SUPPLEMENTARY INFORMATION

Structures of NHC Hg(II) and Ag(I) Complexes and Selective Recognition of Nitrate Anion

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Contents

1. CCDC numbers for complexes 1-8.

CCDC 976658, 976659, 976656, 976652, 976655, 976657, 976653 and 976654 contains the supplementary crystallographic data for complexes **1-8**. 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, Figures and Tables associated with this article can be found in the online version.

2. Tables S1-S3

Table S1 In the same ligand, the dihedral angles between two benzene rings from phenol ether (**A**), and dihedral angles between benzimidazole (or imidazole) rings and adjacent benzene rings from phenol ether (**B**) for complexes **1-8**. The dihedral angles (˚) between two benzimidazole (or imidazole) rings in NHC-Metal-NHC units (**C**) for complexes **1-4** and **6-7**

Compounds	**A**	**B**	**C**
1	30.0(4)˚	77.3(6)˚, 77.8(7)˚	36.1(3)˚
2	46.4(3)˚	73.1(8)˚, 82.4(3)˚	23.9(4)˚
3	81.9(1)˚	78.7(5)˚, 81.2(3)˚	8.6(5)˚
4	7.5(1)˚	81.3(0)˚, 88.4(0)˚	33.9(9)˚
5	72.3(0)˚	72.6(1)˚, 79.8(6)˚	-
6	89.2(4)˚	61.3(1)˚, 76.9(0)˚	28.3(2)˚
7	76.2(1)˚	83.6(8)˚, 85.0(7)˚	31.8(1)˚
8	15.5(6)˚	81.0(1)˚, 81.6(7)˚	-

Table S2 Distances (Å) of π-π interactions, and distances (Å) and angles (°) of C-H···π contacts for **1**-**4** and **6**-**8**

	π-π		C-H···π	
Complex	Face-to-face	Center-to-center	H···π	C-H···π
1	3.585(6) (benzimidazole) 3.443(6) (benzimidazole to pyridine)	3.715(1) (benzimidazole) 3.869(1) (benzimidazole to pyridine)	_	_
2	3.396(8) (benzene)	3.610(1) (benzene)	_	_
3			3.165(9)	134.2(3)
4	_	_	3.310(4)	101.0(1)
6	3.425(1) (benzimidazole)	3.634(2) (benzimidazole)	2.961(2)	153.3(6)
7	_	_	2.624(2)	143.2(2)
8	_	_	2.854(1)	147.5(2)
			2.890(1)	127.3(2)

Table S3 H-Bonding geometry (Å, °) for complexes **2**-**6**

Compounds	D-H···A	D-H	H···A	D···A	D-H···A
2	C(31)-H(31)···Cl(1)^{i}	0.930(5)	2.775(1)	3.703(5)	175.2(3)
	C(3)-H(3A)···Cl(3)^{i}	0.970(4)	2.754(1)	3.671(4)	157.8(2)
3	C(19)-H(19B)···O(3)^{i}	0.970(0)	2.696(6)	3.642(8)	165.1(3)
	C(27)-H(27B)···O(4)^{i}	0.970(0)	2.268(4)	3.177(6)	155.6(2)
	C(4)-H(4)···O(5)^{iii}	0.930(0)	2.511(5)	3.418(8)	165.1(3)
4	C(34)-H(34)··· I(1)^{i}	0.931(1)	2.940(8)	3.751(1)	146.2(9)
	C(21)-H(21)··· I(3)^{i}	0.929(1)	3.177(9)	3.893(1)	135.2(7)
5	C(15)-H(15B)···Cl(1)	0.970(1)	2.801(2)	3.628(1)	143.6(7)
	C(26)-H(26A)···Cl(5)^{i}	0.970(1)	2.818(2)	3.620(8)	140.6(6)
6	C(34)-H(34B)··· I(4)^{i}	0.970(1)	3.006(8)	3.882(1)	150.6(6)

Symmetry code: i: 3/2 - *x*, -1/2 + *y*, 1/2 - *z* for **2**; i: 1 - *x*, 3 - *y*, -*z*, iii: 1 + *x*, -1 + *y*, *z* for **3**; i: 2 - *x*, 2 - *y*, 1 - *z* for **4**; i: *x*, 1.5 - y, 0.5 + *z* for **5**; i: 1.5 + *x*, 3.5 - y, 0.5 + *z* for **6**.

3. The crystal packings of complexes 1-8

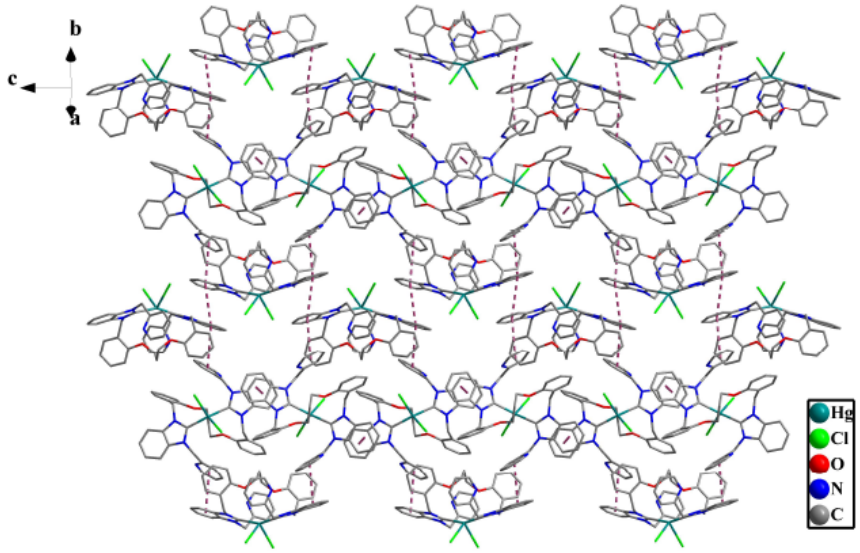


Fig. S1(a) 2D supramolecular layer of complex **1** via π-π interactions. All hydrogen atoms were omitted for clarity.

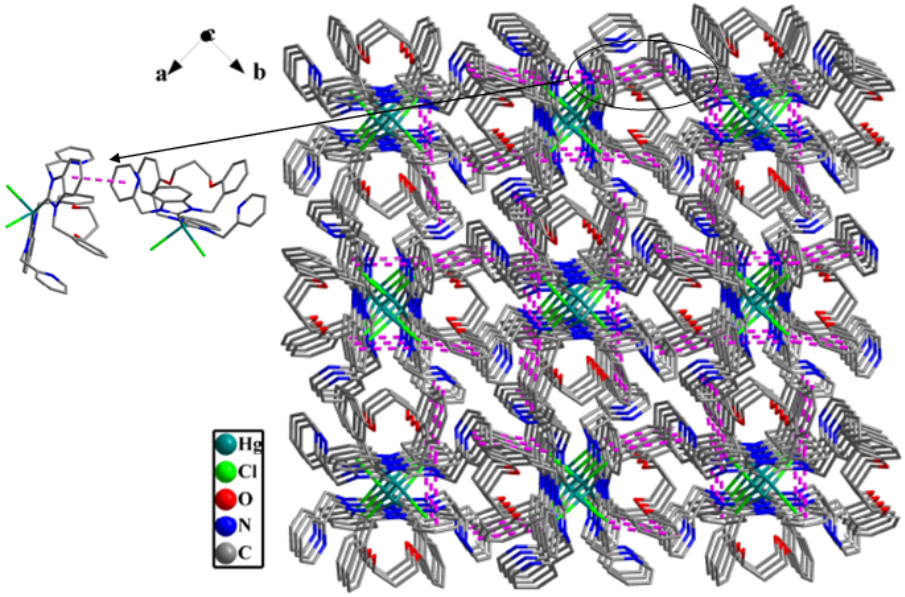


Fig. S1(b) 3D supramolecular network of complex **1** via π-π interactions. All hydrogen atoms were omitted for clarity.

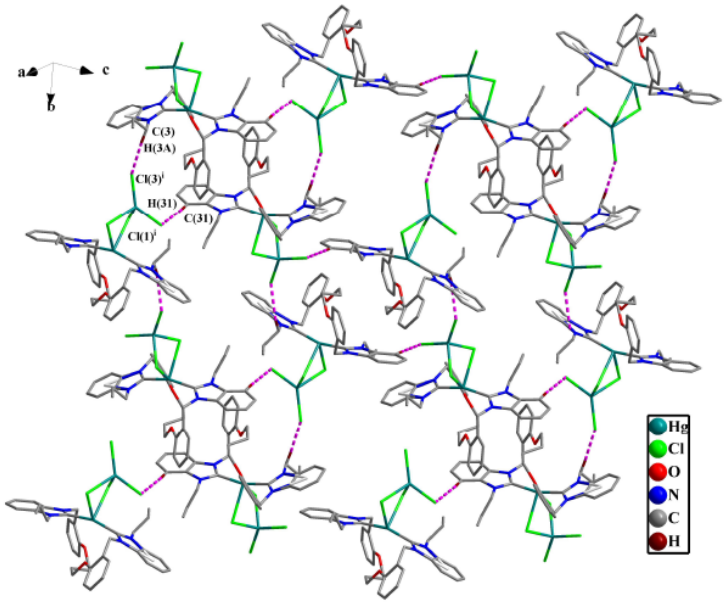


Fig. S2(a) 2D supramolecular layer of complex **2** via C-H···Cl hydrogen bonds. All hydrogen atoms except those participating in the C-H···Cl hydrogen bonds were omitted for clarity. Symm. Code: i: 3/2 - *x*, -1/2 + *y*, 1/2 - *z*.

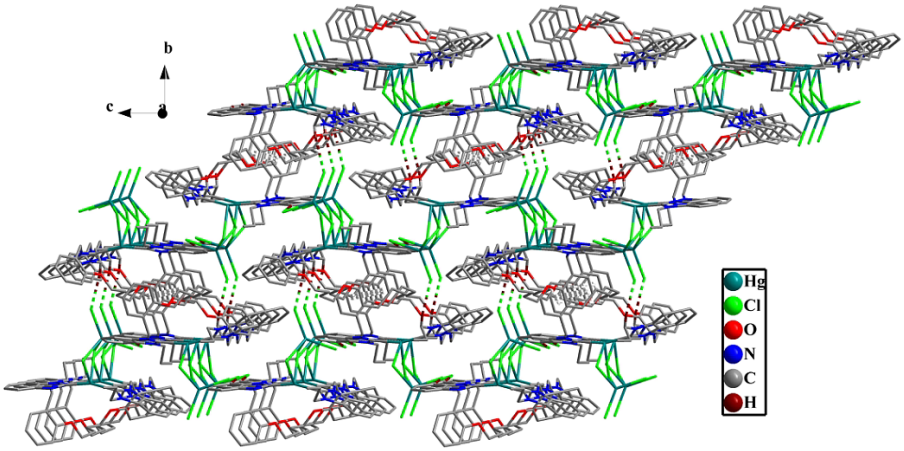


Fig. S2(b) 3D supramolecular network of complex **2** via C-H···Cl hydrogen bonds and π-π interactions. All hydrogen atoms except those participating in the C-H···Cl hydrogen bonds were omitted for clarity.

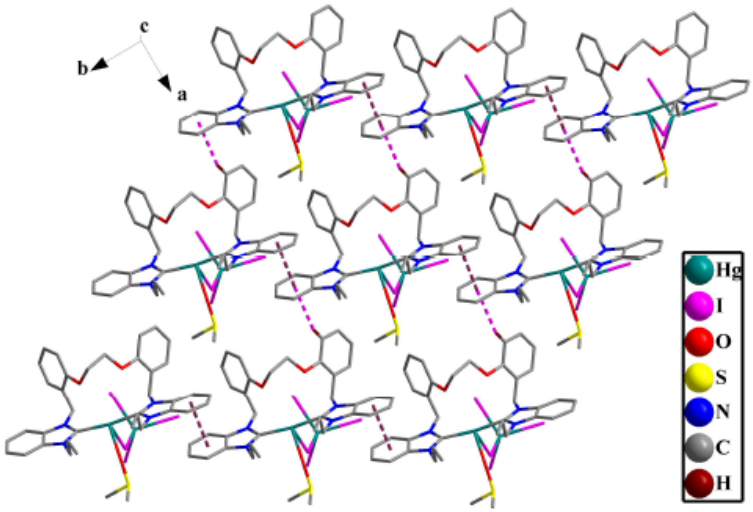


Fig. S3(a) 2D supramolecular layer of complex **3** via C-H···π contacts and π-π interactions. All hydrogen atoms except those participating in C-H···π contacts were omitted for clarity.

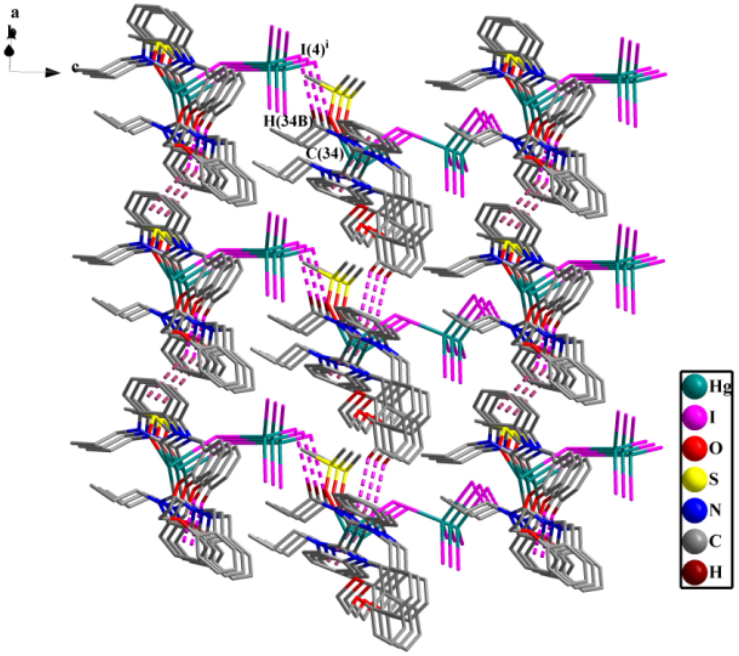


Fig. S3(b) 3D supramolecular network of complex **3** via C-H···π contacts, π-π interactions and C-H···I hydrogen bonds. All hydrogen atoms except those participating in C-H···π contacts and C-H···I hydrogen bonds were omitted for clarity. Symm. Code: i: 1.5 + *x*, 3.5 - y, 0.5 + *z*.

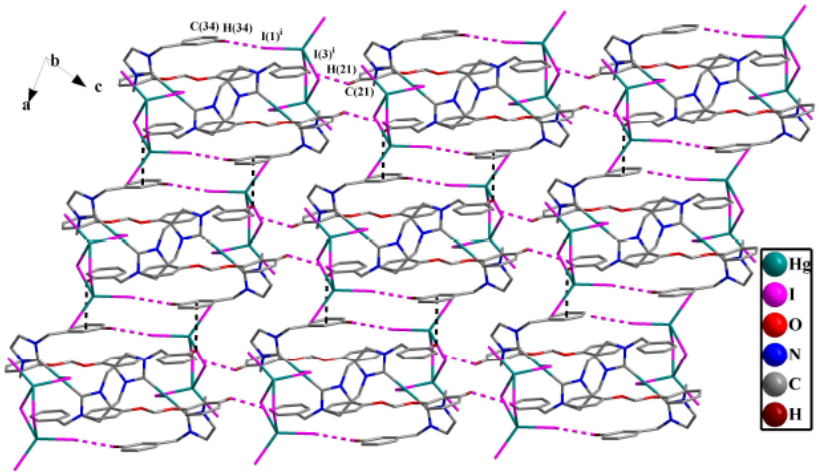


Fig. S4 2D supramolecular layer of complex **4** via C-H···I hydrogen bonds and C-H···π contacts. All hydrogen atoms except those participating in the C-H···I hydrogen bonds and C-H···π contacts were omitted for clarity. Symm. Code: i: 2 - *x*, 2 - *y*, 1 - *z*.

