

Strong Solvatochromic Fluorescence from the Intramolecular Charge-Transfer State Created by Excited-State Intramolecular Proton Transfer

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Significant interest has existed in the fundamental investigation and the application of organic molecules exhibiting excited-state intramolecular proton transfer (ESIPT) because of their four-level photophysical scheme, spectral sensitivity to the surrounding medium and a large Stokes'-shifted fluorescence.¹ ESIPT is a phototautomerization, that is, enol (E) to keto (K) transformation in the excited state via an intramolecular hydrogen bond involving the transfer of hydroxyl proton to the electronegative atom, which occurs extremely fast in the subpicosecond time scale.² After the relaxation of the keto form to the ground state, the energetically favored enol form is recovered spontaneously by reverse proton transfer, to complete the cyclic four-level scheme. Consequently, this process gives rise to the transient chemical change from enol to keto tautomer, leading to the transient alternation of the electronic properties such as electron density distribution, energies of electronic states, and dipole moments, etc. Recently, it has been demonstrated that the proper structural design of the ESIPT molecule leads to the peculiar photoexcitation-gated properties, including electrochromic modulation,³ perturbation of electronic state by variation of solvent polarity,⁴ and anion emission.⁵

In this communication, we report an unusually large positive solvatochromic shift in ESIPT keto fluorescence originating from the creation of an intramolecular charge-transfer (ICT) state after the ESIPT process. Molecules investigated in this work are 2-(2'-hydroxyphenyl)benzoxazole (HBO) derivatives with conjugative electron acceptors (HBOCE and HBODC; Figure 1), which are capable of rearranging themselves into the dipolar push-pull structure after ESIPT.

It was peculiarly observed that the keto emission of HBODC and HBOCE showed large bathochromic shift with increasing solvent polarity in contrast to the negligible shift of enol emission, which is, in addition, totally different from the small negative solvatochromism of keto emission in nonsubstituted HBO.^{2,6} Most probably, it is speculated that the large difference in electronic properties between the enol and keto forms is associated with the ESIPT-gated transient evolution of amine in keto tautomer from imine in enol tautomer, resulting in the significantly enhanced charge-transfer interaction with conjugative electron acceptor in the keto tautomer. To identify the transient alternation of electronic properties between the enol and keto forms, their first hyperpolarizabilities (β) were evaluated using the MOPAC 97 program with PM3 method (Supporting Information). For HBOCE, the calculated β value was 22.99×10^{-30} esu for enol and 28.56×10^{-30} esu for the keto tautomer. Similar enhancement (25%) was also obtained in the relative β values of HBODC, providing a generality of β enhancement for this class of molecules. Enhanced β value of keto tautomer is attributed to the transient push-pull structure reinforced and modulated by the ESIPT process. This structure is similar to those of 2-(4-diethylamino-benzylidene)-malononitrile and its analogues, which have been intensively investigated as the second-order nonlinear optical chromophores.⁷ Therefore, it is considered

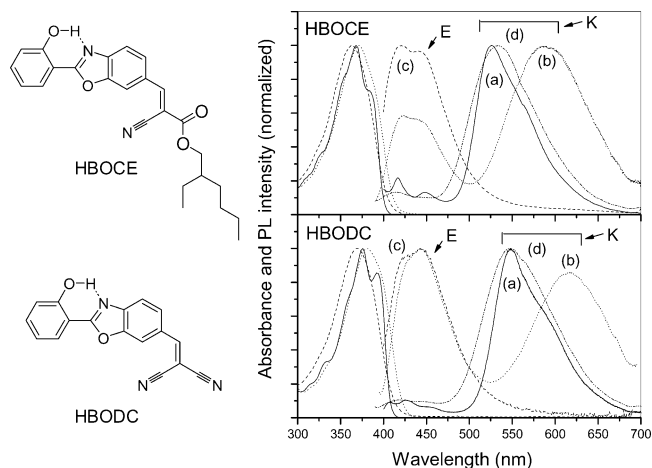


Figure 1. Absorption and fluorescence spectra of HBOCE and HBODC excited at the wavelength of absorption maxima in (a) cyclohexane, (b) chloroform, (c) methanol, and (d) PMMA film doped with 2 wt % of each dye.

