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

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A series of bis-benzimidazolium (or bis-imidazolium) salts, and their eight N-heterocyclic carbene mercury(II) and silver(I) complexes **1-8** have been synthesized and characterized. Complexes **1-4** and **6** contain similar macrometallocycles formed via one bidentate carbene ligand and one metal ion. Their major differences are anionic units, which are related to the amount of metal sources added. In complex **7**, one 30-membered macrometallocycle is generated via two ligands and two silver(I) atoms in dilute solution. For open structure of complexes **5** and **8**, **5** contains an anionic unit $[Hg_3Cl_8]^{2-}$, and **8** is formed as a dimer through two monomers $[L^3Ag_2Cl_2]$. The study of selective recognition of anions on the basis of fluorescent and UV/vis spectroscopic titrations indicates that macrometallocycle **6** is an effective chemosensor for nitrate anion.

Introduction

The design and synthesis of receptors for the selective recognition of anions are one of the most significant areas of host-guest chemistry.[1] Most anion receptors have amide, pyrrole, or urea groups as binding sites to form N-H···X hydrogen bonds or the positively charged ammonium groups (or guanidinium groups) that involve N^+-H···X^--type hydrogen bonds (X = O, N, F, Cl, Br and I).[2] In recent years, the receptors with imidazolyl groups have attracted intensive attention due to their strong

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binding abilities to anionic guests via nonclassical C-H···X hydrogen bonds.[3, 4] Although a great progress has been made, the receptors with special selectivity and high sensitivity are seldom reported. During the course of searching for receptors bearing cavities, we became interested in cyclic N-heterocyclic carbene (NHC) metal complexes. N-heterocyclic carbenes are a type of important ligand due to their strong σ-donating property,[5] and they can coordinate with many metals to form complexes with various structures including tweezer,[6] tripod,[7] macrocycle[8] and groove.[9] The special structures and multi-bonding sites of these complexes made them be useful receptors.[10]

Nitrate salt as the environmental pollutant exists extensively in natural world (such as water, vegetable and food). When crops are irrigated by polluted water, the nitrate salt can be absorbed. After these crops (such as the vegetable and food) are consumed by human, the nitrate salt can be transformed into the nitrite salt, and the latter will make the person poisoning.[11, 12] Therefore, the determination of nitrate group in vegetable and food is of considerable importance for the environment and human health. There are many methods to detect nitrate group, such as fluorescence[13] and UV/vis spectrophotometry,[14] ion chromatography[15] and electrochemical methods.[16] Among these methods, the fluorescence and UV/vis spectrophotometry have received more attention due to the high sensitivity and easy-operation.[17] In this paper, we report the preparation of eight bis-benzimidazolium (or bis-imidazolium) salts (**$L^1H_2\cdot Cl_2$-$L^6H_2\cdot Cl_2$, $L^7H_2\cdot(PF_6)_2$** and **$L^8H_2\cdot(PF_6)_2$**), as well as the synthesis and structures of eight NHC mercury(II) and silver(I) complexes (**1**-**8**). Particularly, the selective recognition of nitrate anion using macrometallocycle **6** as a chemosensor was studied on the basis of fluorescent and UV/vis spectroscopic titrations.

Results and discussion

Synthesis and general characterizations of bis-benzimidazolium (or bis-imidazolium) salts

As shown in Scheme 1, the salicylic aldehyde as starting material was etherificated with 1,n-dibromoalkane (n = 1, 2, 3 or 4), followed by reduction of aldehyde groups with sodium borohydride to form 1,n-bis(2-hydroxymethylphenoxy)alkylene.

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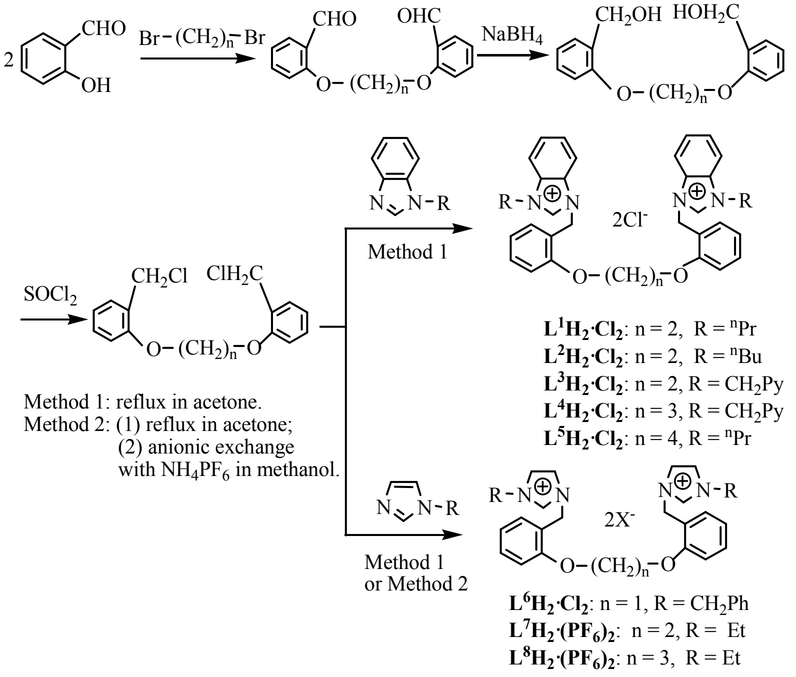
Chlorination of two hydroxy groups in 1,n-bis(2-hydroxymethylphenoxy)alkylene using thionyl chloride gave 1,n-bis[2-(chloromethyl)phenoxy]alkylene, which further reacted with N-R-benzimidazole or N-R-imidazole afforded 1,n-bis[2-(N-R-benzimidazoliumylmethyl)phenoxy]alkylene chloride **$L^1H_2·Cl_2$-$L^5H_2·Cl_2$** and 1,n-bis[2-(N-R-imidazoliumylmethyl)phenoxy]alkylene chloride **$L^6H_2·Cl_2$-$L^8H_2·Cl_2$**. The subsequent anion exchange with ammonium hexafluorophosphate was carried out for **$L^7H_2·Cl_2$** and **$L^8H_2·Cl_2$** in methanol to give **$L^7H·(PF_6)_2$** and **$L^8H_2·(PF_6)_2$**, respectively. These bis-benzimidazolium (or bis-imidazolium) salts are stable to air and moisture, and soluble in DMSO, DMF, CH_2Cl_2 or CH_3CN, but insoluble in diethyl ether or hydrocarbon solvents. In the ^1H NMR spectra of precursors, the benzimidazole (or imidazole) proton signals (NC*H*N) appear at δ = 9.15-10.19 ppm, which are consistent with the chemical shifts of the reported benzimidazolium (or imidazolium) salts.[18]



Scheme 1 Preparation of precursors **$L^1H_2·Cl_2$-$L^6H_2·Cl_2$**, **$L^7H_2·(PF_6)_2$** and **$L^8H_2·(PF_6)_2$**.

Synthesis and general characterization of NHC metal complexes 1-8

As shown in Scheme 2, NHC mercury(II) complexes **1-5** were prepared via the reaction of precursors with mercury(II) salts (such as $Hg(OAc)_2$, $HgCl_2$ or HgI_2) at

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different molar ratios in CH_3CN or CH_3CN/DMSO solution at about 80 ˚C. The reaction of $\mathbf{L^4H_2 \cdot Cl_2}$ with 1.0 mol eq. $Hg(OAc)_2$ afforded monomercury(II) macrocyclic complex $[L^4HgCl_2]$ (**1**) without the presence of bases due to the deprotonation ability of acetate. The complex $[L^5Hg](HgCl_4)$ (**2**) was prepared via the reaction of $\mathbf{L^5H_2 \cdot Cl_2}$ with 2.0 mol eq. $HgCl_2$ in the presence of KO^tBu. The reaction of $\mathbf{L^1H_2 \cdot Cl_2}$ with 2.0 mol eq. HgI_2 in the presence of KO^tBu in CH_3CN/DMSO solution yielded complex $[L^1Hg(DMSO)](HgI_4)$ (**3**), in which the dimethyl sulfoxide (DMSO) participates in coordination with Hg(II) atom. The treatment of $\mathbf{L^6H_2 \cdot Cl_2}$ with 3.0 mol eq. HgI_2 afforded complex $[L^6Hg](Hg_2I_6)$ (**4**) using KO^tBu as base. Similarily, the open $[L^8Hg_2Cl_2](Hg_3Cl_8)$ (**5**) could be formed via the reaction of $\mathbf{L^8H \cdot (PF_6)_2}$ with 5.0 mol eq. $HgCl_2$.

NHC silver(I) complexes **6-8** were prepared via the reaction of precursors with Ag_2O at different molar ratios and different concentrations of reactants in CH_3CN/CH_2Cl_2 solution under refluxing. The monosilver(I) macrocyclic complex $[L^2Ag](Cr_2O_7)_{0.5}$ (**6**) was obtained via the reaction of $\mathbf{L^2H_2 \cdot Cl_2}$ with 0.5 mol eq. Ag_2O in a high concentration solution. In a diluted solution, the disilver(I) macrocyclic complex $[L^7{}_2Ag_2](PF_6)_2$ (**7**) could be generated from $\mathbf{L^7H_2 \cdot (PF_6)_2}$ and 0.5 mol eq. Ag_2O. Treatment of $\mathbf{L^3H_2 \cdot Cl_2}$ with 1.0 mol eq. Ag_2O yieled a dimer $[L^3Ag_2Cl_2]_2$ (**8**).

Complexes **1-8** are stable toward air and moisture, and soluble in acetonitrile or DMSO, but insoluble in diethyl ether or hydrocarbon solvents. Their structures were confirmed by ^1H NMR, $^{13}C\{^1H\}$ NMR spectroscopy and X-ray crystallography. In the ^1H NMR spectra of **1-8**, the resonance signals for the benzimidazolium or imidazolium protons (NC*H*N) have disappeared, which indicates the formation of the expected metal carbene complexes. The chemical shifts of other protons are similar to those of the corresponding precursors. In $^{13}C\{^1H\}$ NMR spectra, the signals for the carbene carbons of **1-5** appear at 170.1-185.4 ppm, which are similar to the known carbene metal complexes.[18] The signals for the carbene carbons of silver(I) complexes **6-8** were not observed. The absence of the carbene carbon resonance is not unusual, and this phenomenon has been previously reported for some silver(I)-carbene complexes, which may result from the fluxional behaviour of the NHC complexes.[19]

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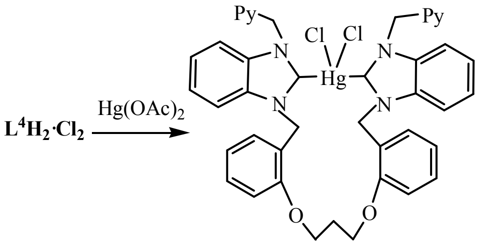

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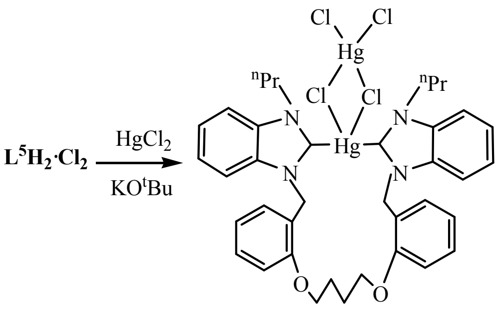

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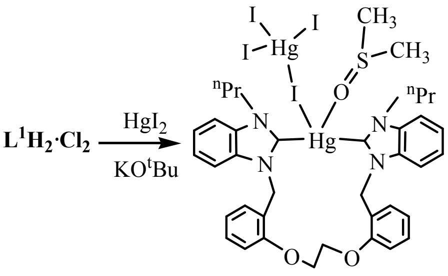

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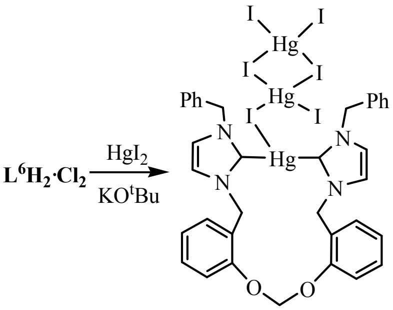

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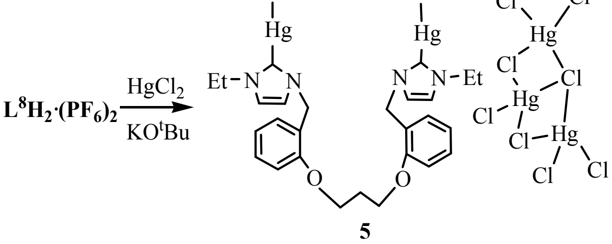

