

Supporting Information

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

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1. Materials and methods

All commercially available reagents and solvents were used without further purification. Silica gel was grade 60N (Spherical, Neutral, 100-200 mesh) from Merck, India. Melting points were determined with a Thermo Scientific melting point apparatus. Cardanol used is purchased locally.

1.1. Photoisomerisation studies

Experiments were performed on degassed solutions of **1** in cyclohexane (1×10^{-5} M) using Oriel optical bench with a 200 W high pressure mercury lamp. The *trans* to *cis* photo isomerisation of **1** was observed by irradiating sample by 350 nm (λ band pass= 350 ± 20 nm) light. The isomerization was monitored through change in UV/Vis absorption spectra. UV-Vis absorption measurements were recorded on a Cary 100 Bio. Temperature dependent studies were carried out on a Shimadzu UV 3101 PC NIR with a thermostat directly attached to the wall of the cuvette holder. The temperature is controlled manually. For the temperature dependent measurements, the initial temperature was set to 15 °C and the data points were collected at every 5 °C increase up to 65 °C for each measurement with a heating rate of 5°C/min.

1.2. Sample Preparation for Microscopy Measurements

A required concentration of **1** (1×10^{-4} M) was prepared by dissolving in cyclohexane by sonication and warming the solution. The solution was subsequently allowed to cool for a few hours followed by drop casting this solution on a carbon coated grid (400 mesh). For the morphology transition experiments, about 500 μ L of the solution was then placed in a 1 cm cuvette and irradiated with appropriate wavelengths (i.e. 350 nm) for **1**.

1.3. Transmission Electron Microscopy

TEM imaging was performed on a JEOL-JEM0310 microscope with an accelerating voltage of 300 kV. Samples were prepared by drop casting the **1** solution in cyclohexane (before and after irradiation) on carbon coated copper grids (400 mesh) and the TEM pictures were obtained without staining. For the morphology evaluation of the irradiated samples, about 500 μ L of the solution was placed in a 1 cm cuvette and irradiated with appropriate wavelengths by monitoring the absorbance changes. Small amounts were withdrawn from this solution in different time intervals and drop casted on the TEM grid and imaged without staining. All samples were imaged after drying in a vacuum oven.

1.5. Atomic Force Microscopy

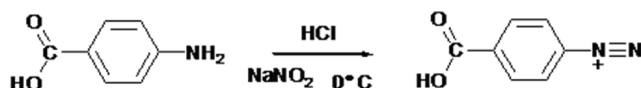
Samples were prepared by drop casting the **1** solution in cyclohexane (before and after irradiation) on mica sheet. A required concentration of **1** (1×10^{-5} M) was prepared in cyclohexane by sonication and warming of the solution and allowed to cool for few hours followed by drop casting on mica sheets. AFM imaging was performed in an Agilent 5500 Scanning Probe Microscope. The tip broadening effect was considered and the actual dimension of the nano spheres were calculated according to the equation

(1) where R is the radius of the tip, r is the actual width of spheres and r_c is the mean apparent width of the spheres.

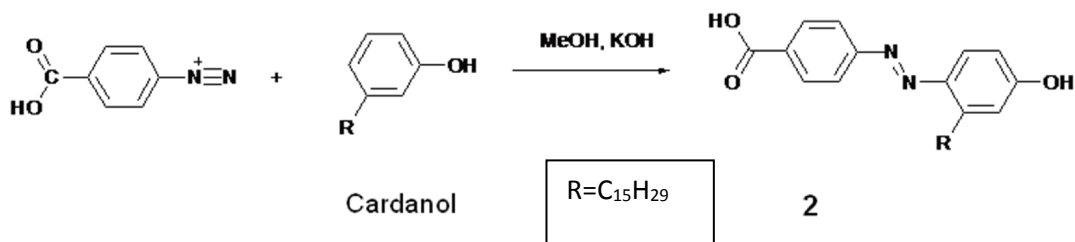
$$r_c = 2\sqrt{Rr} \quad (1)$$

Radius of the tip (Agilent AFM non-contact mode) is 7 nm. The average width of the nano spheres formed from the $c = 1 \times 10^{-4} \text{M}$ solution is 38nm. The actual diameter obtained after calculation is 25.8 nm.

