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Polyvalent Scaffolds. Counting the Number of Seats Available for Eosin Guest Molecules in Viologen-Based Host Dendrimers

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Abstract: We have prepared and investigated two dendrimers based on a 1,3,5-trisubstituted benzenoid-type core, containing 9 and 21 viologen units in their branches, respectively, and terminated with tetraarylmethane derivatives. We have shown that, in dichloromethane solution, such highly charged cationic species give rise to strong host−guest complexes with the dianionic form of the red dye eosin. Upon complexation, the absorption spectrum of eosin becomes broader and is slightly displaced toward lower energies, whereas the strong fluorescence of eosin is completely quenched. Titration experiments based on fluorescence measurements have shown that each viologen unit in the dendrimers becomes associated with an eosin molecule, so that the number of positions ("seats") available for the guest molecules in the hosting dendrimer is clearly established, e.g., 21 for the larger of the two dendrimers. The host−guest interaction can be destroyed by addition of chloride ions, a procedure which permits eosin to escape from the dendrimer's interior in a controlled way and to regain its intense fluorescence. When chloride anions are precipitated out by addition of silver cations, eosin molecules re-enter the dendrimer's interior and their fluorescence again disappears.

Introduction

Dendrimers are complex yet well-defined monodisperse compounds, exhibiting a high degree of constitutional order with the potential to locate selected structural units in predetermined sites within their structures.[1,2] Currently, they are attracting the interest of a large number of scientists, not only because of their unusual chemical and physical properties but also on account of the wide range of potential applications they proffer in such diverse fields as medicine, biology, chemistry, physics, and engineering. An important feature of dendrimers is the presence within them of internal voids, often containing moieties that are capable of interacting with, and, thereby, hosting, small molecules or metal ions.[3] Research on dendrimer-based host−guest systems has been inspired by a number of objectives, including the preparation of encapsulated metal nanoparticles,[4] dioxygen binding,[5] ion transportation,[6] ion sensing,[7] light harvesting,[8,9] stepwise complexation,[10] and self-assembly.[11] Although, in most cases, dendrimers have played the role of hosts, occasionally dendrimer branches have also assumed the

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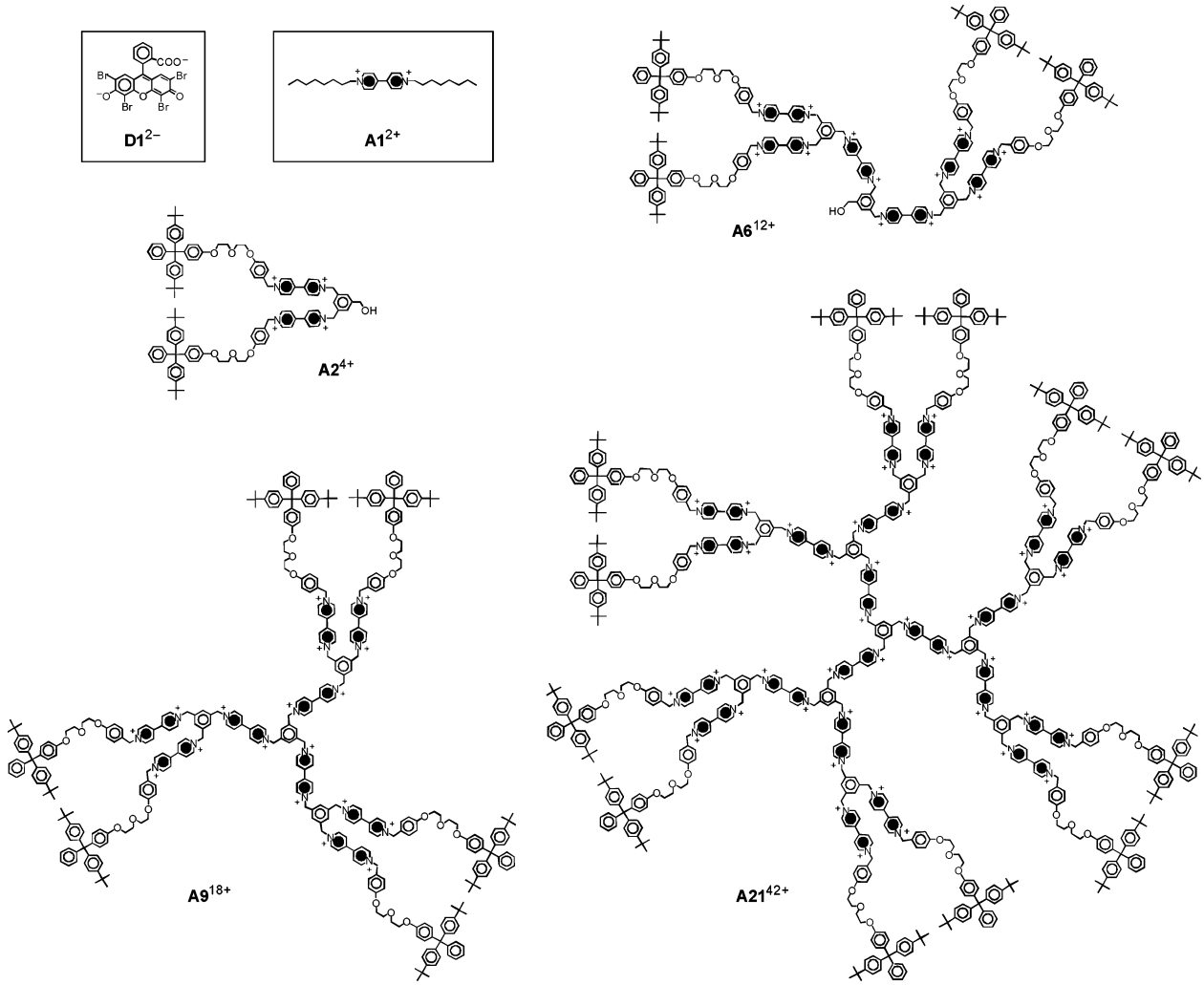
10.1021/ja037318m CCC: $27.50

