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Site-Selective Imination of an Anthracenone Sensor: Selective Fluorescence Detection of Barium(II)

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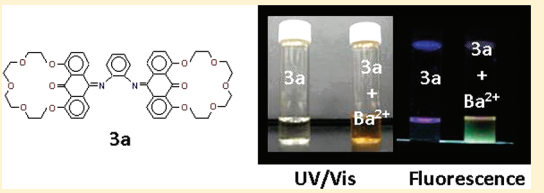
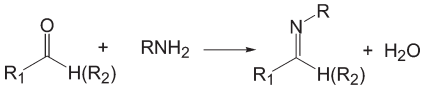
Supporting Information

ABSTRACT: Site-selective imination of anthraquinone-based macrocyclic crown ethers using titanium tetrachloride as the catalyst yields imines where only the external carbonyl group of the anthraquinone forms Schiff-bases. The following aromatic amines yield monomeric compounds (aniline, 4-nitroaniline, 4-pyrrolaniline, and 1,3-phenylenediamine). Reaction of 2 equiv of the macrocyclic anthraquinone host with 1,2- and 1,4-phenylenediamine yields dimeric imine compounds. The 1,2-diimino host acts as a luminescence sensor, exhibiting enhanced selectivity for Ba(II) ion. Spectroscopic data indicate that two barium ions coordinate to the sensor. Due to *E*/*Z* isomerization of the imine, the monomeric complexes are nonluminescent. Restricted rotation about the 1,2 oriented C═N groups or other noncovalent/coordinate-covalent interactions acting between neighboring crown ether rings may inhibit *E*/*Z* isomerization in this example, which is different from current examples that employ coordination of a metal cation with a chelating imine nitrogen atom to suppress *E*/*Z* isomerization and activate luminescence. The 1,4-diimino adduct, where the crown rings remain widely separated, remains nonluminescent.



INTRODUCTION

Since the original discovery of imines by Schiff in the year 1864,[1] imines have been used in a variety of applications such as dyes,[2] catalysts,[2] and macrocycles,[3] and they have served as model compounds that mimic several enzymes and proteins.[4] Imines, also called azomethines or Schiff bases, are typically synthesized starting from primary amines and corresponding aldehydes. Because of their limited reactivity, imines derived from ketones are less common; however, ketones do undergo nucleophilic substitution in the presence of an appropriate catalyst. One system that has recently gained prominence



uses Ti(IV) as the catalyst.[5] Hall et al. has successfully condensed anthraquinones with aromatic amines to make imines and polyimines, using titanium tetrachloride as the catalyst together with DABCO.[5b,6] Recently we have employed this catalyst to react anilines with compound **1** (Scheme 1), which condenses exclusively with the external carbonyl group, even in the presence of excess aromatic amine. The directed synthesis of imines has been limited to simple asymmetric quinones,[7] and has the potential for the selective derivitization of new antistaphylococcal drugs.[8]

Imine-based fluorescence sensors, although only recently employed as a new class of luminescence sensors,[9] are attractive because generally (i) straightforward preparative methods are available, (ii) starting materials are readily available, (iii) selectivity toward metal ions is good,[10−18] and (iv) attractive electronic and photophysical properties result.[19] For this class of sensor, isomerization of the covalently bridged C═N provides an efficient pathway for the nonradiative relaxation of photoexcited states. Coordination of a metal ion to the C═N nitrogen lone pair suppresses C═N isomerization, leading to production of a photodynamic 'ON' state, resulting in enhanced emission.[20]

Here we demonstrate the selective sensing of Ba(II) ion using imine-containing macrocycles, whereas imine-based fluorescence sensors have predominantly been selective for zinc(II) ion in the past. The selective and sensitive detection of barium is important because soluble barium compounds are known to be poisonous and severity is dependent upon the dose of barium. At low doses, barium acts as a muscle stimulant, whereas higher doses affect the nervous system, causing cardiac irregularities, tremors, weakness, anxiety, dyspnea, and paralysis.[21] Studies involving the selective detection of Ba^{2+} have been rarely addressed, however,[22] although the problems related to its toxicity should encourage the development of new detection systems for this analyte. Many of the reported sensors are nonselective in nature,[23] generally containing strong interference from Mg^{2+}, Ca^{2+}, and Sr^{2+} cations within the same alkaline earth family.

