

**Electronic Supplementary Information for:**

**Photodoping-based broadband photochromism  
of semiconductor nanocrystals under air  
operated by a supramolecular gel**

*Yuki Nakai,<sup>a</sup> Yuki Nagai,<sup>a\*</sup> Yoshinori Okayasu,<sup>a</sup> and Yoichi Kobayashi<sup>a\*</sup>*

*<sup>a</sup> Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1  
Nojihigashi, Kusatsu, Shiga 525-8577, Japan.*

E-mail: ynagai@fc.ritsumeai.ac.jp; ykobayas@fc.ritsumeai.ac.jp

**CONTENTS**

<b>1. General Methods</b>	<b>S2</b>
<b>2. Synthesis</b>	<b>S5</b>
<b>3. Photodoping of the TiO<sub>2</sub> NCs in solution</b>	<b>S8</b>
<b>4. Characterization of the gel</b>	<b>S9</b>
<b>5. Photodoping of the TiO<sub>2</sub> NC gel</b>	<b>S10</b>
<b>6. NIR laser irradiation to the TiO<sub>2</sub> NCs gel</b>	<b>S12</b>
<b>7. Photodoping of the ZnO NCs in solution</b>	<b>S13</b>
<b>8. Photodoping of the ZnO NC gel</b>	<b>S14</b>
<b>9. Spatiotemporal emission photopatterning using the ZnO NC gel</b>	<b>S16</b>
<b>10. References</b>	<b>S16</b>

## **1. General Methods**

### **Materials**

Oleylamine (used for measurement), *p*-toluenesulfonic acid, tetramethylammonium hydroxide pentahydrate, Boc-L-glutamic acid, 1-hydroxybenzotriazole, and octadecyl amine were purchased from Tokyo Chemical Industry Co. (TCI). 1-butanol, acetylacetone, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride, oleylamine (used for synthesis), and zinc acetate dihydrate were purchased from FUJIFILM Wako Pure Chemical Co. Titanium (IV) tetrabutoxide was purchased from Sigma-Aldrich Co. Toluene, ethanol (99.5%), dimethyl sulfoxide, ethyl acetate, acetonitrile, tetrahydrofuran, dichloromethane, chloroform, and Chloroform-*d* were purchased from Kanto Chemical Co. All reagents were used without further purification.

### **Microwave synthesis**

Microwave synthesis was conducted using a Discover 2.0 (CEM Corporation).

### **X-ray diffraction (XRD) measurements**

XRD patterns were measured on a Rigaku Ultima IV (Rigaku).

### **Fourier transform infrared (FT-IR) spectroscopy**

FTIR spectra were measured on an FTIR-680 plus (JASCO, resolution: 2 cm<sup>-1</sup>), using KBr pellets.

### **Nuclear magnetic resonance spectroscopy (NMR):**

<sup>1</sup>H-NMR spectra were measured on an ECZ-400 spectrometer (JEOL, 400 MHz).

### **Scanning electron microscope (SEM):**

SEM images were taken on a VE-8800 (KEYENCE, acceleration voltage, 10kV). Before SEM observations, the gel samples were dried under vacuum and treated with Au sputtering.

## **Gel preparation**

Typically, oleylamine-capped TiO<sub>2</sub> or ZnO nanocrystals (NCs) and the gelator (*N,N'*-bis(octadecyl)-L-Boc-glutamic diamide, 45–100 mM for the TiO<sub>2</sub> NCs and ~35 mM for the ZnO NCs), ~2wt% ethanol, and ~3wt% oleylamine were added to toluene, followed by heating at ~50 °C. Subsequent cooling at room temperature for 20 min at least gave NC gels. Although some deviations of the addition amounts of ethanol and oleylamine had little influence on the photochromic behavior, excess addition deteriorated the performance; excess ethanol brought the NC precipitation, and excess oleylamine prevented the gelation. A large amount of the NCs also decreased the gelation ability, probably because of oleylamine adsorbed on the NCs. N<sub>2</sub>-purged gel samples were prepared by N<sub>2</sub> bubbling for the sol state under heating at ~50 °C.

## **Photodoping and oxidation**

For photodoping, TiO<sub>2</sub> or ZnO NC gels were irradiated with continuous UV light (typically, 2 hours for TiO<sub>2</sub> NCs and 3 hours for ZnO NCs) generally using a 365-nm LED light source LC-L1V3 (HAMAMATSU). Spatiotemporal photopatterning in ZnO NC gel was conducted using a UV-LED controller CL-1501 (Asahi Spectra) and a 365-nm LED CL-H1 365-9-1-B (Asahi Spectra) equipped with a rod lens RLQL80-1 (Asahi Spectra). Oxidation of photodoped NC gels was proceeded by shaking the cuvette under air after heating at ~50 °C.

