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Biscrown-Annulated TTFAQ−Dianthracene Hybrid: Synthesis, Structure, and Metal Ion Sensing

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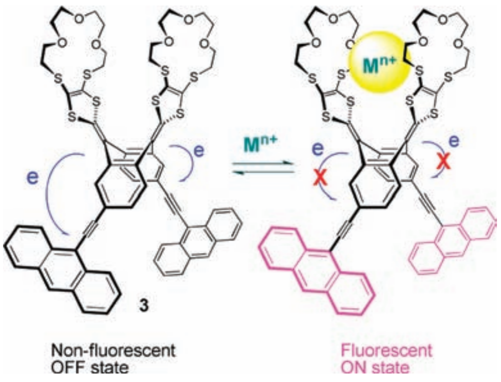
ABSTRACT



A new fluorescence chemosensor (3) made up of a biscrown-annulated TTFAQ receptor and two anthracene fluorophores was designed and synthesized. Its solid-state structure was disclosed by X-ray crystallographic analysis, while fluorescence titrations indicated a high sensitivity for large hard metal cations such as Ba^{2+}.

Tetrathiafulvalene (TTF) possesses well-defined electron-donating and electrochemical properties and has been extensively employed in redox-switchable supramolecular hosts.[1] In particular, TTF constitutes a widely used motif in making redox sensors for cationic metal ions.[1b−e,2] Various π-extended analogues of TTF (exTTFs) also show very rich electronic and redox characteristics, rendering them promising applications in molecular devices.[3] Nevertheless, due to the challenging synthesis of exTTFs, the family of exTTF-based sensors[1b,4] is still considerably smaller than the TTF-based sensors. Continued efforts to develop new synthetic methods and explore useful molecular properties for novel exTTF derivatives are thus highly desirable.

In this communication, we investigate the applicability of the class of anthraquinodimethane-type exTTFs (generally

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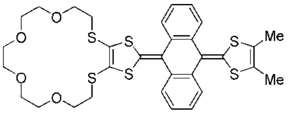
referred to as TTFAQs) in making selective metal cation sensors. TTFAQ is known to have a rigid nonplanar, saddle-like structure in the neutral state.[1a,3,5] Upon oxidation, TTFAQ simultaneously releases two π-electrons to form a stable dication with a planar anthracene unit. In view of its excellent redox behavior, TTFAQ can be used as a redox-responsive signaling unit paired with appropriate receptors to form functional sensors.[4c−f] In terms of metal ion sensing, crown ethers are effective receptors to be integrated into TTF derivatives;[1−3,6] however, crown ether-annulated TTFAQ derivatives were scarcely addressed, with only two examples (**1** and **2**) known in the literature prior to this work.[4d,e] Interestingly, these two compounds exhibited selective voltammetric and spectroscopic responses to various metal cations. The X-ray structure of monocrown-annulated TTFAQ **1** was determined to show a highly curved crown−π molecular framework.[4d] For biscrown-TTFAQ **2**, despite the lack of crystallographic data, it is conceivable that the molecular framework would fold into an arc-shaped conformation with a preorganized and rigid inner cavity, which might enhance the binding with certain cationic species via synergistic crown ether−cation and π−cation interactions (i.e., co-operativity).[8]



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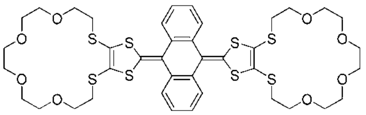

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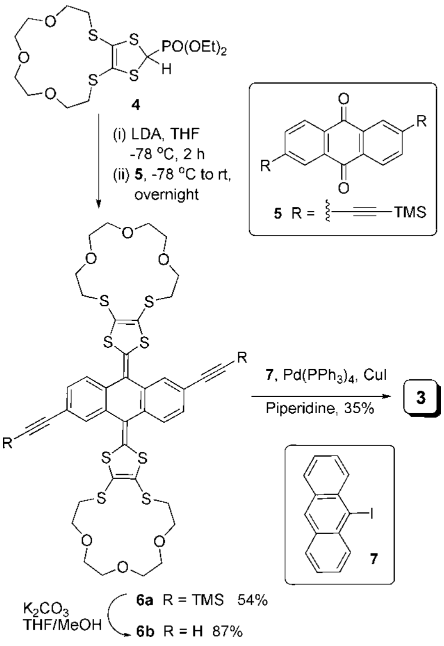
Following the arguments described above, we designed a biscrown-annulated TTFAQ **3** as a prototype of a chemosensor for metal cations. The working principle of sensor **3** is schematically depicted in the graphical abstract. In this mechanism, uncomplexed **3** is supposed to show quenched fluorescence (turn off) as a result of photoinduced electron transfer (PET) from the TTFAQ donor to the anthracene acceptor. After complexation with metal cations, the electron-donating ability of the TTFAQ moiety is attenuated because of cation−π attraction. This effect will in turn suppress the PET process to result in fluorescence enhancement (turn on).

