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Fluorescence spectra of bithiophene and terthiophene single crystals and of their isolated molecules in cyclodextrin

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Abstract

In order to examine the effect of subsumption space of β- and γ-cyclodextrin (CyD) on the photophysics of oligothiophenes, 2, 2′-bithiophene (BT) and 2, 2′: 5′, 2″-terthiophene (TT), the fluorescence spectra were compared with those of the single crystals (SC) at 15, 77 K and room temperature (RT). Both the numbers of BT included in β- and γ-CyD are twin (BT_2). The numbers of TT included in β- and γ-CyD are unit (TT_1) and twin (TT_2), respectively. Electronic excitation of BT encapsulated in β- and γ-CyD gives similar fluorescence spectra, showing bathochromic shift compared with that of BT single crystal, $(BT)_{SC}$. The observation that the fluorescence spectra of encapsulated BT_2 are similar to the spectra of its THF solution suggests the configuration of BT_2 in β- and γ-CyD should be face-to-face configuration $(BT_2)_{\|}$. On the contrary, TT in β- and in γ-CyD afford quite different fluorescence spectra. Encapsulated TT in β-CyD exhibits the hypsochromic shift of fluorescence maxima compared to that of TT single crystal, $(TT)_{SC}$. While the bathochromically shifted fluorescence spectra of TT_2 in γ-CyD is also ascribed to the face-to-face configuration $(TT_2)_{\|}$ as in the case of BT_2 in γ-CyD. Fluorescence spectra show the excited ground state complex of BT_2 and TT_2 in γ-CyD.

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Keywords: Fluorescence spectra; Bithiophene; Terthiophene; Cyclodextrin; Isolated molecule; Excited complex

1. Introduction

Luminescence properties of conjugated polymers have been attracting much interest for these two decades. Polythiophene and thiophene oligomers belong to π-conjugated organic materials, thus they are used as active components in many kinds of optoelectronics devices [1–12].

The absorption and fluorescence spectra of bithiophene and terthiophene molecules have been observed in several solutions and the supramolecular system of cyclodextrin (CyD) in aqueous medium at room temperature (RT) [13–19]. Molecular structures of bithiophene and terthiophene are shown in Fig. 1. Infrared and Raman spectra of thiophene oligomers were well examined by Furukawa et al. [20]. Time-resolved study of oligothiophenes have been studied by several authors [11,21–23]. There is no report for the optical measurements of $(BT)_{SC}$ and $(TT)_{SC}$.

Thiophene oligomers have been synthesized since 1947. Their crystal structure has been analyzed by X-ray diffraction recently [24–26]. The unit cell of $(BT)_{SC}$ is a monoclinic space group $2P1/c$. It contains 4 molecules. Unit cell dimensions are $a = 0.7734$ nm, $b = 0.5729$ nm, $c = 0.8933$ nm, $\beta = 106.72°$ at 133 K. The melting point is 305 K.

The crystal structure of $(TT)_{SC}$ has been investigated by Van Bolhuis et al. [27]. Parameters and volume of its

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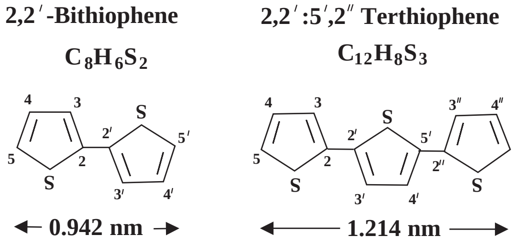

Fig. 1. Molecular structure of trans-bithiophene and terthiopene.

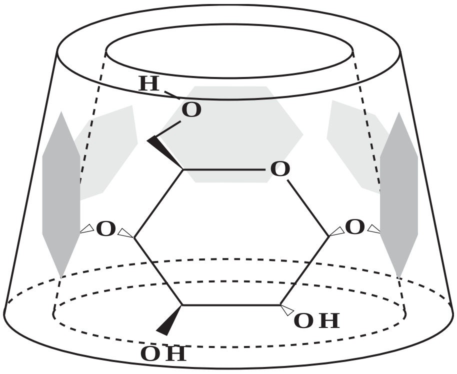

Fig. 2. α-, β- and γ-CyD are consisting of six, seven or eight glucose units, respectively.

