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A Versatile Synthesis for New 9,10-Bis(4-alkoxyphenyl)-2,7-diiodophenanthrenes: Useful Precursors for Conjugated Polymers

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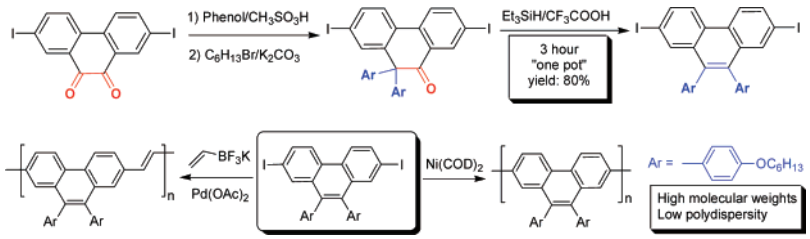
ABSTRACT



A practical synthesis for 9,10-bis(alkoxyphenyl)-2,7-diiodophenanthrenes is described. 9,10-Bis(4-hexyloxyphenyl)-2,7-diiodophenanthrene was selectively obtained by a one-pot reaction of 10,10-bis-(4-hexyloxy-phenyl)-2,7-diiodo-10*H*-phenanthren-9-one with 1 equiv of triethylsilane in trifluoroacetic acid. The target molecular architecture was demonstrated to be a useful precursor for obtaining the corresponding poly-(phenanthrene) and poly(phenanthrylene-vinylene).

In the field of organic light emitting diodes (OLEDs), a considerable interest in obtaining high band gap π-conjugated polymers as stable blue-emitting materials continues to be addressed. In order to limit the delocalization of the π density on the conjugated framework, much attention has been focused on high resonance energy systems. Poly(*p*-phenylenes) (PPPs) and their derivatives[1] have represented the most widely investigated class of π-conjugated polymers. However, the mandatory introduction of solubilizing groups in the polymer backbone of PPPs causes an additional torsion of the phenylene−phenylene angles,[2] which shifts the emission of these polymers to the violet region. The idea of linking two phenylene units by a methine bridge[3] turned out to be successful in terms of color emission, but it introduces easily oxidizable sites, which are responsible for the spectral instability of the corresponding polymers.[4] From a structural point of view, a viable alternative is constituted by phenanthrene, one of the most versatile fused aromatic compounds in the light of its easy functionalizability.

After a report highlighting its potential,[5] a very recent work has pointed out the possibility of a simple introduction of several functional groups in six positions of the phenanthrene system.[6] Furthermore, its high resonance energy and consequent stability[7] grants this molecule the suitable requisites as monomer precursor for obtaining stable blue-emitting poly-

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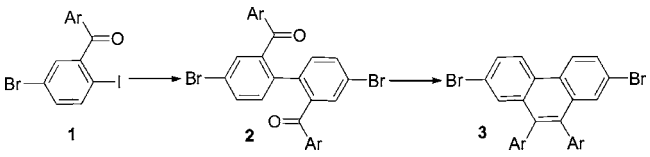
mers. In this framework, it has been ascertained that the presence of aryl groups in the 9,10 positions of phenanthrene is crucial for preserving the optical properties of the corresponding macromolecules in the solid state.[8] The synthesis of 9,-10-diaryl-2,7-dibromophenanthrenes has been recently described by Müllen[8] et al. and the proposed approach, sketched in Scheme 1, envisages as key step the McMurry-type

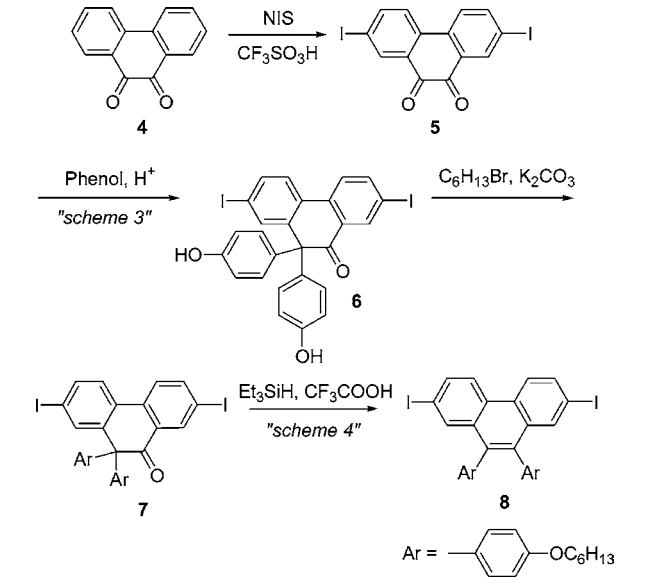
Scheme 1. Synthesis of 9,10-Diaryl-2,7-dibromophenanthrenes According to Ref 8



coupling of carbonyl groups in **2** generating the phenanthrene scaffold. The introduction of the leaving groups (in this case bromides) in the less activated 2,7 positions of phenanthrene is pursued by a selective reductive homocoupling of **1**, exploiting the higher reactivity of iodides toward the Ullmann-type reaction, leading to **2**. However, the potentialities of this synthetic approach are limited by the forced presence on phenanthrene of halogen leaving groups less reactive than iodides.

