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ICT-based Cu(II)-sensing 9,10-anthraquinonecalix[4]crown

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ABSTRACT

A series of calix[4]arene-based chromogenic sensors bearing the 9,10-anthraquinone moiety have been synthesized and examined for their abilities to recognize various cations such as Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} by UV–vis spectroscopy. In acetonitrile, the presence of Cu^{2+} induces the formation of the 1:1 ligand/metal complex, which exhibits a new absorption band centered at 450 nm, and leads to an obvious color change from yellow to red.

The development of specific chemosensors for the efficient detection of metal ion analytes is one of the most important areas in organic and supramolecular chemistry due to their pivotal role in a variety of fundamental physiological processes in organisms ranging from bacteria to mammals.[1,2]

Over the last few decades, chemosensors for the detection and measurement of Cu^{2+} ions have been actively investigated as this metal ion is a significant environmental pollutant and an essential trace element in the human body. Copper(II) also plays an important role in various biological processes. However, it is toxic at higher concentrations and, for example, the accumulation of Cu^{2+} in the liver and kidney may cause gastrointestinal problems, Wilson disease, hypoglycemia, dyslexia, and infant liver damage.[3,4]

Calixarenes have been found to be outstanding platforms for creating attractive host molecules. Modifications of calixarenes give rise to a great variety of derivatives with tunable binding properties. For instance, calix[4]arene derivatives such as esters, amides, crown ethers, azacrown ethers, and carboxylic acids have been shown to extract and form complexes with metal ions, also displaying interesting selectivity.[5,6] As one of the calixarene derivatives, calixcrown compounds in which one crown ether unit or two crown ether units are incorporated into the lower rim of a calix[4]arene skeleton are also well described because of their high selectivity toward metal ions.[7,8]

An anthraquinone chromophoric system may be important as a chemosensor because its optical properties can be significantly perturbed by chemical stimuli. It is also important to note that the carbonyl group of 9,10-anthraquinone ligands is known to interact with various metal ions to cause a pronounced color change.[9,10]

Even though the 9,10-anthraquinone moiety has been recently utilized as a chemosensor for metal ions and anions,[9,10] there have been only a few examples with *p-tert*-butylcalix[4]arene bearing the 9,10-anthraquinone sensing moiety.[11] This report describes the synthesis and binding properties of a series of 9,10-anthraquinone pendant calix[4]crowns amongst which compound **1** displays a highly selective color change for Cu^{2+}.

Our synthesis began with the preparation of the 9,10-anthraquinone derivative **4**. Under a N_2 atmosphere, the treatment of 1,8-dihydroxy-9,10-anthraquinone with 2-(2-chloroethoxy)ethyl 4-methylbenzenesulfonate and Cs_2CO_3 in CH_3CN led to **4**. Subsequently, **1–3** were synthesized using the reaction of **4** with **6–8** in the presence of Cs_2CO_3 in CH_3CN/DMF (1:1 v/v) with a catalytic amount of NaI. As a reference compound, **5** was also obtained by the reaction of 1,8-dihydroxy-9,10-anthraquinone with 2-(2-hydroxyethoxy)ethyl 4-methylbenzenesulfonate and K_2CO_3 in CH_3CN (Scheme 1). Their molecular structures were fully characterized by ^1H NMR, ^{13}C NMR, MS, and X-ray analysis (see Supplementary data). Synthetic details are described in Ref.15.

The UV–vis spectra of the 9,10-anthraquinone-appended calix[4]arenes **1–3** showed a new absorption band at 380 nm in CH_3CN. Excess perchlorate salts (50 equiv) of Li^+, Na^+, K^+, Rb^+, Cs^+,

