Luminescence Switching

DOI: 10.1002/anie.200803975

Switching of Polymorph-Dependent ESIPT Luminescence of an Imidazo[1,2-*a*]pyridine Derivative[**]

Toshiki Mutai, Haruhiko Tomoda, Tatsuya Ohkawa, Yuji Yabe, and Koji Araki**

Organic solid-state luminescent materials have been attracting considerable interest in various fields of application.[1] Switching and tuning of solid-state luminescence properties, particularly by controlling the mode of molecular packing instead of chemical alteration of the molecules, is one of the recent targets of both fundamental research and practical applications. An increasing number of reports on this subject[2] has appeared recently. However, successful examples of achieving efficient switching of solid-state luminescence by means of a dry process are rather limited.[3,4] One reason for this difficulty may be the absence of an effective mechanism to transform the alteration of molecular packing into different luminescence properties. Up to now, successful systems have generally adopted transformation between the monomeric and dimeric/excimeric states as the mechanism of packing-induced emission switching.[3]

Here we report a novel and effective mechanism of switching organic solid-state luminescence based on an excited-state intramolecular proton-transfer (ESIPT)[5] process. Two crystal polymorphs of 2-(2′-hydroxyphenyl)imidazo[1,2-*a*]pyridine (**1**; Scheme 1) exhibit bright photoluminescence of different colors—blue-green and yellow—both of which are due to ESIPT (Figure 1). X-ray crystallographic analysis showed different molecular conformations and modes of packing in these two crystal polymorphs, and interconversion of the polymorphs by a thermal dry process successfully and repeatedly realized switching of ESIPT luminescence.

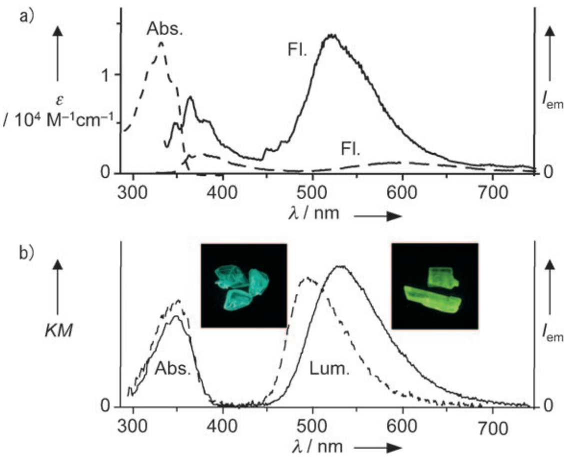
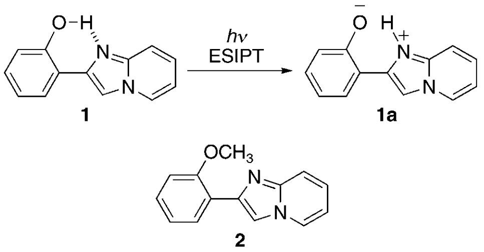


Figure 1. a) Absorption and fluorescence spectra of **1** in THF solution at room temperature (dashed line) and 77 K (solid line). b) Absorption and luminescence spectra of polymorph BG (dotted line) and Y (solid line). Inset: Pictures of both polymorphs under UV irradiation (365 nm).



Scheme 1. Molecular structures of **1**, **1a**, and **2**.

Slow and fast cooling of a hot solution of **1** in aqueous ethanol gave crystal polymorphs BG and Y, respectively. In the IR spectra, an O–H stretching band at around 3135 cm^{-1} for both crystals indicated formation of intramolecular hydrogen bonds between the OH group and nitrogen atom N1 in the imidazopyridine ring.

On excitation at 330 nm, **1** showed weak fluorescence (quantum yield $\Phi = 0.01$–0.08) in the visible region in dilute solution: blue fluorescence at 375 nm in protic ethanol, orange fluorescence with a large Stokes shift at 567 nm in nonpolar cyclohexane, and both blue and orange fluorescence at 377 and 602 nm in THF (Table 1). Figure 1a shows the emission spectra of **1** in THF solution. In contrast, the 2′-methoxy derivative **2**, which does not form an intramolecular hydrogen bond, shows only blue fluorescence, regardless of the solvent. These results indicated that the blue fluorescence is direct emission from a locally excited state, and the orange fluorescence is the ESIPT fluorescence from **1a** (Figure 1a). These assignments are in good agreement with those reported previously by Douhal et al.,[6] who also suggested that the significant Stokes shift of the orange emission is due to solvent rearrangement and/or further conformational change of a zwitterionic ESIPT state.

