

# Syntheses, structural properties, and charge-transfer complexes of pyrenophanes

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Dithia[3.3](4,9)benzenopyrenophanes carrying various functional groups at the inner position or the outer position of the benzene ring have been prepared. The pyrenophanes with the substituent at the inner position of the opposite benzene ring exhibit the conformation in which the pyrene and the benzene components exist in the parallel manner (parallel conformation). On the contrary the conformation characterized by the perpendicular orientation of the pyrene and the benzene components has been confirmed for the pyrenophanes having the substituent at the outer position of the opposite benzene ring (perpendicular conformation). The NH- $\pi$  interaction between the inner amino group on the opposite benzene ring and the pyrene ring was observed. Formation of charge-transfer complexes of the pyrenophanes and tetracyanoethylene (TCNE) was performed. It has been found out that the orientation of two aromatic components and the NH- $\pi$  interaction as well as the electronic nature of the substituent on the opposite benzene ring significantly affect characteristics of the charge-transfer complexes in this pyrenophane system.

## Introduction

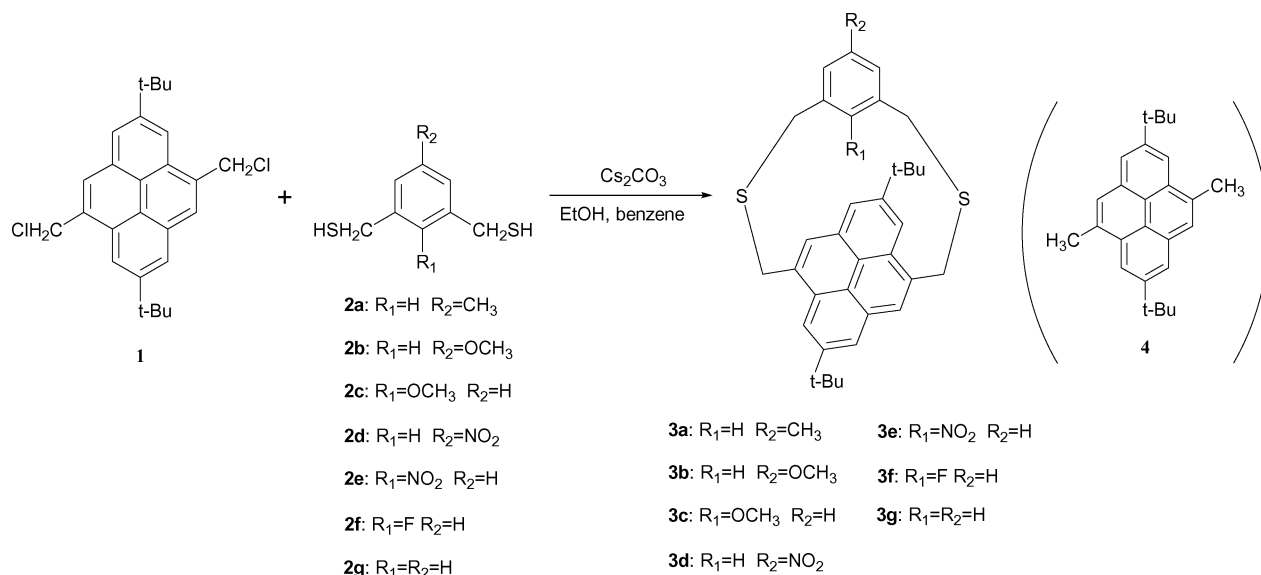
Supramolecular<sup>1</sup> chemistry is based on the association of two or more building molecules through intermolecular interactions, in contrast to molecular chemistry, which is based on the covalent bonding of atoms. Cyclophanes, which are bridged aromatic molecules, have been expanding their interest in the field of supramolecular chemistry. Among them large-sized cyclophanes capable of forming the inner cavity have been playing a crucial role as synthetic receptors in molecular recognition which is one of the central topics of supramolecular chemistry. On the contrary small-sized cyclophanes characterized by the aromatic components which are fixed in close proximity to each other have not appeared so often in this field, however, they could be a good model for the study of weak interactions such as  $\pi$ - $\pi$ , CH- $\pi$ , or NH- $\pi$  interactions related to the  $\pi$ -electron system.<sup>2-4</sup> Especially, cyclophanes composed of the pyrene unit are interesting because they have an extended  $\pi$ -electron system.

