Organic LETTERS

Letter

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Aromatization of Benzannulated Perylene-3,9-diones: Unexpected Photophysical Properties and Reactivity

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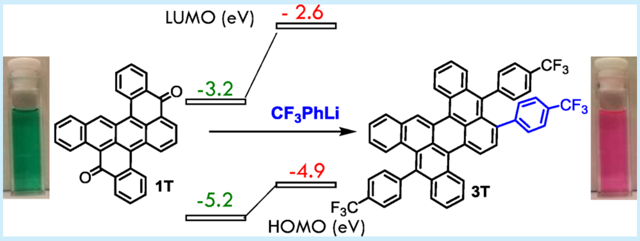
S *Supporting Information*



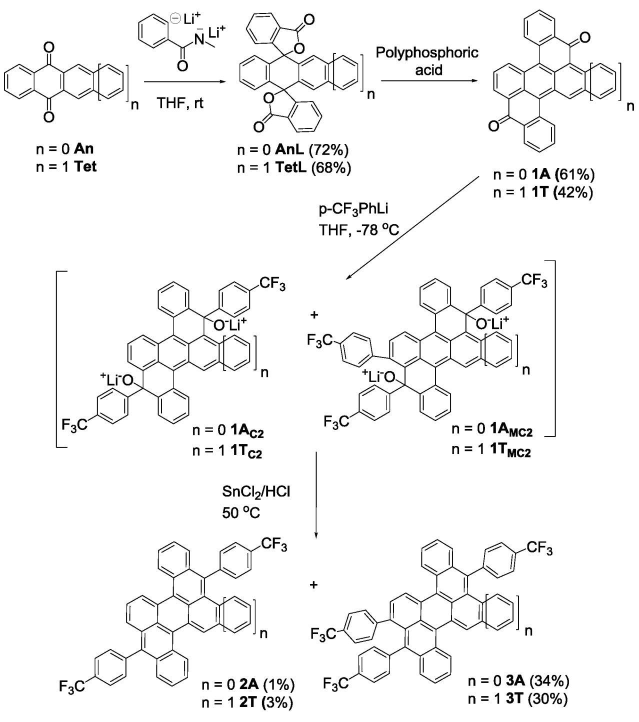
ABSTRACT: Highly unusual properties of acene-based quinones **1A** and **1T** are reported. They undergo an unexpected combination of Michael and carbonyl additions of aryllithium leading to new triarylated benzoperylenes **3A** and **3T**. Uncharacteristically for quinones, **1A** and **1T** display vibronically split absorption bands and small Stokes shifts. The absorption/emission spectra of the highly emissive **1A** are almost indistinguishable from those of the aromatized **3A**. Additional benzene rings cause a counterintuitive blue shift of the aromatic derivatives (**2T**/**3T**), but an expected red shift was observed for the quinone (**1T**). This behavior is fully supported by DFT calculations and rationalized by considering the longest conjugation path.

Acenequinones are key building blocks used to construct functionalized acenes, which are important semiconducting materials for optoelectronic applications.[1,2] The carbonyl groups allow for convenient placement of various substituents on the acene core, thereby improving its solubility and chemical inertness as well as amending the solid-state packing.[3] Such a substitution strategy has greatly benefited the field of organic semiconducting devices[4] by providing materials with an outstanding performance and stability, notably 6,13-bis(triisopropylsilylethynyl)pentacene[5] (hole mobility $\mu^+ > 1$ cm^2 V^{-1} s^{-1}) and rubrene[6] ($\mu^+ \sim 15$ cm^2 V^{-1} s^{-1}). It has also enabled isolation and studies of long oligoacenes, which are otherwise extremely reactive because of closed-shell structure instability.[7]

In designing such materials, the common expectations are that (i) reductive aromatization of quinones and (ii) extending the π conjugation of the resulting polycyclic aromatics will lead to contraction of the HOMO−LUMO gap and red shift of absorption. None of these premises hold true for the anthracene- and tetracene-based quinones **1A** and **1T** described here. These *di*ones show unexpected chemical reactivity, affording *tri*substituted polycyclic aromatic hydrocarbons **3A** and **3T**, and possess highly unusual spectroscopic properties that we report and rationalize in this letter.

