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Excited State Localization and Delocalization of Internal Charge Transfer in Branched Push−Pull Chromophores Studied by Single-Molecule Spectroscopy

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The exciton model is based on the assumption that the interaction between subchromophores is purely electrostatic and can be approximated by dipole−dipole coupling, while all interchromophore charge-transfer (CT) processes are neglected.[1] There is no simple way to directly test the validity of this approximation in dendrimers containing branched intramolecular charge transfer (ICT) interactions because of the intrinsic complexity of the ICT chromophores, which are strongly affected by geometrical confinement and charge symmetry.

Extensive theoretical and experimental investigations of the structure−property relationship of the branching ICT effects in various dendrimers, such as studies using femtosecond anisotropy spectroscopy and two-photon absorption measurements,[2,3] have led to several conflicting findings, such as coherent effects, additive behavior, and even reduction of coupling/optical response. Ensemble studies have shown that delocalized excitations dominate the absorption in all branched ICT dendrimers, whereas emission always comes from the excitation localized on a single branch rather than from a delocalized state.[2] In order to reveal the phenomena possibly hidden in the ensemble measurements, single-molecule (SM) studies are necessary to determine the nature of (de)localization in branched ICT compounds. Very few SM studies investigating the inter-ICT coherence or the effects of disorder within branched push−pull dendrimer molecules have been reported.[4]

We report here a SM analysis of the excited-state localization and delocalization in branched ICT chromophores within the two model ICT compounds shown in Figure 1. Both **S-2** and **TOZ-2** bear a common electron-donating moiety (D) in the central part, connected in each branch to an electron-withdrawing group (A) through a conjugated linker. In contrast to **TOZ-2**, the branches in **S-2** are additionally terminated by electron-donating groups. The study of these two different molecules using SM spectroscopy could help us to determine the nature of interbranch ICT coupling for the electronic delocalization and CT phenomena.

Both **S-2** and **TOZ-2** show two distinct strong absorption bands, as shown in Figure 1. The absorption peaks in the long-wavelength regions at 495 and 415 nm result from the ICT transitions in **S-2** and **TOZ-2**, respectively. The ICT properties of the visible absorption bands are also evident from quantum-chemical calculations (see the Supporting Information). The observed broad structureless fluorescence bands at ~635 nm for **S-2** and ~485 nm for **TOZ-2** are typical of relaxed ICT states. The lifetimes and quantum yields of **S-2** and **TOZ-2** are listed in Table S1 in Supporting Information.

Thin films of polystyrene (PS) film doped with **S-2** and **TOZ-2** for SM measurements were prepared by spin-coating of 10^{-10} M solutions in $CHCl_3$ containing 10 mg/mL PS onto cleaned coverslips. Fluorescence intensities and lifetimes of single **S-2** and **TOZ-2** molecules were measured simultaneously as a function of time. We focus our analysis on the two-step photobleaching molecules (79% of **S-2** and 66% of **TOZ-2** molecules, whereas the others show one-step photobleaching behavior), since they can provide important insight into the interbranch coupling.[5a]

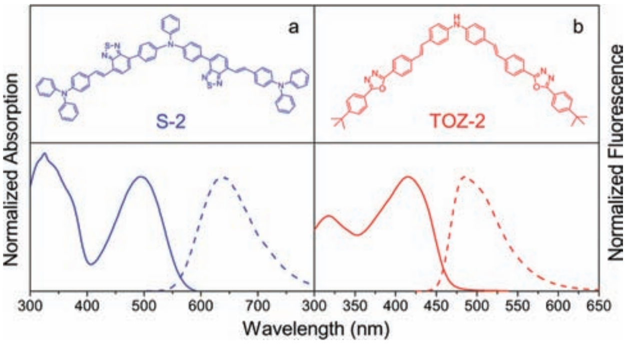

Figure 1. Molecular structures and normalized absorption (solid lines) and fluorescence (dashed lines) spectra in $CHCl_3$ of (a) **S-2** and (b) **TOZ-2**.

Representative **S-2** and **TOZ-2** SM fluorescence intensity time traces are shown in Figure 2a, with the corresponding fluorescence lifetimes indicated at each intensity level. The two-step fluorescence time traces indicate that there are two successive excited-state processes in both **S-2** and **TOZ-2**, as is generally observed in most dimeric aggregates.[5] We analyzed the SM properties of 112 **S-2** and 85 **TOZ-2** molecules with two-step behaviors. The histograms of the step-intensity ratios I_S (the ratio of the lower and the higher step intensities) for **S-2** and **TOZ-2** show different aspects, as displayed in Figure 2b. The distribution of I_S values for **S-2** is centered at 0.5 (81% of the molecules fell in the 0.3−0.7 range), indicating no or weak coupling between the two push−pull branches, whereas for **TOZ-2** molecules, there are two distinct intensity ratio distributions, one around 0.2 (48% in the 0−0.3 range) and the other around 0.5 (52% in the 0.3−0.8 range). The presence of two distinct intensity ratio distributions indicates that there are two different extents of ICT coupling within **TOZ-2**; the I_S value of 0.2 may imply strong coupling between the branches, resulting in superradiance, whereas that around 0.5 points to no (or weak) coupling, similar to the results for **S-2**. Although we could not rule out spectral diffusion and orientation effects (the case when two branches are not arranged in-plane) for the observed two-step intensity traces, the extent of the excited-state ICT delocalization

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over the coupled branches can be further supported by the SM lifetime measurements.[5a]

