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Highly Selective Fluorescent Sensors for Hg^{2+} and Ag^+ Based on Bis-triazole-Coupled Polyoxyethylenes in MeOH Solution

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Fluorescent chemosensors **6**–**9**, with variable length polyoxyethylenes between two triazolylmethyl ether units, have been synthesized under "click" conditions in which the bis-triazoles and polyoxyethylenes were used as metal-ion binding sites and the pyrenes as fluorophores. Of the 15 metal ions screened, the fluorescence of chemosensors **6**–**9** in methanol solution was found to be selectively quenched by only Hg^{2+} and Ag^+. In contrast, the fluorescence of control compound **10**, a [(triazol-4-yl)methoxymethyl]pyrene, was quenched by only Hg^{2+}. These results imply that the recognition of Hg^{2+} does not need the cooperation of two triazole groups. Binding constants for the interactions of **6**–**9** with Ag^+ increased as the chain length of the polyoxyethylene increased. Finally, a very high selectivity of compound **9** towards Hg^{2+} in aqueous methanol solution was observed.

Introduction

Fluorescent chemosensors that can selectively recognize metal ions have attracted considerable attention in the fields of supramolecular chemistry, biology, and medicinal chemistry.[1] An effective fluorescent chemosensor must convert the cation recognition by an ionophore into an easily monitored and highly sensitive light signal from the fluorophore. Mercury ions are severe environmental pollutants, and several diseases are known to be associated with mercury contamination.[2] Silver ions also have adverse biological effects, and there are many reports of silver bioaccumulation and toxicity.[3] Thus, the development of sensitive and selective chemosensors for Ag^+ and Hg^{2+} in various media is of considerable importance for environmental protection and human health.[4] Zhang and co-workers reported that compounds with two tetraphenylethylenes bearing adenine and thymine moieties were fluorescence turn-on chemosensors for Ag^+ and Hg^{2+}.[5] Lee and co-workers reported an NS_2O_2-macrocycle-based fluoroionophore as a highly selective turn-on-type fluorescence chemosensor for Ag^+ in aqueous ethanol solution.[4e]

Pyrene is one of the most useful fluorogenic units because of its characteristic and sensitive emissions from both the monomer and the excimer. Moreover, the ratio of its monomer-to-excimer emission is a sensitive probe for conformational change.[6] It has been reported that two pyrenyl moieties connected by a series of polyoxyethylenes[6b] or dioxaoctanediamides[6f] show moderate-to-excellent selectivity towards Ca^{2+} and Hg^{2+}, respectively. Because triazole is readily made by "click" chemistry[7] from an azide and an alkyne,[6h,8,9c] it prompted us to explore the possibility of combining two terminal pyrenes with bis-triazoles[6h,8,9c] and polyoxyethylenes[6b,6c] for metal-ion screening studies.

We have previously reported the synthesis of a series of 1,*n*-bis-pyrenylmethoxymethyltriazoles linked by methylene chains, which exhibit both monomer and excimer emission quenching in the presence of Pb^{2+} and an enhanced monomer but quenched excimer in the presence of Cd^{2+} and Zn^{2+}.[6h] The metal-ion selectivity in previous systems was relatively poor (it responded to at least five metal ions in CH_3CN) and the fluorescence phenomena, despite being significant, were quite complicated. Furthermore, the solvent system is always a concern in the development of useful metal ion sensors. We chose to replace the methylene chain employed previously by polyoxyethylenes[6b,6c] because they may help the bis-triazole groups to coordinate metal ions. Furthermore, they may also help to increase the solubility of the bis-pyrenyl-triazole system in solvents more polar than CH_3CN.

Results and Discussions

The synthetic pathways for chemosensors **6**–**9**, control compound **10**, and **11**[6h] are summarized in Scheme 1. The polyoxyethylene diazides **1**–**4** were first prepared by treating the corresponding di-*O*-tosyl-polyoxyethylenes with sodium

