Electrochemical investigations of singly and doubly bridged imino[60]fullerenes

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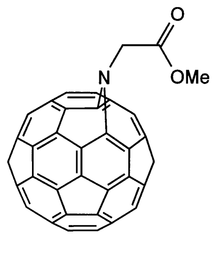
The electrochemical properties of four singly bridged (1–4) and one doubly bridged (5) *N*-substituted imino[60]fullerenes have been investigated with cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The substituents on the imino nitrogen are methoxycarbonylmethyl (1, 2, 5), 4-(pentafluorophenoxycarbonyl)phenyl (3), and 4-(succinimidoxycarbonyl)phenyl (4). [6,6]-Bridged structures (2) with closed and [5,6]-bridged structures (1, 3, 5) with open transannular bonds were compared for the first time. Whereas C_{60} and 1–4 exhibit four successive, reversible reduction peaks in terms of an EEEE mechanism, a chemical reaction followed the cathodic reduction of 5 to $5^{\bullet -}$. This effect is particularly clear in the DPV, where all subsequent reduction peaks were doubled. This can be explained by an ECEEE mechanism, in which 5 after the first E reduction undergoes a chemical transformation into one or two new species, which are further reduced in EEE processes. In the anodic oxidation of 1–5 a two-electron transfer was confirmed. In sharp contrast to all other fullerene derivatives, a quasireversible oxidation of 4 could be observed. To our knowledge, this is the first report of a quasireversible electrochemical oxidation for C_{60} mono adducts. The reduction potentials exhibit good linear relationships with the calculated LUMO energy levels. Significantly, compared to C_{60}, the reductions of the [6,6]-bridged derivative 2 as well as of the doubly [5,6]-bridged compound 5 occur at more negative potentials, whereas those of the singly [5,6]-bridged compounds 1, 3, 4 are found at less negative potentials.

Introduction

The electrochemical investigation of C_{60}[1–17] and its derivatives[18–34] has been an interesting subject since the beginning of preparative fullerene research.[35,36] While the cathodic reduction has received more attention, the anodic oxidation remained largely unexplored. Only a few reversible oxidations of fullerenes (C_{60}, C_{70} and C_{76}) themselves[37–39] and of their poly adducts[42] have been observed. However, to our knowledge, no observations of a reversible electrochemical or chemical oxidation of C_{60} mono adducts have been reported. We describe here the redox properties of a series of imino[60]fullerenes **1**–**5**. Iminofullerenes have recently gained considerable importance, since they can be starting materials for the synthesis of heterofullerenes.[40] Iminofullerenes can either have [6,6]-bridged or [5,6]-bridged structures.[41] The [6,6]-bridged isomers have usually closed and the [5,6]-bridged isomers open transannular bonds and are therefore epimino[60]fullerenes or azahomo[60]fullerenes, respectively. This is due to the principle of minimizing unfavourable double bonds in five-membered rings.[35,36] In open [5,6]-adducts the entire 60 π-electron chromophore remains intact, whereas in [6,6]-bridged mono adducts one double bond is removed, which partially breaks the conjugation within the fullerene framework. This is reflected, for example, in the characteristic electronic absorption spectra and the colours in solution of these two types of compounds.[1,2] Whereas the UV–VIS spectra of [5,6]-bridged mono adducts are very similar to those of free C_{60}, specific changes like a characteristic additional absorption at 430 nm result for [6,6]-bridged adducts. Electrochemical investigations of various [6,6]-adducts have shown a general trend, namely successive shifts of the reduction potentials to more negative values with an increasing number of addends attached to the fullerene framework.[18–34,42] Early electrochemical investigations[43] on singly [5,6]-bridged imino-



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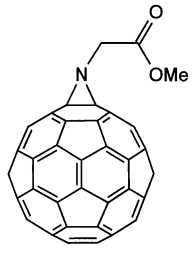

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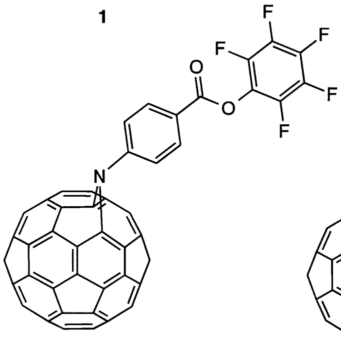

