

Synthesis of Cyano-Substituted Diaryltetracenes from Tetraaryl[3]cumulenes**

Przemyslaw Gawel, Cagatay Dengiz, Aaron D. Finke, Nils Trapp, Corinne Boudon, Jean-Paul Gisselbrecht, and François Diederich*

Dedicated to Professor Armin de Meijere on the occasion of his 75th birthday

Abstract: A versatile, two-step synthesis of highly substituted, cyano-functionalized diaryltetracenes has been developed, starting from easily accessible tetraaryl[3]cumulenes. This unprecedented transformation is initiated by [2+2] cycloaddition of tetracyanoethylene (TCNE) to the proacetylenic central double bond of the cumulenes to give an intermediate zwitterion, which after an electrocyclization cascade and dehydrogenation yields 5,5,11,11-tetracyano-5,11-dihydrotetracenes in a one-pot procedure. A subsequent copper-assisted decyanation/aromatization provided the target 5,11-dicyano-6,12-diaryltetracene derivatives. All of the postulated structures were confirmed by X-ray crystallography. The new chromophores are thermally highly stable and feature promising fluorescence properties for potential use in optoelectronic devices. They are selective chemosensors for Cu^I ions, which coordinate to one of the CN substituents and form a 1:1 complex with an association constant of $K_a = 1.5 \times 10^5 \text{ L mol}^{-1}$ at 298 K.

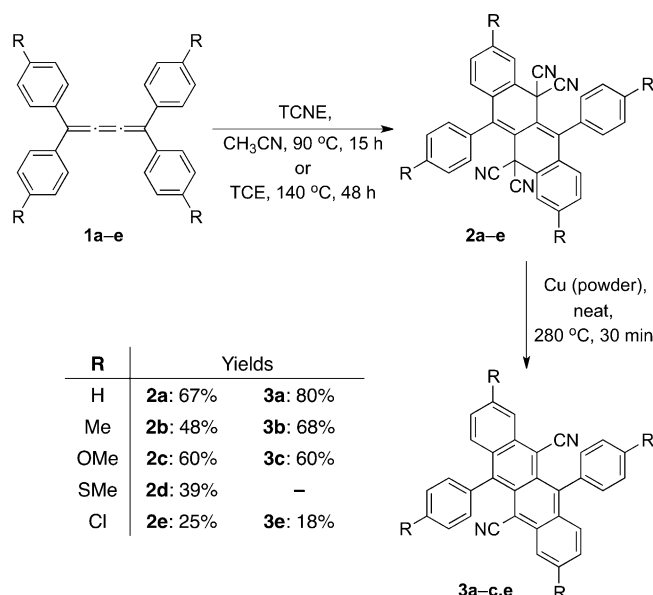
In the early 1920s, Brand reported the first synthesis of tetraarylbuta-1,2,3-trienes ([3]cumulenes).^[1] Since then, [3]cumulenes have attracted increasing attention, and a variety of procedures have been developed for their synthesis.^[2] However, only a limited amount of research has been done to investigate the chemistry of [3]cumulenes themselves.^[3,4]

[3]Cumulenes show the largest bond-length alternation (BLA)^[5] in the $[n]$ cumulene series.^[6] The central C=C bond of [3]cumulenes (average bond length 1.236 Å) is much shorter than the two terminal C=C bonds (average bond length

1.366 Å),^[7] and in polarized push-pull-substituted [3]cumulenes the central C=C bond approaches the length of an acetylenic C≡C triple bond (down to 1.20–1.21 Å).^[8] By applying the [2+2] cycloaddition–retroelectrocyclization (CA-RE) reaction between electron-rich alkynes and electron-deficient alkenes,^[9] we recently observed proacetylenic reactivity in a push-pull-substituted [3]cumulene.^[10] It reacted with tetracyanoethylene (TCNE) via the CA-RE cascade to give a stable zwitterionic product. With this in mind, we became interested in exploring the potential proacetylenic reactivity of the longer central C=C bond of non-polarized tetraaryl[3]cumulenes with TCNE.

Herein, we report a one-pot synthesis of 5,5,11,11-tetracyano-5,11-dihydrotetracenes **2a–e**, which we propose is initiated by the CA-RE reaction of tetraaryl[3]cumulenes **1a–e** with TCNE, and their subsequent Cu-promoted thermal oxidation to 5,11-dicyanotetracenes **3a–c,e** (Scheme 1). We describe the structures and remarkable optoelectronic properties of these new chromophores and their use as a selective chemosensor for Cu^I ions.

