Communication

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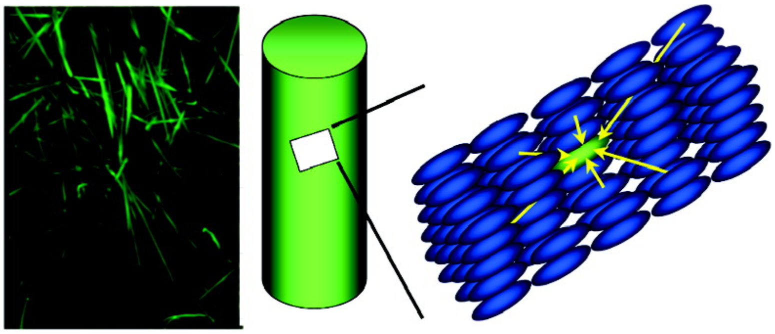

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Energy Transfer in Self-Assembled [*n*]-Acene Fibers Involving ≥100 Donors Per Acceptor

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Energy transfer processes in nanoscale devices and nanostructured materials[1] are of prime importance for applications in photovoltaics, OLEDs, photonics, and biomimetic light-harvesting. In these fields, supramolecular organization of organic compounds has grown in interest. In particular, highly organized nanometric fibers have been obtained by self-assembly[2] and can be envisaged as alternatives to crystals, nanocrystals, and polymers. Networks of these fibers can also lead to solvent-trapping and thus to formation of organogels.[3] This work relates to the use of [*n*]-acenes, including anthracenes, tetracenes, and pentacenes, whose crystals are known to display record charge mobilities[4] and attractive optical properties. Indeed, 2,3-*n*-dialkyloxyacenes[5,6] have been shown to self-assemble into organogel fibers at millimolar concentration at room temperature by non-H-bonding interactions. Previous studies on the didecyl derivative of anthracene (DDOA) have shown that this leads to a high molecular order in the gel fibers, as confirmed by the present study, and is proposed to be similar to that in the crystals of the dihexyl analogue, DHOA.[5]

To investigate the optical properties and the efficiency of light-induced energy transfer in [*n*]-acene gel fibers, we have doped DDOA donor gels with 2,3-*n*-dialkoxytetracene (D*n*OT) acceptors. This mimics tetracene-doped anthracene crystals, where energy transfer occurs very efficiently due to favorable cocrystallization, good spectral overlap, and exciton migration.[7] Even though energy transfer has been observed in organogels,[8] many crucial factors leading to a very high efficiency have not been described yet. Our system offers an original insight as it differs from linearly stacked systems,[2,3] such as those formed with oligo(*p*-phenylenevinylenes) (OPV),[9] by its high chromophore density combined to an unusual molecular arrangement. Indeed, previous spectroscopic studies of aligned DDOA gel fibers, combined to X-ray diffraction on crystals of DHOA and molecular modeling, suggest that DDOA assembles into triads that are packed head-to-tail in layers that wrap around a central axis and form fibers.[5]

The doping of DDOA gels with D*n*OT energy traps reveals compelling evidence for efficient energy transfer from the excited anthracenes to the tetracene derivatives. Indeed, in gels including 1 mol % of DDOT, an almost total quenching of the emission of DDOA occurs, and an emission of DDOT appears with a noteworthy 100 nm Stokes shift. The emission spectra are shown in Figure 1a for 2.0 mM DMSO gels at 293 K with increasing proportions of DDOT. It is remarkable that 0.05% doping with DDOT is sufficient to achieve 35% of the maximum transfer. Besides, the total gel concentration barely influences the process. Indeed, maximum quenching is completed with 1% doping in DDOA gels from 0.020 mM (in methylcyclohexane, MCH, at 170 K; see Figure 2a) up to 4 mM. The tetracene emission intensity remains constant at doping higher than 1%, whereas additions higher than 3% were not investigated in order to avoid tetracene−tetracene interactions or large structure modifications. In solution, due to the low acceptor concentrations used, no diffusion-limited energy transfer occurs and only DDOA emits (Figure 2a).