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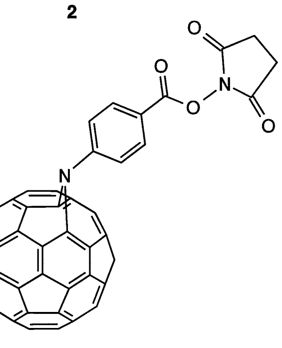

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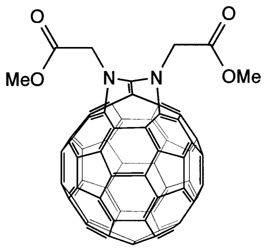

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fullerenes already indicated that within this binding mode the fullerene core preserves its electronegativity more than within other derivatives. Altogether, the reduction potentials of *N*-bridged derivatives are less negative than those of *C*-bridged derivatives.[43]

Experimental

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a Windows-driven BAS 100 W electrochemical analyser (Bioanalytical Systems, West Lafayette, IN). As working electrode a 3 mm-diameter glassy carbon electrode was used. The auxiliary electrode consisted of a Pt wire. $Ag/AgClO_4$ (0.01 M in MeCN/0.1 M Bu_4NPF_6) was used as reference electrode. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc^+) as the internal standard. All measurements were carried out at room temp. under argon in a 1,2-dichlorobenzene solution containing 0.1 M Bu_4NPF_6. The concentration of substrate was *ca.* 0.5 mM.

The semiempirical calculations of the orbital energy were performed on a microcomputer using the Spartan SGI (Version 3.1.3/Wavefunctions, Inc., 18401, Irvine, CA, USA).

J values are in Hz. The synthesis of compounds **1**, **2** and **5** is described elsewhere.[44]

1,6-Aza-[*N*-4′-(pentafluorophenoxycarbonyl)phenyl]homo[60]-fullerene (3)

To a solution of 1.00 g (1.388 mmol) of C_{60} in 70 ml of 1-chloronaphthalene, 1.1 equiv. (530 mg) of pentafluorophenyl *p*-azidobenzoate was added. This mixture was stirred for 3 d at 55 °C. After dilution with 150 ml of toluene the mixture was heated at reflux for 0.5 h. The separation of **3** from unreacted C_{60} was achieved with flash-chromatography using toluene–hexane (3:7) as eluent. Yield: 135 mg (58% relative to consumed C_{60}).

UV (cyclohexane) λ/nm: 658 (br), 596 (br), 553 (br), 467, 323, 261, 213. IR (KBr) ν/cm^{-1}: 511, 527, 542, 571, 596, 606, 685, 754, 841, 974, 1007, 1038, 1090, 1121, 1144, 1175, 1248, 1313, 1346, 1383, 1396, 1429, 1437, 1470, 1518, 1558, 1570, 1603, 1653, 1757, 2860, 2968. δ_H(CS_2–20% C_6D_6, 25 °C): 7.47 (d, *J* 8.85, 2 H), 8.12 (d, *J* 8.85, 2 H). δ_C(CS_2–20% C_6D_6, 25 °C): 115.88, 120.85, 121.68, 132.37, 132.72, 134.98, 136.70, 137.59, 137.92, 138.69, 138.97, 139.22, 140.15, 140.26, 140.99, 141.71, 141.99, 142.45, 143.06, 143.27, 143.38, 143.50, 143.58, 143.81, 143.95, 143.98, 144.26, 144.42, 144.51, 144.58, 144.61, 144.77, 144.84, 144.88, 145.23, 145.46, 145.56, 147.63, 152.90, 161.28. MS (FAB, NBA) *m/z*: 1022 (M^+ + H), 838 ($-C_6F_5O$), 735 ($C_{60}NH^+$), 720 (C_{60}^+).

