Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information for
"Photostability Enhancement of Pentacene Derivative Having Two Nitronyl Nitroxide Radical Substituents"

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General Experimental. **1a** and **1b** were synthesized from 6,13-pentacenedione as a starting material according to the procedures shown in Scheme 1. 6,13-pentacenedione, other reagents and solvents were purchased from either Sigma-Aldrich Co., Inc., Kanto Chemical Co., Inc., Tokyo Kasei Kogyo Co., Ltd., Merck & Co., Inc., or Wako Pure Chemical Ind., Ltd., and used without further purification unless otherwise indicated. Melting points were determined with an AS ONE ATM-1 melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on an either Bruker AVANCE400 (400 MHz, 100 MHz) or Bruker AVANCE300N (300 MHz, 75 MHz) spectrometer. Chemical shifts of ^{1}H NMR and ^{13}C NMR were reported in parts per million (ppm, δ) relative to those of tetramethylsilane (δ = 0 ppm) or solvent residual signals (δ = 7.26 (^{1}H) and 77.1 ppm (^{13}C) in $CDCl_3$, δ = 5.32 (^{1}H) and 53.84 ppm (^{13}C) in CD_2Cl_2, δ = 2.49 (^{1}H) and 39.5 ppm (^{13}C) in $(CD_3)_2SO$). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700(S) for fast atom bombardment (FAB), JEOL AccuTOF LC-plus JMS-T100LP for electrospray ionization (ESI) or direct analysis in real time (DART). Elemental analysis data were obtained on a J-Science MICRO CORDER JM10. All reactions were monitored by thin layer chromatography (TLC), which was performed with precoated plates (Merck silica gel 60 F_{254}) and visualized by using UV lamp. Daiso IR-60 1002W (40/63 mm) was used for flash column chromatography. THF for the syntheses of **1a** and **1b** and spectroscopic measurements were purified by passing through aluminum oxide 90 active basic (Merck & Co., Inc.) prior to the use. Since pentacene framework is known to be unstable under ambient light, the syntheses were carried out in the dark and the experimental apparatuses were covered with aluminum foil.

Synthetic Procedures and Characterization Data

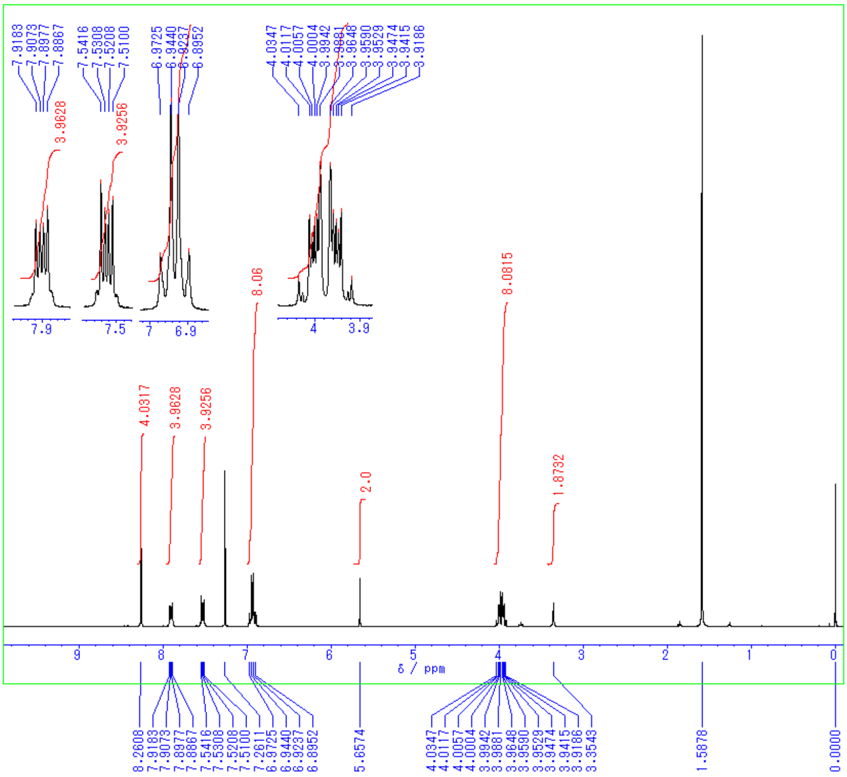
6,13-bis(4-(1,3-dioxolan-2-yl)phenyl)-6,13-dihydropentacene-6,13-diol (2). 2-(4-bromophenyl)-1,3-dioxolane was synthesized according to the literature method.[S1] To a suspension of Mg turning (0.96 g, 51.3 mmol) in anhydrous THF (8 mL) was added I_2 grain (0.02 g, 0.08 mmol) under argon. A solution of 2-(4-bromophenyl)-1,3-dioxolane (11.76 g, 51.3 mmol) in anhydrous THF (20 mL) was inserted in a dropping funnel. To the suspension was added around 1/3 volume of the solution of 2-(4-bromophenyl)-1,3-dioxolane. After reaction was started, the remained THF solution of 2-(4-bromophenyl)-1,3-dioxolane was also added to the suspension dropwise for over 70 min. The mixture was stirred at room temperature for 75 min to give the Grignard reagent.

