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# Dihalo-Substituted Dibenzopentalenes: Their Practical Synthesis and Transformation to Dibenzopentalene Derivatives

**Feng Xu, Lifen Peng, Akihiro Orita,* and Junzo Otera***

*Department of Applied Chemistry, Okayama University of Science, Kita-ku,*
*Okayama 700-0005, Japan*

*orita@high.ous.ac.jp; otera@high.ous.ac.jp*

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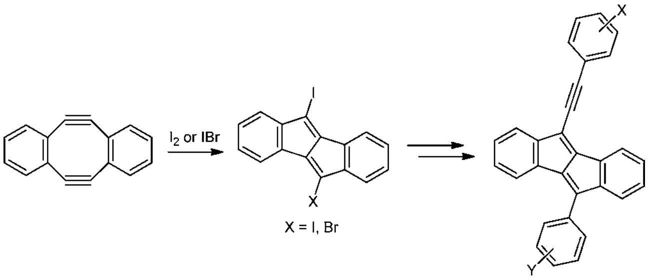
## ABSTRACT



**Diiodo- and bromo, iodo-substituted dibenzopentalenes were obtained by treatment of 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene with $I_2$ and IBr, respectively. These dihalo-substituted pentalenes reacted with terminal ethynes in Sonogashira coupling and with arylboronic acid in Suzuki–Miyaura coupling to give a series of phenylethynyl- and/or aryl-substituted pentalenes. Suzuki–Miyaura coupling of the halopentalenes with in situ prepared pentaleneboronic esters provided bis-, tri-, and tetra(dibenzopentalene)s. It was found that these dibenzopentalene oligomers underwent facile electrochemical reduction and exhibited a bathochromic shift in UV–vis absorption spectra because of their expanded $\pi$-systems.**

Great attention has been paid to polycyclic hydrocarbons which possess expanded $\pi$-conjugation systems such as pentacene and its derivatives[1] because they are promising as field-effect transistor (FET) and electroluminescence (EL) materials.[2] More recently, besides these aromatic compounds, considerable notice has been taken of antiaromatic $\pi$-expanded pentalenes for their potential applications to the organic materials.[3,4] Saito[4a,b] and Yamaguchi[4c] succeeded in synthesis of dibenzopentalenes by reduction of silylethyne with lithium and ketoarylethyne with lithium naphthalenide (LiNaph), respectively.

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[1] For reviews of pentacene, see: (a) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (b) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.

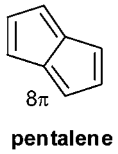
[2] (a) *Functional Organic Materials*; Müller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, 2007. (b) *Organic Light Emitting Devices: Synthesis Properties and Applications*; Mullen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006. (c) *Carbon-Rich Compounds*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006.

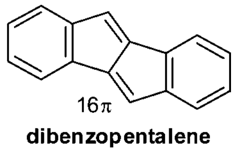
[3] For a recent review of dibenzopentalenes: (a) Saito, M. *Symmetry* **2010**, *2*, 950. For recent examples of $20\pi$ antiaromatic systems: (b) Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11103. (c) Chase, D. T.; Rose, B. D.; McClintock, S. P.; Zakharov, L. N.; Haley, M. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 1127. (d) Shimizu, A.; Tobe, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 6906. For an amino-substituted pentalene: (e) Yin, X.; Li, Y.; Zhu, Y.; Kan, Y.; Li, Y.; Zhu, D. *Org. Lett.* **2011**, *13*, 1520.

[4] (a) Saito, M.; Hashimoto, Y.; Tajima, T.; Ishimura, K.; Nagase, S.; Minoura, M. *Chem.—Asian J.* **2012**, *7*, 480. (b) Saito, M.; Nakamura, M.; Tajima, T. *Chem.—Eur. J.* **2008**, *14*, 6062. (c) Zhang, H.; Karasawa, T.; Yamada, H.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2009**, *11*, 3076. (d) Zerubba, U. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 11012. (e) Zerubba, U. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796. (f) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 7728. (g) Kawase, T.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem.—Eur. J.* **2009**, *15*, 2653. (h) Babu, G.; Orita, A.; Otera, J. *Chem. Lett.* **2008**, *37*, 1296. (i) Willner, I.; Becker, J. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1979**, *101*, 395. (j) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 555. (k) Katsumoto, K.; Kitamura, C.; Kawase, T. *Eur. J. Org. Chem.* **2011**, 4885. (l) Yang, J.; Lakshmikantham, M. V.; Cava, M. P.; Lorcy, D.; Bethelot, J. R. *J. Org. Chem.* **2000**, *65*, 6739.