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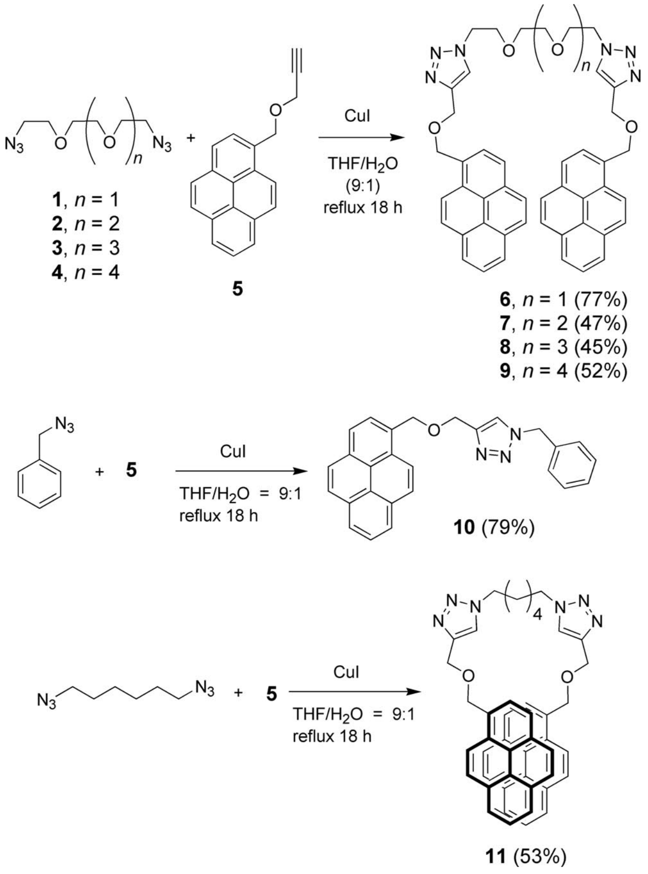
azide. The subsequent reaction of 1-(propagyloxymethyl)-pyrene (**5**)[6h] with the corresponding polyoxyethylene diazides **1**–**4** under click conditions afforded the target molecules **6**–**9** in 45–77% yields, with the triazoles and polyoxyethylenes designed to function as metal-ion binding sites and the pyrenes as reporting fluorophores.[6,9] The formation of triazoles **6**–**9** was monitored by ^{1}H NMR spectroscopy by the appearance of a new singlet arising from the triazole proton at around δ = 7.4–7.7 ppm.[6h,9]



Scheme 1. Synthesis of chemosensors **6**–**9**, control compound **10**, and **11**.[6h]

When excited at 312 nm, compounds **6**–**9** (10 μM in MeOH) showed strong intramolecular excimer emissions at around λ_{max} = 478 nm and weak monomer emission bands at around 376 and 395 nm.[6] The changes in the fluorescence intensities of **6**–**9** (10 μM) in the presence of 10 equiv. of 15 metal perchlorate salts (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Pb^{2+}) were studied and the results are summarized in Figure 1 and Table S1 of the Supporting Information. Figure 1 shows the changes in the fluorescence spectra of **6**–**9** (10 μM in MeOH) upon addition of 10 equiv. of metal ions. Note that there is a gradual increase in fluorescence quenching towards Ag^+ as the chain length of the polyoxyethylenes in compounds **6**–**9** increases. In the presence of Hg^{2+} and Ag^+, the fluorescence spectra of **6**–**9** showed not only a quenched monomer, but also a quenched excimer due to conformational distortion of the polyoxyethylene chains. Job plot experiments were carried out for **6**–**9** and revealed a 1:1 complex for each of them with Hg^{2+} and Ag^+ in MeOH. By using Stern–Volmer plots, the association constants of **6**–**9** with Hg^{2+} were calculated to be 9.9×10^4, 1.5×10^5, 6.6×10^4, and 6.1×10^4 M^{-1}, respectively.[10]

The control compound **10**, bearing a triazolylmethoxymethylpyrene, showed selective quenching of the monomer emissions of pyrene at λ_{em} = 375 and 395 nm upon addition of Hg^{2+} (Figure 2). Under these conditions, compound **10** did not show any excimer emission from the pyrenyl group. This result implies that in MeOH the recognition of Hg^{2+} by **10** does not need the cooperation of two triazole groups; alternatively, the fluorescence of two pyrenyl groups may be quenched by the bound Hg^{2+}.

Figure 3 shows the gradual change in the fluorescence spectra of **9** upon addition of Ag^+ and the corresponding Job plot. By using Stern–Volmer plots, the binding constants of **6**–**9** with Ag^+ in MeOH were calculated to be 7.1×10^3, 1.4×10^4, 3.3×10^4, and 4.3×10^4 M^{-1}, respectively.[10] Note that the binding constants of **6**–**9** with Ag^+ increase as the polyoxyethylene chain increases. The encouraging results obtained with these chemosensors in MeOH led us to explore their metal-ion selectivities in aqueous solvent. When a mixture of H_2O/MeOH (9:1, v/v) was used as the solvent system, **9** showed monomer emission at λ_{em} = 375 and 395 nm and excimer emission at λ_{em} = 490 nm. We found that in aqueous methanol solution, **9** still showed the same selectivity towards Hg^{2+} and Ag^+: Both monomer and excimer emissions were quenched upon complexation (Figure 4, a). From a Stern–Volmer plot, the association constant of **9** with Hg^{2+} in a mixture of H_2O/MeOH (v/v, 9:1) was calculated to be 8.8×10^3 M^{-1}.[10] In sharp contrast, when the fluorescence quenching experiments of **6**–**9** were carried out in MeCN, poor selectivity for metal ions was found, that is, they showed various fluorescence-sensing behavior towards Cu^{2+}, Hg^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, and Pb^{2+} (Table S2 and Figure S14 of the Supporting Information). Part b of Figure 4 shows that the monomer and excimer emissions of the pyrene groups in chemosensor **9** were quenched by Cu^{2+}, Hg^{2+}, Cr^{3+}, and Pb^{2+}; whereas enhanced monomer but quenched excimer emissions were observed for Ca^{2+}, Cd^{2+}, and Zn^{2+}.