To the mixtures of the Grignard reagent was added THF (80 mL) and 6,13-pentacenedione (2.05 g, 6.65 mmol) and, then, the reaction mixture was heated with stirring overnight at 50°C. After addition of THF (100 mL), the mixture was washed with saturated aqueous solution of NH_4Cl (130 mL × 3). The organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. Residual THF was removed by two cycles of 1,2-dichloroethane (50 mL) addition and concentration under reduced pressure. The resulting solid was suspended in 1,2-dichloroethane (50 mL) and filtered off. **2** as a colorless powder was obtained by 3 cycles of 1,2-dichloroethane (50 mL) hot filtration (1.20 g, 30%). mp: 274–275°C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 8.26 (s, 4H), 7.90 (dd, J = 6.18, 3.30 Hz, 4H), 7.53 (dd, J = 6.24, 3.24 Hz, 4H), 6.90–6.97 (m, 8H), 5.66 (s, 2H), 3.92–4.03 (m, 8H), 3.35 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 143.7, 139.7, 137.0, 132.8, 128.1, 127.9, 126.5, 125.9, 125.6, 103.3, 77.2, 65.1; HRMS (FAB+ m/z): $[M+H]^+$ calcd for $C_{40}H_{33}O_6$, 609.2277; found 609.2290; analysis (calcd, found for $C_{40}H_{32}O_6$):C(78.93, 78.72) H(5.30, 5.34).

4,4'-(pentacene-6,13-diyl)dibenzaldehyde (3). To a suspension of **2** (0.43 g, 0.71 mmol) in THF (20 mL) was added a solution of $SnCl_2$ in conc. HCl (2.36 mol L^{-1}, 4 mL). After stirring at room temperature for 30 min, H_2O (150 mL) was added. The resulting dark purple powder was collected by filtration, washed with an excess of H_2O, ethanol and *n*-hexane, and purified by silica gel column chromatography (eluent: CH_2Cl_2) to give **3** as a dark purple powder (0.28 g, 82% yield). mp: >300°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ/ppm 10.34 (s, 2H), 8.31 (s, 4H), 8.30 (d, J = 8.24 Hz, 4H), 7.89 (d, J = 7.92 Hz, 4H), 7.76–7.78 (m, 4H), 7.31–7.33 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ/ppm 192.1, 146.1, 136.2, 136.1. 132.6. 131.3, 130.0, 128.3, 128.1, 125.7, 125.1,; HRMS (ESI+ *m*/*z*): $[M]^+$ calcd for $C_{36}H_{22}O_2$, 486.1620; found 486.1631; analysis (calcd, found for $C_{36}H_{22}O_2$): C(88.87, 88.63), H(4.56, 4.70).

2,2'-(pentacene-6,13-diylbis(4,1-phenylene))bis(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl) (1a) and 4-(13-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)pentacen-6-yl)benzaldehyde (1b). A suspension of 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (0.77 g, 3.13 mmol) and K_2CO_3 (0.76 g, 5.50 mmmol) in MeOH (30 mL) was stirred at room temperature for 80 min under argon. The mixture was filtrated and washed with MeOH (10 mL). The filtrate was taken into a round bottom flask and **3** (0.18 g, 0.37 mmol) in 1,2-dichloroethane (50 mL) was added. The solution was refluxed for 3 days under argon in the dark. The mixture was filtrated, washed with 1,2-dichloroethane, affording **4** (including 1/0.26 (mol/mol) ratio of the precursors for **1a** and **1b** based on ^{1}H NMR) as a dark purple powder, which was employed in the following process without further purification.

To a suspension of **4** (170.2 mg) in CH_2Cl_2 (15 mL) and THF (10 mL) was added a solution of $NaIO_4$ (432.2 mg, 2.02 mmol) in H_2O (20 mL) in the dark. The reaction mixture was stirred at room temperature for 60 min and, then, added to saturated aqueous solution of $NaHCO_3$(aq.) (15 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3), and washed with H_2O (40 mL × 2) and brine. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/ethyl acetate = 9/1) to give **1a** (50.1 mg, 18% from compound **3**) and **1b** (24.3 mg, 9% from compound **3**) as dark blue purple powders. **1a**: mp: 280–281°C (decomp.); TLC (CH_2Cl_2/ethyl acetate = 9/1): R_f = 0.34; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{48}H_{45}O_4N_4$, 743.3441; found 741.3440; analysis (calcd, found for $C_{48}H_{44}O_4N_4 \cdot 0.8C_3H_8O_2$): C(75.87, 75.83), H(6.28, 6.25), N(6.91, 6.97). **1b**: mp: 222–223°C (decomp.); TLC (CH_2Cl_2/ethyl acetate = 9/1): R_f = 0.57; HRMS (*m*/*z*): $[M]^+$ calcd for $C_{42}H_{33}O_2N_3$, 613.2491; found 613.2490.