Table 1
Physical characters of α-, β- and γ-CyD's

	Number of glucoses	Molecular weight	Inner diameter D (nm)	Depth d (nm)
α-CyD	6	972	0.45	0.70
β-CyD	7	1135	0.70	0.70
γ-CyD	8	1297	0.85	0.70

are $a = 1.5225$ nm, $b = 0.5635$ nm, $c = 2.5848$ nm, $\beta = 98.15°$, $V = 2.1952$ nm^3 at 130 K. The melting point is 366–368 K. There are eight molecules in a unit cell.

It is possible to investigate the physical characters of clusters with the use of CyD. The shape seems like a short tube as seen in Fig. 2. The inner diameter increases in the order of α-, β- and γ-CyD as summarized in Table 1 [28]. The electroconductive oligothiophene molecules are able to be inserted in cylindrical organic compound of CyD. They may be designed as a kind of molecular wires with insulator coating of CyD. They are one of the candidates of molecular wires for the use of future nano-technological very large scale integration (VLSI) circuits. Not only long polythiophene chains but also the short chains of oligothiophenes would be useful for highly integrated circuits. It is essential to investigate the physical properties systematically from bithiophene, terthiophene to polythiophene for the future applications.

In the present paper, we will report a detailed experimental study on the temperature-dependent photoluminescence of 2, 2′-bithiophene (BT) and 2, 2′: 5′, 2″-terthiophene (TT) subsumed in β- and γ-CyD prepared as powdered samples and their single crystals. The optical properties of oligothiophenes help us to understand how these molecules are subsumed in CyD.

2. Experimental

2.1. Sample preparation of single crystals of BT and TT

Powder of BT and TT were purchased from Aldrich Chemical Co. The powder purity of BT is 97% and that of TT is 99%. They were purified three times by vacuum sublimation method. The cleaned glass tube was evacuated for 5 h at 593 K with a rotary oil pump. Then the glass tube was cooled to RT and filled with argon gas. The molecular weight of argon is 39, which is heavier than that of air, 29. The glass tube was taken off from the evacuation system by holding the open edge upward, and then was quickly covered with a thin paraffin film (Parafilm). The purified BT was quickly put into the glass tube and then covered again with the film. By these treatments, humid air did not come into the glass tube, because the tube was filled with argon gas, which is heavier than air. The glass tube was again set to the vacuum system and evacuated to 1.86×10^{-3} Pa and filled with argon gas to the pressure of 3.4×10^4 Pa. The glass tube was sealed with gas flame. In this evacuation process two liquid nitrogen traps were inserted between the glass tube and the pumps to prevent the contamination of the pump oil.

A heater was made by winding tungsten wire on the pyrex glass tube. The heater was set in a refrigerator. The bottom part of a sample tube which contained BT powder was inserted into the heater. The length of the heated part of the sample tube was about 8 cm. The temperature inside the refrigerator was kept at 278 K. The glass tube had been kept for 1 week at a temperature range of 290–295 K inside the heater. The melting point of BT is 305 K at atmospheric pressure. Large single crystals were grown in 4 or 5 days on the inside wall of the glass tube. The $(BT)_{SC}$ grows like a thin plate. The color of $(BT)_{SC}$ is transparent. We used SCs of 4×4 mm^2 size in the present experiment.

