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New Platforms Integrating Ethynyl-Grafted Modules for Organogels and Mesomorphic Superstructures

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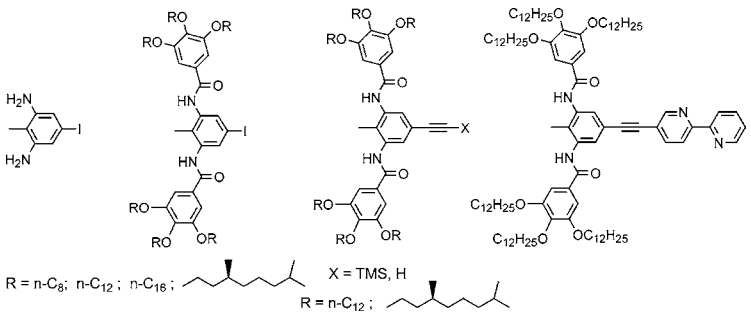
ABSTRACT



A methyldiacylaminophenyl core substituted with gallic derivatives and alkynyl functions has been synthesized from 2,6-diamino-4-iodotoluene. By heating the iodo and ethynyl molecules, typical columnar mesophases are observed and the C_{12} synthons bearing a protected terminal alkyne group gelified acetone, via the formation of interlocked fibers which are promoted by intermolecular hydrogen bonding.

The design and preparation of highly functionalized platforms for applications in material sciences, optoelectronics, electrochromism, light-emitting devices, and sensor chemistry is an important and topical area of research.[1] In addition to the potential applications of mesogenic nanostructures in display technology[2] and charge transport,[3] it appears that liquid crystalline phases in which molecules self-assemble into columnar superstructures recently led to the fabrication of efficient photovoltaic devices.[4] For this purpose, many flat molecules, so-called discoid mesogens (e.g., phthalocyanines, porphyrins, perylenes, dibenzopyrene, and hexa-substituted benzene derivatives), have been engineered to easily arrange in an axial stack in order to ensure charge transport along the column.[5] However, the shape of the molecules is not mandatory for the emergence of columnar mesophases. We recently found that nondiscoid compounds with tetrahedral cores or polycatenar or phasmidic scaffolds also provide columnar arrangements.[6,7]

The implementation of strong intermolecular attractive interactions provided by arene−arene stacking or hydrogen bonding strongly stabilizes mesophases but also favors the emergence of fibrous superstructures such as found in organo-gels. Hydrogen bonds are commonly responsible for solvent immobilization by organogelators[8] and to a lesser

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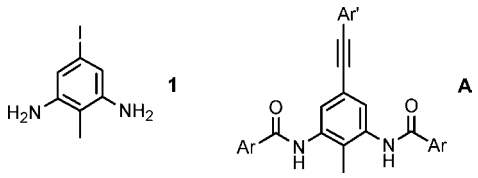
extent to water gelation by hydrogelators.[9] The main representatives of the hydrogen-bond-based gelators are the amide derivatives known to self-assemble into fiberlike structures forming three-dimensional networks.[10,11]

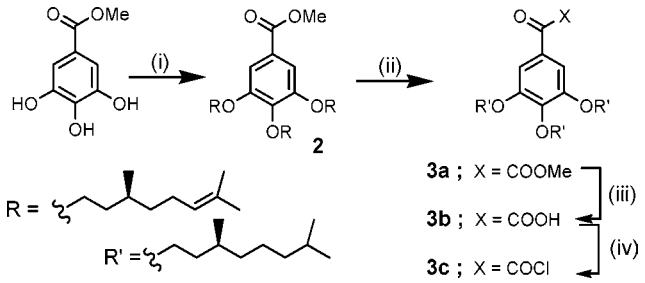
As a matter of fact, the difficulty to overcome in the engineering of such molecules able to achieve solvent gelation and to melt into a mesomorphic state is to find the balance between the tendency of the molecules to dissolve or to aggregate, to melt or to microsegregate into a noncrystalline state. One particular interesting area of investigation is to import within the molecules a chelating center able to interact with an incoming cation, metal salt, or other substrate. The construction of such molecules is dependent on the availability of key building blocks that implement the hydrogen-bonding vectors, the flexible and rigid parts, as well as a function able to be activated under mild conditions to provide the conjugated ligand. Our own experience with conjugated molecular systems allowed us to target molecules featuring easily activable functional groups such as iodine and capable of reacting in the presence of low-valent palladium(0).[12] Among such pivotal starting materials, we sought to develop the preparation of a tetrasubstituted phenyl ring **1** that provides the prerequisite to construct molecules **A** integrating two secondary amides and alkynyl-substituted bipyridine fragments. Recently, one-dimensional organic nanostructures were engineered in solution or self-assembled on the gold surface from hexa-substituted phenyl rings incorporating three amido and three ether or ethynyl functions.[13]



Access to such platforms first requires producing the key starting materials **1**. Reduction of 2,6-dinitro-4-iodotoluene[14] by unstabilized HI[15] gave the desired compound in 91% yield. This path allows the production of large quantities of the novel and chemically stable derivative **1**.

