

# A Luminescent Sensor Responsive to Common Oxoacids: X-ray Crystal Structure of [H<sub>3</sub>O<sup>+</sup>·1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione]ClO<sub>4</sub>

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**Abstract:** 1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione with a reduced cavity size, due to the presence of a carbonyl oxygen within the crown, has been shown by X-ray crystallography to encapsulate a hydronium ion. Hydrogen bonds between the hydronium ion and the crown oxygens are particularly strong, averaging 2.56 Å. The polyether ring also exhibits a pronounced folding to optimize encapsulation of the hydronium ion. The hydronium hydrogen atoms have been unequivocally observed, indicating near ideal pyramidal geometry, due to the absence of hydrogen-bonding disorders previously observed in other [H<sub>3</sub>O<sup>+</sup>·18-crown-6]<sup>+</sup> structure analyses. Intense luminescence is concurrently observed with complexation of the hydronium ion within the polyether ring. Common oxoacids, such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, and CF<sub>3</sub>SO<sub>3</sub>H, result in luminescent intensities approximately 40 times larger than that of 1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione alone, which also correlates with the pK<sub>a</sub>s of these acids. This capability serves a unique pK<sub>a</sub> regimen as a possible sensor molecule for measuring acidities of potent oxo and superacids.

## Introduction

A recent review has described an abundance of unique luminescent sensor systems.<sup>1</sup> These systems all share in common (A) a high sensitivity in detection and (B) “on-off” switchability of luminescence that is controlled by complexation of a guest molecule. In photoinduced electron transfer (PET), an amine is typically protonated that deactivates internal electron transfer from the amine donor to the aromatic lumophore and “turns on” luminescence.<sup>2a</sup> Other variations of this phenomenon include the synthesis of azocrown ether/lumophore pairs sensitive to cation complexation within the host receptor.<sup>2b</sup> Carbonyls are significantly less basic than amines however (pK<sub>b</sub> for anthraquinone equals 22.4),<sup>3</sup> so protonation would require particularly acidic conditions, unless the host/receptor component is specifically designed to correctly position the acidic guest molecule.

In this paper we describe a luminescent molecular sensor sensitive to HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, and CF<sub>3</sub>SO<sub>3</sub>H, based on 1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione, (**1**). **1** has previously found utility as a redox-switchable crown ether that has a high affinity and selectivity for cations in its electrochemically reduced state, compared to its neutral form.<sup>4,5</sup> We have found that the incorporation of a hydronium ion within the polyether ring, in close proximity to one of the carbonyl oxygens, has a profound effect on the luminescence efficiency of this compound.

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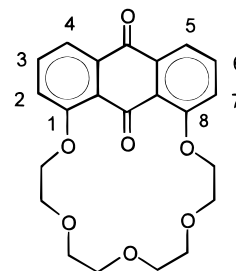
<sup>‡</sup> University of South Dakota.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1997.

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## Experimental Section

Elemental analyses were conducted by MHW Laboratories of Phoenix, AZ. NMR chemical shifts are referenced to the residual proton resonance of the solvent. Titrations to determine acid content were performed with NaOH solutions standardized using potassium hydrogen phthalate. Acetonitrile was CMS Chempure low water grade, used as provided. Fluorescence spectra of solutions were measured at room temperature using a Spex Fluoromax spectrofluorometer. The excitation wavelength for all spectra was 420 nm.

**Preparation of Complexes.** [H<sub>3</sub>O<sup>+</sup>·1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione]ClO<sub>4</sub> (**2**). To 0.208 g of **1**<sup>4</sup> dissolved in 10 mL of acetonitrile is added 3 mL of 60% perchloric acid. The solution is allowed to sit in an ice bath for approximately 20 min. The resulting precipitate is collected on a sintered-glass filter, washed with diethyl ether, and allowed to air dry: yield 0.136 g (50%) of yellow/orange fluorescent solid; mp 145–150 °C; <sup>1</sup>H NMR δ (200 MHz, DMSO-*d*<sub>6</sub>) 7.74 (t, 2 H, J<sub>2(4),3</sub> = 7.7 Hz, 3 and 6-H), 7.67 (dd, 2 H, J<sub>2,3</sub> = 7.6 Hz, J<sub>2,4</sub> = 1.7 Hz, 2 and 7-H), 7.50 (dd, 2 H, J<sub>3,4</sub> = 7.6 Hz, J<sub>2,4</sub>

