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Synthesis of Tetracene Sulfoxide and Tetracene Sulfone via a Cascade Cyclization Reaction

Yi-Chun Lin and Chih-Hsiu Lin*

Institute of Chemistry, Academia Sinica, 128 Academia Road, Nankang,
Taipei, Taiwan

chl@chem.sinica.edu.tw

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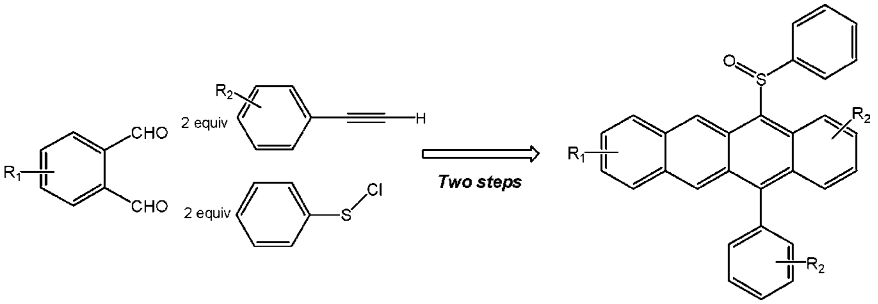
ABSTRACT



A facile synthesis of tetracene sulfoxides and sulfones based on *o*-diallene annulation initiated cascade cyclization was developed. The photophysical behavior of these tetracene derivatives can be generally rationalized by the presence of electron-withdrawing sulfoxides and sulfones at the 5-position.

Nearly 25 years ago, Hoffmann, Chapman, and Kivelson foretold that the small HOMO-LUMO gap in acenes may enable these linearly fused aromatic hydrocarbons to exhibit various unusual material properties than typically associated with metals and semiconductors.[1] The prominent status that acene compounds hold in the current pursuit for organic electronics[2] is the fulfillment of that prophecy. Most notably, pentacene and tetracene derivatives are now regularly employed as the semiconducting layers in field effect transistors.[3] Although the extraordinary hole mobility of pentacene has become the benchmark to which all similar studies are measured, acene-based devices still leave plenty of room for improvement especially concerning the stability and solubility problems in higher acenes. One common approach to optimizing the performance of organic electronic devices is to substitute the parent compounds with various synthetic derivatives. However, in acene-based devices, the systematic change of substitutions on acenes poses a great challenge since there are very few synthetic methodologies that can serve this purpose.[4]

Most acene syntheses that appear in the literature are based on Diels−Alder or aldol condensation.[5] In such strategies,

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(1) (a) Kertesz, M.; Hoffmann, R. *Solid State Commun.* **1983**, *47*, 97. (b) Kivelson, S.; Chapman, O. L. *Phys. Rev. B* **1983**, *28*, 7236.

(2) In field effect transistors: (a) Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159. (b) Ando, S.; Nishida, J.-I.; Fujiwara, E.; Tada, H.; Inoue, Y. I.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2005**, *17*, 1261. In light emitting diodes: (c) Shi, J. M.; Tang, C. W. *Appl. Phys. Lett.* **2002**, *80*, 3201. (d) Danel, K.; Huang, T.-H.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Chem. Mater.* **2002**, *14*, 3860. (e) Huang, T.-H.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Chem. Mater.* **2003**, *15*, 4854. (f) Wolak, M. A.; Jang, B. B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492. (g) Wolak, M. A.; Delcamp, J.; Landis, C. A.; Lane, P. A.; Anthony, J. E.; Kafafi, Z. *Adv. Funct. Mater.* **2006**, *16*, 1943. In light-emitting field effect transistor: (h) Hepp, A.; Heil, H.; Weise, W.; Ahles, M.; Schmechel, R.; von Seggern, H. *Phys. Rev. Lett.* **2003**, *91*, Art. No. 157406. (i) Santato, C.; Capelli, R.; Loi, M. A.; Murgia, M.; Cicoira, F.; Roy, V. A. L.; Stallinga, P.; Zamboni, R.; Rost, C.; Karg, S. E.; Muccini, M. *Synth. Met.* **2004**, *146*, 329. In solar cell: (j) Yoo, S.; Domercq, B.; Kippelen, B. *Appl. Phys. Lett.* **2004**, *85*, 5427. (k) Chu, C. W.; Shao, Y.; Shrotriya, V.; Yang, Y. *Appl. Phys. Lett.* **2005**, *86*, Art. No. 243506. (l) Pandey, A. K.; Dabos-Seignon, S.; Nunzi, J. M. *Appl. Phys. Lett.* **2006**, *89*, Art. No. 113506.

