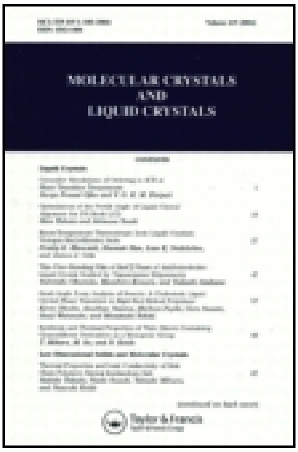

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Fluorescent Molecular Complexes of 9-Hydroxyfluoren-9-yl Substituted Thiophene and Thienothiophenes with 1,2,4,5-Tetracyanobenzene:Crystalline Complexation of Bulky and Conformationally Mobile Molecules

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FLUORESCENT MOLECULAR COMPLEXES OF 9-HYDROXYFLUOREN-9-YL SUBSTITUTED THIOPHENE AND THIENOTHIOPHENES WITH 1,2,4,5-TETRACYANOBENZENE: CRYSTALLINE COMPLEXATION OF BULKY AND CONFORMATIONALLY MOBILE MOLECULES

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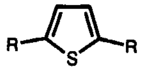
Abstract Bis(9-hydroxyfluoren-9-yl)-substituted thiophene (**1**), thieno-[3,2-*b*]thiophene (**2**), and thieno[2,3-*b*]thiophene (**3**) were recrystallized with 1,2,4,5-tetracyanobenzene (TCNB) from CH_2Cl_2 to afford crystalline complexes $(\mathbf{1})_2$(TCNB), (**2**)(TCNB)(CH_2Cl_2), and (**3**)(TCNB)(CH_2Cl_2), respectively. These crystals are yellow and fluorescent in the solid state. X-ray analyses of $(\mathbf{1})_2$(TCNB) and (**3**)(TCNB)(CH_2Cl_2) revealed that the fluorenyl moieties and the TCNB ring are arranged in a face-to-face manner. The coloring and fluorescent properties are ascribed to a weak charge-transfer (CT) interaction, which is brought about by lattice-controlled packing rather than intrinsic CT interactions. The nature of the fluorescence is discussed on the basis of the crystal structure and the lifetime of the emission.

INTRODUCTION

Recently we have introduced a new family of host compounds for crystalline inclusion complexes.[1] These host compounds, (**1**), (**2**), (**3**), (**4**), and (**5**) are composed of a condensed thiophene as a rigid backbone and two fluorenyl rings as bulky substituents, fitting to general structural requirements as host molecules of crystalline inclusion complexes, *i.e.*, clathrate crystals.[2] Despite of such a non-planar, bulky, and conformationally mobile structure, compound (**4**) has been found to serve as an electron-donor component to afford a crystalline charge-transfer complex with dichlorodicyanoquinone (DDQ) due to the low ionization potential of the constituent π-moieties.[3] This observation is in contrast to the general understanding that crystalline charge-transfer complexes are composed of planar π-donor and acceptor molecules.[4] The conformationally flexible π-donor and acceptor compounds have not attracted attention so far. In continuing our studies on solid-state complexation we are interested in seeing whether a series of compounds (**1**)-(**5**) act as a host component to form crystalline inclusion complexes or as a donor component to give crystalline charge-transfer complexes, when a weak acceptor is employed for complexation. Thus, we have chosen 1,2,4,5-tetracyanobenzene (TCNB) as a counterpart of the complexation; the electron-affinity of TCNB is 2.46 eV,[5] whereas that of DDQ is 3.20 eV. TCNB is known as a typical electron acceptor and to form stable crystalline CT complexes with various aromatic compounds.[6,7] In this paper we demonstrate the behavior of (**1**) - (**5**) in complexation with TCNB and the structural characterization as well as the solid-state coloring and fluorescent properties of their complexes.



