



Halochromic and Hydrochromic Squaric Acid Functionalized Perylene Bisimide

Journal:	<i>ChemComm</i>
Manuscript ID:	CC-COM-02-2015-001691.R1
Article Type:	Communication
Date Submitted by the Author:	18-Mar-2015
Complete List of Authors:	Maeda, Takeshi; Osaka Prefecture University, Department of Applied Chemistry Würthner, Frank; Universität Würzburg, Institute of Organic Chemistry

COMMUNICATION

Halochromic and Hydrochromic Squaric Acid Functionalized Perylene Bisimide

Cite this: DOI: 10.1039/x0xx00000x

Takeshi Maeda^{*a,b} and Frank Würthner^{*a}Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

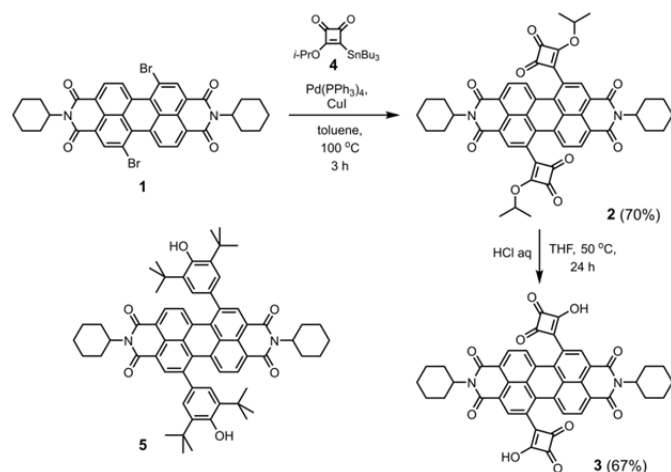
www.rsc.org/

The functionalization of perylene bisimide by squaric acid afforded halochromic dyes with pronounced acidity. The dye senses solvent polarity, pH and humidity by means of pronounced changes in absorption spectra and thin film color through the intramolecular charge transfer between perylene and cyclobutene cores initiated by protonation/deprotonation.

Perylene bisimide (PBI) dyes have attracted considerable interest due to their outstanding absorption and fluorescence properties, thermal and chemical robustness, and strong electron affinity, with the latter arising from the low-lying lowest unoccupied molecular orbital (LUMO) energy caused by electron-withdrawing imide groups.¹ Owing to these properties, PBIs are widely utilized as electron acceptors for photoinduced charge-transfer systems at the intramolecular and supramolecular levels² as well as n-type semiconductors in organic field effect transistors and solar cells.³ The absorption and fluorescence properties, in combination with the low-lying LUMO level, are also highly suitable for sensing applications. Indeed, a number of examples are given in literature for which photoinduced electron-transfer phenomena are exploited to reveal specific guest binding properties or phase transitions in polymers.⁴ Furthermore, guest-induced PBI aggregation or de-aggregation phenomena have been exploited for sensing applications⁵ as well as fluorescence energy-transfer phenomena in confined space as present in PBI-based micelles and vesicles.⁶ Whilst the latter examples from our group provided a unique ratiometric sensing system with pH-dependent blue, white or red colors,^{6b} we have to admit that this system is rather complex and hence not properly suited for practical applications as shown in literatures.⁷ Therefore, in our efforts to establish new PBI-based sensing concepts beyond the principles described before, the recently discovered pronounced halochromism in PBI **5** bearing 4-hydroxyl-3,5-di-tert-butylphenyl units at the 1,7-bay positions⁸ appeared promising to us. For these dyes it was observed that the PBI absorption band shifted from 578 nm to 1185 nm upon addition of strong bases such as tetrabutylammonium hydroxide (TBAH) which could be attributed to the formation of phenoxide anions and their strong intramolecular charge transfer to the electron poor PBI scaffold. Thus, the introduction of bay substituents whose electron donating property being altered through structural conversion in

