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Photochemical synthesis and electronic spectra of fulminene ([6]phenacene)

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Abstract Facile synthesis of fulminene ([6]phenacene) was achieved through the Mallory reaction of 1-(1-naphthyl)-2-(1-phenanthryl)ethene or the 9-fluorenone-sensitized photo-ring-closure of 1-(1-naphthyl)-2-(1-phenanthryl)ethane. The electronic spectral properties of fulminene were investigated for the first time using photoluminescence as well as transient absorption spectroscopy. The spectral features were compared with those of a series of lower phenacene homologs such as phenanthrene ([3]phenacene), chrysene ([4]phenacene), and picene ([5]phenacene). For the [*n*]phenacene series, both the fluorescence and phosphorescence bands linearly red-shifted with an increase in the number of the benzene rings (*n*). Trends in the energy levels of the excited singlet (E_S) and the triplet (E_T) states were expressed as $E_s = -2.6n + 89.1$ (kcal mol^{-1}) and $E_T = -1.8n + 66.2$ (kcal mol^{-1}), respectively. In the case of fulminene, laser flash photolysis displayed a transient spectrum with an absorption maximum (λ_{max}^{T-T}) at 675 nm, which was assigned as the triplet fulminene excited state. The λ_{max}^{T-T} values for the [*n*]phenacene series showed a linear correlation as a function of the ring number *n*, given by an equation, $\lambda_{max}^{T-T} = 60n + 318$ (nm).

This article is dedicated to Professor Kazuhiko Mizuno in memory of his retirement.

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Introduction

Aromatic molecules with an extended π-conjugated electronic system have attracted considerable attention from the theoretical and experimental fields [1]. Polycyclic aromatic compounds are divided into two major structural categories. The first category comprises phenacenes, which contain benzene rings fused in a zigzag manner; the second comprises acenes, which contain linearly bound benzene rings. The structures of the phenacene and the acene conformations as well as those of the phenacenes used in this study are shown in Fig. 1.

Recently, polycyclic aromatic molecules have been used as the active layer in organic thin-film field-effect transistors (OFETs). The use of acenes, typified by pentacene, in OFETs has been extensively investigated [2, 3]. However, acenes are generally not stable enough to use under exposure of light and air, making the practical application in electronic devices difficult. Thus, unsubstituted higher acenes with $n > 5$ were generated and characterized in a polymer film or in a noble-gas matrix [4–6]. Therefore, an aromatic electronic material, which is stable under atmospheric conditions, remains highly desired [7, 8].

Phenacenes are more stable compared with acene structures [9]. Therefore, the phenacene structure has been expanded to an [11]phenacene skeleton, which was reported to be stable [10–12]. Recently, phenacenes have become an important class of compounds in the field of organic electronics. It was shown that picene **3** ([5]phenacene) could be used as an active layer of a *p*-channel OFET with high field-effect mobility, μ = ca. 5 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ [13]. [7]Phenacene also served as an active layer of OFET, showing a field-effect mobility of $\mu = 0.75\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ [14]. As the picene and [7]phenacene thin-film OFETs showed sensitivity toward O_2 and humidity, they were potentially applicable to practical devices such as gas

