Imidazole-Based Excited-State Intramolecular Proton-Transfer Materials: Synthesis and Amplified Spontaneous Emission from a Large Single Crystal

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Abstract: We have synthesized a novel class of imidazole-based excited-state intramolecular proton-transfer (ESIPT) materials, i.e., hydroxy-substituted tetraphenylimidazole (HPI) and its derivative HPI-Ac, which formed large single crystals exhibiting intense blue fluorescence and amplified spontaneous emission (ASE). Transparent, clear, and well-defined fluorescent single crystals of HPI-Ac as large as 20 mm × 25 mm × 5 mm were easily grown from its dilute solution. From the X-ray crystallographic analysis and semiempirical molecular orbital calculation, it was deduced that the four phenyl groups substituted into the imidazole ring of HPI and HPI-Ac allowed the crystals free from concentration quenching of fluorescence by limiting the excessive tight-stacking responsible for intermolecular vibrational coupling and relevant nonradiative relaxation. Fluorescence spectral narrowing and efficient ASE were observed in the HPI-Ac single crystal even at low excitation levels attributed to the intrinsic four-level ESIPT photocycle.

Introduction

Highly fluorescent organic materials including molecular laser dyes and conjugated polymers have been extensively investigated as the active gain media for optically pumped solid-state lasers.1 Different from the various classes of fluorescent dyes investigated so far, the one based on excited-state intramolecular proton transfer (ESIPT) has an intrinsic advantage for stimulated emission because it is harnessed with a favorable four-level photophysical cycle.2 The ESIPT reaction, a fast enol (E)-to-keto (K) prototropy occurring in the excited states of intramolecularly H-bonded molecules, is thus gaining ever increasing interest due to the fundamental importance of the peculiar photophysical processes as well as the potential applications to the laser dyes,3-6 solar energy concentrators,7 chemosensors,8 and electroluminescent materials.9 Because the ESIPT molecules are normally more stable in E forms in the ground states but in K* forms in the excited states, photoexcitation of them is immediately followed by the four-level cyclic proton-transfer reactions (E→E*→K*→K→E) mediated by the intramolecular H-bonds (Scheme 1).2 It is characteristically observed, therefore, that the absorption from E and emission from K* results in an abnormally large Stokes shift with no self-absorption, providing an ideal scheme for the proton-transfer lasers3-6 and UV-photostabilizers.10

To realize a compact and rugged device of high performance, most of the ESIPT applications demand highly dense solid-state...
systems. However, the intermolecular interactions in the condensed phase are often associated with the problem of significant concentration quenching in the fluorescence intensity, which is a serious challenge in the fluorescent ESIPT materials as well. Recently, we have demonstrated that site-isolation by dendritic architecture\textsuperscript{11,12} or specific J-aggregation with favorable intermolecular interaction\textsuperscript{13} could effectively suppress the concentration quenching and even enhance the fluorescence emission in the solid state.

Aiming at the organic-crystal laser of high performance in this work, we have designed and synthesized a novel class of ESIPT materials, hydroxy-substituted tetraphenyl imidazole (HPI) and its acetate-containing derivative, HPI-Ac (see Scheme 2), which readily form strongly fluorescent large single crystals with proper intermolecular stacking. It was initially considered that the four phenyl rings in HPI and HPI-Ac would favorably reduce the intermolecular vibronic interactions which would otherwise induce the nonradiative deactivation process.\textsuperscript{14} In this paper, we report on the crystal structure, photoluminescence, and amplified spontaneous emission (ASE) of HPI and HPI-Ac.

### Experimental Section

Benzil, salicylaldehyde, aniline, 4-aminophenylethyl alcohol, and ammonium acetate were purchased from Aldrich. Glacial acetic acid at room temperature. A 1.07 g amount of K$_2$CO$_3$ (7.72 mmol) and 0.48 mL of iodomethane (7.72 mmol) were added sequentially, and then the mixture was stirred under dark conditions for 12 h. After purification, 1.5 g of white MeOPI powder was obtained quantitatively. MeOPI mp 208 °C; 1 H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] 3.31 (s, 3H), 6.68 (d, 1H), 6.88--6.91 (m, 2H), 7.00 (t, 1H), 7.09--7.34 (m, 12H), 7.60 (d, 2H), 7.65 (d, 1H); MS (EI) calcd for C$_{28}$H$_{22}$N$_2$O: C, 83.56; H, 5.51; N, 6.96. Found: C, 83.32; H, 5.61; N, 6.96.

