Anion–π Interactions | **Very Important Paper**

DOI: 10.1002/ange.201307984

Electron Sharing and Anion–π Recognition in Molecular Triangular Prisms**

Severin T. Schneebeli, Marco Frasconi, Zhichang Liu, Yilei Wu, Daniel M. Gardner, Nathan L. Strutt, Chuyang Cheng, Raanan Carmieli, Michael R. Wasielewski, and J. Fraser Stoddart**

Electronic interactions, as well as through-space electron hopping and delocalization between redox-active aromatic building blocks, play a crucial role in orchestrating electron transport in organic materials.[1] Extensive investigations[2] of orbital overlap associated with both parallel and T-shaped geometries between aromatic rings are paving the way for the design of efficient organic photovoltaics[3] and molecular electronic devices.[4] In any quest to advance these research areas, it is essential to learn how through-space orbital overlap and electron sharing in non-traditional (that is, not parallel or T-shaped) geometries[5] between multiple rings affect the properties of aromatic compounds and their superstructures. With the objective of investigating this phenomenon in molecules with unconventional aromatic stacking geometries, we have designed and synthesized rigid chiral triangular prisms,[6] namely (−)- and (+)-NDI-Δ, with tubular cavities flanked by three naphthalenediimide (NDI) units. Its unique redox properties[7] and accessible functionalization[8] make NDI an ideal building block with which to explore electron-transport and delocalization.[9] Furthermore, the highly electron-deficient nature of NDIs is of current interest for the investigation of anion–π interactions[10] with potential applications in chemosensing,[11] synthetic membrane transport,[12] and selective catalysis.[13]

We demonstrate that cyclic through-space electron sharing[5,14] (which, although geometrically related, differs fundamentally from the three-dimensional through-bond electron delocalization of cycloparaphenylenes)[15] takes place in the NDI-molecular prisms as a consequence of the unique triangular arrangement of their NDI units. Rigid triangular geometries are special in so far as they: 1) allow for efficient orbital overlap on account of the 60° contact angles involved and 2) contain, at the same time, cavities capable of expressing molecular recognition.[16] Moreover, the cyclic orbital overlap in the NDI-based molecular triangular prisms (−)- and (+)-NDI-Δ leads to 3) electronic communication between the NDI units, resulting in no less than six individually accessible redox states; 4) enhanced anion–π recognition with bound linear I_3^- anions; and 5) I_3^--induced π–π stacking into single-handed helical superstructures that are 6) right- (*P*) and left-handed (*M*), respectively, as a result of chirality transfer from the molecule to the supramolecule.

The molecular triangular prisms (−)- and (+)-NDI-Δ[6] were synthesized (Figure 1 a) in a single stereospecific step from two commercially available components, namely, naphthalenetetracarboxylic dianhydride (**1**) and *(RR)* or *(SS)*-*trans*-1,2-cyclohexanediamine (**2**), in 25 and 23 % yields, respectively. The high symmetry of both (−)- and (+)-NDI-Δ is reflected by the relative simplicity of the ^{1}H NMR spectra for the compounds, which show only two sets of signals for the 12 NDI protons (Supporting Information). The rigid molecular structures of (−)- and (+)-NDI-Δ also lead to strong peaks (Figure 1 b) in the circular dichroism (CD) spectra.[17] Both enantiomers of NDI-Δ formed crystals from MeOH/CH_2Cl_2 solutions suitable for single-crystal X-ray diffraction analyses. The crystal structures (for example, for (−)-NDI-Δ

---

[*] Dr. S. T. Schneebeli,[+] Dr. M. Frasconi,[+] Dr. Z. Liu, Y. Wu, N. L. Strutt, C. Cheng, Prof. J. F. Stoddart
Center for the Chemistry of Integrated Systems
Department of Chemistry, Northwestern University
2145 Sheridan Road, Evanston, IL 60208 (USA)
E-mail: stoddart@northwestern.edu

Y. Wu, D. M. Gardner, Prof. R. Carmieli, Prof. M. R. Wasielewski
Argonne-Northwestern Solar Energy Research (ANSER) Center
Department of Chemistry, Northwestern University
2145 Sheridan Road, Evanston, IL 60208 (USA)
E-mail: m-wasielewski@northwestern.edu

[+] These authors contributed equally to this work.