Since the first reports<sup>5-7</sup> 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,<sup>8</sup> as well as (1,3)compounds,<sup>9</sup>

have been described mainly for the purpose of fluorescence studies based on transannular  $\pi$ -electronic interactions. As a mixed pyrenophane, the pyrenophanes incorporating simple aromatic components such as benzene, naphthalene and phenanthrene rings have been synthesized. More recently Yamato *et al.*<sup>10</sup> showed the convenient preparative methods of 4,9-bridged pyrenophanes. The introduction of S into the bridge of a cyclophane should make conformational inversion easier, indicating that a wide variety of conformations can be expected.

We have clarified that conformations and molecular packings of the 4,9-bridged dithiapyrenophanes are strongly affected by the substituent on the opposite benzene ring.<sup>11</sup> However, systematic studies on transannular  $\pi$ -electronic interactions in the pyrenophanes have been very limited. Thus, in order to obtain novel aspects of specific transannular  $\pi$ -electronic interactions and weak interactions related with  $\pi$ -electrons of the pyrene unit, we have focused on the small-sized pyrenophane system containing the substituted benzenes.

Here we report the syntheses, structures, and charge-transfer complexes of novel (4,9)benzenopyrenophanes having various functional groups on the opposite benzene ring.

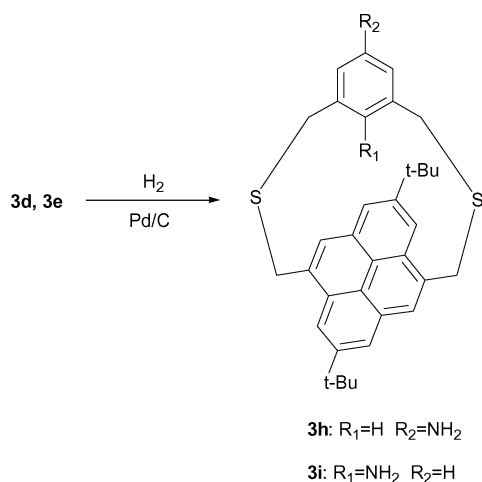


## Results and discussion

### Syntheses of pyrenophanes (3a–i)

Bis(chloromethyl)pyrene **1** was prepared according to the reported method.<sup>10</sup> Derivatives of 2,6- or 3,5-dimethyl benzene were brominated by NBS, followed by treatment with thiourea to give the desired bis(mercaptomethyl) compounds **2a–g**.<sup>12–14</sup> Cyclization of **1** and **2a** using Cs<sub>2</sub>CO<sub>3</sub> as a base under highly dilute condition afforded the corresponding dithiapyrenophane **3a** in 54% yield. Dithiapyrenophanes **3b–f** and **3g**<sup>10</sup> were obtained by the similar method in 28–66% yields.

The nitro compounds **3d** and **3e** were reduced with hydrogen gas in the presence of 10% Pd/C to give the corresponding amino compounds **3h** and **3i** in 62 and 15% yields, respectively. The low yield for **3i** might be due to the steric hindrance of the pyrene component against the nitro group.



### Conformations of pyrenophanes

All pyrenophanes **3a–i** exhibited the protons of both methylene bridges as sets of doublets at room temperature in the <sup>1</sup>H NMR spectra, indicating that the pyrenophanes exist in a rigid conformation. No obvious changes in their <sup>1</sup>H NMR signals were observed in the conventional temperatures. The partial data of the <sup>1</sup>H NMR spectra of **3a–i** are summarized in Table 1.

In the spectrum of **3a** having the hydrogen at the internal position (R<sub>1</sub>) of the opposite benzene ring the pyrene protons appeared as three kinds of signals. Taking this signal pattern into account, the benzene ring can be considered perpendicular to the pyrene ring. This “perpendicular conformation” is expected for the pyrenophanes **3b**, **3d**, **3g** and **3h** carrying the hydrogen at R<sub>1</sub> position since their <sup>1</sup>H NMR spectra show the feature similar

to that of **3a**. The inner proton (R<sub>1</sub>) of **3a** appears shielded at  $\delta$  3.77. Such a strongly shielded effect is consistent with the “perpendicular conformation” described above because the inner proton plunges into the  $\pi$ -cloud of the pyrene component. The inner proton (R<sub>1</sub>) shows more upfield shift in order of **3d**, **3g**, **3a**, **3b** and **3h**, which reflects the Hammett constants of the substituent at the *para* position (R<sub>2</sub>). In these pyrenophanes the inner proton (R<sub>1</sub>) seems to suffer the similar shielded effect of the pyrene component.

