Probing the structural factors influencing columnar mesophase formation and stability in triphenylene discotics†

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Series of structurally related substituted triphenylene derivatives were designed and synthesised to interrogate key features which determine mesophase formation and stability, and to challenge the general conclusions previously proposed by us and others. It is apparent that no single, simple principle can be universally applied.

Discotic and columnar liquid crystals[1] are an intensively investigated class of organic materials. Their discovery in 1977[2] sparked curiosity-driven research with diverse molecular cores demonstrated as scaffolds supporting liquid crystal behaviour[3] and a rich polymesomorphism was discovered.[3–5] Three main classes of discotic cores have received particular attention, namely phthalocyanines,[6] coronenes[7] and triphenylenes[8] (Fig. 1). Applications are diverse and include light-emitting diodes,[9] field-effect transistors[10] and photovoltaic devices[11] as well as optical materials such as compensating films for displays.[12] Electronic applications exploit particular properties of columnar phases which can give rise to easily aligned self-healing (fluid) materials with high charge carrier mobilities.[13]

We and others have focused on the triphenylene core which provides synthetic and structural versatility. Structural features controlling mesophase type and stability[14,15] were found to be extremely subtle but we concluded that only conjugating substituents that were able to extend the triphenylene's π-system supported mesophase formation and that only in very rare cases would mesophase formation be observed when non-conjugating substituents were present. Williams and co-workers[16] recently argued that mesophase behaviour can be rationalised by considering the electron donating/withdrawing character of the substituents. Within a series of substituted azatriphenylene derivatives (**1**) a reasonable correlation between substituent Hammet parameters and mesophase stability was observed. The analysis was extended to triphenylenes themselves and a weaker correlation was described. Symmetrical hexaalkoxy triphenylenes such as **2** (Fig. 2) are the archetypal discotic liquid crystals, typically showing columnar hexagonal mesophases over reasonably wide temperature ranges.[4b] Removal of one alkoxy chain, however, destroys mesophase formation[17] but it is restored when a conjugating substituent is incorporated.[18] The dependence on extension of the core π-system is made clear when similar chain-length substituents are compared (**4** and **5**; **6–9**). It is clear that cyanide **7** results in the most dramatic mesophase stabilisation, but a significant enhancement is found for apolar acetylene **6**.[18a] Non-conjugating methyl substitution destroys mesophase behaviour whereas methoxy supports it.[18b,19] Our assessment is that a number of factors combine to govern mesophase formation and stability in triphenylene discotics. Core extension by substitution with conjugating groups appears to be a crucial factor. It is recognised that non-conjugating systems pose different stereochemical requirements and are likely to destabilise columnar mesophase formation for steric reasons also. Attachment of electron withdrawing substituents to the π-electron-rich alkoxytriphenylene core leads to the greatest enhancement of mesophase stability probably through polarisation and strengthening of π–π interactions between the aromatic cores.[16] Indeed, combination of electron-rich discotic materials with electron-accepting aromatics such as TNF is well known to lead to stabilised columnar mesophases.[20]

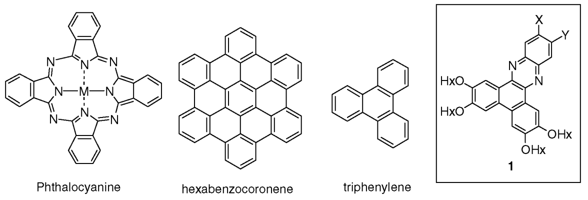

Fig. 1 The most extensively studied discotic liquid crystal cores.

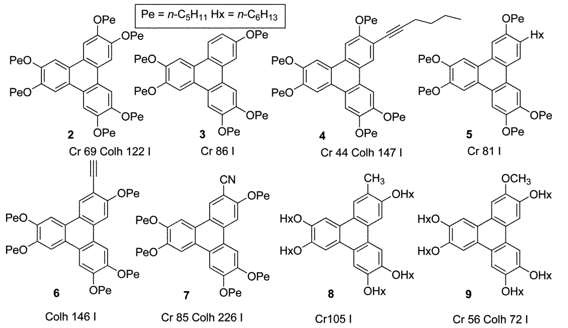

Fig. 2 Selected examples illustrating the sensitivity of mesophase stability to modest structural variation.

