

Supporting Information

Sustainable Electronic Materials: Reversible Phototuning of Conductance in a Noncovalent assembly of MWCNT and Bioresource Derived Photochromic Molecule

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1. Materials and Methods

All commercially available reagents and solvents were used without further purification. Silica gel plates were 250 μm thick, 60 F₂₅₄ grade from Merck. Silica gel was grade 60N (Spherical, Neutral, 100-200 mesh) from Merck, India.

1.1 Photoisomerisation Studies

The Experiments were performed on degassed solutions of **1** in Toluene ($1 \times 10^{-5}\text{M}$) using Oriel optical bench with a 200 W high pressure mercury lamp. The *trans* to *cis* photo-isomerisation of **1** and **1.MWCNT** was observed by irradiating sample by 354 nm (λ band pass= 354 ± 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. In a similar way *cis-trans* isomerization was monitored by irradiating the sample by 600 nm long pass. 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 70 °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) and other samples was prepared by dissolving/dispersing in Toluene by sonication. 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 250 μL of the solution was then placed in a 1 mm cuvette and irradiated with appropriate wavelength (i.e. 354 nm) for **1**.

1.3 Transmission Electron Microscopy (TEM)

TEM imaging was performed on a JEOL-JEM2100 microscope with an accelerating voltage of 200 kV. Samples were prepared by drop casting the **1** solution in Toluene on carbon coated copper grids (400 mesh) and the TEM images were obtained without staining.

1.4 Scanning Electron Microscopy (SEM)

SEM imaging is done using a Zeiss EVO 18 cryo SEM Special Edn with variable pressure detector working at 20-30 kV.

1.5 Atomic Force Microscopy (AFM)

AFM measurements were carried out under ambient conditions by using an Agilent 5500 Scanning Probe Microscope operating in non-contact mode. Silicon cantilevers (Agilent Technologies) with a resonance frequency of ~ 300 kHz were used. The 512×512 pixel images were collected at a rate of 2 scan lines per second. A required concentration of both samples (1×10^{-3} M) was prepared in Toluene by drop casting on mica sheets.

1.6 Nuclear Magnetic Resonance (NMR) Studies

^1H NMR and ^{13}C NMR spectra were recorded using Bruker AV III 500 MHz FTNMR spectrometer using Toluene- d_8 and Acetone- d_6 as solvents with TMS as internal standard

1.7 Mass Studies

Mass spectra were recorded under ESI/HRMS using ThermoScientific Exactive mass spectrometer and also by HRMS-FAB.

1.8 X-ray Diffraction (XRD) Experiment

Small angle X-ray scattering measurements were performed by using XEUSS SAXS system by Xenocs, operated at 50kV and 0.60 mA. The X-ray radiation was collimated with FOX2D mirror and two pairs of scatterless slits from Xenocs. The data were collected in the transmission mode geometry using Cu $K\alpha$ radiation (wavelength $\lambda = 1.54 \text{ \AA}$). The fiber diagrams were recorded using an image plate system (Mar 345 detector) and processed using Fit2D software.

1.9 Dynamic Light Scattering (DLS) experiments

DLS were measured on particle size analyzer (Zetasizer Nano ZS series, Malvern instruments) by using glass cuvette.

1.10 Thermal Analysis

1.10.1 Thermogravimetric Analysis (TGA)

TGA was carried out in TAQ50 instrument under nitrogen atmosphere at a heating rate of 5 °C per minute.

1.10.2 Differential Scanning Calorimetric (DSC) Analysis

DSC was performed on TAQ20 instrument at a heating and cooling rate of 5 °C per minute.

1.11 Conductance Measurements

1.11.1 Electrochemical Work station

The photo-current switching performance of the sample was studied by an advanced electrochemical system with three electrode cell PGSTAT302N electrochemical work station (Autolab, Metrohm, Switzerland). Among the three electrodes one is the Indium Tin Oxide (ITO) working electrode, one is a platinum wire counter electrode and an Ag/AgCl reference electrode. The electrolyte solution used is 0.1M KCl solution. The ITO plates are washed by ultrasonication with water, Extran, acetone and isopropyl alcohol. The plates are then covered by an insulation tape leaving 0.4×0.4 cm² as active area. Then about 50 μL of bare azocompound **1** and non-covalent hybrid solution of **1** and acid functionalized MWCNTs are spin coated on to these plates. Before measurements the plates are kept in vacuum oven at for 24 hours at 25 °C.

1.11.2 Keysight 2-Probe station

About 5 ml of the hybrid solution is spin-coated onto an ITO plate and the conductance measurements are done without UV irradiation and with UV irradiation at different time intervals using EVERBEING INT'L CORP 2-probe station interfaced with an Agilent B2912A SMU, with the whole arrangement controlled by Quick IV computer GUI interface (Keysight).

1.11.3 Keithly 4-Probe station

Conductance measurements on a Keithly 6221A 4-Probe station are done after spin coating both solutions of bare acid functionalized MWCNT and the trans and cis hybrid solutions onto ITO plates. The thickness of the films are measured to be 1 μm using a DEXTAK Profilometer.

The UV irradiation is carried out by using a Spectroline E Series UV lamp with AC input 230V and output 8W at 365 nm.

