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LETTER

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Fabrication of Colorless Organic Materials Exhibiting White Luminescence Using Normal and Excited-State Intramolecular Proton Transfer Processes

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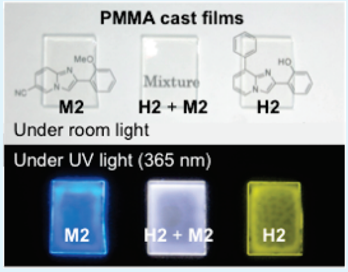
S *Supporting Information*

ABSTRACT: Organic, white luminescent materials were fabricated using a mixture of proton-transfer and nonproton-transfer fluorophores. 2′-Methoxy and 2′-hydroxy derivatives of 2-phenylimidazo[1,2-*a*]pyridine (PIP) have similar UV-absorption properties; however, they exhibit mechanistically different luminescence respectively ascribable to the normal (∼420 nm) and excited-state intramolecular proton transfer processes (∼530 nm) in the solid state. UV-irradiation of mixed solids excites both components concurrently and results in efficient white luminescence composed of two independent emissions without involving energy transfer process. White luminescent solids are easily transformed into vapor-deposited films under mild conditions, and a colorless and transparent thin film by dissolving in PMMA.



KEYWORDS: white luminescence, solid materials, fluorescence, OLED, PMMA, excited-state intramolecular proton transfer, imidazopyridine

INTRODUCTION

Organic solid-state luminescent materials have been attracting considerable interest in various fields.[1−4] Among them, those displaying white emission are of primary interest because of possible application as a new class of light sources.[5−7]

To date, most white emission is the so-called "pseudo-white" luminescence realized by mixing blue- and yellow-emitting species that are a proper combination of energy donors and acceptors,[5] respectively (Figure 1a). However, designing donor−acceptor systems that can function in the solid state is rather complicated because the energy transfer efficiency is sensitive to the concentration and miscibility of components in matrices as well as undesirable intermolecular interaction, among other things. It is also noteworthy that such white-emitting devices are generally yellow-brownish in color, because most low-energy luminescent compounds absorb visible light. Therefore, they are rather unsuitable for applications where good visibility and color rendering properties are required.

An approach to overcome the above-mentioned difficulties is to use yellow-emitting compounds that absorb only UV light, by which the excited-state energy transfer from a blue luminophore is energetically blocked and colorless devices can be developed. However, yellow-emitting compounds that have such a large Stokes′ shift are rather rare.

A photoinduced proton transfer through an intramolecular hydrogen bond is termed the excited-state intramolecular proton transfer (ESIPT), which is a remarkably fast process (rate constant $k \approx 1 \times 10^{13}$ s^{-1}) comparable to the internal conversion.[8,9] Emission from the ESIPT state[10,11] is characterized by a large Stokes′ shift (8000−11 000 cm^{-1}), which enables yellow luminescence by UV-excitation. S. Y. Park and group[12,13] have reported white-light-emitting devices using two ESIPT luminophores having different Stokes′ shift, and a group of P. T. Chou[14] has described a white-light-emitting solution using ESIPT and normal luminophores. However, the development of such systems remains a challenge because compounds exhibiting ESIPT luminescence with a high quantum yield are quite limited, especially in the solid state.

We recently reported[15] that 2′-hydroxy derivative of 2-phenylimidazo[1,2-*a*]pyridine (PIP) **H1**, having an intramolecular hydrogen bond (OH···N1), exhibits efficient ESIPT luminescence in the solid state (yellow, $\Phi = 0.37$), whereas 2′-methoxy PIP (**M1**) having no intramolecular hydrogen bond shows a normal luminescence (blue, $\Phi = 0.24$). Unlike the significant difference in luminescence, the absorption bands of **H1** and **M1**, shown in near-UV region (300−370 nm), are almost identical.

Inspired by the above results, we herein report newly designed white luminescent materials based on PIP derivatives, which exhibit ESIPT and a normal luminescence simply by the introduction/removal of an intramolecular hydrogen bond, and importantly, they do so without causing any changes in the UV-absorption properties (Figure 1b). The advantages of such white luminescent materials are (i) easy concurrent excitation because of energetically matched absorption and (ii) realizing blue and yellow emission through electronically independent luminescent processes. Thus, no donor−acceptor relationship

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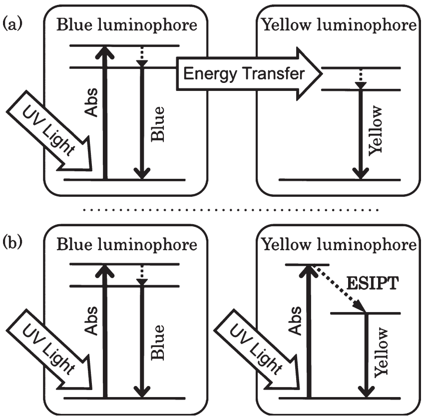


Figure 1. Energy diagrams of white-luminescent materials composed of blue and yellow luminescent species that function as (a) a donor—acceptor system, and (b) independent luminophores.

exists in the relevant mixture. Furthermore, as both luminescent PIPs absorbed only near-UV light, we successfully fabricated a white luminescent polymer film that was colorless and transparent, which would enable its use in novel applications where good visibility and color rendering properties are required.