Chart 1. Examined Compounds[a]



[a] The symbols used indicate the presence of electron-donor (D) or electron-acceptor (A) units, the number of such units, and, as a superscript, the overall electric charge of each compound.

mantle of guests, particularly toward cyclodextrin[12] and cucurbituril[13] hosts. Dendrimers containing photoactive[2a,9,14] and/or electroactive[2b,f,14a,15] units are particularly interesting since such units (i) offer a handle to probe the intricacies of their structures and superstructures, (ii) allow the dendrimer to perform useful functions, such as light harvesting or charge pooling, and (iii) can be useful for sensing purposes with signal amplification.

This paper describes host−guest systems (Chart 1) obtained when two dendrimers containing 9 (**A9**$^{18+}$) and 21 (**A21**$^{42+}$) electron-acceptor viologen units[16] in the branches interact with the dianionic form (**D1**$^{2-}$) of the fluorescent electron-donor eosin. We have shown that, in dendrimers of this family, it is possible to count the number of "seats" available for the eosin guest molecules by fluorescence titration.

Results and Discussion

Synthesis. The routes employed to synthesize the dendrimers **A9**·18PF_6 and **A21**·42PF_6, and their intermediates **1**·4PF_6 and **A6**·12PF_6, are outlined in Schemes 1 and 2. The tetracationic chloride **1**·4PF_6 (Scheme 1) was obtained in 85% yield by reacting the tetracationic alcohol[17] **A2**·4PF_6 with thionyl chloride in dry MeCN in the presence of pyridine. Alkylation of the tricationic salt[18] **2**·3PF_6 with the tetracationic chloride **1**·4PF_6 in the presence of KI in DMF solution gave the dendrimer **A9**·18PF_6 in a yield of 60% after counterion exchange. In Scheme

