

Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

Remarkably, 6,13-bis(phenylthio)pentacene and 6,13-bis(decylthio)pentacene are both considerably longer-lived than TIPS-pentacene.

Introduction

Pentacene is one of the most widely utilized organic semi-conductor compounds.¹ Due to its poor solubility and facile photo-degradation,² numerous groups have prepared pentacene derivatives bearing either solubilizing or stabilizing substituents. Amongst the most commonly prepared derivatives are phenyl substituted pentacenes³ and ethynyl substituted pentacenes⁴ including silylethynyl derivatives.^{68c, 5} Because phenyl substituents lie in a time-averaged orthogonal orientation relative to the acene backbone, they help to diminish intramolecular π - π stacking interactions thereby improving solution solubilities and enabling an exploration of solution phase chemistries.⁶ Phenyl substituted pentacenes have been studied as red emitters in organic light-emitting diode (OLED) applications.^{68d, 7} The first silylethynyl substituted pentacene is less than 10 years old and was prepared for the purpose of studying [60]fullerene Diels-Alder chemistry.^{68c} Silylethynyl substituted pentacenes are, however, more widely known for their electronic properties, especially as they relate to organic field-effect transistor (OFET) applications.^{70b, 8} The most popular of these derivatives is 6,13-bis(triisopropylsilylethynyl)pentacene or TIPS-pentacene.⁹ The literature reveals a general acceptance that silylethynyl substituted pentacenes like TIPS-pentacene are relatively stable species.^{70b} Other pentacene derivatives that have been described as stable include phenylethynyl derivatives^{69b} and those bearing electron withdrawing groups like halogen, cyano and trifluoromethyl.¹⁰ For pentacene compounds, degradation generally involves photo-oxidation⁶⁷ and, to a lesser extent, photodimerization.¹¹ Thus, although the term stability is thermodynamic in origin, it is meant to imply a lack of reactivity or “kinetic stability” (i.e., resistance to photo-oxidation) where acenes are concerned. Despite the large number of assertions concerning the stability of various pentacene derivatives, kinetic data to support these claims is either scarce¹² or missing altogether. Instead, a body of anecdotal evidence has been amassed. For example, the widely held belief that silylethynyl substituted pentacenes like TIPS-pentacene are amongst the most stable pentacene derivatives is seemingly corroborated by the fact that bulky silylethynyl substituents were successfully employed in the synthesis and characterization of persistent hexacene and heptacene derivatives, a significant accomplishment.¹³ Since there are no reports of other persistent hexacene and heptacene derivatives, several important questions arise: Do silylethynyl groups stabilize acenes through an electronic effect, through steric resistance or through a combination of the two? Which effect is more important? Are there other substituent effects at play? Are there other pentacene derivatives that are similarly resistant to photo-oxidation? In order to answer questions like these, a fundamental understanding of substituent effects in acenes, particularly as they relate to photo-oxidative resistance, is required.

In this study, we report a combined experimental and computational study of a series of substituted pentacenes including halogenated, phenylated, silylethynylated and thiolated derivatives. Experimental studies include the synthesis and characterization of both new and known pentacene derivatives and a kinetic study of each derivative under photo-oxidative conditions. Computationally, we calculated the energies of the frontier orbitals of each pentacene derivative at the B3LYP/6-311+G**//PM3 level in order to correlate HOMO and LUMO energies with measured half-lives. The results provide for the first time a quantitative assessment of the photo-oxidative stability of a series of pentacene derivatives as a function of substituents. Overall, the persistence of each pentacene derivative is impacted by three factors, all closely tied

Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

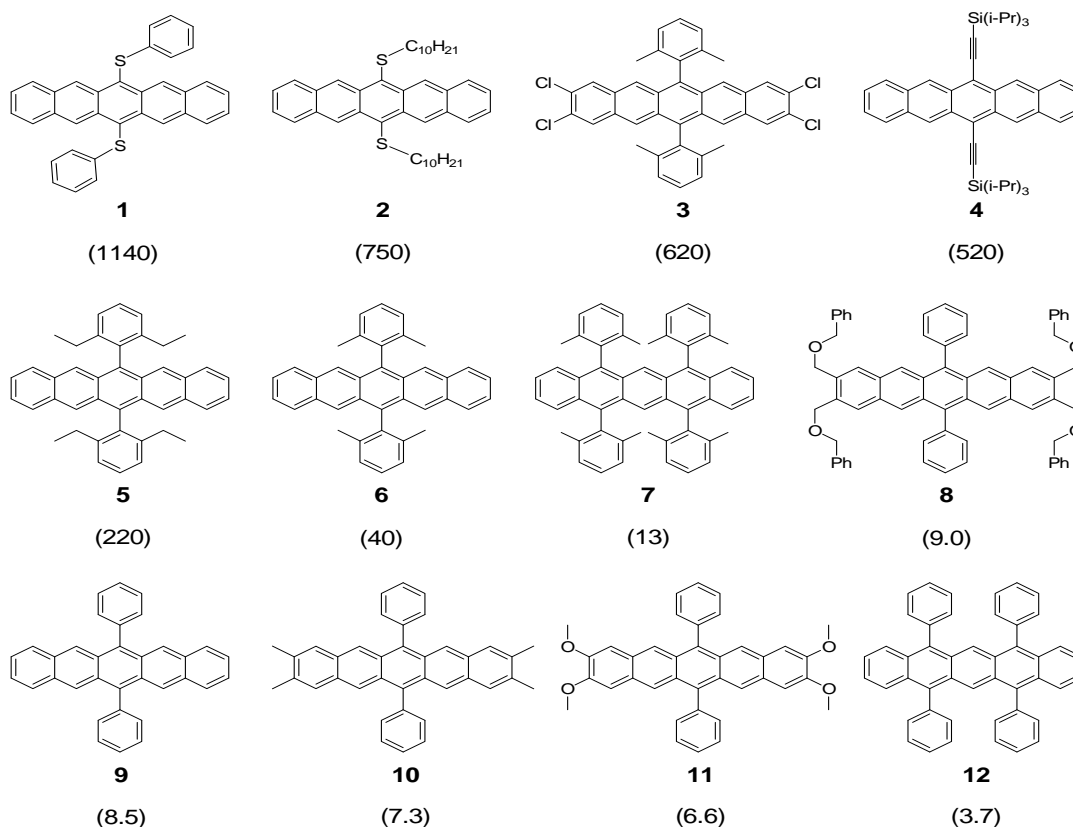


Figure 1. Structures of pentacene derivatives **1** – **12** and their associated half-lives in parentheses. All half-lives were determined for 10^{-4} M solutions in CH_2Cl_2 at 25°C in ambient light and air.

to its reactivity with singlet oxygen, $^1\text{O}_2$: (a) steric resistance, (b) electronic effects and (c) the capacity of each derivative to physically quench $^1\text{O}_2$. Phenyl substituted pentacenes are the least resistant to photo-oxidation, unless the phenyl rings bear *ortho* alkyl groups which are constrained to lie over the acene π -system providing enhanced steric resistance to $^1\text{O}_2$. Halogen substituted pentacenes show enhanced resistance to photo-oxidation via an inductive effect which renders the acene less dienophilic towards $^1\text{O}_2$. A combination of halogen and *o*-alkyl phenyl substituents yields a pentacene derivative that is more resistant to photo-oxidation than TIPS-pentacene. Most interesting, however, is that alkylthio- and arylthiopentacene derivatives, simple to prepare¹⁴ but little studied, are considerably more resistant to photo-oxidation than all other pentacene derivatives tested. We demonstrate that the enhanced persistence of alkylthio- and arylthiopentacenes is due to a combination of effects including a new substituent effect that has not been previously discussed for pentacene derivatives, i.e., physical quenching of $^1\text{O}_2$. These results have significant implications for the field of organic molecular electronics. Soluble, persistent alkylthio- and arylthiopentacenes represent promising, new candidates for thin-film OFET, OLED¹⁵ and organic photo-voltaic¹⁶ (OPV) devices. Alkylthio and arylthio groups also represent promising substituents for the preparation of large, persistent acenes with six or more rings.

Results and Discussion.

Synthesis and Characterization. Soluble pentacenes derivatives **1-12** (Figure 1) were synthesized, purified and then characterized by a combination of ^1H and ^{13}C NMR spectroscopies, UV-vis spectrophotometry, high resolution mass spectrometry and cyclic voltammetry.

Kinetics of Photo-oxidation. For kinetic analyses, the purified pentacenes were separately dissolved in CH_2Cl_2 to give 10^{-4} M solutions and then exposed to ambient light and air at 25°C for prolonged periods. UV-vis spectra were recorded at regular intervals enabling a quantitative

