Excited-State Design

DOI: 10.1002/anie.201404867

A Strap Strategy for Construction of an Excited-State Intramolecular Proton Transfer (ESIPT) System with Dual Fluorescence**

Naoya Suzuki, Aiko Fukazawa, Kazuhiko Nagura, Shohei Saito, Hirotaka Kitoh-Nishioka, Daisuke Yokogawa, Stephan Irle, and Shigehiro Yamaguchi**

***Abstract:** An amine-embedded flexible alkyl strap has been incorporated into an emissive boryl-substituted dithienylpyrrole skeleton as a new entity of excited-state intramolecular proton transfer (ESIPT) chromophores. The π-electron system shows a dual emission, which covers a wide range of the visible region depending on the solvent polarity. The incorporation of the aminoalkyl strap as well as the terminal boryl groups efficiently stabilize the zwitterionic excited-state species resulting from the ESIPT even in an aqueous medium.*

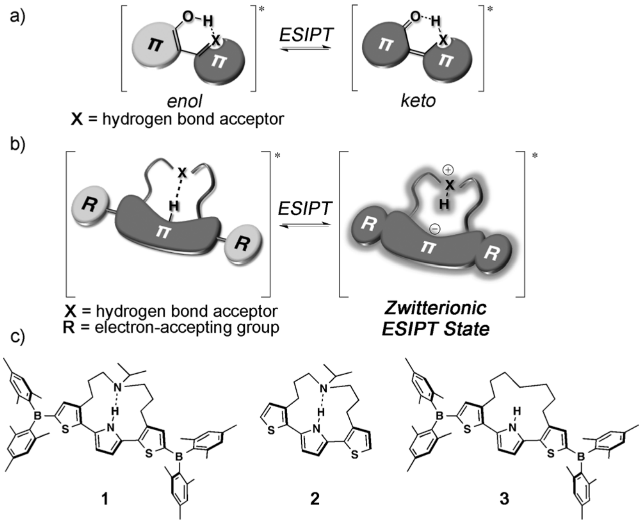


Figure 1. Designs of the excited-state proton transfer (ESIPT) systems based on a) a keto–enol type tautomerism and b) a strap strategy with a basic flexible chain. c) Chemical structures of compounds **1**–**3**.

Luminescence is one of the fundamental properties that lead to attractive molecular functions of organic compounds. Construction of novel π-conjugated skeletons that can yield characteristic luminescence properties would have a significant impact on a broad spectrum of chemistry including not only organic electronics, but also bioimaging and sensors. Among the various fascinating luminescence properties, we now focus the attention on a fluorescence based on the excited-state intramolecular proton transfer (ESIPT).[1] The ESIPT is a photochemical process that produces a tautomer with a totally different electronic structure from the initial excited form. Consequently, the ESIPT state gives rise to a fluorescence with an anomalously large Stokes shift. In addition, the ESIPT chromophores often exhibit a dual emission originating from both the initial excited form and the proton-transferred tautomer, which covers a broad wavelength range. These features of the ESIPT can be the basis of various applications including white light-emitting materials,[2–4] polymorph-dependent light-emitting materials,[5] and fluorescent probes.[6–9] However, as the formation of an intramolecular hydrogen bond is a prerequisite of the ESIPT, the ESIPT chromophores have been limited to only a few variations, such as planar molecules that consist of a phenol or aniline scaffold as a hydrogen-bond donor and an imino/azo-nitrogen- or carbonyl-oxygen-containing ring skeleton as a hydrogen-bond acceptor. The ESIPT in most of these molecules is based on a keto–enol type tautomerization (Figure 1a). An exception is 2-(hydroxyphenyl)imidazo[1,2-*a*]pyridine, whose ESIPT state adopts a zwitterionic form instead of a keto form.[5,10]

