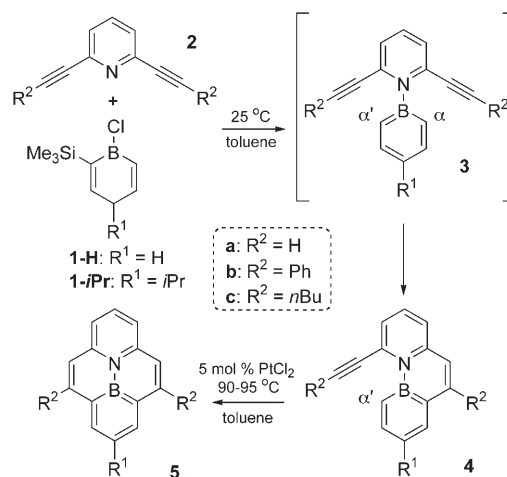


10a-Aza-10b-borapyrenes: Heterocyclic Analogues of Pyrene with Internalized BN Moieties**

Michael J. D. Bosdet, Warren E. Piers,* Ted S. Sorensen, and Masood Parvez

Polycyclic aromatic hydrocarbons (PAHs) have been at the forefront of materials research owing to their exceptional photophysical and electrochemical properties.^[1] In the current drive towards improved molecular devices such as organic light-emitting devices and field-effect transistors, π -conjugated materials containing boron have been intensely investigated, as the incorporation of this heteroatom is known to decrease the HOMO–LUMO gap while simultaneously providing a versatile means of honing physical properties by interaction with various Lewis bases.^[2,3] Examples of polycyclic aromatic heterocycles incorporating boron are scarce, though isoelectronic analogues of the PAHs pyrene,^[4] phenanthrene,^[5] and naphthalene^[6] have been synthesized by BN substitution at the periphery. Herein we report the synthesis and photophysical properties of an *internally* BN-substituted isoelectronic analogue of the ubiquitous fluorophore pyrene.^[7,8]

The BN analogues of pyrene (**5**, Scheme 1) were prepared in two steps starting from boracyclohexadienes **1**^[9] and the bis(*ortho*-alkynyl)-substituted pyridines **2**. The borabenzene–pyridine intermediates **3**^[9,10] rapidly converted into the BN phenanthrene analogues **4**, which in most instances were isolable as pure compounds.^[11] Aza-boraphenanthrenes **4** arise from a cycloisomerization reaction of one of the alkyne moieties in **3**; this reaction requires catalysis in the all-carbon systems.^[12] Here, the facile nature of the uncatalyzed reaction under ambient conditions may be attributed to the nucleophilic character^[5b,13] of the carbon atom in the position α to the boron atom in the transient borabenzene **3**. Although this nucleophilic character is retained in derivatives **4**, computed structures of these derivatives suggest that the distance between the nucleophilic α' carbon atom and the terminal carbon atom of the remaining alkyne group is about 3.5 Å in this more rigid structure versus about 2.9 Å in the adducts **3**. Therefore, treatment of compounds **4** with 5 mol % of PtCl_2 at 90–100 °C is required to induce cyclization of the second



Scheme 1. Synthesis of 10a-aza-10b-borapyrenes **5**.

alkyne moiety to afford the pyrene analogues **5** as orange-brown powders in moderate to high yields.

While the BN phenanthrenes **4** are moderately sensitive to ambient atmosphere, the BN pyrenes **5** are air- and moisture-stable, which allowed them to be purified by column chromatography. Indeed, the pyrenes **5** were found to be thermally and chemically quite robust, undergoing no reaction at the B–N linkage with protic acids like MeOH or even HCl. Thermogravimetric analysis on **5b-H** and **5c-H** revealed $T_{5\%}$ values above 210 °C, whereas **5a-H** displayed a $T_{5\%}$ value of 153 °C.

