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Synthesis of 2,3-Substituted Tetracenes and Evaluation of Their Self-Assembling Properties in Organic Solvents

Jens Reichwagen,[†] Henning Hopf,[*,†] André Del Guerzo,[‡] Colette Belin,[§]
Henri Bouas-Laurent,[‡] and Jean-Pierre Desvergne[*,‡]

Institut für Organische Chemie, TU-Braunschweig, D-38106 Braunschweig, Germany, and Laboratoire de Chimie Organique et Organométallique (CNRS, UMR 5802) and Laboratoire de Physico-Chimie Moléculaire (CNRS, UMR 5803), Université Bordeaux 1, F-33405 Talence, France

h.hopf@tu-bs.de; jp.desvergne@lcoo.u-bordeaux1.fr

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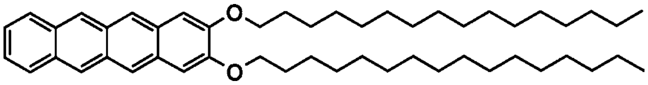
ABSTRACT

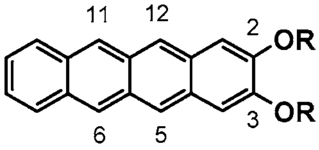


Rod-shaped 2,3-di-alkoxytetracenes, soluble in common organic solvents, have been synthesized and studied for their gelling ability in organic solvents and their unusual UV–visible spectroscopic properties.

The physical properties of linear polycyclic aromatic hydrocarbons (anthracene, tetracene, and pentacene) that are poorly soluble in common organic solvents have been most often studied in the solid state.[1] However, for some applications where deposition on surfaces or introduction into matrixes is required, it is advantageous to use soluble derivatives. This approach was explored recently by the synthesis of novel 5,12-disubstituted and 5,6,11,12-tetrasubstituted tetracenes[2] that showed an improved solubility in organic solvents and electroluminescent properties in homogeneous films. These interesting properties were attributed to aggregation involving π interaction between adjacent molecules, as was attested by the X-ray structure of 5,12-dimethoxy-6,11-bis(triisopropylsilylethynyl)tetracene single crystals.[2]

To enhance the π stacking ability of tetracenes, we have substituted the lateral rings to obtain elongated structures, capable of self-aggregation along the long axis of the nucleus. Such a property was observed with 2,3-di-*n*-decyloxyanthracene (DDOA) as described in recent publications.[3] The substitution in 2,3 positions by alkoxy chains such as O-*n*-$C_{10}H_{21}$ and O-*n*-$C_{16}H_{33}$ would lead to didecyloxytetracene (DDOT) and dihexadecyloxytetracene (DHDOT) of rodlike shape and nanometer size (ca. 2.7 and 3.4 nm in the extended form, respectively), see Scheme 1. When we started our investigations, no 2,3-dialkoxytetracenes had been described, presumably because of preparative difficulties.[4] Indeed, none

Scheme 1. 2,3-Di-*n*-alkoxytetracenes[a]



[a] DDOT: R = $n\mathrm{C}_{10}\mathrm{H}_{21}$. DHDOT: R = $n\mathrm{C}_{16}\mathrm{H}_{33}$.

[†] Institut für Organische Chemie.

[‡] Laboratoire de Chimie Organique et Organométallique (CNRS, UMR 5802), Université Bordeaux 1.

[§] Laboratoire de Physico-Chimie Moléculaire (CNRS, UMR 5803), Université Bordeaux 1.

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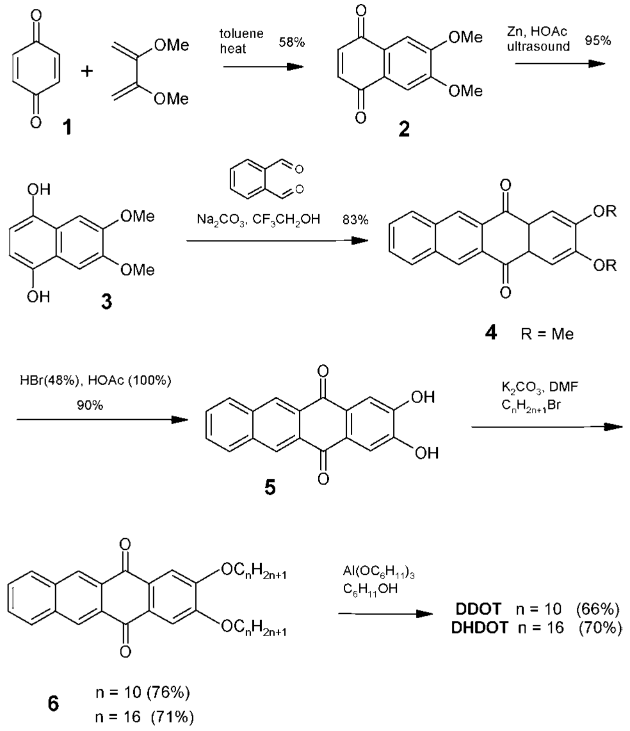
of the conventional methods[5] attempted met with success in our hands, and an original synthetic pathway had to be developed. The products failed to crystallize and formed gels in a variety of poor solvents, at ambient temperature, as anticipated.