In our previous studies,[6h] the bis-triazolylmethoxymethylpyrenes linked by methylene chains showed dual-mode recognition of transition-metal ions in CH_3CN; see Figure 5a for the titration results for compound **11**. However, when we repeated the metal-ion screening experiments using MeOH/MeCN (97.5:2.5, v/v) as solvent,[11] compound **11** showed selective fluorescence quenching only towards Hg^{2+} (Figure 5, b). Based on these results, we believed that in MeOH solution the bis-triazole groups are not effective coordination sites of Ag^+ ions; Ag^+ ions were further stabilized by coordination with the polyoxyethylene ethers. Thus, the polyoxyethylene chains in **6**–**9** not only serve as a spacer for linking the bis-triazoles but also serve as binding sites for Ag^+. Furthermore, the longer chain lengths of the polyoxyethylenes allow more flexible conformational change to achieve a better binding for the Ag^+ ions.

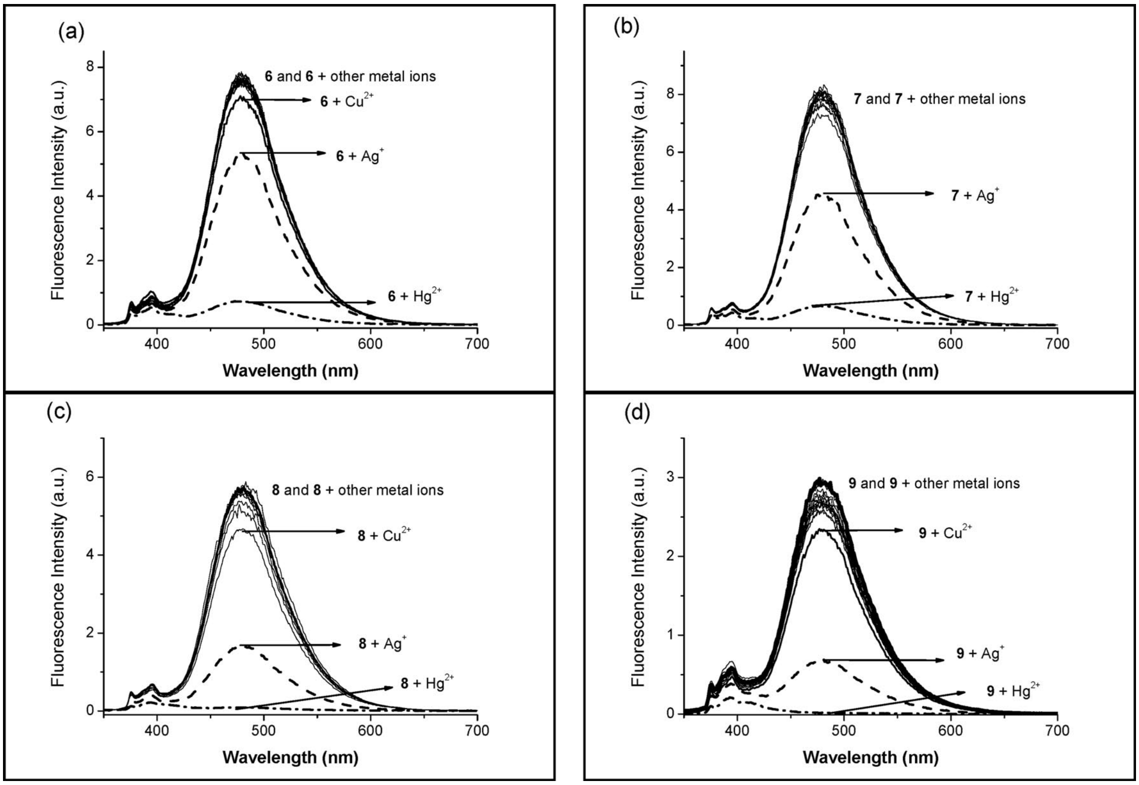


Figure 1. Fluorescence changes for the hosts (a) **6**, (b) **7**, (c) **8**, and (d) **9** (10 μm in MeOH) upon the addition of 15 metal ions (10 equiv., λ_{ex} = 312 nm, 298 K).