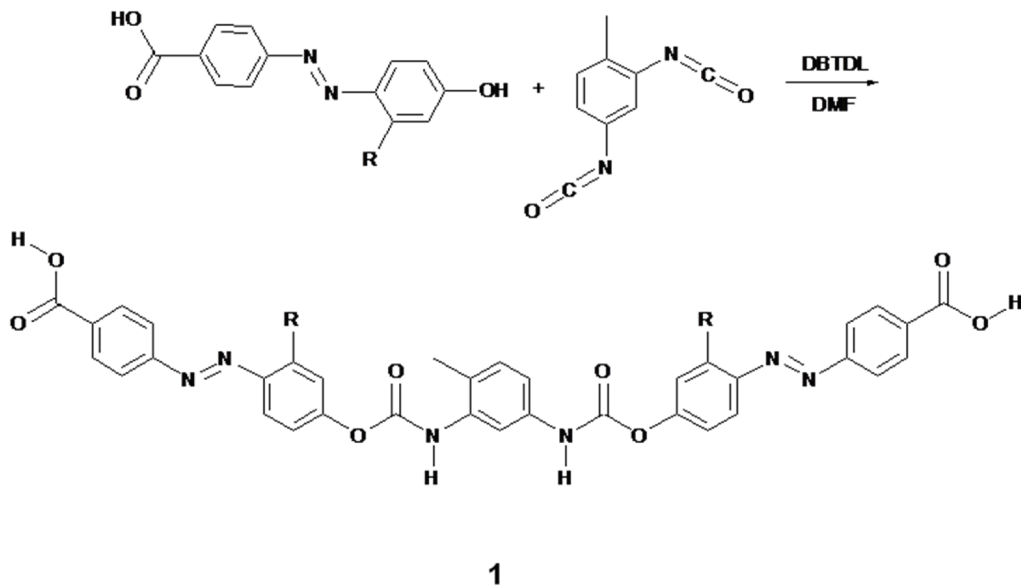
2. Synthesis



Scheme 1: Synthesis of Diazonium salt



Scheme 2: Synthesis of 2 by coupling with the Diazonium salt



Scheme 3: Coupling 2 with TDI to give 1

2.1. Synthesis of 2

To an RB flask equipped with magnetic stirrer was added 0.6-g anhydrous sodium carbonate dissolved in 20 ml of water. The setup was kept in ice bath with continuous stirring. 4-Amino benzoic acid(1.4 g,0.01 M) 4- amino benzoic acid dissolve din 20 ml dilute HCl was then added into the RB. The reaction mixture turns to a red. Cardanol (4 grams, 0.0013), KOH(1 gram, .017M) in 100ml methanol was added slowly to get red precipitates. The compound was extracted from the reaction mixture using chloroform and water. It was further purified using column chromatography. The pure **2** was dissolved in chloroform and precipitated using petroleum ether to give a yield of 34%. m.p. 139-140 °C.

IR (KBr; cm^{-1}): 3298(Ar -OH, -NH), 2920, 2860 (-CH₂-), 1686(Ar-COOH), 3020, 790 (cis-CH=CH-), 1575 (-N=N-).

¹H NMR (500 MHz, *d*₆ Acetone) δ : 8.06-7.82 (d, 2H), 7.62-7.80 (d,2H), 7.53-7.47 (m, 2H), 6.67- 6.77(s, 1H), 6.66-6.59 (d, 1H), 5.18-5.183 (m, CH₂=CH₂),3.04-3.0 (s, 2H), 1.90-1.92 (m, 2H), 1-85-1.92(m, 7H), 1.23-1.57(m,2H), 1.12-1.23 (m, 14H), 0.7-0.75 (m,2H).

¹³C NMR (acetone-*d*₆): δ :13.3; 22.4, 28.5, 29.0, 29.3, 30.8, 31.5, 31.9, 113.9, 114.8, 116.4, 116.8, 121.9, 129.4, 130.5, 131.4, 143.5, 146.6, 155.5, 161.5, 166.4 ppm.

