

Electron Delocalization in Reduced Forms of 2-(BMe₂)pyrene and 2,7-Bis(BMe₂)pyrene

Lei Ji,[†] Robert M. Edkins,[†] Andreas Lorbach,[†] Ivo Krummenacher,[†] Charlotte Brückner,[‡] Antonius Eichhorn,[†] Holger Braunschweig,[†] Bernd Engels,[‡] Paul J. Low,[§] and Todd B. Marder^{*,†}

[†]Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[‡]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Straße 42, 97074 Würzburg, Germany

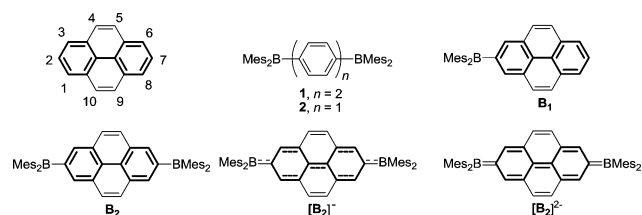
[§]School of Chemistry and Biochemistry, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

Supporting Information

ABSTRACT: Reduction of 2-(BMe₂)pyrene (**B**₁) and 2,7-bis(BMe₂)pyrene (**B**₂) gives rise to anions with extensive delocalization over the pyrenylene bridge and between the boron centers at the 2- and 2,7-positions, the typically unconjugated sites in the pyrene framework. One-electron reduction of **B**₂ gives a radical anion with a centrosymmetric semiquinoidal structure, while two-electron reduction produces a quinoidal singlet dianion with biradicaloid character and a relatively large S₀–T₁ gap. These results have been confirmed by cyclic voltammetry, X-ray crystallography, DFT/CASSCF calculations, NMR, EPR, and UV–vis–NIR spectroscopy.

The design and synthesis of organic open-shell biradicals¹ have attracted much interest because of potential applications in materials science, e.g., energy storage, two-photon absorption, spintronics, and field-effect transistors.² Pyrene derivatives have numerous applications in organic electronics. Most reported pyrene derivatives have been limited to substitution at the 1-, 3-, 6-, and 8-positions (Chart 1), with

Chart 1. Structures of Pyrene, 1, 2, B₁, B₂, [B₂]^{•−}, and [B₂]^{2−}^a



^aThe biphenyl unit of pyrene according to Clar's aromatic π -sextet rule¹² is indicated in bold.

substitution at the 2- and 7-positions being considerably rarer.³ It is difficult to functionalize the 2- and 7-positions of pyrene directly, as these sites are situated on two nodal planes in both the HOMO and LUMO, i.e., those in and perpendicular to the molecular plane.⁴ However, substituents at the 2-position affect the photophysical properties differently than those at the 1-position, leading to differences in the energies and intensities of their lowest-energy transitions and their radiative lifetimes.⁵

The usually poor conjugation to substituents at the 2- and 7-positions of pyrene offers the possibility to form biradicals by the introduction of suitable spin-carrying substituents at these sites.⁶ Müllen studied the dianions of 2,2'-bipyrenyl and 2,2':7',2''-terpyrenyl, which have biradical character with a small S₀–T₁ transition energy.^{6a} Complete active space (CAS[10,10]) calculations by Baumgarten showed that the 2-(anthracen-9-yl)pyrene dianion has a triplet ground state with a small S–T gap of 0.3 kcal mol^{−1} and a spin density distribution similar to the sum of those for the monoradical anions of pyrene and anthracene.^{6b} Pyrenes with two nitroxide-based radical moieties at the 2,7-positions are singlet biradicals with small S–T gaps,^{6d–f} but the spin-carrying atoms are not directly connected to pyrene. Pyrene derivatives with pronounced quinoidal structures have been postulated⁷ but not yet confirmed.

