

Broad-band visible emission from UV-exposed TPD solution

M. P. Joshi^{1*}, S Raj Mohan¹, S. K. Tiwari¹, T. S. Dhama¹, T. Shripath², U.P. Deshpande²,
M. K. Singh³, H. Ghosh¹

¹Laser Physics Application Section,

Raja Ramanna Centre for Advanced Technology, Indore, MP - 452 013, India.

²UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore 452017, India

³Laser Materials and Device Development Division,

Raja Ramanna Centre for Advanced Technology, Indore, MP - 452 013, India.

*mukesh@cat.ernet.in

Abstract: Strong broad band visible emission from *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) is reported when solution of TPD (in halomethane solvents like chloroform or dichloromethane) is exposed to UV light. Emission color changes from originally blue to green with exposure. Uv-visible absorption, FTIR and XPS studies of photoproduct suggest photodegradation of TPD. With UV exposure the photolysis of chloroform first oxidizes TPD and with further exposure a permanent transformation/degradation of TPD to possibly its chloride salt and other low molecular weight compounds. Strong blue-green dual emission is observed from the photoproduct dissolved in different solvents (solvent dependent) and also from vacuum sublimed thin film. Compared to pure TPD an improved electrical conductivity has been observed in photodegraded TPD dispersed polymers films.

Keywords: TPD; photodegradation, visible emission; exciplex

Introduction

N,N'-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) a well-known aromatic diamine dye with emission in blue ($\lambda_{em} \sim 410\text{nm}$) and used extensively in developing organic light emitting diodes (OLEDs)[1] and solid-state dye laser[2]. Due to lone pair of electrons at nitrogen site the TPD molecule is chemically very reactive and easily undergoes charge transfer reactions with electron acceptors. This property also makes TPD structure unstable under certain environmental conditions of certain gases or solvents[3]. Stability of TPD has been addressed but mostly in doped polymers films and with respect to lasing parameters like pump intensity, repetition rate and polymer matrix[4]. Photodegradation of TPD in solutions and resulting changes in optoelectronic properties has not been reported so far.

We report observation broad band visible emission covering the entire blue–green range from TPD when solutions of TPD in halomethane solvents are exposed with UV light. A systematic shift of emission from blue to green is observed with exposure time. We emphasize exclusive use of halomethanes like chloroform and dichloromethane solvents which initiates photochemical reactions and degrade TPD. Resultant solid photoproduct show solvent dependent blue-green broad band emission and is thermally stable as sublimed films also show broad band visible emission. Compared to pure TPD the photoproduct dispersed in polystyrene shows drastic improvement in electrical conductivity. Photoelectron spectroscopy, FTIR and absorption and photoluminescence measurements suggest the

origin of emission in green is presumably the characteristics of TPD based chloride salt or an exciplex emission from TPD and its photoproducts.

Experiment

Solution of TPD (Aldrich, 99.8% pure) in spectroscopic grade chloroform was prepared ($\sim 10^{-4}\text{M}$ concentration) and part of this solution was transferred to a 1 mm path-length quartz cuvette and kept under UV lamp for exposure (we used 4W germicidal lamp, long wavelength UV light ($\lambda_{peak} \sim 365\text{ nm}$), fluence $\sim 8\text{ nJ/m}^2\text{ s}$). With exposure, visible inspection showed gradual change of TPD emission from blue to white to finally green with darkening of solution color. Figure 1 shows exposure time dependent changes in photoluminescence spectrum of TPD-chloroform solution. With increasing exposure, the emission maxima $\sim 410\text{ nm}$ of TPD decreases and growth of new

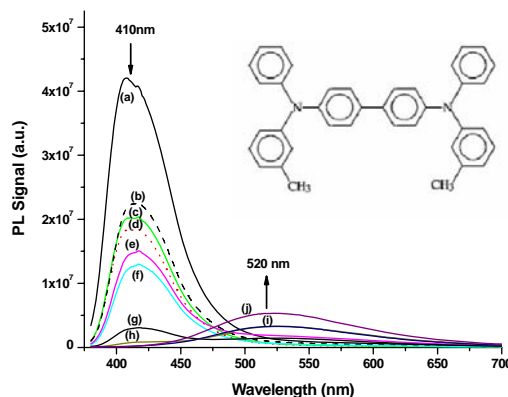


Figure 1: Changes in photoluminescence spectrum of TPD-chloroform solution with UV exposure taken at different exposure durations (a) 0 s, (b) 10s, (c) 30s, (d) 1.5m, (e) 3.5 m, (f) 8.5m, (g) 18.5m, (h) 38.5m, (i) 68.5m, (j) 113.5m. All the data recorded with excitation wavelength at 365 nm. Inset show structure of TPD.

