

Supramolecular fluorescent probes for the detection of mixed alkali metal ions that mimic the function of integrated logic gates

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Two fluorescent probes **1** and **2** are developed that are capable of measuring two different metal ions under basic and acidic conditions, respectively. These probes contain a fluorophore, whose two forms are interconvertible in acidic and basic solutions and have the potential to measure the concentration of each metal ion in a mixture of caesium–potassium or sodium–potassium ions, respectively. Probe molecules **1** and **2** can also be portrayed as logic gates that function as a combination of one AND and one INHIBIT gate.

Introduction

Many researchers are taking steps toward various approaches to make computer-based molecules and molecular-scale components, including quantum arrays, nanoparticles, nanocell, and nanotubes.¹ As the chipmaker is edging closer and closer to fundamental limits on how many transistors and wires can be crammed onto a conventional silicon chip, these molecular electronics are foreseen to be “bottom up” alternative and the salvation of next generation of chips. Molecular devices which function as wires,^{2–5} switches,^{6–12} diodes,^{13–14} and logic gates^{15–21} have indeed been reported. Among these approaches, luminescence is of particular interest because of the advantages of photons as output over electrons, such as reduced “connection problem”. Recently, five basic logic gates, YES, NOT, AND, OR, XOR and two integrated logic functions, OR NOT and INHIBIT^{22,23} based on Photoinduced-Electron Transfer (PET) processes have also been described. The design of more integrated logic gates is underway for more sophisticated logic gates behavior.

Aside from the rapidly-growing interest in the molecular information processing, fluorescent sensors have also been an active topic of research in recent years for their wide application in various chemical and biological processes.²⁴ Fluorescent probes enable researchers to detect a wide range of chemicals from metal ions to complex biomolecular assemblies with exquisite sensitivity and selectivity.^{25–27} A large family of fluorescent sensors is based on photo-induced electron transfer (PET) quenching of the fluorophore by the receptor.^{28–30} Most of the current fluorescent probes are designed to detect only one species. A multicolor labeling experiment entails the deliberate introduction of two or more probes to monitor different species simultaneously. However, only a few such systems have been studied because of the strict requirements to utilize this technique.³¹ These requirements include absorption at a coincident excitation wavelength, a well-separated emission spectra of the two or more fluorophores, the absence of energy transfer between the two fluorophores, the absence of transient excited-state collisional quenching, and the absence of excited state dimer formation. These requirements have created a barrier to the development of such dual or multicolor sensors.

Recently,³² we have designed and synthesized one novel fluorescent probe **1** as shown in Scheme 1. Our results have shown that this molecule can be used to detect caesium ions in acidic conditions, but potassium ions in basic solutions. Based on the same design, we synthesized another probe **2** (Scheme 1). Logically, **2** would be a potassium sensor in basic solutions and a sodium sensor in acidic solutions. In this paper, we report the detailed fluorescence behaviors of both fluorescence probes **1** and **2**. The unique fluorescence behaviors of **1** and **2** suggest that another approach for a mixture of dual components sensing is feasible. Furthermore, the fluorescence behaviors of **1** and **2** may be used as an logic AND or INHIBIT gate switched by H⁺ for nano-computational technology.

Results and discussion

Absorption and fluorescence of **1** and **2** in acidic and basic solutions

The absorption spectra of **2** in basic and acidic solutions are shown in Fig. 1. In basic conditions, addition of K⁺ slightly

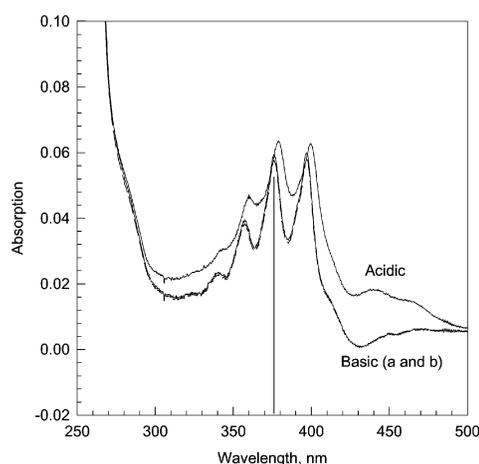
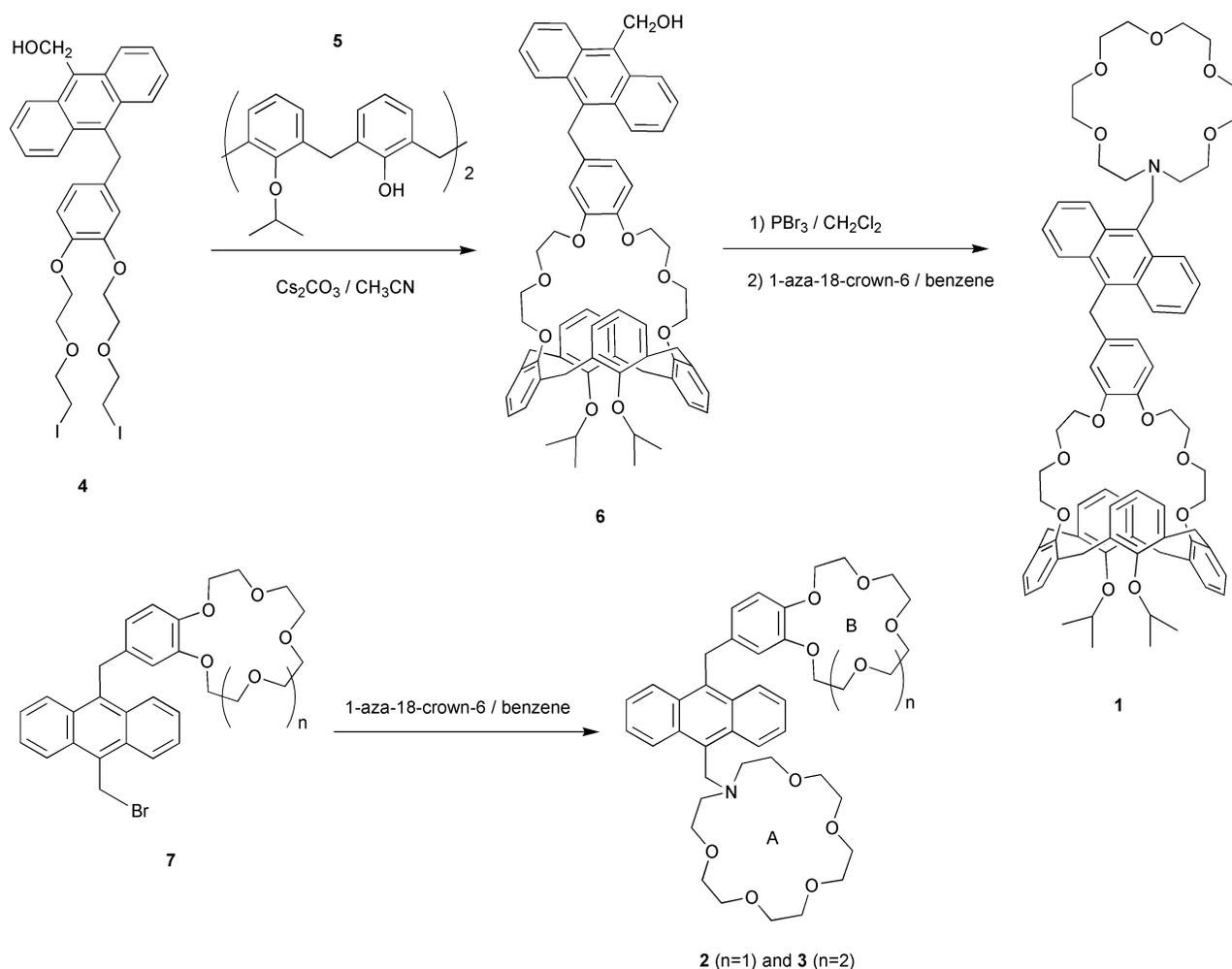


