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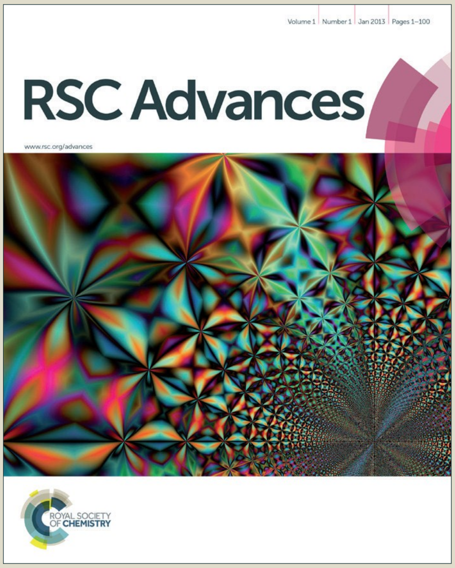

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A NHC silver(I) macrometallocycle: synthesis, structure and selective recognition of iodide anion

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A bis-benzimidazolium salt with oligoether-linker **$LH_2{\cdot}(PF_6)_2$** and its 13-membered N-heterocyclic carbene silver(I) crown ether **1** has been synthesized and characterized. The coordination geometry on the silver(I) ion of **1** is nearly linear with C(7)-Ag(1)-C(23) bond angle of 179.6(1)°. In the crystal packing of **1**, 2D supramolecular layer is formed by π-π stacking interactions from benzimidazole rings. Particularly, the selective recognition of I^- using **1** as a receptor was studied on the basis of fluorescent and UV/vis spectroscopic titrations.

Introduction

The molecular recognition is the process that the host binds selectively guest to produce a specific function.[1] The traditional covalent bond is a main force between host and guest. However, the non-covalent forces, such as van der Waals forces, hydrogen bonds and electrostatic interactions, also play important roles. Recognition of anionic species is a vigorous field of research due to their significance in biology, medicine and environment.[2] The detection, isolation and identification of anions have shown a broad application prospect in membrane transport carrier, chemical sensing and imitation-enzyme-catalyzed organic synthesis.[3] Some anionic receptors that can selectively identify alkaline ions (like fluoride ion and acetate ion) and other anions have been reported.[4-6] Iodine is a trace element toward human beings, and it has important influence on brain function, cell growth, nerve activity, metabolism and thyroid function. The deficiency or excess of iodine in human body can cause goiter, hypothyroidism, hyperthyroidism and some other diseases.[7] Additionally, iodine has also been widely used in the synthesis of drugs.[8] Thus, the analysis and detection of iodide anion is of great importance in our daily life. Common detection methods of iodide anion are GC, capillary electrophoresis and atomic absorption spectroscopy.[9] In general, the iodide anion is difficult to be bound by receptors due to its spherical structure and weak alkaline characteristics. Up to now, only several receptors that can bind iodide selectively have been known.[10] Therefore, the design and synthesis of iodide receptors with relatively simple structure are still a challenging job in host-guest chemistry.

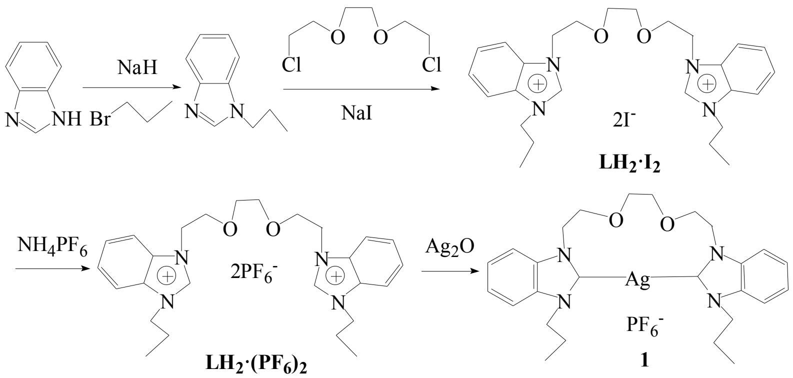
During the course of searching for receptors, we became interested in N-heterocyclic carbene (NHC) metal crown ethers. In this paper, we report the synthesis and structure of a new N-heterocyclic carbene silver(I) crown ether silver-{C,C'-1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl)} hexafluorophosphate (**1**). Particularly, the selective recognition of I^- using **1** as a receptor was studied on the basis of fluorescent and UV/vis spectroscopic titrations.

