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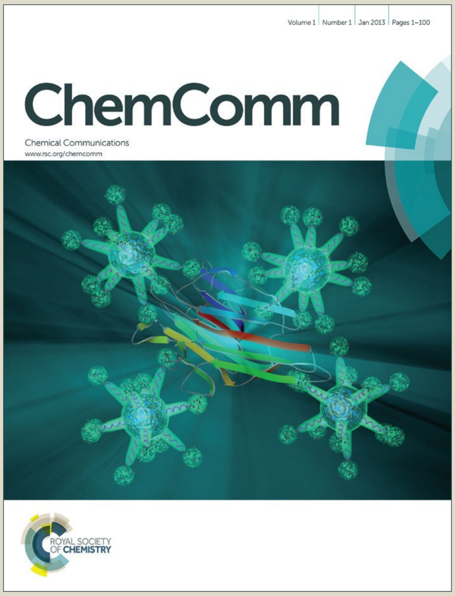

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Photostability Enhancement of Pentacene Derivative Having Two Nitronyl Nitroxide Radical Substituents

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Akihiro Shimizu,[a] Akitaka Ito[a] and Yoshio Teki*[a]

Pentacene derivatives having nitronyl nitroxide radical substituents (1a and 1b) were synthesized, and their photochemical properties were evaluated. 1a with two radical substituents showed remarkable enhancement of photostability compared with pentacene, 6,13-bis(triisopropylsilylethynyl)-pentacene and the monoradical, 1b. This is understood due to the presence of the multiple deactivation pathways in the photoexcited states.

Pentacene (Pn) and its derivatives are promising candidates for organic field-effect transistor (OFET),[1] organic thin-film transistor (OTFT),[2] organic light-emitting diode (OLED)[3] applications, since they act as p-type organic semiconductor owing to its high hole mobility in solid state.[4] However, Pn framework easily decomposes by reacting with oxygen under ambient light.[5] Therefore, development of stable Pn derivatives is an important research theme, and stable Pn derivatives having a bulky and/or electron-withdrawing substituent(s) have been hitherto reported.[2,6,7] As a notable example of such stabilized Pn derivatives, J. E. Anthony and coworkers reported 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn).[6]

Recently, we reported a new strategy for the photostabilization of Pn derivatives. Thus, Pn derivatives having a nitronyl nitroxide radical or dimethyl oxoverdazyl radical substituent (pentacene–radical derivatives) were significantly stable against photodegradation.[8] Detailed analysis for the excited-state dynamics of the pentacene–radical derivatives revealed ultrafast transformation of the Pn moiety from singlet excited state (^{1}Pn*) to triplet excited state (^{3}Pn*) by enhanced intersystem crossing (ISC) and singlet fission, followed by deactivation of ^{3}Pn* to the ground state.[9] These excited-state processes are accelerated in the presence of radical substituent and, thus, result in less photochemical reaction with oxygen. Furthermore, R. R. Tykwinski and coworkers recently reported that Pn derivatives introducing σ-conjugated (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) radical substituent showed electron spin polarization transfer but almost no acceleration of the excited-state processes.[10] Therefore, the π-radical substituent in the pentacene–radical derivatives plays an important role in their attractive and unique behavior. In this study, we synthesized Pn derivatives having one and two nitronyl nitroxide radical substituent(s) (**1b** and **1a**, respectively; Scheme 1) and evaluated the effect of the number of the radical substituents on the spectroscopic and spin properties. Photochemical stability of **1a** was revealed by comparisons with those of **1b**, Pn and TIPS-Pn, which is highly enhanced than that of TIPS-Pn or others.

1a and **1b** were synthesized in the dark using aluminum foil to avoid photodegradation of the Pn moiety. The synthetic route for the derivatives is shown in Scheme 1, and detailed synthetic procedures are described in ESI. 6,13-Dihydropentacene derivative **2** was synthesized from 6,13-pentacenedione by a Grignard reaction with 30% yield and, then, reduced to 4,4'-(pentacene-6,13-diyl)dibenzaldehyde **3** under acidic condition (82% yield). A thermal condensation reaction of **3** with 2,3-bis(hydroxyamino)-2,3-dimethylbutane in a 1,2-dichloroethane/methanol mixture gave crude **4** as a mixture of the derivatives with one and two precursor(s) of the radical substituent. Finally, oxidation of crude **4** by $NaIO_4$ gave **1a** (18% yield) and **1b** (9% yield) which were isolated by silica-gel column chromatography.