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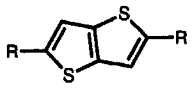

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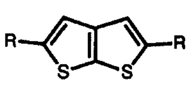

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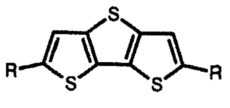

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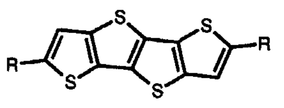

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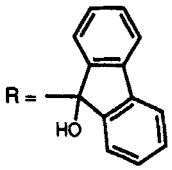

MOLECULAR COMPLEXES

Among a series of host compounds (**1**) - (**5**), (**1**), (**2**), and (**3**) afforded crystalline molecular complexes by recrystallization from dichloromethane together with TCNB. The molecular complex derived from (**1**) has a 2:1 stoichiometry of (**1**):TCNB. On the other hand, compound (**2**) crystallizes in a three-component complex including dichloromethane to give a 1:1:1 composition of (**2**):TCNB:CH_2Cl_2. Similarly, (**3**) forms complex (**3**)(TCNB)(CH_2Cl_2). All the complexes are thermally stable. In contrast, compounds (**4**) and (**5**) afforded no molecular complexes with TCNB, although a variety of solvents such as dichloromethane, chloroform, dioxane, methanol, ethanol, and ether were tried for cocrystallization.

The ionization potential of the constituent π-moieties increases in the order of trithieno-condensed thiophene in (**5**) [7.52 eV] < dithieno-condensed thiophene in (**4**) [7.78 eV] < fluorene [7.93 eV] < thieno[3,2-*b*]thiophene in (**2**) [8.12 eV] < thiophene [8.87 eV].[8] Host (**5**) must be the most electron-donative compound among the present series of compounds. Nevertheless it gave no complex, indicating that the formation of the complex in (**1**), (**2**), and (**3**) is not ascribed merely to charge-transfer complexation.

It should be noted that fluorene, thieno[3,2-*b*]thiophene, and thieno[2,3- *b*]thiophene, which constitute the π-chromophore of compounds (**1**), (**2**), and (**3**), formed no crystalline molecular complexes with TCNB. These observation also seems to suggest that the CT interaction is not a principal factor for cocrystallization and rather the lattice-controlled packing is responsible for the complexation.

CRYSTAL STRUCTURES

An X-ray analysis of $(\mathbf{1})_2$(TCNB) was carried out. Crystal data are as follows; $P2_1/a$, $a = 17.042(4)$, $b = 17.175(2)$, $c = 8.784(1)$ Å, $\beta = 98.10(2)°$, $V = 2551.3(7)$ Å^3, $Z = 2$, $D_{calc.} = 1.389$ gcm^{-3}, $R = 0.044$ for 4552 reflections. Two (**1**) molecules (D) and one TCNB molecule (A) form a trimeric unit and these units stack in parallel along the c axis to line up a DAD sequence in the crystal. The perspective view of 2:1 unit of (**1**) and TCNB is displayed in Figure 1. The trimeric unit is related by an inversion at the center of the TCNB molecule. In the stacks each of (**1**) molecules is arranged in such a way that one of its fluorenyl rings is faced to a TCNB molecule and another is to the fluorenyl ring of the neighboring (**1**) molecule. The least-square plains of the fluorenyl ring and the neighboring TCNB ring make an angle of 14.1°. The shortest contact between D and A is 3.24 Å. The projection of overlapping is shown in Figure 2. The hydroxyl groups of (**1**) are not involved in hydrogen bonding.

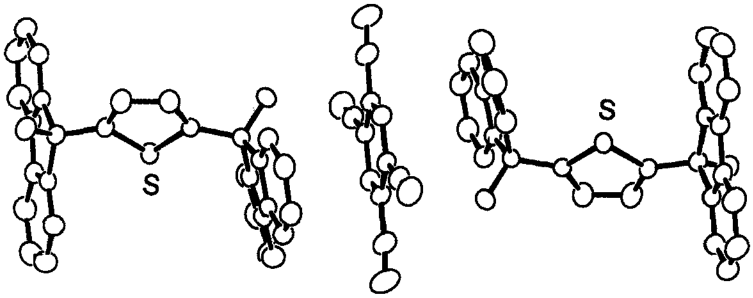

FIGURE 1 Perspective view of the 2:1 unit of (**1**) and TCNB.