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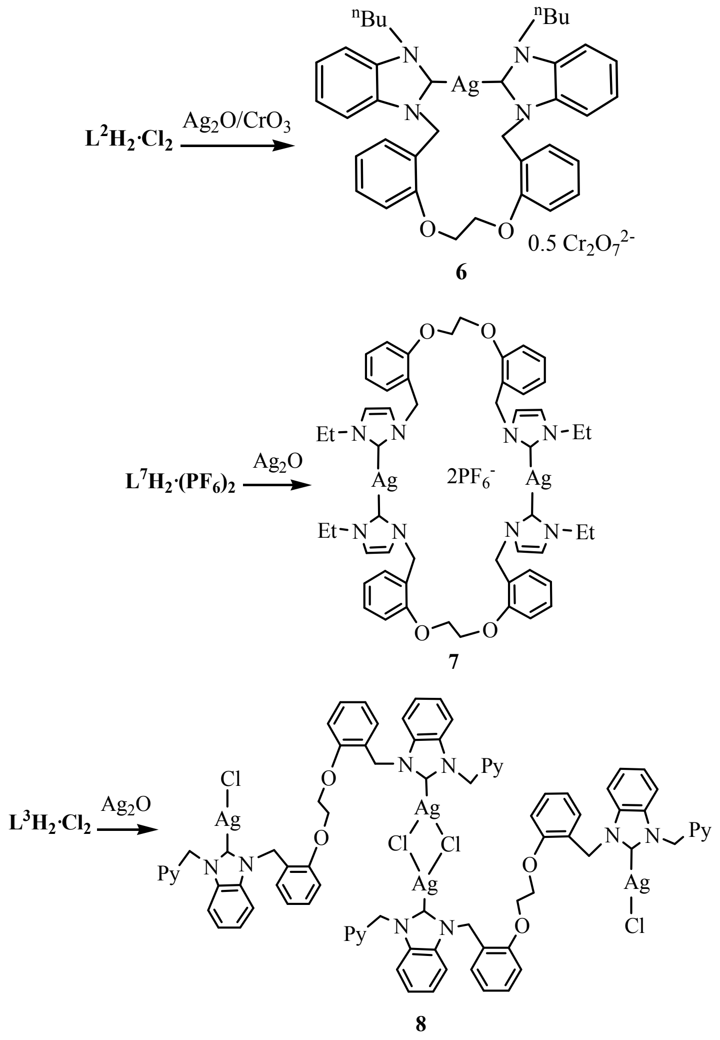

Scheme 2 Preparation of complexes **1-8**.

Crystal structure of NHC complexes 1-8

The crystals of **1-8** (Fig.1-Fig. 8) suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into their CH_3CN or CH_3CN/DMSO solutions. In complexes **1-4** and **6**, each m-membered macrometallocycle (**1**: m = 16, **2**: m = 17, **3** and **6**: m = 15 and **4**: m = 14 and) contains one bidentate carbene ligand and one metal atom (Hg(II) for **1-4** and Ag(I) for **6**). In the same ligand of complexes **1-8**, the dihedral angles between two benzene rings from phenol ether are 7.5(1)-89.2(4)˚ (Table S1 in Supplementary Information), and the dihedral angles between benzimidazole (or imidazole) rings and adjacent benzene rings from phenol ether are from 61.3(1)˚ to 88.4(0)˚. In NHC-metal-NHC units of complexes **1-4**, **6** and **7**, the dihedral angles between two benzimidazole (or imidazole) rings are from 8.6(5)˚ to 36.1(3)˚ (Table

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S1). In complexes **1-8**, the internal ring angles (N-C-N) at the carbene centers are in the range of 102.5(5)-108.3(4)˚, which is comparable to those of known NHC-metal complexes.[20]

In mercury(II) complexes **1-5**, Hg(II) atoms are tetra-coordinated except that Hg(1) in **4** is tri-coordinated and Hg(1) and Hg(2) in **5** are di-coordinated, and the bond distances of Hg-C are from 2.036(9) Å to 2.117(3) Å. In complexes **1-4**, the angles of C-Hg-C are in the range of 154.3(1)-170.6(4)˚.

In complex **1**, the bond angles of C(14)-Hg(1)-Cl(1) and Cl(1)-Hg(1)-Cl(1A) are 91.5(9)˚ and 93.6(5)˚, respectively. The distances of both Hg-Cl bonds are all 2.765(9) Å. The dihedral angle between two pyridine rings is 26.4(4)˚, and the dihedral angle between the benzimidazole ring and adjacent pyridine ring is 72.2(3)˚. The molecule of **1** is situated on a 2-fold axis.

In complex **2**, two ^{n}propyl chains point to the opposite directions. The distances of Hg(1)-Cl(2) and Hg(1)-Cl(4) are 2.864(7) Å and 2.919(8) Å, respectively. In $[HgCl_4]^{2-}$ unit, the bond angles of Cl-Hg(2)-Cl are from 93.8(4)˚ to 127.8(5)˚. The bond distances of Hg(2)-Cl range from 2.387(1) Å to 2.586(1) Å, and these values are slightly shorter than those of Hg(1)-Cl. The Hg(1)···Hg(2) separation of 3.713(3) Å indicates that there is no direct interaction between both metal ions (van der Waals Radii of mercury being 1.70 Å).

In complex **3**, the distance of Hg(1)-O(3) is 2.671(9) Å, and similar to the reported values.[21] The bond angles of C(7)-Hg(1)-O(3) and C(33)-Hg(1)-O(3) are 86.2(3)˚ and 98.6(4)˚, respectively. In $[HgI_4]^{2-}$ unit, the bond distances of Hg(2)-I are from 2.743(9) Å to 2.896(9) Å, which are similar to the reported values.[6b, 22] Additionally, the distance of Hg(1)-I(2) (3.180(3) Å) is slightly longer than those of Hg(2)-I, but shorter than the sum of van der Waals Radii of mercury and iodine (3.68 Å).

In the cation of **4**, the dihedral angle between two benzene rings from benzyls is 6.3(9)˚, and the dihedral angle between imidazole ring and adjacent benzene ring from benzyl is 88.8(1)˚. In the anionic unit of **4**, a building block $[Hg_2I_6]^{2-}$ is formed via two mercury(II) atoms (Hg(2) and Hg(3)) and six iodine atoms (two bridging iodines I(3) and I(4) and four terminal iodines I(1), I(2), I(5) and I(6)). In this building block, the

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bond angles of I-Hg-I are in the range of 92.6(3)-123.5(3)°, and two Hg(2)-I-Hg(3) angles are 82.8(3)° and 80.9(2)°, respectively. The distances of Hg-I$_{terminal}$ (2.661(1)-2.729(1) Å) are slightly shorter than those of Hg-I$_{bridge}$ (2.805(9)-3.004(1) Å). The distance of Hg(2)···Hg(3) (3.840(1) Å) is longer than the sum of van der Waals Radii (3.40 Å), which shows no interaction between the metal ions. Noteworthily, the distance of Hg(1)-I(5) (3.228(8) Å) is slightly longer than those of other Hg-I.

In the cation of complex **5**, an open structure is formed by one carbene ligand $\mathbf{L}^{8}$ and two [HgCl] units. Two C-Hg-Cl arrangements are approximately linear with the angles of 174.5(3)° and 177.5(3)°, and two C-Hg-Cl units point to the opposite directions. The bond distances of Hg-Cl are in the range of 2.288(2)-2.288(3) Å. The anionic unit $[Hg_3Cl_8]^{2-}$ of **5** contain five terminal chlorine atoms (Cl(3), Cl(4), Cl(8), Cl(9) and Cl(10)) and three bridging chlorine atoms (Cl(5), Cl(6) and Cl(7)). Among three bridging chlorine atoms, Cl(6) and Cl(7) are di-coordinated, and Cl(5) is tri-coordinated. The bond distances of Hg-Cl$_{bridge}$ (2.448(3)-2.969(2) Å) are longer than those of Hg-Cl$_{terminal}$ (2.295(3)-2.348(3) Å). The bond angles of Cl-Hg-Cl and Hg-Cl-Hg are 80.0(7)-159.9(1)° and 83.8(7)-133.3(9)°, respectively.

In silver(I) complexes **6-8**, the bond distances of Ag-C are in the range of 2.058(7)-2.119(4) Å. For both **6** and **7**, the silver(I) atom is di-coordinated with two carbene carbon atoms. The C-Ag-C arrangement is approximately linear with the bond angles of 173.9(1)° for **6** and 177.4(1)° for **7**. These values are similar to those of the reported NHC-silver(I) complexes.[23] In $Cr_2O_7^{2-}$ unit of **6**, an inversion center is observed. Different from **6**, the cation of **7** contains a 30-membered macrometallocycle formed by two bidentate carbene ligands $\mathbf{L}^{7}$ and two silver(I) atoms. The Ag···Ag separation of 3.575(3) Å is longer than the sum of van der Waals Radii (3.44 Å), which suggests no interaction between the metal ions.

In complex **8**, a dimer $[L^3Ag_2Cl_2]_2$ is formed by two monomers $[L^3Ag_2Cl_2]$ via two Ag-Cl bonds, in which an inversion center is observed. In two ends of dimer, Ag(1) or Ag(1A) are di-coordinated with one carbene carbon atom and one chlorine atom. In the center of dimer, the quadrangular Ag_2Cl_2 is coplanar arrangement, where

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each silver(I) atom is tri-coordinated with one carbene carbon atom and two chlorine atoms. The bond angles of the Ag(2)-Cl(2)-Ag(2A) and Cl(2)-Ag(2)-Cl(2A) are 88.3(3)° and 91.7(3)°, respectively. The bond angle of C(30)-Ag(2)-Cl(2) is 136.2(1)°, and this value is less than that of C(13)-Ag(1)-Cl(1) (175.7(1)°). The distance of Ag(2)-Cl(2) are 2.545(1) Å, and this value is slightly longer than that of Ag(1)-Cl(1) (2.339(1) Å). In each monomer, two benzimidazole rings are approximately parallel with the dihedral angle of 1.9(3)°, and the dihedral angle between two pyridine rings is 69.3(2)°. The benzimidazole ring and adjacent pyridine ring are almost perpendicular with the dihedral angle of 87.5(2)°. The Ag(2)···Ag(2A) separation of of 3.567(3) Å is longer than the sum of van der Waals Radii (3.44 Å), which shows no interaction between the metal ions.

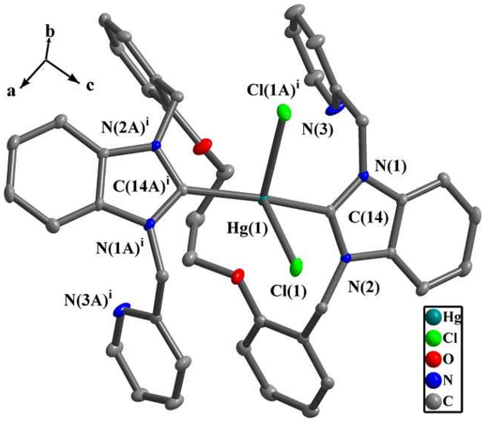

Fig. 1 Perspective view of **1** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity. Symm. Code: i: *y*, *x*, -*z*.

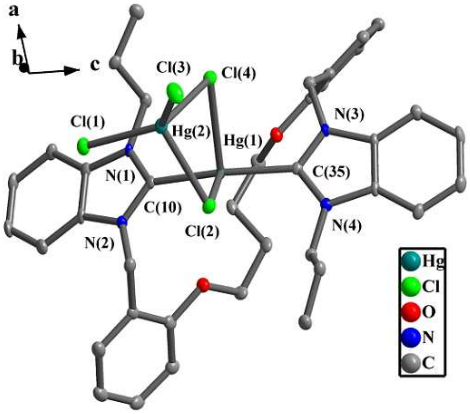

Fig. 2 Perspective view of **2** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity.

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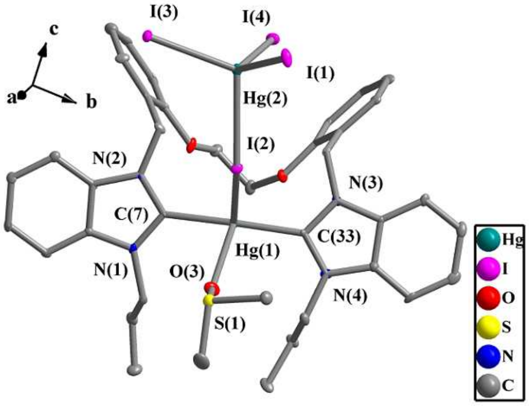

Fig. 3 Perspective view of **3** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity.