broad band emission centered around 520nm take place. Optimum time for appearance of green emission was $\sim 2\text{ hrs}$ for given TPD concentration. Saturation of emission intensity and peak position was observed with further UV exposure. Even for prolonged UV exposure for more than few days there was no change or reduction in green emission intensity. Exclusive use of halomethanes was proved when similar observation were made in dichloromethane but not in other solvents like toluene, dioxane etc. Exclusive use of halomethane solvent seems to be playing an important role in

producing green emission. Emission characteristics were further investigated when the photoproduct (dark red-brown solid) showed solvent dependent dual band emission in blue and green region. Figure 2 and Figure 3 show solvent dependent emission spectra of photodegraded TPD and vacuum sublimed thin film deposited on quartz substrate respectively.

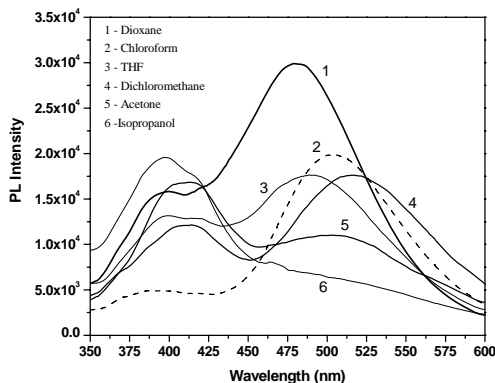


Figure 2: Solvent dependent dual band emission from photoproduct obtained after over exposing (>24 hrs) TPD-chloroform solution. Photoproduct was purified by vacuum sublimation and then re-dissolved in different solvents of similar concentrations ($\sim 10^{-4}$ M).

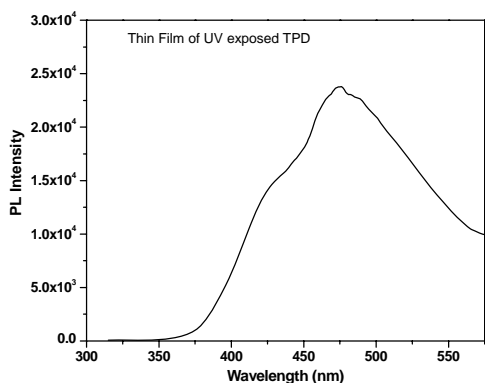


Figure 3: Photoluminescence spectrum of photodegraded TPD film sublimed on quartz substrate. Excited at 300nm. Two well separated bands in blue and green, as observed in solutions, are merged together.

In Figure 2, there are two emission bands clearly visible as blue band and green band. Blue band ranges from 375-425 nm and green band from 475 to 525 nm. With solvents of different polarity and dielectric constant these bands show spectral shifts. Emission in blue region shows some structure with shoulders and humps while green region is smooth and structureless. Dual nature of emission band is seen in all the solvent except for more polar solvent like isopropanol which showed emission in blue region only. Vacuum sublimed thin film of photodegraded TPD also show broad band emission covering the entire blue-green region. Important observation that can be drawn from Figure 3 is that

compared to solution spectrum the thin film spectrum show red-shift of blue band with loss of structures while green band undergoes blue-shift.

Discussion and Analysis

To understand the observed emission characteristics one needs to first look at possible photochemical reactions in UV exposed TPD solution and the nature of resultant photoproduct. It is known that UV photolysis of halomethanes generates chlorine radicals and hydrochloric acid [5] and this property of halomethanes has been exploited extensively to oxidize various organic compounds and synthesize new compounds via photochemical synthesis route[6]. Therefore the primary photochemical reaction between TPD and halomethane is oxidation of TPD (TPD^+)[7]. With further exposure the increase in acid content in the solution may initiate several other photochemical substitution reactions, polymerization etc. to permanently transform TPD to new compound that is possibly responsible for green emission.

