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Photophysics

Excited-State Dynamics of Pentacene Derivatives with Stable Radical Substituents**

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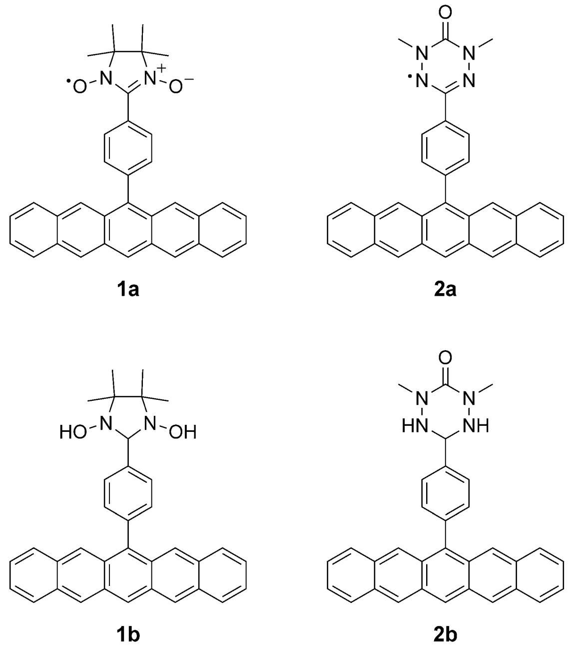
Abstract: *The excited-state dynamics of pentacene derivatives with stable radical substituents were evaluated in detail through transient absorption measurements. The derivatives showed ultrafast formation of triplet excited state(s) in the pentacene moiety from a photoexcited singlet state through the contributions of enhanced intersystem crossing and singlet fission. Detailed kinetic analyses for the transient absorption data were conducted to quantify the excited-state characteristics of the derivatives.*

Organic semiconductor transistors and other devices serve a variety of applications in molecular electronics[1] and organic molecular spintronics.[2] Pentacene and its derivatives[3] have received increasing interest as promising electronic materials for organic field-effect transistors (OFETs)[1c,4] because of their high carrier mobility.[4] However, their photochemical instability in the presence of air prevents their practical applications.[5] Therefore, much effort to improve the stability by derivatization and/or chemical modification has been carried out,[3] with a notable example being 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn).[3a,6]

During the course of our systematic studies on π-conjugated spin systems with high-spin photoexcited states,[7] we discovered that a combination of two unstable species (pentacene and an organic radical) leads to a remarkable protection from photodegradation and enhancement of solubility in common organic solvents.[8] In our previous study, two pentacene–radical hybrids, Pn-Ph-NN (**1a**) and Pn-Ph-OV (**2a**) (Scheme 1; Pn, Ph, NN, and OV denote the pentacene, phenyl, nitronyl nitroxide radical, and oxoverdazyl radical moieties, respectively) were quite stable in dilute solution under ambient light (lifetime under our experimental conditions ($\tau_{\mathrm{stab}} = 2100$ (**1a**) and 960 min (**2a**) in CH_2Cl_2) compared with the relevant precursor compounds **1b** and **2b** ($\tau_{\mathrm{stab}} = 1.9$ (**1b**) and 2.0 min (**2b**)). Although **1a** and **2a** showed these remarkable stabilities, the electrochemical and spectroscopic properties of the derivatives were similar to those of their precursors and pentacene. Therefore, the excited-state dynamics of the pentacene–radical derivatives were studied. Here, we report the detailed excited-state dynamics of the derivatives by employing transient absorption measurements. In the photoexcited states of the pentacene–radical derivatives, the excited singlet state of the pentacene moiety (^{1}Pn*) is rapidly converted into the relevant triplet state (^{3}Pn*) by enhanced (accelerated) intersystem crossing ($^1\mathrm{Pn}^* \rightarrow {}^3\mathrm{Pn}^*$) and singlet fission ($^1\mathrm{Pn}^* + \mathrm{Pn} \rightarrow {}^3\mathrm{Pn}^* + {}^3\mathrm{Pn}^*$). To the best of our knowledge, this is the first example of singlet fission occurring in a pentacene derivative in dilute solution.



Scheme 1. Chemical structures of pentacene–radical derivatives, **1a** and **2a**, and their relevant precursors, **1b** and **2b**.

