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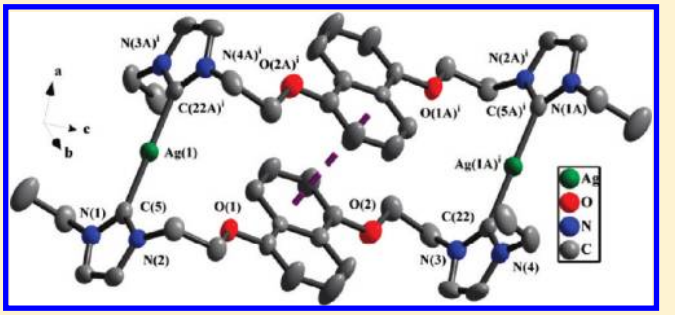
Two N-Heterocyclic Carbene Silver(I) Cyclophanes: Synthesis, Structural Studies, and Recognition for *p*-Phenylenediamine

Qing-Xiang Liu,* Zhao-Quan Yao, Xiao-Jun Zhao, Ai-Hui Chen, Xiao-Qiong Yang, Shu-Wen Liu, and Xiu-Guang Wang

Tianjin Key Laboratory of Structure and Performance for Functional Molecule, College of Chemistry, Tianjin Normal University, Tianjin 300387, People's Republic of China

Supporting Information

ABSTRACT: The diimidazolium salt 1,5-bis[1-ethylimidazoliumylethoxy]naphthalene hexafluorophosphate (**2**) and the dibenzimidazolium salt 1,4-bis[1-(*n*-butyl)benzimidazoliumylethoxy]benzene hexafluorophosphate (**4**), as well as their N-heterocyclic carbene silver(I) cyclophanes [naphthalene-$(OCH_2CH_2imyEt)_2Ag]_2(PF_6)_2$ (**5**) and [benzene$(OCH_2CH_2$-bimy$^nBu)_2Ag]_2(PF_6)_2$ (**6**), have been prepared and characterized. Each cation in complexes **5** and **6** contains a 30-membered macrometallacycle. In the crystal packing of **5** and **6**, 3D architectures are formed via intermolecular weak interactions, including $\pi-\pi$ interactions, hydrogen bonds, and C−H···π contacts. The recognition of neutral *p*-phenylenediamine (PDA) molecules using **5** and **6** as receptors via fluorescent and UV/vis spectroscopic titrations have been investigated.



INTRODUCTION

The development of receptors for recognizing cations and anions has received a significant amount of attention in molecular recognition study and supramolecular chemistry.[1] Additionally, the design and synthesis of receptors capable of binding neutral guests are of crucial importance due to their potential applications in environmental and biological processes.[2] However, this work still remains a great challenge in comparison to the more extensively studied recognition of cations and anions. One of the main strategies for achieving strong affinity and selective recognition for neutral species is the design and synthesis of receptors bearing cavities. In the type of receptor, the acting force between the host and guest mostly derives from several well-known intermolecular weak interactions, including van der Waals forces, classical hydrogen bonds (such as N−H···O and N−H···N hydrogen bonds), aromatic $\pi-\pi$ interactions, and synergistic effects of cavity size.[3] Some other nonclassical hydrogen bonds (such as C−H···X hydrogen bonds, X = O, N, F, Cl, Br, I) have also been reported in recent years.[4] During the course of searching for receptors bearing cavities, we became interested in N-heterocyclic carbene metal cyclophanes. In this paper, we report the synthesis and structures of two new N-heterocyclic carbene silver(I) cyclophanes: [naphthalene$(OCH_2CH_2imyEt)_2$-$Ag]_2(PF_6)_2$ (**5**) and [benzene$(OCH_2CH_2bimy^nBu)_2Ag]_2(PF_6)_2$ (**6**) (imy = imidazol-2-ylidene and bimy = benzimidazol-2-ylidene). In particular, the recognition of *p*-phenylenediamine (PDA) using these cyclophanes as receptors was investigated on the basis of fluorescent and UV/vis spectroscopic titrations.

RESULTS AND DISCUSSION

Synthesis and General Characterization of Precursors 2 and 4. As shown in reaction 1 in Scheme 1, 1,5-dihydroxynaphthalene on etherification with 1,2-dibromoethane followed by a reaction with 1-ethylimidazole to afford the diimidazolium salt 1,5-bis[1-ethylimidazoliumylethoxy]naphthalene bromide and subsequent anion exchange with ammonium hexafluorophosphate in methanol gave 1,5-bis[1-ethylimidazoliumylethoxy]-naphthalene hexafluorophosphate (**2**). The dibenzimidazolium salt 1,4-bis[1-(*n*-butyl)benzimidazoliumylethoxy]benzene hexafluorophosphate (**4**) was prepared in a manner analogous to that of **2** (Scheme 1, reaction 2). Precursors **2** and **4** are stable toward air and moisture, are soluble in polar organic solvents such as dichloromethane and acetonitrile, and are scarcely soluble in benzene, diethyl ether, and petroleum ether. In the ^1H NMR spectra of **2** and **4**, the imidazolium (or benzimidazolium) proton signals (NC*H*N) appear at δ 9.38 and 9.95 ppm, which are consistent with the chemical shifts of reported imidazolium (or benzimidazolium) salts.[5]

Synthesis and General Characterization of NHC Silver(I) Cyclophanes 5 and 6. The reaction of precursors **2** and **4** with silver(I) oxide in acetonitrile afforded the N-heterocyclic carbene silver(I) cyclophanes **5** and **6**, respectively (Scheme 2). Complexes **5** and **6** in the solid state are stable toward air and moisture, are slightly light sensitive, are soluble in DMSO, and are insoluble