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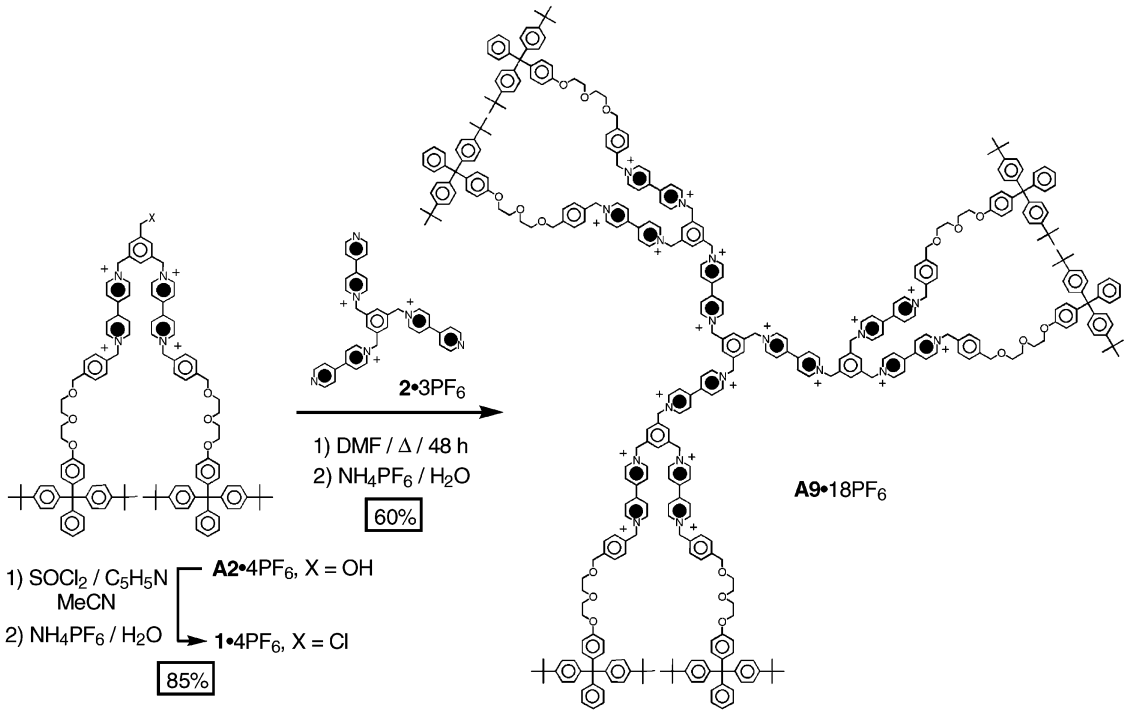
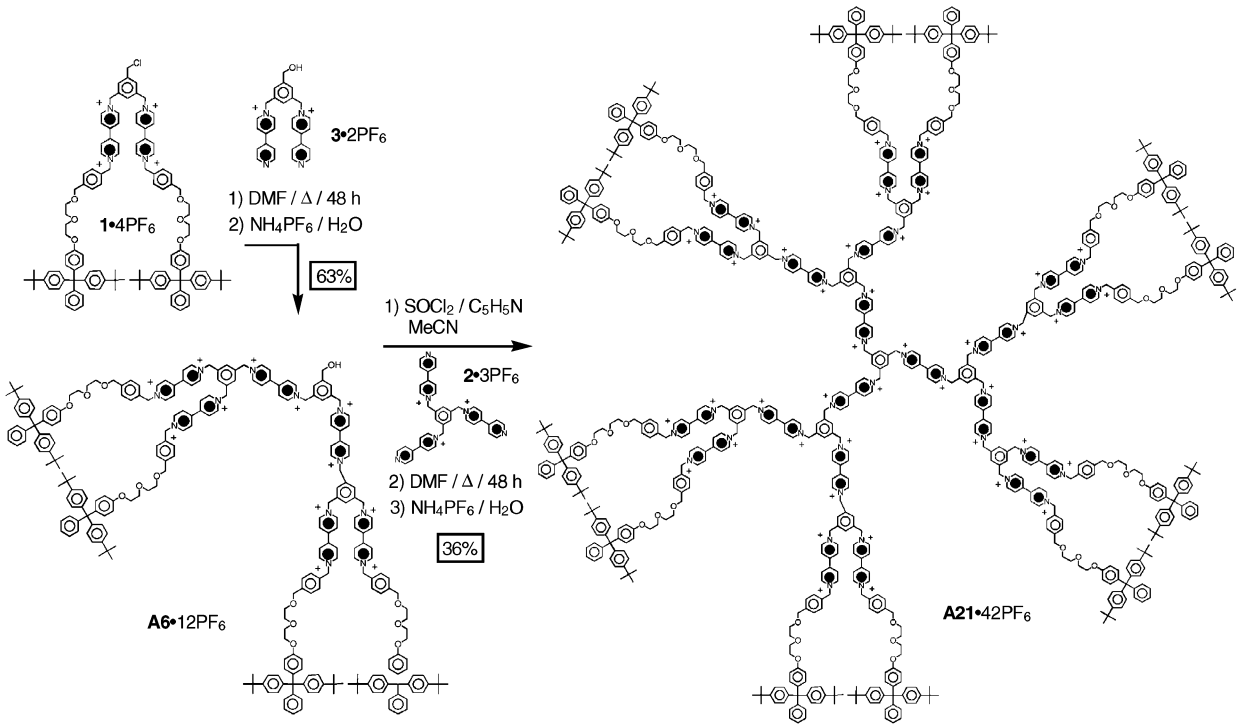
Scheme 1



Scheme 2



2, reaction of the tetracationic chloride[17] **1**·4PF_6 with the dicationic salt **3**·2PF_6, followed by counterion exchange, afforded the dodecacationic alcohol **A6**·12PF_6 in 63% yield. The alcohol **A6**·12PF_6 was treated with thionyl chloride to obtain the chloride intermediate which was then reacted with the tricationic salt[18] **2**·3PF_6 to give the dendrimer **A21**·42PF_6 in an overall yield of 36% after counterion exchange.

