Tuning Excited-State Charge/Proton Transfer Coupled Reaction via the Dipolar Functionality

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Based on design and synthesis of **I**, **II**, and **III**, we demonstrate an ingenious approach to fine-tuning the excited-state intramolecular charge transfer (ESICT) coupled excited-state intramolecular proton transfer (ESIPT) reaction via the dipolar functionality of the molecular framework. Both **I** and **II** exhibit remarkable dual emission due to the different solvent-polarity environment between ESICT and ESIPT states, while the interplay of two charge-transfer entities in **III** leads to ESIPT decoupling from the solvent-polarity effect, resulting in a unique proton-transfer tautomer emission. The results make further rational design of the ESICT/ESIPT coupled systems feasible simply by tuning the net dipolar effect. Accordingly, systematic investigation of the correlation in regards to the difference in dipolar vectors between ESICT and ESIPT versus solvent-polarity induced barriers becomes possible.

Due to its fundamental importance in chemical reactions, the excited-state intramolecular proton transfer (ESIPT) reaction has received much attention.[1] One important issue of current interest regarding ESIPT reactions should be ascribed to the ESIPT coupled excited-state intramolecular charge transfer (ESICT). Considering that the Franck−Condon excited state of an ESIPT molecule undergoes a gigantic dipolar change due to the charge separation, the normal and proton-transfer tautomer equilibrium polarizations might be far separated. Since the large dipolar change in solution is normally coupled to solvent polarization effects, the relative energies between normal and tautomer in the excited state are a function of the solvent polarization coordinate. As a result, the long-range polarization interactions may result in a solvent-induced barrier channeling into the proton-transfer reaction.

Seminal studies on molecules exhibiting remarkable solvent polarization dependent ESIPT reaction dynamics should be ascribed to two prototypical systems, namely 4′-*N*,*N*-diethylamino-3-hydroxyflavones (**I**) (see Scheme 1)[2a−d] and *para-N*,*N*-dimethylamino-methylsalicylate.[2e,f] For the case of system **I**, on one hand, ESICT takes place from the diethylamino nitrogen (electron donor) to the carbonyl oxygen (electron acceptor). On the other hand, similar to its parent molecule 3-hydroxyflavone (3HF),[3] **I** also undergoes ESIPT from the hydroxyl proton to the carbonyl oxygen (see Scheme 1). The difference in solvent-polarity environment between charge transfer (CT) and proton transfer (PT) states leads to a remarkable ESICT/ESIPT coupled reaction. In polar, aprotic solvents, in contrast to a unique PT tautomer emission observed in 3HF,[3] dual emissions are resolved, consisting of CT and PT bands.[2a−d] Applying the Marcus electron-transfer model, Swinney and Kelley[2c] were able to describe the overall reaction dynamics as well as to deduce the solvent-induced barrier for **I** by a combination of solvent polarity and proton-transfer reaction coordinates. In contrast to the ultrafast rate (<50 fs) of ESIPT in 3HF,[4] the proton tunneling rate for **I** in polar solvents is slower than the rate of solvent relaxation. Thus, a nonadiabatic type of proton transfer takes place essentially after solvent equilibration is established in the excited state.[2c] Such an intriguing ESICT/ESIPT coupled property has led to intensive studies on **I** and its analogues. Most of the approaches focus on the wavelength tunability upon replacing the 2-phenyl ring by other functionalized aromatics,[5] the applications in metal ion recognition,[6] and the use of CT/PT emission intensity ratio as indicators to probe the empirical solvent polarity.[7]

Based on the chemical design, we herein demonstrate an ingenious approach to fine-tuning the ESICT/ESIPT coupled reaction via the dipolar orientation of the molecular framework. The synthetic strategy lies in that if the dialkylamine, which acts as an electron donor at the C(4′) position in **I**, plays a key role in ESICT, then switching the diethylamine from C(4′) to C(7) position, forming **II** (Scheme 1), may result in a similar ESICT/ESIPT coupled reaction. However, the resulting net dipole moment, the orientation of which is affected by the CT effect, is expected to alter with respect to that of **I**. Moreover, if 2-phenyl pyrone (region **A** in Scheme 1) and flavone (region **B**) chromophores are strongly coupled so that electrons are delocalized throughout the entire molecular framework, it would be intriguing to functionalize 3HF by adding dialkylamine at both the C(4′) and C(7) positions, forming **III**, of which the net dipole moment may be associated with the interplay between two charge-transfer systems, namely **I** and **II**. Thus, switching the dipolar property of the CT state may greatly tune the ESICT/ESIPT coupling behavior among **I**−**III**.

