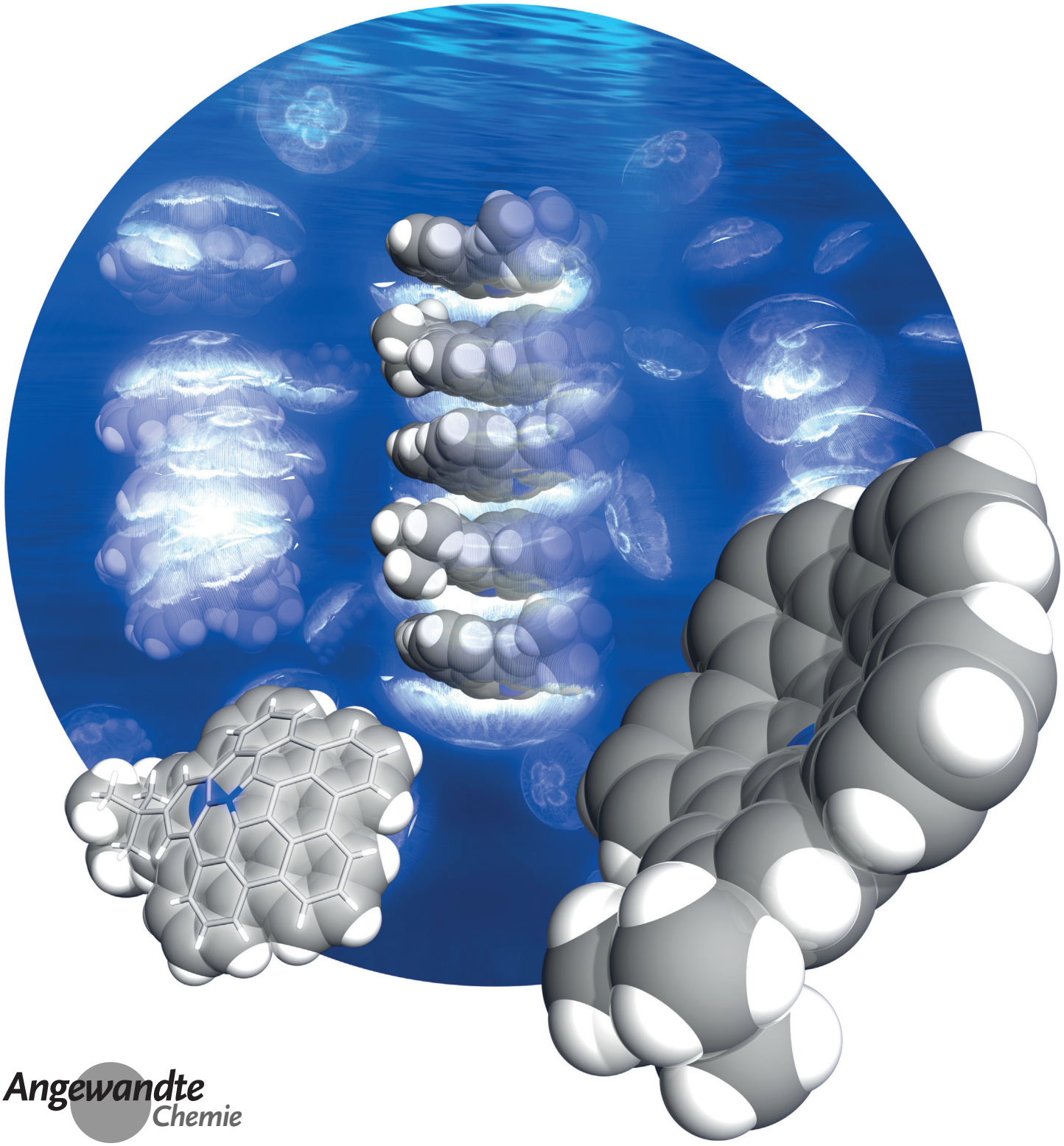
Angewandte Zuschriften

Corannulenes

Deutsche Ausgabe: DOI: 10.1002/ange.201502599
Internationale Ausgabe: DOI: 10.1002/anie.201502599