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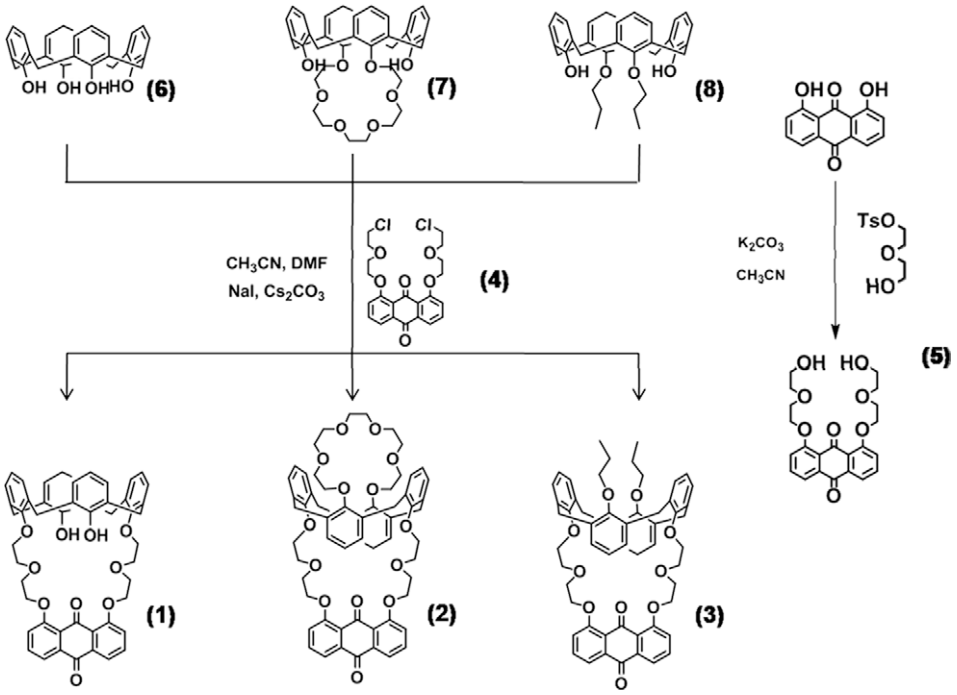

Scheme 1. Synthetic route to chromogenic ligands **1**–**3**.

Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} (a total 16 metal ions) were tested to evaluate the metal ion-binding properties of **1**–**3**. Interestingly, we found unusual UV–vis changes in **1**; the addition of Cu^{2+} produced a new absorbance band at 450 nm in a solution of CH_3CN, as shown in Figure 1a. Based on the UV band and color changes, we noticed that compound **1** shows a pronounced selectivity for Cu^{2+} over other metal cations, whereas **2** and **3** do not show any UV and color changes (Fig. 1b).

In a function of Cu^{2+} concentration, the intensity of the new red-shifted absorption band centered at 450 nm increased. This band at 450 nm is attributable to an Internal Charge Transfer (ICT)[12] transition made possible by coordination of Cu^{2+} to **1**. When the Cu^{2+} ion interacts strongly with the lone pair electrons of the carbonyl oxygen atoms ($Cu^{2+}\cdots O{=}C$) with the aid of the two proximal OHs of the calix[4]arene platform, then the charge transfer from the 1,8 oxygen atoms to the electron-deficient carbonyl group becomes stronger (Fig. 3).

To elucidate how the two proximal OHs in **1** act to promote selective Cu^{2+} ion binding, **a** calixcrown having a dipropyl unit (**3**) was also prepared. However, we observed no absorbance changes of **3** toward any metal ions, including Cu^{2+} (Fig. 1b). In addition, **5** was synthesized to investigate the role of the calix[4]-

