Polyviologen Dendrimers as Hosts and Charge-Storing Devices

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Abstract: Two dendrimers were designed and synthesized that contain a 1,3,5-trisubstituted benzenoid core and incorporate 9 and 21 viologen (4,4′-bipyridinium) units in their branches in addition to hydrophilic (aryloxy) terminal groups. For comparison purposes, model compounds containing one and two viologen units were also studied. These polycationic dendrimers form strong host–guest complexes with the dianionic form of the red dye eosin in dilute CH_2Cl_2 solutions. Titration experiments, based on fluorescence measurements, showed that each viologen unit in the dendritic structures becomes associated with an eosin dianion. Electrochemical (in MeCN) and photosensitization (in CH_2Cl_2) experiments revealed that only a fraction of the viologen units present in the dendritic structures can be reduced. This fraction corresponds to the number of viologen units present in the outer shells of the dendrimers. The reasons for incomplete charge pooling are discussed. Comparison with the behavior of polyviologen dendrimers that are terminated with bulky tetraarylmethane groups and were studied previously enabled the role played by the terminal groups in the redox and hosting properties to be elucidated.

Keywords: dendrimers · electrochemistry · host–guest systems · photosensitization · viologens

Introduction

Dendrimers are repetitively branched, yet constitutionally well-defined, macromolecules exhibiting high monodispersity.[1] These nanoscopic compounds can contain selected chemical units in predetermined sites of their structure (core, branches, periphery), mutual interactions of which can lead to unusual, sometimes unpredictable, physicochemical properties that result in a wide range of potential applications.[2] Dendrimers containing photoactive and/or electroactive moieties are currently attracting much attention, since they can be designed to perform useful functions, such as light harvesting,[3] charge pooling,[4,5,6] ion sensing with signal amplification,[7] and molecular recognition.[8]

Dendrimers $B9^{18+}$ and $B21^{42+}$ (Scheme 1), discussed in this paper, are based on a 1,3,5-trisubstituted benzenoid core and contain 9 and 21 4,4′-bipyridinium (viologen) units, respectively, in their branches, and 6 and 12 aryloxy groups, respectively, at their peripheries. Viologen is a well-known electroactive species that undergoes two successive one-electron, reversible reduction processes[9, 10] and exhibits peculiar spectroscopic features in both its dicationic and radical-cationic forms. Viologen units are also known to give strong donor–acceptor complexes with electron-donating species.[10]

We report 1) the synthesis of dendrimers $B9^{18+}$ and $B21^{42+}$ as their hexafluorophosphate salts, 2) their interaction with the eosin dianion (Ey^{2-}, Scheme 1), and 3) their electrochemical and photosensitized reduction. For comparison purposes, we also investigated the properties of monoviologen compounds 1,1′-dibenzyl-4,4′-bipyridinium (dbV^{2+}) and 1,1′-dioctyl-4,4′-bipyridinium (doV^{2+}), as well as dendron $B2^{4+}$, which contains only two viologen units (Scheme 1).

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B21⁴²⁺ appears as: B21^{42+}

Ey^{2-}

dbV^{2+}

doV^{2+}

B9^{18+}

B2^{4+}
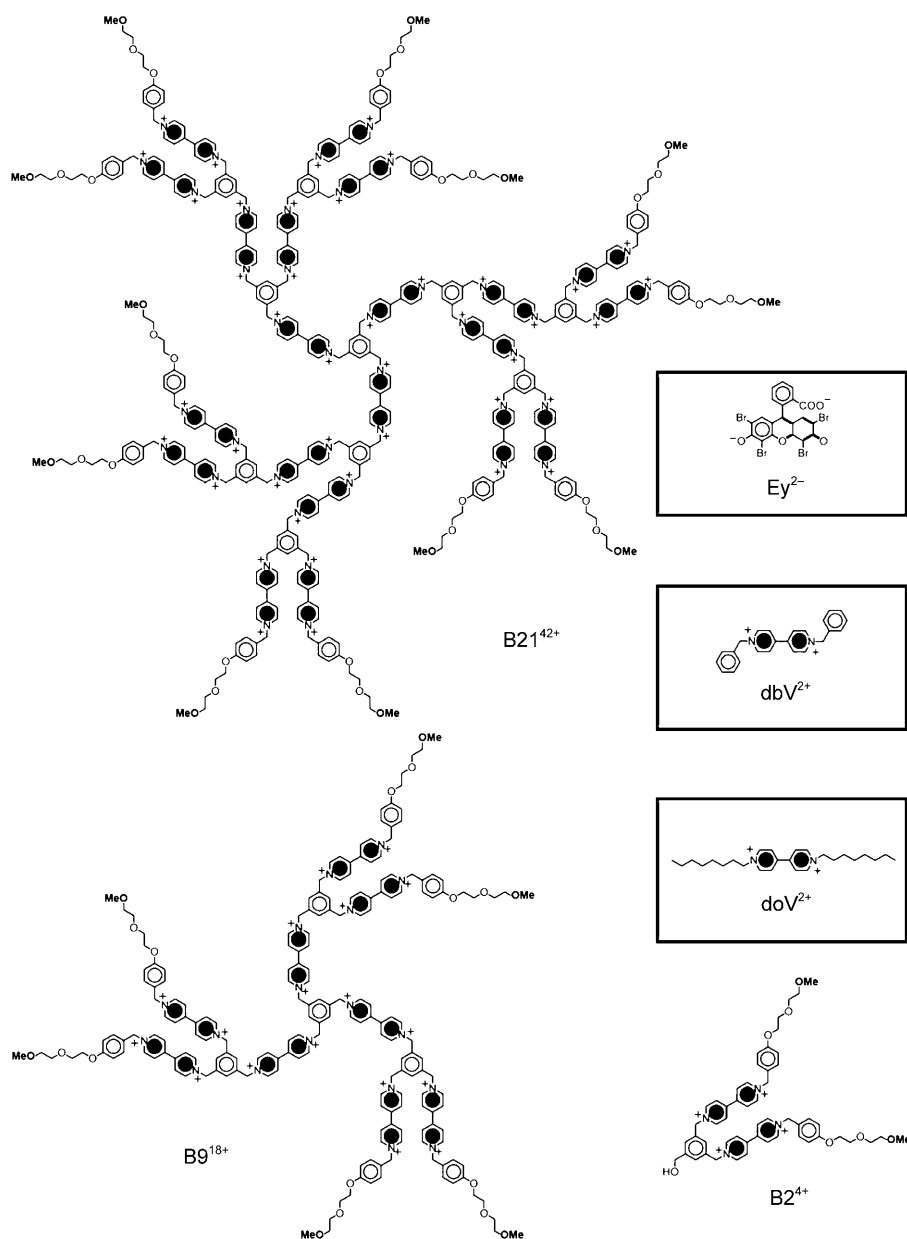
Scheme 1. Structural formulas of the investigated compounds. Symbols **B**n^{2n+} indicate the number of viologen units in the dendritic structure (**n**) and the overall electric charge ($2n$) on each compound.

