Discrepant Gas Adsorption in Isostructural Heterometallic Coordination Polymers: Strong Dependence of Metal Identity

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Synthesis:

Pd(2,4-Hpydc)$_2$. To a MeOH solution (30 mL) of pyridine-2,4-dicarboxylic acid (2.00 mmol, 0.33 g), was added sodium methanol (2.00 mmol, 0.11 g). After stirring in half an hour, a MeOH solution (10 mL) of $PdCl_2(CH_3CN)_2$ (1.00 mmol, 0.26 g) was slowly added. A pale yellow precipitate was formed immediately. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with MeOH and ethyl ether, and dried in vacuo to afford a pale yellow powder. Yield: 94%. Anal. Calcd for $C_{14}H_8N_2O_8Pd$: C, 38.33; H, 1.84; O, 29.18. Found: C, 38.01; H, 2.16; O, 29.71.

Cu(2,4-Hpydc)$_2$. The DMF solution (10 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (1.00 mmol, 0.24 g) was slowly added to the DMF solution (10 mL) of pyridine-2,4-dicarboxylic acid (2.00 mmol, 0.33 g) under vigorous stirring. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with DMF and MeOH, and dried in vacuo to afford a blue powder. Yield: 95%. Anal. Calcd for $C_{14}H_8N_2O_8Cu$: C, 42.49; H, 2.04; O, 32.34. Found: C, 42.36; H, 2.16; O, 32.44.

Cu(2,5-Hpydc)$_2$. The DMF solution (10 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (1.00 mmol, 0.24 g) was slowly added to the DMF solution (20 mL) of pyridine-2,5-dicarboxylic acid (2.00 mmol, 0.33 g) under vigorous stirring. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with DMF and MeOH, and dried in vacuo to afford a blue powder. Yield: 97%. Anal. Calcd for $C_{14}H_8N_2O_8Cu$: C, 42.49; H, 2.04; O, 32.34. Found: C, 42.33; H, 2.19; O, 32.39.

Co[Co(2,5-Hpydc)$_3$]$_2\cdot 6H_2O$. The DMF solution (10 mL) of $Co(NO_3)_2\cdot 6H_2O$ (1.00 mmol, 0.29 g) was slowly added to the DMF solution (20 mL) of pyridine-2,5-dicarboxylic acid (2.00 mmol, 0.33 g) under vigorous stirring. The

mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with DMF and MeOH, and dried in vacuo to afford a pink powder. Yield: 96%. Anal. Calcd for $C_{42}H_{36}N_6O_{30}Co_3$: C, 39.36; H, 2.83; O, 37.45. Found: C, 39.23; H, 2.93; O, 37.51.

Ni[Ni(2,5-Hpydc)$_3$]$_2$·6H$_2$O. The DMF solution (10 mL) of $Ni(NO_3)_2·6H_2O$ (1.00 mmol, 0.29 g) was slowly added to the DMF solution (20 mL) of pyridine-2,5-dicarboxylic acid (2.00 mmol, 0.33 g) under vigorous stirring. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with DMF and MeOH, and dried in vacuo to afford a green powder. Yield: 93%. Anal. Calcd for $C_{42}H_{36}N_6O_{30}Ni_3$: C, 39.38; H, 2.83; O, 34.47. Found: C, 39.26; H, 2.93; O, 34.53.

Zn[Zn(2,5-Hpydc)$_3$]$_2$·6H$_2$O. The DMF solution (10 mL) of $Zn(NO_3)_2·6H_2O$ (1.00 mmol, 0.30 g) was slowly added to the DMF solution (20 mL) of pyridine-2,5-dicarboxylic acid (2.00 mmol, 0.33 g) under vigorous stirring. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with DMF and MeOH, and dried in vacuo to afford a colorless powder. Yield: 95%. Anal. Calcd for $C_{42}H_{36}N_6O_{30}Zn_3$: C, 38.78; H, 2.79; O, 36.90. Found: C, 38.69; H, 2.86; O, 37.01.

