# Acid–Base-Responsive Intense Charge-Transfer Emission in Donor– Acceptor-Conjugated Fluorophores

## Toshifumi Inouchi, Takuya Nakashima,\* and Tsuyoshi Kawai\*<sup>[a]</sup>

Abstract: Herein we report on the synthesis and acid-responsive emission properties of donor-acceptor (D-A) molecules that contain a thienothiophene unit. 2-Arylthieno[3,2-b]thiophenes were conjugated with an *N*-methylbenzimidazole unit to form acid-responsive D-A-type fluorophores. The D-A-conjugated fluorophores showed intense intramolecular charge-transfer (ICT) emission in response to

acid. The effect of the substitution on their photophysical properties as well as their solvent-dependence indicated non-twisting ICT emission in protonated D–A molecules. The quinoidal character of 2-arylthienothiophene as

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a donor part is discussed, as it is assumed that it contributes to suppression of the molecular twisting in the excited state, therefore decreasing the nonradiative rate constant, thereby resulting in the intense ICT emission. Acid–base-sensitive triple-color emission was also achieved by the introduction of a base-responsive phenol group in the donor part.

## Introduction

Understanding and tuning the photophysical properties of organic fluorophores is of importance for a wide range of applications.<sup>[1]</sup> Recently, with an eye on the excited-state properties that are a result of electronic and geometric structures, much effort has been made to develop intensively fluorescent molecules. For example, aggregation-induced emission (AIE) molecules exhibit restricted intramolecular rotations in the excited state, which leads to a highly emissive aggregate with suppressed nonradiative decay processes.<sup>[2]</sup> Thermally activated delayed fluorescence (TADF) employs twisted molecular structures to separate HOMO and LUMO spatially, thereby decreasing the energy gap between S<sub>1</sub> and T<sub>1</sub> states to enhance the probability of thermal activation from the T<sub>1</sub> to S<sub>1</sub> states.<sup>[3]</sup> Excited-state intramolecular proton transfer (ESIPT) usually takes place faster than fluorescence, thus leading to a redshifted emission with a large Stokes shift and a strong solvatochromic effect.<sup>[4]</sup> Emission from the intramolecular charge-transfer (ICT) states has also been an important subject because of the environment-sensitive emission derived from a large dipole moment in the excited CT state.<sup>[5]</sup> Excited-state relaxation to an ICT state often accompanies the rotation between a donor (D) and an acceptor (A) part, which is known as twisted intramolecular charge-transfer (TICT) emission.<sup>[6]</sup>

 [a] Dr. T. Inouchi, Dr. T. Nakashima, Prof. T. Kawai Graduate School of Materials Science Nara Institute of Science and Technology, NAIST 8916-5 Takayama, Ikoma, Nara 630-0192 (Japan) E-mail: ntaku@ms.naist.jp tkawai@ms.naist.jp

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Twisting in the excited state often sacrifices the emission efficiency<sup>[6,7]</sup> because of the nonradiative decay processes coupled with the rotation. To avoid such a twisting in the excited state, Yang and co-workers<sup>[8]</sup> introduced a spiroconjugation-like ICT emission, although it gave suppressed emission quantum yields in polar solvents. Meanwhile, non-twisting planar ICT emission was demonstrated by covalently rigidized molecules<sup>[9]</sup> and donor-substituted tridurylboranes.<sup>[10]</sup>

In our previous work, we reported a T-shaped conjugated molecule with an *N*-methylbenzimidazole<sup>[11]</sup> junction that showed TICT emission in response to acid, whereby the charge transfer took place between two orthogonally arranged  $\pi$  systems.<sup>[12]</sup> The increase in quinoidal character in a  $\pi$  component of the T-shaped conjugated molecule led to non-twisting ICT emission with a higher emission quantum yield.<sup>[13]</sup> Thus we proposed the introduction of quinoidal character into the excited state for the design of fluorophores that showed non-twisting ICT emission, whereas the emission efficiency of the T-shaped molecule was 0.43 at the most. We herein describe a simple D–A conjugated system composed of an acid-responsive *N*-methylbenz-imidazole moiety and a 2-arylthieno[3,2-*b*]thiophene group (Scheme 1).