We now disclose a new design of the ESIPT chromophore, which does not rely on the keto–enol tautomerism, but is based on a strap strategy making use of a functional flexible chain. To equip the chromophore with an alkyl chain strap has been used as a simple strategy to constrain a conformation of the π-conjugated skeleton[11–14] or to insulate it.[15–18] In contrast, our idea is to employ an alkyl strap embedding an amine moiety, thereby endowing it with the function of a base. We install this strap in an emissive π-conjugated scaffold bearing a relatively acidic proton (Figure 1b). As the π skeleton, we chose a pyrrole-containing oligoarene. The appropriate chain length of the aminoalkyl strap would ensure the formation of an intramolecular hydrogen bond between a nitrogen atom in the strap and the pyrrole N−H proton. In the excited state, the acidity of the pyrrole N−H would increase[19] similar to that of a phenol O−H.[20] This behavior would be enhanced by introduction of an electron-accepting group in the pyrrole-containing π-conjugated skeleton to impart a donor–acceptor type character. Based on this consideration, we designed compound **1** that has an electron-donating dithienylpyrrole skeleton with electron-accepting boryl groups at the termini. We found that the ESIPT indeed occurred in this molecule to produce a zwitter-

---

[*] N. Suzuki, Prof. Dr. A. Fukazawa, Dr. K. Nagura, Dr. S. Saito,
Dr. H. Kitoh-Nishioka, Prof. Dr. D. Yokogawa, Prof. Dr. S. Irle,
Prof. Dr. S. Yamaguchi
Institute of Transformative Bio-molecules (WPI-ITbM) and
Department of Chemistry, Graduate School of Science
Nagoya University
Furo, Chikusa, Nagoya 464-8602 (Japan)
E-mail: sirle@chem.nagoya-u.ac.jp
yamaguchi@chem.nagoya-u.ac.jp

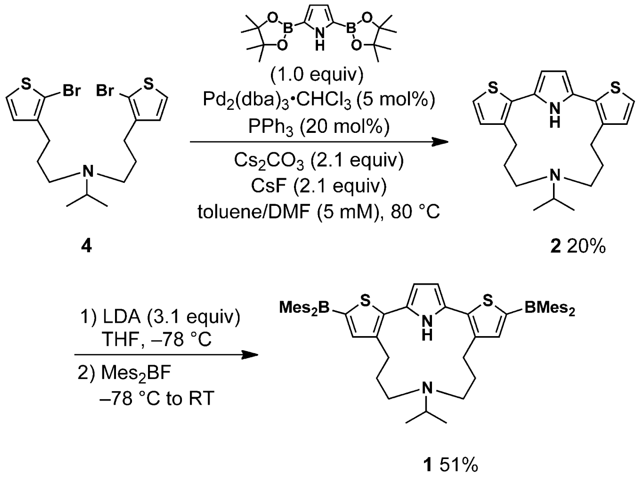
[**] This work was partly supported by JST, CREST (S.Y. and S.I.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404867.

ionic excited state. Here we present the synthesis and characteristic fluorescence properties of **1**. The time-resolved fluorescence spectroscopy and the quantum chemical calculations as well as the comparison with pertinent reference compounds, a nonborylated (**2**) and an alkyl-strapped (**3**) analogue, provide deeper insight into the ESIPT emission.

Compound **1** was synthesized in two steps from a dialkylamine-tethered dithiophene **4** (Scheme 1). The Pd-catalyzed cross-coupling of the dibromide **4** with pyrrole-2,5-diboronate in 5 mM toluene/dimethyl formamide (DMF) produced the strapped dithienylpyrrole **2** in 20 % yield. Compound **2** was dilithiated with 3.1 equiv of LDA followed by treatment with Mes_2BF to afford the diborylated derivative **1**. This compound was stable enough to purify by silica gel column chromatography and 51 % yield was obtained. The alkyl-strapped reference compound **3** was obtained in a similar manner (see Scheme S2 in the Supporting Information, SI).

The structure of **1** was determined by X-ray crystallography (Figure 2). The aminoalkyl strap constrains the conformation of the dithienylpyrrole framework in a twisted form. The dihedral angles between the central pyrrole ring and the adjacent thiophene rings are 43.5° and −19.6°. The close proximity between the nitrogen atom in the alkyl strap and the pyrrole N−H is noteworthy. The distance between the two nitrogen atoms N1 and N2 is 3.26 Å, indicative of a weak hydrogen bond between the amine moiety and the N−H proton of the pyrrole ring.[21] The resonance signal of the N−H proton in the ^1H NMR spectrum of **1** in C_6D_6 appeared at 12.8 ppm, which is significantly downfield-shifted compared to that of the alkyl-strapped analogue **3** (7.71 ppm). This difference suggested that the hydrogen bonding is retained even in solution (Figure S41).



Scheme 1. Synthesis of compound **1**.