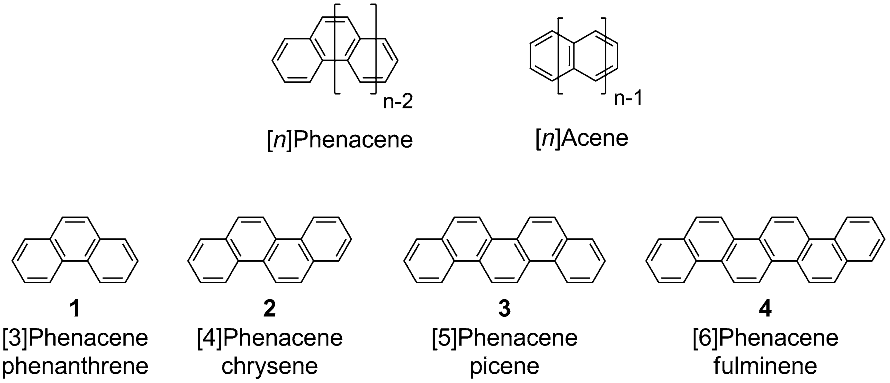


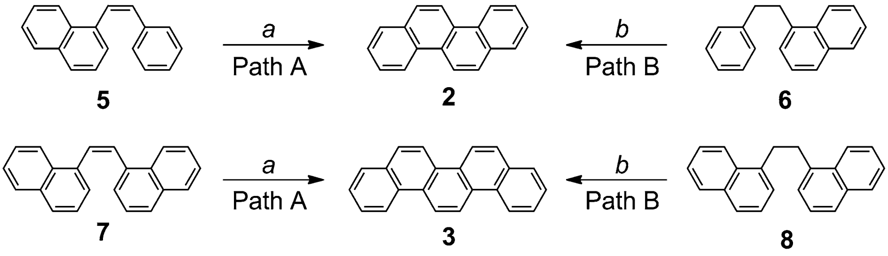
Fig. 1 General structures of phenacene and acene (*upper*), and the structures of [*n*]phenacenes (n = 3–6) used in this study (*lower*)

sensors [15, 16]. Furthermore, picene **3** doped with an alkaline metal such as potassium displayed superconductivity with a high superconducting transition temperature ($T_c = 18$ K). The potassium-doped picene was the first aromatic hydrocarbon-derived superconductor [17]. Very recently, phenanthrene **1** also showed superconductivity ($T_c = 5$ K) upon potassium doping [18, 19]. These findings clearly indicate that phenacenes and their derivatives are a novel and promising class of compounds for organic electronics [20].

Phenacenes were discovered decades ago (i.e., picene **3** and fulminene **4** were isolated from coal tar in the 1950s [21]). However, compared with acenes, considerably less effort has been made to synthesize such higher phenacenes and fabricate an electronic device utilizing them. Therefore, insufficient strategies for systematic synthesis of higher phenacene skeletons and only limited information about their electronic features, such as absorption spectra [21, 22], are currently available. Therefore, it would be highly desirable to establish an efficient synthetic pathway to a series of higher phenacenes, and to systematically elucidate their electronic features. Such studies on phenacenes would initiate new chemistry, physics, and material-science progress in the area of expanded aromatic organics from the viewpoint of their application to electronic devices.

Conventionally, phenacene frameworks (e.g., chrysene **2** and picene **3**) have been constructed by photochemical ring closure of a stilbene-like diarylethene precursor followed by an oxidative aromatization, also referred to as the Mallory reaction (Scheme 1, path A) [23]. Previously, it was reported that phenacene skeletons such as picene **3** ([5]phenacene) could be readily prepared through a 9-fluorenone (**9F**)-sensitized photolysis of a diarylethane (Scheme 1, path B) [24]. These two methodologies have yet to be applied to the preparation of fulminene **4** ([6]phenacene). Furthermore, detailed electronic features of fulminene **4** have not been experimentally investigated. Thus, preparation and electronic spectral characterization of fulminene **4** would contribute to the design and development of phenacene-based organic electronic devices.

In the present study, we investigated the preparation of fulminene **4** via both the Mallory reaction and the **9F**-sensitized photolysis. The characterization of fulminene **4** using photoluminescence and transient absorption spectroscopy is also reported here. Furthermore, the spectral features of fulminene **4** were compared with those of lower phenacenes to establish correlation between the spectral behavior and the structure of the phenacenes as related to the number of the benzene rings, *n*.



Scheme 1 Photochemical synthesis of chrysene **2** and picene **3**. Reagents: *a* $h\nu$, I_2, O_2; *b* **9F**, $h\nu$, $CHCl_3$

Experimental

Instruments

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected on a Varian 400MR (400 MHz) or Varian NMR System 600 MHz (600 MHz) spectrometer. Infrared (IR) spectra were measured using a Shimadzu IR Prestige-21 spectrophotometer. Absorption spectra were recorded on a Jasco U-best 50 or Jasco V-530 spectrophotometer. Emission spectra were recorded on a Hitachi fluorescence spectrometer F-7000. Fluorescence quantum yields were determined by using an absolute photoluminescence quantum yield measurement system (Hamamatsu Photonics C9920-02). Fluorescence lifetimes were determined by using a time-correlated single-photon counting fluorimeter (Hamamatsu Photonics TAU System). Elemental analyses were performed using a PerkinElmer 2400II Analyzer in the Micro Elemental Analysis Laboratory of Okayama University. Steady-state photolysis was carried out using a Rayonet photoreactor (Southern New England Ultraviolet Company, RPR-100) equipped with 350-nm fluorescent lamps (RPR-3500, 16 × 16 W).