that HBODC and HBOCE constitute a new class of second-order nonlinear optical materials whose hyperpolarizability can be modulated by light absorption. Another consequence of the ESIPT-induced transient push-pull structure is a unique spectral change depending on the solvent polarity to be discussed below.

HBOCE and HBODC were synthesized using a Knoevenagel condensation of the aldehyde-substituted HBO with cyano-acetic acid 2-ethyl-hexyl ester and malononitrile, respectively (Scheme 1 of Supporting Information).

Figure 1 shows representative absorption and emission spectra of HBOCE and HBODC in the aprotic nonpolar (cyclohexane, a), polar (chloroform, b), and protic (methanol, c) solvents as well as in the solid state (PMMA film, d). Ground-state enol absorptions in three solvents indicate no significant spectral dependency on the solvent nature. Dual emissions (E and K) from the enol and keto forms are observed in aprotic solvents (Figure 1a,b), where the keto emission is much stronger and far separated from the absorption band with a Stokes' shift more than 150 nm. In contrast, only a single enol emission with normal Stokes' shift (<75 nm) is observed in protic solvent (Figure 1c) because the intramolecular hydrogen-bonding ($-\text{OH} \cdots \text{N}-$) needed for the ESIPT process is interrupted in this solvent. Characteristic dual emissions from HBOCE and HBODC in different aprotic solvents are contrasted with the virtual single keto emission from HBO,^{2,6} which is most likely attributed to the increased energy barrier between the tautomer states due to the incorporation of conjugated polar substituents.⁸ In the solid solution in PMMA, fluorescence emission spectra of enol and keto forms are similar to those in nonpolar solvent except for their slightly broader shape. Irrespective of the solvents, all the enol fluorescences are located in the limited spectral range of blue emission compared to the keto emission. However, it is peculiarly

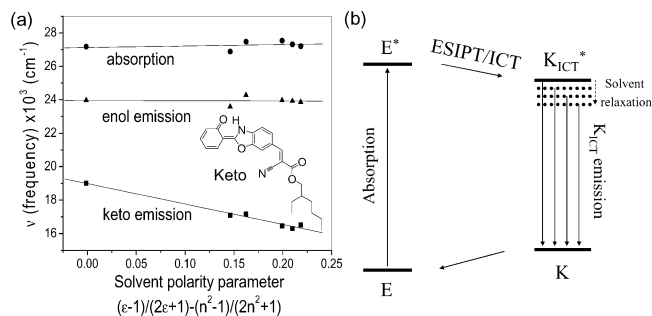


Figure 2. (a) Plot of absorption (●) and emission maxima in enol (▲) and keto (■) forms of HBOCE as a function of solvent polarity parameter. n and ϵ are the refractive index and dielectric constant of solvent, respectively. (b) Proposed consecutive photophysical process.

noted that the spectral positions of keto emission are largely varied from the green to the orange range with increasing polarity in aprotic solvents. This positive solvatochromism of keto emission is just opposite to the spectral trend in nonsubstituted HBO.^{2,6} In view of the positive solvatochromic shift, keto emission of HBOCE seems to be unusual and unique in comparison to that of HBO. For HBODC, the same effect is observed, but the stronger electron-accepting dicyanovinyl group than the 2-cyano-acrylate group in HBOCE resulted in the larger red shifts in the absorption and emission bands. Such an unusual spectral behavior of HBODC and HBOCE suggests that their keto emission is likely to be related to a more complicated process rather than the common ESIPT phenomena.

