Supporting information

Conformation driven *in situ* interlock: from discrete metallocycles to infinite polycatenane

Hui Xue,[a,b] Feilong Jiang,[a] Qihui Chen,*[a] Daqiang Yuan,[a] Jiandong Pang,[a,b] Guangxun Lv,[a,b] Xiuyan Wan,[a,b] Linfeng Liang,[a,b] and Maochun Hong*[a]

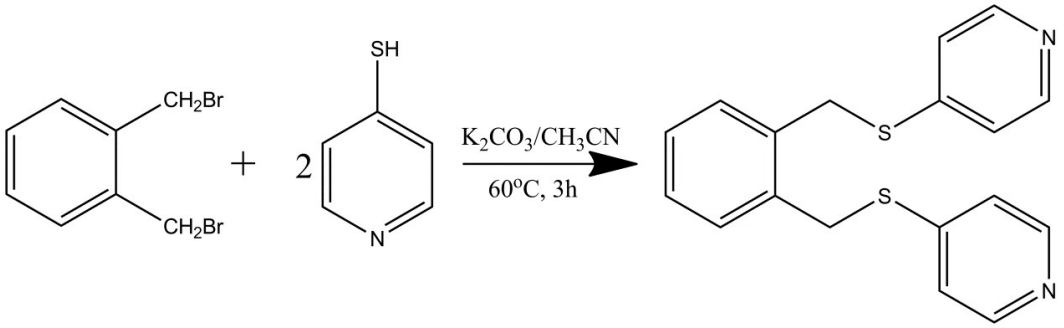
[a]*State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China*
[b]*University of Chinese Academy of Sciences, Beijing, 10049, China*

Content

Experimental methods

General: All of reagents were commercially available and used as purchased. C, H, and N microanalyses were measured using an elemental Vairo EL analyzer, ^{1}HNMR spectra were recorded at Bruker AM-400 (400 MHZ) spectrometer, IR spectra were recorded on a Shimadzu IR-440 spectrometer.

The synthesis process of ligand （L）



A solution of 1,2-bis(bromomethyl) benzene (1.32g, 5mmol), pyridine-4-thiol (1.11g, 10mmol) and potassium carbonate (1.38g, 10mmol) in 50ml MeCN was heated to 60°C for 3h with vigorous stirring. After cooling, the pale fuchsia solution was filtered. Removal of the solvent gave an oil, which afforded a fuchsia powder on recrystallization from CH_2Cl_2–Et_2O–hexane (yield: 1.41g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (dd, *J* = 4.9, 1.5 Hz, 4H, Py-H), 7.44 (dd, *J* = 5.5, 3.5 Hz, 2H, Ph-H), 7.34 (dd, *J* = 5.5, 3.5 Hz, 2H, Ph-H), 7.26 (dd, *J* = 4.9, 1.5 Hz, 4H, Py-H), 4.41 (s, 4H, CH_2). ESI-MS (m/z): 324 ($M+H^+$).

Self-assembly of three different metallocycles

$[Hg_2L_2Cl_4]$ metallocycle

The ligand L (16mg, 0.04mmol) and $HgCl_2$ (12mg, 0.04mmol) were put into CH_3CN/ H_2O solution, and stirring this solution at room temperature for 1 hours, the white power was obtained. ESI-MS confirmed that the metallocycle $[Hg_2L_2Cl_4]$ can be synthesized quickly, the 1154 peak corresponds to $[Hg_2L_2Cl_3]^+$ in Fig S1.

$[Ag_2L_2(CF_3SO_3)_2]$ metallocycle

The ligand L (16mg, 0.04mmol) and $AgCF_3SO_3$ (10mg, 0.04mmol) were put into CH_3CN/ H_2O solution, and stirring this solution at room temperature for 1 hours, the white power was obtained. ESI-MS confirmed that the metallocycle $[Ag_2L_2(CF_3SO_3)_2]$ can be synthesized quickly, the 1013 peak corresponds to $[Ag_2L_2(CF_3SO_3)]^+$ in Fig S2.

$[Zn_2L_2Cl_4]$ metallocycle

The ligand L (16mg, 0.04mmol) and $ZnCl_2$ (6mg, 0.04mmol) were put into CH_3CN/

H_2O solution, and stirring this solution at room temperature for 1 hours, the white power was obtained. ESI-MS confirmed that the metallocycle $[Zn_2L_2Cl_4]$ can be synthesized quickly, the 885 peak corresponds to $[Zn_2L_2Cl_3]^+$ in Fig S3.

