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Excited-State Dynamics of Non-Luminescent and Luminescent π-Radicals

Yoshio Teki*[a]

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Abstract: Recently, the potential use of organic π-radicals and related spin systems has been expanded to modern technological applications. The unique excited-state dynamics of organic π-radicals can be useful to improve the stability of photochemically unstable organic compounds, make the polarization transfer applicable to information technology, and achieve effective up-conversion of interest for luminescence bioimaging, among others. Furthermore, highly luminescent stable π-radicals have been recently reported, which are especially interesting for application in organic light-emitting devices due to their potential to provide an internal quantum efficiency of 100%. Thus, the excited-state nature of stable π-radicals as well as the control of their excited-state spin dynamics are emerging topics both in fundamental science and related technological applications. In this minireview, we focus on the excited-state dynamics of both photostable non(weakly)-luminescent and luminescent π-radicals, which are located opposite to each other. In particular, we cover the following topics: (1) effective generation of high-spin photoexcited states and control of the excited-state dynamics using non-luminescent π-radicals, (2) unique excited-state dynamics of luminescent π-radicals and radical excimers, and (3) applications utilizing excited-state dynamics of π-radicals.

1. Introduction

Stable organic π-radicals (unpaired π-spin systems delocalized through π-conjugation), which are persistent under air atmosphere, possess fascinating open-shell electronic structures built up from light elements (H, C, N, O, and S). Their electronic, magnetic, and optical properties have been investigated in view of potential uses as building blocks for functional molecular materials.[1-2] Most studies have focused on their unique open-shell nature in their electronic ground states, since organic radicals usually exhibit strong non-radiative energy relaxation pathways, thus being weakly or non-luminescent. Even when a luminescent chromophore is attached to a radical, its intrinsic nature leads to weakly emissive or emissionless low energy states due to the enhanced intersystem crossing (EISC). [3-10] Herein, we use the term "π-radical/π-radical moiety" to denote a spin system in which unpaired π-electron(s) is delocalized in the molecule/moiety through π-conjugation. Thus, π-radical moieties can act as spin catalysts,[10] causing non-radiative intersystem crossing (ISC). However, these properties can be used to effectively generate high-spin photoexcited states[11-15] as well as improve the stability of photochemically unstable aromatic compounds such as pentacene.[16-18] The appending of π-radical moieties to chromophore/functional moiety can be used to control or modify the excited-state dynamics.[19-31] Furthermore,

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luminescent organic π-radicals have also been developed.[32-48] One of the straightforward applications of luminescence is organic light-emitting devices (OLED).[49] Luminescent radicals have the potential to rise the upper limit of the internal quantum efficiency to 100% owing to their unique electronic/spin structures.[37, 39] The tris(2,4,6-trichlorophenyl)methyl (TTM) radical and its derivatives have been found to be promising candidates to produce novel materials for OLED.[37, 39-40, 43-44, 47-48] In this review, we focus on the excited-state and dynamics of photostable non(weakly)-luminescent as well as luminescent π-radicals, which are located on counter side to each other.

2. Classification of Excited-State π-Radical

Herein, we classify the excited-state dynamics of π-radicals and related spin systems into three categories according to their pathways up to the lowest photoexcited state, as shown in Figure 1. Figure 1(a) shows the case when no accessible excited states exist between the first excited doublet state (D_1) and ground state (D_0). Figures 1(b) and 1(c) show the situation when compounds are constituted of both a radical and chromophore moiety (or another functional moiety such as a donor-bridge-acceptor), whose excited state is located lower in energy compared to the first excited doublet state (D_n) generated by direct photoexcitation or rapid internal conversion after photoexcitation. In this case, the lowest excited state corresponds to the triplet excited state or charge-separated state of the chromophore/functional moiety, which is coupled to the radical moiety. For a chromophore/functional moiety linked to a π-radical system, lower energy doublet (D) and quartet (Q) states are generated upon interaction between the radical moiety and the triplet state of the
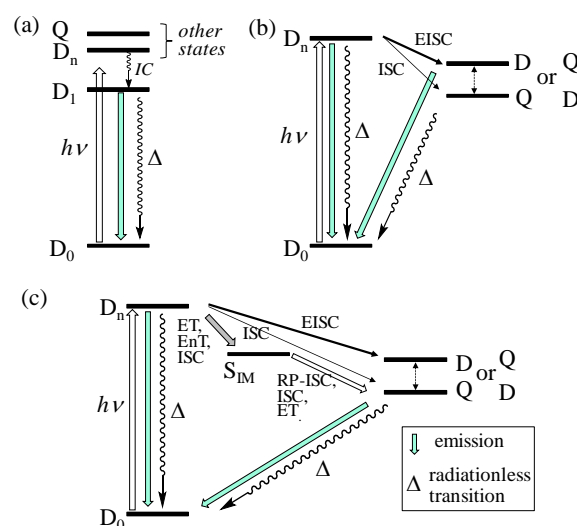

Figure 1. Typical three cases of the excited-state dynamics of π-radicals. (a) The lowest excited state is the first excited doublet state of the radical. (b) The lowest excited state is the first excited state of the chromophore, which is coupled to the radical moiety. D_n generated by the photo-excitation moves rapidly to D and/or Q by EISC. (c) The case that the D and Q are generated via an intermediate state (S_{IM}).

chromophore/functional moiety, as shown in Figures 1(b) and 1(c). These D and Q states resemble to so-called trip-doublet and trip-quartet in Cu-porphyrin complexes,[50-51] although the wavefunction of the radical moiety couples relatively much stronger to that of the chromophore/functional moiety in organic π-radical systems. In Figure 1(b), the D state is the lowest photoexcited doublet state, i.e., D_1 state. The doublet excited state (D_n) generated upon photoexcitation directly moves to a lower energy doublet state (D) and/or quartet state (Q), due to EISC induced by the radical moiety and/or a normal spin-orbit intersystem crossing (SO-ISC). Figure 1(c) shows the case where the D and Q states are generated via an intermediate state (S_{IM}). Thus, at first, the D_n state rapidly moves to the S_{IM} state by electron transfer (ET), energy transfer (EnT), intersystem crossing (ISC), or other means. Then, D and Q states are generated from the S_{IM} state by either normal SO-ISC, radical-pair intersystem crossing (RP-ISC), [52-55] EnT, etc. The D or Q states in Figures 1(b) and 1(c) are usually weakly luminescent as a result of energy gap law,[56] EISC to the ground-state (D_0), and spin-forbidden nature. Therefore, the energy location shown in Figure 1(a) is a mandatory condition for a radical to be luminescent. The molecular orbitals of a luminescent π-radical fall into this category.[36] Another required condition for a radical to be luminescent may be a weak coupling to the nonradiative pathway (vibrational mode, etc.). In this case, the excited-state dynamics is very simple as it only consists of emissive and/or radiationless energy relaxation pathways directly towards the ground state. In contrast, a variety of excited-state dynamics can be expected in Figure 1(c). In this case, the control of the excited-state dynamics is possible by appending a radical moiety; this can be used for polarization transfer with potential applications in information technology, modification of the charge recombination (CR) rate in donor-acceptor-radical triad (functionality linked π-radical) systems, lifetime control of the charge-separated (CS) excited states in metal complexes with radical ligands, and so forth. Figure 1(b) illustrates the typical behavior of chromophore linked π-radicals. A radical induced EISC occurs in this case. The EISC can be used to improve the photostability, as shown in the later section. Figures 1(b) and 1(c) refer to the category of the non-luminescent π-radicals. However, in the special case where D_n is dominantly constituted by the excited state of a radical moiety with a poor spatial overlap to the chromophore moiety, the EISC mechanism does not work well. [44] In this case, the radical system may be luminescent, since there are no effective pathways to D and Q as shown in Figure 1(b). This classification is valid when a radical is under isolated or diluted conditions, such as when it is dissolved in diluted organic solvents. However, even when a radical belongs to the category shown in Figure 1(a), the excited-state dynamics may become more complicated upon aggregation. Such instance will be discussed later in the section dealing with the luminescent π-radicals. π-Radicals offer the following advantages from the viewpoint of materials science: (1) π-conjugation leads to a strong exchange coupling, which is important for the spin control of the physical properties and dynamics of the materials; (2) design of spin systems with the desired spin states is possible by taking into account the network structure of the π-conjugation (π-topology); and (3) radical

induced EISC mechanism is available. This opens the way for the effective generation of photoexcited triplet states within chromophores.

## 3. Excited-State Dynamics of Non-Luminescent π-Radical

In this section, we describe the excited-state spin dynamics of organic π-radicals linked to a chromophore/functional moiety. Specifically, the radical induced EISC, effective generation of high-spin photoexcited states, control of the excited-state dynamics utilizing π-radical spin are reviewed.

3.1. EISC in Chromophore Linked π-Radicals

Paramagnetic species such as nitroxide radicals promote the exchange-induced EISC of chromophores from their singlet to the triplet excited state.[3-6] A rapid quenching occurs when triplet molecules collide with paramagnetic species like oxygen or nitroxide.[5, 7, 57] In 1969, Hoytink first proposed two possible quenching mechanisms, i.e., a borrowing mechanism of the transition intensity from the allowed transition and an electron-exchange mechanism,[4] namely EISC. The electron-exchange EISC functions efficiently for chromophore-linked π-radicals owing to the extent of π-conjugation between the chromophore and radical moieties. A schematic diagram of the excited-state dynamics in chromophore-linked radical systems is illustrated in Figure 1(b). Figure 2 shows a schematic picture of EISC occurring in the chromophore-linked radical systems. Two possible mechanisms to enhance/accelerate ISC can be considered in π-radicals.