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[a] *Division of Molecular Material Science, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan. E-mail: teki@sci.osaka-cu.ac.jp*

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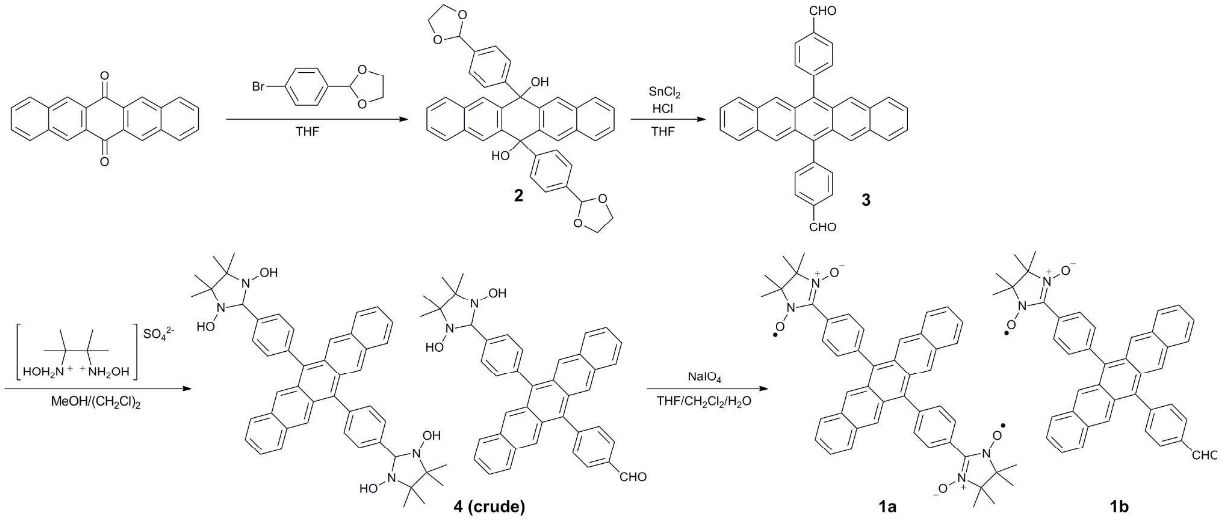


Scheme 1. Synthetic route for **1a** and **1b**.

Electron spin resonance (ESR) spectra of the derivatives in degassed toluene at room temperature are shown in Figures 1a and 1b. The spectrum of **1b** was adequately analyzed as nitronyl nitroxide mono-radical,[11] using a hyperfine coupling constant of two equivalent nitrogen atoms (a_{N}) and g factor of 0.73 mT and 2.0062, respectively. ESR spectrum of **1a** exhibited 9 line signals, which differs from that of **1b**. This result indicates the existence of the exchange interaction between two nitronyl nitroxide radical substituents. Therefore, the spectrum of **1a** was simulated by including exchange interaction, whose spin Hamiltonian is giving by:

$$\mathcal{H} = g_1\beta_e \boldsymbol{B}\cdot\boldsymbol{S_1} + \textstyle\sum_{\boldsymbol{j}} a_{j(\mathrm{N})}\cdot\boldsymbol{S_1}\cdot\boldsymbol{I_1} + g_2\beta_e\boldsymbol{B}\cdot\boldsymbol{S_2} + \textstyle\sum_{\boldsymbol{k}} a_{k(\mathrm{N})}\cdot \boldsymbol{S_2}\cdot\boldsymbol{I_2} - 2J\boldsymbol{S_1}\cdot\boldsymbol{S_2} \qquad (1)$$

In Eq (1), g_1 and g_2 are g factors. β_e is Bohr magneton. $\boldsymbol{B}$ is external magnetic field. $\boldsymbol{S_1}$ and $\boldsymbol{S_2}$ are electron spin operators. $\boldsymbol{I_1}$ and $\boldsymbol{I_2}$ are nuclear spin operators. a_j and a_k are hyperfine coupling constants in the radical moieties. J is exchange coupling constant. Simulated spectrum of **1a** agreed with observed one by using $|J| \geq 2.5 \times 10^8$ Hz, $a_{j(\mathrm{N})} = a_{k(\mathrm{N})} = 0.74$ mT for four equivalent nitrogen atoms and $g_1 = g_2 = 2.0065$ mT. Thus, two radical substituents in **1a** couple through strong exchange interaction.