Results and discussion

Synthesis and general characterization of bis-benzimidazolium salt $LH_2\cdot(PF_6)_2$ and NHC silver(I) crown ether 1

As shown in Scheme 1, benzimidazole as a starting material was alkylated with 1-bromopropane, followed by quarterization with 1,2-bis(2-chloroethoxy)ethane in the presence of NaI to afford bis-benzimidazolium salt, 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propylbenzimidazolium-1-yl) diiodide ($LH_2\cdot I_2$). Then anion exchange was carried out with ammonium hexafluorophosphate in methanol to give $LH_2\cdot(PF_6)_2$. Precursor $LH_2\cdot(PF_6)_2$ is stable to air and moisture, and soluble in organic solvents such as dichloromethane and acetonitrile, and scarcely soluble in diethyl ether, petroleum ether and water. The structure of **$LH_2{\cdot}(PF_6)_2$** was confirmed by its ^{1}H NMR and ^{13}C NMR spectroscopy and elemental analysis. In the ^{1}H NMR spectra of **$LH_2{\cdot}(PF_6)_2$**, the benzimidazolium proton signal (NC*H*N) appears at $\delta = 9.58$ ppm, which is consistent with the chemical shifts of the known benzimidazolium salts.[11]

Reaction of precursor **$LH_2{\cdot}(PF_6)_2$** with Ag_2O in CH_2Cl_2 to afford a N-heterocyclic carbene silver(I) complex silver-{C,C'-1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl)} hexafluorophosphate (**1**). Complex **1** is soluble in DMSO and CH_3CN, and almost insoluble in diethyl ether. The complex **1** is slightly light-sensitive in the solution, but light-stable as solid. In the ^{1}H NMR spectra of **1**, the resonance for the benzimidazolium proton (NC*H*N) has disappeared, and the chemical shifts of other protons are similar to those of the corresponding precursor **$LH_2{\cdot}(PF_6)_2$**. In the ^{13}C NMR spectra of **1**, the signal of the carbene carbon was not observed. The absence of the carbene carbon resonance is not unusual, and this phenomenon has been reported for some silver(I)-carbene complexes, which may result from the fluxional behavior of the NHC complexes.[12]



Scheme 1 Preparation of the bis-benzimidazole salt **$LH_2{\cdot}(PF_6)_2$** and complex **1**.

Structure of NHC silver(I) crown ether 1

The formation of silver(I) carbene complex **1** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy and X-ray crystallography. The crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of CH_2Cl_2 in air. The cation of complex **1** contains a 13-membered NHC silver crown ether formed by a silver(I) ion and a chelate biscarbene ligand with a flexible linkage as shown in Fig. 1. The both benzimidazole rings within each molecule form a dihedral angle of 16.5°, and two n-propyl group chains point to contrary directions. The coordination geometry on the silver(I) ion is nearly linear with C(7)-Ag(1)-C(23) bond angle of 179.5(8)°. The $Ag-C_{carbene}$ bond distance is 2.090(3) Å. The internal ring angle (N-C-N) at the carbene center is 106.3(3)°. These values are similar to the corresponding values of other NHC silver complexes reported.[13] The Ag···O separations are 3.344(3) Å and 3.533(3) Å, respectively, which shows that Ag···O interactions can be neglected (Sum of van der Waals radii of silver and oxygen = 3.10 Å).

In the crystal packing of **1**, 2D supramolecular layer (Fig. 2) is formed by π-π stacking interactions from benzimidazole rings with a face-to-face distance of 3.479(4) Å (the distance of center-to-center being 4.276(7) Å).[14]