response to the surrounding chemical conditions should confer stimuli-responsive optical properties onto PBIs. However, whilst the pronounced spectral shifts for PBI **5** nicely sense the deprotonation, this molecule is less appealing for pH sensing applications because it only responds to rather strong bases. For this reason we became interested in replacing the hydroxyphenyl substituent by a more acidic group that exhibits similarly strong electronic coupling through electron donation to the electron poor PBI scaffold. Towards this goal, 3,4-dihydroxycyclobut-1-ene-1,2-dione (squaric acid) appeared to be quite attractive because it is an oxocarbonic acid that shows appreciably high acidity originating from the resonance stabilization of its dianion form, whose 2 π -electron system is aromatic according to the Hückel rule.⁹ Squaric acid can react with nucleophiles such as activated arenes and methylene compounds to afford either mono- or disubstituted condensation products known as semi-squaraines and squaraines.^{10,11} Owing to the high acidity of the remaining hydroxyl groups after condensation of squaric acid, semi-squaraines could be successfully utilized for proton-exchange membranes in fuel cells and photosensitizers for TiO₂-based solar cells in which squaric acid residues act as anchors for TiO₂.¹² Herein we report that the newly designed PBI dye **3** (Scheme 1) bearing 3-hydroxycyclobutenedione moieties at the 1,7 bay positions indeed displays an impressive sensitivity to pH changes, solvent polarity and even humidity.

Organometallic C-C cross-coupling reactions have been amply employed for the preparation of substituted rylene bisimides having functional groups other than the squaric acid residue.^{13,14} We have approached the synthesis of our target PBIs containing squaric acid residues by cross-coupling reaction utilizing a stannyl derivative of squaric acid.¹⁵ As shown in Scheme 1, the synthesis of PBI **3** could be accomplished in a quite straightforward manner starting from stannyl cyclobutenedione derivative **4** and 1,7-dibrominated PBI **1**¹⁶ in a Stille-type cross-coupling reaction and subsequent acidic hydrolysis of the isopropoxy precursor **2**. It is noteworthy that PBI **2** is highly soluble in common organic solvents such as chloroform, dichloromethane, toluene, acetone, THF, and DMSO which is presumably entailed by the sterically demanding squaric acid residues that prohibit π -stacking of the PBIs.¹⁷ In contrast, PBI **3** is insoluble in chlorinated solvents and toluene but displays exceptional solubility in polar solvents, including DMSO, DMF, acetone, THF, methanol, and water.



Scheme 1. Synthesis of PBIs **2** and **3** bearing squaric acid residues.

PBIs **2** and **3** show broad absorption bands in THF attributed to S_0-S_1 transition with maxima at 569 nm and 570 nm, respectively (Fig. 1). Compared to the absorption maximum of the parent PBI chromophore ($\lambda_{\max} = 522$ nm in THF¹⁸), these bands are bathochromically shifted with significant band broadening. These spectral features can be explained by an electron donating effect of the squaric acid substituents at the 1,7 positions of PBIs **2** and **3** which is even stronger than given by 1,7-diphenoxy substituents ($\lambda_{\max} \sim 550$ nm¹⁷). In contrast to common PBIs and also to PBI **2**, pronounced differences in the UV/Vis spectra are observed for PBI **3** upon variation of the solvent (Fig. 1). Thus, whilst the absorption spectrum of **3** in acetone ($\lambda_{\max} = 565$ nm) is comparable to that in THF, the lowest energy absorption band in DMSO and DMF (both with $\lambda_{\max} = 667$ nm) are bathochromically shifted with a concomitant broadening of the band and a decrease of absorption intensity. The use of methanol and water as solvents leads to less spectrally displaced, almost structureless spectra and a reduction of molar absorptivity. Thus, **3** displays an apparent solvent effect in its absorption property as a consequence of the introduction of acidic squaric acid residues.

