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Introduction

Charge-transfer (CT) is a pivotal process in determining the performance of photoelectric or electrochemical devices. A typical CT from electron donor (D) to electron acceptor (A) occurs in a molecule where D and A are clearly distinguished.^{1–4} In contrast, this kind of CT does not occur in a molecule where D and A are not well resolvable, such as 1-phenylpyrene (Py-Benz). Because the building units of Py-Benz, that is benzene and pyrene, have unfavorable redox potentials, the typical CT between D and A is not operational.⁵ As such examples are numerous, it is desirable to develop a strategy to induce CT in a molecule made of such building units.

Toward this goal, we hypothesized that electronic coupling (EC) in a symmetric multi-chromophore system (MCS) can be

used to induce CT.6 Extensive experimental and theoretical studies have been conducted to understand and control EC.^{7,8} As a result, it is known that EC can be perturbed by substitutions with various functional groups and the change of environmental factors such as solvent polarity.⁹ The perturbation of EC induces the reduction of the energy gap or the inversion of the excited state manifolds, so-called electronic state mixing (ESM). ESM results in significant changes in the photophysical properties of a chromophore such as the oscillator strengths for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, the emission quantum yield and the emission lifetime, as well as in the excited-state relaxation dynamics in the excited state.¹⁰⁻¹² For example, Manathunga et al. showed that the photoisomerization of the retinal protonated Schiff base chromophore is decelerated by the ESM accompanied with the substitution with an electron-withdrawing group.¹³ Liu and Schanze reported that the photophysical properties of a π -conjugated metalorganic oligomer can be modulated by solvent polarity.¹⁴ They suggested that the change in the photophysical properties is due to the mixing of the two low-lying excited states, the ${}^{3}\pi,\pi^{*}$ and triplet metal-to-ligand charge transfer states.¹⁴ This result implies that when the excited state manifolds are energetically

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Charge transfer induced by electronic

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Charge transfer (CT) from electron donor (D) to acceptor (A) plays an important role in photoelectric or electrochemical devices and is a useful concept for a molecule with D and A well distinguishable. Here, we report our finding that even in a molecule with D and A not resolvable, CT can be induced by electronic state mixing (ESM) in a symmetric multi-chromophore system (MCS), namely 1,4-di(1-pyrenyl)benzene (Py-Benz-Py). Unlike Py and Py-Benz, Py-Benz-Py exhibits unique photophysical properties attributable to the reduction of the energy gap between two electronic states induced by ESM. The ESM for Py-Benz-Py is due to the extended π -conjugation owing to the further introduction of Py into Py-Benz, and consequently leads to the favorable intramolecular CT, followed by the planarization due to the twisting motion between Py and phenyl moieties. Time-resolved spectroscopic data demonstrate that the twisting process of the Py moiety in acetonitrile occurs with two unequal time constants, suggesting the localized CT state and the asynchronous twisting dynamics of two Py moieties unlike the delocalized CT state in nonpolar and low-polarity solvents leading to the synchronous twisting of two Py moieties. This means that the symmetry-breaking CT in MCSs

can induce an asynchronous twisting motion. The results reported here support that a molecule without CT can be turned into another molecule with CT induced by ESM and demonstrate that the excited-state

relaxation dynamics can be regulated through the ESM induced by introducing the substituents or changing

multi-chromophore system[†]

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the environmental factors such as solvent polarities.

state mixing in a symmetric X-Y-X-type

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close to each other, the configuration mixing between states is controlled by the change of solvent polarity.

For our purpose, we chose 1,4-di(1-pyrenyl)benzene (Py-Benz-Py) (Fig. 1a), which is one of the simplest MCSs as our model target system. Pyrene (Py) shows weak $S_0 \rightarrow S_1$ and strong $S_0 \rightarrow S_2$ transitions, which are polarized along the short y-axis and long z-axis, respectively and is a prototypical chromophoric system to show the effects of chemical and physical modifications on ESM (Scheme 1). In Py, the two lowest excited states, L_b (S₁) and L_a (S₂) with Platt's notation, are closely related to the absorption and emission behavior.^{15,16} ESM can easily occur in Py due to the small



Fig. 1 (a) Molecular structures of pyrene (Py), 1-phenylpyrene (Py-Benz), and 1,4-di(pyrenyl)benzene (Py-Benz-Py). Comparison of UV-visible absorption (b) and emission (c) spectra of Py, Py-Benz, and Py-Benz-Py. The UV-visible absorption and emission spectra of Py and Py-Benz measured in acetonitrile (MeCN) are shown as black solid lines and black dashed lines, respectively. The excitation wavelength is 340 nm. The UV-visible absorption and emission spectra of Py-Benz-Py measured in cyclohexane (CHX), diethyl ether (EE), tetrahydrofuran (THF), dichloromethane (DCM), and MeCN are shown as red, orange, green, blue, and magenta solid lines, respectively. The excitation wavelength is 380 nm.



