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Department Electrochemistry and conducting polymers

Zentrum für Spektroelektrochemie

Center for Spectro-electrochemistry at IFW Dresden

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Elektrochemie an Kohlenstoff-Nanostrukturen

Hanau, Materials Valley 24.1.2013

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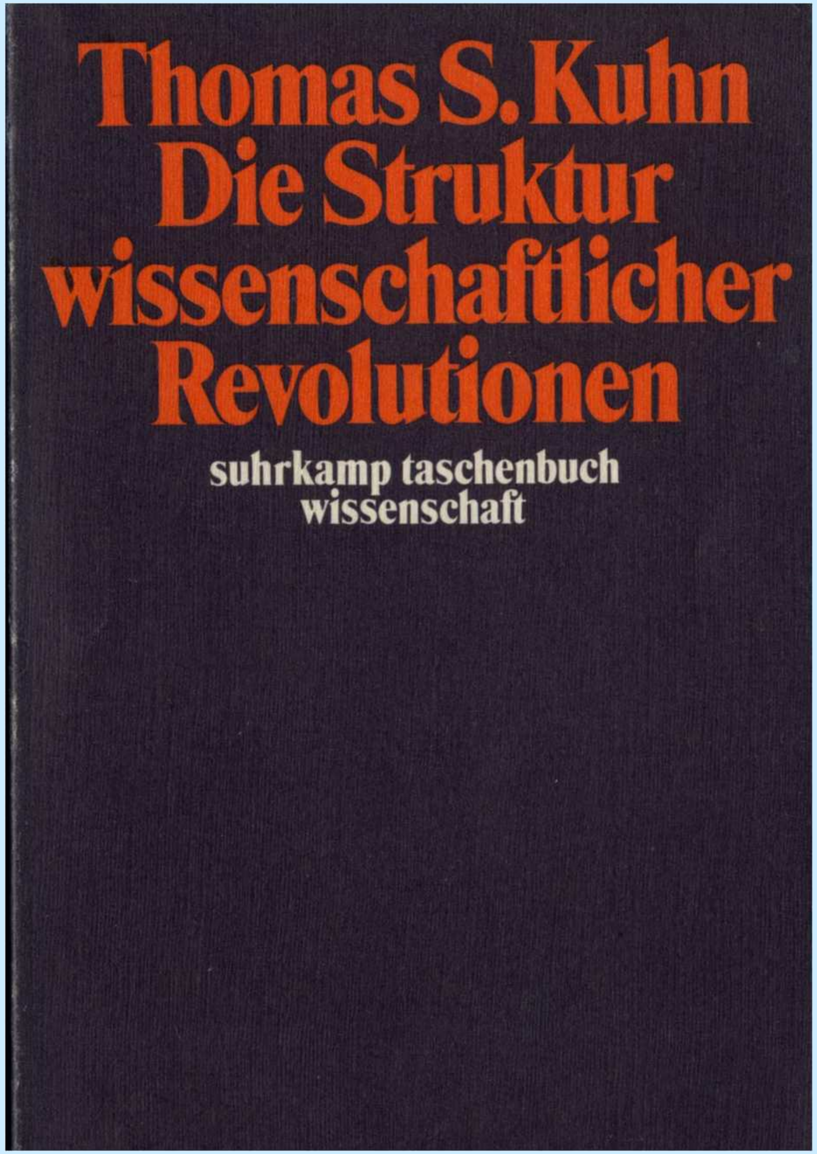

Thomas S. Kuhn (1922-1996)

Paradigmawechsel — das Wort wird Thomas S. Kuhn einfach nicht mehr los. Es machte ihn zum bekanntesten Wissenschaftshistoriker unserer Zeit und sickerte selbst in die unwissenschaftlichste Plauderei ein. An Lavoisiers Sauerstofftheorie etwa oder Röntgens Entdeckung demonstrierte Kuhn, der in Harvard, Berkeley, Princeton lehrte und seine Karriere am MIT krönte, in seinem Buch "Die Struktur wissenschaftlicher Revolutionen", wie wissenschaftliche Wahrheit entsteht.

Die Zeit, 1995

Paradigma — nach Thomas S. Kuhn ist es die „Gesamtheit aller eine Disziplin in einem Zeitabschnitt beherrschenden Grundauffassungen hinsichtlich Gegenstandsbereich und Methode.“
(Der Große Brockhaus, 20. Auflage)

Paradigmen — nach Platon „die Urbilder der sinnlich wahrnehmbaren Dinge.“
(Der Große Brockhaus, 20. Auflage)

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B

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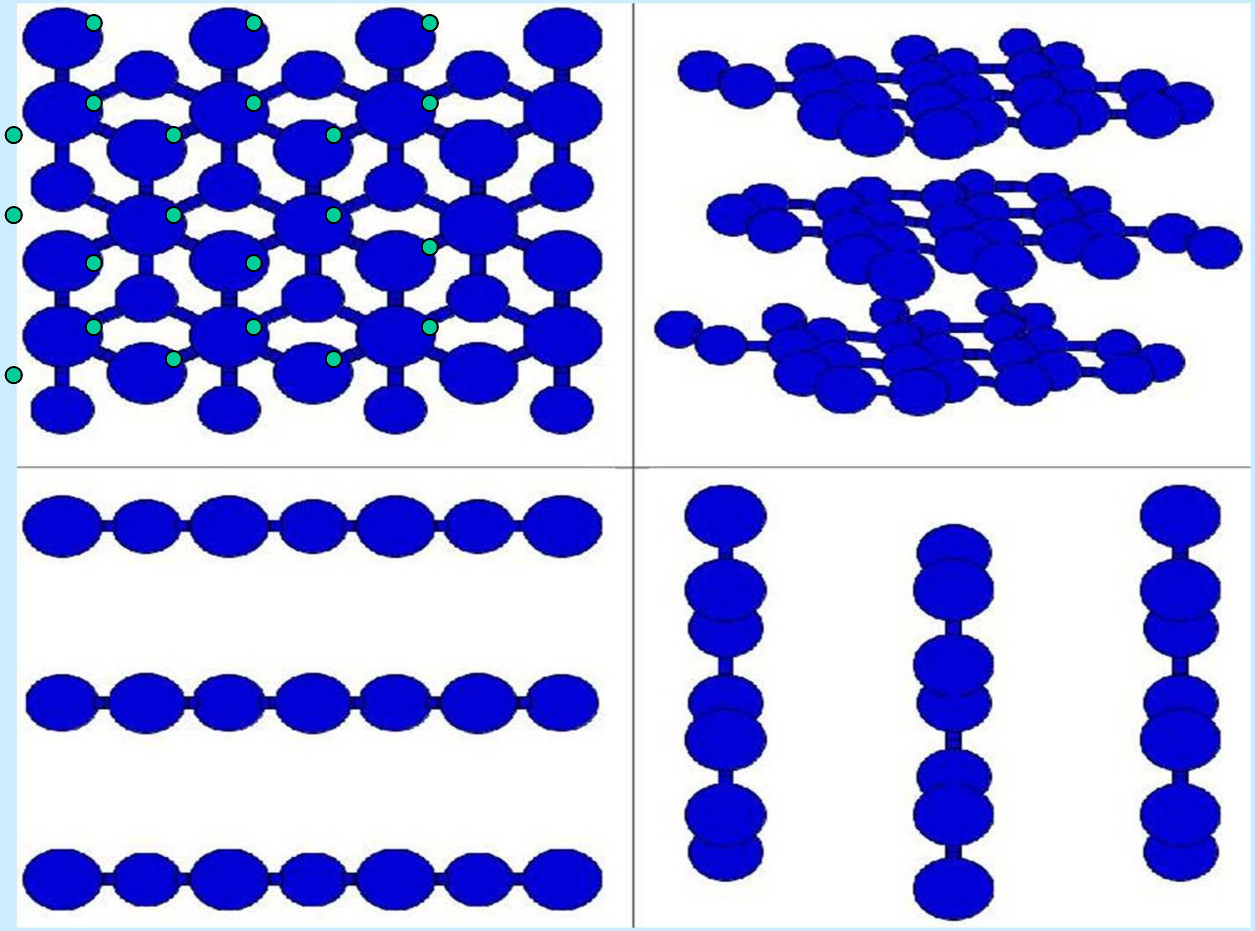
A

Hexagonaler Graphit: sp^2 Hybridisierung



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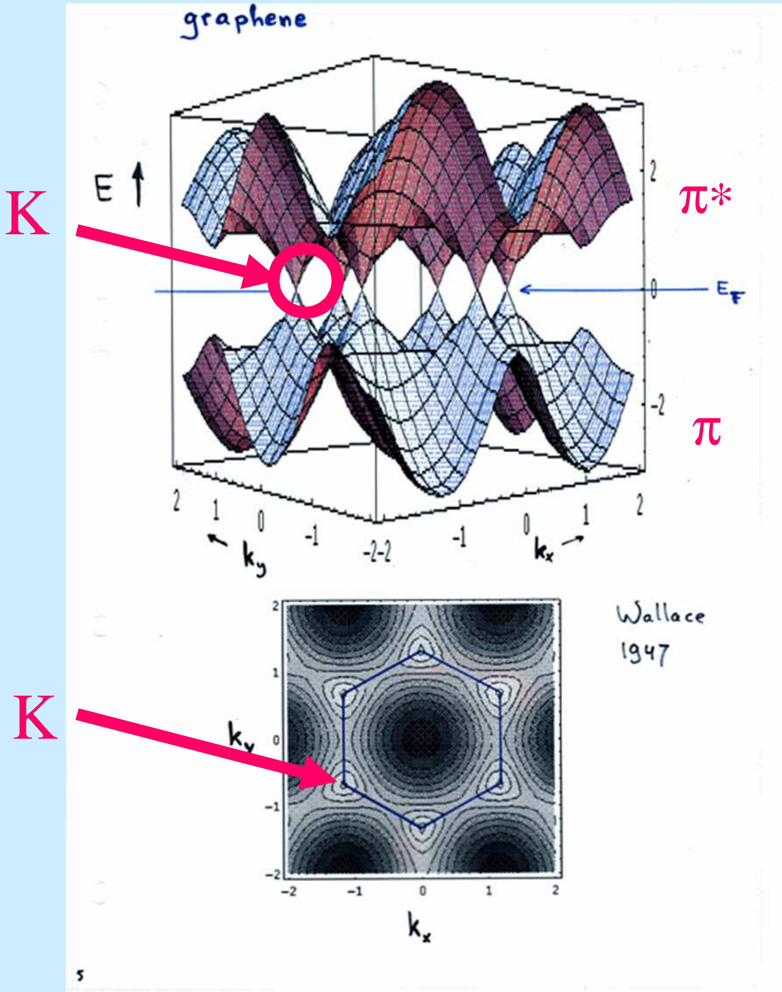
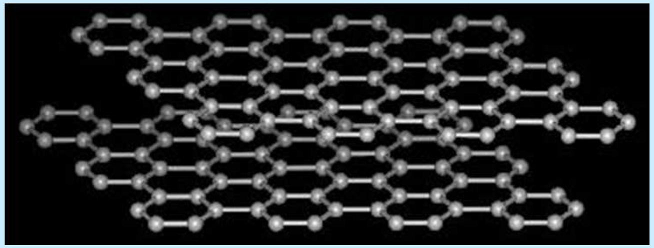
Bandstruktur der p-Elektronen in der Graphitschicht





Graphit ist ein „zero-gap“ Halbleiter = Halbmetall

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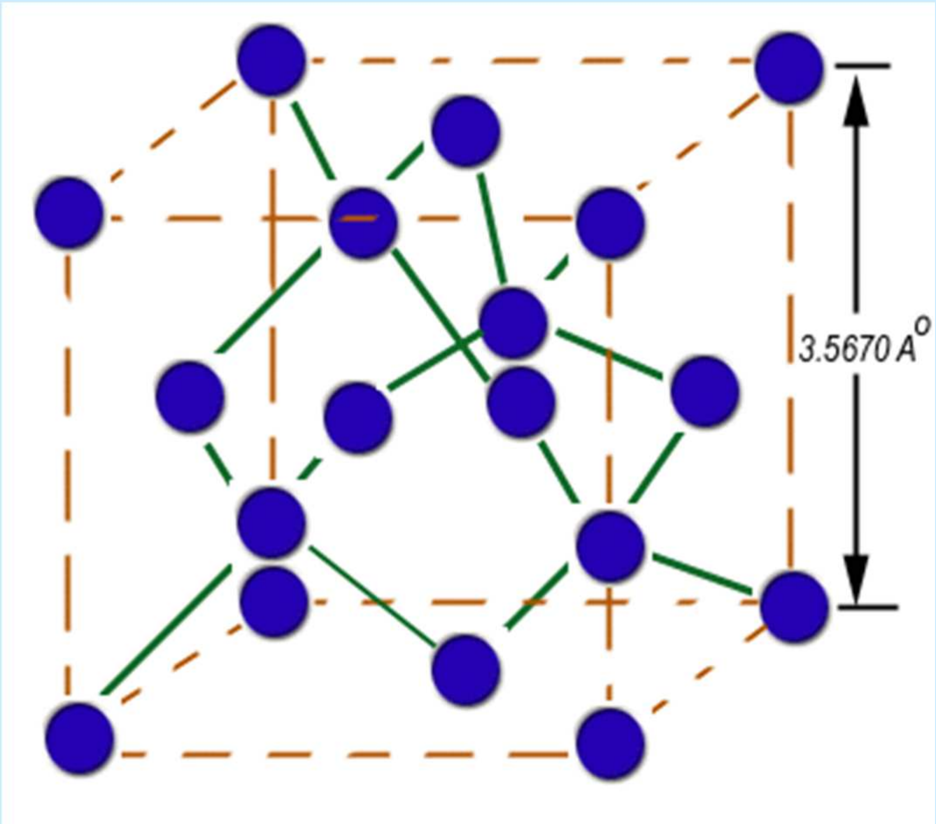
Diamant: sp^3 Hybridisierung



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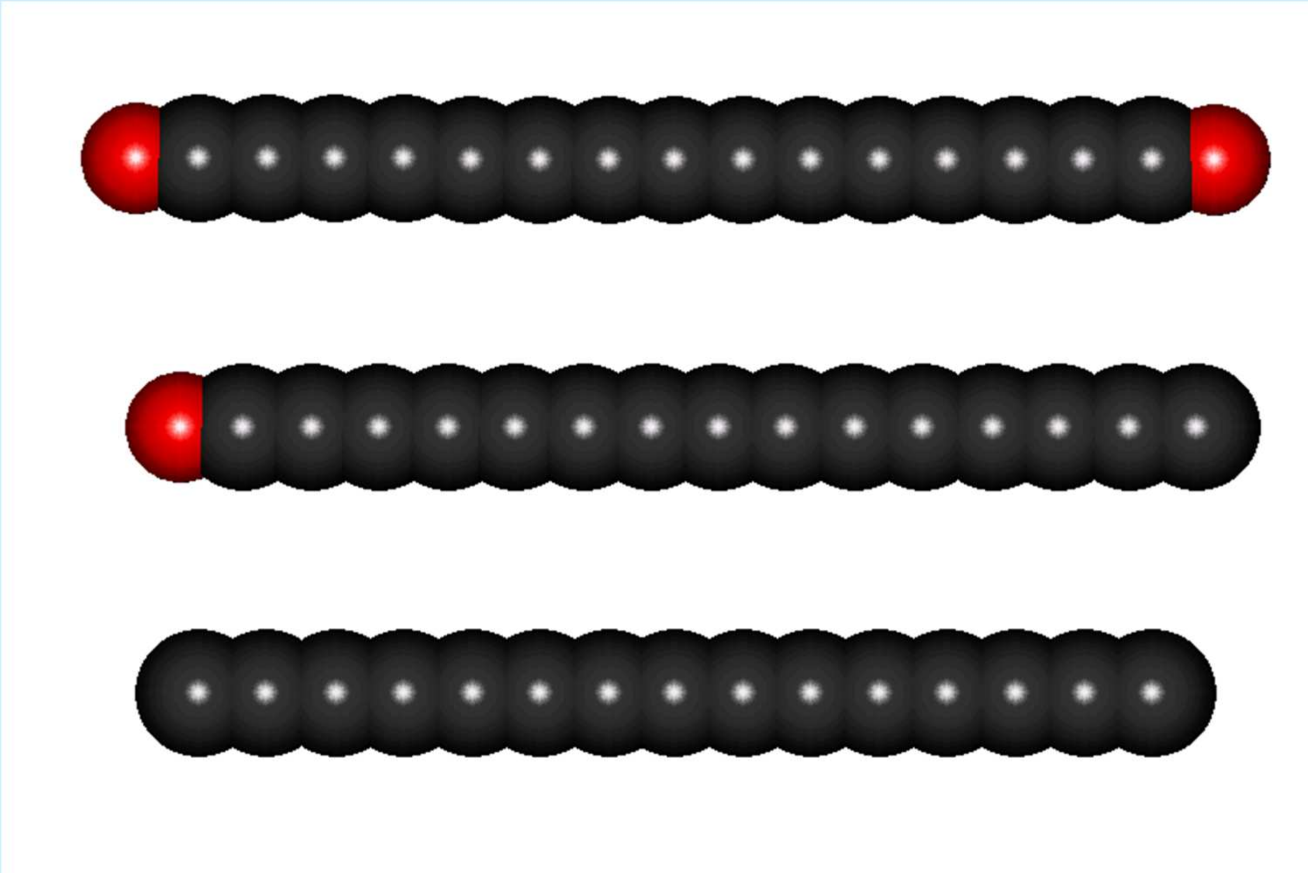
Kumulene …C=C=C=C=C….: sp Hybridisierung



