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# Making Nonsymmetrical Bricks: Synthesis of Insoluble Dipolar Sexiphenyls

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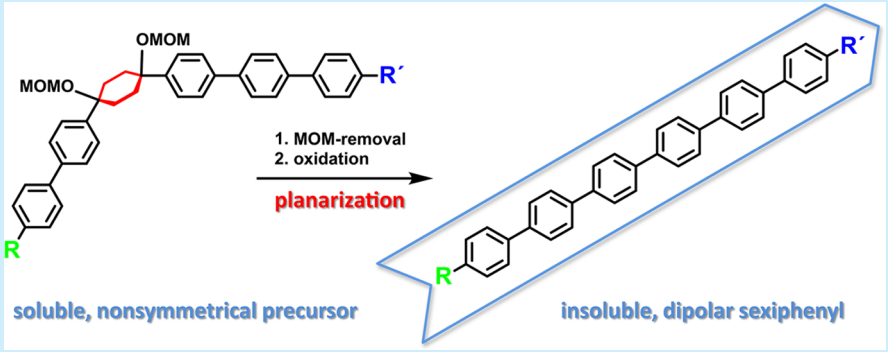
Supporting Information




**ABSTRACT:** A versatile synthesis of nonsymmetrical, terminally substituted *p*-sexiphenyl (**6P**) derivatives has been developed. The synthesis makes use of a nonsymmetrical starting material as well as modular functionalization using Suzuki cross-coupling to yield a soluble precursor, which finally is converted to the insoluble target **6P** derivatives. These derivatives display similar electronic and optical properties to the parent **6P**, yet the permanent dipole along their molecular axis allows for tuning of their self-assembly on various substrate surfaces.

Any optoelectronic device consists of several components responsible for specific functions, such as injecting and ejecting charges, transporting holes and electrons, absorbing and emitting photons, among others, and the interface between these different materials is of utmost importance for the overall device performance. Among the various interfaces, the one between organic molecules and inorganic solid surfaces is highly relevant yet the control over its structure and energetics remains challenging. To engineer this interface, one can either tailor the solid substrate surface or the organic molecule. While the first approach is somewhat limited to specific surfaces and their reconstructions, tuning the molecular structure seems to offer endless opportunities. However, there are few privileged small molecules that have received a lot of attention and they typically consist of planar and rigid, extended $\pi$-systems.[1]

Among the best studied molecules is *p*-sexiphenyl (**6P**), which is known to grow in well-ordered thin films on surfaces, such as KCl(001), GaAs(001), mica(001), $TiO_2$(110), Au(111), or Al(111).[2] Options to control the self-assembly and therefore properties of the first interfacial layers have been rather limited, in particular to different deposition techniques and rates as well as sample temperatures.[2] Although substituted **6P** derivatives should grant the desired control over self-assembly, such compounds have thus far remained elusive due to the lack of solubility precluding their synthesis. Here, we describe the synthesis of various **6P** derivatives with different substituents on their termini. Such **6P** derivatives having a permanent dipole along their molecular axis display distinct self-assembly behavior on various substrate surfaces and therefore provide an effective means to tune interfacial energetics.[3]

The desired optical and electronic properties of the organic semiconductor require both sufficient oligomer length and coupling between the repeat units to ensure for efficient $\pi$-conjugation.[4] However, in the series of unsubstituted oligo(*p*-phenylene)s the solubility decreases rapidly with the length of the *p*-phenylene chain.[5] Introduction of solubilizing side chains is problematic as they can cause an increased phenyl−phenyl twist and hence lead to decoupling of the repeat units.[6] Furthermore, such long alkyl side chains increase the molecular weight considerably, therefore precluding vacuum-processing of the organic material by thermal evaporation.[7] Due to the challenging preparation and purification primarily caused by the low solubility, only shorter dipolar oligomers such as *p*-quarterphenylenes[8,9] and hydroxyl *p*-quinquiphenyl[10] have been synthesized thus far. With regard to **6P**, which was first prepared by Pummerer and Bittner as early as in 1924,[11] only a few terminally substituted derivatives are known; however, all of them are symmetrical. To meet this challenge, we developed a new modular synthetic route involving a nonsymmetric, soluble precursor, which after desired terminal functionalization is converted to the dipolar, insoluble **6P** in the final step of the synthesis.