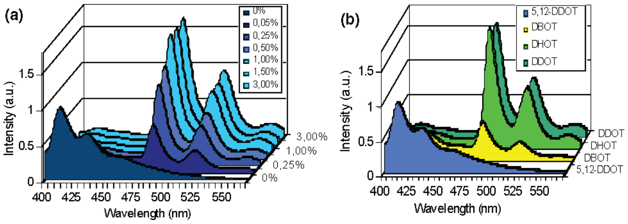

Figure 1. Emission spectra of doped DDOA (2.0×10^{-3} M) gels in DMSO at 293 K, $\lambda_{exc} = 384$ nm; (a) with increasing proportions of DDOT (mol %); (***b***) with 1 mol % of 5,12-DDOT, DBOT, DHOT, and DDOT, respectively.

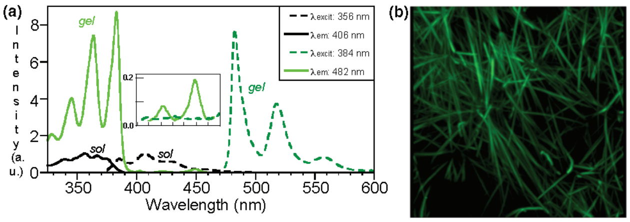

Figure 2. (a) Excitation (—) and emission (- - -) spectra of DDOA, 2.0×10^{-5} M, doped with 1 mol % of DHOT in MCH: (green) gel at 170 K; (inset) enlargement of spectra between 400 and 470 nm; (black) sol at 293 K. (b) Fluorescence confocal microscopy image (50×50 μm) of DDOA gel in DMSO at 298 K with 2 mol % of DDOT; $\lambda_{exc} = 405$ nm, $500 < \lambda_{em} < 600$ nm.

Like in a cocrystallization, we can expect that tetracene incorporation occurs by "replacing" a DDOA in the native structure and should be favored by structural and chemical similarity between the tetracene and DDOA. To verify this and its influence on the energy transfer process, the doping of DDOA gels in DMSO with four different tetracene derivatives has been investigated. The three 2,3-disubstituted tetracenes (DDOT, DHOT, and DBOT) differ by their chain length (*d*ecyl, *h*exyl, and *b*utyl), whereas 5,12-DDOT is substituted in positions 5,12. Of these, only DDOT is a gelator in the same conditions as DDOA. The addition of DDOT or DHOT affords almost identical emission spectra (Figure 1b). In contrast, DBOT is a less efficient acceptor, and 5,12-DDOT does not influence DDOA emission at all. In addition, fluorescence confocal microscopy imaging of a DDOA/DDOT mixed gel (Figure 2b) shows that DDOT emission results quite homogeneously and only from the fibers. These data confirm that incorporation and dispersion of the acceptor in the donor fiber only occur with an appropriate

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2,3-substitution and chain length, and that these aspects are fundamental to achieve efficient energy transfer.[10] Moreover, tetracene incorporation in the place of a DDOA results in a parallel orientation of the dipolar moments of donor and acceptor chromophores, which is optimal for resonant energy transfer.

The gels with low concentrations of DDOA (0.02 mM) have been prepared in order to perform quantitative measurements that require low optical densities. When doped with 1% DHOT, the excitation spectrum of the gel (Figure 2a) displays almost exclusively the absorption features of DDOA. By direct excitation of tetracene, an emission 54 times weaker is observed. This clearly demonstrates that DHOT emission originates after light absorption by DDOA and subsequent energy transfer to the tetracene. This indirect excitation has been measured to occur within 1 ns. In the gels, the tetracene emits like an isolated chromophore, and its emission is slightly red-shifted as compared to MCH solution emission. Its spectral structure, which is finer than in solution (fwhm of 430 cm^{-1} in gel vs 650 cm^{-1} in solution), is reminiscent of that of nonsubstituted tetracene in doped anthracene crystals[7] and corroborates the high molecular order described earlier[5] for the DDOA gels. As compared to solution ($\tau_{sol} = 5.7$ ns, 298 K, air), emission of tetracene in the gel decays slower ($\tau_{gel} = 21$ ns), independently of concentration, solvent, or temperature. These features suggest that in the gel the tetracene is in a more rigid environment, clearly confirming the tight bond between the tetracene and the DDOA fiber.