$(TT)_{SC}$ was prepared by the same method as that of $(BT)_{SC}$. The purified TT powder was put into a cleaned glass tube and evacuated to 1.86×10^{-3} Pa with a diffusion pump. The glass tube was sealed with argon gas of 3.4×10^4 Pa. The glass tube was heated up to 361–365 K and kept in the these temperature range for 2 weeks. The melting point of $(TT)_{SC}$ is 366–368 K, thus these treatments were proceeded not in the refrigerator but in a room. The color of $(TT)_{SC}$ is thin yellow. In the present experiments, we used nearly 1.5 × 5 mm^2 size of crystals.

2.2. Sample preparation of isolated molecules in CyD and BT solution in tetrahydrofuran (THF)

It is possible to insert BT and TT molecules into the cylindrical cavity of β- and γ-CyD. In comparison of the inner diameter of α-CyD and the molecular sizes of BT and TT, they are not able to be inserted into the cavity of α-CyD.

The cleaned glass tube was evacuated with a rotary oil pump and heated to 593 K for 5 h and was filled with argon gas as the same way mentioned above to make single crystals. The white powder of β-CyD (or γ-CyD) was put into the bottom of a glass tube and evacuated to 1.86×10^{-3} Pa with a diffusion pump. Furthermore, the glass tube was heated up to 393 K (or 413 K for γ-CyD). Then the glass tube was gradually cooled to RT and filled with argon gas. Sublimated fresh single crystals were put into the glass tube with CyD. They were put in the glass tube by separating from CyD. The glass tube was again evacuated to 1.86×10^{-3} Pa with a diffusion pump. The tube was sealed and kept in a heating glass tube that was wound with tungsten heater. It had been heated for 3 days at 300 and 361 K for BT and TT, respectively. The day before measurement one of the sealed tube edges was pulled out of the heating tube. Excess BT (or TT) was recrystallized at the cooled edge from the CyD surface. The CyD powder encapsulating BT (or TT) was taken out by breaking the glass tube and then was quickly pressed with a glass plate on double-sided adhesive tape which was fixed on the sample holder. This kind of CyD powder preparation is our original method [29,30].

BT solutions were prepared by solvating it in tetrahydrofuran (THF) (99.9%, Aldrich). THF was used without further purification. It did not show any absorption or emission in the wavelength region of 190–650 nm. Freshly sublimated samples were dissolved in THF and prepared as several solutions with different concentrations between 0.006 and 24.136 mol/l. The solubility of BT in water is less than 2×10^{-5} mol/l [15].

2.3. Measurements

Freshly grown samples were used for each fluorescence measurements. One of them was quickly set to the sample holder of a closed-cycle helium cryostat (Janis Research Co., Inc., Model CCS-150 and Helix Corp., CTI-CRYOGENICS 22CP). The fluorescence spectra of $(BT)_{SC}$ and $(TT)_{SC}$ were measured at 15, 77 K and RT. The background pressure in the cryostat chamber was 1.86×10^{-3} Pa. Temperatures were adjusted within ± 0.01 K with an autotuning temperature controller (Lake Shore Cryotronics, Inc., Model-330). A deuterium lamp (Hamamatsu Photonics L1314, 150 W) light was used for fluorescence measurements in the energy range of 2.0–3.8 eV. Excitation light for fluorescence measurements was 320 nm (3.9 eV) which was monochromated with Nikon G250 monochromator. It was focused on the sample with fused quartz lenses. Emitted light from the sample was focused with a concave mirror and detected with a charge-coupled device (CCD) detector (Princeton Instruments) through monochromator (Acton Research Corp., Spectra Pro-500).

It was very difficult to obtain the fluorescence spectra of thin $(BT)_{SC}$, because of its low melting temperature and of the sublimation character. The SC easily sublimates within 30 min in the process of evacuation. Thus, we devised a new sample holder cell. It is composed of indium plate ring. Inner diameter of the indium plate ring is 10 mm, outside diameter is 20 mm. The thickness is approximately 3 mm. Both side of the thick indium plate ring were slightly coated by CAF-1 silicone sealant (ROCKGATE Co.) and put on a quartz plate with 25 mm diameter and 1 mm thick. The $(BT)_{SC}$ was fixed on the sample holder plate which was set inside the indium ring. The sample holder plate was tilted a little in the opposite direction of optical concave mirror to separate emitted light from reflection. Another quartz plate was fixed on the indium ring. These treatments were done at 281 K in a cold room. The sealed indium cell was fixed on the sample holder of the cryostat with bolts as illustrated in Fig. 3.