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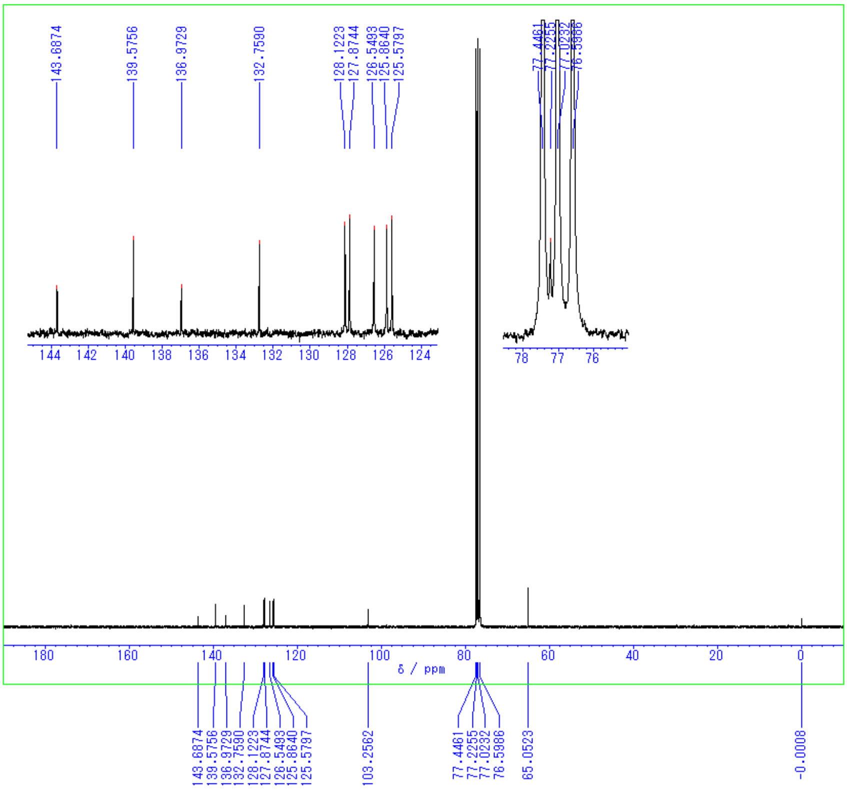
^{1}H NMR spectrum of **2**



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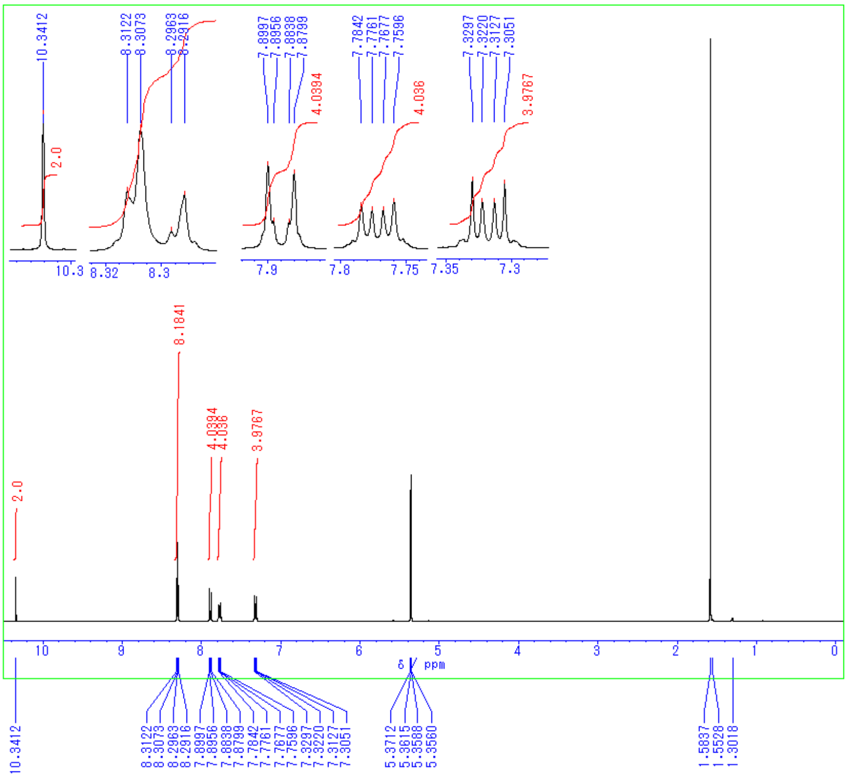

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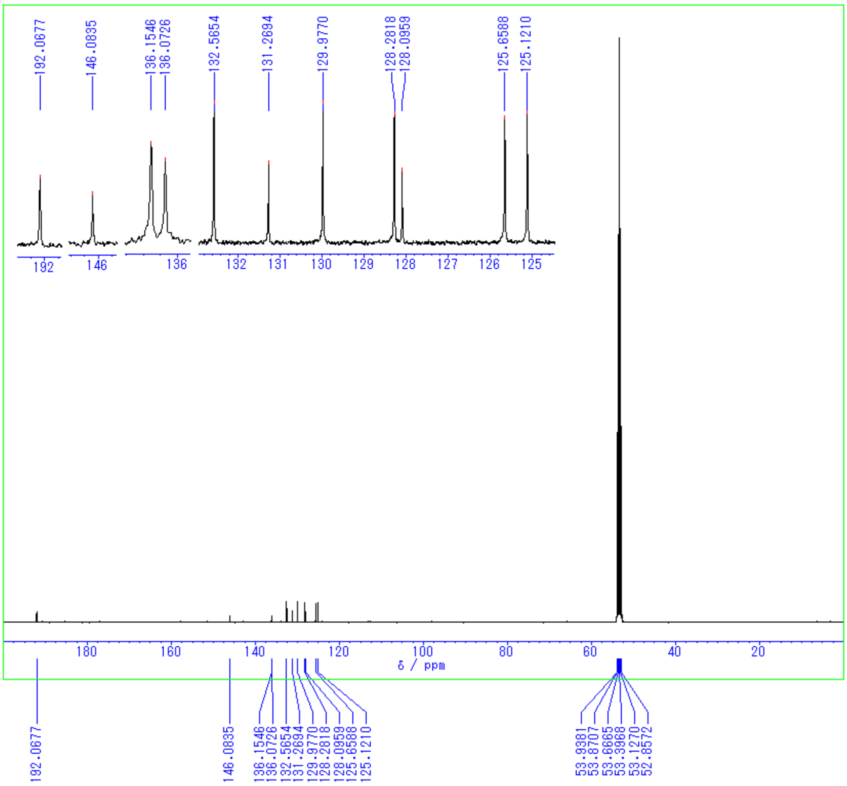

