Facile Synthesis of 9,10-Diarylphenanthrenes and Poly(9,10-diarylphenanthrene)s

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ABSTRACT
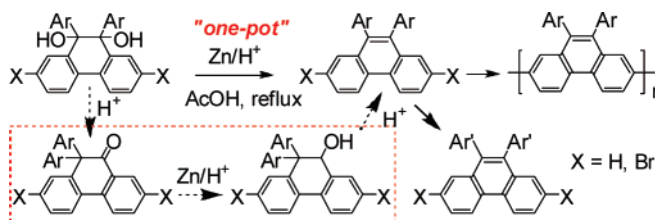
One-pot reduction of 9,10-diaryl-9,10-dihydrophenanthrene-9,10-diols to 9,10-diarylphenanthrenes was achieved with Zn/H⁺ in acetic acid. Accordingly, various novel phenanthrenes and polyphenanthrenes with efficient blue emission were easily synthesized.

Conjugated oligomers and polymers have been intensively explored for their applications in electronics, photonics, and optoelectronics in the last two decades.[1] Further improvement of the device performance such as efficiency and lifetime relies on not only the development of new fabrication techniques and device configurations, but also on the incessant exploration of new materials. Research has therefore focused on the design and synthesis of phenylene-based stepladder conjugated polymers, which have shown unique and promising optoelectronic properties.[2]

Phenanthrene (PhA) is one of the most stable fused aromatics.[3] Its high resonance energy qualifies it as an ideal building block for conjugated systems with a high energy gap. However, only a few conjugated oligomers or polymers containing PhA have been reported to date.[4−6]Particularly, the synthesis of soluble polyphenanthrenes (PPhAs)[6] is still rather difficult for lack of facile methods to prepare polymerizable PhA derivatives carrying the necessary solublizing groups.

PhAs with halogen atoms at the 2,7-positions and solublizing groups at the 9,10-positions have so far been synthesized in two different ways: (1) McMurry coupling of carbonyl groups in 4,4′-dibromo-2,2′-di(4-decylbenzoyl)-1,1′-biphenyl[6a] and (2) Friedel−Crafts reaction of phenanthrenequinone (PhAQ) with phenol followed by alkoxylation.[6b] However, these protocols are limited by multistep reactions or their narrow scope. MacLachlan et al. also reported the

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(3) Hepworth, J. D.; Waring, D. R.; Waring, M. J. *Basic Concepts in Chemistry*: *Aromatic Chemistry*; John-Wiley & Sons, New York, 2003.

(4) (a) Tian, H.; Shi, J.; Dong, S.; Yan, D.; Wang, L.; Geng, Y. H.; Wang, F. *Chem. Commun.* **2006**, 3498−3500. (b) Tian, H.; Wang, J.; Shi, J.; Yan, D.; Wang, L.; Geng, Y. H.; Wang, F. *J. Mater. Chem.* **2005**, *15*, 3026−3033.

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(6) (a) Yang, C.; Scheiber, H.; List, E. J. W.; Jacob, J.; Müllen, K. *Macromolecules* **2006**, *39*, 5213−5221. (b) Grisorio, R.; Suranna, G. P.; Mastrorilli, P.; Nobile, C. F. *Org. Lett.* **2007**, *9*, 3149−3152.

synthesis of 2,7-diiodo-3,6,9,10-tetraalkoxy-PhAs;[5] however, the $-OCH_3$ groups at the 3,6-positions could induce significant steric hindrance for the preparation of PPhAs. The established synthetic route toward 9,10-diaryl(Ar)-PhAs from PhAQ (Scheme 1) can afford PhAs with different Ar from
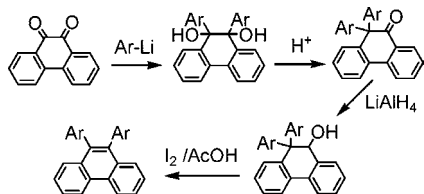
the same substrate, but the reduction of diol precursors to PhAs requires several steps.[7] Here we report a one-pot reduction of 9,10-diaryl-9,10-dihydrophenanthrene-9,10-diols to 9,10-diaryl-PhAs by which a variety of PhAs and PPhAs become accessible.