$C_{15}O_2$

$C_{15}O$

C_{15}

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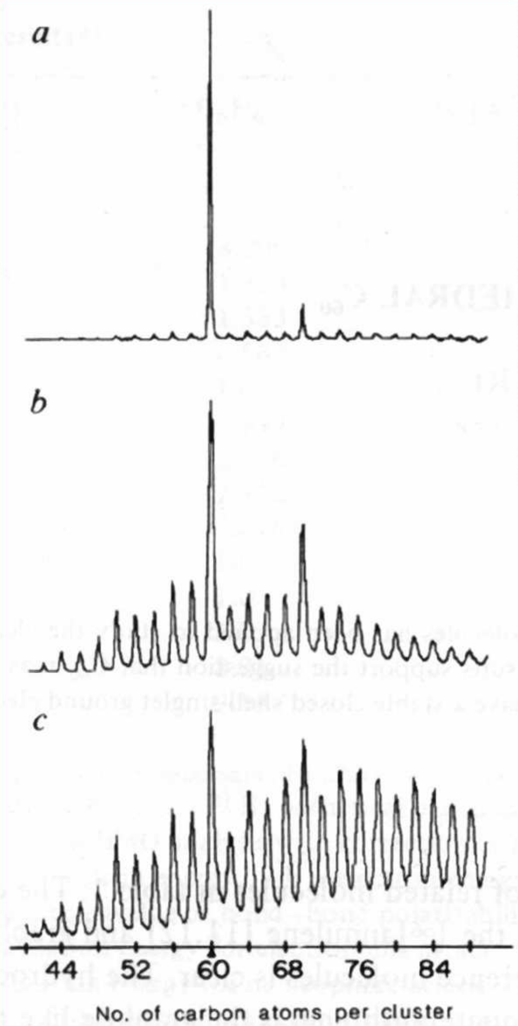
Eine neue Kohlenstoffstruktur: C_{60}



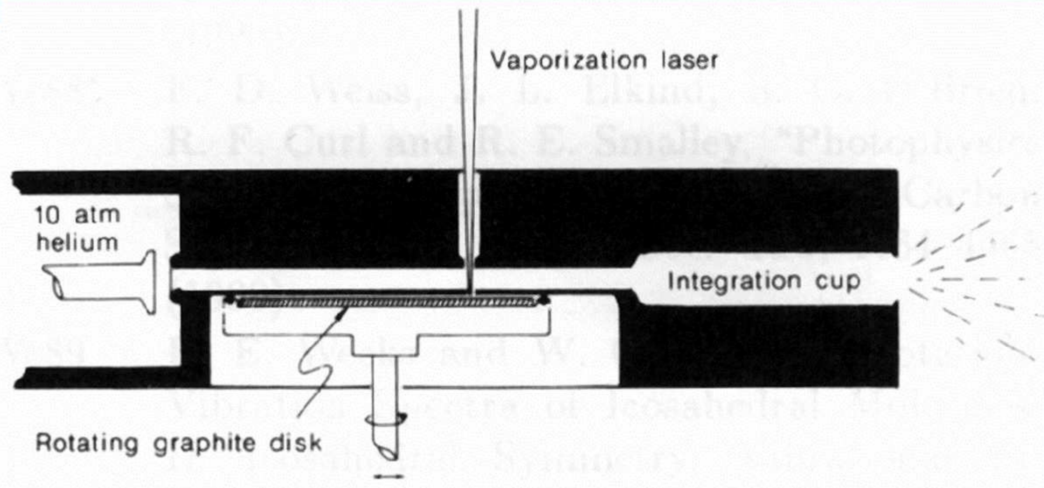


Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In *c*, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in *b* was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in *a* was obtained by maximizing these cluster thermalization and cluster–cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

Kroto et al., *Nature* 318, 1985, 162

Das Ikosaedermodell des C_{60}

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Reprinted with permission from Nature
Vol. 318, No. 6042, pp. 162–163, 14 November 1985

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

graphite fused six-membered ring structure. We believe that the distribution in Fig. 3*c* is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp^2 valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered

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Der Lohn:

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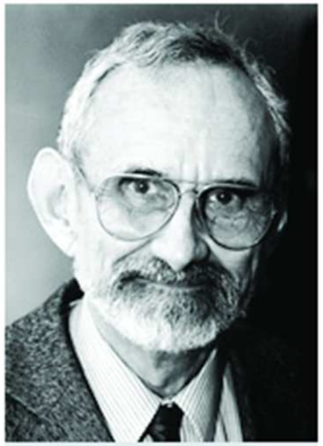
By Year | Nobel Prize in Physics | **Nobel Prize in Chemistry** | Nobel Prize in Medicine | Nobe

Chemistry

The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"



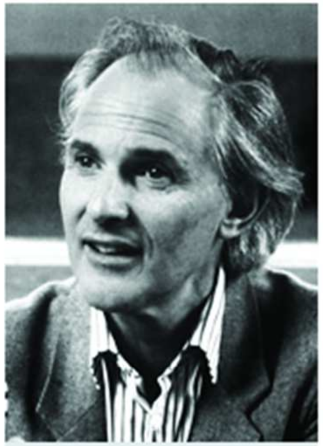
Robert F. Curl Jr.

1/3 of the prize

USA

Rice University
Houston, TX, USA

b. 1933



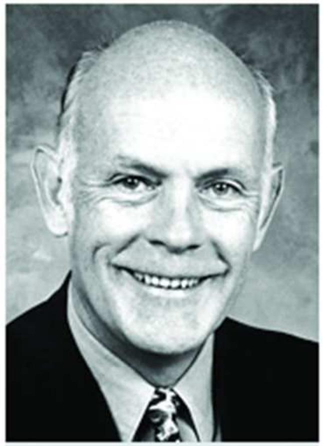
Sir Harold W. Kroto

1/3 of the prize

United Kingdom

University of Sussex
Brighton, United Kingdom

b. 1939



Richard E. Smalley

1/3 of the prize

USA

Rice University
Houston, TX, USA

b. 1943
d. 2005

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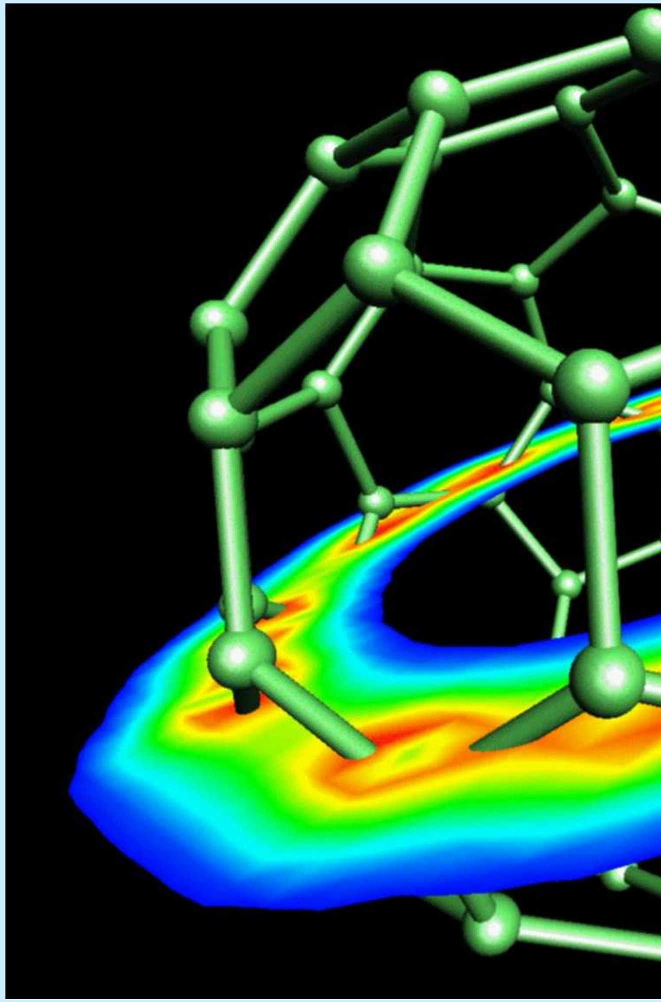
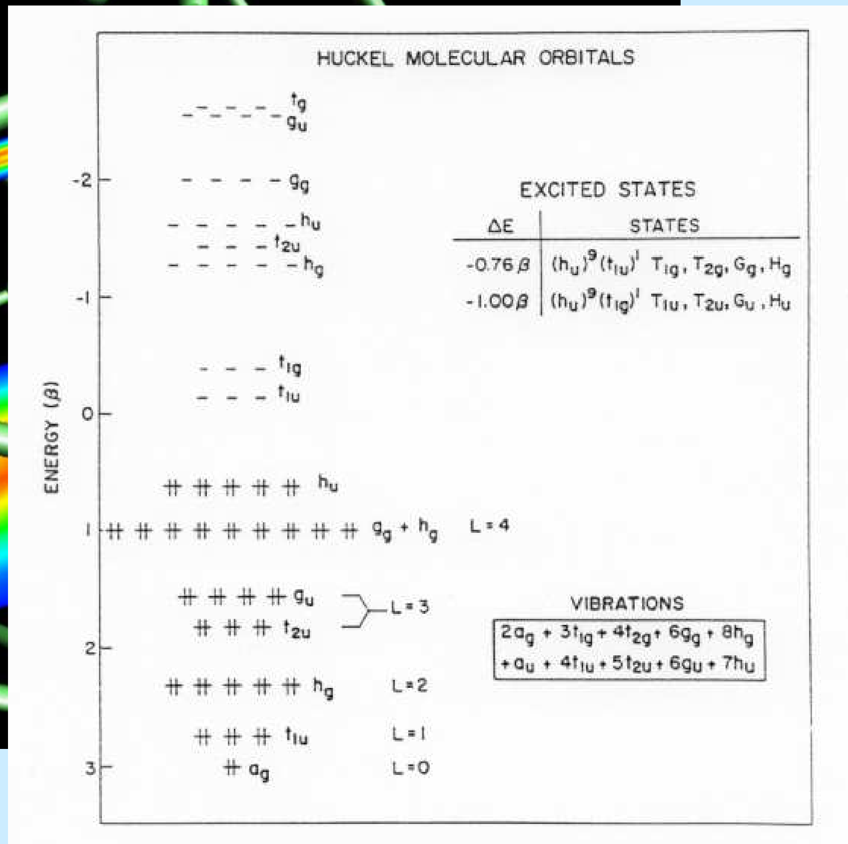
The new world of fullerenes





HMO energy level diagram for C_{60} (unscaled β, see text).

Haddon 1986: Transfer of up to 12 electrons

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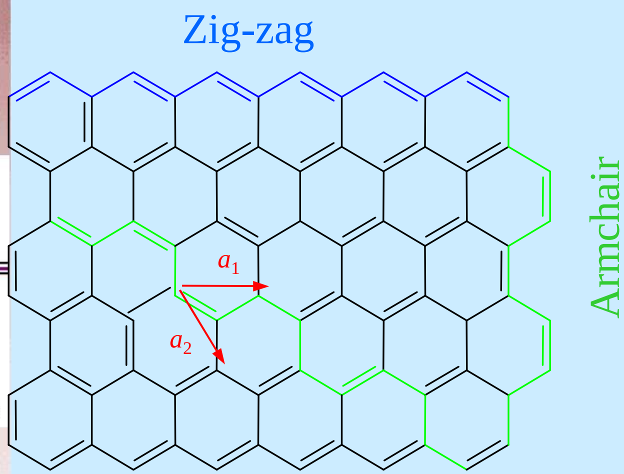
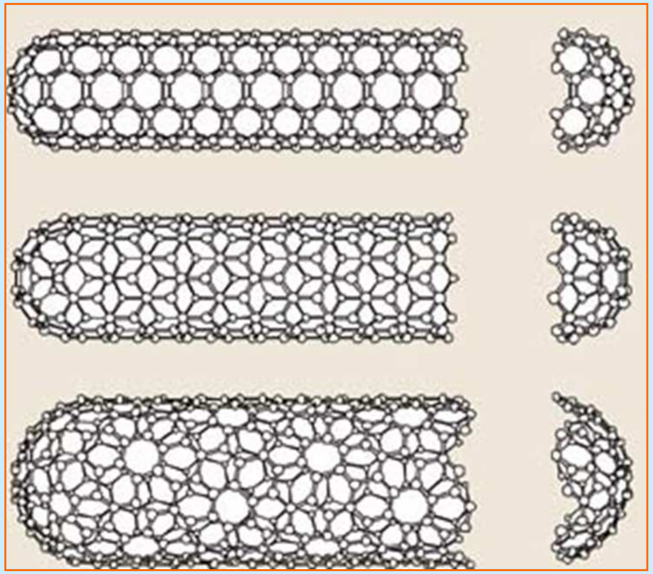
SWCNT from graphene





Armchair nT
(n=m) metal

Zig-zag nT
(n-m) = 3i metal
(n-m) ≠ 3i semicond.

Chiral nT
(n-m) = 3i metal
(n-m) ≠ 3i semicond.

Chiral vector: $\mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2}$

$\mathbf{a_1}$, $\mathbf{a_2}$ …. Unit vectors of 2D-hexagonal lattice

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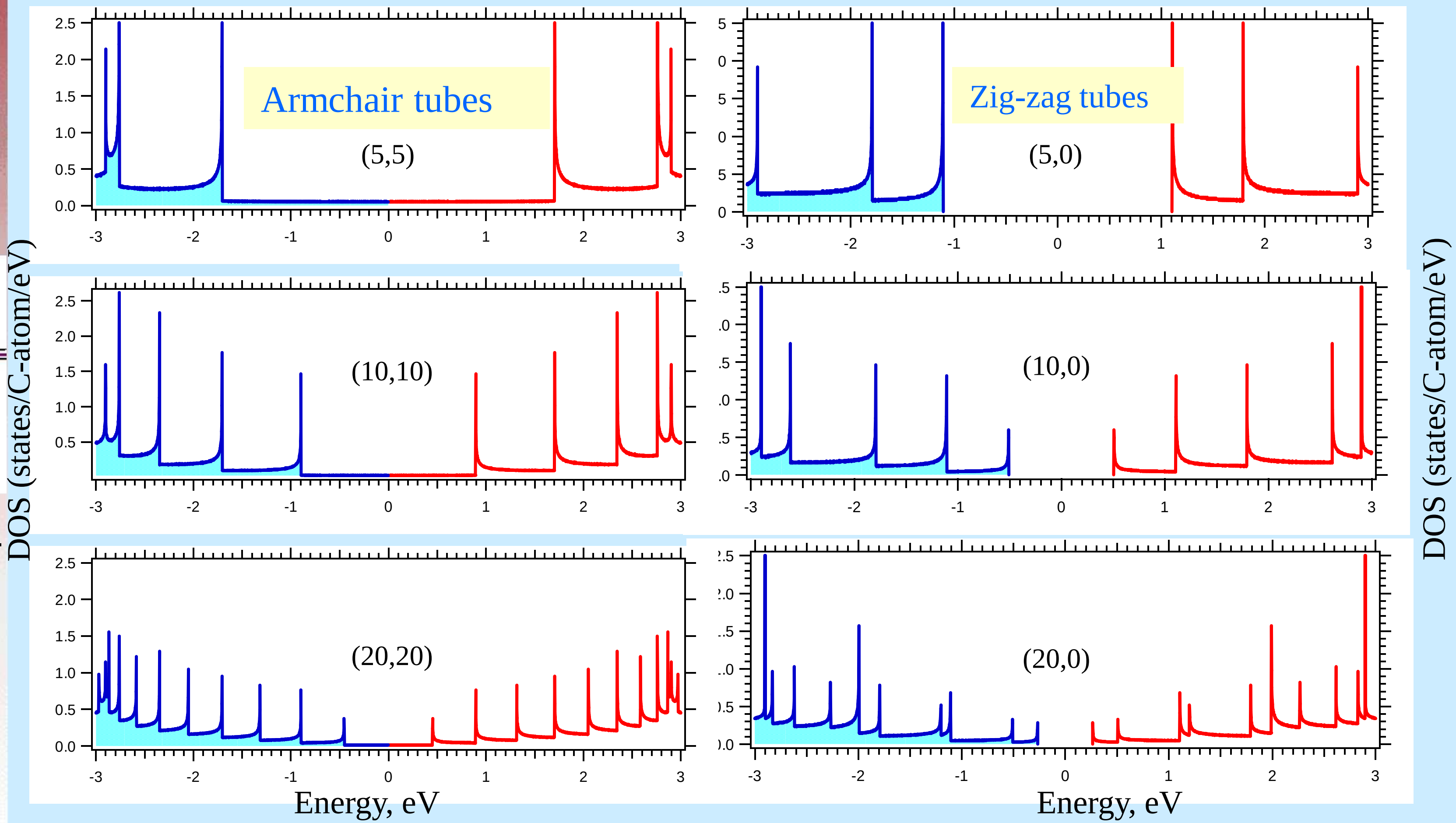
Density of states (DOS) in SWCNT
→*Van Hove singularities*



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Peapods

Ausblick

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Electrochemistry of “empty” fullerenes