[**] We thank Dr. Saman Shafaie for collecting high-resolution mass-spectrometric data, Dr. Amy A. Sarjeant and Charlotte Stern for solving the single-crystal X-ray structures, and Dr. Nicolaas A. Vermeulen, Dr. Andrew C. Sue, and Dr. Jianing Li for helpful discussions. The authors thank our joint collaborators Dr. Turki S. Al-Saud and Dr. Nezar H. Khdary from the King Abdulaziz City of Science and Technology (KACST) in Saudi Arabia for their interest in this research. M.R.W. is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy, DOE, under grant no. DE-FG02-99ER-14999. S.T.S. thanks the International Institute for Nanotechnology (IIN) at Northwestern University (NU) for an IIN Postdoctoral Fellowship and the QUEST high-performance computing center at NU for a research allocation of computer time. M.F. was supported by the Non-Equilibrium Energy Research Center (NERC), which is an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Basic Energy Sciences (DOE-BES) under Award DE-SC0000989. Y.W. thanks the Fulbright Scholars Program for a Graduate Research Fellowship. D.M.G. was supported by the Department of Defense through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program. N.L.S. acknowledges the National Science Foundation (NSF) for a Graduate Research Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307984.

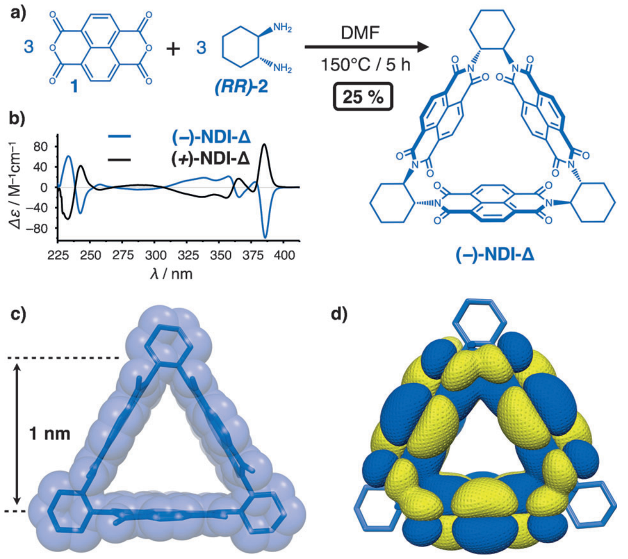

Figure 1. a) Stereospecific synthesis of the rigid triangular molecular prism (−)-NDI-Δ from (*RR*)-**2**. The enantiomer (+)-NDI-Δ was prepared in a similar yield from (*SS*)-**2**, following the same procedure as that used to prepare the (−)-enantiomer. b) CD spectra of (−)- and (+)-NDI-Δ recorded at 298 K in CH_2Cl_2 solutions. c) Tubular representation of the single-crystal X-ray structure of (−)-NDI-Δ with the corresponding space-filling representation superimposed upon it in a semi-transparent fashion. d) Graphical representations of the DFT-calculated (B3LYP/6-31G**) lowest unoccupied molecular orbital (LUMO) of (−)-NDI-Δ. Orbital isosurfaces are illustrated at 0.004 electrons Bohr^{-3}.

shown in Figure 1) confirm the rigid geometries of the hollow, equilateral, triangular prisms with a base-to-apex distance of about 1.0 nm. The faces of the NDI units in (−)-NDI-Δ, and also in (+)-NDI-Δ, are arranged with respect to each other in an orthogonal fashion, resembling the faces of triangular prisms. These rigid three-dimensional frameworks therefore constitute a unique geometrical arrangement of the NDI molecular orbitals for cyclic through-space electron sharing.

The electron-sharing hypothesis is supported by density functional theory (DFT) calculations that reveal the presence of delocalized frontier molecular orbitals in (−)-NDI-Δ. The highly delocalized LUMO (Figure 1 d) of (−)-NDI-Δ is populated with one electron in $[(-)\text{-NDI-}\Delta]^{\bullet-}$ radical anion, resulting in a SOMO which resembles the LUMO of (−)-NDI-Δ closely in shape. This result suggests that the unpaired electron in $[(-)\text{-NDI-}\Delta]^{\bullet-}$ is shared among all three NDI-units of the triangular prism, thus constituting a rare example of a purely organic mixed-valence[9a,14c,18] radical in which the unpaired electron is surrounding a triangular cavity.

