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Tris(triazolyl)triazine via Click-Chemistry: A C_3 Electron-Deficient Core with Liquid Crystalline and Luminescent Properties

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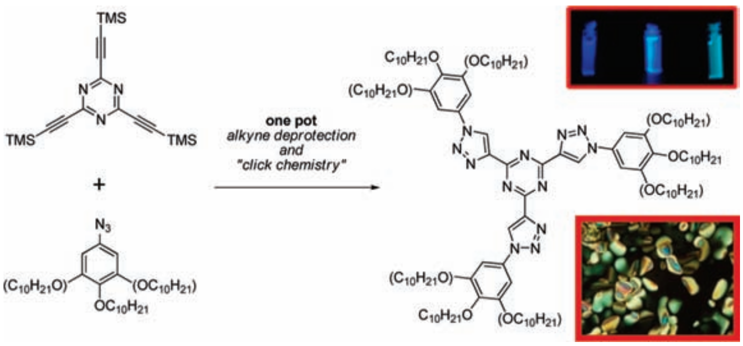
ABSTRACT



The synthesis of a novel core based on tris(triazolyl)triazine has been accomplished by a one-pot procedure that combines a 3-fold deprotection of alkyne groups and "click chemistry" of the aromatic alkyne and azide precursors. The procedure is straightforward for the preparation of functional materials for organic electronics. Indeed, compounds with low reduction potential are obtained. These compounds also show liquid crystalline behavior, displaying columnar mesophases at room temperature, and are luminescent in the visible region both in solution and in thin films.

Since the first report of the Cu(I)-catalyzed 1,3-dipolar cycloaddition of azides to alkynes,[1] a "click-chemistry" reaction, the number of applications has grown dramatically to cover a wide range of fields from synthetic chemistry to biomedicine and materials science.[2] Reactions proceed regioselectively and give high yields in reasonable reaction times and with tolerance to a large number of functional groups. Most of these cycloaddition reactions involve aliphatic azides and terminal alkynes, with less evidence for the use of aromatic azide precursors.[2a,3] Exploitation of aromatic click-chemistry opens up the path to novel organic conjugated systems for organic electronics. We have focused our attention on the versatile 1,3,5-triazine scaffold as it could be triply functionalized with triazole rings by click-chemistry to give the C_3-symmetrical system 2,4,6-tris(triazolyl)-1,3,5-triazine (TTT). This azaheterocyclic core, to the best of our knowledge, has not been reported to date and the structure consists of a highly electron-deficient system that could be

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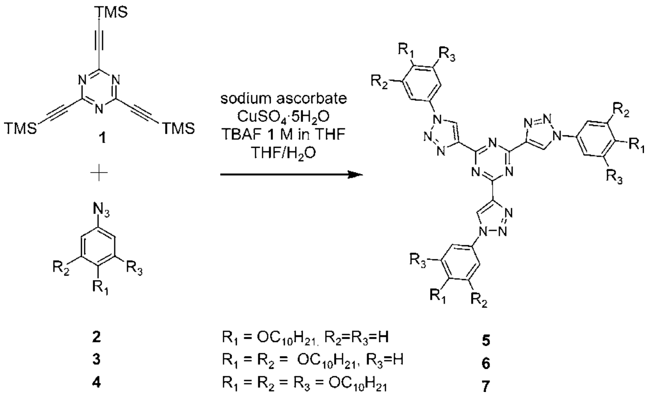
of interest for n-type organic semiconductors.[4] Furthermore, extension of the conjugation of the new heterocyclic core with aromatic rings should give molecules with luminescent properties.[5] Moreover, this core shows clear potential for multifunctional materials. Indeed, appropriate substitution at the periphery of the molecules can provide access to novel discotic liquid crystals, which are interesting from the point of view of their one-dimensional self-organizing ability. Disc-like aromatic compounds that form columnar liquid crystals have great potential in the field of organic semiconductors due to the overlap of π-orbitals, which results in uniaxial charge carrier mobility with performances approaching those of conjugated polymers.[6]

