Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

The Role of Weak Interactions in Controlling the Mode of Interpenetration in Hybrid Ultramicroporous Materials

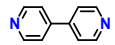
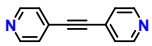
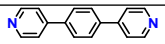
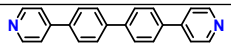
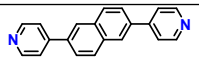
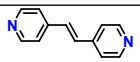
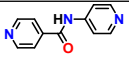
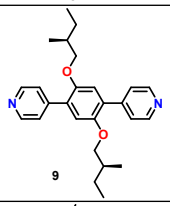
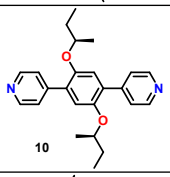
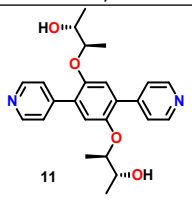
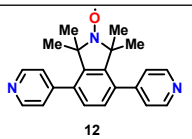
Alankriti Bajpai, Matteo Lusi and Michael J. Zaworotko*

Department of Chemical Sciences and Bernal Institute, University of Limerick, Castletroy, Co. Limerick, Ireland.

xtal@ul.ie

Table of Contents

Table S1. List of **MFSIX-L-M'(-i)** compounds reported in the literature

Ligand	MFSIX-L-M'(-i)	REFCODE	Year	Reference
 1	**SIFSIX-1-Zn**	ZESFUY	1995	1
	SIFSIX-1-Cu	GORWUF	2000	2
	GEFSIX-1-Cu	AFEHUO	2002	3
	SIFSIX-1-Cu	AFEKAX		
	SIFSIX-1-Zn	WONZIJ	2009	4
	SIFSIX-1-Cu	HAPKOA	2013	5
	TIFSIX-1-Cu	PETWIW		
	SNFSIX-1-Cu	PETWES		
 2	**SIFSIX-2-Zn**	WONZOP	2009	4
	SIFSIX-2-Cu	YEMTER	2013	6
	SIFSIX-2-Cu-i	YEMTIV		
 3	**SIFSIX-3-Zn**	FUDQIF	2009	7
	SIFSIX-3-Zn	FUDQIF	2013	6
	SIFSIX-3-Cu	WONKOB	2014	8
	SIFSIX-3-Ni	-	2015	9
				10
				11
	SIFSIX-3-Co			
 4	**SIFSIX-4-Zn**	WONZUV	2009	4
 5	**SIFSIX-5-Zn-i**	LIFWII	2011	12
 6	**SIFSIX-6-Zn-i**	LIFWOO		
 7	**SIFSIX-7-Cu**	HAPKUG	2012	13
 8	**SIFSIX-8-Cu**	GIKPIB	2013	14
 9	**SIFSIX-9-Zn**	SERWET	2013	15
 10	**SIFSIX-10-Zn**	SERWIX		
 11	**SIFSIX-11-Zn**	SERWAP		
 12	**SIFSIX-12-Cu**	VOLQAQ	2014	16
 13	**SIFSIX-13-Zn**	FORKOO, FORKUU	2015	17

SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS

All reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar or AK Scientific, and used as received.

Compounds **15** and **16** were prepared by Pd^0-catalysed Sonogashira coupling of 4-ethynylpyridyine hydrochloride with the corresponding diiodo derivatives by following the procedure reported in the literature.[18]

SIFSIX-15-Zn-i. A blank layer of MeOH/$CHCl_3$ (2 mL; 1:1 *v/v*) was carefully layered over a solution solution of **15** in 2 mL of $CHCl_3$ (5 mg, 0.02 mmol). Over this was layered a solution of zinc hexafluorosilicate (0.01 mmol) in 2 mL of MeOH. Colourless needles were obtained after 10 d. Yield 67%.

SIFSIX-15-Cu-i. A blank layer of MeOH/$CHCl_3$ (2 mL; 1:1 *v/v*) was carefully layered over a solution solution of **15** in 2 mL of $CHCl_3$ (5 mg, 0.02 mmol). Over this was layered a solution of copper hexafluorosilicate (0.01 mmol) in 2 mL of MeOH. Violet needles were obtained after 8 d. Yield 74%.

Crystals of **SIFSIX-15-Zn-i** and **SIFSIX-15-Cu-i** were also isolated when the solvent of crystallization was changed from MeOH/$CHCl_3$ to EtOH/$CHCl_3$, MeOH/ethylene glycol/H_2O or *n*-BuOH/ethylene glycol/H_2O.

SIFSIX-16-Zn-i. A solution of zinc hexafluorosilicate (0.01 mmol) in 2 mL of EtOH was carefully layered over a solution of **16** in 2 mL of $CHCl_3$ (5 mg, 0.01 mmol). Colourless needles were obtained after 3 d. Yield 35%.

X-RAY CRYSTALLOGRAPHIC DETAILS

X-ray diffraction data for all compounds were collected on a Bruker Quest D8 equipped with a Cu Microfocus tube (Cu-Kα radiation λ = 1.5418 Å) and PHOTON CMOS detector. The crystals were cooled *in situ* at 100(2) K with an Oxford CRYOSTREAM 700 cold finger. Indexing and data reduction were conducted using the Bruker APEX2 suite and corrected for absorption using the SADABS software[20] implemented in the Bruker APEX2 suite. All structures were solved by direct methods (SHELXS-97), and refined (SHELXL-97) by full least-squares on all F_{obs} data.[21, 22] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions (riding model). Crystallographic data and refinement parameters for all structures are given in Table S2.