Comparison of the cyclic voltammogram (CV) of (−)-NDI-Δ with that of a NDI reference compound (NDI-Ref) (Figure 2) provides experimental evidence for the DFT-predicted cyclic electron sharing in (−)-NDI-Δ. While the CV of NDI-Ref possesses two sequential one-electron cathodic waves, observed at −709 ± 5 and −1131 ± 9 mV vs. Ag/AgCl, corresponding to the formation of the $[\text{NDI-Ref}]^{\bullet-}$ radical anion and the $[\text{NDI-Ref}]^{2-}$ dianion, respectively, the CV of (−)-NDI-Δ reveals a dramatic splitting into six distinct reversible one-electron waves. This observation indicates that electronic communication between the three equivalent NDI redox centers is occurring within the triangular molecular prisms. Furthermore, the potential ($E_1 = -567 \pm 7$ mV), corresponding to the first reduction of (−)-NDI-Δ, is shifted by 142 mV towards more positive potentials compared to the E_1 of NDI-Ref.[19] Similar shifts in redox potentials have been observed[9] previously for covalently bonded, parallel π–π stacked NDI- and PDI-derivatives, which also display through-space electron sharing. The observed shift in redox potentials has also been rationalized quantitatively by DFT calculations employing a continuum solvent model with the B3LYP-functional, that is, the same functional used to compute the frontier molecular orbitals of (−)-NDI-Δ. The good correlation observed (Figure 2, inset) between the DFT-calculated and the experimental reduction potentials for (−)-NDI-Δ, NDI-Ref, (+)-PMI-Δ, and PMI-Ref adds further credibility to the DFT-description of the (−)-NDI-Δ frontier molecular orbitals.

While the UV/Vis spectrum[20] (Supporting Information, Figure S8) of $[(-)\text{-NDI-}\Delta]^{\bullet-}$ also hints[21] at electronic communication between the NDI units in the triangular prisms, even stronger experimental evidence for electron sharing in $[(-)\text{-NDI-}\Delta]^{\bullet-}$ is provided by continuous wave (cw) electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopies. When compared to the EPR spectrum of $[\text{NDI-Ref}]^{\bullet-}$, that of $[(-)\text{-NDI-}\Delta]^{\bullet-}$ shows a decrease in line-width by a factor of 1.75 at 265 K (Figure 3 a). This result is in good agreement with EPR theory for electron-delocalized systems,[22] which predicts a reduction in EPR linewidth by $\sqrt{n} = 1.73$ for sharing of an electron by three ($n = 3$) NDI units. Moreover, the proton

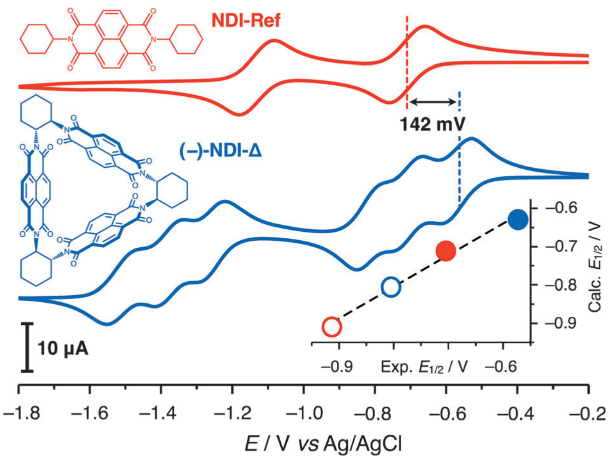

Figure 2. Cyclic voltammograms (CVs) of a reference NDI compound (NDI-Ref) with cyclohexyl substituents (red curve) and (−)-NDI-Δ (blue curve) recorded (scan rate 50 mV s^{-1}) using a glassy carbon electrode. All of the experiments were performed at 298 K in argon-purged CH_2Cl_2 solutions (0.5 mM) with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. The inset shows the correlation between the DFT-calculated and the experimental half-wave potentials ($E_{1/2}$ vs. Ag/AgCl) for the first reductions of (−)-NDI-Δ (blue ●), NDI-Ref (red ●), and the corresponding compounds (○) with all of the NDI groups replaced with pyromellitic diimide (PMI) functional groups. A linear fit to the data ($y = 1.20x + 0.16$ V) gave a coefficient of correlation (R^2) of 0.99.