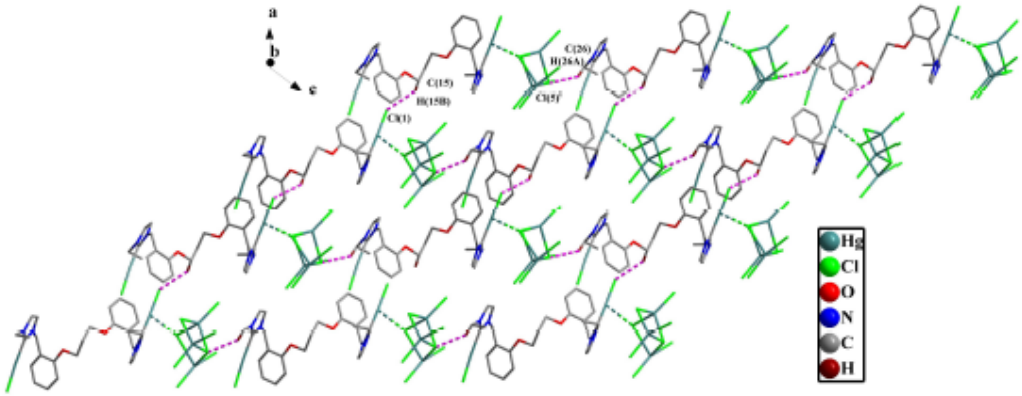


Fig. S5 2D supramolecular layer of complex **5** via C-H···Cl hydrogen bonds. All hydrogen atoms except those participating in the C-H···Cl hydrogen bonds were omitted for clarity. Symm. Code: i: *x*, 1.5 - y, 0.5 + *z*.

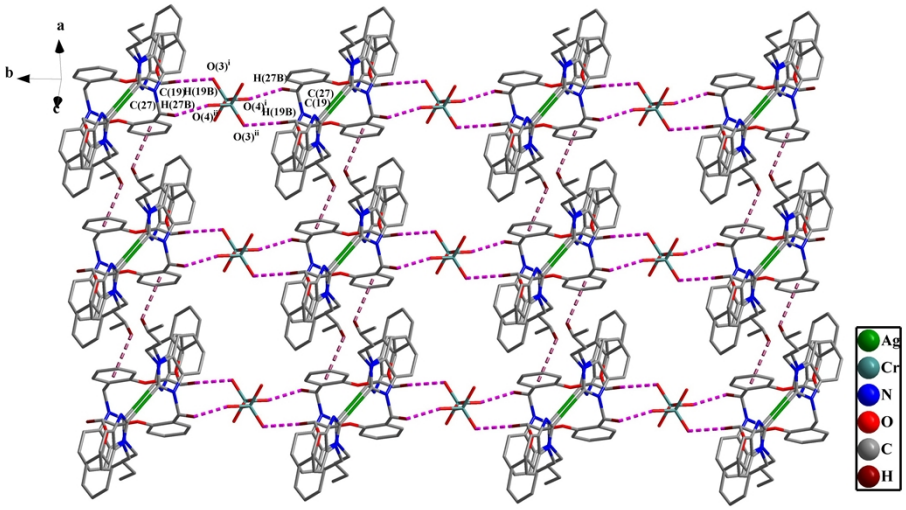


Fig. S6(a) 2D supramolecular layer of complex **6** via two types of C-H···O hydrogen bonds and C-H···π contacts. All hydrogen atoms except those participating in C-H···O hydrogen bonds and C-H···π contacts were omitted for clarity. Symm. Code: i: 1 - *x*, 3 - *y*, -*z*.

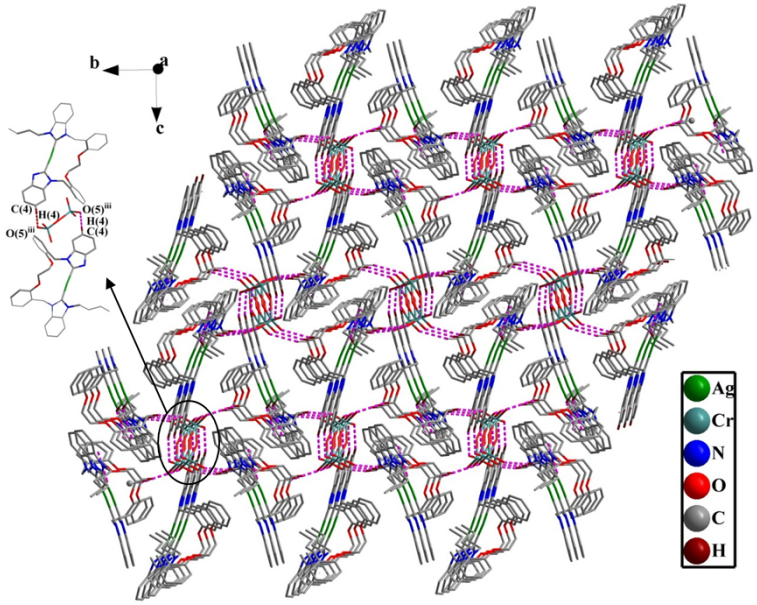


Fig. S6(b) 3D supramolecular network of complex **6** via C-H···O hydrogen bonds and C-H···π contacts. All hydrogen atoms except those participating in the C-H···O hydrogen bonds and C-H···π contacts were omitted for clarity. Symm. Code: iii: 1 + *x*, -1 + *y*, *z*.

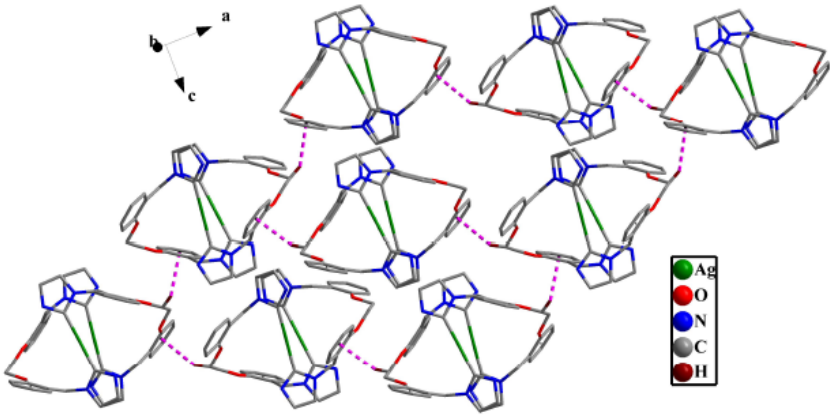


Fig. S7(a) 2D supramolecular layer of complex **7** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity.

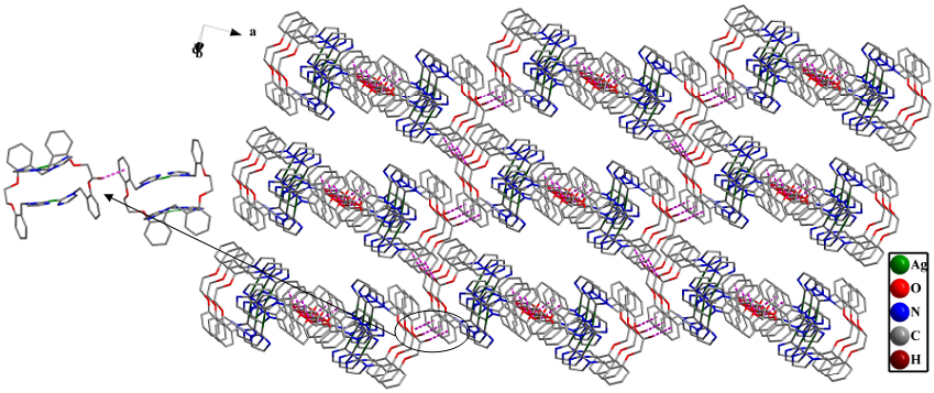


Fig. S7(b) 3D supramolecular architecture of complex **7** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity.

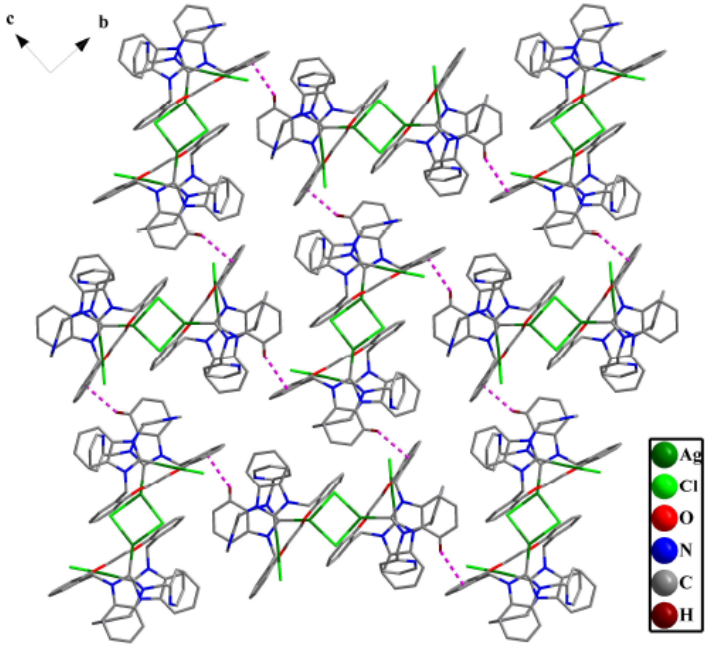


Fig. S8(a) 2D supramolecular layer of complex **8** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity.

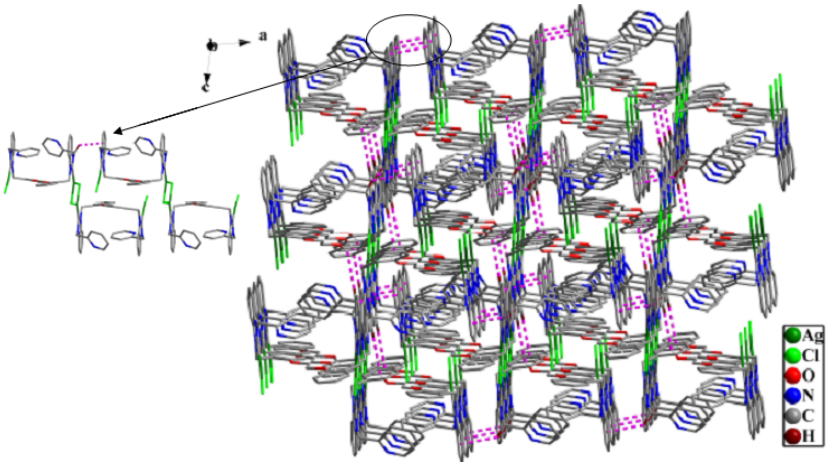


Fig. S8(b) 3D supramolecular network of complex **8** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity.

4. The figures of fluorescence and UV/vis spectroscopies for 6

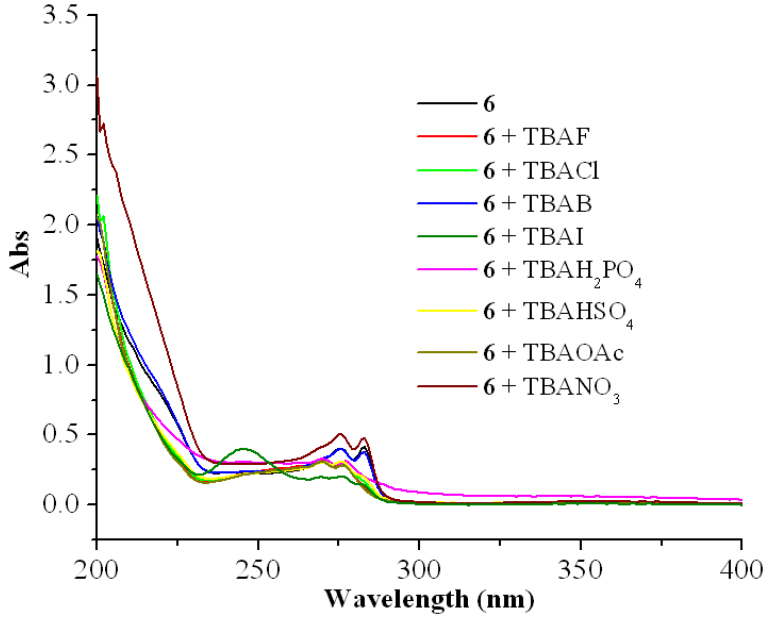


Fig. S9 UV-vis absorption spectra of **6** (1×10^{-5} mol/L) and upon the addition of the tetrabutyl ammonium salts of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, OAc^- and NO_3^- in acetonitrile at 25˚C.

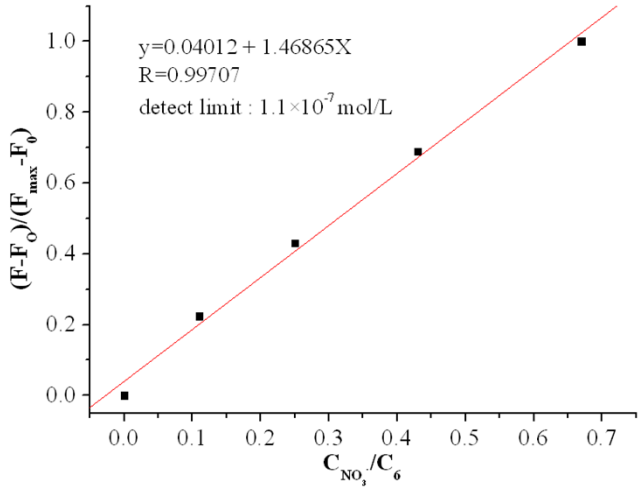


Fig. S10 Emission (at 254 nm) of **6** at different concentrations of NO_3^- (0, 0.11, 0.25, 0.43, 0.67 μM) added, normalized between the minimum emission (0.0 μM NO_3^-) and the emission at 0.67 μM NO_3^-. The detection limit was determined to be 1.1×10^{-7} mol/L.

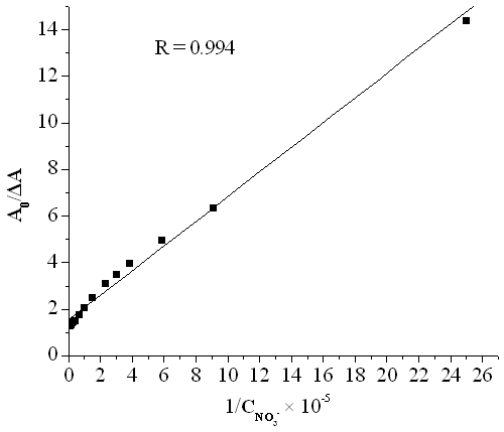


Fig. S11 Benesi-Hildebrand plot of **6** (1 × 10^{-5} mol/L) in the presence of NO_3^- in acetonitrile at 25 ˚C. The concentrations of NO_3^- are 0.04, 0.11, 0.17, 0.26, 0.33, 0.43, 0.67, 1, 1.5, 2.4, 3, 4, 6, 9 mol/L.

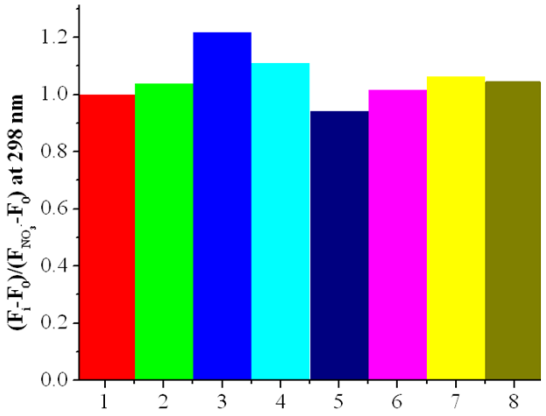


Fig. S12 Change ratio ((F_i-F_0)/(F_{NO3}--F_0)) of fluorescence intensity of **6** upon addition of 1 equiv. NO_3^- in the presence of 5 equiv. of background anions. 1: NO_3^-; 2: NO_3^- + F^-; 3: NO_3^- + Cl^-; 4: NO_3^- + Br^-; 5: NO_3^- + I^-; 6: NO_3^- + $H_2PO_4^-$; 7: NO_3^- + HSO_4^-; 8: NO_3^- + OAc^- in acetonitrile at 25 ˚C.

