Organic LETTERS

Letter

pubs.acs.org/OrgLett

Cyano-Substituted Perylene Diimides with Linearly Correlated LUMO Levels

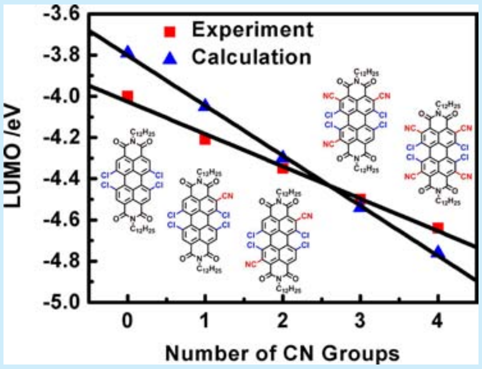
Jing Gao,[†,‡] Chengyi Xiao,[†,‡] Wei Jiang,*[,†] and Zhaohui Wang*[,†]

[†]Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: A series of nonbay region cyano-substituted tetrachloroperylene diimides with tunable LUMO energy levels from −4.21 to −4.64 eV were developed. The excellent linear correlation between LUMO energy levels and the number of cyano groups indicated that the LUMO energy levels could be lowered effectively and predictably by incorporating cyano groups.



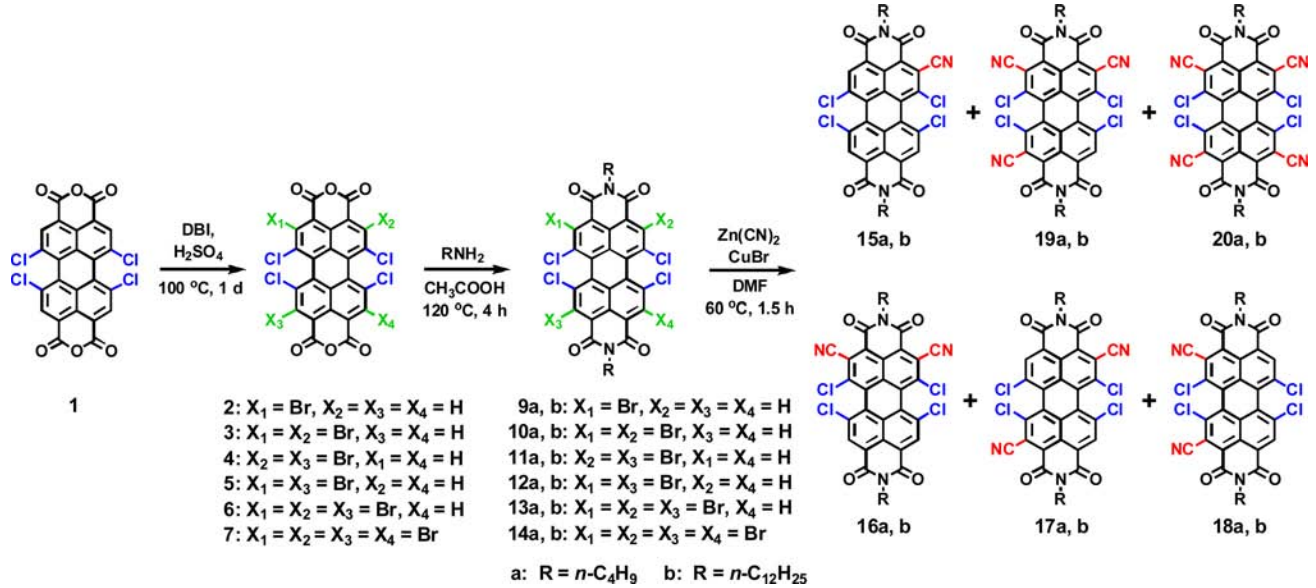
Intensive interest in organic semiconducting materials based on π-molecules is driven by their potential applications in various electronic and optoelectronic devices, including organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and dye-sensitized solar cells (DSSCs).[1] Among these organic semiconductors, the development of electron-transporting (n-type) materials has significantly lagged behind their hole-transporting (p-type) counterparts,[2] primarily due to their instability under ambient conditions.[3] Attaching strong electron-withdrawing groups, such as F, CN, etc.[4] to the conjugated core, tends to lower the lowest unoccupied molecular orbital (LUMO) energy levels sufficiently, which facilitates electron injection and transportation.[5] Marks reported dicyano-substituted perylene diimide (PDI) derivatives with LUMO levels below −4.3 eV that appeared to have good air stabiliy and excellent n-channel performance in ambient conditions.[6] Recently, Chi reported a series of cyanated naphthalene diimide (NDI) derivatives with lowered LUMO levels and reported that these NDI derivatives become unstable as the LUMO levels approach −4.6 eV.[7] Tuning LUMO levels via incorporating electron-withdrawing groups is vital and virtual for the electron-transporting and ambient stability of n-type organic semiconductors.