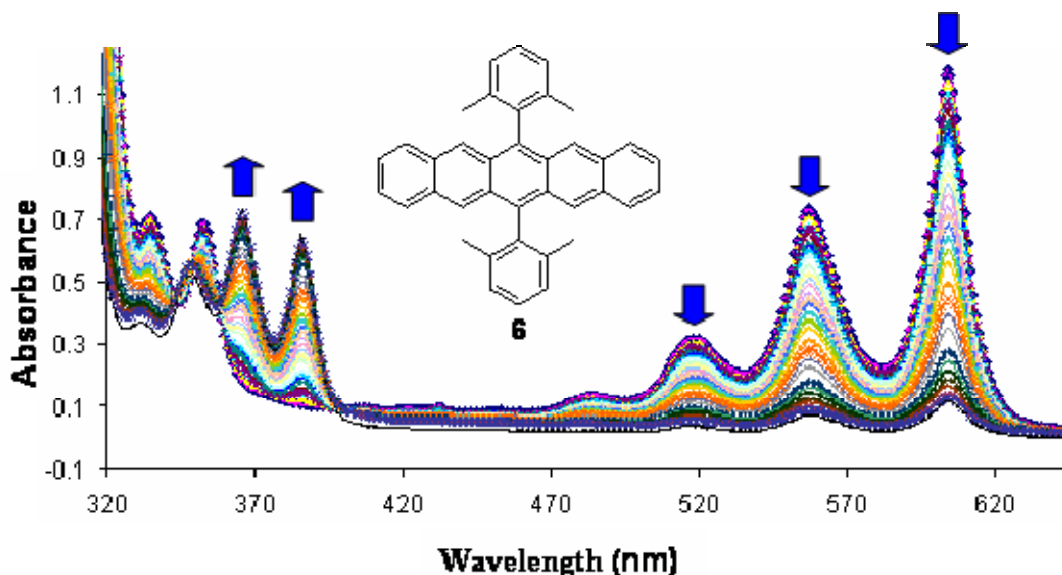
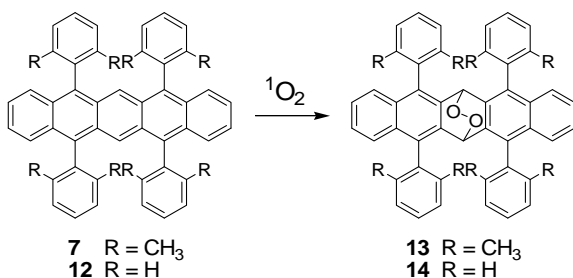


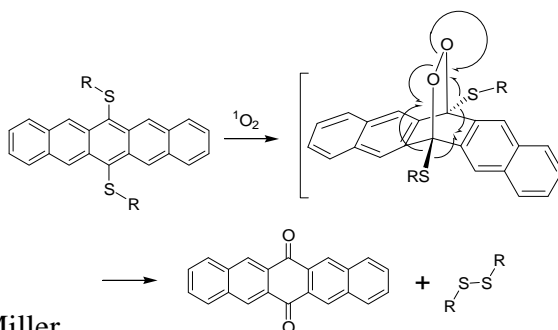
Figure 2. UV-vis spectra associated with the photo-oxidation of **6**.

determination of absorbance-time profiles for both the starting pentacenes as well the corresponding pentacene oxidation products. Figure 2 is illustrative. Here, the long wavelength bands of 6,13-bis(*o*-methylphenyl)pentacene, **6**, at 604, 557 and 518 nm are all observed to diminish with reaction progress while a new set of bands at 386 and 366 nm corresponding to oxidation products are observed to grow. Oxidation products were characterized by ^1H and ^{13}C

Scheme 1. $^1\text{O}_2$ oxidation of **7** and **12** to give Diels-Alder adducts **13** and **14**.



Scheme 2. Proposed mechanism for oxidation of phenylthiopentacene **1** and decylthiopentacene **2** to afford 6,13-pentacenedione and a disulfide.



Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

NMR spectroscopy. Most acenes did not oxidize to give a single oxidation product in a clean reaction with compounds **7** and **12** representing exceptions. In these cases, $^1\text{O}_2$ adducts **13** and **14** formed cleanly (Scheme 1) and were subsequently isolated and characterized. Phenylthiopentacene **1** and decylthiopentacene **2** oxidize slowly to give predominantly 6,13-pentacenedione and either diphenyl disulfide or didecyl disulfide, respectively (Scheme 2).

Absorbance-time profiles (Figure 3) were determined for each pentacene derivative and they revealed a relative ordering of photo-oxidative resistance as follows:

6,13-bis(phenylthio)pentacene > 6,13-bis(decylthio)pentacene
> 2,3,9,10-tetrachloro-6,13-bis(2',6'-dimethylphenyl)pentacene
> 6,13-TIPS-pentacene > 6,13-bis(*o*-alkylphenyl)pentacenes
> other phenyl substituted pentacenes.

