Electronic Supporting Information

Novel Mn(II) based metal-organic frameworks isolated in ionic liquids

Ling Xu[†‡], Young-Uk Kwon[*‡], Baltazar de Castro[†] and Luís Cunha-Silva[*†]

[†] *REQUIMTE & Department of Chemistry and Bichemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal.*

[‡] *Department of Chemistry, BK-21 School of Chemical Materials Science, SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-176 Korea.*

* Corresponding authors E-Mails: *l.cunha.silva@fc.up.pt* and *ywkwon@skku.edu*

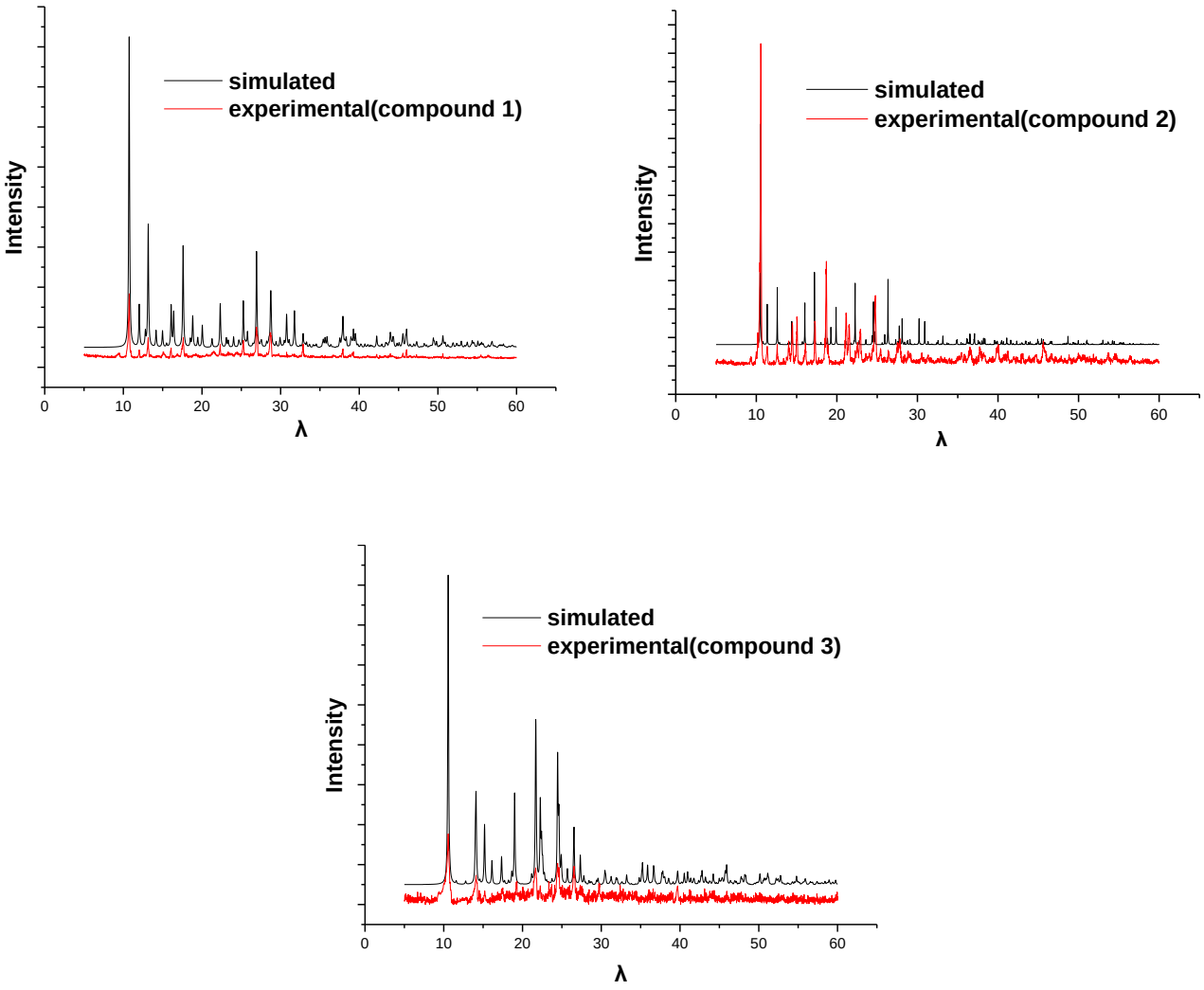


Figure S1. The powder X-ray diffraction patterns for the compounds **1-3** and the comparison with the respective simulated difractogram.

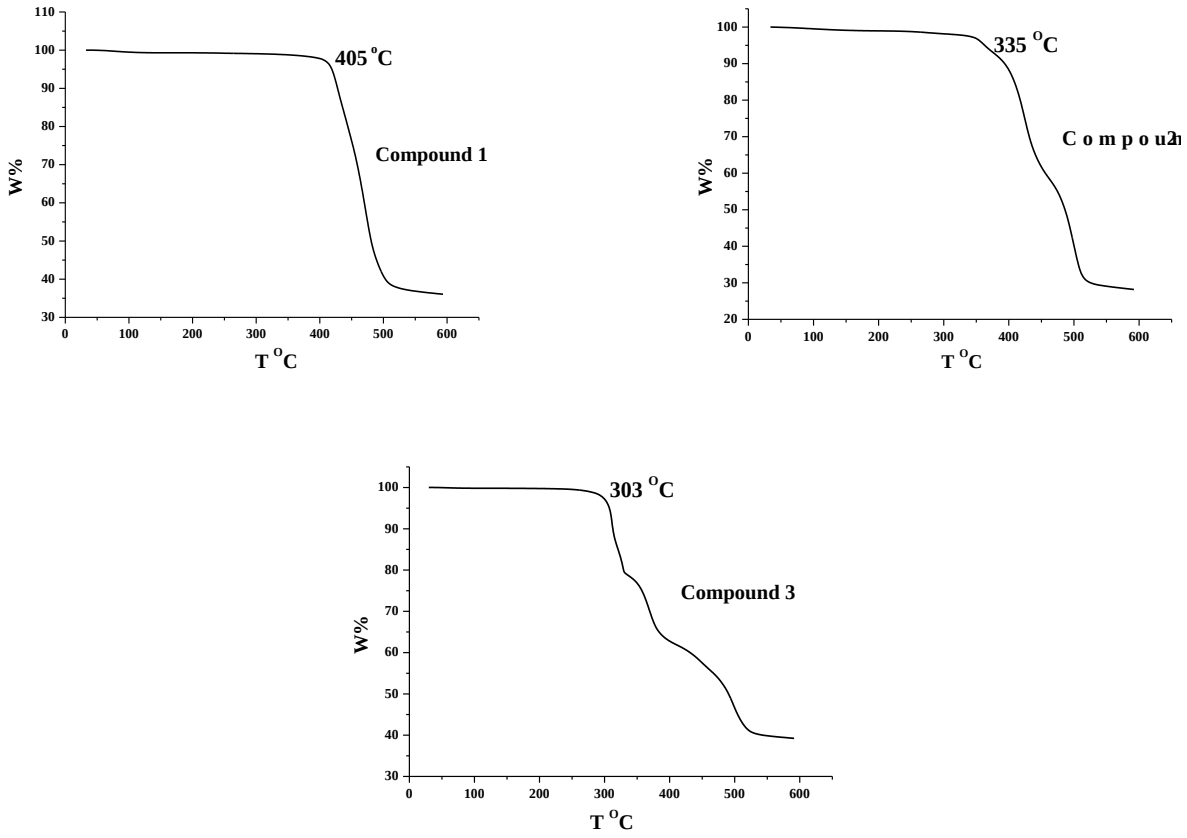


Figure S2. TG curves of compounds **1** - **3**.

