Dibenzoanthradiquinone Building Blocks for the Synthesis of Nitrogenated Polycyclic Aromatic Hydrocarbons

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T he synthesis of increasingly large polycyclic aromatic hydrocarbons $(PAHs)^1$ is attracting growing attention due to their potential applications in electronics, photonics, energy storage and conversion, sensing, and information storage, among others. PAHs can be considered small cut outs of graphene that show discrete HOMO-LUMO gaps and energy levels that can be tuned with the number of fused rings, their arrangement, and the number and position of embedded heteroatoms, providing an infinite number of possibilities to prepare organic semiconductors with different properties.

Cyclocondesation reactions between o-quinone and odiamine precursors have been widely used for the construction of nitrogen-doped PAHs (N-PAHs).^{1b-f} On one hand this type of condensation fuses together the π -systems of both precursors through the formation of a pyrazine ring, while, on the other hand, it introduces simultaneously two electronwithdrawing nitrogen atoms in the framework. Our ability to increase structural complexity by using such cyclocondensation reactions depends on the development of efficient methods to synthesize PAHs with sets of o-quinones and o-diamines in different positions. To date there is a number o-quinones that have been used in the synthesis of complex N-PAHs, some of which include *o*-quinones of anthracene,² phenanthrene,³ phenantroline,^{3b} pyrene,^{1f,4} coronene,⁵ hexabenzocoronene,⁶ and graphene quantum dots.' However, the methods for the introduction o-quinones in PAHs are not always straightforward or general. Not surprisingly, their use depends directly on their synthetic availability. For example, although, the synthesis of pyrene o-quinones was reported in 1937,^{4a} it was not until 2005^{4b} when they became accessible through a one-step method from pyrene derivatives, which resulted in a substantial increase in their interest.

Dibenzo[a,h]anthracene (1a) is constituted by five fused rings and can be structurally described as a planarized tri-pphenylene group fused to two additional rings in opposite bays (Figure 1). Electronically, this arrangement gives rise to three



Figure 1. Dibenzo[a,h] anthracenes (1a and 1b) and dibenzo[a,h]-anthracene-di-o-quinones (2a and 2b). Library of N-PAHs 3a, 3b, 4, and 5.

Clar sextets, one on each ring of the tri-*p*-phenylene residue, and to two K-regions with a double bond character. The

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oxidation of the K-regions of dibenzo[a,h]anthracene to the dio-quinone (**2a**) and its subsequent derivatization with ophenylenediamine to produce the corresponding diquinoxaline have been described by Stephenson in 1949.⁸ However, dibenzo[a,h]anthracene-di-o-quinone **2a** was obtained as a byproduct of the synthesis of the mono-o-quinone and its isolation was only partially achieved by fractional sublimation. Since then, to the best of our knowledge, there has been an additional report describing diquinone **2a**, but just as an undesired oxidation byproduct in 1958.⁹ Therefore, alternative methods need to be sought.

Herein, we make available a straightforward method for the synthesis of dibenzo [a,h] anthracene-5,6,12,13-diquinones 2a and 2b from their respective dibenzo [a,h] anthracenes 1a and 1b. In addition, we describe a synthetic methodology to prepare dibenzo [a,h] anthracenes 1a and 1b in a gram scale that does not involve any chromatographic purification. To showcase the usefulness of di-o-quinones 2a and 2b as building blocks, a series of N-PAHs (3a, 3b, 4, and 5) have been synthesized by cyclocondensation with different *o*-diamines leading to a small library of derivatives that show different electronic absorption and fluorescence properties that cover the visible and the NIR, different redox properties, and pseudoconductivy values that illustrate their potential as organic semiconductors.