The synthesis of the phenyl rings carrying the paraffin chains required the alkylation of the methyl ester of gallic acid with the alkyl bromide as depicted in Scheme 1 for the (*S*)-(+)-citronellyl derivative. Saponification provides the corresponding acids that are converted to the acid chloride by reaction with neat $SOCl_2$ (Scheme 1). The C_8, C_{12}, and C_{16} derivatives were produced in a similar way.[16]

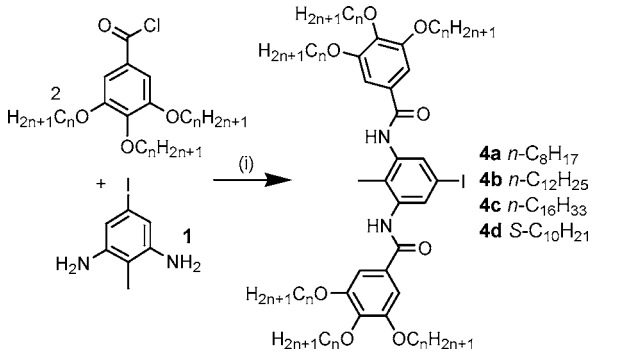
Scheme 1[a]



[a] Key: (i) (*S*)-(+)-citronellylbromide, Na_2CO_3, CH_3CN, reflux, 27%; (ii) H_2 (40 Bar), Pd/C, 89%; (iii) KOH, EtOH/H_2O, reflux, 90%; (iv) $SOCl_2$, quantitative.

With this viable protocol in hand, we turned our attention toward the condensation of these derivatives with the diamino compound **1** (Scheme 2). Utilizing an anhydrous acetone solution and dry Na_2CO_3, the target iodo platforms **4a**−**d** were isolated in good yields.

Scheme 2[a]



[a] Key: (i) Na_2CO_3, acetone, 27% for **4a**, 86% for **4b**, 76% for **4c**, and 33% for **4d**.

Next, we chose to investigate the coupling of these iodo molecules with a variety of terminal acetylenes in THF using diisopropylamine to quench the nascent acid. We first targeted trimethylsilylacetylene, and we were able to produced the ethynyl grafted molecules **5a** and **5b** in good yields (73−83%) using a Pd-promoted cross-coupling reaction. Deprotection of the alkynes is straightforward in the presence of KF/methanol or NaOH/methanol and afforded **6a** and **6b** in good yields (Scheme 3).

We then decided to probe the cross-coupling reaction in a stoichoimetric ratio with 5-ethynyl-2,2′-bipyridine or 5,5′-diethynyl-2,2′-bipyridine[12b] with molecule **4b** in order to form molecules bearing donor sites for the chelation of potentially

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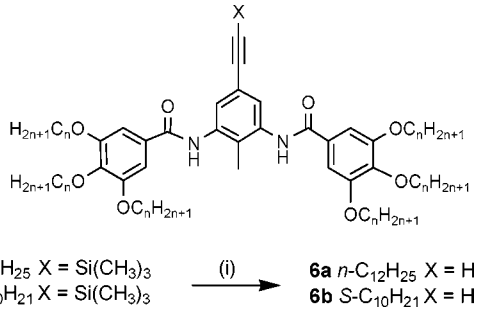
Scheme 3[a]

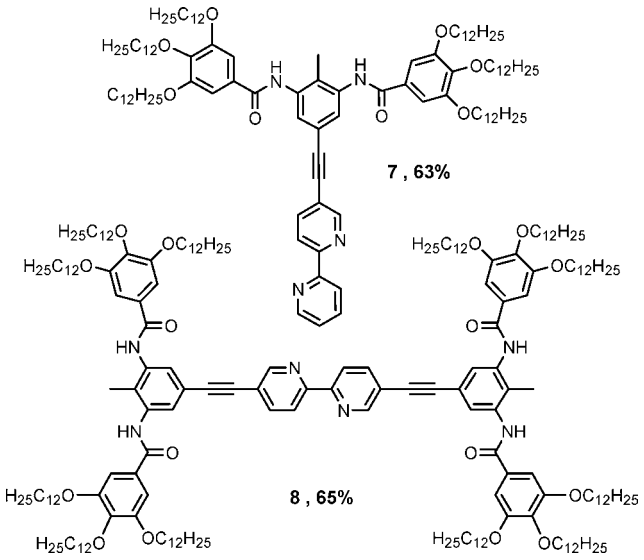


5a *n*-$C_{12}H_{25}$ X = $Si(CH_3)_3$
5b *S*-$C_{10}H_{21}$ X = $Si(CH_3)_3$
(i) →
6a *n*-$C_{12}H_{25}$ X = H
6b *S*-$C_{10}H_{21}$ X = H

