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# Thermal transition behavior and crystal structure of octakis(phenylsulfanyl)naphthalene

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## Abstract

The conformational properties of octakis(phenylsulfanyl)naphthalene (ophn) were examined by their X-ray structural and thermal analyses. Ophns have been prepared in two different conformations, i.e. the red and yellow forms. The yellow form consists of the **aabbaabb** and **bbaabbaa** isomers (the descriptions **a** and **b** denote side-chain phenyl moieties projecting above or below, respectively). Both isomers are alternately arrayed in the direction parallel to the *c*-axis. This crystal structure will not be formed with only the chiral compounds. From the DTA results, the crystal melting point ($T_{m1}$) of the red form appeared at around 201.3 °C, for the yellow form, $T_{m2}$ appeared at around 174.5 °C and the crystallization point ($T_{c2}$) is 114.5 °C. Both crystals indicate an amorphous phase during cooling after melting, then the $T_g = 60$ °C. The phase transformation observed for the red and yellow forms is summarized on the basis of the thermal analysis and powder X-ray diffraction pattern.

*Keywords:* Octakis(phenylsulfanyl)naphthalene; X-ray crystal structure; Thermal analysis; Chromism; Polymorphism

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## 1. Introduction

Polymorphism is commonly understood as connoting the ability of a compound to crystallize in more than one distinct crystal structure. According to McCrone, “A polymorph is a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state” [1]. Because polymorphs have different structures, they may significantly differ in density, hardness, solubility, and optical and electrical properties. Octa-substituted naphthalene is known as a polymorphism compound. MacNicol and co-workers reported some octa-substituted naphthalenes in their study of inclusion compounds [2–5]. One of these compounds, octakis(phenylsulfanyl)naphthalene, was isolated in two different conformations. Interestingly, when one presses crystals of the yellow form on, for example, a glass slide, red crystals are produced at the point of pressure application, so that a solid–solid transformation seems to occur in the crystal lattice. The red form and yellow form of octakis(phenylsulfanyl)naphthalene were isolated and determined by X-ray crystal analysis. Also, the difference in the conformation energies of both structures is small based on AM1 calculations [6]. Some investigations about octa-substituted naphtha-

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lene have been reported except for that mentioned above. However, a detailed study of the relation between the crystal structure and thermal analysis of octakis(phenylsulfanyl)naphthalene has not yet been carried out. In this paper, we describe the preparation of octakis(phenylsulfanyl)naphthalene, its crystal structure and thermal properties. Furthermore, the structure and thermal analyses were studied from the viewpoint of its thermo-chromism properties.

## 2. Result and discussion

### 2.1. Molecular structure

Ophn was crystallized from chloroform-pentane to give red crystals and from DMI-diethylether to give yellow crystals. As their X-ray crystal structures have already been reported by MacNicol and co-workers [3], we present a summary of their molecular structures. An ORTEP view of the red and yellow forms with selected atom labeling is shown in Fig. 1a and b, respectively. The descriptions **a** and **b** denote the side-chain phenyl moieties projecting above or below, respectively, the mean plane of the naphthalene core. The side-phenyl groups are perpendicular to the naphthalene ring plane, however, the conformation of the red form is **aababbab**. The core naphthalene ring has almost a planar structure. In contrast, the conformation of the yellow form is **aabbaabb**, and it is interesting to note that the two benzene rings in the core naphthalene ring have a torsion angle of 31° at the 9- and 10-position carbon. The distances S···S of the 1- and 8-position into the naphthalene ring are 2.94 Å (red) and 3.23 Å (yellow), respectively. This is considerably shorter than twice the van der Waals radius of 3.70 Å. Considering an individual molecule, the yellow form seems to be more stable than the red form. The crystal packing structures of both ophns are shown in Fig. 2. In the red form, each molecule with the **aababbab** conformation is closely packed in the direction parallel to the *c*-axis. From the molecular packing structure of the red form, the intermolecular naphthalene–naphthalene distances

