

Stable Pentacenes

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.^[1-4] Unsubstituted pentacene, however, presents a number of challenges, such as photo-oxidative 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;^[5,6] these substituents improve the solubility of pentacene, but unless specifically designed to do so,^[7] generally do not improve acene stability.^[8] 6,13-diarylpentacene derivatives have found use as emissive species in organic light emitting devices (OLEDs).^[9,10]

Anthony and coworkers 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 (¹O₂), cycloaddition

with which is a major decomposition pathway of most pentacenes,^[17] by these materials.^[18] 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 coworkers have developed alkyl- and arylthiol-substituted acenes that show remarkable stability.^[7,21] Electron-withdrawing fluorine substituents have also been shown to improve acene stability.^[22,23]

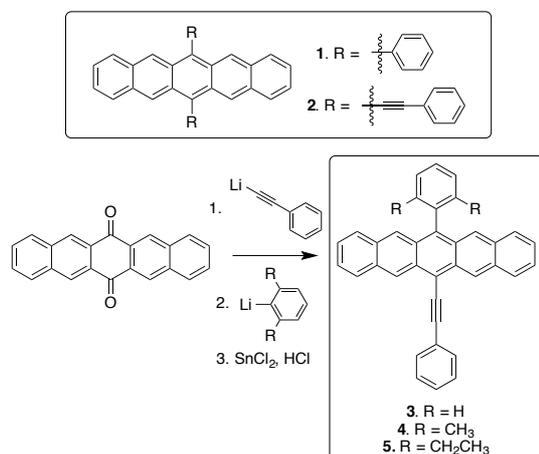
Nearly all reports of acenes with backbones longer than anthracene are substituted symmetrically with respect to the long axis of the molecule. Therefore, although these approaches to acene design have yielded groundbreaking results, such a limitation on structure restricts the chemical space for discovering 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.^[24-26] Earlier this year, the same group reported three 6-anthryl-13-ethynylpentacene derivatives, one of which showed ambipolar behavior in thin film transistors.^[27]

Our group has developed a general approach to ¹O₂-responsive luminescent materials that rely on energy transfer from a light-harvesting chromophore to acene; subsequent acene-¹O₂ cycloaddition reactions yield a robust, ratiometric response in luminescence.^[28,29] Designing next generations of these materials for new applications requires fine control over acene absorbance, luminescence, reactivity with ¹O₂, and selectivity for this reaction over other acene decomposition pathways such as alkyne-acene cycloaddition and [4+4] "butterfly" dimerization.^[30-33] Our overall goal in this project is to determine how substitution could control band gap and reactivity with ¹O₂ of substituted pentacene derivatives, including unsymmetric aryl-ethynyl pentacenes. 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**^[10] and 6,13-diphenylethynylpentacene **2**^[13] 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 SnCl₂ in aqueous HCl yielded the target pentacene derivatives, each of which was purified by column

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chromatography followed by recrystallization. Compound **3** simply combines the two types of substituents present 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, **4** and **5** have methyl or ethyl groups, respectively, in *ortho* positions.



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

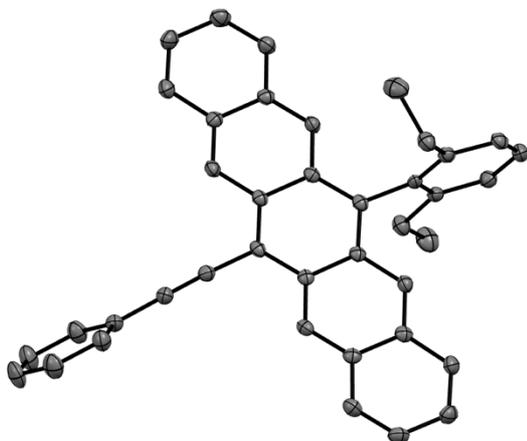


Figure 1. X-ray crystal structure of compound **5**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms and a disordered CH₂Cl₂ molecule have been omitted for clarity.