Benzene-Fused Azacorannulene Bearing an Internal Nitrogen Atom**

Shingo Ito, Yuki Tokimaru, and Kyoko Nozaki**



Angewandte Chemie

Abstract: *A novel nitrogen-doped corannulene derivative, 8-tert-butyl-6b²-azapentabenzo[bc,ef,hi,kl,no]corannulene, was synthesized by 1,3-dipolar cycloaddition of a polycyclic aromatic azomethine ylide with a diarylethyne and subsequent palladium-catalyzed intramolecular cyclization. This molecule represents the first example of a corannulene derivative bearing an internal heteroatom, and exhibits unique structural and physical properties caused by the introduction of the nitrogen atom and extended π-conjugation, as compared to the parent corannulene.*

Bowl-shaped polycyclic aromatic molecules such as C_{5v}-symmetric corannulene[1] and C_{3v}-symmetric sumanene[2,3] have attracted significant attention owing to their unique properties and partial fullerene- and carbon-nanotube-like structures. Synthetic chemists have, therefore, devoted substantial effort toward the synthesis and derivatization of bowl-shaped polyaromatic molecules. However, few studies have focused on the synthesis of heteroatom-doped derivatives, although doping of heteroatoms into polycyclic aromatic hydrocarbons is a powerful method to alter their intrinsic properties, including band structures and electrocatalytic activity.[4,5] To the best of our knowledge, the only reported examples of such heteroatom-doped derivatives include heteroatom-doped sumanenes, which contain nitrogen,[6] silicon,[7,8] and sulfur[9] atoms in their peripheral positions. Heteroatom-doped corannulene derivatives are more challenging to synthesize and are elusive compounds, although theoretical calculations[10] and attempts toward their synthesis[1b,11] have been reported. The lack of heteroatom-doped corannulene derivatives prompted us to pursue their synthesis. We decided to use nitrogen as the heteroatom, because it is a second-row element, the same as carbon. Because of the difference in the valences of carbon and nitrogen atoms, the simple replacement of a trigonal carbon atom at either the hub ($2a^1$) or spoke ($2a$) position[12] of corannulene with a trigonal nitrogen atom leads to the formation of cationic species, which seem to be rather unstable (Figure 1). Therefore, an effective method to fabricate a stable neutral species would be the fusion of five benzene rings to form $6b^2$-azapentabenzo[*bc*,*ef*,*hi*,*kl*,*no*]corannulene,[13] which is the target of this study.

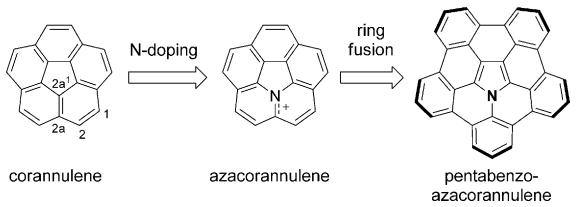
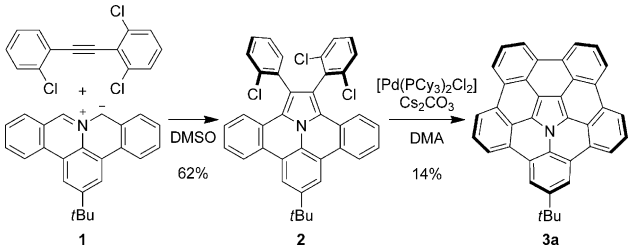


Figure 1. Corannulene and azacorannulenes.

