Supporting Information for

Diverse Structural Ag(I) Supramolecular Complexes Constructed from Multidentate Dicyanoisophorone-Based Ligands: Structure and Enhanced Luminescence

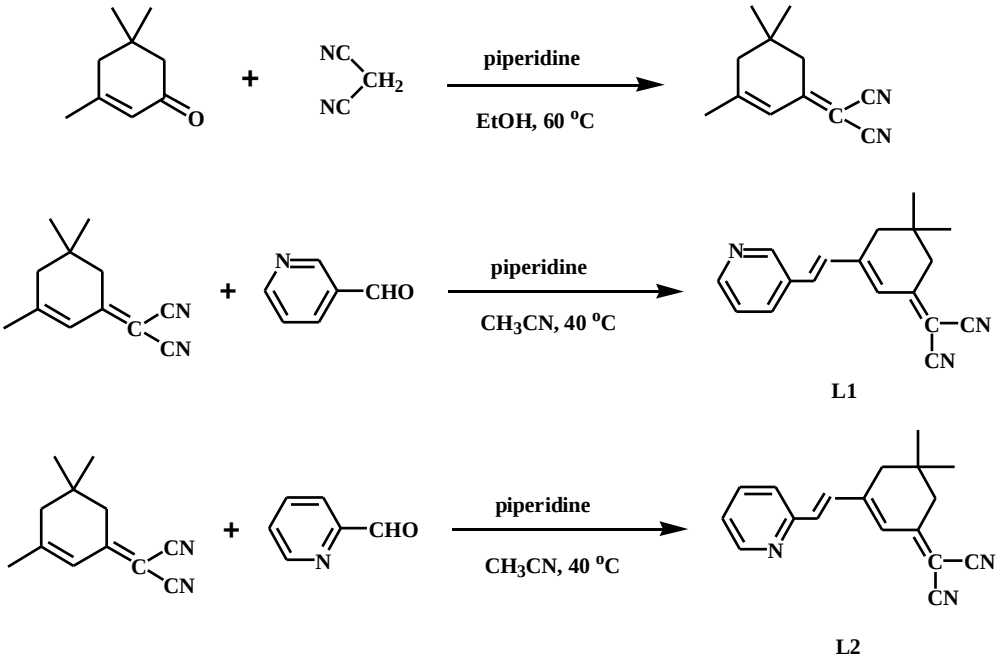
Feng Jin,[†,‡] Ying Zhang,[†] Hui-Zhen Wang,[†] Hui-Zhi Zhu,[†] Yan Yan,[†] Jun Zhang,[†] Jie-Ying Wu,[†] Yu-Peng Tian,[†] Hong-Ping Zhou[*,†]

[†]School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P. R. China

[‡]Department of Chemistry, Fuyang Normal College, Fuyang 236041, P. R. China

[*]Corresponding author. *E-mail*: zhpzhp@263.net (H. -P. Zhou).

Contents:



Scheme S1 Synthetic route to **L1** and **L2**

Experimental section

Synthesis of Ligands.

2-{5,5-Dimethyl-3-[2-(pyridin-2-yl)-ethenyl]cyclohex-2-enylidene}propanedinitrile (L1) 2-(3, 5, 5-Trimethylcyclohex-2-enylidene)malononitrile (2.60 g, 14 mmol), CH_3CN (100 mL), pyridine-2-carboxaldehyde (1.50 g, 14 mmol) and piperidine (2 mL) were added to a round-bottom flask. The reaction mixture was kept stirring for 12 h at 40 ^oC. After cooled to room temperature, the yellow crystals formed slowly. The product was filtered and recrystallized from MeOH. Yield: 2.90 g (75%). ^1H NMR (400 MHz, $CDCl_3$): 1.03(s, 6H), 2.57(s, 2H), 2.64(s, 2H), 6.95(s,1H), 7.28(d, 2H), 7.64(d, 2H), 7.81~7.87(m, 1H), 8.61(d, 1H); IR $\nu(cm^{-1})$: 2596 (s), 2931 (s), 2868 (s), 2219 (s), 1567 (s), 1526 (s), 1417 (s), 1401 (s), 1335 (s), 1312 (s), 1212 (s), 1162 (s), 1126 (s), 1024 (s), 965 (s); Anal. Calcd. (%) for $C_{18}H_{17}N_3$: C 78.45; H 6.17; N 15.25; Found (%): C 78.48; H 6.21; N 15.28. MS (EI) (*m/z*): Calc. for $C_{18}H_{17}N_3$: 276.15 $[HM]^+$; Found: 276.15 $[HM]^+$.

