Development of Imidazo[1,2-a]pyridine Derivatives with an Intramolecular Hydrogen-Bonded Seven-Membered Ring Exhibiting Bright ESIPT Luminescence in the Solid State

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S Supporting Information

ABSTRACT: Imidazo [1,2-*a*] pyridine derivatives with different hydroxyaryl units (1-3), which could potentially form an intramolecular hydrogen-bonded seven-membered ring in either a planar or a twisted conformation, were newly developed, and the effect of conformation and steric repulsion on the excited-state intramolecular proton transfer (ESIPT) luminescence was evaluated. Among them, 1 and 2 formed an intramolecular hydrogen-bonded seven-membered ring in the crystalline state and exhibited efficient ESIPT luminescence in the solid state (quantum yield up to 0.45).



The development of new organic compounds exhibiting bright emission in the solid state is an important research direction in both fundamental and applied chemistry.¹ Excitedstate intramolecular proton transfer (ESIPT) fluorescence is the emission from a proton-transferred species generated upon the photoexcitation of an intramolecularly hydrogen-bonded molecule and is characterized by a large Stokes shift (~10 000 cm^{-1}), which realizes long-wavelength emission by UV, namely, short-wavelength excitation (Figure S1).² To date, compounds exhibiting efficient ESIPT fluorescence in the solid state mostly have five- or six-membered intramolecular hydrogen-bonded rings,³ in which 2-(2'-hydroxyphenyl) benzimidazole (HBI, X = NH, Scheme 1) and 2-(2'-hydroxyphenyl)benzoxazole (HBO, X = O, Scheme 1) are very well-known ESIPT luminescent fluorophores.

On the other hand, studies on the ESIPT fluorescence of compounds with a larger intramolecular hydrogen-bonded ring are lacking.⁴⁻⁸ Chou et al. reported two types of compounds with an intramolecular hydrogen-bonded seven-membered ring: N-H...N hydrogen-bonded pyrrole-pyridine compound in solution^{4,5} and the solid state⁵ and analogues of a greenfluorescent protein dye.⁶ A compound with an eight-membered ring was also studied.7 Arai et al. reported weak ESIPT fluorescence of a N-H…N hydrogen-bonded seven-membered ring compound in the solution state.⁸ To date, only a few compounds with a hydrogen-bonded seven-membered ring exhibiting efficient ESIPT luminescence in the solid state have been reported.^{5,6}

We previously studied the ESIPT luminescence properties of imidazo[1,2-a]pyridine (IP) having hydrogen-bonded sixmembered rings (i.e., 2-hydroxyphenyl-IP (2HPIP), Scheme 1) and obtained a good efficiency in the solid state ($\Phi \sim 0.5$) and

Scheme 1. Molecular Structure of HBI (X = NH), HBO (X = O), 2-(2'-Hydroxyphenyl)-IP (2HPIP), 8-(2'-Hydroxyphenyl)-IP (8HPIP, 1), 8-(3'-Hydroxythiophen-2yl)-IP (2), 8-(6'-Fluoro-2'-hydroxyphenyl)-IP (3), and 4-(2'-Hydroxyphenyl)-1-methylbenzimidazole (4)



definite polymorph dependence on luminescence color.^{9,10} The ESIPT luminescence of a series of 2HPIP derivatives¹¹ and polymorph-dependent luminescence¹² was also reported. Despite being structurally similar to HBI and HBO in the enol form in the ground state, the structure of the ESIPT species of 2HPIP is definitely different (Figure S1). Whereas HBI and HBO formed typical keto tautomers, such a neutral tautomer cannot be drawn for 2HPIP. Instead, the ESIPT species of 2HPIP forms a zwitterionic structure, which is further rotatable

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in a fluid environment,^{13,14} and these might be the reason for displaying characteristic luminescence behavior.

2HPIP derivatives are generally fixed to a planar conformation in the crystal. Therefore, we considered introducing a "flexible" part to allow either planar or twisted conformation with keeping the intramolecular hydrogen bond. To meet this concept, we synthesized 8-hydroxyphenyl-IP (8HPIP, 1) and its derivatives 2 and 3 that could potentially form an intramolecular hydrogenbonded seven-membered ring (Scheme 1). We then examined their luminescence properties. In addition, the effect of steric hindrance between the two aromatic rings was studied. For comparison, a derivative of HBI (4) was also studied.

Compounds 1-4 were synthesized by Suzuki coupling of the brominated heterocyclic core (8-bromo-IP for 1-3 and 4-bromobenzimidazole for 4) and the corresponding hydroxyaryl boronic acid (see Supporting Information for details).