Recently our group,[14] as well as Feng and Müllen,[15] independently developed the 1,3-dipolar cycloaddition of the polycyclic aromatic azomethine ylide **1** (Scheme 1) with



Scheme 1. Synthesis of 8-*tert*-butyl-$6b^2$-azapentabenzo[*bc*,*ef*,*hi*,*kl*,*no*]corannulenes (**3a**) from the polycyclic aromatic azomethine ylide **1**.

diarylethynes and subsequent oxidative dehydrogenation to afford fused 1,2,3,4,5-pentaarylpyrroles. We envisioned that subsequent cyclization would lead to the formation of the $6b^2$-azapentabenzo[*bc*,*ef*,*hi*,*kl*,*no*]corannulenes **3**. Herein we disclose the first bottom-up synthesis of 8-*tert*-butyl-$6b^2$-azapentabenzo[*bc*,*ef*,*hi*,*kl*,*no*]corannulene (**3a**), which is a novel bowl-shaped polycyclic aromatic molecule bearing a nitrogen atom in an internal position, by the palladium-catalyzed intramolecular cyclization of the fused 1,2,3,4,5-pentaarylpyrrole **2** as the key reaction.

The synthetic scheme is shown in Scheme 1. For the successful cyclization of partially fused 1,2,3,4,5-pentaarylpyrroles, it is necessary to introduce some functionality which enables carbon–carbon bond formation between neighboring aryl groups in **2**. Toward this end, we focused on the palladium-catalyzed intramolecular arylative cyclization of a trichlorinated compound, previously employed in the synthesis of diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysenes.[16] Thus, 2,2′,6-trichlorodiphenylethyne was used as a coupling partner for the 1,3-dipolar cycloaddition of **1**. The reaction was carried out using an optimized procedure,[17] and it generated **2** in 62% yield. Subsequent intramolecular cyclization of **2** was performed in the presence of [Pd-$(PCy_3)_2Cl_2$] and a stoichiometric amount of cesium carbonate (Cs_2CO_3) in *N*,*N*-dimethylacetamide (DMA) to **3a** in 14% yield.

The structure of **3a** was confirmed by nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (HRMS). The ^{1}H NMR spectra of **3a** in [D_6]benzene revealed the presence of seven different aromatic protons: one singlet, four doublets, and two triplets, thus indicating that **3a** possesses C_s symmetry. The HRMS of

[*] Dr. S. Ito, Y. Tokimaru, Prof. K. Nozaki
Department of Chemistry and Biotechnology
Graduate School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: ito_shingo@chembio.t.u-tokyo.ac.jp
nozaki@chembio.t.u-tokyo.ac.jp

[**] This work was partially supported by the Japan Society for the Promotion of Science (JSPS) and Japan Science and Technology Agency (JST). Financial support from the Yazaki Memorial Foundation for Science and Technology is gratefully acknowledged. We thank U. Takeda, Dr. K. Harano, and Prof. E. Nakamura (UTokyo) for HPLC separation, R. Mogaki, Dr. Y. Itoh, and Prof. T. Aida (UTokyo) for fluorescence analysis, and H. Waragai (UTokyo) for quantum yield measurement.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201502599.

3a exhibited an *m*/*z* value of 493.1848, which corresponds to an ion mass of $C_{38}H_{23}N$ (*m*/*z*: 493.1830). Finally, single crystals of **3a** that were suitable for X-ray analysis were obtained by recrystallization of **3a** from dichloromethane and diethyl ether. The X-ray crystallographic analysis, shown in Figure 2,

