

# New *N*-heterocyclic carbene silver(I) and mercury(II) 2-D supramolecular layers by the $\pi$ – $\pi$ stacking interactions

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Received 4 March 2007; received in revised form 11 April 2007; accepted 1 May 2007

Available online 8 May 2007

## Abstract

The precursor 1-(9-anthracenylmethyl)-3-alkylbenzimidazolium chlorides (**1a**, alkyl = C<sub>4</sub>H<sub>9</sub>, **1b**, alkyl = C<sub>6</sub>H<sub>13</sub>) and their three new NHC silver(I) and mercury(II) complexes {[1-(9-anthracenylmethyl)-3-alkylbimy]MCl}<sub>2</sub> (**2a**, alkyl = C<sub>4</sub>H<sub>9</sub>, M = Ag; **2b**, alkyl = C<sub>6</sub>H<sub>13</sub>, M = Ag; **3a**, alkyl = C<sub>4</sub>H<sub>9</sub>, M = Hg; bimy = benzimidazol-2-ylidene) have been prepared and characterized. The crystal structures of **2a**, **2b** and **3a** showed that 2-D supramolecular layers are formed by both benzimidazole ring head to tail  $\pi$ – $\pi$  stacking interactions and anthracene ring face-to-face  $\pi$ – $\pi$  stacking interactions.

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**Keywords:** Carbene complex; Silver; Mercury;  $\pi$ – $\pi$  Stacking interactions

## 1. Introduction

In recent years, *N*-heterocyclic carbenes (NHCs) have attracted considerable attention due to their strong  $\sigma$ -donor ability to complexes with transition metals and main group elements [1]. A large number of metal complexes with NHCs have been synthesized [2]. While some of these carbenes are isolable, less stable relatives may be generated and used *in situ* [3]. The NHC metal complexes are remarkably stable toward heat, air, and moisture [4], and they have been applied to a broad spectrum of catalytic reactions including Heck, Suzuki, Kumada couplings, and olefin metathesis [5].

NHC silver complexes have played an important role in the rapid development of NHC metal complexes [6]. One reason for this is that carbene silver complexes are readily accessible through deprotonation of *N,N'*-disubstituted imidazolium salts, which can be easily derived. Another reason for this is that carbene silver complexes can be used as carbene transfer reagent for synthesis of Pd, Pt, Au and

Rh carbene complexes, such a route affords a convenient method for the preparation of these carbene metal complexes [7]. In addition, the potential use of NHC silver complexes has also been realized as antimicrobial agents [8]. We are interested in NHC complexes exhibiting fluorescence [9] owing to their potential application as fluorescent switch. Herein we wish to report the synthesis, structure and fluorescent emission spectra of {[1-(9-anthracenylmethyl)-3-alkylbimy]MCl}<sub>2</sub> (**2a**, alkyl = C<sub>4</sub>H<sub>9</sub>, M = Ag; **2b**, alkyl = C<sub>6</sub>H<sub>13</sub>, M = Ag; **3a**, alkyl = C<sub>4</sub>H<sub>9</sub>, M = Hg; bimy = benzimidazol-2-ylidene).

## 2. Results and discussion

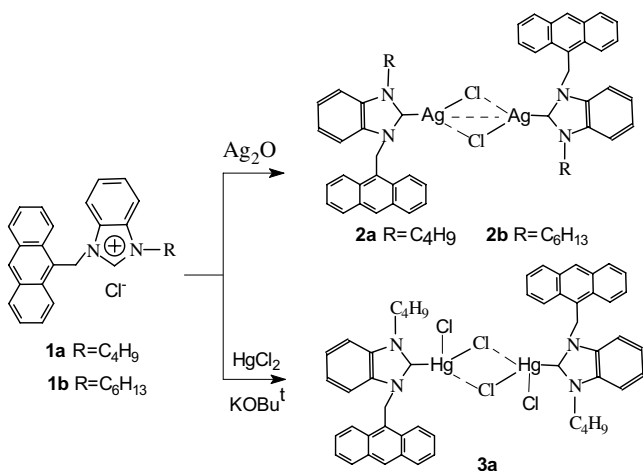
### 2.1. Synthetic strategy

1-(9-Anthracenylmethyl)-3-alkylbenzimidazolium chlorides (**1a**, alkyl = C<sub>4</sub>H<sub>9</sub>, **1b**, alkyl = C<sub>6</sub>H<sub>13</sub>) were prepared from benzimidazole by stepwise alkylation with 1-haloalkane followed by 9-chloromethylantracene in sequence. Precursors **1a** and **1b** are stable to air and moisture, and soluble in polar organic solvents such as dichloromethane, acetonitrile, methanol, scarcely soluble in benzene, and insoluble in diethyl ether and petroleum ether. The **1a** or

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**1b** were treated with silver oxide (1/2 mole equivalent) to afford complexes  $\{[1-(9\text{-anthracylmethyl})\text{-}3\text{-alkylbimy}]\text{AgCl}\}_2$  (**2a**, alkyl =  $\text{C}_4\text{H}_9$ , **2b**, alkyl =  $\text{C}_6\text{H}_{13}$ ). Complex  $\{[1-(9\text{-anthracylmethyl})\text{-}3\text{-butylbimy}]\text{HgCl}_2\}_2$  (**3a**) was prepared by the reaction of **1a** and  $\text{HgCl}_2$  in the presence of  $\text{KOBU}^t$  in the solution of  $\text{CH}_3\text{CN}$  and THF (Scheme 1). The complexes **2a**, **2b** and **3a** are stable in air and moisture, and soluble in DMSO and insoluble in diethyl ether and hydrocarbon solvents.



Scheme 1. Preparation of complexes **2a**, **2b** and **3a**.