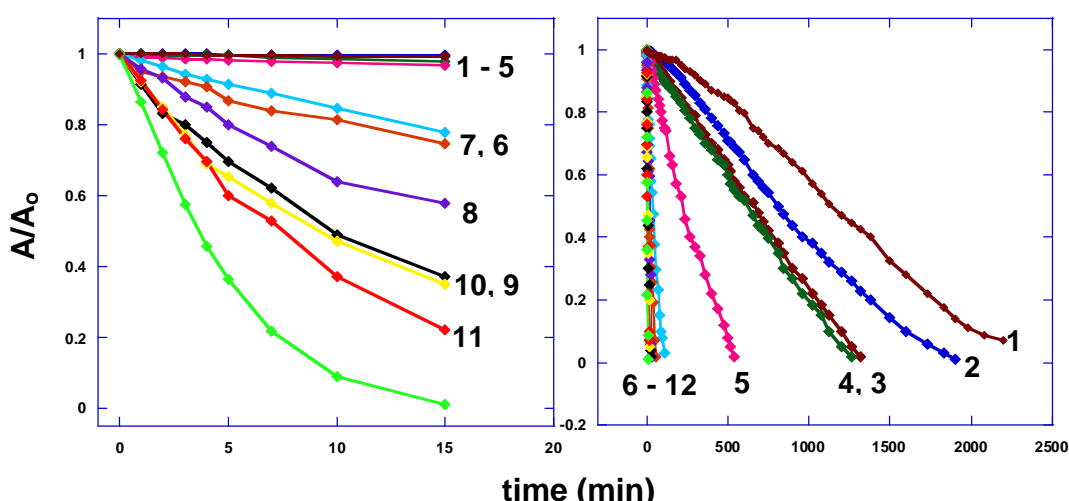


Figure 3. Absorbance-time profiles for pentacene derivatives **1** – **12**.

Although limited stages of several oxidation reactions appear to follow first order kinetics, the reactions are not first order processes. In a first order reaction, the associated half-life, $t_{1/2}$, would be independent of acene concentration and this is not observed in any case. Moreover, plots of $\ln(A_t/A_0)$ versus time (A_t is the absorbance of acene at a given wavelength at time t ; A_0 is the initial absorbance of acene at the same wavelength at time zero) are not linear over significant percentage conversions for any of the pentacene derivatives tested. This result is in direct conflict with the first order kinetics reported by Ono and co-workers^{67a} for the photo-oxidation of 6,13-diphenylpentacene, **9**, under similar conditions. These authors report a first-order rate constant but reveal no absorbance-time data and no details concerning the analysis. Maliakal and co-workers compared the photo-oxidation of TIPS-pentacene to that of pentacene in THF solution.⁷⁷ They report that TIPS-pentacene is approximately 50 times more stable than pentacene based upon measured half-lives. However, as the photo-oxidation reactions are not first order, the measured half-lives depend upon the initial concentrations of the molecules, a detail not provided in the Maliakal paper. Thus, unless the TIPS-pentacene and pentacene samples were prepared at the same concentration (TIPS-pentacene is vastly more soluble than pentacene in THF), the comparison of half-lives is of limited value.

Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

In our reactions, all pentacene derivatives were treated to identical conditions such that the measured half-lives (Fig. 1) could be directly compared. This approach allows for the first time a quantitative assessment of the photo-oxidative resistance of a series of pentacene derivatives as a function of substituents.

Steric Effects. The least persistent of the acenes tested are the phenyl substituted derivatives **5-12**. Within this series, it is clear that steric resistance is an important contributor to overall pentacene persistence. Thus, both 6,13-bis(2',6'-dimethylphenyl)pentacene, **6**, and 5,7,12,14-tetrakis(2',6'-dimethylphenyl)pentacene, **7**, are more resistant to photo-oxidation than their counterparts that are missing *o*-methyl groups, 6,13-diphenylpentacene, **9**, and 5,7,12,14-tetraphenylpentacene, **12**, respectively. This is because the low energy conformations place the phenyl rings in near orthogonal orientations relative to the pentacene backbone and this in turn constrains the *o*-methyl groups of **6** and **7** to lie directly over and under the pentacene π -systems, effectively shielding the π -systems. Figure 4 is illustrative for compounds **6** and **7**. The positional location of phenyl substituents along the acene backbone is also important. Thus, **6** is less prone to photo-oxidation than **7** despite the fact that it has half the number of phenyl substituents. The greater persistence of **6** reflects the fact that its phenyl substituents provide greater shielding to the most reactive ring on pentacene, i.e., the center ring.¹⁷ Specifically, the 6,13 carbons of **6**, sites for potential Diels-Alder reactions with $^1\text{O}_2$, are better shielded in **6** as compared to **9** (Fig. 4). Likewise, **9** is more persistent than **12** for the same reason. Combining steric resistance and positional location considerations, it is not surprising that 6,13-bis(2',6'-diethylphenyl)pentacene, **5**, is considerably more persistent than **6**, **7**, **9** or **12**.