We are particularly interested in the π-expanded PDI and NDI systems fused along the equatorial axis to achieve air-stable, electron-poor molecules that featured low-lying LUMO levels and excellent n-channel performances. A series of graphene-like triply linked PDI arrays up to four units were obtained, and particularly, 4Cl-diPDIs possessing LUMO levels of about −4.3 eV exhibited excellent electron mobilities as high as 4.65 cm^2 V^{-1} s^{-1} based on single crystal OFETs.[8] Moreover, hybrid rylene arrays involving NDI and PDI moieties were also reported as air-stable electron-transporting materials with LUMO levels below −4.2 eV.[9] Herein, we present a new straightforward synthetic appproach toward nonbay region cyano-substituted tetrachloroperylene diimides (xCN-4Cl-PDIs), and also a new synthetic strategy for the selective funtionalization of the nonbay positions of PDIs is developed. Accordingly, the careful investigation of photophysical properties and single-crystal analysis are presented to elucidate the influence of the incorporation of CN groups on the electronic properties and molecular packing arrangement in the solid state.

The synthesis of xCN-4Cl-PDIs (**15**−**20**) is shown in Scheme 1. The starting material was prepared by bromination of commercially available tetrachloroperylene dianhydride (4Cl-PDA) with 1.5 equiv of dibromoisocyanuric acid (DBI) in oleum (50% SO_3) and 98% sulfuric acid at 100 °C for 24 h in excellent yield. Imidization of the mixture of xBr-4Cl-PDA **2**−**7** with *n*-butylamine or *n*-dodecylamine in glacial acetic acid for 4 h afforded the corresponding xBr-4Cl-PDIs **9**−**14**. The cyanation was successfully carried out in the presence of $Zn(CN)_2$ and CuBr in DMF at 60 °C for 1.5 h, and then the desired products (**15**−**20**) with different numbers of CN groups were effectively obtained respectively in one pot in high yields. Due to the different number and positions of CN groups greatly affecting the molecular polarity, the cyanated series was separated successfully. All of the products show good solubility in common organic solvents such as dichloromethane,

Received: November 12, 2013
Published: January 6, 2014

Scheme 1. Synthesis of a Series of Nonbay Region Cyano-Substituted 4Cl-PDIs



chloroform, tetrahydrofuran, toluene, and chlorobenzene at room temperature. Their structures were fully characterized and verified by ^{1}H, ^{13}C NMR spectroscopy and MALDI-TOF.

Their UV absorption and fluorescence spectra were investigated, and the results are summarized in Tables 1 and S1. In comparison to cyano-free 4Cl-PDI (**8b**), the incorporation of cyano substituents on the nonbay region does not significantly affect the absorption and emission properties in solution.[10] The absorption maxima of xCN-4Cl-PDIs are just red-shifted about 4−16 nm, with respect to 520 nm of 4Cl-PDI. The optical band gaps of xCN-4Cl-PDIs estimated from the onset absorption wavelength are very similar, i.e. 2.25 eV, except for that of compound **16b** which is about 2.19 eV. This small difference for compound **16b** was speculated to be due to the increased longitudinal intramolecular dipole along the N−N axis that results from the two cyano substituents introduced at the 2-,5-positions.[11]

Table 1. Summary of Optical, Electrochemical Properties of Compounds 15b−20b, with Cyano-Free Compound 4Cl-PDI (8b) as Reference

compd	abs$_{max}$^{a} [nm]	E_{1r}^{b} [V]	E_{2r}^{b} [V]	LUMO^c [eV]	E_g^{d} [eV]
4Cl-PDI^e	520	−0.85	−1.05	−4.00	2.27
15b	526	−0.66	−0.92	−4.21	2.24
16b	536	−0.44	−0.79	−4.41	2.19
17b	524	−0.50	−0.80	−4.35	2.25
18b	526	−0.50	−0.80	−4.36	2.24
19b	528	−0.35	−0.70	−4.50	2.23
20b	524	−0.20	−0.54	−4.64	2.24

^{a}Measured in dilute $CHCl_3$ solution (1.0×10^{-5} M). ^{b}Half-wave reduction potentials (vs Fc/Fc$^+$) measured in CH_2Cl_2 at a scan rate of 0.1 V/s. ^{c}Estimated from the onset potential of the first reduction wave. ^{d}Obtained from the edge of the absorption spectra. ^{e}*N*,*N*′-Di-*n*-dodecyl-1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylic acid diimide.

