

Photochemical synthesis of diphenylphenanthrenes, and the photophysical properties studied by emission and transient absorption measurements

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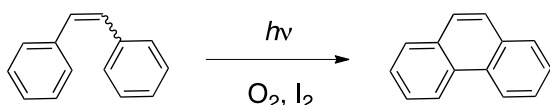
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ABSTRACT: Novel diphenylphenanthrenes (DPPs) were prepared by a photocyclization method, and the substituent effects of the phenyl groups on the photophysical properties of the phenanthrene chromophore were investigated based on measurements of fluorescence yields, lifetimes, and transient absorption. Fluorescence activities in DPPs are increased by introducing phenyl rings that can enhance the transition moment along the short axis of the phenanthrene skeleton. Intersystem crossing from the fluorescent states to the triplet manifolds is shown to be operative through the triplet-triplet absorption spectra obtained by laser photolysis techniques.

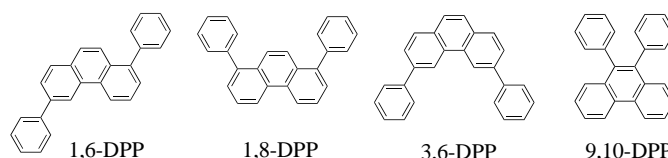
Some aromatic molecules with extended π systems can be divided into two major groups from the molecular shapes. One is acenes representative of anthracene, tetracene and pentacene having linearly aligned benzene rings. In these two decades, acenes have been paid attention due to the potentials for organic semiconductor such as active layers of organic field effect transistors (OFET)¹⁻³ although they are generally unstable on exposure to oxygen and light.⁴⁻⁶ The other group is phenacenes, such as phenanthrene, chrysene, picene, fulminene, etc. having benzene rings fused in a zigzag manner. Phenacenes had not been subjected for chemical material researches because of the difficulties in the organic synthesis processes until our findings. We have reported a facile synthetic process for preparing phenacenes using photochemical reactions of diarylethanes using aromatic carbonyls as a sensitizer (photosensitization method).⁷ With this method, we prepared picene ([5]phenacene) and fulminene ([6]phenacene).⁸ We have found that these phenacenes show excellent OFET performance^{9,10} and that potassium-doped picene presents superconductivity at 20 K.¹¹ Because phenacenes are quite stable on exposing to oxygen and light, they are promising organic electronic materials.¹² It is also of interest from the viewpoint of photophysics that picene provides fluorescence emission from the second lowest excited singlet (S_2) state in the vapor phase.¹³ However, the phenanthrene skeleton cannot be formed with the sensitized photolysis method.

Scheme 1. The chemical process of the Mallory photocyclization.



Instead of the photosensitization method, Mallory photoreaction is an excellent procedure for phenacene synthesis via photocyclization of stilbene (Scheme 1).¹⁴ The fluorescence yield of anthracene, the smallest acene, is established to be 0.27 in ethanol as a reference material for fluorescence measurements by IUPAC.¹⁵ It is known that introduction of two phenyl groups into the anthracene skeleton, instead of 9,10-diphenylanthracene, enhances the fluorescence yield to be 0.95.¹⁶ Substitution effects of two phenyl groups on the fluorescence features of phenanthrene have not been investigated except for 9,10-diphenylphenanthrene^{17,18} because of difficulties of the preparations. In the present work, we are successfully prepared a variety of diphenylphenanthrenes (DPPs, Chart 1) using the Mallory photocyclization procedure. Based on fluorescence and transient absorption measurements, the photophysical and photochemical features are investigated from the viewpoint of the substituent effect for increasing the fluorescence yields.

Chart 1. Molecular structures of DPPs used in the present work.



