**New Synthetic Strategies and Disconnections in the Synthesis of Liquid Crystals Enabled by Photoredox Cross-Coupling Reactions**

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**Abstract**

In this letter we describe the application of metallaphotoredox cross-electrophile couplings to the synthesis of liquid crystals using dual nickel and iridium catalysis. Given the proliferation of aryl and alkyl bromides in liquid crystal research we consider that the silyl-radical mediated cross coupling of alkyl bromide with an aryl bromide (to afford a direct alkyl-aryl bond) will become an extremely powerful tool in the synthesis of liquid crystalline materials, and we use this to synthesise several well-known materials (PCH32, 5CB, CB7CB and CB15) in a single synthetic step from inexpensive and commercially available building blocks. The metallaphotoredox decarboxylative sp3-sp2 cross-coupling of an aryl bromide with an alkyl carboxylic acid provides a complimentary method to form alkyl-aryl bonds, and we use this to successfully prepare *trans* PCH5 in a single synthetic step from commercially available building blocks. We also prepare novel methylene linked materials in a single synthetic step, one of which exhibit the topical TB phase.

**Introduction**

The development of palladium catalysed cross-coupling reactions in the late 20th century (1) radically altered how the synthesis of liquid crystals was approached, (2) providing new disconnections to organic chemists and enabling the synthesis of complex aromatic core units from basic and easily prepared or procured building blocks. (3) We are of the opinion that recent developments in photoredox coupling have the potential to catalyse a similar revolution in organic chemistry. (4-9) In particular we note the silyl radical-mediated cross-coupling of alkyl and aryl bromides under dual nickel/iridium catalysis reported by Macmillan *et al* (10) is likely to be extremely attractive to those synthesising liquid crystalline matter, as is the related decarboxylative arylation reported by Macmillan *et al.* (11)

In this letter we detail how we have successfully applied these new synthetic techniques to the synthesis of liquid crystalline materials with direct aryl-alkyl bonds which are currently topical due, in part, to the discovery of the twist-bend modulated nematic phase in these systems. (12, 13) Forming such bonds typically involves multiple steps for example: acylation followed by ketone reduction; (14, 15) Sonogashira cross-coupling followed by hydrogenation; (16) hydroboration followed by sp2-sp3 Suzuki cross coupling; (17) transmetallation followed by iron catalysed coupling. (18-20) The sp2-sp3 silyl-radical mediated photoredox cross-coupling (10) provides an alternative one-step alkyl-aryl coupling from widely available and inexpensive reagents, and we successfully employ it herein. The decarboxylative arylation provides a similar transformation, albeit using carboxylic acids rather than alkyl bromides, and again we successfully demonstrate its utility in the synthesis of well-known liquid crystalline material that has historically required a lengthy synthetic pathway.

Both reactions greatly simplify the synthesis of many materials and we are of the opinion that they, and other related photoredox synthetic transformation(s), are likely to have significant impact in the field of liquid crystals.

**Experimental**

Several of the chemical intermediates used herein have been described by previously: ***i3***, ***i4*** and ***i5*** in ref (21). The photocatalyst [Ir{dF(CF3)ppy}2(dtbbpy)]PF6 was prepared according to ref (22). 1,2-Dimethoxy ethane was distilled from CaH prior to use and stored over 4Å molecular sieves under dry nitrogen. 2,6-Lutidine and tris(trimethylsilyl)silane were distilled upon receiving from SigmaAldrich and Fluorochem respectively. Barton’s base was purchased from Fluorochem and used without purification. ***i1*** was purchased from Fluorochem, ***i2*** was purchased previously from BDH, 4-bromobenzonitrile was purchased from Aldrich and *trans* 4-pentylcyclohexane carboxylic acid was purchased from Synthon GMBH. Photoredox couplings were performed in 25 ml reaction tubes (Sigma Aldrich, part no. Z515981). Reactions were irradiated two LED emitters (Mouser, part no. LZ1-10UB00-00U8, 410 nm peak output, 1050 mW radiant flux) mounted on anodised aluminium heatsinks (Mouser, part no. 984-ATSEU-077B-C6-R0) at opposite sides of the reaction tube at a distance of approximately 1 cm from the wall of the reaction tube. The LED and reactor assembly was cooled with a fan during operation - failure to cool the reaction leads to reduced yields and increased side products. Full experimental details are given in the SI.

