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# A Three-Step Synthesis of 4*H*-Cyclopenta[*def*]phenanthrene from Pyrene

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4*H*-Cyclopenta[*def*]phenanthrene (CPP) is a valuable building block in the production of photoactive polymers, which find use in a wide range of organic electronic applications. Of particular importance is their use in the development of blue-colored, organic light-emitting diodes (OLEDs), which remains a challenge in the field. Unfortunately, commercial sources and synthetic procedures known in the literature are unable to provide enough CPP for large scale implementation. Herein, we report on the development of a novel, gram-scale synthesis of CPP in three steps, starting from pyrene. The key steps in our methodology are the ring contraction of pyrene-4,5-dione to oxoCPP in a single step, as well as the direct reduction of oxoCPP to CPP. Apart from the small number of synthetic steps, our methodology benefits from the use of relatively non-hazardous reagents, together with optimized purification procedures, making CPP accessible in useful quantities.

Organic light-emitting diodes (OLEDs) show significant advantages over the now commonplace inorganic ones, including simpler manufacturing, lower power consumption and better durability, to name just a few.<sup>[1]</sup> Of the three primary colors, blue colored OLEDs have proven to be especially elusive, making them the focus of much research.<sup>[2]</sup> Thin film, multi-layer devices using low molecular weight polymers incorporating the 4*H*-cyclopenta[*def*]phenanthrene (CPP) motive hold promise in this regard, generally showing stable emissions and good color purity.<sup>[3]</sup> Other electro-luminescent and photovoltaic devices,<sup>[4]</sup> including dye-sensitized solar cells,<sup>[5]</sup> also benefit from the low band gap of CPP-based polymers, which is responsible for its superior qualities.<sup>[4e]</sup> Some typical examples of polymeric constructs incorporating the CPP motive are shown in Figure 1. They can consist entirely of repeating CPP units (Figure 1A,<sup>[3b]</sup>

Figure 1C<sup>[3f]</sup>), or alternate with other specific aromatic moieties to tune the HOMO–LUMO levels (Figure 1B).<sup>[4c]</sup> It can sometimes be fortuitous to cap the polymer with aromatic moieties, to suppress the broad emission bands that originate from excimer formation (Figure 1C).<sup>[6]</sup> Synthesis of these constructs usually starts from the parent CPP molecule **1**, which is first doubly alkylated on the C4 position to increase solubility, and then hydrogenated to the 8,9-dihydro compound, to allow site selective dibromination. Back-oxidation then yields a general building block which is then further diversified, *i.e.* by conversion to or coupling with boronic acids in Suzuki-type cross coupling reactions, or *via* a Yamamoto type homo-coupling (Scheme 1A).

One important factor that hampers the large-scale production of CPP based polymers is the high cost associated with commercial samples of **1**. In addition, reported synthetic procedures to obtain **1** are either lengthy, poor yielding, or require the use of hazardous materials, making them unamendable for large scale synthesis (Scheme 1B).<sup>[7]</sup> In this paper, we report on an economic, three-steps procedure to obtain **1** on a gram scale, starting from pyrene, with an overall yield of 10% (Scheme 1C).

The oxidation of pyrene **2** to the 4,5-dione **3** using a NaIO<sub>4</sub>/RuCl<sub>3</sub> system has been reported several times in literature, including a detailed description on a 15 gram scale by Walsh *et al.*<sup>[8]</sup> One of the major drawbacks associated with this reaction is the formation of a dark-colored, intractable suspension which is difficult to filter off, seriously hampering the work-up. However, we found that, when the NaIO<sub>4</sub> was carefully added as an aqueous solution, rather than as a solid, to a solution of **2** and RuCl<sub>3</sub> in DCM:THF, and the addition was stopped when the reaction starts to warm up, a much finer suspension could be obtained. This can then be filtered off using a standard glass fritted filter, significantly expediting the work-up procedure, without negatively affecting the yield of **3** obtained from the filtrate (~50%) (Figure 2A). The product can be purified by column chromatography over silica gel using neat DCM as eluent, which can be recovered and reused to reduce the total amount of solvent needed.<sup>[8]</sup>

The crucial step in our synthesis is the direct conversion of **3** to **4**. We initially tried to accomplish this conversion by pyrolysis of **3** at 245–260 °C in an evacuated tube in the presence of lead(II) oxide.<sup>[9]</sup> This provided the desired product **4** as a yellow sublimate but only in poor yields (2–8%). When the reaction was performed on a one-gram scale, trace amounts of phenanthrene-4,5-lactone **5** were also obtained as ascertained by comparison with an authentic