The steady-state absorption and fluorescence spectra of the derivatives were recorded in CH_2Cl_2 (Figure 1), and the spectroscopic properties are summarized in Table 1. All the derivatives exhibited highly structured $^1\pi\pi^*$ absorption bands of the pentacene moiety at around 590 ($S_0 \rightarrow S_1$) and 350 nm ($S_0 \rightarrow S_2$). These features are quite similar for all the derivatives, thus indicating that there is no specific electronic

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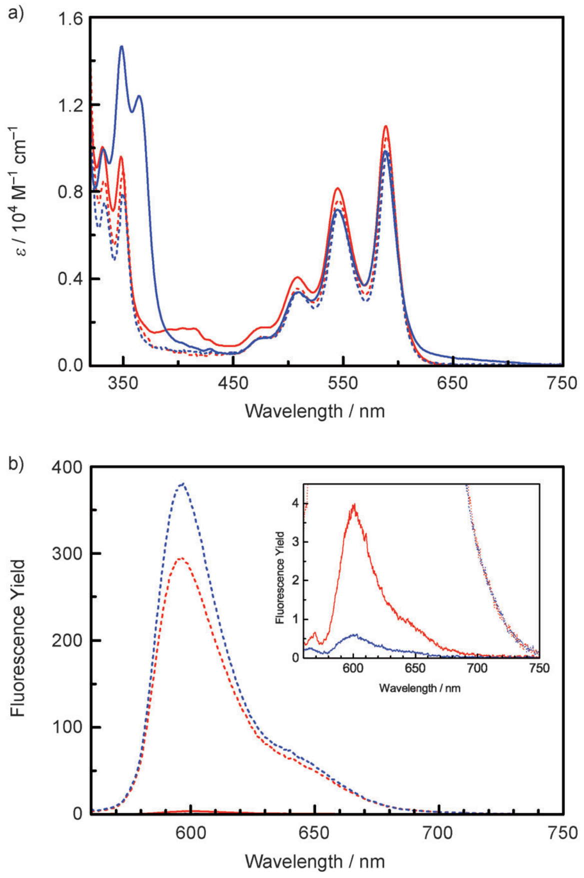

Figure 1. Steady-state absorption (a) and fluorescence spectra (b) of **1a** (blue solid curves), **1b** (blue broken curves), **2a** (red solid curves), and **2b** (red broken curves) in CH_2Cl_2.

Table 1: Spectroscopic properties of the derivatives in CH_2Cl_2.

Derivative	λ_a [nm] ($\varepsilon/10^3$ M^{-1}cm^{-1})			λ_f [nm]	$\Phi_f/\Phi_{f,1a}$
1a	349 (14.7)	365 (12.4)	588 (9.87)	600	1
1b	350 (7.87)		590 (9.87)	596	460
2a	348 (9.60)	415 (1.71)	589 (11.0)	600	5.6
2b	350 (8.98)		590 (10.5)	596	390

interaction between the pentacene and radical or precursor moieties. Additional features ascribed to a $^2\pi\pi^*$ transition in the radical substituents were observed at around 365[9] and 415 nm[10] in the absorption spectra of **1a** and **2a**, respectively. In addition, **1a** showed a weak and structureless absorption band originating from a $^2n\pi^*$ transition in the nitronyl nitroxide radical substituent at about 640 nm.[9]

The fluorescence spectra of the derivatives were very similar. They can be best characterized as a $^1\pi\pi^*$-based fluorescence of the pentacene moiety, and are indicative of the absence of strong electronic interactions between the pentacene and substituents, as evident in the absorption spectra. In contrast, the fluorescence intensity was greatly reduced by introducing a radical substituent. As summarized in Table 1, the fluorescence quantum yield (Φ_f) of **1a** was 460 times smaller than that of the relevant precursor **1b**, and that of **2a** was 70 times smaller than that of **2b**. Since decomposition of a pentacene derivative is known to occur mainly from the singlet excited state,[11] the huge quenching of the fluorescence observed for **1a** and **2a** would be related to their remarkable photostability. There are two possible pathways to explain the fluorescence quenching observed in the pentacene–radical derivatives (Figure 2): energy transfer (EnT) and enhanced intersystem crossing (ISC). In the former system, a radical moiety in a derivative acts as an intramolecular energy scavenger ($^2[^1\text{Pn}^*\text{-Ph-R}^\bullet]^* \rightarrow {}^2[\text{Pn-Ph-}^2\text{R}^{\bullet *}]^*$) and fast nonradiative decay occurs to the electronic ground state ($^2[\text{Pn-Ph-}^2\text{R}^{\bullet *}]^* \rightarrow {}^2[\text{Pn-Ph-R}^\bullet]$). In the latter, the excited singlet state of the pentacene moiety ($^2[^1\text{Pn}^*\text{-Ph-R}^\bullet]^*$) is quickly converted into the relevant triplet state ($^3\text{Pn}^*$). We previously reported that ISC in anthracene was enhanced by introducing radical substituent(s),[7a] and a similar phenomenon was also observed as ultrafast ISC for perylene-3,4:9,10-bis(dicarboximide) derivatives with radical substituent(s).[12] In such a π-radical hybrid system, spin–orbit coupling due to the spin–orbit interaction of spin-doublet radical substituent(s) contributes to the excited-state characteristics of a molecule. Furthermore, ISC in the system is expected to be largely spin-allowed, since the spin state of the whole molecule does not change upon the transition.[13]

