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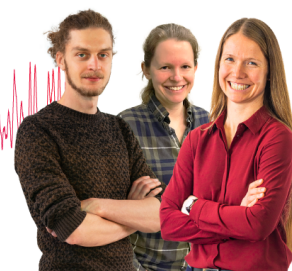
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ABSTRACT

Molecular donor-acceptor (D-A) linked systems have attracted significant attention due to their potential to address D-A interactions in excited states. In these systems, it is crucial to understand the interplay between electrons and spin behaviors, atomic nucleus movements (including vibration, rotation, fluctuation, and transfer), and collective motion (electron-phonon coupling) over time. Through intentional manipulation of locally excited, charge-transfer excited, and charge-separated states, along with modulation of dynamic effects (enhancement or restraint), we expect to unlock the full potential of D-A systems for photofunctions in electronics, energy, healthcare, and functional materials. In this perspective, we present our recent examples of D-A linked systems and related ones that address the aforementioned issues as part of our “Dynamic Exciton” research project in Japan.

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INTRODUCTION

Molecular donor-acceptor (D-A) linked systems have attracted significant attention because of their role in addressing D-A interactions in excited states.¹ These systems have served as models for understanding the factors that control photoinduced energy transfer (EnT) and electron transfer (ET), including applications in photosynthesis, photocatalysis, and organic solar cells (OSCs). More recently, these systems have also found applications in thermally activated delayed fluorescence (TADF), photoredox catalysts, and singlet fission and upconversion molecules, all featuring a D-A linked structure. Within this context, the classical Marcus’s ET theory has made significant contributions to the field.² However, the impact of atomic nucleus movements on the behavior of electrons and spins during ET reactions over time has received less attention.

In this context, we initiated the “Dynamic Exciton” project in Japan in 2020.^{3–5} Initially, we redefine the term “exciton.” Originally, a molecular exciton referred to the excited state of a molecule in

molecular crystals. However, over the past 60 years, the concept has evolved alongside advancements in molecular science and technology. Here, “exciton” is not only redefined as the locally excited (LE) state in molecular D-A systems but also encompasses the charge-transfer (CT) excited and charge-separated (CS) states. This broader definition emphasizes the hole-electron pair interactions. Our goal is to manipulate these three distinct states through mutual transformation in photochemistry. Another important aspect of “exciton” is its dynamic nature. In molecular D-A systems, understanding the mutual interactions between electron and spin behaviors, atomic nucleus movements (including vibration, rotation, fluctuation, and transfer), and collective motion (electron-phonon coupling) over time is essential. Through deliberate manipulation of these three states and modulation of dynamic effects (enhancement or restraint), we anticipate fully harnessing the photofunctional potential of D-A systems in electronics, energy, medicine/medical care, and functional materials. Taking this perspective, we will present recent examples of D-A linked systems and related research addressing the mentioned issues.

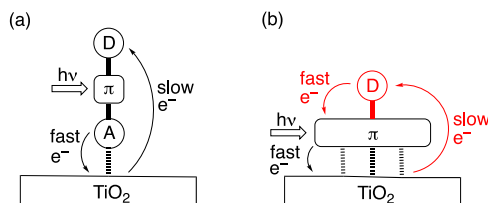


FIG. 1. Schematic representation of the adsorption structure and electron transfer processes at the dye/ TiO_2 interfaces. (a) Vertical orientation for conventional rod-shaped D- π -A type dyes with a mono-anchoring group. (b) Horizontal orientation for flat planar π -conjugated dye with multiple anchoring groups. The donor moiety is fixed on top of the π moiety to slow down the charge recombination.

MODELS FOR PHOTOINDUCED CHARGE TRANSFER AND SEPARATION AT HETEROINTERFACES

In recent decades, D-A heterointerfaces, comprising photoactive organic molecules and inorganic nanostructures, have drawn considerable attention due to their potential role in solar energy conversion.^{6–8} A prime example is dye-sensitized solar cells (DSSCs), which offer promising alternatives to conventional photovoltaics. Their advantages include high power conversion efficiency (PCE), low-cost production, facile fabrication, and suitability for indoor use.^{9,10} According to the operational principles of DSSCs, the dye-sensitized TiO_2 electrode (dye/ TiO_2) is the most important component for high photovoltaic performance. Advances in dye development and redox shuttles have enhanced DSSC performance, with donor- π -acceptor (D- π -A) type dyes

achieving impressive PCEs.^{11–20} Typically, D- π -A type dyes exhibit enhanced light-harvesting properties due to their push-pull electronic structure.^{21–23} Moreover, the rod-shaped structure, featuring a single anchoring group, allows molecules to align vertically on TiO_2 . This arrangement promotes rapid electron injection from the dye excited state to TiO_2 , minimizing charge recombination and leading to a high PCE [Fig. 1(a)]. Nevertheless, this approach does not apply to flat planar dyes (such as highly light-harvesting porphyrins and corroles) with multiple anchoring groups. These dyes tend to orient horizontally on TiO_2 by binding at multiple sites.^{24–26} Unfortunately, due to the robust electronic coupling between the dye and TiO_2 , rapid charge recombination occurs between the oxidized dye radical cation (dye^+) and an electron in TiO_2 (TiO_2^-). This diminishes the PCE despite efficient electron injection.^{27–30} To address this challenge, a donor moiety can be positioned atop the planar π -conjugated dye on TiO_2 (forming a donor-dye/ TiO_2 structure). The triad D-D-A scheme, widely employed by Gust, Moore, and others for decades, offers a potential solution.^{31–36} If charge recombination competes with intramolecular ET from the donor moiety to the oxidized dye, the resultant long-lived CS state (donor $^+$ -dye/ TiO_2^-) can suppress charge recombination, enhancing the PCE in the rigid donor-dye/ TiO_2 configuration [Fig. 1(b)].

To demonstrate this proof of concept, Imahori and colleagues focused on *meso*-triaryl-corroles. The photovoltaic performance of the corrole-based DSSCs strongly depends on the central metal. In fact, a gold(III) corrole dye with three *meta*-carboxyphenyl groups at *meso*-positions (AuCor) showed the highest PCE among all metallo-corroles studied (Fig. 2).^{37,38} Although the heavy metal effect induces very fast intersystem crossing ($\sim 10^{12} \text{ s}^{-1}$) from the singlet excited state to the triplet excited state, which is energetically lower than the

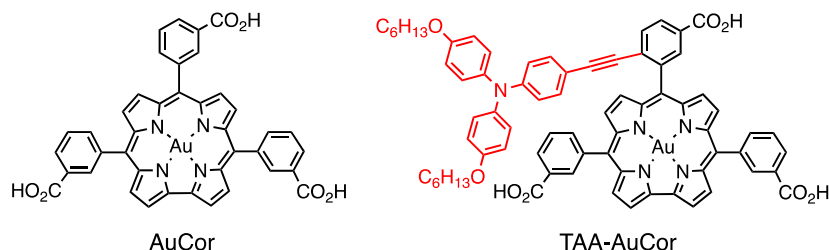


FIG. 2. Molecular structures of gold corroles AuCor and TAA-AuCor.

