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Electrochemical Switching and Size Selection in Cucurbit[8]uril-Mediated Dendrimer Self-Assembly**

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Dendrimer self-assembly is an efficient approach to building sizable, soft-matter nanostructures without paying a large entropic cost, as the assembling units or building blocks are already macromolecules of considerable size. Several approaches have been described to assemble dendrimers which take advantage of π–π stacking,[1] fluorophobic,[2] solvophobic,[3] hydrogen-bonding,[4] ion–dipole,[5] metal coordination,[6] and other intermolecular interactions.[7] Recently, we reported a dendrimer self-assembly system under redox control,[8] in which dendronized 4,4′-bipyridinium (viologen) derivatives were efficiently dimerized by one-electron reduction in the presence of a cucurbit[8]uril (CB8) host.[9] This host greatly stabilizes the formation of viologen radical cation dimers[10] and, thus, its presence is crucial for the successful redox-driven dimerization or assembly of the dendrimers. CB8 is also an excellent host for charge-transfer complexes formed by the combination of an aromatic electron-deficient molecule (π acceptor) with a partner containing an aromatic electron-rich residue (π donor).[11] Here, we report on the preparation of a new series of dendrimers, **D1**–**D3**, which contain a *para*-dialkoxybenzene aromatic donor unit in their apical positions (Scheme 1). These dendrimers can form CB8-mediated, charge-transfer assemblies with the already reported dendronized viologens **A1**–**A3**.[12] Furthermore, one-electron reduction of the viologen unit disrupts the donor–acceptor complexes and leads to the dimerization of the viologen dendrimers as their radical cations.

The preparation of the π-donor dendrimers starts by reaction of **1** with each of the amine building blocks (Newkome dendrons) that we had already available.[13] This reaction was conducted in dry DMF with *N*-[(dimethylamino)-1*H*-1,2,3-triazole[4,5-*b*]-pyridin-1-ylmethylene]-*N*-methylmethanaminium hexfluorophosphate (*n*-HATU) and 1,8-bis(dimethylamino)naphthalene (proton sponge) to facilitate the coupling. The *tert*-butyl ester groups on the periphery of the resulting dendrimers were hydrolyzed with formic acid

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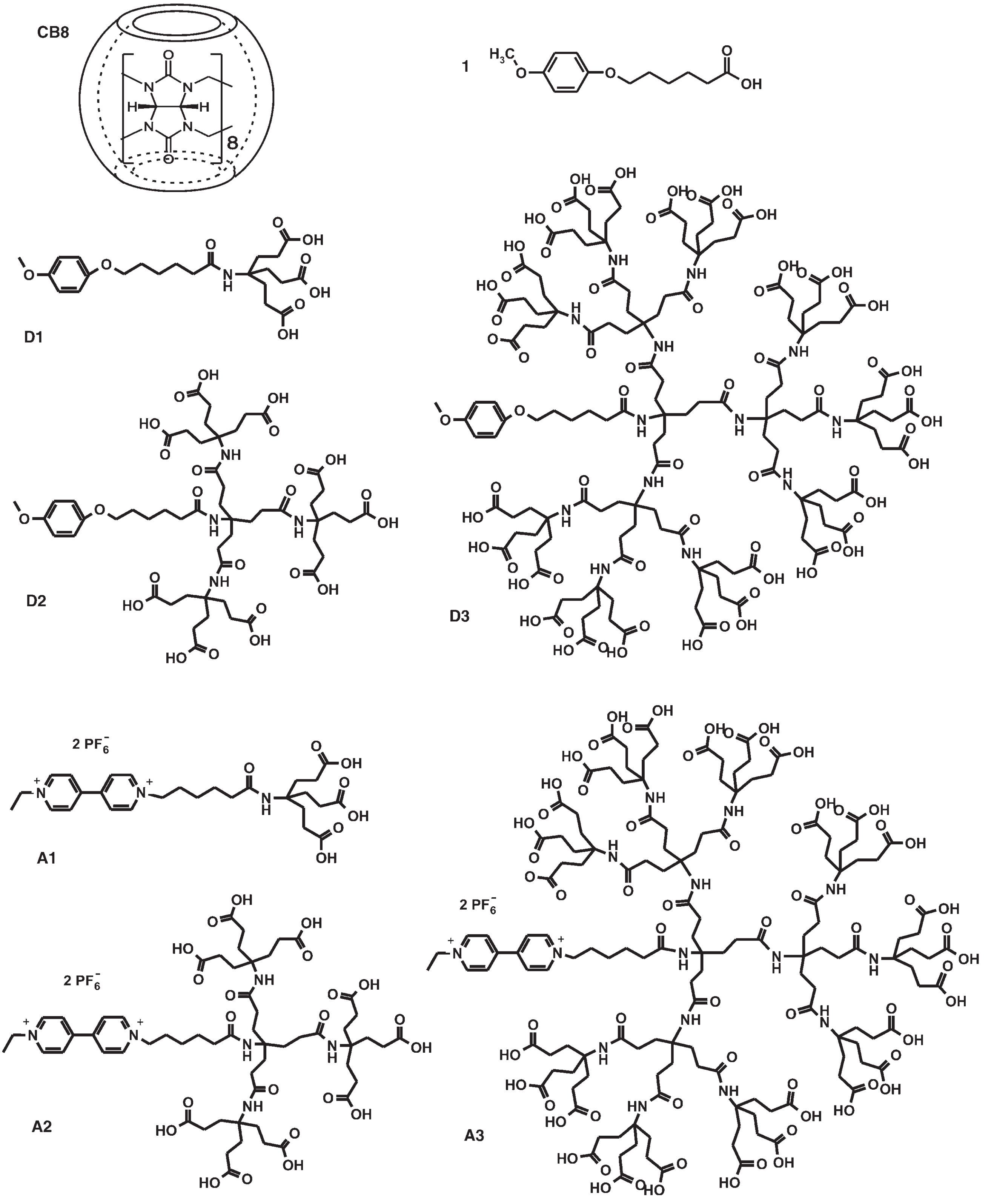

