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Novel fluorescent sensor for Ag^+ and Hg^{2+} based on the BINOL-pyrene derivative via click reaction

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ABSTRACT

A novel BINOL-pyrene derivative sensor **1** for Ag^+ and Hg^{2+} incorporating the triazole moieties and pyrenes was synthesized via click reaction. Binding of Ag^+ ion induces the formation of 1:1 Ag^+–**1** chelating complex, and occurs in a ratiometric manner through an enhanced monomer and declining excimer emission, which make it possible to ratiometrically detect Ag^+. The competitive experiment shows **1** can be used as an Ag^+ specific fluorescence sensor over a wide range of competing cations. In the meanwhile, the sensor **1** was found to be selectively quenched by only Hg^{2+} at both monomer and excimer emission. Furthermore, we obtained evidences for different fluorescence signaling behaviors with Ag^+ and Hg^{2+} by ^1H NMR titration experiments.

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1. Introduction

Fluorescent sensors for selective and sensitive detection of heavy and transition metal ions have been widely investigated due to their important function and/or toxicity to the environment and biological systems.[1] Among the important metal ions, silver (I) has attracted considerable attention due to its bioaccumulation and toxic effects.[2] Therefore, the need for a highly sensitive and selective determination of silver ion arises from its long-term toxicity to humans and to the environment. However, there are only few reports on Ag^+ ion sensors and even less on Ag^+ ratiometric fluorescent sensors based on metal–ligand coordination.[3] This is due to the fact that Ag^+ has a moderate coordination ability making it quite difficult to be discriminated from other chemically similar heavy ions. Thus, the design of a suitable chemical method for the ratiometric measurement for Ag^+ is still a challenge.

As fluorogenic units, pyrenes (Py) are one of the most useful scaffolds for the construction of fluorogenic chemosensors for the detection of a variety of important chemical species.[4] More interestingly, unique monomer, and excimer emissions are observed at considerably different wavelengths depending on the relative proximity between pyrene moieties.[5] During coordination events to a certain ion, the host molecule could be fine-tuned to yield a monomer and/or excimer emissions depending on the orientation of the two pyrene moieties. This feature of the pyrene moieties involves the observation of changes in the ratio of the intensities of the emission at monomer versus excimer, and should meet a requirement of the ratiometric fluorescent sensors.[6] At present, many investigations have been conducted to fabricate ratiometric fluorescent probes for Hg^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+} etc., utilizing the pyrene moiety of monomer versus excimer.[7] However, few reports based on the pyrene system for Ag^+ have been explored.[3b,d]

Optically active 2,2′-binaphthol (BINOL) and its derivatives have attracted particular interests in asymmetric catalysis and fluorescent chemosensors due to their versatile backbone, which can be modified by strategic placement of functional groups based on steric and electronic properties.[8] In terms of high efficiency and technical simplicity, the 'Click' reaction has been used extensively for the preparation of particular synthetic materials. The copper(I)-catalyzed Huisgen [3+2] dipolar cycloaddition (CuAAC) between alkynes and azides, which is described by Kolb et al. as the 'cream of the crop' is an exemplary click reaction.[9] Several papers describing the binding properties of click-generated 1,2,3-triazoles and the use of CuAAC reaction to construct sensors for heavy metal ions have been reported.[10] As part of our continued interest in fluorogenic chemosensors via 'click chemistry',[11] we hereby report a novel chemosensor **1** (see Fig. 1) based on (*S*)-BINOL incorporating 1,2,3-triazole and pyrene moieties via click reaction. Our results indicate that this kind of the BINOL-pyrene derivative sensor can be used as

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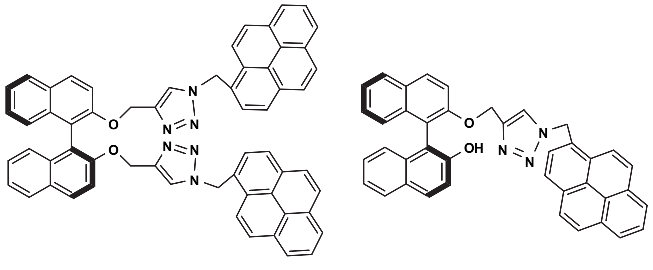
a ratiometric fluorescence sensor for Ag^+ detection through an enhanced monomer and declining excimer emission. Meanwhile, the sensor **1** was found to be selectively quenched by only Hg^{2+} at both monomer and excimer emission.