We envisage that the contribution of quinoid structure of a  $\pi$  component suppresses the rotation about the D-A bridge with the aid of NH/S hydrogen bonding in the excited state (Scheme 1a), thus leading to intense charge-transfer emission in protonated fluorophores. To vary the quinoidal and electron-donating properties, several thiophene derivatives were introduced as a  $\pi$  component. The order of increase in the quinoidal character may follow the order shown in Scheme 1b, which roughly corresponds to the orders of decrease in the aromatic resonance energy of the donor part as well as the increase in the extent of charge

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Scheme 1. a) Design concept for planarizing the molecular geometry in the excited state of a protonated fluorophore by a combination of quinoid character and an NH/S interaction. b) Molecular structures of benzimidazole-based fluorophores.

separation in the whole structure.<sup>[14]</sup> An electron-donating and an electron-withdrawing unit, methoxy and trifluoromethyl groups, respectively, were introduced as a substituents on the 2-arylthieno[3,2-*b*]thiophene moiety to study their effect on the photophysical property. The acid-responsive optical properties of these molecules were evaluated. Both the acid- and base-responsive dual ICT emission with quantum yields as high as 0.8 were also demonstrated by introducing a base-responsive phenol group in the donor part.

## **Results and Discussion**

#### Synthesis

Arylthienothiophene-benzimidazole-conjugated D-A molecules were synthesized as shown in Scheme 2. Newly synthesized molecules were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. The arylthienothiophene parts with substituents were synthesized according to the modified method reported in the literature,<sup>[15]</sup> followed by the stannylation at the 5-position of 2-substituted thienothiophene. Since the stannylated arylthienothiophenes (6) were easily decomposed to the protonated ones (5) in a silica gel column, they were purified through a silica gel column that contained 10 wt % anhydrous potassium carbonate.<sup>[16]</sup> Stille cross-coupling reactions between *N*-methyl-2-bromobenzimidazole<sup>[13]</sup> and the stannylated arylthienothiophene unit led to the synthesis of arylthienothiophene-benzimidazole conjugated molecules. OHPhTTIm was readily derivatized by the deprotection of the methoxy group in OMePhTTIm by using BBr<sub>3</sub>. Other molecules that contained various thiophene derivatives as a donor part were also synthesized as reference compounds through Pd-catalyzed cross-coupling reactions between N-methyl-2-bromobenzimidazole and stannylated or borylated donor units (see the Supporting Information for details).

#### **Photophysical Properties**

Absorption and fluorescence spectra of fluorophores were measured in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). To study the acid-responsive photophysical properties, an excess amount of trifluoroacetic acid (TFA, 0.01 mL) was added to the solutions in  $CH_2Cl_2$  (1.0×10<sup>-5</sup> M, 3 mL) that was excessive enough to protonate all the molecules in CH<sub>2</sub>Cl<sub>2</sub>.<sup>[13]</sup> The optical properties of compounds in neutral and protonated forms



Scheme 2. Synthesis of arylthienothiophene-benzimidazole conjugated molecules: a)  $K_2CO_3$  (2 M, aqueous), [Pd(PPh\_3)\_4], 1,4-dioxane/toluene; b) 1-iodo-4-(trifluoromethyl)benzene, KF, [PdCl<sub>2</sub>(PPh\_3)\_2], DMSO; c) *n*BuLi, DMF, dry THF; d) ethyl mercaptoacetate,  $K_2CO_3$ , DMF; e) NaOH, ethanol, water; f) CuO, quinoline; g) *n*BuLi, *n*Bu<sub>3</sub>SnCl, dry THF; h) [Pd(PPh\_3)\_4], DMF; and i) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>.

are summarized in Table 1 together with the data on emission quantum yield and time-correlated single-photon counting (TCSPC) measurements. All compounds exhibited moderate emission intensity with quantum yields ( $\Phi_f$ ) in the range of 0.2–0.6. The absorption and emission bands shifted to longer wavelength depending on the extent of  $\pi$ -conjugated systems both for the neutral and protonated states (see