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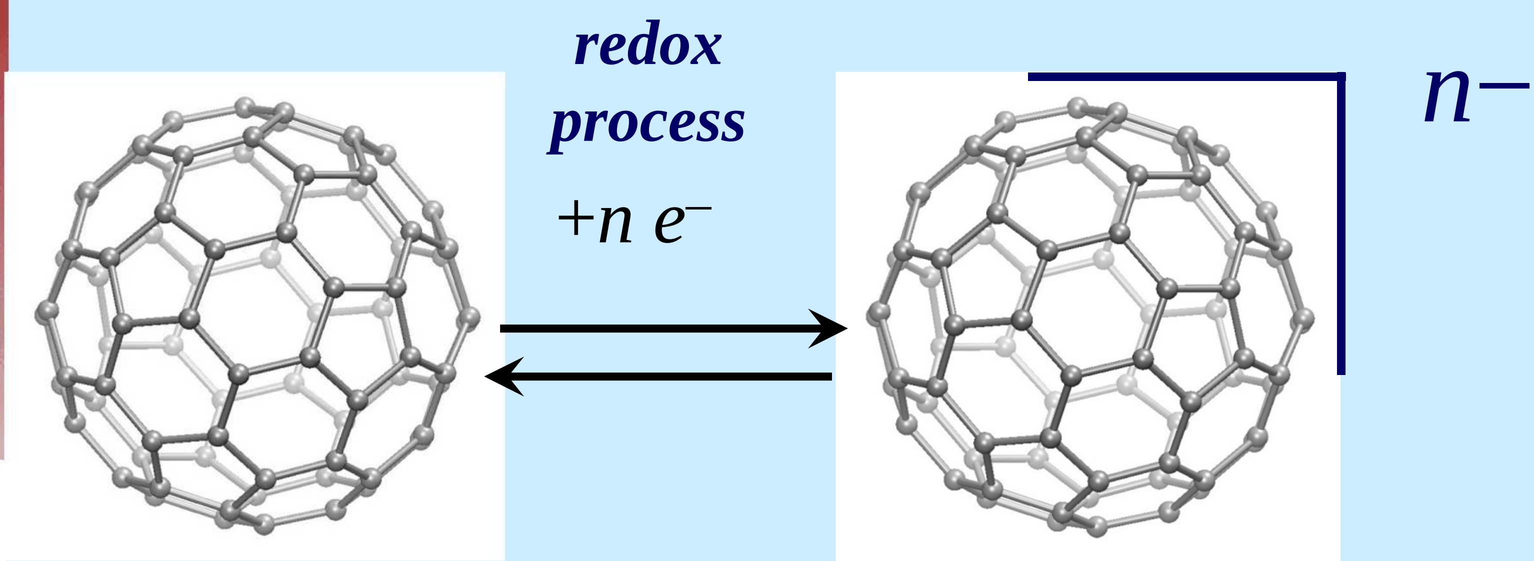

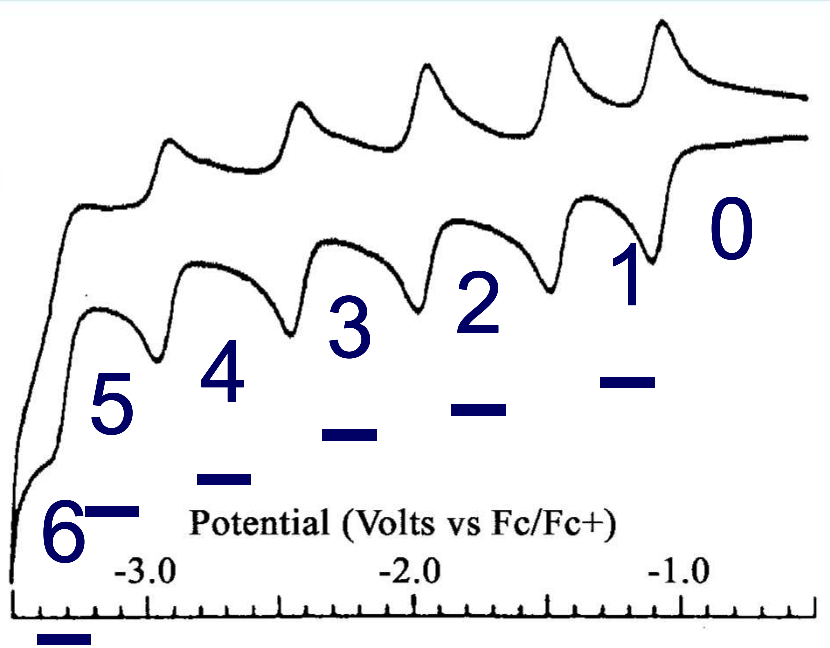

Cyclic voltammetry of C_{60}

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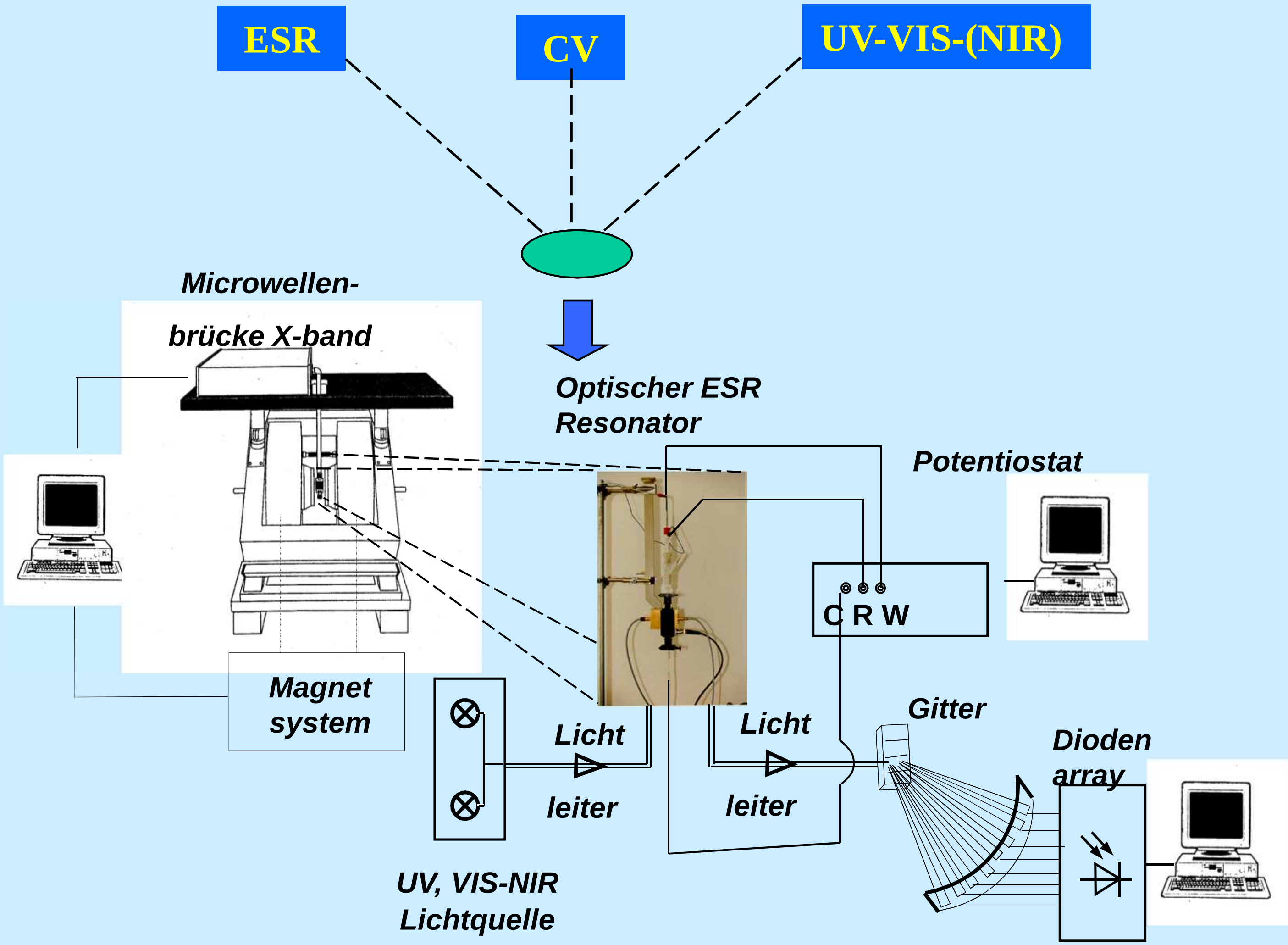
In situ ESR/UV-ViS-NIR Spectroelectrochemistry



Vis-NIR spectroelectrochemistry: C_{60}^{-}

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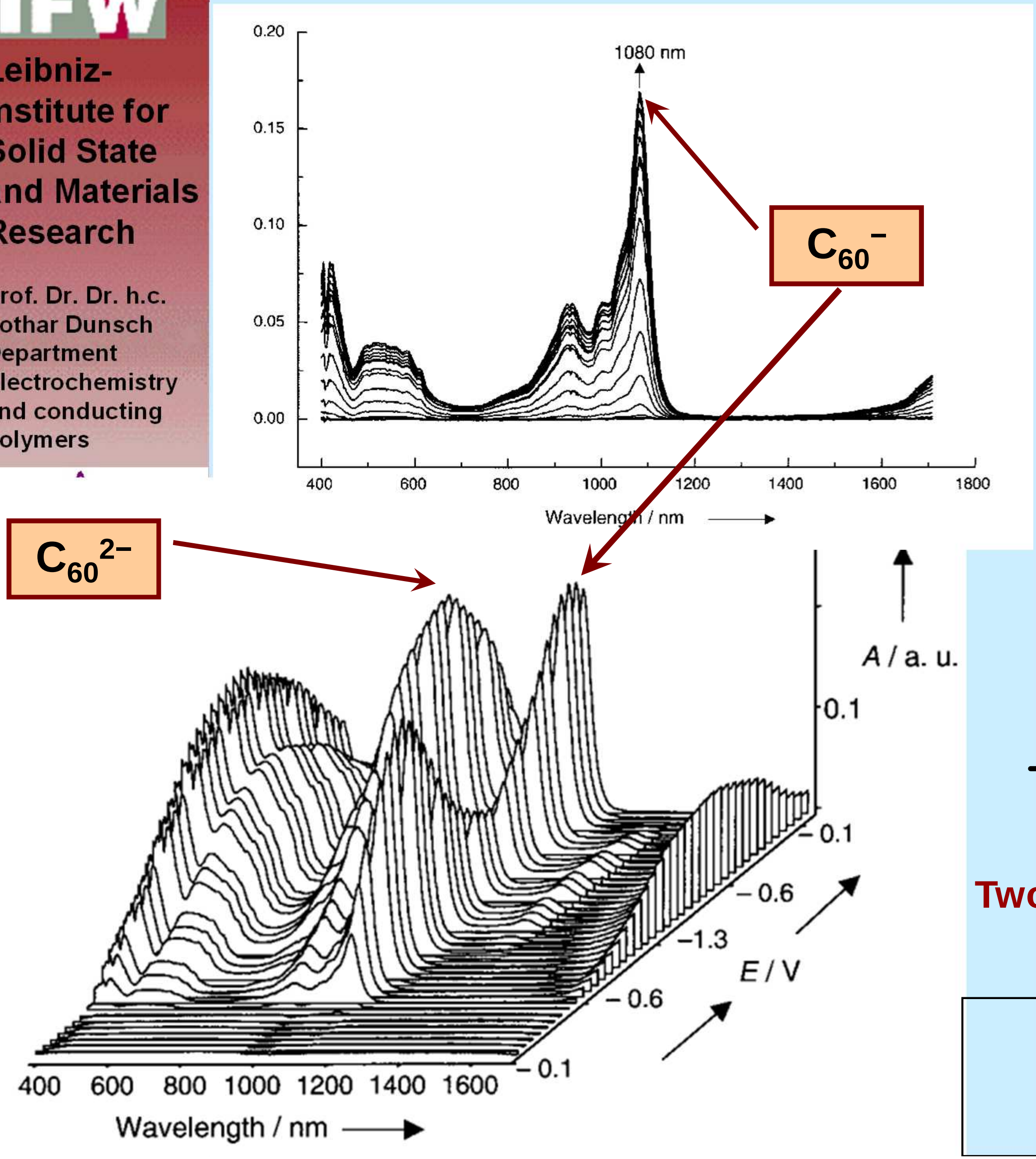

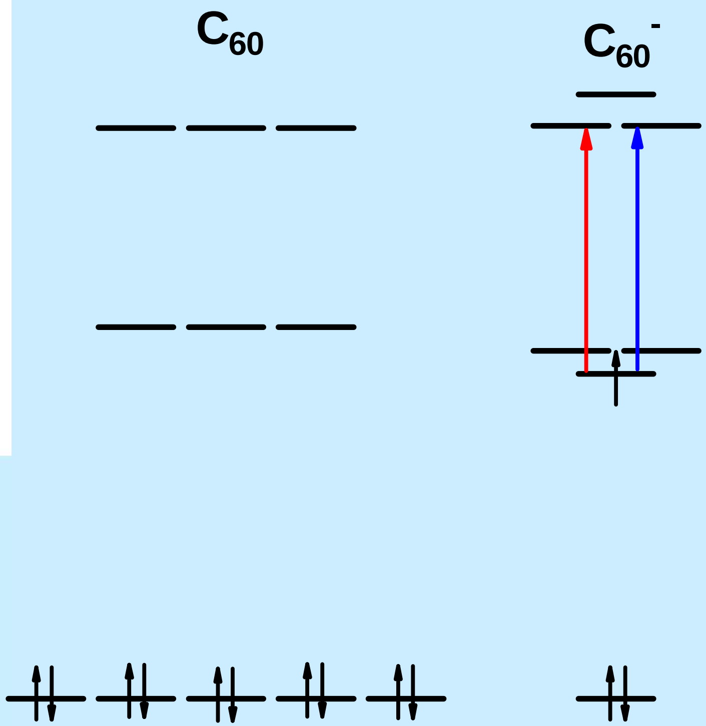

Two-fold degenerate transition. Should be split in anions of derivatives.

P. Rapta, A. Bartl, A. Gromov, A. Stasko, L. Dunsch. *ChemPhysChem* **2002**, *4*, 351-356

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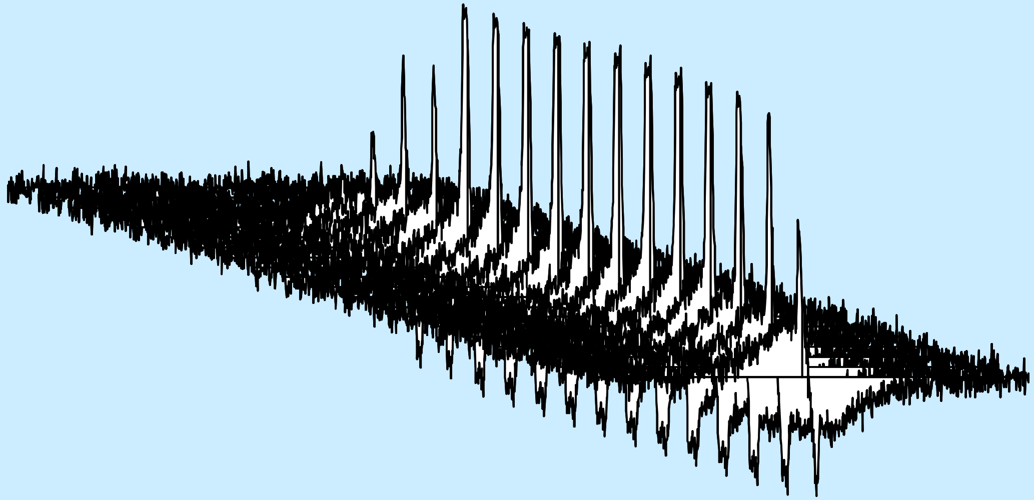
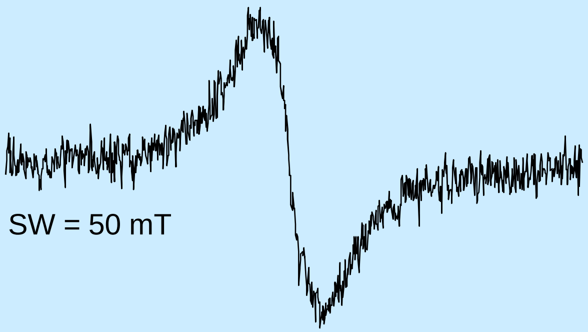
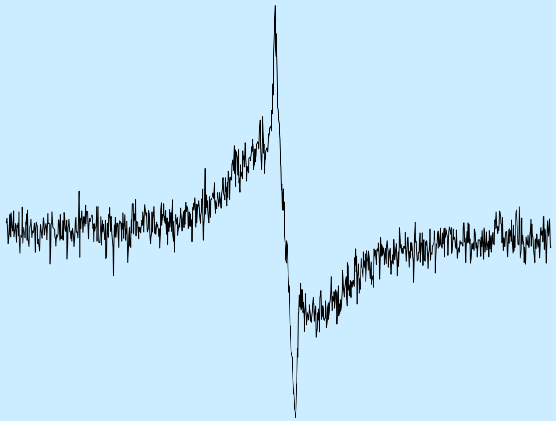
ESR spectra of electrochemically reduced C_{60}