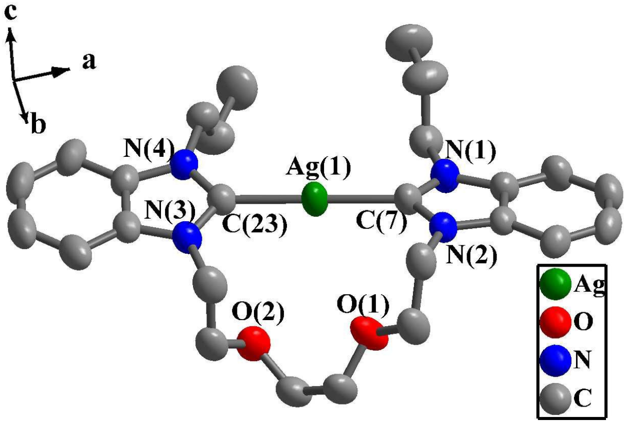


Fig. 1 Perspective view of **1** and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)-C(7) 1.353(6), N(2)-C(7) 1.355(4), N(4)-C(23) 1.348(6), N(3)-C(23) 1.351(5), Ag(1)-C(7) 2.090(3), Ag(1)-C(23) 2.087(9); N(1)-C(7)-N(2) 106.3(1), N(3)-C(23)-N(4) 105.9(9), C(7)-Ag(1)-C(23) 179.5(8).

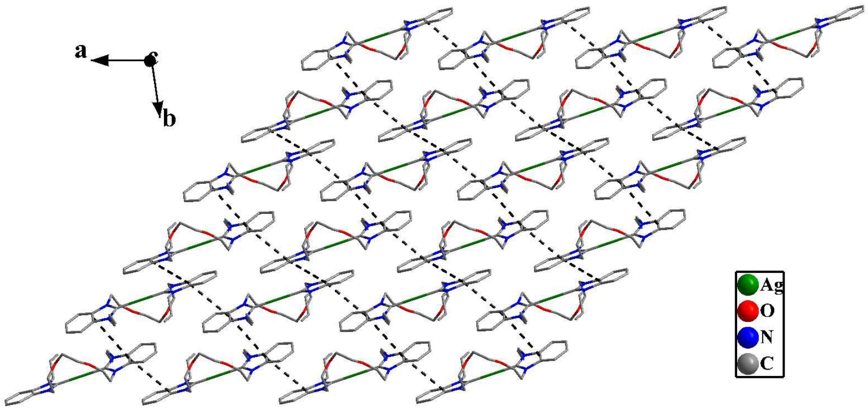


Fig. 2 2D supramolecular layer of complex **1** via π-π stacking interactions. All hydrogen atoms were omitted for clarity.

Recognition of NHC silver(I) crown ether 1 for iodide anion

The selective recognition of some anions (F$^-$, Cl$^-$, Br$^-$, I$^-$, $H_2PO_4^-$, HSO_4^-, OAc$^-$ and NO_3^-, and their cation being tetrabutyl ammonium (TBA$^+$)) using **1** as a receptor was investigated by fluorescent and UV/vis titrations in acetonitrile at 25 ˚C. As shown in Fig. 3, the receptor **1** displays an emission at 362 nm (λ_{ex} = 235 nm, the excitation and emission slit: 3 nm and 3 nm), which is attributed to the emission of benzimidazole. Upon the addition of 15 equiv. of F$^-$, Cl$^-$, Br$^-$, $H_2PO_4^-$, HSO_4^-, OAc$^-$ and NO_3^-, respectively, the fluorescence emission intensity of **1** does not obviously change, whereas the addition of the same amount of I$^-$ causes a great decrease of emission intensity at 362 nm.

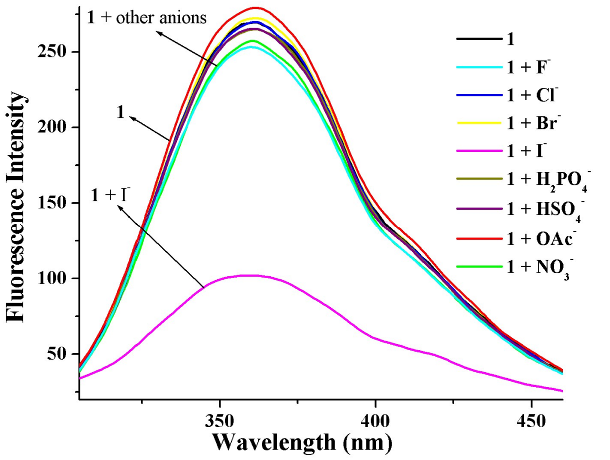


Fig. 3 Fluorescence spectra of **1** (1.0×10^{-5}mol/L) upon addition of different tetrabutyl ammonium salts (15.0 equiv.) in acetonitrile (λ_{ex} = 235 nm).

