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Fluorescence of Diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium Salts Under Various Conditions

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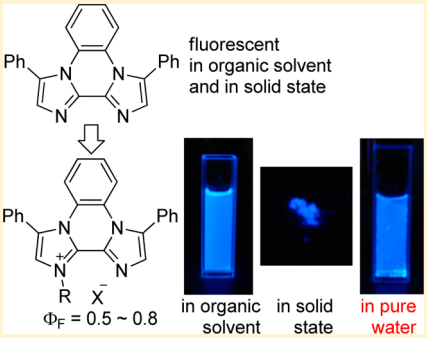
Supporting Information

ABSTRACT: The synthesis and photophysical properties of diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium salts were examined for different counteranions. The ethyl-substituted diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium salt with tosylate anion (categol-ized in ionic liquid) showed good fluorescence (Φ_F = 0.77) in organic solvent. The 3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium salts showed absorption and fluorescence peaks resembling those of the former diimidazoquinoxaline. The salt also emitted under various conditions such as in organic solvents, water, and even in the solid state, while retaining a good fluorescence quantum yield (Φ_F = 0.5−0.8). Furthermore, the fluorescence was quenched efficiently through the introduction of an electron-donating substituent on the alkyl side chain.

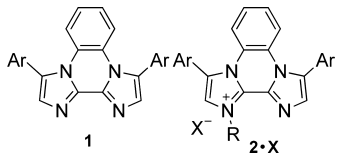


INTRODUCTION

The development of organic fluorophores is essential for progress in many areas of chemistry and functional materials research. Various fluorescence materials based on planar π conjugation have been explored.[1] However, the application of the chromophores under desired circumstances sometimes requires consideration at the stage of synthesis planning. For instance, hydrophilic poly(ethylene glycol) (PEG) has been attached to fluorophores for dissolution in water, and the PEG block is sometimes introduced in the early or middle stages of their synthesis.[2] One of the simplest methods for changing the character of a compound is the formation of the ionic form when the chromophore possesses an sp^2 nitrogen atom in its π conjugation, such as in pyridine and imidazole. For example, phosphonated cyanines have been formed by the substitution reaction of alkyl bromide with benzothiazole.[3] They show enhanced in fluorescent intensity upon the addition of $Ca(ClO_4)_2$. The synthesis and physical properties of a 2,2′-bibenzimidazolium compound have been investigated by Shi and Thummel,[4] and 2,2′-bibenzimidazolium salts have been explored as synthetic reagents with electron donors.[5] Bielawski and co-workers reported fluorescent materials consisting of benzobis(imidazolium) salts,[6] which showed interesting physical and optical properties. Furthermore, compounds containing an ionic structure in the fused cyclic system also exhibited fluorescence ability.[7,8] This implies that it is also possible to utilize the ionic structure as a fluorophore. Some imidazolium salts exist as ionic liquids, which are useful as reaction solvents[9] and electrolytes.[10] Furthermore, it is possible to provide further functionality and introduce additional properties at the alkyl chain in imidazolium-type ionic structures. Therefore, the ionization of the heterocyclic system has potential for the development of novel functional materials.

Recently, we reported the luminescent properties of diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline derivatives (**1**) with a high quantum yield (~70%) in the blue region (Chart 1).[11] These

Chart 1



materials have an sp^2 nitrogen atom that can introduce a substituent through alkylation. Herein, we report the physical properties of diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium salts (**2·X**), which showed fluorescence properties resembling those of the parent diimidazo[1,2-*a*:2′,1′-*c*]quinoxalines (**1**) in organic solvents. **2·X** exhibited luminance under various conditions, including in the solid state and in aqueous solution. Furthermore, the quenching of luminance by the introduced substituent is also demonstrated. Fluorophores with solubility in water as well as quenching ability are promising materials for utilization as chemical and biological sensors.[12,13]

RESULTS AND DISCUSSION

Compound **1** was alkylated with alkyl iodide in CH_3CN under reflux to give the corresponding salt **2·I** (Scheme 1). Double alkylation never occurred even with excess alkyl halide present. The compound (**2·OTs**) bearing tosylate as the counteranion was also obtained through the reaction of **1** with alkyl tosylate.

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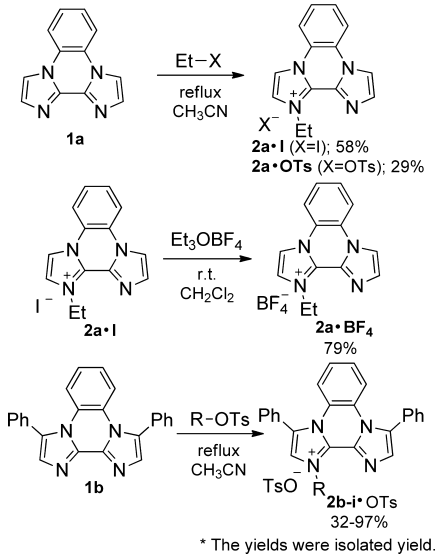
Scheme 1. Formation of Diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium Salts



The tetrafluoroborate derivative (**2a·BF$_4$**) was obtained from **2a·I** by anion exchange using triethyloxonium tetrafluoroborate.[14]

The physical properties of **1** and **2·X** are summarized in Table 1. We first examined the influence of the counteranion and the substituent on the melting point. The melting point decreased upon the introduction of an ethyl group at the sp^2 nitrogen atom in the case of the compounds with no substituent at the 3- and 10-positions (**1a** vs **2a·X**). The tosylate anion gave the lowest melting point (89−90 °C) among the three different anions used (entries 2−4), yielding a compound that is categorized as an "ionic liquid."[15] On the contrary, there was little effect on the melting point upon salt formation in the case of the 3,10-diphenyl compounds (**1b** vs **2b·OTs**) (entries 5 and 7). Similar melting points were obtained even upon the introduction of linear and branched alkyl chains (**2b·OTs**, **2c·OTs**, **2d·OTs**, and **2e·OTs**) (entries 7, 12, 13, and 14). It suggests that the interaction in between neighboring diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium moieties is more efficient to give crystal packing than that in the alkyl chain. However, a decrease in melting point of about 100 °C was observed when the phenyl group was attached to the substituted alkyl group (**2f·OTs**) (entry 15), which would be caused by somewhat change in the crystal structure with new interaction between diimidazoquinoxalinium structure and phenyl ring on the side chain.