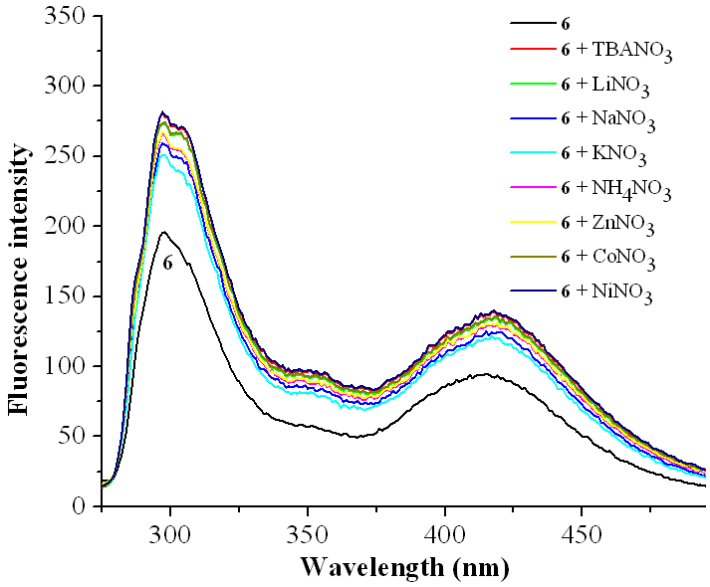


Fig. S13 Fluorescence spectra of **6** (1×10^{-5} mol/L) upon addition of nitrate salts (15×10^{-5} mol/L) with different cations (Li^+, Na^+, K^+, NH_4^+, Zn^{2+}, Co^{2+} and Ni^{2+}).

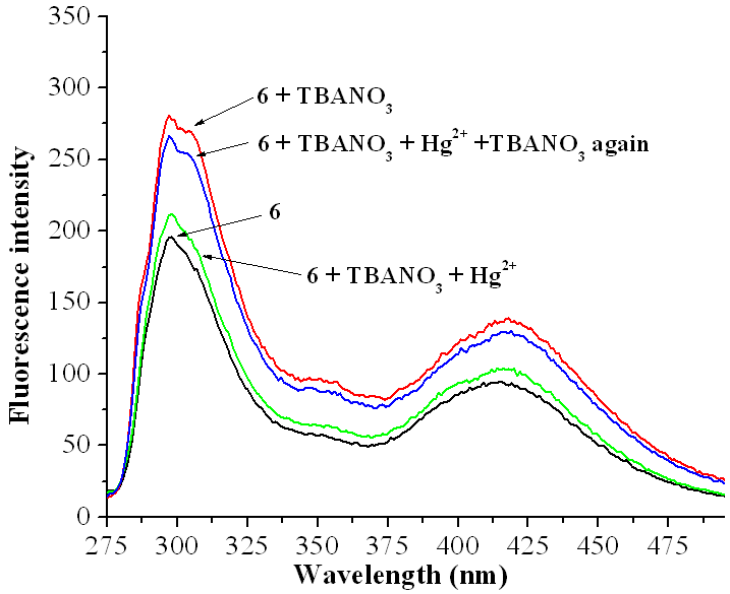


Fig. S14 Fluorescence spectra of **6** (1.0×10^{-5} mol/L) upon the addition of 15 equiv. of NO_3^- in acetonitrile. Hg^{2+} (7.5 equiv.) was added to **6** and NO_3^- mixture to show the reversible binding nature of NO_3^- with **6**.

5. The changes of ^{1}H NMR spectra in benzene rings for 6 and 6/NO_3^- and Scheme S1

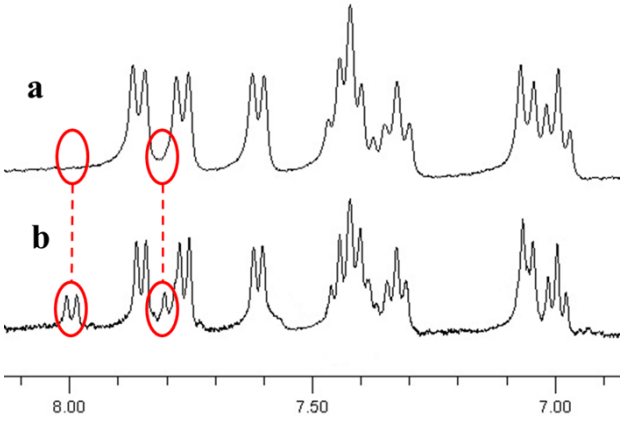
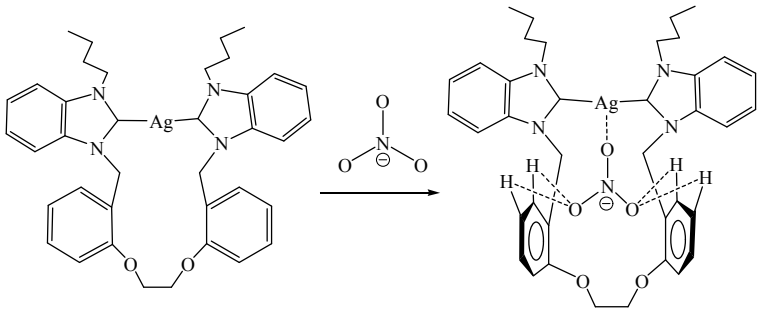


Fig. S15 ^{1}H NMR (400 MHz, DMSO-d_6): The changes of ^{1}H NMR spectra in benzene rings of phenol ether for **6** and **6**/NO_3^-. a: complex **6**, b: **6**/NO_3^-.



Scheme S1 The interactions of NO_3^- with complex **6**.

6. Preparation of bis-benzimidazolium (or bis-imidazolium) salts $L^2H_2\cdot Cl_2$-$L^6H_2\cdot Cl_2$ and $L^8H_2\cdot(PF_6)_2$, and complexes $[L^1Hg(DMSO)](HgI_4)$ (3), $[L^6Hg(Hg_2I_6)]$ (4), $[L^8Hg_2Cl_2](Hg_3Cl_8)$ (5) and $[[L^3Ag_2Cl_2]_2$ (8).

Preparation of 1,2-bis[2-(N-^{n}butylbenzimidazoliumylmethyl)phenoxy]ethylene chloride ($L^2H_2\cdot Cl_2$)

This compound was prepared in a manner analogous to that of $L^1H_2\cdot Cl_2$, only N-^{n}butylbenzimidazole (2.578 g, 14.8 mmol) was used instead of N-^{n}butylbenzimidazole. Yield: 4.022 g (91%). M.p.: 274-276 ˚C. Anal. Calcd for $C_{38}H_{44}O_2N_4Cl_2$: C, 69.18; H, 6.72; N, 8.49%. Found: C, 69.44; H, 6.51; N, 8.68%. ^{1}H NMR (400 MH_Z, DMSO-d_6): δ

0.84 (t, *J* = 7.4 Hz, 6H, C*H*$_3$), 1.26 (m, 4H, C*H*$_2$), 1.80 (m, 4H, C*H*$_2$), 4.30 (s, 4H, OC*H*$_2$), 4.37 (t, *J* = 7.2 Hz, 4H, C*H*$_2$), 5.57 (s, 4H, C*H*$_2$), 7.12 (m, 4H, Ar*H*), 7.43 (m, 4H, Ar*H*), 7.60 (m, 4H, Ar*H*), 7.78 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.98 (d, *J* = 8.4 Hz, 2H, Ar*H*), 9.70 (s, 2H, 2-bimi*H*). ^{13}C{^{1}H} NMR (100 MH$_Z$, DMSO-d$_6$): δ 13.2 (*C*H$_3$), 19.0 (*C*H$_2$), 30.5 (*C*H$_2$), 45.9 (*C*H$_2$), 46.3 (*C*H$_2$), 66.6 (*C*H$_2$), 112.4 (Ph*C*), 113.6 (bimi*C*), 113.7 (bimi*C*), 121.0 (bimi*C* or Ph*C*), 121.6 (bimi*C* or Ph*C*), 126.3 (Ph*C*), 130.8 (bimi*C* or Ph*C*), 142.5 (2-bimi*C*), 156.4 (Ph*C*).

Preparation of 1,2-bis[2-(N-picolylbenzimidazoliumymethyl)phenoxyl]ethylene chloride ($L^3H_2 \cdot Cl_2$)

This compound was prepared in a manner analogous to that of **$L^1H_2 \cdot Cl_2$**, only N-picolylbenzimidazole (3.096 g, 14.8 mmol) was used instead of N-^{n}butylbenzimidazole. Yield: 3.327 g (68%), M.p.: 174-176 ˚C. Anal. Calcd for $C_{42}H_{38}O_2N_6Cl_2$: C, 69.13; H, 5.24; N, 11.51%. Found: C, 69.47; H, 5.66; N, 11.34%. ^{1}H NMR (400 MH$_Z$, DMSO-d$_6$): δ 4.31 (s, 4H, C*H*$_2$), 5.69 (s, 4H, C*H*$_2$), 5.92 (s, 4H, C*H*$_2$), 7.04 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.15 (m, 2H, Ar*H*), 7.42 (m, 4H, Ar*H*), 7.52 (t, *J* = 6.0 Hz, 2H, Ar*H*), 7.66 (t, *J* = 8.0 Hz, 4H, Ar*H*), 7.90 (m, 6H, Ar*H*), 8.24 (d, *J* = 4.0 Hz, 2H, Ar*H*), 10.14 (s, 2H, 2-bimi*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 46.2 (*C*H$_2$), 50.6 (*C*H$_2$), 66.2 (*C*H$_2$), 112.3 (Ph*C*), 113.7 (bimi*C*), 113.8 (bimi*C*), 120.9 (bimi*C* or Ph*C*), 121.3 (bimi*C* or Ph*C*), 122.6 (Ph*C* or Py*C*), 123.4 (Ph*C* or Py*C*), 126.3 (Ph*C*), 126.5 (Ph*C*), 130.8 (bimi*C* or Ph*C*), 130.9 (bimi*C* or Ph*C*), 131.1 (Py*C*), 137.4 (Py*C*), 143.5 (2-bimi*C*), 149.3 (Py*C*), 152.8 (Py*C*), 156.4 (Ph*C*) (Py = pyridine).

Preparation of 1,3-bis[2-(N-picolylbenzimidazoliumymethyl)phenoxyl]propylene chloride ($L^4H_2 \cdot Cl_2$)

This compound was prepared in a manner analogous to that of **$L^1H_2 \cdot Cl_2$**, only 1,3-dibromopropane (10.740 g, 53.2 mmol) and N-picolylbenzimidazole (3.096 g, 14.8 mmol) were used instead of 1,2-dibromoethane and N-^{n}butylbenzimidazole. Yield: 3.523 g (70%). M.p.: 192-194 ˚C. Anal. Calcd for $C_{43}H_{40}O_2N_6Cl_2$: C, 69.44; H, 5.42; N, 11.30%.

Found: C, 69.71; H, 5.47; N, 11.58%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.04 (t, J = 6.0 Hz, 2H, CH_2), 4.02 (t, J = 5.8 Hz, 4H, CH_2), 5.78 (s, 4H, CH_2), 6.00 (s, 4H, CH_2), 7.62 (m, 4H, Ar*H*), 7.70 (d, J = 7.6 Hz, 4H, Ar*H*), 7.88 (q, J = 5.1 Hz, 4H, Ar*H*), 7.94 (q, J = 8.0 Hz, 4H, Ar*H*), 8.00 (q, J = 8.0 Hz, 4H, Ar*H*), 8.01 (d, J = 12.0 Hz, 2H, Ar*H*), 8.39 (d, J = 4.0 Hz, 2H, Ar*H*), 10.18 (s, 2H, 2-bimi*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 28.1 (*C*H$_2$), 48.5 (*C*H$_2$), 50.6 (*C*H$_2$), 64.6 (*C*H$_2$), 112.0 (Ph*C*), 113.9 (bimi*C*), 120.6 (bimi*C* or Ph*C*), 121.1 (bimi*C* or Ph*C*), 122.7 (Ph*C* or Py*C*), 123.6 (Ph*C* or Py*C*), 126.4 (Ph*C*), 126.5 (Ph*C*), 130.8 (bimi*C* or Ph*C*), 130.9 (bimi*C* or Ph*C*), 131.2 (Py*C*), 137.4 (Py*C*), 143.5 (2-bimi*C*), 149.4 (Py*C*), 152.9 (Py*C*), 156.6 (Ph*C*).

Preparation of 1,4-bis[2-(N-^{n}propylbenzimidazoliumymethyl)phenoxyl]butylene chloride ($L^5H_2\cdot Cl_2$)

This compound was prepared in a manner analogous to that of $\mathbf{L^1H_2\cdot Cl_2}$, only 1,4-dibromobutane (11.486 g, 53.2 mmol) and N-^{n}propylbenzimidazole (2.371 g, 14.8 mmol) were used instead of 1,2-dibromoethane and N-^{n}butylbenzimidazole. Yield: 3.223 g (72%) M.p.: 198-200 ˚C. Anal. Calcd for $C_{38}H_{44}O_2N_4Cl_2$: C, 69.18; H, 6.72; N, 8.49%. Found: C, 69.52; H, 6.83; N, 8.74%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.89 (t, J = 8.0 Hz, 6H, CH_3), 1.67 (s, 4H, CH_2), 3.36 (m, 4H, CH_2), 3.98 (s, 4H, CH_2), 4.51 (t, J = 6.0 Hz, 4H, CH_2), 5.69 (s, 4H, CH_2), 7.05 (q, J = 8.1 Hz, 4H, Ar*H*), 7.40 (m, 2H, Ar*H*), 7.54 (q, J = 18.7 Hz, 2H, Ar*H*), 7.67 (m, 4H, Ar*H*), 7.97 (q, J = 4.0 Hz, 2H, Ar*H*), 8.13 (d, J = 8.0 Hz, 2H, Ar*H*), 9.88 (s, 2H, 2-bimi*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 10.5 (*C*H$_3$), 22.1 (*C*H$_2$), 25.0 (*C*H$_2$), 48.0 (*C*H$_2$), 55.9 (*C*H$_2$), 67.3 (*C*H$_2$), 112.1 (Ph*C*), 113.7 (bimi*C*), 113.8 (bimi*C*), 120.5 (bimi*C* or Ph*C*), 121.2 (bimi*C* or Ph*C*), 126.5 (Ph*C*), 130.6 (bimi*C* or Ph*C*), 130.7 (bimi*C* or Ph*C*), 131.0 (bimi*C* or Ph*C*), 142.5 (2-bimi*C*), 156.5 (Ph*C*).

Preparation of 1,1-bis[2-(N-benzylimidazoliumylmethyl)phenoxy]methylene chloride ($L^6H_2\cdot Cl_2$)

This compound was prepared in a manner analogous to that of $\mathbf{L^1H_2\cdot Cl_2}$, only 1,1-dibromomethane (9.248 g, 53.2 mmol) and N-benzylimidazole (2.341 g, 14.8 mmol)

were used instead of 1,2-dibromoethane and N-^{n}butylbenzimidazole. Yield: 3.786 g (92%). M.p.: 190-192 ˚C. Anal. Calcd for $C_{35}H_{34}O_2N_4Cl_2$: C, 68.51; H, 5.58; N, 9.13%. Found: C, 68.23; H, 5.61; N, 9.59%. ^{1}H NMR (400 MH$_Z$, DMSO-d$_6$): δ 5.36 (s, 4H, CH_2), 5.46 (s, 4H, CH_2), 6.04 (s, 2H, OCH_2), 7.10 (s, 2H, ArH), 7.46 (m, 16H, ArH), 7.75 (s, 2H, ArH), 7.84 (s, 2H, ArH), 9.75 (s, 2H, 2-imi$H$). ^{13}C{^{1}H} NMR (100 MH$_Z$, DMSO-d$_6$): δ 47.9 (CH$_2$), 51.7 (CH$_2$), 114.0 (PhC), 122.3 (PhC), 122.4 (PhC), 122.8 (PhC), 122.9 (PhC), 128.2 (PhC), 128.6 (PhC), 128.9 (PhC), 130.8 (imi$C$ or PhC), 131.0 (imi$C$ or PhC), 134.9 (PhC), 136.5 (2-imi$C$), 154.1 (PhC) (imi = imidazole).

