Extended Aromatic Structures | **Hot Paper**

Deutsche Ausgabe: DOI: 10.1002/ange.201603135
Internationale Ausgabe: DOI: 10.1002/anie.201603135

Extended Bis(benzothia)quinodimethanes and Their Dications: From Singlet Diradicaloids to Isoelectronic Structures of Long Acenes

*Shaoqiang Dong, Tun Seng Herng, Tullimilli Y. Gopalakrishna, Hoa Phan, Zheng Long Lim, Pan Hu, Richard D. Webster, Jun Ding, and Chunyan Chi**

***Abstract:** Extended bis(benzothia)quinodimethanes and their dications were synthesized as stable species. The neutral compounds mainly have a quinoidal structure in the ground state but show increased diradical character with extension of the central quinodimethane unit. The dications exhibit similar electronic absorption spectra, NMR spectra, NICS values, and diatropic ring currents to their aromatic all-carbon acene analogues and thus can be regarded as genuine isoelectronic structures of pentacene, hexacene, and heptacene, respectively. Our research gave some insights into the design and synthesis of stable longer acene analogues.*

Acenes and their analogues have attracted tremendous interest owing to their unique physical properties and potential applications in optoelectronics.[1] However, the existence of only one aromatic sextet ring and extended successive *cis*-1,3-butadienes bring along intrinsic instability problems.[2] Common strategies to improve the stability of acenes include introduction of bulky substituents to avoid dimerization[3] or electron-withdrawing groups to lower the HOMO energy levels.[4] Our group recently reported an efficient method by *peri*-annulation of a π-conjugated cyclopenta-ring onto the zigzag edges of acenes.[5] At the same time, we also developed a new strategy to disturb the diene-like conjugation, by fusing two benzothia groups with a *p*-quinodimethane (*p*-QDM) unit to form a quinoidal bis(benzothia)quinodimethane structure (Figure 1).[6] The new quinoidal dithiapentacene analogue exhibited much better chemical stability compared with pentacene. Extension of the central *p*-QDM to 2,6-naphthoquinodimethane (*p*-NQDM) and 2,6-anthraquinodimethane (*p*-AQDM) would give longer hexacene and heptacene analogues. These quionoidal molecules can be regarded as pro-aromatic compounds and have a tendency to be diradicals by recovering aromaticity of the central quinodimethane units (Figure 1) and thus their diradical characters and physical properties are of interest.[7] On the other hand, these molecules have $4n$ π electrons with two more π electrons compared with their respective aromatic acenes. Therefore, oxidation of these neutral dithia compounds by losing two electrons would lead to the corresponding isoelectronic structures of pentacene, hexacene, and heptacene. These charged species are supposed to be stable as demonstrated in many sulfur-containing conjugated molecules.[8] It is worth noting that Bertinger and Einholz have successfully prepared the acene dications containing $4n$ π electrons, which are still stable because two aromatic sextets can be drawn for the dication forms.[9] Neckers and De reported sulfur-containing heptacene analogues,[10] but fundamentally they contain a mix of -cene and -phen type of structures. Our group recently reported two dipolar *p*-QDM containing pentacene and nonacene analogues but they contain more than one aromatic sextet rings and thus exhibit intrinsically different properties from pentacene and nonacene.[11] In our new design, the dicationic molecules have the same number of π electrons to the corresponding acenes and there is only one aromatic sextet ring in the closed-shell resonance forms (Figure 1). Therefore, they can be regarded as the genuine isoelectronic structures of all-carbon acenes. To validate this hypothesis, in this work, three bis(benzothia)-quinodimethane compounds BBB-Pen, BNB-Hex, and BAB-Hep (Figure 1) and their dications were synthesized and their physical properties were investigated both experimentally and theoretically. Bulky mesityl (Mes) groups are strategically introduced to the most reactive sites with high spin density to obtain stable and soluble materials.

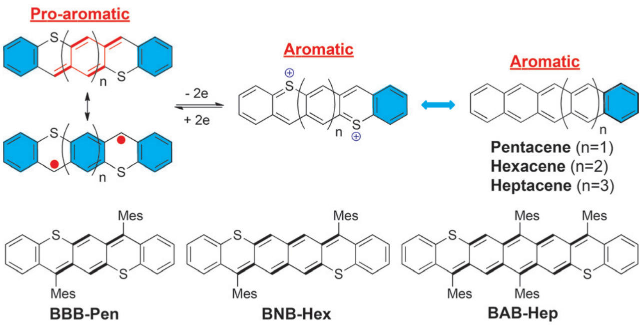


Figure 1. Structures of the bis(benzothia)quinodimethanes, their dications, and their acene analogues. The aromatic sextet ring is shaded in blue.