The results are discussed in comparison with those reported previously for two analogous dendrimers (**A 9**[18+] and **A 21**[42+]) terminated with tetraarylmethane bulky moieties instead of aryloxy groups.[5, 11] The properties of dendron **A 2**[4+], analogous to **B 2**[4+], were also investigated in order to complete the comparison between the two families of compounds.

Results

Synthesis: The synthetic routes to dendrimers **B 9**·18 PF$_6$ and **B 21**·42 PF$_6$ and their intermediates **5**·4 PF$_6$ and **8**·12 PF$_6$ are outlined in Schemes 2 and 3. Bromide **5**·4 PF$_6$ (Scheme 2) was obtained in 61 % yield by treating alcohol **B 2**·4 PF$_6$ with CBr$_4$ in dry MeCN in the presence of PPh$_3$. Alkylation of salt **6**·3 PF$_6$ with bromide **5**·4 PF$_6$ in MeCN gave dendrimer **B 9**·18 PF$_6$ in 25 % yield after counterion exchange. Reaction of bromide **5**·4 PF$_6$ with salt **4**·2 PF$_6$ followed by counterion exchange afforded alcohol **7**·12 PF$_6$ in 65 % yield (Scheme 3). Alcohol **7**·12 PF$_6$ was treated with CBr$_4$ in dry MeCN in the presence of PPh$_3$ to obtain bromide **8**·12 PF$_6$, which was then treated with salt **6**·3 PF$_6$ to give dendrimer **B 21**·42 PF$_6$ in an overall yield of 15 % after counterion exchange.
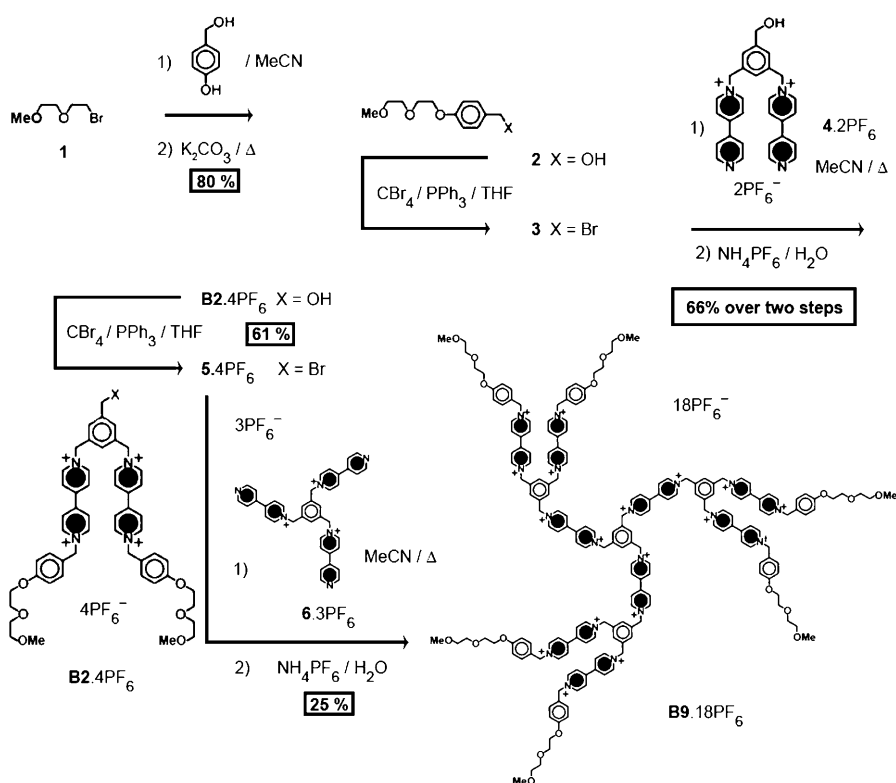
Abstract in Italian: *Sono stati progettati e sintetizzati due dendrimeri contenenti un'unità benzenica sostituita nelle posizioni 1,3,5 come core, 9 e 21 unità viologeno (4,4'-dipiridinio), rispettivamente, nelle ramificazioni e gruppi idrofilici di tipo arilossi come unità periferiche. In CH$_2$Cl$_2$ questi dendrimeri policationici interagiscono con la forma dianionica dell'eosina dando complessi host–guest in cui, come mostrato chiaramente dalle titolazioni basate su misure di fluorescenza, ogni unità viologeno contenuta nella struttura dendritica si associa con un anione eosina. Esperimenti di riduzione elettrochimica (in MeCN) e fotochimica (in CH$_2$Cl$_2$ e in presenza di un opportuno fotosensibilizzatore) hanno inoltre messo in evidenza che non tutte le unità viologeno contenute nei dendrimeri possono essere ridotte; in particolare, sembra che siano riducibili solo quelle presenti nel guscio dendritico piú esterno. Il confronto con il comportamento di composti modello, contenenti una e due unità viologeno, e di dendrimeri precedentemente investigati, che differiscono da quelli discussi in questo lavoro per la presenza di gruppi terminali piú ingombranti di tipo tetraarilmetano, ha fatto luce sui motivi che inibiscono la riduzione di tutte le unità viologeno contenute nelle strutture dendritiche e ha chiarito se e come la natura dei gruppi terminali influenza le proprietà redox e complessanti di questi dendrimeri.*

Scheme 2. Synthesis of dendron **B2**·4PF$_6$ and dendrimer **B9**·18PF$_6$.

Absorption spectra: Figure 1 shows the absorption spectra in MeCN of dendrimers **B9**$^{18+}$ and **B21**$^{42+}$ in comparison

with that of **dbV**$^{2+}$, employed as model compound of the dendrimer viologen units, at concentrations 9 and 21 times higher than those of **B9**$^{18+}$ and **B21**$^{42+}$, respectively. Evidently, the absorption spectra of the dendrimers are not identical to that of the model compound, and the differences are much more pronounced for **B21**$^{42+}$. In particular, its spectrum is less intense than that of the model compound in the spectral region around the maximum and shows broad and weak absorption features that are also present to a minor extent in the spectrum of **B9**$^{18+}$ and emerge from the low-energy tail of the intense UV band.