Eosin Complexation. The absorption spectra of dioctyl viologen **A1**$^{2+}$,[19] the dendrons **A2**$^{4+}$ and **A6**$^{12+}$ and the dendrimers **A9**$^{18+}$ and **A21**$^{42+}$ recorded in dichloromethane are dominated by the bands of the viologen units, with the molar absorption coefficients related to the number of such units contained in each compound. The absorption and fluorescence spectra of eosin **D1**$^{2-}$ as its tetrabutylammonium salt are displayed in Figure 1. The absorption spectrum is characterized by a strong and narrow band (λ_{max} = 530 nm, ϵ = 105 000 M^{-1} cm^{-1}). The fluorescence band (λ_{max} = 560 nm) is very intense (Φ = 0.75) and short-lived (τ = 3.8 ns).

It is well-known that the dicationic viologen units are strong

(19) Although dibenzyl viologen would no doubt be a better reference compound for the viologen units contained in the dendrimers, it is not soluble in dichloromethane. It was for this reason that we used dioctyl viologen.

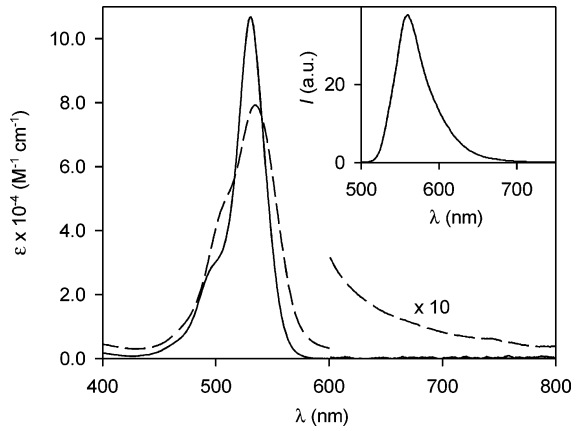


Figure 1. Full line: absorption and (inset) fluorescence spectra of the tetrabutylammonium salt of eosin dianion $\mathbf{D1}^{2-}$ recorded in dichloromethane. Dashed line: absorption spectrum observed after addition of a stoichiometric amount of dioctyl viologen $\mathbf{A1}^{2+}$ (as its PF_6^- salt); the fluorescence band is completely quenched.

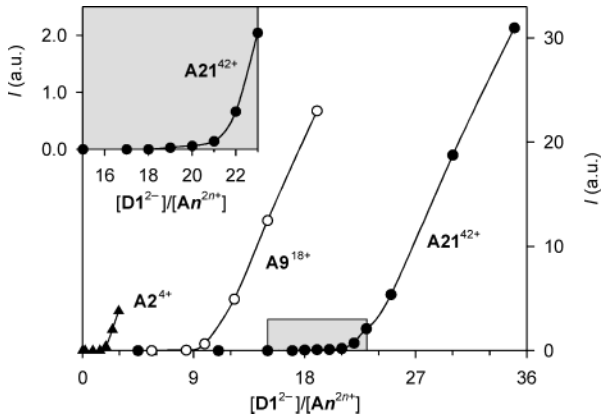


Figure 2. Fluorescent titration experiments performed in dichloromethane solutions. Diagram of the intensity of the eosin $\mathbf{D1}^{2-}$ fluorescence band (λ_{ex} = 500 nm; λ_{em} = 560 nm) as a function of the $[\mathbf{D1}^{2-}]/[\mathbf{An}^{2n+}]$ ratio (n is the number of viologen units in each compound).

electron acceptors,[20] while the eosin dianion is a moderate electron donor.[21] It can therefore be expected that dicationic viologen units $\mathbf{A1}^{2+}$ associate with dianionic eosin molecules $\mathbf{D1}^{2-}$ to yield charge-transfer (CT) complexes. Crystalline 1:1 complexes between $\mathbf{D1}^{2-}$ and both the *N*,*N*′-dimethyl-4,4′-bipyridinium and *N*,*N*′-dibenzyl-4,4′-bipyridinium dications have been described.[22] Complex formation in dimethylformamide[22] and in aqueous solution[23] has also been investigated and even exploited for signal transduction purposes.[24]

