Angewandte
International Edition Chemie

DOI: 10.1002/anie.201303738

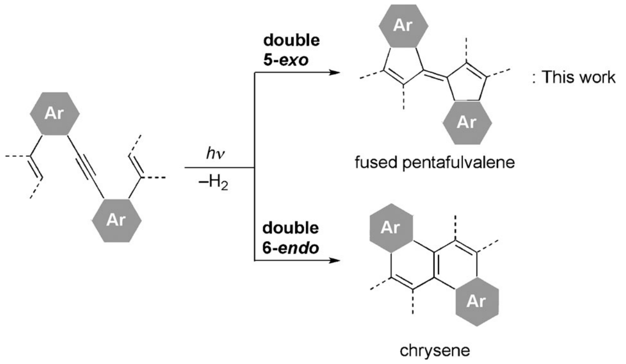
Alkyne Cyclization

Photochemical Double 5-*exo* Cyclization of Alkenyl-Substituted Dithienylacetylenes: Efficient Synthesis of Diarylated Dithienofulvalenes**

Aiko Fukazawa, Takashi Karasawa, Hongyu Zhang, Kazumitsu Minemura, Cristopher Camacho, Jian Wang, Stephan Irle,* and Shigehiro Yamaguchi**

Pentafulvalene is a hydrocarbon that possesses two cyclopentadiene rings formally cross-conjugated through an exocyclic double bond.[1] Whereas the parent pentafulvalene is thermally unstable,[2,3] it can be stabilized by ring fusion[3–5] or the introduction of peripheral substituents.[6,7] Pentafulvalene exhibits characteristic redox properties, because it forms a stable radical anion and a dianion with Hückel 6π aromaticity. Utilization of its dianion as a ligand for metal complexes has been extensively studied.[7b,8,9] The other notable feature is its high electron-accepting character, which renders itself being a potent core skeleton for electron-accepting π-conjugated materials, such as n-type semiconducting materials. For example, Wudl and co-workers have recently reported the application of arene-fused pentafulvalene derivatives as an electron-transporting material for organic photovoltaic cell.[10]

From this point of view, the development of a facile and versatile synthetic method of the arene-fused pentafulvalenes is crucial to accelerate this chemistry. Most of the hitherto reported methods are based on the dimerization of cyclopentadiene derivatives, such as diazo compounds,[2,10,11] cyclopentadienone,[5a,c] and thione derivatives.[10] Tobe and co-workers recently reported the Pd-catalyzed domino Heck-type double cyclization of diaryldienynes as an alternative synthetic method of the arene-fused pentafulvalenes.[12] Meanwhile, we have recently reported the photochemical double 5-*exo* cyclization of *o*-arylcarbonyl-substituted diphenylacetylenes, which produced 3,3′-diaryl-1,1′-bi(isobenzofuran)s.[13] This result prompted us to explore the intramolecular cyclization of *o*-alkenyl-substituted diarylacetylenes, which have the olefin moieties in place of the carbonyl double bonds. As shown in Scheme 1, the dehydrogenative intramolecular cyclization may have two possible reaction modes, namely: 1) the double 5-*exo* cyclization that produces a fused pentafulvalene framework; and 2) the double 6-*endo* cyclization that produces a chrysene-type framework. We now report that the photocyclization of dithienylacetylene derivatives as the diarylacetylene precursor exclusively produces a thiophene-fused pentafulvalene framework. This simple and versatile method enables us to produce a series of 3,3′-diarylated dithienopentafulvalenes, which have an attractive electronic diversity toward the application as organic electronic materials.



Scheme 1. Possible cyclization modes in an intramolecular double cyclization of *o*-alkenyl-substituted diarylacetylenes.

