Angewandte
Zuschriften

Biradical Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201507039
Internationale Ausgabe: DOI: 10.1002/anie.201507039

Perylene Bisimide Radicals and Biradicals: Synthesis and Molecular Properties

David Schmidt, Minjung Son, Jong Min Lim, Mei-Jin Lin, Ivo Krummenacher,
Holger Braunschweig, Dongho Kim, and Frank Würthner**

Dedicated to Professor Todd B. Marder on the occasion of his 60th birthday

Abstract: *Unprecedented neutral perylene-3,4:9,10-tetracarboxylic acid bisimide (PBI) radicals and biradicals were synthesized by facile chemical oxidation of 4-hydroxyaryl-substituted PBIs. Subsequent characterization by optical and magnetic spectroscopic techniques, as well as quantum chemical calculations, revealed an open-shell singlet biradical ground state for the PBI biradical* **OS-2**$^{\bullet\bullet}$ ($\langle s^2\rangle = 1.2191$) *with a relatively small singlet–triplet energy gap of 0.041 eV and a large singlet biradical character of* $y = 0.72$.

Polycyclic aromatic hydrocarbons (PAHs) with open-shell biradicaloid ground states[1] have attracted continuous interest owing to their critical role in understanding the fundamental nature of chemical reactions,[2] and versatile applicability in electronic devices,[3] non-linear optics,[4] energy storage devices,[5] organic spintronics,[6] and singlet fission.[7] Despite the inherent instability of such open-shell molecules that are often susceptible to degradation reactions with oxygen, several classes of stable π-conjugated biradicaloids have been realized by generating a stabilizing environment, such as those intrinsically given for *p*-quinodimethanes,[8] bisphenalenyls,[9] or zethrenes.[10] Therefore, a common approach to enhance the stability of such biradicaloids is to design a quinoidal PAH framework that is in resonance with a singlet biradical structure containing a polycyclic aromatic core and radical centers at the terminal carbon atoms.[11]

In this regard, perylene-3,4:9,10-tetracarboxylic acid bisimides (PBIs) with an aromatic perylene core should, in principle, offer another promising scaffold for constructing stable functional open-shell systems. Along with other well-recognized properties of PBIs, such as photostability and outstanding fluorescence behavior,[12] recent investigations on PBI derivatives have focused on their applications in photovoltaics and optoelectronic devices by virtue of their n-type semiconducting properties owing to the presence of two electron-withdrawing bisimide subunits.[13] The capability of these electron-deficient aromatic bisimides to form fairly stable reduced species[14] was exploited very recently for the isolation of ambient stable PBI radical anions[15] and dianions.[16] Although it is expected that the synthesis of PBI biradicals with open-shell electronic ground states should be feasible owing to the stabilizing effect of the polycyclic and electron deficient aromatic core, there has been no report on the formation and characterization of stable PBI biradicals thus far.

Herein, the first example of a stable PBI-centered biradical formed by successive deprotonation and chemical oxidation of the 1,7-di(4-hydroxyaryl)-substituted PBI derivative **2** is reported (Scheme 1).[17] A comprehensive characterization of its molecular properties by various optical and magnetic spectroscopic techniques revealed a singlet biradical ground state that was further corroborated by quantum chemical calculations and by comparison with its mono(4-hydroxyaryl)-substituted radical analogue **1**$^{\bullet}$.

The reaction mechanisms for the generation of (bi)radicals **1**$^{\bullet}$ and **2**$^{\bullet\bullet}$ from the 4-hydroxyaryl-substituted PBIs **1** and **2** are outlined (Scheme 1; Supporting Information, Figures S1, S2). As a consequence of the electron-withdrawing dicarboximide units, PBIs **1** and **2** exhibit strongly acidic 4-hydroxyaryl substituents at the bay positions, which are readily deprotonated to form the corresponding (di)anions **1**$^{-}$ and **2**$^{2-}$ upon addition of tetrabutylammonium fluoride (TBAF).[17] The formation of **1**$^{-}$ and **2**$^{2-}$ was confirmed by the appearance of prominent charge-transfer (CT) absorption bands at the near-infrared (NIR) region (Figure 1) and substantiated by ^{1}H NMR spectroscopy.[17] Subsequent reaction of the (di)anions with lead(IV) tetraacetate dissolved in dichloromethane under inert atmosphere at room temperature led to the desired neutral monoradical **1**$^{\bullet}$ and biradical **2**$^{\bullet\bullet}$. Alternatively, PBIs **1** and **2** can also be deprotonated and oxidized heterogeneously in a one-step procedure by adding PbO_2 to the corresponding toluene solutions followed by filtration of the excess amount of oxidant. Interestingly, for **2**$^{\bullet\bullet}$, several resonance structures can be drawn, one of which is characterized by a closed-shell Kekulé structure (**CS-2** in