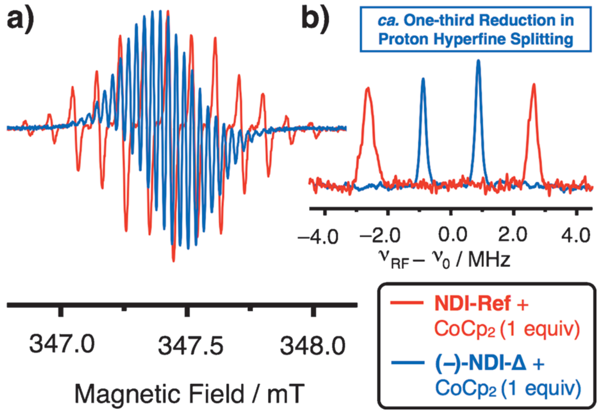

Figure 3. Evidence for electron-sharing in (−)-NDI-Δ by a) cw-EPR and b) cw-ENDOR spectroscopy. a) EPR spectra of NDI-Ref (red curve) and (−)-NDI-Δ (blue curve) after reduction with 1.0 equiv of cobaltocene ([CoCp$_2$]). All of the spectra were recorded in CH$_2$Cl$_2$ (0.3 mM) at 265 K. The decrease in the EPR-linewidth for [(−)-NDI-Δ]$^{\bullet-}$ by a factor of about 1.75 indicates sharing of the unpaired electron over all three NDI units. b) In the case of [(−)-NDI-Δ]$^{\bullet-}$, this observation has also been confirmed by the ENDOR spectrum, which shows a near-perfect one-third reduction of the proton hyperfine interactions.

hyperfine splittings in the cw-ENDOR spectra for the monoradical anion [(−)-NDI-Δ]$^{\bullet-}$ are also reduced by about a factor of three (Figure 3b) when compared with the reference compound, providing yet further evidence[23] for the sharing of the unpaired electron among the three symmetrically equivalent NDI subunits.[24]

The fact that electronic communication between the redox centers in (−)- and (+)-NDI-Δ increases the electron-affinity of the NDI units in the prisms, as shown by the CV data, should in turn also result in enhanced charge-transfer interactions with anions in the context of anion–π interactions.[12b,c,25] Thus, we envisioned that the tubular, electron-deficient cavities of (−)- and (+)-NDI-Δ could provide an ideal electronic and geometrical fit for the accommodation of the linear I_3^- anion. To test this hypothesis, the (−)-NDI-Δ host was titrated with solutions of [Bu$_4$N][I$_3$] in CD$_2$Cl$_2$ and the binding constant (K_a) was evaluated by ^{1}H NMR spectroscopy. Employing a 1:1 binding model, which was confirmed by a Job Plot (Supporting Information, Figure S3), we determined[26] a modest K_a value of $25 \pm 2\,\text{L mol}^{-1}$ for the binding of I_3^- by the (−)-NDI-Δ host.

Structural evidence for the binding of I_3^- inside the cavities of (−)- and (+)-NDI-Δ was obtained by single-crystal X-ray diffraction. Slow vapor diffusion of *n*-hexane into 1,2-dibromoethane solutions of (−)- or (+)-NDI-Δ, containing [Bu$_4$N][I$_3$], resulted in brown single crystals, which were found to be inclusion complexes of I_3^- anions located inside (−)- and (+)-NDI-Δ, respectively. The solid-state superstructures (Figure 4a) reveal that the linear I_3^- anions almost completely fill up the tube-shaped cavities of the triangular molecular prisms, with anion–π distances of about 3.8 Å.[27] With the I_3^- anions buried completely inside the triangular prisms, there is no space for the Bu$_4$N$^+$ cations to reside close to the anions, leading to ion-pair separation[27] upon guest binding. In the present case, it is clear that anion–π interactions within a neutral host are therefore able to break up ion-pairing in non-polar solvents, highlighting the significance of such supramolecular interactions inside a triangular prismatic cavity.