Fig. 1 The absorption spectra of **2** in methanol solution under basic conditions ((a) in the absence and (b) presence of 10^{-3} mol L⁻¹ K⁺) using benzyltrimethylammonium hydroxide, 1×10^{-2} M as proton scavenger and under acidic conditions (1×10^{-2} mol L⁻¹ HCl).



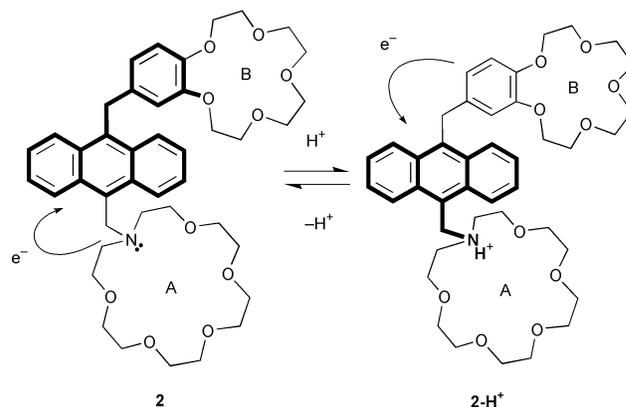
Scheme 1 The structures and synthetic routes of **1**, **2** and **3**.

increases the extinction coefficients of **2**, but does not alter the fluorescence profile of **2**. The absorption spectra of **2** in acidic conditions, however, showed a 3 nm red-shift of the maximum absorption peak of **2** (380 nm) compared with basic solutions (377 nm) with an isosbestic point excitation at 376 nm. This red-shift of absorption observed is attributed to the electrostatic stabilization of the anthracene excited singlet state by the electron-withdrawing ammonium methyl group. The absorption spectra of **1** in acidic and basic solutions are similar to that of **2**.

Similar to the absorption spectra of **2**, the emission ($\lambda_{\text{ex}} = 376$ nm, isosbestic point excitation in both acidic and basic conditions) peak of **2** (1×10^{-6} mol L $^{-1}$) in MeOH under acidic conditions (429 nm) red-shifts 4 nm compared with basic conditions (425 nm) because of the protonation of the aminomethyl group as shown in Fig. 2 (a and b).

In molecule **2**, two receptors are connected with an anthracene molecule. One receptor is benzocrown-5, which is a good host for sodium ions.³³ The other is aza-crown-6, which has the right cavity size for K $^{+}$ complexation.³⁴

Under basic conditions (using 1×10^{-3} mol L $^{-1}$ benzyltrimethylammonium hydroxide as the proton scavenger³⁵) in methanol, a weak emission from **2** is observed (curve a in Fig. 2a) owing to quenching of anthracene emission by the aminomethyl moiety in the crown ring A (Scheme 2, $\Delta G \approx -0.1$ eV¹⁷). Addition of K $^{+}$ ions (1×10^{-4} mol L $^{-1}$), which forms a strong complex with crown ring A, causes a 7.2 fold enhancement in the fluorophore emission (curve b, Fig 2a). Addition of Na $^{+}$ (1×10^{-4} mol L $^{-1}$, curve c in Fig. 2a), on the other hand, does not alter the fluorescence intensity of **2**, suggesting a weak complexation constant between the crown ring A and sodium. It should be mentioned that even though ring B



Scheme 2 The two PET processes in **2** switched by H $^{+}$.

can complex with sodium ions under basic conditions, such complexation does not have any effects on the PET quenching process.

In acidic media, the fluorescence intensity of **2** (in the form of **2-H $^{+}$**) in MeOH does not change significantly (curve a, Fig. 2b) even though the nitrogen atom of ring A, an electron donor component that quenches the fluorescence of anthracene, is protonated. This is due to the formation of a new PET fluorophore–receptor pair, in which the emission of anthrylmethylammonium is quenched by the dialkoxybenzene moiety of crown ring B (see Scheme 2). The driving force, ΔG , is calculated to be -0.1 eV¹⁷ (as a comparison, in basic conditions, the $E_{1/2}^{\text{red}}$ of the fluorophore does not change upon complexation of K $^{+}$ with right-hand ring A, so the K $^{+}$ –ring A complexation does not trigger the formation of such a new

