Luminescence and Structural Comparisons of Strong-Acid Sensor Molecules. 2

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Anthraquinone-containing cyclic polyether hosts form 1:1 complexes with hydronium ion, producing large enhancements in luminescence via inversion of nπ* and $\pi\pi$* exited states. We have characterized the binding of hydronium ion within these host molecules and have synthesized a large variety of analogous hosts that contain different structural and electronic features that allow better understanding of what controls binding and luminescence capacity in this class of fluorescent sensor molecules. X-ray crystallography of an anthraquinone host that contains terminal amine functional groups rather than terminal ether groups is investigated, and complete proton transfer to carbonyl groups is observed in concentrated sulfuric acid media that also produces a previously unobserved luminescence.

Introduction

There are numerous classes of fluorescent sensors in the burgeoning field of molecular recognition.[1] One of these classes includes host molecules that contain a low-lying nπ* state that are typically nonemissive in solution. When a binding event occurs with the nonbonding electron pair(s) of the host, the nπ* state is destabilized with respect to the $\pi\pi$* state, which now becomes the lowest energy excited state and emission is switched “on” in the system. Inversion of nπ*−$\pi\pi$* states has been employed using azoaromatic molecules containing nitrogen lone pairs that bind Lewis acids (typically alkali metal cations),[2] and inversion has also been previously observed for pyrene-1-carboxaldehyde, which is nonemissive in aprotic solvents but becomes luminescent in methanol.[3] Here, hydrogen bonding by the protic solvent to the carbonyl lone pair(s) is sufficient to invert excited states and produce emission. However, to our knowledge, the design of fluorescent sensors employing inversion of nπ* and $\pi\pi$* exited states initiated through hydrogen bonding has not been previously investigated. Numerous cyclic polyether compounds have been made that complex hydronium ion, but none are luminescent in solution.[4]

As we have reported earlier, X-ray crystallography has shown that hydronium ion has a high affinity for the anthraquinone-containing polyether compound, **1**, and forms three strong hydrogen bonds to two polyether oxygens and the intraannular carbonyl group (binding sites are indicated by a dashed line in **1**).[5] The hydrogen bond to the anthraquinone lumophore results in nπ*−$\pi\pi$* inversion, producing a significant increase in luminescence. Other oxoacids, under identical conditions, produce different emission intensities, allowing the possibility of developing an anion sensor based in strong acid media.

In this paper, we further characterize the binding of hydronium ion with **1**, and we have synthesized numerous host analogues containing different structural and electronic features that allow better understanding of what controls binding and luminescence ability in this class of fluorescent sensor molecules. In the past, **1** has also been utilized as an alkali metal cation sensor, where the electrochemical reduction of the quinone is dependent on the different cation binding affinities of the host.[6] The identical cyclic polyether/intraannular motif of **1** is found in similarly substituted xanthones, which have also been used as cation sensors.[7]

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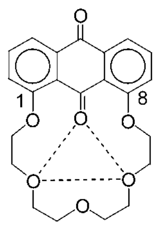

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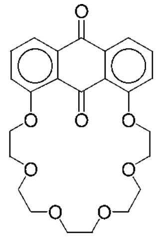

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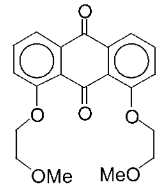

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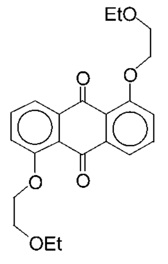

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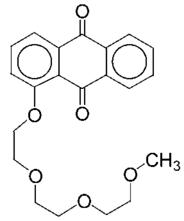

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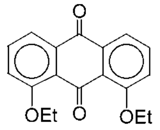

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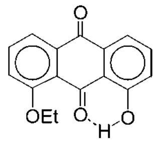

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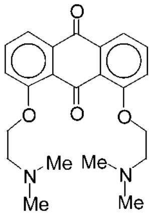

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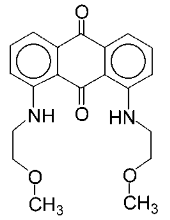

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Experimental Section

The solvents used in the syntheses were standard reagent grade. The compounds were purchased from commercial suppliers.

Preparation of Complexes. 1,8-Oxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione (1). Synthesized according to ref 6a: mp = 153−156 °C (lit.[6a] mp 155−156 °C).

