

**Supporting Information for:**

**Negative Photochromism Based on Molecular Diffusion  
Between Hydrophilic and Hydrophobic Particles in the  
Solid-State**

**Tetsuo Yamaguchi<sup>†</sup>, Ayan Maity,<sup>‡</sup> Vivek Polshettiwar<sup>‡</sup> and Makoto Ogawa<sup>\*†</sup>**

*<sup>†</sup>School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555 Moo 1, Payupnai, Wangchan, Rayong 21210, Thailand*

*<sup>‡</sup>Division of Chemical-Sciences, Tata Institute of Fundamental Research (TIFR), Homi Bhabha Road*

E-mail: *makoto.ogawa@vistec.ac.th*

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## 1. Experimental methods

### Materials

1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (SP) was purchased from Tokyo Chemical Industry Co., Ltd. and was used without further purification.

DFNS was synthesized according to the reported procedure<sup>1</sup> as follows, hexadecyltrimethylammonium bromide (CTAB) (3 g, 8.23 mmol) and urea (3.6 g, 60 mmol) were first dissolved in deionized water (300 mL) by vigorously stirring at 1400 rpm for 10 minutes in a 2 L conical flask. To the above mixture, a solution of tetraethoxysilane (TEOS) (72 mmol) in cyclohexane (300 mL) was added dropwise under stirring and then stirred for 10 min. 1-Pentanol (18 mL) was, then, added to above mixture and the mixture was further stirred for several minutes. The reaction mixture was then transferred into a 1 L microwave reactor and exposed to microwave radiation (maximum power- 800 W) to 120 °C via a 30-minute ramp in the Ethos-1 microwave reactor and kept for 1 hour. The solid product was isolated by centrifugation and washed with EtOH (3 times) and water (3 times), followed by air drying. The product was calcined at 550 °C for 6 h in air to yield DFNS. DFNS was characterized by scanning electron microscopy (SEM), and N<sub>2</sub> adsorption analysis.

Diocetyl dimethyl ammonium anion intercalated montmorillonite was used as organophilic clay.

### Sample preparation and photochemical reaction

The red powder of DFNS contained MC was prepared by following procedure. DFNS 40 mg was added to toluene and sonicated for 1 min. the toluene solution of SP was added to the suspension of DFNS and the final solution was fixed with 20 mL. The concentration of spiropyran (SP) was fixed with  $7.45 \times 10^{-4}$  M and  $6.2 \times 10^{-6}$  M. After 1 hour stirring with magnetic stirrer, the homogeneous suspension was irradiated UV light for 2 min and filtrated immediately. The resulting red powder was dried in vacuum condition overnight in the dark.

The organoclay with long alkyl chain 50 mg was mixed with DFNS/MC(High) 50 mg in the agate mortar for 10 min in the dark.

### Equipment

UV spot light (365 nm), Ushio SPL-2 with 95 mW/cm<sup>2</sup>, was used for the UV irradiation. The visible light irradiation was performed by 100 W Xe lamp, ABET technologies Sunlite solar simulator. UV-vis absorption spectra were recorded on a UV-vis spectrophotometer (PerkinElmer LAMDA 1050).

## 2. UV-vis absorption spectra

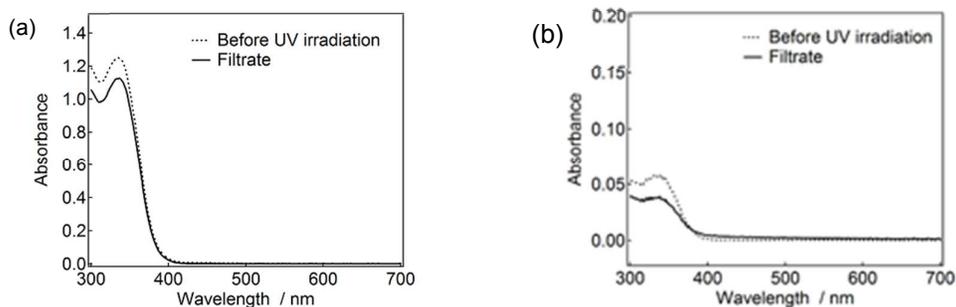


Figure S1. UV-vis absorption spectra of (a)  $7.45 \times 10^{-4}$  M and (b)  $6.2 \times 10^{-6}$  M of SP solution contained DFNS (2 g/L) before UV irradiation and after filtrate.