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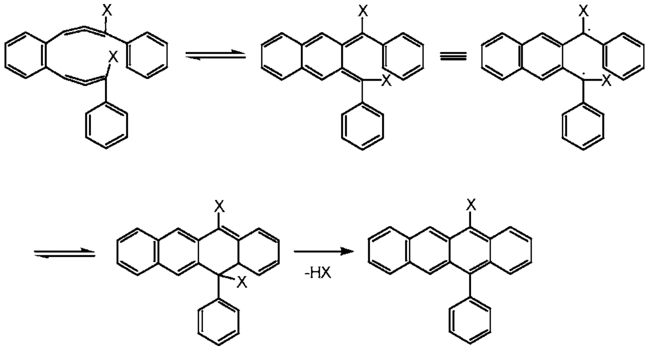
the Diels−Alder or aldol adducts invariantly need to undergo further redox manipulations to furnish the acene structure. However, the redox steps can cause problems with more sensitive acene products. We hereby propose a one-step synthesis of tetracene via a bisallenyl annulation cascade cyclization reaction without employing such redox operations.

Allene is a very useful structure motif to trigger annulation reactions. Such reactions are often employed in the synthesis of exotic aromatic systems.[6] The application of *o*-diallene to construct various linearly fused aromatic systems was also well-documented in the literature.[7] In such transformations, the starting *o*-diallenyl compounds first undergo annulation to form transient *o*-quinonedimethane intermediates. To reach a stable product, the diradicaloid intermediates can be trapped by internal hydrogen abstraction or inter- or intramolecular cyclization.[8] When the diradicaloids derived from *o*-diallenyl phenylene undergo intramolecular electrocyclic reaction with a phenyl group, as reported by Saá et al.,[8a] the intermediate will lead to a dihydrotetracene-type product. We further reasoned that such a cyclization can be made irreversible if a leaving group is incorporated into the system to trigger a post-annulation elimination reaction and furnish the tetracene structure. We shall use such a proposed mechanism as our working model in the subsequent investigation.

Scheme 1. Cascade Cyclization of *o*-Bisallenyl Compounds to Tetracene Derivatives



Among the numerous choices to generate the transient *o*-bisallenyl intermediates,[9] the 2,3-sigmatropic rearrangement of propargylic sulfenate or sulfinate seems best suited to our purpose. Such reactions are generally carried out under very mild conditions and the yields of allenic products are generally very high. More importantly, the sulfoxide or sulfone functional groups produced after such rearrangements can serve as the leaving groups to facilitate the post-annulation elimination reaction. Such a strategy opened an access to the tetracene derivatives with a facile one-pot four-step reaction (rearrangement, two annulations, and elimination).

The strategy was first carried out with the simplest substrate-α,α'-bis(phenylethynyl)-1,2-benzenedimethanol at ambient temperature. With three different sulfenyl and sulfinyl reagents (sulfenyl chloride, *p*-tolylsulfinyl chloride, and *p*-nitrobenzenelsulfenyl chloride) of a wide range of reactivity,[10] we discovered that the reaction rates or the yields of desired products are quite similar (Scheme 2). These results indicated that the formation of the sulfenyl (or sulfinyl) esters is not likely to be the rate-determining step.