1,6-Aza-[*N*-4′-(succinimidoxycarbonyl)phenyl]homo[60]-fullerene (4)

To a solution of 835 mg (1.159 mmol) of C_{60} in 70 ml of 1-chloronaphthalene 1.1 equiv. (332 mg) of *N*-hydroxysuccinimidyl *p*-azidobenzoate was added. This mixture was stirred for 3 d at 55 °C. After dilution with 150 ml of toluene the mixture was heated at reflux for 0.5 h. The separation of **4** from unreacted C_{60} was achieved with flash-chromatography using toluene–ethyl acetate (8:2) as eluent. Yield: 156 mg (60% relative to consumed C_{60}).

UV (CH_2Cl_2) λ/nm: 657 (br), 598 (br), 550 (br), 463, 323, 261. IR (KBr) ν/cm^{-1}: 527, 690, 752, 839, 991, 1018, 1065, 1177, 1200, 1242, 1256, 1313, 1348, 1360, 1383, 1396, 1427, 1512, 1533, 1558, 1603, 1740, 1769. δ_H($C_2D_2Cl_4$, 25 °C): 2.86 (s, 4 H), 7.57 (d, *J* 8.24, 2 H), 8.13 (d, *J* 8.24, 2 H). MS (FAB, NBA) *m/z*: 953 (M^+ + H), 838 (—SuccO), 720 (C_{60}^+).

Results and discussion

Fig. 1 shows the cyclic voltammograms (CVs) of C_{60} and **1**–**5**, obtained on cathodic reduction. C_{60} and **1**–**4** exhibit four well separated reduction peaks (Ir–IVr) and the four corresponding re-oxidation peaks (Io–IVo) [Fig. 1(*a*–*e*)]. Sequential electron-transfer processes are clearly observed for the four reversible reduction steps, which may be described as an EEEE mechanism. The cathodic reduction peak potentials (E^r) and the potential differences between reduction and corresponding re-oxidation peak potentials (ΔE) are listed in Table 1. The reduction potentials differ from one compound to the other, depending on the nature of the substituent at the *N*-bridges as well as on the addition mode. Significantly, in contrast to the [6,6]-bridged adduct **2**, the first reduction peak potentials (E^{r1}) of **1**, **3** and **4** are less negative than that of C_{60}, reflecting their

