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Fluorescence from Bound Ionic States of Neat Molecular Crystals: *p*-Substituted *N*,*N*-Dimethylanilines[1)]

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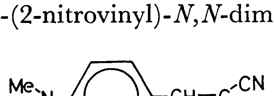
Synopsis. Fluorescences were detected from bound ionic states (*i.e.*, charge-transfer exciton states) of two neat molecular crystals, each formed by a single molecular component. These fluorescent compounds are *p*-(2,2-dicyanovinyl)-*N*,*N*-dimethylaniline and *p*-(2-nitrovinyl)-*N*,*N*-dimethylaniline. They are dimorphic in the solid state.

Interest in charge-transfer (CT) properties of molecular solids[2)] has increased greatly due to the recent observation of a high conductivity anomaly in a mixed molecular crystal TTF-TCNQ.[3)] It is now well-known that transitions to bound ionic states (*i.e.*, CT exciton states) are observed in the optical spectra of such mixed crystals.[4,5)] Here, a CT exciton means an intermolecular CT excitation in the solid.[2)] However, the corresponding states of neat molecular crystals had long eluded direct observation, until in 1968 Tanaka and Shibata detected a CT excitation in the 9,10-dichloroanthracene crystal.[6)] One of the most serious difficulties in studying CT excitons has been heavy interference from neutral Frenkel excitons (*i.e.*, excitons caused by the intramolecular excitations) energetically degenerate with them.[7)]

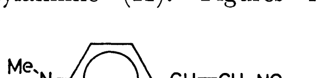
In previous papers,[8)] we showed that a CT exciton band can be shifted to the low energy side, lower than any Frenkel exciton band, if one uses an appropriate aromatic compound with a strong electron-attracting chromophore. This idea was verified by a recent X-ray crystallographic analysis of 2-(*p*-methoxyphenyl)-*p*-benzoquinone crystals.[9)] Component molecules are therein arranged so as to promote intermolecular CT interactions. In this note we report the first observation of fluorescence from the bound ionic states of neat molecular solids of this type.[10)]

Results and Discussion

After an extensive search two aromatic compounds, each with a strong electron-attracting chromophore, were found to be fluorescent in the solid state.[11)] They are *p*-(2,2-dicyanovinyl)-*N*,*N*-dimethylaniline (I) and *p*-(2-nitrovinyl)-*N*,*N*-dimethylaniline (II). Figures 1 and 2 show electronic spectra of these two compounds both in chloroform solution and in the solid state. Fluorescence spectra were recorded on a Hitachi MPA-2A fluorescence spectrophotometer, and were corrected for the spectral response of the analyzing system, unless otherwise stated. All absorption spectra were measured with a Beckman DK-2A spectrophotometer with reflectometric equipment. Solid-state absorption spectra were derived from diffuse reflection spectra of the solids dispersed in the powdered sodium chloride.



I



II

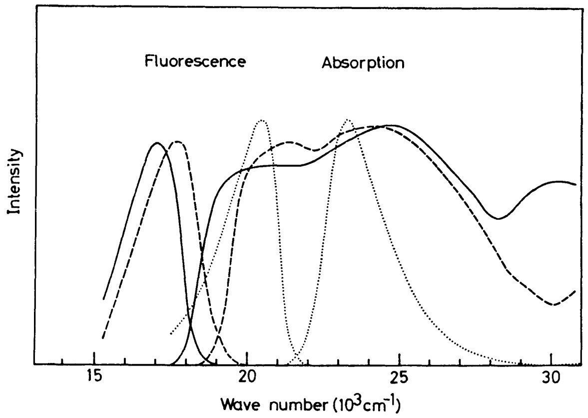


Fig. 1. Electronic spectra of Compound I in two solid states (—— and ----) and in chloroform solution (······).

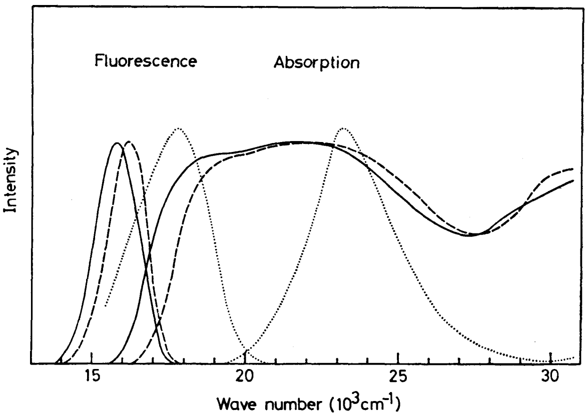


Fig. 2. Electronic spectra of Compound II in two solid states (—— and ----) and in chloroform solution (······).

