# Spectral Properties and Charge-transfer Complexes of the Cyclophanes Having the Pyrene Moiety

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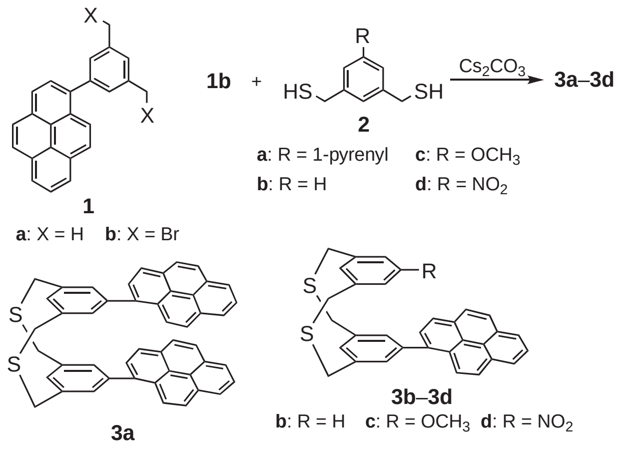
Novel cyclophanes having the pyrene moiety have been synthesized. The fluorescence and phosphorescence properties have been examined in terms of their structure. It has been found out that their charge-transfer complexes reflect the transannular $\pi$–$\pi$ interaction based on the structure.

Small-sized cyclophanes[1] characterized by the aromatic components in close proximity could be a good model for the study of weak interactions[2] such as $\pi$–$\pi$, CH–$\pi$, or NH–$\pi$ interactions based on $\pi$-electrons. From these points of view, it is no doubt that cyclophanes consisting of the pyrene ring deserve an intensive research.

Since the first reports[3–5] on [2.2](2,7)pyrenophanes, various kinds of pyrenophanes with other bridging such as (1,6), (1,6)(2,7), and (1,8)pyrenophanes,[6] as well as (1,3)compounds,[7] have been described mainly for the purpose of spectral studies concerning transannular $\pi$-electronic interactions. We clarified that conformations and molecular packings of the mixed 4,9-bridged pyrenophanes consisting of the pyrene and the benzene components are strongly affected by the functional group on the opposite benzene ring.[8] We also disclosed that the electronic state of the opposite benzene component in the mixed pyrenophanes plays a crucial role in formation of the charge-transfer complexes.[9] The pyrenophanes ever prepared so far have the bridging part on the pyrene ring itself, which might cause the strained ring.

Thus, the cyclophanes in which the pyrene ring is directly connected to the cyclophane skeleton has occurred to my mind as shown in Scheme 1.

Here, we describe the synthesis of novel cyclophanes having the pyrene moiety and their structural and spectral properties including transient absorption spectra as well as their charge-transfer complexes with TCNE.



**Scheme 1.**

The Suzuki couplimg of 1-bromopyrene and 3,5-dimethylphenylboronic acid gave the compound **1a**, which was brominated with NBS to afford the bromomethyl compound **1b** in 74% yield. The sulfanylmethyl compound **2a** was obtained by the reaction of **1b** and thiourea in 83% yield. Cyclization of **1b** and **2a**–**2d**[10–12] using $Cs_2CO_3$ as a base under highly dilute condition afforded the corresponding dithiacyclophanes **3a**–**3d** in 19–50% yields.

Cyclophanes **3a** and **3b**–**3d** exhibited the protons of both methylene bridges as one singlet and two singlets, respectively, at room temperature in their $^1$H NMR spectra, indicating that the cyclophanes exist in a flexible conformation. The inner aromatic proton on the benzene unit for the anti conformation in such a dithia[3.3]metacyclophane system should be subject to upfield shift ($\delta$ 6.62–6.86).[10] However, no upfield shift ($\delta$ 7.21–7.39)[13] for this proton was observed for **3a**–**3d**, thus, these cyclophanes seem to assume the syn conformation.

Emission properties for **3a**–**3d** together with **1a** are shown in Tables 1 and 2. Fluorescence bands due to locally excited (LE) singlet state of a pyrene moiety were observed for **1a** and **3b**–**3d** while an excimeric fluorescence band with weak LE fluorescence was obtained for **3a**, which arises from its syn conformation due to intramolecular excimer formation. A decay lifetime of LE fluorescence of **3a** was determined to be 185 ps which was in agreement with a rise lifetime of the corresponding excimer fluorescence.[13]

This agreement indicates that a favorable conformation for the excimeric state is formed with a time constant of 185 ps at 295 K via the molecular motion of the pyrenyl moieties of **3a**. Phosphorescence was observed from **1a** and **3a**–**3d** at 77 K and the shape of the spectra was similar to each other. Transient absorption spectra having a maximum absorbance around 460–470 nm were obtained upon 355 nm laser photolysis of dichloromethane solutions of **1a** and **3a**–**3c**.[13] They were due to triplet–