[Ni(cyclam)Pd(2,4-pydca)$_2$·4H$_2$O]$_n$ 1. $Pd(2,4\text{-}Hpydca)_2$ (1.00 mmol, 0.44 g) was added to an aqueous solution of NaOH (2.00 mmol, 0.08 g). After stirring in half an hour, an aqueous solution of $[Ni(cyclam)](ClO_4)_2$ (1.00 mmol, 0.46 g) was slowly added. A deep yellow precipitate was formed immediately. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with H_2O and THF, and dried in air to afford a pale yellow powder. Yield: 91%. Anal. Calcd for $C_{24}H_{38}N_6NiO_{12}Pd$: C, 37.55; H, 4.99; O, 25.01. Found: C, 37.14; H, 5.23; O, 25.46. IR (KBr, cm^{-1}): 3429 (m), 3212 (m), 1670 (s), 1381 (s), 1315 (s), 1105 (m), 947 (m), 780 (w).

[Ni(cyclam)Cu(2,5-pydc)$_2$·3H$_2$O] $Cu(2,5\text{-}Hpydc)_2$ (1 mmol, 0.39 g) was added to an aqueous solution of NaOH (2.00 mmol, 0.08 g). After stirring in half an hour, filtering and an aqueous solution of $[Ni(cyclam)](ClO_4)_2$ (1.00 mmol, 0.46 g) was added and

stirred in an hour. The resulting solution was evaporated to obtain the pure compound. The solid was collected by filtration, washed with H_2O and dried in air to afford a light blue powder. Yield: 85%. Anal. Calcd for $C_{24}H_{36}N_6NiO_{11}Cu$: C, 40.78; H, 5.13; O, 24.90. Found: C, 40.88; H, 5.03; O, 24.82.

[Cu(cyclam)Cu(2,5-pydc)$_2$·2H$_2$O] Cu(2,5-Hpydc)$_2$ (1 mmol, 0.39 g) was added to an aqueous solution of NaOH (2.00 mmol, 0.08 g). After stirring in half an hour, filtering and an aqueous solution of [Cu(cyclam)](ClO$_4$)$_2$ (1.00 mmol, 0.46 g) was added and stirred in an hour. The resulting solution was evaporated to obtain the pure compound. The solid was collected by filtration, washed with H_2O and dried in air to afford a blue powder. Yield: 87%. Anal. Calcd for $C_{24}H_{34}N_6O_{10}Cu_3$: C, 41.56; H, 4.94; O, 23.07. Found: C, 41.65; H, 5.92; O, 23.01.

[Ni(cyclam)Cu(2,4-pydc)$_2$·10H$_2$O]$_n$ Cu(2,4-Hpydc)$_2$ (1 mmol, 0.39 g) was added to an aqueous solution of NaOH (2.00 mmol, 0.08 g). After stirring in half an hour, filtering and an aqueous solution of [Ni(cyclam)](ClO$_4$)$_2$ (1.00 mmol, 0.46 g) was added and stirred in an hour. The resulting solution was evaporated to obtain the pure compound. The solid was collected by filtration, washed with H_2O and dried in air to afford a light blue powder. Yield: 89%. Anal. Calcd for $C_{24}H_{50}N_6NiO_{18}Cu$: C, 34.61; H, 6.05; O, 34.58. Found: C, 34.68; H, 6.01; O, 34.52.

[Cu(cyclam)Pd(2,4-pydc)$_2$·Guest]$_n$. Pd(2,4-Hpydc)$_2$ (1.00 mmol, 0.44 g) was added to an aqueous solution of NaOH (2.00 mmol, 0.08 g). After stirring in half an hour, an aqueous solution of [Cu(cyclam)](ClO$_4$)$_2$ (1.00 mmol, 0.46 g) was slowly added. A purple precipitate was formed immediately. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with H_2O and THF, and dried in air to afford a purple powder. Yield: 87%. IR (KBr, cm^{-1}): 3451 (m), 3235 (m), 3169 (m), 2946(w), 1676 (s), 1552 (w), 1375 (s), 1297 (s), 1113 (m), 1021(w), 956 (m), 883(m), 780(w).

