A GENUINELY MULTIDISCIPLINARY JOURNAL

CHEMPLUSCHEM

CENTERING ON CHEMISTRY

Accepted Article

Title: Novel aza-BODIPY derivatives containing BF(CN) and B(CN)2 structures

Authors: Tian-yi Li, Zaifei Ma, Zhi Qiao, Christian Körner, Koen Vandewal, Olaf Zeika, and Karl Leo

To be cited as: *ChemPlusChem* 10.1002/cplu.201600479

Link to VoR: http://dx.doi.org/10.1002/cplu.201600479

A Journal of ChemPubSoc Europe

WILEY-VCH

www.chempluschem.org

Novel aza-BODIPY derivatives containing BF(CN) and $B(CN)_2$ structures

Tian-yi Li*, Zaifei Ma, Zhi Qiao, Christian Körner, Koen Vandewal Olaf Zeika, and Karl Leo[a]

Abstract: Two novel aza-BODIPY derivatives with the fluorine atoms in the BF_2 moiety replaced by cyano groups are synthesized. The introduction of cyano groups changes the phenyl substituents on the 3, 5 positions from parallel to antiparallel. The HOMO/LUMO energy levels are stabilized gradually when increasing the number of cyano groups and the photophysical properties show corresponding shifts. With high thermal stability, the derivatives can be purified by sublimation and to prepare vacuum deposited thin films. Our research extends the family of aza-BODIPY with cyano substituted derivatives.

The development of boron dipyrromethene (BODIPY) dyes has been an attractive topic in numerous research fields, such as organic photovoltaics,[1] thin film transistors,[2] electroluminescence,[3] energy transfer cassettes,[4] and chiroptics.[5] However, the absorption and emission peaks of traditional BODIPY dyes are restricted to the range of 480–540 nm.[6] In order to extend to the red or near infrared (NIR), many efforts have been undertaken to modify the BODIPY molecular structures. One of the most effective methods is replacing the meso-carbon atom with a nitrogen atom to form aza-BODIPY dyes (Figure. 1). Normally, aza-BODIPY dyes present large bathochromic shifts compared to their BODIPY analogues without damaging their outstanding photophysical properties such as high molar extinction coefficient, sharp Gaussian shaped absorption bands and decent photostability.[7]

Several molecular modifications of aza-BODIPYs, with the goal to realize certain properties and to accomplish specific applications have been reported. Electron-donating moieties were introduced in 1,3,7,5 positions to achieve further bathochromic shifts in both absorption and emission.[8] Also, heterocyclic rings were attached to these positions to form chemical sensors and indicators.[9] In case of substitution of the 2,6 positions by bromine atoms, the production of singlet oxygen was increased, which was favourable for photodynamic therapy.[8b] Aza-BODIPYs with extended structures were synthesized by connecting the 2,6 positions with the aryl substituents on 3,5 positions. The resulting rigid dyes presented high molar extinction coefficients and even further red shifted absorptions.[10] Recently, benzannulated aza-BODIPYs with fused rings on 1,2 positions were prepared and are promising as NIR absorbing donor materials in organic photovoltaics.[11]

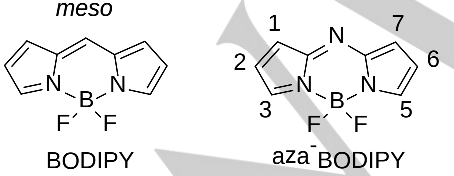
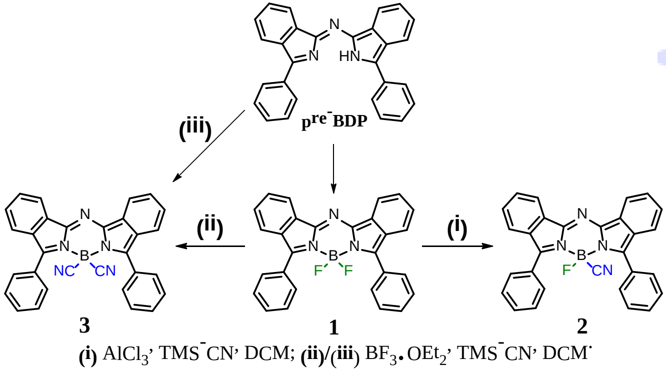


Figure 1. The core structure of BODIPY and aza-BODIPY.