Preparation of 1,3-bis[2-(N-ethylimidazoliumylmethyl)phenoxy]propylene hexafluorophosphate ($L^8H_2\cdot(PF_6)_2$)

This compound was prepared in a manner analogous to that of **$L^7H_2\cdot(PF_6)_2$**, only 1,3-dibromopropane (10.740 g, 53.2 mmol) was used instead of 1,2-dibromoethane. Yield: 2.402 g (81%). M.p.: 112-114 ˚C. Anal. Calcd for $C_{27}H_{34}O_2N_4P_2F_{12}$: C, 44.03; H, 4.65; N, 7.60%. Found: C, 44.32; H, 4.81; N, 7.52%. ^{1}H NMR (400 MH$_Z$, DMSO-d$_6$): δ 1.40 (t, J = 7.2 Hz, 6H, CH_3), 2.22 (m, 2H, CH_2), 4.19 (m, 8H, OCH_2), 5.34 (s, 4H, PhCH_2), 7.03 (t, J = 7.6 Hz, 2H, ArH), 7.09 (d, J = 8.4 Hz, 2H, ArH), 7.39 (t, J = 8.2 Hz, 2H, ArH), 7.43 (d, J = 7.6 Hz, 2H, ArH), 7.67 (s, 2H, ArH), 7.77 (s, 2H, imi$H$), 9.14 (s, 2H, 2-imi$H$). ^{13}C{^{1}H} NMR (100 MH$_Z$, DMSO-d$_6$): δ 15.1 (CH$_3$), 28.4 (CH$_2$), 44.2 (CH$_2$), 48.0 (CH$_2$), 64.5 (CH$_2$), 111.9 (PhC), 120.7 (PhC), 122.1 (PhC), 122.7 (PhC), 130.4 (imi$C$ or PhC), 130.8 (imi$C$ or PhC), 135.7 (2-imi$C$), 156.3 (PhC).

Preparation of [L^1Hg(DMSO)](HgI_4) (3)

This compound was prepared in a manner analogous to that of complex **2**, only **$L^1H_2\cdot Cl_2$** (0.189 g, 0.3 mmol) and HgI_2 (0.272 g, 0.6 mmol) were used instead of **$L^5H_2\cdot Cl_2$** (0.197 g, 0.3 mmol) and $HgCl_2$ (0.163 g, 0.6 mmol) in CH_3CN/DMSO solution (15 mL, 2:1, v/v) at about 80 ˚C. Yield: 0.091 g (19%). Mp: 242-244 ˚C. Anal. Calcd for $C_{38}H_{44}Hg_2I_4N_4O_3S$: C, 29.52; H, 2.86; N, 3.62%. Found: C, 29.21; H, 2.64; N, 3.55%. ^{1}H NMR (400 MH$_Z$, DMSO-d$_6$): δ 0.82 (d, J = 6.4 Hz, 6H, CH_3), 2.08 (q, J = 4.6 Hz, 4H,

CH_2), 4.03 (s, 4H, CH_2), 4.29 (s, 4H, OCH_2), 5.62 (s, 4H, CH_2), 7.00 (q, J = 6.7 Hz, 4H, Ar*H)*, 7.27 (d, J = 8.4 Hz, 2H, Ar*H*), 7.41 (q, J = 9.4 Hz, 6H, Ar*H*), 7.84 (m, 4H, Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 12.7 (*C*H_3), 24.8 (*C*H_2), 48.9 (*C*H_2), 51.4 (*C*H_2), 65.1 (*C*H_2), 112.8 (bimi*C*), 113.0 (bimi*C*), 121.1 (bimi*C* or Ph*C*), 124.4 (bimi*C* or Ph*C*), 130.3 (bimi*C* or Ph*C*), 133.5 (bimi*C* or Ph*C*), 134.1 (Ph*C*), 156.5 (Ph*C*), 188.5 ($C_{carbene}$).

Preparation of [$L^6Hg(Hg_2I_6)$] (4)

This compound was prepared in a manner analogous to that of complex **2**, only **$L^6H_2 \cdot Cl_2$** (0.184 g, 0.3 mmol) and HgI_2 (0.408 g, 0.9 mmol) were used instead of **$L^5H_2 \cdot Cl_2$** (0.197 g, 0.3 mmol) and $HgCl_2$ (0.163 g, 0.6 mmol). Yield: 0.353 g (61%). M.p.: 168-170 ˚C. Anal. Calcd for $C_{35}H_{32}Hg_3I_6N_4O_2$: C, 22.08; H, 1.69; N, 2.94%. Found: C, 22.43; H, 1.71; N, 2.72%. ^{1}H NMR (400 MH$_Z$, DMSO-d_6): δ 5.24 (s, 4H, CH_2), 5.69 (s, 2H, OCH_2), 5.79 (s, 4H, PhCH_2), 7.08 (t, J = 3.0 Hz, 4H, Ar*H*), 7.20 (d, J = 9.2 Hz, 6H, Ar*H*), 7.45 (t, J = 7.2 Hz, 4H, Ar*H*), 7.65 (q, J = 14.1 Hz, 8H, Ar*H*). ^{13}C{^{1}H} NMR (100 MH$_Z$, DMSO-d_6): δ 51.7 (*C*H_2), 53.9 (*C*H_2), 92.9 (*C*H_2), 114.5 (Ph*C*), 122.8 (Ph*C*)), 123.9 (Ph*C*), 124.1 (Ph*C*), 125.1 (Ph*C*), 127.6 (Ph*C*), 128.3 (Ph*C*), 129.0 (Ph*C*), 131.1 (imi*C* or Ph*C*), 131.8 (imi*C* or Ph*C*), 136.7 (Ph*C*), 153.8 (Ph*C*), 177.4 ($C_{carbene}$).

Preparation of [$L^8Hg_2Cl_2$](Hg_3Cl_8) (5)

This compound was prepared in a manner analogous to that of complex **2**, only **$L^8H_2 \cdot (PF_6)_2$** (0.220 g, 0.3 mmol) and $HgCl_2$ (0.407 g, 1.5 mmol) were used instead of **$L^5H_2 \cdot Cl_2$** (0.197 g, 0.3 mmol) and $HgCl_2$ (0.163 g, 0.6 mmol). Yield: 0.310 g (57%). M.p.: 188-190 ˚C. Anal. Calcd for $C_{27}H_{32}Cl_{10}Hg_5N_4O_2$: C, 17.99; H, 1.78; N, 3.10%. Found: C, 18.24; H, 1.53; N, 3.43%. ^{1}H NMR (400 MH$_Z$, DMSO-d_6): δ 1.39 (t, J = 3.5 Hz, 6H, CH_3), 2.22 (t, J = 5.7 Hz, 2H, CH_2), 4.18 (t, J = 7.6 Hz, 4H, OCH_2), 4.29 (q, J = 9.3 Hz, 4H, CH_2), 5.50 (t, 4H, PhCH_2), 7.08 (m, 4H, Ar*H*), 7.40 (m, 4H, Ar*H*), 7.76 (q, J = 12.6 Hz, 4H, Ar*H*). ^{13}C{^{1}H} NMR (100 MH$_Z$, DMSO-d_6): δ 17.6 (*C*H_3), 29.8 (*C*H_2), 47.2 (*C*H_2), 50.8 (*C*H_2), 65.7 (*C*H_2), 109.9 (Ph*C*), 123.1 (Ph*C*), 123.2 (Ph*C*), 123.8 (Ph*C*), 123.9 (Ph*C*), 125.1 (Ph*C*), 131.0 (imi*C*), 157.1 (Ph*C*), 167.6 ($C_{carbene}$).

Preparation of $[L^7{}_2Ag_2](PF_6)_2$ (7)

Silver oxide (0.034 g, 0.15 mmol) was added to a CH_3CN/CH_2Cl_2 (15 mL, 2:1, v/v) solution of precursor $\mathbf{L^7H_2 \cdot (PF_6)_2}$ (0.216 g, 0.3 mmol), and the suspension solution was stirred for 24 hours under refluxing. The resulting solution was filtered and concentrated to 10 mL, and Et_2O (5 mL) was added to precipitate a yellow powder. Isolation by filtration yields complex **7**. Yield: 0.136 g (66%). M.p.: 182-184 ˚C. Anal. Calcd for $C_{26}H_{30}AgF_6N_4O_2P$: C, 45.69; H, 4.42; N, 8.19%. Found: C, 45.33; H, 4.52; N, 8.54%. ^{1}H NMR (400 MH_Z, DMSO-d_6): δ 1.40 (t, J = 10.0 Hz, 12H, CH_3), 4.14 (q, J = 6.9 Hz, 8H, CH_2), 4.26 (s, 4H, OCH_2), 4.44 (s, 4H, OCH_2), 5.33 (d, J = 12.0 Hz, 8H, PhCH_2), 7.08 (m, 8H, Ar*H*), 7.48 (m, 16H, Ar*H*). ^{13}C{^{1}H} NMR (100 MH_Z, DMSO-d_6): δ 18.6 (*C*H_3), 47.3 (*C*H_2), 51.6 (*C*H_2), 67.1 (*C*H_2), 112.4 (Ph*C*), 121.2 (Ph*C*), 122.0 (Ph*C*), 123.1 (Ph*C*), 125.1 (Ph*C*), 130.4 (bimi*C* or Ph*C*), 131.1 (bimi*C* or Ph*C*), 143.5 (Ph*C*), 156.4 (Ph*C*). The carbene carbon was not observed.

Preparation of $[L^3Ag_2Cl_2]_2$ (8)

This compound was prepared in a manner analogous to that of complex **7**, only $\mathbf{L^7H_2 \cdot (PF_6)_2}$ (0.218 g, 0.3 mmol) and silver oxide (0.069 g, 0.3 mmol) were used instead of $\mathbf{L^7H_2 \cdot (PF_6)_2}$ (0.216 g, 0.3 mmol) and silver oxide (0.034 g, 0.15 mmol). Yield: 0.131 g (46%). Mp.: 254-256 ˚C. Anal. Calcd for $C_{42}H_{36}Ag_2Cl_2N_6O_2$: C, 53.47; H, 3.84; N, 8.90%. Found: C, 53.52; H, 3.75; N, 8.67%. ^{1}H NMR (400 MH_Z, DMSO-d_6): δ 4.29 (s, 8H, OCH_2), 5.78 (d, J = 8.0 Hz, 8H, CH_2), 5.86 (s, 8H, CH_2), 7.01 (t, J = 7.2 Hz, 8H, Ar*H*), 7.29 (m, 4H, Ar*H*), 7.37 (m, 16H, Ar*H*), 7.74 (q, J = 7.4 Hz, 16H, Ar*H*), 8.38 (d, J = 4.4 Hz, 4H, Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 46.2 (*C*H_2), 50.6 (*C*H_2), 66.2 (*C*H_2), 112.3 (Ph*C*), 113.7 (bimi*C*), 113.8 (bimi*C*), 120.9 (bimi*C* or Ph*C*), 121.3 (bimi*C* or Ph*C*), 122.6 (Ph*C* or Py*C*), 123.4 (Ph*C* or Py*C*), 126.3 (Ph*C*), 126.5 (Ph*C*), 130.8 (bimi*C* or Ph*C*), 130.9 (bimi*C* or Ph*C*), 131.1 (Py*C*), 137.4 (Py*C*), 143.4 (Ph*C* or Py*C*), 149.3 (Py*C*), 152.8 (Py*C*), 156.4 (Ph*C*). The carbene carbon was not observed.

6. The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of precursors $L^{1}H_2 \cdot Cl_2$-$L^{6}H_2 \cdot Cl_2$, $L^{7}H_2 \cdot (PF_6)_2$-$L^{8}H_2 \cdot (PF_6)_2$ and complexes 1-8

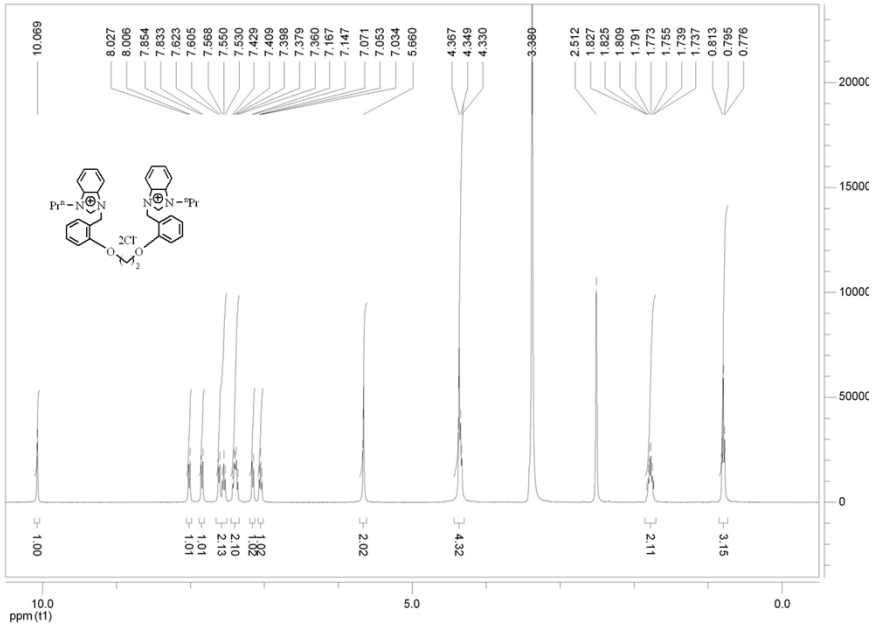


Fig. S16 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^{1}H_2 \cdot Cl_2}$.

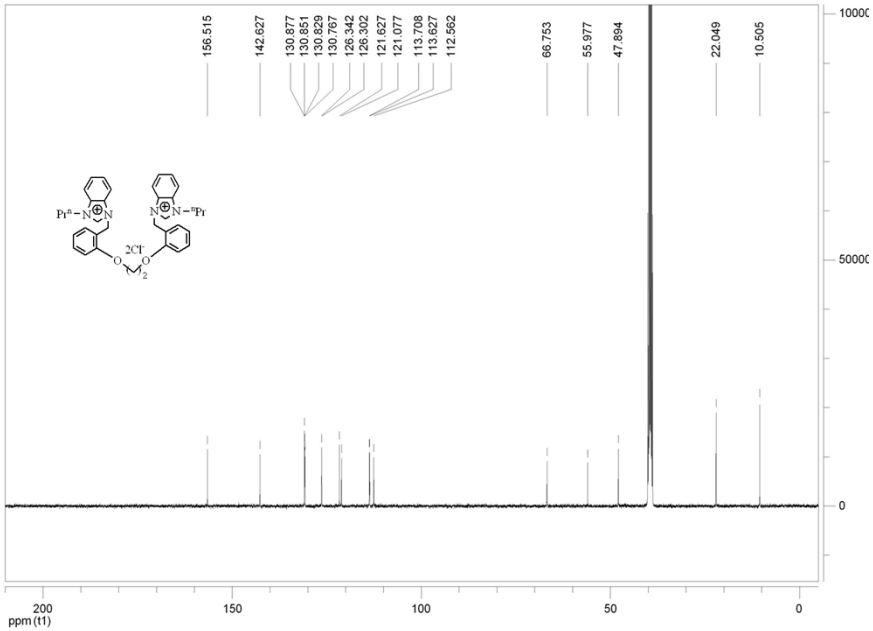


Fig. S17 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^{1}H_2 \cdot Cl_2}$.