In this study, we report the site-selective synthesis of a series of anthraquinone-imine derivatives along with fluorescence screening with common metal cations and associated stoichiometric studies. Compound **1**, without imine formation, and its derivatives have previously demonstrated selective fluorescence with a variety of biological and environmentally important cations.[24]

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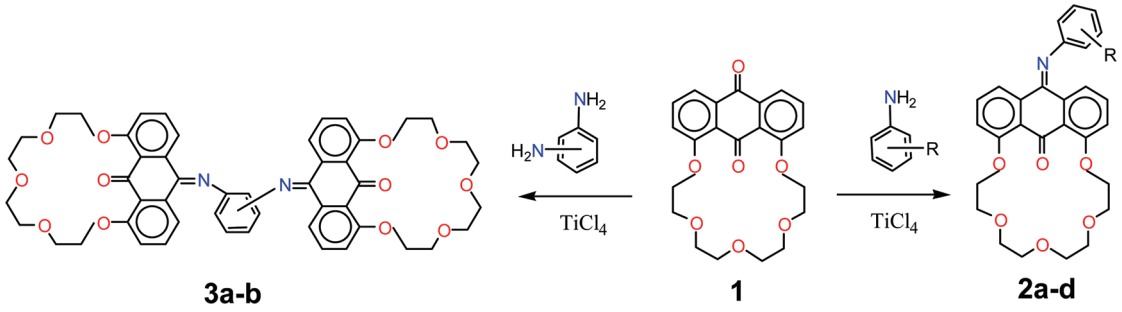
Scheme 1[a]



[a] **2a**, R = H; **2b**, R = 4-NO_2; **2c**, R = 4-(1*H*-pyrrol-1yl); **2d**, R = 3-NH_2; **3a** = 1,2-diimino; **3b**, 1,4-diimino.

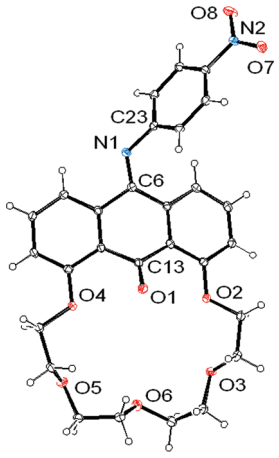


Figure 1. Thermal ellipsoid diagram (30%) for compound **2b**. C(13)−O(1) = 1.215(2) Å; N(2)−O(6) = 1.227(2) Å ; N(2)−O(8) = 1.231(2) Å.

RESULTS

The reaction of 1 equiv of the anthraquinone macrocycle **1** with 1 equiv of $TiCl_4$ and a slight excess of an aromatic aniline (Scheme 1) yields the site-selective synthesis of compounds **2a**−**d** where only the extraannular carbonyl group has been converted to the corresponding imine. The identities of these new imines have all been confirmed by elemental analyses and NMR results. In addition, the X-ray crystal structures of compound **2b** (Figure 1) and **2c** (Figure S1, Supporting Information), the *p*-nitro and pyrrole adducts, confirm that imine formation occurs only at the external carbonyl group. The imine bond for **2b** equals 1.288(2) Å in length, typical of a C═N double bond, and the imine bond angle equals C(6)−N-(1)−C(23) 125.99(15)° where the *p*-nitrophenyl ring is also rotated away from the anthraquinone plane to avoid steric interference from the aromatic hydrogen atom of the anthraquinone. Since two carbonyl groups are available, the production of only one possible imine isomer indicates that the cyclic polyether ring may trap the Lewis acid catalyst adjacent to the intraannular carbonyl, preventing loss of H_2O after nucleophilic attack by the amine nitrogen at the carbonyl carbon. Only two bands, the starting material **1** and the product band, were observed upon purification by column chromatography after each synthesis. The directed synthesis of amines in this system is different than what has previously been observed by Hall et al. for the diimination/polymerization of both carbonyl groups in anthraquinones that do not contain a cyclic polyether.[5,6]