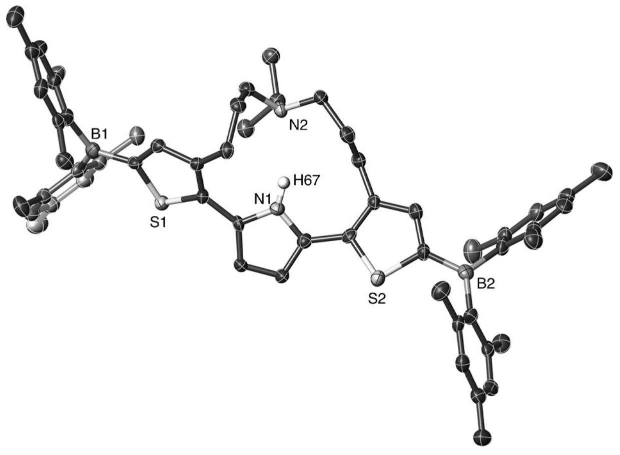


Figure 2. Thermal ellipsoid plot of **1** (50 % probability). Hydrogen atoms are omitted for clarity except for the N−H proton on the pyrrole ring.

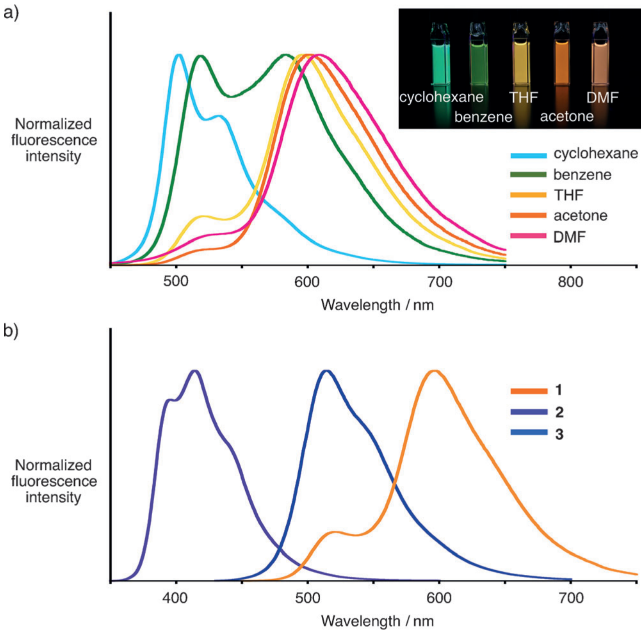


Figure 3. a) Fluorescence spectra of **1** in various solvents excited at 390 nm (inset: photographs under the irradiation with a 365 nm lamp) and b) fluorescence spectra of **1**, **2**, and **3** in THF (excitation wavelength: 390 nm for **1** and **3**, 330 nm for **2**).

Compound **1** showed remarkable solvent-dependent fluorescence. In cyclohexane, **1** has a strong absorption band with the maximum at 451 nm and exhibited a bluish-green fluorescence at 500 nm with the quantum yield Φ_F of 0.21 (Figure 3 a and Table 1). When the solvent was changed to benzene, the absorption maximum did not change significantly, but the emission band was slightly shifted to 520 nm and, most notably, a new intense band appeared at 581 nm. As a result, the dual emission bands from a single molecule cover a wide range in the visible region. As the solvent polarity was further increased by using acetone or DMF, the intensity of the shorter emission band significantly decreased and the longer emission band became dominant, giving rise to an orange or reddish-orange fluorescence (Figure 3 a, inset). In conjunction with these changes, the Φ_F also increased in the more polar solvents. The highest Φ_F value of 0.46 was obtained in acetone.

To elucidate the origin of the dual emission, we conducted several measurements. First, the excitation spectra of **1** were

Table 1: Photophysical data of **1**, **2**, and **3** in various solvents.