Scheme 1. Structures of precursor compound **1**, all the dendrimers studied, and the CB8 host.

to yield the water-soluble dendrimers **D1**–**D3**. All the new dendrimers were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by FAB and MALDI-TOF mass spectrometry.

Dendrimers **D1**–**D3** form stable charge-transfer complexes with the viologen-containing dendrimers in the presence of the CB8 host. This is clearly evidenced by the development of a charge-transfer band when a dendrimer from the **D1**–**D3** series and a dendrimer from the **A1**–**A3** series are mixed in the presence of CB8. Figure 1 shows the charge-transfer band at 490 nm that develops upon mixing **D2** (2.0 mM), **A2** (2.0 mM), and CB8 (2.0 mM). The charge-transfer band is essentially undetectable unless CB8 is added to the solution and its intensity increases linearly with increasing concentration of CB8, at least until approaching 1.0 equivalents, at which point the solution turns turbid because of the low solubility of the host. Similar bands are observed when any two dendrimers (**A*n***–**D*n***, ***n*** = **1–3**), one from each series, are mixed in the presence of CB8. However, the band intensities tend to decrease as the sizes of the two assembling dendrimers increase, which probably reflects the increasing steric bulk and repulsive electrostatic interactions (from the peripheral carboxylate groups) in the formation of the complex.[8]

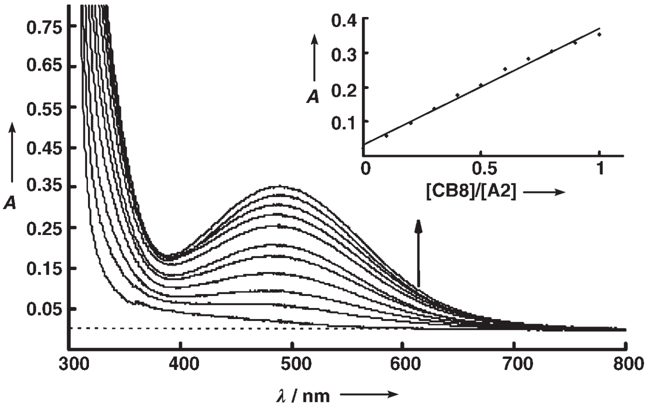

Figure 1. Charge-transfer absorption bands observed with a mixture of 2.0 mM **D2** and 2.0 mM **A2** in Na_3PO_4 buffered at pH 7.0 ($[Na^+] = 0.1$ M) in the presence of increasing concentrations of CB8 (from 0 to 2.0 mM in the direction of the arrow). The inset plots the dependence of the maximum absorbance on [CB8].

NMR spectroscopic data also confirm the formation of the **A*n***–**D*n***–CB8 charge-transfer complexes. For example, Figure 2 shows the partial ^{1}H NMR spectra corresponding to a 1:1 mixture of dendrimers **A2** and **D2**. In the absence of CB8, the aromatic protons on the viologen residue of **A2** (at $\delta = 9.12$ and 8.56 ppm) and the aromatic benzyl protons of **D2** (at $\delta = 6.94$ ppm) resonate at essentially the same chemical shifts as observed in the spectra of each dendrimer before mixing, thus suggesting that the charge-transfer complex is not formed under these conditions. However, addition of the CB8 host shifts all these aromatic proton resonances to higher fields, with a CB8-induced shift that increases with the host concentration. This observation is also consistent with the formation of a charge-transfer complex in which the aromatic residues of dendrimers **A2** and **D2** share the cavity of CB8. Similar data were obtained with all other **A*n***–**D*n*** combinations. We can thus conclude that CB8 mediates the formation of stable charge-transfer complexes between the viologen (π acceptor) and alkoxymethoxybenzene (π donor) residues of dendrimers **A*n*** and **D*n***, respectively, thus giving rise to the formation of well-defined **A*n***–**D*n***–CB8 assemblies.

