

Self-assembling and light-harvesting properties of fluorescent linear condensed aromatic gelators*

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Abstract: The self-assembling and photophysical properties of soluble fluorescent linear condensed aromatic gelators are reported. The gels formed by 2,3-alkoxy derivatives are constituted of *nanofibers* weaving a 3-dimensional supramolecular network and imprisoning the solvent. These nanofibers are efficient light-harvesting systems in which complete energy transfer toward a fluorescent acceptor can be achieved at doping levels below 1 mol % of acceptor.

Keywords: organogelators; energy transfer; fluorescence; tetracene; pentacene.

INTRODUCTION

The development of nanostructures with designed optical properties represents a major interest for applications in photonics, OLEDs, optoelectronics, photovoltaics, and biomimetic light-harvesting. *Linear acenes* (i.e., linear condensed aromatic hydrocarbons such as anthracene, tetracene, and pentacene) have been appreciated for years in solid-state photonics for their exceptional optical properties, and in the design of optically active molecular constituents for their efficient fluorescence and photochemistry [1]. Tetracene and pentacene have, furthermore, raised much interest due to their high charge mobility in the solid state [2–4], showing potential as organic semiconductors for the fabrication of organic thin-film transistors, electronic papers, and flexible displays. Until recently, a limited solubility of pure acenes and synthetic challenges has limited their applications and the knowledge of their properties (especially for tetracene and pentacene). Developing soluble acene derivatives is a current challenge. Our strategy is to develop compounds that self-assemble out of solution into nanostructured assemblies with controlled molecular arrangements, in order to obtain fibers with designed optic properties or nanostructured films deposited onto surfaces with semi-conducting properties.

In these lines, we have shown that the substitution of the anthracene nuclei by two long linear alkoxy chains (O-*n*-C₁₀H₂₁) greatly improved the solubility of the compounds [5] and of their corresponding photodimers usually known for their great insolubility in organic media. The large improvement of the solubility of these photochromic materials should find application in information storage devices. Along these studies, we have discovered that the 2,3-di-*n*-decyloxy derivative (DDOA) was

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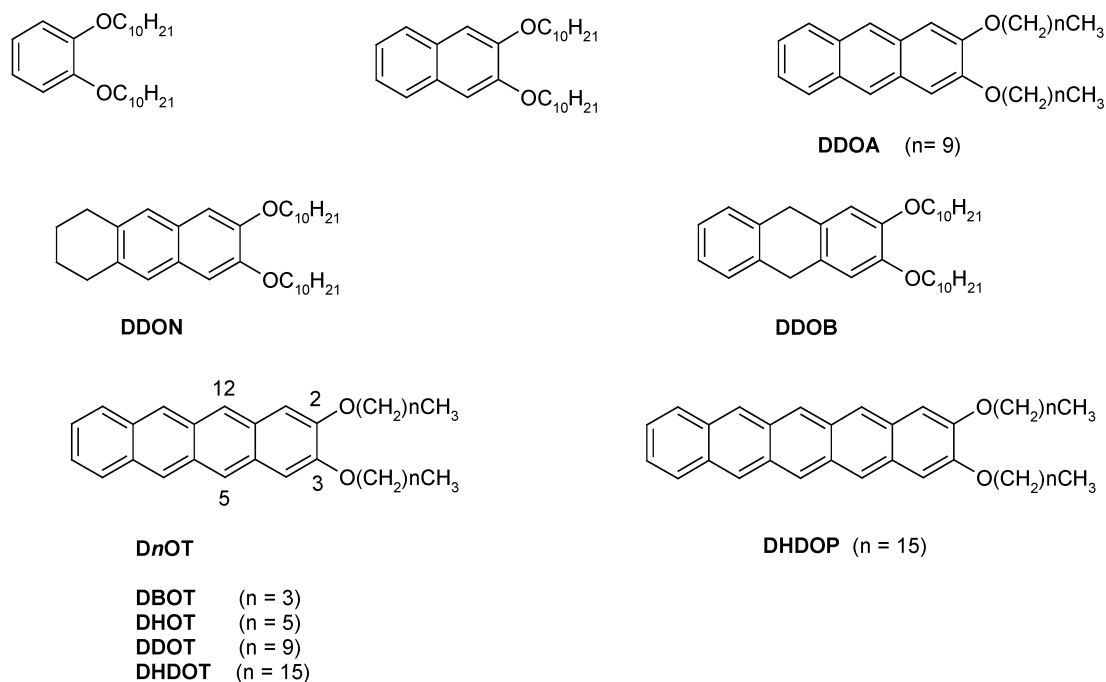
able to gelify a series of solvents at very low concentration [6]. The gelification process rests on a 3-dimensional supramolecular network of nanosized fibers resulting from DDOA stacking [7]. As already reported, the phase transition (sol-gel) is accompanied by large and specific spectral changes (UV, fluorescence, IR) which is due to the specific molecular DDOA organization. Similarly, the 2,3 disubstitution of tetracene or pentacene with two long alkoxy chains produces soluble materials, displaying also organogelating properties.