2. Synthesis

2.1 Synthesis of 4-[(4-Cardanyl)azo]benzoic acid(AZOC1) (3)

4-Aminobenzoic acid (1.371 g, 0.01 mol) (Sigma Aldrich, Mumbai) was dissolved in dilute HCl and diazotised with sodium nitrite (0.690 g, 0.01 mol in 2 ml of water) solution at 0°C with stirring. Cardanol (3.005 g, 0.1 mol) (obtained by distillation of cashewnut shell liquid under vacuum dissolved in a chilled solution of potassium hydroxide (1.077 g, 0.019 mol) in methanol (10 ml) was added drop-wise to the above solution diluted with chilled methanol (40 mL). The red dye formed was stirred for further 2 hour and poured into dilute HCl solution with stirring. The red solid separated was filtered, washed thoroughly with water, and dried. The dye was then purified by column chromatography on silica gel (100–200 mesh) using mixture of Petroleum ether and Ethyl acetate as eluent. The solvent was removed and recrystallised from a petroleum ether.¹

Yield: 3.02 g (67%), red flakes; m.p.134-135 °C.

IR(KBr; cm⁻¹): 3298(Ar-OH), 2860(-CH₂-), 1686 (Ar-COOH), 3020, 790 (-CH=CH), 1575(-N=N-)

¹H NMR (500 MHz, Acetone d₆) 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, -CH=CH-), 3.04-3.0 (s,2H), 1.90-1.92 (m,2H), 1.85-1.92(m,6H), 1.23-1.57(m,2H), 1.12-1.23(m,14H), 0.7-0.75(m,2H) ppm

¹³C NMR (Acetone d₆) 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]⁺ Calculated for C₂₈H₃₈N₂O₃: 450.29, found: 450.81

2.2 Synthesis of 4-[4-dodecyloxycarbonyloxy-2-pentadecylphenylazo]benzoic acid (DOAZOC1) (1)

3 (2 gm, .0030mol) was dissolved in 50 ml methanol and 2 ml Conc.H₂SO₄ is added to it. The mixture is kept for refluxing for 24 hour. Then the methanol is evaporated in a rotary vapour. To the residue 50ml N,N-DMF is added and 7.5 g of KOH is added. The mixture is kept for refluxing at 80°C, after 10 minutes 20ml of 1-Bromododecane is added. The solution is again kept for 96 hour. The compound is extracted using dichloromethane after acidifying with dilute HCl. It is then purified by column chromatography on neutral alumina using petroleum ether as eluent. The solvent is removed and the recrystallised from Tetrahydrofuran.^{2,3}

Yield: 1.5gm(55%), red coloured viscous liquid.

IR(KBr; cm^{-1}): 3461(Ar-COOH), 2920, 2847(-CH₂-), 1726(Ar-COOH), 3012, 777(-CH=CH-), 1594 (-N=N-), 1212(Ar-C-O-), 1113 (R-C-O-Ar).

¹H NMR (500 MHz, Toluene d₈) δ : 8.25-8.23(d,2H), 7.96-7.94(d,2H), 7.09(s,1H), 6.79-6.78(d,1H), 6.62-6.60(d,1H), 5.43-5.39(m,CH=CH-), 4.21-4.19(t,2H), 3.20-3.17(t,3H), 2.09-1.99(m, 5H), 1.74-1.57(m,4H), 1.39-1.25(m,32H), 0.94-0.88(m,6H) ppm.

¹³CNMR(Toluene,d₈) δ : 13.7, 14.1, 22.6, 22.8, 26.0, 27.2, 28.7, 28.9, 29.2, 29.3, 29.5, 29.8, 31.7, 31.9, 32.2, 112.5, 114.6, 117.0, 122.4, 129.7, 129.9, 130.5, 131.3, 144.6, 146.5, 155.6, 162.7, 166.2 ppm.

ESI-MS: [M+1] Calculated for C₄₀H₆₂N₂O₃: 619.48, Found: 619.48

2.3 Synthesis of Acid functionalized MWCNT.

About 1 gram of MWCNT is purchased from Sigma Aldrich and it is then taken in a two-necked 500 ml RB flask. To this about 80 ml of concentrated nitric acid is added and the mixture is kept for refluxing at 110 °C about 6 hour. The sample is then filtered using a Milli pour filter unit. It is then washed with distilled water till pH becomes 7. The sample is then dried at 120 °C for 12 hours.⁴

IR (KBr; cm^{-1}): 3443(Ar-COOH), 1715(Ar-COOH), 1540(Ar-C=C-), 1187(Ar-C-O-).

2.4 Preparation of Non-covalent hybrid with 1 and Acid functionalized MWCNT (1.MWCNT)

To a 5 ml (1×10^{-3} M) solution of 1 in Toluene, 5 mg of the acid functionalized MWCNT is added. The solution is then made up to 10ml in a glass vial. It is then probe sonicated for 2 hours. A dispersion is formed. The dispersion is then spin-coated on to ITO plates.

IR (KBr; cm^{-1}): 3663(-OH, hydrogen bonded), 2925, 2853(-CH₂-), 1720(Ar-COOH), 3002, 768 (-CH=CH-), 1594(-N=N-), 1571 (Ar-C=C-), 1109(Ar-C-O-).