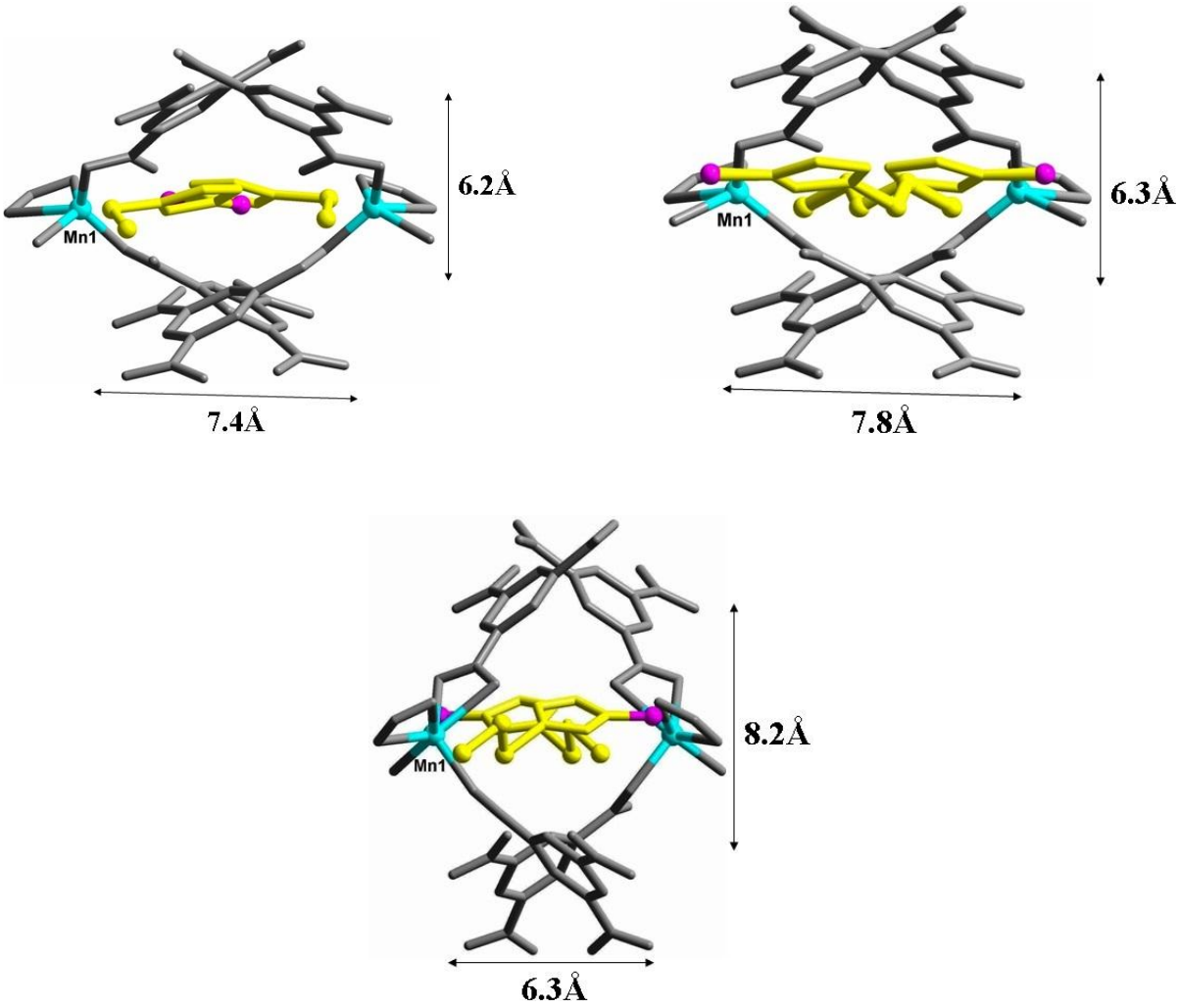


Figure S3. The cavities and the arrangement modes of $[rmi]^+$ in compounds **1** (top left)**, 2** (top right) and **3** (bottom). $-CH_3$ groups are represented by purple cycles.

