Angewandte
Chemie

Photoisomerization

DOI: 10.1002/ange.200602088

Hierarchical Self-Assembly of Donor–Acceptor-Substituted Butadiene Amphiphiles into Photoresponsive Vesicles and Gels**

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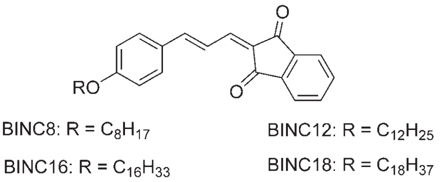
The construction of supramolecular architectures by the spontaneous self-assembly of molecules is currently a subject of great interest in areas that range from chemistry and biology to materials science.[1] Of particular interest is the design of externally addressable molecules that contain self-assembly elements, as these can give rise to so-called "smart materials".[2] Such addressable molecules could include among others, photochromics, which can be used to bring about light-induced changes in the self-assembly[3,4] or environment-sensitive luminophores, which can provide valuable insight into the nature of the molecular aggregation within such assemblies.[5] Herein, we present a novel class of donor–acceptor-substituted amphiphilic butadienes (Scheme 1) capable of undergoing spontaneous concentration-dependent hierarchical self-assembly from vesicles to gels. The self-assembly process was associated with unique changes in the fluorescence of the system. Moreover, the presence of a photoisomerizable chromophore makes these



Scheme 1. Structures of the molecules used in this study.

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[**] This study was supported by the Department of Science and Technology (DST), Government of India (New Delhi), and Council of Scientific and Industrial Research (CSIR, Task Force Program, CMM 22). The authors thank Robert Philip for assistance with AFM studies, M. R. Chandran for SEM measurements, Dr. J. D. Sudha for the rheological studies, and Dr. M. R. Pillai (Director of the Rajiv Gandhi Centre for Biotechnology, Trivandrum) for TEM and confocal laser scanning microscopy experiments. N.S.S.K., S.V., and G.N. thank the CSIR (Government of India) for research fellowships (This is manuscript no. RRLT-PPS-218).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

materials photoresponsive. Such stimuli-responsive vesicles and gels are becoming increasingly important because of their obvious implications in controlled-release systems.[4d,6,7]

The butadiene derivatives were synthesized in a multistep process, and their structures were established by FTIR and ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectro metry, and elemental analysis.[8] ^{1}H NMR spectroscopic analysis revealed that the compounds existed as their *E* isomers.[8] All the derivatives formed transparent gels in polar solvents, such as alcohols, acetonitrile, and dimethyl sulfoxide (DMSO).[8] As BINC18 gels were the most stable, detailed studies were carried out on this molecule. BINC18 was observed to be capable of gelating polar solvents at very low concentrations. Its critical gelator concentration (CGC), which ranged from 1.3 to 1.7×10^{-3} M,[8] was comparable to that of some of the best low-molecular-weight gelators.[5f,6i,9]

Microscopic investigations of solutions of BINC18 provided clear evidence for a hierarchical build-up of supramolecular assemblies, which started from small-sized vesicles at lower concentrations to larger vesicles at intermediate concentrations, until gel formation occurred in the millimolar concentration range. The formation of aggregates was spontaneous and did not require any special effects, such as ultrasonication or the use of mixed solvents. Atomic force microscopy (AFM) imaging of films deposited on mica sheets from freshly prepared 5×10^{-6} M solutions of BINC18 in methanol indicated the formation of small nanospheres of nearly uniform size, with an average diameter of 200 nm (Figure 1 a). Films cast from the same solutions, but which were aged for about 24 hours, indicated the formation of much larger polydisperse spherical aggregates, with sizes that ranged from 1 to 2 µm, many of which were found to be adhered together (Figure 1 b). Apart from aging, the size of the spherical aggregates was also observed to be dependent on the initial concentration of the solution. Thus AFM images of films deposited from a freshly prepared 1×10^{-4} M solution of BINC18 in methanol indicated the formation of polydisperse spherical structures, with an average diameter of about 500 nm.[8] Aging of these solutions also resulted in an increase in the size of the spherical aggregates from 1 to 2 µm.[8] In the millimolar concentration range, in which BINC18 formed transparent gels, AFM analysis indicated that the large spherical aggregates interconnected to form a continuous globular network (Figure 1 c).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images indicated a vesicular structure for the spherical aggregates (Figure 1 d,e). SEM analysis of samples prepared from 1×10^{-4} M aged solutions of BINC18 in methanol (Figure 1 d) showed spheres with diameters that ranged from 1 to 2 µm, which was similar to that observed by AFM images under identical conditions.[8] In several cases, half-opened vesicular aggregates that resulted from wall collapse were observed, which can be attributed to the high vacuum applied during the preparation of the sample. In the millimolar concentration range, in which gelation occurred, the SEM images indicated a morphology that matched closely that of the AFM images.[8]