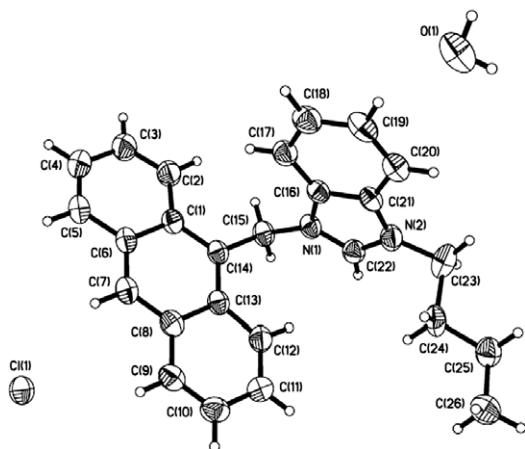


Fig. 1a. Perspective view of **1a** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

## 2.2. Structure of precursor **1a**, complexes **2a**, **2b** and **3a**

Yellow crystals of **1a** suitable for X-ray diffraction were obtained by evaporating slowly its  $\text{CH}_2\text{Cl}_2$ /acetone solution at room temperature. In molecular structure of **1a** both the anthracene ring and benzimidazole form a dihedral angle of  $84.1^\circ$  as shown in Fig. 1a. Analysis of the crystal packing of **1a** revealed that the 1-D chains are formed by face-to-face  $\pi$ - $\pi$  interactions from intermolecular anthracene rings and benzimidazole rings (Fig. 1b) with the inter-planar separation of  $3.489 \text{ \AA}$  (center-to-center separation:  $3.853 \text{ \AA}$ ) [10].

The pale yellow crystals of **2a** and  $\text{2b} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}$  suitable for X-ray diffraction were grown by evaporating slowly their  $\text{CH}_2\text{ClCH}_2\text{Cl}/\text{CH}_3\text{OH}$  solution at room temperature, and the pale yellow crystals of **3a** were obtained by slow diffusion of diethyl ether into its DMSO solution. Molecular structures of the complexes **2a** and **3a** are depicted in Fig. 2a and Fig. 3a, respectively (**2b** and **2a** have similar molecular structures). In complexes **2a** and **2b** the dimeric units of  $\{[1-(9\text{-anthracylmethyl})\text{-}3\text{-alkylbimy}]\text{AgCl}\}_2$  are formed by the two  $[1-(9\text{-anthracylmethyl})\text{-}3\text{-alkylbimy}]\text{AgCl}$  moieties with the aid of two weak  $\text{Ag} \cdots \text{Cl}$  bonds ( $\text{Ag} \cdots \text{Cl}$  separation:  $3.142 \text{ \AA}$  for **2a** and  $3.048 \text{ \AA}$  for **2b**, regular  $\text{Ag}-\text{Cl}$  bond length being  $2.3\text{--}2.4 \text{ \AA}$ ) [7,11]. This pairwise association formed a rhombic  $\text{Ag}_2\text{Cl}_2$  arrangement. In the rhombus the  $\text{Ag}(1\text{A})-\text{Cl}(1\text{A})$  distance is  $2.342 \text{ \AA}$  for **2a** and  $2.396 \text{ \AA}$  for **2b**, and the  $\text{Ag}(1\text{A})-\text{Cl}(1\text{A}) \cdots \text{Ag}(1\text{B})$  and  $\text{Cl}(1\text{A}) \cdots \text{Ag}(1\text{B})-\text{Cl}(1\text{B})$  bond angles are  $81.8^\circ$  and  $98.2^\circ$ , respectively, for **2a** (corresponding values are  $89.2^\circ$  and  $90.8^\circ$  for **2b**), as well as the  $\text{Ag}(1\text{A})-\text{Ag}(1\text{B})$  distance is  $3.640 \text{ \AA}$  for **2a** and  $3.850 \text{ \AA}$  for **2b**, which indicates a weak metal-metal interaction [12]. The  $\text{C}-\text{Ag}$  distance is  $2.085 \text{ \AA}$  for **2a** and  $2.088 \text{ \AA}$  for **2b**, and the internal ring angle ( $\text{N}-\text{C}-\text{N}$ ) at the carbene center is  $106.2(2)^\circ$  for **2a** and  $105.3(3)^\circ$  for **2b**, and these data are similar to those of some known NHC silver complexes [13]. The two benzimidazole rings are parallel within each dimeric unit, and form a dihedral angle of  $56^\circ$  for **2a** and  $80.3^\circ$  for **2b** with the centric  $\text{Ag}_2\text{Cl}_2$  plane. In same moiety the dihedral angle of benzimidazole ring and anthracene ring is  $98^\circ$  for **2a** and  $84.6^\circ$  for **2b**.

The complex **3a** like **2a** and **2b** forms also a dinuclear dimeric unit  $\{[1-(9\text{-anthracylmethyl})\text{-}3\text{-alkylbimy}]\text{HgCl}_2\}_2$  through both weak  $\text{Hg} \cdots \text{Cl}$  bonds ( $\text{Hg} \cdots \text{Cl} = 3.140 \text{ \AA}$ , regular  $\text{Hg}-\text{Cl}$  bond length being  $2.4\text{--}2.5 \text{ \AA}$ ) as shown in

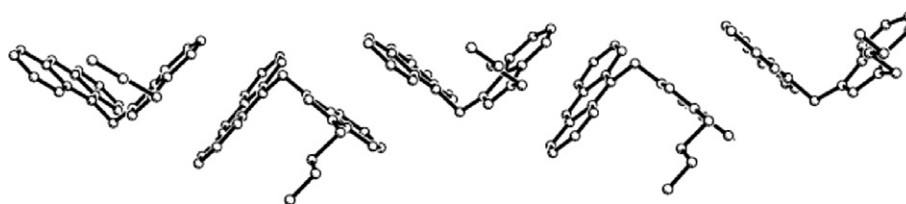


Fig. 1b. The 1-D chains by  $\pi$ - $\pi$  stacking interactions from anthracene rings and benzimidazole rings in **1a**.