---

[*] Dr. T. Mutai, T. Ohkawa, Prof. Dr. K. Araki
Institute of Industrial Science, The University of Tokyo
4-6-1, Komaba, Meguro-ku, Tokyo 153-8505 (Japan)
Fax: (+81) 3-5452-6364
E-mail: araki@iis.u-tokyo.ac.jp
mutai@iis.u-tokyo.ac.jp
Prof. Dr. H. Tomoda, Y. Yabe
Department of Applied Chemistry, Shibaura Institute of Technology,
Toyosu, Kouto-ku, Tokyo 108-8548 (Japan)

[**] This work was supported by a Grant-in-Aid (No. 18310076, 18710077, and 20510094) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. ESIPT = excited-state intramolecular proton-transfer.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803975.

Table 1: Absorption and emission of **1** and **2** in various states.

	λ_{abs} [nm]	λ_{em} [nm] (Φ)	τ [ns]
1			
THF (RT)	332, 346	377 (0.08)	2.63
		602 (0.02)	0.52
THF (77 K)	332[a], 349[a]	370	2.69
		521	5.26
polymorph BG	339[b]	496 (0.50)	5.91
polymorph Y	337[b]	529 (0.37)	5.84
amorphous	337[b]	527 (0.39)	6.39
2			
THF (RT)	332	378 (0.11)	2.56
THF (77 K)	329[a], 344[a]	348, 366, 383	2.81
powder	312[b]	382 (0.24)	2.75

[a] Excitation spectrum. [b] Kubelka–Munk spectrum.

When solutions of **1** and **2** in THF were frozen at 77 K, the fine-structured blue fluorescence from the locally excited state remained unchanged, but the ESIPT fluorescence of **1** shifted to 521 nm. Since this dual blue and yellow emission of **1** was also observed in a polystyrene matrix at room temperature, the shift of the ESIPT fluorescence of **1** from orange to yellow in rigid matrices is ascribed to suppression of the stabilization of the excited zwitterionic species through solvent rearrangement and/or further conformational changes of the substrate. A similar color change of the ESIPT fluorescence of **1** from orange to yellow in poly(methyl methacrylate) was also reported.[6b]

Absorption bands of both crystal polymorphs appeared at around 340 nm, close to that observed in a dilute THF solution (Figure 1 b). On excitation at 330 nm, the BG and Y polymorphs exhibited blue-green (496 nm) and yellow luminescence (529 nm), respectively, with considerable quantum yield ($\Phi = 0.37$–0.50). Amorphous solid **1**, prepared by the freeze-drying method, showed a yellow luminescence similar to that of polymorph Y. Though their luminescence colors were different, their Stokes shifts of 9300–10800 cm^{-1} were large enough to be well within the range of typical ESIPT fluorescence.[5] Since the structureless spectral shape and luminescence lifetime of the crystalline and amorphous solids of **1** were essentially identical to those observed in the frozen dilute solution, the observed yellow and blue-green luminescence of the solids with significant Stokes shifts were assigned as ESIPT luminescence. Thus, ESIPT luminescence is sensitive to the environment, not only to the type of solvent and matrix rigidity, but also to the mode of molecular packing in the solid state. On the other hand, the fine-structured blue luminescence (ca. 380 nm) emitted directly from the locally excited state was little affected by the environment, either in solution or in the solid. Moreover, the ESIPT luminescence is a monomeric emission, since no apparent difference was observed between the diluted and condensed states. To understand the role of the molecular packing in the solid-state luminescence of **1**, X-ray crystallographic analyses of crystal polymorphs BG ($Pbca$, $Z = 8$) and Y ($P2_1/c$, $Z = 8$) were performed at room temperature.[7] The asymmetric unit is composed of one and two molecules in polymorphs BG and Y, respectively, and each molecule clearly shows formation of an O−H⋯N1 intramolecular hydrogen bond (Figures S3 and S4 in Supporting Information). The most notable conformational difference is the N1-C2-C1′-C2′ dihedral angle θ between the phenyl and imidazopyridine rings. While the two aromatic rings are nearly coplanar ($\theta = -1.0$ and 1.3°) in polymorph Y, the conformation of **1** is twisted in polymorph BG ($\theta = 5.8°$). The distances O⋯N1 representative of the length of the intramolecular hydrogen bond showed only a slight difference (less than 0.02 Å).

In frozen solutions, amorphous polymer matrices, or pure amorphous solids, where no organized molecular assembly is present, substrates tend to be in energetically stable conformation on average. Geometry optimization by HF/6-31G(d) calculation indicated a coplanar conformation as the lowest energy structure.