The solid-state superstructures of (−)- and (+)-NDI-Δ also indicate that the formation of the I_3^- inclusion complexes with (−)- and (+)-NDI-Δ leads to dramatic changes in the extended supramolecular interactions between the triangular prisms themselves. When they bind I_3^- anions, π–π stacking of the triangular prisms is observed in the solid state (Figure 4a), wherein two NDI units of each prism stack face-to-face with

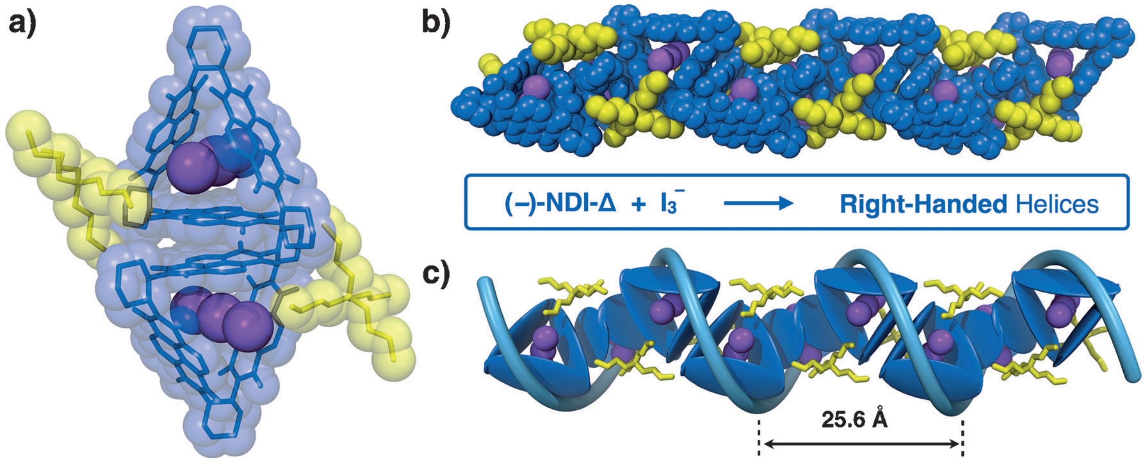

Figure 4. Space-filling and graphical representations of the single-crystal X-ray superstructure of (−)-NDI-Δ with [Bu$_4$N][I$_3$]. a) Face-to-face π-stacked dimer, which is further stabilized with electrostatic and [C−H⋯O] interactions.[30] Note that the superstructures (Supporting Information, Figure S4) of the NDI-Δ molecules without [Bu$_4$N][I$_3$] did not exhibit any π-stacking. b), c) Space-filling and graphical representations of the right-handed, π-stacked supramolecular (*P*)-helices present in the solid-state superstructure of (−)-NDI-Δ. As expected, in the case of (+)-NDI-Δ, the corresponding left-handed (*M*)-helices were formed stereospecifically. (−)-NDI-Δ molecules are illustrated in blue, I_3^- anions in purple, and Bu$_4$N$^+$ counterions in yellow. The helical nature of the stacked wires is illustrated on overlaying a light-blue helix. Hydrogen atoms are omitted for the sake of clarity.

their neighbors at a near-perfect π–π stacking distance of about 3.4 Å with a cross-angle[28] of 60°. On examining the packing in the solid state of the empty triangles, no π–π stacking is detected (Supporting Information, Figure S4), indicating that the binding of I_3^- seems to induce this extended supramolecular phenomenon. The anion-induced π–π stacking of the triangular prisms (Figure 4 b) leads to the stereocontrolled formation of single-handed helices,[29] with every three triangles constituting one pitch of the helix with a repeat of 25.6 Å. The helicity of the resulting superstructures is controlled by the inherent chirality of the NDI-Δ prisms themselves; that is, while the (−)-NDI-Δ prisms form only right-handed (*P*)-helices in the solid-state, exclusively left-handed (*M*)-helices are formed from the corresponding (+)-enantiomer.

In summary, we have demonstrated, both by experiment and by the application of theory, through-space orbital interactions and the associated electron sharing phenomena in triangular, redox-active NDI prisms. The resulting electronic communication among the NDI units leads to six individually accessible redox states in the prisms, which is an unusually large number for such a relatively small organic molecule. Compounds with many readily accessible redox states (which include C_{60} as a well-known and much investigated example)[30] open the door to potential applications[31] in the field of molecular electronics. The orbital interactions between the NDI units in the molecular prisms also render their electron deficient cavities ideal for studying anion–π interactions. This property is demonstrated by the encapsulation of linear I_3^- anions inside the prismatic cavities, causing a profound change in the packing of the prisms in the extended solid-state superstructures. The inclusion of I_3^- anions induces π–π stacking of the chiral prisms into one-handed supramolecular helices, providing us with a rare emergent example of anion-induced self-assembly with potential as ion-channels.[12] The chirality invested in the six stereogenic centers in the occupied prisms dictates the handedness associated with their packing in the solid state to be either right- or left-handed.