The absorption and fluorescence spectra of the diimidazoquinoxalinium salts were measured in CH_3CN (Table 1). In comparison with **1a**, a slight longer wavelength of the absorption maximum peak (λ_{max}) was obtained upon the introduction of alkyl groups in **2a·I** (entry 2 and Figure 1). The fine structure was also observed in the absorption spectra, which suggests that the diimidazoquinoxalinium has a rigid structure. The fluorescence peak (λ_{em}) of **2a·I** was at 353 nm with a 14-nm hypsochromic shift compared with that of **1a**

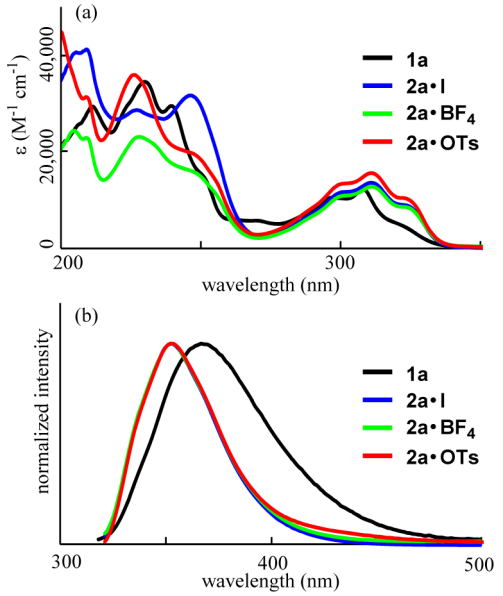


Figure 1. (a) Absorption (3.0 × 10^{-5} M in CH_3CN) and (b) fluorescence (3.0 × 10^{-7} M in CH_3CN) spectra of **1a**, **2a·I**, **2a·BF$_4$**, and **2a·OTs**.

Table 1. Physical Properties of 1 and 2·X

entry	compd	Ar	R	X	mp[a] (°C)	solvent	λ_{max} (nm) [ε (M^{-1} cm^{-1})][b]	λ_{em} (nm)[c] [Φ_F][d]
1	**1a**	H			261	CH_3CN	307.5 [12200]	367 [0.70]
2	**2a·I**	H	Et	I	157−158	CH_3CN	311 [13700]	353 [0.68]
3	**2a·BF$_4$**	H	Et	BF_4	240−241	CH_3CN	311 [12700]	353 [0.78]
4	**2a·OTs**	H	Et	OTs	89−90	CH_3CN	311 [15500]	353 [0.77]
5	**1b**	Ph			203−204	CH_3CN	329 [14200]	424 [0.47]
6						THF	335 [11500]	428 [0.82][e]
7	**2b·OTs**	Ph	Et	OTs	223−224	CH_3CN	335.5 [17700]	429 [0.63]
8						THF	336.5 [17900]	433 [0.72]
9						H_2O	334 [16800]	429 [0.72]
10						aq NaOH (pH = 11.8)	334.5 [19100]	430 [0.65]
11						aq HCl (pH = 2.2)	334 [19100]	430 [0.66]
12	**2c·OTs**	Ph	*n*-Bu	OTs	203−204	CH_3CN	335.5 [17800]	428 [0.78]
13	**2d·OTs**	Ph	*i*-Bu	OTs	209−210	CH_3CN	336.5 [17600]	428 [0.65]
14	**2e·OTs**	Ph	*n*-Hex	OTs	203−204	CH_3CN	335.5 [18500]	428 [0.22]
15	**2f·OTs**	Ph	$-(CH_2)_3Ph$	OTs	105−107	CH_3CN	336 [18600]	427 [0.65]

[a]Melting points are uncorrected. [b]Concentration: 3.0 × 10^{-5} M. [c]Concentration: 3.0 × 10^{-7} M. [d]Determined by *p*-terphenyl (Φ_F = 0.87, excited at 265 nm) as a standard. [e]Determined by quinine sulfate (Φ_F = 0.55, excited at 366 nm) as a standard.

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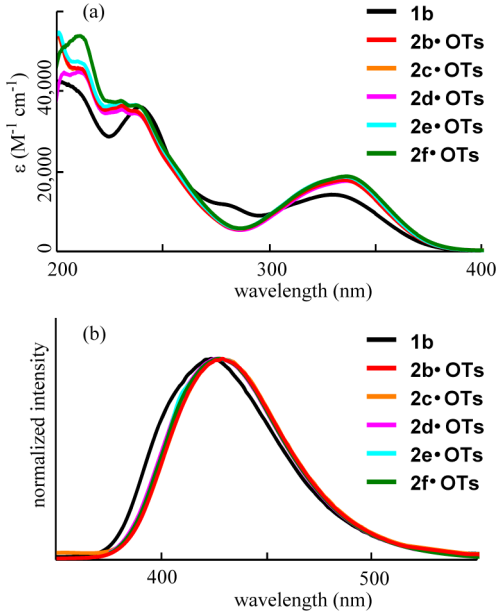

Figure 2. (a) Absorption (3.0×10^{-5} M in CH_3CN) and (b) fluorescence (3.0×10^{-7} M in CH_3CN) spectra of **1b** and **2b–f·OTs**.

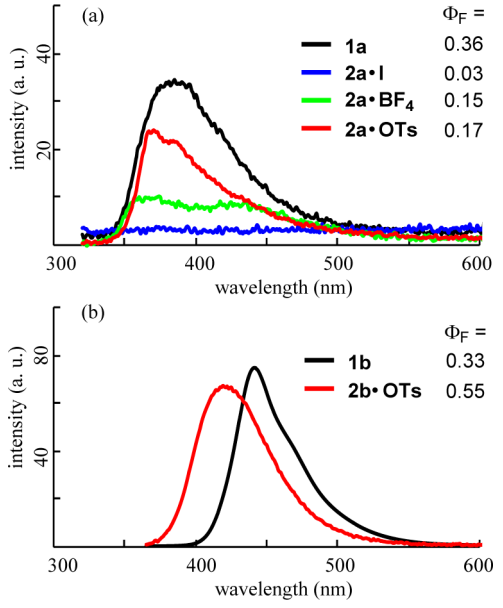

Figure 3. Fluorescence spectra in the solid state with integration sphere system: (a) **1a**, **2a·I**, **2a·BF_4**, and **2a·OTs** excited at 311 nm; (b) **1b** and **2b·OTs** excited at 335 nm. Φ_F values were determined by using a calibrated integration sphere system.