In polymorph Y, the molecules of **1** packed in the structure very close to the coplanar conformation. Since these solids showed identical yellow ESIPT luminescence, the most stable conformation of **1** is likely to be the coplanar structure. On the other hand, that blue-green ESIPT luminescence is emitted only from polymorph BG suggests a substantial effect of the mode of the molecular packing. As the molecular geometry is fixed in a twisted conformation in polymorph BG, this packing-induced small deviation of the molecular conformation may affect the ESIPT process and lead to higher-energy ESIPT luminescence.

We then examined the thermal properties of both polymorphs. In the first heating curve of differential scanning calorimetry (DSC), polymorph BG showed an endothermic peak at the melting point (141 °C). On the other hand, both polymorph Y and the amorphous solid displayed a small peak at around 131 °C in addition to the melting peak at 141 °C (Figure S5 in Supporting Information), and the former was found to correspond to the phase transition to polymorph BG. When powdered crystals of polymorph Y or the amorphous solid were heated at 135 °C for 1 min on a glass plate, the XRD pattern of the heated powder (Figure 2 d) was different from that of starting polymorph Y (Figure 2 c) or the amorphous solid and was comparable to the pattern of polymorph BG (Figure 2 a). Accordingly, the luminescence turned from yellow to blue-green. The resultant blue-green-emitting powder was then melted and kept at 150 °C for 1 min. Quick cooling of the heated glass plate by ice cubes yielded a yellow-emitting solid. The XRD pattern showed only a vague diffraction image, that is the major state of the solid was amorphous.

Based on the above findings, we examined the switching ability of the polymorph-dependent luminescence of **1**. Starting from polymorph Y, powdered crystals were kept at 135 °C for 1 min to convert them to the blue-green-emitting state. They were then heated at 150 °C for 3 min and rapidly cooled to give the yellow-emitting state. Performing the switching cycle six times without deterioration (Figure 3) demonstrated that the color of the efficient luminescence of **1** is switched easily and reproducibly by the thermal dry process.

In summary, reproducible switching of organic solid-state luminescence was achieved on the basis of the highly efficient ESIPT luminescence of **1** ($\Phi = 0.37$–0.50) by thermal control

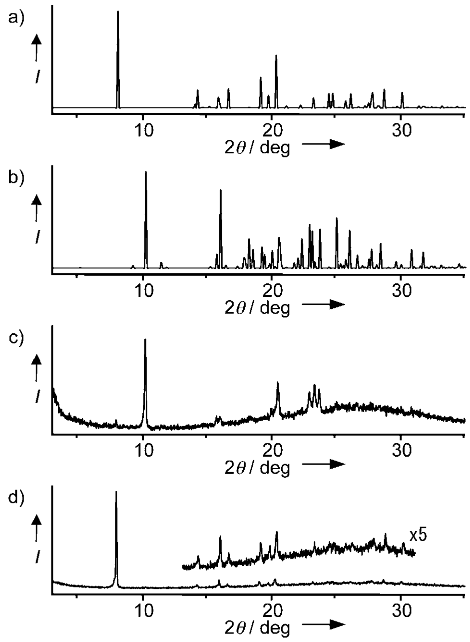


Figure 2. XRD profiles of crystal polymorphs BG (a) and Y (b) calculated from corresponding crystal structures, and observed profiles of polymorph Y at room temperature (c) and after heating at 135 °C for 1 min (d).

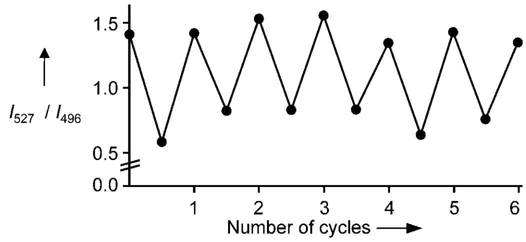


Figure 3. Plot of the intensity ratio of yellow and blue-green luminescence (I_{527}/I_{496}) against the number of switching cycles.

of the molecular packing. The clear switching of the luminescence color demonstrates that the ESIPT process is a promising mechanism for packing-to-luminescence transduction and amplification that offers a novel design concept for tunable organic luminescent solids. Further studies on the detailed mechanism, especially the relationship between crystal structure and the luminescence properties are underway.

Received: August 12, 2008

Keywords: hydrogen bonds · luminescence · nitrogen heterocycles · polymorphism · solid-state structures

---

[1] a) S. R. Forrest, *Nature* **2004**, *428*, 911–918; b) G. Barbarella, M. Melucci, G. Sotgiu, *Adv. Mater.* **2005**, *17*, 1581–1593; c) Y. Taniguchi, *J. Photopolym. Sci. Technol.* **2002**, *15*, 183–184; d) A. Montali, C. Bastiaansen, P. Smith, C. Weder, *Nature* **1998**, *392*, 261–264.