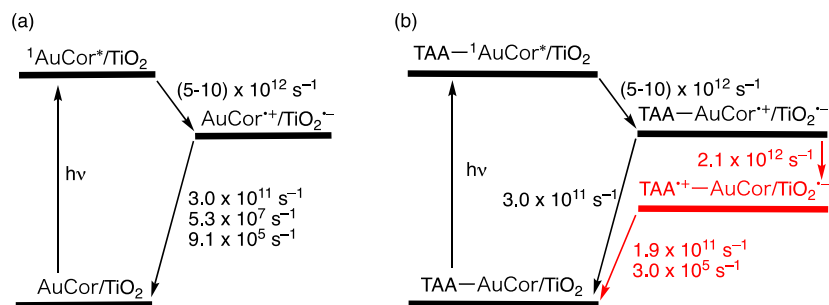


FIG. 3. Relaxation pathways of corrole-sensitized TiO_2 films (a) AuCor/ TiO_2 and (b) TAA-AuCor/ TiO_2 based on the analysis of time-resolved TA measurements.

conduction band (CB) of TiO_2 , the electron injection occurs sufficiently quickly to compete with intersystem crossing, resulting in optimal PCE. Additionally, AuCor adopts a face-to-face horizontal orientation on TiO_2 through the binding of its three carboxy groups to TiO_2 . Therefore, AuCor was selected as a model system for validating this concept.³⁹ By arranging an appropriate donor moiety, specifically triarylamine (TAA), atop AuCor, it is possible to manipulate the dye⁺/ TiO_2 ⁻ state (TAA-AuCor), thereby improving photocurrent generation and subsequent PCE. To achieve this configuration, they tethered TAA at an *ortho*-position of a *meso*-phenyl group at the 10-position via a triple bond (Fig. 2). The anticipated fixed donor-dye/ TiO_2 configuration was confirmed by theoretical calculations using density functional theory (DFT).

To examine the ET processes at the interface, the picosecond time-resolved transient absorption (TA) spectroscopic measurements were carried out for the corrole-sensitized TiO_2 films (AuCor/ TiO_2 and TAA-AuCor/ TiO_2) deposited on a CaF_2 substrate (Fig. 3).³⁹ The fingerprint TA signal at 5000 nm was used to track free electrons in the CB of TiO_2 . Electron injection from the excited singlet state of gold(III) corroles occurred at an extremely rapid rate $\{(5\text{--}10) \pm 0.1\} \times 10^{12} \text{ s}^{-1}$, surpassing the intersystem crossing $[(1.0 \pm 0.1) \times 10^{12} \text{ s}^{-1}]$ for AuCor. In the subsequent picosecond time range (10–1000 ps), AuCor/ TiO_2 exhibited charge recombination between the CB electrons and Cor^+ , whereas TAA-AuCor/ TiO_2 showed negligible recombination within this time-frame (Fig. 4). The extended lifetime of electrons in the CB of TiO_2 for TAA-AuCor is consistent with its higher electron collection efficiency. Simultaneously, the TA spectra of AuCor/ TiO_2 in the 400–1000 nm range displayed characteristic absorption at 450 nm and weak, broad absorption at 600–750 nm, corresponding to Cor^+ . This absorption decayed with a time constant of $(3.0 \pm 0.1) \times 10^{11} \text{ s}^{-1}$. In contrast, the TA spectra of TAA-AuCor/ TiO_2 exhibited broad absorption in the 700–800 nm range, corresponding to TAA⁺. Namely, the TA spectra revealed that intramolecular ET from the TAA moiety to Cor^+ takes place with a time constant of $(2.1 \pm 0.1) \times 10^{12} \text{ s}^{-1}$ upon photoexcitation of TAA-AuCor. The intramolecular ET efficiency for TAA-AuCor/ TiO_2 was calculated to be 88%. The decay rates of the dye radical cation in the picosecond–nanosecond–microsecond regions $[(3.0 \pm 0.1) \times 10^{11} \text{ s}^{-1}, (5.3 \pm 0.1) \times 10^7 \text{ s}^{-1}, (9.1 \pm 0.1) \times 10^5 \text{ s}^{-1}]$ for AuCor/ TiO_2 ; $(1.9 \pm 0.1) \times 10^{11} \text{ s}^{-1}, (3.0 \pm 0.1) \times 10^5 \text{ s}^{-1}$ for TAA-AuCor/ TiO_2] could be attributed to charge recombination between electrons in the shallow trap state of TiO_2 and the dye radical cation, along with heterogenous ET coupling.³⁹ Alternatively, enhanced spin–orbital coupling by the Au atom, along with dynamic effects due to vibration and fluctuation, could promote spin conversion from the singlet CS state to the triplet CS state, leading to multiple CR processes.³ In contrast, introducing the TAA moiety retards undesirable charge recombination by generating a longer-lived CS state (TAA⁺-AuCor/ TiO_2 ⁻). Overall, rational molecular design allows us to manipulate CS states at D–A heterointerfaces, improving charge separation efficiency and extending the lifetime for highly efficient DSSCs.

Although D–A heterointerfaces involving two-dimensional (2D) layered materials have been extensively studied,⁴⁰ understanding CT and charge separation behaviors at D–A heterointerfaces remains a challenge. Despite the straightforward and practical nature of the noncovalent approach, understanding the fundamental

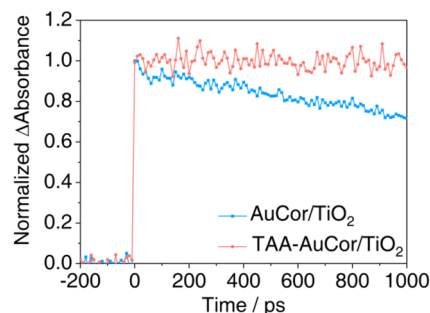


FIG. 4. TA profiles of AuCor/ TiO_2 (blue line) and TAA-AuCor/ TiO_2 (red line) at 5000 nm. The samples were excited by a $2 \mu\text{J}$ 570 nm laser pulse at a frequency of 500 Hz with a duration of 90 fs, and data were accumulated over 10 000 scans.

aspects of photoinduced CS at the heterojunction remains elusive due to the amorphous nature of organic layers composed of numerous molecules on few-layered 2D materials.⁴¹ Conversely, the covalent approach provides a powerful means to control interactions between organic and inorganic materials through covalent linkages at the molecular level.^{42,43} However, the limited reactivity at the 2D layered surface has impeded covalent modifications by organic molecules with well-defined structures. Imahori and colleagues created a heterointerface between a photoactive molecule (pyrene, Py) and a semiconducting 2D inorganic monolayer (MoS_2) using a precisely defined nanoscale bridge (Py- MoS_2).⁴⁴ Py and MoS_2 are connected via a short, semi-rigid bridge called *N*-benzylsuccinimide (BSI) (Fig. 5). Pérez and co-workers demonstrated that BSI groups can be densely grafted onto the MoS_2 surface through a reaction with *N*-benzylmaleimide (BMI).^{45,46} Thermogravimetric analysis and atomic force microscopy revealed that the BSI moieties densely form a monolayer on MoS_2 . Moreover, the terminal Py moieties are

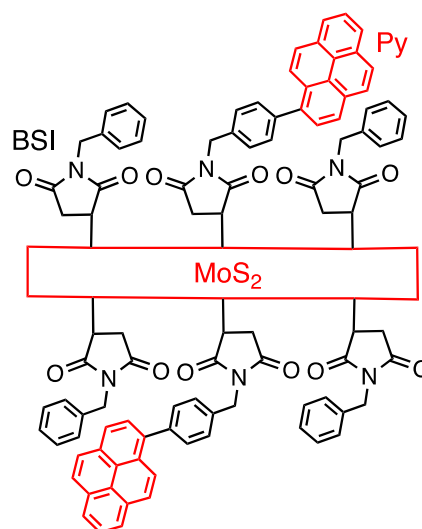


FIG. 5. Schematic illustration of Py- MoS_2 , where a pyrene (Py) is linked to a semiconducting 2D inorganic monolayer (MoS_2) with a well-defined bridge *N*-benzylsuccinimide (BSI).

