

Fullerene van der Waals Oligomers as Electron Traps

Tatyana E. Shubina,^a Dmitry I. Sharapa,^a Christina Schubert,^b Dirk Zahn,^c Marcus Halik,^d Paul A. Keller,^e Stephen G. Pyne,^e Sreenu Jennepalli,^e Dirk M. Guldi,^b and Timothy Clark^{*,a,f}

^a Computer-Chemie-Centrum and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Department Chemie und Pharmazie, Nögelsbachstraße 25, 91052 Erlangen, Germany.

^b Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany.

^c Lehrstuhl für Theoretische Chemie and Computer-Chemie-Centrum, Friedrich-Alexander-Universität Erlangen-Nürnberg, Department Chemie und Pharmazie, Nögelsbachstraße 25, 91052 Erlangen, Germany.

^d Organic Materials & Devices, Institute of Polymer Materials, Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstrasse 7, 91058 Erlangen, Germany.

^e School of Chemistry, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia.

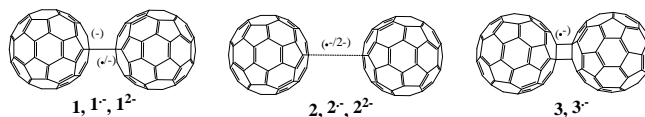
^f Centre for Molecular Design, University of Portsmouth, King Henry Building, King Henry I Street, Portsmouth, PO1 2DY, United Kingdom.

Supporting Information Placeholder

ABSTRACT: Density-functional theory (DFT) calculations indicate that van der Waals fullerene dimers and larger oligomers can form interstitial electron traps in which the electrons are even more strongly bound than in isolated fullerene radical anions. The fullerenes behave like “super atoms” and the interstitial electron traps represent one-electron intermolecular σ -bonds. Spectroelectrochemical measurements on a *bis*-fullerene-substituted peptide provide experimental support. The proposed deep electron traps are relevant for all organic electronics applications in which non-covalently linked fullerenes in van der Waals contact with one another serve as n-type semiconductors.

Fullerenes, and particularly C₆₀, have found use as organic n-type semiconductors in electronic devices,¹⁻⁴ and especially in organic photovoltaics.⁵⁻⁷ The high electron-accepting ability of fullerenes (the first electron affinity of C₆₀ is 2.67 eV,⁸⁻¹⁰ the second approximately -0.2 eV¹¹) makes them almost unique among organic molecules. Fullerenes are used extensively as electron acceptors, for instance in phenyl-C₆₀-butyric acid methyl ester (PCBM) based organic solar cells and in devices based on polycrystalline fullerene films. In most cases, van der Waals interactions between fullerenes are present. An exciting possibility for low-voltage organic field-effect transistors (FETs) is to combine the dielectric and the semiconductor functionalities in a single molecule that can form a self-assembled monolayer (SAM).¹² When the semiconductor moiety in such molecules is a substituted fullerene, an n-type semiconductor layer results that can become negatively charged under conductance conditions.

This results in considerable hysteresis in the voltage-current characteristics of the device.¹³ When analyzing semiempirical molecular orbital calculations on such SAMs,¹⁴ we noticed that the local electron affinity^{15,16} indicated electron traps in the interstitial volumes between adjacent fullerenes in the semiconductor layer and that these traps were particularly deep when three fullerenes were involved.¹⁴ A literature survey revealed that several groups have studied covalently linked fullerenes, their radical anions and dianions,¹⁷⁻³⁰ but that little attention has been paid to non-bonded van der Waals aggregates of fullerenes.³¹ The covalently bonded C₆₀-dimer radical anion/dianion, **1**^{•-/2-} can be considered to be the result of an addition to a C_{sp2}-C_{sp2} bond in the fullerene cage, whereas a reduced van der Waals dimer, **2** can form one-electron bonds³² between fullerene “super atoms”.³³ A third possibility is the dimer adduct formed by a formal [2+2] cycloaddition of two 5,6-bonds, **3**.¹⁷