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**Table 1.** Crystallographic Data for [H<sub>3</sub>O<sup>+</sup>·1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione]ClO<sub>4</sub> (**2**)

chem form	C <sub>22</sub> H <sub>25</sub> ClO <sub>12</sub>	form wt	516.87
<i>a</i> =	11.5996(2) Å	space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>b</i> =	7.0079(2) Å	<i>T</i> =	173(2) K
<i>c</i> =	28.4827(2) Å	<i>λ</i> =	0.71073 Å
<i>β</i> =	96.176(1)	<i>ρ</i> <sub>obs</sub> =	1.498 g cm <sup>-3</sup>
<i>V</i> =	2291.79(9) Å <sup>3</sup>	<i>μ</i> =	0.0233 cm <sup>-1</sup>
<i>Z</i> =	4	<i>R</i> <sub>1</sub> <sup>a</sup> =	0.0517
		<i>R</i> <sub>w</sub> <sup>2 b</sup> =	0.1244

<sup>a</sup> *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|. <sup>b</sup> *R*<sub>w</sub><sup>2</sup> = [Σ[w(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]]<sup>1/2</sup>, where *w* = *q*/σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*aP*)<sup>2</sup> + *bP*.

= 1.7 Hz, 4 and 5-H), 4.73 (s, 3H, H<sub>3</sub>O<sup>+</sup>), 4.22–3.58 (m, 16 H, m, CH<sub>2</sub>S). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>ClO<sub>12</sub>: C, 51.12; H, 4.87; Cl, 6.87. Found: C, 50.08 (50.70); H, 4.95 (4.87); Cl, 5.55 (8.53), values in parentheses represent a second sample.

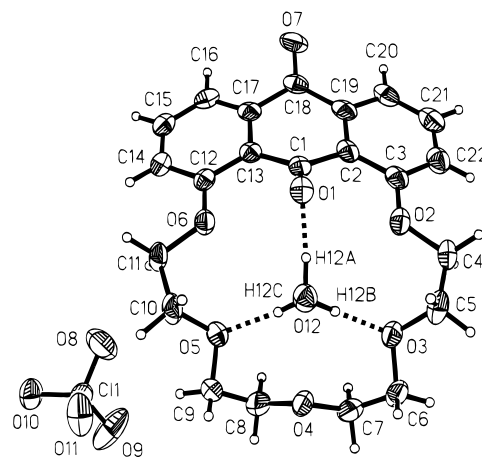
**[H<sub>3</sub>O<sup>+</sup>·1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione][Cl-H-Cl] (**3**).** In a sealed glass jar, 10 mL of a toluene solution of **1** was allowed to sit with 10 mL of concentrated HCl (separate vial). After 2 weeks, the toluene solution was filtered to yield **2**, a yellow solid. Yields were unrecorded: mp 145–150 °C; <sup>1</sup>H NMR δ (200 MHz, CDCl<sub>3</sub>) 7.82 (d, 2 H, *J*<sub>2,3</sub> = 7.6 Hz, 2 and 7-H), 7.61 (t, 2 H, *J*<sub>2(4),3</sub> = 7.8 Hz, 3 and 6-H), 7.24 (d, 2 H, *J*<sub>3,4</sub> = 7.6 Hz, 4 and 5-H), 4.26–3.80 (m, 16 H, CH<sub>2</sub>S), 3.72 (s, 3 H, H<sub>3</sub>O<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 53.99; H, 5.35; Cl, 14.49. Found: C, 55.19; H, 5.33; Cl, 13.01.

**[H<sub>3</sub>O<sup>+</sup>·1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione][BF<sub>4</sub>] (**4**).** **1** (0.105 g) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and 10 mL of 48% HBF<sub>4</sub> are stirred for 15 min. The layers are separated, and the extraction is repeated with another 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic layers are combined, and the solvent is evaporated to dryness. Yield is 0.127 g (95%) of a light yellow solid: mp 150–155 °C; <sup>1</sup>H NMR δ (200 MHz, DMSO-*d*<sub>6</sub>) 7.74 (t, 2 H, *J*<sub>2(4),3</sub> = 7.8 Hz, 3 and 6-H), 7.68 (d, 2 H, *J*<sub>2,3</sub> = 7.6 Hz, 2 and 7-H), 7.51 (d, 2 H, *J*<sub>3,4</sub> = 7.6 Hz, 4 and 5-H), 4.26–3.56 (m, 16 H, CH<sub>2</sub>S), 3.52 (s (broad), H<sub>3</sub>O<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>BF<sub>4</sub>O<sub>8</sub>: C, 52.40; H, 5.00. Found: C, 54.64; H, 4.93.

