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# A Bifunctional Chromogenic Calix[4]arene Chemosensor for Both Cations and Anions: A Potential Ca<sup>2+</sup> and F<sup>-</sup> Switched INHIBIT Logic Gate with a YES Logic Function

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A bifunctional chromogenic calix[4]arene **3**, which contains both triazoles and hydroxy azophenols as both cationic and anionic recognition sites and the azophenol moiety as a coloration unit, was designed and synthesized. The recognition of  $Ca^{2+}$  by **3** gave rise to a marked colour change from green-

## Introduction

The development of naked-eye chemosensors capable of recognizing and sensing anions and cations is one of the most challenging fields in supramolecular chemistry.<sup>[1]</sup> In the past two decades, the colour-inducing azophenol dyes have been widely used in chromoionophores because they change their absorption spectra upon the binding of anions<sup>[2]</sup> or metal ions.<sup>[3]</sup> Hong and co-workers reported the use of a series of azophenol derivatives as chromogenic units to selectively trigger colour change upon complexation with various anions.<sup>[2a-2d]</sup> Moreover, an azobenzenebased chemosensor, which can be used under physiological pH conditions, was reported for the colorimetric detection of the Cu<sup>2+</sup> ion.<sup>[3a]</sup> Calix<sup>[4]</sup>arenes have been utilized as an excellent scaffold for creating attractive host molecules with ion-sensing properties.<sup>[4]</sup> Shinkai and co-workers reported that calix[4]arene containing a 4-(4-nitrophenyl)azophenol unit with three ethyl ester groups showed a perfect lithium ion selectively with respect to the UV/Vis band shift.<sup>[4a,4b]</sup> Chang et al. showed that a bathochromic shift of a *p-tert*butylcalix[4]arene bearing a 1,3-diazophenol unit was observed upon calcium ion complexation.<sup>[4d]</sup> Chen et al. also reported that azocalix[4]arene derivatives allowed not only for highly sensitive and selective detection but also for easy colorimetric differentiation of F-, AcO- and H2PO4- of similar basicity, depending on the azocalix[4]arene structure.<sup>[4q]</sup>

There is considerable interest in the development of calix[4]arene derivatives that behave as molecular logic gates.<sup>[5]</sup> Since the pioneering work by de Silva,<sup>[5a]</sup> remark-

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ish to bright yellow, whereas the recognition of  $F^-$  by **3** showed a colour change from light green to bluish. The colour changes of **3** by the inputs of Ca<sup>2+</sup> and  $F^-$  have been implemented to construct a combinational logic circuit at the molecular level.

able progress has been made in the development and application of molecular logic gates.<sup>[5]</sup> A large number of molecular systems showing logic algebra, such as AND, OR, NOR, INHIBIT, XOR, YES, NOT and XNOR have been reported.<sup>[5,6]</sup> These systems change their properties, such as absorptions, fluorescence and redox potential in a specific fashion in response to a particular input. We have been interested in the design, synthesis and evaluation of chromogenic<sup>[7]</sup> and fluorogenic<sup>[8]</sup> chemosensors. For example, recently we reported a new chromogenic sensor for  $Ca^{2+}$  and Pb<sup>2+</sup> ions based on triazole- and azo-coupled calix[4]arene 5:<sup>[7c]</sup> however, it did not exhibit any chromogenic change toward any anions added. Surprisingly, with a subtle change in its *para*-substituent, compound **3** is not only sensitive to metal ions but also anions; thus, it allows us to test its function as a logic gate. We report herein the synthesis of a bifunctional chromogenic calix[4]arene 3 that exhibits an INHIBIT logic gate with a YES logic function by using  $Ca^{2+}$  and  $F^{-}$  ions as chemical inputs (Figure 1).



Figure 1. Azocalix[4]arenes 3 and 5 and control compound 4.