The synthesis of dibenzo[a,h] anthracene (Scheme 1) started with the iodination of the commercially available 1,4-

Scheme 1. Synthetic Route for the Preparation of the Dibenzo[*a*,*h*]anthracene-5,6,12,13-diquinones



dibromobenzene **6** into diiodide 7. Next, (trimethylsilyl)ethynyl groups were introduced by Sonogashira coupling on the iodide positions to generate dibromide **8**, which was subsequently subjected to Suzuki coupling with phenylboronic acid to yield **9a**. Desilylation of **9a** into **10a** took place quantitively. Benzannulation of **10a** using PtCl₂ yielded dibenzo[*a*,*h*]anthracene **1a** in a 57% yield. All these synthetic steps required no chromatographic purification, and therefore **1a** could be prepared in a straightforward manner. Chemoselective oxidation of the K-regions was first attempted using NaIO₄ and RuCl₃, but only small amounts of the desired diquinone **2b** (>1%) were obtained after chromatographic purification. Longer reaction times or reoxidation of the crude under the same conditions did not alter the outcome of this reaction. Notably, after workup a large amount of a dark reddish crude mixture was obtained, which we suspected was a mixture of different oxidation intermediates of dibenzo[a,h]anthracene diquinone. When we subjected this crude mixture to a subsequent oxidation process using K₂Cr₂O₇, the yields after chromatography improved substantially to 14%. Diquinone **2a** showed very limited solubility and could only be characterized by IR. Diquinone **2a** was then allowed to react with *o*-phenylenediamine **11**¹⁰ in a 3:1 mixture of CHCl₃/AcOH yielding **3a** in 59% as a yellow solid (Scheme 2). It was

Scheme 2. Synthesis of N-PAHs 3a, 3b, 4, and 5 by Condensation of Dibenzo[a,h]anthracene-5,6,12,13diquinones 2a and 2b with the Corresponding *o*-Diamines 11, 12, and 13



found that **3a** was scarcely soluble in common organic solvents such as $CHCl_3$ or toluene, but still thanks to the four tri*iso*-propylsilyl (TIPS) groups, it was possible to establish its structure by NMR (¹H and ¹³C) and MS, which confirmed not only the structure of **3a** but also that of diquinone **2a**.

Given the low solubility of **2a** and **3a**, we decided introduce *tert*-butyl groups in positions 3 and 10 of the dibenzo[*a*,*h*]anthracene core. To do so, a *tert*-butyl substituted phenylboronic acid was employed in the Suzuki reaction step that generated **9b** (87%) with two *tert*-butyl groups in the tri-*p*phenylene core. Then, the same synthetic route was used for **2a**. Tri-*p*-phenylene **9b** was subjected to desilylation into **10b** (>99%) and subsequently to PtCl₂ catalyzed benzanulation (63%) to provide 3,10-di-*tert*-butyl-dibenzo[*a*,*h*] anthracene **1b** in a gram scale without any chromatographic purification. Then oxidation of **1b** using NaIO₄/RuCl₃ and subsequently $K_2Cr_2O_7$ yielded the desired 3,10-di-*tert*-butyldibenzo[*a*,*h*]anthracene-5,6,12,13-diquinone **2b** (17%). Diquinone **2b** was highly soluble in comparison to **2a**, and it could be characterized by NMR (¹H and ¹³C) and HRMS.

At this stage, we assessed the reactivity of diquinone **2b** with different diamines with an increasingly long aromatic core. Diquinone **1b** was allowed to react with 1,2-phenylenediamine **11**, 5,6-diaminobenzothiadiazole **12**,¹¹ and 2,3-diaminophenazine **13**,¹² in a 3:1 mixture of CHCl₃/AcOH (Scheme 2). *N*-Doped PAHs **3a** (76%), **4** (22%), and **5** (37%) were isolated, respectively, by flash chromatography as yellow, dark red, and purple solids, respectively, and were highly soluble in halogenated or aromatic solvents at room temperature, which allowed their characterization by NMR (¹H and ¹³C) and HRMS.