2-{5,5-Dimethyl-3-[2-(pyridin-3-yl)-ethenyl]cyclohex-2-enylidene}propanedinitrile (L2) 2-(3, 5, 5-Trimethylcyclohex-2-enylidene)malononitrile (2.60 g, 14 mmol), CH_3CN (100 mL), pyridine-3-carboxaldehyde (1.50 g, 14 mmol) and piperidine (2

mL) were added to a round-bottom flask. The reaction mixture was kept stirring for 12 h at 40 ^{o}C, then the solvent was removed with a rotary evaporator to give the black oil. EtOH (20 mL) was added to the black oil, and the yellow solid product formed slowly. The product was filtered and recrystallized from EtOH. Yield: 2.63 g (68%). ^{1}H NMR(400 MHz, $CDCl_3$): 1.09(s, 6H), 2.48(s, 2H), 2.62(s, 2H), 6.88(s,1H), 7.03(s, 2H), 7.33~7.36(m, 1H), 7.85, 7.87(d, 1H), 8.56~8.57(t, 1H), 8.70(d, 1H); IR v(cm^{-1}): 2953 (s), 2914 (s), 2870 (s), 2218 (s), 1566 (s), 1530 (s), 1467 (s), 1427 (s), 1390 (s), 1330 (s), 1316 (s), 1156 (s), 972 (s); Anal. Calcd. (%) for $C_{18}H_{17}N_3$: C 78.45; H 6.17; N 15.25; Found (%): C78.41; H 6.14; N 15.21. MS (EI) (*m/z*): Calc. for $C_{18}H_{17}N_3$: 276.15 $[HM]^+$; Found: 276.15 $[HM]^+$.

Table S1 The data of IR spectra of all compounds

compound	IR(assignment)
L1	2219 (C≡N stretching)
1	2216 (C≡N stretching); 1182/1030/1007 (TsO^-)
2	2252 (C≡N stretching); 1092 (ClO_4^-)
3	2220 (C≡N stretching); 1337/1317 (NO_3^-)
L2	2218 (C≡N stretching)
4	2249/2219 (C≡N stretching); 1388/1300 (NO_3^-)
5	2254/2221 (C≡N stretching); 1090 (ClO_4^-)
6	2217 (C≡N stretching); 841(PF_6^-)

Table S2 Selected Bond Lengths (Å) and Angles (°) of Complexes **1-6**

1			
N(2)–Ag(1)#1	2.193(3)	Ag(1)–N(1)	2.190(3)
Ag(1)–N(2)#1	2.193(3)	Ag(1)–O(4)	2.465(3)
Ag(1)–O(2)	2.555(3)	N(2)#1–Ag(1)–O(4)	95.3(1)
N(1)–Ag(1)–N(2)#1	147.6(1)	N(1)–Ag(1)–O(4)	114.0(1)
N(1)–Ag(1)–O(2)	99.4(1)	N(2)#1–Ag(1)–O(2)	97. 9(1)
O(4)–Ag(1)–O(2)	81.9(1)		
2			
Ag(1)–N(1)	2.170(4)	Ag(2)–N(3)	2.189(4)
Ag(1)–O(1)#2	2.592(6)	N(1)#–Ag(1)–O(1)#3	88.6(2)
Ag(2)–N(2)#4	2.145(4)	N(1)–Ag(1)–O(1)#2	88.6(2)
N(1)#1–Ag(1)–O(1)#2	91.4(2)	N(1)–Ag(1)–O(1)#3	91.4(2)
N(2)#4–Ag(2)–N(3)	167.0(2)		