---

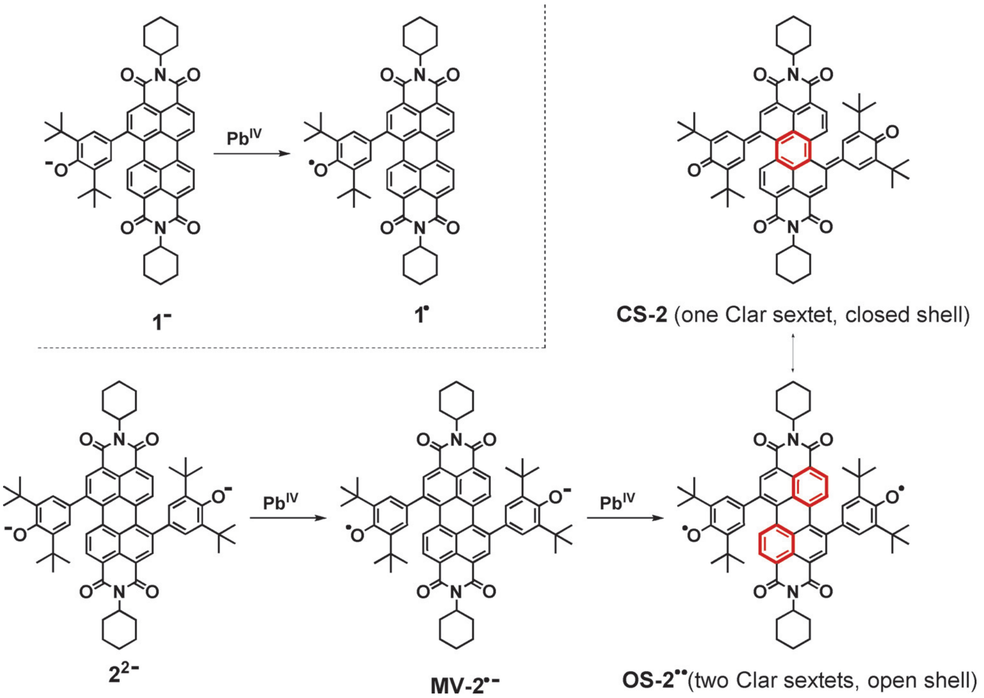
[*] Dr. D. Schmidt,[+] Dr. M.-J. Lin, Prof. Dr. F. Würthner
Universität Würzburg, Institut für Organische Chemie and
Center for Nanosystems Chemistry
Am Hubland, 97074 Würzburg (Germany)
E-mail: wuerthner@chemie.uni-wuerzburg.de

M. Son,[+] Dr. J. M. Lim, Prof. Dr. D. Kim
Yonsei University,
Spectroscopy Laboratory for Functional π-Electronic Systems, and
Department of Chemistry
Seoul 120-749 (Korea)
E-mail: dongho@yonsei.ac.kr

Dr. I. Krummenacher, Prof. Dr. H. Braunschweig
Universität Würzburg, Institut für Anorganische Chemie
Am Hubland, 97074 Würzburg (Germany)

[+] These authors contributed equally to this work

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507039.



Scheme 1. Synthesis of PBI (bi)radicals **1**$^{\bullet}$ and **2**$^{\bullet\bullet}$ studied in this work.