Eosin complexation: 4,4′-Bipyridinium dications interact strongly with the dianionic form of eosin (**Ey**$^{2-}$) to yield charge-transfer (CT) complexes.[11,12] We observed previously that addition of **doV**$^{2+}$, as its hexafluorophosphate salt, to a solution of **Ey**$^{2-}$ in
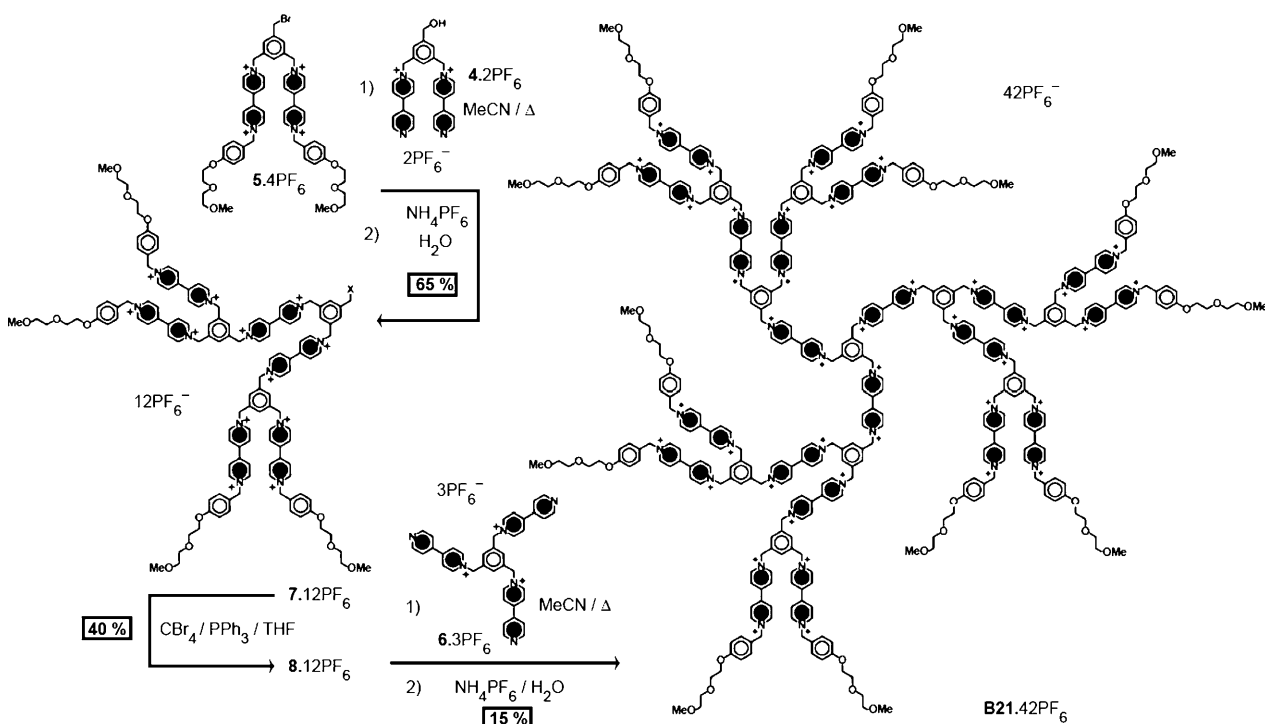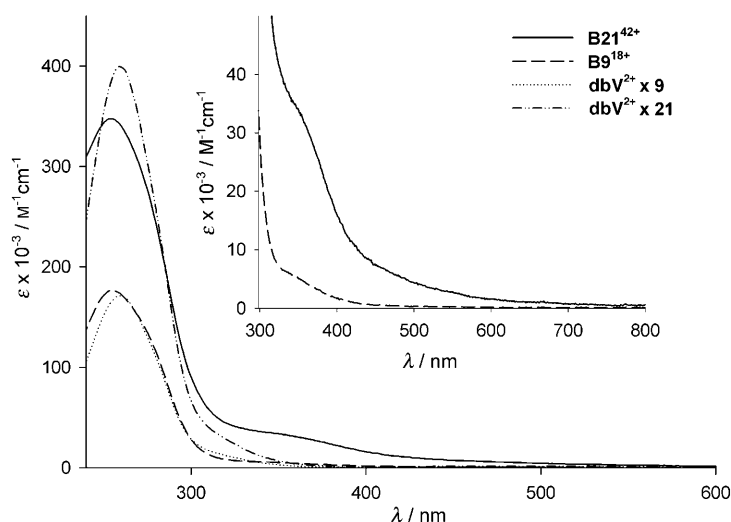

Scheme 3. Synthesis of dendrimer **B21**·42PF$_6$.

Figure 1. Absorption spectra in MeCN of dendrimers $B9^{18+}$ (dashed line) and $B21^{42+}$ (solid line) compared with the spectra of 9 (dotted line) and 21 (dashed and dotted line) dbV^{2+} units. Inset: Enlarged view ($\lambda >$ 300 nm) of the spectra of the dendrimers.

CH_2Cl_2, as its tetrabutylammonium salt, causes 1) noticeable perturbations in the visible absorption band of Ey^{2-}, and 2) complete quenching of its fluorescence because of the formation of a strong 1:1 complex ($K_{ass} > 10^6 M^{-1}$).[11]

Fluorescence titration experiments were performed to investigate the interaction between Ey^{2-} and dendrimers $B9^{18+}$ and $B21^{42+}$. The experimental data, obtained by titrating solutions of $B9^{18+}$ and $B21^{42+}$ in CH_2Cl_2 (each containing ca. 1×10^{-5} M viologen units) with a solution of Ey^{2-} in acetonitrile (1 mM) (Figure 2), show that the eosin fluorescence signal appears only when the number of added Ey^{2-} exceeds the number of viologen units contained in each dendrimer.

These results demonstrate that $B9^{18+}$ and $B21^{42+}$ can quench the fluorescence of 9 and 21 eosin dianions, respectively; that is, each viologen unit of the dendrimers associates with one eosin dianion. Titration of dendron $B2^{4+}$ (9.0×10^{-6} M viologen units) confirms the stoichiometric formation of 1:1 complexes between the viologen units and eosin (Figure 2). The quenching of eosin fluorescence by association with the quencher (static mechanism) is confirmed by the fact that dynamic quenching can be ruled out considering the short lifetime ($\tau = 3.8$ ns) of the eosin excited state and the low concentration ($<5\times10^{-5}$ M) of the quencher.

Electrochemical reduction: Electrochemical experiments were carried out in argon-purged MeCN. The half-wave potentials, number of exchanged electrons, and diffusion coefficients of dbV^{2+} and dendrimers $B9^{18+}$ and $B21^{42+}$ are listed in Table 1, in which results previously obtained[5] for dendrimers $A9^{18+}$ and $A21^{42+}$ are also reported for comparison purposes (see Discussion section).

Table 1. Half-wave reduction potentials, numbers of exchanged electrons, and diffusion coefficients in argon-purged MeCN solution at 298 K.

	$E_{1/2}^1$ [a] [V vs. SCE]	$E_{1/2}^2$ [a] [V vs. SCE]	n_{el} [b]	n [c]	$10^5 D$ [cm^{2}s^{-1}]
dbV^{2+}	−0.35	−0.77	1	1	1.60
$B9^{18+}$	−0.30	−0.78[d]	6	9	0.45
$B21^{42+}$	−0.30	−0.73[d]	11	21	0.27
$A9^{18+}$[e]	−0.29	−0.75[d]	5	9	0.32
$A21^{42+}$[e]	−0.30	−0.76[d]	14	21	0.27

[a] Glassy carbon working electrode, TBAPF$_6$ supporting electrolyte. [b] Number of exchanged electrons obtained by chronoamperometric experiments (estimated error ±20%). [c] Overall number of viologen units present in the compound, as confirmed by eosin complexation experiments. [d] Process affected by adsorption. [e] From reference [5].