X-ray crystallography of compound **5** (Figure 1) revealed that the pentacene core in this molecule is highly planar (twist angle ~ 3°). Consistent with previous reports on aryl-substituted pentacenes, the plane defined by the aryl substituent is 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 CH₂Cl₂, while Table 1 summarizes their steady-state photophysical properties. Absorbance spectra of the new pentacene derivatives in CH₂Cl₂ showed no alteration in shape between 30 mM and 0.3 mM,

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 π -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.^[13,34] Alkyl substitution on the aryl groups caused virtually no change in the absorbance or fluorescence spectra of compounds in comparing **4** and **5** 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-aryl-pentacenes 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 non-radiative decay.

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.

	$\lambda_{\text{onset,abs}}$ (nm)	$\lambda_{\text{max,abs}}$ (nm)	ϵ (M ⁻¹)	$\lambda_{\text{max,fl}}$ (nm)	Φ_f
1	630	516, 554, 599	12,700	610	0.09
2	695	311, 562, 605, 660	27,300	675	0.13
3	680	309, 588, 630	9,400	688	0.02
4	680	309, 587, 630	14,000	672	0.03
5	680	309, 588, 631	13,000	675	0.04

Photochemical decomposition of pentacene derivatives, particularly in the presence of O₂, can limit their utility. Among the most prevalent degradation pathways is a photoexcited pentacene derivative donating energy to O₂ to generate ¹O₂. ¹O₂ then undergoes fast [4+2] cycloaddition with the central ring of the pentacene to yield the corresponding endoperoxide with bimolecular rate constants 10⁸–10⁹ M⁻¹s⁻¹. To characterize the photochemical reactions of these new unsymmetrically substituted pentacenes, we first determined the products of photooxidation of **3** in CDCl₃. Either i) direct irradiation of **3** using visible light (> 400 nm), or ii) 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 minutes, yielding a major product with ¹H NMR and ¹³C 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 ¹H 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.^[5]

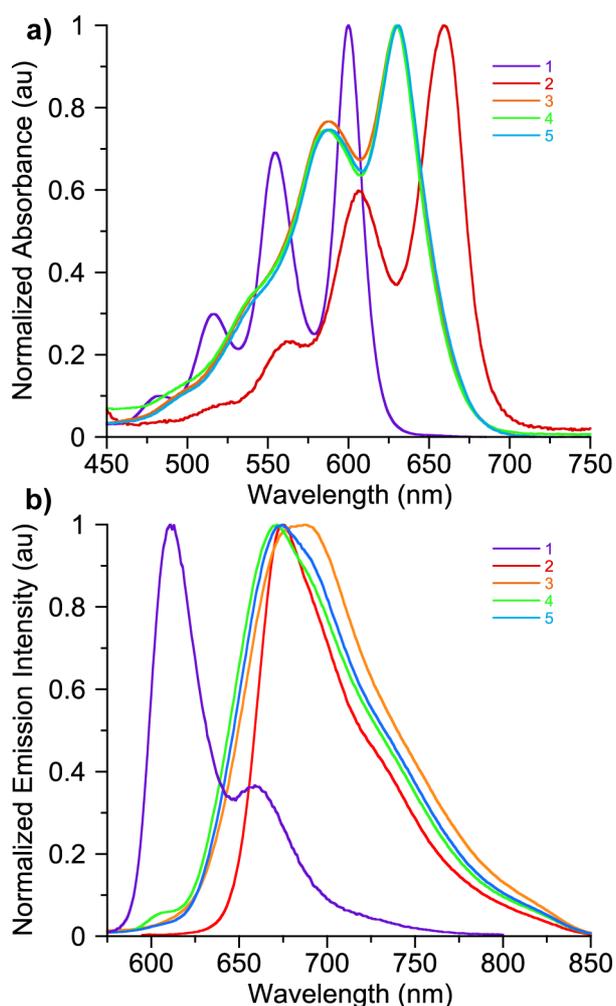
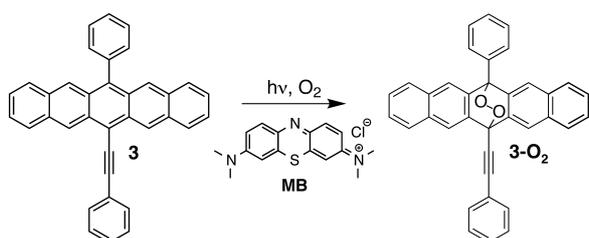


Figure 2. Normalized UV/vis absorbance and fluorescence emission spectra of pentacenes 1-5.



