

**Accelerated Recombination of Lophyl Radicals and Control of the Surface Tension  
with Amphiphilic Lophine Dimers**

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**Supplementary Information**

## 1. Materials

Solvents and reagents were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) or Wako Pure Chemical Co. (Osaka, Japan) and used without further purification. All reaction mixtures and fractions eluted by column chromatography were monitored using thin layer chromatography (TLC) plates (Merck, Kieselgel 60 F254). The TLC plates were observed under UV light at 254 and 365 nm. Flash column chromatography over silica gel (Wakosil C-200, 64–201  $\mu\text{m}$ ) was used for the separations.

## 2. Measurements

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured at 298 K from  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$  or  $\text{D}_2\text{O}$  solution of the samples using a JEOL model JNM-AL300 (300 MHz) or JNM-ECP500 (500 MHz) spectrometer with  $\text{Si}(\text{CH}_3)_4$  as an internal standard. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are reported in parts per million (ppm) and Hertz (Hz), respectively. ESI-MS spectra were measured using a JASCO model JMS-T100CS instrument. High-resolution mass (HRMS) spectra (ESI-negative) were recorded using a JEOL model JMS-MS700 system. Elemental analysis was performed with a PE 2400II (PerkinElmer) system. UV/vis absorption spectra were measured using an Agilent 222 UV/vis spectrophotometer with a quartz cuvette (1.0 cm path length). A dynamic light scattering (DLS) measurement was carried out with Litesizer 500 instrument (Anton-Paar).

## 3. Synthesis and the structural characterization

Synthetic routes for **3TEG-LPD** and **TEG-LPD** are shown in Scheme S1. **1**<sup>1</sup>, **2**<sup>2</sup>, **4**<sup>3</sup> as intermediates were prepared according to the literature. A synthesis of **TEG-LPD** was performed according to the reported procedure<sup>5</sup>.



### Synthesis of 3TEG-LPD

In a 300 mL round-bottomed flask, a mixture of **3** (0.857 g, 0.950 mmol), potassium ferricyanide (15.6 g, 47.0 mmol) and dichloromethane (150 mL) was stirred at room temperature for 1.5 hour. 105 mL of aqueous potassium hydroxide solution (5.31 g, 94.9 mmol) was added slowly to the mixture and stirred for 1.5 h. The reaction mixture was washed with water and the organic layer was dried by sodium sulfate. After evaporating the solvent, the crude product was subjected to silica gel column chromatography (dichloromethane/methanol = 20/1, v/v). After removal of the solvent, the product was dried in a vacuum oven at 70 °C. The yield was 30% (0.332 g). <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 6.95–7.60 (m, 32H), 4.14–4.22 (m, 12H), 3.38–3.80 (m, 60H), 3.20–3.24 (m, 18H) ppm. HRMS (ESI, +ve) calcd. for C<sub>98</sub>H<sub>122</sub>N<sub>4</sub> NaO<sub>28</sub>: 1825.8143, found: 1825.8140. IR (KBr): 1280 cm<sup>-1</sup> (C-N stretching). Calculated for C<sub>98</sub>H<sub>122</sub>N<sub>4</sub>O<sub>28</sub>: %C, 65.25; %H, 6.82; %N, 3.11. Found: %C, 64.53; %H, 6.71; %N, 2.81.

### Synthesis of TEG-LPD<sup>5</sup>

In a 50 mL round-bottomed flask, a mixture of **4** (0.229 g, 0.500 mmol), potassium ferricyanide (0.592 g, 1.8 mmol) and dichloromethane (16 mL) was stirred at room temperature for 1.5 h. 5 mL of 3 M aqueous sodium hydroxide solution was added slowly to the mixture and was stirred for 48 h. The mixture was washed with water and was dried by sodium sulfate. After removal of the solvent, the crude product was subjected to silica gel column chromatography (ethyl acetate). After removal of the solvent, the product was dried in a vacuum oven at 70 °C. The yield was 13% (0.123 g). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.58–7.26 (m, 10H), 7.26–6.18 (m, 18H), 4.31–3.48 (m, 24H), 3.42–3.31 (m, 6H) ppm. IR (KBr): 1310 cm<sup>-1</sup> (C-N stretching). HRMS (ESI, +ve) calcd. for C<sub>56</sub>H<sub>58</sub>N<sub>4</sub>NaO<sub>8</sub>: 937.4152, found: 937.4153.

## 4. Characterization

### 4.1 Estimation of the number of TEG-LPD in a micelle

We estimated the number of TEG-LPD molecules in a micelle on the aqueous 0.5 mM TEG-LPD/50 mM CTAB solution as follows.

The concentration of CTAB, forms the micelles, is 49 mM, considering the critical micelle concentration (cmc) of CTAB (= 50 mM – 1 mM). Since the aggregation number of the CTAB micelles is 151 according to the report<sup>4</sup>, the concentration of the

CTAB micelle is 0.32 mM. Thus, the number of **TEG-LPD** molecules in a micelle is 2 (= 0.5 mM/0.32 mM).

#### **4.2 Surface and interfacial tension measurements**

The static surface tension was measured with a platinum plat at room temperature (ca. 25 °C) by a Krüss K100 auto surface tensiometer. The surface tension was assumed to be equilibrated when the value became constant.