2.5 Pattern of hydrogen bonding in heterodimer formed between Acid Functionalized MWCNT and 1

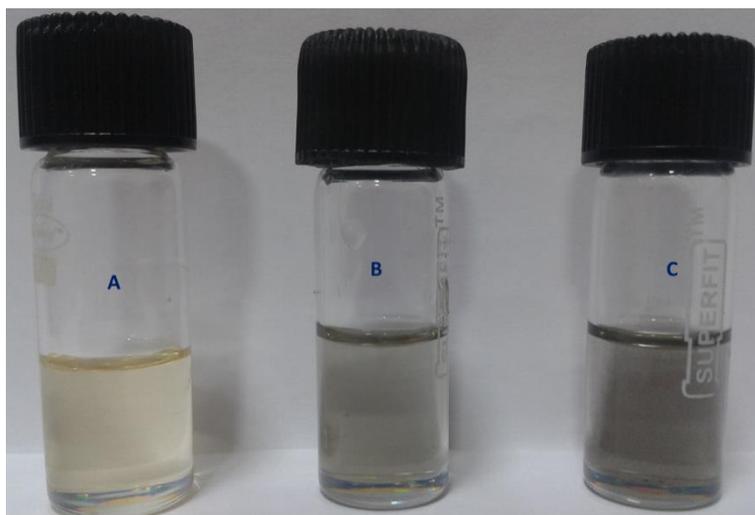
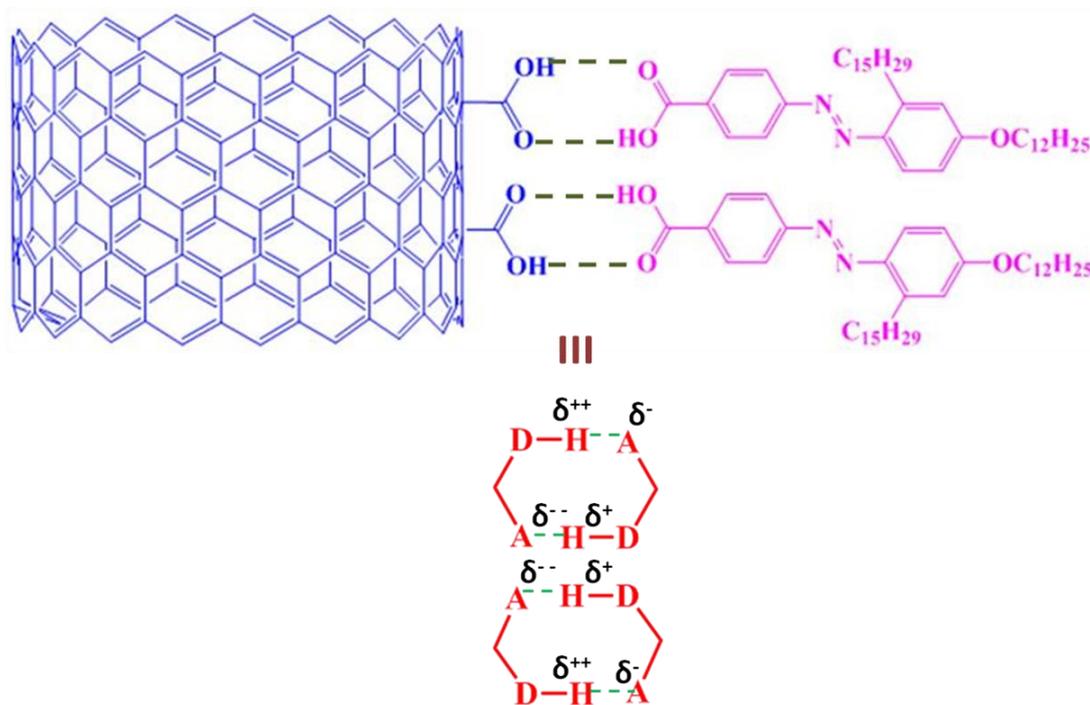


Figure S1: Visible light Photographs of solutions of A) 1, B) 1.MWCNT and C) MWCNT in Toluene