Our investigations were prompted by the observation that a dichloromethane solution of dendrimer $\mathbf{A21}\cdot 42PF_6$ is able to extract eosin from aqueous solution. Extraction can be easily followed from the bleaching of the aqueous phase and the increase in the color intensity of the organic phase. The extracted eosin, in fact, maintains its red color but loses its fluorescence. The amount of eosin extracted depends on the concentration and pH of the aqueous phase.[25]

We then decided to study the formation of complexes between dendrimers and eosin[26] in a more systematic way, employing the tetrabutylammonium salt of eosin dianion $\mathbf{D1}^{2-}$ which is soluble in dichloromethane. We have found that addition of the hexafluorophosphate salt of dioctyl viologen $\mathbf{A1}^{2+}$ to a dichloromethane solution of $\mathbf{D1}^{2-}$ causes (Figure 1) a strong perturbation in the visible absorption band and a complete quenching of the fluorescence of $\mathbf{D1}^{2-}$. A titration curve showed that a strong 1:1 complex is formed ($K_{ass} > 10^6$ M^{-1}). Formation of a CT complex is also evidenced (Figure 1) by the weak absorption tail arising above 580 nm.

Qualitatively similar results were obtained on mixing the tetrabutylammonium salt of the eosin dianion $\mathbf{D1}^{2-}$ with the hexafluorophosphate salts of the dendron $\mathbf{A2}^{4+}$ and the dendrimers $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$.[27] Fluorescent titration experiments were then performed. Dichloromethane solutions of $\mathbf{A2}^{4+}$, $\mathbf{A9}^{18+}$, and $\mathbf{A21}^{42+}$ (each containing 4.2×10^{-5} M viologen units) were titrated with a solution of $\mathbf{D1}^{2-}$. The results show (Figure 2) that the eosin fluorescence signal appears only when the number of added $\mathbf{D1}^{2-}$ equivalents exceeds the number of $\mathbf{A}^{2+}$ units contained in each compound. These results demonstrate that compounds $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$ are capable of quenching, by a static mechanism,[28] the fluorescence of 9 and 21 eosin molecules, respectively. In other words, each dicationic viologen unit in the dendrimers associates with an eosin dianion. Therefore, compounds $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$ can be viewed as polyvalent scaffolds which provide a well-defined number of separate compartments ("seats") where single eosin molecules can be hosted. Whereas for most dendrimers it is not known whether the guest species are hosted in their interiors or on the peripheries of their structures, in the present case, it is clear that the $\mathbf{D1}^{2-}$ molecules are hosted in the interiors of $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$.

We have also observed that the host−guest complexes can be destroyed by the addition of an excess of chloride ions. In a solution containing 4.0×10^{-6} M $\mathbf{A9}^{18+}$ and 8.0×10^{-6} M $\mathbf{D1}^{2-}$, eosin fluorescence is completely quenched and the eosin absorption maximum appears at 535 nm, indicating that the $\mathbf{D1}^{2-}$ molecules are encapsulated in the dendrimer. Upon addition of an excess (2×10^{-2} M) of tetrabutylammonium chloride, the absorption maximum of eosin moved[29] to 540 nm and an intense emission band appears with λ_{max} = 560 nm. The same spectroscopic data were obtained for a dichloromethane solution containing the same amounts of $\mathbf{D1}^{2-}$ and tetrabutylammonium chloride in the absence of the dendrimers. These results show that $\mathbf{D1}^{2-}$ does escape from the dendrimer upon addition of Cl^- ions. At this stage, addition of Ag^+ as its

(20) The first reduction process of the hexafluorophosphate salt of $\mathbf{A1}^{2+}$ in dichloromethane occurs at −0.27 V vs SCE.
(21) The first oxidation process of the tetrabutylammonium salt of $\mathbf{D1}^{2-}$ in dichloromethane occurs at +0.65 V vs SCE.
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(25) Similar behavior is observed in the extraction of eosin from aqueous into dichloromethane solutions containing poly(propylene amine) dendrimers: Balzani, V.; Ceroni, P.; Gestermann, S.; Gorka, M.; Kauffmann, C.; Vögtle, F. *Tetrahedron*, **2002**, *58*, 629.
(26) For a molecular dynamics simulation of the complexes formed between eosin and a poly(propylene amine) dendrimer, see: Teobaldi, G.; Zerbetto, F. *J. Am. Chem. Soc.* **2003**, *125*, 7388.
(27) These experiments could not be performed for dendron $\mathbf{A6}^{12+}$ because an insufficient amount of compound was available.
(28) Dynamic quenching of the eosin fluorescence by the viologen units of the dendrimers can be ruled out because of the short lifetime (τ = 3.8 ns) of the eosin excited state and the low concentration ($<2.1 \times 10^{-5}$ M) of the quencher.
(29) The absorption maximum of eosin in dichloromethane in the presence of an excess of tetrabutylammonium chloride occurs at 540 nm.