## **UV-Vis-NIR absorption spectroscopy**

Steady-state UV-Vis-NIR spectra were measured on a UV-3600 spectrometer (SHIMADZU). 1-mm, 2-mm or 1-cm quartz cuvettes were used.

## **Fluorescence spectroscopy**

Steady-state emission spectra were measured on an FP-6500 spectrofluorometer (JASCO). The excitation wavelength was 380 nm, and a 1-cm quartz cuvette was used.

## **NIR laser irradiation to NC gels**

NCs gels were irradiated with continuous-wave (CW) 975-nm laser using MDL-III-975-500mW (Changchun New Industries Optoelectronics). A temperature data logger Ondotori TR75A (T&D Corporation) equipped with a T-type thermocouple was used for temperature measurements. The measurement sample setup example is shown in Fig. S8. For photodoping before the decoloration measurement, TiO<sub>2</sub> NC gel was irradiated with UV light (365 nm, 57 mW cm<sup>-2</sup>) for 1 hour.

### **Measurements of the time evolution of absorption and emission**

Absorption and emission changes were traced by an OCEAN FX spectrometer (Ocean Optics) as a detector and a DH-2000-BAL deuterium-halogen light source (Ocean Optics) as a probe light source. For the concurrent measurement of absorption and emission changes of the ZnO NC gel, the probe light and the UV LED light were controlled using a homemade MATLAB code in the following ways; The absorption spectra were recorded with the probe light on and the UV LED light off, while the emission spectra were recorded with the probe light off and the UV LED light on.

## 2. Synthesis

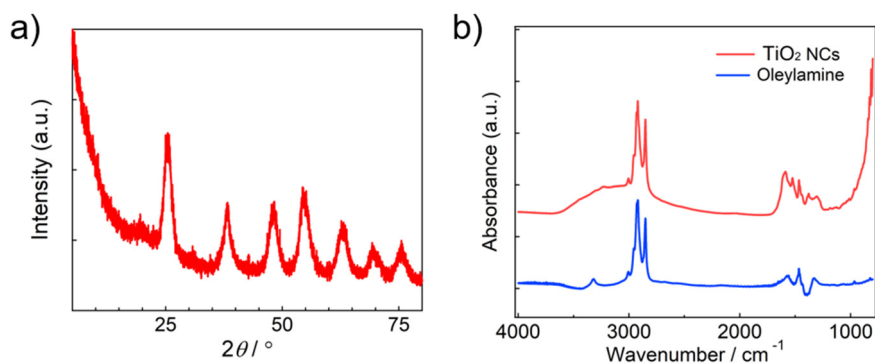
All syntheses were performed under an air atmosphere.

### Synthesis of oleylamine-capped TiO<sub>2</sub> NCs

Oleylamine-capped TiO<sub>2</sub> NCs were according to a previous report by Hirsimäki *et al.*,<sup>1</sup> with some modifications. Titanium (IV) tetrabutoxide (12.0 g, 35.2 mmol) was slowly dropped in a mixed solution of 1-butanol (20 mL) and acetylacetone (12 mL), followed by stirring for 15 min. An aqueous solution (6 mL) of *p*-toluenesulfonic acid monohydrate (1.33 g, 6.99 mmol) was added to the solution and heated at 200 °C for 3 min by the microwave synthesizer (300 W, 220 psi). The yellow solution was added with hexane to form precipitates, and the precipitates were collected by centrifugation (9500 rpm, 15 min) and decantation. For further purification, the collected precipitates were dispersed in ethanol, and precipitates were formed and collected again by the addition of hexane, centrifugation, and decantation. This purification was repeated twice, and the precipitates were dried under vacuum to give a pale yellow solid.

The isolated pale yellow solid and oleylamine (29.9 g, 111 mmol) were dissolved in chloroform (40.0 mL), followed by stirring at room temperature for 15 hours. The solution was added with acetonitrile to form precipitates, and the precipitates were collected by centrifugation (9500 rpm, 10 min) and decantation. For further purification, the collected precipitates were dissolved in chloroform, and precipitates were formed and collected again by the addition of acetonitrile, centrifugation, and decantation. This purification was repeated twice. Drying the precipitates under vacuum gave a pale yellow solid.

XRD measurement revealed that the obtained TiO<sub>2</sub> NCs were anatase crystals, and the average diameter was estimated as ~5.1 nm from the Scherrer equation. FT-IR spectra confirmed the successful coordination of oleylamine onto the NC surface.