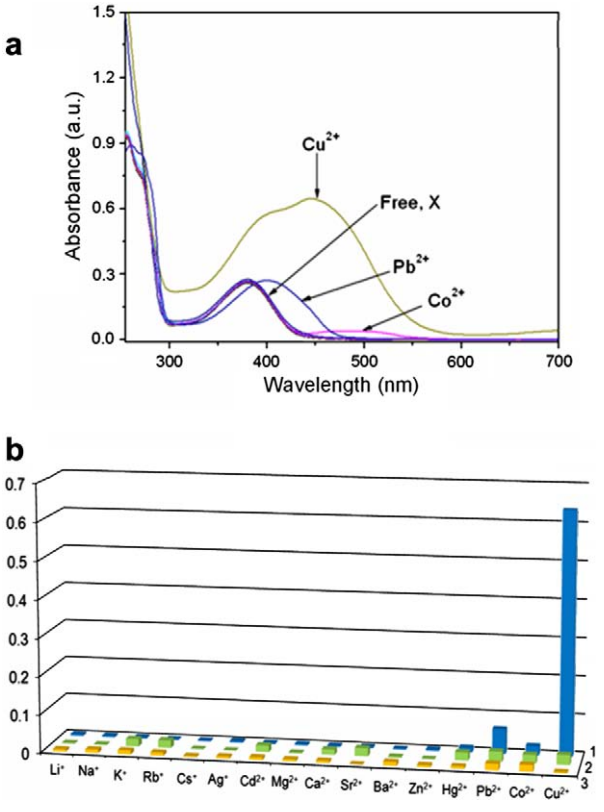

Figure 1. Absorption spectra of **1** (50.0 μM) (a) and relative responses at 450 nm of **1**–**3** (50.0 μM), (b) with the addition of ClO_4^- salts of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} (50 equiv, respectively) in CH_3CN.

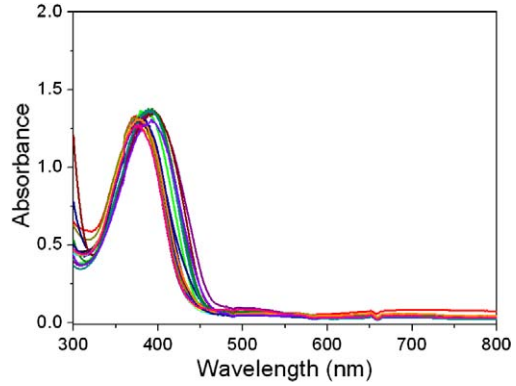

Figure 2. Absorption spectra of **5** (50.0 μM) with addition of ClO_4^- salts of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} (50 equiv, respectively) in CH_3CN.

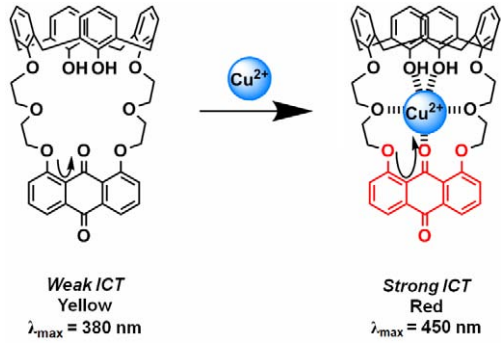

Figure 3. Plausible complexation mechanism of **1** for Cu^{2+} ion.

arene framework for the complexation mechanism but it shows no significant changes upon metal cation addition (Fig. 2). This may be firm evidence that the two proximal OHs and calix[4]arene moiety of the compound **1** play a critical role in the selective complexation of the copper(II) ion to give a UV band shift as well as a color change.

To obtain insight into any allosteric effect on the ligand-metal complexation, calixcrown-6 (**2**) having recognizably binuclear crown groups was also synthesized. Upon addition of various metal cations, however, the absorption band changes of **2** showed the same pattern as those of **3** (Fig. 1b), revealing that no metal ion is encapsulated in the 9,10-anthraquinone part of the calixcrown. A crystal of [**2**+Pb^{2+}] was obtained by slow evaporation from the solution of CH_2Cl_2/CH_3CN and the structure, as determined by X-ray crystallography, is depicted in Figure 4. Interestingly, from the X-ray crystal structure and UV–vis spectral change of [**2**+Pb^{2+}], we noticed that the Pb^{2+} ion is encapsulated in the crown-6 group and not in the crown-anthraquinone cavity, which is obviously unable to induce the UV–vis spectral changes of **2**. For the Cu(II) complexation of **2**, we therefore assume that the Cu(II) ion is entrapped by the crown-5 unit instead of by the 9,10-anthraquinoline unit mainly due to the lack of two proximal OHs of the calix[4]arene. So, it is noteworthy that the new ICT band of **1**–Cu(II) complex at 450 nm originates from the complexation of the 9,10-anthraquinone moiety associated with two phenoxy oxygen atoms.