In this communication we report the synthesis and properties of substituted triphenylene discotics designed to probe the relationship between molecular structure and mesophase behaviour and to provide derivatives with device potential. For this study we kept the parent triphenylene intact and investigated the introduction of aryl substituents with varying electronic characteristics. In order to preserve the

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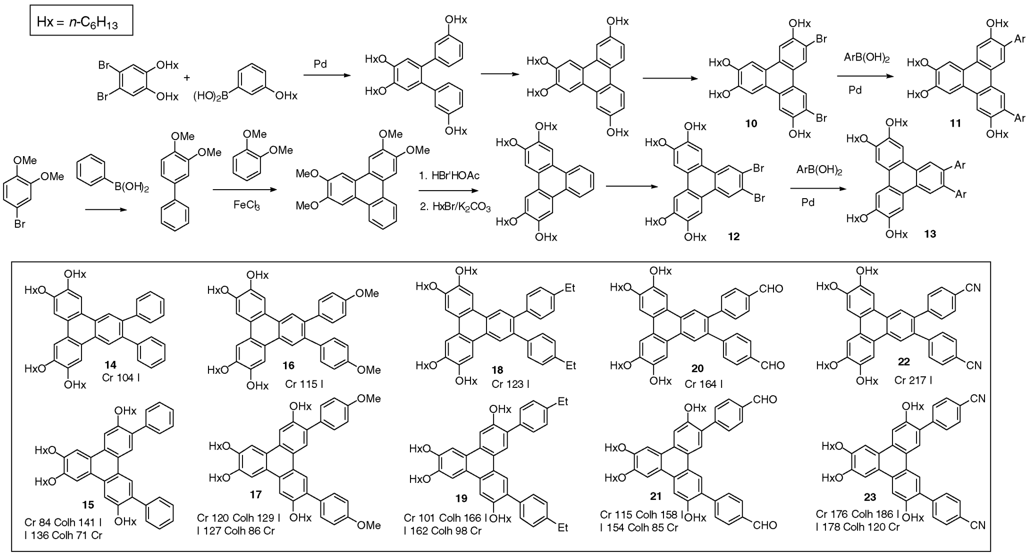

Scheme 1 Synthesis and mesophase properties of new 2,3- and 3,6-substituted triphenylenes.

basic molecular shape as disc (or oval), the study focused on introduction of new substituents at the triphenylene 2,3- or 3,6-positions.[15,21]

The key intermediates were dibromides **10** and **12**, synthesised by bromination of the corresponding tetraalkoxytriphenylenes. Suzuki–Miyaura coupling[22] of **10** and **12** with appropriate aryl boronic acids afforded the target triphenylene discotics (Scheme 1). The thermal behaviour (determined by polarised optical microscopy and DSC) of the first set of new triphenylenes is also shown in Scheme 1.

Within this series of triphenylenes, the diphenyl derivatives can be considered as parent structures. The 2,3-diphenyltriphenylene **14** does not show a mesophase whereas the corresponding derivative bearing the same substituents at positions 3- and 6- shows a columnar hexagonal mesophase. This general trend of behaviour is mirrored through most of the series, with 2,3-diaryl triphenylenes **16**, **18**, **20** and **22** melting directly to isotropic liquids and their 3,6-substituted counterparts showing hexagonal mesophases. Within the series of 3,6-diaryl derivatives it can be seen that introduction of electron donating groups (compound **17**) has little effect on the mesophase behaviour compared to parent triphenylene **15**. However, this comparison is perhaps not ideal because extra substituents have been introduced in **17**. Within the two series we minimised additional substituent effects by choosing groups with similar (2 atom) lengths but different electronic properties. Diethyl derivative **19**, which can be considered essentially neutral in terms of electronic effects, exhibits a significantly more stable mesophase than **17** and has properties intermediate between **21** and **23** which bear electron withdrawing aldehyde and nitrile groups, respectively. The trend is therefore not strong, although the most powerful electron withdrawing substituents (nitriles on **23**) lead to the most stable mesophase. Interestingly, this derivative shows particularly strong tendency for homeotropic alignment between glass slides such that it is formed instantly and spontaneously as the material is cooled into the mesophase. Crystals suitable for X-ray diffraction were obtained for **23** (Fig. 3).[23] Within slipped columns it can be seen that the flat triphenylene cores stack in an antiparallel sense and it seems reasonable to assume that this relationship is preferred as the molecules assemble into symmetrical columns within the mesophase.[16]