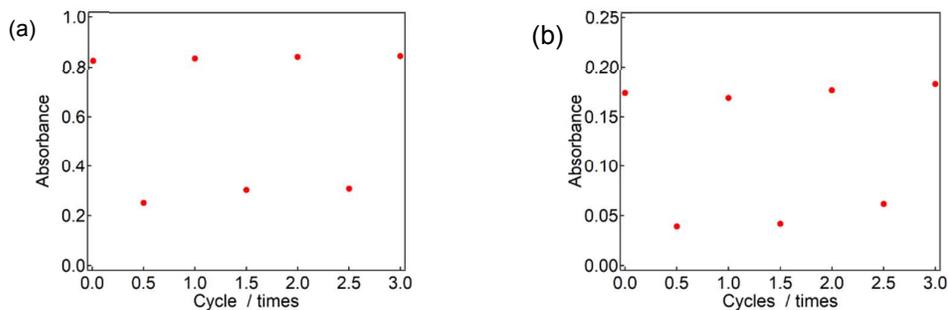


Figure S2. Photo decoloration/ thermal coloration cycles of (a) DFNS/MC(High) and (b) DFNS/MC(Low). The photo decoloration was carried out by visible light irradiation for 2 min and thermal coloration was observed by storing in the dark for 10 h at room temperature.

## 3. TEM images

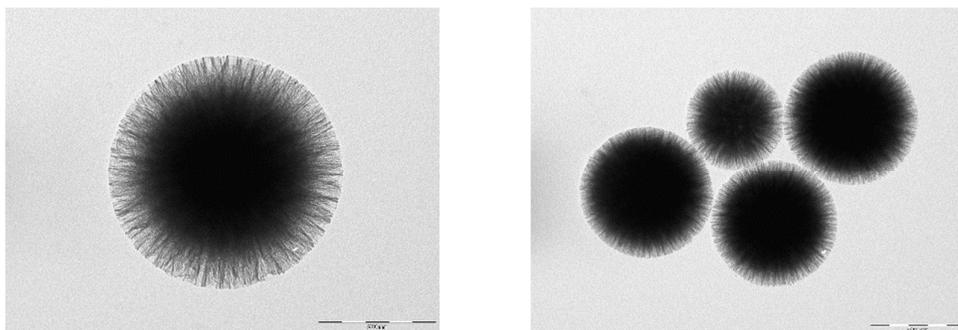


Figure S3. TEM images of DFNS.

#### 4. N<sub>2</sub> adsorption

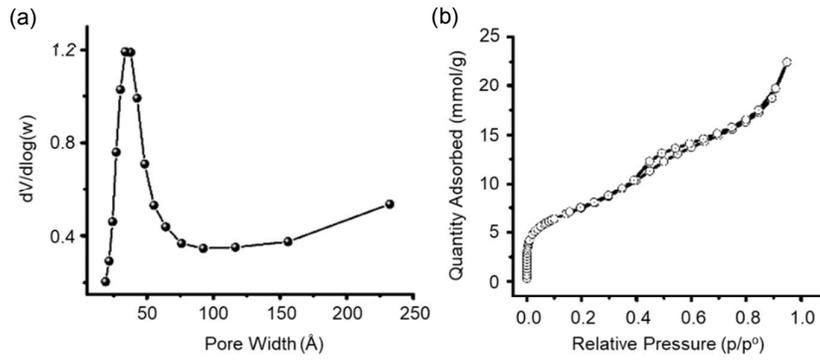


Figure S4. N<sub>2</sub> adsorption study of DFNS: (a) pore size distribution and (b) N<sub>2</sub>

