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High Triplet Yield from Singlet Fission in a Thin Film of 1,3-Diphenylisobenzofuran

Justin C. Johnson,[†] Arthur J. Nozik,[†,‡] and Josef Michl*[,‡,§]

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, United States, Department of Chemistry and Biochemistry, University of Colorado, 215 UCB, Boulder, Colorado 80309-0215, United States, and Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

Received May 21, 2010; E-mail: michl@eefus.colorado.edu

Abstract: Direct observation of triplet absorption and ground-state depletion upon pulsed excitation of a polycrystalline thin solid film of 1,3-diphenylisobenzofuran at 77 K revealed a 200 ± 30% triplet yield, which was attributed to singlet fission.

In singlet fission,[1,2] [$S_1S_0 \rightarrow {}^1(T_1T_1)$], a singlet excited chromophore shares its energy with a nearby ground-state chromophore to yield a triplet excited state of each. If the two triplets behave independently, up to two charge separation events per photon could occur in a solar cell, resulting in a large efficiency enhancement.[3] A high triplet yield, Φ_T, has been inferred in solid tetracene,[4] but all direct measurements have yielded low Φ_T values (e.g., 0.4% for polydiacetylene[5] and 25−30%[6] and 5−10%[7,8] for carotenes in light-harvesting complexes).

Since only Φ_T values close to 200% followed by efficient charge separation would be of practical significance, we are searching for routes to optimal chromophores and interchromophore coupling modes. We have identified biradicaloids and large alternant hydrocarbons as two likely classes of parent π-electron systems by consideration of S_1, T_1, and T_2 excitation energies.[9] Work is underway on design criteria for coupling,[2] both direct via the matrix element[10] $<S_1S_0|\hat{H}|{}^1(T_1T_1)>$ and mediated, involving charge-transfer states.[11] We find that slip-stacked dimers are favorable when S_1 is of the HOMO → LUMO type.

1,3-Diphenylisobenzofuran (**1**, Figure 1A) is a thoroughly characterized[12] biradicaloid chromophore. Solid **1** meets both the state energy and coupling criteria, with excitation energies $E(S_1) \approx 22\,000$ cm^{-1}, $E(T_1) \approx 11\,400$ cm^{-1} (solid), and $E(T_2) \approx 24\,000$ cm^{-1} (solution) and slip-stacked dimers in the crystal structure[12] (Figure 1B). We report that transient absorption in a thin layer of polycrystalline **1** has revealed a Φ_T value close to 200%.

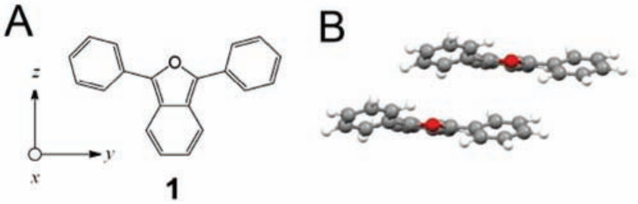

Figure 1. (A) Molecular axes in **1**. (B) Two molecules of **1** within the published[2] crystal lattice, selected to exhibit the presence of slip stacking.

Thin (∼100 nm) layers of **1** were sublimed onto sapphire substrates. The only strong line in the X-ray diffraction pattern was the (002) reflection ($d = 9.681$ Å, cf. 9.605 Å predicted from the crystal structure[12]). Pole figure analysis suggested that the film consists of crystallites oriented with the *c* axis approximately along the surface normal and the *a* and *b* axes distributed randomly around it. Thus, the *z* axes of both molecules in the unit cell are perpendicular to the surface, and the *x* and *y* axes are parallel to it (Figure 1A). Measurement of polarized absorption at normal and tilted incidence confirmed these results. The film is close to uniaxial, with the surface normal as the unique axis.