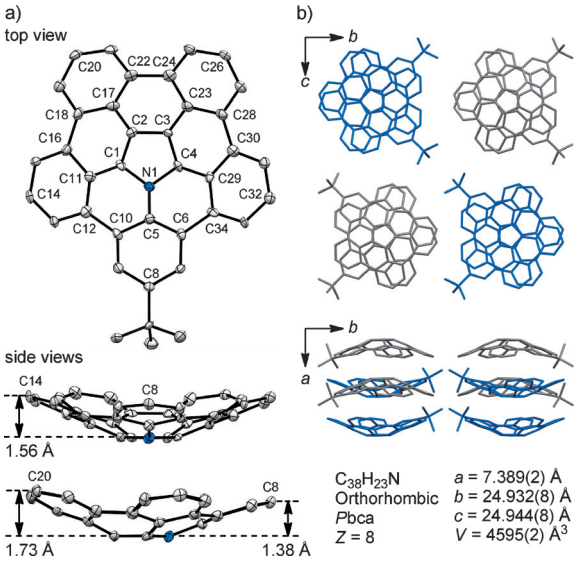


Figure 2. a) X-ray structure of **3a** with thermal ellipsoids of 50% probability. Hydrogen atoms in both views and *tert*-butyl groups in side views are omitted for clarity. b) Packing structure of **3a**.

revealed a C_s-symmetrical bowl-shaped structure consisting of 34 sp^2-carbon atoms and 1 sp^2-nitrogen atom.[18] The bowl depths, defined as the perpendicular distance from the center of the hub pyrrole ring to the parallel planes containing carbon atoms C8, C14, and C20, are 1.38, 1.56, and 1.73 Å, respectively (Figure 2a). The bowl is deeper than that of corannulene (0.87 Å)[1] and that of sumanene (1.11 Å).[2,3] The lengths of the bonds comprising the five peripheral benzene rings (C5-C10, C11-C16, C17-C22, C23-C28, and C29-C34) range between 1.38 to 1.43 Å, and are within the common range of carbon–carbon bond lengths in benzene rings. The lengths of the bridging bonds, C6-C34, C10-C12, C16-C18, C22-C24, and C28-C30, are within 1.49–1.51 Å, which is similar to that of carbon–carbon single bonds. This trend could be explained by the major contribution of the bond alternation pattern consisting of one pyrrole ring and five Clar-type benzene rings. As shown in Figure 2b, **3a** exhibited a one-directional concave-to-convex π-stacking structure along the *a* axis. The stacking distance is 3.69 Å, which is slightly shorter than that of sumanene (3.84 Å). Notably, corannulene does not adopt a concave-to-convex π-stacking structure because of dominant CH–π interactions.[19] Each **3a** molecule in the column is shifted by about 80–83° because the *tert*-butyl moiety in **3a** occupies the vacant space generated by insertion of the pseudocircular column of **3a** into a square of the unit cell. The neighboring columns are oriented toward opposite directions: this phenomenon was also observed in hemifullerene ($C_{36}H_{12}$),[20] some corannulene derivatives,[21] and monooxosumanene,[22] but not observed in the parent corannulene[19] or sumanene.[2] It is worth noting that the aromatic signals of **3a** in the ^{1}H NMR spectrum shifted slightly upfield with increased concentration of **3a**.[17] This phenomenon suggests that some self-aggregation of **3a** occurs in the solution state. The association constant determined by using an indefinite noncooperative (isodesmic) model[23] at 25 °C was $(5.0 \pm 0.4)\,\text{M}^{-1}$.[17] This concentration dependence is commonly observed for disklike polycyclic aromatic compounds,[24] but to the best of our knowledge, no report exists detailing the phenomenon in bowl-shaped polycyclic aromatic molecules.

The photophysical properties of **3a** were investigated, as shown in Figure 3. A solution of **3a** in dichloromethane (2.8×10^{-6} M) exhibited bright yellow color and showed weak and broad absorption bands at $\lambda = 300$–500 nm with maximum

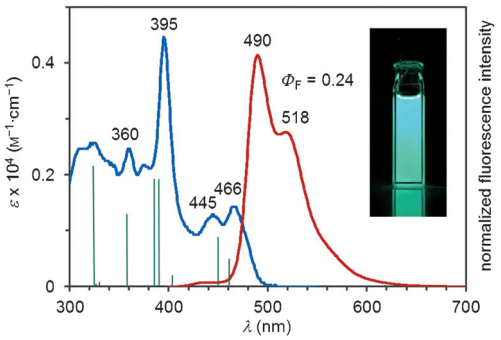


Figure 3. UV/Vis absorption spectrum (blue line) and fluorescence spectrum excited at $\lambda = 320$ nm (red line) of **3a** in CH_2Cl_2 solution (2.8×10^{-6} M), along with the oscillator strengths (green bars) obtained by TD-DFT calculations at the B3LYP/6-311+G(2d,p) level of theory. Inset photograph shows a solution of **3a** under irradiation with a $\lambda = 365$ nm lamp.

