Dyes and Pigments 87 (2010) 44-48

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Ultrafast solvation and anisotropy dynamics in a tri-branched molecule based on a triphenylamine core

M. Fakis^{a,*}, V. Giannetas^a, J. Mikroyannidis^b

^a Department of Physics, University of Patras, 26504 Patras, Greece ^b Department of Chemistry, University of Patras, 26504 Patras, Greece

ARTICLE INFO

Article history: Received 4 November 2009 Received in revised form 17 February 2010 Accepted 18 February 2010 Available online 1 March 2010

Keywords: Femtosecond spectroscopy Tri-branched molecules Solvation Time resolved anisotropy

ABSTRACT

The steady-state spectra and the isotropic and anisotropic fluorescence dynamics of a tri-branched molecule comprising a triphenylamine core and 2,3-di(2-thienyl)acrylonitrile branches were studied in solution and solid film in the femtosecond regime. Isotropic fluorescence dynamics revealed an ultrafast decay component (ranging from 0.3 ps to 6.7 ps depending on solvent and emission wavelength) that was observed only in solution and was attributed to solvation; a slow decay component (~ 1 ns), attributed to radiative population decay, was also observed. The solvation process was studied in three different solvents of different polarities and viscosities. The solvation efficiency increased with increasing solvent polarity whilst solvation time was greatest in the solvent of highest viscosity. Anisotropy dynamics showed an ultrafast decay in the fs regime indicating strong intramolecular interactions among the branches.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

In the past decade a large amount of research has been devoted to the design, synthesis and photophysical characterization of multibranched conjugated organic molecules owing to their potential applications in non-linear optics (NLO), light emitting diodes, lasers and solar cells [1–10]. The advantage of multi-branched molecules. compared to the conventional linear conjugated compounds, is that such compounds provide a large number of branched chromophores in an ordered geometry. The non-linear optical properties of multi-branched molecules can be greatly enhanced compared to their linear counterparts due to a cooperative effect amongst the branched chromophores imparted by electron coupling [11–14]. When this coupling is weak, the NLO parameters are the sum of those of each chromophore. In order to exceed this additive behavior [15,16], strong interbranch coupling leading to delocalized excitations is required. The strength of coupling is greatly influenced by the nature of the core and it has been shown that tri-branched molecules with a nitrogen core favour excitation coupling among branches compared to their counterparts having a carbon, phosphorus or benzene core [17].

Steady-state and time resolved spectroscopic techniques are employed for the examination of multi-branched molecules,

* Corresponding author. E-mail address: fakis@upatras.gr (M. Fakis).

especially for understanding the nature of the coupling between the branches and for determining structure-property relationships [18,19]. Ultrafast isotropic and anisotropic fluorescence techniques are valuable tools for probing energy migration and for differentiating between coherent and incoherent energy transfer. Time resolved isotropic fluorescence dynamics may probe different kinds of dynamic processes such as intra- or inter-molecular energy transfer, intramolecular rearrangement (e.g. twisting of a functional group), solvation and radiative population decay. All of these phenomena can occur within the time scale of tens of picoseconds or less except for radiative population decay, which, typically, occurs within hundreds of picoseconds. In addition, time resolved anisotropic fluorescence dynamics may simultaneously probe exciton migration and overall molecular rotation. However, these processes typically occur over different time scales since exciton migration occurs in the fs to ps regime whereas overall rotation occurs in the ps to ns regime.

The photophysics and dynamics of conjugated molecules are dramatically affected by the nature of the solvent. Understanding solvent—solute interactions is of great importance in photophysics since by changing a solvent, the decay pathways of a molecule may be completely altered. Especially, solvent polarity affects both steady-state and time-resolved fluorescence spectra [20,21]. In polar solvents an Intramolecular Charge Transfer (ICT) state is formed especially when the solute molecule contains donor and acceptor groups. In some cases, intramolecular charge separation requires rotation of a group leading to a Twisted Intramolecular





^{0143-7208/\$ –} see front matter \circledast 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2010.02.002

Charge Transfer state (TICT) [20–22]; additionally, solvent viscosity affects reorientational motion and solvation dynamics [23,24]. From the above, it is apparent that combinatorial isotropic and anisotropic fluorescence studies undertaken in various solvents and in the solid state are required in order to thoroughly investigate the photophysics of a molecule.