**Results**

As an initial test of the applicability of the silyl radical-mediated metallaphotoredox cross-electrophile coupling (“the cross coupling”) reported by MacMillan *et al*. (10) we attempted the synthesis of ***PCH32***, a useful non-volatile isotropic solvent for the measurement of dipole moments. (23) Synthesis of this material from commercially available precursors *via* classical methodology requires three steps; Sonogashira coupling with TMS acetylene, deprotection and finally hydrogenation of the alkyne (shown in grey, Figure 1). Using 2,6-lutidine as a base the cross coupling reaction afforded 87% conversion to ***PCH32*** within 1 hour (Scheme 1). Following chromatography and removal of excess tris(trimethylsilyl)silane (“TTMS”) *in vacuo* (70 °C, 1 mBar) we obtained ***PCH32*** as an isotropic liquid. The structure was confirmed by NMR (1H/13C{1H}).

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**Figure 1:** Synthesis of ***PCH32*** via metallophotoredox cross-electrophile coupling (top) and *via* classical disconnections (middle, greyed out).

As ***PCH32*** is non mesogenic, and an isotropic liquid at ambient temperature, we did not record transitional data. We next prepared three well-known materials (Figure 2), the calamitic ***5CB*** (24, 25) and the bimesogen ***CB7CB***, (12, 14) as well as the non-mesogenic chiral dopant ***CB15*** shown in Scheme 2, all from a commercially available building block (***i2***). We obtained ***5CB*** in 91% yield from ***i2*** and 1-bromopentane, ***CB7CB*** was obtained in 72% yield from ***i2*** and 1,7-dibromoheptane, and ***CB15*** was obtained in a 84% yield from ***i2*** and (S)-1-bromo-2-methylbutane.

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**Figure 2:** The synthesis of ***5CB***, ***CB7CB*** and ***CB15*** from a common intermediate (***i2***) *via* metallophotoredox cross-electrophile coupling.

Following chromatography and recrystalisation the transition temperatures and associated enthalpies of ***5CB*** and ***CB7CB*** were determined by microscopy and DSC, with both found to be in excellent agreement with literature data, as shown in Table 1. As ***CB15*** is non mesogenic, and an isotropic liquid at ambient temperature, we did not record transitional data.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| No. |  | **MP** | **TB-N** | **N-Iso** |
| ***5CB*** | T | 23.0 [23.7] | - | 35.1 [35.3] |
| ΔH | 21.9 [22.6] | - | 0.3 [0.3] |
| ***CB7CB*** | T | 104.2 [104.4] | 106.3 [106.5] | 118.6 [118.9] |
| ΔH | 23.0 [23.1] | 0.4 [0.4] | 0.8 [0.8] |

**Table 1:** Transition temperatures (T, °) and associated enthalpies of transition (ΔH, kJ mol-1) for 5CB and CB7CB with literature values presented in square parenthesis [] and taken from refs (26, 27).

Having demonstrated the success of this reaction at producing known materials we now turn to the synthesis of novel materials that would require lengthy synthetic pathways to obtain. In particular, we considered the possibility of methylene-linked dimers incorporating *trans* phenylcyclohexyl mesogenic unit(s) to be particular attractive; these are trivial to prepare with an ether linking group (28) but the combination of a methylene linker and all *trans* cyclohexane is difficult to realise presently. A proposed classical synthesis would be similar to our synthesis of CB8OCB (16) or CBCC4OCB, (27) Sonogashira followed by hydrogenation and Mitsunobu etherification. In Figure 1 we used an excess of alkyl bromide as ethyl bromide is cheap and easily removed, however in Figure 3 we considered the polarity of the alkyl halideand **CBO5PCH3** **and CBO6PCH3** would be similar (experimentally we find ΔRf ≈ 0.05), whereas ***i1*** is non-polar; we therefore inverted the alkyl/aryl bromide ratio to simplify purification and this has minimal effect on isolated yields (71% and 78 % respectively). Structures were confirmed by NMR (1H/13C{1H}) and MS (APCI).