However, all these modifications of aza-BODIPY are limited on the dipyrrolemethene section. In this contribution, we therefore focus on the BF_2 moiety and replaced the fluorine atoms with cyano groups, aiming to develop a versatile synthetic route for aza-BODIPY derivatives. As shown in Scheme 1, the well-studied benzannulated aza-BODIPY **1** was synthesized according to a previously described method from the precursor **pre-BDP**.[12] The exchange of the fluorine atom with a cyano group was carried out by reacting **1** and trimethylsilyl cyanide together with a Lewis acid according to route **(i)** and **(ii)**. Aza-BODIPY **1** and two *equiv* of Lewis acid were added in anhydrous DCM and stirred at reflux for 10 min. Then, ten *equiv* of trimethylsilyl cyanide were added into the system dropwise at room temperature. We found that, when aluminium chloride was used as the Lewis acid, the final product was **2** in spite of the excessive trimethylsilyl cyanide and the reaction can be completed within one hour. A prolongation of the reaction time to overnight did not influence the final product. When the boron trifluoride etherate was employed, **2** is observed at the beginning of the reaction. However, after several hours, **2** disappeared gradually and **3** started to accumulate. The complete conversion of **1** into **3** was observed after 10 h of stirring. This observation reveals that the replacement of two fluorine atoms with cyano groups can be considered as a two-step process. The strong electron deficiency and relatively small molecular volume of boron trifluoride etherate play a significant role in this exchange reaction. Moreover, we tried to synthesize **3** from **pre-BDP** directly with five *equiv* of boron trifluoride etherate and ten *equiv* of



Scheme 1. The molecular structures and synthetic route of aza-BODIPY derivatives with cyano groups.

---

[a] Li, Dr. Ma, Qiao, Dr. Körner, Prof. Dr. Vandewal, Dr. Zeika, Prof. Dr. Leo
Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP)
Technische Universität Dresden
George-Bähr-Str.1, 01069 Dresden, Germany
E-mail: tianyi.li@iapp.de

Supporting information for this article is given via a link at the end of the document.

trimethylsilyl cyanide via route **(iii)**. As a result, the yield of route **(iii)** is around 56%, which is similar to that of route **(i)** and **(ii)**. Consequently, with a yield of around 60% from **pre-BDP** to **1**, the yield of **3** is doubled when using route **(iii)** instead of route **(i)**. The newly synthesized aza-BODIPY derivatives are fully characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and MS. Single crystal X-ray diffraction measurements are carried out to determine the exact molecular structures.

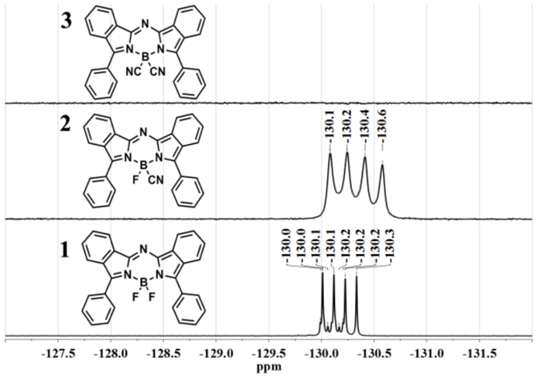


Figure 2. The ^{19}F NMR spectra of the compounds.