The structure of unsubstituted **5a-H** has been confirmed by X-ray crystallography (Figure 1a).^[14] The B–N bond is short (1.456(4) Å; compare borabenzene–pyridine: 1.558(3) Å),^[15] which suggests significant B–N double-bond character. This value is in close agreement with comparable BN PAH analogues with internalized BN moieties, such as BN naphthalene (1.461(1) Å)^[16] and B_2N_2 triphenylene (1.464(4) Å).^[17] The borabenzene and pyridine rings within the pyrene framework retain significant π -electron delocalization, whereas the C_4BN rings contain localized C–C double bonds (ca. 1.36 Å) between the peripheral carbon atoms. The localization of these double bonds together with the very slight deviation from planarity (Figure 1b) indicate structural features analogous to those of pyrene.^[18] NICS(1) calculations^[19] support this view, revealing values of –13.7 and –15.1 for the pyridine and borabenzene rings, respectively, and a value of –9.5 for the C_4BN ring, suggesting that the pyridine and borabenzene rings have significantly greater aromaticity than the C_4NB rings (Table S1 in the Supporting Information). Comparative values for the all-carbon pyrene molecule

[*] M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez
Department of Chemistry
University of Calgary
2500 University Drive N.W., Calgary, Alberta, T2N 1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: wpiers@ucalgary.ca
Homepage: <http://www.chem.ucalgary.ca/groups/wpiers>

[**] M.J.D.B. acknowledges NSERC and AIF (Canada) for financial support, Prof. D. Cramb, Prof. R. Turner, and Dr. C. A. Jaska of this institution for invaluable discussions and/or access to instrumentation, and H. Tuononen for help with SOMO computations.

Supporting information for this article, including full experimental details, is available on the WWW under <http://www.angewandte.org> or from the author.

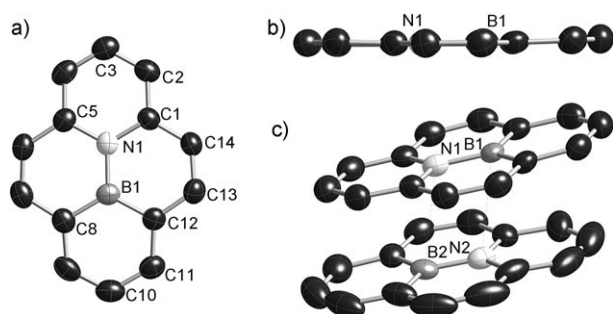


Figure 1. a) Molecular structure of **5a-H** (thermal ellipsoids shown at 50% probability). H atoms have been omitted for clarity. b) Side view of **5a-H**. c) Crystal packing of **5a-H** as viewed down the crystallographic *a* axis. Select bond lengths [Å] and angles [°] (one of two independent molecules): B1–N1 1.456(4), B1–C8 1.502(4), B1–C12 1.492(4), C1–C14 1.423(4), C13–C14 1.357(4), C12–C13 1.423(4), N1–C1 1.407(3), N1–C5 1.398(3); C1–N1–B1 119.8(2), N1–B1–C8 119.2(3), C9–C8–B1 116.1(3), C10–C11–C12 121.8(3), C13–C12–B1 117.2(3), C8–B1–C12 121.1(3), C11–C12–C13 126.5(3); C1–N1–B1–C8 179.1(2).

are -14.0 and -7.9 for the apical and flanking rings, respectively.

Introduction of a dipolar BN unit affects the packing of **5a-H**, which shows dimeric head-to-tail π stacking (Figure 1c), in which the BN dipoles oppose each other within each dimer. The dimers exhibit an average separation of 3.50 Å between the molecular planes, and an intermolecular B $\cdots$ N separation of 4.067 Å. The packing behavior of these dimers differs from the herringbone motif observed in crystalline pyrene.^[18]

The substituted BN pyrene **5c-iPr**^[20] shows analogous metrical parameters to **5a-H** (Figure 2a), but significantly different solid-state packing (Figure 2b). The molecules are arranged in parallel sheets, such that the dipoles of one sheet are situated opposite to those of neighboring sheets. Notably, there are no π -stacking interactions (closest π - π overlap: 7.24 Å) and consequently the closest intermolecular B $\cdots$ N separation is very large (7.378 Å).