The synthesis of functionalized [3]cumulenes **1a–e** followed a well-established procedure,^[2,11] and gave the desired compounds in multigram quantities in four steps, starting



Scheme 1. Synthesis of 5,11-dihydrotetracenes **2a–e** and tetracenes **3a–c,e**. In the first step, the second set of conditions is used only for **1e**. TCNE: tetracyanoethylene; TCE: 1,1,2,2-tetrachloroethane.

[*] P. Gawel, C. Dengiz, Dr. A. D. Finke, Dr. N. Trapp, Prof. Dr. F. Diederich
Laboratorium für Organische Chemie, ETH Zürich
Vladimir-Prelog-Weg 3, HCI, 8093 Zürich (Switzerland)
E-mail: diederich@org.chem.ethz.ch

Prof. Dr. C. Boudon, Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide,
Institut de Chimie-UMR 7177, C.N.R.S., Université de Strasbourg
4, rue Blaise Pascal, 67000 Strasbourg (France)

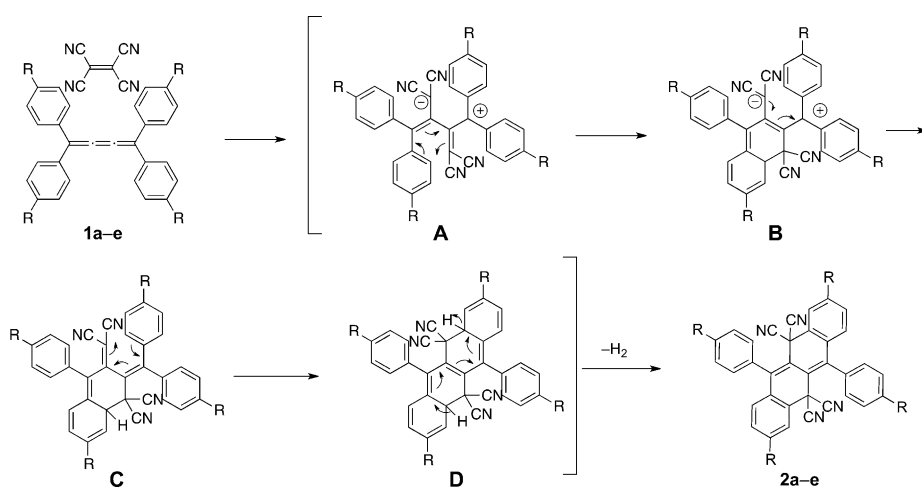
[**] This work was supported by the Swiss National Science Foundation and the ERC Advanced Grant No. 246637 ("OPTELOMAC"). We thank Dr. Ori Gidron for help with the determination of fluorescence quantum yields, Dr. David Schweinfurth with the complexation studies, and Dr. Bruno Bernet for NMR interpretation. X-ray services were provided by the Small Molecule Crystallography Center of ETH Zürich (<http://www.smocc.ethz.ch>).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201402299>.

from *para*-substituted benzophenones (Supporting Information, Section S2). X-ray crystal structures of **1b–e** showed no influence of the substituents on the butatriene moiety with the length of the central C=C bond varying between 1.24 and 1.25 Å and of the two terminal C=C bonds between 1.33 and 1.35 Å (for details on the butatrienes, see the Supporting Information, Sections S3, S4, S7, S8).

Upon heating **1a–d** in acetonitrile with TCNE, 5,11-dihydrotetracenes **2a–d** were obtained in good yields (39–67 %, Scheme 1). The polar solvent and the elevated temperature (90 °C) seem to be essential for the reaction.^[12] [3]Cumulene **1e** required higher temperatures (140 °C) and a different solvent (1,1,2,2-tetrachloroethane, TCE) to undergo this reaction with TCNE.