To gain some insight on the nature of photoproduct we studied changes in uv-visible absorption of TPD-chloroform solution as a function of UV exposure and characterized the resultant solid photoproduct using FTIR and X-ray photoelectron spectroscopy. As shown in Figure 4, two major absorption peaks of TPD at 305nm and 354nm show gradual changes in intensity with exposure. Within very short exposure time (~ 1 minute) the low energy peak at 354nm almost disappeared while peak at 305nm remained almost same with minor changes in intensity and peak position. With further increase of UV exposure a broad hump in visible region is also seen. The implications of drastic reduction of

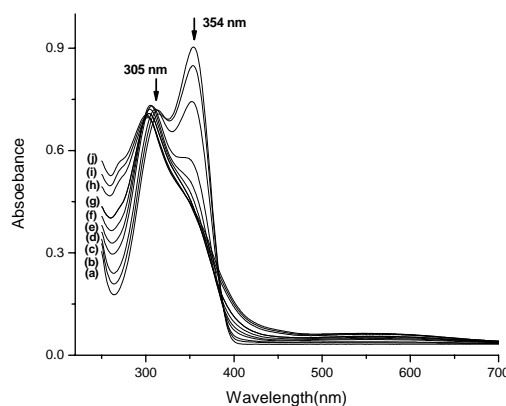


Figure 4: Changes in absorption spectrum of TPD-chloroform solution with UV exposure. Data recorded after exposure duration (a) 0 s, (b) 10s, (c) 30s, (d) 1.5m, (e) 3.5 m, (f) 8.5m, (g) 18.5m, (h) 38.5m, (i) 68.5m, (j) 113.5m

low energy peak at 354nm is studied theoretically by structural optimization of TPD using DFT-based 'D-mol' code and using well known multireference single double configuration interaction (MRSDCI) *ab-initio* many body method within π -electron basis to obtain electronic structure.

Theoretical simulation of optical absorption spectrum of TPD molecule is in very close agreement with the experimentally observed absorption spectrum.

The low energy transition (peak at 354nm) corresponds to Highest occupied molecular orbital (HOMO)- Lowest occupied molecular orbital (LUMO) transition and graphical representation of electron densities of LUMO levels, as shown in Figure 5, suggests electron density in LUMO is heavily centered on the biphenyl group.

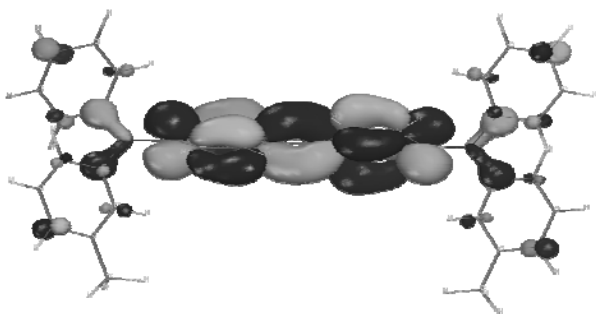


Figure 5: Electron density isocontours of LUMO level of TPD

Therefore the drastic reduction in absorbance at 354nm may be due to either breaking of TPD into two identical triphenyl amine (TPA) units or some bond formation at nitrogen sites or carbon atoms of central phenyl groups which reduces electron density at central biphenyl group of TPD. It has been reported that various substitution reactions on TPD structure drastically affect electron density at central biphenyl unit[8]. Possibility of breaking of TPD into two TPA units seems possible as we observe blue shifted emission in blue band i.e. emission below 410nm (see Figure2, the blue band extends below TPD emission). Therefore the emission band in blue region seems to be due to mixtures of unreacted TPD and other short π -conjugated compounds. Although the origin of strong and solvent dependent green emission still remains interesting.

FTIR spectrum of photoproduct film sublimed on ZnSe substrate showed appearance of new frequencies and changes in relative intensities with broadening of several IR absorption bands of TPD. Complicated FTIR spectrum indicate multicomponent photoproduct (Figure 6). More pronounced effect was seen as a broad hump around 3300cm^{-1} which corresponds to N-H stretching [9]. This is missing in pure TPD as nitrogen is connected to three phenyl groups but not directly to any hydrogen. Acidic content that is generated upon UV photolysis of chloroform may protonate TPD and produce N-H stretching. Therefore the protonation of TPD seems an important consequence of UV exposure.