The fluorescence measurements of powder samples of BT and TT inserted in β- and γ-CyD were performed at RT and low temperatures by the same way as the single crystals.

Absorption spectra of $(BT)_{SC}$ and $(TT)_{SC}$ were measured with a UV-VIS-NIR scanning spectrophotometer

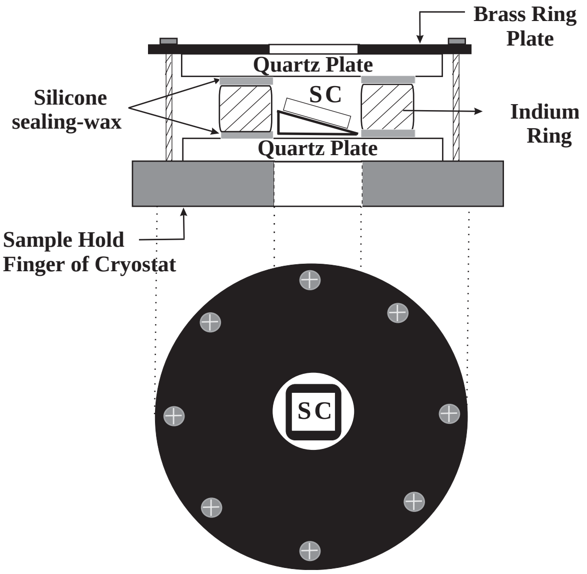

Fig. 3. A cross-section view of a quartz plate system with indium ring.

(Shimadzu UV-3100PC) at RT. Only the steep rise of the fundamental absorption was able to be measured. It was measured to clarify the edge of fundamental absorption energy, because the absorption edge spectra usually becomes indistinct, which are obtained by the Kramers–Kronig analysis from the reflectivity data.

For optical measurements of BT in THF, the prepared solution was put into a fused quartz cell with a $12 \times 12 \times 45\ \mathrm{mm}^3$ size. Fluorescence measurements were also carried out at RT by the same way as that of single crystal and powder samples of BT using the fused quartz cell. The excitation light was 300 nm (4.13 eV).

3. Experimental results

Not only $(\mathrm{BT})_{\mathrm{SC}}$ but also BT molecules encapsulated in β- and γ-CyD show a weak blue luminescence at RT. The fluorescence spectra of $(\mathrm{BT})_{\mathrm{SC}}$ are shown in Fig. 4(a). The absorption edge is also shown with thick line around 3.40 eV. The fluorescence spectra of $(\mathrm{BT})_{\mathrm{SC}}$ show one broad band at RT around 3.18 eV. The intensity at RT is very weak, thus it is shown by multiplying six times. The fluorescence intensity increases as the temperature decreases from RT to 15 K. There are two peaks at 3.18 and 3.29 eV at 77 and 15 K. Furthermore, they show small hump at high-energy side at 3.38 and 3.47 eV (Fig. 4(a)).