SW = 50 mT



Two paramagnetic C_{60} species

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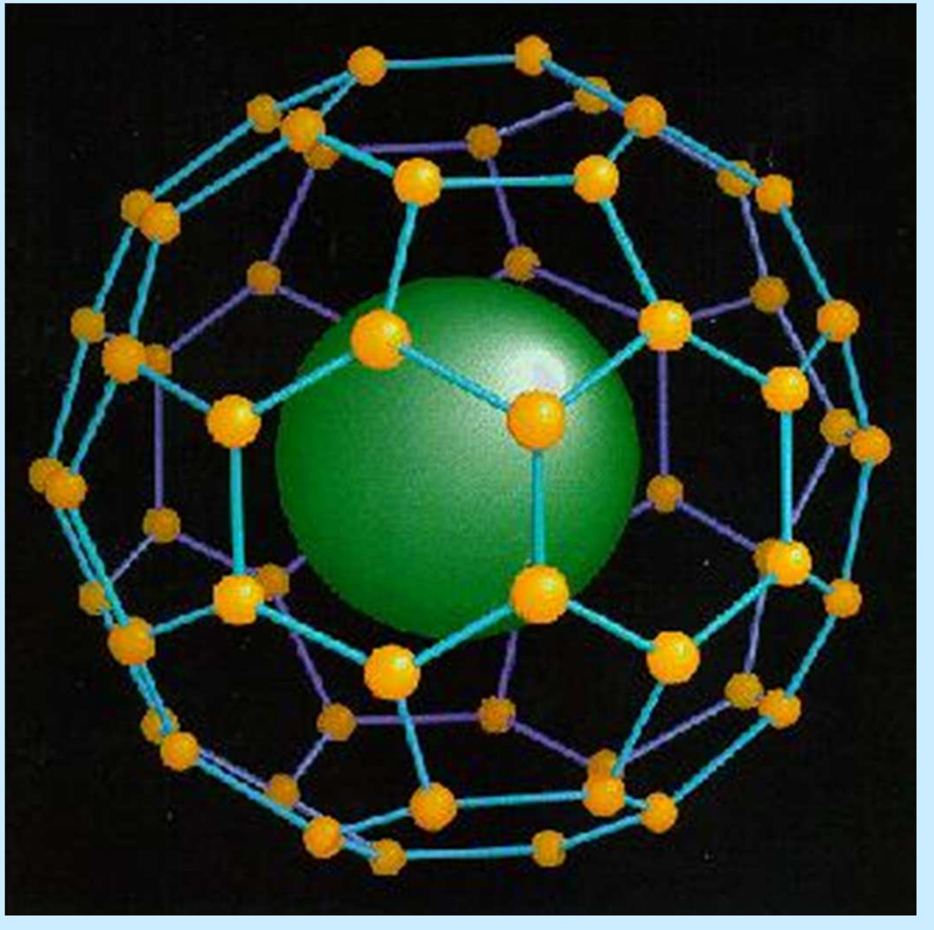
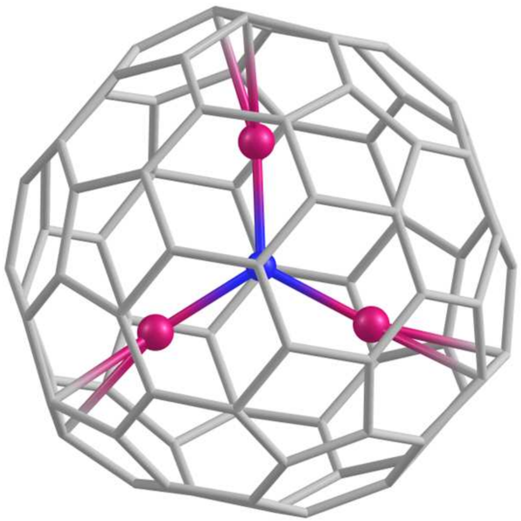
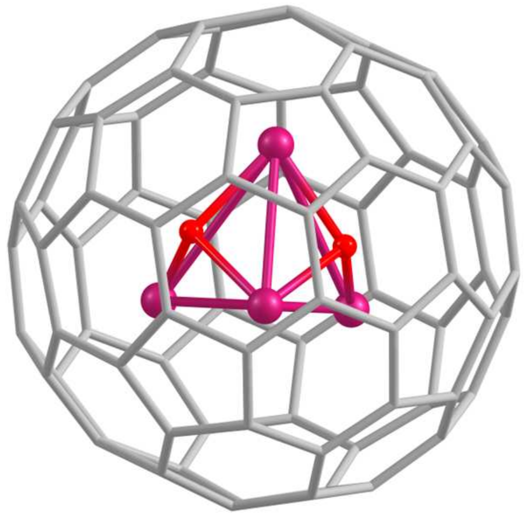
Endohedral Fullerenes



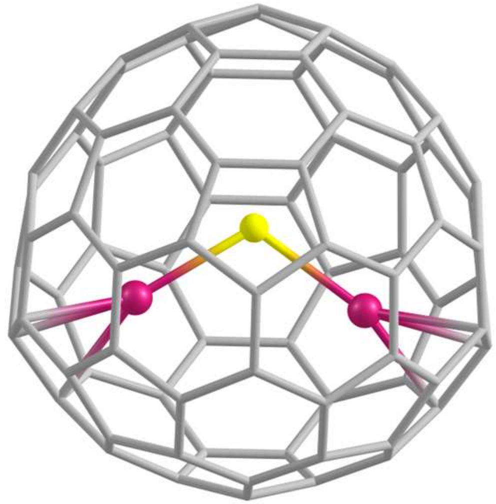
Clusterfullerenes



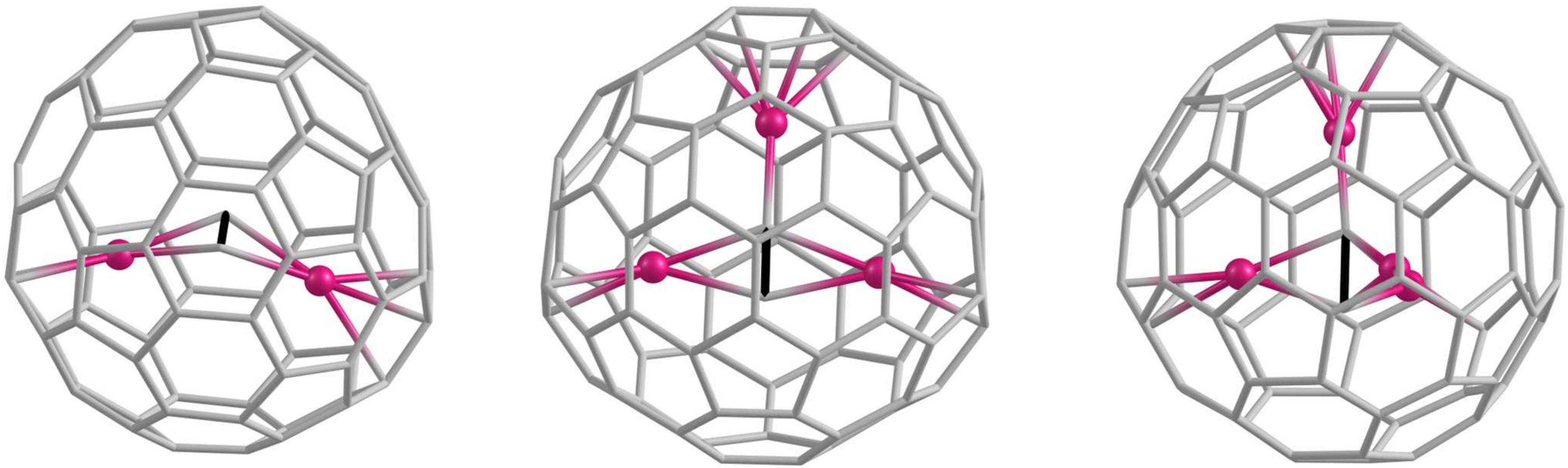
$M_3N@C_{2n}$ nitride



$Sc_4O_{2,3}@C_{80}$ oxide



$M_2S@C_{2n}$ sulfide



$Sc_2C_2@C_{82}$, $Sc_{3,4}C_2@C_{80}$ carbide

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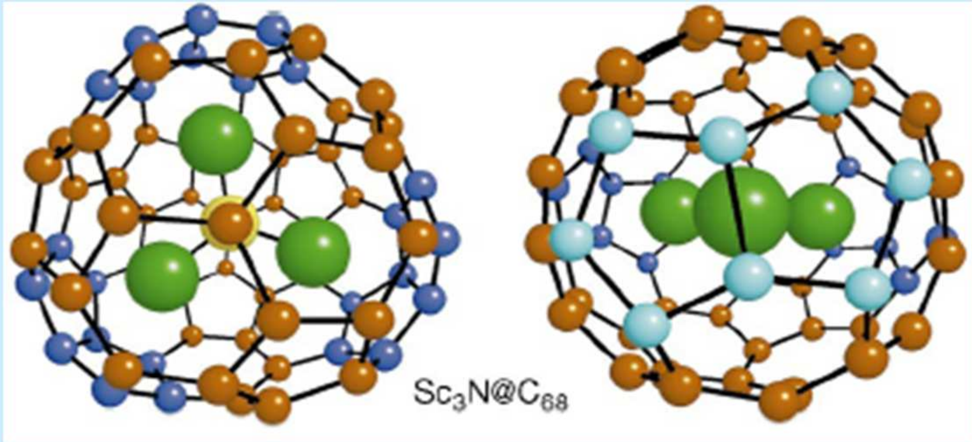
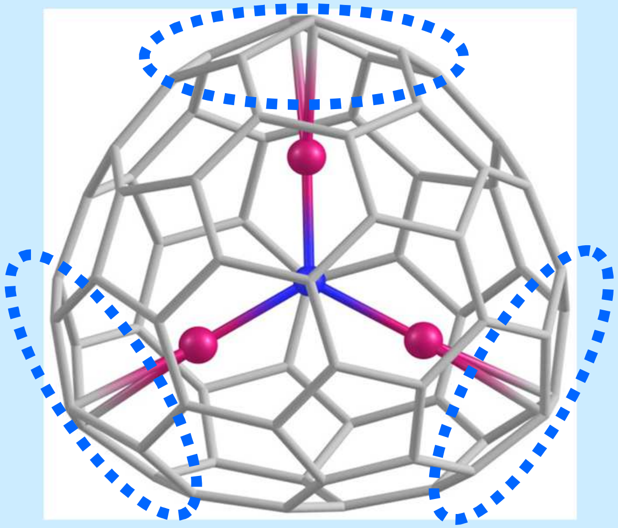
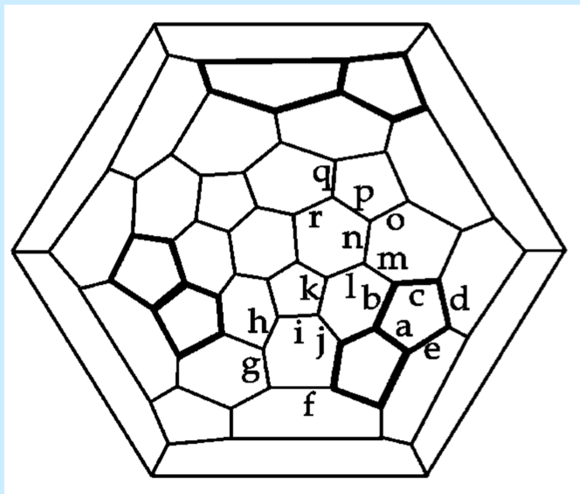
$Sc_3N@C_{68}$ (D_3): A Non-IPR Fullerene



(S. Stevenson, et al., *Nature* 2000, **408**, 427.)





Yang, S., Kalbac, M., Popov, A., Dunsch, L. *Chem. Eur. J.* **2006** , 12, 7856.

Cyclovoltammetry of $Sc_3N@C_{68}$

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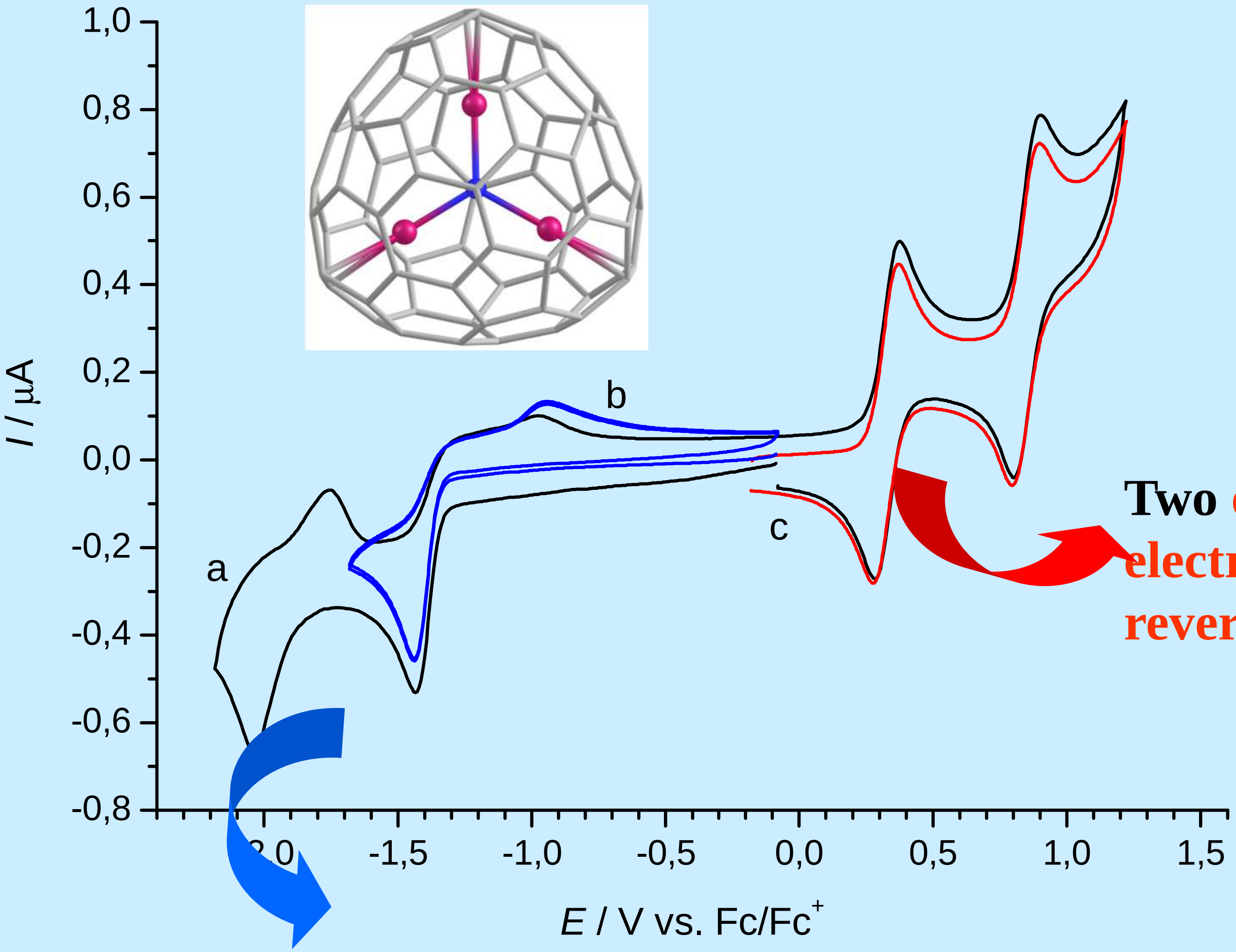

Two oxidation steps: electrochemical reversible!