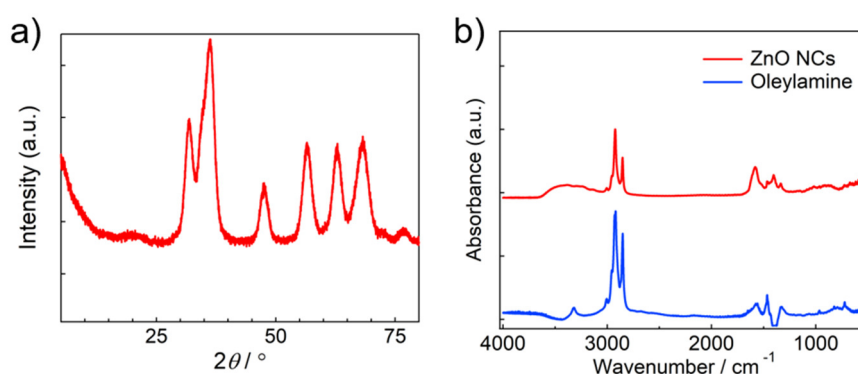
**Fig. S1** (a) XRD pattern of the TiO<sub>2</sub> NCs. (b) FT-IR spectra of the TiO<sub>2</sub> NCs and oleylamine.

## Synthesis of oleylamine-capped ZnO NCs

Oleylamine-capped ZnO NCs were synthesized according to a previous report by Mayer *et al.*,<sup>2</sup> with some modifications. Zinc acetate dihydrate (3.30 g, 15.0 mmol) was dissolved in a mixed solution of ethanol (50 mL) and dimethyl sulfoxide (100 mL). An ethanol solution (50 mL) of tetramethylammonium hydroxide tetrahydrate (4.41 g, 24.3 mmol) was dropped to the solution at 1.7 mL/min in the ice bath. The solution was heated at 50 °C for 30 min. The clear solution was added with ethyl acetate to form precipitates, and the precipitates were collected by centrifugation (9000 rpm, 10 min) and decantation. The precipitates were dispersed in ethanol, and precipitates were formed and collected again by the addition of hexane, centrifugation, and decantation. The precipitates were dried under vacuum to give a colorless solid.

The colorless solid and oleylamine (19.4 g, 72.5 mmol) were dissolved in chloroform (27 mL), followed by stirring at room temperature for 16 hours. The solution was added with acetonitrile to form precipitates, and the precipitates were collected by centrifugation (9000 rpm, 10 min) and decantation. For further purification. The collected precipitates were dispersed in chloroform, and precipitates were formed and collected again by the addition of acetonitrile, centrifugation, and decantation. This purification was repeated twice. Drying the precipitates under vacuum gave a colorless solid.

XRD measurement revealed that the obtained ZnO NCs were wurtzite crystals, and the average diameter was estimated as ~5.6 nm from the Scherrer equation. FT-IR spectra confirmed the successful coordination of oleylamine onto the NC surface.