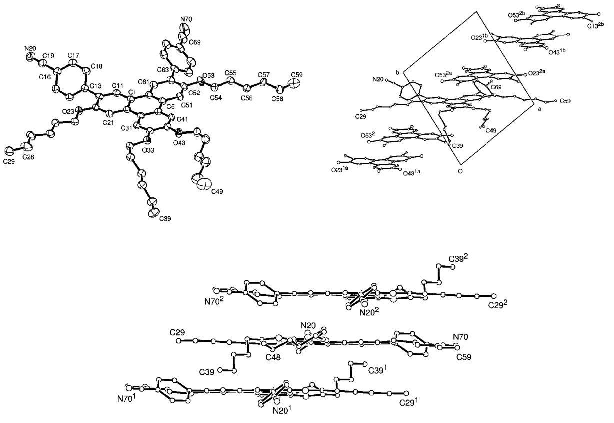

Fig. 3 X-Ray crystal structure of **23**.

The above observations suggested modifications to parent systems **14** and **15** to investigate the importance of the electronic character of the substituent further and determine whether its electronic character is a general controlling factor governing mesophase stability. The phenyl substituents of **14** and **15** were therefore swapped, respectively, for electron deficient pyridines and electron-rich thiophenes and furans, again using straightforward Suzuki–Miyaura coupling (Scheme 1). The thermal behaviour of the new materials is shown in Fig. 4. It is immediately clear from the results in Fig. 4 that mesophase behaviour in these compounds does not follow a trend where electron withdrawing substituents favour columnar phases. In fact, the opposite trend is apparent with electron poor pyridine substituents destroying mesophase behaviour completely. π-Excessive thiophenes however result in columnar mesophase formation through all compounds studied. Once again introduction of the new aryl groups at

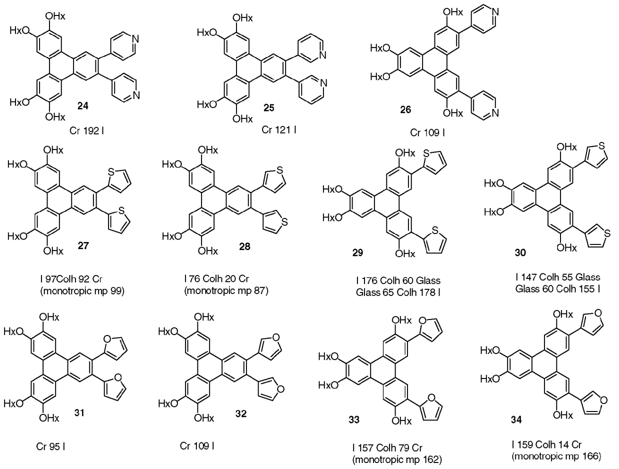

Fig. 4 Mesophase behaviour of heterocycle-substituted triphenylenes.

the 3,6-positions results in much more stable columnar mesophases compared to 2,3-substitution. Comparison of isomers **27**/**28** and **29**/**30** reveals a weak link between mesophase stability and the position of thiophene substitution (α *versus* β).

The observation that introduction of thiophene substituents supports columnar mesophase formation could prove particularly important because such materials can be considered as through-conjugated discotic analogues of the extensively investigated oligothiophenes.[24] The furan substituted derivatives also show formation of mesophases and their behaviour, which is more closely related to electron deficient derivatives **21**/**23**, further contradicts a simple correlation between mesophase stability and electronic nature of substituent.

In conclusion we have designed and synthesised series of structurally related substituted triphenylene derivatives in order to interrogate key features which determine mesophase formation and stability. It is apparent that no single, simple principle can be widely applied. Structural features, proposed by us and others, such as the importance of conjugating substituents or the electronic nature of the substituents, provide useful guidelines but are insufficient to reliably predict and explain all the observed trends in isolation. Perturbation of molecular structure through variation of substituent (nature, position, number *etc.*) has wider impact on bulk phase properties and it is impossible to change, for example, electronic properties without concomitant steric and conformational change. These effects must therefore be considered in concert to achieve the fine balance of properties which lead to mesophase formation at the expense of crystallinity or disorder.

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