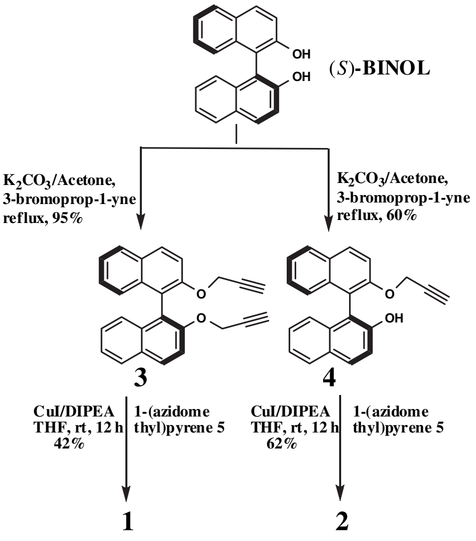


1 **2**

Fig. 1. Sensors **1** and **2**.

2. Result and discussion

The synthetic route for compounds **1** and **2** is depicted in Scheme 1. First, dipropargyl **3**[12] and mono-**4**[13] derivatives of (*S*)-BINOL were prepared according to the literature. Cu(I)-catalyzed 1,3-dipolar cycloaddition of dipropargyl **3** with 1-(azidomethyl) pyrene **5**[7b] afforded the intense fluorescent sensor **1** in 42% yield while applying similar procedure this time using mono-**4** derivative gave **2** in 62% yield. The structure of the products was identified by using ^{1}H NMR, ^{13}C NMR, and HRMS.



Scheme 1. Synthetic route for compounds **1** and **2**.

The optical properties of both **1**, featuring two triazole binding sites, and **2**, which incorporates a single triazole binding site were studied. The UV–vis spectra of **1** and **2** are shown in Fig. 2(a). The absorption spectrum of **1** reveals the typical pyrene absorption bands at 231, 275, 326 nm, and 342 nm, and **2** gives the similar absorption.[7c,14] As is seen in Fig. 2(b), the maximum absorption wavelength of the pyrene in **1** displays both monomer and excimer emissions at 374, 394, and 484 nm upon excitation at 340 nm, respectively, whereas **2** produced only a monomer emission at 374, 394, and 415 nm. It was noted that the formation of the excimer emission in **1** is caused by an intramolecular interaction between Py (the ground state pyrene) and Py* (the photoinduced excited state pyrene) where two pyrenes are likely to be in parallel.[7b]

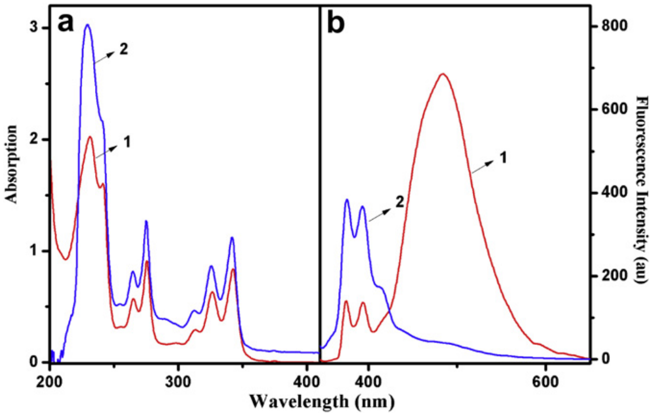


Fig. 2. (a) UV–vis spectra of compounds **1** and **2** (21 μM) in MeOH. (b) Fluorescence spectra of compounds **1** (λ_{ex}=340 nm, 10 μM) and **2** (λ_{ex}=336 nm, 10 μM) in MeOH.