A Lextra 50 XeCl excimer laser (308 nm, Lambda Physik) was used as the excitation light source for transient absorption spectral measurements. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere [25]. The transient absorption spectra were obtained using a Unisoku USP-554 system, which provided a transient absorption spectrum with one laser pulse. The obtained transient spectral data were analyzed using the least-squares best-fitting method.

$CHCl_3$ (fluorimetry grade from Kanto Chemical) was used as solvent for absorption and fluorescence measurements, while a mixture of methylcyclohexane (UVasol, Dojin) and 2-methylbutane (Fluka) (MP, 3:1 v/v) was used for phosphorescence measurements as a glass matrix at 77 K. All the samples (as $CHCl_3$ solution) in a quartz cell with 1-cm path length for measurements of transient absorption, fluorescence quantum yields, and lifetimes were deaerated by bubbling with extrapure argon gas for 20 min at room temperature. The optical density of the samples was adjusted to be ca. 0.8 at 308 nm.

Materials

Compounds **9**, **10**, and **11** were prepared by the previously reported procedures [10]. Phenanthrene **1** and chrysene **2** were purchased from Aldrich and Wako Pure Chemical Industries, Ltd., respectively. Picene **3** was prepared according to the previously reported procedure [24, 26].

*Preparation of fulminene **4** by the Mallory reaction* To a solution of phosphonium salt **11** (533 mg, 1.0 mmol) and 1-naphthaldehyde (156 mg, 1.0 mmol) in 20 mL CH_2Cl_2 was dropwise added a 50 % aqueous soln. of NaOH (ca. 1 mL). The mixture was vigorously stirred at room temperature for 1 h. To the resulting mixture was added small amount of anhyd. Na_2SO_4, and the salt was filtered off. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel (hexane) to afford naphthylphenanthrylethene **12** as an *E*/*Z* mixture (314 mg). The mixture was used in the following Mallory reaction without further separation or purification. A solution of compound **12** (314 mg) and iodine (240 mg) in toluene (80 mL) was irradiated at 350 nm under aerated conditions for 13 h. The precipitated product **4** was collected and washed with toluene (147 mg, 45 % from **11**). An analytical sample was obtained by sublimation under reduced pressure.

Colorless plates, mp 479 °C (determined by differential scanning calorimetry, Lit. [21] 466–469 °C). ^{1}H NMR (600 MHz, $CDCl_3$, cf. Fig. 2) δ 9.05 (d, 2H, $J = 9.1$ Hz, $H_{8,16}$), 9.00 (d, 2H, $J = 9.1$ Hz, $H_{7,15}$), 8.89 (d, 2H, $J = 7.6$ Hz, $H_{1,9}$), 8.88 (d, 2H, $J = 9.1$ Hz, $H_{6,14}$), 8.08 (d, 2H, $J = 9.1$ Hz, $H_{5,13}$), 8.04 (d, 2H, $J = 7.6$ Hz, $H_{4,12}$), 7.77 (t, 2H, $J = 7.6$ Hz, $H_{2,10}$), 7.69 (t, 2H, $J = 7.6$ Hz, $H_{3,11}$). IR (neat) ν_{max} 3,086, 3,050, 3,027, 1,601, 1,439, 1,428, 1,278, 1,269, 807, 762, 741 cm^{-1}. Anal. Found: C, 95.02; H, 4.59 %. Calc. for $C_{26}H_{16}$: C, 95.09; H, 4.91.

*1-(1-Naphthyl)-2-(1-phenanthryl)ethane **13*** A mixture of compound **12** (247 mg, 0.75 mmol) and 5 % Pd/C (38 mg) in an AcOEt–EtOH mixture (1:1 v/v, 100 mL) was stirred under an atmosphere of hydrogen for 18 h. The Pd/C was filtered off, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane) to afford naphthylphenanthrylethane **13** (235 mg, 94 %).