Scheme 1 (a) Concept of electronic state mixing (ESM) by bichromophoric interaction in Py-Benz-Py. (b) Principle Cartesian coordinate system with Platt's notation for pyrene (Py). (c) Dominant orbitals of each excitation in Py.

energy gap between the two states as they are easily perturbed and mixed by substitutions. 5,17

Despite many experimental and theoretical studies on ESM, the detailed understanding of ESM phenomena is still elusive. So far, most experimental studies on ESM have been conducted in a diluted solution to exclude the effect owing to the chromophorechromophore interaction. In contrast, the chromophore-chromophore interaction in a high concentration solution and in optoelectronic and photovoltaic devices with high coverage of a chromophore results in unique physical properties such as rapid excimer formation, up-conversion, and singlet fission (SF).¹⁸⁻²¹ SF, which is a conversion process from one singlet exciton into two triplet excitons to overcome the limit of Shockley-Queisser power conversion efficiency, has been shown to proceed either intermolecularly or intramolecularly in the solid and solution phases.²²⁻²⁴ Recent studies reported that dyad systems where two identical chromophores are covalently linked can induce an efficient SF process through a charge-transfer species or an excimer as an intermediate.^{25,26} These studies lead to the hypothesis that a covalently linked dimeric system can induce ESM via chromophore-chromophore interaction and the resulting ESM is more complicated compared with that occurring in single-chromophore systems. Thus, more systematic studies are required to understand the ESM phenomena occurring in MCSs including a covalently linked dimeric system.

Regarding the photophysical properties of Py derivatives, Crawford *et al.* reported the substituent effects on the UV-visible absorption and emission spectra and their lifetimes.¹⁰ Raytchev and coworkers have systematically interrogated the substituent effect of the ultrafast internal conversion (IC) from S₂ to S₁, which is influenced by ESM.⁵ In this regard, Py-Benz-Py containing two identical Pys is a good model system to observe the ESM phenomenon induced by the chromophore–chromophore interaction in MCSs. In the present study, we investigated the excited-state relaxation dynamics of Py-Benz-Py using combined femtosecond

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transient absorption (fs-TA) spectroscopy and theoretical calculations. Unlike Py and its derivatives, Py-Benz-Py exhibits the characteristic photophysical properties, such as a broad absorption band, a short fluorescence lifetime, and the absence of internal conversion (IC) from S_2 to S_1 state, caused by ESM. In addition, the ESM in Py-Benz-Py induces the efficient intramolecular CT (ICT), followed by the twisting motion between Py and phenyl moieties. Py-Benz-Py in MeCN shows unusual torsional dynamics, which can be interpreted in terms of the asynchronous twisting of two Py moieties owing to symmetry-breaking CT. Our results presented in this work demonstrate that the symmetry-breaking CT in MCSs can be regulated through the ESM induced by introducing the substituents or changing the environmental factors such as solvent polarities.