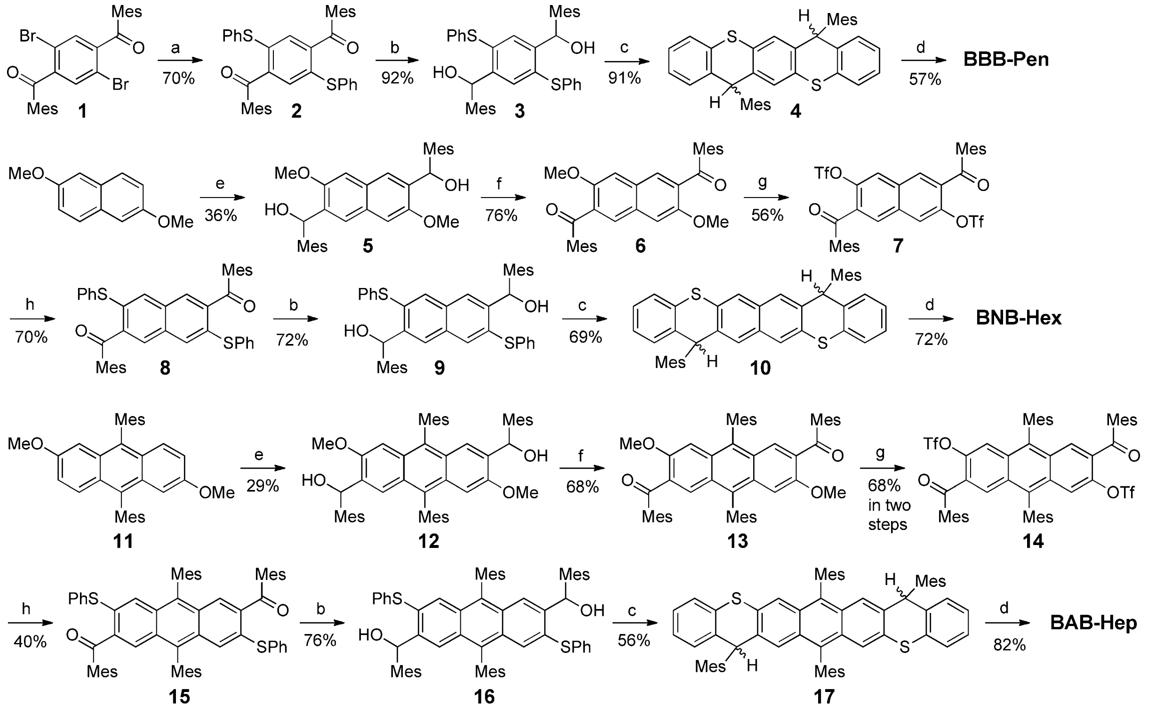
---

[*] Dr. S. Dong, Dr. T. Y. Gopalakrishna, Dr. H. Phan, Z. L. Lim, P. Hu, Prof. C. Chi
Department of Chemistry
National University of Singapore
3 Science Drive 3, 117543, Singapore (Singapore)
E-mail: chmcc@nus.edu.sg

Dr. T. S. Herng, Prof. J. Ding
Department of Materials Science and Engineering
National University of Singapore
119260, Singapore (Singapore)

Prof. R. D. Webster
Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University
21 Nanyang Link, 637371, Singapore (Singapore)

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201603135.



Scheme 1. Synthetic routes of BBB-Pen, BNB-Hex, and BAB-Hep: a) thiophenol, CuI, K_2CO_3, DMF; b) $LiAlH_4$, THF; c) $BF_3\cdot Et_2O$, DCM; d) DDQ, toluene; e) i) *n*-BuLi, THF; ii) mesitaldehyde; f) PCC, DCM; g) i) BBr_3, DCM; ii) Tf_2O, pyridine, DCM; h) thiophenol, $Pd_2(dba)_3$, Xantphos, Cs_2CO_3. Mes = mesityl; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; PCC = pyridinium chlorochromate, DCM = CH_2Cl_2.