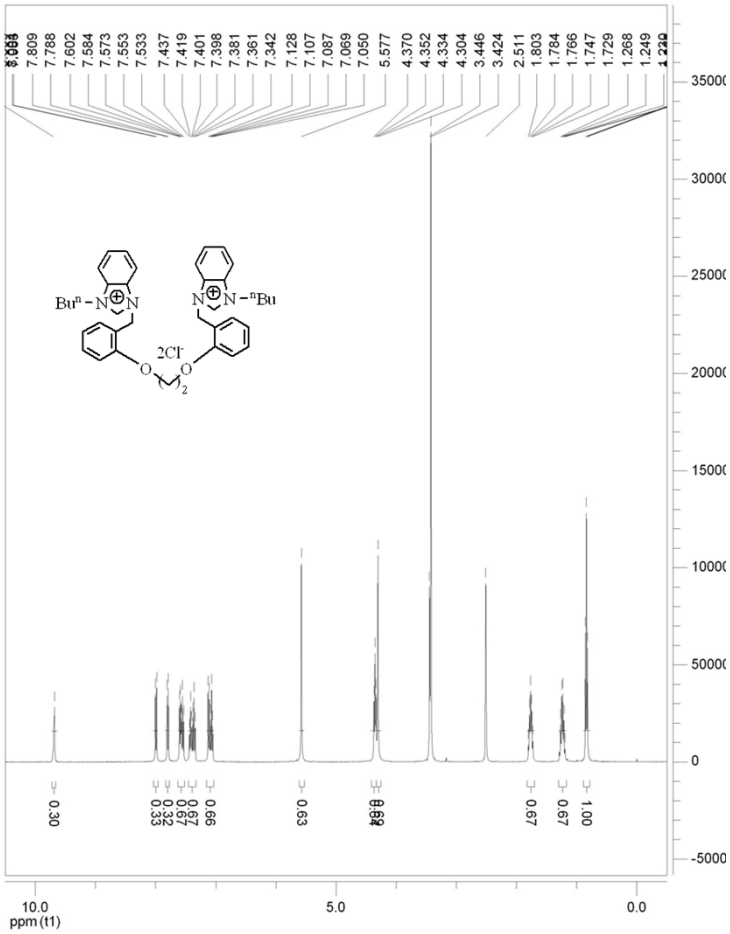


Fig. S18 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^2H_2 \cdot Cl_2}$.

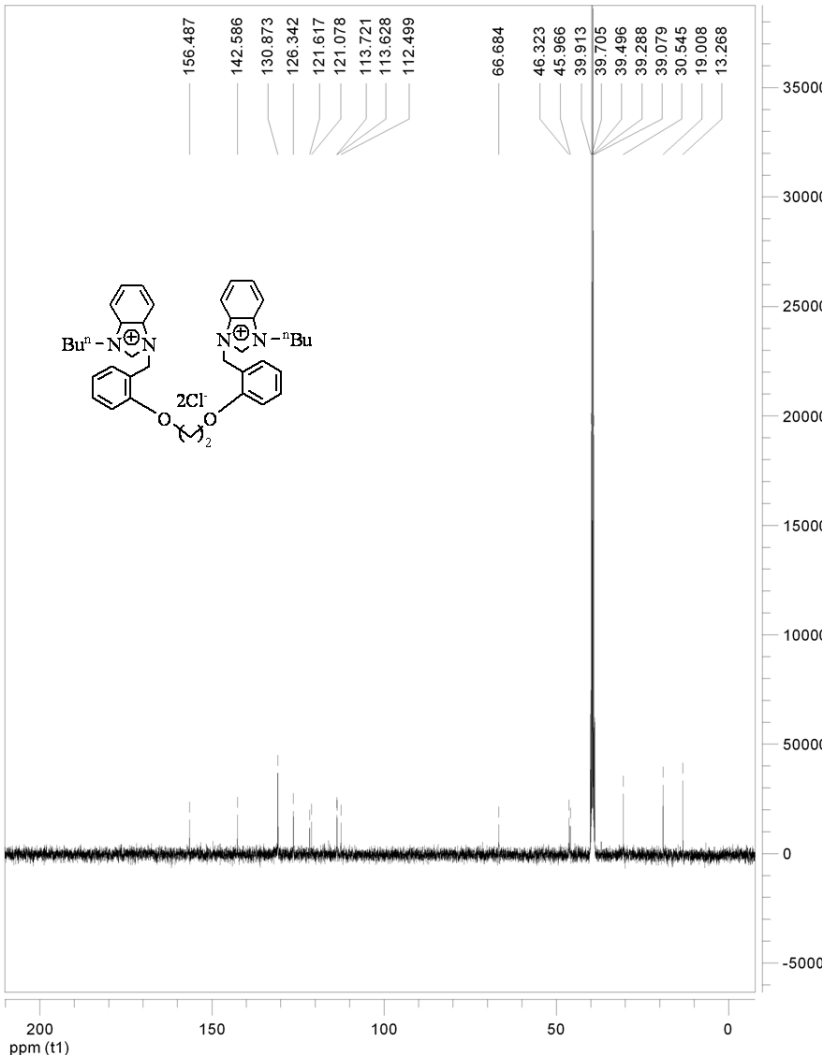


Fig. S19 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^2H_2 \cdot Cl_2}$.

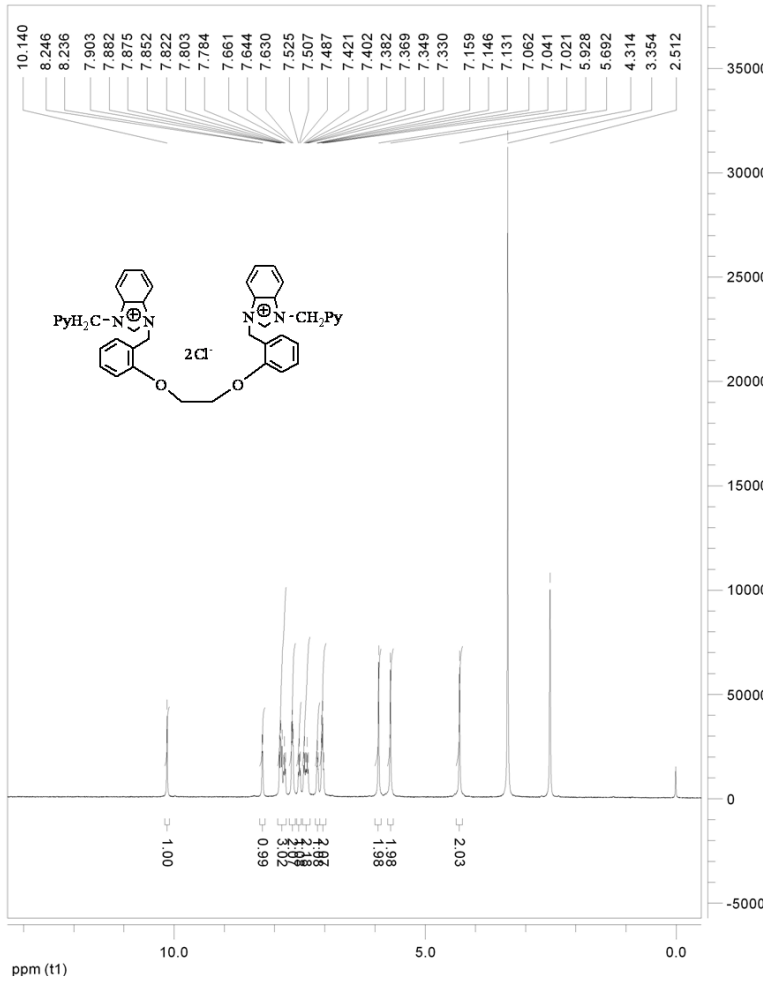


Fig. S20 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^3H_2 \cdot Cl_2}$.

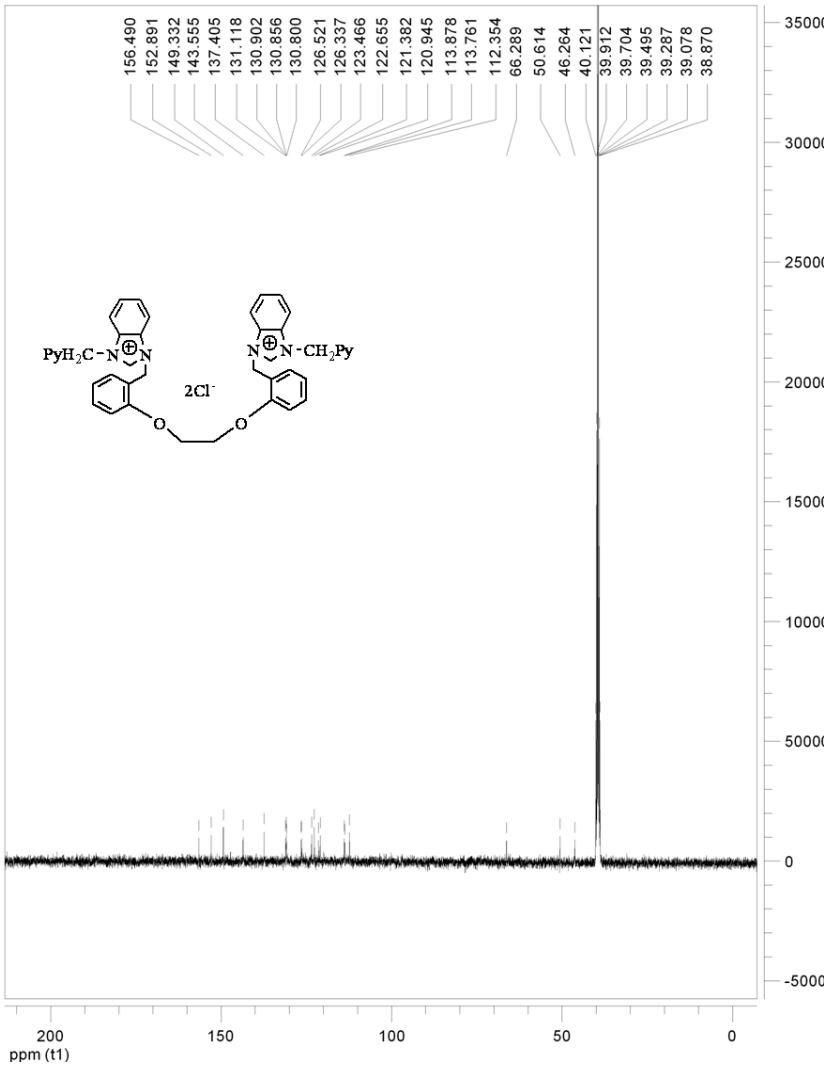


Fig. S21 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^3H_2 \cdot Cl_2}$.

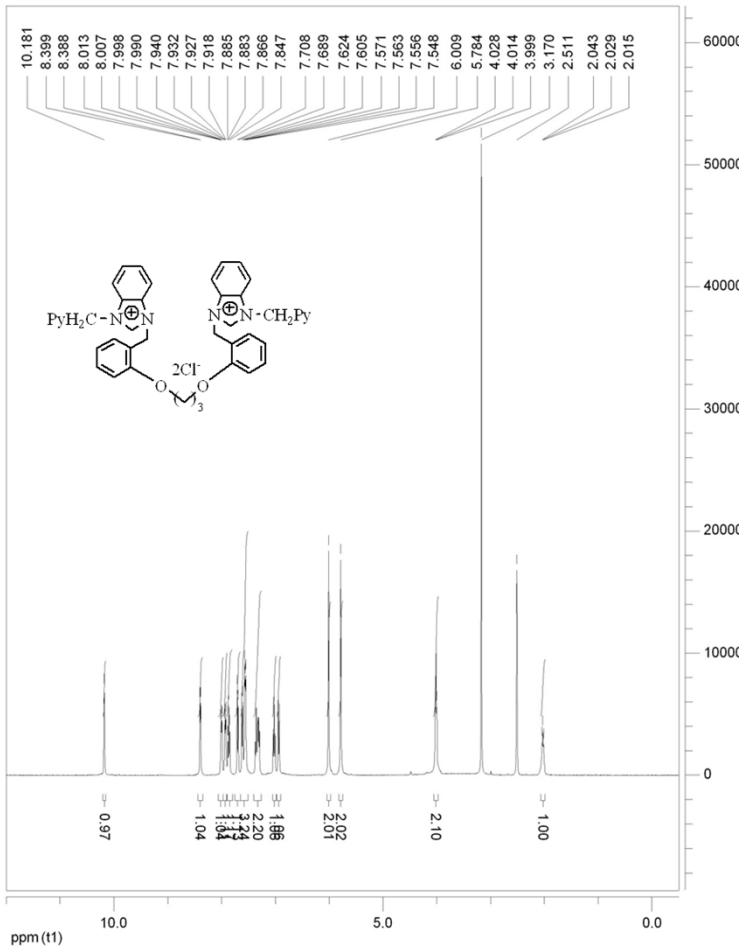


Fig. S22 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^4H_2 \cdot Cl_2}$.

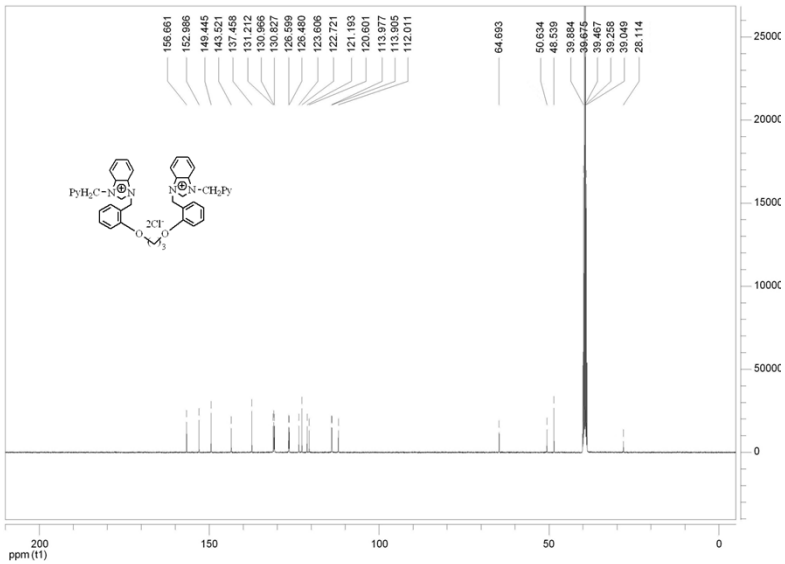


Fig. S23 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^4H_2 \cdot Cl_2}$.

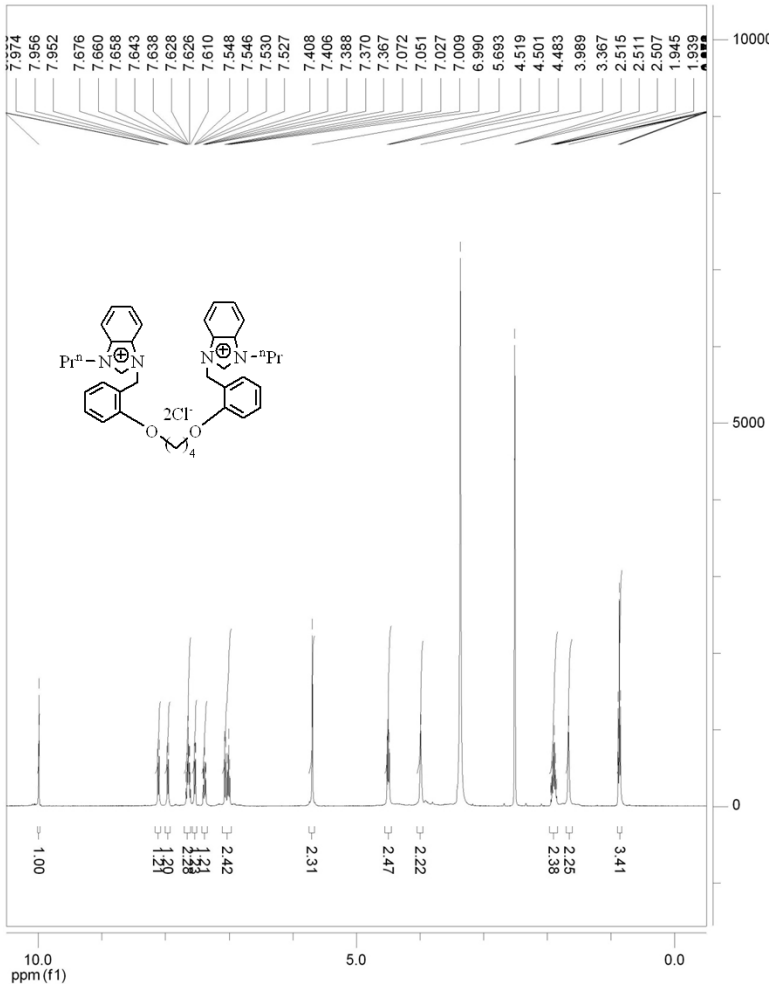


Fig. S24 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^5H_2 \cdot Cl_2}$.

