Supplementary Materials

Diverse Ag(I) complexes constructed from asymmetric pyridyl- and pyrimidyl amide ligands: roles of Ag---Ag and π - π interactions

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(b)



(c)

Fig. S2. A packing diagram of **4** showing that the cations are linked by the ClO_4^- anions to form a 2D net.



Fig. S3. The molecules of **5** are interlinked through C-H---O hydrogen bonds to form a 2D net.



Fig. S4. The cations of **6** are interlinked by the ClO_4^- anions to form a 2D net.



Fig. S5. Fluorescent emission spectra of (a) 1, (b) 2 - 4, (c) 5 - 6 and (d)





(b)

Wavelength (nm)

Fig. S5. Fluorescent emission spectra of (a) 1, (b) 2 - 4, (c) 5 - 6 and (d) 7 - 9 and their corresponding ligands. (cont.)



(d)

Fig. S6. Uv spectra of (a) 1, (b) 2 - 4, (c) 5 - 6 and (d) 7 - 9 and their corresponding ligands.



(b)

Fig. S6. Uv spectra of (a) 1, (b) 2 - 4, (c) 5 - 6 and (d) 7 - 9 and their corresponding ligands. (cont.)



(d)

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ag(1)-N(1)	2.196 (2)	N(1)-Ag(1)-O(7)	129.1 (1)
$\begin{array}{cccccccc} Ag(1)-O(10) & 2.365 (2) & O(10)-Ag(1)-O(7) & 84.2 (1) \\ Ag(2)-N(3) & 2.242 (2) & N(3)-Ag(2)-O(10) & 173.0 (1) \\ Ag(2)-O(8A) & 2.590 (2) & N(3)-Ag(2)-O(8A) & 92.8 (1) \\ Ag(2)-O(10) & 2.246 (2) & O(10)-Ag(2)-O(8A) & 90.2 (1) \\ \mbox{2} \\ Ag(1)-N(1) & 2.191 (1) & N(1)-Ag(1)-N(1A) & 180.0 \\ Ag(2)-O(4) & 2.291 (2) & O(4)-Ag(2)-O(5) & 52.3 (1) \\ Ag(2)-O(5) & 2.552 (1) & O(4)-Ag(2)-O(4B) & 180.0 \\ O(5)-Ag(2)-O(5B) & 180.0 \\ O(5)-Ag(2)-O(5B) & 180.0 \\ \mbox{3} \\ Ag-N(1) & 2.159 (2) & N(1)-Ag-N(1A) & 180.0 \\ \mbox{4} \\ Ag-N(1) & 2.172(2) & N(1)-Ag-N(3) & 173.6(1) \\ Ag-N(3) & 2.178(2) \\ \mbox{5} \\ Ag-N(1) & 2.138(2) & N(1)-Ag-N(3) & 174.1(1) \\ Ag-N(3) & 2.139(2) \\ \mbox{6} \\ Ag-N(1) & 2.141(2) & N(4)-Ag-N(1) & 174.6(1) \\ Ag-N(3) & 2.141(2) \\ \end{array}$	Ag(1)-O(7)	2.372 (2)	N(1)-Ag(1)-O(10)	139.6 (1)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Ag(1)-O(10)	2.365 (2)	O(10)-Ag(1)-O(7)	84.2 (1)
$\begin{array}{ccccccc} Ag(2)-O(8A) & 2.590\ (2) & N(3)-Ag(2)-O(8A) & 92.8\ (1) \\ Ag(2)-O(10) & 2.246\ (2) & O(10)-Ag(2)-O(8A) & 90.2\ (1) \\ \hline 2 \\ Ag(1)-N(1) & 2.191\ (1) & N(1)-Ag(1)-N(1A) & 180.0 \\ Ag(2)-O(4) & 2.291\ (2) & O(4)-Ag(2)-O(5) & 52.3\ (1) \\ Ag(2)-O(5) & 2.552\ (1) & O(4)-Ag(2)-O(4B) & 180.0 \\ & O(5)-Ag(2)-O(5B) & 180.0 \\ \hline 3 \\ Ag-N(1) & 2.159\ (2) & N(1)-Ag-N(1A) & 180.0 \\ \hline 4 \\ Ag-N(1) & 2.172(2) & N(1)-Ag-N(3) & 173.6(1) \\ Ag-N(3) & 2.178(2) \\ \hline 5 \\ Ag-N(1) & 2.138(2) & N(1)-Ag-N(3) & 174.1(1) \\ Ag-N(3) & 2.139(2) \\ \hline 6 \\ Ag-N(1) & 2.141(2) & N(4)-Ag-N(1) & 174.6(1) \\ Ag-N(3) & 2.141(2) \\ \hline \end{array}$	Ag(2)-N(3)	2.242 (2)	N(3)-Ag(2)-O(10)	173.0(1)