The synthesis of diimines was also achieved by the addition of 1,2- and 1,4-phenylenediamines with **1** (Scheme 1, compounds **3a** and **3b**, respectively). The asymmetry of the anthraquinone aryl protons, integration of aryl vs alkyl proton resonances, elemental analyses data, and the ESI-MS results confirm the formation of dimeric compounds, which also are a darker red-orange in color than the imine monomers (orange) due to increased conjugation. When using only 1 equiv of **1**, reaction with 1,3-phenylenediamine yielded only the resulting monomer, compound **2d**. Reaction of 1,2- and 1,4-phenylenediamine with 1 equiv of **1** only yielded dimeric compounds upon isolation and purification.

Selectivity of these new imines as potential metal ion sensors was examined by adding 10 equiv of metal perchlorate salts to compounds **2a**−**d** and **3a**−**b** in acetonitrile and collecting the resulting emission spectra (Figures S2−S7, Supporting Information). With the exception of **3a**, none of the imines shows selectivity for any of the different metal ions tested. Compound **3a** does show a marked selectivity for the addition of Ba(II) ion, however. Figure S7 also shows that **3a** is mildly selective for other alkaline earth metals, albeit with reduced sensitivity, increasing in emission intensity as descending down the periodic table. A competition study for Ba(II) with the same cations (Figure 2) shows that Ba(II) selectivity has increased 7-fold over the ligand, while Sr(II) increases ∼2.5 fold and Ca(II) increases 1.5 fold in comparison. Luminescence for the most part is maintained for Ba(II) even in the presence of most other metal ions, except for a few paramagnetic transitional metals and Hg and Pb heavy atoms.

The Job's plot using fluorescence data to determine the number of barium(II) ions that associate with **3a** is provided in Figure 3. The apex point of the plot approximates 0.667, which is the ideal mole ratio for a 1:2 ligand:metal complex, i.e., [Ba]/([L] + [Ba]) = 0.667. This supports a 1:2 ligand: metal association reaction, L + 2 M ↔ LM_2 where two Ba(II) ions are involved in production of luminescence.

The titration of compound **3a** with increasing amounts of Ba(II) ion is shown in Figure 4. Ba(II) has been added until the emission intensity saturates, and the insert plots fluorescence intensity versus Ba(II) concentration. The data points (squares) follow a sigmoidal curve rather than the standard saturation behavior that would be expected for a simple 1:1 ligand: metal association reaction (dotted line in the insert). Higher order

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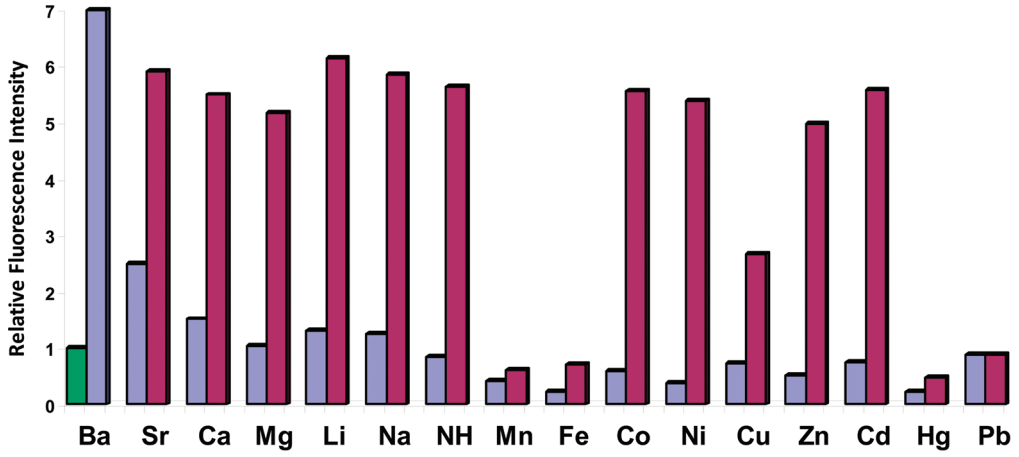