Synthesis procedures and analytical data for DPPs are deposited in the Supporting Information. 3,6- and 9,10-DPPs were successfully prepared by photocyclization of the corresponding diphenylstilbenes (DPS) while 1,6- and 1,8-DPPs were difficult to produce from the 2,4'- and 2,2'-DPSs, respectively. Therefore, for synthesizing 1,6- and 1,8-DPPs, Suzuki coupling of the corresponding dibromophenanthrenes with phenylboronic acid was, respectively, applied. Interestingly, it is notable that formation of 9-biphenylphenanthrene is supposed upon conducting the Mallory photocyclization of 2,4'-DPS. The mechanism is proposed in the Supporting Information. It seems that the substituting position of the phenyl group on the phenanthrene skeleton affects the reactivity in Mallory photoreactions. Mallory et al. reported that 9,10-DPP undergoes the Mallory photocyclization yielding dibenzo[g,p]chrysene,¹⁴ although we were unable to reproduce the process with the use of our microflow photoreactor.¹⁹

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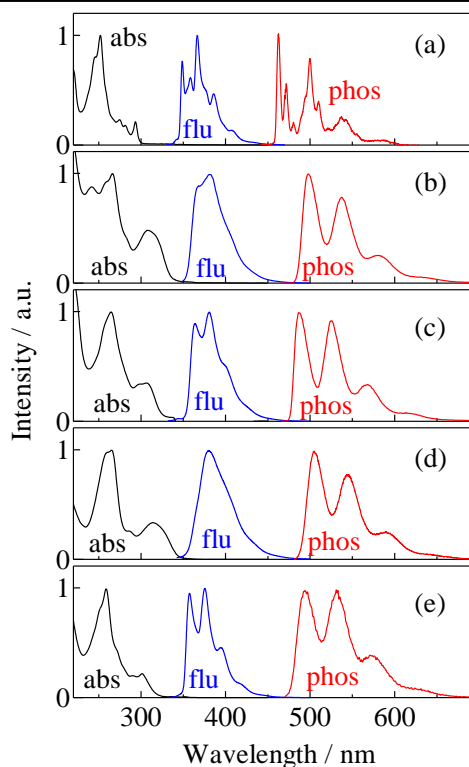


Figure 1. Absorption and fluorescence spectra in cyclohexane at 295 K and phosphorescence spectra in MP at 77 K for phenanthrene (a), 1,6-DPP (b), 1,8-DPP (c), 3,6-DPP (d) and 9,10-DPP (e).

Figure 1 shows absorption and emission spectra of phenanthrene (Phen) and DPPs. The measured emission excitation spectra agreed with the corresponding absorption spectra. The first absorption band of Phen located at 295 nm characterizing the $S_1 \leftarrow S_0$ absorption is originated from the transition moment along the short axis of the phenanthrene skeleton, what is called the 1L_b band.²⁰ Conversely, the $S_2 \leftarrow S_0$ character due to the transition along the long axis of the phenanthrene skeleton (the 1L_a band) can be seen at 250 nm. Absorption, fluorescence and phosphorescence spectral features of Phen and DPPs are similar to each other although the 1L_b absorption bands, fluorescence and phosphorescence spectra of DPPs have less vibrational structures compared to those of Phen. These observations indicate that the substituted phenyl groups influence the fluorescence properties by affecting the short axis transition in the phenanthrene moiety. Fluorescence yields (Φ_f), fluorescence lifetimes (τ_f), fluorescence rate (k_f), nonradiative deactivation yields (Φ_{nr}), nonradiative rates (k_{nr}) and triplet energies (E_T) of phenanthrene (Phen) and DPPs are listed in Tables S1-3 deposited in the Supporting Information.

Figure 2 shows plots of these photophysical parameters of Phen and DPPs for comparison at a glance. The Φ_f values of DPPs except for 3,6-DPP are greater than that of Phen whereas the k_f values of all the DPPs deserve the enhanced fluorescence processes by substituting with the phenyl groups. The substitution effect by the phenyl groups is similar to that along the short axis in 9,10-diphenylanthracene.

