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A new form of discotic metallomesogens: the synthesis of metal-bridged triphenylene discotic dimers

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Preliminary communication

A new form of discotic metallomesogens: the synthesis of metal-bridged triphenylene discotic dimers

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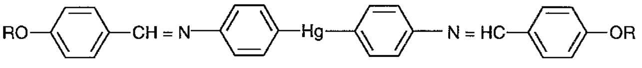
Discotic metallomesogens are becoming increasingly important due to their electronic and optoelectronic properties. Preliminary results on the synthesis and characterization of a new form of discotic metallomesogens in which a Hg atom is covalently linked with two substituted triphenylene moieties are presented.

Liquid crystalline compounds incorporating metal atoms are now commonly known as metallomesogens. Like pure organic materials, they exhibit various mesophases such as, nematic, smectic, columnar, cubic, etc. As the introduction of a metal into liquid crystal compounds may induce novel properties, interest is growing in the field of metallomesogens. The chemistry and physics of metallomesogens have recently been described in several review articles [1–4].

Metallomesogens are known to form both calamitic (rod-like) and discotic (disc-like) architectures. A majority of these compounds are coordination complexes and only a few are organometallic complexes. Symmetrical linear mercury(II) derivatives where the mercury atom is covalently linked with two phenyl groups (structure below) were described by Vorlander in 1923 [5]. These symmetrical, as well as non-symmetrical, mercury complexes were reported to form smectic phases [3, 5]. Formation of a smectic A mesophase was also observed in bis(*p-n*-hexyloxyphenyl)mercury [6]. Substituted biphenyls connected by a mercury atom were reported by Chandrasekhar but their mesophases could not be characterized due to chemical instability [7]. The synthesis and characterization of chiral smectic C* mesophases of azoxymercury complexes has also been reported recently [8]. Organometallic compounds possessing a direct metal–carbon bond have been considered chemically and thermally unstable; however, it is known that the metal–alkynyl linkage is significantly more stable [3]. Several new series of liquid crystalline materials covalently linked with various metals such as palladium, platinum, gold, etc., have appeared in the literature [3, 9].



While various metal-bridged dimers of calamitic molecules are documented in the literature, there has so far been no example in which the metal is covalently linked with two discotic moieties. Here, we report the first examples of organometallic discotic liquid crystals in which a mercury atom is located between two substituted triphenylene molecules.

The synthesis of bis-(penta-alkoxy triphenylene-ethynyl)-mercury complexes is outlined in the scheme.

The key precursor monobromo-penta-alkoxytriphenylene **1** can be prepared by two methods: (1) from monohydroxy-penta-alkoxytriphenylene via the reduction of the phenolic group by activation with a tetrazole unit followed by catalytic hydrogenation [10], or (2) via the biphenyl route using the oxidative coupling of a tetra-alkoxybiphenyl with alkoxybromobenzene [10, 11]. Compound **1a** was prepared by route 1 as reported by us previously [10] while compound **1b** was prepared using the biphenyl route. Palladium-copper catalysed alkynylation of **1a** and **1b** with 2-methyl-3-butyn-2-ol followed by hydrolysis yielded acetylenes **2a** and **2b** in high yields. The mercuric salts were prepared by adding 2 equivalents of alkaline mercuric iodide to a cold solution of acetylene (**2a** or **2b**) in ether-ethanol [12]. The resultant precipitate was filtered and washed with ethanol and ether. The solid product was dissolved in chloroform and filtered through a $0.2\,\mu$ syringe filter. Solvent was removed under vacuum and the product