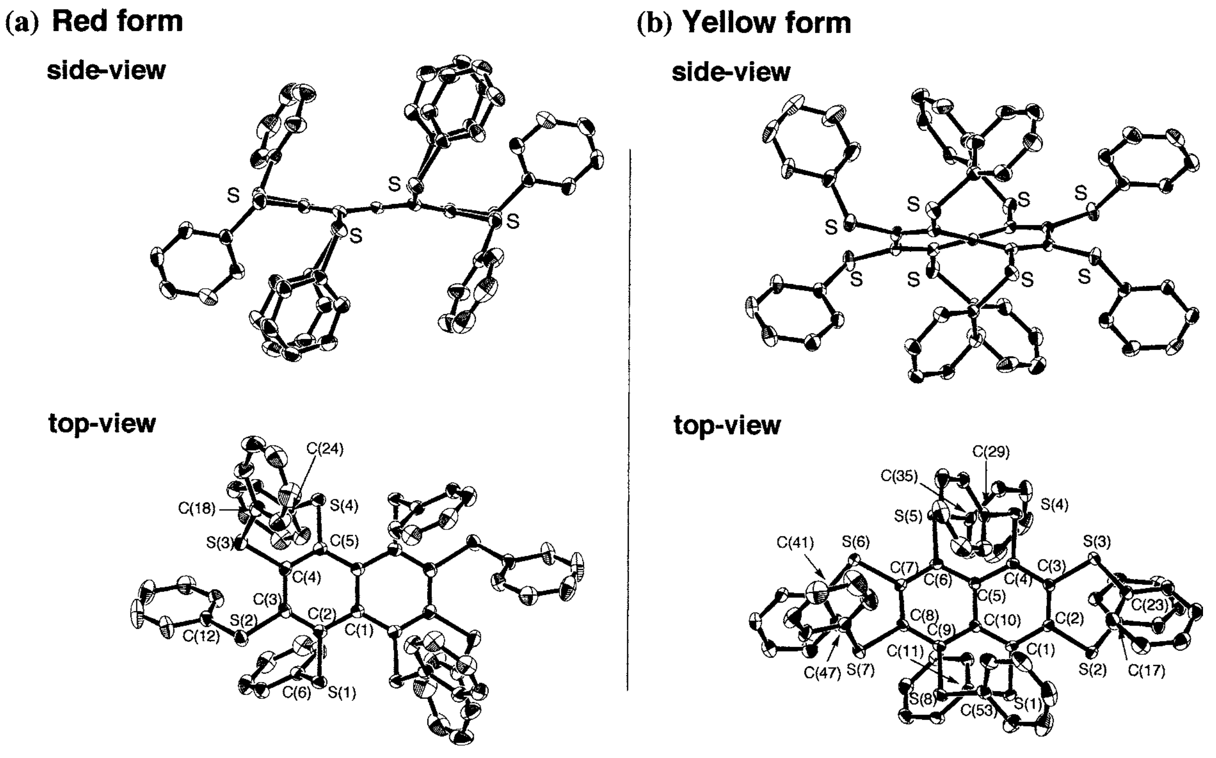
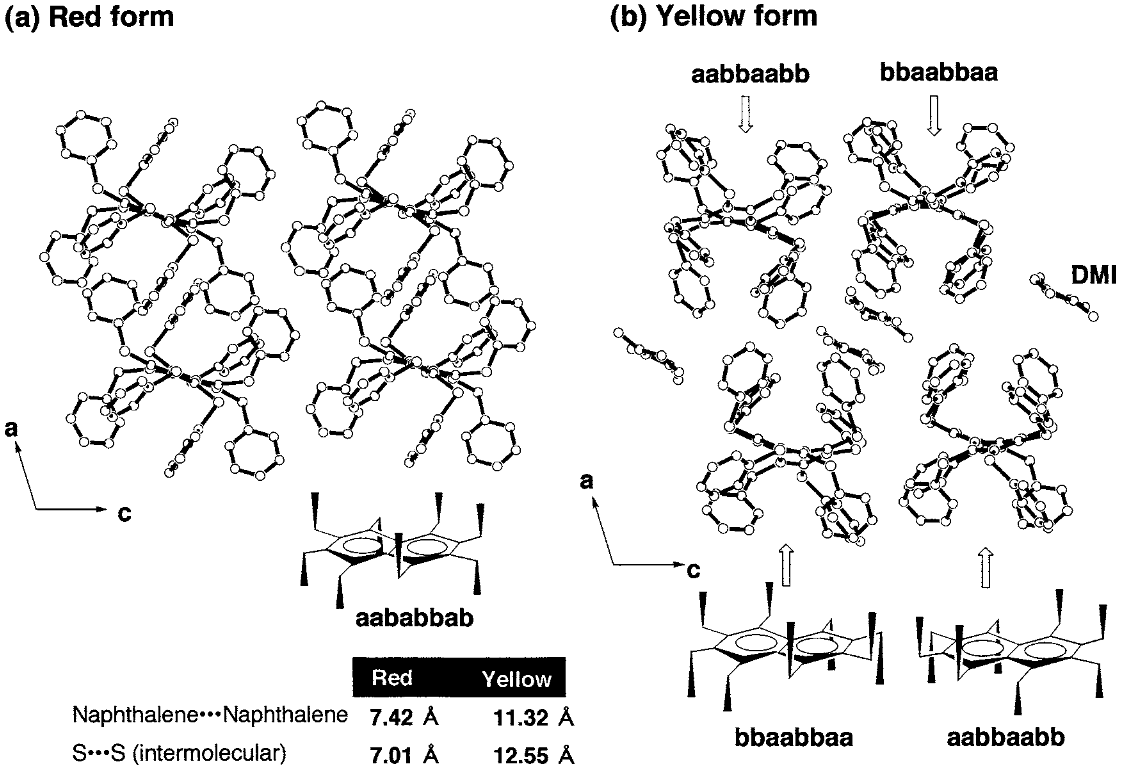