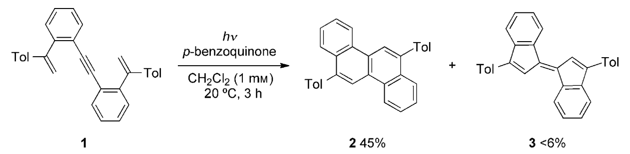
We first conducted a photochemical reaction using bis[*o*-(1-tolylethenyl)phenyl]acetylene **1** as a starting material (Scheme 2). Photoirradiation of **1** using a high-pressure mercury lamp in CH_2Cl_2 (1 mM) for 3 h in the presence of *p*-benzoquinone as an oxidant led to the cyclization producing 6,12-di(*p*-tolyl)chrysene **2** in 45 % yield as a major product. A small amount of the by-product, 3,3′-di(*p*-tolyl)-bi(indenylidene), was also produced through the double 5-*exo* cyclization, the yield of which was less than 6 %. This regioselectivity is consistent with the fact that the intramolecular photocyclization of *o*-vinyl-substituted diphenylacetylene proceeds in a 6-*endo* fashion to produce 2-phenylnaphthalene.[14]

---

[*] Dr. A. Fukazawa, T. Karasawa, Dr. H. Zhang, K. Minemura, Dr. C. Camacho, Dr. J. Wang, Prof. Dr. S. Irle, Prof. Dr. S. Yamaguchi
Department of Chemistry, Graduate School of Science
Nagoya University, Furo, Chikusa, Nagoya 464-8602 (Japan)
E-mail: aiko@chem.nagoya-u.ac.jp
sirle@iar.nagoya-u.ac.jp
yamaguchi@chem.nagoya-u.ac.jp
Homepage: http://orgreact.chem.nagoya-u.ac.jp/en/Home.html
Prof. Dr. S. Yamaguchi
Research Center for Materials Science, Nagoya University
Furo, Chikusa, Nagoya 464-8602 (Japan)
Prof. Dr. S. Irle, Prof. Dr. S. Yamaguchi
Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, and CREST Japan Science and Technology Agency (JST)
Furo, Chikusa, Nagoya 464-8602 (Japan)

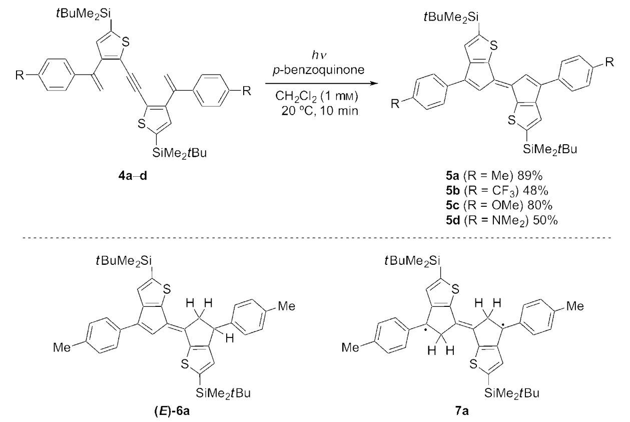
[**] This work was partly supported by Grant-in-Aid (No. 19675001) from MEXT (Japan) (S.Y.), JST, CREST (S.Y. and S.I.), and JST, ACT-C (A.F.). A.F. thanks the Hayashi Memorial Foundation for Female Natural Scientists for financial support. S.I. thanks Prof. Thomas Niehaus (University of Regensburg) for providing the TD-DFTB code.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303738.



Scheme 2. Photochemical double cyclization of bis(*o*-alkenylphenyl)acetylenes (Tol = *p*-methylphenyl).