In **SIFSIX-15-Cu-i**, the large atomic displacement of the equatorial fluorine atoms is likely an effect of high thermal motion. The displacement parameters have been constrained to ISOR values of 0.05, 0.05. After structure solution, the reflection intensities were treated with the PLATON SQUEEZE program to eliminate residual electron density due to unresolved solvent molecules.

TABLE S2. Crystal Data and Refinement Details

Compound	**SIFSIX-15-Zn-i**	**SIFSIX-15-Cu-i**	**SIFSIX-16-Zn-i**
Formula	$C_{41}H_{24}N_4F_6OSiZn$	$C_{40}H_{24}N_4F_6SiCu$	$C_{52}H_{16}N_4F_6O_4SiZn$
MW ($gmol^{-1}$)	796.10	766.26	968.15
T (K)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic	Tetragonal
Space group	*Cmcm*	*Cmcm*	*I4/mmm*
Z	4	4	2
a (Å)	29.756(4)	29.9341(13)	24.9961(7)
b (Å)	29.000(4)	28.0390(13)	24.9961(7)
c (Å)	7.6262(11)	7.9233(4)	7.4414(2)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V ($Å^3$)	6580.8(15)	6650.2(5)	4649.4(3)
ρ_{calc} (gcm^{-3})	0.804	0.765	0.692
μ (mm^{-1})	1.030	0.946	0.810
Measured/independent reflections (R_{int})	8655/2151 (0.0782)	46517/2835 (0.0821)	29037/1242 (0.1938)
Observed reflections [I > 2σ(I)]	1509	2416	1158
R_1[a], wR_2[b] [I > 2σ(I)]	0.1558, 0.3735	0.1026, 0.2759	0.0740, 0.1987
R_1, wR_2 (all data)	0.1867, 0.3922	0.1151, 0.2877	0.0886, 0.2024
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e $Å^{-3}$)	-1.025, 0.920	-2.527, 1.244	-0.902, 0.950
Goodness-of-fit on F^2	1.080	1.041	1.087

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2\sum F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}$.

REFERENCES

1. S. Subramanian and M. J. Zaworotko, *Angew. Chem. Int. Ed.*, 1995, **34**, 2127-2129.
2. S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem. Int. Ed.*, 2000, **39**, 2082-2084.
3. S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, 2002, **124**, 2568-2583.
4. M. J. Lin, A. Jouaiti, N. Kyritsakas and M. W. Hosseini, *CrystEngComm*, 2009, **11**, 189-191.
5. P. Nugent, V. Rhodus, T. Pham, B. Tudor, K. Forrest, L. Wojtas, B. Space and M. J. Zaworotko, *Chem. Commun.*, 2013, **49**, 1606-1608.
6. P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Q. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80-84.
7. K. Uemura, A. Maeda, T. K. Maji, P. Kanoo and H. Kita, *Eur. J. Inorg. Chem.*, 2009, 2329-2337.
8. O. Shekhah, Y. Belmabkhout, Z. J. Chen, V. Guillerm, A. Cairns, K. Adil and M. Eddaoudi, *Nat. Commun.*, 2014, **5**, 7.
9. A. Kumar, D. G. Madden, M. Lusi, K. J. Chen, E. A. Daniels, T. Curtin, J. J. Perry and M. J. Zaworotko, *Angew. Chem. Int. Ed.*, 2015, **54**, 14372-14377.
10. O. Shekhah, Y. Belmabkhout, K. Adil, P. M. Bhatt, A. J. Cairns and M. Eddaoudi, *Chem. Commun.*, 2015, **51**, 13595-13598.
11. S. K. Elsaidi, M. H. Mohamed, H. T. Schaef, A. Kumar, M. Lusi, T. Pham, K. A. Forrest, B. Space, W. Q. Xu, G. J. Halder, J. Liu, M. J. Zaworotko and P. K. Thallapally, *Chem. Commun.*, 2015, **51**, 15530-15533.
12. M. J. Lin, A. Jouaiti, N. Kyritsakas and M. W. Hosseini, *CrystEngComm*, 2011, **13**, 776-778.
13. S. D. Burd, S. Q. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 3663-3666.
14. S. S. Xiong, Y. B. He, R. Krishna, B. L. Chen and Z. Y. Wang, *Cryst. Growth Des.*, 2013, **13**, 2670-2674.
15. P. Larpent, A. Jouaiti, N. Kyritsakas and M. W. Hosseini, *Chem. Commun.*, 2013, **49**, 4468-4470.
16. L. C. Li, R. Matsuda, I. Tanaka, H. Sato, P. Kanoo, H. J. Jeon, M. L. Foo, A. Wakamiya, Y. Murata and S. Kitagawa, *J. Am. Chem. Soc.*, 2014, **136**, 7543-7546.
17. J. J. Liu, Y. J. Hong, Y. F. Guan, M. J. Lin, C. C. Huang and W. X. Dai, *Dalton Trans.*, 2015, **44**, 653-658.
18. A. Bajpai, H. S. Scott, T. Pham, K. J. Chen, B. Space, M. Lusi, M. L. Perry and M. J. Zaworotko, *IUCrJ*, 2016, **3**, 430-439.
19. APEX - Bruker (2010). APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.
20. SADABS - Sheldrick, G. M. (2008). SADABS. Program for Empirical Absorption Correction. University of Gottingen, Germany.
21. Sheldrick, G. M. SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
22. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.