First, the absorption and fluorescence spectra were measured in 2-methyltetrahydrofuran (MeTHF), which forms a glassy solid at 77 K and in a nonpolar cyclohexane solution. In the fluid MeTHF solution, compound 1 exhibits a π – π * absorption band at 285 nm and a shoulder band at approximately 320 nm (Figure 1a). In cyclohexane, on the other hand, the absorption band is observed mostly in a longer wavelength region (327 nm) (Figure 1c). Such a difference in the absorption band has also been reported for HBI¹⁵ and HPIP,¹³ in which case the absorption bands in the longer and shorter wavelength regions were assigned to intramolecular hydrogen-bonded species and



Figure 1. Absorption (gray), fluorescence (solid), and excitation (dotted and dashed) spectra of 1: (a) MeTHF solution at room temperature, (b) frozen MeTHF solution at 77 K, and (c) cyclohexane solution at room temperature. Asterisks (*) indicate the Raman scattering peaks.

non-hydrogen-bonded species, respectively. Upon excitation at 285 nm, a weak fluorescence band (389 nm) and an additional tail (550-700 nm) are observed in MeTHF. In contrast, a largely Stokes-shifted fluorescence (589 nm) is found in cyclohexane, indicating a probable ESIPT fluorescence. Furthermore, when the MeTHF solution was frozen to transparent glass at 77 K, a similar Stokes-shifted fluorescence was observed in addition to the normal fluorescence (Figure 1b).¹⁶ Although the excitation spectrum of the long-wavelength fluorescence (dashed line) was found at over 330 nm, that of the short-wavelength fluorescence (dotted line) is observed at the relatively higher energy region. The DFT and TD-DFT calculations of 1 indicate the lower absorption energy of the hydrogen-bonded enol species compared to the non-hydrogenbonded species (Figure S2). Furthermore, the relative energy levels of the ground (S_0) and excited (S_1) states of the enol and proton-transferred (PT) species are S_0 (enol) < S_0 (PT) and $S_1(enol) > S_1$ (PT), supporting that the ESIPT luminescence may occur. These results show that the short-wavelength fluorescence is a normal fluorescence from the non-hydrogenbonded species of 1, and the largely Stokes-shifted fluorescence can be assigned to the ESIPT fluorescence. Similar to 2HPIP, a zwitterionic, rotatable structure can be drawn for the ESIPT state of 1 (Figure S1b). The notable blue shift of the ESIPT fluorescence in rigid media can be explained by suppression of the rotating motion of the ESIPT state, which has been reported in 2HPIP (Figure S1b) by Douhal et al.¹⁴ and our group.^{9,11}

Compounds 2 and 3 exhibit normal fluorescence with an additional weak ESIPT fluorescence in fluid MeTHF (Figure S3) and cyclohexane (Figure S4). On the other hand, compound 4 exhibits only normal fluorescence. The fluorescence quantum yields of 2–4 are generally low (Tables S1 and S2). In glassy MeTHF at 77 K, 2 and 4 exhibit an emission assignable to the ESIPT fluorescence, whereas 3 does not.

The emission decay of the normal and ESIPT regions was measured in nonpolar cyclohexane (Tables S2). The dominant components (>90%) of lifetimes are shorter than 0.1 ns, except for the ESIPT fluorescence of 3. The values of the rate constant of the radiative process (k_r) are found to be within the range of typical singlet allowed $\pi - \pi^*$ emission.¹⁷ Therefore, the low quantum yield of these emissions is mainly due to efficient nonradiative deactivation processes, which is indicated by large values of the rate constant of the nonradiative process (k_{nr}).

To study the luminescence properties in the solid state, the molecular packing of 1-4 was examined by performing X-ray crystallographic analysis (Table S3). Figure 2 shows the ORTEP drawings of the asymmetric units of 1-4. In the crystals of 1-3, the two aromatic rings in each molecule are connected at different dihedral angles (θ): 40.58, 3.32, and 57.85°, respectively. This might be due to the different steric hindrances between 7-H of the IP ring and 6'-X (X = H (1), F (3)). Although the dihedral angles of 1 and 2 were significantly different, the O…N distance within a molecule in 1 (2.659 Å) and 2 (2.559 Å) indicates the formation of an intramolecular hydrogen-bonded seven-membered ring in both compounds. The nearly planar conformation of 2 may be a result of the minor steric repulsion between 7-H and the thienyl sulfur atom. No noticeable intermolecular interaction is observed within the crystals of 1 (Figure S5), and the slipped-stacked dimer-like structure, which further forms a herringbone-like packing, is observed in the crystals of 2 (Figure S6). In the crystals of 3, on the other hand, the distance between O and N in an adjacent molecule is 2.802 Å, and an intermolecular hydrogen bonding



Figure 2. ORTEP drawings of the asymmetric unit of (a) 1, (b) 2, (c) 3, and (d) 4. The dihedral angle between the two aromatic rings (1-4) and the O···N distance corresponding to the intramolecular hydrogen bond (1, 2, and 4) are also shown.

ribbon is formed along the *b*-axis (Figure S7). For the HBI derivative 4, a molecule is twisted ($\theta = 37.39^\circ$) similar to that in 1, and the O…N distance (2.626 Å) is well within the intramolecular hydrogen bonding. The molecular packing suggests no specific intermolecular interaction (Figure S8).