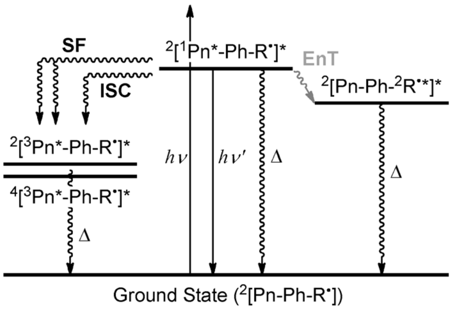

Figure 2. Excited-state processes of the pentacene–radical derivatives. Pn, Ph, and R$^\bullet$ denote the pentacene, phenyl, and radical moieties, respectively.

To elucidate the excited-state dynamics of the pentacene–radical derivatives, transient absorption measurements were conducted. Figure 3 shows the transient absorption spectra of the derivatives in CH_2Cl_2. The spectra 0.1 ps after photoexcitation are dominated by the $^1\text{Pn}^*$ state,[14] with an intense and broad excited-state absorption at about 450 nm and a relatively weak ground-state bleach at around 590 nm, irrespective of the derivative. The excited-state absorption of **1a** or **2a** disappeared over several or several tens of picoseconds, respectively, and a new structured absorption feature at about 510 nm, which can be best characterized as corresponding to the $^3\text{Pn}^*$ state,[14,15] appeared in the same timescale, while the spectra of **1b** and **2b** changed only slightly in the picosecond timescale (see Figure S2 in the Supporting Information). Similar spectroscopic changes were also observed for **1b** and **2b**, with the typical lifetime of the singlet excited state of the pentacene derivatives (ca. 6 ns)[16] as shown in Figure 3. The presence of $^3\text{Pn}^*$ states was also confirmed by time-resolved electron spin resonance measure-

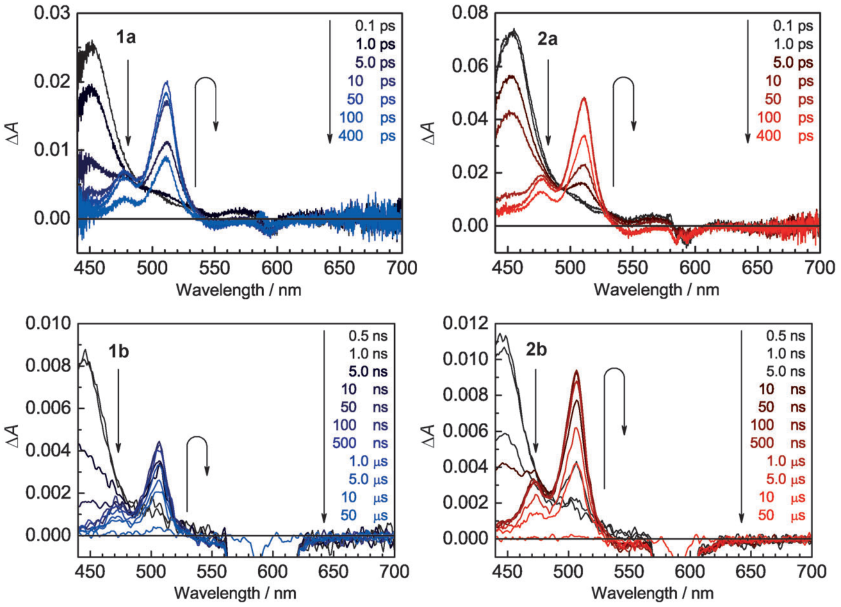

Figure 3. Transient absorption spectra of the derivatives in CH_2Cl_2.

ments (see the Supporting Information). The detailed kinetics of the derivatives are evaluated below. It is noteworthy that there was no evidence for an energy-transfer product (^{2}[Pn-Ph-^{2}R•]*) from our transient absorption measurements.