^{19}F NMR spectra provide the most obvious evidence for the demonstration of the new derivatives containing two, one and zero fluorine atoms. As illustrated in Figure. 2, **1** presents a set of structured signals with four main peaks and several splitting peaks in the range of –130.0 to –130.3 ppm. When one fluorine atom is replaced, the peaks in the spectrum of **2** broaden and the fine structures are smeared out. Only four peaks with similar strength are observed in the region from –130.1 to –130.6 ppm. For **3**, there is no resonance signal, telling that both of the fluorine atoms are replaced by cyano groups.

The molecular structures of **1**, **2** and **3** are illustrated in Figure. 3. The structure of **1** has been reported by Kobayashi and Lukyanets *et.al.*[13] Single crystal samples of **2** and **3** for X-ray diffraction measurements are obtained by slow diffusion of iso-hexane into the DCM solutions. The boron centres adopt a slightly disordered tetrahedral geometry. The B-F1 bond (1.38 Å) in **2** is the shortest in the coordination sphere. For both **2** and **3**, B-N1 (1.55 Å) and B-N2 (1.55 Å) have almost the same length, but slightly shorter than those of **1**, indicating that replacing the fluorine atoms with cyano groups strengthens the B-N bonds. The bond lengths between boron and cyano groups (B-C1: 1.60, 1.59 Å for **2** and **3**; B-C2: 1.60 Å for **3**) are the longest (Table S2). When looking into the structure of **1**, it is interesting to note that the two phenyl moieties are in the parallel positions and the corresponding H atoms had intermolecular interactions with both F atoms in the BF_2 moiety. In contrast, for **2** and **3**, these two phenyl rings are antiparallel to each other and the only F atom in **2** can have intermolecular interaction with both of ortho-H atoms in the phenyl rings.

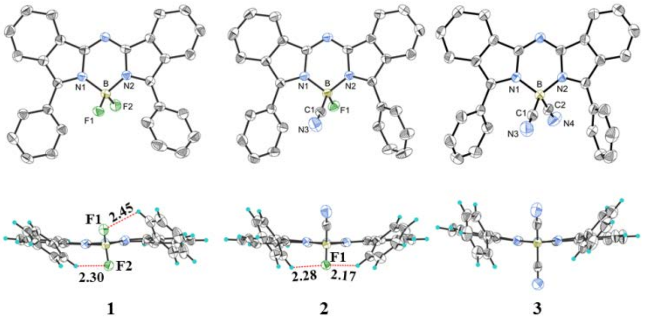


Figure 3. The ORTEP structures of **1**, **2** and **3** with the thermal ellipsoids set at 60% probability (up: top view; down side view; C: black, N: blue, F: green, B: dark yellow).

The thermal properties of **2** and **3** are investigated by thermal gravimetric analysis (TG, Figure. S3). Both of the derivatives display a good thermal stability with decomposition temperatures over 300 ℃. Therefore, these derivatives can be purified by vacuum gradient sublimation at a temperature lower than 250℃ with reasonable yield around 60%. The photostability of all the compounds is studied in DCM solution under the radiation of 6000 W m^{-2} for 12 h (Figure S5). Aza-BODIPY **1** shows the best photo stability and the extinction coefficient keeps as constant during the radiation. The derivative **3**, whose extinction coefficient decreases around 16%, has better photo stability than **2**.

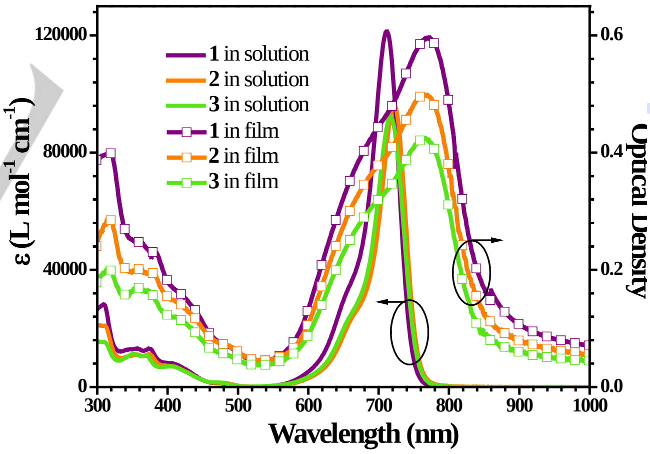


Figure 4. The absorption spectra of **1**, **2** and **3** in DCM solution and in solid state (50 nm thin film on glass).