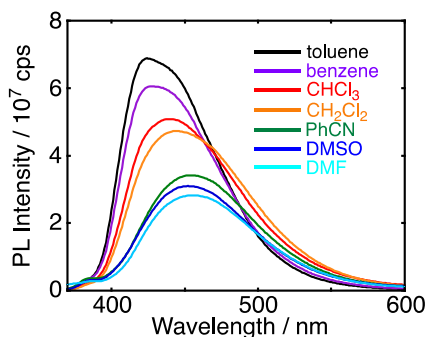


FIG. 6. Photoluminescence (PL) spectra of Py-MoS₂ in various solvents excited at 345 nm. At the excitation wavelength, the absorption intensities were 0.13 in all solvents.

significantly tilted toward the BSI-modified MoS₂ and are anchored to the BSI moieties at an approximate separation distance of 1 nm, as indicated by theoretical calculations (*vide infra*). Notably, the Py moiety is attached to the *para*-position of the phenyl group by Suzuki coupling following the initial tethering on MoS₂. The modification ratio through Suzuki coupling is relatively low, with only $(30 \pm 3)\%$ of the BSI on MoS₂ being modified with the Py moiety. Consequently, the excited singlet state of Py interacts primarily with MoS₂, leading to the formation of CT excited and/or CS states at the well-defined heterointerface of Py-MoS₂.

The photoluminescence spectra of Py-MoS₂ and a pyrene reference were also measured in DMF.⁴⁴ The pyrene reference, when excited at 345 nm, exhibited strong emission peaks at 382 and 402 nm with an emission quantum yield of $56\% \pm 1\%$. Upon measuring the photoluminescence spectrum of Py-MoS₂ with an excitation wavelength of 345 nm, pyrene emission was significantly quenched, and a broad, red-shifted intense emission appeared at 453 nm (Fig. 6). The emission decay profiles revealed that the photoluminescence rate constant for Py-MoS₂ is $(3.7 \pm 0.1) \times 10^8 \text{ s}^{-1}$, significantly lower than that of the pyrene reference $[(1.3 \pm 0.1) \times 10^7 \text{ s}^{-1}]$. As solvent polarity increased from toluene to DMF, Py-MoS₂ exhibited a systematic red-shift and reduced emission intensity, attributable to CT emission. It should be pointed out that the emission quantum yield of Py-MoS₂ ($68\% \pm 1\%$ in toluene) is remarkably high, especially when compared to the typical intermolecular CT excited states between pyrene derivatives and *N,N*-dimethylaniline ($\sim 20\%$ in non-polar solvents).⁴⁴ This may result from the fixed orientation and the short separation distance between the pyrene and MoS₂ through the BSI moieties on MoS₂, which stabilize the CT excited state and suppress nonradiative decay.

The picosecond TA spectroscopic measurements of Py-MoS₂ were conducted with an excitation wavelength of 345 nm, where the Py moiety predominantly absorbs the excitation light.⁴⁴ From the global analysis, three components [$k_1 = (1.1 \pm 0.1) \times 10^{12} \text{ s}^{-1}$, $k_2 = (8.5 \pm 0.1) \times 10^9 \text{ s}^{-1}$, and $\tau_3 = (3.6 \pm 0.1) \times 10^8 \text{ s}^{-1}$] were obtained. The first and second decay components, associated with bleach arising from the MoS₂ excited states, corresponded to the decay of the hot and cooled MoS₂ excited states. The third component, showing broad positive signals in the visible and NIR regions with a peak around 860 nm, arises from the decay of the CT excited

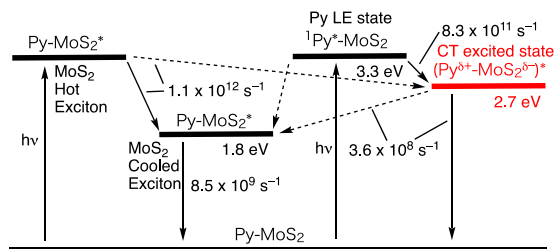


FIG. 7. Relaxation pathways of Py-MoS₂ in DMF. The energy level of the CT excited state was determined by the peak position of the emission. The plausible pathways are shown as a black dotted arrow.

state, in agreement with the emission rate constant of Py-MoS₂ $[(3.7 \pm 0.1) \times 10^8 \text{ s}^{-1}]$. The rise component at 850 nm indicates the formation of the CT excited state with a rate constant of $(8.3 \pm 0.1) \times 10^{11} \text{ s}^{-1}$. The relaxation pathways of Py-MoS₂ are illustrated in Fig. 7.

Theoretical studies were performed for the Py-MoS₂ model using a MoS₂S₆₃ nanosheet, where one Py-BSI unit and two BSI units are covalently bonded to sulfur atoms. Geometry optimization of the Py-MoS₂ model showed the nearly horizontal orientation of the Py moiety, which aligns with the small thickness of the experimentally obtained Py-MoS₂ (2.6 nm).⁴⁴ Moreover, the time-dependent density functional theory (TDDFT) and the three-dimensional reference interaction site model (3D-RISM) were employed to examine the emission behavior of Py-MoS₂. The LUMO of the Py moiety interacts with the MoS₂ vacant orbitals, suggesting the formation of the CT state through interaction between the MoS₂ vacant orbitals and the Py excited state. Namely, photoexcitation of the Py moiety in the Py-MoS₂ covalently linked system effectively formed the long-lived, highly emissive CT excited state that extends across the heterointerface of pyrene and mono-layered MoS₂. This unique, highly emissive CT excited state may provide insight into how to reduce the voltage loss derived from nonradiative charge recombination in OSCs. As several groups have proposed,^{3,4,47} if the CT excited state is more emissive and its energy level is close to that of the LE state, the two states will hybridize. This will inhibit nonradiative vibrational charge recombination, thereby reducing the voltage loss. Therefore, this study paves the way for utilizing organic-inorganic 2D heterointerfaces in energy conversion and optoelectronic devices and sensors.

MODELS FOR SINGLET FISSION

Singlet fission (SF) is a photophysical process that generates two individual triplet excited states ($T + T$) from one photon absorption through a correlated triplet pair (TT) in two nearby chromophores.^{48–55} SF is expected to provide an option for efficient exciton generation and subsequent transport processes in molecular assemblies.^{56,57} For instance, tetracene (Tc) satisfies the energy level condition where the lowest-lying singlet excited state [$E(S_1) = 2.4 \text{ eV}$] matches two triplet excited state [$E(T_1) = 1.2 \text{ eV}$] [i.e., $E(S_1) \geq 2E(T_1)$]. Kobori and colleagues successfully achieved quantitative individual triplet generation via intramolecular SF in biphenyl-bridged Tc dimers.^{56,57} Building on this success, they proposed a molecular design for efficient exciton transport in linear Tc

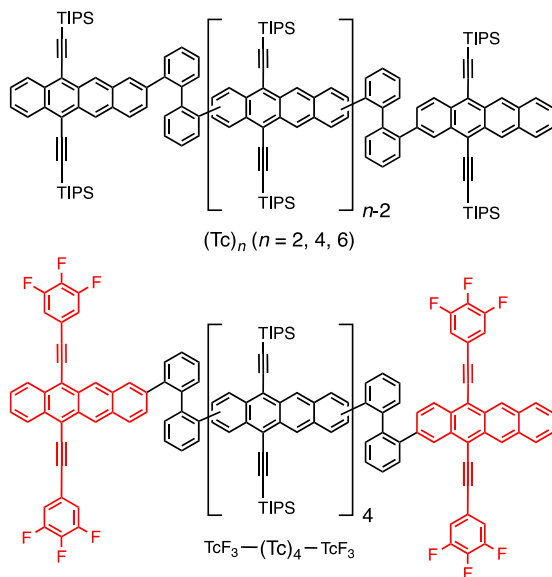


FIG. 8. Molecular structures of Tc-oligomers and reference. TIPS: triisopropylsilyl group.

oligomers by promoting TT dissociation and controlling subsequent exciton trapping processes.⁵⁸ To examine the effect of entropic gain on the number of Tc moieties, a series of Tc-homo-oligomers with 2,2'-biphenylene bridges were designed [(Tc)_n; n = 2, 4, 6] (Fig. 8).