The 1:1 stoichiometry of compound **1** with Cu(II) was proven by a mole-ratio plot, shown in Figure 5a. In the Job plot,[13] the maximum absorbance change was observed when the molar fraction of ionophore **1** versus Cu^{2+} was 0.5, indicative of a 1:1 complex (Fig. 5b). The K_{assoc} value was estimated as $1.80 \times 10^2\ M^{-1}$.[14]

UV–vis spectral changes (Fig. 6) of **1** in competitive metal ion complexation were also undertaken in the presence of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, and Co^{2+} in acetonitrile (perchlorate counter anion). The miscellaneous competitive cations did not lead to any significant changes in the visible region. In the presence of miscellaneous competitive cations, compound **1** still showed a UV band shift as well as a color change from yellow to red, indicating that the wavelength shift of absorbance resulting from the addition of the Cu^{2+} ion is not influenced by any subsequent addition of miscellaneous cations. All these experiments imply that the selectivity of **1** for the Cu^{2+} ion over other competitive cations is remarkably high.

The distinctive color change of a ligand on complexation with certain metal ions has an important role in a possible sensing system. In our system, we observed that **1** shows a selective color change from yellow to red (**1**+Cu^{2+}) as seen in Figure 7, leading to practical applications such as in industrial and environmental fields.

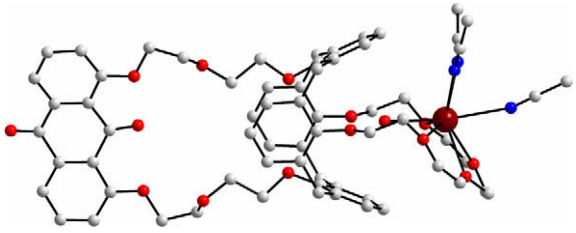

Figure 4. Solid-state structure of **1**–Pb^{2+} (ClO_4^-) showing displacement atomic ellipsoids drawn at the 50% probability level.

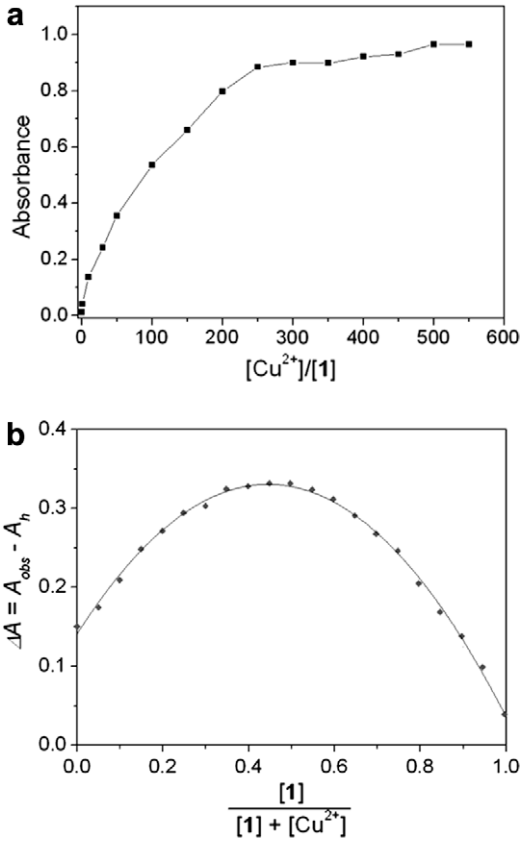

Figure 5. (a) λ_{max} (450 nm) values versus Cu^{2+}/**1** molar ratio. (b) Job plot of a 1:1 complex of **1** and Cu^{2+}ion, where the difference in absorbance intensity at 450 nm was plotted against the mole fraction of **1** at an invariant total concentration of 50 μM in CH_3CN.

