Opposite substituent effects in the ground and excited states on the acidity of N–H fragments involved in proton transfer reaction in aromatic urea compounds

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Abstract

To investigate substitution effects on excited-state intermolecular proton transfer (ESPT) reactions as well as acidity of proton donating fragments in the ground state, we synthesized substituted anthracen-2-yl-3-phenylurea derivatives that form a hydrogen bonds with acetate anions and undergo ESPT reaction. Fluorescence lifetime measurements and their kinetic analyses revealed that the trifluoromethyl group on the phenyl ring as an electron-withdrawing group caused a slow ESPT reaction despite an increase in the acidity of the N–H fragment in the ground state. In contrast, the methoxy group as a donating group leads to a fast ESPT reaction despite a reduction of the acidity of the N–H fragment in the ground state. These effects of substituents on ESPT reaction are due to their influence on the charge transfer reaction, which occurs from the N–H fragment to the anthryl ring to increase the acidity of N–H followed by ESPT reaction, over the urea unit by a combination of resonance and inductive effects. These opposing effects of substituents on the acidity of the urea unit in the ground and excited states provide an important insight in balancing the reactivity of proton transfer reaction in both the excited and ground states.

Keywords Substitution effects · Proton transfer · Anthracene · Urea compounds · Ground state · Excited state

1 Introduction

Excited-state proton transfer reactions have been actively studied for decades [1–6]. The reactions facilitate applications in optoelectronic [7], fluorescence sensor [8–12], and bioimaging technologies [13, 14] and are used in light-emitting devices such as white OLEDs [15–17]. The reactions occur in some compounds that form hydrogen bonds in the ground state. Upon photoirradiation, the redistribution of electron density in a molecule causes changes in pK_a value of the proton donor and acceptor sites followed by a tautomeric process including a proton transfer (deprotonation) reaction. Consequently, the reaction shows dual emission comprising an emission from normal form (N^*) and a large Stokes-shifted emission from tautomer form (T^*) generated via the proton transfer reaction.

Since an excited-state proton transfer reaction shows a large Stokes-shifted emission from T^* , it has been focused to modify the proton transfer reaction [7, 18, 19]. In particular, the effect of substituents on the proton transfer reaction has been widely reported [20–24]. For example, Chou et al. investigated the excited-state intramolecular proton transfer (ESIPT) reaction of a series of 2-(2'-aminophenyl)-benzothiazole derivatives, in which the amino hydrogen was replaced with electron-donating/withdrawing groups [6, 25]. Their report demonstrated empirical correlations among the hydrogen bonding strengths including N–H bond distances and proton acidity, ESIPT kinetics, and thermodynamics. Replacing with an electron-withdrawing group next to the proton donor N–H leads to an increase in the acidity of the N–H moiety followed by a faster ESIPT reaction and a more exergonic reaction thermodynamics. In contrast, an electron-donating group produces a kinetic and thermodynamically unfavorable ESIPT reaction.

However, it is difficult to adjust the acidity including hydrogen bonding strength and proton transfer reactions in both the ground and excited states by introducing substituents since substituents have similar effects on the ground

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state as well as on the excited state. Therefore, it is challenging to facilitate a proton transfer reaction in the excited state while suppressing a proton transfer reaction in the ground state. In addition, it is difficult to suppress a proton transfer reaction in the excited state while increasing hydrogen bonding strength in the ground state. To address these issues, it is important to shed light on molecular designs in which the substituents can have different effects in the ground and excited states.

Herein, we have investigated the excited-state intermolecular proton transfer (ESPT) reactions in several derivatives of urea compounds, which served as hydrogen bond donors [26–30], in the presence of acetate anions (Ac) [31–38]. In the presence of tetrabutylammonium acetate (TBAAC), anthracen-*n*-yl-3-phenylurea (*n*PUA; *n* = 1, 2, and 9) forms a complex with Ac to undergo ESPT reactions, as shown in Scheme 1. In this case, the complex before ESPT reaction is referred to as normal form while the complex after ESPT reaction is referred to as tautomer form. An important feature of aromatic urea compounds such as *n*PUA, which has fluorescent dyes and substituted phenyl groups on both wings of the urea unit, is their easy synthesis.