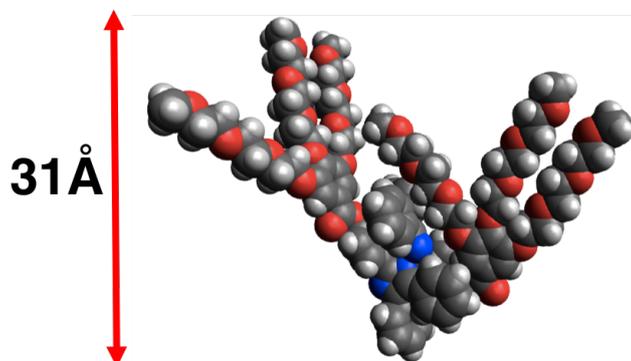
#### **4.3 Photoisomerization of the lophine dimers**

UV light irradiation was carried out using a 200 W Hg-Xe Lamp (SUPERCUR UVF-203S, SAN-EI ELECTRONIC). Irradiation wavelength (260–390 nm) was accomplished using a color filter (U340, HOYA). Each solution was irradiated with light (20 mW/cm<sup>2</sup>) in a 1.0 cm path quartz cuvette.

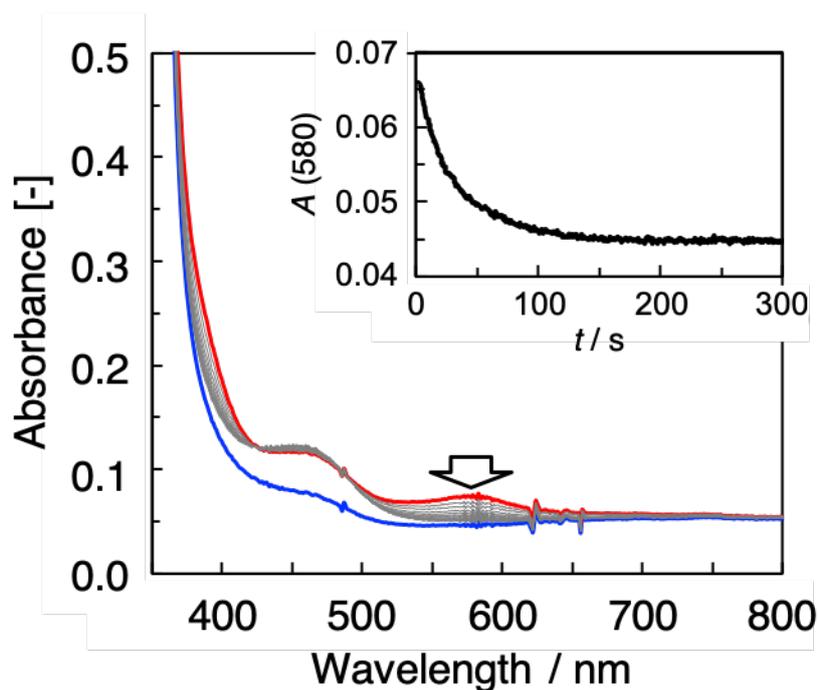
#### **4.4 Reversible control of surface tension with photoirradiation**

5 mM of aqueous lophine dimer **2** solution (ca. 10 mL) was equipped in a petri dish. UV light (260–390 nm, 20 mW/cm<sup>2</sup>) was irradiated to top of the aqueous solution, and the distance between the light and the solution was ca. 1 cm. Continuous measurement of the surface tension at every 5 s was performed with platinum plate method.

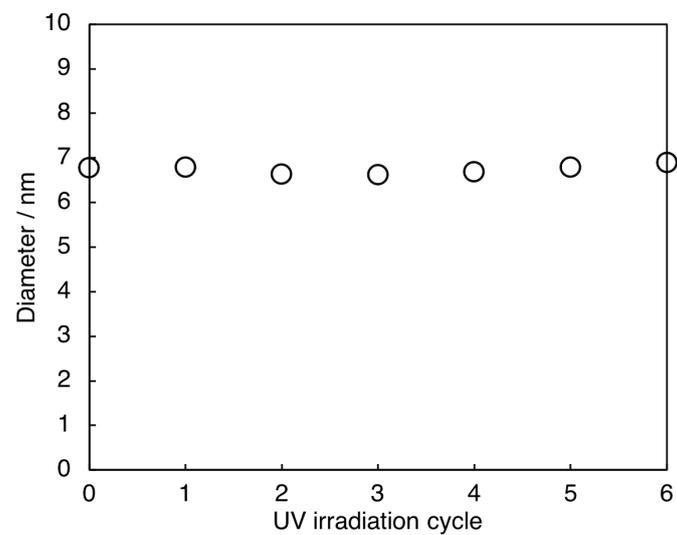
## 5. Supplementary figures



**Fig. S1** Stabilized molecular structure of 3TEG-LPD. Red arrow shows a maximum scale of the molecule.



**Fig. S2** Variations in the UV-Vis absorption spectra of the 0.5 mM 3TEG-LPD aqueous solution. The inset shows the transient changes in absorbance due to the lophyl radical production by UV irradiation.



**Fig. S3** Diameters of the micelles, formed by 0.5 mM **3TEG-LPD** aqueous solution after several times of UV light irradiations.





## References

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