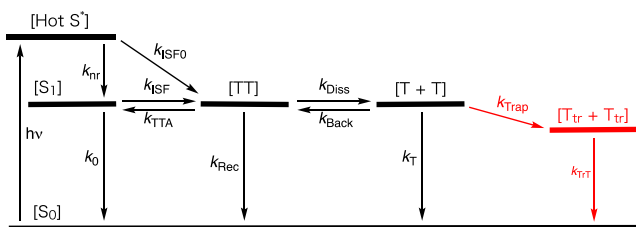


FIG. 9. Proposed kinetic scheme for (Tc)_n (n = 2, 4, 6) and TcF₃-(Tc)₄-TcF₃.

A Tc-hetero-oligomer [TcF₃-(Tc)₄-TcF₃] was also synthesized to assess vibronic coupling effects for entropic gain. The molecular modifications involved replacing triisopropylsilyl (TIPS) groups at the terminal Tc moieties in [(Tc)_n] with 3,4,5-trifluorophenyl groups, slightly lowering the energy level of T₁ for the TcF₃ moiety (1.06 eV) relative to that for the Tc moiety (1.13 eV).

To monitor the generation and dissociation of TT, time-resolved electron paramagnetic resonance (TREPR) measurements were conducted in 2-methyltetrahydrofuran at 80 K ($\lambda_{\text{ex}} = 532 \text{ nm}$).⁵⁸ The electron spin polarization (ESP) of the microwave absorption (A) and emission (E) in the quintet state ⁵(TT) at the center field and the dissociated states T + T at the outer fields were detected in (Tc)₆ and TcF₃-(Tc)₄-TcF₃ (Fig. 9). The E/A/E/A pattern polarization in the quintet TT state was rationalized by vibronic effects, assuming the varying exchange interaction (*J*) model in TT coupled to the TT conformation after intramolecular SF. This suggests that vibrational motions play a significant role in generating the quintet ⁵(TT) due to the *J* modulation, rather than exciton hopping from ⁵(T + T)₀ with the help of the SQ₀ mixing. The final triplet yields (Φ_T) were determined to be $165\% \pm 6\%$ for (Tc)₂, $173\% \pm 9\%$ for (Tc)₄, $182 \pm 10\%$ for (Tc)₆, and 176% for TcF₃-(Tc)₄-TcF₃ by picosecond TA measurements (Table I). The Φ_T value increases with the number of Tc moieties. Furthermore, in TcF₃-(Tc)₄-TcF₃, localized triplet states at the terminal TcF₃ moieties with a time constant (k_{TTr}) of $3.3 \times 10^3 \text{ s}^{-1}$ were seen after efficient exciton migration. The kinetic parameters obtained from TA spectroscopies are consistent with those obtained from TREPR spectroscopy at 80 K.

The thermodynamic parameters for the TT dissociations were also evaluated by temperature-dependent TA measurements (Table II).⁵⁸ The endothermicity of enthalpy, $\Delta H \approx +1 \text{ kJ mol}^{-1}$ for (Tc)_n and TcF₃-(Tc)₄-TcF₃, results from the stabilization of the TT relative to the T + T due to the CT character in the strongly coupled multiple excitons of ³Tc* - ³Tc* and ³TcF₃* - ³Tc*. Additionally, from activation enthalpy, $\Delta H^\ddagger > \Delta H$, conformational changes are found to be essential for the activations. The exergonicity of TT dissociation (Gibbs free energy, $\Delta G < 0$) stems from the entropy change, i.e., the increase number of states in T + T relative to TT. Therefore, entropy ΔS increases with the number of Tc moieties. Remarkably, both ΔS and activation entropy $\Delta S^\ddagger$ of TcF₃-(Tc)₄-TcF₃ are larger than those of (Tc)₆, supporting the importance of dynamic effects such as molecular vibration and rotation at the TcF₃ moieties.

TABLE I. Kinetic parameters at 293 K.

Compound	k_{ISFO}^a (10^{11} s^{-1})	k_{ISF}^a (10^9 s^{-1})	k_{TTA}^a (10^8 s^{-1})	k_{Diss}^b (10^7 s^{-1})	k_{Rec}^b (10^6 s^{-1})	k_{Back}^b (10^6 s^{-1})	k_{T}^c (10^3 s^{-1})	k_{Trap}^b (10^6 s^{-1})	k_{TTr}^c (10^3 s^{-1})	Φ_T (Φ_{TTr}^d) (%)
(Tc) ₂	1.5	6.2	3.0	5.5	16	4.7	3.7	...	...	165 ± 6
(Tc) ₄	1.5	6.3	3.0	6.5	13	3.7	3.0	...	...	173 ± 9
(Tc) ₆	1.4	6.9	2.9	7.2	10	2.6	2.7	...	...	182 ± 10
TcF ₃ -(Tc) ₄ -TcF ₃	1.9	5.4	3.0	9.2	9.0	1.6	2.9	9.8	3.3	176

^aEstimated by target analysis of femtosecond TA spectra.

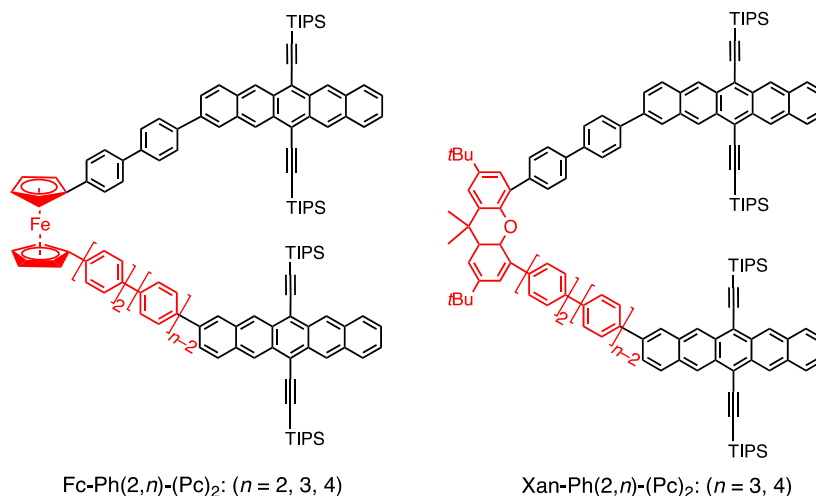
^bEstimated by target analysis of picosecond TA spectra.

^cCalculated by $k_{\text{T}} = \tau_{\text{T}}^{-1}$, which was estimated by nanosecond TA spectra.

^dCalculated by $k_{\text{TTr}} = \tau_{\text{TTr}}^{-1}$, which was estimated by nanosecond TA spectra.

TABLE II. Thermodynamic parameters regarding TT dissociation.

