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6,13-Dibromopentacene [2,3:9,10]-Bis(dicarboximide): A Versatile Building Block for Stable Pentacene Derivatives

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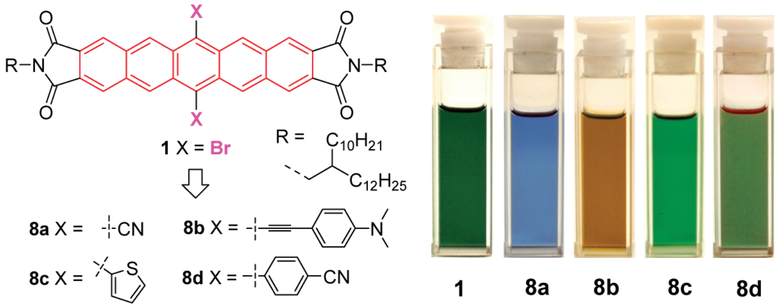

6,13-Dibromopentacene [2,3:9,10]-bis(dicarboximide) (1) was synthesized for the first time by using in situ generated benzo[1,2-*c*:4,5-*c*′]difuran as a key intermediate. Compound 1 exhibits good photostability in comparison to other pentacene derivatives and it can be further functionalized by Pd-catalyzed coupling reactions to give a series of soluble and stable functional pentacenes.

Acenes, linear fused aromatic hydrocarbons, have been the subject of extensive studies due to their potential applications in organic electronics.[1] Pentacene, a benchmark molecule in organic field effect transistors, represents the fourth member of the acene family. Whereas pentacene without any substituent is unstable under ambient condition and insoluble in a variety of organic solvents, chemical modification to introduce substituents has been developed to prepare its stable and soluble derivatives.[2] A typical approach toward most functional pentacene derivatives involves the functionalization of pentacenequinones, i.e., a pentacenequinone is treated with aryl or alkyne lithium or Grignard reagent followed by aromatization of the as-formed diol.[3−5] In addition, other strategies such as the ZnI_2-mediated reaction of pentacene-6,13-diol with thiols followed by oxidative dehydrogenation,[6] Diels−Alder cycloaddition between isobenzofuran derivatives and *p*-benzoquinone, followed by reductive aromatization[7] and zirconocene-mediated cyclization of diynes[8] were also reported.

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(1) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (b) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (c) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.

(2) (a) Li, Y.; Wu, Y.; Liu, P.; Prostran, Z.; Gardner, S.; Ong, B. S. *Chem. Mater.* **2007**, *19*, 418. (b) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980. (c) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138. (d) Bénard, C. P.; Geng, Z.; Heuft, M. A.; VanCrey, K.; Fallis, A. G. *J. Org. Chem.* **2007**, *72*, 7229. (e) Llorente, G. R.; Dufourg-Madec, M.-B.; Crouch, D. J.; Pritchard, R. G.; Ogier, S.; Yeates, S. G. *Chem. Commun.* **2009**, 3059.

(3) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15. (c) Anthony, J. E.; Gierschner, J.; Landis, C. A.; Parkin, S. R.; Sherman, J. B.; Bakus, R. C., II *Chem. Commun.* **2007**, 4746. (d) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.

(4) (a) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274. (b) Lehnherr, D.; Murray, A.; McDonald, R.; Tykwinski, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6190. (c) Lehnherr, D.; McDonald, R.; Tykwinski, R. R. *Org. Lett.* **2008**, *10*, 4163. (d) Lehnherr, D.; Gao, J.; Hegmann, F. A.; Tykwinski, R. R. *Org. Lett.* **2008**, *10*, 4779. (e) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090.

(5) (a) Palayangoda, S. S.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2007**, *72*, 6584. (b) Jiang, J.; Kaafarani, B. R.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 2155.

(6) Kobayashi, K.; Shimaoka, R.; Kawahata, M.; Yamanaka, M.; Yamaguchi, K. *Org. Lett.* **2006**, *8*, 2385.

(7) Rainbolt, J. E.; Miller, G. P. *J. Org. Chem.* **2007**, *72*, 3020.