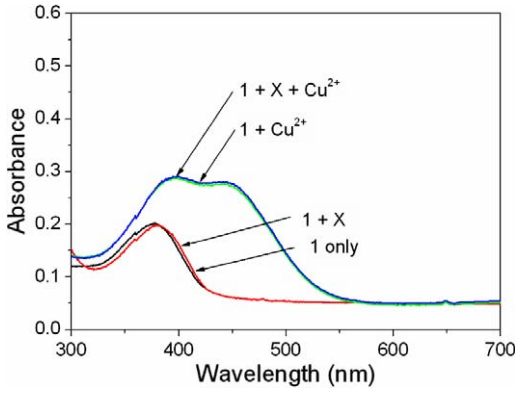

Figure 6. UV–vis spectra of **1** (50.0 μM) in CH_3CN in the presence of Cu^{2+} ion and miscellaneous cations including Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, and Co^{2+} (5 equiv).

Figure 7. Visual color changes of **1** (50.0 μM) upon addition of various metal ions in CH_3CN. From left to right: free **1**, Cu^{2+}, Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, and Co^{2+} (250.0 equiv).

In conclusion, we have presented a series of calix[4]crowns bearing the 9,10-anthraquinone unit as a colorimetric selective chemosensor. We then observed that among the calixcrown derivatives synthesized, compound **1** shows a selective change in UV absorption and color toward the Cu^{2+} cation in CH_3CN. High selectivity and sensitivity of **1** for Cu^{2+} ion are mainly due to the presence of two proximal OHs of the calix[4]arene framework and the polyether pendant 9,10-anthraquinone moiety. Competition experiments and the visual change of **1** give a solid foundation for the design of an optimal host molecule for Cu(II) ion which can be applied to the industrial and environmental fields.

Acknowledgments

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Supplementary data

Supplementary data associated with this paper can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.149.