Received: September 11, 2013

Keywords: anion–π interactions · helical π–π stacking · macrocycles · mixed-valence compounds · radical anions

---

[1] a) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Bredas, *Chem. Rev.* **2007**, *107*, 926–952; b) H. Bässler, A. Köhler, *Top. Curr. Chem.* **2012**, *312*, 1–65.

[2] a) M. Kiguchi, T. Takahashi, Y. Takahashi, Y. Yamauchi, T. Murase, M. Fujita, T. Tada, S. Watanabe, *Angew. Chem.* **2011**, *123*, 5826–5829; *Angew. Chem. Int. Ed.* **2011**, *50*, 5708–5711; b) S. T. Schneebeli, M. Kamenetska, Z. L. Cheng, R. Skouta, R. A. Friesner, L. Venkataraman, R. Breslow, *J. Am. Chem. Soc.* **2011**, *133*, 2136–2139; c) A. Saeki, Y. Koizumi, T. Aida, S. Seki, *Acc. Chem. Res.* **2012**, *45*, 1193–1202.

[3] B. C. Thompson, J. M. J. Fréchet, *Angew. Chem.* **2008**, *120*, 62–82; *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77.

[4] a) S. J. Tans, A. R. M. Verschueren, C. Dekker, *Nature* **1998**, *393*, 49–52; b) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99–117.

[5] a) D. Sun, S. V. Rosokha, J. K. Kochi, *Angew. Chem.* **2005**, *117*, 5263–5266; *Angew. Chem. Int. Ed.* **2005**, *44*, 5133–5136; b) S. V. Rosokha, I. S. Neretin, D. Sun, J. K. Kochi, *J. Am. Chem. Soc.* **2006**, *128*, 9394–9407.

[6] For the sake of simplicity, we refer to the *(RRRRRR)*-enantiomer of NDI-Δ as (−)-NDI-Δ and to the *(SSSSSS)*-enantiomer as (+)-NDI-Δ. This notation is based on the signs of the optical rotations at $\lambda_{max} = 385$ nm in the CD spectra (Figure 1 b) of the two compounds. In an analogous fashion (based on the compound's optical rotation at $\lambda_{max} = 225$ nm) we refer to *(RRRRRR)*-PMI-Δ, the CD spectrum of which has been published elsewhere (see reference [17]), as (+)-PMI-Δ.

[7] a) C. Thalacker, C. Röger, F. Würthner, *J. Org. Chem.* **2006**, *71*, 8098–8105; b) F. Schlosser, J. Sung, P. Kim, D. Kim, F. Würthner, *Chem. Sci.* **2012**, *3*, 2778–2785.

[8] a) S. V. Bhosale, C. H. Jani, S. J. Langford, *Chem. Soc. Rev.* **2008**, *37*, 331–342; b) N. Ponnuswamy, F. B. Cougnon, J. M. Clough, G. D. Pantos, J. K. M. Sanders, *Science* **2012**, *338*, 783–785; c) S. P. Black, A. R. Stefankiewicz, M. M. J. Smulders, D. Sattler, C. A. Schalley, J. R. Nitschke, J. K. M. Sanders, *Angew. Chem.* **2013**, *125*, 5861–5864; *Angew. Chem. Int. Ed.* **2013**, *52*, 5749–5752.

[9] a) A. Takai, T. Yasuda, T. Ishizuka, T. Kojima, M. Takeuchi, *Angew. Chem.* **2013**, *125*, 9337–9341; *Angew. Chem. Int. Ed.* **2013**, *52*, 9167–9171; b) F. Schlosser, M. Moos, C. Lambert, F. Würthner, *Adv. Mater.* **2013**, *25*, 410–414.