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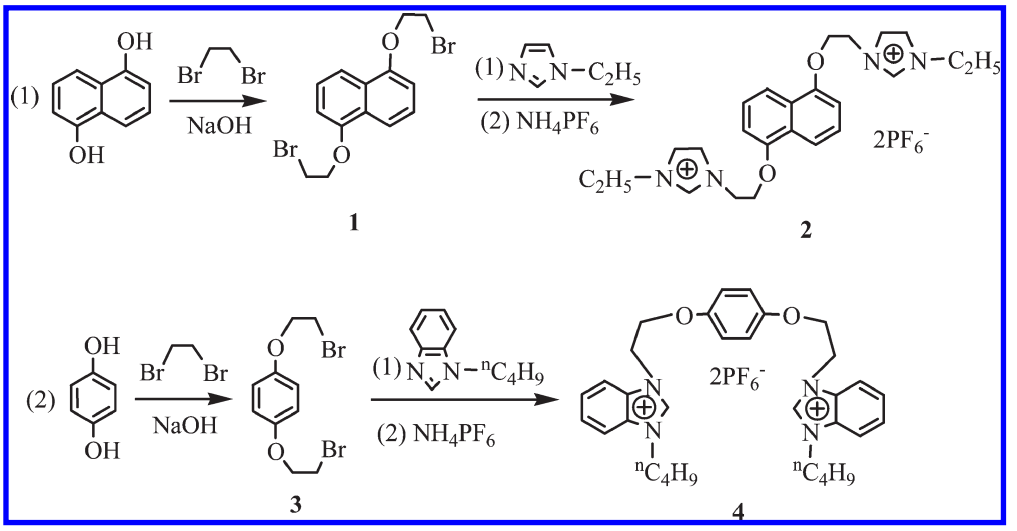
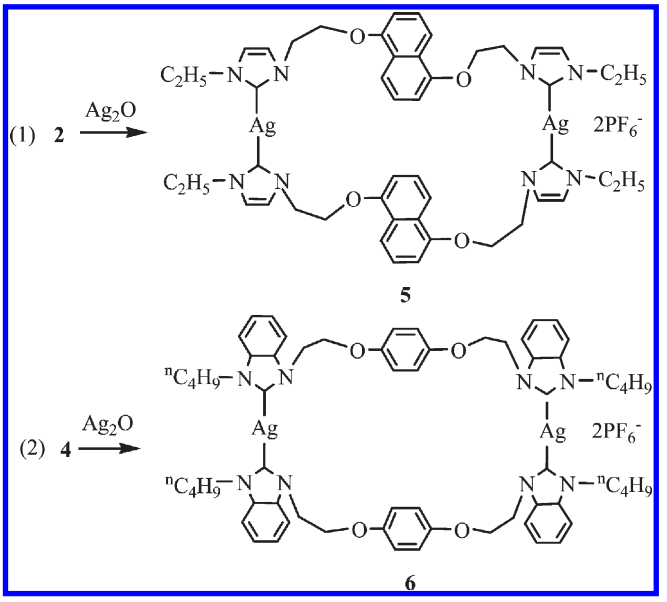
Scheme 1. Preparation of Precursors 2 and 4



Scheme 2. Preparation of Complexes 5 and 6



in diethyl ether and hydrocarbon solvents. In the ^{1}H NMR spectra of **5** and **6**, the disappearance of the resonances for the imidazolium (or benzimidazolium) protons (NC*H*N) shows the formation of the expected metal carbene complexes, and the chemical shifts of other hydrogens are similar to those of the corresponding precursors. In ^{13}C NMR spectra, the signal for the carbene carbon of **5** appears at 206.2 ppm, which is similar to signals for known carbene silver(I) complexes.[6] The signal of the carbene carbon in **6** was not observed. Similar results have been reported for some carbene silver(I) complexes, which may result from the fluxional behavior of the NHC complexes.[7]

Structures of NHC Silver(I) Cyclophanes 5 and 6. Colorless crystals of **5** and **6** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into their DMSO and CH_3OH/C_2H_5OH solutions. In complexes **5** and **6**, each cation contains a 30-membered macrometallacycle formed by two bidentate carbene ligands and two silver(I) atoms (Figures 1a and 2a), in which each silver(I) atom is dicoordinated with two carbene carbon atoms to adopt an almost linear arrangement (C−Ag−C = 179.6(1)° for **5** and 175.1(1)° for **6**), and the Ag−C distance is in the range 2.074(5)−2.093(3) Å. In **5** and **6**, two C−Ag−C units are parallel, and the intramolecular separation Ag−Ag in the macrometallacycle is 11.680(4) Å for **5** and 9.551(8) Å for **6**. These data show us that the hosts molecules **5** and **6** have large cavity structures which can contain and have astrong affinity for *p*-phenylenediamine. Because the longest distance between two hydrogen atoms in *p*-phenylenediamine is 6.74 Å, it is suitable for the size of these two cavities. The X-ray crystal structure analyses of **5** and **6** show that inversion centers exist in these complexes. Two imidazole (or benzimidazole) rings in the NHC−Ag−NHC units form dihedral angles of 3.0° for **5** (11.8° for **6**). Two imidazole (or benzimidazole) rings in the same ligand form dihedral angles of 2.9° for **5** (13.3° for **6**). The dihedral angles of imidazole (or benzimidazole) rings and naphthalene (or benezene) rings in the same ligand are 72.3 and 77.7° for **5** (70.3 and 82.3° for **6**). In **5**, $\pi-\pi$ stacking interactions between two parallel naphthalene rings are observed with a face-to-face distance of 3.596(7) Å (center-to-center distance 3.634(1) Å).[8] In **6**, two benzene rings are also parallel, but no $\pi-\pi$ stacking interactions are observed.

