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Crown ether containing (1,3)pyrenophanes **1-6** were synthesized, and UV absorption and fluorescence spectroscopic studies were carried out to determine their abilities to form complexes with metal and ammonium ions. Fluorescence spectra of 1.0 × 10^{-5} M solutions of **1**, **2**, **4** and **6** in 1:1 v/v CH_2Cl_2:CH_3CN were comprised of both monomer and intramolecular excimer emission bands, while only monomer emission bands were present in the fluorescence spectra of **3** and **5**. The intensities of intramolecular excimer emission bands of **1**, **2**, **4** and **6** in 1:1 v/v CH_2Cl_2:CH_3CN decreased and those of the monomer emission increased in conjunction with the existence of isoemissive points upon addition of increasing concentrations of various metal perchlorates. The fluorescence spectral changes were dependent on sizes of crown ether rings and metal ions and, as such, they reflected equilibrium constants for formation of metal-crown ether complexes. Addition of *n*-$Bu_2NH_2^+PF_6^-$ or $(PhCH_2)_2NH_2^+PF_6^-$ to solutions of the (1,3)pyrenophane linked crown ethers, which brought about similar fluorescence spectral changes, led to formation of pseudo-rotaxanes as was evidenced by analysis of ^1H NMR spectra and Job's plots. The fluorescence changes of **1** occurred during 5 cycles of repetitive addition and removal of Ba^{2+}. The ratio of intensities of the monomer to intramolecular excimer emission bands of **1**, **2**, **4** and **6** increased as the temperature decreased. Based on the experimental observations and the results of DFT calculations, it is concluded that the (1,3)pyrenophanes exist in solution as equilibrium mixtures of *anti* monomer emitting and *syn* intramolecular excimer emitting conformers and the equilibrium favors the *anti* form when the crown ether moieties form complexes with metal or ammonium ions.

Introduction

Owing to its high fluorescence quantum yield, dual monomer and excimer fluorescence character and high photostability, pyrene has been widely used as a fluorescent reporter compound.[1-12] In addition, crown ethers have found many uses owing to their ring size dependent selectivity for binding metal cations.[13-19] Thus far, substances containing both pyrene fluorophores and crown ether moieties have been extensively investigated as fluorescent sensors for detection of metal cations.[20-48] Sensors of this type can be grouped into three types. The first two groups include sensors that display metal cation promoted turn-ON[22-29] and turn-OFF[30-32] of pyrene fluorescence caused by the introduction or blocking of photoinduced electron transfer (PET) or by enabling a heavy atom effect. The third type of sensors operates by switching between monomer and excimer emission[33-48] that are induced by changes in the spatial location and orientation of two pyrene moieties. Because the pyrene and crown ether units in most of these sensors are linked through flexible chains, which contain for example simple methylene,[22-26,33,34] ether,[35] oligoethylene glycol,[36-39] ester,[27] amide,[30-32,40-46] imine,[28] sulfoxide[29] and DNA[47] groups, their singlet excited state lifetimes and thus fluorescence intensities are not necessarily high because of bond rotation induced thermal deactivation.

Pyrenophanes, cyclophanes that include pyrene in the rings, have attracted much attention in view of their structural and fluorescence properties, as well their molecular recognition abilities.[3,49-82] We previously demonstrated that dioxa-, dithia-, and diselena-[3.3](1,3)pyrenophanes exist as mixtures of interconverting *syn* and *anti* conformers, and that the conformer ratios are dependent on solvent polarity and temperature, and they govern fluorescence characteristics.[83] In addition, we observed that fluorescence efficiencies are enhanced by attaching silyl substituents to the pyrene fluorophore,[84-91] and that substances in which the pyrene and crown ether groups are either fused[92] or linked by a rigid phenylethynyl group[93] serve as efficient fluorescent sensors for the detection of metal cations.

In the study described below, we designed and synthesized several (1,3)pyrenophanes that contain covalently linked crown ether moieties, and assessed how their UV absorption

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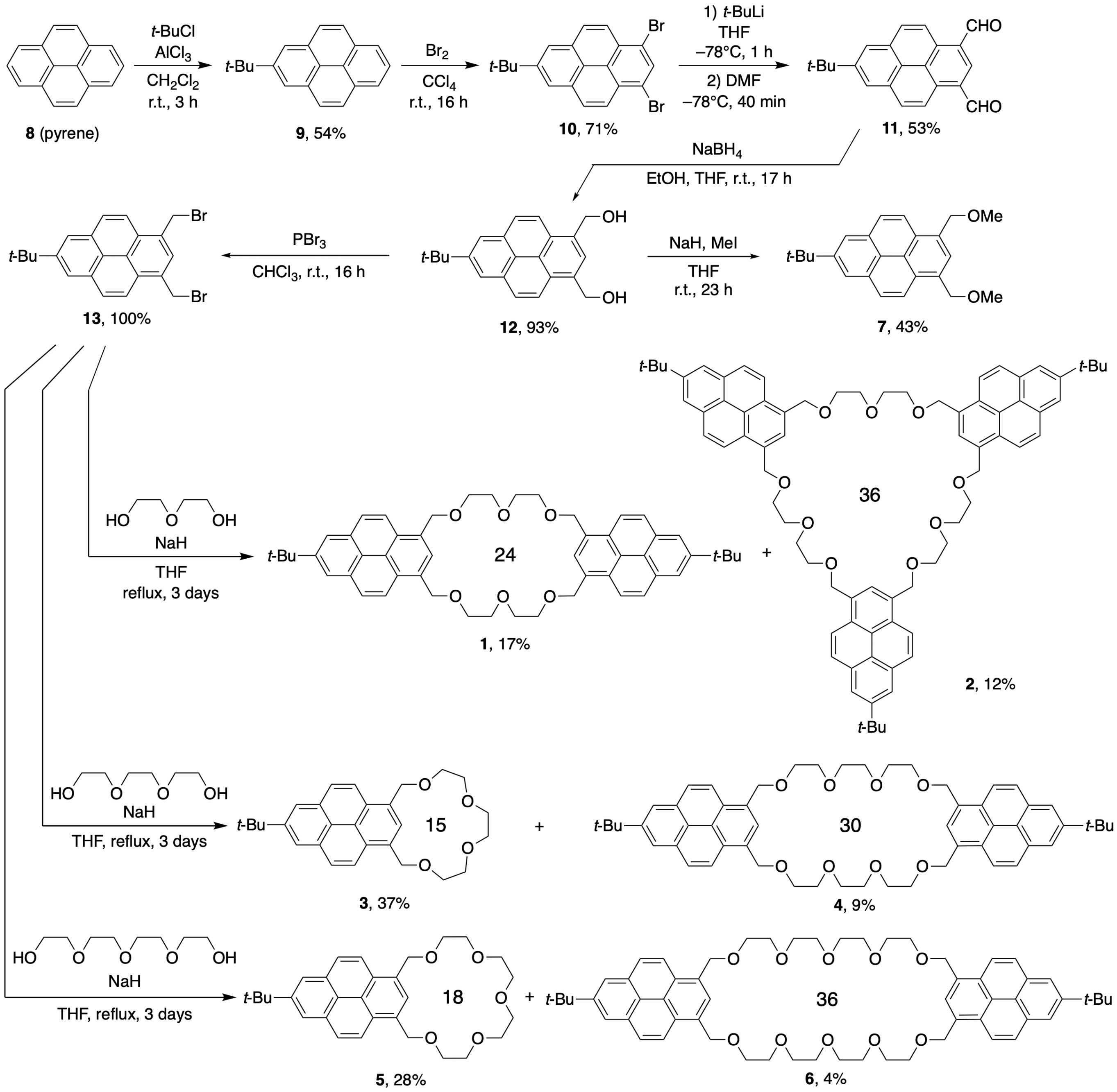
and fluorescence spectral properties were perturbed by metal and dialkylammonium ions. The results showed that these types of cations caused concentration dependent changes in the intensities of monomer and excimer emission from these substances as a consequence of alterations in their *anti*/*syn* conformer populations. As a result, the (1,3)pyrenophane-crown ethers conjugates served as selective and sensitive fluorescent sensors for metal and dialkylammonium ions.