Fig. 1. ORTEP view of ophn with the atomic labeling scheme (a) red form and (b) yellow form.



| | Red | Yellow |
|---|---|---|
| Naphthalene•••Naphthalene | 7.42 Å | 11.32 Å |
| S•••S (intermolecular) | 7.01 Å | 12.55 Å |

Fig. 2. Crystal packing structure of ophn (a) red form and (b) yellow form.

and the shortest S ··· S distances are of 7.42 and 4.20 Å, respectively. In the yellow form, the crystal consists of the **aabbaabb** and **bbaabbaa** isomers. Since both isomers are alternately arrayed in the direction parallel to the *c*-axis, this structure will not be formed with only the chiral compounds. Furthermore, DMI molecules from the synthesis solvent are inserted in the crystal. Therefore, the intermolecular naphthalene–naphthalene distances and the shortest S ··· S distances are of 11.32 and 4.09 Å, respectively. This is the reason why the color change of the ophn organic crystals is regarded with torsion in the naphthalene ring and lose packing structure. The ophns have a thermochromic property between the red and yellow forms as follows.

### 2.2. Thermal analysis and morphology

It is possible to investigate the change in the DTA characteristics of the red form as a function of multiple heating/cooling cycles, and the resulting calorimetry traces are shown in Fig. 3. For these measurements, the heating rates were 3 °C/min and cooling rates were 30 °C/min. In the first scan, one observes a $T_{\mathrm{m1}}$ at 201.3 °C. The sample was taken to a maximum temperature of 215 °C. On the first cooling cycles, no crystallization was observed for this sample. A powder diffraction analysis of this sample revealed no diffraction peaks. This means that this sample is in a glass state for a super-cooled liquid, consistent with a lack of long-range order. During the second cycle, both the $T_{\mathrm{g}}$ (60 °C) and $T_{\mathrm{c2}}$ (111.2 °C) were observed. Also, a new endotherm peak appeared at $T_{\mathrm{m2}} = 174.4$ °C and the $T_{\mathrm{m1}}$ disappeared. Note the appearance of a $T_{\mathrm{g}}$ at 60 °C after one cycle. In the cooling cycles, crystallization becomes progressively less pronounced. The glass state sample changes from red to yellow at around $T_{\mathrm{c2}}$ and then follows a change to red again at around $T_{\mathrm{m2}}$. Therefore, the $T_{\mathrm{c2}}$ and $T_{\mathrm{m2}}$ are identical to the crystallization