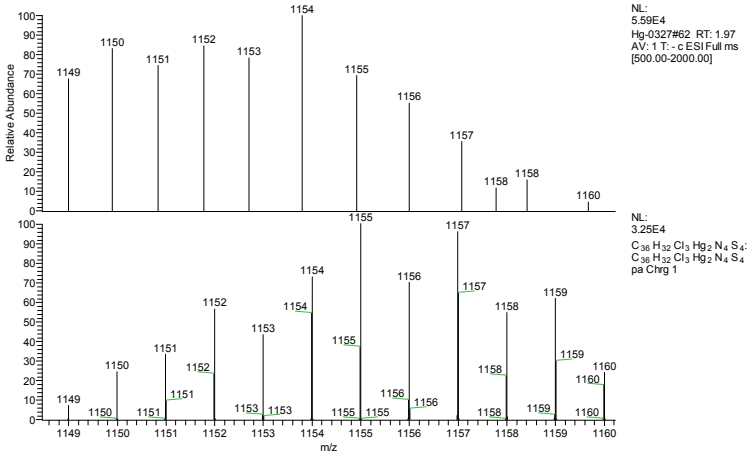


Fig. S1 Experimental (up) and simulated (down) ESI-MS spectra of $[Hg_2L_2Cl_3]^+$.

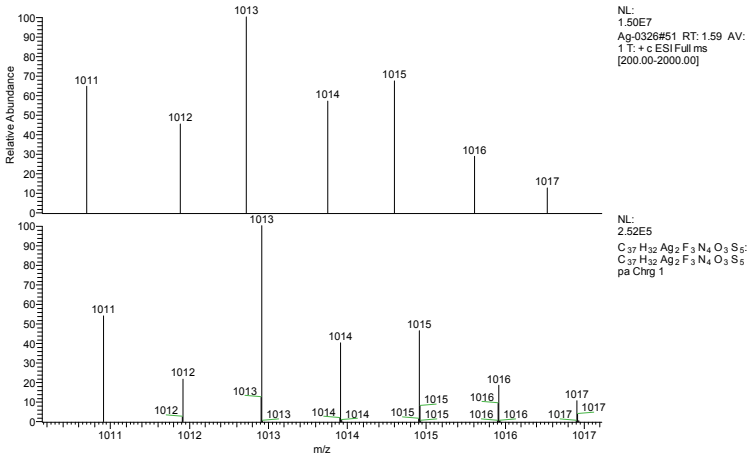


Fig. S2 Experimental (up) and simulated (down) ESI-MS spectra of $[Ag_2L_2(CF_3SO_3)]^+$.

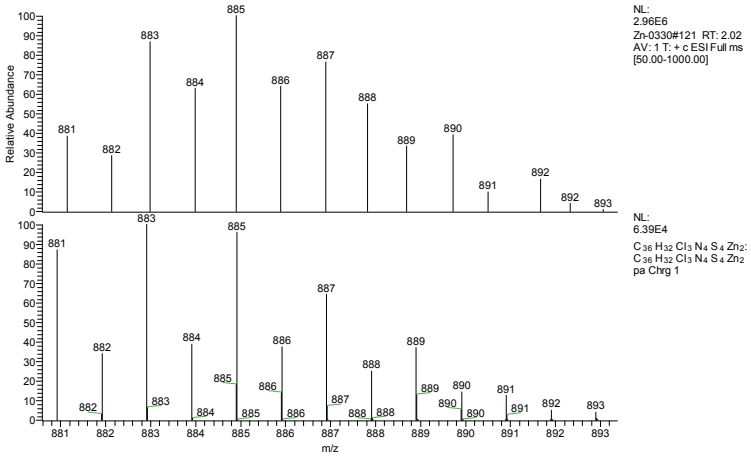


Fig. S3 Experimental (up) and simulated (down) ESI-MS spectra of $[Zn_2L_2Cl_3]^+$.

The synthesis process of compound 1

Layering a CH_3CN solution of ligand L (8mg, 0.02mmol) with a H_2O solution of $HgCl_2$ (6mg, 0.02mmol), about three days later, colorless rodlike crystal compound **1** were obtained in a 50% yield. Anal. Calcd for $C_{18}H_{16}C_{l2}HgN_2S_2$ (Mr = 595.96) n(%): C, 36.24; H, 2.68; N, 4.70; Found (%): C, 36.10; H, 2.65; N, 4.68. IR (cm^{-1}): 3450(w), 3056(w), 1589(s), 1483(m), 1422(m), 1221(m), 1106(m), 1068(m), 1008(m), 816(m), 779(w), 749(w), 718(s), 489(m).

The synthesis process of compound 2

Layering a CH_3CN solution of ligand L (8mg, 0.02mmol) with a H_2O solution of $AgCF_3SO_3$ (5mg, 0.02mmol), about three days later, colorless rodlike crystal compound **2** were obtained in a 75% yield. Anal. Calcd for $C_{19}H_{19}AgN_2O_3S_3F_3$ (Mr = 584.43) n(%): C, 39.01; H, 3.25; N, 4.79; Found (%): C, 38.97; H, 3.20; N, 4.81. IR (cm^{-1}): 3481(w), 3150(w), 1592(s), 1488(m), 1429(m), 1275(s), 1159(m), 1114(m), 1033(s), 806(m), 728(m), 636(s), 568(w), 495(m).