Electrochemically, pyrene is subject to multiple reductive processes, with radical anionic, dianionic,^[21] trianionic,^[22] and even tetraanionic^[23] species having been reported. Cyclic voltammetry on compounds **5** indicates they exhibit a reversible one-electron reduction at potentials anodic to that of pyrene. For example, **5a-H** had a reversible one-electron reduction at -1.98 V (Figure S1 in the Supporting Information), whereas pyrene exhibits a first reduction at -2.11 V.^[24] Stirring a THF solution of **5a-H** over a lithium mirror for 24 h at 25°C afforded the radical anion $\text{Li}^+[\text{5a-H}]^-$ as a deep purple solution, which was indefinitely stable under an atmosphere of argon at -35°C but immediately oxidized back to neutral **5a-H** upon exposure to oxygen. Radical formation was further confirmed by EPR, with a singlet at $g_{\text{iso}} = 2.003$ (Figure S2 in the Supporting Information). The EPR spectra were observed to be featureless with no hyperfine coupling, even when the radical anion was generated in situ electrochemically with a $[\text{nBu}_4\text{N}]^+$ counterion. The SOMO of **5a-H** (Figure S3 in the Supporting Information) shows that the unpaired electron is located predominantly on the carbon atoms, and thus only minimal hyperfine coupling

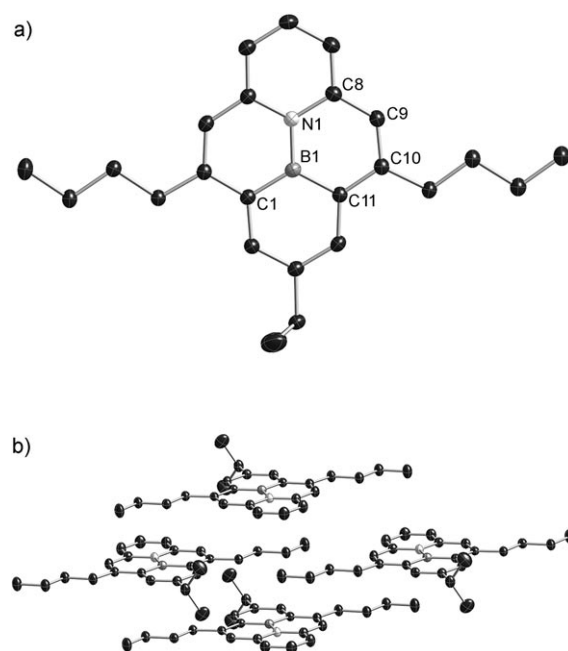


Figure 2. a) Molecular structure of **5c-iPr** (thermal ellipsoids shown at 50% probability). H atoms have been omitted for clarity. b) Crystal packing of **5c-iPr** showing molecules from three parallel sheets (see also the Supporting Information). Interplanar distance: 3.6 Å; closest π - π overlap: 7.2 Å. Select bond lengths [Å] and angles [°] of the monomer: B1–N1 1.454(2), B1–C1 1.498(2), B1–C11 1.507(2) C8–C9 1.425(2), C9–C10 1.378(2), C10–C11 1.435(2), N1–C8 1.399(2); N1–B1–C1 119.47(13), N1–B1–C11 119.41(13); C8–N1–B1–C1 180.0 .

from B or N is anticipated; indeed a node exists along the C_2 axis.^[25]

Pyrene is a ubiquitous fluorophore that has found application in various sensors^[26] and as a probe in biochemical labeling studies.^[7,27] As such, the photophysical properties of BN pyrenes **5** were of interest. The absorption spectra of derivatives **5** show a strong band in the UV region (320 – 332 nm), with relatively weak visible bands (439 – 483 nm; Table 1). Excitation of **5a-c** in cyclohexane was found to result in green fluorescence ($\lambda_{\text{max}} = 488$ – 498 nm), with low

Table 1: UV/Vis and fluorescence data for BN pyrenes **5**.

