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Preliminary communication

Iodo-substituted triphenylene-based discogens: by metal-mediated oxidative cross-coupling

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New monoiodopentakis(alkoxy)triphenylene derivatives were synthesized and characterized. The metal-mediated oxidative coupling of 2-iodoalkoxybenzene with 3,3′,4,4′-tetraalkoxybiphenyl by $MoCl_5$ as oxidizing reagent yields 2-iodopentakis(alkoxy)triphenylene. These products were purified by repeated column chromatography; their liquid crystalline properties were studied by polarizing optical microscopy and differential scanning calorimetry. All the derivatives exhibit a columnar mesophase over a wide temperature range.

Triphenylene (TP) based organic materials [1] have been studied for various applications, e.g. photoconductors, electroluminescence, as hole- and electron-transporting materials in organic light-emitting diodes, photovoltaic cells, gas sensors and optical data storage materials [2] and for their ferroelectric switching properties [3]. The first commercial application has been developed by Fuji Photo Film Co, Japan, in the form of a phase-compensation film from a photopolymerized triphenylene-based discotic nematic liquid crystal, used to improve the viewing angle of a twisted nematic liquid crystal [4]. We suggest that triphenylene-based discotic liquid crystals (TP DLCs) will show great application potential in forthcoming organic electronic devices. A variety of mesophases has been obtained by structural modifications of TP, such as fluoroalkoxy side chains and branched side chain combinations of alkoxy–thioethers, ether–ester and mixed alkoxy–alkoxy [5].

Oxidative trimerization of 1,2-dimethoxybenzene was used to form hexamethoxy-TP in concentrated sulfuric acid using chloranil or Iron(III)chloride as oxidizing agent. This is a multistep process for the synthesis of TP DLCs having long alkyl chains. The Ringsdorf group, using 70% H_2SO_4 at 80°C, achieved hexasubstituted TP in about 20% yield. Later, the Boden group reported direct synthesis of symmetrical hexasubstituted TP exhibiting liquid crystalline behaviour using $FeCl_3$ as oxidizing agent in a catalytic amount of H_2SO_4, in moderate to good yield [6]. Recently, the Kumar group has reported a highly improved synthesis of TP DLCs using $MoCl_5$ and $VOCl_3$ as oxidant in excellent yield [7]. These reactions are the exceptional case of the Scholl reaction where more than one aryl–aryl bond are formed. This is noteworthy since both the classical trimerization of substituted benzene as well as the biphenyl route to functionalized TP required electron-rich starting materials. The direct cross-coupling reaction using oxidizing reagents provides a method for creating C–C bond formation. Aryl halides can be dehalogenated by a Lewis acid. This reaction is more successful if the aromatic core contains iodine, and is accomplished by various reducing agents [8]. Since iodo substituents offer straightforward introduction of various functionalities, an electronegative iodo moiety allows a number of functional groups to interchange reactions, opening up further variations in the molecular structure. Direct synthesis of monofunctionalized hexasubstituted TP with distortion of its planar geometry is yet to be explored. This is an extremely important precursor for the synthesis of dimers, oligomers and polymers, and represents a valuable precursor in the molecular engineering of TP DLCs [9].

Only a few examples of 2-bromopentakis(alkoxy)triphenylene have so far been reported [10]. Our keen interest is to replace the bromo (covalent radius 1.14 Å) functional group by an iodo group having a large covalent radius (1.33 Å) to obtain TP-I, and to study the effect on molecular geometry and mesomorphism. Our continued search has now led to the synthesis of iodo-substituted triphenylene without cleavage of the iodine

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moiety. Here we describe the efficient synthesis of novel 2-iodopentakis(alkoxy)triphenylene (TP-I) derivatives and the study of their liquid crystalline properties. We have discovered that $MoCl_5$ is a milder reagent for the cross-coupling reactions of 3,3′,4,4′-tetraalkoxybiphenyl with 2-iodoalkoxybenzene to yield TP-I. Synthesis of the compounds is outlined in scheme 1.

