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Fullerene Cyanation Does Not Always Increase Electron Affinity: Experimental and Theoretical Study

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The electron affinities of C_{70} derivatives with trifluoromethyl, methyl and cyano groups were studied experimentally and theoretically using low-temperature photoelectron spectroscopy (LT PES) and density functional theory (DFT). The electronic effects of these functional groups were determined and found to be highly dependent on the addition patterns. Substitution of CF_3 for CN for the same addition pattern increases the experimental electron affinity by 70 meV per substitution. The synthesis of a new fullerene derivative, $C_{70}(CF_3)_{10}(CN)_2$, is reported for the first time.

Introduction

Introduction of electron-withdrawing groups (EWGs) into organic molecules is known to generally enhance their electron acceptor properties, and this approach has been actively used to design new *n*-type organic semiconductor materials.[1,2] Among organic electronic devices, organic photovoltaics (OPVs) are regarded as a commercially viable renewable energy source that have already achieved efficiencies over 10% by utilizing conducting polymers and fullerenes as electron-donors and electron-acceptors, respectively.[3] Energy level engineering of donor-acceptor pairs directly affects the optimal driving force for maximum charge transfer in OPV active layers.[4] As new low-band-gap polymers are synthesized, new fullerene molecules with increased electron accepting strength (higher electron affinity (EA), or deeper LUMO levels) must follow in order to match the frontier orbitals of the donor and achieve the optimal driving force for maximizing charge transfer. Modification of fullerene core with EWGs has been widely used to tune E(LUMO) levels and achieve better OPV performance. For example, $C_{60}(CF_3)_2$,[5] and $C_{60}(CN)_2$[6] were reported as favorable alternatives to PCBM and C_{60}(indene) fullerene cycloadducts in certain active layer formulations. Furthermore, an electron-withdrawing CN moiety was intentionally attached to C_{60}(indene) acceptor to match the orbital energies of a low-band-gap polymer, and OPV device performance showed improved power conversion efficiency compared to underivatized C_{60}(indene).[7] Cyanation of trifluoromethylated C_{60} resulted in large increases in EA for the $C_{60}R_5$ structures with skew pentagonal pyramid addition motif.[8] Direct comparison of electron-withdrawing effects of CF_3 and CN groups on E(LUMO) in the isostructural compounds revealed that cyanation is more potent than trifluoromethylation.[9]

Herein we report several examples of cyanated C_{70} derivatives for which an opposite effect on EA upon addition of CN groups was observed. Therefore, one cannot consider cyanation as a general and straightforward approach for boosting acceptor properties in fullerenes and their derivatives.

Results and Discussion

General Remarks

In the research community developing OPV materials and optimizing device performance, acceptor strength of organic molecules are commonly referred to as materials with low-lying LUMO levels (i.e., lowest unoccupied molecular orbitals). The quantitative value of LUMO energy has been conveniently (but not always consistently and correctly)[10] derived from the measured reversible first reduction potential ($E_{1/2}$ value) using cyclic voltammetry with typical uncertainties of 10-20 mV. Determination of solid-state EA of organic materials is now becoming available via inverse photoelectron spectroscopy (IPES), but with lower precision and accuracy; errors as high as 300 meV are typically reported.[11,12] Gas-phase EA measured by low-temperature photoelectron spectroscopy (LT PES) represents the most fundamental intrinsic measure of a molecule's ability to accept electrons, and uncertainties as low as 5-10 meV can be readily achieved in modern state-of-the-art instruments, allowing for reliable comparisons of compounds even with very small differences in EA, for example C_{60} and C_{70}.[13,14] This method is indispensable when organic acceptors do not exhibit reversible electrochemical behavior in solution, and when the amounts of materials are too small to be used for IPES which is frequently the case at the exploratory stage of research.