Based on the structure of aromatic urea compounds, a substituent on the phenyl group might influence the acidity of N–H fragments. Specifically, an electron-withdrawing group on a phenyl ring, which reduces the electron density of urea groups, might increase the acidity of N–H fragments in the ground state. Similarly, an electron-donating group on the phenyl group might increase the electron density of the urea group, resulting in the reduction of the acidity of N–H fragments. In contrast to these substituent effects in the ground state, those on the proton transfer reaction in the excited state might be more complicated since ESPT reaction is closely related to charge transfer reactions [5]. In the case of *n*PUA, the charge transfer in the excited state occurs from the N–H fragment to the anthryl ring, which increases the acidity of N–H leading to a proton transfer reaction. In other words, the charge transfer reaction is the driving force of ESPT reaction to generate T* that is located on the

anthryl ring. When the effect of the substituents on charge transfer is considered, an electron-withdrawing group on the phenyl ring would weaken the charge transfer reaction to the anthryl ring, leading to suppression of ESPT reaction despite of an increase in acidity in the ground state. Similarly, an electron-donating group on the phenyl ring may promote ESPT reaction in contrast to the reduction in acidity in the ground state.

In this work, we synthesized anthracen-2-yl-3-(4-trifluoromethylphenyl)urea (CF₃-2PUA), which has a CF₃ group as an electron-withdrawing group, and anthracen-2-yl-3-(4-methoxyphenyl)urea (OMe-2PUA), with a methoxy group (OMe) as a donating group, to investigate the effects of substitution on 2PUA derivatives in the ground and excited states as shown in Fig. 1. ¹H NMR and absorption spectra, as well as both steady-state and time-resolved fluorescence spectra, were measured for CF₃-2PUA and OMe-2PUA in the absence and presence of TBAAC and were compared with those of 2PUA. In addition, we also conducted a kinetic analysis for the fluorescence lifetimes to determine the rate constants of the ESPT reaction. Finally, we found that aromatic urea compounds with substituent groups caused slow and fast ESPT reactions despite the strengthening and weakening of hydrogen bonding in the ground state by electron-withdrawing and electron-donating groups, respectively.

2 Experimental methods

2.1 Synthesis

2.1.1 2PUA

The synthesis of 2PUA was described in our previous report [32].

2.1.2 CF₃-2PUA

2-Aminoanthracene (117 mg, 0.605 mmol), dry dichloromethane (15 mL), and 4-(trifluoromethyl) phenylisocyanate (75 μ L, 0.525 mmol) were added to a 50-mL three-neck flask. The mixture was then refluxed for 6 h; subsequently, the supernatant was removed by suction filtration. The residue, the crude desired product, was recrystallized from the water–ethanol mixture to produce

Scheme 1 ESPT reaction between *n*PUA (*n* = 1, 2, and 9) and Ac

Fig. 1 Structure of CF₃-2PUA (left) and OMe-2PUA (right)

a light-yellow solid (163 mg, 0.429 mmol, 81.7% yield). ^1H NMR (DMSO- d_6 , 400 MHz): δ 9.55 (s, 1H), 9.44 (s, 1H), 8.49 (s, 1H), 8.42 (s, 1H), 8.31 (s, 1H), 8.06–8.03 (m, 3H), 7.74 (d, $J=8.5$ Hz, 2H), 7.66 (d, $J=8.5$ Hz, 2H), 7.54–7.44 (m, 3H). ^{13}C NMR (DMSO- d_6 , 400 MHz): δ 152.9, 143.9, 136.8, 132.3, 132.2, 130.7, 129.4, 128.7, 128.6, 128.1, 126.7, 126.6, 126.5, 126.4, 126.1, 125.2, 125.0, 121.4, 118.4, 112.8. Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{N}_2\text{O}$: C, 69.47; H, 3.97; N, 7.36; O, 19.2; found: C, 69.33; H, 4.18; N, 7.29.

2.1.3 OMe-2PUA

2-Aminoanthracene (105 mg, 0.543 mmol), dry dichloromethane (20 mL), and 4-methoxyphenyl isocyanate (75 μL , 0.583 mmol) were added to a 50-mL three-neck flask. The mixture was then refluxed for 4.5 h; subsequently, the supernatant was removed by suction filtration. The residue, the crude desired product, was recrystallized from *N,N*-dimethylformamide to produce a light-yellow solid (94 mg, 0.275 mmol, 50.6% yield). ^1H NMR (DMSO- d_6 , 400 MHz): δ 9.02 (s, 1H), 8.74 (s, 1H), 8.47 (s, 1H), 8.39 (s, 1H), 8.27 (s, 1H), 8.04–8.01 (m, 3H), 7.48–7.41 (m, 5H), 6.90 (d, $J=8.0$ Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (DMSO- d_6 , 400 MHz): δ 155.0, 153.3, 137.4, 133.1, 132.5, 132.2, 130.5, 129.3, 128.6, 128.1, 126.3, 126.0, 125.1, 124.7, 121.5, 120.6, 114.5, 112.0, 55.7. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$: C, 77.17; H, 5.30; N, 8.18; O, 9.35; found: C, 76.97; H, 5.27; N, 8.27.