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Table 1.	Photophy	ysical p	roperties of	of	benzimida	azole-l	based	fluorop	nores.
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Compound	$\lambda_{abs} \ [nm]^{[a]}$	$\lambda_{em} [nm]^{[a]}$	$\Delta v_{st} \times 10^{-3} \ [cm^{-1}]^{[a,b]}$	$\Phi_{\mathrm{f}} \left( \Phi_{\mathrm{f}}^{\mathrm{H}} / \Phi_{\mathrm{f}}  ight)^{\mathrm{[a]}}$	τ [ns] <sup>[a]</sup>	$k_{\rm r}  [{\rm ns}^{-1}]^{[{\rm a}]}$	$k_{ m nr}  [{ m ns}^{-1}]^{[a]}$	$k_{ m r}/k_{ m nr}{}^{[ m a]}$	$\Delta \mu  [\text{debye}]^{[c]}$
OMePhTTIm	367	444	4.81	0.40	0.59	0.67	1.0	0.66	4.81
OMePhTTIm+H <sup>+[d]</sup>	398	500	5.26	0.86 (2.15)	1.7	0.48	$7.8 \times 10^{-2}$	6.1	10.7
PhTTIm	361.5	431	3.25	0.31	0.52	0.59	1.3	0.45	4.07
<b>PhTTIm</b> + $H^{+[d]}$	382	453	4.08	0.91 (2.93)	1.6	0.58	$5.6 \times 10^{-2}$	$1.0 \times 10^1$	7.02
CF <sub>3</sub> PhTTIm	366	438	4.52	0.35	0.58	0.60	1.1	0.54	5.79
$CF_3PhTTIm + H^{+[d]}$	375.5	433	4.36	0.88 (2.51)	1.4	0.64	$9.2 \times 10^{-2}$	7.0	3.54
PhThIm	343.5	420	5.37	0.60	1.3	0.45	0.30	1.5	3.24
<b>PhThIm</b> + $H^{+[d]}$	356	433	5.10	0.94 (1.57)	1.8	0.53	$3.5 \times 10^{-2}$	15	4.11
2-ThIm	312	376	5.62	0.32	1.1	0.29	0.61	0.48	2.98
<b>2-ThIm</b> + $H^{+[d]}$	316.5	378	5.23	0.32 (1.00)	1.1	0.30	0.63	0.48	2.25
3-ThIm	296	338	4.30	0.25	0.69	0.36	1.1	0.33	2.79
$3-ThIm + H^{+[d]}$	296.5	353	5.46	0.19 (0.76)	0.62	0.31	1.3	0.24	1.00
BzThIm	320.5	380	4.95	0.24	0.67	0.36	1.1	0.32	1.35
$BzThm + H^{+[d]}$	328.5	396	5.20	0.08 (0.33)	0.63	0.12	1.5	0.082	3.12

[a] In CH<sub>2</sub>Cl<sub>2</sub> ( $1.0 \times 10^{-5}$  M). [b] Obtained using  $\lambda^2$ -corrected fluorescence spectra. [c] Obtained from the solvent-dependent Stokes shifts. [d] In the presence of TFA (0.01 mL) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL).

the Supporting Information). The protonation on the *N*-methylbenzimidazole moiety caused a redshift in absorption spectra for all molecules, thus suggesting the stabilization of the LUMO level by the introduction of a cationic charge.<sup>[17]</sup>