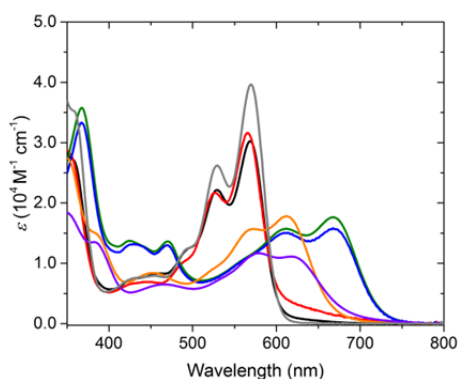


Fig. 1 Absorption spectra of **2** (gray) in THF and **3** in THF (black), acetone (red), methanol (orange), water (purple), DMF (blue), and DMSO (green).

To shed light into the origin of these spectral changes, we monitored the absorption spectral changes in THF upon successive addition of up to 3 equivalents of Hünig's base (Fig. 2A). An increase in the amount of the added base resulted in the emergence of an absorption band with a maximum at 641 nm, in conjunction

with a decrease of the original absorption of **3**. The well-defined transformation from the original to the final UV/Vis spectra upon base addition could be attributed to the conjugate base of **3** formed by the deprotonation at squaric acid residues. Upon subsequent addition of trifluoroacetic acid (TFA), the original absorption of **3** reappears with concomitant decrease of absorption of deprotonated species (Fig. 2B). Whilst two molar equivalents of Hünig's base were sufficient to completely transform the bifunctional PBI **3** into its dianion, the neutralization required a large excess of TFA (ca. 3000 equiv.), indicating that acid-base equilibrium is biased towards the formation of the conjugate base form (3^{2-}). The acidity of **3** was further evaluated in a THF-water mixture by titration experiments and evaluation of the pH-dependency of the absorbance using the least-square method (Fig. S1). PBI **3** proved to exhibit the expected high acidity with values of $pK_{a1} = -0.3$ and $pK_{a2} = 2.7$ that are close to those of sulfuric acid ($pK_{a1} = -3$ and $pK_{a2} = 1.9$). The pK_{a1} value of **3** is also comparable to that previously reported for semisquaric acid with electron withdrawing functionality indicating that a strong $-M$ effect of the PBI scaffold contributes to the high acidity.¹⁹ The pK_{a2} for the second deprotonation is decreased, probably due to delocalization of the first deprotonated state along the π -scaffold.

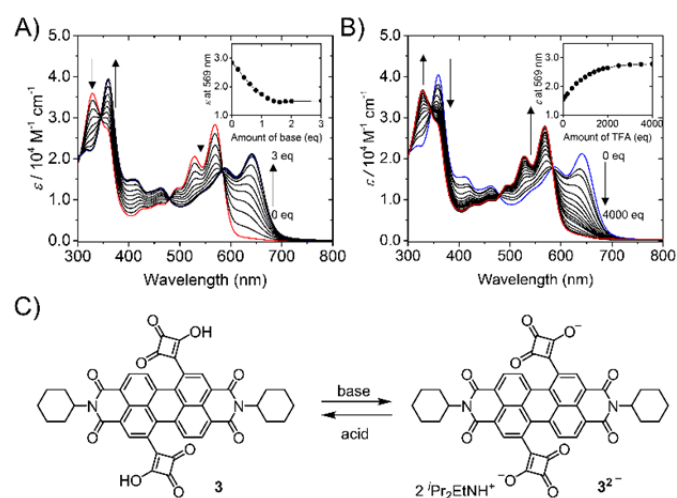


Fig. 2 Absorption spectral change of **3** upon addition of Hünig's base (diisopropylethylamine) (A) and the consecutive addition of TFA (B). Insets show the apparent extinction coefficient at 569 nm vs molar equivalents of Hünig's base and TFA. A scheme for the interconversion of **3** and its conjugate base 3^{2-} through the addition of base and acid is also shown (C).