Scheme 1. Synthesis of Sensor **3**



The synthetic route to compound **3** is outlined in Scheme 1.[7] Compound **3** is an orange crystalline solid showing reasonably good solubility in common organic solvents. The molecular structure of compound **3** was convincingly characterized by NMR, IR, and MS analyses, and its solid-state structure was unraveled by single-crystal X-ray crystallography.[7]

As shown in Figure 1, the saddle-shaped TTFAQ core of **3** together with two crown ether rings form a "clawlike"

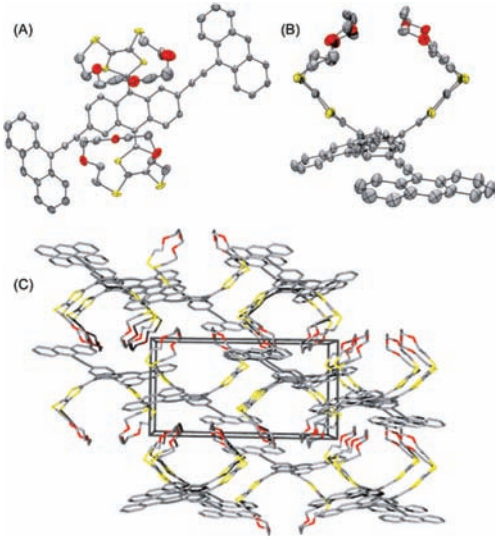


Figure 1. ORTEP presentations of compound **3** (30% ellipsoid probability). (A) Front view. (B) Side view. (C) Crystal packing viewed down the *b*-axis.

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(8) For cooperative binding of biscrown receptors with metal ions, see: (a) Fery-Forgues, S.; Al-Ali, F. *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 139–153. (b) Kondo, S.-i.; Kinjo, T.; Yano, Y. *Tetrahedron Lett.* **2005**, *46*, 3183–3186.

structure, with the two crown ether groups curling up inwardly at a close edge-to-edge distance within the van der Waals contact. Such a structure creates a cylindrical inner cavity (ca. 10.8 Å from two opposite S atoms, Figure 1B). The accessible void within the cavity was calculated using a Monte Carlo process, revealing a maximum radius of 2.12 Å.[7] The two anthracene units show a rather small twist angle with respect to the two benzene rings of TTFAQ. The nearly coplanar orientation must result from a significant conjugation effect. Also worth noting is the packing motif of **3** in the solid state, wherein two anthracene moieties of adjacent molecules show intimate face-to-face π-stacking in a distance of ca. 3.44 Å. The intimate and ordered intermolecular stacking hence allows for the formation of hollow channels as revealed in Figure 1C. This crystallographic feature suggests a potential use of **3** as a supramolecular scaffold for various cavitates or clathrates in crystal engineering.

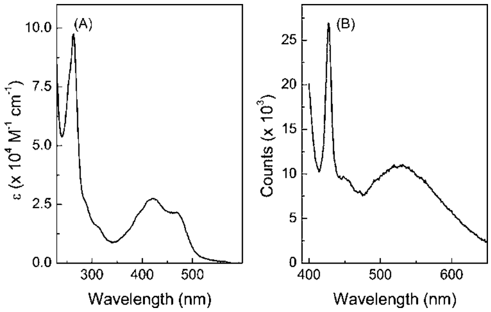

Figure 2. (A) UV−vis and (B) fluorescence spectra of compound **3** measured in degassed THF at room temperature ($\lambda_{exc} = 365$ nm, $\Phi = 6.9 \times 10^{-3}$).

