Normal and Twisted Intramolecular Charge Transfer (TICT) Fluorescence of P-(N,N-diphenylamino)benzoic acid methyl ester (DPABME) in Various Solvents

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Abstract

The steady state fluorescence of P-(N,N-diphenylamino)benzoic acid methyl ester (DPABME) in ethanol is broad and is composed mainly of the intramolecular charge transfer (ICT) band ~490 nm and a shoulder ~400 nm due to normal fluorescence of charge transfer character. In acetonitrile only the long fluorescence (ICT) band ~480 nm could be observed. In n-butylchloride, only the short fluorescence ~420 nm could be observed. The competition between the two fluorescence bands is discussed and confirmed by fluorescence decay, time resolved fluorescence (TRF) spectra and red edge effect (REE) results.

Keywords: Fluorescence; Intramolecular charge transfer; Charge transfer; Time resolved fluorescence (TRF); Red edge effect (REE); P-(N,N-diphenylamino)benzoic acid methyl ester (DPABME); Solvent effect.

Introduction

Aromatic compounds possessing strong donor and strong acceptor chromophors and exhibit dual fluorescence have found their ways to probe various solvents, polymers and cyclodextrins (CDx) [1-7]. These kinds of molecules have great potential to be applied in industry as molecular electronic devices [8] especially if they can be connected in conjugation with polymers. Such properties are found in triphenylamine (TPA) and related compounds and most probably will find their ways in industry applying electronic devices, photography-lithography and photocopying [9].

Our goal in this paper is to understand the optical and luminescence properties of P-(N,N-diphenylamino)benzoic acid methyl ester (DPABME), a derivative of TPA, and compare it to the results previously obtained by Rettig and coworkers [10] for cyanophenyl carbazol (CPC) and by Chen et al. [11] for hexadecyl-4-biphenyl aminobenzoate (HBAB) respectively. For CPC, Rettig and coworkers found it to emit either from a locally excited (LE) (λ = 340 nm) state if present in nonpolar hydrocarbon solvent or from a twisted intramolecular charge transfer (TICT) (λ = 435 nm) state if present in polar acetonitrile solvent. In polar acetonitrile, they argued that CPC is

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pretwisted (around carbazol-benzonitrile bond) in the ground state and consider it to resemble that of 3,5-dimethyl-N,N-diethyl-4-aminobenzonitrile (3,5 D-DMABN). Phillips and coworkers however, attributed the long fluorescence observed by Rettig and coworkers, using supersonic jet experiment, to specific solute-solvent interaction between twisted CPC and acetonitrile and not to a TICT state.

On the other hand Chen et al. attributed the fluorescence of HBAB in various polar and nonpolar solvents to be due to TICT, ICT and LE states. Moreover they considered triphenylamine as the donor and the hexadecyl ester group as the acceptor and argued that twisting occurs around the phenyl-carboxyl bond. This is unreasonable and has no theoretical or experimental support when TICT proposal is used.

These contradictory interpretations motivated us to investigate the role of various solvents on the fluorescence of DPABME, a similar probe to CPC and HBAB. In hydrocarbon and acetonitrile, we found its fluorescence similar to those obtained by Rettig and coworkers. In n-butylchloride and acetonitrile we found its fluorescence to resemble those obtained by Chen et al. In water however, the main fluorescence observed ~425 nm (shorter than when in acetonitrile) however, with a tail extends beyond 500 nm. The long fluorescence ~500 nm was found to enhance with the addition of α-CD while the band ~420 nm stay almost unchanged. This is similar to the observation made for 4-(N,N-diethylamino)benzoic acid ethyl ester (DEABMEE), a well known TICT probe and therefore their emission is interpreted in terms of TICT-mechanism suggested for 4-(dimethylamino)benzonitrile (DMABN) and related compounds.

**Experimental**

P-(N,N-diphenylamin)benzoic acid methyl ester (DPABME) was synthesized previously.

The solvents, ethanol, acetonitrile, n-butylchloride and pantane are of spectral grades and the concentration of DPABME samples were ~1 x 10^{-5} M.

Fluorescence (corrected) and excitation spectra were measured using SPF-500 spectrofluoremeter from SLM instruments Inc.

Fluorescence decay and time resolved fluorescence (TRF) spectra were measured using a picosecond applied photophysics photon-counting system described elsewhere.