The excited doublet state directly generated upon photoexcitation is expressed as the D_n state, which is located higher in energy than the D and Q states. In the electron-exchange mechanism shown in Figure 2(a), the spin allowed pathway from the D_n to the D state corresponds to the key process in Figure 1(b). The efficiency of this mechanism depends on (J_1-J_2)/ΔE_{SD-TD}, where J_1 and J_2 are the exchange couplings between the radical and two unpaired electrons in the triplet state of the chromophore, and ΔE_{SD-TD} is the energy difference between the sing-doublet and trip-doublet states.[50] In Figures 1(b) and 1(c), D_n and D correspond to the sing-doublet and trip-doublet states,

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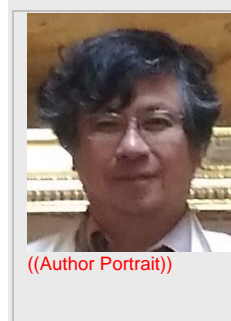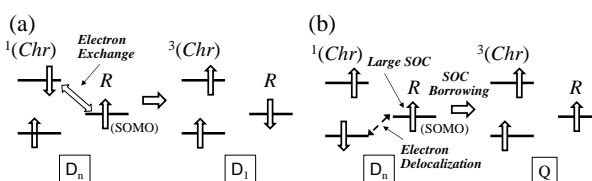
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Figure 2. Two possible mechanisms to enhance the intersystem crossing in π-radicals. (a) Spin-exchange mechanism. (b) Spin-orbit interaction borrowing mechanism.

respectively. The spin exchange mechanism can accelerate only the $D_n \rightarrow D$ pathway, however it does not work for the $D_n \rightarrow Q$ pathway, since this mechanism conserves the spin quantum numbers S and M_s. Therefore, although the spin-exchange mechanism in radical induced EISC increases the triplet quantum yield of the chromophore moiety in D, this mechanism does not lead to an enhancement of the ISC process to Q. To increase the Q state generation (i.e., accelerate the ISC of $D_n \rightarrow Q$), other or additional mechanisms are necessary. It should be noted that the polarization transfer from D to Q through a radical triplet pair mechanism (RTPM) like that occurring in solution [58-60] can be ruled out in the case of triplet–radical linked spin systems with a fixed molecular structure, because RTPM requires a change of distance between the chromophore and radical. A dipolar mixing between the D and Q states is one possible additional mechanism leading to an acceleration of the intersystem crossing to Q. Such dipolar mixing also may generate a net polarization for the transition between $|D_{+1/2}\rangle$ and $|D_{-1/2}\rangle$ near the center of the spectrum.[13, 61-62] Hereafter, we will use the ket vectors $|D_{Ms}\rangle$ or $|Q_{Ms}\rangle$ to express the doublet or quartet state, respectively, with a magnetic quantum number Ms. This mechanism is expected to be effective in the case of a small/moderate exchange interaction (J), since the mixing is inversely proportional to the energy splitting between the D and Q states ($2J = \Delta E_{DQ} = E(D) - E(Q)$). However, in π-conjugated spin systems such as π-radicals, the magnitude of the exchange interaction J is much larger than that of the dipolar interaction. In such a case, an effective enhancement of the $D_n \rightarrow Q$ ISC due to the dipolar mixing seems to be difficult. It should be noted that the effective delocalization of the wavefunction of the chromophore to the radical moieties occurs in π-conjugated spin systems. Therefore, in addition to the acceleration of $D_n \rightarrow D$, the borrowing of the transition intensity through the delocalization of the wavefunction of the chromophore to the radical moiety is possible in π-radicals, which is expected to lead to the effective generation of the Q state, as shown in Figure 2(b).[12] For purely organic chromophores such as acene derivatives, the spin-orbit interaction in the radical moiety is much larger than that of the chromophore moiety, owing to the localized electronic structure of the molecular orbital with the unpaired electron (a singly occupied molecular orbital: SOMO). Thus, in the ISC of the chromophore moiety, the spin-orbit coupling of the radical moiety can be available via the wavefunction delocalization, as shown in Figure 2(b).[12] This effect is expected to be effective in π-radicals with a large J value since a more extended delocalization leads to a larger J value. Although the spin-orbit interaction does not directly mix between

D and Q, the higher energy doublet (quartet) state (e.g., D_2 and Q_2) can mix with the Q (D) state. This D_2–Q mixing leads to a net polarization of the $|Q_{+1/2}\rangle \leftrightarrow |Q_{-1/2}\rangle$ transition, as proposed by Kandrashkin and van der Est. In this study,[63-64] the origin of the observed net polarization[62] was deduced to differ from the dipolar mixing [13, 61-62] mentioned earlier. A similar mixing mechanism is also possible in the case of π-radicals with a relatively larger ΔE_{DQ}. Therefore, the intensity borrowing via the D_2–Q mixing due to the spin-orbit interaction is also possible. Thus, the ISC to the Q state is expected to be accelerated via the D_2–Q mixing by an electron-exchange EISC mechanism to the higher energy doublet state. Such higher energy doublet or quartet state is expected to correspond to the $D(n\pi^*)$ or $Q(n\pi^*)$ state, respectively, in π-radicals shown latter.[12]

3.2. Effective Generation of High-Spin Photoexcited States and π-Topological Control of the Excited Spin States

Stable radicals such as nitroxides have been known as good quenchers of excited singlet and triplet states since 1957[3] and the 1970's, respectively.[7-9] Dynamic electron polarization (DEP) is a non-equilibrium condition (non-Boltzmann population) among electron spin sublevels. The DEP generated by the interaction between a triplet excited-state molecule and nitroxide stable radical was detected in 1986[65] by using time-resolved electron spin resonance (ESR) spectroscopy.[66] This phenomenon was found to occur upon mixing of spin sublevels due to a hyperfine interaction followed by an exchange interaction of the reencounter pair between triplet and doublet molecules in solution.[58-60, 67] This DEP generation mechanism was hereafter named as radical-triplet pair mechanism (RTPM). Since then, the interactions between excited-triplet (T) and radical (R) pairs in solution have been extensively investigated by using the time-resolved ESR technique. Although Kothe *et al.* reported for the first time the time-resolved ESR detection of the excited quartet state of the decacylene anion radical as early as 1980,[68] no other examples of excited high-spin states of organic compounds followed for more than a decade. In 1995, Corvaja *et al.* observed the first example of excited quartet state in a triplet-radical pair in solution for a C_{60} derivative covalently (σ-bonding) linked to a nitroxide radical.[69] The corresponding time-resolved ESR spectrum is
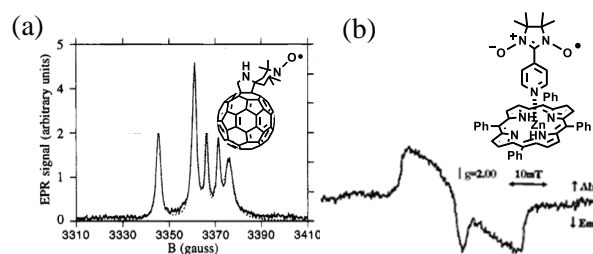

Figure 3. Time-resolved ESR spectra of σ-bonded C_{60} derivative covalently (σ-bonding) linked nitroxide radical and Zn-TTP-nipy. (a) Time-resolved ESR spectrum of C_{60} linked nitroxide radical at 1 μs in toluene solution. (b) Time-reolved ESR spectrum of Zn-TTP-nipy at 0.5 μs in toluene glass matrix. Reproduced with permission from ref. [69] and [70]. Copyright 1995 and 1996, American Chemical Society.

shown in Figure 3(a). Yamauchi *et. al.* reported the excited quartet state of a radical-triplet pair in solid phase.[70] Figure 3(b) shows the time-resolved ESR spectrum of a quartet state with a fine-structure splitting observed for tetraphenylporphilinato-zinc(II) coordinated by *p*-pyridyl nitronyl-nitroxide (Zn-TTP-nipy) diluted in a toluene glass matrix. Later, additional homologous systems have been also reported.[71-90] Furthermore, Ishii *et al.* described the correlation occurring among the electron spin polarization, excited-state dynamics, and electron exchange interaction in phthalocyaninatosilicon(SciPc)–nitroxide radical systems.[91-92] Details of these studies were reviewed previously.[13, 15, 93] In these systems, stable radicals coupled to excited triplet chromophores through either sigma bonds or coordination, in which the spin exchange interactions were relatively small in magnitude, although high-spin states could be observed by time-resolved ESR measurements. From the viewpoint of materials chemistry, robust excited high-spin systems are desired to overcome thermal fluctuations. Therefore, robust spin systems such as π-radicals are important not only in the field of spin chemistry but also in materials science. Hereafter, the main sections of this review will focus on the excited states of π-radicals and related spin systems.

