

# Electronic Supplementary Information

Reduced graphene oxide/liquid crystalline oligomer composites based on reversible covalent chemistry

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## Synthesis of LCO

The liquid crystalline monomer cholesteryl 4-(allyloxy)benzoate ( $M_1$ ) was prepared according to previously reported synthetic method.<sup>1</sup> It showed the following phase transition: Crystalline (112 °C), chiral nematic (240 °C), and isotropic fluid, the detailed chemical parameters of  $M_1$  were as follows, IR (KBr,  $\text{cm}^{-1}$ ): 3057(=CH), 2971-2860(-CH<sub>3</sub>, -CH<sub>2</sub>-), 1703(C=O), 1645 (C=C), 1604, 1493(Ar-), 1271, 1173 (C-O-C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.99-7.98 (d, 2H, Ar-H), 6.92 (d, 2H, Ar-H), 6.05 (m, 1H, CH<sub>2</sub>=CH-), 5.44-5.41 (t, 2H, CH<sub>2</sub>=CH-), 5.32-5.31 (m, 1H, =CH- in cholesteryl), 4.59-4.58 (d, 2H, -OCH<sub>2</sub>-), 2.03-0.67 (m, 43H, cholesteryl-H).

4'-hydroxy-[1,1'-biphenyl]-4-yl undec-10-enoate ( $M_3$ ) was synthesized according to reference,<sup>2,3</sup> the detailed chemical parameters of  $M_3$  were as follows, (mp=126 °C). IR (KBr,  $\text{cm}^{-1}$ ): 3385 (-OH); 3090 (=C-H); 2983, 2872 (-CH<sub>2</sub>-); 1754 (C=O); 1647 (C=C); 1606, 1508  $\text{cm}^{-1}$  (Ar-). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.24-1.28 (10H, s, CH<sub>2</sub>=CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>-); 1.73-1.79 (2H, m, -CH<sub>2</sub>CH<sub>2</sub>COO-); 1.92-2.03 (2H, m, CH<sub>2</sub>=CHCH<sub>2</sub>-); 2.37-2.41 (2H, m, -CH<sub>2</sub>CH<sub>2</sub>COO-); 4.95-5.12 (2H, m, CH<sub>2</sub>=CH-); 5.16 (s, 1H, -OH); 5.75 (1H, m, CH<sub>2</sub>=CH-); 6.74-8.06 (8H, m, Ar-H).

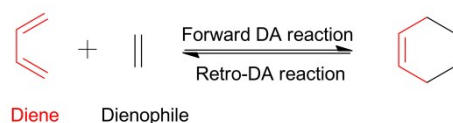
4-maleimido benzoic acid (MBA) and 4-maleimido benzoic acid chloride (MBAC) were synthesized according to reference,<sup>4,5</sup> the detailed chemical parameters of MBA were as follows, IR (KBr,  $\text{cm}^{-1}$ ): 3102 (-COOH), 1711 (C=O of maleimide). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): d 7.24 (s, 2H, -CH=CH-), 7.51 (d, J = 8.4 Hz, 2H, Ar-H), 8.06 (d, J = 9.3 Hz, 2H, Ar-H), 13.13 (s, 1H, -COOH).

LCO was synthesized as following:  $M_1$ ,  $M_2$  and  $M_3$  were added to

polymethylhydrogensiloxane (PMHS, Aldrich). After the addition of platinum catalyst (chloroplatinic acid), the polymerization was carried out at 80 °C under nitrogen atmosphere with magnetic stirring until the infrared spectra showed no Si-H absorption peak at 2166cm<sup>-1</sup>.<sup>6,7</sup> The polymer solution was dried over anhydrous magnesium sulfate and filtered, then, 4-maleimido benzoic acid chloride was dissolved in tetrahydrofuran (THF) and added dropwise to the solution of polymers at 25 °C. The mixture was stirred at room temperature under dry air for 4 h, then heated to 60 °C and kept for 20 h in an oil bath to ensure that the reaction finished. The solution was poured into a beaker filled with 200mL of methanol, the crude product was obtained by filtration and recrystallized from ethanol.<sup>8</sup> The liquid crystalline oligomer (LCO) was obtained.

