

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**

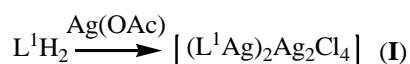
Complexes	π - π		C-H... π	
	face-to-face	center-to-center	H... π	C-H... π
1	3.380(2) (benzene)	3.761(2) (benzene)	2.521(1)	150.2(5)
	3.646(2) (benzimidazole)	3.938(2) (benzimidazole)		
3	3.405(1) (benzene)	3.679(1) (benzene)	2.751(1)	144.7(4)
	3.342(1) (benzimidazole)	3.507(1) (benzimidazole)		
4	3.409(3) (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)	4.086(3) (benzimidazole)	–	–
	3.422(3) (benzene)	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 **L¹H₂** with Ag(OAc)^[a]



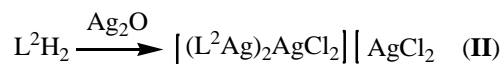
L ¹ H ₂ /Ag(OAc) (equiv/equiv)	Entry	Time (h)	Temp. (°C)	Crude product ^[b]	Ag(OAc) yield (%)
1:1	1	14	40	I	41
	2	16	40	I	64
	3	18	40	I	62
	4	18	25	I	50
1:2	5	16	40	I	64
	6	16	40	I	61

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

[a] Reaction conditions: the solvent CH₂Cl₂ in N₂.

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

Table S6 The reaction of ligand L²H₂ with Ag₂O^[a]

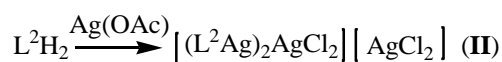


L ² H ₂ /Ag ₂ O (equiv/equiv)	Entry	Time (h)	Temp. (°C)	Crude product ^[b]	Ag ₂ O yield (%)
1:1	1	6	40	II	51
	2	8	40	II	64
	3	10	40	II	63
	4	10	25	II	48
1:2	5	8	40	II	61
	6	8	40	II	63
1:3	7	8	40	II	65
	8	8	40	II	63

[a] Reaction conditions: the solvent CH₂Cl₂ in N₂.

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

Table S7 The reaction of ligand L²H₂ with Ag(OAc)



L ² H 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 CH₂Cl₂ in N₂.

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