Since the two annulation steps are likely to be reversible before elimination occurs, the success of these reactions

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(3) Pentacene and pentacene derivative based devices: (a) Brown, A. R.; Jarrett, C. P.; deLeeuw, D. M.; Matters, M. *Synth. Met.* **1997**, *88*, 37. (b) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854. (c) Rost, C.; Gundlach, D. J.; Karg, S.; Riess, W. *J. Appl. Phys*. **2002**, *95*, 5782. (d) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812. (e) Podzorov, V.; Sysoev, S. E.; Loginova, E.; Pudalov, V. M.; Gershenson, M. E. *Appl. Phys. Lett.* **2003**, *83*, 3504. (f) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138. (g) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986. (h) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340. Tetracene and tetracene based devices: (i) Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. *Science* **2004**, *303*, 1644. (j) Tulevski, G. S.; Miao, Q.; Fukuto, M.; Abram, R.; Ocko, B.; Pindak, R.; Steigerwald, M. L.; Kagan, C. R.; Nuckolls, C. *J. Am. Chem. Soc.* **2004**, *126*, 15048. (k) Moon, H.; Zeis, R.; Borkent, E.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Christian Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322. (l) Merlo, J. A.; Newman, C. R.; Gerlach, C. P.; Kelley, T. W.; Muyres, D. V.; Fritz, S. E.; Toney, M. F.; Frisbie, C. D. *J. Am. Chem. Soc.* **2005**, *127*, 3997. Heteroacene based devices: (m) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664.

(4) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106* (12), 5028. (b) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (c) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15. (d) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163. (e) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028. (f) Lin, C.-H.; Radhakrishnan, K. *Chem. Commun.* **2005**, 504. (g) Radhakrishnan, K.; Lin, C.-H. *Synlett* **2005**, 2179. (h) Reichwagen, J.; Hopf, H.; Desvergne, J.-P.; Del Guerzo, A.; Bouas-Laurent, H. *Synthesis* **2005**, 3505. (i) Jiang, J. Y.; Kaafarani, B. R.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 2155. (j) Kobayashi, K.; Shimaoka, R.; Kawahata, M.; Yamanaka, M.; Yamaguchi, K. *Org. Lett.* **2006**, *8*, 2385.

(5) (a) Reichwagen, J.; Hopf, H.; Guerzo, A. D.; Desvergne, J. P.; Belin, C.; Laurent, H. B. *Org. Lett.* **2005**, *7*, 971. (b) Reichwagen, J.; Hopf, H.; Guerzo, A. D.; Desvergne, J. P.; Belin, C.; Laurent, H. B. *Org. Lett.* **2005**, *7*, 971. (c) Chan, S. H.; Yick, C. Y.; Wong, H. N. C. *Tetrahedron* **2002**, *58*, 9413. (d) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, 122, 12876. (e) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967. (f) Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 4085. (g) Chen, Z.; Muller, P.; Swager, T. M. *Org. Lett.* **2006**, *8*, 273. (h) Chan, S. H.; Lee, H. K.; Wang, Y. M.; Fu, N. Y.; Chen, X. M.; Cai, Z. W.; Wong, H. N. C. *Chem. Commun.* **2005**, 66. (i) Chen, Y. L.; Hau, C. K.; Wang, H.; He, H.; Wong, M. S.; Lee, A. W. M. *J. Org. Chem.* **2006**, *71*, 3512.

(6) (a) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207. (b) Yang, Y.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 5832. (c) Dai, W.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2004**, *6*, 4355. (d) Kim, D.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2006**, *8*, 2313. (e) Ma, S. M. *Chem. Rev.* **2005**, *105*, 2829. (f) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057.