In this work, the steady-state spectra and ultrafast fluorescence dynamics of a tri-branched molecule with triphenylamine central core and 2,3-di(2-thienyl)acrylonitrile branches are studied in solution and solid film. Both isotropic and anisotropic fluorescence dynamics are presented. Three different solvents were used and the effect of polarity and viscosity on the fluorescence dynamics is discussed. Besides, ultrafast anisotropy dynamics is exhibited indicating strong excitation delocalization among the branches.

2. Experimental

2.1. Materials

The chemical structure of the tri-branched molecule studied is shown in the inset of Fig. 1. It contains triphenylamine central core (i.e. nitrogen atom at the center) and 2,3-di(2-thienyl)acrylonitrile branches and is abbreviated as TPA(DTA)₃. TPA(DTA)₃ was prepared by a three-step synthetic route; the detailed description of the synthesis and chemical characterization has been published elsewhere [25]. Briefly, tris(4-bromophenyl)amine reacted with tributyl(thiophen-2-yl)stannane in the presence of PdCl₂(PPh₃)₂ to afford tris(4-(thiophen-2-yl)phenyl)amine. The latter was reacted with *N*,*N*-dimethylformamide and POCl₃ to yield 5,5′5″-(nitrilotri-4,1phenylene)tris-2-thiophenecarboxaldehyde. Finally, this compound was reacted with 2-(thiophen-2-yl)acetonitrile in anhydrous ethanol in the presence of NaOH to afford TPA(DTA)₃. The chemical structure of TPA(DTA)₃ was confirmed by FT-IR and ¹H NMR spectroscopy as well as elemental analysis.

FT-IR (KBr, cm⁻¹): 3026, 2210, 1658, 1594, 1576, 1528, 1494, 1442, 1322, 1293, 1272, 1253, 1184, 1054, 830, 800, 700. ¹H NMR (CDCl₃, ppm): 7.46 (s, 3H, olefinic); 7.34–7.33 (m, 3H, thiophene protons at position 2); 7.31–7.29 (m, 6H, phenylene protons meta to nitrogen); 7.19–7.12 (m, 12H, thiophene protons at positions 3,4); 7.09–7.06 (m, 6H, phenylene protons ortho to nitrogen). Anal. Calcd. for $C_{51}H_{30}N_4S_6$: C, 68.73; H, 3.39; N, 6.29. Found: C, 67.56; H, 3.30; N, 6.22.



Fig. 1. Absorption spectrum of $TPA(DTA)_3$ in THF and fluorescence spectra in THF, ACP and DMF. The inset shows the chemical structure of $TPA(DTA)_3$.

2.2. Techniques

The steady-state absorption and fluorescence spectra were obtained with a Beckman DU-640 spectrometer and a Perkin Elmer LS45 luminescence spectrometer respectively. The fluorescence spectra were recorded by using an excitation wavelength of 400 nm. The fluorescence dynamics has been studied with a time resolved fluorescence upconversion technique. The experimental set-up has been described in details previously [26,27]. Briefly, a mode-locked Ti:Sapphire femtosecond laser (80 fs pulse duration, 80 MHz repetition rate, tunable from 750 to 850 nm) has been used as the fundamental laser source. The second harmonic of the femtosecond laser was used for the excitation of the samples. The excitation power was typically below 5 mW. The fluorescence of the samples was collected and mixed with the delayed fundamental laser beam into a BBO crystal (type I) generating an upconversion ultraviolet beam. This beam passed through appropriate filters and a monochromator and it was detected though a photomultiplier as a function of the temporal delay between the fundamental laser beam and the fluorescence. The temporal resolution of the technique was 160 fs. Both isotropic and anisotropic decays were measured. The isotropic decays were taken under magic angle conditions while the anisotropic ones were detected with polarization parallel and perpendicular to the excitation beam. The polarized decays were used in order to determine the time resolved anisotropy. The decays were measured for TPA(DTA)₃ in three different solvents namely tetrahydrofuran (THF), acetophenone (ACP) and dimethylformamide (DMF) as well as in a Poly (methyl methecrylate) (PMMA) film. For the formation of the film, appropriate amounts of TPA(DTA)₃ and PMMA were initially dissolved in THF and were magnetically stirred for 24 h. The films were prepared by spin coating onto glass substrates, previously rinsed with acetone. All samples were placed in a rotating holder in order to avoid thermal degradation.