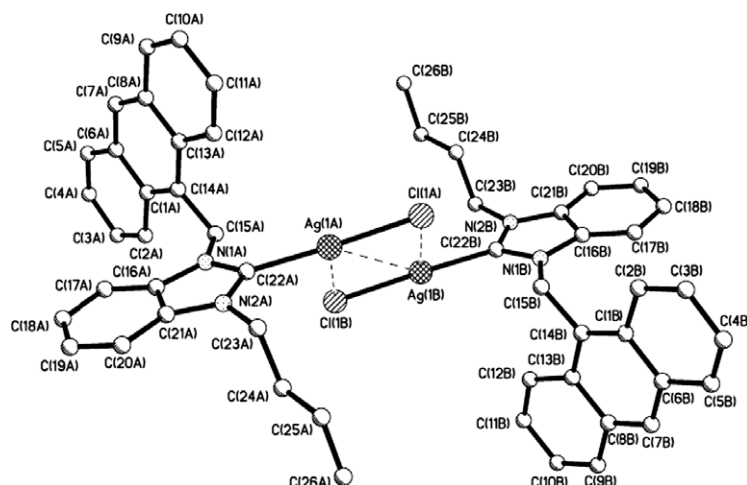


Fig. 2a. Perspective view of **2a** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

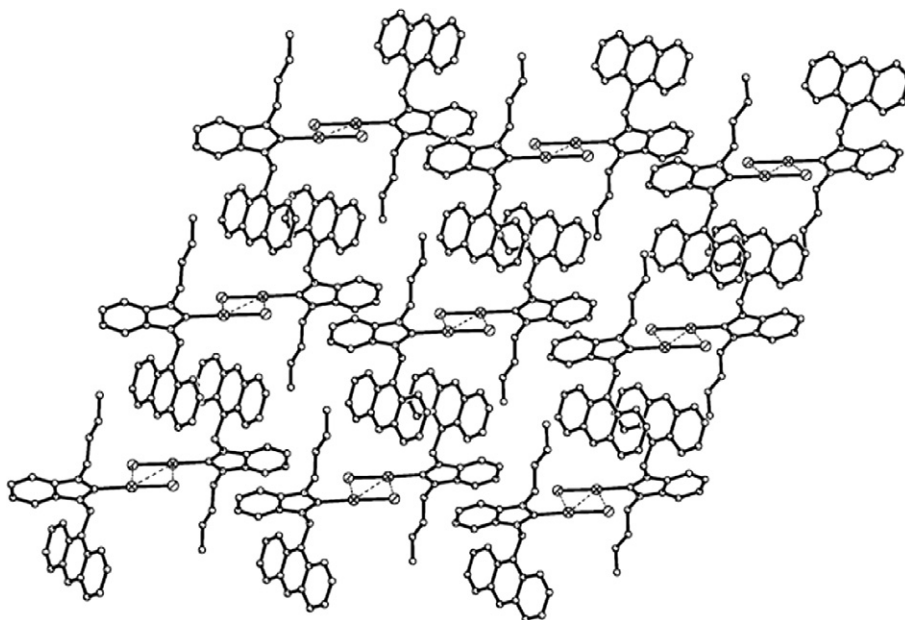


Fig. 2b. The 2-D supramolecular layer by both types of  $\pi$ - $\pi$  stacking interactions in **2a**.

Fig. 3a. However, the coordination chemistry of **3a** has somewhat different from those of **2a** and **2b**. Each mercury atom of **3a** is coordinated by one carbene-carbon and three chlorine atoms (two bridging chlorine, Cl(1A) and Cl(1B), and one non-bridging chlorine atoms, Cl(2A)), and by one oxygen atom and one sulfur atom from solvent DMSO (Hg(1A)–O(1A) = 2.730 Å and Hg(1A)–S(1A) = 3.636 Å) to form a distorted octahedron. The coplanar four atoms Hg(1A), Cl(1A), Hg(1B) and Cl(1B) form a rhombic Hg<sub>2</sub>Cl<sub>2</sub> arrangement (Hg(1A)–Cl(1A)–Hg(1B) = 93.6° and Cl(1A)–Hg(1A)–Cl(1B) = 86.4°). The two non-bridging chlorine ligands lie in both flanks of the rhombic plane (Cl(1A)–Hg(1A)–Cl(2A) = 100.83(9)°), and the distance of non-bridging chlorine and mercury (Hg(1A)–Cl(2A) = 2.421 Å) is shorter than that of bridging chlorine and mercury (Hg(1A)–Cl(1A) = 2.509 Å). The Hg–Hg separation

of 4.140(4) Å shows no metal–metal interactions. The C–Hg distance of 2.114(5) Å is slightly longer than those of known NHC mercury complexes (2.02–2.06 Å) [14], and the internal ring angle (N–C–N) at the carbene center is 108.5(4)°, which is somewhat smaller than that of the precursor **1a** (110.8(3)°) and similar to those of some known mercury complexes. The two benzimidazole rings within each dimeric unit are parallel, and form the dihedral angles of 101.5° and 88.1°, respectively, with rhombic Hg<sub>2</sub>Cl<sub>2</sub> plane and neighboring anthracene ring. In the crystal structure of **2b** one solvent molecule 1,2-dichloroethane is contained, and it is disordered over two positions and these were refined with anisotropic displacement parameters and with C–C, C–H and C–Cl distances restrained to 1.480(3) Å, 0.960(3) Å and 1.720(3) Å, respectively. The occupancy factors are 0.677(4) and 0.323(4), respectively.