The mesomorphic behaviour of unsymmetrical monofunctionalized triphenylene prepared in this work exhibits a columnar (Col) phase over a wide temperature range. Optical microscopy shows classical focal-conic fan texture of the columnar mesophase, which is probably hexagonal. These classical fan textures of the Col mesophase of the compound **TP-I(c)** can be seen in figures 1 and 2. Compound TP-I exhibits only the Col mesophase, whereas the bromo-substituted TP shows Col_x and Col_h mesophases, as reported previously [10c].

The melting points of the corresponding alkoxy substitutions decrease significantly with decreasing chain length. However, the DSC scanning peaks for the transition are reasonably sharp for the Col mesophase, indicating a high degree of purity for the compounds. There is no tendency for decomposition during the heating and cooling cycles, which are reproducible, as shown in figure 3.

The decreasing electronegativity with increasing covalent radius of the halogen substituents led to increasing melting transition temperature with decreasing chain length, but there was little effect on the clearing transition temperature. On cooling, the isotropic to mesophase transition temperature was lower. However, this suggested that the aliphatic side chains of a minimum length were necessary to reduce core–core interaction, and induced enough flexibility into the molecular core to decrease $\pi-\pi$ interaction sufficiently for the formation of the higher ordered Col mesophase.

The synthesis reaction took place under mild conditions in a very short time at room temperature. In a

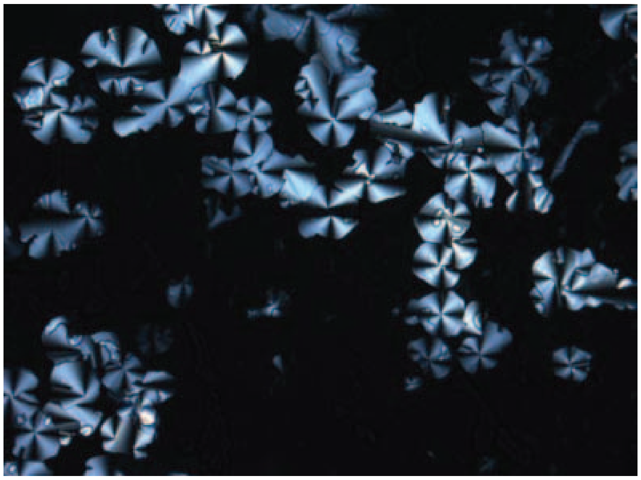


Figure 1. Classical fan texture of the Col mesophase of the compound **TP-I(c)** at 126°C on cooling from the isotropic (200 ×).

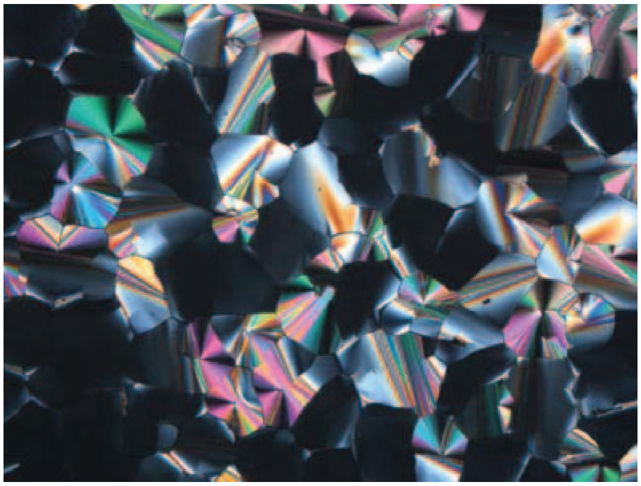
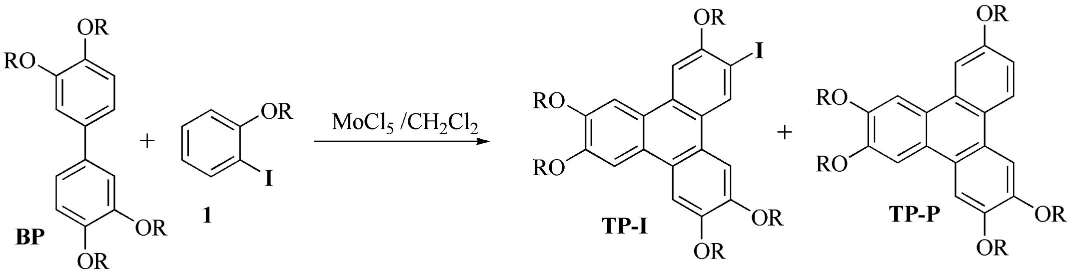