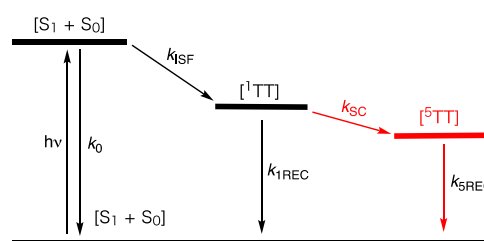
Compound	$\Delta H^\ddagger$ ^a (kJ mol ⁻¹)	$\Delta S^\ddagger$ ^a (kJ mol ⁻¹ K ⁻¹)	$\Delta G^\ddagger$ at 293 K ^b (kJ mol ⁻¹)	$\Delta\Delta W^\ddagger$ ^c	$\Delta H^\ddagger$ ^d (kJ mol ⁻¹)	$\Delta S^\ddagger$ ^d (J mol ⁻¹ K ⁻¹)	ΔG at 293 K ^e (kJ mol ⁻¹)	$\Delta\Delta W^\ddagger$ ^f
(Tc) ₂	3.09 ± 0.09	-86.2 ± 0.3	25.7 ± 0.1	1.00 ± 0.03	1.00 ± 0.10	23.7 ± 0.3	-6.00 ± 0.14	1.00 ± 0.02
(Tc) ₄	3.12 ± 0.07	-84.2 ± 0.2	25.1 ± 0.1	1.28 ± 0.03	1.00 ± 0.08	27.7 ± 0.3	-6.98 ± 0.12	1.62 ± 0.04
(Tc) ₆	3.16 ± 0.07	-83.0 ± 0.3	24.7 ± 0.1	1.46 ± 0.03	1.00 ± 0.10	31.9 ± 0.4	-8.21 ± 0.15	2.70 ± 0.07
TcF ₃ -(Tc) ₄ -TcF ₃	3.33 ± 0.03	-80.8 ± 0.1	24.1 ± 0.1	1.90 ± 0.04	0.78 ± 0.07	36.2 ± 0.2	-9.85 ± 0.10	4.52 ± 0.10

^aEstimated by the Eyring plots.^bCalculated by $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.^cCalculated by $\Delta S^\ddagger - \Delta S^\ddagger_{(Tc)_2} = k_B \ln \Delta W^\ddagger - k_B \ln \Delta W^\ddagger_{(Tc)_2} = k_B \ln \Delta \Delta W^\ddagger$ [W is number of state. $\Delta W^\ddagger = W^\ddagger/W_{TT}$, $\Delta \Delta W^\ddagger = \Delta W^\ddagger/\Delta W^\ddagger_{(Tc)_2}$].^dEstimated by the plot of ΔG vs temperature.^eCalculated by $\Delta G = -RT \ln(k_{Diss}/k_{Back})$.^fCalculated by $\Delta S - \Delta S_{(Tc)_2} = k_B \ln \Delta W - k_B \ln \Delta W_{(Tc)_2} = k_B \ln \Delta \Delta W$ [W is number of state. $\Delta W = W_{T+T}/W_{TT}$, $\Delta \Delta W = \Delta W/\Delta W_{(Tc)_2}$].**FIG. 10.** Molecular structures of PC-dimers and references. Fc-Ph(2,4)-(Pc)₂ has the slipped, parallel conformation of the Pc moieties, whereas Fc-Ph(2,2)-(Pc)₂ has the twisted one.

Analysis by Boltzmann's equation for the change in the number of T + T relative to TT showed that the number of activated states, $\Delta\Delta W^\ddagger$, increases with the number of Tc moieties in (Tc)₆ and with the introduction of energy acceptor moieties at the terminals in TcF₃-(Tc)₄-TcF₃ (Table II). These findings on the thermodynamic control of exciton migration in systematically linked molecular systems provide pivotal, fundamental information for quantum information science and solar energy conversion.

Kobori and colleagues also developed a molecular design strategy for quantitative T + T through intramolecular SF.⁵⁹ They extended this strategy to design Fc-Ph(2,n)-(Pc)₂, where stacking of two pentacene (Pc) moieties is controlled by the number of phenylene (Ph) bridges ($n = 2-4$) through the ferrocene (Fc) moiety as the hinge (Fig. 10). Xan-Ph(2,n)-(Pc)₂ with the xanthene (Xan) moiety as the rigid hinge ($n = 3, 4$) was also prepared as a reference.

The quantum yields of singlet ¹TT (Φ_{1TT}) and triplet ⁵TT (Φ_{5TT}) were estimated by TA measurements (Fig. 11, Table III).⁵⁹ All systems exhibited approximately quantitative singlet ¹TT generation ($\Phi_{1TT} \approx 100\%$). The Φ_{5TT} of Fc-Ph(2,4)-(Pc)₂ (55%) is larger than those of Fc-Ph(2,2)-(Pc)₂ (13%) and Xan-Ph(2,4)-(Pc)₂

**FIG. 11.** Proposed kinetic scheme for Pc-dimers.

(15%) because of the larger conformational flexibility in Fc-Ph(2,4)-(Pc)₂ during spin conversion. To investigate reasons for enhanced quintet generation of TT in Fc-Ph(2,4)-(Pc)₂ relative to the other Pc-dimers, temperature-dependent picosecond TA measurements were conducted in toluene to deduce thermodynamic parameters from the ¹TT state to the transition state (Table IV). The large $\Delta S^\ddagger$ of Fc-Ph(2,4)-(Pc)₂ (-63.0 J mol⁻¹ K⁻¹) relative to other Pc-dimers

TABLE III. Kinetic parameters at 293 K.

Compound	k_0^a (10^8 s $^{-1}$)	k_{ISF}^b (10^{10} s $^{-1}$)	$k_{1\text{REC}}^c$ (10^7 s $^{-1}$)	k_{SC}^d (10^7 s $^{-1}$)	$k_{\text{SC}}/k_{1\text{REC}}$	$k_{5\text{TT}}^e$ (10^4 s $^{-1}$)	$\Phi_{1\text{TT}}^b$ (%)	$\Phi_{5\text{TT}}^a$ (%)
Fc-Ph(2,2)-(Pc) $_2$	4.5	1.9	21	3.1	0.14	2.8	100	13
Fc-Ph(2,3)-(Pc) $_2$	0.83	1.6	34	12	0.35	2.8	100	26
Fc-Ph(2,4)-(Pc) $_2$	0.83	1.6	5.7	7.3	1.3	2.6	100	55
Xan-Ph(2,3)-(Pc) $_2$	0.60	1.7	9.8	0.41	0.042	3.2	100	4.0
Xan-Ph(2,4)-(Pc) $_2$	0.60	1.7	6.5	1.2	0.18	3.0	100	15

^aEstimated by picosecond TA spectra.^bEstimated by femtosecond TA spectra.^cCalculated by $k_{1\text{REC}} = k_{1\text{TT}} - k_{\text{SC}}$.^dCalculated by $k_{\text{SC}} = k_{1\text{TT}} \times \Phi_{5\text{TT}}/\Phi_{1\text{TT}}$.^eCalculated by $k_{5\text{TT}} = \tau_{5\text{TT}}^{-1}$, which was estimated by nanosecond TA spectra.

TABLE IV. Thermodynamic parameters regarding TT dissociation.

Compound	A^a ($\times 10^8$ s $^{-1}$)	$\Delta H^\ddagger$ (kJ mol $^{-1}$)	$\Delta S^\ddagger$ (J mol $^{-1}$ K $^{-1}$)	$-T\Delta S^\ddagger$ at 298 K (kJ mol $^{-1}$)	$\Delta G^\ddagger$ at 298 K ^c (kJ mol $^{-1}$)
Fc-Ph(2,2)-(Pc) $_2$	1.41	1.24 ± 0.02	-96.2 ± 0.96	28.7	29.9
Fc-Ph(2,3)-(Pc) $_2$	12.2	3.96 ± 0.06	-76.4 ± 1.2	22.8	26.7
Fc-Ph(2,4)-(Pc) $_2$	48.8	8.99 ± 0.49	-63.0 ± 1.0	18.8	27.8
Xan-Ph(2,3)-(Pc) $_2$	0.45	4.06 ± 0.02	-109 ± 0.61	32.5	36.6
Xan-Ph(2,4)-(Pc) $_2$	4.95	7.98 ± 0.31	-83.1 ± 0.80	24.7	32.7

^aEstimated by the Arrhenius plots.^bEstimated by Eyring plot.^cCalculated by $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

($-109 \sim -76.4$ J mol $^{-1}$ K $^{-1}$) is highly related to the rotational flexibility of the Fc moiety. Given Boltzmann's formula, the ratio of the density of states in the activated ^1TT , caused by disorder in ^1TT conformations, for Fc-Ph(2,4)-(Pc) $_2$ vs Xan-Ph(2,4)-(Pc) $_2$ was estimated to be 20, consistent with the large $\Delta S^\ddagger$ of Fc-Ph(2,4)-(Pc) $_2$. The values of $-T\Delta S^\ddagger$ (18.8–32.5 kJ mol $^{-1}$) are an order of magnitude larger than those of $\Delta H^\ddagger$ (1.24–8.99 kJ mol $^{-1}$) in all Pc-dimers. This indicates that the low-frequency vibrational modes ($h\nu \ll k_{\text{B}}T$) are responsible for the thermal activation ($\Delta H^\ddagger \approx RT$) of breaking the T–T binding enthalpy to weaken electronic bonds for generating ^5TT .

