## Acenes

## **Combining Electronic and Steric Effects for Highly Stable Unsymmetric Pentacenes**

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Abstract: This paper describes the reactivity of unsymmetrically substituted pentacenes to photochemical oxidation. Acenes in general, and pentacenes in particular, are a key family of compounds for a variety of organic electronics applications. The instability of many pentacene derivatives, particularly to oxidation, is an important restriction in their applicability. Several substitution strategies for decreasing the reactivity of pentacene exist, but these almost always involve symmetrically substituted derivatives, restricting the chemical space of structures from which to choose. In this paper, we demonstrate that combining electronic and steric effects yields highly stable unsymmetrically substituted pentacenes.

Acenes are one of the most successful classes of organic semiconductors, with pentacene among the leaders in performance.<sup>[1-4]</sup> Unsubstituted pentacene, however, presents a number of challenges, such as photooxidative instability and low solubility in organic solvents, which limit its promise in emerging technologies, such as field-effect transistors. There are a number of successful strategies that use substituent effects to ameliorate these drawbacks of pentacene, while still retaining functional properties of the acene. One of the earliest examples was substitution with phenyl groups or other aromatic substituents;<sup>[5,6]</sup> these substituents improve the solubility of pentacene, but unless specifically designed to do so,<sup>[7]</sup> generally do not improve acene stability.<sup>[8]</sup> 6,13-Diarylpentacene derivatives have found use as emissive species in organic light emitting devices (OLEDs).<sup>[9, 10]</sup>

Anthony and co-workers popularized the use of diethynyl acenes, including pentacenes, which show superior optoelectronic properties and are both highly soluble and stable.[11-16] The stability of diethynylpentacenes is at least in part due to physical quenching of singlet oxygen  $({}^{1}O_{2})$ , cycloaddition with which is a major decomposition pathway of most pentacenes,<sup>[17]</sup> by these materials.<sup>[18]</sup> The strategy of combining aryl groups and electronically deactivating ethynyl substituents has yielded stable heptacenes and nonacenes that have been characterized by X-ray crystallography.[19,20] Miller and co-workers

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have developed alkyl- and arylthiol-substituted acenes that show remarkable stability.<sup>[7,21]</sup> Electron-withdrawing fluorine substituents have also been shown to improve acene stability.<sup>[22, 23]</sup>

Nearly all reports of acenes with backbones longer than anthracene are substituted symmetrically with respect to the long axis of the molecule. Therefore, although these approaches to acene design have yielded groundbreaking results, such a limitation on structure restricts the chemical space for discovering new molecules with improved properties. The principal exceptions to this have come from Tykwinski and coworkers, who described several years ago the preparation of unsymmetrically substituted diethynylpentacenes by controlling stoichiometry and rate of addition of ethynyllithium reagents to pentacenequinone.<sup>[24-26]</sup> Earlier this year, the same group reported three 6-anthryl-13-ethynylpentacene derivatives, one of which showed ambipolar behavior in thin film transistors.<sup>[27]</sup>

Our group has developed a general approach to <sup>1</sup>O<sub>2</sub>-responsive luminescent materials that rely on energy transfer from a light-harvesting chromophore to acene; subsequent acene-<sup>1</sup>O<sub>2</sub> cycloaddition reactions yield a robust, ratiometric response in luminescence.<sup>[28, 29]</sup> Designing next generations of these materials for new applications requires fine control over acene absorbance, luminescence, reactivity with <sup>1</sup>O<sub>2</sub>, and selectivity for this reaction over other acene decomposition pathways, such as alkyne-acene cycloaddition and [4+4] "butterfly" dimerization.<sup>[30-33]</sup> Our overall goal in this project is to determine how substitution could control band gap and reactivity with <sup>1</sup>O<sub>2</sub> of substituted pentacene derivatives, including unsymmetric arylethynylpentacenes. Herein we highlight an approach to new, highly stable unsymmetric pentacene derivatives through rational design that incorporates both electronic and steric effects.

Scheme 1 shows the structures of the substituted pentacenes described in this study: symmetric 6,13-diphenylpentacene (1)<sup>[10]</sup> and 6,13-diphenylethynylpentacene (2)<sup>[13]</sup> are known in the literature, while the unsymmetric 6-aryl-13-phenylethynylpentacenes 3-5 are new compounds. Synthesis of 3-5 first involved slow addition of lithiated phenylacetylene followed by protonation and purification of the intermediate hydroxyketone. Subsequent addition of an excess of the appropriate aryllithium to the hydroxyketone followed by reduction of the resulting diol with SnCl<sub>2</sub> in aqueous HCl yielded the target pentacene derivatives, each of which was purified by column chromatography followed by recrystallization. Compound 3 simply combines the two types of substituents pres-

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Scheme 1. Structures of 6,13-disubstituted pentacenes 1-5.

ent in symmetric 1 and 2. To examine the influence of sterically demanding *ortho*-alkyl substituents of the aryl groups on both the photophysics and reactivity of the pentacenes, compounds 4 and 5 have methyl or ethyl groups, respectively, in *ortho* positions.