Three-coordinate boron compounds have found use in various organic electronic materials because the empty p orbital of the boron center makes it a very strong electron acceptor⁸ and spin carrier.⁹ Kaim showed that when compounds containing two boron centers separated by a π -conjugated bridge, such as 1,4-phenylene or 4,4'-biphenylene,¹⁰ are reduced by one electron, class-III mixed-valence species result.¹¹

While the LUMO of most 2- and 2,7-substituted pyrene derivatives has no contribution at the 2-position, the LUMO of the BMe₂ derivative **B**₁ (Mes = 2,4,6-Me₃-C₆H₂) (Chart 1) is constructed by mixing the B_{3u} LUMO+1 of pyrene with the empty p orbital of the boron atom of the BMe₂ fragment, giving rise to a large coefficient at the pyrene 2-position (Figure 1).⁵ Thus, while the LUMO of pyrene is little-affected by the substituent at the 2-position, mixing of its LUMO+1 with boron leads to a switch in the order of the pyrene-like virtual orbitals. DFT calculations show that the LUMO of 2,7-bis(BMe₂)pyrene (**B**₂), which has large coefficients at the 2,7-positions, is distributed over the two boron centers and the whole pyrenylene bridge (Figure 1). Thus, the reduced products of **B**₁ and **B**₂ may be predicted to display extensive delocalization over the pyrene core and the boron center(s). Our combined experimental and theoretical confirmation of this hypothesis is reported herein.

The cyclic voltammograms of **B**₁ and **B**₂ were recorded in THF (Figure 2). The first reduction process of **B**₁ at E_{1/2} = −2.39 V vs Fc/Fc⁺ is reversible and corresponds to formation of the

Received: April 13, 2015

Published: May 7, 2015

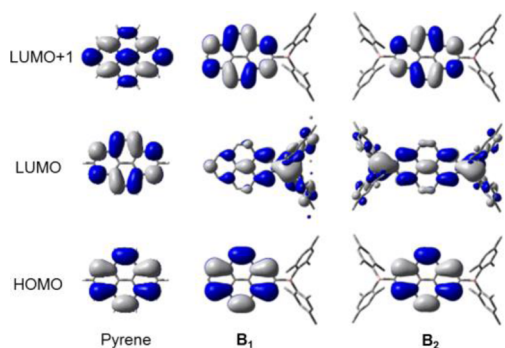


Figure 1. Key orbitals of pyrene, **B**₁, and **B**₂ at their DFT (B3LYP/6-31G*)-optimized geometries.

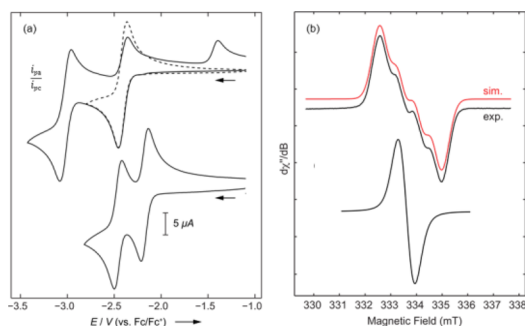


Figure 2. (a) Cyclic voltammograms of (top) **B**₁ and (bottom) **B**₂. The dashed line shows the response upon one-electron reduction (cf. Figures S7 and S8 in the SI). (b) Experimental (black) and simulated (red) continuous-wave X-band EPR spectra of (top) [**B**₁]⁻ and (bottom) [**B**₂]⁻ in THF solution at room temperature.

radical anion, with a reduction potential comparable to that of PhBMes₂ (-2.30 V vs Fc/Fc⁺ in DMF).^{10c} The second reduction wave is ascribed to a pyrene-localized reduction. **B**₂ shows two reversible one-electron reductions at $E_{1/2} = -2.17$ and -2.45 V vs Fc/Fc⁺. The first reduction potential of **B**₂ is 0.22 V more positive than that of **B**₁, indicating that the introduction of the second BMes₂ group stabilizes the LUMO. The separation of the first and second reduction waves ($\Delta E = 0.28$ V) is comparable to that of 4,4'-bis(BMes₂)-1,1'-biphenyl (**1**) ($\Delta E = 0.25$ V),^{10c} suggesting charge delocalization in the one-electron-reduced species¹³ and rendering the monoradical anion stable with respect to disproportionation (comproportionation constant $\approx 5.6 \times 10^4$) and therefore a potential synthetic target.

