

Reliable and Reproducible Separation of 3,9- and 3,10-Dibromoperylenes and the Photophysical Properties of their Alkynyl Derivatives

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Abstract: We developed a reliable and reproducible separation method of 3,9-dibromoperylene and 3,10-dibromoperylene resulted from bromination of perylene by using sequential and repeated recrystallization. Because of the unprecedented purities of the dibromoperylenes, they exhibited the highest melting temperatures so far reported. In addition, various alkynylperylenes were prepared from the dibromoperylenes, and we investigated the photophysical characteristics of these alkynyl derivatives in detail.

Introduction

Since its high fluorescence quantum yield, perylene has long been attractive in a variety of research fields. Indeed, pervlene and the derivatives proved to be possible candidates such as in semiconductors,^[1] organic organic electroluminescence materials,^[2] and biological probes.^[3] To utilize them for materials of optical interest, halogenation, especially bromination of the perylene nucleus is most preferred, bearing in mind the following substitution by organometallic strategies. In this context, preparation of 3-bromoperylene (1) was well established, and the many different kinds of mono-substituted perylenes were synthesized starting from 1.^[4,5] On the other hand, a limited number of preparative methods are available for pure dibromoperylenes owing to the difficulty for separating the arising two regio-isomers of 3,9-dibromoperylene (2) and 3,10dibromoperylene (3). In 1925, Zinke et al. reported the first synthesis and separation of the dibromoperylenes.^[6] After that, Uchida et al. published a different synthetic method for them and determined the isomer possessing a higher melting temperature being **2** by the X-ray structure analysis in 1979.^[7] For both the reports, the separation was performed by repeated recrystallization, while we hardly reproduced the result because the details are unclear. There are a few other reports for separating the isomers, however, their NMR data showed contaminants of another isomer.^[8] This situation causes their melting temperatures to be incompatible among the published papers. Possibly from these reasons, dibromoperylene was usually used as a regio-mixture for the applications, [2c,9] so that there are few reports about the photophysical properties of the

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regioisomerically pure derivatives.^[9c] Very recently, Yamada et al. synthesized 3,9- and 3,10-bis(4-methoxyphenyl)perylenes and investigated the physical properties of their oxidized products. In this study, moderately purified 3,9- and 3,10-dibromoperylenes were used, and further purification was carried out in the next derivatization stage to obtain analytically pure samples.

Our group has reported about the substitution effect of alkynyl-groups on pyrene. As the number of alkynyl-substituents increased in pyrenes, the fluorescence quantum yields increased accompanied by red-shifts of the absorption and emission maxima.^[10] Furthermore, the alkynyl-group could be a good scaffold for fabricating the fluorophores to appropriate structures convenient for their applications. Recently, we reported dialkynylpyrene-based [3] and [4]rotaxanes that emit only blue light from the monomeric pyrene^[11] and that exhibit polarized luminescence from the excimer,^[12] circularly respectively. When extending the system to other fluorophores, we came up against difficulties for obtaining regioisomerically pure dibromoperylene. Herein, we wish to report a reliable and reproducible separation method of 3,9-dibromoperylene and 3,10-dibromoperylene and the photophysical characteristics of their alkynyl derivatives in detail.

Results and Discussion

Dibromoperylenes were synthesized by a similar method to that reported by Uchida et al., as follows.^[7] Pervlene was suspended in benzene, and bromine was slowly added to the suspension at 40 °C. The reaction mixture was stirred for 3 h at the same temperature and filtered after cooling to room temperature. The precipitate was found to be an approximately 1:1 mixture of 3,9dibromoperylene (2) and 3,10-dibromoperylene (3) with some minor products by ¹H NMR measurement. We tried to separate the regioisomers obeying the reported procedures, but all in vain because of lack of details in experimental procedure.^[6-8] After much trial and error, we finally established a reproducible separation method by sequential and repeated recrystallization. Figure 1 shows ¹H NMR spectral changes of dibromoperylenes during the course of the recrystallization process. First, the 1:1 mixture was allowed to recrystallization from anilinenitrobenzene (1:1), and the recrystallization from the same solvent system was repeated until the amount of 2 came to be slightly predominant to that of 3 in the precipitate (Figure 1a). Using only the precipitate and discarding all the mother liquors proved to be crucial for succeeding the final separation. The 2predominated precipitate was further purified by recrystallization from toluene-hexane (3:1). Repeated recrystallization with the

same solvent system (10 times on average) gave pure 2 as micro pale orange needles (29% yields; m.p. 304-306 °C) (Figure 1d). The mother liquors arisen from the recrystallization by using this solvent system were found to contain 3 a little more than 2 (Figure 1e) and now used for isolating 3. Pure 3 was obtained as filamentous yellow crystals (23% yields; m.p. 267-268 °C) by repeated recrystallization from toluene-hexane (4:1~5:1) (Figure 1h). Because of the unprecedented purities of the dibromoperylenes, they exhibited the highest melting temperatures, compared to those so far reported. Each dibromoperylene was identified by comparing the ¹H NMR data to the published ones.^[8c] More detailed information for the separation is provided in Figure S1 in the Supporting Information. For reference, 3-bromoperylene (1) was also synthesized^[4c] and derivatized to mono-substituted perylenes.