3 Results

3.1 In the absence of TBAAc

To investigate the effects of substituent on the electronic state of 2PUA derivatives, ^1H NMR, absorption and fluorescence spectra of 2PUA, CF_3 -2PUA, and OMe-2PUA in the absence of TBAAc were measured.

3.1.1 ^1H NMR

The two N–H signals in CF_3 -2PUA were observed at 9.55 and 9.44 ppm, whereas the signals in 2PUA were observed at 9.13 and 8.97 ppm in DMSO- d_6 as shown Fig. 2. The downfield shifts of the two N–H signals in CF_3 -2PUA relative to those of 2PUA indicated that the CF_3 substituent increased the acidity of N–H in the ground state since the downfield shifts of N–H signals of the urea group correlated with the acidity of an N–H fragment. In contrast, the two N–H signals in OMe-2PUA were observed at 9.02 and 8.74 ppm, which were upfield shifted compared to the N–H signals in 2PUA, indicating that the OMe group decreased the acidity of N–H in the ground state.

3.1.2 Absorption and fluorescence spectra

The absorption spectra exhibited anthracene-like vibrational features in all compounds as shown in Fig. 3. The red-edge band > 370 nm was attributed to a charge transfer band generated by introducing a urea group into the anthracene

Fig. 2 ^1H NMR spectra of **a** 2PUA, **b** CF_3 -2PUA, and **c** OMe-2PUA in the absence and an excess amount of TBAAc

Fig. 3 Absorption and fluorescence spectra of 2PUA, CF₃-2PUA, and OMe-2PUA in the absence of TBAAc in DMSO

ring [32]. A CF₃ substituent unit resulted in a shift in the red-edge band to a shorter wavelength, whereas an OMe substituent unit caused a shift to a longer wavelength. The fluorescence spectrum, which has a charge transfer character, also shifted to a shorter wavelength in CF₃-2PUA and a longer wavelength in OMe-2PUA compared to those in 2PUA. These results in absorption and fluorescence spectra implied that the CF₃ group suppressed the charge transfer reaction whereas the OMe group promoted the charge transfer reaction. It was revealed that the charge transfer interaction from the urea group to the anthryl ring was influenced by a substituent such as CF₃ and OMe groups due to a change in the electron-donating ability of the urea group.

3.2 In the presence of TBAAc

To investigate the effects of substituent on the interaction of 2PUA derivatives with Ac, ¹H NMR, absorption, steady-state fluorescence, fluorescence lifetime measurements, and kinetic analysis were performed in the presence of TBAAc.

3.2.1 ¹H NMR

Figure 2 shows the changes in the ¹H NMR spectra of 2PUA, CF₃-2PUA, and OMe-2PUA upon the addition of TBAAc. The two N–H signals of all urea compounds shifted to downfield after the addition of excess Ac compared to those in the absence of Ac, indicating the formation of a complex via hydrogen bonding between the N–H fragment of urea and Ac. Focusing on the N–H signals of each compound, the N–H signals of CF₃-2PUA were observed at a downfield side compared to those of 2PUA. On the other hand, the signals of OMe-2PUA were observed at the upfield side, similar to that in the absence of TBAAc. These results indicated that the hydrogen bonding strength between the urea compound and Ac was increased by the CF₃ group but decreased by the OMe group in the ground state.

3.2.2 Absorption spectra

The absorption spectra of 2PUA, CF₃-2PUA, and OMe-2PUA upon the addition of TBAAc were measured as shown in Figs. S1–S3. The red-edge absorption band longer than 370 nm, which was attributed to a charge transfer band, red-shifted and the absorbance below 340 nm increased significantly upon the addition of TBAAc in all 2PUA derivatives. Furthermore, isosbestic point was observed in all compounds. These phenomena indicated that all urea compounds formed a 1:1 complex via a hydrogen bond between urea and Ac, as previously reported [32].