We propose a cascade mechanism for the unprecedented transformation to the dihydrotetracenes, initiated by formal [2+2] cycloaddition of TCNE to the central C=C bond of the tetraaryl[3]cumulenes (Scheme 2).^[9,10] Retroelectrocycliza-



Scheme 2. Proposed mechanism for the transformation of tetraaryl[3]cumulenes with TCNE to give 5,11-dihydrotetracenes.

tion of the formed cyclobutene ring generates the zwitterionic species **A** with the negative and positive charges stabilized by the dicyanovinyl and diphenylmethyl groups, respectively. The requirement for stabilization of the highly polar, zwitterionic intermediates explains the favorable influence of the polar solvent acetonitrile on the reaction. A disrotatory $6\pi\text{-e}^-$ electrocyclic closure provides intermediate **B**, followed by charge neutralization to give **C**.^[13] The crystal structure of the previously reported zwitterion formed by a push–pull butatriene shows the right geometry for the proposed disrotatory ring closure.^[10]

Intermediate **C** undergoes a second disrotatory $6\pi\text{-e}^-$ electrocyclic closure to give 4a,5,10a,11-tetrahydrotetracene **D**. We presume that this is possibly the rate-determining step and that the high temperatures are required to enable the right cyclization geometry. A formal 1,8-elimination of hydrogen, driven by gain in benzenoid aromaticity, finishes the reaction cascade.

5,11-Dihydrotetracenes **2a–e** are pale- to deep-yellow solids. Except for **2d**, which gives a black tar at elevated

temperatures (310 °C), all other 5,11-dihydrotetracenes decompose to a mixture of products (including small amounts of target tetracene derivatives **3**, see below) at around 300 °C. X-ray crystallography (Section S3) revealed that the four fused rings of **2b** and **2c** are coplanar, while there is a significant puckering in the dihydrotetracene core of **2a**, with two nitriles in a pseudoaxial and the others in a pseudoequatorial position (Figure 1). Compounds **2a–e** are fluorescent, both in solution (CH_2Cl_2) and in the solid state (Section S5). Compounds **2a** and **2b** exhibit low fluorescence quantum yields ($\Phi_F = 0.10$ in CH_2Cl_2), whereas compounds **2c–e** display higher fluorescence quantum yields ($\Phi_F = 0.22$ for **2c** in CH_2Cl_2 ; for details, see Section S5).

We subsequently transformed the 5,11-dihydrotetracenes into the corresponding tetracenes by formal elimination of cyanogen ($(\text{CN})_2$). Tetracenes feature extraordinary electronic properties and find application in organic devices, such as field effect transistors (FETs), organic light-emitting diodes (OLEDs), and solar cells.^[14] Heating a finely ground mixture of **2a–c** with an excess of copper powder^[15] to 280 °C yielded tetracene derivatives **3a–c** in fair to good yields (18–80 %, Scheme 1). In the case of **2d**, the reaction conditions led to the decomposition of starting material. Other attempts towards oxidative or reductive eliminations failed.^[16]

5,11-Dicyano-6,12-diaryltetracenes **3a–c** are thermally stable solids, sublimable at 230 °C (10^{-6} mbar), and are intensely pink colored with yellow to orange glow in solution and in the solid state. They are structurally similar to rubrene (5,6,11,12-tetraphenyltetracene) and also have

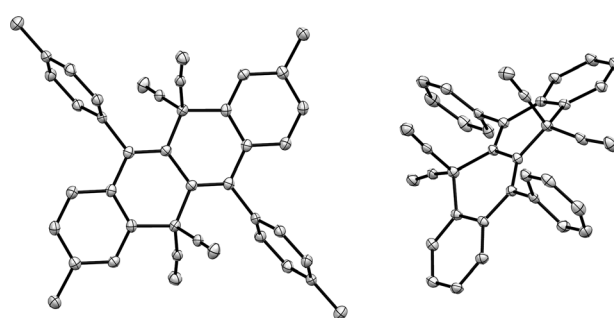


Figure 1. Left: Crystal structure of **2b**. Right: crystal structure of **2a**. $T = 100$ K. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

a similar appearance.^[17] X-ray crystal structures were determined for all obtained compounds. The cyano groups are in plane with the tetracene core, and the phenyl rings at the 6- and 12-positions are nearly orthogonal to it. Repulsion from the orthogonal phenyl rings causes substantial bending of the

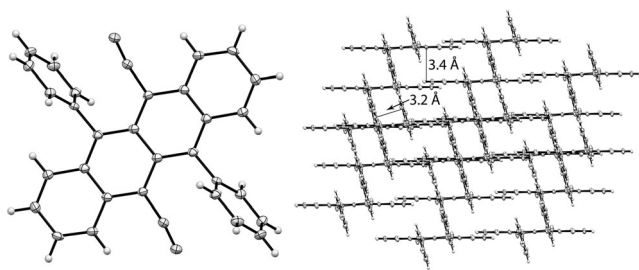


Figure 2. Left: Crystal structure (left) and crystal packing pattern (right) of **3a**. $T = 100$ K. Thermal ellipsoids at 50% probability.