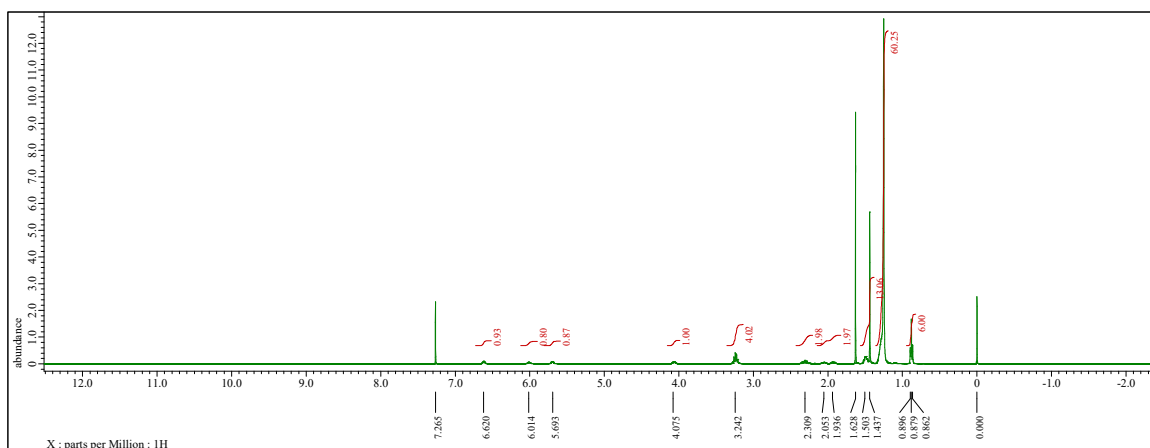


**Fig. S2** (a) XRD pattern of the ZnO NCs. (b) FT-IR spectra of the ZnO NCs and oleylamine.

### Synthesis of the gelator (*N,N'*-bis(octadecyl)-L-Boc-glutamic diamide)

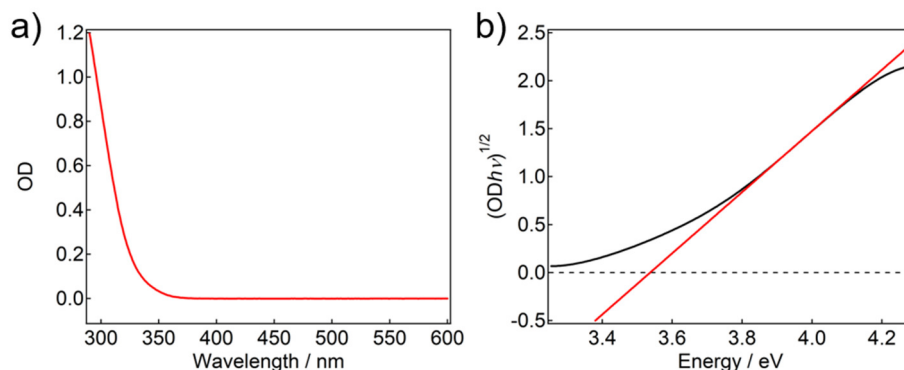
The gelator was synthesized according to a previous report by Liu *et al.*<sup>3</sup> Boc-L-glutamic acid (1.24 g, 4.09 mmol) and octadecyl amine (2.86 g, 10.6 mmol) were added to dichloromethane (120 mL). 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (2.02 g, 10.5 mmol) and 1-hydroxybenzotriazole (1.51 g, 9.86 mmol) were added to the mixture, followed by stirring at room temperature for 72 hours. The obtained colorless solid was collected by filtration. The crude product was dissolved in tetrahydrofuran and reprecipitated by addition of water. Drying the precipitates under vacuum gave a colorless solid (2.69 g, 87% yield).

<sup>1</sup>H-NMR (Chloroform-*d*/TMS, 400 MHz):  $\delta$  6.62 (s, 1H),  $\delta$  6.01 (s, 1H),  $\delta$  5.69 (s, 1H),  $\delta$  4.08 (m, 1H),  $\delta$  3.24 (m, 4H),  $\delta$  2.31 (m, 2H),  $\delta$  1.94–2.05 (m, 2H),  $\delta$  1.45–1.55 (m, 4H),  $\delta$  1.43 (s, 9H),  $\delta$  1.25 (br s, 60H),  $\delta$  0.88 (t,  $J = 6.4$  Hz, 6H).



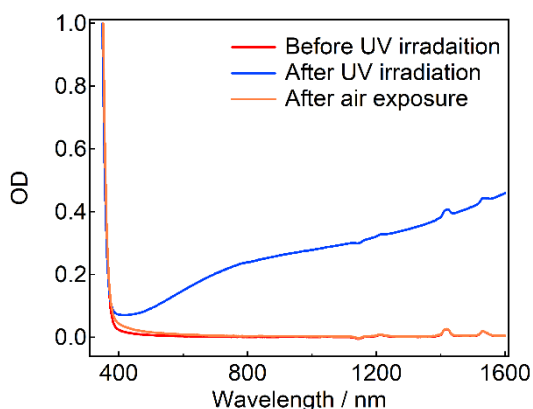
**Fig. S3** <sup>1</sup>H-NMR spectrum of the gelator (Chloroform-*d*/TMS, 400 MHz).

### 3. Photodoping of the TiO<sub>2</sub> NCs in solution



**Fig. S4** Absorption spectrum of the dilute TiO<sub>2</sub> NCs in toluene (without ethanol and additional oleylamine, 1-cm cuvette). (b) Tauc plot for the TiO<sub>2</sub> NC solution.

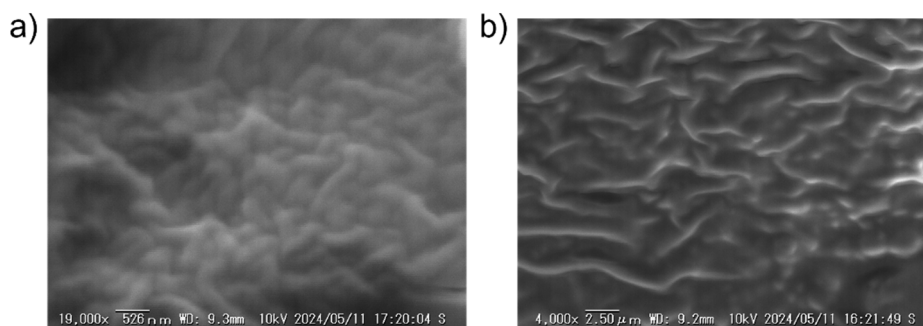
The indirect bandgap of the anatase-type TiO<sub>2</sub> NCs was estimated by the Tauc plot (Fig. S4b). We used  $(ODh\nu)^{1/2}$  instead of  $(\alpha h\nu)^{1/2}$  ( $\alpha$  is the absorption coefficient), because OD is proportional to  $\alpha$ . The bandgap of the TiO<sub>2</sub> NCs was obtained as 3.54 eV. This value was larger than the bandgap of bulk TiO<sub>2</sub> (3.2 eV),<sup>4</sup> because of the quantum size effect (The radius of the TiO<sub>2</sub> NCs:  $\sim$ 2.6 nm, the exciton Bohr radius of TiO<sub>2</sub>: 3.2 nm).<sup>5</sup>