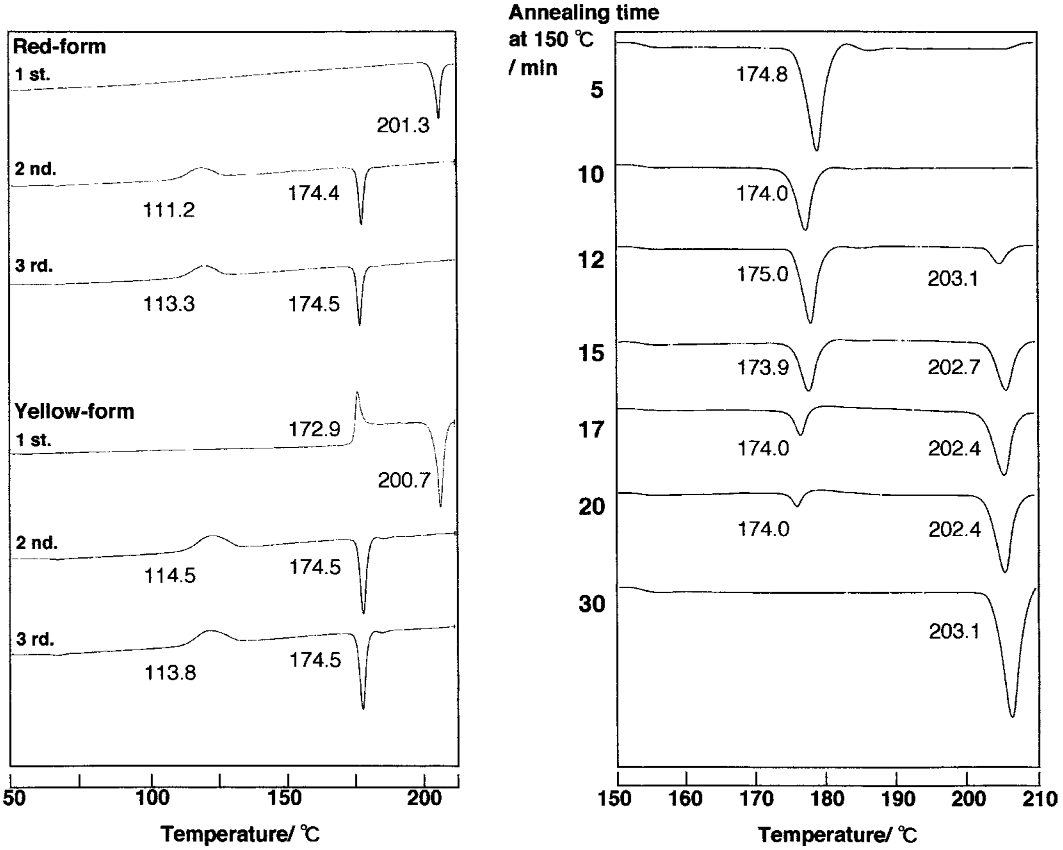


Fig. 3. DTA curves of ophn (a) red form and yellow form, (b) red form annealing (150 °C) sample.

temperature and melting point of the yellow form. The glass state sample was annealed at 150 °C after raising the temperature by 150 °C at a rate of 3 °C/min. The changes in the DTA curve with annealing time are shown in Fig. 3. This indicates $T_{m2}$ at around 174 °C disappeared and $T_{m1}$ at around 203 °C is shown by the crystallization of the red form. The DTA trace of the yellow form shows a sharp crystallization exotherm at $T_s^*$ 172.9 °C, followed by melting transitions at 200.7 °C. The first exotherm corresponds to a solid–solid transition from the yellow to red form, while the second endotherm peak suggests the red form undergoes an isotropic transition. Upon the first cooling cycles, no crystallization was observed for this sample similar to the red form. During the second cycle, both the $T_g$ (60 °C) and $T_{c2}$ (114.5 °C) are observed. Also, an endotherm peak appeared at $T_{m2} = 174.5$ °C again.

The formation of both the amorphous glassy state and the crystalline state (yellow and red forms) was evidenced by the X-ray diffraction powder patterns (Fig. 4). The sample obtained by heating the amorphous glass over 100 °C, where crystallization (yellow form) takes place, show sharp peaks characteristic of the crystal (this pattern is different from the red form), whereas the glassy sample shows only broad halos. Therefore, $T_{c2}$ (114.5 °C) of the DTA corresponds to the yellow form crystallization temperature. On the other hand, the samples obtained by annealing the yellow form over 150 °C, where crystallization (red form) takes place, shows sharp peaks characteristic of the crystal (this pattern is different from the yellow form, and is identified as the simulated pattern from the single crystal X-ray analysis of the red form).

