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Reconfiguration of the Symmetry and Charge-Transfer Characteristics of a Triply Crowned 1,3,5-Tris(arylalkynyl)mesitylene by Successive Metal Ion Complexation

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A triply benzocrown-ether-functionalized trialkynylmesitylene derivative with C_3 symmetry as well as its linear analogue have been synthesized and their optical properties have been studied by UV/Vis absorption, steady-state and time-resolved fluorescencece spectroscopy. The spectroscopic investigation of the uncomplexed compounds revealed the nature of the electronic and excitonic communication pathway in the ground and excited states of the all-*meta*-substituted chromophore system. Upon cation complexation, the octopolar character of the free trialkynyl compound becomes dipolar and finally returns to octopolar in the fully complexed species.

Introduction

Recent advances in acetylenic scaffolding have opened the way to interesting new molecular materials.[1] Linear,[2] cruciform,[3] star-shaped,[4] macrocyclic,[5] three-dimensional[6] and branched chromophore systems[7] have been designed for various applications. These acetylenic dyes are based on a small aromatic platform (benzene, paracyclophane) that carries functional groups and interconnecting spacers in a one- or two-dimensional arrangement. Alkynyl spacers have been increasingly employed as connecting units because they endow the molecular scaffold with rigidity and do not hinder free rotation of the adjacent groups while allowing for efficient electronic communication.[8] A fundamental aspect in all these systems, which will also be addressed in this work, is the conjugation pathway and its effectiveness as imparted by the geometry of the acetylenic scaffold.[3c] A number of examples of linear or branched, mono-, bis- or multi-receptor-containing conjugated π systems have been described as switchable[7a,9] or sensing devices.[3b,10] The latter feature, that is, the use of a chemical input such as a metal cation to modulate the electronic properties of a system, and thus its spectroscopic characteristics, is particularly elegant since it offers high versatility in molecular design and manipulation.

Results and Discussion

Herein, we present the tris(benzocrown)-functionalized arylalkynyl system **1** which possesses C_3 symmetry. Upon addition of suitable cations, the charge-transfer (CT) character can be switched from octopolar (free) to dipolar (mono- and dicationic complex) back to octopolar again for the fully complexed tricationic species. The resulting spectroscopic changes were monitored by UV/Vis and steady-state as well as time-resolved fluorescence spectroscopy. The linear tolane derivative **2** was used as a reference compound in which cation complexation merely affects its dipolar CT character. In both systems the arylethynyl chromophore in combination with the complexation subunit functioned as an integral part of the chromophore. We chose a crown ether moiety as the cationic complexation unit[11] as its supramolecular chemistry is well known and has been extensively studied for decades since the early work of Cram and Lehn.[12] Another obvious motivation is the commercial availability of a large variety of crown ether derivatives, the bromobenzo-18-crown-6 in our particular case, together with a plethora of synthetic work involving crown ethers. The synthesis of the crown ether derivatives **1** and **2** was based on the palladium-catalyzed cross-coupling reaction of an aryl halide with a free arylacetylene. Compound **1** can be obtained upon three-fold coupling of triiodomesitylene with 4′-ethynylbenzo-18-crown-6[13] under Sonogashira conditions in a 36% yield (Scheme 1). The relatively low yield is a consequence of the sterically hindered,