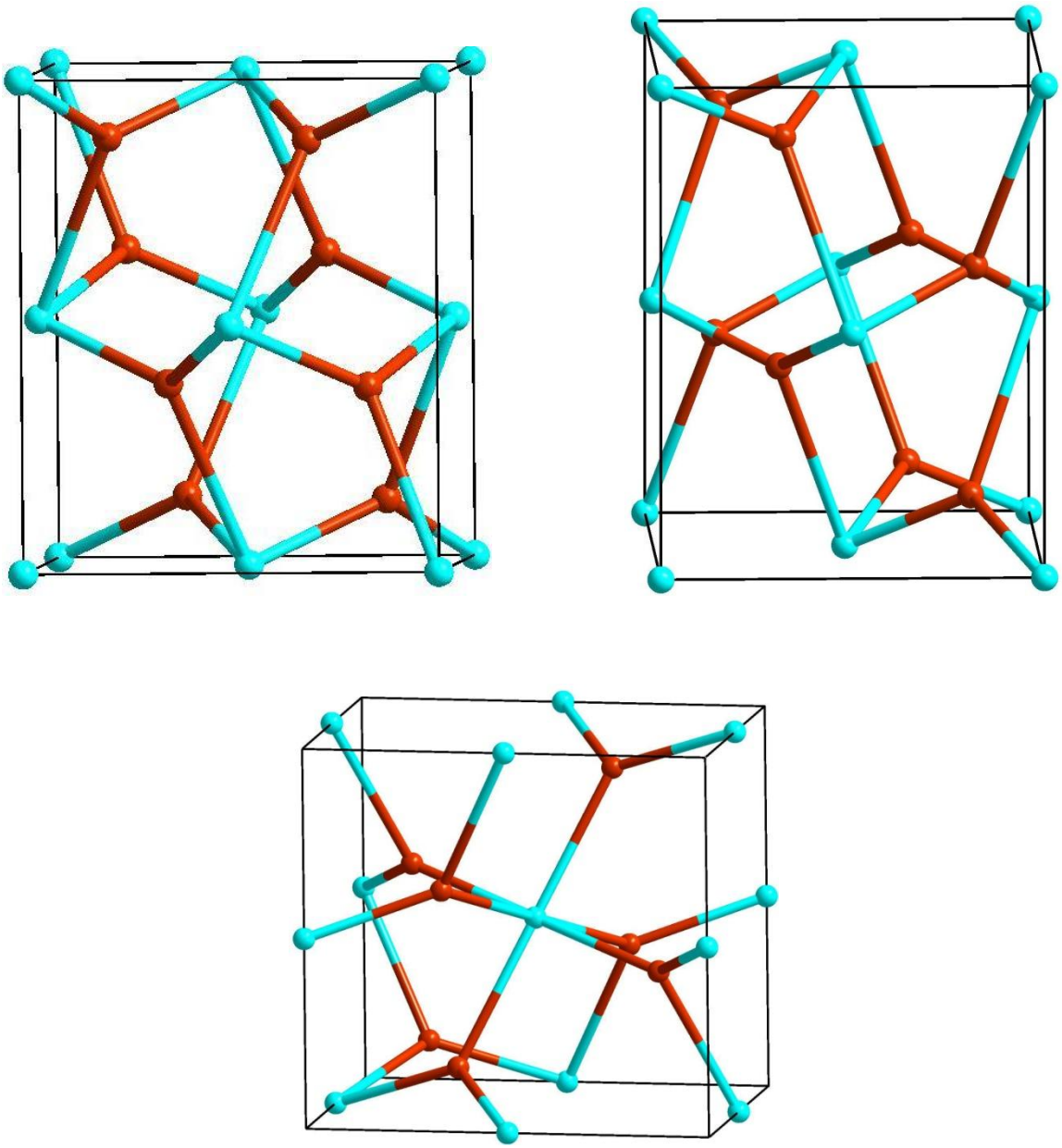
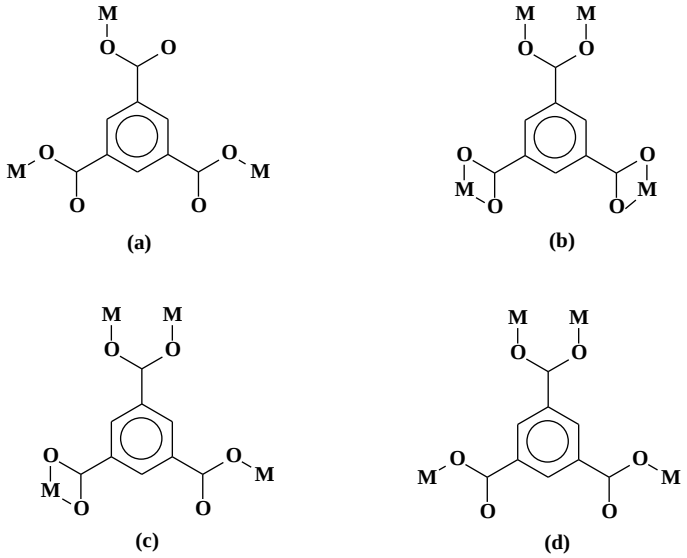