3. Results and discussion

3.1. Steady-state spectroscopy

The steady-state absorption and fluorescence spectra of TPA (DTA)₃ in solutions with different solvents are shown in Fig. 1. Specifically, TPA(DTA)₃ in THF exhibits an absorption peak at 460 nm corresponding to the $\pi - \pi^*$ excitation. The absorption spectrum of TPA(DTA)₃ was not sensitive to the change of the solvent polarity. This is explained since the dipole moment in the ground state is lower than in the excited one. For this reason the absorption spectrum is shown in Fig. 1 only in THF. The fluorescence spectrum of TPA(DTA)₃ in THF exhibits a structureless feature with a peak at 528 nm. When the solvent is changed from THF, which is a low-polarity solvent, to ACP and DMF, which are solvents with higher polarities, the fluorescence spectrum shifts to longer wavelengths. Specifically, TPA(DTA)₃ in ACP and DMF exhibits fluorescence peaks at 536 nm and 545 nm respectively. This redshift is expected, since, after excitation, the solvent molecules reorient or relax around the dipole of the excited state lowering its energy. This effect becomes more significant as the solvent polarity increases [22].

3.2. Fluorescence dynamics

The isotropic fluorescence dynamics of TPA(DTA)₃ in THF solution (10^{-4} M concentration) are shown in Fig. 2 together with the fitting curves for four different emission wavelengths. The excitation wavelength was 400 nm. It is clear that as the detection is shifted from short towards long wavelengths, the decays become



Fig. 2. Fluorescence dynamics of TPA(DTA)₃ in THF, in normalized units (n.u.), at various detection wavelengths. The excitation wavelength was 400 nm while the concentration was 10^{-4} M.

slower. At short wavelengths, the decays are governed by an ultrafast component followed by a slower one. The time constant of the ultrafast component increases with the emission wavelength and it ranges from 1.4 ps to 5.1 ps. Table 1 summarizes the ultrafast decay parameters (time constant and pre-exponential factor) at various emission wavelengths. At the longest wavelength detected i.e. at 600 nm, the dynamics exhibits a slow rise meaning that there is an accumulation process in the population of the low energy states. In Fig. 2, the dynamics at 600 nm is shown within the first 6 ps so that the slow rise is clear. In Table 1 this rise is identified by a negative pre-exponential factor. The slow decay component could not be accurately fitted within the time scale shown in Fig. 2. Thus, the fluorescence decays have been measured on a longer time scale and are shown in Fig. 3 at 530 nm. Fitting these dynamics, the time

Table 1

Fitting parameters of the ultrafast fluorescence decay component in different solvents and detection wavelengths.

Solvent	$\lambda = 500 \text{ nm}$		$\lambda = 540 \text{ nm}$		$\lambda = 580 \text{ nm}$		$\lambda = 600 \text{ nm}$	
	$\overline{\tau_1}$ (ps)	A_1	$\overline{\tau_1}$ (ps)	A_1	$\overline{\tau_1}$ (ps)	A_1	$\overline{\tau_1}$ (ps)	<i>A</i> ₁
THF	1.4	0.80	2.5	0.58	5.1	0.23	0.6	-0.34
ACP	2.2	0.86	4.3	0.63	6.7	0.33	1	-0.2
DMF	0.3	0.95	1	0.75	2.9	0.67	0.4	-0.45

constant of the slow component was determined and it was found \sim 980 ps. The slow decay component showed no detectable dependence on the emission wavelength.

The fluorescence transients shown in Figs. 2 and 3 have been also observed in other similar tri-branched molecules in the past [13,21,28–31]. They have been attributed to different kinds of physical mechanisms such as inter-molecular energy transfer towards aggregates, intramolecular energy migration, single-t-singlet annihilation, solvation or photoinduced conformational changes.

