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ESIPT-based anthraquinonylcalix[4]crown chemosensor for In^{3+}

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ABSTRACT

An ESIPT-based novel fluorescent chemosensor, 1,8-anthraquinonylcalix[4]monocrown-6 (**1**), which displayed a selective fluorescent change with In^{3+} among various metal ions, was rationally designed and synthesized. Upon the addition of In^{3+}, the probe displayed a fluorescence decrease at 625 nm, at the same time, an increase of the band centered at 535 nm was observed. This sensing process was also proved by the ^1H NMR titration and electrochemical tests.

Fluorescent chemosensors are powerful tools for the efficient detection and quantitative determination of target ions or molecules.[1] In particular, the development of fluorescent probes for heavy metal ions, which play critical roles in biological metabolism and environmental processes, has received much interest.[2] In the past decade, the great consumption of indium, a well-known heavy metal widely used in the semiconductor industry and solar cells,[3] aggravated already serious heavy metal pollution. Indium is confirmed to interfere with iron metabolism from the sites of absorption, transportation, utilization, and storage in cells.[4] According to animal studies on the toxicity of In^{3+}, acute intravenous administration of In^{3+}, which is extremely poisonous to the liver and kidney, has been reported.[5] In addition, In^{3+} was found to be capable of causing severe lung damage and the development of fibrosis.[6] Among the traditional techniques to detect and quantify In^{3+}, spectro-photometric titration and equilibrium dialysis techniques have been widely employed.[4] Very few chemosensors with fluorescence enhancement for In^{3+}, which are capable of displaying high selectivity over other metal ions, however, have been reported. Therefore, the exploration of simple, quick, and efficient In^{3+}-selective fluorescent chemosensor is necessary not only for the fundamental research but also for biological application in living systems.

1-Aminoanthraquinone (1-AAQ), a chromofluorophore well known by the excited-state intramolecular proton transfer (ESIPT), has been reported to show intrinsic photophysical properties such as intense luminescence, large Stokes shifts, and significant photostability, and has been applied in various chemical fields.[7,8] However, the anthraquinone-based chemosensor with ESIPT was rarely studied.[8] Therefore, in the design of In^{3+} sensor **1**, anthraquinones were chosen as the signaling unit because the proton of amine substituent, attached to 1- or 8-position of anthraquinone, could form an intramolecular H-bond, which enables a rapid photo-induced proton transfer by converting the keto form of quinone to enol at the excited state.[8] The ESIPT system in **1** was expected to present significant optical signal transitions when the In^{3+} ions were added to the testing system.[7]

In our previous work, we reported a calix[4]arene-based chemosensor, *p-tert*-butylcalix[4]arene-di(1-AQQ) with ESIPT system, exhibiting F^- selectivity over other anions.[8] As calix[4]arenes are famous for basic molecular scaffolds with structural rigidity, special molecular appearance, and facile introduction of fluorophore,[9] in present work, the introduction of calix[4]arenes to aminoanthraquinone would therefore form a rigid scaffold to insure the recognition of In^{3+} ions.

Herein, we report a novel fluorescent chemosensor, 1,8-anthraquinonylcalix[4]monocrown-6 (**1**), which displayed a selective fluorescent change with In^{3+} over various metal ions examined in CH_3CN. Results showed that with the addition of In^{3+} to the solution of **1**, the fluorescence band at 625 nm decreased gradually, at the same time, the increase of the band centered at 535 nm was observed. To the best of our knowledge, this is the first In^{3+} fluorescent chemosensor based on excited-state intramolecular

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proton transfer (ESIPT) with diaminoanthraquinone appended to an calix[4]arene skeleton.

1,8-Diaminoquinoline-appended 1,3-alternate calix[4] arene **1** was prepared by the synthetic route depicted in Scheme 1. To obtain functionalized diaminoanthraquinone unit, compound **2** was first synthesized by the reaction of 1,8-dichloroanthraquinone and 2-(2-aminoethoxy)ethanol in the CH_3CN and then tosylated with 2 equiv of *p*-toluenesulfonyl chloride in the presence of NaOH in THF to give **4**. Calix[4]arene was cyclized with pentaethylene glycol ditosylate to produce calix[4]monocrown-6.[3,10] The target molecule **1** was then prepared by the reaction of **4** with calix[4]monocrown-6 (**3**) in the presence of Cs_2CO_3 in CH_3CN.[15]