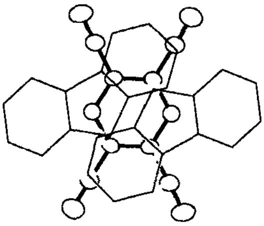

FIGURE 2 Projection of π-overlapping of the fluorenyl ring of (**1**) and the TCNB molecule in (**1**)(TCNB).

With regard to the X-ray structure of (**3**)(TCNB)(CH_2Cl_2), the flip-flop disorder of the thienothiophene ring and the locational disorder of dichloromethane gave a rather larger R value. However, the principal crystal structure is evidently constituted of uniform mixed stacks of -DA-DA-DA- type by the face-to-face overlapping of each of the fluorenyl rings in the host molecules with the TCNB molecule. The perspective view of (**3**) and TCNB is shown in Figure 3. Crystal data for (**3**)(TCNB)(CH_2Cl_2): C2/c, a = 29.806(5), b = 12.786(2), c = 9.943(2) Å, β = 101.43(1)°, V = 3741(1) Å^3, Z = 2, $D_{calc.}$ = 1.355 gcm^{-3}, R = 0.11 for 6188 reflections. The least-square planes of the fluorenyl and TCNB rings make an angle of 3.0° with each other. The overlap of the neighboring donor and acceptor along the stacking direction is shown in Figure 4. The average interplanar spacing between the fluorenyl ring and the TCNB plane is 3.54 Å and the shortest distance between the two planes is 3.42 Å. Hydrogen bonding again plays no role for connecting (**3**) and TCNB molecules. Dichloromethane is enclathrated in the cavity constructed by the (**3**) and TCNB molecules by means of van der Waals force. The isotropic parameters of all atoms in dichloromethane are considerably large, indicating that the guest molecules are loosely embeded in the inclusion cavity.

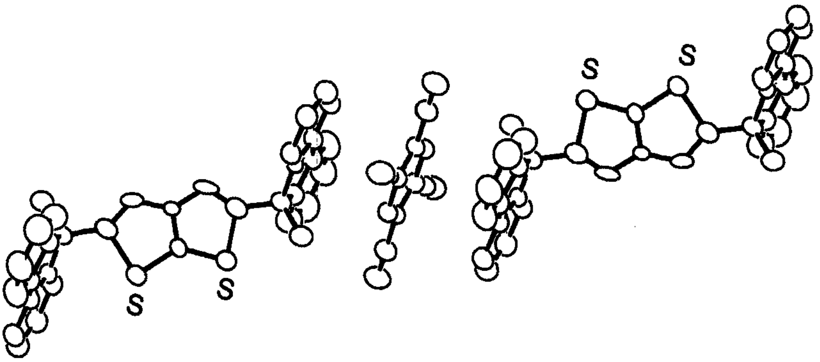

FIGURE 3 Perspective view of (**3**) and TCNB molecules in (**3**)(TCNB)(CH_2Cl_2)

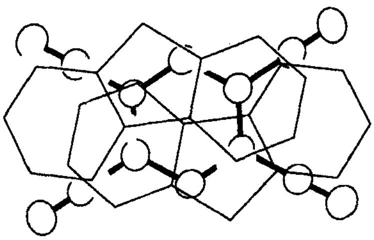

FIGURE 4 Projection of π-overlapping of the fluorenyl ring of (**3**) and the TCNB molecule in (**3**)(TCNB)(CH_2Cl_2).

UV-VIS AND FLUORESCENCE SPECTRA

The UV-vis spectrum of the solid-state complex (**1**)$_2$(TCNB) was measured by means of the diffuse-reflectance (Figure 5). A well-defined band having the maximum intense is observed at 410 nm, whereas this band is not observed in each component compound in the solid-state. Similarly, (**3**)(TCNB)(CH_2Cl_2) exhibited a broad band at 420 nm that is not observable in the solid-state spectra of the individual component. Therefore, the coloration of the crystalline complex is ascribable to the intermolecular charge-transfer (CT) interaction. A mixture of (**1**) and TCNB in a solution shows no such a long wavelength CT absorption; the UV-vis spectra of the mixtures of either (**1**), (**2**), or (**3**) and TCNB in dichloromethane corresponded to the superimpose of that of the individual components. Therefore, the charge transfer is considered to be an event associated with the crystalline state.