Compounds dbV^{2+}, $B9^{18+}$, and $B21^{42+}$ exhibit the two reduction processes typical of viologens. Cyclic voltammetric patterns show that the reducible viologen units in each dendrimer are equivalent and that the first reduction is reversible with Nernstian behavior in all cases (Figure 3), whereas the second process, particularly for $B21^{42+}$, is affected by adsorption of the reduced species on the electrode.

The diffusion coefficients and number of exchanged electrons (Table 1) were determined by chronoamperometric experiments performed at the potential of the first reduction process by using ultramicroelectrodes.[13] As expected, the diffusion coefficient of $B9^{18+}$ is larger than that of $B21^{42+}$. For both dendrimers the number of exchanged electrons is smaller than that expected on the basis of the number of the viologen units in the molecular structure. Apparently, only the external viologen units—6 for $B9^{18+}$ and 12 for $B21^{42+}$—are reduced in electrochemical experiments.

Unfortunately, spectroelectrochemical experiments aimed at obtaining the absorption spectra of the reduced compounds could not be performed because of adsorption of the reduced species on the platinum minigrid used as working electrode.

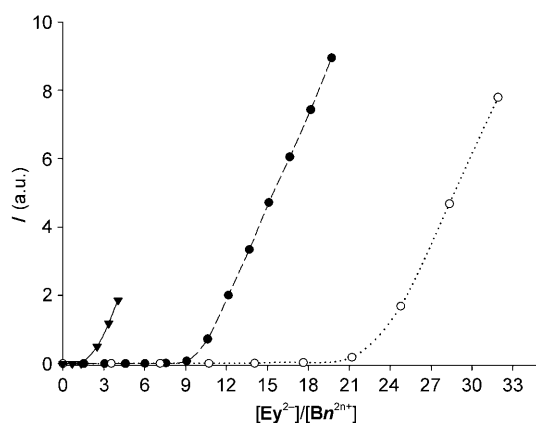**Photosensitized reduction**: One-electron reduction of viologen compounds can be conveniently performed by using

Figure 2. Fluorescence titration experiments performed in CH_2Cl_2 solutions. Intensity of the Ey^{2-} fluorescence band ($\lambda_{ex} = 500$ nm, $\lambda_{em} = 560$ nm) as a function of the $[Ey^{2-}]/[Bn^{2n+}]$ ratio: $B2^{4+}$ (solid triangles), $B9^{18+}$ (solid circles), $B21^{42+}$ (open circles).
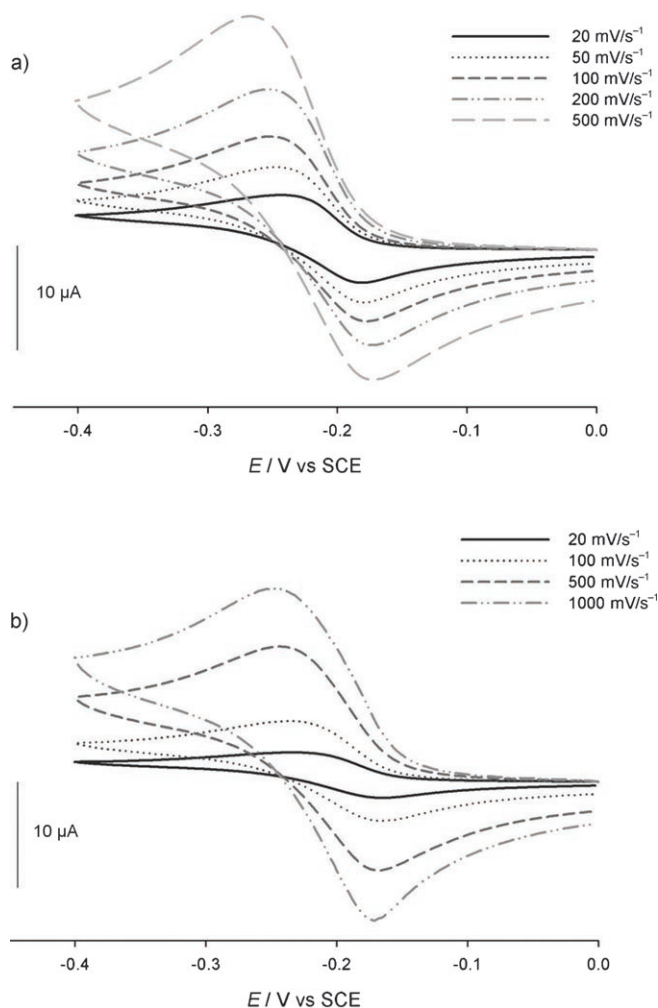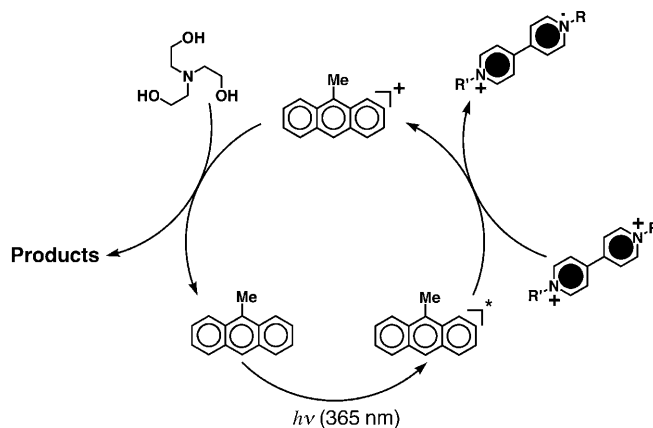
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Figure 3. Cyclic voltammetric behavior as a function of sweep rate for the first reduction process of a) dendrimer $\mathbf{B9}^{18+}$ (1.2×10^{-4} M) and b) dendrimer $\mathbf{B21}^{42+}$ (7×10^{-5} M). Argon-purged MeCN, glassy carbon working electrode, TBAPF$_6$ (0.1 M) supporting electrolyte.

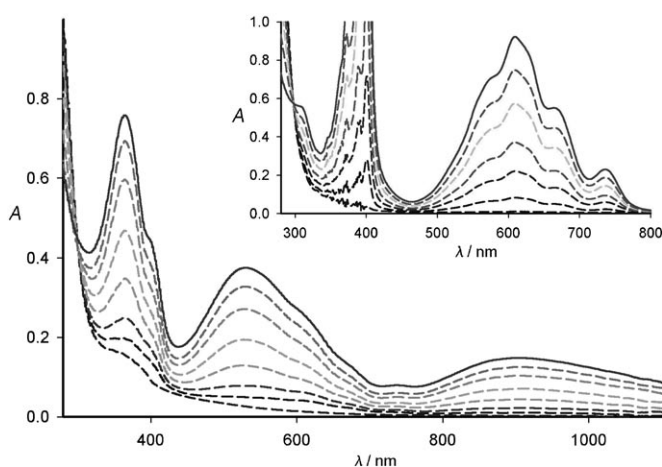Scheme 4. Scheme of photosensitized $\mathbf{doV}^{2+}$ reduction.

