Host–Guest Chemistry

Tweezering the Core of a Dendrimer: A Photophysical and Electrochemical Study**

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Dendrimers[1] are complex, yet well-defined, branched compounds that exhibit a high degree of constitutional order, with the possibility of containing selected chemical units at predetermined sites of their structure (core, branches, periph-

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ery). As a result of their nanoscopic size and fractal structure, dendrimers resemble biocomponents such as viruses, enzymes, and proteins.[2] Dendrimers that contain redox-active units are currently attracting much attention.[3] When a large number of redox-active units are placed in the periphery and/or along the branches, dendrimers can undergo multiple electron-transfer processes and perform, for example, as molecular batteries, sensors, and catalysts.[4] Dendrimers with a single redox site as a core are the simplest examples of systems with an encapsulated redox center,[5] and their redox properties are usually modulated by the size and nature of the dendritic branches.[6]

Despite their large structures, which usually render dendrimers attractive as host molecules, suitably designed dendrimers can be equally involved as guests in molecular-recognition phenomena.[7] In such cases, the host species does not interact with the whole dendritric structure, but only with specific component units. Usually, the guest behavior of the dendrimer is connected with the threading of dendritic branches by ring-shaped molecules such as crown ethers,[8] cyclodextrins,[9] and cucurbiturils.[10]. More recently, Kaifer and co-workers[7,11] prepared several dendrimers that contain a single-site, potential guest unit and have investigated their adducts with cucurbit[7]uril, β-cyclodextrin, and bis-*para*-phenylene[34]crown-10.

When the potential guest unit constitutes the core of a dendrimer, the formation of a host–guest complex through threading of ring-shaped hosts cannot take place. It occurred to us that in such a case, tweezer-shaped molecules could be used to enclose the dendritic core into a host structure. Herein, we show that this strategy works in solution when suitably designed host and guest units are used.[12]

Several molecular tweezers and clips that exhibit electron-donating properties have been prepared recently in one of our laboratories.[13] Molecular tweezer **T**, which comprises one naphthalene and four benzene components bridged by four methylene units, was prepared and purified as previously reported (Figure 1).[14] NMR spectroscopy (see Supporting Information for details) showed that tweezer **T** forms a stable 1:1 complex with 4,4′-*N*,*N*-bis(3,5-di-*tert*-butylbenzyl)-bipyridinium $[\mathbf{D0}]^{2+}$. Solvent-dependent binding constants ($K_a = 730\,\text{M}^{-1}$ in [D$_6$]acetone/$CDCl_3$ (2:1) and $K_a = 8400\,\text{M}^{-1}$ in CD_2Cl_2), and complexation-induced upfield shifts of the chemical shifts for the protons of the guest ($\Delta\delta_{max} = 1.01$ or 0.91 ppm (H^o), and 4.12 or 3.22 ppm (H^m)) were determined by ^{1}H NMR titration experiments (500 MHz, Bruker DRX 500) at 25 °C, and the 1:1 stoichiometry of the complex was determined through Job plot analysis. The observed large $\Delta\delta_{max}$ values and the specific broadening of the ^{1}H NMR signals assigned to the bridgehead protons of the complexed tweezer at low temperature are evidence that one of the pyridinium rings of $[\mathbf{D0}]^{2+}$ is positioned inside the cavity of the tweezer and that tweezer **T** shuttles from one pyridinium ring of $[\mathbf{D0}]^{2+}$ to the other. At room temperature the shuttling process is fast and leads to an averaging of the ^{1}H NMR signals of the guest molecule lying inside/outside of the tweezer cavity, while at −75 °C the process is slow with respect to the NMR timescale ($\Delta G^{\neq}(\text{shuttle}) = 10\,\text{kcal mol}^{-1}$, estimated from the line broadening). As the 3,5-di-*tert*-butylben-