Figure S4. Topological representations of $[Mn(btc)]^-$ strcutrures in compounds **1** (top-left)**, 2** (top-right) and **3** (bottom).



Scheme S1. Connectivity modes of btc^{3-} ligand with metals found in the preferred products.

Table S1. The main IR characteristic absorption peaks for compounds **1-3**.

compounds	$\upsilon_{as}(COO^-)/cm^{-1}$	$\upsilon_{s}(COO^-)/cm^{-1}$	$\delta(C-H)(MI)/cm^{-1}$	$\delta(C-N)(MI)/cm^{-1}$	$\delta(C-H)/cm^{-1}$
1	1628, 1560	1458, 1368	3172, 3101	1163	2982, 2932
2	1624, 1576	1428, 1375	3153, 3104	1166	2968, 2919
3	1615, 1582	1413, 1353	3156, 3104	1166	2970, 2925

Table S2. Selected bond distances (Å) and angles (°) for the Mn1 coordination center of **1**.

Compound **1**		
Mn1– O11 = 2.022(4)	O11– Mn1– O13A = 132.2(2)	O13A– Mn1– O15C = 82.7(1)
Mn1– O13A = 2.107(3)	O11– Mn1– O14B = 80.7(1)	O16C– Mn1– O15C = 60.6(1)
Mn1– O14B = 2.209(3)	O14B– Mn1– O13A=114.0(1)	O11– Mn1– O12 = 64.8(1)
Mn1– O15C = 2.233(3)	O11– Mn1– O16C = 118.5(1)	O14B– Mn1– O12 = 134.9(1)
Mn1– O16C = 2.477(4)	O14B– Mn1– O16C = 76.1(1)	O13A– Mn1– O12 = 75.2(1)
	O13A– Mn1– O16C=109.1(1)	O16C– Mn1– O12 = 145.6(1)
	O11– Mn1– O15C = 118.5(1)	O15C– Mn1– O12 = 87.0(1)
	O14B– Mn1– O15C=136.7(1)	

Symmetry codes: A = *x−1/2, −y−1/2, −z+1;* B =*−x+3/2, , y+1/2, z;* C =*−x+3/2, −y, z+1/2*

Table S3. Selected bond distances (Å) and angles (°) for the Mn1 center in the compound **2**.