As shown in Fig. 4, upon the titration of I^- into the solution of **1**, the fluorescence intensities at 362 nm decrease gradually with the concentration of I^- increases. In the inset of Fig. 4, when the ratio of $C_{I^-}/C_{\mathbf{1}}$ was below 1:1, the fluorescence intensity decreases sharply with increasing concentration of I^-. When the ratio was in range of 1:1 to 20:1, the tendency of the fluorescence intensity decrease becomes slow. When the ratio exceeded 20:1, higher C_{I^-} will not lead to further emission decrease. The Stern-Volmer constant $K_{SV}^{10q\text{-}10s}$ was calculated as 2.3×10^4 M^{-1} (R = 0.994) by using the conventional Stern-Volmer relationship in acetonitrile at 25 ˚C (eqn (1), Fig. S1).

$$F_0/F = 1 + K_{SV}C_{I^-} \qquad (1)$$

where F and F_0 are the fluorescene intensity of **1** in the presence and absence of I^-, respectively; C_{I^-} is the concentrations of I^-; K_{SV} is the Stern-Volmer constant. From the changes in the iodide-dependent fluorescence intensity, the detection limit is estimated to be 6.1×10^{-7} mol/L (Fig. S2).[15]

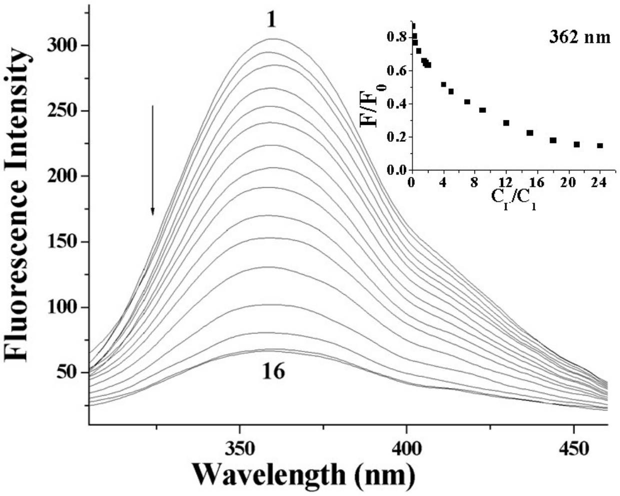


Fig. 4 Fluorescent titration spectra of **1** (1.0×10^{-5} mol/L) in the presence of different concentrations of I^- in acetonitrile at 25 ˚C. C_{I^-} for curves 1-16 are 0, 0.25, 0.33, 0.8, 1.5, 1.75, 2.0, 4.0, 5.0, 7.0, 9.0, 12.0, 15.0, 18.0, 21.0, 24.0×10^{-5} mol/L. Inset: F/F_0 at 362 nm of **1** as a function of $C_{I^-}/C_{\mathbf{1}}$ (λ_{ex} = 235 nm).

In UV/vis titration experiments (Fig. 5), the UV/vis absorption spectra of **1** increased gradually with the enhancement of the molar fraction of I^-. In addition, a red shift at 201-210 nm with the increasing of concentration of I^- was observed, which indicates that π-π transition energy of benzene rings in **1** was decreased by the interactions between **1** and I$^-$.[16] It is notable that a 1:1 complexation stoichiometry for **1**·I$^-$ was established by Job's plot analysis at 205 nm (inset of Fig. 5),[17] where the products ($\chi\Delta A$) between molar fractions and the discrepancy of the absorption bands were plotted against molar fractions (χ) of **1**. When the molar fractions of **1** was 0.5, the $\chi\Delta A$ values for **1**·I$^-$ reach maximum.[18] The stability constant K for **1**·I$^-$ calculated from the plot of $A_0/\Delta A$ versus **1**·I$^-$ based on the standard Benesi-Hildebrand is 1.18 × 10^5 M^{-1} (R = 0.999) (eqn (2), Fig. S3).