Figure 2. Selectivity—competition study of compound **3a** with added M(II) perchlorate salts. 4.0×10^{-5} M = [**3a**]; [M(II)] = 4.0×10^{-4} M. λ_{ex} = 356 nm. Green = **3a**; blue = **3a** + M(II); red = **3a** + M(II) + Ba(II).

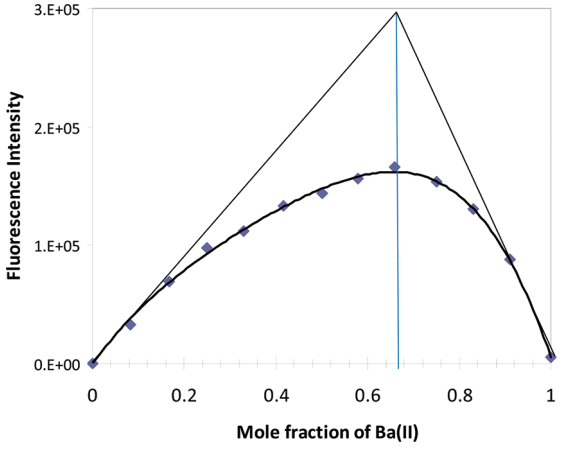

Figure 3. Job's plot showing 1:2 stoichiometry for compound **3a** (L + Ba(II) = constant 2.0×10^{-4} M): The ideal mole ratio for a 1:2 complex [Ba]/([L] + [Ba]) = 0.667, λ_{ex} = 356 nm.

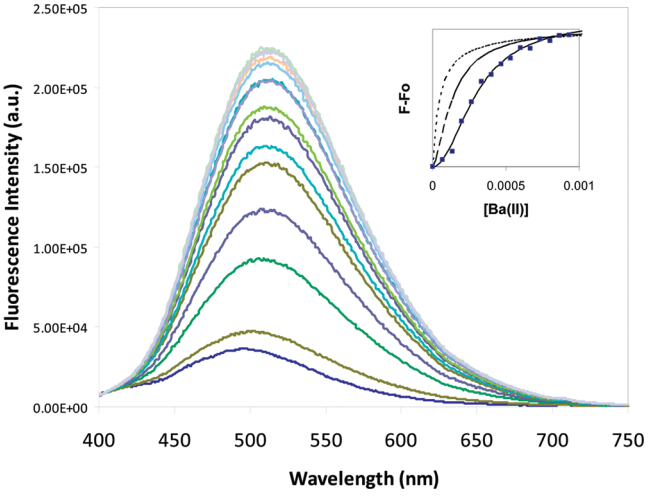

Figure 4. Titration of **3a** (2.0×10^{-4} M) with $Ba(ClO_4)_2$ in acetonitrile, λ_{ex} = 356 nm. Insert: ■ fluorescence data; --- best fit for 1:1 ligand: Ba(II) association; — — — best fit for 1:1.5; — best fit for 1:2. Association constant for 1:2 best fit equals 1.1×10^7 M^{-2}.

association reactions have been modeled to confirm that a second-order association where two metals ions associate with compound **3a** provides the best fit. Also shown in the inset is the fit (dashed line) for a 1:1.5 association, which would represent a 2 L + 3 M ↔ L_2M_3 type model. The 1:2 fit is clearly the appropriate fit and confirms the stoichiometry previously obtained from the Job's plot. The 1:2 association constant equals 1.1×10^7 M^{-2} (±15%) from the best fit and represents the product of the individual association constants of the successive steps: L + M ↔ LM + M ↔ LM_2 = K_1K_2 = 1.1×10^7. K_1 and K_2 (estimated at ~10^2 to 10^4 individually) are not particularly large association constants in either case and account for the shallow saturation in intensity at approximately 2 equiv (0.004 M) of added Ba(II).

