JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Control of Self-Assembly of a 3-Hexen-1,5-diyne Derivative: Toward Soft Materials with an Aggregation-Induced Enhancement in Emission

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Supporting Information

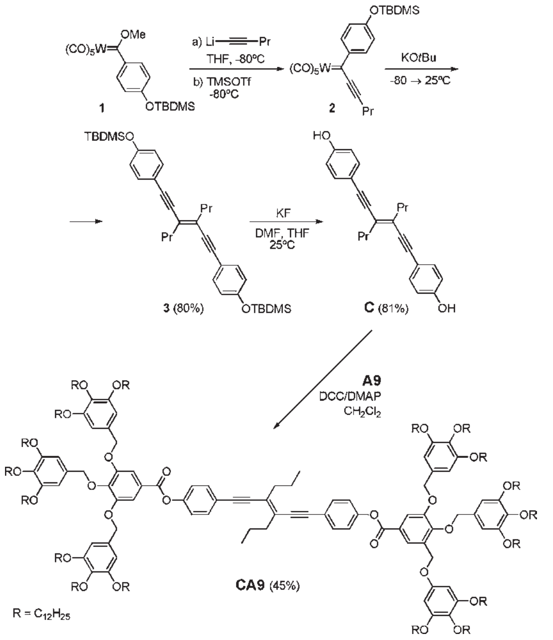
ABSTRACT: The supramolecular architectures of a fluorophore are controlled through the design of a conjugated polycatenar molecule, the self-assembly of which can be addressed toward a columnar liquid-crystalline phase and organogels. Thus, depending on the environmental conditions for self-assembly, compound **CA9** organizes into an unprecedented hexagonal columnar mesophase in the condensed state, in which half a molecule constitutes the slice of the column, or into a rectangular mesomorphic-like organization in the presence of apolar solvents such as cyclohexane and dodecane, at a concentration in which fibers form and gelling conditions are fulfilled. In this Col$_r$-type arrangement, the organization within the columns depends on the solvent. All of the materials prepared show luminescence, and moreover, a remarkable 3-fold increase in fluorescence intensity was observed in going from the solution to the gel state.

Spontaneous self-assembly of simple molecules is a powerful tool that allows complex supramolecular structures to be built. Such systems are suitable for the development of materials with organization-dependent properties.[1] This strategy has been successfully applied to the creation of soft materials of technological interest, such as liquid crystals and organogels containing organic chromophores.[2] A common feature of these materials is the possibility of achieving a high degree of control over the organization of the chromophores at the supramolecular level, which is important for the potential application of organic materials in optoelectronics.[3]

The design of new molecules as building blocks for functional soft materials is a challenge that still proves elusive on two counts: the transfer and enhancement of a given molecular property to the materials and the possibility of controlling the organization of the molecules to allow the transfer of the property to the material.

Organic fluorophores, as constituents of materials with emerging applications in optoelectronics, have one main drawback when organized at the supramolecular level,[4] namely, the formation of aggregates that cause fluorescence quenching. Nevertheless, organic molecules have wide design possibilities, and this represents added value that can help to overcome the aforementioned negative aspect.[5] In this respect, our attention was focused on the conjugated molecule 1,6-bis(4-hydroxyphenyl)-3-hexen-1,5-diyne (**C**), which was prepared as outlined in Scheme 1. Complex **2**, which was generated from **1** via methoxy displacement by acetylide, underwent rapid and selective tail-to-tail dimerization in the presence of KO*t*Bu to provide **3**.[6] Treatment of **3** with KF furnished endiyne **C**, which shows emission in solution that is visible to the naked eye upon illumination with a UV lamp [quantum efficiency of 0.57 in THF calculated with respect to diphenylanthracene (DPA); see the Supporting Information (SI)]. However, in the

Scheme 1. Procedure for the Synthesis of Core C and the Compound CA9



Received: March 2, 2011
Published: May 02, 2011

dx.doi.org/10.1021/ja2018898 | *J. Am. Chem. Soc.* 2011, 133, 8110–8113

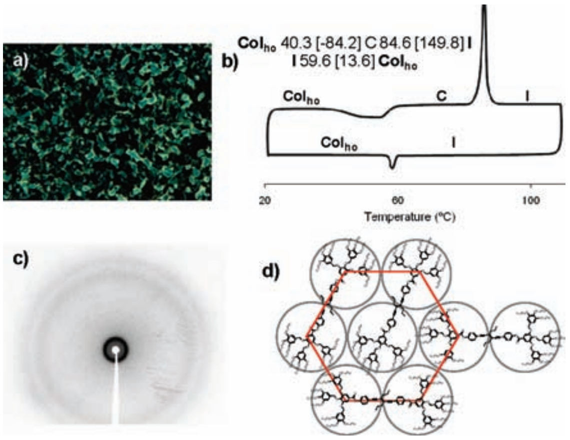


Figure 1. (a) POM photograph (×50) of compound **CA9**, natural texture at 50 °C. (b) DSC thermogram recorded for **CA9** at a heating−cooling rate of 10 °C/min; phase transitions (°C [kJ/mol]) are indicated. (c) XRD pattern of **CA9** at room temperature. (d) Top-view schematic representation of the two-dimensional arrangement proposed for the Col_h mesophase of compound **CA9**. For the sake of clarity, each molecule contains two circles, which correspond to columns in the hexagonal arrangement.