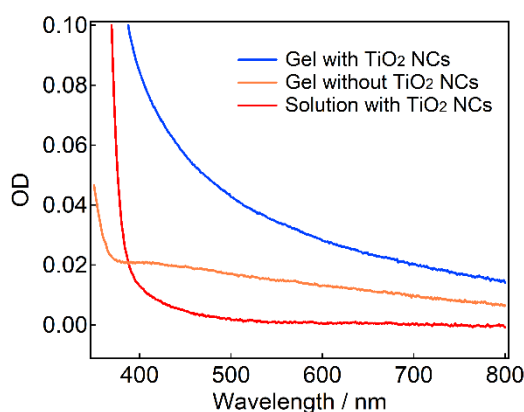
**Fig. S5** Absorption spectra of the N<sub>2</sub>-purged TiO<sub>2</sub> NC solution (1.3wt% TiO<sub>2</sub> NCs, 2wt% ethanol, 3wt% oleylamine, in toluene; 2-mm cuvette) before and after UV light irradiation (365 nm, 105 mW cm<sup>-2</sup>) and after air exposure.



#### 4. Characterization of the gel



**Fig S6.** SEM images of the gels (80 mM of the gelator, 2wt% ethanol, 3wt% oleylamine, upon the gel preparation) after vacuum drying; (a) without TiO<sub>2</sub> NCs, (b) with the TiO<sub>2</sub> NCs (1.5 wt% TiO<sub>2</sub> NCs).

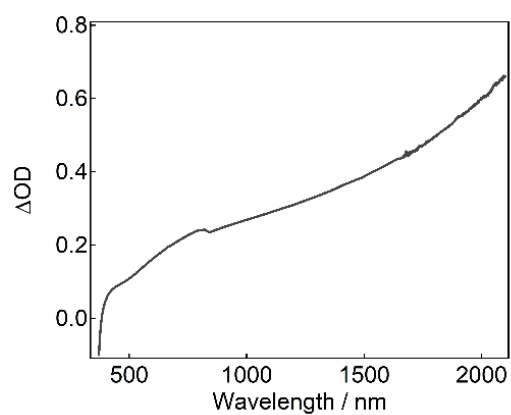


**Fig. S7.** Absorption spectra (2wt% ethanol, 3wt% oleylamine, 1-mm cuvette) of the gels with the TiO<sub>2</sub> NCs (1.5wt% TiO<sub>2</sub> NCs, 83 mM of the gelator) and without TiO<sub>2</sub> NCs (81 mM of the gelator) and the TiO<sub>2</sub> NC solution (1.6wt% TiO<sub>2</sub> NCs).

Fig. S6 shows SEM images of the gels without and with the TiO<sub>2</sub> NCs. In the gel without semiconductor NCs, fibers with the width of 0.2–1 μm were observed. In contrast, the fiber width in the gel with the TiO<sub>2</sub> NCs was 1–2 μm, thicker than the gel without semiconductor NCs.

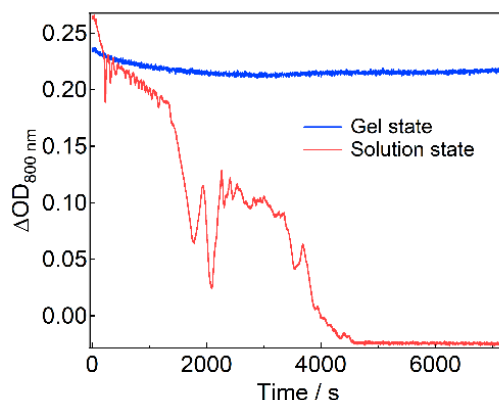
The thickening of the gel fiber was corroborated by a scattering increase in UV-Vis spectroscopy (Fig. S7); The gel with the TiO<sub>2</sub> NCs showed more intense scattering than that of the superposition of the gel without TiO<sub>2</sub> NCs and the solution of TiO<sub>2</sub> NCs. These results suggest that there is some interaction between the gelator and TiO<sub>2</sub> NCs, affecting the supramolecular fiber structure.

## 5. Photodoping of the TiO<sub>2</sub> NC gel



**Fig. S8** Absorption change of the TiO<sub>2</sub> NC gel (1.4wt% TiO<sub>2</sub> NCs, 2-mm cuvette) upon photodoping (The difference between Fig.2a red and blue).

A weak absorption was observed at around 700 nm, which would originate from the Ti<sup>3+</sup> sites (Fig. S8).<sup>1</sup> The absorption was clearer in the solution sample (Fig. S5 blue).