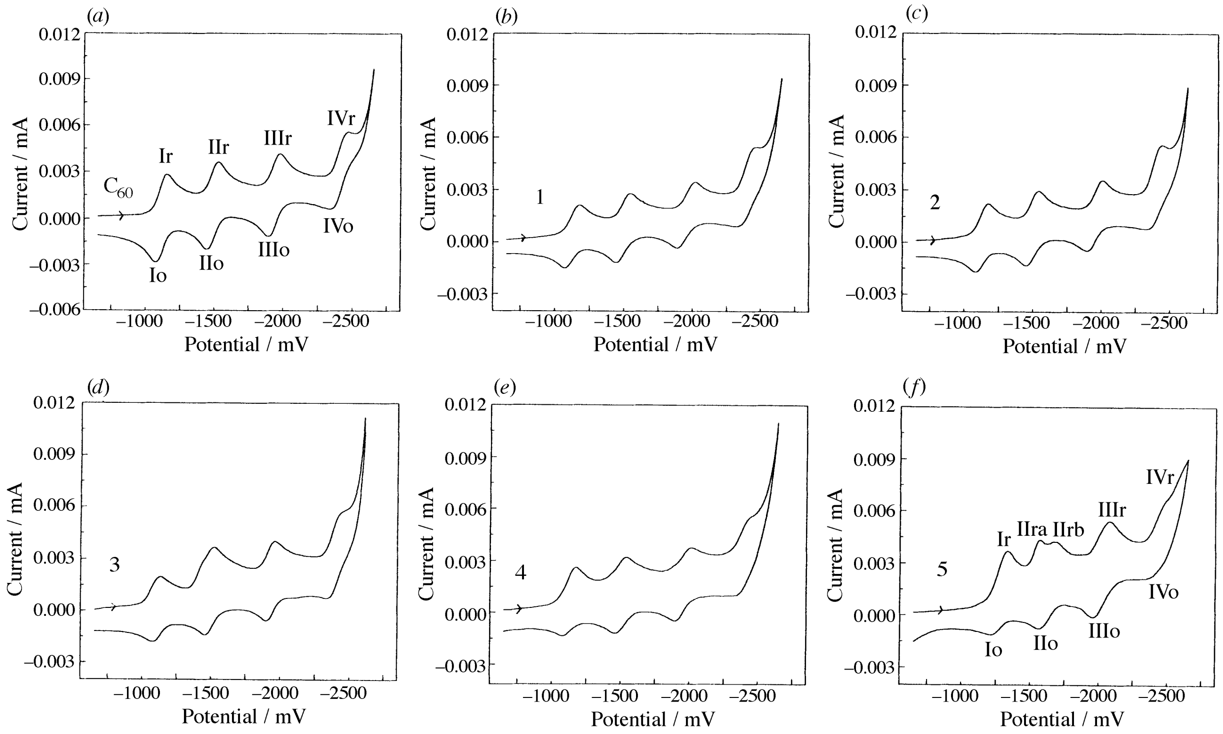

Fig. 1 CVs of the cathodic reduction of C_{60} (*a*) and **1** (*b*)–**5** (*f*) in 1,2-dichlorobenzene solution containing 0.1 M Bu_4NPF_6, scan rate 20 mV s^{-1}

Table 1 Cathodic reduction and anodic oxidation peak potentials[a]

Compd.	$E^{r1}/\Delta E$/mV	$E^{r2}/\Delta E$/mV	$E^{r3}/\Delta E$/mV	$E^{r4}/\Delta E$/mV	E^{o1}/mV
C_{60}	−1174/80	−1532/80	−1990/80	−2465/85	1218
1	−1172/85	−1528/86	−1985/87	−2451/90	1061
2	−1177/83	−1538/85	−2000/85	−2446/87	1150
3	−1126/67	−1515/68	−1958/68	−2433/70	1140
4	−1150/81	−1523/85	−1982/83	−2470/90	1018
5	−1195/80	−1543[b]/88[c]	−1992/87	−2383/90	997

[a] E^{r1}–E^{r4}: first to fourth cathodic reduction peak potentials. Scan rate 20 mV s^{-1}. ΔE: potential differences between cathodic reduction peak and corresponding reoxidation peak. E^{o1}: anodic oxidation peak potentials. Scan rate 20 mV s^{-1}. [b] Potential of IIrb. [c] Potential differences between IIrb and IIo.

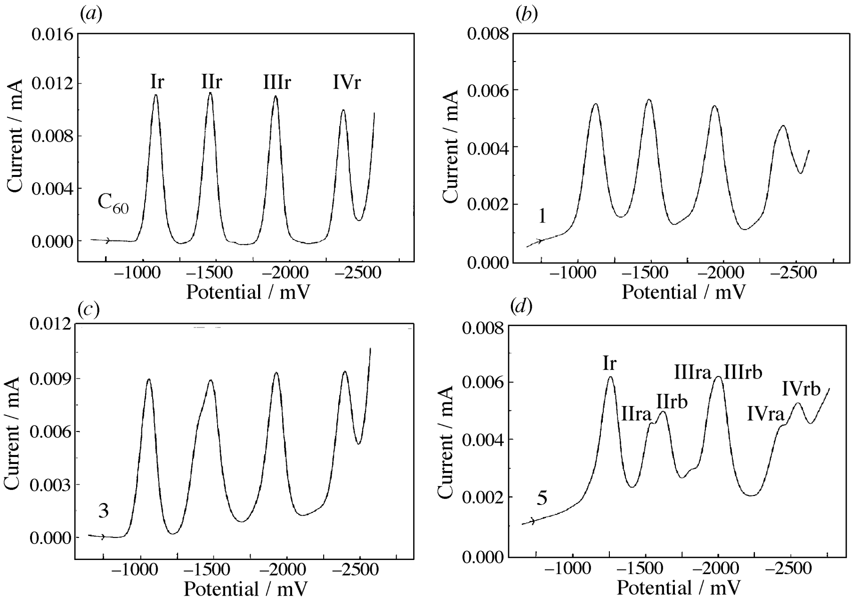

Fig. 2 Differential pulse voltammograms of C_{60} (*a*), **1** (*b*), **3** (*c*) and **5** (*d*) in 1,2-dichlorobenzene solution containing 0.1 M Bu_4NPF_6; scan rate, 20 mV s^{-1}; pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms

stronger electron-accepting ability, while **5** was reduced at more negative potential than C_{60}, resulting from its weaker electron-accepting ability with respect to C_{60}. As can be seen from comparison of the reduction potentials of the mono adducts **1**, **3** and **4** the electron-withdrawing influence of the substituent on the *N*-bridge has a pronounced influence on the redox properties. The E^{r1} of **1** and **2** differ moderately presumably due to the presence of the same substituent on the *N*-bridges. There is also only a small change between their E^{r1} and that of C_{60}, indicating their electron-accepting ability to be close to that of C_{60}. The CV of **5** [Fig. 1(*f*)] is distinguished from those of the other compounds. The second reduction peak (IIr) splits into two separate peaks, IIra and IIrb, each of the peak currents being smaller than those of the corresponding peaks IIr of the other compounds. The reason may be that **5** is reduced to $\mathbf{5}^{\cdot -}$, undergoing a structural change in the sense of isomerization to $\mathbf{5a}^{\cdot -}$ and $\mathbf{5b}^{\cdot -}$, which are further reduced at different potentials, leading to a less pronounced splitting of the following peaks IIIr and IVr. This is shown more clearly in the DPV of **5** [Fig. 2(*d*)]. Though the difference of reduction potentials between IIIra and IIIrb is not so large as between IIra and IIrb, it can still be observed between IVra and IVrb, while the other DPVs [Fig. 2 (*a*)–(*c*)] exhibit sharper peaks. On the basis of the CVs and DPVs discussed, it can be assumed that $\mathbf{5}^{\cdot -}$ undergoes a chemical follow-up reaction, before it is further reduced. The reduction of **5** may be described tentatively as an ECEEE process. The reason that $\mathbf{5}^{\cdot -}$ is not stable may be ascribed to the comparatively large amount of strain energy that is involved in this remarkable addition pattern, where one C-atom is already partially decoupled from the fullerene framework.[44] Note that bisiminofullerenes with this type of addition pattern after further activation *via* amine addition can be transformed in a fragmentation reaction to the heterofullerene $C_{59}N$, which is obtained, for example, as dimer $(C_{59}N)_2$.[40] Hence, it is very interesting in this respect, that the first reduction step of **5** is accompanied by a follow-up reaction, which could be a ring opening reaction or a rearrangement to a mixed [5,6]/[6,6]-bridged intermediate. Electrochemically induced rearrangements from [5,6]- to [6,6]-bridged isomer have been observed for methanofullerenes, but only after the third electron-uptake.[23,33] A more detailed investigation of the reduction mechanism of **5** will be discussed in an upcoming study.

On anodic oxidation, all compounds except **4** exhibit a single, irreversible oxidation peak at a scan rate of 20 mV s^{-1} [Fig. 3(*a*)–(*c*)]; the oxidation also remains irreversible at higher scan rates. Because the oxidized species formed from C_{60} and the above mentioned derivatives are chemically unstable, one or more chemical reactions following or accompanying the electron transfer render the electrochemical oxidation irreversible.[2] Due to the influence of addends on C_{60}, all oxidation peak potentials of **1**–**5** are less positive than that of C_{60}; therefore, such C_{60} derivatives are more readily oxidized than C_{60}. As shown in Fig. 3(*b*), in sharp contrast to the other compounds, a re-reduction peak corresponding to the oxidation of **4** was clearly observed under our experimental conditions, indicating that oxidized **4** is stable on the CV timescale. The potential separation ΔE_p ($= E_p^o - E_p^r$) is 65 mV at 20 mV s^{-1}, and increases with increasing scan rate, indicating that the charge transfer for the oxidation of **4** is electrochemically quasireversible. To our knowledge, there are no other reports of the electrochemically or chemically reversible oxidation of any C_{60} *mono* adduct. The peak current of the irreversible oxidation of C_{60} in a 1,2-