3.2.3 Association constants

The association constants are determined using the following equation:

$$\frac{A_0}{A - A_0} = \frac{A_0}{A_{\max} - A_0} \left(\frac{1}{K_a[Ac]} + 1 \right), \quad (1)$$

where A_0 and A are the absorbance of 2PUA in the absence and presence of Ac, respectively, $[Ac]$ is the total Ac concentration, and $A_{\max}$ is the absorbance of 2PUA that is completely hydrogen bonded with Ac. By Eq. (1), the association constants of 2PUA, CF₃-2PUA, and OMe-2PUA were calculated to be 4300, 11,300, and 3300 M^{−1}, respectively. The association constant of CF₃-2PUA was larger than that of 2PUA, whereas the constant of OMe-2PUA was smaller than that of 2PUA, indicating that the hydrogen bonding strength in the ground state was increased by the substitution of CF₃ but decreased by the substitution of OMe, which is consistent with the ¹H NMR results as mentioned above.

3.2.4 Fluorescence spectra

Figure 4 displays the changes in the fluorescence spectra of 2PUA, CF₃-2PUA, and OMe-2PUA upon the addition of TBAAc. The fluorescence spectra of 2PUA showed a new emission band at 600 nm, which was attributed to the tautomer (T*) generated via ESPT reaction while the fluorescence maximum shifted to 470 nm with a decrease in the fluorescence intensity after the addition of TBAAc as described in a previous work [32]. Although CF₃-2PUA also showed similar changes as those in 2PUA upon the addition of TBAAc, the fluorescence intensity of shorter wavelength emission decreased moderately and the T* emission was relatively greater than those of 2PUA. In contrast, it is noted that OMe-2PUA showed a significant decrease in the intensity of the shorter wavelength emission and negligible T* emission.

Fig. 4 Changes in fluorescence spectra of **a** 2PUA (2.1×10^{-5} M), **b** CF₃-2PUA (2.6×10^{-5} M), and **c** OMe-2PUA (2.0×10^{-5} M) due to the addition of TBAAC excited at isosbestic points of 354, 352, and 353 nm, respectively

3.2.5 Fluorescence lifetime

To investigate ESPT reaction from a kinetic point of view, fluorescence lifetime measurements were performed as shown in Figs. S4–S7. The fluorescence lifetimes obtained in DMSO are listed in Table 1. Here, we noted that almost all 2PUA form a complex in the ground state due to the addition of excessive amounts of TBAAC, as evidenced by the relevant association constants.

In the presence of TBAAC, the lifetimes of 2PUA displayed biexponential decay curves of values 13.1 and 5.1 ns at 440 nm, while the decay curves at 640 nm showed rise and decay components of 4.0 and 13.4 ns, respectively, as reported in our previous report [32]. CF₃-2PUA exhibited decay curves with values of 14.0 and 9.5 ns at 460 nm, while the decay curves at 640 nm showed rise and decay behaviors

Table 1 Fluorescence lifetimes (τ) and their amplitudes (A) of 2PUA, CF₃-2PUA and OMe-2PUA in the absence and presence of TBAAC

Sample	Obs./nm	τ /ns	
		In the absence of TBAAC	In the presence of TBAAC ^a
2PUA	440	18.9 (1.00)	13.1 (0.06), 5.1 (0.94)
	650		13.4 (1.00), 4.0 (– 1.00)
CF ₃ -2PUA	460	18.4 (1.00)	14.0 (0.17), 9.5 (0.83)
	640		16.3 (1.00), 7.7 (– 1.00)
OMe-2PUA	460	1.68 (1.00)	1.47 (0.29), 0.07 (0.71)

^a[TBAAC] = 10 mM

of 7.7 and 16.3 ns, respectively. OMe-2PUA displayed decay curves of values 1.47 and 0.07 ns at 460 nm, while fluorescence lifetimes at longer wavelengths were impossible to be measured due to the quite low fluorescence intensity. The decay curves comprising two components at 460 nm suggested that ESPT reaction occurred in OMe-2PUA in spite of a negligible T* emission in fluorescence spectra. If ESPT did not occur in OMe-2PUA, the shorter wavelength fluorescence would consist of only one lifetime that can be attributed to a complex.