Crystal structures for compound **2b** in the presence of Ca(II) and Zn(II) perchlorate show two very different coordination environments for the metal cations. For the calcium adduct (Figure 5), the calcium is bound completely within the macrocycle and exhibits a coordination sphere where the calcium is complexed to nine oxygen atoms: the intraannular carbonyl oxygen, three polyether oxygens of the polyether ring, and four oxygen atoms from two chelating perchlorate anions, one above and one below the ring. The Ca—O bond distances range from 2.303(3) to 2.643(3) Å, with the carbonyl oxygen to calcium bond distance being the shortest.

The Zn complex is quite different in the solid state as compared to the Ca complex (Figure 6). The Zn(II) ion is not complexed within the macrocyclic ring and has instead a complete octahedral coordination sphere occupied by six water molecules. Two of the water molecules coordinated to the zinc form hydrogen bonds to the carbonyl oxygen, O(1)—O(11) = 2.794(4) Å and O(2)—O(11) = 2.849(3) Å, and a third coordinated water molecule bridges two polyether oxygens, O(3)—O(13) = 2.733(4) Å and O(3)—O(15) = 2.743(4) Å. Two additional hydrogen bonds exist between the coordinated water molecules, a perchlorate anion, and the methanol solvate (not shown). The $[Zn(H_2O)_6]^{2+}$ cation is also centrosymmetric and is sandwiched between two identical imine macrocycles. Within the structure, no hydrogen bonds are found involving the imine nitrogen or the nitro group, however.

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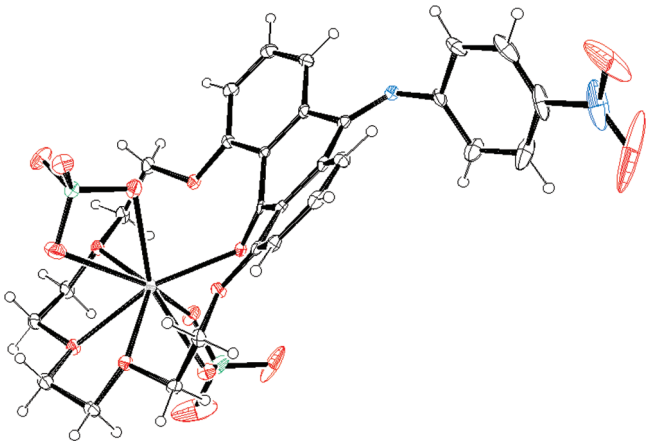

Figure 5. Thermal ellipsoid diagram (30%) of [**2b**·Ca]$(ClO_4)_2$·CH_2Cl_2. The chloroform has been omitted for clarity.