Figure 4. Spectral changes (optical path 1 cm) observed on irradiation with 365 nm light of a solution of 9-methylanthracene (1.2×10^{-4} M), TEOA (5.0×10^{-2} M), and $\mathbf{B21}^{42+}$ (4.0×10^{-6} M) or $\mathbf{doV}^{2+}$ (6.7×10^{-5} M; inset) in degassed CH$_2$Cl$_2$. The solid line corresponds to the photostationary state. A solution containing 9-methylanthracene (1.2×10^{-4} M) in CH$_2$Cl$_2$ was used as reference.

suitable photosensitizers in the presence of sacrificial reductants. Light excitation leads the photosensitizer to a long-lived excited state that can transfer an electron to a viologen during an encounter. The back-electron-transfer reaction between the oxidized photosensitizer and the reduced viologen is prevented by fast reduction of the oxidized photosensitizer by the sacrificial reductant. Such photoinduced processes have been exploited extensively for photogeneration of hydrogen from aqueous solutions[3d, 14] and to power artificial molecular devices and machines.[15]

Previous investigations[5] showed that the photochemical reduction of viologen compounds can be performed efficiently in degassed CH$_2$Cl$_2$ by using 9-methylanthracene[16] as photosensitizer and triethanolamine (TEOA) as sacrificial reductant. Light excitation of a solution of 9-methylanthracene in CH$_2$Cl$_2$ in the presence of TEOA causes reduction of $\mathbf{doV}^{2+}$ to its monomeric radical cation $\mathbf{doV}^{\bullet+}$ (Scheme 4, Table 2, inset of Figure 4).

Figure 4 shows the spectral changes observed on irradiation with 365 nm light of a solution of 9-methylanthracene (1.2×10^{-4} M), TEOA (5.0×10^{-2} M), and $\mathbf{B21}^{42+}$ (4.0×10^{-6} M) in degassed CH$_2$Cl$_2$. The spectral features that arise on irradiation are characteristic of the formation of both monomeric and dimeric reduced viologen species; similar changes were obtained for dendrimer $\mathbf{B9}^{18+}$. The total number of electrons exchanged by dendrimers $\mathbf{B9}^{18+}$ and $\mathbf{B21}^{42+}$ at the photostationary state (Table 2), determined from absorbance measurements, is slightly smaller than that obtained in the chronoamperometric experiments. This discrepancy can be attributed to small amounts of oxidizing impurities contained in the solvent and/or the samples used or, most likely, to underestimation of the dimer concentration because the ε values[17] used refer to a different solvent.

Spectra recorded at different irradiation times showed that the fraction of monomeric and dimeric reduced violo-

Table 2. Ratio between dimerized ($V_d^{.+}$) and monomeric ($V_m^{.+}$) monoreduced viologen units, percentages of the total monoreduced viologen units ($V_{tot}^{.+}$), and numbers of exchanged electrons (n_{phot}) at the photostationary state.[a]

	$V_d^{.+}/V_m^{.+}$	% $V_{tot}^{.+}$	n_{phot}[b]	n[c]
doV^{2+}	0	100	1.0	1
B2^{4+}	0.15	75	1.5	2
B9^{18+}	1.32	53	4.7	9
B21^{42+}	1.10	41	8.5	21
A2^{4+}	0.21	72	1.4	2
A9^{18+}[d]	0.85	48	4.3	9
A21^{42+}[d]	0.82	60	12.6	21

[a] Degassed CH_2Cl_2, irradiation with 365 nm light, 1.2×10^{-4} M 9-methylanthracene, 5.0×10^{-2} M TEOA. [b] Estimated error $\pm 20\%$. [c] Overall number of viologen units present in compounds, as confirmed by eosin complexation experiments. [d] Adjusted from reference [5].

gen species changes with time (Figure 5). At the photostationary state, dendrimer **B9^{18+}** shows prevalence of dimerized (ca. 57%) over monomeric (ca. 43%) viologen units;
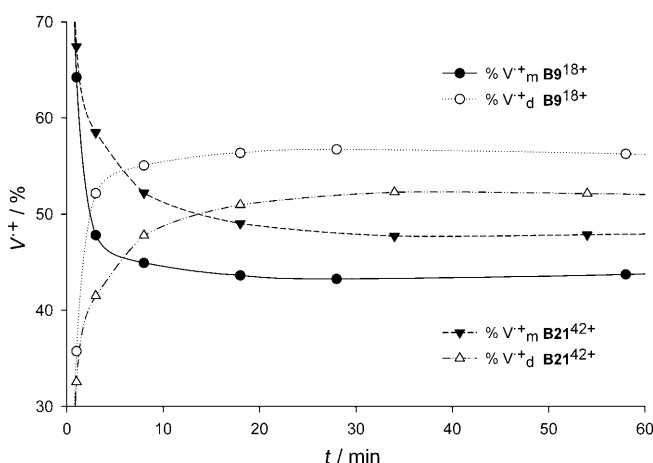

Figure 5. Changes in the percentages of the monomeric ($V_m^{.+}$, solid symbols) and dimerized ($V_d^{.+}$, open symbols) monoreduced viologen units with increasing irradiation time for dendrimers **B9^{18+}** (circles) and **B21^{42+}** (triangles).

for dendrimer **B21^{42+}**, the fraction of dimerized viologen units is slightly lower.

For comparison purposes, we performed photochemical reduction of dendrons **B2^{4+}** and **A2^{4+}** (Table 2) and found that 1) the number of reducible viologen units is slightly smaller than expected and that 2) the percentage of dimerization is low and almost unaffected by the nature of the stoppers.

Discussion

The results presented here are now discussed and compared with those reported previously for similar dendrimers, terminated with bulky tetraarylmethane groups (**A9^{18+}** and **A21^{42+}**, Tables 1 and 2).[5,11]

Absorption spectra: The absorption spectra of dendrimers **B9^{18+}** and especially **B21^{42+}** are different from that of **dbV^{2+}**. The differences could originate from the fact that 1) **dbV^{2+}** is not a fully satisfactory model, at least from the spectroscopic viewpoint, for the viologen units in the dendritic structure, since each unit in the dendrimer shares benzyl groups with other units (Scheme 1) and some benzyl groups carry bismethyleneoxy substituents, and 2) CT interactions between the electron-accepting viologen units and the proximate (through-bond) or remote (through-space) electron-donating aryloxy units, as suggested by the appearance of an absorption tail for $\lambda > 320$ nm.