The electronic properties of the TTFAQ-anthracene derivative **3** were investigated by UV−vis absorption and fluorescence spectroscopy. As can be seen from Figure 2A, the UV−vis absorption spectrum of **3** shows three relatively broad low-energy bands at 472, 423, and 393 nm, which are ascribed to the $\pi \rightarrow \pi^*$ transitions at the central TTFAQ core by comparison to the UV−vis data of other TTFAQ derivatives.[9] In the high-energy region, a shoulder at 315 nm and an intense sharp band at 264 nm are absorptions due to the anthracene moieties.[10] The fluorescence spectrum of **3** exhibits a spectral pattern similar to its absorption profile (see Figure 2B). The sharp emission band peaking at 428 nm and the shoulder at 455 nm are attributed to the 0−0 and 0−1 vibronic bands in anthracene,[10] while the broad featureless hump centering at 532 is tentatively assigned to the anthracene exciplex and/or the TTFAQ core.[9]

Upon titration of **3** with [Ba^{2+}], the two bands at 428 and 455 nm that are characteristics of anthracene increased with increasing [Ba^{2+}]. The emission band at 532 nm remained nearly unchanged. This observation is in line with the proposed turn-on sensing mechanism. Apparently, the binding of [Ba^{2+}] with the biscrown-annulated TTFAQ receptor has resulted in diminished electron density in the TTFAQ unit, which attenuated the efficiency of PET from the TTFAQ donor to the two anthracene fluorophores. Similar fluorescence enhancement was also observed in the titration of **3** with [Li^+]. However, the amounts of [Li^+] required to saturate the fluorescence enhancement appeared to be considerably greater than [Ba^{2+}]. As shown in Figure 3E, saturation point was reached by addition of ca. 200 mol equiv of [Ba^{2+}], whereas for [Li^+] more than 2000 equiv was needed.

The titration of **3** with [Mg^{2+}] (see Figure 3C) showed a consistent trend of enhancement of the two anthracene emission bands, which consumed nearly 6000 mol equiv of [Mg^{2+}] to arrive at saturation (Figure 3E). The low-energy emission band at 532 nm, however, displayed somewhat erratic and random variations with increasing addition of [Mg^{2+}]. This observation suggests that Mg^{2+} might have multiple binding motifs in interacting with the biscrown-TTFAQ units, the details of which await further investigation.

In addition to alkali and alkaline earth metal ions, sensor **3** was also tested with a soft transition metal [Ag^+]. As shown in Figure 3D, with increasing addition of [Ag^+] to **3**, the intensities of two anthracene emission bands increased steadily, and saturation was attained when more than 3000 mol equiv of [Ag^+] was titrated (Figure 3E). In contrast with the other titration results, the emission band at 532 nm was not only significantly enhanced in intensity but also notably blueshifted by ca. 30 nm upon titration of [Ag^+]. Such spectral variation can be related to the softness of the [Ag^+] ion that makes it preferably interact with soft ligands (i.e., S atoms of TTFAQ) rather than hard ligands (O atoms of crown ether) and renders sensor **3** the ability to discriminate transition metal ions from main group metal ions.

Figure 3F compares the sensitivity of sensor **3** toward the four metal cations tested. Upon addition of ca. 200 mol equiv of metal cations, the order of fluorescence enhancement at 428 nm (F/F_0) is found to be: Ba^{2+} (3.22) > Mg^{2+} (1.85) > Li^+ (1.56) > Ag^+ (1.35). This trend indicates that sensor **3** has selectivity for hard metal ions with a relatively large diameter such as Ba^{2+}. The discriminative sensing behavior is likely originated from a complementarity of metal ions and the rigid binding pocket of **3** in terms of size matching and noncovalent (e.g., cation−dipole and cation−π) interactions.

The fluorescence titration data were subjected to a global analysis of equilibrium using the *SPECFIT* program to acquire stability constants for complexation of **3** with metal ions (Table 1).[7] The acquired data should be viewed with some care as there was a certain deviation in the baseline (±5%) as deduced from the absorption spectra. Nevertheless, both 1:1 and 1:2 binding stoichiometries were determined. For 1:1 complexation, [Ba^{2+}] and [Li^+] show stability constants (β_{11}) of the same order of magnitude, while the stability constant for [Ag^+] is much