Figure 1. ¹H NMR spectra of dibromoperylenes during the course of recrystallization process a-d) for 3,9-dibromoperylene and e-h) for 3,10-dibromoperylene.

A series of alkynylperylenes **4–15** were prepared through Sonogashira coupling reaction^[13] between **1–3** and various acetylene derivatives (Scheme 1). Reacting **1–3** with trimethylsilylacetylene afforded 3-(trimethylsilylethynyl)perylene (**4**), 3,9-bis(trimethylsilylethynyl)perylene (**5**), and 3,10bis(trimethylsilylethynyl)perylenes (**6**), respectively (TMS series). Other alkynylperylenes were similarly prepared from **1–3** with a tetraethylene glycol-substituted acetylene (**7–9**: TEG series), 4-(*tert*-butylphenyl)acetylene (**10–13**: *t*BuPh series), and a tetraethylene glycol-substituted phenylacetylene (**13–15**: TEGPh series). The teraethylene glycol-substituted **7–9** and **13–15** were designed in order to disclose their photophysical properties in H₂O.



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Figure 2 revealed UV-vis spectra of the alkynylperylenes **4–15** (1.0 × 10^{-5} M) in CHCl₃, and Table 1 lists their absorption maxima (λ_{abs}) along with the absorption coefficients (ε). The spectra were also measured in cyclohexane, ethanol, and H₂O, and these data are summarized in Figure S2, S3, and Table S1 in the Supporting Information. All the spectra in CHCI₃ showed well-resolved vibrational structures similar to those of parent perylene. The absorption maximum of 3.9bis(trimethylsilylethynyl)perylene (5) appeared at 483 nm, which is bathochromically shifted 21 nanometers than that of monoalkynyl derivative 4, accompanied by the increased absorption coefficient. The 3,10-counterpart 6 displayed the absorption maximum in a little longer wavelength than 5. This tendency was seen not only in this TMS series but also in all the series (TEG, tBuPh, and TEGPh) studied here. The absorption coefficients of the TMS series 4-6 were significantly large, comparing with those of the TEG series 7-9. This is probably because of the π -elongation originated from σ - π interaction between the acetylenic π and the neighboring C-Si σ bonds on 4-6 in the same manner as mono-alkynylperylenes^[5] and alkynylpyrenes.^[10] Absorption maxima of the π -extended *t*BuPh and TEGPh series 10-15 further shifted to longer wavelengths. In addition, the bandwidths of the spectra were rather broadened due to increments in their vibrational states caused by an attachment of the π -extended units. In H₂O, the TEG series 7-9 and especially TEGPh series 13-15 exhibited structure-less, broad absorption spectra, owing to the self-aggregations through stacking of their large π -planes (Figure S3a and S3b in the Supporting Information).



Figure 2. UV-vis spectra of alkynylperylenes 4–15 (1.0 × 10^{-5} M) in CHCl₃. Conditions: 25 °C, path length = 10 mm.

Fluorescence spectra of the alkynylperylenes **4–15** (1.0 × 10^{-6} M) were measured under aerobic conditions in CHCl₃ (Figure 3), cyclohexane, ethanol, and H₂O (Figure S4, S5, and Table S1 in the Supporting Information). Table 2 lists their

fluorescence maxima appearing at the shortest wavelengths (λ_{em}) and fluorescence quantum yields (Φ_{f}) in CHCl₃. The quantum yields were determined by a relative method using 3-(trimethylsilylethynyl)perylene (4) as a reference ($\Phi_{\rm f}$ = 0.88 in cyclohexane^[5]). As well as the absorption spectra, the fluorescence spectra displayed well-resolved vibrational structures. Although the fluorescence quantum yields were found to increase with increasing the number of trimethylsilylethynyl groups in the series of alkynylpyrenes,^[10] bis(trimethylsilylethynyl)-substituted perylenes 5 and 6 showed lower quantum yields ($\Phi_{\rm f}$ = 0.65 and 0.79, respectively) than mono-substituted 4 ($\Phi_f = 0.95$). Yamaji et al. discussed that the intersystem crossing process could be enhanced by interactions such as a vibronic coupling of triple bonds to the perylene nucleus.^[5] The same mechanism might work in this case, causing the lower quantum yields. The emission maxima and quantum yields of the TMS series 4-6 were larger than those of the TEG series 7-9, probably due to the effect of the σ - π interaction above mentioned. In H₂O, the TEGPh series 13-15 strongly aggregated on the basis of the UV-vis spectra, so that no accurate quantum yields were determined even at 1.0×10^{-6} M (Figure S5b and Table S1 in the Supporting Information). At a higher concentration (1.0×10^{-5} M), **13–15** exhibited new broad and structure-less emission bands probably because of the corresponding emissions from their excimers. The emission maxima appeared around 650 nm, and the emission bands approached near-infrared region (Figure S5d in Supporting Information).