Our further efforts to extend this series to other first-row transition metals (Mn^{2+}, Co^{2+}) using similar synthesis protocol, resulted in noncrystalline substance. When the solution of [M(cyclam)](ClO$_4$)$_2$ (M = Mn^{2+}, Co^{2+}) (1.00 mmol) was slowly added to a solution of Pd(2,4-Napydc)$_2$) (0.1 mmol), a stickiness substance were obtained and we

couldn't obtained the precipitate.

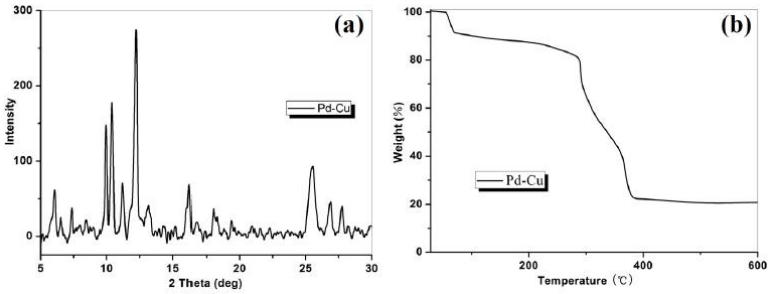

Fig. S1 (a) PXRD patterns for complex Pd-Cu; (b) TGA of complex Pd-Cu

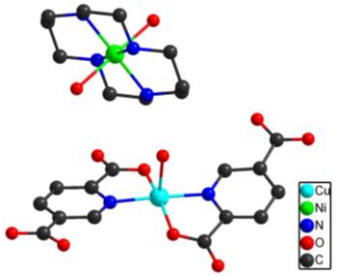