In stark contrast, when we employed bis[3-(1-tolylethenyl)thienyl]acetylene **4a** as a starting material, the reaction proceeded with a totally different selectivity. Thus, the photocyclization of **4a** was completed within 10 min to afford the thiophene-fused pentafulvalene **5a** in 89 % yield of isolated product (Scheme 3). In this case, the double 5-*exo* product was exclusively obtained and no 6-*endo* product was observed. This high 5-*exo* selectivity for the dithienylacetylene precursor has a generality. The double photocyclization of a series of bis[3-(1-arylethenyl)thienyl]acetylenes with 4-trifluoromethylphenyl (**4b**), 4-methoxyphenyl (**4c**), and 4-dimethylaminophenyl (**4d**) as the aryl groups also smoothly proceeded to give the corresponding dithienopentafulvalene derivatives **5b–d** in moderate to good yields. The high 5-*exo* selectivity renders this photoreaction very attractive and useful. In particular, the fact that the dramatic change in selectivity can be induced by simply replacing the benzene rings with the thiophene rings in the diarylacetylene precursor is worthy of note.

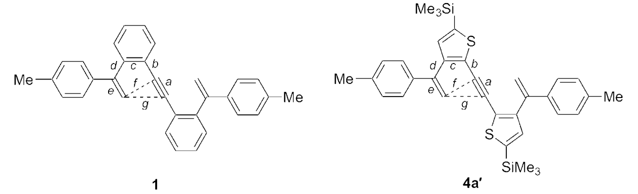


Scheme 3. Photochemical double 5-*exo* cyclization.

To gain insights into the reaction mechanism, we conducted the photoreaction of **4a** in the absence of *p*-benzoquinone as a controlled experiment. The photoirradiation promoted the cyclization and dihydropentafulvalene (*E*)-**6a** was obtained in 83 % yield together with its *Z* isomer in 7 % yield. However, the isolated (*E*)-**6a** remained intact when treated with *p*-benzoquinone in CH_2Cl_2 at room temperature with the protection from light. The photoirradiation to the CH_2Cl_2 solution of (*E*)-**6a** and *p*-benzoquinone for 10 min resulted in a complex mixture, which did not contain dithienopentafulvalene **5a**. These results demonstrate that the dihydropentafulvalene itself is not a reaction intermediate for the formation of dithienopentafulvalene **5** (Supporting Information, Scheme S4). It is most likely produced by the hydrogen shift from a cyclized intermediate, presumably biradical intermediate **7a**.

To elucidate the photo-excited state of the bis(alkenylaryl)acetylene precursors, theoretical calculations of **1** and **4a′** were performed at the B3LYP/def2-SV(P) level of theory using the TURBOMOLE program, where **4a′** is a model compound of bis(3-alkenylthienyl)acetylene **4a** with Me_3Si groups in place of (tBu)Me_2Si groups.[15] Starting from the optimized geometry in the ground state (S_0), the geometry optimization was performed in the lowest excited singlet state (S_1). The optimized geometries in the S_0 and S_1 states are compared in Table 1. Notably, in the S_1 optimized structure for both compounds **1** and **4a′**, the bond length alternation among the bonds *a–e* in the bis(alkenylaryl)acetylene framework becomes smaller compared to that in the S_0 optimized structure. Namely, the photoexcitation from S_0 to the Frank–Condon state in S_1 or higher excited states followed by the structural relaxation produces a cumulenic structure in the S_1 state both for **1** and **4a′**. Several experimental and theoretical studies on the excited-state dynamics of diphenylacetylene derivatives have already indicated that the cumulenic diphenylacetylene in the singlet excited state readily undergoes a structural relaxation to a non-emissive bent geometry with a biradical character.[14b,16] In our reaction, a similar structural relaxation may be responsible for further reactivity toward the double cyclization.

Table 1: Selected bond lengths and interatomic distances in the optimized structures of **1** and **4a′** in the S_0 and S_1 states calculated at the B3LYP/def2-SV(P) level.