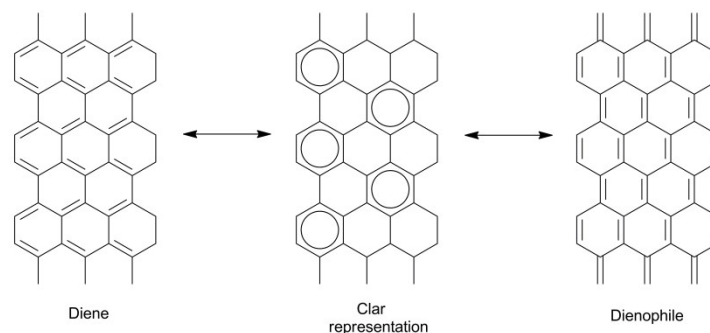
## Canonical Resonance Structures of Graphene and Diels-Alder Reaction

The forward reaction leads to the formation of a six-membered ring via simultaneous creation of two new  $\sigma$ -bonds and one new  $\pi$ -bond and the loss of three  $\pi$ -bonds; alternatively, the process may be viewed as a change in hybridization in which four sp<sup>2</sup> carbon atoms become sp<sup>3</sup> hybridized.<sup>9</sup>



**Scheme 1.** Schematic representation of the Diels-Alder reaction between a Diene (1,3-Butadiene) and Dienophile (Ethylene), illustrating the Diels-Alder cycloaddition and cycloreversion reactions in their simplest form

In contrast to fullerene and carbon nanotubes, which always act as the dienophile in [4 + 2] cycloaddition due to their curvatures, 2-dimensional graphene and its derivatives are able to behave as both diene and dienophile.<sup>10,11</sup>



**Scheme 2.** Resonance Forms of Graphene: Graphene as Diene and Dienophile

### The reasons for using $M_1$ , $M_2$

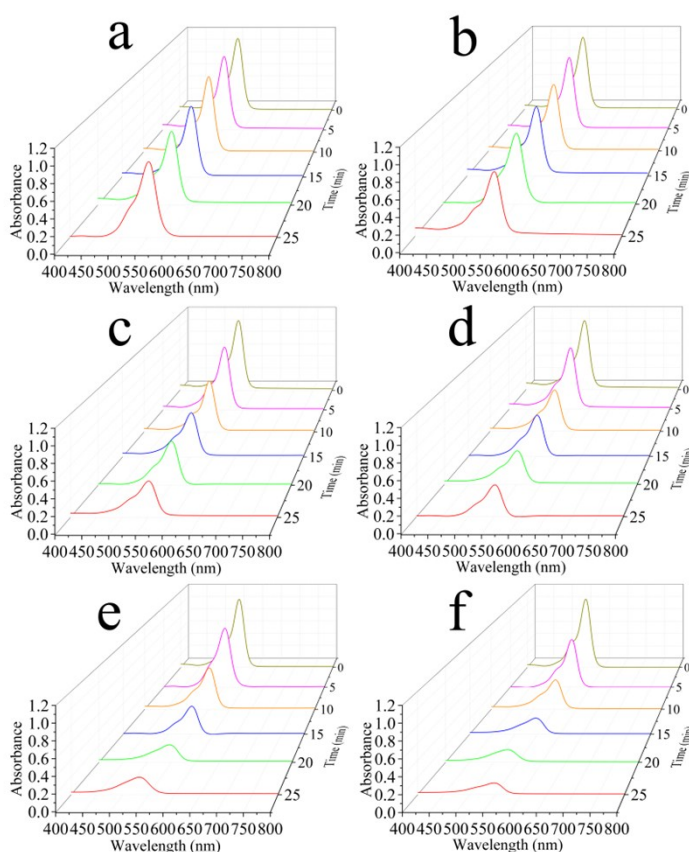
$M_1$  has wide liquid crystalline range (from 112 °C to 240 °C) and the chemical structure possesses high stability for lack of reactive functional groups. The extra spacer in  $M_1$  is used to broaden the liquid crystalline range of  $M_1$ . The reasons for using  $M_2$  are as following: there is long hydrocarbon chain in the molecular structure of  $M_2$  compared with  $M_1$ ,  $M_2$  can bring some flexibility to LCO. Meanwhile,  $M_2$  has carboxyl group, which makes  $R_2$  have good compatibility and solubility.

### The reasons for using LCO modified RGO

The photocatalytic activity of  $TiO_2$  is limited by the aggregation of nanoparticles and the fast electron–hole pair recombination.<sup>12</sup> Graphene sheets, with high specific surface area and unique electronic properties, can be used as a good support for  $TiO_2$  to enhance the photocatalytic activity. Thus, Graphene/ $TiO_2$  nanocrystals hybrid was prepared, in which  $TiO_2$  were dispersed on the surface of graphene sheets. The graphene acted as an electron-acceptor material to effectively hinder the electron–hole pair recombination of  $TiO_2$ .<sup>13</sup> However, pristine graphene usually has poor solubility in both polar and apolar solvents.<sup>14</sup> The surface modification of graphene is often necessary to avoid the aggregation of graphene sheets and to enhance their interactions with the photocatalysts. Thus, the LCO modified RGO was used in our research.