On the contrary the pyrenophane **3c** having the methoxy group at the inner position (R<sub>1</sub>) exhibits a quite different <sup>1</sup>H NMR peak pattern for the pyrene protons. Six kinds of peaks for them are observed, suggesting that the conformation is not a “perpendicular conformation” as seen in **3a**. The chemical shift of methoxy protons in **3c** observed at  $\delta$  2.72 is almost identical with that of the inner methoxy protons in the [2.2]metacyclophane<sup>15</sup> whose two aromatic rings are almost parallel. We have already reported<sup>11</sup> that the pyrenophane **3e** assumes the conformation where two aromatic components are almost parallel in the solid state. From these facts the “parallel conformation” seems to be dominating for **3c**. As <sup>1</sup>H NMR spectral signals similar to **3c** were observed for **3e**, **3f** and **3i**, one can expect the “parallel conformation” for the pyrenophanes when the opposite benzene ring has the substituent at its inner position.

### NH– $\pi$ interaction in pyrenophanes

Although the <sup>1</sup>H NMR signal for the amino protons in **3h** was observed at  $\delta$  3.24, the corresponding signal in **3i** was not detected, meaning that the amino group in **3i** must be situated in the different environment from that for **3h**. In the IR spectrum of **3i** the peaks of the amino group were observed at 3438 and 3298 cm<sup>-1</sup>, which are much lower than the corresponding peaks of 3484 and 3400 cm<sup>-1</sup> in 2,6-dimethylaniline. Such a large shift probably stems from formation of hydrogen bonds which arise from the amino group directed toward the  $\pi$ -cloud of the pyrene component. On the other hand the outer amino group in **3h** shows the peaks at 3480 and 3380 cm<sup>-1</sup>, indicating that there is no specific interaction.

From these results it can be concluded that there exists the NH– $\pi$  interaction between the amino group and the pyrene component in **3i**.

### Charge-transfer complexes of pyrenophanes and TCNE

It has been well known<sup>16</sup> 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

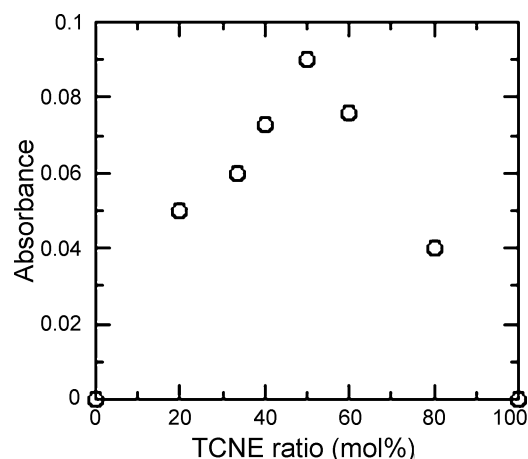
Table 1 Chemical shifts<sup>a</sup> in pyrenophanes