nitrile groups, with a deviation of up to 10° (Figure 2). The crystal packing is dominated by π - π stacking interactions. Packing patterns of **3a**, **c**, **e** are similar, with single molecules oriented on parallel planes in a regular manner. In the case of **3b**, the packing is less regular, where the molecules are located on different nonparallel planes (Figure S24). The UV/Vis spectra of compounds **3a**-**c**, **e** are characteristic for acenes, with a very strong band around 300 nm and vibronically coupled bands with significant fine structure at lower energy (Figure 3). The lowest energy absorption is not a charge transfer band, but rather associated with the π - π^* transition in the tetracene moiety, as evidenced by time-dependent DFT calculations (see Section S8).^[18] The HOMO and LUMO are located on the tetracene core, with no polarization along the molecules. Tetracenes **3a**-**c**, **e** are strong fluorophores

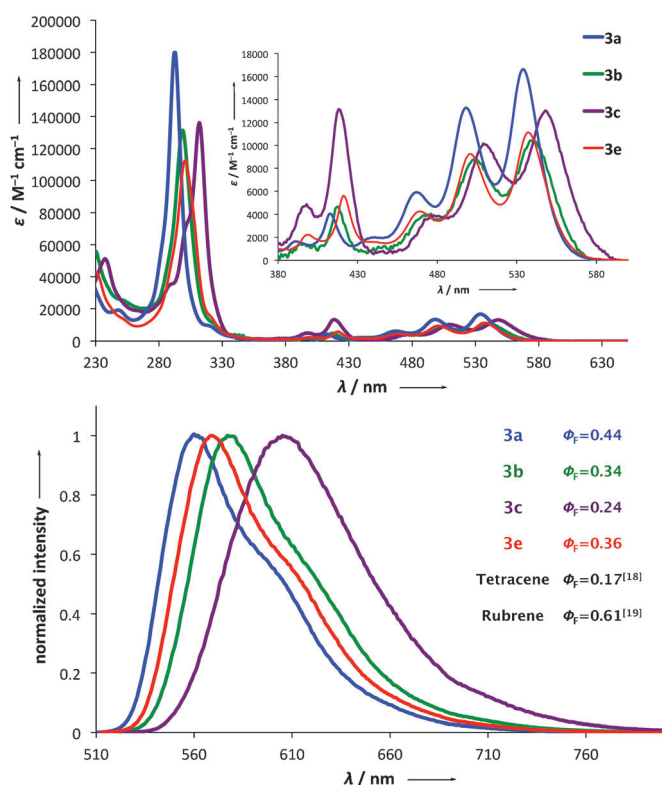


Figure 3. UV/Vis absorption spectra (top) and normalized photoluminescence spectra of **3a**-**c**, **e** (bottom) in CH_2Cl_2 at 298 K. The table gives the fluorescence quantum yields Φ_F (for details, see the Supporting Information, Section S5).

(Figure 3). In comparison to 5,11-dihydrotetracenes **2a**-**e**, tetracenes **3a**-**c**, **e** show reversed substituent dependence on fluorescence efficiency (see Section S5). While unsubstituted **3a** displays the highest fluorescence quantum yield ($\Phi_F = 0.44$), it is almost half as much for methoxy-substituted **3c** ($\Phi_F = 0.24$). The fluorescence quantum yield of **3a** is in between the values for tetracene ($\Phi_F = 0.17$)^[19] and rubrene ($\Phi_F = 0.61$).^[20] Tetracenes **3a**-**c**, **e** show rather constant electrochemical gaps (2.27 V for **3c** to 2.30 V for **3a**), which are in full agreement with the spectroscopically determined gaps (for full electrochemistry data, see Sections S4 and S7).