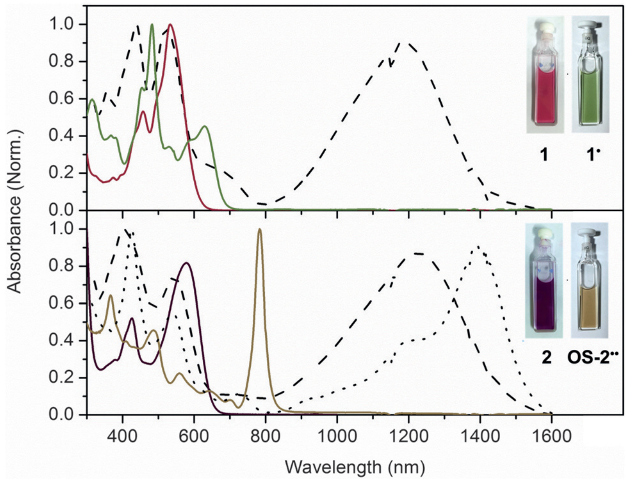


Figure 1. Normalized UV/Vis/NIR absorption spectra of neutral PBIs **1** and **2** (red and violet solid lines, from the top), (di)anionic species 1^{-} and 2^{2-} (black dashed lines, from the top), radical **1**$^{\bullet}$ (green solid line) and mixed-valence **MV-2**$^{\bullet-}$ (black dotted line), and biradical **OS-2**$^{\bullet\bullet}$ (beige solid line).

Scheme 1). However, Clar's aromatic sextet rule, which can be applied to estimate the stability and reactivity of PAHs, predicts that the resonance structure with more aromatic sextets should be the more stable one.[18] Therefore, we conjecture that **2**$^{\bullet\bullet}$ exists as its open-shell singlet biradical form **OS-2**$^{\bullet\bullet}$, which is due to the higher number of aromatic sextet rings (Scheme 1). Although **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ slowly decompose with time, as evidenced by the gradual changes in their time-dependent UV/Vis/NIR absorption spectra (Supporting Information, Figure S1), both (bi)radicals exhibit remarkable stabilities facilitating their unambiguous characterization. Kinetic analyses of the UV/Vis absorption spectral changes revealed a minimum half-life of $\tau_{1/2} \approx 40$ h for **1**$^{\bullet}$, whereas **OS-2**$^{\bullet\bullet}$ appeared to be even more stable, with an estimated minimum half-life of approximately 54 h (Supporting Information, Figure S1 and Table S1).

Upon titration of $\mathbf{1}^{-}$ and $\mathbf{2}^{2-}$ with [Pb(OAc)$_4$] solutions, the broad CT bands at around 1200 nm decrease gradually with the rise of new bands in the visible region, which are accompanied by drastic color changes for both compounds (Figure 1; Supporting Information, Figure S2, Tables S2, S3).

In contrast to the absorption spectrum of **1**$^{\bullet}$ with typical vibronic progressions, the absorption spectrum of biradical **OS-2**$^{\bullet\bullet}$ exhibits an unusual sharp and intense NIR band at 783 nm (Supporting Information, Table S2). The intermediate occurrence of an additional NIR absorption at 1396 nm after adding one equivalent [Pb(OAc)$_4$] to $\mathbf{2}^{2-}$ is attributed to the initial formation of the mixed-valence compound **MV-2**$^{\bullet-}$ (black dotted line, Figure 1; Supporting Information, Figure S2). The bathochromic shifts observed for **OS-2**$^{\bullet\bullet}$ are not as prominent as those in recent reports on similar open-shell π-conjugated systems, implying that the two unpaired electrons do not interact strongly with each other.[19] The generation of the open-shell species **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ was further corroborated by spectroelectrochemistry (Supporting Information, Figure S3), where nearly identical absorption spectra to those obtained through chemical oxidation were observed after electrochemical oxidation at potentials of 400 and 500 mV, respectively. Further electrochemical oxidations at higher potentials (1500 mV) were observed for both systems that presumably arise from the formation of the corresponding cationic frameworks $\mathbf{1}^{+}$ and $\mathbf{2}^{2+}$.

To quantify the amount of **1**$^{\bullet}$ that had been generated when using PbO$_2$ as the oxidant, the number of unpaired electrons per molecule was investigated by ^{1}H NMR spectroscopic experiments according to the Evans method (Supporting Information, Figure S4).[20] Thus, the paramagnetic shift of the solvent residual signal of 16.6 Hz, which is directly related to the effective magnetic moment of **1**$^{\bullet}$ (1.82 μ_B), was used to determine the number of unpaired electrons per molecule to be 1.08, confirming the formation of pure **1**$^{\bullet}$.[20] Similarly, the singlet biradical character of **OS-2**$^{\bullet\bullet}$ was revealed by low-temperature ^{1}H NMR spectroscopy in highly deuterated toluene (99.96 % [D$_8$]toluene). Whereas **2** exhibits sharp and characteristic resonances for all aromatic protons between 7.70 and 8.50 ppm, no signals can be detected for **OS-2**$^{\bullet\bullet}$ at room temperature. However, upon lowering the temperature to 180 K, the signal intensity increased gradually and broad resonances between 7.80 and 8.30 ppm appeared (Supporting Information, Figure S5). This behavior has already been observed for many other PAHs with singlet open-shell ground states and is attributed to thermally excited triplet species with small singlet–triplet energy gaps.[21]

