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The photodimerization characteristics of anthracene pendants within amphiphilic polymer micelles in aqueous solution†

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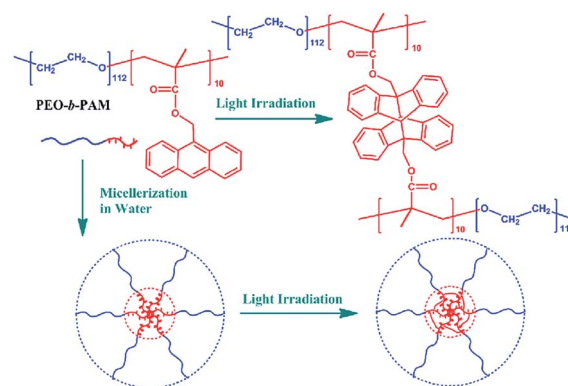
An amphiphilic polymer with anthracene pendants of **PEO-*b*-PAM** has been applied to comprehensively investigate the photodimerization characteristics of anthracene in aqueous solution upon various selected narrow band of light irradiations in the UV-vis-NIR region.

Anthracene and its derivatives are interesting compounds because of their versatile photochemical applications.[1] Owing to their diverse photophysical and photochemical properties, anthracenes have been used in many systems such as functional polymers, triplet sensitizers and molecular fluorosensors.[1–5] Another well-known facet of anthracenes is their typical photodimerization reaction, which occurs favourably in UV light irradiations (250–400 nm) and has been widely investigated for the application of photoresponsive materials.[6–15] Furthermore, the dimerization has been recently accomplished with visible light (400–700 nm) or multiphoton light in order to weaken some side effects during irradiation.[16–18] It is widely accepted that the photodimerization efficiency always depends on the photochemical absorbency of anthracenes to a certain light irradiation. Thus, the photodimerization efficiency can be anticipated according to the characteristic UV-vis absorbance of anthracenes, and it can be easily controlled by adjusting the photon flux.[6] However, to date, reports that comprehensively describe the photodimerization characteristics of anthracene upon various light irradiations in the UV-vis-NIR region are rare. Such reports, apparently, will help further understanding on the photodimerization mechanism of anthracenes, as well as other photo-crosslinkable chromophores, and may improve their opportunities in potential applications, such as nano-fabrication, nanoreactors and biological functional models,

especially when their photophysical and photochemical properties are demanded to be controlled sophisticatedly.[19–22]

Herein, based on our ongoing study of photoresponsive amphiphilic polymers, our attention was drawn to the photo-dimerization characteristics of anthracene pendants within the polymer micelles of poly(ethylene oxide)-*b*-poly(anthracene methyl methacrylate) (**PEO-*b*-PAM**), which was concisely synthesized by ATRP (Scheme 1). Scheme 1 illustrates the amphiphilic structure of such block copolymer and its photo-dimerization upon light irradiation in aqueous solution. Note that the photodimerization efficiency of anthracene always depends on its concentration and molecule mobility,[23] and the typical amphiphilic block copolymer of **PEO-*b*-PAM** can spontaneously form aggregated micelles. Thus, anthracene pendants would be entangled into the confined micelle core with high local concentration and restricted mobility, which may facilitate the dimerization at the start of irradiation and result in the maximum equilibrium extent in the late stages of irradiation.

We first focused on the micellization of **PEO-*b*-PAM** in aqueous solution. The obtained polymer micelle aqueous solution was first diluted gradually to evaluate its stability, and

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Scheme 1 Schematic illustration of the amphiphilic polymer with anthracene pendants (PEO-*b*-PAM) and its photodimerization upon light irradiation in aqueous solution.
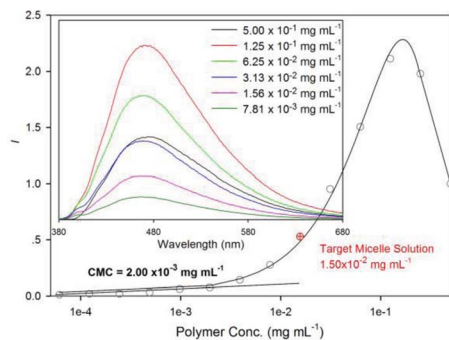
Fig. 1 Normalized fluorescence emission intensity of anthracene at 470 nm (λ_{exc} = 353 nm). Inset: fluorescence emission spectra of **PEO-b-PAM** in aqueous solution.