The $^1Pn^* \rightarrow ^3Pn^*$ quantum yields (Φ_{ST}) of **1a** and **2a** were determined by Equation (1):

$$\Phi_{ST} = \frac{\Delta A(\text{triplet})}{\Delta\varepsilon(\text{triplet})} \bigg/ \frac{\Delta A(\text{singlet})}{\Delta\varepsilon(\text{singlet})} \qquad (1)$$

In Equation (1), ΔA and $\Delta\varepsilon$ are the maximum optical density in the transient absorption time course and apparent molar absorption coefficient at the maximum wavelength of each excited-state species (i.e. $^1Pn^*$ and $^3Pn^*$), respectively. The $\Delta\varepsilon$ values of $^1Pn^*$ and $^3Pn^*$ in **1a** or **2a** were estimated by deconvoluting the transient absorption spectra by the steady-state absorption spectra (see Figures S3 and S4 in the Supporting Information), and the values for the $^3Pn^*$ species were comparable with those reported.[15] Surprisingly, the Φ_{ST} values of both **1a** and **2a** calculated from Equation (1) were larger than 1.0 (1.30 and 1.05, respectively). Although the $\Delta\varepsilon$ values possess relatively large errors (ca. 10%), the Φ_{ST} value of **1a** is larger than unity even in the worst case ($\Phi_{ST} = 1.06$). Such an over-stoichiometric Φ_{ST} value obtained for the pentacene–radical derivatives is indicative of the presence of singlet (exciton) fission (SF) in the pentacene moiety, in which two triplet excited states are produced from one singlet excited state and one ground state (Pn), as in Figure 2 and Equation (2):[17]

$$^1Pn^* + Pn \rightarrow {}^3Pn^* + {}^3Pn^* \qquad (2)$$

Singlet fission is the reverse reaction of triplet-triplet annihilation (TTA), and that of tetracene and pentacene derivatives in the crystalline phase and/or solid-state film have been reported.[14,18] Very recently, Friend and co-workers reported SF of TIPS-Pn in concentrated solution.[19] They reported that SF occurred in highly concentrated solution ($>10^{-2}$ mol dm^{-3}) as a consequence of excimer formation. Since our experimental system is relatively dilute (ca. 10^{-4} mol dm^{-3}), the excited-state dynamics of the derivatives were worth studying in detail.

Figure 4 shows the transient absorption decay profiles of the derivatives in CH_2Cl_2. The transient absorption maxima of the $^1Pn^*$ and $^3Pn^*$ species of each derivative were monitored. All the derivatives showed similar photophysical behavior: after photoexcitation at 590 nm, decay of the $^1Pn^*$ state was evident from the band at about 450 nm and an increase of the $^3Pn^*$ state (evident from the band at ca. 510 nm) with the same time constant, followed by a slow decay of the $^3Pn^*$ state. To evaluate the excited-state dynamics of the derivatives in detail, the kinetics in the absence and presence of SF were modeled (see the Supporting Information).