[2] a) R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. P. Rath, N. Tamaoki, S. Das, *J. Phys. Chem. C* **2008**, *112*, 2137–2146; b) H. Tong, Y. N. Hong, Y. Q. Dong, Y. Ren, M. Haussler, J. W. Y. Lam, K. S. Wong, B. Z. Tang, *J. Phys. Chem. B* **2007**, *111*, 2000–2007; c) C. Kitamura, T. Ohara, N. Kawatsuki, A. Yoneda, T. Kobayashi, H. Naito, T. Komatsu, T. Kitamura, *CrystEngComm* **2007**, *9*, 644–647; d) Y. Qian, S. Li, G. Zhang, Q. Wang, S. Wang, H. Xu, C. Li, Y. Li, G. Yang, *J. Phys. Chem. B* **2007**, *111*, 5861–5868; e) H. Y. Zhang, Z. L. Zhang, K. Q. Ye, J. Y. Zhang, Y. Wang, *Adv. Mater.* **2006**, *18*, 2369–2372; f) Y. Mizobe, N. Tohnai, M. Miyata, Y. Hasegawa, *Chem. Commun.* **2005**, 1839–1841; g) K. Hirano, S. Minakata, M. Komatsu, J. Mizuguchi, *J. Phys. Chem. A* **2002**, *106*, 4868–4871; h) N. Sanz, P. L. Baldeck, J. F. Nicoud, Y. Le Fur, A. Ibanez, *Solid State Sci.* **2001**, *3*, 867–875.

[3] a) J. Kunzelman, M. Kinami, B. R. Crenshaw, J. D. Protasiewicz, C. Weder, *Adv. Mater.* **2008**, *20*, 119–122; b) S. C. F. Kui, S. S. Y. Chui, C. M. Che, N. Y. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 8297–8309; c) C. Wang, Z. Wang, D. Q. Zhang, D. B. Zhu, *Chem. Phys. Lett.* **2006**, *428*, 130–133; d) S. Mizukami, H. Houjou, K. Sugaya, E. Koyama, H. Tokuhisa, T. Sasaki, M. Kanesato, *Chem. Mater.* **2005**, *17*, 50–56; e) J. W. Chen, B. Xu, X. Y. Ouyang, B. Z. Tang, Y. Cao, *J. Phys. Chem. A* **2004**, *108*, 7522–7526; f) B. K. An, S. K. Kwon, S. D. Jung, S. Y. Park, *J. Am. Chem. Soc.* **2002**, *124*, 14410–14415; g) N. Chandrasekharan, L. A. Kelly, *J. Am. Chem. Soc.* **2001**, *123*, 9898–9899.

[4] a) T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005**, *4*, 685–687; b) Y. Sagara, T. Mutai, I. Yoshikawa, K. Araki, *J. Am. Chem. Soc.* **2007**, *129*, 1520–1521.

[5] a) S. M. Ormson, R. G. Brown, *Prog. React. Kinet.* **1994**, *19*, 45–91; b) A. U. Khan, M. Kasha, *Proc. Natl. Acad. Sci. USA* **1983**, *80*, 1767–1770.

[6] a) A. Douhal, F. Amat-Guerri, A. U. Acuña, *J. Phys. Chem.* **1995**, *99*, 76–80; b) A. Douhal, F. Amat-Guerri, A. U. Acuña, *Angew. Chem.* **1997**, *109*, 1586–1588; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1514–1516; c) A. Douhal, *Ber. Bunsen-Ges.* **1998**, *102*, 448–451.

[7] a) Crystallographic data for polymorph BG: $C_{13}H_{10}N_2O$, $M = 210.23$, orthorhombic, *Pbca*, $a = 7.6560(2)$, $b = 12.1630(3)$, $c = 22.2380(5)$ Å, $V = 2070.80(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.349$ g cm^{-3}, $T = 298(2)$ K, 18651 measured and 2030 independent reflections, $R_1 = 0.0548$, $wR_2 = 0.1297$, GOF = 1.104; b) crystallographic data for polymorph Y: $C_{13}H_{10}N_2O$, $M = 210.23$, monoclinic, $P2_1/c$, $a = 18.2400(4)$, $b = 5.77300(10)$, $c = 20.3010(5)$ Å, $\beta = 108.1650(10)°$, $V = 2031.15(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.375$ g cm^{-3}, $T = 298(2)$ K, 18482 measured and 3733 independent reflections, $R_1 = 0.0624$, $wR_2 = 0.1732$, GOF = 1.116. CCDC 698144 (polymorph BG) and 698145 (polymorph Y) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.