Prominent electronic and spectroscopic properties, along with the unique molecular environment of the cyano groups in tetracenes **3a**-**c**, **e**, inspired us to explore their use as fluorescent chemosensors for ions with the potential to coordinate to this group.^[21] We exposed compounds **3a**-**c**, **e** to different metal triflates (Li^+ , Mg^{2+} , Ba^{2+} , Ni^{2+} , Cu^{2+} , Cu^+ , Ag^+ , Zn^{2+} , Hg^{2+} , Sn^{2+} , In^{3+}) in CH_2Cl_2 and found them to be highly selective fluorescent molecular sensors for Cu^+ and Ag^+ (see Section S6). These soft ions interact well with the soft nitrogen atoms in cyano groups.^[22] Their selectivity may be controlled by the size of the metal cation, as space is limited by the close proximity of the adjacent phenyl ring. Moreover these ions are known to favorably interact with π -surfaces by undergoing cation- π interactions, while the soft aromatic π -surface is not capable of sufficiently “solvating” the harder ions, such as alkali and alkaline earth metal ions.^[23]

The chromophoric response to the complexation of Ag^+ and Cu^+ ions is substantial and allows for the easy detection of these ions both by absorption and emission spectroscopy in CH_2Cl_2 solution (Figure 4). A change in color occurs upon complexation, which is readily monitored in daylight (Figure S47). With all four cyanotetracenes, Cu^+ ions produce bathochromic shifts of the lowest-energy absorption of approximately 25 nm and Ag^+ ions shifts of approximately 15 nm. Treatment of the tetracenes with these ions leads to lowered fluorescence emission intensity and bathochromic shifts of the emission maxima. We quantified the binding of Cu^+ ions (as the more readily soluble $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ salt) by evaluating absorption and emission titrations (Figure 4), assuring the 1:1 stoichiometry both by the appearance of distinct isosbestic points in the absorption spectra and by Job plot analysis (Figure S59). Non-linear least-square curve fitting of the absorption titration data from multiple runs afforded an association constant $K_a = 130\,600 \pm 20\,000 \text{ L mol}^{-1}$. This value was confirmed by the evaluation of the fluorescence titration, with excitation at the isosbestic point at 513 nm, which yielded $K_a = 170\,000 \pm 22\,000 \text{ L mol}^{-1}$. Fluorescent copper ion sensing is a rapidly developing field owing to the importance of these ions in human metabolism.^[24]

In summary, we reported an unprecedented access to substituted tetracenes in two steps, starting from [3]cumulenes. Their reaction with TCNE in the first step to give 5,5,11,11-tetracyano-5,11-dihydrotetracenes most probably involves the reactivity of the proacetylenic, central cumulenonic bond in a CA-RE reaction. Formal cyanogen elimination in the second step provided functionalized tetracenes with a rubrene-like substitution pattern as thermally stable,

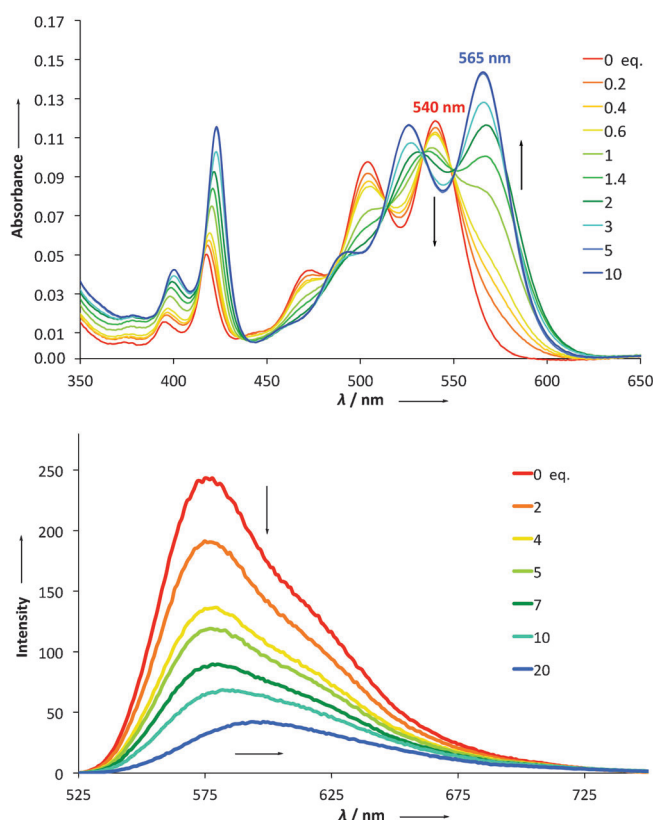


Figure 4. Molecular sensing of Cu^+ ions (as $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$) by absorption (top, $[\text{3b}] = 10^{-5} \text{ M}$) and emission (bottom, $[\text{3b}] = 10^{-6} \text{ M}$) spectroscopy. On the legends on the right side are given the equivalents of Cu^+ . $T = 298 \text{ K}$.

highly fluorescent molecular materials with potential for application in optoelectronic devices.^[25] We have now shown that these new chromophores, with their unique structural feature of coaligned neighboring phenyl and cyano substituents on the tetracene ring, have potential as selective molecular sensors of soft ions such as Cu^+ and Ag^+ . Additional synthetic modifications for chemosensor applications, also in aqueous solution, are planned.