Compd	UV/Vis ^[a] λ_{max} [nm]	Fluorescence ^[b] λ_{max} [nm]	φ_f ^[c]	τ_f ^[b,d] [ns]
5a-H	321 (5.8), 443 (0.29)	480, 493, 498, 506, 514	0.15	70 (7) ^[e]
5b-H	328 (9.7), 446 (0.10)	489, 522	0.11	76
5b-iPr	332 (5.6), 453 (0.19), 483 (0.06)	498, 532	0.11	53
5c-H	320 (8.4), 341 (1.8), 439 (0.12)	478, 511	0.16	79
5c-iPr	323 (8.9), 446 (0.10), 477 (0.02)	488, 521	0.19	59

[a] Recorded in CH_2Cl_2 . Number in parentheses is the molar extinction coefficient, ϵ , in $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. [b] Recorded in cyclohexane with excitation at 330 nm. [c] Quantum yield reported relative to 9,10-diphenylanthracene ($\varphi_f = 0.90$). [d] Fluorescence lifetime. [e] Excimer fluorescence lifetime determined at greater than 10^{-3} M ($\lambda_{\text{ex}} = 430$ nm).

quantum yields ($\varphi_f = 0.11$ – 0.19) and moderate lifetimes ($\tau_f = 53$ – 79 ns; Table 1). Conversely, pyrene fluoresces in the UV region ($\lambda_{\max} = 383$ nm) with both a higher quantum efficiency ($\varphi_f = 0.60$ in cyclohexane) and a longer lifetime ($\tau_f = 450$ ns).^[28] The polar nature of **5a-c** might be expected to give rise to solvatochromic behavior in the emission spectra, but this has not been investigated in detail as of yet.

In all BN pyrenes the red edge of the emission band was seen to increase in intensity with increasing sample concentration (Figure S4 in the Supporting Information), suggestive of excimer formation at higher concentrations. Pyrene is the textbook example of a species which forms an excimer in concentrated solution, the fluorescence from which is a broad, bathochromically shifted peak at 470 nm.^[29] In contrast, the fluorescence from the **5a-H** excimer is only modestly bathochromically shifted relative to the monomer (broadening centered around 510–550 nm), such that no clear maxima could be resolved,^[30] though a second lifetime component was identified in highly concentrated solutions of **5a-H** (see Table 1), which may be attributed to an excimer. Further insight into the fluorescence behavior of this emissive species was gained from a study of the emission and excitation of single crystals of **5a-H** and **5c-iPr**.^[31] Thus, the π -stacked motif of **5a-H** gave rise to a broad emission with $\lambda_{\max} = 520$ nm (Figure 3a), similar to the emission position for concentrated solutions of this species. The excitation spectrum (Figure 3b) shows predominantly bands which correspond to monomer excitation, arguing against the notion of

ground-state dimer absorption/fluorescence. While there is likely some contribution of inner filter effects to the overall shape of the optically dense solutions,^[7] the existence of a second lifetime component in these solutions together with the single-crystal emission maxima is suggestive of an excimeric species. Analogous features exist in the excitation spectrum from a single crystal of **5c-iPr** (Figure S5 in the Supporting Information), in which no π stacking is observed (see above). Clearly, this packing excludes fluorescence from a dimer, and indeed the emission spectrum closely resembles that of the monomer in dilute cyclohexane solution. This result is notable, as BN pyrene **5c-iPr** also displays excimer emission in concentrated solution.

In summary, we report synthetic routes to a new family of heterocycles based on the pyrene framework, with an internalized BN fragment in place of CC. While retaining some of the photophysical properties of pyrenes (excimer formation), the 10a-aza-10b-bora derivatives **5** have higher electron affinities, feature a lower band gap, and incorporate an internal dipole which influences crystal packing. Together these features suggest these compounds may form the basis for n-channel organic semiconductors.^[32] The versatility of the synthetic route presented, along with ongoing functionalization studies of **5a-H**, augurs well for the fine-tuning of photophysical and redox properties for this promising family of compounds.