The synthesis of these bis(benzothia)quinodimethanes was based on an intramolecular Friedel–Crafts alkylation followed by oxidative dehydrogenation approach and the key intermediates are the thiophenol- and mesitylketone-substituted compounds **2**, **8**, and **15** (Scheme 1). The intermediate **2** was synthesized from compound **1** by direct nucleophilic substitution with thiophenol in the presence of K_2CO_3. Subsequent reduction by $LiAlH_4$ gave diol **3**, $BF_3\cdot Et_2O$ mediated cyclization generated compound **4**, and oxidation by DDQ afforded the target compound BBB-Pen. For the synthesis of BNB-Hex, direct lithiation of 2,6-dimethoxynaphthalene with *n*-BuLi and subsequent quenching with mesitaldehyde gave diol **5**, which was converted to diketone via PCC oxidation. Then, the methoxy groups of **6** were converted into triflic groups by demethylation followed by esterification. The key intermediate **8** was synthesized by Pd catalyzed C–S bond formation reaction, and then BNB-Hex was synthesized via similar steps to BBB-Pen. For the synthesis of BAB-Hep, 9,10-dimesityl-2,6-dimethoxyanthracene **11** was first prepared (see details in the Supporting Information). Following a similar synthetic route to BNB-Hex, the BAB-Hep was obtained.

All three compounds showed clear ^{1}H NMR spectra in C_6D_6 solutions at room temperature and the resonances were assigned by 2D NOESY technique (see Supporting Information). Variable-temperature ^{1}H NMR spectra were recorded in [D$_8$]toluene (Figure S1–S3 in the Supporting Information). No obvious NMR spectral broadening was observed for BBB-Pen even at 95 °C, indicating its closed-shell nature in the ground state and this is consistent with its very small calculated diradical character ($y_0 = 0.004$, at UCAM-B3LYP/6-31G(d,p) level of theory; see Supporting Information for details). However, spectral broadening was observed for both BNB-Hex and BAB-Hep at elevated temperatures and the longer BAB-Hep exhibits much more distinctive change. Similar calculations predict that both BNB-Hex and BAB-Hep have a singlet diradical ground state, with a diradical character of 0.195 and 0.384, respectively. Like all other open-shell singlet diradicaloids,[7] the broadened NMR signal can be ascribed to a thermally populated triplet species. Consistent with the NMR results, BBB-Pen was ESR silent while BNB-Hex and BAB-Hep showed a broad ESR signal in solution with $g_e = 2.0039$ and 2.0032, respectively (Figure S4). The spin concentration was estimated to be 0.04 % for BNB-Hex and 0.98 % for BAB-Hep in DCM solution at room temperature by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as standard (Figure S5),[12] indicating a relatively large singlet–triplet energy gap (ΔE_{S-T}) for both. The temperature dependent magnetic susceptibility measurements of the BAB-Hep powder (5–380 K) by SQUID technique revealed a singlet ground state and fitting of the data by Bleaney–Bowers equation gave a ΔE_{S-T} value of $-5.3\,\mathrm{kcal\,mol^{-1}}$ (Figure S6), which is close to the theoretical value ($\Delta E_{S-T} = -5.5\,\mathrm{kcal\,mol^{-1}}$). However, the signal for the powder of BNB-Hex is too weak for reliable analysis presumably owing to the larger singlet–triplet energy gap ($\Delta E_{S-T} = -7.6\,\mathrm{kcal\,mol^{-1}}$ based on similar calculation). The increase of the diradical character and decrease of single-triplet energy gap with extension of the central quinodimethane unit can be simply explained by the increase of the aromatic resonance energy from benzene to naphthalene and further to anthracene.