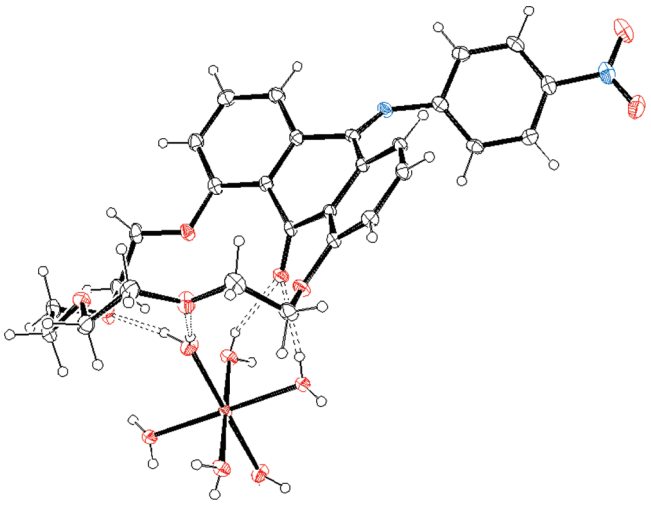

Figure 6. Thermal ellipsoid diagram (30%) of [**2b**·Zn$(H_2O)_6$]$(ClO_4)_2$·MeOH. The methanol solvate and the perchlorate anions have been omitted for clarity. Hydrogen bonds are drawn as dashed lines.

DISCUSSION

Neither Ca(II) or Zn(II) turn on luminescence with any of the monomeric imine compounds, and these structures indicate that complexation of a cation with the intraannular carbonyl is *not* sufficient to turn on emission within these macrocyclic hosts. The uncomplexed imine is ostensibly still free to undergo *E*/*Z* isomerization and nonradiatively deactivate the excited state. This is different behavior than what was previously observed with compound **1** alone (no imine present), which exhibits significantly enhanced luminescence in the presence of Ca(II) and Pb(II).[24b] X-ray crystal structures clearly show complexation of cations within the polyether ring in **1**, similar to the calcium structure found here, including coordination of the intraannular carbonyl oxygen, which is sufficient to enhance luminescence in these other nonimine type systems.

The stoichiometric data above indicates that the addition of 2 equiv of metal cations is sufficient to induce luminescence in the 1,2-dimeric imine compound **3a**. Two possibilities exist for activation of luminescence. Both of the polyether macrocycles could coordinate a metal cation, which promotes internal charge transfer (ICT) of the anthraquinone lumophore, and, at the same time, complexation of the metal ions produce rigidification of the molecule, increasing radiative relaxation/emission. Because the macrocyclic hosts occupy the 1,2 positions of the bridging phenyl group, *E*/*Z* isomerization of the R-C═N group may be restricted. Notably, the 1,4-isomer (**3b**) is nonluminescent, lending credibility to this option, because the binding affinity of the macrocyclic hosts should remain relatively constant; however *E*/*Z* isomerization is still possible, as the two hosts are diametrically opposed to each other across the phenyl spacer. Restricted rotation about the 1,2 oriented C═N groups or other additional noncovalent or coordinate-covalent interactions between metal-occupied neighboring crown rings represents a new photodynamic mechanism for activation of luminescence in *E*/*Z* imine sensors. This is opposed to the common suppression of *E*/*Z* isomerization by coordination of metal ions to the chelating imine nitrogen atom. The possibility still remains, however, that the imine nitrogens in the ortho positions of the phenyl spacer in **3a** act as a potential chelating group, binding to a second metal center and preventing *E*/*Z* isomerization from occurring. Unfortunately, to resolve this issue, we have not been able to isolate single-crystals of **3a** in the presence of Ba(II) or Sr(II). We have made numerous attempts to grow crystals in the presence of different alkaline earth cations, different solvents, different amounts of metal ion, different counteranions, and using different crystal growing methods. Only small clusters with thin, ill-defined shapes have been obtained.

CONCLUSIONS

The organic site-selective synthesis of new imine macrocycles is described, which has not been previously reported. Imine monomers are nonluminescent in the presence of metal cations, as opposed to the title compound from which they are derived. *E*/*Z* isomerization, typical of imines, allows nonradiative deactivation of the excited state. A diimine dimer based on 1,2-phenylenediamine shows luminescence specificity toward Ba(II) in solution. *E*/*Z* Isomerization of the imine groups may be restricted by noncovalent/coordinate-covalent interactions between adjacent crown ether rings and/or steric influences, representing a new mechanism for luminescence enhancement in this class of compounds.