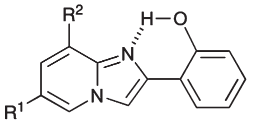
EXPERIMENTAL SECTION

Syntheses of **H1** and **M1** were reported previously,[14] and those of **H2** and **M2** were described in the Supporting Information (SI). All compounds were obtained as a white solid. Mixed solids of **H1** and **M1**, and those of **H2** and **M2** were prepared by grinding the two respective compounds in a mortar.

A thin solid layer of a mixture of **H2** and **M2** was prepared by vapor deposition, which is described as follows. Compounds **H2** (1.5 mg) and **M2** (5 mg) were placed at the bottom of a sublimation tube, and a quartz plate (15 × 15 × 0.15 mm) was positioned on a water-cooled target. The tube was then heated to 140 °C under reduced pressure (2 mmHg) for 2 h to form a white layer on the quartz plate.

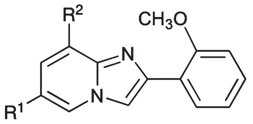
To fabricate the luminescent polymer film, mixed solids of **H2** and **M2** (total 4×10^{-6} mol, *ca.* 1 mg) and poly(methyl methacrylate) (PMMA) (M_w = 120 000, 0.2 g) were dissolved in benzene (2 mL), which was cast on a quartz plate, dried in air for 2 h, and then heated at 100 °C under reduced pressure for 12 h.

A solid-state absorption spectrum was obtained by the Kubelka—Munk conversion of a diffractive reflectance spectrum measured on a JASCO FP-6600 spectrofluorophotometer equipped with a JASCO ILF-533 integral sphere. Samples were prepared from finely ground compounds (1 mg) and powdered sodium chloride (1 g), which were mixed in a glass tube and then placed in a 5 mm quartz cell. The luminescence spectra in the solid state were obtained by spreading finely powdered solid on a quartz plate that was placed in an ILF-533 integral sphere and measured on a JASCO FP-6600 spectrofluorophotometer. The quantum yield in the solid state was obtained using calculation software based on a literature method[16] installed in the spectrofluorophotometer. The *x,y* coordinates on a Commission Internationale de l'Eclairage (CIE) 1931 chromaticity diagram were calculated from an emission spectrum measured on a HAMAMATSU PMA-11 multichannel analyzer equipped with an integral sphere by excitation at 365x nm.



H1, **H2**

	R^1	R^2
H1	H	H
H2	H	C_6H_5



M1, **M2**

	R^1	R^2
M1	H	H
M2	CN	H

Figure 2. Molecular structure of the 2′-hydroxy PIPs (**H1**, **H2**) and 2′-methoxy PIPs (**M1**, **M2**).

Table 1. Absorption and Luminescence Properties in the Solid State

compd	λ_{abs} (nm)[a]	λ_{em} (nm) (Φ)	CIE coordinate
H1	335	529 (0.37)	(0.36, 0.55)
H2	330	536 (0.31)	(0.41, 0.50)
M1	312	382 (0.24)	(0.23, 0.22)
M2	348	422 (0.15)	(0.17, 0.09)

[a] Kubelka-Munk spectra.

RESULTS AND DISCUSSION

Figure 2 shows molecular structures of 2′-hydroxy (**H1** and **H2**) and 2′-methoxy (**M1** and **M2**) derivatives of PIP. In the infrared spectra of **H1** and **H2**, a sharp O—H stretching band appeared at around 3130 cm^{-1}, indicating the formation of an intramolecular hydrogen bond between the O—H and nitrogen (N1) in the imidazopyridine ring in the solid state.

The solid-state absorption and luminescence maxima of **H1**, **H2**, **M1** and **M2** are collected in Table 1. All compounds showed their absorption maxima in the UV region whether they have an intramolecular hydrogen bond or not. Upon excitation at 365 nm, hydroxy PIPs (**H1** and **H2**) exhibited strong luminescence at 529 and 536 nm, respectively, characterized by a large Stokes′ shift due to ESIPT process. Methoxy PIPs (**M1** and **M2**), on the other hand, showed efficient normal luminescence directly from S_1 excited state at 382 and 422 nm, respectively. Because the shapes of the absorption spectra of hydroxy and methoxy PIPs were similar to each other, both yellow and blue luminescence are achieved by photoexcitation at the same wavelength (Figure 3). It should be noted that the absorption bands did not trail into the visible region; this is consistent with the white color of the solid.