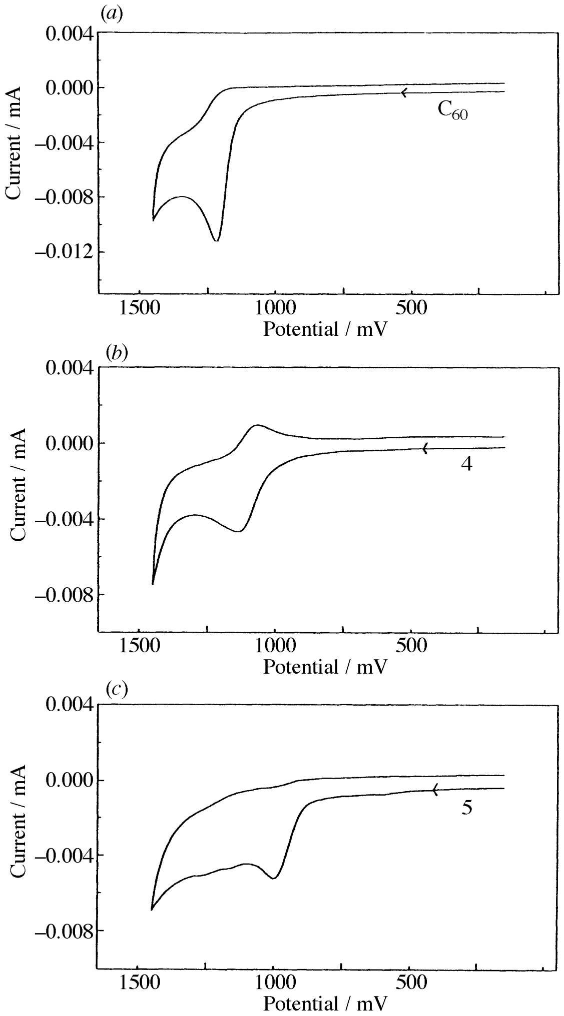

Fig. 3 CVs of the anodic oxidation of C_{60} (*a*), **4** (*b*), **5** (*c*) in 1,2-dichlorobenzene solution containing 0.1 M Bu_4NPF_6, scan rate, 20 mV s^{-1}

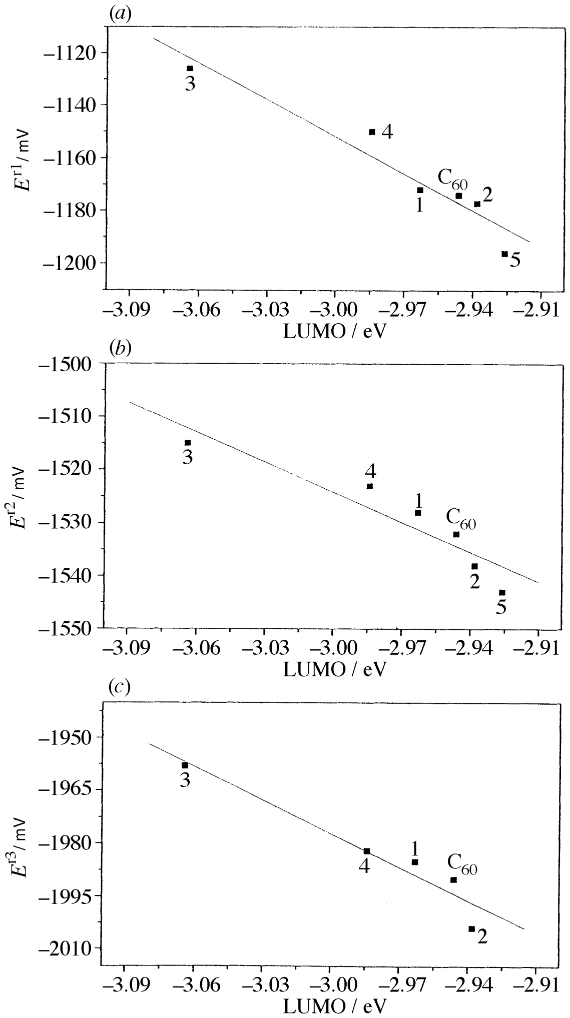

Fig. 4 Plots of reduction peak potentials from Table 1 *vs.* the LUMO energy levels. (*a*) The first reduction potentials (E^{r1}) *vs.* LUMO. (*b*) The second reduction potentials (E^{r2}) *vs.* LUMO. (*c*) The third reduction potentials (E^{r3}) *vs.* LUMO.