In 2000, our group reported the first observation of a high-spin photoexcited state for neutral stable π-radicals.[11] Systematic studies of the relationship between the π-topology and photoinduced spin alignment occurring in photoexcited states were also carried out.[11-12, 17, 94-98] The π-radicals, whose high-spin photoexcited states were detected by our group, are listed in Figure 4. Here, *m* and *p* stand for the *meta* and *para* position, respectively, which correspond to the relative connecting positions of the anthracene and radical moieties relative to the phenyl group. Typical time-resolved ESR spectra of the quartet (S = 3/2) photoexcited state (Q) of **1p** and quintet (S = 2) photoexcited state (Qu) of **4pp** observed in frozen glass matrixes are shown in Figure 5. Although the first excited quartet state of a π-radical anion was reported in 1980,[68] at that time there were no examples of the direct detection of high-spin excited states in
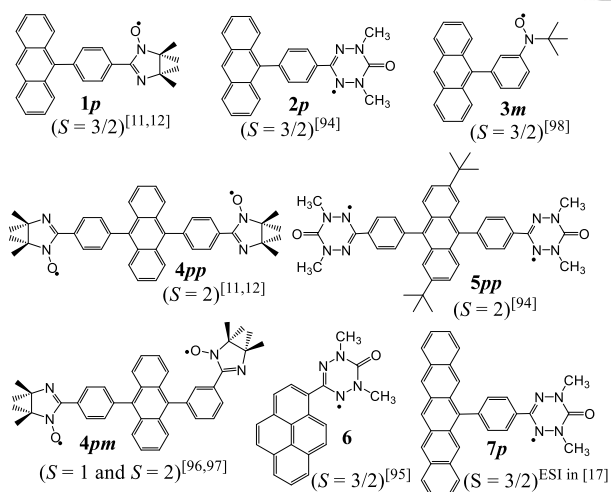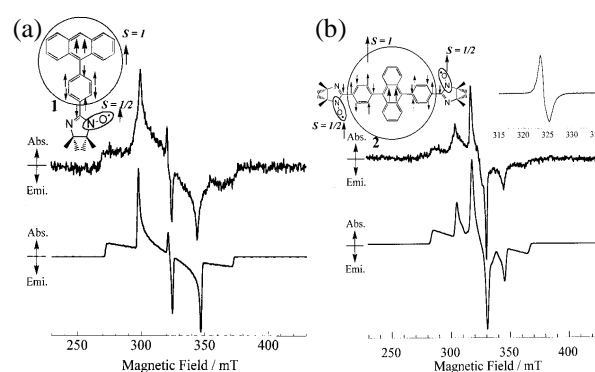

Figure 5. Typical time-resolved ESR spectra of the photoexcited high-spin states at ca. 1 μs in a frozen glass matrix at 30 K. (a) Observed (upper) and simulated (lower) spectra of the quartet (S = 3/2) state of **1p**. (b) Observed (upper) and simulated (lower) spectra of the quintet (S = 2) state of **4pp**. The inset shows the ordinary ESR spectrum of the ground state. Reproduced with permission from ref. [11]. Copyright 2000, American Chemical Society.

neutral π spin systems. Furthermore, Figure 5(b) shows the first example of a quintet photoexcited state of a π-radical. A robust photoinduced spin alignment was achieved between two radical spins through the triplet excited state of the chromophore. A quintet state was also observed for **5pp**, while quartet states were observed in the case of **2p**, **3m**, **6**, and **7p**. In contrast, such high-spin states were not detected for their π-topological isomers **1m**, **3p**, and **4mm** (not shown in Figure 4), according to time-resolved ESR measurements.[12, 98] In the case of **4pm**, a high-spin quintet state was also observed together with a unique triplet state.[96-97] Thus, the photoexcited states drastically changed depending on the π-topology. The π-topological control of the photoinduced spin alignment was clearly demonstrated in these π-radical systems. In **4pm**, the triplet-state (open-shell) spin coupler is expected to mix the spin-wavefunctions of two triplet excited states (T_1 and T_2), leading to the unique triplet state arising from four unpaired electrons that are closely locate near the quintet (Qu) state. The spin-wavefunction mixing was also found to lead to a reduced fine-structure splitting.[96-97] The generation of these high-spin excited-states was induced by appending a π-radical moiety, which produced a radical induced enhanced/accelerated ISC. Their excited-state dynamics can be classified as the category shown in Figure 1(b). This radical induced enhanced ISC probably corresponds to the type of mechanism illustrated in Figure 2(b). The details of the justification for this argument can be found in the original report.[12] Only a few points are discussed here. In **4pp** and **5pp**, the diphenylanthracene unit plays the role of a photoexcited triplet-state spin coupler that aligns two radical spins, leading to a photoexcited quintet state. However, diphenylanthracene has a fluorescent quantum yield close to unity.[99] Thus, the intrinsic triplet quantum yield of the chromophore moiety by normal SO-ISC is very low (a very low efficiency of ISC from S_1 to T_1). In addition, the signal intensity of the verdazyl radicals (**2p** and **5pp**) was much stronger than that of the iminonitroxide radicals (**1p** and **4pp**), although a larger energy gap between D and Q was predicted by theoretical calculations.[100] The magnitude of the intramolecular

Figure 4. A series of π-Radicals in which the photoexcited high-spin states were detected. Their detected spin-states are given in the parentheses. In **4pm**, a superimposed spectrum of triplet and quintet states were detected. The corresponding literatures are indicated in parentheses.

ferromagnetic exchange interaction (J = 123 cm^{-1} [calcd.][100] and 117 $\pm$ 20 cm^{-1} [estimated from exp.] [101]) was much larger than that of the dipolar interaction. Therefore, the possibility of a dipolar mixing to take place could be ruled out. Therefore, the radical induced ISC mechanism shown in Figure 1(b) (spin-orbit interaction borrowing) is the most plausible pathway leading to the effective generation of robust high-spin photoexcited states of π-radicals.[12]

The effective generation of high-spin photoexcited states as well as the role of EISC were supported from the kinetic point of view by the studies carried out on systems constituted of perylene-3,4:9,10-bis(dicarboximide) (PDI) and nitroxide radical (Figure 6).[14] In this study, Wasielewski *et al.* determined the rate constants and quantum efficiency (Φ_T) of EISC from the singlet state (^{1}PDI) to the triplet state (^{3}PDI) of the PDI moiety as well as the lifetimes of the D and Q states by using ultra-fast transient absorption spectroscopy. The ultra-fast ISC from ^{1}PDI to ^{3}PDI occurred in ca. 2 ps, and the Φ_T increased up to 0.3 by appending a radical moiety. The ultra-fast ISC induced by appending the π-radical moiety (EISC) in the covalently linked three spin systems was theoretically investigated, while the factors producing the EISC were discussed using the Hubbard type model Hamiltonian.[102] It should be noted that it was not possible to distinguish whether the recorded optical spectra corresponded to the ^{3}PDI of Q or that of D. Therefore, the confirmation of the Q state generation by time-resolved ESR is crucial. Both the Q and D states due to DEP were detected in solution at 295 K by W-band time-resolved ESR measurements. Therefore, the occurrence of EISC to the Q state was confirmed. In this study, the ISC mechanism to Q was explained as a dipolar mixing between the D and Q states[13] owing to the fine-structure term of the PDI moiety. It was speculated that even though D and Q are well separated in energy, the dipolar interaction can mix D and Q in these systems.[14] Nonetheless, the efficient generation of high-spin photoexcited states in π-radical systems was also confirmed by the kinetic standpoint.
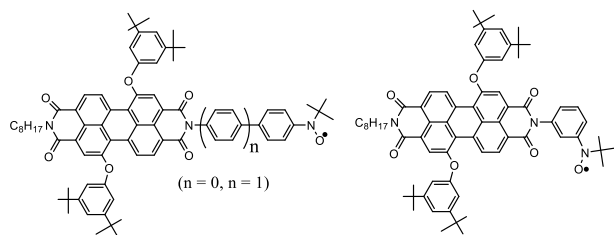

Figure 6. PDI linked nitroxide radicals in which their ultra-fast ISC was investigated in ref. [14].

3.3. Control of Excited-State Dynamics by π-Radical

The control of the excited-state dynamics is of crucial importance for the development of molecular-based photofunctional materials and well as applications in artificial photosynthesis, molecular spintronics, and organic molecular-based devices such as OLED. The presence of an unpaired spin appended to either the chromophore (C) or donor (D)-acceptor (A) system plays a key role in controlling the corresponding excited-state dynamics. The

understanding of the excited-state dynamics for π-radical systems, which belong to the category shown in Figure 1(c), may provide a fundamental knowledge about the photocontrol of the organic materials and device properties.
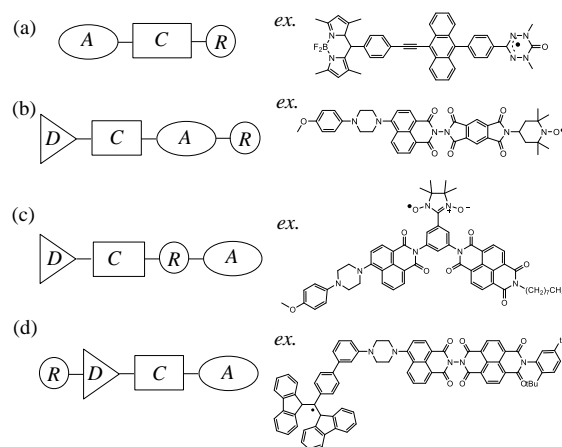

Figure 7. A variety of π-radicals and related spin systems in which the impact of the third spin to the excited-state dynamics were investigated. Here, D, A, C, and R are electron donor, acceptor, chromophore, and radical moieties, respectively.