Received: February 11, 2014
Published online: March 24, 2014

Keywords: [2+2] cycloaddition · [3]cumulenes · chemosensors · electrocyclization · tetracenes

- [1] a) K. Brand, *Chem. Ber.* **1921**, *54*, 1987–2006; b) K. Brand, F. Kercher, *Chem. Ber.* **1921**, *54*, 2007–2017.
- [2] a) H. Hopf in *The Chemistry of Ketenes, Allenes and Related Compounds* (Ed.: S. Patai), Wiley-Interscience, London, **1980**, pp. 780–901; b) H. Hopf, *Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives*, Wiley-VCH, Weinheim **2000**, pp. 178–196; c) L. Leroyer, V. Maraval, R. Chauvin, *Chem. Rev.* **2012**, *112*, 1310–1343.
- [3] a) H. Maurer, H. Hopf, *Angew. Chem.* **1976**, *88*, 687–688; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 628–629; b) A. Roedig, G. Zaby, *Chem. Ber.* **1980**, *113*, 3342–3351; c) J. K. Crandall, D. M.

- Coppert, T. Schuster, F. Lin, *J. Am. Chem. Soc.* **1992**, *114*, 5998–6002; d) J.-D. van Loon, P. Seiler, F. Diederich, *Angew. Chem.* **1993**, *105*, 1235–1238; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1187–1189; e) P.-H. Liu, L. Li, J. A. Webb, Y. Zhang, N. S. Goroff, *Org. Lett.* **2004**, *6*, 2081–2083; f) T. Asakawa, M. Iinuma, T. Furuta, S. Fujii, T. Kan, K. Tanaka, *Chem. Lett.* **2006**, *35*, 512–513.
- [4] a) M. Iyoda, S. Tanaka, M. Nose, M. Oda, *J. Chem. Soc. Chem. Commun.* **1983**, 1058–1059; b) M. Iyoda, S. Tanaka, H. Otani, M. Nose, M. Oda, *J. Am. Chem. Soc.* **1988**, *110*, 8494–8500.
- [5] BLA in cumulenes is reported as the difference in bond length between the two central-most bonds; see Ref. [6].
- [6] J. A. Januszewski, D. Wendinger, C. D. Methfessel, F. Hampel, R. R. Tykwinski, *Angew. Chem.* **2013**, *125*, 1862–1867; *Angew. Chem. Int. Ed.* **2013**, *52*, 1817–1821.
- [7] Average bond lengths were calculated from CSD entries of [3]cumulenes not bound to transition metals ($n = 68$). F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380–388.
- [8] D. Bouvy, Z. Janousek, H. G. Viehe, B. Tinant, J.-P. Declercq, *Tetrahedron Lett.* **1993**, *34*, 1779–1782.
- [9] a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, 737–739; b) S.-i. Kato, F. Diederich, *Chem. Commun.* **2010**, *46*, 1994–2006; c) M. Štefko, M. D. Tzirakis, B. Breiten, M.-O. Ebert, O. Dumele, W. B. Schweizer, J.-P. Gisselbrecht, C. Boudon, M. T. Beels, I. Biaggio, F. Diederich, *Chem. Eur. J.* **2013**, *19*, 12693–12704.
- [10] Y.-L. Wu, F. Tancini, W. B. Schweizer, D. Paunescu, C. Boudon, J.-P. Gisselbrecht, P. D. Jarowski, E. Dalcanele, F. Diederich, *Chem. Asian J.* **2012**, *7*, 1185–1190.
- [11] For first syntheses of some of the [3]cumulenes reported herein, see: a) Ref. [1]; **1a**, **1c**, **1e**; b) K. Brand, G. Wendel, *J. Prakt. Chem.* **1927**, *115*, 335–350; **1b**.
- [12] N. Islam, M. Tsukayama, Y. Kawamura, *Int. J. Mod. Phys. B* **2006**, *20*, 4619–4624; these authors also reported the transformation of **1c** with TCNE, however at room temperature in CH_2Cl_2 . Under these conditions, they obtained a dihydronaphthalene derivative, as confirmed by X-ray analysis. The transformation of **1b** to **2b** in our study also works with lower yields in DMF at 100°C .
- [13] In case of identical atom positions, **B** and **C** are of course resonance structures.
- [14] a) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945; b) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028–5048; c) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460–492; *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483; For N-heteroacenes, see: d) U. H. F. Bunz, J. U. Engelhart, B. D. Lindner, M. Schaffroth, *Angew. Chem.* **2013**, *125*, 3898–3910; *Angew. Chem. Int. Ed.* **2013**, *52*, 3810–3821.
- [15] A similar cyanogen elimination from tetracyanoquinodimethanes on Cu(100) surfaces was recently reported: C. Urban, Y. Wang, J. Rodriguez-Fernandez, R. Garcia, M. A. Herranz, M. Alcamí, N. Martín, F. Martín, J. M. Gallego, R. Miranda, R. Otero, *Chem. Commun.* **2014**, *50*, 833–835.
- [16] G. Jayamurugan, O. Dumele, J.-P. Gisselbrecht, C. Boudon, W. B. Schweizer, B. Bernet, F. Diederich, *J. Am. Chem. Soc.* **2013**, *135*, 3599–3606.
- [17] For the synthesis of rubrene and derivatives, see: a) A. S. Paraskar, A. R. Reddy, A. Patra, Y. U. Wijssboom, O. Gidron, L. J. W. Shimon, G. Leitun, M. Bendikov, *Chem. Eur. J.* **2008**, *14*, 10639–10647; For applications of rubrene in field-effect transistors, see: b) V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644–1646; c) K. A. McGarry, W. Xie, C. Sutton, C. Risko, Y. Wu, V. G. Young, Jr., J.-L. Brédas, C. D. Frisbie, C. J. Douglas, *Chem. Mater.* **2013**, *25*, 2254–2263;