Interchromophore interactions (exciton coupling) in the solid are weak, as the fluorescence and the absorption below 35 000 cm^{-1} (*y*-polarized[12]) were nearly identical to those in solution except for a small red shift (Figure S1 in the Supporting Information). The absorption above 35 000 cm^{-1} (largely *z*-polarized[12]) was suppressed, as expected for an oriented sample. The fluorescence quantum yield was $\Phi_F = 0.10-0.15$ (cf. 0.95−0.99 in solutions). The decay was multiexponential and nearly temperature-independent. Most emission decayed with a time constant (amplitude) of 0.8 ns (85%), and some with <0.1 ns (<5%), ∼3 ns (10%), and 10−20 ns (<2%); cf. single exponential lifetimes of 5.5−7.5 ns in solutions.[12]

At times shorter than 1 ps, the 150-fs pulse excited transient absorption of the film observed between 10 000 and 23 000 cm^{-1} (Figures 2 and 3) showed a ground-state bleach above 22 000 cm^{-1} and overlapping *y*-polarized T_1-T_6 and T_1-T_8 peaks near 21 000 cm^{-1} (the *z*-polarized T_1-T_7 peak that contributes to the T−T absorption band in solution was missing, causing an appearance of a spectral hole; see Figure S2). It also showed weak stimulated emission near 19 600 cm^{-1} and weak, broad S_1-S_n and T_1-T_n absorptions at 13 000−18 000 cm^{-1} (all assignments were taken

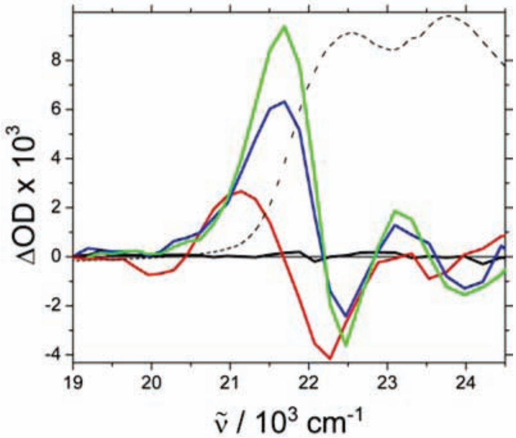

Figure 2. Photoinduced absorption/bleaching spectra of a film of **1** collected at 77 K with time delays of 0 (black), 1 (red), 20 (blue), and 200 ps (green). The steady-state absorption spectrum (dashed curve) is also shown.

[†] National Renewable Energy Laboratory.
[‡] University of Colorado.
[§] Academy of Sciences of the Czech Republic.

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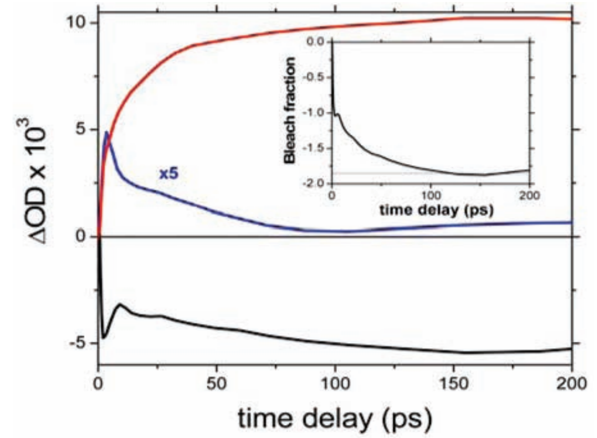

Figure 3. Photoinduced absorption/bleaching kinetics of a film of **1** at 77 K, with the probe centered at 22 500 (black), 21 500 (red), and 16 500 cm^{-1} (blue). Inset: Bleach fraction (extrapolated to 1.0 at 200 fs) after correction for overlapping triplet absorption. Dashed line is shown at the value −1.85.

from solution work and calculations[12]). During the first 5 ps, the triplet absorption sharpened and the peak was blue-shifted to ∼21 800 cm^{-1}, presumably due to vibrational cooling.