Results and discussion

Steady-state absorption/emission spectra and fluorescence lifetime

To elucidate the photophysical properties of Py-Benz-Py, we first inspected the steady-state UV-visible absorption and emission spectra of Py-Benz-Py in various solvents and compared them with those of Py and Py-Benz in MeCN (Fig. 1b and c). As shown in Fig. 1b, Py-Benz-Py in all solvents shows the broad absorption band at 300-400 nm whereas Py and Py-Benz exhibit the vibrationally well-resolved ones at 300-350 nm and the slightly structured ones at 300-360 nm, respectively. The red-shifted, broader absorption band of Py-Benz-Py with respect to Py and Py-Benz is indicative of conformational flexibility due to the rotation around the single bond between Py and phenyl moieties. Such a spectral difference between Py-Benz-Py and Py is also observed for the emission spectra. Py-Benz-Py has a broad emission band around 420 nm whereas Py and Py-Benz show the vibrationally resolved ones at 350-450 nm (Fig. 1c). It is known that for Py the intense absorption band at 300-350 nm and the emission bands at 350–400 nm correspond to the $S_0 \rightarrow S_2$ and $S_1 \rightarrow S_0$ transitions, respectively.5,10 In addition, the absorption band of Py for the forbidden $S_0 \rightarrow S_1$ transition at 350–400 nm is well separated from that of the $S_0 \rightarrow S_2$ transition, but visible only when greatly magnified, due to its much weaker oscillator strength. Unlike Py and Py-Benz, Py-Benz-Py shows a single, broad, strong absorption extended up to 400 nm, which suggests that the forbidden $S_0 \rightarrow S_1$ transition of Py is also allowed in Py-Benz-Py. Thus, the broad, single band makes the straightforward assignment of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions impossible. Such a broad absorption band indicates that the energy gap between S1 and S2 is much reduced or even that the two states are mixed into two degenerate states. If such an ESM happens, the fluorescence lifetime can also be shortened compared to that of Py. While the absorption of Py-Benz-Py does not show noticeable dependence on solvent polarity, its emission is weakened and greatly red-shifted as the solvent polarity increases (Table 1). Furthermore, Py-Benz-Py in various solvents exhibits fluorescence lifetimes in the range of 1.4-2.1 ns (Table 1 and Fig. S6, ESI[†]), which are much shorter than that of Py $(\tau_{\rm f} = 354 \text{ ns}).^{10}$ Such a broader absorption band and a shorter

Table 1 Absorption and emission maxima, Stoke shifts, emission quantum yields (Φ), emission lifetimes (τ), radiative rate constants ($k_{\rm R}$), and non-radiative rate constants ($k_{\rm NR}$) of Py-Benz-Py in various solvents

Solvent	λ_{abs} (nm)	λ _{emi} (nm)	Stokes shift (cm ⁻¹)	Φ	τ (ns)	$k_{ m R} \ (10^7 \ { m s}^{-1})$	$k_{\rm NR} \ (10^7 \ { m s}^{-1})$
CHX	348	416	4656	0.68	1.4	49	23
EE	346	417	4834	0.76	1.6	48	15
THF	351	423	4946	0.62	1.4	44	27
DCM	353	423	5003	0.61	1.5	41	26
MeCN	349	445	6166	0.57	2.1	27	20

fluorescence lifetime compared with Py and Py-Benz were also observed in a previous study, where Crawford *et al.* reported that various Py derivatives with the substitution at the 1-position of Py have a broad absorption band and a much shorter fluorescence lifetime ($\tau_{\rm f}$ = a few ns) than that of Py ($\tau_{\rm f}$ = 354 ns) by the perturbation of the first two excited states (S₁ and S₂) of Py.¹⁰ On the basis of our experimental results and the previous study for Py derivatives, we suggest that the unique photophysical properties of Py-Benz-Py originate from ESM.

On the other hand, as mentioned above, the emission of Py-Benz-Py shows the dependency on the solvent polarity. The Stokes shifts in cyclohexane (CHX) and MeCN are determined to be 4656 and 6166 cm^{-1} , respectively. These large Stokes shifts mean that the emission comes from the CT state, indicating that CT in Py-Benz-Py efficiently occurs even in the nonpolar solvent such as CHX. In contrast, Weigel et al. showed that the emission in Py-Benz is not influenced by the solvent polarity, suggesting the absence of CT dynamics.²⁷ Considering the structures of Py-Benz and Py-Benz-Py, the efficient CT dynamics for Py-Benz-Py is probably due to the further introduction of Py into Py-Benz. It is known that the substituent influences the energy gap between the excited states. In this regard, the further introduction of Py into Py-Benz may induce the stronger perturbation of the first two excited states compared with that in Py-Benz, consequently resulting in the reduction of the energy gap between two electronic states induced by ESM as well as the efficient CT. The CT dynamics will be discussed in detail later.