Needle-shaped crystals suitable for X-ray diffraction were obtained for 3a, 3b, 4, and 5, which further confirmed their structure (Figure 2). The X-ray structures show that the



Figure 2. Front view (left) and packing (right) of (a) 3a, (b) 3b, (c) 4, and (d) 5 observed on the crystal structures.

aromatic cores are virtually flat in all cases, but in the case of **3b**, one of the quinoxaline arms is out-of-plane. Conversely, the packing is quite different. In the case of **3a** the molecules are $\pi - \pi$ stacked (3.49 Å), while in the case of **3b** with the *tert*butyl group the packing is herringbone. The crystal structure of compound **4** combined $\pi - \pi$ (3.55 Å) and herringbone stacking. The structure of **5** showed a clear $\pi - \pi$ stacking (3.41 Å) between molecules.

The nuclear independent chemical shift (NICS) values were calculated for 3a, 3b, 4, and 5 (Figure S1). The NICS(0) values of the tri-*p*-phenylene residue of the dibenzo[a,h]-anthracene core oscillate between -3.9 and -6.0 ppm, while NICS(0) values of the K-region rings oscillate between +2.9 and +5.1 ppm, which is consistent with the aromatic and antiaromatic character, respectively, predicted by Clar rules. The NICS(0) values of the additional rings oscillate between -3.4 and -14.9 ppm, which is consistent with the quinoxaline, diazanaphthothiadiazole, and tetraazatetracene character of 3, 4, and 5, respectively.

Solutions of 3, 4, and 5 show the same bright colors as the corresponding solids. Compounds 3a and 3b show a similar bright yellow color, while the solutions of 4 and 5 are red and dark red, respectively (Figure S2). The UV–vis absorption of 3a and 3b (Figure 3a and Table S1) show similar absorption features with a small bathochromic shift of the band for 3b around 450 nm. The absorption spectra of 4 and 5 show the same set of bands observed for 3a and 3b, but bathochromic cally shifted. The shifts increase with the number of rings fused to the dibenzoanthracene core. TD-DFT calculations carried out at the B3LYP-CH₂Cl₂-6-311+g(2d,p)/B3LYP-6-31g(d,p) level showed the same trend in the absorption maxima (Figure S3 and Table S2). The lowest energy band corresponds in all



Figure 3. (a) Molar absorptivity coefficients in CHCl₃. (b) Normalized fluorescence spectra and quantum yields in CHCl₃. (c) CV curves in 0.1 M solution of nBu_4NPF_6 in CH₂Cl₂. Potentials versus Fc/Fc⁺. (d) FP-TRMC (λ = 355 nm, I_0 = 9.1 × 10¹⁵ photons cm⁻²) of products **3a**, **3b**, **4**, and **5**.

cases to the HOMO-LUMO transition. The optical HOMO-LUMO gaps were estimated from the onset of the longest wavelength absorption (2.63, 2.49, 1.94, and 1.82 eV, respectively, for **3a**, **3b**, **4**, and **5**) and show the same trends as the calculated ones (Table S2).

The solutions of 3 and 4 under UV light show a green and red fluorescence, while no fluorescence could be observed for 5 with the naked eye (Figure S2). The fluorescence spectrum of **3b** ($\lambda_{max} = 502 \text{ nm}; \Phi = 0.09$) appears bathochromically shifted in comparison to that of 3a ($\lambda_{max} = 470 \text{ nm}; \Phi = 0.08$), in agreement with the electronic absorption spectra (Figure 3b and Table S1). The fluorescence spectra of 4 ($\lambda_{max} = 632 \text{ nm}; \Phi = 0.36$) and 5 ($\lambda_{max} = 670 \text{ nm}; \Phi = 0.10$) extend between the red and the NIR regions.