#### 5. Lamp intensity

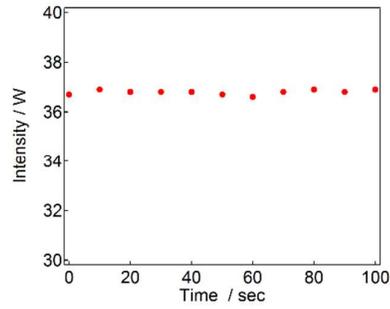


Figure S5. Light flux of the excitation Xe lamp.

## 6. Photographs



Figure S6. Photographs of the photo decoloration/ thermal coloration cycles of DFNS/MC(High) by 2 min visible light irradiation and storing in the dark for 10 hours.

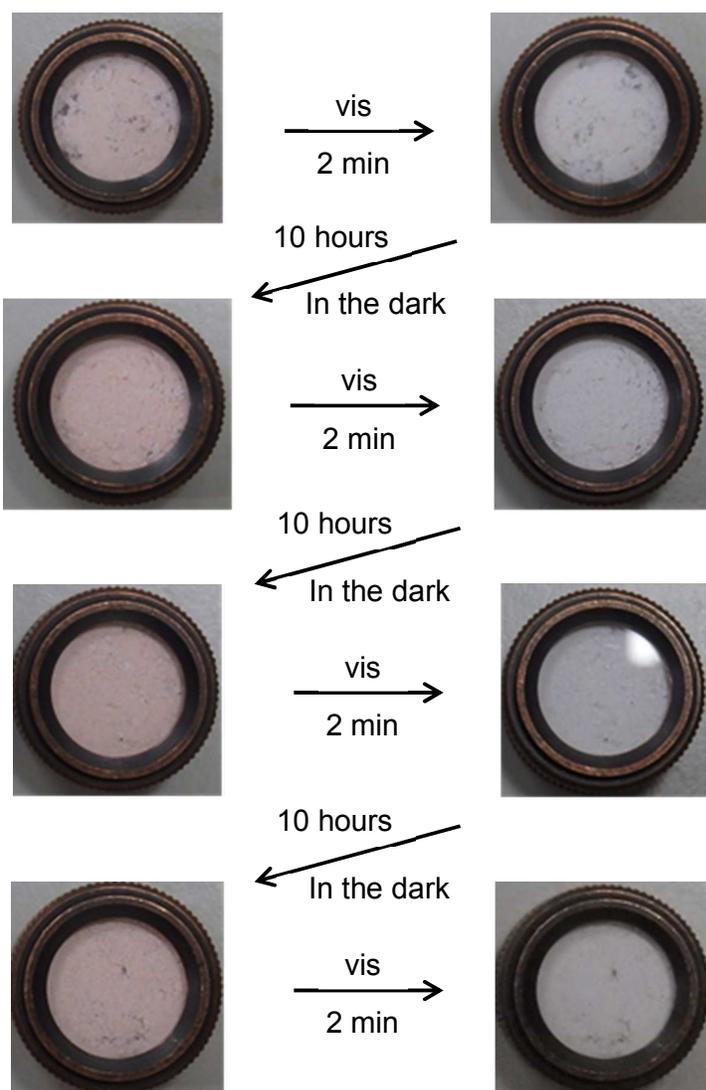


Figure S7. Photographs of the photo decoloration/ thermal coloration cycles of DFNS/MC(Low) by 2 min visible light irradiation and storing in the dark for 10 hours.



Figure S8. Photographs of the photo decoloration/ thermal coloration cycles of organophilic clay-DFNS/MC(Low) by 2 min visible light irradiation and storing in the dark for 10 hours.

## 7. Reference

- 1 Polshettiwar, V.; Cha, D.; Zhang, X. and Basset, J. M. *Angew. Chem. Int. Ed.*, 2010, **49**, 9652–9656.