

Preparation of Photofunctional Organic - Inorganic Nanocomposites

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Sulfonated spiropyran dye intercalated into the interlayers of layered double hydroxides showed reversible photochromism in the presence of co-intercalated organic acid. The effects of reaction conditions on the photochemical properties were clarified and slow rate of decoloration and stable reversible photochromism were attained. Intercalates composed of two photochromic compounds and organic acid also showed photochromic properties. Furthermore, new organic - inorganic hybrids including spiropyran dye and organic acid among silica matrices were prepared by sol-gel reaction. They also showed stable and reversible photochromic properties.

1. INTRODUCTION

Many studies have been reported on the photochromism of spiropyrans (SPs) because of their potential usefulness as photoresponsive materials [1,2]. SP forms merocyanine (MC) reversibly on the light irradiation. In a non - polar solvent, SP is stable. When SP is exposed to UV light, SP undergoes ring opening to MC. In a non polar solvent, MC is fairly unstable and isomerized to SP immediately. The thermal reversion of photoinduced MC to the starting SP is influenced by the surrounding matrix. Many matrices such as polymer films, monolayers, liquid crystals, smectite clays, biomolecules and micelles are the subjects of intensive research. We have been interested in the preparation of organic - inorganic nanocomposites [3-6] and prepared various organic intercalation compounds into inorganic layer compounds. We have already reported that SP intercalated into the interlayers of layered double hydroxide (LDH) revealed stable and reversible photochromism [7-9]. In the case of Mg/Al and Zn/Al LDHs the co-intercalation of organic acid was essential to attain photochromism.

In this study to attain reversible and stable photochromism, new organic - inorganic nanocomposites were prepared by considering the kinds of matrix, spiropyran and organic acid.

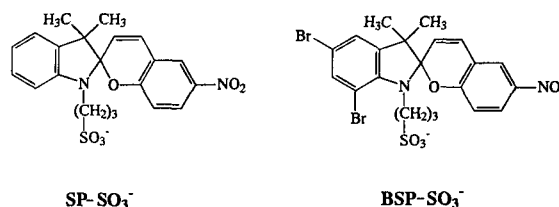


Fig.1 Structure of spiropyrans used in this study

2. EXPERIMENTAL

Two SPs, Sulfonated spiropyran (SP-SO₃⁻) and dibrominated SP-SO₃⁻ (BSP-SO₃⁻) were used. LDHs were prepared by the reaction of a mixture of M(II)(NO₃)₂ with Al(NO₃)₃. p-Toluenesulfonic acid (PTS), p-aminobenzenesulfonic acid or naphthalene sulfonic acid were co-intercalated into the LDH. In the intercalation, SP-SO₃⁻ and BSP-SO₃⁻ were reacted usually at 60°C for 1 h in an aqueous suspension of LDH [7,8].

Powder X-ray diffraction spectra of the organic - inorganic nanocomposites were recorded on a Rigaku powder diffractometer unit using CuK α (filtered) radiation at 40KV and 20mA. Upon intercalation, interlayer spacings of LDH increased from 7.8 Å to larger values. UV irradiation was carried out using a 400W high-pressure mercury lamp. Visible light irradiation was carried out using a 500W Xenon lamp.

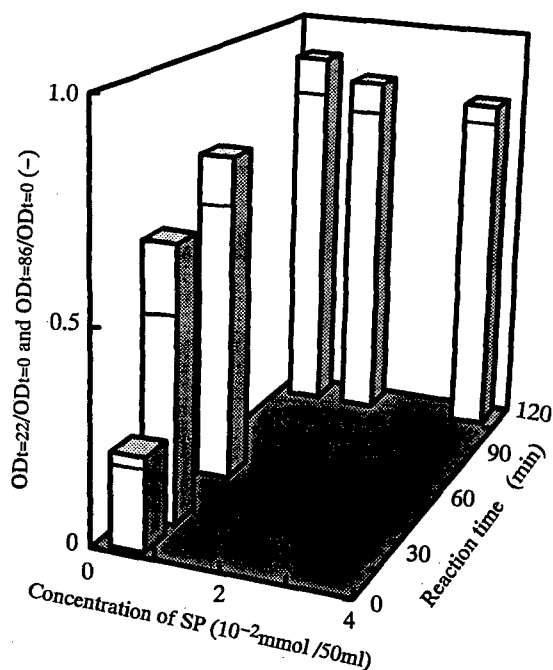


Fig.2 The effects of reaction time and the concentration of SP-SO_3^- in the reactant on optical density of intercalate at 535 nm