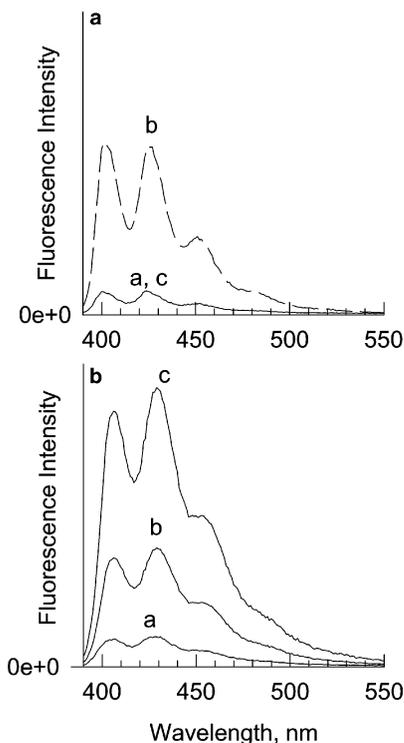


Fig. 2 (a) Fluorescence spectra of **2** (1×10^{-6} mol L⁻¹) in methanol under basic conditions (curve a) using benzyltrimethylammonium hydroxide, 1×10^{-2} mol L⁻¹ as proton scavenger in the presence of K^+ (1×10^{-4} mol L⁻¹) and Na^+ (1×10^{-4} mol L⁻¹) ions (curves b and c, respectively). (b) Fluorescence spectra of **2-H⁺** (1×10^{-6} mol L⁻¹) in methanol (1×10^{-2} mol L⁻¹ HCl) without (curve a) and with K^+ (2×10^{-2} mol L⁻¹) or Na^+ (2×10^{-2} mol L⁻¹) ions present (curves b and c, respectively). Excitation at the isosbestic point (376 nm) for both **2** and **2-H⁺**.

fluorophore–receptor pair). In consequence, the emission of **2-H⁺** increases 9.4 fold upon addition of Na^+ ions (3×10^{-2} mol L⁻¹) (curve c, Fig. 2b), but only 4 fold (curve b, Fig. 2b) upon addition of K^+ ions (3×10^{-2} mol L⁻¹). When the amine group is protonated, metal ions can no longer bind to the crown ring A because of the electrostatic repulsion between the protonated amine and the positive ion. The observed PET effect upon metal ion complexation under these conditions can thus be attributed to a change in the energetic such that the oxygen lone pair electrons of dialkoxybenzene in crown ring B can no longer fully participate in the PET process causing an enhancement in the emission of the fluorophore molecule (fluorescence turned on).¹⁷ The fluorescence behavior of **1** is similar to that of **2** except that it is Cs^+ sensitive in acidic solutions.

Solvent effect on the fluorescence of **2**

Since the emission behavior and fluorescence intensity enhancement of **1** and **2** could be influenced by the solvent polarity,³⁶ the changes in fluorescence intensity (428 nm) of **2** as a function of MeOH composition in CH_2Cl_2 –MeOH solvent mixture in both acidic and basic conditions were investigated and shown in Fig. 3. In basic conditions, the fluorescence intensity of **2** decreases while the ratio of MeOH increases due to the known polarity effect on the electron transfer process. In acidic conditions, the maximum emission intensity for **2** is obtained in the solvent mixture containing 10% methanol in dichloromethane. The observed increase in the emission intensity upon addition of a small amount of methanol to dichloromethane suggests an interaction between methanol and the crown ether-5, which was also observed in the cyanoanthracene system.³⁶ The interaction of methanol with the crown ether through hydrogen bonding can suppress the electron transfer process (PET) and enhance the fluorescence intensity of **2**. As the ratio of MeOH is

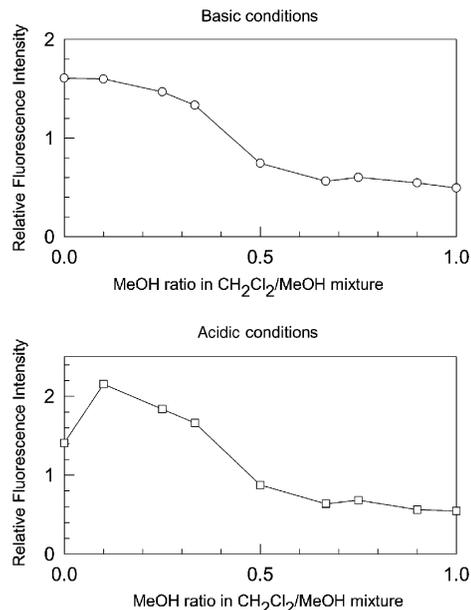


Fig. 3 The solvent effects on the fluorescence intensity of **2** (1×10^{-6} mol L⁻¹) in CH_2Cl_2 –MeOH mixture.

increased, the polarity effect on the electron transfer process begins to dominate and results in a decrease in fluorescence intensity. The fluorescence quantum yields of **2** and the maximum quantum yields upon complexation with K^+ (in basic conditions) and Na^+ (in acidic conditions) are shown in Fig. 4 and the complexation constants of **2** with metal ions in

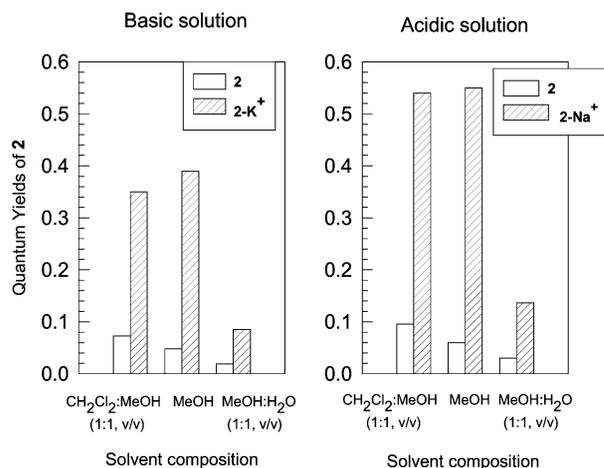


Fig. 4 The solvent effect on the fluorescence enhancements of **2** in basic and acidic solutions upon complexation with K^+ and Na^+ , respectively.

both acidic and basic conditions are listed in Table 1. The reported fluorescence quantum yields were measured relative to 9,10-diphenylanthracene in MeOH ($\phi_f = 0.94$).³⁷

The complexation constants, K , are calculated from the emission intensity profiles using equation (1)

$$\frac{I - I_0}{I_\infty - I} = K \left([M]_t - [L]_t \frac{I - I_0}{I_\infty - I_0} \right) \quad (1)$$

where I is the fluorescence intensity of the solution at certain metal ion concentrations, I_0 is the fluorescence intensity of the probe in the absence of metal ions, I_∞ is the fluorescence intensity when no further changes in the emission occur upon addition of the metal ion, L is the concentration of probe molecule **2** or **2-H⁺** and M represents metal ion concentration.