[a] Key: (i) KF (for **6a**, 62%) or NaOH (for **6b**, 80%), MeOH.

luminescent transition metals. In the initial studies, the cross-coupling in the presence of $[Pd^0(PPh_3)_4]$ at 60 °C failed due to a very efficient oxidative homocoupling reaction of the terminal alkyne providing the butadiyne derivatives. After some experimentation, the most suitable method we found involves the use of $[Pd^{II}(PPh_3)_2Cl_2]$ and CuI as reducing agent at rt, providing ligand **7** in fair yields (Scheme 4).

Scheme 4



During the preparation of **8**, it was soon established by thin-layer chromatography that the monosubstituted derivatives are preferentially formed at the early stage of the reaction and a steady-state concentration of this compound is always present. The isolation of this monosubstituted derivative is not targeted in this context but is auspicious for the potential engineering of dissymmetric molecules bearing different polarized vectors.

The thermal and polymorphic behavior of iodo and ethynyl platforms was investigated by thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), and polarized optical microscopy (POM). From TGA analyses, except for **6a** and **6b** which decompose above the clearing point at 200 and 218 °C, respectively, all of the compounds were found to be stable up to 260 °C. DSC analyses shows that compounds exhibit reversible first-order thermal transitions after heating to the isotropic melt. Their phase behavior is summarized in Table 1. The liquid−crystalline behavior of the functionalized platforms was probed by the observation of optical textures showing homogeneous, birefringent, and

Table 1.

compd	T (°C), ΔH (J g^{-1})[a]
4a	Cr 172 (18.6) Col dec > 255.0
4b	Cr 95 (35.2) Col_1 159 (10.4) Col_2 236 (11.3) I
4c	Cr 95 (61.8) Col_1 154 (7.7) Col_2 215 (8.4) I
4d	Cr < −50 Col 256 (26.2) I
5a	Cr 82 (24.2) Col 203 (14.3) I
5b	Cr 174 (23.1) Col 185 (9.8) I
6a[b]	Cr 94 (41.7) Col_1 183 (13.9) Col_2 200 (5.7) I
6b[b]	Cr 122 (19.8) Col 218 (13.3) I
7	Cr 86 (29.3) Col_1 177 (19.7) Col_2 210 (5.5) I
8	Cr 94 (12.4) Col dec > 289.5

[a] Transition temperature (T) and enthalpies ΔH associated to each transition are given in parentheses, dec = decomposition temperature. [b] Transition temperature and enthalpy values obtained on the first heating curve.

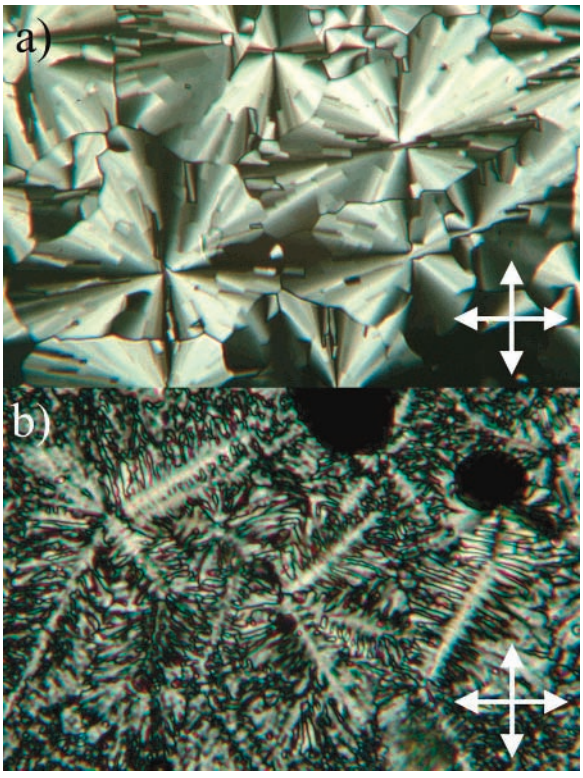


Figure 1. Liquid crystalline compounds viewed by optical microscopy under crossed-polarizers (symbolized by the cross in the corner of the picture): (a) compound **4c** at 203 °C and (b) compound **5a** at 199 °C.

fluid domains. The optical texture observed upon slow cooling from the isotropic melt clearly show the existence of columnar phase associated with the appearance of the pseudo focal-conic-like patterns for **4c** or dendritic texture for **5a** (Figure 1).[17] The described platforms are mesomorphic and one can note that compound **4d** is liquid crystal from room temperature to 256 °C. X-ray experiments are currently under progress in order to determine the exact symmetries of these columnar phases.