The cyclic voltammograms of 3a, 3b, 4, and 5 were recorded in CH_2Cl_2 using nBu_4NPF_6 as the electrolyte and ferrocene (Fc/Fc^{+}) as the reference (Figure 3c). In products 3a, 3b, and 4 two different reduction processes were observed. In the case of 3a a small cathodic current at low potentials was attributed to aggregation as noted for similar compounds.¹³ The redox potentials (Table S3) were similar for 3a and 3b (-1.52 and -1.72 V; -1.54 and -1.71 V, respectively), while they were less cathodic than in the case of 4 (-0.93 and -1.04 V). The voltammograms of 5 showed the same set of two reduction processes but at even lower cathodic potentials and with an additional reduction wave (-0.69, -0.81, and -1.23 V). None of these products shows any redox process in the oxidative scan. The electrochemical LUMO levels (or electron affinities) were estimated from the onset of the first reduction are -3.59, -3.60, -3.92, and -4.17 eV for 3a, 3b, 4, and 5, respectively (Table S4). These values are in a reasonable agreement with the ones calculated at the B3LYP-CH₂Cl₂-6-311+g(2d,p)/ B3LYP-6-31g(d,p) level of theory (Table S5).

The charge transporting properties of **3a**, **3b**, **4**, and **5** were evaluated by flash-photolysis time-resolved microwave conductivity (FP-TRMC)¹⁴ directly on the powder solids (Figures 3d and S4). This contactless technique allows measuring directly the pseudoconductivity ($\varphi \Sigma \mu_{max}$) that can be considered the minimum/intrinsic mobility of the material. $\varphi \Sigma \mu_{max}$ values approaching 10⁻⁴ cm² V⁻¹ s⁻¹ were obtained in all cases. Compounds **3a** and **3b** (0.69 × 10⁻⁴ and 0.65 × 10⁻⁴ cm² V⁻¹ s⁻¹, respectively) showed similar $\varphi \Sigma \mu_{max}$ values, which were slightly lower for **4** and **5** (0.54 × 10⁻⁴ and 0.44 × 10⁻⁴ cm² V⁻¹ s⁻¹, respectively). These values are in the same range as those observed on molecular organic semiconductors.^{14,15}

The frontier orbitals calculated at the B3LYP-6-31g(d,p) level show that the electron densities in both the HOMO and the LUMO spread throughout the whole aromatic core, indicating that these are highly conjugated systems (Figure 4).



Figure 4. Frontier orbitals at the B3LYP-6-31g(d,p) level for 3a, 3b, 4, and 5.

In the case of the HOMO, the densities over the external rings of the tri-*p*-phenylene residue decrease as the number of rings increase along the K-regions. In the case of the LUMOs, the electron densities are mostly localized over the extended Kregions and appear to be conjugated through the central ring of the tri-*p*-phenylene residue.

In summary, we have reported a methodology to prepare and isolate two inaccessible and valuable building blocks for the synthesis of N-PAHs, namely dibenzo[*a*,*h*]anthracene di-*o*quinones 2a and 2b, including a gram scale synthesis of the corresponding dibenzo [a,h] anthracene precursors that does not involve any chromatographic purification. To showcase, the usefulness of di-o-quinones 2a and 2b as building blocks, a series of N-PAHs (3a, 3b, 4, and 5) have been synthesized by cyclocondensation with different o-diamines leading to a small library of derivatives. Optoelectronic, redox, and theoretical studies on 3a, 3b, 4, and 5 confirm that dibenzo [a,h]anthracene di-o-quinones are a highly tunable platform to prepare N-PAHs with a broad range of absorbing and emitting properties that extend from the visible into the NIR, which, combined with their low LUMO levels and $\varphi \Sigma \mu_{\rm max}$ values approaching 10^{-4} cm² V⁻¹ s⁻¹, illustrate their potential as organic semiconductors. Overall this work makes accessible a family of derivatives that have received virtually no attention since 1949, expanding the building block toolbox for the synthesis of N-PAHs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01536.

Figures S1–S4, Table S1–S5, general methods and full synthesis and characterization details of **3a**, **3b**, **4**, and **5** (PDF)

Accession Codes

CCDC 1916388–1916391 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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