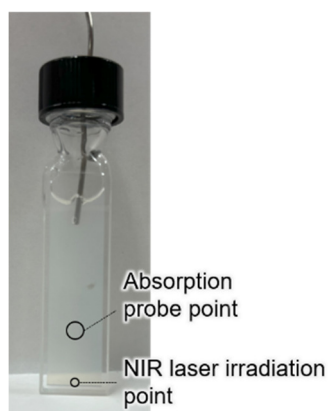


**Fig. S9** Coloration decay at 800 nm for the TiO<sub>2</sub> NC gel and solution after UV irradiation (1wt% TiO<sub>2</sub> NCs, 2-mm cuvette).

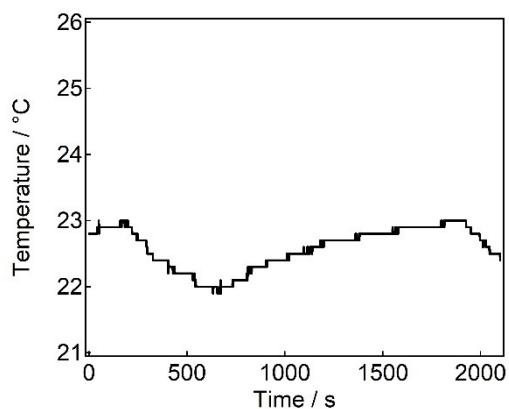
In the oxygen blocking by the gel, suppression of convective diffusion owing to the semi-solid nature of the gel plays an important role. On the other hand, oxygen permeation via molecular diffusion from the air-gel interface occurred even in the gel (roughly ~2 mm per hour, from observation with naked eyes).

Yanai and Kimizuka *et al.* reported that incorporation of photofunctional compounds into supramolecular gel fibers is important for oxygen blocking in the molecular level.<sup>6</sup> However, in our case, we have no evidence for the incorporation of semiconductor NCs into the gel fibers and the microscopic oxygen blocking, although the thickening of the gel fiber by the addition of the TiO<sub>2</sub> NCs suggests that there would be some interaction between the gelator and TiO<sub>2</sub> NCs.

## 6. NIR laser irradiation to the TiO<sub>2</sub> NC gel

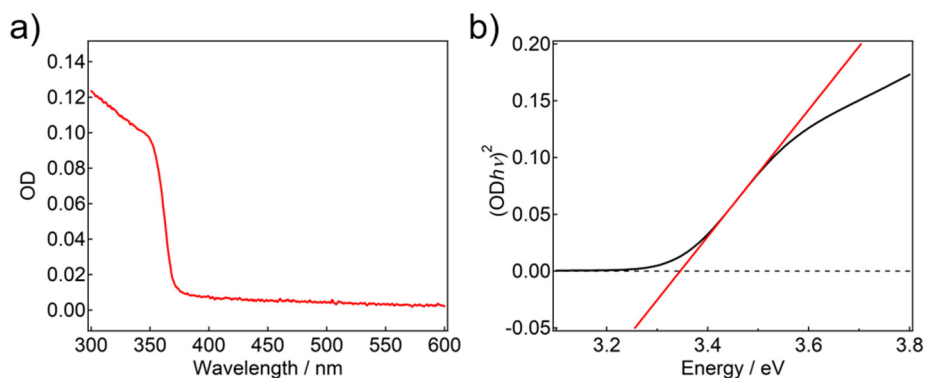


**Fig. S10** The measurement sample setup for NIR laser irradiation to the TiO<sub>2</sub> NC gel.



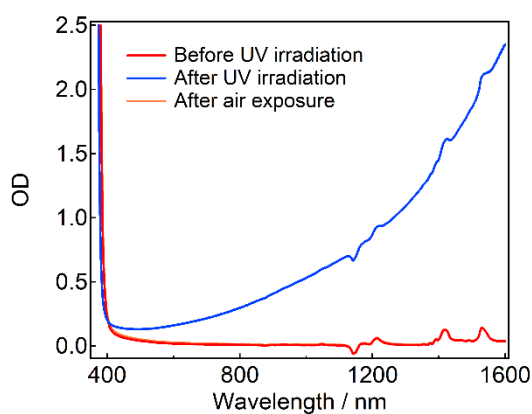
**Fig. S11** Temperature changes of the TiO<sub>2</sub> NC gel (10wt% TiO<sub>2</sub> NCs, 2-mm cuvette) without photodoping under NIR laser (975 nm, 500 mW) irradiation.