$$A_0/(A_0\text{-}A) = [\varepsilon_r/(\varepsilon_r\text{-}\varepsilon_c)](1/KC_{I^-} + 1) \qquad (2)$$

where A_0 is the absorption of host **1** in the absence of I$^-$, and A_0-A is the discrepancy of absorption between the absence and presence of I$^-$; ε_r and ε_c are the molar extinction coefficients of **1** and **1**·I$^-$, respectively; C_{I^-} is the concentration of I$^-$. The stability constant K is given by the ratio of intercept/slope.[19]

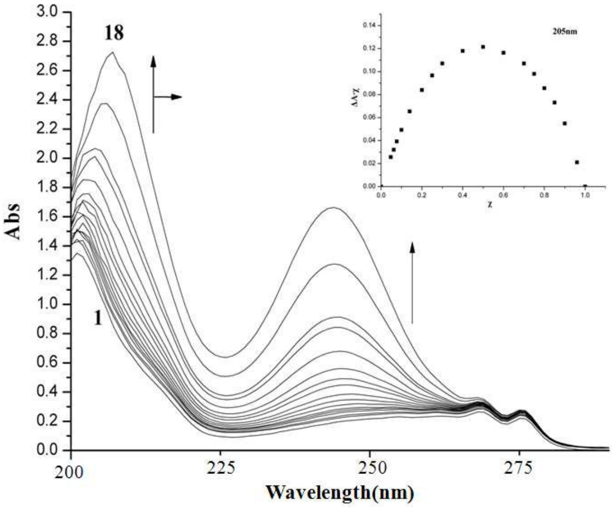


Fig. 5 Absorption spectra of **1** (1.0×10^{-5} M) upon titration of I$^-$ in acetonitrile. C_{I^-} for curves 1-18 are: 0, 0.04, 0.11, 0.17, 0.25, 0.33, 0.43, 0.67, 1.0, 1.5, 2.4, 3.0, 4.0, 6.0, 9.0, 12.0, 15.0, 20.0 × 10^{-5} mol/L. Inset: The Job's plot for **1**·I$^-$ complex at 205 nm. χ is the molar fraction of **1**.

In order to further explore the special selective ability of I$^-$ using **1** as a receptor, the competition experiments were conducted. The receptor **1** (1.0×10^{-5} mol/L) is firstly mixed with 5 equiv. of various anions (F$^-$, Cl$^-$, Br$^-$, $H_2PO_4^-$, HSO_4^-, OAc$^-$ and NO_3^-), and then 5 equiv. of I$^-$ was added. The fluorescent spectra are exploited to monitor the competition events. As displayed in Fig. S4, only $H_2PO_4^-$ cause the fluorescence intensity increased about 20% compared with that in the presence of I^- alone. The fluorescence intensities of other anions are similar to that in the presence of I^- alone. The results show that host **1** can discriminate between I^- and other anions.

Fluorescence decrease similar to Fig. 3 was also observed after the addition of other iodide salts (15.0×10^{-5} mol/L) with different countercations (K^+, Na^+, NH_4^+, Cu^+ and Hg^{2+}) to **1** (1.0×10^{-5} mol/L) (Fig. S5). Thus, the different cations had no obvious influence on the binding between **1** and iodide anion.

Interactions of 1 with I^-

From the structure of **1**, we can see that the silver(I) ion is the most likely binding site for I^- via Ag···I interactions. To obtain detailed information on the binding mode between **1** and I^-, ^{1}H NMR titration experiments were carried out in DMSO-d_6. The spectral differences are depicted in Fig. 6 (whole ^{1}H NMR spectra change being given in Fig. S6 in Supporting Information). The signals of *H*d, *H*g, *H*e and *H*f on benzimidazole were upfield shifted by 0.03-0.04 ppm upon addition of 1 equiv of I^-, and the signals of *H*c and *H*h on CH_2 around benzimidazole (Scheme 2) were upfield shifted by 0.05 ppm upon addition of 1 equiv of I^-. These changes should be attributed to the interactions between I^- and Ag^+. As expected, this observation shows that the iodide anion is captured by Ag^+ via Ag···I interactions. In addition, the signals of protons above-mentioned have not obvious change upon addition of more equivalents of I^- (Fig. 6(c) and Fig. 6(d)). This indicates that **1** and I^- are 1:1 complexation. In High-resolution mass spectra (HRMS) of **1**·I^- (Fig. S7), M^+ (669.07) of **1**·I^- is observed, which provided additional evidence for the formation of a 1:1 complex between **1** and I^-. These results are consistent with the results of UV/vis titration experiments (in insets of Fig. 5).