3. Visible light irradiation experiments of cis-1 in Toluene

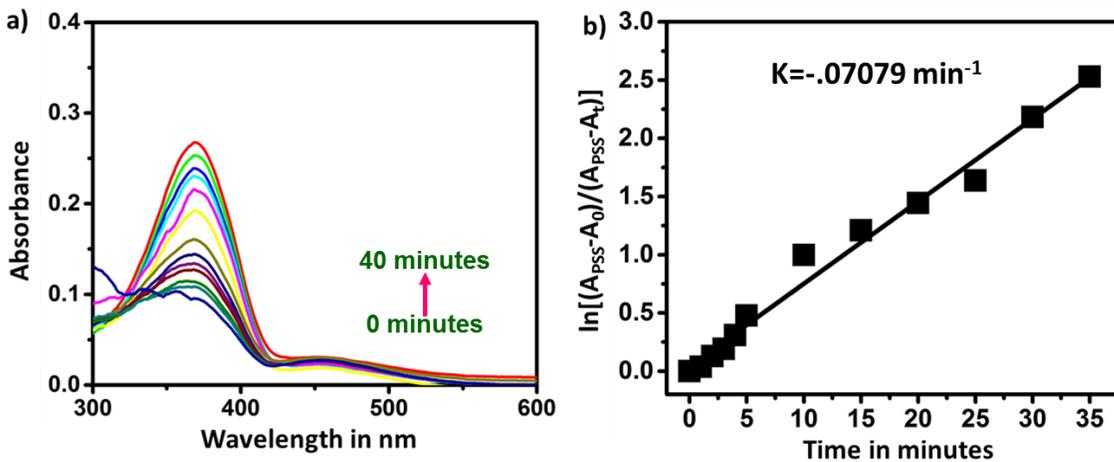


Figure S2: a) UV-Visible spectra for irradiation of 1 at 600 nm b) Rate constant for cis-trans isomerization is $.07079 \text{ min}^{-1}$

4. Visible light irradiation experiments of cis-1.MWCNT hybrid in Toluene

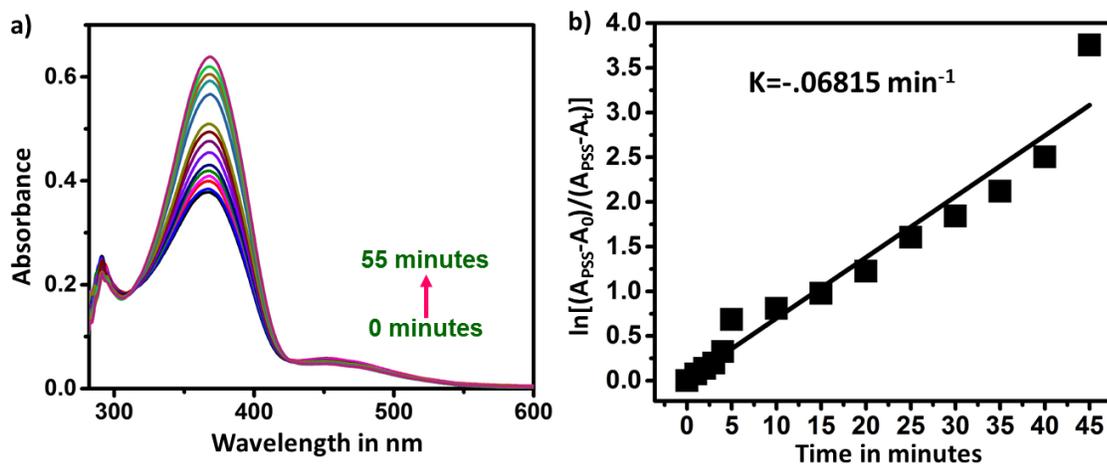


Figure S3: a) UV-Visible spectra for irradiation of 1 at 600 nm b) Rate constant for cis-trans isomerization is $.06815 \text{ min}^{-1}$

5. Thermal irradiation experiments of 1 in Toluene

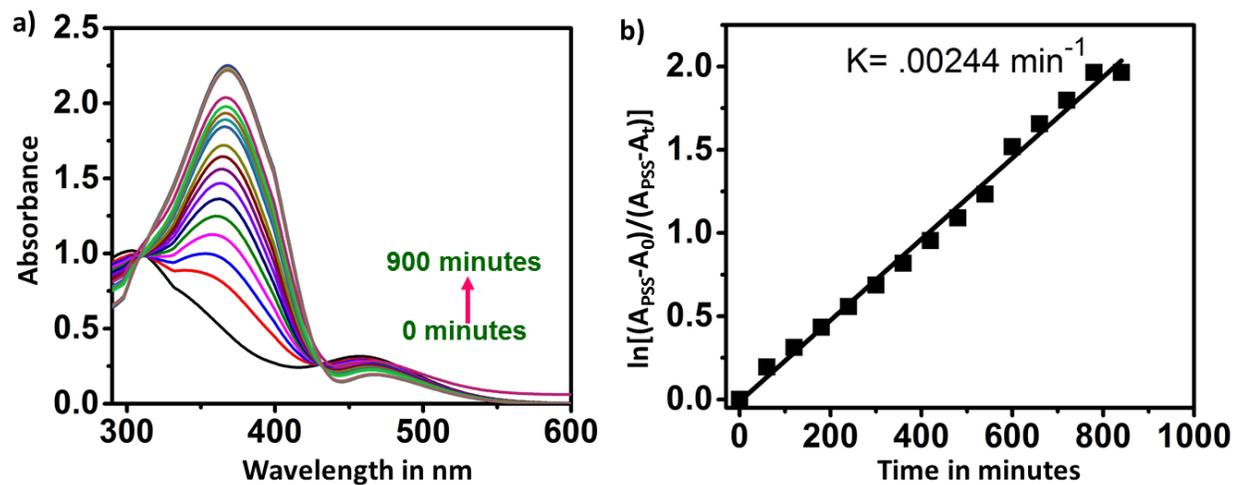


Figure S4: a) UV-Visible spectra for thermal irradiation of 1 b) Rate constant for cis-trans isomerization is $.00244 \text{ min}^{-1}$