**BzThIm** showed the reduced  $\Phi_{\rm f}$  (0.08) and an increase in the Stokes shift after protonation, which are indicative of the TICT emission in **BzThIm**+H<sup>+</sup>. Owing to the aromatic character of the annulated benzene ring, BzThIm appears to have the least quinoid character among the present molecules.<sup>[18]</sup> Compounds 2-ThIm and 3-ThIm seem to have an enhanced quinoid character relative to BzThIm, whereas they possess shorter  $\pi$  systems than **BzThIm**. Therefore, those molecules gave higher emission quantum yields than  $BzThIm + H^+$  in their protonated forms. The comparison between 2-ThIm and 3-ThIm may well demonstrate the effects of quinoid nature and intramolecular NH/S hydrogen bonds<sup>[19]</sup> in their protonated states. The former is expected to have larger quinoid character and involve the NH/S interaction in the excited state, thus giving the unchanged  $\Phi_{
m f}$  and nonradiative rate constant  $(k_{nr})$  after the protonation. Meanwhile, the protonation led to a decrease in the  $\Phi_{\rm f}$  and an increase in the  $k_{\rm nr}$  for the latter probably due to the absence of NH/S interaction and the less quinoid character anticipated from the shorter  $\pi$  system in the excited state. The extension of a  $\pi$  system from **2-ThIm** to **PhThIm** gave an increase in the quinoid character, thereby resulting in the highest  $\Phi_{\rm f}$ of 0.94 in the protonated form  $(PhThIm + H^+)$ . The suppression of rotation in the excited state by the cooperative effects of the NH/S hydrogen bonding and the quinoid character of  $\pi$  components are also suggested by the prominent decrease in the  $k_{nr}$  after protonation for the molecules with phenylthiophene and arylthienothiophene units.

The compounds that contain an arylthienothiophene unit showed a marked increase in the  $\Phi_{\rm f}$  values upon protonation with the ratios of  $\Phi_{\rm f}^{\rm H+}/\Phi_{\rm f}$  over 2, which is larger than that of **PhThIm** ( $\Phi_{\rm f}^{\rm H+}/\Phi_{\rm f}=1.57$ ). The introduction of an arylthienothiophene unit gave an elevation in the HOMO level as estimated by cyclic voltammetry (see the Supporting Information), which suggests an increased electron-donating property. The protonation increases the electron-accepting capability of the benzimidazole unit and also the extent of charge separation in the ground state. The substituent at the donor part had an impact on their photophysical properties. **OMePhTTIm**+H<sup>+</sup> led to a redshift both in the absorption and emission spectra with respect to **PhTTIm**+H<sup>+</sup>, whereas **CF<sub>3</sub>PhTTIm**+H<sup>+</sup> gave a blueshift (Figure 1). The stabiliza-



Figure 1. a) Absorption and b) emission spectra of 2-arylthieno[3,2b]thiophene-containing conjugated molecules in the presence of TFA in CH<sub>2</sub>Cl<sub>2</sub> ( $1.0 \times 10^{-5}$  M with 0.01 mL of TFA). Solid lines: **PhTTIm**+H<sup>+</sup>, broken lines: **CF<sub>3</sub>PhTTIm**+H<sup>+</sup>, and dotted lines: **OMePhTTIm**+H<sup>+</sup>.

tion and the destabilization of the excited-state energy with the electron-donating (OMe) and electron-withdrawing (CF<sub>3</sub>) groups, respectively, clearly indicated the contribution of quinoidal CT property to the excited state (Scheme 3). The degree of spectral shift from **PhTTIm**+H<sup>+</sup> to substituted ones was larger in the emission spectra than in the absorption spectra. This result suggested that the quinoidal



Scheme 3. Diagram of the emission process for the protonated forms of 2-arylthienothiophene-benzimidazole molecules. EDG: electron-donating group, EWG: electron-withdrawing group.

structure most likely contributes to the state responsible for emission rather than the Franck–Condon state formed right after the excitation. The fact that **CF<sub>3</sub>PhTTIm** gave a redshift in the absorption spectrum but a blueshift in the emission band upon protonation also supports the proposed destabilization of the quinoidal ICT state by the electron-withdrawing group. Furthermore, the significant elongation of the emission lifetime for these molecules upon protonation clearly implies the adiabatic excited state reaction from the locally excited state to the ICT state.<sup>[13]</sup>