Colorless crystals, mp 131–132 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, 1H, $J = 8.4$ Hz), 8.67 (d, 1H, $J = 8.4$ Hz), 8.19 (d, 1H, $J = 6.0$ Hz), 8.10 (d, 1H, $J = 9.0$ Hz), 7.94 (m, 2H), 7.84 (d, 1H, $J = 9.0$ Hz), 7.80 (d, 1H, $J = 7.4$ Hz), 7.70 (ddd, 1H, $J = 8.4, 7.8, 1.3$ Hz), 7.65 (t, 1H, $J = 7.8$ Hz), 7.62−7.54 (m, 3H), 7.49 (d, 1H, $J = 7.2$ Hz), 7.44 (t, 1H, $J = 7.2$ Hz), 7.38 (d, 1H, $J = 7.2$ Hz), 3.59 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 137.9, 133.9, 131.8, 131.6, 130.8, 130.7, 130.1, 128.9, 128.4, 127.1, 126.9, 126.8, 126.6, 126.5, 126.2, 125.95, 125.93, 125.6, 125.5, 123.6, 122.9, 122.3, 121.2, 34.5, 34.4. IR (neat) ν_{max} 3,045, 2,937, 1,597, 1,508, 1,465, 1,456, 1,396, 827, 204, 794, 779, 756 cm^{-1}. Anal. Found: C, 93.83; H, 5.89 %. Calc. for $C_{26}H_{20}$: C, 93.94; H, 6.06.

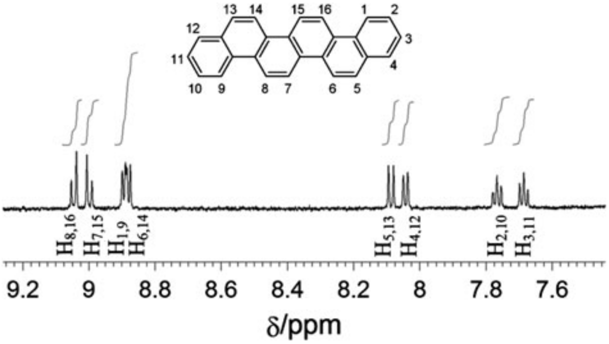


Fig. 2 ^{1}H NMR spectrum (aromatic region) of fulminene **4** (600 MHz, $CDCl_3$)

*Preparation of fulminene **4** by the **9F**-sensitized photolysis of naphthylphenanthrylethane **13*** A solution of naphthylphenanthrylethane **13** (99.7 mg, 0.30 mmol) and **9F** (162 mg, 0.90 mmol) in 15 mL $CHCl_3$ was purged with nitrogen and irradiated at 350 nm for 3 days. The precipitate formed was collected and washed with $CHCl_3$ to afford fulminene **4** (7.4 mg, 7.5 %). The ^1H NMR spectral data were identical to those observed for the product obtained in the above-mentioned photolysis of naphthylphenanthrylethene **12**.