Table 1 The complexation constants, K , of **2** with K^+ and **2-H** $^+$ with Na^+ in different solvents or solvent mixtures (1×10^{-6} mol L $^{-1}$)

Solvents	CH ₂ Cl ₂ -MeOH (1 : 1, v/v)	MeOH	MeOH-H ₂ O (1 : 1, v/v)
K/L mol $^{-1}$ of aza-crown in 2 with K^+	1.2×10^6	6.3×10^4	1.9×10^3
K of 2-H $^+$ with Na^+	1.2×10^3	6.2×10^2	100

Table 2 The maximum fluorescence quantum yield (Φ) and complexation constants, K , for the complexation of various alkali metal ions by **1** and **1-H** $^+$ (1×10^{-6} mol L $^{-1}$) in CH₃OH. λ_{ex} = 376 nm at the isosbestic point for both **1** and **1-H** $^+$. The quantum yields were determined relative to 9,10-diphenylanthracene in MeOH, $\Phi_r = 0.94$ ³⁹

Metal ion M $^+$	Free	Li $^+$	Na $^+$	K $^+$	Rb $^+$	Cs $^+$
Φ_{em} of 1	0.061	0.064	0.068	0.42	0.32	0.15
K of aza-crown in 1 with ions	–	15	6.4×10^2	7.94×10^4	1.29×10^4	7.60×10^2
Φ_{em} of 1-H $^+$	0.094	0.096	0.13	0.25	0.20	0.36
K for 1-H $^+$	–	10	9.1×10^3	3.24×10^4	1.15×10^6	7.08×10^6

Table 1 shows that the complexation constants of **2** with metal ions are severely affected by the solvent composition. The complexation of **2** with K^+ or Na^+ in CH₂Cl₂-MeOH (1 : 1 v/v) is much stronger than in MeOH. The complexation of **2** with metal ions is weaker in the MeOH-H₂O mixture than in MeOH. These results further prove the existence of the interactions between polar protic solvents, such as H₂O and MeOH, with crown ether, which would weaken the binding of crown ether with metal ions. However, although the complexation constants of **2** with metal ions are stronger in CH₂Cl₂-MeOH mixtures than in MeOH, the most significant fluorescence enhancement of **2** upon addition of metal ions are observed in MeOH solution (8.1 fold upon binding with K^+ in basic solutions, 9.2 fold upon binding with Na^+ in acidic solutions) as shown in Fig. 4. This is because of the relatively lower quantum yields of **2** in MeOH than in CH₂Cl₂-MeOH mixtures due to the polarity effect but similar maximum fluorescence quantum yields of **2-K** $^+$ or **2-Na** $^+$ in both MeOH and CH₂Cl₂-MeOH solutions as shown in Fig. 4.

The pK_a of **2** in MeOH-H₂O (1 : 1 v/v) was calculated to be 7.8 according to equation (2).³⁸

$$\text{Log} \frac{I_{F_{\max}} - I_F}{I_F - I_{F_{\min}}} = \text{pH} - \text{p}K_a \quad (2)$$

Where I_F is the fluorescence intensity of **2** in the solution at a certain pH, $I_{F_{\min}}$ is the fluorescence intensity of the unprotonated form of probe **2**, $I_{F_{\max}}$ is the fluorescence intensity of the protonated form of probe **2**.

Complexation study of **1** and **2** in acidic and basic solutions

The effects of various alkali metal ions concentration on the emission of **2** in a basic media are shown in Fig. 5a. Both Li $^+$ and Na $^+$ ions show no effect on the emission behavior of **2** and the most dramatic enhancement under these conditions is observed for K^+ ions with the onset at 10^{-6} M. Although both crown rings A and B present in **2** can bind alkali metal ions, the fact that emission is quenched by the free amine group¹⁷ present in ring I (under neutral or basic conditions) suggests that the observed enhancement is due to complexation of ions with this ring disabling nitrogen lone pair electrons from participation in the PET process. This is consistent with the reported results for a derivative of aza-18-crown-6, which acts as a good K^+ receptor.^{24,39}

The change in emission behavior of **2** in MeOH under acidic conditions (1×10^{-2} M of HCl) as a function of alkali metal ion concentration is shown in Fig. 5b. It is shown that addition of Li $^+$ and Cs $^+$ ions (up to 10^{-2} mol L $^{-1}$ concentration) to **2-H** $^+$ solution slightly increases the emission intensity while K^+ and Rb $^+$ ions induce a reasonable enhancement in the emission. The most dramatic enhancement in the emission behavior of **2-H** $^+$ is observed for Na^+ ions with the onset at 10^{-5} mol L $^{-1}$ concen-

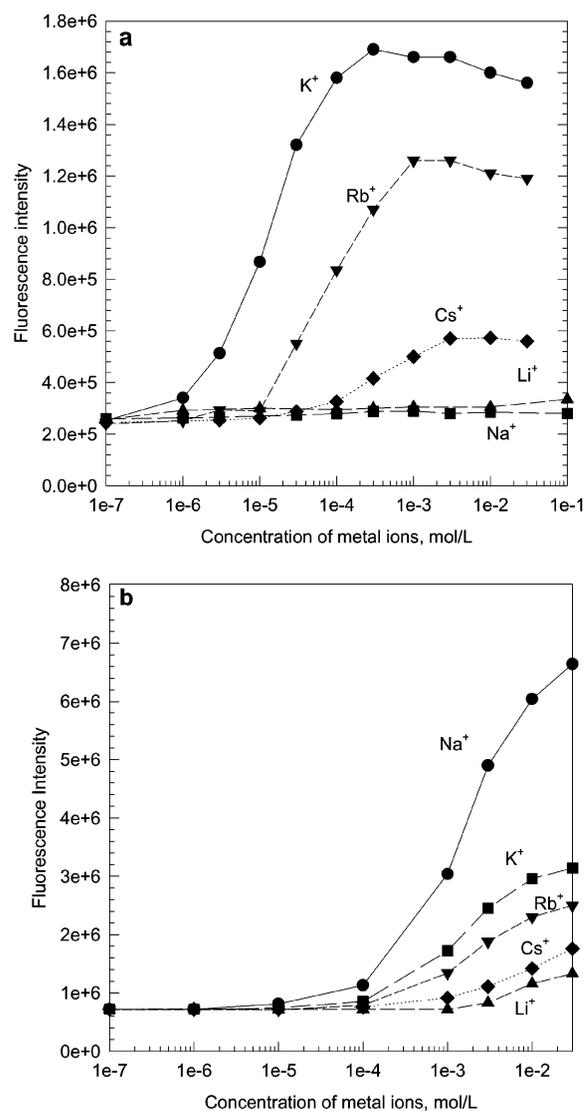


Fig. 5 (a) Changes in the fluorescence intensity of **2** (1×10^{-6} mol L $^{-1}$) in basic methanol (benzyltrimethylammonium hydroxide, 1×10^{-2} mol L $^{-1}$ as proton scavenger) as a function of concentration of various alkali metal ions; (b) Change in the emission intensity of **2-H** $^+$ (1×10^{-6} mol L $^{-1}$) in acidic methanol (1×10^{-2} mol L $^{-1}$ HCl) as a function of concentration of various alkali metal ions. Excitation at the isosbestic point for both **2** and **2-H** $^+$ is at 376 nm.

