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Photochromism and Self-Assembly of Soluble Tetracenes

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Photochromism and Self-Assembly of Soluble Tetracenes

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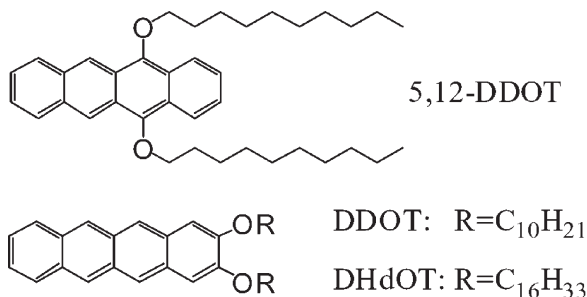
Irradiation of 5,12-didecyloxytetracene leads to a plano- and a centrosymmetric photodimer, inducing a large spectral shift; the monomer is restored by gentle heating or irradiation at $\lambda \leq 300$ nm. In addition, self-assembly of 2,3-didecyloxytetracene affords organogel nanofibers.

Keywords: photochromism, soluble tetracenes, organol gel, self-assembly

[*n*]acenes such as tetracenes and pentacenes [1] are at the center of recent developments in optoelectronics due to their significant charge mobility, intense colored absorption and emission, and valuable photo-reactivity and photochromism [2]. Tetracene displays a very low solubility in organic solvents which confines its studies and applications to the solid state [3]. By substituting tetracene with long chain alkoxy

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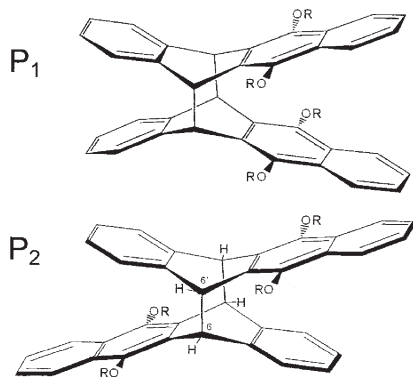


SCHEME 1 Soluble tetracene derivatives.

groups in positions 5,12 or 2,3, a significant solubility is achieved in common organic solvents. In this paper, we describe some properties of the soluble tetracenes 5,12-di-*n*-decyloxytetracene (**5,12-DDOT**, Scheme 1), 2,3-di-*n*-decyloxytetracene (**DDOT**) and 2,3-di-*n*-hexadecyloxytetracene (**DHdOT**).

The synthesis of **5,12-DDOT**, **DDOT** and **DHdOT** have been described elsewhere [4,5]. An overall yield of 38% has been obtained for **5,12-DDOT**, whereas overall yields of *ca.* 20% have been achieved for **DDOT** and **DHdOT**. Their preparation was repeated several times and gram quantities were obtained.

Two photoproducts, **P₁** and **P₂** (Scheme 2), have been obtained in 1:1 ratio by irradiation of **5,12-DDOT** and have been isolated by chromatography (reaction yield = 6.5×10^{-3} with 8.3×10^{-3} M concentration of monomer). The ^1H NMR spectra (CDCl_3) revealed the presence of signals characteristic of 4 bridgehead protons (6,11 and



SCHEME 2 Photoproducts obtained by irradiation of **5,12-DDOT**. $R = C_{10}H_{21}$.

6',11' positions) at δ : 5.35 (**P**₁) and δ : 5.32 (**P**₂) [6]. Attempts to obtain single crystals suitable for X-ray structure determination did not meet with success. The back reaction to the monomer was shown to occur in solution under gentle heating; by irradiation at $\lambda \leq 300$ nm a photostationary state could be attained.

A strong spectral shift is associated to this photoreaction. Indeed, as seen in the absorption spectra (Fig. 1), the maximum absorption wavelength shifts from 506 nm in the monomer to about 310 nm in the dimers ($\Delta\nu \approx 12500$ cm⁻¹). Compelling evidence of the hh structure of **P**₁ (and hence ht structure of **P**₂) came from fluorescence spectroscopy. The absorption (**5,12-DDOT**, **P**₁, **P**₂) and fluorescence (**P**₁, **P**₂) spectra are represented in Figure 1. **P**₁ and **P**₂ exhibit the normal monomer fluorescence of a substituted naphthalene derivative (emitting between 340 and 425 nm); additionally, and in contrast to **P**₂, **P**₁ presents a non-structured and red-shifted band (λ_{max} : 424 nm, ν_{max} : 23585 cm⁻¹). This emission is typical of an excimer, as confirmed by the excitation spectra (spectra of **P**₁ at 340 and 425 nm match the absorption spectrum) and the kinetic analysis. Indeed, the short decay time of the high energy emission (352 nm, $\tau = 1.3$ ns) is very similar to the rise time of the lower energy emission (424 nm, $\tau = 1.6$ ns), as typically expected for excimer states populated by S₁ excited states [7]. The excimer decay lifetime is 6.6 ns.

