

Fluorescence of *p*-*N,N*-Dimethylaminobenzonitrile Incorporated in Pores of Molecular Sieves

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The donor-acceptor-substituted aromatic molecule *p*-*N,N*-dimethylaminobenzonitrile (DMABN) is known to show a characteristic dual twisted intramolecular charge transfer (TICT) fluorescence with a pronounced solvent dependence. Despite the two-band structure of the fluorescence from DMABN incorporated within pores of the molecular sieves AlPO-5, SAPO-5, ZSM-5, and silicalite, there is no indication for TICT-state emission.

KEY WORDS: *p*-*N,N*-Dimethylaminobenzonitrile; molecular sieves; twisted intramolecular charge transfer.

INTRODUCTION

p-*N,N*-Dimethylaminobenzonitrile (DMABN) shows an anomalous fluorescence, characterized by a single broad fluorescence at about 350 nm in nonpolar solvents and a dual fluorescence in polar organic solvents, with emissions at about 350 nm and between 420 and 600 nm. According to the widely accepted twisted intramolecular charge transfer (TICT) theory [1], this anomalous fluorescence is due to the possibility of forming an emitting TICT state as shown schematically in Fig. 1. Since dual fluorescence and TICT states sensitively reflect changes in the environment of emitting molecules even in rigid matrices, DMABN can be used as a probe for testing the microenvironment of the molecule [2,3]. For this reason, we have investigated the fluorescence of DMABN incorporated in zeolites. It is known that dipolar organic molecules spontaneously form self-assembled chain-like structures within the pores of zeolites [5-7]. Analyzing the fluorescence emission and their polarization, we have studied if the highly organized adsorbate system of DMABN in molecular sieve pores allows the twisting of individual molecules excited by light absorption.

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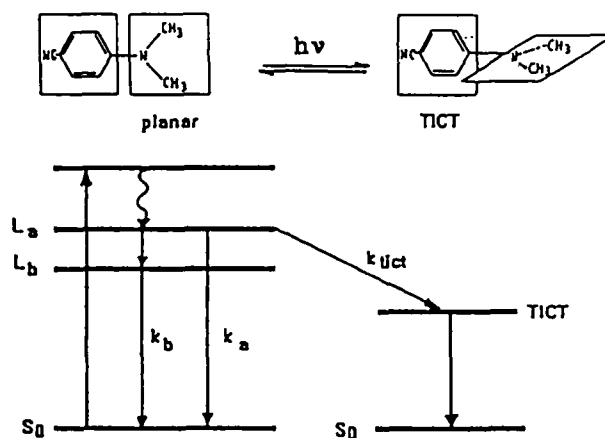


Fig. 1. Schematic energy levels of *p*-*N,N*-dimethylaminobenzonitrile.

EXPERIMENTAL

The aluminosilicate ZSM-5 with Si/Al \approx 40 and its Al-free analogon silicalite as well as the alumophosphate AlPO-5 and its Si-containing structural isotype SAPO-5 were used as host materials. The DMABN molecules were introduced into the molecular sieve pores by a gas-phase adsorption process [6]. Emission spectra of pow-

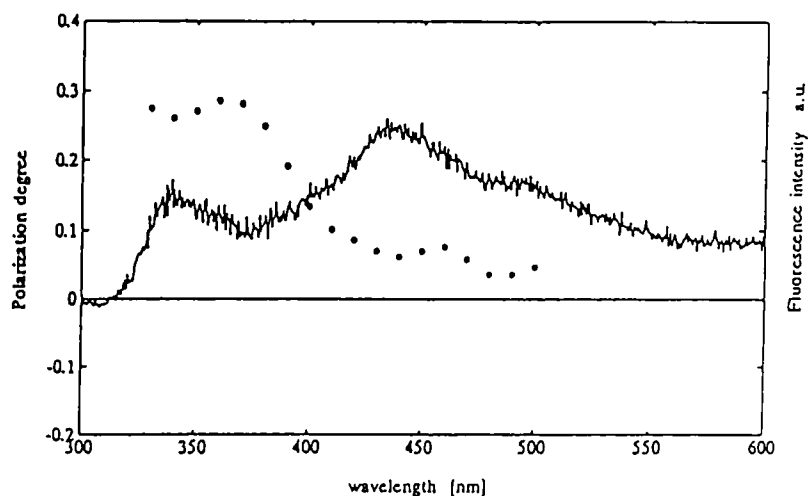


Fig. 2. Fluorescence spectrum (solid line) and polarization degree (open circles) of DMABN in ZSM-5.