4700

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#### **Results and Discussion**

The synthesis of host 3 is illustrated in Scheme 1. The diazo coupling reaction of 25,27-bis(O-propargyl)calix[4]arene (1),<sup>[9]</sup> by using *p*-nitroaniline in HCl and NaNO<sub>2</sub>, gave the desired product 2 in 81% yield. The Cu<sup>I</sup>-catalyzed 1,3-dipolar cycloaddition reaction of 2 with 1-(azidomethyl)benzene under Click conditions afforded the 5,17-bis(pnitrophenyl)azo-25,27-bis(1,2,3-triazole)calix[4]arene (3) in 64% yield. Control compound  $4^{[10]}$  was synthesized in 80%yield by using a method similar to that used in the preparation of **2**. All compounds synthesized in this work were fully characterized by spectroscopic data including <sup>1</sup>H and <sup>13</sup>C NMR, MS and HRMS. The absorption maxima ( $\lambda_{max}$ ) and molar extinction coefficients of the chromogenic calix[4]arenes and control compounds synthesized in this work are summarized in Table 1. Next, we investigated the affinities of these azo compounds 2–4 for a series of groups 1A, 2A, transition-metal ions and anions in MeCN/CHCl<sub>3</sub> (v/v = 1000:4) solution.



Scheme 1. Synthetic route for 3: Reagents and conditions: (i) *p*-nitroaniline/acetone, NaNO<sub>2</sub>/4  $\times$  HCl, pyridine, 0 °C, 24 h. (ii) 1-(azidomethyl)benzene, CuI, THF/H<sub>2</sub>O, 50 °C, 18 h.

Table 1. The absorption  $\lambda_{\text{max}}$  and corresponding extinction coefficients of azo compounds **2–4** in MeCN/CHCl<sub>3</sub> ( $\nu/\nu = 1000$ :4).

Compound	$\lambda_{\max}$ [nm]	$\varepsilon  [\mathrm{M}^{-1}  \mathrm{cm}^{-1}]$
2	390	26,000
3	390	32,000
4	384	23,000

Excess (10 equiv.) perchlorate salts of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Ag<sup>+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup> and Cr<sup>3+</sup> were tested to evaluate the metal-ion binding properties of **2–4**. Ligand concentration in all titration experiments was fixed at 10  $\mu$ M in MeCN/CHCl<sub>3</sub> ( $\nu/\nu = 1000:4$ ). Free hosts **2**, **3** and **4** exhibited absorption bands at 390, 390 and 384 nm in MeCN/CHCl<sub>3</sub> ( $\nu/\nu = 1000:4$ ), respectively. The triazole–azophenol host **3**, containing triazoles as the metal-ligating groups, is found to exhibit remarkable selectivity toward Ca<sup>2+</sup>, Pb<sup>2+</sup> and Ba<sup>2+</sup> over all other metal ions. The addition of 10 equivalents of Ca<sup>2+</sup>, Pb<sup>2+</sup> and Ba<sup>2+</sup> induced a bathochromic shift of the triazole–azophenol **3** from  $\lambda_{max} = 390$  to 496, 501 and 485 nm, respectively (Figure 2). However, the UV/Vis spectra of **2**, which does not contain the triazole groups, showed only weak batho-



chromic shifts to  $Ca^{2+}$ ,  $Pb^{2+}$  and  $Ba^{2+}$ , respectively. Moreover, the UV/Vis spectra of control compound **4** did not show any change in the presence of 10 equivalents of thirteen different metal perchlorates (see Figures S5 and S6 in the Supporting Information).



Figure 2. UV/Vis spectra of **3** (10  $\mu$ M) before and after adding an 100  $\mu$ M concentration of various metal perchlorates in MeCN/CHCl<sub>3</sub> ( $\nu/\nu = 1000$ :4).

The two triazole moieties of **3** are proven to form an efficient metal-ion binding site, whereas compounds **2** and **4**, which lack such an efficient metal-ion binding site, showed either little or no binding affinities toward all the metal ions studied here. The geometry of the binding site of the host, comprising the two nitrogen atoms of triazole units and two hydroxys of the azophenol units, seems to be ideal in terms of size and arrangement for the recognition of doubly charged metal cations. Among all attractive forces, the electrostatic interaction of metal cations with two azophenol moieties and the ion-dipole interaction of metal ions with the triazole units are of primary importance.