Previously studied dendrimers **A9^{18+}** and **A21^{42+}** exhibited similar behavior; however, a quantitative analysis shows that **A21^{42+}** has an absorption due to CT interactions that is less intense (about one half) and shifted towards lower energy compared to **B21^{42+}**. These results show that the terminal stoppers play some role in determining the spectroscopic properties of such dendrimers.

Host properties toward eosin: Both **A**- and **B**-type dendrimers can host a number of eosin dianions equal to the number of viologen units in their branches. Thus, neither the dendrimer generation nor the nature of the peripheral groups play a role in the formation of viologen/eosin complexes. Clearly, eosin anions can penetrate into the interior of the positively charged dendrimers, replacing the PF_6^- counterions. The dendrimers can be viewed as polyvalent scaffolds with a well-defined number of independent sites where single eosin dianions can be hosted.

Charge pooling: The electrochemical and photosensitization experiments performed on **A**- and **B**-type dendrimers (Tables 1 and 2) revealed that, in all cases, only a fraction of the viologen units can be reduced. Within experimental error, this fraction corresponds to the number of viologen units in the outer shell (6 for **A9^{18+}** and **B9^{18+}**, 12 for **A21^{42+}** and **B21^{42+}**).

The fact that the number of reducible viologen units is smaller than that expected cannot be attributed to lack of branches in the structures of the dendrimers, because the results obtained for eosin complexation show clearly that the compounds examined do contain 9 (**A9^{18+}** and **B9^{18+}**) and 21 (**A21^{42+}** and **B21^{42+}**) viologen units, in agreement with the ^{1}H NMR spectroscopic and mass-spectrometric characterization.

The electrochemical reduction experiments showed that, in each dendrimer, the first reduction process of all of its reducible viologen units occurs at the same potential and that the first reduction process of all of the reducible viologen units in all of the dendrimers occurs at the same potential. Interestingly, the reduction potential of a reducible unit is not affected by the state of the other reducible units, and this is an ideal property for a charge-pooling system. Furthermore, the nature of the peripheral groups—tetraarylmethane and aryloxy units for **A**- and **B**-type families, respectively—affects neither the number of reducible viologen

units nor the first reduction potential. Two concomitant effects can be taken into account to explain the lack of complete electrochemical reduction: 1) on reduction of the external viologen shell, shrinkage of the dendrimer structure, favored by dimerization of the reduced units, prevents the internal viologen units "seeing" the electrode, and 2) the internal viologen units, engaged in tight ionic couples with the hexafluorophosphate counterions, become more difficult to reduce, whereby electron hopping from external to internal viologen units is prevented.

Experiments on photosensitized reduction showed that the numbers of viologen units reducible under the photochemical conditions are in reasonable agreement with those obtained by chronoamperometric experiments, that is, only the viologen units in the external shells can be reduced. These experiments also reveal that formation of the one-electron reduced viologen units is accompanied by their dimerization. The lack of reduction of all the viologen units in such experiments can be explained by considering that 1) the uncharged photosensitizer cannot displace the counterions assembled in the proximity of the highly charged core of the dendrimer, and 2) the interaction between the photosensitizer and the internal viologen units can be prevented by dimerization of the external reduced units, a phenomenon which shrinks the dendrimer structure. We have also discovered that dimerization is not a strongly favored process, as shown by the fact that it does not occur for the mono-viologen **doV**$^{2+}$ species and leads to only 15–20 % of associated species in the case of dendrons **B2**$^{4+}$ and **A2**$^{4+}$ (Table 2), which are structurally preorganized for dimerization. For the dendrimers, the fraction of dimerized viologen units is higher, by about 45 and 57 % for the **A**- and **B**-type families, respectively, than expected because of the possibility of producing dimers also between reduced units belonging to different dendrons. The results also show that the bulky tetraarylmethane peripheral moieties disfavor formation of dimers compared with the smaller aryloxy groups.

Conclusion

We have found that polyviologen dendrimers, independently of the nature and bulkiness of the terminal groups (**A9**$^{18+}$, **A21**$^{42+}$, **B9**$^{18+}$, and **B21**$^{42+}$), can act as polytopic receptors toward electron-donor substrates and host a number of eosin dianions equal to the number of viologen units in their branches. The data obtained show clearly that the host–guest interactions that drive complex formation in low-polarity media are affected by neither the steric hindrance of the terminal groups nor the electronic interactions that these groups establish with the viologen units. These results are of interest for the design and construction of dendrimers capable of performing functions related to drug-delivery or sensing applications.

In principle, polyviologen dendrimers can behave as molecular batteries,[4–6] as they are potentially capable of storing, at easily accessible potentials, a number of electrons

twice that of the viologen units. Although it has been reported[4] that in dendrimers very similar to those described here all the viologen units are reducible, our results show clearly that only a fraction of these units can be reduced. This observation throws light on the reasons why charge pooling is incomplete and on the role played by the terminal groups.

The fact that the number of reducible viologen units is smaller than that expected cannot be attributed to lack of branches in the structures of the dendrimers, because the results obtained for eosin complexation indicate that the compounds examined do contain 9 (**A9**$^{18+}$ and **B9**$^{18+}$) and 21 (**A21**$^{42+}$ and **B21**$^{42+}$) viologen units.

Photosensitized reduction experiments revealed that, for both the **A**- and **B**-type families of dendrimers, a fraction of the monoreduced viologen units undergoes dimerization and that this process prevails for the dendrimers in which the bulky tetraarylmethane terminal groups have been removed.

We have also identified a dendrimer effect in the dimerization process involving the reduced viologen units. The dendritic structure of compounds **B9**$^{18+}$, **B21**$^{42+}$, **A9**$^{18+}$, and **A21**$^{42+}$ provides an environment that favors dimerization, since it forces the reduced viologen units to occupy close positions yet is flexible enough to enable interactions not only between the reduced units belonging to the same branch (intradendron interactions), but also between reduced units located in different branches (interdendron interactions).

Experimental Section

Electrochemical experiments: Cyclic voltammetric (CV) experiments were carried out in argon-purged MeCN (Romil Hi-Dry) at room temperature with an Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm², Amel); its surface was routinely polished with 0.3 μm alumina/water slurry on a felt surface immediately prior to use. In all cases, the counterelectrode was a Pt spiral, separated from the bulk solution by a fine glass frit, and an Ag wire was used as a quasireference electrode. Ferrocene ($E_{1/2} = +0.395$ V vs. SCE) was present as an internal standard. In all the electrochemical experiments the concentration of the compounds was in the range 1×10^{-4} to 7×10^{-5} M, and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) with 100 times higher concentration was added as supporting electrolyte. Cyclic voltammograms were obtained with sweep rates in the range 0.02–1.0 V s^{-1}; the IR compensation implemented within Autolab 30 was used, and every effort was made throughout the experiments to minimize the resistance of the solution. At any instance, the full reversibility of the voltammetric wave of ferrocene was taken as an indicator of the absence of uncompensated resistance effects. The reversibility of the observed processes was established by using the criteria of 1) separation of 60 mV between cathodic and anodic peaks, 2) a ratio of the intensities of the cathodic and anodic currents close to unity, and 3) constancy of the peak potential on changing sweep rate in the cyclic voltammograms. The experimental error in the potentials was estimated to be ±10 mV. The diffusion coefficients and the numbers of exchanged electrons were obtained independently by chronoamperometry, as described in the literature.[13] A Pt disk with a diameter of 50 μm was used as working electrode, and the experiments were carried out for 5 s, with 0.05 s sample time, at potentials of −0.40 V for **dbV**$^{2+}$ and −0.35 V for **B9**$^{18+}$ and **B21**$^{42+}$. The current intensities under steady-state conditions were determined from CV experiments by using the same

working electrode as the chronoamperometric experiments and a sweep rate of 10 mV s^{-1}.