Using fluorescence spectroscopy, we first investigated the selective fluorionophoric properties of **1** and **2** toward Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Pb^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, and Pd^{2+} ions. After systematically looking for selective signaling toward a special target, all the fluorescence measurements were carried out in MeOH/H_2O (v/v=200:1, [**1**]=10 μM, [**M**]=50 μM). The fluorescence changes are shown in Fig. 3. Addition of Ag^+ ion to the solution of **1** bearing pyrene-triazoles as metal ions chelating ligands induced a marked ratiometry, whereas the monomer emission increased as its excimer emission declined due to the separation of the two pyrene rings and off–on PET for monomer emission. By contrast, no significant spectral changes were observed upon addition of most of the other metal ions; however, when Hg^{2+} was added to the solution of **1**, we observed unexpectedly a quenched fluorescence in both monomer and excimer emissions due to heavy metal ion effect or a reverse PET, that is, the pyrene units behaved as PET donors and the metal ion bound triazoles behaved as electron acceptors.[10e] In contrast, **2** bearing only one pyrene unit, showed no significant or slight spectral changes upon addition of any of the metal ions used (see Fig. S5, Supplementary data). The two triazole units of **1** were thus proven to form an efficient and selective metal ion binding site, whereas **2**, which features only one triazole binding site, is unable to form effective complexes despite the inclusion of an additional hydroxyl group. Furthermore, the geometry of the binding site of the sensor **1**, in which the two N atoms of triazole rings are arranged distally on the binaphthalene scaffold, which seems to be ideal in terms of arrangement and size for recognition of Ag^+ in ratiometric measurement. Moreover, similar fluorescence variation

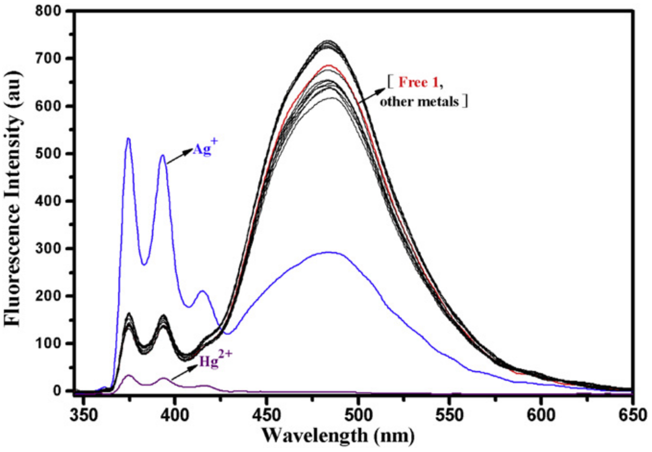


Fig. 3. Fluorescence spectra of **1** (λ_{ex}=340 nm, 10 μM) in the presence of metal ions in MeOH/H_2O (v/v=200:1). Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Pb^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, and Pd^{2+} ions (5.0 equiv) were added, respectively.

was observed after addition of Ag salts with different anions (NO_3^-, $CF_3SO_3^-$, BF_4^-) and addition of $Hg(NO_3)_2$ (see Figs. S6 and S7, Supplementary data).

The UV–vis spectra of **1** were evaluated in MeOH/H_2O (v/v=200:1) upon addition of Ag^+ and Hg^{2+} (see Figs. S8 and S9, Supplementary data). We found that a little change in the UV–vis spectra of **1** is observed upon addition of (0–2.2) equiv Ag^+ and it is unobvious to identify the isosbestic points. Upon addition of (0–3.2) equiv Hg^{2+}, the absorbance at 265, 275, 326, 342 nm showed a slight enhance; moreover, an isosbestic point at 344 nm could be observed (see Fig. S10, Supplementary data).

An important feature of many prospective metal ion sensors is their ability to detect metal ion selectively over other cations. To utilize **1** as an ion-selective fluorescence chemosensor for Ag^+, the competitive experiments were conducted in the presence of 10.0 equiv Ag^+ mixed with 10.0 equiv other cation, respectively. The enhancement ratio of I_F/I_0 at 374 nm (here, I_0 indicates the fluorescence intensity of free **1** and I_F indicates the fluorescence intensity upon addition of the mixture of Ag^+ and competitive cations) as shown in Fig. 4. For Ag^+, the I_F/I_0 value at 374 nm was almost 4.5. No considerable changes in the values were observed in the presence of other metal ions aside from Hg^{2+}. Although the quenching effect of mercury ions abolishes the enhancement of Ag^+, it is comparable to the most effective sensors reported.[3] On the other hand, the fluorescent quenching ratio ($1-I_F/I_0$) at 484 nm was not significantly affected by the interaction with surveyed metal ions except Hg^{2+} (see Fig. S11, Supplementary data, ($1-I_F/I_0$) measured=0.51 (Ag^+), 0.99 (Hg^{2+}), 0.48–60 (the other metal ions)). Thus, it is notable that **1** can be used as an Ag^+ specific fluorescence sensor in the absence of Hg^{2+}.