To investigate the 3D conformation of calix[4]arene scaffold and ESIPT feature, a single crystal of **1**, growing by diffusion of diethyl ether into a dichloromethane solution, was tested by X-ray crystallography. According to the data, it is confirmed that calix[4]arene framework is in an 1,3-alternate conformation and is connected with both 1,8-diaminoanthraquinone and crown-6 ring (Fig. 1). As expected, the oxygen atom O(1), occupying 9-position of anthraquinone, forms intramolecular H-bonds with two protons of neighboring secondary amines with the distances of N(1)–H(1)···O(1) = 1.917 Å and N(2)–H(2)···O(1) = 1.904 Å, respectively. NMR spectra also support the crystal structure of **1** featuring 1,3-alternate conformation, showing a singlet peak at 3.8 ppm in ^1H NMR as well as a single peak at 38 ppm in ^{13}C NMR spectra (Figs. S4 and S5).

To gain an insight into the ESIPT pattern of **1**, the UV–vis and fluorescence spectra of **1** in various solvents were obtained. As shown in Figure 2, no obvious change of UV–vis spectra (Fig. 2a) but considerable changes depending on the solvents in fluorescence spectra (Fig. 2b)[12,13] were observed, which proved a typical pattern of the ESIPT system in **1** as indicated in Scheme 2.[11] In aprotic non-polar solvents, such as toluene, emissions peaks mainly appeared at 620 nm, while in protic polar solvents, such as methanol, blue-shifted emission band centered at 525 nm was found.

The blue-shifted emission band could be attributed to an intramolecular H-bond blocking by polar solvent inhibiting the ESIPT phenomena (Fig. 2b).[12,13]

To evaluate the selectivity of **1** for In^{3+} ion, UV–vis and fluorescence intensity changes upon addition of ClO_4^- salts of a wide range of metal cations were measured in CH_3CN solution.

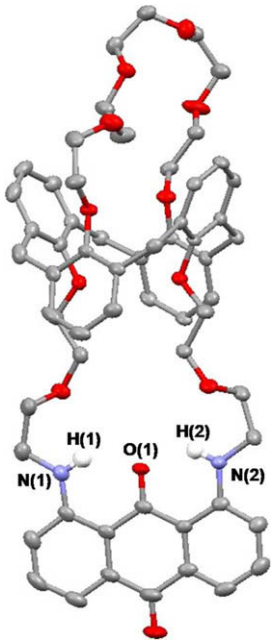
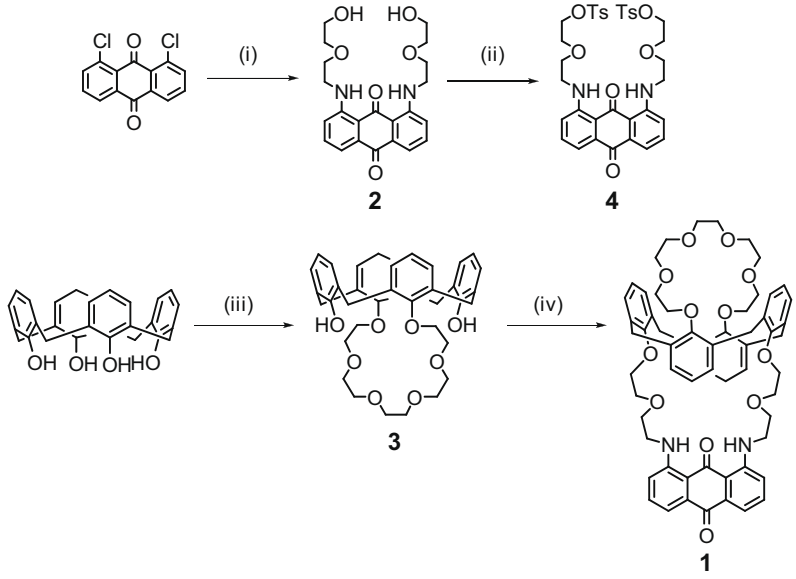


Figure 1. Crystal structure of **1** showing displacement atomic ellipsoids drawn at the 50% probability level. Hydrogen and dichloromethane molecules were omitted for clarity.

Results showed no obvious change in the UV–vis spectra upon the addition of all the metal ions (Fig. S1). However, in the fluorescent spectra, **1** presented a selective fluorescent change with a fluorescent increase at 535 nm for In^{3+} ion over other cations such as Li^+, Na^+, K^+, Cs^+, Ag^+, Mg^{2+}, Sr^{2+}, Cu^{2+}, Ba^{2+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, and Hg^{2+} (Fig. 3).