X-ray crystallographic analysis of all three compounds further elaborated their ground-state structures (Figure 2).[13] Large bond-length alteration was observed for the central *p*-QDM, *p*-NQDM, and *p*-AQDM units, indicating a major contribution of the quinoidal resonance form to the ground-state geometry in all cases. BBB-Pen and BNB-Hex both have a nearly planar geometry and the latter has a larger C1−C2 bond length, in agreement with its larger diradical character. BAB-Hep in principle should have an even larger C1-C2 bond length but it is actually similar to that of BNB-Hex, presumably a result of its distorted nonplanar structure (deviation from planarity up to 13°). Calculations also show that the nucleus-independent chemical shift (NICS(1)zz) values of the central quinodimethane units gradually change from $\delta = 1.65$ ppm (ring C) in BBB-Pen to $\delta = -9.86$ ppm (ring C) in BNB-Hex and $\delta = -10.24$ ppm (ring C)/ $\delta = -15.85$ ppm (ring D) in BAB-Hep, indicating an increase of aromaticity and diradical character with extension of the molecular length (as a reference, the NICS(1)zz value of benzene ring is calculated to be $\delta = -29.68$ ppm).

BBB-PEN and BNB-Hex in DCM display an intense absorption band at $\lambda_{max} = 555$ and 620 nm, respectively, which is similar to the *p* band of many closed-shell polycyclic aromatic hydrocarbons (PAHs), such as acenes and rylenes (Figure 3).[14] BAB-Hep also exhibits an intense absorption at $\lambda_{max} = 662$ nm, but a shoulder peak at 716 nm was observed. This weak absorption band can be regarded as a signature of open-shell singlet diradicaloids[7c] and it is proposed to be due to the presence of a low-lying double exciton state.[15] BBB-Pen and BNB-Hex exhibit maximum emission at 617 and 689 nm (Figure S8), with a fluorescence quantum yield of 0.13 and 0.10, respectively. No obvious fluorescence was detected for BAB-Hep owing to its larger diradical character. Note that all three compounds exhibit excellent photostability with a half-life time of more than 1 month in DCM under ambient light and air conditions.

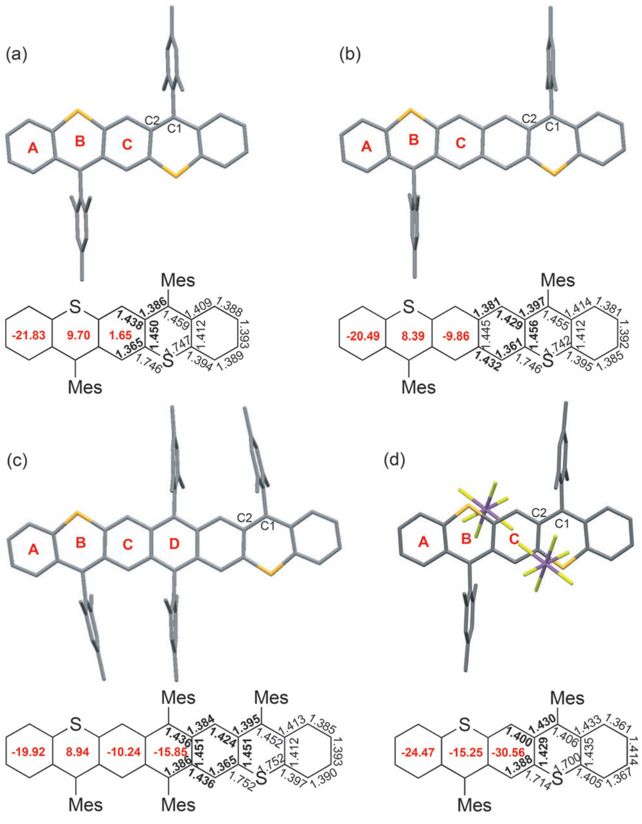


Figure 2. X-ray crystallographic structures, selected bond lengths from single-crystal structures, and calculated NICS(1)zz values (red) of a) BBB-Pen, b) BNB-Hex, c) BAB-Hep, and d) BBB-Pen^{2+}. Hydrogen atoms are omitted for clarity.