We also measured photophysical properties in various solvents to gain further insight into the emission mechanism. The solvent-polarity-dependent Stokes shifts afforded a change in the dipole moment  $(\Delta \mu)$  between the ground and the excited states through a Lippert-Mataga plot (see the Supporting Information for details).<sup>[20]</sup> All compounds without TFA showed solvent-independent structured emission, which could be clearly assigned to the LE emission. Meanwhile, Stokes shift showed an increase with increasing solvent polarity for the protonated compounds. The absorption peak shifted to shorter wavelength in polar solvents for the protonated forms, thus indicating the stabilization of the ground state of the ionic forms. However, polar solvents gave the emission band at longer wavelength than less polar solvents, which suggests the stabilization of the excited state in polar media in a similar manner to the effect of electrondonating group on the quinoidal ICT state (Scheme 3). While polar solvents are expected to stabilize both the ground and excited state of protonated molecules, they afforded the larger values of Stokes shift than less polar solvents. This result is suggestive of the more polarized nature in the excited state than in the ground state. PhTTIm showed an increase in the  $\Delta \mu$  value from 4.07 to 7.02 upon protonation. **CF<sub>3</sub>PhTTIm** exhibited a decrease in the  $\Delta \mu$ after protonation, whereas  $OMePhTTIm + H^+$  showed the most prominent solvent dependence with a  $\Delta \mu$  value of 10.7 debye. The electron-donating character of the OMe group could facilitate the formation of polarized CT state, in which the positive charge was accepted by the arylthienothiophene unit (Scheme 3). These results also supported the introduction of ICT character in the excited state for the arylthienothiophene-containing fluorophores.

#### Acid–Base-Responsive Emission

The phenol group becomes a strong electron-donating unit specifically in the deprotonated state under basic conditions,<sup>[21]</sup> thus giving a base-enhanced D–A character. **OHPhTTIm** was thus expected to form D–A systems responsive to both acid and base. Scheme 4 shows the acid-base response of **OHPhTTIm** and subsequent resonances with quinoidal structures. Interestingly, both the (**O**<sup>–</sup>)**PhTTIm** and **OHPhTTIm** +H<sup>+</sup> states could give a very similar  $\pi$ -conjugation backbone to their quinoidal resonance structures, which would contribute to stabilizing the excited states with CT character.



Scheme 4. Acid–base response of **OHPhTTIm** and their resonance with quinoid structures.

Protonation and deprotonation in the ground state on the *N*-methylbenzimidazole and phenol unit, respectively, were confirmed by <sup>1</sup>H NMR spectroscopic measurements (Figure 2). The assignment of peaks was based on the result of correlation <sup>1</sup>H NMR spectroscopic experiments (see the Supporting Information). The addition of equimolar TFA was enough to complete the spectral shift in the <sup>1</sup>H NMR spectroscopic profile, whereas the large excess amount of



Figure 2. Parts of <sup>1</sup>H NMR spectra and signal assignment (CD<sub>3</sub>OD, 600 MHz, 298 K) of **OHPhTTIm** under different conditions. Top: With TFA (1.0 equiv); middle: blank; bottom: with *t*BuOK (200 equiv).

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potassium tert-butoxide (tBuOK) was needed for the deprotonation of phenol group. The relative acidity between TFA and N-methylbenzimidazole and between tBuOK and the phenol part might determine the amount of acid and base to complete protonation and deprotonation, respectively. The N-methyl signal (d) and protons on the benzimidazole moiety (a-c) were shifted downfield in the presence of TFA owing to the deshielding effect of the protonated benzimidazolium cation.<sup>[22]</sup> The cationic charge also had an effect on the protons (e, f) attached to the thienothiophene ring to give downfield shifts. However, the deprotonation of the phenol group with the excess amount of tBuOK resulted in the upfield shifts of protons on the donor moiety including the phenol (h,g) and thienothiophene (e,f) units. It should be noted that the protons on the phenol and thienothiophene units still appeared in the aromatic region above  $\delta =$ 6.5 ppm under both the acidic and basic conditions, which suggested the small contribution of nonaromatic quinoidal structure in the ground state.