Upon interaction with Ca(ClO<sub>4</sub>)<sub>2</sub>, the chromogenic sensor **3** in MeCN/CHCl<sub>3</sub> ( $\nu/\nu = 1000:4$ ) solution experienced a marked bathochromic shift in its  $\lambda_{max}$  from 390 to 496 nm ( $\Delta\lambda_{max} = 106$  nm; Figure 3). The greenish solution of free **3** turned a bright-yellow colour upon complexation with Ca<sup>2+</sup> and exhibited an isosbestic point at 426 nm. The spectral features in Figure **3** are consistent with a 1:1 binding ratio between calix[4]arene **3** and Ca<sup>2+</sup>. Further support of the 1:1 binding ratio comes from a Job plot<sup>[11]</sup> experiment, in



Figure 3. UV/Vis spectra of **3** (10  $\mu$ M) upon titration with various equivalents of Ca(ClO<sub>4</sub>)<sub>2</sub> in MeCN/CHCl<sub>3</sub> ( $\nu/\nu$  = 1000:4).

which the absorbances of the complexes at 496 nm were plotted against molar fractions of **3** under the conditions of an invariant total concentration. As a result, the concentration of complex **3**·Ca<sup>2+</sup> approached a maximum when the molar fraction of  $[3]/([3] + [Ca^{2+}])$  was about 0.5 (see Figure S7 in the Supporting Information).

From the titration experiment, the association constant for  $3 \cdot Ca^{2+}$  in MeCN/CHCl<sub>3</sub> (v/v = 1000:4) was determined to be  $1.01 \times 10^5 \text{ m}^{-1}$  by a Benesi–Hildebrand plot<sup>[12]</sup> (see Figure S8 in the Supporting Information). Similar UV/Vis titration behaviour and 1:1 binding stoichiometry was observed in the cases of  $3 \cdot Pb^{2+}$  and  $3 \cdot Ba^{2+}$ , respectively (see Figures S9–S14 in the Supporting Information), and the association constants for complexation of  $Pb^{2+}$  and  $Ba^{2+}$  by 3 were estimated, yielding  $3 \cdot Pb^{2+} = 6.35 \times 10^4 \text{ m}^{-1}$  and  $3 \cdot Ba^{2+} = 2.53 \times 10^4 \text{ m}^{-1}$ .

In addition to the metal ions binding properties, we have also investigated the sensing properties of azo compounds 2-4 towards anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>,  $H_2PO_4^-$  and  $NO_3^-$ ) by using tetrabutylammonium as a counter cation. In the absence of cations or anions, the UV/ Vis spectrum of **3** is characterized by the presence of one absorption band with a  $\lambda_{max}$  at 390 nm. The addition of F<sup>-</sup>, AcO<sup>-</sup> and  $H_2PO_4^-$  to 3 induced a red absorption band in its UV/Vis spectra to a different extent, whereas no obvious spectral change was observed in the addition of the other anions. The new absorption bands were found to have  $\lambda_{max}$ at 626 nm for F<sup>-</sup>, 618 nm for AcO<sup>-</sup> and 622 nm for  $H_2PO_4^{-}$ , respectively, corresponding to a maximum absorption intensity trend of  $F^- > AcO^- > H_2PO_4^-$  (see Figure 4). It is known<sup>[1a]</sup> that the electronic excitation of an azophenol chromophore generally occurs through a charge transfer from the donor oxygen atom of the phenol to the acceptor substituent  $(NO_2)$  of the chromophore. The extent of the bathochromic shifts by the basic anions (F-, AcO- and  $H_2PO_4^{-}$ ) may be due to the subtle balance between the deprotonation of the azophenol and complexation induced release of protons from the azophenol units. Similar observation in chromogenic sensing of anions by azocalix[4]arene derivatives, reported by Chen et al.,<sup>[4q]</sup> was also ascribed to the hydrogen-bonding ability and basicity of the anions to the azophenols of the calix[4]arenes.



Figure 4. UV/Vis spectra of 3 (10  $\mu$ M) before and after adding an 100  $\mu$ M concentration of various anions in MeCN/CHCl<sub>3</sub> ( $\nu/\nu$  = 1000:4).

Upon interacting with  $TBA^{+}F^{-}$ , the chromogenic sensor 3 in MeCN/CHCl<sub>3</sub> (v/v = 1000:4) solution experienced a marked bathochromic shift in its  $\lambda_{max}$  as shown in Figure S15 (Supporting Information). The absorption maximum at 390 nm gradually decreased in intensity with the formation of a new absorption band at approximately 626 nm ( $\Delta \lambda_{max}$  = 236 nm). An isosbestic point at 452 nm was observed in the titration spectra of 3 by  $TBA^+F^-$ . Job plot experiments were carried out for 3 and revealed a 1:1 complex for 3 with  $F^-$  (see Figure S16 in the Supporting Information). From the titration, the association constant of 3 with F<sup>-</sup> is calculated to be  $4.38 \times 10^4$  m<sup>-1</sup> (see Figure S17 in the Supporting Information). Similar UV/Vis titration behaviour and 1:1 binding stoichiometry was observed in the cases of  $3 \cdot AcO^{-}$  and  $3 \cdot H_2PO_4^{-}$ , respectively (see Figures S18-S23), and the association constants for complexation of  $AcO^{-}$  and  $H_2PO_4^{-}$  by 3 were estimated, yielding  $3 \cdot \text{AcO}^- = 2.50 \times 10^4 \text{ m}^{-1}$  and  $3 \cdot \text{H}_2 \text{PO}_4^ 5.50 \times 10^3 \text{ m}^{-1}$ .