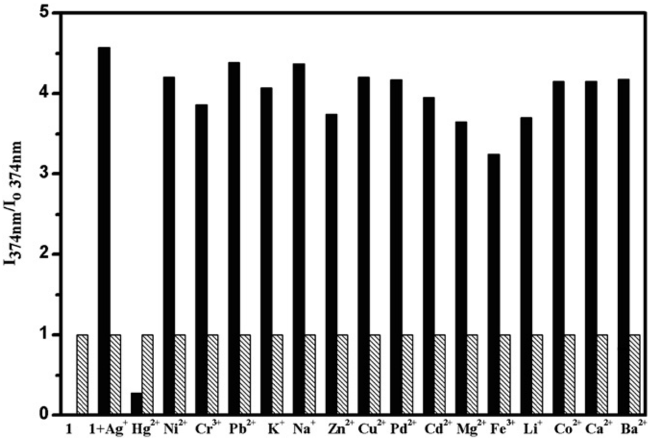


Fig. 4. The emission response of **1** (λ_{ex}=340 nm, 10 μM) in the presence of both Ag^+ and another competing metal ion (both 10.0 equiv) at 374 nm. Slant line bar, no metal but free **1** added; black bar, Ag^+ and the competing metal ion added. Conditions: Methanol/H_2O (v/v=200:1).

Fig. 5 shows the titration profiles of **1** during Ag^+ addition. When Ag^+ was added to solution of **1**, a significant increase in the monomer emission at 374 nm and a significant decrease in the emission at excimer emission at 484 nm, which was attributed to the formation of **1**–Ag^+ chelating complex. The inset in Fig. 5 features the dependence of the intensity ratios of emission at 374 nm to those at 484 nm (I_{374nm}/I_{484nm}) on [Ag^+]. This curve serves as the calibration plot for the detection of Ag^+. The association constant (K_a) of **1** with Ag^+ was found to be 3.419×10^5 M^{-1} based on a nonlinear curve fitting of the fluorescence titration results (R=0.980) according to the formation of **1**–Ag^+ complex of 1:1 stoichiometry (Fig. S15, Supplementary data). The 1:1 binding mode was confirmed from ESI-MS spectral data (see Fig. S12, Supplementary data). The peak at m/z=985.17, which corresponds to the [**1**–Ag^++H^+] was observed, and thus supports our claim on the existence of a 1:1 binding ratio between **1** and Ag^+. This was further proven by the Job's plot experiment (see Fig. S13, Supplementary data), in which the emission of the complexes at 374 nm were plotted against molar fractions of **1** under the conditions of an invariant total concentration. As a result, the concentration of complex **1**–Ag^+ approached a maximum when the molar fraction of [**1**]/([**1**]+[Ag^+]) was about 0.5. It indicated that 1:1 complex was formed.

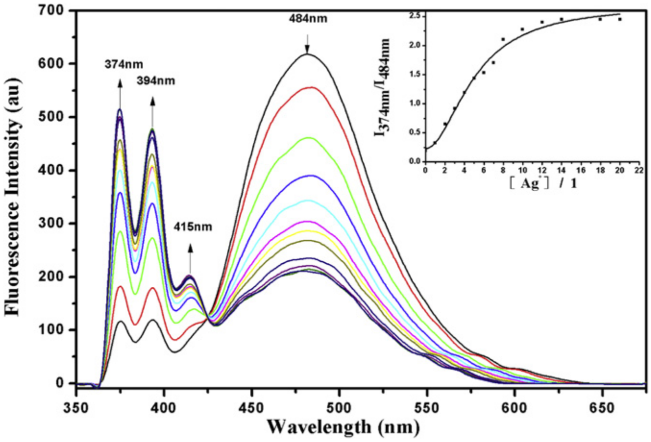


Fig. 5. Fluorescence spectra of **1** in MeOH/H_2O (v/v=200:1, [1]=10 μM, λ_{ex}=340 nm) in the presence of increasing amount of $AgClO_4$ (0–20 equiv) predissolved in MeOH/H_2O (v/v=200:1). The inset features the dependence of the intensity ratios of emission at 374 nm to those at 484 nm (I_{374nm}/I_{484nm}) on [Ag^+].