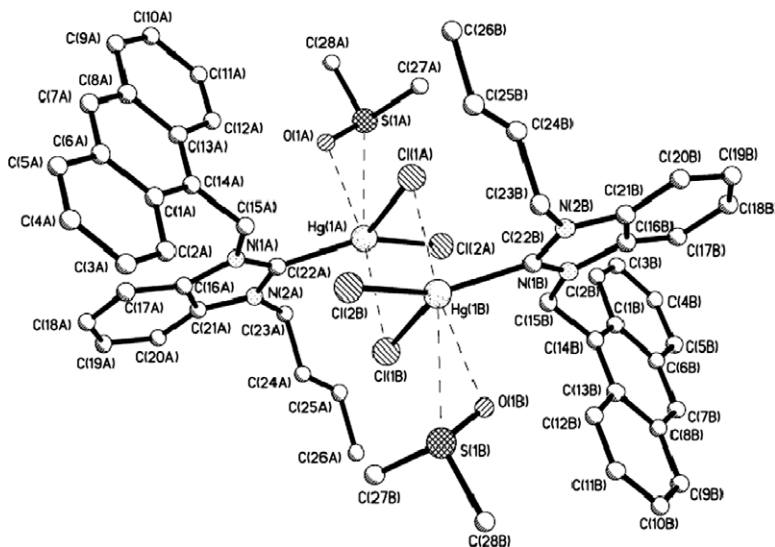


Fig. 3a. Perspective view of **3a** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

An interesting feature in the packing diagrams of **2a**, **2b** and **3a** is that both types of aromatic  $\pi$ - $\pi$  stacking interactions are observed [10] (Fig. 2b for **2a**, Fig. 3b for **3a**, **2b** and **2a** have similar packing diagram). One type is the head to tail  $\pi$ - $\pi$  stacking interactions from inter-unit benzimidazole rings with the inter-planar separation of 3.569 Å for **2a**, 3.343 Å for **2b** and 3.507 Å for **3a** (center-to-center separation: 3.918 Å for **2a**, 4.469 Å for **2b** and 3.623 Å for **3a**), which form 1-D infinite chains. Another type is the face-to-face  $\pi$ - $\pi$  interactions from inter-chain anthracene rings, which extends the above 1-D polymeric chains into 2-D supramolecular layers. In the packing diagrams the distance of neighboring parallel anthracene rings is 3.533 Å

for **2a**, 3.399 Å for **2b** and 3.430 Å for **3a** with center-to-center separation of 3.818 Å for **2a**, 4.078 Å for **2b** and 3.734 Å for **3a**. Thus aromatic  $\pi$ - $\pi$  stacking interactions are mainly responsible for expanding the dimeric units to 2-D supramolecular layers in **2a**, **2b** and **3a**.

### 2.3. Fluorescent emission spectra of precursor **1a**, complexes **2a** and **3a**

The fluorescent emission spectra of **1a**, **2a** and **3a** are shown in Fig. 4 (the fluorescent emission spectra of **1b** and **2b** are similar to those of **1a** and **2a**). In dichloromethane **2a** and **3a** showed an anthracene-type fluorescence

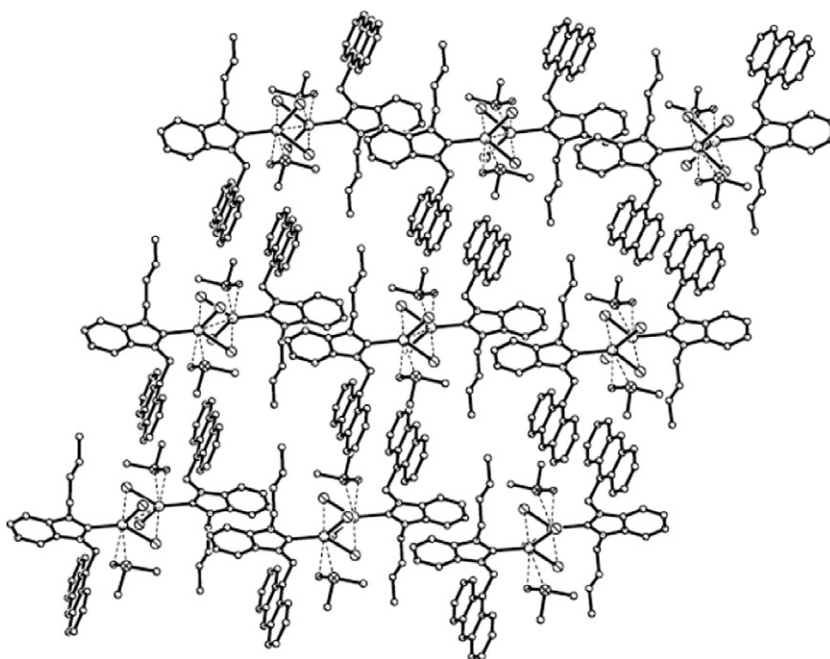


Fig. 3b. The 2-D supramolecular layer by both types of  $\pi$ - $\pi$  stacking interactions in **3a**.