The absorption spectra of **1**, **2** and **3** are recorded in both diluted DCM solution and for vacuum deposited thin films (Figure. 4, Table 1). In solution, both derivatives **2** and **3** have similar absorption profiles as **1**, consisting of an extremely intensive single absorption band in the long wavelength region from 600 nm to 750 nm and a broad but weak absorption tail extending from 500 nm to the UV region. This observation demonstrates that the introduction of cyano groups has only minor influence on the photoinduced electronic transitions. However, it is worth to note that the absorption peaks present interesting shifts with the number of cyano groups. When introducing one cyano group, the main absorption peak of **2** bathochromically shifts by 11 nm from 711 nm to 722 nm, as compared to **1**. Surprisingly, further introduction of the second cyano group in **3** brings a small hypsochromic shift of 5 nm and the absorption peak is found at 717 nm. This reveals that the HOMO-LUMO energy gap decreases with the introduction of one cyano group. However, this gap does not decrease further with the introduction of a second cyano group and **2** remains the smallest gap. The optical properties of all the compounds in the solid state are investigated using vacuum thermal deposited thin films with a thickness of 50 nm. The obvious broadening and bathochromic shifts observed for all the compounds indicate that these three dyes have J-aggregation effects.[14] The absorption coefficients of these three dyes are all higher than 1×10^5 cm^{-1} (Figure S4). Furthermore, the molar extinction coefficients decreased along with the increasing number of cyano groups in both solution and film. The theoretical calculation results below will give evidence for the decreasing absorbing abilities. The emission spectra of all the compounds were also recorded in DCM solutions (Figure S6) and present perfect mirror-image relationship with the absorption spectra. The emission peaks were in the NIR region from 745 to 752 nm with rather small stokes shifts in the range of 32 to 35 nm.

Table 1 The spectroscopic data of **1**, **2** and **3**

Dye	Solution				Thin film	
	λ_{abs}/nm[a]	ε/$M^{-1}cm^{-1}$ [a]	ΔE_{opt} /eV[b]	λ_{em} ($\Delta\lambda_{Stokes}$)/ nm[c]	λ_{abs} [*O.D.*] / nm [%][d]	ΔE_{opt}/eV[b]
1	711	121 500	1.66	745 (34)	763 [0.50]	1.36
2	722	96 360	1.62	754 (32)	766 [0.50]	1.38
3	717	92 250	1.64	752 (35)	766 [0.42]	1.41

[a] The absorption spectra were measured in 1×10^{-5} mol L^{-1} DCM solutions; [b] The band gaps were calculated with the onset wavelength of the absorption spectra λ_{onset} by $\Delta E_{opt}=1240/\lambda_{onset}$; [c]The emission spectra were recorded in 5×10^{-5} mol L^{-1} DCM solutions; [d] The absorption was measured according to the optical density (*O.D.*) and the transmission rate can be determined as $T=10^{(-O.D.)}\times100\%$.

