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Communication

Self-assembly of Cardanol Based Supramolecular Synthons to Photoresponsive Nanospheres: Light Induced Size Variation at Nanoscale

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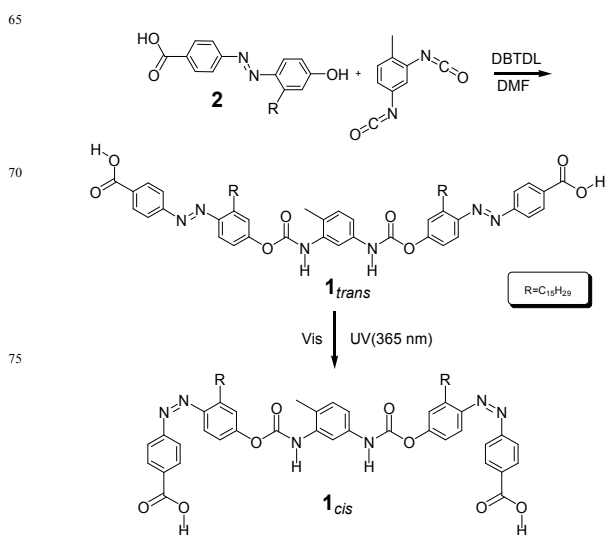
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The development of soft nanomaterials by the controlled self-assembly of molecules derived from renewable sources has become a major area of interest for scientists across the world. Our attempt in this paper is to report the self-assembly of Cardanol based photoswitchable molecule in non polar solvents such as cyclohexane. The self-assembly of Molecule 1 leads to the formation of nanospheres and it transforms with UV light. This could be seen an example of light induced size variation at Nanoscale

Recent trends in scientific research show an increasing interest in studying nanostructures fabricated from bioresources. This is on account of their ability for specific molecular recognition, simple chemical and biological modification and easy availability for bottom-up fabrication.¹ Plant/crop based feed stocks are already used extensively in the preparation of various materials such as plastics, solvents, lubricants etc. Among the various bioresources, cardanol has been considered the most exciting molecule based on its functional flexibility due to three main structural and chemical features: (i) the presence of reactive phenolic –OH group offering synthetic flexibility, (ii) the presence of meta alkyl chain with non-isoprenoid *cis* double bonds that lead to amphiphilic and lipidic character and (iii) the existence of the aromatic ring which allows for π - π stacking and functionalization. These features make cardanol an acceptable precursor for chemical modifications to generate a library of amphiphiles and functional monomers used in the production of soft materials.² There exists a plethora of reports based on cardanol centred polymers and polymeric materials in scientific literature³ and they continue to enjoy their status as a major focus of research.

The self-assembly of cardanol and its derivatives into diverse nanostructures have been intensely studied by various research groups.⁴ However, studies on the self-assembly of cardanol based molecules are limited to extended architectures, fibres and gels.^{2,4,5} Controlling their self-assembly is important for the development of novel soft materials from bioresources (Cardanol). Self-assembly can be controlled by various stimuli such as pH, temperature, molecular design and light⁶. Among these, light happens to be a powerful tool to manipulate the

properties of molecules and materials⁷. For example, light induced changes of azobenzene derived photochromic molecules have been exploited to control properties of molecular, macromolecular and supramolecular architectures⁸. Among various photochromic molecules, azobenzene is of immense scientific relevance due to its reversible E-Z photoisomerization that proceeds with large dipole moment and volume change leading to significant modulation of the macroscopic properties. Here we report the controlled self-assembly of Cardanol (a common bioresource extracted from cashew nut shell liquid) based molecule **1** into nanospheres and its transformation under exposure to light into microspheres. The cardanol linked photoactive molecule **1** was synthesized through a two-step process (Scheme 2 & 3 in supporting information). Cardanol on diazotization⁹ gives **2** and it was then coupled with toluene diisocyanate to get **1**.¹⁰



Scheme 1 Schematic representation of synthesis of **1**

The product was characterised by IR and ^1H NMR Spectroscopy. The absorption spectra of **1** in cyclohexane shows a peak at 365 nm corresponding to π - π^* transition and the peak at 450 nm corresponding to the n - π^* transition of the azo moiety.