3.2.6 Kinetic analysis of ESPT reaction

To determine the rate constants of ESPT reaction, kinetic analysis of the ESPT process was conducted. When we assumed that the ESPT reaction kinetics of 2PUA could be described by the reaction diagram shown in Scheme 2, the kinetic equations for the population of both the excited state normal (N*) and tautomer forms (T*) could be expressed as shown in the following equations [38, 39]:

$$\frac{[N^*]}{[N^*]_0} = \frac{1}{1/\tau_1 - 1/\tau_2} \left\{ \left(X - \frac{1}{\tau_2} \right) \exp \left(-\frac{1}{\tau_1} t \right) - \left(X - \frac{1}{\tau_1} \right) \exp \left(-\frac{1}{\tau_2} t \right) \right\} \quad (2)$$

Scheme 2 ESPT processes of 2PUA with the relevant rate constants

$$\frac{[T^*]}{[N^*]_0} = \frac{k_{PT}}{1/\tau_1 - 1/\tau_2} \left\{ \exp\left(-\frac{1}{\tau_2}t\right) - \exp\left(-\frac{1}{\tau_1}t\right) \right\} \quad (3)$$

where $X = k_{N^*} + k_{PT}$, $Y = k_{T^*} + k_{-PT}$, $Z = k_{PT} \times k_{-PT}$

$$\frac{1}{\tau_1} = \frac{1}{2} \left\{ (X + Y) + \sqrt{(X - Y)^2 + 4Z} \right\}$$

$$\frac{1}{\tau_2} = \frac{1}{2} \left\{ (X + Y) - \sqrt{(X - Y)^2 + 4Z} \right\}.$$

Equation (2) could be also given as the following equation, which corresponded to the decay curve of N^* :

$$\frac{[N^*]}{[N^*]_0} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (4)$$

where $A_1 + A_2 = 1$, $A_1 = (X - 1/\tau_2)/(1/\tau_1 - 1/\tau_2)$. The following equations could be given in terms of A_1 , τ_1 , τ_2 , and k_{N^*} :

$$k_{PT} = X - k_{N^*} = 1/\tau_2 + A_1(1/\tau_1 - 1/\tau_2) - k_{N^*} \quad (5)$$

$$k_{-PT} = \frac{Z}{X - k_{N^*}} = \frac{A_1(1 - A_1)(1/\tau_1 - 1/\tau_2)^2}{1/\tau_2 + A_1(1/\tau_1 - 1/\tau_2) - k_{N^*}} \quad (6)$$

$$k_{T^*} = Y - \frac{Z}{X - k_{N^*}} = 1/\tau_1 - A_1(1/\tau_1 - 1/\tau_2) - \frac{A_1(1 - A_1)(1/\tau_1 - 1/\tau_2)^2}{1/\tau_2 + A_1(1/\tau_1 - 1/\tau_2) - k_{N^*}}. \quad (7)$$

As can be seen from Eqs. (5)–(7), k_{T^*} , k_{PT} , and k_{-PT} could be calculated from three experimental values (τ_1 , τ_2 , and A_1 in the decay curve of N^*) when k_{N^*} is obtained. Based on the results of our previous work, the inverse of the lifetime of 2PUA derivatives in the absence of TBAAc can be used as k_{N^*} [38]. Table 2 lists the rate constants that were determined under the assumption that k_{N^*} was equal to the inverse of the lifetime of 2PUA derivatives in the absence of TBAAc. Focusing on the rate constants of k_{PT} and k_{-PT} , the values in CF_3 -2PUA were about half as small as those of 2PUA, indicating that ESPT reaction in CF_3 -2PUA was slower than that in 2PUA. In contrast, the rate constants k_{PT} and k_{-PT} in OMe-2PUA were significantly larger than those in 2PUA,

Table 2 The rate constants determined for ESPT reactions of 2PUA, CF_3 -2PUA, and OMe-2PUA

Sample	Rate constants/ 10^7 s^{-1}				Equilibrium constant $K_{PT} (k_{PT}/k_{-PT})$
	k_{PT}	k_{-PT}	k_{N^*}	k_{T^*}	
2PUA	12	0.69	7.1	7.7	17
CF_3 -2PUA	4.5	0.36	5.4	7.4	13
OMe-2PUA	970	390	60	72	2.5

Scheme 3 Resonance structures of 2PUA derivatives

implying that ESPT reaction in OMe-2PUA was extremely fast compared to that in 2PUA.