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14. Association constants were obtained using the computer program ENZFITTER, available from Elsevier-BIOSOFT, 68 Hills Road, Cambridge CB2 1LA, United Kingdom: Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
15. Unless otherwise noted, reagents were obtained from commercial suppliers and were used without further purification. Melting points were taken in evacuated and sealed capillary tubes with a Mel-Temp apparatus and were uncorrected. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX 400 spectrometer. Chemical shifts are recorded in parts per million relative to TMS as an internal standard.
*Preparation of (**1**) <cone-calix[4]arene anthraquinone>:* To a solution of **4** (600 mg, 1.3 mmol) in dried MeCN and DMF, calix[4]arene (500 mg, 1.2 mmol), Cs_2CO_3 (470 mg, 1.5 mmol), and NaI (catalytic amount) were added. The reaction mixture was refluxed for 2 days. The solution was washed with water and CH_2Cl_2. The organic layer, after drying over anhydrous Na_2SO_4, was filtered and evaporated. Column chromatography on silica gel with EtOAc–hexane (2:1) as eluents gave 400 mg (yellow solid, 20%) of **1**. Mp: 273–275 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 2H, O*H*), 7.81 (dd, 2H, $Ar_{anthra}H$, J = 7.67 Hz), 7.58 (t, 2H, $Ar_{anthra}H$, J = 8.18 Hz), 7.30 (dd, 2H, $Ar_{anthra}H$, J = 8.28 Hz), 6.89 (d, 4H, $Ar_{cal}H$, J = 10.22 Hz), 6.87 (d, 4H, $Ar_{cal}H$, J = 10.30 Hz), 6.71 (t, 2H, $Ar_{cal}H$, J = 7.70 Hz), 6.54 (t, 2H, $Ar_{cal}H$, J = 7.51 Hz), 4.33–4.34 (m, 8H, OCH_2CH_2O), 4.22–4.28 (m, 12H, OCH_2CH_2O, $Ar_{cal}CH_2Ar_{cal}$), 3.22 (d, 4H, $Ar_{cal}CH_2Ar_{cal}$, J = 13.00 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): 185.3, 182.5, 158.6, 156.6, 154.4, 135.0, 134.4, 134.3, 134.1, 134.0, 133.8, 133.7, 133.0, 131.7, 129.8, 129.6, 129.4, 129.3, 128.4, 125.8, 125.7, 124.1, 123.1, 122.9, 120.8, 119.7, 77.8, 77.7, 77.4, 77.1, 74.5, 73.0, 71.1, 70.9, 70.8, 70.5, 70.4, 70.3, 30.7 ppm. FAB MS m/z (M^+): calcd, 804.29. Found, 805.4. IR (KBr plate, cm^{-1}): 3423, 1668, 1461, 1587.
*Preparation of (**2**) <1,3-alternate calix[4]crown-6 anthraquinone>:* To a solution of **4** (390 mg, 0.86 mmol) in dried MeCN and DMF, calix[4]crown-6 (400 mg, 0.61 mmol), Cs_2CO_3 (760 mg, 2.33 mmol), and NaI (catalytic amount) were added. The reaction mixture was refluxed for 2 days. The solution was washed with water and CH_2Cl_2. The organic layer, after drying over anhydrous $MgSO_4$, was filtered and evaporated. Column chromatography on silica gel with EtOAc–hexane (1:1) as eluents gave 243 mg (yellow solid, 40%) of **2**. Mp: 198–200 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, 2 H, $Ar_{anthra}H$, J = 7.70 Hz), 7.62 (t, 2 H, $Ar_{anthra}H$, J = 8.14 Hz), 7.30 (d, 2H, $Ar_{anthra}H$, J = 8.07 Hz), 7.11 (d, 4H, $Ar_{calix}H$, J = 2.41 Hz), 7.09 (d, 4H, $Ar_{calix}H$, J = 2.43 Hz), 6.88 (t, 4H, $Ar_{calix}H$, J = 7.40 Hz), 4.22 (t, 4 H, OCH_2, J = 4.13 Hz), 3.87 (s, 8H, $Ar_{calix}CH_2Ar_{calyx}$; 4H, OCH_2), 3.70 (s, 4H, OCH_2), 3.64–3.54 (m, 12H, OCH_2), 3.44 (t, 4H, OCH_2, J = 4.97 Hz), 3.27 (q, 8H, OCH_2). ^{13}C NMR (400 MHz, $CDCl_3$): 184.4, 184.1, 182.6, 158.7, 158.6, 157.0, 156.9, 156.5, 156.2, 155.8, 155.4, 142.8, 135.0, 134.1, 133.8, 133.0, 129.4, 125.8, 122.8, 119.8, 102.1, 69.8, 69.7, 69.5, 68.5, 38.3, 38.2 ppm. FAB MS m/z (M^+): calcd, 1008.43. Found, 1007.0. IR (KBr plate, cm^{-1}): 1672, 1585, 1457, 1135.