[1·H_3O]ClO_4 (2). Synthesized according to ref 5.

1,8-Oxyethyleneoxybis(ethyleneoxyethyleneoxy)anthracene-9,10-dione (3). Synthesized according to ref 8: mp = 119−120 °C (lit.[8b] mp 116−117 °C); ^{1}H NMR δ 7.81 (2 H, d, 4 and 5-H) 7.58 (2 H, t, 3 and 6-H), 7.24 (2 H, d, 2 and 7-H), 4.23−3.70 (20 H, four multiplets and one singlet, −OCH_2). Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 65.13; H, 6.13.

1,8-Bis(2-methoxyethoxy)anthracene-9,10-dione (4). A mixture of 4.16 g (15.0 mmol) of 1,8-dichloroanthraquinone, 2.16 g (30.0 mmol) 2-methoxyethanol, and 60 mL of THF was slowly added to a warm solution of 1.8 g of NaH and 20 mL of THF under nitrogen and refluxed for 3.5 h. Column chromatography with alumina (CH_2Cl_2−2% methanol) yielded 0.636 g (12%) of a light yellow solid. Recrystallized from absolute ethanol: mp = 123−125 °C; ^{1}H NMR 7.81 (2 H, d, 4 and 5-H), 7.58 (2 H, t, 3 and 6-H), 7.30 (2 H, d, 2 and 7-H), 4.24 (4 H, t, aryl-OCH_2), 3.86 (4 H, t, MeOCH_2) 3.50 (6 H, s, −OCH_3); GC−MS *m/e* calcd 356.4, found 356. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.65. Found: C, 67.61; H, 5.80.

1,5-Bis(2-ethoxyethoxy)anthracene-9,10-dione (5). The synthesis is the same as **4**. The reactants used were 1,5-dichloroanthraquinone and 2-ethoxyethanol: mp 129−132 °C (lit.[9a] mp 129−132 °C, lit.[9b] 132 °C); ^{1}H NMR 7.88 (2 H, d, 4 and 8-H), 7.63 (2 H, 3 and 7-H), 7.29 (2 H, d, 2 and 6-H), 4.29 (4 H, t, aryl-OCH_2), 3.92 (4 H, t, EtOCH_2), 3.68 (4 H, q, −OCH_2-CH_3), 1.22 (6 H, t, −CH_3); GC−MS *m/e* calcd 384.4, found 384. Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.78; H, 6.15.

1-(2-(2-Methoxyethoxy)ethoxy)anthracene-9,10-dione (6). Synthesized according to ref 6e: mp 50−52 °C (lit.[6e] mp 55−57 °C); ^{1}H NMR 8.21 (2 H, m, 5, and 8-H), 7.94 (1 H, d, 4-H), 7.71 (2 H, m, 6 and 7-H), 7.62 (1 H, t, 3-H), 7.35 (1 H, d, 2-H), 4.30−3.50 (12 H, six multiplets, −OCH_2), 3.33 (3 H, s, −OCH_3); GC−MS *m/e* calcd 370.4, found 370. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 67.90; H, 6.02.

1,8-Diethoxyanthracene-9,10-dione (7). Synthesized following ref 10b. The product was recrystallized from acetic acid: mp 166−169 °C (lit.[10a] mp 170 °C, lit.[10b] mp 173 °C); ^{1}H NMR 7.79 (2H, d, 4 and 5-H), 7.56 (2H, t, 3 and 6-H), 7.25 (2H, d, 2 and 7-H), 4.22 (4H, q, −OCH_2), 1.55 (6H, t, −CH_3); GC−MS *m/e* calcd 296.3, found 297. Anal. Calcd for $C_{18}H_{16}O_4$. C, 72.96; H, 5.44. Found: C, 72.93; H, 5.65.

1-Ethoxy-8-hydroxyanthracene-9,10-dione (8). Samples of **7** were eluted down a silica gel column using dichloromethane, and a quantitative amount of product was collected, dried, and recrystallized from ethanol: mp 179−180 (mp lit.[10] 176 °C); ^{1}H NMR δ 8.54 (1 H, s,-OH), 7.88 (1 H, d, 4-H), 7.70 (1 H, d, 5-H), 7.65 (1 H, t, 6-H), 7.55 (1 H, t, 3-H), 7.27 (1 H, d, 2-H), 7.23 (1 H, d, 7-H), 4.22 (2 H, q, −OCH_2-), 1.54 (3 H, t, −CH_3); GC−MS *m/e* calcd 268.3, found 268. Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C,72.40; H, 4.87.