The “super atom” picture of fullerenes is interesting in this context because the lowest unoccupied molecular orbitals of C₆₀ are triply degenerate. This means that additional electrons can occupy low-lying intermolecular molecular orbitals, leading to the fascinating possibility that larger van der Waals C₆₀-oligomer dianions can form multi-center two-electron bonds to give trimers (**4**) analogous to H₃⁺^{34,35} and tetramers (**5**) analogous to the 1,3-dehydro-5,7-adamantdiyl dication.³⁶

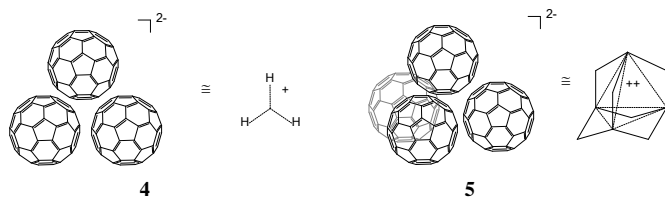


Table 1 shows the results obtained from density-functional theory (RI-BP86^{37,38}/TZV³⁹) calculations on fullerene dimers, trimers and tetramers and one- and two-electron reduced forms. We have used an empirical correction to account for dispersion,⁴⁰ although the correctness of such treatments for fullerenes has recently been placed in doubt.⁴¹ We have investigated the three structures 1-3 described above for $(C_{60})_2^{\bullet-}$ and $(C_{60})_2^{2-}$. **1** has a long covalent bond of 1.6 to 1.7 Å, whereas **2** features a shortened van der Waals contact distance of around 2.6 Å between the fullerenes (the van der Waals radius of carbon is 1.7 Å). Perhaps surprising in view of previous interest in the covalently bonded isomer, **1**, the non-bonded structure **2** is found to be more stable (by up to 11.3 kcal mol⁻¹ for the radical anion and 4.8 kcal mol⁻¹ for the singlet dianions). The D3-dispersion correction lowers these values (stabilizes the dimers) by approximately 5 kcal mol⁻¹.

Species	E_{Rel}	EA	Dissociation	
			Reaction	ΔE_{R}
C_{60}		2.82		
2	0.0 (0.0)	3.24	$\rightarrow 2C_{60}$	+11.9
3	+1.2 (-5.4)	3.25	$\rightarrow 2C_{60}$	+17.3
4		3.49	$\rightarrow 3C_{60}$	+34.2
5		3.62	$\rightarrow 4C_{60}$	+66.9
<hr/>				
$C_{60}^{\bullet-}$		-0.21		
1^{•-}	+11.3 (+6.0)	2.98	$\rightarrow C_{60}+C_{60}^{\bullet-}$	+15.8
2^{•-}	0.0 (0.0)	1.11	$\rightarrow C_{60}+C_{60}^{\bullet-}$	+21.7
3^{•-}	+1.53 (-5.6)	1.03	$\rightarrow C_{60}+C_{60}^{\bullet-}$	+27.3
4^{•-}		1.58	$\rightarrow 2C_{60}+C_{60}^{\bullet-}$	+49.7
5^{•-}		1.86	$\rightarrow 3C_{60}+C_{60}^{\bullet-}$	+85.6

Table 1. Relative energies (E_{Rel} , kcal mol⁻¹) of C_{60} oligomers 1-5, the corresponding anions and dianions, relevant Electron Affinities (EA, eV) and reaction energies (ΔE_{R} , kcal mol⁻¹) calculated at the RI-BP86/TZV level of theory.