In the case of bodipy-bridge-chromophore molecules with an appended π-radical as illustrated in Figure 7(a) (bodipy: fluorophore boron dipyrromethene), our group reported the first observation of photoexcited quartet high-spin states with an unusual DEP pattern (*aee/aae* pattern; *a/e*: absorption/emission of the microwave), as shown in Figure 8(a). This unusual DEP pattern could be rationalized as a selective population (polarization) within high-field spin sublevels.[19-20] Later, similar DEP patterns were also observed for other acceptor-bridge-chromophores linked to π-radical systems[103] as well as a chromophore linked to an σ-bonded radical.[27] Such unusual DEP patterns polarized in the high-field spin sublevels (*aee/aae*) have been previously observed only in the case of systems in which a radical pair was formed and underwent RP-ISC followed by charge recombination to the local triplet state in either a mutated photosynthetic reaction center[53] or its model systems.[104] Figures 8(a) and 8(b) show the typical time-resolved ESR spectra of a bodipy-bridge-chromophore linked to a π-radical system[19-20] and a TEMPO-PDI σ-bonded radical system,[27] respectively. Since DEP corresponds to a non-equilibrium physical quantity, it depends on the specific pathway how an observed state is generated, i.e., its excited-state dynamics. Photoexcited high-spin states usually exhibit a characteristic DEP pattern due to a non-Boltzmann population in the zero-field spin sublevels (*aaa/eee* pattern, see Figure 5), which is similar to that of the usual photoexcited triplet states generated by SO-ISC (*aa/ee* pattern). Thus, the direct pathway illustrated in Figure 1(b) leads to a common DEP pattern. However, for chromophore-radical linked spin systems connecting with functional groups, an indirect pathway via an intermediate state (S$_{IM}$) is possible, as illustrated in Figure 1(c). It was first speculated[19-20] and later confirmed theoretically[21-22] that changes in the spin wavefunction from
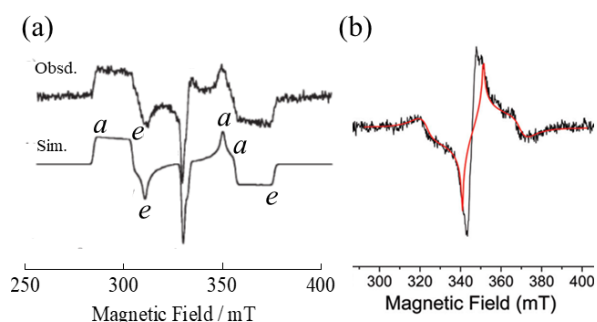
Figure 8. Typical time-resolved ESR spectra of the bodipy-bridge-chromophore linked π-radical system and the TEMO-PDI σ-bonded radical system. (a) Bodipy-bridge-chromophore linked π-radical system shown in Figure 7(a). Here, a and e correspond to the absorption and emission of the microwave, respectively. Upper is the time-resolved ESR spectrum observed at 0.3 μs after the excitation of the bodipy absorption band of $\lambda_{ex} = 505$ nm in a frozen toluene glass matrix at 30 K. Lower is the spectral simulation which is obtained by a superposition mainly of the high-field polarization and the normal DEP. (b) TEMO-PDI σ-bonded radical system. Black spectrum is the observed time-resolved ESR spectrum at 1 μs after the excitation of the PDI absorption band of $\lambda_{ex} = 532$ nm in a frozen toluene glass matrix at 85 K. Red is the simulation. Reproduced with permission from ref. [19] (Figure 8(a)) and ref. [27] (Figure 8(b)). Copyright 2006, John Wiley and Sons and Copyright 2010, American Chemical Society.

Figure 9. Model of the DEP generation via the doublet-quartet QM state (ϕ_1 - ϕ_6), which is constructed by a weak exchange coupling between the doublet and the triplet moieties. The selective population appears due to the doublet character of the quantum-mixed spin sublevels (ϕ_2 - ϕ_5) from the higher energy photo-excited doublet state. The circles between the sublevels express the quantum coherence among the spin sublevels. CS, CR, and EISC denote the charge-separation (ET), the charge recombination (back ET), and the enhanced intersystem-crossing, respectively. In the cases of ex.1, ex.2 and ex.3, this mechanism can be available. Reproduced with permission from ref. [22]. Copyright 2012, Royal Society of Chemistry.

quantum-mixed (QM) states ($\phi_1-\phi_6$) to the pure D and Q states upon either a charge-recombination or polarization transfer (Figure 9) can lead to an unusual DEP, when the S_{IM} state is a QM state between the quartet (Q_{IM}) and doublet (D_{IM}) states. Here, it should be noted that the spin parts (spin functions) in the wavefunctions of the D_{IM} and Q_{IM} states ($|Q_{IMM,s}>$ and $|D_{IM,Ms}>$) and those of the D and Q states (($|Q_{M,s}>$ and $|D_{Ms}>$) can be expressed by the same formula. Therefore, when the wavefunction mixing between the chromophore and radical moiety is negligible (the limiting case is represented by a weakly exchange coupling), the spin functions of the D and Q states ($|Q_{Ms}>$ and $|D_{Ms}>$) can be related to the weakly coupled QM states (($|\alpha T_{Ms'}>$ and $|\beta T_{Ms'}>$) according to the following Equation:

$$\phi_1 \sim |\alpha T_{+1}> = |Q_{+3/2}> \tag{1a}$$

$$\phi_2 \sim |\alpha T_0> = \sqrt{2/3}\,|Q_{+1/2}> - \sqrt{1/3}\,|D_{+1/2}> \tag{1b}$$

$$\phi_3 \sim |\alpha T_{-1}> = \sqrt{1/3}\,|Q_{-1/2}> - \sqrt{2/3}\,|D_{-1/2}> \tag{1c}$$

$$\phi_4 \sim |\beta T_{+1}> = \sqrt{1/3}\,|Q_{+1/2}> + \sqrt{2/3}\,|D_{+1/2}> \tag{1d}$$

$$\phi_5 \sim |\beta T_0> = \sqrt{2/3}\,|Q_{-1/2}> + \sqrt{1/3}\,|D_{-1/2}> \tag{1e}$$

$$\phi_6 \sim |\beta T_{-1}> = |Q_{-3/2}> \tag{1f}$$

For π-radicals, the above relationship may hold approximately since the spin wavefunctions of the chromophore and radical moieties mix upon π-conjugation. In the initial stage after photoexcitation, selective populations of the $\phi_2-\phi_5$ of the S_{IM} states (QM state) occur due to their doublet character that makes the spin allowed to the D_n state or the M_s conservation of EISC from the D_n state (Figure 9). These selective populations are transferred to the D and Q states upon either charge-recombination or population transfer due to EnT, and so forth, thus leading to a unique DEP. A similar unique DEP pattern was
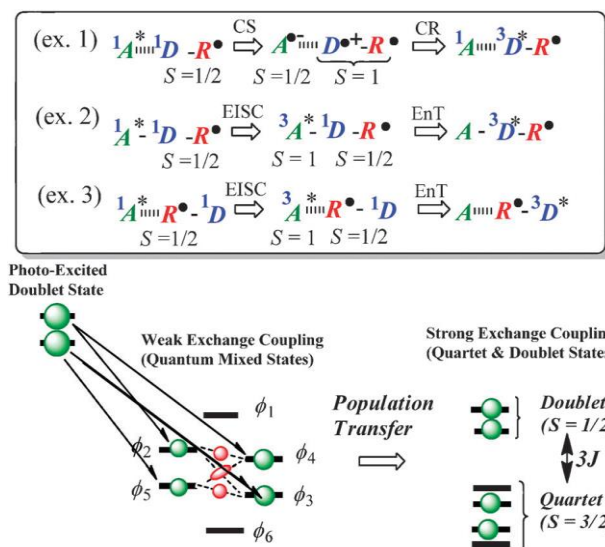
also reported in a chromophore linked to an σ-bonded radical.[27] In this molecule, the chromophore is a σ-bonded perylene-3,4:9,10-bis-(dicarboximide) (PDI) moiety, while the radical part is a stable 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). A solvent dependency of the TA spectra was observed for this molecule. TEMPO quenched ^{1}PDI by EISC in toluene and electron transfer from TEMPO to PDI in THF. A unique DEP pattern in this system was only observed in a frozen toluene matrix at 85 K. In this study, the origin of the unique DEP pattern was speculatively discussed. A pathway like the ^{1}S*–$T_{\pm1}$ transition was assumed to exist under a weak exchange coupled regime between the triplet excited state and ground state radical spin, in which the M_s change of ^{3}PDI* was compensated by the change from α to β of the radical. Although the spin wavefunction changes were not included in this mechanism, similar QM states ($\phi_1-\phi_6$) were assumed to occur also in this system.