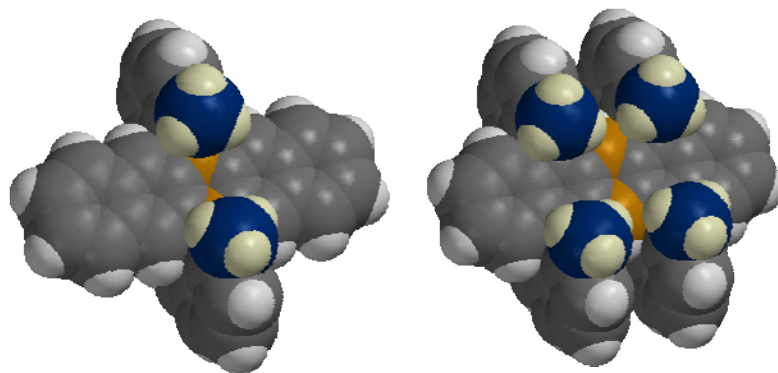


Figure 4. Calculated structures for 6,13-bis(2',6'-dimethylphenyl)pentacene, **6** (left), and 5,7,12,14-tetrakis(2',6'-dimethylphenyl)pentacene, **7** (right). For clarity, methyl carbons are shown in blue, methyl hydrogens in beige and the 6,13 carbons in orange.

Electronic Effects. Electronic effects are also important contributors to overall pentacene longevity. An examination of measured half-lives (Fig. 1, Table 1) for compounds **3**, **4** and **8-11** reveals that the addition of electron withdrawing (EW) groups leads to longer-lived species while electron donating (ED) groups have just the opposite effect. However, the magnitude of electronic effects are far smaller for ED groups as compared to EW groups. For example, placement of ED groups on the 2,3,9,10 positions as in 2,3,9,10-tetra((phenylmethoxy)methyl)-6,13-diphenylpentacene, **8**, 2,3,9,10-tetramethyl-6,13-diphenylpentacene, **10**, and 2,3,9,10-tetramethoxy-6,13-diphenylpentacene, **11**, only modestly impacts photo-oxidative resistance as compared to **9** which lacks 2,3,9,10 substituents. Thus, pentacene **11** with methoxy groups (Hammett $\sigma_p = -0.27$ ¹⁸) is the least persistent in this series followed by **10** with methyl groups

Glen P. Miller
Department of Chemistry & Materials Science Program
University of New Hampshire

Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

(Hammett $\sigma_p = -0.17^{83}$) and finally **8** with (phenylmethoxy)methyl groups which are slightly EW (Hammett $\sigma \sim +0.08$).^{83,19} In the case of **8**, the additional steric resistance provided by the large (phenylmethoxy)methyl groups may also enhance its longevity but the effect should be modest as these groups are well removed from the reactive, center ring. Most impressive are the EW chlorine substituents (Hammett $\sigma_p = +0.23^{83}$) in 2,3,9,10-tetrachloro-6,13-bis(2',6'-dimethylphenyl)pentacene, **3**, which effectively increase the half-life of **3** by more than an order of magnitude as compared to **6**. With a combination of EW chlorine substituents and sterically demanding 2',6'-dimethylphenyl substituents, **3** is in fact more persistent than TIPS-pentacene, **4**, widely regarded as one of longest-lived pentacene derivatives.^{70b}

Of all the pentacene derivatives tested, the most persistent are 6,13-bis(phenylthio)pentacene, **1**, and 6,13-bis(decylthio)pentacene, **2**. Both are considerably longer-lived than TIPS-pentacene **4**. Clearly, steric resistance cannot account for the enhanced longevity of **1** and **2** as compared to other pentacene derivatives tested. The phenylthio and decylthio groups of **1** and **2** are not constrained to lie over their respective pentacene π -systems, as are for example the *ortho*-methyl groups of **6** and **7** (Fig. 4). In fact, the phenylthio and decylthio groups of **1** and **2** are not expected to substantially shield their respective pentacene π -systems.