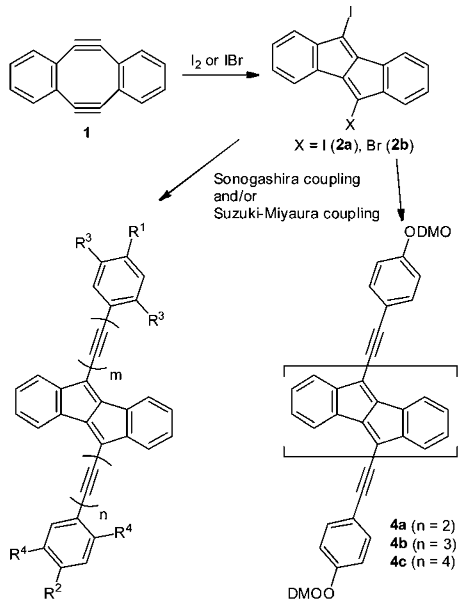
10.1021/ol3017353

Tilley[4d,e] and Kawase[4f,g] reported new methodologies for synthesis of pentalenes taking advantage of transition-metal-catalyzed dimerization of haloarylethynes, and Kawase evaluated their charge mobilities in OFET devices.[4f] We already established the synthesis of dibenzopentalenes by use of a highly strained acetylene 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**)[5] which could be obtained in a practical manner: nucleophilic addition of alkyllithium to **1** followed by transannulation and nucleophilic addition of the resulting pentalenyl anion to electrophiles provided the desired dibenzopentalenes.[4h]





Herein a similar transannulation which is effected by electrophilic dihalogenation ($I_2$ or IBr) to give dihalodibenzopentalenes (Figure 1) is described.[6] We postulated that if **2** could be used in transition-metal-catalyzed C–C bond formation such as in Sonogashira and Suzuki–Miyaura coupling, a new, practical avenue for a variety of $\pi$-expanded dibenzopentalenes **3** and dibenzopentalene oligomers **4** would be developed. We report these synthetic results and several physical properties of the newly prepared dibenzopentalenes such as UV–vis absorption spectra and cyclic voltammetry (CV).

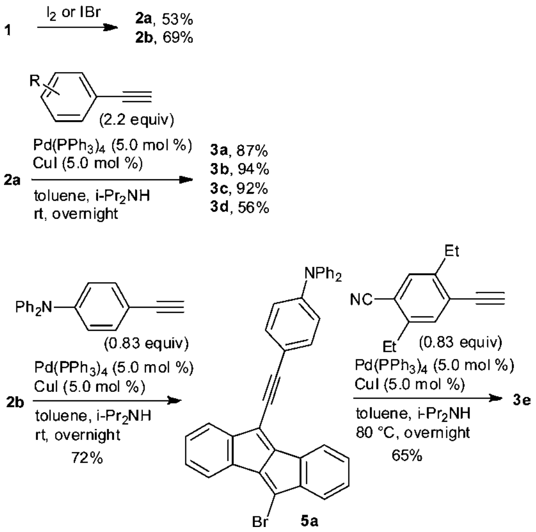


$R^1 = R^2 = R^3 = R^4 = H$, m = n = 1 (**3a**)
$R^1 = R^2$ = DMOO, $R^3 = R^4 = H$, m = n = 1 (**3b**)
$R^1 = R^2 = Ph_2N$, $R^3 = R^4 = H$, m = n = 1 (**3c**)
$R^1 = R^2$ = CN, $R^3 = R^4$ = Et, m = n = 1 (**3d**)
$R^1 = Ph_2N$, $R^2$ = CN, $R^3$ = H, $R^4$ = Et, m = n = 1 (**3e**)
$R^1 = Ph_2N$, $R^2$ = CN, $R^3 = R^4$ = H, m = n = 0 (**3f**)
$R^1 = Ph_2N$, $R^2$ = CN, $R^3 = R^4$ = H, m = 0, n = 1 (**3g**)
$R^1 = Ph_2N$, $R^2$ = CN, $R^3 = R^4$ = H, m = 1, n = 0 (**3h**)
DMOO: (±)-3,7-dimethyloctyloxy