		Absorption		Fluorescence			
	Solvent	λ_{abs}[a] [nm]	ε [$\times 10^4$ $M^{-1}cm^{-1}$]	λ_{em}[b] [nm]	Φ_F[c]	τ_1[d] [ns]	τ_2[e] [ns]
1	cyclohexane	451	4.78	500, 530	0.21	0.46	1.1
	benzene	456	4.81	520, 581	0.21	0.41	0.71
	THF	451	5.05	520, 594	0.37	0.37	1.5
	acetone	450	4.80	520, 602	0.46	1.0	2.3
	DMF	453	4.60	525, 609	0.41	0.87	2.6
2	THF	334	2.12	396	0.29	0.85	–[f]
3	THF	428	2.79	514	0.14	0.84	–[f]

[a] Only the longest absorption maximum wavelengths are shown. [b] Emission maxima upon excitation at 390 nm. [c] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error. [d] Fluorescence lifetimes of the shorter-wavelength emission bands. [e] Fluorescence lifetimes of the longer-wavelength emission bands. [f] Not observed.

similar to the absorption spectra regardless of the monitored wavelengths, 510 nm or 610 nm, as well as the solvents used (Figures S2–S6). This fact demonstrates that the two emission bands originate from the identical ground state. Secondly, the picosecond time-resolved fluorescence spectroscopy revealed that these two emission bands have distinct lifetimes from each other. Thus, the lifetimes of the shorter-wavelength and longer-wavelength emission bands range from 0.37 to 1.0 ns and from 0.71 to 2.6 ns, respectively. These results lead to the conclusion that these two emission bands originate from two distinct states.

The comparison of **1** with the structurally relevant compounds **2** and **3** demonstrated the necessity of the amino group in the strap and the terminal boryl groups to obtain the dual emission (Figures 3b, S7, and S8). Thus, in stark contrast to the dual emission of **1**, the nonborylated derivative **2** only showed a single-component emission at $\lambda_{em} = 396$ nm ($\tau_{FL} = 0.85$ ns) in THF. This fluorescence did not show a significant solvent dependence (Figure S7). These results demonstrate that the introduction of the electron-accepting boryl groups to the terminal positions is crucial for the dual emission. The alkyl-tethered analogue **3** also exhibited a single-component fluorescence with the λ_{em} of 514 nm in THF, whose fluorescence lifetime τ_{FL} was 0.84 ns. These values are comparable to those of the shorter-wavelength emission band of **1**. Thus, the shorter-wavelength emission band of **1** should be correlated to the diborylated dithienylpyrrole skeleton itself and the longer-wavelength emission band of **1** should result from the contribution of the intramolecular N−H···N hydrogen bond. Hence, we assigned the two bands to the emissions from a locally excited state (LE) and an ESIPT state, respectively. The temperature-dependent fluorescence measurement of **1** in 2-methyltetrahydrofuran showed that the longer-wavelength emission band became dominant as the temperature decreased from 294 K to 170 K (Figure S16). Thus, the two distinct states responsible for each emission band are in thermal equilibrium.

A characteristic feature of the ESIPT emission of **1** is its solvent dependence. The longer emission band of **1** at 581 nm in benzene showed a bathochromic shift to 609 nm in DMF (Figure 3a and Table 1). This is in contrast to the conventional ESIPT systems based on the keto–enol tautomerism, which generally shows a hypsochromic shift with increasing solvent polarity due to the less polar nature of the keto form in the ESIPT state than the corresponding geometry in the ground state.[9a,22,23] The present result indicates that the ESIPT state in **1** has a highly polarized character.

To gain deeper insights into the character of the excited state of **1**, calculations on both the ground state (S_0) and the lowest-energy excited singlet state (S_1) in the gas phase and in acetone were conducted using the CAM-B3LYP functional with the 6-31G+(d) (for N atoms), 6-31G(d,p) (for the migrating H atom), and 6-31G(d) basis sets (for the other atoms). Truhlar's SMD solvation model[24] was used to take the solvent effect into account. The TD-DFT vertical excitation calculations[25] suggested that the lowest-energy transition from S_0 to S_1 is attributable to the HOMO→LUMO transition. The HOMO and LUMO are inherently the π and π* orbitals delocalized on the 2,5-dithienylpyrrole moiety. The LUMO also has a significant contribution of the vacant p orbitals of the boron atoms. Accordingly, the HOMO→LUMO transition is the π–π* transition with a pronounced charge transfer character similar to the known boron-containing π-electron systems (Figure S22).[26]

Geometry optimizations in S_1 starting from the Franck–Condon state and the proton-transferred structure as initial guesses indeed gave two local minima corresponding to the LE and ESIPT states. The plausible potential energy surfaces are shown in Figure 4. The energies of the LE and ESIPT states relative to the optimized geometry in S_0 are +2.94 eV and +3.47 eV in the gas phase, and +2.78 eV and +2.81 eV in acetone, respectively. Notably, the ESIPT state is significantly stabilized in the polar solvent and consequently comparable to the LE state in energy. The dipole moments of the LE and ESIPT states are 4.07 D and 10.4 D in the gas phase, and 6.65 D and 17.1 D in acetone, respectively. The significant increase in the dipole moment of the ESIPT state in the polar solvent is consistent with the solvent effect observed in the fluorescence spectra. The large magnitude of the dipole moment vector and its direction in the ESIPT state of **1** strongly support its zwitterionic character (Figures S19 and S21).