## 7. Photodoping of the ZnO NCs in solution



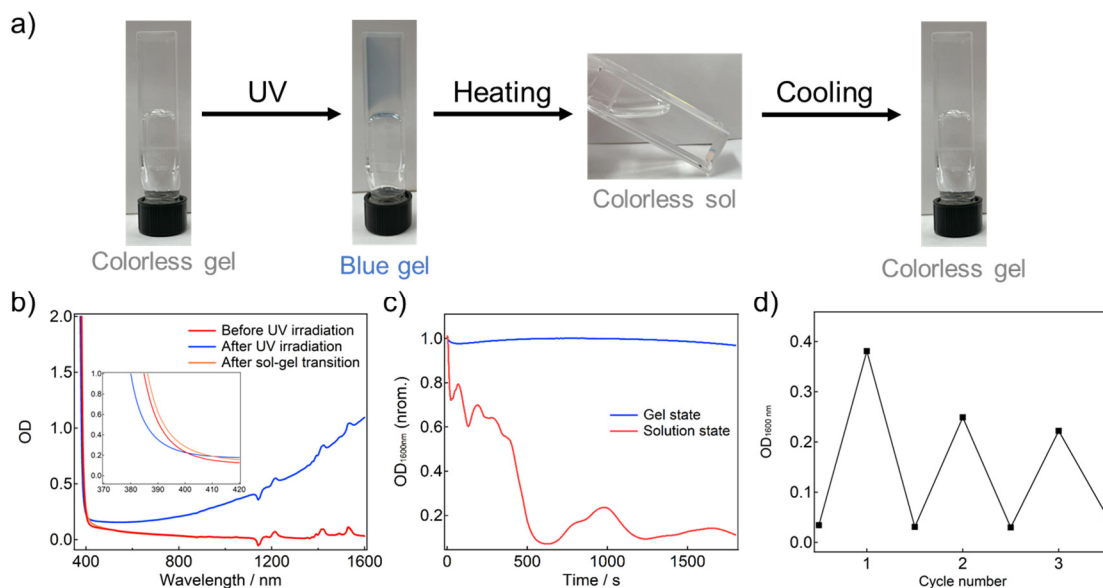
**Fig. S12** Absorption spectrum of the dilute ZnO NCs in toluene (without ethanol and additional oleylamine, 1-cm cuvette). (b) Tauc plot for the ZnO NC solution.

The direct bandgap of the ZnO NCs was estimated (Fig. S12b) using the Tauc plot (Fig. S5). The direct bandgap of the ZnO NCs was calculated as 3.34 eV. This value was almost comparable to the bandgap of ZnO (3.4 eV),<sup>7</sup> because the radius of the ZnO NCs (~2.8 nm) was larger than the exciton Bohr radius of ZnO (2.34 nm).<sup>8</sup>

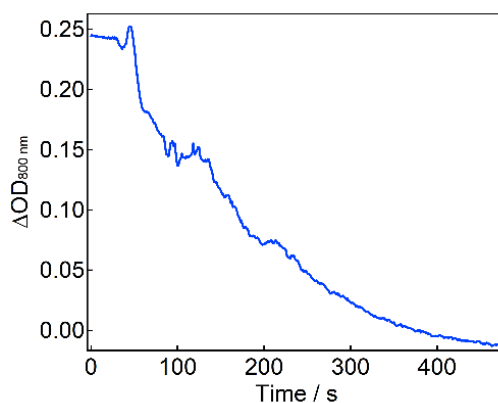


**Fig. S13** Absorption spectra of the N<sub>2</sub>-purged ZnO NC solution (18wt% ZnO NCs, 1wt% ethanol, 4wt% oleylamine, in toluene; 1-cm cuvette) before and after UV light irradiation (365 nm, 108 mW cm<sup>-2</sup>) and after air exposure.

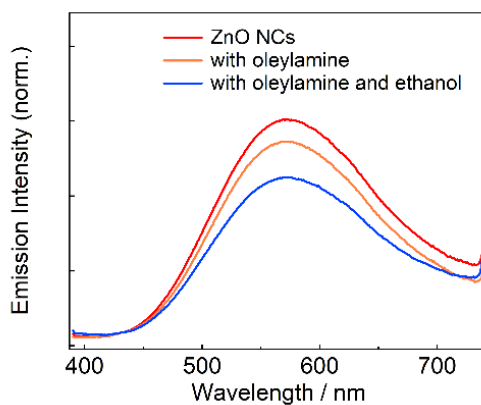
## 8. Photodoping of the ZnO NC gel



**Fig. S14** (a) Sample image of the ZnO NC gel (11wt% ZnO NCs, 1-cm cuvette) upon UV irradiation and the sol-gel transition. (b) Absorption spectra of the ZnO gel (11wt% ZnO NCs, 1-cm cuvette) before and after UV light irradiation (365 nm, 106 mW cm<sup>-2</sup>) and the sol-gel transition. (c) Coloration decay at 1600 nm for the ZnO NC gel and solution after UV irradiation (1wt% ZnO NCs, 1-cm cuvette). (d) Repeatability of the UV light-induced coloration (365 nm, 35 mW cm<sup>-2</sup>) and heating-induced decoloration (11 wt% ZnO NCs, 1-cm cuvette).

