Preparation of substituted triphenylenes via nickel-mediated Yamamoto coupling†

Zachary W. Schroeder, Joshua LeDrew, Vanessa M. Selmani and Kenneth E. Maly✉

Substituted triphenylenes show promise as organic semiconductors because of their ability to form columnar liquid crystalline phases featuring extended π-stacked arrays. While there are several methods for preparing triphenylenes, including oxidative cyclization reactions such as the Scholl reaction, as well as transition metal-catalyzed arylene cyclotrimerization, these methods are not effective for electron-deficient triphenylenes. Here we demonstrate that the nickel-mediated Yamamoto coupling of o-dibromoarenes is a concise and efficient way to prepare substituted triphenylenes, including electron-deficient systems that are otherwise challenging to prepare. We also demonstrate the application of this approach to prepare electron deficient discotic mesogens composed of triphenylenes bearing imide and thioimide groups.

Introduction

A key component in the design of organic semiconducting materials is the ability to tune properties such as the frontier molecular orbital energies and molecular packing. Promoting π-stacking favours molecular orbital overlap that is important for charge transport in these systems. One strategy to promote effective π-stacking is to design disk-shaped molecules that form columnar mesophases, where molecules self-organize into π-stacked arrays, making them attractive candidates as organic semiconducting materials.1-3

Substituted triphenylenes have been extensively explored and are well-established discotic mesogens.4-6 These triphenylenes are usually prepared via oxidative aryl–aryl bond forming reactions such as the Scholl reaction,7,8 which works very well for electron-rich systems but is not effective for electron-poor compounds. Other common approaches for the preparation of triphenylenes include cross-coupling followed by oxidative cyclization, as well as palladium-catalyzed arylene cyclotrimerization.9 Despite these methods, access to electron-deficient triphenylenes remains a challenge.10

The design and synthesis of electron deficient triphenylenes would provide access to potential n-type materials with low LUMO energies. Furthermore, several studies have shown that electron-withdrawing groups on discotic mesogens promote the formation of stable columnar liquid crystalline phases, likely through improved π-stacking interactions.11-14 These observations suggest that the preparation of electron-deficient triphenylenes may lead to discotic liquid crystals with broad mesophase ranges. Therefore, there is impetus to develop new approaches for the preparation of electron-deficient triphenylene derivatives.

The Yamamoto coupling consists of a homocoupling of aryl bromides in the presence of a Ni(0) complex to form a new aryl–aryl bond. This reaction has been used for the synthesis of biaryls,15-16 as well as the preparation of conjugated polyarylenes17-19 and extended two- and three-dimensional macro-molecular frameworks.20 When ortho-dibromobenzene is subjected to Yamamoto coupling conditions, cyclotrimerization occurs to form the corresponding 3-fold symmetric triphenylene (Scheme 1).21 Recently, this approach has been used to prepare 3-fold symmetric polycyclic aromatic hydrocarbons such as trinaphthylenes and larger starphene derivatives.22-24 The use of the Yamamoto coupling to prepare substituted triphenylenes, however, has received little attention. This reaction should be amenable to the preparation of triphenylenes, including electron deficient triphenylenes that are not readily prepared by other methods.

Here we report the use of the nickel-mediated Yamamoto coupling to prepare a series of triphenylenes 2a-f and compare this approach to other methods for preparing the same

**Scheme 1** Cyclotrimerization of o-dibromobenzene using the Yamamoto coupling.21

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The design and synthesis of electron deficient triphenylenes would provide access to potential n-type materials with low LUMO energies. Furthermore, several studies have shown that electron-withdrawing groups on discotic mesogens promote the formation of stable columnar liquid crystalline phases, likely through improved π-stacking interactions.11-14 These observations suggest that the preparation of electron-deficient triphenylenes may lead to discotic liquid crystals with broad mesophase ranges. Therefore, there is impetus to develop new approaches for the preparation of electron-deficient triphenylene derivatives.

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compounds. In particular, we focus on electron-deficient triphenylenes, which are otherwise challenging to prepare using established methods. We demonstrate that this method is viable for the preparation of triphenylenes and in several cases offers the advantage of a more concise and high yielding synthesis as compared to other approaches. We also demonstrate that this approach can be used to prepare electron-deficient discotic compounds such as triphenylene trisimide (3) and its thionated analog (4) in order to compare their mesomorphic properties.

Results and discussion

To explore the potential of the Yamamoto coupling, a series of substituted o-dibromobenzenes were used. o-Dibromobenzene (1a), 1,2-dibromo-4,5-difluorobenzene (1e), and 1,2-dibromo-3,4,5,6-tetrafluorobenzene (1f) were obtained from commercial sources. 4,5-Dibromo-o-xylene(1b) and dimethyl 4,5-dibromophthalate(1c) were prepared according to literature procedures, and 4,5-dibromophthalaldehyde (1d) was prepared in two steps from 4,5-dibromophthalic acid (refer to ESI† for details).