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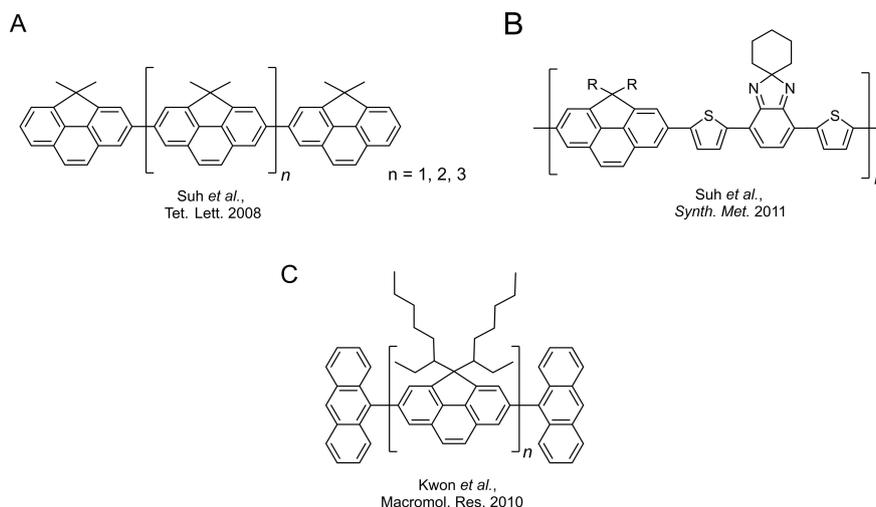
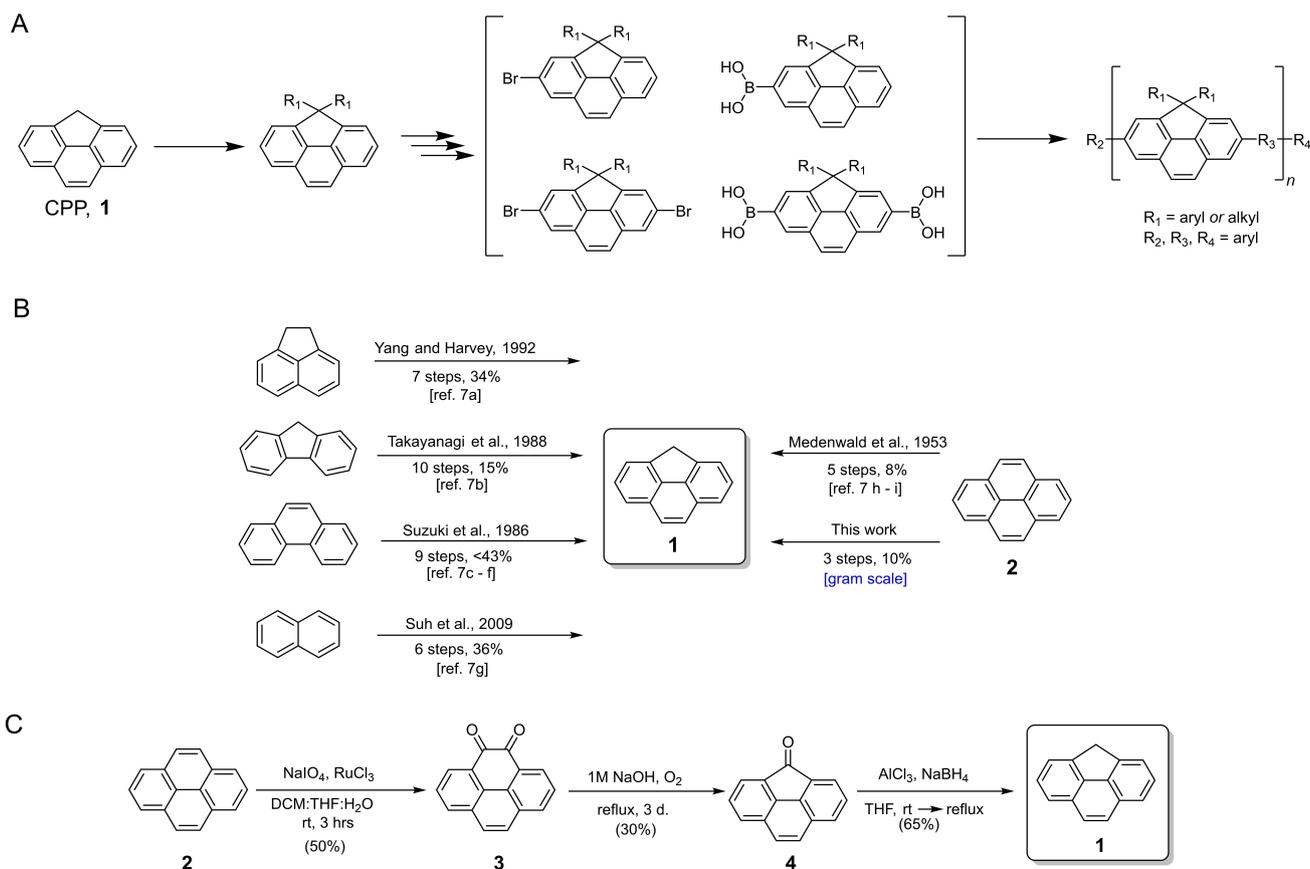


