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Preparation and Structure of NHC Hg(II) and Ag(I) Macrometallocycles

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A series of functionalized bis-azolium salts, 1,8-bis[2'-(N-R-azoliumyl)ethoxy]-9,10-anthraquinone hexafluorophosphate $\mathbf{L^1H_2\cdot(PF_6)_2}$-$\mathbf{L^4H_2\cdot(PF_6)_2}$ (R = Et, CH_2Ph and CH_2Py, azoliumyl = benzimidazoliumyl or imidazoliumyl), as well as their seven N-heterocyclic carbene mercury(II) and silver(I) complexes $[(L^2HgBr)_2](HgBr_4)$ (**1**), $[L^2Hg(HgI_4)]_2$ (**2**), $[L^1Hg(HgI_4)]$ (**3**), $[L^4Hg(HgI_4)]$ (**4**), $[L^1Ag](PF_6)$ (**5**), $[L^3Ag](PF_6)$ (**6**) and $[L^4Ag](PF_6)$ (**7**) have been prepared and characterized. In complexes **1** or **2**, two 16-membered macrometallocycles are connected together via two bridging halide ions (two bridging bromide ions for **1**, and two bridging iodide ions for **2**). In complexes **3**-**7**, each molecule contains one 16-membered macrometallocycle formed by one biscarbene ligand ($\mathbf{L^1}$ for **3** and **5**, $\mathbf{L^3}$ for **6**, $\mathbf{L^4}$ for **4** and **7**) and one metal ion (Hg(II) for **3** and **4**, Ag(I) for **5**-**7**). In crystal packings of **1**-**7**, 2D supramolecular layers and 3D supramolecular architectures are formed via intermolecular weak interactions (such as the hydrogen bonds, π-π interactions and C-H···π contacts). In addition, the fluorescence emission spectra of complexes and bis-azolium salts were described. The cyclic voltammetry study for silver(I) complexes **5**-**7** were conducted.

Introduction

After the isolation of the first stable free N-heterocyclic carbene (NHC) by Arduengo et al. in 1991,[1] N-heterocyclic carbenes have received considerable attention in

organometallic chemistry.[2] Because NHC ligands can be easily derived through changing the substituents on imidazole rings, the various functionalized NHC ligands can be provided for metal-organic materials. N-heterocyclic carbenes can coordinate with most transition metal ions in the periodic table to form interesting metal complexes, such as macrocycles,[3] molecular rectangles[4, 5] and grooves.[6] The strong electron-donating ability of NHCs leads to high stability of their metal complexes toward heat, moisture and air,[7] and these metal complexes have widely been applied in catalytic field[8] and materials science.[9]

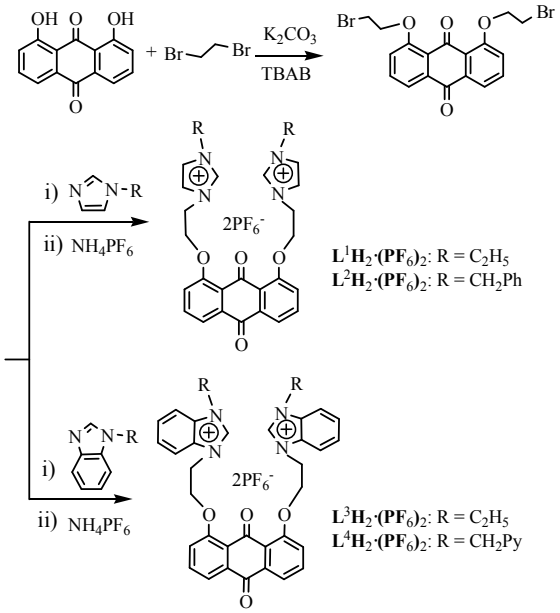
Among NHC metal complexes, the NHC silver(I) and mercury(II) complexes have played important roles in the development of carbene chemistry. NHC silver(I) complexes can be used as carbene transfer reagents for synthesizing other NHC metal complexes (such as Ni, Pd, Pt, Cu, Au, Rh, Ir and Ru).[10] Besides, NHC silver(I) complexes have also shown interesting biological activity as antimicrobial and antimitochondrial agents.[11] As the first known NHC metal complex, NHC mercury(II) complexes also attracted the attention of researchers owing to their various coordination mode and interesting characteristics of structures.[12]

We are interested in NHC metal complexes with fluorophore owing to their potential application in fluorescent field.[13] In this paper, we report the preparation of four bis-azolium salts, 1,8-bis[2'-(N-R-azoliumyl)ethoxy]-9,10-anthraquinone hexafluorophosphate $\mathbf{L^1H_2{\cdot}(PF_6)_2}$-$\mathbf{L^4H_2{\cdot}(PF_6)_2}$ (R = Et, CH_2Ph and CH_2Py, azoliumyl = benzimidazoliumyl or imidazoliumyl), as well as the preparation and structure of their seven NHC mercury(II) and silver(I) complexes $[(L^2HgBr)_2](HgBr_4)$ (**1**), $[L^2Hg(HgI_4)]_2$ (**2**), $[L^1Hg(HgI_4)]$ (**3**), $[L^4Hg(HgI_4)]$ (**4**), $[L^1Ag](PF_6)$ (**5**), $[L^3Ag](PF_6)$ (**6**) and $[L^4Ag](PF_6)$ (**7**). Additionally, the fluorescence emission spectra of the bis-azolium salts and complexes are described. The cyclic voltammetry study for silver(I) complexes **5-7** were conducted.

Results and discussion

Synthesis and characterization of precursors $L^1H_2\cdot(PF_6)_2$-$L^4H_2\cdot(PF_6)_2$

As shown in Scheme 1, 1,8-dihydroxy-9,10-anthraquinone as a starting material was treated by 1,2-dibromoethane to afford 1,8-bis(2'-bromoethoxy)-9,10-anthraquinone, which is further reacted with N-R-azole (R = Et, CH_2Ph or CH_2Py, azole = benzimidazole or imidazole) to afford bis-azolium salts $\mathbf{L^1H_2\cdot(Br)_2}$-$\mathbf{L^4H_2\cdot(Br)_2}$, and subsequent anion exchange with ammonium hexafluorophosphate in methanol was carried out to give 1,8-bis[2'-(N-R-azoliumyl)ethoxy]-9,10-anthraquinone hexafluorophosphate $\mathbf{L^1H_2\cdot(PF_6)_2}$-$\mathbf{L^4H_2\cdot(PF_6)_2}$. Precursors $\mathbf{L^1H_2\cdot(PF_6)_2}$-$\mathbf{L^4H_2\cdot(PF_6)_2}$ are stable toward heat, air and moisture, soluble in organic solvents such as DMSO, dichloromethane and acetonitrile, and scarcely soluble in benzene, diethyl ether and petroleum ether. In the ^{1}H NMR spectra of $\mathbf{L^1H_2\cdot(PF_6)_2}$-$\mathbf{L^4H_2\cdot(PF_6)_2}$, the azolium proton signals (NC*H*N) appear at δ = 9.29-10.03 ppm, which are consistent with the chemical shifts of reported imidazolium or benzimidazolium salts.[6, 14]

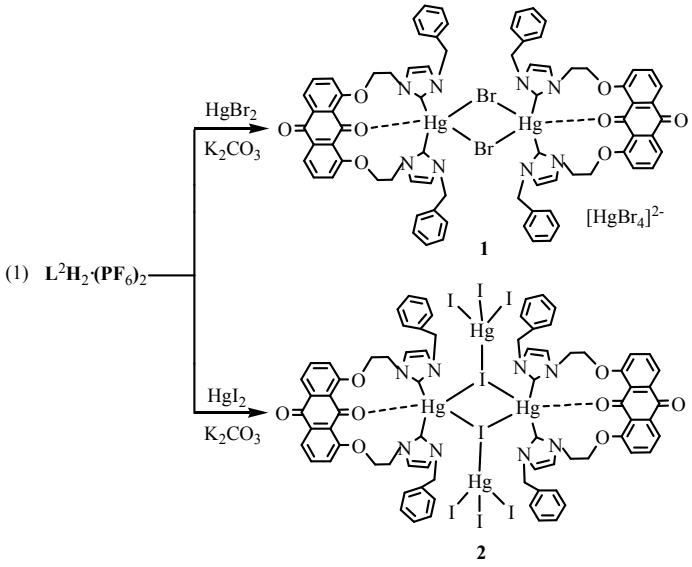


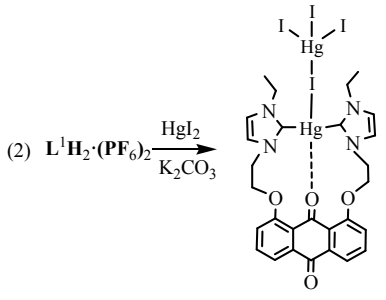
Scheme 1 Preparation of precursors $\mathbf{L^1H_2\cdot(PF_6)_2}$-$\mathbf{L^4H_2\cdot(PF_6)_2}$.

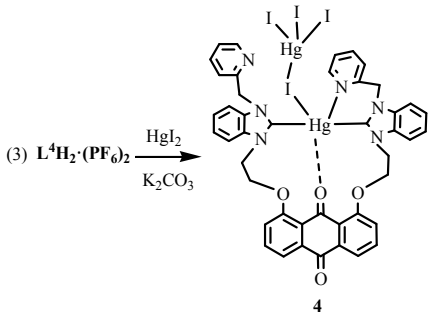
Synthesis and characterization of complexes 1-7

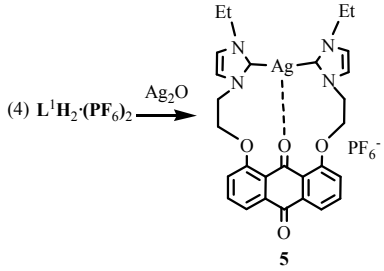
Complexes **1-4** were prepared by the reactions of $\mathbf{L^1H_2 \cdot (PF_6)_2}$, $\mathbf{L^2H_2 \cdot (PF_6)_2}$ or $\mathbf{L^4H_2 \cdot (PF_6)_2}$ with $HgBr_2$ or HgI_2 in the presence of K_2CO_3 in CH_3CN/DMSO (Schemes 2(1)-2(3)). Complexes **5-7** were prepared by the reactions of precursors $\mathbf{L^1H_2 \cdot (PF_6)_2}$, $\mathbf{L^3H_2 \cdot (PF_6)_2}$ or $\mathbf{L^4H_2 \cdot (PF_6)_2}$ with Ag_2O in CH_3CN (Schemes 2(4) and 2(5)).

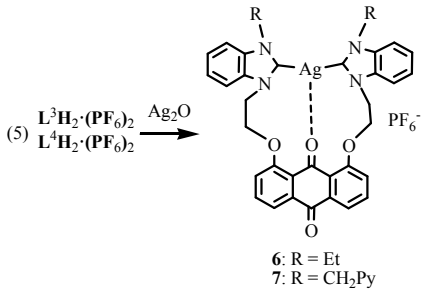
Complexes **1-7** are stable toward heat, air and moisture, soluble in DMSO and scarcely soluble in diethyl ether and hydrocarbon solvents, and their single crystals suitable for X-ray diffraction are obtained by slow diffusion of diethyl ether into their CH_3CN/DMSO or CH_3CN solution at room temperature. The structures of complexes **1-7** are confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy and X-ray crystallography. In the ^{1}H NMR spectra of complexes **1-7**, the disappearance of the resonances for the azolium protons (NC*H*N) shows the formation of the expected metal carbene complexes, and the chemical shifts of other hydrogen atoms are similar to those of corresponding precursors. For ^{13}C NMR spectra of complexes **1-4**, the signals of the carbene carbons appear at 175.5-179.5 ppm, which are similar to known carbene metal complexes.[15] In silver(I) complexes **5-7**, the signals for the carbene carbons are not observed. The absence of the carbene carbon resonance is not unusual, and this phenomenon has been reported for some silver(I) carbene complexes, which may result from the fluxional behavior of the NHC complexes.[16] Silver complexes **5-7** are slightly light-sensitive in the solution, but light-stable as solid.