The stimulated emission decayed within 25 ps. The S_1-S_4 absorption decayed almost completely with time constants of ∼2 and 25 ps before exhibiting a slight rise on a 100 ps time scale and remaining nearly constant thereafter until 1 ns. The ground-state bleach appeared to decrease in the first 2 ps (because of overlap with triplet absorption) and then grew with a time constant of 25 ps to ∼185% of its initial value (at 77 K, after correction for overlapping triplet absorption). The ratio of the bleach seen at $t < 0.2$ ps (a measure of the number of S_0 molecules lost to excitation by the initial photon pulse) to the additional bleach seen at $t > 100$ ps (a measure of the number of S_0 molecules lost to excitation by energy transfer from S_1 to S_0 to yield $2T_1$) yielded a total value Φ_T of 185%. The T_1-T_n absorption grew with rate constants of ∼2 and 25 ps and decayed less than 10% in 1 ns. We conclude that T_1 is formed from S_1 with rate constants $k = 5 \times 10^{11}$ (45%) and $k' = 4 \times 10^{10}$ (55%) s^{-1} at 77 K, which increase by a factor of only ∼3 between 12 K and room temperature. Only <5% of the fluorescence was prompt and the rest was delayed, originating in the isoergic $T_1 + T_1 \rightarrow S_1 + S_0$ process, which competes with all other triplet decay modes. The relative longevity of the triplet is presumably aided by the endoergicity of the $T_1 + T_1 \rightarrow T_2 + S_0$ process.

An independent estimate of Φ_T from a comparison of the ground-state bleach at 22 500 cm^{-1} and the transient triplet absorbance at 21 500 cm^{-1} at normal incidence is possible if we assume that the absorption coefficients for S_0 and T_1 absorption are in the same ratio as in solution (23×10^3 and 32×10^3 M^{-1} cm^{-1}, respectively).[12] The result for the period 0.2−1 ns after excitation would be ∼140% at 77 K if the film were isotropic. After correction for anisotropy (see the Supporting Information), the triplet yield at 77 K becomes 200 ± 30%. It decreased to ∼175% at 12 K and ∼125% upon going to 300 K. Since the triplet formation rate constant changes little with temperature, the changes in Φ_T primarily reflect the temperature dependence of other processes.

The fast transformation of the S_1 state into the T_1 state is clearly due to singlet fission: (i) For **1** in solution[12] and for its linearly linked covalent dimers in nonpolar solvents,[13] Φ_T is less than 1% and the fluorescence rate constant is $(1.5-2.5) \times 10^8$ s^{-1}, hence the rate constant for $S_1 \rightarrow T_1$ intersystem crossing induced by spin−orbit coupling is less than $\sim 2 \times 10^6$ s^{-1}. It is highly unlikely that this process could be accelerated by 4−5 orders of magnitude in a polycrystalline film. (ii) The sum of Φ_F and Φ_T exceeds 100%. (iii) After the initial excitation pulse, the S_0 state is consumed to the expected extent within the experimental error and at the rate at which S_1 decays and T_1 is formed.

The rate constants k and k' observed for triplet formation most likely reflect the occurrence of singlet fission before and after thermal equilibration with the lattice. They can be compared with the thermally activated rate constant in a room-temperature tetracene crystal, which is usually quoted as $\sim 10^{10}$ s^{-1}.[2]

At 77 K, fluorescence and triplet formation account for all the absorbed photons within experimental error. At other temperatures, the fate of a fraction of the photons is unclear, as we did not observe any unassigned peaks in the transient spectra. The known[12] intense spectra of the radical cation and anion of **1** were not observed, eliminating significant charge separation (<5%). The formation of weakly emissive excimers cannot be excluded, but it seems improbable that they would be transparent throughout the visible region. The likely fate of the excitations for which no account can be given is that they also undergo singlet fission but emerge from the initial manifold of nine mixed-spin sublevels as a hot $S_0 + T_n$ or $S_0 + S_0$ combination. Since T_2 is too high in energy[12] and T_1 and especially S_0 are too low, these processes are disfavored by the energy gap law, which could explain why their role is only minor.

In conclusion, the structural design guidance provided by theory[2,9,11,14] appears to be helpful in that it has led to an examination of a previously unexplored solid with a remarkably high Φ_T from singlet fission, 200 ± 30% at 77 K, and a triplet that is stable for at least 1 ns.

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Supporting Information Available: Sample preparation, X-ray diffraction, steady-state and time-resolved spectroscopy, quantum yield determination, and complete ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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