Fig. 6 shows the fluorescent quenching of **1** is almost complete upon 1:4 M ratio of mercury salt solution at both monomer and excimer emission. Job's plot experiment was carried out between **1** and Hg^{2+}, and it revealed a 1:2 complex of **1**:Hg^{2+} (see Fig. S14, Supplementary data). However, we can't determine the association constant (K_a) of **1** with Hg^{2+} from the fluorescence titration curve since it is too steep (the inset of Fig. 6).[15] Thus, the association constant (K_a) of **1** with Hg^{2+} can be obtained as high as 4.332×10^8 M^{-2} according to a nonlinear curve fitting of the UV–vis titration curve (R=0.993, see Fig. S16, Supplementary data).

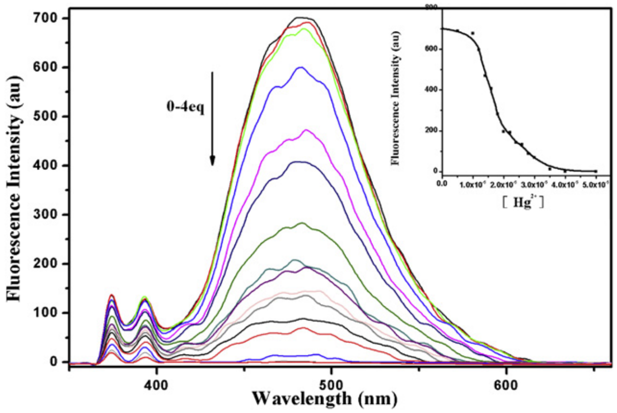


Fig. 6. Fluorescence spectra of **1** in MeOH/H_2O (v/v=200:1, [1]=10 μM, λ_{ex}=340 nm) in the presence of increasing amount (0–4 equiv) of $Hg(ClO_4)_2$ predissolved in MeOH/H_2O (v/v=200:1). The inset: the fluorescence titration curve at 484 nm on [Hg^{2+}].

To further determine the complexation mode of Ag^+ with **1**, we performed ^1H NMR titration experiments in (DMSO-d_6/CD_3OD=3:4), which was shown in Fig. 7. In detail, upon addition of 1.0 equiv of Ag^+, considerable changes were noted in the chemical shifts of protons in the triazole groups of chemosensor **1**. H_b labeled

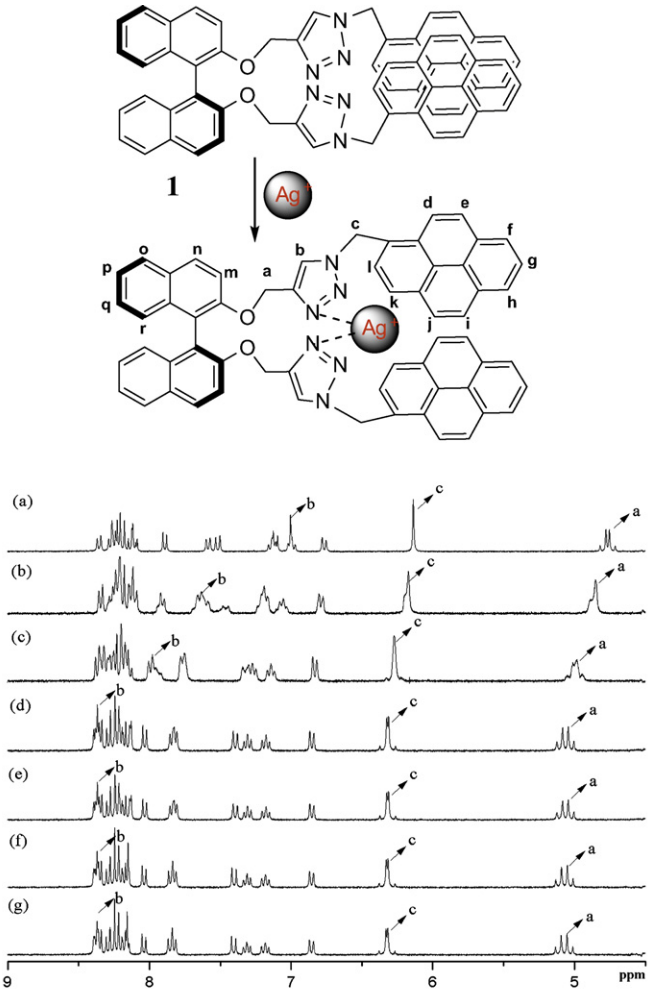


Fig. 7. The proposed structure for **1** and **1**:Ag^+, and partial ^1H NMR spectra of (a) **1**; (b) addition of 0.5 equiv of $AgClO_4$; (c) addition of 1.0 equiv of $AgClO_4$; (d) addition of 1.5 equiv of $AgClO_4$; (e) addition of 2.0 equiv of $AgClO_4$; (f) addition of 2.5 equiv of $AgClO_4$; (g) addition of 3.0 equiv of $AgClO_4$.