Wasielewski and co-workers intensively investigated the influence of appending a radical spin to a donor-bridge-acceptor. [23-31] The excited-state dynamics of several types of molecules was studied by transient absorption and time-resolved ESR spectroscopy. It is well known that the recombination dynamics of radical pairs is spin-selective and affected by the external magnetic field.[10, 52, 105] Therefore, the presence of a stable radical as third spin interacting with the photogenerated radical ion pairs can modulate the excited-state dynamics. The influence of a third spin on the charge recombination (CR) lifetimes of photogenerated radical pairs was first examined using electron donor-bridge-acceptor systems appended to σ-substituted stable-

radicals (Figure 7(b)).[23, 25, 28] In these systems, the radical spin influenced the CR rate (lifetime) of the photogenerated radical ion pairs, which depended on the relative ordering of the energy levels of the radical ion pairs as well as the local neutral triplet state. In addition, a DEP transfer occurred from the spin-correlated radical ion pairs to the stable radical moiety, leading to a net electron spin polarization of the radical moiety, whose degree depended on the exchange between the donor (D) and acceptor(A). Normally, the net spin polarization is not produced from the spin dynamics of correlated radical ion pairs. This phenomenon demonstrates a remarkable impact of the appended radical as the third spin. In contrast, the third spin had little or no impact on the spin-spin exchange interaction and charge-separation (CS) time constants within the radical ion pairs as well as the quartet state generation.[23, 25, 28] The charge and spin transfer dynamics of the donor-bridge(R)-acceptor molecules shown in Figure 7(c) were also investigated. [24, 26] In these molecules, the bridge moiety exhibits a π-conjugation to the appended stable π-radical (R). In these systems, similar phenomena described above for the molecules of Figure 7(b) were also observed; in particular, the appended radical influenced the spin dynamics of photogenerated charge-separated triradical states (D$^{+\bullet}$–C–R$^{\bullet}$–A$^{-\bullet}$), thus resulting in a slower CR rate compared to the corresponding molecules lacking an appended radical moiety. In contrast, no influence on the spin-spin exchange interaction between D$^{+\bullet}$ and A$^{-\bullet}$ was detected. A net polarization of the radical moiety was also observed. These phenomena were qualitatively explained as the result of an equilibrium between the triradical states (D$^{+\bullet}$–C–R$^{\bullet}$–A$^{-\bullet}$) and local triplet states of the acceptor moiety (^{3}A*) coupled to a stable radical spin (D–C–R$^{\bullet}$–^{3}A*). The excited-state dynamics proposed in this study is shown in Figure 10. Here, the dipolar mixing between the D$_2$ and Q$_2$ states in (D–C–R$^{\bullet}$–^{3}A*) was assumed as the origin of the net
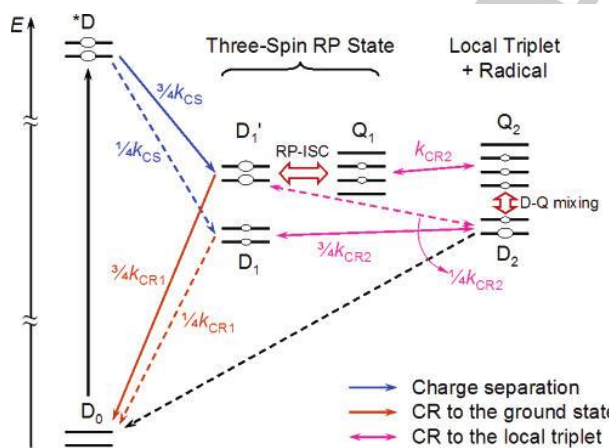

Figure 10. Energy level diagram in an external magnetic field. Blue arrows denote charge separation; orange arrows, charge recombination to the ground doublet state; and magenta arrows, reversible D-D and Q-Q. Dashed lines mean less-probable transitions. Red double arrows stand for processes that mix the spin sublevels of the relevant D and Q states. The size of the ellipse represents its population qualitatively. Reproduced with permission from ref. [24]. Copyright 2006, American Chemical Society.

polarization.[24, 26] The slower charge recombination found for the radical appended system was attributed to the EISC induced by R$^{\bullet}$ (enhanced RP-ISC), which increased the rate of mixing between D$_1$' [^{2}(D$^{+\bullet}$–C–R$^{\bullet}$–A$^{-\bullet}$)] and Q$_1$ [^{4}(D$^{+\bullet}$–C–R$^{\bullet}$–A$^{-\bullet}$)], along with an equilibrium between the nearly isoenergetic Q$_1$ and Q$_2$ states. The influence of the radical spin on the spin polarization transfer from a photogenerated radical ion pair to a stable radical (DEP generation to the ground state) was also investigated using the R$^{\bullet}$– D–C–A system shown in Figure 7(d). The polarization transfer rate was found to be strongly solvent dependent.[30] The third spin accelerated the radical pair recombination lifetimes down to a picosecond timescale via a triplet channel.[29]

The polarization transfer from an excited high-spin state to the ground state was also observed for a strongly exchange-coupled π-conjugated pyrene based biradical system, namely 4,5,9,10-tetramethoxypyrene-2,7-bis(*tert*-butylnitroxide).[106] This biradical was found to exist in a semi-quinoid form with an unprecedented strong intramolecular antiferromagnetic magnetic exchange interaction of $2J/k_B = -1185$ K. Thus, the ground state was a singlet state (S$_0$) with a low lying triplet state (T$_0$), which were located at a fairly large energy separation of $2J/k_B$. A dynamically electron spin polarized triplet state was observed upon photoexcitation, which could be assigned to the T$_0$ state due to the fine-structure splitting. Thus, the T$_0$ state could be populated via photoexcited states (S$_1$ T$_1$, T$_2$, and Qu$_1$) that were generated by exchange coupling between the photoexcited triplet state of the pyrene moiety and two connecting NO radicals. The transition to T$_0$ from T$_1$ and T$_2$ was allowed since the total spins were the same ($S = 1$). A similar phenomenon (the polarization of a low lying T$_0$ state) was previously reported in a weakly exchange-coupled σ-bonded phthalocyanine-bis(radical) system, and the origin of the T$_0$ polarization was explained as a dipolar mixing occurring among T$_1$, T$_2$, and Qu$_1$.[91, 107] However, the mechanism of the DEP generation to the T$_0$ for this pyrene based biradical π-spin system may be different from that previously reported due to a very large intramolecular exchange coupling that prevents the dipolar mixing to occur among photoexcited states with different spin states.

The impact of the π-radical spin on the charge-separated excited-state dynamics was also investigated in metal complexes containing π-radical ligands.[108-109] As shown in Figure 11(a), Shultz, Kirk and co-workers synthesized radical complexes of the (*t*-Bu$_2$bpy)Pt(Cat-R) type, where Cat, bpy, and R stand for 3-tertbutyl-ortho-catecholate, bipyridine, and nitronylnitroxide radical (NN), respectively, and investigated their photoexcited states by magnetic circular dichroism (MCD) spectroscopy. In these complexes, upon excitation of the ligand-to-ligand charge transfer (LL'CT) band, a photoinduced charge transfer occurs from Cat to bpy, leading to a (bpy$^{\bullet}$)Pt(SQ$^{\bullet}$NN$^{\bullet}$) three-spin system. For three spin systems, the spin-wavefunctions of the sing-doublet ($|S_1,1/2\rangle$) and trip-doublet ($|T_1,1/2\rangle$) undergo mixing depending on the λ, which is given by

$$\lambda = (1/2)\tan^{-1}\{\sqrt{3}J_{\text{SQ-NN}}/(2J_{\text{SQ-bpy}} - J_{\text{SQ-NN}})\}. \quad (2)$$

Where $J_{\text{SQ-NN}}$ and $J_{\text{SQ-bpy}}$ are the excited state pairwise exchange interactions between the three spin centers SQ$^{\bullet}$, bpy$^{\bullet}$, and NN$^{\bullet}$ in
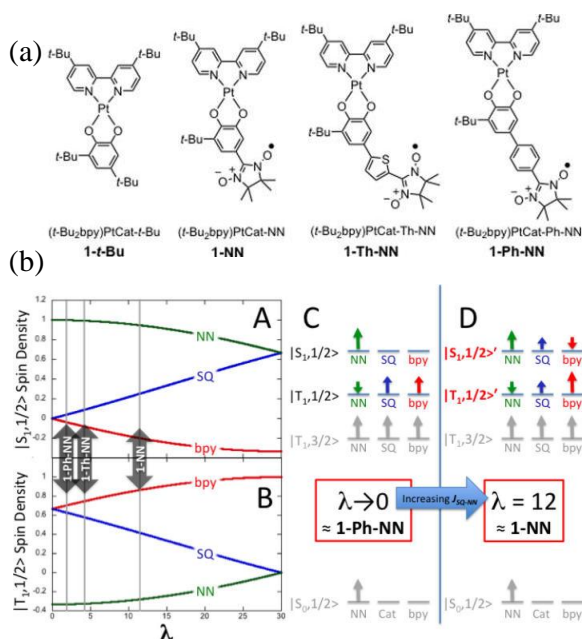
Figure 11. Molecular structures and spin populations. (a) Molecular structures of the parent and radical-elaborated (*t*-Bu₂bpy)Pt(Cat-R) complexes. (b) Spin populations of $|S_1,1/2\rangle$ (A) and $|T_1,1/2\rangle$ (B) states for the three spin centers (bpy•, SQ and NN, color-coded to match C and D) as a function of λ of equation (2). Gray vertical lines indicate "experimental" values of λ for **1-Ph-NN** (1.83), **1-Th-NN** (4.25), and **1-NN** (11.5). C and D show the graphical depictions of J_{SQ-NN}-modulated excited state spin populations on NN, SQ, and bpy for $\lambda \rightarrow 0$ ($\approx$ weak J_{SQ-NN}; C) and for $\lambda = 12$ ($\approx$ strong J_{SQ-NN}; D), respectively, in photoexcited (*t*-Bu₂bpy)Pt(Cat-R) complexes. Reproduced with permission from ref. [108]. Copyright 2018, American Chemical Society.