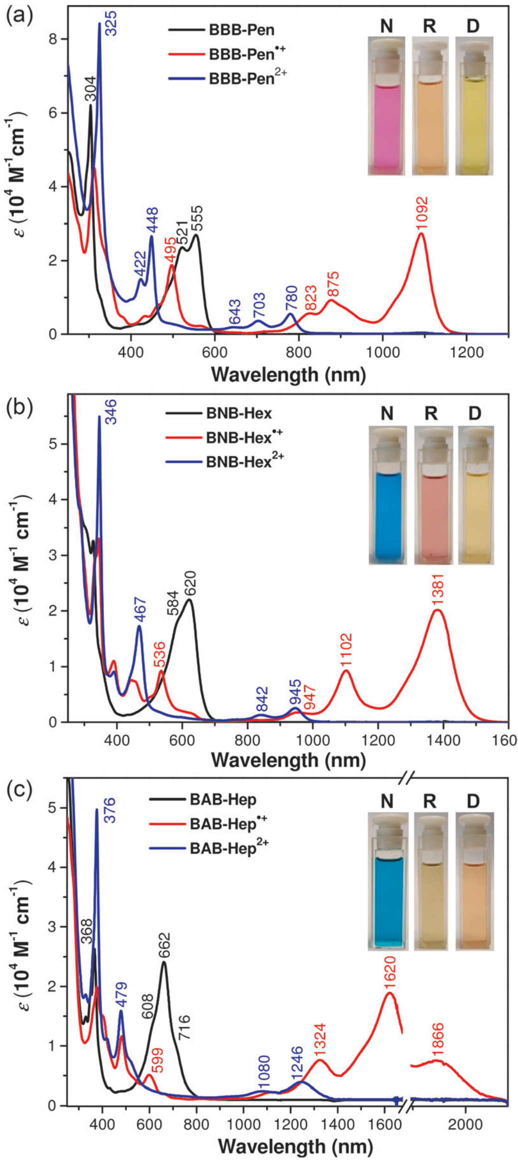


Figure 3. UV/Vis-NIR absorption spectra of the neutral (N), cationic radical (R), and dicationic (D) states of a) BBB-Pen, b) BNB-Hex, and c) BAB-Hep in DCM. Inset: are photos of the solutions.

Electrochemical measurements revealed that all three compounds exhibited two reversible oxidation, with half-wave potential at 0.07, 0.63 V for BBB-Pen, −0.04, 0.44 V for BNB-Hex, and −0.11, 0.31 V for BAB-Hep (vs. Fc$^+$/Fc couple; Fc = $[(\eta\text{-}C_5H_5)_2Fe]$) (Figure S9 and Table S1), indicating that they can be easily oxidized into stable species. Chemical oxidation by one and two equivalent of $NOSbF_6$

gave their corresponding radical cations and dications, which can be reversibly reduced back to neutral compounds via addition of triethylamine. The radical cations show long-wavelength absorption with maximum at 1092 nm for BBB-Pen$^{\cdot+}$, 1381 nm for BNB-Hex$^{\cdot+}$ and 1620 nm for BAB-Hep$^{\cdot+}$ (Figure 3), and intense one-line ESR spectra with $g_e = 2.0042$, 2.0036, and 2.0033, respectively (Figure S10). The dications are all ESR silent and display blue-shifted absorption compared to the respective radical cations, with λ_{max} at 780 nm for BBB-Pen^{2+}, 945 nm for BNB-Hex^{2+} and 1246 nm for BAB-Hep^{2+} in long wavelength absorption band (Figure 3). Interestingly, the band structures of the absorption spectra of the dications are very similar to their corresponding trialkylsilylethynyl-substituted pentacene ($\lambda_{max} = 642$ nm), hexacene ($\lambda_{max} = 738$ nm), and heptacene ($\lambda_{max} = 852$ nm), indicating that they have similar electronic structures.[3a,b,14b]

^{1}H NMR spectra of the three dications were recorded in [D$_2$]dichloromethane solution via in situ oxidation by two-fold NOSbF$_6$ (Figure 4 and Figure S11). Largely downfield shifted resonances were observed for all three dications, indicating the formation of aromatic compounds. NICS(1)zz value calculations also support this conclusion, as large negative values were calculated for all the dithiapentacene framework (Figure 2d). In addition, anisotropy of the induced current-density (AICD) plots of the dications clearly show clockwise ring currents delocalized along the periphery (Figure 4), which is similar to the corresponding acenes (Figure S14–16). However, for the neutral quinoidal compounds, the clockwise ring currents are mainly localized on the lateral benzene rings.

