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Mechanofluorochromism of heteropolycyclic donor–π-acceptor type fluorescent dyes

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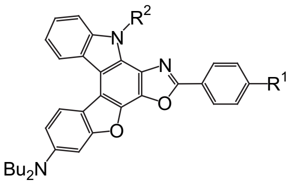
ABSTRACT

This paper reports that mechanofluorochromism is found for a series of benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-type fluorophores (**1a**–**5a**) with different *p*-substituted phenyl groups as acceptor and dibutylamino groups as donor. Grinding of as-recrystallized dyes **1a**–**3a** with strong electron-accepting group induces a fluorescent color change with an enhanced quantum yield and the fluorescent color is recovered by heating or exposure to solvent vapor. On the basis of experimental results and semi-empirical molecular orbital calculations (AM1 and INDO/S), we clarified that the mechanofluorochromism is attributed to a reversible switching between crystalline and amorphous states with changes of dipole–dipole interaction and intermolecular π–π interaction by changes of the densities of the solids before and after grinding.

1. Introduction

Mechanofluorochromism found recently denotes a change in fluorescent color induced by mechanical stress to organic crystal, being accompanied by a reversion to the original fluorescent color by heating or exposure to solvent vapor. Although it has received an increasing interest both in the fundamental research field of solid-state photochemistry and in the applied field of optoelectronic devices, the number of organic dyes exhibiting the mechanofluorochromism is still limited and the mechanism is a matter, which requires intensive debates.[1]

In our previous work, the mechanofluorochromism is found for a series of benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-type fluorophores **1a**–**d** having cyano groups as acceptor and dibutylamino groups as donor (Scheme 1). Grinding of as-recrystallized dyes **1a**–**d** induces a fluorescent color change with an enhanced quantum yield and the fluorescent color is recovered by heating or exposure to solvent vapor.[2] On the basis of the time-resolved fluorescence spectroscopy, X-ray powder diffraction (XRD), and differential scanning calorimetry (DSC), the mechanofluorochromism observed with this new class of fluorescent dyes is found to accompany a reversible switching between crystalline and amorphous states with changes of molecular arrangement.



1a : R^1 = CN, R^2 = H
1b : R^1 = CN, R^2 = *n*-butyl
1c : R^1 = CN, R^2 = benzyl
1d : R^1 = CN, R^2 = 5-nonyl
2a : R^1 = COOMe, R^2 = H
3a : R^1 = COOH, R^2 = H
4a : R^1 = H, R^2 = H
5a : R^1 = *t*-Bu, R^2 = H

Scheme 1. Benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-type fluorophores **1a**–**d** and **2a**–**5a**.

In this paper, in order to clarify molecular structures necessary for manifestation of the mechanofluorochromism, we have designed and synthesized a new class of heteropolycyclic donor–π-acceptor (D–π-A) type fluorescent dyes **2a**–**5a**[3] having a structure similar to **1a**–**d**, but different *p*-substituted phenyl groups as acceptor with a special interest on the effects of dipolar characteristics of the dyes on the mechanofluorochromism.

2. Results and discussion

In 1,4-dioxane, the fluorophores **1a**–**5a** exhibit intense absorption band at around 390–430 nm assigned to the ICT excitation from the donor (dibutylamino group) to the acceptor (*p*-substituted phenyl group) and intense fluorescence band at around 455–540 nm.[3] The

