Supporting information

Molecular and supramolecular architecture of silver (I) and copper (II) complexes with a new semi-rigid sulfonyl ligand

Zhaoxian Qin[a,b,‡] Li Zhao[a,‡] Qian Xiao[a], Xinzhan Sun[a], Aimin Li[a], Zhiwen Li [b,c], Shanli Tian[b], Yuheng Deng[a], Jiangwei Zhang[b,*] and Chongqing Wan[a,*]

[a]Beijing Key Laboratory for Optical Materials and Photonic Devices, Department of Chemistry, Capital Normal University, Beijing 100048, P.R. China. E-mail: wancq@cnu.edu.cn (C.W.)

[b]Gold Catalysis Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China. E-mail: jwzhang@dicp.ac.cn (J.Z.)

[c]Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, 116029, P.R.China.

[‡]These authors contributed equally to this publication.

I. Synthesis of 2-((pyridin-2-ylsulfide)methyl)pyridine (a)

To a round-bottom flask equipped with a magnetic stirrer, 2-(chloromethyl)pyridine hydrochloride (1.312 g, 8 mmol) and NH_3 (640 mg, 16 mmol) dissolved in ethanol were added, followed by the addition of 2-mercaptopyridine (890 mg, 8 mmol) with stir. The mixture was Kept stirring and refluxing for 16 hours. Upon completion, the mixture was filtrated and the filtrate was concentrated by rotary evaporation. The yellow oil obtained was further purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. 2-((pyridin-2-ylsulfide)methyl)pyridine was obtained as a yellow oil (970 mg). Yield: 60%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.54 (d, 1H), 8.43 (d, 1H), 7.59 (t, 1H), 7.46 (m, 2H), 7.21 (d, 1H), 7.14 (t, 1H), 6.98 (t, 1H), 4.59 (s, 2H).

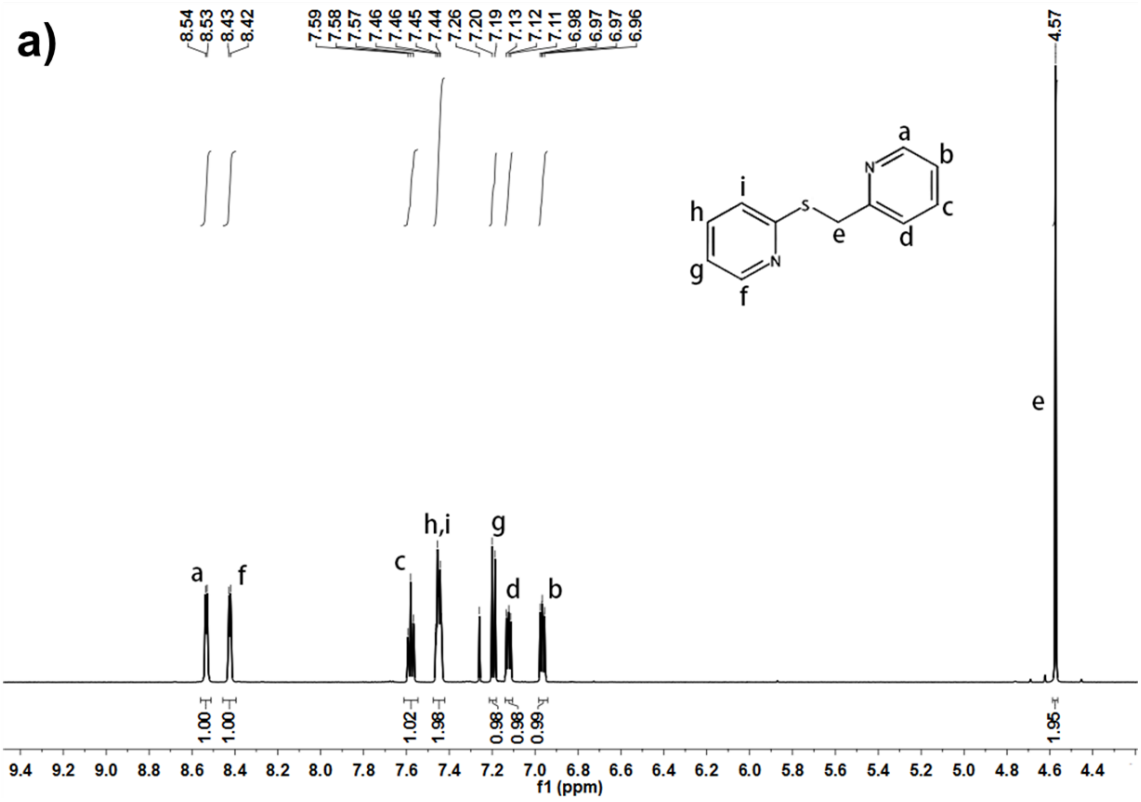

Figure S1.. ^{1}H NMR (600 MHz, $CDCl_3$) of 2-((pyridin-2-ylsulfide)methyl)pyridine.