In this paper, we propose a very practical alternative synthetic method for the preparation of 9,10-diaryl-2,7-diiodophenanthrenes. The reaction sequence is outlined in Scheme 2. The commercially available phenanthrenequinone was con-

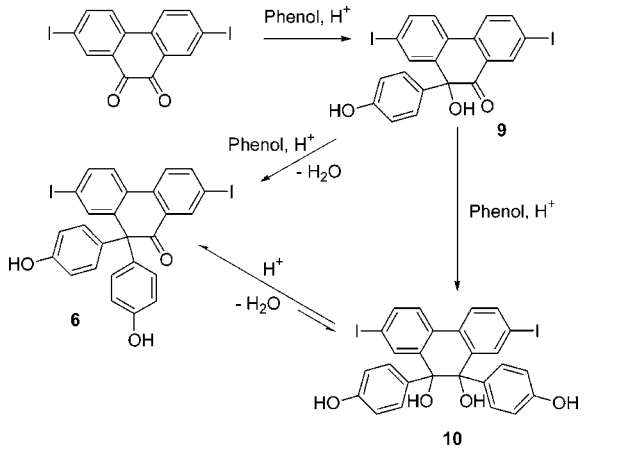
Scheme 2. Synthesis of **8**



verted into the corresponding 2,7-diodo derivative **5** using *N*-iodosuccinimide in triflic acid, according to a literature procedure.[9] Compound **5** was then submitted to a Friedel−Crafts reaction with an excess of phenol and methanesulfonic acid in CCl_4 at 80 °C to afford the corresponding product **6** in 90% yield. Remarkably, the carbonyl compound **6** was obtained in one pot, bypassing the adoption of the known multistep procedures[10] which use Grignard reagents that are incompatible with the presence of iodides in the molecule.[11]

The plausible mechanism yielding **6** is shown in Scheme 3. The aromatic electrophilic substitution of the protonated

Scheme 3. Plausible Mechanism for Obtaining **6**



form of phenanthrenequinone onto phenol affords the intermediate **9**, possessing two sites for the subsequent proton attack: the carbonyl and the hydroxyl group. The protonation of the carbonyl would lead to the formation of the corresponding pinacol compound **10**, which transforms into **6** through acid-promoted pinacol/pinacolone rearrangement. On the other hand, following protonation of the C-9 hydroxyl group, the ketonic product **6** could be directly obtained. It is reasonable to suppose that the two pathways are both plausible and that the pinacol/pinacolone rearrangment is strongly favored in the acidic reaction medium. It is remarkable how, notwithstanding the excess of phenol used, the reaction does not lead to the tetrasubstituted derivative, probably because of the severe steric hindrance exerted by the two aryl groups, hampering further aromatic electrophilic substitutions.

As illustrated in Scheme 2, the presence of the hydroxyl functionalities in **6** ensured a straightforward introduction of alkyl chains of the desired length by means of a nucleophilic substitution on the appropriate alkyl bromide. In our case, compound **7** was obtained in 73% yield by reaction of **6** and hexyl bromide in methyl-isobutylketone in the presence of K_2CO_3 as base.

At this point of the synthetic sequence, the construction of the 9,10-diarylphenanthrene scaffold, according to literature approaches,[10] should require the reduction of the ketone