[10] a) A. Frontera, P. Gamez, M. Mascal, T. J. Mooibroek, J. Reedijk, *Angew. Chem.* **2011**, *123*, 9736–9756; *Angew. Chem. Int. Ed.* **2011**, *50*, 9564–9583; b) S. Guha, F. S. Goodson, L. J. Corson, S. Saha, *J. Am. Chem. Soc.* **2012**, *134*, 13679–13691; c) G. Aragay, A. Frontera, V. Lloveras, J. Vidal-Gancedo, P. Ballester, *J. Am. Chem. Soc.* **2013**, *135*, 2620–2627; d) P. Ballester, *Acc. Chem. Res.* **2013**, *46*, 874–884; e) H. T. Chifotides, K. R. Dunbar, *Acc. Chem. Res.* **2013**, *46*, 894–906; f) D. X. Wang, M. X. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 892–897.

[11] a) L. M. Salonen, M. Ellermann, F. Diederich, *Angew. Chem.* **2011**, *123*, 4908–4944; *Angew. Chem. Int. Ed.* **2011**, *50*, 4808–4842; b) L. E. Santos-Figueroa, M. E. Moragues, E. Climent, A. Agostini, R. Martinez-Manez, F. Sancenon, *Chem. Soc. Rev.* **2013**, *42*, 3489–3613.

[12] a) A. Hennig, L. Fischer, G. Guichard, S. Matile, *J. Am. Chem. Soc.* **2009**, *131*, 16889–16895; b) R. E. Dawson, A. Hennig, D. P. Weimann, D. Emery, V. Ravikumar, J. Montenegro, T. Takeuchi, S. Gabutti, M. Mayor, J. Mareda, C. A. Schalley, S. Matile, *Nat. Chem.* **2010**, *2*, 533–538; c) A. Vargas Jentzsch, A. Hennig, J. Mareda, S. Matile, *Acc. Chem. Res.* **2013**, DOI: 10.1021/ar400014r.

[13] a) S. Lin, E. N. Jacobsen, *Nat. Chem.* **2012**, *4*, 817–824; b) Y. Zhao, Y. Domoto, E. Orentas, C. Beuchat, D. Emery, J. Mareda, N. Sakai, S. Matile, *Angew. Chem.* **2013**, *125*, 10124–10127; *Angew. Chem. Int. Ed.* **2013**, *52*, 9940–9943.

[14] a) K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655–2686; b) M. J. Tauber, R. F. Kelley, J. M. Giaimo, B. Rybtchinski, M. R. Wasielewski, *J. Am. Chem. Soc.* **2006**, *128*, 1782–1783; c) J. Hankache, O. S. Wenger, *Chem. Rev.* **2011**, *111*, 5138–5178.

[15] a) R. Jasti, J. Bhattacharjee, J. B. Neaton, C. R. Bertozzi, *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647; b) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem.* **2010**, *122*, 769–771; *Angew. Chem. Int. Ed.* **2010**, *49*, 757–759.

[16] A. Sautter, D. G. Schmid, G. Jung, F. Würthner, *J. Am. Chem. Soc.* **2001**, *123*, 5424–5430.

[17] For a detailed discussion of Cotton effects in a related trianglar prism [(+)-PMI-Δ] with the NDI building blocks replaced by

pyromellitic diimide (PMI) units, see: J. Gawroński, M. Brzostowska, K. Gawrońska, J. Koput, U. Rychlewska, P. Skowronek, B. Nordén, *Chem. Eur. J.* **2002**, *8*, 2484 – 2494.

[18] a) P. Day, N. S. Hush, R. J. Clark, *Philos. Trans. R. Soc. London Ser. A* **2008**, *366*, 5 – 14; b) A. Heckmann, C. Lambert, *Angew. Chem.* **2012**, *124*, 334 – 404; *Angew. Chem. Int. Ed.* **2012**, *51*, 326 – 392; c) D. Sakamaki, A. Ito, K. Furukawa, T. Kato, M. Shiro, K. Tanaka, *Angew. Chem.* **2012**, *124*, 12948 – 12953; *Angew. Chem. Int. Ed.* **2012**, *51*, 12776 – 12781.

[19] Further reduction of $[(-)\text{-NDI-}\Delta]^{\bullet-}$ occurs at a significantly lower potential ($E_2 = -704 \pm 5$ mV) as a consequence of the enhanced Coulombic repulsion between the electrons in the multiply charged prismatic anions.

[20] a) S. F. Rak, T. H. Jozefiak, L. L. Miller, *J. Org. Chem.* **1990**, *55*, 4794 – 4801; b) D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas, M. R. Wasielewski, *J. Phys. Chem. A* **2000**, *104*, 6545 – 6551.