(entry 2 and Figure 2). The fluorescence quantum yield (Φ_F) remained at ≈70% even upon introduction of an alkyl chain. No influence of the counteranion was observed on the peaks of the absorption and fluorescence spectra (**2a·I**, **2a·BF_4**, and **2a·OTs**) (entries 2–4). However, Φ_F differed slightly (0.68 for **2a·I**, 0.78 for **2a·BF_4**, and 0.77 for **2a·OTs**).

Interestingly, a change of below 6 nm for λ_{max} and λ_{em} was observed between **1b** and **2b·OTs** bearing phenyl groups (entries 5 and 7 in Table 1, and Figure 2), and Φ_F was increased upon changing from the diphenyldiimidazoquinoxaline to the diphenyldiimidazoquinoxalinium structure, which is caused by restriction of the rotation of phenyl ring to introduce the alkyl chain. Focused on the difference in the alkyl chain, **2e·OTs** bearing a long alkyl chain gave a decrease in Φ_F (entry 14). This is because nonradiative decay through the motion of the alkyl chain was increased. However, the phenyl group attached to the edge of the introduced alkyl group did not affect the optical properties in the absorption and fluorescence spectra (entry 15).

In order to obtain further information, we investigated the fluorescence properties of the various materials under different conditions. As mentioned in our previous paper, **1b** shows luminescence in the solid state.[11] Therefore, we examined the fluorescence properties of diimidazoquinoxalinium derivatives in the solid state. We selected **1a** and **2a·X** as the objective substrates because not only the structural change but also the counteranion would affect the optical properties under the aggregated conditions. Compound **1a** was illuminated by photoirradiation with medium quantum yield (Φ_F = 0.36) (Figure 3a). Compounds **2a·BF_4** and **2a·OTs** also exhibited photoluminescence with a decrease in Φ_F (0.15 and 0.17, respectively). However, the fluorescence of **2a·I** was strictly quenched because of the heavy atom effect of the iodide counteranion. The emission peak of **2a·OTs** showed a hypsochromic shift compared with **1a**, and **2a·BF_4** exhibited two broadened peaks. Compounds **1b** and **2b·OTs** also showed emission in the solid state (Figure 3b). Furthermore, an increase in Φ_F was observed upon the attachment of phenyl rings at the 3- and 10-positions in **1b** with a hypsochromic shift of the emission peak, which is a different result from that obtained in solution. From these results, it was found that these 3,10-diaryldiimidazoquinoxaline and 3,10-diaryldiimidazoquinoxalinium structures potentially have emission properties in the solid state upon photoirradiation, even though they have different fluorescence properties in solution.

The solvent effect on the absorption and fluorescence spectra of **1b** and **2b·OTs** is represented in Figure 4. Because of its ionic structure, **2b·OTs** could be dissolved in H_2O without any organic cosolvent. A slight influence on the absorption and fluorescence peaks was observed in both **1b** and **2b·OTs**. Although a decrease in Φ_F was observed for **1b** in a polar solvent (entries 5 and 6 in Table 1), Φ_F of **2b·OTs** was maintained in various solvents (entries 7–11). It was found that **2b·OTs** could be utilized as a good fluorophore, emitting in the visible region even in acidic, basic, and neutral H_2O (entries 9, 10, and11).

The absorption and fluorescence properties of **1b** and **2b·OTs** were consistent with the results of DFT calculations. From the results of the DFT and TDDFT calculations at the B3LYP/6-31+G level (Figure 5), the orbitals of both structures derived in the ground state (from DFT) and excited state (from TDDFT) were delocalized in the biimidazole moiety and substituted phenyl groups at the 3- and 10-positions in the HOMOs of the **1b** and **2b** cation. The LUMOs also exist in the biimidazole and phenyl parts with the region on the phenylene moiety of the diimidazoquinoxaline structure. Therefore, there is little charge transfer in the ground and excited states, which leads to a less pronounced solvent effect on λ_{max} and λ_{em}. The orbital energies of both the HOMO and LUMO decrease upon introduction of an alkyl group to form the diimidazoquinoxalinium structure. However, there is little change in the energy separation between the HOMO and LUMO in the **1b** and **2b** cation (ΔE = 4.101 eV for **1b** and 4.044 eV for **2b** cation from DFT calculations; ΔE = 3.102 eV for **1b** and 3.129 eV for **2b** cation from TDDFT calculations). Thus, the small wavelength

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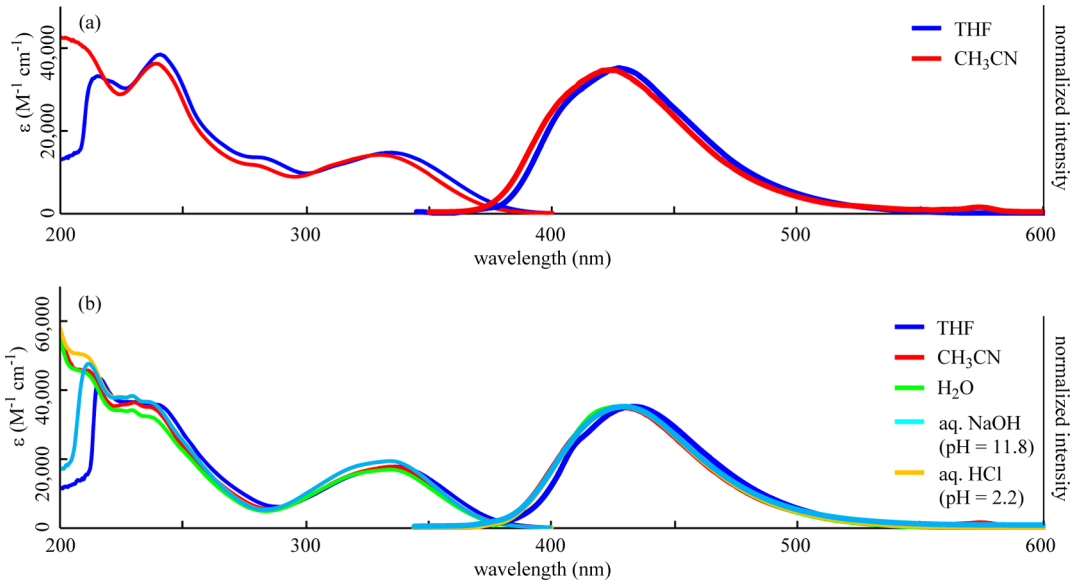

Figure 4. Absorption (narrow line, 3.0×10^{-5} M) and fluorescence (bold line, 3.0×10^{-7} M) spectra of (a) **1b** and (b) **2b·OTs** in THF, CH_3CN, H_2O, aq NaOH (pH = 11.8), and aq HCl (pH = 2.2).