The fluorescence spectra of BT_2 in β- and γ-CyD are shown in Figs. 4(b) and (c). The fluorescence spectra of BT_2 in β- and in γ-CyD are quite similar to each other from 15 K to RT. The fluorescence maxima of BT_2 are at 2.87, 3.03 and 3.2 eV in β-CyD shown in Fig. 4(b), and at 2.82, 2.99 and 3.17 eV in γ-CyD at 15 K shown in Fig. 4(c). The similar maxima are observed at 77 K. The fluorescence maxima of BT_2 in β-CyD at 3.03 eV and BT_2 in γ-CyD at 2.99 eV show red shifts of 0.26 and 0.30 eV from the fluorescence maxima of $(\mathrm{BT})_{\mathrm{SC}}$ at 3.29 eV. Furthermore, the center of mass of fluorescence bands located at around 3.20, 2.95 and 2.93 eV for $(\mathrm{BT})_{\mathrm{SC}}$, BT_2 in β-CyD and BT_2 in γ-CyD, respectively. The center of mass of BT_2 fluorescence in β-CyD and that in γ-CyD show red shifts nearly 0.25 and 0.27 eV from the center of mass of $(\mathrm{BT})_{\mathrm{SC}}$, respectively.

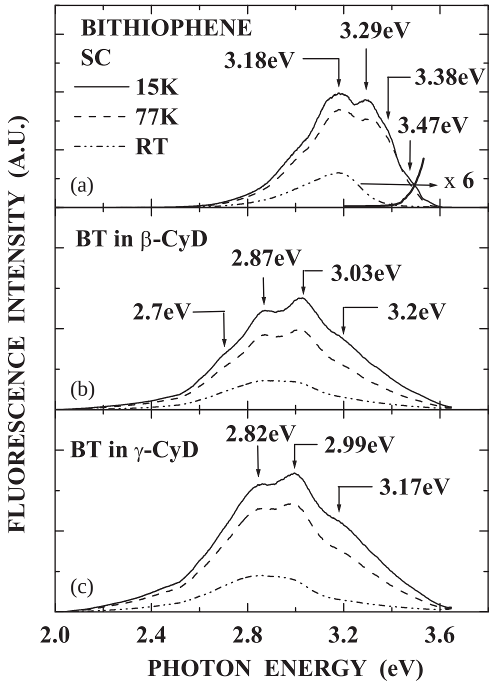

Fig. 4. Fluorescence spectra of BT single crystal and BT isolated molecules in cyclodextrins.

The fluorescence spectra of BT in THF at RT are shown in Fig. 5 with several concentrations of 0.006, 7.874 and 24.136 mol/l. The fluorescence spectra show broad peak located at 3.27 eV at low concentration of 0.006 mol/l. The spectral peak and shape do not change for lower concentration than 0.006 mol/l, although the intensity and the S/N ratio decrease. The fluorescence intensity gradually decreases with increasing BT concentration and new peak appears around 2.85 eV. The fluorescence peaked at 3.27 eV comes from the isolated single molecule of BT.

The fluorescence spectra of $(\mathrm{TT})_{\mathrm{SC}}$, exhibiting weak green, are shown in Fig. 6(a). The fundamental absorption edge at RT is shown with thick curve which is steeply rising around 2.40 eV.

It should be noted that the fluorescence intensity of $(\mathrm{TT})_{\mathrm{SC}}$ is affected by the temperature. The most strongest fluorescence spectrum of $(\mathrm{TT})_{\mathrm{SC}}$ at 15 K has the fine structures in the region from 2.36 to 2.79 eV. The most highest fluorescence intensity of 2.70 eV at 15 K shows nearly five times stronger than that at 77 K. Three main peaks, 2.56, 2.64 and 2.72 eV are observed in the fluorescence spectra of $(\mathrm{TT})_{\mathrm{SC}}$ at 77 K. At RT $(\mathrm{TT})_{\mathrm{SC}}$ affords extremely weak fluorescence spectrum.

The fluorescence spectra of TT_1 in β-CyD depicted in Fig. 6(b). They show blue shift of 0.16 eV from the

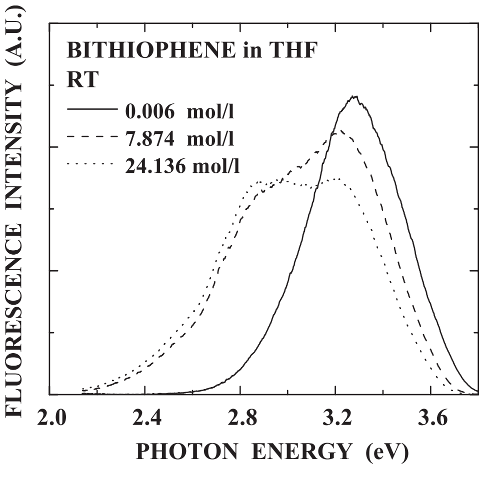

Fig. 5. Fluorescence spectra of BT in THF.