The presence of amide tethers on these ambipolar structures led us to probe the gelation ability of molecules **5a** and **5b**. Compound **5a** displayed gelation abilities in acetone with a minimum gelation concentration (MGC) of 1.4 g·L^{-1} (Figure 2a), whereas compound **5b** is soluble in acetone in this range of concentrations (Figure 2b). Turbid gels were formed in acetone at 25 °C after the hot and homogeneous fluid solution of **5a** was cooled. The sol to gel phase transitions are thermally reversible.

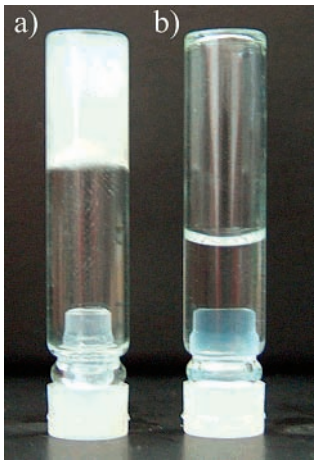


Figure 2. Gelation test in acetone: (a) **5a** (2.4 gL^{-1}) and (b) **5b** (11.0 gL^{-1}). Gel formation is confirmed by observing that the sample does not flow when the test tube is inverted. Upon cooling below the temperature of gelation, the complete volume of solvent is immobilized and can support its own weight without collapsing.

SEM experiments were used to examine the morphology of the formed gels. Images obtained from a diluted gel of compound **5a** in acetone (1.25 g L^{-1}) freeze-dried onto silicon wafer reveals the presence of a 3D network of interlocked bundle of fibers with an average diameter of ~150 nm extending over several tens of micrometers (Figure 3). It is likely that the formation of a 3D network of interlocked fiberlike aggregates is responsible for the gelation of acetone. The width of the fibers is large compared to the dimension of the molecule. Therefore, the observed fibers correspond to the bundle of smaller elongated molecular assemblies.

The formation of elongated fiberlike aggregates indicates that the self-assembly of compound **5a** is driven by strong

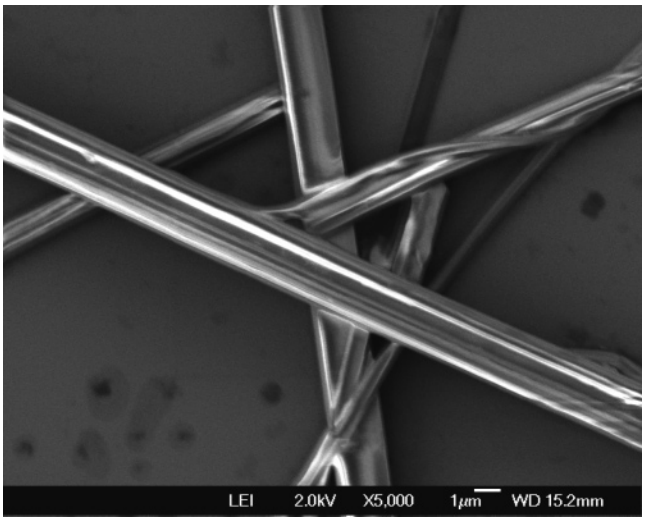


Figure 3. SEM picture of a freeze-dried gel from compound **5a** in acetone (1.25 g L^{-1}) deposited on silicon wafer showing the presence of interlocked bundle of fiber.

directional intermolecular interactions. To ascertain whether H-bonding plays a role in the formation of the observed fibers, infrared spectroscopy was performed in these gels. Single C═O and NH stretching vibrations were observed for compound **5a**, respectively, at 1638 and 3413 cm^{-1} in the gelated state. These spectroscopic data are an unambiguous signature of hydrogen-bonded amides inducing a hydrogen bonded network,[18] in line with the aggregation of the platform into elongated fibers. It is also surmised that $\pi-\pi$ interaction of the phenyl subunits might add additional stabilization interactions.

In conclusion, we have been able to prepare new segmented compounds bearing a controlled number of interconnected fragments by a rational approach, using transition-metal-catalyzed coupling reactions. In preliminary experiments it has been observed that these compounds may be used successfully as solvent gelators and for the emergence of columnar nanostructures. The next phase of this work is to complex the empty coordination sites in a controlled manner with specific transition metal salts and to study their properties in the gels or mesophases. It is foreseen that the triple bond will serve as an efficient conduit for shuttling information and the amide will stabilize the supramolecular edifice via hydrogen bonding. Future investigations will be tailored toward applications in material science.

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Supporting Information Available: Experimental procedures and characterization for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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