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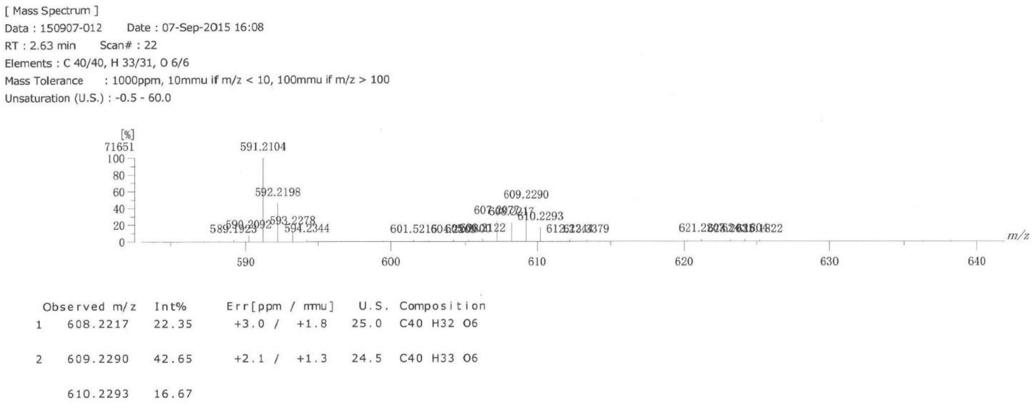
^{13}C NMR spectrum of **3**

HRMS of **2**



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Mass Tolerance : 1000ppm, 10mmu if m/z < 10, 100mmu if m/z > 100
Unsaturation (U.S.) : -0.5 - 60.0

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 Observed m/z  Int%     Err[ppm / mmu]   U.S.  Composition
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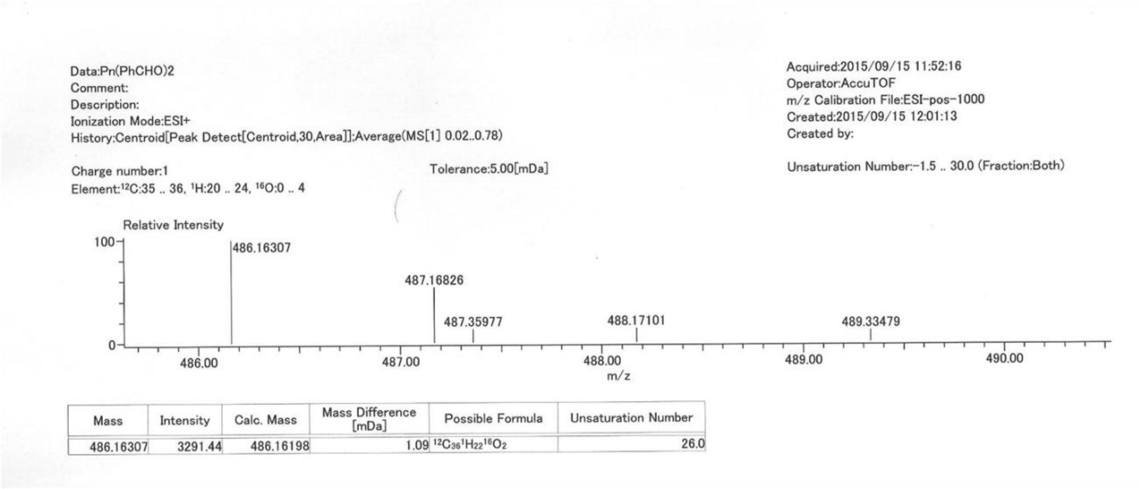
2   609.2290   42.65     +2.1 /  +1.3    24.5  C40 H33 O6