In this work we studied electronic properties of the new $C_{70}(CF_3)_n(CN)_m$ fullerene acceptors using LT PES and DFT calculations. Their synthesis and structural characterization have been published recently; however, electrochemical properties were not reported because of electrochemical irreversibility and insufficient sample amounts for some minor products. An original conception of the project was to develop more powerful acceptors than trifluoromethylfullerenes (TMFs) by adding more electron-withdrawing CN groups to TMF substrates. Our theoretical E(LUMO) predictions[9] as well as experimental evidence by us[8] and others[7,15] for the cyanated C_{60} derivatives indicated that a considerable enhancement of acceptor properties occur when CN groups are attached to a parent C_{60}, $C_{60}(CF_3)_{2n}$ or C_{60}(indene). Furthermore, gas-phase studies of $C_{70}(CN)_n$ species by electrospray mass spectrometry accompanied by semi-empirical theoretical analysis demonstrated the propensity of C_{70} to form stable singly- and doubly-charged $C_{70}(CN)_n$ anions, where n = 1–6.[16] No bulk samples of $C_{70}(CN)_n$ compounds have been reported in the literature, to our knowledge.

The family of $C_{70}(CF_3)_n$ compounds that were chosen as substrates for cyanation in this study currently includes dozens of structurally and spectroscopically characterized molecules, some of which can be prepared selectively and in large quantities.[17,18] Several isomers of $C_{70}(CF_3)_n$ possess unique photophysical properties, i.e., they were proven to be the brightest fluorophores of all fullerenes.[19] Electronic properties of C_{70} TMFs were studied by cyclic voltammetry and theoretically using DFT method, see Figure 1 for DFT calculated E(LUMO) for $C_{70}(CF_3)_n$.[17]

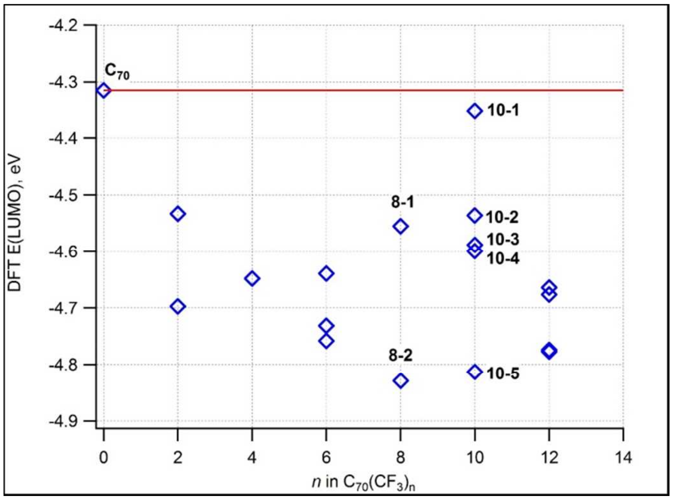

Figure 1. DFT calculated E(LUMO) for known $C_{70}(CF_3)_n$ (n = 0-12) compounds.[17]

These studies revealed that all but one $C_{70}(CF_3)_n$ molecule have significantly lower-lying LUMOs than the parent C_{70}, with $0.218 < \Delta E(\mathrm{LUMO}, \text{vs. } C_{70}) < 0.514$, and thus are much better acceptors than parent C_{70}. The exception, an E(LUMO) shift of only 0.036 eV was calculated for the most abundant isomer of $C_{70}(CF_3)_{10}$ (denoted here as **10-1,** where **10** is number of CF_3 groups, **1** is the isomer number in $C_{70}(CF_3)_{10}$, similar notations are used for other isomers throughout the text). Such an unexpected result was in line with the observed small negative shift in $E_{1/2}$ vs. C_{70}. In case of all the other $C_{70}(CF_3)_n$ compounds, large positive shifts in $E_{1/2}$ vs. C_{70} were measured, and up to three quasi-reversible reductions were recorded. It was found that **8-2** had the highest positive shift in $E_{1/2}$ as well as the lowest-lying LUMO in the entire series (Figure 1).[17]

For the studies of cyanation effect on electronic properties of C_{70} TMFs, two $C_{70}(CF_3)_n$ substrates were chosen, C_s-$C_{70}(CF_3)_8$ (**8-1**) and C_1-$C_{70}(CF_3)_{10}$ (**10-1**). Both compounds represent the most thermodynamically stable isomers among respective compositions, they form most abundantly in high-temperature syntheses, and thus can be readily prepared and isolated in practical amounts following previously reported literature procedures.[17,18] Notably, **10-1** contains a subset of addition pattern of **8-1** plus the addition of 2 CF_3 groups (see Figure 2 for Schlegel diagrams).