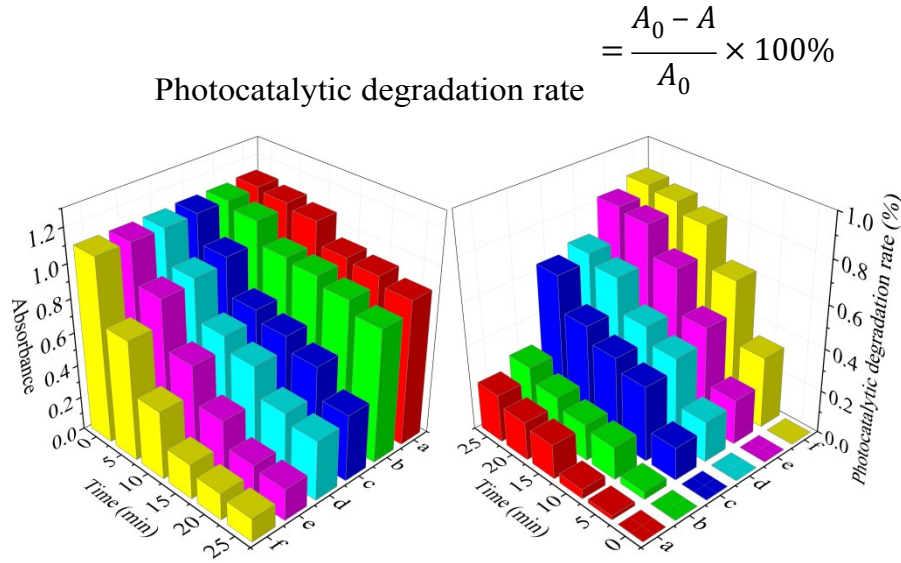
## Photocatalytic degradation experiments

The substrate was 60 mL of Rhodamine B ( RB ) aqueous solution (10 mg/L), the used catalysts (five kinds) in this experiment were 0.21 mg RGO, 5.0 mg TiO<sub>2</sub>, 5.0 mg TiO<sub>2</sub> + 0.21 mg RGO, 5.0 mg TiO<sub>2</sub> + 7.0 mg composite (the mass ratio of LCO and RGO is 50:1), 5.0 mg TiO<sub>2</sub> + 7.0 mg composite (the mass ratio of LCO and RGO is 100:3). First of all, the adsorption-desorption equilibrium of mixtures (the catalyst and RB) was established by stirring for 35 min in the dark, then the dispersions were irradiated with ultraviolet light (300 W, 365 nm) under continuous stirring. At given time intervals, aliquots of the samples were collected and removed the catalyst by centrifugation, at last analyze the photocatalytic efficiency of catalyst by UV-vis spectroscopy at 553 nm.



**Fig. S1** UV-Vis absorption spectra of RB aqueous solutions (10 mg/L) at different time intervals, (a) no catalyst, (b) 0.21 mg RGO, (c) 5.0 mg TiO<sub>2</sub>, (d) 5.0 mg TiO<sub>2</sub> + 0.21 mg RGO, (e) 5.0 mg TiO<sub>2</sub> + 7.0 mg composite (the mass ratio of LCO and RGO is 50:1), (f) 5.0 mg TiO<sub>2</sub> + 7.0 mg composite (the mass ratio of LCO and RGO is 100:3).

The UV-Vis absorption spectra of RB aqueous solutions are listed in Fig. S1, the relevant absorbances at 553 nm are presented in Fig. S2. The efficiency of the photocatalytic degradation can be quantified by the photocatalytic degradation rate, where  $A_0$  is the initial concentration of RB, and  $A$  is the residual concentration of RB after photodegradation. The photocatalytic degradation rate of samples are presented in Fig. S2.



**Fig. S2** Absorbances at 553 nm of UV-Vis absorption spectra of RB aqueous solutions (10 mg/L) at different time intervals (the left bar graph), and the photocatalytic degradation rate of samples (the right bar graph). (a) no catalysts, (b) 0.21 mg RGO, (c) 5.0 mg  $\text{TiO}_2$ , (d) 5.0 mg  $\text{TiO}_2$  + 0.21 mg RGO, (e) 5.0 mg  $\text{TiO}_2$  + 7.0 mg composite (the mass ratio of LCO and RGO is 50:1), (f) 5.0 mg  $\text{TiO}_2$  + 7.0 mg composite (the mass ratio of LCO and RGO is 100:3)

Fig. S2 shows that there is less photodegradation in single RB aqueous solutions. The photodegradation efficiency of RB solution with RGO is a little higher than that of single RB solution, The photodegradation efficiency of RB solution with  $\text{TiO}_2$  is gradually raised, the photocatalytic efficiency of 5.0 mg  $\text{TiO}_2$  + 0.21 mg RGO is higher than that of 5.0 mg  $\text{TiO}_2$  and the photocatalytic efficiency of 5.0 mg  $\text{TiO}_2$  + 7.0 mg composite (the mass ratio of LCO and RGO is 50:1) is higher than that of 5.0 mg  $\text{TiO}_2$  + 0.21 mg RGO. Furthermore, the photocatalytic efficiency of  $\text{TiO}_2$  + RGO-LCO composites tends to increase with increasing the content of RGO.

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