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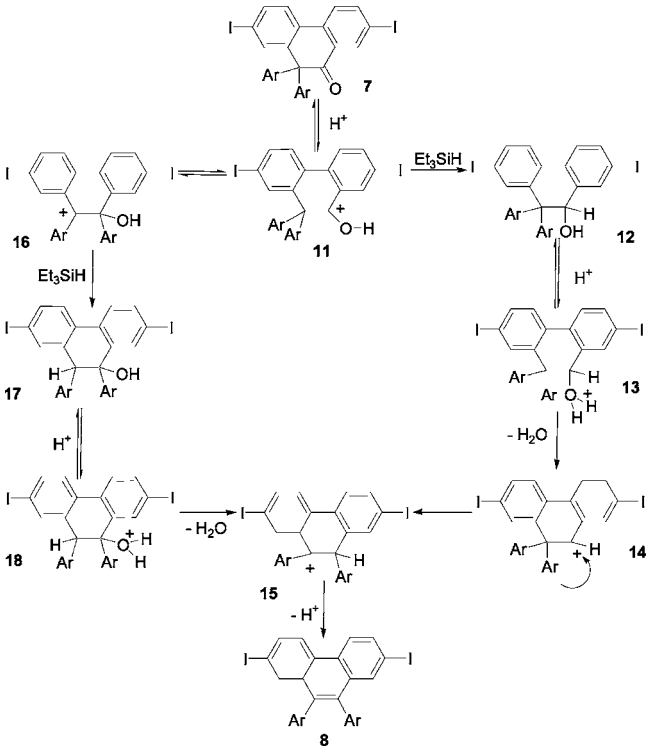
in **7** to the −OH group followed by a rearrangement of the aryl groups and subsequent dehydration catalyzed by proton sources to afford **8**. In order to avoid the use of $LiAlH_4$ for obtaining the −OH group in this highly bulky substrate (its employment might have led to a simultaneous dehalogenation of the substrate,[12] forming impurities that are extremely difficult to remove) we chose milder conditions for the reductive step in the synthesis of **8**.

We were pleased to find that reaction of **7** with one equivalent of triethylsilane in trifluoroacetic acid at 80 °C did not simply afford the ketone reduction product but the target molecule **8**, with unexpected high selectivity, in a fast (3 h), high-yielding (80%) one-pot reaction. The product could be straightforwardly purified and was fully characterized by NMR, IR, and elemental analysis. The selectivity of this reaction is quite surprising, considering all the possible byproducts that could be obtained during the reaction. It is known that triethylsilane formally acts as a hydride source for carbocations,[13] and its versatility has been demonstrated for the conversion of ketones to methylene groups.[14] The use of triethylsilane requires a protic source (trifluoroacetic acid) necessary to generate the suitable carbocations.

For these reasons, it is realistic to consider two simultaneous reaction pathways for the obtainment of **8**, as depicted in Scheme 4.

Scheme 4. Plausible Mechanisms for Obtaining **8**

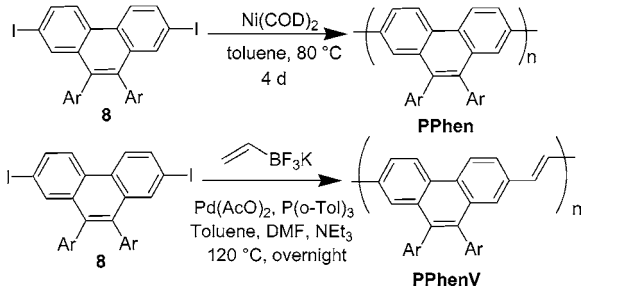


Protonation of **7** leads to the carbocation **11**, which can act as hydride acceptor. The alcohol **12** can be further protonated yielding, after loss of a water molecule, the carbocation **14**. The latter intermediate would then undergo the aryl shift yielding the more stable carbocation **15** and subsequent aromatization leading to the target molecule **8**. On the other hand, another reaction pathway can start from the rearrangement of **11** yielding the more stable carbocation **16**, which, in turn, can act as hydride acceptor forming **17**. Dehydration of **17** leads again to the intermediate **15**, followed by aromatization through proton elimination, giving the target molecule **8**. The high selectivity of the reaction is explained by assuming that the rearrangement of carbocation **14** and the aromatization of **15** are faster processes with respect to reaction of these species with triethylsilane.

The advantages of having built up an iodophenanthrene building block were demonstrated by carrying out polymerization tests for the obtainment of poly(2,7-phenanthrene)s and poly(2,7-phenanthrylenevinylene)s.

As a first test, the polymerizaton of **8** by $Ni(COD)_2$-promoted reductive homocoupling was carried out affording the corresponding polymer **PPhen** in 76% yield (Scheme 5). The obtained polymer was soluble in $CHCl_3$, CH_2Cl_2, and THF and was characterized by ^1H NMR, FT-IR, and gel permeation chromatography (GPC).

Scheme 5. Synthesis of **PPhen** and **PPhenV** from **8**



Its number average molecular weight (against polystyrene standards) was estimated as 31 000 Da (~60 repeating units) and, noteworthy, could be obtained with fairly low polydispersity ($M_w/M_n = 1.5$).