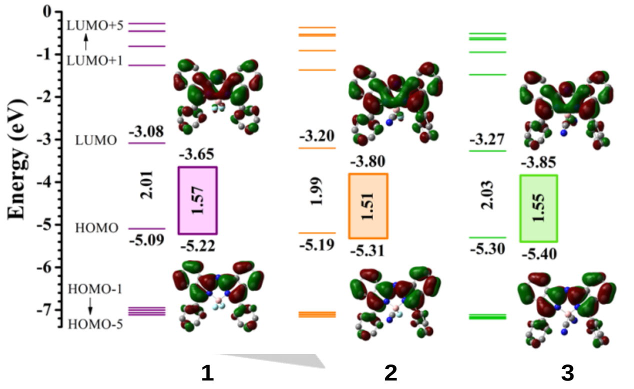


Figure 5. The frontier molecular orbital positions of **1**, **2** and **3** from CV measurements (right) and DFT calculations (left) together with the plots of HOMOs and LUMOs.

In order to obtain a deeper insight in the frontier molecular orbitals, both cyclic voltammetry (CV) measurements and density functional theory (DFT) calculations are conducted (Figure 5, Figure S7 and S8). The aza-BODIPY **1** has a reversible redox wave with an oxidation potential at 0.86 V. A similar reversible wave is observed for **2** with a positively shifted oxidation potential at 0.95 V. This oxidation becomes partial reversible for **3** and the oxidation peak potential is further shifted to 1.05 V. For **1** the redox potential in the negative region is reversible and these waves become irreversible for **2** and **3**. The reduction peaks are found at –0.78 V, –0.65 V and –0.59 V respectively. The HOMO energy level of **1** is measured to be –5.22 eV. When one of the fluorine atom is replaced, the HOMO decreases by 0.09 eV to –5.31 eV. Adding a second cyano group, the HOMO is stabilized to –5.40 eV with further decrease of 0.09 eV. The LUMO energy level however shows a different trend. First it decreases by 0.15 eV from –3.65 eV for **1** to –3.80 eV for **2**, but then decrease to –3.85 eV for **3** with only 0.05 eV. Consequently, the smallest energy band gap was found for **2** with one cyano group. The energy gap of **3** with two cyano groups is in the middle. This result explains the observed hypsochromic shift in the absorption spectra between compounds **2** and **3**. From the theoretical calculation results, both the HOMO and LUMO are mainly located on the upper aza-diisoindole moieties and the phenyl substituents. This is the reason for the almost identical absorption profiles of these three compounds. However, due to the subtle disturbance from cyano groups, the electron density contribution to the HOMOs from BF_2, BF(CN) and $B(CN)_2$ are 0.12%, 0.11% and 0.18% respectively. These numbers become 1.36%, 3.54% and 5.45%. This means aza-BODIPY **1** has the biggest overlap between HOMO and LUMO and the overlap decreases gradually in **2** and **3**. Thus, the lower extinction coefficients for the derivatives are explained. Although the exact trend in LUMO energy levels is too small to be revealed by the CV measurements, the stepwise decrease in HOMO energy levels by 0.1 eV is reproduced.

In conclusion, we have successfully developed a novel synthetic route for aza-BODIPY derivatives with BF(CN) and $B(CN)_2$ structures and have prepared two NIR dyes **2** and **3** based on benzannulated aza-BODIPY. Due to the lack of F–H interactions, the phenyl substituents on 3,5 positions turned from parallel into antiparallel in both aza-BODIPY derivatives. The absorption maxima of the derivatives **2** and **3** display bathochromic shifts of 11 nm and 6 nm respectively compared to the aza-BODIPY **1**. By increasing the number of cyano groups, the HOMO energy level decreases gradually. However, the LUMO of **2** is lower than **3**, making the energy gap of the derivative with one cyano group the lowest. Similar as the former research in replacing fluorine by alkyne fragments in BODIPY,[15] neither electron donating nor electron withdrawing moieties linked to boron makes significant disturbing on the optical and FMOs properties. Furthermore, both the new derivatives present an outstanding thermal stability and can be purified by vacuum sublimation. This results in thin film of high purity and quality, indicating them suitable as candidates for vacuum processed NIR organic electronic devices. Considering the growing research interest of aza-BODIPY, more functional aza-BODIPY derivatives with BF(CN) and $B(CN)_2$ structures can be developed and present realistic applications in various fields of optoelectronics and beyond.