Compound **2**		
Mn1−O11A = 1.958(5)	O11A−Mn1– O16C=121.9(8)	O13B– Mn1−O15=132.7(2)
Mn1−O13B = 2.293(5)	O11A−Mn1−O13B=119.2(2)	O11A−Mn1−O14B=123.7(2)
Mn1−O14B = 2.454(5)	O16C−Mn1−O13B = 86.5(2)	O16C−Mn1−O14B = 114.3(2)
Mn1−O15 = 2.295(4)	O11A−Mn1−O15 = 82.6(2)	O13B−Mn1−O14B=59.4(2)
Mn1−O16C = 2.122(4)	O16C−Mn1−O15 = 118.8(2)	O15−Mn1−O14B=73.5(2)

Symmetry codes: A = *−x+1/2, y−1/2, z;* B = *x,− y+1/2, z+1/2;* C = *−x+1, −y, −z+1*

Table S4. Selected bond distances (Å) and angles (°) for the Mn1 center in the compound **3**.

Compound **3**		
Mn1−O11 = 2.201(4)	O14B−Mn1−O12A = 79.9(2)	O15C−Mn1−O13B = 102.4(2)
Mn1−O12A = 2.135(4)	O14B−Mn1−O15C = 119.1(2)	O11−Mn1−O13B = 96.6(2)
Mn1−O13B = 2.249(5)	O12A−Mn1−O15C = 93.7(2)	O14B−Mn1−O16C = 136.8(2)
Mn1−O14B = 2.122(4)	O14B−Mn1−O11 = 102.7(2)	O12A−Mn1−O16C = 138.0(2)
Mn1−O15C = 2.186(5)	O12A−Mn1−O11 = 94.6 (2)	O15C−Mn1−O16C = 54.1(2)
Mn1−O16C = 2.462(5)	O15C−Mn1−O11 = 138.2(2)	O11−Mn1−O16C = 95.0(2)
	O14B−Mn1−O13C = 60.8(2)	O13B−Mn1−O16C = 78.4(2)
	O12A−Mn1−O13C= 140.6(2)	

Symmetry code: A =*−x, −y, −z+1;* B = *x+1/2, −y+1/2, −z+1;* C = *−x−1/2, −y, z−1/2*.

Table S5. The MOF materials synthesized by ionothermal reactions.

ligands	metal	compounds	Ref
1,3-bis(4-pyridyl- propane) (bpp)	Cu	$[Cu(bpp)]BF_4$	[1]
1,3,5-triazine (tpt)	Cu	$[Cu_3(tpt)_4](BF_4)_3\cdot(tpt)_{2/3}\cdot 5H_2O$	[2]
1,4-benzene-dicarboxylate acid (H_2bdc)	Cd	$[bmi]_2[Cd_3(bdc)_3Br_2]$	[3]
	Co	$[Co_3(IM)_2(bdc)_3]$	[4]
1,3-benzene-dicarboxylate acid (1,3-H_2bdc)	Co	$[emi]_2[Co_3(1,3\text{-}bdc)_4]$	[5]
	Ni	$[emi]_2[Ni_3(1,3\text{-}bdc)_4]$	[5]
	Mn	$[emi]_2[Mn_3(1,3\text{-}bdc)_4]$	[5]
1,2,4,5-benzene-tetracarboxylate acid (H_4btec)	Cd	$[emi]_2[Cd_2(btec)Br_2]$	[6]
	Zn	$[emi]_2[Zn_3(btec)_2]\cdot 2H_2O$	[7]
Achiral 4,4'-oxybis(benzoic acid) (H_2obb)	In	$[emi]_3[In(obb)_2](Es)_2(H_2O)$	[8]
Tetrafluorosuccinic acid (H_2tfs)	Co	$[emi]_2[Co(H_2O)_2(tfd)]$	[9]
Hexafluoroglutaric acid (H_2hfg)	Co	$[emi]_2[Co_3(H_2O)_4(hfg)]$	[9]
1,4-naphthalenedicarboxylate (1,4-ndc)		$[emi]_2[Zn_7(\mu_4\text{-}O)_2(1,4\text{-}ndc)_6]$	[10]
1,4-phenylenebis-(methylene)diphosphonic acid (H_4pmd)	Ce	$Ce(Hpmd)(H_2O)$	[11]
	Pr	$Pr(Hpmd)(H_2O)$	[11]
1,3-biscarboxy-alkylimidazolium salt (HA)	Ca	$Ca_2[A_3Br]\cdot 5H_2O$	[12]
	Sr	$Sr[ABr]\cdot 5.5H_2O$	[12]
	Ba	Ba[ABr]	[12]
	Cs	$CsA\cdot 4H_2O$	[12]
5-tert-butyl-isophthalic acid (H_2tbip)	Co	$[Co_3(tbip)_3(H_2O)_4]\cdot 2H_2O$	[13]
D-camphoric (D-H_2cam)	In	$[emi][In(D\text{-}cam)_2]$	[8]
	In	$[Pr_4N][In(D\text{-}cam)_2]$	[8]
	In	$[Pr_4N][In(DL\text{-}cam)_2]$	[8]
	In	$[emi]_2[In_2(D\text{-}cam)_3(D\text{-}Hcam)_2]$	[8]
	In	$[bmi]_2[In_2(D\text{-}cam)_3(D\text{-}Hcam)_2]$	[8]
	Co	$[emi][Co_2(D\text{-}cam)_2(OAc)])$	[14]
1,3,5-benzene-tricarboxylate (H_3btc)	Ni	$[emi]_2[Ni_3(btc)_2(OAc)_2]$	[15]
	Ni	$[pmi]_2[Ni_3(btc)_2(OAc)_2]$	[16]
	Ni	$[bmi]_2[Ni_3(btc)_2(OAc)_2]$	[16]
	Ni	$[pmi]_2[Ni_3(Hbtc)_4(H_2O)_2]$	[16]
	Ni	$[bmi]_2[Ni_3(Hbtc)_4(H_2O)_2]$	[17]
	Ni	$[bmi]_2[Ni(Hbtc)_2(H_2O)_2]$	[17]
	Ni	$[ami][Ni_3(btc)_2(OAc)(MI)_3]$	[18]

