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Synthesis and Solid-state Optical Properties of 2,3-Dialkyl- and 2,3,8,9-Tetraalkyltetracenes

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We prepared 2,3-dialkyl- and 2,3,8,9-tetraalkyltetracenes by way of Diels–Alder reactions between 1,4-anthraquinones and 3,4-dialkylthiophene-1,1-dioxides and obtained mainly orange and yellow solids, respectively. The differences in optical properties in the solid state were probably due to different intermolecular interactions.

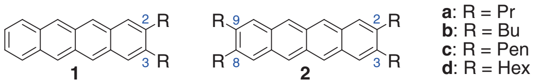
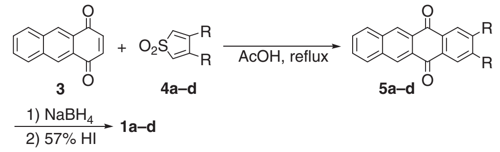
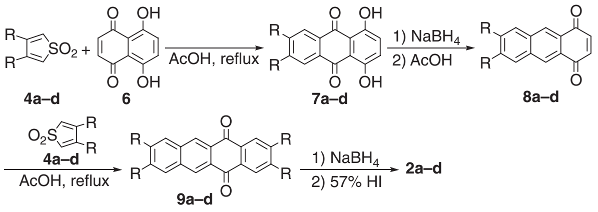


Figure 1. Structures of alkyl-substituted tetracenes.



Scheme 1. Synthesis of 2,3-dialkyltetracenes **1a**–**1d**.



Scheme 2. Synthesis of 2,3,8,9-tetraalkyltetracenes **2a**–**2d**.

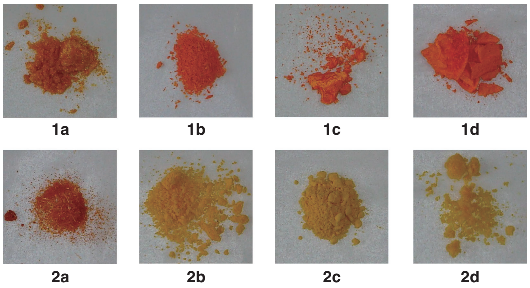


Figure 2. Photographs of tetracenes **1a**–**1d** and **2a**–**2d** in powder form.

Tetracene is a promising organic semiconducting molecule for OFETs, OLEDs, and solar cells.[1] However, unsubstituted tetracene is barely soluble in common organic solvents and is inadequate for the fabrication of devices over large areas because of its high costs. To decrease the manufacturing costs, soluble organic semiconductors are necessary; numerous soluble tetracene derivatives with substituents have been prepared.[2] From this perspective, we have recently prepared alkyl-substituted tetracenes (1,4,7,10-tetraalkyl and 1,4-dialkyl derivatives).[3] We have found that the alkyl-substituted tetracenes are not only promising semiconductors but also interesting chromophores. Thus, depending on the length, shape, and the number of alkyl side chains, the solid-state color of the tetracenes varies through yellow, orange, and red. To investigate the effects of the substitution position on the solid-state color, we attempted to prepare new tetracenes possessing alkyl side chains other than at the 1,4,7,10-positions (Figure 1). We report here the synthesis and optical properties of 2,3-dialkyltetracenes **1a**–**1d** and 2,3,8,9-tetraalkyltetracenes **2a**–**2d** (alkyl = propyl to hexyl).

First, **1a**–**1d** were prepared as shown in Scheme 1.[4] We applied the anthraquinone synthesis using 1,4-naphthoquinone and 3,4-disubstituted thiophene-1,1-dioxides developed by Williams et al.[5] into a tetracenequinone synthesis. Diels–Alder reactions between 1,4-anthraquinone (**3**) and 3,4-dialkylthiophene-1,1-dioxides **4a**–**4d**, followed by the loss of sulfur dioxide and oxidation, in refluxing acetic acid produced 2,3-dialkyl-5,12-tetracenequinones **5a**–**5d** in 19%–42% yields. Then, reduction with $NaBH_4$, followed by treatment with hydroiodic acid, gave **1a**–**1d** in 17%–63% yields. Next, we prepared **2a**–**2d** as shown in Scheme 2.[4] Diels–Alder reactions between **4a**–**4d** and 5,8-dihydroxy-1,4-naphthoquinone (**6**), followed by the loss of sulfur dioxide and oxidation, provided 6,7-dialkyl-1,4-dihydroxy-9,10-anthraquinones **7a**–**7d** in 38%–50% yields. 6,7-Dialkyl-1,4-anthraquinones **8a**–**8d** were readily prepared by the reduction of **7a**–**7d** with $NaBH_4$ and the following acidic work-up.[6] Second, Diels–Alder reactions between **4a**–**4d** and **8a**–**8d**, followed by the loss of sulfur dioxide and oxidation, afforded 2,3,8,9-tetraalkyl-5,12-tetracenequinones **9a**–**9d** in 20%–53% yields. Finally, reduction with $NaBH_4$, followed by treatment with hydroiodic acid, provided **2a**–**2d** in 29%–39% yields. All the molecules had suitable solubilities in common organic solvents, except for **1a**, which had a slightly poor solubility. We obtained all the tetracenes in powder form, although 1,4,7,10-tetraalkyl[3b] and 1,4-dialkyl[3c] derivatives were crystalline. Interestingly, the solid-state color of isolated tetracenes was visually orange-yellow for **1a**, orange for **1b**–**1d** and **2a**, and yellow for **2b**–**2d** (Figure 2). Thus, a significant color variation dependent on the number of alkyl side chains was observed, while there were very small changes in the solid-state color dependent on the alkyl side-chain length. These results were completely different from those of 1,4,7,10-tetraalkyltetracenes,[3b] suggesting an intrinsic substituent effect by the alkyl groups at the 2,3- and 2,3,8,9-positions. Because alkyl side chains had little ability to control the electronic structure of the tetracene rings, the above-mentioned color