TEM images of samples prepared by drop-casting aged 1.2×10^{-4} M solutions onto a Formvar-coated copper grid also indicated circular structures with diameters in the range 1–1.5 µm (Figure 1 e), similar to that observed by SEM and AFM. The hollow nature of the spherical aggregates was clearly indicated by the sharp contrast between the periphery and center.[6e,g] The images also revealed that the vesicles were sufficiently robust enough to retain their spherical shape under the conditions of the TEM experiments. Further support for the concentration-dependent hierarchical formation of vesicles, joined vesicles, and gels was obtained by confocal laser scanning microscopy (CLSM) (Figure 1 f–h).

Self-assembly of BINC18 was also indicated by changes in the absorption and emission spectra as a function of temperature (Figure 2 a). With decreasing temperature, a reduction in the intensity of the main peak at 432 nm and concomitant increase in absorption at 330 nm, with clear isosbestic points at 372 and 274 nm, were observed. The process was completely reversible on heating. The temperature-dependent changes in the absorption spectrum of BINC18 in methanol were also accompanied by changes in its fluorescence behavior. Whereas the solution of BINC18 (1.2×10^{-4} M) exhibited a weak fluorescence band centered at 540 nm at room temperature (quantum yield, $\Phi_\text{f}=0.004$), a nearly 40-fold enhancement in fluorescence accompanied by a shift in the maximum to 602 nm was observed at 7 °C (Figure 2 b). A significant enhancement in the fluorescence lifetimes was also observed with a decrease in temperature (Figure 2 b, inset). Mainly a long-lived component with a lifetime of 1.0 ns was observed at 13 °C, whereas the lifetime of the species was within the time resolution of the instrument (< 100 ps) at 40 °C.[8] These effects can be attributed to the formation of H aggregates, which involves a parallel interaction mode of the chromophores.[10] Excitonic splitting in

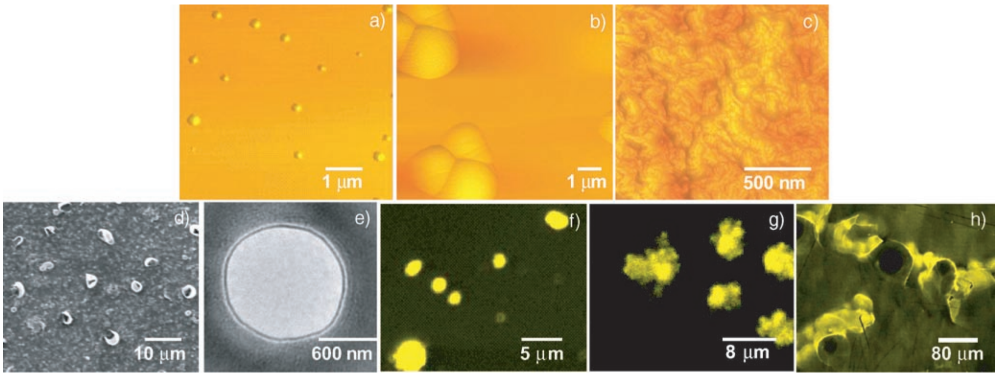

Figure 1. Microscopic images of aggregates of BINC18 deposited from methanolic solutions. The concentration of the solutions and conditions are indicated. (a–c) AFM height images on mica: a) 5×10^{-6} M; b) 5×10^{-6} M, aged 24 h; and c) 1.5×10^{-3} M. d) SEM image at 1×10^{-4} M, aged 24 h; e) TEM image at 1.2×10^{-4} M, aged 24 h. (f–h) CLSM images ($\lambda_\text{ex}=488$ nm; $\lambda_\text{em}=500$–800 nm): f) 1×10^{-4} M; g) 1×10^{-4} M, aged 24 h; and h) dried gel.