Two reduction steps: electrochemically irreversible but chemically reversible

(Yang, S., Rapta, P., Dunsch, L. *Chem. Commun.* **2007**)

$Sc_3N@C_{68}$
Spectroelectrochemistry: The stable radical cation

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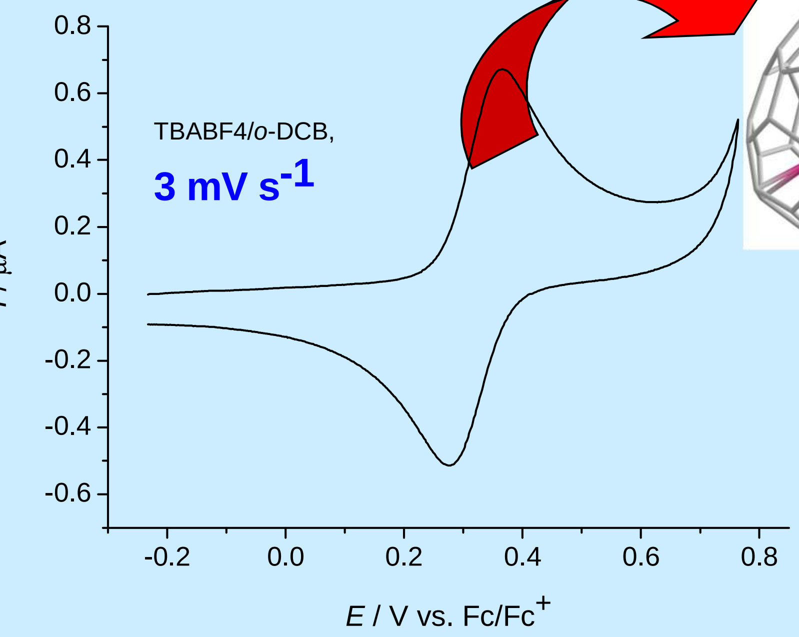

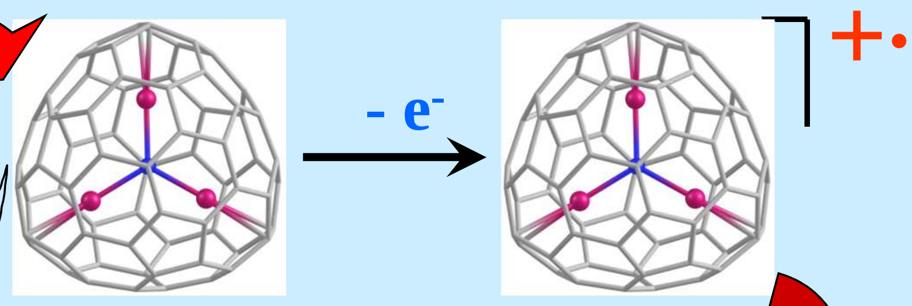

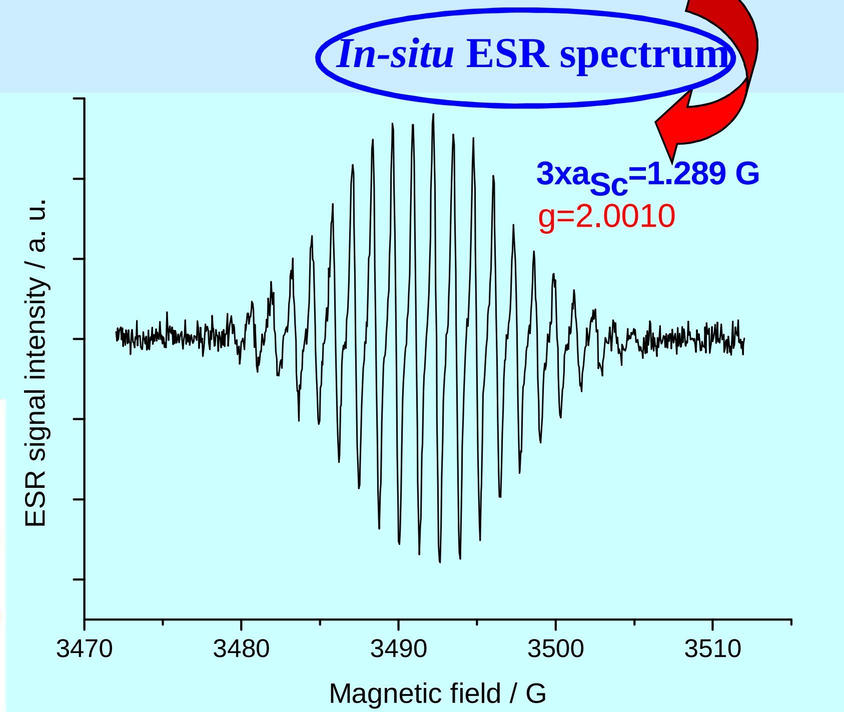

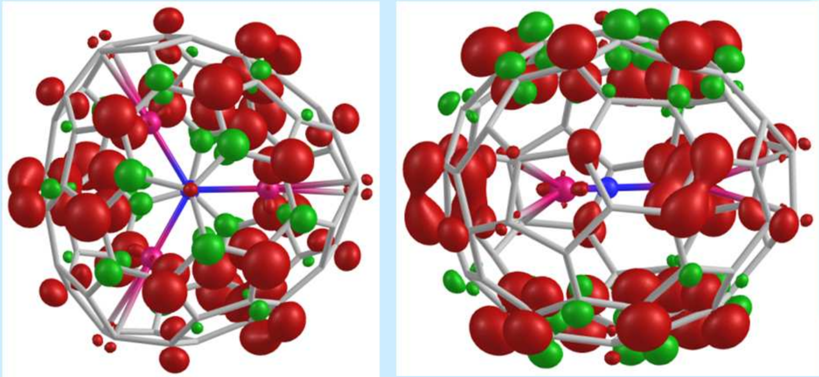

Spin density at $Sc_3N@C_{68}^{+\cdot}$, PBE0/6-311G*Ber: a_{Sc}=-1.469 G

•Yang, S., Rapta, P., Dunsch, L. *Chem. Commun.* **2007**, 189.

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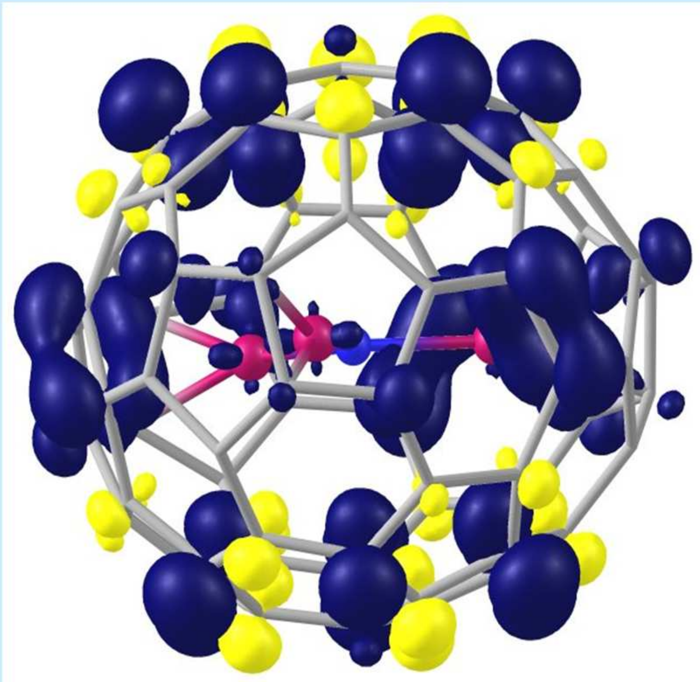
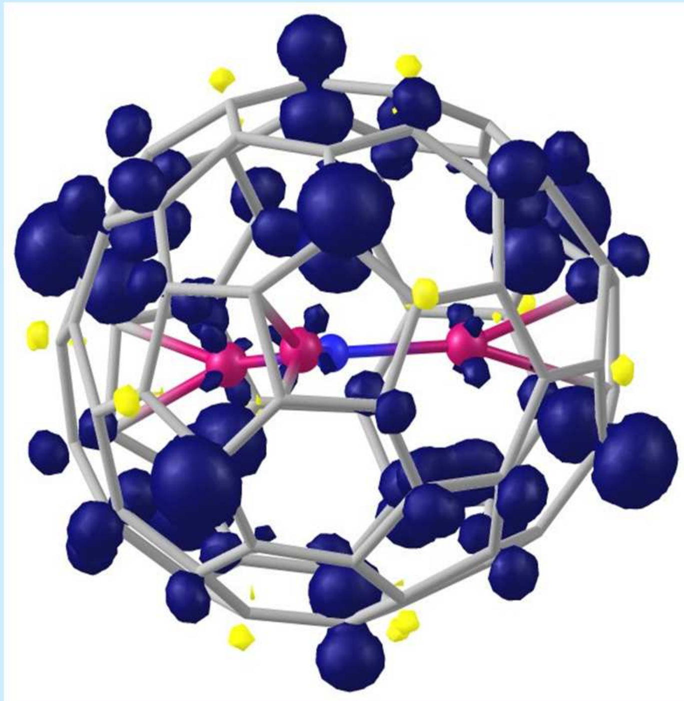
Spin density distribution in $Sc_3N@C_{68}^{+}$ (left) and $Sc_3N@C_{68}^{-}$ (right)





⇨ spin density distribution on the carbon cage is substantially different in the cation and the anion, which explains the differences in *a*(Sc)

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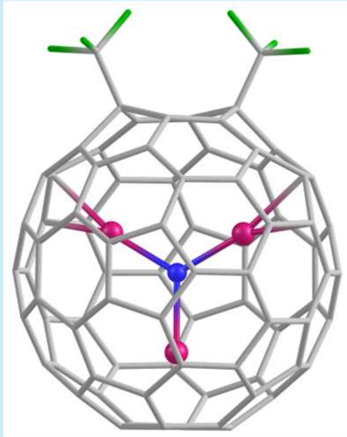
Trifluoromethylation of $Sc_3N@C_{80}$

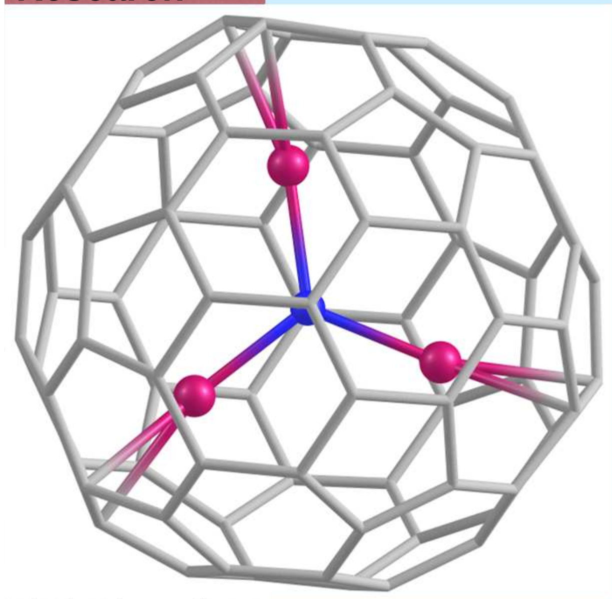
Group of S. Strauss and O. Boltalina

Colorado State University, Fort Collins, USA



$Sc_3N@C_{80}(CF_3)_2$

Shustova, Popov, Mackey, Coumbe, Phillips, Stevenson, Strauss, Boltalina. *JACS* **2007,** *129*, 11676



$+ 2n \bullet CF_3 \longrightarrow Sc_3N@C_{80}(CF_3)_{2n}$, $2n = 2–16$

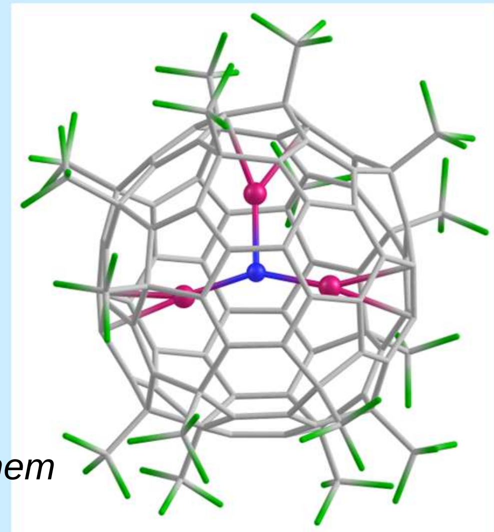
electrochemistry at IFW Dresden

$Sc_3N@C_{80}$-$I_h(7)$

Stevenson et al., *Nature* **1999**, *401, 55.*

Krause, Dunsch, *ChemPhysChem* **2005,** *5*, 1445

http://www.ifw-dresden.de/iff/14



$Sc_3N@C_{80}(CF_3)_{14,16}$

Shustova, Chen, Mackey, Coumbe, Phillips, Stevenson, Popov, Boltalina, Strauss. *JACS* **2009,** *131,* 17630

$Sc_3N@C_{80}(CF_3)_2$: cyclic voltammetry

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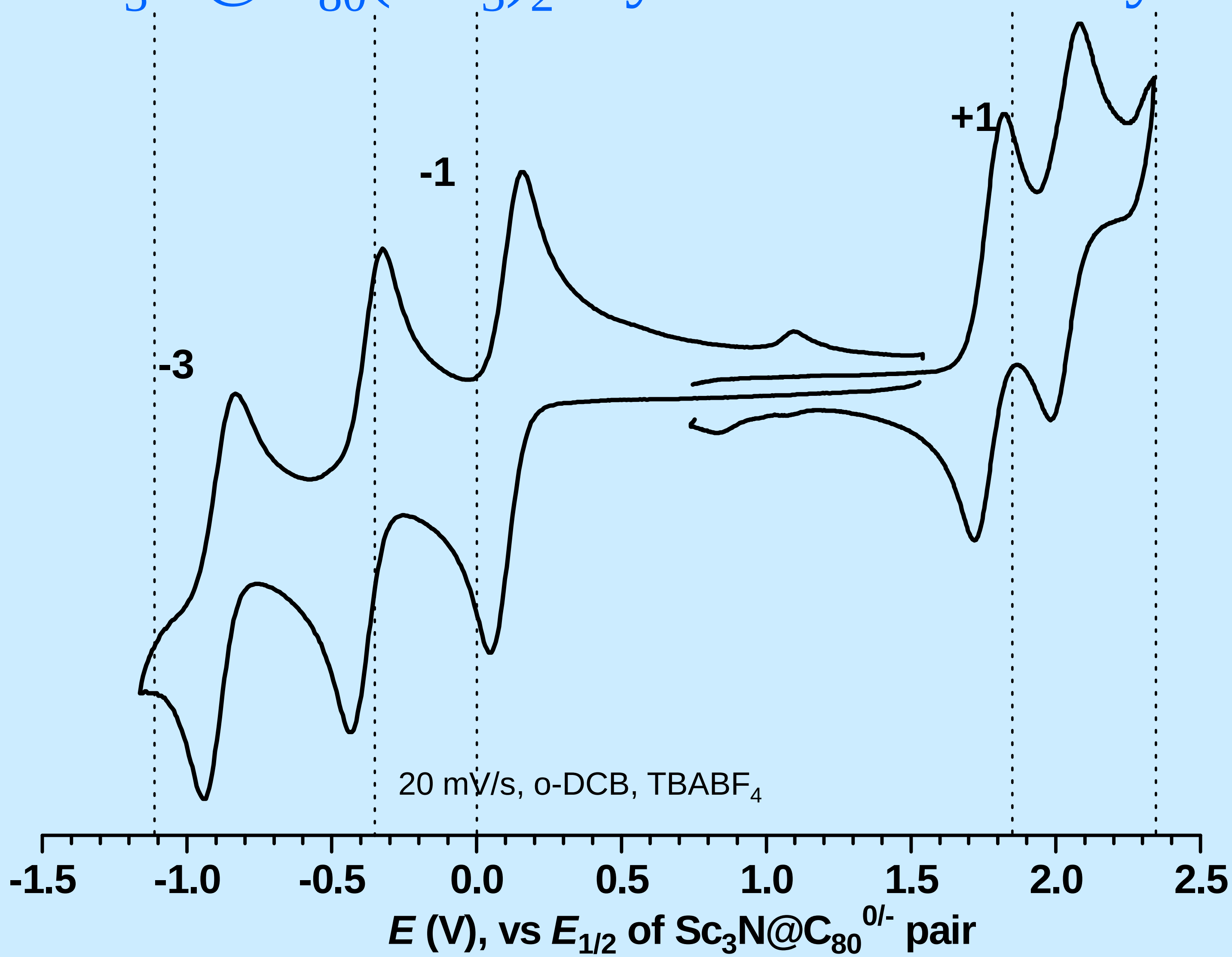

A. A. Popov, N. B. Shustova, A. Svitova, M. A. Mackey, C. E. Coumbe, J. P. Philips, S. Stevenson, S. H. Strauss, O.V. Boltalina, L. Dunsch, *Chem. Eur. J.* 16:16 (2010) 4721-4724