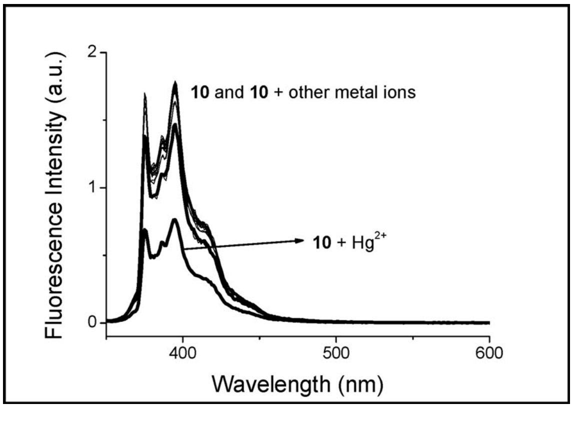


Figure 2. Fluorescence changes for the control compound **10** (10 μm in MeOH) upon addition of 15 metal ions (10 equiv., λ_{ex} = 312 nm, 298 K).

To obtain structural information and conformational change in the complexes formed between **9** and Hg^{2+} (and Ag^{+}), we carried out ^{1}H NMR titration experiments in CD_3CN/CD_3OD (1:4, v/v) solution. Figure 6 shows the stacked plots of the ^{1}H NMR spectra of **9** (5 mm) in the absence and presence of 1 equiv. of Hg^{2+} at 25 °C. The ^{1}H NMR spectra of **9** (5 mm) with various amounts of Hg^{2+} are shown in Figure S13 of the Supporting Information. Upon complexation with 1 equiv. of Hg^{2+}, the 5-triazole proton H_c and the methylene protons H_b and H_d were strongly shifted upfield ($\Delta\delta$ = –0.42, –0.33, and –0.79 ppm, respectively). These results imply that complexation of **9** with Hg^{2+} induces a large conformational change that causes these protons to be shielded by pyrene rings. The protons of the polyoxyethylenes also showed some chemical shift changes, which suggests that the polyoxyethylene moieties are also involved in the coordination with Hg^{2+}.

Figure 7 shows the stacked plots of the ^{1}H NMR spectra of **9** (5 mm) in the absence and presence of 1 equiv. of Ag^{+} at 25 °C. Upon complexation with 1 equiv. of Ag^{+}, only the protons H_b showed a significant upfield shift ($\Delta\delta$ = –0.30 ppm); the oxyethylene protons (H_d–H_f, H_h, and H_i) did not show much change. For more detailed titration plots of **9** (5 mm) in the absence and presence of various amounts of Ag^{+}, see Figure S14 of the Supporting Information. Despite the nonsystematic changes in the chemical shifts of these protons, the observations suggest that both the polyoxyethylenes and the bis-triazoles try to reorient themselves to coordinate the Ag^{+}. It is expected that the coordination of **9** with Ag^{+} should be very close to the triazole and oxygen atoms of the ether groups that distort the original conformation.

The results of the fluorescence quenching suggest that the pyrene units behave as PET donors and the metal-ion-bound triazole groups behave as electron acceptors.[6h,12] As the chain length of the polyoxyethylene increases, the binding ability of chemosensors **6**–**9** towards Ag^{+} increases. Based on the ^{1}H NMR titration results and fluorescence changes, we propose that Hg^{2+} and Ag^{+} are bound between

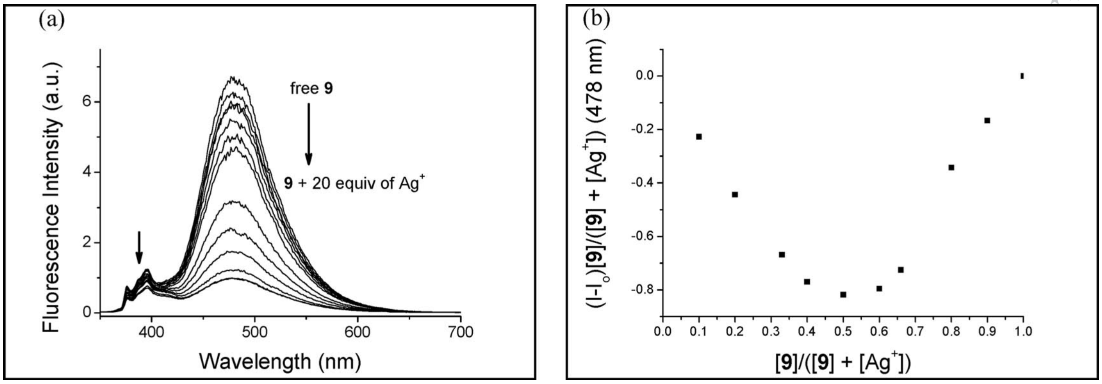


Figure 3. (a) Changes in the fluorescence spectra (λ_{ex} = 312 nm) of **9** (10 μM in MeOH) upon addition of various amounts of Ag^+ and (b) job plot for **9** with Ag^+ at 298 K.