The phase transformation observed for the red and yellow forms is summarized in Scheme 1. It is of

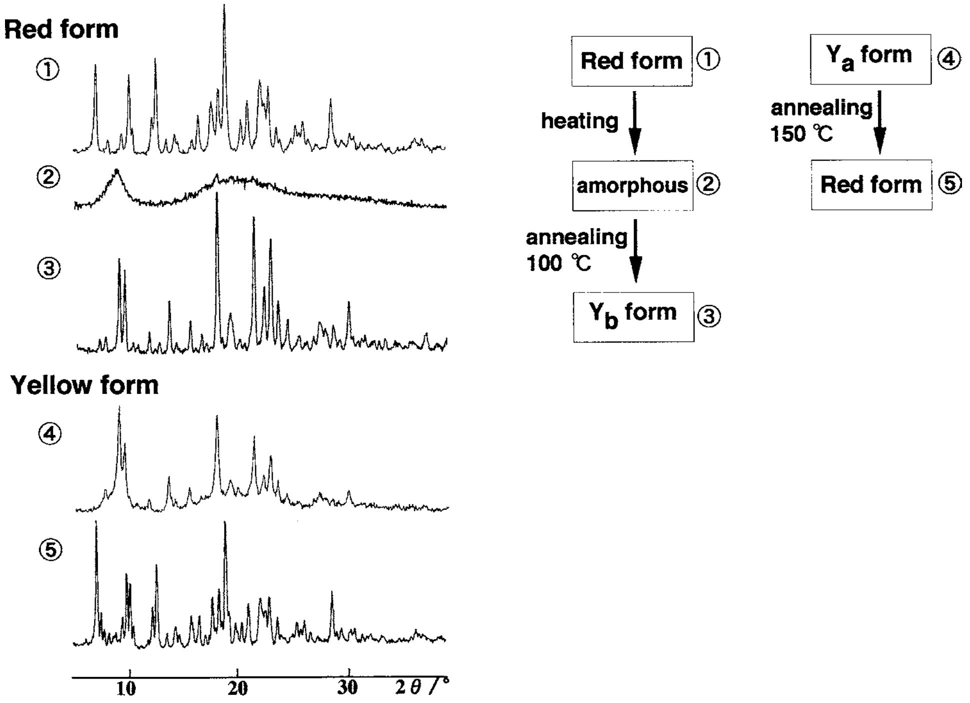
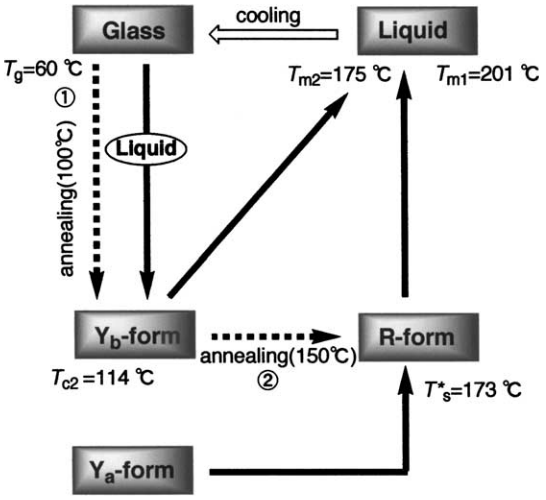


Fig. 4. Powder X-ray diffraction pattern of ophn (①) red form ② amorphous phase after melting ③ annealed (at 100 °C) sample of amorphous (change to yellow) ④ yellow form ⑤ annealed (at 150 °C) sample of yellow form (change to red).



Scheme 1. Phase transformation of ophn.

interest to note that the mode of phase transition drastically changes by a change in the molecular structure. That is, the red form undergoes solid–solid phase transitions from the crystal yellow form. The difference in the intermolecular packing in the molecular assemblies of ophn may be responsible for the difference in the mode of phase transition.