$\begin{array}{ccccccc} Ag(2) - O(10) & 2.246 \ (2) & O(10) - Ag(2) - O(8A) & 90.2 \ (1) \\ \textbf{2} & & & & & & \\ Ag(1) - N(1) & 2.191 \ (1) & N(1) - Ag(1) - N(1A) & 180.0 \\ Ag(2) - O(4) & 2.291 \ (2) & O(4) - Ag(2) - O(5) & 52.3 \ (1) \\ Ag(2) - O(5) & 2.552 \ (1) & O(4) - Ag(2) - O(4B) & 180.0 \\ & & & & & \\ O(5) - Ag(2) - O(5B) & 180.0 \\ \textbf{3} & & & & \\ Ag - N(1) & 2.159 \ (2) & N(1) - Ag - N(1A) & 180.0 \\ \textbf{4} & & & \\ Ag - N(1) & 2.172(2) & N(1) - Ag - N(1A) & 180.0 \\ \textbf{4} & & & \\ Ag - N(3) & 2.178(2) & \\ \textbf{5} & & & \\ Ag - N(1) & 2.138(2) & N(1) - Ag - N(3) & 173.6(1) \\ Ag - N(3) & 2.139(2) & & \\ \textbf{6} & & & \\ Ag - N(1) & 2.141(2) & N(4) - Ag - N(1) & 174.6(1) \\ Ag - N(3) & 2.141(2) & \\ \end{array}$	Ag(2)-O(8A)	2.590 (2)	N(3)-Ag(2)-O(8A)	92.8 (1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ag(2)-O(10)	2.246 (2)	O(10)-Ag(2)-O(8A)	90.2 (1)
$\begin{array}{ccccccc} {\rm Ag(1)-N(1)} & 2.191\ (1) & {\rm N(1)-Ag(1)-N(1A)} & 180.0\\ {\rm Ag(2)-O(4)} & 2.291\ (2) & {\rm O(4)-Ag(2)-O(5)} & 52.3\ (1)\\ {\rm Ag(2)-O(5)} & 2.552\ (1) & {\rm O(4)-Ag(2)-O(4B)} & 180.0\\ & {\rm O(5)-Ag(2)-O(5B)} & 180.0\\ \hline {\rm 3} & & & & \\ {\rm Ag-N(1)} & 2.159\ (2) & {\rm N(1)-Ag-N(1A)} & 180.0\\ {\rm 4} & & & & \\ {\rm Ag-N(1)} & 2.172(2) & {\rm N(1)-Ag-N(3)} & 173.6(1)\\ {\rm Ag-N(3)} & 2.178(2) & & \\ {\rm 5} & & & \\ {\rm Ag-N(1)} & 2.138(2) & {\rm N(1)-Ag-N(3)} & 174.1(1)\\ {\rm Ag-N(3)} & 2.139(2) & & \\ {\rm 6} & & & \\ {\rm Ag-N(1)} & 2.141(2) & {\rm N(4)-Ag-N(1)} & 174.6(1)\\ {\rm Ag-N(3)} & 2.141(2) & & \\ \end{array}$	2			
$\begin{array}{ccccccc} {\rm Ag(2)-O(4)} & 2.291\ (2) & {\rm O(4)-Ag(2)-O(5)} & 52.3\ (1) \\ {\rm Ag(2)-O(5)} & 2.552\ (1) & {\rm O(4)-Ag(2)-O(4B)} & 180.0 \\ & {\rm O(5)-Ag(2)-O(5B)} & 180.0 \\ {\rm O(5)-Ag(2)-O(5B)} & 180.0 \\ {\rm J} \\ {\rm Ag-N(1)} & 2.159\ (2) & {\rm N(1)-Ag-N(1A)} & 180.0 \\ {\rm J} \\ {\rm Ag-N(1)} & 2.172\ (2) & {\rm N(1)-Ag-N(3)} & 173.6\ (1) \\ {\rm Ag-N(3)} & 2.178\ (2) \\ {\rm S} \\ {\rm Ag-N(1)} & 2.138\ (2) & {\rm N(1)-Ag-N(3)} & 174.1\ (1) \\ {\rm Ag-N(3)} & 2.139\ (2) \\ {\rm 6} \\ {\rm Ag-N(1)} & 2.141\ (2) & {\rm N(4)-Ag-N(1)} & 174.6\ (1) \\ {\rm Ag-N(3)} & 2.141\ (2) \\ \end{array}$	Ag(1)-N(1)	2.191 (1)	N(1)-Ag(1)-N(1A)	180.0