Zn/H^+ is a well-known reductant system, with which pinacol rearrangement and reduction of ketone intermediate in the established route[7] should be able to be accomplished in one step. In fact, when a mixture of diol **1a**, Zn powder, and concd HCl was refluxed in AcOH, **1a** disappeared completely in 5 min accompanied by the appearance of **3a** (major) and **2a** (minor), as monitored by thin-layer chromatography (TLC). Further refluxing led to gradual conversion of **3a** to **2a**. Addition of Zn and HCl in portions gave a better yield. In a typical optimized condition, Zn (10 equiv) and HCl (4.8 equiv) were added in two portions, and **2a** was obtained in a yield of 86% (see the Supporting Information). To prove **3a** as the key intermediate, its reduction was performed under similar conditions. Compound **2a** was obtained in 93% yield. On the basis of the above observations, a reaction pathway is proposed as shown in Scheme 2: **1a** is
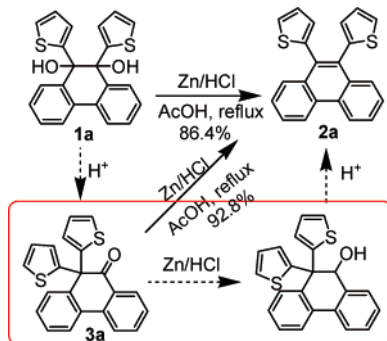
first converted to pinacolone intermediate **3a** via a typical pinacol rearrangement in the presence of H^+, then **3a** is reduced by Zn/H^+. The resultant intermediate is rapidly

converted to **2a** via a Wagner−Meerwein rearrangement under the protic conditions.[7] We also found that the existence of both strong acid and water was crucial. For different acids, the yield increased in the order of HCl ≥ H_2SO_4 > CF_3SO_3H > CF_3COOH.

The above approach is applicable to the synthesis of various PhAs. As shown in Table 1, the yield of **2** is in the range

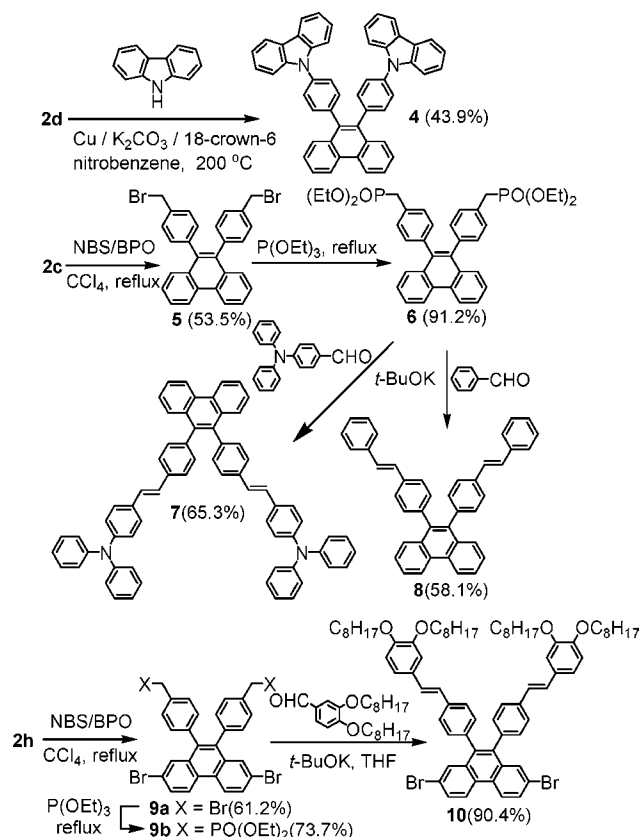| entry	X	Ar	compd/yield (%)
1	H		**2a**/86.4
2	H		**2b**/80.1
3	H		**2c**/97.8
4	H		**2d**/87.1
5	H		**2e**/60.1
6[a]	H		**2f**/22.4
7	Br		**2g**/43.2
8	Br		**2h**/75.7
9	Br		**2i**/81.3

[a] The diol was directly used without purification.