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ICT absorption and fluorescence maxima (λ^{abs}_{max} and λ^{em}_{max}) of **1a**–**5a** show red-shifts in the order of **5a** (387 and 455 nm)<**4a** (388 and 453 nm)<**3a** (416 and 526 nm)<**2a** (418 and 532 nm)<**1a** (428 and 539 nm), with increasing the electron-accepting ability of *p*-substituted phenyl group (Fig. 1). The fluorescence quantum yields of **1a**–**5a** are 0.96–0.99. The time-resolved fluorescence spectroscopy of **1a**–**5a** indicated that the decay profile fitted satisfactorily a single exponential function with τ=2.7–4.1 ns. On the other hand, colors of the fluorophores recrystallized from acetone were yellow for **1a** and **2a**, and yellowish-orange for **3a**, and light-yellow for **4a** and **5a**, and the fluorescent colors were yellowish-green for **1a**–**3a**, green for **4a**, and bluish-green for **5a**. The fluorescence excitation and emission maxima (λ^{ex}_{max} and λ^{em}_{max}) of **1a**–**5a** in the crystalline state were red-shifted by 55–115 nm and 15–40 nm, respectively, compared with those for the corresponding dyes in 1,4-dioxane, being accompanied by the considerable decrease in the fluorescence quantum yield (Φ_F) (Table 1). For donor–π-acceptor type fluorescent dyes, in general, the red-shifts of λ^{ex}_{max} and λ^{em}_{max}, and the lowering of Φ_F by changing from solution to the crystalline state are quite common and explained in terms of the formation of intermolecular π–π interactions in the crystalline state leading to delocalization of excitons or eximers.[4] We see from Table 1 that the red-shifts of λ^{ex}_{max} and λ^{em}_{max} for **3a** in the crystalline state relative to that in solution are exceptionally larger than the other dyes. Most likely, this may be caused from the formation of intermolecular hydrogen bondings between the carboxyl groups in **3a**, which are also responsible for the significant fluorescence quenching observed with **3a** in the solid state.[5]

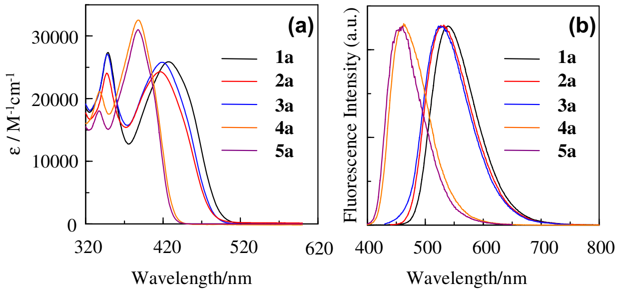

Figure 1. (a) Absorption and (b) fluorescence spectra of **1a**–**5a** in 1,4-dioxane.

Table 1
Solid-state photophysical data for **1a**–**5a** before and after grinding

Dye	Excitation λ^{ex}_{max}/nm	Emission λ^{em}_{max}/nm	Φ_F[a]	τ_1/ns[b] (A_1/%)[c]	τ_1/ns[b] (A_2/%)[c]
1a (before)	507	561	<0.02	0.6 (77)	3.2 (23)
1a (after)	561	614	0.06	0.9 (37)	4.0 (63)
2a (before)	486	548	<0.02	0.4 (99)	3.7 (1)
2a (after)	526	589	0.03	0.3 (87)	2.2 (13)
3a (before)	531	564	—[d]	—[d]	—[d]
3a (after)	568	596	—[d]	—[d]	—[d]
4a (before)	460	500	0.09	0.6 (57)	2.5 (43)
4a (after)	475	518	0.13	0.6 (60)	2.8 (40)
5a (before)	443	471	0.05	0.3 (96)	1.6 (4)
5a (after)	443	474	0.09	0.3 (83)	1.8 (17)

[a] Fluorescence quantum yield.
[b] Fluorescence lifetime.
[c] Fractional contribution.
[d] Too weak.