I−**III** were synthesized by the Claisen condensation.[2a] While **I** has been reported, detailed synthetic schemes for **II** and **III** as well as their corresponding methoxyl derivatives, $\mathbf{II_a}$ and $\mathbf{III_a}$, respectively, are elaborated in the Supporting Information. Figure 1 shows the emission spectra of **I**−**III** in various polar solvents, and detailed photophysical data are listed in Table 1 (see Supporting Information for the absorption spectra). Similar to the steady-state emission behavior of **I** shown in Figure 1A,[2] **II** exhibits dual emission, in which the peak wavelength of the higher energy band is strongly dependent on the solvent polarity

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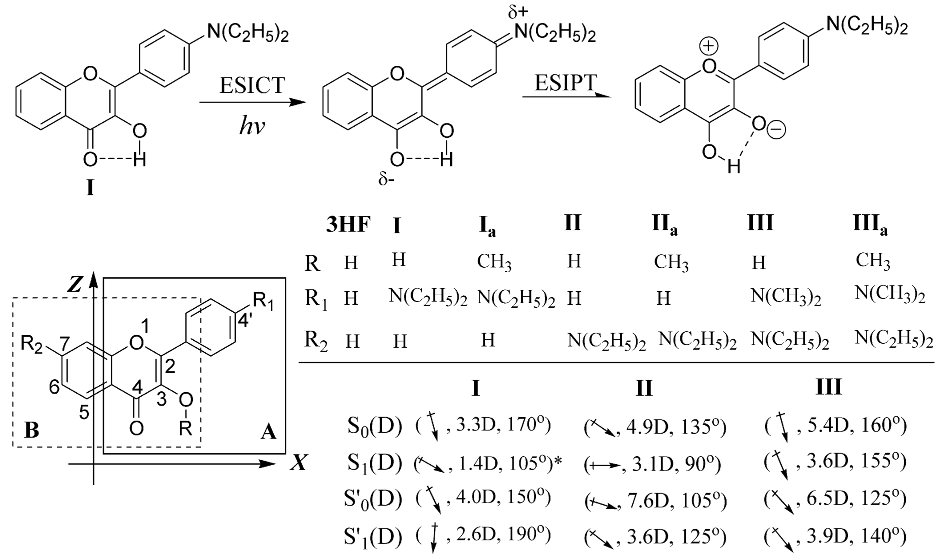
SCHEME 1. Structures of Various Systems Studied and the Calculated (see text) Dipole Moments (arrows show components along the *z*−*x* plane) for I, II and III in Singlet normal (S) and Proton Transfer (S′) States (angle specified clockwise to the *z*-axis)



	3HF	**I**	**I$_a$**	**II**	**II$_a$**	**III**	**III$_a$**
R	H	H	CH_3	H	CH_3	H	CH_3
R$_1$	H	$N(C_2H_5)_2$	$N(C_2H_5)_2$	H	H	$N(CH_3)_2$	$N(CH_3)_2$
R$_2$	H	H	H	$N(C_2H_5)_2$	$N(C_2H_5)_2$	$N(C_2H_5)_2$	$N(C_2H_5)_2$

	I	**II**	**III**
S_0(D)	(↓, 3.3D, 170°)	(↘, 4.9D, 135°)	(↓, 5.4D, 160°)
S_1(D)	(↘, 1.4D, 105°)*	(→, 3.1D, 90°)	(↓, 3.6D, 155°)
S'_0(D)	(↘, 4.0D, 150°)	(↘, 7.6D, 105°)	(↘, 6.5D, 125°)
S'_1(D)	(↓, 2.6D, 190°)	(↘, 3.6D, 125°)	(↘, 3.9D, 140°)

