

Structural variations in a family of orthodialkoxyarenes organogelators

Pierre Terech^{a,*}, Gilles Clavier^b, Henri Bouas-Laurent^b, Jean-Pierre Desvergne^b, Bruno Demé^c,
Jean-Luc Pozzo^b

^a UMR 5819 CEA-CNRS–Univ. J. Fourier, DRFMC-SI3M, CEA-Grenoble 17, rue des Martyrs, 38054 Grenoble Cedex 9, France

^b Laboratoire de Chimie Organique et Organométallique, LCOO, UMR 5802 CNRS, Université Bordeaux 1, 351, Cours de la Libération, 33405 Talence, France

^c Institut Laue Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

Received 1 March 2006; accepted 29 June 2006

Available online 4 July 2006

Abstract

A series of low mass organic gelators (LMOGS) **1** to **6** whose chemical structures have in common an orthodialkoxyarene feature was prepared in order to compare the shape of their fibrillar network as investigated by small-angle neutron scattering (SANS) experiments. All members of the family exhibit a pronounced tendency to bundle formation by merging isolated fibers in extended packets of average diameter >500 Å. Variations of the 2D packing symmetry are observed from hexagonal to square orderings with close derivatives of the reference member 2,3-didecyloxyanthracene (DDOA). Networks in which the fraction of isolated fibers is significant enough to allow for their SANS identification are those for 6,7-dichloro-2,3-didecyloxyanthracene (Cl₂DDOA) and 2,3-dodecyloxy-9,10-anthraquinone (**5**). For this latter, the monodispersity of the cross-sections (thickness = 74 Å) is remarkable and the rectangular shape ($b/a \sim 0.12$) accounts for a merging mechanism into anisotropic bundles (ribbons).

© 2006 Elsevier Inc. All rights reserved.

Keywords: Gel; Neutron scattering; Structures; Network; Fiber; Bundles

1. Introduction

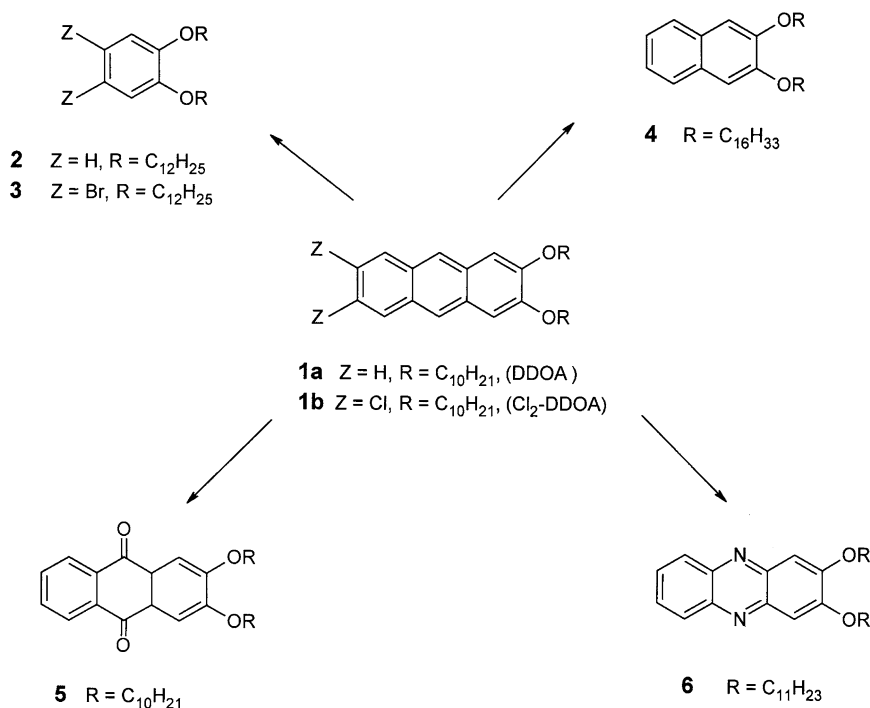
Molecular gels are innovative materials in the field of thermoreversible gels. The emergent [1–6] domain of research in soft condensed matter takes advantage of the spontaneous self-assembling phenomenon to form giant meshes of fibers from small molecules ($M_W \leq 1000$) [7–19]. The cohesive energies characteristic of the fibers and their nodal zones in the gel networks are of the order of the thermal energy accounting for the remarkable reversibility between the sol and gel states and the associated structures and properties involved at various scales. Water [20] or organic liquids [1] and mixtures can be gelled by specialist molecules part of an increasing large library. Frequently, low molecular mass organic gelators (LMOGs) [21] bear hydroxyl groups useful to develop electrostatic interactions (hydrogen bonds) generating the linear assemblies. Here, we focus on a subclass of aromatic compounds, 2,3-di-*n*-alk-

oxyanthracenes (**1**, Scheme 1) without such hydroxyl groups and shown [12,22–25] to gelate apolar hydrocarbons, alcohols, nitriles, amides, etc. Despite some interesting attempts using molecular modeling [11], the design of LMOGs remains largely empirical due to a subtle solvent-LMOG affinity parameter and the analysis of experimental investigations remains a privileged approach.