Compd	R <sub>1</sub> proton	R <sub>2</sub> proton	Pyrene proton		
	( $\delta$ /ppm)	( $\delta$ /ppm)	( $\delta$ /ppm)	( $J$ /Hz)	( $J$ /Hz)
<b>3a</b>	3.77 (s, 1H)	1.82 (s, 3H)	7.77 (s, 2H)	7.92 (d, <i>J</i> 1.6, 2H)	8.33 (d, <i>J</i> 1.6, 2H)
<b>3b</b>	3.61 (s, 1H)	3.54 (s, 3H)	7.77 (s, 2H)	7.93 (d, <i>J</i> 1.5, 2H)	8.33 (d, <i>J</i> 1.5, 2H)
<b>3c</b>	2.72 (s, 3H)	5.85 (t, <i>J</i> 7.7, 1H)	7.69 (s, 1H)	7.72 (d, <i>J</i> 1.6, 1H)	7.82 (s, 1H)
			8.13 (d, <i>J</i> 1.5, 1H)	8.23 (d, <i>J</i> 1.6, 1H)	8.34 (d, <i>J</i> 1.5, 1H)
<b>3d</b>	4.38 (s, 1H)	—	7.82 (s, 2H)	7.91 (d, <i>J</i> 1.2, 2H)	8.33 (d, <i>J</i> 1.2, 2H)
<b>3e</b>	—	6.13 (s, 1H)	7.75 (d, <i>J</i> 1.6, 1H)	7.83 (s, 2H)	8.16 (d, <i>J</i> 1.5, 1H)
			8.25 (d, <i>J</i> 1.6, 1H)	8.33 (d, <i>J</i> 1.5, 1H)	
<b>3f</b>	—	5.56 (t, <i>J</i> 7.0, 1H)	7.72 (s, 1H)	7.74 (d, <i>J</i> 1.5, 1H)	7.90 (s, 1H)
			8.19 (d, <i>J</i> 1.2, 1H)	8.25 (d, <i>J</i> 1.5, 1H)	8.38 (d, <i>J</i> 1.5, 1H)
<b>3g</b>	3.96 (s, 1H)	6.15 (t, <i>J</i> 7.6, 1H)	7.77 (s, 2H)	7.92 (d, <i>J</i> 1.4, 2H)	8.33 (d, <i>J</i> 1.4, 2H)
<b>3h</b>	3.44 (s, 1H)	3.24 (s, 2H)	7.80 (s, 2H)	7.98 (d, <i>J</i> 1.3, 2H)	8.37 (d, <i>J</i> 1.3, 2H)
<b>3i</b>	—	5.58 (s, 1H)	7.78 (s, 1H)	7.79 (d, <i>J</i> 1.5, 1H)	7.85 (s, 1H)
			8.14 (d, <i>J</i> 1.2, 1H)	8.30 (d, <i>J</i> 1.5, 1H)	8.39 (d, <i>J</i> 1.2, 1H)

<sup>a</sup> In CDCl<sub>3</sub> at 27 °C.

into the aromatic ring on the TCNE complexes of cyclophanes has been known in [2.2]paracyclophanes.<sup>17</sup> Previously it was reported<sup>18</sup> that substituted and unsubstituted [2.2]metacyclophanes formed exclusively 1 : 1 complexes with TCNE. These facts led us to investigate the charge-transfer complexes of the pyrenophanes in order to know the relationship between charge-transfer transition and characteristic transannular  $\pi$ - $\pi$  interaction and/or NH- $\pi$  interaction in the pyrenophane system.

**3a** was found to form 1 : 1 charge-transfer complexes with TCNE in dichloromethane, which was deduced from the Job's plots (Fig. 1).<sup>19</sup> Other pyrenophanes can be considered to form likewise a 1 : 1 complex.



**Fig. 1** Job's plot of charge-transfer complexes with of **3a** with TCNE in dichloromethane.

An extensive bathochromic shift for all complexes highly indicates that a TCNE molecule binds the pyrene component of the pyrenophane. The stability constant ( $K$ ) for formation of the complexes was also obtained by employing a Benesi-Hildebrand plot.<sup>20</sup> The results are summarized in Table 2.

The absorption maxima and the stability constants are significantly dependent on the substituent on the opposite benzene ring. As seen in **3a**, **3b**, **3c** and **3h** substitution of the benzene ring with the electron-donating group leads to lower energy charge-transfer transition due to transannular interaction between the benzene and the pyrene components, resulting in a bathochromic shift. On the contrary a hypsochromic shift is observed for **3d**, **3e** and **3f**, probably due to the electron-withdrawing group on the opposite benzene ring enhancing higher energy charge-transfer transition through transannular interaction.