Bond [Å]	1 S_0	1 S_1	1 $\Delta(S_1-S_0)$	4a′ S_0	4a′ S_1	4a′ $\Delta(S_1-S_0)$
a	1.220	1.249	+0.029	1.225	1.252	+0.027
b	1.429	1.388	−0.041	1.407	1.368	−0.039
c	1.425	1.466	+0.041	1.401	1.445	+0.044
d	1.495	1.469	−0.026	1.484	1.462	−0.022
e	1.348	1.367	+0.019	1.350	1.364	+0.014
f	3.109	3.008	−0.101	3.121	3.194	+0.073
g	3.653	3.536	−0.117	3.729	3.787	+0.058

Although we calculated the viable biradical intermediates for the double 5-*exo* or 6-*endo* cyclization both in the S_1 and T_1 states of **1** and **4a′**, the 6-*endo* intermediates were always more stable than the 5-*exo* congeners. Therefore, the different selectivity in **1** and **4a** is likely to be due not to the thermodynamic control, but to the kinetic control. In the S_1 optimized geometries, whereas **1** and **4a′** have quite similar cumulenic structures to each other in terms of the lengths of the bonds *a–e*, the nonbonded interatomic distances between the terminal carbon atoms of the alkenyl groups and the acetylene carbon atoms (that is, *f* and *g* in Table 1) were different from each other. The dithienylacetylene **4a′** has longer interatomic distances for both the *f* and *g* than those in the diphenylacetylene **1** (the distance *f* corresponding to the 5-*exo* cyclization: 3.008 and 3.194 Å for **1** and **4a′**; the distance *g* corresponding to the 6-*endo* cyclization: 3.536 and 3.787 Å for **1** and **4a′**, respectively). These differences are due to the different bond angles between the 6-membered-ring benzene and the 5-membered-ring thiophene. These geometric differences in the S_1 state may play a role for producing the selectivity in the photocyclization, although the detailed mechanism remains elusive at this stage.[17]

The highly selective intramolecular cyclization has produced a series of 3,3′-diarylated dithienopentafulvalenes **5a–d** that have several structural advantages and characteristics. First, the thiophene-fused structure not only promises further facile functionalization at the 5-position of the thiophene rings, but also thermodynamically stabilizes the inherently unstable pentafulvalene skeleton. Indeed, no decomposition was observed for all the derivatives **5a–d** even upon heating to 300 °C, contrasting to the fact that the parent pentafulvalene decomposes above −50 °C.[2,3]

Secondly, the aryl groups at the 3,3′-positions effectively extend the π-conjugation of the pentafulvalene framework and impart the electronic diversity. According to the molecular structure of **5b** verified by X-ray crystallography (Figure 1), the 3,3′-diphenyl groups adopt rather a coplanar conformation with the pentafulvalene framework with the dihedral angle of 31.1(5)°.[18] Consequently, the aryl groups at the 3,3′-positions should give a significant perturbation on the electronic structure of the pentafulvalene skeleton.

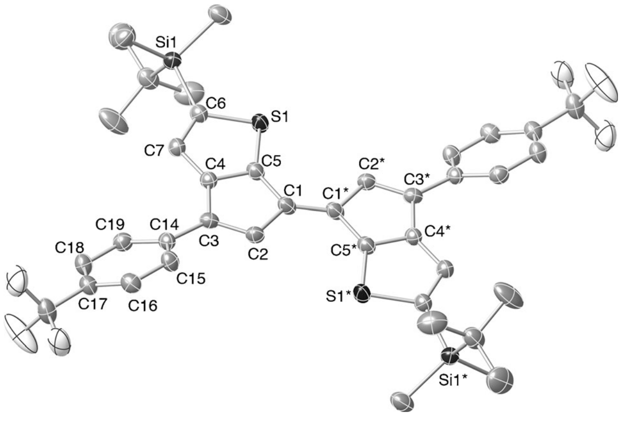


Figure 1. X-ray crystal structure of **5b**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: C1–C1* 1.366(7), C1–C2 1.462(5), C2–C3 1.360(5), C3–C4 1.486(5), C4–C5 1.390(5), C5–S1 1.700(4), S1–C6 1.737(4), C6–C7 1.378(5), C7–C4 1.404(5); C1-C2-C3 110.4(3), C2-C3-C4 108.0(3), C4-C5-C1 109.3(3), C5-C1-C2 104.9(3); C2-C1-C1*-C2* 180, C2-C3-C14-C15 −31.1(5).