Cation and anion-induced chemical-shift changes in the <sup>1</sup>H NMR spectra supports the fact that Ca<sup>2+</sup> is bound to one of the two nitrogen atoms of the triazole units and the two hydroxy azophenol groups of 3 (see Figure 5, b); however, F<sup>-</sup> is bound to the two hydroxy azophenol groups of 3 by hydrogen bonding (see Figure 5, c). In the presence of one equivalent of Ca<sup>2+</sup>, chemical shifts of protons H<sub>a</sub>-H<sub>d</sub> on the azophenol unit of 3 changed significantly; the peaks of  $H_a$  and  $H_b$  were shifted upfield by 0.07 and 0.33 ppm, respectively, but the peak of H<sub>d</sub> was shifted downfield by 2.35 ppm. In particular, the peak of H<sub>c</sub> was split into two peaks, one shifted upfield by 0.16 ppm and the other shifted downfield by 0.06 ppm. Furthermore, the signals of methylene bridges, H<sub>g</sub>, were also split into two sets of signals and the peak of H<sub>i</sub> on the triazole group was shifted downfield by 0.12 ppm. These results suggest that  $Ca^{2+}$  is not only bound by triazole-azophenol host 3; the metal complex also breaks the symmetry of the host molecule.<sup>[7c]</sup> By contrast, upon adding one equivalent of TBA<sup>+</sup>F<sup>-</sup> to the solution of 3, the peak of  $H_d$  on the hydroxy of the azophenol



Figure 5. <sup>1</sup>H NMR spectra of **3** (2.5 mM) in a  $\text{CDCl}_3/\text{CD}_3\text{CN}$  (3:1) solution (a) and in the presence of 1.0 equiv. of (b)  $\text{Ca}(\text{ClO}_4)_2$  and (c) TBA<sup>+</sup> F<sup>-</sup>, in which \* denotes external standards CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>.

unit disappeared, which can be explained by the participation of the OH of the azophenol group in  $F^-$  complexation. The high-field shifts of all protons of **3** in the presence of one equivalent of  $F^-$  supported the statement that deprotonation of one of the azophenols occurred due to the basicity of the anion. <sup>1</sup>H NMR titration spectra of **3** with various aliquots of TBA<sup>+</sup> F<sup>-</sup> are shown in Figure S24 (Supporting Information).

Since different colours were observed when compound **3** was treated with either  $Ca^{2+}$  or  $F^-$ , we further utilized our system as molecular logic gates. In the absence of any chemical input, the receptor **3** shows the absorption band at 390 nm. Addition of 10 equivalents of  $Ca^{2+}$  to the solution of **3** shows the absorption band at 496 nm. The addition of 10 equivalents of F<sup>-</sup> to **3** induced a red absorption band at 626 nm. Note that no such red absorption band at 626 nm was observed when 10 equivalents of F<sup>-</sup> were added to the solution of **3**  $\cdot$ Ca<sup>2+</sup> (1:10; see Figure 6). As a consequence of the UV/Vis spectral behaviour of **3** toward Ca<sup>2+</sup> and F<sup>-</sup> ions, the molecular system **3** provides us with a promising structure to mimic an INHIBIT logic gate with a YES logic function.



Figure 6. UV/Vis spectra of **3** (10  $\mu$ M) before and after adding an 100  $\mu$ M concentration of Ca(ClO<sub>4</sub>)<sub>2</sub>, TBA<sup>+</sup>F<sup>-</sup> and Ca(ClO<sub>4</sub>)<sub>2</sub> with TBA<sup>+</sup>F<sup>-</sup> in MeCN/CHCl<sub>3</sub> ( $\nu/\nu$  = 1000:4).