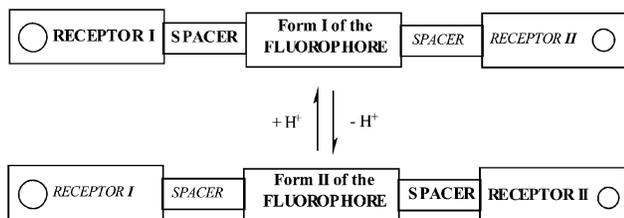
tration of this ion. Similarly, the fluorescence behaviors of **1** suggest that **1** is Cs $^+$ sensitive in acidic solution and K^+ sensitive in basic solutions. Tables 2 and 3 list the maximum fluorescence quantum yields for **1** and **2** when complexed with different alkali metal ions under basic and acidic conditions.

Table 3 The maximum fluorescence quantum yield (Φ) and complexation constants, K , for the complexation of various alkali metal ions by **2** and **2-H⁺** (1×10^{-6} mol L⁻¹) in CH₃OH. $\lambda_{\text{ex}} = 376$ nm at the isosbestic point for both **2** and **2-H⁺**. The quantum yields were determined relative to 9,10-diphenylanthracene in MeOH, $\Phi_{\text{f}} = 0.94$ ³⁹

Metal ion M ⁺	Free	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Φ_{em} of 2	0.048	0.060	0.053	0.39	0.31	0.12
K of aza-crown in 2 with ions	–	10	7.4×10^2	6.30×10^4	1.26×10^4	2.82×10^3
Φ_{em} of 2-H⁺	0.060	0.098	0.55	0.26	0.22	0.15
K of 2-H⁺	–	65	6.2×10^2	6.0×10^2	3.9×10^2	1.5×10^2

The complexation constants, K , for ring A of **2** and ring B of **2-H⁺** with alkali metal ions can be calculated from the emission intensity profiles shown in Figs 5a and 5b using equation (1) and the figure reported before³² for **1**. The complexation constants (K) reported in Tables 2 and 3 were calculated using a non-linear curve-fitting method⁴⁰ for equation (1) to fit the observed experimental emission data. These data clearly show that under basic conditions (where crown ring B is passive and makes no contribution to PET) alkali metal ion binding to crown ring A in **2** results in the observed changes in the fluorophore emission by PET in the following order $\text{K}^+ > \text{Rb}^+ \gg \text{Cs}^+ \gg \text{Na}^+$. The role of ring B in the PET process is pronounced under acidic conditions where the nitrogen atoms are prohibited from participating in the PET process. The affinity of crown ether-5 to preferentially complex Na⁺ relative to K⁺ ions is in good agreement with a previous report.⁴¹

Probe molecules **1** and **2** have been shown to be remarkable dual sensors capable of detecting two ions in solution at two different pHs. In general, a PET sensor consists of a guest binding site as the receptor and a photointeraction site (fluorophore) for signal transduction. In our system, the two forms (anthracene and anthrylmethylammonium) of the fluorophore are interconvertible being switched by H⁺ and OH⁻ as shown in Scheme 3. Under basic conditions, receptor **I** and one form of



Scheme 3 A PET dual component fluorescent sensor switched by H⁺.

the fluorophore (anthracene) forms a PET pair and the sensing behavior depends on the status of receptor **I** (activated or passive) while receptor **II** makes no contribution to the PET process. In contrast, in acidic media, the PET pair becomes the other form of the fluorophore (anthrylmethylammonium) with receptor **II**, and the sensing behavior will be solely dependent on the status of receptor **II** (receptor **I** becomes inactive). Protons can play this role by switching the emission response of the fluorophore in **2** on (in acidic media) and off (in basic media) for sodium and *vice versa* for potassium. This unique capability renders probe molecule **2** the potential to detect both sodium and potassium ions by changing the pH of the media.

The fluorescence behaviors of **1** are very similar to that of **2** except for Cs⁺ sensitivity in acidic conditions.³²

Fluorescence behavior of **1** and **2** in mixed ions solutions

Further studies on the changes in the fluorescence intensities of **1** and **2** were conducted in MeOH solutions containing mixtures of different concentration of Cs⁺ and K⁺, or Na⁺ and K⁺, respectively, at two pH conditions (acidic and basic conditions). The results are shown as three-dimensional maps in Figs. 6 and 7. For example, in basic solution (Fig. 6a), the fluorescence

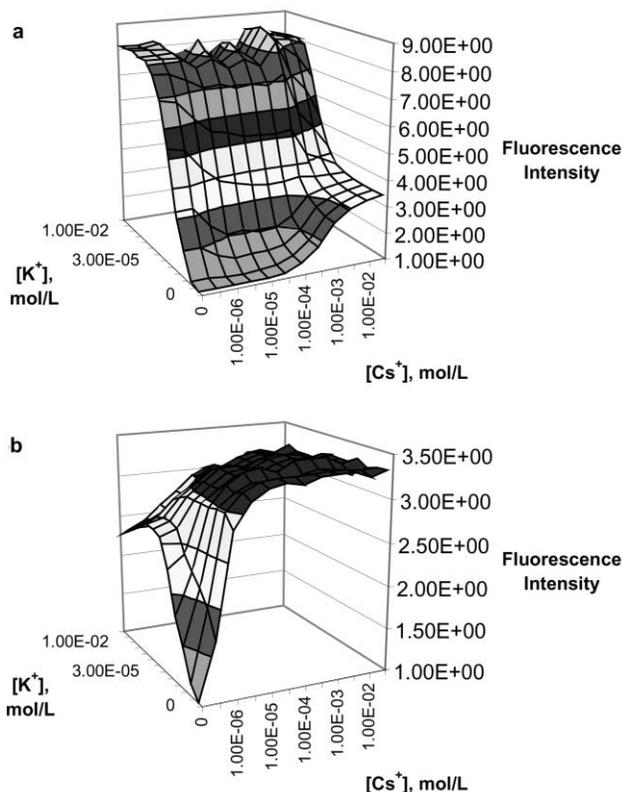


Fig. 6 (a) Changes in the fluorescence intensity of **1** (1×10^{-6} mol L⁻¹) in basic methanol (benzyltrimethylammonium hydroxide, 1×10^{-2} mol L⁻¹ as proton scavenger) as a function of different concentrations of K⁺ and Cs⁺; (b) Change in the emission intensity of **1-H⁺** (1×10^{-6} mol L⁻¹) in acidic methanol (1×10^{-2} mol L⁻¹ HCl) as a function of different concentrations of K⁺ and Cs⁺. Excitation at the isosbestic point for both **1** and **1-H⁺** is at 376 nm.