In order to develop a methodology for the preparation of such mixed-valence anions, we initially focused on the reduction of the well-studied compound **2**^{8a,10} (Chart 1) and were able to isolate and determine the crystal structure of its K⁺ salt (K⁺ = [K(18-crown-6)(THF)₂]⁺; see the Supporting Information (SI)). Encouraged by this, we sought to isolate and characterize the monoanions of **B**₁ and **B**₂ and the dianion of **B**₂. **B**₁K₁ and **B**₂K₁ were synthesized by addition of K⁺ anthracene to THF solutions of **B**₁ and **B**₂, respectively. **B**₂Li₂ (Li⁺ = [Li(THF)₄]⁺) was prepared by reduction of **B**₂ with excess lithium naphthalenide.

B₁K₁ has an EPR hyperfine coupling constant ($g_{\text{iso}} = 2.003$, $a(^{11}\text{B}) = 6.5$ G) that is smaller than those of other triarylborane radical anions, e.g., [BMes₃]⁻ (9.87–10.3 G) and [BPh₃]⁻ (7.84 G),¹⁴ indicating considerable spin delocalization into the pyrene unit in [**B**₁]⁻. In contrast, the EPR spectrum of **B**₂K₁ shows no hyperfine splitting ($g_{\text{iso}} = 2.003$, half width at half-maximum

(HWHM) = 3 G). The absence of resolved hyperfine coupling is likely due to the many different couplings arising from a highly delocalized structure in which the spin density of the unpaired electron is distributed over the pyrene and BMes₂ units.^{10f} The doubly reduced compound **B**₂Li₂ is EPR-silent in solution at room temperature, indicative of a singlet state. The ¹¹B NMR signal of **B**₂Li₂ ($\delta = 38$ ppm) is shifted to significantly higher field than that of **B**₂ ($\delta_{\text{iso}} = 75$ ppm, solid state) because of the higher electron density on the boron centers after reduction. While the ¹H NMR signals of the mesityl protons of **B**₂Li₂ ($\delta = 6.42$ (8H), 2.12 (24H), 2.04 (12H) ppm) are similar to those of **B**₂, those of the pyrene protons are shifted significantly to higher field ($\delta = 4.33$ (4H), 4.20 (4H) ppm). This upfield shift, while smaller than that of pyrene dianion¹⁵ from neutral pyrene, still signifies considerable electron delocalization onto the pyrene unit. There is no line broadening in either the ¹H or ¹³C{¹H} NMR spectrum, confirming that T₁ is not thermally accessible in solution up to 40 °C.

In the X-ray structures of the neutral compounds **B**₁ and **B**₂ (Figure 3 and Table S3 in the SI), the B–C bond lengths *a* and *b*

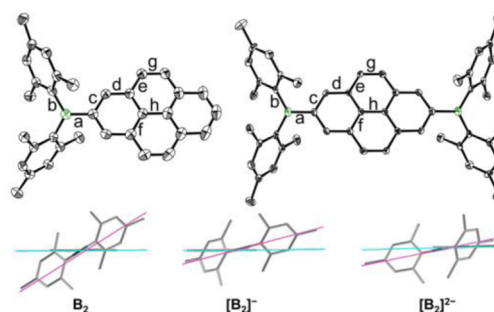


Figure 3. (top) X-ray structures of (left) **B**₁ and (right) **B**₂ (C, black; B, green; H atoms omitted for clarity). (bottom) Side views of the twist between the BC₃ (magenta) and pyrene (cyan) planes in the structures of **B**₂, [**B**₂]⁻, and [**B**₂]²⁻ (one BMes₂ group omitted for clarity).

are similar. While the biphenyl unit (Chart 1) has typical aromatic C–C bond lengths (bonds *c*, *d*, and *f*), bond *g* (**B**₁, 1.353(3); **B**₂, 1.354(5) Å) is more typical of a C=C double bond, indicating that the structure of pyrene obeys Clar's sextet rule,¹² i.e., it can be viewed as a biphenyl unit constrained to be planar by two –CH=CH– groups.