Fig. S2 Crystal structure of complex **A1**

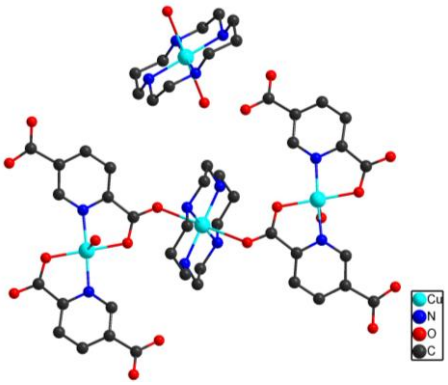

Fig. S3 Crystal structure of complex **A2**

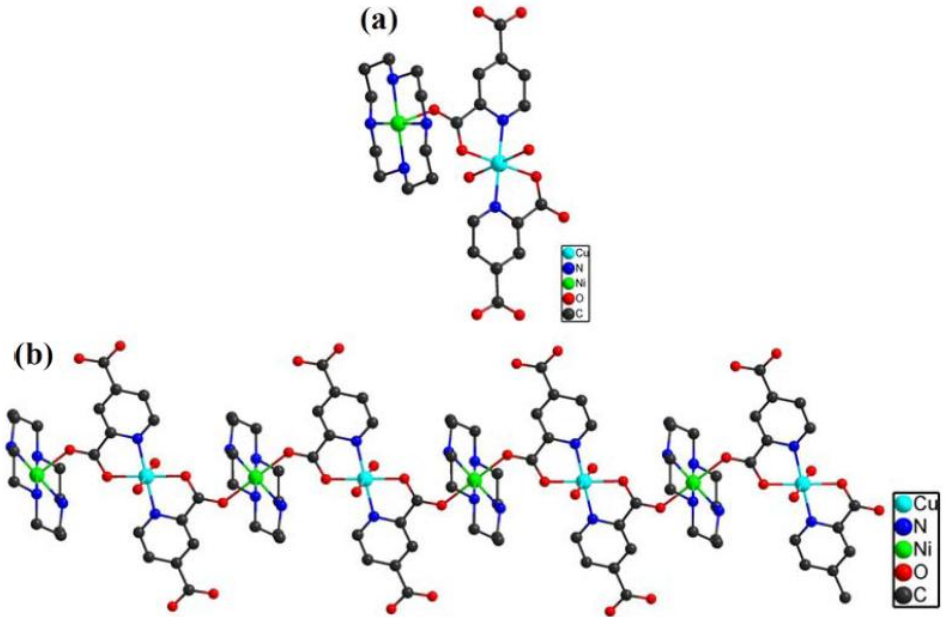

Fig. S4 Crystal structure of complex **A3**

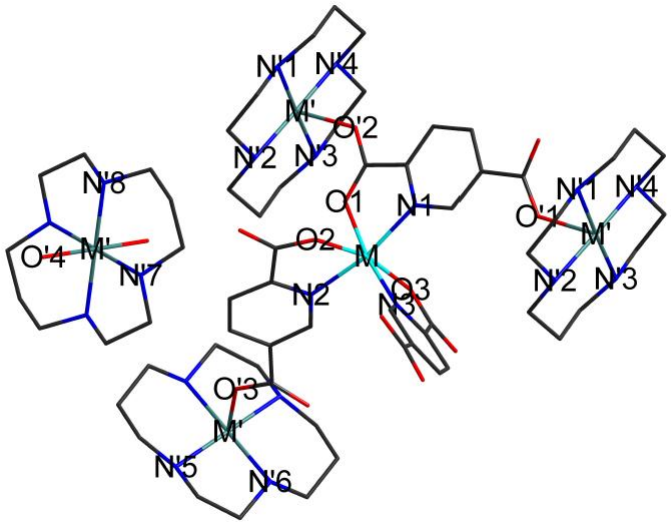

Fig. S5 The coordination modes of $[M(2,5\text{-pydc})_3]^{4-}$ in all the complexes **3 - 7**

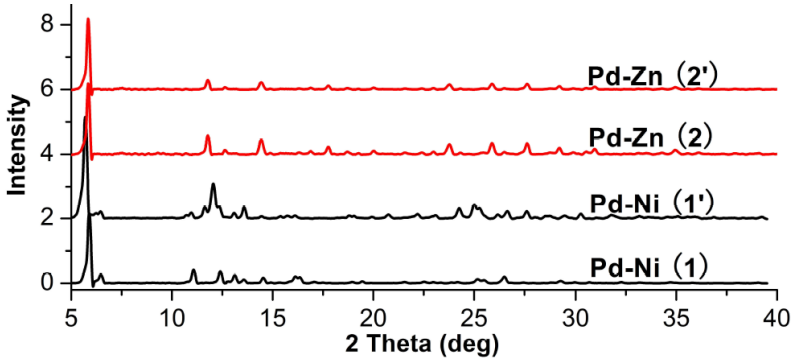

Fig. S6 PXRD patterns for different samples

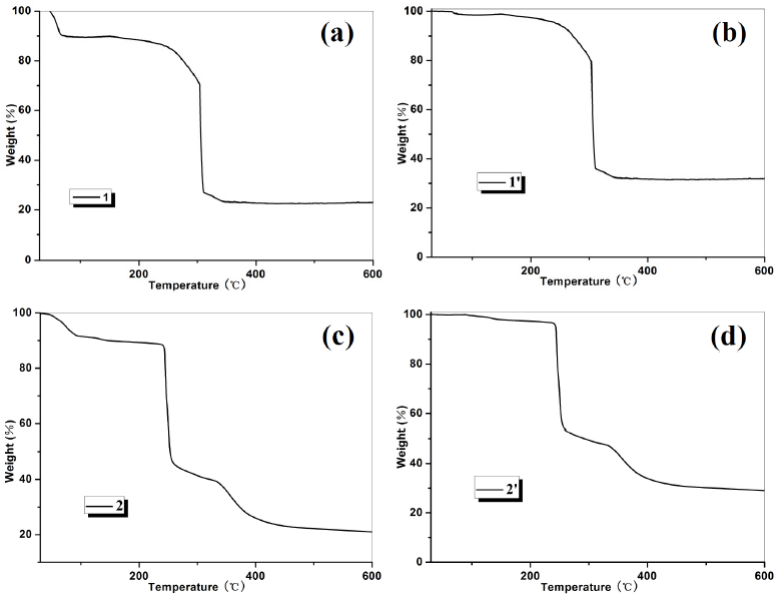

Fig. S7 TGA of complexes **1**(a), **1'**(b), **2**(c) and **2'**(d)