**Figure 1.** Synthetic process for dibenzopentalenes from **2**.

When **1** was treated with $I_2$ (2.0 equiv) in propionitrile at −78 °C to rt and with IBr (1.1 equiv) in $CH_2Cl_2$ at −78 °C, **2a** and **2b** were obtained in 53% and 69% yield, respectively (Scheme 1). Diiodopentalene **2a** and bromo, iodopentalene **2b** were air-stable brown powders which could be purified by column chromatography on silica gel. The halopentalenes **2a** and **2b** served as a coupling component in Sonogashira and Suzuki–Miyaura coupling to provide the corresponding substituted dibenzopentalenes **3**. When **2a** reacted with 2.2 equiv of phenylethyne in the presence of 5.0 mol % of palladium and copper catalysts, C–C bond formation proceeded, and **3a** was obtained in 87% yield as an air-stable dark green powder. By using Sonogashira coupling, dibenzopentalenes bearing an electron-donating and -withdrawing group, **3b**–**d**, were obtained in moderate to good yields as well: 94% for **3b**, 92% for **3c**, and 56% for **3d**, respectively (Scheme 1). It was found that **2b** was a convenient building block for the synthesis of unsymmetrically substituted diethynylpentalene **3e** because Sonogashira coupling of **2b** with aminophenylethyne proceeded selectively at the pentalenyl iodide moiety to afford **5a** in a good yield (Scheme 1). Because the cyano-substituted pentalenes **3d** and **3e** showed poor solubility, it was required to attach ethyl groups on benzene(s) in order to improve the solubility. Subjection of **2b** to Suzuki–Miyaura coupling with 4-(diphenylamino)phenylboronic acid provided **5b**, and subsequent coupling of **5b** with 4-cyanophenylboronic acid and with 4-cyanophenylethyne afforded amino- and cyano-substituted dibenzopentalenes

**Scheme 1.** Syntheses of Dihalodibenzopentalenes **2a,b** and Sonogashira Coupling of **2a,b** with Terminal Ethynes



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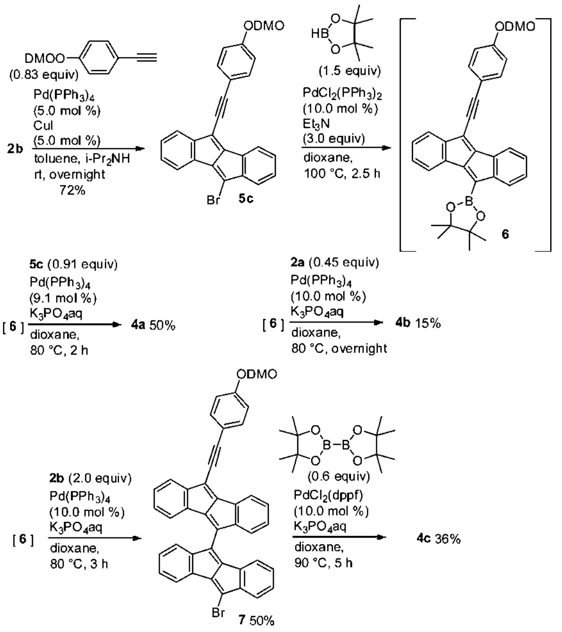
(5) Orita, A.; Hasegawa, D.; Nakano, T.; Otera, J. *Chem.—Eur. J.* **2002**, *8*, 2000.

(6) Synthesis of dibromodibenzopentalene was achieved by bromination of tetrahydrodibenzopentalene followed by dehydrobromination: Cava, M. P.; Pohlke, R.; Mitchell, M. J. *J. Org. Chem.* **1963**, *28*, 1861. Treatment of 5,10-disilyldibenzopentalene with $Br_2$ and $I_2$ afforded dibromo- and diiododibenzopentalenes (**2a**), respectively; see ref 4b.

**3f** and **3g**, respectively (Scheme S1). Coupling of the acetylenic bromide **5a** with 4-cyanophenylboronic acid proceeded smoothly to give **3h** which was a regioisomer of **3g**.

When bromopentalene **5c**, which was prepared by selective coupling of **2b** at the iodide moiety with 3,7-dimethyloctyloxy(DMOO)-substituted phenylethyne, was subjected to one-pot homocoupling, bis(dibenzopentalene) **4a** was successfully obtained in 50% yield (Scheme 2). In this process, boronic ester **6** was prepared and applied to the subsequent Suzuki–Miyaura coupling without purification because of the instability of **6**. Since Suzuki–Miyaura coupling of bromopentalene **5c** afforded bis(dibenzopentalene) **4a** effectively, we applied this protocol to the synthesis of tri- and tetra(dibenzopentalene)s **4b** and **4c** (Scheme 2). In situ preparation of **6** and the subsequent coupling of **6** with **2a** gave **4b** in 15% yield. For preparation of **4c**, the two-step procedure was carried out: Suzuki–Miyaura coupling between **6** and **2b** proceeded selectively at the iodopentalene moiety to give **7** in 50% yield, and the following homocoupling of **7** by treatment with the diborane/$PdCl_2$(dppf) system afforded **4c** in 36% yield. Tri- and tetra(dibenzopentalene)s **4b** and **4c** are black crystalline powders and can be purified by column chromatography followed by reprecipitation.