Here we report the synthesis of 2,3-di-*n*-decyloxytetracene (DDOT) and 2,3-di-*n*-hexadecyltetracene (DHDOT) and describe their gelling ability as well as some distinct spectroscopic properties attesting to the π interaction between the molecules in the aggregates.

As outlined in Scheme 2, DDOT and DHDOT have been prepared in six steps, starting from benzoquinone, a commercial compound, in satisfactory overall yields (ca. 20%).

Scheme 2. Synthetic Pathway to 2,3-Di-*n*-alkoxytetracenes[a]



[a] Overall yields from *p*-benzoquinone: DDOT and DHDOT ca. 20%.

Since tetracene and hydroxytetracenes are very sensitive to oxidation, it was advisable to form the tetracene core in the last step and protect the phenol groups as methoxy ethers, stable in basic media. The strategy consisted of starting from 1,4-dihydroxy-6,7-dimethoxynaphthalene (**3**) as the main building block and constructing 2,3-dimethoxytetracenequinone (**4**) using the condensation of orthodiformylbenzene with **3** in the presence of Na_2CO_3. Smooth demethylation was followed by a classical Williamson alkylation with the long chains to give **6** in reasonable yields. DDOT and DHDOT were finally isolated after Meerwein–Pondorff–Verley reduction. The preparation was repeated several times, and gram quantities were obtained. Spectroscopic data, detailed in Supporting Information (1), are consistent with the proposed structures.

Upon drop casting of warm solutions of dissolved gelator at a concentration (1.4×10^{-3} M) higher than the critical gel concentration (cc, i.e., the lowest concentration at which a gel can be obtained at ambient temperature) and then cooling to room temperature, the topography images obtained by AFM of a thick deposit revealed a network of entangled fibers and fiber bundles, whereas no fiber termination was observed (Figure 1).

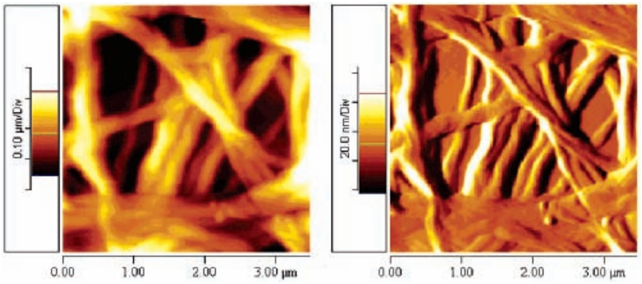


Figure 1. AFM topography (left) and signal error images (right) of DHDOT in $C_{14}H_{30}$, concentration = 1.4×10^{-3} M, after casting on mica; fiber width ca. 100–200 nm.

Table 1. Selected Solvents and Concentrations at Which Room Temperature Gels Are Found for DDOT and DHDOT, from Light Diffusion Measurement[a]

solvent	DDOT concn = 10^{-3} M	DHDOT concn = 10^{-3} M
n-hexanol	0.4*	0.3*
n-heptane		0.9
n-$C_{14}H_{30}$		1.4*
cyclohexane	1.9	0.5

[a] Concentrations are critical concentrations (cc) except for those marked with an asterisk (*), for which the cc values were not determined. Gels were also formed in DMSO and for DHDOT, in dichloromethane and acetone

Solvent screening for gel-forming ability was performed with a variety of solvents, using the inverted tube method.[6] A selection of solvents and critical concentrations are listed in Table 1. One observes than DHDOT is more efficient than DDOT; in addition, DHDOT gelifies dichloromethane and acetone, in contrast to DDOT. DHDOT shows a cc of 0.5×10^{-3}

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(4) Our synthetic work was achieved before the preparation of 2,3-dihydroxytetracene was reported: Tulewski, G. S.; Miao, Q.; Fukuto, M.; Abram, R.; Ocko, B.; Pindak, R.; Steigerwald, M. L.; Kagan, C. R.; Nuckolls, C. *J. Am. Chem. Soc.* **2004**, *126*, 15048–15050. Our method differs in several ways from that of the authors.

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M (0.04 wt %) in cyclohexane, acting as one of the best known supergelators.[7] At a much lower concentration, e.g., 2×10^{-5} M, a gel can be obtained in methylcyclohexane (MCH) at 190 K.

