Photoisomerization-induced Change in the Size of Ferrocenylazobenzene-attached Dendrimers

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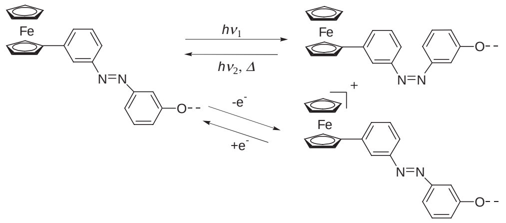
A family of 3-ferrocenylazobenzene-attached dendrimers, 9mer, 27mer, and 81mer, which is the first series of redox-active photochromic dendrimers exhibit photochromism responding to three different light sources, i.e., 365, 436, and 546 nm lights. Decreases in the size of the dendrimers induced by trans-to-cis photoisomerization appeared and became more significant with increases in the size of the dendrimers up to 81mer. Electrochemical treatment of the 81mer provided a photo-sensitive and redox-active dendrimer film-coated electrode.

Dendrimers with functional molecular units inside or outside of their framework have recently attracted much attention due to their potential application in sensors, molecular machines, drug delivery capsules, catalysts, and many other potential uses.[1] Photochromic molecules[2] and redox-active molecules are considered as possible candidates for the functionalization of dendrimers.[3] We recently demonstrated that 3-ferrocenylazobenzene (3-FcAB, **1**) assumes unique photochromic properties due to the combination of a redox change in the ferrocene unit with a redox change leading to reversible isomerization using a single green light source.[4] Here, we report the synthesis of a family of three 3-FcAB-attached dendrimers, i.e., 9mer (**2**), 27mer (**3**), and 81mer (**4**); this is the first series of redox-active photochromic dendrimers to be reported in the literature (Figure 1). These dendrimers exhibited photochromism responding to three different light sources, i.e., UV (365 nm), blue (436 nm), and green (546 nm) lights. Electrochemical measurements have shown that the cis form of the dendrimers has a higher diffusion coefficient, and is accordingly smaller than, the trans form in solution. This dendritic effect became more significant with increases in the size of the dendrimers up to 81mer. Moreover, electrochemical treatment of **4** gave a photo-sensitive and redox-active dendrimer-modified film-coated electrode.

The dendrimers were prepared by the reaction of the corresponding iodomethyldimethylsilyl-terminated dendrimers with 3-ferrocenylphenylazophenol, **5**.[5] The dendrimers were characterized using standard analytical and spectroscopic techniques, including MALDI-TOF mass spectroscopy. The UV–vis spectra of **1**, **2**, and **3** showed an intense azo π–π^* band at $\lambda_{\max} = 354$ nm and a weak visible band at 430 nm, the latter of which was primarily ascribable to the ferrocene e_{1g}–azo π^* transition.[4]



Scheme 1. Photo and redox reactions of a ferrocene moiety in **2**, **3**, and **4**.

The irradiation of **2**, **3**, and **4** with 546-nm green light and with 365-nm UV light led to a decrease in the absorbance of the π–π^* band, which was indicative of trans-to-cis isomerization (Figure 2). The cis yields of all dendrimers in the photostationary state (PSS) were 8 and 80%, respectively, both of which were higher yields than those of the phenol monomer, **5**, i.e., 2 and 53% (the cis yields for **1** were 35 and 61%), respectively. The low cis yield obtained at 546-nm light irradiation for the alkoxy or hydroxyl-substituted 3-FcAB was thought to be due to the electron-donating effect of the substituent.[4b] Remarkably, the kinetics of the photoisomerization depended on the size of the dendrimer; the largest dendrimer, **4**, took a longer time to reach the PSS than did the smaller dendrimers. The 436-nm blue light irradiation of the sample in the cis-rich state following exposure to UV light irradiation induced cis-to-trans isomerization; the trans form was not entirely recovered, and the cis molar ratio obtained was 20%.

In the cyclic voltammogram (CV) of **4** in Bu_4NClO_4–CH_2Cl_2, the redox wave at $E^{0'} = 0.027$ V vs ferrocenium/ferro-

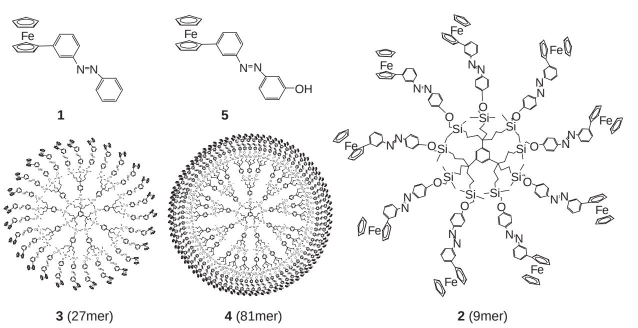


Figure 1. Structures of monomers and dendrimers. **3** and **4** are higher generation dendrimers of **2** with the same backbone chemical structure.