To assign the spin states (i.e., ^1TT and ^5TT) and understand the effect of molecular motions in ^5TT , TREPR measurements were conducted for Fc-Ph(2,4)-(Pc) $_2$ in a toluene/paraffin mixture (1/9, v/v) at 298 K ($\lambda_{\text{ex}} = 656$ nm).⁵⁹ The initial A pattern spin polarization at a delay time of 0.1 μs after excitation was assigned to anisotropic singlet–quintet conversion during rapid conformational dynamics between the stabilized quintet state of $^5\text{TT}_1$ (with a dihedral angle (β) of 20° between the aromatic planes of a triplet exciton and the other exciton) and the activated state of $^5\text{TT}_2$ (with $\beta = 47^\circ$) via quintet–singlet interconversion from $^1\text{TT}_2$. The conformational dynamics of the multiexciton between TT_1 and TT_2 result from low-frequency torsional motion in phenylene and Fc bridges. The subsequent E pattern quintet spin polarization at a delay time of 0.5 μs was also assigned to reverse quintet–singlet conversions. The SF-induced E-polarization via the singlet TTA was explained by singlet deactivation in the presence of exchange coupling after the rapid spin-relaxation due to conformational dynamics. The significant torsional motion during activation is attributed to the hybridization

of the hole level of the Pc moiety to the Fc moiety in TT. This hybridization in ^5TT also contributes to entropy gains for the long-lived, strongly coupled multiple exciton in the quintet states. These findings provide crucial basic information for OSCs and magnetic switching devices.

NEW TYPES OF DONORS AND ACCEPTORS

The creation of new types of electron donors and acceptors is essential for expanding our understanding of D–A interactions and for exploiting new photofunctions based on these interactions. However, the synthesis of new donors and acceptors remains challenging. Akiyama and colleagues successfully created a new type of acceptor, perfluorocubane, C $_8$ F $_8$ [Fig. 12(a)].⁶⁰ Polyhedral fluorocarbons (CF) $_n$ are predicted to localize an electron within their cages upon reduction.^{61–63} Their unique electron-accepting character results from a stabilized vacant orbital within the cage, originating from the overlapping of multiple σ^* orbitals of C–F bonds. These “particle in a box” type molecules can confine an electron inside their cages. This is in sharp contrast to planar and curved aromatic molecules, where an electron is delocalized across both molecular surfaces. Theoretical calculations suggest that C $_8$ F $_8$ exhibits significant electron-accepting character (LUMO = -2.77 eV vs vacuum level, -2.03 V vs Fc/Fc $^+$).⁶⁰ This LUMO level is higher than the calculated LUMO of C $_{60}$ by 0.8 eV (-3.6 eV vs vacuum level).⁶⁴

As for the synthetic route of C $_8$ F $_8$, it is not realistic to introduce eight F atoms onto a cubane one by one.^{65,66} The most promising strategy is to introduce multiple fluorine atoms through radical

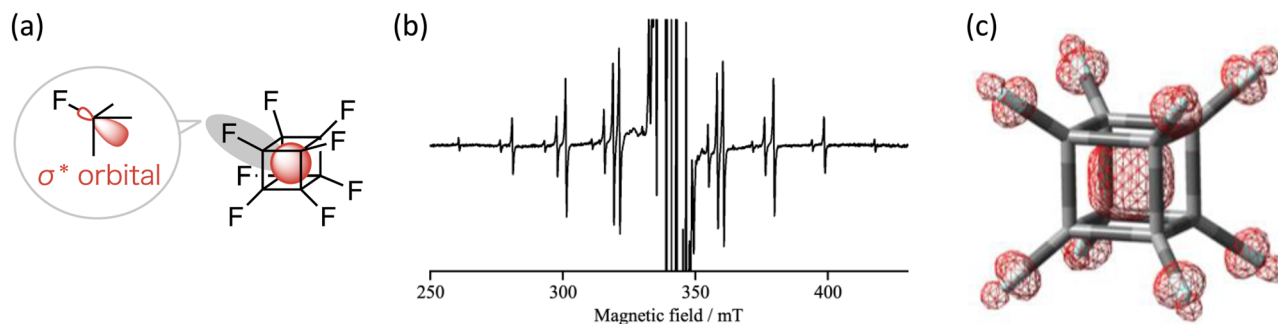


FIG. 12. (a) Molecular structure of C_8F_8 , (b) ESR spectrum of C_8F_8 in a hexamethylethane matrix after γ -ray radiolysis at 77 K, and (c) spin density (contour = 0.005) in the radical anion $C_8F_8^{\cdot-}$, calculated at the UB3LYP/6-311++G(d,p) level of theory.

C–H fluorination using fluorine gas, although controlling the highly reactive fluorine gas is essential for success. They then adopted the liquid-phase direct fluorination, designated as the “PERFECT” method, where the direct fluorination of a partially fluorinated ester with an excess of fluorine gas in a fluorous solvent affords the corresponding perfluorinated product without damaging the cubic skeleton.^{67,68}

The molecular structure of C_8F_8 was fully characterized by 1H , ^{13}C , ^{19}F NMR, FTIR, and Raman spectroscopies as well as x-ray diffraction analysis.⁶⁰ It should be noted that in the crystal structure, one fluorine atom of C_8F_8 interacts with the center of the cyclobutane ring of the nearest molecule, which accords with the previous prediction that C_8F_8 can act as a strong carbon-bonding donor interacting with anions.⁶⁹ The LUMO level of C_8F_8 in THF was determined to be -2.67 eV vs the vacuum level electrochemically (-2.13 V vs Fc/Fc^+ in THF), which is in good agreement with the calculated value (-2.77 eV). Finally, matrix-isolation electron spin resonance (ESR) spectroscopy, in combination with γ -ray radiolysis at 77 K, was used to examine the electronic structure of the radical anion of C_8F_8 . The ESR spectrum of $C_8F_8^{\cdot-}$ in a hexamethylethane matrix exhibited characteristic nine peak bands, which align well with the theoretical simulation with the total nuclear spin quantum number, $M_I = \pm 4, \pm 3, \pm 2, \pm 1, 0$ [Fig. 12(b)]. The large $a(^{19}F)$ hyperfine coupling constant (hfcc = 19.62 mT) agrees well with the calculated value (19.24 mT), where the spin density is mainly distributed inside the cubane cage [Fig. 12(c)]. Accordingly, perfluorinated cage compounds are highly promising as a new type of acceptors for D–A linked model systems as well as organic electronics such as OSCs. For instance, heptafluorocubane-carboxylate ester, which can be obtained in a similar manner, will be connected to a donor molecule with an amide bond.⁶⁰

CONCLUDING REMARKS AND OUTLOOK

We have highlighted representative examples of the “Dynamic Exciton” research project in D–A linked systems, along with associated model systems and their D and A building blocks over the past 4 years. Our demonstrations show that it is effective to rationally manipulate LE, CT excited, and CS states by either enhancively or restraints modulating the dynamic effects in D–A linked systems and similar model systems. Notably, specific intramolecular

vibrations in D–A linked systems, induced by infrared light following initial electronic excitation of the molecules, can alter the ET efficiency.^{70,71} Further rational molecular design of D–A linked systems will enable ET processes to be remarkably accelerated or decelerated by external stimuli. From the perspective of quantum information science, the dynamic effects of chirality-induced spin selectivity are particularly interesting.^{72,73} The “Dynamic Exciton” project promises to reshape photochemistry and pave the way for novel photofunctions in the future.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

H.I. and M.A. researched and wrote the initial paper. All contributed to editing and finalizing the paper.