In our recent study[8] of diaryldibenzoperylene **2A**, prepared by arylation of the known dibenzo[*a*,*j*]perylene-8,16-dione **1A**, we noticed an unusually low yield (12%) of the isolated product along with the formation of a triarylated derivative (5%), which is now identified as triaryldibenzoperylene **3A**. Reaction of **1A** with an excess of aryllithium (20 equiv) followed by reductive aromatization of the resulting tertiary alcohol using SnCl$_2$ afforded **3A** as the major product in 34% isolated yield (with a 1% trace of **2A**, Scheme 1). This behavior is general: the tetracene-based quinone **1T**, prepared from acid-catalyzed cyclization of tetracene lactone (**TetL**), also produces triarylated **3T** in 30% yield (along with a 3% yield of **2T**).

Scheme 1. Synthesis of Benzannulated Perylenes 2 and 3



The formation of **3A** and **3T** can thus be rationalized as a combination of one Michael (1,4-) addition to the benzene ring and two nucleophile-to-carbonyl (1,2-) additions. Nucleophilic 1,4-addition of organometallic reagents to an *aromatic* system is not unprecedented but generally requires that the carbonyl

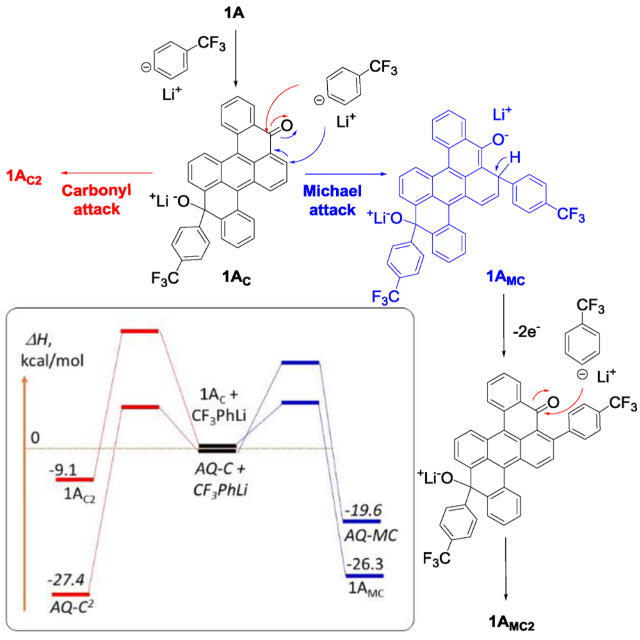
Received: May 30, 2016

DOI: 10.1021/acs.orglett.6b01559
Org. Lett. XXXX, XXX, XXX−XXX

electrophile is deactivated either sterically or electronically (e.g., "masked" as an oxazoline[9]).[10] Organometallic 1,4-addition is also not uncommon for benzo- and naphtho-1,4-quinones.[11] However, such chemical behavior is uncharacteristic for fully benzannulated quinones lacking aliphatic C=C bonds, and a standard 1,2-addition is considered a highly reliable method for their derivatization.[7,12] The only exception of which we are aware is the fourfold Michael addition of arylmagnesium to fused bispentacenequinone reported by Wu's group,[13,17] which was attributed to low reactivity of the carbonyl groups due to the extended conjugation and activation of the C=C bonds by a ring distortion. In their case, no 1,2-addition to carbonyls was observed; in contrast, we have noticed no higher Michael addition products across a broad range of reaction conditions (aryllithium concentration, temperature, reaction time). Thus, **1A** and **1T** present a rare case where an aromatic ketone is amenable to combined nucleophilic attacks on both the benzene ring and the carbonyl group.