	Co	[emi][Co_2(Hbtc)$_2$(4,4'-bpy)$_3$]Br	[19]
	Co	[emi][Co(Hbtc)(4,4'-bpy)$_2$](4,4'-bpy)Br	[19]
	Co	[emi][Co(btc)(H-Im)]	[19]
	Co	[emi]$_2$[Co(btc)$_2$(H_2TED)]	[19]
	Co	[emi]$_2$[Co_3(btc)$_2$(OAc)$_2$]	[20]
	Co	[emi][Co(btc)]	[20]
	Co	[emi][Co_2(btc)$_4$$H_7$(2,2'-bpy)$_2$]	[20]
	Co	[pmi]$_2$[Co_2(btc)$_2$(H_2O)$_2$]	[4]
	Zn	[bmi][Zn_2(btc)(OH)I]	[21]
	Zn	[bmi]$_2$[Zn_4(btc)$_3$(OH)(H_2O)$_3$]	[22]
	Zn	[ami][Zn_2(btc)(OH)Br]	[22]
	Zn	[emi][Zn(btc)]	[22]
	Zn	[pmi][Zn(btc)]	[22]
	Cd	[emi][Cd_2(btc)Cl_2]	[23]
	Cd	[emi][Cd(btc)]	[24]
	Cd	[pmi][Cd(btc)]	[23]
	Mn	[emi][Mn(btc)] (**1**)	This work
	Mn	[pmi][Mn(btc)] (**2**)	
	Mn	[pmi][Mn(btc)] (**3**)	

Table S6. Preferred M-btc coordination polymers synthesized in ionothermal reactions and their coordination modes classified according the Scheme S1.