1,8-Bis(2-(*N*,*N*-dimethylamino)ethoxy)anthracene-9,-10-dione·2$HClO_4$ (9). A warm solution of *N*,*N*-dimethylethanolamine (5.35 g, 60 mmol) and 1,8-dichloroanthraquinone (4.16 g, 15 mmol) in 75 mL of THF was slowly added to a refluxing mixture of NaH (3.6 g, 75 mmol, 50% oil) in 45 mL of THF. After being refluxed for 5.5 h, the solution was cooled, the solvent evaporated, 100 mL of water added, and the solution extracted with 100 mL of CH_2Cl_2. The extract was washed with brine and the solvent evaporated. The product was added to 50 mL of 1 M HCl, filtered, and neutralized with NaOH. The slightly basic solution was extracted with CH_2Cl_2 (2 × 25 mL), and column chromatography (alumina, CH_2Cl_2−acetone) yielded 0.3 g (~5%) of a yellow-brown solid: mp = 257−260 °C dec; ^{1}H NMR δ 7.79 (2 H, d, 4 and 5-H), 7.59 (2 H, t, 3 and 6-H), 7.23 (2 H, d, 2 and 7-H), 4.20 (4 H, t, −OCH_2), 2.87 (4 H, t, −NCH_2), 2.40 (12 H, s, −CH_3). Crystals for X-ray analysis were grown from $HClO_4$/CH_3CN/Ether. The sample submitted for elemental analyses had been air-dried and does not include solvent molecules found in the X-ray structure. Anal. Calcd for [(**9**)H_2]$(ClO_4)_2$ ($C_{22}H_{28}Cl_2N_2O_{12}$): C, 45.30; H, 4.84; N, 4.80. Found: C, 45.00; H, 4.77; N, 4.67.

1,8-Bis((2-methoxyethyl)amino)anthracene-9,10-dione (10). A 1.0 g sample of 1,8-dichloroanthraquinone, 10 mL of 2-methoxyethylamine, and 20 mL of pyridine were heated at 100 °C for 6 h. The cooled solution was combined in a large amount of water and the precipitate collected and dried. Column chromatography (silica/CH_2Cl_2−acetone) yields 0.34 g (27%) of a crystalline purple solid: mp = 202−204 °C; ^{1}H NMR δ 9.75 (2 H, t, NH), 7.53 (2 H, d, 4 and 5-H), 7.46 (2 H, t, 3 and 6-H), 7.02 (2 H, d, 2 and 7-H), 3.70 (4 H, t, −OCH_2), 3.51 (4 H, q, −NCH_2), 3.45 (6 H, s, −OCH_3). Anal. Calcd for $C_{20}H_{22}N_2O_4$. C, 67.78; H, 6.25; N, 7.90. Found: C, 68.00; H, 6.40; N, 8.03.

Spectroscopic Binding Constant Measurements. $HClO_4$, H_2SO_4, and HNO_3 stock solutions, each with different

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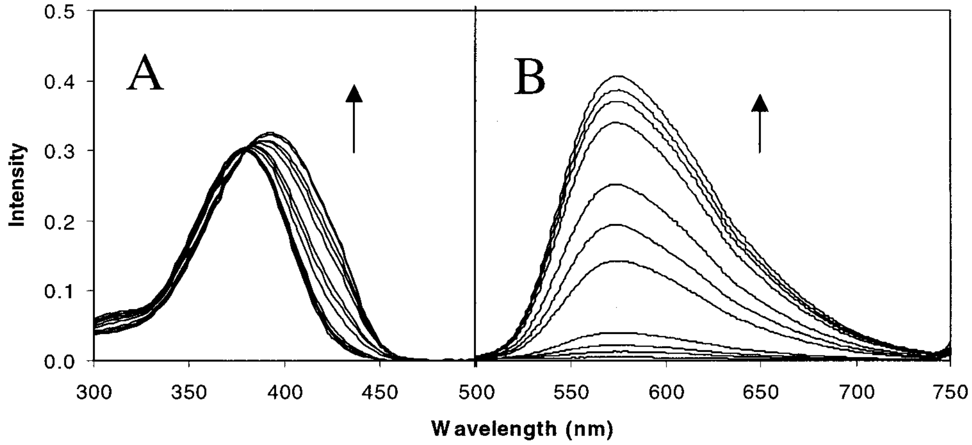