DFT and TDDFT calculations

To investigate the nature of the two low-lying excited states of Py-Benz-Py, we carried out the DFT and TDDFT calculations for Py and Py-Benz-Py. The calculation results using both B3LYP and CAM-B3LYP show that Py-Benz-Py has a larger oscillator strength for the $S_0 \rightarrow S_1$ transition than for the $S_0 \rightarrow S_2$ transition, regardless of the calculation conditions we used (Table S2 and Fig. S7, ESI[†]). Similarly, several Py derivatives substituted at the 1-position showed a brighter first excited state compared to the second excited state.¹⁰ Such higher oscillator strengths for the $S_0 \rightarrow S_1$ transition are attributed to the ESM of the $S_0 \rightarrow S_1$ (L_b) and $S_0 \rightarrow S_2$ (L_a) transitions. Thus, these previous calculation results for Py derivatives substituted at the 1-position lead to the hypothesis that unlike Py, the change in oscillator strengths for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in Py-Benz-Py is due to ESM. Indeed, for Py-Benz-Py, the molecular orbitals (MOs) of the transition to the lowest excited state resembles the MOs of the $S_0\,\rightarrow\,S_2$

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transition (La) of Py (Fig. S8 and S9, ESI⁺). Therefore, we conclude that the large oscillator strength for the $S_0 \rightarrow S_1$ transition in Py-Benz-Py is due to ESM, resulting in the broad absorption band and the short fluorescence lifetime. It is known that the first two low-lying excited states of Py can be perturbed when its π conjugation is expanded by the substitution. Besides, it was revealed that the substitution at the 1-position of Py strongly influences both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, resulting in the higher oscillator strength for the $S_0 \rightarrow S_1$ transition. For example, Py-Benz, a 1-position substituted Py derivative, showed a broader absorption band and a faster IC process than unsubstituted Py. Py-Benz-Py has two 1-position substituted Pys by the further introduction of Py into Py-Benz. The further introduction of Py induces the increase of the π -conjugation length and the degree of the perturbation of the excited states. In this regard, the significant ESM phenomenon for Py-Benz-Py is probably due to the further introduction of Py into Py-Benz. On one hand, it is also known that the low-lying two excited states of a molecule can be perturbed by the substitution of an electron-withdrawing group. Manathunga et al. reported that the electron-withdrawing substituents into the rPSB chromophore cause an increase in the ESM of the first two excited states.¹³ Many studies on Py showed that Py can act as both electron donor and acceptor groups.²⁸⁻³⁰ In this respect, Py acts as an electronwithdrawing group in Py-Benz-Py, resulting in the ESM of the first two excited states. To further clarify the character of S1 and S_2 states for Py-Benz-Py, we represent the MOs of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of Py-Benz-Py calculated with the ADC(2) method and def-TZVP basis set, which show higher accuracy for the excitation energy.^{31,32} As shown in Fig. S9, the calculation results demonstrate that each of the S_0 \rightarrow S_1 and S_0 \rightarrow S_2 transitions of Py-Benz-Py is characterized by a linear combination of four singly excited configurations. The $S_0 \rightarrow S_1$ transition is described by the linear combination of HOMO \rightarrow LUMO+2 (27.3%), HOMO-1 \rightarrow LUMO+3 (24.1%), HOMO-2 \rightarrow LUMO (23.1%), and HOMO-3 \rightarrow LUMO+1 (19.7%) single excitations, which do not show any CT features. The $S_0 \rightarrow S_2$ transition is described by the linear combination of HOMO \rightarrow LUMO+3 (27.8%), HOMO-1 \rightarrow LUMO+2 (24.3%), HOMO-3 \rightarrow LUMO (22.4%), and HOMO-2 \rightarrow LUMO+1 (19.6%) single excitations. Although these single excitations exhibit weak CT features, the CT characters are not aligned in the same direction. For example, the first two main excitations show the CT features in opposite directions. As a result, the overall excitation in the $S_0 \rightarrow S_2$ transition does not have a CT feature. Thus, we suggest that the mixed state of S₁ and S₂ is a locally excited (LE) state.

On the other hand, the calculated minimum energy structures of Py-Benz-Py in the ground and excited states using DFT and TDDFT shows that Py-Benz-Py in the ground state has two dihedral angles (φ_1 and φ_2) between Py and phenyl moieties (Fig. 2a). Py-Benz-Py in the excited state shows relatively planarized geometry ($\varphi_1 = 36^\circ$ and $\varphi_2 = 146^\circ$) compared to that in the ground state (Fig. 2b). This calculation result indicates that after photoexcitation, Py-Benz-Py undergoes planarization. As shown in Fig. S10 (ESI†), the planarization process in the ground state is an uphill pathway. However, the potential energy surface along the dihedral angle of Py-Benz-Py in the