Scheme 1. Synthesis of TTT Compounds **5−7**



The work reported here involved the straightforward synthesis of TTT derivatives and the study of their liquid crystalline, optical, and redox properties. Aromatic azides and the precursor 2,4,6-tris(ethynyl)-1,3,5-triazine are required for the synthesis of the TTT core by click-chemistry (Scheme 1). The latter compound is quite unstable and, for this reason, we prepared and stored the corresponding TMS-protected compound, 2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine (**1**).[7]

The orthogonality of click-chemistry, which allows multiple chemical transformations to occur in solution without interference,[8] enables the click cycloaddition of aliphatic azides to alkyne monomers to occur at the same time as alkyne deprotection.[9] Taking advantage of this feature, we tested a one-pot reaction in which the alkyne groups of intermediate **1** are triply deprotected and made to react in situ with the corresponding aromatic azide **2−4** in the presence of catalytic Cu(I) (Scheme 1). The reactions were carried out at room temperature to give the TTT derivatives **5−7** in moderate yields (45−51%). The ^{1}H NMR spectra of **5−7** display one singlet for the proton of the heterocyclic rings at about 9.17 ppm, which is consistent with the formation of 1,4-disubstituted triazole rings.

All TTT compounds exhibit liquid crystalline behavior (Table 1, Figure 1) and are thermally stable above their clearing point according to thermogravimetric analysis. **6** and **7** display textures that are typical of hexagonal columnar phases (Col$_h$) by polarized optical microscopy (Figures 1b,c). **5** does not show a characteristic texture in pure state (Figure 1a), but a Col$_h$ mesophase is displayed in miscibility tests with **6**. The X-ray diffraction patterns only show a sharp maximum in the low-angle region in all cases. Although this pattern does not unambiguously confirm the hexagonal symmetry of the mesophase, it rules out other columnar symmetries like rectangular or oblique phases. Similar behavior has also been found in other structures previously described as hexagonal columnar phases,[10] and it is due to a minimum in the form factor, which precludes the observation of peaks in this angle region.

5 has only three lateral chains and displays a monotropic columnar mesophase, which is quite unusual.[6b] The as-obtained product is a crystalline solid at room temperature and this melts to an isotropic liquid at 150 °C. On cooling, the compound does not crystallize but becomes glassy, and depending on the cooling rate, a mesophase starts growing at 123 °C (broad peak with maximum at 107 °C, Figure 1a). In the second heating process there is a cold recrystallization at 120 °C, with the material again becoming crystalline above this temperature until the melting point. An X-ray diffraction study was performed on a sample cooled from the isotropic liquid and slowly allowed to reach room temperature. Only a maximum at low angles and a diffuse halo at wide angles were observed. Assuming that the low-angle maximum should correspond to the d(10) reflection of a hexagonal arrangement gives rise to a cell parameter (a) of 35.6 Å.

6, which contains six n-decyloxy terminal chains, showed a mesophase with homeotropic and birrefringent domains (Figure 1b). Only one peak was observed in the DSC thermograms both on heating and cooling, indicating that the mesophase is thermodynamically stable at room temperature. The X-ray diffraction analysis is consistent with a hexagonal columnar mesomorphism (Col$_h$) that has a cell parameter of 37.2 Å. Additionally, in the wide-angle region a diffuse halo at 4.5 Å typical of the liquid-like order between the aliphatic chains and a relatively narrow diffuse ring at 3.5 Å are observed. In partially oriented patterns, this latter

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Table 1. Thermal Properties, X-ray Diffraction Data, and Optical Properties for **5**−**7**

compd	phase transition[a] temp (°C) and enthalpies (kJ mol^{-1})	a (Å)[b]	c (Å)[b]	λ_{abs}^{THF} (nm) (log ε)	λ_{em}^{THF} (nm)[c]	λ_{em}^{bulk} (nm)[c]	Φ[d]
5	I 107 (2.1) Col$_h$ 50 g g 55 Col$_h$ 120 (−16.9)[e] Cr 150 (26.1) I	35.6		257 (4.33), 289 (4.47), 299^{sh}	416	416	0.35
6	I 185 (4.0) Col$_h$ 18 g g 28 Col$_h$ 194 (5.3) I	37.2	3.5	264 (4.69), 304 (4.62)	448	450	0.43
7	I 172 (10.6) Col$_h$ 18 g g 23 Col$_h$ 183 (10.6) I	32.9	3.5	266 (4.62), 301 (4.63)	471	481	0.18

