Electronic Supplementary Material (ESI) for *CrystEngComm*

Supporting Information

Multi-functional Metal-organic frameworks based on H4mdip: Crystal structure, photoluminescence, selective metal ions absorption and catalysis

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Table S1. Crystal Data and structure Refinement Parameters for Compound **1-4**.

	1	2	3	4
Formula	$C_{17}H_8InO_8$	$C_{41}H_{28}N_4O_8Zn_2$	$C_{37}H_{24}Co_2N_4O_8$	$C_{69}H_{51}Co_4N_7O_{18}$
Mr	455.05	835.41	770.46	1501.89
T (K)	150	200	293	293
Radiation, wavelength (Å)	Cu Kα, 1.54184	Mo Kα, 0.71073	Cu Kα, 1.54184	Mo Kα, 0.71073
crystal System	orthorhombic	orthorhombic	orthorhombic	trigonal
space group	*P*nma	*A*ba2	*P*ca2$_1$	*P*32
a [Å]	17.379(5)	14.687(5)	26.6496(5)	19.8876(4)
b [Å]	9.906(5)	18.524(5)	11.4204(2)	19.8876(4)
c [Å]	22.043(5)	16.622(5)	17.5511(3)	19.1704(6)
V [Å^3]	3795(2)	4522(2)	5341.66(16)	6566.4(3)
Z	4	4	4	3
ρ_{calCo} [g cm^{-3}]	0.796	1.227	0.958	1.139
F(000)	892	1704	1568	2298
θ range /°	3.24-62.80	2.15-24.14	3.32-62.75	3.13-23.26
Reflns collected	12091	5393	15032	19457
Independent reflns	3165	2564	7101	11628
Goodness-of-fit	1.027	1.040	1.002	1.050
R_1[a] (I > 2σ (I))	0.0695	0.0425	0.0355	0.0732
wR_2[b] (I > 2σ (I))	0.1774	0.1106	0.0713	0.2113

aR1 = Σ||F_o| − |Fc||/Σ|F_o|. bwR2 = [Σ[w(F_o2 − Fc2)2]/Σw(F_o2)2]1/2.

Table S2.Selected bond lengths (Å) and bond angles (°) of compounds **1-4**

1

In1 – O3	2.187 (3)	In1 – O5C	2.227 (0)
In1 – O4	2.357 (0)	In1 – O6C	2.363 (2)
In1 – O5B	2.227 (0)	In1 – O2	2.271 (4)
In1 – O6B	2.363 (2)	In1 – O1	2.244 (9)
O2 In1 O3	81.116 (19)	O5C In1 O1	83.432 (87)
O4 In1 O5B	83.709 (11)	O5C In1 O6B	133.008 (17)
O5B In1 O5C	76.578 (16)	O5C In1 O4	83.709 (11)
O6C In1 O3	87.208 (86)	O6C In1 O4	91.858 (89)
O6C In1 O2	85.613 (97)	O6C In1 O5B	133.008 (17)
O6C In1 O1	89.979 (13)	O5C In1 O3	126.498 (12)
O1 In1 O3	138.409 (19)	O2 In1 O4	138.412 (16)

2

Zn1 – O1	1.975 (6)	Zn1 – N2	2.074 (7)
Zn1 – O2	2.486 (9)	Zn1 – N1B	2.054 (1)
Zn1 – O3A	1.937 (6)		
O3A Zn1 O1	108.999 (14)	N2 Zn1 O2	93.942 (13)
O3 Zn1 N1B	105.949 (16)	N2 Zn1 O3A	91.279 (14)
O2 Zn1 N1B	86.618 (15)	N2 Zn1 O1	110.531 (15)
O2 Zn1 O1	56.648 (13)	N2 Zn1 N1B	97.567 (19)