A tentative mechanism accounting for the formation of di- and triarylated species starts with an aryllithium attack on the carbonyl group to afford monoadduct **1A$_{\mathrm{C}}$** (Scheme 2). This can be followed by either an attack on the second carbonyl to produce **1A$_{\mathrm{C2}}$** or a Michael addition to afford **1A$_{\mathrm{MC}}$**. With an excess of aryllithium present, the latter can be deprotonated, and the formed trianion is sufficiently electron-rich to be oxidized (most likely by electron transfer to quinone **1A**), regenerating the carbonyl group, which is subject to subsequent nucleophilic addition to produce **1A$_{\mathrm{MC2}}$**. Reduction of the thus-formed diolates (**1A$_{\mathrm{C2}}$** and **1A$_{\mathrm{MC2}}$**) with $SnCl_2$ produces the isolated dibenzoperylenes **2A** and **3A**. The proposed mechanism explains a different ratio of products **2A** and **3A** upon variation of the CF_3PhLi concentration. When only 2 equiv of aryllithium is used, **1A$_{\mathrm{MC}}$** could still be the major product, but it is not able to convert into **1A$_{\mathrm{MC2}}$** because of the insufficient amount of aryllithium and thus cannot aromatize into a stable isolable compound upon reduction with $SnCl_2$. Also, the low yield of the reaction is explained by **1A** playing a role of a sacrificial electron acceptor, oxidizing the deprotonated **1A$_{\mathrm{MC}}$** trianion.

Scheme 2. Proposed Mechanism of Arylation of 1A; the Inset Shows the DFT-Calculated Energy Diagram for Michael/Carbonyl Addition to 1A in Comparison with 9,10-Anthraquinone (AQ)



To support such a mechanistic hypothesis, we performed DFT calculations of Michael (**1A$_{\mathrm{MC}}$**) and carbonyl (**1A$_{\mathrm{C2}}$**) intermediates at the B3LYP/6-31G(d) level, applying a continuum solvent model (THF). Although the reaction is not expected to be under thermodynamic control, following the Bell–Evans–Polanyi principle, the difference of the activation energies within each series is expected to be proportional to the difference of the corresponding reaction enthalpies. The enthalpy of formation of **1A$_{\mathrm{MC}}$** from **1A$_{\mathrm{C}}$** was found to be 17 kcal/mol more favorable than that for the formation of **1A$_{\mathrm{C2}}$**, supporting the observed selectivity. To validate this finding, we performed the same set of calculations with anthraquinone (**AQ**), which showed that the corresponding Michael addition leading to **AQ-MC** is *less* favorable than the carbonyl addition forming **AQ-C^{2}** by 8 kcal/mol, in agreement with the known reactivity of **AQ** and other acenequinones.[7]

Such unusual reactivity of quinones **1A** and **1T** also echoes the reported earlier facile photooxidation of **1A**,[14] which in our experience decomposes readily upon exposure to laboratory light. We have considered a biradical form of **1A** as an origin of this behavior. However, DFT calculations suggest that the triplet state of **1A** lies above a closed-shell singlet by 1.0 eV, and no paramagnetic broadening was observed in its NMR spectrum up to 140 °C.

Deep-purple single crystals of **3A** suitable for X-ray diffraction analysis were grown via slow diffusion of diethyl ether into CH_2Cl_2 solution of **3A** (under nitrogen, protected from light). The perylene backbone has a highly contorted structure with a dihedral angle of 28.7° between the two anthracene planes (Figure 1). Steric congestion of the adjacent aryl substituents bestows a slightly higher distortion (5.5°) to the corresponding anthracene moiety compared with its monosubstituted counterpart (1.9°). A considerable bond length elongation (0.01–0.03 Å) is also noticed for **3A** compared with **2A** in the Michael acceptor benzene ring.

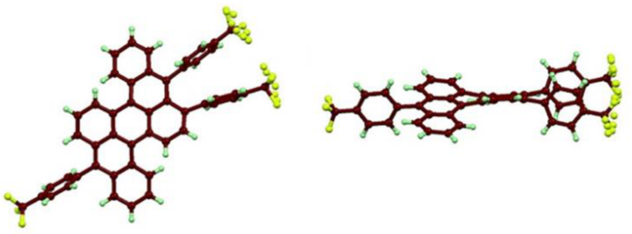


Figure 1. Crystal structure of **3A**.