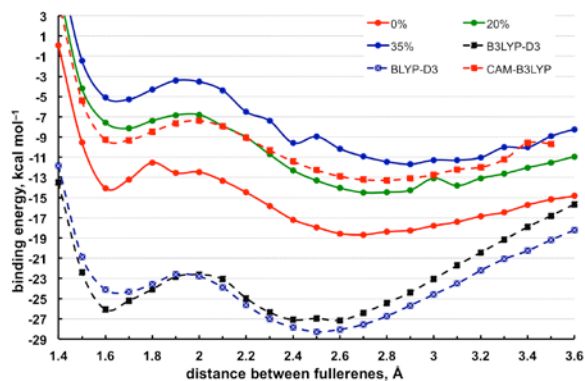
Because this result could easily be caused by the self-interaction error in DFT, we also calculated the energies of **1^{•-}** and **2^{•-}** using increasing amounts (0 to 50%) of Hartree-Fock exchange in a modified hybrid B3LYP functional^{42,43} and performed additional calculations using the long-range corrected CAM-B3LYP⁴⁴ functional. The results are shown in Figure 1.

The data shown in Table 1 and Figure 1 are remarkable in many ways. They demonstrate that the van der Waals dimer radical anion and dianion are probably more stable than the covalently bound isomer **1** investigated previously or comparable to the [2+2] adduct **3** in the same oxidation states.

These values lie between those obtained at the RI-BP86-D3/TZV level (-15.8 and -21.7 kcal mol⁻¹, for **1^{•-}** and **2^{•-}**, respectively, see Supporting Information). All calculations find the deepest minimum to be **2** with a significantly shortened van der Waals contact (between 2.4 and 2.9 Å).

Thus, the range of DFT functionals tested agrees that **2^{•-}** is more stable than **1^{•-}**. However, the results depend very much on the choice of functional and whether the D3-dispersion correction is used or not.

Figure 1. Calculated potential energy diagrams for the dissociation of $(C_{60})_2^{\bullet-}$. The calculational levels are defined in the Supporting Information. Zero on the binding energy scale corresponds to separated $C_{60} + C_{60}^{\bullet-}$.



These variations are not surprising as it is difficult to imagine a system for which DFT might be expected to have more problems. Both the absence of dispersion and the self-interaction error must be important. In order to investigate the effect of the wavefunctions possibly being artificially symmetrical as a result of the self-interaction error, we used the HF-DFT approach, in which the DFT energies are evaluated using electron densities taken from Hartree-Fock calculations. This method has been shown to perform remarkably well for calculations of electron affinities and potential-energy surface scans for systems with odd numbers of electron, for which standard DFT is often unreliable.⁴⁵⁻⁴⁷ HF-TPSS and HF-PBE calculations with the def2-SVP basis set also predict **2^{•-}** to be more stable than **1^{•-}** by 15 kcal mol⁻¹, with a barrier of ca. 3 kcal mol⁻¹ between them.

In order to remove all doubt, we also performed CASSCF⁴⁸/CASPT2^{49,50}(5,4) calculations on DFT-optimized geometries to verify the DFT and HF-DFT results. CASPT2(5,4) calculations also show that **1^{•-}** and **2^{•-}** are close in energy, with a barrier of 6.2 kcal mol⁻¹ between them. Unfortunately, the size of the system limits calculations to the CASPT2(5,4)/ANO-L-VDZ level.⁵¹⁻⁵³

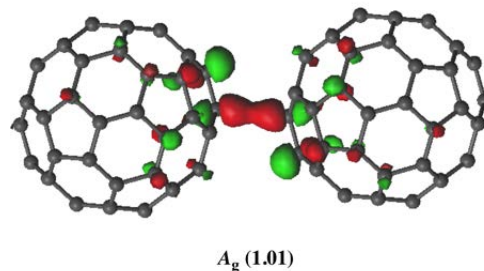


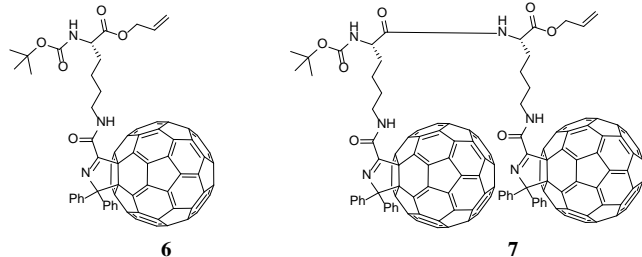
Figure 2. CAS (5,4) formally singly occupied orbital of **2^{•-}**. The calculated occupancy is given in parentheses. This orbital corresponds to a one-electron σ -bond between the two fullerenes. Further CAS(5,4) molecular orbitals are shown in the Supporting Information.