To investigate the electronic structure of both (bi)radicals, **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ were further analyzed by EPR spectroscopy in toluene solutions at 250 K. While **OS-2**$^{\bullet\bullet}$ is EPR-silent, presumably owing to an antiparallel coupling of the unpaired electrons and cancellation of the magnetic moments,[21a] a well-resolved EPR signal centered at $g_{\mathrm{iso}} = 2.004$ was detected for monoradical **1**$^{\bullet}$ (Figure 2 a).

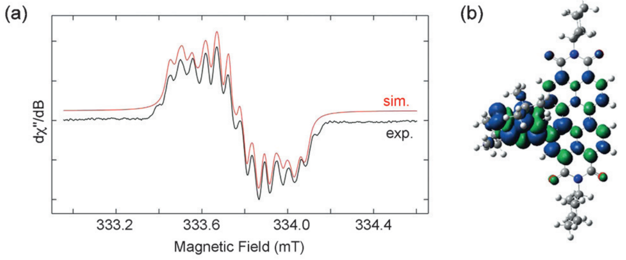


Figure 2. a) Experimental (black) and simulated (red) X-band (9.4 GHz) EPR spectrum of monoradical **1**$^{\bullet}$ in toluene solutions (0.1 mM) at 250 K. b) Calculated spin density distribution of **1**$^{\bullet}$ (UCAM-B3LYP/6-31G(d), isovalue = 0.0007 a.u.). Blue and green surfaces represent positive and negative spin densities, respectively.

The measured EPR spectrum is in good agreement with the simulated spectrum, where several interactions between the unpaired electron and the aromatic hydrogen atoms ($A(^{1}\mathrm{H}) = 0.1$–1.7 G; Supporting Information, Table S4) contribute to the hyperfine splitting, indicating that the electron is generally delocalized over the whole aromatic system. Nevertheless, a significant portion of the spin density seems to be located on the phenoxyl substituent as evidenced by the largest hyperfine interaction of $A(^{1}\mathrm{H}) = 1.7$ G. These findings are supported by the calculated spin density plot of **1**$^{\bullet}$, where the largest coefficients are found on the phenoxyl substituent as well (Figure 2 b).

To gain a deeper understanding of the nature of the PBI-centered (bi)radicals, we calculated the optimized ground-state geometry, spin density distribution, and vertical excitation energies of **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ by using the unrestricted broken-symmetry density functional theory method (UCAM-B3LYP/6-31G(d)). These calculations are in excellent agreement with our previous observations that the singlet biradical ground state ($\langle s^{2}\rangle = 1.2191$) is energetically the most stable form of **OS-2**$^{\bullet\bullet}$ (Supporting Information, Table S5). It is noteworthy that **OS-2**$^{\bullet\bullet}$ exhibits a relatively small singlet–triplet energy gap ($\Delta E_{\mathrm{S\text{-}T}}$) of 0.94 kcal mol^{-1} (0.041 eV), which directly reflects the weak exchange interactions of $J/k_{\mathrm{B}} = -1.05$ kcal mol^{-1} between the two unpaired electrons (Supporting Information, Eq. S5).[22] This weak coupling strength between the two unpaired electrons is well in line with the moderate bathochromic shifts of the absorption maxima observed by UV/Vis/NIR absorption spectroscopy (see above).[19] Furthermore, the singlet–triplet energy gap $\Delta E_{\mathrm{S\text{-}T}}$ is directly related to the singlet biradical character y, which can be estimated to be 0.72 (Supporting Information, Eq. S6).[23] This remarkably high value is consistent with the small degree of exchange interactions between the two unpaired electrons in **OS-2**$^{\bullet\bullet}$.[24] The non-linear optical properties of **OS-2**$^{\bullet\bullet}$ were evaluated by the open-aperture Z-scan technique and revealed a maximum two photon absorption cross-section value of 350 GM at 775 nm (Supporting Information, Figure S6).