[a] DSC data for first cooling and second heating processes, 10 deg/min, peak temperatures, I = isotropic liquid, Col$_h$ = hexagonal columnar mesophase, g = glass transition, Cr = crystal. [b] Hexagonal cell parameters. [c] Excitation wavelength at 300 nm. [d] Quantum yields in cyclohexane solutions relative to diphenylanthracene (Φ = 0.9 in cyclohexane solution).[11] [e] Cold crystallization.

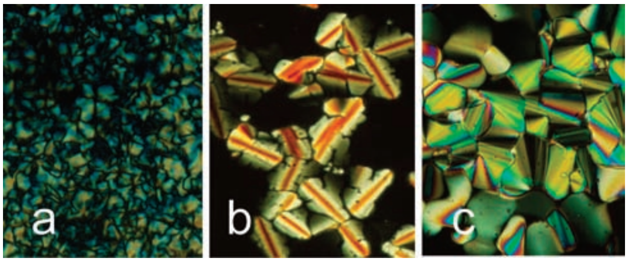

Figure 1. Polarized optical photomicrographs of mesophases for **5** at 92 °C (a), **6** at 25 °C (b), and **7** at 145 °C (c).

reflection is reinforced along the column axis, which is indicative of the periodic stacking of the cores at a mean distance of 3.5 Å, typical of π-stacked systems.

7, which contains nine *n*-decyloxy peripheral chains, also exhibits a hexagonal columnar mesophase that is stable at room temperature, with a cell parameter of 32.9 Å and a stacking distance of 3.5 Å.

It can be seen from the results in Table 1 that the cell parameter of the hexagonal lattice (a) increases from **5** to **6**, but decreases in **7**. This is unexpected given the increasing size of the individual molecules (from three peripheral chains to nine) but it can be explained in terms of the number of molecules per unit cell, Z. Indeed, a reasonable density value in the range 0.9−1.1 g·cm^{-3} is obtained if we consider two molecules per unit cell (Z = 2) for **5** and **6**. In both cases, the column must consist of stacked discs formed by two TTT molecules. However, for **7**, the Z value calculated corresponds to one molecule per unit cell and a density value of 0.9 g·cm^{-3} (Table S1, SI). These findings can be accounted for by the strong tendency of the triazine core to give columnar assemblies regardless of the number of surrounding flexible tails. Three or six tails are not sufficient to fill efficiently the space around the column and this is overcome by the stacking of pairs of molecules in **5** and **6**. For **7**, nine peripheral tails efficiently fill the space around the column and stabilize a columnar mesophase with only one molecule per stacking unit.[10c]

The UV−vis absorption and photoluminescence of **5**−**7** were measured in tetrahydrofuran (THF) solutions. The results are summarized in Table 1. The maximum absorption wavelengths are located in the UV region, at around 300 nm, and are attributed to $\pi-\pi^*$ transitions due to the high absorption coefficients. All TTT compounds are luminescent, emitting in the blue-green part of the visible spectrum (Figure 2 and abstract figure). A remarkable red-shift in the emission maximum is observed as the number of peripheral alkoxy chains increases. The compounds also show luminescence in thin films at room temperature with emission wavelengths similar to those of the solutions. The large Stokes shifts are consistent with a strong charge transfer character and/or a conformational relaxation in the excited state, of higher polarity when increasing the number of alkoxy chains. This trend has also been observed in other luminescent mesogens.[10b]