In general, the absorption properties of PBIs are rarely dependent on the environmental conditions such as solvents.¹ Insensitivity of the absorption properties toward solvent polarity indicates that the optical transitions are not attributable to dipolar charge-transfer character. Accordingly, solvents have no significant influence on the absorption properties of the acidic form **3** as shown for THF, acetone, or methanol-TFA mixture ($\lambda_{\max} \sim 570$ nm). In contrast, the conjugate base form 3^{2-} shows distinguishable absorption spectra in various solvent systems such as methanol ($\lambda_{\max} = 612$ nm), acetone-Hünig's base ($\lambda_{\max} = 623$ nm), THF-Hünig's base ($\lambda_{\max} = 641$ nm), DMF ($\lambda_{\max} = 667$ nm), and DMSO ($\lambda_{\max} = 667$ nm) (Fig. S2, Table S1). Thus, the absorption properties of 3^{2-} are prone to a significant solvent effect. The exceptional solubility of PBI **3** in polar solvents suggests that the squaric acid residues were strongly solvated in their basic form, supporting the solubilization of hydrophobic PBI cores in these solvents.

In order to obtain insights into the origin of the halochromism of **3**, the electron distribution of the frontier orbitals of **3** was calculated by the density functional method at the rB3LYP/6-31+G(d) level.²⁰ According to these calculations, both the HOMO and LUMO are delocalized on the entire PBI scaffold, resembling the frontier orbitals of the parent PBI with an additional extension on the cyclobutenedione cores (Fig. 3, Fig. S6). In striking contrast to **3**, deprotonated **3**²⁻ shows a clear spatial separation of the HOMO and LUMO. Thus, whilst the LUMO still resembles the one of PBI **3** and other PBIs, the HOMO of deprotonated **3**²⁻ is mainly located on the cyclobutenedione subunits. This indicates that the bathochromically shifted absorption of **3**²⁻ is attributable to an intramolecular charge-transfer transition from deprotonated electron-rich squaric acid residues to the electron-deficient PBI core. In this regard PBI **5**²⁻ with phenolate substituents at the bay region provided similar effects. The by far higher acidity of squaric acid compared to phenol, however, should enable more interesting responsiveness of PBI **3** towards ambient conditions, which is indeed the case as shown in the following.

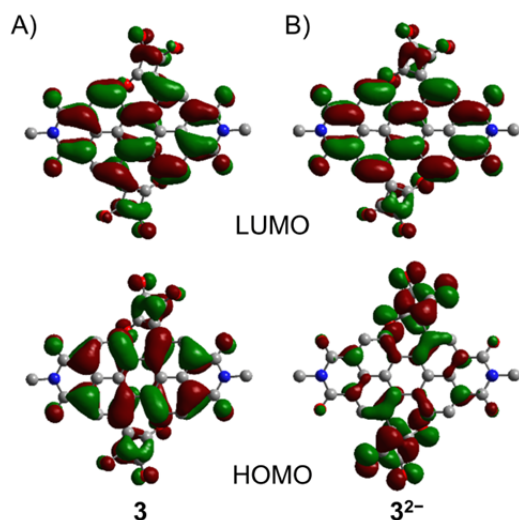


Fig. 3 Electron distribution of frontier orbitals of **3** (A) and its conjugate base form **3**²⁻ (B) optimized at rB3LYP/6-31+G(d) level.

A closer inspection of the absorption spectrum of **3** in THF shown in Fig. 1 reveals a weak absorbance at the low energy edge (ca. 630 nm), which is appreciably enhanced at the lower concentration of 2×10^{-6} M (Fig. S3). This indicates that **3** is partially deprotonated and existing as its conjugate base at the lower concentration because of residual water traces in THF solvent (Fig. S4). Indeed, upon addition of small amounts of water (up to 15 vol%) a change of the absorption spectra was observed that complies with the transformation of **3** to **3**²⁻ (Fig. 4A). This effect is not limited to THF solvent but can be transferred to polymeric matrices as shown in Fig. 4B. A thin film consisting of **3** and hydrophilic polyethylene glycol (PEG, $M_w = 2000$) was fabricated by spin casting of the dissolved components from a chloroform solution onto a quartz glass substrate. Interestingly, the initial red-purple color of the film changed instantaneously into blue-green upon exposure to humid air. The red-purple film could be regenerated by drying of the humidified film. The hydrophilic PEG matrix is known to swell on exposure to water. This process can be colorimetrically monitored by dye **3** which is converted to its conjugate base form **3**²⁻ similarly as observed in THF solution. The color change originating from the dissociation of acidic proton at squaric acid residues was reasonably