Results and discussion

The pathways used to synthesize the crown ether containing (1,3)pyrenophanes **1**-**6** are displayed in Scheme 1. Briefly, preparation of the 1,3-bis(bromomethyl)-7-*tert*-butylpyrene (**13**) serving as the key intermediate in the sequences, began with Friedel-Crafts mono-*tert*-butylation of pyrene (**8**) followed by bis-bromination to generate 1,3-dibromo-7-*tert*-butylpyrene (**10**). Formylation of **10** produced bis-aldehyde **11**, which was transformed to the corresponding diol **12** by $NaBH_4$ reduction. PBr_3 promoted bromination of **12** then formed the key intermediate **13**. Reaction of **13** with diethylene glycol in the presence of NaH produced a mixture of the crown ether containing (1,3)pyrenophanes **1** (17%) and **2** (12%), which respectively possess 24 and 36 membered crown ether ring systems. Reactions of **13** with tri- and tetra-ethylene glycol generated the respective pyrenocrown ethers **3** (37%) and **5**



Scheme 1 Synthesis of crown ether containing (1,3)pyrenophanes **1**-**6** and model **7**.

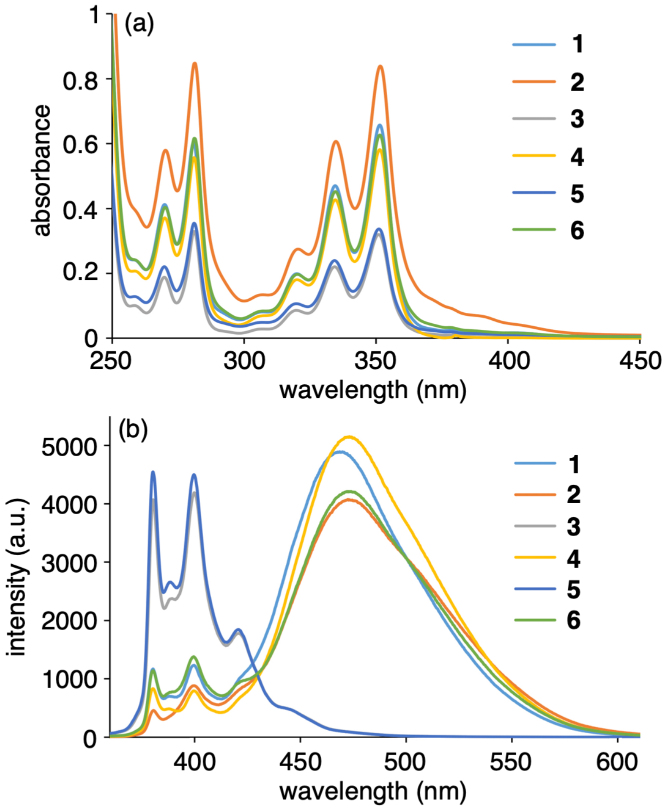


Fig. 1 (a) UV-vis absorption and (b) fluorescence spectra of **1**-**6** (1.0×10^{-5} M in 1:1 $CH_2Cl_2:CH_3CN$, λ_{ex} = 351 nm for **1**-**3** and **5** and 352 nm for **4** and **6**.

(28%), along with corresponding 30- and 36-membered crown ethers **4** (9%) and **6** (4%). Finally, bis-methyl ether **7** was prepared for reference purposes by methylation of diol **12**.

The UV-vis absorption spectra of 1.0×10^{-5} M 1:1 $CH_2Cl_2:CH_3CN$ solutions of **1**-**6** contained absorption bands, arising from π-π^* transitions of the pyrene chromophore, with molar extinction coefficients that increased as the number of pyrene rings increases (Fig. 1a). The fluorescence spectra of the solutions of **3** and **5**, each of which contains one pyrene fluorophore contained monomer emission bands between 380-410 nm, whereas spectra of **1**, **2**, **4** and **6**, bearing two or three pyrene moieties, contained intense bands associated with intramolecular excimer emission at ca. 470 nm along with weaker bands corresponding to monomer emission between 380-410 nm (Fig. 1b).

Solvent dependencies of the UV-vis absorption and fluorescence spectra of **1**, **2**, **4**, and **6** were assessed using toluene, THF, $CHCl_3$, CH_2Cl_2, and DMF as solvents (Fig. S1-S4). The data showed that UV-vis absorption spectra of these substances were not dependent on these solvents, but that the ratios of the intensities of intramolecular excimer to monomer emission (I_{460}/I_{380}) in the fluorescence spectra were affected by solvent changes. This was especially true for **1**, which had the largest I_{460}/I_{380} (2.09) in CH_2Cl_2 and smallest I_{460}/I_{380} (1.09) in $CHCl_3$ (Table S1).

Studies were conducted to determine the best solvent for use in studies of the metal cation dependence of the nature of fluorescence spectra of the crown ether containing (1,3)pyrenophanes. We observed that addition of $Ba(ClO_4)_2$ (0-2000 equiv) to a 1.0×10^{-5} M 1:1 $CH_2Cl_2:CH_3CN$ solution of **1** caused a decrease in the intensity of intramolecular excimer emission band and a simultaneous increase in the intensity of the monomer emission band (Fig. 2a). This change was associated with a fluorescence color change from greenish blue to purple upon addition of 2000 equiv of $Ba(ClO_4)_2$ (Fig. 2b,c). Addition of $Ba(ClO_4)_2$ to a solution of **1** in 1:1 toluene:CH_3CN brought about similar fluorescence spectral changes but to a lesser degree (Fig. S5). Moreover, when $Ba(ClO_4)_2$ was added to a 1:1 THF:CH_3CN solution of **1**, only small changes in the emission spectrum occurred. It is assumed that the changes in the fluorescence spectrum of **1** promoted by $Ba(ClO_4)_2$ are associated with complexation of