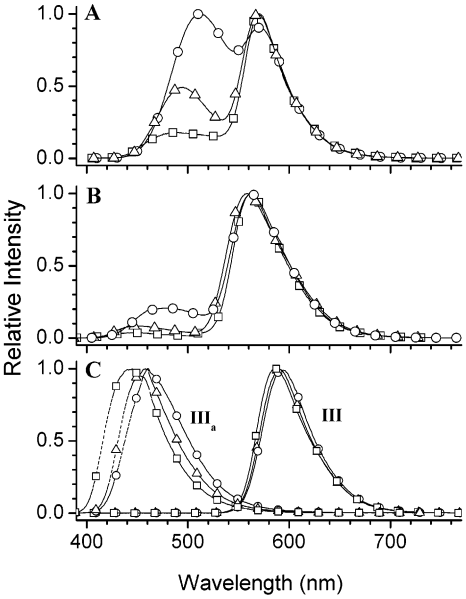


Figure 1. Emission spectra of (A) **I**, (B) **II**, and (C) **III** (solid line) and **III$_a$** (dash line) in ethyl acetate (□), CH_2Cl_2 (△), and CH_3CN (○). The excitation wavelength is 350 nm.

TABLE 1: Photophysical Properties of I−III in Various Solvents at Room Temperature

		Em (nm) (τ (ns) [preexponential factor])		
	Abs (nm)	N[d]	T[e]	QY(%)[f]
I	401[a]	475 (0.47)	570 (0.38)	5
	411[b]	495 (0.72)	572 (0.78)	17
	405[c]	516 (0.42)	574 (0.41)	9.6
II	374	445 (0.12)	566 (0.11[−1.00], 1.30[1.02])	13.8
	380	460 (0.15)	564 (0.17[−1.00], 3.25[0.93])	45.5
	382	490 (0.39)	566 (0.39[−1.00], 1.80[1.15])	19.7
II$_a$	362	452 (0.40)		3.3
	365	465 (0.79)		11.2
	367	513 (4.05)		29.3
III	401		589 (3.41)	26.3
	406		589 (3.65)	46.3
	409		594 (2.81)	71.1
III$_a$	376	453 (0.42)		16.2
	384	458 (0.95)		45.2
	388	460 (1.07)		46.6

[a] In ethyl acetate. [b] In CH_2Cl_2. [c] In CH_3CN. [d] Normal band. [e] PT tautomer. [f] For **I** and **II**, QY(%)% is the sum of dual emission intensity. Note that negative preexponential values indicate rise components.

and is reasonably ascribed to a CT emission incorporating a charge transfer from C(7)-diethylamine to carbonyl oxygen. Conversely, the lower energy band with an anomalously large Stokes shift of >7000 cm^{-1} reveals negligibly small solvent-polarity dependence and is clearly assigned to a PT tautomer emission. The charge-transfer property in **II** could be further supported by its methoxyl derivative **II$_a$**, in which ESIPT was prohibited and the resulting emission showed similar solvent-polarity dependence with that of the CT band in **II** (see Table 1). Figure 1C depicts the emission spectra of **III** in various solvents. In contrast to both **I** and **II**, **III** exhibits predominantly a proton-transfer emission, of which the peak wavelength reveals negligible solvent-polarity dependence. The results indicate that the dipolar change in the excited state for **III** must be small between normal and PT tautomer species so that ultrafast ESIPT takes place. This viewpoint can be firmly supported by the non-ESIPT analogue **III$_a$**, which exhibits a nearly solvent-polarity independent, normal Stokes shifted emission (see Table 1 and Figure 1C). The results lead us to propose that, upon excitation, the interplay between two charge-transfer dipole vectors in **III** yields a net dipole moment nearly the same as that of the PT tautomer. ESIPT is thus decoupled from the solvent polarity effect, resulting in a dominant PT tautomer emission.