wavelengths (λ_{abs}) at 360, 395, 445, and 466 nm.[25] These observed values are longer than those of corannulene[26] and multibenzocorannulenes,[27] and comparable to those of multiindenocorannulenes.[28] Another remarkable feature of **3a** is its fluorescence. Specifically, **3a** exhibited blue/green fluorescence with maximum emission wavelengths (λ_{em}) at 490 nm and a shoulder band at $\lambda = 518$ nm with a quantum yield of $\Phi_F = 0.24$ (2.8×10^{-6} M).[29] Corannulene is known to show weaker fluorescence with a quantum yield of $\Phi_F = 0.024$–0.070[26b,30] in solution. Therefore, the introduction of the nitrogen atom into corannulene and extended π-conjugation derived from peripheral pentabenzo moieties significantly alters its optical properties.

To understand the observed photophysical properties, theoretical calculations were performed for **3b**, in which the *tert*-butyl group of **3a** is replaced by a hydrogen atom, using density functional theory (DFT) at the B3LYP/6-311+G(2d,p) level of theory (Figure 4). The bond lengths and angles of the calculated bowl structure are in good agreement with those of **3a**, as determined by X-ray crystallographic analysis.[17] The lowest unoccupied molecular orbital (LUMO; −1.95 eV) and LUMO+1 (−1.94 eV) are similar, which differs from those of corannulene which has doubly generated LUMOs.[31] The lone pair on the nitrogen atom contributes to π-conjugation in HOMO−1 and LUMO+1. Time-depen-

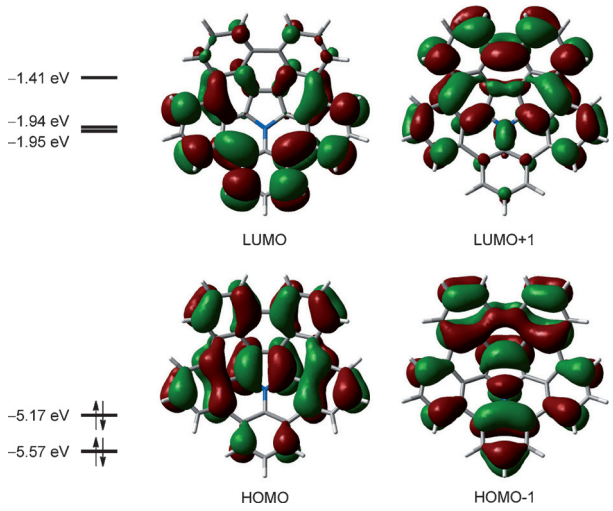


Figure 4. Kohn–Sham molecular orbitals (from HOMO−1 to LUMO+1) of **3b** calculated at the B3LYP/6-311+G(2d,p) level of theory.

dent (TD) DFT calculations using the same method revealed that the transition energies and oscillator strengths show good agreement with the observed values. The calculated bands at $\lambda = 462$ and 449 nm could be assigned to the transitions of HOMO→LUMO and HOMO→LUMO+1, respectively. The strongest absorption band at $\lambda = 395$ nm (Figure 3) could be attributed to the HOMO−1→LUMO/LUMO+1 transitions. The aromaticity of **3b** was evaluated by nucleus-independent chemical shift (NICS) analysis (Figure 5a).