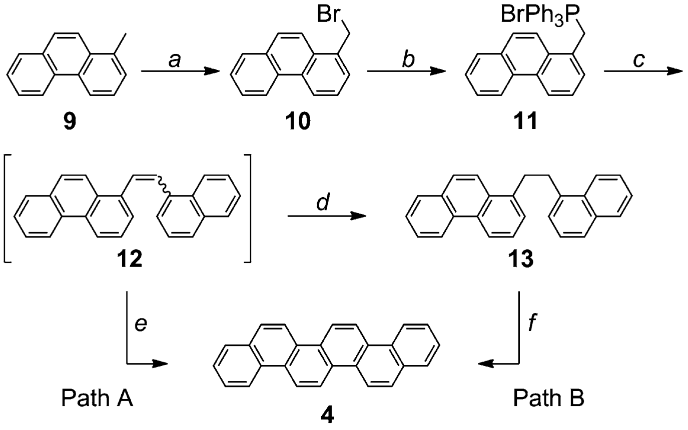
Results and discussion

Preparation of fulminene 4

The synthetic pathways for fulminene **4** are shown in Scheme 2. Phosphonium bromide **11** was prepared by the previously reported procedure [10]: 1-Methylphenanthrene **9** was brominated with *N*-bromosuccinimide (NBS) in the presence of benzoylperoxide (BPO) to afford 1-bromomethylphenanthrene **10**, which was treated with triphenylphosphine to form phosphonium salt **11**. A Wittig reaction of the phosphonium salt **11** and 1-naphthaldehyde using NaOH as a base in a CH_2Cl_2-H_2O mixture produced naphthylphenanthrylethene **12**. The ^1H NMR spectrum of the obtained product **12** displayed complex signals, presumably because the product contained both *E*- and *Z*-isomers. Therefore, the structure of compound **12** was only confirmed after hydrogenation of the double bond: Compound **12** was reacted with hydrogen in the presence of Pd/C to afford naphthylphenanthrylethane **13** in 94 % yield. The structure of compound **13** was confirmed by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. From the characterization of naphthylphenanthrylethane **13**, compound **12** was established to possess the naphthylphenanthrylethene framework.

First, the Mallory photocyclization [23] of compound **12** was investigated (Scheme 2, path A). A solution of compound **12** and iodine in aerated toluene was irradiated at 350 nm and room temperature. After 13 h of photolysis, fulminene **4** was obtained as a precipitate in 45 % yield based on phosphonium salt **11**. The structure of fulminene **4** was confirmed by ^1H NMR and IR spectroscopy as well as elemental analysis. The analytical sample was obtained by sublimation under reduced pressure [26]. IR spectrum of fulminene **4** was identical to the reported data [21]. It has been noted that, due to fulminene's poor solubility in organic solvents, ^1H NMR measurement was not possible [22]. However, by using a high-field NMR spectrometer (600 MHz), we successfully obtained the ^1H NMR spectrum; the results are shown in Fig. 2. The signals of the protons at the bay regions ($H_{1,9}$, $H_{6,14}$, $H_{7,15}$, $H_{8,16}$) appear at lower field (8.9–9.1 ppm), while the protons at both edges of the molecule ($H_{2,10}$, $H_{3,11}$) show two triplet signals at higher field (~7.7 ppm). These features are consistent with the reported ^1H NMR spectra of related phenacenes [22, 24]. Unfortunately, the ^{13}C NMR spectrum of fulminene **4** could not be observed due to poor solubility.

Subsequently, the **9F**-sensitized photocyclization [24, 26] of naphthylphenanthrylethane **13** was investigated (Scheme 2, path B). When a $CHCl_3$ solution of



Scheme 2 Synthesis of fulminene **4**. Reagents: (*a*) NBS, BPO, CCl_4, 74 %; (*b*) PPh_3, dimethylformamide (DMF), 91 %; (*c*) 1-naphthaldehyde, NaOH aq., CH_2Cl_2; (*d*) H_2, Pd/C, AcOEt–EtOH, 94 %; (*e*) *hν*, I_2, O_2, 45 % from **11**; (*f*) **9F**, *hν*, $CHCl_3$, 7.5 %

compound **13** and **9F** was irradiated at 350 nm and room temperature for 3 days, fulminene **4** was obtained as a precipitate in 7.5 % yield. The spectral data of the fulminene **4** obtained by the **9F**-sensitized photocyclization were identical to those prepared by the Mallory reaction. Although the yield was not high, it was discovered that the **9F**-sensitized photocyclization of 1,2-diarylethane [24] was useful for systematic synthesis of [*n*]phenacene skeletons.

Electronic spectra of [*n*]phenacenes

Figure 3 shows the electronic absorption, fluorescence, and phosphorescence spectra of a series of [*n*]phenacenes ($n = 3$–6) in nonpolar media. All the spectra consist of well-resolved vibrational structures. The 0–0 origins of the absorption and fluorescence spectra are clearly seen with a Stokes shift of $<300\ \mathrm{cm}^{-1}$. The excitation spectra for the fluorescence and phosphorescence were identical to the corresponding absorption spectrum of phenacenes.