HRMS-FAB: [M]⁺ calcd for C₂₈H₃₈N₂O₃: 450.29; found: 450.81

2.2 Synthesis of 1

To a solution of **1** (0.5 grams, 0.001 M) in 6 ml of DMF taken in an RB flask, toluene diisocyanate (0.2 grams, 0.001M) was added drop wise. A few drops of the catalyst dibutyl tin dilaurate (DBTDL) were also added and the reaction mixture was kept overnight. The temperature is then increased to 60 °C and the stirring was continued for 6 hours. The precipitate was collected and purified by column chromatography (silica gel 60-120 mesh using ethyl acetate as solvent). Pure compound was dissolved in THF and precipitated by cyclohexane to give a yield of 72%. m.p. 133-134 °C.

IR(KBr; cm^{-1}): 3323(Ar -OH, -NH), 1698(Ar-COOH), 1595 (-N=N-).

¹H NMR (500 MHz, DMSO- *d*₆): δ 10.31(2H, COOH) 8.62(s, 2H, Ar), 8.31(2H, NH), 8.11-8.09(d, 4H, Ar), 7.85-7.86 (d, 4H, Ar) 7.63-7.65(d, 2H), 6.79(s,1, H, Ar), 6.75-6.72 (m,2H, Ar), 5.26-5.31(m, CH₂=CH₂), 3.04-0.7.1(m,4H,CH₂), 2.6-2.7(m,CH₃)).

¹³C NMR (DMSO- *d*₆): δ : 14.36, 14.43, 22.56, 28.68, 28.94, 29.0, 29.07, 29.16,29.38, 29.45, 31.16, 31.5, 31.42, 31.54,31.75, 32.10, 39.44, 39.61, 39.78, 39.94, 40.11, 40.28, 40.37, 40.44, 99.99, 109.61, 114.71, 115.28,116.10,116.78,117.36,119.79,121.9,122.49,125.48,126.93,128.19,128.78,129.36,130.01,130.13,131.07 150.18, 207.05 ppm.

HRMS-FAB: [M]⁺ calcd for C₆₅H₈₂N₆O₈: 1074.62, found: 1075.4

3. Variable Temperature Absorption Spectra of 1

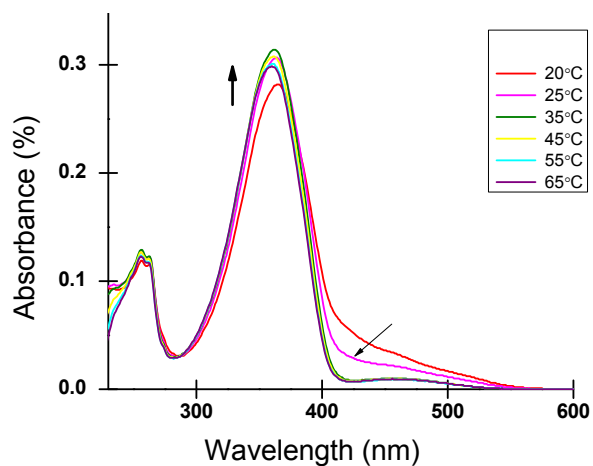


Figure S1. Temperature dependent UV/Vis absorption spectrum of 1 (from 20 °C to 65 °C)