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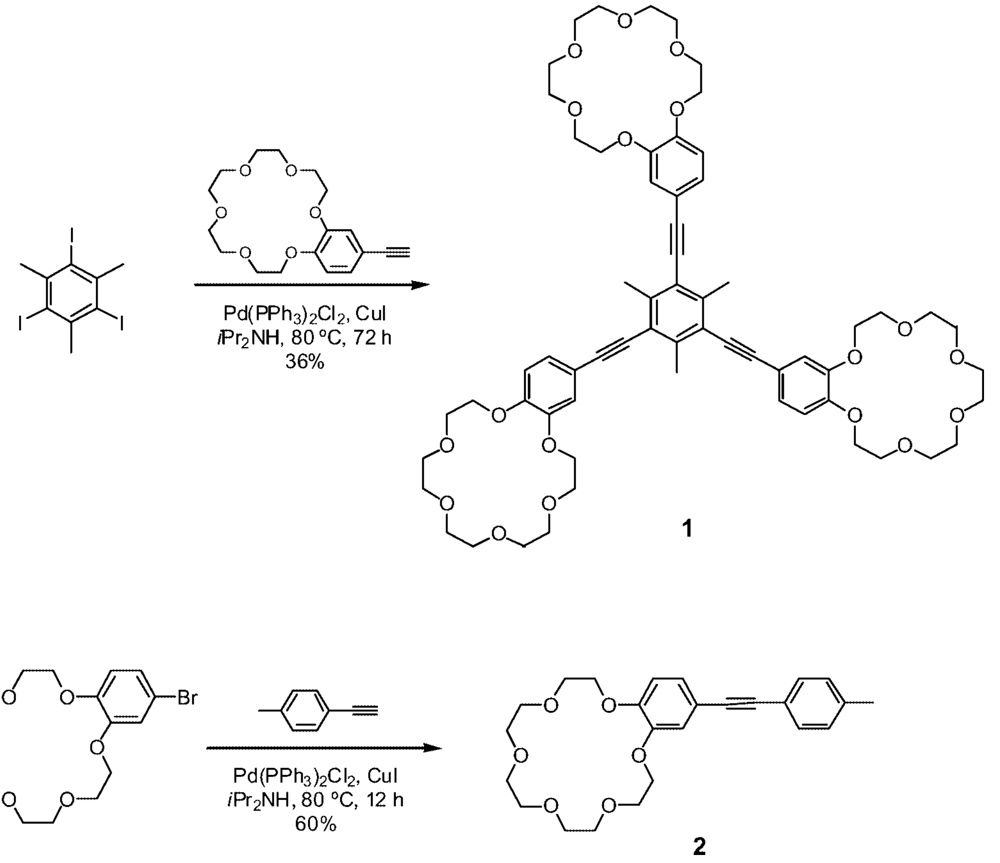


Scheme 1. Synthesis of **1** and **2** by Sonogashira coupling.

electronically rich aryl halide favouring the formation of a significant amount of a butadiynyl homocoupling product.[14] The molecular structure of **1** is unequivocally confirmed by ^{1}H and ^{13}C NMR spectrocopy, MS and HRMS. Sonogashira coupling of 4′-bromobenzo-18-crown-6 with 4-ethynyltoluene afforded **2** in 60% yield (Scheme 1). In both cases, a 1.5-fold excess of the ethynyl compound was employed.

Optical Spectroscopy of Uncomplexed 1 and 2: The spectroscopic properties of donor–acceptor (D–A) acetylene dyes that carry strong electron-donating and -withdrawing substituents have been studied most commonly. Typically, they exhibit broad and unstructured absorption and emission bands with large Stokes shifts.[2] As will be demonstrated below, the same general tendencies are observed for **1** and **2**, however, the effects are much more subtle owing to the weak donor or acceptor strength of the respective substituents.

The absorption and fluorescence behaviour of **1** and **2** in the absence and presence of alkali and alkaline-earth metal ions was investigated in acetonitrile solution at room temperature. From Figure 1, a representation of the steady-state spectra of both compounds in MeCN, the unique features of the C_3-symmetric, octopolar chromophore **1** become apparent. Compared with the linear dipolar reference **2**, the absorption spectrum of **1** is only slightly shifted to longer wavelengths, that is, the maximum of the lowest-energy transition is centred at 314 nm for **1** and 301 nm for **2**. (These values correspond to the maxima of fits of the slightly structured low-energy absorption bands up to ca. 250 nm.)

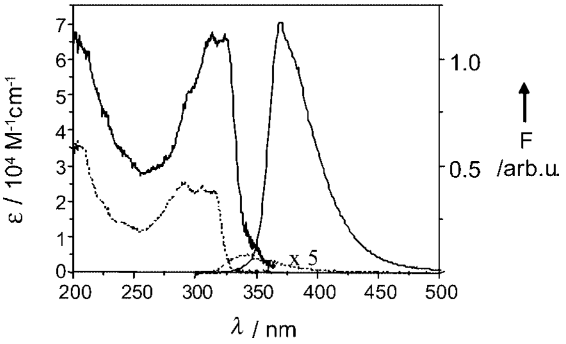
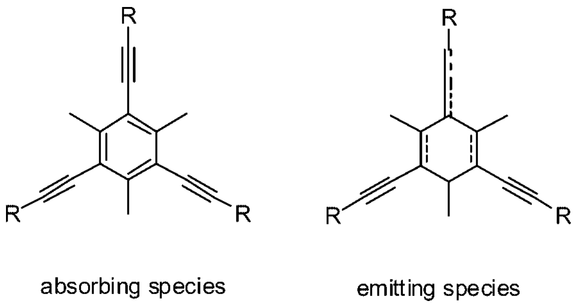


Figure 1. Absorption and emission spectra of **1** (solid line) and **2** (dotted line) in MeCN at 298 K. The emission spectra are directly proportional to the respective fluorescence quantum yields.

