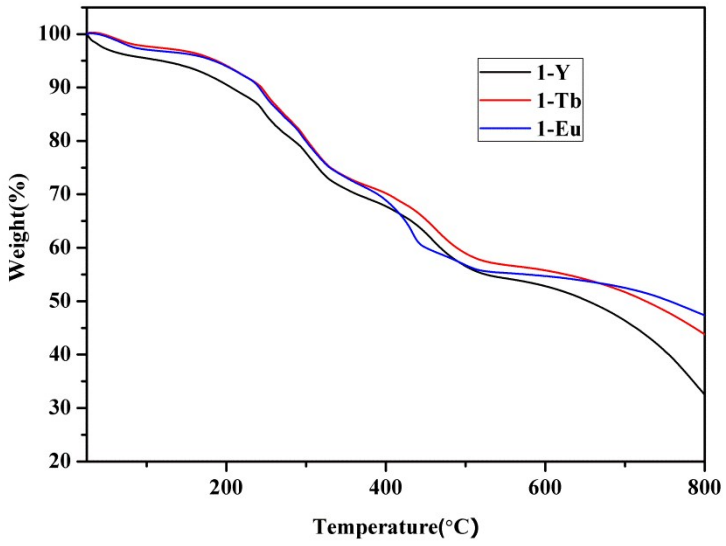

Figure S8 TGA curves of **1-Ln**.

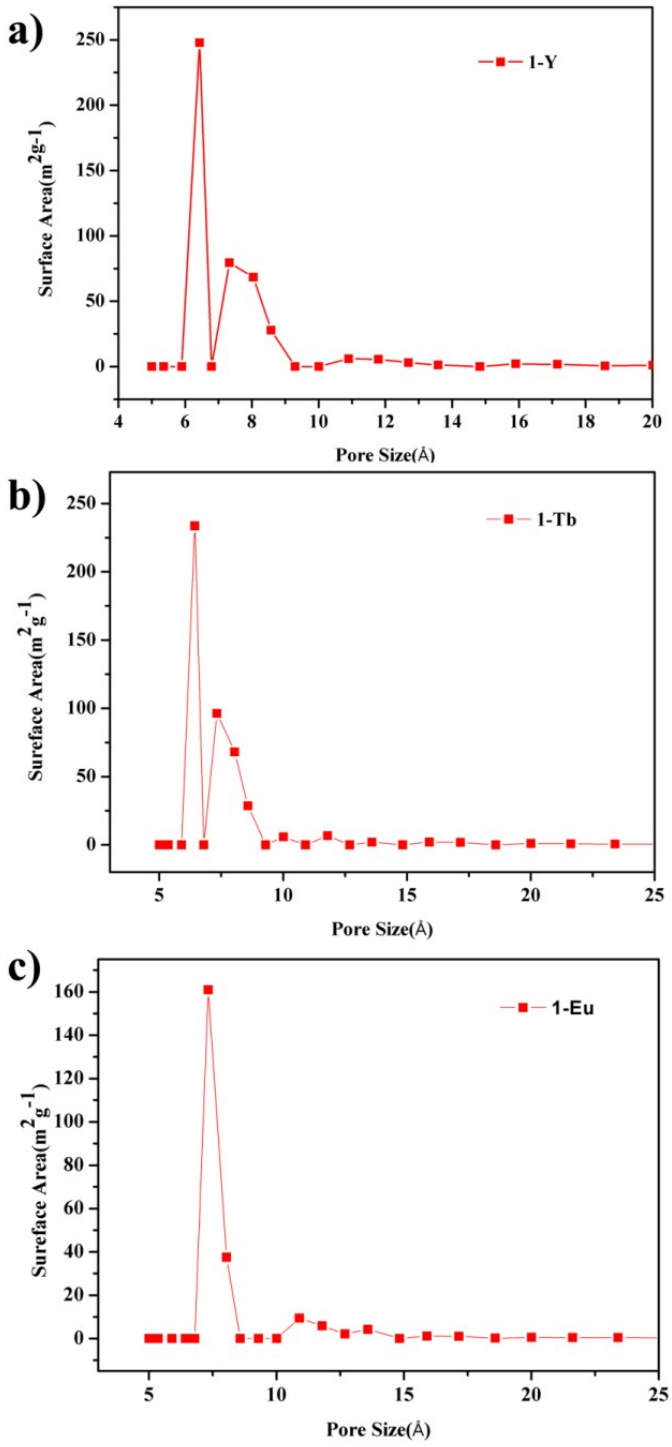

Figure S9 The pore size distributions of **1-Ln**.