Experimental Section

5a-H: Under argon, a solution of **1-H** (90 mg, 0.49 mmol) in toluene (1 mL) was added to a solution of **2a** (62 mg, 0.49 mmol) in toluene (6 mL) and stirred for 3 days. Volatile components were removed in vacuo and the brown solid was subsequently slurried in *n*-hexane (10 mL), sonicated for 30 minutes, and filtered through a swivel frit. After several washes with *n*-hexane, the solvent was removed in vacuo, and the brown solid was slurried in toluene and filtered through celite to afford an orange solution. PtCl_2 (3 mg, 11 μmol) was added, and the mixture stirred for 16 h at 95 °C. After cooling and removing the toluene in vacuo, the brown solid was dissolved in Et_2O (10 mL) and filtered through neutral alumina. Yellow plates suitable for X-ray analysis were obtained by slow evaporation from this solution at 25 °C. Yield: 43 mg (43 %). ^1H NMR (C_6D_6): $\delta = 8.84$ (d, 2H, $^3J_{\text{H,H}} = 7.5$ Hz, CH^7), 8.78 (d, 2H, $^3J_{\text{H,H}} = 8.5$ Hz, CH^5), 8.25 (t, 1H, $^3J_{\text{H,H}} = 7.5$ Hz, CH^8), 7.62 (d, 4H, $^3J_{\text{H,H}} = 8.3$ Hz, $\text{CH}^2 + \text{CH}^4$), 7.45 ppm (t, 1H, $^3J_{\text{H,H}} = 7.5$ Hz, CH^1); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 139.42$ (s, C^3), 138.92 (s, CH^5), 133.04 (s, C^6), 130.44 (s, CH^7), 127.27 (s, CH^1), 123.69 (s, C^8), 120.42 (s, CH^2), 117.35 ppm (s, CH^4); $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 22.3$ (brs); UV/Vis (ϵ given in $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$): $\lambda_{\max}(\text{CH}_2\text{Cl}_2) = 443$ (0.3), 321 (5.8), 285 (2.2) nm; $\lambda_{\max}(n\text{-hexane}) = 479$ (0.1), 447 (0.3), 322 (5.6), 286 (2.3) nm; fluorescence (cyclohexane): $\lambda_{\max} = 480$, 493, 498, 506, 514 nm; $\varphi_f = 0.15$, $\tau_f = 70$ ns ($\chi^2 = 0.30$); cyclic voltammetry (in THF, vs. SCE): $E_{1/2} = -1.98$ V. HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{N}^{11}\text{B}$ ($[M]^+$): 203.09063; found: 203.09112. TGA: $T_{\text{onset}} = 101$ °C, $T_{5\%} = 153$ °C. M.p. 138 °C (differential scanning calorimetry).

Received: February 8, 2007

Published online: April 5, 2007

Keywords: aromaticity · boron · cycloisomerization · fluorescence · heterocycles

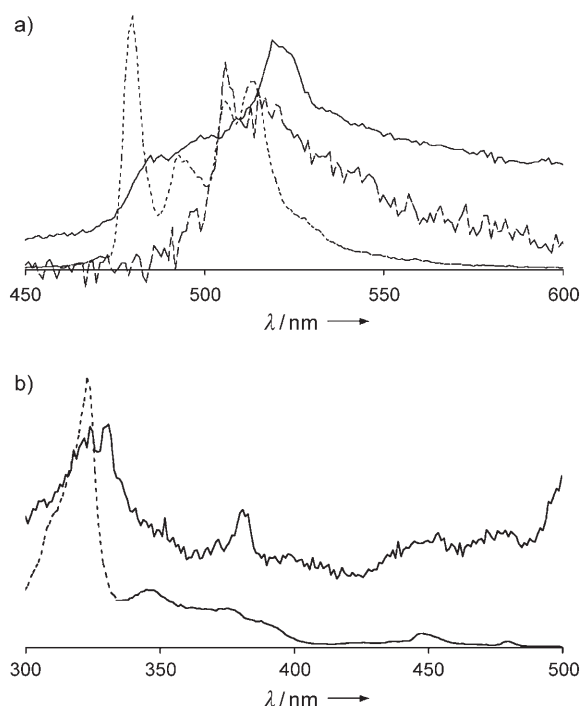


Figure 3. a) Emission spectra ($\lambda_{\text{ex}} = 330$ nm) of **5a-H** single crystal and cyclohexane solutions normalized at 510 nm. Solid line: single crystal; dashed line: 4.92 mM solution; dotted line: 5.91 μM solution. b) Excitation spectra ($\lambda_{\text{em}} = 520$ nm) of **5a-H** single crystal and dilute cyclohexane solution. Solid line: single crystal; dotted line: 5.91 μM solution. For single-crystal spectra, excitation and emission bandwidths were set to 2.5 and 10 nm, respectively.