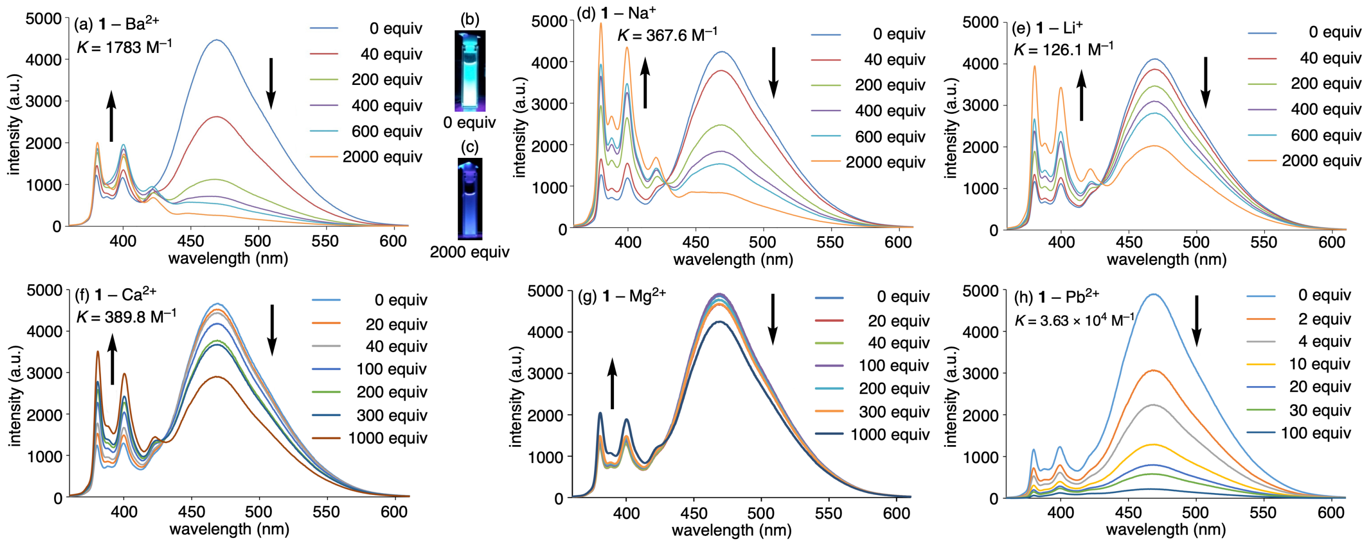


Fig. 2 (a) Fluorescence spectra of **1** (1.0×10^{-5} M in 1:1 $CH_2Cl_2:CH_3CN$, λ_{ex} = 351 nm) upon addition of $Ba(ClO_4)_2$ (0-2000 equiv). (b)(c) Image showing **1** (1.0×10^{-5} M in $CH_2Cl_2:CH_3CN$, λ_{ex} = 254 nm) before and after addition of $Ba(ClO_4)_2$ (2000 equiv). Fluorescence spectra of **1** (1.0×10^{-5} M in 1:1 $CH_2Cl_2:CH_3CN$, λ_{ex} = 351 nm) upon addition of (d) $NaClO_4$ (0-2000 equiv), (e) $LiClO_4$ (0-2000 equiv), (f) $Ca(ClO_4)_2$ (0-1000 equiv), (g) $Mg(ClO_4)_2$ (0-1000 equiv), and (h) $Pb(ClO_4)_2$ (0-100 equiv).

Ba^{2+} to the crown ether ring (see below) and that the attenuation of the effects in toluene:CH_3CN is a result of cation-π interaction of toluene with Ba^{2+} and in THF:CH_3CN is a consequence of competitive coordination of this metal cation with THF.

The results described above led to the selection of CH_2Cl_2:CH_3CN as the solvent for studies of the metal cation dependence of fluorescence spectra of the crown ether containing (1,3)pyrenophanes. The response of the fluorescence spectrum of **1** (1.0×10^{-5} M) in 1:1 CH_2Cl_2:CH_3CN to the presence of $NaClO_4$, $LiClO_4$, $Ca(ClO_4)_2$, and $Mg(ClO_4)_2$ was determined (Fig. 2d-g). In a manner that is similar to the effect caused by $Ba(ClO_4)_2$, the intensity of the intramolecular excimer emission band of **1** decreased and that of monomer emission increased with the existence of isoemissive points when these salts were added but the degrees of the changes were smaller. Interestingly, when $Pb(ClO_4)_2$ was added to a 1:1 CH_2Cl_2:CH_3CN solution of **1**, the intensities of both intramolecular excimer and monomer emission decreased, a likely consequence of heavy atom enhancement of intersystem crossing (heavy atom effect)[94] in the excited states of the pyrene moieties (Fig. 2h). Complexation constants (*K*), obtained by analysis of the fluorescence spectral changes, are provided in Fig. 2. The UV-vis absorption spectrum of **1** in 1:1 CH_2Cl_2:CH_3CN was not changed by addition of $Ba(ClO_4)_2$, $NaClO_4$, $LiClO_4$, $Ca(ClO_4)_2$, $Mg(ClO_4)_2$, and broadening and a long wavelength shift of the absorption band was caused by addition of $Pb(ClO_4)_2$ (Fig. S6).

In order to determine if the size of the crown ether ring influences metal cation binding propensities, various metal perchlorates were added to 1.0×10^{-5} M 1:1 CH_2Cl_2:CH_3CN solutions of **2**, **4**, and **6** (Fig. S7-S12). In most cases, the salts had no effect on the UV-vis absorption spectra of these substances. However, like in the case of **1,** addition of $Pb(ClO_4)_2$ led to broadening and a shift to longer wavelengths of the absorption bands of **2**, **4**, and **6**. Moreover, addition of $Ba(ClO_4)_2$ to solutions of both **2** and **4**, and $Ca(ClO_4)_2$ to a solution of **6** also caused the UV-vis absorption bands to shift to longer wavelength. Also, like in the case of **1**, the intensities of intramolecular excimer emission bands dramatically decreased and those of monomer emission simultaneously increased. The changes in fluorescence were remarkable when $Ba(ClO_4)_2$ was added to solutions of **2** , **4** and **6**, and $Ca(ClO_4)_2$ was added to solutions of **4** and **6**, $NaClO_4$ was added to a solution of **4**, and $Mg(ClO_4)_2$ was added to a solution of **6**. As with **1**, $Pb(ClO_4)_2$ promoted quenching of the fluorescence of **2**, **4** and **6**. The degree of the metal cation induced emission changes was lower in the case of the tris-pyrene derivative **2** than it was in the bis-pyrene derivatives **4** and **6**. A comparison of the fluorescence spectral changes taking place with **1**, **4**, and **6** indicated that smaller quantities of $Ba(ClO_4)_2$ were required to quench intramolecular excimer emissions as the crown ether ring size increases. Specifically, 2000 equiv of $Ba(ClO_4)_2$ was required to quench intramolecular excimer emission from **1**, whereas 100 and 20 equiv of this salt were sufficient to quench intramolecular excimer emission from **4** and **6**. These observations show that an increase in the number of oxygen atoms and/or increased molecular flexibility in the linked-crown ether rings lead(s) to an increase in the metal cation complexation ability of the (1,3)pyrenophanes. Analysis of Job's plots[95-97] showed that the stoichiometry of each of the complexes formed between $Ba(ClO_4)_2$, $NaClO_4$, and $LiClO_4$ and **1**, **2**, **4** and **6** in 1:1 CH_2Cl_2:CH_3CN is 1:1 (Fig. S13-S16).

Information about the proposed complexation of the crown ether linked (1,3)pyrenophanes came from ^1H NMR analysis of $CDCl_3$ solutions of **1** before and after addition of $Ba(ClO_4)_2$ and $LiClO_4$ (Fig. S17). Specifically, addition of $Ba(ClO_4)_2$ to a $CDCl_3$ solution of **1** led to splitting of the peaks at 3.71-3.76 ppm (m, 16H), ascribable to protons in the diethylene glycol moiety, into two sets of peaks at 3.73-3.77 (m, 8H) and 3.78-3.82 (m, 8H) ppm. However, the chemical shifts of resonances associated with protons in the pyrene moiety were not significantly changed. Moreover, addition of $LiClO_4$ to a solution of **1** did not result in significant changes in the chemical shifts of resonance associated with the diethylene glycol moiety and only caused peak broadening. These observations support the suggestion that Ba^{2+} interacts with diethylene glycol moiety in **1**.