Fig. 2 UV-vis spectra changes (0.015 mg mL^{-1} × 1 mL) upon the 371 ± 5 nm (1.20 mW cm^{-2}) light irradiation. Inset: enlarged view from 260 to 420 nm and the definition of photodimerization degree (PD) by comparing the absorption at 371 nm before and after irradiation.

the dilution process was traced by fluorescent spectroscopy and DLS instrument. As shown in the inset of Fig. 1, the anthracene emission spectra in aqueous solution are easily detected with broad fluorescence emission covering 380–680 nm intervals. The maximum emission peak around 470 nm is not always weaken during the dilution. In fact, it is strengthened at the beginning and then becomes weak upon further dilution. This phenomenon can often be found in the assemblies of anthracene-containing polymers.[13] The self-quenching effect of anthracene decreases with the decreasing concentration of anthracene pendants first, and then the fluorescence decreases with the further decrease in the concentration of anthracene.[24,25] Furthermore, as shown in Fig. 1, the plot of normalized maximum emission below polymer concentration of 2.00 × 10^{-3} mg mL^{-1} shows a relatively gentle and linear decrease along with the dilution, while the DLS examinations (S2 in ESI†) show narrow size distributions around 50 nm above 2.00 × 10^{-3} mg mL^{-1} and large fluctuations below this concentration. Thus, we assigned this value as the critical micelle concentration (CMC) of **PEO-b-PAM** in aqueous solution. The nanostructures of polymer micelles before and after photodimerization were also visualized by AFM images with uniformly spherical micelles (S3 in ESI†). Taking both the micelle stability and the demands of the real-time UV-vis spectroscopy into consideration, the polymer concentration used in photodimerization was kept at 0.015 mg mL^{-1}.

In order to comprehensively investigate the photodimerization characteristics of anthracene pendants in polymer micelles, an adjustable double grating monochromator of Omni-λ1805i equipped with a broadband laser-driven light source of EQ-1500 LDLS™ and a set of six optical filters was assembled to afford the adjustable narrow band wavelength of light between 250 and 950 nm. Under the used conditions, 1 mL of polymer micelle solution (0.015 mg mL^{-1}) was sealed in the fluorescence cuvette and photodimerization of anthracene pendants was performed directly on an optical bench at 25 °C with gentle stirring. As designed, the anthracene micelle solution was first photodimerized with 371 ± 5 nm (1.20 mW cm^{-2}) wavelength light, which corresponded to one of the characteristic absorbance bands of anthracene pendants in aqueous solution. As shown in Fig. 2, the UV-vis spectrum before
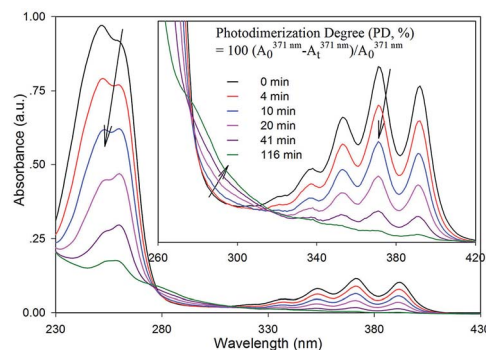
irradiation showed a broad absorption band around 260 nm, and a series of vibrationally spaced absorption structures at 320, 338, 353, 371 and 392 nm (finger like absorption bands), which are typical of anthracenes.[9] During irradiation, accompanied with the weak ascending between 280 and 310 nm, all the absorbance bands decreased significantly, strongly indicating the ongoing photodimerization of anthracene in the polymer micelle core.[9] Moreover, because of its linear degradation and higher signal-to-noise ratio, the absorption band intensity at 371 nm was used as the baseline to measure the time-dependent photodimerization changes, resulting in the definition of photodimerization degree (PD) by comparing the peak absorption at 371 nm.

As shown in Fig. 3a, upon 371 ± 5 nm light irradiation, the time-dependant PD values for anthracene pendants synchronously decreased with the lowering of irradiation intensities. For 1.20 mW cm^{-2} irradiation, it showed saturating behaviour, affording a linear quick increase in the initial stage (up to 40%), a relatively slow increase thereafter (from 40% to 70%), and finally levelled off above 90%. The time-dependences of these
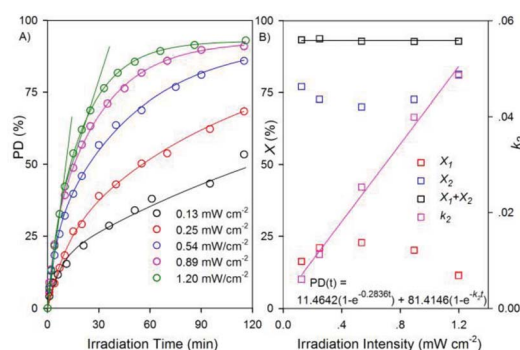

Fig. 3 (a) The time-dependent PD of anthracenes upon 371 ± 5 nm light irradiation with different intensities. The solid curves are four parameter biexponential fits to eqn (1). (b) The intensity dependence of X_1, X_2, $X_1 + X_2$ values according to the four parameters biexponential fitting, and the linear dependence of k_2 according to the one parameter biexponential fitting.