Scheme 2 Preparation of complexes **1-7**.

Structure of Complexes 1-7

In each molecule of complexes **1** or **2** (Fig. 1(a) and Fig. 2(a)), two 16-membered macrometallocycles are connected together via two bridging halide ions (two bridging bromide ions for **1**, and two bridging iodide ions for **2**) to form a dimer, in which each 16-membered macrometallocycle is constructed by one ligand $\mathbf{L^2}$ and one mercury(II) ion. As shown in Fig. 3(a)-Fig. 7(a), each molecule of complexes **3-7** contains one 16-membered macrometallocycle formed via one biscarbene ligand ($\mathbf{L^1}$ for **3** and **5**, $\mathbf{L^3}$ for **6**, $\mathbf{L^4}$ for **4** and **7**) and one metal ion (Hg(II) ion for **3** and **4**, Ag(I) ion for **5-7**).

In complexes **1-7**, each O(2) atom from anthraquinone ring participates in coordination with metal ion. The bond distances of Hg(1)-O(2) for **1-4** are in the range of 2.827(6)-2.942(8) Å, and the bond distances of Ag(1)-O(2) for **5-7** are from 2.632(4) to 3.042(6) Å (Table S1, van der Waals Radii of mercury, silver and oxygen being 1.70 Å, 1.72 Å and 1.52 Å, respectively). In complexes **1-4**, the bond distances of Hg-C are from 2.055(3) Å to 2.095(3) Å. The bond angles of C-Hg-C are from 165.1(4)˚ to 172.1(7)˚. In complexes **5-7**, the bond distances of Ag-C are from 2.052(7) Å to 2.096(9) Å. The bond angles of C-Ag-C are from 172.8(2)˚ to 174.8(2)˚. These values are similar to those of known NHC metal complexes.[15, 17]

In complex **1**, Hg(1) is penta-coordinated with two carbene carbon atoms, two bridging bromide ions and one oxygen atom from anthraquinone to adopt a trigonal bipyramidal geometry. A distorted Hg_2Br_2 quadrangular arrangement is formed by

Hg(1), Br(4), Hg(3) and Br(7). In the Hg_2Br_2 quadrangular, the dihedral angle between Br(4)-Hg(1)-Br(7) plane and Br(4)-Hg(3)-Br(7) plane is 30.2(8)˚. The bond distances of Hg-Br are from 3.024(5) Å to 3.152(3) Å, and these values fall within the normal range of Hg-Br bond.[18] The bond angles of Br-Hg-Br and Hg-Br-Hg are from 81.8(3)˚ to 83.3(3)˚ and from 91.4(2)˚ to 94.4(5)˚, respectively. The separation between Hg(1) and Hg(3) is 4.445(4) Å, which shows that there is no direct interaction between both mercury(II) ions. Two anthraquinone rings in complex **1** form the dihedral angle of 56.7(2)˚. In the both flanks of Hg_2Br_2 quadrangular, two pairs of opposite imidazole rings form the dihedral angles of 20.7(1)˚ and 22.7(0)˚, respectively, and the distances of two imidazole rings in each pair are about 3.8 Å and 6.9 Å, respectively.

In complex **2**, an inversion center is observed. Hg(1) is penta-coordinated with two carbene carbon atoms, two bridging iodide ions and one oxygen atom from anthraquinone to adopt a trigonal bipyramidal geometry. Hg(2) is tetra-coordinated with four iodide ions to adopt a slightly distorted tetrahedral geometry. Around Hg(2), the bond distances of Hg(2)-I are from 2.737(8) Å to 2.938(8) Å, and the bond angles of I-Hg(2)-I are in the range of 102.7(2)-124.3(2)˚. These values fall in normal ranges.[19] In the center of the dimer, a coplanar parallelogram is formed by Hg(1), I(1), Hg(1A) and I(1A). Each bridging iodide ion is connected to three mercury(II) ions. The bond angles of Hg(1)-I(1)-Hg(2) and I(1)-Hg(1)-I(1A) are 112.8(1)˚ and 67.1(1)˚, respectively. The bond distances of Hg(1)-I(1) and Hg(1)-I(1A) are 3.399(9) Å and 3.519(9) Å, respectively, and these values are longer than those of normal distances of Hg-I. The separation between Hg(1) and Hg(1A) is 5.765(2) Å, which indicates that there is no direct interaction between both mercury(II) ions.

Hg(1) in complex **3** is tetra-coordinated with two carbene carbon atoms, one iodide ion and one oxygen atom from anthraquinone to adopt a tetrahedral geometry.

Hg(2) is surrounded by four iodide ions to form the $[HgI_4]^{2-}$ unit, in which the bond distances of Hg(2)-I are from 2.724(8) Å to 2.952(8) Å, and the bond angles of I-Hg(2)-I are from 102.8(2)˚ to 119.4(3)˚. These values are similar to those of complex **2**. The bond distance of Hg(1)-I(1) (3.280(9) Å) is longer than that of normal distance of Hg-I.

Hg(1) in **4** is tetra-coordinated with two carbene carbon atoms, one nitrogen atom from the pyridine ring and one iodide ion from a $[HgI_4]^{2-}$ unit. The bond distance of Hg(1)-N(6) is 2.734(1) Å. $[HgI_4]^{2-}$ unit of **4** is similar to that of **3**. The bond distance of Hg(1)-I(6) is 3.118(5) Å, and it is longer than that of normal distance of Hg-I.

Each silver(I) ion in **5-7** is tri-coordinated with two carbene carbon atoms and one oxygen atom from anthraquinone. Two ethyl groups in **5** or **6** point to the opposite directions, respectively. Two pyridine rings in **7** form the dihedral angle of 56.6(4)˚.

In each 16-membered macrometallocycle of **1-7**, the dihedral angles between anthraquinone and two azole rings are from 53.2(2)˚ to 85.6(5)˚ (Table S2 in the Supporting Information). In each macrometallocycle of complexes **1**, **2**, **4** and **7**, the dihedral angles between benzene (or pyridine) rings and adjacent azole rings are from 60.7(7)˚ to 88.9(0)˚. The dihedral angles between two azole rings in the same NHC-M-NHC units for **1-7** are from 7.1(3)˚ to 39.8(7)˚.

Each O(2) atom in **1-7** lie in the outside of anthraquinone plane, and the slip angles between O(2) atoms and anthraquinone planes are from 9.9(8)˚ to 16.5(9)˚ (Table S1). The internal ring angles (N-C-N) at the carbene centers for **1-7** are from 103.4(7)˚ to 108.1(0)˚, which are similar to those of known NHC metal complexes.[15, 17]

Crystal packings of complexes 1-7

In the crystal packing of **1** (Fig. 1(b)), 2D supramolecular layer is formed through

C-H···Br hydrogen bonds.[20] In the hydrogen bonds, the hydrogen atoms are from anthraquinone rings or CH_2 of ethoxy groups (the data of hydrogen bonds being given in Table S3).

2D supramolecular layer of **2** (Fig. 2(b)) is formed by C-H···O hydrogen bonds.[21] In the hydrogen bonds, the hydrogen atoms are from anthraquinone rings. Additionally, 2D supramolecular layers are further extended into 3D supramolecular architecture through C-H···π contacts (Fig. 2(c)).[22] In C-H···π contacts, the hydrogen atoms are from CH_2 of ethoxy groups and π systems are from benzene rings (the data of C-H···π contacts being given in Table S4).

2D supramolecular layer of **3** (Fig. 3(b)) is formed via π-π stacking interactions[23] from intermolecular imidazole rings and anthraquinone rings (Table S4).

As shown in Fig. 4(b), 2D supramolecular layer of **4** is formed through C-H···I hydrogen bonds[20] and C-H···O hydrogen bonds. In C-H···I hydrogen bonds, the hydrogen atoms are from benzimidazole rings. In C-H···O hydrogen bonds, the hydrogen atoms are from CH_2 of picolyl groups. Additionally, 2D supramolecular layers are further extended into 3D supramolecular architecture via new C-H···I hydrogen bonds (Fig. 4(c)). In the new hydrogen bonds, the hydrogen atoms are from CH_2 of ethoxy groups.

2D supramolecular layer of **5** (Fig. 5(b)) is formed by C-H···F hydrogen bonds.[24] In the hydrogen bonds, the hydrogen atoms are from imidazole rings, CH_2 of ethoxy groups or CH_3 of ethyl groups, respectively.

2D supramolecular layer of **6** (Fig. 6(b)) is formed by C-H···F hydrogen bonds and π-π interactions from intermolecular anthraquinone rings and benzimidazole rings. In the hydrogen bonds, the hydrogen atoms are from benzimidazole rings.

2D supramolecular layer of **7** (Fig. 7(b)) is formed by C-H···F hydrogen bonds, C-H···N hydrogen bonds[20] and C-H···O hydrogen bonds. In these hydrogen bonds,

the hydrogen atoms are from the benzimidazole rings, CH_2 of picolyl groups and the benzimidazole rings, respectively.

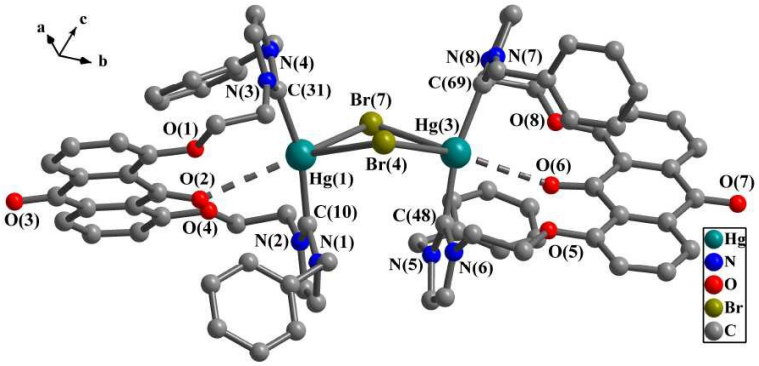


Fig. 1(a) Perspective view of **1**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (˚): Hg(1)-C(10) 2.093(0), Hg(1)-C(31) 2.087(0), Hg(3)-C(48) 2.073(0), Hg(3)-C(69) 2.095(3), Hg(1)-Br(4) 3.057(1), Hg(1)-Br(7) 3.031(7), Hg(3)-Br(4) 3.152(3), Hg(3)-Br(7) 3.024(5); N(1)-C(10)-N(2) 105.8(8), C(10)-Hg(1)-C(31) 165.1(4), C(48)-Hg(3)-C(69) 166.9(1), Hg(1)-Br(4)-Hg(3) 91.4(2), Hg(1)-Br(7)-Hg(3) 94.4(5), Br(4)-Hg(1)-Br(7) 83.3(3), Br(4)-Hg(3)-Br(7) 81.8(3).