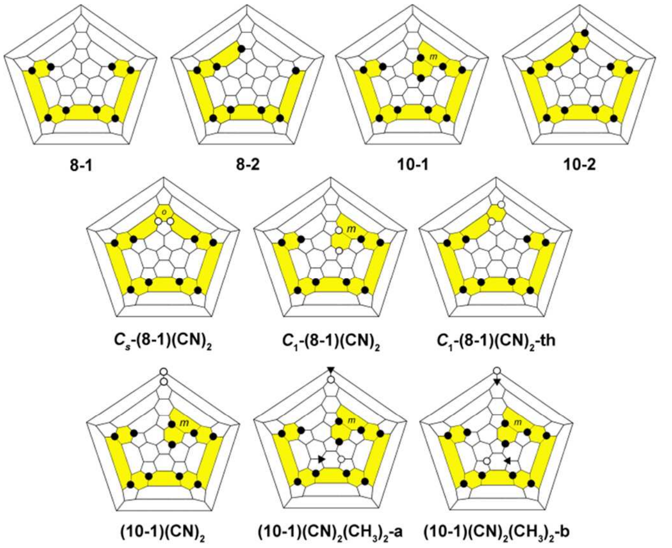

Figure 2. Schlegel diagrams of C_{70} TMFs and their cyanated derivatives studied by DFT method. Filled and open circles represent cage carbon atoms of bonded CF_3 and CN, respectively, triangles represent location of CH_3 additions. Yellow indicates continuous ribbon of edge sharing p-, m-, and o-C_6X_2 hexagons. Meta and ortho C_6X_2 hexagons are labeled with m and o, respectively.

Electron Affinity of $C_{70}(CF_3)_8$ and $C_{70}(CF_3)_{10}$

First, we determined gas-phase EAs of **8-1** and **10-1**. Figure 3 (bottom panel) and Figure 4 (bottom panel) show the photoelectron spectra of the mono-anions of **8-1** and **10-1,** respectively, recorded at 266 nm (4.661 eV) using acetonitrile solutions of each fullerene mixed with appropriate donors using a magnetic-bottle time-of-flight PES coupled with an ESI source and a cryogenic ion-trap for size-selected anions as described previously.[20]

The experimentally determined adiabatic EA of **8-1** is 3.08(1) eV which is 0.315 eV higher than the EA value of parent C_{70} measured using the PES technique,[14] whereas the EA value measured here for **10-1** is only 2.93(1) eV. A 150 meV decrease in EA of **10-1** compared to **8-1** is likely caused by destabilization of the fullerene π system due to the introduction of two additional CF_3 groups to **8-1** structure, and it is not compensated by the electron-withdrawing effect of the CF_3 groups. These measured EA values are in qualitative agreement with the previously calculated E(LUMO) for these molecules, i.e., **8-1** was predicted to have a 0.204 eV lower-lying LUMO than **10-1**. We also calculated their EA values by DFT method in this work, which agree well with the experiment: the relative differences in EA between **8-1** and **10-1** are ΔEA_{DFT} = 0.202 eV. This validation of the DFT-derived EA values was further used for the comparison of the electronic properties for the pair of C_2-$C_{70}(CF_3)_8$ **(8-2)** and C_2-$C_{70}(CF_3)_{10}$ **(10-2)** compounds, the latter has the **8-2** substructure in its addition pattern as shown on the Schlegel diagrams, Figure 2. The **8-2** molecule was predicted to be a stronger acceptor than **10-2** based on E(LUMO) values and reduction potentials,[17] which is now supported by comparing their new DFT data for EAs: EA_{DFT}(**8-2**) = 3.224 eV, which is 0.272 eV higher than that of **10-2**. Remarkably, **8-2** appears to be even a stronger acceptor than F4-TCNQ,[21] and comparable to fluorinated fullerenes, $C_{60}F_{18}$ and $C_{60}F_{36}$,[22] the latter has been widely used as a *p*-dopant in organic electronics,[23-25] and for enhancement of diamond surface conductivity.[26] It makes **8-2** a promising alternative to a fluorofullerene for doping applications, not only due to comparable EA values, but also because it is chemically more inert towards hydrolysis.[27,28]