Moreover, the absorption energies of yellow-luminescent species (**H1** and **H2**) are greater than the luminescence energies of **M1** and **M2**, indicating that photoexcited energy transfer between hydroxy and methoxy PIPs is energetically blocked.

We then prepared mixtures of the parent compounds **H1** and **M1**, and examined their luminescence properties in the solid state. At a ratio of **H1**:**M1** = 1:100 by weight, the powder displayed a bright whitish luminescence that consisted of a prominent blue luminescence at 386 nm and a broad luminescence band in the low-energy range of 470—650 nm (see Figure S1 in the Supporting Information), which were clearly assignable to those of **M1** and **H1**, respectively. Thus, it is demonstrated that the whitish luminescence is a summation of the luminescence from **H1** and **M1**, which is also the reason for the linear

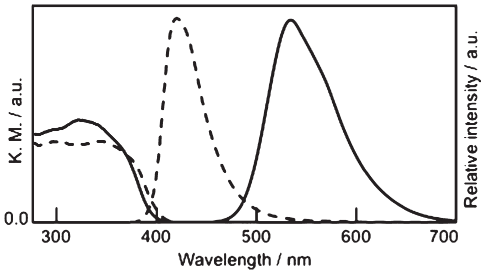


Figure 3. Solid-state absorption (Kubelka−Munk) and luminescence spectra of **H2** (solid line) and **M2** (broken line).

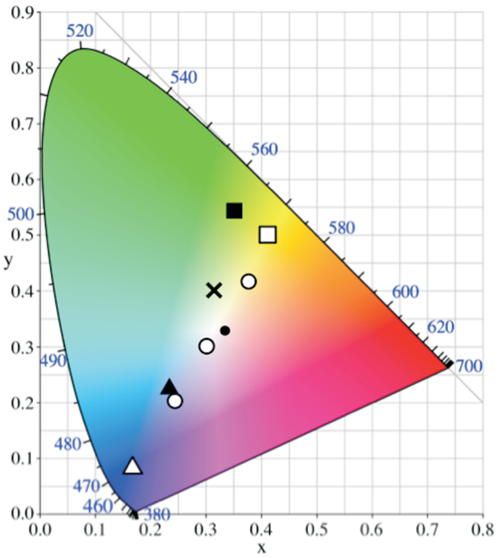


Figure 4. A CIE chromaticity diagram of **H1** (filled square), **H2** (open square), **M1** (filled triangle), **M2** (open triangle), a mixture of **H1** + **M1** (1:100; cross), and **H2** + **M2** (1:10, 3:10, and 10:10; open circle; from left to right). A black dot indicates the ideal white (x,y = 0.33, 0.33).

relationship of the x,y coordinates among each species (**H1** and **M1**) with the whitish luminescence ((x,y) = (0.32, 0.40)) in the CIE chromaticity diagram (Figure 4).

In the CIE chromaticity diagram, a line connecting the points of **H2** and **M2** runs quite close to the point of pure white light ((x,y) = (0.33, 0.33)). Therefore, a mixture of **H2** and **M2** is expected to be more suitable as a white luminescent material. The solid-state absorption spectra of a mixture of **H2** and **M2** were a summation of those of each compound, just as in the case of a mixture of **H1** and **M1**, indicating negligible electronic interaction in the ground state. A mixed solid with a ratio of **H2**:**M2** = 3:10 by weight displayed a bright white luminescence ($\Phi = 0.24$) at the x,y coordinate of (0.30, 0.31), which indicates almost pure white luminescence. The spectrum consisted of normal and ESIPT luminescence bands with maximum wavelengths at 416 and 535 nm, respectively.

The intensity ratio of the two luminescence bands varied according to the mixing ratio of **H2** and **M2**, and it resulted in a linear plot in the CIE chromaticity diagram (Figure 4). It should be emphasized that the shape and intensity of these dual luminescence spectra, including the white luminescence, were reasonably reproduced from those of **H2** and **M2** by considering absorption coefficient and quantum yield of each component as well as mixing ratio (see Figure S2 in the Supporting Information). Moreover, a decrease of luminescence lifetime of **M2**, a crucial evidence of excited-state energy transfer, was not observed, proving the lack of energy transfer from **M2** to **H2** (see the Supporting Information). Thus, it is concluded that **H2** and **M2** emit independently, and any intermolecular interactions that have a complex effect on the luminescence properties can be neglected. A prolonged illumination of UV light showed that the CIE coordinate of the white-luminescent mixture remained unchanged for 33 h in air, although the intensity of the luminescence decreased (see the Supporting Information).