In this contribution, the gelling behavior and supramolecular organization of some 2,3-di-*n*-alkoxyanthracenes, tetracene and pentacene analogs are reported together with the description of efficient energy transfers occurring within the nanosized fibers woven in the gels.

GELLING PROPERTIES OF LINEAR CONDENSED AROMATIC COMPOUNDS

As previously shown, 2,3-di-*n*-alkoxyanthracenes and analogs [6] are very efficient gelators toward a large variety of organic fluids at room temperature. In fact, these compounds, and especially the substrate bearing two decyloxy chains (DDOA), have been recognized to act as supergelators [8,9]. Thus, linear alcohols, toluene, acetone, diethylether, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), CH_2Cl_2 , CCl_4 , propylene carbonate, aliphatic amines, and other organic fluids (alkanes...) are readily gelified. Similarly, liquid crystals [10], electrolytes [11], and supercritical CO_2 [12] form gels, whereas pure water is resistant.

As demonstrated, the length of the two alkoxy chains and the 2,3 substitution on the aromatic ring are critical for the expression of gelating properties (Scheme 1). Moreover, a subtle balance between the respective dimensions of the aromatic and the chain is prevailing (the latter has to be a linear alkane and not a branched chain), probably in order to afford an optimized mutual overlap within the fibers (C-H/aromatic π -cloud interactions). Figure 1 clearly shows that the 10-carbon chain is quasi-ideal for



Scheme 1 General formulae of rod-like aromatic organogelators. The active molecules bear 2 alkoxy chains at C-2 and C-3; any modification of this substitution pattern or any change in the shape of the aromatic part renders the compounds inactive.

anthracene, whereas the 16-carbon chain (DHDOT) is preferable for tetracene [13]. In addition, the shape and size of the aromatic subunit are also of importance: at least three aligned and fused rings are necessary to get an efficient gelator [phenyl and naphthyl groups are not as favorable as anthracene, tetracene (DnOT) or pentacene (DHDOP)], and any modification of the aromatic shape leads to inactive materials (nonlinear aromatics such as stilbene, pyrene, phenanthrene, etc. produce non-gelling agents). Finally, the active molecules have to display a rod-like geometry, which probably induces a specific packing mode in the crystalline phases (when obtained), where molecules are organized in layers [14]. Of note is the absence of any hydrogen-bonding groups borne by the substrates as usually encountered with other small-sized organogelators, these groups being recognized to be the major driving force for the aggregative process. For DDOA and analogs, the driving force essentially rests on hydrophobic interactions (π - π stacking, van der Waals forces...) which control the mutual molecular orientation and the supramolecular arrangement.

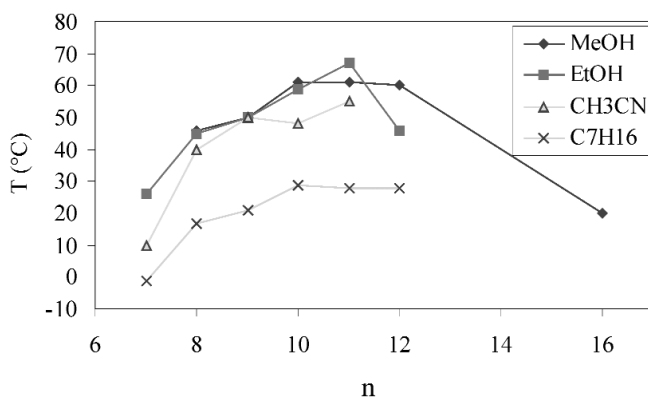


Fig. 1 Dependence of DDOA gelling properties vs. alkane chain length (the number of carbons in the chain varying from 7 to 16). For DHOA, $n = 6$ (hexyl chain), depending on the experimental conditions, both crystals and gel could be obtained.