Interestingly, comparing **3b** and **3c** the inner-substituted pyrenophane **3c** induces a shift to longer wavelength than the outer-substituted one **3b**, implying that the electron-donating effect of the methoxy group in **3c** works more effectively

**Table 2** Absorption maxima and stability constants of charge-transfer complexes<sup>a</sup> of **3a-i** and **4**

Compound	$\lambda_{\max}$ /nm	Stability constant/mol <sup>-1</sup>
<b>3a</b>	819	5.50
<b>3b</b>	820	6.50
<b>3c</b>	835	7.66
<b>3d</b>	795	1.75
<b>3e</b>	775	1.25
<b>3f</b>	810	4.30
<b>3g</b>	814	4.33
<b>3h</b>	842	8.58
<b>3i</b>	763	1.25
<b>4</b>	817	10.0

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

than that in **3b** through transannular  $\pi$ - $\pi$  interaction. This difference probably arises from the conformational properties of the pyrenophanes because much stronger transannular  $\pi$ - $\pi$  interaction can be expected for a face-to-face orientation of two aromatic components in the "parallel conformation" than an edge-to-face orientation in the "perpendicular conformation". A similar shift can be seen between **3d** and **3e**. In this case electron-withdrawing effect can be emphasized in the "parallel conformation", resulting the shift to a shorter wavelength in **3e**.

With increasing donor strength of the pyrene component the complexes become more stable, indicated by the large stability constant. For methoxy-substituted pyrenophanes **3b** and **3c** 6.50 and 7.66 mol<sup>-1</sup> were obtained as the stability constant, respectively. As expected, nitro-substituted pyrenophanes **3d** and **3e** gave small values (1.75 and 1.25 mol<sup>-1</sup>). These values also reflect the "parallel" and "perpendicular" conformations. Substitution with an electron-donating group in the "parallel conformation" leads to a larger increase in stability of the complexes than in the "perpendicular conformation". In agreement with this explanation, a larger decrease in stability of the complexes is achieved in the "parallel conformation" by substitution with an electron-withdrawing group.

The pyrenophane **3i** having the amino group on the opposite benzene ring is expected to assume the "parallel conformation", nevertheless, its behavior for complexation with TCNE is unexpectedly unique. Considering the electron-donating effect of the amino group a bathochromic shift would have been expected, however, the  $\lambda_{\max}$  of the complex of **3i** underwent a hypsochromic shift showing 763 nm in comparison with 842 nm for the complex of **3h**.

Other factors except for transannular  $\pi$ - $\pi$  interaction have to be considered to explain such an unexpected result. The NH- $\pi$  interaction possibly exists between the amino protons and the pyrene component as described above. Thus, such a unique hypsochromic shift for the complex of **3i** may be related to the NH- $\pi$  interaction since the less  $\pi$ -basic pyrene component could be induced by the NH- $\pi$  interaction.

The  $K$  value of the reference compound **4** is larger than those of the pyrenophanes. Although a precise reason for that is currently unclear, a somewhat distorted pyrene ring in the pyrenophanes might be responsible for decrease in its  $\pi$ -basicity.

## Conclusion

It has been found out that [3.3](4,9)benzenopyrenophanes assume two kinds of conformations, that is, "perpendicular conformation" and "parallel conformation" depending on the position of the substituent on the opposite benzene ring.

In the pyrenophane carrying the amino group at the inner position the NH- $\pi$  interaction was confirmed between the pyrene component and the amino group.

In this cyclophane system the complex formation of the TCNE-pyrene component is much affected by the nature of the substituent on the opposite benzene ring through transannular  $\pi$ - $\pi$  electronic interaction. It should be noted that this transannular interaction is enhanced in the "parallel conformation" and reduced in the "perpendicular conformation".

For the first time we have also clarified that the NH- $\pi$  interaction can have a significant influence on the formation of charge-transfer complexes based on the  $\pi$ -basicity of the aromatic ring.

## Experimental

### Typical procedure for coupling reaction

A solution of **1** (2.0 g, 4.9 mmol) and **2a** (0.9 g, 4.9 mmol) in a mixture of ethanol and benzene (200 ml) was added dropwise over 15 h to a stirred suspension of Cs<sub>2</sub>CO<sub>3</sub> (4.0 g, 12 mmol) in ethanol (2 L) at a refluxing temperature. The reaction mixture was concentrated and the residue was extracted