II. Synthesis of 2-((pyridin-2-ylsulfone)methyl)pyridine (L)

To a solution of 2-((pyridin-2-ylsulfide)methyl)pyridine (970 mg, 4.8 mmol) in glacial acetic acid (30 ml), H_2O_2 (30% w/w, 2.5 ml) was added with stirring at room temperature. Then, the mixture was stored at room temperature for a week, followed by concentrating in vacuo. Water (40 ml) was added into the residue to afford a white precipitate. The crude product was collected by filtration and purified by chromatography on silica gel. The 2-((pyridin-2-ylsulfone)methyl)pyridine (617 mg) was obtained. Yield: 55%. ^{1}H NMR: (600 MHz, $CDCl_3$) δ: 8.81 (d, 1H), 8.45 (d, 1H), 7.87 (d, 2H), 7.66 (t, 1H), 7.54 (m, 1H), 7.42 (d, 1H), 7.21 (m, 1H), 4.84 (s, 2H).

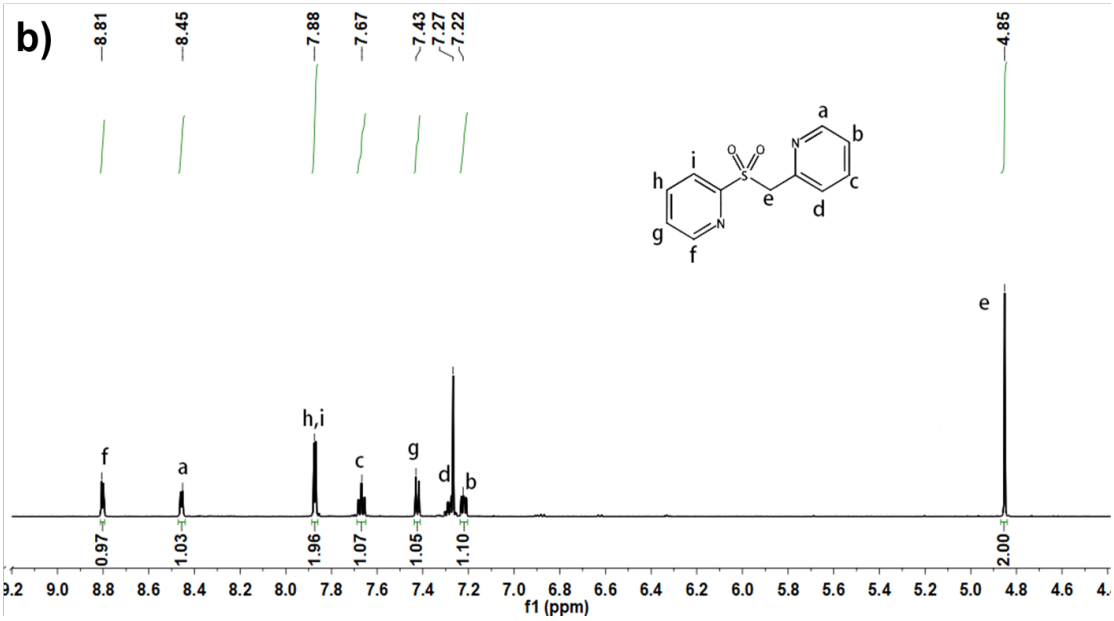

Figure S2.. ^{1}H NMR (600 MHz, $CDCl_3$) of L.

Table S1. Crystallographic data of the ligand L and complexes **1-5**.