Fig. 2 Calculated geometries of Py-Benz-Py in the ground state (a) and excited state (b) using DFT and TDDFT, respectively. In each panel, the front and side views are shown on the left and right sides, respectively. The orange-shaded and green-shaded balls are used to indicate the dihedral angles φ_1 and φ_2 , respectively.

ground state is quite flat at 52° and 128°, suggesting that various geometries can exist and small conformational changes are relatively easy in solution. This calculation result implies that in the ground state the rotational barriers for Py-Benz-Py in the range of $35^{\circ}-65^{\circ}$ and $110^{\circ}-150^{\circ}$ are very small (~0.05 eV). Meanwhile, the planarization process of Py-Benz-Py in the excited state is a downhill pathway, indicating a barrierless relaxation (Fig. S10, ESI[†]).

Excited-state dynamics

To elucidate the excited state relaxation dynamics upon ESM in Py-Benz-Py, we measured the fs-TA spectra of Py-Benz-Py in various solvents with 350 nm excitation. For comparison, the fs-TA spectra of Py-Benz, which has the same ordering for the first and second excited states as Py, were also measured in toluene and DCM (Fig. 3a and Fig. S11, ESI[†]). As shown in Fig. 3a and b, the fs-TA spectra for Py-Benz are characterized by a broad positive signal corresponding to the excited-state absorption (ESA). The broad positive signal around 620 nm significantly decreases with the delay time, whereas the intense positive signal around 510 nm slightly increases (Fig. 3a). Raytchev et al. assigned the intense absorption band at 510 nm to the $S_1 \rightarrow S_n$ transition, and the broad absorption band at 620 nm to the $S_2 \rightarrow S_n$ transition.⁵ Based on their assignments, we conclude that the spectral change in fs-TA spectra for Py-Benz is due to the IC from S_2 to S_1 within the sup-picosecond time scale. As shown in Fig. 1b, Py-Benz exhibits a broad absorption band and a shorter fluorescence lifetime ($\tau_{\rm f}$ = 109 ns in MeCN)³³ than that of Py $(\tau_f = 354 \text{ ns})^{10}$ suggesting the existence of ESM by the substituent effect. However, Py-Benz showed the more structured absorption and emission bands and the longer fluorescence lifetime than those of Py-Benz-Py, indicating the ESM for Py-Benz is weaker than that for Py-Benz-Py. Thus, we suggest that although the substitution at the 1-position of Py induces

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Fig. 3 (a) Transient absorption spectra of Py-Benz in toluene. The excitation wavelength is 350 nm. (b) Time profiles monitored at selected wavelengths (orange circle: 520 nm, and blue circle: 650 nm). (c and e) Transient absorption spectra of Py-Benz-Py in MeCN. The excitation wavelength is 350 nm. (d) Time profiles monitored at selected wavelengths (black circle: 450 nm, red circle: 520 nm, orange circle: 640 nm, and blue circle: 710 nm). Fit curves are shown in black solid lines. (f) The spectral relaxation is well fit by the single-exponential function with a time constant of 3.0 ± 0.1 ps. The fit curve is shown as the black solid line.

ESM, the ordering for the first and second excited states for Py-Benz is not changed.

In contrast to Py-Benz, the fs-TA spectra for Py-Benz-Py in MeCN are characterized by a negative signal around 450 nm and an intense and broad positive signal around 600 nm, as shown in Fig. 3c and e. The negative and positive signals correspond to the stimulated emission (SE) and ESA of Py-Benz-Py, respectively. In the early delay times (<10 ps), the negative and positive signals are red- and blue-shifted, respectively, indicating the relaxation from a higher energy state to a lower energy state. The time evolutions of the TA spectra at specific wavelengths were globally fit to quantify the kinetics in the excited state. The time profiles of Py-Benz-Py in MeCN were fit well by a tri-exponential function with three relaxation times of 3.8 \pm 0.1, 155 \pm 16, and 2190 \pm 50 ps. Py-Benz-Py in CHX, a nonpolar solvent, shows a negative signal around 435 nm and a broad positive signal over 500 nm corresponding to SE and ESA, respectively, and all time profiles monitored at several wavelengths can also be fit by a tri-exponential function with shared relaxation times of 11.0 \pm 0.2, 323 \pm 43, and 1410 ± 40 ps (Fig. S12, ESI[†]). The TA spectra for Py-Benz-Py in EE, THF, and DCM show similar spectral features and all time profiles monitored at several wavelengths can also be expressed by a tri-exponential function (Fig. S13-S15, ESI†). Time constants determined from TA measurements for Py-Benz-Py in various solvents are summarized in Table 2. The evolution-associated difference spectra and population changes for Py-Benz-Py are represented in Fig. S16 (ESI[†]). We observed no spectral change representing the IC from S₂ to S₁ in Py-Benz-Py in all solvents. Based on the steady-state spectroscopic and theoretical calculation results, we suggest that the absence of IC from S₂ to S₁ in Py-Benz-Py is due to the much-