Triphenylenes 2a-f were chosen as targets because they have all been prepared previously by different methods, permitting a comparison of the Yamamoto coupling with previously reported approaches. They were also selected because they included a range of electron-donating and electron-withdrawing groups. Compounds 1a-f were each subjected to reaction with stoichiometric Ni(COD)2 (1.25 eq.), COD (2 eq.), and 2,2'-bipyridine (1.25 eq.) in THF at room temperature overnight to afford the corresponding triphenylenes in modest to good yields (Table 1).

Triphenylene (2a) has been prepared by a number of different methods, including the Yamamoto coupling. The previous report of the formation of triphenylene in 60% yield using the Yamamoto coupling used Ni(COD)2 in the presence of PPh3 in DMF at 70 °C. It should be noted that the reported yield was not an isolated yield but was measured by gas chromatography. We employed conditions adapted from Rüdiger et al., who used Ni(COD)2 in the presence of COD and 2,2'-bipyridine (bpy) in THF at room temperature, thereby avoiding the use of DMF as a solvent and the need for elevated temperatures. Gratifyingly, we obtained triphenylene 2a in 59% isolated yield, comparable to that reported previously.

Using the same conditions, hexamethyltriphenylene 2b was prepared in a 58% yield. To evaluate the utility of the Yamamoto, we compared this synthesis with the previously reported synthetic approaches to 2b. There are two previously described synthetic approaches to 2b. The first involves palladium-catalyzed aryne cyclotrimerization using the corresponding trimethylsilyl aryl triflate. While the second approach involves oxidative cyclization of the corresponding terphenyl, which was prepared by Suzuki coupling (Scheme 2). The aryne cyclotrimerization reaction is reported to proceed in 34% yield, and also requires several steps to prepare the aryne precursor, requiring cryogenic conditions. Alternatively, Rathore and coworkers showed that oxidative cyclization of the o-terphenyl

![Table 1](image)

| Substrate | Product | Yield (%) |
|-----------|---------|-----------|
| 1a (X = H, Y = H) | 2a | 59 |
| 1b (X = CH3, Y = H) | 2b | 58 |
| 1c (X = CO2CH3, Y = H) | 2c | 74 |
| 1d (X = CHO, Y = H) | 2d | 0 |
| 1e (X = F, Y = H) | 2e | 44 |
| 1f (X = Y = F) | 2f | 20 |

![Scheme 2](image)

Scheme 2: Previously reported synthetic approaches to compound 2b.
derivative proceeded in quantitative yield.\textsuperscript{29} However, the preparation of the \( o \)-terphenyl precursor via Suzuki-coupling proceeded in a modest 32% over two steps. Clearly, each of these approaches has its disadvantages and the Yamamoto coupling represents a much more concise synthesis and improved yield as compared to both methods.

Having demonstrated that the Yamamoto coupling offers and improved synthesis of electron-rich triphenylenes, we turned our attention to electron-deficient triphenylenes (2c-f). Compound 2c, which bears ester groups on the triphenylene, has been synthesized previously.\textsuperscript{31} Since oxidative cyclizations are not generally effective for the synthesis of electron-deficient triphenylenes, the previous synthesis by Osawa \textit{et al.} made use of a Cava reaction as a key step to form the triphenylene (Scheme 3). Specifically, the synthesis began by benzylic bromination of the relatively expensive hexamethylbenzene to form hexakis(bromomethyl)benzene in quantitative yield. The Cava reaction of hexakis(bromomethyl)benzene with dimethyl acetylene-dicarboxylate (DMAD) in the presence of sodium iodide gave the hexahydrotriphenylene in 14% yield, which was oxidized with \( \text{MnO}_2 \) in 95% yield to give 2c. This synthesis has the drawbacks of starting with the relatively expensive hexamethylbenzene and the low yield of the Cava reaction. In contrast, Yamamoto coupling of 1c, which is readily prepared in two steps from 1b,\textsuperscript{26} proceeds in a yield of 74%. This reaction demonstrates that electron-poor triphenylenes can be prepared using this approach, providing an alternative to existing methods.

In contrast to the preparation of hexaester 2c, efforts to prepare hexaaldehyde 2d were unsuccessful, resulting in a complex mixture with no evidence of the desired product. One potential explanation for the failure of the Yamamoto coupling of 1d is that aldehydes are known to react directly with zerovalent nickel complexes, undergoing reactions such as homodimerization to form esters.\textsuperscript{32} This observation highlights a limitation in the scope of the Yamamoto coupling when other reactive functional groups are present.