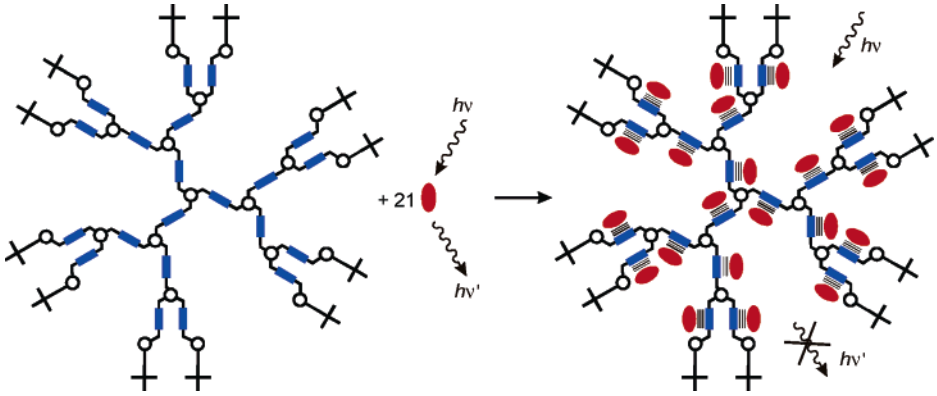

Figure 3. Filling up the "seats" in the polycationic dendritic host with dicationic guests. The red elipsoids are dianions of eosin, and the blue rectangles are dicationic bipyridinium units.

trifluoroacetate salt precipitates out Cl^- ions as AgCl and the changes in the absorption and fluorescence spectra show that $\mathbf{D1}^{2-}$ re-enters the dendrimer.

Conclusions

We have prepared and studied two dendrimers, $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$, constructed around a 1,3,5-substituted benzenoid-type core, bearing 9 and 21 viologen units in their branches, respectively, and terminated with tetraarylmethane groups. We have shown that each viologen unit of the dendrimers can associate with a molecule of the red dye eosin as its dianion $\mathbf{D1}^{2-}$. Therefore, the number of "seats" available (Figure 3) for the guest molecules is 9 and 21 for $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$, respectively. In such compounds, it is clear that the $\mathbf{D1}^{2-}$ guest molecules are hosted in the interior of the dendrimer. Host−guest interactions, which are signaled by the changes in the absorption spectrum and the complete quenching of the intense fluorescence of eosin, can be destroyed by the addition of chloride ions. Eosin is therefore allowed to escape from the dendrimer scaffold in a controlled way, thus regaining its fluorescence. The host−guest complexation can be restored when chloride ions are precipitated out by addition of silver ions.

We would like to note that these dendrimers are quite flexible structures, with rapidly moving branches, and that the association between each eosin molecule and its viologen "seat" is not a static but a dynamic process. In a scaffold each item occupies a well-defined place; in our case, however, it is probable that the guest molecules move from seat to seat, like in a merry-go-round.

These results are of interest for the design and preparation of dendrimers that can act as controllable polytopic receptors and for the development of supramolecular systems capable of performing functions related to, for example, drug delivery or sensing applications.

Experimental Section

The tetrabutylammonium salt of eosin dianion $\mathbf{D1}^{2-}$ was prepared from the disodium salt of eosin, also called eosin Y (Aldrich), dissolved in water by addition of tetrabutylammonium chloride. Dioctyl viologen $\mathbf{A1}^{2+}$, as its bis(hexafluorophosphate) salt, was kindly supplied by Prof. A. Arduini (University of Parma). The equipment and procedures used to obtain absorption spectra and emission spectra, decays, and quantum yields have been previously described.[7] The preparation, characterization, and properties of the dendrons $\mathbf{A2}^{4+}$ and $\mathbf{A6}^{12+}$, and the dendrimers $\mathbf{A9}^{18+}$ and $\mathbf{A21}^{42+}$ (as their hexafluorophosphate salts) are described below with the exception of $\mathbf{A2}^{4+}$ which has already been reported in the literature.[17]