compound	L	**1**	**2**	**3**	**4**	**5**
Chemical formula	$C_{11}H_{10}N_2O_2S$	$C_{11}H_{10}AgClN_2O_6S$	$C_{13}H_{10}Ag\ F_3N_2O_4S$	$C_{14}H_{10}AgF_5N_2O_4S$	$C_{11}H_{10}Cl_2CuN_2O_2S$	$C_{11}H_{10}C_7Cu\ N_2O_{3.5}S_1$
Formula weight	234.27	441.59	455.16	505.17	368.71	392.71
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic	triclinic
Space group	P 21/c	P -1	P 21/c	P b c a	P 21/n	P -1
a (Å)	6.1391(5)	8.1846(4)	9.2069(6)	13.5906(5)	7.7548(5)	7.6414(5)
b (Å)	12.3196(9)	9.1335(6)	10.3554(6)	15.3623(6)	13.6358(10)	8.3115(6)
c (Å)	14.8420(9)	10.3479(6)	16.4755(11)	16.9588(6)	12.7451(9)	12.1704(9)
α (º)	90	85.194(4)	90	90	90	92.816(5)
β (º)	97.954(6)	79.853(4)	101.116(4)	90	100.228(4)	97.234(5)
γ (º)	90	70.598(4)	90	90	90	100.802(5)
Unit cell Volume ($Å^3$)	1111.72(14)	717.94(7)	1541.32(17)	3540.7(2)	1326.29(16)	751.12(9)

Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Z	4	2	4	8	4	2
Reflection collected/unique	13825/2267	9859/ 2938	22286/ 3155	54676/ 4307	10697/ 2705	10220/ 3593
R_{int}	0.0713	0.0325	0.0536	0.0340	0.0436	0.0449
Final R_1 values[a]($I > 2\sigma(I)$)	0.0385	0.0346	0.0423	0.0279	0.0369	0.0413
Final $wR(F^2)$ values[b] (all data) ($I > 2\sigma(I)$)	0.0866	0.0691	0.0992	0.0678	0.0573	0.0898
Final R_1 values (all data)	0.0734	0.0534	0.0802	0.0347	0.0687	0.0687
Final $wR(F^2)$ values (all data)	0.0974	0.0780	0.1187	0.0721	0.0661	0.1019
Goodness-of-fit (GOD) on F^2	1.076	1.059	1.048	1.036	1.047	1.051

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

Table S2. Hydrogen-bonding geometry (Å, º).

Complexes	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (º)	Symmetry code of A
L	C6-H6B···N2	0.970	2.683	3.640(3)	169.43	$-x+1, -y, -z+1$
	C8-H8···O2	0.930	2.522	3.374(3)	152.48	$x+1, y, z$
	C2-H2···O6	0.930	2.612	3.228(2)	124.16	$x+1, y, z$
1	C4-H4···O3	0.930	2.648	3.509(3)	154.23	x, y, z
	C6-H6A···O5	0.970	2.611	3.578(3)	174.43	$-x+1, -y+1, -z$
	C6-H6A···O5	0.970	2.597	3.217(4)	122.00	$-x+1, -y+1, -z$
	C6-H6B···O6	0.970	2.337	3.243(3)	155.14	x, y, z
	C8-H8···O3	0.930	2.656	3.407(3)	138.35	$x, y-1, z$
	C10-H10···O1	0.930	2.550	3.240(3)	131.26	$x-1, y, z$
2	C6-H6A···O3	0.970	2.576	3.462(2)	151.94	x, y, z
	C6-H6B···O4	0.970	2.304	3.257(2)	167.01	$x-\frac{1}{2}, y, -z+\frac{1}{2}$
	C11-H11···O2	0.930	2.577	3.318(3)	136.94	$x-\frac{1}{2}, y, -z+\frac{1}{2}$
3	C4-H4···O4	0.930	2.626	3.542(3)	168.65	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$
	C6-H6A···O2	0.970	2.224	3.094(3)	148.70	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$
	C1-H1···O1	0.930	2.505	3.259(3)	138.28	$x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$
	C4-H4···Cl2	0.930	2.553	3.472(4)	169.35	$x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$
4	C6-H6A···Cl1	0.970	2.864	3.664(4)	140.31	x, y, z
	C6-H6B···Cl1	0.970	2.640	3.414(3)	136.99	$x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$
	C10-H10···Cl2	0.930	2.978	3.554(2)	121.50	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$
	C11-H11···Cl2	0.930	2.798	3.482(3)	131.17	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$
	C2-H2···Cl1	0.930	2.909	3.679(3)	141.02	$x, y+1, z$
	C2-H2···O2	0.930	2.502	3.284(3)	141.88	$x, y+1, z$
5	C4-H4···Cl2	0.930	2.982	3.552(4)	121.02	$-x+1, -y+1, -z+1$
	C6-H6A···O1	0.970	2.416	3.330(2)	156.97	$-x, -y, -z+1$
	C6-H6B···Cl2	0.970	2.607	3.515(3)	156.00	$x-1, y, z$
	C11-H11···Cl1	0.930	2.641	3.466(3)	148.24	$-x+1, -y, -z$