Fluorinated triphenylenes 2e and 2f are of interest in the context of crystal engineering and supramolecular chemistry because of their ability to engage in arene–perfluoroarene interactions in the solid state.\textsuperscript{33–38} These two compounds could be prepared via the Yamamoto coupling of the corresponding dibromoarenes 1e and 1f in modest yields. Compound 2e has been prepared previously by palladium catalyzed arylene cyclotrimerization reactions.\textsuperscript{39,40} The initial report of the arylene cyclotrimerization used the corresponding trimethylsilyl aryl triflate as the arylene precursor and gave compound 2e in 52% yield. However, the synthesis of the arylene precursor required three steps from commercially available 2-bromo-4,5-difluorophenol, with some of these steps having modest yields.\textsuperscript{9,39} More recently, Greaney and coworkers reported an arylene cyclotrimerization method using the appropriate bromoaryl boronate ester and showed that 2e could be prepared in

![Scheme 3](image3.png)

\textbf{Scheme 3} Synthesis of compound 2c reported by Osawa \textit{et al.}.\textsuperscript{31}

![Scheme 4](image4.png)

\textbf{Scheme 4} Synthesis of compounds 3 and 4.

![Fig. 1](image1.png)

\textbf{Fig. 1} UV-visible spectra of 3 (blue line) and 4 (red line) in \( \text{CH}_2\text{Cl}_2 \) (2 \( \times \) 10\textsuperscript{-6} M).
bronze at high temperature, furnishing a Mann coupling of 1,2-diiodotetra-
hexamethylbenzene, followed by a Cava reaction with the starting material.

The Yamamoto coupling and used 18% over three steps. Given the low yield and use of expensive
product of the reaction was then treated with bromine and
imide (Scheme 4). 4,5-Dibromo-o-xylene was oxidized to the corre-
sponding phthalic acid in moderate yield as described previ-
ously and then converted into the anhydride in quantitative
yield. Anhydride 5 was then reacted with octyl amine in the
presence of Ni(OAc)₂ and Ac₂O in a modification of a method
described by Branda and coworkers to give imide 6.

Compound 6 was then subjected to the Yamamoto coupling
conditions using Ni(COD)₂, COD, and 2,2’-bipyridine (bpy) in
THF to furnish the desired compound 3 in 65% yield.

An investigation of the mesomorphic properties of 3 by
polarized optical microscopy and differential scanning calo-
rimetry showed that the compound indeed exhibited an ordered
columnar mesophase as described previously by Wu and
coworkers. The observed mesomorphic properties are consis-
tent with those previously reported, showing a clearing point at
c. 228 °C.

Previous studies on imide materials have shown that thio-
nation can be used to improve electron-accepting ability of
imides by lowering the LUMO energy, producing materials with
lower HOMO–LUMO gaps. We have also shown that
thionation of imide containing discotic liquid crystalline
compounds has only a small impact on liquid crystallinity while
altering the electronic properties significantly. We therefore
sought to explore the effect of thionation on the mesomorphic
properties of compound 4. Compound 4 was readily accessed by
6-fold thionation of 3 giving the desired product in 60% yield.

Thioimide 4 shows a red shift in the absorption compared to
the corresponding imide as shown by UV-visible spectroscopy (Fig. 1). This red shift is consistent with previously re-
ported thionated imides, which show a lowering of the
HOMO–LUMO energy.

Preliminary investigation of the mesomorphic properties of
compound 4 by polarized optical microscopy showed
compound 4 underwent a transition to the isotropic phase at
approximately 320 °C. Upon cooling, a phase transition to
a columnar mesophase was observed. Polarized optical
microscopy revealed dendritic textures consistent with a
columnar hexagonal phase (Fig. 2). This texture was preserved
approximately 320 °C. Upon cooling, a phase transition to
a columnar mesophase was observed. Polarized optical
microscopy revealed dendritic textures consistent with a
columnar hexagonal phase (Fig. 2). This texture was preserved
room temperature, suggesting a glass formation. Unfortu-
nately, heating above 300 °C also appeared to result in at least
partial decomposition. Consequently, the phase transition
temperatures were reduced with each heating and cooling cycle.
As such, the phase transitions were not readily observed by
differential scanning calorimetry, nor is it possible to make
meaningful characterization of the mesophase, or comparison
of the mesophase characteristics with compound 3. That said,
in this system, thionation has the effect of dramatically
increasing the clearing point of these compounds to the point
of decomposition. These observations are in contrast to
previous studies on the thionation of imide liquid crystals,
where thionation had only a small impact on the mesophase
range. In this case, where all six imide oxygen atoms are
replaced by sulfur has a dramatic effect on the phase transition
temperatures.

Conclusions

In summary, we have shown that the nickel-mediated Yama-
moto coupling of o-dibromoarenes can be used for the prepa-
ration of substituted triphenylenes. This approach is more
concise and high yielding than several existing synthetic
approaches, in particular for electron-deficient systems that are

Fig. 2 Polarized optical micrograph of thioimide 4 upon cooling from
isotropic liquid.
not readily prepared by oxidative cyclization methods. One drawback of this approach is the use of stoichiometric amounts of Ni(COD)₂. We applied this method to the preparation of electron-deficient discotic mesogen 3 bearing imide groups, and converted it to the corresponding thioimide (4). Compound 4 shows evidence for a columnar mesophase with a high clearing point, but decomposition near the clearing point prevents a clear comparison with compound 3.

Conflicts of interest
There are no conflicts to declare.

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