3			
Ag(1)–N(1)	2.159(3)	N(1)–Ag(1)–N(1)#1	180.0(1)
Ag(1)–N(2)	2.398(3)	N(2)#2–Ag(2)–N(2)	99.0(2)
Ag(2)–O(4)	2.455(2)	N(2)–Ag(2)–O(4)	134.84(9)
O(4)#2–Ag(2)–O(4)	105.3(1)	N(2)#2–Ag(2)–O(4)	94.8(1)
4			
Ag(1)–N(3)	2.194(3)	Ag(1)-N(1)	2.218(3)
Ag(1)–O(1)	2.530(3)	N(3)–Ag(1)–O(1)	115.6(1)
N(3)–Ag(1)–N(1)	144.0(1)	N(1)–Ag(1)–O(1)	99.1(1)
5			
Ag–N(1)	2.154(3)	N(1)#1–Ag–N(1)	180.000(1)
6			
Ag(1)–N(1)	2.180(4)	Ag(1)–N(2)	2.182(4)
N(1)–Ag(1)-N(2)	162.5(1)		

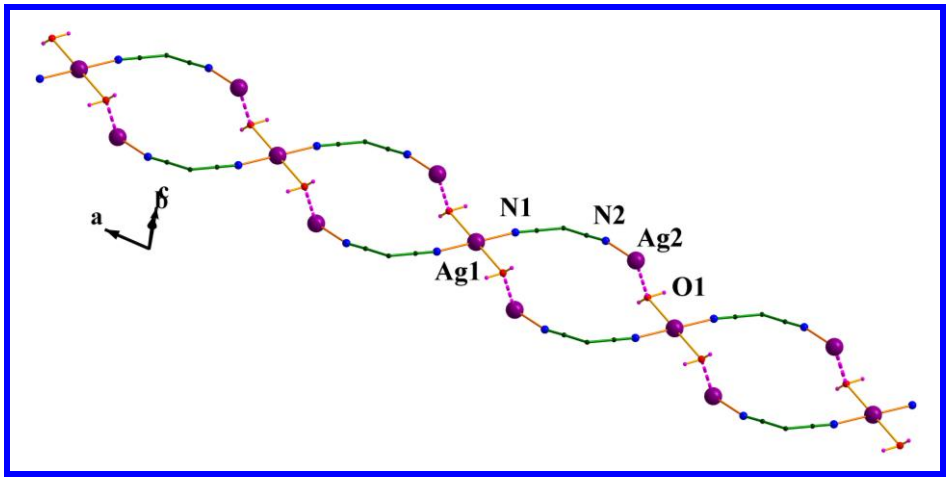


Figure S1 The crossed double-chain of **2** in the 2D structure.