Figure 2. Homogeneous fan texture of the Col mesophase of the compound **TP-I(c)** at 45°C (200 ×).



TP-I (a) : R = R' = C_4H_9
TP-I (b) : R = R' = C_5H_{11}
TP-I (c) : R = R' = C_6H_{13}
TP-I (d) : R = R' = C_7H_{15}

Scheme 1. Synthesis of 2-iodopentakis(alkoxy)triphenylenes via oxidative cross-coupling.

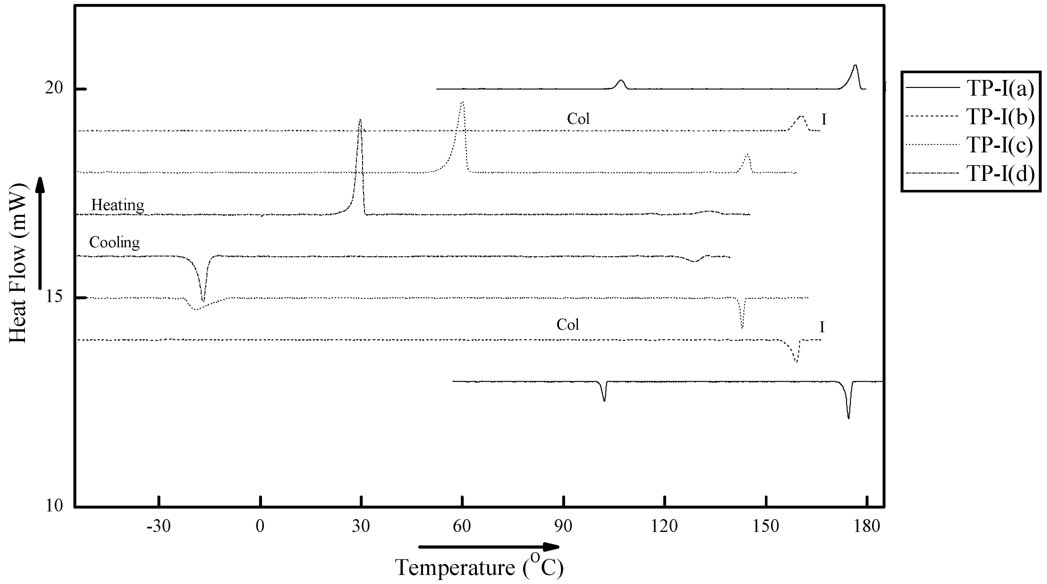


Figure 3. Second heating and cooling DSC thermograms of 2-iodopentakis(alkoxy) TP derivatives.

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typical reaction, anhydrous $MoCl_5$ (0.83 g, 3 mmol) was added in portions to a stirred solution of BP (1 mmol) and 2-iodoalkoxybenzene (2 mmol) in 20 ml dichloromethane (dried over calcium hydride), and the mixture was stirred for 30 min under anhydrous conditions at room temperature, carefully quenching with chilled methanol (10 ml). Water was added to the reaction mixture which was extracted with dichloromethane (3×50 ml); the organic layer was separated, washed with water and brine, dried with anhydrous Na_2SO_4, concentrated *in vacuo* and purified by repeated column chromatography on silica gel, eluting dichloromethane/hexane (1/5). Recrystallization from diethyl ether and ethanol gave a white solid. Tetraalkoxybiphenyl was prepared by classical Ullaman coupling of dialkoxymonoiodobenzene. The hydro-dehalogenation occurred due to the presence of iodine as the exiting group under these reaction conditions. The products were characterized by their spectra.