4 Discussion

4.1 Assumptions of the driving force of 2PUA derivatives based on their asymmetry structure

To facilitate the following discussion, we assumed that ESPT reaction in 2PUA derivatives has two electronically different N–H fragments: the N–H_p fragment on the phenyl group side and the N–H_A fragment on the anthryl side. The π -conjugations of the phenyl and anthryl rings extend to their adjacent N–H as depicted in the resonance structure shown in Scheme 3. In contrast, the π -conjugation part including the phenyl ring and N–H_p shortly extends to another π -conjugation part including the anthracene ring and N–H_A over the C=O unit. Comparing the acidity of the two N–H fragments, N–H_A may be more acidic than N–H_p since the anthryl ring has a large resonance (*R*) effect caused by extensive π -conjugation compared to the phenyl ring.

In the excited state, the electron-donating ability of N–H_A and the electron-accepting ability of the anthryl ring are enhanced, leading to a favorable charge transfer from N–H_A to the anthryl ring that has a larger *R* effect than the phenyl ring. The charge transfer reaction in the excited state provides poor electron density in N–H_A, resulting in enhanced acidity of N–H_A. When 2PUA form hydrogen bonds with a base such as Ac, a proton transfer reaction takes place between Ac and N–H_A in the excited state due to the increasing acidity of N–H_A. Herein, we assumed that the driving force of ESPT reaction involving 2PUA is a charge transfer from N–H_A to the anthryl ring and ESPT reaction is related to the transfer of H_A. The following discussion is based on the assumptions of ESPT reaction as described above.

4.2 Effects of substituents on the acidity of N–H in the ground state

Substituents including CF_3 and OMe groups influenced the acidity of N–H as shown in their respective ^1H NMR spectra and association constants in Sect. 3. The CF_3 group, which is an electron-withdrawing group increased the acidity of N-H_A and N-H_P , leading to enhanced hydrogen bonding strength between a urea moiety and Ac in the ground state, which was confirmed by its association constant. These phenomena are explained by a decrease in the electron density of two N–H fragments due to the electron-withdrawing property of the CF_3 group. This phenomenon is consistent with previous reports that an electron-withdrawing group such as NO_2 enhanced hydrogen bond donor tendencies to promote deprotonation in urea-based anion receptors [27, 40]. Moreover, it is noted that the CF_3 group on the phenyl ring influenced not only N-H_P but also N-H_A as shown in the ^1H NMR spectra although the π -conjugation in the phenyl ring shortly extended to the anthryl ring over a urea moiety. This result suggested that the effect of the CF_3 group on the anthryl ring involved not only the resonance (*R*) effect through π -conjugation but also the inductive (*I*) effect through σ -bonding in N–C–N in a urea moiety.

In the OMe-2PUA case, the ^1H NMR spectra showed that the OMe group, which is an electron-donating group, decreased the acidity of N-H_A and N-H_P in the ground state. This phenomenon is explained by an increase in the electron density of two N–H fragments due to the electron-donating property of the OMe group.

4.3 Effects of substituents on the charge transfer interaction in the excited state

Substituents including CF_3 and OMe influenced the charge transfer from N-H_A to anthryl ring as mentioned in Sect. 3. The red-edge band of the absorption spectrum longer than 370 nm, which was attributed to a charge transfer band, red-shifted in the order of CF_3 -2PUA, 2PUA, and OMe-2PUA as shown in Fig. 3. Moreover, the order of the red-shift in the fluorescence spectra was also the same as that of the absorption spectra as shown Fig. 3. These results indicated that the substitution of CF_3 suppressed the charge transfer from the urea moiety to the anthryl ring whereas the substitution of OMe promoted the charge transfer. The suppression of charge transfer reaction in CF_3 -2PUA would cause the low acidity in N-H_A in the excited state since a weak charge transfer provided high electron density on N-H_A . In contrast, the promotion of charge transfer of OMe-2PUA would enhance the increase of acidity in N-H_A by photoirradiation since a large charge transfer reaction significantly provided a lack of electron density on N-H_A .

4.4 Effects of substituents on ESPT reaction of CF_3 -2PUA

Substituents including CF_3 influenced the relevant rate constants of the ESPT reaction as shown in Sect. 3. The rate constants including k_{PT} and $k_{-\text{PT}}$ in CF_3 -2PUA showed that the rates of ESPT reaction are slower than those in 2PUA as listed in Table 2. In general, the acidity including the hydrogen bonding strength empirically correlates with the rate constants of proton transfer [6, 25]. Therefore, CF_3 -2PUA may have a weaker acidity of N-H_A than 2PUA in the excited state although CF_3 -2PUA has more acidity of N-H_A than 2PUA in the ground state. The weaker acidity in CF_3 -2PUA in the excited state may be due to the suppression of the charge transfer from N-H_A to the anthryl ring. Since the driving force of ESPT reaction is the increase in acidity of N-H_A by the charge transfer from N-H_A to the anthryl ring, a weak charge transfer in the CF_3 -2PUA caused a small increase in the acidity of N-H_A in the excited state to slow down ESPT reaction.