A thermoreversible gel[8] has the property of reverting to an isotropic liquid when heated (the so-called melting process) and forming a gel again when the solution is cooled (the gelification process). The processes generally involve hysteresis.[3b,8] Phase transition diagrams are obtained by plotting the temperatures of gelification (T_{gel}) or melting (T_m) versus gelator concentrations. These diagrams were established for DDOT and DHDOT in several solvents, especially in *cyclohexane*. An example is given in Supporting Information (2A). From these data, the thermodynamic parameters $\Delta H°$ and $\Delta S°$ were calculated (using classical equations developed in Supporting Information 2B, 3) for the sol−gel transition and collected in Table 2, together with some relevant data on DDOA. The data concerning the gelification process have been selected because T_{gel} values are more reliable (from sample to sample) than T_m values.[3b] The salient features of Table 2 are the great importance of the entropic factor and the trend of increasing stability from DDOA to DHDOT in hydrocarbon media (for solubility reasons, it was not possible to compare DDOA and tetracenes in the same solvent). Other data indicate that tetracene gels are stronger in *n*-hexanol than in cyclohexane and that DHDOT gels are more robust than those of DDOT (see Supporting Information, 2C).

Table 2. Thermodynamic Parameters ($\Delta H°$, $\Delta S°$) and Free Enthalpy ($\Delta G°$ at 298 K) of Gelification in *n*-Heptane[a] (DDOA) and Cyclohexane (DDOT, DHOT) (Accuracy ±10%)

substrate/solvent	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})
DDOA/*n*-heptane	−60	−155	−13.8
DDOT/cyclohexane	−78	−192	−21.0
DHDOT/cyclohexane	−76	−178	−23.0

[a] Data taken from ref 3b.

In solution, as shown in Figure 2 for DHDOT, both tetracene derivatives absorb in the UV−visible range up to 510 nm[9,10] and emit a green fluorescence (450−650 nm) with quantum yields ≥0.2 (in degassed cyclohexane).[11] The gel absorption spectrum is similar to that of DHDOT microcrystalline powder in KBr pellet (Figure 2, inset). This is reminiscent of the DDOA behavior.[4] The marked red-shift of the $S_1 \leftarrow S_0$ (^1L_a) transition by 790 cm^{-1} and the fine structure reveal a well-defined molecular organization of DHDOT with partial overlapping of chromophores.[3b] Furthermore, the clear hypochromism[12] of the $S_2 \leftarrow S_0$ (^1L_b) transition at 403 nm is typical of *exciton splitting*[15] and strongly suggests some degree of alignment between the long axis of the aromatic nuclei. The fluorescence and excitation spectra of DHDOT in the gel phase and in solution are represented in Figure 3.

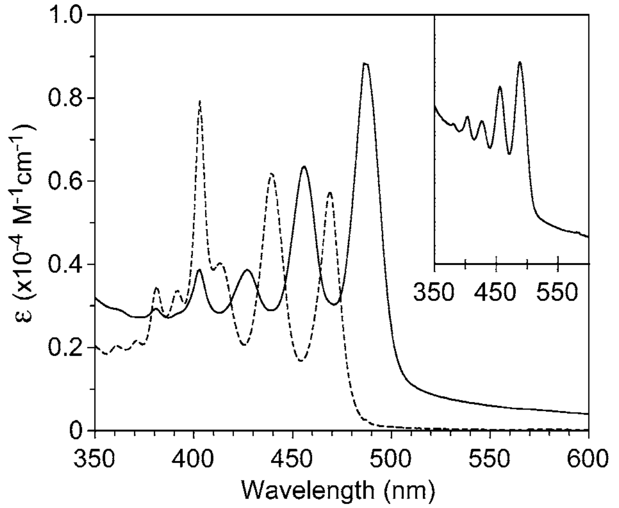

Figure 2. Absorption spectra of DHDOT in a cyclohexane gel at 298 K (−) and in the isotropic phase at 343 K (···); concentration = 1.6×10^{-3} M; $\Delta\nu$(0−0) sol−gel = −790 cm^{-1}. Inset: absorption spectrum of DHDOT gel in KBr. The spectra in the gel phase and the KBr matrix display an important contribution of light diffusion.

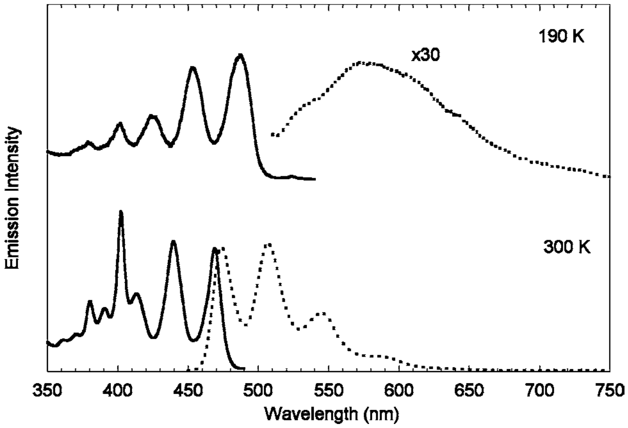

Figure 3. Excitation (−) and emission spectra (···) of DHDOT in methylcyclohexane, concentration = 2×10^{-5} M, at 300 K ((−) λ_{obsd} = 507 nm and (···) λ_{exc} = 440 nm) and at 190 K (gel state) ((−) λ_{obsd} = 580 nm and (···) λ_{exc} = 488 nm).