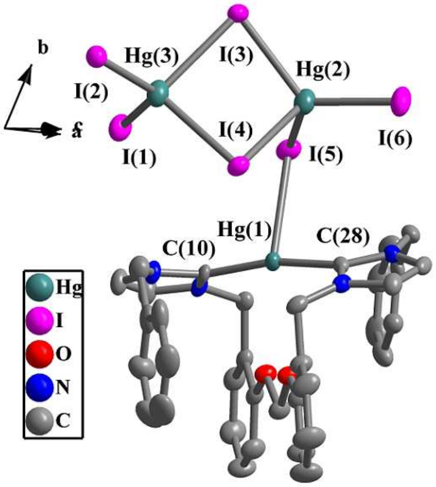

Fig. 4 Perspective view of **4** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity.

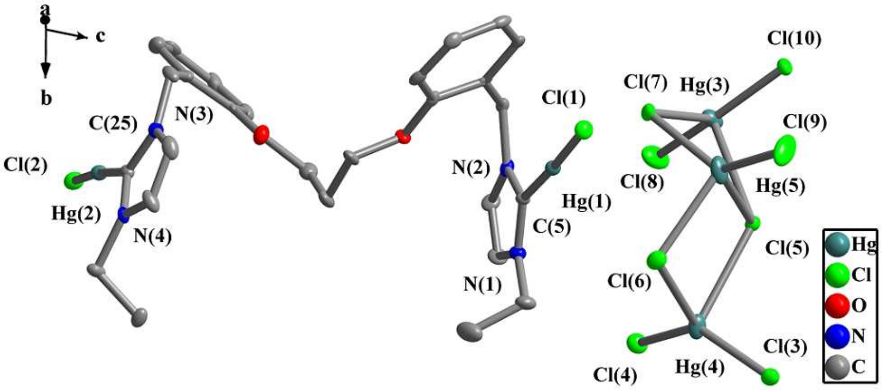

Fig. 5 Perspective view of **5** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity.

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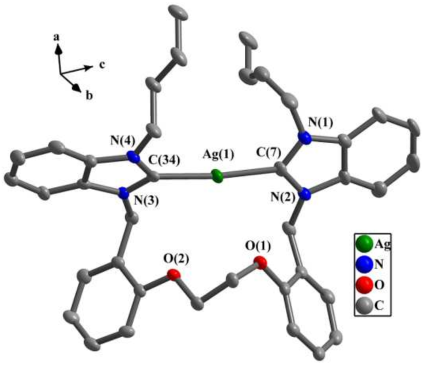

Fig. 6 Perspective view of **6** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity.

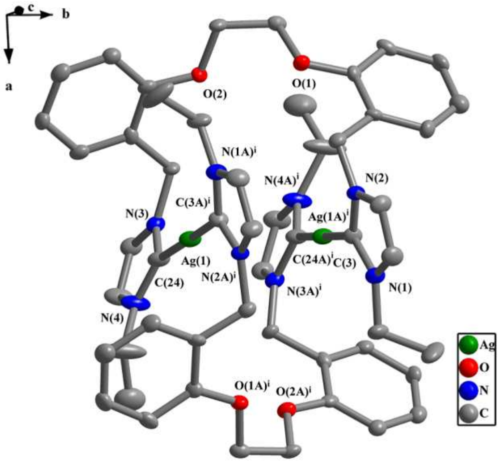

Fig. 7 Perspective view of **7** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity. Symm. Code: i: 0.5 - *x*, 1.5 - *y*, *z*.

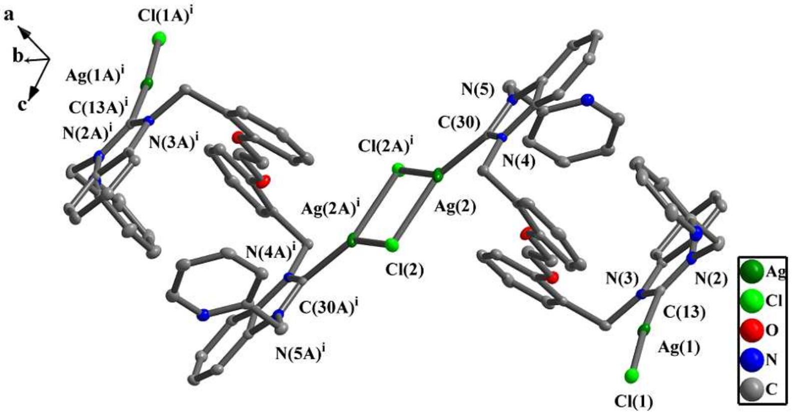

Fig. 8 Perspective view of **8** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms were omitted for clarity. Symm. Code: i: 2 - *x*, 1 - *y*, 2 - *z*.

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The crystal packings of complexes 1-8

In the crystal packing of **1**, 2D supramolecular layer (Fig. S1(a) in Supplementary Information) and 3D supramolecular architecture (Fig. S1(b)) are formed via two types of π-π stacking interactions[24] (the data of π···π interactions being given in Table S2). One is between intermolecular benzimidazole rings and benzene rings, and another is between intermolecular benzene rings and pyridine rings.

As shown in Fig. S2(a), 2D supramolecular layer of **2** is formed through two types of C-H···Cl hydrogen bonds[25] (the data of hydrogen bonds being given in Table S3). The hydrogen atoms in the hydrogen bonds are from methylene groups or benzimidazole rings. Additionally, 2D supramolecular layers are further extended into 3D supramolecular architecture through π-π stacking interactions from benzene rings (Fig. S2(b)).

In the crystal packing of **3**, the 2D supramolecular layers (Fig. S3(a)) are formed by C-H···π contacts[26] and π···π interactions from intermolecular benzimidazole rings. In C-H···π contacts, the hydrogen atoms are from benzene rings and π systems are from benzimidazole rings (the data of C-H···π contacts being given in Table S2). The 2D supramolecular layers are further extended into 3D supramolecular architecture (Fig. S3(b)) through C-H···I hydrogen bonds.[27] In C-H···I hydrogen bonds, the hydrogen atoms are from methylene groups.

In the crystal packing of **4** (Fig. S4), 2D supramolecular layer is formed through C-H···π contacts and two types of C-H···I hydrogen bonds. In C-H···π contacts, the hydrogen atoms are from benzene rings and π systems are from benzene rings. In C-H···I hydrogen bonds, the hydrogen atoms are from benzene rings.

In the crystal packing of **5** (Fig. S5), 2D supramolecular layer is formed by two types of C-H···Cl hydrogen bonds. In the hydrogen bonds, the hydrogen atoms are from different methylene groups.

In the crystal packing of **6**, 2D supramolecular layer (Fig. S6(a)) is formed through C-H···π contacts and two types of C-H···O hydrogen bonds.[28] In C-H···π contacts, the hydrogen atoms are from CH_2 of ^{n}butyl groups and π systems are from benzene rings. In the hydrogen bonds, oxygen atoms are from $[Cr_2O_7]^{2-}$ units, and the hydrogen atoms are from CH_2 of benzyl groups or ether chains. Additionally, 2D supramolecular layers are further extended into 3D supramolecular network via new C-H···O hydrogen bonds (Fig. S6(b)). In the hydrogen bonds, the oxygen atoms are from $[Cr_2O_7]^{2-}$ units, and the hydrogen atoms are from benzimidazole rings.

In the crystal packing of **7** (Fig. S7(a) and Fig. S7(b)), 2D supramolecular layer and 3D network are formed via the same C-H···π contacts. In C-H···π contacts, the hydrogen atoms are from methylene groups and π systems are from the benzene rings.

In the crystal packing of **8**, 2D supramolecular layer (Fig. S8(a)) is formed by C-H···π contacts. In C-H···π contacts, the hydrogen atoms are from benzimidazole rings and π systems are from benzene rings. 2D supramolecular layers are further extended into 3D supramolecular architecture through new C-H···π contacts (Fig. S8(b)). In new C-H···π contacts, the hydrogen atoms are from methylene groups of picolyl and π systems are from benzimidazole rings.

The conformations of NHC mercury(II) and silver(I) complexes based on the bidentate carbene ligands with different linkers

In order to further undersand the influence of different precursors and different metal sources on the conformations of metal complexes in solid state, in the paper, eight precursors and different metal sources ($HgCl_2$, HgI_2, $Hg(OAc)_2$ and Ag_2O) are used for the preparation of metal complexes. In these precursors, there exist differences in four positions as shown in Scheme 1, namely, (a) the size of linkers ($(CH_2)_n$, n = 1-4), (b) the different R (Et, ^{n}Pr, ^{n}Bu, CH_2Ph or CH_2Py), (c) the imidazole or benzimidazole, and (d) the different anions (Cl^- and PF_6^-). Complexes **1-8** contain three types of conformations as shown in Scheme 2: the mononuclear macrocycle (*e.g.*, complexes **1-4** and **6**), the dinuclear macrocycle (*e.g.*, complex **7**), and the open structure (*e.g.*, complexes **5** and **8**). The differences of these conformations are mainly related to the ratios of precursors to metal sources and the concentrations of reactants as shown in Table 1, while the differences of precursors or metal sources have little influence on these conformations. In NHC-Hg(II) complexes **1-5**, the different molar ratios of precursors to mercury salts lead to diverse connectivities. For example, complexes **1-4** contain similar cationic macrometallocycles (Scheme 2(1)-(4)), but their anionic units

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are different. Anions are highly dependent on the amount of mercury salts added. When mercury salts are excessive, the different anionic units $[Hg_pY_q]^{2-}$ can be formed (Y = Cl or I; p = 1, 2 or 3; q = 4, 6 or 8), and the similar cases have been reported.[19a, 29] By contrast, the formation of cyclic NHC-Ag(I) complexes **6** and **7** are related mainly to the concentration of reactants. Upon precursor and Ag_2O at a 1:0.5 molar ratio, a high concentration of reactants affords the mononuclear macrocycle **6** as main product, however, a dilute solution of reactants gives dinuclear macrocycle **7** as dominating product. This phenomenon has also been reported by Xu and Saito.[30]

Table 1 The molar ratios of precursors to metal sources for **1-8**

	Precursors:metal sources	Complexes
NHC-Hg(II)	1:1	**1**
	1:2	**2** or **3**
	1:3	**4**
	1:5	**5**
NHC-Ag(I)	1:0.5 in high conc.	**6**
	1:0.5 in dilute conc.	**7**
	1:1	**8**

Based on literature reports and our results obtained here, NHC mercury(II) and silver(I) complexes, which are formed via the reaction of the bidentate imidazolium (or benzimidazolium) salts (**A**) bearing different linkers with mercury(II) compounds or silver(I) compounds, contain mainly five types of conformations (**I**)-(**V**) as shown in Scheme 3: (1) the mononuclear macrocycle (**I**) with one bidentate carbene ligand, such as complexes **1-4**, **6** and known complexes with different linkers (linkers: phenelene[6(b), 31] pyridyl, [31(i), 31(n), 32] and ether chain[29(a), 29(b), 31(c), 33]). Compared with known complexes, **1-4** and **6** show similar cationic macrometallocycles, and their major differences are the anionic units (such as Cl^-, Br^-, I^-, PF_6^-, OAc^- or $[Hg_pY_q]^{2-}$). The high concentration of reactants is usually favorable for the preparation of this type of macrometallocycle. (2) The dinuclear macrocycle (**II**) with two bidentate carbene ligands, such as complex **7** and known complexes with different linkers (linkers: phenelene,[10(a), 10(b), 31(o), 31(r), 32(s), 34] pyridyl,[19(a), 23(a), 31(e), 31(i), 31(r), 35] ether chain[8(b), 29(c)] and alkyl[9(b), 31(g), 31(q), 31(t), 36]). For these complexes, the diverse distortions of macrometallocycle are the major different due to the flexibility and

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length of linkers. The dilute concentration of reactants[30] and hexafluorophosphate as counteranion[10(a), 31(g), 31(s), 37] are usually helpful to the preparation of this type of macrometallocycle. (3) The dinuclear macrocycle (**III**) with one bidentate carbene ligands,[9(b), 30(a), 31(g), 31(o), 31(t)-31(v)] which is likely to be obtained upon precursor and metal ion at a 1:2 molar ratio. (4) The open structure (**IV**) (such as complex **5** and known complexes[6(b), 19(b), 31(g), 31(s), 38]). (5) The oligomer (such as complex **8** and known complexes[31(k), 31(w), 39]). The conformations of complexes **5** and **8** are similar to those of known complexes with different linkers.