The X-ray structure of **B**₁K₁ reveals electron delocalization between the boron center and pyrene, including shortening of the B–C(pyrene) bond by 0.049 Å relative to **B**₁, a decreased dihedral angle between the pyrene and BC₃ planes (8.7(1)° vs 36.32(6)° in **B**₁), and changes in the C–C bond lengths of the ring directly bonded to the BMes₂ group (bonds *c*, *d*, and *f*). DFT (UB3LYP/6-31G*) optimization of [**B**₁]⁻ also shows delocalization of the excess electron, with the spin density distributed between the pyrene (40%) and BMes₂ (60%) groups.

The fact that in **B**₂K₁ the anion is located on a crystallographic inversion center without disorder (see the SI), the significant reduction of the angle α between the BC₃ and pyrene planes from 31.7(1)° in **B**₂ to 14.2(1)° in [**B**₂]⁻, and the observed bond-length alternation (BLA) of the biphenyl unit (0.033 Å), testifying to a semiquinoidal structure, indicate strong conjugation between the boron centers and the pyrenylene bridge. The spatial distribution of the α highest occupied spin orbital (α -HOSO) of [**B**₂]⁻ is similar to that of the LUMO of **B**₂, i.e., there is significant delocalization of the excess electron across the whole molecule.

In the X-ray structure of B_2Li_2 , the $[B_2]^{2-}$ anion lies on a crystallographic inversion center. The angle between the BC_3 and pyrene planes decreases further to $9.8(1)^\circ$, which is much smaller than that in B_2 or even $[B_2]^-$, consistent with effective π -orbital overlap between the boron centers and the pyrenylene bridge. The B–C(pyrene) bond *a* is shortened significantly to $1.510(3)$ Å, which is in the range of known B=C(aryl) double bonds.^{9m,16} The lengthening of the *c* and *f* bonds, as well as the shortening of the *d* and *h* bonds, leads to a quinoidal structure. The BLA of the biphenyl unit (0.058 Å) is significantly enhanced compared with those of $[B_2]^-$ and the recently reported semiquinoidal structure of a pyrene derivative with nitroxide substituents at the 2,7-positions (0.020 Å),^{6e} indicating enhanced quinoidal structure. The experimental BLA is similar to that of the optimized closed-shell structure (0.054 Å) but larger than that calculated for the broken-symmetry open-shell singlet (0.032 Å), although the latter is affected by spin contamination, as is typical for this type of calculation. The bond lengths and BC_3 /pyrene torsion angle in the X-ray structure of $[B_2]^{2-}$, as well as their changes relative to B_2 , are closer to the calculated closed-shell singlet structure (see the SI). The presence of an unrestricted, broken-symmetry singlet solution below the restricted solution in energy indicates that the wave function is not well described by a single determinant; thus, we used multiconfigurational methods to determine more accurate energies. A CASSCF[10,10]/cc-pVDZ calculation of the singlet state of $[B_2]^{2-}$ at the DFT RB3LYP/6-31G* D_2 -symmetry-constrained optimized geometry gave natural orbital occupation numbers (NOONs) of 1.48 (b_3 HOMO) and 0.52 (b_2 LUMO). In the corresponding multistate CASPT2 computation, the second most important configuration ($LUMO^2 \leftarrow HOMO^2$) contributes around 13%. This indicates partial biradicaloid character in the lowest singlet state. These values can be compared to those for the 2,5-bis(borolyl)thiophene dianion (NOONs: 1.65 (HOMO), 0.35 (LUMO); 18% doubly excited configuration),^{16b} which show that the two molecules have similar biradicaloid character. This CASPT2 calculation provided an estimated S_0 – T_1 energy gap of 13 kcal mol⁻¹. This relatively large energy spacing is consistent with experiment (i.e., no thermal population of T_1 at room temperature) and is larger than that of the 2,5-bis(borolyl)thiophene dianion (6.2 kcal mol⁻¹).^{16b}

