Supporting Information

Self-assembly, Photoresponsive Behavior and Transport Potential of Azobenzene Grafted Dendronized Polymeric Amphiphiles

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1. Photoisomerization Study of Polymers Below the CAC in Aqueous Solution. The photoisomerization behavior of both the polymers was studied below the CAC in the aqueous solution. The rate of *trans-cis* photoisomerization was studied by analyzing the change in absorbance at 351 nm with time on irradiating the samples at 365 nm. The system reaches the photostationary state in 20-30 seconds for both the polymers below the CAC value (Figures S1A and S2A).

2. Calculation of Rate Constant for *trans-cis-trans* Photoisomerization. The rate constant of *trans-cis* photoisomerization was calculated by using the first-order rate law by measuring absorbance at 351 nm at different time intervals for both the polymers (**4a** and **4b**) below their CAC while from the absorbances at 351 and 337 nm for polymer **4a** and **4b** respectively above their CAC, using **Equation S1**.^{1,2}

$$\ln\left(\frac{A_{\infty} - A_t}{A_{\infty} - A_0}\right) = -k_{t-c}t$$

Equation S1

Where, A_{∞} = absorbance at photostationary state

 A_t = absorbance at time 't'

 A_0 = absorbance at time '0'

k_{t-c} = rate constant for *trans-cis* photoisomerization

t = time of irradiation at 365 nm

The isomerization rate constant (k_{t-c}), for polymers **4a** and **4b**, below their CAC, was calculated to be 0.141 and 0.131 s⁻¹ however above CAC, it decreases significantly to 0.039 and 0.018 s⁻¹, respectively. The rate of *trans-cis* isomerization below CAC was found to be approximately 4 times higher for polymer **4a** while it is 7 times higher for **4b** as compared to above CAC value. The rate constant for *cis-trans* photoisomerization was also calculated by measuring absorbance at 351 nm for both of the polymers below their CAC while from the absorbances at 351 and 337 nm for polymer **4a** and **4b** respectively, above CAC, at the photostationary state by using the first-order rate law, using **Equation S2**.^{1,2}

$$\ln\left(\frac{A_{\infty} - A_0}{A_{\infty} - A_t}\right) = k_{c-t}t$$

Equation S2

Where, A_{∞} = absorbance at photostationary state

At = absorbance at time 't'

 A_0 = absorbance at time '0'

t = time of irradiation at 254 nm

The isomerization rate constant (k_{c-t}), was calculated to be 0.114 and 0.118 s⁻¹ below CAC while it decreased to 0.0104 and 0.0086 s⁻¹ for polymers **4a** and **4b** respectively above CAC. The rate of *cis-trans* isomerization below CAC was found to be approximately 11 times higher for polymer **4a** while it is 14 times higher for **4b** as compared to above the CAC value.

3. Calculation of % release of Nile red using fluorescence measurements. The % release of Nile red from the miceller nanostructures on photoisomerization was calculated by measuring the fluorescence intensity of Nile red before and after *trans-cis-trans* isomerization by using the Equation S3.

% Release of Nile red =
$$\frac{I_d}{I_i} \times 100$$

Where, $I_d = I_i - I_r$

Where, I_i = Initial fluorescence intensity for encapsulated sample before irradiation

Ir = Regained fluorescence intensity after trans-cis-trans isomerization

I_d = Decrease in fluorescence intensity on *trans-cis-trans* isomerization

4. Control Experiment for Photobleaching of Nile red. Control experiments were performed so as to confirm if the net decrease in the fluorescence intensity of Nile red on photoirradiating the aqueous solution of dye encapsulated polymeric amphiphiles is not because of photobleaching of Nile red (either due to chemical degradation or non-specific reactions with the surrounding). Since the Nile red has a very insignificant solubility in aqueous medium, it was dissolved in pure methanol and a mixture of water and methanol in 1 : 1 and 2 : 1 ratio keeping the dye concentration (0.4 mM) same as used for encapsulation studies. Solutions of lower concentrations of Nile red were also studied as the amount of Nile red encapsulated in polymeric amphiphiles was lower than that used for encapsulation studies. From these experiments, we have observed that at the concentration of Nile red used for encapsulation studies and even below this concentration. We have not observed any significant change in the intensity on photoirradiating the samples at 365 and 254 nm, the wavelength used for studying the photoisomerization behavior of azobenzene grafted polymers. The exemplary plots for variation in fluorescence intensity of Nile red on the photoisomerization of azobenzene moiety as a result of photoirradiation is because of a net release of Nile red from the core of polymeric amphiphiles

5. Figures





Figure S1. Photoisomerization of polymer 4a in aqueous solution below critical aggregation concentration, (A) Irradiation at 365 nm (*trans-cis*); (B) Irradiation at 254 nm (*cis-trans*).