crystalline state, the luminescence was not visible to the naked eye, and only noisy luminescence spectra were obtained upon excitation at 335 nm. The reason for this finding may lie in the presence of head-to-head aggregates, as deduced from its crystal structure (see the SI).

Our interest in the design of organized functional materials through the control of supramolecular columnar assemblies[7] led us to design **CA9** bearing two bulky end groups derived from 3,4,5-tris(3,4,5-trihydroxybenzyloxy)benzoic acid (**A9**) (Scheme 1).[8] This acid shows a cubic mesophase[8a] and was chosen to impart a promesogenic molecular shape. Interestingly, the proposed molecular structure proved favorable for columnar self-organization through π stacking both in the bulk material and in solvents, yielding liquid-crystalline and organogel materials, respectively. The mesomorphic behavior of **CA9** was studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). When **CA9** was cooled from the isotropic state, a *schlieren*-type texture was observed, suggesting hexagonal columnar mesomorphism (Figure 1a; also see the SI). The DSC thermogram (Figure 1b) shows the transition from the isotropic state to the mesophase at 59.6 °C in the cooling process, and a crystallization peak was not observed down to room temperature. However, the mesophase underwent cold crystallization upon heating.

X-ray diffraction (XRD) experiments were carried out to determine the type of mesophase. The wide-angle X-ray scattering diagram (Figure 1c) shows a single diffraction maximum at small angles. In the absence of higher-order reflections, it is difficult to unambiguously assign the mesophase type on the basis of XRD data alone.[5b,9] Nevertheless, according to texture observations before and after shearing, we propose a hexagonal columnar mesophase with a lattice parameter of a = 33.9 Å, as determined from the maximum at small angles. Moreover, the outer diffuse halo observed at 3.9 Å helped to confirm the long-range correlation order of the columnar mesophase (Col_{ho}) and represents the mean stacking distance between the molecular cores along the column (h parameter of the Col_h mesophase).

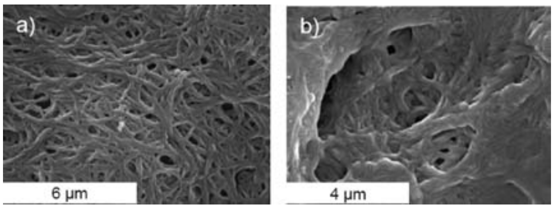


Figure 2. SEM images corresponding to (a) dodecane (×10000) and (b) cyclohexane (×14000) xerogels.

A partially aligned X-ray diagram could be registered on mechanically treated samples, which is consistent with a columnar phase in which columns are oriented along the rubbing direction (see the SI).

On the basis of the parameters measured using XRD, the density of the compound was calculated to be 1.95Z, where Z is the number of molecules per unit cell (see the SI). Since the density values of organic mesomorphic materials must be close to 1 g cm^{-3}, Z must have a value of 0.5, which means that each column slice (or hexagonal network node) contains half a molecule of compound **CA9**. Accordingly, each molecule would be located in two contiguous columns, and this disposition would be randomly distributed among columns from one molecule to the adjacent one along the column (Figure 1d). Such an arrangement, in which two columns are connected through the mesogenic core of the liquid-crystal molecule, is congruent with the C2 symmetry of the mesogen and has not been seen previously in columnar mesophases. Indeed, other shape-related mesogens (e.g., twin-tapered benzamides) have been reported to form columnar mesophases in which the stacking units consist of either one or two molecules.[10]

A number of examples have been reported in which the lack of directional intermolecular interactions such as hydrogen bonds[11] or the ability to generate mesophases prevents the formation of gels.[12] Even though the **CA9** molecule fulfills both of these criteria, it is able to promote the formation of supramolecular fibers that encapsulate certain organic solvents. Thus, it forms gels in cyclohexane and dodecane at concentrations of ∼3 wt %, and these are stable at room temperature. The dodecane gel was obtained at room temperature, whereas the formation of the gel in cyclohexane required low temperatures (0 °C). However, once formed, the gel was stable at room temperature.

Gels of compound **CA9** from dodecane and cyclohexane appeared in scanning electron microscopy (SEM) images as fibers with lengths of several tens of nanometers entangled to form a network that can encapsulate the solvent (Figure 2).