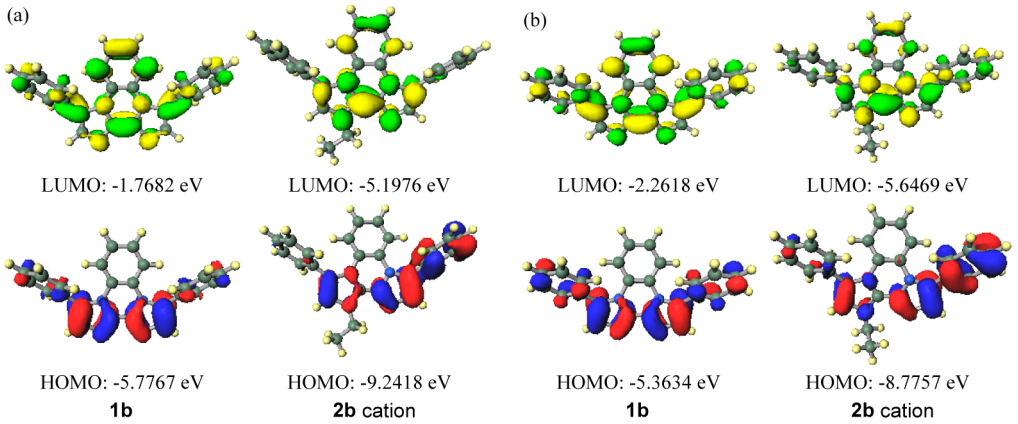

Figure 5. Orbitals and energies of HOMO and LUMO of **1b** and **2b** cation estimated by (a) DFT and (b) TDDFT (nstate = 10) calculations for structure optimization at the B3LYP/6-31+G level.

change in the absorption and fluorescence peaks would be observed by lowering the orbital energies of the HOMO and LUMO by the same degrees.

From the consideration of the result of the DFT calculations, fluorescence quenching of **2b·OTs** was observed upon the introduction of a moiety with electron-donating ability. To reveal the possibility to such phenomenon directly, the fluorescent intensity of **2b·OTs** under solvent-free conditions was reduced by mixing about the same volume of **2b·OTs** with each electron-donating substrate, 3,4,5-trimethoxytoluene and anthracene, whereas they were less effective in **1b** which has higher LUMO orbital energies than **2b** cation (Figure 6). Upon mixing **2b·OTs** with anthracene, the fine structure observed in the fluorescence spectrum shown in Figure 6b is due to emission from the anthracene. In solution, the quenching phenomenon was also observed upon the combination of **2b·OTs** and 3,4,5-trimethoxytoluene, although an excess of the donating 3,4,5-trimethoxytoluene (over 100 equiv) was necessary for efficient quenching (Figure 7).

Furthermore, we examined the intramolecular quenching due to the electron-donating property of the alkyl chain. The optical properties of compounds **2g·OTs**, **2h·OTs**, and **2i·OTs** bearing a 3,4,5-trimethoxyphenyl group or an anthryl group on the alkyl chain are summarized in Table 2 and Figure 8. The data for **2f·OTs**, which is their phenyl analogue with a propylene linker, is also represented for reference. Fluorescence quenching of **2h·OTs** and **2i·OTs** was observed in dilute conditions (3.0×10^{-7} M) (entries 3 and 4), whereas **2g·OTs** showed fluorescence with $\Phi_F = 0.50$. It is suggested that the length of the alkyl chain is important for quenching the fluorescence, and that the propylene linker gives the appropriate alignment for the interaction between the electron-donating substituent and the diimidazoquinoxalinium part. In terms of the quenching ability of the different substituents, it was found that the fluorescence of **2i·OTs** was quenched more effectively than that of **2h·OTs** ($\Phi_F = 0.03$ for **2i·OTs** vs 0.16 for **2h·OTs**). The ionization potential of anthracene (7.23 eV)[16] is lower than that of 1,2,3-trimethoxybenzene (7.74 eV).[17] Therefore, we believe that the quenching mechanism can be explained rationally by the acceptor-excited photoinduced electron transfer depicted in Scheme 2.[18,19] The diimidazoquinoxalinium part (**A**) is excited by photoirradiation to give the "SOMO" state (Scheme 2 (ii)). When an electron-donating substrate (**B**) is present in the appropriate position of **A**, the

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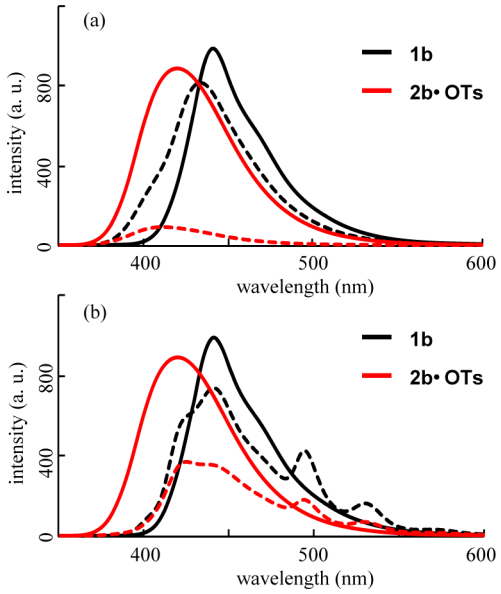


Figure 6. Fluorescence spectra in solid state excited at 335 nm: (a) **1b** (solid black line), **1b** + 3,4,5-trimethoxytoluene (ca. 1:1 (v/v)) (dashed black line), **2b·OTs** (solid red line), and **2b·OTs** + 3,4,5-trimethoxytoluene (ca. 1:1 (v/v)) (dashed red line); (b) **1b** (solid black line), **1b** + anthracene (ca. 1:1 (v/v)) (dashed black line), **2b·OTs** (solid red line), and **2b·OTs** + anthracene (ca. 1:1 (v/v)) (dashed red line).

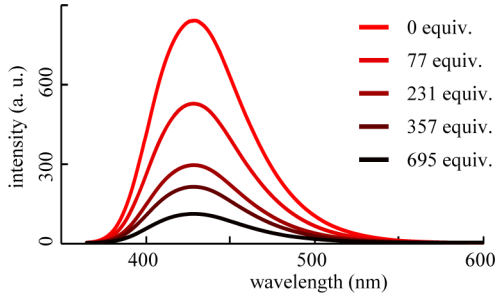


Figure 7. Fluorescence spectra (3.0×10^{-5} M in CH_3CN) of **2b·OTs** with various amounts of 3,4,5-trimethoxytoluene (excited at 355 nm).