Quinones **1** and their corresponding aromatic derivatives **2** and **3** are readily soluble in common organic solvents, and their photophysical properties were analyzed in CH_2Cl_2 solution (Figure 2 and Table 1). **1A** displays a sharp vibronically structured absorption band at $\lambda_{\mathrm{max}}^{\mathrm{abs}} = 575$ nm (2.16 eV). Quite surprisingly, the absorption spectrum of this quinone **1A** is barely distinguishable from those of its diarylated derivative **2A**[8] and triarylated **3A** (Figure 2). Furthermore, **1A** is significantly more emissive ($\Phi_f = 58\%$) than its aromatized derivatives **2A** and **3A** ($\Phi_f = 8$ and 13%,[15] respectively), which is uncharacteristic for quinones because of usually fast intersystem crossing. As expected, the extended π conjugation in quinone **1T** leads to a

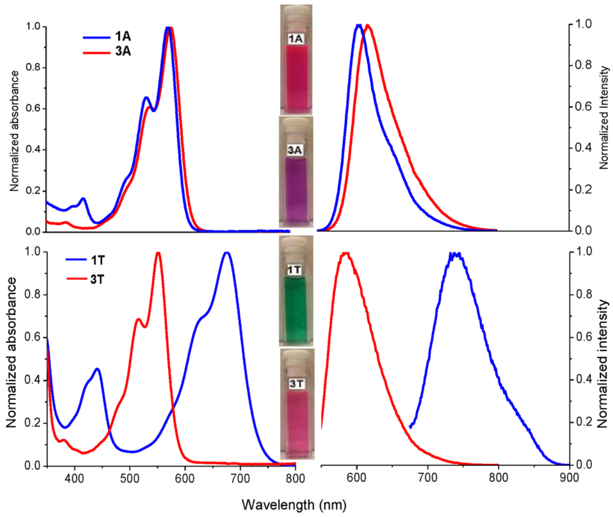


Figure 2. Absorption (left) and emission (right) spectra of anthracene-based **1A**/**3A** (top) and tetracene-based **1T**/**3T** (bottom) in CH_2Cl_2. The insets show photographs of CH_2Cl_2 solutions of **1** and **3**.

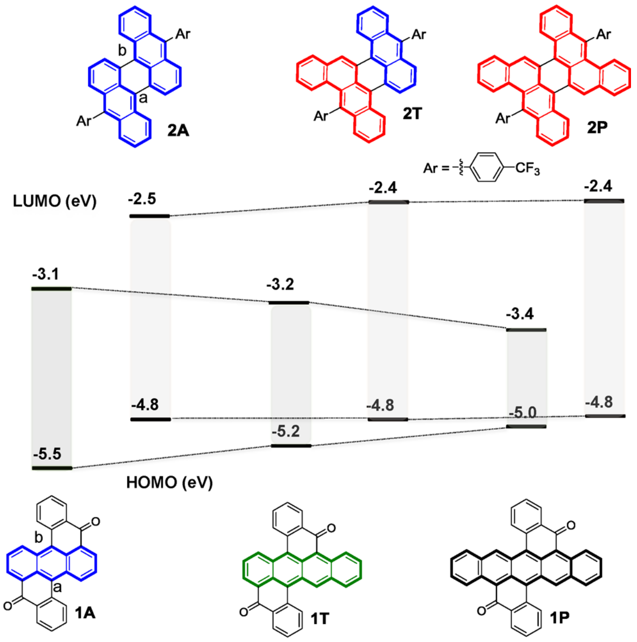


Figure 3. DFT-calculated HOMO–LUMO energies of quinones **1** and their corresponding aromatics **2**.

significantly red-shifted (vs **1A**) absorption centered at 675 nm (1.84 eV).