the (bpy)Pt(Cat-R) complexes. Equation (2) is an approximation since the mixing between the sing-doublet and trip-doublet actually depends on the $(J_{SQ-NN} - J_{bpy-NN})/(2J_{SQ-bpy} - J_{SQ-NN})$ ratio, however J_{bpy-NN} can be neglected in this case as it is expected to be very small as explained in their own work.[109] Their exchanges were evaluated using experimental data. Thus, the J_{SQ-NN} value was estimated from the temperature dependence of the magnetic susceptibility of the relevant ground state biradicals.[110] The magnitude of the J_{SQ-NN} exchange interaction was directly addressed from the low temperature MCD. The MCD intensity depended on the J_{SQ-bpy} via the mixing of the wavefunction with the coefficient λ. Figure 11(b) shows the excited doublet net spin populations of the NN, SQ, and bpy centers (green, blue, and red, respectively) calculated according to the Heitler-London approach using the J data. The net spin population was induced upon mixing of the wavefunction between $|S_1,1/2\rangle$ and $|T_1,1/2\rangle$ due to the spin exchange interactions (the mixing coefficient, sin λ). Here, the $S_1(T_1)$ in the $|S_1(T_1),1/2\rangle$ function indicates the excited state spin singlet (triplet) nature of the (t-Bu₂bpy)Pt(Cat) chromophore and the "1/2" indicates the total spin of the system constructed from the chromophore and radical spin (Notice: the definition used in this study differs to $|Q_{Ms}\rangle$ etc. used in eqs.(1a) –(1f).). Thus, in these systems, the dynamic spin polarization could be created by magnetic exchange interactions, which require neither intersystem crossing nor magnetic resonance techniques. In

addition, the wavefunction mixing can be also expected to lead to a highly efficient internal conversion (IC) process. Thus, the π-radical spin can impact the excited-state dynamics. The control of the lifetime of a charge-separated excited-state was demonstrated by varying the exchange interaction between the radical and charge-separated excited state.[109]

4. Excited-State Dynamics of Luminescent π-Radical

As described in the previous section, organic radicals are usually non-luminescent due to the EISC or other non-radiative energy-relaxation pathways shown in Figures 1(b) and 1(c), even when a chromophore is attached to the radical. However, a stable luminescent radical was first reported in 2006,[32] since then, the luminescent properties of stable organic π-radicals have become a research topic of great interest.[32-48] Typical luminescent organic π-radicals are shown in Figure 12. In the first report of a luminescent radical, the maximum quantum yield (Φ_F) was 53% for a fluorescence emission of $\lambda = 628$ nm in a cyclohexane solution of TTM-NCz.[32] In the case of OLED based on conventional diamagnetic (closed-shell) molecules, the luminescence occurs only from the excited singlet state (25%), not from the excited triplet (75%) state. Unlike the photoexcited
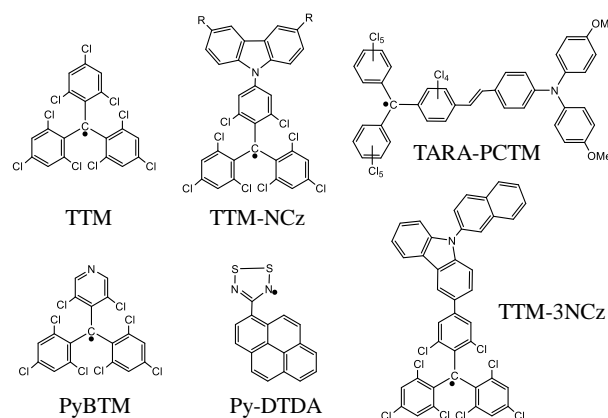

Figure 12. Variety of luminescent π-Radicals.

state of conventional closed-shell molecules, mono-radicals do not exhibit an intrinsic radiationless energy relaxation pathway such as the singlet–triplet ISC; thereby, a high luminescence efficiency is expected in electroluminescent devices when other non-radiative energy relaxation are suppressed.[36] Thus, their characteristic electronic structure offers the potential to increase the upper limit of the internal quantum efficiency (IQE) to 100%.[37, 39] When the ground-state closed-shell molecule is excited, one electron stays in the HOMO, while the other moves to the lowest unoccupied molecular orbital (LUMO). Their spin configuration is either singlet or triplet, as shown in Figure 13(a). Li *et al.* reasoned that when a ground-state radical species is excited, one electron is promoted to the lowest singly unoccupied molecular orbital (SUMO), while the SOMO is empty, as shown in Figure 13(b).[37]
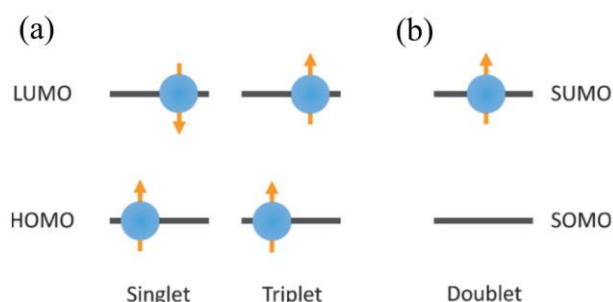
Figure 13. Schematic diagram of the spin configuration of the excited states shown in ref. [24] by Li *et al.*. (a) For closed-shell molecules, the singlet or triplet spin configuration is possible. (b) For open-shell molecules, only the doublet spin configuration is possible. Reproduced with permission from ref. [37]. Copyright 2015, John Wiley and Sons.

Thus, the transition of the excited electron back to the SOMO is spin-allowed. As a consequence, for OLED using radical species as emitters, the upper limit of IQE would theoretically be 100%. Therefore, photostable highly luminescent π-radicals are attractive materials to be used for OLED[49] or other applications based on luminescence. Here, we would like to point out the above mechanism since Figure 13(b) may lead to a misleading interpretation, although the hypothesis of the potential 100% IQE achievable by OLED is correct. The higher energy SUMO exists as a result of the electron repulsion that occurs only when the corresponding SOMO is occupied. Nevertheless, the attainment of a 100% IQE is theoretically possible in the case both hole and electron transfer take place simultaneously. Thus, a hole derives from the adjacent radical site (or connecting functionality moiety), while an electron in the SUMO simultaneously makes a transition to the SOMO. Li *et al.* first developed a radical based OLED using TTM-NCz.[37] Figure 14 shows the corresponding device structure along with the spectrum of the OLED with a maximum external quantum efficiency (η_{EQE}) of 2.4%. Recently, an OLED with a η_{EQE} of 27% at a wavelength of 710 nm has been reported using a luminescent radical emitter (TTM-3NCz in Figure 12), which is the highest value for deep-red and infrared LEDs.[47] These luminescent radicals belong to the π-radical family and most of them are derivatives of the triphenylmethyl (TM) radical,[111] which has been investigated for a long time.[1] Rawson *et al.* have
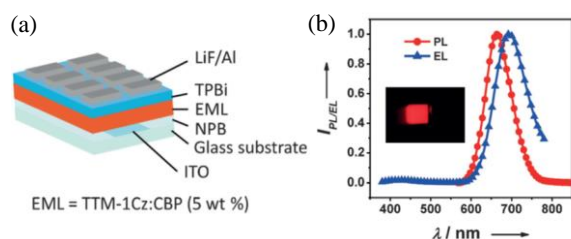
recently reported the pyrene linked dithiadiazolyl (Py-DTDA) radical shown in Figure 12, which differs from the TM-radical species.[44] This luminescent π-radical exhibits fluorescence in the deep-blue region of the visible spectrum (440 nm) with a modest fluorescence quantum yield (Φ_F = 50%) upon excitation at 241 nm. The energy mismatch and poor spatial overlap between the DTDA radical SOMO and pyrene π manifold efficiently inhibit the non-radiative electron exchange relaxation pathway, leading to a modest quenching of emission. Such suppression of the non-radiative relaxation pathway may expand the category of luminescent organic π-radicals. The study of their excited-state dynamics will contribute to applications in radical chemistry as well as their fundamental basic science.

However, most studies concerning luminescent radicals have been so far focused on the improvement of their luminescent properties, photostability as well as device applications. The excited-state dynamics of most luminescent radicals is expected to belong predominantly to the category shown in Figure 1(a) owing to their unique electronic structures. Figure 15 shows the calculated spin density distribution as well as spin configurations of the ground state and lowest excited state of the (3,5-dichloro-4-pyridyl)bis(2,4,6-trichloro-phenyl)methyl radical (PyBTM) reported by Kusamoto, Nishihara and co-workers, which is one of the most photostable luminescent π-radicals.[36] In fact, DFT calculations clarified that the lowest photoexcited state of the PyBTM radical is a doublet state corresponding to the one-electron excitation from β-HOMO to β-SOMO (SUMO). The lowest photoexcited state of the weak CT type luminescent π-radicals was also a doublet state corresponding to the one-electron intramolecular charge-transfer excitation from β-HOMO in the carbazole (NCz in Figure 12) moiety to β-SOMO (SUMO) in the PTM (perchloroperchloro-triphenylmethyl) moiety, according to the DFT calculations.[48] It should be noted that α-SOMO is occupied in the lowest photoexcited doublet state (D_1) of these typical luminescent radicals. The excited-state dynamics of TARA-PCTM radicals exhibiting strong CT bands were investigated by time-resolved spectroscopies, which behave as open-shell mixed valence donor-acceptor compounds.[35] A strong fluorescence was observed for a highly polar excited charge-transfer state in the visible and NIR spectral region. Time-resolved fluorescence and transient absorption spectroscopy
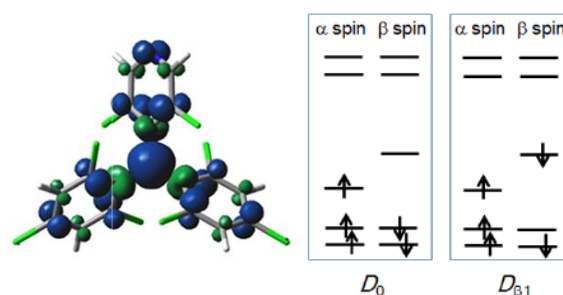

Figure 14. Radical-based OLED performance. a) The schematic diagram of the device structure of OLED. b) The electro-luminescence (EL) spectrum (7 V) of the OLED accompanied by the photo-luminescence (PL) spectra of the doped thin film. The inset shows a photograph of the OLEDs operating at 7 V. Reproduced with permission from ref. [37]. Copyright 2015, John Wiley and Sons.