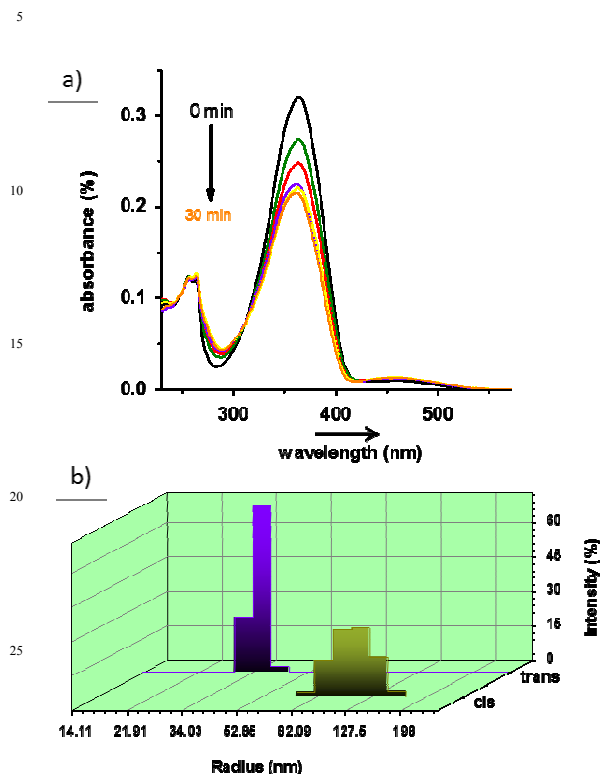


Figure. 1 a) The spectral changes of **1** upon photoirradiation in cyclohexane ($1 \times 10^{-5} \text{ mol dm}^{-3}$) using 350 nm light at 25 °C. b) DLS profiles showing the intensity-averaged hydrodynamic radius (R_h) of the self-assemblies before (blue) and after (green) photoirradiation with 350 nm light (25 °C)

The presence of four potential hydrogen bonding moieties i.e. two carboxylic groups and two urethane groups in the molecular structure of **1** can give rise to the formation of self assembly. Temperature dependent UV spectrum of **1** supports the report that self-assembly is present in **1** in non-polar solvents like cyclohexane (Figure S1). The absorption spectrum in cyclohexane ($1 \times 10^{-5} \text{ M}$) after sonication and subsequent cooling to 25 °C shows a peak at 365 nm with a molar extinction coefficient of ($\epsilon=25000 \text{ M}^{-1}\text{cm}^{-1}$). The intensity of absorption maxima in cyclohexane is enhanced ($\epsilon=29840 \text{ M}^{-1}\text{cm}^{-1}$) upon heating to 60 °C along with a slight blue shift (5 nm). The increase in the intensity of absorption signifies the breaking of aggregates. This in turn leads to an increase in the effective number of absorbing bodies, thereby proving the breaking of self-assembled structures. We have investigated the light responsiveness of **1** in cyclohexane by irradiating the sample ($c = 1 \times 10^{-5} \text{ M}$) using a band pass filter (λ band pass = $350 \pm 20 \text{ nm}$, LOT-Oriel 200 W high-pressure Hg Lamp) for up to 30 minutes with UV-Vis spectrum taken at various intervals (Figure 1b). The cis-trans isomerisation has been confirmed by the decrease in the π - π^* transitions and a slight increase in the n - π^* transition of the cis isomer. The photo stationary state (PSS) was reached in 30

minutes with a conversion efficiency of 37 %. For an insight into light induced morphology transition, Dynamic Light Scattering (DLS) analysis was performed in cyclohexane ($1 \times 10^{-4} \text{ M}$). A consistent particle size of around $35 \pm 5 \text{ nm}$ was obtained which indicates the aggregation of **1**. After irradiation (350 nm, 5 min) an increase in the R_h value has been observed with an average size of 100 nm indicating a change in the morphology of the aggregates. (Figure 1b)

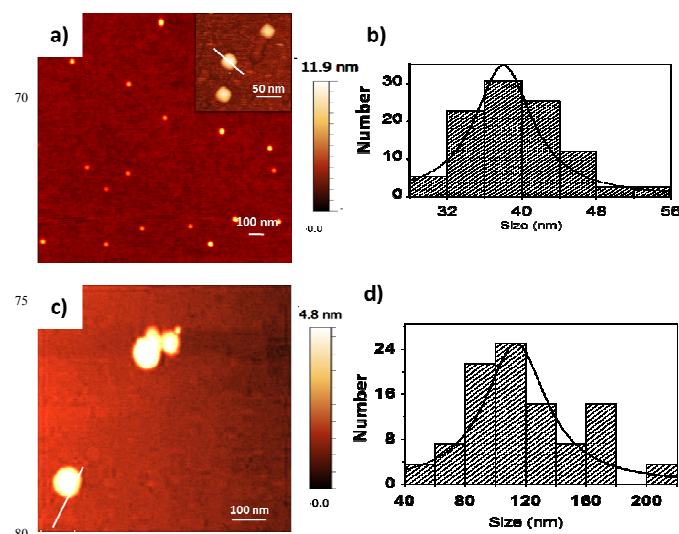


Figure. 2 AFM images of assemblies in cyclohexane ($1 \times 10^{-4} \text{ M}$, 25 °C) a) nano spheres of **1**_{trans}. b) Size distribution c) Microspheres of **1**_{cis} d) Size distribution

