# Tetralithiated Tetraazaperopyrene as a Key Intermediate for the Synthesis of Functionalized Derivatives

Lena Hahn, Hubert Wadepohl, and Lutz H. Gade*

Anorganisch-Chemisches-Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

S *Supporting Information*

ABSTRACT: A new synthetic approach to core-functionalized tetraazaperopyrenes (TAPP) is reported. In-situ reaction of 4-fold lithiated TAPP with electrophiles results in the formation of various unprecedented TAPP derivatives, which are highly emissive fluorophores, show promising photophysical and electrochemical properties and act as valuable starting materials. Thus, lithiation of the TAPP core opens up a facile way for developing new organic materials.

E = PPh$_2$, SnR$_3$, SiMe$_3$, I   R = CF$_3$, F
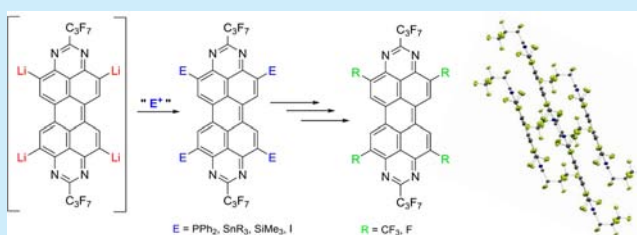
Over the past one and a half decades the field of organic materials has experienced a remarkably dynamic development. Much of the attention has been devoted to polycyclic aromatic hydrocarbons (PAH),[1−3] and among these particularly to perylene-3,4,9,10-tetracarboxydiimides (PDIs)[4−6] and naphthalenediimides (NDIs)[7] due to their manifold applications as functional fluorescence dyes or as organic semiconductors in transistors or light emitting diodes (LED).[8,9] Modification at the core positions has proven to be most effective in altering the photo- and redoxchemical properties of PAHs.[4,10−13] For example, the current strategy to obtain air stable n-type semiconductors with appropriately low LUMO energies is the introduction of suitably placed electron withdrawing groups to the polycyclic aromatic core resulting in lowering of LUMO energies.[14−19]

Several years ago we developed an efficient synthesis for 1,3,8,10-tetraazaperopyrenes (TAPP) which possess photophysical and electrochemical properties found to be related to the intensely studied PDIs.[20,21] TAPP derivatives have given promising results as biological fluorescence markers as well as organic semiconductors.[22−24]

Key intermediates in the synthesis of the latter have been 4-fold core chlorinated as well as brominated TAPP derivatives[22,23] which have proven to be excellent starting materials for a range of transformations such as nucleophilic substitutions, cross-coupling reactions and Buchwald Hartwig aminations.[12] However, in the functionalization of TAPPs, these synthetic modifications remained primarily restricted to the introduction of aryl and alkyne substituents. The introduction of other, especially of electron-withdrawing substituents, such as fluoro or trifluoromethyl groups by transition metal catalyzed reactions, remained unsuccessful. Therefore, a fundamentally different approach for further derivatization of the TAPP core was required.

We herein report a convenient method for the synthesis of a wide range of functionalized TAPP derivatives which is complementary to the previously established synthetic strategies. This is based on the lithiation of the TAPP core in the 4,7,11,14-

positions and the subsequent reaction with electrophilic reagents (Scheme 1). Furthermore, some of the products obtained via this route serve as starting materials for the synthesis of other previously inaccessible TAPPs.

**Scheme 1. Synthetic Strategy to Core-Functionalized TAPP Derivatives**
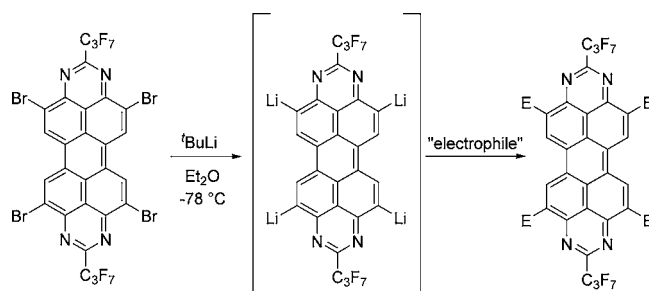
Lithiation was achieved by treatment of the previously reported 4-fold brominated TAPP with an excess of *tert*-butyllithium in ether at −78 °C and the 4-fold lithiated TAPP was then reacted in situ with a range of electrophiles. All attempts to isolate the tetralithiated species in the presence of coligands/donor solvents have been unsuccessful.[25,26] The reported reaction conditions are the result of an extensive screening and optimization process.