Additional support for this conclusion comes from the observation that the UV-vis absorption and fluorescence emission spectra of pyrene itself (**8**) and 2-*tert*-butyl-6,8-bis(methoxymethyl)pyrene (**7**), each missing a crown ether moiety were not changed by addition of the $Ba(ClO_4)_2$ (Fig. S18). In contrast, $Pb(ClO_4)_2$ quenched the fluorescence of pyrene (**8**) and **7** as a consequence of a heavy atom effect.

Because pyrenophane **1** contains a 24 membered crown ether ring, it is expected to be an ideal host for complexation with dialkylammonium ions.[98-101] To probe this issue, ^1H NMR spectroscopy was employed to assess change occurring when n-$Bu_2NH_2^+PF_6^-$ was added to a $CDCl_3$ solution of **1** (Fig. 3a-c). Fig. 3a and 3c contain respective ^1H NMR spectra of **1** and n-$Bu_2NH_2^+PF_6^-$ alone, and a spectrum of a mixture of **1** and n-$Bu_2NH_2^+PF_6^-$ is shown in Fig. 3b. Analysis of these spectra showed that n-$Bu_2NH_2^+PF_6^-$ promoted upfield shifts in the resonances for hydrogens on the pyrene ring and pyrenylmethyl group of **1**, and protons in the *n*-butyl group of n-$Bu_2NH_2^+PF_6^-$ also experienced an upfield shift. In addition, resonances for protons in the diethylene glycol group of **1** were splitted when n-$Bu_2NH_2^+PF_6^-$ was present.

Analysis of fluorescence spectral changes demonstrated that the intensity of the intramolecular excimer emission band associated with **1** (1.0×10^{-5} M in 1:1 CH_2Cl_2:CH_3CN) decreased and that of monomer emission increased with the existence of an isoemissive point upon addition of n-$Bu_2NH_2^+PF_6^-$(Fig. 3d). Job's plot analysis showed that a 1:1 complex was formed between **1** and n-$Bu_2NH_2^+PF_6^-$ (Fig. 3e). Similar ^1H NMR spectroscopic, fluorescence spectral and Job's plot observations were made when $(PhCH_2)_2NH_2^+PF_6^-$ was added to solutions of **1** (Fig. S19). The results suggested the possibility that pseudo-rotaxanes are generated between the n-$Bu_2NH_2^+$ and $PhCH_2)_2NH_2^+$ ions as the axle and **1** as the wheel owing to NH_2^+•••O hydrogen bonding interactions.

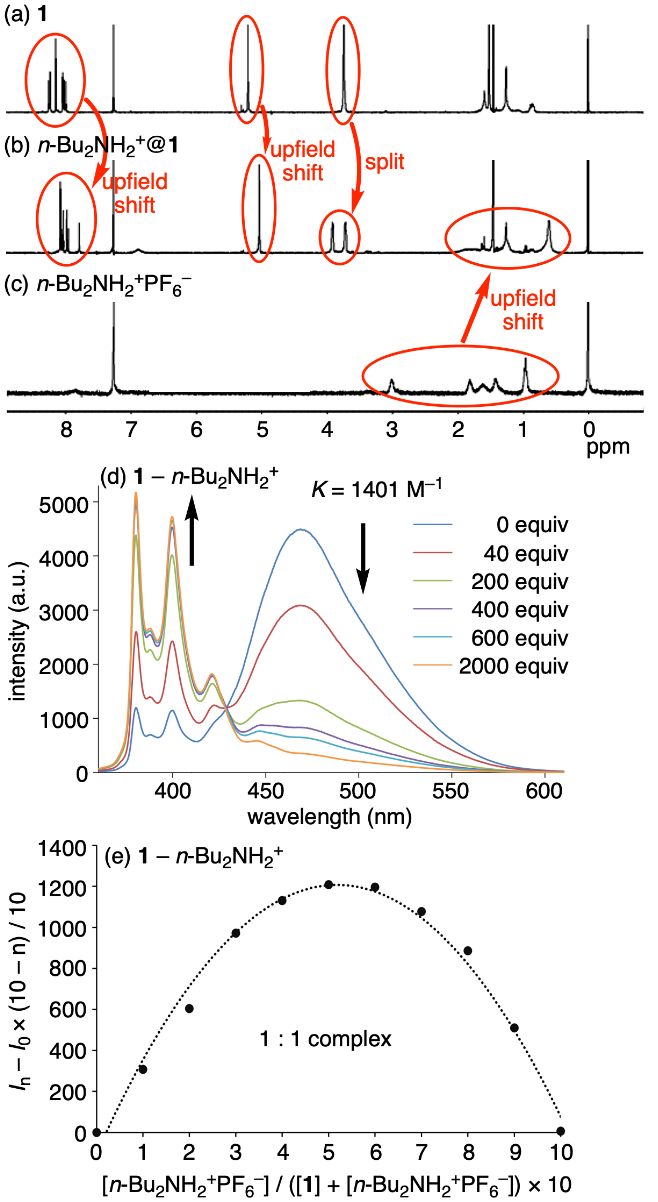


Fig. 3 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) **1**, (b) a mixture of **1** with n-$Bu_2NH_2^+PF_6^-$, and (c) n-$Bu_2NH_2^+PF_6^-$. (d) Fluorescence spectra of **1** (1.0×10^{-5} M in 1:1 CH_2Cl_2:CH_3CN, λ_{ex} = 351 nm) upon addition of n-$Bu_2NH_2^+PF_6^-$ (0-2000 equiv). (e) Job's plot for complex formation between **1** and n-$Bu_2NH_2^+$, obtained using measurements of fluorescence intensities at 468 nm in 1:1 CH_2Cl_2:CH_3CN, [**1**] + [n-$Bu_2NH_2^+PF_6^-$] = 1.0×10^{-5} M.

Changes of UV-vis absorption and fluorescence spectrum of **1**, **2**, **4**, and **6** caused by addition of n-$Bu_2NH_2^+PF_6^-$, $(PhCH_2)_2NH_2^+PF_6^-$ and $NH_4^+PF_6^-$ are summarized in Fig. S20-S23. Analysis of the fluorescence spectra showed that the emission bands of **1** were remarkably altered when $NH_4^+PF_6^-$ was present while only small changes in the emission spectrum of **2** occurred when all three ammonium salts were added. Moreover, in the cases of **4** and **6**, remarkable emission spectral changes took place when n-$Bu_2NH_2^+PF_6^-$ and $(PhCH_2)_2NH_2^+PF_6^-$ were added, but $NH_4^+PF_6^-$ had little effect. The findings show that size matching of the ammonium salt guests and crown ether host is an important factor in governing the degree of complex formation with the (1,3)pyrenophanes. Finally, proton ^{1}H NMR analysis of solutions containing combinations of **1**–$NH_4^+PF_6^-$ and **2**–n-$Bu_2NH_2^+$ showed that resonances for protons in the oligoethylene glycol tethers of **1** and **2** were splitted by interactions between the axle and wheel components (Fig. S24, S25).

Inspection of complexation constants *K*,[102] calculated using fluorescence spectral changes, and ionic radius data displayed in Table 1 show that Ca^{2+}, Ba^{2+} and Pb^{2+} binded most strongly with the crown ether linked (1,3)pyrenophanes **1**, **2**, **4** and **6**. In addition, the (1,3)pyrenophanes displayed modestly selective binding to metal cations that matched the expected sizes of their crown ether ring systems. It should be noted that the *K* values are smaller than those of normal non-pyrene containing crown ethers and dibenzocrown ethers.[18,104] This is likely a consequence of restrictions in the crown ether rings in the (1,3)pyrenophanes caused by connections to the 1,3-positions of pyrene.