Figure 15. Spin density distribution in the ground-state (D_0) and the spin configurations in the D_0 and the lowest excited state (D_1) of PyBTM calculated using DFT and TD-DFT calculations (UB3LYP/6-31G(d)). Reproduced with permission from ESI of ref. [36]. Copyright 2014, John Wiley and Sons.
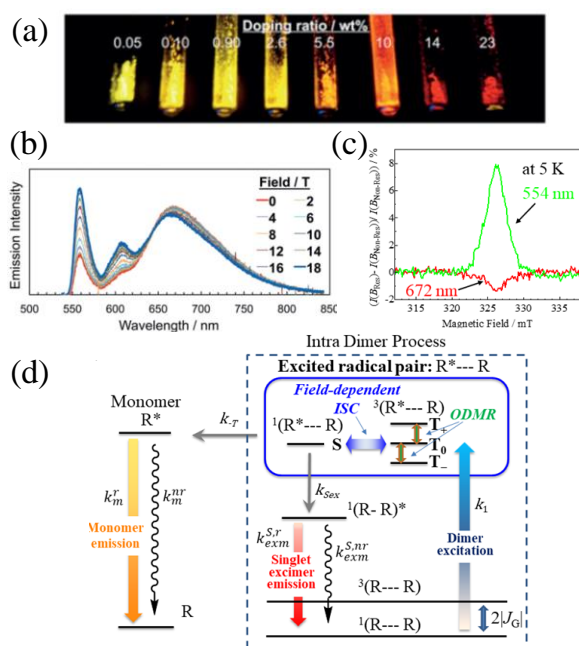
Figure 16. Photograph of the color changes depended on the concentration of PyBTM doped into the host crystal, magnetic-field dependence of the emission and ODMR spectra. (a) Photograph (λ_{ex}=365 nm). (b) Magnetic field effect of the emission spectra at 4.2 K (Dope concentration: 10w%). The emissions with peak at λ_{em}= 563 nm and 597 nm are assigned to the monomer emission and the broad emission appeared at λ_{em}= 680 nm is due to the excimer emission. (c) Steady-state ODMR spectra (Dope concentration: 10.1w%). The upper and lower spectra are ODMR signals monitored the emission bands of 554 nm (the monomer emission) and 672 nm (the excimer emission), respectively. (d) Excited-state dynamics clarified based on the experimental data and the Quantum dynamics simulation. Reproduced with permission from ref. [45] ((a) and (b)) and ref. [117] ((c) and (d)). Copyright 2018 and 2019, John Wiley and Sons.

revealed that a remarkably slow back-electron transfer was the origin of the strong fluorescence observed for these TARA-PCTM radicals. Kusamoto, Nishihara and co-workers reported that PyBTM showed a very high photostability [36] in organic solvents together with a high emission quantum yield of 89% in a mixed crystal doped into the host crystal of the precursor (αH-PyBTM).[45] Recently, Ratera, Terenzian and co-workers reported the formation of excimers of the tris(2,4,6-trichlorophenyl)methyl (TTM) radical showing a red/NIR emission using organic nanoparticles and doped polymeric films.[42] A similar excimer emission was also observed for mixed crystals of PyBTM/αH-PyBTM.[45] The excited-state dynamics of these radical-excimers belongs to the simplest case (Figure 1(a)), when they are under isolated or diluted conditions in organic solvents. However, the excited-state dynamics becomes more complicated when they undergo aggregation, leading to the formation of excimers or oligomers in their photoexcited states. In fact, in addition to the excimer formation, a large magnetic-field-effect (MFE) for the monomer and excimer emissions (magneto-luminescence) was detected for mixed PyBTM/αH-PyBTM crystals.[45] Thus, the intensity ratio of the monomer and excimer bands could be drastically modulated by applying a magnetic field up to 18 T at

4.2 K. Figure 16(a) shows the photograph of the dependence of the color change on the concentration of PyBTM doped in the host crystal of αH-PyBTM. Figure 16(b) depicts the MFE of the emission spectra. The intensity ratio of the monomer and excimer emission bands was modulated drastically by applying a magnetic field. This is the first evidence of MFE ascribed to the luminescence of organic radicals, although the MFE on molecular luminescence in the singlet ground-state has been studied extensively.[112-116] Our group investigated the excited-state dynamics of PyBTM and its excimer formation in a mixed crystal by using optically detected magnetic resonance (ODMR) and time-resolved emission spectroscopy.[117] Quantum-dynamics simulations of the excited-state dynamics was also carried out using a stochastic Liouville equation based on the kinetic constants obtained experimentally. ODMR signals with opposite signs were detected when monitoring the monomer and excimer emissions in the crystal at a high concentration of PyBTM, as shown in Figure 16(c). This is the first observation of an ODMR signal by stable organic radicals. In a radical system, the unpaired electron can be used as probe for studying the electronic state and its dynamics. The excited-state dynamics of a π-radical and its excimer has been clarified, as depicted in Figure 16(d). Thus, a very weakly coupled excited-state radical pair is formed in the initial stage after photoexcitation. Then, the spin selective pathway from the singlet spin configuration of the spin-correlated radical pair to the singlet excimer state leads to the excimer formation (rate constant: k_{Sex}). A dissociation process also occurs from the triplet spin configuration of the spin-correlated radical pair (rate constant: k_{-T}), leading to a monomer emission. The S-T_0 mixing (field-induced ISC) combined to the microwave induced population changes between the triplet-state spin sublevels may lead to opposite signs of the ODMR. The observed ODMR is due to the microwave induced change of the yield between the dissociation to the monomer and the formation of the excimer. Therefore, this ODMR is a novel type of reaction-yield detected magnetic resonance (RYDMR).[118] The initial process of excimer formation has been clarified for the first time from the viewpoint of the spin-dynamics.

5. Applications Using Excited-State Dynamics of π-Radicals

5.1. Photochemical Stabilization

A simple application of the unique excited-state dynamics of π-radicals exploits their EISC mechanism to improve the photostability of photochemically unstable compounds such as pentacene. When a radical species is appended to a chromophore compound, a rapid deactivation of the singlet excited state of the chromophore is expected upon radical induced EISC. We applied this idea to extremely photochemically unstable pentacene derivatives and demonstrated a remarkable radical induced photostabilization effect (radical photo-stabilization).[16-18] Pentacene and its derivatives have received increasing interest as promising electronic materials for organic field-effect transistors (OFETs) owing to their high hole-carrier mobility. Pentacene derivatives also have the potential to serve
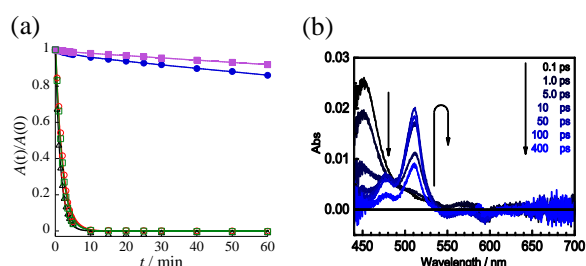
Figure 17. Photochemical stability improvement and the ultra-fast ISC of Pentacene derivatives appended to π-radical. (a) Photochemical stability check. Blue (**7p** in Figure 4), Violet (the compound in which the verdazyl radial moiety in **7p** was replaced to nitronyl-nitroxide radical.), Red and Green are correspond to their precursors and black is pentacene. (b) Time course of the transient absorption spectra of pentacene derivative linked nitronyl-nitroxide radical. Reproduced with permission from ref. [16] and ref. [17]. Copyright 2013 and 2014. John Wiley and Sons.

as spin-current transport media in spintronics devices.[119-121] However, their photochemical instability in the presence of air prevents their practical applications. Figure 17(a) shows the results of the photochemical stability tests conducted on pentacene derivatives appended to π-radical, their relevant precursors, as well as pentacene. The pentacene derivatives appended to a nitronyl-nitroxide (NN) and oxoverdazyl (OV) radical were quite stable in a diluted solution under ambient light (decomposition lifetime under our experimental conditions; τ_{dec} = 2100 (NN) and 960 (OV) min in CH_2Cl_2) compared with the relevant precursor compounds and pentacene itself (τ_{dec} = 1.9 and 2.0 min for the precursors, and τ_{dec}= 1.9 min for pentacene).[16] Figure 17(b) shows the time course of the transient absorption (TA) spectra of the NN compound. The TA spectrum given by the excited-singlet state rapidly decayed, and was quickly converted to the TA spectrum of the relevant excited-triplet state. The characteristic EISC time was ca. 5 and 20 ps for the NN and OV derivatives, respectively.[17] Therefore, the combination of two unstable species (photochemically-unstable pentacene and a radical) can lead to a remarkable protection from photodegradation along with an enhancement of solubility in common organic solvents. In contrast, almost no acceleration of the excited-state processes was observed when σ-conjugated TEMPO was used as radical substituent.[122] Therefore, the π-radical substituents play a key role in determining their attractive and unique behavior. The photochemical stabilization using π-radical substituent(s) is a promising approach applicable to other compounds. Furthermore, pentacene derivatives bearing π-radical substituents are expected to be useful for applications in molecular spintronics.