As seen in Figure 7, we constructed two logic circuits along with the truth Table for the absorption bands at 496 and 626 nm upon the addition of two input signals (Ca<sup>2+</sup> and  $F^{-}$ ). The two input signals are Ca<sup>2+</sup> (input 1) and  $F^{-}$ (input 2). The output signals are output 1 (absorption band at 496 nm) and output 2 (absorption band at 626 nm). As can be seen from the truth table in Figure 7, monitoring the absorption band at 496 nm (output 1), upon addition of Ca<sup>2+</sup>, F<sup>-</sup> and an equimolar mix of Ca<sup>2+</sup> and F<sup>-</sup> leads to a YES logic gate. The YES logic gate is a single input device that delivers the same output signal given by the input. However, output 2 results in an INHIBIT logic gate. An INHIBIT (INH) logic gate is a result of concatenation of AND and NOT gates, but in contrast to other logic gates with concatenated NOT, the logic inversion concerns not the output but one of the input.<sup>[6]</sup> So the strength of the INHIBIT gate is acknowledged in combination with a YES logic gate to lead to the construction of a combinational logic circuit. Last but not least, we have also investigated the ditopic binding ability of ligand 3 with  $CaF_2$ . The UV/



Vis spectra of **3** (10  $\mu$ M) did not show any change after adding 100 equivalents of CaF<sub>2</sub>. The results indicated that compound **3** is not a ditopic receptor to recognizing the ion pair of Ca<sup>2+</sup> and F<sup>-</sup> (see Figure S25 in the Supporting Information).



Figure 7. Logic diagram of the combinational logic circuit and truth table.

#### Conclusions

We have developed a novel bifunctional chromogenic calix[4]arene sensor **3** with bistriazoles and azophenols as the binding site for both cations and anions and azophenols as the signal transduction unit, which showed selective coloration toward not only  $Ca^{2+}$ ,  $Pb^{2+}$  and  $Ba^{2+}$ , but also F<sup>-</sup>,  $AcO^-$  and  $H_2PO_4^-$ . The recognition of  $Ca^{2+}$  by **3** gave rise to a marked colour change from greenish to bright yellow. In sharp contrast, the recognition of F<sup>-</sup> by **3** showed a colour change from light green to bluish. In addition, a dual output molecular switch is designed when the system is operated by inputs of  $Ca^{2+}$  and F<sup>-</sup>. The concept presented here contributes to the construction of a miniaturized and integrated molecular level device with logic gate functions.

### **Experimental Section**

**General:** All melting points are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 300 MHz instruments. Data are reported as follows: chemical shifts in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, br. s = broad singlet, m = multiplet), coupling constant (Hz), integration, and interpretation. Mass spectra were obtained on a Micromass-Trio 2000 GC-MS instrument. High resolution mass spectra were recorded on a JMS-700 high performance mass spectrometer. Column chromatography was performed with SiO<sub>2</sub> [Merck Silica Gel 60 (230–400 mesh)]. UV/Vis spectra were recorded by using a HP-8453 spectrophotometer with a diode array detector, and the resolution was set at 1 nm.

**5,17-Bis**(*p*-nitrophenyl)azo-25,27-dipropargyloxy-26,28-dihydroxycalix[4]arene (2): A solution of *para*-nitroaniline (0.14 g, 1.01 mmol) in acetone (8 mL) was added to an ice-cold solution of NaNO<sub>2</sub> (0.14 g, 2.02 mmol) in HCl (4 N, 6 mL) and the mixture was stirred for 30 s. The combined solution was then added to an other ice-cold solution of 25,27-dipropargyloxy-26,28-dihydroxycalix[4]arene (1) (0.10 g, 0.20 mol) in pyridine (12 mL) to produce a coloured solution. The reaction mixture was stirred at 0 °C for 24 h and then treated with HCl (4 N, 50 mL) to give a coloured precipitate. The solid residue was recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/ methanol mixture to give 2 (0.13 g, 81%) as a red solid; m.p. 214– 216 °C.  $R_f = 0.23$  (hexane/ethyl acetate = 3:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 8.37 (d, *J* = 8.9 Hz, 4 H, H<sub>a</sub>), 8.04 (s, 2 H, H<sub>d</sub>), 7.97 (d, *J* = 8.9 Hz, 4 H, H<sub>b</sub>), 7.83 (s, 4 H, H<sub>c</sub>), 6.99 (d, *J* = 7.5 Hz, 4 H, H<sub>f</sub>), 6.81 (t, *J* = 7.5 Hz, 2 H, H<sub>c</sub>), 4.87 (d, *J* = 2.3 Hz, 4 H, H<sub>h</sub>), 4.48 (d, *J* = 13.5 Hz, 4 H, H<sub>g</sub>), 3.60 (d, *J* = 13.5 Hz, 4 H, H<sub>g</sub>), 2.66 (t, *J* = 2.3 Hz, 2 H, H<sub>i</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.4 MHz):  $\delta$  = 157.8 (Cq), 156.2 (Cq), 151.2 (Cq), 148.0 (Cq), 145.8 (Cq), 132.5 (Cq), 129.5 (CH), 128.8 (Cq), 126.1 (CH), 124.7 (CH), 124.7 (CH), 122.9 (CH), 77.8 (Cq), 63.7 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>) ppm. FABMS: *m/z* (%) 799 [M<sup>+</sup> + 1, 6], 459 (6), 306 (100). HR-FABMS: calcd. for C<sub>46</sub>H<sub>35</sub>N<sub>6</sub>O<sub>8</sub> 799.2516; found 799.2506 [M + H<sup>+</sup>].