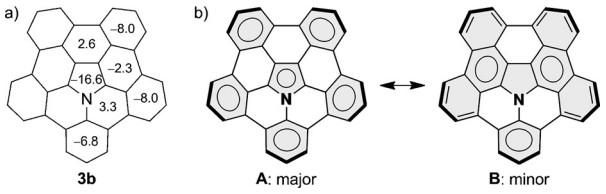


Figure 5. a) NICS(0) values of **3b** calculated at the B3LYP/6-311+G-(2d,p) level of theory. b) Bond alternation pattern of **3b**.

NICS(0) values of −16.6 for the central pyrrole ring and those varying from −7.0 to −6.8 for the peripheral benzene rings suggest a major contribution of structure **A** consisting of one pyrrole ring and five benzene rings, and a minor contribution of structure **B** comprising two phenanthrene rings (Figure 5b). This trend is opposite to that observed with corannulene, in which the central five-membered ring exhibits anti-aromatic characteristics and the six-membered rings exhibit aromatic characteristics.[32]

An important feature of bowl-shaped molecules is their bowl-to-bowl inversion behavior. DFT calculations using the B3LYP function revealed activation energies ranging from 15.3 to 17.0 kcal mol^{-1}, depending on which basis set was utilized.[33] The calculated barriers are higher than those of corannulene (experimental value: 10–11 kcal mol^{-1}[34] and theoretical value: 10.4 kcal mol^{-1}[35]), but lower than those of sumanene (experimental values: 19.6–20.4 kcal mol^{-1} [2a,36] and theoretical values: 16.8–19.1 kcal mol^{-1} [37]). The higher barrier than that of corannulene could be attributed to the presence of peripheral pentabenzo moieties, which retard bond shrinkage required for the transition state in the bowl-to-bowl inversion. This data is in good accordance with the general trend that deeper bowl depths typically lead to high activation energies for bowl-to-bowl inversions.[10,38]

In summary, we developed the first bottom-up synthesis of 8-*tert*-butyl-6*b*^{2}-azapentabenzo[*bc*,*ef*,*hi*,*kl*,*no*]corannulene (**3a**) by 1,3-dipolar cycloaddition of the azomethine ylide **1** and subsequent palladium-catalyzed intramolecular cyclization of the fused 1,2,3,4,5-pentaarylpyrrole **2**. The advantages of azacorannulene over parent corannulene include: 1) the unique structure with C_s symmetry because of the introduction of a trigonal nitrogen atom, 2) formation of one-directional bowl-in-bowl π-stacking in the solid state, and 3) efficient fluorescence with longer emission wavelengths resulting from extended π-conjugation of five fused benzene rings. Detailed analyses and derivatization of the benzene-fused azacorannulene are currently in progress in our laboratory and will be reported in due course.

Keywords: azomethine ylide · corannulenes · polycycles · supramolecular chemistry · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7256–7260
Angew. Chem. **2015**, *127*, 7364–7368