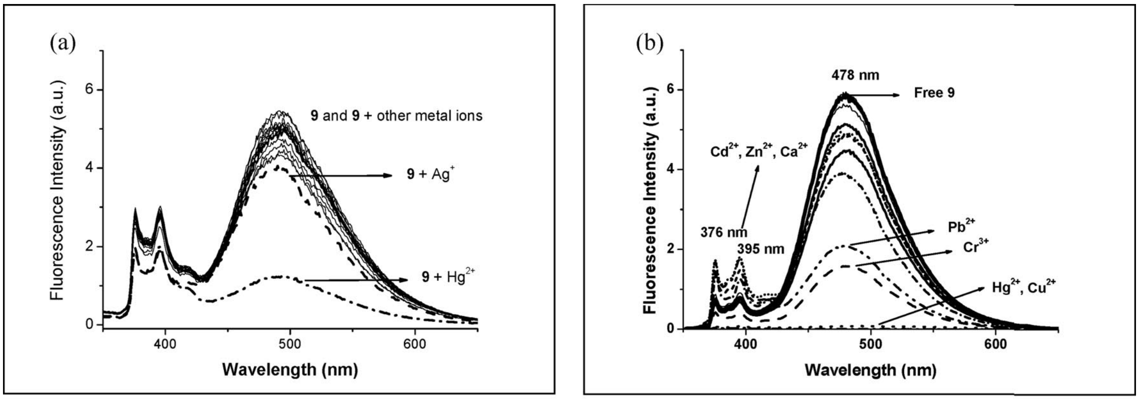


Figure 4. Fluorescence changes for compound **9** (10 μM) upon addition of 15 metal ions (10 equiv.) in (a) H_2O/MeOH (9:1, v/v; λ_{ex} = 333 nm, 298 K) and (b) MeCN solution (λ_{ex} = 312 nm, 298 K).

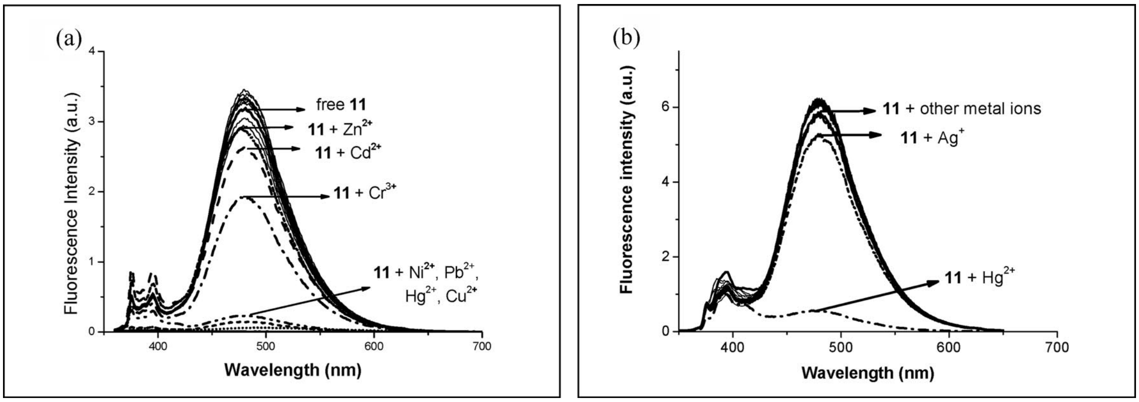


Figure 5. Fluorescence changes for compound **11** (10 μM) upon addition of 15 metal ions (10 equiv.) in (a) MeCN and (b) MeOH/MeCN (97.5:2.5, v/v) solution (λ_{ex} = 312 nm, 298 K).

the 3-N atoms of the bis-triazoles, the pyrenylmethyl ether groups, and the polyoxyethylene bridge of **9** (Scheme 2), which distorts the original conformation and thus quenches both the monomer and excimer emissions of the pyrenes.

Because metal ions can be detected by molecule **9** through fluorescence in a 10 % aqueous methanol solution, we further tested its fluorescence response as a function of pH. The fluorescence intensity of the pyrene monomer (monitored at 376 nm) in **9** exhibited two stepwise changes: It reached a maximum above pH 9, entered a plateau region in the range pH 6–8, and reached a minimum below pH 3 (see Figure S16 of the Supporting Information). Two sets of experiments were then carried out on **9** at pH 4 and 9. The fluorescence responses of **9** towards Hg^{2+} were less sensitive than that at pH 7. Thus, the fluorescent chemosensor **9** in H_2O/MeOH (9:1, v/v) works well only under neutral conditions.