The calculated spin density distributions of **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ (Figure 2 b; Supporting Information, Figure S7 a) reveal a strongly delocalized nature of the spin density, although the largest coefficients are found on the phenoxyl bay substituents. Moreover, the singly occupied molecular orbital (SOMO) profiles of the singlet biradical **OS-2**$^{\bullet\bullet}$ display characteristic disjoint features with α and β spin density localized on the PBI core with contributions of each phenoxyl substituent (Supporting Information, Figure S7 b). The ground-state absorption spectra of both (bi)radicals were simulated with the time-dependent DFT (TD-DFT) method using the respective optimized open-shell ground-state geometries of **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ (Supporting Information, Figures S8, S9). The calculated vertical excitation energies are consistent with the experimental absorption spectra, where the lowest-energy transitions for **1**$^{\bullet}$ are only weakly allowed ($f = 0.0001$ at 1026 nm) in contrast to **OS-2**$^{\bullet\bullet}$ ($f = 0.2100$ at 784 nm). The MOs that contribute to the lowest-energy transitions of **1**$^{\bullet}$ reveal a significant CT character from the phenoxyl substituent to the PBI core, whereas those of **OS-2**$^{\bullet\bullet}$ correspond to the characteristic SOMO–LUMO transitions without perceptible CT contributions.

The excited-state dynamics of the open-shell species **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ were further investigated by femtosecond transient absorption (TA) spectroscopy (Figure 3). Both (bi)radicals remained stable throughout the measurements, reflecting the unusual photostability of these open-shell systems, which is comparable to other known bisimide-functionalized biradicaloid π-skeletons.[21a] The TA spectra of both compounds show negative ground-state bleach signals at regions that correspond to their steady-state absorptions as well as intense positive excited-state absorption signals. Compared to their closed-shell counterparts **1** and **2,** which exhibit long singlet excited-state lifetimes of 5.7–6.1 ns (Supporting Information, Figure S10), the excited-states of **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$ were found to decay much faster with time constants of 1.9 and 11 ps, respectively (Supporting Information, Figure S11). These short excited-state lifetimes are consistent with the non-fluorescent behavior of the open-shell PBIs **1**$^{\bullet}$ and **OS-2**$^{\bullet\bullet}$. The shorter excited-state lifetime of monoradical **1**$^{\bullet}$ compared to that of **OS-2**$^{\bullet\bullet}$ can be attributed to the intramolecular CT process (see above).

In summary, we report for the first time the generation of neutral PBI radicals and biradicals and their unambiguous characterization by various optical and magnetic spectro-

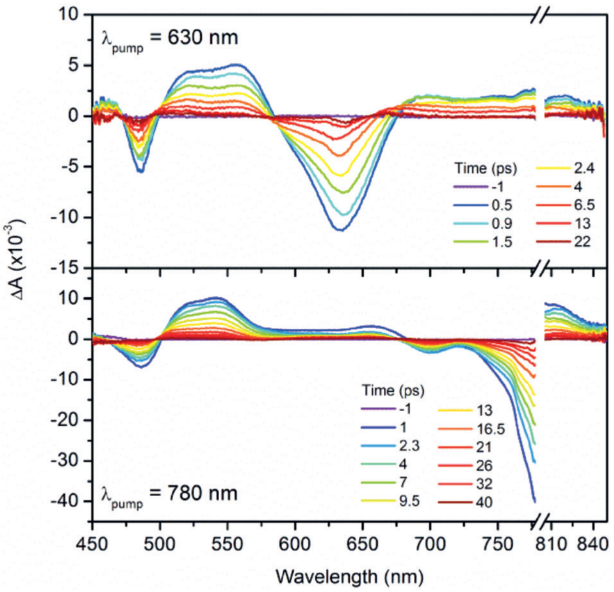


Figure 3. Femtosecond transient absorption spectra of **1**$^{\bullet}$ (top) and **OS-2**$^{\bullet\bullet}$ (bottom) measured in dichloromethane at room temperature.

scopic techniques. Through a comprehensive study including TD-DFT calculations we have demonstrated that **OS-2**$^{\bullet\bullet}$ exists in its singlet open-shell ground state with a relatively small singlet–triplet energy gap. The large singlet biradical character is in excellent agreement with Clar's aromatic sextet rule for polycyclic aromatic hydrocarbons, which predicts the resonance structure with more aromatic sextets to be the energetically favorable form. The remarkable stability accomplished by delocalization of spin density from phenoxyl radicals into electron-withdrawing π-scaffolds might offer an entry into a new class of functional materials based on open-shell organic colorants. Current efforts in our laboratories are accordingly directed towards the generalization of our concept for other electron-deficient π-scaffolds.