Table 1. Electrochemical and optical properties of pentacene derivatives **1** – **12**.

pentacene derivative ($t_{1/2}$)	$E_{1/2}$ [O] (mV)	$E_{1/2}$ [red] (mV)	low energy λ_{max} (nm)	E_g (eV) optical ^a	E_g (eV) CV ^b	E_g (eV) B3LYP/6-311+G**//PM3
1 (1140)	---	---	624, 575, 534	1.86	---	2.17
2 (750)	755, 936	-1229, -1726	617, 570, 529	1.88	1.98	2.19 ^c
3 (620)	899	-1227	605, 559, 520	1.94	2.13	---
4 (520)	789	-1054	643, 591, 548	1.81	1.84	2.01
5 (220)	713	-1485	605, 558, 520	1.95	2.20	---
6 (40)	695	-1478	604, 557, 518	1.96	2.17	2.22
7 (13)	638, 1372	-1543	618, 569, 529	1.90	2.18	---
8 (9.0)	627, 1224	-1430	600, 554, 515	1.93	2.06	---
9 (8.5)	682	-1396	604, 558, 519	1.94	2.08	2.23
10 (7.3)	536, 1171	-1521	602, 556, 518	1.92	2.06	---
11 (6.6)	464, 1081	-1651	583, 539, 501	2.01	2.12	---
12 (3.7)	635, 1183	-1407	621, 573, 532	1.88	2.04	2.21

^aOptical band gaps determined from onset of lowest energy visible band; ^bElectrochemical band gaps determined from onset of 1st oxidation and 1st reduction waves in cyclic voltammograms; ^cBand gap calculation is for analogous 6,13-bis(methylthiophenyl)pentacene rather than **2**.

The nature of any electronic effects associated with alkylthio and arylthio substituents was investigated using UV-vis spectroscopy and cyclic voltammetry. The UV-vis spectra for **1** and **2** reveal red-shifted absorptions at 624 and 617 nm, respectively, amongst the longest wavelength bands observed in the series **1** – **12** (Table 1). Only TIPS-pentacene **4**, 5,7,12,14-tetrakis(*o*-methylphenyl)pentacene, **7**, and 5,7,12,14-tetraphenylpentacene **12** show similar absorptions with wavelengths greater than 615 nm. Likewise, these five compounds possess the smallest optical band gaps in the series **1** - **12**. Similar trends are observed for **1**, **2**, **4**, **7** and **12** when comparing electrochemical band gaps from cyclic voltammetry experiments and computational band gaps calculated at the B3LYP/6-311+G**//PM3 level (Table 1). Of these compounds, TIPS-pentacene **4** has the longest wavelength absorption and the smallest band gap, presumably because the

Glen P. Miller

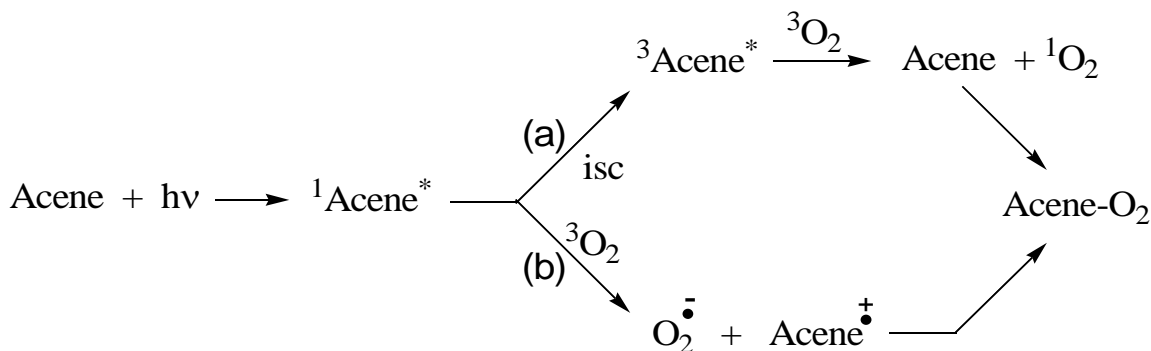
Department of Chemistry & Materials Science Program
University of New Hampshire

Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

alkynyl group is fully conjugated to the pentacene π -system. Diphenyl substituted pentacenes like **3**, **5**, **6** and **9-11** are only partially conjugated because the phenyl rings cannot achieve a co-planar conformation with respect to the pentacene π -system. Additional *ortho* alkyl substitution as in **5** and **6** ($\lambda_{\text{max}} = 604\text{-}5\text{ nm}$) does not lead to significant changes in the UV-vis spectrum as compared to **9** ($\lambda_{\text{max}} = 604\text{ nm}$) suggesting that the unsubstituted phenyl groups in **9** are already significantly rotated with respect to the pentacene π -system. Additional phenyl groups do, however, lead to red-shifted absorptions as in **7** and **12** due to overall enhanced π -delocalization. Conversely, placing chlorine at the 2,3,9,10 positions does not lead to significant changes in the UV-vis spectrum as illustrated by a comparison of **3** and **6**.