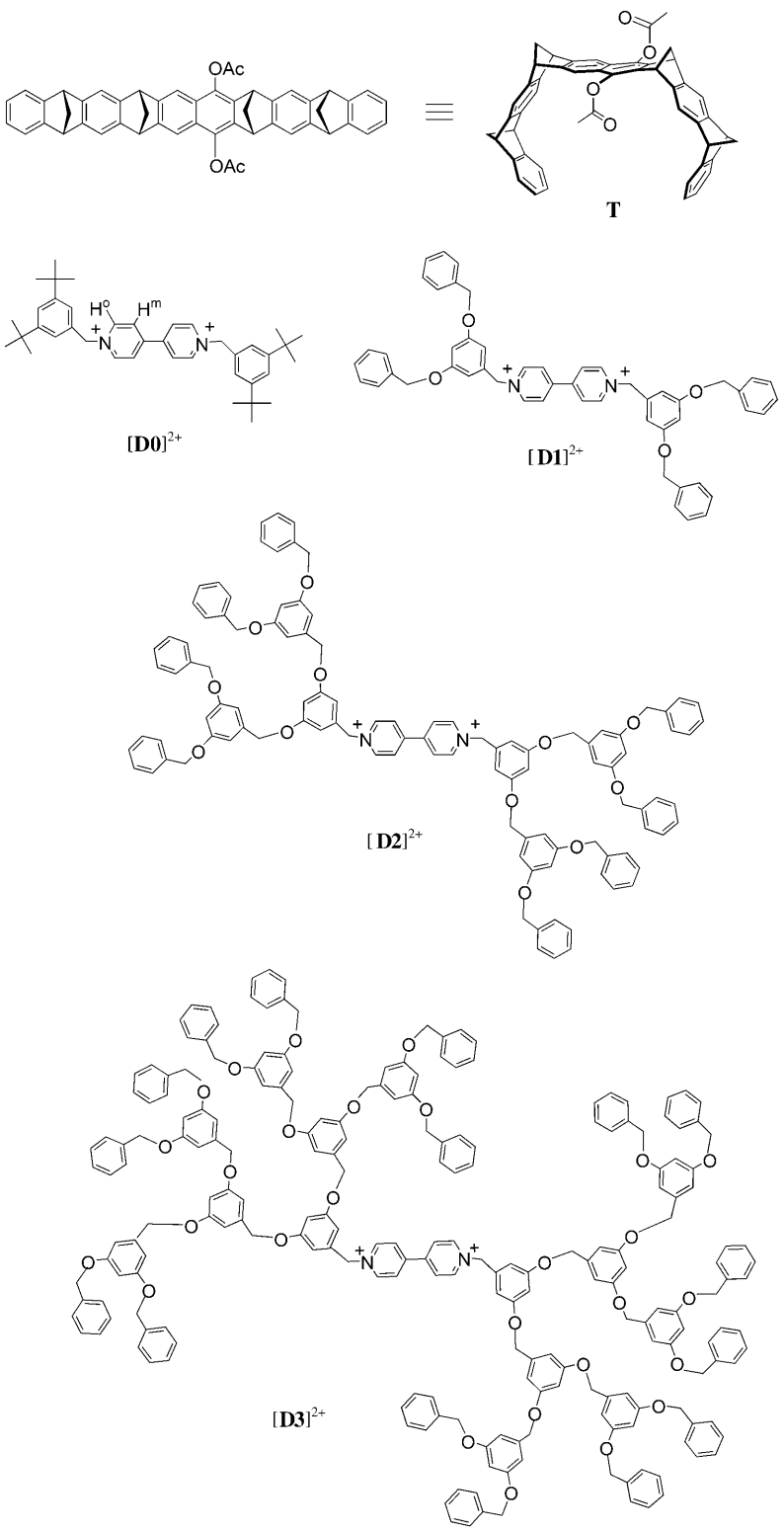

Figure 1. Formulae of the investigated tweezer (**T**) and dendrimeric compounds (**D*n*** where ***n*** indicates the dendron generation: ***n*** = 0,1,2,3).

zyl stopper groups in $[\mathbf{D0}]^{2+}$ are already too bulky to form a complex with tweezer **T** by threading and as the complexation has to proceed by clipping of the guest molecule through the tips of the tweezer, we thought that **T** should also be able to interact with the bipyridinium core (bpy^{2+}) of the first-, second-, and third-generation dendrimers $[\mathbf{D}n]^{2+}$ ($n = 1, 2$ and 3; see Figure 1). NMR spectroscopy, however, could not provide information on the formation of a complex in the case of the dendrimers because of solubility problems and line broadening. Therefore we carried out a photophysical and electrochemical investigation of the interactions.

The hexafluorophosphate salts of the $[\mathbf{D}n]^{2+}$ dendrimers had been prepared during the course of previous work.[15] The equipment used for the photophysical and electrochemical measurements has been described elsewhere.[16] All the experiments were performed at room temperature (293 K) in air-equilibrated solution. Quantum yields of fluorescence were measured following the methods of Demas and Crosby[17], using terphenyl in cyclohexane ($\Phi = 0.82$) as the standard.[18] Dichloromethane was used as the solvent for the photophysical experiments, and mixtures of dichloromethane/acetonitrile (3:1 or 9:1 v/v) were used for the electrochemical experiments. The association constants were obtained from fluorescence titration experiments.