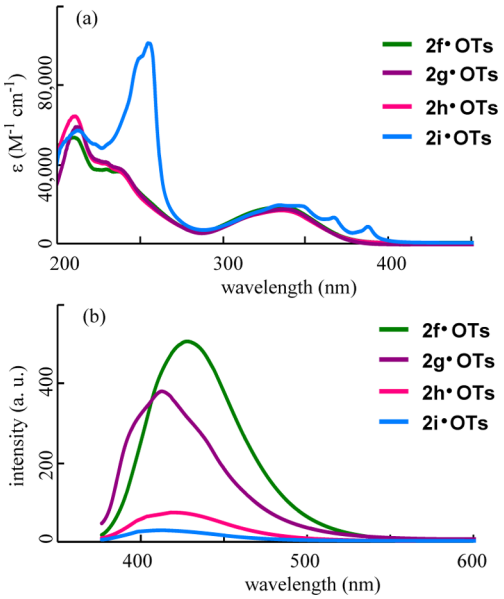


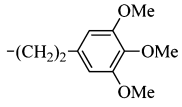
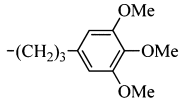
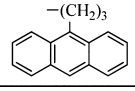
Figure 8. (a) Absorption (3.0×10^{-5} M in CH_3CN) and (b) fluorescence (3.0×10^{-7} M in CH_3CN) spectra of **2f–i·OTs**.

"HOMO" electron of **B** is easily transferred to the lowering "SOMO" of **A** (Scheme 2 (iii)). As a result, further electron transfer between **B** and **A** occurs, followed by nonradiative decay to reach the ground state (Scheme 2 (iv)). From these findings, we suggest that the fluorescence of diimidazoquinoxalinium is controllable by the functionality introduced though the alkyl side chain at the 1-position.

■ CONCLUSION

We have synthesized various diimidazo[1,2-*a*:2′,1′-*c*]-quinoxalinium salts through substitution reactions with alkylation reagents and the exchange of the counteranions and examined their optical properties under various conditions. Fine fluorescence properties with $\Phi_F \approx 0.8$ were obtained in solution. The 3,10-diphenyldiimidazaoquinoxalinium derivatives showed absorption and emission peaks resembling those of the original diimidazoquinoxaline (**1b**). Furthermore, the diimidazoquinoxalinium salts exhibited fluorescence in various

Table 2. Physical Properties of 2·X with Aryl Group Attached

entry	Compound	Ar	R	X	λ_{max} (nm) [ε (M^{-1} cm^{-1})]^a	λ_{em} (nm)^b [Φ_F]^c
1	**2f•OTs**	Ph	$-(CH_2)_3$-Ph	OTs	336 [18,600]	427 [0.65]
2	**2g•OTs**	Ph		OTs	337 [17,700]	412 [0.50]
3	**2h•OTs**	Ph		OTs	337 [16,400]	425 [0.16]
4	**2i•OTs**	Ph		OTs	335, 367, 388 [19,100, 12,800, 8,100]	421 [0.03]

^{a}Measured in CH_3CN (3.0×10^{-5} M). ^{b}Measured in CH_3CN (3.0×10^{-7} M). ^{c}Determined by *p*-terphenyl (Φ_F = 0.87, excited at 265 nm) as a standard.

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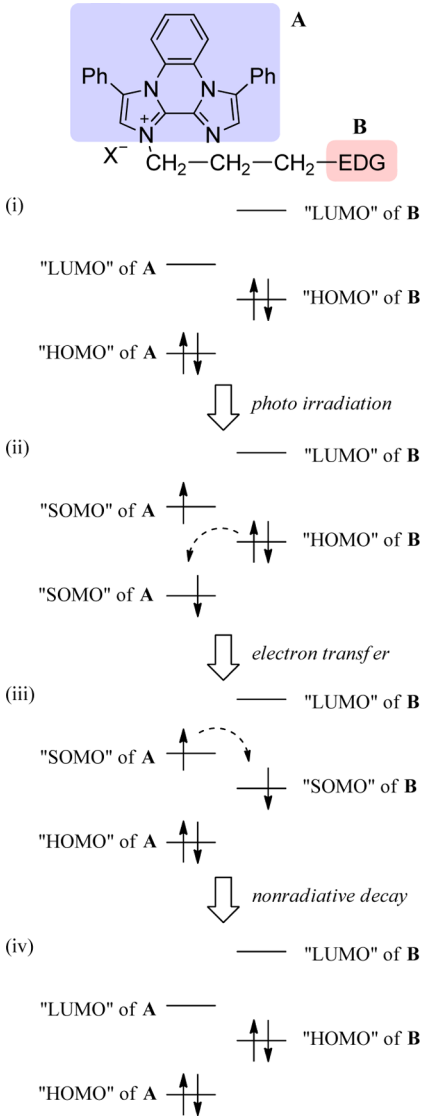
Scheme 2. Proposed Fluorescence Quenching Mechanism for 2b Based on Photoelectron Transfer



solvents, especially in H_2O with Φ_F = 0.72, and even illuminated in the solid state. Therefore, they can be utilized as fluorophores under various conditions. The long length of the alkyl chain decreased the fluorescence intensity. The counteranion such as iodide anion had decreased the fluorescence in the solid state, but was less effective in solution. We further examined the electron-donating effect of the substituent attached on the alkyl side chain, and found that substrates with electron-donating character led to efficient quenching of the fluorescence because of the photoelectron transfer. This result implies that novel functional fluorophores can be designed using this interaction between the diimidazoquinoxalinium structure and the group attached on the alkyl side chain. From these findings, it is suggested that diimidazoquinoxalinium salts have potential for application not only as fluorophores utilized under various conditions, but also in the fields of sensors, biological fluorescence imaging, biolabeling, and so on. The applications of this diimidazoquinoxaline structure as a sensor are under investigation.