The synthesis process of compound 3

Layering a CH_3CN solution of ligand L (8mg, 0.02mmol) with a H_2O solution of $ZnCl_2$ (3mg, 0.02mmol), about three days later, colorless rodlike crystal compound **3** were obtained in a 40% yield. Anal. Calcd for $C_{20}H_{19}N_3S_2ZnCl_2$ (Mr = 501.81) n(%): C, 47.83; H, 3.79; N, 8.37; Found (%): C, 47.79; H, 3.76; N, 8.30. IR (cm^{-1}): 3398(w), 3202(w), 1669(s), 1450(w), 1407(m), 1349(s), 1255(m), 1110(m), 1008(m), 867(w), 795(m), 649(s), 470(m).

X-ray crystallography

Data collections were all performed on a Mercury CCD diffractometer with graphite monochromated Cu Ka radiation (λ = 0.71073 Å). The structures were solved by direct methods, and all calculations were performed using the SHELXL package. The structures **1-4** were refined by full matrix least-squares with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were generated geometrically and treated as riding. The crystallographic data are summarized in Table S1-S5. CCDC 1054664, 1054665, 1054666, 1058370 contain the supplementary crystallographic data for **1-4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and refinement results for **1-4**.

Formula	$C_{18}H_{16}N_2S_2HgCl_2$(**1**)	$C_{19}H_{19}N_2S_3AgO_3F_3$(**2**)	$C_{20}H_{19}N_3S_2ZnCl_2$(**3**)	$C_{18}H_{12}N_2S_2HgI_2$(**4**)
Formula weight	595.96	584.43	501.81	774.81
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	$P2_1/c$	*C*2/*c*
a (Å)	26.6229	23.7546	8.5494	26.4973
b (Å)	10.0005	9.6388	18.8079	10.4756
c (Å)	13.9461	18.5295	13.9638	14.4782
α (°)	90	90	90	90
β (°)	93.414	93.688	99.017	94.642
γ (°)	90	90	90	90
Volume ($Å^3$)	3706.45	4233.84	2217.58	4005.61
T (K)	100	100	100	100
Z	8	8	4	8
F (000)	2272.0	2320.0	1024.0	2816.0
R1 (I>2(I))	0.0358	0.0280	0.0290	0.0424
wR2 (reflections)	0.0967	0.0722	0.0722	0.1167
Goodness of fit on F2	1.066	1.027	1.053	1.041

Bond	(Å)
Hg1—Cl2	2.3708 (12)
Hg1—Cl1	2.3741 (13)
Hg1—N2^{i}	2.393 (4)
Hg1—N1	2.420 (5)
Angle	(º)
Cl2—Hg1—Cl1	151.28 (5)
Cl2—Hg1—N2^{i}	102.12 (11)
Cl1—Hg1—N2^{i}	98.90 (10)
Cl2—Hg1—N1	97.85 (11)
Cl1—Hg1—N1	97.42 (11)
N2^{i}—Hg1—N1	100.25 (14)

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) for compound **1**.

Symmetry codes: (i) 1-x, 1-y, 1-z.

Table S3 Selected Bond Lengths (Å) and Bond Angles (°) for compound **2**.

Bond	(Å)
Ag1—N2^{i}	2.127 (2)
Ag1—N1	2.131 (2)
Ag1—Ag1^{i}	3.2259 (4)
Angle	(º)
N2^{i}—Ag1—N1	170.82 (10)
N2^{i}—Ag1—Ag1^{i}	82.21 (7)
N1—Ag1—Ag1^{i}	102.87 (6)

Symmetry codes: (i) 1-x, 1-y, 1-z.

Bond	(Å)
Zn1—N1	2.0346 (19)
Zn1—N2^{i}	2.0537 (19)
Zn1—Cl2	2.2275 (6)
Zn1—Cl1	2.2303 (6)
Angle	(º)
N1—Zn1—N2^{i}	106.15 (7)
N1—Zn1—Cl2	106.60 (6)
N2^{i}—Zn1—Cl2	107.99 (6)
N1—Zn1—Cl1	107.27 (5)
N2^{i}—Zn1—Cl1	102.10 (6)
Cl2—Zn1—Cl1	125.37 (2)

Table S4 Selected Bond Lengths (Å) and Bond Angles (°) for compound **3**. Symmetry codes: (i) 1-x, 1-y, 1-z.

Table S5 Selected Bond Lengths (Å) and Bond Angles (°) for compound **4**.

Bond	(Å)
Hg1—N2	2.432 (7)
Hg1—N1^{i}	2.441 (7)
Hg1—I1	2.6433 (6)
Hg1—I2	2.6454 (7)
Angle	(º)
N2—Hg1—N1^{i}	103.9 (2)
N2—Hg1—I1	102.70 (16)
N1^{i}—Hg1—I1	100.18 (17)
N2—Hg1—I2	105.65 (15)
N1^{i}—Hg1—I2	97.76 (17)
I1—Hg1—I2	141.47 (2)

Symmetry codes: (i) 1-x, 1-y, 1-z.