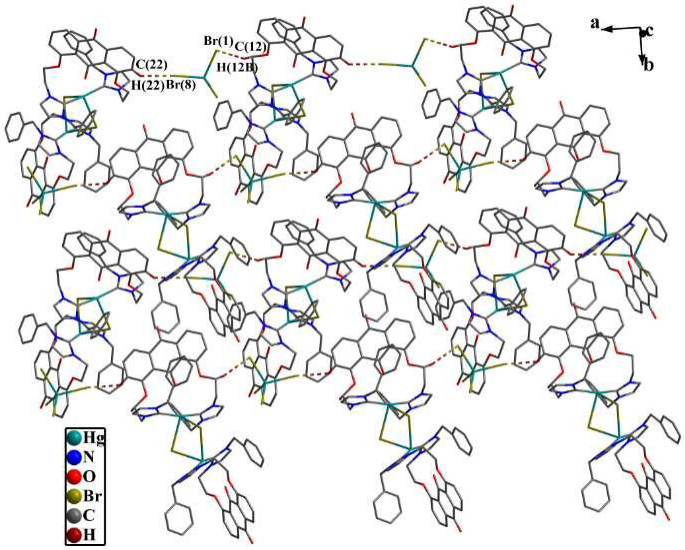


Fig. 1(b) 2D supramolecular layer of **1** via C-H···Br hydrogen bonds. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

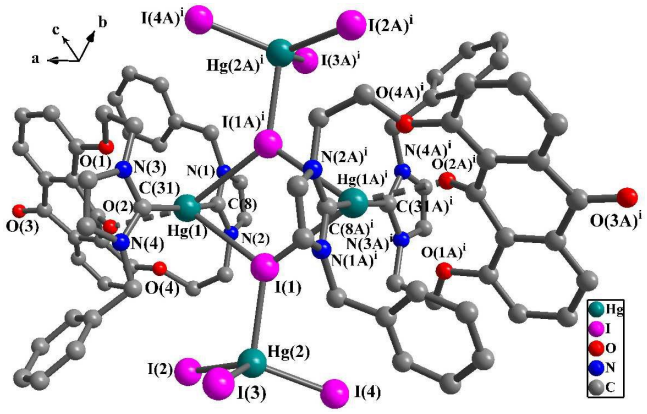


Fig. 2(a) Perspective view of **2**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)-C(8) 2.082(9), Hg(1)-C(31) 2.074(9), Hg(1)-I(1) 3.399(9), Hg(2)-I(1) 2.938(8), Hg(2)-I(2) 2.760(8), Hg(2)-I(3) 2.775(8), Hg(2)-I(4) 2.737(8), Hg(1)-O(2) 2.845(6); N(1)-C(8)-N(2) 107.8(8), C(8)-Hg(1)-C(31) 168.1(4), Hg(1)-I(1)-Hg(2) 119.3(2), I(1)-Hg(2)-I(3) 103.4(2), I(1)-Hg(2)-I(4) 102.7(2). Symmetry code: i: - *x*, 1 - *y*, 1 - *z*.

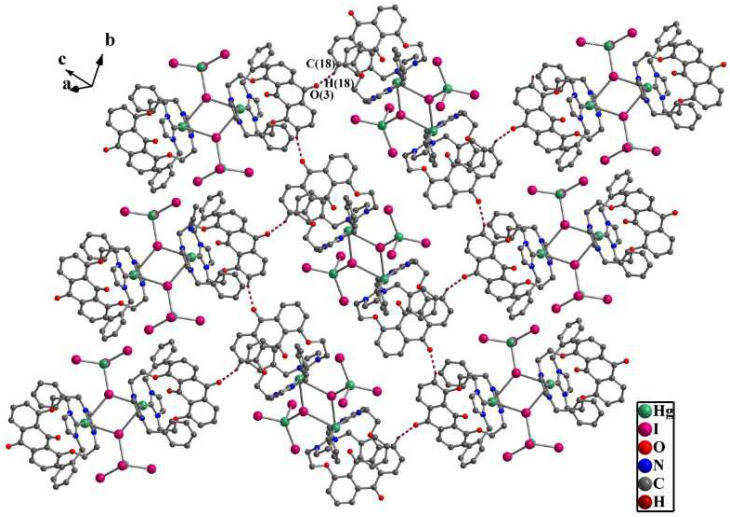


Fig. 2(b) 2D supramolecular layer of **2** via C-H···O hydrogen bonds. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

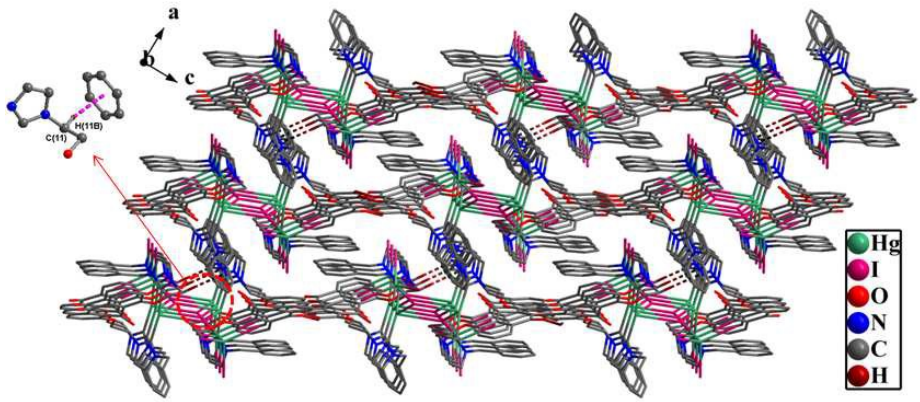


Fig. 2(c) 3D supramolecular architecture of **2** via C-H···O hydrogen bonds and C-H···π contacts. All hydrogen atoms except those participating in C-H···O hydrogen bonds and C-H···π contacts were omitted for clarity.

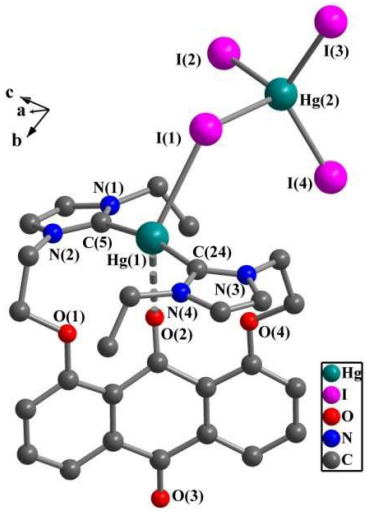


Fig. 3(a) Perspective view of **3**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)-C(5) 2.069(8), Hg(1)-C(24) 2.076(1), Hg(1)-I(1) 3.280(9), Hg(2)-I(1) 2.952(8), Hg(1)-O(2) 2.827(6); N(1)-C(5)-N(2) 107.0(7), C(5)-Hg(1)-C(24) 167.3(3), Hg(1)-I(1)-Hg(2) 122.0(4), I(1)-Hg(2)-I(3) 104.2(2).

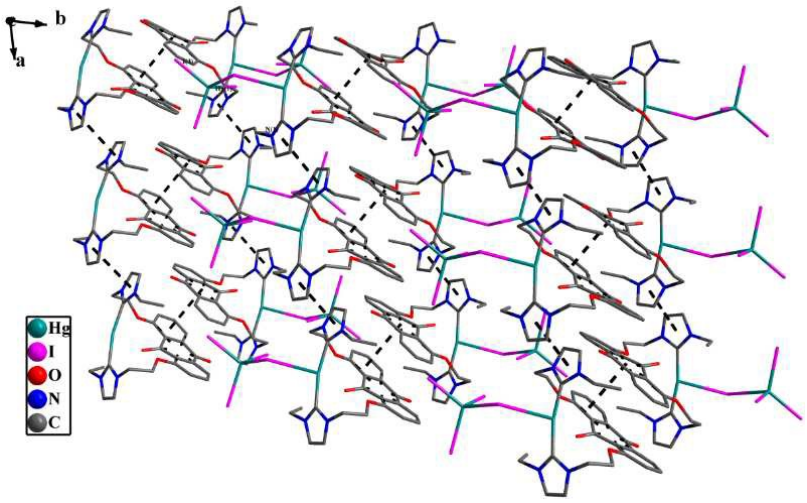


Fig. 3(b) 2D supramolecular layer of **3** via π-π interactions. All hydrogen atoms were omitted for clarity.

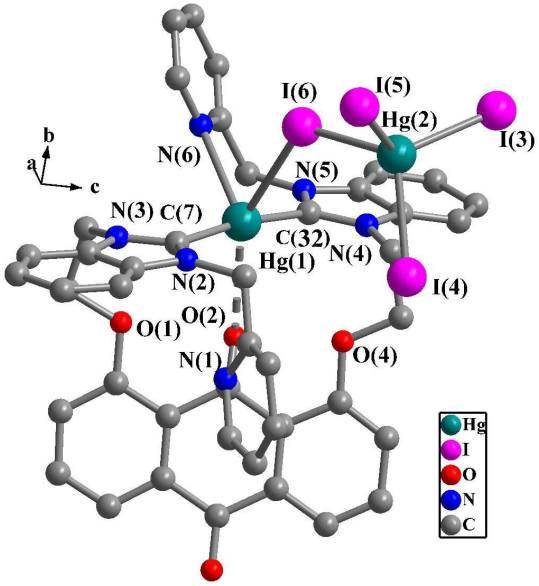


Fig. 4(a) Perspective view of **4**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (˚): Hg(1)-C(7) 2.082(2), Hg(1)-C(32) 2.055(3), Hg(1)-I(6) 3.118(5), Hg(2)-I(4) 2.798(4) Hg(1)-N(6) 2.734(1), Hg(1)-O(2) 2.879(8); N(2)-C(7)-N(3) 108.1(0), C(7)-Hg(1)-C(32) 172.1(7), Hg(2)-I(6)-Hg(1) 122.2(4), I(6)-Hg(2)-I(4) 110.8(6).

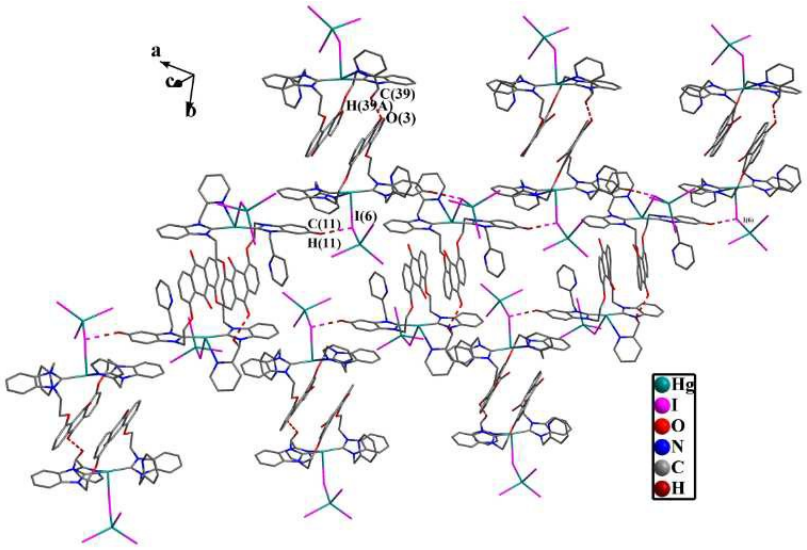


Fig. 4(b) 2D supramolecular layer of **4** via C-H···O hydrogen bonds and C-H···I hydrogen bonds. All hydrogen atoms except those participating in these hydrogen bonds were omitted for clarity.