#### Measurements.

CW absorption and emission/excitation spectra were obtained by using a UV/vis spectrometer (Scinco, S-3100) and a fluorimeter consisting of a 6-in. integrating sphere (Labsphere, 3P-GPS-060-SF) equipped with a 325-nm CW He-Cd laser (Omnichrome, Series 56) and a PMT detector (Hamamatsu, PD471) attached to a monochromator (Acton Research, Spectrapro-300i). The detailed analytical procedure to obtain solid-state crystal $\Phi_{PL}$ has been described elsewhere.\textsuperscript{15} Fluorescence kinetic profiles were measured by using an actively/passively mode-locked Nd:YAG laser.
Both HPI and HPI-Ac were readily synthesized according to the classical method of lophine synthesis in good yields (see Scheme 2).\(^{(17)}\) In the synthesis of HPI-Ac, acetyl-blocking of the aliphatic alcohol group was automatically effected due to the reactivity of glacial acetic acid used as the reaction medium. Large single crystals of HPI and HPI-Ac were easily grown from dilute solutions, both of which belong to the triclinic system and \(P\overline{1}\) space group (vide infra). Particularly, HPI-Ac tended to form transparent, clear, and well-defined fluorescent single crystals, as large as 20 mm \(	imes\) 25 mm \(	imes\) 5 mm (see Figure 1). When observed under a crossed Nicols configuration of the polarizer and analyzer, bright and dark images of the crystals were strictly switched at each 45° rotation, suggesting that the morphology of the crystals are not polycrystalline.\(^{(18)}\) Single crystals are free of grain boundary defects, in contrast to conventional solution-processed thin films. Therefore, high-quality single crystals with strong fluorescence emission are important research targets for the fabrication of organic diode lasers. However, only a few investigations have been reported so far on the fluorescence emission and ASE from single crystals because of the difficulty in obtaining large single crystals showing efficient luminescence properties.\(^{(18,19)}\)

In the design of the HPI molecule, four phenyl groups were deliberately incorporated into the central imidazole unit to adjust the intermolecular interactions, considering that the molecular packing modes strongly affect the solid-state photoluminescence. The incorporation of steric groups on the chromophore can improve the emission properties by limiting the excessively tight packing and consequent intermolecular vibronic relaxation. Among the four phenyl rings, two of them, at 2- and 4-positions, while the other two are intended to provide a steric restriction between structures of HPI and HPI-Ac are triclinic and the two phenyl rings at the 1- and 5-positions of the central imidazole ring are twisted almost perpendicular to the chromophore plane. It is presumed that these two twisted phenyl rings are appropriately preventing direct stacking of the active chromophores in a zigzag manner and maintaining proper intermolecular distances, suppressing the concentration quenching of fluorescence, and thus keeping the single crystals strongly fluorescent (Figure 5b).\(^{(14)}\) The fluorescence quantum efficiencies (\(\Phi_{\text{PL}}\)) of HPI and HPI-Ac in CHCl\(_3\) solutions were both measured to be 0.18. On the other hand, \(\Phi_{\text{PL}}\) of HPI-Ac crystal was measured to be 0.32, indicating the enhanced fluorescence emission due to the reduced intermolecular interaction in the crystalline state.
Figure 3. Absorption and emission (excitation at 318 nm) spectra of HPI-Ac (solid) and MeOPI (dotted) in CHCl₃ (1.0 × 10⁻⁵ M) and a single crystal of HPI-Ac (dashed) at room temperature. The excitation spectrum, monitored at 530 nm, of the HPI-Ac solution (circles) is also depicted. Inset: Fluorescence kinetics of crystalline HPI-Ac, excited at 315 nm (1 μJ cm⁻² s⁻¹) and monitored at 380 nm (a) and 530 nm (b).

Figure 4. Peak-normalized emission spectra of a single crystal of HPI-Ac at various pulse excitation energies: (a) 0.11, (b) 0.38, (c) 0.49, (d) 0.79, and (e) 3.5 mJ cm⁻² pulse⁻¹.