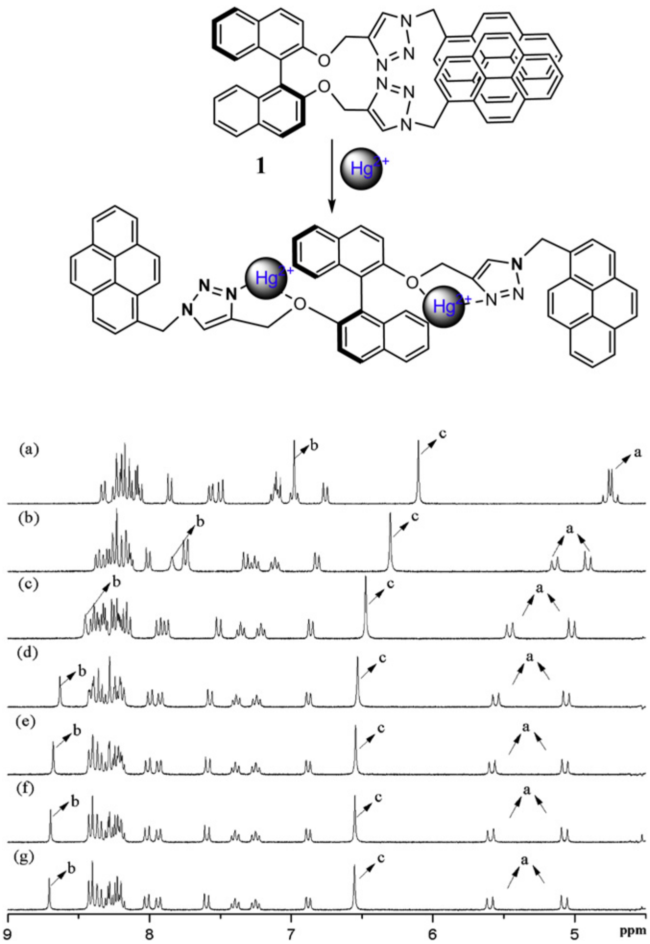


Fig. 8. The possible binding mechanism of **1** with Hg^{2+} and partial ^1H NMR spectra of (a) **1**; (b) addition of 0.5 equiv of $Hg(ClO_4)_2$; (c) addition of 1.0 equiv of $Hg(ClO_4)_2$; (d) addition of 1.5 equiv of $Hg(ClO_4)_2$; (e) addition of 2.0 equiv of $Hg(ClO_4)_2$; (f) addition of 2.5 equiv of $Hg(ClO_4)_2$; (g) addition of 3.0 equiv of $Hg(ClO_4)_2$.

protons in the triazole rings underwent a downfield shift by $\Delta\delta$=0.97 ppm from 7.00 ppm to 7.97 ppm, whereas the OCH_2-triazole linker proton H_a showed a slight shift in the downfield, which indicates that oxygen atoms are not involved in the coordination with Ag^+. The H_c peak proximal to the pyrene did not undergo a significant change in the presence of Ag^+. These spectral changes suggest that Ag^+ is only bound to the nitrogen atoms of the triazole rings. Based on the result of the ^1H NMR experiments, the possible binding mechanism of **1** with Ag^+ is schematically depicted in Fig. 7. When Ag^+ is bound by two triazole nitrogen atoms in chemosensor **1**, the transformation into unfolded conformation would prevent the two pyrene molecules from maintaining the π–π interaction necessary for excimer emission, but instead would force their separation and lead to the increasing monomer emission of **1**. It is in line with the fluorescence changes observed as the induced conformational changes of the triazole units by 1:1 chelating complexation.