The UV–vis–NIR absorption spectra of B_1 , B_2 , and their anions were measured in dry Et₂O solutions under Ar (Figure 4). Like other 2- and 2,7-substituted pyrene compounds,⁵ the $S_1 \leftarrow S_0$ transitions of B_1 (413 nm, $\epsilon = 2100$ M⁻¹ cm⁻¹) and B_2 (444 nm, $\epsilon = 2800$ M⁻¹ cm⁻¹) are weak with stronger $S_2 \leftarrow S_0$ transitions.

Compared with the $S_1 \leftarrow S_0$ bands of the neutral compounds, the lowest-energy bands of the anions $[B_1]^-$, $[B_2]^-$, and $[B_2]^{2-}$ are very intense and red-shifted, similar to those of the radical anions of their phenylene and biphenylene analogues.^{10c} Blue-colored B_1K_1 has a strong transition at 782 nm ($\epsilon = 22000$ M⁻¹ cm⁻¹), which is bathochromically shifted by 1660 cm⁻¹ from that of the PhBMes₂ radical anion (692 nm, $\epsilon \approx 1900$ M⁻¹ cm⁻¹).^{10c} The band position is reproduced moderately well by TD-DFT (CAM-B3LYP/6-31G*, Et₂O CPCM solvation), which predicts a value of 1.90 eV ($f = 0.42$) of α -LUSO \leftarrow α -HOSO character (experiment 1.62 eV). A transition at 0.93 eV is predicted to have very low oscillator strength ($f = 0.002$) and is not experimentally observed. The shapes of all of the absorption bands of B_2K_1 are similar to those of $[1]^-$,^{10c} but the band positions differ. The lowest-energy transition of B_2K_1 (1405 nm, $\epsilon \approx 48000$ M⁻¹

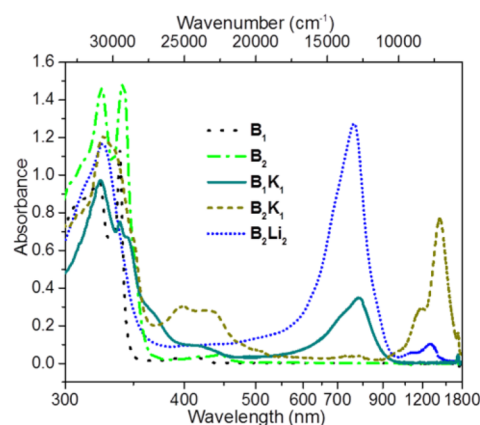


Figure 4. UV–vis–NIR absorption spectra of B_1 , B_2 , and their anions (1.6×10^{-5} M in Et₂O). The weak absorption band between 1100 and 1800 nm in the spectrum of B_2Li_2 is due to traces of the monoanion.

cm⁻¹) is red-shifted by 550 cm⁻¹ relative to that of $[1]^-$ (1305 nm, $\epsilon = 31200$ M⁻¹ cm⁻¹). Such intense long-wavelength absorption bands are usually interpreted as intervalence charge transfer (IVCT), or charge resonance, bands of class-III mixed-valence systems,^{11d} but the inability of a two-state model to describe accurately the electron distribution over the pyrene bridge in $[B_2]^-$ leads us to prefer the term “completely delocalized”. The vibrational splitting of 1500 cm⁻¹ (by band deconvolution) is similar to that of $[1]^-$ and other biphenylene-bridged monoradicals.^{10c} These data indicate that the pyrenylene unit acts here as a conjugated, planarized biphenylene bridge. TD-DFT calculations within the Tamm–Dancoff approximation (see the SI) gave a value of 0.88 eV (experiment 0.89 eV) with α -LUSO \leftarrow α -HOSO character for the low-energy, strongly allowed ($f = 0.71$) transition.