An evaluation of durability of the crown ether linked (1,3)pyrenophane **1** as a fluorescent sensor for metal cations was carried out using the scheme summarized in Fig. 4a. For this purpose, analysis was carried out on 1.0×10^{-5} M 1:1 CH_2Cl_2:CH_3CN solutions of **1** before (ON1) and after (OFF1) addition of 1000 equiv of $Ba(ClO_4)_2$. Following their preparation, both solutions were diluted with a mixture of 1 M HCl aq and $CHCl_3$, and the resulting mixture was shaken then separated into organic and aqueous layers. The organic layers, containing recovered **1** and no $Ba(ClO_4)_2$, were concentrated in vacuo, giving a residue that was dissolved in a quantity of 1:1

Table 1 Ionic radii and complexation constants for metal and ammonium ions.[a]

ion	ionic radius (pm)[b]	*K* (M^{-1}) **1**	**2**	**4**	**6**
Li^+	60	126.1 ± 2.2	126.7 ± 16.9	2386 ± 303	464.0 ± 29.6
Mg^{2+}	65	–[c]	926.3 ± 81.0	260.7 ± 11.2	850.2 ± 15.6
Na^+	95	367.6 ± 7.5	91.0 ± 8.3	–[c]	45.6 ± 3.3
Ca^{2+}	99	164.2 ± 4.6	9051 ± 939	$(1.19 \pm 0.02) \times 10^4$	$(1.59 \pm 0.04) \times 10^4$
Pb^{2+}	120	$(3.63 \pm 0.03) \times 10^4$	$(2.17 \pm 0.08) \times 10^4$	$(8.11 \pm 0.03) \times 10^5$	$(3.98 \pm 0.07) \times 10^6$
Ba^{2+}	135	1783 ± 26	703.2 ± 49.6	$(1.63 \pm 0.07) \times 10^4$	$(3.66 \pm 0.17) \times 10^5$
NH_4^+	–	664.1 ± 13.0	890.5 ± 81.4	2009 ± 159	–[c]
n-$Bu_2NH_2^+$	–	1401 ± 15	243.3 ± 14.7	136.2 ± 3.0	174.3 ± 5.7
$(PhCH_2)_2NH_2^+$	–	273.7 ± 4.2	589.0 ± 43.7	165.3 ± 2.7	257.8 ± 3.3

[a] Complexation constants calculated by using TitrationFit 2014-0630 based on fluorescence changes. [b] Data from ref. 103. [c] Fluorescence changed, but complexation constants were not obtained.

CH_2Cl_2:CH_3CN that would give 1.0×10^{-5} M if **1** was completely recovered. This series of operations was repeated five times. The contents of Ba^{2+} complexed and free **1** in the five generated pairs of respective ON and OFF solutions were determined by using fluorescence spectroscopy (Fig. 4b). A plot of the intensity of emission at 468 nm (I_{468}) at each pair of ON and OFF points demonstrated that **1** can be utilized at least five times as a fluorescent sensor for Ba^{2+} (Fig. 4c).

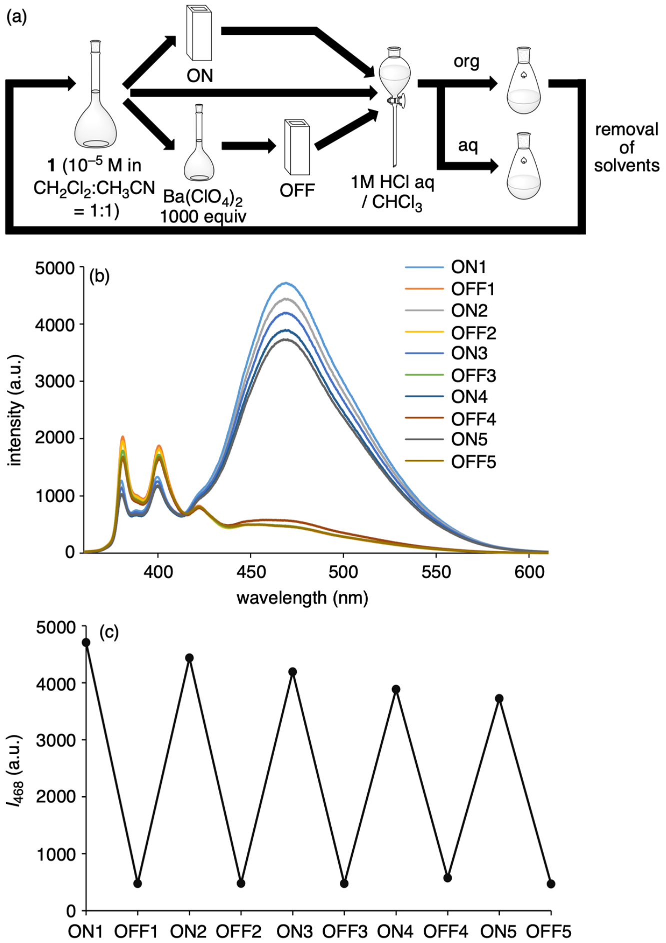


Fig. 4 (a) Experimental procedure for evaluating the durability of **1** in the detection of Ba^{2+} ion. (b) Fluorescence spectra of **1**, 1.0×10^{-5} M in 1:1 CH_2Cl_2:CH_3CN (λ_{ex} = 351 nm). (c) Fluorescence intensity at 468 nm (λ_{ex} = 351 nm), following repeated addition and removal of $Ba(ClO_4)_2$.

The final phase of this investigation was aimed at obtaining information about conformations of the crown ether linked (1,3)pyrenophanes before and after metal cation binding. For this purpose, the temperature dependencies of the fluorescence and ^1H NMR properties of **1**, **2**, **4**, and **6** were assessed. Fluorescence spectra of $CHCl_3$, toluene and DMF solutions of **1**, **2**, **4**, and **6** were recorded at intervals of 20°C in the ranges of –60°C to 60°C for $CHCl_3$ and DMF, and from –80°C to 60°C for toluene (Fig. S26-S29). The results showed that the intensities of monomer emission bands of the (1,3)pyrenophanes increased with decreasing temperature, and the intramolecular excimer emission bands increased with increasing temperature.

Variable temperature ^1H NMR studies were conducted on $CDCl_3$ or toluene-d_8 solutions of **1**, **2**, **4**, and **6** in the temperature ranges of –60°C to 60°C for $CDCl_3$ and of –80°C to 60°C for toluene-d_8 (Fig. S30-S33). Analysis of the results showed that while changes in chemical shifts of protons took place, peak coalescence did not occur.

In an attempt to clarify the results of the temperature dependent fluorescence studies, DFT calculations were carried out (Fig. 5, S34, Table S2). Geometry optimization followed by energy determination for the *syn* and *anti* conformers of **1**, carried out by using B3LYP/3-21G//B3LYP/6-31G(d,p), indicated that *anti*-**1** is more stable than *syn*-**1** ($\Delta\Delta H$(*syn*–*anti*) = 18.2 kJ/mol). The entropy difference ($\Delta\Delta S$(*syn*–*anti*)) between *anti*-**1** and *syn*-**1** was calculated to be 13.3 J/mol•K at 25°C. Based on a consideration of the relationship $\Delta\Delta G = \Delta\Delta H - T\Delta\Delta S$, we expect that the proportion of the enthalpically favored *anti*-**1** conformer should increase with decreasing temperature, whereas the proportion of entropically favored *syn*-**1** should increase with increasing temperature. This conclusion is consistent with results of variable-temperature fluorescence studies which demonstrate that monomer emission, likely arising from *anti*-**1**, became preferred at lower temperature and excimer emission, likely coming from *syn*-**1**, predominated at higher temperature.