3

Co1 – O1A	2.235 (6)	Co2 – O7A	2.206 (8)
Co1 – O2A	2.204 (3)	Co2 – O8A	2.209 (1)
Co1 – O5B	2.025 (0)	Co2 – O6B	2.026 (3)
Co1 – O3	2.013 (4)	Co2 – O4	2.007 (3)
Co1 – N1	2.158 (4)	Co2 – N3	2.142 (0)
Co1 – N2	2.161 (7)	Co2 – N4	2.182 (4)
O1A Co1 N2	88.917 (14)	O4 Co2 N3	90.140 (12)
O2A Co1 N2	93.558 (16)	O6B Co2 N3	86.973 (15)
O5B Co1 N2	89.295 (12)	O8A Co2 N3	90.580 (14)
O3 Co1 N2	92.462 (13)	O7A Co2 N3	92.355 (16)
O1A Co1 O3	90.591 (14)	O7A Co2 O4	89.552 (13)
O3 Co1 O5B	120.661 (13)	O4 Co2 O6B	122.249 (13)
O2A Co1 O1	58.587 (13)	O6B Co2 O8A	88.969 (13)
O2A Co1 O5B	90.404 (13)	O7A Co2 O8A	59.218 (13)
O1A Co1 N1	92.591 (14)	O4 Co2 N4	89.560 (12)

O2A Co1 N1	87.089 (16)	O6B Co2 N4	93.276 (15)
O5B Co1 N1	89.089 (16)	O8A Co2 N4	89.276 (15)
O3 Co1 N1	87.693 (13)	O7A Co2 N4	87.538 (16)

4

O2 – Co1	2.017 (7)	O18 – Co3	2.159 (7)
O1 – Co1	2.141 (4)	O4A – Co3	2.057 (6)
O8A – Co1	2.035 (6)	O6B – Co3	2.0387 (5)
O15A – Co1	2.040 (1)	N6 – Co3	2.256 (2)
N2 – Co1	2.147 (5)	N5 – Co3	2.144 (5)
O10 – Co2	2.078 (6)	O13 – Co4	2.074 (9)
O3 – Co2	2.070 (7)	O18 – Co4	2.142 (7)
O1 – Co2	2.145 (4)	O17A– Co4	2.092 (6)
N1 – Co2	2.156 (2)	O7B – Co4	2.097 (4)
O14A – Co2	2.051 (1)	N3 – Co4	2.152 (5)
N8 – Co2	2.148 (7)	N4 – Co4	2.213 (8)
O12 – Co3	2.056 (6)		

O15A Co1 O2	98.734 (29)	N5 Co3 O12	94.646 (30)
O15A Co1 O1	91.623 (25)	N5 Co3 O4A	87.36 (33)
O15A Co1 O8	101.616 (29)	O18 Co3 N6	90.050 (30)
O15A Co1 N2	97.532 (32)	O18 Co3 O6B	93.358 (28)
O8 Co1 N2	86.021 (36)	O18 Co3 O12	88.504 (25)
O2 Co1 N2	90.182 (36)	O18 Co3 O4A	88.962 (33)
O2 Co1 O1	92.657 (28)	N6 Co3 O4A	84.230 (34)
O8 Co1 O1	87.959 (28)	N6 Co3 O6B	83.962 (33)
N8 Co2 N1	88.370 (31)	O12 Co3 O6B	95.534 (29)
N8 Co2 O3	89.518 (28)	O12 Co3 O4A	96.326 (29)
N8 Co2 O10	89.975 (30)	O13 Co4 N4	88.254 (34)
N8 Co2 O14A	89.179 (30)	O13 Co4 N3	91.087 (39)
O1 Co2 N1	92.739 (28)	O13 Co14 O18	89.908 (26)
O1 Co2 O3	89.373 (25)	O13 Co4 O7B	90.071 (31)
O1 Co2 O10	89.902 (26)	O17A Co4 N4	91.317 (29)
O1 Co2 O14A	90.974 (26)	O17A Co4 N3	90.292 (25)
O14A Co2 N1	89.517 (35)	O17A Co4 O18	87.514 (38)
O10 Co2 N1	88.905 (35)	O17A Co4 O7B	91.616 (33)
O3 Co2 O10	91.449 (31)	O7B Co4 N4	87.380 (31)
O3 Co2 O14A	90.098 (32)	N4 Co4 N3	88.302 (37)
N5 Co3 N6	86.834 (33)	O7B Co4 O18	89.735 (25)
N5 Co3 O6B	89.806 (33)	N4 Co4 N3	94.621 (32)

Symmetry transformations used to generate equivalent atoms: for **1**: A) 1/2–x, y, 1/2+z; B) 1/2+x,

–y, z; for **2**: A) –x, –y, z; B) 1/2–x, 1/2+y, z; C) 1/2+x, 1/2–y, z; D) 1/2–x, y, 1/2+z; for **3**: A) 1/2+x, 1/2–y, 1/2–z; B) –x, 1/2+y, –z; C) –x, –y, –z; D) x, 1/2–y, z; for **4**: A) –x, x–y, 2/3+z; B) –x+y, –x, 1/3+z.