[21] The UV/Vis spectroscopic characterization of (−)-NDI-Δ was performed in different redox states obtained by electrochemical and chemical reduction, using a one-electron reductant, cobaltocene ($[\mathrm{CoCp_2}]$). The reduction of (−)-NDI-Δ to the monoradical anion $[(-)\text{-NDI-}\Delta]^{\bullet-}$ reveals (Supporting Information, Figure S6 – S8) an absorption spectrum typical for $[\mathrm{NDI}]^{\bullet-}$ radical anions. A red-shift compared to $[\text{NDI-Ref}]^{\bullet-}$ was, however, observed for the one long-wavelength ($\lambda > 700$ nm) absorption assigned (see: W. S. V. Kwan, J. F. Penneau, L. L. Miller, *J. Electroanal. Chem.* **1990**, *291*, 295 – 299) to the $D_0 \rightarrow D_1$ transition of the $[(-)\text{-NDI-}\Delta]^{\bullet-}$ radical anion, an observation which is consistent with the hypothesis of electronic communication within the $[(-)\text{-NDI-}\Delta]^{\bullet-}$ radical anion itself.

[22] J. R. Norris, R. A. Uphaus, H. L. Crespi, J. J. Katz, *Proc. Natl. Acad. Sci. USA* **1971**, *68*, 625 – 628.

[23] T. M. Wilson, M. J. Tauber, M. R. Wasielewski, *J. Am. Chem. Soc.* **2009**, *131*, 8952 – 8957.

[24] Given that the largest hyperfine splitting of NDI is about 10 MHz, the EPR and ENDOR experiments are consistent with electron sharing between the three NDI molecules on a time scale of more than $10^7\,\mathrm{s^{-1}}$, but they do not address whether the electron is rapidly hopping between NDI sites or is delocalized. True delocalization of the electron requires that the position of the electron on any individual NDI site is indistinguishable on at least the vibrational time scale (ca. $10^{13}\,\mathrm{s^{-1}}$).

[25] S. Guha, S. Saha, *J. Am. Chem. Soc.* **2010**, *132*, 17674 – 17677.

[26] Titration of $[\mathrm{Bu_4N}][\mathrm{I_3}]$ into solutions of NDI-Ref did not lead to any measurable shifts of the ^{1}H NMR signals, suggesting a very low association constant (K_a) for the $[\mathrm{Bu_4N}][\mathrm{I_3}]\cdot$NDI-Ref complex. K_a values for $\mathrm{I^-}$ binding to single NDI cores have been reported previously (see Ref. [12a]) to lie in the range of 0.2–0.4 $\mathrm{L\,mol^{-1}}$.

[27] Ion-pair separation is demonstrated in the solid-state superstructures of $[\mathrm{Bu_4N}][\mathrm{I_3}\subset\text{NDI-}\Delta]$ by the relatively large centroid-to-centroid distances (> 8.5 Å) observed between oppositely charged ions, compared to ion-pair distances of 5.8 Å in crystal structures (CCDC 707270; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, private communication 2008) of pure $[\mathrm{Bu_4N}][\mathrm{I_3}]$.

[28] The cross angle between π–π stacked NDI-Δ molecules was calculated as the minimum angle between the two vectors v_1 and v_2 (which describe the orientation of two adjacent π–π stacked NDI units 1 and 2) projected onto the same plane. Thereby, v_i ($i = 1, 2$) was defined as the vector connecting both nitrogen atoms in NDI plane$_i$.

[29] a) A. R. A. Palmans, E. W. Meijer, *Angew. Chem.* **2007**, *119*, 9106 – 9126; *Angew. Chem. Int. Ed.* **2007**, *46*, 8948 – 8968; b) N. Ponnuswamy, G. D. Pantos, M. M. J. Smulders, J. K. M. Sanders, *J. Am. Chem. Soc.* **2012**, *134*, 566 – 573; c) W. Zhang, W. Jin, T. Fukushima, N. Ishii, T. Aida, *J. Am. Chem. Soc.* **2013**, *135*, 114 – 117.

[30] P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Am. Chem. Soc.* **1991**, *113*, 1050 – 1051.

[31] S. S. Babu, H. Möhwald, T. Nakanishi, *Chem. Soc. Rev.* **2010**, *39*, 4021 – 4035.