To further understand the complexation behavior of **1** and I^-, the infrared spectra of **1** and **1**·TBAI were measured. In the infrared spectra (Fig. S8), we observed that the ν(C-N) absorption bands move from 1122 cm^{-1} in free **1** to 1140 cm^{-1} in **1**·I^-, which is attributed to electron-donating effect of I^- as shown in Scheme 2.

By comprehensive analysis of the structure of **1**, ^{1}H NMR spectra, high-resolution mass spectra and infrared spectra of **1** and **1**·TBAI, we can see that the binding force of **1** and I$^-$ originates mainly from Ag···I interactions due to strong affinity of silver(I) ion toward I$^-$. When I$^-$ is bound by silver(I) ion, the remarkable decrease of fluorescence intensity of **1** may be attributed to the metal (d_π) to ligand (π^*) charge transfer (MLCT) process promoted by electron-donating effect of I$^-$.[20]

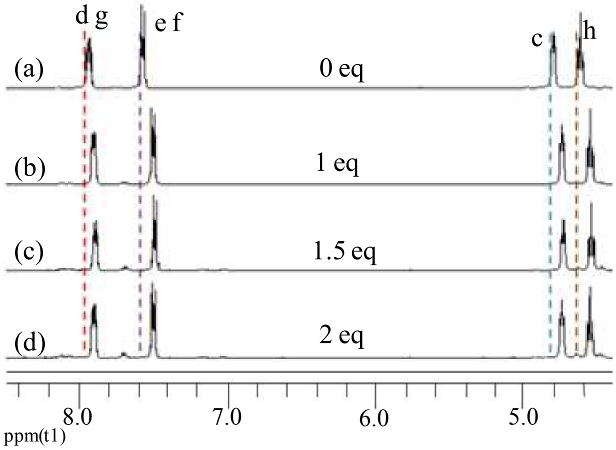
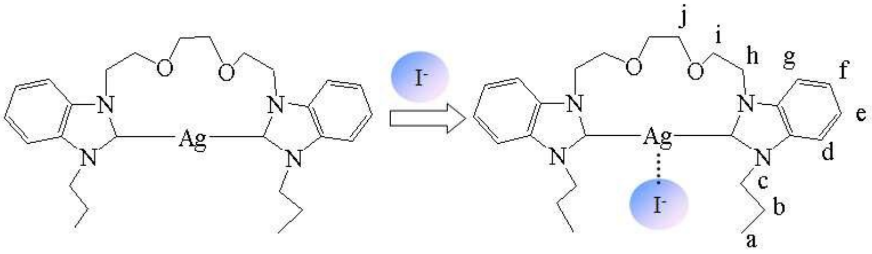


Fig. 6 Partial ^{1}H NMR spectra in DMSO-d_6. (a) Complex **1**; (b) **1** and 1 equiv. of TBAI; (c) **1** and 1.5 equiv of TBAI; (d) **1** and 2 equiv. of TBAI.



Scheme 2 The interactions of **1** with I$^-$

Conclusions

In summary, a new NHC silver(I) crown ether **1** has been synthesized and characterized. The fluorescent and UV/vis spectroscopic titrations indicate that complex **1** has great affinity to I$^-$. ^{1}H NMR spectra, HRMS and IR spectra show that I$^-$ is captured through Ag···I interactions. The special selective ability of **1** for I$^-$ make that it can discriminate I$^-$ and other anions in acetonitrile. Even if the detection limit is down to the 6.1 × 10^{-7} mol/L, the detection of **1** to I$^-$ is also sensitive. The high selectivity and sensitivity and the great affinity to I$^-$ make this complex has a potential application for quantitative measurement of I$^-$.

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 used without further purification. Melting points were determined with a Boetius Block apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. *J* values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. The luminescent spectra were conducted on a Cary Eclipse fluorescence spectrophotometer. UV-vis spectra were obtained using a JASCO-V570 spectrometer. EI mass spectra were recorded on a VG ZAB-HS mass spectrometer (VG, U.K.). IR spectra (KBr) were taken on an Bruker Equinox 55 spectrometer.