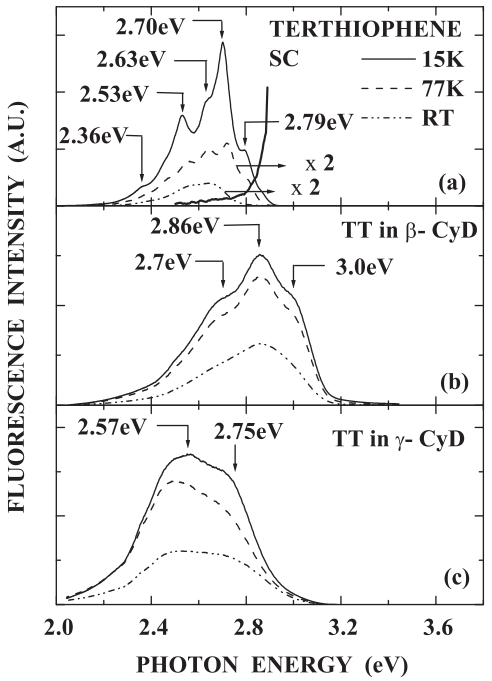

Fig. 6. Fluorescence spectra of TT single crystal and TT isolated molecules in CyD.

highest fluorescence maxima of $(TT)_{SC}$. The fluorescence maxima of TT_1 in β-CyD at 15 K are 2.7, 2.86 and 3.0 eV. On the other hand, quite different fluorescence spectra were obtained for TT_2 in γ-CyD as seen in Fig. 6(c). The fluorescence maxima of TT_2 in γ-CyD at 15 K are 2.57 and 2.75 eV. The bathochromic shift of 0.29 eV is evaluated by the comparison of the highest maxima of TT_2 in γ-CyD, 2.57 eV with that of TT_1 in β-CyD, 2.86 eV. Furthermore, the center of mass of fluorescence bands located at around 2.63, 2.83 and 2.59 eV for $(TT)_{SC}$, TT_1 in β-CyD and TT_2 in γ-CyD, respectively. The center of mass of TT_1 fluorescence in β-CyD shows blue shift of 0.20 eV from the mass center of $(TT)_{SC}$, and the TT_2 fluorescence in γ-CyD shows red shift of 0.24 eV from the mass center of TT_1 fluorescence in β-CyD. It should be mentioned that the fine structure of TT_2 in γ-CyD becomes indistinct. The bathochromically shifted fluorescence of TT_2 in γ-CyD suggests that the orientation should be face-to-face configuration $(TT_2)_{\parallel}$ like BT_2 in γ-CyD. The configuration of TT_2 in γ-CyD will be discussed in following section.

4. Discussion and conclusion

The fluorescence spectra of $(BT)_{SC}$ and $(TT)_{SC}$ show the fine structures at low temperatures as shown in Figs. 4(a) and 6(a). The energy differences between the adjacent fine peaks are approximately 0.07–0.11 eV for these single crystals. On the other hand, the energy differences between adjacent peaks of isolated BT and TT molecule in CyD are nearly 0.16–0.18 eV as seen in Figs. 4(b) and (c) and 6(b) and (c). Infrared and Raman spectra of oligothiophenes show the CH out-of-plane bending vibration energy, 0.08 eV and the breathing mode vibration energy, 0.18 eV for BT and TT [20]. Thus, these fine structures of single crystals and isolated molecules in CyD are attributed to the molecular vibrations of CH out-of-plane mode and breathing mode. The CH out-of-plane bending vibration modes are seen only in the fluorescence spectra of BT and TT single crystals.