The gelification produces a soft and translucent material (Fig. 2) with spectroscopic properties that are directly related to the molecular organization in the nanofibers (section ca. 100–200 nm, length of several μm) weaving the supramolecular architecture. A molecular arrangement has been proposed where the DDOA molecules are arranged in triads, themselves stacked head-to-tail into sheets that wrap around the long axis of the fibers [7] (see Fig. 2). This model is based on the crystal structure of the closely related gelator 2,3-di- n -hexyloxyanthracene (DHOA) (DHOA can form either crystals or gels, whereas DDOA never crystallizes) and on infrared dichroism, molecular modeling [7], and birefringence [15] studies performed on aligned DDOA gel fibers. Due to similar spectroscopic behaviors, it was anticipated that all the organogelators in the series (i.e., anthracene, tetracene [13], and pentacene derivatives [16]), experience a molecular organization comparable to that of DDOA. This conclusion is reinforced by the similarity of the shapes of the fibers (revealed by electronic or atomic force microscopy) and of the thermodynamic parameters deduced from the phase transition diagrams [6,13]. Moreover, the straightforward realization of mixed gels with these compounds (*vide infra*) strongly confirms the structural analogy of the packing in the fibers.

On the other hand, it has been shown that the gels formed with $[n]$ -acenes display interesting properties connected with their sensitivity to a mechanical stress or an oriented magnetic field which, for instance, allows the fibers to align in a specific direction. These fibers oriented through external stimuli could find interest in various fields such as stabilization of deformed nanoreactors or nanocapsules [17].

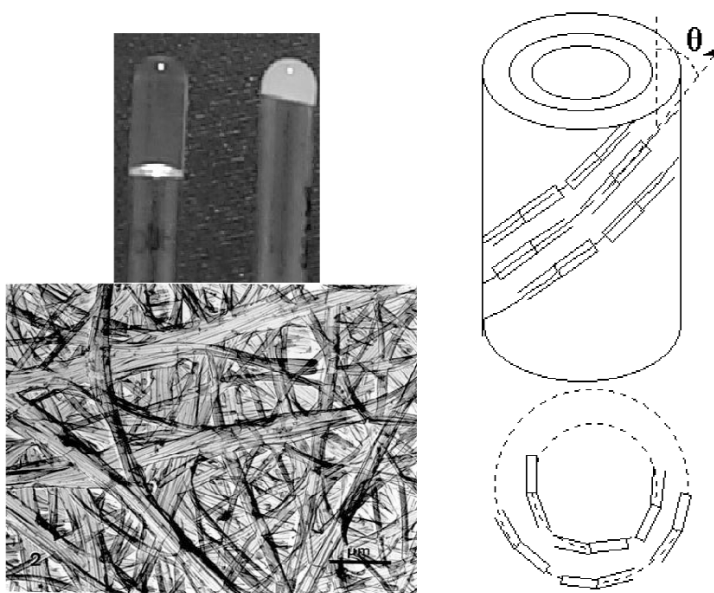


Fig. 2 *Left*: Freeze-fracture transmission electron microscopy (TEM) image of gels formed with DDOA and propanol: the section of the fibers is ca. 100–200 nm (inset: gel photographed in an inverted tube, the gel is translucent at low DDOA concentration and turbid at higher concentration). *Right*: Stacking of DDOA inside the fibers as revealed from molecular modeling. Adapted from [7] with permission: copyright © 2003 American Chemical Society.

ENERGY TRANSFER IN SELF-ASSEMBLED [*n*]-ACENE FIBERS

In order to investigate the efficiency of light-induced energy transfer in [*n*]-acene gel-fibers, DDOA donor gels were doped with 2,3-*n*-dialkoxytetracene (DnOT) acting as acceptor [18]. An almost total quenching of the emission of DDOA occurs in gels including 1 mol % DDOT and an emission of DDOT appears with a 100-nm Stokes shift. It is noteworthy that 0.05 % doping with DDOT achieves ca. 1/3 of the maximum transfer, and maximum quenching is completed with 1 % doping in DDOA gels (Fig. 3a). In isotropic solution, due to the low acceptor concentrations used, no diffusion-limited energy transfer occurs and only emission of DDOA could be recorded.