Acknowledgements

The research at the University of Würzburg is supported by the DFG research training group 2112 on "Molecular Biradicals". The work at Yonsei University is supported by the Global Research Laboratory Program (2013K1A1A2A02050183) by the Ministry of Science, ICT & Future, Korea.

Keywords: biradicals · dyes · perylene bisimides · pigments · radicals

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13980–13984
Angew. Chem. **2015**, *127*, 14186–14190

---

[1] a) A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893; b) H. F. Bettinger, *Pure Appl. Chem.* **2010**, *82*, 905–915; c) C. Lambert, *Angew. Chem. Int. Ed.* **2011**, *50*, 1756–1758; *Angew. Chem.* **2011**, *123*, 1794–1796; d) Z. Sun, J. Wu, *J. Mater. Chem.* **2012**, *22*, 4151–4160; e) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857–7889; f) M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088.

[2] a) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem. Int. Ed.* **2003**, *42*, 502–528; *Angew. Chem.* **2003**, *115*, 518–546; b) W. R. Roth, H. Hopf, C. Horn, *Chem. Ber.* **1994**, *127*, 1765–1779.

[3] a) M. Chikamatsu, T. Mikami, J. Chisaka, Y. Yoshida, R. Azumi, K. Yase, A. Shimizu, T. Kubo, Y. Morita, K. Nakasuji, *Appl. Phys. Lett.* **2007**, *91*, 043506; b) D. T. Chase, A. G. Fix, S. J. Kang, B. D. Rose, C. D. Weber, Y. Zhong, L. N. Zakharov, M. C. Lonergan, C. Nuckolls, M. M. Haley, *J. Am. Chem. Soc.* **2012**, *134*, 10349–13052.

[4] K. Kamada, K. Ohta, T. Kubo, A. Shimizu, Y. Morita, K. Nakasuji, R. Kishi, S. Ohta, S. I. Furukawa, H. Takahashi, M. Nakano, *Angew. Chem. Int. Ed.* **2007**, *46*, 3544–3546; *Angew. Chem.* **2007**, *119*, 3614–3616.

[5] Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato, T. Takui, *Nat. Mater.* **2011**, *10*, 947–951.

[6] Y. W. Son, M. L. Cohen, S. G. Louie, *Phys. Rev. Lett.* **2006**, *97*, 216803.

[7] M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891–6936.

[8] a) J. Thiele, H. Balhorn, *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1463–1470; b) C. R. Flynn, J. Michl, *J. Am. Chem. Soc.* **1974**, *96*, 3280–3288.

[9] a) K. Ohashi, T. Kubo, T. Masui, K. Yamamoto, K. Nakasuji, T. Takui, Y. Kai, I. Murata, *J. Am. Chem. Soc.* **1998**, *120*, 2018–2027; b) T. Kubo, M. Sakamoto, M. Akabane, Y. Fujiwara, K. Yamamoto, M. Akita, K. Inoue, T. Takui, K. Nakasuji, *Angew. Chem. Int. Ed.* **2004**, *43*, 6474–6479; *Angew. Chem.* **2004**, *116*, 6636–6641.

[10] Z. Sun, Z. Zeng, J. Wu, *Acc. Chem. Res.* **2014**, *47*, 2582–2591.

[11] a) Z. Zeng, S. Lee, J. L. Zafra, M. Ishida, X. Zhu, Z. Sun, Y. Ni, R. D. Webster, R.-W. Li, J. T. López Navarrete, C. Chi, J. Ding, J. Casado, D. Kim, J. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 8561–8565; *Angew. Chem.* **2013**, *125*, 8723–8727; b) L. Ji, R. M. Edkins, A. Lorbach, I. Krummenacher, C. Brückner, A. Eichhorn, H. Braunschweig, B. Engels, P. J. Low, T. B. Marder, *J. Am. Chem. Soc.* **2015**, *137*, 6750–6753.