Figure 1. (A) UV−vis titration of **1** (5.0×10^{-5} M) with perchloric acid. (B) Fluorescence titration under identical conditions. $[HClO_4]$ ($\times 10^5$) = 0, 2.5, 5.0. 10.0, 30.0, 60.0, 110, 310, 610, 1110 M.

initial acid concentrations (0.010, 0.10, and 1.0 M) were prepared in acetonitrile, using aqueous 60% $HClO_4$, 96% H_2SO_4, and 70% HNO_3. Water was added to the H_2SO_4 and HNO_3 stock solutions to keep the concentration of water equal when comparing titrations of different acids. To a glass cuvette were combined 3.0 mL of acetonitrile and 15 μL of 0.01 M polyether compound, and the UV−vis or fluorescence spectrum recorded. Aliquots of the appropriate acid were then added according to the amount shown given in Table S1 (Supporting Information), and the spectroscopic measurements were repeated. The total concentration of **1** in the cuvette was 5.0×10^{-5} M, and the minor volume change associated with added acid (4%) during the titration was ignored.

Quantum Yields. Emission quantum yields were determined according to ref 11, using the following equation:

$$\Phi_{\text{test}} = \frac{\Phi_{\text{ref}} A_{\text{test}} (1 - 10^{-\epsilon \text{cl}}{}_{\text{ref}}) n^2{}_{\text{test}}}{A_{\text{ref}} (1 - 10^{-\epsilon \text{cl}}{}_{\text{test}}) n^2{}_{\text{ref}}}$$

In this equation, Φ is the quantum yield, A is the area of the emission spectrum, and ($-\epsilon$cl) is the absorbance of the solutions at 420 nm. The emission spectra were obtained in signal/reference (s/r) mode. The value of n^2, the refractive index, drops out of the equation because the same solvent was used for both the test and reference compounds. The tested compounds (6.7×10^{-5} M) in the presence of 1.0 M $HClO_4$ and the reference compound, $Ru(bipy)_3{}^{2+}$ (1×10^{-5} M), were run in acetonitrile. The quantum yield for $Ru(bipy)_3{}^{2+}$ in acetonitrile has been previously given as 0.061.[12] There was no difference in quantum yield between degassed and nondegassed solutions of **1**. Only the reference compound was degassed with high purity argon before examination, all other solutions were not degassed. Anhydrous acetonitrile was used; however addition of aqueous mineral acids involves adding water. In order that a valid comparison can be made between the different acids, water was added, if necessary, so that a constant 3.7 M H_2O concentration was achieved. 3.7 M was used because this much water is introduced when using 60% $HClO_4$.

X-ray Data Collection, Structure Determination, and Refinement. Crystals of **9** were grown by slow evaporation of the compound in acetonitrile after adding 2−3 drops of concentrated perchloric acid. The crystals were attached to a glass fiber and mounted on the Siemens SMART system for data collection at 173(2) K. A summary of data collection and refinement information is given in ref 13 and the Supporting Information (Table S2). The structure was solved and refined using SHELXS-86 and SHELX-97.[14]

The space group $P2_1/n$ was determined based on systematic absences and intensity statistics. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, except the hydrogen atoms connected to the nitrogens, which were found from the final electron difference map.

The perchlorate counterions were refined with rigid-body restraints; DELU instructions were used to restrain the displacement parameters along the bond to be equal. Additionally, the SAME instruction was used in order to restrain bond lengths in the disordered perchlorates to be similar to those that were not disordered. The compound was found to be a racemic twin in 72:28 enantiomorphic ratio. Final cell constants were calculated from a set of 3742 strong reflections from the actual data collection after integration.[15]

Results and Discussion

Binding Constant Determinations. Figure 1 illustrates the changes that occur when **1** is titrated with dilute perchloric acid in acetonitrile. The UV−vis spectra in Figure 1A show the conversion of **1** into the hydronium ion adduct, **2**, and the band at 375 nm shifts ~25 nm to higher wavelength, with a clean isosbestic point present at 384 nm. Figure 1B shows the concomitant increase in fluorescence intensity under conditions identical to 1A. Nonluminescent solutions of **1** become brightly emissive (yellow-orange in color) after addition of acid.