(8) (a) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-I. *J. Org. Chem.* **2006**, *71*, 7967. (b) Li, S.; Li, Z.; Nakajima, K.; Kanno, K.-I.; Takahashi, T. *Chem. Asian J.* **2009**, *4*, 294.

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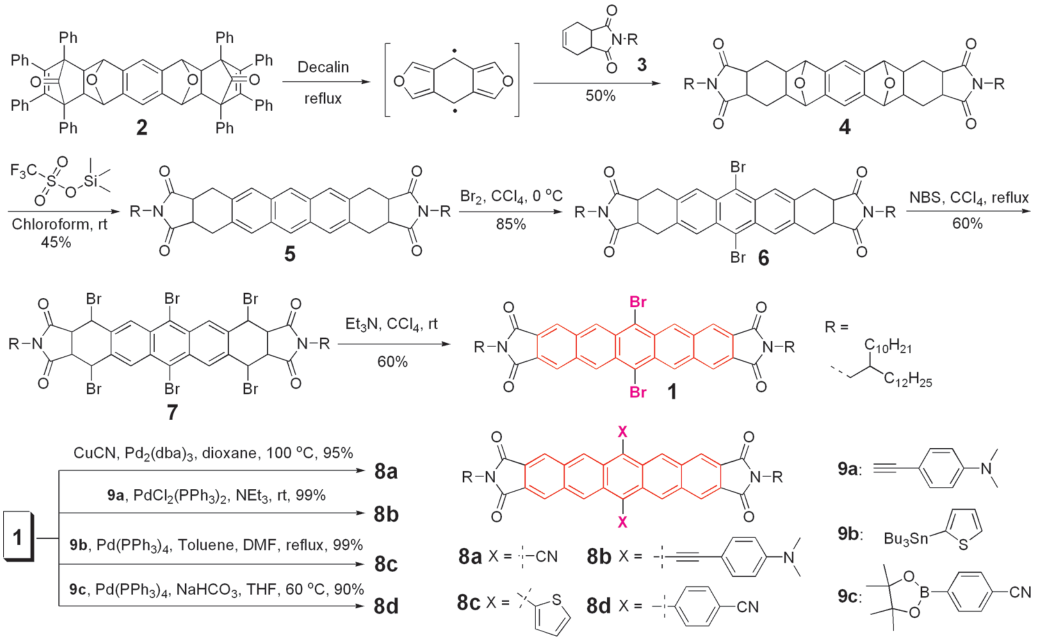
Scheme 1. Synthetic Route of Stable Pentacene Diimides **1** and **8a**−**d**



An ideal pentacene building block for further functionalizations is brominated pentacene with the Br-groups at specific sites, e.g., the *meso*-6,13-positions. However, synthesis of well-defined brominated pentacenes is challenging and direct bromination by using bromine or *N*-bromosuccinimide (NBS) is not feasible due to the high reactivity and poor solubility of pentacene. Dibromo- and tetrabromopentacene derivatives have been reported by several groups and in all cases, the bromine atoms are attached to the first and fifth ring of the pentacene framework.[9] However, dibromopentacenes with the bromine atoms regioselectively located at the *meso*-6,13-positions have never been reported. Another concern is the relatively poor photostability of most of the pentacene derivatives due to their high HOMO energy level. Recent works from our groups and other groups indicate that attachment of electron-withdrawing groups onto the highly reactive higher order acenes and *peri*-fused acenes is an efficient approach to obtain stable materials.[10] Herein, we report the first synthesis of a 6,13-dibromopentacene [2,3:9,10]-bis(dicarboximide) (**1**, Scheme 1), which can be used as a versatile building block for the synthesis of a series of soluble and stable pentacene derivatives by Pd-catalyzed cross-coupling reactions.