**Results and Discussion**

Figure 1 shows similar absorption spectra (λ_{max} ~335 nm) of TPABME in polar (ethanol), slightly polar (n-butylchloride) and nonpolar (pentane) solvents. Figure 2 and Table I however, show the fluorescence spectra of TPABME to undergo dramatic red shift, ~6700 cm^{-1} when in ethanol, ~5600 cm^{-1} in acetonitrile and ~3200 cm^{-1} in n-butylchloride relative to its fluorescence in pentane. These observations are in line with dipole moment enhancement of DPABME accompanied by larger interactions with the solvents in the excited state relative to the ground state. Moreover, the Stoke's shifts...
(Table I) measured from their $\lambda_{\text{max}}$ of absorption and fluorescence are extremely large: (~10000 cm$^{-1}$) as in ethanol or acetonitrile, medium (~6000 cm$^{-1}$) as in n-butylchloride and small (~3200 cm$^{-1}$) as in pentane. These shifts and the values of the half-band widths ($\Delta\nu_{1/2}$) of fluorescence, Table I, correlate with the decrease of their polarities and are good indications that DPABME emits from LE state of charge transfer character (CT) character as in n-butylchloride, from TICT as in acetonitrile and from both states LE and TICT-states as in ethanol, depending on the polarity of the solvent. Moreover, as mentioned in the introduction section these observations are in line with previous observations made for CPC in acetonitrile [10] and for HBAB in various solvents [11]. The larger effects observed for the fluorescence of DPABME relative to CPC emphasize the role of angle pretwist expected to be larger for DPABME as compared to CPC. The two phenyls of the donor (-diphenylamine) in DPABME are disconnected as compared to carbazol in CPC compound. Therefore one expects a larger pretwist angle between the two moieties (diphenylamine and methylbenzoate) of DPABME as compared to CPC. This is in line with our previous expectation and fluorescence results obtained for p-(N,N-diethylamino)benzoic acid ethyl ester (DEABEE) as compared to 4-pyrolaminobenzoic acid methyl ester [5,18,19]. Moreover and since the ethyl benzoate are considered better acceptor relative to benzonitrile (due to absence and presence of canonical intersections [20,21], in their potential energy curves, during their excited states life times, respectively) one expects DPABME to reach its TICT state more feasible as compared to CPC in polar solvents.

Table I. Spectroscopic data for p-(N,N-diphenylamino)benzoic acid methyl ester (DPABME) in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$/nm Absorption</th>
<th>$\lambda_{\text{max}}$/nm Fluorescence</th>
<th>Fluorescence decay lifetimes /ns</th>
<th>Half band width/cm$^{-1}$</th>
<th>Stock’s shift/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>335</td>
<td>375</td>
<td>1.1</td>
<td>3000</td>
<td>3200</td>
</tr>
<tr>
<td>n-butylchloride</td>
<td>335</td>
<td>425</td>
<td>4.2</td>
<td>4040</td>
<td>6300</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>335</td>
<td>480</td>
<td>6.8</td>
<td>4370</td>
<td>9000</td>
</tr>
<tr>
<td>ethanol</td>
<td>335</td>
<td>390</td>
<td>1.8</td>
<td>shoulder</td>
<td>~4200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490</td>
<td>4.3</td>
<td>5340</td>
<td>9400</td>
</tr>
</tbody>
</table>
Figure 1: Absorption spectra of $\sim 1.0 \times 10^{-5}$ M DPABME in pentane (1), in ethanol (2), and in n-butyl chloride (3), at room temperature.

Figure 2: Fluorescence spectra (corrected) of $\sim 1 \times 10^{-5}$ M DPABME in pentane (1), n-butyl chloride (2), acetonitrile (3), and ethanol (4) at room temperature.
The angle of pretwist plays a major role in the distribution of various conformers of these probes in different salvation sites of their solvents. This is usually reflected on their emission spectra and response to red edge excitation especially if the medium is slightly rigid and/or polar \([7,22,23]\).