Supplementary description of the structure for compound 2 and 4.

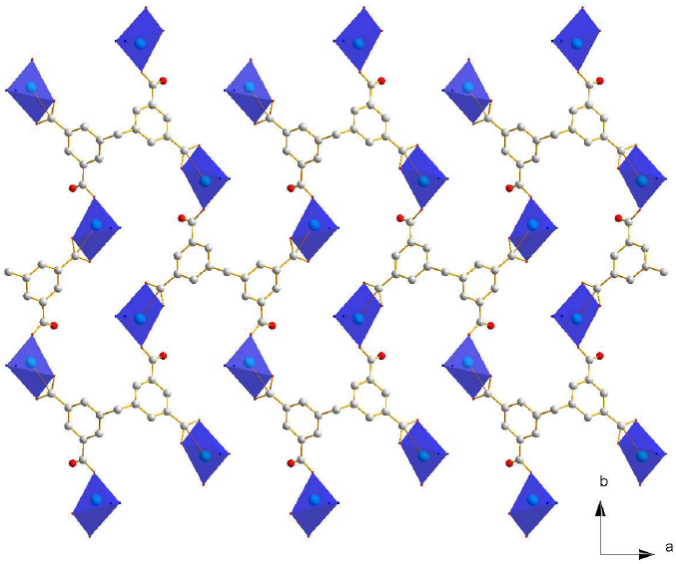

Fig. S1 The single 2D layer constructed by $mdip^{4-}$ ligands and Zn^{2+} cations viewed along the *c* axis.

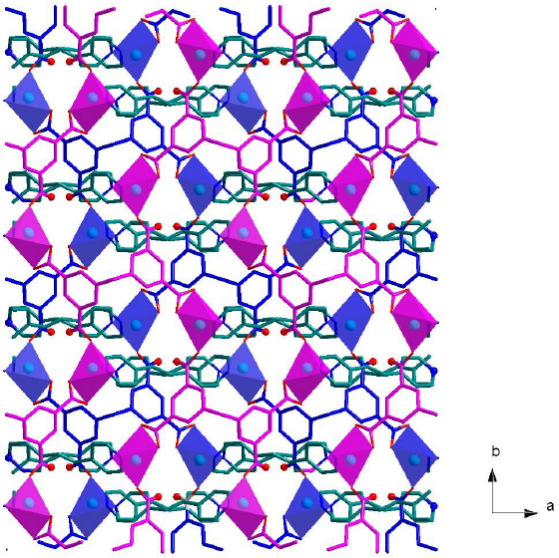

Fig. S2 The ABAB accumulated 2D layers are linked by bpe molecules viewed along the *c* axis.

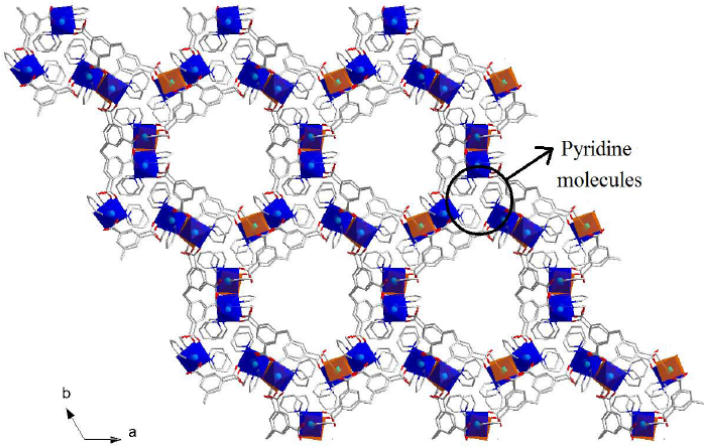

Fig. S3 The small channels among the regular triangular helical chains have been occupied by the pyridines molecules.

Powder X-ray Diffraction (PXRD) for compounds 1, 2, 3 and4.