Mechanistic considerations. Photo-excited pentacenes are believed to sensitize $^1\text{O}_2$ formation^{77,85a,85b,85c} and numerous examples of acene- $^1\text{O}_2$ Diels-Alder adducts are known^{67a,20} in addition to those reported here. The formation of Diels-Alder adducts seems to implicate $^1\text{O}_2$ as a reactant in a mechanism involving $^1\text{O}_2$ sensitization (Scheme 3, path a). It is however possible to achieve the same products via an alternative mechanism involving electron transfer from photo-excited pentacene to $^3\text{O}_2$ followed by O-C couplings (Scheme 3, path b). Indeed, Malikal and co-workers have argued that $^1\text{O}_2$ sensitization can be ignored for TIPS-pentacene **4** because the singlet-triplet energy gap calculated for **4** was well below the 22.5 kcal/mol singlet-triplet energy gap for $^1\text{O}_2$.⁷⁷ Malikal and co-workers further argue⁷⁷ that the lower LUMO energy of **4** as compared to pentacene results in enhanced photo-stabilization as the barrier to electron transfer

Scheme 3. Possible mechanisms for the photo-oxidation of acenes **1-12**



(Scheme 3, path b) is proportionately greater. We find these arguments unconvincing for two reasons: (1) the calculations⁷⁷ were performed at a dangerously low level of theory (B3-LYP/6-31+G*); (2) conclusions are drawn based on a comparison of only two molecules. Regarding the first point, it is documented that B3-LYP DFT calculations are well suited for predicting a wide range of geometries at the 6-31G* level. However, it has been shown²¹ that triple-zeta quality AO basis sets represent a minimum requirement for accurate energy calculations and that the 6-31G* basis set should be avoided in accurate work. Our B3LYP/6-311+G**//PM3 calculations do not show a correlation between LUMO energies and measured half-lives.

Given the totality of data collected here, we conclude that both steric and electronic effects are important contributors to pentacene longevity and that it is possible to rationalize these effects within the context of a single photo-oxidation pathway involving $^1\text{O}_2$ sensitization (Scheme 3, path a). We are not prepared to dismiss an electron transfer mechanism of the type illustrated in path b of Scheme 3, but we believe that it is likely of secondary importance.

Substituent Effects in Pentacenes: Longest-Lived Pentacene Derivatives Revealed

Conclusions

Alkylthio- and arylthiopentacenes are soluble, long-lived pentacene derivatives that represent promising, new candidates for thin-film OFET, OLED²² and organic photo-voltaic²³ (OPV) devices.

More Information

For more information about substituent effects in pentacenes, see:

Kaur, I., Jia, W., Kopreski, R., Selvarasah, S., Dokmeci, M. R., McGruer, N. and Miller, G. P., “**Substituent Effects in Pentacenes: Gaining Control Over HOMO-LUMO Gaps and Photo-oxidative Resistances,**” *J. Amer. Chem. Soc.*, **2008**, *130*, 16274–16286

and contact:

Glen P. Miller
Professor of Chemistry & Materials Science
University of New Hampshire
23 Academic Way – Parsons Hall
Durham, NH 03824
glen.miller@unh.edu

¹ Chason, M.; Brazis, P. W., Jr.; Zhang, J.; Kalyanasundaram, K.; Gamota, D. R. *Proc. IEEE* **2005**, *93*, 1348-1356.

² (a) Ono, K.; Totani, H.; Hiei, T.; Yoshino, A.; Saito, K.; Eguchi, K.; Tomura, M.; Nishida, J.; Yamashita, Y. *Tetrahedron* **2007**, *63*, 9699-9704. (b) Palayangoda, S. S.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2007**, *72*, 6584-6587. (c) Etienne, A.; Beauvois, C. *Compt. Rend.* **1954**, *239*, 64-6.

³ (a) Allen, C. F. H.; Bell, A. *J. Amer. Chem. Soc.* **1942**, *64*, 1253-1260. (b) Miller, G. P.; Mack, J. *Org. Letters*, **2000**, *2*, 3979-3982. (c) Miller, G. P.; Mack, J.; Briggs, J. *Org. Letters*, **2000**, *2*, 3983-3986. (d) Jang, B.-B.; Lee, S. H.; Kafafi, Z. H. *Chem. Mater.* **2006**, *18*, 449-457. (e) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Amer. Chem. Soc.* **2006**, *128*, 1340-1345.

⁴ (a) Miller, G. P., Mack, J., and Briggs, J. B. *Fullerenes- Volume 11, Proceedings of the International Symposium on Fullerenes, Nanotubes, and Carbon Nanoclusters*, P.V Kamat, D.M. Guldi, and K.M. Kadish, Eds., The Electrochemical Soc.: Pennington, NJ, **2001**, 202-206. (b) Li, Y.; Wu, Y.; Liu, P.; Prostran, Z.; Gardner, S.; Ong, B. S. *Chem. Mater.* **2007**, *19*, 418-423.