$\begin{array}{ccccccc} {\rm Ag}(2){\rm -O}(5) & 2.552(1) & {\rm O}(4){\rm -Ag}(2){\rm -O}(4{\rm B}) & 180.0 \\ & {\rm O}(5){\rm -Ag}(2){\rm -O}(5{\rm B}) & 180.0 \\ {\rm 3} & & & & \\ {\rm Ag}{\rm -N}(1) & 2.159(2) & {\rm N}(1){\rm -Ag}{\rm -N}(1{\rm A}) & 180.0 \\ {\rm 4} & & & & \\ {\rm Ag}{\rm -N}(1) & 2.172(2) & {\rm N}(1){\rm -Ag}{\rm -N}(3) & 173.6(1) \\ {\rm Ag}{\rm -N}(3) & 2.178(2) & & \\ {\rm 5} & & & \\ {\rm Ag}{\rm -N}(1) & 2.138(2) & {\rm N}(1){\rm -Ag}{\rm -N}(3) & 174.1(1) \\ {\rm Ag}{\rm -N}(3) & 2.139(2) & & \\ {\rm 6} & & & \\ {\rm Ag}{\rm -N}(1) & 2.141(2) & {\rm N}(4){\rm -Ag}{\rm -N}(1) & 174.6(1) \\ {\rm Ag}{\rm -N}(3) & 2.141(2) & & \\ \end{array}$	Ag(2)-O(4)	2.291 (2)	O(4)-Ag(2)-O(5)	52.3 (1)
$\begin{array}{c cccc} O(5)-Ag(2)-O(5B) & 180.0 \\ \hline 3 & & & & \\ Ag-N(1) & 2.159\ (2) & N(1)-Ag-N(1A) & 180.0 \\ \hline 4 & & & & \\ Ag-N(1) & 2.172(2) & N(1)-Ag-N(3) & 173.6(1) \\ Ag-N(3) & 2.178(2) & & \\ 5 & & & & \\ Ag-N(1) & 2.138(2) & N(1)-Ag-N(3) & 174.1(1) \\ Ag-N(3) & 2.139(2) & & \\ \hline 6 & & & \\ Ag-N(1) & 2.141(2) & N(4)-Ag-N(1) & 174.6(1) \\ Ag-N(3) & 2.141(2) & \\ \end{array}$	Ag(2)-O(5)	2.552 (1)	O(4)-Ag(2)-O(4B)	180.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			O(5)-Ag(2)-O(5B)	180.0
Ag-N(1) $2.159 (2)$ N(1)-Ag-N(1A)180.04 $Ag-N(1)$ $2.172(2)$ N(1)-Ag-N(3)173.6(1)Ag-N(3) $2.178(2)$ S I I $Ag-N(1)$ $2.138(2)$ N(1)-Ag-N(3)174.1(1) $Ag-N(3)$ $2.139(2)$ G I I $Ag-N(1)$ $2.141(2)$ N(4)-Ag-N(1)174.6(1) $Ag-N(3)$ $2.141(2)$ I I I	3			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ag-N(1)	2.159 (2)	N(1)-Ag-N(1A)	180.0
Ag-N(1) $2.172(2)$ N(1)-Ag-N(3) $173.6(1)$ Ag-N(3) $2.178(2)$ 5 Ag-N(1) $2.138(2)$ N(1)-Ag-N(3) $174.1(1)$ Ag-N(3) $2.139(2)$ 6 Ag-N(1) $2.141(2)$ N(4)-Ag-N(1) $174.6(1)$ Ag-N(3) $2.141(2)$ N(4)-Ag-N(1) $174.6(1)$	4			
Ag-N(3) $2.178(2)$ 5 $4g-N(1)$ $2.138(2)$ $N(1)-Ag-N(3)$ $174.1(1)$ Ag-N(3) $2.139(2)$ 6 Ag-N(1) $2.141(2)$ $N(4)-Ag-N(1)$ $174.6(1)$ Ag-N(3) $2.141(2)$ $N(4)-Ag-N(1)$ $174.6(1)$	Ag-N(1)	2.172(2)	N(1)-Ag-N(3)	173.6(1)
5Ag-N(1) $2.138(2)$ N(1)-Ag-N(3) $174.1(1)$ Ag-N(3) $2.139(2)$ 6 Ag-N(1) $2.141(2)$ N(4)-Ag-N(1) $174.6(1)$ Ag-N(3) $2.141(2)$	Ag-N(3)	2.178(2)		
Ag-N(1) $2.138(2)$ N(1)-Ag-N(3)174.1(1)Ag-N(3) $2.139(2)$ 6 Ag-N(1) $2.141(2)$ N(4)-Ag-N(1)174.6(1)Ag-N(3) $2.141(2)$	5			
Ag-N(3) 2.139(2) 6 2.141(2) N(4)-Ag-N(1) 174.6(1) Ag-N(3) 2.141(2) 1100000000000000000000000000000000000	Ag-N(1)	2.138(2)	N(1)-Ag-N(3)	174.1(1)
6Ag-N(1)2.141(2)N(4)-Ag-N(1)174.6(1)Ag-N(3)2.141(2)	Ag-N(3)	2.139(2)		
Ag-N(1)2.141(2)N(4)-Ag-N(1)174.6(1)Ag-N(3)2.141(2)	6			
Ag-N(3) 2.141(2)	Ag-N(1)	2.141(2)	N(4)-Ag- $N(1)$	174.6(1)
	Ag-N(3)	2.141(2)		