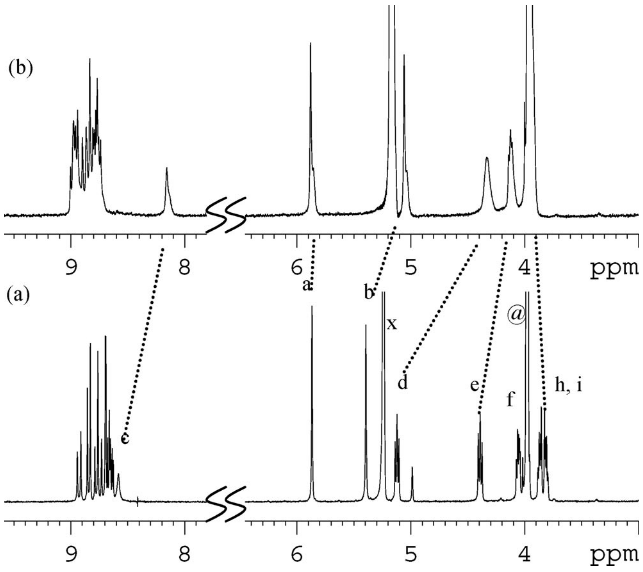


Figure 6. The ^{1}H NMR titration spectra of (a) **9** (5 mM) and (b) **9** in the presence of 1 equiv. of Hg^{2+} in CD_3CN/CD_3OD (1:4, v/v): x and @ represent solvent signals.

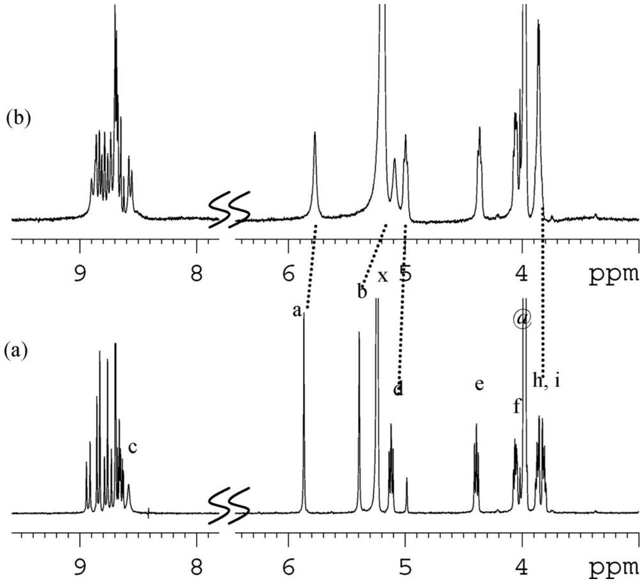
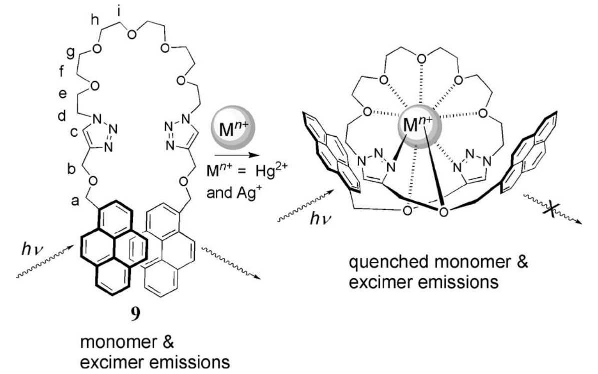


Figure 7. ^{1}H NMR titration of (a) **9** (5 mM) and (b) **9** in the presence of 1 equiv. of Ag^+ in CD_3CN/CD_3OD (1:4, v/v): x and @ represent solvent signals.

Conclusions

A series of new fluoroionophores **6**–**9** with bis-triazoles and polyoxyethylenes as cationic binding sites and pyrenes as the reporting units have been synthesized. In MeOH solution, of the 15 metal ions screened, chemosensors **6**–**9** responded selectively to Hg^{2+} and Ag^+. Under similar conditions, the control compound **10**, a [(triazol-4-yl)methoxymethyl]pyrene, showed selective fluorescence quenching only towards Hg^{2+}. These results imply that the recognition of Hg^{2+} does not need the cooperation of two triazole groups. Note that the binding constants of **6**–**9** towards Ag^+ increased as the chain length of the polyoxyethylenes increased. Finally, the very high selectivity of compound **9** towards Hg^{2+} in aqueous methanol solution shows that the readily synthesized [(triazol-4-yl)methoxymethyl]pyrene system is a potential fluorogenic sensor for the environmental or biological detection of Hg^{2+} ions.



Scheme 2. Possible binding modes of **9** with Hg^{2+} and Ag^+ in MeOH.

Experimental Section

General: All reported yields are isolated yields. Flash column chromatography was performed by using silica gel (70–230 mesh). Melting points were determined with a Yanaco MP500D apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz with the solvent peak (usually $CDCl_3$) as the internal standard and ^{13}C NMR spectra were recorded at 75.4 MHz. Mass spectra were recorded in the FAB mode with *m*-nitrobenzyl alcohol (NBA) as the matrix. UV/Vis spectra were recorded with a HP-8453 spectrophotometer, fluorescence spectra were measured with an Aminoco Bowman Series-2-type spectrofluorimeter, and solvents were of HPLC grades.