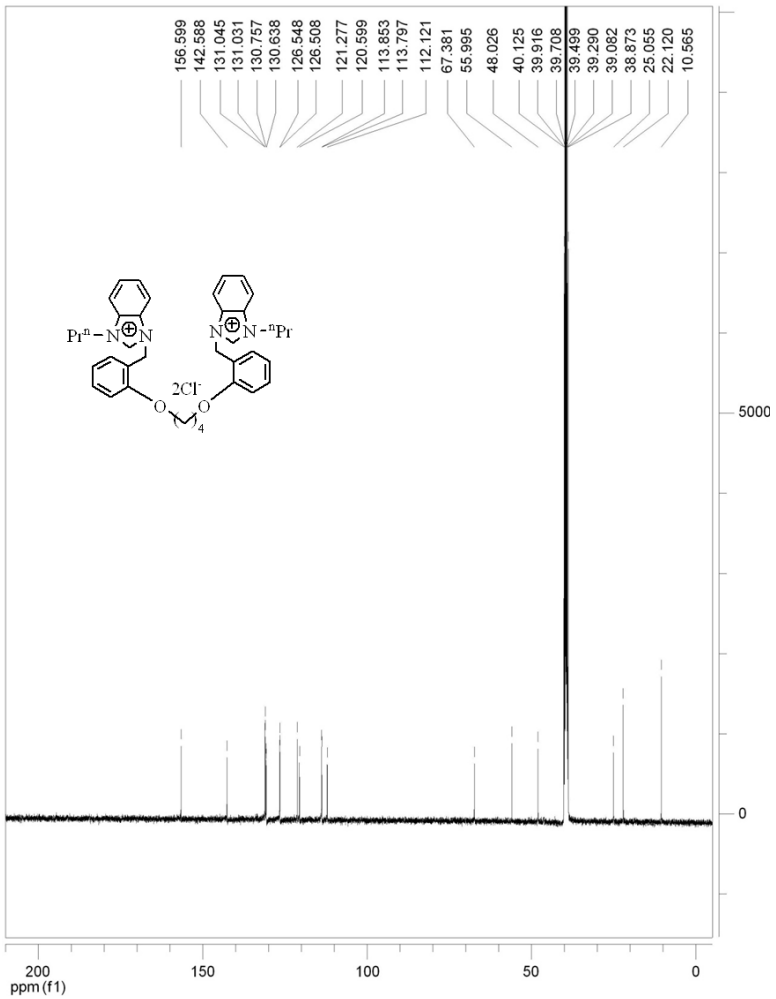


Fig. S25 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^5H_2 \cdot Cl_2}$.

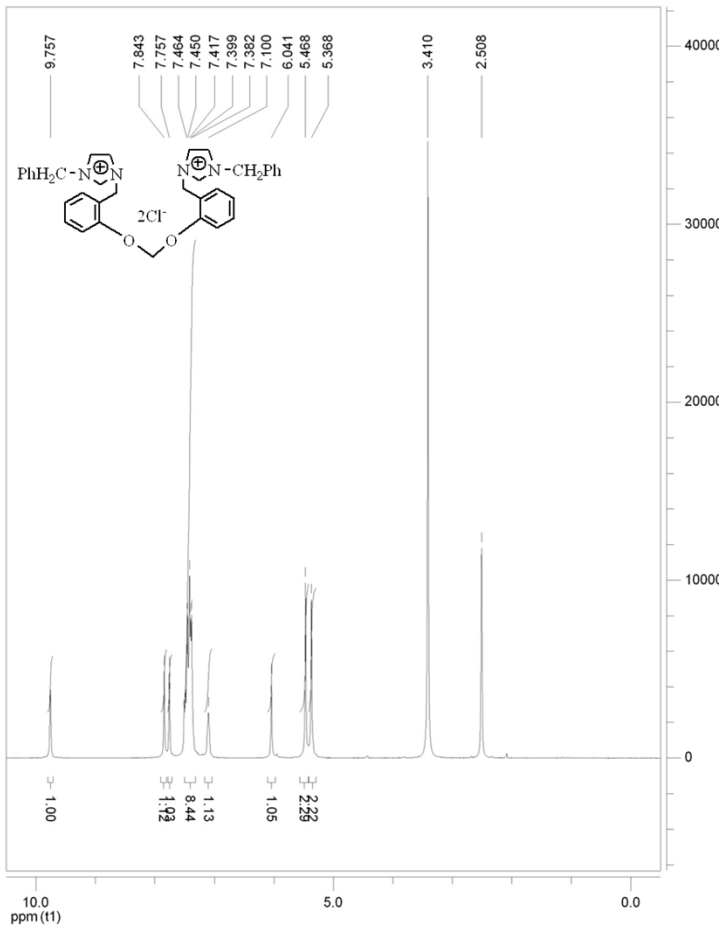


Fig. S26 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^6H_2 \cdot Cl_2}$.

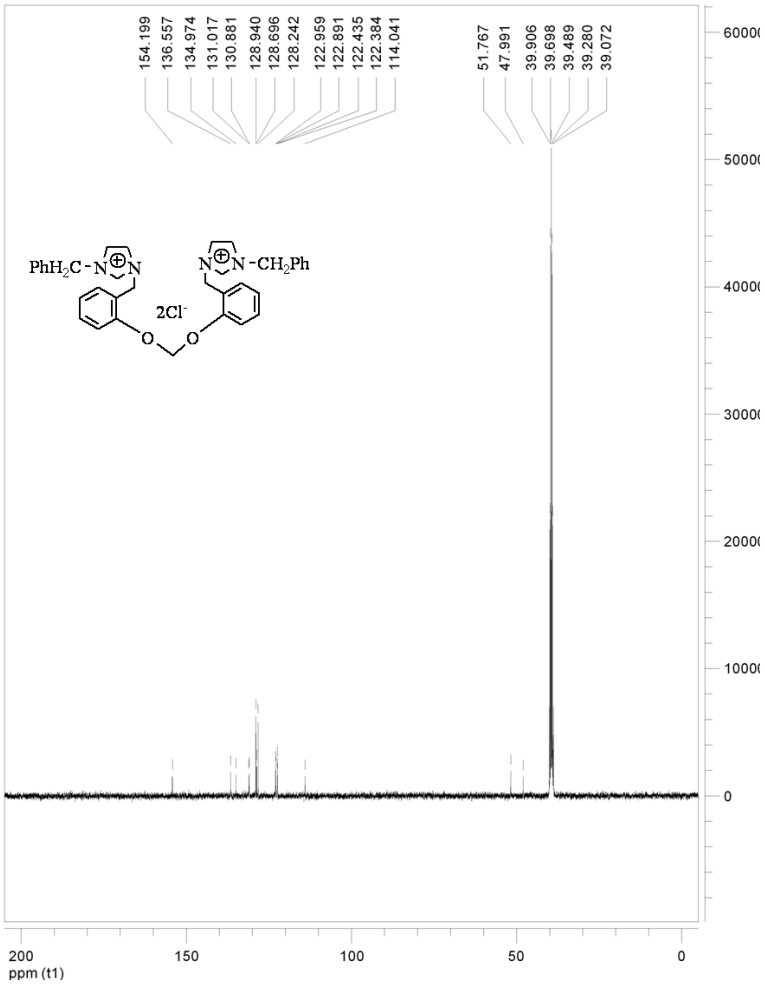


Fig. S27 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^6H_2 \cdot Cl_2}$.

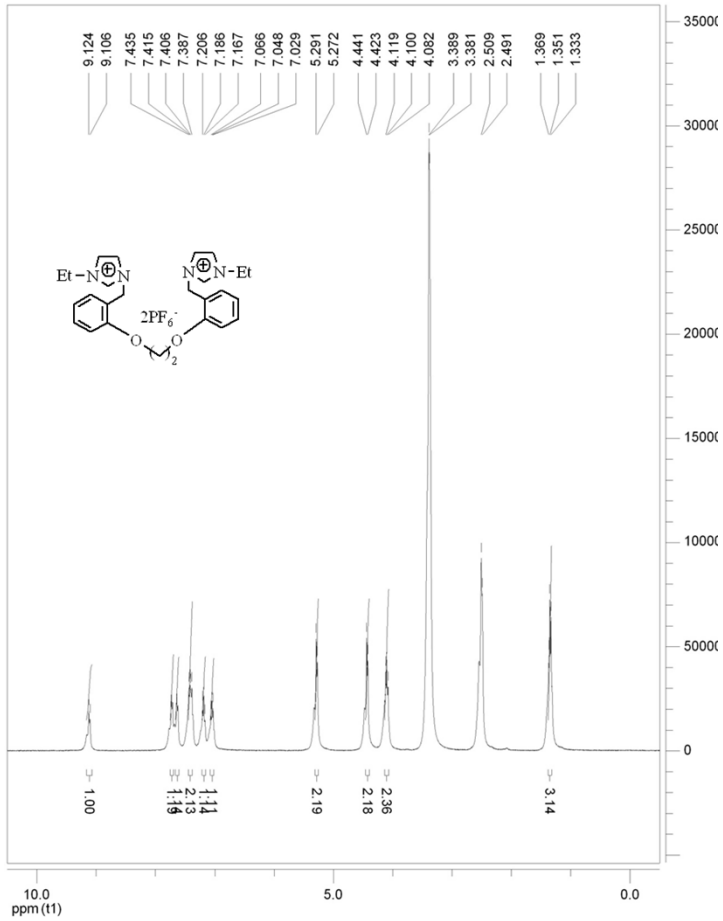


Fig. S28 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^7H_2 \cdot (PF_6)_2}$.

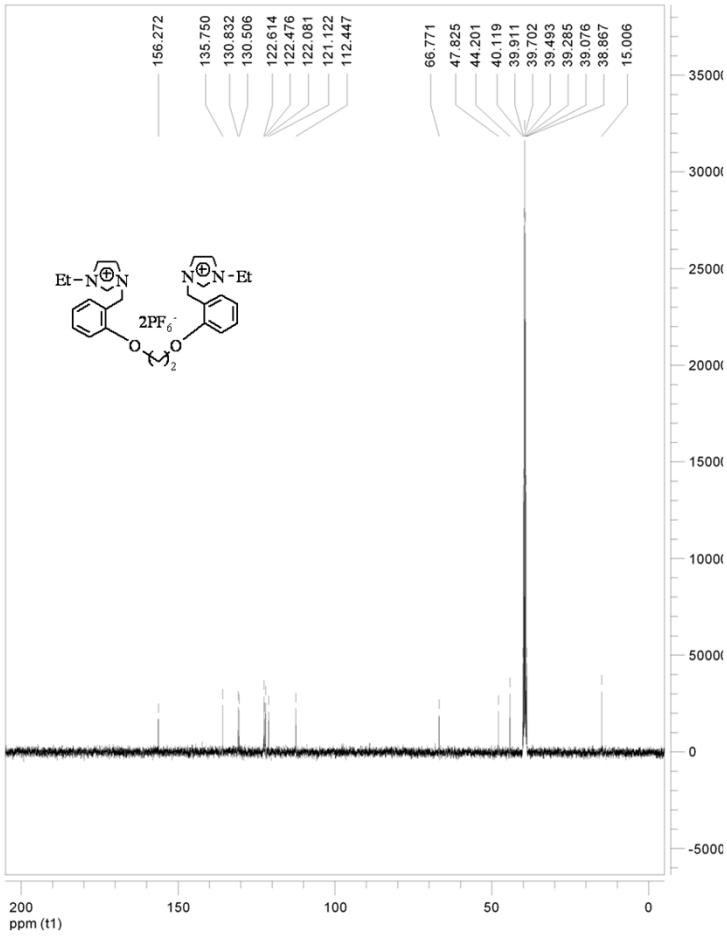


Fig. S29 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^7H_2 \cdot Cl_2}$.

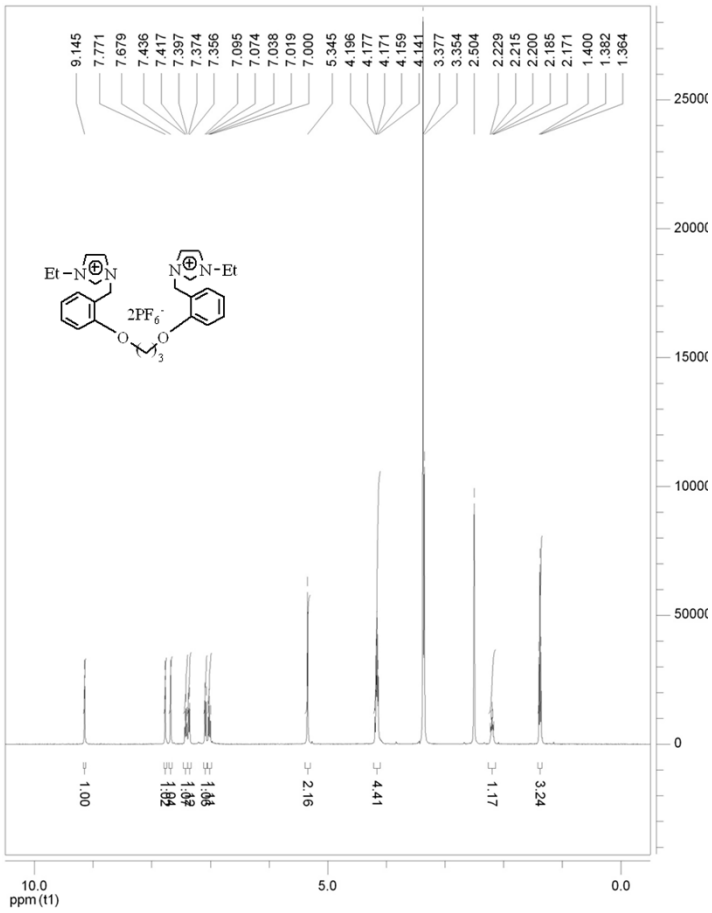


Fig. S30 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^8H_2 \cdot (PF_6)_2}$.

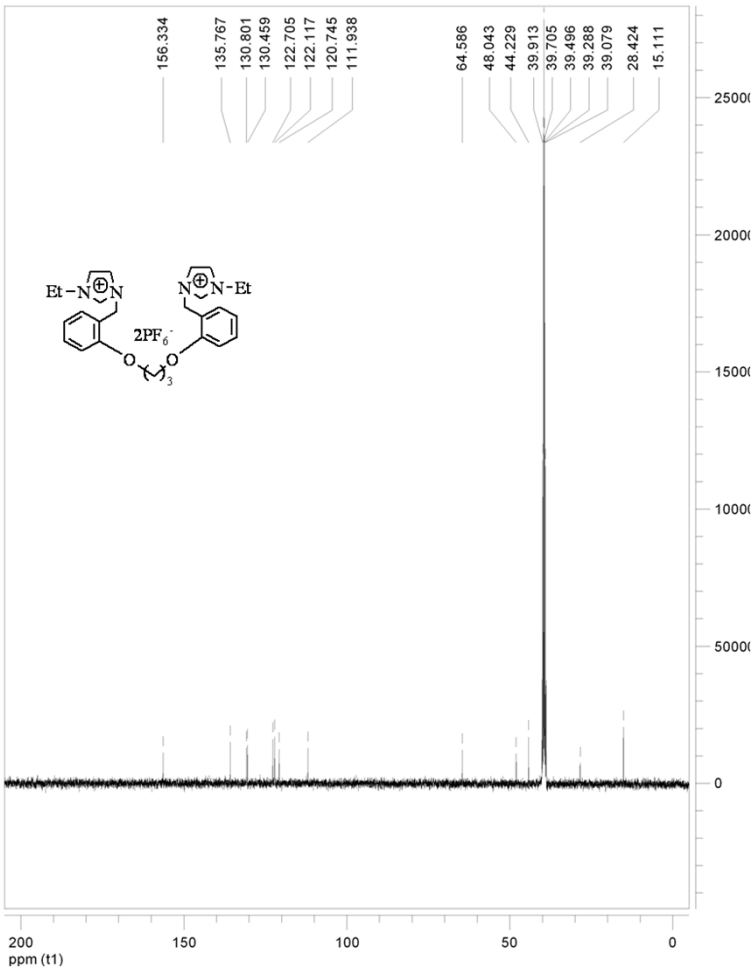


Fig. S31 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^8H_2 \cdot Cl_2}$.