TP-I(a): MS: m/z (relative intensity): 713 (6%), 714 (7%), 715 (97%), 716 (44%), 717 (13%): calculated for $C_{38}H_{51}IO_5$. ^{1}H NMR (400 MHz): δ=8.79 (s, 1H), 7.84 (s, 1H), 7.78 (s, 3H), 7.67 (s, 1H), 4.23 (t, 10H), 1.92 (m, 10H), 1.63 (m, 10H) and 1.05 (m, 15H). ^{13}C NMR: δ=155.7, 149.6, 149.2, 148.9, 134.3, 125.1, 124.9, 123.2, 122.8, 107.9, 107.6, 107.1, 106.6, 104.5, 86.9, 69.6, 69.2, 31.5, 31.3, 19.3 and 13.9. **TP-I(b)**: MS: m/z (relative intensity): 783 (21%), 784 (20%), 785 (100%), 786 (61%), 787 (28%): calculated for $C_{43}H_{61}IO_5$. ^{1}H NMR (400 MHz): δ=8.81 (s, 1H), 7.86 (s, 1H), 7.80 (s, 3H), 7.69 (s, 1H), 4.23 (t, 10H), 1.95 (m, 10H), 1.50 (m, 20H) and 0.97 (t, 15H). ^{13}C NMR (100 Hz): δ=155.7, 150.2, 149.5, 148.9, 134.3, 130.3, 125.1, 123.2, 122.8, 107.9, 107.5, 107.1, 106.5, 104.5, 86.9, 69.6, 69.6, 29.1, 28.9, 28.4, 22.5, and 14.0. **TP-I(c)**: MS: m/z (relative intensity): 853.8 (18%), 854.8 (16%), 855.8 (100%), 856.8 (56%), 857.9 (16%): calculated for $C_{48}H_{71}IO_5$. ^{1}H NMR (400 MHz): δ=8.80 (s, 1H), 7.86 (s, 1H), 7.79 (t, 3H), 7.68 (s, 1H), 4.22 (m, 10 H), 1.94(m, 10H), 1.59 (m, 10H), 1.40 (m, 20H) and 0.94(m, 15H). ^{13}C NMR (100 Hz): δ=155.7, 150.2, 149.5, 149.2, 148.9, 134.2, 130.3, 124.9, 123.2, 122.8, 107.9, 107.6, 107.1, 106.6, 104.5, 86.8, 69.9, 69.6, 31.6, 29.4, 29.2, 25.8, 22.6, and 13.9. **TP-I(d)**: MS: m/z (relative intensity): 923.8 (7%), 925.7 (29%), 926 (15%): calculated for $C_{53}H_{81}IO_5$. ^{1}H NMR (200 MHz): δ=8.81 (s, 1H), 7.87 (s, 1H), 7.80 (s, 3H), 7.69 (s, 1H), 4.21 (m, 10 H), 1.94 (m, 10H), 1.45 (m, 40H) and 0.91 (m, 15H). ^{13}C NMR (100 Hz): δ=155.7, 150.2, 149.5, 149.2, 148.9, 134.2, 130.3, 125.1, 124.9, 123.2, 122.8, 107.9, 107.6, 107.1, 106.6, 104.5, 86.8, 70.0, 69.6, 31.8, 29.5, 29.2, 26.1, 22.6, and 14.1.

In conclusion, we have reported the first four examples of TP-I synthesized by the oxidative coupling reaction of electron-rich biphenyl with electron-deficient substituted benzenes, using $MoCl_5$. To the best of our knowledge, these are the first examples where the iodo moiety is incorporated into triphenylene discotic molecules. The liquid crystalline behaviour of these derivatives clearly indicates that the increasing covalent radius of the substituents leads to highly ordered Col mesophase, such as columnar plastic and helical. Cross-coupling reactions using these oxidants, with or without additive, will be investigated in order to understand the role of hydrochloric acid formation in this reaction.

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