4. UV Spectra of 1 in Various Solvents

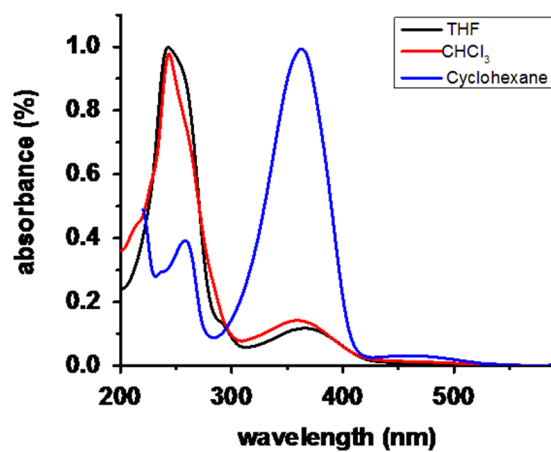


Figure S2: Absorption spectra of 1 in various solvents

5. UV Spectra of 2 in Various Solvents

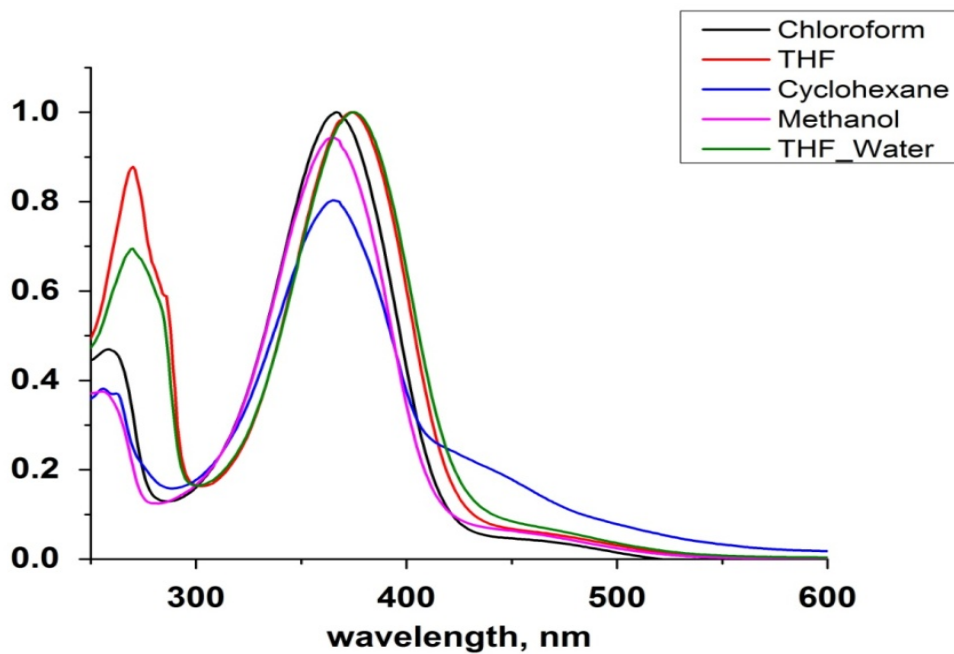


Figure S3: Absorption spectra of 2 in various solvents

6. AFM Images of 1 in various solvents

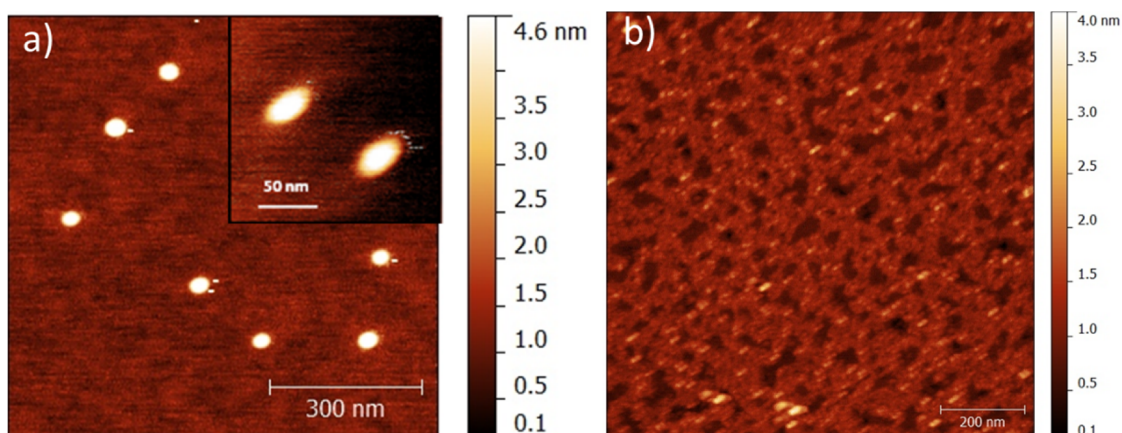


Figure S4: AFM image of 1 a) In cyclohexane (1×10^{-5} M) b) In chloroform (1×10^{-5} M)