The DFT calculations at the B3LYP/6-31G(d) level of theory revealed that the 3,3′-diaryl groups as well as the thiophene-fused structure significantly alter the electronic structure of the pentafulvalene. Figure 2 illustrates the comparison of the Kohn–Sham MOs of the relevant pentafulvalene derivatives. In comparison to the parent pentafulvalene **8**, the thiophene-fused analogue **9** has a higher-lying HOMO by 0.27 eV. This is due to the orbital interaction of the pentafulvalene skeleton with the thiophene moieties as well as the desymmetrization of the pentafulvalene skeleton, which alters the character of the HOMO from a π orbital of pentafulvalene to a delocalized π orbital along the hexatriene skeleton. Moreover, the comparison between **9** and **5a′** (a model compound of **5a**) demonstrates that the introduction of phenyl groups onto the dithienopentafulvalene skeleton results in the effective delocalization of the HOMO. In particular, the electron-donating 4-(*N*,*N*-dimethylamino)phenyl groups in **5d′** (a model compound of **5d**) increase the HOMO level by 0.86 eV. These results imply that the HOMO of this π-conjugated skeleton is significantly influenced by the terminal aryl groups. In contrast, the LUMOs of the aryl-substituted dithienopentafulvalnes **5a′** and **5d′** are almost localized on the central pentafulvalene moiety, reflecting the high electron-accepting character of the pentafulvalene skeleton itself (see below).

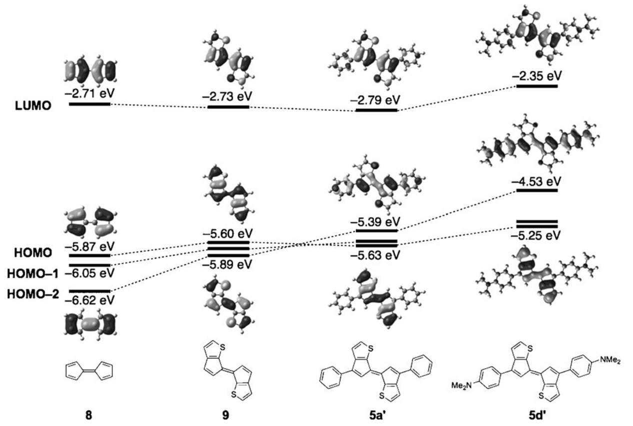


Figure 2. Energy diagrams and pictorial representations of the Kohn–Sham MOs for pentafulvalene **8**, dithienopentafulvalene **9**, and the model compounds of diaryl-substituted dithienopentafulvalenes **5a′** and **5d′**, calculated at the B3LYP/6-31G(d) level.

The characteristic electronic structures of the 3,3′-diarylated dithienopentafulvalenes **5** reflect their electronic spectra. Figure 3 shows the UV/Vis/NIR absorption spectra of **5a–d** in THF. Their data are summarized in Table 2. Compound **5a** exhibited a weak shoulder absorption band around 600 nm in addition to a strong absorption band with the maximum wavelength (λ_{max}) of 479 nm. These wavelengths are red-

Table 2: Absorption Properties of Dithienopentafulvalenes.[a]

Compound	λ_{abs} [nm] ($\varepsilon/10^4$)		
5a	540 (sh)	479 (6.46)	450 (5.05)
5b	550 (sh)	478 (4.84)	449 (3.95)
5c	580 (sh)	487 (5.80)	456 (4.52)
5d	624 (2.07)	524 (4.47)	491 (3.60)
7[b,c]	422 (–[d])	398 (–[d])	378 (–[d])

[a] In THF. [b] Ref. [12b]. [c] A mixture of *E* and *Z* isomers (*E*/*Z* = 95:5). [d] Not reported.