with CH<sub>2</sub>Cl<sub>2</sub>. The extract was dried over MgSO<sub>4</sub>, concentrated and chromatographed using a 1 : 1 mixture of chloroform and hexane as an eluent to give **3a** (1.4 g, 54%) as colorless prisms; mp 211–213 °C (chloroform–hexane); (Found: C, 80.2; H, 7.3. Calc. for C<sub>35</sub>H<sub>38</sub>S<sub>2</sub>: C, 80.4; H, 7.3%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.61 (18H, s), 1.82 (3H, s), 2.68 (2H, d, *J* 16.8), 2.79 (2H, d, *J* 16.8), 3.77 (1H, s), 4.22 (2H, d, *J* 12.0), 4.93 (2H, d, *J* 12.0), 6.24 (2H, s), 7.77 (2H, s), 7.92 (2H, d, *J* 1.6), 8.33 (2H, d, *J* 1.6); *m/z* (EI) 522 (M<sup>+</sup>).

#### Dithia[3.3](4,9)pyrenophane 3b

White powder; mp 244–245 °C (chloroform–hexane); (Found: C, 77.8; H, 7.1. Calc. for C<sub>35</sub>H<sub>38</sub>OS<sub>2</sub>: C, 78.0; H, 7.1%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.61 (18H, s), 2.70 (2H, d, *J* 16.7), 2.80 (2H, d, *J* 16.7), 3.54 (3H, s), 3.61 (1H, s), 4.22 (2H, d, *J* 12.1), 4.93 (2H, d, *J* 12.1), 6.02 (2H, s), 7.77 (2H, s), 7.93 (2H, d, *J* 1.5), 8.33 (2H, d, *J* 1.5); *m/z* (EI) 538 (M<sup>+</sup>).

#### Dithia[3.3](4,9)pyrenophane 3c

White powder; mp 238–240 °C (chloroform–hexane); (Found: C, 77.7; H, 7.2. Calc. for C<sub>35</sub>H<sub>38</sub>OS<sub>2</sub>: C, 78.0; H, 7.1%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.59 (9H, s), 1.64 (9H, s), 2.72 (3H, s), 2.76 (1H, d, *J* 17.4), 2.87 (1H, d, *J* 17.4), 2.89 (1H, d, *J* 16.6), 3.28 (1H, d, *J* 16.6), 4.10 (1H, d, *J* 12.0), 4.31 (1H, d, *J* 12.1), 4.71 (1H, d, *J* 12.1), 5.12 (1H, d, *J* 12.0), 5.85 (1H, t, *J* 7.7), 6.19 (1H, d, *J* 7.7), 6.75 (1H, d, *J* 7.7), 7.69 (1H, s), 7.72 (1H, d, *J* 1.6), 7.82 (1H, s), 8.13 (1H, d, *J* 1.5), 8.23 (1H, d, *J* 1.6), 8.34 (1H, d, *J* 1.6); *m/z* (EI) 538 (M<sup>+</sup>).

#### Dithia[3.3](4,9)pyrenophane 3d

Yellow prisms. mp 263–264 °C (toluene); (Found: C, 73.3; H, 6.5; N, 2.2. Calc. for C<sub>34</sub>H<sub>35</sub>NO<sub>2</sub>S<sub>2</sub>: C, 73.7; H, 6.4; N, 2.5%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.57 (18H, s), 2.75 (2H, d, *J* 16.8), 2.86 (2H, d, *J* 16.8), 4.26 (2H, d, *J* 12.1), 4.38 (1H, s), 4.94 (2H, d, *J* 12.1), 7.32 (2H, s), 7.82 (2H, s), 7.91 (2H, d, *J* 1.2), 8.33 (2H, d, *J* 1.2); *m/z* (EI) 553 (M<sup>+</sup>).

#### Dithia[3.3](4,9)pyrenophane 3e

Yellow prisms; mp 260–262 °C (toluene); (Found: C, 73.5; H, 6.7; N, 2.2. Calc. for C<sub>34</sub>H<sub>35</sub>NO<sub>2</sub>S<sub>2</sub>: C, 73.7; H, 6.4; N, 2.5%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.62 (9H, s), 1.63 (9H, s), 2.78 (1H, d, *J* 16.4), 2.87 (1H, d, *J* 16.4), 2.92 (1H, d, *J* 16.6), 3.28 (1H, d, *J* 16.6), 4.13 (1H, d, *J* 12.0), 4.31 (1H, d, *J* 12.0), 4.69 (1H, d, *J* 12.0), 5.09 (1H, d, *J* 12.0), 6.13 (1H, t, *J* 7.8), 6.47 (1H, d, *J* 7.8), 7.06 (1H, d, *J* 7.8), 7.75 (1H, d, *J* 1.6), 7.83 (1H, s), 8.16 (1H, d, *J* 1.5), 8.25 (1H, d, *J* 1.6), 8.33 (1H, d, *J* 1.5); *m/z* (EI) 553 (M<sup>+</sup>).