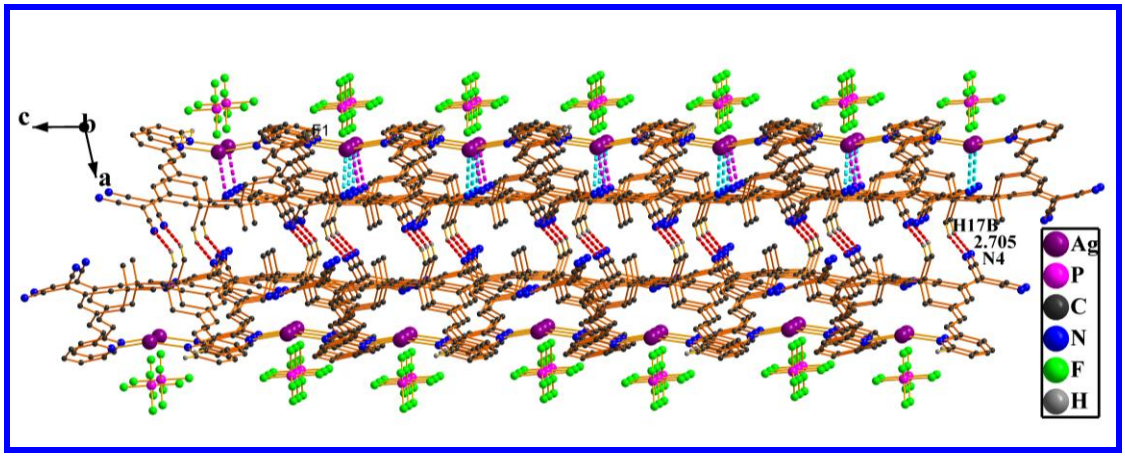


Figure S2 The double-sheet of complex **6** formed by C–H···N interactions. The red dotted lines represent the weak interactions. The hydrogen atoms are omitted for clarity.

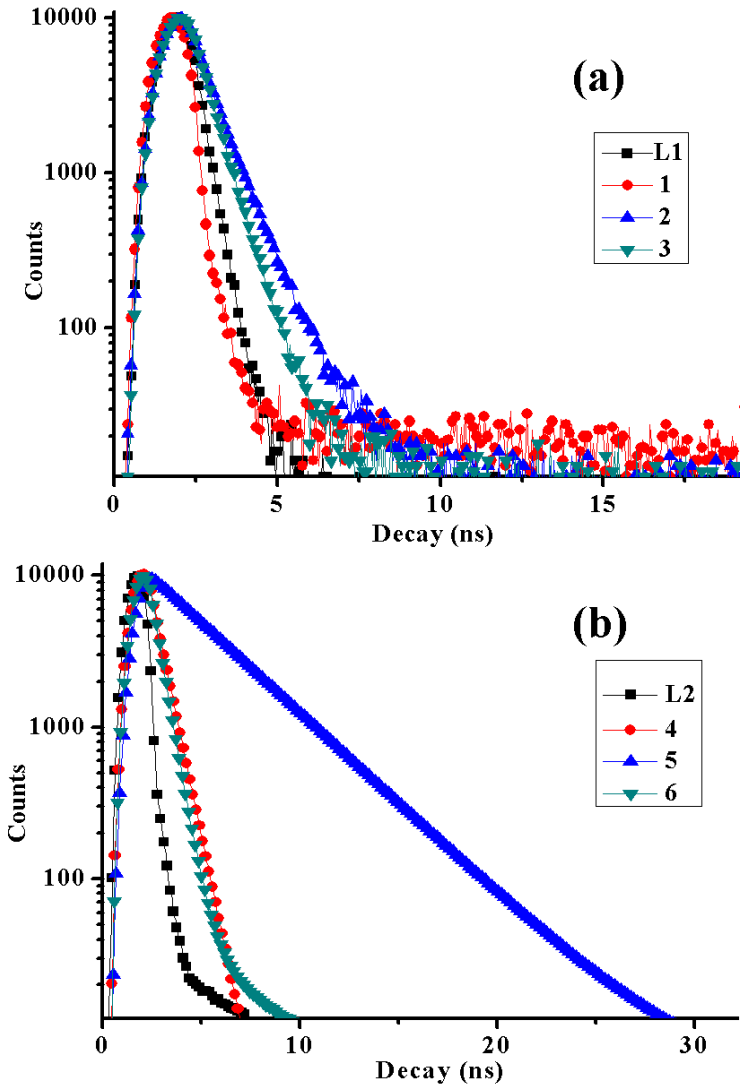


Figure S3 (a) Time-resolved fluorescence curves of **L1** and complexes **1**-**3** in the solid state at room temperature; (b) Time-resolved fluorescence curves of **L2** and complexes **4**-**6** in the solid state at room temperature.