In the optimized structure of **1** in the ESIPT state in acetone, the N···H distance between the strap amine and the pyrrole hydrogen (1.041 Å) indeed becomes shorter to a considerable extent compared to that (2.301 Å) in the LE state. In agreement with this change, the B−C bond between the boryl group and the thienyl group is also shortened from 1.534 and 1.528 Å in the LE state compared to 1.523 Å in the ESIPT state. According to the natural population analysis (NPA), upon the change from the LE to ESIPT state, the sums of the natural charges in the 2,5-dithienylpyrrole moiety and in the two Mes_2B moieties become more negative by −0.213 and −0.098 in the gas phase, and −0.263 and −0.121 in acetone, respectively.[27] Namely, the total negative charge of the diborylated dithienylpyrrole moiety increases in the polar solvent, and a substantial amount of the negative charge is accommodated on the Mes_2B moiety. These results clearly demonstrate that the terminal boryl groups play a pivotal role

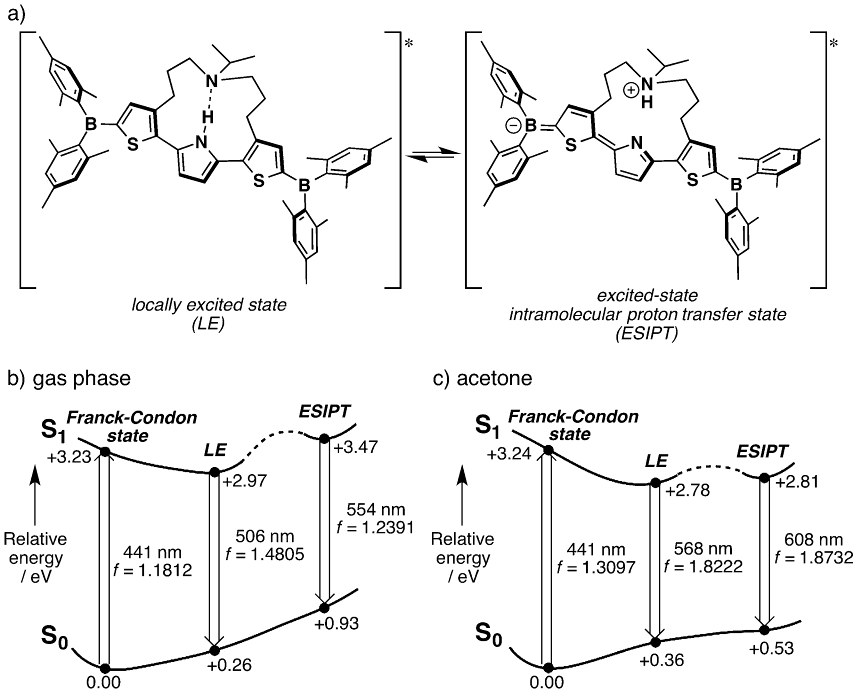


Figure 4. a) Schematic representation of **1** in the LE and ESIPT states. Potential energy surfaces b) in the gas phase and c) in acetone. The relative energies calculated with the CAM-B3LYP functional are given in kcal mol^{-1} relative to the optimized geometry in S_0. The TD-DFT vertical excitation energies and oscillator strengths (*f*) are calculated with the PBE0 functional. Solvents are considered using the SMD model.

as the electron-accepting groups in the excited state, giving rise to the significant stabilization of the zwitterionic ESIPT state.