The fluorescence changes were also monitored upon the addition of various amounts of In^{3+} in CH_3CN solution. The titration of In^{3+} to the solution of **1** (50 μM) resulted in a gradual decrease of the peak at 625 nm and a progressive increase of a new peak around 535 nm (Fig. 4). The marked blue-shift signaled that the In^{3+} ions might coordinate to nitrogen atoms and therefore prohibited the formation of intramolecular H-bonding of anthraquinone.



Scheme 1. Synthetic route of **1**. Reagents and conditions: (i) 2-(2-aminoethoxy)ethanol, reflux, CH_3CN (71%); (ii) *p*-toluenesulfonyl chloride, NaOH/THF, reflux (21%); (iii) pentaethylene glycol ditosylate, CH_3CN, reflux (60%); (iv) **4**, Cs_2CO_3, CH_3CN, reflux (69%).

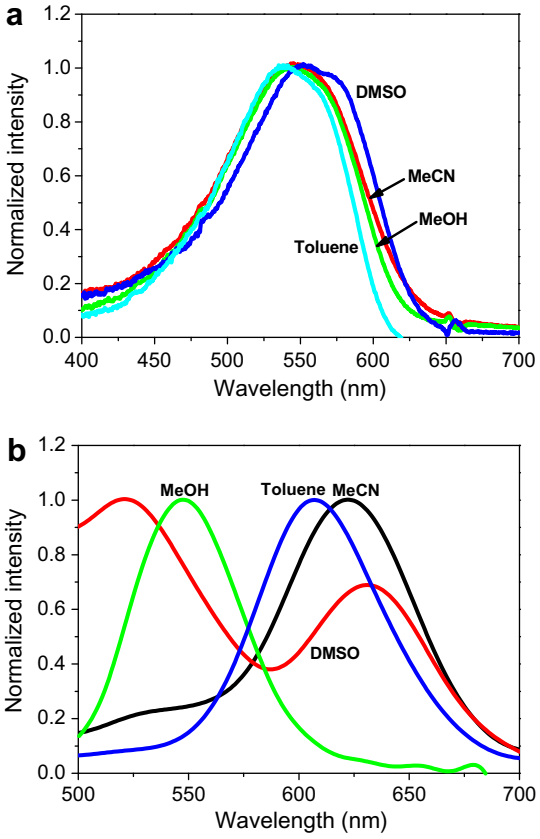
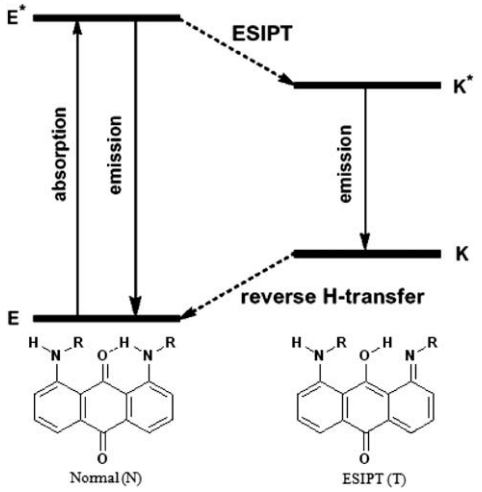


Figure 2. (a) Normalized UV–vis and (b) fluorescence spectra of **1** (50 μM) in various solvents (excitation at 485 nm).



Scheme 2. Excited-state intramolecular proton transfer (ESIPT) system.

The observed blue-shifted emission band in the fluorescence spectra is in good agreement with the fluorescent changes caused by polar solvents prohibiting ESIPT phenomena.

To confirm that the ESIPT is blocked through the coordination of In^{3+} with the nitrogen atoms of **1**, we investigated the ^1H NMR spectra of **1** upon the addition of In^{3+} and compared it with that of free **1**. When In^{3+} was added to **1**, the two NH protons became broad and finally diminished, and the six protons of anthraquinone ring moved toward the downfield region (δ 6.8–7.0) as shown in Figure S4, which support that two nitrogen atoms on anthraquinone may participate in binding with In^{3+}.