We then examined the absorption and luminescence properties in the solid state. The Kubelka–Munk spectra of 1-4 converted from the diffuse reflectance spectra (Figure S9) are observed in a region similar to that of the absorption spectra in the solution, indicating no obvious intermolecular interaction in the ground state.

Figure 3 shows the normalized luminescence spectra of the crystalline solid at ambient temperature. The ESIPT lumines-



Figure 3. Normalized emission spectra of 1 (solid line), 2 (dashed line), 3 (dash-dotted line), and 4 (dotted line) in the solid state.

cence of compounds 1 and 2 is observed at approximately 500 nm, with a significantly higher quantum yield of up to 0.45 compared with that in the solution (Table 1). Note that the onset of the absorption and luminescence spectra of 2 are quite similar, which is seemingly a normal emission. However, the luminescence maxima (471 nm) are near the ESIPT luminescence in the rigid MeTHF (484 nm), and the quantum chemical study (Figure S10) supports the ESIPT mechanism of 2 in the crystal, indicating that the emission of 2 in the crystal is

Table 1. Kubelka–Munk and Luminescence Maxima in the Solid State

	$\lambda_{\rm KM}/nm$	$\lambda_{ m em}/ m nm~(\Phi)$	$ au_{ m em}/ m ns$	$k_{\rm r}/10^8~{ m s}^{-1}$	$k_{\rm nr}/10^8 {\rm \ s}^{-1}$
1	324	528(0.32)	0.04(46)	1.02	2.18
			5.75(54)		
2	359	471(0.45)	1.15(26)	1.29	1.57
			4.32(74)		
3	309	387(0.03)	0.62(83)	0.28	8.96
			3.34(17)		
4 ^{<i>a</i>}	285	378, 493(<10 ⁻²)	0.30(99)	0.28	27.9
			5.84(1)		
${}^{a} au_{\rm em}$ was measured at 510 nm.					

from the ESIPT species. In contrast, 3 exhibits only weak normal luminescence at 387 nm. The luminescence behaviors of the IP derivatives 1-3 are in good accordance with the results of the crystallographic studies: a compound forming intramolecular and intermolecular hydrogen bonds in the crystal exhibited ESIPT and normal luminescence, respectively. The emission decay profiles were fitted with a biexponential curve, indicating short (ca. 1 ns) and long (3.3-5.8 ns) lifetimes (Figure S11). However, the ratios of the two lifetimes between the efficiently luminescent (1 and 2) and weakly luminescent (3) compounds are remarkably different (Table 1). The values of k_r and k_{nr} estimated from the weighted average of the two lifetimes indicate that k_r values for 1-3 are within the range of the singlet allowed $\pi - \pi^*$ emission.¹⁷ The k_{nr} value for 3 is similar to those observed for 1-3 in fluid cyclohexane. On the other hand, those for 1 and 2 are considerably smaller, showing that suppression of the nonradiative process could be a major reason for the high quantum yields.

The HBI derivative 4 exhibited dual emission, but the quantum yield was very low ($\Phi < 10^{-2}$). Although 1 and 4 formed similar conformation and intramolecular hydrogen bonds in the crystal, the significantly lower quantum yield and higher value of $k_{\rm nr}$ suggest that there exist notably efficient nonradiative deactivation pathways in the photoexcited state, which might be because the structure of the ESIPT species of 4 would be remarkably different from that of luminescent HBI (Figure S1).

In summary, we synthesized IP (1-3) and HBI (4) derivatives that could potentially form an intramolecular hydrogen-bonded seven-membered ring. An X-ray crystallographic analysis confirmed that 1 and 2 formed an intramolecular hydrogen-bonded seven-membered ring in the crystal. On the other hand, 3 formed an intermolecular (and not intramolecular) hydrogen bond, probably because of the steric repulsion between 6'-F and 7-H. A bright emission ($\Phi \sim 0.45$) attributed to ESIPT luminescence was observed in 1 and 2 in the solid state, whereas a weak normal luminescence was detected in 3. This was in good agreement with the results of the crystallographic studies.

The above results confirm the formation of a new series of ESIPT luminescent compounds based on a hydrogen-bonded seven-membered ring. Their characteristic luminescent properties, such as high efficiency in the solid state and complete changeability by slight modification in the molecular structure, pave the way for designing ESIPT systems for optoelectronic materials. Further study on the electronic structure including quantum calculation with high level of theory will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00455.

Detailed synthetic procedures, ¹H and ¹³C NMR spectra, absorption and fluorescence spectra, and crystallographic data (PDF)

Accession Codes

CCDC 1885155–1885158 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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