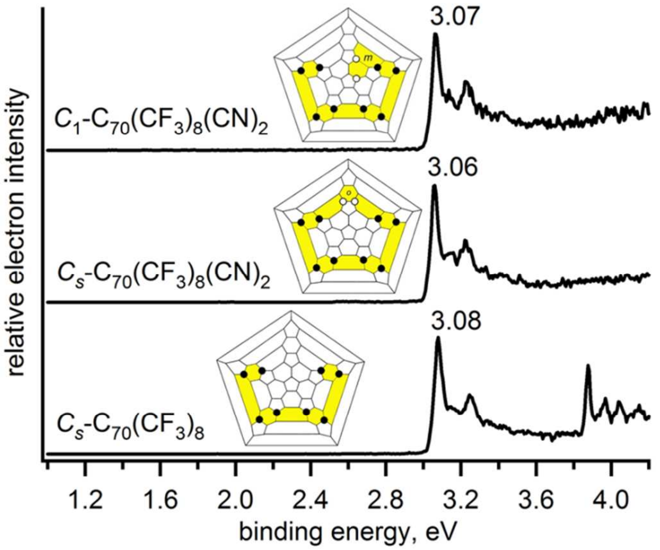

Figure 3. The low temperature (12K) photoelectron spectra at 266 nm of C_s-$C_{70}(CF_3)_8$ **(8-1)**, C_s-$C_{70}(CF_3)_8(CN)_2$ **(C_s-(8-1)(CN)$_2$)**, and C_1-$C_{70}(CF_3)_8(CN)_2$ **(C_1-(8-1)(CN)$_2$)**.

Electron Affinity of Cyanated $C_{70}(CF_3)_8$

We then investigated if the destabilization resulting from two CF_3 additions to **8-1** as observed in **10-1** could be overcome by adding stronger electron-accepting groups than CF_3, and whether the locations of these EWGs on the cage influence the EAs. Two products of cyanation of **8-1** were prepared for this work using a recently published method,[8] **C_s-(8-1)(CN)$_2$** and **C_1-(8-1)(CN)$_2$**. They were studied by LT PES, and the resulting spectra, together with the Schlegel diagrams, are shown in Figure 3. These results reveal that introducing two CN groups to **8-1** does not actually increase the EA in these two cyanated derivatives, as one might expect, but it even results in slight decreases of 10-20 meV. The strong electron-withdrawing nature of CN groups was not enough to overcome destabilization caused by the changed π system for these two isomers. These slight decreases in EA compared to parent **8-1** were confirmed by DFT calculated EA values as shown in Table 1.

To examine if placing CN group(s) on different cage carbon atoms in **8-1** may cause an opposite effect, i.e., lead to an increased EA value, we used DFT to study a theoretical isomer of $C_{70}(CF_3)_8(CN)_2$ **(C_1-(8-1)(CN)$_2$-th)** that has the same addition pattern as **10-2** and only differs from **C_s-(8-1)(CN)$_2$** by the location of one CN moiety (see Figure 2). Indeed, this minimal change in addition pattern leads to a large increase in EA of 0.213 eV compared to **8-1** (Table 1). Thus, the introduction of two CN groups to **8-1** can either increase or decrease EA based on addition pattern. The calculated EA of three isomers of $C_{70}(CF_3)_8(CN)_2$ differ by as much as 0.255 eV, which manifests strong dependence of electronic properties on the location of each substituent on fullerene core. In contrast, small-molecule acceptors with polycyclic aromatic cores exhibit linear incremental dependence on the number of EWGs, and isomeric molecules within the same composition preserve very similar EAs.[29,30]

Our results indicate that relative electron-withdrawing effect of a CN group is larger than that of CF_3 group when *ipso*-substitution of a CF_3 group takes place. For pairs of isostructural $C_{70}(CF_3)_8(CN)_2$ and $C_{70}(CF_3)_{10}$ with the **10-1** and **10-2** addition patterns, incremental increase in DFT-calculated EA(per one CN group) is ca. 90 meV and 100 meV, respectively, which is in agreement with the recently reported incremental EA value of 80 meV per one CN group for the isostructural pair of $C_{60}(CF_3)_5$ and $C_{60}(CF_3)_4CN$ species.[8] Experimental data from photoelectron spectroscopy reported here provide an unequivocal support for these conclusions derived from the DFT data: the measured EA of **C_1-(8-1)(CN)$_2$** is 140 meV higher than that of **10-1**, indicating that substituting CF_3 for CN results in an increase of EA by 70 meV per substitution. Furthermore, the $C_{70}(CF_3)_8(CN)_2$ and $C_{70}(CF_3)_{10}$ isomers with the **10-2** addition pattern have an increased EA over the **10-1** pattern by 238 meV and 220 meV, respectively.