Scheme 2. Photooxidation of 3 to endoperoxide 3-O₂.

To understand the effect of substitution on the photochemical stability of these pentacene derivatives, we measured the kinetics of their disappearance upon exposure to ¹O₂ generated by irradiation of **MB** in an air-equilibrated CHCl₃ solution by UV/vis spectrophotometry. In these experiments, the initial concentrations of the pentacene derivative and methylene blue were 50 μM and 80 μM, respectively. Because **1-5** have absorbance 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 acene. We also adjusted the decomposition kinetics to reflect only the

Table 2: Kinetics of photooxidations of **1-5** in CHCl₃. Reported relative rates are from fits of initial rate data to first-order kinetics and were determined relative to that for **DPA** ($k = 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) 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 $\leq 10\%$ of the means.

	Relative Rate (sensitized) ^a	t _{1/2} (s) λ > 400 nm
1	~30	< 4
2	0.27 ^b ± 0.17	1040
3	10 ^c ± 1	30
4	0.33 ^c ± 0.13	810
5	0.18 ^c ± 0.01	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

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 the methylene blue, and 2) subtracting the absorbance of methylene blue from all UV/vis spectra before determining the remaining concentration of pentacene. To correct for experimental variability, we compared all kinetics to the **MB**-mediated photooxidation of 9,10-diphenylanthracene (**DPA**), which has a bimolecular rate constant of $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, 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 ¹O₂ increased during the reaction; this scenario is possible if acene-¹O₂ reactions (a combination of physical and chemical quenching) compete with unimolecular decay of ¹O₂.^[35] In all cases, we fit the initial data to a pseudo first-order kinetics model (Figure 3); Table 2 summarizes the relative rates of acene decomposition under these conditions. In addition, we also monitored the disappearance of acene upon irradiation under identical conditions (λ > 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 λ > 665 nm.

One critical trend in structure-property relationships is that unsymmetrically substituted arylethynyl compound **3** shows a rate of reaction with photosensitized ¹O₂ that is intermediate between diphenyl pentacene **1** and diphenylethynylpentacene **2**: the rate of reaction of **3** is approximately three-fold smaller than **1**, with a rate constant with ¹O₂ similar to that of diaryltetracenes, indicating that one ethynyl group stabilizes the pentacene towards photooxidation 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 ¹O₂ by ethynylpentacenes.^[18]