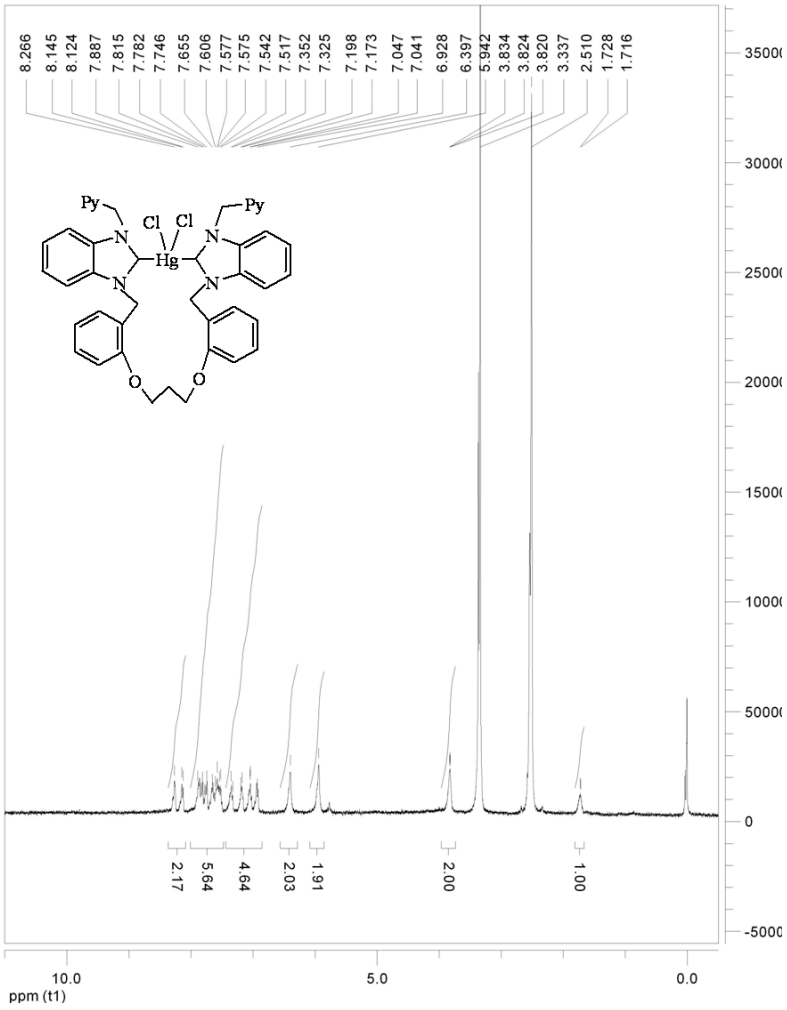


Fig. S32 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **1**.

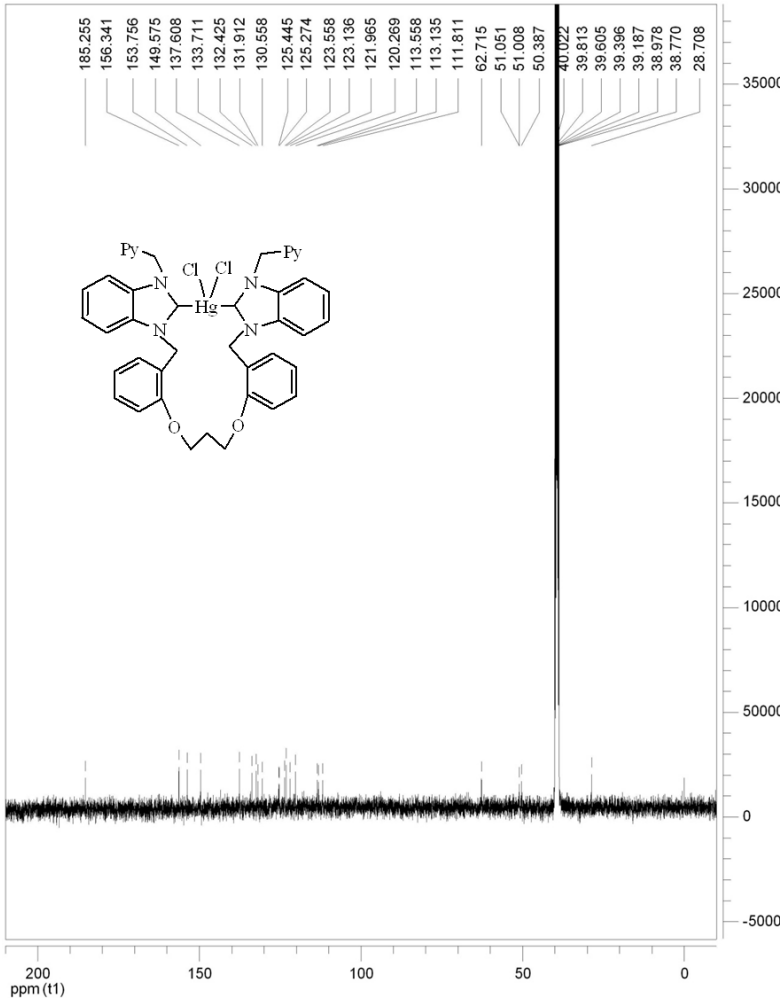


Fig. S33 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **1**.

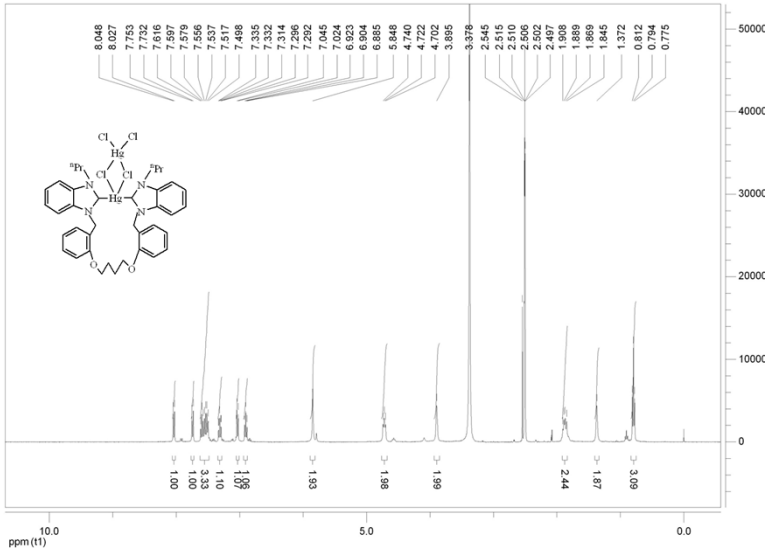


Fig. S34 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **2**.

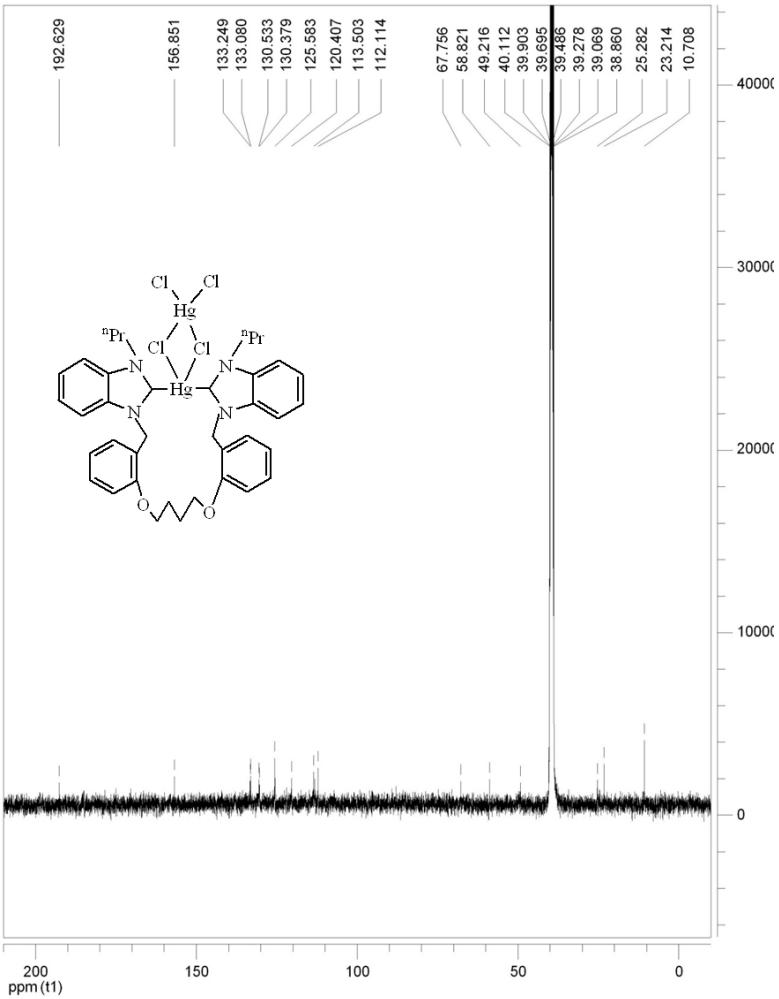


Fig. S35 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **2**.

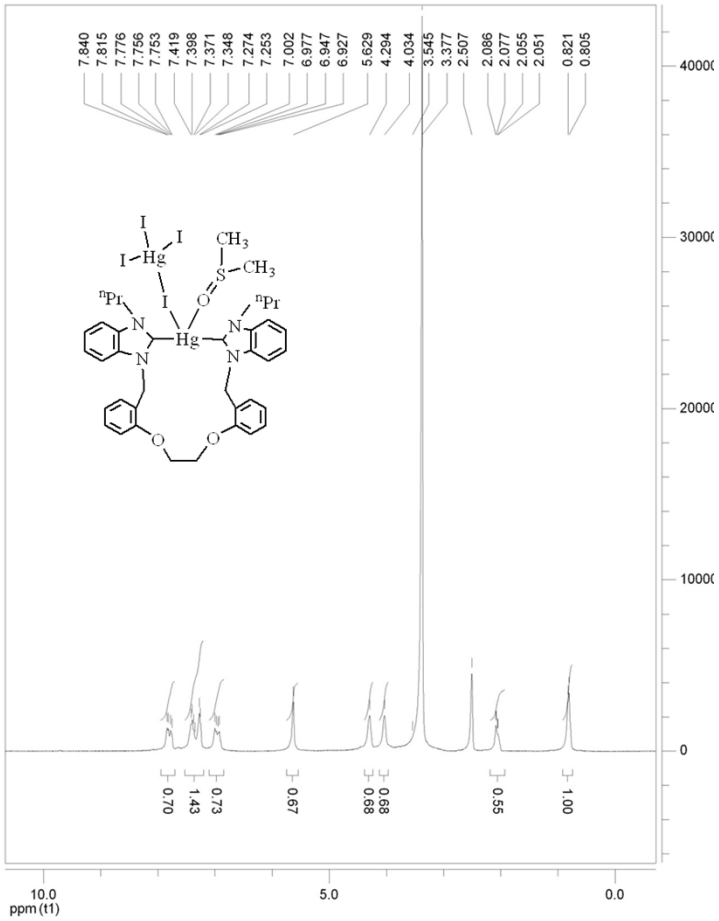


Fig. S36 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **3**.

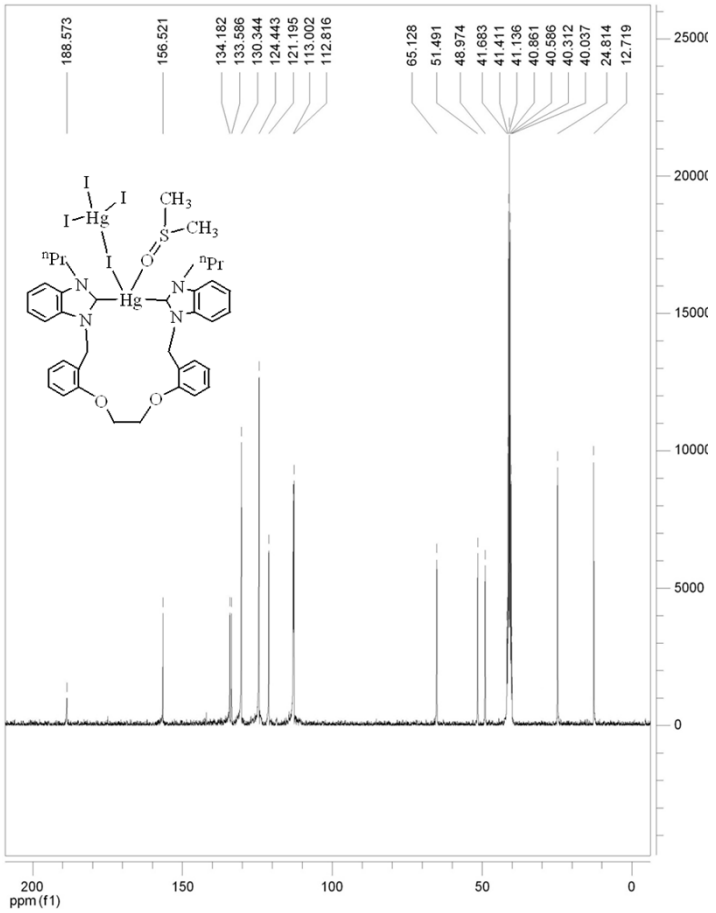


Fig. S37 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **3**.

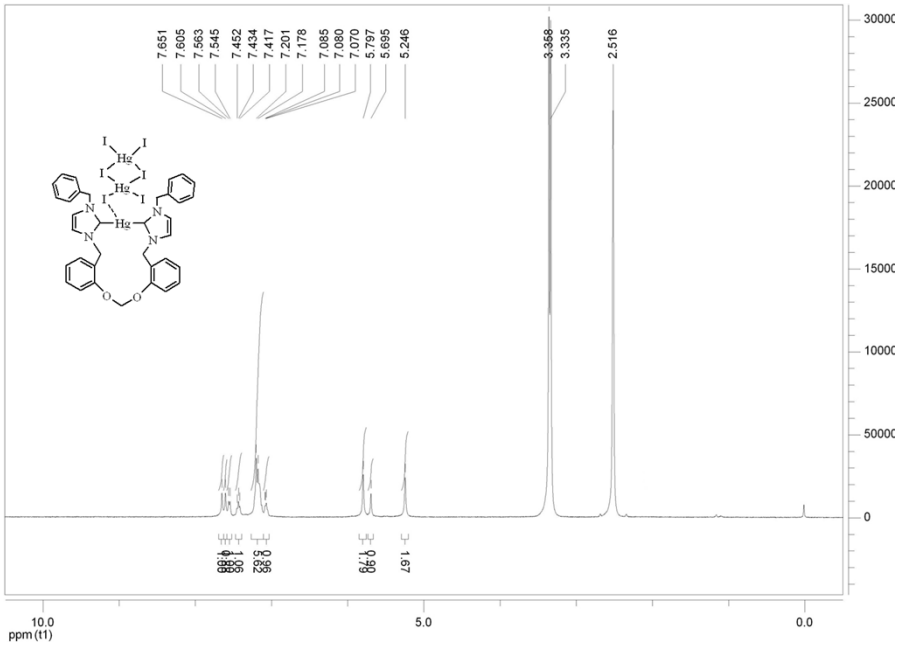


Fig. S38 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **4**.

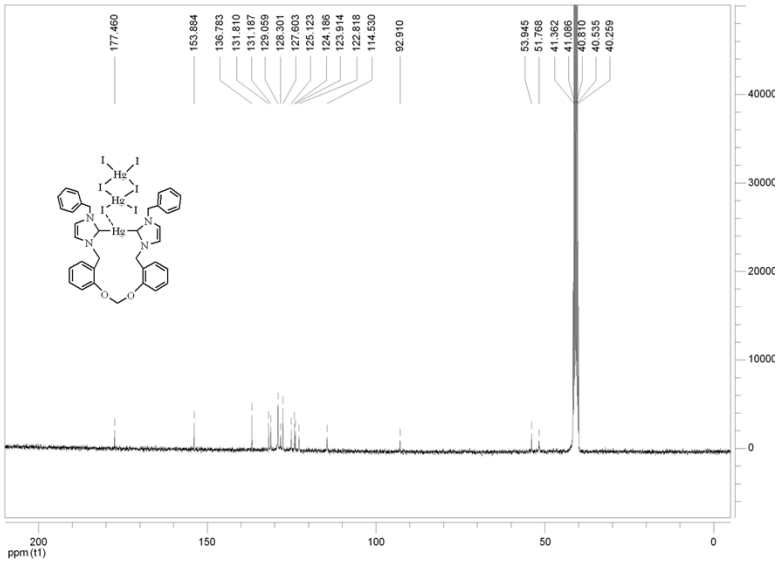


Fig. S39 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **4**.