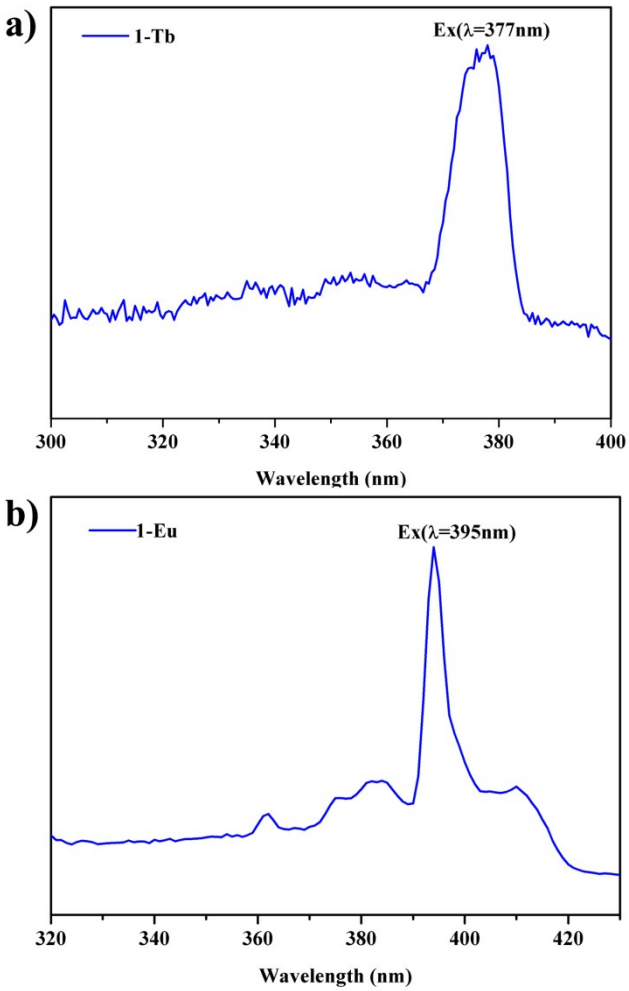

Figure S10 The excitation spectra of **1-Tb** and **1-Eu** at room temperature.

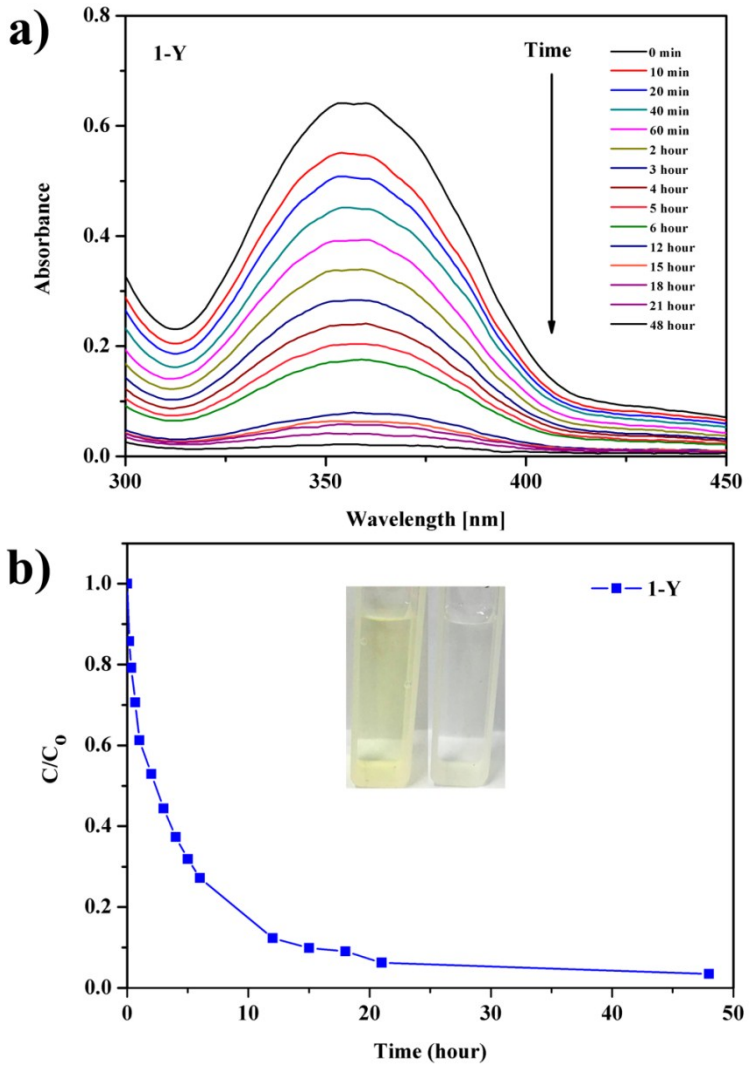

Figure S11 (a) UV/Vis spectra of $K_2Cr_2O_7$ aqueous solution during anion exchange with **1-Y.** (b) The adsorption rate of **1-Y.** Inset: The photographs show the color of the $K_2Cr_2O_7$ solution before (left) and after (right) ion-exchange for 48 h.