1,8-Bis[4-(pyren-1-ylmethoxymethyl)-1*H*-1,2,3-triazole-1-yl]-3,6-dioxaoctane (6): A mixture of 1-[(prop-2-ynyloxy)methyl]pyrene (0.27 g, 1.0 mmol), 1,8-diazido-3,6-dioxaoctane (0.1 g, 0.5 mmol), and CuI (about 5 mg, 0.02 mmol) in THF and water (9:1, v/v, 30 mL) was stirred vigorously at 70 °C for 18 h. The mixture was extracted thrice (5 mL × 3) with chloroform. The chloroform layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified through a silica gel column eluting with ethyl acetate/MeOH (30:1, v/v) to give 0.28 g (77 %) of **6**. Yellow oil; R_f = 0.325 (EtOAc/MeOH = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.26 (d, J = 9.2 Hz, 2 H, CH_{pyrene}), 8.14–7.94 (m, 16 H, CH_{pyrene}), 7.45 (s, 2 H, $CH_{5\text{-triazole}}$), 5.22 (s, 4 H, $C_{pyrene}CH_2O$), 4.73 (s, 4 H, $OCH_2C_{4\text{-triazole}}$), 4.20 (t, J = 4.5 Hz, 4 H, $N_{1\text{-triazole}}CH_2C$), 3.52 (t, J = 4.5 Hz, 4 H, CCH_2O), 3.29 (s, 4 H, OCH_2CH_2O) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 144.8 (C_q), 131.3 (C_q), 131.1 (C_q), 130.8 (C_q), 130.6 (C_q), 129.3 (C_q), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 125.9 (CH), 125.2 (CH), 125.2 (CH), 124.7 (C_q), 124.5 (C_q), 124.4 (CH), 123.7 (CH), 123.3 (CH), 71.0 (CH_2), 70.0 (CH_2), 69.0 (CH_2), 63.7 (CH_2), 49.9 (CH_2) ppm. HRMS (FAB): calcd. for $C_{46}H_{40}N_6O_4$ $[M]^+$ 740.3111; found 740.3116.

1,11-Bis[4-(pyren-1-ylmethoxymethyl)-1*H*-1,2,3-triazole-1-yl]-3,6,9-trioxaundecane (7): A mixture of 1-[(prop-2-ynyloxy)methyl]pyrene (0.27 g, 1.0 mmol), 1,11-diazido-3,6,9-trioxaundecane (0.12 g, 0.50 mmol), and CuI (about 5 mg, 0.02 mmol) in THF and water

(9:1, v/v, 30 mL) was stirred vigorously at 70 °C for 18 h. The mixture was extracted thrice (5 mL × 3) with chloroform. The chloroform layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified through a silica gel column eluting with ethyl acetate/MeOH (30:1, v/v) to give 0.18 g (47%) of **7**. Yellow oil; R_f = 0.18 (EtOAc/MeOH = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.29 (d, J = 9.2 Hz, 2 H, CH_{pyrene}), 8.16–7.95 (m, 16 H, CH_{pyrene}), 7.57 (s, 2 H, $CH_{5\text{-triazole}}$), 5.25 (s, 4 H, $C_{pyrene}CH_2O$), 4.76 (s, 4 H, $OCH_2C_{4\text{-triazole}}$), 4.32 (t, J = 5.0 Hz, 4 H, $N_{1\text{-triazole}}CH_2C$), 3.57 (t, J = 5.0 Hz, 4 H, CCH_2O), 3.28 (br. s, 8 H, OCH_2CH_2O) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 144.7 (C_q), 131.3 (C_q), 131.1 (C_q), 130.9 (C_q), 130.7 (C_q), 129.4 (C_q), 127.7 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 125.9 (CH), 125.2 (CH), 125.2 (CH), 124.8 (C_q), 124.6 (C_q), 124.4 (CH), 123.8 (CH), 123.4 (CH), 71.0 (CH_2), 70.2 (CH_2), 70.1 (CH_2), 69.0 (CH_2), 63.6 (CH_2), 50.1 (CH_2) ppm. HRMS (FAB): calcd. for $C_{48}H_{44}N_6O_5$ $[M]^+$ 784.3373; found 784.3380.