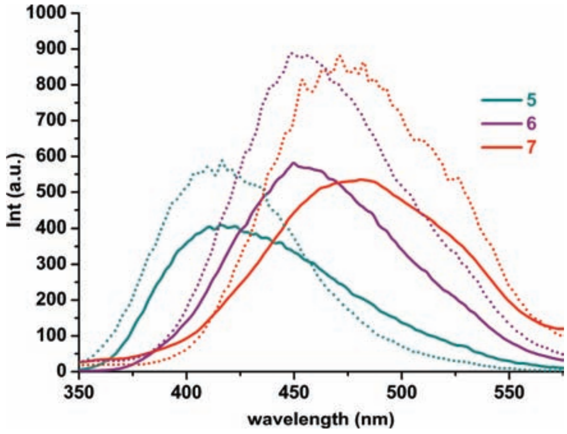

Figure 2. Emission spectra of **5**−**7** in THF solution (dashed lines) and thin films at rt (solid lines).

Discotic aromatic compounds that form columnar liquid crystals have great potential in the field of organic electronics

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Table 2. Cyclic Voltammetry results for **5**−**7**

compd	E_{red} (V)[a]	$E^{\mathrm{opt}}_{\mathrm{sol}}$ (eV)[c]	LUMO (eV)
5	−1.28, −2.24[b]	3.66	−3.52
6	−1.33, −2.15[b]	3.50	−3.47
7	−1.33	3.53	−3.47

[a] $E_{1/2}$ reduction potentials. [b] E_{p} of the irreversible process. [c] Calculated from solution absorption edges.

as one-dimensional semiconductors.[5] In particular, columnar liquid crystals with nitrogenated aromatic cores have an electron-accepting character for which n-type semiconducting properties have been described.[4,12] In this respect, TTT compounds should be reasonably good electron-accepting molecules since the introduction of the three triazole rings should increase further the electron-deficient nature of the triazine ring.[13] The redox behavior of the TTT compounds was studied by cyclic voltammetry in oxygen-free dichloromethane solutions. All potentials are referenced against ferrocene/ferrocenium (FOC) as the internal standard (Table 2). **5**−**7** did not show any oxidation process at positive potentials from 0 to +2.2 V. However, **5** showed a reversible reduction process at a half-wave potential of −1.28 V. In addition, an irreversible reduction process was found at −2.24 V. **6** showed the same behavior, with reversible and irreversible reduction processes (−1.33 and −2.15 V, respectively). In contrast, only one reversible reduction process was found, at a half-wave potential of −1.33 V, for **7**. Under the premise that the energy level of ferrocene/ferrocenium is 4.8 eV below vacuum level,[14]we obtained the LUMO energy levels as the difference between −4.8 eV and E_{red} (eV). Thus, LUMO energy levels of −3.52 eV for **5** and −3.47 eV for **6** and **7** were calculated from the first reduction potentials. These reduction potentials and LUMO values are consistent with an enhancement of the electron-deficient nature of the aromatic core due to the presence of the triazolyl rings. Other triazine derivatives have been reported to show higher reduction potentials,[13] for example, 2,4,6-triphenyl-1,3,5-triazine shows a reversible reduction potential at −2.09 V vs FOC and this corresponds to a LUMO energy of −2.71 eV.[13a]

It is interesting to note that the LUMO values obtained are also considerably lower than that of tris(8-hydroxyquinoline)aluminum (Alq$_3$), the most commonly used molecular electron-transport hole-blocking material for OLEDs (E_{LUMO}(Alq$_3$) = −2.9 eV),[15] and similar to those of other well-known electron-accepting materials.[16] Consequently, promising characteristics for electron injection from standard cathode metals such as magnesium−silver alloy (work function of Mg = −3.7 eV)[15] can be envisaged for these materials.

In summary, novel electron-deficient organic compounds can be prepared by a straightforward synthesis through click-chemistry. The materials show good liquid crystalline properties, exhibiting ordered columnar mesophases. TTT compounds also show luminescence from the blue to green region of the visible spectrum depending on the peripheral substitution. Electrochemical measurements confirmed the electron-deficient nature of this class of compounds and their potential for electron transport. Further studies on these molecules for multifunctional materials are in progress.

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Supporting Information Available: Detailed experimental procedures and characterization data, and X-ray diffractograms with tabulated data, UV−vis absorption spectra, and CV plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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