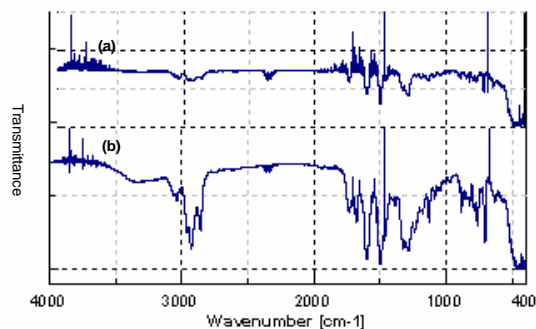


Figure 6: FTIR spectrum of (a) TPD and (b) photodegraded TPD

More important information is obtained from the XPS survey spectrum which was made on sublimed films of TPD and photoproduct onto Si substrates. The X-ray photoelectron spectra were recorded in a VSW ESCA instrument using Al $K\alpha$ (1486.6eV) radiation (resolution of 0.9eV) at a base vacuum of 2×10^{-9} torr. Apart from carbon and nitrogen we also detected chlorine in the photoproduct. Binding energies peak of Cl 2p is shown in Figure 7. The presence of chlorine peak around

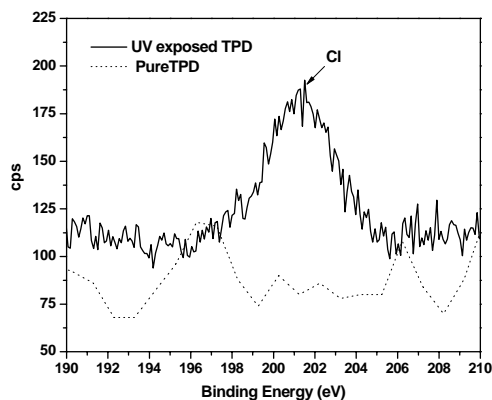


Figure 7: Cl 2p core-level spectrum from photodegraded TPD.

200.5eV indicates chlorine is bonded or part of the photodegraded product of TPD. The exact nature and location of chlorine bonding is difficult but most likely to form chloride salt of TPD. Binding energy peak of N 1s in most of nitrogen containing compound is normally obtained in narrow region of 399-401 eV depending upon the oxidation states and the level of protonation of nitrogen[10]. We observed N 1s peak around 400.2 eV suggesting positively charged nitrogen atom ($-N^+-H-$)[11].

Based on FTIR, XPS and uv-visible absorption studies it seems upon UV exposure the TPD dye is undergoing structural transformation from oxidation to substitution reaction to possibly a chloride salt. The exact origin of green emission is still unresolved but some conclusion can be drawn

from the comparison of Figures 2 and 3. Two clear band (blue and green) as observed in solutions show contrasting spectral shift in solid form i.e. red-shift of blue band and blue shift of green band. This suggests that the origins of dual band emission is very different. Blue band seems to originate from locally excited molecular transition while green band is an outcome of coupling of excited states of photoproducts. Mechanisms like charge (proton, electron) transfer, exciplex transition etc. are possible sources of green emission. Efficiencies of these processes depend strongly on the environment (solvent dependence). There can be mechanisms other than the protonated dye or exciplex emission like defect luminescence that can not be ignored[12]. A more detailed analysis of photoluminescence using time resolved and temperature dependence are being carried to unravel the same.

The important effect of UV exposure of TPD solution, as far as materials for display applications is concerned, is the natural and unintentional photochemical synthesis of a new compound/s with broad-band blue-green visible emission. One can make use of simple technique of UV exposure for developing white light OLEDs. Novel emission processes like proton transfer, exciplex excitation transfer are commonly utilized to develop white light OLEDs[13]. The photoproduct, apart from giving a broad-band visible emission, also showed a drastic improvement in electrical conductivity. Current density in the case of photodegraded (dispersed in polystyrene) was observed to increase ~ 5 times that of pure TPD dispersed in polystyrene. Threshold voltage also decreased in photodegraded sample. Improvements in optical and electrical characteristics of TPD upon UV exposure are advantageous for display device applications. Efforts are being made to obtain electroluminescence from degraded TPD dispersed in polymers like PVK, PMMA etc.

Conclusion

UV exposed TPD-chloroform solution show gradual shift of emission originally from blue to strong and broad visible emission. Photolysis of chloroform under UV excitation initiates photochemical reaction to transform or degrade TPD structure. The photoproduct, new compound/s formed out of degradation of TPD, show improved electrical conductivity and broad band visible emission. The mechanism of visible

emission in green is likely to be due to protonated TPD or an exciplex emission from degraded photoproducts.

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