- [1] a) K. Müllen, J. P. Rabe, *Ann. N. Y. Acad. Sci.* **1998**, 852, 205; b) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, 101, 1267; c) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, 104, 4891; d) J. E. Anthony, *Chem. Rev.* **2006**, 106, 5028.
- [2] a) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, 16, 4574; b) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2000**, 122, 6335; c) S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, 124, 8816; d) A. Wakamiya, T. Ide, S. Yamaguchi, *J. Am. Chem. Soc.* **2005**, 127, 14859; e) W. L. Jia, M. J. Moran, Y. Y. Yuan, Z. H. Lu, S. Wang, *J. Mater. Chem.* **2005**, 15, 3326; f) K. Parab, K. Venkatasubbaiah, F. Jäkle, *J. Am. Chem. Soc.* **2006**, 128, 12879.
- [3] S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, 34, 2.
- [4] M. J. S. Dewar, R. Dietz, *J. Chem. Soc.* **1959**, 2728.
- [5] a) M. J. S. Dewar, V. P. Kubba, R. Pettit, *J. Chem. Soc.* **1958**, 3073; b) M. J. D. Bosdet, C. A. Jaska, W. E. Piers, T. S. Sorensen, M. Parvez, *Org. Lett.* **2007**, 9, 1395.
- [6] P. Paetzold, C. Stanesco, J. R. Stubenrauch, M. Bienmüller, U. Englert, *Z. Anorg. Allg. Chem.* **2004**, 630, 2632.
- [7] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed., Springer, Heidelberg, **1999**.
- [8] P. Somerharju, *Chem. Phys. Lipids* **2002**, 116, 57.
- [9] D. A. Hoic, J. Robbins-Wolf, W. M. Davis, G. C. Fu, *Organometallics* **1996**, 15, 1315.
- [10] When R^2 = trimethylsilyl this intermediate is isolable.
- [11] Full characterization of **4a-H** and **4b-H** has not been provided in the Supporting Information, as analytically pure samples proved difficult to attain. Complete characterization of the remaining derivatives **4** has been provided.
- [12] V. Mamane, P. Hannen, A. Furstner, *Chem. Eur. J.* **2004**, 10, 4556.
- [13] a) I. Ghesner, W. E. Piers, M. Parvez, R. McDonald, *Organometallics* **2004**, 23, 3085; b) J. Pan, J. W. Kampf, A. J. Ashe III, *Org. Lett.* **2007**, 9, 679.
- [14] Crystal data for **5a-H**: $C_{14}H_{10}BN$, M_r = 203.04, monoclinic, space group $P2_1/c$, a = 8.471(6), b = 17.106(13), c = 14.372(6) Å, α = 90°, β = 102.14(4)°, γ = 90°, V = 2036(2) Å³, Z = 8, ρ_{calcd} = 1.325 g cm⁻³, MoK α radiation, λ = 0.71073 Å, T = 173(2) K, 8518 measured reflections, 4639 unique (R_{int} = 0.0843), 1661 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$, μ = 0.076 mm⁻¹, min/max transmission 0.9894 and 0.9955, $R1(I > 2\sigma)$ = 0.0637, $wR2$ = 0.1251, GoF = 0.974, 289 parameters, final difference map within +0.169 and -0.175 e Å⁻³. CCDC-636012 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.
- [15] R. Boese, N. Finke, J. Henkelmann, G. Maier, P. Paetzold, H. P. Reisenauer, G. Schmid, *Chem. Ber.* **1985**, 118, 1644.
- [16] X. Fang, H. Yang, J. W. Kampf, M. M. Banaszak Holl, A. J. Ashe III, *Organometallics* **2006**, 25, 513.
- [17] C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *J. Am. Chem. Soc.* **2006**, 128, 10885.
- [18] A. Camerman, J. Trotter, *Acta Crystallogr.* **1965**, 18, 636.