1,14-Bis[4-(pyren-1-ylmethoxymethyl)-1*H*-1,2,3-triazole-1-yl]-3,6,9,12-tetraoxatetradecane (8): A mixture of 1-[(prop-2-ynyloxy)methyl]pyrene (0.380 g, 1.42 mmol), 1,14-diazido-3,6,9,12-tetraoxatetradecane (0.20 g, 0.71 mmol), and CuI (about 5 mg, 0.02 mmol) in THF and water (9:1, v/v, 30 mL) was stirred vigorously at 70 °C for 18 h. The mixture was extracted thrice (5 mL × 3) with chloroform. The chloroform layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified through a silica gel column eluting with ethyl acetate/MeOH (30:1, v/v) to give 0.26 g (45%) of **8.** Yellow oil; R_f = 0.2 (EtOAc/MeOH = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.29 (d, J = 9.2 Hz, 2 H, CH_{pyrene}), 8.15–7.94 (m, 16 H, CH_{pyrene}), 7.65 (s, 2 H, $CH_{5\text{-triazole}}$), 5.26 (s, 4 H, $C_{pyrene}CH_2O$), 4.78 (s, 4 H, $OCH_2C_{4\text{-triazole}}$), 4.39 (t, J = 5.0 Hz, 4 H, $N_{1\text{-triazole}}CH_2C$), 3.67 (t, J = 5.0 Hz, 4 H, CCH_2O), 3.38–3.30 (m, 12 H, OCH_2CH_2-OCH_2) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 144.8 (C_q), 131.2 (C_q), 131.1 (C_q), 130.9 (C_q), 130.7 (C_q), 129.3 (C_q), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 125.9 (CH), 125.2 (CH), 125.2 (CH), 124.8 (C_q), 124.5 (C_q), 124.4 (CH), 123.9 (CH), 123.3 (CH), 70.9 (CH_2), 70.2 (CH_2), 70.2 (CH_2), 70.1 (CH_2), 69.1 (CH_2), 63.6 (CH_2), 50.1 (CH_2) ppm. HRMS (FAB): calcd. for $C_{50}H_{48}N_6O_6$ $[M]^+$ 828.3635; found 828.3615.

1,17-Bis[4-(pyren-1-ylmethoxymethyl)-1*H*-1,2,3-triazole-1-yl]-3,6,9,12,15-pentaoxaheptadecane (9): A mixture of 1-[(prop-2-ynyloxy)methyl]pyrene (0.27 g, 1.0 mmol), 1,17-diazido-3,6,9,12,15-pentaoxaheptadecane (0.17 g, 0.50 mmol), and CuI (about 5 mg, 0.02 mmol) in THF and water (9:1, v/v, 30 mL) was stirred vigorously at 70 °C for 18 h. The mixture was extracted thrice (5 mL × 3) with chloroform. The chloroform layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified through a silica gel column eluting with ethyl acetate/MeOH (30:1, v/v) to give 0.23 g (52%) of **9**. Yellow oil; R_f = 0.25 (EtOAc/MeOH = 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.30 (d, J = 9.2 Hz, 2 H, CH_{pyrene}), 8.16–7.94 (m, 16 H, CH_{pyrene}), 7.69 (s, 2 H, $CH_{5\text{-triazole}}$), 5.27 (s, 4 H, $C_{pyrene}CH_2O$), 4.79 (s, 4 H, $OCH_2C_{4\text{-triazole}}$), 4.43 (t, J = 5.0 Hz, 4 H, $N_{1\text{-triazole}}CH_2C$), 3.72 (t, J = 5.0 Hz, 4 H, CCH_2O), 3.42–3.37 (m, 16 H, $OCH_2CH_2OCH_2$-CH_2O) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 144.8 (C_q), 131.2 (C_q), 131.1 (C_q), 130.9 (C_q), 130.6 (C_q), 129.3 (C_q), 127.6 (CH), 127.3 (CH), 127.3 (CH), 127.1 (CH), 125.8 (CH), 125.1 (CH), 124.7 (C_q), 124.5 (C_q), 124.4 (CH), 123.9 (CH), 123.3 (CH), 70.8 (CH_2), 70.3 (CH_2), 70.2 (CH_2), 70.2 (CH_2), 70.1 (CH_2), 69.2 (CH_2), 63.6 (CH_2), 50.1 (CH_2) ppm. HRMS (FAB): calcd. for $C_{52}H_{52}N_6O_7$ $[M]^+$ 872.3898; found 872.3889.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for **6**–**9** (Figures S1–S8), percentage fluorescence changes for hosts **6**–**9** in CH_3OH upon addition of various metal ions at 298 K (Table S1), fluorescence titration spectra for **6**–**9** with various amounts of Hg^{2+} and Ag^+ in CH_3OH solution (Figures S9–S12), ^{1}H NMR titrations of **6**–**9** in the presence of various amounts of metal ions Hg^{2+} and Ag^+ (Figures S13 and S14), percentage fluorescence changes for hosts **6**–**9** (10 μM in CH_3CN) upon addition of various metal ions (Table S2), and fluorescence changes for hosts **6**–**9** upon addition of 15 metal ions (Figure S15).

Acknowledgments

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[10] The fluorescence titration results are shown in the Supporting Information.

[11] As a result of the poor solubility of previous series of compounds in pure MeOH, a small amount of CH_3CN was needed for their complete dissolution. Thus, metal-ion screening experiments were carried out in $MeOH/CH_3CN$ (97.5:2.5, v/v).

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