The absorption and emission spectra of tweezer **T** in dichloromethane are shown in Figure 2. The strong fluorescence emission band at $\lambda_{max} = 344$ nm ($\tau = 9.5$ ns, $\Phi = 0.53$)

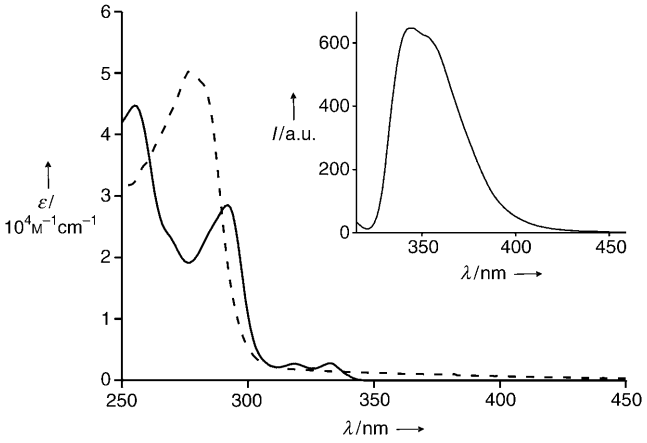

Figure 2. Absorption spectra of tweezer **T** (——) and dendrimer $[\mathbf{D3}]^{2+}$ (as PF_6^- salt; -----) in dichloromethane at room temperature. Inset: Emission spectrum of tweezer **T** in dichloromethane at 293 K ($\lambda_{ex} = 334$ nm).

can be assigned to the naphthalene unit. The absorption spectra of dendrimers $[\mathbf{D}n]^{2+}$ (see Figure 2 for an example) display a strong absorption band around $\lambda = 260$ nm from the bipyridinium unit, while the 1,3-dimethyleneoxybenzene units of the dendrons show an absorption around $\lambda =$ 280 nm. The fluorescence of the 1,3-dimethyleneoxybenzene units is completely quenched in the dendrimers.[15]

In a solution of 9:1 dichloromethane/acetonitrile, tweezer **T** shows an irreversible oxidative process at $+1.6$ V, whereas no reduction process could be observed in the potential window of the solvent used (up to -2.0 V vs. SCE). The $[\mathbf{D}n]^{2+}$ dendrimers[15,19] show two one-electron-transfer processes that correspond to the successive reductions of the 4,4′-bipyridinium core: $bpy^{2+} \rightarrow bpy^{+}$ and $bpy^{+} \rightarrow bpy$. The values of the potentials are gathered in Table 1, and the cyclic voltammetric curve for $[\mathbf{D2}]^{2+}$ is shown in Figure 3.

Table 1: Half-wave potentials versus SCE (saturated calomel electrode)[a] and association constants.[b]

	$bpy^{2+} \rightarrow bpy^{+}$ [V]	$bpy^{+} \rightarrow bpy$ [V]	$K_a \times 10^{-3}$ [M^{-1}]
$[\mathbf{D1}]^{2+}$[c]	−0.25	−0.73	
$[\mathbf{D1}]^{2+}\cdot\mathbf{T}$[c]	−0.30	−0.73	27
$[\mathbf{D2}]^{2+}$	−0.24	−0.72	
$[\mathbf{D2}]^{2+}\cdot\mathbf{T}$	−0.31	−0.72	18
$[\mathbf{D3}]^{2+}$	−0.24	−0.72	
$[\mathbf{D3}]^{2+}\cdot\mathbf{T}$	−0.30	−0.72	9

[a] Solvent: dichloromethane/acetonitrile (9:1), unless otherwise noted; $(NBu_4)PF_6$ (0.1 M); under these conditions more than 95% of the electroactive species are in the complexed form. [b] Solvent: dichloromethane; from fluorescence titration experiments. [c] Solvent: dichloromethane/acetonitrile (3:1).

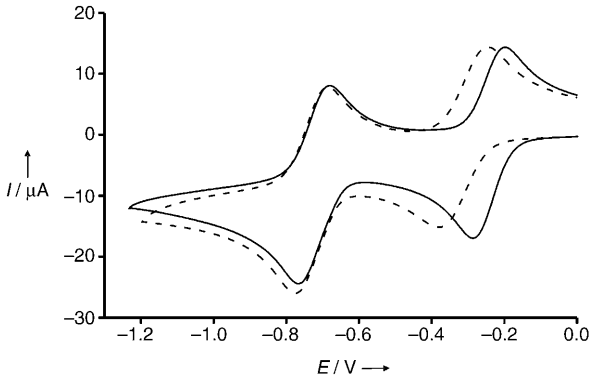

Figure 3. Cyclic voltammetry (CV) curves for a solution of $[\mathbf{D2}]^{2+}$ at 1.0×10^{-3} M in dichloromethane/acetonitrile (9:1) in the absence (——) and presence (-----) of tweezer **T** (3.2×10^{-3} M). Scan rate: 0.2 V s^{-1}; $(NBu_4)PF_6$ (0.1 M).Under such conditions, the association constant (Table 1) shows that about 98% of the species are associated.