However, the molar absorptivity of **1** is almost three times greater than that of **2**, reaching values of about 6.6×10^{4} $\text{M}^{-1}\,\text{cm}^{-1}$ at 315 and 325 nm. Such values are commonly only found for intensely absorbing cyanine or related dyes.[15] Both of these facts suggest that **1** is composed of three linear subchromophores in an all-*meta* arrangement that are only weakly coupled through the central benzene core in their ground-state geometry.[16] The fluorescence emission data on the other hand reveal clear differences between the two dyes. Despite the fact that **2** is a linear, highly conjugated, D–A-substituted system in which the benzocrown unit formally exemplifies the donor and the *p*-tolyl group the acceptor,[17] the C_3-symmetric octopole **1** shows an even larger Stokes shift of 5130 cm^{-1} as compared with 4240 cm^{-1} for **2**.[18] Moreover, in both cases, solvatochromism is observed with a reduction in the Stokes shift upon decreasing the polarity of the solvent (Table 1). Together with the fact that the fluorescence bands are rather unstructured and broad in MeCN, the title compounds can be classified as chromophores with moderate CT character.[19] This behaviour suggests that the emitting state in **1** is rather different from the absorbing state. In accordance with the experimental and theoretical results of a study of phenylethynyl dendrimer models published recently by Gaab et al.,[20] we tentatively assume that the relaxed excited state of **1** also has a more cumulenic structure and thus exhibits clear features of asymmetric CT chromophores, that is, stronger coupling of the formally *meta*-isolated subchromophores (Scheme 2).[21]

Table 1. Spectroscopic data for **1** and **2** in selected solvents at 298 K: acetonitrile, tetrahydrofuran and di-*n*-butyl ether (BOB).

	Solvent	λ_{abs} [nm]	λ_{em} [nm]	$\sim\nu_{abs-em}$ [cm^{-1}]	Φ_f
1	MeCN	314	374	5130	0.32
	THF	315	371	4800	0.22
	BOB	314	361	4160	0.08
2	MeCN	301	345	4240	7×10^{-3}
	THF	301	340	3810	6×10^{-3}
	BOB	301	332	3160	7×10^{-3}



Scheme 2. Electronic and structural differences of the absorbing and emitting species as proposed in ref.[20].

Differences between the classical linear and the branched fluorophore are also apparent from the kinetic fluorescence data. Whereas **1** has a very high fluorescence quantum yield Φ_f of 0.32 in MeCN, which is of a similar magnitude to that of similar star-shaped phenylethynyls,[22] **2** is only weakly emissive with $\Phi_f = 7\times10^{-3}$. Fluorescence lifetime measurements support these findings showing that **1** decays in the nanosecond (τ_f = 6.10 ns) and **2** (τ_f = 0.28 ns) in the subnanosecond time domain in this solvent. Here, the weak fluorescence of **2** is strongly reminiscent of the weak emission of other diphenylacetylenes that carry *para* substituents of similar donor strength and most probably involves linear-to-bend geometry change in the excited state (to a "*trans*-stilbene-like" geometry) that subsequently facilitates efficient internal conversion and intersystem crossing.[23]

Optical Spectroscopy of the Cationic Complexes of 1 and 2: In general, the addition of cations of the first and the second main group of the periodic table to acetonitrile solutions of **1** and **2** leads to distinct spectroscopic changes with the cation selectivities being in line with those reported by other researchers for the benzo-18-crown-6 receptor.[10a–10c,11] However, as compounds **1** and **2** were not conceived as sensor molecules but as chromophore systems with cation-reconfigurable symmetry, we focused our studies on Sr^{2+}, the ion that induces the strongest effects due to its optimum fit-in-size and high charge density. Further details of its general complexation behaviour are included in the Supporting Information. Before describing these results in detail, it is important to note that we used both crowned dyes at concentrations of 1 and 3 μM. These concentrations are more than one order of magnitude lower than those commonly used in such studies[10] and have deliberately been chosen to avoid aggregation phenomena in order to be able to study only the effect of the successive formation of the complexes on the CT characteristics of the dyes.