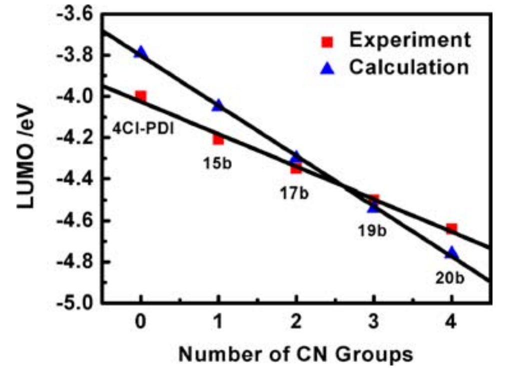


Figure 1. Plots of calculated and experimental LUMO energy levels of 4Cl-PDI (**8b**), compounds **15b**, **17b**, **19b**, and **20b** depending on the number of CN groups on the nonbay regions.

The electrochemical properties of compounds **15−20** were investigated by cyclic voltammery in CH_2Cl_2 (Figures S2 and S3). All compounds exhibit two reversible reduction waves, while no oxidation wave was observed within the available potential range. The introduction of electron-withdrawing CN groups on the nonbay regions indeed induces a notable positive shift of the reduction potentials. The first half-wave reduction potentials ranged from −0.66 V (**15b**) to −0.20 V (**20b**) vs Fc/Fc$^+$ that increased by ca. 0.15 V for the increasing number of CN groups, while the second half-wave reduction potentials ranged from −0.92 V (**15b**) to −0.54 V (**20b**) that increased by ca. 0.13 V. Thus, the estimated LUMO levels of compounds **15b**−**20b** fall from −4.21 eV to −4.64 eV, which coincided with the calculated values (DFT at B3LYP/6-31G* level) from −3.79 eV to −4.76 eV. And the experimental values based on the cyano-free to tetracyano compounds also gained a good linear relationship by the introductory number of CN groups with a regression coefficient $R^2 = 0.991$ (Figure 1). The excellent linear relationship indicated that the LUMO energy levels could be lowered effectively and predictably by incorporating CN groups on the nonbay regions. It is worth noting that tri- and tetracyanated derivatives (**19b** and **20b**) showed LUMO energy levels below −4.50 eV. Especially, the tetracyanated one (**20b**) with an ultralow LUMO level of −4.64 eV possessed among the lowest LUMO level ever reported for the PDI family. The deep LUMO levels of compounds **15b**−

20b rendered them good candidates for air-stable electron-transporting materials.[12]

To assess the effect of cyano-substitution on the molecular packing arrangement in the solid state, single crystals of compounds **15a**, **16a**, **17a**, and **20a** featuring butyl substituents on the imide positions were grown by slow evaporation of the dichloromethane/methanol solutions at room temperature. A single crystal of 4Cl-PDI (**8a**) was also obtained for comparison. The repulsion between the chlorine atoms in the bay positions distort the PDI plane,[13] which results in a twisting of the two naphthalene subunits, also giving rise to the presence of *P* and *M* atropo-enantiomers in the solid state with dimer pair formation occurring in the series of 4Cl-PDI derivatives.[14] The torsion angles in the bay area of all of these CN-substituted 4Cl-PDIs were about 35°−39°, which indicate that the CN-substitution on the nonbay regions only slightly affected the PDI core.

The cyano-free molecules of 4Cl-PDI are arranged in a side-shifted columnar arrangement along the *c*-axis with an overlap between the nearest neighboring naphthalene subunits (Figure 2a). The minimum interplanar distance is 3.55 Å, which agrees very well with the reported value for tetrachloro-substituted PDI.[15] In the case of cyano-substituted derivatives (xCN-4Cl-PDIs), the molecules are liable to form dimers by the presence of CN groups. For molecules of **15a**, the incorporation of one CN group on the nonbay region would generate an antiparallel configuration, producing a columnar structure along the *a*-axis. Two different distances are observed along the stacks with a plane-to-plane distance of 3.30 Å between dimer pairs and 3.43 Å between each stack (Figure 2b). 2CN-4Cl-PDIs **16a** and **17a** have notably different packing arrangements for the different substituted positions of the two CN groups. The molecules **16a** with 2,5-cyano substitution (Figure 2c) adopt a herringbone-like arrangement stacked along the *c*-axis, and dimers are packed tightly between columns with a plane-to-plane distance of 3.30 Å, whereas the crystal structures of **17a** (Figure 2d) exhibit a sandwich-herringbone packing with a close interplanar spacing of 3.64 Å between each dimer. The crystal structure of 4CN-4Cl-PDI **20a** (Figure 2e) reveals a marked difference in solid-state packing resulting in the molecules being stacked in herringbone-like arrangements along both the *a*- and *b*-axis. The results indicated that the introduction of CN groups only slightly influences the PDI core, but the number and positions of CN groups greatly altered the crystal packing motifs.