EXPERIMENTAL SECTION

General Information. Melting points were uncorrected. NMR measurements were recorded with a 300 MHz spectrometer for ^{1}H NMR and with a 75 MHz spectrometer for ^{13}C NMR. Chemical shifts (δ) of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane in $CDCl_3$ (δ = 0) or DMSO-d_5 (δ = 2.49) as an internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), bs (broadened singlet), and coupling constants (J) are reported in hertz units. Chemical shifts (δ) of ^{13}C NMR are expressed in parts per million downfield or upfield from $CDCl_3$ (δ = 77.0) or DMSO-d_6 (δ = 39.6) as an internal standard. Infrared spectra (IR) were recorded on a KBr disk. UV−vis and PL spectra were measured in a quartz cell. The absolute fluorescence quantum yield in solid state was measured with the integrating sphere unit. Anhydrous CH_3CN was distilled from sodium hydride and was stored with MS 3 Å. Anhydrous $CHCl_3$ was distilled from P_2O_5 after washing with MeOH and drying with $CaCl_2$, and was stored with MS 4 Å. Anhydrous THF was distilled from sodium benzophenone ketyl immediately prior to use. The reactions were performed under nitrogen atmosphere.

1-Ethyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium Iodide (2a·I). To a solution of diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline (**1a**)[11] (62.3 mg, 0.299 mmol) in CH_3CN (1.2 mL) was added iodoethane (82.4 mg, 0.528 mmol). The mixture was stirred under reflux conditions for 24 h. After being cooled to room temperature, the reaction mixture was concentrated in vacuo. From ^{1}H NMR of the crude products, the reaction proceeded almost quantitatively. The residual mixture was recrystallized from CH_3CN and hexane to give 1-ethyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium iodide (**2a·I**) (63.2 mg, 0.174 mmol) in 58% isolated yield as a white solid: mp 240.1−241.1 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.57 (t, J = 7.1 Hz, 3H), 4.93 (q, J = 7.2 Hz, 2H), 7.81 (t, J = 7.3 Hz, 1H), 7.88 (t, J = 6.5 Hz, 1H), 7 95 (s, 1H), 8.43 (d, J = 2.1 Hz, 1H), 8.57 (d, J = 7.3 Hz, 1H), 8.60 (d, J = 7.9 Hz, 1H), 8.99 (s, 1H), 9.10 (d, J = 2.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 15.0, 44.7, 115.6, 116.8, 117.7, 118.0, 122.5, 124.4, 124.7, 127.9, 129.4, 129.8, 130.6, 134.1; IR (KBr) 3072, 3021, 1644, 1583, 1503, 1455, 1434, 1332, 774, 677 cm^{-1}. Anal. Calcd for $C_{14}H_{13}IN_4 \cdot {}^3/_5H_2O$: C, 44.84; H, 3.82; N, 14.94. Found: C, 44.88; H, 3.54; N, 14.83.

1-Ethyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium Tetrafluoroborate (2a·BF_4). To a solution of 1-ethyldiimidazo[1,2-*a*:2′,1′-*c*]-quinoxalinium iodide (**2a·I**) (36.4 mg, 0.100 mmol) in CH_3CN (3 mL) was added a solution of triethyloxonium tetrafluoroborate in CH_2Cl_2 (1 M; 0.1 mL, 0.1 mmol). After being stirred at room temperature for 28 h, the reaction mixture was concentrated in vacuo. From ^{1}H NMR of the crude products, the reaction proceeded almost quantitatively. The reaction residue was recrystallized from CH_3CN and hexane to give 1-ethyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium tetrafluoroborate (**2a·BF_4**) (25.8 mg, 79.6 mmol) in 80% isolated yield as white solid: mp 156.5−157.8 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.56 (t, J = 7.3 Hz, 3H), 4.92 (q, J = 7.2 Hz, 2H), 7.81 (t, J = 7.5 Hz, 1H), 7.88 (t, J = 7.3 Hz, 1H), 7.95 (s, 1H), 8.42 (d, J = 1.6 Hz, 1H), 8.56 (d, J = 7.6 Hz, 1H), 8.58 (d, J = 7.7 Hz, 1H), 8.99 (s, 1H), 9.08 (d, J = 1.8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 15.0, 44.7, 115.5, 116.7, 117.7, 118.0, 122.5, 124.4, 124.7, 127.9, 129.4, 129.9, 130.6, 134.1; IR (KBr) 3050, 3022, 1644, 1583, 1505, 1456, 1435, 1333, 774, 678 cm^{-1}. Anal. Calcd for $C_{14}H_{13}BF_4N_4 \cdot {}^1/_6H_2O$: C, 51.41; H, 4.11; N, 17.13. Found: C, 51.68; H, 4.10; N, 16.88.

1-Ethyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2a·OTs). To a solution of **1a** (63.0 mg, 0.302 mmol) in CH_3CN (1.2 mL) was added ethyl *p*-toluenesulfonate (104 mg, 0.519 mmol). The mixture was stirred at 60 °C for 24 h. After being cooled to room temperature, the reaction mixture was concentrated in vacuo. From ^{1}H NMR of the crude products, the reaction almost proceeded quantitatively. The residual mixture and was recrystallized from CH_3CN and hexane to give 1-ethyldiimidazo[1,2-*a*:2′,1′-*c*]-quinoxalinium *p*-toluenesulfonate (**2a·OTs**) (36.0 mg, 0.0881 mmol) in 29% isolated yield as white solid: mp 89.4−90.3 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.56 (t, J = 7.3 Hz, 3H), 2.72 (s, 3H), 4.92 (q, J = 7.3 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.9 Hz, 2H),

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7.81 (t, J = 7.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7 95 (s, 1H), 8.42 (d, J = 1.5 Hz, 1H), 8.58 (t, J = 7.9 Hz, 2H), 8.98 (s, 1H), 9.08 (d, J = 1.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 15.0, 20.8, 44.7, 115.6, 116.8, 117.7, 118.0, 122.5, 124.4, 124.7, 125.5, 127.9, 128.1, 129.4, 129.8, 130.5, 134.1, 137.6, 145.8; IR (KBr) 3092, 3066, 1644, 1505, 1456, 1432, 1332, 1195, 776, 690 cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_4O_3S{\cdot}H_2O$: C, 59.14; H, 5.20; N, 13.14. Found: C, 59.02; H, 5.12; N, 13.10.