The objective of the present study is to design new gelators related to compounds **1** (especially DDOA) through structural modifications of the aromatic part and of the chain length but not of the nature and number (two alkoxy groups) nor the mutual position (ortho substituted along the molecular long axis) of the substituents. Previous experiments have shown that the gel-forming ability of DDOA is also present in benzene derivatives [12] (but **2** is less efficient than **3**) or in 2,3-dihexadecyloxynaphthalene (**4**), or by replacing, in a symmetrical way, the “CH” groups of the middle ring (in compounds **1**) by two “C=O” (**5**) [24] or “N” (**6**) [25], respectively. The new syntheses are conducted so as to maintain or increase the dipole–dipole interactions. Structural consequences of these

* Corresponding author.

E-mail address: pierre.terech@cea.fr (P. Terech).



Scheme 1. Investigated family of aromatic gelators structurally related to **1** by modification of the cyclic skeleton in a symmetrical fashion.

molecular modifications on the supramolecular aggregates of the gels are expected. Using the small angle neutron scattering (SANS) technique, we report on the structural features of gels formed with compounds **3**, **4**, **5**, and **6** selected for their optimal stability at ambient temperature.

2. Experimental

Melting temperatures were determined in capillary tubes of a Buchi 510 apparatus. FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer. ¹H and ¹³C NMR spectra used a Bruker 250 AC instrument for solutions in CDCl₃ unless stated otherwise. Chemical shifts are in ppm and *J* values are in Hz. Chromatography separations were performed on SDS Silica Chromagel (70–210 μm). Mass spectra were obtained on an AutoSpec EQ spectrometer. Elemental analyses were performed by the Microanalytical Service, Institut du Pin, University Bordeaux 1. Electronic absorption spectra and transmission spectra were measured on a Hitachi U-3300 spectrophotometer equipped with a thermo-controlled cell (10 mm optical path-length). For TEM measurements, gels were deposited on formvar coated copper grids in thin slices prepared by ultracryomicrotomy. A carbon coating preceded the examination (JEOL 2000 apparatus).

Gelation tests used the inverted test tube method [4]. The gel-to-sol phase transition temperatures *T_m* (see Appendix A) were determined using an inverted septum-capped glass tube immersed in a thermo-controlled bath, the temperature being raised at 2 °C min⁻¹. The reported values are the average of several measurements (reproducibility ±1 °C). Details of the syntheses of **3**, **5**, and **6** are given in Appendix A. Alteration of the structures developed in the gels by the isotopic composi-

tion of the systems was assumed to be inexistent considering the variety of organic liquids that can be gelled (see Appendix A) and the absence of previous similar observations in the class of low-mass organogels. The gelators were purified and dried (Appendix A), deuterated ethanol and acetonitrile were high quality grades so that the role that might be played by trace amounts of water on the structures was assumed negligible.

Small angle neutron scattering (SANS) measurements were performed using the D11 diffractometer at the Institut Laue Langevin (ILL, Grenoble, France) [26]. Deuterated organic solvents were used (Aldrich) to restrict the level of incoherent scattering of the gels to the contribution of the gelator molecules themselves. The sample–detector distances and neutron wavelengths were adjusted to deliver a scattered wave vector *Q*-range 0.002 Å⁻¹ < *Q* < 0.25 Å⁻¹ (*Q* = 4π/λ sin θ, λ being the neutron wavelength and θ half the scattering angle). Standard corrections and calibration procedures have been used to precede with the radial averaging of isotropic 2D arrays of neutron counts collected on the detector. The level of incoherent background (mainly due to the presence of H atoms of the gelators) to be subtracted from the scattered intensity, was adjusted from a *IQ*⁴ versus *Q* plot assuming sharp interfaces of the fibrillar aggregates. Intensities represented in all figures are expressed in cm⁻¹. Detailed and rigorous formalisms and protocols concerning the use of the SANS technique for such self-assembled systems are presented elsewhere [27] and references cited therein.

3. Results and analysis

The electron micrograph of Fig. 1 shows that the solid-like part of the gel network for the **4**/ethanol system is made up of

Download English Version:

<https://daneshyari.com/en/article/612936>

Download Persian Version:

<https://daneshyari.com/article/612936>

[Daneshyari.com](https://daneshyari.com)