An interesting feature in the crystal packing of **5** (Figure 1b) is that the 2D supramolecular layers are formed by C−H···O hydrogen bonds[9] and $\pi-\pi$ stacking interactions from intermolecular imidazole rings with a face-to-face distance of 3.478(5) Å (center-to-center distance 4.210(1) Å). In the C−H···O hydrogen bonds, the hydrogen atoms are from CH_2 groups of ether chains (data for the C−H···O hydrogen bonds are given in Table 1). In addition, PF_6^- groups are packed between successive 2D supramolecular layers and hold the layers together via C−H···F hydrogen bonds[10] (Table 1) to expand 2D layers into a 3D supramolecular architecture (Figure 1c).

In the crystal packing of **6**, a 2D supramolecular layer is formed via two types of C−H···π contacts,[11] as shown in Figure 2b. In the first C−H···π contacts, the hydrogen atoms are from CH_2 groups of ether chains and π systems are from benzimidazole rings (H···π distance 2.673(2) Å and C−H···π angle

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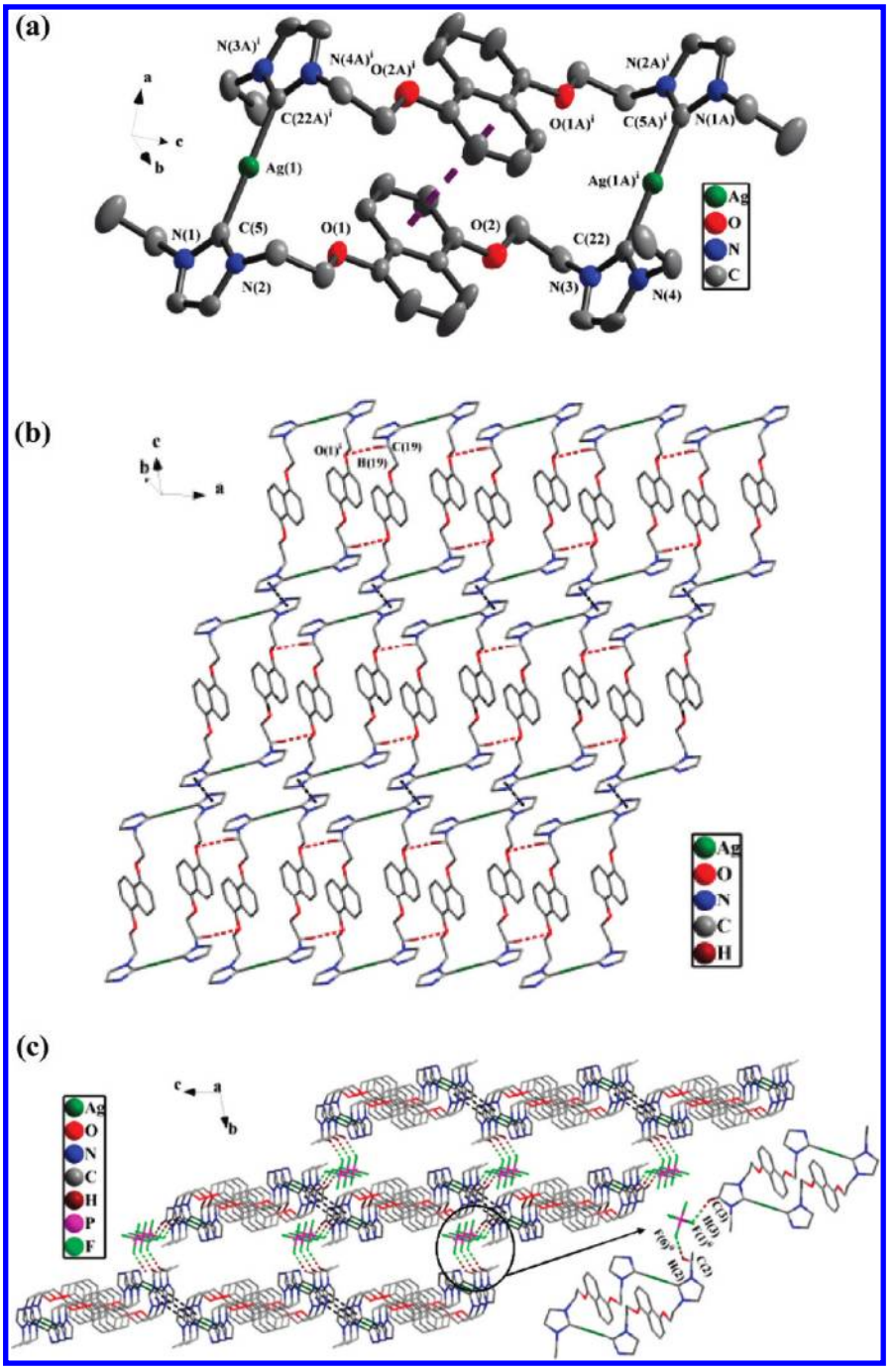

Figure 1. (a) Perspective view of **5** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms and the PF_6^- anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−C(5) = 2.075(5), Ag(1)−C(22A) = 2.074(5); C(5)−Ag(1)−C(22A) = 179.6(1), N(1)−C(5)−N(2) = 104.1(4). Symmetry code: (i) $2 - x, -y, 1 - z$. (b) 2D supramolecular layer of **5** showing $\pi-\pi$ interactions and C−H···O hydrogen bonds. All hydrogen atoms, except those participating in the hydrogen bonds, and all ethyl groups on nitrogen atoms are omitted for clarity. (c) 3D supramolecular architecture of **5** with $\pi-\pi$ interactions and C−H···O and C−H···F hydrogen bonds. All hydrogen atoms, except those participating in the hydrogen bonds, and irrelevant ethyl groups are omitted for clarity. Symmetry code: (ii) $x, 1 + y, z$.