A further dynamic approach allows us to establish a precursor−successor relationship between CT and PT bands for **II**. For example, in CH_3CN the decay time of 390 ps in **II** monitored at the CT band is identical to the rise time of the PT band (see Table 1 and Figure 2). The results are in contrast to **I**, in which the excited-state equilibrium between CT and PT is established, as supported by their identical population lifetimes (see Table 1 and also ref 2c). For the case of **III**, the rate of ESIPT is too fast to be resolved by our time-correlated single photon counting system (~15 ps response time), supporting the solvent-polarity decoupled ESIPT mechanism for **III**.

Theoretical approaches at an INDO/S-CI level based on AM1 geometry optimized ground state structures have been performed in an attempt to rationalize the experimental results. All singly

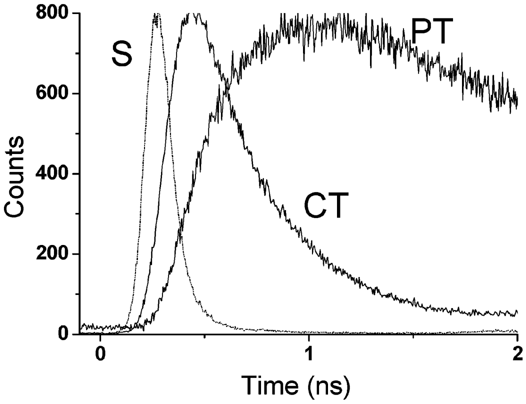


Figure 2. Time-resolved spectra of compound **II** (CT: monitored at 460 nm; PT: monitored at 640 nm; S: system response function).

excited configurations from the 10 highest occupied to the 10 lowest unoccupied molecular orbitals were involved in the computation (see Supporting Information). Dipole moments were calculated for **I**, **II**, and **III** in both ground and excited states, and the dipole vectors along the $z-x$ plane are depicted in Scheme 1. For **III**, the orientation of the dipole moment is similar between the normal ground (S_0, 160°) and excited (S_1, 155°) states, while significant differences were obtained for both **I** and **II** (see Scheme 1). More importantly, while the dipole vectors of excited CT (S_1) and PT (S_1') states are substantially different for both **I** and **II** (see Scheme 1), they are similar in **III** (S_1, (3.6 D, 155°), S_1'(3.9 D, 140°)). Although this approach, to a certain extent, is qualitative on the magnitude of the dipole moment, according to different dipole orientations, ESICT/ESIPT coupled reactions are expected for **I** and **II**, and solvent polarities should play a key role in describing the reaction dynamics and/or thermodynamics. Conversely, negligible changes in dipolar orientations for **III** lead to a fast, solvent decoupled ESIPT, consistent with experimental results.

We have thus demonstrated for the first time a prominent dipole orientation tuning ESICT/ESIPT coupled reaction. The preservative net dipolar effect in **III** leads us to conclude that 2-phenyl pryone and flavone moieties are strongly coupled so CT in **III** is essentially delocalized in the entire molecule. This makes feasible further rational design of ESICT/ESIPT systems by altering the net dipolar vector. Accordingly, systematic investigation of the correlation in regards to the difference in dipolar vectors between ESICT and ESIPT as well as the solvent-polarity induced barrier becomes possible, which may be crucial to gain fundamental insights into research fields of current interest regarding, e.g., proton-coupled electron transfer in living systems.[8] Unfortunately, for **I**−**III** possessing five-membered ring hydrogen bonds, the intramolecular hydrogen bonding strength is relatively weak. Thus, in protic solvents such as ethanol and water, our preliminary studies have shown that certain percentage of C=O- - -H−O− intramolecular hydrogen bond in compound **I**−**III** is ruptured by forming intermolecular hydrogen bond with protic solvents. As a result, excited-state deprotonation instead of ESIPT takes place in these protic solvents. This makes the discussion of the ESICT/ESIPT reaction solely based on the solvent polarity very complicated. Studies on the ESICT/ESIPT coupled reaction, in combination with the excited-state deprotonation, for compounds **I**−**III** in protic systems are currently in progress.

Supporting Information Available: Detailed experimental procedures, absorption, emission, time-resolved and X-ray studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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