On the whole, the conformations of NHC mercury(II) and silver(I) complexes based on the bidentate carbene ligands with different linkers are mainly related to the following factors: (a) the ratio of precursor to metal source; (b) the concentration of reactants; (c) the flexibility and length of linkers in ligands; (d) the anionic types in reaction system (involving: the anions from precursors or metal sources (such as PF_6^-, Cl^-, Br^-, I^-, OAc^-, CO_3^{2-} or NO_3^-), and new formation of anions in the reactions (such as $[Hg_pY_q]^{2-}$ or $Cr_2O_7^{2-}$)). In addition, some solvents (such as CH_3CN, DMSO or DMF), which can participate in coordination with metal ions, may have also some effects on the conformations of complexes. The other factors, such as benzimidazole or imidazole rings, have probably little influence on the formation of diverse conformations.

Additionally, in the preparations of NHC mercury(II) and silver(I) complexes, whether or not the bases (such as KO^tBu, K_2CO_3 or NaOAc) are used depends mainly on metal sources. When the metal sources are alkaline oxide (like Ag_2O) or metal salts with OAc^- or CO_3^{2-} anions (such as AgOAc, Ag_2CO_3 or $Hg(OAc)_2$, which have capability to snatch proton of NC*H*N from benzimidazolium or imidazolium salts), the base is not required. However, when the anions of metal sources are Cl^-, Br^-, I^- or NO_3^- (such as: $HgCl_2$, $HgBr_2$, HgI_2 or $AgNO_3$), the base must be used.

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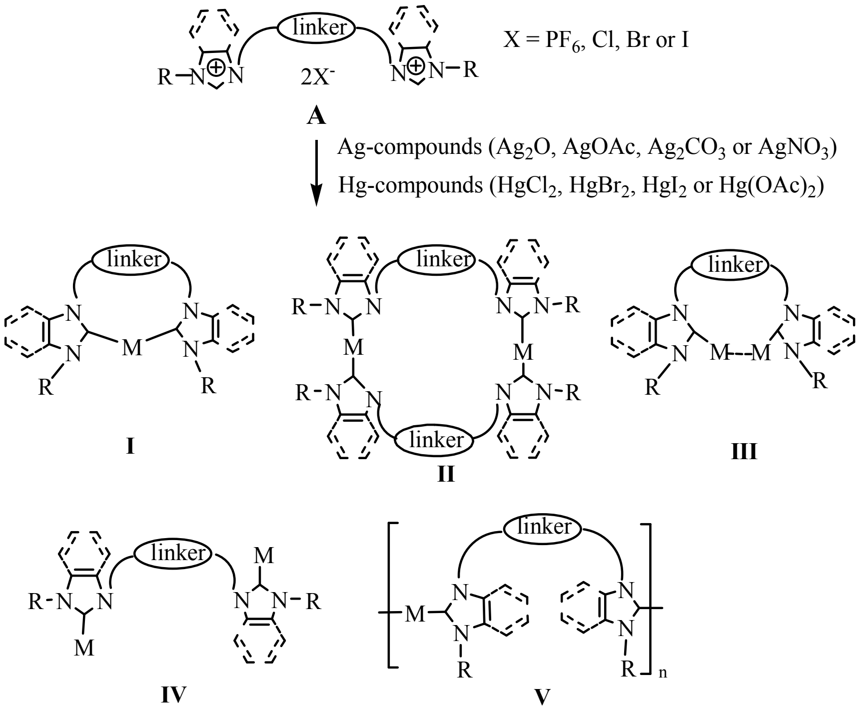

Scheme 3 The conformations of NHC mercury(II) and silver(I) complexes.

Recognition of nitrate anion using 6 as a chemosensor

According to the size of cavity and structural characteristics of **6**, the selective recognition of some anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, OAc^- and NO_3^-, and their cations being tetrabutyl ammonium (TBA^+)) using **6** as a chemosensor was investigated by fluorescent and UV/vis spectroscopic methods in acetonitrile at 25 ˚C (Fig. 9 and Fig. S9 in Supplementary Information).

As shown in Fig. 9, the chemosensor **6** exhibits double emission at *ca*. 296 nm and 415 nm (λ_{ex} = 254 nm; the excitation and emission slits are 5 nm and 3 nm, respectively). The peak at 296 nm is attributed to the emission of benzimidazole. The peak at 415 nm was due to anion induced eximer formation, and the similar emission peak is also observed in the literature of benzimidazole derivatives.[40] Upon the addition of 10.0 mol eq. F^-, Cl^-, Br^-, $H_2PO_4^-$, HSO_4^- and OAc^-, the fluorescence emission intensity of **6** does not obviously change. The addition of same amount of iodide anion resulted in the slight decrease of emission intensity at 296 nm and 415 nm, which is derived from heavy atom effect of iodine.[41] Whereas the addition of

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same amount of nitrate anion causes a great enhancement of emission intensity at 296 nm and 415 nm. According to the size of cavity (0.47 nm × 0.32 nm) and structural characteristics of **6**, the size of nitrate anion (0.21 nm × 0.21 nm) may match with complex **6**, and nitrate anion can be captured effectively by **6**. The main force between nitrate anion and **6** is electrostatic attraction coming from silver(I) atom and oxygen atom of nitrate anion (Scheme S1 in Supplementary Information). Upon the addition of nitrate anion into the solution of **6**, the remarkable enhancement of fluorescence intensity may be attributed to the electron-donating effect of oxygen atom of nitrate anion. Thus, complex **6** can be functioned as a highly selective fluorescent chemosensor for nitrate anion. In order to further understand the interactions of nitrate anion with **6**, the ^{1}H NMR spectra of **6**/NO_3^- are compared with those of **6**. As depicted in Fig. S15, the signals of protons from the benzene rings of phenol ether have split, and new peaks appear at δ 7.80 ppm and 8.00 ppm. This change may result from the formation of N-O···H hydrogen bonds between nitrate anion and hydrogen atoms from benzene rings of phenol ether. Thus N-O···H hydrogen bonds may inhance the combination of nitrate anion and **6**.

As shown in Fig. 10, upon the titration of nitrate anion into the solution of **6**, the fluorescence intensity at 296 nm and 415 nm increases gradually due to the interactions between nitrate anion and **6**.[42] In the inset of Fig. 10, when the ratio of $C_{NO_3^-}/C_{\mathbf{6}}$ was below or equal to 1:1, the fluorescence intensity shows a linear enhancement with the increasing concentration of nitrate anion. When the ratio was in range of 1:1 to 4:1, the tendency of the fluorescence intensity enhancement becomes slow. When the ratio exceeded 4:1, higher $C_{NO_3^-}$ will not lead to further emission enhancement. From the changes in nitrate-dependent fluorescence intensity, the detection limit is estimated to be 1.1×10^{-7} mol/L (Fig. S10).[43] The association constant *Ks* for **6**/NO_3^- was calculated as 3.67×10^5 M^{-1} (R = 0.992) by using the nonlinear least-square analysis (Equation 1, Fig. 10),[44]

$$F/F_0=1+(F_{max}/2F_0-1/2)\{1+C_{NO_3^-}/C_{\mathbf{6}}+1/K_SC_{\mathbf{6}}-[(1+C_{NO_3^-}/C_{\mathbf{6}}+1/KsC_{\mathbf{6}})^2-4C_{NO_3^-}/C_{\mathbf{6}}]^{1/2}\} \quad (1)$$

where *F* and *F*$_0$ are the fluorescence intensity of **6** in the presence and absence of

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NO_3^-, respectively; $F_{\max}$ is the maximum fluorescence intensity in the titration experiment; $C_{NO_3^-}$ and C_6 are the concentrations of nitrate anion and **6**, respectively; *Ks* is the association constant.

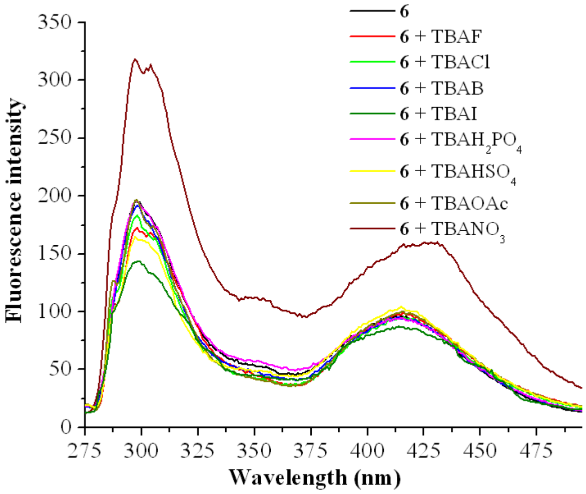

Fig. 9 Fluorescence spectra of **6** (1×10^{-5} mol/L) upon the addition of the tetrabutyl ammonium salts of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, OAc^- and NO_3^- (10.0 mol eq.) in acetonitrile at 25 ˚C.

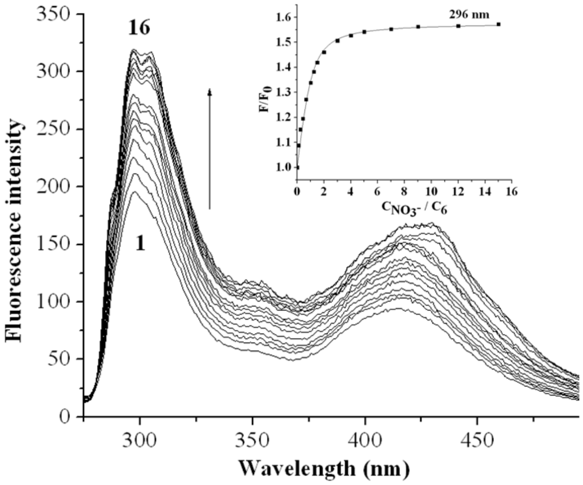

Fig. 10 Fluorescence titration spectra of **6** (1.0×10^{-5} mol/L) in the presence of different concentrations of nitrate anion in acetonitrile at 25 ˚C. $C_{NO_3^-}$ for curves 1-16 (from bottom to top) are 0, 0.11, 0.25, 0.43, 0.67, 1.0, 1.25, 1.5, 2.0, 3.0, 4.0, 5.0, 7.0, 9.0, 12.0, 15.0 × 10^{-5} mol/L. Inset: the fluorescence at 296 nm of **6** as a function of nitrate anion concentration.

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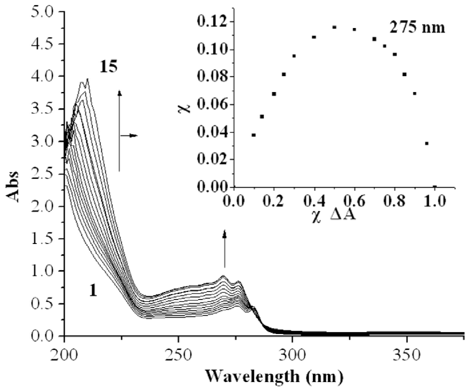

Fig. 11 UV/vis absorption spectra of **6** (1.0×10^{-5} mol/L) in acetonitrile at 25 ˚C. The concentrations of nitrate anion for curves 1-15 (from bottom to top) are: 0, 0.04, 0.11, 0.17, 0.26, 0.33, 0.43, 0.67, 1.0, 1.5, 2.4, 3.0, 4.0, 6.0, 9.0×10^{-5} mol/L. Inset: The Job plot for **6**/NO_3^- complex in acetonitrile at 275 nm.