By grinding the solids in a mortar with a pestle, the dyes **1a** and **2a** changed their colors to orange and exhibited strong reddish-orange fluorescence. On the other hand, a little change of the color and fluorescent color was observed in dye **4a**. The photophysical data of **1a**–**5a** before and after grinding of as-recrystallized dyes are summarized in Table 1. After grinding, the λ^{ex}_{max} and λ^{em}_{max} for **1a**–**4a** are red-shifted by 15–54 nm and 16–53 nm, respectively. The degrees of the red-shift ($\Delta\lambda^{ex}_{max}$, $\Delta\lambda^{em}_{max}$) decrease in the order of **1a** (54, 53)>**2a** (40, 41)>**3a** (37, 32)>**4a** (15, 18), agreeing with the order of increasing the electron-accepting ability of *p*-substituted phenyl group. It is worth noting here that the Φ_F values are enhanced by grinding from 0.02, 0.02, and 0.09–0.06, 0.03, and 0.13 for **1a**, **2a**, and **4a**, respectively. When the ground samples were heated at 120–180 °C (over recrystallization (T_c), described later) or exposed to organic solvents, such as acetone for several minutes, the dyes except **3a** recovered to the original colors. The color and fluorescent color changes for powder of **1a** by grinding and heating are typically shown in Figure 2a and the excitation and fluorescence spectral changes are also shown in Figures 2a and c. In contrast to the dyes **1a**–**4a**, the dye **5a** did not exhibit appreciable changes of λ^{ex}_{max} and λ^{em}_{max} by grinding, although a slight increase of Φ_F was observed.

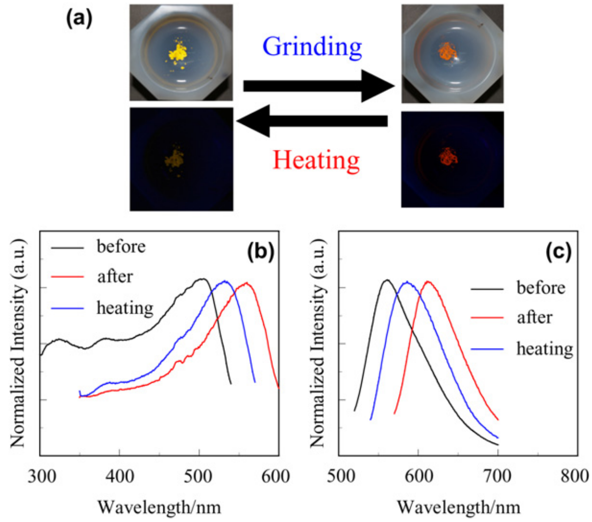

Figure 2. (a) Photographs of powder of **1a** under room light (top) and under UV irradiation (down) before and after grinding and (b) excitation and (c) fluorescence spectra of **1a** before and after grinding, and after heating the ground solid at 150 °C.

The time-resolved fluorescence spectroscopy with the dyes **1a**, **2a**, **4a**, and **5a** revealed that, irrespective of grinding, the fluorescence decay profiles fitted biexponential curves with fluorescence lifetimes of τ_1=0.3–0.9 ns and τ_2=1.6–4.0 ns. The emission wavelengths in the time-resolved measurements (λ^{trs}_{max}) were dependent on the time window: for the as-recrystallized dye, **1a**: 559 nm for 0–5 ns to 587 nm for 7–20 ns, **2a**: 555 nm for 0–5 ns to 595 nm for 7–20 ns, **4a**: 510 nm for 0–5 ns to 530 nm for 7–20 ns, and **5a**: 470 nm for 0–5 ns to 500 nm for 7–20 ns; for the ground dye, **1a**: 614 nm for 0–5 ns and 620 nm for 7–20 ns, **2a**: 595 nm for 0–5 ns to 610 nm for 7–20 ns, **4a**: 520 nm for 0–5 ns to 540 nm for 7–20 ns, and **5a**: 470 nm for 0–5 ns to 500 nm for 7–20 ns. The ratios of fractional contributions (A_1/A_2) decreased in common by grinding: $(A_1/A_2)_{after}/(A_1/A_2)_{before}$=0.18, 0.04, 1.13, and 0.20 for **1a**, **2a**, **4a**, and **5a**, respectively. The fluorescence decay profiles indicate the existence of two distinct emitting states before and after grinding.

The XRD measurements with as-recrystallized dyes **1a**–**5a** exhibited diffraction peaks ascribable to well-defined microcrystalline structures. After grinding, they almost disappeared, showing that the crystal lattice was significantly disrupted by grinding. Except **3a**, the diffraction peaks of the ground dyes after being heated were quite similar to those before grinding, suggestive of recovery of the microcrystalline structure by heating. The DSC analysis was made to clarify thermal properties of these dyes. The results indicated that the dyes (except **3a**, which showed decomposition) before grinding showed only one sharp endothermic peak associated with melting. On the other hand, the ground solids underwent an endothermic glass transition (T_g) and then recrystallization (T_c) before melting (T_m).