A plot of total acid concentration vs absorbance/fluorescence intensity is given in Figure 2 for perchloric acid (circles), sulfuric acid (diamonds), and nitric acid (squares).

Sulfuric and particularly nitric acid do not produce as large a change in absorbance or fluorescence intensity as does perchloric acid, which we attribute to weaker binding of hydronium ion with **1**, due to competitive binding of H_3O^+ with stronger conjugate bases ($NO_3^- > HSO_3^- > ClO_4^-$).

Table 1 provides binding constants for the best fit in each case, based on the equilibrium expression in eq 1,

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[13] Crystallographic data for $2([\mathbf{9}H_2](ClO_4)_2)\cdot CH_3CN\cdot H_2O$: MW = 1225.8; monoclinic; space group, $P2(1)$; $a = 16.434(3)$ Å, $b = 7.015(1)$ Å, = 24.463(4) Å, $\beta = 106.729(3)°$; $V = 2700.9(7)$ Å^3; $Z = 2$; density (calcd) = 1.52 g cm^{-3}; Mo Kα radiation, $\lambda = 0.710\ 73$; Siemens CCD area detector diffractometer; R1 = 0.0540, wR2 = 0.1194. Additional crystallographic data is also provided in the Supporting Information (Table S2).

[14] SHELXTL-Plus V5.1, Siemens Industrial Automation, Inc., Madison, WI.

[15] SAINT 6.0, Bruker, 1999.

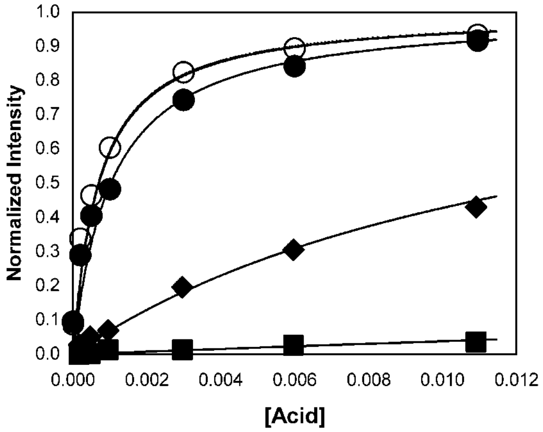

Figure 2. Normalized binding constant study. Fluorescence titration using $HClO_4$ = ○; UV−vis titration using $HClO_4$ = ●, UV−vis titration using H_2SO_4 = ◆; UV−vis titration using HNO_3 = ■.

Table 1. Binding Constants and Quantum Yields of Anthraquinone-Containing Polyether Compounds in Acetonitrile

compd	acid	Φ without acid	Φ with acid	emission λ_{max}	binding constant method	p*K*
1	$HClO_4$	0.0006	0.0145	574	UV−vis	3.0
					fluorescence	3.1
	H_2SO_4	0.0006	0.0073	575	UV−vis	1.9
	HNO_3	0.0006	0.0012	571	UV−vis	0.6
3	$HClO_4$	0.0019	0.0130	574	fluorescence	4.0
4	$HClO_4$	0.0015	0.0130	576	UV−vis	1.4
					fluorescence	1.7
5	$HClO_4$	0.0012	0.0004	580		
6	$HClO_4$	0.0023	0.0034	568	UV−vis	2.1
					fluorescence	2.3
7	$HClO_4$	0.0050[a]	0.0098	581	fluorescence	0.8
8	$HClO_4$	0.0073[b]	0.0062	595		
9	$HClO_4$	0.0024	0.0030	571		

[a] Emission peak maximum = 593 nm. [b] Emission peak maximum = 592 nm.

where CE represents the unbound macrocycle.

$$CE + H_3O^+ ... A^- \rightleftarrows [CEH_3O^+] ... A^- \qquad (1)$$

A 10-fold difference in binding affinity is observed between perchloric acid and sulfuric acid, and again between sulfuric acid and nitric acid. The degree of hydronium ion complexation using $HClO_4$ is 3 orders of magnitude smaller than that previously found with 18-crown-6 in acetonitrile, but comparable with hydronium formation with dibenzo-18-crown-6.[16] Quantum yields of **1** (Table 1) in the presence of different acids also parallel the same trend found for binding constants.