1-Ethyl-3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2b·OTs). This compound was prepared in 55% isolated yield (0.115 g, 0.204 mmol) from 3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxaline (**1b**)[11] (0.135 g, 0.373 mmol) at 60 °C for 24 h according to a procedure similar to that mentioned for **2a·OTs**: pale yellow solid; mp 222.8−224.0 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.75 (t, J = 7.2 Hz, 3H), 2.24 (s, 3H), 5.27 (q, J = 7.2 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 7.17 (ddd, J = 1.3, 7.03, and 8.5 Hz, 1H), 7.25 (ddd, J = 1.6, 7.0, and 8.3 Hz, 1H), 7.54−7.61 (m, 12H), 7.70 (s, 1H), 7.75 (diffused d, J = 8.0 Hz, 2H), 8.47 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3, 21.1, 46.2, 118.5, 119.6, 124.0, 125.6, 125.9, 126.3, 126.5, 126.7, 128.0, 128.2, 128.7, 129.4, 129.6, 129.7, 130.2, 130.4, 130.56, 130.63, 130.7, 130.9, 132.6, 135.4, 138.1, 144.5; IR (KBr) 3056, 2981, 1645, 1579, 1491, 1469, 1447, 1403, 1202, 1122 cm^{-1}. Anal. Calcd for $C_{33}H_{28}N_4O_3S$: C, 70.69; H, 5.03; N, 9.99. Found: C, 70.22; H, 5.12; N, 9.90.

1-*n*-Butyl-3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2c·OTs). This compound was prepared in 41% isolated yield (48.3 mg, 0.0820 mmol) from **1b** (72.1 mg, 0.200 mmol) at 70 °C for 24 h according to a procedure similar to that mentioned in **2a·OTs**: pale yellow solid; mp 202.5−203.6 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (t, J = 7.3 Hz, 3H), 1.54 (sext, J = 7.6 Hz, 2H), 2.10 (quint, J = 7.5 Hz, 2H), 2.24 (s, 3H), 5.22 (t, J = 7.5 Hz, 2H), 6.96 (d, J = 7.9 Hz, 2H), 7.16 (ddd, J = 1.4, 7.2, and 8.7 Hz, 1H), 7.24 (ddd, J = 1.5, 7.2, and 8.4 Hz, 1H), 7.53−7.61 (m, 12H), 7.69 (s, 1H), 7.77 (dd, J = 1.7 and 8.0 Hz, 2H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.6, 19.7, 21.2, 31.9, 50.5, 118.5, 119.7, 124.1, 125.91, 125.93, 126.4, 126.6, 126.7, 128.1, 128.2, 128.8, 129.5, 129.6, 129.8, 130.2, 130.5, 130.7, 130.79, 130.84, 131.0, 132.6, 135.4, 138.2, 144.4; IR (KBr) 3058, 2959, 2872, 1645, 1579, 1492, 1468, 1447, 1403, 1213 cm^{-1}. Anal. Calcd for $C_{35}H_{32}N_4O_3S$: C, 71.40; H, 5.48; N, 9.52. Found: C, 71.19; H, 5.50; N, 9.41.

1-Isobutyl-3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2d·OTs). This compound was prepared in 33% isolated yield (39.1 mg, 0.0664 mmol) from **1b** (72.1 mg, 0.200 mmol) with 4 equiv of isobutyl *p*-toluenesulfonate under reflux conditions for 72 h according to a procedure similar to that mentioned in **2a·OTs**: pale yellow solid; mp 208.7−209.6 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.12 (d, J = 6.7 Hz, 6H), 2.34 (s, 3H), 2.52 (nonet, J = 7.0 Hz, 1H), 5.07 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 7.16 (ddd, J = 1.2, 7.3, and 8.2 Hz, 1H), 7.24 (ddd, J = 1.2, 7.3, and 8.5 Hz, 1H), 7.54−7.63 (m, 12H), 7.68 (s, 1H), 7.78 (dd, J = 1.7 and 7.8 Hz, 2H), 8.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.6, 21.1, 29.2, 57.0, 118.5, 119.6, 124.0, 125.9, 126.29, 126.33, 126.5, 126.7, 128.0, 128.2, 128.7, 129.4, 129.6, 129.7, 130.2, 130.49, 130.53, 130.7, 130.97, 131.00, 132.6, 135.3, 138.1, 144.5; IR (KBr) 3057, 2962, 2873, 1642, 1579, 1492, 1469, 1447, 1402, 1193 cm^{-1}. Anal. Calcd for $C_{35}H_{32}N_4O_3S{\cdot}^2/_3CHCl_3$: C, 64.10; H, 4.93; N, 8.38. Found: C, 63.81; H, 4.90; N, 8.37.

1-*n*-Hexyl-3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2e·OTs). This compound was prepared in 38% isolated yield (46.9 mg, 0.0760 mmol) from **1b** (72.2 mg, 0.200 mmol) at 70 °C according for 24 h to a procedure similar to that mentioned in **2a·OTs**: pale yellow solid; mp 202.6−203.6 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J = 7.0 Hz, 3H), 1.29−1.40 (m, 4H), 1.46−1.57 (m, 2H), 2.11 (quint, J = 7.6 Hz, 2H), 2.24 (s, 3H), 5.21 (t-like, J = 7.6 Hz, 2H), 6.96 (d, J = 7.9 Hz, 2H), 7.16 (ddd, J = 1.3, 7.2, and 8.7 Hz, 1H), 7.24 (ddd, J = 1.5, 7.0, and 8.4 Hz, 1H), 7.54−7.61 (m, 12H), 7.67 (s, 1H), 7.78 (dd, J = 1.8 and 8.0 Hz, 2H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 21.2, 22.4, 26.1, 29.9, 31.2, 50.7, 118.5, 119.7, 124.1, 125.87, 125.94, 126.4, 126.6, 126.7, 128.1, 128.2, 128.8, 129.4, 129.6, 129.8, 130.2, 130.6, 130.7, 130.79, 130.82, 131.0, 132.6, 135.4, 138.1, 144.4; IR (KBr) 3055, 2955, 28592, 1645, 1579, 1491, 1468, 1447, 1404, 1203 cm^{-1}. Anal. Calcd for $C_{37}H_{36}N_4O_3S{\cdot}^1/_3H_2O$: C, 71.36; H, 5.93; N, 9.00. Found: C, 71.33; H, 5.84; N, 8.98.