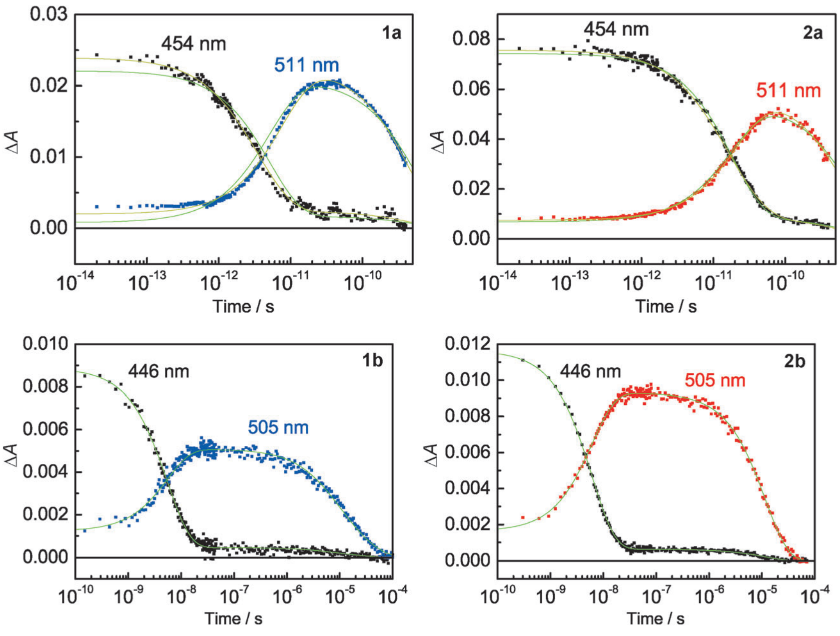

Figure 4. Transient absorption decay profiles of the derivatives in CH_2Cl_2. Green and yellow curves represent the theoretical best fits to Equations (S7) and (S17), respectively.

Table 2: Theoretical fitting parameters for transient absorption decay profiles of the derivatives to Equation (S7).

Derivative	λ_{max} [nm]	A_S	A_T	k_1 [s^{-1}] (τ_S)	k_T [s^{-1}] (τ_T)	k_{TT}' [s^{-1}]
1a	454	0.022	0.0017	1.9×10^{11}	1.8×10^{9}	N.D.
	511	0.0008	0.021	(5.3 ps)	(560 ps)	
1b	446	0.0089	0.0005	1.8×10^{8}	2.3×10^{4}	8.0×10^{4}
	505	0.0012	0.0051	(5.6 ns)	(43 μs)	
2a	454	0.074	0.0085	5.4×10^{10}	1.2×10^{9}	N.D.
	511	0.0068	0.055	(19 ps)	(830 ps)	
2b	446	0.012	0.0006	1.6×10^{8}	8.7×10^{4}	N.D.
	505	0.0016	0.0093	(6.3 ns)	(11 μs)	

The transient absorption decays of the derivatives were fitted by an equation that does not include SF process (see Equation (S7) in the Supporting Information). The fitting parameters obtained by a global fit between the ^{1}Pn* and ^{3}Pn* time courses are summarized in Table 2. As expected from the transient absorption spectra, the time courses of **1b** and **2b** can be adequately reproduced by Equation (S7), and the lifetimes of the ^{1}Pn* species (τ_S) were determined to be 5.6 and 6.3 ns, respectively. Although the τ_S value of **1b** is slightly smaller than that of **2b**, the Φ_f values showed a reverse trend. The fluorescence rate constants ($k_f = \Phi_f/\tau_S$) of the derivatives are expected to be almost constant, since the molar absorption coefficients of $^1\pi\pi^*$ bands are comparable. Such a photophysical conflict between **1b** and **2b** can be explained by a TTA contribution. As shown from the kinetic fitting, only **1b** showed TTA, presumably due to its long-lived ^{3}Pn* nature ($\tau_T = 43$ (**1b**) and 11 μs (**2b**)). Therefore, the relatively large Φ_f value observed for **1b** includes a fluorescence from ^{1}Pn* generated by TTA.