The XRD patterns and DSC curves for **1a** are shown in Figure 3 (see Table S1 in the supplementary data for the XRD data and DSC data). The XRD and DSC studies suggest strongly that the mechanofluorochromism of **1a**–**5a** is not just a matter of events originating from a reversible change between crystalline and amorphous states by grinding and heating, because the dye **5a** did not exhibit such a mechanofluorochromism. In order to know the change in the molecular packing before and after grinding, we measured the densities of the solids before and after grinding by Archimedian method. The densities were found to be increased by grinding from 1.32, 1.37, and 0.96 g cm^{-3} to 1.36, 1.41, and 1.01 g cm^{-3} for **1a**, **2a**, and **4a**, respectively, showing that the dye molecules are more densely packed after grinding. Unfortunately, it was not possible to measure the densities of the solids for the other compounds, because it is soluble in solvents used in performing the measurement.

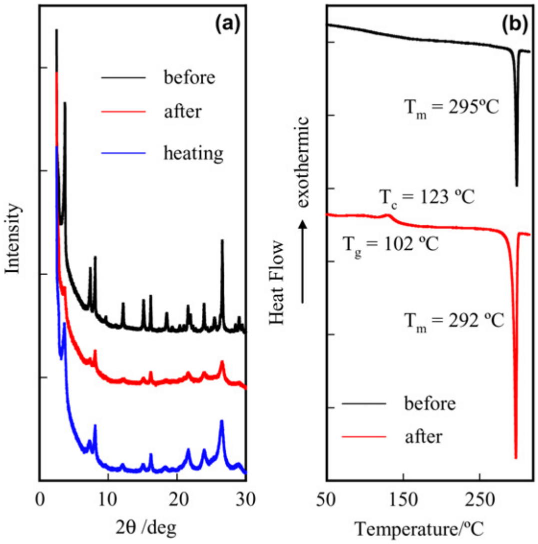

Figure 3. (a) XRD patterns and (b) DSC curves (scan rate: 10 °C min^{-1}) of **1a** before and after grinding, and after heating the ground solid.

As mentioned above, in the case of **1a**–**5a**, the red-shifts of λ_{max}^{ex} and λ_{max}^{em}, and lowering of Φ_F by changing from solution to the crystalline state are explainable in terms of strong π–π interactions in the crystalline state. When the dyes are in the crystalline state, the π–π interactions between adjacent molecular planes give rise to stacking of the dye molecules and the stacking will be also realized so as to arrange dipole moments in parallel orientation. In fact, a single-crystal X-ray structural analysis for **1d** indicates that the overlapping between π-planes of the fluorescent molecules have a centrosymmetry.[2] On the other hand, by grinding as-recrystallized dyes, the molecules may move closer to each other so as to minimize the dipole–dipole interaction energy (so as to arrange adjacent dipole moments in head-to-tail orientation) as well as the intermolecular π–π interaction energy, as evidenced by the increased densities for the dyes in amorphous state. The former interaction energy will be enhanced for dyes with greater dipole moments. The dipole moments (μ_g) of **1a**–**5a** in the ground states were evaluated from semi-empirical molecular orbital (MO) calculations by the INDO/S method after geometrical optimizations by the MOPAC/AM1 method.[6,7] The μ_g values of **1a**–**3a** were 5.21, 6.03, and 7.18 D, respectively, much greater than 1.47 D for **4a** and 1.65 D for **5a**, reflecting that the dyes **1a**–**3a** have fairly large π-conjugated planes with strong electron-accepting and donating moieties on both ends of the molecules. On these bases, it may be inferred that the red-shifts of λ_{max}^{em} and λ_{max}^{ex} observed with **1a**–**3a** by changing from the crystalline state to the amorphous state are caused by strong dipole–dipole interactions, whereas a negligible mechanofluorochromism for **4a** and **5a** is ascribable to their weak dipole characters. On the other hand, the Φ_F values in amorphous state are higher than those in the crystalline state. This suggests that a non-radiative decay route for the excited states is relatively discouraged by the π–π interactions in the amorphous states for this series of dyes.