Interestingly, Compound I was dimorphic. The yellow crystal was obtained from a benzene solution, whereas the orange crystal was obtained by recrystallization from methanol. The visible spectra of these solids consist of two broad absorption bands, one around 20000 cm^{-1} and one around 24000 cm^{-1}. As before,[8,12)] the first absorption band of each crystalline form can be assigned to the transition to the bound ionic state, *i.e.*, an intermolecular CT transition, because of the dual charge-transfer properties of the component molecule.[13)] The second absorption band has a counterpart in the solution absorption spectrum, and should hence be a neutral Frenkel exciton band.

The difference in color between the two crystalline forms is evidently related to a considerable shift of the CT exciton band. The spectral shift amounts to about 1000 cm^{-1}.

Here, one should note that a remarkable red shift in the fluorescence maximum of Compound I occurs on going from solution to solids. The fluorescent levels of the solids are obviously different from that of the solution. By inspection of the spectra, the fluorescence of each solid can naturally be identified as arising from the bound ionic state (*i.e.*, CT exciton state). The fluorescence maxima are located at 17700 cm^{-1} for the yellow crystal and 17000 cm^{-1} for the orange crystal. The energy difference between the two fluorescence bands is comparable to that between the corresponding CT exciton bands. In contrast to the spectral behavior, the structural difference between the two crystalline forms is too small to discern by means of the X-ray powder patterns.

Compound II also exists in two different crystalline forms. They are red and red-violet crystals obtained from the methanol and benzene solutions, respectively. As shown in Fig. 2, a CT absorption band of the red-violet crystal is about 700 cm^{-1} shifted to the low energy side compared with that of the red one. The shift of the fluorescence band due to dichromism appears to be in the same direction and of the same amount as that of the absorption edge, although these solid-state fluorescence spectra are uncorrected. The spectral shift of the bound ionic state suggests a change in the intermolecular interactions in the solid.

The importance of these bound ionic states mostly stems from their involvement in electron transfer and electron-hole recombination processes in neat molecular crystals.[2,3,13] The existence of the CT exciton level may also be responsible for the shifts of local excitation bands in the solid-state spectrum.[5] In this sense, the present finding of fluorescent CT exciton bands provides an important clue to a substantial characterization of the CT exciton state, and might help to clarify its role in electron and energy transfers in the neat molecular crystals.

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References

1) Part V of "Organic Charge-Transfer Self-Complexes;" Part IV : J. Aihara, *Bull. Chem. Soc. Jpn.*, **47**, 2899 (1974).

2) F. Gutman and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y. (1967), Chap. 5; M. Pope and H. Kallmann, *Discuss. Faraday Soc.*, **51**, 7 (1971).

3) "Low-Dimensional Cooperative Phenomena," ed by H. J. Keller, Plenum, New York, N. Y. (1975); "Chemistry and Physics of One-Dimensional Metals," Plenum, New York, N. Y. (1977).

4) D. B. Tanner, C. S. Jacobsen, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **13**, 3381 (1976); J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).

5) J. Tanaka, M. Tanaka, T. Kawai, T. Tanabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976).

6) J. Tanaka and M. Shibata, *Bull. Chem. Soc. Jpn.*, **41**, 34 (1968); S. C. Abbi and D. M. Hanson, *J. Chem. Phys.*, **60**, 319 (1974).

7) J. Tanaka, *Bull. Chem. Soc. Jpn.*, **36**, 1237 (1963); **38**, 86 (1965); J. Tanaka, T. Kishi, and M. Tanaka, *ibid.*, **47**, 2376 (1974).

8) J. Aihara, G. Kushibiki, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **46**, 3584 (1973); J. Aihara, *ibid.*, **47**, 2063 (1974).

9) G. R. Desiraju, I. C. Paul, and D. Y. Curtin, *J. Am. Chem. Soc.*, **99**, 1594 (1977).

10) It goes without saying that not a few charge-transfer complexes are fluorescent in the solid state. See, *e.g.*, S. Iwata, J. Tanaka, and S. Nagakura, *J. Am. Chem. Soc.*, **89**, 2813 (1967).

11) Unfortunately, fluorescence of the solid 2-(*o*- or *p*-methoxyphenyl)-*p*-benzoquinone could not be detected. Fluorescences of many tricyanovinyl aromatics and several *p*-substituted *N*,*N*-dimethylanillines were not appreciable in the solid state, either.

12) R. L. Hansen and J. J. Neumayer, *J. Phys. Chem.*, **71**, 3047 (1967).

13) R. L. Hansen, *J. Phys. Chem.*, **70**, 1646 (1966).

14) See, *e.g.*, M. Pope, J. Burgos, and J. Giachino, *J. Chem. Phys.*, **43**, 3367 (1965); M. Pope and J. Burgos, *Mol. Cryst.*, **1**, 395 (1966); G. T. Pott and D. F. Williams, *J. Chem. Phys.*, **51**, 203 (1969); H. P. Schwob and D. F. Williams, *ibid.*, **58**, 1542 (1973).