Whereas reaction with diphenylphosphine chloride resulted in the formation of **1** as an air and moisture sensitive red solid, addition of an excess of trimethylsilyl chloride as well as the reaction with trimethyl- and tri(*n*-butyl)tin chloride, resulted in the formation of compounds **2-4**, respectively which were isolated as yellow powders after column chromatography (Scheme 2). Single crystals of the tri(*n*-butyl)stannylated derivative **4** suitable for X-ray diffraction where grown from a
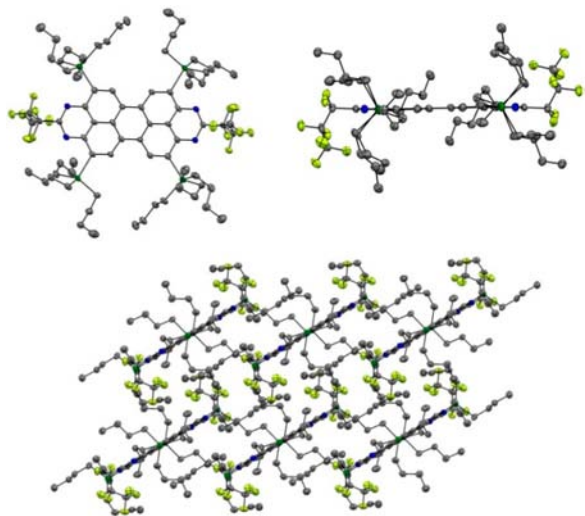
Scheme 2. Functionalization of the TAPP Core
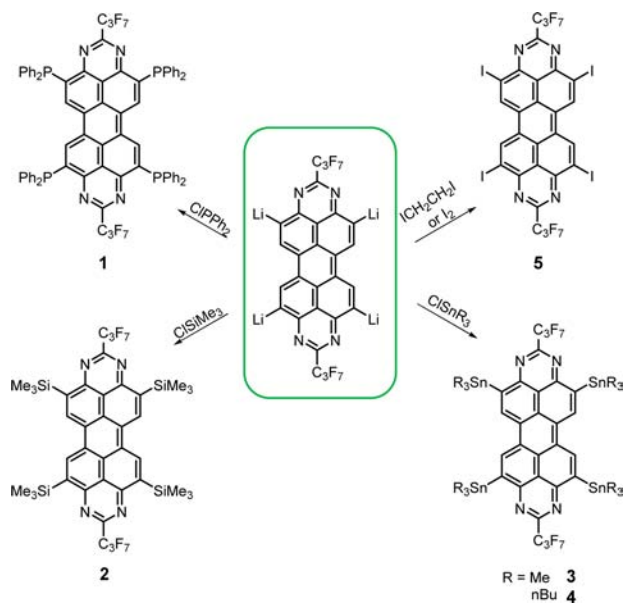
concentrated solution of the compound in acetone. Two views of its molecular structure are displayed in Figure 1. The

Figure 1. Molecular structure of **4**. View orthogonal to the aromatic core (top left) and along the principal axis side view (top right) and side view of packing pattern (bottom). Thermal ellipsoids are drawn at a 55% probability level; hydrogen atoms were omitted for clarity.

tetraazaperopyrene core is almost planar with the two perfluoropropyl groups pointing in opposite directions above and below the tetraazaperopyrene plane. The intermolecular packing pattern is characterized by a slip-stacked face-to-face arrangement as found for other TAPP derivatives. The interplanar distance of 7.03 Å, however, is much greater than observed for other core substituted TAPPs[12,22,23] which is probably due to the steric demand of the butyl groups preventing efficient π-stacking.

Iodination of the TAPP core to give compound **5** was achieved by reacting lithiated TAPP with sources of electrophilic iodine, such as 1,2-diiodoethane or I₂. On the other hand, the analogous synthesis of fluorinated and trifluoromethylated derivatives using "F⁺" and "CF₃⁺" sources was unsuccessful. These transformations

were of particular interest since both fluorination and introduction of perfluorinated alkyl groups were expected to significantly stabilize the LUMO energy level in such aromatics, thus rendering those TAPP derivatives potentially interesting compounds for the application as n-type semiconductors. Therefore, alternative reaction pathways were explored.