In order to examine whether the ultrafast dynamics is attributed to aggregates or other concentration dependent species, the fluorescene dynamics was detected in THF solutions with different concentrations ranging from $0.5.10^{-4}$ M up to 10^{-3} M. The dynamics are shown in Fig. 4(a) at excitation and detection wavelengths of 400 nm and 530 nm respectively. In all concentrations the decays are similar meaning that aggregates are not formed and that no other concentration dependent component affects the dynamics (at least within the concentration range used).

Furthermore, in order to identify whether intensity dependent phenomena occur, the fluorescence dynamics has been studied for two different excitation powers and the results are shown in Fig. 4(b). The dynamics are identical meaning that intensity dependent effects like singlet—singlet annihilation can be excluded within our excitation power regime.

The fluorescence dynamics of TPA(DTA)₃ has also been studied in solid film. For the formation of the film, TPA(DTA)₃ was dispersed into PMMA matrix (0.1 wt%). The fluorescence decay of the TPA (DTA)₃–PMMA film at 530 nm is shown in Fig. 4(c) together with the corresponding results of TPA(DTA)₃ in THF (10⁻⁴M). It is clear that in solid film, TPA(DTA)₃ exhibits a relatively slow decay with no ultrafast decay component.

From all the above results it is concluded that ultrafast fluorescence dynamics of TPA(DTA)₃ occurs only in solution and that it is not due to aggregates or singlet—singlet annihilation. Therefore it can be plausibly attributed to solvation. An influence from photoinduced conformational changes on the dynamics could not be excluded. In many cases, solvation and photoinduced conformational changes (such as twisting of a functional group around a bond or cis—trans isomerization) co-exist and constitute competing relaxation mechanisms occurring within the same temporal regime [32,33]. However, the co-existence of these mechanisms would probably require the introduction of an additional exponential decay term to satisfactorily fit the fluorescence transients.



Fig. 3. Long scale fluorescence dynamics of $TPA(DTA)_3$ in THF, ACP and DMF at 530 nm (excitation wavelength: 400 nm, concentration: 10^{-4} M).



Fig. 4. The dependence of the fluorescence dynamics of $TPA(DTA)_3$ on (a) concentration and (b) excitation power. In both figures the excitation wavelength was 400 nm and the detection one was 530 nm. The curves in (a) and (b) have been slightly shifted for clarity. Figure (c) shows the fluorescence dynamics of $TPA(DTA)_3$ at 530 nm in a PMMA film and in a THF solution. The excitation wavelength was 400 nm.

The ultrafast process has been studied in two additional solvents namely ACP and DMF and the role of solvent polarity and viscosity was examined. In Fig. 5, the fluorescence dynamics of TPA(DTA)₃ is shown in these solvents at four wavelengths. The dynamics of TPA (DTA)₃ in THF is also shown for a comparison. As shown in Fig. 5 and in Table 1 the fluorescence in DMF (the most polar solvent) initially decays much faster than in the other two solvents. Additionally, the ultrafast mechanism is more efficient in DMF as it is evident by its very high pre-exponential factor. The decay dynamics in DMF can be explained taking into account its higher polarity than the other solvents. It is well known that in highly polar solvents, an ICT state is formed becoming the energetically lowest lying state. The ultrafast decay in DMF is therefore due to the relaxation from the initially excited state to the ICT. The fluorescence of the relaxed ICT state is detected at long wavelengths. Although, an ICT state could also be the fluorescent state in the other solvents (i.e. THF and ACP), the ultrafast relaxation is much more efficient in DMF meaning that the activation barrier for ICT formation is decreased in the polar solvent.

On the other hand, the decay features in ACP, which is a solvent of intermediate polarity are more complicated. At short wavelengths, the fluorescence in ACP initially decays more slowly than in



Fig. 5. Early fluorescence dynamics of $TPA(DTA)_3$ in THF, ACP and DMF at four wavelengths.