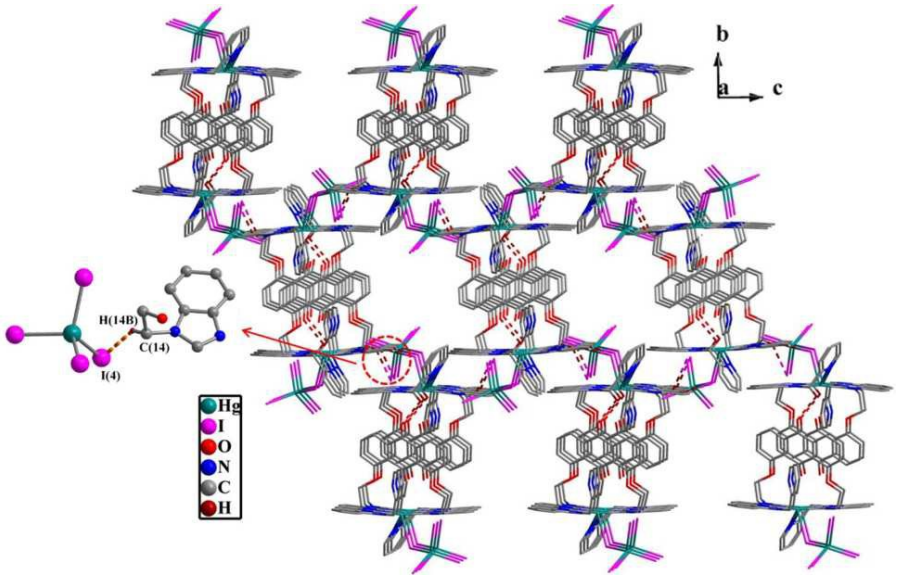


Fig. 4(c) 3D supramolecular architecture of **4** via C-H···O hydrogen bonds and C-H···I hydrogen bonds. All hydrogen atoms except those participating in these hydrogen bonds were omitted for clarity.

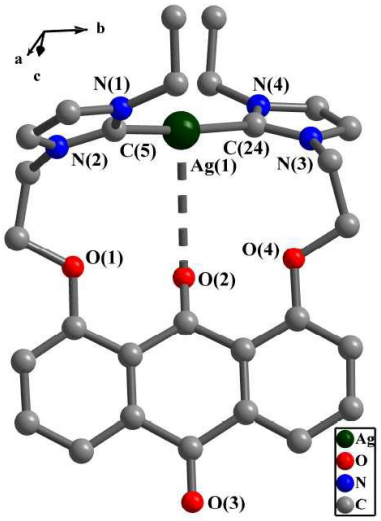


Fig. 5(a) Perspective view of **5**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (˚): Ag(1)-C(5) 2.088(2), Ag(1)-C(24) 2.087(6), Ag(1)-O(2) 2.954(1); N(1)-C(5)-N(2) 103.4(7), C(5)-Ag(1)-C(26) 174.8(2).

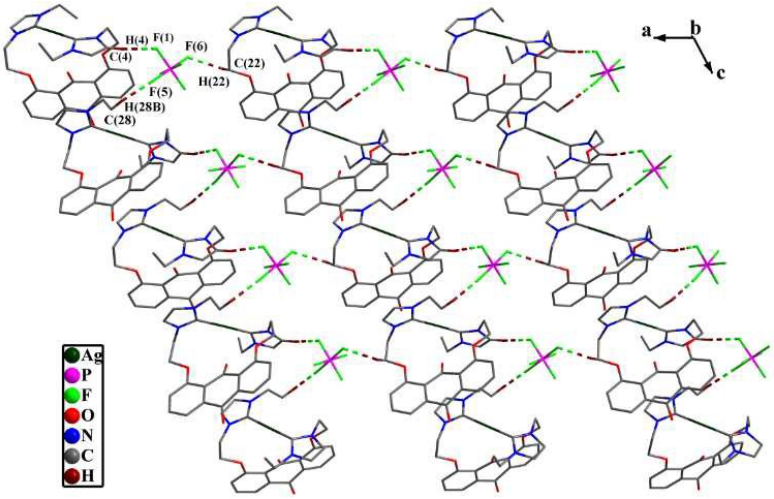


Fig. 5(b) 2D supramolecular layer of **5** via C-H···F hydrogen bonds. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

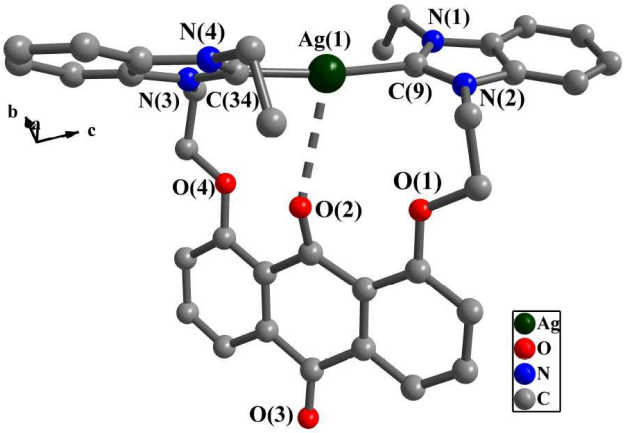


Fig. 6(a) Perspective view of **6**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (˚): Ag(1)-C(9) 2.078(6), Ag(1)-C(34) 2.052(7), Ag(1)-O(2) 3.042(6); N(1)-C(9)-N(2) 107.4(3), C(9)-Ag(1)-C(34) 172.9(2).

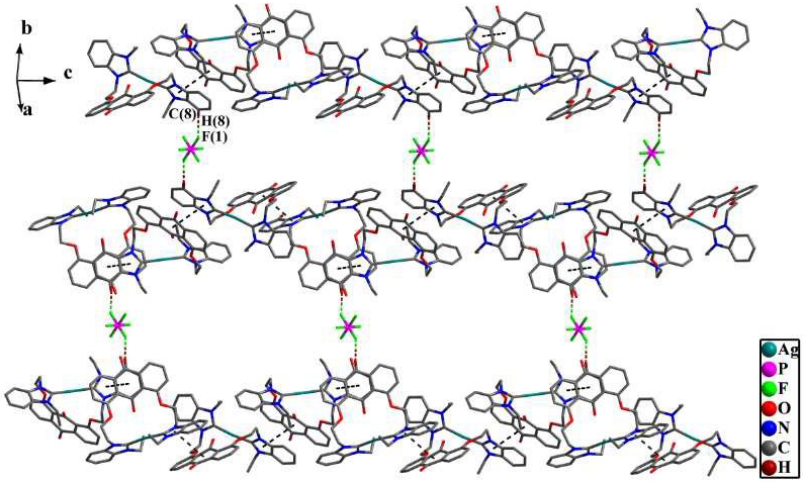


Fig. 6(b) 2D supramolecular layer of **6** via C-H···F hydrogen bonds and π-π interactions. All hydrogen atoms except those participating in the hydrogen bonds were omitted for clarity.

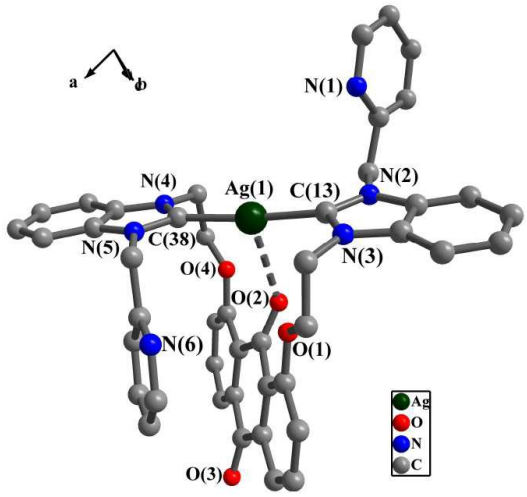


Fig. 7(a) Perspective view of **7**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (˚): Ag(1)-C(13) 2.096(9), Ag(1)-C(38) 2.091(9), Ag(1)-O(2) 2.632(4); N(2)-C(13)-N(3) 105.7(6), C(13)-Ag(1)-C(38) 172.8(2).

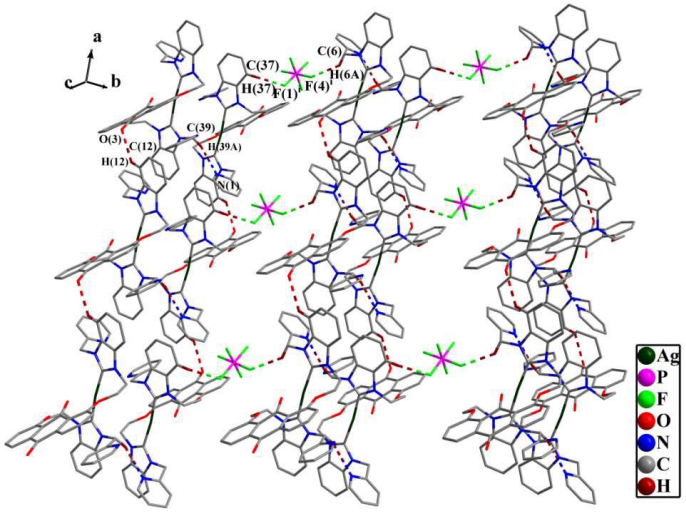


Fig. 7(b) 2D supramolecular layer of **7** via C-H···F, C-H···O and C-H···N hydrogen bonds. All hydrogen atoms except those participating in these hydrogen bonds were omitted for clarity.

Fluorescence Emission Spectra of precursor $L^1H_2\cdot(PF_6)_2$ and complexes 1, 3 and 5

As shown in Fig. 8, the fluorescence emission spectra of precursors $L^1H_2\cdot(PF_6)_2$ and complexes **1**, **3** and **5** in acetonitrile at room temperature are obtained upon excitation at 267 nm. Precursors $L^1H_2\cdot(PF_6)_2$-$L^4H_2\cdot(PF_6)_2$ exhibit similar emission bands in the

region of 400-450 nm, corresponding to intraligand n-π* transitions. The fluorescence emissions of complexes **1**, **3** and **5** are weaker than those of corresponding precursors (complexes **1** and **2** showing similar fluorescence intensity, complexes **3** and **4** showing similar fluorescence intensity, and complexes **5-7** showing similar fluorescence intensity), which may be attributed to the metal perturbed intraligand processes.[25]

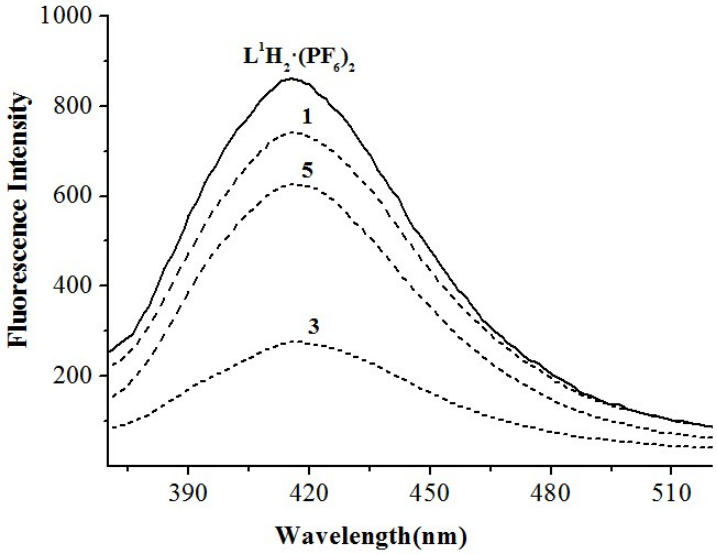
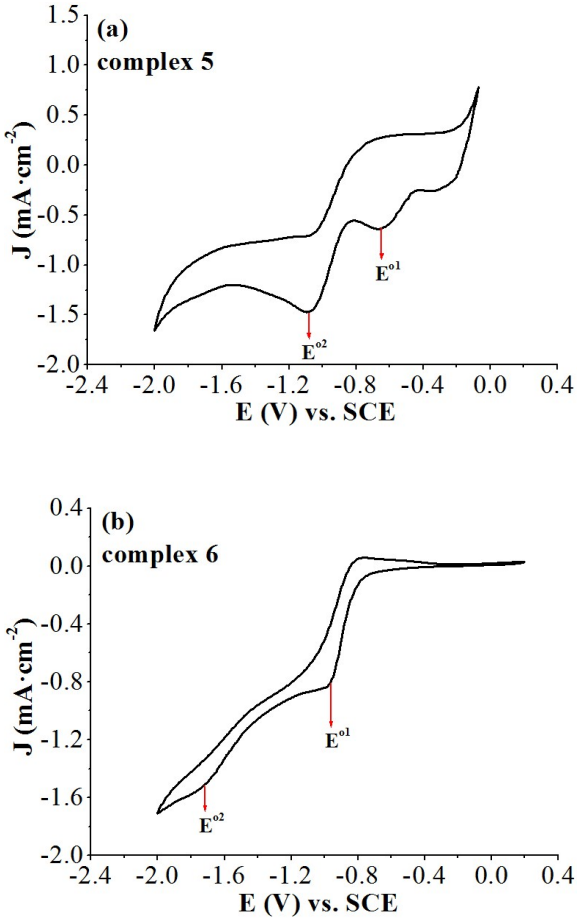


Fig. 8 Emission spectra of $\mathbf{L^1H_2\cdot(PF_6)_2}$ and complexes **1**, **3** and **5** at room temperature in CH_3CN (1.0×10^{-5} M) solution (slit: ex = 5 nm and em = 5 nm).