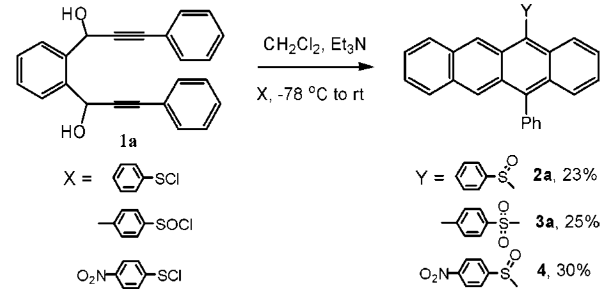
(7) (a) Braverman, S.; Duar, Y.; Segev, D. *Tetrahetron. Lett.* **1976**, *36*, 3181. (b) Braverman, S.; Duar, Y. *J. Am. Chem. Soc*. **1990**, *112*, 5830. (c) Braverman, S.; Zafrani, Y.; Gottlieb, H. E. *Tetrahedron* **2001**, *57*, 9177. (d) Braverman, S.; Cherkinsky, M.; Birsa, M. L.; Zafrani, Y. *Eur. J. Org. Chem.* **2002**, 3198.

(8) (a) Rodríguez, D.; Castedo, L.; Domínguez, D.; Saá, C. *Org. Lett.* **2003**, *5*, 3119. (b) Kitagaki, S.; Ohdachi, K.; Mukai, C. *Org. Lett.* **2006**, *8*, 95.

(9) Krause, N.; Hashmi, A. K. *Modern Allene Chemistry*; Wiley-VCH: Weinheim, Germany, 2004.

(10) (a) Braverman, S.; Mechoulam, H. Y. *Isr. J. Chem.* **1967**, *5*, 71. (b) Braverman, S.; Stabinsky, Y. *Isr. J. Chem.* **1967**, *5*, 125. (c) Braverman, S. Rearrangements involving sulfones. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988, Chapter 13. (d) Braverman, S. Rearrangements involving sulfoxides. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988, Chapter 14.

Scheme 2. Cascade Synthesis of Tetracene Solfoxide (**2a**, **4**) and Sulfones (**3a**) with Various Sulfenyl and Sulfinyl Reagents



should largely depend on the efficiency of the rearrangement and elimination steps. On the basis of this line of reasoning, we successfully optimized the reaction yield by slightly raising the reaction temperature since it is well-known that the elimination of sulfoxide and sulfone is thermally activated. When the reactions were performed in refluxing methylene chloride, tetracene sulfoxide **2a** and sulfone **3a** were obtained in 79% and 66% yields, respectively. To confirm our structural assignment, a single crystal of **2a** was obtained and its structure was unambiguously established by X-ray crystallography (Figure 1). The yields of various tetracene derivatives from this cascade reaction are listed in Scheme 3.

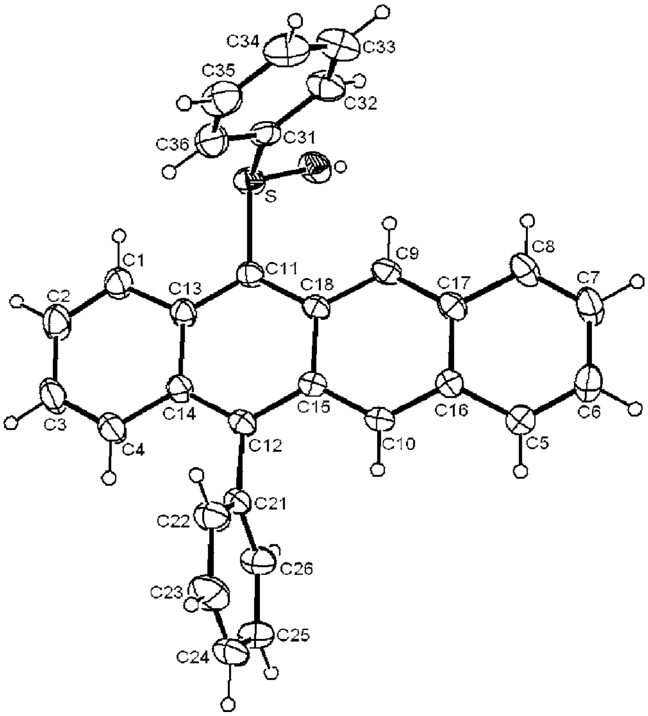
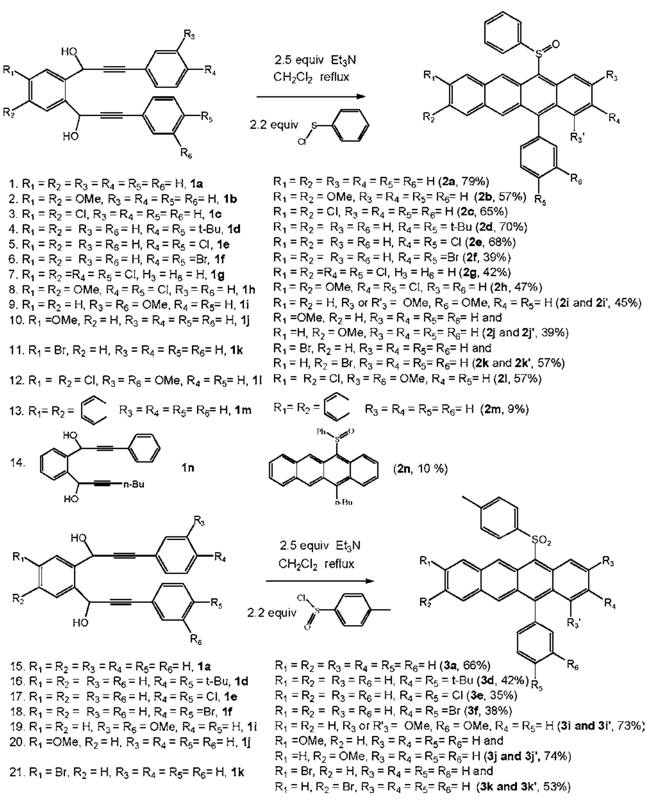


