Charge-Transfer Complex Formation by Grinding Crystals of Donor and Acceptor

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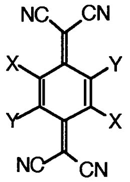
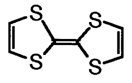
By grinding tetracyanoquinodimethane and tetrathiafulvalene or tetrathianapthacene powders, the corresponding charge-transfer complexes were formed, which showed similar electrical conductivity to those prepared by a recrystallization method.

Charge-transfer (CT) complexes between donors such as tetrathiafulvalene (**2**) or tetrathianapthacene (**3**) and acceptors such as tetracyanoquinodimethane (**1a**), and its tetrafluoro- and dimethyl-substituted derivatives (**1b** and **1c**) show high electrical conductivity at room temperature as a result of segregated column formation of donor and acceptor molecules.[1-4] These complexes are usually prepared by mixing of the donor and the acceptor in an appropriate solvent. We found that these complexes can be prepared by mixing powdered crystals of donor and acceptor and that the complexes prepared by this method show similar electrical conductivity to those of the complexes prepared by the solution method. These data suggest that donor and acceptor molecules can move freely in the solid state to lead to the CT complex formation.



1

a : X=Y=H
b: X=Y=F
c : X=Me; Y=H



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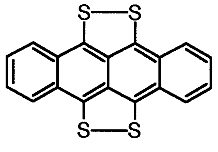

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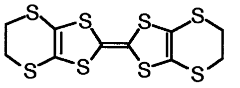

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For example, when a mixture of yellow crystals of **1a** (0.204 g, 1 mmol) and orange crystals of **2** (0.204 g, 1 mmol) was ground occasionally for 1 h by using an agate mortar and pestle, the CT complex of **2-1a** was formed as a black crystalline powder. The complex showed CN stretching absorption ν_{CN} at 2200 cm^{-1} in its IR spectrum, although TCNQ itself shows the corresponding absorption at 2224 cm^{-1}. The shift by 24 cm^{-1} to lower frequency is attributed to the formation of the CT complex.[2,5] The room temperature electrical conductivity of the complex was found to be 0.70 S cm^{-1} by a four-probe method on the compressed pellet. The value is comparable to that (21 S cm^{-1}) measured by the same method as above for the complex prepared by recrystallization from MeCN according to the reported procedure.[1-4]

A similar occasional grinding of yellow crystals of **1a** (0.204 g, 1 mmol) and dark green crystals of **3** (0.352 g, 1 mmol) for 1 h gave a black crystalline powder of the CT complex of **3-1a** (ν_{CN}=2201cm^{-1}), which shows electrical conductivity of 0.024 S cm^{-1}. The observed electrical conductivity is comparable to that (1.3 S cm^{-1}) measured for the complex prepared by recrystallization from MeCN according to the reported procedure.[1-4]

The stronger acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**1b**) and the weaker acceptor 2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane (**1c**) also formed CT complexes with **2** or **3** by the grinding method. For example, occasional grinding of a mixture of **2** and **1b** (ν_{CN} 2228 cm^{-1}) or **1c** (ν_{CN} 2222 and 2210 cm^{-1}) for 1 h gave CT complexes, **2-1b** (ν_{CN}=2194 cm^{-1}) and **2-1c** (ν_{CN}=2194 cm^{-1}), respectively.

A relatively weak donor, bis(ethylenedithio)tetrathiafulvalene (**4**) formed no CT complex with **1a** by the grinding method. However **4** formed a CT complex (ν_{CN}=2195 cm^{-1}) with **1b**.

We have reported so far that grinding of alcohol host compounds and various kinds of guest compounds gives inclusion compounds which are constructed through hydrogen bond formation.[6] The present data clearly show that donor and acceptor molecules move around even in the solid state and mutually arrange to form CT complex.

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References and Notes

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