EXPERIMENTAL SECTION

Elemental analyses results are the average of two or more determinations. ^1H (200 MHz) and ^{13}C (50 MHz) spectra were obtained at room temperature in $CDCl_3$ and referenced to the residual solvent peak. 1,8-Oxybis(ethylenethoxyethylenethoxy)-9,10-anthraquinone (**1**) was synthesized by a previously reported method.[25] Melting points were determined in an open capillary and are uncorrected. ESI-MS spectra were obtained using an ion trap mass spectrometer.

General Synthesis. In a round-bottom flask, 2.0 mmol of the aromatic amine (**2a**−**d**) and 7.5 mmol of DABCO were dissolved in 10 mL of toluene and heated at 90 °C for 10 min. Titanium tetrachloride (1.87 mmol) in 5 mL of toluene was added dropwise. Compound **1** (1.87 mmol) was then added to the above mixture and refluxed for 15 h. The solvent was removed at reduced pressure, and 50 mL of CH_2Cl_2 was added and washed several times with brine solution. The organic layer was collected, dried, and purified by column chromatography (neutral alumina) using CH_2Cl_2 and CH_2Cl_2/CH_3OH (9/1) as eluents, to obtain pure solids.

1,8-Oxybis(ethylenoxyethylenoxy)-10-(phenylimino)anthracen-9(10*H*)-one (2a). Yield, 80%, melting point = 208−210 °C, elemental analyses calculated for $C_{28}H_{29}N_1O_6$: C, 70.72; H, 6.15; N,

2.95%. Found: C, 70.86; H, 5.83; N, 3.19%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.70−4.30 (m, 16H, CH_2−O, polyether); 6.60−6.75 (t, 1H); 6.80−7.00 (m, 3H); 7.00−7.20 (t, 3H); 7.25−7.40 (t, 2H); 7.45−7.65 (t, 1H); 7.75−7.90 (d, 1H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 68.7; 69.3; 70.1; 70.3; 71.00; 109.7, 114.5, 117.9; 119.3; 120.9; 123.7; 129.2; 131.2; 132.8; 150.8; 156.4; 157.1; 183.1.

1,8-Oxybis(ethylenoxyethylenoxy)-10-[(4-nitrophenyl)-imino]anthracen-9(10*H*)-one (2b). Yield, 83%, melting point = 220−222 °C, elemental analyses calculated for $C_{28}H_{28}N_2O_8.H_2O$: C, 62.45; H, 5.57; N, 5.21%. Found: C, 62.74; H, 5.40; N, 5.22%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.7−4.3 (m, 16H, CH_2−O, polyether); 6.75−7.20 (dd, 5H); 7.3−7.5 (br, 2H); 8.10−8.25 (d, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 68.7; 69.4; 70.2; 71.0; 115.5; 119.2; 125.5; 132.4; 143.6; 156.8; 157.5, 158.0, 183.2

1, 8-Oxybis(ethylenoxyethylenoxy)-10-{[4-(1*H*-pyrrol-1yl)-phenyl]imino}anthracen-9(10*H*)-one (2c). Yield, 74%, melting point = 222−224 °C, elemental analyses calculated for $C_{32}H_{30}N_2O_6.H_2O$: C, 69.05; H, 5.76; N, 5.03%. Found: C, 68.42; H, 5.67; N, 4.93%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.7−4.3 (m, 16H, CH_2−O, polyether); 6.2−6.4 (*s*, 2H); 6.6−6.8 (d, 1H); 6.8−7.0 (t, 3H); 7.0−7.2 (m, 4H); 7.3−7.4 (d, 2H); 7.4−7.5 (t, 2H); 7.7−8.0 (d, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 69.1, 69.3, 70.6, 71.2, 110.6, 114.8, 118.1, 119.4, 121.1, 121.4, 131.7, 133.3, 137.3, 139.8, 148.6, 157.5, 157.6, 183.7.