Based on the molecular structure and thermal property, ophn exhibits polymorphism—the existence of more than one crystal structure. In molecular crystals, the free energy difference between polymorphs is usually quite small, a matter of a few kilocalories per mole at most, and depends on temperature, mainly because of the entropic contribution to the free energy. Because of the thermodynamic relation $G = H - TS$, the form with the higher entropy will tend to become the thermodynamically more stable form as the temperature is raised (Fig. 5). Here the $Y_a$-form means the yellow form crystal phase obtained from solution, and the $Y_b$-form means the yellow form crystal phase obtained from the melt state. Based on the DTA, thus, over a small temperature range, and particularly

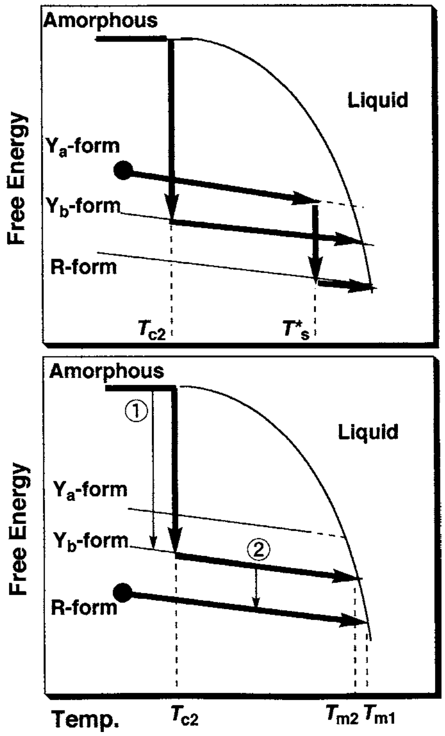


Fig. 5. Free energy and temperature curves.

between room temperature and the melting point, one polymorph or another can change from being the stable form to being metastable. In the case of ophn, the thermodynamic transition temperature is below the melting point, the polymorphic system is known to be enantiotropic and the transition is in principle reversible. Therefore, the color change phenomenon by thermal treatment is related to polymorphism.

### 2.3. Powder reflectance spectra

As shown in Fig. 6, the powder reflectance spectra are clearly different. The spectra of the red and yellow forms have $\lambda_{max}$ values of 578 and 539 nm, respectively.

In conclusion, we have reported the crystal structure and thermal analysis of ophn with two isomers, the red-form and yellow-form. The phase transformation observed for the red and yellow forms is summarized on the basis of a thermal analysis and the powder X-ray diffraction pattern.

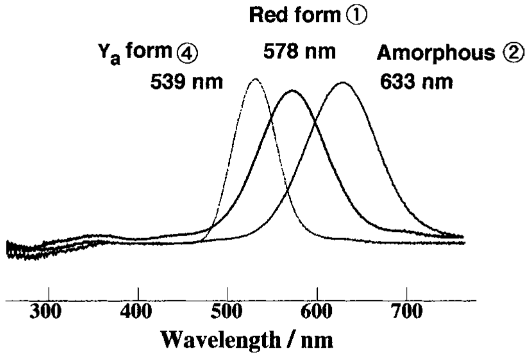


Fig. 6. Powder reflectance spectra of ① red form ② amorphous phase ④ yellow form.

## 3. Experimental

The preparations were performed using the usual Schlenk techniques. Solvents were dried using standard procedures and distilled under an argon atmo-

Table 1
Crystallographic data for red form and yellow form

| | Red form | Yellow form |
|---|---|---|
| Chemical formula | $C_{58}H_{40}S_8$ | $C_{63}H_{50}N_2OS_8$ |
| Formula weight | 993.43 | 1,107.58 |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P*1 (no. 2) | C2$_1$/c (no. 14) |
| Unit cell dimensions | | |
| $a$ (Å) | 9.086(1) | 22.565(6) |
| $b$ (Å) | 11.398(3) | 12.199(3) |
| $c$ (Å) | 12.384(4) | 19.900(6) |
| $\alpha$ (°) | 101.166(8) | |
| $\beta$ (°) | 96.365(4) | 100.429(4) |
| $\gamma$ (°) | 109.601(2) | |
| Unit cell volume | | |
| $V$ (Å) | 1,163.7(5) | 5,387(2) |
| $Z$ | 1 | 4 |
| $\mu$(Mo Kα) (cm$^{-1}$) | 4.25 | 3.77 |
| Number of reflections measured | 12,289 | 42,917 |
| Number of observed reflections | 4,665 | 10,348 |
| $[I > 2\sigma(I)]$ | | |
| $R$ | 0.030 | 0.065 |
| $R$w | 0.076 | 0.103 |
| $T$ (K) | 200.0 | 150.0 |

$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, $R\text{w} = [\Sigma\omega(Fo^2-Fc^2)^2/\Sigma\omega(Fo^2)^2]^{1/2}$.