[1] a) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843–4867; b) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868–4884; c) B. M. Schmidt, D. Lentz, *Chem. Lett.* **2014**, *43*, 171–177.
[2] a) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878; b) H. Sakurai, T. Daiko, H. Sakane, T. Amaya, T. Hirao, *J. Am. Chem. Soc.* **2005**, *127*, 11580–11581.
[3] For reviews, see: a) S. Higashibayashi, H. Sakurai, *Chem. Lett.* **2011**, *40*, 122–128; b) T. Amaya, T. Hirao, *Chem. Commun.* **2011**, *47*, 10524–10535; c) T. Amaya, T. Hirao, *Chem. Rec.* **2015**, *15*, 310–321.
[4] For recent reviews of heteroatom-doped graphenes, see: a) X. Wang, G. Sun, P. Routh, D.-H. Kim, W. Huang, P. Chen, *Chem. Soc. Rev.* **2014**, *43*, 7067–7098; b) X.-K. Kong, C.-L. Chen, Q.-W. Chen, *Chem. Soc. Rev.* **2014**, *43*, 2841–2857; c) F. López-Urías, R. Lv, H. Terrones, M. Terrones in *Graphene Chemistry: Theoretical Perspectives*, (Eds.: D. Jiang, Z. Chen), Wiley, Chichester, **2013**, pp. 183–207; d) H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781–794.
[5] For reviews of azafullerenes, see: a) M. D. Tzirakis, M. Orfanopoulos, *Chem. Rev.* **2013**, *113*, 5262–5321; b) O. Vostrowsky, A. Hirsch, *Chem. Rev.* **2006**, *106*, 5191–5207.
[6] Q. Tan, S. Higashibayashi, S. Karanjit, H. Sakurai, *Nat. Commun.* **2012**, *3*, 891.
[7] S. Furukawa, J. Kobayashi, T. Kawashima, *J. Am. Chem. Soc.* **2009**, *131*, 14192–14193.
[8] M. Saito, T. Tanikawa, T. Tajima, J. D. Guo, S. Nagase, *Tetrahedron Lett.* **2010**, *51*, 672–675.
[9] K. Imamura, K. Takimiya, Y. Aso, T. Otsubo, *Chem. Commun.* **1999**, 1859–1860.
[10] a) G. N. Sastry, U. D. Priyakumar, *J. Chem. Soc. Perkin Trans. 2* **2001**, 30–40; b) P. A. Denis, *J. Phys. Chem. C* **2008**, *112*, 2791–2796; c) A. Reisi-Vanani, L. Alihoseini, *Surf. Sci.* **2014**, *621*, 146–151.
[11] V. M. Tsefrikas, S. Arns, P. M. Merner, C. C. Warford, B. L. Merner, L. T. Scott, G. J. Bodwell, *Org. Lett.* **2006**, *8*, 5195–5198.

[12] A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 1921 – 1923.

[13] X. Gao, S. B. Zhang, Y. Zhao, S. Nagase, *Angew. Chem. Int. Ed.* **2010**, *49*, 6764 – 6767; *Angew. Chem.* **2010**, *122*, 6916 – 6919.

[14] S. Ito, Y. Tokimaru, K. Nozaki, *Chem. Commun.* **2015**, *51*, 221 – 224.

[15] a) R. Berger, A. Giannakopoulos, P. Ravat, M. Wagner, D. Beljonne, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2014**, *53*, 10520 – 10524; *Angew. Chem.* **2014**, *126*, 10688 – 10692; b) R. Berger, M. Wagner, X. Feng, K. Müllen, *Chem. Sci.* **2015**, *6*, 436 – 441.

[16] H.-I. Chang, H.-T. Huang, C.-H. Huang, M.-Y. Kuo, Y.-T. Wu, *Chem. Commun.* **2010**, *46*, 7241 – 7243.

[17] See the Supporting Information for details.

[18] CCDC 1057910 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] J. C. Hanson, C. E. Nordman, *Acta. Crystallogr. Sect. B* **1976**, *32*, 1147 – 1153.

[20] M. A. Petrukhina, K. W. Andreini, L. Peng, L. T. Scott, *Angew. Chem. Int. Ed.* **2004**, *43*, 5477 – 5481; *Angew. Chem.* **2004**, *116*, 5593 – 5597.

[21] a) A. Sygula, H. E. Folsom, R. Sygula, A. H. Abdourazak, Z. Marcinow, F. R. Fronczek, P. W. Rabideau, *J. Chem. Soc. Chem. Commun.* **1994**, 2571 – 2572; b) Y.-T. Wu, T. Hayama, K. K. Baldridge, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870 – 6884.

[22] T. Amaya, M. Hifumi, M. Okada, Y. Shimizu, T. Moriuchi, K. Segawa, Y. Ando, T. Hirao, *J. Org. Chem.* **2011**, *76*, 8049 – 8052.

[23] M. Bogdan, C. G. Floare, A. Pîrnau, *J. Phys. Conf. Ser.* **2009**, *182*, 012002.