THF and DMF. At long wavelengths, the fluorescence in ACP, initially decays similarly to THF. The difference in polarity alone cannot explain the fluorescence dynamics observed in ACP. Since ACP has an intermediate polarity we would expect the fluorescence decay in this solvent to be faster than THF and slower than DMF. However, as it is shown in Fig. 5, this is not observed. In order to explain the results, the solvent viscosity has to be considered. ACP is the most viscous solvent among the three solvents used in this work. Solvation is considered as the reorientation (relaxing) of the solvent molecules around the excited solute molecules lowering the energy of the excited state. Since this reorientation is retarded in solvents of high viscosity, the solvation dynamics is also retarded and consequently the fluorescence decay due to solvation becomes slower. However, the dynamics in ACP also shows another important feature. Although this dynamics is slower in ACP than in THF, the drop of the fluorescence intensity, because of the ultrafast component, is bigger in ACP than in THF (the pre-exponential factor for the ultrafast component is higher in ACP than in THF). Consequently, the overall drop in fluorescence intensity because of the solvation process (i.e. the solvation efficiency), follows the increase of the solvent polarity meaning that it is enhanced as the polarity increases. On the other hand, the solvation time is greatly affected by the viscosity meaning that solvation becomes slower in the most viscous solvent i.e. ACP.



Fig. 6. Polarized fluorescence dynamics of $TPA(DTA)_3$ in THF and ultrafast anisotropy decay. The excitation and detection wavelengths were 400 nm and 530 nm respectively and the concentration was $10^{-4}M$.

The long-scale fluorescence dynamics of $TPA(DTA)_3$ in ACP and DMF are shown in Fig. 3. As in the case of THF, a wavelength independent long decay component (~1 ns decay constant) is observed in both solvents attributed to radiative population decay.

3.3. Time resolved anisotropy

The anisotropy decay is a powerful method for determining whether exciton transfer occurs among the branches of multibranched molecules. Anisotropy dynamics can also provide information about the nature of this transfer. Energy hopping among branches (incoherent process) or excitation delocalization (coherent process) can occur affecting the polarization of the fluorescence and thus the anisotropy dynamics. If this is the case, a fast depolarization of the emission would be observed leading to a fast drop of the anisotropy [19,29]. For this reason the ultrafast polarized dynamics of TPA(DTA)₃ (concentration 10^{-4} M) were detected at 530 nm. The results are shown in Fig. 6 together with the calculated anisotropy decay within the ultrafast time scale. The anisotropy decays to a residual value of 0.13 with an ultrafast decay within the temporal resolution of our technique. This ultrafast anisotropy decay is too fast and cannot be due to a hopping mechanism [34,35]. It is strongly associated to excitation delocalization to an area larger than one branch due to interactions among branches. These interactions are supported by the nitrogen central core which has been found to enhance excitation coupling among branches [17]. Strong interbranch interactions are desirable and are associated with the enhancement of non-linear optical properties in tri-branched molecules.

4. Conclusions

A tri-branched molecule with triphenylamine central core and 2,3-di(2-thienyl)acrylonitrile branches has been studied in solution and solid film concerning the steady-state spectra and time

resolved fluorescence dynamics. The tri-branched molecule, in solutions, exhibits ultrafast solvation decay. Solvation rate was affected by both polarity and viscosity, being greatest in DMF, a solvent of high polarity and lowest in ACP, a solvent of high viscosity. In contrast, solvation efficiency was affected only by solvent polarity and was enhanced as polarity increased. Anisotropy dynamics revealed ultrafast decay indicating excitation delocalization among the branches, which is desirable in the context of the enhancement of non-linear optical properties.