enhancement region of **1** takes place at $[\text{K}^+] = 1 \times 10^{-6} - 1 \times 10^{-4}$ mol L⁻¹ in the absence or presence of low concentration of Cs⁺. However, although the complexation constant for ring I of **1** with Cs⁺ is low, higher concentrations of Cs⁺ could competitively complex with ring I of **1**. Consequently, a higher concentration of K⁺ is required to replace or compete with Cs⁺ to fully complex with ring I of **1**. At high concentration of Cs⁺ (e.g. 3×10^{-2} mol L⁻¹), the fluorescence enhancement region of **1** is shifted to when $[\text{K}^+] = 1 \times 10^{-5} - 1 \times 10^{-2}$ mol L⁻¹. In acidic solution (Fig. 6b), **1** is converted to **1-H⁺**, and the fluorescence enhancement region of **1-H⁺** takes place when $[\text{Cs}^+] = 1 \times 10^{-7} - 1 \times 10^{-5}$ mol L⁻¹ in the absence of K⁺. However, since K⁺ could also complex with **1-H⁺** and cause a relatively weaker fluorescence enhancement, the Cs⁺ sensing regions of **1** in the absence or presence of K⁺ are different as shown in Fig. 6b.

These results suggest that probe **1** and **2** could potentially function as fluorescent sensors to determine the presence of different ions in a mixture containing both Cs⁺ and K⁺, or Na⁺ and K⁺, respectively. The fluorescence behaviors of **1** or **2** in a solution containing a mixture of metal ions are different from that with only one metal ion present. For instance, when a mixture containing 5×10^{-3} mol L⁻¹ Na⁺ and 1×10^{-3} mol L⁻¹ K⁺ is used, an eight-fold enhancement in the fluorescence intensity

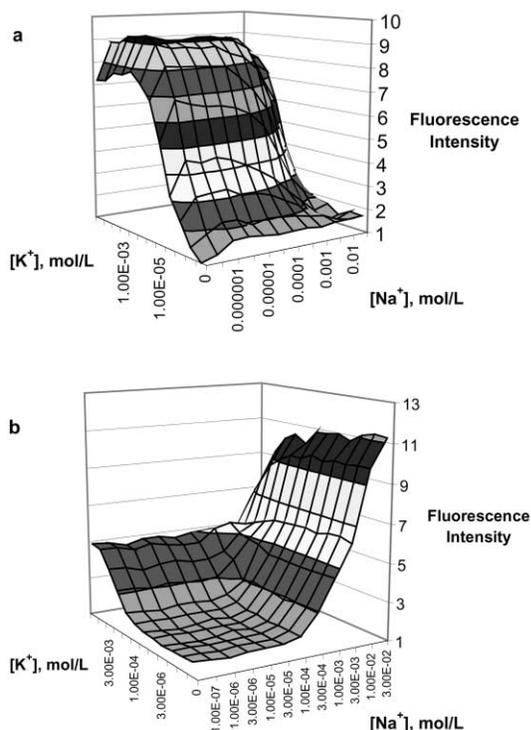


Fig. 7 (a) Changes in the fluorescence intensity of **2** ($1 \times 10^{-6} \text{ mol L}^{-1}$) in basic methanol (morpholine, $1 \times 10^{-2} \text{ mol L}^{-1}$ as proton scavenger) as a function of different concentrations of K^+ and Na^+ ; (b) Change in the emission intensity of 2-H^+ ($1 \times 10^{-6} \text{ mol L}^{-1}$) in acidic methanol ($1 \times 10^{-2} \text{ mol L}^{-1}$ HCl) as a function of different concentrations of K^+ and Na^+ . Excitation at the isosbestic point for both **2** and 2-H^+ is at 376 nm.

of **2** is observed in both acidic and basic media. However, in a solution that contains only $5 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}^+$, and no K^+ , **2** shows an eight-fold fluorescence enhancement in acidic solution, and no fluorescence increase in basic solution. On the other hand, in a solution that contains only $1 \times 10^{-4} \text{ mol L}^{-1}$ of K^+ , and no Na^+ , **2** shows an eight-fold fluorescence enhancement, but no fluorescence increase in an acidic media. By data analysis of the fluorescence intensities of **2** determined in both acidic and basic solutions, the concentrations of both K^+ and Na^+ could be determined simultaneously.

The fluorescence behavior of **3** in basic and acidic conditions

Compound **3** was also synthesized based on the same design described above as a useful supplementation. It is known that both benzo-18-crown-6 and aza-18-crown-6 are K^+ receptors, but their complexation constants with K^+ are different. Based on our above discussion, the K^+ detection range of **3** under basic or acidic conditions would be different. Our results show that these expectations are realized as shown in Fig. 8. In basic solution, the fluorescence enhancement region of **3** takes place at $[\text{K}^+] = 1 \times 10^{-6} - 3 \times 10^{-4} \text{ mol L}^{-1}$, while in the acidic solution, the fluorescence enhancement region of **3** takes place at $[\text{K}^+] = 1 \times 10^{-7} - 1 \times 10^{-4} \text{ mol L}^{-1}$. The complexation constants of **3** with K^+ are calculated to be 5.3×10^4 and $2.2 \times 10^5 \text{ L mol}^{-1}$, in basic and acidic conditions, respectively. Overall, compound **3** can be used to measure the K^+ concentration from $1 \times 10^{-7} \text{ mol L}^{-1}$ to $3 \times 10^{-4} \text{ mol L}^{-1}$, which is broader than a single fluorescent probe containing only aza-18-crown-6 or benzo-18-crown-6 receptor.