fast and reversible (Movie S1). We further explored the impact of different humidity levels on the absorption spectra of the PBI/PEG film (Fig. S5). According to these studies the absorption spectrum of the dried film is almost identical to that of the film at the relative humidity of 40%. Then a pronounced change of absorption occurred with increase of humidity level from 40% to 50% whilst at higher humidity levels up to 90% again only small changes are observed. Accordingly, there is a “switch-on” response of PBI/PEG films at humidity levels of about 50%.

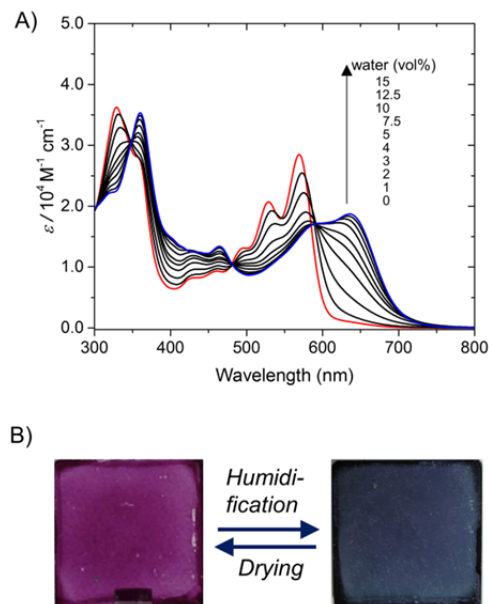


Fig. 4. A) Absorption spectral changes of **3** in THF upon increasing water content. B) Photographs of **3** in a PEG matrix indicating the reversible color change upon the cycle of humidification and drying.

In conclusion, a novel PBI derivative **3** bearing squaric acid residues as bay substituents showed pronounced halochromic properties due to a change in the electron-donation strength caused by protonation and deprotonation at hydroxyl groups on the cyclobutene skeleton. Owing to the high acidity of the squaric acid residues, the deprotonation occurred already in moderately basic solvents and even by traces of water in THF or PEG matrix. Thus, PBI **3** exhibits the property known as hydrochromism²¹ that was shown to be useful for colorimetric humidity sensing.

Notes and references

^aUniversität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg, Germany. E-mail: wuerthner@chemie.uni-wuerzburg.de

^bOsaka Prefecture University, Department of Applied Chemistry, Graduate School of Engineering, Naka-ku, Sakai 599-8531, Japan. E-mail: tmaeda@chem.osakafu-u.ac.jp

Electronic Supplementary Information (ESI) available: Synthetic details and product characterization; NMR ESI-MS; pH-dependent absorption spectra, detailed data for halochromic effect; spectral study upon dilution in THF; a movie for humidity sensing; DFT calculations. See DOI: 10.1039/c000000x/