The spectral changes of **OHPhTTIm** in the presence of TFA and *t*BuOK were measured in solutions in methanol  $(1.0 \times 10^{-5} \text{ M}, 3 \text{ mL})$ . Greater amounts of TFA (2 equiv) and *t*BuOK (2000 equiv) were needed to quench the original emission from the neutral state, probably on account of the intermolecular proton transfer in the excited states (see the Supporting Information). Both the acidic and basic states gave a similar redshifted absorption profile (Figure 3a). The blue-colored emission in the neutral state changed to green



Figure 3. a) Absorption and b) emission spectral change of **OHPhTTIm** (black) in the presence of 2.0 equiv TFA (red) and 2000 equiv *t*BuOK (blue) in methanol  $(1.0 \times 10^{-5} \text{ M})$ . c) Photographs of **OHPhTTIm** in methanol taken under 365 nm UV light.

by the addition of TFA, whereas it turned to yellow-green emission with tBuOK (Figure 3c). The degree of redshift in the fluorescence spectra was thus more pronounced in the basic state (Figure 3b). The most plausible explanation might be that the ICT state is more stabilized for (O<sup>-</sup>)PhTTIm by the electron-donating phenolate group relative to **OHPhTTIm**+H<sup>+</sup>. While the  $\Phi_{\rm f}$  increased from 0.62 to 0.82 upon protonation in a similar manner to OMePhTTIm, it was also enhanced under the basic conditions to 0.77. The nonradiative rate constant decreased from  $0.36 \text{ ns}^{-1}$  in the neutral state to  $0.10 \text{ ns}^{-1}$  in the deprotonated one (see the Supporting Information). Since the NH/S interaction did not operate without TFA, the intense greenvellow emission under basic conditions could be explained by the contribution of the quinoidal ICT state. The emission lifetime increased from 1.0 to 2.0 and 2.3 ns under the acidic and basic conditions, respectively, as in the case with other molecules that contained the arylthienothiophene unit (see the Supporting Information). Finally, we investigated the pH-dependent emission spectra of OHPhTTIm under aqueous conditions (see the Supporting Information). OHPhT-TIm successfully gave triple-color emission depending on the pH conditions with a sharp spectral response in aqueous solutions.

#### Conclusion

We synthesized acid-responsive D–A conjugated molecules that contained an arylthienothiophene unit as a donor component. The contribution of a quinoidal resonance structure in the excited state promoted the non-twisting ICT emission with strong intensity. The acid–base-responsive ICT emission from the phenol-containing fluorophore under aqueous conditions suggested the potential application of the present system to biological sensing.

## **Experimental Section**

Benzimidazole-based D-A-conjugated molecules with a variety of donor components were synthesized through Pd-catalyzed cross-coupling reaction between N-methyl-2-bromobenzimidazole and stannylated or borylated donor moieties (see the Supporting Information for details). <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded with a JEOL JNM-AL300 instrument. <sup>1</sup>H NMR (600 MHz) spectra were recorded with a JEOL JNM-ECA600. Recycling preparative GPC and normal-phase HPLC were performed with a LC-9110NEXT (Japan Analytical Industry) and LaChrom Elite (Hitachi), respectively. Elemental analysis were performed for C, H, and N with a Perkin-Elmer 2400IICHNS/O instrument. Mass spectroscopy and high-resolution mass spectroscopy (HRMS) were measured with a JEOL JMS-Q1000TD and JMS-700 MStation, respectively. UV/Vis absorption and fluorescence spectra were obtained with a JASCO V-660 spectrophotometer and a Hitachi F-7000 fluorescence spectrophotometer, respectively. Fluorescence lifetimes and absolute fluorescence quantum yields of compounds were measured with a FluoroCube 3000U (Horiba) and Hamamatsu C9920-02, respectively. Cyclic voltammetry was performed with a  $\mu$ -AUTOLAB III potentiostat/galvanostat equipped with an electrochemical analysis system software in an argon-filled glovebox. A platinum wire was used as a counter electrode, an Ag/Ag+ electrode was used as a reference elecCHEMISTRY

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trode, and a platinum disk electrode was used as a working electrode. The measurements were conducted in a solution of  $0.1\,{\rm M}$  tetrabutylammonium hexafluorophosphate (TBAPF\_6) in dichloromethane at a scan rate of  $100\,{\rm mV\,s^{-1}}$  at room temperature in an argon-filled glovebox.

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