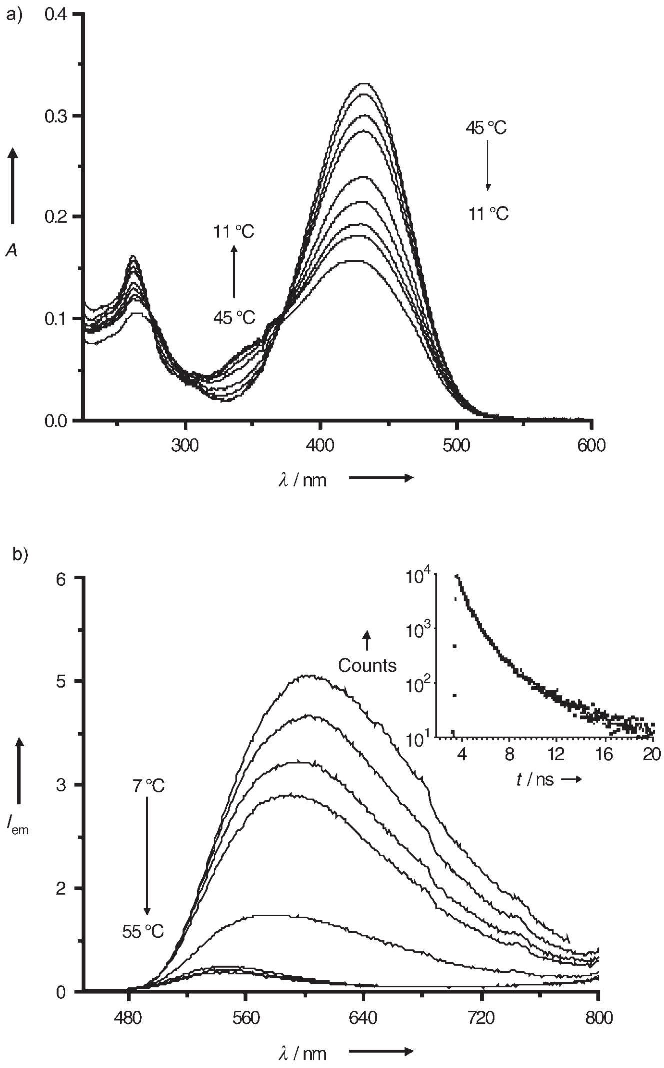

Figure 2. Temperature-dependent changes in a) absorption ($l = 1$ mm) and b) emission spectra ($\lambda_{ex} = 370$ nm; 1 cm × 1 cm) of a 1.2×10^{-4} M solution of BINC18 in methanol. The inset shows the fluorescence decay profile monitored at 13 °C ($\lambda_{ex} = 375$ nm; $\lambda_{em} = 600$ nm).

H aggregates is known to give rise to a high-energy allowed transition and a low-energy forbidden band. In such systems, absorption is dominated by the high-energy band, which results in a blue shift relative to the monomer absorption band, whereas long-lived and strongly red-shifted fluorescence occurs from the low-energy band.[5e,10]

The formation of H aggregates indicates a close π-stacked arrangement of the molecules. These results are also in support of the presence of an outer-membrane-like structure in the supramolecular aggregates.[11] The thickness of the wall of the vesicles (≈38 nm) measured from TEM images (Figure 1e) was almost ten times larger than the contour length of BINC18 (3.72 nm), thus suggesting a multilamellar structure for the walls of the vesicles. A model for the vesicle that is consistent with the spectroscopic studies and the TEM images would consist of about three to four closed bilayers, with the solvent layers existing in the center and between the bilayer membranes.[12] A schematic representation of the supramolecular assembly of BINC18 that leads to gel formation is provided in Figure 3.

Photoirradiation of a solution of BINC18 in methanol with 445-nm light resulted in a decrease in intensity of the main absorption band and was accompanied by a slight increase in absorption intensity at the lower wavelengths (Figure 4a). These changes can be attributed to a photoisomerization process (Figure 4b) similar to that reported earlier for donor–acceptor-substituted butadienes.[13] The rate of thermal reversal to the *E* isomer in such butadienes is known to depend on the electron-donating and -accepting strengths of the substituents.[13] For BINC18, a lifetime of 8.2×10^3 s was determined for the recovery of the *E* isomer by monitoring the growth of the 432-nm peak (Figure 4c). Photochemical isomerization and complete thermal reversal of BINC18 could be achieved over several cycles.