X-ray crystallography of compound **5** (Figure 1) revealed that the pentacene core in this molecule is highly planar (twist angle ca.  $3^{\circ}$ ). Consistent with previous reports on aryl-substituted pentacenes, the plane defined by the aryl substituent is



Figure 1. X-ray crystal structure of compound 5. Thermal ellipsoids shown at 50% probability. Hydrogen atoms and a disordered  $CH_2CI_2$  molecule have been omitted for clarity.

nearly perpendicular (86°) to the plane defined by the pentacene core. The phenyl ring of the phenylethynyl substituent is also twisted (torsional angle of 58°), which we attribute to a combination of the low barrier of rotation of this group and crystal packing forces.

Figure 2 shows the UV/Vis absorbance and fluorescence emission spectra of pentacenes 1-5 in  $CH_2Cl_2$ , while Table 1 summarizes their steady-state photophysical properties. Ab-



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Figure 2. Normalized UV/Vis a) absorbance and b) fluorescence emission spectra of pentacenes 1–5.

 
 Table 1. Steady-state absorbance and fluorescence parameters of pentacenes 1–5. Molar extinction coefficients are reported at the longest wavelength maximum for each compound.

	λ <sub>onset,abs</sub> [nm]	$\lambda_{\max,abs}$ [nm]	ε [м <sup>-1</sup> ]	λ <sub>max,fl</sub> [nm]	$arPhi_{ m f}$
1	630	516, 554, 599	12700	610	0.09
2	695	311, 562, 605, 660	27 300	675	0.13
3	680	309, 588, 630	9400	688	0.02
4	680	309, 587, 630	14000	672	0.03
5	680	309, 588, 631	13000	675	0.04

sorbance spectra of the new pentacene derivatives in  $CH_2CI_2$  showed no alteration in shape between 30 and 0.3  $\mu$ M, indicating the absence of aggregation of the chromophores in solution at concentrations suitable for measurement of absorbance and fluorescence spectra of these compounds. All absorbance spectra showed vibronic structure, as is characteristic for linear acenes. An immediately noticeable trend is that the magnitude of the band gaps of these pentacenes, as determined by the onset of absorbance, increases in the order **2** (1.78 eV) < **3**–**5** (1.82 eV) < **1** (1.94 eV). This trend correlates with the degree of  $\pi$ -conjugation present in these pentacene derivatives. The aryl substituents attached directly to the pentacene core are highly



twisted and contribute less additional delocalization to the pentacene core than arylethynyl groups that can adopt a more coplanar conformation, resulting in the observed decrease in band gap with increasing phenylethynyl substitution.<sup>[13,34]</sup> Alkyl substitution on the aryl groups caused virtually no change in the absorbance or fluorescence spectra of compounds **4** and **5** relative to **3**. Consistent with larger conformational reorganization in the excited state for aryl-substituted acenes, compounds **1** and **3–5** showed larger Stokes shifts (42–58 nm) than **2** (15 nm). The ethynyl–arylpentacenes also showed low quantum yields of fluorescence, between 2–4%, which we attribute to these compounds having a combination of features from both **1**—vibrational modes from twisting around the aryl–acene bond—and **2**—a narrow HOMO–LUMO gap—that leads to increased rates of nonradiative decay.

Photochemical decomposition of pentacene derivatives, particularly in the presence of  $O_2$ , can limit their utility. Among the most prevalent degradation pathways is a photoexcited pentacene derivative donating energy to  $O_2$  to generate  ${}^1O_2$ , which then undergoes fast [4+2] cycloaddition with the central ring of the pentacene to yield the corresponding endoperoxide with bimolecular rate constants  $10^8-10^9 \text{ m}^{-1} \text{ s}^{-1}$ . To characterize the photochemical reactions of these new unsymmetrically substituted pentacenes, we first determined the products of photooxidation of **3** in CDCl<sub>3</sub> (Scheme 2). Either 1)



Scheme 2. Photooxidation of 3 to endoperoxide 3-O<sub>2</sub>.