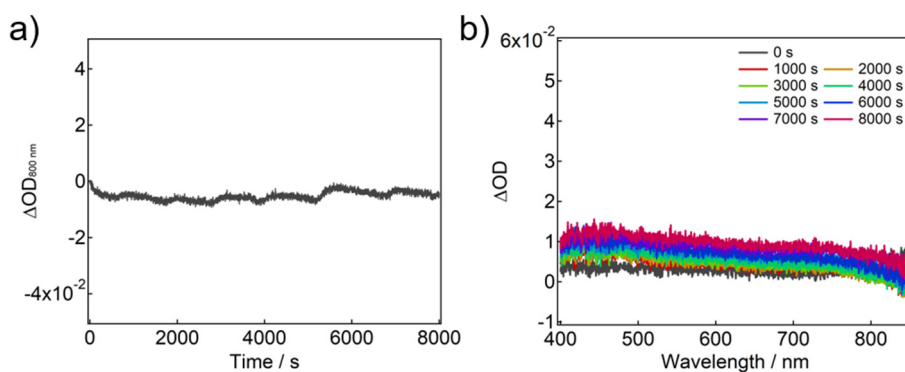


**Fig. S15** Absorption (at 800 nm) changes of the ZnO NC gel (11wt% ZnO NCs, 1-cm cuvette) under NIR laser irradiation (975 nm, 500 mW).



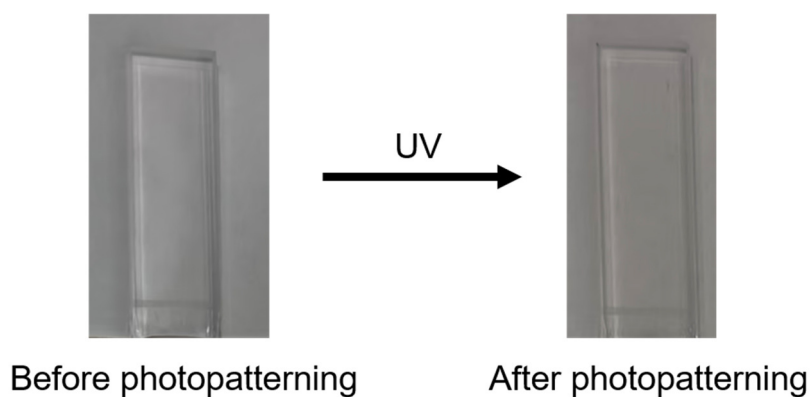
**Fig. S16** Emission spectra of the ZnO NC toluene solution ( $\lambda_{\text{ex}}$ : 380 nm); red) toluene without additional oleylamine and ethanol, orange) toluene with 3wt% oleylamine, blue) toluene with 3wt% oleylamine and 2wt% ethanol.

Even the addition of only oleylamine brought some quenching of the emission of ZnO NCs (Fig. S16 orange). This result suggests that oleylamine works as a hole scavenger similarly to ethanol.



**Fig. S17** Time evolutions of (a) absorbance at 800 nm and (b) absorption spectra of the ZnO NC gel (0.02wt% ZnO NCs, 1-cm cuvette) under UV irradiation (365 nm,  $63 \text{ mW cm}^{-2}$ ). These absorption data were measured concurrently with the emission data shown in Fig. 4c.

## 9. Spatiotemporal emission photopatterning using the ZnO NC gel



**Fig. S18** Sample images of the ZnO NC gel under white light before and after the photopatterning.

## 10. References

- 1 U. Joost, A. Šutka, M. Oja, K. Smits, N. Döbelin, A. Loot, M. Järvekülg, M. Hirsimäki, M. Valden and E. Nõmmiste, *Chem. Mater.*, 2018, **30**, 8968–8974.
- 2 J. N. Schrauben, R. Hayoun, C. N. Valdez, M. Braten, L. Fridley and J. M. Mayer, *Science*, 2012, **336**, 1298–1301.
- 3 Y. Li, T. Wang and M. Liu, *Soft Matter*, 2007, **3**, 1312–1317.
- 4 H. Tang, H. Berger, P. E. Schmid, F. Lévy and G. Burri, *Solid State Commun.*, 1993, **87**, 847–850.
- 5 E. Baldini, L. Chiodo, A. Dominguez, M. Palummo, S. Moser, M. Yazdi-Rizi, G. Auböck, B. P. P. Mallett, H. Berger, A. Magrez, C. Bernhard, M. Grioni, A. Rubio and M. Chergui, *Nat. Commun.*, 2017, **8**, 13.
- 6 P. Duan, N. Yanai, H. Nagatomi and N. Kimizuka, *J. Am. Chem. Soc.*, 2015, **137**, 1887–1894.
- 7 D. C. Look, *Mater. Sci. Eng. B*, 2001, **80**, 383–387.
- 8 R. T. Senger and K. K. Bajaj, *Phys. Rev. B*, 2003, **68**, 045313.