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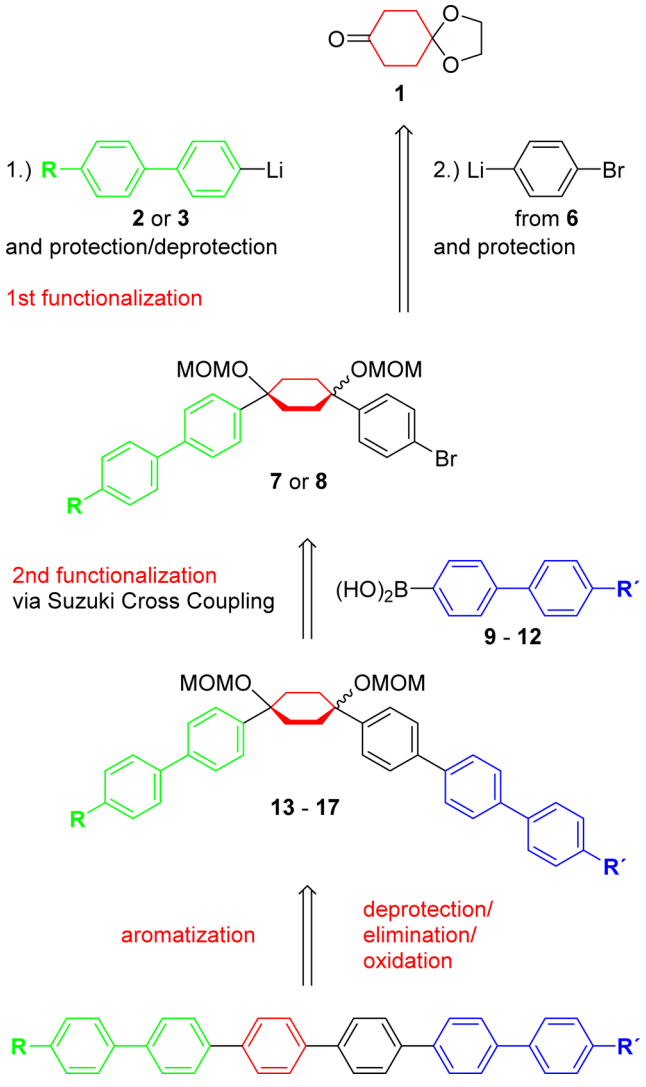
Our synthetic efforts have been inspired by the work of Mayer and Schiffner, who in 1932 discovered the synthetic access to *p*-phenylenes by addition of a phenyl Grignard reagent to cyclohexane-1,4-dione followed by elimination of water from the formed diol and aromatization.[12] This strategy was rediscovered three decades later, when Kern et al. synthesized methyl and methoxy side chain substituted *p*-phenylenes up to *p*-octiphenyl[5] and rejuvenated by Itami and co-workers in their elegant synthesis of cyclic oligo(*p*-phenylene)s.[13] For this purpose, the latter authors introduced methyloxymethyl groups to stabilize their nonplanar intermediates. An alternative elegant route again involving a soluble precursor has been developed by Unroe and Reinhardt leading to unsubstituted (and hence symmetrical) oligo(*p*-phenylene)s up to *p*-octiphenyl.[14]

Retrosynthetically, the target nonsymmetrical **6P** compounds were disected into two terminally functionalized biphenyl units, one phenylene extension, and the original solubilizing cyclohexane fragment (Scheme 1). The latter (shown in red, see Scheme 1) was envisioned to originate from commercially available monoketal-protected cyclohexa-1,4-dione **1**, circumventing a desymmetrization in a statistical fashion (to avoid potentially cumbersome purification). Initial attachment of one terminal biphenyl unit (green) was followed by introduction of the phenyl spacer (black) carrying a halogen functionality for subsequent connection to the other terminal biphenyl unit (carrying the substituent R′). The resulting **6P** precursors should display sufficient solubility due to the central cyclohexane kink, thereby allowing for facile chromatographic purification. The final sequence of deprotection, elimination, and oxidation leads to aromatization of the former saturated cyclohexane fragment and installs the last missing phenylene unit. Isolation of the formed **6P** derivatives is enabled by both their low solubility (allowing for removal of all other soluble byproducts by extensive washing) as well as their crystallinity and thermal stability (allowing for recrystallization and final sublimation).

**Scheme 1. Retrosynthetic Analysis of Nonsymmetric 6P Derivatives**




Our actual syntheses (Scheme 2) involved addition of lithiated biphenyls **2** or **3**, followed by acidic ketal removal and subsequent MOM-protection of the tertiary alcohol to yield intermediates **4** and **5**, respectively. Nucleophilic addition of the monolithiated dibromobenzene **6** followed again by MOM-protection gave access to compounds **7** and **8**, which carry a bromine substituent for further functionalization. These advanced intermediates (**7** and **8**) were prepared on a 2 g scale and readily functionalized by Suzuki cross-coupling with various biphenyl boronic acids **9**–**12** to install the second terminus and yield the nonsymmetric 6P precursors **13**–**17**. Because of their excellent solubility in a variety of organic solvents, such as ethyl acetate, methylene chloride, THF, among others, precursors **13**–**17** were readily purified by column chromatography. The final deprotection–elimination–oxidation sequence was performed in one pot using $NaHSO_4 \cdot H_2O$ at 150 °C with *p*-chloranil as the oxidant, according to a procedure developed by Itami and co-workers.[15,16] The green intermediate elimination product proved somewhat resistant to undergo final aromatization, presumably due to its low solubility even at 150 °C in a DMSO/xylene mixture.[5,17] However, when raising the temperature to 210 °C with 1,2,4-trichlorobenzene as solvent and using *p*-chloranil or air as the oxidant complete aromatization was accomplished. After being cooled to room temperature, the products were collected by simple filtration and purified by crystallization from 1,2,4-trichlorobenzene and final gradient sublimation.