Focusing on the equilibrium constant K_{PT} , which was calculated by $k_{\text{PT}}/k_{-\text{PT}}$, CF_3 -2PUA has a smaller K_{PT} than 2PUA. Although K_{PT} indicated that T^* in CF_3 -2PUA has less population than 2PUA, the fluorescence spectra of CF_3 -2PUA showed intense T^* emission compared to that of 2PUA. This result suggested that the ratio of the fluorescence quantum yield of T^* relative to that of N^* , $\Phi_{\text{T}^*}/\Phi_{\text{N}^*}$, of CF_3 -2PUA is larger than that of 2PUA. In addition, the separated T^* emission including 2PUA and CF_3 -2PUA is displayed in Figs. S8–S10. The separated T^* emission of CF_3 -2PUA obviously shifted to a shorter wavelength, indicating an energy gap between T, and T^* was reduced in CF_3 -2PUA. This change in the energy gap is consistent with the fact that the CF_3 group increased the acidity in the ground state to stabilize T, whereas the CF_3 group decreased the acidity in the excited state followed by destabilizing T^* .

In the above discussion, we assumed that H_A is deprotonated during ESPT reaction. However, it is necessary to discuss a possibility of the deprotonation of H_P . As an electron-accepting group, CF_3 may increase the electron-accepting capacity of the phenyl ring and there is possibility of H_P deprotonation. However, CF_3 -2PUA has similar absorption and fluorescence spectra to those of 2PUA, implying that the electronic state in the excited state is localized on the anthryl ring, as in the case of 2PUA. These results suggested that the charge transfer reaction occurred from N-H_A to the anthryl ring in CF_3 -2PUA, leading to the deprotonation of H_A during ESPT reaction. In addition, the assumption of the deprotonation of H_P is inadequate to explain the phenomenon that ESPT reaction rate of CF_3 -2PUA is slower than that of 2PUA.

4.5 Substituent effects on ESPT reaction of OMe-2PUA

The rate constants including k_{PT} and k_{-PT} in OMe-2PUA suggested that ESPT reaction involving OMe-2PUA is much faster than that in 2PUA as listed in Table 2. The fast reaction in OMe-2PUA might also relate to the charge transfer. The enhancement of charge transfer due to the OMe group, which has an electron-donating ability, causes a considerable increase in the acidity of N–H_A in the excited state, leading to a fast reaction.

Despite the kinetically promoted ESPT reaction in OMe-2PUA, the equilibrium constant K_{PT} of OMe-2PUA is smaller than that of 2PUA, suggesting that the ESPT reaction of OMe-2PUA was thermally suppressed compared to that of 2PUA. We do not have enough explanation of the thermally suppressed reaction of OMe-2PUA. Thus, we need to investigate substituent dependence of the energy gap between N* and T*.

Based on the fluorescence spectra, OMe-2PUA showed a negligible T* emission, which may be explained by the poor emissive property of OMe-2PUA due to a large non-radiative rate constant as well as thermally suppressed ESPT reaction. In the absence of TBAAC, OMe-2PUA showed a small fluorescence quantum yield and a large nonradiative deactivation rate constant, k_{nr} , as listed in Table 3. This large k_{nr} might be caused by the OMe group having an electron-donating ability that promotes an electron-transfer-quenching reaction from the phenyl ring to the anthryl ring [41–43]. This explanation is consistent with the fact that the k_{nr} of OMe-2PUA depends on the magnitude of solvent polarity [44–46], i.e., the k_{nr} of OMe-2PUA is $5.7 \times 10^8 \text{ s}^{-1}$ in DMSO, $1.5 \times 10^8 \text{ s}^{-1}$ in MeCN, and $1.8 \times 10^7 \text{ s}^{-1}$ in THF as listed in Table 3. Similarly, the T* of OMe-2PUA in the presence of Ac is assumed to have a large nonradiative deactivation rate constant, $k_{nr}^{T^*}$, due to electron-transfer quenching, compared to those of other 2PUA derivatives. This is supported by the

fact that OMe-2PUA showed a relatively large k_{T^*} , which is deactivation rate constant of T*, compared to 2PUA and CF₃-2PUA. Thus, negligible T* emission of OMe-2PUA can be explained by its large $k_{nr}^{T^*}$.