- 1 (a) S. Huang, S. Barlow, and S. R. Marder, *J. Org. Chem.*, 2011, **76**, 2386–2407; (b) F. Würthner, *Chem. Commun.*, 2004, 1564–1579; (c) H. Langhals, *Heterocycles*, 1995, **40**, 477–500.
- 2 (a) V. M. Blas-Ferrando, J. Ortiz, L. Bouissane, K. Ohkubo, S. Fukuzumi, F. Fernandez-Lazaro, and A. Sastre-Santos, *Chem. Commun.*, 2012, **48**, 6241–6243; (b) J. Huang, Y. Wu, H. Fu, X. Zhan, J. Yao, S. Barlow, and S. R. Marder, *J. Phys. Chem. A*, 2009, **113**, 5039–5046; (c) E. H. Beckers, S. C. J. Meskers, P. H. J. Schenning, Z. Chen, F. Würthner, M. Marsal, D. Beljonne, J. Cornil, and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2006, **128**, 649–657; (d) M. P. O’Neil, M. P. Niemczyk, W. A. Svec, D. Gosztola, G. L. Gaines III, and M. R. Wasielewski, *Science*, 1992, **257**, 63–65.
- 3 (a) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, and S. R. Marder, *Adv. Mater.*, 2011, **23**, 268–284; (b) F. Würthner, and M. Stolte, *Chem. Commun.*, 2011, **47**, 5109–5115.
- 4 (a) E. A. Stephen, S. W. Morton, P. H. Hammond, and T. M. Swager, *Adv. Mater.*, 2013, **25**, 4504–4510; (b) M. Xu, J.-M. Han, Y. Zhang, X. Yang, and L. Zang, *Chem. Commun.*, 2013, **49**, 11779–11781; (c) D. Aigner, S. M. Borisov, P. Petritsch, and I. Klimant, *Chem. Commun.*, 2013, **49**, 2139–2141; (d) J. R. Siekierzycka, C. Hippus, F. Würthner, R. M. Williams, and A. M. Brouwer, *J. Am. Chem. Soc.*, 2010, **132**, 1240–1242; (e) Y. Che, X. Yang, S. Loser, and L. Zang, *Nano Lett.*, 2008, **8**, 2219–2223; (f) L. Zang, R. Liu, M. Holman, K. Nguyen, and D. A. Adams, *J. Am. Chem. Soc.*, 2002, **124**, 10640–10641.
- 5 (a) X. Feng, Y. An, Z. Yao, C. Li, and G. Shi, *ACS Appl. Mater. Interfaces*, 2012, **4**, 614–618; (b) B.-P. Jiang, D.-S. Guo, and Y. Liu, *J. Org. Chem.*, 2010, **75**, 7258–7264.
- 6 (a) X. Zhang, D. Görl, and F. Würthner, *Chem. Commun.*, 2013, **49**, 8178–8180; (b) X. Zhang, S. Rehm, M. M. Safont-Sempere, and F. Würthner, *Nature Chem.*, 2009, **1**, 623–629.
- 7 (a) S. Rivadehl, E. F. Reid, C. F. Hogan, S. V. Bhosale, and S. J. Langford, *Org. Biomol. Chem.*, 2012, **10**, 705–709; (b) C. Vijayakumar, G. Tobin, W. Schmitt, M.-J. Kim, and M. Takeuchi, *Chem. Commun.*, 2010, **46**, 874–876.
- 8 M.-J. Lin, B. Fimmel, K. Radacki, and F. Würthner, *Angew. Chem. Int. Ed.*, 2011, **50**, 10847–10850.
- 9 (a) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, 1959, **81**, 3480; (b) G. Maahs, and P. Hegenberg, *Angew. Chem. Int. Ed.*, 1966, **5**, 888–893; (c) R. Gelb, *Anal. Chem.*, 1971, **43**, 1110–1113.
- 10 (a) R. R. Avirah, K. Jyothish, C. H. Suresh, E. Suresh, and D. Ramaiah, *Chem. Commun.*, 2011, **47**, 12822–12824; (b) M. W. Reed, D. J. Pollart, S. T. Perri, L. D. Foland, and H. W. Moore, *J. Org. Chem.*, 1988, **53**, 2477–2482; (c) L. S. Liebesking, R. W. Fengele, K. R. Wirtz, and T. T. Shawe, *J. Org. Chem.*, 1988, **53**, 2482–2488; (d) E. Terpetschnig, and J. R. Lakowicz, *Dyes Pigms.*, 1993, 227–234; (e) L. S. Liebesking, and J. Zhang, *J. Org. Chem.*, 1991, **56**, 6379–6385.