Synthesis. Solvents were purchased from Aldrich and purified according to literature procedures. Reagents and compounds were purchased from Aldrich, except for $\mathbf{A2}\cdot 4PF_6$,[17] $\mathbf{2}\cdot 3PF_6$,[17] and $\mathbf{3}\cdot 2PF_6$.[18] Thin-layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60F (Merck 5554). The plates were inspected by UV light and, if required, developed in I_2 vapor. Column chromatography was carried out by using silica gel 60 (Merck 9385, 230−400 mesh). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. All ^1H and ^{13}C NMR spectra were recorded on either (i) a Bruker ARX500 (500 and 125 MHz, respectively) or (ii) a Bruker Avance500 (500 and 125 MHz, respectively), using residual solvent as the internal standard. Samples were prepared using CD_3COCD_3 or CD_3CN purchased from Cambridge Isotope Labs. All chemical shifts are quoted using the δ scale, and all coupling constants (J) are expressed in hertz (Hz). Fast atom bombardment (FAB) mass spectra were obtained using a ZAB-SE mass spectrometer, equipped with a krypton primary atom beam, utilizing a *m*-nitrobenzyl alcohol matrix. Cesium iodide or poly(ethylene glycol) was employed as a reference compound.

(i) Tetrakis(hexafluorophosphate) Salt $\mathbf{1}\cdot 4PF_6$. Thionyl chloride (0.3 mL, 1.55 mmol) and pyridine (0.25 mL, 3.1 mmol) were added separately to a solution of the tetracationic alcohol $\mathbf{A2}\cdot 4PF_6$ (2.3 g, 1.0 mmol) in dry MeCN (20 mL), and the reaction mixture was stirred at 40 °C overnight. After removal of solvent, the residue was treated with a 5% aqueous solution (50 mL) of NH_4PF_6. The precipitate was collected by filtration, washed with H_2O (200 mL), dried, and subjected to column chromatography (SiO_2: 10 mM NH_4PF_6 in Me_2CO). The resulting product was washed with H_2O and dried to afford the tetracationic chloride $\mathbf{1}\cdot 4PF_6$ (1.96 g, 85%). M.p. > 250 °C. MS (FAB): m/z = 2151 $[M - PF_6]^+$, 2006 $[M - 2PF_6]^+$, 1860 $[M - 3PF_6]^+$. ^1H NMR [500 MHz, CD_3COCD_3]: δ 9.45 (4 H, d, J = 7 Hz), 9.38 (4 H, d, J = 7 Hz), 8.74 (8 H, d) 7.88 (1 H, s) 7.86 (2 H, s), 7.62 (4 H, d, J = 9 Hz), 7.30−7.03 (34 H, m), 6.84 (4 H, d, J = 9 Hz), 6.18 (4 H, s), 6.09 (4 H, s), 4.70 (2 H, s), 4.21−4.08 (8 H, m), 3.92−3.81 (8 H, m), 1.29 (36 H, s).

(ii) Octadecakis(hexafluorophosphate) Salt $\mathbf{A9}\cdot 18PF_6$. A solution of the tricationic salt[18] $\mathbf{2}\cdot 3PF_6$ (26 mg, 0.025 mmol), the tetracationic chloride $\mathbf{1}\cdot 4PF_6$ (468 mg, 0.2 mmol), and KI (50 mg, 0.3 mmol) in DMF (1 mL) was stirred at 50 °C in the dark under an argon atmosphere for 2 days. After cooling to room temperature, H_2O (50 mL) and NH_4PF_6 (1.0 g, 6.1 mmol) were added into the reaction mixture. The precipitate was collected by filtration, dried, and subjected to column chromatography (SiO_2, Me_2CO, and then 5 mM, 10 mM, and saturated solutions of NH_4PF_6 in Me_2CO consecutively). The resulting product was washed with H_2O and dried to afford $\mathbf{A9}\cdot 18PF_6$ (127 mg, 60%). M.p. > 250 °C. ^1H NMR [500 MHz, CD_3COCD_3]: δ 9.40−9.20 (36 H, m), 8.64 (32 H, m), 8.00 (9 H, br s) 7.97 (3 H, br s), 7.58 (12 H,

d, $J = 9$ Hz), 7.28−6.96 (102 H, m), 6.82 (12 H, d, $J = 9$ Hz), 6.14−6.03 (36 H, m), 4.17−4.05 (24 H, m), 3.88−3.78 (24 H, m), 1.34 (108 H, s).