In contrast to **1b** and **2b**, the fittings to the transient absorption decay profiles of **1a** and **2a** by Equation (S7) were less satisfactory (see Figure 4). The deviation is due to a contribution of SF to the excited-state dynamics. Therefore, the transient absorption dynamics of **1a** and **2a** were fitted by the kinetic model including SF (Equation (S17) in the Supporting Information), as shown in Figure 4. The fitting parameters are summarized in Table 3. The theoretical fits to Equation (S17) were much better than those to Equation (S7), especially for **1a**, thus indicating the presence of SF. To compare the lifetime of the ^{1}Pn* species, the normalized ^{1}Pn* time courses reproduced from the fitting parameters were integrated ($\int([^1\mathrm{Pn}^*]_t/[^1\mathrm{Pn}^*]_0)\mathrm{d}t$). The resulting average lifetimes ($\langle\tau_S\rangle$) of **1a** and **2a** were 4.1 and 20 ps, respectively. The extremely short-lived ^{1}Pn* species demonstrate not only a huge acceleration of ISC but also the contribution of SF to produce ^{3}Pn* from ^{1}Pn* in the pentacene–radical derivatives. The lifetime of the ^{3}Pn* species (τ_T) were also remarkably shortened by the introduction of the radical substituents ($\tau_T = 450$ ps for **1a** and 680 ps for **2a**). Such ultrafast formation and deactivation of ^{3}Pn* in the pentacene–radical derivatives were presumably caused by "spin-allowed" intersystem crossing and spin–orbit coupling as a result of the presence of the spin-doublet radical substituent. This class of the derivatives possesses two different ^{3}Pn* species, $^4[^3\mathrm{Pn}^*\text{-Ph-R}^\bullet]^*$ and $^2[^3\mathrm{Pn}^*\text{-Ph-R}^\bullet]^*$, the energy difference of which is expected to be ca. 100 cm^{-1} as a result of the presence of spin-doublet radical substituents. During the transition from $^2[^1\mathrm{Pn}^*\text{-Ph-R}^\bullet]^*$ to $^2[^3\mathrm{Pn}^*\text{-Ph-R}^\bullet]^*$ followed by deactivation to the ground state ($^2[\mathrm{Pn}\text{-Ph-R}^\bullet]$), the total spin character of a molecule does not change while the pentacene moiety undergoes ISC. Therefore, the transition would be largely spin-allowed, and the quartet state is expected to form and deactivate quickly. The concentration dependence is expected, since SF is a bimolecular reaction. The Φ_{ST} value was slightly enhanced for both **1a** and **2a** by an increase in the concentration of the derivatives (ca. 1 mM; see the Supporting Information).

In conclusion, the introduction of a radical substituent on a pentacene greatly accelerates intersystem crossing in the pentacene moiety and notably induces singlet (exciton) fission even in dilute solution. Singlet fission in the pentacene moiety, in which two triplet excited states are produced by only one photon, is a fascinating reaction and a possible candidate for the photochemical applications, such as artificial photosynthesis and solar cells. While it is known that SF dynamics can be treated as a pseudo-double-exponential function,[20] the kinetic model we derived in this study would be more realistic. Although the rate constants of the singlet fission obtained in the present study exceed the diffusion-controlled limit (see the Supporting Information), the rapid SF reaction observed for the pentacence–radical derivatives even in highly dilute solution might arise from the presence of an SF-active domain (or microaggregates) mediated by molecular interactions, presumably through the presence of the radical substituent in the derivatives. An introduction of the spin-doublet radical substituent in a derivative is expected to cause a singlet fission reaction even in incredibly dilute solution as a result of highly "spin-allowed" $^1\mathrm{Pn}^*\rightarrow{}^3\mathrm{Pn}^*$ transition and spin–orbit coupling.[21]

Table 3: Theoretical fitting parameters for transient absorption decay profiles of **1a** and **2a** to Equation (S17).

Derivative	λ_{max} [nm]	A_S	A_T	k_1' [s^{-1}] (error)[a]	k_2' [s^{-1}] (error)[a]	β [s^{-1}] (error)[a]	$\alpha\gamma$ [s^{-2}] (error)[a]	k_T [s^{-1}] (error)[a]	$\langle\tau_S\rangle$ [ps]	τ_T [ps]
1a	454	0.024	0.0024	2.0×10^{11}	8.8×10^{10}	1.3×10^{11}	7.3×10^{6}	2.2×10^{9}	4.1	450
	511	0.0020	0.023	(3.8×10^{8})	(2.4×10^{9})	(2.4×10^{9})	(7.2×10^{14})	(1.5×10^{8})		
2a	454	0.076	0.0086	3.9×10^{10}	2.6×10^{10}	4.4×10^{10}	4.9×10^{8}	1.5×10^{9}	20	680
	511	0.0075	0.058	(1.9×10^{9})	(3.0×10^{9})	(1.5×10^{9})	(4.8×10^{19})	(4.9×10^{7})		

[a] Standard error of the fit.

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[20] The dynamics of **1a** and **2a** could be also treated by a pseudo-double exponential function. The time constants of the ISC and SF were estimated from the fitting to be 1.8 and 4.7 ps, respectively, for **1a** and 8.2 and 24 ps, respectively, for **2a**.

[21] E. C. Greyson, J. Vura-Weis, J. Michl, M. A. Ratner, *J. Phys. Chem. B* **2010**, *114*, 14168–14177; herein, the condition of maximizing singlet fission, in which the pathways given by spin–orbit coupling were neglected, was examined. The existence of a non-negligible spin–orbit coupling will open the additional pathway.