Hiroshi Imahori: Conceptualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Midori Akiyama:** Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES

- ¹J. Jortner and M. Bixon, *Electron Transfer—from Isolated Molecules to Biomolecules* (John Wiley & Sons, New York, 1999).
- ²R. A. Marcus, *Angew. Chem., Int. Ed. Engl.* **32**, 1111 (1993).
- ³H. Imahori, Y. Kobori, and H. Kaji, *Acc. Mater. Res.* **2**, 501 (2021).
- ⁴H. Imahori, *Bull. Chem. Soc. Jpn.* **96**, 339 (2023).
- ⁵H. Imahori and M. Akiyama, *J. Porphyrins Phthalocyanines* **28**, 319 (2024).
- ⁶V. M. Agranovich, Y. N. Gartstein, and M. Litinskaya, *Chem. Rev.* **111**, 5179 (2011).
- ⁷H. Jin, J. Li, J. Iocozzia, X. Zeng, P.-C. Wei, C. Yang, N. Li, Z. Liu, J. H. He, T. Zhu, J. Wang, Z. Lin, and S. Wang, *Angew. Chem., Int. Ed.* **58**, 15206 (2019).
- ⁸C. Zang, M. Xu, L. Zhang, S. Liu, and W. Xie, *J. Mater. Chem. C* **9**, 1484 (2021).
- ⁹B. O'Regan and M. Grätzel, *Nature* **353**, 737 (1991).
- ¹⁰Y. Ren, D. Zhang, J. Suo, Y. Cao, F. T. Eickemeyer, N. Vlachopoulos, S. M. Zakeeruddin, A. Hagfeldt, and M. Grätzel, *Nature* **613**, 60 (2023).
- ¹¹H. Imahori, T. Umeyama, and S. Ito, *Acc. Chem. Res.* **42**, 1809 (2009).
- ¹²A. Yella, C.-L. Mai, S. M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh, and M. Grätzel, *Angew. Chem., Int. Ed.* **53**, 2973 (2014).
- ¹³S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, and M. Grätzel, *Nat. Chem.* **6**, 242 (2014).
- ¹⁴K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa, and M. Hanaya, *Chem. Commun.* **51**, 15894 (2015).
- ¹⁵Y. Kurumisawa, T. Higashino, S. Nimura, Y. Tsuji, H. Iiyama, and H. Imahori, *J. Am. Chem. Soc.* **141**, 9910 (2019).
- ¹⁶J.-M. Ji, H. Zhou, Y. K. Eom, C. H. Kim, and H. K. Kim, *Adv. Energy Mater.* **10**, 2000124 (2020).
- ¹⁷Y. Ren, N. Flores-Díaz, D. Zhang, Y. Cao, J.-D. Decoppet, G. C. Fish, J.-E. Moser, S. M. Zakeeruddin, P. Wang, A. Hagfeldt, and M. Grätzel, *Adv. Funct. Mater.* **30**, 2004804 (2020).
- ¹⁸D. Zhang, M. Stojanovic, Y. Ren, Y. Cao, F. T. Eickemeyer, E. Socie, N. Vlachopoulos, J.-E. Moser, S. M. Zakeeruddin, A. Hagfeldt, and M. Grätzel, *Nat. Commun.* **12**, 1777 (2021).
- ¹⁹T. Higashino and H. Imahori, *ACS Energy Lett.* **7**, 1926 (2022).
- ²⁰Y. Zhang, T. Higashino, and H. Imahori, *J. Mater. Chem. A* **11**, 12659 (2023).
- ²¹A. Mishra, M. K. R. Fischer, and P. Bäuerle, *Angew. Chem., Int. Ed.* **48**, 2474 (2009).
- ²²P. Brogdon, H. Cheema, and J. H. Delcamp, *ChemSusChem* **11**, 86 (2018).
- ²³J.-M. Ji, H. Zhou, and H. K. Kim, *J. Mater. Chem. A* **6**, 14518 (2018).
- ²⁴W. M. Campbell, A. K. Burrell, D. L. Officer, and K. W. Jolley, *Coord. Chem. Rev.* **248**, 1363 (2004).
- ²⁵J. Rochford, D. Chu, A. Hagfeldt, and E. Galoppini, *J. Am. Chem. Soc.* **129**, 4655 (2007).
- ²⁶S. Rangan, S. Coh, R. A. Bartynski, K. P. Chitre, E. Galoppini, C. Jaye, and D. Fischer, *J. Phys. Chem. C* **116**, 23921 (2012).
- ²⁷H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S. E. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chábera, A. P. Yartsev, and V. Sundström, *J. Phys. Chem. A* **115**, 3679 (2011).
- ²⁸S. Ye, A. Kathiravan, H. Hayashi, Y. Tong, Y. Infahsaeng, P. Chábera, T. Pascher, A. P. Yartsev, S. Isoda, H. Imahori, and V. Sundström, *J. Phys. Chem. C* **117**, 6066 (2013).
- ²⁹A. S. Hart, C. B. Kc, H. B. Gobeze, L. R. Sequeira, and F. D'Souza, *ACS Appl. Mater. Interfaces* **5**, 5314 (2013).
- ³⁰L. Si and H. He, *J. Phys. Chem. A* **118**, 3410 (2014).
- ³¹T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemeth, and A. L. Moore, *Nature* **307**, 630 (1984).
- ³²M. R. Wasielewski, G. L. Gaines III, G. P. Wiederrecht, W. A. Svec, and M. P. Niemczyk, *J. Am. Chem. Soc.* **115**, 10442 (1993).
- ³³H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata, and S. Fukuzumi, *J. Am. Chem. Soc.* **123**, 6617 (2001).
- ³⁴H. Imahori, Y. Sekiguchi, Y. Kashiwagi, T. Sato, Y. Araki, O. Ito, H. Yamada, and S. Fukuzumi, *Chem. - Eur. J.* **10**, 3184 (2004).
- ³⁵H. Imahori, *Bull. Chem. Soc. Jpn.* **80**, 621 (2007).
- ³⁶A. B. Munoz-Garcia, I. Benesperi, G. Boschloo, J. J. Concepcion, J. H. Delcamp, E. A. Gibson, G. J. Meyer, M. Pavone, H. Pettersson, A. Hagfeldt, and M. Freitag, *Chem. Soc. Rev.* **50**, 12450 (2021).
- ³⁷A. B. Alemanyeh, N. U. Day, T. Mani, A. B. Rudine, K. E. Thomas, O. A. Geder-aas, S. A. Vinogradov, C. C. Wamser, and A. Ghosh, *ACS Appl. Mater. Interfaces* **8**, 18935 (2016).
- ³⁸T. Higashino, Y. Kurumisawa, A. B. Alemanyeh, R. F. Einrem, D. Sahu, D. Packwood, K. Kato, A. Yamakata, A. Ghosh, and H. Imahori, *ACS Appl. Energy Mater.* **3**, 12460 (2020).
- ³⁹Q. Guo, T. Higashino, R. Adachi, C. Wechwithayakhlung, D. Packwood, A. Yamakata, and H. Imahori, *ChemSusChem* **17**, e202301661 (2024).
- ⁴⁰G. R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano, V. R. Cooper, L. Liang, S. G. Louie, E. Ringe, W. Zhou, S. S. Kim, R. R. Naik, B. G. Sumpter, H. Terrones, F. Xia, Y. Wang, J. Zhu, D. Akinwande, N. Alem, J. A. Schuller, R. E. Schaak, M. Terrones, and J. A. Robinson, *ACS Nano* **9**, 11509 (2015).
- ⁴¹T. R. Kafle, B. Kattel, P. Yao, P. Zereski, H. Zhao, and W.-L. Chan, *J. Am. Chem. Soc.* **141**, 11328 (2019).
- ⁴²R. Canton-Vitoria, H. B. Gobeze, V. M. Blas-Ferrando, J. Ortiz, Y. Jang, F. Fernández-Lázaro, Á. Sastre-Santos, Y. Nakanishi, H. Shinohara, F. D'Souza, and N. Tagmatarchis, *Angew. Chem., Int. Ed.* **58**, 5712 (2019).
- ⁴³R. Canton-Vitoria, Y. Sayed-Ahmad-Baraza, M. Pelaez-Fernandez, R. Arenal, C. Bittencourt, C. P. Ewels, and N. Tagmatarchis, *npj 2D Mater. Appl.* **1**, 13 (2017).
- ⁴⁴T. Umeyama, D. Mizutani, Y. Ikeda, W. R. Osterloh, F. Yamamoto, K. Kato, A. Yamakata, M. Higashi, T. Urakami, H. Sato, and H. Imahori, *Chem. Sci.* **14**, 11914 (2023).
- ⁴⁵M. Vera-Hidalgo, E. Giovanelli, C. Navío, and E. M. Pérez, *J. Am. Chem. Soc.* **141**, 3767 (2019).
- ⁴⁶R. Quirós-Ovies, M. Vázquez Sulleiro, M. Vera-Hidalgo, J. Prieto, I. J. Gómez, V. Sebastián, J. Santamaría, and E. M. Pérez, *Chem. - Eur. J.* **26**, 6629 (2020).
- ⁴⁷T. Saito, S.-i. Natsuda, K. Imakita, Y. Tamai, and H. Ohkita, *Sol. RRL* **4**, 2000255 (2020).
- ⁴⁸N. R. Monahan, D. Sun, H. Tamura, K. W. Williams, B. Xu, Y. Zhong, B. Kumar, C. Nuckolls, A. R. Harutyunyan, G. Chen, H.-L. Dai, D. Beljonne, Y. Rao, and X.-Y. Zhu, *Nat. Chem.* **9**, 341 (2017).
- ⁴⁹N. Alagna, J. Han, N. Wollscheid, J. L. Perez Lustres, J. Herz, S. Hahn, S. Koser, F. Paulus, U. H. F. Bunz, A. Dreuw, T. Buckup, and M. Motzkus, *J. Am. Chem. Soc.* **141**, 8834 (2019).
- ⁵⁰C. Hetzer, B. S. Basel, S. M. Kopp, F. Hampel, F. J. White, T. Clark, D. M. Guldi, and R. R. Tykwinski, *Angew. Chem., Int. Ed.* **58**, 15263 (2019).
- ⁵¹A. T. Gilligan, E. G. Miller, T. Sammakia, and N. H. Damrauer, *J. Am. Chem. Soc.* **141**, 5961 (2019).
- ⁵²J. Kim, H. T. Teo, Y. Hong, J. Oh, H. Kim, C. Chi, and D. Kim, *Angew. Chem., Int. Ed.* **59**, 20956 (2020).
- ⁵³S. Paul, C. Govind, and V. Karunakaran, *J. Phys. Chem. B* **125**, 231 (2021).
- ⁵⁴M. Dvořák, S. K. K. Prasad, C. B. Dover, C. R. Forest, A. Kaleem, R. W. MacQueen, A. J. Petty, R. Forecast, J. E. Beves, J. E. Anthony, M. J. Y. Tayebjee, A. Widmer-Cooper, P. Thordarson, and T. W. Schmidt, *J. Am. Chem. Soc.* **143**, 13749 (2021).
- ⁵⁵M. B. Smith and J. Michl, *Chem. Rev.* **110**, 6891 (2010).
- ⁵⁶K. Miyata, F. S. Conrad-Burton, F. L. Geyer, and X.-Y. Zhu, *Chem. Rev.* **119**, 4261 (2019).
- ⁵⁷S. Nakamura, H. Sakai, H. Nagashima, Y. Kobori, N. V. Tkachenko, and T. Hasobe, *ACS Energy Lett.* **4**, 26 (2019).
- ⁵⁸S. Nakamura, H. Sakai, M. Fuki, R. Oioe, F. Ishiwari, A. Saeki, N. V. Tkachenko, Y. Kobori, and T. Hasobe, *Angew. Chem., Int. Ed.* **62**, e202217704 (2023).
- ⁵⁹R. Hayasaka, H. Sakai, M. Fuki, T. Okamoto, R. Khan, M. Higashi, N. V. Tkachenko, Y. Kobori, and T. Hasobe, *Angew. Chem., Int. Ed.* **63**, e202315747 (2024).
- ⁶⁰M. Sugiyama, M. Akiyama, Y. Yonezawa, K. Komaguchi, M. Higashi, K. Nozaki, and T. Okazoe, *Science* **377**, 756 (2022).