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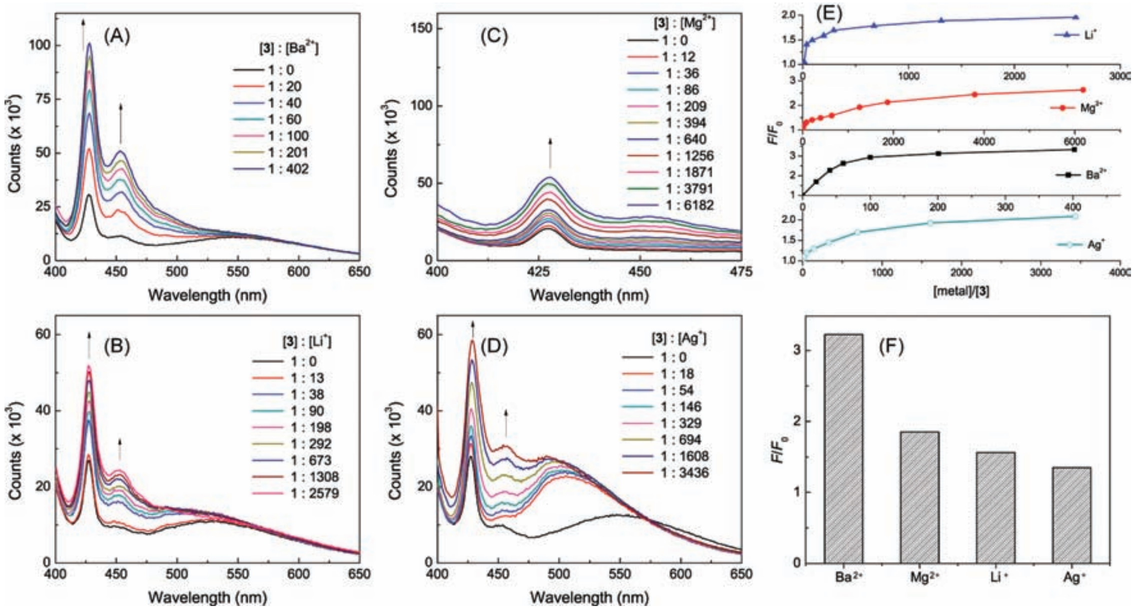

Figure 3. Fluorescence spectra monitoring the titration of compound **3** (10^{-6} M) with various metal cations in THF: (A) with [Ba^{2+}]; (B) with [Li^+]; (C) with [Mg^{2+}]; and (D) with [Ag^+]. (E) Plots of F/F_0 (at 428 nm) vs [metal]/[**3**]. (F) Comparison of fluorescence enhancement (at 428 nm) upon titration of **3** with various metal ions (ca. 200 mol equiv).

Table 1. Stability Constants for **3** Binding with Different Metal Ions in THF Solutions

metal ion	ionic radius	log β_{11} (M^{-1})	log β_{12} (M^{-2})
Ba^{2+}	135 pm	4.51 ± 0.42	8.76 ± 0.45
Li^+	76 pm	4.25 ± 0.12	6.48 ± 0.26
Ag^+	115 pm	5.42 ± 0.17	7.83 ± 0.18

greater than the other two by approximately 1 order of magnitude, likely as a result of the strong Ag−S interactions. For 1:2 complexation, [Ba^{2+}] affords the largest cumulative stability constant (β_{12}) among the other metal ions, which is in line with the highest sensitivity for [Ba^{2+}] revealed in Figure 3F. In general, a 15-crown-5 receptor should favor to strongly bind with small metal cations such as [Na^+] or [Li^+].[11] A cautious interpretation of the usually large β_{12} value for [Ba^{2+}] in comparison with [Li^+] suggests a significant positive cooperation effect taking place in the formation of the 1:2 complex of **3** with [Ba^{2+}].[12]

In conclusion, we have designed and synthesized a new type of fluorescence chemosensor **3** based on a biscrown-annulated TTFAQ receptor and two anthrancene fluorophores. The structure of sensor **3** possesses a "clawlike" biscrown-TTFAQ framework that endows **3** with fluorescence sensing capability to various metal ions, with a particularly high sensitivity for large alkaline earth metal cations like [Ba^{2+}]. Our results validate the applicability of biscrown-annulated TTFAQ as a sensitive donor and selective metal cation receptor in constructing fluorophore-based chemosensors.

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Supporting Information Available: Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] It is known for biscrown receptors that when the two crowns act independently with respect to complexation the ratio of stability constants (K_2/K_1) is equal to 0.25. When the ratio is lower than 0.25, a negative cooperation effect is encountered, whereas when the ratio is greater than 0.25 a positive effect is said to take place.[8a]