Figure 3. Fluorescence spectra of alkynylperylenes **4–15** (1.0 × 10⁻⁶ M) in CHCl₃. Conditions: 25 °C, λ_{ex} = 450 nm, path length = 10 mm.

Table 1. Summary of photophysical properties of alkynylperylenes $\mbox{4-15}$ in $\mbox{CHCI}_3.$

Alkynylperylene		Absorption ^a		Fluorescence	
		$\lambda_{\rm abs}$ (nm)	\mathcal{E} (×10 ⁴ M ⁻¹ cm ⁻¹)	λ _{em} ^b (nm)	$arPsi_{f}^{c}$
4	TMS series	462	4.4	470	0.95
5		483	6.3	490	0.65
6		486	7.1	493	0.79
7	TEG series	460	2.5	468	0.69
8		478	3.7	485	0.47
9		480	3.1	487	0.42
10	<i>t</i> BuPh series	468	4.5	481	0.54
11		496	6.9	512	0.54
12		499	6.7	516	0.73
13	TEGPh series	470	2.7	481	0.62
14		496	4.3	511	0.62
15		500	4.6	516	0.46

^a [Alkynylperylene] = 1.0 × 10 ⁻⁵ M, each λ_{abs} is an absorption band appearing at the longest wavelength. ^b [Alkynylperylene] = 1.0 × 10 ⁻⁶ M, λ_{ex} = 450 nm, each λ_{em} is an emission band appearing at the shortest wavelength. ^c Each ϕ_{f} was determined by using 3-(trimethylsilylethynyl)perylene (ϕ_{f} = 0.88^[5] in cyclohexane) as a reference compound.

Conclusions

In summary, we developed a reliable and reproducible method to separate the two regioisomers, 3,9-dibromoperylene and 3,10-dibromoperylene by sequential and repeated recrystallization. Their purities were guaranteed on the basis of the ¹H NMR spectra and of the highest melting temperatures. In addition, various alkynylperylenes were prepared from the dibromoperylenes, and their photophysical properties were investigated in detail. We would feel amply rewarded if the present study proved helpful to whom it may concern. Of course, rotaxane formation using regioisomerically pure the dialkynylperylenes is now underway in our laboratory.

Experimental Section

General Methods

NMR spectra were recorded using tetramethylsilane (TMS) as an internal reference on a JEOL ECA 500 II at 500 MHz (¹H) and a JEOL ECA 500 II at 125 MHz (¹³C) spectrometers at 25 °C or 40 °C. IR spectra were measured on a JASCO FT/IR-460 plus spectrometer. Mass spectra were obtained by the ESI method on a JEOL JMS-T100LC mass spectrometer. Absorption and fluorescence spectra were recorded using a JASCO V-560 and JASCO FP-6500 spectrometers, respectively. Melting points were determined with Yanaco MP-500D and not corrected.

Spectroscopic Measurements

Steady state absorption and fluorescence were recorded at 25 $^{\circ}$ C using a 10 mm path length cell. The fluorescence quantum yields (ϕ_i) of **4-15** at

450 nm was determined by using 3-(trimethylsilylethynyl)perylene (4) (λ_{ex} = 450 nm, $\Phi_{f} = 0.88^{[5]}$ in cyclohexane) as a reference compound and calculated according to the following equation ($\Phi_{sample} = \Phi_{standard} \times [A_{standard} / A_{sample}] \times [I_{sample} / I_{standard}] \times [n_{sample}^{2} / n_{standard}^{2}]$). In this equation, Φ_{sample} and $\Phi_{standard}$ are the quantum yields of a sample and standard, respectively. A_{sample} , I_{sample} , and n_{sample} are the optical density, the integrated emission intensity at the excitation wavelength, and the refractive index for the sample, respectively. $A_{standard}$, $I_{standard}$ and $n_{standard}$ are those for the standard.

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