*Preparation of (**3**) <1,3-alternate dipropyloxycalix[4]arene anthraquinone>:* To a solution of **4** (0.98 g, 2.14 mmol) in dried MeCN and DMF, 25, 27-dipropyloxycalix[4]arene (1.0 g, 1.97 mmol), Cs_2CO_3 (0.76 g, 2.33 mmol), and NaI (catalytic amount) were added. The reaction mixture was refluxed for 2 days. The solution was washed with water and CH_2Cl_2. The organic layer, after drying over anhydrous $MgSO_4$, was filtered and evaporated. Column chromatography on silica gel with EtOAc–hexane (1:2) as eluents gave 120 mg (yellow solid, 6.3%) of **3**. Mp: 238–240 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, 2 H, $Ar_{anthra}H$, J = 7.69 Hz), 7.60 (t, 2H, $Ar_{anthra}H$, J = 8.18 Hz), 7.31 (dd, 2H, $Ar_{anthra}H$, J = 8.34 Hz), 7.09 (d, 4H, $Ar_{calix}H$, J = 7.47 Hz), 7.01 (d, 4H, $Ar_{calix}H$, J = 7.47 Hz), 6.81 (quintet, 4H, $Ar_{calix}H$), 4.25 (t, 4H, OCH_2, J = 4.35 Hz), 3.91 (t, 4H, OCH_2, J = 4.82 Hz), 3.80 (s, 8H, $Ar_{calix}CH_2Ar_{calix}$), 3.53 (t, 4H, OCH_2, J = 6.16 Hz), 3.41–3.33 (m, 8H, OCH_2), 1.27 (sextet, 4H, $CH_3CH_2CH_2$, J = 7.57 Hz), 0.70 (t, 6H, CH_3CH_2, J = 7.39 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): 184.1, 182.7, 158.7, 157.2, 156.4, 156.1, 155.5, 135.0, 134.4, 134.2, 134.0, 133.8, 129.1, 125.8, 122.4, 121.0, 119.9, 115.8, 112.0, 72.0, 70.6, 70.5, 70.4, 70.0, 69.9, 69.0, 38.5, 38.4, 38.1, 23.0, 22.8, 22.7, 10.3 ppm. FAB MS m/z (M^+): calcd, 891.05. Found, 891.0. IR (KBr plate, cm^{-1}): 1668, 1585, 1454.
*Preparation of (**4**) <1,8-bis(2-(2-chloroethoxy)ethoxy)anthraquinone >:* A mixture of 1,8-dihydroxyanthraquinone (5.0 g, 0.02 mol), 2-(2-chloroethoxy)ethyl 4-methylbenzenesulfonate (11.15 g, 0.04 mol), and Cs_2CO_3 (6.52 g, 0.02 mol) in dried MeCN (250 mL) was refluxed for 6 h. The solution was washed with water, and the organic layer was dried over anhydrous $MgSO_4$. Removal of the organic solvent was carried out by evacuation. Column chromatography on silica gel with EtOAc–hexane (1:2) as eluents gave 1.8 g (yellow solid, 19%) of **4**. Mp: 86–88 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, 2H, Ar*H*, J = 7.71 Hz), 7.62 (t, 2H, Ar*H*, J = 8.24 Hz), 7.33 (dd, 2*H*, Ar*H*, J = 8.35 Hz), 4.31 (t, 4H, OCH_2, J = 4.54 Hz), 4.03 (t, 4H, OCH_2, J = 5.01 Hz), 3.99 (t, 4H, OCH_2, J = 5.58 Hz), 3.71 (t, 4H, OCH_2, J = 5.98 Hz).). ^{13}C NMR (400 MHz, $CDCl_3$): 184.0, 182.3, 158.6, 134.9, 134.0, 124.9, 120.4, 119.8, 72.0, 70.0, 69.7, 43.3 ppm. FAB MS m/z (M^+): calcd, 452.08. Found, 453.7. IR (KBr plate, cm^{-1}): 1666, 1581.ed.; 1999; Chapter 13.
*Preparation of (**5**) <1,8-bis(2-(2-hydroxyethoxy)ethoxy)anthraquinone >:* A mixture of 1,8-dihydroxyanthraquinone (1.0 g, 0.0041 mmol), 2-(2-hydroxyethoxy)ethyl 4-methylbenzenesulfonate (2.7 g, 0.01 mol), and K_2CO_3 (5.75 g, 0.04 mol) in dried MeCN (250 mL) was refluxed for 12 h. The solution

was washed with water, and the organic layer was dried over anhydrous $MgSO_4$. Removal of the organic solvent was carried out by evacuation. Column chromatography on silica gel with EtOAc as eluents gave 1.1 g (orange oil, 63.5%) of **5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 2H, Ar*H*, *J* = 7.83 Hz), 7.56 (t, 2H, Ar*H*, *J* = 7.87 Hz), 7.24 (d, 2*H*, Ar*H*, *J* = 8.43 Hz), 4.24 (t, 4H, OCH_2, *J* = 5.27 Hz), 3.94 (t, 4H, OCH_2, *J* = 4.03 Hz), 3.78 (m, 8H, OCH_2, $CHCl_2$). ^{13}C NMR (400 MHz, $CDCl_3$): 183.8, 183.4, 158.8, 158.7,l 134.9, 134.8 l, 134.7, 134.1, 130.0, 128.1, 126.0, 123.8, 119.3, 72.4, 68.7, 64.0, 63.9, 63.7, 61.8, 61.7, 61.6, 21.8, 21.1 ppm. FAB MS *m*/*z* (M^+): calcd, 416.15. Found, 417.0. IR (KBr plate, cm^{-1}): 1658, 1577.