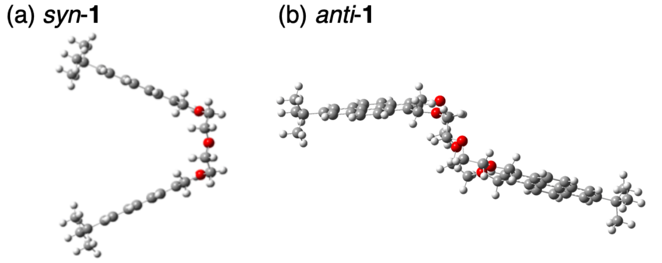
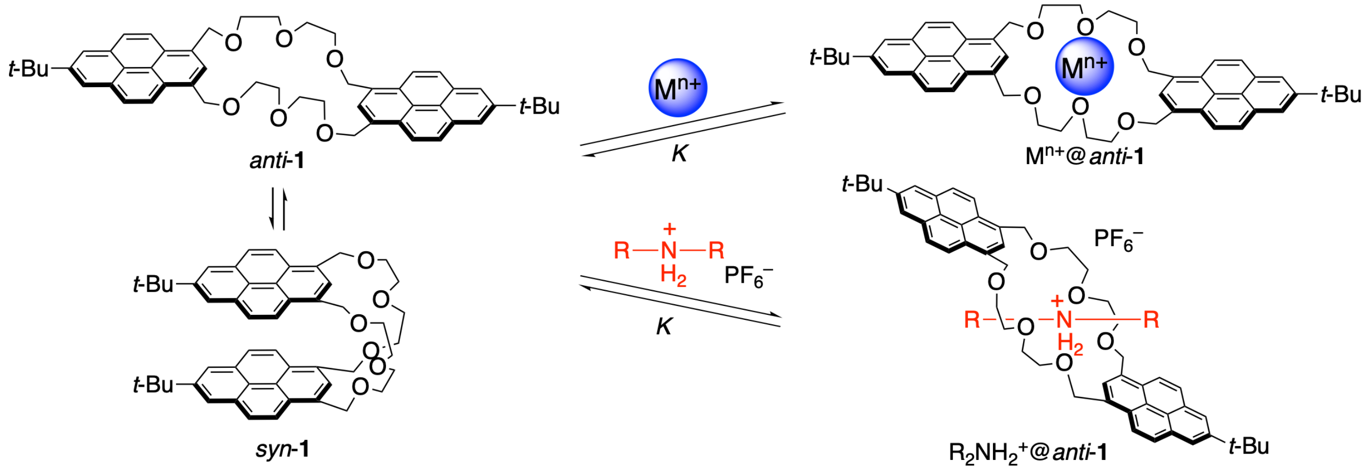


Fig. 5 Optimized structures of (a) *syn*-**1** and (b) *anti*-**1** calculated by using B3LYP/6-31G(d,p).

There are some additional related factors for the temperature dependency. One is solvent exclusion model.[83] Since *anti* conformer has a larger molecular surface area, it should be well solvated. On the other hand, conversion of the *anti* to the more compact *syn* form takes place with the release of solvent molecules, therefore, it brings a further increase in entropy. In addition, it is known that excimer to monomer ratio (I_{ex}/I_{mon}) in fluorescence spectra is influenced by solvent viscosity that decreases with increasing temperature, therefore, higher temperature causes the increase of the ratio.[105] This temperature dependency obtained in this study is the same tendency with those of unsubstituted pyrene (**8**)[2] and flexible 1,3-di(1-pyrenyl)propane,[106,107] however, it is opposite with that of largely *anti*-favored and rigid [2.2](1,3)pyrenophane.[53]

Conformational changes occurring when metal or ammonium ions are added to solutions of the pyrenophane containing crown ether **1** are depicted in Scheme 2. In the absence of metal or ammonium ions, **1** exists as an equiliblium mixture of *anti*-**1** and *syn*-**1** conformers, along with other miscellaneous conformers arising from molecular motion of the diethylene glycol ring. In the presence of metal and ammonium ions, **1** adopts the respective *anti* conformations M^{n+}@*anti*-**1** and $R_2NH_2^+$@*anti*-**1**. Speculation that complexation mainly occurs on the *anti* form is based on the observation that the intensity of the intramolecular excimer emission decreases and that of the monomer emission band increases in the presence of metal and ammonium ions. However, the possibility that *syn*-type complexes[108] are formed in the cases of larger crown ether bearing ring systems in **2**, **4**, and **6**, and small ions such as Li^+ and NH_4^+can not be excluded because only small fluorescence spectral changes were observed in such combinations. Detecting the excimer and monomer emission, we observe the conformational change upon addition of metal or ammonium ions, not directly the complex formation between ions and the (1,3)pyrenophanes. Therefore, it may be possible that some molecules do not form complexes so efficiently but change the conformation very easily once they form complexes.



Scheme 2 Equilibrium between *syn* and *anti*-**1** and their metal and ammonium complexes.

Conclusions

In this study, the crown ether containing (1,3)pyrenophanes **1**, **2**, **4**, and **6** were synthesized and evaluated as fluorescent sensors for metal and ammonium ions. Addition of perchlorate salts containing Ba^{2+}, Na^+, Li^+, Ca^{2+}, and Mg^{2+} to 1.0×10^{-5} M 1:1 CH_2Cl_2:CH_3CN solutions of the (1,3)pyrenophanes was found to cause an increase in the intensity of monomer emission and a decrease in that of intramolecular excimer emission, with isoemissive points existing in most cases. The degree of the fluorescence spectral changes, which correspond to complexation constants, occurring upon increasing concentrations of the cationic guests showed that size matching between the crown ethers and metal ions governs cation binding propensities. Moreover, addition of Pb^{2+} ion to solutions of the (1,3)pyrenophanes resulted in quenching of both monomer and intramolecular excimer emissions. Addition of ammonium salts (n-$Bu_2NH_2^+$, $(PhCH_2)_2NH_2^+$) to solutions of **1**, **4**, and **6** brought about formation of pseudo-rotaxanes. Analysis of Job's plots demonstrated that 1:1 complexes were produced. The temperature dependence of the nature of fluorescence spectra of **1** showed that the intensity of monomer emission increased as temperature decreases and that an increase in the intensity of intramolecular excimer emission occurred at higher temperature. The results of a durability test showed that **1** can be used for fluorescence sensing of Ba^{2+} repeatedly for at least five times. It is believed that these novel (1,3)pyrenophanes containing crown ether moieties could be valuable and efficient fluorescent sensors for recognition of metal and ammonium ions.