In most of the conventional ESIPT systems, the ESIPT is prohibited in an aqueous medium due to the formation of intermolecular hydrogen bonding with the protic solvent.[1,28,29] To retain the ESIPT emission even in the aqueous medium, it requires a specific structure that significantly favors the intramolecular hydrogen-bonded conformer[24] or a special treatment to prevent the interaction with the solvent, such as the formation of an inclusion complex of the ESIPT system with a host molecule like cyclodextrin.[30–32] In stark contrast, the present aminoalkyl-strapped **1** showed the ESIPT emission even in water-containing solvents (Figure 5). Upon increasing the water content in the THF/water mixture from 0% to 40%,[33] the intensity of the longer-wavelength emission band continuously increased and, eventually, the fluorescence quantum yield Φ_F in the 60:40 (v/v) THF/water solution reached 54%. The relative intensities of the two emission bands were almost proportional to the water content of the THF/water mixture (for the detailed discussion, see SI and Figure S17). This characteristic feature is likely due to either the structural constraint of the pyrrole and alkylamine moieties, or the steric protection of the hydrogen-bonded N−H⋯N moiety from the solvent molecules by the aliphatic aminoalkyl strap. This feature would be beneficial to various applications that are exerted in an aqueous medium, such as bioimaging or sensory materials.

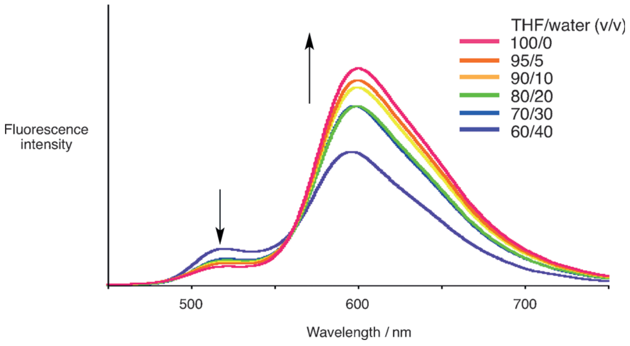


Figure 5. Fluorescence spectra of **1** in THF/water mixtures from 100:0 to 60:40 THF/H_2O (v/v).

In summary, we have developed a new ESIPT chromophore consisting of an aminoalkyl-strapped dithienylpyrrole bearing boryl groups. The π-electron system shows dual emission bands with high luminescence quantum yields, which cover a wide range in the visible region depending on the solvent polarity. Our “functional strap” strategy endows two remarkable features totally different from those of the conventional ESIPT system based on the keto–enol tautomerism: 1) the significant zwitterionic character, and 2) no disruption of the ESIPT emission even in an aqueous medium. These features are potential advantages for the application as environment-responsive fluorophores. Further investigation along this line as well as the systematic study regarding the effect of the strap length, the substituents on the aminoalkyl moiety, and the terminal boryl groups are now in progress in our group.

Received: May 1, 2014

Keywords: boron · ESIPT · fluorescence · hydrogen bonds · π conjugation

---

[1] Recent reviews: a) A. P. Demchenko, K.-C. Tang, P.-T. Chou, *Chem. Soc. Rev.* **2013**, *42*, 1379; b) J. Zhao, S. Ji, Y. Chen, H. Guo, P. Yang, *Phys. Chem. Chem. Phys.* **2012**, *14*, 8803; c) J. E. Kwon, S. Y. Park, *Adv. Mater.* **2011**, *23*, 3615; d) C.-C. Hsieh, C.-M. Jiang, P.-T. Chou, *Acc. Chem. Res.* **2010**, *43*, 1364.
[2] a) S. Kim, J. Seo, H. K. Jung, J.-J. Kim, S. Y. Park, *Adv. Mater.* **2005**, *17*, 2077; b) S. Park, J. E. Kwon, S. H. Kim, J. Seo, K. Chung, S.-Y. Park, D.-J. Jang, B. M. Medina, J. Gierschner, S. Y. Park, *J. Am. Chem. Soc.* **2009**, *131*, 14043.
[3] H. Shono, T. Ohkawa, H. Tomoda, T. Mutai, K. Araki, *ACS Appl. Mater. Interfaces* **2011**, *3*, 654.
[4] K.-C. Tang, M.-J. Chang, T.-Y. Ling, H.-A. Pan, T.-C. Fang, K.-Y. Chen, W.-Y. Hung, Y.-H. Hsu, P.-T. Chou, *J. Am. Chem. Soc.* **2011**, *133*, 17738.

[5] T. Mutai, H. Tomoda, T. Ohkawa, Y. Yabe, K. Araki, *Angew. Chem.* **2008**, *120*, 9664; *Angew. Chem. Int. Ed.* **2008**, *47*, 9522.

