Electronic Supplementary Material (ESI) for CrystEngComm

Manuscript ID CE-ART-03-2012-025365

Supplementary material

CCDC 818678-818682 for **1-5** and 794736-794738 for **6-8** contain the supplementary crystallographic data. These data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data and Figures associated with this article can be found, in the online version.

Table S1 Dihedral angles (˚) between two benzimidazole rings (**A**) on the same ligand, dihedral angles (˚) between benzimidazole ring and adjacent benzene ring on the same ligand (**B**), and dihedral angles (˚) between two benzene rings on the same ligand (**C**) for complexes **1**-**5**

Complexes	**A**	**B**	**C**
1	14.1	80.9, 78.5	82.1
2	13.1	79.1, 88.5	49.5
3	12.5	80.1, 77.4	88.1
4	2.6	80.0, 81.1	80.2
5	2.2	77.3, 76.7	68.8

Table S2 Dihedral angles (˚) between two benzimidazole rings (**A**) on the same ligand, dihedral angles (˚) between the mesitylene plane and two benzimidazole rings on the same ligand (**B**), and dihedral angles between benzimidazole ring and adjacent benzene ring of benzyl group (or pyridine ring) (**C**) for complexes **6**-**8**

Compounds	**A**	**B**	**C**
6	13.1	71.1, 80.3	-
7	6.6	88.1, 88.1	74.4, 67.7
8	10.5	80.8, 89.0	73.4, 78.3

Table S3 Distances (Å) of π-π interactions, and distances (Å) and angles (˚) of C-H···π contacts for **1** and **3-7**

Complexes	π-π		C-H···π	
	face-to-face	center-to-center	H···π	C-H···π
1	3.380(2) (benzene) 3.646(2) (benzimidazole)	3.761(2) (benzene) 3.938(2) (benzimidazole)	2.521(1)	150.2(5)
3	3.405(1) (benzene) 3.342(1) (benzimidazole)	3.679(1) (benzene) 3.507(1) (benzimidazole)	2.751(1)	144.7(4)
4	3.409(3) (benzimidazole)	3.672(3) (benzimidazole)	_	_
5	3.402(77) (benzimidazole)	3.672(1) (benzimidazole)	_	_
6	_	_	3.376(3)	137.2(7)
7	3.613(3) (benzimidazole) 3.422(3) (benzene)	4.086(3) (benzimidazole) 3.719(3) (benzene)	_	_

Table S4 H-Bonding Geometry (Å, ˚) for **2** and **6-8**

	D-H···A	D-H	H···A	D···A	D-H···A
2	C(38)-H(38A)···Cl(3)	0.96(1)	2.674(1)	3.594(6)	161.0(4)
6	C(8)-H(8)···I(5)^{i}	0.93(1)	2.998(3)	3.787(5)	143.7(1)
	C(38)-H(38)···I(6)^{i}	0.93(1)	2.661(2)	3.495(3)	149.7(1)
7	C(4)-H(4)···Br(3)^{i}	0.97(1)	2.949(1)	3.831(2)	158.8(6)
	C(24)-H(24)···Br(2)	0.93(1)	2.908(1)	3.781(2)	150.3(6)
	C(6)-H(6)···N(6)	0.97(1)	2.487(1)	3.452(2)	173.1(6)
8	C(35)-H(35)···O(1)^{i}	0.93(1)	2.369(2)	3.124(2)	138.2(1)
	C(12)-H(12)···O(2)^{ii}	0.93(1)	2.500(2)	3.420(3)	170.0(1)

Symmetry code: i: -2-*x*, 2-*y*, 1-*z* for **6**. i: *x*, 1+*y*, *z* for **7**. i: 1+*x*, *y*, *z*; ii: 1-*x*, 1-*y*, -*z* for **8**.

Table S5 The reaction of ligand $\mathbf{L^1H_2}$ with Ag(OAc)[a]

$$L^1H_2 \xrightarrow{Ag(OAc)} \left[(L^1Ag)_2Ag_2Cl_4\right] \quad (\mathbf{I})$$

L^1H_2/Ag(OAc) (equiv/equiv)	Entry	Time (h)	Temp. (˚C)	Crude product[b]	Ag(OAc) yield (%)
1:1	1	14	40	**I**	41
	2	16	40	**I**	64
	3	18	40	**I**	62
	4	18	25	**I**	50
1:2	5	16	40	**I**	64
	6	16	40	**I**	61

1:3	7	16	40	**I**	62
	8	16	40	**I**	63

[a] Reaction conditions: the solvent CH_2Cl_2 in N_2.

[b] Crude product was characterized by ^1H NMR, element analysis and melting point.

Table S6 The reaction of ligand $\mathbf{L^2H_2}$ with Ag_2O[a]

$$L^2H_2 \xrightarrow{Ag_2O} [(L^2Ag)_2AgCl_2][AgCl_2] \quad (\mathbf{II})$$

L^2H_2/Ag_2O (equiv/equiv)	Entry	Time (h)	Temp. (˚C)	Crude product[b]	Ag_2O yield (%)
1:1	1	6	40	**II**	51
	2	8	40	**II**	64
	3	10	40	**II**	63
	4	10	25	**II**	48
1:2	5	8	40	**II**	61
	6	8	40	**II**	63
1:3	7	8	40	**II**	65
	8	8	40	**II**	63

[a] Reaction conditions: the solvent CH_2Cl_2 in N_2.

[b] Crude product was characterized by ^1H NMR, element analysis and melting point.

Table S7 The reaction of ligand $\mathbf{L^2H_2}$ with Ag(OAc)

$$L^2H_2 \xrightarrow{Ag(OAc)} [(L^2Ag)_2AgCl_2][AgCl_2] \quad (\mathbf{II})$$

L^2H_2/Ag(OAc) (equiv/equiv)	Entry	Time (h)	Temp. (˚C)	Crude product[a]	Ag(OAc) yield (%)
1:1	1	14	40	**II**	38
	2	16	40	**II**	66
	3	18	40	**II**	64
	4	18	25	**II**	51
1:2	5	16	40	**II**	64
	6	16	40	**II**	62
1:3	7	16	40	**II**	63
	8	16	40	**II**	62

[a] Reaction conditions: the solvent CH_2Cl_2 in N_2.

[b] Crude product was characterized by ^1H NMR, element analysis and melting point.