Cyclic voltammetry

Electrochemical properties were obtained by cyclic voltammetric experiments in 0.1 M tetrabutylammonium tetrafluoroborate ($^nBu_4NBF_4$) using CH_3CN as solvent for complexes **5-7** and their corresponding precursors $\mathbf{L^1H_2\cdot(PF_6)_2}$, $\mathbf{L^3H_2\cdot(PF_6)_2}$ and $\mathbf{L^4H_2\cdot(PF_6)_2}$. Experiments were performed with a three-electrode system (Pt foil as working electrode, Pt wire as counter electrode, and SCE as reference electrode). As shown in Fig.9(a)-Fig.9(c), the reduction peak of silver(I) center is not observed in complexes **5-7**, which indicates that the complexed silver(I) ion is relatively more difficult to reduce due to coordination with carbene carbon atoms.[26] The characteristic, first and second, one-electron anthraquinone reduction potentials[27] for complexes **5-7** and their corresponding precursors $\mathbf{L^1H_2\cdot(PF_6)_2}$, $\mathbf{L^3H_2\cdot(PF_6)_2}$ and $\mathbf{L^4H_2\cdot(PF_6)_2}$ are observed (the cyclic voltammograms of precursors $\mathbf{L^1H_2\cdot(PF_6)_2}$, $\mathbf{L^3H_2\cdot(PF_6)_2}$ and $\mathbf{L^4H_2\cdot(PF_6)_2}$ being shown in Fig.S1(a)-Fig.S1(c) of Supplementary Information). But the anthraquinone reduction potentials in **5-7** have changed in different degrees

compared with corresponding precursors. Anthraquinone's first one electron reduction potential (E^{o1}) and the second one electron reduction potential (E^{o2}) of **5** shifted towards positive potentials by 0.31 V and 0.39 V, respectively, while E^{o1} of **6** or **7** have hardly changed, and E^{o2} of **6** or **7** have only little changes (shifting towards positive potentials by 0.06 V for **6** and 0.05 V for **7**) (Table S5). According to literature reports, the anthraquinone reduction potentials are sensitive to subtle electronic changes on their peripheries,[28] and the charge density of silver(I) center in **5-7** should be an important influence factor on anthraquinone reduction potentials. As can be seen from the structures of **5-7** (Fig.5(a)-Fig.7(a)), the charge density of silver(I) center is related to the size of π-conjugated system of azolylidenes (imidazolylidene for **5** and benzimidazolylidene for **6** and **7**).[29] Benzimidazolylidene has more large π-conjugated system by comparison to imidazolylidene, and it can more effectively disperse positive charge of silver(I) center. Thus, the positive charge density of silver(I) center in **5** is greater than in **6** or **7**. As a result, the anthraquinone reduction potential in **5** is more significantly affected than in **6** or **7**.



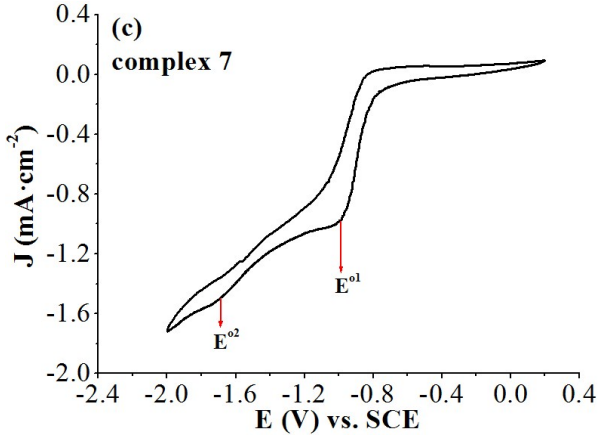


Fig. 9 Cyclic voltammograms of complexes **5**-**7** in CH_3CN using 0.1 M $^nBu_4NBF_4$ as the supporting electrolyte.

Conclusions

In summary, four bis-azolium salts $\mathbf{L^1H_2\cdot(PF_6)_2}$-$\mathbf{L^4H_2\cdot(PF_6)_2}$ and their seven N-heterocyclic carbene Hg(II) and Ag(I) complexes **1**-**7** have been prepared and characterized. In complexes **1** or **2**, two 16-membered macrometallocycles are connected together via two bridging halide ions (two bridging bromide ions for **1**, and two bridging iodide ions for **2**). In complexes **3**-**7**, each molecule contains one 16-membered macrometallocycle formed by one bidentate ligand and one metal ion. In crystal packings of **1**-**7**, 2D supramolecular layers and 3D supramolecular architectures are formed via intermolecular weak interactions, including hydrogen bonds, π-π stacking interactions and C-H···π contacts. Further studies on new organometallic complexes from these ligands and analogous ligands are underway.

Experimental

General procedures

All manipulations were performed using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for synthesis and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian

Mercury Vx 400 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. *J* values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. The fluorescence spectra were performed using a Cary Eclipse fluorescence spectrophotometer. Cyclic voltammetry (CV) measurements were measured using HSV-110 (Automatic Polarization System), HOKUTO DENKO (HD) in CH_3CN solution with tetrabutylammonium tetrafluoroborate ($^{n}Bu_4NBF_4$) as the supporting electrolyte.

Preparation of 1,8-bis(2'-bromoethoxy)-9,10-anthraquinone

An acetone (50 mL) suspension of 1,8-dihydroxy-9,10-anthraquinone (1.081 g, 4.5 mmol), K_2CO_3 (3.726 g, 27.0 mmol), TBAB (0.200 g, 0.6 mmol) and 1,2-dibromoethane (5.072 g, 27.0 mmol) was stirred under refluxing for 3 days. After removing the solvent, H_2O (50 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3 × 30 mL) and the extracting solution was dried over anhydrous $MgSO_4$. After removing CH_2Cl_2, a yellow solid of 1,8-bis(2'-bromoethoxy)-9,10-anthraquinone was obtained. Yield: 1.246 g (61%). M.p.: 122-124 ˚C. Anal. Calcd for $C_{18}H_{14}Br_2O_4$: C, 47.60; H, 3.10%. Found: C, 47.83; H, 3.44%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.84 (t, *J* = 5.8 Hz, 4H, CH_2), 4.49 (t, *J* = 5.8 Hz, 4H, CH_2), 7.57 (q, *J* = 3.2 Hz, 2H, Ar*H*), 7.75 (t, *J* = 2.8 Hz, 4H, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.9 and 180.7 (*C*=O), 157.3, 134.2, 134.1, 124.2, 121.5 and 119.2 (Ar*C*), 69.7 (O*C*H_2CH$_2$), 30.8 (OCH$_2$*C*H$_2$).

Preparation of $L^1H_2 \cdot (PF_6)_2$

An acetone (50 mL) solution of N-ethylimidazole (0.846 g, 8.8 mmol) and 1,8-bis(2'-bromoethoxy)-9,10-anthraquinone (1.816 g, 4.0 mmol) was stirred under refluxing for 3 days, and a yellow precipitate was formed. The product was filtered and washed by acetone to give a pale yellow powder of 1,8-bis[2'-(N-ethylimidazoliumyl)ethoxy]-

9,10-anthraquinone dibromide (**$L^1H_2 \cdot Br_2$**). Yield: 2.275 g (88%). M.p.: 260-262 ˚C. Anal. Calcd for $C_{28}H_{30}Br_2N_4O_4$: C, 52.03; H, 4.67; N, 8.66%. Found: C, 52.45; H, 4.32; N, 8.82%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.42 (t, J = 7.4 Hz, 6H, CH_3), 4.22 (q, J = 7.3 Hz, 4H, CH_2), 4.57 (t, J = 4.6 Hz, 4H, CH_2), 4.71 (t, J = 4.6 Hz, 4H, CH_2), 7.59 (q, J = 3.1 Hz, 2H, ArH), 7.78 (m, 4H, ArH), 7.87 (s, 2H, ArH), 8.08 (s, 2H, ArH), 9.34 (s, 2H, 2-imi$H$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.8 and 182.0 (C=O), 157.1, 136.4, 134.8, 134.1, 123.1, 122.9, 121.8, 120.1 and 119.2 (ArC or imi$C$), 67.5 (OCH$_2$CH$_2$), 48.3 (CH$_2$), 44.2 (CH$_2$), 14.9 (CH$_3$) (imi = imidazole).

NH_4PF_6 (0.652 g, 4.0 mmol) was added to the methanol (40 mL) solution of **$L^1H_2 \cdot Br_2$** (1.293 g, 2.0 mmol), and the mixture was stirred for 48 h at room temperature. The 1,8-bis[2'-(N-ethylimidazoliumyl)ethoxy]-9,10-anthraquinone hexafluorophosphate (**$L^1H_2 \cdot (PF_6)_2$**) was obtained as a yellow solid through filtering. Yield: 1.305 g (84%). M.p.: 218-220 ˚C. Anal. Calcd for $C_{28}H_{30}F_{12}N_4O_4P_2$: C, 43.31; H, 3.89; N, 7.21%. Found: C, 43.55; H, 3.63; N, 7.52%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.42 (t, J = 7.4 Hz, 6H, CH_3), 4.21 (q, J = 7.3 Hz, 4H, CH_2), 4.57 (s, 4H, CH_2), 4.70 (s, 4H, CH_2), 7.59 (d, J = 7.6 Hz, 2H, ArH), 7.80 (t, J = 6.8 Hz, 6H, ArH), 8.07 (s, 2H, ArH), 9.29 (s, 2H, 2-imi$H$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.0 and 181.0 (C=O), 157.1, 136.4, 134.6, 134.1, 123.1, 122.9, 121.8, 120.1 and 119.2 (ArC or imi$C$), 67.4 (OCH$_2$CH$_2$), 48.3 (CH$_2$), 44.3 (CH$_2$), 14.9 (CH$_3$).