⁵ (a) Troisi, A.; Orlandi, G.; Anthony, J. E. *Chem. Mater.* **2005**, *17*, 5024-5031. (b) Anthony, J. E. *Angew. Chem Int. Edit.* **2008**, *47*, 452-483. (c) Benard, C. P.; Geng, Z.; Heuft, M. A.; VanCrey, K.; Fallis, A. G. *J. Org. Chem.* **2007**, *72*, 7229-7236.

⁶ Briggs, J. B.; Miller, G. P. *C. R. Chim.* **2006**, *9*, 916-927.

⁷ (a) Wolak, M. A.; Jang, B.-B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492-5499. (b) Picciolo, L. C.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **2001**, *78*, 2378-2380.

⁸ (a) Park, S. K.; Jackson, T. N.; Anthony, J. E.; Mourey, D. A. *Appl. Phys. Lett.* **2007**, *91*, 063514/1-063514/3. (b) Lee, W. H.; Kim, D. H.; Jang, Y.; Cho, J. H.; Hwang, M.; Park, Y. D.; Kim, Y. H.; Han, J. I.; Cho, K. *Appl. Phys. Lett.* **2007**, *90*, 132106/1-132106/3. (c) Park, J. G.;

Glen P. Miller
Department of Chemistry & Materials Science Program
University of New Hampshire

- Vasic, R.; Brooks, J. S.; Anthony, J. E. *J. Low Temp. Phys.* **2006**, *142*, 387-392. (d) Kim, Y.-H.; Lee, Y. U.; Han, J.-I.; Han, S.-M.; Han, M.-K. *J. Electrochem. Soc.* **2007**, *154*, H995-H998. (e) Park, S. K.; Anthony, J. E.; Jackson, T. N. *IEEE Electr. Device L.* **2007**, *28*, 877-879.
- ⁹ Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Amer. Chem. Soc.* **2001**, *123*, 9482-9483.
- ¹⁰ Okamoto, T.; Senatore, M. L.; Ling, M.-M.; Mallik, A. B.; Tang, M. L.; Bao, Z. *Adv. Mater.* **2007**, *19*, 3381-3384.
- ¹¹ (a) Coppo, P.; Yeates, S. G. *Adv. Mater.* **2005**, *17*, 3001-3005. (b) Birks, J. B.; Appleyard, J. H.; Pope, R. *Photochem. Photobiol.* **1963**, *2*, 493-495.
- ¹² Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980-4986.
- ¹³ Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Amer. Chem. Soc.* **2005**, *127*, 8028-8029.
- ¹⁴ Kobayashi, K.; Shimaoka, R.; Kawahata, M.; Yamanaka, M.; Yamaguchi, K. *Org. Letters*, **2006**, *8*, 2385-2388.
- ¹⁵ Lee, S.; Koo, B.; Park, J.-G.; Moon, H.; Hahn, J.; Kim, J. M. *MRS Bull.* **2006**, *31*, 455-459.
- ¹⁶ Rand, B. P.; Genoe, J.; Heremans, P.; Poortmans, J. *Prog. Photovoltaics* **2007**, *15*, 659-676.
- ¹⁷ (a) Chien, S.-H.; Cheng, M.-F.; Lau, K.-C.; Li, W.-K. *J. Phys. Chem A* **2005**, *109*, 7509-7518. (b) Cheng, M.-F.; Li, W.-K. *Chem. Phys. Lett.* **2003**, *368*, 630-638. (c) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Letters* **2001**, *3*, 3643-3646.
- ¹⁸ Dean, J. A. *Handbook of Organic Chemistry*, McGraw-Hill: New York, 1987. pp. 7.1 – 7.7.
- ¹⁹ A σ_p value for the -CH₂-OH is referenced in place of -CH₂-O-CH₂Ph.
- ²⁰ (a) Kaur, I. and Miller, G. P., *New J. Chem.* **2008**, *32*, 459-463. (b) Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Uno, H.; Ogawa, T.; Ohara, K.; Ono, N. *Chem-Eur J* **2005**, *11*, 6212-6220. (c) Gollnick, K. *Adv. Chem. Ser.* **1968**, No. 77, 78-101. (d) Zhou, X.; Kitamura, M.; Shen, B.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2004**, *33*, 410-411.
- ²¹ Grimme, S.; Steinmetz, M.; Korth, M. *J. Org. Chem.* **2007**, *72*, 2118-2126.
- ²² Lee, S.; Koo, B.; Park, J.-G.; Moon, H.; Hahn, J.; Kim, J. M. *MRS Bull.* **2006**, *31*, 455-459.
- ²³ Rand, B. P.; Genoe, J.; Heremans, P.; Poortmans, J. *Prog. Photovoltaics* **2007**, *15*, 659-676.