[12] a) H. Langhals, *Heterocycles* **1995**, *40*, 477–500; b) F. Würthner, *Chem. Commun.* **2004**, 1564–1579; c) C. Huang, S. Barlow, S. R. Marder, *J. Org. Chem.* **2011**, *76*, 2386–2407.

[13] C. Li, H. Wonneberger, *Adv. Mater.* **2012**, *24*, 613–636.

[14] a) M. A. Iron, R. Cohen, B. Rybtchinski, *J. Phys. Chem. A* **2011**, *115*, 2047–2056; b) V. V. Roznyatovskiy, D. M. Gardner, S. W. Eaton, M. R. Wasielewski, *Org. Lett.* **2014**, *16*, 696–699.

[15] D. Schmidt, D. Bialas, F. Würthner, *Angew. Chem. Int. Ed.* **2015**, *54*, 3611–3614; *Angew. Chem.* **2015**, *127*, 3682–3685.

[16] a) J. Gao, C. Xiao, W. Jiang, Z. Wang, *Org. Lett.* **2014**, *16*, 394–397; b) S. Seifert, D. Schmidt, F. Würthner, *Chem. Sci.* **2015**, *6*, 1663–1667.

[17] M.-J. Lin, B. Fimmel, K. Radacki, F. Würthner, *Angew. Chem. Int. Ed.* **2011**, *50*, 10847–10850; *Angew. Chem.* **2011**, *123*, 11039–11042.

[18] E. Clar, *The Aromatic Sextet*, Wiley, London, **1972**.

[19] Z. Zeng, M. Ishida, J. L. Zafra, X. Zhu, Y. M. Sung, N. Bao, R. D. Webster, B. S. Lee, R.-W. Li, W. Zeng, Y. Li, C. Chi, J. T. López Navarrete, J. Ding, J. Casado, D. Kim, J. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 6363–6371.

[20] a) D. F. Evans, *J. Chem. Soc.* **1959**, 2003–2005; b) S. K. Sur, *J. Magn. Reson.* **1989**, *82*, 169–173; c) D. H. Grant, *J. Chem. Educ.* **1995**, *72*, 39–40; d) E. M. Schubert, *J. Chem. Educ.* **1992**, *69*, 62; e) J. I. Hoppe, *J. Chem. Educ.* **1972**, *49*, 505.

[21] a) Z. Sun, K.-W. Huang, J. Wu, *J. Am. Chem. Soc.* **2011**, *133*, 11896–11899; b) Z. Sun, S. Lee, K. H. Park, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, S. Das, Y. Li, C. Chi, R.-W. Li, K.-W. Huang, J. Ding, D. Kim, J. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 18229–18236; c) T. Kubo, A. Shimizu, M. Sakamoto, M.

Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Angew. Chem. Int. Ed.* **2005**, *44*, 6564–6568; *Angew. Chem.* **2005**, *117*, 6722–6726; d) A. Shimizu, M. Uruichi, K. Yakushi, H. Matsuzaki, H. Okamoto, M. Nakano, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, *Angew. Chem. Int. Ed.* **2009**, *48*, 5482–5486; *Angew. Chem.* **2009**, *121*, 5590–5594; e) J. Liu, P. Ravat, M. Wagner, M. Baumgarten, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2015**, DOI: 10.1002/anie.201502657; *Angew. Chem.* **2015**, DOI: 10.1002/ange.201502657.

[22] K. Yamaguchi, Y. Takahara, T. Fueno in *Applied Quantum Chemistry* (Eds.: V. H. Smith, Jr., H. F. Schaefer III, K. Morokuma), D. Reidel, Dordrecht, **1986**, p. 155.

[23] K. Kamada, K. Ohta, A. Shimizu, T. Kubo, R. Kishi, H. Takahashi, E. Botek, B. Champagne, M. Nakano, *J. Phys. Chem. Lett.* **2010**, *1*, 937–940.

[24] Y. Li, W.-K. Heng, B. S. Lee, N. Aratani, J. L. Zafra, N. Bao, R. Lee, Y. M. Sung, Z. Sun, K.-W. Huang, R. D. Webster, J. T. López Navarrete, D. Kim, A. Osuka, J. Casado, J. Ding, J. Wu, *J. Am. Chem. Soc.* **2012**, *134*, 14913–14922.

Received: July 29, 2015