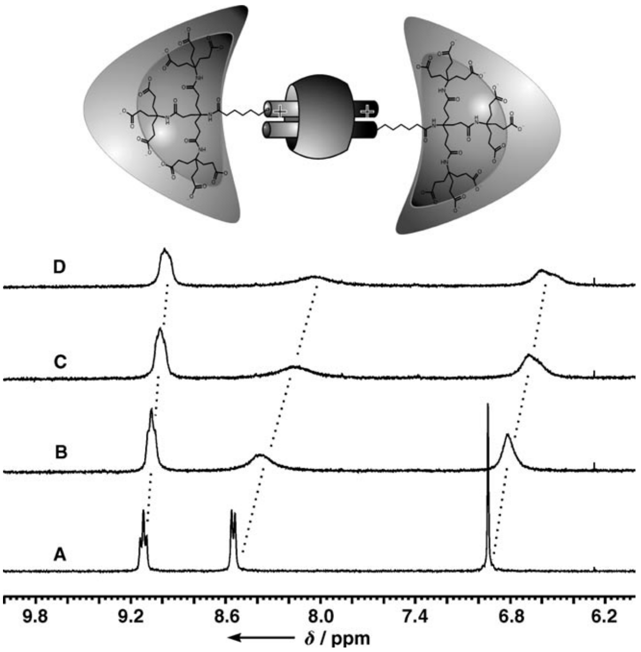

Figure 2. Partial ^{1}H NMR spectra (300 MHz, 0.1 M Na_3PO_4/D_2O, pD = 7.0) showing the effect of the CB8 host on the aromatic protons of dendrimers **A2** and **D2**: A) 0 equiv, B) 0.2 equiv, C) 0.4 equiv, and D) 0.6 equiv CB8.

The cyclic voltammetric behavior of the dendronized viologen derivatives **A1**–**A3** has already been described.[12] Viologen-containing dendrimers have the unique property of retaining relatively fast electrochemical kinetics through the first three generations of growth.[12,14] In the presence of CB8, one-electron reduction of the viologen units in **A1**–**A3** leads to the formation of highly stable viologen radical cation dimers inside the host cavity, while dimerization takes place to a very low extent in the absence of CB8. Figure 3 shows the cyclic voltammetric behavior recorded with an equimolar mixture of dendrimers **A1** and **D2** with and without added CB8. In the absence of CB8, the cathodic voltammetric behavior is dominated by the two consecutive one-electron

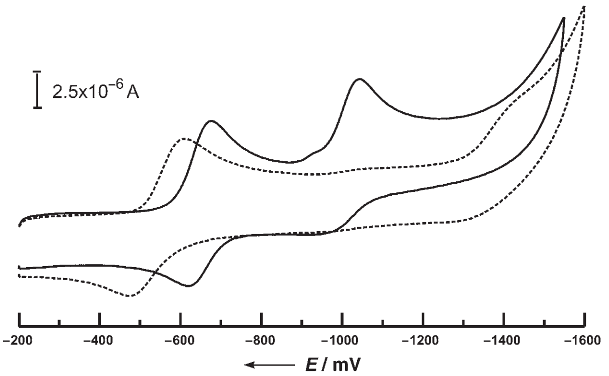

Figure 3. Cyclic voltammetric behavior on glassy carbon (0.07 cm^2) of a solution containing 0.5 mM **A1**, 0.5 mM **D2**, and Na_3PO_4 buffered at pH 7.0 ($[Na^+] = 0.1$ M) in the absence (solid line) and the presence (discontinuous line) of CB8. The potential is reported relative to an Ag/AgCl reference electrode. Scan rate: 0.10 V s^{-1}.

reductions of the viologen unit on **A1**. The half-wave potentials are similar to those measured in the absence of **D2**, again suggesting that the charge-transfer complex is not stable in the absence of CB8. However, addition of the host alters the voltammetric behavior substantially. The first reduction wave shifts to less negative values and the second reduction wave shifts to more negative values, thereby revealing a considerable differential stabilization of the one-electron-reduced, radical cation form of the viologen dendrimer **A1**. In fact, when a suitable concentration (0.5 equiv or more) of host CB8 is present in the solution, the voltammetric behavior observed for **A1** in the presence of **D2** is essentially identical to that observed in the absence of the π-donor dendrimer, thus suggesting that dimerization of the viologen radical cation takes place in the presence of **D2** as long as CB8 is also present in the system. Similar voltammetric results were obtained with other dendrimer combinations.