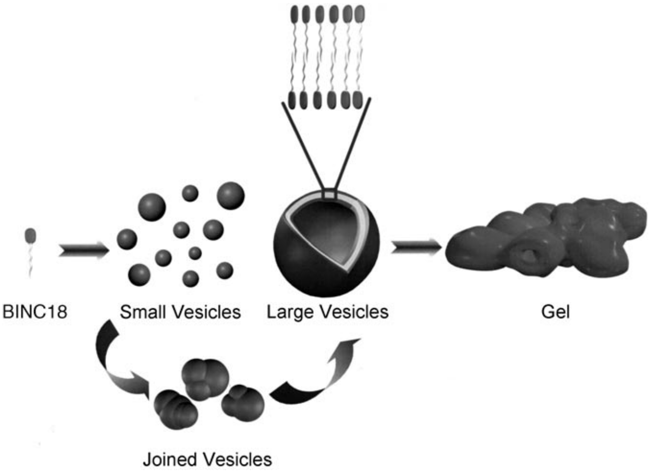

Figure 3. Schematic representation of the hierarchical organization from small to large vesicles and finally to gels. The molecular self-assembly of only one bilayer is indicated.

Photoirradiation of BINC18 also resulted in disruption of its supramolecular aggregates. Figure 5a,b depicts the effect of photoisomerization and thermal recovery of vesicles of BINC18. The AFM image of a film obtained from a non-irradiated aged 5×10^{-6} M solution of BINC18 showed the existence of large joined vesicular aggregates described earlier (Figure 1b). On irradiation, destruction of the larger vesicles and formation of small spherical aggregates was observed (Figure 5a), whereas AFM images obtained from the irradiated solutions kept in the dark for 24 hours clearly indicated recovery of the large vesicular aggregates (Figure 5b).

The effects of photoisomerization and thermal reversal on gel formation are shown in Figure 5c. Increased transparency and loss of fluorescence in a region of the gel photoirradiated at 445 nm through a mask (Figure 5c, film 2) suggested the destruction of the gel nature. Recovery of the fluorescence and scattering nature in the irradiated portion was observed on keeping the film in the dark for 24 hours, although persistence of a faint residual image indicated that the recovery was not complete under these conditions (Figure 5c, film 3).