Acknowledgements

T.Li thanks the China Scholarship Council (CSC No. 201406190164) and the German Federal Ministry for Education and Research (BMBF) through the InnoProfile project “Organische p-i-n Bauelemente 2.2” (03IPT602X). Z.Ma thanks the Alexander von Humboldt Foundation for a fellowship.

Keywords: aza-BODIPY • Cyano substituents • Near infrared • Sublimation • Tuneable FMOs

[1] a) S. Erten-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli, E. U. Akkaya, *Org. Lett.* **2008**, *10*, 3299-3302; b) T. Rousseau, A. Cravino, T. Bura, G. Ulrich, R. Ziessel, J. Roncali, *Chem. Commun.* **2009**, 1673-1675; c) S. Kolemen, O. A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J. H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Gratzel, E. U. Akkaya, *Chem. Sci.* **2011**, *2*, 949-954; d) W. X. Liu, J. N. Yao, C. L. Zhan, *RSC Adv.* **2015**, *5*, 74238-74241; e) T. Jadhav, R. Misra, S. Biswas, G. D. Sharma, *PCCP* **2015**, *17*, 26580-26588; f) G. H. Summers, J. F. Lefebvre, F. A. Black, E. S. Davies, E. A. Gibson, T. Pullerits, C. J. Wood, K. Zidek, *PCCP* **2016**, *18*, 3358-3358.

[2] a) T. Bura, N. Leclerc, S. Fall, P. Leveque, T. Heiser, P. Retailleau, S. Rihn, A. Mirloup, R. Ziessel, *J. Am. Chem. Soc.* **2012**, *134*, 17404-17407; b) H. Usta, M. D. Yilmaz, A. J. Avestro, D. Boudinet, M. Denti, W. Zhao, J. F. Stoddart, A. Facchetti, *Adv. Mater.* **2013**, *25*, 4327-4334; c) M. Ozdemir, D. Choi, G. Kwon, Y. Zorlu, B. Cosut, H. Kim, A. Facchetti, C. Kim, H. Usta, *ACS Appl. Mater. Interfaces* **2016**, *8*, 14077-14087.

[3] a) A. B. Nepomnyashchii, M. Bröring, J. Ahrens, R. Krüger, A. J. Bard, *J. Phys. Chem. C* **2010**, 114, 14453-14460; b) A. B. Nepomnyashchii, M. Bröring, J. Ahrens, A. J. Bard, *J. Am. Chem. Soc.* **2011**, 133, 19498-19504.

[4] a) R. Sharma, H. B. Gobeze, F. D’Souza, M. Ravikanth, *Chemphyschem.* **2016**, 17, 2516-2524; b) T. K. Khan, M. S. Shaikh, M. Ravikanth, *Dyes Pigments*, **2012**, 94, 66-73; c) C. Thivierge, J. Han, R. M. Jenkins, K. Burgess, *J. Org. Chem.* **2011**, 76, 5219-5228.

[5] a) T. Bruhn, G. Pescitelli, S. Jurinovich, A. Schaumlöffel, F. Witterauf, J. Ahrens, M. Bröring, G. Bringmann, *Angew. Chem. Int. Ed.* **2014**, 53, 14592-14595; b) T. Bruhn, G. Pescitelli, F. Witterauf, J. Ahrens, M. Funk, B. Wolfram, H. Schneider, U. Radius, M. Bröring, *Eur. J. Org. Chem.* **2016**, 4236-4243.

[6] A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891-4932.

[7] a) S. Shimizu, T. Iino, Y. Araki, N. Kobayashi, *Chem. Commun.* **2013**, *49*, 1621-1623; b) G. Fan, L. Yang, Z. J. Chen, *Frontiers of Chemical Science and Engineering* **2014**, *8*, 405-417.