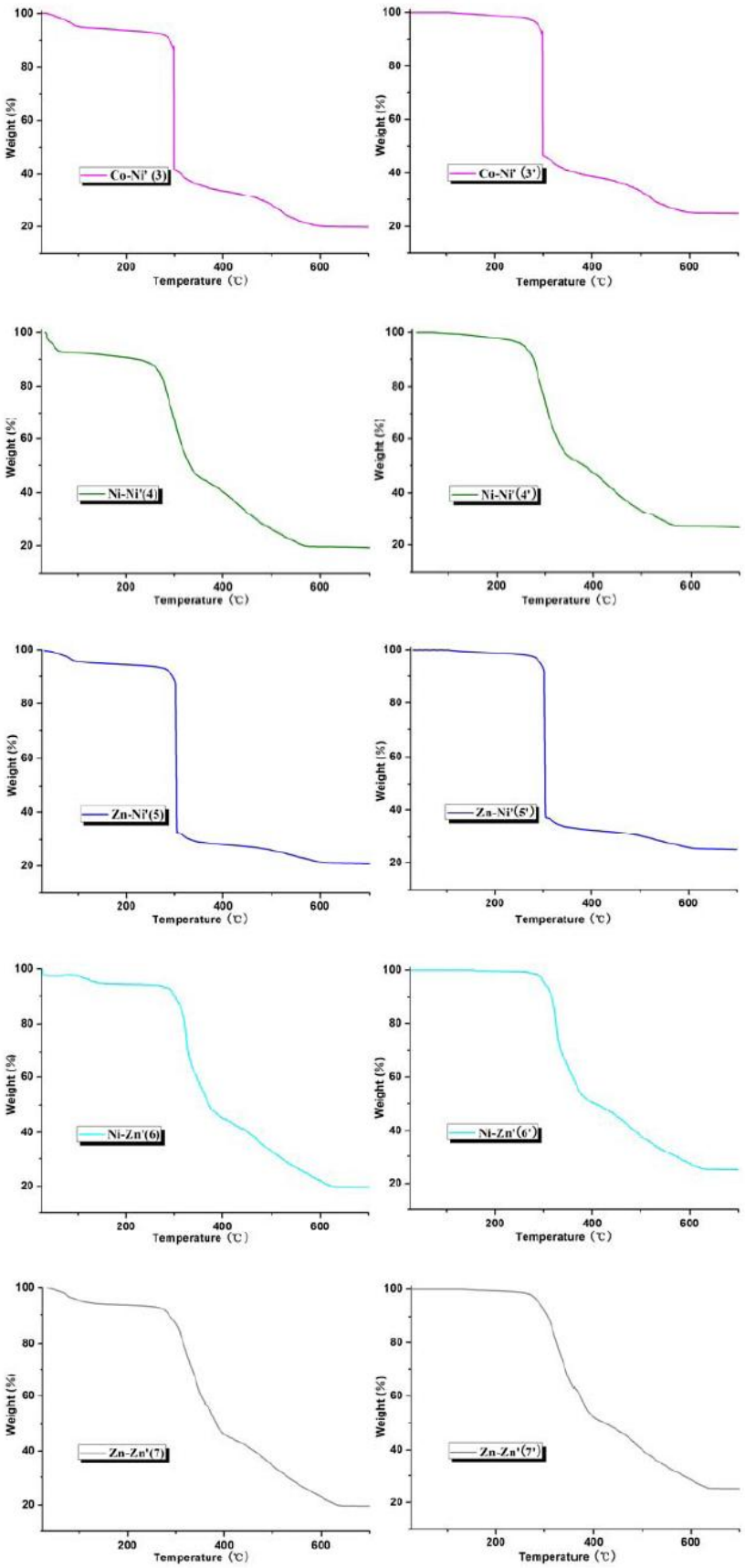

Fig. S8 TGA of complexes **3** – **7** and **3' - 7'**

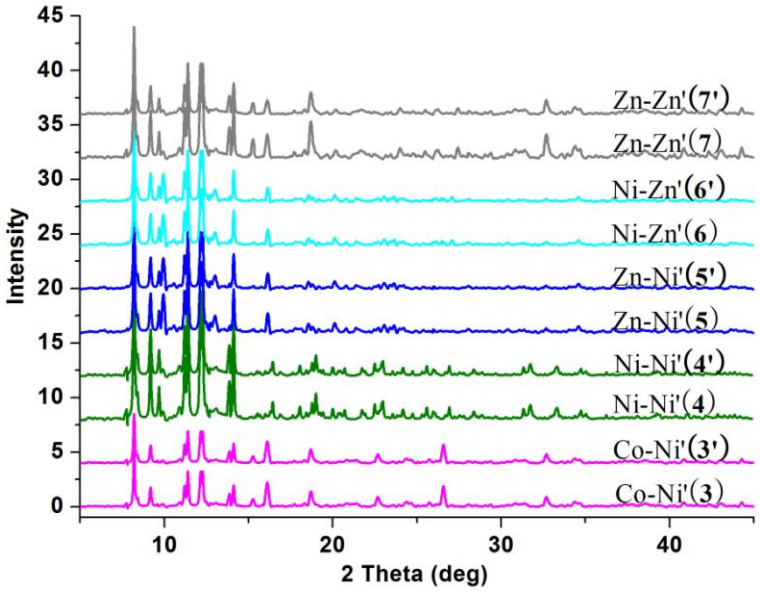

Fig. S9 PXRD patterns for different samples

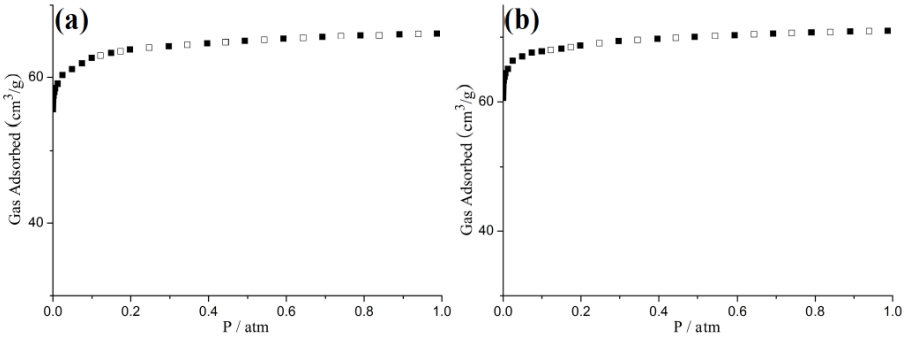

Fig. S10 N_2 sorption curves (77 K) of **1'** (a) and **2'** (b)