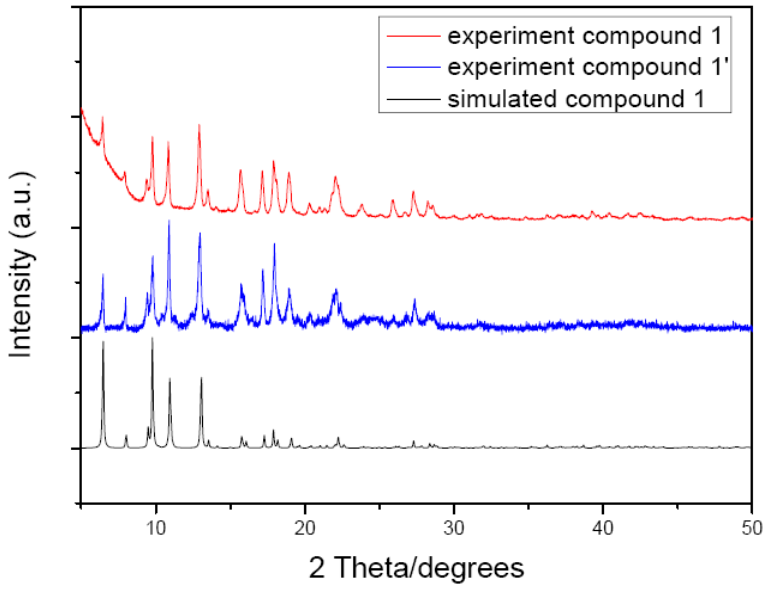

Figure S4. PXRD analysis for compound **1** (Red line: fresh compound **1** was measured by "Philips X'Pert PRO S" X-ray Diffractometer. Blue line: fresh compound **1** was measured by "Theta Theta Rotating anode X-ray Diffractometer")