Figure S2. Photoisomerization of polymer **4b** in aqueous solution below critical aggregation concentration, **(A)** Irradiation at 365 nm (*trans-cis*); **(B)** Irradiation at 254 nm (*cis-trans*).



Figure S3. Changes in the fluorescence intensity of encapsulated Nile red, on 1st cycle of *trans-cis-trans* reverse photoisomerization for polymer **4a**, **(A)** Irradiation at 365 nm causes *trans-cis* isomerization with a decrease in its fluorescence intensity; **(B)** Irradiation at 254 nm causes *cis-trans* isomerization with an increase in its fluorescence intensity leading to partial regain, indicated net photo-induced release.





Figure S4. Changes in the fluorescence intensity of encapsulated Nile red, on 2nd continuous cycle of *trans-cis-trans* reverse photoisomerization for polymer **4a**, **(A)** Irradiation at 365 nm causes *trans-cis* isomerization with a decrease in its fluorescence intensity; **(B)** Irradiation at 254 nm causes *cis-trans* isomerization with an increase in its fluorescence intensity leading to complete regain indicating no net release.



Figure S5. Changes in the fluorescence intensity of encapsulated Nile red, on 1st cycle of *trans-cis-trans* reverse photoisomerization after thermal restoration for 16 h in darkness, for polymer **4a**, **(A)** Irradiation at 365 nm causes *trans-cis* isomerization with a decrease in its fluorescence intensity; **(B)** Irradiation at 254 nm causes *cis-trans* isomerization with an increase in its fluorescence intensity leading to partial regain, indicated net photo-induced release.



Figure S6. Changes in the fluorescence intensity of encapsulated Nile red, on 2nd continuous cycle of *trans-cis-trans* reverse photoisomerization after thermal restoration for 16 h in darkness, for polymer **4a**, **(A)** Irradiation at 365 nm causes *trans-cis* isomerization with a decrease in its fluorescence intensity; **(B)** Irradiation at 254 nm causes *cis-trans* isomerization with an increase in its fluorescence intensity leading to complete regain indicating no net release.



Figure S7. Changes in the fluorescence intensity of encapsulated Nile red, on 1st cycle of *trans-cis-trans* reverse photoisomerization after thermal restoration for 2 h in darkness, for polymer **4a**, **(A)** Irradiation at 365 nm causes *trans-cis* isomerization with a decrease in its fluorescence intensity; **(B)** Irradiation at 254 nm causes *cis-trans* isomerization with an increase in its fluorescence intensity leading to partial regain, indicated net photo-induced release.



Figure S8. Control experiment for studying the photobleaching of Nile red in 1 : 1 mixture of water : methanol on photoirradiation at (A) 365 nm; (B) 254 nm.



Figure S9. Gel permeation chromatogram of polymer 1; \overline{M}_{w} = 13,579 g/mol, \overline{M}_{n} = 10,583 g/mol, \overline{M}_{z} = 16,927g/mol, D = 1.3, Detector: RI, Eluent: THF, Flow rate: 1 mL/min, Standard: Pullulan.



Figure S10. Fluorescence spectra of curcumin encapsulated polymeric solution (A) in water; (B) in methanol.



Figure S11. DLS plots of polymers in aqueous solution above CAC.



Figure S12. DLS plots of polymers in aqueous solution below CAC.



Figure S13. ¹H and ¹³C NMR spectra of compound 2.



Figure S14. ¹H and ¹³C NMR spectra of polymer 4a.



Figure S15. ¹H and ¹³C NMR spectra of polymer 4b.



Figure S16. ²D HETCOR NMR spectra of polymer 4b.

6. References

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