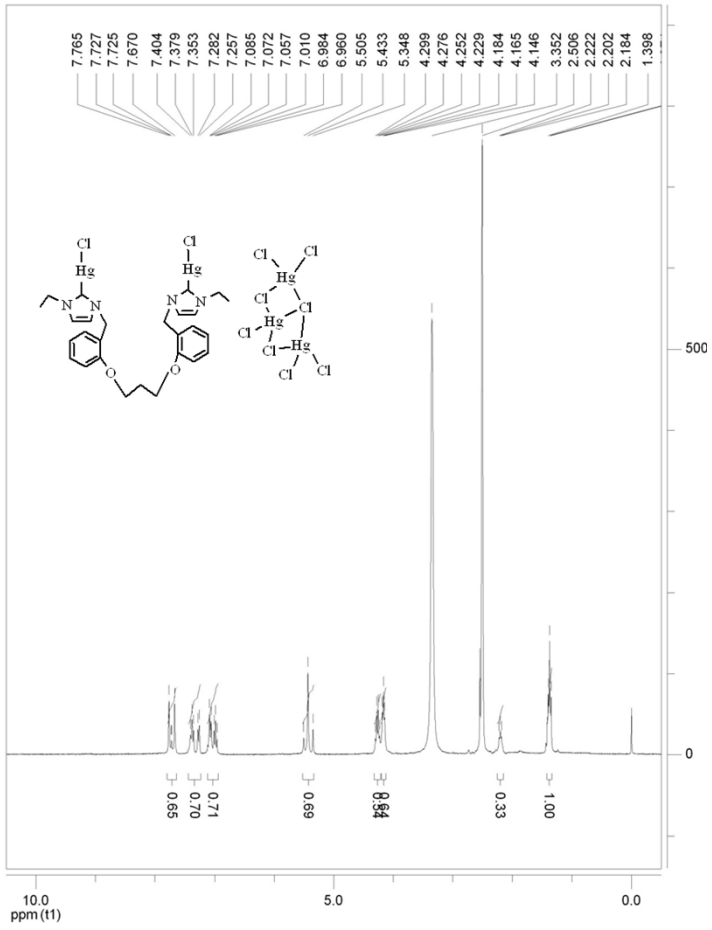


Fig. S40 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **5**.

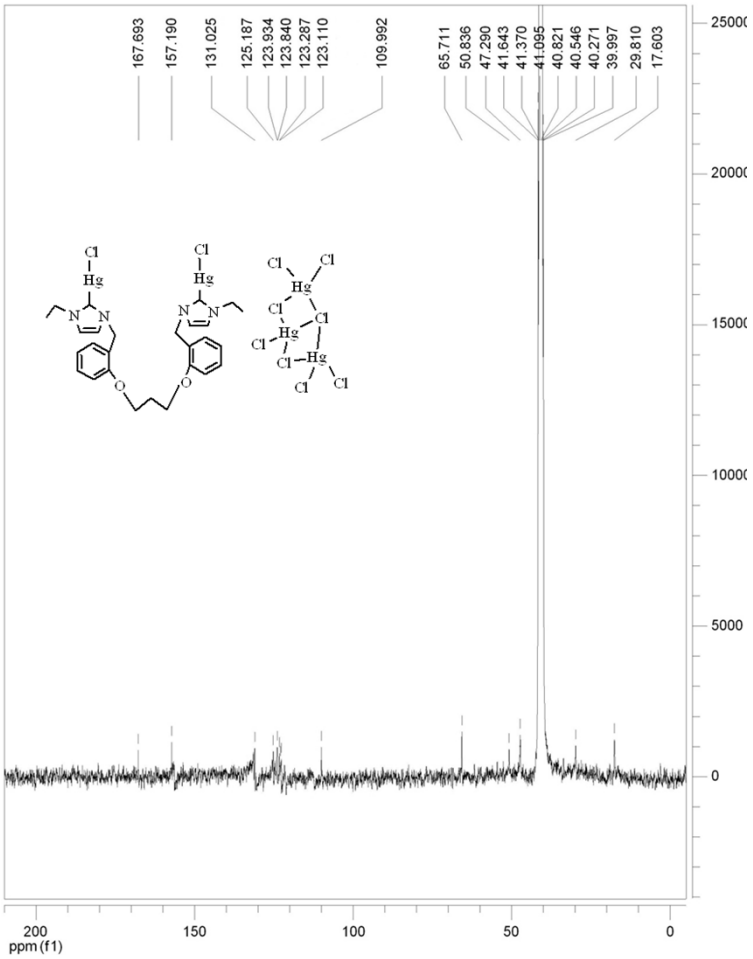


Fig. S41 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **5**.

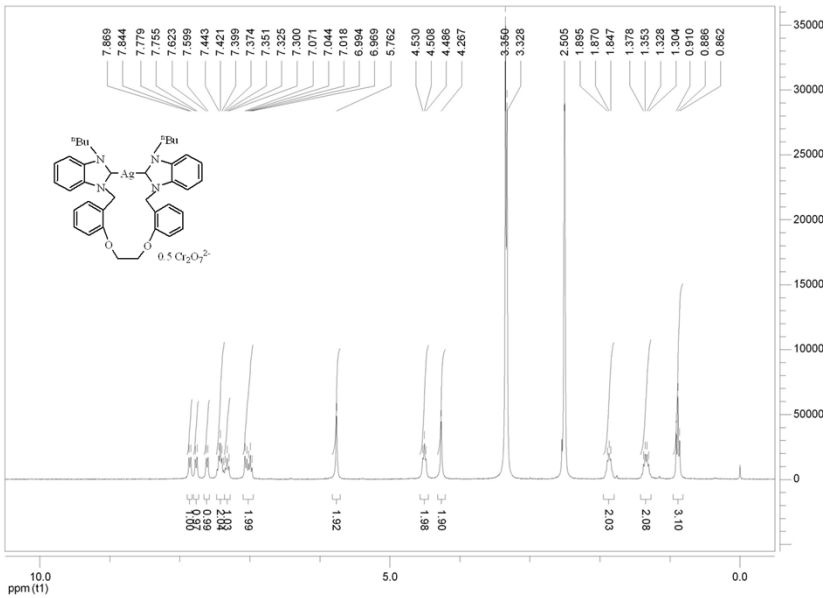


Fig. S42 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **6**.

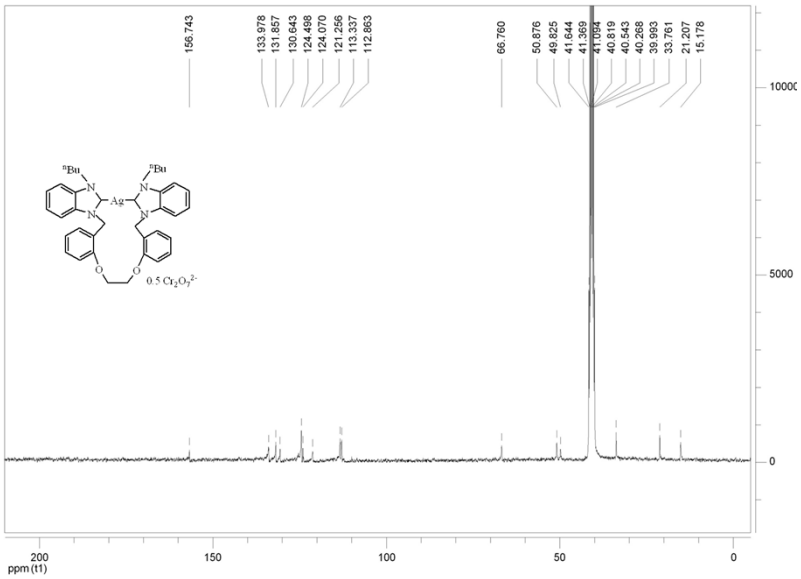


Fig. S43 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **6**.

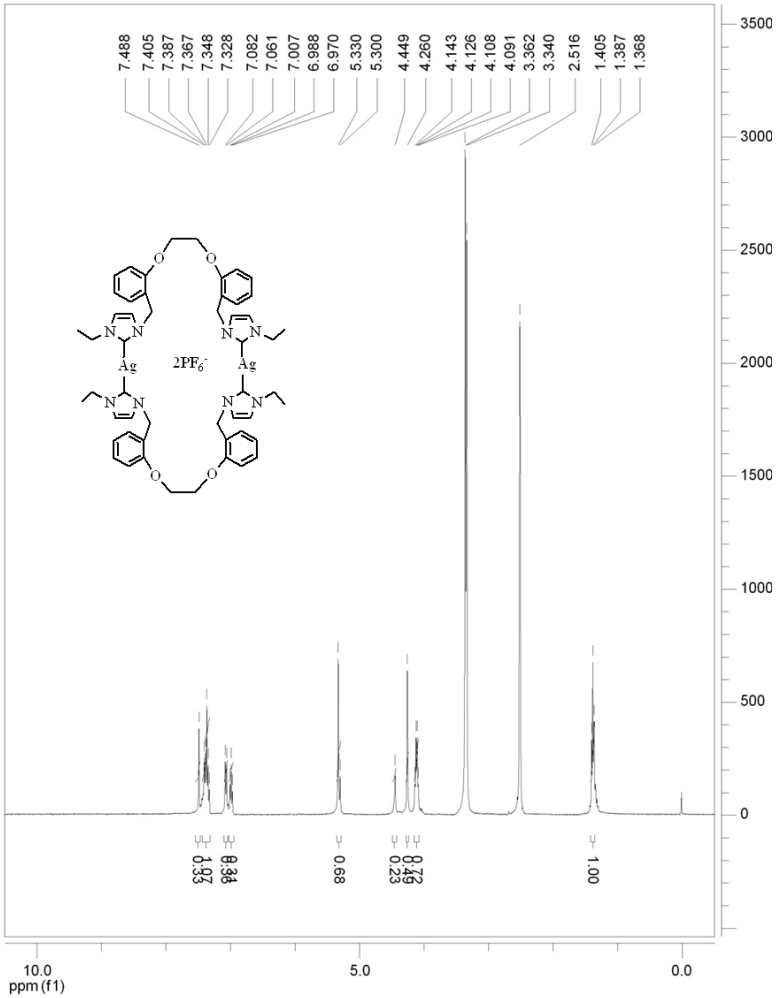


Fig. S44 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **7**.

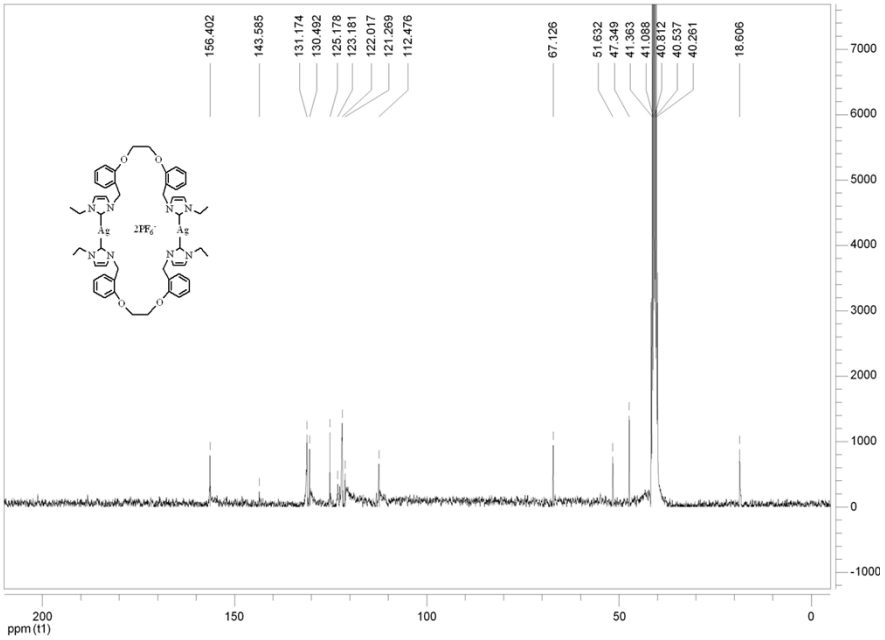


Fig. S45 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **7**.

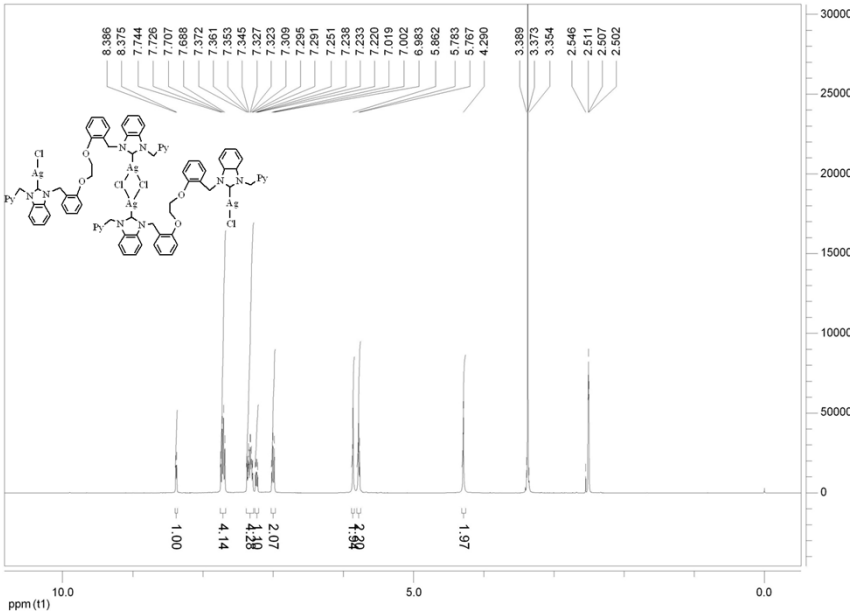


Fig. S46 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **8**.

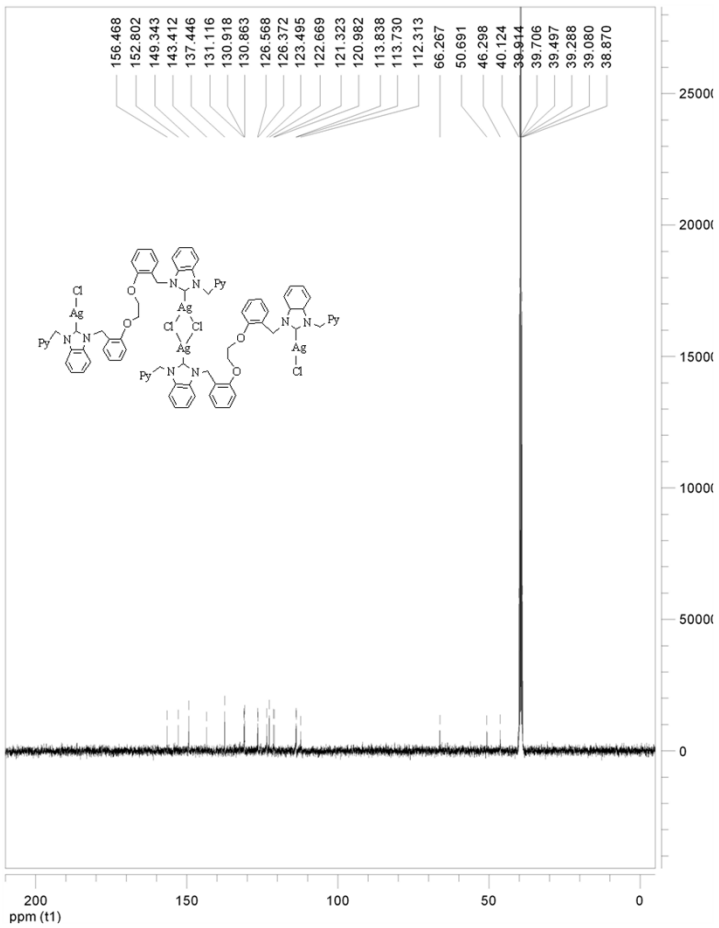


Fig. S47 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **8**.