- [19] The NICS method is a measure of the abnormal proton chemical shift of aromatic molecules by the induced ring current that is due to cyclic σ - or π -electron delocalization, and whose values can either be negative (suggestive of diatropic ring currents and aromaticity) or positive (suggestive of paratropic ring currents and antiaromaticity). The standard method for NICS calculations is NICS(1), which is calculated at a distance of 1 Å above the plane of the ring in order to minimize the influence from the σ framework while maximizing the contributions from the π system.
- [20] Crystal Data for **5c-iPr**: $C_{25}H_{32}BN$, M_r = 357.33, monoclinic, space group $P2_1/m$, a = 12.295(6), b = 7.242(3), c = 12.806(7) Å, α = 90°, β = 114.731(19)°, γ = 90°, V = 1035.7(9) Å³, Z = 2, ρ_{calcd} = 1.146 g cm⁻³, MoK α radiation, λ = 0.71073 Å, T = 173(2) K, 5716 measured reflections, 3205 unique (R_{int} = 0.0356), 2191 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$, μ = 0.064 mm⁻¹, min/max transmission 0.9872 and 0.9923, $R1(I > 2\sigma)$ = 0.0538, $wR2$ = 0.1397, GoF = 1.037, 160 parameters, final difference map within +0.342 and -0.253 e Å⁻³. CCDC-636013 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.
- [21] K. Müllen, *Helv. Chim. Acta* **1978**, 61, 2307.
- [22] K.-H. Thiele, S. Bambirra, J. Sieler, S. Yelonek, *Angew. Chem.* **1998**, 110, 3016; *Angew. Chem. Int. Ed.* **1998**, 37, 2886.
- [23] M. Rabinovitz, A. Minsky, *Pure Appl. Chem.* **1982**, 54, 1005.
- [24] This value was obtained under identical experimental conditions in this work (see the Supporting Information). A value of -2.54 V has recently been reported in THF: J. Daub, R. Engl, J. Kurzawa, S. E. Müller, S. Schneider, A. Stockmann, M. R. Wasielewski, *J. Phys. Chem. A* **2001**, 105, 5655, and references therein.
- [25] SOMO computations for the radical anion of pyrene show a nodal plane along the same axis, though the hyperfine coupling can be resolved; see: R. F. C. Claridge, C. M. Kirk, B. M. Peake, *Aust. J. Chem.* **1973**, 26, 2055, and reference [21].
- [26] a) H. Maeda, T. Maeda, K. Mizuno, K. Fujimoto, H. Shimizu, M. Inouye, *Chem. Eur. J.* **2006**, 12, 824; b) K. S. Foscaneanu, J. C. Scaiano, *Photochem. Photobiol. Sci.* **2005**, 4, 817; c) Y. Zhang, R. Yang, F. Liu, K. Li, *Anal. Chem.* **2004**, 76, 7336; d) Y. Fujiwara, Y. Amao, *Sens. Actuators B* **2003**, 89, 58; e) J. S. Yang, C. S. Lin, C. Y. Hwang, *Org. Lett.* **2001**, 3, 889; f) B. Bodenant, T. Weil, M. Businelli-Peurcel, F. Fages, B. Barbe, I. Pianet, M. Laguerre, *J. Org. Chem.* **1999**, 64, 7034.
- [27] a) H. Maeda, T. Maeda, K. Mizuno, K. Fujimoto, H. Shimizu, M. Inouye, *Chem. Eur. J.* **2006**, 12, 824; b) C. Yao, H. Kraatz, R. P. Steer, *Photochem. Photobiol. Sci.* **2005**, 4, 191.
- [28] J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York, **1970**.
- [29] a) I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, **1971**; b) A. Sharma, S. G. Schulman, *Introduction to Fluorescence Spectroscopy*, Wiley Interscience, New York, **1999**.
- [30] Limited solubility prevented photophysical studies at higher concentrations.
- [31] Single-crystal emission and excitation spectra of pyrene afforded some of the early confirmation of excimer formation in solution; see: B. Stevens, *Spectrochim. Acta* **1962**, 18, 439.
- [32] C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Brédas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, 16, 4436.