Preparation of $L^2H_2 \cdot (PF_6)_2$

This compound was prepared in a manner analogous to that for **$L^1H_2 \cdot (PF_6)_2$**, only N-benzylimidazole (1.392 g, 8.8 mmol) was used instead of N-ethylimidazole. Yield: 3.206 g (89%). M.p.: 208-210 ˚C. Anal. Calcd for $C_{38}H_{34}F_{12}N_4O_4P_2$: C, 50.67; H, 3.80; N, 6.22%. Found: C, 50.41; H, 3.52; N, 6.46%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.86 (t, J = 5.6 Hz, 4H, CH_2), 4.50 (t, J = 5.4 Hz, 4H, CH_2), 5.47 (s, 4H, CH_2), 7.35 (q, J = 2.4 Hz, 5H, ArH), 7.55 (q, J = 2.4 Hz, 3H, ArH), 7.81 (m, 10H, ArH), 8.11 (s,

2H, Ar*H*), 9.45 (s, 2H, 2-imi*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.9 and 181.3 (*C*=O), 157.0, 137.1, 134.6, 134.5, 134.0, 128.9, 128.1, 123.8, 122.1, 121.1, 119.7, 119.1 and 119.0 (Ar*C* or imi*C*), 67.2 (O*C*H$_2$CH$_2$), 52.0 (*C*H$_2$), 48.5 (*C*H$_2$).

Preparation of $L^3H_2\cdot(PF_6)_2$

This compound was prepared in a manner analogous to that for **$L^1H_2\cdot(PF_6)_2$**, only N-ethylbenzimidazole (1.286 g, 8.8 mmol) was used instead of N-ethylimidazole. Yield: 2.981 g (85%). M.p.: 190-192 ˚C. Anal. Calcd for $C_{36}H_{34}F_{12}N_4O_4P_2$: C, 49.32; H, 3.90; N, 6.39%. Found: C, 49.71; H, 3.57; N, 6.27%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.63 (t, J = 7.2 Hz, 6H, C*H*$_3$), 3.91 (t, J = 5.6 Hz, 4H, C*H*$_2$), 4.56 (t, J = 5.8 Hz, 4H, C*H*$_2$), 5.06 (t, J = 4.6 Hz, 4H, C*H*$_2$), 7.56 (q, J = 3.0 Hz, 2H, Ar*H*), 7.74 (q, J = 3.4 Hz, 4H, Ar*H*), 7.78 (d, J = 3.2 Hz, 4H, Ar*H*), 8.13 (q, J = 2.8 Hz, 2H, Ar*H*), 8.27 (q, J = 3.0 Hz, 2H, Ar*H*), 9.97 (s, 2H, 2-bimi*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.9 and 181.5 (*C*=O), 157.5, 134.6, 134.1, 131,0, 130.7, 126.6, 126.5, 119.8, 119.3, 119.0, 116.8 and 113.8 (Ar*C* or bimi*C*), 66.1 (O*C*H$_2$CH$_2$), 45.8 (*C*H$_2$), 42.3 (*C*H$_2$), 14.1 (*C*H$_3$) (bimi = benzimidazole).

Preparation of $L^4H_2\cdot(PF_6)_2$

This compound was prepared in a manner analogous to that for **$L^1H_2\cdot(PF_6)_2$**, only N-picolylbenzimidazole (1.736 g, 8.8 mmol) was used instead of N-ethylimidazole. Yield: 3.250 g (83%). M.p.: 231-233 ˚C. Anal. Calcd for $C_{44}H_{36}F_{12}N_6O_4P_2$: C, 52.70; H, 3.61; N, 8.38%. Found: C, 52.51; H, 3.43; N, 8.55%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.66 (s, 4H, C*H*$_2$), 5.08 (s, 4H, C*H*$_2$), 5.89 (s, 4H, C*H*$_2$), 7.16 (t, J = 6.0 Hz, 2H, Ar*H*), 7.51 (q, J = 2.6 Hz, 2H, Ar*H*), 7.62 (m, 6H, Ar*H*), 7.78 (m, 6H, Ar*H*), 7.92 (d, J = 7.6 Hz, 2H, Ar*H*), 8.19 (d, J = 5.6 Hz, 4H, Ar*H*), 10.03 (s, 2H, 2-bimi*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.8 and 181.5 (*C*=O), 157.6, 157.2, 156.9, 152.7, 149.3, 149.2, 144.6, 137.3, 134.5, 134.0, 133.8, 131.0, 126.7, 126.6, 126.4, 123.5, 123.4, 123.1, 122.8, 122.5, 122.4, 121.5, 120.0, 119.3, 114.0 and 113.7 (Ar*C* or bimi*C*), 66.3

(O*C*H$_2$CH$_2$), 51.0 (*C*H$_2$), 50.9 (*C*H$_2$), 46.2 (*C*H$_2$), 46.0 (*C*H$_2$).

Preparation of complex [(L^{2}HgBr)$_2$](HgBr$_4$) (1)

A CH$_3$CN/DMSO (30 mL, v:v = 2:1) suspension of HgBr$_2$ (0.108 g, 0.3 mmol), K$_2$CO$_3$ (0.249 g, 1.8 mmol) and **L^{2}H$_2$·(PF$_6$)$_2$** (0.270 g, 0.3 mmol) was stirred for 12 h at 80 ˚C in N$_2$ protection. The mixture was filtered and concentrated to 5 mL, and Et$_2$O (10 mL) was added to precipitate a pale yellow powder. Isolation by filtration yields complex **1**. Yield: 0.283 g (41%). M.p.: 216-218 ˚C. Anal. Calcd for C$_{76}$H$_{64}$Br$_6$Hg$_3$N$_8$O$_8$: C, 39.71; H, 2.80; N, 4.87%. Found: C, 39.93; H, 2.61; N, 4.52%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.30 (t, J = 4.2 Hz, 8H, C*H*$_2$), 4.85 (s, 8H, C*H*$_2$), 5.92 (d, J = 0.8 Hz, 8H, C*H*$_2$), 6.83 (t, J = 7.4 Hz, 4H, Ar*H*), 6.90 (t, J = 6.8 Hz, 8H, Ar*H*), 7.15 (d, J = 7.2 Hz, 8H, Ar*H*), 7.41 (d, J = 8.4 Hz, 4H, Ar*H*), 7.80 (m, 12H, Ar*H*), 7.89 (d, J = 2.0 Hz, 4H, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.7 and 179.9 (*C*=O), 177.1 ($C_{carbene}$), 157.6, 135.9, 134.7, 133.6, 128.2, 127.5, 126.8, 124.9, 123.1, 121.5, 118.9 and 118.6 (Ar*C* or imi*C*), 67.1 (O*C*H$_2$CH$_2$), 53.0 (*C*H$_2$), 50.5 (*C*H$_2$).

Preparation of complex [L^{2}Hg(HgI$_4$)]$_2$ (2)

This complex was prepared in a manner analogous to that for complex **1**, only HgI$_2$ (0.136 g, 0.3 mmol) was used instead of HgBr$_2$. Yield: 0.229 g (49%). M.p.: 237-239 ˚C. Anal. Calcd for C$_{38}$H$_{32}$Hg$_2$I$_4$N$_4$O$_4$: C, 30.07; H, 2.12; N, 3.69%. Found: C, 30.42; H, 2.41; N, 3.43%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.32 (t, J = 4.0 Hz, 8H, C*H*$_2$), 4.81 (s, 8H, C*H*$_2$), 5.88 (s, 8H, C*H*$_2$), 6.85 (t, J = 7.2 Hz, 4H, C*H*$_2$), 6.93 (t, J = 7.4 Hz, 8H, C*H*$_2$), 7.14 (d, J = 7.6 Hz, 8H, Ar*H*), 7.42 (d, J = 7.6 Hz, 4H, Ar*H*), 7.82 (m, 12H, Ar*H*), 7.92 (d, J = 1.6 Hz, 4H, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.5 and 178.9 (*C*=O), 175.5 ($C_{carbene}$), 156.4 (O*C*H$_2$CH$_2$), 134.6, 133.6, 132.4, 127.1, 126.4, 125.6, 124.0, 122.1, 120.2, 117.8 and 117.5 (Ar*C* or imi*C*), 65.9, 51.9 (*C*H$_2$), 49.5 (*C*H$_2$).

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

This complex was prepared in a manner analogous to that for complex **1**, only HgI_2 (0.136 g, 0.3 mmol) and **$L^1H_2\cdot(PF_6)_2$** (0.232 g, 0.3 mmol) were used instead of $HgBr_2$ and **$L^2H_2\cdot(PF_6)_2$**. Yield: 0.188 g (45%). M.p.: 257-259 ˚C. Anal. Calcd for $C_{14}H_{14}HgI_2N_2O_2$: C, 24.13; H, 2.02; N, 4.02%. Found: C, 24.43; H, 2.31; N, 4.38%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.38 (t, J = 6.6 Hz, 6H, CH_3), 4.57 (t, J = 9.8 Hz, 8H, CH_2), 4.99 (s, 4H, CH_2), 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.70 (d, J = 7.6 Hz, 2H, ArH), 7.80 (m, 2H, ArH), 7.82 (s, 2H, ArH), 7.89 (s, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.4 and 181.3 (C=O), 176.2 ($C_{carbene}$), 157.4, 134.8, 133.8, 124.1, 122.8, 122.2, 119.2 and 118.8, (ArC or imi$C$), 67.8 (OCH$_2$CH$_2$), 50.5 (CH$_2$), 45.6 (CH$_2$), 16.1 (CH$_3$).

Preparation of complex [$L^4Hg(HgI_4)$] (4)

This complex was prepared in a manner analogous to that for complex **1**, only HgI_2 (0.136 g, 0.3 mmol) and **$L^4H_2\cdot(PF_6)_2$** (0.200 g, 0.2 mmol) was used instead of $HgBr_2$ and **$L^2H_2\cdot(PF_6)_2$**. Yield: 0.105 g (40.8 %). M.p.: 256-258 ˚C. Anal. Calcd for $C_{44}H_{34}Hg_2I_4N_6O_4$: C, 32.63; H, 2.11; N, 5.18%. Found: C, 32.45; H, 2.32; N, 5.47%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.48 (s, 4H, CH_2), 5.29 (s, 4H, CH_2), 6.32 (s, 4H, CH_2), 7.07 (m, 2H, ArH), 7.40 (d, J = 7.6 Hz, 2H, ArH), 7.73 (m, 12H, ArH), 8.14 (t, J = 4.6 Hz, 2H, ArH), 8.24 (t, J = 4.6 Hz, 2H, ArH), 8.31 (d, J = 4.4 Hz, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 184.8 and 182.4 (C=O), 179.5 ($C_{carbene}$), 157.2, 153.4, 149.9, 138.0, 134.5, 133.7, 133.6, 131.4, 125.9, 125.7, 123.6, 122.8, 122.3, 119.0, 118.7, 113.1 and 112.9 (ArC or bimi$C$), 65.6 (OCH$_2$CH$_2$), 51.6 (CH$_2$), 40.3 (CH$_2$).

Preparation of complex [L^1Ag](PF_6) (5)

An acetonitrile (30 mL) suspension of silver oxide (0.082 g, 0.3 mmol) and **$L^1H_2\cdot(PF_6)_2$** (0.232 g, 0.3 mmol) was stirred for 12 h at 40 ˚C in N_2 protection. The

mixture was filtered and concentrated to 5 mL, and Et_2O (10 mL) was added to precipitate a pale yellow powder. Isolation by filtration yields complex **5**. Yield: 0.201 g (90%). M.p.: 234-236 ˚C. Anal. Calcd for $C_{28}H_{28}AgF_6N_4O_4P$: C, 45.60; H, 3.82; N, 7.59%. Found: C, 45.84; H, 3.53; N, 7.77%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.44 (t, J = 7.4 Hz, 6H, CH_3), 4.26 (q, J = 7.4 Hz, 4H, CH_2), 4.45 (t, J = 4.4 Hz, 4H, CH_2), 4.71 (t, J = 4.2 Hz, 4H, CH_2), 7.48 (d, J = 8.0 Hz, 2H, ArH), 7.55 (d, J = 1.6 Hz, 2H, ArH), 7.59 (d, J = 1.6 Hz, 2H, ArH), 7.70 (d, J = 7.6 Hz, 2H, ArH), 7.75 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.8 and 180.4 (C=O), 157.4, 134.3, 133.8, 122.7, 122.1, 120.6, 118.8 and 118.4 (ArC or imi$C$), 68.1 (OCH$_2$CH$_2$), 51.0 (CH$_2$), 46.0 (CH$_2$), 17.0 (CH$_3$). The carbene carbon was not observed.