In UV/vis titration experiment of **6**, the UV/vis absorption spectra increases gradually at 204-280 nm (Fig. 11) with the increasing of nitrate anion concentration, where a red shift at 204-225 nm is observed. The phenomenon indicates that interactions between nitrate anion and **6** reduce $\pi \rightarrow \pi^*$ transition energy of benzene rings.[45] It is notable that a 1:1 complexation stoichiometry for **6**/NO_3^- complex is established by Job's plot analysis at 275 nm (inset of Fig. 11),[9a, 46] which is in consistent with the fluorescence titration result as displayed in inset of Figure 10. The stability constant K for **6**/NO_3^- calculated from the plot of $A_0/\Delta A$ versus **6**/$C_{NO_3^-}$ based on the standard Benesi-Hildebrand equation (Equation 2) is $2.88 \times 10^5\ M^{-1}$ (R = 0.994) (Fig. S11),

$$A_0/(A_0\text{-}A)=\varepsilon_r(1/KC_{NO_3^-}+1)/(\varepsilon_r - \varepsilon_c) \quad (2)$$

where A_0 is the absorption of chemosensor **6** in the absence of nitrate anion, and A_0-A is the discrepancy of absorption between the absence and presence of nitrate anion; ε_r and ε_c are the molar extinction coefficients of **6** and **6**/NO_3^-, respectively; $C_{NO_3^-}$ is the concentration of nitrate anion. The stability constant K is given by the ratio of intercept/slope.[47]

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In order to further study the special selective ability of **6** as a chemosensor for nitrate anion, the competition experiments were conducted. Complex **6** (1.0×10^{-5} mol/L) was first mixed with 5.0 mol eq. various anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^- and OAc^-), and then 1.0 mol eq. nitrate anion was added and the competition events were monitored by fluorescent spectra. According to the fluorescent spectra, no obvious interference in the presence of 5.0 mol eq. various anions was observed (Fig. S12). In the case of chloride anion, the fluorescence intensity increased about 20% than that in the presence of nitrate anion alone. The fluorescence intensities of other anions were almost identical to that in the presence of nitrate anion alone. The results show that chemosensor **6** can discriminate between nitrate anion and other anions, especially dihydrogen phosphate anion and fluoride anion, which are common interfering anions in many cases.[48]

Fluorescent enhancement similar to Fig. 9 was also observed after the addition of other nitrate salts (15.0×10^{-5} mol/L) with different countercations (Li^+, Na^+, K^+, NH_4^+, Zn^{2+}, Co^{2+} and Ni^{2+}) to **6** (1×10^{-5} mol/L) (Fig. S13). Thus, the different cations had no obvious influence on the binding between **6** and nitrate anion. Reversible binding of **6** with nitrate anion was also carried out (Fig. S14). The addition of 7.5 mol eq. mercury(II) cation to a mixture of **6** (1.0×10^{-5} mol/L) and nitrate anion (15.0×10^{-5} mol/L) resulted in the decrease of fluorescence intensity at 296 nm and 415 nm, and the fluorescence intensity is approximately equal to **6**, which signifies the regeneration of the free **6**. The fluorescence intensity increased upon addition of nitrate anion again. This result shows that **6** is a good chemosensor for nitrate anion with admirable ability of reversibility and regeneration.

Conclusions

In summary, a series of bis-benzimidazolium (or bis-imidazolium) salts and their eight N-heterocyclic carbene mercury(II) and silver(I) complexes have been synthesized and characterized. Each of complexes **1-4**, **6** and **7** contains one macrometallocycle. Complex **5** is an open structure and complex **8** is a dimer. The different connectivities of complexes **1-8** are mainly related to the ratios of precursors to metal sources and the concentrations of reactants, while the differences of

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precursors or metal sources have little influence on the conformations of complexes **1-8**. The selective recognition of nitrate anion using macrometallocycle **6** as a chemosensor was studied by the methods of fluorescent and UV/vis spectroscopic titrations. *Ks* value of 3.67×10^5 M^{-1} based on the nonlinear least-square analysis and *K* value of 2.88×10^5 M^{-1} based on the standard Benesi-Hildebrand equation are similar to each other.[49] Large *Ks* and *K* values show that macrometallocycle **6** has great affinity to nitrate anion. The special selective ability of **6** for nitrate anion make that it can discriminate nitrate anion and other anions in acetonitrile. From the changes in nitrate-dependent fluorescence intensity, the detection limit was estimated to be 1.1×10^{-7} mol/L. The high selectivity and sensitivity and the great affinity to nitrate anion mean that the chemosensor has a potential application for quantitative measurement of nitrate anion. Further studies on the synthesis of new organometallic compounds from precursors $\mathbf{L^1H_2{\cdot}Cl_2}$-$\mathbf{L^6H_2{\cdot}Cl_2}$, $\mathbf{L^7H_2{\cdot}(PF_6)_2}$ and $\mathbf{L^8H_2{\cdot}(PF_6)_2}$, and the recognition for other guests 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 $^{13}C\{^1H\}$ 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 ^1H and ^{13}C NMR. *J* values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. The luminescent spectra were conducted on a Cary Eclipse fluorescence spectrophotometer. UV-vis spectra were obtained using a JASCO-V570 spectrometer.

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

A DMF (80 mL) soulution of salicylic aldehyde (15.601 g, 127.7 mmol), 1,2-dibromoethane (10.000 g, 53.2 mmol) and anhydrous K_2CO_3 (17.656 g, 127.7

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mmol) was stirred for 24 hours at 50 ˚C under nitrogen protection. The resulting brown solution was poured into water (200 mL), and a brown precipitate was formed. The product was filtered to give a brown powder of 1,2-bis[2-(formyl)phenoxy]ethylene. Yield: 12.196 g (83%). M.p.: 146-148 ˚C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 4.44 (t, J = 8.0 Hz, 4H, C*H*$_2$), 7.03 (m, 4H, Ph*H*), 7.53 (t, J = 8.8 Hz, 2H, Ph*H*), 7.80 (d, J = 8.0 Hz, 2H, Ph*H*), 10.53 (s, 2H, C*H*O).

Sodium borohydride (3.359 g, 88.8 mmol) was slowly added to a THF/C_2H_5OH (150 mL, 1:1, v/v) solution of 1,2-bis[2-(formyl)phenoxy]ethylene (10.000 g, 37.0 mmol) with stirring for 2 hours in the ice-water bath. Then the solution was stirring under refluxing for 10 hours. After the solvent was removed with a rotary evaporator, H_2O (150 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3 × 30 mL) and the organic phase was dried over anhydrous $MgSO_4$. After removing CH_2Cl_2, a white solid of 1,2-bis[2-(hydroxymethyl)phenoxy]ethylene was obtained. Yield: 9.192 g (90%). M.p.: 122-124 ˚C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.42 (s, 2H, O*H*), 4.31 (s, 4H, C*H*$_2$), 4.49 (s, 4H, C*H*$_2$OH), 6.95-7.00 (m, 4H, Ph*H*), 7.18 (t, J = 10.0 Hz, 2H, Ph*H*), 7.37 (d, J = 7.6 Hz, 2H, Ph*H*).

To a solution of 1,2-bis[2-(hydroxymethyl)phenoxy]ethylene (10.012 g, 36.5 mmol) in $CHCl_3$ (100 mL) was added thionyl chloride (17.348 g, 145.8 mmol). The mixture was refluxed for 12 hours and poured into water (300 mL) after cooling. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed and a white solid of 1,2-bis[2-(chloromethyl)phenoxy]ethylene was obtained. Yield: 8.475 g (74%). M.p.: 96-98 ˚C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 4.43 (s, 4H, OC*H*$_2$), 4.70 (s, 4H, C*H*$_2$Cl), 6.96 (d, J = 7.2 Hz, 2H, Ph*H*), 7.14 (d, J = 8.4 Hz, 2H, Ph*H*), 7.34-7.41 (m, 4H, Ph*H*).

An acetone (100 mL) solution of N-^{n}propylbenzimidazole (2.371 g, 14.8 mmol) and 1,2-bis[2-(chloromethyl)phenoxy]ethylene (2.085 g, 6.7 mmol) was stirred for 3 days under refluxing, and a white precipitate was formed. The product was filtred and washed with small portions of acetone to give a white powder of 1,2-bis[2-(N-^{n}butylbenzimidazoliumylmethyl)phenoxy]ethylene chloride (**L^{1}H$_2$·Cl$_2$**). Yield: 3.750 g (88%). M.p.: 160-162 ˚C. Anal. Calcd for $C_{36}H_{40}O_2N_4Cl_2$: C, 68.45; H,

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6.38; N, 8.87%. Found: C, 68.67; H, 6.54; N, 8.67%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.81 (t, J = 7.4 Hz, 6H, C*H*$_3$), 1.82 (m, 4H, C*H*$_2$), 4.36 (t, J = 7.6 Hz, 8H, C*H*$_2$), 5.66 (s, 4H, C*H*$_2$), 7.07 (t, J = 7.4 Hz, 2H, Ar*H*), 7.16 (d, J = 8.4 Hz, 2H, Ar*H*), 7.42 (m, 4H, Ar*H*), 7.62 (m, 4H, Ar*H*), 7.85 (d, J = 8.4 Hz, 2H, Ar*H*), 8.02 (d, J = 8.4 Hz, 2H, Ar*H*), 10.06 (s, 2H, 2-bimi*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 10.5 (*C*H$_3$), 22.0 (*C*H$_2$), 47.8 (*C*H$_2$), 55.9 (*C*H$_2$), 66.7 (*C*H$_2$), 112.5 (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*), 130.7 (bimi*C* or Ph*C*), 130.8 (bimi*C* or Ph*C*), 142.6 (2-bimi*C*), 156.5 (Ph*C*) (bimi = benzimidazole).

Bis-benzimidazolium (or bis-imidazolium) salts **$L^2H_2\cdot Cl_2$-$L^6H_2\cdot Cl_2$** were prepared in a manner analogous to that of **$L^1H_2\cdot Cl_2$** (the data of analyses being given in Supplementary Information).

Preparation of 1,2-bis[2-(N-ethylimidazoliumylmethyl)phenoxy]ethylene hexafluorophosphate ($L^7H_2\cdot(PF_6)_2$)

This compound was prepared through two steps of reactions, and the first step is in a manner analogous to that of **$L^1H_2\cdot Cl_2$**, only N-ethylimidazole (1.422 g, 14.8 mmol) was used instead of N-^{n}butylbenzimidazole. The second step is anionic exchange with NH_4PF_6. NH_4PF_6 (1.467 g, 9.0 mmol) was added to a methanol (60 mL) solution of **$L^7H_2\cdot Cl_2$** (2.013 g, 4.0 mmol) with stirring, and a white precipitate was formed immediately. A white powder of 1,2-bis[2-(N-ethylimidazoliumylmethyl)phenoxy]ethylene hexafluorophosphate (**$L^7H_2\cdot(PF_6)_2$**) was obtained after filtration and washing with small portions of cold methanol. Yield: 2.513 g (86%). M.p.: 216-218 ˚C. Anal. Calcd for $C_{26}H_{32}O_2N_4P_2F_{12}$: C, 43.22; H, 4.46; N, 7.75%. Found: C, 43.51; H, 4.68; N, 7.91%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.36 (t, J = 7.2 Hz, 6H, C*H*$_3$), 4.11 (t, J = 7.4 Hz, 4H, C*H*$_2$), 4.44 (d, J = 7.2 Hz, 4H, OC*H*$_2$), 5.29 (d, J = 7.6 Hz, 4H, C*H*$_2$), 7.06 (t, J = 7.4 Hz, 2H, Ar*H*), 7.20 (t, J = 7.8 Hz, 2H, Ar*H*), 7.40 (d, J = 6.4 Hz, 4H, Ar*H*), 7.43 (d, J = 7.6 Hz, 2H, Ar*H*), 9.10 (s, 2H, Ar*H*), 9.12 (s, 2H, 2-imi*H*). ^{13}C{^{1}H} NMR (100 MH$_Z$, DMSO-d$_6$): δ 15.0 (*C*H$_3$), 44.2 (*C*H$_2$), 47.8 (*C*H$_2$), 66.7 (*C*H$_2$), 112.4 (Ph*C*), 121.1 (Ph*C*), 122.0 (Ph*C*), 122.4 (Ph*C*), 122.6 (Ph*C*), 130.5 (imi*C* or Ph*C*), 130.8 (imi*C* or Ph*C*), 135.7 (2-imi*C*), 156.2 (Ph*C*).

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Bis-imidazolium salt **$L^8H_2·(PF_6)_2$** was prepared in a manner analogous to that of **$L^7H_2·(PF_6)_2$** (the data of analyses being given in Supplementary Information).

Preparation of [L^4HgCl_2] (1)

A CH_3CN (30 mL) suspension of **$L^4H_2·Cl_2$** (0.223 g, 0.3 mmol) and $Hg(OAc)_2$ (0.095 g, 0.3 mmol) was stirred at about 80 ˚C for 12 hours, and an orange solution was formed. 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 **1**. Yield: 0.091 g (32%)，Mp: 240-242 ˚C. Anal. Calcd for $C_{43}H_{38}Cl_2HgN_6O_2$: C, 54.80; H, 4.06; N, 8.91%. Found: C, 54.62; H, 4.33; N, 8.58%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.72 (d, J = 4.8 Hz, 2H, C*H*$_2$), 3.83 (t, J = 2.8 Hz, 4H, C*H*$_2$), 5.94 (s, 4H, C*H*$_2$), 6.39 (s, 4H, C*H*$_2$), 6.92 (s, 2H, C*H*$_2$), 7.04 (d, J = 2.4 Hz, 2H, Ar*H*), 7.19 (d, J = 10.0 Hz, 2H, Ar*H*), 7.35 (d, J = 10.8 Hz, 2H, Ar*H*), 7.65 (m, 6H, Ar*H*), 7.88 (m, 6H, Ar*H*), 8.14 (d, J = 8.0 Hz, 2H, Ar*H*), 8.26 (s, 2H, Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 28.7 (*C*H$_2$), 50.3 (*C*H$_2$), 51.0 (*C*H$_2$), 62.7 (*C*H$_2$), 111.8 (Ph*C*), 113.1 (bimi*C*), 113.5 (bimi*C*), 120.2 (bimi*C* or Ph*C*), 121.9 (bimi*C* or Ph*C*), 123.1 (Ph*C* or Py*C*), 123.5 (Ph*C* or Py*C*), 125.2 (Ph*C*), 125.4 (PhC), 130.5 (bimi*C* or Ph*C*), 131.9 (Py*C*), 132.4 (PyC), 133.7 (Py*C*), 137.6 (Py*C*), 149.5 (Py*C*), 153.7 (Py*C*), 156.3 (Ph*C*), 185.2 (C_{carbene}).