**X-ray Data Collection, Structure Determination, and Refinement.** A crystal of the compound was attached to a glass fiber and mounted on the Siemens SMART system for data collection at 173(2) K. An initial set of cell constants was calculated from 35 reflections harvested from three sets of 20 frames. Final cell constants were calculated from a set of 4948 strong reflections from the actual data collection. A summary of data collection and refinement information is given in Table 1. The space group *P*2<sub>1</sub>/*n* was determined on the basis of systematic absences and intensity statistics.<sup>6</sup> A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydronium protons were refined as free atoms with relative isotropic displacement parameters. Atomic coordinates for all non-hydrogen atoms are given in the Supporting Information.

## Results

The addition of concentrated perchloric acid to a solution of **1** in acetonitrile yields a fluorescent yellow-orange precipitate of composition [H<sub>3</sub>O<sup>+</sup>·1,8-oxybis(ethyleneoxyethyleneoxy)-



**Figure 1.** Thermal ellipsoid (50%) diagram of [H<sub>3</sub>O<sup>+</sup>·1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione]ClO<sub>4</sub> (**2**). Selected bond distances (Å) and bond angles (deg): C(1)–O(1), 1.235; C(18)–O(7), 1.226; O(1)···O(12), 2.597; O(3)···O(12), 2.547; O(5)···O(12), 2.557; O(2)···O(5), 5.42; O(3)···O(6), 5.44; O(2)···O(6), 4.94; O(3)···O(5), 4.41; H(12a)–O(12)–H(12b), 105.6; H(12a)–O(12)–H(12c), 113.9; H(12b)–O(12)–H(12c), 108.0.

anthracene-9,10-dione]ClO<sub>4</sub> (**2**). Formation of this complex has been confirmed by titration with strong base, NMR spectroscopy, elemental analysis, and X-ray crystallography. Titration of a known amount of solid **2** in water with standardized NaOH reveals that 1.0 ± 5% equiv of acid is present. Additionally, the <sup>1</sup>H NMR spectrum shows the resonance for H<sub>3</sub>O<sup>+</sup> (4.73 ppm) shifted considerably downfield, as compared to the resonance of only wet solvent.

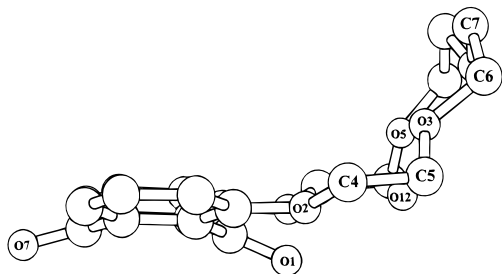
The synthesis of HCl, **3**, and HBF<sub>4</sub>, **4**, adducts are also reported in the Experimental Section. Titration with base confirms that 2 equiv of acid are present in **3**. This adduct is probably similar to the hydrogen dichloride [Cl-H-Cl]<sup>-</sup> salts of [H<sub>3</sub>O<sup>+</sup>·1,8-crown-6]<sup>+</sup> previously reported;<sup>7</sup> although the method of synthesis is quite different here. Melting points for all of the mineral acid adducts formed with **1** are not particularly informative, since all the adducts lose water and acid between 100 and 110 °C and then melt slightly lower than the reported value of **1** (155–156 °C).<sup>4</sup>

**2** was redissolved in acetonitrile, and X-ray quality crystals were grown by slow evaporation of solvent. The asymmetric unit in this structure contains a perchlorate anion and the anthraquinone-containing crown ether that encapsulates a single hydronium ion: [H<sub>3</sub>O<sup>+</sup>·1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione]ClO<sub>4</sub>. The crown ether has approximate C<sub>s</sub> symmetry as shown in Figures 1 and 2. The O–C–C–O torsion angles in the polyether ring alternate ±*g* (except for the aryl carbons which are synclinal); however not all of the bond torsions in the polyether chain adopt idealized conformations (~70° for *gauche* O–C–C–O and ~180° for *anti* C–O–C–C). The torsion angles for C(4)–C(5)–O(3)–C(6) and C(9)–O(5)–C(10)–C(11) are 139.3 and –127.7°, respectively, which is approaching the lower limit of what is considered *anti* (120–180°).<sup>8</sup> Likewise O(2)–C(4)–C(5)–O(3) and O(5)–C(10)–C(11)–O(6) of 60.9 and –60.31° are small for usual *gauche* conformations. The combined effect of these small torsion angles is the formation of two pseudocorners within the polyether chain that folds the ring considerably above the plane of the anthraquinone (Figure 2). This folding has the striking

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(8) Dale, J. *Israel J. Chem.* **1980**, *20*, 3.