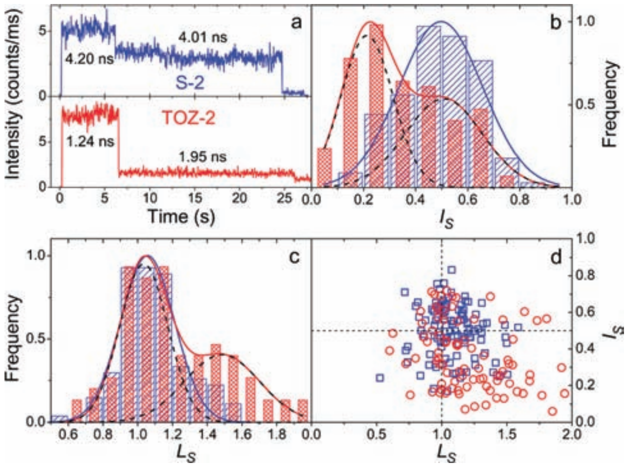

Figure 2. (a) Representative SM fluorescence-intensity time traces, (b) intensity-ratio and (c) lifetime-ratio histograms for the molecules, showing two-step photobleaching, and (d) the corresponding L_S/I_S correlation plots for **S-2** (blue) and **TOZ-2** (red).

The fluorescence lifetimes were recovered by exponential fitting of the decays at each intensity level. The ratio L_S of the lifetimes of the lower- and higher-intensity steps directly yields the superradiance coherence size of ICT over the entire duration of the excited-state relaxation. The L_S histograms for **S-2** and **TOZ-2** are shown in Figure 2c. As illustrated by the distribution of **S-2** L_S values centered at 1.06 (73% of the molecules were in the 0.8−1.2 range), no significant change in the fluorescence lifetime occurred with sequential photobleaching, indicating no (or weak) coupling within **S-2**. Two distinct L_S distributions were evident for **TOZ-2**, one centered at 1.03 (53% in the 0.8−1.2 range) and the other at 1.49 (36% in the 1.2−1.8 range), similar to its intensity ratio histogram. $L_S \approx 1$ indicates no (or weak) coupling of the two ICT branches, as observed for **S-2** and partly for **TOZ-2**. The distribution of L_S values around 1.5 in **TOZ-2**, however, provides clear evidence of fluorescence stemming from the excited ICT state being delocalized over two branches rather than localized on a single branch, as is typically observed in ensemble measurements.[2] Furthermore, the correlation plot of the fluorescence intensity and lifetime ratios (I_S vs L_S) (Figure 2d) shows a clear correspondence between these two quantities. While the **S-2** molecules are mainly located around the $I_S = 0.5$, $L_S = 1$ region (weak coupling), a significant fraction of the **TOZ-2** molecules is characterized by $L_S > 1.2$ and $I_S < 0.3$ (strong coupling). This illustrates the usefulness of SM measurements in the determination of the nature of interbranch ICT coupling in branched chromophores, which is usually hidden in ensemble measurements.

Furthermore, the decreased lifetimes observed in the more highly emissive levels in **TOZ-2** reflect the fluorescence from the delocalized ICT excited state, where the coherence size of $L_S \approx 1.5$ (compared with the ideal situation of $L_S = 2$ for a dimer) indicates that the fluorescence stems from excitation that is not fully delocalized over the two branches in **TOZ-2** molecules, which results from the typical effect of torsional disorder in push−pull molecules.

The structural difference in **S-2** and **TOZ-2** is reflected through the different ICT coupling of the excited states. The geometrical conformations (i.e., planar cores) of **S-2** and **TOZ-2** share a central nitrogen atom, favoring increased conjugation. The coupling in both **S-2** and **TOZ-2** is mediated by intervening orbitals from the central electron-donating part. The charge redistribution upon photoexcitation from the core to the periphery in **TOZ-2** leads to a symmetrical and distant twofold-degenerate ICT state. Unlike rigid dimers, where the transitions from two independent dipole chromophores are equal in energy and occur with equal probability,[5] the symmetry of the flexible ICT-like chromophores is easily broken after excitation because of the intrinsic torsional disorder in push−pull molecules. The molecules with two independent symmetry-kept ICT-like states upon excitation show strong coupling, whereas the symmetry-broken molecules show no (or weak) coupling. As a result, two distinct peaks in the lifetime ratio distribution are observed for **TOZ-2**. In contrast, the symmetry of the branched ICT branches in **S-2** from the periphery to the middle of the branches is easily broken by the central electron-donating triphenylamine moiety.[2a] In other words, the exciton-like delocalization between the two ICT quadrupoles is very weak. Such a case with no (or weak) coupling becomes more pronounced in dimeric molecules with a D−A−D structure (such as **S-1** and **DAD**; see the Supporting Information), where the charge redistribution upon photoexcitation from the periphery to the core in each branch leads to a large mixture of ICTs at the central core (acting as one new ICT chromophore) and then results in no (or weak) coupling.

In conclusion, we have shown that SM spectroscopy can be a powerful technique for studying exciton-like ICT coupling dynamics in dendritic systems. The strong coupling and stepwise photobleaching of the ICT branches in the dendrimers, which depends on torsional disorder, have been demonstrated at the SM level. The fluorescence from the delocalized ICT state over two branches in push−pull molecules, which cannot be distinguished by means of conventional experiments probing the average behavior of large ensembles of molecules,[2] has been observed at SM level.

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Supporting Information Available: Materials, general and computational methods, and additional information. This material is available free of charge via the Internet at http://pubs.acs.org.

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