We also carried out ^1H NMR experiments so as to further seek the detailed information on the complexation of Hg^{2+} with **1** in (DMSO-d_6/CD_3OD=3:4). As shown in Fig. 8, while the amount of Hg^{2+} is beyond 2.0 equiv, the shifts tend to saturation, which reveals the formation of a 1:2 complex and suggests high affinity between **1** and Hg^{2+}. In detail, addition of 2.0 equiv Hg^{2+} can lead to a significant downshift of the H_a, $-OCH_2-$ linking triazole groups from 4.76 ppm to 5.06 ppm and 5.58 ppm, and the H_c, proximal to the pyrene from 6.13 to 6.54 ppm. Meanwhile, the H_b, in the triazole rings undergoes a dramatic downfield shift by $\Delta\delta$=1.67 ppm from 7.00 ppm to 8.67 ppm. These data confirm the conclusion that both triazole moiety and oxygen of **1** are involved in the coordination with Hg^{2+}, which is totally different from that of Ag^+. The possible binding mechanism of **1** with Hg^{2+} is depicted in Fig. 8. Compared with Ag^+-induced the fluorescence ratiometric manner, the Hg^{2+}-induced ‘ON–OFF’ type signaling behavior of the monomer and excimer emission is due to the metal ion induced conformational changes from folded to open-winged conformations when triazole moiety and oxygen of **1** are involved in the coordination with Hg^{2+}.[4e] Thus, evidences for different fluorescence signaling mechanisms with Ag^+ and Hg^{2+} were obtained by ^1H NMR titration experiments.

3. Conclusion

In summary, we have developed a novel fluorescent sensor 1 for Ag^+ and Hg^{2+} based on the BINOL-pyrene derivative via click reaction. The binding of Ag^+ ion occurs in a ratiometric manner through an enhanced monomer and declining excimer emission which make it possible to detect Ag^+ ratiometrically. The competitive experiments show **1** can be used as an Ag^+ specific fluorescence sensor over a wide range of competing cations. Meanwhile, the sensor **1** was found to be selectively quenched by only Hg^{2+} at both monomer and excimer emission. Evidences for different fluorescence signaling mechanisms with Ag^+ and Hg^{2+} were obtained by NMR titration experiments. This work opens up the possibility of a family of highly selective sensors for a wide range of cations based on tunable BINOL platforms.

4. Experimental section

4.1. General considerations

All the solvents were of analytic grade and THF was dried according to the standard methods prior to use. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. ^{1}H NMR and ^{13}C NMR were measured on a Bruker APX-300 spectrometer with chemical shifts reported in parts per million (in DMSO-d_6, or $CDCl_3$, TMS as internal standard). ESI-MS and HRMS spectral data were recorded on a Thermofisher LCQ and a Thermofisher LTQ-Orbitrap XL, respectively. Optical rotations were measured on Rudolph Research Analytical Autopol III Automatic Polarimeter with a 100 mm cell. Fluorescence spectra were determined on a Perkin–Elmer LS 55. All emission spectra were recorded at 24±1 °C. Stock solutions for analysis were prepared (2×10^{-4} M for compound **1** and **2** in MeOH) immediately before the experiments. The solutions of metal ions were prepared from $Hg(ClO_4)_2\cdot3H_2O$, $AgClO_4$, $Cr(NO_3)_3\cdot9H_2O$, $Zn(NO_3)_2\cdot6H_2O$, $Ba(NO_3)_2$, KNO_3, $NaNO_3$, $LiClO_4$, $Fe(NO_3)_3\cdot6H_2O$, Ca $(NO_3)_2\cdot4H_2O$, $Co(NO_3)_2\cdot6H_2O$, $Pd(OAc)_2$, $Ni(NO_3)_2\cdot6H_2O$, Cd $(NO_3)_2\cdot21/2H_2O$, $Cu(NO_3)_2\cdot2H_2O$, $Pb(NO_3)_2$, $Mg(NO_3)_2$.