observed PD changes upon various irradiation intensities are fit reasonably with a biexponential equation:

$$PD(t) = X_1(1 - e^{-k_1 t}) + X_2(1 - e^{-k_2 t}) \quad (1)$$

where $PD(t)$ corresponds to the time-dependent photo-dimerization degree, k_1 and k_2 are rate constants, X_1 and X_2 are the relative weighting fractions. Note that the sum of X_1 and X_2 determines the maximum photodimerization extent (PD_{max}) that the anthracene pendants could reach after sufficient irradiation time. Fig. 3b shows the obtained fractions of X_1 and X_2 at different irradiation intensities, whose sum fluctuated weakly around 93% and afforded a good zero-order linear fit, indicating that the PD_{max} of anthracenes upon 371 ± 5 nm light irradiation is always intensity-independent. Thus, in order to better verify the intensity-dependence of the photodimerization kinetics, $X_1 = 11.4642$, $k_1 = 0.2836$ min^{-1} and $X_2 = 81.4146$ obtained from the biexponential fitting of 1.20 mW cm^{-2} irradiation were used as constants to obtain a one parameter biexponential fit of eqn (1) for another four intensity irradiations. As shown in Fig. 3b, with these constraints, the obtained k_2 ranged from 0.0061 min^{-1} at 0.13 mW cm^{-2} to 0.0486 min^{-1} at 1.20 mW cm^{-2} and increased linearly as a function of 371 ± 5 nm light intensity, indicating the existence of two different populations of anthracene pendants: one that is insensitive to irradiation intensity and reacts with rate $k_1 = 0.2836$ min^{-1}, and another that is sensitive to intensity, corresponding to k_2.[11]

In order to better understand the photodimerization kinetics dependency of irradiation conditions, and according to the characteristic absorbance bands of anthracene pendants in aqueous solution, another five narrow band UV light of 261, 300, 338, 353, 392 $\pm$ 5 nm and four vis-NIR light of 416, 550, 700 and 900 $\pm$ 5 nm were chosen as the irradiation light. As shown in Fig. 4a, when irradiated by these various wavelengths from the double grating monochromator with the same slits (their irradiation intensities corresponding to the highest values in Fig. 4b), the obtained time dependences of PD are fit very well to

the four parameter biexponential of eqn (1), and all the UV light irradiations gave faster dimerization rates and higher dimerization extents than the vis-NIR light at the same time. The solid linear lines in Fig. 4b are zero-order linear fits of $X_1 + X_2$ values obtained by changing the irradiation intensities of the above selected light. All the $X_1 + X_2$ values obtained by the UV light irradiations were above 90%, despite there being large gaps in light absorbency of the selected UV light according to the characteristic absorbance bands of anthracenes (see the curve line in Fig. 4b). Even for the latter four vis-NIR light irradiations, in which region anthracenes have nearly no absorptions, they still afforded considerable efficiencies with PD_{max} values of 55%, 35%, 25% and 32% for 416, 550, 700 and 900 $\pm$ 5 nm light irradiations, respectively, which can be ascribed to the multi-photon effect. These results strongly show that the photodimerization extent (PD_{max}) of anthracenes always favours UV light rather than vis-NIR light and is independent of the intensities of a certain light irradiation.

To summarize, we have synthesized an amphiphilic block copolymer of **PEO-*b*-PAM** with anthracene pendants, which can afford the high local concentration and restricted mobility of anthracene pendants in the confined micelle core and thus facilitate the dimerization of anthracenes upon light irradiations. Most efforts have been dedicated to the photodimerization of anthracenes; however, to the best of our knowledge, our study is the first attempt to comprehensively describe it using various narrow band wavelength light in the UV-vis-NIR region. The result shows that the photodimerization of anthracene pendants occurs more favourably in UV light than vis-NIR light, and for a certain light irradiation, the dimerization extent that anthracenes can reach is always independent of light intensities. This indicates that anthracenes cannot afford the similar photodimerization efficiencies of UV light by simply strengthening the power of vis-NIR light.

Acknowledgements

Fig. 4 (a) The time-dependence of PD upon selected narrow band light irradiations derived from the monochromator with the same slits. The solid curves are four parameter biexponential fits to eqn (1). (b) The UV-vis-NIR absorbance spectrum of polymer micelles (0.015 mg mL^{-1}) and the zero-order intensity dependence of $X_1 + X_2$ values for the selected light irradiations.

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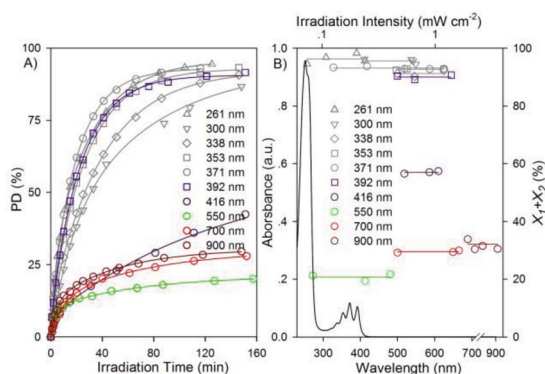4 B. Fabre, D.-M. Bassani, C.-K. Liang, S. Lhenry and P. Hapiot, *J. Phys. Chem. C*, 2013, **117**, 12725.

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