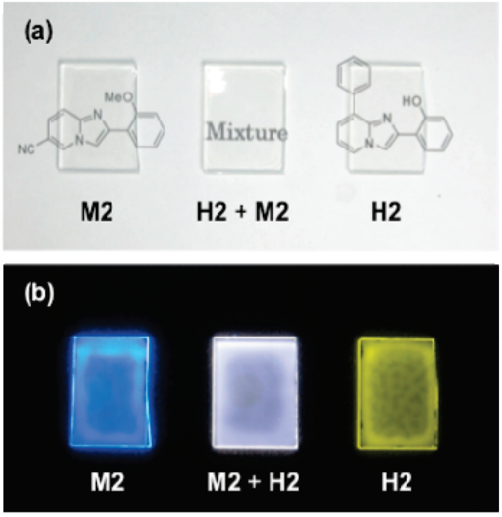


Figure 5. Images of PMMA films containing **M2**, **H2**+**M2** (11:7), and **H2** (from left to right) under (a) room light and (b) a UV lamp (365 nm).

The white-luminescent mixture of **H2** and **M2** was then applied to a vapor deposition process. Under a mild condition (140 °C, 3 mmHg), the mixed solid completely vaporized within 2 h and a quartz plate was uniformly coated with an opaque white layer (see Figure S3 in the Supporting Information). The content ratio of **H2** and **M2** determined by ^{1}H NMR was 3:10, which was identical to that of the starting mixed solid. The layer displayed a strong, nearly pure white luminescence ($\Phi = 0.18$; (x,y) = (0.30, 0.31)) (see Figure S4 in the Supporting Information). These results demonstrate that a white-luminescent layer can be readily fabricated by a common industrial method.

We also examined luminescence properties of **H2**, **M2** and their mixture in PMMA films. They were all colorless and transparent, and accordingly, the absorption spectra were observed at the UV region (see Figure S5 in the Supporting Information). It should be noted that the absorption spectrum of the mixture was a summation of those of **H2** and **M2**, and the spectrum showed no rise of the baseline that would imply light scattering, indicating that both compounds were well dissolved in PMMA matrix. At the ratio of **H2**:**M2** = 11:7 by weight, a PMMA film exhibited bright white luminescence ($\Phi = 0.22$) with the x,y coordinate (0.36, 0.33), which again indicated a linear plot with that of **H2** and **M2** in the CIE chromaticity diagram (see Figure S6 in the Supporting Information). Similar to the mixed solids, the shape and intensity of the spectrum were reasonably reproduced by the summation of those of **H2** and **M2**, revealing that compounds **H2** and **M2** independently exhibit luminescence both in concentrated and diluted environment.

Figure 5 shows photographs of PMMA cast films containing **H2**, a white-luminescent mixture (**H2**:**M2** = 11:7 by weight), and **M2** (from left to right). Because the films were colorless and transparent under room light regardless of the components, illustrations on a white paper appeared the same through and without these films. On the other hand, distinctive luminescence of blue, yellow and white were observed under a UV lamp (365 nm). It is therefore concluded that a colorless and transparent white-luminescent material that absorbs UV light only was realized.

CONCLUSIONS

In summary, we prepared white luminescent organic materials composed of two PIP-based compounds exhibiting normal and ESIPT luminescence as blue- and yellow-emitting species, respectively. Because there is a lack of spectral overlap between the absorption and luminescence bands, the two components do not have donor—acceptor relationship, which is generally the case for most white luminescent materials. Indeed, the intensity ratio of dual luminescence fairly reflected the mixing ratio of the two compounds, indicating that the excited-state intermolecular energy transfer between luminescent species was negligible even in the solid state. Thus, these results provide a useful strategy for designing white luminescent materials, as the electronic interaction between functional components could often be problematic in the solid state.

The use of compounds with similar molecular structures is advantageous, because these compounds are on a same synthetic route and are expected to have similar physical properties. Owing to the similar UV-absorption properties of PIP derivatives, colorless white luminescent materials are realized. They also showed good processability for a vapor-deposited layer and a polymer thin film under mild condition. Of particular interest is a white luminescent PMMA film that is colorless and transparent, which is preferable for use in novel applications, where for example, good visibility and color rendering properties are required.

ASSOCIATED CONTENT

Supporting Information. Synthesis of **H2** and **M2**, and additional spectral data of the absorption and luminescence (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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