In another polymerization experiment, monomer **8** was submitted to a cascade Suzuki−Heck reaction, a method recently reported by us for obtaining poly(arylenevinylene)s,[15] which employs the use of potassium vinyltrifluoroborate[16] as ethylene equivalent. The macromolecule **PPhenV** was obtained in a one-pot reaction with potassium vinyltrifluoroborate, palladium(II) acetate/tri(*o*-tolyl)phosphane as catalyst, and triethylamine as base in toluene/DMF at 120 °C. This polymer was obtained in 71% yield as a green powder,

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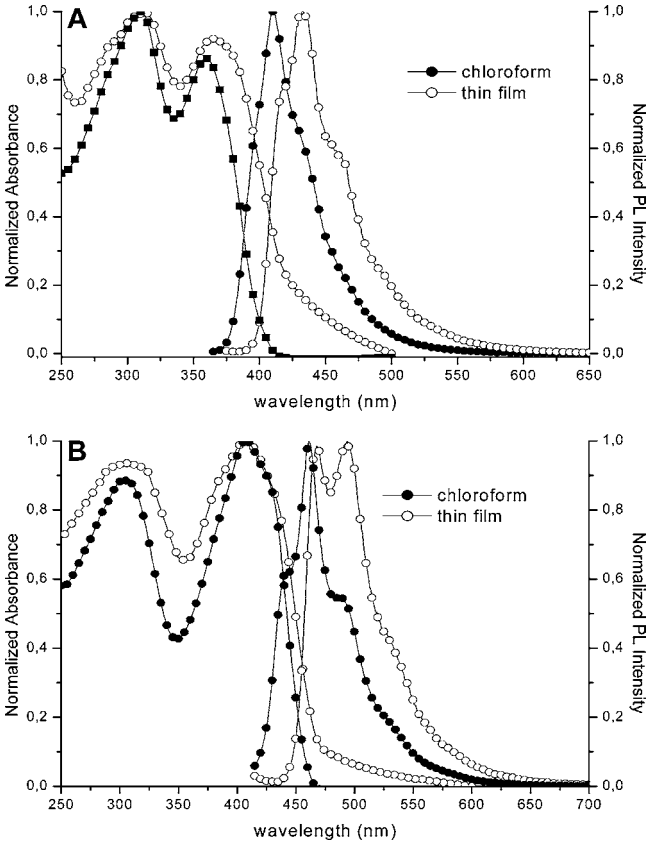

Figure 1. UV−vis and photoluminescence spectra of **PPhen** (A) and **PPhenV** (B) in chloroform solution and as a thin film on quartz.

soluble in chlorinated solvents, which was characterized by ^{1}H NMR and FT-IR spectroscopy. Its number average molecular weight was found to be 7500 Da (∼14 repeating units) with a polydispersity of 2.2. Noteworthy, this is the poly(2,7-phenanthrylene-vinylene) with the highest reported relative molecular weights.[6]

A preliminary investigation of the physical properties of the two polymers was carried out by means of UV−vis and photoluminescence both in chloroform solution and in the solid state (Figure 1). The optical band gap of the two polymers was estimated by the onset of the absorption as 2.97 eV (**PPhen**) and 2.63 eV (**PPhenV**). Consequently, **PPhen** shows a blue-emission (λ_{max} = 409 nm) while **PPhenV** emits in the blue-green region (λ_{max} = 461 nm) in solution. In the solid state, structured bands can be observed with maxima at 433 nm (**PPhen**) and 493 nm (**PPhenV**). As expected, the emission features of both polymers show no evidence for aggregation phenomena (broadening of emission band) in the solid state because of the beneficial effect of the two phenyl groups in the phenanthrene 9,10-positions, orthogonally placed with respect to the conjugated backbone, preserving the molecules from strong intermolecular interactions.

In conclusion, we have synthesized a 2,7-diiodo-9,10-diaryl-phenanthrene by means of a versatile synthetic approach, envisaging as key step a reaction of the suitable carbonyl precursor with triethylsilane in trifluoroacetic acid. This reaction proceeds with a simultaneous hydride donation, dehydration and an aryl 1,2-shift to construct the phenanthrene scaffold in high yield and selectivity. In addition to these synthetic aspects, the approach grants the obtainment of monomers affording poly(2,7-phenanthrene)s and poly(2,7-phenanthrylenevinylene)s with relatively high molecular weigths and low polydispersities. Our current efforts are devoted to testing the scope width of the reaction and to the use of our monomer typology for obtaining suitable phenanthrene-based copolymers for applications as active layers in OLEDs.

Supporting Information Available: Synthetic procedures and characterization data of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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