Electron Affinity of Cyanated $C_{70}(CF_3)_{10}$

The electronic properties of the three cyano derivatives of **10-1** were also studied by LT PES and DFT. Two isomers of C_1-$C_{70}(CF_3)_{10}(CN)_2(CH_3)_2$ **((10-1)(CN)$_2$(CH$_3$)$_2$-a and (10-1)(CN)$_2$(CH$_3$)$_2$-b)**, were synthesized using a previously reported procedure.[8] A new compound, C_1-$C_{70}(CF_3)_{10}(CN)_2$ **((10-1)(CN$_2$))**, was prepared from **10-1** according to a modified literature procedure (see footnote for complete experimental details).[8] The addition of NEt_4CN to **10-1** resulted in one predominant isomer of C_1-$C_{70}(CF_3)_{10}(CN)^-$ that was subsequently quenched with *p*-TsCN to produce one predominant product, **(10-1)(CN)$_2$**. The ^{19}F NMR spectrum of this new fullerene exhibited ten CF_3 multipets that differ from the ten multiplets of **10-1** as shown in Figure 5, and practically identical to the ^{19}F NMR spectra of previously characterized derivative C_1-$C_{70}(CF_3)_{10}(CN)(CH_3)$.[8] Therefore, the new derivative most likely has the same addition pattern as the latter, where two cyano groups are added to the most reactive cage carbons, as shown on Figure 5.

Table 1 Experimental and DFT-calculated electron affinities (EA) of fullerene compounds from this work

Compound	Abbreviation	Experimental EA (eV)[a]	DFT EA (eV)
C_{70}	C_{70}	2.765(1)[b], 2.72(5)[c]	2.522
C_s-$C_{70}(CF_3)_8$	**8-1**	3.08	2.934
C_2-$C_{70}(CF_3)_8$	**8-2**	not measured	3.224
C_s-$C_{70}(CF_3)_8(CN)_2$	**C_s-(8-1)(CN)$_2$**	3.06	2.892
C_1-$C_{70}(CF_3)_8(CN)_2$	**C_1-(8-1)(CN)$_2$**	3.07	2.909
C_1-$C_{70}(CF_3)_8(CN)_2$-th	**C_1-(8-1)(CN)$_2$-th**	n/a	3.147
C_1-$C_{70}(CF_3)_{10}$	**10-1**	2.93	2.732
C_2- $C_{70}(CF_3)_{10}$	**10-2**	not measured	2.952
C_1-$C_{70}(CF_3)_{10}(CN)_2$	**(10-1)(CN)$_2$**	3.14	3.000
C_1-$C_{70}(CF_3)_{10}(CN)_2(CH_3)_2$-a	**(10-1)(CN)$_2$(CH$_3$)$_2$-a**	2.97	2.849
C_1-$C_{70}(CF_3)_{10}(CN)_2(CH_3)_2$-b	**(10-1)(CN)$_2$(CH$_3$)$_2$-b**	2.97	2.850

a – uncertainty is ±10 meV ; b) see ref.[14] c) see ref.[31]

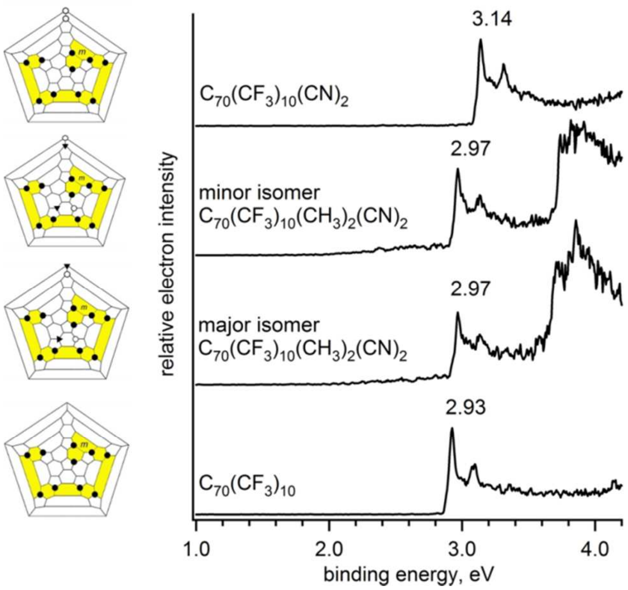

Figure 4. Photoelectron spectra of cyanated derivatives of **10-1** and corresponding Schlegel diagrams.