of 22−98% for different Ar. Diol intermediates **1** were synthesized according to the reported procedure[7c] and details are included in the Supporting Information. It should be noted that the low yield of **2f** is due to the impure diol **1f**, which is not stable enough for chromatographic purification. The reduction of **1** to **2** also proceeds smoothly without debromination for entries 7−9, which allows easy preparation of various PhA monomers. Since different diaryl-PhAs can be synthesized from the same commercially available starting material, PhAQ, in two steps, this approach is a practical method to make functionalized PhAs. Of note, facile halogenation of PhAQ has been achieved.[8] Therefore, polymerizable PhAs carrying different aryl substituents become available.

The successful synthesis of various PhAs allows us to prepare PhAs with structurally complex substituents via postfunctionalization. Accordingly, three types of materials, i.e., arylamine substituted PhAs **2f** and **4**, phenylene-vinylene

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Table 2. Solution Absorption and PL Maxima (λ), Energy Bandgaps (ΔE), and PL Quantum Yields (Φ) of **7**, **8** and **P1**−**3**

compd	λ_{abs} (nm)[a]	λ_{PL} (nm)[a]	ΔE (eV)[b]	Φ[c]
7	371, 280, 298	428	2.97	0.80
8	305, 281	394	3.41	0.64
P1	381, 306	403, 425	3.04	0.56
P2	367	410, 430	3.00	0.10
P3	332, 390	412, 436	2.90	0.83

[a] Measured in toluene. [b] Estimated from absorption onset. [c] Measured in toluene with 9,10-diphenylanthracene as a standard.

Thermal properties of **2f**, **4**, **7**, **8**, and **P1**−**3** were studied by means of differential scanning calorimetry (DSC). Com-

Figure 1. Solution absorption and PL spectra of **7** and **8** (a, 10^{-5} M) and **P1**−**3** (b, 10^{-5} M for repeating units) in toluene and film absorption and PL spectra of **P1**−**3** (c).

substituted PhAs **7** and **8**, and PPhAs **P1**−**3** with different aryl substituents at the 9,10-positions, were provided to support the versatility of the current approach. As shown in Scheme 3, carbazole-containing **4** was synthesized from **2d** via a typical Ullmann coupling reaction[9] in a yield of 44%. The bromination of **2c** with NBS/BPO (benzoyl peroxide) afforded **5** in a yield of 54%, which was converted to the corresponding phosphonate ester **6**. The compounds **7** and **8** were obtained via Wittig reactions[10] in yields of 65% and 58%, respectively. Likewise, compound **10** with Br atoms at the 2,7-positions was prepared as shown in Scheme 3.

Three PPhAs with different Ar groups were synthesized by means of the Yamamoto coupling reaction,[11] as shown in Scheme 4. All of these polymers are soluble in common organic solvents such as THF, chloroform, and toluene. The number-average molecular weight (M_n) of **P1**−**3** is 140 800, 54 700, and 34 100 g/mol, respectively, as measured by gel-permeation chromatography (GPC) with polystyrene as the standard.