After excitation DPABME is expected to relax toward a more planer state and thus emits from its LE (of some CT character) state, or towards a less planer state and thus emits from a TICT state. Two or one fluorescence bands are therefore expected for DPABME in various solvents. Their relative positions and intensities are determined by many complicated factors that vary from the size, donacity, ionization potential and angle of pretwist of the donor to the electron affinity of the acceptor and to polarity and viscosity of the medium. These factors also determine the relative positions and the height of the barrier between the two states, as well as the stabilization of the TICT-state and its position relative to the ground state.

In pentane (a nonpolar solvent) only the normal fluorescence \(\sim 375\) nm is observed. The Stoke's shift however is large \(\sim 3200\) cm\(^{-1}\) (Table I) and could reflect some CT character of the b-state resulted from dispersion interaction between the solute and solvent during the excited state lifetime. In acetonitrile (a polar solvent) only the long fluorescence \(\sim 480\) nm is observed and is attributed to a TICT state and consistent with the observation made by Rettig and coworkers on CPC in acetonitrile. In water only one fluorescence band is observed \(\sim 420\) nm, however its tail extends beyond 500 nm. Upon inclusion with \(\alpha\)-CD aqueous solution the TICT fluorescence \(\sim 510\) nm started to appear. This is attributed to destabilization of the TICT state that lead to reducing quenching with water molecules according to energy gap rule\([24,25]\). The short fluorescence \(\sim 420\) nm in water is therefore due to normal fluorescence from LE excited state with CT character, while the long fluorescence \(\sim 510\) nm which is enhanced by inclusion is due to TICT state.

In ethanol, the fluorescence of DPABME is however broader and undergoes a larger Stoke's shift relative to pentane or acetonitrile (Table I). Moreover the b-band appeared as a shoulder at the blue side of the TICT fluorescence band. Their relative intensity vary with the wavelength of excitation. Exciting at the red edge of the absorption band selects either more or less planer conformers, relative to the bulk and thus reflected on the relative intensity of the normal fluorescence band with respect to the TICT band depending on \(\lambda_{\text{exc.}}\)
Figure 3 shows that the TICT band is enhanced relative to the b-band upon increasing $\lambda_{\text{exc}}$ from 280 nm to 360 nm. The presented results put no doubts that two states, b- and TICT-state are present in the excited state of DPABME. This is confirmed by the time resolved fluorescence (TRF) spectra of Figures 4 & 5 and fluorescence decay results, Table I. The TRF spectra results show:

1- The fluorescence of DPABME in ethanol, Figure 4, is broad and composed of two fluorescence bands, a b-band and a TICT-band of almost equal opportunities reflected by equal intensities using different time windows. Their lifetimes are 1.8 ns at 380 nm and 4.2 ns at 480 nm.

This is consistent with the steady state fluorescence of DPABME in ethanol, Figure 2 - spectrum # 4.

2- The fluorescence of DPABME in acetonitrile, Figure 5, is narrow and constitute the red part of the fluorescence spectra in ethanol and therefore attributed to emission from a TICT state. Its lifetime is 6.2 ns. This is also consistent with the steady state fluorescence of DPABME in acetonitrile, Figure 2- spectrum # 3.
Figure 4: Time – resolved fluorescence spectra of ~1x10⁻⁶ M DPABME in ethanol using different time windows. (1) Δt = 100 ps, (2) Δt = 1ns, (3) Δt = 10 ns, at room temperature.

Figure 5: Time - resolved fluorescence spectra of ~1x10⁻⁶ M DPABME in n-butyl chloride (1), acetonitrile (2), and ethanol (3), at room temperature using 10 ns time windows.

3- The fluorescence of DPABME in n-butyl chloride, Figure 5, is also narrow, however it constitutes the blue part of the fluorescence spectra in ethanol and is therefore attributed to emission from a b-state. Its lifetime is 4.2 ns. This is
consistent with the steady state fluorescence of DPABME in n-butylchloride, Figure 2- spectrum #2.

Actually the sum of the half-band widths of the fluorescence of DPABME in n-butylchloride and in acetonitrile, measured from TRF spectra results of Figure 5 equal the half-band width of fluorescence of DPABME in ethanol. This is an indication that the b-state is apparently inemissive in acetonitrile and the TICT-state is apparently inemissive in n-butylchloride. However, both states are emissive in ethanol.

To further understand the role of solvent on the excited state of DPABME we are in the process of investigating its fluorescence in various alcohols, various polymers and various CD aqueous solutions.

References