Substituents were chosen according to several criteria, most notably, (i) to provide electronic variation ranging from electron-donating to strongly electron-accepting groups (based on inductive and resonance effects), (ii) to aid characterization of the compounds' self-assembly structures (for example by XPS and NEXAFS), and (iii) to be compatible with the reaction conditions throughout the synthetic sequence. The last requirement precluded the introduction of strong tertiary amine donors, since both aniline as well as *N*,*N*-dimethylaniline (as model compounds) decomposed when exposed to the high-temperature, strongly acidic aromatization conditions. Hence, a methoxy group was chosen as donor while chloro, trifluoromethyl, and cyano groups were selected as acceptor moieties (of increasing strength). In a first set of monofunctional **6P** derivatives, the one and only substituent (−OMe, −Cl, or −CN) was introduced late in the sequence by Suzuki cross-coupling with the appropriate biphenyl boronic acids. In a second set of **6P** derivatives, targeting donor–**6P**–acceptor architectures, the methoxy donor was introduced in the beginning of the sequence as it is compatible with the subsequently employed organolithium reagents. The opposite,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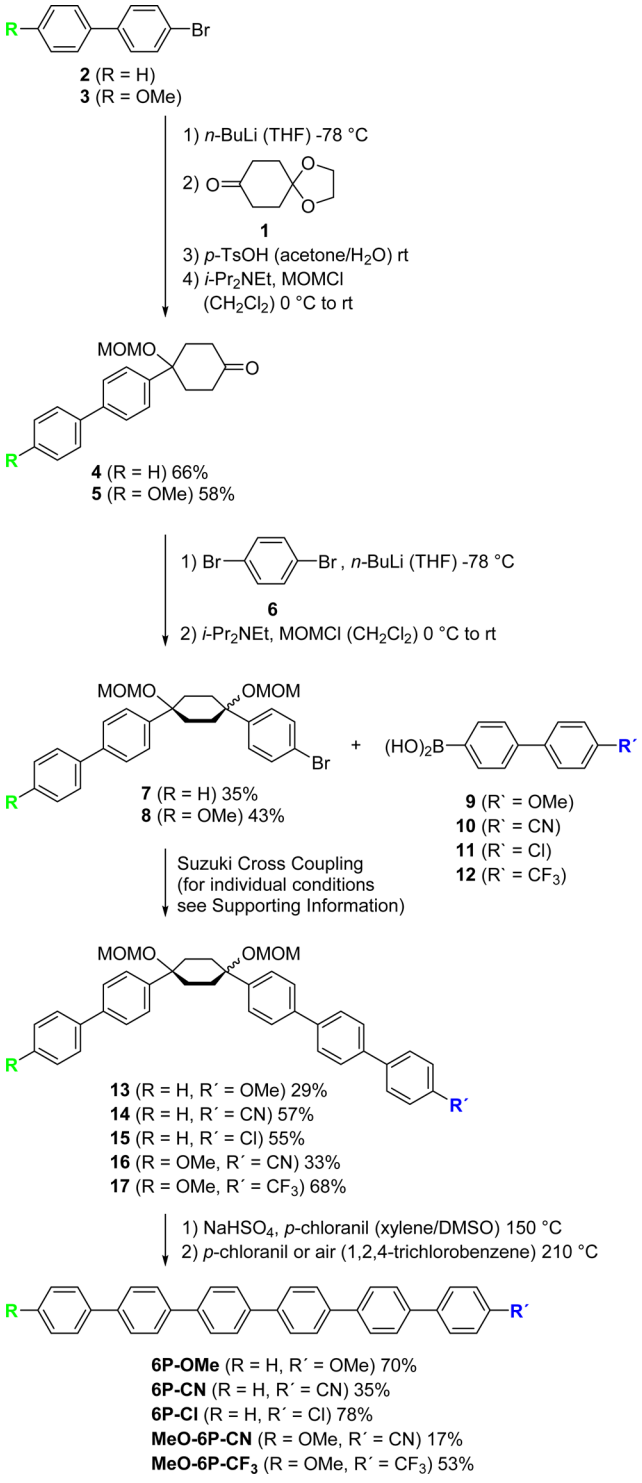
**Scheme 2. Synthesis of New *p*-Sexiphenyl Derivatives**




electron-withdrawing groups ($-CF_3$ or $-CN$) were introduced afterward again by employing mild Suzuki cross-coupling conditions. In all cases, the final deprotection−elimination−oxidation steps could successfully be performed and yielded the desired mono- and difunctional *p*-sexiphenyls.