6. UV-Visible switching cycle of 1 in Toluene

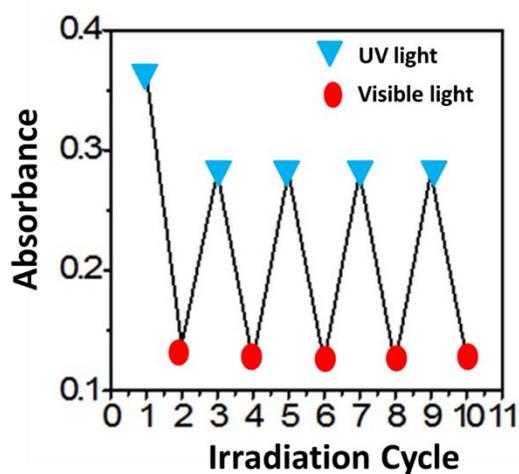


Figure S5: Alternate UV-Visible switching of 1 at 354 nm and 600 nm

7. ^1H NMR studies of 1 in Toluene

7.1 UV irradiation studies

7.1.1 Before irradiation

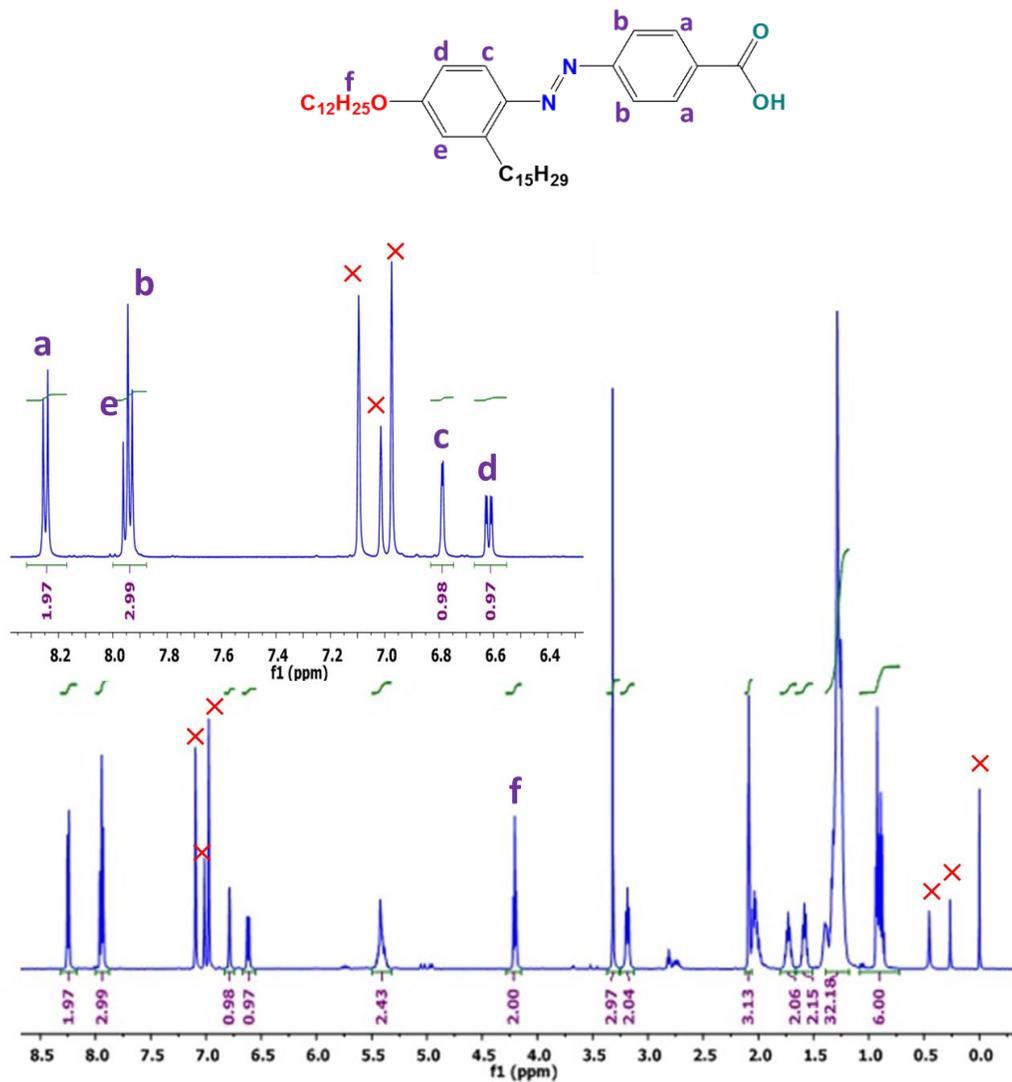


Figure S6: ^1H NMR spectra of 1 in Toluene before irradiation. The inset shows the zoomed region between 6.3-8.4 ppm.