Table S1: Summary of reported heterometallic cluster organic frameworks based on lanthanide clusters and cuprous-halide clusters.

Formula of compounds	Ligand	Structural Feature	Ref.
$[Ln_2(H_2O)_8]_2(Cu_4I_4)(pdc)_4][NO_3]_4$•solvent (**Ln** = Y, Tb, Eu)	H_2pdc = 3,5-pyridinedicarboxylic acid	two types of heterometallic coordination cages frameworks	This work
$[Ln_2Cu_2(\mu_2\text{-}X)(hma)(ina)_4(H_2O)_2]_n \cdot 2nH_2O$ (**Ln** = La, Nd, X =Cl, X = Br , X = I) $[Ln_3Cu_{4.5}I_{3.5}(\mu_3\text{-}OH)(hma)(ina)_6(H_2O)]_n$•$nH_2O$ (**Ln** = Pr, Nd) $[LnCu_{0.5}(hma)(ina)(H_2O)]_n$•$nH_2O$ (**Ln** = La, Ce, Pr)	Hina =isonicotinic acid H_3hma =hemimellitic acid	3D pillared-layer frameworks	S1
$La_6Cu_3ClL_{12}(ox)_3(OH)_2 \cdot 8H_2O$ $La_6Cu_4X_3L_{12}(ox)_3(OH)_2 \cdot H_3O$ (X = Br/I)	HL=4-(3-pyridyl)benzoic acid, ox = oxalate	wheel cluster frameworks	S2
$[Ln_6(\mu_3\text{-}O)_2](IN)_{18}[Cu_8(\mu_4\text{-}I)_2(\mu_2\text{-}I)_3 \cdot H_3O$ (**Ln**=Y , Nd , Dy , Gd , Sm, Eu , Tb)	HIN =isonicotinic acid	sandwich cluster frameworks	S3
$[La_6(\mu_3\text{-}OH)_2(ox)_3L_{12}Cu_{11}(\mu_3\text{-}X)_6(\mu_2\text{-}X)_3] \cdot 8H_2O$ (X=Br/Cl); $[Ln_4(OAc)_3(H_2O)_4L_9][Cu(\mu_3\text{-}I)]@[Cu_{10}(\mu_3\text{-}I)(\mu_4\text{-}I)_6(\mu_5\text{-}I)_3] \cdot 7H_2O$ (**Ln**=Pr/Nd/Sm/Eu)	HL = 4-pyridin-4-ylbenzonic acid	sandwich cluster frameworks	S4
$Eu_6(OH)_2Cu_9I_6L_{12}(ox)_3 \cdot H_2O \cdot ClO_4$; $Eu_6Cu_7I_7L_{12}(OAc)_6(H_2O)_2 \cdot 2H_2O$	HL=4-pyridin-4-ylbenzonic acid ox=oxalate OAc=acetate	sandwiched cluster frameworks	S5
$Ln_2Cu_2I_2(OH)_2(pca)_2(na)_2$ (**Ln** =Y, Er , Yb)	Hna = nicotinic acid Hpca = 2-pyrazinecarboxylic acid	heterometallic frameworks	S6
$[NaLn_2Cu_6I_5(IN)_6(ox)(H_2O)_4] \cdot H_2O$ (**Ln** = La, Eu, Gd , Tb)	HIN =isonicotinic acid ox= oxalate	3D pillared-layer frameworks	S7
$[Gd_4L_{12}(Cu_{10}I_8)(H_2O)_{10}] \cdot 2ClO_4 \cdot 4H_2O$; $[La_4(Ox)_2L_8(Cu_7I_5)(H_2O)_4] \cdot 2ClO_4 \cdot 4H_2O$; $[La_4Na(Ox)_3L_8(Cu_7I_6)(H_2O)_2] \cdot 5H_2O$	Ox = oxalate, HL = 4-pyridin-4-ylbenzonic acid	3D pillared-layer frameworks	S8
$[Sm_3Cu_5I_4L_6(\mu_3\text{-}OH)_2(OAc)(H_2O)_3] \cdot ClO_4 \cdot 2H_2O$; $[Sm_6Cu1_4I_{12}L_{14}(\mu_3\text{-}OH)_4(H_2O)_5] \cdot 2ClO_4 \cdot 8H_2O$	OAc=acetate, HL=4-pyridin-4-ylbenzoic acid	heterometallic frameworks	S9
$Ln_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3$ (**Ln** =Nd, Pr)	HIN =isonicotinic acid, HOAc= acetic acid	heterometallic frameworks	S10
$[Ce_2(ina)_5(na)_2(H_2O)_2][Cu_5Br_4]$; $[Er_4(ina)_8(bdc)_2(OH)(H_2O)_5][Cu_8I_7]$; $[Ce_3(ina)_8(bdc)(H_2O)_4][Cu_7Br_6]$	na =nicotinic acid	heterometallic frameworks	S11