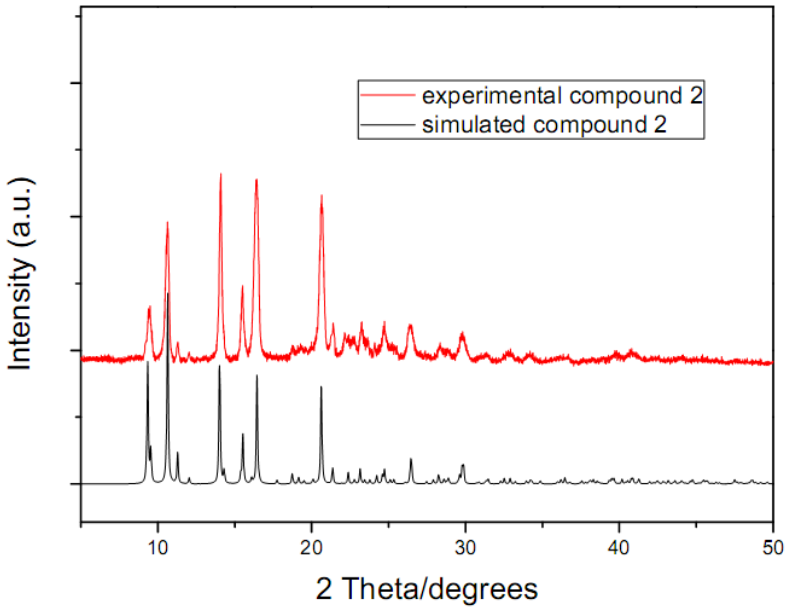

Figure S5. PXRD analysis for compound **2**

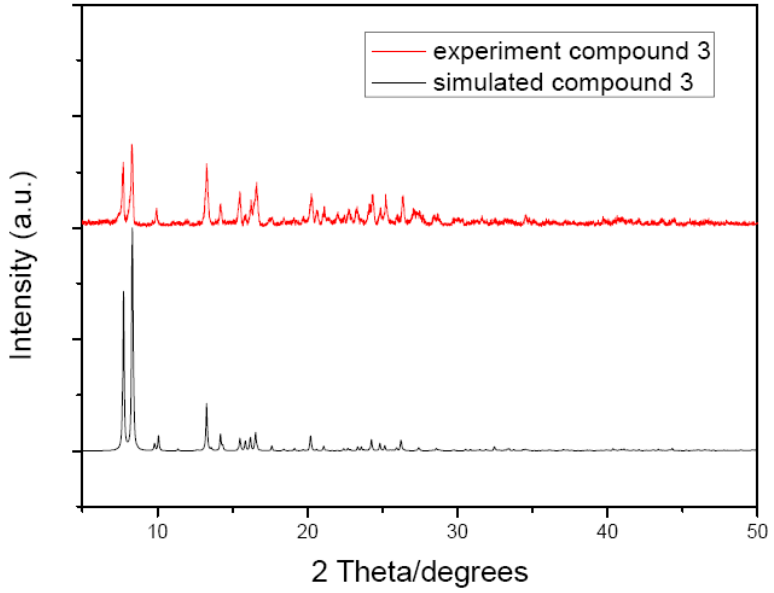

Figure S6. PXRD analysis for compound **3**

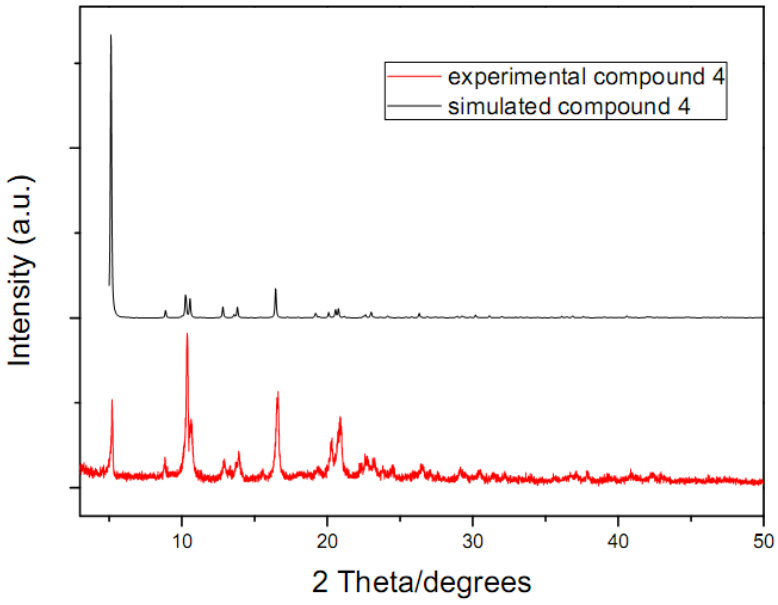

Figure S7. PXRD analysis for compound **4**

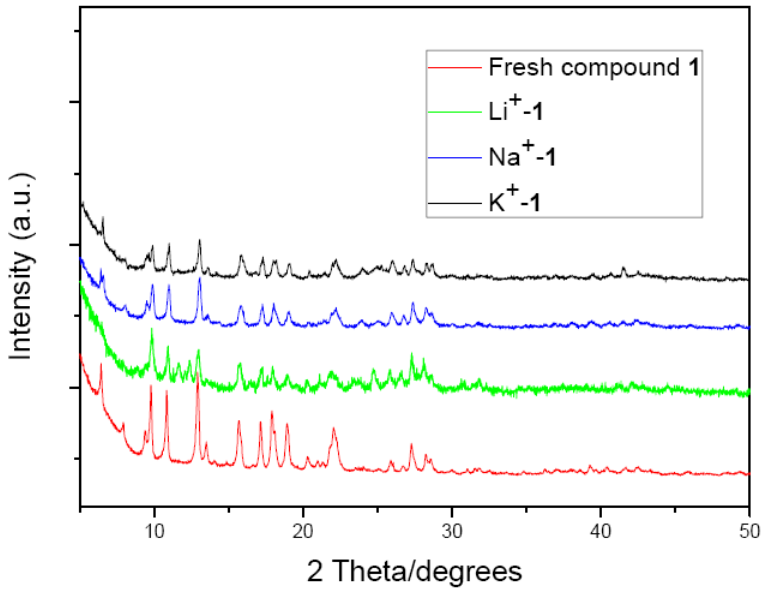

Figure S8. PXRD analyses for Li^{+}-**1**, Na^{+}-**1**, K^{+}-**1.**