**Scheme 2.** Syntheses of **4a–c** by Suzuki–Miyaura Coupling



With dibenzopentalenes **3a–h** and **4a–c** in hand, we evaluated their physical properties such as NMR, UV–vis absorption, and cyclic voltammetry. When the $^{13}$C NMR of **3a** was recorded in $CDCl_3$, two sp$^2$ carbons were observed at a particularly low magnetic field, 148.3 and 149.1 ppm. This finding is consistent with simulation results: DFT calculations (B3LYP/6-31G(d)) suggested that two quartenary carbons at the ring junction would be observed at 143.3 and 147.1 ppm.[7] In order to investigate the antiaromaticity of **3a**, the nucleus-independent chemical shift (NICS) calculation was carried out.[8] Calculations at the B3LYP/6-31G(d) level showed that NICS (0) values of the six- and five-membered rings of **3a** were −4.5 and +8.5, respectively. Because negative and positive NICS values indicate the presence of diatropic and paratropic ring currents, respectively, it is demonstrated that the peripheral benzenes are aromatic and five-membered rings are antiaromatic.[9]

UV–vis absorption spectra of **3a–h** and **4a–c** were recorded in $CH_2Cl_2$ (Figures 2a and b), and in Table S1, $\lambda_{max}$ and $\varepsilon_{max}$ were summarized. Dibenzopentalene **3a** exhibited an absorption band at 495 nm ($\varepsilon$ 3.3 × 10$^4$ L mol$^{-1}$ cm$^{-1}$), and the wavelength of $\lambda_{max}$ appeared at a longer wavelength by 31 nm in comparison with that of 9,10-di(phenylethynyl)anthracene (**8**) while the $\varepsilon_{max}$ of **3a** was 1.6 L mol$^{-1}$ cm$^{-1}$ smaller than that of **8**.[7] The larger wavelength of **3a** indicated that the dibenzopentalene motif had a more largely expanded $\pi$-system than anthracene. TD-DFT calculations (LC-BLYP/6-31G(d)) suggested that the 495-nm absorption band of **3a** was attributable to HOMO → LUMO transition ($S_0$–$S_2$ band).[7]

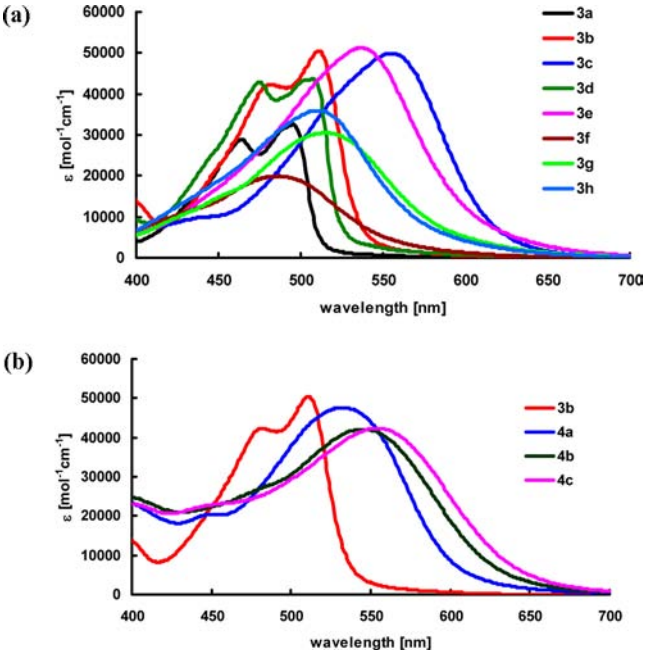


**Figure 2.** (a) UV–vis absorption spectra of **3a–h** in $CH_2Cl_2$; (b) UV–vis absorption spectra of **3b** and **4a–c** in $CH_2Cl_2$.

When electron-donating and/or -withdrawing substituents were attached to ethynylbenzenes of dibenzopentalenes,

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[7] See Supporting Information for details.

[8] Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P.; von, R. *Chem. Rev.* **2005**, *105*, 3842.

