

## NEW PHENOMENA OF EMISSION DEPENDENCE OF INTRAMOLECULAR EXCITED STATE COMPLEXES OF DMNP IN POLAR SOLVENTS ON EXCITATION WAVELENGTH

Guangyuan GE, Duolu LI, Nailiang TIAN, Guangnan XIONG, Xurong XU, Qingfu ZHOU\* and Huijun XU\*

Changchun Institute of Physics, Academia Sinica, Changchun, China

The photophysical properties of the intramolecular excited state complexes (ESC) of N,N'-Di- $\beta$ -naphthylmethyl-piperazine (DMNP) have been studied in solvents of different polarities. New phenomena of excitation dependent fluorescence were observed.

## 1. INTRODUCTION

The investigation on the nature of excited state complexes (excimers and exciplexes) has been one of the most interested subjects due to its important role in photochemical and photobiological systems<sup>[1,2]</sup>. In the present paper, we report some new phenomena on ESC in solutions. Both intramolecular excimer and exciplex were proposed to be formed in the compound, DMNP<sup>[3]</sup>. The emission dependence of ESC on excitation was observed for first time as our knowledge.

## 2. EXPERIMENTAL

Absorption spectra were recorded using a Perkin-Elmer 124 double-beam spectrophotometer. Corrected emission spectrum were measured using a Hitachi MPF-4 spectrofluorometer. Benzene, methylanide, chloroform and ethylacetate were used without further purification. None of the solvents used seemed to contain fluorescent contaminants on excitation in the wavelength region of experimental interest. Very dilute solution, the concentration  $10^{-4}$  M, were used in order to avoid practical intermolecular interaction. All experiments were carried out at room temperature.

## 3. RESULTS AND DISCUSSION

\* Institute of Photographic Chemistry, Academia Sinica, Beijing, China

In the emission spectrum of DMNP, the emission band near 340nm is the monomeric fluorescence of naphthalene chromophore. The broad, structureless and red-shifted bands peaked at 410, 460, 480nm in CH<sub>3</sub>CN, C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub> respectively and 400, 490nm in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> are proposed to be the emission bands of intramolecular ESC of DMNP. Fig. 1 shows the excitation spectrum monitoring at 400, 410, 460 and 480nm for the four solutions of DMNP. In neutral solvent, benzene, the excitation band is near 295nm which changes in position in polar solvents. There is however another excitation band red-

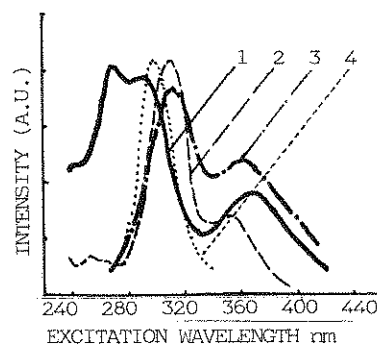
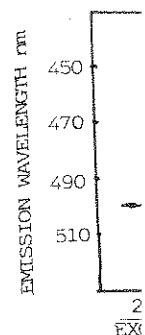


FIGURE 1

The excitation spectrum of the ESC's fluorescence of DMNP. Monitoring the wavelength: 480nm in CHCl<sub>3</sub> (1); 410nm in CH<sub>3</sub>CN (2); 400nm in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> (3); 460nm in C<sub>6</sub>H<sub>6</sub> (4).



The dependence of ESC in DMNP in CHCl<sub>3</sub>; (2) in

shifted to solvents, CH<sub>3</sub>CN were observed. The excitation band near

With the terms of the ESC, 480nm is unambiguous. The 490nm in CH<sub>3</sub>CN and Fig. 2 explain the peak position. With the excitation wavelength, as in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> respectively. To ever, with the excitation wavelength from 340 to 460nm are blue-shifted from 340 to 460nm in CH<sub>3</sub>CN, nevertheless, the excitation of monomeric ESC in polar solvents is the phenomenon.

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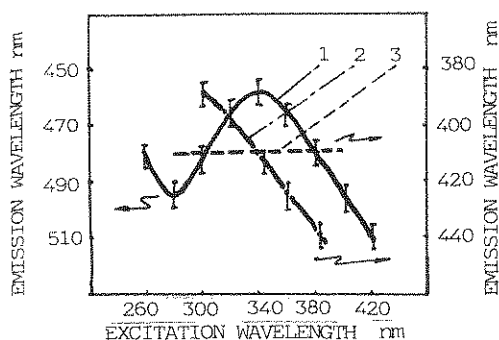


FIGURE 2

The dependence of emission wavelength of the ESC in DMNP on excitation wavelength (1) in CHCL3; (2) in CH3COOC2H5; (3) in CH3CN.

shifted to 350, 360 and 370nm in polar solvents, CH3CN, CH3COOC2H5 and CHCL3 respectively were observed. The origin of the second excitation band need to be studied further.

With the different excitation wavelength in terms of the excitation spectrum, we observed that the peak position of emission bands of ESC, 480nm in CHCL3, 400nm in CH3COOC2H5 shift unambiguously. But there is no such effect for the 490nm band in CH3COOC2H5, 410nm band in CH3CN and 460nm band in C6H6. The curves in Fig. 2 express the dependence of the emission peak position of ESC on the excitation wavelength. With the increase of excitation wavelength, as seen in the Fig., the 400nm ESC band in CH3COOC2H5 will be red-shifted progressively. To the 480nm ESC band in CHCL3, however, with the increase of excitation wavelength from 280nm to 340nm, the peak positions are blue-shifted from 500 to 460nm. And excited from 340 to 420nm, the peak positions red-shifted from 460 to 510nm. For the 410nm band in CH3CN, no such effect exist. We could not nevertheless ignore the phenomenon that with the excitation wavelength lying to the red-side of monomeric emission band, the emissions of ESC in polar solvent exist yet. Fig. 3 shows the phenomenon in CH3CN and CHCL3 respectively.

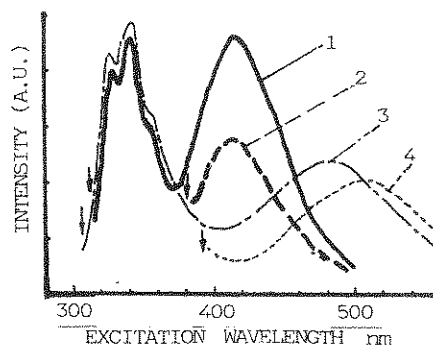


FIGURE 3

The fluorescence spectra of DMNP under different excitation, 310nm (1), 380nm (2) in CH3CN; 300nm (3), 390nm (4) in CHCL3.

The phenomena observed in the work cannot be interpreted by previous theories<sup>[4]</sup>. It seems that the electronic structure of the ESC changes due to excitation. In the compound, the distributions of piperazine chromophore to the ESC may be significant due to the interactions of its isolated pair electrons with one or two naphthalene chromophores (in ground or excited state). So it may not be classified the ESC as the excimer or exciplex simply. And the interaction of chromophores in DMNP (in ground, especially excited state) with solvent should be considered. The processes of dipolar relaxation and energy transfer also cannot be neglected. To reveal the mechanism of the phenomena, kinetic spectroscopy is required. Details of these and related work will be published in the future.

#### 4. REFERENCES

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