The lowest excited singlet state energies (E_S) in the phenacenes were determined from the averaged energies of the 0–0 origins of the corresponding absorption and fluorescence spectra while the excited triplet state energies (E_T) were estimated from the 0–0 origins of the phosphorescence spectra. The obtained values of E_S and E_T are listed in Table 1 along with the 0–0 transition wavelengths ($\lambda_{0\text{–}0}^{\mathrm{ABS}}$, $\lambda_{0\text{–}0}^{\mathrm{FL}}$) and the Stokes shift. Also, the lifetimes (τ_f), quantum yields (Φ_f), and rate constants (k_f) of fluorescence determined in the present work are listed. Additionally, the photophysical parameters of the related acenes are summarized in Table 2. The rate constants of fluorescence (k_f) were obtained by Eq. 1.

$$k_\mathrm{f} = \Phi_\mathrm{f}\tau_\mathrm{f}^{-1}. \tag{1}$$

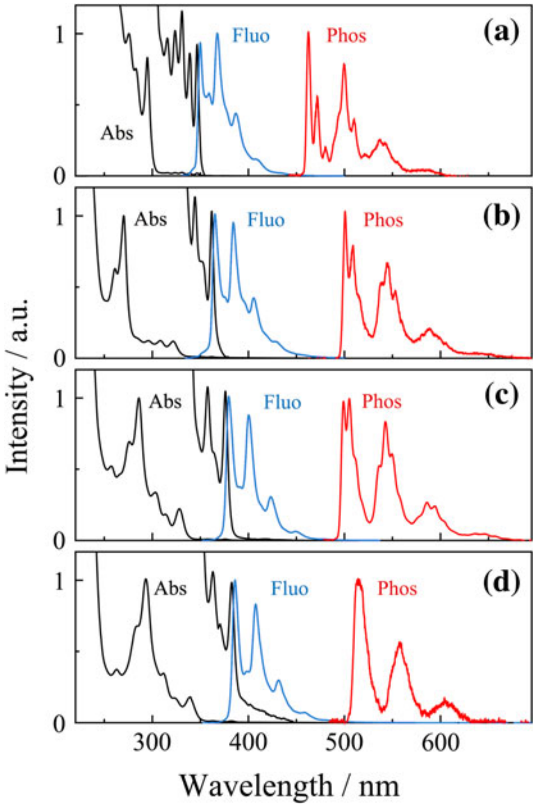


Fig. 3 Absorption (*black line*) and fluorescence (*blue line*) spectra in $CHCl_3$ at 295 K and phosphorescence (*red line*) spectra (normalized) of phenanthrene **1** (**a**), chrysene **2** (**b**), picene **3** (**c**), and fulminene **4** (**d**) in a 3:1 methylcyclohexane:2-methylbutane mixture at 77 K. The intensity of the absorption spectra in the longer wavelength region was arbitrarily enlarged for clear expression. (Color figure online)

The estimated k_f values are all in the magnitude of 10^6 s^{-1}, which indicates that the fluorescence process is of π,π^* type.

Transient absorption spectra of the phenacenes were obtained by means of flash photolysis techniques using a nanosecond laser pulse. Figure 4 compares the transient absorption spectra obtained at 100 ns upon 308-nm laser photolysis of degassed $CHCl_3$ solution of phenacenes at 295 K. The intensity of all the transient absorption decreased within tens of microseconds, and the decay was accelerated by the presence of dissolved oxygen. From these observations, the obtained transient signals can be ascribable to the triplet–triplet (T–T) absorption of [*n*]phenacenes. The absorption maximum wavelengths ($\lambda_{\max}^{\mathrm{T-T}}$) of the obtained T–T absorption spectra are listed in Table 1.

It would be of interest to find the relationship between the obtained spectroscopic features and the number of benzene rings, *n*, in the phenacene series. Additionally, this relationship was compared with that of an [*n*]acene series reported previously to clarify the difference in the spectral behavior between phenacene and acene series. In Fig. 5a, b, the E_S and E_T, and $\lambda_{\max}^{\mathrm{T-T}}$ values are, respectively, plotted as a function of *n*. With increasing *n* values, the E_S and E_T values linearly decrease, and the $\lambda_{\max}^{\mathrm{T-T}}$ values increase. Therefore, E_S, E_T, and $\lambda_{\max}^{\mathrm{T-T}}$ are expressed using Eqs. 2–4 and 5–7 as a function of *n* for the [*n*]phenacene and [*n*]acene series, respectively.