Preparation of complex [L^{3}Ag](PF$_6$) (6)

This complex was prepared in a manner analogous to that for complex **5**, only **L^{3}H$_2$·(PF$_6$)$_2$** (0.175 g, 0.2 mmol) was used instead of **L^{1}H$_2$·(PF$_6$)$_2$**. Yield: 0.171 g (81%). M.p.: 266-268 ˚C. Anal. Calcd for $C_{36}H_{32}AgF_6N_4O_4P$: C, 51.63; H, 3.85; N, 6.68%. Found: C, 51.73; H, 3.52; N, 6.71%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.54 (t, J = 7.2 Hz, 6H, CH_3), 4.58 (t, J = 4.2 Hz, 4H, CH_2), 4.70 (q, J = 7.0 Hz, 4H, CH_2), 5.18 (t, J = 4.2 Hz, 4H, CH_2), 7.52 (m, 6H, PhH), 7.63 (d, J = 6.8 Hz, 2H, ArH), 7.71 (t, J = 4.0 Hz, 2H, ArH), 7.87 (q, J = 2.8 Hz, 2H, ArH), 7.98 (q, J = 2.8 Hz, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.6 and 180.8 (C=O), 157.3, 134.4, 133.7, 133.3, 133.2, 132.4, 132.3, 124.0, 123.8, 122.6, 118.8, 118.4 and 112.1 (ArC or bimi$C$), 66.2 (OCH$_2$CH$_2$), 49.0 (CH$_2$), 43.7 (CH$_2$), 15.9 (CH$_3$). The carbene carbon was not observed.

Preparation of complex [L^{4}Ag](PF$_6$) (7)

This complex was prepared in a manner analogous to that for complex **5**, only **L^{4}H$_2$·(PF$_6$)$_2$** (0.200 g, 0.2 mmol) was used instead of **L^{1}H$_2$·(PF$_6$)$_2$**. Yield: 0.191 g

(84%). M.p.: 239-241 ˚C. Anal. Calcd for $C_{44}H_{34}AgF_6N_6O_4P$: C, 54.84; H, 3.55; N, 8.72%. Found: C, 54.52; H, 3.67; N, 8.44%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.46 (t, J = 4.4 Hz, 4H, CH_2), 5.15 (t, J = 4.4 Hz, 4H, CH_2), 5.99 (s, 4H, CH_2), 7.07 (J = 4.1 Hz, 2H, Ar*H*), 7.35 (d, J = 8.0 Hz,, 2H, Ar*H*), 7.49 (m, 8H, Ar*H*), 7.74 (m, 4H, Ar*H*), 7.80 (J = 7.6 Hz, 2H, Ar*H*), 7.96 (d, J = 8.0 Hz, 2H, Ar*H*), 8.38 (d, J = 4.0 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.7 and 180.4 (*C*=O), 157.4, 155.7, 149.1, 136.9, 134.4, 134.1, 133.7, 132.3, 124.1, 123.9, 122.8, 122.3, 121.7, 118.8, 118.4, 112.4 and 112.1 (Ar*C* or bimi*C*), 65.9 (O*C*H$_2$CH$_2$), 53.4 (*C*H$_2$), 48.7 (*C*H$_2$). The carbene carbon was not observed.

Cyclic voltammetry experiment

Cyclic voltammetry experiments were measured using HSV-110 (Automatic Polarization System), HOKUTO DENKO (HD) at a scan rate of 50 mV/s for **5**-**7**. The electrolyte is 0.1 M tetrabutylammonium tetrafluoroborate (^{n}Bu$_4$NBF$_4$). The conventional three-electrode electrochemical cell including the Pt foil electrode as a working electrode, a Pt wire as a counter electrode, and a saturated calomel electrode as a reference electrode was used.

X-ray data collection and structure determinations

X-ray single-crystal diffraction data for complexes **1**-**7** were collected by using a Bruker Apex II CCD diffractometer at 173(2) K for **1**, **2** and **4**-**7** and 296(2) K for **3** with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. There was no evidence of crystal decay during data collection in all cases. Semiempirical absorption corrections were applied by using SADABS and the program SAINT was used for integration of the diffraction profiles.[30] All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL[31] by the full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. Hydrogen atoms bonded to C atoms were placed geometrically

and presumably solvent H atoms were first located in difference Fourier maps and then fixed in the calculated sites. Further details for crystallographic data and structural analysis are listed in Table 1 and Table 2. Fig.s were generated by using Crystal-Maker.[32]

Table 1 Summary of crystalographic data for complexes **1-3**

	1	**2**·CH_3CN	**3**·0.25DMSO
Chemical formula	$C_{76}H_{64}Br_6Hg_3N_8O_8$	$C_{38}H_{32}Hg_2I_4N_4O_4$·$CH_3CN$	$C_{14}H_{14}HgI_2N_2O_2$ ·0.25DMSO
Formula weight	2298.58	1558.51	716.19
Cryst syst	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	17.792(1)	9.108(2)	8.908(4)
b, Å	17.744(1)	15.513(3)	14.540(3)
c, Å	28.263(1)	30.601(7)	15.730(3)
α, deg	90	90	71.4 (7)
β, deg	97.5 (2)	90.4 (7)	89.9 (8)
γ, deg	90	90	77.6 (7)
V, Å^3	8846.8(1)	4323.5(1)	1882.4(7)
Z	4	4	4
D_{calcd}, Mg m^{-3}	1.726	2.394	2.527
Abs coeff, mm^{-1}	7.955	9.995	11.492
F(000)	4360	2856	1298
Cryst size, mm	0.18 × 0.17 × 0.15	0.18 × 0.17 × 0.16	0.18 × 0.17 × 0.16
θ_{min}, θ_{max}, deg	1.15, 25.01	2.59, 28.32	2.35, 28.48
T, K	173(2)	173(2)	296(2)
No. of data collected	44964	9979	9505
No. of unique data	15577	7622	6588
No. of refined	917	497	421
Goodness-of-fit on F^2 [a]	1.076	1.098	1.016
Final R indices[b] [$I > 2\sigma(I)$]			
R_1	0.0495	0.0422	0.0470
wR_2	0.1117	0.0976	0.1257
R indices (all data)			
R_1	0.0732	0.0473	0.0508
wR_2	0.1170	0.0996	0.1297

[a] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined. [b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2 Summary of crystalographic data for complexes **4-7**

	4·1.5DMSO	**5**	**6**·DMSO	**7**·DMSO·2.5H_2O
Chemical formula	$C_{44}H_{34}Hg_2I_4N_6O_4$ ·1.5DMSO	$C_{28}H_{28}AgF_6N_4O_4P$	$C_{36}H_{32}AgF_6N_4O_4P$ ·DMSO	$C_{44}H_{34}AgF_6N_6O_4P$ ·DMSO·2.5H_2O
Formula weight	1736.74	737.38	915.62	1086.78
Cryst syst	Monoclinic	Monoclinic	Rhombohedral	Triclinic
Space group	$P2_1/n$	$P2_1/c$	R_3	$P\bar{1}$
a, Å	12.513(9)	14.903(4)	29.601(6)	12.716(3)
b, Å	26.971(9)	14.579(9)	29.601(6)	14.533(2)
c, Å	16.546(0)	15.114(8)	22.500(3)	14.628(2)
α, deg	90	90	90	62.5 (8)
β, deg	92.4 (1)	117.7 (7)	90	83.1 (5)
γ, deg	90	90	120	74.1 (1)
V, Å^3	5579.7(6)	2905.9(4)	17074(2)	2308.1(6)
Z	4	4	18	2
D_{calcd}, Mg m^{-3}	2.067	1.685	1.603	1.564
Abs coeff, mm^{-1}	7.813	0.830	0.708	0.600
F(000)	3228	1488	8388	1110
Cryst size, mm	0.18 × 0.17 × 0.16	0.18 × 0.17 × 0.16	0.18 × 0.17 × 0.16	0.18 × 0.17 × 0.16
θ_{min}, θ_{max}, deg	2.46, 27.89	2.79, 28.34	1.20, 25.01	2.30, 28.18
T, K	173(2)	173(2)	173(2)	173(2)
No. of data collected	28565	8345	29535	10551
No. of unique data	9822	5112	6693	7986
No. of refined params	541	419	482	629
Goodness-of-fit on F^2 [a]	1.071	1.056	1.065	1.037
Final R indices[b] [$I > 2\sigma(I)$]				
R_1	0.0607	0.0325	0.1147	0.0548
wR_2	0.1696	0.0866	0.2926	0.1317
R indices (all data)				
R_1	0.0695	0.0356	0.1483	0.0765
wR_2	0.1747	0.0894	0.3146	0.1485

$^{a}GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined. $^{b}R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

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Supplementary Information

Tables, Figures and CIF files giving crystallographic data for complexes **1-7**, and ^{1}H NMR and ^{13}C NMR spectra for all precursors and complexes with this article can be found in the online version.

References

1 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361-363.

2 (*a*) S. P. Nolan, N-Heterocyclic Carbenes in Synthesis, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006; (*b*) P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596-609; (*c*) J. A. Mata, M. Poyatos and E. Peris, *Coord. Chem. Rev.*, 2007, **251**, 841-859; (*d*) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746-1787; (*e*) C. Samojłowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 3708-3742.

3 (*a*) F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape and D. L. Van, *Angew. Chem., Int. Ed.*, 2005, **44**, 3759-3763; (*b*) R. McKie, J. A. Murphy, S. R. Park, M. D. Spicer and S. Z. Zhou, *Angew. Chem., Int. Ed.*, 2007, **46**, 6525-6528; (*c*) H. M. Bass, S. A.

Cramer, J. L. Price and D. M. Jenkins, *Organometallics*, 2010, **29**, 3235-3238; (*d*) E. Suzanne and P. S. Howson, *Dalton Trans.*, 2011, **40**, 10268-10277; (*e*) X. Q. Zhang, Y. P. Qiu, B. Rao and M. M. Luo, *Organometallics*, 2009, **28**, 3093-3099.

4 D. B. Qin, X. S. Zeng, Q. S. Li, F. B. Xu, H. B. Song and Z. Z. Zhang, *Chem. Commun.*, 2007, 147-149.

5 (*a*) A. Rit, T. Pape, A. Hepp and F. E. Hahn, *Organometallics*, 2011, **30**, 6393-6401; (*b*) S. Saito, M. Saika, R. Yamasaki, I. Azumaya and H. Masu, *Organometallics*, 2011, **30**, 1366-1373.

6 (*a*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122-3172; (*b*) Q. X. Liu, Z. Q. Yao, X. J. Zhao, Z. X. Zhao and X. G. Wang, *Organometallics*, 2013, **32**, 3493-3501.

7 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290-1309; (*b*) H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687-703; (*c*) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed.*, 1997, **36**, 2162-2187; (*d*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122-3172; (*e*) T. Droege and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940-6952; (*f*) H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 2784-2790.