(6) SHELXTL-Plus V5.0, Siemens Industrial Automation, Inc., Madison, WI.

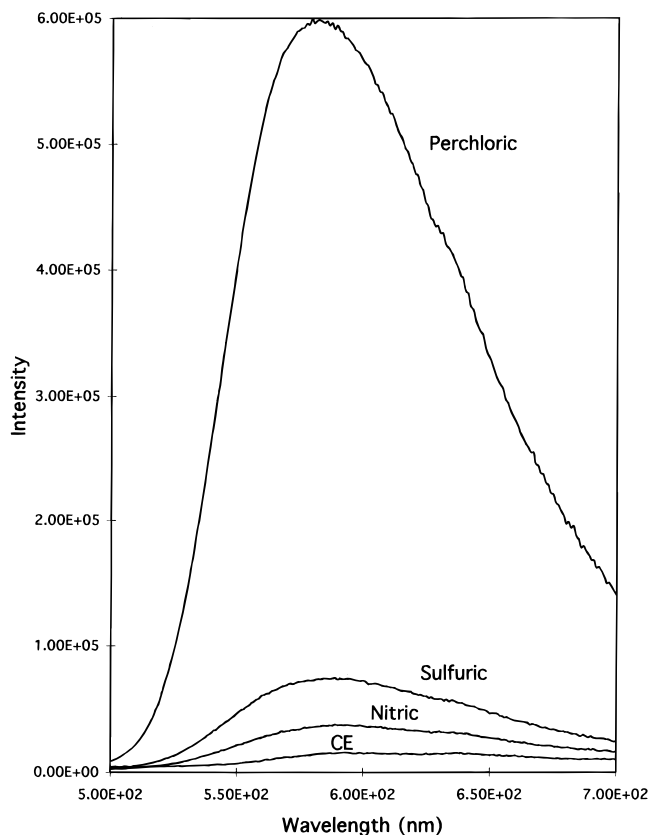


**Figure 2.** Side-view ball-and-stick diagram of **2** showing the pseudocorners in the polyether ring. The perchlorate ion, the hydronium ion, and hydrogen atoms have been omitted.

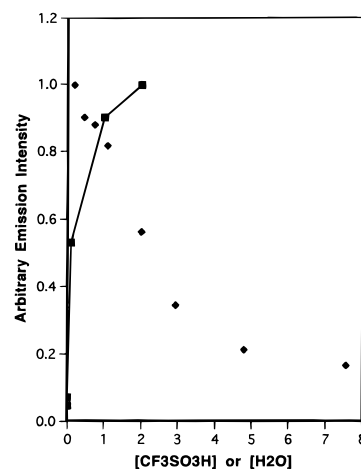
effect of bringing the polyether oxygens much closer together. O(2)⋯O(5) and O(3)⋯O(6) distances of 5.42 and 5.44 Å are approximately 0.4–0.6 Å shorter than those found in other 18-crown-6 structures previously determined.<sup>7,9</sup> Within the macrocycle, bond distances and bond angles average O–C(alkyl) = 1.44 Å, O–C(aryl) = 1.36 Å, C(alkyl)–C(alkyl) = 1.50 Å, C(alkyl)–O–C(alkyl) = 112.4°, C(alkyl)–O–C(aryl) = 118.1°, O–C(alkyl)–C(alkyl) = 107.5°, and O–C(aryl)–C(aryl) = 117.9°, typical for other 18-crown-6 type structures. Additionally, in the structure of **2**, the anthraquinone is not planar. The two phenyl rings in the anthraquinone form a “v” intersecting at C(1) and C(18) forming a dihedral angle of 3.1°. O(1) and O(7) are also bent considerably out of the anthraquinone plane (Figure 2).