The extremely poor solubility of the target compounds excludes conventional characterization techniques relying on reasonably concentrated solutions of the analyte, most notably NMR spectroscopy.[18] Hence, all **6P** derivatives were characterized by high-resolution mass spectrometry (using electron ionization), which in combination with the proven structure of the purified precursors provides sound evidence for the structural identity of the target **6P** derivatives. Additional proof stems first of all from the observed (and expected) drastically lowered solubility during the aromatization step and from the excitation and emission spectra showing the presence of the characteristic **6P** optical transition as well as the IR data. The latter proved to be particularly insightful for **6P-CN** and **MeO-6P-CN** as the characteristic C≡N stretching mode can be observed. Interestingly, donor-substitution gave rise to an increased wavenumber (**MeO-6P-CN**: 2231.7 $cm^{-1}$ as compared to **6P-CN**: 2228.1 $cm^{-1}$), which surprisingly is opposite to the expected decreased stretching vibration.[19] Despite their low solubility,[20] the optical properties of the **6P** derivatives, in particular their optical gaps, could be evaluated since the compounds are very emissive, and therefore, even at extremely low concentrations, fluorescence spectra could be recorded. Note that in contrast to fluorescence spectra, absorption spectra could not be obtained due to the insufficient optical density. Instead, the intense fluorescence emission enabled the corresponding excitation spectra to be obtained (Figure 1). Furthermore, note that fluorescence emission and

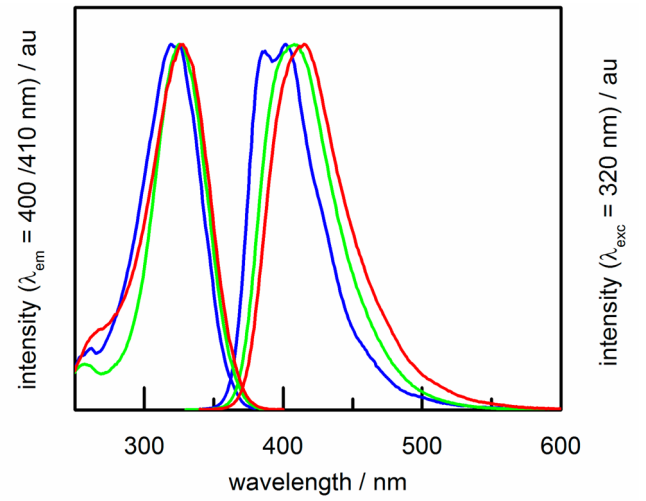



**Figure 1.** Fluorescence emission (right) and corresponding excitation (left) spectra of **6P-OMe** (blue line), **6P-CN** (green line), and **MeO-6P-CN** (red line) at extremely low concentration (<$5{\cdot}10^{-6}$ M) in $CHCl_3$ at 25 °C. All spectra have been normalized to the same intensities.

excitation spectroscopy proved to be the analytical method of choice to monitor the completeness of the aromatization sequence, because the not completely aromatized intermediate dihydro-**6P** derivatives, present after deprotection and 2-fold water elimination, can be detected even in traces due to their red-shifted emission.

The detailed spectroscopic data (Figure 1 as well as Table S1 in the Supporting Information) show that substitution with donors and/or acceptors causes a bathochromic shift of both the fluorescence excitation as well as emission spectra when compared to the parent unsubstituted *p*-sexiphenyl. The more pronounced red-shift of acceptor-substituted **6P-CN** as compared to donor-substituted **6P-OMe** can be explained by the slightly more extended π-system of the cyano group. Not unexpectedly, the combination of both donor and acceptor moieties in the case of **MeO-6P-CN** results in the largest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bathochromic shift. The corresponding optical gap amounts to 3.39 eV (onset) as compared to 3.46 eV for the unsubstituted *p*-sexiphenyl. While methoxy or chloro substitution does not affect the vibronic fine structure of the emission spectra typical for the parent unsubstituted *p*-sexiphenyl,[21] introduction of cyano or trifluoromethyl groups leads to suppression of these vibronic features. Note that although the structural identity of the investigated **6P** derivatives has been established (vide supra), their low solubilities and relatively high molecular weights preclude liquid and gas chromatography to estimate their purity, which could only be assessed via elemental analysis.[22]

In summary, we have developed a synthetic route to previously inaccessible dipolar *p*-sexiphenyl derivatives. Currently, we are investigating the influence of their dipolar structure on their self-assembly behavior at various solid substrate surfaces[23] and the resulting interfacial energy level alignment.[3,24]

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details including synthesis and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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