    610.2293   16.67
```

HRMS of **3**



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Comment:
Description:
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Charge number:1
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Tolerance:5.00[mDa]

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m/z Calibration File:ESI-pos-1000
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Created by:

Unsaturation Number:-1.5 .. 30.0 (Fraction:Both)

Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Possible Formula	Unsaturation Number
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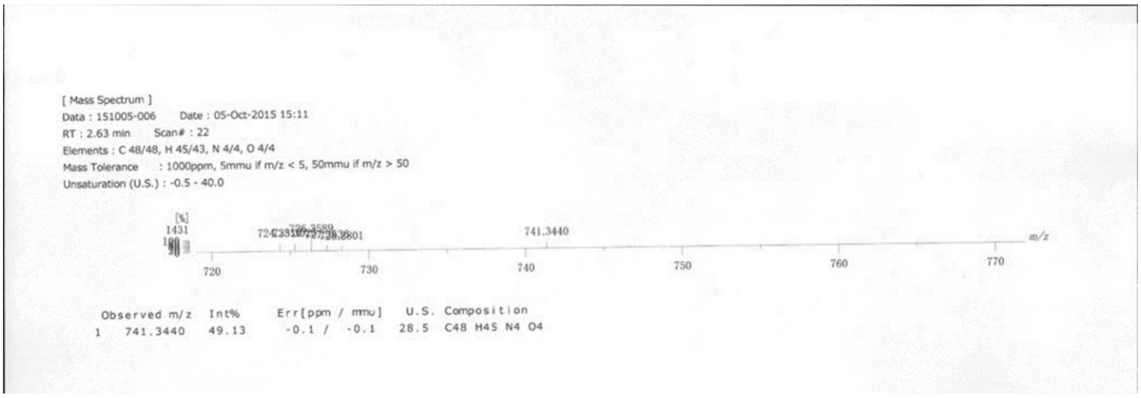
HRMS of **1a**



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  Observed m/z   Int%      Err[ppm / mmu]   U.S.  Composition
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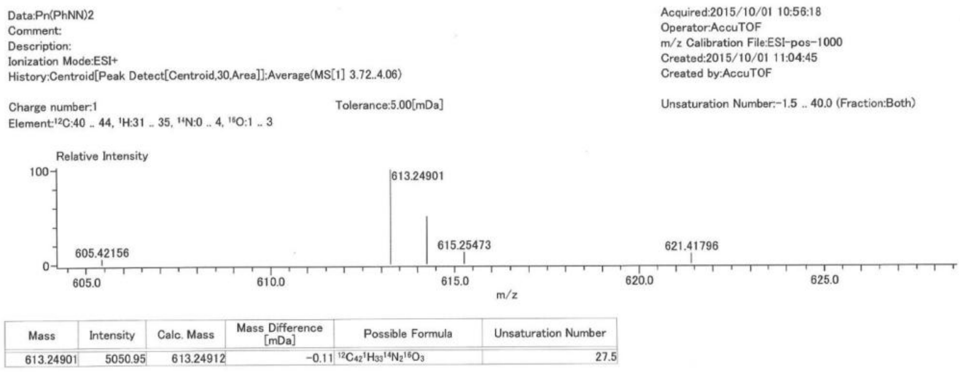
HRMS of **1b**



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Charge number:1
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Tolerance:5.00[mDa]

Unsaturation Number:-1.5 .. 40.0 (Fraction:Both)

Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Possible Formula	Unsaturation Number
613.24901	5050.95	613.24912	-0.11	$^{12}C_{42}{}^{1}H_{33}{}^{14}N_2{}^{16}O_3$	27.5

Spectroscopic Measurements

Steady-state absorption and fluorescence spectra of the derivatives were measured by a Hitachi U-3500 spectrophotometer and a Hitachi F-7000 spectrofluorometer, respectively. Molar absorption coefficients of the derivatives in THF were determined by concentration dependence of the absorption spectrum. For the fluorescence measurements of the derivatives in THF, the absorbance of a sample solution at the excitation wavelength (λ^{ex} = 554 nm) was set at <0.05 to avoid self-absorption and inner filter effects.

The absolute fluorescence quantum yields of Pn and TIPS-Pn in aerated THF were measured by an Otsuka Electronics QE-2000-3095C quantum efficiency measurement system equipped with an integrating hemisphere and a low stray-light spectrometer using 530- and 550-nm light for excitation, respectively. Since the fluorescence from **1a** or **1b** was very weak and their absolute fluorescence