$Ln_2Cu_7I_6(ina)_7(H_2O)_6 \cdot H_2O$ (**Ln**=Ce, Sm) $Er_4(OH)_4Cu_5I_4(ina)_6(na)(2,5\text{-}pdc) \cdot 0.3H_2O$	ina = isonicotinic acid, na = nicotinic acid 2,5-pdc =2,5-pyridinedicarboxylic acid	3D pillared-layer frameworks	S12
$[Dy_2(pca)_2(npa)_2(H_2O)_3](Cu_2I_2)$	pca=2-pyrazinecarboxylic acid, npa=1,8-naphthalenedicarboxylic acid	heterometallic frameworks	S13
$[Ln_2(H_2O)_4(DMSO)](CuI)_4(Ina)_4(ox)$ (**Ln** = Pr, Sm, Eu)	HIna = isonicotinic acid H_2ox =oxalic acid	2D pillar-chained frameworks	S14
$[LnCuI(L1)_2(OAc)(H_2O)]_n$ (**Ln** = Pr, Nd, Sm, Eu, Gd); $[Ln_2Cu_4I_3(L_2)_7(H_2O)]_n$ (**Ln** = La, Pr); $[Nd_2Cu_7I_6(L_2)_7(H_2O)_6]_n \cdot 2.5nH_2O$	L1=4-(4-pyridyl)benzoate L2=isonicotinate	heterometallic frameworks	S15
$Er_3Cu_5I_4L_{10}(H_2O)$	L = 4-pyridin-3-yl-benzonate	heterometallic frameworks	S16
$\{La_2Cu_7I_6(IN)_7(H_2O)_6 \cdot 2H_2O\}_n$	HIN = isonicotinic acid	heterometallic frameworks	S17
$[Er_2L_6(H_2O)][Cu_2I_2]$; $[ErL_3][CuI]$; $[Dy_2L_6(BPDC)_{0.5}(H_2O)_4][Cu_3I_2]$	HL=4-pyridin-3-yl-benzoicacd H_2BPDC=4,4′-biphenyldi- carboxylicacid	heterometallic polymer	S18
$[La_2Cu_4I_3(Hina)_7(H_2O)]_n$	Hina = isonicotinic acid	3D pillared-layer frameworks	S19
$[Ln_5(\mu_3\text{-}OH)_4(\mu\text{-}H_2O)Cu_8I_8L_{11}] \cdot H_2O$ (**Ln** = Dy, Eu)	HL=4-pyridin-4-yl-benzoic acid	heterometallic frameworks	S20
$[Ln_2Cu_4I_3(IN)_7(H_2O)]_n$; $[LnCu_{3.5}I_3(IN)_{3.5}(H_2O)_3]_n \cdot nH_2O$ (**Ln** = Nd, Gd, La, Eu)	HIN = isonicotinic acid	heterometallic frameworks	S21
$[Dy_2(Cu_4I_4)(nia)_6(DMF)_2]$	Hnia= nicotinic acid	heterometallic frameworks	S22
$\{[Pr_2(Hina)_4(NO_3)_4(H_2O)_4](NO_3)_2\}_n$; $\{[Pr_3Cu_7\text{-}I_7(ina)_8(HCOO)(CH_3NO)_4] \cdot 2H_2O\}_n$	Hina = isonicotinic acid	heterometallic frameworks	S23
$[Gd_2(Cu_2I_2)(C_6H_4NO_2)_6(C_3H_7NO)(H_2O)] \cdot (C_3H_7NO)$; $[Gd_2(Cu_4I_4)(C_6H_4NO_2)_6(C_3H_7NO)_2]$; $[Gd_2(Cu_6I_6)(C_{12}H_8NO_2)_6(C_2H_6O)_2(H_2O)_2]$; $[Gd_2(Cu_8I_8)(C_{12}H_8NO_2)_6(H_2O)_4] \cdot {}_5(C_4H_8O_2)$	Hna =nicotinic acid Hpba= 3-(pyridin-4-yl)benzoic acid	heterometallic frameworks	S24
$[Gd_3Cu_{12}I_{12}(IN)_9(DMF)_4]_n \cdot nDMF$; $[Gd_4Cu_4I_3(CO_3)_2(IN)_9(HIN)_{0.5}(DMF)(H_2O)]_n \cdot nDMF \cdot nH_2O$	HIN = isonicotinic acid	heterometallic frameworks	S25
$[Er_7(\mu_3\text{-}O)(\mu_3\text{-}OH)_6(bdc)_3](ina)_9[Cu_3X_4]$ (X=Cl or Br)	H_2bdc=1,2-benzenedicarboxyc acid Hina = isonicotinic acid	heterometallic frameworks	S26

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