The $S_1 \leftarrow S_0$ transition of the dianion B_2Li_2 at ca. 760 nm ($\epsilon \approx 81000$ M⁻¹ cm⁻¹) is red-shifted from those of $[2]^{2-}$ (665 nm, $\epsilon \approx 11700$ M⁻¹ cm⁻¹)^{10c} and $[1]^{2-}$ (736 nm, $\epsilon = 67700$ M⁻¹ cm⁻¹). The red shift of the pyrene–BMes₂ compounds relative to their phenyl analogues is likely due to the enlarged π bridge of the pyrene system.

In conclusion, we have demonstrated that the anions of B_1 and B_2 show strong communication between the boron center(s) and pyrene across the 2- and 2,7-positions. Through effective mixing of the LUMO+1 of the pyrene fragment and the B 2p orbitals of the strongly electron-accepting BMes₂ substituents located at the 2- or 2,7-positions, the LUMOs of B_1 and B_2 have reasonably large orbital coefficients at these positions (unlike the LUMO of pyrene) as well as on the boron atoms. By chemical reduction of B_1 and B_2 , it was possible to isolate and structurally characterize the mono- and dianions $[B_1]^-$, $[B_2]^-$, and $[B_2]^{2-}$. The unpaired electron in $[B_2]^-$ is completely delocalized over the B–pyrene–B molecular backbone, which has a centrosymmetric semiquinoidal structure and a low-energy NIR absorption band (1405 nm). Sharp NMR peaks and EPR silence reveal that $[B_2]^{2-}$ has a singlet ground state without any noticeable population of the triplet state up to 40 °C, which agrees well with CASPT2 calculations predicting a ca. 13 kcal mol⁻¹ S–T gap. Comparison of the geometries of the X-ray and DFT-optimized structures suggests that the ground state of $[B_2]^{2-}$ is not far from a closed-shell singlet, while broken-symmetry DFT and CASSCF calculations indicate some biradicaloid character. Our results show that with a judicious choice of substituents at the 2,7-positions, pyrene provides an effective, rigid, conjugated

alternative to the widely employed biphenylene linker for various optoelectronic materials with potentially enhanced properties.

■ ASSOCIATED CONTENT

Supporting Information

Procedures, additional data, and a CIF file. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03805.

■ AUTHOR INFORMATION

Corresponding Author

*todd.marder@uni-wuerzburg.de

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the DFG and the Bavarian State Ministry of Science, Research, and the Arts (Collaborative Research Network “Solar Technologies Go Hybrid”) and the Alexander von Humboldt Foundation (postdoctoral fellowships to R.M.E. and A.L.) for support and Dr. R. Bertermann for NMR measurements.