Table 1 Photophysical parameters of [*n*]phenacenes ($n = 3$–6)[a]

Compd. (*n*)	$\lambda_{0-0}^{\mathrm{ABS}}$ (nm)	$\lambda_{0-0}^{\mathrm{FL}}$ (nm)	Stokes shift $(\mathrm{cm})^{-1}$	Φ_F	τ_f (ns)	k_f[b] (10^6 s^{-1})	E_S[c] (kcal mol^{-1})	E_T[d] (kcal mol^{-1})	$\lambda_{\max}^{\mathrm{T-T}}$ (nm)
Phenanthrene **1** (3)	347	350	247	0.049	18.9	2.6	81.9	61.8	490
Chrysene **2** (4)	362	365	227	0.045	10.3	4.4	78.5	57.0	570
Picene **3** (5)	376	380	280	0.088	17.0	5.2	75.5	57.3	615
Fulminene **4** (6)	382	386	271	0.120	16.0	7.5	74.3	55.6	675

[a] In $CHCl_3$ at 295 K

[b] Estimated by $k_f = \Phi_f \tau_f^{-1}$

[c] Estimated from the 0–0 origins of the absorption and fluorescence spectra

[d] Estimated from the 0–0 origins of phosphorescence spectra in a mixture of methylcyclohexane and 2-methylbutane (3:1 v/v) at 77 K

Table 2 Photophysical parameters of [*n*]acenes ($n = 3$–5)[a]

Compd. (*n*)	Φ_F	τ_f (ns)	k_f[b] (10^6 s^{-1})	E_S (kcal mol^{-1})	E_T (kcal mol^{-1})	$\lambda_{\max}^{\mathrm{T-T}}$ (nm)
Anthracene (3)	0.30	5.3	56	77.2	42.5	433
Tetracene (4)	0.17	6.4	26	58.6	29.3	465
Pentacene (5)	0.08	–	–	49.0	17.9	505

[a] Data taken from [27]

[b] Estimated by $k_f = \Phi_f \tau_f^{-1}$

For the [*n*]phenacene series:

$$E_s = -2.6n + 89.1\ \left(\mathrm{kcal\ mol^{-1}}\right), \tag{2}$$

$$E_T = -1.8n + 66.2\ \left(\mathrm{kcal\ mol^{-1}}\right), \tag{3}$$

$$\lambda_{\max}^{\mathrm{T-T}} = 60n + 318\ (\mathrm{nm}). \tag{4}$$

For the [*n*]acene series:

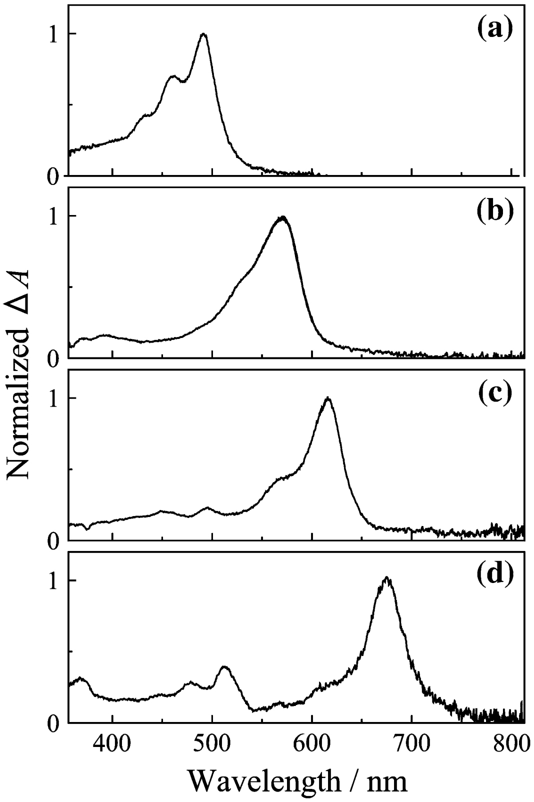
$$E_s = -13.6n + 116\ \left(\mathrm{kcal\ mol^{-1}}\right), \tag{5}$$

$$E_T = -12.4n + 79.4\ \left(\mathrm{kcal\ mol^{-1}}\right), \tag{6}$$

$$\lambda_{\max}^{\mathrm{T-T}} = 36n + 324\ (\mathrm{nm}). \tag{7}$$

According to the plots of E_S and E_T versus *n*, the slopes for the phenacene series were smaller than for the acene series. This finding indicates that, on increasing the number of benzene rings in acenes and phenacenes, the energy levels of the excited states of phenacenes are less influenced than those of acenes. The decreased influence is attributed to the difference in the molecular structures, i.e., zigzag versus linear. The slopes for the shift in the $\lambda_{\max}^{\mathrm{T-T}}$ values were appreciably the same