 Table 2
 Time constants determined from TA measurements for

 Py-Benz-Py in various solvents
 Figure 1

Solvent	τ_1 (ps)	$\tau_2 \text{ (ps)}$	τ_3 (ns)
CHX	11 ± 0.2	323 ± 43	1.41 ± 0.04
EE	4.2 ± 0.1	144 ± 11	1.61 ± 0.01
THF	5.4 ± 0.1	53 ± 3.9	1.43 ± 0.01
DCM	3.3 ± 0.1	27 ± 1.5	1.40 ± 0.01
MeCN	3.8 ± 0.1	155 ± 16	2.19 ± 0.05

reduced energy gap between S1 and S2, leading to the formation of energetically degenerate states or inversion in the energy-level ordering. In practical terms, the bichromophoric interaction in Py-Benz-Py can induce the reduction of energy gap or inversion in the energy-level ordering as a result of ESM (Scheme 1a). Indeed, our calculation result using an ADC(2)34 method and def-TZVP basis set shows that the two lowest states of Py-Benz-Py degenerated and their vertical excitation energies are found to be 3.670 and 3.672 eV. Also, the energy gap between the low-lying excited states tended to decrease in the order of Py, Py-Benz, and Py-Benz-Py (Fig. 4). The low-lying excited states of Py-Benz-Py are derived from La and Lb states of Py. Although Py-Benz-Py has similar excited states to Py in terms of the transition in MOs, Py-Benz-Py exhibits significantly different photophysical properties. Thus, the change in photophysical properties of Py-Benz-Py compared to Py is attributed to the ESM in Py-Benz-Py.

Here, we consider the excited-state relaxation dynamics upon the ESM for Py-Benz-Py. The earliest kinetic component (τ_1) can be interpreted either as the vibrational relaxation from the initially populated local excited state or ICT process. As shown in Table 2, Paper



Fig. 4 The excitation energies (eV) of the L_a and L_b states of pyrene (Py), 1-phenylpyrene (Py-Benz), and 1,4-di(pyrenyl)benzene (Py-Benz-Py) using the ADC(2) method and def-TZVP basis set.

the τ_1 time constants become smaller as the solvent polarity increases. It is known that the ICT process is greatly affected by solvent polarity. Moreover, the formation of the CT state has been explained with the spectral shift of the TA spectra because the stabilization of the CT state by interaction with solvent molecules induces a red- and blue-shift in the absorption bands corresponding to the SE and the ESA, respectively.³⁵⁻³⁹ As depicted in Fig. 3, Py-Benz-Py in a highly polar solvent such as MeCN shows red- and blue-shifts in bands corresponding to SE and ESA, respectively. In addition, the spectral relaxation for Py-Benz-Py measured in MeCN is fit by the single-exponential function with a time constant of 3.0 \pm 0.1 ps (Fig. 3f), which is consistent with the τ_1 time constant from the global fitting. Furthermore, the 3 ps dynamics is much slower than the average solvation dynamics of MeCN (0.26 ps).⁴⁰ With these considerations, we attribute the τ_1 time constant, which shows the dependence on the solvent polarity, to the ICT process.