A pentacene bis(dicarboximide) analogue of **1** without the dibromo groups was reported by Takahashi et al.[8b] but it tends to dimerize easily. As shown in Scheme 1, our key synthetic strategy toward the pentacene diimide framework is to utilize the Diels−Alder reaction between the reactive benzo[1,2-*c*:4,5-*c*′]difuran intermediate[11] and the dienophile dicarboxylic imide **3** (see the Supporting Information (SI) for synthesis), followed by stepwise aromatization reactions. The dove-tail alkyl chains are introduced to the imide units to provide sufficient solubility for the final products. A retro-Diels−Alder reaction of compound **2**[11] upon heating to 190−200 °C generated benzo-[1,2-*c*:4,5-*c*′]difuran in situ, which then reacted with **3** to give the addition product **4** in 50% yield. Dehydration of **4** with trimethylsilyl triflate in chloroform afforded the anthracene derivative **5** in 45% yield. Bromination of **5** with 2 equiv of Br_2 at 0 °C in the dark selectively provided the desired *meso*-dibromoanthracene compound **6** in 85% yield. Dehydrogenation of **6** by heating together with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or Pd/C failed to give the target compound **1** and most of the starting material was recovered. Alternatively, **6** was brominated with NBS in refluxing CCl_4 and the obtained compound **7** was treated with triethylamine to give the title product **1** in 36% yield for two steps.[12]

The potential of **1** as a useful synthon for various pentacene derivatives was then tested by various Pd-catalyzed coupling reactions (Scheme 1). Pd-catalyzed cyanation of **1** with CuCN in dioxane worked smoothly and the

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(9) (a) Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2007**, *129*, 10308. (b) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163. (c) Zhao, Y. W.; Mondal, R.; Neckers, D. C. *J. Org. Chem.* **2008**, *73*, 5506. (d) Zhao, Y. W.; Cai, X. C.; Danilov, E.; Li, G. F.; Neckers, D. C. *Photochem. Photobiol. Sci.* **2009**, *8*, 34.

(10) (a) Qu, H.; Chi, C. *Org. Lett.* **2010**, *12*, 3360. (b) Yao, J.; Wu, J.; Chi, C.; Loh, K. P. *Chem.*—*Eur. J.* **2009**, *15*, 9299. (c) Li, J.; Zhang, K.; Zhang, X.; Huang, K.; Chi, C.; Wu, J. *J. Org. Chem.* **2010**, *75*, 856. (d) Jiao, C.; Huang, K.; Luo, J.; Zhang, K.; Chi, C.; Wu, J. *Org. Lett.* **2009**, *11*, 4508.

(11) Luo, J.; Hart, H. *J. Org. Chem.* **1988**, *53*, 1341.

(12) (a) Wang, Z.; Kim, C.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 13362. (b) Yin, J.; Qu, H.; Zhang, K.; Luo, J.; Zhang, X.; Chi, C.; Wu, J. *Org. Lett.* **2009**, *11*, 3028.

Table 1. Summary of Photophysical and Electrochemical Properties of Compounds **1** and **8a**−**d**[a]

	λ_{abs} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	E_{ox}^{1} (V)	E_{ox}^{onset} (V)	E_{red}^{1} (V)	E_{red}^{2} (V)	E_{red}^{onset} (V)	HOMO (eV)	LUMO (eV)	E_g^{opt}
1	352, 622	113220	0.76	0.71	−1.17	−1.56	−1.04	−5.51	−3.76	1.93
8a	361, 638	81040	NA	NA	−0.75	−1.28	−0.61	NA	−4.19	1.88
8b	344, 750	78890	0.16	0.11	−1.25	−1.57	−1.15	−4.91	−3.65	1.52
8c	355, 620	107270	0.78	0.65	−1.36	−1.78	−1.27	−5.45	−3.53	1.92
8d	353, 614	93200	0.79	0.70	−1.30	−1.77	−1.21	−5.50	−3.59	1.95

[a] E_{ox}^{n} and E_{red}^{n} are half-wave potentials for respective redox waves with Fc/Fc^{+} as reference. HOMO and LUMO energy levels were calculated from the first oxidation and reduction wave onset according to the equations HOMO = $-(4.8 + E_{ox}^{onset})$ eV and LUMO = $-(4.8 + E_{red}^{onset})$ eV.[14]