Preparation of [L^5Hg]($HgCl_4$) (2)

A CH_3CN (30 mL) suspension of **$L^5H_2·Cl_2$** (0.197 g, 0.3 mmol), $HgCl_2$ (0.163 g, 0.6 mmol) and KO^{t}Bu (0.078 g, 0.7 mmol) was stirred at about 80 ˚C for 12 hours, and an orange solution was formed. 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 **2**. Yield: 0.153 g (45%), Mp: 257-259 ˚C. Anal. Calcd for $C_{38}H_{42}Cl_4Hg_2N_4O_2$: C, 40.39; H, 3.74; N, 4.95%. Found: C, 40.52; H, 3.95; N, 4.71%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.81 (t, J = 6.0 Hz, 6H, C*H*$_3$), 1.37 (s, 4H, C*H*$_2$), 1.90 (q, J = 8.0 Hz, 4H, C*H*$_2$), 3.89 (s, 4H, C*H*$_2$), 4.74 (t, J = 6.0 Hz, 4H, C*H*$_2$), 5.84 (s, 4H, C*H*$_2$), 6.92 (t, J = 8.0 Hz, 2H, Ar*H*), 7.04 (d, J = 8.0 Hz, 2H, Ar*H*), 7.31 (t, J = 4.0 Hz, 2H, Ar*H*), 7.61 (m, 6H, Ar*H*), 7.75 (d, J = 8.0 Hz, 2H, Ar*H*), 8.04 (d, J = 8.0 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 10.7 (*C*H$_3$), 23.2 (*C*H$_2$), 25.2

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(CH_2), 49.2 (CH_2), 58.8 (CH_2), 67.7 (CH_2), 112.1 (Ph*C*), 113.5 (bimi*C*), 120.4 (bimi*C* or Ph*C*), 125.5 (Ph*C*), 130.3 (bimi*C* or Ph*C*), 130.5 (bimi*C* or Ph*C*), 133.0 (bimi*C* or Ph*C*), 133.2 (bimi*C* or Ph*C*), 156.8 (Ph*C*), 192.6 ($C_{carbene}$).

Complexes $[L^1Hg(DMSO)](HgI_4)$ (**3**), $[L^6Hg(Hg_2I_6)]$ (**4**) and $[L^8Hg_2Cl_2](Hg_3Cl_8)$ (**5**) were prepared in a manner analogous to that of complex **2** (the data of analyses being given in Supplementary Information).

Preparation of $[L^2Ag](Cr_2O_7)_{0.5}$ (6)

Silver oxide (0.034 g, 0.15 mmol) and CrO_3 (0.029 g, 0.3 mmol) were added to a CH_3CN/CH_2Cl_2 (15 mL, 2:1, v/v) solution of precursor $\mathbf{L^2H_2 \cdot Cl_2}$ (0.197 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 **6**. Yield: 0.173 g (71%). M.p.: 218-220 ˚C. Anal. Calcd for $C_{38}H_{42}AgCrN_4O_{5.5}$: C, 56.86; H, 5.27; N, 6.98%. Found: C, 56.44; H, 5.56; N, 6.76%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.91 (t, J = 7.2 Hz, 6H, CH_3), 1.37 (q, J = 9.8 Hz, 4H, CH_2), 1.89 (t, J = 9.6 Hz, 4H, CH_2), 4.26 (s, 4H, OCH_2), 4.53 (t, J = 6.6 Hz, 4H, NCH_2), 5.76 (s, 4H, CH_2Ph), 7.07 (m, 4H, Ar*H*), 7.44 (m, 6H, Ar*H*), 7.62 (d, J = 9.6 Hz, 2H, Ar*H*), 7.77 (d, J = 9.6 Hz, 2H, Ar*H*), 7.86 (d, J = 9.6 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 15.1 (CH_3), 21.2 (CH_2), 33.7 (CH_2), 49.8 (CH_2), 50.8 (CH_2), 66.7 (CH_2), 112.8 (bimi*C*), 113.3 (bimi*C*), 121.2 (bimi*C* or Ph*C*), 124.0 (bimi*C* or Ph*C*), 124.4 (bimi*C* or Ph*C*), 130.6 (bimi*C* or Ph*C*), 131.8 (bimi*C* or Ph*C*), 133.9 (Ph*C*), 156.7 (Ph*C*). The carbene carbon was not observed.

Complexes $[L^7{}_2Ag_2](PF_6)_2$ (**7**) and $[L^3Ag_2Cl_2]_2$ (**8**) were prepared in a manner analogous to that of complex **6** (the data of analyses being given in Supplementary Information).

UV titrations

UV titrations were performed on a JASCO-V570 spectrometer using a 1 cm path-length quartz cuvette. Acetonitrile used in the titrations was freshly distilled over calcium hydride. Titrations were carried out by placing the receptor **6** (1×10^{-5} mol/L) into the 4 mL cuvette and adding increasing amounts of nitrate anion ($0\text{-}9.0 \times 10^{-5}$

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mol/L) using a microsyringe. The absorption spectra were recorded in the range of 200-400 nm. After each addition, an equilibration time of 8-10 min was allowed before the absorption spectra were recorded. Statistical analysis of the data was carried out using Origin 8.0.

Fluorescence titrations

Fluorescence titrations were performed on a Cary Eclipse fluorescence spectrophotometer using a 1 cm path-length quartz fluorescence cell. Acetonitrile used in the titrations was freshly distilled over calcium hydride. Titrations were carried out by placing the receptor **6** (1×10^{-5} mol/L) into the 4 mL cuvette and adding increasing amounts of nitrate anion ($0\text{-}15.0 \times 10^{-5}$ mol/L) using a microsyringe. The receptor solution was excited at 254 nm, and the emission spectra were recorded in the range of 264-500 nm. After each addition, an equilibration time of 8-10 min was allowed before the fluorescence intensity was recorded. Statistical analysis of the data was carried out using Origin 8.0.

X-ray data collection and structure determinations

For complexes **1-8**, selected single crystals were mounted on a Bruker APEX II CCD diffractometer at 173(2) K for **1** and **8**, and 293(2) K for the others with *Mo-K* radiation (λ = 0.71073 Å) by ω scan mode. Data collection and reduction were performed using the SMART and SAINT software[50] with frames of 0.6° oscillation in the range of $1.8° < \theta < 25°$. An empirical absorption correction was applied using the SADABS program.[51] The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package.[52] All hydrogen atoms were generated geometrically, assigned appropriated isotropic thermal parameters and included in the final calculations. Crystalographic data were summaried in Tables 2-4 for **1-8**.

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Table 2 Summary of crystalographic data for **1-3**

	1·H_2O	**2**	**3**
Chemical formula	$C_{43}H_{38}Cl_2HgN_6O_2 \cdot H_2O$	$C_{38}H_{42}Cl_4Hg_2N_4O_2$	$C_{38}H_{44}Hg_2I_4N_4O_3S$
Formula weight	960.30	1129.74	1545.61
Cryst syst	Tetragonal	Monoclinic	Monoclinic
Space group	$P4_12_12$	$P2_1/n$	Cc
a/Å	14.5037(6)	11.4527(6)	11.7672(9)
b/Å	14.5037(6)	20.9738(11)	19.2956(9)
c/Å	18.1126(10)	15.9974(8)	19.0562(11)
α/deg	90	90	90
β/deg	90	99.6210(10)	90.2920(10)
γ/deg	90	90	90
V/Å^3	3810.1(3)	3788.6(3)	4326.8(5)
Z	4	4	4
D_{calcd}, Mg/m^3	1.674	1.981	2.373
Abs coeff, mm^{-1}	4.230	8.417	10.030
$F(000)$	1912	2168	2848
Cryst size, mm	0.15 × 0.14 × 0.13	0.15 × 0.13 × 0.12	0.15 × 0.14 × 0.13
θ_{min}, θ_{max}, deg	1.99, 25.00	1.62 , 25.01	2.03, 25.01
T /K	173(2)	296(2)	296(2)
No. of data collected	19292	19043	10601
No. of unique data	3337	6678	5605
No. of refined params	250	453	473
Goodness-of-fit on F^2 [a]	1.004	1.049	1.057
Final R indices[b] [$I > 2\sigma(I)$]			
R_1	0.0220	0.0259	0.0384
wR_2	0.0545	0.0628	0.0917
R indices (all data)			
R_1	0.0235	0.0311	0.0390
wR_2	0.0556	0.0695	0.0920
Flack params	-0.010(6)		0.019(5)

[a] $GOF = [\Sigma\omega(F_o^2 - F_c^2)^2 /(n-p)]^{1/2}$, 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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Table 3 Summary of crystalographic data for **4-6**

	4	**5**	**6**
Chemical formula	$C_{35}H_{32}Hg_3I_6N_4O_2$	$C_{27}H_{32}Cl_{10}Hg_5N_4O_2$	$C_{38}H_{42}AgCrN_4O_{5.5}$
Formula weight	1903.82	1802.02	802.63
Cryst syst	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	11.3111(15)	14.4160(12)	10.840(4)
b/Å	13.5636(18)	15.8007(13)	13.647(5)
c/Å	16.321(2)	23.0337(14)	25.631(9)
α/deg	81.613(2)	90	90
β/deg	75.368(2)	127.396(3)	102.500(13)
γ/deg	67.987(2)	90	90
V/Å^3	2242.5(5)	4168.3(5)	3702(2)
Z	2	4	4
D_{calcd}, Mg/m^3	2.820	2.872	1.440
Abs coeff, mm^{-1}	14.408	19.025	0.871
F(000)	1688	3232	1652
Cryst size, mm	0.15 × 0.14 × 0.13	0.01 × 0.01 × 0.01	0.22 × 0.20 × 0.15
θ_{min}, θ_{max}, deg	1.29, 25.01	1.70, 25.01	1.63, 25.01
T /K	296(2)	296(2)	296(2)
No. of data collected	11504	20652	17003
No. of unique data	7865	7307	6469
No. of refined params	451	435	467
Goodness-of-fit on $F^{2\ a}$	1.037	1.011	1.066
Final R indices^b [$I > 2\sigma(I)$]			
R_1	0.0471	0.0370	0.0603
wR_2	0.1245	0.0788	0.1639
R indices (all data)			
R_1	0.0584	0.0539	0.0677
wR_2	0.1326	0.0895	0.1718
Flack params			

[a] $GOF = [\Sigma\omega(F_o^2 - F_c^2)^2 /(n-p)]^{1/2}$, 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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Table 4 Summary of crystalographic data for **7** and **8**

	7·2CH_3CN	**8**·CH_2Cl_2
Chemical formula	$C_{26}H_{30}AgF_6N_4O_2P$	$C_{42}H_{36}Ag_2Cl_2N_6O_2$
Formula weight	765.49	1028.33
Cryst syst	Orthorhombic	Monoclinic
Space group	*Fdd*2	$P2_1/c$
a/Å	44.800(3)	10.8182(5)
b/Å	17.1348(13)	20.4671(10)
c/Å	17.7314(14)	18.6333(9)
α/deg	90	90
β/deg	90	101.7600(10)
γ/deg	90	90
V/Å^3	13611.3(17)	4039.1(3)
Z	16	4
D_{calcd}, Mg/m^3	1.494	1.691
Abs coeff, mm^{-1}	0.709	1.281
F(000)	6240	2064
Cryst size, mm	0.14 × 0.13 × 0.12	0.17 × 0.16 × 0.14
θ_{min}, θ_{max}, deg	2.14, 25.01	1.92 , 25.01
T /K	296(2)	173(2)
No. of data collected	16885	20330
No. of unique data	5992	7093
No. of refined params	419	514
Goodness-of-fit on $F^{2\ a}$	1.027	1.046
Final R indices[b] $[I > 2\sigma(I)]$		
R_1	0.0310	0.0354
wR_2	0.0867	0.0877
R indices (all data)		
R_1	0.0356	0.0442
wR_2	0.0912	0.0934
Flack params	-0.07(3)	

[a] $GOF = [\Sigma\omega(F_o^2 - F_c^2)^2 /(n-p)]^{1/2}$, 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

Text, experimental procedures, tables, figures, and CIF files giving crystallographic data for **1-8**, fluorescence and UV spectra for **6**, and general considerations, characterization data, the changes of ^{1}H NMR spectra in benzene rings for **6** and **6**/NO_3^-, and ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra for all precursors and complexes.