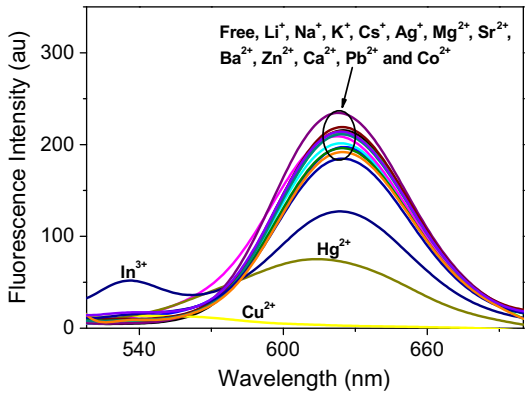


Figure 3. Fluorescence spectra of **1** (50 μM) with the addition of ClO_4^- salts of Li^+, Na^+, K^+, Cs^+, Ag^+, Mg^{2+}, Sr^{2+}, Cu^{2+}, Ba^{2+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+}, and In^{3+} (20 equiv, respectively) in CH_3CN.

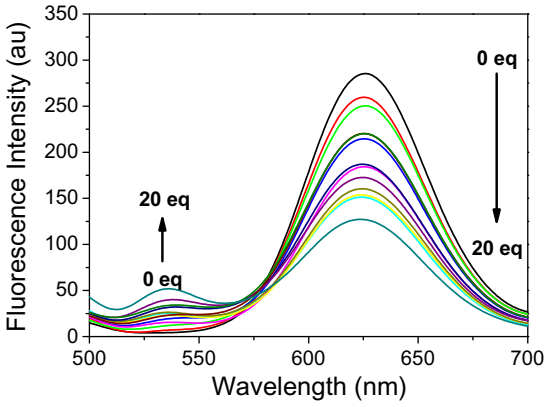


Figure 4. Fluorescence spectra of **1** (50 μM) upon the addition of various amounts of In^{3+} in CH_3CN with an excitation at 485 nm.

The In^{3+} coordination to the amine groups of **1** was also proven by observing electrochemical behaviors of **1** in both the absence and the presence of In^{3+}. Since the electroactive group, that is, quinone, is close to the amine groups of **1**, we expected different electrochemical behaviors of **1** when the In^{3+} binds close to the amine groups. So, we investigated the electrochemical behaviors of **1** by differential pulse voltammetry (DPV) of **1** in 0.1 M TBAP/CH_3CN solution.

Differential pulse voltammograms of **1** (0.2 mM) are shown in Figure 5 as a function of added In^{3+}. In the absence of In^{3+}, two

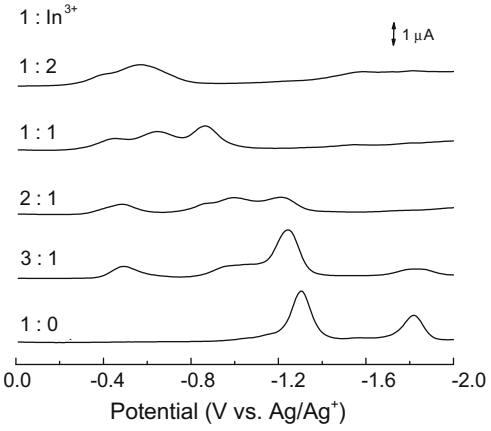


Figure 5. Differential pulse voltammograms of **1** (0.2 mM) in the absence and the presence of In^{3+} ions. Electrolyte: 0.1 M TBAP in CH_3CN. Pulse amplitude: 50 mV.

well-defined cathodic peaks of free **1** (**1**:In^{3+} = 1:0) were observed at −1.3 and −1.8 V, which correspond to two successive one-electron transfers to two anthraquinone moieties of **1**.[14] Upon the addition of successive amounts of In^{3+}, however, the original two cathodic peaks of free **1** disappeared and new additional cathodic peaks resulting from the reduction processes of **1**·In^{3+} complexes were observed. These results indicate that In^{3+} ions form complexes with **1** and interact with the amine groups close to the electroactive quinone of **1**.

Differential pulse voltammograms of **1** (0.2 mM) were also obtained in the presence (1 equiv) of other cations such as Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Sr^{2+}, Cu^{2+} , Ba^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Ru^{2+}, Co^{2+}, and Zn^{2+} in CH_3CN with 0.1 M TBAP as the supporting electrolyte. As we observed in the presence of In^{3+}, 1 equiv addition of Hg^{2+} or Pb^{2+} cations to **1** resulted in significant changes in the voltammograms while the addition of alkali, alkali earth, or other transition metal caused comparably negligible voltammetric changes (Figs. S15–S17). Figure 6 shows the differential pulse voltammograms of **1** in the presence (1 equiv) of In^{3+}, Hg^{2+}, or Pb^{2+}. One equivalent addition of In^{3+}, Hg^{2+}, or Pb^{2+} caused the disappearance of the original cathodic peaks of free **1** and the appearance of new cathodic peaks at more positive potentials, which also indicates an interaction of the metal cations with the amine groups located next to the electroactive quinone of **1**. However, the potential shifts of **1** upon the addition of In^{3+}, Hg^{2+}, or Pb^{2+} are the biggest in the complexation of **1** with In^{3+}. The potential shifts of **1** in the presence of 1 equiv of In^{3+}, Pb^{2+}, or Hg^{2+} are summarized in Table 1.