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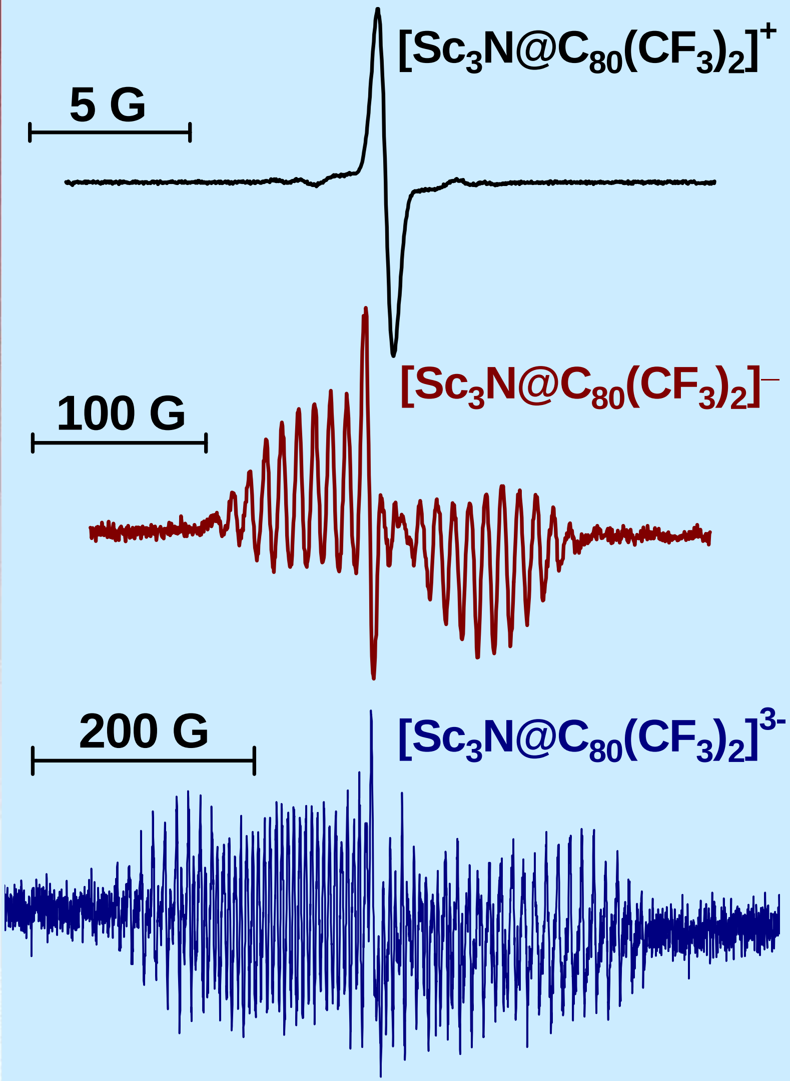
Summary of the ESR Spectra



no ^{45}Sc or ^{19}F splitting

***g* = 2.0018**

a(Sc) = 2 x 9.34 G, 10.7 G

***g* = 1.9958**

a(Sc) = 2 x 10.8 G, 49.2 G

***g* = 2.0006**

Spin density on the Sc_3N cluster

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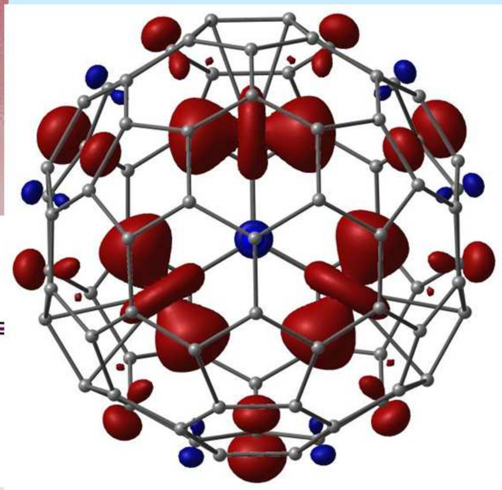
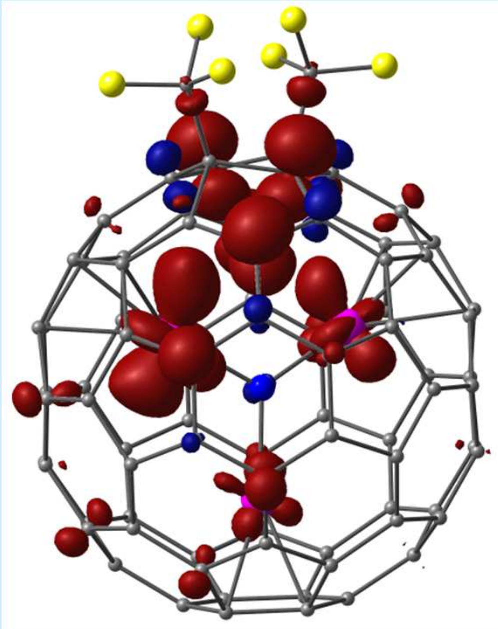


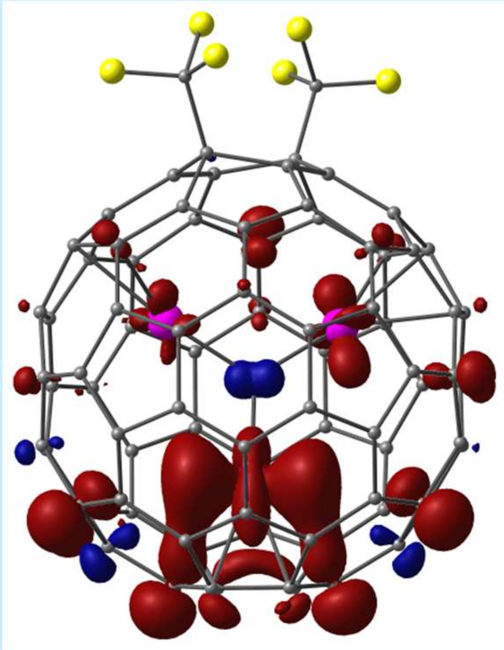
g-factor 1.9992;
***a*(Sc)** 3 x 55.4 G

$Sc_3N@C_{80}^{-\bullet}$



g-factor 1.9958;
***a*(Sc)** 10.7 G and 2 x 9.4 G

$Sc_3N@C_{80}(CF_3)_2^{-\bullet}$



g-factor 2.0006;
***a*(Sc)** 49.2 G and 2 x 10.8 G

$Sc_3N@C_{80}(CF_3)_2^{3-\bullet}$

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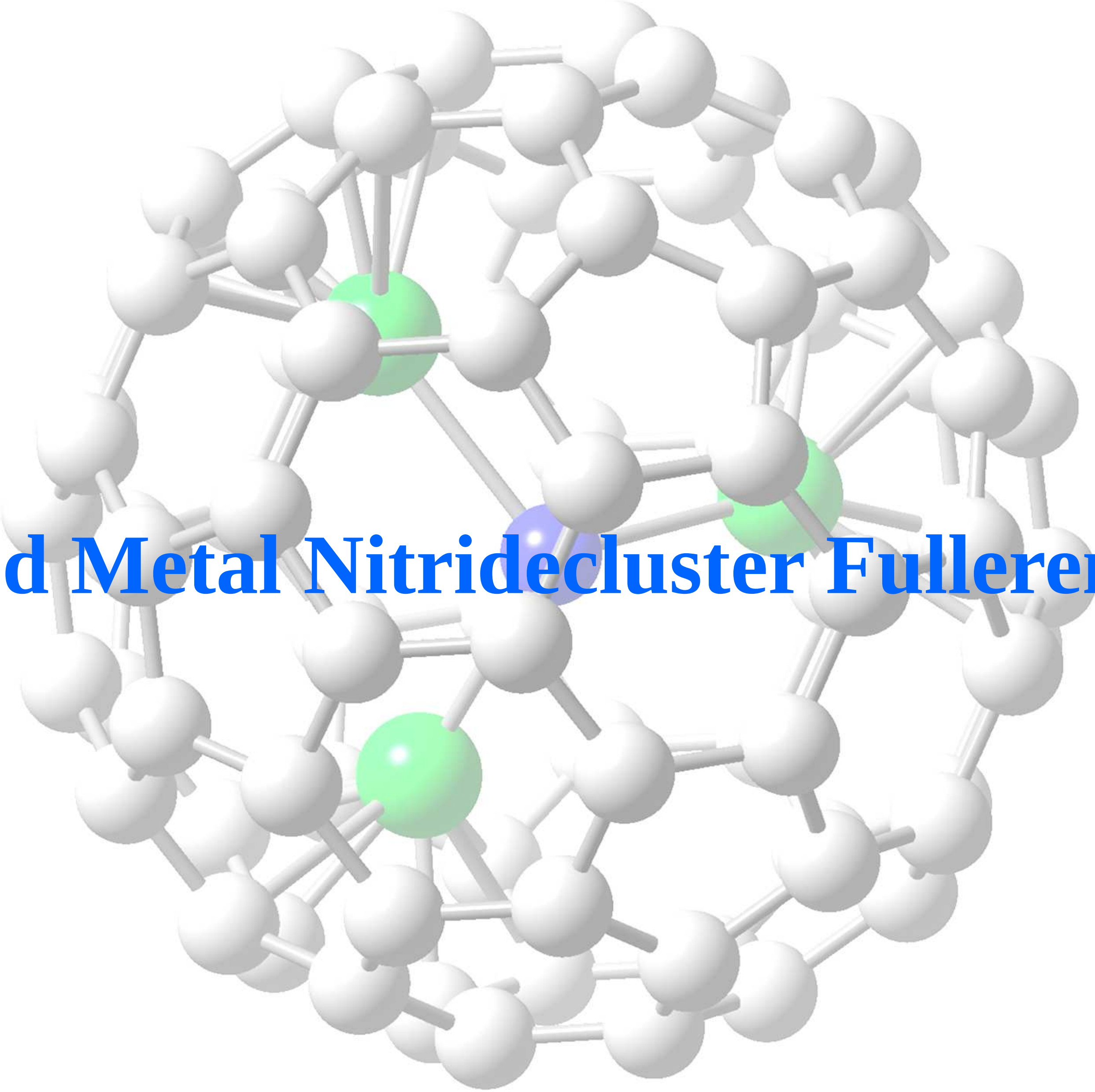
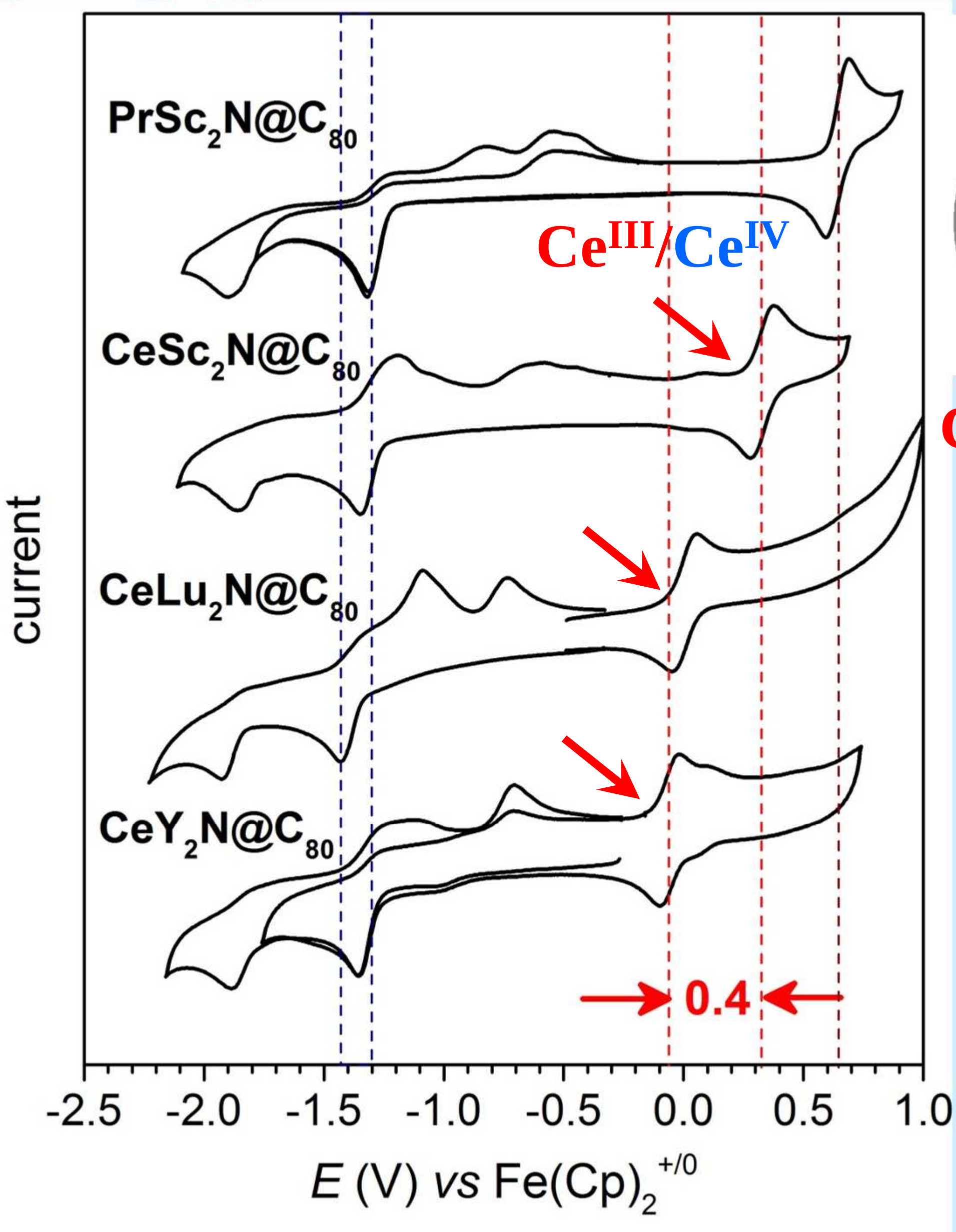
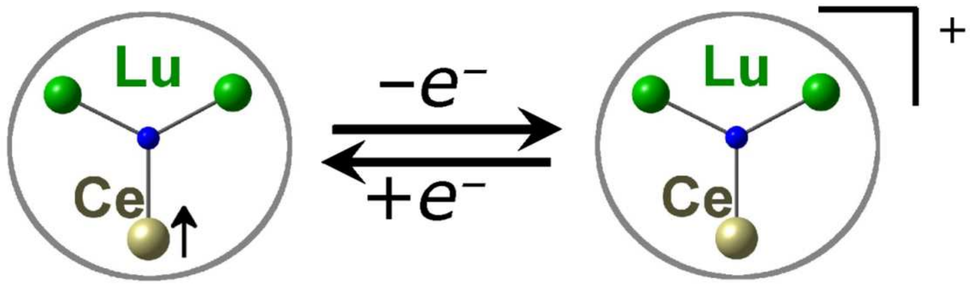