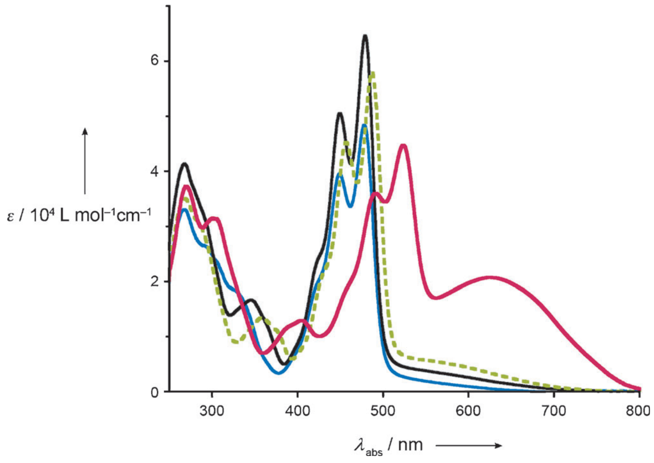


Figure 3. UV/Vis/NIR absorption of **5a–d** in THF: **5a** (R = Me, black solid line); **5b** (R = CF_3, blue solid line); **5c** (R = OMe, green broken line); **5d** (R = NMe_2, red solid line).

shifted by 57 nm compared to the non-substituted **7**.[12b] This absorption spectra is significantly altered by various 3,3′-diaryl substituents in **5b–d**. Thus, the shoulder-like absorption band around 600 nm are red-shifted with an increase in the absorption coefficient, as the aryl group becomes more electron-donating ongoing from CF_3 (**5b**), Me (**5a**), OMe (**5c**), to NMe_2 (**5d**). In particular, the Me_2N-substituted **5d** exhibited an obvious absorption band in the long-wavelength region with the λ_{max} of 624 nm. Thus, the photophysical properties of the diaryl-substituted dithienopentafulvalenes can be modulated to a great extent by the choice of the aryl groups at the 3,3′-positions.

The electrochemical properties of **5a–d** also depend on the electronic effects of the 3,3′-diaryl groups. The cyclic voltammetry (Table 3; Supporting Information, Figure S44) showed that their peak anodic potentials for oxidation significantly decreased as the electron-donating ability of the terminal aryl groups increased (E_{pa} = +1.01 V, +0.73 V, +0.63 V, and +0.06 V vs. Fc/Fc$^+$ for **5b**, **5a**, **5c**, and **5d**, respectively). In particular, the oxidation potential of the Me_2N-substituted **5d** is comparable to that of ferrocene, demonstrating its high electron-donating character.

Table 3: Electrochemical Properties of **5a–d** in CH_2Cl_2.[a]

Compound	Oxidation potential	Reduction potential	
	E_{pa} [V][b]	E_{pc1} [V][b]	E_{pc2} [V][b]
5a	+0.73	−1.41 (−1.36)	−1.85
5b	+1.01	−1.27 (−1.19)	−1.60 (−1.54)
5c	+0.63	−1.46 (−1.39)	−1.91
5d	+0.06	−1.52 (−1.47)	−1.97

[a] Determined by cyclic voltammetry under the following conditions: Sample 1 mM; $Bu_4N^+PF_6^-$ 0.1 M in CH_2Cl_2; scan rate 100 mV s^{-1}. [b] Peak anodic potential (E_{pa}) and peak cathodic potential (E_{pc}) against the ferrocene/ferrocenium couple are given. For reversible processes, the corresponding half redox potentials ($E_{1/2}$) are given in the parentheses.