References

1 (*a*) P. Metrangolo, T. Pilati, G. Terraneo, S. Biella and G. Resnati, *Coord. Chem. Rev.*, 2006, **250**, 2917-3244; (*b*) V. Vajpayee, Y. H. Song, M. H. Lee, H. Kim, M. Wang, P. J. Stang and K. W. Chi, *Chem. Eur. J.*, 2011, **17**, 7837-7844; (*c*) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79-128; (*d*) C. R. Bondy and S. J. Loeb, *Coord. Chem. Rev.*, 2003, **240**, 77-99; (*e*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486-516; (*f*) A. Chakraborty, R. Gunupuru, D. Maity, S. Patra, E. Suresh and P. Paul, *Inorg. Chem. Commun.*, 2010, **13**, 1522-1526; (*g*) A. Ghosh, B. Ganguly and A. Das, *Inorg. Chem.*, 2007, **46**, 9912-9918.

2 (*a*) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 191-221; (*b*) E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon and K. C. Nam, *J. Am. Chem. Soc.*, 2003, **125**, 12376-12377; (*c*) J. L. Sessler and D. Seidel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5134-5157; (*d*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609-1646; (*e*) C. Schmuck, *Coord. Chem. Rev.*, 2006, **250**, 3053-3067; (*f*) M. D. Best, S. L. Tobey and E. V. Anslyn, *Coord. Chem. Rev.*, 2003, **240**, 3-15.

3 (*a*) M. V. Bake, M. J. Bosnich, D. H. Brown, L. T. Byrne, V. J. Hesle, B. W. Skelton, A. H. White and C. C. Williams, *J. Org. Chem.*, 2004, **69**, 7640-7652; (*b*) K. Sato, S. Arai and T. Yamagishi, *Tetrahedron Lett.*, 1990, **40**, 5219-5222; (*c*) S. K. Kim, N. J. Singh, H. G. Kim, J. K. Kim, J. W. Lee, K. S. Kim and J. Yoon,

CrystEngComm Accepted Manuscript

Org. Lett., 2003, **5**, 2083-2086.

4 Q. S. Lu, L. Dong, J. Zhang, L. Jiang, Y. Huang, S. Qin, C. W. Hu and X. Q. Yu, *Org. Lett.*, 2009, **11**, 669-672.

5 (*a*) A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361-363; (*b*) A. J. Arduengo III, R. H. V. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530-5534; (*c*) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 772-780; (*d*) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller and R. H. Crabtree, *Organometallics*, 2002, **21**, 700-706; (*e*) V. M. Baker, D. H. Brown, V. J. Hesler, B. W. Skelton and A. H. White, *Organometallics*, 2007, **26**, 250-252; (*f*) F. Hanasaka, K. Fujita and R. Yamaguchi, *Organometallics*, 2006, **25**, 4643-4647; (*g*) W. A. Herrmann, L. J. Goossen and M. Spiegler, *Organometallics*, 1998, **17**, 2162-2168; (*h*) S. Grundemann, M. Albrecht, A. Kovacevic, J. W. Faller and R. H. Crabtree, *J. Chem. Soc., Dalton Trans.*, 2002, 2163-2167; (*i*) K. E. Krahulic, G. D. Enright, M. Parvez and R. Roesler, *J. Am. Chem. Soc.*, 2005, **127**, 4142-4143.

6 (*a*) M. V. Baker, D. H. Brown, R. A. Haque, B. W. Skelton and A. H. White, *Dalton Trans.*, 2004, 3756-3764; (*b*) Q. X. Liu, A. H. Chen, X. J. Zhao, Y. Zang, X. M. Wu, X. G. Wang and J. H. Guo, *CrystEngComm*, 2011, **13**, 293-305.

7 C. E. Ellul, G. Reed, M. F. Mahon, S. I. Pascu and M. K. Whittlesey, *Organometallics*, 2010, **29**, 4097-4104.

8 (*a*) D. B. Qin, F. B. Xu, X. J. Wan, Y. J. Zhao, Z. Z. Zhang, *Tetrahedron Lett.*, 2006, **47**, 5641-5643; (*b*) Q. X. Liu, Z. Q. Yao, X. J. Zhao, A. H. Chen, X. Q. Yang, S. W. Liu and X. G. Wang, *Organometallics*, 2011, **30**, 3732-3739.

9 (*a*) J. S. Wang, S. G. Bodige, W. H. Watson and C. D. Gutsche, *J. Org. Chem.*, 2000, **65**, 8260-8263; (*b*) Q. X. Liu, X. Q. Yang, X. J. Zhao, S. S. Ge, S. W. Liu, Y. Zang, H. B. Song, J. H. Guo and X. G. Wang, *CrystEngComm*, 2010, **12**, 2245-2255.

10 (*a*) C. X. Lin, X. F. Kong, Q. S. Li, Z. Z. Zhang, Y. F. Yuan, F. B. Xu, *CrystEngComm*, 2013, **15**, 6948-6962; (*b*) Q. X. Liu, Z. Q. Yao, X. J. Zhao, Z. X. Zhao and X. G. Wang, *Organometallics*, 2013, **32**, 3493-3501; (*c*) D. B. Qin, X. S. Zeng, Q. S. Li, F. B. Xu, H. B. Song and Z. Z. Zhang, *Chem. Commun.*, 2007,

CrystEngComm Accepted Manuscript

147-155.

11 (*a*) C. S. Bruning-Fann and J. B Kaneene, *Veter. Human Toxicol.*, 1993, **35**, 521-538; (*b*) L. Knobeloch, B. Salna, A. Hogan, J. Postle and H. Anderson, *Environ. Health Perspect.*, 2000, **108**, 675-678.

12 G. H. Ke, P. Wang and Z. Yang, *Environ. Sci. & Tech.*, 2006, **29**, 45-47.

13 (*a*) T. Gunnlaugsson, A. P. Davis, J. E. O'Brien and M. Glynn, *Org. Lett.*, 2002, **4**, 2449-2452; (*b*) S. Y. Liu, L. Fang, Y. B. He, W. H. Chan, K. T. Yeung, Y. K. Cheng and R. H. Yang, *Org. Lett.*, 2005, **7**, 5825-5828; (*c*) S. H. Kim, H. C. Choi, J. Kim, S. J. See, D. T. Quang and J. S. Kim, *Org. Lett.*, 2010, **12**, 560-563; (*d*) S. E. Garcia-Garrido, C. Caltagirone, M. E. Light and P. A. Gale, *Chem. Commun.*, 2007, 1450-1452; (*e*) G. Q. Zhang and H. Q. Zhang, *Chin. J. Anal. Chem.*, 1994, **22**, 1006-1008.

14 (*a*) F. Qian, C. Zhang, Y. Zhang, W. He, X. Gao, P. Hu and Z. Guo, *J. Am. Chem. Soc.*, 2009, **131**, 1460-1468; (*b*) N. Weibel, L. J. Charbonnière, M. Guardigli, A. Roda and R. Ziessel, *J. Am. Chem. Soc.*, 2004, **126**, 4888-4896; (*c*) Y. Yu, W. J. Shi and N. F. Yang, *Spectrosc. Spec. Anal.*, 2007, **27**, 573-576.

15 D. B. Shi, *Chin. J. Health Laboratory Tech.*, 2008, **18**, 245-247.

16 H. M. Qin, *Environ. Sci. & Tech.*, 2001, **5**, 30-31.

17 (*a*) Y. M. Hu, X. M. Wang, D. Fei, F. Q. Dong and L. S. Ding, *Acta Chim. Sinica.*, 2008, **66**, 1245-1251; (*b*) S. F. Li, H. L. Wu, A. L. Xia, S. H. Zhu, J. F. Nie, Y. C. Bian, J. Liu and R. Q. Yu, *Acta Chim. Sinica.*, 2008, **66**, 947-952.

18 (*a*) D. J. Nielsen, K. J. Cavell, B. W. Skelton and A. H. White, *Organometallics*, 2006, **25**, 4850-4856; (*b*) J. C. C. Chen and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 839-840; (*c*) M. Alcarazo, S. J. Roseblade, A. R. Cowley, R. Fernandez, J. M. Brown and J. M. Lassaletta, *J. Am. Chem. Soc.*, 2005, **127**, 3290-3292; (*d*) J. W. Wang, F. H. Meng and L. F. Zhang, *Organometallics*, 2009, **28**, 2334-2337; (*e*) Q. X. Liu, S. J. Li, X. J. Zhao, Y. Zang, H. B. Song, J. H. Guo and X. G. Wang, *Eur. J. Inorg. Chem.*, 2010, 983-988; (*f*) X. L. Liu, W. Z. Chen, *Organometallics*, 2013, **31**, 6614-6622; (*g*) Q. Li, X. Li, J. Yang, H. B. Song and L. F. Tang, *Polyhedron*, 2013, **59**, 29-37; (*h*) J. H. Chen, X. Q. Zhang, Q. Feng and

CrystEngComm Accepted Manuscript

M. M. Luo, *J. Organomet. Chem.*, 2006, **691**, 470-474.

19 (*a*) J. C. Garrisen, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *Organometallics*, 2001, **20**, 1276-1278; (*b*) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, *J. Chem. Soc., Dalton Trans.*, 2000, 4499-4506; (*c*) O. Guerret, S. Sole, H. Gornitzka, M. L. Teichert, G. Teingnier and G. Bertrand, *J. Am. Chem. Soc.*, 1997, **119**, 6668-6669; (*d*) C. K. Lee, K. M. Lee and I. J. B. Lin, *Organometallics*, 2002, **21**, 10-12; (*e*) A. J. R. Arduengo III, H. V. Dias, J. C. Calabrese and F. Davidson, *Organometallics*, 1993, **12**, 3405-3409; (*f*) R. Z. Ku, J. C. Huang, J. Y. Cho, F. M. Kiang, K. R. Reddy, Y. C. Chen, K. J. Lee, J. H. Lee, G. H. Lee, S. M. Peng and S. T. Liu, *Organometallics*, 1999, **18**, 2145-2154; (*g*) B. Liu, C. Y. Chen, Y. J. Zhang, X. L. Liu and W. Z. Chen, *Organometallics*, 2013, **32**, 5451-5460; (*h*) F. E. Hahn, M. C. Jahnke and T. Pape, *Organometallics*, 2006, **25**, 5927-5936.

20 (*a*) I. J. B. Lin and C. S. Vasam, *Coord. Chem. Rev.*, 2007, **251**, 642-670; (*b*) W. N. O. Wylie, A. J. Lough and R. H. Morris, *Organometallic*s, 2009, **28**, 853-862; (*c*) X. M. Zhang, Z. X. Xi, A. L. Liu and W. Z. Chen, *Organometallics*, 2008, **27**, 4401-4406.

21 R. D. Rogers, A. H. Bond and J. L. Wolff, *J. Coord. Chem.*, 1993, **29**, 187-207.

22 (*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; (*c*) Q. X. Liu, L. N. Yin and J. C. Feng, *J. Organomet. Chem.*, 2007, **692**, 3655-3663.

23 J. Huang, E. D. Stevens and S. P. Nolan, *Organometallics*, 2000, **19**, 1194-1197.

24 (*a*) A. J. Black, G. Baum, N. R. Champness, S. S. M. Chung, P. A. Cooke, D. Fenske, A. N. Khlobystov, D. A. Lemenovskii, W. S. Li and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2000, 4285-4291; (*b*) L. H. Zhao, Y. P. Quan, A. H. Yang, J. Z. Cui, H. L. Gao, F. L. Lu, W. Shi and P. Cheng, *CrystEngComm*, 2009, **11**, 1427-1432.

25 M. L. Cole and P. C. Junk, *CrystEngComm*, 2004, **6**, 173-176.

26 F. Neve and A. Crispini, *CrystEngComm*, 2003, **5**, 265-268.

CrystEngComm Accepted Manuscript

27 (*a*) R. P. A. Bettens, D. Dakternieks, A. Duthie, F. S. Kuan and E. R. T. Tiekink, *CrystEngComm*, 2009, **11**, 1362-1372; (*b*) C. R. Girija, N. S. Begum, A. A. Syed and V. Thiruvenkatam, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, o611.