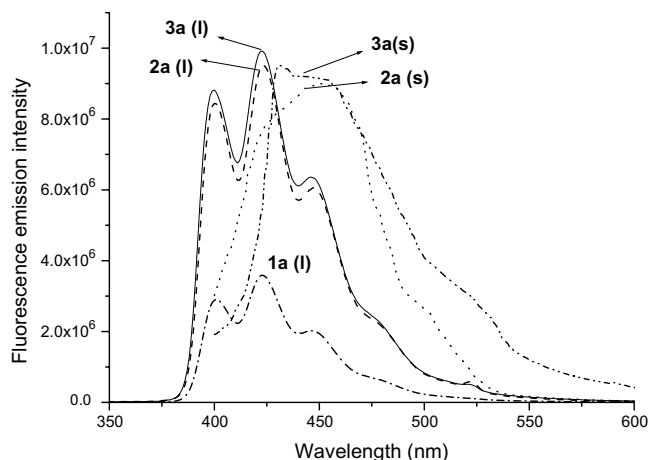


Fig. 4. Emission spectra of **1a(l)** (---), **2a(l)** (—), **2a(s)** (···), **3a(l)** (— · —) and **3a(s)** (— — —) at 298 K in  $\text{CH}_2\text{Cl}_2$  ( $5.0 \times 10^{-6}$  M) solution and in solid state.

emission in 370–550 nm similar to but stronger than that of corresponding precursor **1a**. This can be attributed to the electron-withdrawing effect of silver(I) and mercury(II), which inhibits the photoinduced electron transfer (PET) process of the lone-pair electron of the nitrogen atom to the anthracene ring [15a]. In solid state the intensity of fluorescent emission spectra of **2a** and **3a** are similar to those of them in solution, which suggests that **2a** and **3a** may have same dimer structures in solid state and solution. In solid state the red-shift for fluorescence peak of **2a** and **3a** from their corresponding solution emission may be ascribed to an excimer formation arising from  $\pi$ – $\pi$  stacking interactions [15b,15c,15d], which suggests that the  $\pi$ – $\pi$  stacking interactions occur mainly in the solid state.

#### 2.4. Thermogravimetric analysis of complexes **2a**, **2b** and **3a**

Complexes **2a**, **2b** and **3a** are air stable at ambient conditions and the thermogravimetric experiments were performed to explore their thermal stabilities. The TGA curve of **2a** reveals that the complex starts to decompose beyond 235 °C with two steps of weight losses (peaks at 282 °C and 356 °C) and does not stop until heating ends at 750 °C. The TGA curve of **2b** suggests that the first weight loss of 2.05% in the region of 102–138 °C (peaking at 120 °C) is corresponds to the expulsion of the lattice 1,2-dichloroethane molecules (calculated: 1.56%). The starting decomposition of the residuary section occurs at 228 °C with two steps of weight losses (peaks at 269 °C and 359 °C) and does not stop until heating ends at 750 °C. The TGA curve of **3a** suggests that the first weight loss of 1.57% in the region of 162–190 °C (peaking at 180 °C) is corresponds to the expulsion of the coordination dimethylsulfoxide molecules (calculated: 1.09%). The residual section starts to decompose at 198 °C with a series of complicated weight losses (peaks at 240, 261, 298 and 387 °C), and further heating to 750 °C suggests a continuous weight loss.

### 3. Conclusion

In summary, three new NHC silver(I) and mercury(II) 2-D supramolecular layers formed by both types of the aromatic  $\pi$ – $\pi$  stacking interactions have been synthesized. The fluorescent intensities of these complexes are stronger than those of their precursors. Further studies on new organometallic compounds from precursor **1** and analogous ligands are underway.

### 4. Experimental

#### 4.1. General procedures

All manipulations were performed using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for syntheses and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Varian Mercury Vx 300 spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts,  $\delta$ , are reported in ppm relative to the internal standard TMS for both  $^1\text{H}$  and  $^{13}\text{C}$  NMR.  $J$  values are given in Hz. Elemental analyses were measured using a Perkin–Elmer 2400C elemental analyzer. The luminescent spectra were conducted on Cary eclipse fluorescence spectrophotometer.

#### 4.2. Preparation of 1-(9-anthracenylmethyl)-3-butylbenzimidazolium chloride (**1a**)

A THF solution of benzimidazole (10.170 g, 86 mmol) was added to a suspension of oil-free sodium hydride (3.977 g, 94.7 mmol) in THF (150 mL) and stirred for 1 h at 60 °C. Then THF (100 mL) solution of *n*-butyl iodide (16.634 g, 90.4 mmol) was dropwise added to above solution. The mixture was continued to stir for 48 h at 60 °C and a yellow solution was obtained. The solvent was removed with a rotary evaporator and  $\text{H}_2\text{O}$  (500 mL) was added to the residue. Then the solution was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 100$  mL), and the extracting solution was dried with anhydrous  $\text{MgSO}_4$ . After removing  $\text{CH}_2\text{Cl}_2$ , a yellow liquid 1-butylbenzimidazole was obtained. Yield: 14.5 g (96.7%).

A solution of 9-butylbenzimidazole (6.840 g, 39.3 mmol) and 9-chloromethylantracene (8.480 g, 37.4 mmol) in THF (150 mL) was stirred for three days under reflux, and a yellow precipitate was formed. The yellow product was filtered and washed with THF. The yellow crystals of 1-(9-anthracenylmethyl)-3-butylbenzimidazolium chloride (**1a**) are obtained by recrystallization from acetone/diethyl ether. Yield: 12.800 g (85.0%). M.p.: 239–241 °C. Anal. Calc. for  $\text{C}_{26}\text{H}_{25}\text{ClN}_2$ : C, 77.89; H, 6.29; N, 6.99. Found: C, 77.80; H, 6.33; N, 6.76%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02 (t,  $J = 5.4$ , 3H,  $\text{CH}_3$ ), 1.46 (m, 2H,  $\text{CH}_2$ ), 2.04 (m, 2H,  $\text{CH}_2$ ), 4.57 (t,  $J = 5.4$ , 2H,  $\text{CH}_2$ ), 6.92 (d,  $J = 6.3$ ,

1H, PhH), 6.99 (s, 2H, CH<sub>2</sub>), 7.12 (t, *J* = 6.3, 1H, PhH), 7.38 (t, *J* = 6.3, 1H, PhH), 7.54 (d, *J* = 6.3, 1H, PhH), 7.68 (t, *J* = 8.4, 2H, AnH) (An: anthracene), 7.72 (t, *J* = 8.4, 2H, AnH), 8.10 (d, *J* = 8.4, 2H, AnH), 8.56 (d, *J* = 8.4, 2H, AnH), 8.59 (s, 1H, AnH), 12.17 (s, 1H, 2-benzimiH) (benzimi: benzimidazole).