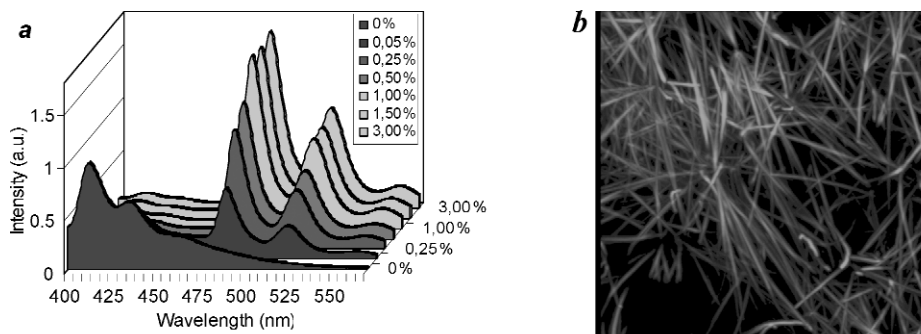


Fig. 3 Emission spectra of doped DDOA (2.0×10^{-3} M) gels in DMSO at 293 K, λ_{exc} : 384 nm; (a) with increasing proportions of DDOT (mol %); (b) Fluorescence confocal microscopy image ($50 \times 50 \mu\text{m}$) of DDOA gel with 2 mol % DDOT, λ_{exc} : 405 nm, $500 < \lambda_{\text{em}} < 600$ nm. Adapted from [18] with permission: copyright © 2005 American Chemical Society.

Like in a cocrystallization (energy transfer has been shown to efficiently occur in tetracene-doped anthracene crystals due to favorable cocrystallization, good spectral overlap, and exciton migration [19]), it was envisioned that tetracene incorporation occurs by “replacing” a DDOA in the native structure of the gel, the replacement being favored by structural and chemical similarity of the constituents. This point was confirmed by doping DDOA gels (DMSO) with five different tetracenes: four of them being 2,3-disubstituted with hexadecyl (DHDOT), decyl (DDOT), hexyl (DHOT), and butyl (DBOT) chains, and one compound substituted in positions 5,12 (5,12-DDOT) with a decyl chain, the latter substitution breaking the rod-like shape of the molecule. The addition of DDOT or DHOT produces identical emission spectra (Fig. 4a). In contrast, due to the smaller incorporation or dispersion, DBOT (Fig. 4a) and DHDOT (Fig. 4b) are less efficient acceptors and 5,12-DDOT, the non-rod-like shape molecule, does not influence DDOA emission. Similarly, DHDOT disperses better in DHDOA (hexadecyl chain) than in DDOA (Fig. 4b). The fluorescence confocal microscopy imaging of a DDOA/DDOT mixed gel (Fig. 3b) demonstrates that DDOT emission results homogeneously from all the fibers and that the energy-transfer process occurs within the fibers.

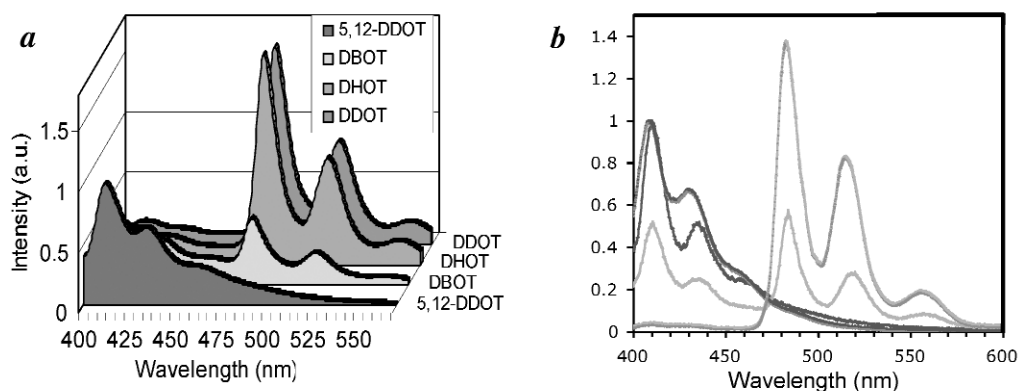


Fig. 4 Relative emission spectra of anthracene gels (2.0×10^{-3} M) in DMSO at 293 K, λ_{exc} : 384 nm: (a) DDOA with 1 mol % of 5,12-DDOT, DBOT, DHOT, and DDOT, respectively; (b) In the spectral region 400–470 nm, from top to bottom: DHDOA, DDOA, DDOA/DHDOT (1 %), DHDOA/DHDOT (1 %); emission intensity increases correspondingly in the region 470–600 nm. Adapted from [18] with permission: copyright © 2005 American Chemical Society.