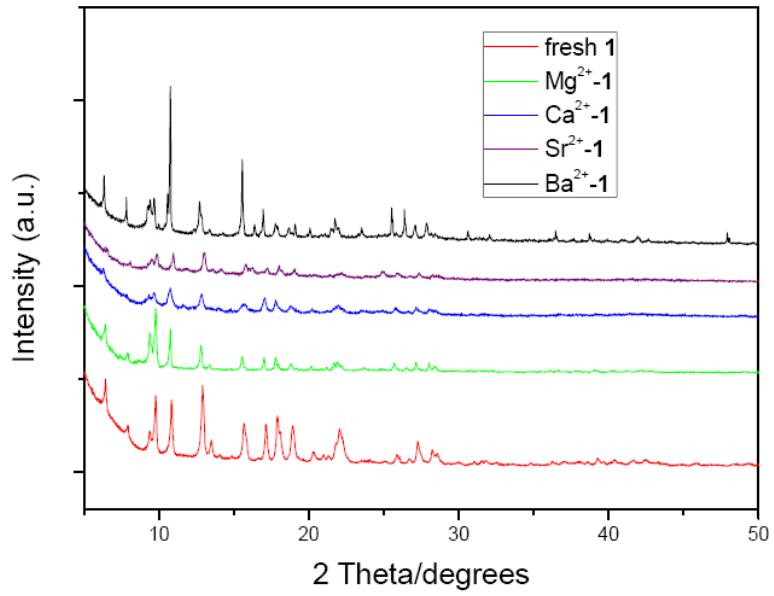

Figure S9. PXRD analyses for Mg^{2+}-**1**, Ca^{2+}-**1**, Sr^{2+}-**1,** Ba^{2+}-**1.**

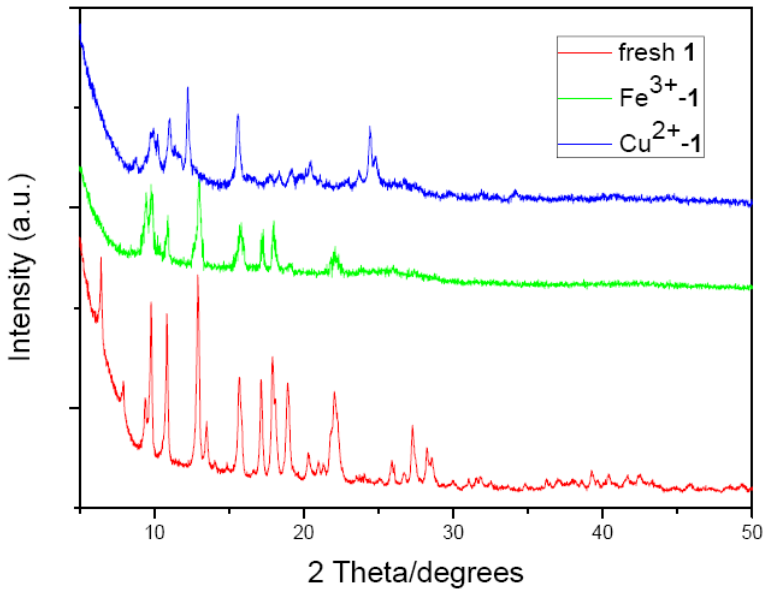

Figure S10. PXRD analyses for Cu^{2+}-**1**, Fe^{3+}-**1**.

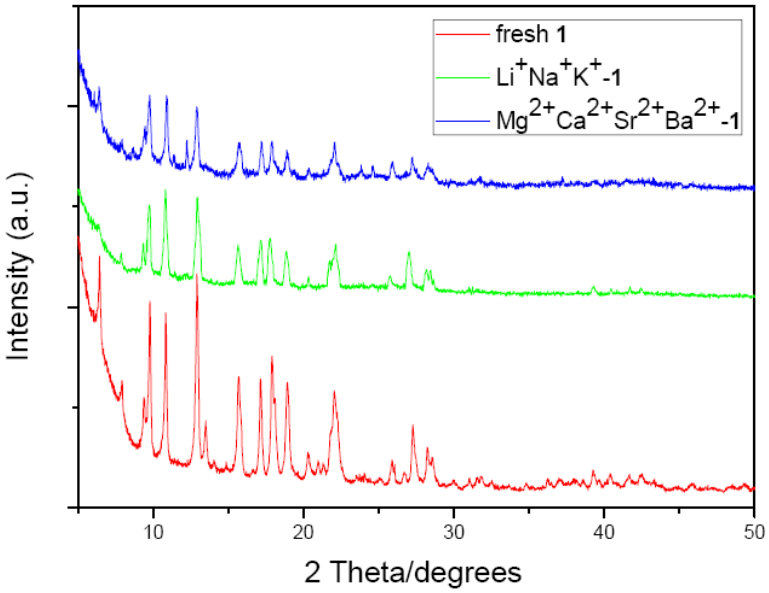

Figure S11. PXRD analyses for $Li^{+}Na^{+}K^{+}$-**1**, $Mg^{2+}Ca^{2+}Sr^{2+}Ca^{2+}$-**1**.