1,8-Oxybis(ethylenoxyethylenoxy)-10-[(3-aminophenyl)-imino]anthracen-9(10*H*)-one (2d). Yield, 73%, melting point = 178−180 °C, elemental analyses calculated for $C_{28}H_{28}N_2O_6$: C, 68.85; H, 5.74; N, 5.74%. Found: C, 69.08; H, 5.88; N, 5.50%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.7−4.3 (m, 16H, CH_2−O, polyether); 6.0−6.2 (m, 1H); 6.3−6.5 (m, 1H); 6.7−7.2 (m, 5H); 7.4−7.6 (t, 2H); 7.7−7.8 (d, 1H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 68.7; 69.0; 70.0; 70.2; 70.9; 105.5; 109.2; 110.7; 114.3; 117.9; 121.0; 130.0; 147.6; 151.9; 157.0; 183.5.

Bis{1,8-oxybis(ethylenoxyethylenoxy)anthracen-9(10*H*)-one}-10-(1,2-phenylene-diimino) (3a). Compound **3a** was synthesized from 2 equiv of **1** and 1,2-phenylenediamine using the above-mentioned procedure. Yield, 72%, melting point = 244−246 °C, elemental analyses calculated for $C_{50}H_{48}N_2O_{12}\cdot H_2O$: C, 67.71; H, 5.68; N, 3.16%. Found: C, 67.42; H, 5.56; N, 3.38%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.75−4.3 (m, 32H, CH_2−O, polyether), 6.77 (d, 2H), 6.8 (s, 4H), 6.9 (d, 2H), 7.05 (t, 2H), 7.08 (d, 2H), 7.5 (t, 2H), 7.8 (d, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 69.1, 69.4, 70.3, 70.5, 71.1, 114.4, 114.5, 117.9, 119.2, 121.2, 124.1, 125.9, 131.6, 132.7, 133.3, 133.8, 139.9, 147.4, 157.1, 157.4, 157.5, 183.9.

Bis{1,8-oxybis(ethyleneoxyethylenoxy)anthracen-9(10*H*)-one}-10-(1,4-phenylene-diimino) (3b). Compound **3b** has been synthesized from 2 equiv of **1** and 1,4-phenylenediamine. Yield, 70%, melting point = 278−280 °C, elemental analyses calculated for $C_{50}H_{48}N_2O_{12}$: C, 69.12; H, 5.53; N, 3.23% Found: C, 69.06; H, 6.50; N, 3.57%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.74−4.31 (m, 32H, CH_2−O, polyether), 6.76 (d, 2H), 6.8 (s, 4H), 6.9 (d, 2H), 7.06 (t, 2H), 7.07 (d, 2H), 7.51 (t, 2H), 7.81 (d, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 68.8, 70.1, 70.2, 70.8, 114.2, 114.3, 117.7, 120.9, 123.9, 125.7, 131.2, 132.4, 132.9, 139.6, 147.1, 156.8, 157.1, 157.3, 183.5.

Crystallography. Crystallographic data were collected at 100 K using Mo K_α radiation on a Bruker CCD APEXII diffractometer. Cell constants were determined after integration from approximately 8000 reflections.[26] Structures were solved by direct methods using SIR97[27] and refined using SHELXL-97.[28] Data reduction and refinement were completed using the WinGX suite of crystallographic software.[29] All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, with the exception of $[\mathbf{2b}\cdot Zn(H_2O)_6](ClO_4)_2\cdot MeOH$ where the hydrogen atoms on the coordinated water molecules were found from the difference map. The methanol hydroxyl proton was not found, however, even though a close donor−acceptor distance of 2.76 Å exists between the OH of the methanol and a perchlorate anion, representative of a traditional hydrogen bond. A single DFIX instruction restrained the C−O distance in the methanol solvate as well. For $[\mathbf{2b}\cdot Ca](ClO_4)_2\cdot CH_2Cl_2$, the nitro group is disordered and has been modeled over two positions in a 64:36 ratio and the smaller occupancy kept isotropic. Table S1 in Supporting Information lists additional crystallographic and refinement information.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic data, NMR data and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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