#### 4.3. Preparation of 1-(9-anthracenylmethyl)-3-hexylbenzimidazolium chloride (**1b**)

The precursor **1b** was prepared in a manner analogous to that for **1a**, only with *n*-hexyl bromide instead of *n*-butyl iodide. Compound **1b** was obtained as a yellow powder (yield: 64.1%). M.p.: 156–158 °C. Anal. Calc. for C<sub>28</sub>H<sub>29</sub>ClN<sub>2</sub>: C, 78.39; H, 6.81; N, 6.53. Found: C, 78.55; H, 6.39; N, 6.79%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.85 (t, *J* = 5.4, 3H, CH<sub>3</sub>), 1.30 (m, 6H, 3CH<sub>2</sub>), 1.89 (m, 2H, CH<sub>2</sub>), 4.57 (t, *J* = 5.4, 2H, CH<sub>2</sub>), 6.87 (d, *J* = 6.3, 1H, PhH), 6.99 (s, 2H, CH<sub>2</sub>), 7.10 (t, *J* = 6.3, 1H, PhH), 7.26 (t, *J* = 6.3, 1H, PhH), 7.37 (d, *J* = 6.3, 1H, PhH), 7.52 (t, *J* = 8.4, 2H, AnH) (An: anthracene), 7.67 (t, *J* = 8.4, 2H, AnH), 8.06 (d, *J* = 8.4, 2H, AnH), 8.55 (d, *J* = 8.4, 2H, AnH), 8.56 (s, 1H, AnH), 12.19 (s, 1H, 2-benzimiH) (benzimi: benzimidazole).

#### 4.4. Preparation of {[1-(9-anthracylmethyl)-3-butylbimy]AgCl}<sub>2</sub> (**2a**)

Silver oxide (0.058 g, 0.249 mmol) was added to a solution of compound **1a** (0.200 g, 0.499 mmol) in dichloromethane (30 mL) and the suspension solution was stirred for 24 h at refluxing. The resulting solution was filtered and concentrated to 5 mL, and Et<sub>2</sub>O (20 mL) was added to precipitate a pale yellow powder. Isolation by filtration yields **2a**. Yield: 0.132 g (52.2%). M.p.: 260–262 °C. Anal. Calc. for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>ClAg: C, 61.50; H, 4.76; N, 5.52%. Found: C, 61.59; H, 4.87; N, 5.33%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 0.98 (t, *J* = 5.4, 3H, CH<sub>3</sub>), 1.30 (m, 2H, CH<sub>2</sub>), 1.76 (m, 2H, CH<sub>2</sub>), 4.35 (t, *J* = 5.4, 2H, CH<sub>2</sub>), 6.92 (d, *J* = 6.3, 1H, PhH), 6.99 (s, 2H, CH<sub>2</sub>), 7.12 (t, *J* = 6.3, 1H, PhH), 7.21 (t, *J* = 6.3, 1H, PhH), 7.30 (d, *J* = 6.3, 1H, PhH), 7.35 (t, *J* = 8.4, 2H, AnH) (An: anthracene), 7.47 (t, *J* = 8.4, 2H, AnH), 8.10 (d, *J* = 8.4, 2H, AnH), 8.31 (d, *J* = 8.4, 2H, AnH), 8.60 (s, 1H, AnH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): δ 172.5 (C<sub>carbene</sub>), 132.2, 131.9, 130.3, 129.4, 128.2, 125.0, 124.9, 118.3 and 114.2 (AnC or PhC), 54.4 (NCH<sub>2</sub>An), 53.0 (NCH<sub>2</sub>C), 32.1 (CCH<sub>2</sub>C), 28.4 (CCH<sub>2</sub>C), 13.7 (CH<sub>3</sub>).

#### 4.5. Preparation of {[1-(9-anthracylmethyl)-3-hexylbimy]AgCl}<sub>2</sub> (**2b**)

This complex was prepared in a manner analogous to that for **2a**, only with 1-(9-anthracenylmethyl)-3-hexylbenzimidazolium chloride (**1b**) instead of 1-(9-anthracenylmethyl)-3-butylbenzimidazolium chloride (**1a**). Yield: 0.130 g, (52.1%). M.p.: 214–216 °C. Anal. Calc. for

C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>ClAg: C, 62.76; H, 5.27; N, 5.23. Found: C, 62.44; H, 5.48; N, 5.34%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 0.84 (t, *J* = 5.4, 3H, CH<sub>3</sub>), 1.27 (m, 6H, 3CH<sub>2</sub>), 1.84 (m, 2H, CH<sub>2</sub>), 4.35 (t, *J* = 5.4, 2H, CH<sub>2</sub>), 6.47 (d, *J* = 6.3, 1H, PhH), 6.94 (s, 2H, CH<sub>2</sub>), 7.13 (t, *J* = 0.63, 1H, PhH), 7.30 (t, *J* = 6.3, 1H, PhH), 7.41 (d, *J* = 6.3, 1H, PhH), 7.53 (t, *J* = 8.4, 2H, AnH) (An: anthracene), 7.68 (t, *J* = 8.4, 2H, AnH), 8.10 (d, *J* = 8.4, 2H, AnH), 8.21 (d, *J* = 8.4, 2H, AnH), 8.56 (s, 1H, AnH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): δ 174.0 (C<sub>carbene</sub>), 133.1, 130.9, 129.8, 128.5, 124.9, 123.8, 118.5 and 113.8 (AnC