$\text{OD}_{t=0}$, $\text{OD}_{t=22}$ and $\text{OD}_{t=86}$ are optical density of intercalate at $t=0$, 22 and 86 h, respectively.

3. RESULT AND DISCUSSION

3.1 Photochromic properties of co-intercalate of SP-SO_3^- and organic acid

By UV light irradiation to co-intercalate of SP-SO_3^- and organic acid, the color changed from yellow to red. The absorption maximum of the colored intercalate was at 535 nm. The half life time of photoinduced MC in toluene solution is only a few seconds at room temperature. However, between the interlayers of LDH, MC form was highly stable and the half life time of photoinduced MC reached more than 200 h in the presence of PTS. As shown in Fig. 1, the preparation time was important for the photochromic properties. Weight of intercalated SP were 3.2 - 7.0 % for intercalates obtained by the reaction of PTS (0.6 mmol per 50 ml) and SP-SO_3^- (0.01 - 0.04 mmol per 50 ml). Their MC forms were highly stable and only <20% of initial optical density after UV light irradiation decreased after 86 h.

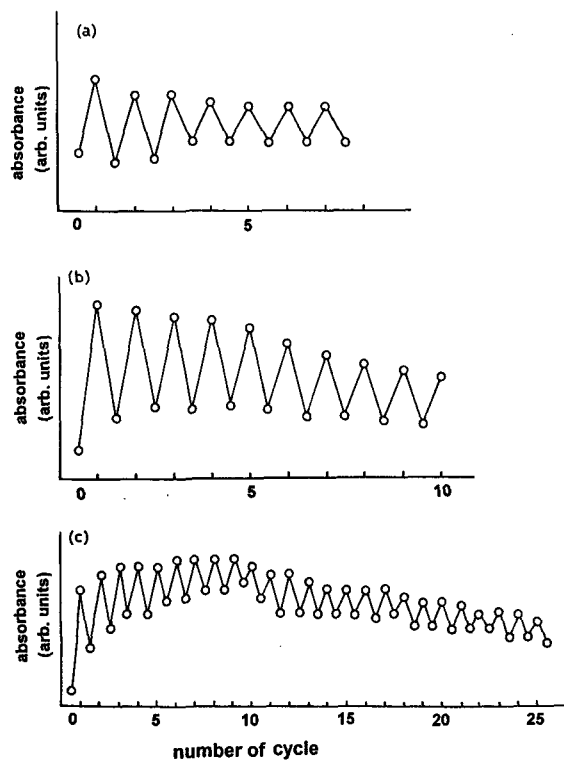


Fig. 3 Reversible photochromism of organic acid and SP-SO_3^- co-intercalates

- p-aminobenzensulfonic acid was used instead of PTS
- 365 nm light was irradiated as UV light
- UV was irradiated for 5 min instead of 20 min irradiation

Reversible photochromic properties of SP depended on the kinds of organic acids, wavelength of irradiation light and irradiation time. p-Aminobenzene sulfonic acid and naphthalene sulfonic acids were used instead of PTS. In the case of PTS, after four times of repetition of light irradiation, the difference of optical density after and before visible light irradiation decreased to a half of the initial difference. By using p-aminobenzene sulfonic acid, the reversibility improved to eight cycles. It is already reported that the reaction of the triplet state of SP caused irreversible deactivation of photochromic properties of SP [2]. Despite the effort to avoid the undesirable reaction using naphthalene sulfonic acid instead of PTS, no improvement of the photochromic property was observed.