Photochemical reduction: The experiments were performed in solutions of **doV**$^{2+}$, **A2**$^{4+}$, **B2**$^{4+}$, **B9**$^{18+}$, or **B21**$^{42+}$ in CH$_2$Cl$_2$ with 9-methylanthracene as photosensitizer and triethanolamine as sacrificial reductant. The solutions (3 mL) were degassed by repeated freeze–pump–thaw cycles and irradiated at 365 nm with light from a medium-pressure Hg lamp equipped with an interference filter.

Concentrations of the monomeric and dimeric forms of the monoreduced viologens: The monomer (c_M) and dimer (c_D) concentrations of the monoreduced viologen units were determined from the absorbance at 605 and 537 nm (A_{605} and A_{537}) by using Equations (1) and (2)

$$c_M = (A_{605}\varepsilon_{D537} - A_{537}\varepsilon_{D605})/(\varepsilon_{M605}\varepsilon_{D537} - \varepsilon_{M537}\varepsilon_{D605}) \tag{1}$$

$$c_D = (A_{537}\varepsilon_{M605} - A_{605}\varepsilon_{M537})/(\varepsilon_{M605}\varepsilon_{D537} - \varepsilon_{M537}\varepsilon_{D605}) \tag{2}$$

in which ε_{D537} and ε_{D605} represent the molar absorption coefficients of the dimer at the two selected wavelengths; their values were taken from the literature[17] and correspond to 29000 and 2350 M^{-1} cm^{-1}, respectively. For ε_{M605} and ε_{M537}, the molar absorption coefficients of the monomer, the values used were 14000 and 5770 M^{-1} cm^{-1}, respectively, in agreement with those reported in reference [17]. The concentration of the dimerized one-electron-reduced viologen units corresponds to $2 \times c_D$.

Materials and methods: All chemicals were purchased from Aldrich and used without further purification. Solvents were purchased from Aldrich and purified according to literature procedures. Thin-layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60F (Merck 5554). The plates were inspected by UV light. Column chromatography was performed on silica gel 60 (Merck 40–60 nm, 230–400 mesh). HPLC-grade MeCN was purchased from Aldrich and degassed by bubbling He. Known amounts of the compounds were dissolved in MeCN (HPLC grade) to afford stock solution of known concentration (0.001 M). The resulting solutions (injected volume 10 μL) were analyzed at ambient temperature by HPLC (flow rate 1.0 mL min^{-1}; mobile phase, pump A 0.1% CF$_3$CO$_2$H in H$_2$O, pump B MeCN/0.1% CF$_3$CO$_2$H in H$_2$O (95:5); time [min]/pump A [%] = 0/100, 8/100, 28/0, 42/0, 45/100) by employing a Hypersil BDS C18 column (length 25 cm, inside diameter 5.6 cm) operated by HP 1090 (Hewlett-Packard) connected to a thermo surveyor UV/Vis diode-array detector. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. ^{1}H and ^{13}C spectra were recorded on Bruker Avance500 (500 and 125 MHz, respectively) with residual proton signals of solvents as internal standard. Samples were prepared in CD$_3$CN or (CD$_3$)$_2$CO purchased from Cambridge Isotope Laboratories. Electron impact mass spectra (EIMS) were obtained on a VG Prospec mass spectrometer.

B2·4PF$_6$: A solution of **4·2PF$_6$** (1.0 g, 1.38 mmol), prepared by the literature procedure,[18] in dry MeCN (10 mL) was added dropwise to a solution of **3**[19] (1.0 g, 3.45 mmol) in dry MeCN (10 mL) under reflux and an argon atmosphere for 2 h. The reaction mixture was stirred for 2 d and then cooled to ambient temperature; the solvent was removed under vacuum and the residue subjected to column chromatography (SiO$_2$, MeOH:2 M NH$_4$Cl$_{aq}$:MeNO$_2$ 7:2:1). Excess MeNO$_2$ and MeOH were then removed under vacuum such that the product still remained dissolved, and a saturated solution of NH$_4$PF$_6$ was added dropwise. The solid was filtered off, washed with H$_2$O (4 × 50 mL), and dried to afford **B2·4PF$_6$** as a yellow solid (1.3 g, 66% in two steps). M.p. > 250 °C; ^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ = 9.45 (d, J = 10 Hz, 4H), 9.41 (d, J = 10 Hz, 4H), 8.76 (d, J = 10 Hz, 8H), 7.93 (s, 1H), 7.89 (s, 2H), 7.66 (d, J = 8.5 Hz, 4H), 7.08 (d, J = 6.5 Hz, 4H), 6.21 (s, 4H), 6.11 (s, 4H), 4.74 (s, 2H), 4.21–4.17 (m, 4H), 3.86–3.82 (m, 4H), 3.68–3.65 (m, 4H), 3.52–3.50 (m, 4H), 3.31 ppm (s, 6H); HRMS (ESI): m/z: 1299.32 [M−PF$_6$]$^+$.

5·4PF$_6$: Alcohol **B2·4PF$_6$** (2 g, 1.38 mmol) was dissolved in dry THF:MeCN (3:1, 4 mL), and CBr$_4$ (2.3 g, 6.9 mmol) and Ph$_3$P (1.82 g, 6.9 mmol) were added under vigorous stirring. The reaction mixture was

stirred under argon at room temperature to completion, during which 1.25 equiv of CBr$_4$ and Ph$_3$P were added at 30 min intervals until TLC showed no starting material. The reaction mixture was then poured into H$_2$O, extracted with CH$_2$Cl$_2$ (3 × 25 mL), and the combined extracts were evaporated to dryness. The residue was subjected to column chromatography (SiO$_2$, Me$_2$CO, and then 5 mM solution of NH$_4$PF$_6$ in Me$_2$CO). The resulting product was washed with H$_2$O and dried to afford the desired product **5·4PF$_6$** (1.27 g, 61%) as a dark brown solid. M.p. > 250 °C; ^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ = 9.42 (d, J = 10 Hz, 4H), 9.37 (d, J = 9 Hz, 4H), 8.72 (d, J = 6 Hz, 8H), 7.86 (s, 1H), 7.84 (s, 2H), 7.61 (d, J = 10 Hz, 4H), 7.04 (d, J = 6 Hz, 4H), 6.16 (s, 4H), 6.15 (s, 4H), 4.58 (s, 2H), 4.14–4.13 (m, 4H), 3.79–3.77 (m, 4H), 3.61–3.60 (m, 4H), 3.47–3.45 (m, 4H), 3.25 ppm (s, 6H): HRMS (ESI): m/z: 1363.26 [M−PF$_6$]$^+$.