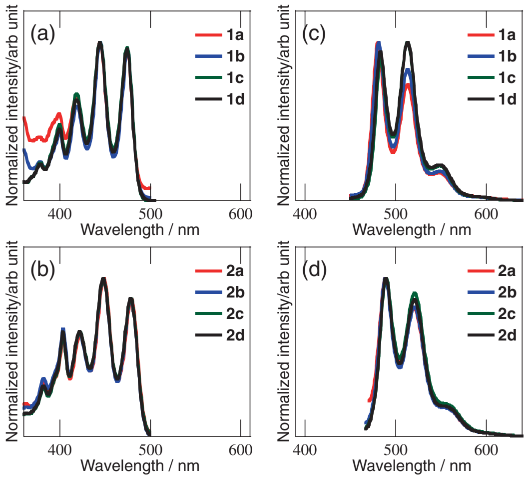


Figure 3. UV–vis absorption spectra of (a) **1a**–**1d** and (b) **2a**–**2d** and fluorescence spectra of (c) **1a**–**1d** and (d) **2a**–**2d** in hexane.

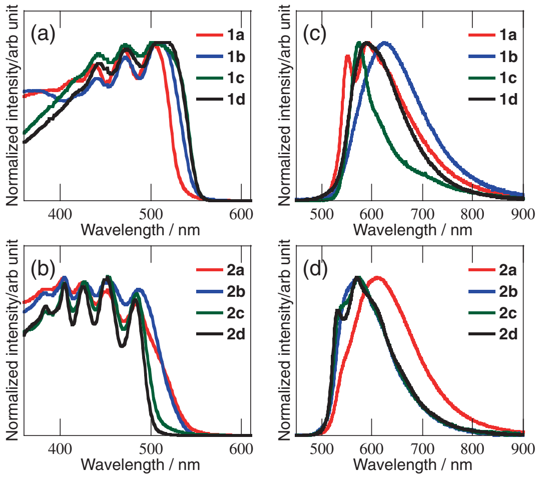


Figure 4. Kubelka–Munk spectra of (a) **1a**–**1d** and (b) **2a**–**2d** in KBr pellets and fluorescence spectra of (c) **1a**–**1d** and (d) **2a**–**2d** in powder form.

variation was most likely due to crystallochromy,[3b,7] namely, a color change caused by different intermolecular interactions based on different molecular arrangements.

Optical properties of **1a**–**1d** and **2a**–**2d** both in solution and in the solid state were measured,[4] as shown in Figures 3 and 4. In solution, both the absorption and fluorescence spectra showed structured bands. There were no significant differences in the spectral shapes, the wavelengths of the absorption and fluorescence peaks, or the fluorescence quantum yields (Φ_F values were around 0.1) between **1a**–**1d** and **2a**–**2d** (Figure 3 and Table S1[4]), indicating that the length and the number of the alkyl side chains hardly affected the electronic structures of the tetracene rings.

On the other hand, in the solid state, the spectral shapes of absorption (Kubelka–Munk) and fluorescence and the fluorescence quantum yields (Φ_F values varied from 0.01 to 0.18) differed between **1a**–**1d** and **2a**–**2d** (Figure 4 and Table S2[4]). The absorption spectra in diluted KBr pellets illustrated structured bands. The longest absorption maxima of **1a**–**1d** (500–512 nm) were red shifted compared with those of **2a**–**2d** (482–486 nm). The latter values were comparable with the absorption maxima of **2a**–**2d** in solution (479 nm), indicating, in the case of **1a**–**1d**, the presence of stronger intermolecular interactions in the solid state with respect to **2a**–**2d**. The different absorption edges might reflect different aggregation structures. We believe that the four alkyl side chains at the two sides in **2a**–**2d** prevented close molecular orientation between the tetracene rings. In contrast, similar to 1,4-dialkyltetracenes,[3c] **1a**–**1d** would adopt a herringbone structure by edge-to-face interactions between adjacent tetracene rings because of the nonexistence of alkyl side chains at the 7,8,9,10-positions. We have already observed that the herringbone structure of tetracene moieties can cause red shifts.[3b] All the fluorescence spectra in the solid state were not only red shifted compared with those in solution but also differed significantly among each other, suggesting the presence of different intermolecular interactions. The different intermolecular interactions based on different molecular arrangements probably led to the difference in optical properties in the solid state. The solid-state optical properties differed slightly because of the difference in the alkyl side-chain lengths but considerably due to the difference in the numbers of alkyl side chains. These results were completely different from those of 1,4,7,10-tetraalkyltetracenes. An investigation of structural information in the solid state is under way.

In conclusion, we prepared 2,3-dialkyl- and 2,3,8,9-tetraalkyltetracenes to examine the effects of the substitution position on the solid-state color. In solution, optical properties were almost the same between **1a**–**1d** and **2a**–**2d**. The solid-state color of **1a**–**1d** was red shifted compared with that of **2a**–**2d**. The difference in the solid-state color was probably caused by different intermolecular interactions.

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