[24] For representative examples, see: a) J. Wu, A. Fechtenkötter, J. Gauss, M. D. Watson, M. Kastler, C. Fechtenkötter, M. Wagner, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 11311 – 11321; b) M. Kastler, W. Pisula, D. Wasserfallen, T. Pakula, K. Müllen, *J. Am. Chem. Soc.* **2005**, *127*, 4286 – 4296; For reviews, see: c) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546; d) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687 – 5754.

[25] The UV spectra are not dependent on the concentration of **3a**. See the Supporting Information for details.

[26] a) A. L. Lafleur, J. B. Howard, J. A. Marr, T. Yadav, *J. Phys. Chem.* **1993**, *97*, 13539 – 13543; b) M. Yamaji, K. Takehira, T. Mikoshiba, S. Tojo, Y. Okada, M. Fujitsuka, T. Majima, S. Tobita, J. Nishimura, *Chem. Phys. Lett.* **2006**, *425*, 53 – 57.

[27] G. Mehta, P. V. V. S. Sarma, *Chem. Commun.* **2000**, 19 – 20.

[28] B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 10537 – 10545.

[29] Quantum yields of fluorescence depend on the concentration of **3a**: $\Phi_F = 0.24$ (2.8×10^{-6} M), 0.20 (2.8×10^{-5} M), and < 0.01 (2.8×10^{-4} M).

[30] J. Dey, A. Y. Will, R. A. Agbaria, P. W. Rabideau, A. H. Abdourazak, R. Sygula, I. M. Warner, *J. Fluoresc.* **1997**, *7*, 231 – 236.

[31] a) A. Ayalon, M. Rabinovitz, P.-C. Cheng, L. T. Scott, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1636 – 1637; *Angew. Chem.* **1992**, *104*, 1691 – 1692; b) M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1995**, *117*, 6254 – 6257.

[32] a) M. V. Frash, A. C. Hopkinson, D. K. Bohme, *J. Am. Chem. Soc.* **2001**, *123*, 6687 – 6695; b) T. C. Dinadayalane, S. Deepa, A. S. Reddy, G. N. Sastry, *J. Org. Chem.* **2004**, *69*, 8111 – 8114.

[33] Since the activation energy, ΔG, of bowl-to-bowl inversion is known to depend on which basis sets are utilized (Ref. [37c]), geometry optimization and energy calculations were performed using the following basis sets: B3LYP/6-31G(d): 15.3 kcal mol^{-1}, B3LYP/6-31G(d,p): 15.9 kcal mol^{-1}, B3LYP/6-311G(d,p): 16.7 kcal mol^{-1}, B3LYP/6-311 + G(2d,p): 17.0 kcal mol^{-1}.

[34] a) T. J. Seiders, K. K. Baldridge, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **2001**, *123*, 517 – 525; b) L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920 – 1921.

[35] K. Kawasumi, Q. Zhang, Y. Segawa, L. T. Scott, K. Itami, *Nat. Chem.* **2013**, *5*, 739 – 744.

[36] T. Amaya, H. Sakane, T. Muneishi, T. Hirao, *Chem. Commun.* **2008**, 765 – 767.

[37] a) U. D. Priyakumar, G. N. Sastry, *J. Phys. Chem. A* **2001**, *105*, 4488 – 4494; b) T. C. Dinadayalane, G. N. Sastry, *Tetrahedron* **2003**, *59*, 8347 – 8351; c) T. Amaya, H. Sakane, T. Nakata, T. Hirao, *Pure Appl. Chem.* **2010**, *82*, 969 – 978.

[38] a) S. Higashibayashi, R. Tsuruoka, Y. Soujanya, U. Purushotham, G. N. Sastry, S. Seki, T. Ishikawa, S. Toyota, H. Sakurai, *Bull. Chem. Soc. Jpn.* **2012**, *85*, 450 – 467; b) B. B. Shrestha, S. Karanjit, S. Higashibayashi, H. Sakurai, *Pure Appl. Chem.* **2014**, *86*, 747 – 753.

Received: March 20, 2015
Published online: April 27, 2015