The gas-phase EA of the newly synthesized **(10-1)(CN)$_2$** was determined by PES and compared to **10-1**. Cyanation of **10-1** resulted in a 210 meV increase of EA. Remarkably, comparison of **10-1** and two isomers of C_1-$C_{70}(CF_3)_{10}(CN)_2(CH_3)_2$ for which photoelectron spectroscopy data were also obtained in this work, shows slightly higher EA values for the latter despite the presence of two electron-donating CH_3 groups in their structures and decreased π-system of C_{70} core. The measured EA values of two C_1-$C_{70}(CF_3)_{10}(CN)_2(CH_3)_2$ isomers are virtually the same: apparently, difference in relative positions of CN and CH_3 do not have effect on their electronic properties. DFT calculations confirm the observed trend of increasing EA from **10-1** to **(10-1)(CN)$_2$(CH$_3$)$_2$** to **(10-1)(CN)$_2$** (Table 1 and Figure 5). In contrast to the unanticipated trends in electronic properties of cyanated $C_{70}(CF_3)_8$ compounds described above, these three examples of chemical modifications of **10-1** appear to follow the expected trend where electron-withdrawing CN groups increase EA and electron-donating CH_3 groups decrease EA.

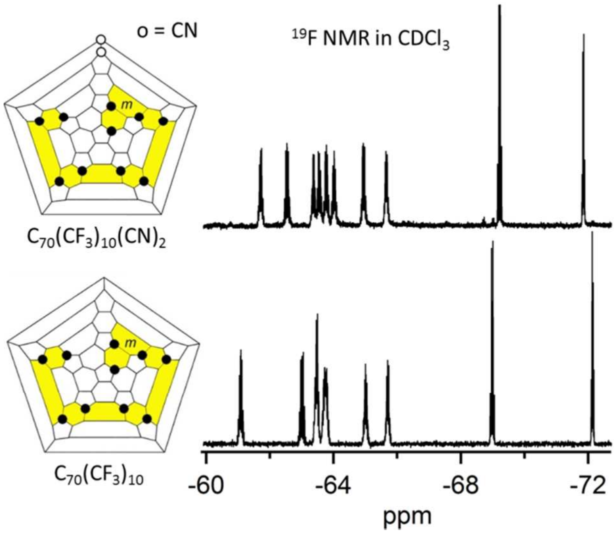

Figure 5. Fluorine-19 NMR spectra of **10-1** and **(10-1)(CN)$_2$** and corresponding Schlegel diagrams.

Conclusions

We have studied effects of trifluoromethylation and cyanation on the electron affinity of seven C_{70} fullerene derivatives using LT PES and DFT. In some cases, the addition of electron-withdrawing CF_3 or CN groups leads to the improvement of electron accepting properties, whereas in the several other cases cyanation led to the decreased EA. In the case of two fullerene derivatives with the same addition pattern, CN substitution of CF_3 results in an EA increase of 70 meV per substitution, as determined experimentally, and an increase of 90-100 meV was predicted by DFT. DFT calculations on two different $C_{70}(CF_3)_8(CN)_2$ isomers demonstrated that the difference in location of only one CN group can change the EA by 255 meV. Overall, excellent correlation between the experimentally determined and DFT calculated EA values (with systematic underestimation of DFT values of ca. 150 meV) were observed for seven studied compounds (Figure 6). These results highlight the usefulness of the validated theoretical analysis of electronic properties prior to practical synthesis of new acceptor materials which design is based solely on the chemical intuition. Complex and mutually cancelling effects of the electron-withdrawing functional groups, saturation of the fullerene π system and addition pattern type are difficult to predict empirically, whereas modern DFT theory allows for reliable, if not quantitative, data, and trends to be revealed for these classes of molecules.