The steady-state absorption spectra of **1a** and **1b** were measured in THF, which are shown in Figure 1c together with those of Pn and TIPS-Pn. The $^1\pi\pi^*$ transition in the Pn moiety was observed at around 599 nm, which was irrespective of the derivatives. The molar absorption coefficient (ε) of **1a** was almost identical to that of **1b**. Their $^1\pi\pi^*$ bands were shifted to longer wavelength region compared with that of Pn, indicative of $^1\pi\pi^*$ stabilization by introducing two phenylene groups. These characteristics of the spectra were well reproduced by TD-DFT calculations for **1a**, **1b**, Pn and 6,13-diphenylpentacene: see ESI. Additional features in the spectra of **1a** and **1b** were observed around 700 and 365 nm, which are attributed to nπ and ππ* transitions in the nitronyl nitroxide radical substituent(s), respectively.[11] The ε values of the bands of **1a** (3700 and 31400 $\mathrm{M^{-1}\,cm^{-1}}$ at 700 and 365 nm, respectively) are almost twice larger than those of **1b** (1900 and 18100 $\mathrm{M^{-1}\,cm^{-1}}$ at 700 and 365 nm, respectively), which evidences the assignments of the bands (i.e., nπ and ππ* transitions in nitronyl nitroxide radical substituent(s)).

Fluorescence spectra of **1a**, **1b** and Pn were also measured in THF (see Figure S2 in ESI). The band shapes of fluorescence from **1a** and **1b** were similar to that from Pn, but their intensities were greatly reduced. As summarized in Table 1, the fluorescence quantum yields (Φ_{f}) of **1a** and **1b** are quite small (<0.0004 and <0.0008, respectively), while Pn and TIPS-Pn are fluorescent (Φ_{f} = 0.13 and 0.30, respectively).

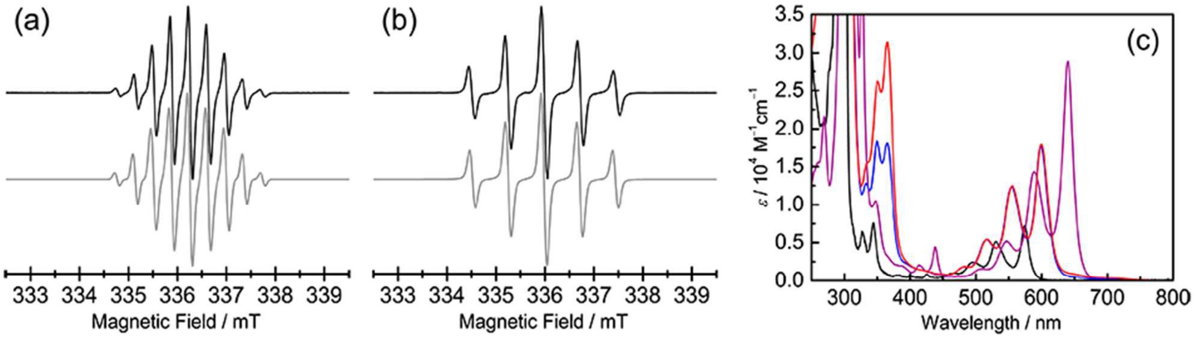


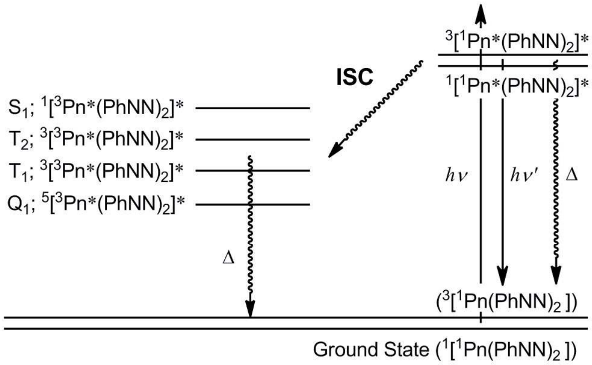
Figure 1. Observed ESR spectra of **1a** (a) and **1b** (b) in oxygen-free toluene at room temperature (black curve) and steady-state absorption spectra of **1a** (red), **1b** (blue), Pn (black) and TIPS-Pn (purple) in THF (c). Gray curves in (a) and (b) represent simulated ESR spectra by the parameters in Table 1.

Table 1. Spectroscopic and photochemical properties of the derivatives in air-saturated THF and parameters for ESR simulation.