128.2(1)°). In the second C−H···π contacts, the hydrogen atoms are from benzimidazole rings and π systems are from benzene rings (H···π distance 2.859(2) Å and C−H···π angle 149.2(3)°). Similar to the case for **5**, PF_6^- groups in **6** are also packed between successive 2D supramolecular layers and hold the layers together via C−H···F hydrogen bonds (Table 1) to expand 2D layers into a 3D supramolecular architecture (Figure 2c).

Recognition of *p*-Phenylenediamine (PDA) Using 5 and 6 as Receptors. In the NHC silver(I) cyclophanes **5** and **6**, each cycle of cation contains several types of binding sites (such as oxygen atoms, nitrogen atoms, and π systems). In accord with the sizes of cavities and structural characteristics of **5** and **6**, the selective recognition of some neutral molecules using **5** and **6** as receptors can be measured. During the experiments, we

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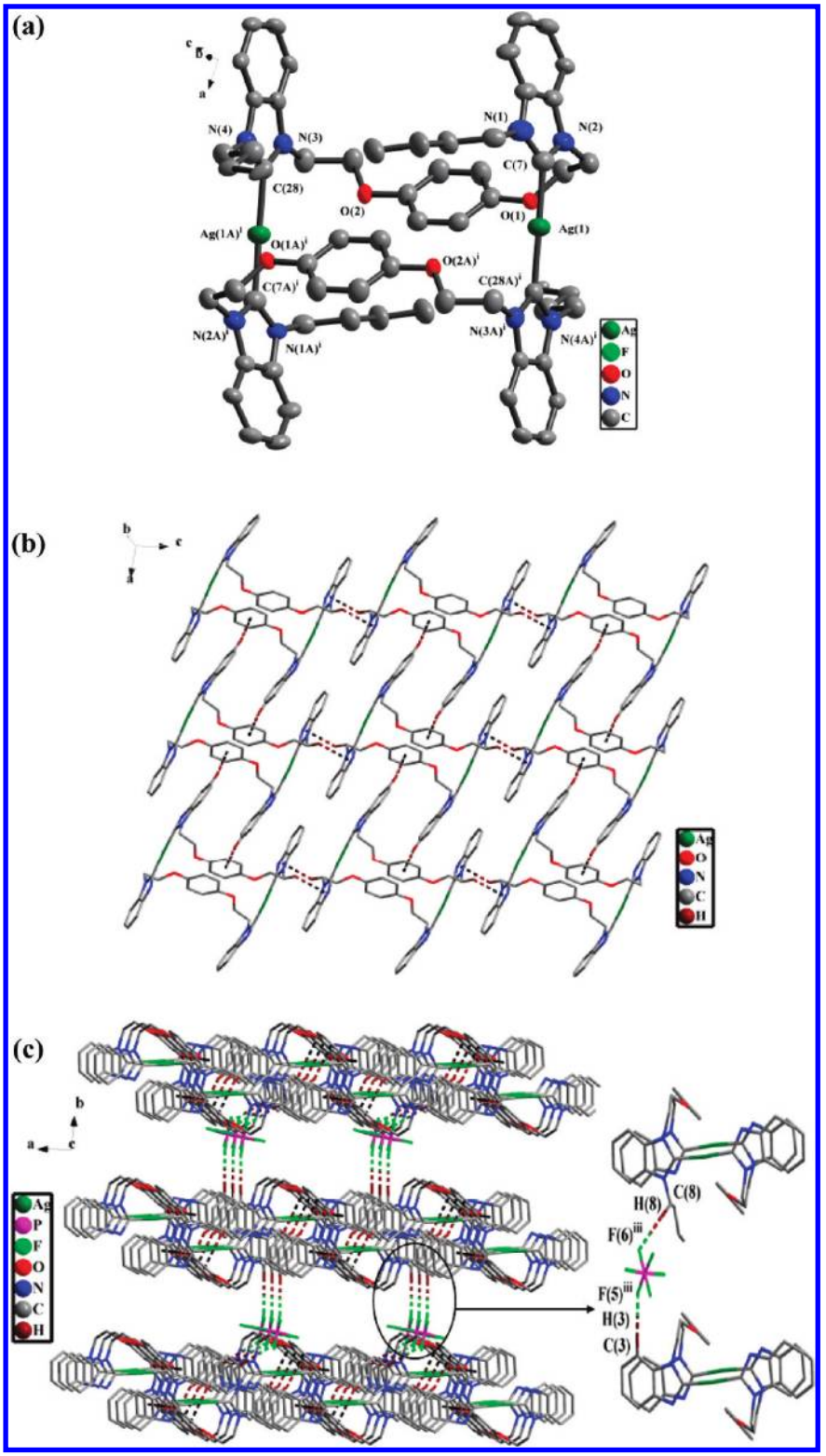

Figure 2. (a) Perspective view of **6** and anisotropic displacement parameters depicting 30% probability. All hydrogen atoms and the PF_6^- anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−C(7) = 2.093(3), Ag(1)−C(28A) = 2.086(3); C(7)−Ag(1)−C(28A) = 175.1(1), N(1)−C(7)−N(2) = 106.2(3). Symmetry code: (i) 2 − *x*, −*y*, −*z*. (b) 2D supramolecular layer of **6** with C−H···π contacts. All hydrogen atoms, except those participating in C−H···π contacts, and all butyl groups on nitrogen atoms are omitted for clarity. (c) 3D supramolecular architecture of **6** with C−H···π contacts and C−H···F hydrogen bonds. All hydrogen atoms, except those participating in the hydrogen bonds and C−H···π contacts, and irrelevant butyl groups were omitted for clarity. Symmetry code: (iii) 1 − *x*, −*y*, −*z*.