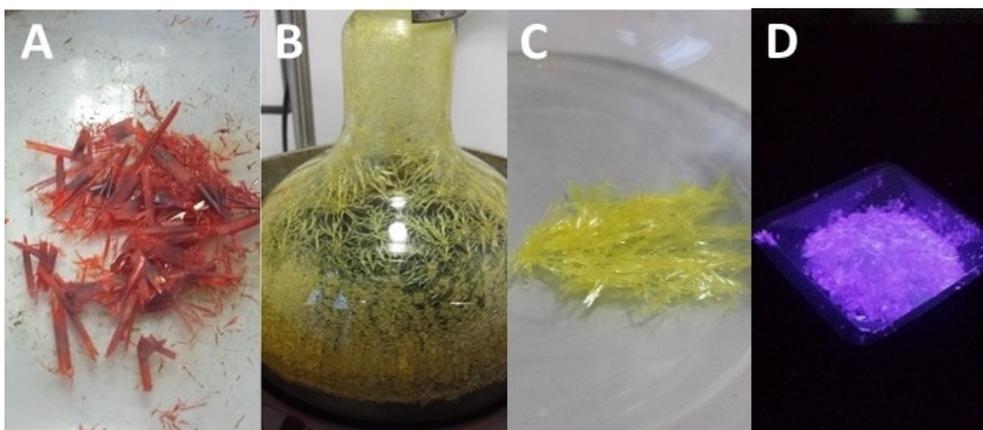
Figure 1. Some selected polymeric structures incorporating the CPP motive, designed for use in organic electronic applications.



Scheme 1. A) General synthesis route for the production of brominated CPP and CPP-boronic acids, and CPP-based polymers therefrom. B) Our and known literature procedures for the synthesis of CPP from different polycyclic aromatic hydrocarbon precursors. C) Three-step, gram scale synthesis of CPP from pyrene.

sample (See SI). A more satisfactory yield of 30% of **4** was obtained by boiling of compound **3** in an aqueous 1 M NaOH solution for three days, which resulted in deposition of the desired product as a bright yellow sublimate on the walls of

the reaction flask, as well as in the air-cooled condenser fitted to it (Figure 2B and Figure 2C).<sup>[10]</sup> Boiling for a longer period of time did not produce any more material, nor did the use of a more concentrated (10 M) NaOH solution (10%).



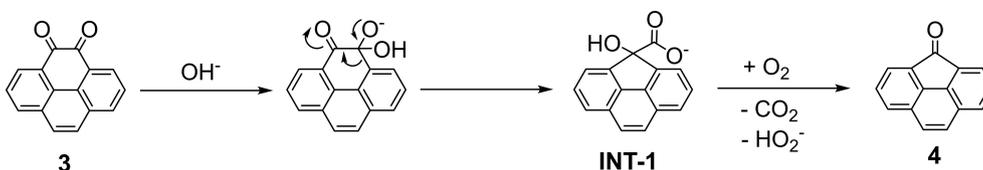
**Figure 2.** Images of the different products. A) Crystals of pyrene-4,5-dione, **3**; B) Deposition of oxoCPP **4** on the wall of a flask; C) Recovered, sublimated product **4**; D) One gram of product **1** under UV light.

To facilitate the easy recovery of the sublimated oxoCPP product, a custom reaction vessel was designed. The reaction vessel consists of a Duran beaker with removable lid, to allow the sublimate to be washed out with DCM after the reaction had finished, eliminating the need for further purification (For details see SI).