Experimental

Materials and equipment

THF was distilled from CaH_2 and then from $Na/Ph_2C{=}O$. Toluene and CH_2Cl_2 were distilled from CaH_2. $CHCl_3$ was distilled from Na_2SO_4. DMF was distilled without drying agent. Spectral grade of $CHCl_3$, CH_2Cl_2, and DMF were purchased and used without further purification for spectroscopic studies. $NH_4^+PF_6^-$ was used as purchased, and n-$Bu_2NH_2^+PF_6^-$ was prepared using a literature procedure.[109] Most other chemical substances were used after purification by distillation or recrystallization. ^1H and ^{13}C NMR spectra were recorded using a JEOL JMN LA-400 (400 MHz and 100 MHz, respectively) or a JEOL ECA-500 (500 MHz and 125 MHz, respectively) spectrometer with Me_4Si as an internal standard. IR spectra were determined using a Shimadzu FTIR-8300 spectrometer. Low- and high-resolution mass spectra were taken on a JEOL JMS-AM50 and a JEOL JMS-SM102A instrument, respectively. UV-vis spectra were recorded using a Hitachi U-2900 spectrophotometer. Fluorescence spectra were recorded using a Hitachi F-2500 or a Jasco FP-8000 spectrophotometer. HPLC separations were performed on recycling preparative HPLC instruments, Japan Analytical Industry Co. Ltd., LC-908 equipped with a JAIGEL-H (GPC) column. Column chromatography was conducted by using Kanto-Chemical Co. Ltd., silica gel 60 N (spherical, neutral, 0.04–0.05 mm). Thin-layer chromatography was done with Merck Kiesel gel 60 F_{254} plate, and spots were detected by using UV light and a phosphomolybdic acid ethanol solution with heating. Theoretical calculations were performed by using B3LYP/6-31G(d,p) or ωB97XD/6-31G(d,p) basis sets in a Gaussian 09 software package. Complexation constants were calculated by using TitrationFit 2014-0630 based on changes of fluorescence spectra.

1,3-Bis(bromomethyl)-7-*tert*-butylpyrene (13)

To an argon-purged, stirred CH_2Cl_2 solution (90 mL) of pyrene (**8**, 8.09 g, 40 mmol) and *t*-BuCl (3.70 g, 40 mmol) was added $AlCl_3$ (8.01 g, 60 mmol) at 0°C. The resulting solution was stirred at room temperature for 3 h. Ice water (100 mL) was added. The solution was extracted with $CHCl_3$ (30 mL × 3). The combined organic layers were washed with saturated NH_4Cl aqueous solution (30 mL × 3). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization of the residue from hexane-EtOH gave 2-*tert*-butylpyrene (**9**, brown solid, 5.57 g, 54% yield). Lit.[83,110]

To a stirred CCl_4 (20 mL) solution of 2-*tert*-butylpyrene (**9**, 1.23 g, 5 mmol) was added CCl_4 (2.5 mL) solution of Br_2 (1.60 g, 10 mmol), and the solution was stirred at room temperature for 18 h. NaOH aqueous solution (0.2 M, 20 mL) was added. The solution was filtered and concentrated in vacuo. Recrystallization of the residue from toluene (20 mL) gave 1,3-dibromo-7-*tert*-butylpyrene (**10**, gray solid, 1.40 g, 71% yield). Lit.[83,111]

To an argon-purged, stirred THF (40 mL) solution of 1,3-dibromo-7-*tert*-butylpyrene (**10**, 2.92 g, 7.0 mmol) was added dropwise *t*-BuLi (1.77 M in pentane, 16.8 mL, 29.7 mmol) at –78°C, and the solution was stirred at –78°C for 1 h. To the solution was added DMF (4.3 mL, 56 mmol) at –78°C, and the solution was stirred at –78°C for 40 min, then at room temperature for 2 h. H_2O (100 mL) was added. The solution was filtered and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (eluent: $CHCl_3$) to give 2-*tert*-butyl-6,8-diformylpyrene (**11**, orange solid, 1.18 g, 53% yield). Lit.[83,112]

To a stirred THF (80 mL) and EtOH (10 mL) solution of 2-*tert*-butyl-6,8-diformylpyrene (**11**, 1.10 g, 3.5 mmol) was added $NaBH_4$ (661 mg, 17.6 mmol), and the solution was stirred at room temperature for 19 h. H_2O (100 mL) was added. The solution was filtered and concentrated in vacuo to give 2-*tert*-butyl-6,8-bis(hydroxymethyl)pyrene (**12**, white solid, 1.04 g, 93% yield). Lit.[83]

To an argon-purged, stirred $CHCl_3$ (20 mL) solution of 2-*tert*-butyl-6,8-bis(hydroxymethyl)pyrene (**12**, 340 mg, 1.1 mmol) was added dropwise $CHCl_3$ (10 mL) solution of PBr_3 (0.3 mL, 3.2 mmol), and the solution was stirred at room temperature for 29 h. Saturated NH_4Cl aqueous solution (30 mL) was added. The solution was extracted with $CHCl_3$ (30 mL × 3). The combined organic layers were washed with saturated NH_4Cl aqueous solution (30 mL × 3). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo to give 1,3-bis(bromomethyl)-7-*tert*-butylpyrene (**13**, pale green solid, 480 mg, 100% yield). Lit.[83]

Pyrenophanes 1 and 2

To an argon-purged, stirred mixture of NaH (220 mg, 5.5 mmol) and THF (30 mL) was added THF (10 mL) solution of diethylene glycol (161 mg, 1.5 mmol), and the mixture was stirred at reflux for 2 h. After cooling to room temperature, a mixture of KCl (398 mg, 5.3 mmol) and THF (10 mL) was added. To the solution was added dropwise THF (40 mL) solution of 1,3-bis(bromomethyl)-7-*tert*-butylpyrene (**13**, 550 mg, 1.2 mmol) over a 2.5 h period, and the solution was stirred at reflux for 66 h. H_2O (30 mL) and HCl aqueous solution (1 N, 10 mL) were added. The solution was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl aqueous solution. The organic layer was separated and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (eluent: $CHCl_3$:EtOH = 1:1) followed by recycling preparative HPLC (GPC, eluent: $CHCl_3$) to give 14,33-di-*tert*-butyl-2,5,8,21,24,27-hexaoxa[9.9](1,3)pyrenophane (**1**, 84 mg, 17% yield) and 14,33,52-tri-*tert*-butyl-2,5,8,21,24,27,40,43,46-nonaoxa[9.9.9](1,3)pyrenophane (**2**, 59 mg, 12% yield). Data for **1**: pale yellow solid; mp 234-237°C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.52 (s, 18H), 3.73 (d, *J* = 2.3 Hz, 16H), 5.20 (s, 8H), 7.99 (s, 2H), 8.02 (d, *J* = 9.0 Hz, 4H), 8.14 (s, 4H), 8.24 (d, *J* = 9.5 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.78, 35.05, 69.51, 70.80, 71.36, 122.54, 122.93, 123.00, 125.00, 127.39, 127.64, 128.80, 130.53, 130.61, 148.85 ppm; IR (KBr) 837, 876, 1100, 1227, 1350, 1458, 1593, 2963 cm^{-1}; MS (EI) *m/z* (relative intensity, %) = 57 (15), 285 (48), 300 (20), 388 (14), 776 (M^+, 44); HRMS (FAB+) calcd for $C_{52}H_{57}O_6$: 777.4155, found: 777.4163. Data for **2**: yellow solid; mp 82-85°C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 27H), 3.62 (d, *J* = 10.5 Hz, 24H), 5.14 (s, 12H), 7.93 (s, 3H), 7.96 (d, *J* = 9.2 Hz, 6H), 8.12 (s, 6H), 8.23 (d, *J* = 8.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.83, 35.08, 69.45, 70.72, 71.54, 122.57, 122.92, 123.17, 125.03, 127.61, 127.68, 128.97, 130.58, 130.63, 148.88 ppm; IR (KBr) 817, 880, 1100, 1227, 1361, 1462, 1597, 2954 cm^{-1}; MS (FAB+) *m/z* (relative intensity, %) = 284 (100), 388 (14), 662 (2), 1165 (M^+, 5); HRMS (FAB+) calcd for $C_{78}H_{84}O_9$: 1164.6115, found: 1164.6126.