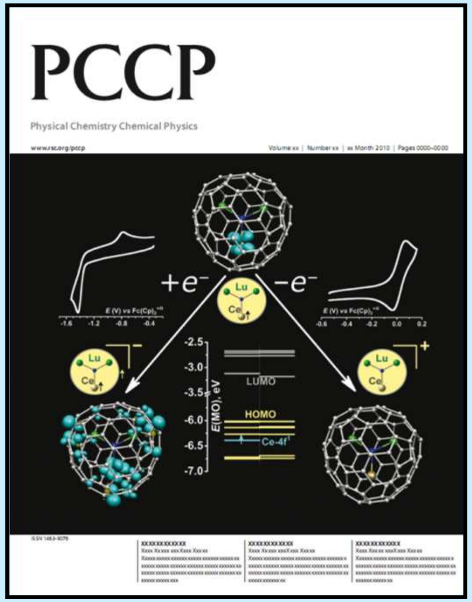
Mixed Metal Nitridecluster Fullerenes

$CeM_2N@C_{80}$: the endohedral Ce^{III}/Ce^{IV} redox pair



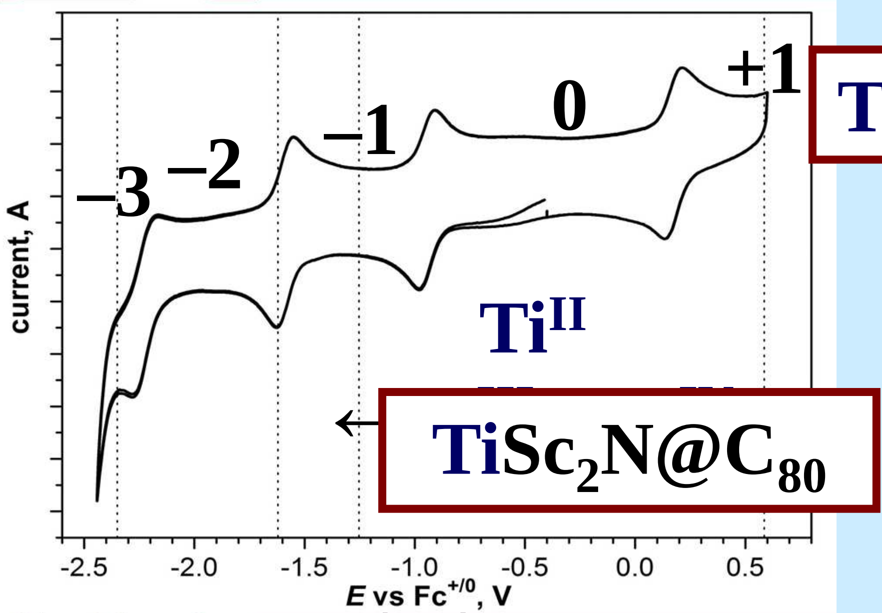


$Ce^{III}M_2N@C_{80}$ $Ce^{IV}M_2N@C_{80}$

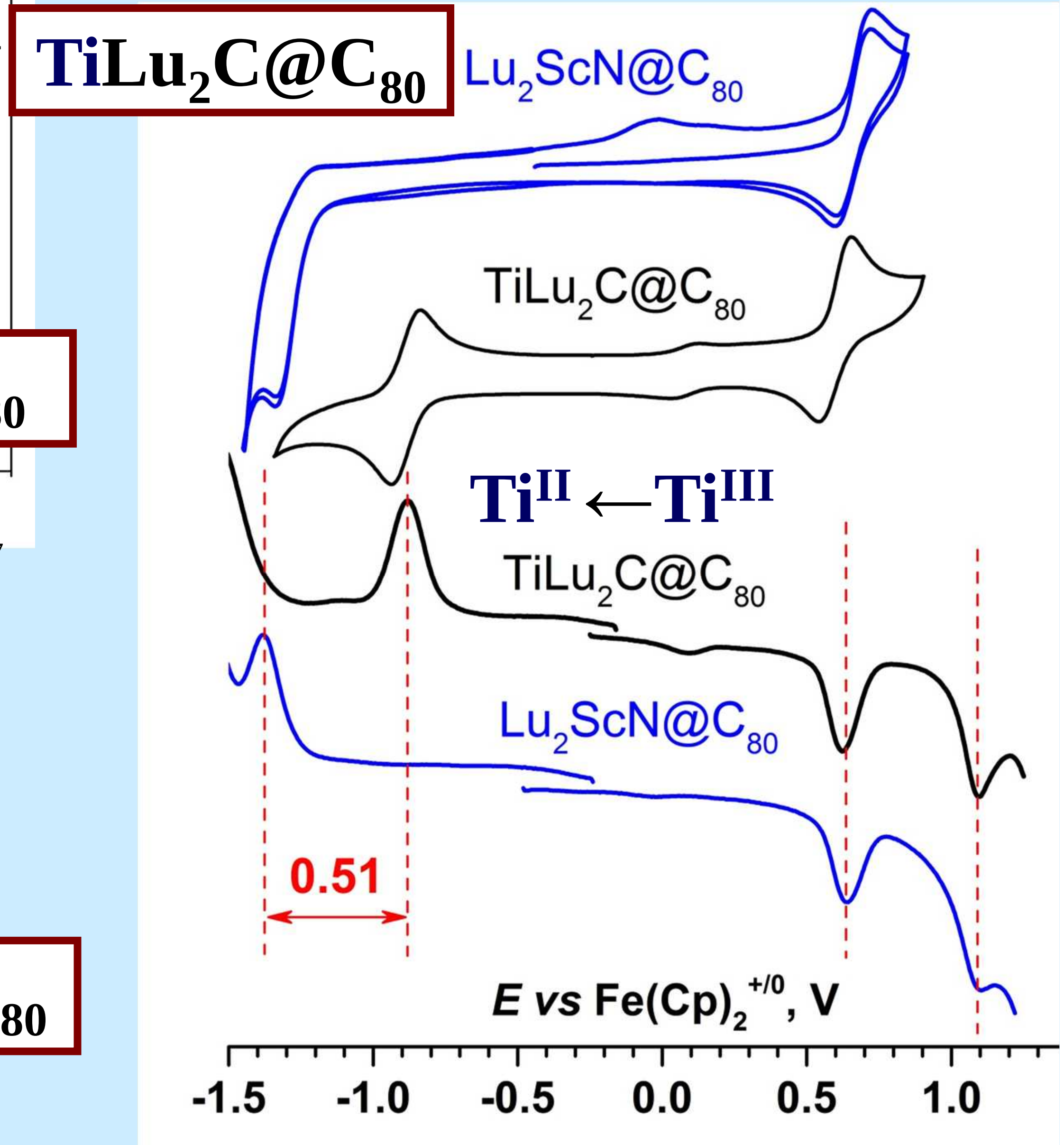


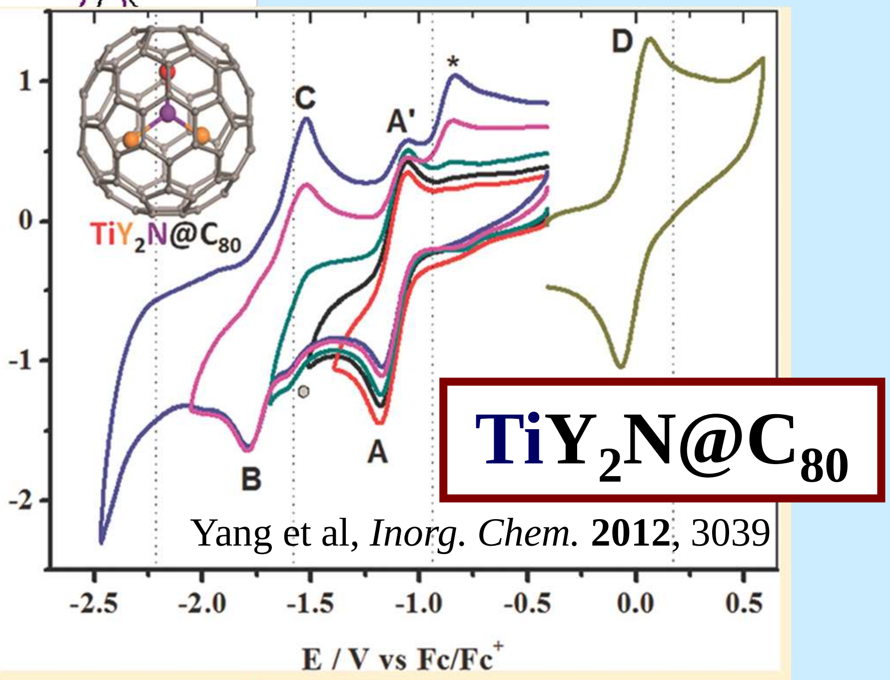
Zhang, Popov, Yang, Klod, Rapta, Dunsch, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7840.

Redox-active Ti in TiM_2N and TiM_2C clusters



Popov, Yang, Dunsch, et al. *ACS Nano* **2010**, *4*, 4857





Yang et al, *Inorg. Chem.* **2012**, 3039

Svitova, Popov, Dunsch, *in press*

$Sc_4O_2@C_{80}$: redox-active cluster

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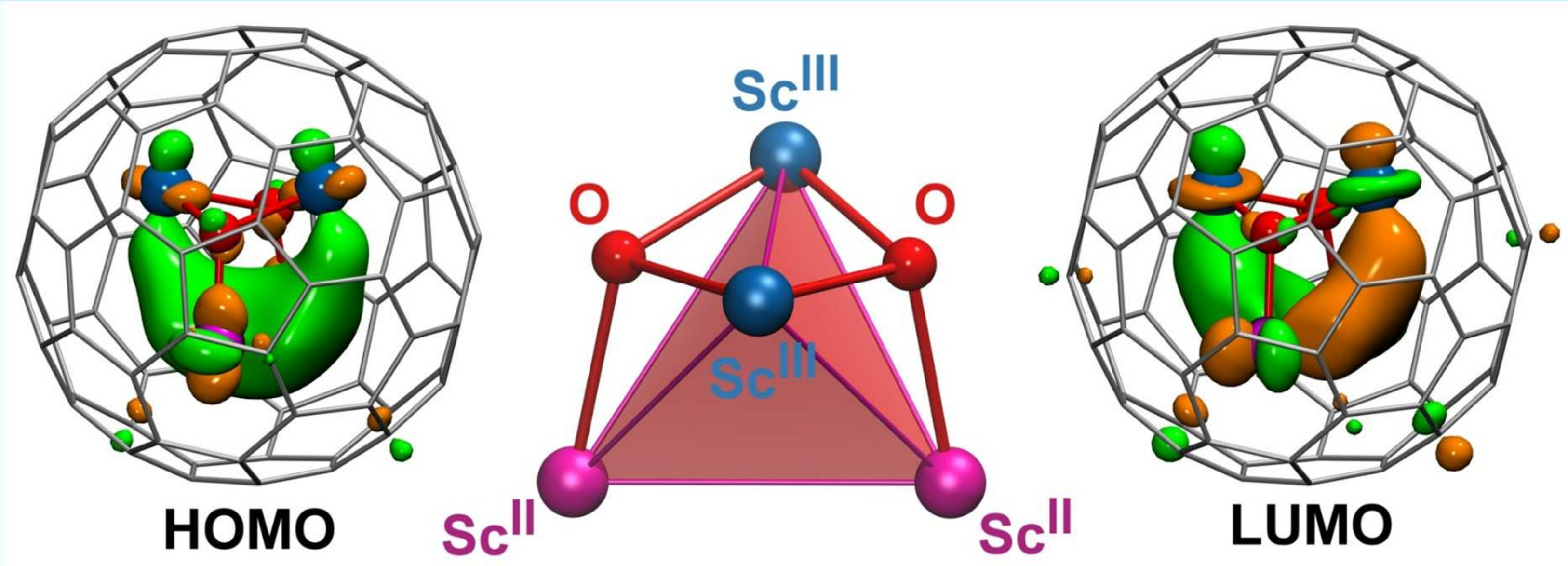
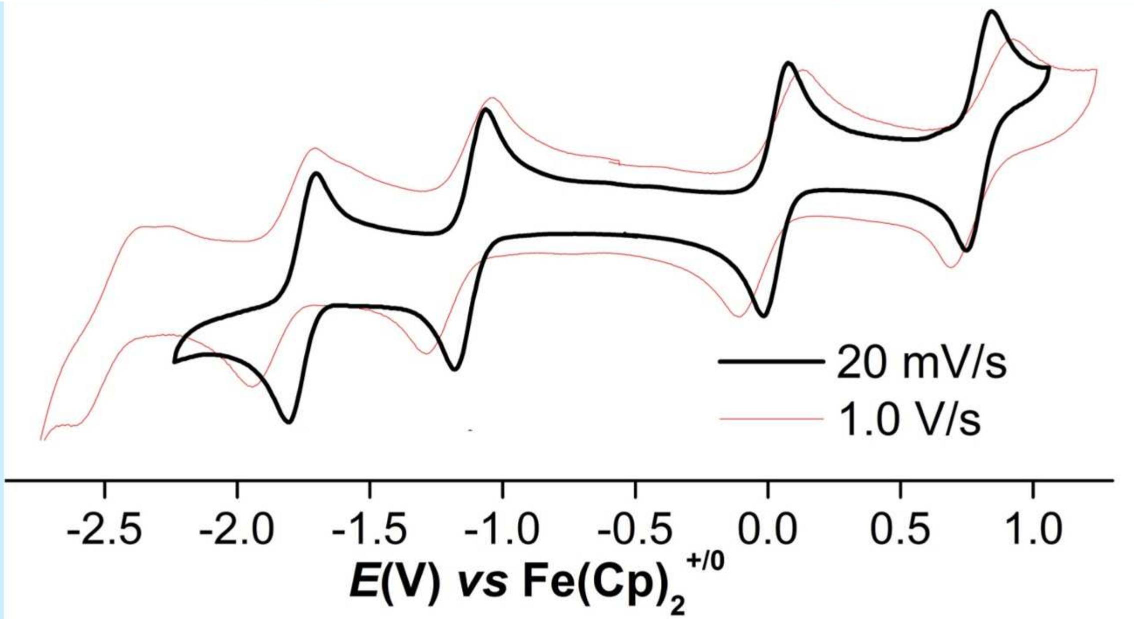
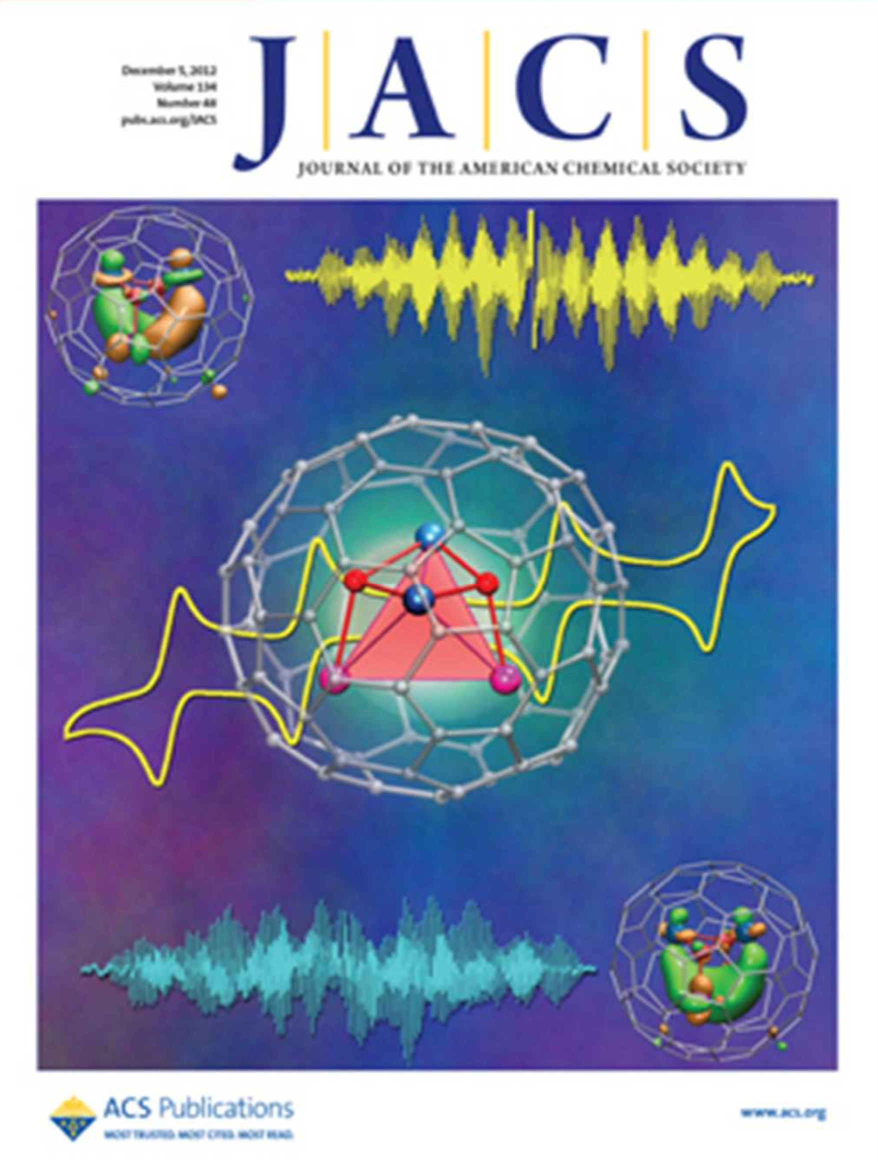
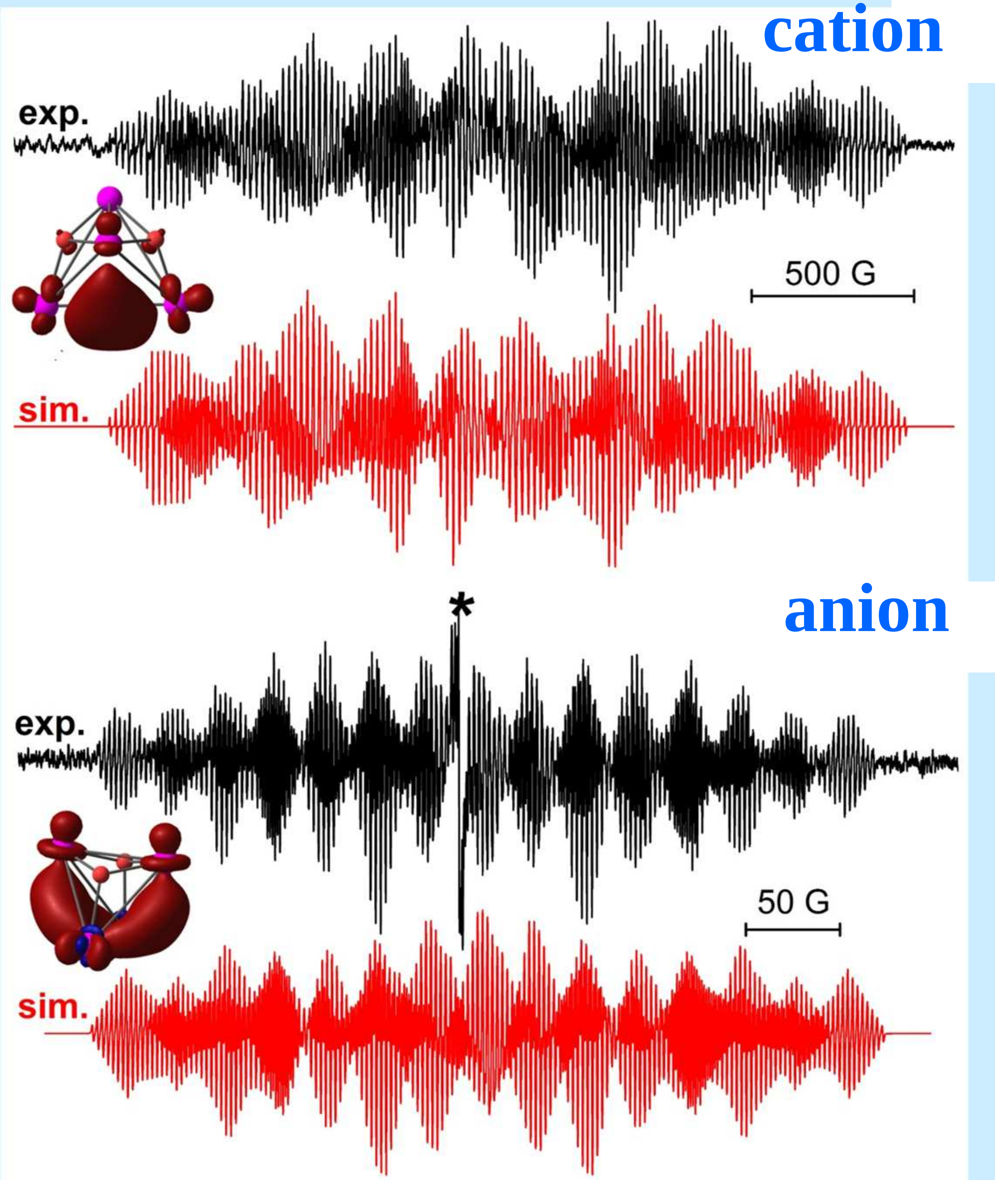