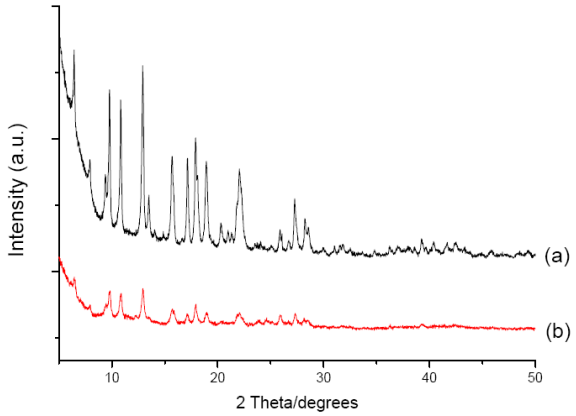

Figure S12. Powder XRD pattern analyses for (a) fresh compound **1**, (b) three times reused for the Michael addition of pyrrole to nitroolefins.

TGA analyses of compounds 1-4.

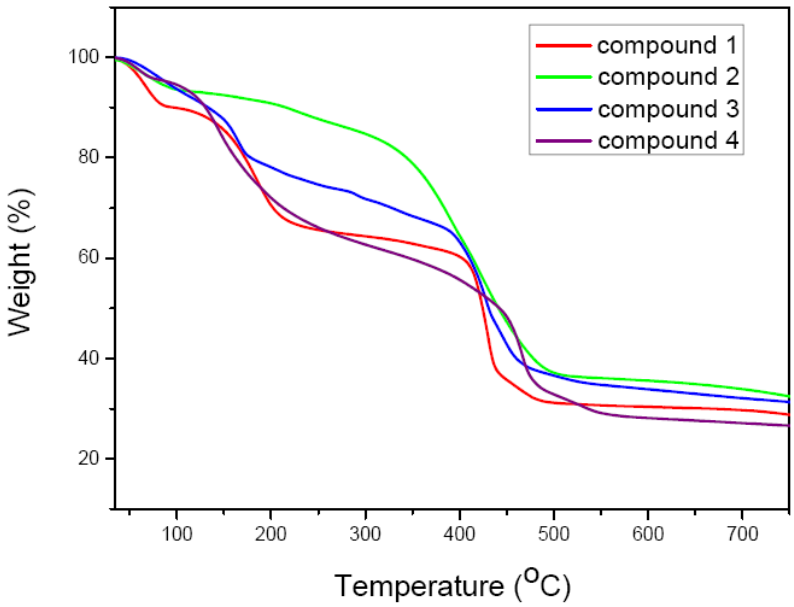

Figure S13. TGA analyses of compounds **1**-**4**.

Typical procedure for detection of metal ions by ICP-OES.

Approximate 6~10 mg of Li^{+}-**1**, Na^{+}-**1**, K^{+}-**1**, Mg^{2+}-**1**, Ca^{2+}-**1**, Sr^{2+}-**1**, Ba^{2+}-**1**, Cu^{2+}-**1**, $Li^{+}Na^{+}K^{+}$-**1** and $Mg^{2+}Ca^{2+}Sr^{2+}Ba^{2+}$-**1** were dissolved with a small amount of concentrated HNO_3 in 25ml volumetric flasks respectively. Then solutions were diluted into 25 ml for detection of the corresponding metal ions by ICP-OES.

Typical procedure for Friedel-Crafts alkylation of pyrrole with nitroolefins.

To a solution of 5mg catalyst (indium nitrate, compounds **1**, **3** and **4**), 0.15 mmol nitroalkenes, 0.45mmol pyrrole in 0.5 ml water was stirred for 1 hour at roomtemperature. After completion of reaction, 5 ml ethyl acetate and 2.5 μl nitrobenzene (used for internal standard) was added in the solution. After absolutely mixing, the supernatant organic solution was analyzed by GC-MS to check the conversion and yield of the reaction.

Experimental procedure for reusability tests of compound 1.

At the end of the reaction, the solution was operated according to "Typical procedure for reaction". And then the mixture of aqueous phase and organic phase were filtered. The catalyst was wash by ethyl acetate several times. The reused catalyst was dried for the second run.