Table 2
Selected bon lengths (Å) and bond angles (°) for red form and yellow form

| | | | |
|---|---|---|---|
| Red form | | | |
| S(1)–C(2) | 1.786(1) | S(1)–C(6) | 1.779(1) |
| S(2)–C(3) | 1.762(2) | S(2)–C(12) | 1.767(1) |
| S(3)–C(4) | 1.775(2) | S(3)–C(18) | 1.776(1) |
| S(4)–C(5) | 1.778(2) | S(4)–C(24) | 1.780(1) |
| C(2)–S(1)–C(6) | 97.40(6) | C(3)–S(2)–C(12) | 105.81(7) |
| C(4)–S(3)–C(18) | 101.58(7) | C(5)–S(4)–C(24) | 98.71(6) |
| Yellow form | | | |
| S(1)–C(1) | 1.773(2) | S(1)–C(11) | 1.771(3) |
| S(2)–C(2) | 1.767(3) | S(2)–C(17) | 1.772(3) |
| S(3)–C(3) | 1.766(2) | S(3)–C(23) | 1.770(3) |
| S(4)–C(4) | 1.776(2) | S(4)–C(29) | 1.779(2) |
| S(5)–C(6) | 1.770(3) | S(5)–C(35) | 1.777(3) |
| S(6)–C(7) | 1.771(3) | S(6)–C(41) | 1.761(3) |
| S(7)–C(8) | 1.765(3) | S(7)–C(47) | 1.778(3) |
| S(8)–C(9) | 1.778(3) | S(8)–C(53) | 1.783(3) |
| C(1)–S(1)–C(11) | 102.5(1) | C(2)–S(2)–C(17) | 106.2(1) |
| C(3)–S(3)–C(23) | 105.9(1) | C(4)–S(4)–C(29) | 100.6(1) |
| C(6)–S(5)–C(35) | 101.9(1) | C(7)–S(6)–C(41) | 103.8(1) |
| C(8)–S(7)–C(47) | 105.2(1) | C(9)–S(8)–C(53) | 100.6(1) |

sphere prior to use. The standard chemicals were obtained from Wako Chemical Co., Japan, and used without further purification. The IR spectra were measured as KBr disks on a JASCO FT/IR-8000 spectrometer, and the $^1$H NMR with a Varian Mercury 300 FT-NMR spectrometer at 23 °C. Tetramethylsilane was used as the internal reference. The thermal analyses were performed on a Rigaku Co. Ltd., TG 8120 with a scanning rate of 3 °C/min when heating in an atmosphere of nitrogen (100 ml/min). The samples were dried at 100 °C/2 h under high vacuum before DTA measurements. The diffuse reflection spectra were obtained with a Hitachi U-4000 in the 350–800 nm range.

### 3.1. Octa(phenylsulfanyl)naphthalene (ophn)

Ophn was synthesized essentially according to a literature [3] method. Recrystallization from chloroform-n-pentane yielded orange columns (84%), mp 196–198 °C. IR $\nu_{max}$ KBr disc/cm 3067w, 3015w, 1578m, 1474m, 1438m, 1068m, 733s, 686s; $^1$H-NMR $\delta_H$(300 MHz; $CDCl_3$)/ppm 6.46–6.53 (8 H, m), 6.72–6.84 (16 H, m) and 7.08–7.16 (16 H, m); EI-Mass *m*/*z* 992 ($M^+$, 100%).

### 3.2. X-ray analysis of red and yellow form

Crystal data for the red and yellow forms are given in Table 1. The structures were solved by a direct method [7] and refined by full-matrix least-squares analysis on $F^2$. Data collection for these compounds was performed on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation. All the full-occupancy non-hydrogen atoms were anisotropically refined. The positions of all the hydrogen atoms were determined from the difference electron density maps and included, but not refined. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources [8]. Computations were carried out using TEXSAN [9]. The selected bond lengths and bond angles for the red and yellow forms are listed in Table 2.

## 4. Supplementary material

Tables of crystal data, intensity measurements, structure solution and refinement, atomic coordinates and thermal parameters, intermolecular bond lengths and angles, and least-squares planes for ophn. The

X-ray crystallographic files are in the CIF format. This material is available from the authors upon request.

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