Table 1  
Selected bond lengths (Å) and angles (°) for **1a** and **3a**

<b>1a</b>		<b>3a</b>	
N(1)–C(22)	1.323(4)	Hg(1A)–C(22A)	2.114(5)
N(1)–C(16)	1.390(4)	Hg(1A)–Cl(2A)	2.421(2)
N(1)–C(15)	1.480(4)	Hg(1A)–Cl(1A)	2.509(2)
N(2)–C(22)	1.331(4)	N(1A)–C(22A)	1.327(6)
N(2)–C(21)	1.380(4)	N(1A)–C(16A)	1.404(6)
N(2)–C(23)	1.457(4)	N(1A)–C(15A)	1.474(7)
N(1)–C(22)–N(2)	110.8(3)	N(2A)–C(22A)	1.341(7)
C(22)–N(1)–C(16)	108.0(3)	N(2A)–C(21A)	1.386(6)
C(22)–N(1)–C(15)	124.7(3)	N(2A)–C(23A)	1.455(7)
C(16)–N(1)–C(15)	127.3(2)	C(22A)–Hg(1A)–Cl(2A)	136.2(1)
C(22)–N(2)–C(21)	107.9(3)	C(22A)–Hg(1A)–Cl(1A)	122.9 (1)
C(22)–N(2)–C(23)	125.0(3)	Cl(2A)–Hg(1A)–Cl(1A)	100.8 (9)
C(21)–N(2)–C(23)	127.0(3)	C(22A)–N(1A)–C(16A)	109.7(4)
		C(22A)–N(1A)–C(15A)	123.9(4)
		C(16A)–N(1A)–C(15A)	126.3(4)
		C(22A)–N(2A)–C(21A)	109.1(5)
		C(22A)–N(2A)–C(23A)	125.3(5)
		C(21A)–N(2A)–C(23A)	125.5(5)
		N(1A)–C(22A)–N(2A)	108.5(4)
		N(1A)–C(22A)–Hg(1A)	127.3(4)
		N(2A)–C(22A)–Hg(1A)	124.2(4)

Table 2  
Selected bond lengths (Å) and angles (°) for **2a** and **2b**

<b>2a</b>		<b>2b</b>	
Ag(1A)–C(22A)	2.085(3)	Ag(1A)–C(22A)	2.088(4)
Ag(1A)–Cl(1A)	2.342(8)	Ag(1A)–Cl(1A)	2.396(1)
N(1A)–C(22A)	1.353(3)	N(1A)–C(22A)	1.363(5)
N(1A)–C(16A)	1.390(3)	N(1A)–C(16A)	1.399(5)
N(1A)–C(15A)	1.479(3)	N(1A)–C(15A)	1.469(5)
N(2A)–C(22A)	1.350(3)	N(2A)–C(22A)	1.354(5)
N(2A)–C(21A)	1.382(4)	N(2A)–C(21A)	1.386(6)
N(2A)–C(23A)	1.468(3)	N(2A)–C(23A)	1.474(6)
C(22A)–Ag(1A)–Cl(1A)	170.4(7)	C(22A)–Ag(1A)–Cl(1A)	156.7(1)
C(22A)–N(1A)–C(16A)	110.6(2)	C(22A)–N(1A)–C(16A)	111.2(3)
C(22A)–N(1A)–C(15A)	122.5(2)	C(22A)–N(1A)–C(15A)	122.3(3)
C(16A)–N(1A)–C(15A)	126.7(2)	C(16A)–N(1A)–C(15A)	126.1(3)
C(22A)–N(2A)–C(21A)	111.2(2)	C(22A)–N(2A)–C(21A)	111.5(3)
C(22A)–N(2A)–C(23A)	123.0(2)	C(22A)–N(2A)–C(23A)	122.6(4)
C(21A)–N(2A)–C(23A)	125.6(2)	C(21A)–N(2A)–C(23A)	125.9(4)
N(2A)–C(22A)–N(1A)	106.2(2)	N(2A)–C(22A)–N(1A)	105.3(3)
N(2A)–C(22A)–Ag(1A)	125.4(2)	N(2A)–C(22A)–Ag(1A)	124.2(3)
N(1A)–C(22A)–Ag(1A)	128.3(2)	N(1A)–C(22A)–Ag(1A)	130.5(3)

or PhC), 53.2 (NCH<sub>2</sub>An), 53.1 (NCH<sub>2</sub>C), 32.2, 29.0, 27.7 and 23.1 (CCH<sub>2</sub>C), 14.0 (CH<sub>3</sub>).