Supporting the disparate binding abilities of hydronium ion produced by different oxoacids are NMR titrations using perchloric and nitric acids. In the presence of perchloric acid, a greater shift in proton resonances of $-OCH_2$ groups adjacent to the ether oxygen/hydronium ion binding site is observed (Figure 3). This contrasts greatly with nitric acid where virtually no change in chemical shift is observed.

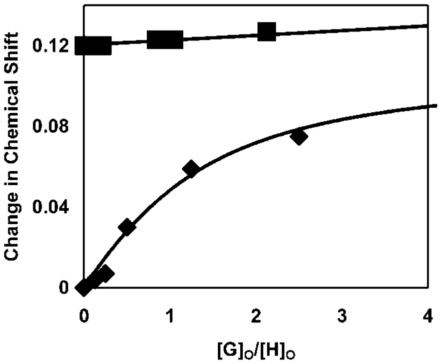

Figure 3. NMR titration of 0.04 M **1** using $HClO_4$ (◆) and HNO_3 (■). $[G]_o$ and $[H]_o$ are initial guest (acid) and host (**1**) concentrations, respectively. Average chemical shifts (ppm) are measured for the methylene protons attached to the third carbon removed from the aromatic ether oxygens. The HNO_3 data has been vertically offset on the *y*-axis by 0.12 ppm for clarity.

Previous X-ray crystal structures of **1** in the presence of perchloric acid[5] and nitric acid,[17] supply additional evidence that the degree of formation of a hydronium ion adduct is strongly dependent upon the counterion. At high perchloric acid concentrations in acetonitrile, a precipitate results that, when recrystallized, reveals H_3O^+ encapsulated within the polyether cavity. However, by slow evaporation of a nitric acid/acetonitrile solution, HNO_3 is only found hydrogen-bonded to water molecules surrounding the polyether ring.

All the above data suggest that perchloric acid in acetonitrile has traditional "superacid" character,[18] directly observable in the spectroscopic and structural characterizations of these compounds. The ratios of binding constants for different acids in this system provide some measure of counterion strength in acetonitrile. Whereas strong mineral acids are traditionally leveled in aqueous solution, this system is able to differentiate acidities of strong oxoacids in acetonitrile. Contributions from dynamic quenching by the anion can also be ruled out as the binding constant for **1**, determined by fluorescence spectroscopy (Figure 2, open circles, p*K* = 3.1), is of the same magnitude as the binding constant determined by the ground-state absorption data (p*K* = 3.0, closed circles). This is also observed for compounds **4** and **6**.

Binding constants have also been determined for compounds **3**, **4**, **6**, and **7**. Most notably, **3** has a greater affinity for hydronium ion than does **1**. The larger cyclic polyether in **3** produces less ring strain upon coordination of H_3O^+ within the macrocycle. Compound **4**, the open-chain analogue, has a smaller affinity for hydronium ion, however. This is attributed to the macrocyclic effect relating smaller entropy changes with larger binding constants for guest/host associations of preorganized cyclic structures. Compound **6**, containing a single long-chain polyether, also has a smaller binding constant than the cyclic structures but is larger than **4**. We have also observed that an extended polyether chain(s) containing

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dialkyl ether oxygens is not structurally necessary to cause inversion of nπ^* and $\pi\pi^*$ states. Although small, compound **7**, the simple diethoxy derivative, weakly binds H_3O^+, and a new emission band appears with a λ_{max} similar to the other 1,8-disubstituted compounds.

Quantum Yields. Quantum yields for compounds **1**–**9** with added perchloric acid are given in Table 1. No difference in quantum yield was found between degassed and nondegassed solutions of **1**, and all the quantum yields reported are for nondegassed solutions. Quantum yields for 1,8-disubstituted anthraquinones **1**, **3**, and **4** are approximately 10–40 times larger in the presence of perchloric acid than without added acid. The quantum yields are also similar in magnitude, which is consistent with their sizable binding constants and formation of >98% of the hydronium ion lumophore, $[CEH_3O]^+$, under these conditions (eq 1). The quantum yield for **7**, which has the smallest binding constant, is not as large. However, the emission of **7** is complicated by a sizable emission band and quantum yield that is present prior to adding acid. The emission band for **7** with no added acid compares well with the emission of 1-ethoxy-8-hydroxyanthraquinone, **8**. Compound **8** has been isolated in quantitative yield by simple elution of **7** through a silica gel column using dichloromethane. This has previously been observed in the synthesis of 1-(2-ethoxyethoxy)-5-hydroxyanthracene-9,10-dione.[9b] Characterization data for **7**, recrystallized from acetic acid, are consistent with substitution by two ethoxy groups and reported literature values however. Luminescence in this case is either due to a small remaining impurity of **8** or the hydrolysis of an ethoxy group. The addition of $HClO_4$ to **7** does cause an increase in the quantum yield and a new emission band appears at ~580 nm, analogous to addition of acid to **1**, **3**, and **4**.