For both **1** and **2**, full complexation of Sr^{2+} was reached with a three-fold excess of cation to ligand, that is, at a ratio of 1:1 of cation to receptor unit. Figure 2 and Figure 3 show typical spectral changes found for both compounds upon binding to the spectroscopically active cation. In the absorption spectra, hypsochromic shifts of comparable magnitude are observed independent of the dye molecule (and of the metal cation, see Table 2 and the Supporting Information). This is due to the fact that coordination of a cation at a crown ether oxygen atom, especially the oxygen atom *para* to the ethynyl spacer, leads to a reduction in the electron-donating ability of this atom, resulting in a reduction of its CT character. Again, these results reveal that the three branches in **1** are electronically rather isolated in the ground state and strongly resemble linear **2**.

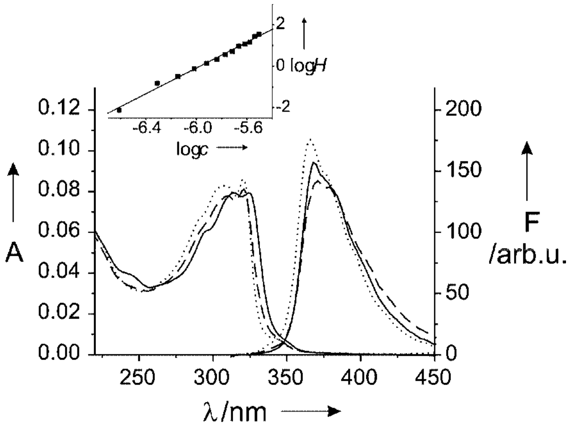


Figure 2. Absorption and emission spectra of **1** (solid line), **1**·Sr^{2+} (dashed line) and **1**·$(Sr^{2+})_3$ (dotted line) in MeCN; $c = 1\times10^{-6}$ M. The spectra of **1**·$(Sr^{2+})_2$ have been omitted for clarity. The inset shows a Hill plot of the absorption data at 300 nm (A), expressed as $\log H = \log (A - A_{min})/(A_{max} - A)$ vesus $\log c_M$ (r = 0.986).

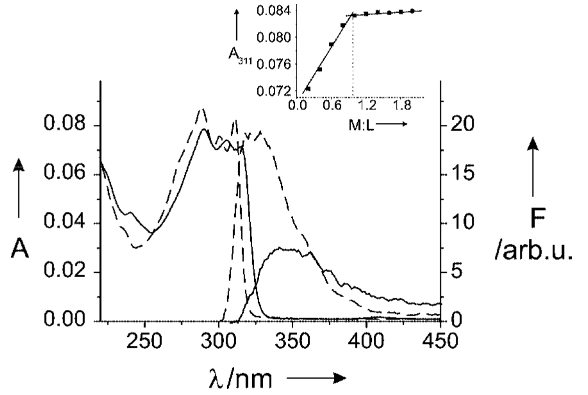


Figure 3. Absorption and emission spectra of **2** (solid line) and **2**·Sr^{2+} (dashed line) in MeCN; $c = 3\times10^{-6}$ M. The inset shows a plot of the absorption at 311 nm versus the metal-to-ligand ratio M:L.

Table 2. Spectroscopic data for **1** and **2** in the absence and presence (full complexation) of Sr^{2+} in MeCN.

