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Photoinduced intramolecular charge-transfer dynamics of a red-emitting dicyanovinyl-based triarylamine dye in solution

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ABSTRACT

The photophysics of a red-emitting push–pull triarylamine compound (fvin) comprising a triphenylamino electron donor core and a dicyanovinylene electron acceptor group is investigated by steady-state absorption and emission and femtosecond time-resolved absorption spectroscopy in room-temperature *n*-hexane, toluene, ethanol, and acetonitrile solvents. Fvin is strongly fluorescent in apolar solvents upon excitation of the $S_0 \rightarrow S_1$ intramolecular charge transfer (ICT) transition, but hardly emissive in polar solvents. Time-resolved spectra reveal a strong dependence of the excited-state dynamics on both the solvent polarity and viscosity. Unlike *n*-hexane solutions where the fluorescent ICT excited state remains weakly solvated and keeps a structure close to that of the Franck–Condon level, significant stabilization of the ICT state operates in toluene, leading to a relaxed fluorescent ICT′ form with stronger charge transfer character. This was featured by a notable dynamic Stokes shift of the stimulated emission (SE) band occurring in 15 ps. However the similarly high fluorescence quantum yield and lifetime in *n*-hexane and toluene excludes any large structural distortion on going from ICT to ICT′. In acetonitrile and ethanol, the SE shift dynamics is enhanced and clearly biphasic. The first step can be ascribed to an ICT → ICT′ conformational relaxation as in toluene. The second step, accompanied by a drastic drop of the SE intensity and a strong evolution of the excited-state absorption spectrum (time-constant 1.5 ps in acetonitrile, 9 ps in ethanol), corresponds to the appearance of a new ICT″ state with enhanced charge localization and separation, most probably associated with a rotation of the phenyldicyanovinylene group. This large-amplitude distortion is followed by fast internal conversion to the ground state (9 ps in acetonitrile, 21 ps in ethanol), accounting for the almost nonemissive character of fvin in polar solvents.

1. Introduction

Red-light emitting organic materials are highly sought for applications in biphotonic bioimaging where biological tissue autofluorescence is to be avoided [1,2], as well as in organic electronics as electroluminescent layers in monochromatic or white light organic emitting diodes. Most of the systems involve long π-conjugated backbones prone to deleterious π–π stacking, which causes concentration quenching at high material density. Thus, doped matrices have often been used, thereby conducting to reduced performances due to limited amounts of photoactive units. To overcome this hurdle, a new class of small molecule-based materials has been elaborated and involves bulky substituents preventing the molecules from aggregating with each other to produce amorphous thin films with no scattering defect [3,4]. However, need to minimize reabsorption of the emitted light when working with neat films was crucial. Compounds exhibiting large Stokes shift have therefore appeared as ideal candidates, which requires strong geometry discrepancy between their ground and radiative excited states. To this aim, push–pull compounds exhibiting large charge-transfer over a short π-conjugated pathway were devised and yielded high fluorescence despite competitive relaxation of the distorted excited state through radiationless internal conversion [5]. Prediction of the photophysical behavior is complexified by the high sensitivity with regard to the environment polarity usually encountered with charge-transfer systems. In this context, we have investigated by femtosecond and nanosecond transient absorption spectroscopies the photophysical properties of a new triarylamine compound, 4-di(4′-tert-butylbiphenyl-4-yl)amino-4′-dicyanovinylbenzene (*fvin*, see Scheme 1), that has been successfully employed to fabricate nondoped red-light emitting diodes [6], optically pumped red-emitting lasers [7], as well as emissive nanoparticles to generate hybrid magnetofluorescent nanowires [8] and image murine cells under two-photon excitation

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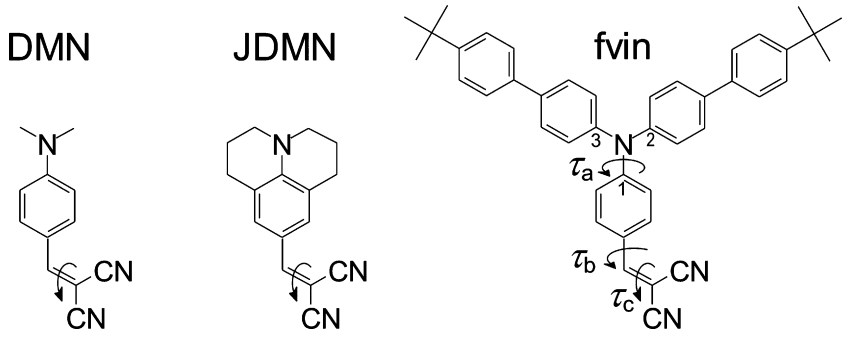

Scheme 1. Structure of the fvin compound and its N,N-dialkylamino analogs DMN and JDMN, working as molecular rotors along the indicated rotation coordinates.