5.2. Possible Applicable to Information Technology

The application of the excited-state radical dynamics to information technology[123] is still at a basic stage of investigation. Salikhov et al. proposed the role of the observer for the third spin in time-resolved ESR spectra of a light-induced radical pair,[124] and its potential application to a quantum teleportation which is one of the modern technologies of the information transfer.[125-126] The role of the third spin in the initial state preparation (information

input) was discussed in relation to the quantum teleportation. The studies about the spin qubits and the quantum teleportation which are strongly related to the quantum information science were carried out on photogenerated radical pair systems by Wasielewski and coworkers.[127-129] Initially entangled radical pairs constituted of D–C–A triad systems (cf. Figure 7) could serve as coupled spin qubits in quantum information science applications, provided that the spin coherence lifetimes of these systems are long.[127] A rapid electron hopping promoted the spin decoherence in $D^{+•}-C-A_2^{3+•}$, while the interaction between the radical-pair electron spins and nuclear spins of the solvent had little or no effect on the spin dynamics. These observations provided basic information for designing molecular spin qubits with long coherence times, which may be useful for quantum information technology applications. It was also demonstrated that pulse-EPR technique could be used to probe spin coherence of radical pairs that can function as qubit pairs in DNA.[128] The experiment of the quantum teleportation using a covalent donor-acceptor-radical (D–A–R•) molecular system has been also carried out.[129] In this experiment, a specific electron spin state on R• in a magnetic field was prepared by microwave pulse (information input), an entangled charge separated radical pair ($D^{•+}–A^{•-}$) was generated by a photoexcitation (Bell-state formation). Ultrafast electron transfer from $A^{•-}$ to R• carried out spin-state teleportation, that is, the input information on R• moved to $D^{•+}$ by the spin-selective chemical reaction $D^{•+}–A^{•-}–R^• \rightarrow D^{•+}–A–R^-$ through the agency of quantum entanglement. Although the basic teleportation experiment has been demonstrated, the role of the third spin as illustrated in Figure 7 for the information science is still worth of investigation.

5.3. Effective Up-Conversion

The radical induced EISC was utilized to produce an efficient triplet-triplet annihilation (TTA) photon up-conversion.[130] Yaglioglu et al. used a flexible framework bearing σ-conjugated TEMPO (not a π-radical). The flexible framework was introduced to make RTPM possible in solution. A long-lived triplet excited state of the well-known fluorophore boron dipyrromethene (bodipy) was generated with a high triplet quantum yield (Φ_T = 80%) in a toluene solution by EISC, and was used to perform the TTA up-conversion (quantum yield Φ_{UC} = 6.7%). The proposed mechanism of this radical induced efficient up-conversion is shown in Scheme 1. This does not represent an application of the excited-state dynamics of π-radicals. However, if the π-radical induced EISC mechanism shown in Figure 2 could be used to efficiently generate a triplet-state, the radical enhanced TTA up-
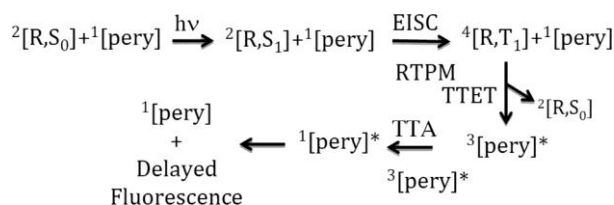
Scheme 1. Proposed Mechanism for the EISC-Promoted TTA Up-conversion. Reproduced with permission from ref. [130]. Copyright 2017, American Chemical Society.

conversion might be possible in the solid phase, since the mechanism of Figure 2 can be available in a fixed framework.

Stable luminescent π-radicals were also employed to attain the TTA photon up-conversion utilizing a doublet-triplet energy transfer.[41] Liu *et al.* used a neutral π-radical such as TTM-NCz (Figure 12) with a remarkable doublet emission, which could be used as triplet sensitizer to initiate the photophysical process of the TTA up-conversion. Figure 18 shows the proposed idea of this radical induced TTA up-conversion. Generally, the energy loss ΔE_{ST} during singlet-triplet ISC is inevitable for the usual photon up-conversion using closed-shell ground state molecules. When a doublet-triplet energy transfer (DTET) occurs upon direct excitation of an organic π–radical, the issue of energy loss can be expected to be overcome, as shown in Figure 18(a) (^{2}D* state in Figure 18(b) should be replaced to the excited doublet state corresponding to the one-electron excitation from β-HOMO to β-SOMO.) The Dexter-like DTET (according to the author's definition) shown in Figure 16(b) leads to an excited triplet state of the acceptor molecules. The authors provided the experimental evidence of the TTA photon up-conversion using TTM-NCz as a triplet sensitizer for 9,10-diphenylanthracene (DPA). By sensitizing the DPA triplet with TTM-1Cz, the incident red light (λex = 635 nm) was successfully upconverted to blue light (λex = 432 nm) in solution, although the up-conversion quantum yield (Φ_{UC}) was low (a saturated value of 0.25%). Here, we wish to highlight that the radical induced electron-exchange EISC mechanism[4] described in this review can be also available to triplet sensitizers for promoting the TTA up-conversion. These are possible new applications of stable luminescent π-radicals
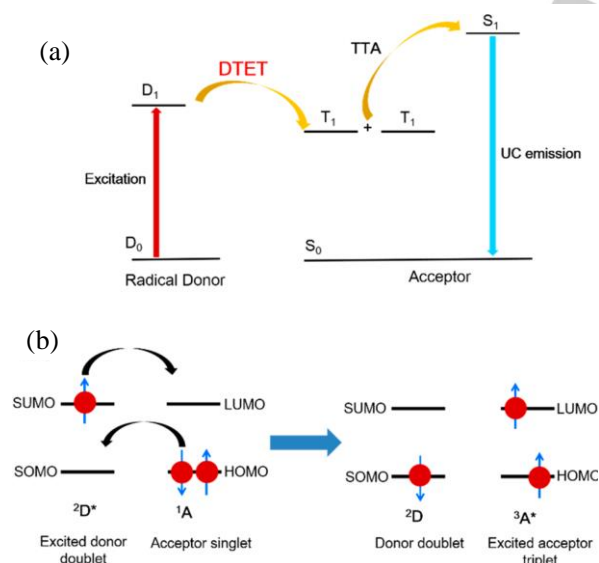

Figure 18. Proposed idea of the radical induced TTA up-conversion. (a) Illustration of TTA-based up-conversion sensitized by doublet exciton. (b) Electron-exchange-based Dexter-like doublet−triplet energy transfer (corresponding to electron-exchange EISC). Reproduced with permission from ref. [41]. Copyright 2017, American Chemical Society.

6. Summary and Outlook

Organic stable π-radicals are fascinating open-shell molecules, which have many potential applications. To date, a huge number of studies have been reported concerning their electronic structures, magnetic properties, chemical reactions, etc. However, many of these reports are focused on their ground-state properties, since organic radicals are usually weakly or non-luminescent. Recently, highly luminescent and stable π-radicals have also emerged, which offer potential application in the development of efficient OLED. Furthermore, the control of the excited state dynamics utilizing organic π-radicals has been described. Potential applications have been demonstrated in the fields of photochemical stabilization, polarization transfer applicable to information technology, and effective up-conversion. However, the following issues remain with regard to the excited-state dynamics of π-radicals: (1) the role of the third spin was clarified only in the case of weakly coupled triad systems, in which the charge separation makes the spin coupling weak. Such role is still unclear for fully π-conjugated systems, in which a radical spin couples strongly to a donor-acceptor system; (2) for π-conjugated biradical systems, their excited-state dynamics has not yet been resolved, including the mechanism of polarization transfer both in the excited and ground-state; (3) the relationship between the electronic structure and luminescent properties has not yet been established. The mechanism that prevents the non-radiative energy-relaxation pathways is little understood; (4) the excited-state dynamics of the π–radicals in the solid phase (single crystal, doped crystal, etc.) is scarcely known, although this knowledge is crucial for technological applications such as OLED, photocontrol of organic magnetism and emission properties, etc. This review may give some useful hints to address the above issues.

The use of organic π-radicals may rapidly expand to modern technological applications. Thus, understanding the unique excited-state dynamics of organic π–radicals and related spin systems will continue to gain importance, especially in view of contributions to modern technology as well as basic science. The unique excited-state dynamics of luminescent and non-luminescent organic π-radicals will attract increasing attention owing to the research interest in a next generation of functional materials.

Acknowledgements

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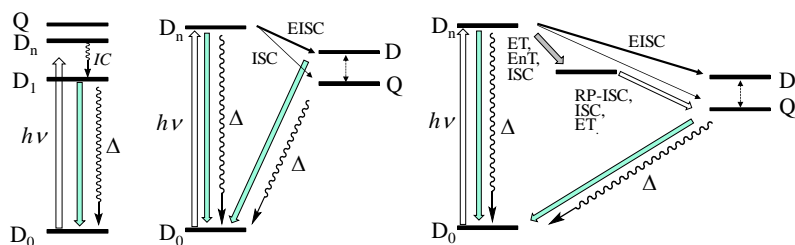**Entry for the Table of Contents** (Please choose one layout)

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Luminescent and non-luminescent π-radicals are located opposite to each other. This review focus on their excited-state dynamics. The following topics on the counter sides are covered: (1) effective generation of high-spin photoexcited states and control of the excited-state dynamics using non-luminescent π-radicals, (2) unique excited-state dynamics of luminescent π-radicals and radical excimers, and (3) applications utilizing excited-state dynamics of π-radicals.

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