Logic gates

Molecules **1** and **2** also exhibit a unique logic gate system that combines an AND gate and an INHIBIT gate as described in Fig. 9 by two representations. For example, **2** combines an AND gate and an INHIBIT gate with the input notations IN_1 , IN_2 ,

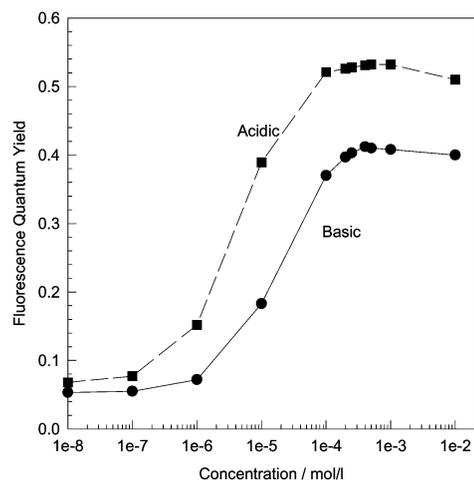


Fig. 8 Changes in the fluorescence intensity of **3** ($1 \times 10^{-6} \text{ mol L}^{-1}$) in basic methanol (benzyltrimethylammonium hydroxide, $1 \times 10^{-2} \text{ mol L}^{-1}$ as proton scavenger) and in acidic methanol ($1 \times 10^{-2} \text{ mol L}^{-1}$ HCl) as a function of $[\text{K}^+]$. Excitation at the isosbestic point for both **3** and 3-H^+ is at 376 nm.

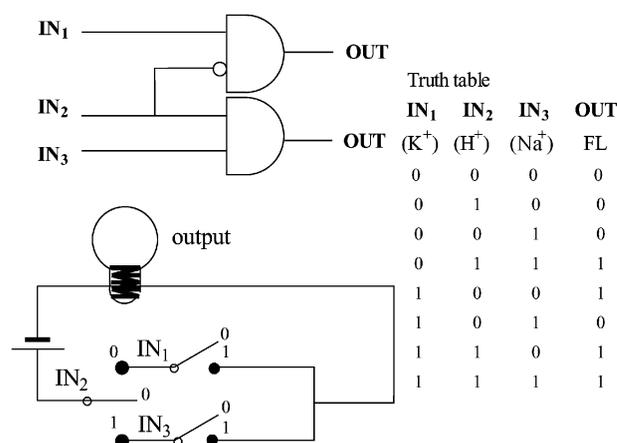


Fig. 9 Schematic representation of **2** showing an AND gates and an INHIBIT gate logics switched by H^+ . Inset shows the truth table for this logical gating performance.

and IN_3 signifying presence (1) or absence (0) of potassium ion (K^+), proton (H^+), and sodium ion (Na^+) in solution. Notation OUT refers to fluorescence of **2** being on (1) or off (0). The truth table shown in the inset of Fig. 9 was constructed based on the fluorescence data in MeOH (Fig. 2) and the scheme depicted in Scheme 2 to demonstrate the logic gating behavior of **2**. The emission of **2** is on in the presence of both Na^+ and H^+ , or in the presence of K^+ and absence with H^+ . H^+ acts as a switch in this unique logic system. However, a defect exists for **2** as shown in Fig. 2, in acidic conditions, the fluorescence intensity of molecules **2** increases by a factor of 9.2 when $10^{-2} \text{ mol L}^{-1}$ of sodium are present, but also increases by a factor of 4.3 when $10^{-2} \text{ mol L}^{-1}$ of K^+ are present. **1** would be a better such combined logic system based on the fluorescence data in Fig. 6 when $2 \times 10^{-6} \text{ mol L}^{-1}$ of Cs^+ and K^+ are used. In acidic conditions, addition of $2 \times 10^{-6} \text{ mol L}^{-1}$ of Cs^+ increases the fluorescence intensity of **1** by a factor of 3.4, but no fluorescence intensity change of **1** is observed upon addition of $2 \times 10^{-6} \text{ mol L}^{-1}$ of K^+ .

Experimental

Instrumentation

^1H NMR spectra were obtained in chloroform- d on a 400 MHz Bruker spectrometer. Fluorescence spectra were measured with

a Spex fluorolog 2 or a Hitachi F4010 spectrophotometer. UV-absorption spectra were obtained on a Shimadzu UV-2401PC spectrophotometer. Matrix assisted laser desorption/ionization-Fourier transform ion cyclotron resonance is presented by the acronym MALDI-FTICR. Mass spectra were acquired on a Finnigan FT/MS 2001 Fourier transform ion cyclotron resonance mass spectrometer equipped with a nitrogen laser (337 nm, Laser Photonics).

Materials

Benzyltrimethylammonium hydroxide (Aldrich), caesium acetate (Aldrich, 99.9%), rubidium acetate (Aldrich, 99.9%), potassium acetate (99.9%), *p*-H-calix[4]arene (Aldrich) were used as received, 25,27-bis(2-propoxy)-26,28-dihydroxy-*p*-H-calix[4]arene (**5**) was synthesized according to a method described in the literature.⁴² Methylene chloride (Merck, 99.98%), methanol (Merck, HPLC grade), benzene (Merck, GR grade), hexane (Merck, GR grade), sodium acetate (Fisher, 100%), lithium acetate (Alfa, GR grade) were all used as received.

Syntheses

1,2-Bis(5-iodo-3-oxa-1-pentoxo)-4-(10-hydroxymethyl-9-anthrylmethyl)benzene (4). Compound **4** was synthesized using the previously reported procedure.³⁶