The calculated IR and UV-Vis spectra suggest that **1^{•-}** and **2^{•-}** can be distinguished easily. Figure S3 shows the calculated infrared spectra. **2^{•-}** is characterized by very intense absorptions at 1430-1486 and 1600 cm⁻¹ that are far weaker in the separated monomers and **1^{•-}**.

The computed UV/Vis spectra are shown in Figure S4. Once again, the van der Waals dimer radical anion **2^{•-}** is clearly distinguished by a strong absorption in the infrared at 1760 nm (5672 cm⁻¹). This absorption is far more intense than that found at

slightly longer wavelength (1848 nm) for $1^{\bullet-}$, which also exhibits a second weaker absorption at 1441 nm. Separated fullerene and its radical anion do not absorb in this region.

Data for the dimer dianions are shown in the Supporting Information, which demonstrates that a singlet-triplet crossing occurs on dissociation. However, the results obtained with different functionals vary strongly, so that we simply present the results.



In order to investigate the proposed effect experimentally, we performed cyclic voltammetry and spectroelectrochemical experiments on the fullerene-substituted peptides **6** and **7**.⁵⁴ These two compounds offer the opportunity to observe and compare a system in which interactions between non-bonded fullerenes are possible (**7**) with one in which they are not (**6**). The redox properties of the mono- and dipeptides were studied by means of cyclic voltammetry (CV). The measurements were performed at room temperature in chlorobenzene with tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. Chlorobenzene, an aprotic solvent, was chosen to avoid protonation of the charged species. Figure 3 shows the reductive scans between -0.2 to -1.6 V of **6** and **7**. We compare the spectra obtained upon fast and slow scanning. Both compounds show a reduction, which is assigned to the one-electron reduction of C₆₀. At fast scan rates (0.2 Vs⁻¹), the reduction appears to be quasi-reversible and occurs at nearly the same potential for both **6** and **7**. In contrast, slowing down the scan rate to 0.005 Vs⁻¹ leads to an irreversible reduction of **7**, while **6** remains reversible. Moreover, at slower scan rates **7** is more easily reduced than **6**. The change to an irreversible reduction of **7** at slower scan rates is consistent with the formation of a van der Waals dimer of the fullerenes in **7**.

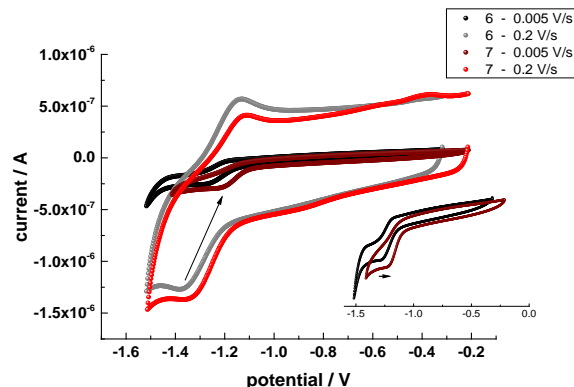


Figure 3. Cyclic voltammograms of **6** and **7** with a scan rate of 0.0050 Vs⁻¹ and 0.200 Vs⁻¹. Measurements were performed in chlorobenzene containing 0.05 M TBAPF₆ as supporting electrolyte with a glassy carbon working electrode, a platinum counter electrode, and a silver pseudo-reference electrode. Corrected for ferrocene as an internal standard.

With this information in hand, we carried out spectroelectrochemical experiments to gather information about the absorption features of the reduced species. A differential absorption spectra for **7** in chlorobenzene solution is shown in Figure 4. The corresponding spectrum for **6** (Figures S7 and S8) shows the features known from literature for *N*-methylfulleropyrrolidine.⁵⁵ In partic-

ular, a sharp peak with a 1028 nm maximum is observed for the one electron reduced C₆₀. In contrast, the differential spectrum of **7** is characterized by a broad absorption between 700 and 1200 nm and with a local maximum at 860 nm. These spectral attributes are assigned to van der Waals dimer of **7** and are in sound agreement with the calculated spectrum shown for the relevant conformation of **7^{•-}** shown in Figure S7 of the supporting information.