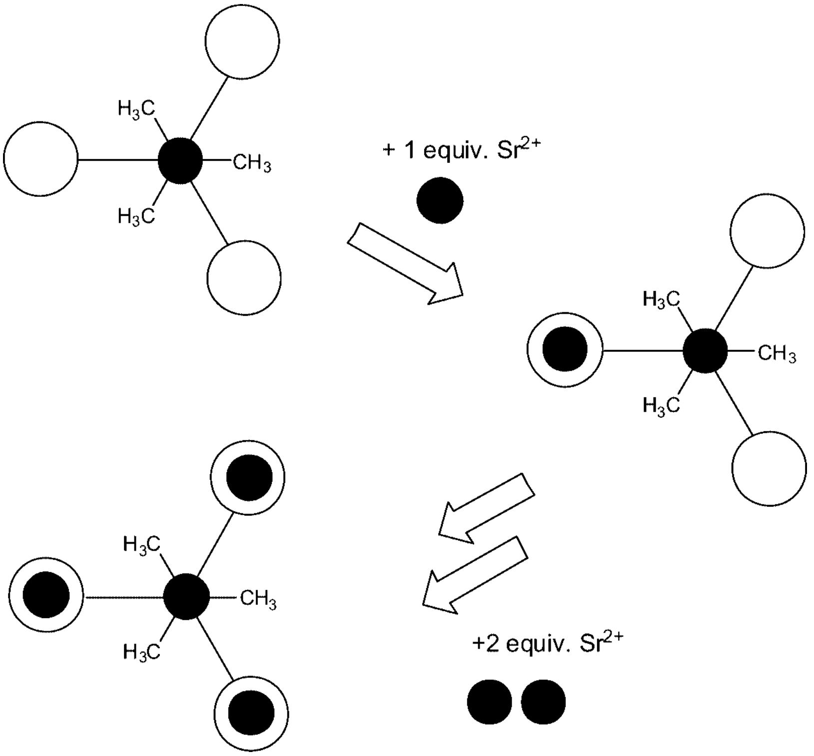
	λ_{abs}[a] [nm]	λ_{em}[a] [nm]	Φ_f
1	325	370	0.32
1·$(Sr^{2+})_3$	321	367	0.36
2	315	345	7×10^{-3}
2·$(Sr^{2+})_3$	311	324	11×10^{-3}

[a] The values correspond to the maxima of the 0–0 transitions obtained by deconvolution of the respective band.

By taking a closer look at Figure 2, the special features of star-shaped **1** become apparent. The binding of 1 equiv. of Sr^{2+} leads to the expected blue shift in absorption. However, a red shift is observed for the emission band. Apparently, when one of the three receptor units is occupied by a positively charged species, this asymmetric distortion reinforces the excited-state CT character and leads to bathochromically shifted fluorescence, the Sr^{2+}-containing crown in a cumulenic structure, as shown in Scheme 2, most probably acting as the acceptor. Adding a further equivalent of cation leads to a progressive shift in the absorption band, but does not induce significant changes in emission. This can be understood in terms of a simple reversion of one of the unbound donor groups to an acceptor, the entire ensemble still maintaining its dipolar character. Finally, upon full complexation, a further shift in the absorption band is noticed, now accompanied by a return of the fluorescence band virtually to its initial position. Thus, the system is switched back from a dipolar to an octopolar system. At the same time, some increase in the fluorescence quantum yield is found, most probably due to the reduced flexibility of the whole quaternary complex. The enhanced fluorescence yield is also reflected in increased fluorescence decay times, for example, 7.20 and 7.48 ns for **1**·Sr^{2+} and **1**·$(Sr^{2+})_3$. The inset in Figure 2 depicts a Hill analysis of the absorption data at 300 nm, which shows progressive changes throughout the entire titration in accord with Equation (1).

$$\log(A - A_{\min})/(A_{\max} - A) = n\log c_M + \log K_d \qquad (1)$$

Here, A is the absorption at the respective wavelength, min and max denote the values at the start and endpoint of the titration, n denotes the n:1 M/L stoichiometry and K_d is the overall stability constant. The results of the plot shown in Figure 2 yield $n = 3.1$ and $\log K_d = 18$, revealing



Scheme 3. Schematic representation of the cation-induced reconfiguration of the charge-transfer features of **1**.

the formation of an M$_3$L complex. The stoichiometric course of the successive binding, as revealed by the different shifts in absorption and emission and the very weak changes in the overall fluorescence output between **1** and **1**·(Sr^{2+})$_3$ suggest that aggregation or sandwich-type complexation can indeed be ruled out in our case. For instance, Xia et al. found a strong increase in emission in bis- as well as tris-crowned linear and star-shaped sensor molecules which indicates metal ions by self-assembling fluorescence enhancement or sandwich formation.[10a,10b] A schematic representation of the cation-steered reconfiguration of the electronic properties and charge-transfer characteristics of **1** is given in Scheme 3.

Model compound **2** exhibits the typical behaviour of linearly substituted D–A-type CT-active sensor molecules with the receptor serving as electron donor, that is, hypsochromic shifts in both absorption and emission upon cation binding and the absence of any stoichiometry effects, that is, the clear formation of a 1:1 complex (inset of Figure 3).[24] The moderate fluorescence enhancement further suggests that formation of the complex does not entirely switch off any of the efficient nonradiative deactivation channels but merely leads to some modification of the factors governing radiationless decay in such dyes as discussed above.