6,13-dicyanopentacene dicarboximide **8a** was obtained in 95% yield. The Hagihara−Sonogashira coupling between **1** and 4-dimethylaminophenylacetylene (**9a**) can even be carried out at room temperature and gave **8b** in nearly quantitative yield. Such a high reactivity of C−Br bond in **1** can be attributed to the activation effect by the electron-withdrawing imide groups. Stille coupling reaction between **1** and tributyl(thiophen-2-yl)stannane (**9b**) also afforded the thienyl-substituted pentacene dicarboximide **8c** in nearly quantitative yield. Suzuki coupling reaction of **1** with 4-cyanophenylboronic ester (**9c**) by using the Pd-$(PPh_3)_4$−$NaHCO_3$ system in THF/H_2O successfully gave compound **8d** in 90% yield. However, attempts to introduce vinylene substituents through Heck reaction with styrene have so far been unsuccessful presumably due to the low stability of the final products and decomposition of **1** at high reaction temperature (100 °C). Further optimization of reaction conditions will be carried out in the future.

All the new pentacene bis(dicarboximide)s show good solubility in normal organic solvents due to the attachment of the dove-tail alkyl chains. The solutions of compounds **1** and **8a**−**d** in toluene are all in deep color and the UV−vis absorption spectra are shown in Figure 1a and the data are summarized in Table 1. In comparison to the parent pentacene, which shows absorption maximum at 303 nm (β-band) and 582 nm (p-band) in trichlorobenzene,[13] the 6,13-dibromopentacencene dicarboximide **1** exhibits a similar well-resolved band structure but with significant red-shift of the whole spectrum, for example, the β-band and p-band maxima are now shifted to 352 and 622 nm, respectively. Such bathochromic shift can be explained by intramolecular donor (pentacene)−acceptor (dicarboxylic imide) interactions as observed in many aromatic imides.[10] Compounds **8a**, **8c**, and **8d** show similar vibronic band structures to **1** as they basically hold the same pentacene chromophore. The absorption spectrum of **8a** is red-shifted in comparison to that of **1** because of extended π-conjugation along the cyano groups. The absorption spectra of **8c** and **8d** are just slightly different from that of **1**, indicating that the π-conjugation between the pentacence core and the aryl substituents is relatively weak as usually observed for other pentacenes. The fluorescence spectra of **1**, **8a**, **8c**, and **8d** are quite similar, with the emission at 500−750 nm (see Figure S1 in the Supporting Information (SI)). In contrast, **8b** displays a broad absorption with maximum at 750 nm. Such significant spectral broadening and red-shift can be explained by the strong intramolecular donor−acceptor interactions which narrow the optical energy gap. Compound **8b** shows two emission bands in toluene, one centered at 581 nm and the other located at 811 nm. The latter emission band arises from the intramolecular charge transfer character of **8b**, which is further supported by the positive solvatochromism effect (see Figure S2 and Table S1 in the SI). The fluorescence quantum yields in toluene are determined as 0.2%, 6.0%, 0.8%, 1.3%, and 8.5% for **1** and **8a**−**d**, respectively.

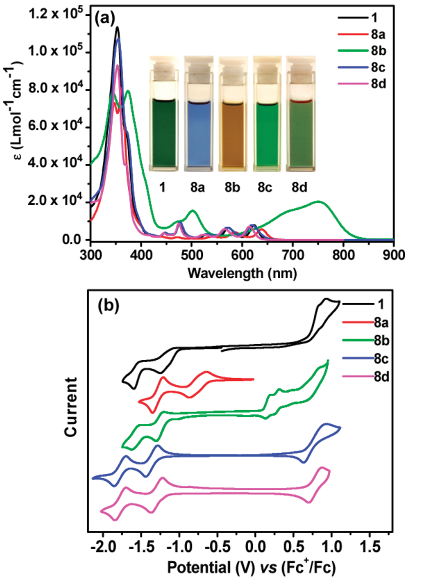

Figure 1. (a) UV−vis−NIR absorption spectra of **1**, **8a**−**d** in toluene. Insert: A picture of the solutions of these compounds in toluene. (b) Cyclic voltammograms of **1** and **8a**−**d** in chlorobenzene with 0.1 M Bu_4NPF_6 as supporting electrolyte, $AgNO_3$/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s.

The electrochemical properties of these new pentacene dicarboximides were studied by cyclic voltommetry in dry chlorobenzene (Figure 1b and Table 1). All of them showed two reversible reduction waves (quasireversible

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(13) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, UK, 1964; Vol. 1, p 425.