Derivatives	λ_a / nm (ε / 10^3 M^{-1} cm^{-1})				λ_f / nm	Φ_f	*g* factor	$a_{(N)}$ / mT	k / s^{-1}
1a	351 (26.2)	365 (31.4)	600 (17.9)	700 (0.37)	604	< 0.0004	2.0065	0.74	3.9×10^{-7}
1b	349 (18.3)	365 (18.1)	599 (17.6)	700 (0.19)	609	< 0.0008	2.0062	0.73	1.0×10^{-6}
Pn	344 (7.6)		574 (7.2)		581	0.13 (±0.02)			1.7×10^{-3}
TIPS-Pn	347 (10.4)	438 (04.4)	640 (28.9)		647	0.30 (±0.03)			1.3×10^{-6}, 5.4×10^{-6}

Photochemical stabilities of **1a** and **1b** in air-saturated THF at room temperature under irradiation of He-Ne laser (543.5 nm) were evaluated by comparing with Pn and TIPS-Pn. As shown in Figure 2, the $^1\pi\pi^*$ bands in the Pn moiety were reduced over time, indicative of a cutoff of π-conjugation in the Pn moiety. It should be noted that Pn and TIPS-Pn showed negative signals at 590–670 and 660–790 nm, respectively, during laser irradiation, which are attributed to fluorescence from Pn moiety by the excitation light. In contrast to rapid disappearance of the $^1\pi\pi^*$ band of Pn within ~10 min (Figure 2c), the $^1\pi\pi^*$ bands of **1a**, **1b** and TIPS-Pn in the Pn moiety did not change almost at all within these timescales and spectral changes were observed in several tens of hours.

Time variations of absorbance for the derivatives are shown in Figure 3, in which absorbance at 543.5 nm are subtracted by those at 800 or 900 nm to remove the effect of baseline drift. Their decays were adequately fitted by Eq (S9), in which the decrease in the absorbance at the excitation wavelength was taken into account (see ESI), and the rate constants (k) as measures of the decomposition reaction were determined to be 3.9×10^{-7} (**1a**), 1.0×10^{-6} (**1b**), 1.7×10^{-3} (Pn), and 1.3×10^{-6} and 5.4×10^{-6} s^{-1} (TIPS-Pn)[12]: see Table 1. Photochemical stability of **1a** is larger than those of TIPS-Pn and **1b** presumably due to the presence of two radical substituents. It should be noted that **1a** and **1b** showed quite weak fluorescence in spite of intense fluorescence from TIPS-Pn. This finding indicates the difference in the photostabilization mechanisms between **1a**/**1b** and TIPS-Pn. This means the existence of the rapid pathways to deactivate the ^{1}Pn* through lower-lying ^{3}Pn* in **1a** and **1b**. We previously reported that ISCs in Pn and anthracene derivatives were enhanced by introducing radical substituent(s),[9,13] and a similar phenomenon was also observed as ultrafast ISC for perylene-3,4:9,10-bis(dicarboximide) derivatives with radical substituent(s).[14] The ^{1}Pn* in **1a** is expected to be converted to ^{3}Pn* more efficiently than that in **1b** by enhanced spin–orbit ISCs arising from two radical moieties. In addition, multiple pathways to deactivate ^{1}Pn* to other excited spin states with lower energy are expected as a schematic illustration for **1a** is shown in Scheme 2. Three spin-allowed pathways, in which overall spin multiplicities of the molecule do not change, ($^3[^1\text{Pn}^*(\text{PhNN})_2]^* \rightarrow {}^3[^3\text{Pn}^*(\text{Ph}^*\text{NN})_2]^*$ (T_1) $\rightarrow {}^3[^1\text{Pn}(\text{PhNN})_2]$ (T_0), $^3[^1\text{Pn}^*(\text{PhNN})_2]^* \rightarrow {}^3[^3\text{Pn}^*(\text{Ph}^*\text{NN})_2]^*$ (T_2) $\rightarrow {}^3[^1\text{Pn}(\text{PhNN})_2]$ (T_0), $^1[^1\text{Pn}^*(\text{PhNN})_2]^* \rightarrow {}^1[^3\text{Pn}^*(\text{Ph}^*\text{NN})_2]^*$ (S_1) $\rightarrow {}^1[^1\text{Pn}(\text{PhNN})_2]$ (T_0)) exist in **1a**. As a result, ^{1}Pn* in **1a** deactivates to the ground state more rapidly than that in **1b** and, thus, **1a** shows larger photochemical stability since photoinduced reaction of Pn derivatives mainly occurs in ^{1}Pn*.[15]



Scheme 2. Excited-state processes of **1a**. Pn, Ph and NN denote the pentacene, phenylene, and nitryonyl nitroxide radical moieties, respectively. S, T and Q denote the singlet, triplet and quintet excited states, respectively.