[9]. The existence of strong fluorescence in hydrocarbon solvents at room temperature (Φ_F = 0.27 in hexane and Φ_F = 0.22 in toluene) contrasts with the absence of emission for dialkylaminobenzylidene malononitriles DMN and JDMN (Scheme 1) that have been widely used as "molecular rotors" to probe solvent and biological tissue viscosities [10,11]. Recent photophysical and theoretical studies of these systems have demonstrated that isomerization around the vinylene double bond represents the main barrierless excited state deactivation pathway in solution operating in less than 5 ps [12–14].

The aim of this study is to determine the excited state dynamics of the free fvin molecule in solution and clarify how the solvent polarity dramatically influences the evolution of the radiative k_F and non-radiative k_{nr} rate constants. Ultrafast spectroscopy measurements reveal the formation of a long-lived intramolecular charge transfer excited state (ICT) in apolar and weakly polar solvents. In contrast, in polar solvents, they show efficient quenching of the excited state within a few picoseconds, following a large-amplitude distortion of the ICT excited-state structure, which is tentatively ascribed to a 90° twist between the di(biphenyl)amino and phenyldicyanovinylene moieties (torsion τ_a). It is concluded that such a strong distortion and stabilization of the S_1 structure in polar solvents permits high vibrational coupling between the ground and excited electronic potential surfaces, favoring efficient internal conversion and extinguishing the fluorescence emission. Given the simple structure of fvin and its strongly solvent dependent excited state dynamics, fvin could be ranked in the future as a novel red-emitter ICT archetype whose geometry and relaxation pathways can be switched by the solvent polarity and viscosity.

2. Experimental

The synthesis procedure and structural characterizations of the 4-di(4′-tert-butylbiphenyl-4-yl)amino-4′-dicyanovinylbenzene compound (fvin) have been detailed elsewhere [15]. Acetonitrile, ethanol, *n*-hexane, and toluene solvents were of spectrophotometric grade and purchased from Aldrich.

X-ray diffraction data were collected using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). A crystal of 0.3 mm × 0.1 mm × 0.1 mm was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at 100 K by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. A full sphere of data was collected by φ and ω axis rotation with an increment of 1° and 30 s exposure per degree. Denzingering was accomplished by measuring each frame twice. The data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97 [16] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97 [17] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as riding model with isotropic thermal parameters. All calculations were performed using the Crystal Structure crystallographic software package WINGX [18]. X-ray data is presented in Table S1 (see Supporting Information). The asymmetric unit consists of one molecule of the compound with one acetone solvent molecule. The final conventional R is 0.0520 for 9574 $F_0 > 4\sigma(F_0)$, 450 parameters and 0 restraints, and 0.1000 for all 15,011 data, wR (F^2) = 0.15 for all reflections, $w = 1/[\sigma^2(F_0)^2 + (0.0678P)^2 + 1.1649P]$ where $P = (F_0^2 + 2F_c^2)/3$. The largest difference peak and hole are 0.583 and −0.461 e Å^{-3}. The molecular structure is depicted in Fig. S1. CCDC 841526 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

UV–visible absorption spectra were recorded on a Varian Cary 5E spectrophotometer. Emission spectra were collected on a Spex Fluorolog 1681 spectrofluorimeter and corrected to the emission of a NIST tungsten lamp. Fluorescence quantum yields were determined from a solution of Coumarine 540 A in ethanol (Φ_F = 0.38 [19]) or diphenylanthracene in cyclohexane (Φ_F = 0.90 [20]) absorbing equally at the excitation wavelength.

Fluorescence intensity decays were measured by the time-correlated single-photon counting method (TCSPC) with a picosecond laser excitation at 330 nm provided by a Spectra-Physics setup composed of a titanium–sapphire Tsunami Laser pumped by an argon ion laser, and doubling LBO crystals and tripling BBO crystals. Light pulses were selected by an opto-acoustic crystal at a repetition rate of 4 MHz. Fluorescence photons were detected at 630 nm through a monochromator by a Hamamatsu MCP photomultiplier R3809U connected to a constant-fraction discriminator. Pulse deconvolution was performed from the time profile of the exciting pulse recorded under the same conditions by using a Ludox solution.

Nano-microsecond transient absorption experiments were performed using a conventional laser flash photolysis setup. Excitation pulses at 460 nm (5 ns, 1 mJ) were provided by an OPO (Panther, Continuum) pumped by a 10-Hz Nd:YAG laser (Surelite II, Continuum). The probe light was provided by a Xe flash lamp (XBO 150W/CR OFR, OSRAM). Samples (OD value of ≈1.0 at 460 nm) were placed in a quartz cell (10 mm × 10 mm section) and deaerated by bubbling N_2 except those used for measuring the effect of quenching by O_2. The transmitted light was analyzed with a photomultiplier (R1477-06; Hamamatsu) coupled to a digitalized oscilloscope (TDS 540; Tektronix). Kinetics at each wavelength was accumulated over 9 laser shots.

The femtosecond transient absorption setup has been already described elsewhere [21]. Briefly, it involves a 1 kHz Ti-sapphire laser system based upon a Coherent (MIRA 900D) oscillator and a BM Industries (ALPHA 1000) regenerative amplifier. Pump