Evolution as a function of the pump intensity, where the emission was collected from the edge of the crystal. The diameter of the pump beam was 9 mm, and the intensity was tuned from 0.11 to 3.5 mJ cm⁻² pulse⁻¹ onto the sample without focusing. Even though the spectral narrowing was observed easily with the nonfocused beam, a loss of spectral narrowing was also monitored when the diameter of the pump beam was below a certain size, which is one of the characteristics associated with ASE. The fluorescence emission and ASE of the sample shown in Figure 4 were collected in a direction perpendicular to the excitation beam under the optimized geometry of polarization, as shown in Figure 5a. At a low pump fluence of 0.11 mJ cm⁻² pulse⁻¹, the emission spectrum was initially very broad and the full width at half-maximum (fwhm) was approximately 67 nm. When the pump fluence was gradually increased, the fwhm decreased to 13 nm in this system. To optimize the gain-narrowing condition, we used a cylindrical lens to form a line focus (500 μm × 9 mm, Figure 5b) on the front surface of the sample. The polarization direction of the pump was varied with a half-wave plate. The gain-narrowing of HPI-Ac crystal was strongly dependent on the pump polarization, as expected. When the polarization was aligned parallel to the active chain orientation, the gain-narrowing was observed at a lower pump fluence, and the fwhm was also decreased to 9 nm (see Figure S-4 in the Supporting Information).

Figure 6a shows the evolution of the fwhm and the hyperlinear dependency of integrated emission for the HPI-Ac crystal as a function of the pump intensity. It is noted that the emission intensity is approximately proportional to the pump fluence up to 250 μJ cm⁻² pulse⁻¹, after which the characteristic hyperlinear dependence is clearly developed. The observation that the narrowing of line shape and the hyperlinear dependence occur at the similar pump energy indicates that both effects are the results of light amplification at the wavelength where the single crystal has a high gain. The onset of significant spectral narrowing, which we will call the phenomenological threshold, was determined to be around 200 μJ cm⁻² pulse⁻¹ in the nonfocused state and 6 μJ cm⁻² pulse⁻¹ in the line-focused state, respectively. Above this “threshold”, spontaneous emission from one emitter efficiently stimulates emission as it propagates along...
the excited region of the sample. Amplification occurs preferentially where the stimulated-emission cross-section is maximum, leading to gain-narrowing. The main mechanism for the observed gain-narrowing is attributed to ASE by the observations of the waveguiding property and the effect of excitation beam shape in light amplification.11,24

The picosecond kinetics in Figure 6b gives direct evidence of light amplification via an ASE mechanism. The emission profiles show the reduction of lifetime compared with the spontaneous emission (4000 ps); lifetime decreases from 1400 ps (at 37 μJ cm−2 pulse−1) to 80 ps (at 1900 μJ cm−2 pulse−1) with increasing excitation energy. The inversely proportional dependence of the decay time on the pump energy is consistent with the excited-state population-depletion model explaining ASE phenomena.27 The intrinsic four-level nature of ESIPT contributes to the easy population inversion, and thus the phenomenological ASE threshold of HPI-Ac is lower than that of conventional laser dyes.19,24,28,29 Such low-threshold ASE is a promising property for the application of this crystal as a medium for optical amplifiers or lasers. Moreover, HPI-Ac single crystals have long-term photostability and thermostability when compared with dye-doped polymer films. Although the crystal was repeatedly exposed to 355-nm picosecond pulses (4 × 104 shots), no discernible photobleaching or decomposition was observed under an excitation power of 2 mJ cm−2 pulse−1.

In conclusion, the strongly fluorescent large single crystal of a hydroxy-substituted tetraphenylimidazole derivative (HPI-Ac) was successfully synthesized and characterized to show very efficient amplified spontaneous emission (ASE) associated with the excited-state intramolecular proton transfer (ESIPT) process. From the X-ray crystallographic analysis and semiempirical molecular orbital calculation, it was found that the four phenyl groups substituted in the imidazole ring of HPI-Ac provided the positive steric effect toward the improved fluorescence emission by limiting the excessive tight-stacking responsible for the intermolecular vibrational coupling and relevant nonradiative relaxation.

Acknowledgment. This work was supported by the Ministry of Science and Technology of Korea through the National Research Laboratory (NRL) program, awarded to Prof. Soo Young Park. We are grateful for the instrumental support from the equipment facility of CRM-KOSEF, Korea University. D.-J.J. and O.-H.K. thank the Korea Research Foundation for Grant KRF-2004-015-C00230 and the Brain Korea 21 Program, respectively.

Note Added after ASAP Publication. Incorrect bibliographic information was reported in reference (9) of the version published ASAP June 15, 2005. The corrected version was published ASAP June 21, 2005.

Supporting Information Available: Optical characteristics and crystallographic information (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.