4-fold fluorination of the TAPP core was achieved by following a Ag-catalyzed fluorination protocol reported by Ritter et al.[27] using the stannylated derivative **4** as starting material (Scheme 3,

Scheme 3. Fluorination (Top) and Trifluoromethylation (Bottom) of the TAPP Core (phen = Phenanthroline)
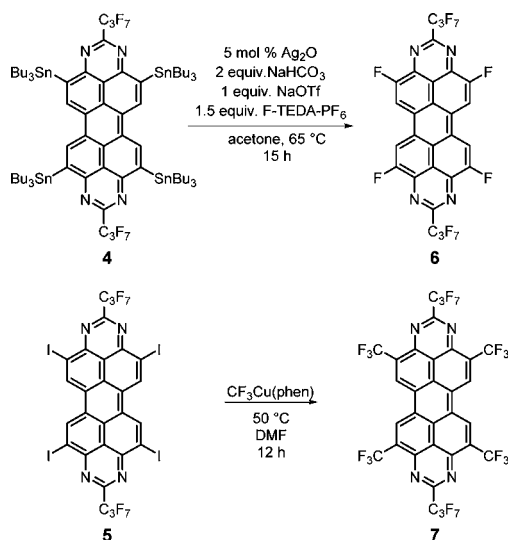
top). NMR spectroscopy revealed full conversion of **4**, however in addition to the 4-fold fluorinated compound **6** approximately 8% of partially protodestannylated byproduct was formed. The pure target product was obtained by recrystallization from chloroform. Trifluoromethylation of the 4,7,11,14-positions was achieved via a synthetic protocol by Hartwig et al.[28] using a trifluoromethylcopper(I) complex as CF₃-source and **5** as starting material (Scheme 3, bottom). The tetrakis-(trifluoromethyl)TAPP-derivative **7** was obtained in 63% yield after aqueous work up. Notably, all attempts to synthesize **7** by the same route but using the core brominated TAPP proved to be unsuccessful.

Single crystals suitable for X-ray diffraction were grown from a solution of **7** in toluene. The molecular structure of **7** is shown in Figure 2. As in the crystal structure of compound **4**, the two axial perfluoralkyl groups are pointing in opposite directions above and below the TAPP plane. The intermolecular packing pattern of **7** also corresponds to a slip-stacked face-to-face arrangement with a interplanar distance of 3.61 Å which is greater than the corresponding value observed for the tetrachlorinated and tetrabrominated derivatives (3.38 and 3.39 Å, respectively).

The UV/vis absorption spectra of compounds **1**−**7** were recorded in THF (Figure 3). The absorption maxima are in the range of 427−519 nm. Compounds **1**−**6** display bathochromic shifts in comparison to the parent core unsubstituted C₃F₇−TAPP (436 nm) with absorption maxima of 452, 453, 459, 468, 494, and 519 nm, respectively, while compound **7** displays a hypsochromic shift with absorption maxima of 427 nm.