Unlike 18-crown-6, itself, not all of the ether oxygens in **2** are available to participate in hydrogen bonding to a centered hydronium guest molecule, due to the extension of one of the anthraquinone carbonyl oxygens into the polyether ring. In this case, the hydronium ion hydrogen bonds to only three oxygens, O(1) (the carbonyl oxygen), O(3), and O(5), which has not been previously observed. The hydronium ion has almost perfect pyramidal geometry as defined by the H–O–H bond angles (H(12a)–O(12)–H(12b) = 105.6°, H(12a)–O(12)–H(12c) = 113.9°, H(12b)–O(12)–H(12c) = 108.0°) and O(12) lies 0.30 Å above the H(12A)–H(12B)–H(12C) plane. Additionally, O(12), the hydronium oxygen, lies 0.74 Å below the plane containing the three oxygens involved in hydrogen bonding (O(1), O(3), and O(5)), indicating, again, that the hydronium ion is not planar. Oxygen–oxygen separations for O(1)⋯O(12), O(3)⋯O(12) and O(5)⋯O(12) are 2.597, 2.547, and 2.557(6) Å, respectively, indicating that particularly strong hydrogen bonding occurs between the hydronium ion and the crown ether. Hydronium–ether contacts in other 18-crown-6 structures range from 2.7 to 2.85 Å.<sup>7</sup> The carbonyl that participates in hydrogen bonding within the ring also shows a slight lengthening of the C–O bond (C(1)–O(1) = 1.235(3) Å), compared to the carbonyl external to the ring (C(18)–O(7) = 1.226(3) Å). The perchlorate anion is symmetric and [H<sub>3</sub>O·1,8-oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione]<sup>+</sup> units lie at van der Waals contacts, only, within the crystal.

Most intriguing is the addition of mineral acids to dilute solutions of **1** that cause strong luminescence to occur. Under similar conditions, **1** in the presence of HClO<sub>4</sub> has an emission



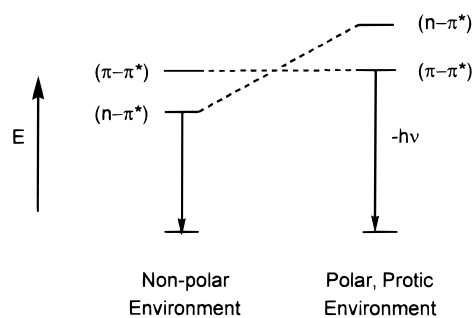
**Figure 3.** Corrected emission spectra of  $6.7 \times 10^{-5}$  M **1** (CE) in the presence of 1.0 M mineral acids. Water concentration is a constant 3.7 M.



**Figure 4.** (Connected squares) Dependence of emission intensity on increasing CF<sub>3</sub>SO<sub>3</sub>H concentration, CE =  $1 \times 10^{-5}$  M, H<sub>2</sub>O = 0.6 M. (Unconnected diamonds) Dependence of emission intensity on increasing water concentration, CE =  $1 \times 10^{-4}$  M, CF<sub>3</sub>SO<sub>3</sub>H = 1.0 M.

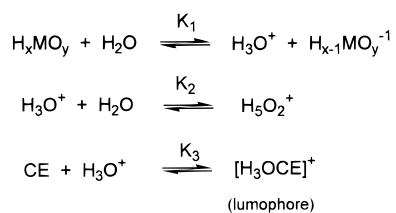
intensity approximately 40 times stronger than that of the crown ether alone (Figure 3). Emission bands are broad, and the maxima vary only 10 nm between solutions of **1** and those that contain mineral acids. All absorption, excitation, and emission spectra remain essentially unchanged as compared to that of **1**, except for increases in the intensity of excitation and emission, which is dependent on the type of acid added, the concentration of the acid, and the amount of water present. Figure 4 shows the corresponding increase in emission intensity with increasing acid concentration and also decreasing emission intensity with increasing amounts of water added. Trifluoromethanesulfonic acid (98%) was used in these determinations because of its superacidic character and low water content. The beginning of

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**Figure 5.** Inversion of  $n-\pi^*$  and  $\pi-\pi^*$  states depending upon hydrogen-bonding environment.

### Scheme 1



an inner filter effect can be seen at high concentrations of added  $\text{CF}_3\text{SO}_3\text{H}$ . Absorption spectra after addition of  $\text{HClO}_4$  are essentially identical to that of **1** and only exhibited a slight red shift. Addition of the same acids to either anthraquinone or 1,5-diethoxyanthraquinone in acetonitrile did not produce any emission.