#### Dithia[3.3](4,9)pyrenophane 3f

Colorless prisms; mp 261–263 °C (chloroform–hexane); (Found: C, 77.1; H, 7.0. Calc. for C<sub>34</sub>H<sub>35</sub>FS<sub>2</sub>: C, 77.5; H, 6.7%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.59 (9H, s), 1.63 (9H, s), 2.65 (1H, d, *J* 17.4), 2.74 (1H, d, *J* 17.4), 2.88 (1H, d, *J* 16.8), 3.16 (1H, d, *J* 16.8), 4.14 (1H, d, *J* 12.2), 4.34 (1H, d, *J* 12.2), 4.74 (1H, d, *J* 11.9), 5.14 (1H, d, *J* 11.9), 5.56 (1H, t, *J* 7.0), 6.18 (1H, d, *J* 7.0), 6.75 (1H, d, *J* 7.0), 7.72 (1H, s), 7.74 (1H, d, *J* 1.5), 7.90 (1H, s), 8.19 (1H, d, *J* 1.2), 8.25 (1H, d, *J* 1.5), 8.38 (1H, d, *J* 1.2); *m/z* (EI) 526 (M<sup>+</sup>).

#### Typical procedure of reduction of nitro pyrenophane

To a suspension of **3d** (92 mg, 17 mmol) and Pd/C (1.1 g) in benzene (100 mL) was introduced hydrogen gas under stirring

at room temperature for 4 h. After the filtration of Pd/C, the filtrate was evaporated *in vacuo* to leave the residue, which was chromatographed with chloroform and hexane (1 : 1) as an eluent to give **3h** (54 mg, 62%) as pale yellow prisms; mp 220–222 °C (chloroform–hexane); (Found: C, 77.6; H, 7.2; N, 2.4. Calc. for C<sub>34</sub>H<sub>37</sub>NS<sub>2</sub>: C, 78.0; H, 7.1; N, 2.7%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.64 (18H, s), 2.68 (2H, d, *J* 16.6), 2.78 (2H, d, *J* 16.6), 3.24 (2H, s), 3.44 (1H, s), 4.24 (2H, d, *J* 12.0), 4.96 (2H, d, *J* 12.0), 5.79 (2H, s), 7.80 (2H, s), 7.98 (2H, d, *J* 1.3), 8.37 (2H, d, *J* 1.3); *m/z* (EI) 523 (M<sup>+</sup>).

#### Dithia[3.3](4,9)pyrenophane 3i

Pale yellow prisms; mp 293–296 °C (dichloromethane–methanol); (Found: C, 77.8; H, 7.2; N, 2.5. Calc. for C<sub>34</sub>H<sub>37</sub>NS<sub>2</sub>: C, 78.0; H, 7.1; N, 2.7%); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.60 (9H, s), 1.61 (9H, s), 2.54 (1H, d, *J* 16.8), 2.76 (1H, d, *J* 16.8), 2.89 (1H, d, *J* 16.5), 3.08 (1H, d, *J* 16.5), 4.19 (1H, d, *J* 12.8), 4.33 (1H, d, *J* 12.2), 4.80 (1H, d, *J* 12.2), 5.10 (1H, d, *J* 12.8), 5.58 (1H, t, *J* 7.6), 6.19 (1H, d, *J* 7.6), 6.67 (1H, d, *J* 7.6), 7.78 (1H, s), 7.79 (1H, d, *J* 1.5), 7.85 (1H, s), 8.14 (1H, d, *J* 1.2), 8.30 (1H, d, *J* 1.5), 8.39 (1H, d, *J* 1.2); *m/z* (EI) 523 (M<sup>+</sup>).

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