Table S1. Selected bond distances (Å) and angles (°) for 1 - 6.

Symmetry code A: -x + 2, -y - 2, -z for **1**; A: -x + 1, -y + 2, -z; B: -x + 2, -y + 1, -z for **2**; A: -x + 1, -y, -z for **3**; A: -x + 1, -y + 1, -z + 1 for **4**; A: -x + 1, -y, -z for **5**.

	7	<u> </u>	0
		0	,
Ag-N(4)	2.277(3)	2.275(5)	2.280(3)
Ag-N(1)	2.334(2)	2.337(4)	2.314(3)
Ag-O(4)	2.394(2)	2.391(4)	2.404(3)
Ag-O(1)	2.423(2)	2.411(4)	2.443(3)
N(4)-Ag-N(1)	166.5(1)	165.4(2)	169.0(1)
N(4)-Ag-O(4)	77.4(1)	77.7(2)	76.9(1)
N(1)-Ag-O(4)	93.1(1)	91.8(2)	94.8(1)
N(4)-Ag-O(1)	115.0(1)	115.7(2)	114.4(1)
N(1)-Ag-O(1)	73.6(1)	73.5(1)	73.8(1)
O(4)-Ag-O(1)	166.1(1)	164.3(1)	168.6(1)

 Table S2. Selected bond distances (Å) and angles (°) for 7 - 9.

\mathbf{L}^{1}	203, 241, 285	4	202, 236, 277
L^2	203, 240, 280	5	202, 241, 266
L^3	202, 246,271	6	202, 241, 267
L^4	196, 249	7	199, 248
1	199, 238, 283	8	198, 248
2	205, 235, 276	9	196, 247
3	202, 236, 277		

Table S3. Th	e Uv absorption wavelengths o	of $\mathbf{L}^1 - \mathbf{L}^4$ and $1 - 9$
in	$1 \text{ CH}_3 \text{CN} (\text{nm}).$	

Table S4.	The ¹ H NMR chemical shifts of $1 - 9$ in DMSO-d ₆ .
Complex	Chemical shifts (ppm)
	11.00 (1H, s, NH), 8.40 (1H, d, H-py), 8.18 (1H, d, H-py),
1	8.11 (4H, dd, H-bz), 7.87 (1H, t, H-py), 7.20 (1H, t, H-py),
	3.89 (3H, s, OCH ₃)
	10.70 (1H, s, NH), 8.97 (1H, d, H-py), 8.34 (1H, d, H-py),
2	8.22 (1H, d, H-py), 8.11 (4H, dd, H-bz), 7.47 (1H, q,
	H-py), 3.90 (3H, s, OCH ₃)
3	10.69 (1H, s, NH), 8.97 (1H, d, H-py), 8.34 (1H, d, H-py),
	8.22 (1H, d, H-py), 8.11 (4H, dd, H-bz), 7.46 (1H, q,
	H-py), 3.90 (3H, s, OCH ₃)
	10.70 (1H, s, NH), 8.93 (1H, d, H-py), 8.34 (1H, d, H-py),
4	8.20 (1H, d, H-py), 8.10 (4H, dd, H-bz), 7.47 (1H, q,
	H-py), 3.90 (3H, s, OCH ₃)
5	10.90 (1H, s, NH), 8.52 (1H, d, H-py), 8.10 (4H, dd,
5	H-bz), 7.86 (2H, d, H-py), 3.90 (3H, s, OCH ₃)
6	10.83 (1H, s, NH), 8.50 (1H, d, H-py), 8.09 (4H, dd,
	H-bz), 7.82 (2H, d, H-py), 3.90 (3H, s, OCH ₃)
7	11.23 (1H, s, NH), 8.76 (2H, d, H-pm), 8.06 (4H, dd,
	H-bz), 7.29 (1H, d, H-pm), 3.89 (3H, s, OCH ₃)
8	11.24 (1H, s, NH), 8.79 (2H, d, H-pm), 8.06 (4H, dd,
	H-bz), 7.30 (1H, d, H-pm), 3.89 (3H, s, OCH ₃)
9	11.24 (1H, s, NH), 8.77 (2H, d, H-pm), 8.06 (4H, dd,
	H-bz), 7.30 (1H, d, H-pm), 3.89 (3H, s, OCH ₃)