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Table 1. H-Bonding Geometry for Complexes 5 and 6

D−H···A[a]	D−H, Å	H···A, Å	D···A, Å	D−H···A, deg
		Complex **5**		
C(19)−H(19)···O(5)^{i}	0.97(5)	2.565(3)	3.629(6)	172.6(3)
C(3)−H(3)···F(1)^{ii}	0.93(4)	2.537(3)	3.320(5)	142.2(3)
C(2)−H(2)···F(6)^{ii}	0.97(5)	2.520(3)	3.281(6)	135.3(2)
		Complex **6**		
C(3)−H(3)···F(5)^{iii}	0.93(4)	2.528(4)	3.457(6)	176.1(3)
C(8)−H(8)···F(6)^{iii}	0.97(4)	2.573(3)	3.536(5)	171.7(2)

[a] Symmetry code: (i) $2-x, 1-y, 2-z$; (ii) $x, 1+y, z$; (iii) $1-x, -y, -z$.

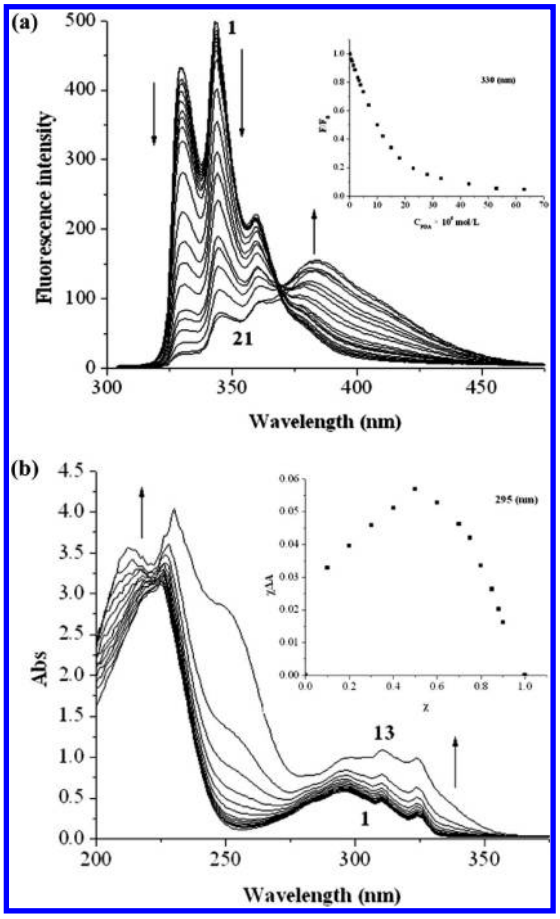

Figure 3. (a) Emission spectra (λ_{ex} 294 nm) of **5** (1.0×10^{-5} mol/L) in the presence of *p*-phenylenediamine (PDA) in acetonitrile at 25 °C. The concentrations (10^{-5} mol/L) of *p*-phenylenediamine for curves 1−21 (from top to bottom) are 0, 0.25, 0.67, 1, 1.5, 2, 3, 3.5, 4, 5, 7, 10, 12, 15, 18, 23, 28, 33, 43, 53, and 63. Inset: variation of fluorescence quenching F/F_0 of **5** with increasing *p*-phenylenediamine concentration. (b) UV/vis absorption spectra of receptor **5** (1.0×10^{-5} mol/L) in acetonitrile at 25 °C. The concentrations (10^{-5} mol/L) of *p*-phenylenediamine for curves 1−13 (from bottom to top) are 0, 0.11, 0.13, 0.17, 0.25, 0.33, 0.43, 0.67, 1, 1.5, 2.4, 4, and 9. Inset: Job plot for the **5**/*p*-phenylenediamine complex in acetonitrile solution at 295 nm.

found that each cycle in **5** and **6** has a strong affinity for the neutral *p*-phenylenediamine molecule, and these compounds exhibit interesting *p*-phenylenediamine complexation properties