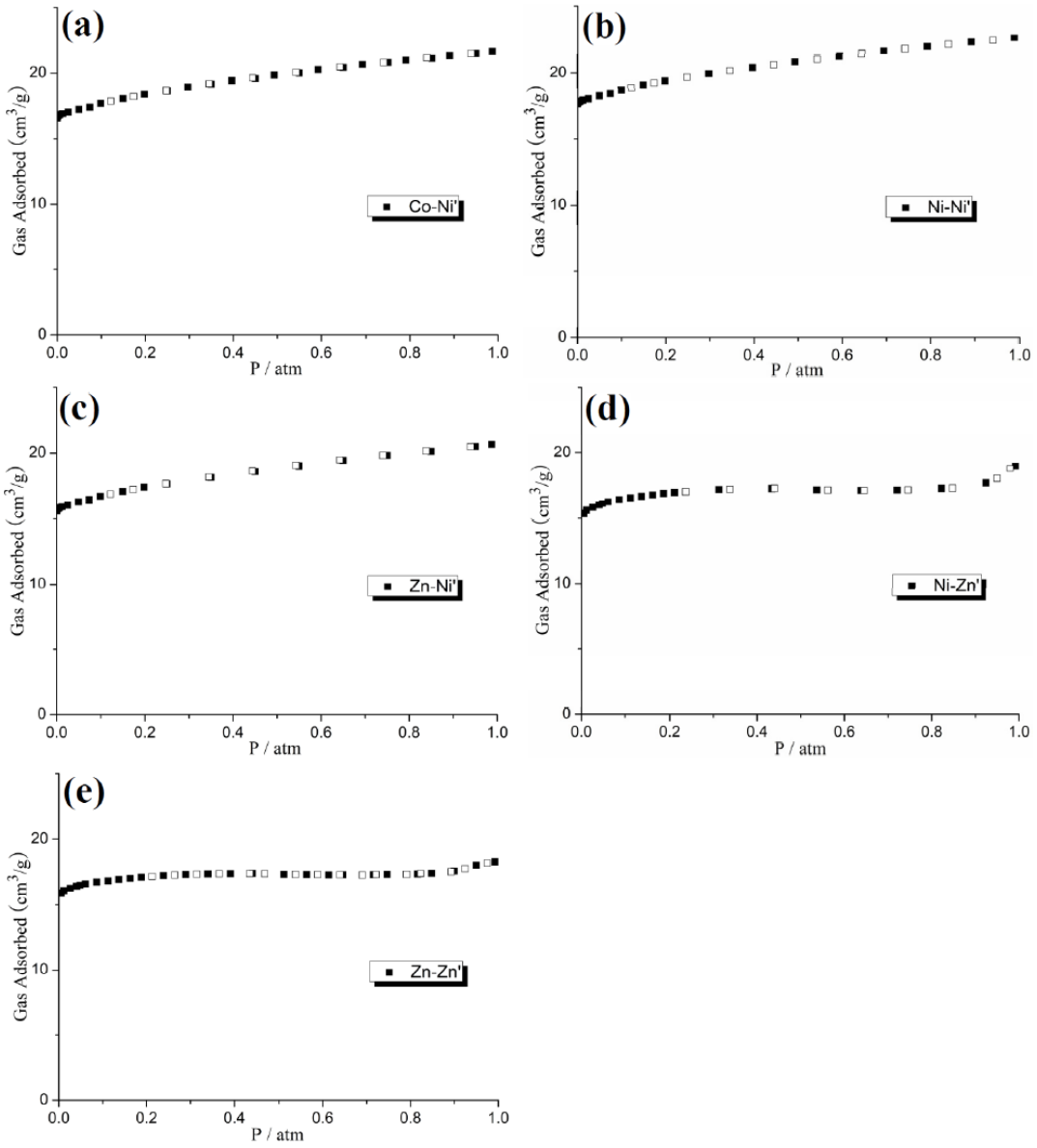

Fig. S11 N_2 sorption curves (77 K) of **3'** (a), **4'** (b), **5'** (c), **6'** (d) and **7'** (e)

The permanent porosity of compound was investigated by N_2 uptake measurements. Based on the nitrogen adsorption isotherm, the BET surface areas were 79 m^2/g (**3**), 82 m^2/g (**4**), 73 m^2/g (**5**), 71 m^2/g (**6**) and 75 m^2/g (**7**), respectively.

Table **S1** Selected bond lengths (Å) of complexes **3** - **7**.