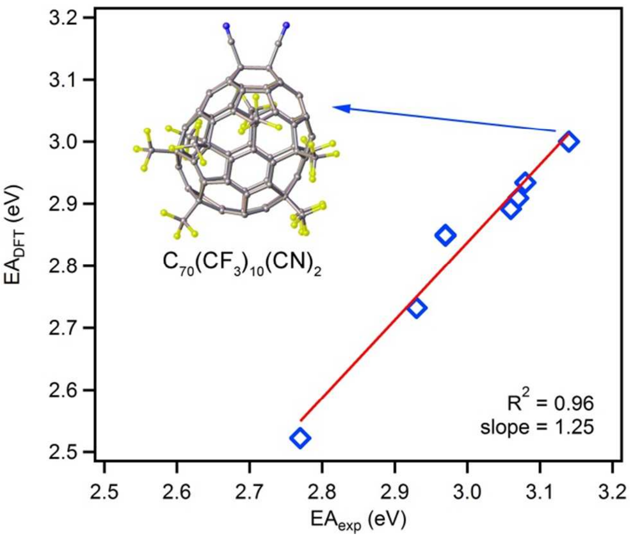

Figure 6. Correlation of DFT calculated and experimental electron affinities for fullerenes studied in this work. A 3D model of the fullerene with the highest electron affinity, **(10-1)(CN)**$_2$, is shown.

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Notes and references

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† Synthesis of **(10-1)(CN)**$_2$: The $C_{70}(CF_3)_{10}(CN)^-$ anion was generated by adding an aliquot of a 6.41 mM ACN solution of NEt_4CN (5.20 mL, 33.3 μmol CN^-) to a yellow solution of **10-1** (25.7 mg, 16.8 μmol) in toluene (15 mL) at 23(2) °C (CN^-:**10-1** mol ratio = 2.00). The reaction mixture immediately became dark green. An aliquot of the solution (10.1 mL, 8.4 μmol $C_{70}(CF_3)_{10}(CN)^-$) was reacted with a 75 mM toluene solution of *p*-TsCN (5 mL, 376 μmol "CN^+", 45 equiv.) and the solution became yellow after 3 h. The solution was exposed to air, washed four times with water, and dried with $MgSO_4$. The solvent was removed and the remaining solids were analyzed by ^{19}F NMR and separated by HPLC: Cosmosil Buckyprep semi-preparative column, toluene/heptane = 60/40 mobile phase, 5 mL min^{-1}, 300 nm detection, retention time = 3.2 minutes. Negative-ion Atmospheric Pressure Chemical Ionization mass spectrometry (NI-APCI-MS): calculated 1581.96, observed 1582.07 *m/z*.

PES measurements: The spectroscopy and procedures used were described previously.[20] Anions of C_{70} fullerene derivatives were generated by electrospraying a 0.1 mM acetonitrile solutions of each fullerene mixed with TDAE donors. Anions generated were transported by RF ion guides into a cryogenic ion trap, where they were accumulated and cooled to 12 K, before being pulsed out at 10 Hz into an extraction zone of a time-of-flight (TOF) mass spectrometer. Mass-selected anions were first maximally decelerated and then intersected by 266 nm (4.661 eV) photons from a Nd:YAG laser in the photodetachment zone. The laser was operated at a 20 Hz repetition rate with ion beam off at alternating shots, enabling shot-by-shot background substraction. Photoelectrons were collected at nearly 100% efficienncy by the magnetic-bottle and analyzed in a 5.2 m long photoelectron flight tube. The TOF photoelectron spectrum was converted to the kinetic energy spectrum, calibrated by the known I^- and ClO_2^- spectra. The binding energy spectrum presented in the paper was obtained by subtracting the kinetic energy spectrum from the photon energy used. The gas-phase EA of each compounds was determined from the 0–0 transition in the 12 K LT-PES spectrum of each radical anion with an accuracy of 10 meV.

DFT calculations: Molecular structures of all studied species were optimized at the PBE/TZ2P level using Priroda code.[33,34] Then, single point energy B3LYP[35,36] calculations with def2-TZVP bases set[37] were performed using Orca suite.[38]

See DOI: 10.1039/b000000x/

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