Conclusions

Our study described herein demonstrates that the optical spectroscopic processes in octopolar compounds equipped with multiple binding sites can be conveniently modulated by chemical inputs and the choice of the desired stoichiometric ratio. Moreover, our results show that employing alkynyl spacers in the design of such molecular ensembles harbours the advantage of intrinsically high fluorescence signals. Independent of the species created, **1**, **1**·Sr^{2+}, **1**·(Sr^{2+})$_2$ or **1**·(Sr^{2+})$_3$, the fluorescence quantum yields remain above 0.30. The complexation-induced changes in the symmetry of the receptor–complex ensemble can be monitored without being disturbed by potential conformational changes arising from the ligand itself.

Experimental Section

1,3,5-Tris[(benzo-18-crown-6)-4′-ylethynyl]-2,4,6-trimethylbenzene (1): 1,3,5-Triiodomesitylene (150 mg, 0.3 mmol) and 4′-ethynylbenzo-18-crown-6 (500 mg, 1.5 mmol) were stirred together with Pd(PPh$_3$)$_2$Cl$_2$ (62 mg, 0.09 mmol), CuI (18 mg, 0.09 mmol) and K$_2$CO$_3$ (288 mg, 2.0 mmol) in degassed diisopropylamine (10 mL) at 80 °C for 72 h. The solvent was removed, the remaining solid was suspended in water (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo to give the resulting crude product, which solidifies upon trituration with MeOH. Recrystallization from acetonitrile gave pure **1** as a pale orange solid. Yield: 122 mg, 36%; m.p. 92–95 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): δ = 7.13 (d, J = 6.6 Hz, 3 H), 7.05 (s, 3 H), 6.84 (d, J = 8.0 Hz, 3 H), 4.19 (t, J = 4.8 Hz, 12 H), 3.93 (t, J = 4.8 Hz, 12 H), 3.77–3.68 (m, 36 H), 2.70 (s, 9 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 149.5, 148.5, 141.3, 125.1, 121.3, 116.9, 116.1, 113.6, 97.2, 85.5, 70.7, 70.6, 69.4, 69.1, 68.9, 20.2 ppm. FAB$^+$ HRMS: calcd. for C$_{63}$H$_{78}$O$_{18}$: 1122.5188; found: 1122.5183. R_f = 0.27 (CH$_2$Cl$_2$/MeOH, 20:1).

4′-(*p*-Tolylethynyl)benzo-18-crown-6 (2): 4′-Bromobenzo-18-crown-6 (391 mg, 1.0 mmol) was stirred together with Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) in degassed diisopropylamine (10 mL) at room temp. for 30 min. 4-Ethynyltoluene (253 µL, 2.0 mmol) was added and the mixture was heated at 80 °C for 12 h. The solvent was removed and the remaining solid was suspended in water (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo to give the resulting crude product, which was purified by column chromatography (40:1 CH$_2$Cl$_2$/MeOH) and finally recrystallized from MeOH to give pure **2** as an off-white solid. Yield: 254 nm, 60%; m.p. 68–70 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): δ = 7.38 (d, J = 7.5 Hz, 2 H), 7.15–6.98 (m, 4 H), 6.81 (d, J = 8.1 Hz, 1 H), 4.16 (t, J = 4.3 Hz, 4 H), 3.92 (t, J = 4.3 Hz, 4 H), 3.90–3.69 (m, 12 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 149.3, 148.5, 138.1, 131.3, 129.1, 125.2, 120.3, 116.8, 116.0, 113.5, 88.7, 88.1, 70.9, 70.8, 70.7, 69.5, 69.0, 21.5 ppm. FAB$^+$ HRMS: calcd. for C$_{25}$H$_{30}$O$_6$: 426.2042; found: 426.2039. R_f = 0.68 (CH$_2$Cl$_2$/MeOH, 20:1).

Supporting Information: Further details concerning general experimental and spectroscopic methods, UV/Vis and fluorescence spectroscopic changes of **1** and **2** upon addition of various alkaline and alkaline-earth metals as well as the ^{1}H NMR spectra of **1** and **2** are included in the Supporting Information (five pages).

Acknowledgments

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