Compounds **5** and **6** have different substitution motifs. Compound **5**, a 1,5-disubstituted anthraquinone, remains totally nonluminescent after addition of acid, and **6** shows only a moderately small enhancement in luminescence. Both of these systems underscore the importance of electronic contributions to the nπ^*–$\pi\pi^*$ inversion of excited states. Whereas **6** has a greater affinity for hydronium ion than either **4** or **7**, quantum yields are larger for 1,8-disubstituted compounds, indicating that 1,8-dialkoxy substitution is the optimal substitution pattern for the examples we have studied.

Compounds **9** and **10** are structurally similar to **4**; however, nitrogens replace either the aromatic ethers or the terminal ether groups. Compound **9** replaces the two terminal ethers groups with amines. Only a small enhancement in luminescence is observed after addition of acid, and protonation of the amines is discussed later in combination with the crystallographic results. Compound **10** has the same connectivity; however amine nitrogens replace the oxygens substituents in the anthraquinone 1 and 8 positions. This substitution shifts the absorbance of **10** significantly to the red ($\lambda_{max} = 524$ nm), changing the color to purple, instead of the usual yellow color of the aromatic ethers. In the presence of perchloric acid, one nitrogen is protonated (unpublished X-ray crystallographic results), but no emission is observed.

Crystallography. X-ray quality crystals of **9**, in the presence of perchloric acid/acetonitrile were grown by slow evaporation of solvent. The structure of **9** is found as alternating π-stacks of anthraquinone units. Two different anthraquinone units, four perchlorate counterions, one acetonitrile molecule, and one water molecule are present in the asymmetric unit (Figure S1, available as Supporting Information), where both of the amine nitrogens in **9** are protonated (hydrogens on the nitrogens were found in the final electron difference map). The water molecule (O9) associated with only one of the anthraquinone units is hydrogen bonded to one of the protonated amines (N4–H···O9 = 2.788 Å) and is also hydrogen bonded to the carbonyl oxygen (O3) of a neighboring anthraquinone (O9–H···O3 = 2.772 Å). N3, the other amine nitrogen, is rotated away from O9, and is hydrogen bonded to a perchlorate anion. Bond distances O9–N4 (water–amine) and O9–O3 (water–carbonyl oxygen of an adjacent anthraquinone) are normal for hydrogen bonds for neutral water. Since the basicity of alkyl tertiary amines (p$K_a \approx 10$)[19] far exceed the basicity of water or the ether oxygens of the host, it is reasonable that these sites are protonated. Most importantly, although a water molecule participates in hydrogen bonding to a carbonyl oxygen in **9** in the solid-state, the lack of luminescence of this compound indicates that nπ^*–$\pi\pi^*$ inversion has not occurred. Luminescence, it seems, requires formation of a stronger hydrogen bond between hydronium ion and a carbonyl oxygen as observed in our previously published crystal structure of **2**.[5] In the presence of excess acid in solution, the amines are protonated and can no longer provide host binding sites for hydronium ion, resulting in the low quantum yield observed for **9**.

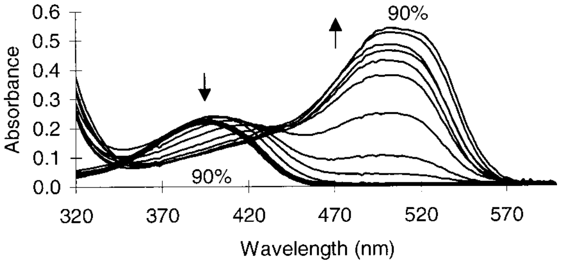

Figure 4. UV–vis titration of **1** in acetonitrile/concentrated sulfuric acid solution. Volume percent sulfuric acid is 10 (dark line), 20, 30, 40, 45, 50, 55, 60, 65, 70, 75, 80, 90%, respectively.