Fig. 4 Transient absorption spectra obtained at 100 ns after 308-nm laser photolysis of phenanthrene **1** (**a**), chrysene **2** (**b**), picene **3** (**c**), and fulminene **4** (**d**) in $CHCl_3$



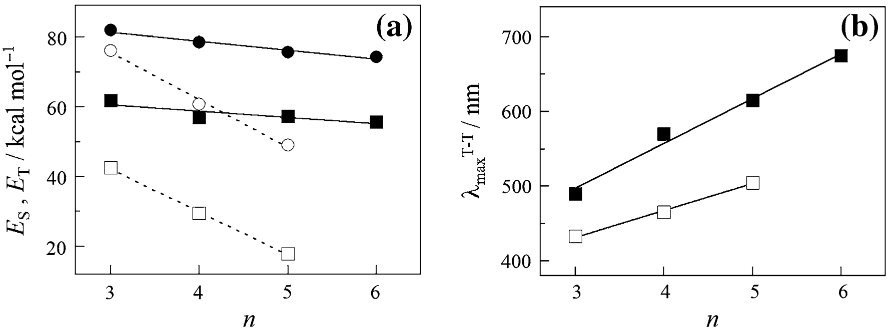


Fig. 5 **a** Plots of the excited singlet (E_S) and triplet (E_T) state energies for [*n*]phenacenes and [*n*]acenes as a function of *n*; E_S (*filled circle*) and E_T (*filled square*) of [*n*]phenacenes, E_S (*open circle*) and E_T (*open square*) of [*n*]acenes. **b** λ_{max}^{T-T} of [*n*]phenacenes (*filled square*) and [*n*]acenes (*open square*) plotted as a function of *n*. Data for [*n*]acenes quoted from Ref. [27]

between the phenacene and acene series. However, the value for phenacene at a certain *n* number tends to drift towards longer wavelength regions compared with the corresponding acene series. The relationship between E_S, E_T, λ_{max}^{T-T}, and *n* expressed using Eqs. 2–7 will be useful for estimating those values for phenacenes and acenes with n values greater than 7, because they are anticipated to have very low solvent solubility. Moreover, acenes with $n > 5$ are known to be too unstable to undergo spectroscopic measurements in solution at room temperature [4–6].

It has been noted that, for the phenacene and acene series, the absorption band corresponding to the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap linearly red-shifted as a function of n as expressed by Eqs. 8 and 9 [11, 28].

For the [n]phenacene series:

$$\lambda_{\max} = 9n + 279\ (\mathrm{nm}). \tag{8}$$

For the [n]acene series:

$$\lambda_{\max} = 98n + 88\ (\mathrm{nm}). \tag{9}$$

Thus, it can be concluded that, for phenacenes with higher n values, the electronic properties concerning absorption, fluorescence (E_S), phosphorescence (E_T), and T–T absorption ($\lambda_{\max}^{T-T}$) can be predicted by Eqs. 2–4 and 8.

Conclusions

Fulminene **4** ([6]phenacene) was prepared by both the Mallory reaction of naphthylphenanthrylethene **12** and the **9F**-sensitized photocyclization of naphthylphenanthrylethane. The photoluminescence spectra for the series of [n]phenacenes ($n = 3$–6) were obtained and compared under the same conditions. The fluorescence and phosphorescence spectra red-shifted with an increase of n, thus linear relationships between n and the excited state energy levels were determined as $E_s = -2.6n + 89.1$ (kcal mol^{-1}) and $E_T = -1.8n + 66.2$ (kcal mol^{-1}). The triplet excited state for fulminene, which displayed a T–T absorption band at 675 nm, was detected using transient absorption measurements. The $\lambda_{\max}^{T-T}$ also linearly red-shifted depending on n, with the relationship $\lambda_{\max}^{T-T} = 60n + 318$ (nm). These results indicate that the photoluminescence and T–T absorption properties of higher phenacenes could be predicted. The linear correlations reported here could provide useful property estimations for future phenacenes and provide guidance in designing organic electronic molecular devices using higher phenacene skeletons.

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