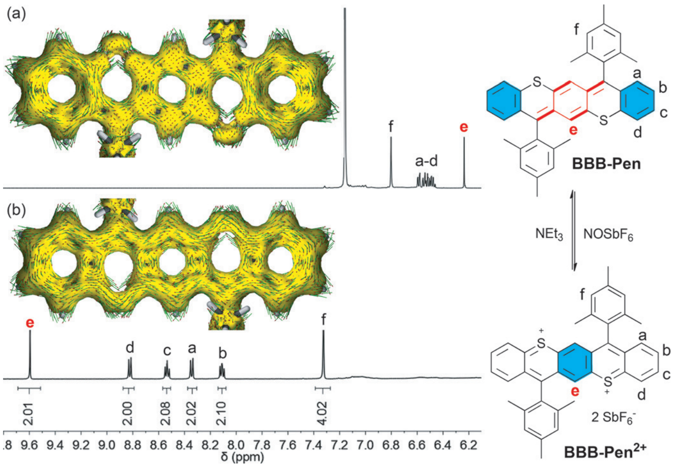


Figure 4. ^{1}H NMR spectra of a) neutral BBB-Pen and b) its dication in the aromatic region. Insets: the corresponding AICD plots and the external magnetic field is applied orthogonal to the plane.

Single crystals of the dication BBB-Pen^{2+} suitable for X-ray crystallographic analysis were successfully obtained (Figure 2d),[16] while the longer dications degraded during the growing process. A clear decrease of the bond length of the two C–S bonds (1.700, 1.714 Å) was observed compared with the neutral BBB-Pen (1.746, 1.747 Å), indicating their partial double-bond character. In addition, the bond-length alternation of the original *p*-QDM unit now becomes much smaller. This result again indicates that the dication indeed has an acene-like structure. Calculations also show that all the dications have negligible diradical characters (Table S2).

In summary, we have successfully synthesized three stable bis(benzothia)-fused quinodimethanes and demonstrated their chain-length dependent diradical character and physical properties. More importantly, their dications can be regarded as the genuine isoelectronic structures of acenes up to heptacene, which was well elaborated by experimental evidence (NMR, electronic absorption spectrum, X-ray crystallographic analysis) and theoretical calculations (NICS value and AICD plot). Our study provides a new way to design and synthesize stable longer acene analogues with similar electronic structures to the traditional all-carbon acenes.

Acknowledgements

C.C. acknowledges financial support from the MOE Tier 1 grant (R-143-000-623-112), Tier 2 grant (MOE2014-T2-1-080) and Tier 3 programme (MOE2014-T3-1-004). We thank Dr. Bruno Donnadieu and Dr. Tan Geok Kheng for the crystallographic analysis.

Keywords: acenes · aromaticity · dications · diradicals · heteroacenes

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9316–9320
Angew. Chem. **2016**, *128*, 9462–9466

---

[1] a) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891; b) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028; c) J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452; *Angew. Chem.* **2008**, *120*, 460; d) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857; e) K. Takimiya, I. Osaka, T. Mori, M. Nakano, *Acc. Chem. Res.* **2014**, *47*, 1493; f) U. H. F. Bunz, J. U. Engelhart, B. D. Lindner, M. Schaffroth, *Angew. Chem. Int. Ed.* **2013**, *52*, 3810; *Angew. Chem.* **2013**, *125*, 3898; g) Q. Miao, *Adv. Mater.* **2014**, *26*, 5541; h) U. H. F. Bunz, *Acc. Chem. Res.* **2015**, *48*, 1676.

[2] a) M. M. Payne, S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2004**, *6*, 3325; b) B. Purushothaman, M. Bruzek, S. R. Parkin, A. F. Miller, J. E. Anthony, *Angew. Chem. Int. Ed.* **2011**, *50*, 7013; *Angew. Chem.* **2011**, *123*, 7151; c) W. Fudickar, T. Linker, *J. Am. Chem. Soc.* **2012**, *134*, 15071; d) J. U. Engelhart, O. Tverskoy, U. H. F. Bunz, *J. Am. Chem. Soc.* **2014**, *136*, 15166.

[3] a) J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, *4*, 15; b) M. M. Payne, S. R. Parkin, J. E. Anthony, *J. Am. Chem. Soc.* **2005**, *127*, 8028; c) D. Chun, Y. Cheng, F, Wudl, *Angew. Chem. Int. Ed.* **2008**, *47*, 8380; *Angew. Chem.* **2008**, *120*, 8508; d) H. Qu, C. Chi, *Org. Lett.* **2010**, *12*, 3360.