Concentrated Acid Media. Figure 4 shows the changes in the UV–vis spectra of **1** in acetonitrile when the amount of concentrated sulfuric acid is increased. At low sulfuric acid concentrations, only a small shift in the absorbance band is observed, similar to Figure 1A, attributed to the formation of the hydronium ion complex, and a concomitant increase in fluorescence intensity at 570 nm (due to nπ^*–$\pi\pi^*$ inversion) is observed as well (not shown). At approximately 40% sulfuric acid, the solution turns red and a new absorption band at 502 nm begins to appear, which we attribute to the complete transfer of a proton to a carbonyl oxygen on the anthraquinone as the activity of water begins to decrease. A new fluorescence band at 648 nm also begins to grow in at approximately the same acidity (Figure 5). Solutions of **1** in concentrated sulfuric acid are stable indefinitely. There is no isosbestic point in Figure 4 since the reaction proceeds through an intermediate, the hydronium ion/crown ether complex.

The titration was repeated in aqueous/H_2SO_4 mixtures that produced similar spectroscopic changes as the ac-

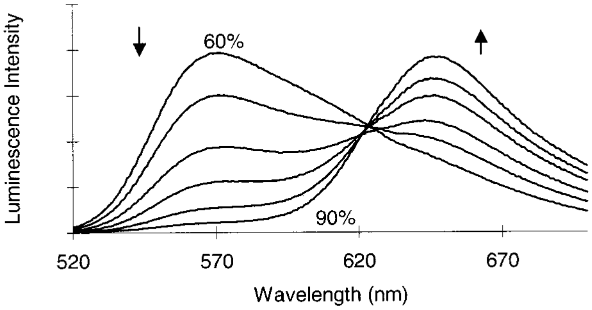

Figure 5. Luminescence changes with addition of concentrated sulfuric acid. Volume percent sulfuric acid is 60, 65, 70, 75, 80, 90%.

etonitrile/H_2SO_4 titrations in Figures 4 and 5. Absorbances at 502 nm were plotted versus acidity function, H_o, based on weight percents of H_2SO_4 in solution (Figure S2, available as Supporting Information).[20] The equivalence point is observed at $H_o = -5.4$ for the H_2SO_4/H_2O titration. Protonation of **1** occurs at significantly lower acidity than for anthraquinone itself ($H_o \cong -8.3$).[21a] As expected, the alkoxy substituents in the 1,8-positions stabilize the protonated form, as previously observed with other hydroxy and methoxy substituted anthraquinone derivatives.[21b,c] **1** is significantly less basic than the similarly substituted xanthones however ($\sim H_o = -2$), where protonation of the xanthone can be stabilized by resonance interactions with the cyclic oxygen para to the carbonyl.[7a]

Conclusion

Ether substituents in both the 1,8 positions of an anthraquinone scaffold provide optimal conditions for luminescence upon hydronium ion complexation. An open, as opposed to closed, polyether ring system is also a suitable host, provided that more basic amine substituents are not present which are preferentially protonated; however the binding constant is significantly smaller. Quantum yields and luminescence intensities with added oxoacids in acetonitrile decrease in the order $HClO_4 > H_2SO_4 > HNO_3$, which parallels their acidities in aqueous solution. Additionally, whereas hydroxyl protons adjacent to the carbonyls (i.e., in 1-ethoxy-8-hydroxyanthracene-9,10-dione) or a complexed hydronium ion are adequate to cause $n\pi^*-\pi\pi^*$ inversion, simple hydrogen bonding to carbonyl oxygens from a water of hydration in the solid state is not sufficient to produce luminescence. Finally, under very strong acid conditions, where the activity of water is low, complete transfer of a proton to the carbonyl is achieved. A new luminescence is observed that does not occur with unsubstituted anthracene-9,10-dione alone.

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Supporting Information Available: Table S1, Volumes/Concentrations Used in Spectroscopic Titrations, and Table S2, Crystal Parameters, Collection and Refinement Data for **9**. Figure S1, Thermal Ellipsoid Diagram of $2[\mathbf{9}H_2](ClO_4)_2 \cdot CH_3CN \cdot H_2O$, and Figure S2, Spectroscopic titration of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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