To get an insight into the different solvatochromic behaviors of enol and keto forms, the spectral dependency of HBOCE on solvent polarity was studied on the basis of the Lippert–Mataga model,⁹ as shown in Figure 2a. The solvents used and the corresponding polarity parameters⁹ are: cyclohexane (~0), chloroform (0.146), diethyl ether (0.162), ethyl acetate (0.199), tetrahydrofuran (0.210), and dichloromethane (0.218). It is seen that the spectral positions of the absorption as well as the enol emission do not vary with solvent polarity and the spectral change is within 10 nm over the entire range of solvents examined. On the other hand, keto emission shows a significant bathochromic shift in the broad range of 526–614 nm with increasing solvent polarity. A good linear correlation with large slope ($12\,000 \text{ cm}^{-1}$) between the emission frequency and solvent polarity strongly suggests that the spectral behavior of keto emission is related to ICT characteristic.^{9,10} Comparing the spectral behaviors of enol and keto emission, it is concluded that the ICT must be developed after the ESIPT process.¹¹

One acceptable explanation for this observation is the creation of specific molecular structure via ESIPT, which is capable of effective charge transfer into the electron acceptor unit. Practically in HBOCE, imino nitrogen in the para position of the electron acceptor is converted into an amine group by the process of ESIPT (see the chemical structure in Figure 2a), which triggers the strong push–pull ICT interaction. Additionally, the aromatic delocalization energy for ICT is no longer needed as much as that in the enol tautomer due to the breakage of heteroaromatic oxazole in the keto tautomer. Therefore, the excited ICT state (K_{ICT}^*) of HBOCE is most probably and easily generated from ICT immediately after ESIPT process (Figure 2b). According to this model, K_{ICT}^* stabilized by solvent relaxation dependent on its polarity is then deactivated to K by radiative or nonradiative decay, and finally, E is recovered from K through reverse proton transfer. Such a consecutive photophysical process (ICT after ESIPT, depicted in Figure 2b) is clearly distinguished from the general photophysical scheme of common ESIPT materials since the K_{ICT}^* stabilized by

the solvent relaxation clearly explains the large positive solvatochromism of keto emission as well as the insensitivity of enol emission with increasing solvent polarity as shown in Figure 2b. It must be noted that keto tautomers of common ESIPT materials including the unsubstituted HBO were more influenced by solvent stabilization for ground state than for excited state, showing a negative solvatochromic keto emission.^{2,6} Additional evidence for this consecutive photophysical process was obtained by the temperature-dependent photoluminescence study (Figure 3a,b of Supporting Information). HBOCE in chloroform solution shows bright orange emission ($\lambda_{\text{em}} = 585 \text{ nm}$) at room temperature, which changes to yellowish white emission ($\lambda_{\text{em}} = 540 \text{ nm}$) in the frozen state at 205 K. It should be noted that the latter one is identical to the keto emission observed in the nonpolar solvent (compare the spectra with those in Figure 1a). Such a unique evolution of keto emission toward higher energy at low temperature is mainly due to the restricted solvent relaxation. Consistent with this point of view, keto emission in the solid film state was also observed to be almost identical to that in nonpolar solvent due to the hampered molecular relaxation in the solid media (Figure 1d).

In summary, the introduction of a conjugative electron acceptor in HBO caused a strong positive solvatochromism in ESIPT keto emission. This unique spectral change was attributed to the consecutive ESIPT/ICT process in the acceptor-substituted HBO compounds. Potential application of HBOCE and HBODC as the fast hyperpolarizability modulators was demonstrated by the semiempirical calculation.

Acknowledgment. This work was supported in part by CRM-KOSEF.

Supporting Information Available: Synthetic and experimental details, temperature-dependent photoluminescence spectra of HBOCE, and calculation details for hyperpolarizability. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) HBODC exhibited the same spectral behavior due to ICT after ESIPT, although the fluorescence intensity of keto and enol emission was quite low compared to that of HBOCE.

JA047815I