**Table 1.** Spectral properties ($\lambda_{max}$/nm)[a] of **3a**–**3d** and **1a**

| Compd | Absorption[b] | Fluorescence[b] [excitation/nm] | Phosphorescence[c] | |
|---|---|---|---|---|
| **3a** | 344 | 439 [344] | 614 | 681 |
| **3b** | 344 | 381 399 [345] | 605 | 668 |
| **3c** | 345 | 382 400 [344] | 605 | 668 |
| **3d** | 344 | 381 397 510[d][280] | 609 | 676 |
| **1a** | 343 | 381 400 [343] | 604 | 665 |

[a]In cyclohexane, $c = 1.0 \times 10^{-5}$ M. [b]$T = 295$ K. [c]Excitation = 345 nm, $T = 77$ K. [d]$T = 77$ K.

**Table 2.** Decay lifetime ($\tau_f$), quantum yields ($\Phi_f$), and rates ($k_f$) of fluorescence obtained for **3a**–**3d** and **1a**[a]

| Compd | $\tau_f$[b]/ns | $\Phi_f$[c] | $k_f$[d]$/10^7\ s^{-1}$ |
|---|---|---|---|
| **3a** | 27.8[e] | 0.48 | 1.7 |
| **3b** | 57.6 | 0.33 | 0.57 |
| **3c** | 52.1 | 0.38 | 0.73 |
| **3d** | 97.7 | $<10^{-4}$ | $<10^{-4}$ |
| **1a** | 106 | 0.47 | 8.0 |

[a] In cyclohexane at 295 K. [b] Determined by the single photon counting method. [c] Determined by comparing with the fluorescence yield of anthracene in ethanol (0.27 ± 0.03). [d] Obtained by the equation, $k_f = \Phi_f \tau_f^{-1}$. [e] A decay lifetime of exicimeric fluorescence at 450 nm.

**Table 3.** Absorption maxima and stability constants of charge-transfer complexes[a] of **3a**–**3d** and **1a** with TCNE

| Compd | $\lambda_{max}$/nm | Stability constant/$M^{-1}$ |
|---|---|---|
| **3a** | 782 | 2.51 |
| **3b** | 779 | 1.86 |
| **3c** | 797 | 3.12 |
| **3d** | 757 | 1.25 |
| **1a** | 769 | 4.54 |

[a] In $CH_2Cl_2$.

triplet absorption of the corresponding pyrene moiety. Excimer triplet of **3a** was not recognized in the transient absorption at 295 K. Appreciable transient absorption was not observed for **3d**, indicating that intersystem crossing and fluorescence processes are inefficient in **3d**, namely, that the deactivation process of the lowest excited singlet state, $S_1$ of **3d** is governed mainly by internal conversion at room temperature.

It has been well known[14] that charge-transfer complexes of cyclophane compounds with tetracyanoethylene (TCNE) can give information of the $\pi$ basicity of the aromatic rings in such systems. A transannular effect of the substituent introduced into the aromatic ring on the TCNE complexes of cyclophanes has been known in [2.2]paracyclophanes.[15]

**3a** and **3b** were found to form 1:1 charge-transfer complexes with TCNE in dichloromethane, which was deduced from their Job's plots.[16] Other cyclophanes can be considered to form likewise the 1:1 complex. The stability constant ($K$) for formation of the complexes was also obtained by employing a Benesi–Hildebrand plot.[13,17] The absorption maxima and stability constants for the complexes are summarized together with those of **1a** in Table 3. As seen in **3a** and **3b**, the transannular $\pi$–$\pi$ interaction between two aromatic components located in close proximity leads to lower energy charge-transfer transition resulting in a bathocchromic shift. Such a shift is enhanced by the electron-donating substituent such as a methoxy group on the opposite benzene ring in **3c**.

On the contrary a hypsochromic shift is observed for **3d**, probably due to the electron-withdrawing effect of the nitro group through transannular interaction. With increasing donor strength of the pyrene component the complexes become more stable, indicated by the large stability constant. The methoxy-substituted pyrenophane **3c** gave $3.12\,M^{-1}$ that is larger than those for **3a** and **3b**. As expected the small value ($1.25\,M^{-1}$) was obtained for the nitro-substituted cyclophane **3d**. The stability constant of the reference compound **1a** is larger than those of the cyclophanes. Although a precise reason for that is currently unclear, a conformational mobility or a cyclic structure in the cyclophane system might be involved in decrease of the $\pi$-basicity.

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