Pyrenophanes 3 and 4

To an argon-purged, stirred mixture of NaH (171 mg, 4.3 mmol) and THF (30 mL) was added THF (50 mL) solution of triethylene glycol (98 mg, 0.7 mmol), and the mixture was stirred at reflux for 1 h. After cooling to room temperature, KCl (754 mg, 10 mmol) was added. To the solution was added dropwise a THF (30 mL) solution of 1,3-bis(bromomethyl)-7-*tert*-butylpyrene (**13**, 220 mg, 0.5 mmol) over a 2 h period, and the solution was stirred at reflux for 72 h. H_2O (30 mL) and HCl aqueous solution (1 N, 10 mL) were added. The solution was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl aqueous solution, separated, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (eluent: $CHCl_3$:EtOH = 1:1) followed by recycling preparative HPLC (GPC, eluent: $CHCl_3$) to give 17-*tert*-butyl-2,5,8,11-tetraoxa[12](1,3)pyrenophane (**3**, 80 mg, 37% yield) and 17,39-di-*tert*-butyl-2,5,8,11,24,27,30,33-octaoxa[12.12](1,3)pyrenophane (**4**, 20 mg, 9% yield). Data for **3**: pale yellow solid; mp 207-209°C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 9H), 3.82 (s, 4H), 3.80-3.91 (m, 8H), 5.43 (s, 4H), 8.06 (d, *J* = 9.2 Hz, 2H), 8.13 (d, *J* = 10.8 Hz, 2H), 8.21 (s, 2H), 8.76 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.87, 35.13, 69.70, 69.75, 70.80, 70.87, 122.08, 122.44, 123.26, 123.96, 124.74, 126.97, 127.22, 130.69, 131.71, 148.74 ppm; IR (KBr) 806, 876, 1358, 1446, 2963 cm^{-1}; MS (EI) *m/z* (relative intensity, %) = 57 (6), 256 (4), 299 (45), 432 (M^+, 100); HRMS (FAB+) calcd for $C_{28}H_{32}O_4$: 432.2301, found: 432.2292. Data for **4**: yellow solid; mp 170-175 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 18H), 3.63-3.70 (m, 24H), 5.14 (s, 4H), 7.91 (s, 2H), 8.01 (d, *J* = 4.0 Hz, 4H), 8.17 (s, 4H), 8.23 (d, *J* = 8.0 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.84, 35.10, 69.40, 70.70, 70.80, 71.47, 122.56, 122.89, 123.19, 124.97, 127.62, 128.93, 129.29, 130.52, 130.63, 148.89 ppm; IR (KBr) 814, 876, 1112, 1231, 1362, 1593, 2955 cm^{-1}; MS (FAB+) *m/z* (relative intensity, %) = 57 (15), 271 (20), 285 (84), 343 (6), 864 (M^+, 27); HRMS (FAB+) calcd for $C_{56}H_{64}O_8$: 864.4679, found: 865.4684.

Pyrenophanes 5 and 6

To an argon-purged, stirred mixture of NaH (600 mg, 15 mmol) and THF (70 mL) was added tetraethylene glycol (191 mg, 0.98 mmol), and the mixture was stirred at reflux for 30 min. To the solution was added dropwise THF (15 mL) solution of 1,3-bis(bromomethyl)-7-*tert*-butylpyrene (**13**, 334 mg, 0.75 mmol) over a 30 min period at room temperature, and the solution was stirred at reflux for 53 h. H_2O (30 mL) and HCl aqueous solution (1 N, 10 mL) were added. The solution was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl aqueous solution, separated, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (eluent: $CHCl_3$:EtOH = 1:1) followed by recycling preparative HPLC (GPC, eluent: $CHCl_3$) to give 20-*tert*-butyl-2,5,8,11,14-pentaoxa[15](1,3)pyrenophane (**5**, 101 mg, 28% yield) and 20,45-di-*tert*-butyl-2,5,8,11,14,27,30,33,36,39-decaoxa[15.15](1,3)pyrenophane (**6**, 15 mg, 4% yield). Data for **5**: pale yellow solid; mp 127-129°C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.58 (s, 9H), 3.85-3.74 (m, 16H), 5.41 (s, 4H), 8.06 (d, *J* = 9.5 Hz, 2H), 8.21 (d, *J* = 9.5 Hz, 2H), 8.21 (s, 2H), 8.41 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.90, 35.17, 69.37, 70.65, 70.88, 71.37, 122.58, 122.65, 123.20, 125.00, 125.73, 127.51, 127.98, 130.75, 131.23, 148.89 ppm; IR (KBr) 806, 876, 1358, 1466, 2924 cm^{-1}; MS (FAB+) *m/z* (relative intensity, %) = 55 (100), 285 (8), 476 (M^+, 71); HRMS (FAB+) calcd for $C_{30}H_{36}O_5$: 476.2563, found: 476.2551. Data for **6**: pale yellow solid; mp 95-100°C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 18H), 3.61 (m, 16H), 5.15 (s, 8H), 7.94 (s, 2H), 8.02 (d, *J* = 9.2 Hz, 4H), 8.19 (s, 4H), 8.24 (d, *J* = 9.2 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.94, 31.87, 69.46, 70.64, 70.67, 71.60, 122.63, 122.97, 123.27, 125.10, 127.73, 127.76, 129.12, 130.59, 130.72, 148.98 ppm; IR (KBr) 799, 876, 1350, 1454, 2951 cm^{-1}; MS (FAB+) *m/z* (relative intensity, %) = 285 (48), 952 (M^+, 4); HRMS (FAB+) calcd for $C_{60}H_{72}O_{10}$: 952.5125, found: 952.5083.

2-*tert*-Butyl-6,8-bis(methoxymethyl)pyrene (7)

To an argon-purged, stirred mixture of NaH (240 mg, 6 mmol) and THF (30 mL) was added 2-*tert*-butyl-6,8-bis(hydroxymethyl)pyrene (**12**, 318 mg, 1 mmol), and the mixture was stirred at room temperature for 1 h. To the solution was added MeI (1.10 g, 7.5 mmol), and the solution was stirred room temperature for 23 h. Saturated NH_4Cl aqueous solution (20 mL) was added. The solution was extracted with $CHCl_3$ (30 mL × 3). The combined organic layers were washed with saturated NaCl aqueous solution (30 mL) and then with saturated NH_4Cl aqueous solution (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (eluent: $CHCl_3$) to give 2-*tert*-butyl-6,8-bis(methoxymethyl)pyrene (**7**, 148 mg, 43% yield). Lit.[83]

Dibenzylammonium hexafluorophosphate

To stirred $(PhCH_2)_2NH$ (2.142 g, 10.9 mmol) was added HCl aqueous solution (2 M, 110 mL), and the suspension was stirred at room temperature for 4 h. The solid was collected by filtration and dissolved in H_2O (200 mL). Saturated $NH_4^+PF_6^-$ aqueous solution was added until formation of precipitation was saturated. The white solid was collected by filtration and identified as $(PhCH_2)_2NH_2^+PF_6^-$ (1.782 g, 48% yield). Lit.[113]

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For Graphical Abstract

(1,3)Pyrenophanes containing crown ether moieties as fluorescence sensors for metal and ammonium ions
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Fluorescence properites of (1,3)pyrenophanes containing crown ether moieties were studied focussing on conformational change and complex formation with metal or ammonium ions.