We have presented calculations on a system for which it is difficult to obtain definitive results because of its size and the electronic characteristics. However, standard functionals with and without dispersion corrections, HF-DFT calculations, modified functionals with increasing amounts of HF-exchange and long-range corrected functionals all give consistent results that indicate that fullerene can function as a “super-atom” that forms a one-electron intermolecular bond, resulting in an electron trap that is even more stable than the isolated fullerene, which is itself an unusually strong electron acceptor.

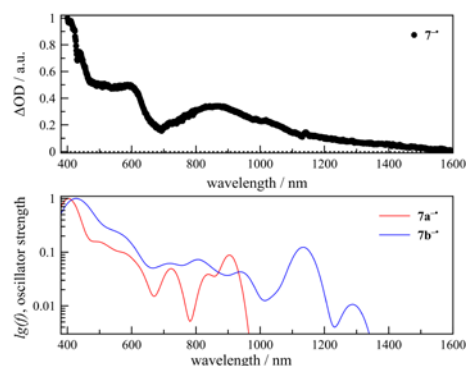


Figure 4. Normalized differential absorption spectra of **7** with an applied voltage of -0.85 V (black line). Measurements were performed in chlorobenzene containing 0.05 M TBAPF₆ as supporting electrolyte with a platinum gauze as working electrode, a platinum plate as counter electrode, and a silver wire as pseudo-reference electrode. The calculated spectra for **7a^{•-}** and **7b^{•-}** (conformations shown in the Supporting Information; **7a^{•-}** has separated fullerenes, **7b^{•-}** fullerenes in van der Waals contact) are shown in red and blue, respectively.

These experimental results are all consistent with **7** existing as at least two conformations in solution, with a minority conformation having a van der Waals contact between the two fullerenes (e.g. **7b** of the Supporting Information). At slow CV scan rates, **7b** can be formed by rearrangement and stabilized by the interfullerene one-electron bond. At fast scan rates, only the majority conformations without inter-fullerene contact are observed. The observed spectrum of **7^{•-}** corresponds to a superposition of those of the majority non-contact conformation and **7b^{•-}** or a similar conformation.

Although definitive calculations are not yet possible, we used standard density-functional theory to calculate the electron affinities of fullerene van der Waals oligomers. The results are shown in Figure 5. The first electron affinity increases from 2.7 eV for the monomer to 3.6 for the tetramer, which exhibits a second electron affinity of almost 2 eV. The tetramer is also calculated just to be able to bind a third electron.

Van der Waals fullerene oligomers can thus exhibit first electron affinities as much as one electron volt more strongly binding than the isolated fullerene and second electron affinities up to approximately 2 eV. These interstitial electron traps represent an unexpected feature of non-covalently bonded aggregates of fullerenes that can affect the performance of electronic devices strongly. Deep electron traps can be expected in amorphous and crystalline fullerene layers or in self-assembled monolayers of fullerene-

substituted organic molecules, all of which are often used as n-type semiconductor components in organic electronics.

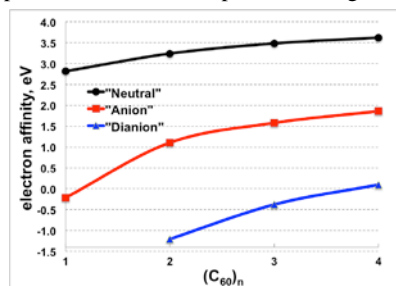


Figure 5. Calculated (RI-BP/TZV) electron affinities (eV) of (C₆₀)_n.

ASSOCIATED CONTENT

Supporting Information.

Details of all calculations and results for different functionals demonstrating the effect of HF-exchange and long-range corrected functionals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Tim.Clark@fau.de

No competing financial interests have been declared.

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SYNOPSIS TOC