(iii) Dodecakis(hexafluorophosphate) Salt A6·12PF$_6$. A solution of the dicationic salt[17] **3**·2PF$_6$ (0.16 g, 0.217 mmol), the tetracationic chloride **1**·4PF$_6$ (1.5 g, 0.653 mmol), and KI (200 mg, 1.2 mmol) in DMF (3 mL) was stirred at 50 °C in the dark under an argon atmosphere for 2 days. After cooling to room temperature, H_2O (150 mL) and NH_4PF_6 (3.0 g, 18.4 mmol) were added into the reaction mixture. The precipitate was collected by filtration, dried, and subjected to column chromatography (SiO_2, Me_2CO, and then 5 mM, 10 mM, and saturated solutions of NH_4PF_6 in Me_2CO consecutively). The resulting product was washed with H_2O and dried to afford the alcohol **A6**·12PF$_6$ (0.75 g, 63%). M.p. > 250 °C. MS (FAB): $m/z = 5258$ $[M - 2PF_6]^+$, 5113 $[M - 3PF_6]^+$, 4968 $[M - 4PF_6]^+$. ^{1}H NMR [500 MHz, CD_3COCD_3]: δ 9.33 (24 H, d), 8.65 (24 H, m), 8.03 (6 H, br s), 7.81 (1 H, s), 7.77 (2 H, s), 7.62 (8 H, d, $J = 9$ Hz), 7.30−7.03 (68 H, m), 6.83 (8 H, d, $J = 9$ Hz), 6.32−5.88 (24 H, m), 4.69 (2 H, s), 4.30−4.03 (16 H, m), 4.01−3.70 (16 H, m), 1.29 (72 H, s). ^{13}C NMR [125 MHz, CD_3COCD_3]: δ 160.2, 156.8, 150.5, 150.2, 148.2, 147.3, 145.8, 145.5, 144.1, 139.2, 135.4, 134.1, 131.8, 131.7, 131.2, 130.7, 130.4, 128.6, 127.4, 127.3, 127.2, 125.7, 124.8, 124.1, 115.3, 113.1, 69.5, 69.3, 67.6, 67.2, 64.4, 64.2, 63.7, 63.3, 33.8, 30.7.

(iv) Dotetracosakis(hexafluorophosphate) Salt A21·42PF$_6$. Thionyl chloride (0.03 mL, 0.155 mmol) and pyridine (0.030 mL, 0.37 mmol) were added separately to the solution of the alcohol **A6**·12PF$_6$ (350 mg, 0.063 mmol) in dry MeCN (3 mL). The reaction mixture was stirred at 50 °C under argon for 4 h. After removal of solvent, the residue was treated with of 5% aqueous solution (5 mL) of NH_4PF_6. The resulting solid was collected by filtration, washed with H_2O (20 mL), dried, and subjected to column chromatography (SiO_2: 10 mM NH_4PF_6 in Me_2CO). The resulting product was washed with H_2O and dried to afford the chloride intermediate (280 mg, 80%) which was added to the solution of tricationic salt[18] **2**·3PF$_6$ (13 mg, 0.013 mmol) and KI (20 mg, 0.12 mmol) in DMF (1 mL). The reaction mixture was stirred at 50 °C in the dark under an argon atmosphere for 2 days. After cooling to room temperature, H_2O (25 mL) and NH_4PF_6 (0.5 g, 3 mmol) were added to the mixture. The resulting precipitate was filtered, dried, and subjected to column chromatography (SiO_2, Me_2CO, and then 5 mM, 10 mM, and saturated solutions of NH_4PF_6 in Me_2CO consecutively). The resulting product was washed with H_2O and dried to afford dendrimer A21·42PF$_6$ (84 mg, 36%). M.p. > 250 °C. ^{1}H NMR [500 MHz, CD_3COCD_3]: δ 9.40−9.08 (72 H, m), 8.95−8.48 (96 H, m), 8.03 (30 H, br s), 7.61 (24 H, br s), 7.55−6.95 (204 H, m), 6.85 (24 H, br s), 6.14−6.03 (36 H, m), 4.21−4.09 (48 H, m), 3.91−3.82 (48 H, m), 1.29 (216 H, s).

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Supporting Information Available: ^{1}H NMR spectra of **A6**·12PF$_6$ and **A21**·42PF$_6$ at 500 MHz in CD_3CN at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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