28 S. A. Baudron, D. Salazar-Mendoza and M. W. Hosseini, *CrystEngComm*, 2009, **11**, 1245-1254.

29 (*a*) Q. X. Liu, J. Yu, X. J. Zhao, S. W. Liu, X. Q. Yang, K. Y. Li and X. G. Wang, *CrystEngComm*, 2011, **13**, 4086-4096; (*b*) Q. X. Liu, X. J. Zhao, X. M. Wu, J. H. Guo and X. G. Wang, *J. Organomet. Chem.*, 2007, **692**, 5671-5679; (*c*) A. Caballero, E. Díez-Barra, F. A. Jalón, S. Merino and J. Tejeda, *J. Organomet. Chem.*, 2001, **395**, 617-618; (*d*) B. Bildstein, M. Malaun, H. Kopacka, K. H. Ongania and K. Wurst, *J. Organomet. Chem.*, 1998, **552**, 45-61.

30 (*a*) C. X, Lin, L. Guo, Q. S. Li, Z. Z. Zhang, Y. F. Yuan and F. B. Xu. *J. Organomet. Chem.*, 2014, **749**, 180-187; (*b*) S. Saito, M. Saika, R. Yamasaki, I. Azumaya and H. Masu, *Organometallics*, 2011, **30**, 1366-1373.

31 (*a*) B. N. Ahamed and R. D. P. Ghosh, *Inorg. Chem.*, 2013, **52**, 4269-4276; (*b*) Y. S. Liu, X. J. Wan and F. B. Xu, *Organometallics*, 2009, **28**, 5590-5592; (*c*) S. Saito, T. Kobayashi, T. Makino, H. Yamaguchi, H. Muto, I. Azumaya, K. Katagiri and R. Yamasaki, *Tetrahedron*, 2012, **68**, 8931-8936; (*d*) R. A. Haque, A. W. Salman, T. S. Guan and H. H. Abdallah, *J. Organomet. Chem.*, 2011, **696**, 3507-3512; (*e*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122-3172; (*f*) M. V. Baker, D. Brown, R. A. Haque, B. W. Skelton and A. H. White, *J. Incl. Phenom. Macrocycl. Chem.*, 2009, **65**, 97-109; (*g*) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978-4008; (*h*) R. A. Haque, M. Z. Ghdhayeb, A. W. Salman, S. Budagumpi, M. B. K. Ahamed and A. M. S. A. Majid, *Inorg. Chem. Commun.*, 2012, **22**, 113-119; (*i*) M. V. Baker, D. H. Brown, R. A. Haque, P. V. Simpson, B. W. Skelton, A. H. White and C. C. Williams, *Organometallics*, 2009, **28**, 3793-3803; (*j*) Z. Lu, S. A. Cramer and D. M. Jenkins, *Chem. Sci.*, 2012, **3**, 3081-3087; (*k*) T. Fahlbusch, M. Frank, G. Maas and J. Schatz, *Organometallics*, 2009, **28**, 6183-6193; (*l*) A. W. Salman, R. A. Haque and S. Budagumpi,

CrystEngComm Accepted Manuscript

Polyhedron, 2012, **42**, 18-23; (*m*) R. A. Haque, H. Z. Zulikha, M. Z. Ghdhayeb, S. Budagumpi and A. W. Salman, *Heteroat. Chem.*, 2012, **23**, 486-497; (*n*) D. C. F. Monteiro, R. M. Phillips, B. D. Crossley, J. Fieldena and C. E. Willans, *Dalton Trans.*, 2012, **41**, 3720-3725; (*o*) X. J. Wan, F. B. Xu, Q. S. Li, H. B. Song and Z. Z. Zhang, *Organometallics*, 2005, **24**, 6066-6068; (*p*) C. Tubaro, A. Biffis, R. Gava, E. Scattolin, A. Volpe, M. Basato, M. M. Díaz-Requejo and P. J. Perez, *Eur. J. Org. Chem.*, 2012, 1367-1372; (*q*) V. Gierz, A. Seyboldt, C. Maichle-Mössmer, K. W. Törnroos, M. T. Speidel, B. Speiser, K. Eichele and D. Kunz, *Organometallics*, 2012, **31**, 7893-7901; (*r*) A. Rit, T. Pape and F. E. Hahn, *Organometallics*, 2011, **30**, 6393-6401; (*s*) P. Marshall, R. L. Jenkins, W. Clegg, R. W. Harrington, S. K. Callear, S. J. Coles, I. A. Fallisa and A. Dervisi, *Dalton Trans.*, 2012, **41**, 12839-12846; (*t*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290-1309; (*u*) J. Cure, R. Poteau, I. C. Gerber, H. Gornitzka and C. Hemmert, *Organometallics*, 2012, **31**, 619-626; (*v*) Q. X. Liu, L. X. Zhao, X. J. Zhao, Z. X. Zhao, Z. Q. Wang, A. H. Chen and X. G. Wang, *J. Organomet. Chem.*, 2013, **731**, 35-48; (*w*) M. Mechler, K. Latendorf, W. Frey and R. Peters, *Organometallics*, 2013, **32**, 112-130.

32 S. Budagumpi, R. A. Haque, A. W. Salman and M. Z. Ghdhayeb, *Inorg. Chim. Acta*, 2012, **392**, 61-72.

33 J. W. Wang, Y. Guo, G. Y. Dong, Y. Guc and D. S. Bai, *Acta Crystallogr.*, *E*, 2012, **68**, m302.

34 (*a*) R. A. Haque, S. Budagumpi, S. Y. Choo, M. K. Choong, B. E. Lokesh and K. Sudesh, *Appl. Organomet. Chem.*, 2012, **26**, 689-700; (*b*) M. A. Iqbal, R. A. Haque, S. Budagumpi, M. B. K. Ahamed and A. M. S. A. Majid, *Inorg. Chem. Commun.*, 2013, **28**, 64-69; (*c*) M. A. Iqbal, R. A. Haque, M. B. K. Ahamed, A. M. S. A. Majid and S. S. Al-Rawi, *Med. Chem. Res.*, 2013, **22**, 2455-2466; (*d*) R. A. Haque, M. A. Iqbal, S. Budagumpi, M. B. K. Ahamed, A. M. S. A. Majid and N. Hasanudin, *Appl. Organomet. Chem.*, 2013, **27**, 214-223.

35 (*a*) V. Gierz, C. Maichle-Mössmer and D. Kunz, *Organometallics*, 2012, **31**, 739-747; (*b*) A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A.

CrystEngComm Accepted Manuscript

Tessier and W. J. Youngs, *J. Am. Chem. Soc.*, 2005, **127**, 2285-2291; (*c*) D. Pugh, A. Boyle and A. A. Danopoulos, *Dalton Trans.*, 2008, 1087-1094; (*d*) A. Poethig and T. Strassner, *Organometallics*, 2011, **30**, 6674-6684.

36 (*a*) G. Papini, M. Pellei, G. G. Lobbia, A. Burini and C. Santini, *Dalton Trans.*, 2009, 6985-6990; (*b*) F. Godoy, C. Segarra, M. Poyatos and E. Peris, *Organometallics*, 2011, **30**, 684-688; (*c*) F. Dominique, H. Gornitzka and C. Hemmert, *J. Organomet. Chem.*, 2008, **693**, 579-583; (*d*) A. L. Liu, X. M. Zhang, W. Z. Chen and H. T. Qiu, *Inorg. Chem. Commun.*, 2008, **11**, 1128-1131; (*e*) X. M. Zhang, S. J. Gu, Q. Q. Xia and W. Z. Chen, *J. Organomet. Chem.*, 2009, **694**, 2359-2367; (*f*) G. Papini, G. Bandoli, A. Dolmella, G. G. Lobbia, M. Pellei and C. Santini, *Inorg. Chem. Commun.*, 2008, **11**, 1103-1106; (*g*) K. M. Lee, J. C. C. Chen and I. J. B. Lin, *J. Organomet. Chem.,* 2001, **617-618**, 364-375.

37 J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561-3598.

38 (*a*) V. J. Catalano, M. A. Malwitz and A. O. Etogo, *Inorg. Chem.*, 2004, **43**, 5714-5724; (*b*) A. A. Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham and M. B. Hursthouse, *Dalton Trans.*, 2003, 1009-1015; (*c*) R. E. Douthwaite, J. Houghton and B. M. Kariuki, *Chem. Commun.*, 2004, 698-699; (*d*) T. A. P. Paulose, J. A. Olson, J. W. Quail and S. R. Foley, *J. Organomet. Chem.*, 2008, **693**, 3405-3410.

39 (*a*) X. Q. Zhang, Y. P. Qiu, B. Rao and M. M. Luo, *Organometallics*, 2009, **28**, 3093-3099; (*b*) Q. X. Liu, M. C. Shi, Z. Q. Wang, S. W. Liu, S. S. Ge, Y. Zang, X. G. Wang and J. H. Guo, *Polyhedron*, 2010, **29**, 2121-2126; (*c*) 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.

40 D. Y. Lee, N. Singh, M. J. Kim and D. O. Jang, *Org. Lett.*, 2011, **13**, 3024-3027.

41 (*a*) A. R. Watkins, *J. Phys. Chem.* 1974, **78**, 1885-1893; (*b*) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 1966, **66**, 199-241; (*c*) M. Vetrichelvan, R. Nagarajan and S. Valiyaveettil, *Macromolecules*, 2006, **39**, 8303-8310.

42 E. M. Pérez, L. Sánchez, G. Fernández and N. Martín, *J. Am. Chem. Soc.*, 2006,

CrystEngComm Accepted Manuscript

128, 7172-7173.

43 A. Caballero, R. Martınez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina and J. Veciana, *J. Am. Chem. Soc.*, 2005, **127**, 15666-15667.

44 (*a*) K. A. Connors, *Binding Constants, the Measurement of Molecular Complex Stability*, John Wiley & Sons, New York, 1987; (*b*) B. Valeur, *Molecular Fluorescence Principles and Applications*, Wiley-VCH Verlag GmbH, New York, 2001.

45 (*a*) M. Ayabe, A. Ikeda, S. Shinkai, S. Sakamoto and K. Yamaguchi, *Chem. Commun.* 2002, 1032-1033; (*b*) D. C. Guo, P. L. Wu, H. Tan, L. Xia and W. H. Zhou, *J. Lumin.*, 2011, **131**, 1272-1276.

46 J. Polster and H. Lachmann. *Spectrometric Titrations*, VCH, Weinheim, 1989, 256-259.

47 A. Easwaran, A. Ayyappanpillai and D. Jorg, *J. Am. Chem. Soc.*, 2005, **127**, 3156-3164.

48 J. Yoon, S. K. Kim, N. J. Singh, J. W. Lee, Y. J. Yang, K. Chellappan and K. S. Kim, *J. Org. Chem.*, 2004, **69**, 581-583.

49 G. Shyamaprosad, H. Anita, C. Rinku and K. F. Hoong, *Org. Lett.*, 2009, **11**, 4350-4353.

50 *SMART 5.0 and SAINT 4.0 for Windows NT, Area Detector Control and Integration Software*; Bruker Analytical X-Ray Systems, Inc., Madison, WI, USA, 1998.

51 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; Univ. of Göttingen, Germany, 1996.

52 G. M. Sheldrick, *SHELXTL 5.10 for Windows NT, Structure Determination Software*; Brucker Analytical X-Ray Systerms, Inc., Madison, WI, USA, 1997.

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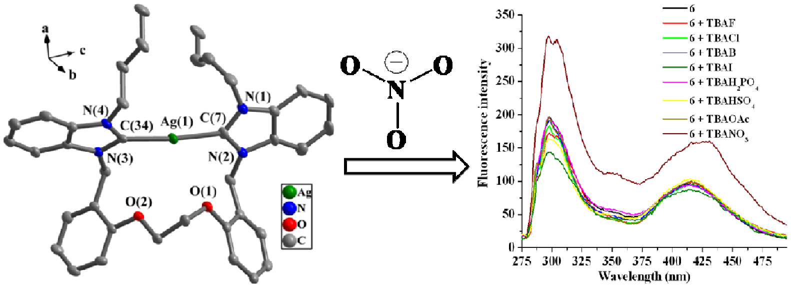
A table of contents entry:

Eight N-heterocyclic carbene Hg(II) and Ag(I) complexes were prepared, and the selective recognition of nitrate anion was studied.



Software of graphics:

Scheme 1-Scheme 3: Chem Draw 8.0

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