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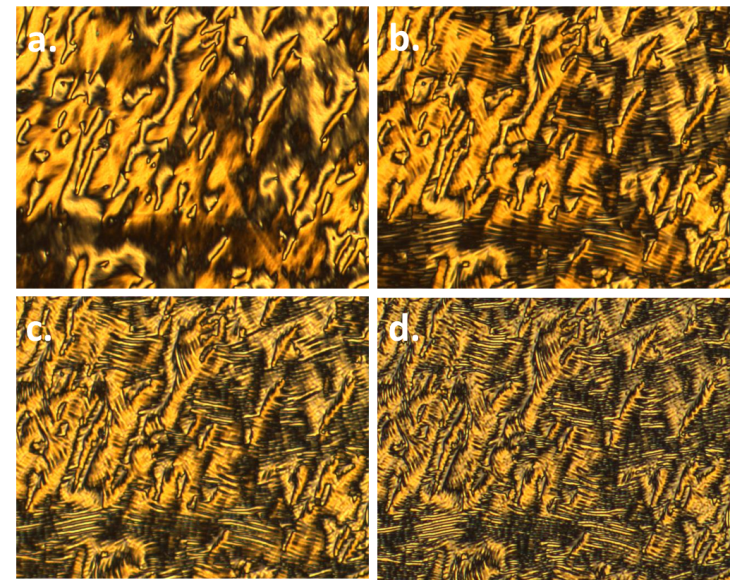
**Figure 3:** The synthesis of the **CBOnPCH3** bimesogens *via* silyl-radical mediated metallophotoredox cross-electrophile coupling (top). A proposed synthesis of **CBO6PCH3** *via* classical disconnections to commercially available building blocks (bottom).

**CBO6PCH3** is structurally related to the dimer *CB6OCB* reported by Paterson *et al*. (29, 30)as well as the cyanobiphenyl/phenylcyclohexyl dimers reported by Pocock *et al*., (28) both of which exhibit nematic and twist-bend modulated nematic phases. **CBO6PCH3** was found to exhibit nematic and TB phases, whereas the related even parity material **CBO5PCH3** exhibits only a nematic phase. The clearing point of the even parity material, **CBO5PCH3,** is significantly higher than that of the bent material, **CBO6PCH3**. Transition temperatures and associated enthalpies of transition for **CBO5PCH3** and **CBO6PCH3** are presented in Table 2.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **No.** |  | **MP** | **TB-N** | **N-Iso** |
| **CBO5PCH3** | T | 120.3 | - | 179.5 |
| ΔH | 22.3 | - | 3.2 |
| **CBO6PCH3** | T | 103.2 | 63.6\* | 95.3\* |
| ΔH | 22.0 | <0.1 | 1.3 |

**Table 2:** Transition temperatures (T, °) and associated enthalpies of transition (ΔH, kJ mol-1) for **CBO5PCH3** and **CBO6PCH3**. \* Monotropic phase transition, observed only on cooling.

The monotropic nature of the TB phase in **CBO6PCH3** unfortunately precludes study by SWAXS, and so phase identification was made solely by optical microscopy. Photomicrographs of the TB phase are presented in Figure 4. The ability to prepare unsymmetrical bimesogens such as **CB6OPCH3** in a single synthetic step from commercially available intermediates is a particularly welcome development, and we will report in detail on the properties of these materials along with their homologues and analogues in future publications. In a similar vein this method could greatly simplify the synthesis of liquid crystalline oligomers which have attracted attention due to their propensity to exhibit the TB phase. (31-35)



**Figure 4:** Photomicrographs (x100) of: (a) the nematic phase of **CBO6PCH3** at 75 °C; the TB phase of **CBO6PCH3** at 63 °C (b), 62 °C (c) and 55 °C (d).