The OFET devices based on the series **15b**−**20b** were fabricated in a bottom gate top contact (BGTC) configuration. The active layer was deposited onto the octadecyltrichlorosilane-treated SiO_2/Si substrate by spin-coating from $CHCl_3$ solution. The device fabrication and measurement occurred in ambient conditions, revealing the device based on **20a** exhibited a moderate electron mobility of 0.03 $cm^2\ V^{-1}\ s^{-1}$ in ambient conditions (for detailed results, see Supporting Information).

In summary, we reported a series of nonbay region cyano-substituted 4Cl-PDI derivatives with tunable low-lying LUMO levels. The incredible linear relationship indicated that the LUMO energy levels could be lowered effectively and predicted accurately by the number of CN groups introduced in the nonbay regions based on 4Cl-PDIs. 4CN-4Cl-PDI with an ultralow LUMO level of −4.64 eV served as an air-stable n-type semiconductor with moderate electron mobilities. Further studies of precise LUMO level tuning engineering are currently underway.

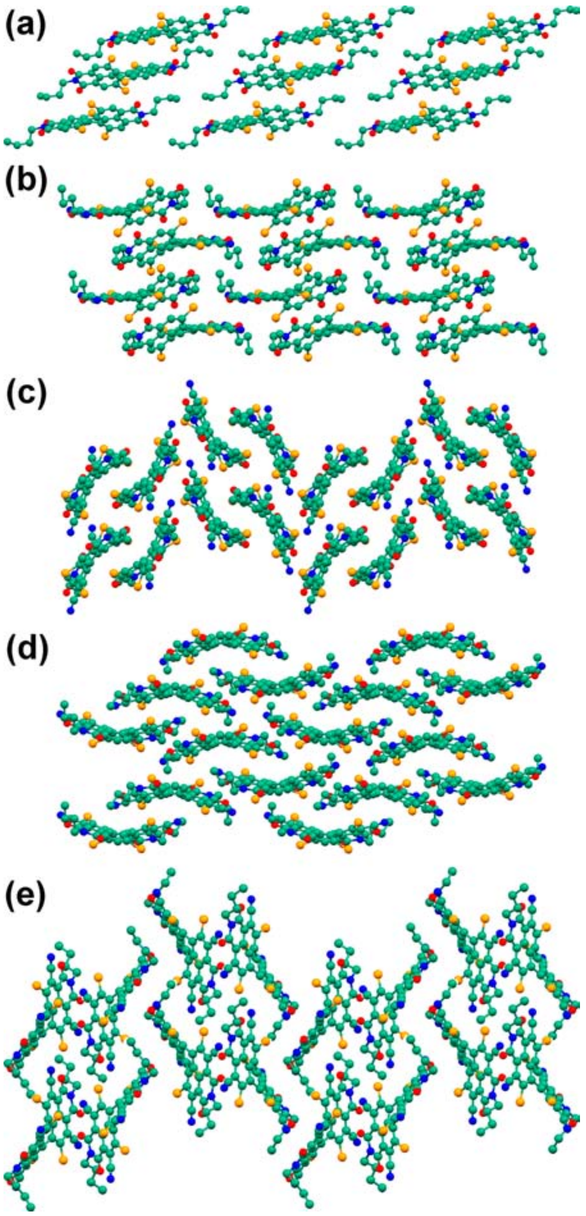


Figure 2. Crystal packing arrangement of **4Cl-PDI** (a), **15a** (b), **16a** (c), **17a** (d), and **20a** (e).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data of new compounds, the CIF information of compounds 4Cl-PDI, **15a**, **16a**, **17a**, and **20a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jiangwei@iccas.ac.cn.
*E-mail: wangzhaohui@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

For financial support of this research, we thank the National Natural Science Foundation of China (21225209, 91027043, and 91233207), 973 Program (Grant 2011CB932301 and 2013CB933500), NSFC-DFG Joint Project TRR61, and Chinese Academy of Sciences.