In addition, it was shown by excitation spectroscopy that tetracene emission originates after light absorption by DDOA and subsequent energy transfer to the acceptor. In the gels, the tetracene emits like an isolated chromophore and its spectral structure is reminiscent of that of non-substituted tetracene in doped anthracene crystals [19], and corroborates the high molecular order described earlier [7] for the DDOA gels.

For a DDOA/DHOT (1 %) gel at room temperature (170 K), it was shown when DDOA is excited that the fluorescence quantum yields, only due to the emission of DHOT, is equal to 0.32. This value compatible with a weak energy waste in the fibers is lower than the intrinsic emission quantum yield of DHOT in the gel-fibers (ca. 0.60), and indicates that 54 % excited DDOA transfer their energy to the tetracene acceptor. Moreover, it was estimated in 0.05 % DDOA/DDOT doped gels (at room temperature) that the extent of the energy transfer can involve at least up to 700 molecules of anthracene (indeed, 1 DDOA out of 3 was quenched). This very high number is largely higher than those found for other organogels [20–21], or by comparison, those for light-harvesting dendrimeric antennae [22]. This high efficiency suggests a combination of two effects, direct resonant energy transfer (essentially by Förster mechanism) between the donor and the acceptor, and to some extent exciton migration between neighboring donors. The latter process has yet to be clearly demonstrated in self-assembled fibers, but

can be estimated in our case to be less favorable than in anthracene crystals [23] probably because of a slightly different chromophore packing in the gels, and the spatial confinement into fibers (diameter ca. 100 nm).

Similar photophysical behaviors would be logically anticipated with analogous rod-like shape organogelators in the series. It was indeed perfectly demonstrated on the benzenic and naphthalenic derivatives (DDOB and DDON, respectively) doped with <1 % DDOA as an acceptor. Although the spectral overlap is not as favorable as for tetracene derivatives and DDOA, very efficient energy transfers occur from the excited benzene chromophore to the DDOA (Fig. 5). Whereas the fluid solution only displays the fluorescence of DDOB or DDON (no energy transfer occurs due to the large dilution, ca. 10^{-5} M for the gelators and less than 10^{-7} M for DDOA), the emission of the gel, which acts as a very powerful light-harvesting antenna, is solely that of DDOA.

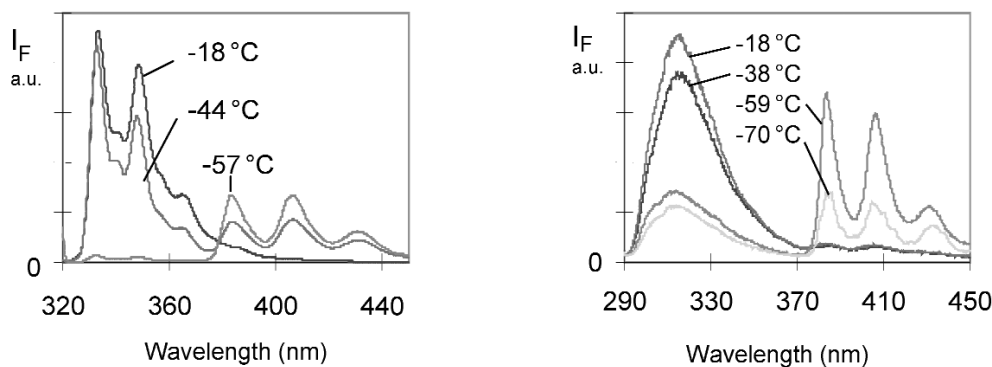


Fig. 5 *Left*: fluorescence spectra of DDON gels with 1 mol % DDOA in methanol vs. T (λ_{exc} : 317 nm, $c = 2.3 \times 10^{-5}$ M); *Right*: fluorescence spectra of DDOB gels with <1 mol % DDOA in methanol vs. T (λ_{exc} : 285 nm, $c = 1.3 \times 10^{-5}$ M).

CONCLUSION

Linear [*n*]acenes substituted at C-2 and C-3 by long alkoxy chains are efficient organogelators yielding soft 3-dimensional architected materials imprisoning the isotropic fluid via intertwined nanofibers. These fibers, which could be organized upon mechanical or magnetic stimuli, were found to be efficient light-harvesting systems. Doping the gels with a few percent of acceptor showed that these fibers are excellent channels for energy transfer. These systems open the way of the design of a new class of hybrid materials including two (or more) independent chromophoric compounds gifted with different (and/or complementary) photophysical and photochemical properties. The self-assembled [*n*]acene fibers are of interest in various fields and could especially be applied in organic optoelectronics.

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