(14) Chi, C.; Wegner, G. *Macromol. Rapid Commun.* **2005**, *26*, 1532.

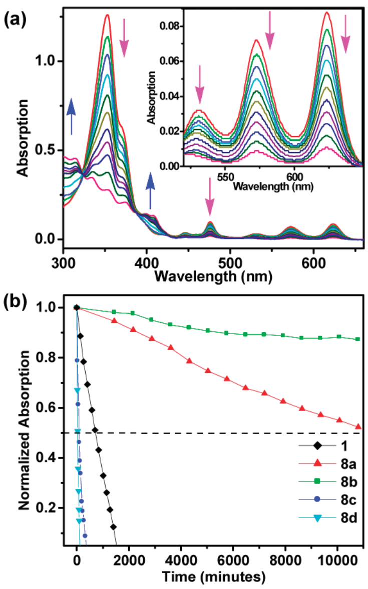

Figure 2. (a) Change of the UV−vis−NIR absorption spectra of **1** in toluene (1×10^{-5} M) with time when exposed to ambient light irradiation; (b) change of the optical density at the corresponding longest wavelength of absorption maximum of **1** and **8a**−**d** as a function of irradiation time at ambient condition.

reduction waves for **1**), indicating that they can be reduced into the corresponding radical anion and dianion, which are stabilized by the delocalized pentacene unit and the electron-withdrawing carboximide groups. For the cyanated compound **8a**, a significantly higher reduction half-wave potential (−0.75 V vs Fc/Fc^+) was observed due to the strong electron-withdrawing character of CN-groups. A very low-lying LUMO level of −4.19 eV was estimated based on the reduction onset, indicating that **8a** could be a good candidate for n-type semiconductors.[14] Due to its high electron affinity, oxidation waves were not observed for **8a** in the available electrochemical window. For **1**, **8c**, and **8d**, one (quasi-)reversible oxidation wave was observed with slightly different half-wave potentials. Accordingly, they have a similar HOMO energy level. Compound **8b** exhibited multiple oxidative waves with the first oxidative half-wave potential negatively shifted due to the existence of electron-donating dimethylamino groups.

The photostability of these pentacene diimides in toluene was investigated under ambient light irradiation and white light (60 W) irradiation in air (Figure 2). For example, upon irradiation with ambient light, the solutions of compound **1** gradually decomposed with a decrease of the optical intensity at the longer wavelength band and the appearance of a new absorption band in the shorter wavelengths (ca. 306 and 410 nm) (Figure 2a). At ambient condition, the half-life times ($t_{1/2}$) of around 700, 11000, 90, and 30 min were estimated for compounds **1**, **8a**, **8c**, and **8d**, respectively, by plotting the absorption intensity at the longest wavelength of absorption maximum with the irradiation time (Figure 2b). The high photostability of **1** and **8a** can be explained by the further stabilization induced by the electron-withdrawing Br- and CN-groups. Interestingly, compound **8b** exhibited extremely high photostability although it owns the highest HOMO energy level. A half-life time ($t_{1/2}$) of nearly one month can be estimated by extrapolation of the degradation curve (Figure 2b)! Such high stability may be related to the intramolecular charge transfer character of **8b** in excited states. For comparison, 6,13-di(triisopropylsilylethynyl)pentacene as one of the most stable pentacene derivatives showed a half-life time of about 9 h under ambient conditions .[4a]

In summary, 6,13-dibromopentacene [2,3:9,10]-bis-(dicarboximide) **1** was successfully synthesized and used as a versatile building block to prepare a series of soluble and stable pentacene derivatives with tunable optical and electronic properties. Our method opens new opportunities to make useful pentacene or even higher order acene-based opto-electronic materials with good stability. Research work on further chemical functionalizations and exploitation of their material applications are underway in our laboratory.

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Supporting Information Available. Synthetic procedures and characterization data of all new compounds, fluorescence spectra, solvatochromism effect of **8b**, and photo-oxidative resistance studies. This material is available free of charge via the Internet at http://pubs.acs.org.