■ REFERENCES

- (1) (a) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (b) Breher, F. *Coord. Chem. Rev.* **2007**, *251*, 1007. (c) Lambert, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 1756. (d) Sun, Z.; Wu, J. *J. Mater. Chem.* **2012**, *22*, 4151. (e) Sun, Z.; Ye, Q.; Chi, C.; Wu, J. *Chem. Soc. Rev.* **2012**, *41*, 7857. (f) Abe, M. *Chem. Rev.* **2013**, *113*, 7011.
- (2) (a) Chikamatsu, M.; Mikami, T.; Chisaka, J.; Yoshida, Y.; Azumi, R.; Yase, K.; Shimizu, A.; Kubo, T.; Morita, Y.; Nakasui, K. *Appl. Phys. Lett.* **2007**, *91*, No. 043506. (b) Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasui, K.; Kishi, R.; Ohta, S.; Furukawa, S.-i.; Takahashi, H.; Nakano, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3544. (c) Nakano, M.; Yoneda, K.; Kishi, R.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Botek, E.; Champagne, B. *J. Chem. Phys.* **2009**, *131*, No. 114316. (d) Koide, T.; Furukawa, K.; Shinokubo, H.; Shin, J.-Y.; Kim, K. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2010**, *132*, 7246. (e) Morita, Y.; Nishida, S.; Murata, T.; Moriguchi, M.; Ueda, A.; Satoh, M.; Arifuku, K.; Sato, K.; Takui, T. *Nat. Mater.* **2011**, *10*, 947. (f) Morita, Y.; Suzuki, S.; Sato, K.; Takui, T. *Nat. Chem.* **2011**, *3*, 197.
- (3) (a) Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260. (b) Casas-Solvas, J. M.; Howgego, J. D.; Davis, A. P. *Org. Biomol. Chem.* **2014**, *12*, 212.
- (4) (a) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172. (b) Crawford, A. G.; Liu, Z.; Mkhald, I. A. I.; Thibault, M.-H.; Schwarz, N.; Alcaraz, G.; Steffen, A.; Collings, J. C.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Chem.—Eur. J.* **2012**, *18*, 5022. (c) Liu, Z.; Wang, Y.; Chen, Y.; Liu, J.; Fang, Q.; Kleeberg, C.; Marder, T. B. *J. Org. Chem.* **2012**, *77*, 7124. (d) Ji, L.; Fucke, K.; Bose, S. K.; Marder, T. B. *J. Org. Chem.* **2015**, *80*, 661.
- (5) Crawford, A. G.; Dwyer, A. D.; Liu, Z.; Steffen, A.; Beeby, A.; Pålsson, L.-O.; Tozer, D. J.; Marder, T. B. *J. Am. Chem. Soc.* **2011**, *133*, 13349.
- (6) (a) Kreyenschmidt, M.; Baumgarten, M.; Tyutyulkov, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1957. (b) Karabunarliev, S.; Baumgarten, M. *Chem. Phys.* **2000**, *254*, 239. (c) Suzuki, S.; Takeda, T.; Kuratsu, M.; Kozaki, M.; Sato, K.; Shiomi, D.; Takui, T.; Okada, K. *Org. Lett.* **2009**, *11*, 2816. (d) Ravat, P.; Ito, Y.; Gorelik, E.; Enkelmann, V.; Baumgarten, M. *Org. Lett.* **2013**, *15*, 4280. (e) Ravat, P.; Teki, Y.; Ito, Y.; Gorelik, E.; Baumgarten, M. *Chem.—Eur. J.* **2014**, *20*, 12041. (f) Ravat, P.; Baumgarten, M. *Phys. Chem. Chem. Phys.* **2015**, *17*, 983.
- (7) (a) Maxfield, M.; Willi, S. M.; Cowan, D. O.; Bloch, A. N.; Poehler, T. O. *J. Chem. Soc., Chem. Commun.* **1980**, 947. (b) Acton, N.; Hou, D.; Schwarz, J.; Katz, T. J. *J. Org. Chem.* **1982**, *47*, 1011. (c) Maxfield, M.; Bloch, A. N.; Cowan, D. O. *J. Org. Chem.* **1985**, *50*, 1789. (d) Boldt, P.; Bruhnke, D. *J. Prakt. Chem.* **1994**, *336*, 110.
- (8) (a) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. *J. Solid State Chem.* **2000**, *154*, 5. (b) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927. (c) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574. (d) Jäkle, F. *Coord. Chem. Rev.* **2006**, *250*, 1107. (e) Yamaguchi, S.; Wakamiya, A. *Pure Appl. Chem.* **2006**, *78*, 1413. (f) Jäkle, F. Boron: Organoboranes. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; Wiley: Chichester, U.K., 2005. (g) Yin, X.; Chen, J.; Lalancette, R. A.; Marder, T. B.; Jäkle, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 9761. (h) Zhang, Z.; Edkins, R. M.; Nitsch, J.; Fucke, K.; Eichhorn, A.; Steffen, A.; Wang, Y.; Marder, T. B. *Chem.—Eur. J.* **2015**, *21*, 177. (i) Zhang, Z.; Edkins, R. M.; Nitsch, J.; Fucke, K.; Steffen, A.; Longobardi, L. E.; Stephan, D. W.; Lambert, C.; Marder, T. B. *Chem. Sci.* **2015**, *6*, 308.