5,17-Bis(p-nitrophenyl)azo-25,27-bis(1-benzyl-1H-1,2,3-triazolylmethyloxy)-26,28-dihydroxycalix[4]arene (3): A mixture of compound 2 (0.15 g, 0.19 mmol), 9-(azidomethyl)benzene (0.06 g, 0.45 mmol) and CuI (about 1 mg, 0.005 mmol) in THF and water (v/v = 2:1, 15 mL) was stirred vigorously at 50 °C for 18 h. The mixture was extracted thrice with chloroform. The chloroform layer was dried with MgSO4 and the solvent was removed under reduced pressure. The residue obtained was purified over a silicagel column eluting with hexane/ethyl acetate (v/v = 1:1) to give 3 (0.13 g, 64%) as a red solid; m.p. 191–193 °C.  $R_{\rm f} = 0.18$  (hexane/ ethyl acetate = 1:1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 8.56 (s, 2 H,  $H_{d}$ ), 8.39 (d, J = 9.0 Hz, 4 H,  $H_{a}$ ), 8.00 (d, J = 9.0 Hz, 4 H,  $H_{b}$ ), 7.89 (s, 2 H, H<sub>i</sub>), 7.84 (s, 4 H, H<sub>c</sub>), 7.42–7.36 (m, 10 H, H<sub>1-n</sub>), 7.03 (d, J = 7.5 Hz, 4 H, H<sub>f</sub>), 6.85 (t, J = 7.5 Hz, 2 H, H<sub>e</sub>), 5.65 (s, 4 H, H<sub>i</sub>), 5.24 (s, 4 H, H<sub>h</sub>), 4.21 (d, J = 13.3 Hz, 4 H, H<sub>g</sub>), 3.41 (d,  $J = 13.3 \text{ Hz}, 4 \text{ H}, \text{H}_{g}$  ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.4 MHz):  $\delta =$ 158.2 (Cq), 156.6 (Cq), 151.8 (Cq), 148.4 (Cq), 146.2 (Cq), 135.2 (Cq), 132.9 (Cq), 130.0 (CH), 129.5 (CH), 129.2 (CH), 129.0 (Cq), 128.5 (CH), 126.4 (CH), 125.1 (CH), 125.1 (CH), 123.3 (CH), 70.1 (CH<sub>2</sub>), 54.9 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>) ppm. FABMS: m/z (%) 1065 [M<sup>+</sup> + 1, 11], 1064 [M<sup>+</sup>, 5], 467 (23), 391 (52), 136 (100). HR-FABMS: calcd. for C<sub>60</sub>H<sub>49</sub>N<sub>12</sub>O<sub>8</sub> 1065.3796; found 1065.3784 [M + H<sup>+</sup>].

**Supporting Information** (see also the footnote on the first page of this article): <sup>1</sup>H and <sup>13</sup>C NMR spectra for compounds **2** and **3**. UV/Vis titration spectra, Job Plots and Benesi–Hildebrand plots of compounds **2–4** with cations and anions. <sup>1</sup>H NMR titration spectra of **3** with various equivalents of TBA<sup>+</sup>F<sup>-</sup>.

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