365 nm light irradiation instead of 254 nm irradiation was effective for the improvement of photochromic properties and reversibility increased to 10 cycles. It indicates that the exposure to higher energy light was one of the reasons of deactivation of SP. Furthermore, by 5 min UV light irradiation instead of 20 min irradiation, the reversibility improved to 25 as shown in Fig. 3 although the difference of optical density before and after light irradiation was small compared to the values of 20 min irradiation.

We have attained stable and reversible photochromism of spiropyran by intercalating SP between the interlayers with organic acid such as PTS. Inner surface of the LDH was covered by hydroxyl groups and polar. Certainly by the intercalation of SP only, MC form was stable between the layers. The toluene part of PTS constitute hydrophobic regions between the layers. The presence of hydrophobic layers between the layers was essential for the photochromic properties.

3.2 Photochromic properties of intercalate composed of SP-SO_3^- and BSP-SO_3^-

It is well known that the bromination of colored compounds causes red shift of the absorption spectra of them. Therefore, we have prepared dibrominated SP-SO_3^- . Certainly, bromination of SP-SO_3^- caused red shift of the absorption peak from 535 nm to 570 nm.

We have prepared co-intercalates of SP-SO_3^- and BSP-SO_3^- having different absorption peaks. By the intercalation of SPs and PTS, interlayer spacing increased from 7.8 Å to 17.9 Å in the case of Mg/Al (0.7/0.3) LDH. By UV light irradiation to the intercalate, colored intercalate was obtained indicating the formation of photoinduced MC. The MC form was stable in dark. 520 nm light was irradiated to the colored co-intercalate. It promoted the decrease of absorption at near 500 nm more than at 610 nm. Also 605 nm irradiation promoted the decrease of absorption at 610 nm more than at 500 nm. The properties depended on the kind of center metals of the LDHs. Pronounced effects of light depended changes of absorption spectra were observed in the cases of Mg/Al (0.8/0.2) LDH and Li/Al (0.33/0.67) LDH. These results indicated that by 520 nm irradiation MC form of SP-SO_3^- isomerized to SP-SO_3^- more than that of BSP-SO_3^- .

Also by 605 nm irradiation MC form of BSP-SO_3^- isomerized to BSP-SO_3^- more than that of SP-SO_3^- .

It suggests that the intercalate including two SPs having different absorption peaks has potential utility as multiple optical memory materials.

Table 1 The effects of reaction conditions on the reactivity of hybrid compounds

PTS/ SP-SO_3^-	gelation	photochromism
0	×	×
0.2	○	○
0.4	○	○
0.5	○	○
0.7	○	○
0.9	○	○
1.0	○	○
10	○	×
50	○	×
100	○	×

3.3 Photochromic properties of SP-SO_3^- trapped in silica matrix

By sol - gel method using tetraethoxysilane or ethyltriethoxysilane, SP-SO_3^- and PTS in an aqueous solution were included in silica matrix. In the case of ethyltriethoxysilane, colored film was obtained.

Table 1 shows the reaction conditions to obtain gel solid. When only SP-SO_3^- was used without PTS, colored solution was obtained. However, no gelation occurred within a week. It indicates that the presence of PTS was essential to obtain gel solid in these reaction conditions. Certainly, PTS/ SP-SO_3^- ratio in the reactant was important factor.

When the gel was obtained in the conditions of PTS/ SP-SO_3^- ratio from 0.2 to 1.0, the obtained hybrid including SP-SO_3^- exhibited reversible photochromism. By UV light irradiation, the colored powder or film was obtained and the color disappeared by visible light irradiation. However, when the gel was obtained in the conditions of PTS/ SP-SO_3^- ratio over 10, the obtained hybrid was yellow and no formation of MC was confirmed even by UV light irradiation.