dichlorobenzene solution is about four times that of each of the one-electron reduction peaks, indicating that by the oxidation of C_{60} four electrons are abstracted. This result is consistent with that observed for a benzonitrile solution.[2] However, for **1**–**5**, the current ratios of the single anodic oxidation and the first cathodic reduction peaks are about two instead of four, indicating that the anodic oxidation of **1**–**5** corresponds to a two-electron transfer. Controlled-potential electrolyses of **1**–**5** further confirm this conclusion. This means that **1**–**5** are oxidized to the dications $\mathbf{1}^{2+}$–$\mathbf{5}^{2+}$, a process which, as judged from the CV, seems to be of the EE type, at least for **4**.

Since the reduction peak potentials E^{ri} of **1**–**5** show a specific dependence on the addition pattern and the nature of the addends but still lie in the same range as those of C_{60}, it can be expected that the corresponding LUMOs are fullerene centred. Indeed, as shown in Fig. 4(*a*)–(*b*), the first and second reduction peak potentials of **1**–**5** and C_{60} exhibit linear relationships with their AM1-calculated LUMO energy levels.[16] However, it has to be stated that for a direct comparison of the potentials of the second reduction the LUMOs of the corresponding mono-anions have to be considered. AM1-calculations of open shell species, however, are not trivial. It is interesting to note that the correlation of the second reduction potentials of **1**–**5** as well as of C_{60} with the LUMO energies are very good. This means that low-lying unoccupied molecular orbitals of these fullerenes are affected in the same relative direction upon uptake of one electron. This is additionally corroborated by the comparison of the energies of the LUMO, LUMO + 1 and LUMO + 2 of **1**–**5**. These orbitals originate from the triply degenerate LUMO of C_{60}. In all cases the LUMO and LUMO + 1 have almost the same energy and especially for the cases of the singly [5,6]-bridged compounds **1**, **3** and **4** these orbitals are almost degenerate. Here the largest energy difference between the two orbitals is 0.006 eV. The third reduction potentials also correlate well with the LUMO energy levels of the compounds except **5** [Fig. 4(*c*)]. As described above, a chemical change follows the reduction of **5** to $\mathbf{5}^{\bullet -}$; therefore, the calculated orbital energy level no longer corresponds to the third reduction peak of **5**. A correlation between the calculated HOMOs and the oxidation peak potentials E^{o1} is not reasonable, because (*i*) we could detect only one (quasi)reversible process (**4**), (*ii*) the oxidation process of C_{60} involves four electrons, that of **1**–**5** two electrons, (*iii*) in a multi-electron process not all electrons are necessarily taken from one and the same MO. However, it is significant that derivatives **1**–**5** are easier to oxidize than C_{60}. MO calculations (AM1) show that the HOMOs have highest coefficients at the nitrogen bridges as well as on the bridge-head C-atoms of the fullerene core, which means that the removal of electrons mainly takes place at those areas of the molecules where the addends are located. The energy differences between the HOMO and HOMO − 1 in **1**–**5**, which originate from the fivefold degenerate HOMOs of C_{60}, are much larger than those between LUMO and LUMO + 1. The corresponding values lie in the range of 0.13 and 0.30 eV. This result is consistent with the fact that two instead of four electrons are removed from the HOMOs upon the observed electrochemical oxidations of **1**–**5**. The HOMO energies of **1**–**5**, ranging from −9.457 to −9.297 eV, are always higher than that of C_{60} (9.643 eV), which supports the fact that these iminofullerenes are easier to oxidize than C_{60}. Interestingly, the largest gap between HOMO and HOMO − 1 of 0.3 eV is found for **4**, which is the only derivative in this series which shows a quasireversible two-electron oxidation.

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