*4.1.1. (S)-2,2′-Bis((1-(pyren-1-ylmethyl)-1H-1,2,3-triazol-4-yl)methoxy)-1,1′-binaphthyl (**1**).* A mixture of **3** (0.362 g, 1.0 mmol), 1-(azidomethyl)pyrene **5** (0.62 g, 2.4 mmol), DIPEA (0.7 mL, 4.0 mmol), and CuI (10 mg, 5 mol %) was stirred under room temperature for 12 h at N_2. The mixture was separated directly by silica gel column chromatography (SiO_2, petroleum ether/EtOAc, 1:1 to EtOAc) to give the desired product **1** (0.37 g, 42%) as a light-yellow solid; $[\alpha]_{D^{22}}$ −9.46 (*c* 0.01, $CHCl_3$); mp: 165–170 °C; R_f=0.4 (petroleum ether/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=4.84 (d, J=12.3 Hz, 2H, H^a), 4.91 (d, J=12.6 Hz, 2H, H^a), 6.17 (s, 4H, H^c), 6.70 (d, J=8.7 Hz, 2H, H^r), 6.93–6.97 (m, 2H, H^p), 7.07–7.12 (m, 2H, H^q), 7.28 (s, 2H, H^b), 7.33 (d, J=9.3 Hz, 2H, H^m), 7.64 (d, J=6.9 Hz, 2H, H^o), 7.67 (d, J=9 Hz, 2H, H^n), 7.85 (d, J=7.8 Hz, 2H, CH_{pyrene}), 8.04–8.33 (m, 16H, CH_{pyrene}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ=51.74, 63.64, 115.17, 120.12, 121.53, 122.13, 123.41, 124.14, 124.59, 124.90, 125.60, 125.70, 126.01, 126.18, 126.37, 127.01, 127.30, 127.51, 128.05, 128.53, 128.74, 128.92, 128.96, 130.25, 130.86, 131.68, 133.39, 144.60, 153.18 ppm. HRMS (ESI$^+$): calcd for $[C_{60}H_{40}N_6O_2+H]^+$ 877.3213; found 877.3262.

*4.1.2. (S)-2′-((1-(Pyren-1-ylmethyl)-1H-1,2,3-triazol-4-yl)methoxy) 1,1′-binaphthyl-2-ol (**2**).* A mixture of **4** (0.324 g, 1.0 mmol), 1-(azidomethyl)pyrene **5** (0.31 g, 1.2 mmol), DIPEA (0.35 mL, 2.0 mmol), and CuI (10 mg, 5 mol %) was stirred under room temperature for 12 h at N_2. The mixture was separated directly by silica gel column chromatography (SiO_2, petroleum ether/EtOAc, 1:1 to EtOAc) to give the desired product **2** (0.36 g, 62%) as a light-white solid; $[\alpha]_{D^{22}}$ −4.57 (*c* 0.007, $CHCl_3$); mp: 135–140 °C; R_f=0.3 (petroleum ether/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=4.86 (d, J=12.6 Hz, 1H, $-OCH_2-$). 4.91 (d, J=13.2 Hz, 1H, $-OCH_2-$), 5.65 (s, 2H, $-CH_2-$), 6.40 (s, 1H, OH), 6.81–6.97 (m, 4H, CH_{BINOL}), 7.11 (d, J=3.9 Hz, 2H, CH_{BINOL}), 7.18–7.23 (m, 2H, CH_{BINOL}), 7.28–7.34 (m, 2H, $CH_{BINOL}+CH_{triazole}$), 7.46 (d, J=7.8 Hz, 1H, CH_{BINOL}), 7.67 (d, J=8.7 Hz, 2H, CH_{BINOL}), 7.73 (d, J=9.0 Hz, 1H, CH_{pyrene}), 7.80 (d, J=9.0 Hz, 1H, CH_{pyrene}), 7.86–8.01 (m, 6H, CH_{pyrene}), 8.07 (d, J=7.5 Hz, 1H, CH_{pyrene}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=52.21, 63.77, 115.36, 116.11, 117.97, 118.03, 121.88, 122.65, 123.06, 124.54, 124.58, 124.80, 124.94, 125.01, 125.27, 125.94, 126.04, 126.35, 126.51, 126.59, 127.27, 127.34, 127.64, 127.99, 128.33, 128.41, 128.86, 128.97, 129.15, 129.56, 129.94, 130.63, 130.73, 131.24, 132.10, 133.88, 133.98, 144.58, 151.70, 154.45 ppm. HRMS (ESI+): calcd for $[C_{40}H_{27}N_3O_2+H]^+$, 582.2103; found 582.2160.

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Supplementary data

^{1}H and ^{13}C NMR spectra for compounds **1** and **2**. Fluorescence spectra of **2** upon addition of a variety of the metal ions. The emission (484 nm) response of **1** (10 μM) in the presence of Ag^+ and another competing metal ion (both 10.0 equiv). UV–vis titration spectra. Job's Plots. Determination of the association constants of **1** with Ag^+ and Hg^{2+}. ESI-MS of [**1**+Ag^+]. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.03.024.

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