Photo-Induced Mode Change for CO₂ Capture/Release on Spiropyran in Polar-Gradient Environment

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1. Experimental procedures

1.1. Reagents

1,3,3-Trimethylindolino-8'-methoxy-benzopyrylospiran (SP, Tokyo Chemical Industry Co., Ltd.) and cetyltrimethylammonium bromide (CTAB, FUJIFILM Wako Pure Chemical Co., Ltd.) were utilized as photochromic molecule and surfactant, respectively. Montmorillonite (**Mont**) and toluene were obtained from The Clay Science Society of Japan and FUJIFILM Wako Pure Chemical Co., Ltd., respectively.



Figure S1. Chemical structures of 1,3,3-Trimethylindolino-8'-methoxybenzopyrylospiran (SP) and cetyltrimethylammonium bromide (CTAB).

1.2. Intercalation of CTA⁺ into interlayer of Mont

Insertion of cetyltrimethylammonium cation (CTA⁺) into the interlayer of **Mont** was performed by referring to the literature.^{S1} 2.00 g of **Mont** was suspended in 100 mL of ion-exchanged water under continuous stirring at 900 rpm. After that, 2.25×10^{-2} mol dm⁻³ of CTAB aqueous solution (100 mL) was added to the stirred **Mont** suspension little by little, and then was further stirred at 900 rpm and 60 °C for 3 h. The resulting suspension was filtered, and the precipitate was washed with water. The given solid was dried at 80 °C overnight, and CTA⁺-intercalated **Mont** (**CTA⁺/Mont**) was obtained.

1.3. Introduction of SP into interlayer of CTA⁺/Mont

The SP was introduced into CTA⁺/Mont by following a reference.^{S2} 9.01 × 10^{-5} mol of SP in toluene was added to 800 mg of CTA⁺/Mont on a mortar and mixed for 10 min in a dark. Resulting yellowish slurry transferred to petri-dish was dried at 80 °C overnight, which afforded SP-introduced CTA⁺/Mont (SP/CTA⁺/Mont).

1.4. X-ray diffraction (XRD)

The XRD analysis was performed using Ultima-IV apparatus (Rigaku Co., Ltd). All samples were irradiated with Cu K α ($\lambda = 0.154$ nm) at a voltage of 40 kV and current of 40 mA. The scanning speed was set to 1.0° min⁻¹ for all the measurements. A lattice plane distance (*d*) and crystalline size (*D*) were respectively calculated by Bragg's equation (S1) and Scherrer equation (S2) as shown below:

$$d = \frac{n\lambda}{2\mathrm{sin}\theta} \tag{S1}$$

$$D = \frac{K\lambda}{\beta \cos\theta}$$
(S2)

where, n, θ , K, and β are diffraction order, Bragg angle, shape factor, and full width at half maximum, respectively.

1.5. Diffuse reflectance UV-vis spectroscopy

Measurement of absorption spectra was carried out using a spectrophotometer (V-750, JASCO Co., Ltd.). Samples were placed in the optical cell and irradiated with light at the range of 200–900 nm. The scanning rate was set to 200 nm min⁻¹. Reflectance (R) was observed and absorption was calculated with 1–R.

1.6. N₂ and CO₂ adsorption/desorption isotherms

Adsorption/desorption isotherms were recorded by a BELSORP-mini II apparatus (MicrotracBEL Co., Ltd.). The sample was placed in a cell and was heated at 80 °C for 2 h in vacuo as pre-treatment. N₂ adsorption experiments were performed at -196 °C and the CO₂ adsorption ability of the prepared samples was investigated at 27 °C.

1.7. Photo-isomerization from SP to MC

The prepared **SP/CTA⁺/Mont** was illuminated with the light ($\lambda < 325$ nm) using a 300 W Xe lamp (Asahi Spectra Co., Ltd.). Absorption spectra during the photo-irradiation were tracked by the UV-vis spectrophotometer.

1.8. Density functional theory (DFT) calculation

DFT calculation was performed using Gaussian 16W and the optimized structures visualized by GaussView 6. On the energy minimization, distances between SP or MC and CO₂ were varied under designations, whilst the structure of each component was fixed to the optimized orientation calculated alone. The basis set was ω B97XD/6-31+G(d,p).

2. Supporting results



Figure S2 (a,c) Dependences of relative energies on the distance between (a) CO₂ and SP and (c) CO₂ and MC. The dashed lines at 0 indicate the sum of the CO₂ and SP or MC calculated alone. (b,d) Distributions of the wave function at HOMO of (b) SP_CO₂ and (d) MC_CO₂ systems. The DFT calculation was performed with of ω B97XD/6-31+G(d,p) basis set.

Figure S3. (a–c) Images of as-prepared (a) SP/Mont, (b) SP/CTA⁺/Mont, and (c) those after drying at 80 °C overnight. (d) XRD patterns and (e) diffuse reflectance absorption spectra of SP/Mont (black) and SP/CTAB/Mont (red).

Figure S4. Optimized structure of SP and lengths along short axes of benzopyran and indole ring. The DFT calculation was performed with of ω B97XD/6-31+G(d,p) basis set.

Figure S5. N_2 adsorption/desorption isotherms of Mont, SP/Mont, CTA⁺/Mont, and SP/CTA⁺/Mont at -196 °C.

Table S1. Basal spacings (*d*), interlayer distances (r_{inter}), crystalline sizes (*D*), and Brunauer-Emmett-Teller surface areas (S_{BET}) of Mont, SP/Mont, CTA⁺/Mont, and SP/CTA⁺/Mont.

| Sample | <i>d</i> / nm | <i>r</i> _{inter} / nm | D / nm | $S_{\rm BET}$ / m ² g ⁻¹ |
|---------------------------|---------------|--------------------------------|--------|------------------------------------------------|
| Mont | 1.26 | 0.26 | 7.76 | 10.75 |
| SP/Mont | 1.20 | 0.24 | 4.66 | 5.02 |
| CTA ⁺ /Mont | 1.95 | 0.99 | 13.53 | 1.29 |
| SP/CTA ⁺ /Mont | 1.96 | 1.00 | 13.56 | 1.13 |

Figure S6. CO₂ adsorption isotherm over SP/Mont.

Figure S7. Time profile of absorption spectra of (a) **SP/CTA⁺/Mont** under UV light ($\lambda < 365$ nm) irradiation for 90 min and (b) and subsequent visible light ($\lambda = 560$ nm) irradiation for 420 min.

Figure S8. (a) Absorption spectra of **SP/CTA⁺/Mont** before UV irradiation (Blue), after UV light irradiation for 90 min (Green), and subsequent aging in a dark for 7 h (Red). (b) Time course of absorption at 590 nm arising from MC on an aging in a dark.

3. Supporting references

- S1. T. Yui, H. Yoshida, H. Tachibana, D. A. Tryk, and H. Inoue, *Langmuir* 2002, 18, 891–896.
- S2. T. Yamaguchi, K. J. Imwiset, and M. Ogawa, *Langmuir* **2021**, *37*, 3702–3708.