[4] a) Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato, S. Tokito, *J. Am. Chem. Soc.* **2004**, *126*, 8138; b) H. Qu, W. B. Cui, J. Li, J. Shao, C. Chi, *Org. Lett.* **2011**, *13*, 924; c) S. Katsuta, D. Miyagi, H. Yamada, T. Okujima, S. Mori, K. I. Nakayama, H. Uno, *Org. Lett.* **2011**, *13*, 1454; d) S. Katsuta, K. Tanaka, Y. Maruya, S. Mori, S. Masuo, T. Okujima, H. Uno, K. I. Nakayama, H. Yamada, *Chem. Commun.* **2011**, *47*, 10112.

[5] a) A. N. Lakshminarayana, J. Chang, J. Luo, B. Zheng, K.-W. Huang, C. Chi, *Chem. Commun.* **2015**, *51*, 3604; b) G. Dai, J. Chang, J. Luo, S. Dong, N. Aratani, B. Zheng, K. Huang, H.

Yamada, C. Chi, *Angew. Chem. Int. Ed.* **2016**, *55*, 2693; *Angew. Chem.* **2016**, *128*, 2743.

[6] Q. Ye, J. Chang, X. Shi, G. Dai, W. Zhang, K.-W. Huang, C. Chi, *Org. Lett.* **2014**, *16*, 3966.

[7] a) Z. Sun, Z. Zeng, J. Wu, *Acc. Chem. Res.* **2014**, *47*, 2582; b) T. Kubo, *Chem. Rec.* **2015**, *15*, 218; c) Z. Zeng, X. Shi, C. Chi, J. T. L. Navarrete, J. Casado, J. Wu, *Chem. Soc. Rev.* **2015**, *44*, 6578; d) T. Kubo, *Chem. Lett.* **2015**, *44*, 111.

[8] a) K. Asmus, *Acc. Chem. Res.* **1979**, *12*, 436; b) C. Rovira, J. Veciana, N. Santaló, J. Tarrés, J. Cirujeda, E. Molins, J. Llorca, E. Espinosa, *J. Org. Chem.* **1994**, *59*, 3307; c) V. Coropceanu, O. Kwon, B. Wex, B. R. Kaafarani, N. E. Gruhn, J. C. Durivage, D. C. Neckers, J. Brédas, *Chem. Eur. J.* **2006**, *12*, 2073; d) T. Nishinaga, A. Wakamiya, D. Yamazaki, K. Komatsu, *J. Am. Chem. Soc.* **2012**, *134*, 3163; e) C. E. Smith, S. O. Odoh, S. Ghosh, L. Gagliardi, C. J. Cramer, C. D. Frisbie, *J. Am. Chem. Soc.* **2015**, *137*, 15732.

[9] R. Einholz, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2013**, *52*, 9818; *Angew. Chem.* **2013**, *125*, 10000.

[10] P. K. De, D. C. Neckers, *Org. Lett.* **2012**, *14*, 78.

[11] X. Shi, W. Kueh, B. Zheng, K.-W. Huang, C. Chi, *Angew. Chem. Int. Ed.* **2015**, *54*, 14412; *Angew. Chem.* **2015**, *127*, 14620.

[12] Y. Zheng, M. Miao, G. Dantelle, N. D. Eisenmenger, G. Wu, I. Yavuz, M. L. Chabinyc, K. N. Houk, F. Wudl, *Adv. Mater.* **2015**, *27*, 1718.

[13] CCDC no. for BBB-Pen, BNB-Hex, and BAB-Hep are 1463884, 1463885 and 1463883, respectively.

[14] a) T. Weil, T. Vosch, J. Hofkens, K. Peneva, K. Müllen, *Angew. Chem. Int. Ed.* **2010**, *49*, 9068; *Angew. Chem.* **2010**, *122*, 9252; b) J. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452; *Angew. Chem.* **2008**, *120*, 460.

[15] S. D. Motta, F. Negri, D. Fazzi, C. Castiglioni, E. V. Canesi, *J. Phys. Chem. Lett.* **2010**, *1*, 3334.

[16] CCDC no. for BBB-Pen^{2+} is 1468505. When crystal growth was conducted under ambient condition, the radical cation BBB-Pen$^{\cdot+}$ was obtained. See crystallographic structure (CCDC no. 1468894) (Figure S17 and Table S6).

Received: March 30, 2016