- ⁶¹K. K. Irikura, *J. Phys. Chem. A* **112**, 983 (2008).
- ⁶²O. V. Boltalina and T. Nakajima, *New Fluorinated Carbons: Fundamentals and Applications* (Elsevier, Amsterdam, NY, 2017).
- ⁶³Y.-F. Wang, Y. Li, Z.-R. Li, F. Ma, D. Wu, and C.-C. Sun, *Theor. Chem. Acc.* **127**, 641 (2010).
- ⁶⁴K. Akaike, K. Kanai, H. Yoshida, J. Tsutsumi, T. Nishi, N. Sato, Y. Ouchi, and K. Seki, *J. Appl. Phys.* **104**, 023710 (2008).
- ⁶⁵E. W. Della and N. J. Head, *J. Org. Chem.* **60**, 5303 (1995).
- ⁶⁶H. Irngartinger and S. Strack, *J. Am. Chem. Soc.* **120**, 5818 (1998).
- ⁶⁷T. Okazoe and J. Fluor, *J. Fluorine Chem.* **174**, 120 (2015).
- ⁶⁸G. Sandford and J. Fluor, *J. Fluorine Chem.* **128**, 90 (2007).
- ⁶⁹A. Bauzá, T. J. Mooibroek, and A. Frontera, *Phys. Chem. Chem. Phys.* **16**, 19192 (2014).
- ⁷⁰Z. Lin, C. M. Lawrence, D. Xiao, V. V. Kireev, S. S. Skourtis, J. L. Sessler, D. N. Beratan, and I. V. Rubtsov, *J. Am. Chem. Soc.* **131**, 18060 (2009).
- ⁷¹M. Delor, P. A. Scattergood, I. V. Sazanovich, A. W. Parker, G. M. Greetham, A. J. H. M. Meijer, M. Towrie, and J. A. Weinstein, *Science* **346**, 1492 (2014).
- ⁷²B. P. Bloom, Y. Paltiel, R. Naaman, and D. H. Waldeck, *Chem. Rev.* **124**, 1950 (2024).
- ⁷³H. J. Eckvahl, N. A. Tcyrulnikov, A. Chiesa, J. M. Bradley, R. M. Young, S. Carretta, M. D. Krzyaniak, and M. R. Wasielewski, *Science* **382**, 197 (2023).