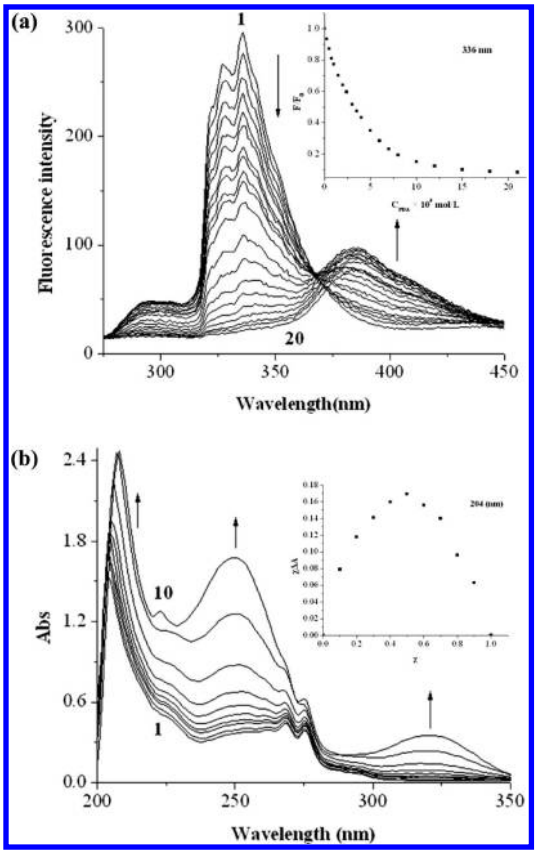

Figure 4. (a) Emission spectra (λ_{ex} 287 nm) of **6** (1.0×10^{-5} mol/L) in the presence of *p*-phenylenediamine in acetonitrile at 25 °C. The concentrations (10^{-5} mol/L) of *p*-phenylenediamine for curves 1−20 (from top to bottom) are 0, 0.25, 0.5, 0.75, 1, 1.5, 2, 2.4, 3, 3.5, 4, 5, 6, 7, 8, 10, 12, 15, 18, and 21. Inset: variation of fluorescence quenching F/F_0 of **6** with increasing *p*-phenylenediamine concentration. (b) UV/vis absorption spectra of receptor **6** (1.0×10^{-5} mol/L) in acetonitrile at 25 °C. The concentrations (10^{-5} mol/L) of *p*-phenylenediamine for curves 1−10 (from bottom to top) are 0, 0.11, 0.25, 0.43, 0.67, 1, 1.5, 2.4, 4, and 9. Inset: Job plot for the **6**/*p*-phenylenediamine complex in acetonitrile solution at 204 nm.

in acetonitrile at 25 °C. To further study the recognition of *p*-phenylenediamine by **5** or **6**, fluorescence titrations were conducted (Figures 3a and 4a). The fluorescence intensities of **5** and **6** (at about λ_{em} 330−365 nm for **5** and λ_{em} 320−345 nm for **6**) decreased markedly with increasing concentration of *p*-phenylenediamine until the fluorescence intensities did not change. The quenching behaviors of *p*-phenylenediamine on the fluorescence of **5** or **6** were found to follow a conventional Stern−Volmer relationship[12−16] (Figures S1a and S2a, -Supporting Information), which may be attributed to the charge transfer interaction between aromatic systems in the host and *p*-phenylenediamine

$$F_0/F = 1 + K_s C_{PDA}$$

where F_0 and F are the fluorescence intensities of **5** or **6** in the absence and presence of *p*-phenylenediamine, respectively, and C_{PDA} is the concentration of *p*-phenylenediamine. The equations reveal that F_0/F increases in direct proportion to the increasing concentration of *p*-phenylenediamine, and the quenching constant K_s defines the quenching efficiency of *p*-phenylenediamine. As shown by the Stern−Volmer plot in Figures S1a and S2a (inset), the K_s values of *p*-phenylenediamine are 0.1×10^5 M^{-1}

for **5** and 0.28×10^5 M^{-1} for **6**, and the linear ranges are $(0-1.0) \times 10^{-4}$ M for **5** and $(0-4.0) \times 10^{-5}$ M for **6**.

The fluorescence intensity for **5** or **6** at about λ_{em} 385 nm increased gradually with increasing concentration of *p*-phenylenediamine (Figures 3a and 4a), which may derive from the fluorescence emission of *p*-phenylenediamine, because the pure *p*-phenylenediamine molecule has fluorescence emission in this position but cyclophanes **5** and **6** have no fluorescence emission in this position.

On addition of *p*-phenylenediamine to the solutions of **5** and **6** in acetonitrile at 25 °C, the UV/vis absorption spectra increased gradually in intensity (Figures 3b and 4b). The absorption enhancement of **5** or **6** followed a Benesi–Hildebrand type equation[17]

$$\frac{A_0}{A_0 - A} = \frac{\varepsilon_r}{\varepsilon_r - \varepsilon_c}\left(\frac{1}{KC_{PDA}} + 1\right)$$

where A_0 is the absorption intensity of receptor **5** or **6** in the absence of *p*-phenylenediamine, $A_0 - A$ is the discrepancy of absorption intensity between the absence and presence of *p*-phenylenediamine, ε_r is the molar extinction coefficient of **5** or **6**, ε_c is the molar extinction coefficient of the *p*-phenylenediamine complex with **5** or **6**, and C_{PDA} is the concentration of *p*-phenylenediamine. The stability constant *K* between **5** or **6** and *p*-phenylenediamine is given by the ratio of intercept to slope (Figures S1b and S2b, Supporting Information; $K = 0.45 \times 10^5$ M^{-1} for **5** and 1.06×10^5 M^{-1} for **6**).

It is notable that a 1:1 complexation stoichiometry for *p*-phenylenediamine complexes with **5** and **6** was established by a Job plot analysis as shown in the insets to Figures 3b and 4b,[18] where the products ($\chi\Delta A$) between molar fractions and the discrepancy of the absorption bands at 295 nm for **5** and at 204 nm for **6** were plotted against molar fractions (χ) of **5** or **6** under the conditions of a constant total concentration. As such, the concentration of *p*-phenylenediamine complexes with **5** and **6** approached a maximum when the molar fractions of hosts/guest were about 0.5.