A very different and counterintuitive trend was observed for the aromatized di/triarylated derivatives (Table 1; discussed below for triarylated compounds). Both the absorption and emission bands of **3A** ($\lambda_{\max}^{\text{abs}}$ = 579 nm, $\lambda_{\max}^{\text{em}}$ = 620 nm) undergo a *blue* shift upon extension of the conjugation in **3T** ($\lambda_{\max}^{\text{abs}}$ = 551 nm, $\lambda_{\max}^{\text{em}}$ = 582 nm).

In fact, the divergent evolution of the energy gaps for the aromatized structures and their convergent evolution for the quinones was predicted by DFT at the outset of this work, prompting us to synthesize the tetracene derivatives.[16] Figure 3 shows that as the conjugation is extended in the quinone series from **1A** to **1P**, the HOMO–LUMO gap decreases from 2.37 to 1.59 eV. On the contrary, the same extension of conjugation in the aromatic series leads to an increase in the HOMO–LUMO gap from 2.24 to 2.41 eV. The same trend was also calculated for unsubstituted (Ar = H) and triarylated (**3A**, **3T**) aromatic series (see the Supporting Information), thus ruling out the Ar-induced twist as an origin of this unusual behavior.

To rationalize these observations, one should consider the longest conjugation path in these compounds (highlighted in bold in Figure 3). Within this framework, quinones **1** are best viewed as acenes substituted at their peri positions, explaining the large red shift/contracting HOMO–LUMO gap in going from **1A** to **1T** and **1P**. On the contrary, such a central acene moiety does not exist in the aromatized derivatives, and **2A**/**3A** can be viewed as two connected anthracene moieties. Analysis of calculated (and X-ray-measured) bond lengths shows 0.06 Å contraction and 0.05 Å elongation of bonds *a* and *b*, respectively, going from **1A** to **2A**, in accord with the drawn resonance structures (Figure 3). Additional fused benzene rings in **2T** and **2P** break the acene structure, resulting in a small blue shift, similar to that observed upon [*a*]benzannulation of anthracene ($\lambda_{\max}^{\text{abs}}$ = 378 nm vs 364 nm for tetraphene).

Analysis of the electrochemical properties by cyclic voltammetry reveals the same trends established above by DFT and photophysical measurements (Figure 4). All of the compounds exhibit amphoteric multistage redox behavior: two reversible reduction waves and one reversible oxidation wave for the quinones and two reversible oxidations and one reversible reduction for the aromatized derivatives. Extending the π-electron system in quinones (**1T** vs **1A**) lowers the oxidation and reduction potentials by 0.2 and 0.3 V, respectively (Table 1).

Aromatization of the quinones leads to expected negative shift of both oxidation (by 0.4–0.6 V) and reduction (by 0.5–0.8 V) potentials. The CF_3Ph substituents, being orthogonal to the π-conjugated system, have a very small electron-withdrawing effect, noticed as ~0.01 V more positive redox potentials in triarylated **3A**/**3T** versus diarylated **2A**/**2T**. Within the di- and triarylated series, the extension of the π-electron system from an anthracene-based to a tetracene-based core leads to slightly higher oxidation (by 0.06 V) and lower reduction (by 0.05 V)

Table 1. Electrochemical and Optical Data for 1–3[a]

compd	$E^{1/2}_{\text{ox}}$[b] (V)	$E^{1/2}_{\text{red}}$[b] (V)	E_g[c] (eV)	λ_{abs} (nm)	λ_{em} (nm)	Φ (%)	E_g[d] (eV)
1A	0.94	−1.29, −1.50	2.24	575	607	58	2.16
1T	0.74, 1.18	−0.98, −1.22	1.72	675	737	–	1.84
2A[8]	0.29, 0.83	−1.82	2.11	571	595	13	2.08
3A	0.30, 0.81	−1.81	2.11	579	620	8	2.14
2T	0.35, 0.82	−1.77	2.13	548	570	19	2.26
3T	0.36, 0.83	−1.77	2.13	551	582	9	2.25

[a] Measured in CH_2Cl_2. [b] Redox potentials are reported with respect to ferrocene (Fc) oxidation. [c] Electrochemical gap, $E_g = E^{1/2}_{\text{ox}} - E^{1/2}_{\text{red}}$. [d] Optical gap, $E_g = 1240/\lambda_{\text{abs}}^{\max}$.