References

- [1] Wang Y, He GS, Prasad PN, Goodson III T. J Am Chem Soc 2005;127:10128.
- [2] Wang D, Wang X, He Q, Zhou M, Rui W, Tao X, et al. Tetrahedron Lett 2008;49:5871.
- [3] Wang Z, Wang X, Zhao J, Jiang W, Yang P, Fang X, et al. Dyes Pigm 2008;79:145.
 [4] Mazzucato S, Fortunati I, Scolaro S, Zerbetto M, Ferrante C, Signorini R, et al.
- Phys Chem Chem Phys 2007;9:2999.
- [5] Halim M, Pillow JNG, Samuel IDW, Burn PL. Synth Met 1999;102:922.
- [6] Bera RN, Cumpstey N, Burn PL, Samuel IDW. Adv Funct Mater 2007;17:1149.[7] Lawrence JR, Turnbull GA, Samuel IDW, Richards GJ, Burn PL. Opt Lett
- 2004;29:869.
- [8] Andronov A, Gilat SL, Frechet JMJ, Ohta K, Neuwahl FVR, Fleming GR. J Am Chem Soc 2000;122:1175.
- [9] Cao D, Liu Z, Deng Y, Li G, Zhang G. Dyes Pigm 2009;83:348.
- [10] Ning Z, Tian H. Chem Commun; 2009:5483.
- [11] Terenziani F, Droumaguet CL, Katan C, Mongin O, Blanchard-Desce MB. ChemPhysChem 2007;8:723.
- [12] Katan C, Terenziani F, Mongin O, Werts MHV, Porres L, Pons T, et al. J Phys Chem A 2005;109:3024.
- [13] Macak P, Luo Y, Norman P, Ågren H. J Chem Phys 2000;113:7055.
- [14] Jiang Y, Wang Y, Hua J, Qu S, Qian S, Tian H. J Polym Sci Part A Polym Chem 2009;47:4400.
- [15] Chung SJ, Kim KS, Lin TC, He GS, Swiatkiewicz J, Prasad PN. J Phys Chem B 1999;103:10741.
- [16] Drobizhev M, Karotki A, Dzenis Y, Rebane A, Suo Z, Spangler SW. J Phys Chem B 2003;107:7540.
- [17] Goodson III T. Acc Chem Res 2005;38:99.
 [18] Lor M, Viaene L, Pilot R, Fron E, Jordens S, Schweitzer G, et al. J Phys Chem B 2004:108:10721.
- [19] Varnavski O, Samuel IDW, Palsson LO, Beavington R, Burn PL, Goodson III T. J Chem Phys 2002;116:8893.
- [20] Yan Y, Li B, Liu K, Dong Z, Wang X, Qian S. J Phys Chem A 2007;111:4188.
- [21] Li B, Tong R, Zhu R, Meng F, Tian H, Qian S. J Phys Chem B 2005;109:10705.
- [22] Lakowicz JR. Principles of fluorescence spectroscopy. New York: Kluwer Academic, Plenum Publishers; 1999.
- [23] Chakrabarty D, Harza P, Chakraborty A, Seth D, Sarkar N. Chem Phys Lett 2003;381:697.
- [24] Burdzinski G, Buntinx G, Poizat O, Toele P, Zhang H, Glasbeek M. Chem Phys Lett 2004;392:470.
- [25] Stylianakis MM, Mikroyannidis J, Dong Q, Pei J, Liu Z, Tian W. Sol Energ Mater Sol Cel 2009;93:952.
- [26] Fakis M, Anestopoulos D, Giannetas V, Persephonis P, Mikroyannidis J. J Phys Chem B 2006;110:12926.
- [27] Fakis M, Anestopoulos D, Giannetas V, Persephonis P. J Phys Chem B 2006;110:24897.
- [28] Li B, Tong R, Zhu R, Hua J, Tian H, Qian S. J Lumin 2006;119-120:116.
- [29] Varnavski O, Leanov A, Liu L, Takacs J, Goodson III T. Phys Rev B 2000;61:12732.
- [30] de Belder G, Jordens S, Lor M, Schweitzer G, De R, Weil T, et al. J Photochem Photobiol A Chem 2001;145:61.
- [31] Davis BL, Melinger JS, McMorrow D, Peng Z, Pan Y. J Lumin 2004;106:301.
- [32] Singh PK, NAth S, Kumbhakar M, Bhasikuttan AC, Pal H. J Phys Chem A
- 2008;112:5598.
- [33] Nad S, Kumbhakar M, Pal H. J Phys Chem A 2003;107:4808.
- [34] Varnavski O, Yan X, Mongin O, Blanchard-Desce M, Goodson III T. J Phys Chem C 2007;111:149.
- [35] Varnavski OP, Ostrovski JC, Sukhomlinova L, Twieg RJ, Bazan GC, Goodson III T. J Am Chem Soc 2002;77:1120.