In order to gain deeper insight into the molecular architecture within the fibers, XRD studies were carried out. X-ray patterns registered for both organogels (Figure 3) indicated that the supramolecular arrangement of compound **CA9** along the fibers corresponds to a columnar mesomorphic-like organization. According to the maxima observed in the small-angle region (see the SI), a rectangular two-dimensional arrangement of the columns was deduced for both materials. Furthermore, at wide angles (∼4.5 Å), a diffuse maximum appeared in each case, corresponding to aliphatic chains with conformational disorder and the solvent. These results are also consistent with the observation of the xerogel by POM (see the SI).

Even though both organogels show the same type of columnar order (i.e., Col_r) within their corresponding fibers, it is surprising

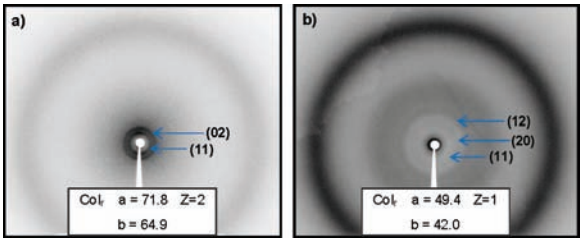


Figure 3. X-ray patterns of gels in (a) dodecane and (b) cyclohexane. Insets: lattice parameters (in Å) and number of molecules per unit cell (Z). The distances measured by XRD are gathered in the SI.

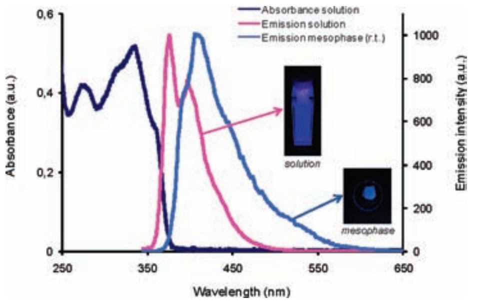


Figure 4. Normalized absorption and emission spectra in THF solution and in the mesophase at room temperature. The insets show the blue emission of the solution and the mesophase of compound **CA9** under illumination by a 365 nm UV lamp.

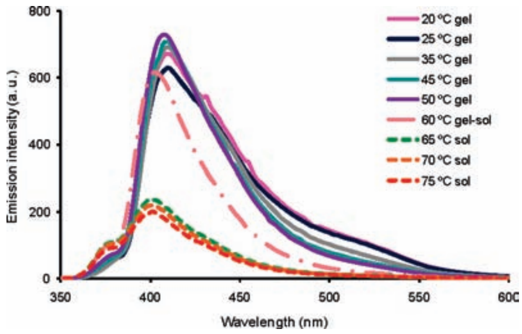


Figure 5. Emission spectra of gelator **CA9** in dodecane at a concentration of 3 wt % at different temperatures (λ_{ex} = 335 nm).

that the structural parameters are so different for the cyclohexane and dodecane gels (Figure 3). Density calculations helped to elucidate the organization of the molecules within the column. In this case, an h parameter related to long stacking order along the column was not detected in the pattern, and this did not allow the calculation of the volume of the unit cell and hence the density. For this reason, the density of the material was estimated as that of the solvent (0.8 g/cm^3 for cyclohexane and 0.75 g/cm^3 for dodecane). From these density values, h values of 4.5Z for the cyclohexane gel and 2.0Z for the dodecane gel were estimated. The parameter c must be close to 4 Å, which is a typical value for columnar stacking and close to that of the mesomorphic material (i.e., 3.9 Å), and hence, the values Z = 1 for the cyclohexane gel and Z = 2 for the dodecane gel were calculated. This means that a different supramolecular organization is present in the fibers of the organogels depending on the solvent. For a rectangular columnar network, the number of columns per unit cell is 2 (see the SI), and these results therefore indicate that in the former there is half a molecule per column slice and in the latter there is one molecule per column slice. A plausible explanation for this finding is based on the interactions established between the molecule and the different solvents. The interactions in cyclohexane must be stronger than those in dodecane since **CA9** is soluble in cyclohexane at room temperature and the solution must be cooled in order to form the corresponding gel. It is also possible that the differences in the degree of interaction depending on the solvent are more significant for the central part of the molecule (which is the most solvophobic part). In this situation, more or less solvent interaction with the central core of the molecule could influence the type of columnar organization (half a molecule or one molecule) within the Col$_r$ arrangement.