DOI: 10.1021/acs.orglett.6b01559
Org. Lett. XXXX, XXX, XXX–XXX

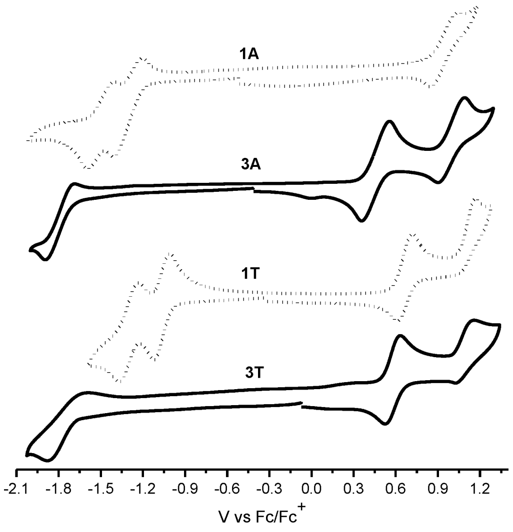


Figure 4. Cyclic voltammograms of quinones **1** and arylated compounds **3** in 0.2 M Bu_4NPF_6 in CH_2Cl_2.

potentials, in line with the increasing HOMO−LUMO gap. Overall, in going from anthracene- to tetracene-based structures, the electrochemical gap is significantly contracted in quinones **1A**/**1T** (by 0.52 eV) and slightly expanded in the aromatized derivatives **2A**/**2T** and **3A**/**3T** (by 0.02 eV).

In summary, we have reported unusual properties of polycyclic quinones **1**, which undergo a selective *tri*arylation with an excess of aryllithium. The proposed mechanism, supported by DFT, involves two carbonyl additions and one Michael addition with an intermittent electron transfer step. Thus, aromatized **3A** and its precursor quinone **1A** have almost indistinguishable photophysical properties, except for a higher fluorescence quantum yield of the quinone (58%). Even more surprisingly, the increase in the π-electron system in the aromatic series **3A**/**2A** to **3T**/**2T** leads to an unexpected blue shift of the absorption/emission bands, while a "normal" red shift is observed for the corresponding quinones (**1A** to **1T**). The dissimilar behavior (converging vs diverging band gap evolution) of the quinoidal and aromatic systems was predicted by DFT and rationalized by considering the longest conjugation path of the molecules. This work impacts the field of designed π-electron systems by (i) proposing a potential approach toward rubrene-like polycyclic aromatics and (ii) showing the limitations of the established design rules (band gap vs conjugation length; nonemissivity of quinones).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01559.

> Synthetic procedures and characterization data for the synthesized compounds; computational protocols and the detailed results on the photophysical properties (PDF)
> Crystallographic data for **3A** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by NSERC of Canada. MRR thanks FQRNT for PBEEE fellowship.

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(12) As a control experiment, we reacted anthracene- and tetracenequinones with a large excess of CF_3PhLi, but in both cases only diarylated products of carbonyl addition were isolated in good yield (∼80%).

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(15) A smaller Φ_f of 0.9% was mistakenly reported for **2A** earlier.[8] The current datum was confirmed by absolute quantum yield measurements in an integrating sphere and reference measurements versus cresyl violet (Φ_f = 54%).

(16) To date, our attempts to extend the series to the pentacene derivatives have failed: contrary to **1A** and **1T**, quinone **1P** could not be prepared by intramolecular cyclization of the corresponding lactone **PenL**, presumably because of its instability under the reaction conditions.

(17) Note added in proof: after submission of this manuscript another example of Michael addition to fully benzannulated quinone was reported by Tykwinski's group: Reus, C.; Lechner, M. P.; Schulze, M.; Lungerich, M.; Diner, C.; Gruber, M.; Stryker, J. M.; Hampel, F.; Jux, N.; Tykwinski, R. R. *Chem. - Eur. J.* **2016**, *22*, 9097.