On the other hand, upon increasing the solvent polarity, the τ_2 time constant measured for Py-Benz-Py became smaller and then larger, as shown in Table 2. Raytchev et al. suggested that in the case of Py derivatives such as 1-biphenyl-4-yl-pyrene (BPh-P) and Py-Benz, the structural relaxation in the S₁ state takes place in several tens of picoseconds timescale.5 Their time-resolved spectroscopic results, for example, showed that after photoexcitation, BPh-P in MeCN undergoes the initial planarization with a time constant of 2 ps.5 Then, the additional twisting motion between biphenyl and Py moieties takes place with a time constant of about 40 ps.⁵ In this regard, we speculate that the τ_2 time constant corresponds to the twisting motion between Py and phenyl moieties. Our TDDFT calculation for Py-Benz-Py presents the possibility of planarization in the excited state (see Fig. 2). To confirm the twisting motion between phenyl and Py moieties, we measured and compared the UV-visible absorption and emission spectra of Py-Benz-Py in DCM (dielectric constant: 8.93, viscosity at 20 °C: 0.43 cP) and triacetin (dielectric constant: 7.01, viscosity at 20 °C: 23 cP). As shown in Fig. S17 (ESI[†]), the emission intensity significantly increases with solvent viscosity, although the absorbance values at the excitation wavelength, 380 nm, are almost the same. Generally, it is known that the increased emission quantum yield accompanied by the increase of the solvent viscosity is due to the restricted intramolecular motion.41 Thus, we conclude that the twisting process of the Py moiety occurs in the excited state.



Scheme 2 Schematic of two types of twisting motion of Py-Benz-Py in nonpolar and low-polar solvents (a) and in a high-polar solvent (b).

According to the structure of Py-Benz-Py with two dihedral angles between Py and phenyl moieties, two types of twisting motions in Py-Benz-Py need to be considered; (i) synchronous twisting of two Py moieties and (ii) asynchronous twisting of two Py moieties with different time constants (see Scheme 2). It has been suggested that generally the twisting motion between the electron donor (D) and acceptor (A) groups can be influenced by the charge localization and delocalization in a molecular system.42,43 With respect to charge distribution, the spectroscopic results reveal that Py-Benz-Py exhibits the ICT dynamics in the excited state. To further understand the relation between the twisting motion and the charge distribution difference, we plot the Stokes shifts against the orientation polarizability (Δf) using the Lippert-Mataga equation (see Fig. S18, ESI[†]). As depicted in Fig. S18 (ESI[†]), only the Stokes shift measured in MeCN largely deviates from the linearity, whereas the values measured in nonpolar and low-polarity solvents give good linearity. This result indicates that the charge distribution in the excited Py-Benz-Py in MeCN is different from those in nonpolar and low-polarity solvents. Indeed, many studies on ICT dynamics have suggested that in a D-A-D (or A-D-A) system, the CT state localized on one of the branches is formed by symmetrybreaking CT in the high-polarity solvent, whereas the delocalized CT state is preserved in nonpolar and low-polarity solvents.⁴³⁻⁴⁷ In addition, symmetry-breaking CT induces a significant change in the photophysical properties of an excited molecule. Because Py-Benz-Py can be considered as a A-D-A triad, the non-linearity in the Lippert-Mataga plot is probably due to the change in the charge distribution from the delocalized CT state to the localized CT state (see Fig. 5). That is, our result indicates that Py-Benz-Py in MeCN has a localized CT state. According to the nature of a CT state, two Py moieties in the delocalized CT state likely have nearly



Fig. 5 Schematic of excited-state dynamics of Py-Benz-Py depending on the solvent polarity.

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identical environments. Consequently, in the delocalized CT state, two Py moieties have an uncharged or partially charged character, leading to the synchronous twisting of two Py moieties ($\tau_{\text{twisting1}} =$ $\tau_{\text{twisting2}}$). In contrast, two Py moieties in the localized CT state should have different environments with one Py moiety having a charged character and the other having an uncharged or partially charged character. Therefore, Py-Benz-Py in MeCN may show asynchronous twisting of two Py moieties with unequal time constants ($\tau_{twisting1} \neq \tau_{twisting2}$), as shown in Scheme 2. In this respect, it is noteworthy that the τ_2 time constant (323 and 144 ps, respectively) for the twisting dynamics in CHX and EE is much larger than that (27 ps) in DCM. These results indicate that the twisting motion between Py and phenyl moieties accelerates with the increase of the solvent polarity. In other words, this means that the twisting of the charged Py moiety is much faster than that of the uncharged Py moiety. As shown in Table 2, the time constant for the twisting dynamics measured in MeCN is close to that determined in EE. This means that the environment of the partially charged (or uncharged) Py moiety in MeCN is similar to that of the Py moiety in EE. Thus, we suggest that the τ_2 time constant (155 ps) observed in MeCN corresponds to the slow twisting motion of the partially charged (or uncharged) Py moiety. On the one hand, as shown in Table 2, the twisting motions significantly depend on the solvent polarity in the range of the solvent polarity index (P) of 0.2-3.1. Considering the high-polarity (P = 5.8) of MeCN compared to other solvents, the time constant for the twisting dynamics of the charged Py moiety should be less than that (27 ps) measured in DCM. In such a scenario, the twisting dynamics of the charged Py moiety in MeCN would occur as fast as the ICT process. Indeed, the ICT process measured in MeCN is slightly slower than that measured in DCM, as shown in Table 2. Therefore, we suggest that the relatively slow ICT process in MeCN may reflect the fast twisting dynamics of the charged Py moiety.