quantum yields were not measurable, the fluorescence quantum yields of **1a** and **1b** in aerated THF were estimated relatively to that of Pn in the same solvent ($\Phi_f = 0.13 \pm 0.02$ determined by the absolute method) based on an equation, $\Phi_{f,sample} = \Phi_{f,Pn} \times (S_{sample}/A_{sample})/(S_{Pn}/A_{Pn})$ where the subscripts of “sample” and “Pn” denote sample and pentacene, respectively, and S and A are the area of a fluorescence spectrum in a wavenumber scale and the absorbance at an excitation wavelength (554 nm), respectively. The emission intensity at each wavelength ($I(\lambda)$) was converted into the photon number in a wavenumber scale ($n(\tilde{\nu})$) by using an equation, $n(\tilde{\nu}) = I(\lambda) \times \lambda^3$.[S2]

Electron Spin Resonance (ESR) Measurements

ESR spectra of **1a** and **1b** were measured in toluene at room temperature by a JEOL JES-TE300 ESR spectrometer. Sample solutions were degassed by freeze-pump-thaw method. Typical experimental parameters are as follows; 100 kHz magnetic field modulation, 0.02 mT modulation width, 0.1 sec time constant. The microwave frequency and power were 9.442 GHz and 1.01 mW for **1a**, and 9.434 GHz and 1.00 mW for **1b**.

Theoretical Calculations

Molecular-orbital calculations for the derivatives were carried out with Gaussian 09W.[S3] Optimization of their molecular structures in the ground state was performed by using DFT with the UB3LYP (for **1a** (triplet state) and **1b** (doublet state)) and B3LYP (for Pn, TIPS-Pn and 6,13-diphenylpentacene (singlet states)) functional, respectively. The 6-31G(d,p) basis sets were chosen in all calculations. TD-DFT calculations were performed to estimate transition energies and oscillator strengths for the optimized geometries of the derivatives. The solvation effect of THF was taken into account in the calculations by using a Polarizable Continuum Model (PCM). Calculated squares of the total spin angular momentum of **1a** and **1b** were 2.0061 (2.1174 before annihilation) and 0.7505 (0.8091 before annihilation), respectively.

Time Variation Measurements of Absorption Spectra