7.1.2 After irradiation

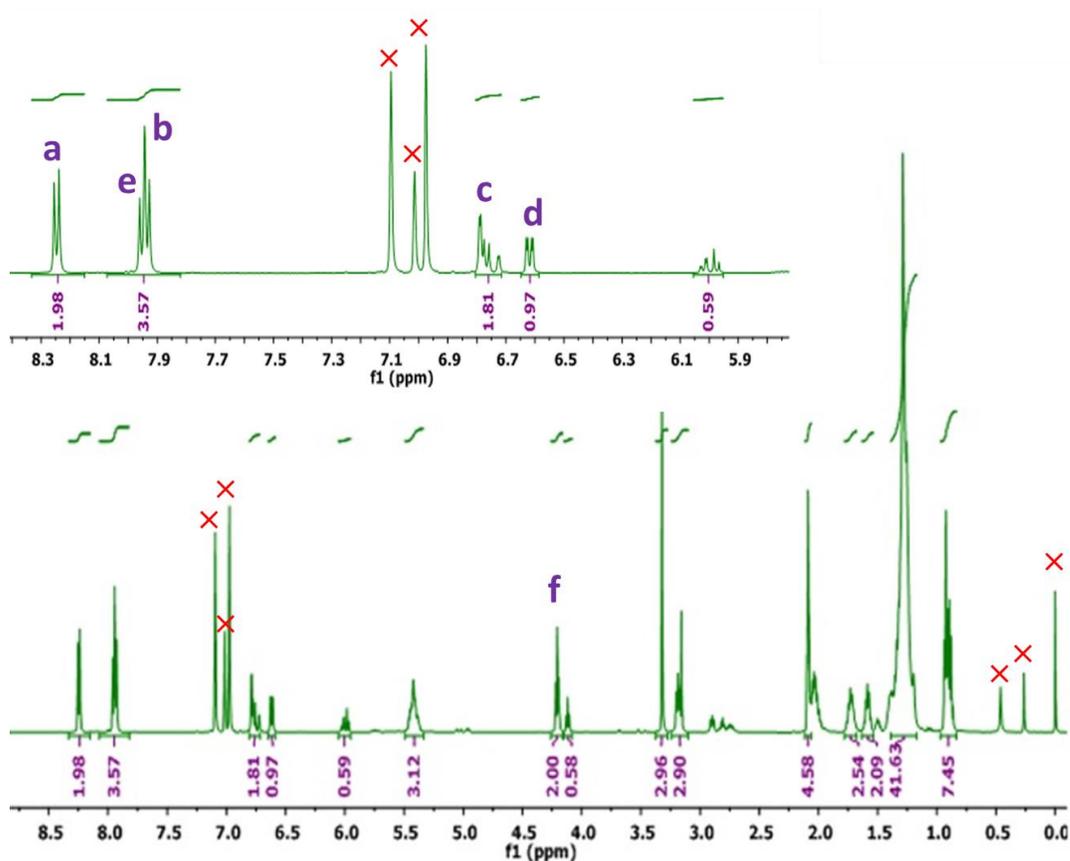


Figure S7: ^1H NMR spectral changes of 1 at PSS in Toluene. The percentage conversion is calculated by the integration of appropriate peaks. The inset shows the zoomed region between 5.9-8.4 ppm.

8. Dynamic Light Scattering (DLS) experiment

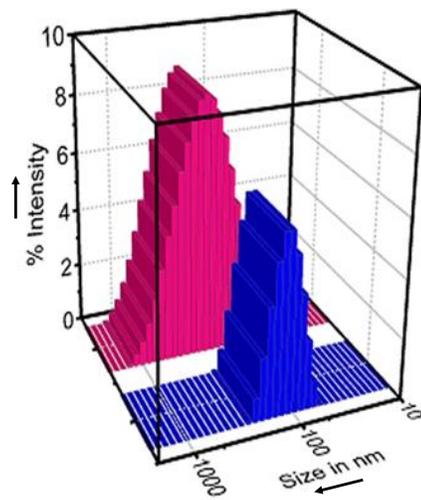


Figure S8: Profiles showing the intensity- averaged hydrodynamic radius (R_h) of the self-assemblies of 1 before (blue) and after (pink) photo-irradiation with 365 nm.