Finally, the longest time constant, τ_3 , can be interpreted in terms of the population relaxation of the structurally planarized ICT state (PICT) to the ground state. As shown in Tables 1 and 2, the τ_3 time constant is very close to the fluorescence lifetime, indicating that τ_3 is the lifetime of the PICT state formed by the structural relaxation.

Energy diagram

The excited-state relaxation dynamics taking into account the ESM of Py-Benz-Py in nonpolar, low-polarity, and high-polarity solvents proposed based on the experimental and theoretical calculation results are shown in Fig. 5. After photoexcitation, Py-Benz-Py is excited to the S_1/S_2 mixed state, which is a LE state and then exhibits the dynamics of a few picoseconds corresponding to the ICT process. The CT states formed in nonpolar and low-polarity solvents are delocalized states, whereas the CT state in the high-polarity solvent (MeCN) is a localized CT state. The formed CT state undergoes the structural relaxation dynamics corresponding to the twisting motion between Py and phenyl moieties to form the PICT state. Notably, the twisting dynamics of the Py moiety in MeCN significantly are slow compared with that in DCM with a low-polarity but

are similar to those in CHX and EE. The slow twisting dynamics measured in MeCN is attributed to the twisting dynamics of the uncharged Py moiety, which is much slower than that of the charged Py moiety.

Conclusions

In this study, we explored a new concept of generating CT via ESM in a symmetric MCS, Py-Benz-Py. Even if Py-Benz does not exhibit CT, Py-Benz-Py shows ICT along with significant ESM reflected by a broad absorption band and a short fluorescence lifetime. The additional introduction of Py into Py-Benz induces the increase of EC as well as the π -conjugation. Consequently, the enhanced EC and the extended π -conjugation result in the reduction of the energy gap between two low-lying electronic states and the CT state formation. The resulting S₁/S₂ mixed state and CT state are energetically close to each other, leading to the efficient transition from the S₁/S₂ mixed state to the CT state. DFT and TDDFT calculations also support the ESM for Py-Benz-Py owing to the expansion of π -conjugation and Py substitution as an electron-withdrawing group. ESM of Py-Benz-Py induces the perturbation of the ultrafast excited-state relaxation dynamics such as the absence of IC from S₂ to S₁ which is commonly observed in Py and its derivatives. Furthermore, unlike Py-Benz, Py-Benz-Py exhibits the dynamics of a few picoseconds corresponding to ICT. Based on the experimental results, we suggest that Py-Benz-Pys in nonpolar and lowpolarity solvents have a delocalized CT state, whereas Py-Benz-Py in high-polarity solvent (MeCN) has a localized CT state. The CT state undergoes the structural relaxation dynamics corresponding to the twisting motion between Py and phenyl moieties. Py-Benz-Py in MeCN shows the twisting process that is significantly slower than that in DCM but is similar to those in CHX and EE. The slow twisting process in MeCN is attributed to the twisting of the uncharged Py moiety, which is much slower than that of the charged Py moiety. We suggest that such photophysical properties is significantly different from those of Py and its derivatives originate from ESM due to the existence of two Pys. In addition, we carried out TDDFT calculations using CAM-B3LYP/cc-pVTZ to elucidate the effect of the substituent such as electron withdrawing or donating groups for Py-Benz-Py. Based on the calculation results, substituted Py-Benz-Pys exhibit reduced energy gaps between excited state manifolds compared to Py-Benz-Py (Fig. S19, ESI[†]). This result means that the substituent can assist in further strengthening the efficient ESM. Our observation will give further insight into the control of the photophysical properties via regulating of ESM and will lead to the strategic material design for improving the performance of photoelectric or electrochemical devices.

Conflicts of interest

There are no conflicts to declare.

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