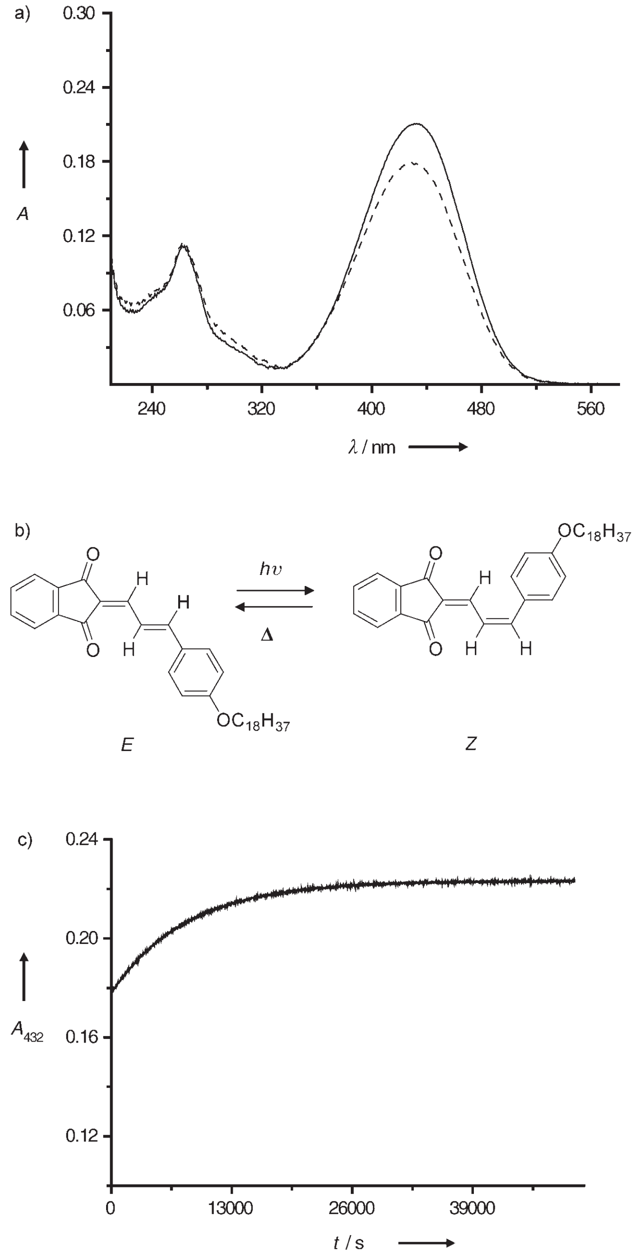

Figure 4. a) The effect of irradiation on the absorption spectrum of BINC18 in methanol (——) before and (-----) after irradiation with 445-nm light for 2 minutes ($c = 5\times10^{-6}$ M). b) Scheme depicting photo- and thermal isomerization of BINC18. c) Time-dependent recovery of the absorbance at 432 nm in the irradiated solution.

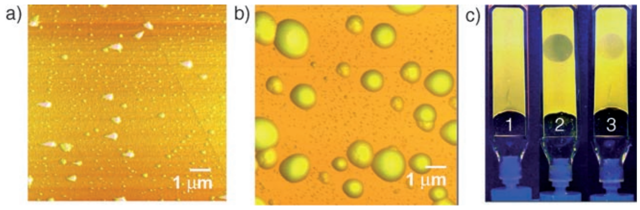

Figure 5. Effect of photoirradiation on vesicles and gels of BINC18. a) AFM tapping mode height image of film deposited from aged 5×10^{-6} M solution in methanol irradiated with 445-nm light for 2 minutes. b) AFM height image of film obtained from the same photoirradiated solution kept in the dark for 24 h. c) Photographic image of BINC18 gel in *n*-butanol kept under low-intensity 365-nm light which indicates yellow fluorescence of the gelated region ($l = 1$ mm, $c = 9.5\times10^{-3}$ M): 1) gel film before irradiation; 2) gel film irradiated with 445-nm light[8] for 30 minutes using a mask; and 3) irradiated gel film kept in the dark for 24 h.

The reversible photoinduced destruction of the gel was also confirmed by viscosity measurements. Rheological studies on BINC18 (4×10^{-3} M) in *n*-butanol were indicative of the formation of fairly stable gels.[8] Frequency-sweep measurements showed that the elastic modulus (G′) and the loss modulus (G″) were almost independent of frequency over a wide range. The studies also indicated that these gels were not thixotropic, which is a common feature with most known low-molecular-weight gelators.[9a] Irradiation of BINC18 gels (3×10^{-3} M) in *n*-butanol at wavelengths greater than 385 nm from a 200-W mercury lamp for 3 hours resulted in a gel-to-sol conversion, as observed by the free-flowing nature of the irradiated sample. The viscosity changes of the gel phase before and after irradiation were measured using a stress-controlled rheometer at low shear (0.02–1 s^{-1}) at 25 °C.[14] At a shear rate of 0.027 s^{-1}, the viscosity of the gel was 2.7×10^{5} cP. Following irradiation, a considerable decrease in viscosity (5.1×10^{4} cP) was observed at the same shear rate. Keeping the irradiated solution in the dark for 24 hours resulted in the reformation of the gel, as indicated by its nonflowing nature and increased viscosity (9.4×10^{4} cP at a shear rate of 0.027 s^{-1}).

In conclusion, we have synthesized a novel class of amphiphilic donor–acceptor butadienes capable of spontaneous hierarchical self-assembly, which first involves the formation of smaller vesicles that merge to form larger ones until they finally link together to form gels that consist of globular aggregates with solvent entrapped within them. This type of gelation is rather uncommon, as with a very few recent exceptions[15] most reported gels are formed through self-aggregation of gelator molecules into long intertwined fibrous networks that hold the solvents in between predominantly by surface tension. The photoresponsive nature of these materials makes them potentially useful in controlled release systems, and we are currently exploring some of these possibilities.

Received: May 25, 2006

Keywords: gels · isomerization · photoresponsive materials · self-assembly · vesicles

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