9. Atomic Force Microscopy (AFM) images

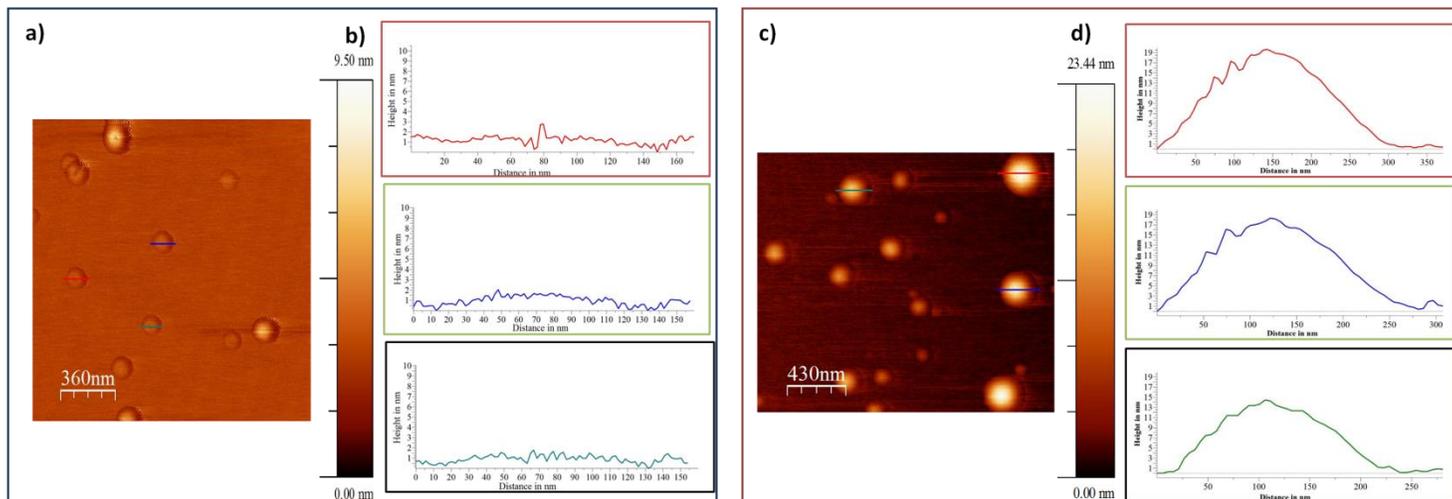


Figure S9: AFM images of 1 with height profiles a) & b) before irradiation c) & d) after irradiation.

10. Thermogravimetric Analysis (TGA) and Differential Thermogravimetric Analysis (DTA)

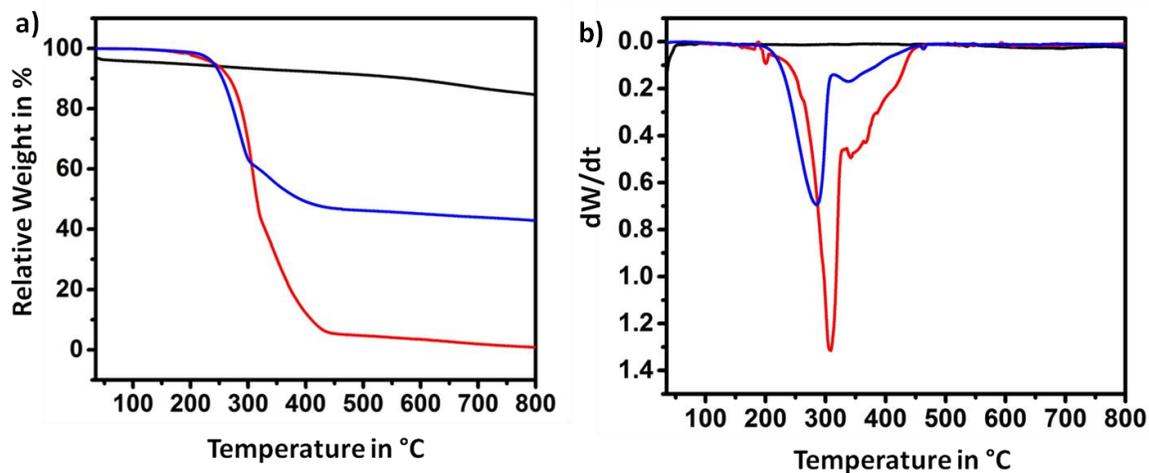


Figure S10: a) TGA b) DTA curves at a rate of 5 °C per minute of MWCNT (black), 1 (red), 1.MWCNT hybrid (blue)

This curve very well illustrates the difference in pyrolytic temperatures of 1, MWCNT and 1.MWCNT hybrid.

11. Differential Scanning Calorimetric (DSC) experiment

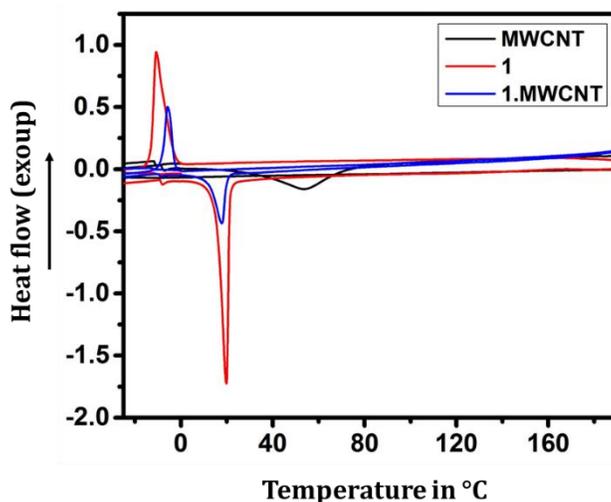


Figure S11: DSC curve at a rate of 2 °C per minute of MWCNT (black), 1 (red) and 1.MWCNT hybrid (blue)

From the DSC curves 1 shows the melting transition temperature of -10.7 °C and 1.MWCNT shows around -6 °C in the heating cycle. In the cooling cycle the phase transition of 1 occurs at 20.2 °C, MWCNT at 54 °C and that of hybrid 1.MWCNT at 17 °C. There was no significant peak in the heating cycle for MWCNT.