3. Conclusions

We have synthesized a new class of heteropolycyclic D–π-A mechanofluorochromic dyes to figure out the molecular structure required for manifestation of the mechanofluorochromism. It is found that the mechanofluorochromism is attributed to a reversible switching between crystalline and amorphous states with changes of dipole–dipole interaction and intermolecular π–π interaction by changes of the densities of the solids before and after grinding. This study demonstrates that the most important point for developing mechanofluorochromic dyes is to design heteropolycyclic dye molecules with large dipole moments and thus strong D–π-A characters.

4. Experimental section

4.1. General

Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields (Φ) were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system (λ_{ex}=325 nm). Fluorescence lifetimes were determined with a HAMAMATSU Photonics C4334/C8898 time-resolved spectrophotometer by excitation at 375 nm (laser diode). Powder X-ray diffraction measurements were performed on a Buruker D8 diffractometer with Cu Kα radiator. Differential scanning calorimetry (DSC) of the samples was carried out using a Shimadzu DSC-60. The densities of the solids were evaluated with a Shimadzu AUW220D balance equipped with SMK-401 saucer by Archimedian method.

4.2. Computational methods

The semi-empirical calculations were carried out with the WinMOPAC Ver. 3.9 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were made using the AM1 method.[6] All geometries were completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Dipole moments of the compounds were evaluated from the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic).[7] All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field–configuration interaction), which includes the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.07.018. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. (a) Mizukami, S.; Houjou, H.; Sugaya, K.; Koyama, E.; Tokuhisa, H.; Sasaki, T.; Kanesato, M. *Chem. Mater.* **2005**, *17*, 50; (b) Sagara, Y.; Mutai, T.; Yoshikawa, I.; Araki, K. *J. Am. Chem. Soc.* **2007**, *129*, 1520; (c) Kunzalman, J.; Kinami, M.; Crenshaw, B. R.; Protasiewicz, J. D.; Weder, C. *Adv. Mater.* **2008**, *20*, 119; (d) Ito, H.; Saito, T.; Oshima, N.; Kitamura, N.; Ishizaka, S.; Hinatsu, Y.; Wakeshima, M.; Kato, M.; Tsuge, K.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 10044.
2. Ooyama, Y.; Kagawa, Y.; Fukuoka, H.; Ito, G.; Harima, Y. *Eur. J. Org. Chem.* **2009**, *31*, 5321.
3. Ooyama, Y.; Ito, G.; Kushimoto, K.; Komaguchi, K.; Imae, I.; Harima, Y. *Org. Biomol. Chem.* **2010**, *8*, 2756.
4. (a) Langhals, H.; Potrawa, T.; Nöth, H.; Linti, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 478; (b) Yeh, H.-C.; Wu, W.-C.; Wen, Y.-S.; Dai, D.-C.; Wang, J.-K.; Chen, C.-T. *J. Org. Chem.* **2004**, *69*, 6455; (c) Ooyama, Y.; Okamoto, T.; Yamaguchi, T.; Suzuki, T.; Hayashi, A.; Yoshida, K. *Chem.—Eur. J.* **2006**, *12*, 7827.
5. (a) Ooyama, Y.; Nakamura, T.; Yoshida, K. *New J. Chem.* **2005**, *29*, 447; (b) Ooyama, Y.; Uwada, K.; Kumaoka, H.; Yoshida, K. *Eur. J. Org. Chem.* **2009**, *34*, 5979.
6. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
7. (a) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111; (b) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223; (c) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21; (d) Kurtz, H. A.; Stewart, J. J.; Dieter, D. M. *J. Comput. Chem.* **1990**, *11*, 82.