■ REFERENCES

(1) (a) Kim, H. N.; Guo, Z.; Zhu, W.; Yoon, J.; Tian, H. *Chem. Soc. Rev.* **2011**, *40*, 79. (b) Jiang, W.; Li, Y.; Wang, Z. *Chem. Soc. Rev.* **2013**, *42*, 6113. (c) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2012**, *112*, 2208. (d) Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723. (e) Wang, Q.; Ma, D. *Chem. Soc. Rev.* **2010**, *39*, 2387. (f) Yan, Q.; Zhou, Y.; Zheng, Y.-Q.; Pei, J.; Zhao, D. *Chem. Sci.* **2013**, *4*, 4389.

(2) (a) Mas-Torrent, M.; Rovira, C. *Chem. Soc. Rev.* **2008**, *37*, 827. (b) Pron, A.; Gawrys, P.; Zagorska, M.; Djurado, D.; Demadrille, R. *Chem. Sov. Rev.* **2010**, *39*, 2577. (c) Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489.

(3) (a) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011**, *44*, 501. (b) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876. (c) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268. (d) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070.

(4) (a) Schmidt, R.; Ling, M. M.; Oh, J. H.; Winkler, M.; Konemann, M.; Bao, Z. N.; Würthner, F. *Adv. Mater.* **2007**, *19*, 3692. (b) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.

(5) (a) Li, Y.; Tan, L.; Wang, Z.; Qian, H.; Shi, Y.; Hu, W. *Org. Lett.* **2008**, *10*, 529. (b) Lei, T.; Dou, J.-H.; Ma, Z.-J.; Yao, C.-H.; Liu, C.-J.; Wang, J.-Y.; Pei, J. *J. Am. Chem. Soc.* **2012**, *134*, 20025. (c) 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. (d) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259.

(6) Jones, B. A.; Ahrens, M. J.; Yoon, M. H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363.

(7) (a) Chang, J.; Ye, Q.; Huang, K.-W; Zhang, J.; Chen, Z.-K.; Wu, J.; Chi, C. *Org. Lett.* **2012**, *14*, 2964. (b) Ye, Q.; Chang, J.; Huang, K.-W.; Shi, X.; Wu, J.; Chi, C. *Org. Lett.* **2013**, *15*, 1194.

(8) (a) Qian, H.; Wang, Z.; Yue, W.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 10664. (b) Qian, H.; Negri, F.; Wang, C.; Wang, Z. *J. Am. Chem. Soc.* **2008**, *130*, 17970. (c) Zhen, Y.; Wang, C.; Wang, Z. *Chem. Common.* **2010**, *46*, 1926. (d) Lv, A.; Puniredd, S. R.; Zhang, J.; Li, Z.; Zhu, H.; Jiang, W.; Dong, H.; He, Y.; Jiang, L.; Li, Y.; Pisula, W.; Meng, Q.; Hu, W.; Wang, Z. *Adv. Mater.* **2012**, *24*, 2626. (e) Zhang, J.; Tan, L.; Jiang, W.; Hu, W.; Wang, Z. *J. Mater. Chem. C* **2013**, *1*, 3200.

(9) (a) Yue, W.; Lv, A.; Gao, J.; Jiang, W.; Hao, L.; Li, C.; Li, Y.; Polander, L. E.; Barlow, S.; Hu, W.; Di Motta, S.; Negri, F.; Marder, S. R.; Wang, Z. *J. Am. Chem. Soc.* **2012**, *134*, 5770. (b) Li, X.; Xiao, C.; Jiang, W.; Wang, Z. *J. Mater. Chem. C* **2013**, *1*, 7513.

(10) Battagliarin, G.; Zhao, Y.; Li, C.; Müllen, K. *Org. Lett.* **2011**, *13*, 3399.

(11) Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Müllen, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 9068.

(12) (a) 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. (b) Molinari, A. S.; Alves, H.; Chen, Z.; Facchetti, A.; Morpurgo, A. *J. Am. Chem. Soc.* **2009**, *131*, 2463.

(13) (a) Zhen, Y.; Yue, W.; Li, Y.; Jiang, W.; Di Motta, S.; Di Donato, E.; Negri, F.; Ye, S.; Wang, Z. *Chem. Commun.* **2010**, *46*, 6078. (b) Hao, L.; Xiao, C.; Zhang, J.; Jiang, W.; Xu, W.; Wang, Z. *J. Mater. Chem. C* **2013**, *1*, 7812.

(14) Osswald, P.; Würthner, F. *J. Am. Chem. Soc.* **2007**, *129*, 14319.

(15) Chen, Z.; Debije, M. G.; Debaerdemaeker, T.; Osswald, P.; Würthner, F. *ChemPhysChem* **2004**, *5*, 137.

■ NOTE ADDED AFTER ASAP PUBLICATION

The TOC/abstract graphic was incorrect in the version published ASAP January 6, 2014; the correct version reposted January 7, 2014.