[6] M. Fischer, P. Wan, *J. Am. Chem. Soc.* **1999**, *121*, 4555.

[7] a) S. Ercelen, A. S. Klymchenko, A. P. Demchenko, *Anal. Chim. Acta* **2002**, *464*, 273; b) A. S. Klymchenko, A. P. Demchenko, *Phys. Chem. Chem. Phys.* **2003**, *5*, 461; c) A. S. Klymchenko, A. P. Demchenko, *J. Am. Chem. Soc.* **2002**, *124*, 12372; d) A. S. Klymchenko, A. P. Demchenko, *Langmuir* **2002**, *18*, 5637; e) A. S. Klymchenko, G. Duportail, T. Ozturk, V. G. Pivovarenko, Y. Mély, A. P. Demchenko, *Chem. Biol.* **2002**, *9*, 1199.

[8] D. A. Yushchenko, V. V. Shvadchak, A. S. Klymchenko, G. Duportail, V. G. Pivovarenko, Y. Mély, *J. Phys. Chem. A* **2007**, *111*, 10435.

[9] a) C. J. Fahrni, M. M. Henary, D. G. VanDerveer, *J. Phys. Chem. A* **2002**, *106*, 7655 – 7663; b) M. M. Henary, Y. Wu, C. J. Fahrni, *Chem. Eur. J.* **2004**, *10*, 3015.

[10] a) A. Douhal, F. Amat-Guerri, A. U. Acuña, *J. Phys. Chem.* **1995**, *99*, 76; b) A. Douhal, F. Amat-Guerri, A. U. Acuña, *Angew. Chem.* **1997**, *109*, 1586; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1514.

[11] a) T. Ando, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 172; b) M. Kataoka, T. Ando, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 177; c) M. Kataoka, T. Ando, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1909; d) F. Toda, T. Ando, M. Kataoka, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1914.

[12] a) S. Eisler, R. McDonald, G. R. Loppnow, R. R. Tykwinski, *J. Am. Chem. Soc.* **2000**, *122*, 6917; b) A. Spantulescu, T. Luu, Y. Zhao, R. McDonald, R. R. Tykwinski, *Org. Lett.* **2008**, *10*, 609.

[13] D. Vonlanthen, A. Mishchenko, M. Elbing, M. Neuburger, T. Wandlowski, M. Mayor, *Angew. Chem.* **2009**, *121*, 9048; *Angew. Chem. Int. Ed.* **2009**, *48*, 8886.

[14] a) K. Sugiyasu, Y. Honsho, R. M. Harrison, A. Sato, T. Yasuda, S. Seki, M. Takeuchi, *J. Am. Chem. Soc.* **2010**, *132*, 14754; b) Y. Ouchi, K. Sugiyasu, S. Ogi, A. Sato, M. Takeuchi, *Chem. Asian J.* **2012**, *7*, 75; c) R. Shomura, K. Sugiyasu, T. Yasuda, A. Sato, M. Takeuchi, *Macromolecules* **2012**, *45*, 3759.

[15] J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martín-Alvarez, F. Hampel, J. A. Gladysz, *Angew. Chem.* **2002**, *114*, 1951; *Angew. Chem. Int. Ed.* **2002**, *41*, 1871.

[16] C. Klinger, O. Vostrowski, A. Hirsch, *Eur. J. Org. Chem.* **2006**, 1508.

[17] K. Sugiyasu, M. Takeuchi, *Chem. Eur. J.* **2009**, *15*, 6350.

[18] Y. Fujiwara, R. Ozawa, D. Onuma, K. Suzuki, K. Yoza, K. Kobayashi, *J. Org. Chem.* **2013**, *78*, 2206.

[19] a) C. A. Taylor, M. A. El-Bayoumi, M. Kasha, *Proc. Natl. Acad. Sci. USA* **1969**, *63*, 253; b) F. T. Vert, I. Z. Sanchez, A. O. Torrent, *J. Photochem.* **1983**, *23*, 355; c) O. A. Borg, B. Durbeej, *J. Phys. Chem. B* **2007**, *111*, 11554.