In the recognition of *p*-phenylenediamine molecules using **5** and **6** as receptors via fluorescent and UV/vis methods, the quenching constant K_s values (0.1×10^5 M^{-1} for **5** and 0.28×10^5 M^{-1} for **6**) from the Stern–Volmer equation (fluorescence method) and the stability constant *K* values (0.45×10^5 M^{-1} for **5** and 1.06×10^5 M^{-1} for **6**) from the Benesi–Hildebrand equation (UV/vis method) are similar to each other.[19] To the best of our knowledge, these are the largest K_s or *K* values, which show that the cyclophanes **5** and **6** are efficient macrocyclic receptors for *p*-phenylenediamine molecules in acetonitrile. Notably, K_s or *K* values in **6** are somewhat larger than those in **5**, which show that the binding capability between **6** and *p*-phenylenediamine is slightly stronger than that between **5** and *p*-phenylenediamine.

In order to understand the interactions of **5** or **6** with *p*-phenylenediamine at the molecular level, we attempted to determine the solid-state structures of *p*-phenylenediamine complexes with **5** and **6**. Unfortunately, no crystals could be obtained.

CONCLUSIONS

In summary, the two new NHC silver(I) cyclophanes **5** and **6** have been synthesized and characterized. In **5** and **6**, each cation possesses a 30-membered macrometallacycle, in which several types of binding sites (such as oxygen atoms, nitrogen atoms, and π systems) are included. By using the methods of fluorescent and UV/vis spectroscopic titrations, the values of K_s based on the Stern–Volmer equation and *K* based on the standard Benesi–Hildebrand equation are similar to each other, which shows that the cyclophanes **5** and **6** are efficient receptors for *p*-phenylenediamine molecules in acetonitrile. Further studies on the synthesis of new organometallic compounds from precursors **2** and **4**, as well as analogous ligands, are underway.

EXPERIMENTAL SECTION

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 were used without further purification. Melting points were determined with a Boetius Block apparatus. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury Vx 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. *J* values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. The luminescent spectra were conducted on a Cary Eclipse fluorescence spectrophotometer. UV–vis spectra were obtained using a JASCO-V570 spectrometer.

Preparation of 1,5-Bis(bromoethoxy)naphthalene (1). A water solution (30 mL) of NaOH (2.997 g, 74.9 mmol) and tetrabutylammonium bromide (TBAB; 0.201 g, 0.6 mmol) was added to a solution of 1,5-dihydroxynaphthalene (2.000 g, 12.5 mmol) in 1,2-dibromoethane (40 mL) and stirred for 12 h at 80 °C. The brown organic layer was obtained by separating it from the water layer. 1,2-Dibromoethane in the organic layer was removed with a rotary evaporator, and H_2O (80 mL) was added to the residue. Then the solution was extracted with $CHCl_3$ (3 × 30 mL), and the extracting solution was dried over anhydrous $MgSO_4$. After $CHCl_3$ was removed, a pale brown powder of 1,5-bis(bromoethoxy)naphthalene (**1**) was obtained. Yield: 2.737 g (59%). Mp: 140–142 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.95 (t, *J* = 6.5, 4H, CH_2), 4.49 (t, *J* = 6.5, 4H, CH_2), 7.03 (d, *J* = 3.8, 2H, Ph *H*), 7.43 (d, *J* = 3.8, 2H, Ph *H*), 7.80 (d, *J* = 3.8, 2H, Ph *H*).

Preparation of 1,5-Bis[1-ethylimidazoliumylethoxy]-naphthalene Hexafluorophosphate (2). A solution of 1-ethylimidazole (2.468 g, 25.7 mmol) and 1,5-bis(bromoethoxy)naphthalene (4.000 g, 10.7 mmol) in THF (150 mL) was stirred for seven days under refluxing, and a yellow precipitate was formed. The product was filtered and washed with THF to give a yellow powder of 1,5-bis[1-ethylimidazoliumylethoxy]naphthelene bromide. Yield: 4.542 g (75%). M.p.: 166–168 °C.

NH_4PF_6 (1.382 g, 8.5 mmol) was added to the methanol solution of 1,5-bis[1-ethylimidazoliumylethoxy]naphthelene bromide (2.000 g, 3.5 mmol) with stirring, and a yellow precipitate was formed immediately. The yellow powder was collected by filtration and washed with small portions of methanol to give 1,5-bis[1-ethylimidazoliumylethoxy]-naphthelene hexafluorophosphate (**2**). Yield: 1.810 g (81%). M.p.: 200–202 °C. Anal. Calcd for $C_{24}H_{30}F_{12}N_4O_2P_2$: C, 41.38; H, 4.34; N, 8.04%. Found: C, 41.57; H, 4.62; N, 8.47%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.42 (t, *J* = 7.2, 6H, CH_3), 4.25 (q, *J* = 7.2, 4H, CH_2), 4.47 (t, *J* = 4.4, 4H, CH_2), 4.75 (t, *J* = 4.4, 4H, CH_2), 7.04 (d, *J* = 8.0, 2H, Ph *H*), 7.35 (t, *J* = 8.0, 2H, Ph *H*), 7.64 (d, *J* = 8.0, 2H, Ph *H*), 7.83 (s, 2H, 4 or 5-imi *H*), 7.95 (s, 2H, 4 or 5-imi *H*), 9.38 (s, 2H, 2-imi *H*) (imi = imidazole).

Preparation of 1,4-Bis(bromoethoxy)benzene (3). This compound was prepared in a manner analogous to that of 1,5-bis(bromoethoxy)naphthalene, only 1,4-dihydroxybenzene was used instead of 1,5-dihydroxynaphthalene. Yield: 3.216 g (55%), Mp: 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60 (t, *J* = 6.0, 4H, CH_2), 4.24 (t, *J* = 6.0, 4H, CH_2), 6.86 (s, 4H, Ph *H*).