direct irradiation of **3** using visible light (> 400 nm), or 2) irradiation of a mixture of **3** and the photosensitizing dye methylene blue (MB) with a 665 nm long-pass filter, using a 200 W Hg/Xe lamp proceeded to completion within 15 min, yielding a major product with <sup>1</sup>H NMR and <sup>13</sup>C NMR data consistent with endoperoxide formation across the central 6 and 13 positions (see Supporting Information). Neither [4+4] butterfly dimerization nor alkyne-acene cycloaddition was evident from the <sup>1</sup>H NMR spectrum of the irradiated samples. Diphenylpentacene **1** is also known to give a structurally analogous endoperoxide across the 6- and 13-positions upon irradiation in air.<sup>[5]</sup>

To understand the effect of substitution on the photochemical stability of these pentacene derivatives, we measured the kinetics of their disappearance upon exposure to  ${}^{1}O_{2}$  generated by irradiation of MB in an air-equilibrated CHCl<sub>3</sub> solution by UV/vis spectrophotometry. In these experiments, the initial concentrations of the pentacene derivative and methylene blue were 50 and 80  $\mu$ m, respectively. Because **1–5** have ab-

sorbance spectra that overlap significantly with the absorbance spectrum of MB, we used a 665 nm long-pass filter to ensure the majority of incident light was absorbed by the MB. We also adjusted the decomposition kinetics to reflect only the decomposition due to absorbance of light by MB with the following corrections: 1) correcting the observed rate by the fraction of light that was absorbed directly by MB, and 2) subtracting the absorbance of MB from all UV/vis spectra before determining the remaining concentration of pentacene. To correct for experimental variability, we compared all kinetics to the MBmediated photooxidation of 9,10-diphenylanthracene (DPA), which has a bimolecular rate constant of  $3 \times 10^{6} \,\mathrm{m^{-1} s^{-1}}$ , under identical conditions (concentrations of acene and MB, light flux, etc.). Kinetic data of the pentacene derivatives deviated from pseudo-first-order behavior by reacting faster than predicted by initial kinetics as the concentration of pentacene decreased, which suggests that the steady-state concentration of <sup>1</sup>O<sub>2</sub> increased during the reaction; this scenario is possible if acene-<sup>1</sup>O<sub>2</sub> reactions (a combination of physical and chemical quenching) compete with unimolecular decay of <sup>1</sup>O<sub>2</sub>.<sup>[35]</sup> In all cases, we fit the initial data to a pseudo-first-order kinetics model (Figure 3); Table 2 summarizes the relative rates of

**Table 2.** Kinetics of photooxidations of 1–5 in CHCl<sub>3</sub>. Reported relative rates are from fits of initial rate data to first-order kinetics and were determined relative to that for DPA ( $k=3\times10^6\,{\rm m}^{-1}\,{\rm s}^{-1}$ ) and are the means of 2–3 independent experiments; each error is one standard deviation from the mean. Maximum measured deviations in half-lives upon direct irradiation are  $\leq10\%$  of the means.

<b>1</b> ca. 30 <4
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<b>2</b> (0.27±0.17) <sup>10</sup> 1040
<b>3</b> (10±1) <sup>[c]</sup> 30
<b>4</b> (0.33±0.13) <sup>[c]</sup> 810
5 (0.18±0.01) <sup>[c]</sup> 1100

[a] Relative rate of DPA decomposition is set at 1. [b] Rate of decomposition was 25% of this value when MB was not present. [c] Rate of decomposition was 5-7% of this value when MB was not present.

acene decomposition under these conditions. In addition, we also monitored the disappearance of acene upon irradiation under identical conditions ( $\lambda > 665$  nm), in the absence of MB. In these control experiments, only compound **2**, because of its red-shifted absorbance that overlaps strongly with that of MB, showed significant decomposition—a rate of 25% of that observed in the presence of MB. In the absence of MB, **3–5** showed only 5–7% of the rate of decomposition upon irradiation at  $\lambda > 665$  nm.