Compound	**3** M = Co; M' = Ni	**4** M = Ni; M' = Ni	**5** M = Zn; M' = Ni	**6** M = Ni; M' = Zn	**7** M = Zn; M' = Zn
M-O1	2.074(3)	2.046(2)	2.082(3)	2.047(2)	2.086(2)
M-O2	2.075(3)	2.055(3)	2.099(3)	2.058(2)	2.111(3)
M-O3	2.072(3)	2.054(3)	2.102(3)	2.062(2)	2.107(3)
M-N1	2.125(3)	2.078(3)	2.145(3)	2.077(2)	2.150(3)
M-N2	2.120(3)	2.079(3)	2.129(3)	2.070(2)	2.134(3)

M-N3	2.094(3)	2.048(3)	2.108(3)	2.050(2)	2.125(3)
M'-O'1	2.127(3)	2.123(2)	2.120(3)	2.164(2)	2.283(2)
M'-O'2	2.138(3)	2.126(2)	2.140(3)	2.234(2)	2.171(3)
M'-O'3	2.155(3)	2.159(2)	2.168(3)	2.247(2)	2.278(2)
M'-O'4	2.133(3)	2.130(3)	2.127(3)	2.212(3)	2.223(3)
M'-N'1	2.072(4)	2.075(3)	2.068(4)	2.099(3)	2.084(4)
M'-N'2	2.073(4)	2.074(4)	2.062(4)	2.092(3)	2.095(3)
M'-N'3	2.062(4)	2.064(3)	2.087(4)	2.090(3)	2.100(4)
M'-N'4	2.083(3)	2.069(3)	2.072(3)	2.088(3)	2.115(3)
M'-N'5	2.069(3)	2.068(4)	2.069(3)	2.095(2)	2.102(3)
M'-N'6	2.072(3)	2.064(3)	2.069(3)	2.089(3)	2.092(3)
M'-N'7	2.055(4)	2.060(4)	2.074(4)	2.095(3)	2.111(4)
M'-N'8	2.047(4)	2.046(4)	2.068(4)	2.084(3)	2.093(4)

Table S**2**. Selected bond lengths (Å) and angles (°) of compounds **1** and **2**.

1		**2**	
Pd(1)-N(1)	1.997(4)	Pd(1)-N(1)	1.987(3)
Pd(1)-O(1)	1.990(3)	Pd(1)-O(1)	1.989(2)
Ni(1)-N(2)	2.054(6)	Zn(1)-N(3)	2.078(5)
Ni(1)-N(3)	2.060(8)	Zn(1)-N(2)	2.101(5)
Ni(1)-O(3)	2.145(4)	Zn(1)-O(3)	2.261(3)
N(1)#1-Pd(1)-N(1)	180.0	N(1)-Pd(1)-N(1)#1	180.00(16)
O(1)-Pd(1)-N(1)#1	97.66(15)	N(1)-Pd(1)-O(1)	82.27(11)
O(1)-Pd(1)-N(1)	82.34(15)	N(1)#1-Pd(1)-O(1)	97.73(11)
O(1)#1-Pd(1)-O(1)	180.0	O(1)-Pd(1)-O(1)#1	180.00(14)
N(2)#2-Ni(1)-N(2)	179.998(1)	N(3)#2-Zn(1)-N(3)	179.998(1)
N(3)#2-Ni(1)-N(3)	179.998(1)	N(2)#2-Zn(1)-N(2)	179.999(1)
O(3)-Ni(1)-O(3)#2	180.0(2)	O(3)#2-Zn(1)-O(3)	180.0

Symmetry transformations used to generate equivalent atoms: For **1**, #1 -x,-y,-z+1; #2 -x+1/2,-y+1/2,-z; For **2**, #1 -x,-y,-z+2; #2 -x+1/2,-y+1/2,-z+1

Table S**3**. The single-component gas separation ratios of **1'** and **2'**

			298K	273K
1'	CO_2/CH_4	0.1 atm	10.6	13.6
		1 atm	5.9	5.3

	CO_2/N_2	0.1 atm	25.7	48.3
		1 atm	17.3	17.1
	CH_4/N_2	0.1 atm	2.4	3.6
		1 atm	2.9	3.4
2'	CO_2/CH_4	0.1 atm	9.8	12.5
		1 atm	6.5	5.7
	CO_2/N_2	0.1 atm	24.1	34.7
		1 atm	18.0	15.1
	CH_4/N_2	0.1 atm	2.4	2.8
		1 atm	2.8	3.0