The experimental data discussed here indicate that, in the presence of CB8, the dendronized viologens **A1**–**A3** form stable charge-transfer complexes with the π-donor dendrimers **D1**–**D3**, as long as the former are present in their oxidized (+2) electron-acceptor forms. However, one-electron reduction of the viologen units leads to the disruption of the charge-transfer complexes and the formation of stable viologen radical cation dimers. Recently, Kim and co-workers have taken advantage of similar interactions to control the behavior of a molecular loop.[11g] In our case, the redox-controlled selection of assembling partners for the dendronized viologens can be used to determine the size of the predominant dendrimer assembly. For example, assume that a mixture of **A1** and **D3** is prepared in the presence of CB8. From the data already presented here it should be clear that the **A1**–**D3**–CB8 charge-transfer complexes will self-assemble in this solution. Upon one-electron reduction of **A1**, however, we should expect the formation of homodimeric **A1**–**A1**–CB8 assemblies and this is indeed the case as shown by the electronic absorption spectra (see the Supporting Information). In fact, the extent of dimerization can be estimated from the ratio of absorbances at 364 and 390 nm, as shown by our research group almost 20 years ago.[15] From the electronic absorption data we estimate that 80 % of the viologen radical cation undergoes dimerization. Therefore, one-electron reduction of the viologen units in **A1** leads to a substantial change in the effective size and molecular weight of the predominant assembly in the solution. Specifically, the molecular weight decreases from 5076 Da in **A1**–**D3**–CB8 to 2387 Da after reduction of **A1** to give the homodimeric assembly **A1**–**A1**–CB8. This conversion is fully reversible: exposure of the solution to oxygen regenerates the dicationic form of **A1** and leads again to the formation of the heavier **A1**–**D3**–CB8 assembly.

The results shown here are similar to those obtained with other combinations of dendrimers (**A*n***–**D*n***), although in some cases the experiments are limited by the poor solubility of CB8. In general terms, dendrimer assembly becomes less efficient as the size of the dendritic components increase. Furthermore, one-electron reduction of the viologen subunit is kinetically hampered in large assemblies of the type **D3**–**A3**–CB8. Furthermore, in this case reduction would lead to the **A3**–**A3**–CB8 assembly (with a very similar molecular weight), thereby resulting in relatively trivial changes (and no size selection) upon electrochemical switching. The system composed of dendrimers **A1** and **D3** (Figure 4) is ideally suited for electrochemical switching and size selection, as it maximizes the change in molecular weight brought about by the one-electron reduction of the dendronized viologen.

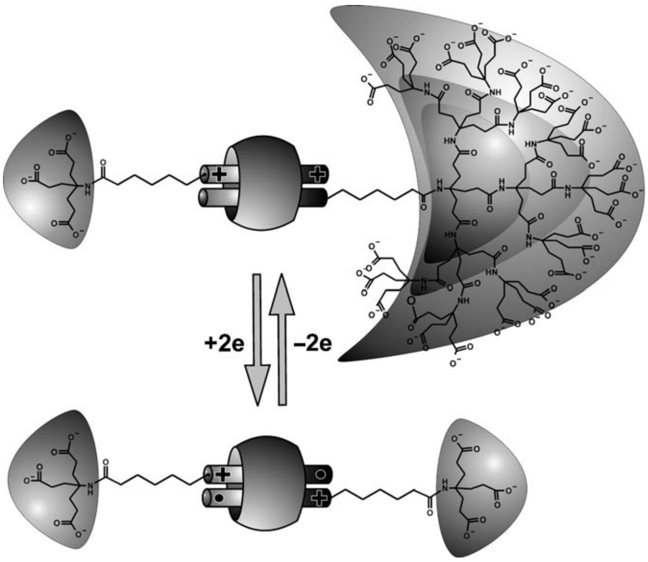

Figure 4. Pictorial representation of redox control on the size of the CB8-mediated dendrimer assemblies.

The study presented here takes advantage of the host properties of CB8 to mediate in a highly effective way the formation of charge-transfer complexes between dendrimers containing accessible π-donor and π-acceptor units. This dendrimer self-assembly system offers excellent possibilities for electrochemical switching and redox control over the type and size of the resulting macromolecular assemblies.

Experimental Section

Full synthetic and characterization details for dendrimers **D1**–**D3** are given in the Supporting Information. All other materials were prepared as previously described.[12] The cyclic voltammetric experiments were done in a single-compartment electrochemical cell fitted with glassy carbon working, auxiliary, and Ag/AgCl reference electrodes. All solutions were deoxygenated with purified nitrogen gas before cathodic voltammetric scans. Exhaustive one-electron reduction of the viologen dendrimers was carried out by exposure of the solution to Zn powder in an inert nitrogen atmosphere.

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