Compounds **2**, **3**, **5**, and **6** were found to be fluorescent, and the emission spectra recorded in THF are shown in Figure 3. While compounds **2**, **3**, and **6** displayed strong emission bands at
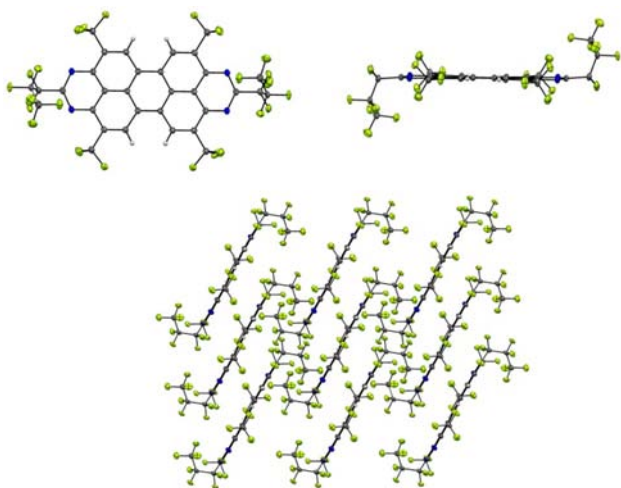
Figure 2. Crystal structure of **7**. Side view (top left), top view (top right), and side view of packing pattern (bottom).
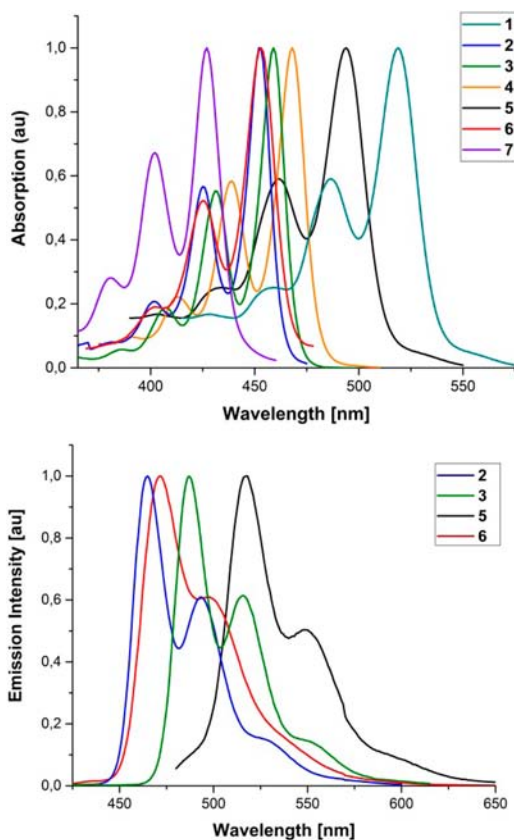

Figure 3. Normalized UV/vis spectra of compounds **1–7** in THF (top) and fluorescence spectra of **2**, **3**, **5**, and **6** (bottom).

465, 486, and 471 nm with quantum yields of 59%, 68%, and 70%, respectively, compound **5** is only weakly fluorescent (ϕ = 0.02). In contrast, compounds **1**, **4**, and **7** exhibit no fluorescence. The nonfluorescent nature of compound **7**, even at high dilution, has been unexpected. We tentatively attribute this behavior to nonradiative deactivation due to internal rotation of the CF_3 groups. An overview of the optical properties is given in Table 1.

To elucidate the influence of the substituents on the energy levels of the molecular frontier orbitals, the electrochemical properties of compounds **2**, **3**, **5**, **6**, and **7** were investigated by

Table 1. Photophysical Properties of 1–7 Recorded in THF

	λ_{max} (abs) (nm) (log ε)	λ_{max} (em) (nm) (Stokes shift)	ϕ_{Em}
1	519 (4.44)		
2	452 (4.94)	465 (619 cm^{-1})	0.68
3	459 (4.93)	486 (1210 cm^{-1})	0.59
4	468 (4.93)		
5	494 (4.93)	518 (938 cm^{-1})	0.02
6	453 (4.82)	471 (844 cm^{-1})	0.70
7	427 (4.54)		

cyclic voltammetry (CV).[29] The cyclic voltammograms of compounds **2**, **3**, **5**, and **6** display two reversible reduction waves indicating the formation of stable mono- and dianions, respectively (Figure 4). The data derived from CV measurements are summarized in Table 2.
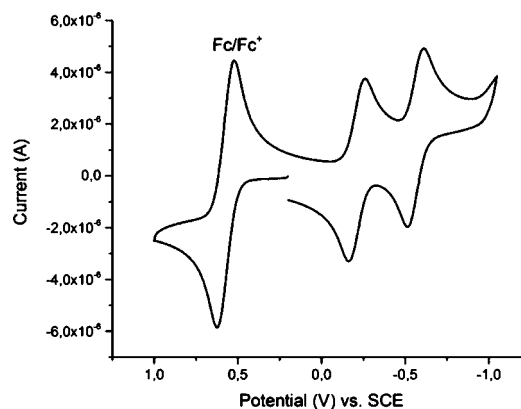

Figure 4. Cyclic voltammogram of **5** recorded in THF (sweep rate 50 mVs^{-1}; supporting electrolyte Bu$_4$NPF$_6$, reference SCE).