1,3-Alternate 25,27-bis(2-propoxy)-26,28-[4-(10-hydroxymethyl-9-anthrylmethyl)-1,2-phenylenebis(5-dioxy-3-oxapentyl)]-calix[4]arene (6). Compound **6** was synthesized according to a procedure described before.⁴² A mixture of 0.20 g (0.39 mmol) of 25,27-bis(2-propoxy)-26,28-dihydroxycalix[4]arene (**5**), 0.29 g (0.4 mmol) of 1,2-bis(5-iodo-3-oxa-1-pentoxo)-4-(10-hydroxymethyl-9-anthrylmethyl)benzene and 1.63 g (5 mmol) of Cs₂CO₃, in 100 ml acetonitrile was refluxed with stirring for 3 days. After cooling to room temperature, the solvents were removed under reduced pressure. The residue was extracted with CH₂Cl₂ and washed using 2 M HCl, NaCl solution, and water respectively. The CH₂Cl₂ layer was dried using anhydrous Na₂SO₄, and the solution was concentrated under reduced pressure. The mixture was purified by flash chromatography giving 0.28 g (70% yield) of a yellow powder, C₆₄H₆₆O₉ requires (C, 78.50%; H, 6.79%; O, 14.70%), found: C, 78.14%; H 6.45%; O, 15.03%; ¹H NMR (CDCl₃), δ 8.50 (d, 2H, Ar), 8.32 (d, 2H, Ar), 7.56 (t, 2H, Ar), 7.47 (t, 2H), 7.04–6.59 (m, 15H, Bz), 5.70 (s, 2H, ArCH₂O), 5.09 (s, 2H, ArCH₂Bz), 4.22 (m, 2H, OCH), 4.07–3.28 (m, 24H, CH₂), 0.94 (d, 12H, CH₃).

1,3-Alternate 25,27-bis(isopropoxy)-26,28-[4-(10-bromomethyl-9-anthrylmethyl)-1,2-phenylenebis(5-dioxy-3-oxapentyl)]-calix[4]arene. 0.2 g of 25,27-bis(isopropoxy)-26,28-[4-(10-hydroxymethyl-9-anthrylmethyl)-1,2-phenylenebis(5-dioxy-3-oxapentyl)]calix[4]arene and 1 g of PBr₃ were mixed in dry methylene chloride (50 ml) in an ice bath and the solution was stirred for 6 h at 0 °C. After adding 100 ml of water, the mixture was twice extracted with methylene chloride. The organic layer was washed with water twice and then dried with anhydrous Na₂SO₄ overnight. The solvent was removed under reduced pressure affording 0.19 g crude product (89%), which was used in the next step without further purification.

1,3-Alternate 25,27-bis(isopropoxy)-26,28-[4-[10-(1-aza-4,7,10,13,16-pentaoxacyclooctadecanylemethyl)-9-anthrylmethyl]-1,2-phenylenebis(5-dioxy-3-oxapentyl)]calix[4]arene (1). 0.15 g of 25,27-bis(isopropoxy)-26,28-[4-(10-bromomethyl-9-anthrylmethyl)-1,2-phenylenebis(5-dioxy-3-oxapentyl)]calix[4]arene (0.14 mmol) was dissolved in benzene (30 ml) and a solution of 52.4 mg (0.2 mmol) of 1-aza-18-crown-6 in benzene (15 ml) was added. The solution was refluxed for 12 h. After the solution was cooled to room temperature, the solvent was evap-

orated and the product was purified by flash chromatography using methylene chloride–acetone (1 : 1 volume) as eluant to afford 0.13 g yellow powder (76%). Mp 110 °C. C₇₆H₈₉NO₁₃ requires: (C, 74.55%; H, 7.33%; O, 16.99%), found: C, 74.74%; H, 6.97%; O, 17.09%; ¹H NMR (CDCl₃) δ 8.62 (d, 2H, Ar), 8.28 (d, 2H, Ar), 7.55–7.40 (m, 4H, Ar), 7.10–6.56 (m, 15H, Bz), 4.96 (s, 2H, ArCH₂Bz), 4.65 (s, 2H, ArCH₂N), 4.25 (m, 2H, OCH), 4.10–2.86 (m, 48H, OCH₂), 0.94 (d, 12H, CH₃). Molecular weight was determined by MALDI and gave *m/z* M⁺ 1224.3, calcd *m/z* 1224.5.

2,3,5,6,8,9,11,12-Octahydro-15-[10'-(bromomethyl)-9'-anthrylmethyl]-1,4,7,10,13-benzopentaoxacyclopentadecin (7). Compound **7** was synthesized following the literature procedure.¹⁷

2,3,5,6,8,9,11,12-Octahydro-15-[10'-(1-aza-4,7,10,13,16-pentaoxacyclooctadecanylemethyl)-9'-anthrylmethyl]-1,4,7,10,13-benzopentaoxacyclopentadecin (2). 0.22 g (0.4 mmol) of 2,3,5,6,8,9,11,12-octahydro-15-[10'-(bromomethyl)-9'-anthrylmethyl]-1,4,7,10,13-benzopentaoxacyclopentadecin was dissolved in benzene 30 ml and a solution of 1-aza-18-crown-6 (0.104 g, 0.4 mmol) in benzene (15 ml) was added to it. The solution was refluxed for 12 h. After the solution cooled to room temperature, the solvent was evaporated and the product was purified by flash chromatography using methylene chloride–acetone (1 : 1 volume) as eluant to afford 0.23 g of a yellow sticky oil (79% yield). C₄₂H₅₅NO₁₀ requires (C, 68.74%; H 7.55%; N, 1.91%; O, 21.80%), found: C, 68.24%; H, 7.45%; O, 22.30%; ¹H NMR (CDCl₃), δ 8.60 (d, 2H, Ar), 8.27 (d, 2H, Ar), 7.52–7.38 (m, 4H, Ar), 6.80–6.54 (m, 3H, Bz), 4.90 (s, 2H, BzCH₂Ar), 4.53 (s, 2H, ArCH₂N), 3.92–2.66 (m, 40H, OCH₂). MS, *m/z* M⁺ 734, calcd *m/z* 733.89

2,3,5,6,8,9,11,12,14,15-Decahydro-18-[10'-(1-aza-4,7,10,13,16-pentaoxacyclooctadecanylemethyl)-9'-anthrylmethyl]-1,4,7,10,13,16-benzohexaoxacyclohexadodecin (3). Compound **3** was synthesized based on the same procedure described above for **2** with a total of 12% yield starting with benzo-18-crown-6 instead of benzo-15-crown-5. C₄₄H₅₉NO₁₁ requires (C, 67.93%; H, 7.64%; N, 1.80%; O, 22.62%), found: C, 66.94%; H, 7.76%; O, 23.24%; ¹H NMR (CDCl₃) δ 8.62 (d, 2H, Ar), 8.26 (d, 2H, Ar), 7.55–7.37 (m, 4H, Ar), 6.83–6.53 (m, 3H, Bz), 4.94 (s, 2H, BzCH₂Ar), 4.56 (s, 2H, ArCH₂N), 3.96–2.61 (m, 44H, OCH₂). MS, *m/z* M⁺ 778, calcd *m/z* 777.95

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