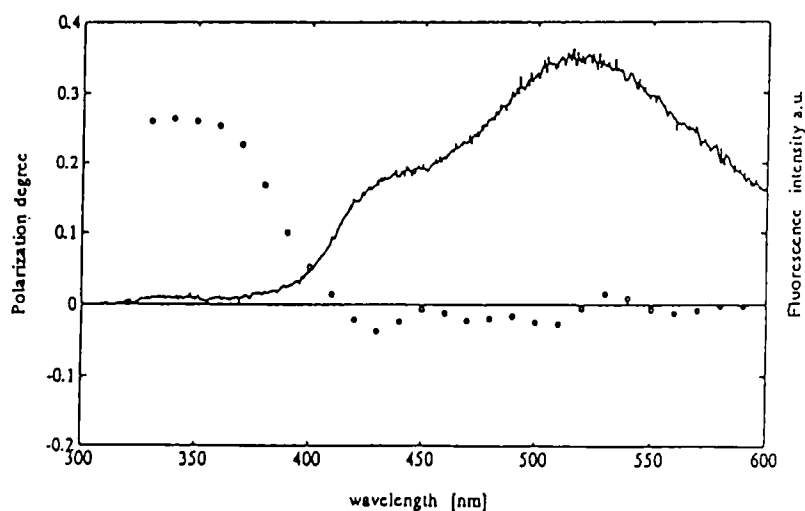


Fig. 3. Fluorescence spectrum (solid line) and polarization degree (open circles) of DMABN in A1PO-5.

der samples were recorded using an SPEX Fluorolog-2 (FL112) spectrofluorometer in back scattering geometry, with subsequent background separation of scattered light [10].

RESULTS AND DISCUSSION

As demonstrated in Fig. 2 for ZSM-5, the fluorescence of DMABN adsorbed on internal surfaces of mo-

lecular sieves shows a two-band structure (A and B), with $\lambda_A > \lambda_B$. DMABN incorporated in A1PO-5 shows the same fluorescence bands and an additional emission in the long-wavelength region (Fig. 3). It is assumed that this low-energy emission is due to an aggregation of DMABN [3]. To identify the nature of the dual fluorescence of DMABN within the channels of molecular sieves, the relative polarization degree $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ was determined. In polar solutions $P(A) > P(B)$ was found, therefore the B fluorescence originates

from an L_b - state and the A fluorescence from the TICT state with the same symmetry as L_a [4]. Contrary to DMABN in polar solutions, in the pores of zeolites we found the high-energy fluorescence positively polarized but the low-energy emission with a weak polarization $P(A) < P(B)$. After excitation in the L_a band (with a transition dipole moment parallel to the long donor-acceptor molecular axis) of DMABN, the B emission must therefore arise from a state with the same symmetry, i.e., from L_a . Therefore there is no symmetry change connected with the B fluorescence. We assign the observed dual fluorescence to relaxation processes k_a and k_b from the energy levels L_a and L_b of the untwisted molecule (see Fig. 1). From our investigation of fluorescence polarization, we have found no indication for the TICT motion with k_{TICT} of DMABN in the pores of molecular sieves. We assume that the strong intermolecular dipole interactions of organic guest molecules within the narrow pores of zeolites [5-9] stabilize the conformation of the individual DMABN molecules, thus causing the suppression of TICT motions.

CONCLUSIONS

Despite its two-band structure, the fluorescence of DMABN in zeolites tested is not caused by a TICT-state emission of the adsorbed molecules. From the polarization of the fluorescence bands, we conclude that the two bands arise from two untwisted excited states [10]. Twisting of the donor group of DMABN is probably

suppressed because of the intermolecular interaction within the chain-like adsorbate structure in the narrow channels of the molecular sieves ZSM-5, silicalite, AIPO-5, and SAPO-5.

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