8 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290-1309; (*b*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768-2813; (*c*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676; (*d*) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677-3707; (*e*) H. B. Song, D. N. Fan, Y. Q. Liu, G. H. Hou and G. F. Zi, *J. Organomet. Chem.*, 2013, **729**, 40-45; (*f*) S. C. Wang, F. Ren, Y. P. Qiu and M. M. Luo, *J. Organomet. Chem.*, 2015, **788**, 27-32; (*g*) G. Bastug and S. P. Nolan, *Organometallics*, 2014, **33**, 1253-1258.

9 (*a*) A. J. Boydston, K. A. Williams and C. W. Bielawski, *J. Am. Chem. Soc.*, 2005, **127**, 12496-12497; (*b*) A. J. Boydston and C. W. Bielawski, *Dalton Trans.*, 2006, 4073-4077; (*c*) A. G. Tennyson, J. W. Kamplain and C. W. Bielawski, *Chem. Commun.*, 2009, 2124-2126; (*d*) L. Mercs, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Dalton Trans.*, 2009, 7168-7178.

10 (*a*) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, *J. Chem. Soc., Dalton Trans.*, 2000, 4499-4506; (*b*) I. J. B. Lin and C. S. Vasam, *Coord. Chem. Rev.*, 2007, **251**, 642-670; (*c*) K. J. Cavell, D. J. Nielsen, B. W. Sketon and A. H. White, *Organometallics*, 2006, **25**, 4850-4856; (*d*) A. Rit, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2010, **132**, 4572-4573; (*e*) D. D. Yang, Y. G. Tang, H. B. Song and B. Q. Wang, *Organometallics*, 2015, **34**, 2012-2017; (*f*) J. W. Wang, Q. S. Li, F. B. Xu, H. B. Song and Z. Z. Zhang, *Eur. J. Org. Chem.*, 2006,1310-1314; (*g*) X. L. Liu and W. Z. Chen, *Organometallics*, 2013, **32**, 209; (*h*) B. Liu, Q. Q. Xia and W. Z. Chen, *Angew. Chem., Int. Ed.*, 2009, **48**, 5513-5516; (*i*) S. Hameury, P. de Frémont, P. A. R. Breuil, H. Olivier-Bourbigoub and P. Braunstein, *Dalton Trans.*, 2014, **43**, 4700-4710.

11 (*a*) A. Melaiye, R. S. Simons, A. Milsted, F. Pingitore, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *J. Med. Chem.*, 2004, **47**, 973-977; (*b*) A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier and W. J. Youngs, *J. Am. Chem. Soc.*, 2005, **127**, 2285-2291; (*c*) R. A. Haque, P. O. Asekunowo, M. R. Razali and F. Mohamad, *Heteroat. Chem.*, 2014, **25**, 194-204.

12 (*a*) H. W. Wanzlick and H. J. Schönherr, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 141-142; (*b*) K. M. Lee, J. C. C. Chen and I. J. B. Lin, *J. Organomet. Chem.*, 2001, **364**, 617-618; (*c*) X. J. Wan, F. B. Xu, Q. S. Li, H. B. Song and Z. Z. Zhang, *Organometallics*, 2005, **24**, 6066-6068; (*d*) U. J. Scheele, S. Dechert and F. Meyer, *Inorg. Chim. Acta*, 2006, **359**, 4891-4900; (*e*) T. Weskamp, V. P. W. Böhm and W. A.

Herrmann, *J. Organomet. Chem.*, 2000, **600**, 12-22; (*f*) J. C. Garrison, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *Organometallics*, 2001, **20**, 1276-1278; (*g*) A. Caballero, E. Díez-Barra, F. A. Jalón, S. Merino and J. Tejeda, *J. Organomet. Chem.*, 2001, **395**, 617-618.

13 (*a*) Q. X. Liu, Q. Wei, R. Liu, X. J. Zhao and Z. X. Zhao, *RSC Adv.*, 2015, **5**, 28435-28447; (*b*) Q. X. Liu, Z. X. Zhao, X. J. Zhao, Q. Wei, A. H. Chen, H. L. Li and X. G. Wang, *CrystEngComm*, 2015, **17**,1358 -1373.

14 (*a*) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978-4008; (*b*) D. J. Nielsen, K. J. Cavell, B. W. Skelton and A. H. White, *Organometallics*, 2006, **25**, 4850-4856; (*c*) J. C. C. Chen and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 839-840; (*d*) M. Alcarazo, S. J. Roseblade, A. R. Cowley, R. Fernandez, J. M. Brown and J. M. Lassaletta, *J. Am. Chem. Soc.*, 2005, **127**, 3290-3291; (*e*) B. Liu, Q. Xia and W. Z. Chen, *Angew. Chem., Int. Ed.*, 2009, **48**, 5513-5516; (*f*) M. L. Li, H. B. Song and B. Q. Wang, *Organometallics*, 2015, **34**, 1969-1977; (*g*) H. B. Song, Y. Q. liu, D. N, Fan and G. F. Zi, *J. Organomet. Chem.*, 2011, **696**, 3714-3720.

15 (*a*) J. J. Van Veldhuizen, J. E. Campbell, R. E. Giudici and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2005, **127**, 6877-6882; (*b*) D. J. Nielsen, K. J. Cavell, B. W. Skelton and A. H. White, *Inorg. Chim. Acta.*, 2003, **352**, 143-150; (*c*) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978-4008; (*d*) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247-2273; (*e*) J. C. Lin, Y. Huang, R. T. W. Lee, C. S. A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561-3598; (*f*) C. V. Georgios and H. G. Robert, *Chem. Rev.*, 2010, **110**, 1746-1787; (*g*) J. W. Wang, F. H. Meng and L. F. Zhang, *Organometallics*, 2009, **28**, 2334-2337; (*h*) Q. Li, Y. F. Xie, B. C. Sun, J. Yang, H. B. Song and L. F. Tang, *Organometallics*, 2013, **745**, 106-114; (*i*) J. D. Holbrey, A. E. Visser, S. K. Spear, W. M. Reichert, R. P. Swatloski, G. A. Broker and R. D. Rogers, *Green Chem.*, 2003, **5**, 129-135.

16 (*a*) C. K. Lee, K. M. Lee and I. J. B. Lin, *Organometallics*, 2002, **21**, 10-12; (*b*) A. J. Arduengo III, H. V. Dias, J. C. Calabrese and F. Davidson, *Organometallics*, 1993, **12**, 3405-3409; (*c*) J. C. Garrison, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *Organometallics*, 2001, **20**, 1276-1278; (*d*) O. Guerret, S. Sole, H. Gornitzka, M. L. Teichert, G. Teingnier and G. Berte, *J. Am. Chem. Soc.*, 1997, **119**, 6668-6669; (*e*) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, *Dalton Trans*., 2000, 4499-4506.

17 (*a*) U. J. Scheele, S. Dechert and F. Meyer, *Inorg. Chim. Acta*, 2006, **359**, 4891-4900; (*b*) K. M. Lee, J. C. C. Chen, C. J. Huang and I. J. B. Lin, *CrystEngComm*, 2007, **9**, 278-281.

18 S. C. Chen, H. H. Hsueh, C. H. Chen, C. S. Lee, F. C. Liu, I. J. B. Lin, G. H. Lee and S. M. Peng, *Inorg. Chim. Acta*, 2009, **362**, 3343-3350.

19 G. Mahmoudi and A. Morsali, *CrystEngComm*, 2007, **9**, 1062-1072.

20 (*a*) J. Y. Kwon, N. J. Singh, H. N. Kim, S. K. Kim and J. Yoon, *J. Am. Chem. Soc.*, 2004, **126**, 8892-8893; (*b*) J. Yoon, S. K. Kim, N. J. Singh, J. W. Lee, Y. J. Yang and K. Chellappan, *J. Org. Chem.*, 2004, **69**, 581-583; (*c*) S. K. Kim, N. J. Singh, S. J. Kim, H. G. Kim, J. K. Kim, J. W. Lee, K. S. Kim and J. Yoon, *Org. Lett.*, 2003, **5**, 2083-2086; (*d*) H. Ihm, S. Yun, H. G. Kim, J. K. Kim and K. S. Kim, *Org. Lett.*, 2002, **4**, 2897-2900; (*e*) K. Sato, S. Arai and T. Yamagishi, *Tetrahedron Lett.*, 1999, **40**, 5219-5222; (*f*) K. Chellappan, N. J. Singh, I. C. Hwang, J. W. Lee and K. S. Kim, *Angew. Chem., Int. Ed.*, 2005, **44**, 2899-2903.

21 R. J. Santos-Contreras, F. J. Martínez-Martínez, N. A. Mancilla-Margalli, A. L. Peraza-Campos, L. M. Morín-Sánchez, E. V. García-Báez and I. I. Padilla-Martínez, *CrystEngComm*, 2009, **11**, 1451-1461.

22 R. P. A. Bettens, D. Dakternieks, A. Duthie, F. S. Kuan and E. R. T. Tiekink, *CrystEngComm*, 2009, **11**, 1362-1372.

23 A. L. Pickering, G. Seeber, D. L. Long and L. Cronin, *CrystEngComm*, 2005, **7**, 504-510.

24 W. Wei, M. Y. Wu, Y. G. Huang, Q. Gao, F. L. Jiang and M. C. Hong, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2623-2628.

25 (*a*) J. P. Desvergne, F. Fages, H. Bouas-Laurent and P. Marsau, *Pure Appl. Chem.*, 1992, **64**, 1231-1238; (*b*) V. W. W. Yam, K. L. Yu, K. M. C. Wong and K. K. Cheung, *Organometallics*, 2001, **20**, 721-726; (*c*) S. C. Chan, M. C. W. Chan, Y. Wang, C. M. Che, K. K. Cheung and N. Zhu, *Chem. Eur. J.*, 2001, **7**, 4180-4190; (*d*) K. J. Wei, Y. S. Xie, J. Ni, M. Zhang and Q. L. Liu, *Cryst. Growth Des.*, 2006, **6**, 1341-1350.

26 F. D'Souzaa and V. Krishnan, *J. Chem. Soc. Dalton Trans.*, 1992, 2873-2876.

27 (*a*) K. Mariappan, P. N. Basa, V. Balasubramanian, S. Fuoss and A. G. Sykes, *Polyhedron*, 2013, **55**, 144-154; (*b*) K. Mariappan and P. N. Basa, *Inorg. Chim. Acta*, 2011, **366**, 344-349.

28 (*a*) M. D. Sanderson, J. W. Kamplain and C. W. Bielawski. *J. Am. Chem. Soc.*, 2006, **128**, 16514-16515; (*b*) M. Bauscher and W. Mantele, *J. Phys. Chem.*, 1992, **96**, 11101-11108; (*c*) M. Kadarkaraisamy, E. Dufek, D. L. Elk and A. G. Sykes, *Tetrahedron*, 2005, **61**, 479-484.

29 (*a*) H. Valdés, M. Poyatos, G. Ujaque and E. Peris, *Chem. Eur. J.*, 2015, **21**, 1578-1588; (*b*) J. A. Therrien, M. O. Wolf and B. O. Patrick, *Inorg. Chem.*, 2014, **53**, 12962-12972.

30 Bruker AXS, *SAINT Software Reference Manual*; Madison, WI, 1998.

31 G. M. Sheldrick, *SHELXTL NT (Version 5.1), Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

32 D. C. Palmer, *CrystalMaker 7.1.5, CrystalMaker Software*, Yarnton, UK, 2006.

A table of contents entry:

A series of bis-azolium salts and their seven NHC metal (Hg(II) and Ag(I)) complexes have been prepared and characterized.

Software of Graphics:

Scheme 1 and Scheme 2: Chem Draw 8.0

Fig. 1-Fig. 7: Diamand 3.0

Fig. 8 and Fig. 9: Origin 8.0