- (9) (a) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 4235. (b) Scheschke, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1880. (c) Chiu, C. W.; Gabbai, F. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1723. (d) Matsumoto, T.; Gabbai, F. P. *Organometallics* **2009**, *28*, 4252. (e) Ueng, S.-H.; Solovye, A.; Yuan, X.; Geib, S. J.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Newcomb, M.; Walton, J. C.; Curran, D. P. *J. Am. Chem. Soc.* **2009**, *131*, 11256. (f) Lalevée, J.; Blanchard, N.; Tehfe, M.-A.; Chany, A.-C.; Fouassier, J.-P. *Chem.—Eur. J.* **2010**, *16*, 12920. (g) Kinjo, R.; Donnadiu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610. (h) Aramaki, Y.; Omiya, H.; Yamashita, M.; Nakabayashi, K.; Ohkoshi, S.-i.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 19989. (i) Braunschweig, H.; Dyakonov, V.; Jimenez-Halla, J. O. C.; Kraft, K.; Krummenacher, I.; Radacki, K.; Sperlich, A.; Wahler, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 2977. (j) Kushida, T.; Yamaguchi, S. *Organometallics* **2013**, *32*, 6654. (k) Bertermann, R.; Braunschweig, H.; Dewhurst, R. D.; Hörl, C.; Kramer, T.; Krummenacher, I. *Angew. Chem., Int. Ed.* **2014**, *53*, 5453. (l) Bissinger, P.; Braunschweig, H.; Damme, A.; Krummenacher, I.; Phukan, A. K.; Radacki, K.; Sugawara, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 7360. (m) Feng, P. Y.; Liu, Y. H.; Lin, T. S.; Peng, S. M.; Chiu, C. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 6237.
- (10) (a) Kaim, W.; Schulz, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 615. (b) Schulz, A.; Kaim, W. *Chem. Ber.* **1989**, *122*, 1863. (c) Fiedler, J.; Zališ, S.; Klein, A.; Hornung, F. M.; Kaim, W. *Inorg. Chem.* **1996**, *35*, 3039. (d) Zališ, S.; Kaim, W. *Main Group Chem.* **2007**, *5*, 267. (e) Kaim, W.; Hosmane, N. S.; Zališ, S.; Maguire, J. A.; Lipscomb, W. N. *Angew. Chem., Int. Ed.* **2009**, *48*, 5082. (f) Lichtblau, A.; Kaim, W.; Schulz, A.; Stahl, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1497.
- (11) (a) Grigsby, W. J.; Power, P. P. *Chem. Commun.* **1996**, 2235. (b) Grigsby, W. J.; Power, P. P. *Chem.—Eur. J.* **1997**, *3*, 368. (c) Hoefelmeyer, J. D.; Gabbai, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 9054. (d) Heckmann, A.; Lambert, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 326. (e) Braunschweig, H.; Dewhurst, R. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3574. (f) Hübner, A.; Diehl, A. M.; Diefenbach, M.; Endeward, B.; Bolte, M.; Lerner, H. W.; Holthausen, M. C.; Wagner, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 4832. (g) Asakawa, H.; Lee, K. H.; Furukawa, K.; Lin, Z.; Yamashita, M. *Chem.—Eur. J.* **2015**, *21*, 4267.
- (12) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964.
- (13) Winter, R. F. *Organometallics* **2014**, *33*, 4517.
- (14) (a) Leffler, J. E.; Watts, G.; Tanigaki, T.; Dolan, E.; Miller, D. S. *J. Am. Chem. Soc.* **1970**, *92*, 6825. (b) Elschenbroich, C.; Kühlkamp, P.; Behrendt, A.; Harms, K. *Chem. Ber.* **1996**, *129*, 859.
- (15) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 2307.
- (16) (a) Bartlett, R. A.; Power, P. P. *Organometallics* **1986**, *5*, 1916. (b) Braunschweig, H.; Dyakonov, V.; Engels, B.; Falk, Z.; Hörl, C.; Klein, J. H.; Kramer, T.; Kraus, H.; Krummenacher, I.; Lambert, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 12852.