Thermoreversible physical organogels of **DDOT** were obtained with a large variety of solvents, such as alcohols, cyclohexane, methylcyclohexane (MCH) and DMSO. **DHdOT** is more efficient than **DDOT** and, in addition, gelifies alkanes, dichloromethane and acetone. At

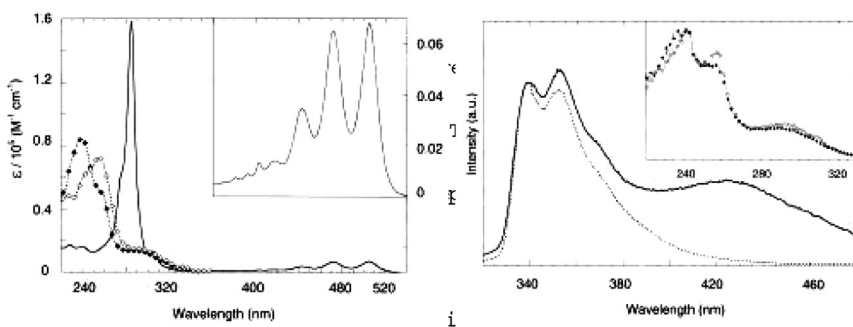


FIGURE 1 (left) UV-Vis absorption coefficients (ϵ) of (—) **5,12-DDOT**, (---◆---) **P**₁ and (····◇····) **P**₂ in CH₂Cl₂. Inset: **1** from 360 to 540 nm. (right) Fluorescence spectra of (—) **P**₁ and (····) **P**₂ in hexane. Conc.: 1.5×10^{-5} M at ambient temperature, λ_{exc} : 310 nm (the same spectra are obtained with λ_{exc} : 240 nm). Inset: Excitation spectra of **P**₁ at λ_{em} : 340 nm and λ_{exc} : 425 nm.

room temperature, the lowest critical concentration (*c.c.*) was 0.4×10^{-3} M (0.03% w) and was exhibited by **DHdOT** in cyclohexane. The topography images obtained by AFM (Fig. 2 left) of a *thick* deposit of organogel on freshly cleaved mica revealed a network of entangled fibers and fiber bundles, whereas no fiber termination was observed. The fibers typically display a width of 100–200 nm.

DDOT and **DHdOT** absorb *visible* light and emit in solution (quantum yield of 0.2 for **DHdOT** in degassed cyclohexane). Figure 2 shows the variation of the absorption spectrum of **DHdOT** upon gel formation. The gel absorption is similar to that of **DHdOT** microcrystalline powder in a KBr pellet, reminiscent of the behaviour of DDOA [8]. The marked red-shift of the $S_1 \leftarrow S_0$ (1L_a) transition by $\Delta\nu$: *ca* -800 cm^{-1} reveals a well-defined molecular organization of **DHdOT** into aggregates with partial chromophore overlapping [9]. The fluorescence intensity of **DHdOT** (not shown) is substantially decreased upon condensation into a gel, which suggests the existence of non-fluorescent low-energy traps.

In summary, this study shows that soluble tetracene substituted in 5,12 position form photo-dimers upon irradiation in the visible. This photoreaction is accompanied by a large shift, resulting in the decoloration of a yellow-orange solution. Their photochromic properties were observed.

Besides, 2,3-bis-*n*-alkoxy substitution allows tetracenes to self-assemble into stable nano-fibers which could act as an optical confining media and thus as a waveguide. These characteristics pave the way for

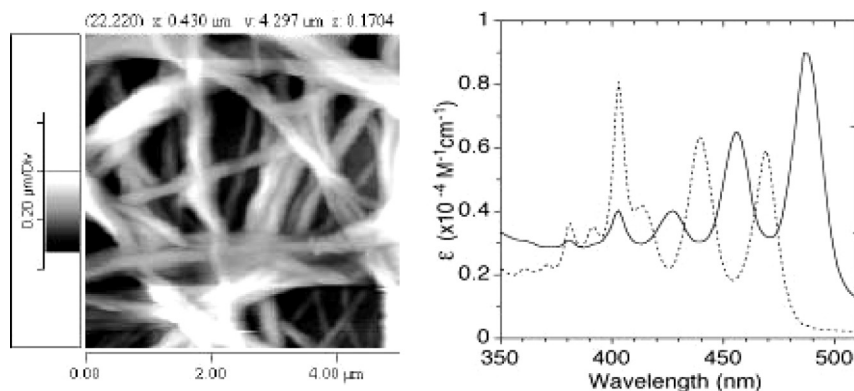


FIGURE 2 (left) Topography AFM images of a **DHdOT** organogel (solvent: $C_{14}H_{30}$). **(right)** Absorption spectra of **DHdOT** (1.6×10^{-3} M) in cyclohexane (...) in the *isotropic sol* at 360 K and (—) in the *gel* at 298 K.

the use of such tetracene derivatives in the field of opto-electronics. Moreover, extension of this work to pentacene is promising.

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