B9·18PF$_6$: A solution of **6·3PF$_6$**[20] (73.5 mg, 0.072 mmol) in dry MeCN (1 mL) was added dropwise to a solution of **5·4PF$_6$** (647.3 mg, 0.43 mmol) in dry MeCN (2 mL) under reflux and an argon atmosphere over 2 h. The reaction mixture was stirred for 48 h and then cooled to ambient temperature. The solvent was removed under vacuum and the residue subjected to HPLC (Hypersil BDS C18 column, flow rate 1.0 mL min^{-1}; mobile phase, pump A 0.1% CF$_3$CO$_2$H in H$_2$O, pump B MeCN/0.1% CF$_3$CO$_2$H in H$_2$O (95/5); time [min]/pump A [%] = 0/100, 8/100, 28/0, 42/0, 45/100). Excess MeCN and H$_2$O were evaporated under vacuum such that the product still remained dissolved, and a saturated aqueous solution of NH$_4$PF$_6$ was added dropwise. The solid was collected by filtration, washed with H$_2$O (4 × 20 mL), and dried under vacuum to afford **B9·18PF$_6$** as a light brown solid (616 mg, 25%). M.p. > 250 °C; ^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ = 8.91–8.87 (m, 36H), 8.38–8.31 (m, 36H), 7.62 (br s, 9H), 7.60 (br s, 3H), 7.44 (d, J = 8.5 Hz, 12H), 7.00 (d, J = 7.5 Hz, 12H), 5.80–5.72 (m, 36H), 4.11–4.09 (m, 12H), 3.76–3.74 (m, 12H), 3.60–3.58 (m, 12H), 3.47–3.45 (m, 12H), 3.26 ppm (s, 18H); ^{13}C NMR (125 MHz, CD$_3$CN): δ = 160.1, 150.5, 150.4, 149.9, 145.7, 145.6, 145.2, 134.7, 134.6, 131.7, 131.2, 127.3, 127.2, 124.2, 115.3, 71.4, 70.0, 68.9, 67.6, 63.5, 57.8 ppm; HRMS (ESI): m/z: 1289.80 [M−4PF$_6$]$^+$.

7·12PF$_6$: A solution of **4·2PF$_6$**[18] (0.20 g, 0.27 mmol) in dry MeCN (2 mL) was added dropwise to a solution of **5·4PF$_6$**[19] (1.44 g, 0.95 mmol) in dry MeCN (2 mL) under reflux and an argon atmosphere over 2 h. The mixture was stirred for 48 h and then cooled to ambient temperature, the solvent removed under vacuum, and the residue subjected to column chromatography (SiO$_2$, Me$_2$CO, and then 5 mM, 10 mM, and saturated solutions of NH$_4$PF$_6$ in Me$_2$CO consecutively). The resulting product was washed with H$_2$O and dried to afford alcohol **7·12PF$_6$** (2.47 g, 65%). M.p. > 250 °C; ^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ = 9.05–8.90 (m, 24H), 8.50–8.30 (m, 24H), 7.75–7.60 (br s, 9H), 7.50 (d, J = 6 Hz, 8H), 7.05 (d, J = 6 Hz, 8H), 5.90–5.70 (m, 24H), 4.70 (s, 2H), 4.25–4.10 (m, 8H), 3.85–3.70 (m, 8H), 3.65–3.60 (m, 8H), 3.55–3.45 (m, 8H), 3.30 ppm (s, 12H); HRMS (ESI): m/z: 1843.2 [M−2PF$_6$]$^+$, 1180.1 [M−3PF$_6$]$^+$, 849.5 [M−4PF$_6$]$^+$.

B21·42PF$_6$: Alcohol **7·12PF$_6$** (500 mg, 0.126 mmol) was dissolved in dry THF:MeCN (3:1, 4 mL), and CBr$_4$ (62 mg, 0.188 mmol) and Ph$_3$P (49 mg, 0.188 mmol) were added under vigorous stirring over 30 min. The reaction mixture was stirred under argon at room temperature to completion, during which 1.25 equiv of CBr$_4$ and Ph$_3$P were added in 30 min intervals until TLC showed no starting material. The reaction mixture was poured into H$_2$O, extracted with CH$_2$Cl$_2$ (3 × 25 mL), and the combined extracts were dried and evaporated to dryness. The residue was subjected to column chromatography (SiO$_2$, Me$_2$CO, and then 5 mM, 10 mM, and saturated solutions of NH$_4$PF$_6$ in Me$_2$CO consecutively). The resulting product was washed with H$_2$O and dried to afford the desired product (203 mg, 40%) as a dark brown solid, which was added to a solution of **6·3PF$_6$**[20] (9 mg, 0.0084 mmol) in MeCN (1 mL). The reaction mixture was stirred for 5 d under reflux and an argon atmosphere and then cooled to ambient temperature. The solvent was removed under vacuum and the residue subjected to HPLC on a Hypersil BDS C18 column, flow rate 1.0 mL min^{-1}; mobile phase, pump A 0.1% CF$_3$CO$_2$H in H$_2$O, pump B MeCN/0.1% CF$_3$CO$_2$H in H$_2$O (95/5); time [min]/pump A [%] = 0/100, 8/100, 28/0, 42/0, 45/100). Excess MeCN and H$_2$O were evaporated off under vacuum such that the product still remained dissolved, and a saturated aqueous solution of NH$_4$PF$_6$ was added dropwise. The solid

was filtered off, washed with H_2O (4×20 mL), and dried under vacuum to afford **B21**·42PF$_6$ as a light brown solid (0.1, 15%). M.p. > 250°C; ^1H NMR (500 MHz, (CD$_3$)$_2$CO): $\delta = 8.91 - 8.67$ (m, 84H), 8.36–8.11 (m, 84H), 7.60 (br s, 27H), 7.56 (br s, 3H), 7.42 (d, $J = 8.5$ Hz, 24H), 6.90 (d, $J = 7.5$ Hz, 24H), 5.78–5.70 (m, 84H), 4.00–3.69 (m, 24H), 3.70–3.68 (m, 24H), 3.56–3.45 (m, 24H), 3.42–3.37 (m, 24H), 3.24 ppm (s, 36H); ^{13}C NMR (125 MHz, CD$_3$CN): $\delta = 160.9$, 146.4, 146.0, 135.6, 135.5, 132.5, 132.0, 128.2, 128.0, 125.0, 118.0, 117.5, 116.1, 72.3, 70.8, 69.8, 68.4, 65.1, 64.3, 58.6 ppm.

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