One critical trend in structure–property relationships is that unsymmetrically substituted arylethynyl compound **3** shows a rate of reaction with photosensitized  ${}^{1}O_{2}$  that is intermediate between diphenylpentacene **1** and diphenylethynylpentacene **2**: the rate of reaction of **3** is approximately threefold smaller than **1**, with a rate constant with  ${}^{1}O_{2}$  similar to that of diaryltetracenes, indicating that one ethynyl group stabilizes the

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**Figure 3.** a) Pseudo-first-order initial kinetics of disappearance of compounds 1–5 and DPA upon exposure to MB (80  $\mu$ M) and irradiation with  $\lambda$  > 665 nm in air-equilibrated CHCl<sub>3</sub>. Absorbance spectra of b) **3** and c) **5** as a function of irradiation time at  $\lambda$  > 665 nm in the presence of MB. The absorbance of MB has been subtracted from each spectrum to reflect the actual concentration of acene.

pentacene towards photooxidiation significantly. This result is consistent with the electronic stabilizing effect that ethynyl substituents supply to the oxidation of acenes, which Fudikar and Linker have ascribed to 1) destabilization of biradical or zwitterionic intermediates for stepwise pathways that are faster than concerted reactions, and 2) physical quenching of <sup>1</sup>O<sub>2</sub> by ethynylpentacenes.<sup>[18]</sup>

Combining this electronic stabilizing effect of ethynyl substituents with steric hindrance due to *ortho*-alkyl substituents on aryl substituents led to pentacene derivatives with persistence under photooxidative conditions that rivals the highly stabilized diethynylpentacenes. Compounds **4** and **5**, which substitute methyl or ethyl groups on the *ortho*-positions of the aryl substituent bound directly to the acene, react with singlet oxygen 30–50 times more slowly than **3**, which has hydrogen atoms as *ortho*-substituents on the aryl substituent. Since the optical spectra of 3, 4, and 5 are nearly identical, there is not a significant difference in conjugation, and therefore it is unlikely that there is significant difference in stabilization of radical or ionic character at the 6- and 13-positions in the transitions states for oxidation of compounds 3-5. The nearly identical energies of HOMOs (-4.78 to -4.80 eV) and LUMOs (-2.81 to -2.83 eV) of these three compounds as determined by DFT calculations (tabulated in the Supporting Information) using the B3LYP functional with the 6-311G(d,p) basis set further support this conclusion. We therefore interpret this striking difference in rate of oxidation to steric shielding of the reactive central positions of pentacene by the alkyl groups above and below the pentacene core from reacting with <sup>1</sup>O<sub>2</sub>. Steric hindrance is known to direct cycloaddition reactions of 6,13-diarylpentacenes with dieneophiles larger than  $O_2$  to the 5,14- or 7,12-positions,<sup>[36-38]</sup> and Miller and co-workers have noted an analogous increase in half-life (up to 25-fold) for diarylpentacenes with o-alkyl substituents.<sup>[7]</sup> The relative rate of decomposition of 4 and 5 is similar to that previously reported for 6,13bis[(triisopropylsilyl)ethynyl]pentacene under photosensitized oxidation conditions with MB, which has a bimolecular rate constant of about  $1\times10^6\,{\ensuremath{\mathsf{m}^{-1}\,\mathsf{s}^{-1}}}.^{\scriptscriptstyle [18]}$ 

Although it is complicated by differences in absorbance spectra of the acenes, and how those spectra overlap with the spectral irradiance curves of light sources, assessing the photostability of acenes upon direct irradiation in the absence of external sensitizers is important for optoelectronic applications. We therefore followed the decomposition of pentacenes 1-5, using UV/Vis spectrophotometry, upon irradiation with  $\lambda$  > 400 nm at a power density of 10 mW cm<sup>-2</sup>—Table 2 shows the half-lives of the pentacenes under these conditions. In agreement with the results of earlier MB-mediated photooxygenation reactions, the half-lives of these compounds span three orders of magnitude, with the order of persistence  $5 \approx 2 > 4 >$ 3 > 1. Direct comparison of 3, 4, and 5, which have nearly identical absorbance spectra and extinction coefficients, agrees with the results from external photosensitization, with sterically hindered 4 and 5 having half-lives about 30-fold longer than less-hindered 3. As evidence for the efficacy of combining steric and electronic factors in our acene designs, diethyl derivative 5 has a half-life nearly identical to that of 2.

This study demonstrates that combining steric and electronic effects can yield unsymmetrically substituted pentacene derivatives that are highly persistent under photooxidative conditions. Each of the substituent effects: 1) the steric hindrance of the central 6- and 13-positions through *o*-alkyl groups on one aryl substituent, and 2) the electronic deactivation of pentacenes through substitution with one ethynyl substituent by inducing physical quenching of  ${}^{1}O_{2r}$  slows the rate of pentacene photoinduced decomposition. This work therefore highlights that new, unsymmetric arylethynylpentacene derivatives can show photostability akin to the more established, symmetrically substituted diethynyl derivatives, significantly broadening the structural space of acene derivatives that may find practical use as organic semiconductors.



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