The nonradiative processes consisted of internal conversion (IC) to the ground state and intersystem crossing (ISC) to the triplet states were investigated by transient

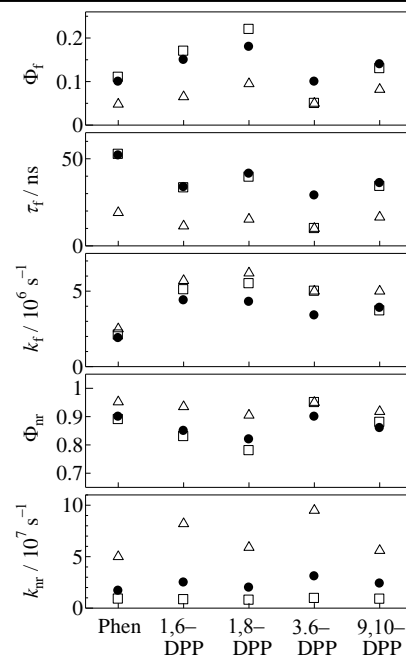


Figure 2. Plots of the photophysical parameters obtained in cyclohexane (●), chloroform (△) and acetonitrile (□).

absorption measurements using laser flash photolysis. Figure 3 shows the transient absorption spectra obtained upon 266 nm laser photolysis of Phen and DPPs. The transient absorption spectrum of Phen is due to the triplet-triplet ($T_n \leftarrow T_1$) absorption.⁸ The spectral shapes of the transient absorption for DPPs differ from that of triplet Phen. The intensities of the transient absorption for 1,6-, 1,8- and 3,6-DPPs decreased with lifetimes (τ_T) in the microsecond time domain, and the decay was accelerated in the presence of the

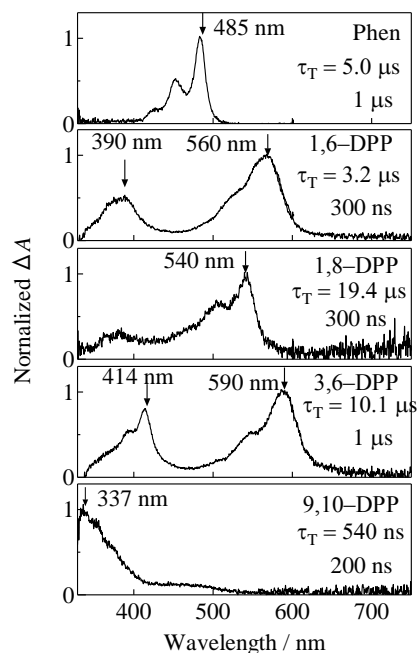


Figure 3. Transient absorption spectra obtained upon 266 nm laser pulsing in Ar-purged cyclohexane solutions at 295 K. The observation times and lifetimes (τ_T) of the transient spectra are superimposed.

dissolved oxygen. Based on these observations, the obtained transient signals could be ascribed to the T-T absorption of the corresponding DPP. The lifetime of the transient signal for 9,10-DPP was too short (500 ns) to be quenched by the dissolved oxygen. We performed triplet sensitization of 9,10-DPP using xanthone as a sensitizer. The transient data upon triplet sensitization are shown in Figure S5 in the Supporting Information. Since the transient absorption spectrum obtained upon triplet sensitization agreed with that obtained upon photolysis of 9,10-DPP, the transient absorption spectrum for 9,10-DPP in Figure 3 is safely assigned to be the T-T absorption. Probably, the phenyl groups substituted at 9- and 10-positions in the vicinity may cause π - π interaction that could shorten the lifetime of the triplet state. Consequently, observations of the T-T absorption indicate that the nonradiative processes of DPPs are governed by ISC.

In conclusion, we have prepared four types of DPP by the photocyclization method, and evaluated the photophysical properties. Fluorescence activities seem to be increased by the introduced phenyl rings that can enhance the transition moment along the short axis of the phenanthrene skeleton. The fluorescent states deactivate via intersystem crossing to the triplet manifolds whose absorption spectra have been identified.

KEYWORDS: Diphenylphenanthrenes, photocyclization, fluorescence lifetime, fluorescence yield, transient absorption

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SUPPORTING INFORMATION

Experimentals; synthetic procedures; photophysical data; triplet sensitization data.

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