In contrast, their redox behavior toward a two-electron reduction reflects the highly electron-accepting character of the pentafulvalene skeleton. The cyclic voltammogram of **5a** in CH_2Cl_2 showed reversible first redox waves at $E_{1/2}$ = −1.36 V and a pseudo-reversible second reduction wave with the E_{pc} of −1.85 V (vs. Fc/Fc$^+$). The reduction potentials for **5a–d** are slightly shifted to positive voltages by increasing the electron-withdrawing ability of the 3,3′-diaryl groups ($E_{1/2}$ = −1.47 V, −1.39 V, −1.36 V, and −1.19 V for **5d**, **5c**, **5a**, and **5b**, respectively). As a result, the first reduction potential of the CF_3-substituted **5b** is close to that of fullerene C_{60} ($E_{1/2}$ = −0.92 V vs Fc/Fc$^+$).[19] These results indicate the potential of the dithienopentafulvalene framework as a building unit of n-type semiconducting materials.

In summary, we have developed the new photochemical cyclization of bis(alkenylthienyl)acetylenes as an efficient synthetic method of diaryl-substituted dithienofulvalenes. The incorporation of the fused thiophene rings is effective to thermodynamically stabilize the pentafulvalene skeleton. Furthermore, the diaryl substituents at the 3,3′-positions impart electronic diversity. The great potential of the dithienofulvalene skeleton as a core skeleton for novel organic dyes and electron-transporting materials would increase the usefulness and importance of this new cyclization reaction. Further study on the synthesis of a variety of dithienofulvalene-based materials is now in progress in our laboratory.

Experimental Section

A general procedure for the photocyclization of **4**. 3,3′-Di(*p*-tolyl)-5,5′-bis(*tert*-butyldimethylsilyl)-1,1′-bi(thieno[2,3-*b*]cyclopenta-2,4-dien-1-ylidene) (**5a**): A Pyrex Schlenk flask was charged with **4a** (130 mg, 0.20 mmol), *p*-benzoquinone (43.2 mg, 0.40 mmol), and CH_2Cl_2 (200 mL). This mixture was irradiated with a high-pressure mercury lamp at 20 °C for 10 min. After concentration under reduced pressure, the mixture was subjected to silica gel column chromatography (5:1 hexane/$CHCl_3$, R_f = 0.63) to afford 115 mg of **5a** (0.178 mmol, 89 % yield) as dark brown solids. M.p.: 273.1–274.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.37 (s, 12 H), 0.99 (s, 18 H), 2.43 (s, 6 H), 6.95 (s, 2 H), 7.29–7.31 (m, 6 H), 7.74 ppm (d, J = 8.0 Hz, 4 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = −4.87, 17.04, 21.50, 26.44, 121.51, 126.84, 127.90, 129.50, 132.34, 134.89, 138.85, 142.48, 143.83, 144.89, 151.38 ppm. HRMS (APCI): Calcd. for $C_{40}H_{49}S_2Si_2$: 649.2814 ([M+H]$^+$). Obs.: 649.2787 ([M+H]$^+$).

Received: May 2, 2013
Revised: July 8, 2013

Keywords: cyclization · pentafulvalene · photoreaction · π conjugation · redox properties

[1] a) M. Neuenschwander, *Pure Appl. Chem.* **1986**, *58*, 55–66; b) B. Halton, *Eur. J. Org. Chem.* **2005**, 3391–3414.
[2] W. B. DeMore, H. O. Pritchard, N. Davidson, *J. Am. Chem. Soc.* **1959**, *81*, 5874–5879.
[3] A. Escher, W. Rutsch, M. Neuenschwander, *Helv. Chim. Acta* **1986**, *69*, 1644–1654.
[4] A. Y. Meyer, H. Yinnon, *Tetrahedron* **1972**, *28*, 3915–3928.
[5] Recent examples on thiophene-fused pentafulvalenes: a) K. Loganathan, E. G. Cammisa, B. D. Myron, P. G. Pickup, *Chem. Mater.* **2003**, *15*, 1918–1923; b) K. Loganathan, P. G. Pickup,

Langmuir **2006**, *22*, 10612 – 10618; c) J. Luo, K.-W. Huang, H. Qu, X. Zhang, L. Zhu, H. S. O. Chan, C. Chi, *Org. Lett.* **2010**, *12*, 5660 – 5663.