Time variations of absorbance in the derivatives were measured by a K-MAC SV2100 spectrophotometer. A continuous-wave Helium-Neon laser (Melles Griot, 543.5 nm, 730 μW) was used as an excitation light to induce reaction, and irradiated through iris diaphragm (laser power: around 540 μW) to the sample solution in THF (~2 mL) vertically from the probe light in the spectrometer. During the measurement, the solution was stirred by a magnetic stirrer (IKA topolino). Pentacene (Pn) was purified by sublimation.

Due to inadequacy of the wavelength correction for the spectrometer, the monitored wavelength indicated in Figure 3 is slightly different (~2.6 nm) from the actual wavelength. We have confirmed that the time variations of the absorbance at 543.5 nm in Figure 3 are not affected by the detection of the excitation light and that trend of the time variation is independent of the monitored wavelength as shown in Figure S4.

Analyses of Time Variation of Absorbance

Reaction scheme of excited-state pentacene with oxygen can be written as

$$^{1}\mathrm{Pn} \xrightarrow{h\nu} {}^{1}\mathrm{Pn}^{*} + \mathrm{O}_2 \xrightarrow{k_{\mathrm{dec}}} \mathrm{Pn}_{\mathrm{dec}} \tag{S1}$$

where k_{dec} is decomposition rate constant of pentacene.

On the basis of the Lambert–Beer law;

$$\mathrm{Abs} = -\log_{10}(I/I_0) = \varepsilon \times c \times l \tag{S2}$$

$$I = I_0 10^{-\mathrm{Abs}} \tag{S3}$$

where ε is molar absorption coefficient, c is molar concentration and l is optical path length, light intensity absorbed by a sample ($I_0 - I$) is given by

$$I_0 - I = I_0(1 - 10^{-\mathrm{Abs}}) \tag{S4}$$

Eq (S4) represents a proportional relationship between the number of excited molecule and $(1 - 10^{-\mathrm{Abs}})$. Therefore, the number of decomposed molecule by photoexcitation (Mn) is given as Eq (S5) using the reaction quantum yield Φ_{dec} and constant α to convert light intensity to photon number (i.e., 2.74×10^{18} photons/J at 543.5 nm).

$$\mathrm{Mn} = \alpha\Phi_{\mathrm{dec}}I_0(1 - 10^{-\mathrm{Abs}}) \tag{S5}$$

Time variation of the absorbance is given as a function of the number of decomposed molecule as in Eq (S6).