The fluorescence spectra of BT in THF show maxima at 3.27 eV at low concentration of 0.006 mol/l as shown in Fig. 5. The fluorescence peak energy shifts to lower energies with increasing BT concentration from 0.006 to 24.136 mol/l. There appears new peak at around 2.85 eV. The fluorescence spectra of BT in THF (0.006 mol/l) shows the same fluorescence spectra with the previous experimental results of very low concentrated BT solution of 10^{-5} M [15]. Thus, we assigned it to the fluorescence spectra of BT single molecule. When the concentration of BT increases in THF, BTs are brought close together. Thus, the nearest twin BTs form an excimer or an excited ground state complex [31].

The fluorescence spectra of BT in β- and γ-CyD are exhibited in Fig. 4(b) and (c). They are quite similar to those of the BT solution with high concentration, 24.136 mol/l as shown in Fig. 5. Taking into account the sizes of BT, they cannot be inserted in α-CyD. On the contrary, there is a sufficient space to insert BT_2 in β- and γ-CyD. In addition, the peak energies shift to lower energies than those of single crystal as shown in Fig. 4(a). It is reasonable to presume that the BT_2 are inserted face-to-face in β- and γ-CyD and they may form an excimer with the irradiated photon energy. On the other hand, the fluorescence spectra of BT in CyD show fine structures at 15 and 77 K. Thus, the fluorescence is attributed to an excited ground state complex [31].

The fluorescence spectra of TT in β- and γ-CyD are considerably different from each other as seen in Figs. 6(b) and (c). The fluorescence maximum of TT in γ-CyD shifts to lower energy than that of TT in β-CyD. The peak energy is also lower than that of single crystal. The appreciable differences come from the resonant state between TT_2 in γ-CyD in their excited states. Observed fluorescence suggests that the TT_2 are inserted in γ-CyD in parallel (face-to-face configuration). On the other hand, the fluorescence spectra of TT_2 in γ-CyD is similar to the emission spectrum of TT dimer which is investigated by Feyter et al. [31]. They investigated photophysical properties of inclusion complexes formed with γ-CyD and TT only at RT. The excited dimer is more long-lived than the locally excited state. They reported the decay times are 4.96 ns for the excited dimer and 0.35 ns for the locally excited state [31].

Only one molecule of TT is able to be inserted in β-CyD, because it has a bent shape in the all *s-trans* conformation as shown in Fig. 1 and it require a wider space to insert TT_2. The fluorescence peak energy of TT_1 in β-CyD shifts to higher energy than that of single crystal. This is the quantum size effect that the energy level separations become larger in a single molecule than those of a single crystal. The TT_2 are able to be inserted in γ-CyD in parallel, that is, face-to-face. The excited energy can resonate between adjacent twin molecules. This affords the fluorescence energy lower than that of isolated single molecule of TT in β-CyD as shown in Fig. 6(c). Nevertheless, the spectra show vibronic structures at 2.57 and 2.75 eV. Thus, TT_2 in γ-CyD also form an excited ground state complex.

In the present paper, we have been presented the fluorescence spectra of $(BT)_{SC}$ and $(TT)_{SC}$ and their isolated molecule in CyD between 15 K to RT. The isolated molecule in CyD were prepared as powder samples. It is difficult to obtain optical absorption and fluorescence spectra of molecule in solution at low temperatures. Furthermore, it is difficult to investigate X-ray powder diffraction of isolated molecule in CyD, because CyDs are arrange randomly in the fine block of CyD powder. If they compose the same single crystals it is possible to make X-ray diffraction measurements. Thus, we clarify isolated uni and twin molecule states of BT and TT from the fluorescence spectra. On the other hand, our devised sample holder cell with indium ring can be applied to obtain the optical measurements of many other crystals which have highly sublimation characters.

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