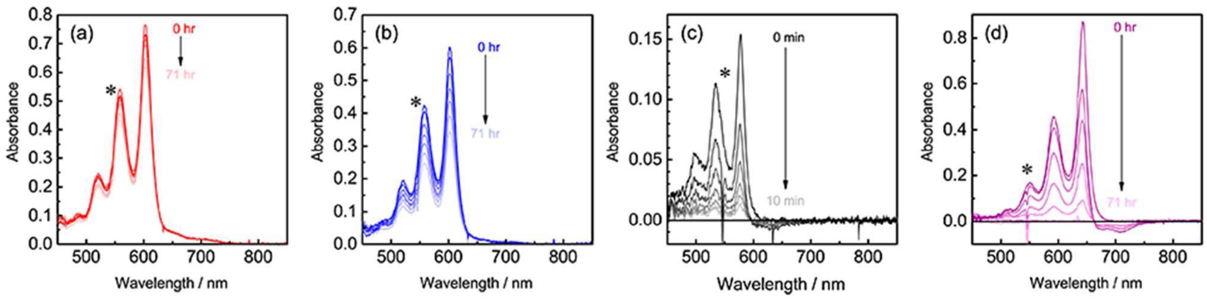


Figure 2. Time variation in absorption spectra of **1a** (a), **1b** (b), Pn (c) and TIPS-Pn (d) in air-saturated THF solution at room temperature upon photoirradiation. *; spike signals at 543.5 nm are due to detection of excitation light.

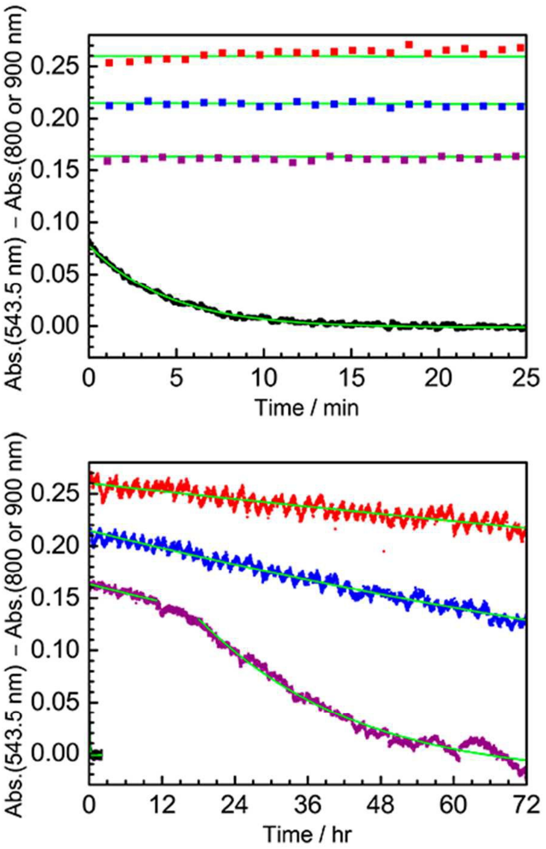


Figure 3. Time variation of absorbance for **1a** (red), **1b** (blue), Pn (black) and TIPS-Pn (purple) in air-saturated THF at room temperature by photoirradiation. Green curves represent the theoretical fit to Eq (S9).

In conclusion, we revealed that Pn derivative (**1a**) having two nitronyl nitroxide radical substituents shows remarkable enhancement of the stability against photodegradation. The photostability exceeded that of the TIPS-Pn as the famous example of stable Pn derivatives. This stabilization of Pn moiety is understood due to the formation of the multiple deactivation pathways in the photoexcited states, that are accelerated due to enhanced ISC by borrowing the spin–orbit interactions of two radical moieties and three spin-allowed pathways from the ^{1}Pn* to the lower-energy spin states.

We can expect that photochemical stabilization using radical substituent(s) is a promising approach applicable to other compounds. Furthermore, Pn derivatives having radical substituents are expected for applications to molecular spintronics.

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