Table 2. Electronic Properties of TAPPs

	$E_{red1}{}^a$ (V)	$E_{red2}{}^a$ (V)	$E_{LUMO}{}^b$ (eV)	$E_{LUMO}{}^c$ (eV)	EA^c (eV)
2	−0.64	−1.12	−3.70	−3.45	2.49
3	−0.66	−1.11	−3.67	−3.41	2.49
5	−0.26	−0.61	−4.02	−4.00	3.28
6	−0.37	−0.81	−3.92	−3.93	3.03
7	−0.35	−0.53	−4.32	−4.44	3.40

^{a}Measured against SCE in THF. ^{b}Determined according to literature methods using Fc/Fc$^+$ as an internal standard (E_{HOMO}(Fc) = −4.8 EV).[29] ^{c}Calculated at the B3LYP/def2-SVP level of theory.

DFT modeling of the electronic properties was carried out to gain additional information about the electron affinity of the compounds. The LUMO energies as well as the electron affinity serve as useful parameters to assess the potential suitability of an organic molecule as an n-type semiconductor.

As observed previously, the nature of the core substituents significantly influences the LUMO energy levels of the functionalized TAPPs. Comparing the LUMO energies of compounds **5–7** (Table 2) to that of the parent unsubstituted C_3F_7–TAPP derivative (3.72 eV) illustrates the degree to which the introduction of electron-withdrawing groups results in reduced LUMO energies. This effect is especially pronounced for the trifluoromethyl-substituted TAPP **7** with a LUMO level as low as −4.32 eV, the lowest determined for a TAPP derivative so far and approaching the values found for fullerenes (for example, C$_{60}$: −4.5 eV). The electrochemical properties suggest

that compounds **5**, **6**, and **7** could be very promising materials for the application as n-type semiconductors.

In summary, the synthetic approach via a 4-fold lithiated TAPP as key intermediate provides a route to previously inaccessible core-substituted derivatives. These display promising photophysical and electrochemical properties and, as shown for the conversions of the stannylated and iodinated TAPPs, may serve as versatile starting materials for the synthesis of other novel TAPPs. Moreover, compounds **6** and **7** provide rare examples[30] in which multiple fluorinations and trifluoromethylations have been selectively achieved using the recently established novel synthetic protocols by Ritter[27] and Hartwig.[28] Future work in our laboratory will focus on the properties of some of these systems as n-type semiconductors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lutz.gade@uni-hd.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Müllen, K., Scherf, U., Eds. In *Organic Light Emitting Devices, Synthesis Properties and Applications*; Wiley-VCH: Weinheim, 2005. (b) Klauk, H. *Organic Electronics: Materials, Manufacturing, and Applications*; Wiley-VCH: Weinheim, 2006.

(2) Reviews: (a) Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037. (b) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (c) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296. (d) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070. (e) Katz, H. E.; Huang, J. *Annu. Rev. Mater. Res.* **2009**, *39*, 71. (f) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586. (g) Klauk, H. *Chem. Soc. Rev.* **2010**, *39*, 2643. (h) Würthner, F.; Meerholz, K. *Chem.—Eur. J.* **2010**, *16*, 9366. (i) Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Müllen, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 9068. (j) Görl, D.; Zhang, X.; Würthner, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 6328.

(3) Selected references: (a) Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363. (b) Würthner, F.; Schmidt, R. *ChemPhysChem* **2006**, *7*, 793. (c) Guo, X.; Ortiz, R. P.; Zheng, Y.; Hu, Y.; Noh, Y.-Y.; Baeg, K.-J.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 1405−1418. (d) Peneva, K.; Mihov, G.; Nolde, F.; Rocha, S.; Hotta, J.; Braeckmans, K.; Hofkens, J.; Uji-i, H.; Herrmann, A.; Müllen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3372.

(4) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386.

(5) Würthner, F. *Chem. Commun.* **2004**, 1564.

(6) Li, C.; Wonneberger, H. *Adv. Mater.* **2012**, *24*, 613.

(7) Suraru, S.-L.; Würthner, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 7428.

(8) Reviews: (a) Würthner, F.; Stolte, M. *Chem. Commun.* **2011**, *47*, 5109. (b) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876.