Each of the molecular complexes exhibited intense solid-state fluorescence as shown in Figure 6.[6] Complex (**1**)$_2$(TCNB) has intense broad emission at λ_{max} = 471 nm. This fluorescence is not observed in a corresponding homogeneous solution. Complex (**2**)(TCNB)(CH_2Cl_2) also exhibited emission at 558 nm. Complex (**3**)(TCNB)(CH_2Cl_2) showed substantially identical behavior with (**2**)(TCNB)(CH_2Cl_2). Solid-state excitation spectra are well corresponding to the electronic spectra in solid.

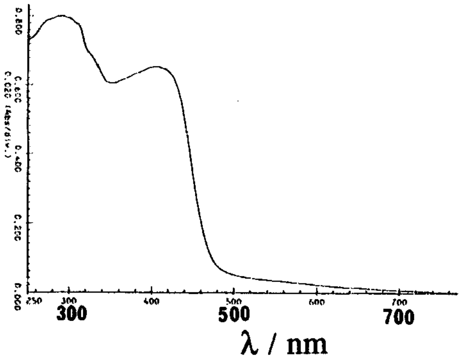

FIGURE 5 Solid-state UV/vis spectrum of (**1**)$_2$(TCNB).

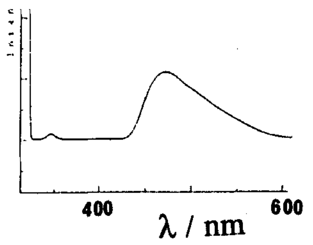

FIGURE 6 Solid-state fluorescence spectrum of (**1**)$_2$(TCNB) [$\lambda_{excitation}$=310 nm].

The possibility of forming excimer or exciplex is considered to be high for molecules which pack in planar pairs. The formation of the excited species in such cases can be considered as a topochemical event. In the crystals of $(\mathbf{1})_2$(TCNB) there are two possibilities of excited parallel orientation, exciplex [D···A]* and triple excimer [D···A···D]*. The formation of the triple excimer in the crystal would require a relatively large change in the geometry. However, the molecular movement for the formation of triple excimer may possible for $(\mathbf{1})_2$(TCNB) crystals, particularly at the defect, where radiative deactivation occurs.

We measured the lifetime of the fluorescence in the solid state. Figure 7 shows that fluorescence decay profiles were fit by the sum of three exponential components and led to two short lifetime (τ = 25.2 ns: 47 %, 941 ns: 8 %) and longer lifetime (τ = 3.9 μs: 45 %). The latter is significantly long decay time for fluorescence and is reminiscent of intervention of triplet-triplet annihilation (delayed fluorescence). It has been known that the high concentration of the excited species in the solid-state facilitates deactivation via triplet-triplet annihilation. Further studies are in progress to deduce the nature of the photoexcited state of the crystalline complexes.

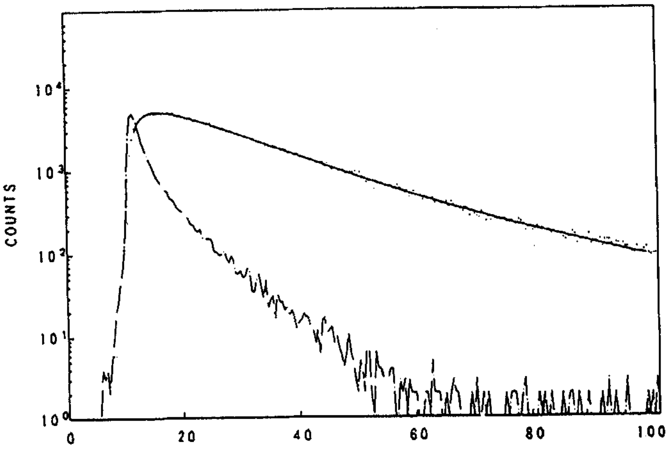

FIGURE 7 Fluorescence decay profile of solid-state $(\mathbf{1})_2$(TCNB) by the nanosecond excimer laser excitation. The excitation pulse (350 nm) shape (broken line) is also shown. The detection wavelength is 470 nm.

ACKNOWLEDGEMENT

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