[6] Perhalogenated pentafulvalenes: a) V. Mark, *Tetrahedron Lett.* **1961**, *2*, 333 – 336; b) V. Mark, *Org. Synth.* **1966**, *46*, 93; V. Mark, *Org. Synth. Coll.* **1973**, *5*, 901 – 903; c) R. West, P. T. Kwitowski, *J. Am. Chem. Soc.* **1968**, *90*, 4697 – 4701; d) H. L. Ammon, G. L. Wheeler, *Tetrahedron* **1973**, *29*, 2695 – 2698.

[7] a) R. Brand, H.-P. Krimmer, H.-J. Linder, V. Sturm, K. Hafner, *Tetrahedron Lett.* **1982**, *23*, 5131 – 5134; b) B. Zhu, O. S. Miljanic, K. P. C. Vollhardt, M. J. West, *Synthesis* **2005**, 3373 – 3379.

[8] M. González-Maupoey, V. Tabernero, T. Cuenca, *Coord. Chem. Rev.* **2009**, *253*, 1854 – 1881, and references therein.

[9] a) B. R. Waldbaum, R. C. Kerber, *Inorg. Chim. Acta* **1999**, *291*, 109 – 126; b) R. Boese, J. K. Cammack, A. J. Matzger, J. Pflug, W. B. Tolman, K. P. C. Vollhardt, T. W. Weidman, *J. Am. Chem. Soc.* **1997**, *119*, 6757 – 6773.

[10] F. G. Brunetti, X. Gong, M. Tong, A. J. Heeger, F. Wudl, *Angew. Chem.* **2010**, *122*, 542 – 546; *Angew. Chem. Int. Ed.* **2010**, *49*, 532 – 536.

[11] P. L. Pauson, B. J. Williams, *J. Chem. Soc.* **1961**, 4153 – 4157.

[12] a) S. M. Abdur Rahman, M. Sonoda, K. Itahashi, Y. Tobe, *Org. Lett.* **2003**, *5*, 3411 – 3414; b) S. M. Abdur Rahman, M. Sonoda, M. Ono, K. Miki, Y. Tobe, *Org. Lett.* **2006**, *8*, 1197 – 1200.

[13] H. Zhang, A. Wakamiya, S. Yamaguchi, *Org. Lett.* **2008**, *10*, 3591 – 3594.

[14] a) P. M. op den Brouw, W. H. Laarhoven, *J. Chem. Soc. Perkin Trans. 2* **1982**, 795 – 799; b) M. C. Sajimon, F. D. Lewis, *Photochem. Photobiol. Sci.* **2005**, *4*, 629 – 636.

[15] R. Ahlrichs, F. Furche, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *TURBOMOLE 5.10*; Cosmologic GmbH & Co. KG.: Leverkusen, Germany, **2008**.

[16] Bent acetylene structures have long been known as a "dark state" in the excited state of diphenylacetylene. See: a) Y. Hirata, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1647 – 1664; b) M. Z. Zgierski, E. C. Lim, *Chem. Phys. Lett.* **2004**, *387*, 352 – 355; c) Y. Amatatsu, M. Hosokawa, *J. Phys. Chem. A* **2004**, *108*, 10238 – 10244.

[17] The quantum chemical calculations suggest that the difference in the flexibility in the S_1 excited state might be partly relevant to the different selectivity in the cyclization of **1** and **4**; see the Supporting Information for details.

[18] For crystal data for **5b**, see the Supporting Information. CCDC 859958 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] P.-M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvares, S. J. Anz, R. L. Whetten, *J. Am. Chem. Soc.* **1991**, *113*, 1050 – 1051.