Titrations of solutions of tweezer **T** at approximately 10^{-5} M in dichloromethane with the dendrimers did not cause any changes in the absorption spectra relative to the spectra expected from the absorptions of the two components. The fluorescence band of **T** ($\lambda_{max} = 344$ nm), however, was quenched, as shown in Figure 4 for the case of $[\mathbf{D3}]^{2+}$. As dynamic quenching can be ruled out because of the short excited-state lifetime of **T** ($\tau = 9.5$ ns), these results indicate that the tweezer and dendrimers give rise to adducts. We also verified that the fluorescence of **T** is not quenched upon addition to the solution of the dendrons used to construct the dendrimers. Therefore we conclude that adduct formation must involve an interaction between the tweezer and the bipyridinium dendritic cores.

To elucidate the stoichiometry and the strength of adduct formation, fluorescence titration experiments were performed by taking into account[20] the fraction of light absorbed

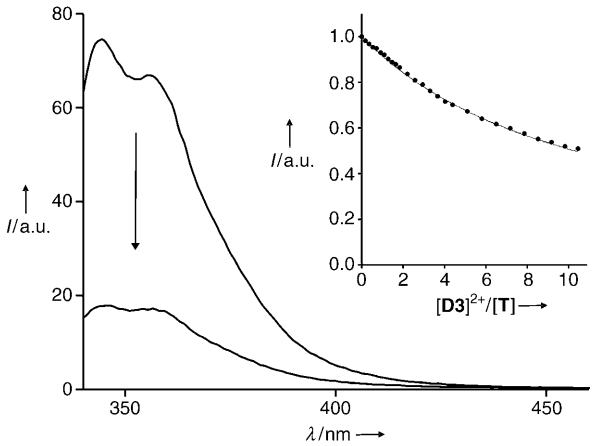

Figure 4. Changes in the fluorescence spectrum of a solution of **T** at 1.6×10^{-5} M in dichloromethane at room temperature upon addition of 10 equivalents of $[\mathbf{D3}]^{2+}$ ($\lambda_{ex}=334$ nm). Inset: The titration curve obtained by plotting the emission intensity at $\lambda=356$ nm as a function of the equivalents of $[\mathbf{D3}]^{2+}$ added, after correction for the fraction of light absorbed by **T**. The solid line shows the fit based on formation of a 1:1 complex. a.u. = arbitrary units.

by the dendrimer. The titration plot obtained for a solution of **T** at 1.6×10^{-5} M in dichloromethane upon addition of $[\mathbf{D3}]^{2+}$ is shown in the inset of Figure 4. As the fluorescence lifetime ($\tau=9.5$ ns) is not affected upon addition of the dendrimer and as there is no evidence of a double-exponential decay, we conclude that even after addition of an excess of dendrimer a significant fraction of tweezer remains uncomplexed in such a dilute solution and that the adducts do not show any appreciable fluorescence.

The results obtained from the titration plots show that 1:1 $[\mathbf{D}\boldsymbol{n}]^{2+}\cdot\mathbf{T}$ adducts are formed, with values for the association constants of the order of $10^4\,\mathrm{M}^{-1}$ which decrease with increasing dendrimer generation (Table 1). A similar dependence of the stability of the complex on the size of the dendrimer was observed in the gas phase by mass spectroscopy.[12] Apparently, even in solution the bipyridinium core is stabilized by "intramolecular solvation", which results from the back-folding of the electron-donor branches, an effect that increases with increasing dendrimer generation.

The CV patterns for reduction of the dendritic cores are affected by the presence of tweezer **T** (Table 1 and Figure 3) which shows that the formation of the adduct involves an interaction between the tweezer and the bipyridinium dendritic cores. In particular, both the cathodic and anodic peaks which correspond to the first one-electron-reduction process of the dendritic core move to more negative values upon addition of the tweezer, whereas the peaks that correspond to the second reduction process are almost unaffected. Such a behavior shows that 1) formation of the adduct is caused by a charge-transfer interaction and 2) the adduct dissociates upon one-electron reduction of the dendritic core.

In conclusion, we have shown that the 4,4′-bipyridinium core of first-, second-, and third-generation $[\mathbf{D}\boldsymbol{n}]^{2+}$ dendrimers that bear Fréchet-type dendrons can be hosted by the molecular tweezer **T**, which comprises a naphthalene moiety and four benzene components bridged by four methylene units. The assembly/disassembly process can be monitored by fluorescence and electrochemical measurements. The tweezering process between **T** and $[\mathbf{D}\boldsymbol{n}]^{2+}$ is quite similar to the threading/dethreading processes observed with bipyridinium-based wire-type units and ring-shaped molecules,[21] with the advantage that tweezering can occur also when the wire-type unit terminates with bulky groups.

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