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(6) Gelation test: 1 cm^3 of solvent was added to a weighed amount of gelator in a septum-capped test tube (ca. 4 cm length and 0.7 cm diameter) in order to obtain the desired concentration. The mixture was warmed to the boiling point until the solid dissolved, and then the mixture was allowed to cool to room temperature. When a gel was formed (generally within several minutes), the sample did not flow when the test tube was inverted.

(7) A "supergelator" is considered to have a cc ≈ 0.3−2.5 mM at rt according to Shinkai (Gronwald, O.; Snip, E.; Shinkai, S. *Curr. Opin. Colloid Int. Sci.* **2002**, *7*, 148−156) and Menger (Menger, F. M.; Caran, K. L. *J. Am. Chem. Soc.* **2000**, *122*, 11679−11691).

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(9) The first electronic band (^1L_a) is comparable with that of tetracene,[10] but the second electronic transition ^1L_b appears clearly in the 350−403 nm range, as enhanced by substitution of a lateral ring (the "b" bands are polarized along the long axis of the nucleus.[10]

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For the gel, one observes the loss of fine structure, a substantial red-shift ($\lambda_{max} = 570$ nm), and a large decrease of the fluorescence intensity. That the fluorescence spectrum of the gel is not the mirror image of the absorption spectrum suggests the presence of exciton traps of lower energy displaying a low radiative probability.[13,14]

In summary, two 2,3-disubstituted tetracene derivatives soluble in common organic solvents have been shown to self-assemble into gels at *very low concentrations*. This must be due to the unique combination of tetracene and long aliphatic chains in rodlike-shaped and nanometer-sized (2.7−3.4 nm) molecules. The superior strength of DHDOT gels reflects the benefit drawn from fine-tuning the chain length in order to favor the best molecular aggregation in the gel phase. Prospectively, such a self-assembly is liable to afford tetracene fibers with semiconducting properties.[1,4,15] The advantage of aggregation in gel fibers has indeed been illustrated in a recent publication.[16] The long-range molecular order that can be achieved by alignment of the organogels fibers mechanically[17] or in a magnetic field[18] appears to be an additional feature to be exploited with these tetracene gels.

Acknowledgment. We are indebted to the Ministère de la Recherche, CNRS, Région Aquitaine, and the Fonds der Chemischen Industrie for financial assistance.

Supporting Information Available: (1) Synthesis of DDOT and DHDOT and spectroscopic data supporting the structures, (2) thermodynamic properties, and (3) equations used to calculate the thermodynamic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Quantum yield was determined using perylene as a standard: $\Phi_F = 0.94$ in cyclohexane. Berlman I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971; pp 399. Φ_F(DDOT) = 0.2; Φ_F(DHDOT) = 0.25.

[12] Hypochromic effects have been also observed in gels by others: (a) Kobayashi, H.; Friggeri, A.; Koumoto, K.; Amaikee, M.; Shinkai, S. *Org. Lett*. **2002**, *4*, 1423−1426. (b) Tamaru, S.; Nakamura, M.; Takeuchi, M.; Shinkai, S. *Org. Lett*. **2001**, *3*, 3631−3634. (c) Tamaru, S.; Uchino, S.; Takeuchi, M.; Ideker, M.; Hatano, T.; Shinkai, S. *Tetrahedron Lett*. **2002**, *43*, 3751−3755.

[13] Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970.

[14] Birks, J. B. *Photophysics of Aromatic Compounds*; Wiley-Interscience: London, 1970. Excimers have no fine structure and are red-shifted, but their excitation spectra may have a fine structure, e.g., for pyrene.

[15] (a) Herwig, P. T.; Müllen, K. *Adv. Mater*. **1999**, *11*, 480−483. (b) Moon, H.; Zeis, R.; Borkent, E. J.; Besnard, C.; Lovinger; A. L.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc*. **2004**, *126*, 15322−15323.

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[18] Shklyarevsky, I. O.; Jonkheijn, P.; Christiansen, P. C. M.; Schenning, A. P. H. J.; Del Guerzo, A.; Desvergne, J.-P.; Meijer, E. W.; Maan, J. C. *J. Am. Chem. Soc*. **2005**, *127*, 1112−1113.