Regardless of the special characteristics of the Col$_r$ organization in the gel, a second aspect that is intriguing is the different columnar architectures of the liquid-crystalline state (Col$_h$) and the fibers of the organogel (Col$_r$). It is accepted that the formation of a Col$_r$ mesophase is caused by repulsions between aliphatic parts, a phenomenon that promotes the approach of the cores by tilting of the mesogens with respect to the column axis.[13] This gives rise to a rectangular symmetry for the columnar arrangement. In the present case, the solvent molecules can increase the steric requirement of the aliphatic part with respect to the core, in contrast to the molecule in bulk material, thus increasing the repulsion between tails, which favors tilting of the rigid cores.

As mentioned above, the conjugated core **C** is a luminophore that emits in solution (see the SI) but does not show fluorescence in the crystalline state. Although **CA9** shows a lower quantum efficiency than the core in dilute THF solution (0.11 with respect to DPA), this compound gives rise to strong fluorescence that is visible to the naked eye in both the mesomorphic state and the organogels. Moreover, luminescent fibers were observed by fluorescence microscopy under illumination at 340−380 nm (see the SI).

The fluorescence in the mesomorphic state was measured at room temperature, and the emission wavelength was compared with that of the solution (Figure 4). Broadening of the emission peak with respect to that in solution was observed, and this led to a single emission maximum and a bathochromic effect with a Stokes shift of ~70 nm (i.e., 30 nm greater than that measured in solution). This finding can be attributed to the intermolecular interactions that exist in the mesophase, which influence the conformational effects and hence the conjugation and optical properties. Moreover, these interactions must impede the formation of head-to-head aggregates as in the crystalline core (see SI), and this prevents fluorescence quenching.

To determine the effect of fiber formation on the luminescence properties, dodecane gels were measured at different temperatures. As observed in Figure 5, the gel was stable from 20 to 50 °C. Within this range, an emission maximum at 410 nm was measured. Upon further heating, the gel−sol transition began to occur at 60 °C, and a blue shift of the maximum was observed while the intensity was maintained. However, upon further heating to 65 °C, the transition to the solution was complete and a significant decrease in luminescence was observed, with the emission maximum at 401 nm and a shoulder at 365 nm. This process was fully reversible upon cooling. As a result, a 3-fold increase in luminescence in going from the solution to the gel occurred, together with a broadening of the

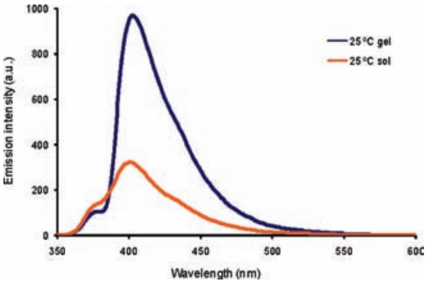


Figure 6. Emission spectra of gelator **CA9** in cyclohexane at a concentration of 3 wt % at room temperature in the sol and gel states (λ_{ex} = 335 nm).

emission band and a bathochromic shift from 401 to 410 nm. Accordingly, quenching did not occur upon aggregation. This behavior is related to the *aggregation-induced enhanced emission (AIEE)* effect, which is probably due to the restriction of intramolecular rotations.[14] This effect was evident throughout the temperature range in which the gel was stable, since variation of the luminescence intensity was not observed until the transition to the sol state.

In an effort to confirm further the occurrence of this effect in this molecule, the influence of temperature was removed by studying the gel in cyclohexane, as this system has a particular behavior with temperature. Unless cooled to 0 °C, the 3 wt % solution of compound **CA9** in cyclohexane is stable at room temperature. Once the gel is formed at low temperature, however, it remains stable at room temperature. The luminescence properties for both sets of conditions are represented in Figure 6. The sol state presented an emission maximum at 401 nm. In the gel state, a slight red shift in the emission was observed (402.5 nm) together with a 3-fold intensity increase. The smaller blue shift of the maximum of the sol state with respect to the gel can be attributed to weaker intermolecular interactions in cyclohexane gels relative to the gel in dodecane. Indeed, it was necessary to decrease the conformational freedom of the molecule upon cooling to reinforce the intermolecular interactions that trigger the gelation process in cyclohexane.

In summary, it has been shown that through the appropriate conjugation to a polycatenar acid, the properties of the 1,6-diphenyl-3-hexen-1,5-diyne fluorophore are not only transmitted but enhanced in going from the molecule to the material. Indeed, the resulting molecular geometry of **CA9** makes it possible to address molecular self-assembly toward liquid-crystalline phases and organogels, which show intense luminescence. Further elaboration of this design and understanding of the formation of the different organizations may lead to functional soft materials with tailor-made columnar architectures.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic procedures, chemical compound information, XRD data (CIF and structural parameters of the mesophase and organogels), POM observations, and fluorescence studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by the MICINN (Projects MAT2009-14636-C03-01, CSD2006-00012, and CTQ-2007-61048), FEDER funding (EU), the Aragon Government, and Principado Asturias (Project IB08-088).

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