- For the electroluminescence of rubrenes, see: d) M. M. Richter, *Chem. Rev.* **2004**, *104*, 3003–3036.
- [18] Gaussian09 (Revision A.1), M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2009**.
- [19] A. M. Müller, Y. S. Avlasevich, K. Mülen, C. J. Bardeen, *Chem. Phys. Lett.* **2006**, *421*, 518–522.
- [20] G. Laurent, N. T. Ha-Duong, R. Mèallet-Renault, R. B. Pansu, *Handai Nanophotonics* (Eds.: M. Hiroshi, K. Satoshi), Elsevier, Amsterdam, **2004**, pp. 89–101.
- [21] a) J. N. Wilson, U. H. F. Bunz, *J. Am. Chem. Soc.* **2005**, *127*, 4124–4125; b) A. J. Zuccherro, J. N. Wilson, U. H. F. Bunz, *J. Am. Chem. Soc.* **2006**, *128*, 11872–11881; c) D. Schweinfurth, K. I. Hardcastle, U. H. F. Bunz, *Chem. Commun.* **2008**, 2203–2205.
- [22] S. F. Rach, F. E. Kühn, *Chem. Rev.* **2009**, *109*, 2061–2080.
- [23] For cation– π interactions of metal ions, see: a) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244–1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250, and references therein. For recent investigations on metal cation– π interactions, see: b) O. Perraud, V. Robert, H. Gornitzka, A. Martinez, J.-P. Dutasta, *Angew. Chem.* **2012**, *124*, 519–523; *Angew. Chem. Int. Ed.* **2012**, *51*, 504–508; c) A. Bauzá, P. M. Deyà, A. Frontera, D. Quinonero, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1322–1326.
- [24] a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566; b) H. S. Jung, P. S. Kwon, J. W. Lee, J. I. Kim, C. S. Hong, J. W. Kim, S. Yan, J. Y. Lee, J. H. Lee, T. Joo, J. S. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 2008–2012.
- [25] For the impact of cyano substituents on the use of acenes in optoelectronic devices, see: a) M.-Y. Kuo, H.-Y. Chen, I. Chao, *Chem. Eur. J.* **2007**, *13*, 4750–4758; b) S. Katsuta, D. Miyagi, H. Yamada, T. Okujima, S. Mori, K.-i. Nakayama, H. Uno, *Org. Lett.* **2011**, *13*, 1454–1457.