Metal center	**ILs**	**products**	**Coordination numbers of M^{2+}**	**Coordination modes of BTC**
Zn	[emi]Br	[emi][Zn(btc)]	4	Mode d: monodentate and bidentate
	[pmi]Br	[pmi][Zn(btc)]	3	Mode a: tri-monodentate
Cd	[emi]Br/I	[emi][Cd(btc)]	6	Mode b: bidentate and chelating
	[pmi]Cl/Br/I	[pmi][Cd(btc)]	5	Mode c: monodentate, bidentate and chelating
Mn	[emi]Br	[emi][Mn(btc)] (**1**)	5	Mode c: monodentate, bidentate and chelating
	[pmi]Cl/Br	[omi][Mn(btc)] (**2**)	5	Mode c: monodentate, bidentate and chelating
	[pmi]I	[pmi][Mn(btc)] (**3**)	6	Mode b: bidentate and chelating

References

(1) Jin, K.; Huang, X. Y.; Pang, L.; Li, J.; Appel, A.; Wherland, S. *Chem. Commun.* **2002**, 2872..

(2) Danil, N. D.; Chun, H. C.; Kim, K. M. *Chem. Commun.* **2004**, 1594.

(3) Liao, J. H.; Huang, W. C. *Inorg. Chem. Commun.* **2006**, *9*, 1227.

(4) Wang, Y. L.; Zhang, N.; Liu, Q. Y.; Yang, X.; Bai, H.; Duan, L. Y.; Liu, H. Y. *Inorg. Chem. Comm.* **2011**, *14*, 380.

(5) Chen,W. X.; Zhuang, G. L.; Zhao, H. X.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Dalton Trans.* **2011**, *40*, 10237.

(6) Xie, Z. L.; Feng, M. L.; Li, J. R.; Huang, X. Y. *Inorg. Chem. Commun.* **2008**, *11*, 1143.

(7) W.J. Ji, Q.G. Zhai, S.N. Li, Y.C. Jiang, M. C. Hu, *Chem. Commun*. **2011**, 47, 3834.

(8) Zhang, J.; Chen, S.; Bu, X. *Angew. Chem. Int. Ed*. **2008**, *47*, 5434.

(9) Hulvey, Z.; Wragg, D. S.; Lin, Z.; Morris, R. E.; Cheetham, A. K. *Dalton Trans.* **2009**, 1131.

(10) Wei, J. J.; Liu, Q. Y.; Wand, Y. L.; Zhang, N.; Wang, W. F. *Inorg. Chem. Comm.* **2012**, *15*, 61.

(11) Shi, F. N.; Trindade, T.; Rocha, J.; Almeida Paz, F. A. *Cryst. Grow. Des.* **2008**, *8*, 3917.

(12) Fei, Z.; Geldbach, T. Scopelliti, J. R.; Dyson, P. J. *Inorg. Chem.* **2006**, *45*, 6331.

(13) Liang, Y. F.; Zhang, Y. R.; Han, Z. B. *Z. Anorg. Allg. Chem.* **2012**, *628*, 423.

(14) Chen, S.; Zhang, J.; Bu, X. *Inorg. Chem.* **2008**, *47*, 5567.

(15) Lin, Z. J.; Wragg, D. S.; Morris, R. E. *Chem. Commun.* **2006**, 2021.

(16) Xu, L.; Yan, S.; Choi, E. Y.; Lee, J. Y.; Kwon, Y. U. *Chem. Commun*. **2009**, 3431.

(17) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880.

(18) Xu, L.; Choi, E. Y.; Kwon, Y. U. *J. Solid. State. Chem.* **2008**, *181*, 3185.

(19) Lin, Z.; Li, Y.; Slawin, A. M. Z.; Morris, R. E. *Dalton Trans*. **2008**, 3989.

(20) Lin, Z.; Wragg, J. E.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 10334.

(21) Xu, L.; Choi, E. Y.; Kwon, Y. U. *Inorg. Chem. Commun.* **2008**, *11*, 150.

(22) Xu, L.; Choi, E. Y.; Kwon, Y. U. *Inorg. Chem.* **2007**, *46*, 10670.

(23) Xu, L.; Choi, E. Y.; Kwon, Y. U. *Inorg. Chem.* **2008**, *47*, 1907.

(24) Liao, J. H.; Wu, P. C.; Huang, W. C. *Cryst. Growth & Des*. **2006**, *6*, 1062.