In conclusion, a new 1,8-diaminoanthraquinone derivative (**1**) involving calix[4]arenemonocrown-6-moieties was explored as the fluorescent sensor of In^{3+} based on ESIPT-blocking system. Compound **1** presented a selective fluorescent change to In^{3+} ion over other cations. The addition of In^{3+} to the solution of **1** resulted in a gradual decrease of the peak at 625 nm and a progressive increase of a new peak around 535 nm. These changes might be attributed to that the intramolecular H-bonds were blocked by the coordination with In^{3+} which therefore led to the inhibition of the ESIPT feature. This sensing process was also proved by the ^1H NMR titration and electrochemical tests. This fluorescent shift may allow probe **1** to be employed for fluorescent detecting In^{3+} in various systems.

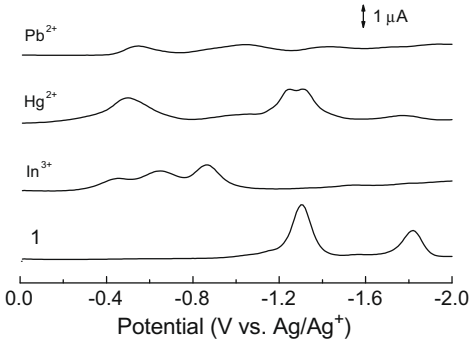


Figure 6. Differential pulse voltammograms of **1** (0.2 mM) in the absence and the presence (1 equiv) of In^{3+}, Hg^{2+}, or Pb^{2+} ions. Electrolyte: 0.1 M TBAP in CH_3CN. Pulse amplitude: 50 mV.

Table 1
Peak potential differences between free and complexed **1** with metal ions determined by differential pulse voltammetry

	In^{3+}	Hg^{2+}	Pb^{2+}
Potential difference (mV) ($\Delta E_p = E_p^{free} - E_p^{complex}$)[a]	845	802	755

[a] E_p^{free} and $E_p^{complex}$ represent the first peak potential of free **1** and **1**·metal ion complex, respectively.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.006.

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15. *General*: Uncorrected melting points (Mps), Buchi 500. ^1H NMR and ^{13}C NMR, Varian 300 MHz (δ in ppm from TMS, *J* in hertz). FAB MS mass spectra, JEOL-JMS-HX 110A/110A high resolution tandem mass spectrometry in Korea University (Korea). All the reactions were run under a nitrogen atmosphere. SiO_2 (Geduran 1.11567) was used for column chromatography. All reagents and solvents were commercial and used without further purification. Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. Stock solutions of **1** (50 μM) were prepared in CH_3CN. For all measurements, excitation was at 485 nm with excitation and emission slit widths at 1.5 nm. Fluorescence titration experiments were performed using 20 μM solutions of **1** in CH_3CN and various concentrations of metal perchlorate in CH_3CN.
All electrochemical experiments were carried out in a conventional three-electrode cell using a Model 440 electrochemical workstation (CH Instruments, Austin, TX) at a room temperature under a dry N_2 atmosphere using 0.1 M tetrabutylammonium perchlorate (TBAP) electrolyte solution. A glassy carbon working electrode (CH Instruments, Inc., TX) was polished with 0.3 μM alumina (Buehler, Lake Bluff, MN). Any residual alumina particles were thoroughly removed by sonicating the working electrode. Then, the working electrode was rinsed with copious amounts of deionized water and CH_3CN, and blown dry with a N_2 stream. A Pt wire and an Ag/Ag^+ (10 mM $AgNO_3$) electrode were used as a counter and a reference electrode, respectively.
Preparation of **1***:* To a solution of **4** (145 mg, 0.21 mmol) in acetonitrile (100 mL) were added calix[4]monocrown-6 (126 mg, 0.21 mmol) and Cs_2CO_3 (470 mg, 1.44 mmol) as a base. The reaction mixture was reflux for 24 h and cooled down to room temperature. CH_2Cl_2 (100 mL) and H_2O (100 mL) were added and the organic layer was washed three times with water, dried over $MgSO_4$, and evaporated in vacuo. Column chromatography of the crude product by silica gel with EtOAc as an eluent gave 88 mg (69%) of **1** as a purple solid. Mp 198–200 °C. IR (KBr, cm^{-1}): 3381, 2881, 1610, 1512, 1412, 1208, 1122, 753. ^1H NMR (300 MHz): δ 9.90 (2H, t, anthraquinone-N*H*), 7.45–7.59 (4H, m, anthraquinone-N*H*), 7.05–7.15 (8H, t, Ar-*H*), 6.90–7.00 (6H, m, Ar-*H*),