#### 4.6. Preparation of {[1-(9-anthracenylmethyl)-3-butylbimyl]HgCl<sub>2</sub>}<sub>2</sub> (**3a**)

A suspension of KOBu<sup>t</sup> (0.090 g, 0.80 mmol), precursor **1a** (0.200 g, 0.499 mmol) and anhydrous mercury(II) chloride (0.136 g, 0.500 mmol) in THF (20 mL) and acetonitrile (20 mL) was refluxed for 24 h. A brown solution was formed and the solvent was removed with a rotary evaporator. The water (30 mL) was added to the residue and the solution extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The extracting solution was dried with anhydrate MgSO<sub>4</sub>, then the solution was concentrated to 10 ml and hexane (2 mL) was added, as a result a pale yellow powder was obtained. Yield: 0.201 g (63%). M.p.: 265–267 °C. Anal. Calc. for C<sub>26</sub>H<sub>24</sub>Cl<sub>2</sub>HgN<sub>2</sub>: C, 49.10; H, 3.80; N, 4.40. Found: C, 49.42; H, 3.55; N, 4.63%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 0.93 (t, *J* = 5.4, 3H, CH<sub>3</sub>), 1.37 (m, 2H, CH<sub>2</sub>), 1.89 (m, 2H, CH<sub>2</sub>), 4.66 (t, *J* = 5.4, 2H, CH<sub>2</sub>), 6.48 (d, *J* = 6.3, 1H, PhH), 6.94 (s, 2H, CH<sub>2</sub>), 7.13 (t, *J* = 6.3, 1H, PhH), 7.22 (t, *J* = 6.3, 1H, PhH), 7.35 (d, *J* = 6.3, 1H, PhH), 7.39 (t, *J* = 8.4, 2H, AnH) (An: anthracene), 7.46 (t, *J* = 8.4, 2H, AnH), 8.12 (d, *J* = 8.4, 2H, AnH), 8.34 (d, *J* = 8.4, 2H, AnH), 8.60 (s, 1H, AnH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): δ 175.4 (C<sub>carbonyl</sub>), 134.2, 132.1, 131.3, 129.5, 128.4, 124.9, 123.7, 119.3 and 113.3 (AnC

Table 3  
Summary of crystallographic data for **1a** and **3a**

	<b>1a</b>	<b>3a</b>
Formula	C <sub>26</sub> H <sub>27</sub> ClN <sub>2</sub> O	C <sub>28</sub> H <sub>30</sub> Cl <sub>2</sub> HgN <sub>2</sub> OS
Color habit	Yellow, block	Yellow, block
Formula weight	418.95	714.09
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	14.9979(12)	12.269(12)
<i>b</i> (Å)	13.9288(12)	20.31(2)
<i>c</i> (Å)	10.6028(9)	11.760(11)
α (°)	90	90
β (°)	90	109.606(12)
γ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	2215.0(3)	2761.0(5)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.256	1.718
Absorption coefficient (mm <sup>-1</sup> )	0.192	5.867
<i>F</i> (000)	888	1400
Crystal size (mm)	0.24 × 0.22 × 0.18	0.28 × 0.24 × 0.20
θ <sub>min</sub> , θ <sub>max</sub> (°)	2.00, 25.03	2.01, 25.03
<i>T</i> (K)	293(2)	293(2)
Number of data collected	11562	14545
Number of unique data	3912	4867
Number of refined parameters	306	354
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.061	1.008
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> <sub>1</sub>	0.0418	0.0340
<i>wR</i> <sub>2</sub>	0.1056	0.0743
<i>R</i> indices (all data)		
<i>R</i> <sub>1</sub>	0.0591	0.0544
<i>wR</i> <sub>2</sub>	0.1164	0.0822

Table 4  
Summary of crystallographic data for **2a** and **2b**

	<b>2a</b>	<b>2b</b>
Formula	C <sub>26</sub> H <sub>24</sub> AgCl N <sub>2</sub>	C <sub>30</sub> H <sub>32</sub> AgCl <sub>3</sub> N <sub>2</sub>
Color habit	Yellow, block	Yellow, block
Formula weight	507.79	634.80
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.0621(6)	11.7195(11)
<i>b</i> (Å)	11.2651(8)	11.950(2)
<i>c</i> (Å)	12.6149(13)	12.2930(12)
α (°)	113.0930(10)	109.109(2)
β (°)	108.1950(10)	116.2730(10)
γ (°)	94.5410(10)	93.937(2)
<i>V</i> (Å <sup>3</sup> )	1095.0(1)	1411.6(3)
<i>Z</i>	2	2
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.540	1.493
Absorption coefficient (mm <sup>-1</sup> )	1.058	1.020
<i>F</i> (000)	516	648
Crystal size (mm)	0.20 × 0.16 × 0.14	0.28 × 0.20 × 0.16
θ <sub>min</sub> , θ <sub>max</sub> (°)	2.02, 25.03	1.86, 25.03
<i>T</i> (K)	293(2)	293(2)
Number of data collected	6005	7685
Number of unique data	3821	4926
Number of refined parameters	272	362
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.052	1.018
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> <sub>1</sub>	0.0287	0.0479
<i>wR</i> <sub>2</sub>	0.0779	0.1344
<i>R</i> indices (all data)		
<i>R</i> <sub>1</sub>	0.0337	0.0620
<i>wR</i> <sub>2</sub>	0.0803	0.1419

or PhC), 53.6 (NCH<sub>2</sub>An), 52.8 (NCH<sub>2</sub>C), 31.1 (CCH<sub>2</sub>C), 27.9 (CCH<sub>2</sub>C), 13.6 (CH<sub>3</sub>).

#### 4.7. X-ray structure determinations

For compounds **1a**, **2a**, **2b** and **3a**, selected single crystals were mounted on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo Kα radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software [16] with frames of 0.6° oscillation in the θ range 1.8 < θ < 25°. An empirical absorption correction was applied using the SADABS program [17]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on *F*<sup>2</sup> using the SHELXTL package [18]. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Selected bond lengths and angles were showed in Tables 1 and 2, and crystallographic data were summarized in Tables 3 and 4 for **1a**, **2a**, **2b** and **3a**.

#### Acknowledgments

This work was financially supported by the National Science Foundation of China (Project Grant No.

20672081) and the Natural Science Foundation of Tianjin (07JCYBJC00300).

### Appendix A. Supplementary material

CCDC 626601, 607253, 607254 and 626600 contain the supplementary crystallographic data for **1a**, **2a**, **2b** and **3a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.005.

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