[20] a) T. Förster, *Naturwissenschaften* **1949**, *36*, 186; b) W. Bartok, P. J. Lucchesi, N. S. Snider, *J. Am. Chem. Soc.* **1962**, *84*, 1842; c) J. L. Rosenberg, I. Brinn, *J. Phys. Chem.* **1972**, *76*, 3558; d) L. G. Arnaut, S. J. Formosinho, *J. Photochem. Photobiol.* **1993**, *75*, 1; e) A. Z. Weller, *Elektrochemie* **1952**, *56*, 662; f) M. Gutman, E. Nachiel, *Biochim. Biophys. Acta Bioenerg.* **1990**, *1015*, 391; g) G. Jackson, G. Porter, *Proc. R. Soc. London, Ser. A* **1961**, *260*, 13; h) J. A. Syage, *J. Phys. Chem.* **1995**, *99*, 5772; i) A. Douhal, F. Lahmani, A. H. Zewail, *Chem. Phys.* **1996**, *207*, 477; j) G. Granucci, J. T. Hynes, P. Millié, T.-H. Tran-Thi, *J. Am. Chem. Soc.* **2000**, *122*, 12243.

[21] T. Steiner, *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48.

[22] F. Rodriguez Prieto, M. C. R. Rodríguez, M. M. Gonzalez, M. A. R. Fernández, *J. Phys. Chem.* **1994**, *98*, 8666.

[23] S. Santra, G. Krishnamoorthy, S. K. Dogra, *J. Phys. Chem. A* **2000**, *104*, 476.

[24] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.

[25] TD-DFT vertical excitation energies and the oscillator strengths were calculated using both CAM-B3LYP and PBE0 functionals. The transition energies obtained with the PBE0 functional are given in Figure 4 because of a better agreement with the experimental results compared to those obtained with the CAM-B3LYP functional. See SI for details.

[26] Reviews on fluorescent tricoordinate organoboron compounds: a) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574; c) S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, *78*, 1413; d) Z. M. Hudson, S. Wang, *Acc. Chem. Res.* **2009**, *42*, 1584; e) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985.

[27] The sums of natural charges for the 2,5-dithienylpyrrole moiety and two $\mathrm{Mes_2B}$ groups are −0.401 and 0.303 in the LE state, −0.614 and 0.205 in the ESIPT state in the gas phase; −0.410 and 0.271 in the LE state, −0.673 and 0.150 in the ESIPT state in acetone, respectively.

[28] M. Kasha, *J. Chem. Soc. Faraday Trans. 2* **1986**, *82*, 2379.

[29] S. J. Formosinho, L. G. Arnaut, *J. Photochem. Photobiol. A* **1993**, *75*, 21.

[30] a) E. L. Roberts, P. T. Chou, T. A. Alexander, R. A. Agbaria, I. M. Warner, *J. Phys. Chem.* **1995**, *99*, 5431; b) E. L. Roberts, J. Dey, I. M. Warner, *J. Phys. Chem.* **1996**, *100*, 19681; c) E. L. Roberts, J. Dey, I. M. Warner, *J. Phys. Chem. A* **1997**, *101*, 5296.

[31] B. K. Paul, A. Samanta, N. Guchhait, *Langmuir* **2010**, *26*, 3214.

[32] F. A. S. Chipem, S. K. Behera, G. Krishnamoorthy, *J. Phys. Chem. A* **2013**, *117*, 4084.

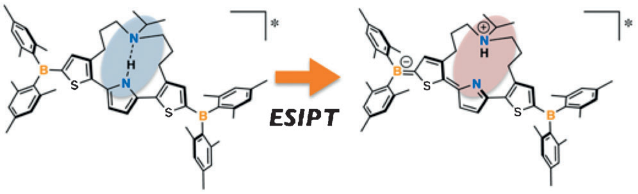
[33] Compound **1** became insoluble when the water content exceeded 50 %.

Communications

Excited-State Design

N. Suzuki, A. Fukazawa, K. Nagura,
S. Saito, H. Kitoh-Nishioka, D. Yokogawa,
S. Irle,* S. Yamaguchi* ______ ■■■■–■■■■

A Strap Strategy for Construction of an Excited-State Intramolecular Proton Transfer (ESIPT) System with Dual Fluorescence



Hold on to the strap: A new type of excited-state intramolecular proton transfer (ESIPT) chromophores has been developed by incorporation of an amine-embedded alkyl strap into an emissive boryl-substituted dithienylpyrrole skeleton. The product's dual fluorescence covers a wide range in the visible region depending on the solvent polarity. The zwitterionic ESIPT state is efficiently stabilized by the aminoalkyl strap and the terminal boryl groups.