Figure 1. ORTEP picture of cascade cyclization product **2a**.

The strategy was applied to a variety of substituted α,α′-bis(phenylethynyl)-1,2-benzenedimethanol compounds (synthesized from various phthalaldehyde and lithium phenyl acetylide) and gave tetracene sulfoxide and sulfone derivatives in good to moderate yields. The dismal yield and poor purity of **2m** in entry 13 must be attributed to the instability of the pentacene product. In entry 14, the butyl chain in **2n** can provide internal hydrogen sources to divert the desired cyclization pathway of the quinonedimethane and leads to the low yield. In reactions where two regioisomeric products are possible, no apparent selectivity was observed except for entry 12 (from **1*l*** to **2*l***). With the exception of **2i** and **2i′**, these isomeric mixtures cannot be easily separated and thus they are characterized as such.

Scheme 3. Yields of Cascade Synthesis of Tetracene Sulfoxides and Sulfones



1. $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$, **1a**	$R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$ (**2a**, 79%)
2. $R_1 = R_2 = OMe$, $R_3 = R_4 = R_5 = R_6 = H$, **1b**	$R_1 = R_2 = OMe$, $R_3 = R_4 = R_5 = R_6 = H$ (**2b**, 57%)
3. $R_1 = R_2 = Cl$, $R_3 = R_4 = R_5 = R_6 = H$, **1c**	$R_1 = R_2 = Cl$, $R_3 = R_4 = R_5 = R_6 = H$ (**2c**, 65%)
4. $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 =$ t-Bu, **1d**	$R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 =$ t-Bu (**2d**, 70%)
5. $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Cl$, **1e**	$R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Cl$ (**2e**, 68%)
6. $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Br$, **1f**	$R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Br$ (**2f**, 39%)
7. $R_1 = R_2 = R_4 = R_5 = Cl$, $H_3 = H_6 = H$, **1g**	$R_1 = R_2 = R_4 = R_5 = Cl$, $H_3 = H_6 = H$ (**2g**, 42%)
8. $R_1 = R_2 = OMe$, $R_4 = R_5 = Cl$, $R_3 = R_6 = H$, **1h**	$R_1 = R_2 = OMe$, $R_4 = R_5 = Cl$, $R_3 = R_6 = H$ (**2h**, 47%)
9. $R_1 = R_2 = H$, $R_3 = R_6 = OMe$, $R_4 = R_5 = H$, **1i**	$R_1 = R_2 = H$, R_3 or $R'_3 = OMe$, $R_6 = OMe$, $R_4 = R_5 = H$ (**2i** and **2i'**, 45%)
10. $R_1 = OMe$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$, **1j**	$R_1 = OMe$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$ and $R_1 = H$, $R_2 = OMe$, $R_3 = R_4 = R_5 = R_6 = H$ (**2j** and **2j'**, 39%)
11. $R_1 = Br$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$, **1k**	$R_1 = Br$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$ and $R_1 = H$, $R_2 = Br$, $R_3 = R_4 = R_5 = R_6 = H$ (**2k** and **2k'**, 57%)