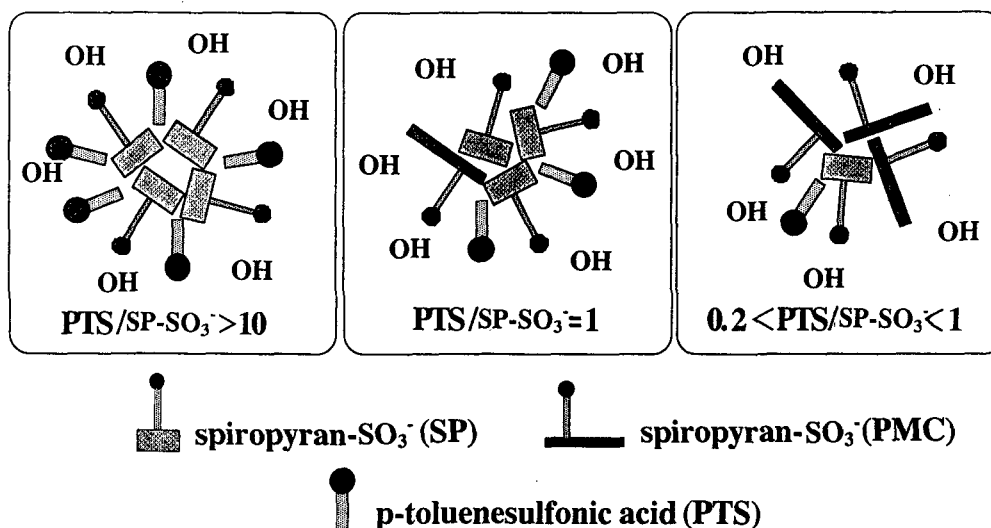


Fig.3 Photochromic properties of SP-SO₃⁻ and PTS attained in silica matrix

From these results, we have considered the molecular orientational structures of SP and PTS included in the silica matrix as shown in Fig. 3. MC form is stable in polar conditions. Silanol groups are considered to constitute polar regions around the portion of organic compounds. At high PTS/SP-SO₃⁻ ratio, photoinduced MC might not contact with silanol group and stable MC form was not obtained. At fairly low PTS/SP-SO₃⁻ ratio, MC form was stable and SP form was not obtained. At the moderate PTS/SP-SO₃⁻ ratio, photoinduced MC might contact with silanol groups and stable.

4. CONCLUSIONS

Reversible and stable photochromic properties were attained by incorporation of spiropyran and organic acid between the interlayers of layered compounds and among silica matrices. The important situation in these systems are that hydrophobic regions and hydrophilic regions are separated. It means that SP is stable in hydrophobic regions and MC form is stable in hydrophilic regions.

Further studies on the control of the proportions of hydrophobic regions and hydrophilic regions should promise preparation of new photofunctional materials.

REFERENCES

1. H. Dürr and H. B-Laurent, *Photochromism: Molecules and Systems*, Elsevier, New York, 1990.
2. M. Irie, T. Tamaki, T. Seki and J. Hibino, *Photochromic Spiroyrans*, Bunshin, Tokyo, 1993.
3. H. Tagaya, S. Ogata, H. Morioka, J. Kadokawa, M. Karasu and K. Chiba, *J. Mater. Chem.*, 6, in press (1996).
4. K. Ara, H. Tagaya, T. Ogata, K. Matsushita, J. Kadokawa, M. Karasu and K. Chiba, *Mater. Res. Bull.*, 321, 283 (1996).
5. H. Morioka, H. Tagaya, M. Karasu, J. Kadokawa and K. Chiba, *J. Solid State Chem.*, 117, 337 (1995).
6. H. Tagaya, S. Sato, H. Morioka, J. Kadokawa, M. Karasu and K. Chiba, *Chem. Mater.*, 5, 1431 (1993).
7. H. Tagaya, T. Kuwahara, S. Sato, J. Kadokawa, M. Karasu and K. Chiba, *J. Mater. Chem.*, 3, 317 (1993).
8. H. Tagaya, S. Sato, T. Kuwahara, J. Kadokawa, M. Karasu and K. Chiba, *J. Mater. Chem.*, 4, 1907 (1994).
9. T. Kuwahara, H. Tagaya and K. Chiba, *Microporous Materials*, 4, 247 (1995).