3.90 (8H, s, ArCH_2Ar), 3.70 (4H, s, OCH_2CH2O), 3.55–3.65 (12H, m, OCH_2CH_2O), 3.40–3.45 (8H, m, OCH_2CH_2O), 3.20–3.25 (4H, t, OCH_2CH_2O), 3.10–3.15(4H, t, OCH_2CH_2O). ^{13}C NMR (100 MHz): 14.41, 21.32, 38.35, 43.49, 53.82, 60.62, 66.54, 69.52, 69.74, 69.91, 70.96, 71.18, 71.29, 114.77, 115.05, 117.70, 123.20, 129.45, 134.01, 134.22, 134.32, 134.45, 151.09, 156.11, 157.01, 171.37, 184.97, 188.90 ppm. FAB-MS (1008.48): 1006.20 [M+2H$^+$].

Preparation of **2***:* 1,8-Dichloroanthraquinone (1.0 g, 3.61 mmol) was added to a solution of 2-(2-aminoethoxy)ethanol (3.61 mL, 34.3 mmol), and heated at reflux for 24 h in MeCN (100 mL). The resulting solid was dissolved in CH_2Cl_2 (100 mL), and the organic layer was washed three times with water, dried over $MgSO_4$, and evaporated in vacuo. The crude product was separated by silica gel with EtOAc as an eluent to give 710 mg (71%) of **2** as a purple solid. Mp 198–200 °C. IR (KBr, cm^{-1}): 3292, 2857, 2346, 1621, 1297, 1214, 1066, 745. ^{1}H NMR (300 MHz): δ 9.90 (2H, s, anthraquinone-N*H*), 7.55–7.60 (2H, d, anthraquinone-*H*), 7.45–7.50 (2H, d, anthraquinone-*H*), 6.97 (2H, d, anthraquinone-*H*), 3.80–3.90 (8H, m, OCH_2CH_2O). ^{13}C NMR (100 MHz): 42.59, 61.70, 68.78, 72.22, 115.73, 115.61, 117.52, 134.15, 150.97, 184.43, 189.01 ppm. FAB-MS (414.95): 415.20 [M+H$^+$].

Preparation of **3***:* Compound **3** was prepared in 80–90% yield by adaptation of synthetic procedures we have previously reported.[10]

Preparation of **4***:* To a THF solution of **2** (1.0 g, 2.43 mmol) was added a solution of *p*-toluenesulfonyl chloride (0.96 g, 5.04 mmol) in THF and added dropwise an aqueous solution of NaOH (1.0 g, excess). The resulting precipitates were dissolved in CH_2Cl_2 (100 mL) and H_2O (100 mL), and the organic layer was washed three times with water, dried over $MgSO_4$, and evaporated in vacuo. Column chromatography of the crude product by silica gel with EtOAc as an eluent provided 0.215 g (21%) of **4** as a purple solid. Mp 198–200 °C. IR (KBr, cm^{-1}): 3286, 2906, 1613, 1513, 1352, 1174, 1076, 913, 746. ^{1}H NMR (300 MHz): δ 9.65 (2H, s, anthraquinone-N*H*), 7.70–7.80 (4H, d, tosylaromatic-*H*), 7.50–7.55 (2H, d, anthraquinone-*H*), 7.40–7.45 (2H, t, anthraquinone-*H*), 7.20–7.25 (4H, d, tosylaromatic-*H*), 6.95–7.00 (2H, d, anthraquinone-*H*), 3.80–3.90 (8H, m, OCH_2CH_2O), 2.30–2.35 (6H, s, tosylmethyl-*H*). ^{13}C NMR (100 MHz): 21.81, 42.82, 68.81, 69.59, 69.99, 114.81, 115.31, 117.89, 128.16, 130.02, 133.16, 133.30, 134.52, 145.04, 151.19 184.68, 188.93 ppm. FAB-MS (722.82): 722.20 [M].