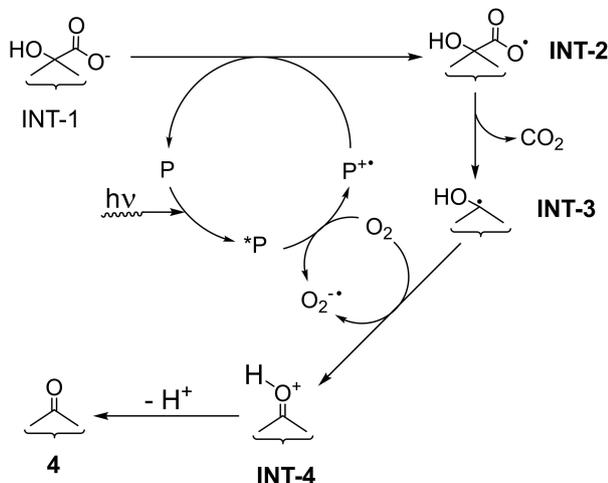
We supposed the conversion of **3** to **4** to proceed *via* a benzylic acid rearrangement in which an initial  $\alpha$ -hydroxycarboxylic acid intermediate (INT-1) undergoes oxidative decarboxylation by oxygen from the air (Scheme 2). The require-

ment of oxygen for this conversion was supported by the fact that no product formation was observed when the reaction was performed under an inert atmosphere. In addition, when the reaction was performed in the dark, no product could be isolated. As no dedicated light source was used, the known photo-sensitizability of phenanthrene was suspected to play a role in the conversion reaction.<sup>[11]</sup> Indeed, examples of self-sensitization of phenanthrene derivatives are known in literature.<sup>[12]</sup>

### Reaction scheme



### Proposed mechanism



**Scheme 2.** Reaction scheme and proposed mechanism for the oxygen mediated oxidative decarboxylation of benzylic acids.

Based on previous work regarding the oxidative decarboxylation of  $\alpha$ -hydroxycarboxylates,<sup>[13]</sup> the reaction is presumed to proceed as shown in Scheme 2. The reaction is initiated by excitation of molecules containing a phenanthrene moiety **P** (i.e. **3** or **4**). The excited species \***P** then undergoes a single electron transfer (SET) to aerial oxygen to produce a superoxide radical and a radical cationic phenanthrene species **P**<sup>•+</sup>. The cationic species reacts with carboxylate (**INT-1**) to yield a carboxyl anion-radical intermediate (**INT-2**), which is accompanied by the re-formation of the ground state phenanthrene species **P**. The radical intermediate (**INT-2**) decomposes with homolytic C–C bond cleavage, resulting in the formation of CO<sub>2</sub> and a secondary alcohol radical (**INT-3**). Another SET with aerial oxygen then yields the protonated carbonyl (**INT-4**), from which the ketone product **4** is formed after deprotonation. The superoxide radicals formed are most likely quenched to form hydrogen peroxide anion. As substituted glycolic acids, like the one supposed to be formed here, are known to be attacked by hydrogen peroxide only slowly, its role is suspected to be insignificant under the present reaction conditions.<sup>[14]</sup> Moreover, despite exhaustive testing, direct treatment of **3** with different peroxides and superoxides, in different solvents and under various reaction conditions, only yielded unreacted starting material and no further identifiable products. Lastly, addition of KMnO<sub>4</sub> as oxidizing agent also did not increase the yield of **4**.

Having developed an efficient route to **4**, we then turned to its reduction to the desired CPP **1**. A procedure for the direct reduction of **4** to **1** via a Wolff-Kishner reaction could be found in literature, with a reported yield of 60%.<sup>[7h]</sup> In order to avoid the use of hazardous hydrazine, however, we tried reduction using Al(BH<sub>4</sub>)<sub>3</sub>, generated *in situ* by adding a solution of AlCl<sub>3</sub> in anhydrous THF to a mixture of NaBH<sub>4</sub> and **4** (Scheme 1).<sup>[15]</sup> After work-up, the product was purified by a standard silica gel column using neat pentane as the eluent. Again, as with the purification of **3**, solvent used for the chromatography could be retrieved and reused, reducing the total amount of solvent needed. Gratifyingly, the reduced product could be isolated on one-gram scale, with a slightly increased yield of 65% (Figure 2D). It is important to note that, when insufficiently dry reagents were used, brown colored reaction mixtures were obtained, which resulted in significantly lower yields of the desired product (10–30%).<sup>[16]</sup>

To conclude, we here reported a convenient three-step, gram scale synthesis of CPP from pyrene. Our methodology benefits from the use of relatively non-hazardous reagents, mild reaction conditions and optimized purification procedures. We have additionally proposed a mechanism to explain the direct conversion of pyrene-4,5-dione to oxoCPP. These results make CPP accessible in quantities that will expedite the development of organic electronics.

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## Conflict of Interest

The authors declare no conflict of interest.

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