7. TEM Images

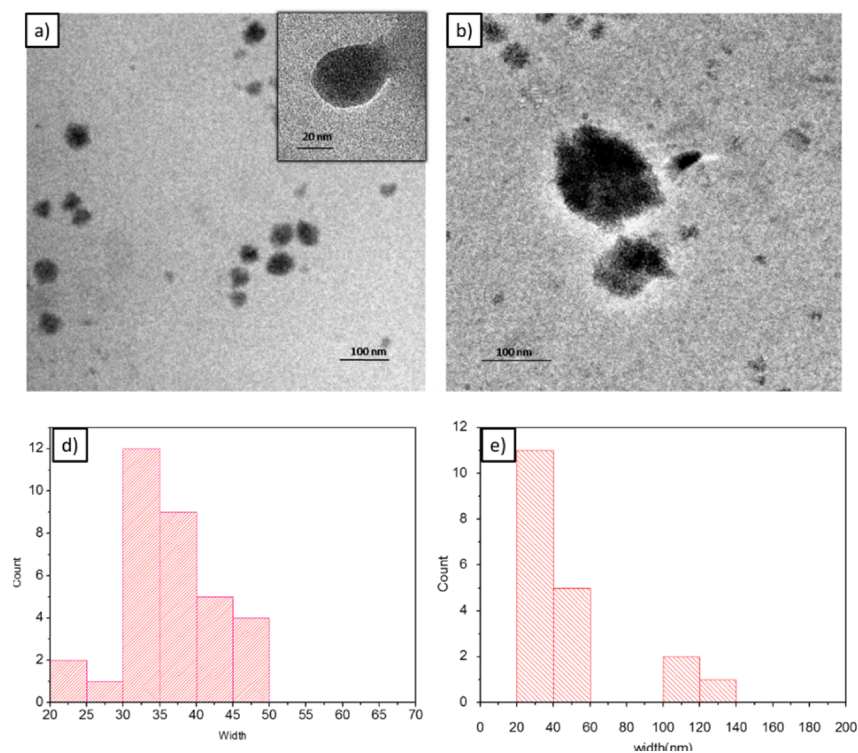


Figure S5: TEM images of **1** in cyclohexane (1×10^{-5} M) a) **1**_{trans} b) **1**_{cis} c) & d) Corresponding Histograms

8. Hydrophilic composite coatings based on **1**

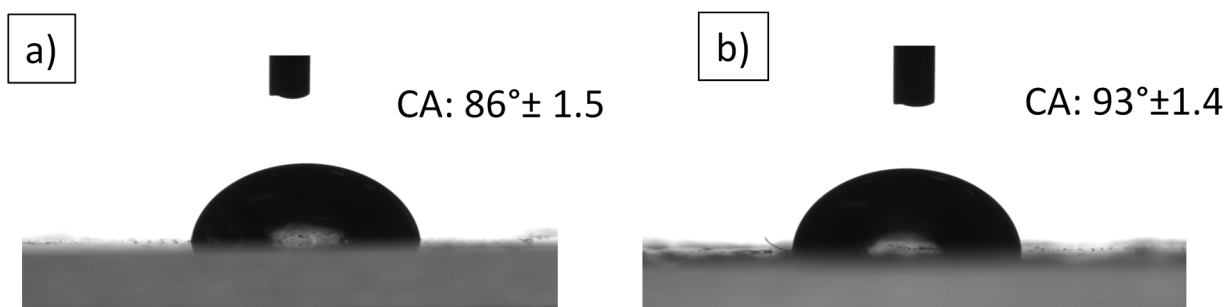


Figure S6: Contact angle measurements of **1** with Carbon Nanotube (CNT) in tetrahydrofuran (THF) a) before irradiation b) after irradiation.

9. References

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