[9] Similar NICS (1) values for six- and five-membered rings were reported in refs 4a and 4g: −5.3 and 6.6 ppm (B3LYP/6-31G(d)** for 5,10-bis($H_3Si$)dibenzopentalene), −6.2 and 5.9 ppm (B3LYP/6-31G** for dibenzopentalene).

both bathochromic and hyperchromic shifts of their largest absorption band were observed in **3b**−**e**, and $Ph_2N$ derivative **3c** demonstrated a larger shift: 60 nm red shift in wavelength of $\lambda_{max}$ and $1.7 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ hyperchromic shift in $\varepsilon_{max}$ in comparison with those of **3a**. Aminophenyl- and/or cyanophenyl-substituted pentalenes **3f**−**h** showed a shorter wavelength of $\lambda_{max}$ than amino- and cyanophenylethynylpentalene **3e** indicating that substitution of the pentalene motif with a phenyl group at 5 and 10 positions would be less efficient in the expansion of its $\pi$-system. In DMOO-substituted dibenzopentalenes **3b** and **4a**−**c**, bis(dibenzopentalene) **4a** had an absorption band at 532 nm without a vibronic structure, and a 21 nm (773 cm$^{-1}$) red shift from that of **3b** was observed (Figure 2b). Although **4b** and **4c** showed a similar bathochromic shift upon homologation of the dibenzopentalene subunit, a significant decrease of the shifts was observed: 13 nm (448 cm$^{-1}$) for **4b** relative to **4a**, 9 nm (298 cm$^{-1}$) for **4c** relative to **4b**. DFT calculations which were performed on a simplified model compound, bis(dibenzopentalene) ($C_{16}H_9$−$C_{16}H_9$) **9**, suggested that **9** adopted a 52.5° or 129.7° dihedral angle between dibenzopentalene subunits in the optimized conformers. The simulation result indicated that the HOMOs and LUMOs in **4a**−**c** were expanded through the staggered $\pi$-system conjugation between dibenzopentalene subunits (Figure S1).[10]

Cyclic voltammetry was recorded for **3a**−**h**, **4a**−**c**, and **8** in $CH_2Cl_2$ (Table S1, Figure S2). All of the dibenzopentalenes underwent a smooth reduction and exhibited their half-wave potentials in a range between −0.96 and −1.33 V while reversible oxidation was observed only in $Ph_2N$-derivatives **3c** and **3e**−**h** (Figures S2a,b). Dibenzopentalene **3a** demonstrated a more positive reduction potential in comparison with that of **8** indicating that a dibenzopentalene motif had a deeper LUMO level than anthracene. It was shown that phenylethynyl-substituted dibenzopentalene **3a** underwent facile reduction in comparison with 5,10-bis(triisopropylsilyl)- and dimethyl-dibenzopentalene ($E^{red} = -1.48$ V[4a] and −1.9 V,[4i] respectively) exhibiting that substitution with pheynylethynyl groups expanded the $\pi$-conjugated system efficiently. The reduction potential of 5,10-diaryldibenzopentalene **3f** was more negative than those of **3a**−**h**, which is diagnostic of the inefficient conjugative interaction of the dibenzopentalene motif with phenyl groups. The electron-withdrawing cyano group enabled a facile reduction in **3d** and **3e**. In a series of DMOO-substituted dibenzopentalenes **3b** and **4a**−**c**, the longer oligomer underwent the more facile reduction (Figure S3). This finding indicated that $\pi$-system expansion between dibenzopentalene subunits played a pivotal role to decrease LUMO levels.

In conclusion, we prepared diiodo- and bromo, iododibenzopentalenes by treatment of highly strained cyclic acetylene with $I_2$ and IBr, respectively. These halo-substituted dibenzopentalenes served as building blocks for the synthesis of a series of phenylethynyl- and/or phenyl-substituted dibenzopentalenes and dibenzopentalene oligomers. Investigation of their UV−vis absorption and cyclic voltammetry revealed that their wavelength of $\lambda_{max}$ and reduction potential could be tuned by changing substituents on the 5,10-positions of the dibenzopentalene motif. In dibenzopentalene oligomers, their $\pi$-system was expanded by a conjugative interaction between dibenzopentalene subunits resulting in a bathochromic shift in $\lambda_{max}$ and facile electrochemical reduction. Further development of these halo-substituted dibenzopentalenes to synthesize substituted pentalenes and their application to organic materials such as OFET are under investigation.

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**Supporting Information Available.** Synthetic procedures and characterization data of all new compounds, Scheme S1, Table S1, Figures S1−3, simulation result for NMR and TD-DFT calculations of **3a**, and UV−vis absorption spectrum of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Although the similar bathochromic shift was observed in a series of oligo(9,10-anthrylenes), the red shift was ascribed to the different substitution patterns because anthrylene subunits were orthogonal to each other: Müller, U.; Adam, M.; Müllen, K. *Chem. Ber.* **1994**, *127*, 437.

The authors declare no competing financial interest.