[8] a) J. Killoran, L. Allen, J. F. Gallagher, W. M. Gallagher, D. F. O'Shea, *Chem. Commun.* **2002**, 1862-1863; b) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2004**, *126*, 10619-10631; c) R. Gresser, H. Hartmann, M. Wrackmeyer, K. Leo, M. Riede, *Tetrahedron* **2011**, *67*, 7148-7155.

[9] a) A. Coskun, M. D. Yilmaz, E. U. Akkaya, *Org. Lett.* **2007**, *9*, 607-609; b) H. Z. Liu, J. Mack, Q. L. Guo, H. Lu, N. Kobayashi, Z. Shen, *Chem. Commun.* **2011**, *47*, 12092-12094; c) Y. T. Chen, D. D. Qi, L. Y. Zhao, W. Cao, C. H. Huang, J. Z. Jiang, *Chem. Eur. J.* **2013**, *19*, 7342-7347; d) S. J. Liu, Z. J. Shia, W. J. Xu, H. R. Yang, N. Xia, X. M. Liu, Q. Zhao, W. Huang, *Dyes Pigments* **2014**, *103*, 145-153.

[10] a) W. L. Zhao, E. M. Carreira, *Angew. Chem. Int. Ed.* **2005**, *44*, 1677-1679; b) W. L. Zhao, E. M. Carreira, *Chem. Eur. J.* **2006**, *12*, 7254-7263.

[11] a) T. Mueller, R. Gresser, K. Leo, M. Riede, *Sol. Energy Mater. Sol. Cells* **2012**, *105*, 328-328; b) J. Min, T. Ameri, R. Gresser, M. Lorenz-Rothe, D. Baran A. Troeger, V. Sgobba, K. Leo, M. Riede, D. M. Guldi, C. J. Brabec, *ACS Appl. Mater. Interfaces* **2013**, *5*, 5609-5616; c) S. Kraner, J. Widmer, J. Benduhn, E. Hieckmann, T. Jaegeler-Hoheisel, S. Ullbrich, D. Schutze, K. S. Radke, G. Cuniberti, F. Ortmann, M. Lorenz-Rothe, R. Meerheim, D. Spoltore, K. Vandewal, C. Koerner, K. Leo, *Phys. Status Solidi A* **2015**, *212*, 2747-2753; d) R. Meerheim, C. Korner, B. Oesen, K. Leo, *Appl. Phys. Lett.* **2016**, *108*.

[12] R. Gresser, M. Hummert, H. Hartmann, K. Leo, M. Riede, *Chem. Eur. J.* **2011**, *17*, 2939-2947.

[13] V. F. Donyagina, S. Shimizu, N. Kobayashi, E. A. Lukyanets, *Tetrahedron Lett.* **2008**, *49*, 6152-6154.

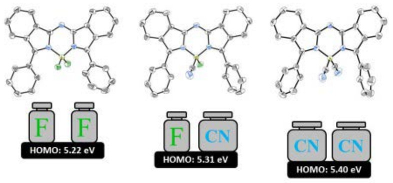
[14] S. Choi, J. Bouffard, Y. Kim, *Chem. Sci.* **2014**, *5*, 751-755.

[15] C. Goze, G. Ulrich, R. Ziessel, *Org. Lett.* **2006**, *8*, 4445-4448.

Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION



Novel aza-BODIPY derivatives: The fluorine atoms in the BF_2 moiety in aza-BODIPY dyes is for the first time replaced by one or two cyano groups and two corresponding derivatives are achieved with the presence of different Lewis acids. The outstanding photophysical properties are kept in the derivatives. The frontier molecular orbital energy levels can be tuned with different numbers of cyano groups.

Tian-yi Li, Zaifei Ma, Zhi Qiao, Christian Körner, Koen Vandewal Olaf Zeika, and Karl Leo*

Page No. – Page No.

Novel aza-BODIPY derivatives containing BF(CN) and B(CN)$_2$ structures