12. Scanning Electron Microscopy (SEM) images

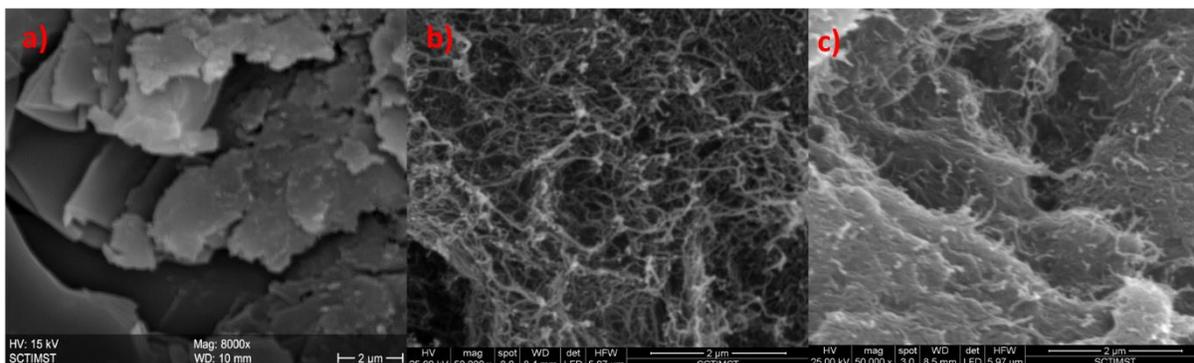


Figure S12: SEM images of a) 1 b) MWCNT and c) 1.MWCNT hybrid in Toluene.

13. X-ray Diffraction (XRD) experiment

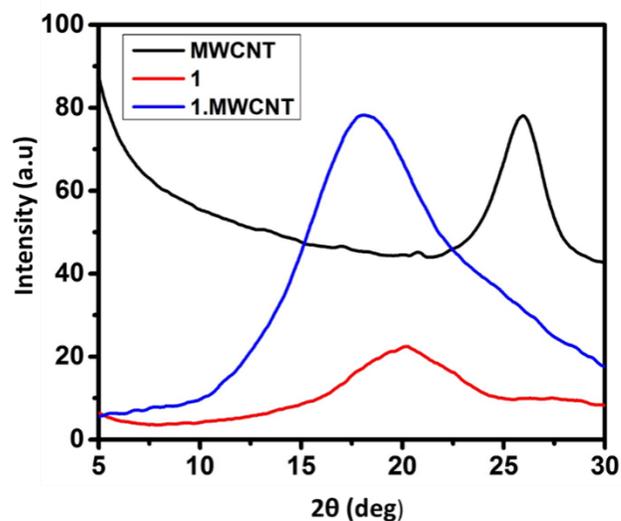


Figure S13: XRD plot of 1, MWCNT and 1.MWCNT hybrid in toluene

14. Table S1: Conductivity studies in a 4-probe station

Compound	Conductivity
MWCNT	168.853 S/cm
Trans-1.MWCNT	3.5905 S/cm
Cis-1.MWCNT	19.4673 S/cm

15. Table S2: Different CNT-AZO hybrids with functionalization, characterization, linkage and application

No	Type of Carbon Nanotube	AZO	Mode of Functionalization	Characterisation Techniques	Application	Reference
1	SWNT	G3azoC11 amphiphile	Non-covalent	UV, Fluorescence	Bundling-debundling	7
2	SWNT	Disperse Red 1 (DR1)	Non-covalent	UV, XPS,NMR	Integrated nanophoto detector	8
3	MWCNT	4-Amino-10-azobenzene 3,4'-disulfonic acid (AY)	Non-covalent	SEM	Sensor	9
4	MWCNT	4'-hexylphenyl[4-(propylbutoxy)phenyl]diazene	Non-covalent	UV,SEM	Conductance Switch	10
5	SWNT	Pyrene-nitroazobenzene	Non-covalent	FTIR,NMR	Colour detector	11
6	SWNT	AZO-pyrene polymers	Non-covalent	NMR,DSC,TGA,TEM	Alignment	12
7	SWNT	AZO-phenylene or vinylene	Non-covalent	UV-Vis-IR, NMR,AFM,TEM	Dispersion	13
8	MWCNT	4-Amino-azobenzene-4'-sodium sulfonic acid	Covalent	Raman,TGA,XPS, TEM	Molecular Switch	14
9	FWCNT	AZO-alkyl spacer	Covalent	FTIR,NMR,TEM	Photoswitch	15
10	MWCNT	2,5-Dimethoxy-4-[4-nitrophenyl]azo] benzenediazonium chloride (FBK)	Covalent	NMR,SEM	Memory storage and sensors	16

16. Calculation of Parameters

16.1 Calculation of Photo-response ratio

The on-off ratio of photocurrent is given by response current, I_{Ph} ,

$I_{Ph} = I_{UV} - I_d$, where I_d is the current in dark and I_{UV} is the current under UV illumination condition. The on-off ratio of photocurrent is I_{Ph}/I_d .⁵

16.2 Calculation of molar extinction coefficient and fraction of aggregates

The molar extinction coefficient (ϵ) can be calculated from the Beer-Lamberts law.

$$A = \epsilon cl$$

Where, **A** is the absorbance of the solution, **c** = concentration of the solution,

l=length of the cuvette in cm.

From variable temperature absorption spectra, the fraction of aggregates ($\alpha_{agg}(T)$).

$$\alpha_{agg}(T) = \frac{A(T) - A_{mon}}{A_{agg} - A_{mon}}$$

A (T), **A_{mon}**, **A_{agg}** are the absorbance in the monomeric form (taken from the UV-Visible spectrum) and absorbance at fully aggregated state at 25 °C.⁶

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