Emission quantum yield values (Φ_{em}) are valuable to describe emissive systems and efficiencies of energy transfer processes, but have not yet been determined in organogels due to their high optical densities at room temperature. In a DDOA/DHOT(1%) gel at 0.02 mM (Figure 2a), Φ_{em} has been measured to be 0.32 (±10%) when DDOA is excited and almost totally quenched. This value is high and indicates quite low energy loss in the fibers, an important feature when envisaging applications. The equivalence of spectra and lifetimes of tetracene emission in doped DDOA gels at 170 and 293 K suggests that, even at 293 K, Φ_{em} of *isolated* gel fibers can be expected to be as high as at 170 K. This will favor the detailed study of their photophysical properties by time-resolved confocal fluorescence microscopy and be a valuable comparison to self-assembled OPV stacks.[9]

Φ_{em} is lower than the intrinsic emission quantum yield of DHOT in the gel fibers, estimated to 0.60 (±15%, $\lambda_{excit} = 440$ nm), showing that out of 100 quenched excited DDOA's 54 transfer their energy to the tetracene. The other excited states deactivate by competitive nonradiative processes; 54 effective donors per tetracene is very high ratio and largely surpasses those derived from other organogels,[8] or by comparison, those of light-harvesting dendrimers.[11] Still, we can estimate that the extent of the energy transfer is even larger, as quenching of as much as 700 molecules of anthracenes by a single tetracene, that is, by the first neighbors in a ~5 nm sphere, occurs at lower doping (0.05% DDOT in DDOA). This high number results from direct energy transfer from the closest donors, but also suggests involvement of exciton migration. This latter process appears yet to be less extended than in anthracene crystals, where the diffusion distance reaches 46 nm.[12] Differences can be due to the fact that chromophore packing is different in the gels (due to the alkyl chains) and to the lower dimension of a fiber (diameter 80−100 nm) as compared to a bulk crystal. Nevertheless, in DDOA gels, the particular molecular arrangement seems to offer multiple pathways for exciton migration and energy transfer (see Figure 3). This contrasts with the stacked gelator systems, where a single linear path is expected for energy transfer, and is believed to favorably influence the energy transfer process.

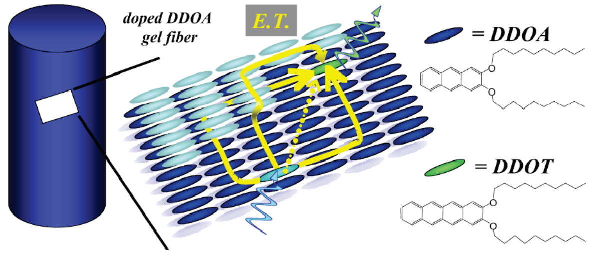

Figure 3. Simplified representation of a doped DDOA gel fiber (enlargement of three layers of sheets of DDOA) is represented, one excited donor (light blue) and one emissive acceptor (green), as well as energy transfer pathways (*E.T.*, yellow arrows) for the direct process (dotted arrow) and several possibilities for exciton migration. Right: Chemical structures of DDOA and DDOT.

Prospectively, preparation of DDOT gel fibers[6a] doped with pentacene derivatives[6b] is envisaged, combining potential charge mobility and optical energy transfer for electrooptical applications. Additionally, long-range organization that has been achieved in bulk organogels and in thin films of DDOA and DDOT by shearing or magnetic field alignment[13] paves the way to preparation of material for waveguiding and directional optical information transfer. Finally, this family of soluble [*n*]-acenes illustrates that self-assembly is a valuable route to access efficient photoactive nanostructured systems.

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Supporting Information Available: Complete refs 1 and 9b. This material is available free of charge via the Internet at http://pubs.acs.org.

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