4.6 Electronic states of T* in CF₃-2PUA and OMe-2PUA

Here, we summarized electronic states of T* of CF₃-2PUA and OMe-2PUA as shown in Scheme 4. ¹H NMR, absorption and fluorescence spectra indicated that CF₃ and OMe groups on the phenyl ring obviously influenced not only N–H_p but also N–H_A even though the π -conjugations of the phenyl and anthracene rings might shortly extend each other. This substituent effect may be related to a combination of R and I effects as described above. In the case of CF₃-2PUA, the CF₃ group having an electron-withdrawing ability on the phenyl ring reduced the electron density of N–H_p by the R effect, and subsequently, the positively charged N–H_p reduced the electron density of N–H_A by the I effect. Then, the reduction of the electron density of N–H_A suppresses the charge transfer from N–H_A to the anthryl ring, resulting in a small increase in the acidity of N–H_A triggered by photoexcitation, leading to suppression of ESPT reaction. This effect on charge transfer can lead to an opposite substituent effect, in which the rate of ESPT reaction decreased despite the increased acidity in the ground state. On the other hand, the OMe group having an electron-donating ability increased the electron density of N–H_A by a combination of R and I effects to enhance the charge transfer, which in turn kinetically promoted ESPT reaction and charge transfer quenching in T* followed by small fluorescence quantum yield of OMe despite the decreased acidity in the ground state.

Table 3 Fluorescence quantum yields, lifetimes, radiate and no-radiate deactivate rate constant of 2PUA derivatives

	Solvent	Φ_F	τ (ns)	k_r (10^7 s^{-1})	k_{nr} (10^7 s^{-1})
2PUA	DMSO	0.48	18.9	2.5	2.8
	MeCN	0.75	19.9	3.8	1.3
	THF	0.67	17.8	3.8	1.9
CF ₃ -2PUA	DMSO	0.83	18.4	4.5	0.9
	MeCN	0.69	15.3	4.5	2.0
	THF	0.63	11.6	5.4	3.2
OMe-2PUA	DMSO	0.05	1.68	3.0	57
	MeCN	0.17	5.59	3.0	15
	THF	0.71	16.2	4.4	1.8

Scheme 4 Electronic states of T* in **a** CF₃-2PUA and **b** OMe-2PUA

5 Conclusions

To investigate the substitution effects on the ground and excited states, we synthesized 2PUA derivatives including CF₃-2PUA having a CF₃ group as an electron-withdrawing group and OMe-2PUA having an OMe group as an electron-donating group. ¹H NMR spectra showed that the CF₃ group enhanced the acidity of N–H_A while the OMe group decreased the acidity in the ground state. Absorption and fluorescence spectra indicated that the CF₃ group suppressed the charge transfer reaction from N–H_A to the anthryl ring whereas the OMe group promoted the charge transfer. These results indicated that the substituent on the phenyl ring influenced the anthryl ring and N–H_A even though the π -conjugations of the phenyl and anthracene rings might shortly extend each other. The substituent on the phenyl group influenced the anthracene and N–H_A beyond the urea group that disrupts the π -conjugation, suggesting that the substitution effect is due to the *I* effect as well as the *R* effect. Furthermore, fluorescence lifetime measurements and their kinetic analyses suggested that the CF₃ group caused the slow ESPT reaction in spite of an increase in the acidity of N–H_A in the ground state. In contrast, the OMe group led to fast reaction in spite of the reduction in the acidity of N–H_A in the ground state. These effects of substituent on ESPT reaction might be due to charge transfer reaction. In other words, the CF₃ group suppressed the charge transfer from N–H_A to the anthryl ring, resulting in a small increase in the acidity of N–H_A. On the other hand, the OMe group enhanced the charge transfer, leading to a large increase in the acidity of N–H_A, which in turn increased the rate constant of ESPT reaction. Thus, the opposing effects of substituents on the acidity in the ground state and excited state are an important insight to balance the reactivity of proton transfer reaction in the excited state and ground state. The present work provides new insights that can be applied to the molecular design for fluorescent material based on an ESPT reaction.

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Availability of data and material Supplementary figures and tables are provided in a separate file.

Declarations

Conflict of interest The authors declare are no conflicts of interest.

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