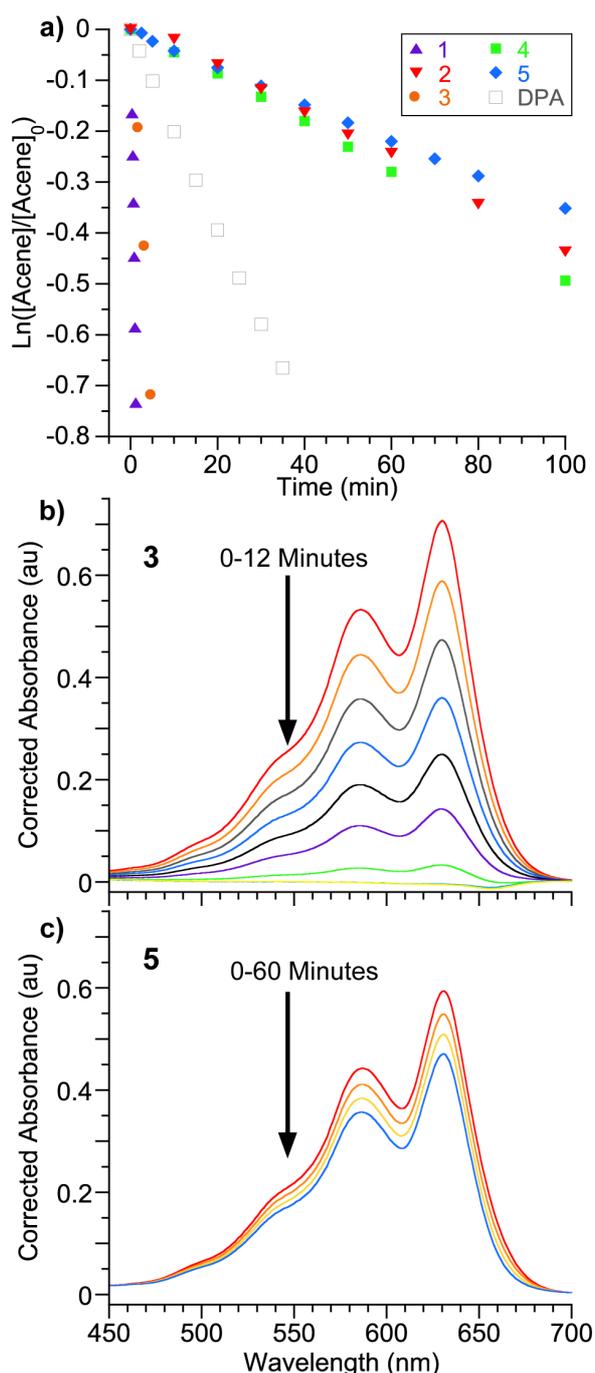


Figure 3. a) Pseudo first-order initial kinetics of disappearance of compounds 3–5 upon exposure to MB 80 (μM) and irradiation with $\lambda > 665$ nm in air-equilibrated CHCl_3 . b, c) Absorbance spectra of 3 (b) and 5 (c) as a function of irradiation time at $\lambda > 665$ nm in the presence of MB. The absorbance of MB has been subtracted from each spectrum to reflect the actual concentration of acene.

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 corresponding aryl ring. 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 transition states for oxidation of compounds 3–5. The nearly identical energies of HOMOs (-4.78 eV – -4.80 eV) and LUMOs (-2.81 eV – -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 $^1\text{O}_2$. 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,^[36–38] and Miller and coworkers have noted an analogous increase in half-life (up to 25-fold) for diarylpentacenes with *o*-alkyl substituents.^[7] The relative rate of decomposition of 4 and 5 is similar to that previously reported for TIPS-pentacene under photosensitized oxidation conditions with MB, which has a bimolecular rate constant of $\sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.^[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^2 —Table 2 shows the half-lives of the pentacenes under these conditions. In agreement with the results of earlier MB-mediated photooxygenations, the half-lives of these compounds span three orders of magnitude, with the order of persistence $5 \sim 2 > 4 > 3 > 1$. 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 ~ 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: i) the steric hindrance of the central 6 and 13 positions through *o*-alkyl groups on one aryl substituent, and ii) the electronic deactivation of pentacenes through substitution with one ethynyl substituent by inducing physical quenching of $^1\text{O}_2$, slows the rate of pentacene photoinduced decomposition. This work therefore highlights that new, unsymmetric aryl-ethynylpentacene 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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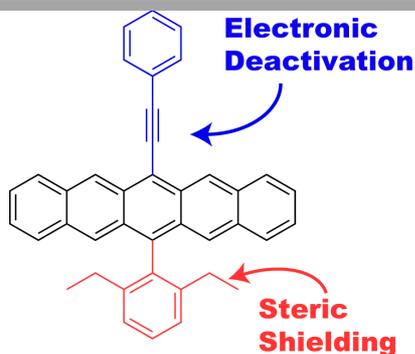
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COMMUNICATION

Highly stable pentacene derivatives are described, which combine an electronically deactivating alkyne substituent with a sterically encumbering dialkylaryl substituent on the reactive 6 and 13 positions. Resistance to photooxidation of these unsymmetrically substituted pentacenes is comparable to diethynylpentacenes, opening a new chemical structural space for the discovery of stable organic semiconductors.



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