We next turned our attention to the decarboxylative arylation as a possible tool for constructing *trans* phenylcyclohexane core units – in this instance the starting 4-alkylcyclohexylbromides are not commercially available. We chose the synthesis of the calamitic material ***PCH5*** (36) as an exemplar for this reaction as existing synthetic routes to this material are long and low yielding. Bezborodov reported a synthesis in 8 steps from 4-pentylcyclohexanone, (37) this is essentially the same route as employed by Dabrowski *et al* who report a route of only 4 steps starting from a more elaborate starting material (38). Using the conditions described by Macmillan *et al*, (39) albeit with 1,2-DME as a solvent rather than DMSO, we were able to obtain all *trans* PCH5 from inexpensive building blocks *via* the dual nickel/photoredox-catalysed decarboxylative arylation reaction. (11) Analysis of the crude material by 1H NMR shows a mixture of *trans*/*cis* products in a 3:1 ratio, fortuitously a single recrystalisation from ethanol (- 20 °C, 0.02 M) yielded only the *trans* product with the *cis* form remaining in solution. The isolated yield of *trans* ***PCH5*** *via* this single step transformation was 55% which is higher than the previous examples noted. The transition temperatures of ***PCH5*** were identical to an authentic sample from BDH.

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**Scheme 4**

**Conclusions**

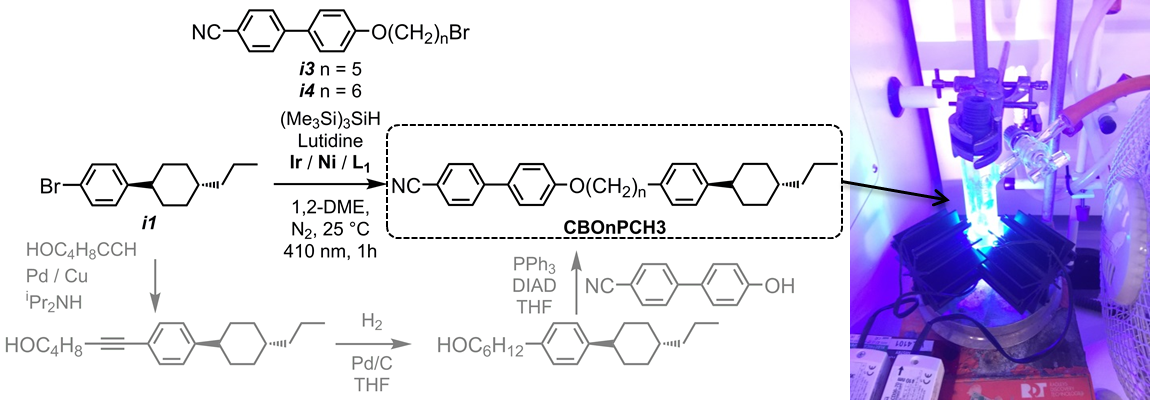
We have successfully applied the silyl radical-mediated metallaphotoredox cross-electrophile coupling reported by Macmillan et al to the synthesis of liquid crystalline materials. We note this method appears to be a robust one-step method for generating methylene-linked materials from commercially available building blocks which are classically prepared in a multi-step synthesis. The reaction conditions are compatible with the nitrile group, and thus we consider this reaction could be widely employed in the synthesis of liquid crystals. In particular the commonly used acylation/reduction or Sonogashira/hydrogenation protocols for introduction of alkyl-aryl bonds are inferior to the present method in both yield and reaction time. We use this reaction to perform one step synthesis for ***PCH32***, ***5CB***, ***CB7CB***, and ***CB15*** - all from commercially available building blocks. We devised novel methylene/ether linked dimers (**CBO5PCH3** and **CBO6PCH3**) which we observe to exhibit nematic and twist-bend phases respectively. Both the alkyl bromide and aryl bromide can be used in excess to ensure high yields, allowing cheaper reagents to be used in large excess to drive reactions to completion (Figure 1) or to take advantage of differences in polarity to simplify purification (Figure 3).

The dual nickel/photoredox-catalysed decarboxylative arylation reaction, also reported by Macmillan *et al*, provides a complimentary method for the formation of alkyl-aryl bonds using an aryl halide and an alkyl carboxylic acid. This allows us to present a one-step synthesis of the well-known material ***PCH5*** which we obtain in 55% yield – higher than all previous multistep synthesis - in 3 hours, while the reaction forms a cis/trans mixture this is in favour of the desired *trans* form (3:1 by 1H NMR) and the two can be separated by chromatography or crystallisation.

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**TOC Entry**

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