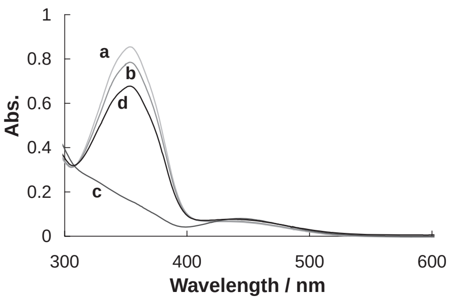


Figure 2. UV–vis absorption spectral change of **4** (1.3×10^{-6} mol dm^{-3}) in solution in toluene upon irradiation with a monochromatic light, first at 546 nm (from a to b), then at 365 nm (from b to c), and then at 436 nm (from c to d).

cene (Fc^+/Fc) corresponding to the ferrocenium/ferrocene couple was quasi-reversible ($\Delta E_p = 64\,mV$), and adsorption on the electrode was noticed ($i_{pc}/i_{pa} = 1.26$) (Figure 3). This finding was indicative of the absorption of the oxidized form of **4**,[3g] which led to a dendrimer-modification of the electrode, as described below. The reduction wave of the azo moiety was chemically irreversible, and the value of the cathodic peak potential E_{pc} was $-1.96\,V$ vs Fc^+/Fc.

One of the characteristic features of azobenzene trans–cis isomerization is known to be substantial physical motion, which in turn results in a significant change in size.[6] Thus, a photo-induced change in size can be expected among dendrimers with shells covered entirely by azobenzene moieties. This dendritic effect on size was examined electrochemically. The CV of **4** prepared by photoirradiation with 365-nm light revealed a significant decrease in the magnitude of the reduction peak of the azo moiety (Figure 3). The CV also showed a quasi-reversible oxidation peak of the ferrocene moieties at $E_{1/2} = 0.026\,V$, i.e., a potential similar to that of all trans isomers. It was recognized that both the anodic and the cathodic peak current values increased by ca. 20% in accord with the trans-to-cis isomerization. This finding is suggestive of an increase of the diffusion coefficient from $D = 3.7 \times 10^{-6}\,cm^2\,s^{-1}$ to $D = 5.6 \times 10^{-6}\,cm^2\,s^{-1}$. This change indicated that the decrease in size of the dendrimers was verified, because *trans*-azobenzene is longer than *cis*- and the results are summarized in Table 1 (see Supporting Information). It should be noted that the value is qualitative, because the samples in the PSS were a mixture of *trans*- and *cis*-azobenzene. We examined the changes in the diffusion coefficients observed before and after 365-nm light photoirradiation for the dendrimers **2**–**4** and for the monomer **1**, cis forms, and the cis yield was not identical to that of the trans form; however, the ratio of $i_{pa}(b)/i_{pa}(a)$ (where $i_{pa}(a)$ and $i_{pa}(b)$ are the anodic currents for the oxidation of the ferrocene moiety before and after 365-nm photoirradiation, respectively) increased clearly in the order of **1** < **2** < **3** < **4**. This result is suggestive of a dendritic effect on the observed change in molecular size induced by photoisomerization of the 3-FcAB moieties.

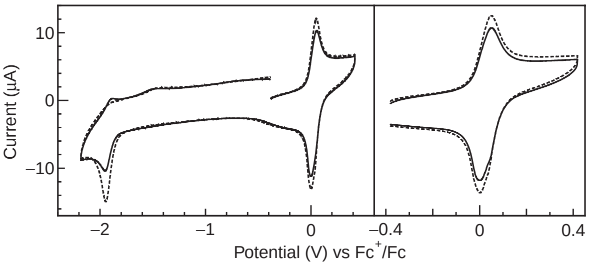


Figure 3. Cyclic voltammograms of **4** ($6.2 \times 10^{-6}\,mol\,dm^{-3}$) at a glassy carbon disk electrode in solution in 0.1 M Bu_4NClO_4–CH_2Cl_2 at $0.1\,V\,s^{-1}$ before (solid line) and after (dotted line) photoirradiation with 365-nm light for 7 h under argon.

Table 1. CV results of **1**–**4** before and after 365-nm photoirradiation[a]

Compd.	$E^{0'}$(a) /mV	$E^{0'}$(b) /mV	$i_{pa}(b)/i_{pa}(a)$	cis yield /%
1	12	12	1.01	23
2	9	3	1.04	26
3	12	5	1.06	14
4	8	4	1.17	10

[a] $E^{0'}$(a) and $E^{0'}$(b) are formal potentials vs Fc^+/Fc before and after photoirradiation.

A **4**-modified ITO electrode was prepared by the repeated potential scans for the redox reaction of ferrocene moieties in the same manner as described in the literature[3g] (see Supporting Information). The **4**-modified ITO electrode was found to possess a UV–vis spectrum containing an azo π–π^* band at $\lambda_{max} = 356\,nm$, which was similar to that in the spectrum of **4** in solution ($\lambda_{max} = 354\,nm$). Nearly no trans-to-cis isomerization took place with 546-nm green light, whereas the cis yield reached by irradiation with UV light corresponded to 26% after 20 min of irradiation. These results indicate that the trans-to-cis photoisomerization was much more inhibited in the film than in solution, probably because of the substantial steric hindrance preventing the movement of the azobenzene moiety in the film. Irradiation of the 26% cis-containing sample with 436-nm blue light gave the PSS after 15 min, and 18% of the trans form was recovered, with 8% of the yield remaining in the cis form. The morphological and structural changes induced by photoirradiation are currently under investigation.

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