Preparation of 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl) dihexafluorophosphate ($LH_2\cdot(PF_6)_2$)

A tetrahydrofuran (THF) (15 mL) solution of benzimidazole (1.000 g, 8.5 mmol) was added to a suspension of oil-free sodium hydride (0.244 g, 10.2 mmol) in THF (25 mL) and stirred for 1 h at 60 ˚C. Then a THF (20 mL) solution of n-propyl bromide (1.145 g, 9.3 mmol) was dropwise added to above mixture. The mixture was continually stirred for 48 h at 60 ˚C. After filtration, a yellow solution was obtained. The solvent was removed with a rotary evaporator and H_2O (30 mL) was added to the residue. The solution was extracted with CH_2Cl_2 (3 × 20 mL), and the extracting solution was dried over anhydrous $MgSO_4$. After removing CH_2Cl_2, a pale yellow oil 1-^{n}propyl-benzimidazole was obtained. Yield: 1.221 g (90%).

A THF (50 mL) suspension of 1-^{n}propyl-benzimidazole (1.429 g, 8.9 mmol) and 1,2-bis(2-chloroethoxy)ethane (0.766 g, 4.1 mmol) in the presence of NaI (1.474 g, 9.8 mmol) was stirred for three days under refluxing, and a white precipitate was formed. The product was filtered and washed with THF. The white powder of 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl) diiodide (**$LH_2·I_2$**) was obtained by recrystallization from methanol/diethyl ether. Yield: 2.207 g (78%). M.p.: 170-172 ˚C. MS (EI): m/z $[M-I^-]^+$ = 563.1869, m/z $[M-2I^-]^+$ = 435.2749.

NH_4PF_6 (1.705 g, 10.5 mmol) was added to a methanol (50 mL) solution of **$LH_2·I_2$** (3.000 g, 4.4 mmol) whilst stirring and a white precipitate was formed immediately. The product was collected by filtration, washed with small portions of cold methanol, and dried in vacuum to give 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl) hexafluorophosphate (**$LH_2·(PF_6)_2$**). Yield: 2.875 g (90%). M.p.: 150-152 ˚C. Anal. Calcd for $C_{26}H_{36}F_{12}N_4O_2P_2$: C, 42.98; H, 5.00; N, 7.71%. Found: C, 42.72; H, 4.63; N, 7.95%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.84 (t, J = 7.2, 6H, CH_3), 1.89 (q, J = 7.2 Hz, 4H, CH_2), 3.46 (s, 4H, CH_2), 4.43 (t, J = 7.2 Hz, 4H, CH_2), 4.58 (t, J = 4.8, 4H, CH_2), 7.63-7.69 (m, 4H, Ph*H*), 7.96-7.98 (q, J = 2.9 Hz, 2H, Ph*H*), 8.02-8.04 (q, J = 3.0 Hz, 2H, Ph*H*), 9.58 (s, 2H, 2-bimi*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 10.4 (CH_3), 21.9 (CH_2), 46.6 (CH_2), 48.0 (CH_2), 67.4 (CH_2), 69.4 (CH_2), 113.5 (Ph*C*), 113.7 (Ph*C*), 126.5 (Ph*C*), 126.6 (Ph*C*), 130.8 (Ph*C*), 131.1 (Ph*C*), 142.1 (2-bimi*C*) (bimi = benzimidazole). MS (EI): m/z $[M-(PF_6^-)]^+$ = 581.2462, m/z $[M-2(PF_6^-)]^+$ = 435.2752.

Preparation of Silver-{C,C'-1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl)} hexafluorophosphate (1)