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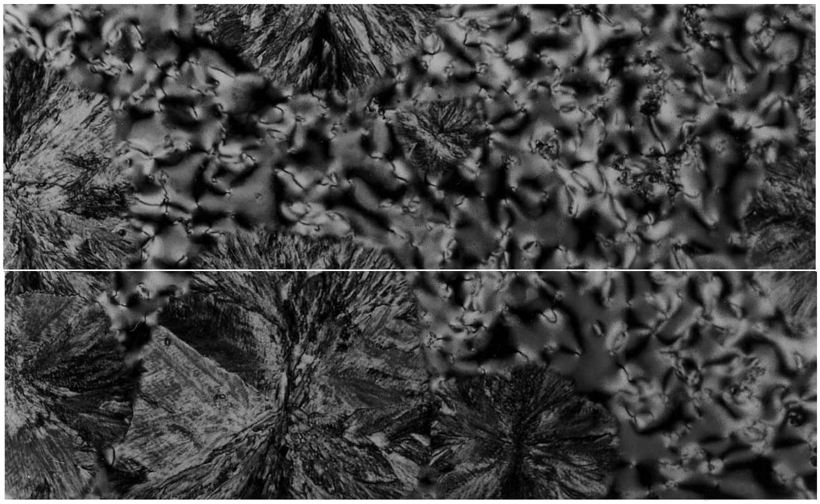
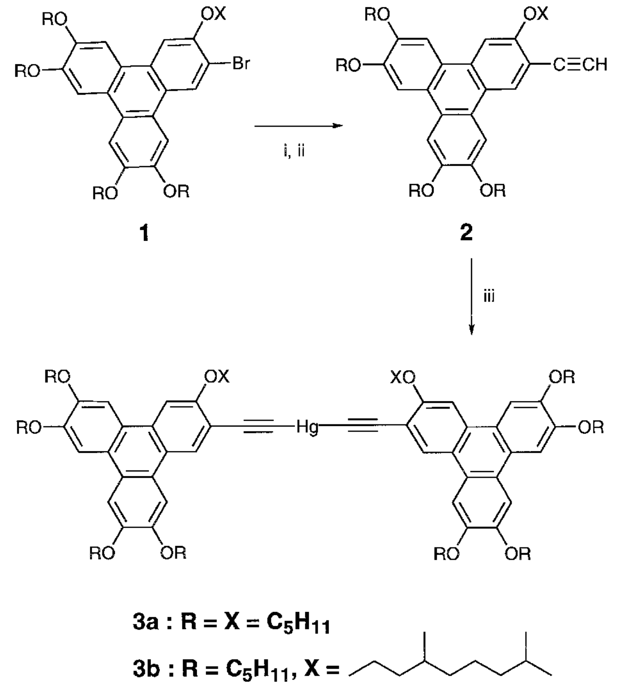


Figure. Optical textures of compound **3b** obtained on cooling from the isotropic liquid at 185°C (crossed polarizers, magnification × 100).



Scheme. Reagents and conditions: (i) 2-methyl-3-butyn-2-ol, $PdCl_2$ $(PPh_3)_2$, CuI, Et_3N, 60–70°C, 15 h; (ii) KOH, toluene, reflux, 1 h; (iii) K_2HgI_4, KOH, EtOH-H_2O.

suspended in ether; it was filtered, washed with ether and dried in vacuum.

3a: MS (FAB): *m/z* 1564.8. ^{1}H NMR ($CDCl_3$): δ 8.59, s, 2H; 7.84, m, 10H; 4.27, m, 20H; 1.96, m, 20H; 1.5, m, 40H; 0.97, m, 30H. IR (KBr): $V_{\max}$ 2800, 2125, 1655, 1560, 1541, 1508, 1425, 1263, 1170 cm^{-1}.

3b: MS (FAB): *m/z* 1704.3. ^{1}H NMR ($CDCl_3$): δ 8.57, s, 2H; 7.84, m, 10H; 4.3, m, 20H; 1.96, m, 20H; 1.5, m, 48H; 0.98, m, 42H. ^{13}C NMR ($CDCl_3$): 158.0, 150.2, 149.5, 148.9, 148.8, 130.5, 129.5, 126.2, 125.4, 125.0, 123.3, 122.9, 122.7, 111.4, 108.0, 107.4, 106.8, 106.2, 104.4, 102.9, 69.8, 69.4, 69.2, 67.7, 39.3, 37.4, 36.1, 30.2, 29.1, 29.0, 28.3, 28.0, 24.8, 22.7, 22.6, 22.5, 20.0 and 14.1.

The thermal behaviour of both dimers was investigated using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope, as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). The crystalline compound **3a** transforms into a highly viscous but shearable fluid phase at about 150°C. On further heating, this mesophase changes to an isotropic phase at about 210°C, but with decomposition. In order to reduce the isotropic temperature, we replaced one of the normal alkyl chains by a branched chain (compound **3b**). This complex on first heating shows a solid to solid transition at about 110°C (peak temperature in the DSC run, $\Delta H = 10.6$ kJ mol^{-1}) and this soft solid transforms into the isotropic phase at 186°C ($\Delta H = 10.9$ kJ mol^{-1}). On cooling the isotropic phase, a metastable nematic discotic phase appears at 185°C. This monotropic mesophase has a high crystallization tendency which starts in the mesophase and is complete at 180°C. On subsequent heating, the first transition at 110°C is not observed and the crystals melt to isotropic liquid at 186°C. The formation of the nematic phase and crystals can be clearly seen in the photomicrograph (see the figure) taken at 185°C on cooling from the isotropic liquid. As mercury compounds strongly absorb X-rays [13], we could not perform X-ray studies on these materials.

In conclusion, we here report the first two examples of discotic liquid crystalline metal complexes in which a Hg atom is covalently linked with two substituted triphenylene molecules. The synthesis of various stable, enantiotropic, discotic mercury complexes is in progress.

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