- 11 (a) L. Beverina, and P. Salice, *Eur. J. Org. Chem.*, 2010, 1207–1225; (b) J. J. Gassensmith, J. M. Baumes, and B. D. Smith, *Chem. Commun.*, 2009, 6329–6338; (c) S. Sreejith, P. Carol, P. Chithra, and A. Ajayaghosh, *J. Mater. Chem.*, 2008, **18**, 264–274; (d) S. Yagi, and H. Nakazumi, *Top. Heterocycl. Chem.*, 2008, **14**, 133–181.
- 12 (a) H. Nakao, T. Maeda, and H. Nakazumi, *Chem. Lett.*, 2013, **42**, 25–27; (b) K. Yoshimura, and L. S. Liebeskind, *Macromol. Rapid Commun.*, 2010, **31**, 1725–1730.
- 13 (a) S. Ito, S. Hiroto, and H. Shinokubo, *Org. Lett.*, 2013, **15**, 3110–3113; (b) Z. An, S. A. Odom, R. F. Kelley, C. Huang, X. Zhang, S. Barlow, L. A. Padilha, J. Fu, S. Webster, D. J. Hagan, E. W. Van Stryland, M. R. Wasielewski, and S. R. Marder, *J. Phys. Chem. A*, 2009, **113**, 5585–5593; (c) H. Qian, F. Negri, C. Wang, and Z. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 17970–17976; (d) W. Qiu, S. Chen, X. Sun, Y. Liu, and D. Zhu, *Org. Lett.*, 2006, **8**, 867–870; (e) U. Rohr, P. Schlichting, A. Böhm, M. Gross, K. Meerholz, C. Bräuchle, and K. Müllen, *Angew. Chem. Int. Ed.*, 1998, **37**, 1424–1437; (f) U. Rohr, C. Kohl, K. Müllen, A. van de Craats, and J. Warman, *J. Mater. Chem.*, 2001, **11**, 1789–1799; (g) Y. Avlasevich, S. Müller, P. Erk, and K. Müllen, *Chem. Eur. J.*, 2007, **13**, 6555–6561; (h) S. Müller, and K. Müllen, *Chem. Commun.*, 2005, 4045–4046.
- 14 (a) E. Sariola-Leikas, M. Niemi, H. Lemmetyinen, and A. Efimov, *Org. Biomol. Chem.*, 2013, **11**, 6397–6406; (b) L. E. Polander, A. S. Romanov, S. Barlow, D. K. Hwang, B. Kippelen, T. V. Timofeeva, and S. R. Marder, *Org. Lett.*, 2012, **14**, 918–921; (c) S. Dey, A. Efimov, and H. Lemmetyinen, *Eur. J. Org. Chem.*, 2011, 5955–5958.
- 15 L. S. Liebesking, and R. W. Fengele, *J. Org. Chem.*, 1990, **55**, 5359–5364.
- 16 F. Würthner, V. Stepanenko, Z. Chen, C. R. Saha-Möller, N. Kocher, and D. Stalke, *J. Org. Chem.*, 2004, **69**, 7933–7939.
- 17 Á. J. Jiménez, M.-J. Lin, C. Burschka, J. Becker, V. Settels, B. Engels, and F. Würthner, *Chem. Sci.*, 2014, **5**, 608–619.
- 18 Z. Chen, B. Fimmel, and F. Würthner, *Org. Biomol. Chem.*, 2012, **10**, 5845–5855.
- 19 (a) L. S. Liebesking, M. S. Yu, and R. W. Fengele, *J. Org. Chem.*, 1993, **58**, 3543–3549; (b) E. J. Smutny, M. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, 1960, **82**, 1793–1801.
- 20 Gaussian 09, for further information see the Supporting Information.
- 21 (a) S. Yamaguchi, and Y. Sasaki, *J. Phys. Chem. B*, 2000, **104**, 9225–9229; (b) L. Sheng, M. Li, S. Zhu, H. Li, G. Xi, Y.-G. Li, Y. Wang, Q. Li, S. Liang, K. Zhong, and S. X.-A. Zhang, *Nature Commun.*, 2014, **5**, 3044.