Silver oxide (0.070 g, 0.3 mmol) was added to a dichloromethane (30 mL) solution of precursor **$LH_2·(PF_6)_2$** (0.200 g, 0.3 mmol) and the suspension was stirred for 24 h under refluxing. The mixture was filtered and concentrated to 5 mL, and diethyl ether (5 mL) was added to precipitate a white powder. Isolation by filtration yields complex **1**. Yield: 0.072 g (38%). M.p.: 230-231 ˚C. Anal. Calcd for $C_{26}H_{34}F_6AgN_4O_2P$: C, 45.43; H, 4.99; N, 8.15%. Found: C, 45.68; H, 4.62; N, 8.53%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.97 (m, J = 1.0, 6H, CH_3), 1.91-1.96 (m, J = 1.6，4H, CH_2), 3.51 (s, 4H, CH_2), 3.78 (t, J = 1.0, 4H, CH_2), 4.56 (t, J = 2.0, 4H, CH_2), 4.74 (t, J = 1.0, 4H, CH_2), 7.46-7.49 (m, J = 1.0, 4H, PhH), 7.86-7.89 (m, J = 0.6, 4H, PhH). ^{13}C NMR (100 MH$_{Z,}$ DMSO-d_6): δ 11.1 (CH_3), 23.2 (CH_2), 48.3 (CH_2), 50.0 (CH_2), 67.7 (CH_2), 69.4 (CH_2), 111.7 (PhC), 112.0 (PhC), 124.0 (PhC), 133.0 (PhC), 133.2 (PhC). The carbene carbon was not observed. MS (EI): m/z [M-(PF_6^-)-1]$^+$ = 541.1733.

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 sensor **1** (1×10^{-5} mol/L) into the 4 mL cuvette and adding increasing amounts of I^- ($0.0\text{-}20.0 \times 10^{-5}$ 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 sensor **1** (1×10^{-5} mol/L) into the 4 mL cuvette and adding increasing amounts of I^- ($0.0\text{-}24.0 \times 10^{-5}$ mol/L) using a microsyringe. The sensor solution was excited at 235 nm, and the emission spectra were recorded in the range of 305-480 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 Structure Determinations

For complex **1** selected single crystals were mounted on a Bruker APEX II CCD diffractometer at 296(2) K with *Mo-K* radiation (λ = 0.71073 Å) by ω scan mode. Data collection and reduction were performed using the SMART and SAINT software[21] with frames of 0.6° oscillation in the range of $1.8^\circ < \theta < 25^\circ$. An empirical absorption correction was applied using the SADABS program.[22] 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.[23] 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. Crystalographic data were summaried in Table 1 for **1**.

Table 1 Summary of crystalographic data for **1**

Chemical formula	$C_{26}H_{34}AgF_6N_4O_2P$	F(000)	700
Formula weight	687.41	Cryst size, mm	0.25 × 0.17 × 0.16
Cryst syst	Triclinic	θ_{min}, θ_{max}, deg	1.82, 25.01
Space group	$P\bar{1}$	T, K	296(2)
a, Å	11.291(2)	No. of data collected	7363
b, Å	11.448(2)	No. of unique data	5021
c, Å	11.816(2)	No. of refined params	418
α, deg	108.288(3)	Goodness-of-fit on $F^{2\ a}$	1.042
β, deg	90.856(3)	Final R indices[b] $[I > 2\sigma(I)]$	
γ, deg	96.519(3)	R_1	0.0382
V, Å^3	1438.7(4)	wR_2	0.0978
Z	2	R indices (all data)	
D_{calcd}, Mg m^{-3}	1.587	R_1	0.0423
Abs coeff, mm^{-1}	0.826	wR_2	0.1016

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

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21172172 and 21572159), Tianjin Natural Science Foundation (No.11JCZDJC22000) and The Program for Innovative Research Team in University of Tianjin (TD12-5038).

Supplementary information

Text, Tables, Fig.s, and CIF files giving crystallographic data and the crystal packings for **LH_2·$(PF_6)_2$** and complex **1**, and ^{1}H NMR and ^{13}C NMR spectra for precursor and complex with this article can be found in the online version.

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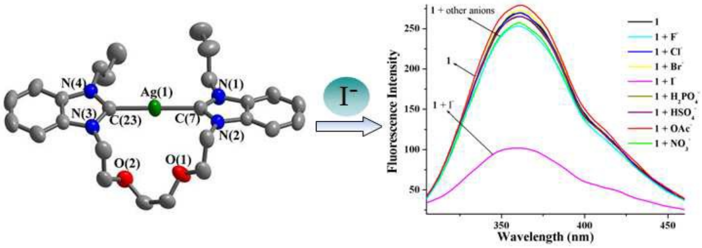
A table of contents entry:

NHC silver(I) crown ether **1** has been synthesized, and the recognition of I^- using **1** as a receptor was studied.



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