### Discussion

For the same concentrations of acid and water (Figure 3), luminescent intensities increase in the order  $\text{HNO}_3 < \text{H}_2\text{SO}_4 \ll \text{HClO}_4$ , which closely parallels the  $\text{p}K_{\text{a}}$ s of these acids ( $\text{HNO}_3 = -1.6$ ,  $\text{H}_2\text{SO}_4 = -3$ , and  $\text{HClO}_4 = -8$ ).<sup>10</sup> Additionally, the higher the acid concentration or the lower the water concentration (Figure 4), the greater the luminescent intensity becomes. Scheme 1 qualitatively describes the complexation of  $\text{H}_3\text{O}^+$  and the conditions that favor production of the lumophore based on the observations above.

$K_1$  is dependent on the specific strength of the acid's conjugate base, perchlorate being the weakest and nitrate the strongest, which controls the formation of hydronium ion which can be complexed by **1** (CE) in the third equilibrium step. Increasing the amount of water promotes formation of higher order hydronium ions which lowers the emission intensity since less  $\text{H}_3\text{O}^+$  can be complexed by **1**. Luminescence is best observed at high concentrations of the strongest acid with minimal water present.

Luminescence is almost certainly caused by the hydronium ion hydrogen bonded to the carbonyl oxygen lone electron pairs within the ring. The lowest energy  $n-\pi^*$  transition in the anthraquinone is raised in energy upon protonation, and is replaced by the strongly emissive  $\pi-\pi^*$  state (Figure 5). Luminescence is only observed when oxoacids are added to solutions of **1** however. The addition of  $\text{HCl}$ ,  $\text{HBr}$ , or  $\text{HI}$  does not produce the same yellow-orange emission, characteristic of the oxoacids. Halogen anions have been shown to be good

quenchers of fluorescent organic cations.<sup>1</sup> The relative emission intensities of **1** in the presence of different oxoacids may, to some degree, also be a function of the quenching ability of the different anions and water. Powder samples of **2**, however, do possess an identical emission band compared to acetonitrile solutions of **1** +  $\text{HClO}_4$ , providing evidence that the crystallography accurately describes the active lumophore responsible for the emission.

Previously, we have reported the synthesis and crystallography of the nitric and sulfuric acid adducts formed with **1**.<sup>11</sup> Complexation of a hydronium ion within the polyether ring does not occur with these acids, even though as mineral acids they are traditionally considered quite powerful acids. Instead, nitric and sulfuric acid are found hydrogen bonded to water molecules surrounding the polyether chain. Perchloric acid in acetonitrile has been known to have "superacid" strength,<sup>12</sup> and it appears that this extreme acidity is necessary to form an ionic  $[\text{H}_3\text{O}\cdot\text{CE}]^+$  type material with **1**. In the nitric and sulfuric adducts, also grown by slow evaporation of  $\text{CH}_3\text{CN}$ , the polyether rings extend outward, in the same plane as the anthraquinone. In contrast to this, when the hydronium ion is present, as in **2**, the chain folds considerable out of the plane, which is energetically unfavorable; this allows the hydronium ion to more favorably access the oxygen atoms in the ring with which it participates in hydrogen bonding.

Finally, the X-ray result for this hydronium ion complex is a direct function of the reduced symmetry of the host. Previous structures of hydronium ion complexes using 18-crown-6 exhibit considerable torsional disorder of the encapsulated  $\text{H}_3\text{O}^+$  ion. In the structure presented here, only one conformation is possible, involving hydrogen bonding to O(1), O(3), and O(5). Twisting of the polyether ring out of the plane of the anthraquinone brings O(3) and O(5) much closer together (4.41 Å) and closer to O(12), producing short hydrogen bonds. The alternative,  $\text{H}_3\text{O}^+$  hydrogen bonding to O(2), O(4), and O(6), is not possible since O(2) and O(6) are firmly fixed at  $\sim 4.94$  Å apart by the anthraquinone. By fortuitous design it appears, hydrogen bonding in this complex includes the carbonyl oxygen, less basic than the other oxygens in the ring but vital for the observed luminescence.

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**Supporting Information Available:** Tables of crystal, collection, and refinement data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for  $\text{C}_{22}\text{H}_{25}\text{ClO}_{12}$  (13 pages). See any current masthead page for ordering and Internet access instructions. This material has also been deposited in CIF format with the ACS.

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