12. $R_1 = R_2 = Cl$, $R_3 = R_6 = OMe$, $R_4 = R_5 = H$, **1l**	$R_1 = R_2 = Cl$, $R_3 = R_6 = OMe$, $R_4 = R_5 = H$ (**2l**, 57%)
13. $R_1 = R_2 =$ $R_3 = R_4 = R_5 = R_6 = H$, **1m**	$R_1 = R_2 =$ $R_3 = R_4 = R_5 = R_6 = H$ (**2m**, 9%)
14. **1n**	(**2n**, 10 %)
15. $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$, **1a**	$R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$ (**3a**, 66%)
16. $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 =$ t-Bu, **1d**	$R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 =$ t-Bu (**3d**, 42%)
17. $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Cl$, **1e**	$R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Cl$ (**3e**, 35%)
18. $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Br$, **1f**	$R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = Br$ (**3f**, 38%)
19. $R_1 = R_2 = H$, $R_3 = R_6 = OMe$, $R_4 = R_5 = H$, **1i**	$R_1 = R_2 = H$, R_3 or $R'_3 = OMe$, $R_6 = OMe$, $R_4 = R_5 = H$ (**3i and 3i'**, 73%)
20. $R_1 = OMe$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$, **1j**	$R_1 = OMe$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$ and $R_1 = H$, $R_2 = OMe$, $R_3 = R_4 = R_5 = R_6 = H$ (**3j and 3j'**, 74%)
21. $R_1 = Br$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$, **1k**	$R_1 = Br$, $R_2 = H$, $R_3 = R_4 = R_5 = R_6 = H$ and $R_1 = H$, $R_2 = Br$, $R_3 = R_4 = R_5 = R_6 = H$ (**3k and 3k'**, 53%)

Attempting to further simplify the procedure, we also tried to perform a multiple-component one-pot reaction by generating the intermediate bis-sulfenyl ester by in situ trapping of the bis-lithium alkoxide with sulfenyl chloride (Scheme 4). Unfortunately, this protocol gave rather unsatisfactory results and it was not pursued further.

The photophysical properties of these tetracene derivatives are tabulated in Table 1. Compared to the parent tetracene,

Scheme 4. Attempted One-Pot Synthesis of Tetracene Sulfoxide

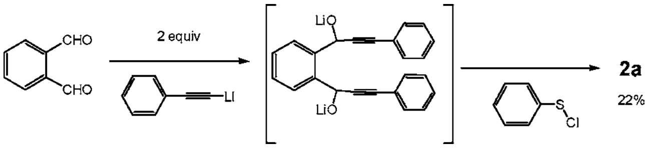


Table 1. Photophysical Data of Tetracene Sulfoxide and Sulfone Compounds

compd	UV λ_{max}/nm	ϵ	PL λ_{max}/nm	Φ PL
tetracene	474	10700	476	
5,12-diphenyl-tetracene	493	13500		
rubrene	528	11500	539	98
2a	511	4030	554	26
2b	510	2784	554	34
2c	512	6783	542	24
2d	508	6196	556	25
2e	511	5266	548	32
2f	512	4793	549	35
2g	512	6731	542	33
2h	515	5590	558	38
2i	495	4307	584	10
2i′	504	6109	579	6
2j, **2j′**	511	5135	561	29
2k, **2k′**	511	6883	549	28
2_l_	526	6045	579	21
2n	513	2331	548	24
3a	503	6693	600	2.7
3d	500	6267	598	2.3
3e	500	7617	591	6.6
3f	499	4003	587	6.5
3i, **3i′**	511	3973	612	0.1
3j, **3j′**	524	5103	596	5.2
3k, **3k′**	499	4040	596	3.0
4	519	4270	551	0.1