The atomic force microscopy (AFM) images of the self-assemblies of solutions of **1** in cyclohexane ($1 \times 10^{-4} \text{ M}$) is shown in Figure 2. These images reveal the self-assembly of **1** to individually dispersed nanospheres. The average diameter of the particles was estimated from the fitted histograms of the size distribution curves (Figure 2 b, d) after subtracting the tip-broadening parameter.¹¹ The histograms, which were obtained from the individual diameters of several particles, show a Lorentzian distribution with an average diameter of $38 \pm 2 \text{ nm}$ and a height of $7 \pm 1 \text{ nm}$ at $1 \times 10^{-4} \text{ M}$.¹² Comparison of the heights and diameter indicate a flattening of the spheres when transferred to the mica surface. Although there might be several causes of this flattening, it is likely that the removal of the solvent after the transfer of the soft particles to the mica surface and the high local force applied by the AFM tip could be the major reasons. The self-assembly was found to be independent of concentration by repeating the experiments in various concentrations (Figure S4a). These soft structures formed by the **1**_{trans} upon irradiation with light ($\lambda = 350 \text{ nm}$) further transforms into microspheres of almost $100 \pm 10 \text{ nm}$ size as proved by the AFM measurements. In order to study the effect of solvents and polarity we have done the Atomic Force Microscopy Measurements in polar solvent such as chloroform. Solvents seem to have an impact on the self-assembly. It was found that **1** form irregular structures in chloroform instead of nano spheres as in cyclohexane (Figure S4b).

In order to confirm this transformation and nature of the nanospheres Transmission Electron Microscopic (TEM) studies were carried out. The TEM images of **1** in cyclohexane (1×10^{-4} M) showed the formation of nanospheres of molecular aggregates. Surprisingly, after irradiation the TEM images revealed the transformation of the nanospheres into microspheres having diameter of 90-120 nm (Figure S5). We hypothesize that the weak E-Z isomerization is restricted to the surface of the aggregates and hence the mechanism of the sphere formation may involve a macroscopic pathway associated with a light driven process as shown in Figure 3.

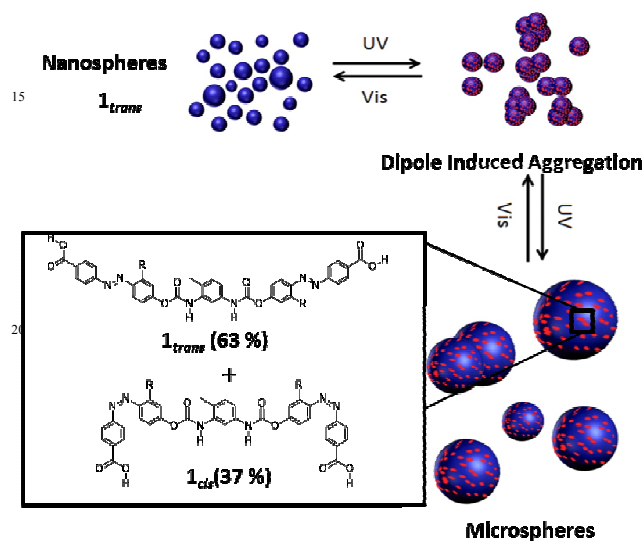


Figure. 3 Light Induced Size variation at Nanoscale-Schematic representation of transformation of nanospheres to microspheres

The observed morphological evolution of the nanospheres into microspheres can be attributed to the photoinduced dipole moment change associated with the E-Z isomerization of the initially formed molecular aggregates. The above suggested mechanism is well supported by the recent reports by Professor Ajayaghosh *et al*^{6c} and Professor Grzybowski *et al*¹³. The observed property changes are recognized as the change in the surface dipole moment as a result of the photoinduced *trans-cis* isomerization. The change in surface polarity of the aggregates was established through the contact angle measurements (Figure S6). During the *trans-cis* isomerization of the azobenzene, the dipole moment increases significantly during the transition from *trans* to *cis* which facilitates inter particle association leading to a structural transformation. Thus, the weak electrostatic repulsion of the aggregates is overcome by the relatively strong dipole-dipole interaction.

To conclude, the light triggered growth of nanospheres through the self-assembly of an azobenzene derivative into microspheres has been identified. The *trans-cis* photoisomerization and the associated surface dipole moment increase are responsible for the association of the nanospheres into microspheres. The observation described here opens up the potential possibilities of using the versatile azobenzene chromophore. The finding is

expected to encourage further studies towards formation of stimuli responsive hierarchical structures from bioresources with controlled morphological features.

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