(9) Selected references: (a) Quante, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1323. (b) Laquindanum, J. G.; Katz, H. E.; Dodabalapur, A.; Lovinger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 11331. (c) Lee, S. K.; Zu, Y.; Herrmann, A.; Geerst, Y.; Müllen, K.; Bard, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 3513. (d) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119. (e) Ahrens, M. J.; Fuller, M. J.; Wasielewski, M. R. *Chem. Mater.* **2003**, *15*, 2684. (f) Zhan, E.; Tan, Z. A.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 7246. (g) Lindner, S. M.; Kaufmann, N.; Thelakkat, M. *Org. Electron.* **2007**, *8*, 69. (h) Liu, C.; Liu, Z.; Lemke, H. T.; Tsao, H. N.; Naber, R. C. G.; Li, Y.; Banger, K.; Müllen, K.; Nielsen, M. M.; Sirrringhaus, H. *Chem. Mater.* **2010**, *22*, 2120. (i) Gsänger, M.; Oh, J. H.; Könemann, M.; Höffken, H. W.; Krause, A.-M.; Bao, Z.; Würthner, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 740. (j) Görl, D.; Zhang, X.; Würthner, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 6328.

(10) Bhosale, S. V.; Jani, C. H.; Langford, S. J. *Chem. Soc. Rev.* **2008**, *37*, 331.

(11) Röger, C.; Würthner, F. *J. Org. Chem.* **2007**, *72*, 8070.

(12) Geib, S.; Martens, S. C.; Märken, M.; Rybina, A.; Wadepohl, H.; Gade, L. H. *Chem.—Eur. J.* **2013**, *19*, 13811.

(13) Dubey, R. K.; Westerveld, N.; Grozema, F. C.; Sudhölter, E. J. R.; Jager, W. F. *Org. Lett.* **2015**, *17*, 1882.

(14) Bao, Z.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207.

(15) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. *Nature* **2007**, *445*, 745.

(16) Oh, J. H.; Suraru, S.; Lee, W.-Y.; Könemann, M.; Höffken, H. W.; Röger, C.; Schmidt, R.; Chung, Y.; Chen, W.-C.; Würthner, F.; Bao, Z. *Adv. Funct. Mater.* **2010**, *20*, 2148.

(17) Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Könemann, M.; Erk, P.; Bao, Z.; Würthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6215.

(18) Weitz, R. T.; Amsharov, K.; Zschieschang, U.; Villas, E. B.; Goswami, D. K.; Burghard, M.; Dosch, H.; Jansen, M.; Kern, K.; Klauk, H. *J. Am. Chem. Soc.* **2008**, *130*, 4637.

(19) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268.

(20) Riehm, T.; De Paoli, G.; Konradsson, A. E.; De Cola, L.; Wadepohl, H.; Gade, L. H. *Chem. - Eur. J.* **2007**, *13*, 7317.

(21) Martens, S. C.; Riehm, T.; Geib, S.; Wadepohl, H.; Gade, L. H. *J. Org. Chem.* **2011**, *76*, 609.

(22) Martens, S. C.; Zschieschang, U.; Wadepohl, H.; Klauk, H.; Gade, L. H. *Chem.—Eur. J.* **2012**, *18*, 3498.

(23) Geib, S.; Zschieschang, U.; Gsänger, M.; Stolte, M.; Würthner, F.; Wadepohl, H.; Klauk, H.; Gade, L. H. *Adv. Funct. Mater.* **2013**, *23*, 3866.

(24) Hahn, L.; Öz, S.; Wadepohl, H.; Gade, L. H. *Chem. Commun.* **2014**, *50*, 4941.

(25) Liu, L.; Zhang, W.-X.; Luo, Q.; Li, H.; Xi, Z. *Organometallics* **2010**, *29*, 278.

(26) Xi, Z. *Acc. Chem. Res.* **2010**, *43*, 1342.

(27) Tang, P.; Furuya, T.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 12150.

(28) Morimoto, H.; Tsubogo, T.; Litvinas, N. D.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 3793.

(29) Seguy, I.; Jolinat, P.; Destruel, P.; Mamy, R.; Allouchi, H.; Courseille, C.; Cotrait, M.; Bock, H. *ChemPhysChem* **2001**, *2*, 448.

(30) Roznyatovskiy, V. V.; Gardner, D. M.; Eaton, S. W.; Wasieleski, M. R. *Org. Lett.* **2014**, *16*, 696.