1-(3-Phenylpropyl)-3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]-quinoxalinium *p*-Toluenesulfonate (2f·OTs). This compound was prepared in 56% isolated yield (0.112 g, 0.172 mmol) from **1b** (0.110 g, 0.306 mmol) under reflux conditions for 48 h according to a procedure similar to that mentioned in **2a·OTs**: colorless solid; mp 105.1−106.7 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 2.53 (quint, J = 7.4 Hz, 2H), 2.90 (t, J = 7.3 Hz, 2H), 5.31 (t, J = 7.3 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 7.01 (m, 1H), 7.08−7.24 (m, 4H), 7.15 (ddd, J = 1.5, 7.4, and 8.7 Hz, 1H), 7.23 (ddd, J = 1.5, 7.1, and 8.4 Hz, 1H), 7.48 (dd, J = 1.2 and 8.5 Hz, 1H), 7.53−7.62 (m, 11H), 7.68 (s, 1H), 7.71 (dd, J = 1.4 and 7.6 Hz, 2H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 30.7, 32.6, 50.4, 118.4, 119.6, 123.9, 125.8, 125.9, 126.0, 126.2, 126.4, 126.7, 128.0, 128.1, 128.21, 128.24, 128.7, 129.5, 129.6, 129.7, 130.26, 130.34, 130.6, 130.7, 130.8, 131.0, 132.6, 135.4, 138.2, 140.5, 144.4; IR (KBr) 3056, 1645, 1579, 1491, 1468, 1447, 1405, 1208, 1119, 1033, 1012, 766, 702, 678, 569, 561 cm^{-1}. Anal. Calcd for $C_{40}H_{34}N_4O_3S{\cdot}^1/_4H_2O$: C, 73.32; H, 5.31; N, 8.55. Found: C, 73.32; H, 5.28; N, 8.55.

1-(3-(3,4,5-Trimethoxyphenyl)ethyl)-3,10-diphenyl-diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2g·OTs). This compound was prepared in 97% isolated yield (53.2 mg, 0.0731 mmol) from **1b** (27.3 mg, 0.0757 mmol) under reflux conditions for 48 h according to a procedure similar to that mentioned in **2a·OTs**: colorless solid; mp 263.7−265.0 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 3.45 (t, J = 7.4 Hz, 2H), 3.76 (s, 3H), 3.80 (s, 6H), 5.52 (t, J = 7.3 Hz, 2H), 6.72 (s, 2H), 6.98 (d, J = 8.0 Hz, 2H), 7.15 (dt, J = 1.3 and 8.6 Hz, 1H), 7.23 (dd, J = 1.5 and 8.9 Hz, 1H), 7.51−7.62 (m, 12H), 7.69 (dd, J = 1.8 and 7.7 Hz, 2H), 7.71 (s, 1H), 8.47 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 36.3, 51.3, 56.2, 60.7, 106.5, 118.5, 119.6, 124.1, 125.9, 126.2, 126.4, 126.5, 126.7, 128.19, 128.24, 128.7, 129.5, 129.6, 129.8, 130.3, 130.4, 130.6, 130.8, 130.9, 131.0, 132.5, 132.8, 135.4, 136.8, 138.3, 144.4, 153.2; IR (KBr) 3446, 3093, 3061, 2999, 2941, 2836, 1645, 1591, 1506, 1468, 1409, 1334, 1215, 1206, 1123, 1035, 1013 cm^{-1}. Anal. Calcd for $C_{42}H_{38}N_4O_6S{\cdot}^1/_7CHCl_3$: C, 68.04; H, 5.17; N, 7.53. Found: C, 67.74; H, 5.20; N, 7.56.

1-(3-(3,4,5-Trimethoxyphenyl)propyl)-3,10-diphenyl-diimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2h·OTs). This compound was prepared in 92% isolated yield (0.209 g, 0.281 mmol) from **1b** (0.110 g, 0.306 mmol) under reflux conditions for 48 h according to a procedure similar to that mentioned in **2a·OTs**: colorless solid; mp 105.3−107.0 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 2.57 (quint, J = 7.1 Hz, 2H), 2.89 (t, J = 7.3 Hz, 2H), 3.69 (s, 3H), 3.73 (s, 6H), 5.32 (t, J = 7.0 Hz, 2H), 6.42 (s, 2H), 6.98 (d, J = 7.6 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 8.1 Hz, 1H), 7.50−7.72 (m, 15H), 8.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 30.7, 33.0, 50.5, 56.1, 60.7, 105.5, 118.5, 119.7, 124.0, 125.9, 126.2, 126.3, 126.4, 126.7, 128.2 (thresh high), 128.7, 129.5, 129.6, 129.7, 130.3, 130.4, 130.7, 130.8, 130.9, 131.0, 132.7, 135.4, 136.2, 136.4, 138.4, 144.3, 152.9; IR (KBr) 3056, 2939, 2839, 1645, 1589, 1507, 1468, 1404, 1195, 1214 cm^{-1}. Anal. Calcd for $C_{43}H_{40}N_4O_6S{\cdot}^6/_7CHCl_3$: C, 62.47; H, 4.88; N, 6.64. Found: C, 62.42; H, 4.98; N, 6.61.

1-(3-(9-Anthryl)propyl)3,10-diphenyldiimidazo[1,2-*a*:2′,1′-*c*]quinoxalinium *p*-Toluenesulfonate (2i·OTs). This compound was prepared in 32% isolated yield (61.8 mg, 0.0823 mmol) from **1b** (92.4 mg, 0.256 mmol) under reflux conditions for 48 h according to a procedure similar to that mentioned in **2a·OTs**: pale yellow solid; mp 147.1−150.5 °C ($CHCl_3$−Et_2O); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 2.72 (sept, J = 7.4 Hz, 2H), 3.91 (t, J = 7.7 Hz, 2H), 5.49 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 7.14 (dt, J = 1.4 and 7.2 Hz, 1H), 7.22 (dt, J = 1.4 and 8.7 Hz, 1H), 7.34 (t, J = 8.0 Hz, 2H), 7.41−7.63 (m, 15H), 7.69 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 8.14 (s, 1H), 8.39 (s, 1H), 8.40 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 24.8, 30.9, 50.4, 118.5, 119.6, 123.9, 124.6, 124.8, 125.6,

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125.8, 125.9, 126.0, 126.2, 126.3, 126.6, 128.1, 128.3 (thresh high), 128.8, 128.9, 129.5, 129.6, 129.7, 130.3 (thresh high), 130.4, 130.7, 131.0, 131.4, 132.5, 133.0, 135.3, 138.4; IR (KBr) 3054, 2971, 1642, 1579, 1492, 1467, 1446, 1403, 1193, 1122 cm^{-1}. Anal. Calcd for $C_{48}H_{38}N_4O_3S\cdot{}^1/_4CHCl_3$: C, 74.23; H, 4.94; N, 7.18. Found: C, 74.49; H, 5.08; N, 7.25.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for new compounds and Cartesian coordinates of the results of DFT and TDDFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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