[a] Spectra are measured in dichloromethane solutions

marked red shifts were observed in both series of compounds in both absorption and emission spectra. These spectroscopic data are in the range of those observed in rubrene-type compounds or 5,12-dialkynyltetracene derivatives reported by Anthony et al.[11] On the contrary, within both series of compounds, the variations of absorption and emission wavelengths are much less pronounced. We therefore deduce that the frontier orbitals are strongly perturbed by the sulfoxide and sulfone at the 5-position, while other functional groups at terminal rings only exert minor influences to the electronic structures of these tetracene derivatives. The more pronounced bathochromic shifts seen in compounds **2_l_** and **3j** are likely due to the cooperative effects of electron-donating methoxy groups and electron-withdrawing chlorides and sulfone groups. While most compounds investigated here have similar absorption spectra around 500−510 nm, two notable discrepancies in the photophysical behavior between sulfoxide and sulfone tetracene derivatives are observed. First, the Stokes shifts of tetracene sulfone compounds are around 100 nm while those of tetracene sulfoxides are only 30−50 nm. Second, the sulfoxide series are on average 5−10 times more efficient emitters than the sulfone series. The only exception is the nitro-substituted tetracene sulfoxide **4**. When the emission spectra of **2a** and **3a** were measured in acetonitrile and ethanol, only **2a** exhibits noteworthy solvatochromic shifts, indicating that the first excited singlet state of sulfoxide tetracene has larger charge-separate character than the sulfone tetracene.

Cyclic voltammetry measurements were performed on the two simplest compounds **2a** and **3a**. The oxidation of **3a** is reversible while that of **2a** is only quasireversible. The oxidation potentials of these two compounds by CV experiments (vs Ag/AgCl electrode with ferrocene as the internal standard) are quite close and surprsingly also very similar to the parent tetracene (0.70 eV for **2a**, 0.77 eV for **3a**, and 0.77 eV for tetracene). These findings indicate sulfoxide and sulfone substitutions both exert influences on the LUMO levels of both tetracene derivatives and cause the red shitfs compared to the parent tetracene. The more electron-withdrawing sulfone group stablizes the LUMO in **3a** more than sulfoxide does **2a** and leads to the larger stokes shifts observed in the tetracene sulfones **3a**−**k**. However, in systems with such large stokes shifts, the LUMO energy cannot be accurately deduced from CV and optical absorption data. TGA analyses indicated the decomposition of **2a** and **3a** starts at 193 and 174 °C, respectively. As expected, the weight loss profiles are consistent with the extrusion of SO and SO_2 fragments. Further gradual weight loss can be observed for both compounds upon pyrolysis up to 500 °C.

In conclusion, we successfully developed a facile synthetic strategy for tetracene sulfoxide and sulfone via a cascade cyclization reaction. Various substituents can be incorporated by using appropriate corresponding starting materials. Due to the presence of sulfone and sulfoxide groups, these compounds show marked red shifts in UV and fluorescence spectra compared to the parent tetracene. The electron-withdrawing sulfone groups also exert subtle influences on their photophysical properties. We will attempt to employ this strategy in higher acene synthesis and explore these compounds in optical or electronic applications in the near future.

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Supporting Information Available: Detailed synthetic procedures, spectroscopic charaterizations (^{1}H, ^{13}C NMR, IR, HRMS) of all reported compounds, absorption, emission, CV, and TGA of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] (a) Burgdorff, C.; Kircher, T.; Lohmannsroben, H.-G. *Specreochim. Acta*, *Part A.* **1988**, *44*, 1137. (b) Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2003**, *5*, 4245.