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Preparation of 1,4-Bis[1-(*n*-butyl)imidazoliumylethoxy]-benzene Hexafluorophosphate (4). This compound was prepared in a manner analogous to that of **2**, only 1,4-bis(bromoethoxy)benzene and 1-(*n*-butyl)benzimidazole were used instead of 1,5-bis(bromoethoxy)-naphthalene and 1-ethylimidazole, respectively. Yield: 1.960 g (82%), Mp: 218−220 °C. Anal. Calcd for $C_{32}H_{40}F_{12}N_4O_2P_2$: C, 47.88; H, 5.02; N, 6.98. Found: C, 47.54; H, 5.47; N, 6.83. ^{1}H NMR (400 MH$_Z$, DMSO-d_6): δ 1.73 (t, J = 5.4, 6H, CH_3), 2.15 (m, 4H, CH_2), 2.19 (m, 6H, CH_2), 4.37 (t, J = 5.6, 4H, CH_2), 4.57 (q, J = 5.4, 2H, CH), 4.92 (t, J = 5.6, 4H, CH_2), 6.86 (m, 4H, Ph H), 7.70 (m, 4H, Ph H), 8.17 (m, 4H, Ph H), 9.95 (s, 2H, benzimi H) (benzimi = benzimidazole).

Preparation of the Cyclophane [naphthalene(OCH$_2$CH$_2$-imyEt)$_2$Ag]$_2$(PF$_6$)$_2$ (5). Silver oxide (0.096 g, 0.4 mmol) was added to a solution of precursor **2** (0.200 g, 0.3 mmol) in acetonitrile (30 mL), and the suspension was stirred for 24 h with refluxing. The resulting solution was filtered and concentrated to 5 mL, and diethyl ether (5 mL) was added to precipitate a white powder. Isolation by filtration yielded cyclophane **5**. Yield: 0.078 g (33%). Mp: 246−247 °C. Anal. Calcd for $C_{48}H_{56}Ag_2F_{12}N_8O_4P_2$: C, 43.85; H, 4.29; N, 8.52. Found: C, 44.13; H, 4.47; N, 8.53. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.40 (t, J = 7.2, 12H, CH_3), 4.25 (q, J = 7.2, 8H, CH_2), 4.51 (t, J = 4.4, 8H, CH_2), 4.76 (t, 8H, CH_2), 7.73−7.78 (m, 12H, Ph H), 7.84 (d, 4H, imi H), 7.94 (d, J = 7.8, 4H, imi H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 206.2 ($C_{carbene}$), 153.3, 136.8, 126.1, 125.9, 123.4, 122.8, 122.1, 112.1, 107.0, and 106.2 (Ph C or imi C), 52.1 (OCH_2), 47.4 (NCH_2), 45.5 (NCH_2), 18.6 (CH_3).

Preparation of the Cyclophane [benzene(OCH$_2$CH$_2$-bimy^{n}Bu)$_2$Ag]$_2$(PF$_6$)$_2$ (6). This complex was prepared in a manner analogous to that of **6**, only **4** was used instead of **2**. Yield: 0.170 g (45%). Mp: 245−247 °C. Anal. Calcd for $C_{64}H_{76}Ag_2F_{12}N_8O_4P_2$: C, 50.34; H, 5.02; N, 7.34. Found: C, 50.65; H, 5.43; N, 7.74. ^{1}H NMR (400 MH$_Z$, DMSO-d_6): δ 0.76 (t, J = 5.6, 12H, CH_3), 1.29 (m, 8H, CH_2), 1.84 (m, 8H, CH_2), 4.23 (t, J = 4.2, 8H, CH_2), 4.58 (t, J = 5.6, 8H, CH_2), 4.99 (t, J = 4.2, 8H, CH_2), 6.40 (s, 8H, Ph H), 7.48 (m, 8H, Ph H), 7.84 (d, J = 6.4, 4H, Ph H), 8.05 (d, J = 6.4, 4H, Ph H). ^{13}C NMR (100 MH$_Z$, DMSO-d_6): δ 152.0, 149.1, 134.2, 133.8, 124.8, 118.3, 115.6, 113.1, and 112.8 (PhC), 67.9 (OCH_2), 49.2 (NCH_2), 48.8 (NCH_2), 32.9 (CCH_2C), 20.3 (CCH_2C), 14.3 (CCH_3). The carbene carbon was not observed.

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 receptors (1×10^{-5} mol/L) into the 4 mL cuvette and adding increasing amounts of the *p*-phenylenediamine ($0-9.0 \times 10^{-5}$ mol/L) using a microsyringe. The absorption spectra were recorded in the range 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.

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 receptors (1×10^{-5} mol/L) into the 4 mL cuvette and adding increasing amounts of *p*-phenylenediamine ($0-63 \times 10^{-5}$ mol/L for **5** and $0-21 \times 10^{-5}$ mol/L for **6**) using a microsyringe. The receptor solution was excited at 294 nm for **5** and 287 nm for **6**, and the emission spectra were recorded in the range 300−450 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.

X-ray Structure Determinations. For complexes **5** and **6** selected single crystals were mounted on a Bruker APEX II CCD diffractometer at 293(2) K with Mo Kα radiation (λ = 0.710 73 Å) in the ω scan mode. Data collection and reduction were performed using SMART and SAINT software[20] with frames of 0.6° oscillation in the range of $1.8° < \theta < 25°$. An empirical absorption correction was applied using the SADABS program.[21] 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.[22] All hydrogen atoms were generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters, and included in the final calculations. Crystallographic data are summarized in Table S1 (Supporting Information) for **5** and **6**.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving additional Stern−Volmer and Benesi−Hildebrand plots and a table and CIF files giving crystallographic data for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: qxliu@eyou.com.

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