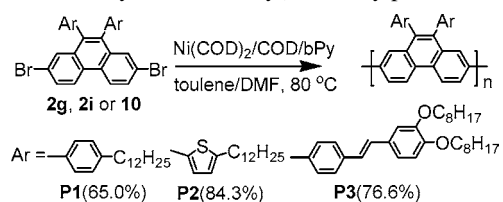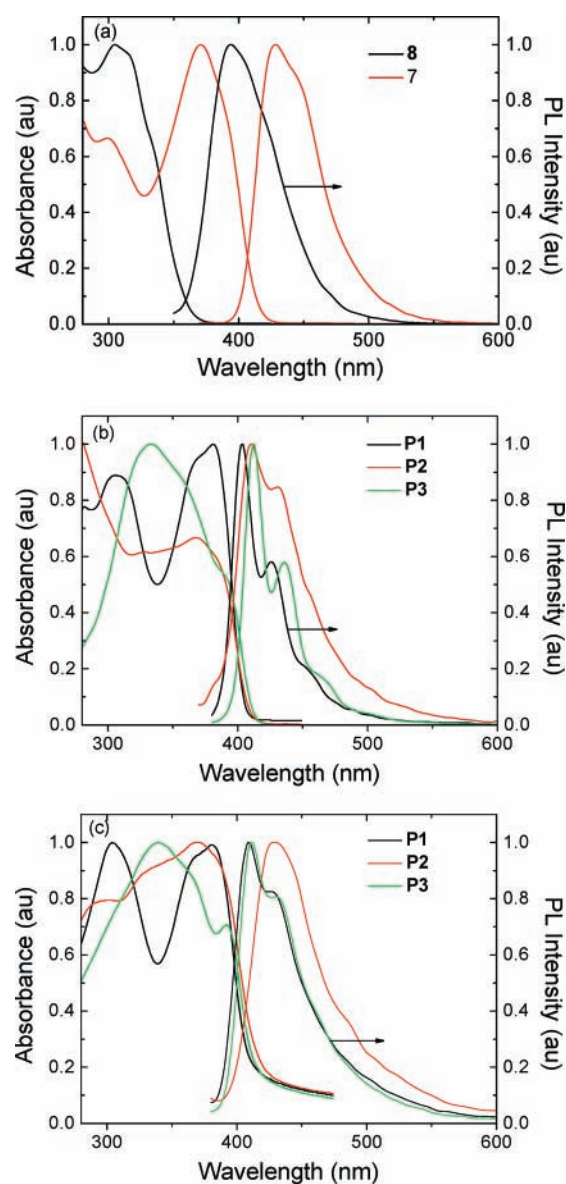**Scheme 4.** Synthesis of Poly(9,10-diarylphenanthrene)s

pound **2f** is a highly crystalline material with a melting point of 270 °C. Compounds **4**, **7**, and **8** form typical molecular glasses with a glass transition temperature (T_g) of 147, 144, and 99 °C, respectively. This high T_g is very important for light-emitting small molecules.[12] Similar to the PPhAs reported previously, no transitions corrsponding to T_g and crystal melting were observed for the polymers **P1**−**3**.[6a]

The electronic absorption maxima (λ_{abs}), the photoluminescence (PL) maxima (λ_{PL}), and the PL quantum yields of **7**, **8**, and **P1**−**3** are summarized in Table 2, and their solution absorption and PL spectra are displayed in Figure 1. Compound **8** emits violet light with a PL maximum of 394 nm and a PL quantum yield of 0.64. The introduction of diphenylamine substituents induces a 34 nm red-shift of the PL maximum (compound **7**). Thereby, the PL quantum yield increases to 0.80. These results suggest that **7** is a highly efficient blue emitter.

Depicted in panels b and c of Figure 1 are absorption and PL spectra of the polymers **P1**−**3**. In toluene solution, emission maxima of **P1**−**3** are at 403, 410, and 412 nm, respectively. Employing electron-richer or larger Ar substituents only results in a red-shift of the PL maximum by less than 10 nm, although these Ar groups are linked with PhA

unit via sp^2 hybrid carbons. PL quantum yields of **P1**−**3** are 0.56, 0.10, and 0.83, respectively. The polymer **P3** exhibits the highest PL quantum yield and is among the most highly efficient light-emitting polymers. Upon going from solution to the film, PL bands of **P1** and **P2** are red-shifted by 6 and 20 nm, respectively. In contrast, the PL spectrum of **P3** is almost unchanged. This indicates that increasing the size of substituents can noticeably suppress the aggregation of the polymer chain in the solid state. Therefore, it is possible to finely adjust the emission color, to improve PL quantum yield, and even to tune the morphological and charge-transporting properties of PPhAs by selecting appropriate Ar substituents.

In summary, we have demonstrated a versatile approach toward various 9,10-diaryl-substituted phenanthrene derivatives, which allows the easy synthesis of polyphenanthrenes with different aryl substituents at the 9,10-positions. Photophysical studies of the resulting materials indicate that phenanthrene is an ideal building block for high energy gap conjugated materials with promising optoelectronic properties.

Supporting Information Available: Experimental procedure for synthesis of all intermediates and target molecules, and characterizations for these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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