$$\frac{d\mathrm{Abs}}{dt} = \varepsilon\frac{dc}{dt}l = -\varepsilon\frac{\alpha\Phi_{\mathrm{dec}}I_0\left(1-10^{-\mathrm{Abs}}\right)}{V}l = -k\left(1 - 10^{-\mathrm{Abs}}\right) \tag{S6}$$

Eq (S6) was facilely converted into Eq (S7) and, then, the time-dependent absorbance Abs(t) was obtained as in Eq (S8).

$$\int_{\mathrm{Abs}(0)}^{\mathrm{Abs}(t)} \frac{1}{1-10^{-\mathrm{Abs}}}\, d\mathrm{Abs} = \int_0^t -kdt \tag{S7}$$

$$\mathrm{Abs}(t) = -\log\left\{\frac{10^{kt}}{\frac{1-10^{-\mathrm{Abs}(0)}}{10^{-\mathrm{Abs}(0)}}+10^{kt}}\right\} = \log\left\{1 + \frac{10^{\mathrm{Abs}(0)}-1}{10^{kt}}\right\} \tag{S8}$$

For fitting of the time variation data, an equation considering a vertical offset (y_0) was employed. It should be noted that the time variations for **1a**, **1b** and early stage of TIPS-Pn were fitted by fixing $y_0 = 0$ since they did not give adequate fits due to the absence of the data to evaluate the offsets.

$$\mathrm{Abs}(t) = \log\left\{1 + \frac{10^{\mathrm{Abs}(0)}-1}{10^{kt}}\right\} + y_0 \tag{S9}$$

Steady-State Absorption and Fluorescence Spectra

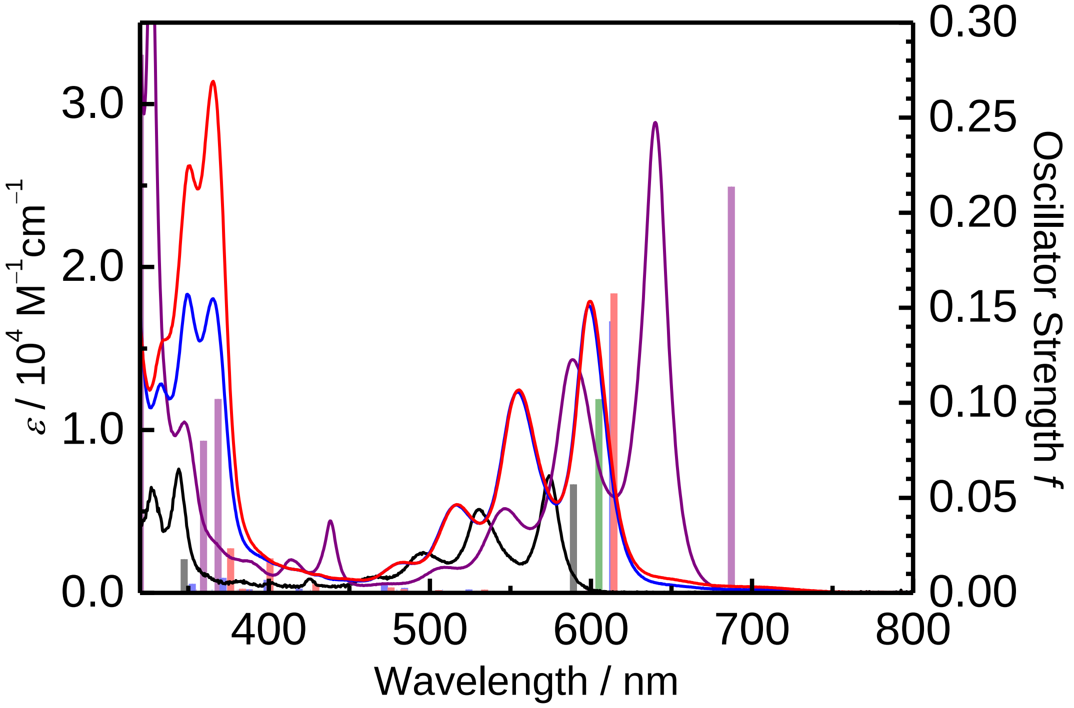
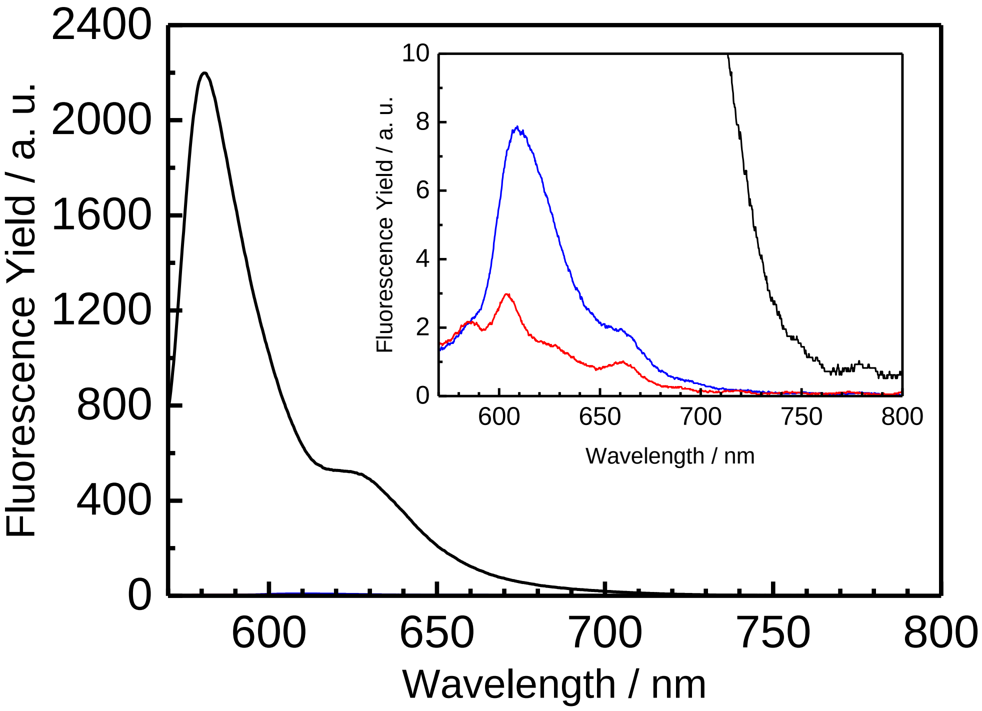


Figure S1. Observed steady-state absorption spectra of **1a** (red),**1b** (blue), Pn (black) and TIPS-Pn (purple) in THF. Vertical bars represent transitions of the derivatives calculated by TD-DFT, together with the calculation for 6,13-diphenylpentacene (green). Calculation results were horizontally shifted to the higher-energy region by a factor of 1.1 in energy to consider underestimation of transition energy by TD-DFT method.[S4]



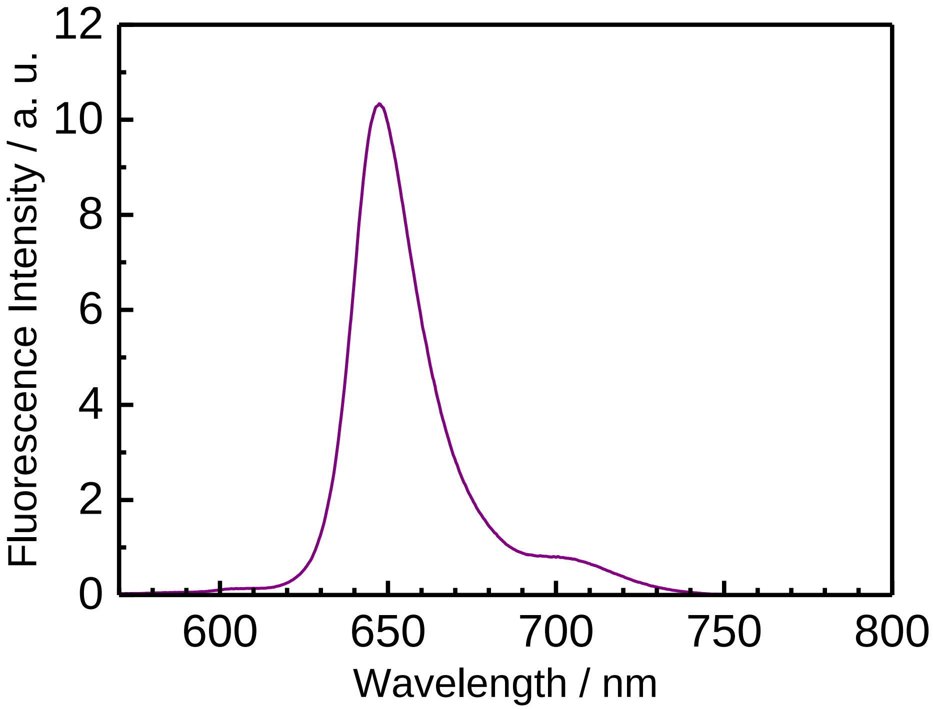


Figure S2. Fluorescence spectra of **1a** (red), **1b** (blue), Pn (black) and TIPS-Pn (purple) in THF.

Spin Densities of the Derivatives in the Ground State

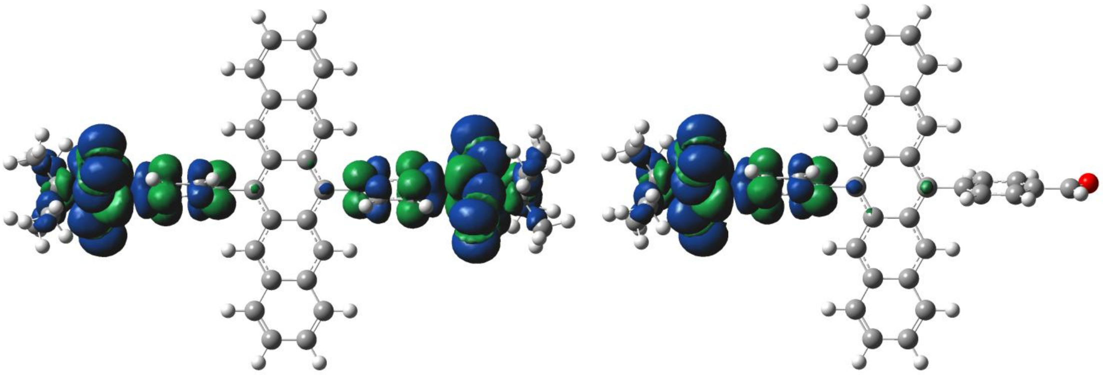
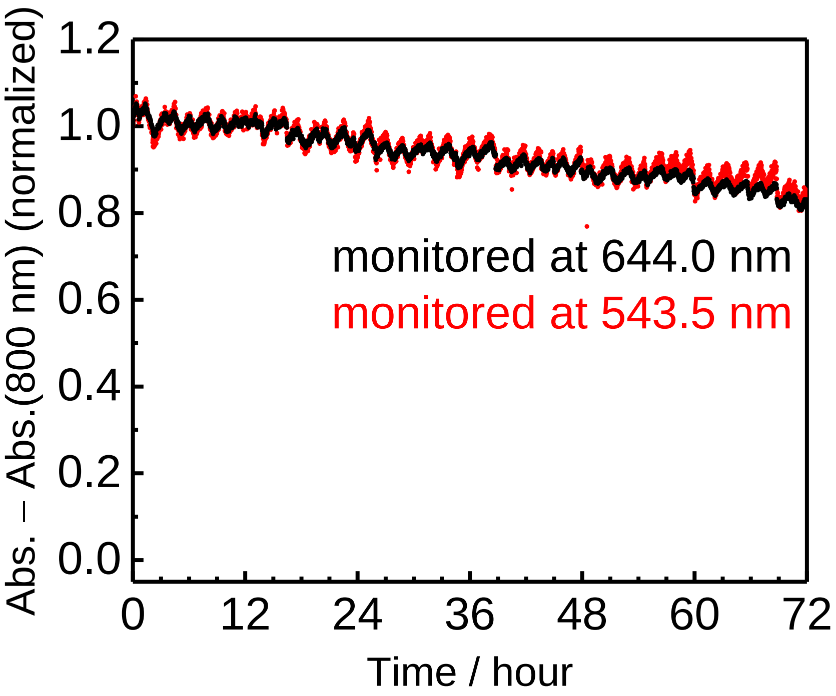


Figure S3. Spin densities of **1a** (left) and **1b** (right) in the ground states.

Monitored-Wavelength Dependence of Time Variation of the Absorbance



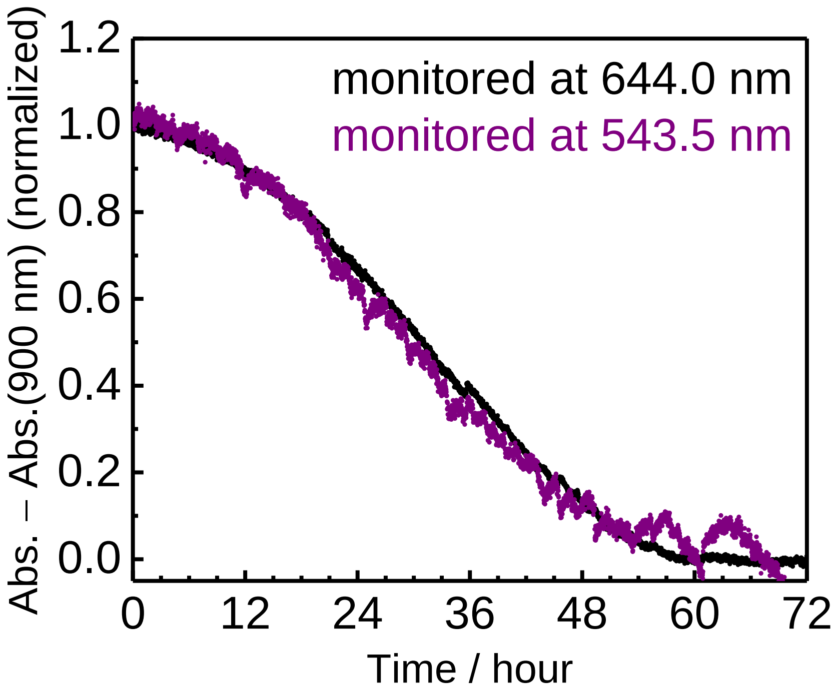


Figure S4. Monitored wavelength dependences of the time variations of the absorbance for **1a** (top) and TIPS-Pn (bottom).

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