Popov, Chen, Pinzon, Stevenson, Echegoyen, Dunsch. *J. Am. Chem. Soc.* **2012**

$Sc_4O_2@C_{80}$: ESR spectra of cation and anion radicals





Popov, Chen, Pinzon, Stevenson, Echegoyen, Dunsch. *J. Am. Chem. Soc.* **2012**

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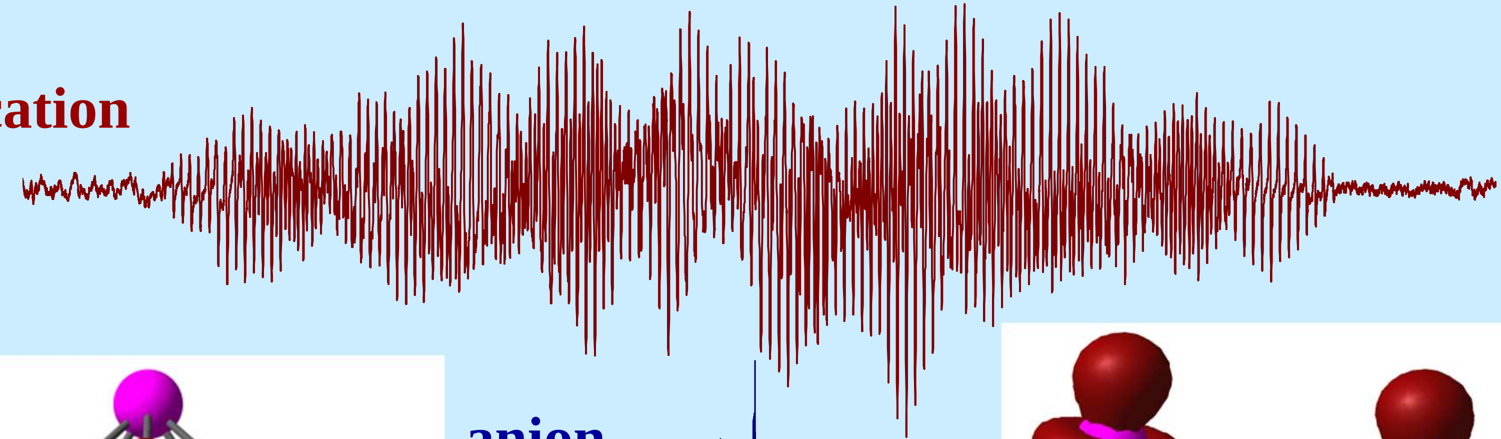
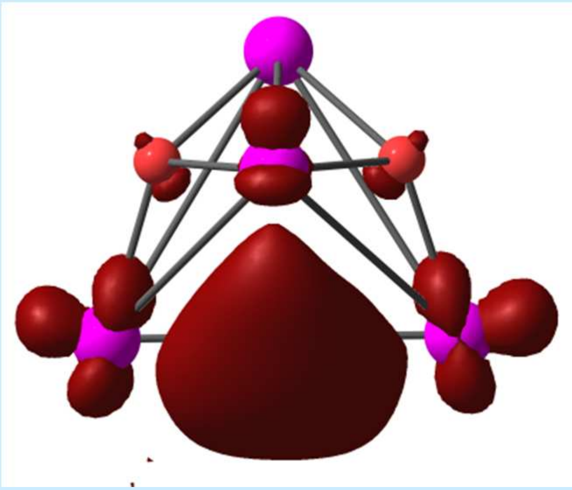
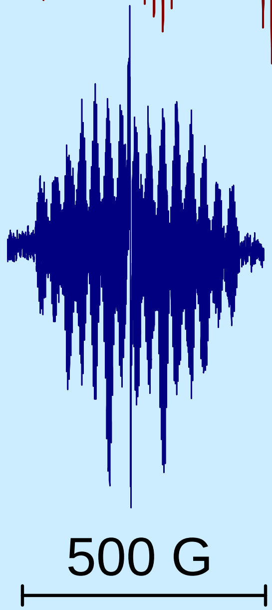
$Sc_4O_2@C_{80}$: charged radicals

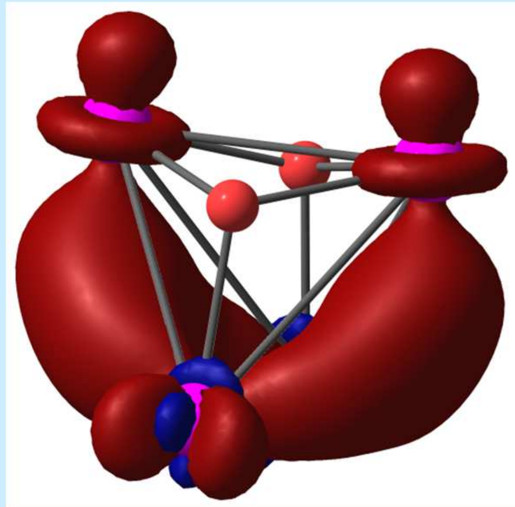
cation



anion







$[Sc_4O_2@C_{80}]^+$
spin density

$[Sc_4O_2@C_{80}]^-$
spin density

2 x *a*(^{45}Sc|1O) = 150.4 G,
2 x *a*(^{45}Sc|2O) = 18.0 G

2 x *a*(^{45}Sc|1O) = 2.6 G,
2 x *a*(^{45}Sc|2O) = 27.4 G

Popov, Chen, Pinzon, Stevenson, Echegoyen, Dunsch. *J. Am. Chem. Soc.* **2012**

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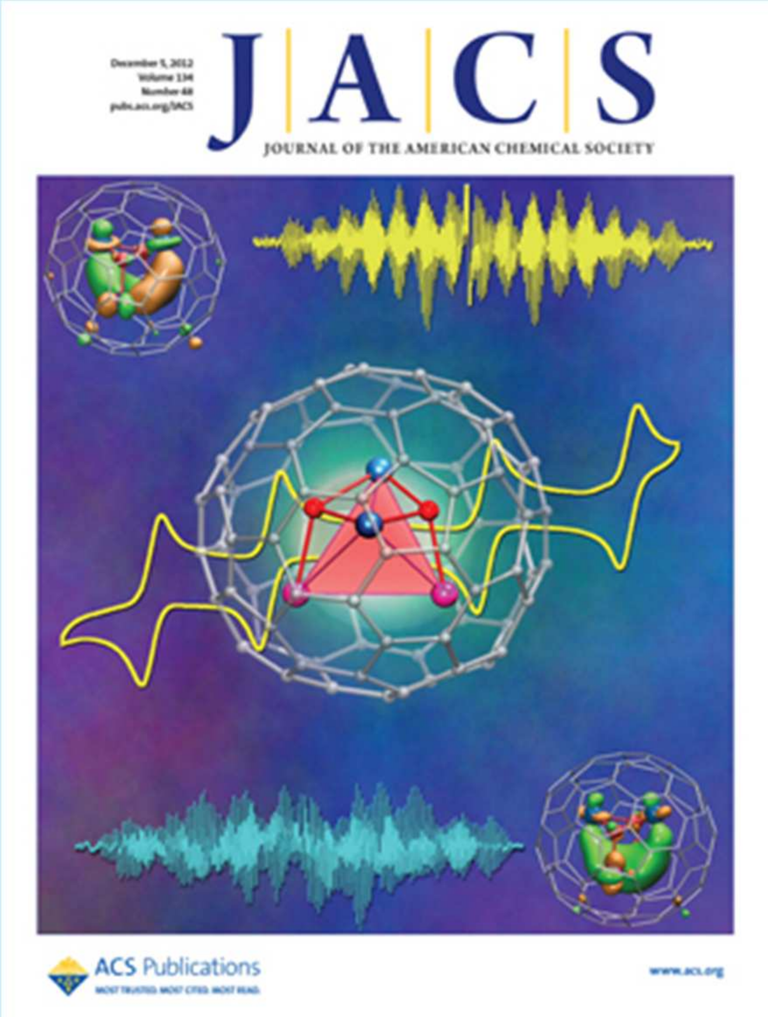
A New Highlight in Endohedral Electrochemistry



$Sc_4O_2@C_{80}$ with mixed-valence state of Sc atoms and metal-based frontier orbitals exhibits unique electrochemical behavior: both reduction and oxidation are localized on the Sc_4O_2 cluster. The endohedral nature of redox reactions is proved by hyperfine structure with large ^{45}Sc coupling constants observed in ESR spectra of the anion and cation radicals.

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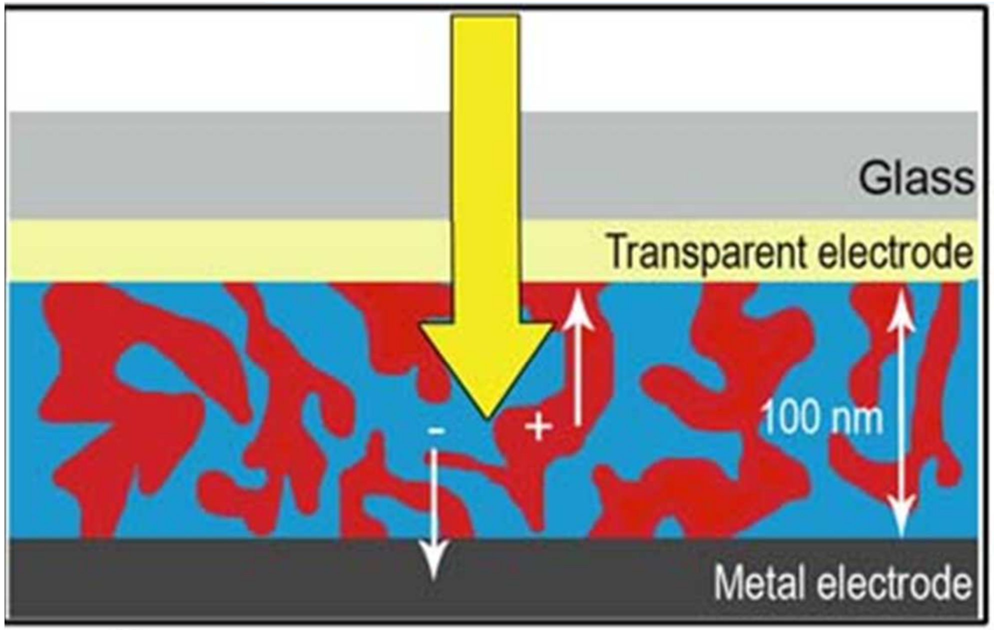
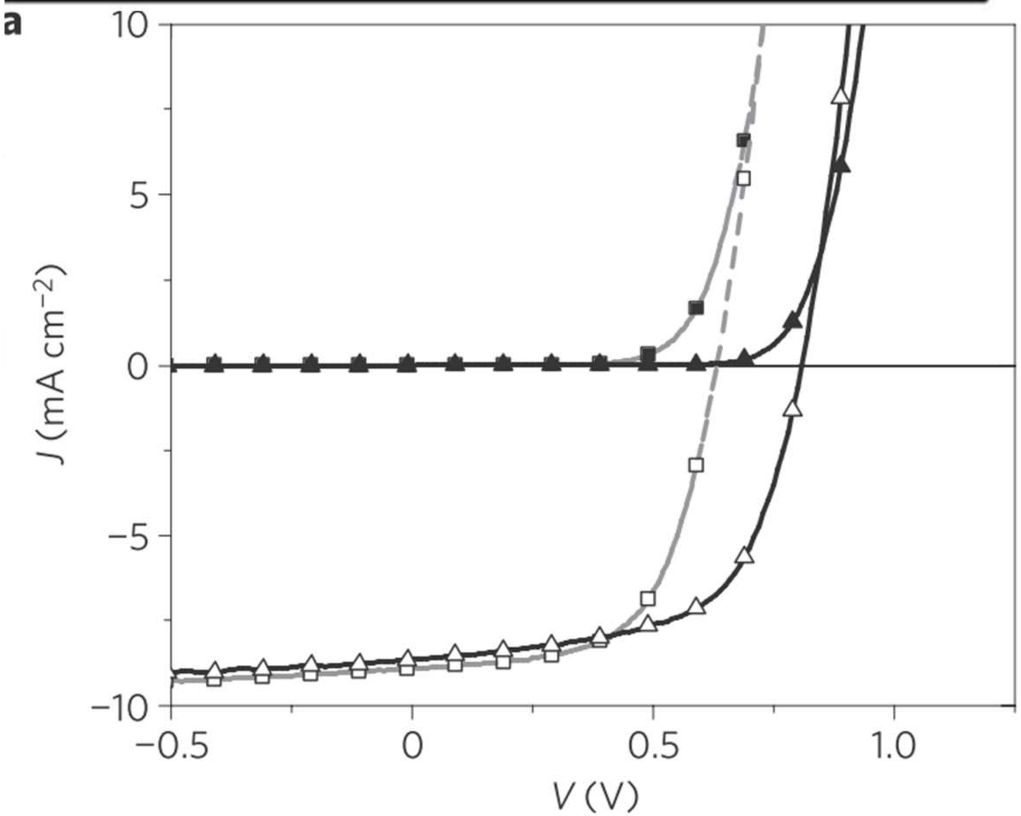
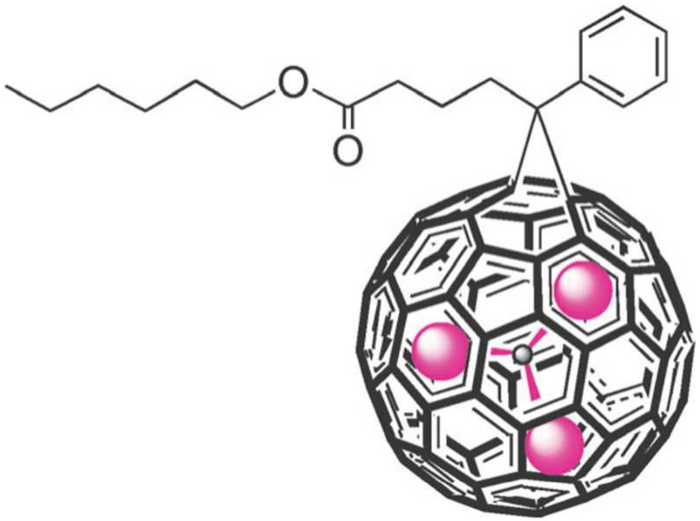
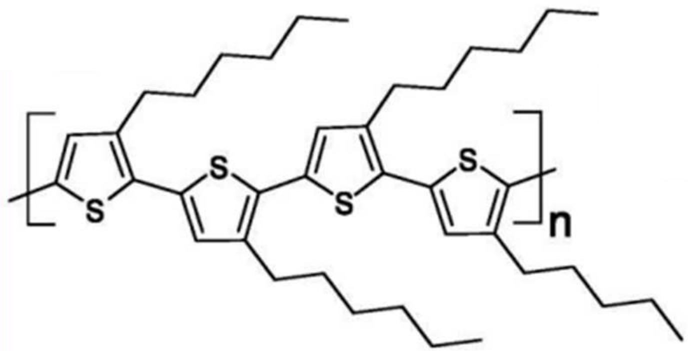
Mögliche Anwendungen

Bulk heterojunction solar cell









Drees et al. *Nat. Mater.* **2009**, *8, 208*.

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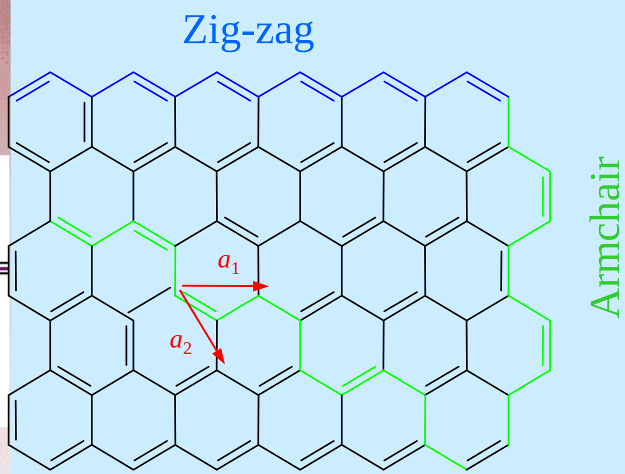
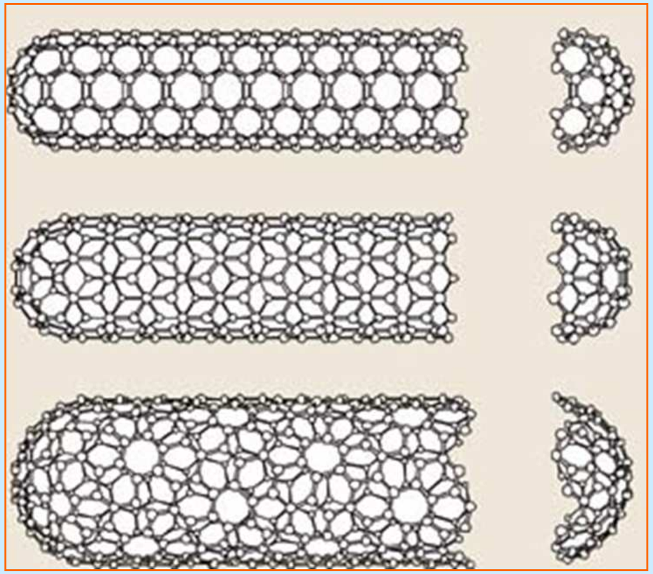
SWCNT from graphene





Armchair nT
(n=m) metal

Zig-zag nT
(n-m) = 3i metal
(n-m) ≠ 3i semicond.

Chiral nT
(n-m) = 3i metal
(n-m) ≠ 3i semicond.

Chiral vector: $\mathbf{C}_\mathbf{h} = n\mathbf{a}_1 + m\mathbf{a}_2$

$\mathbf{a}_1$, $\mathbf{a}_2$ …. Unit vectors of 2D-hexagonal lattice

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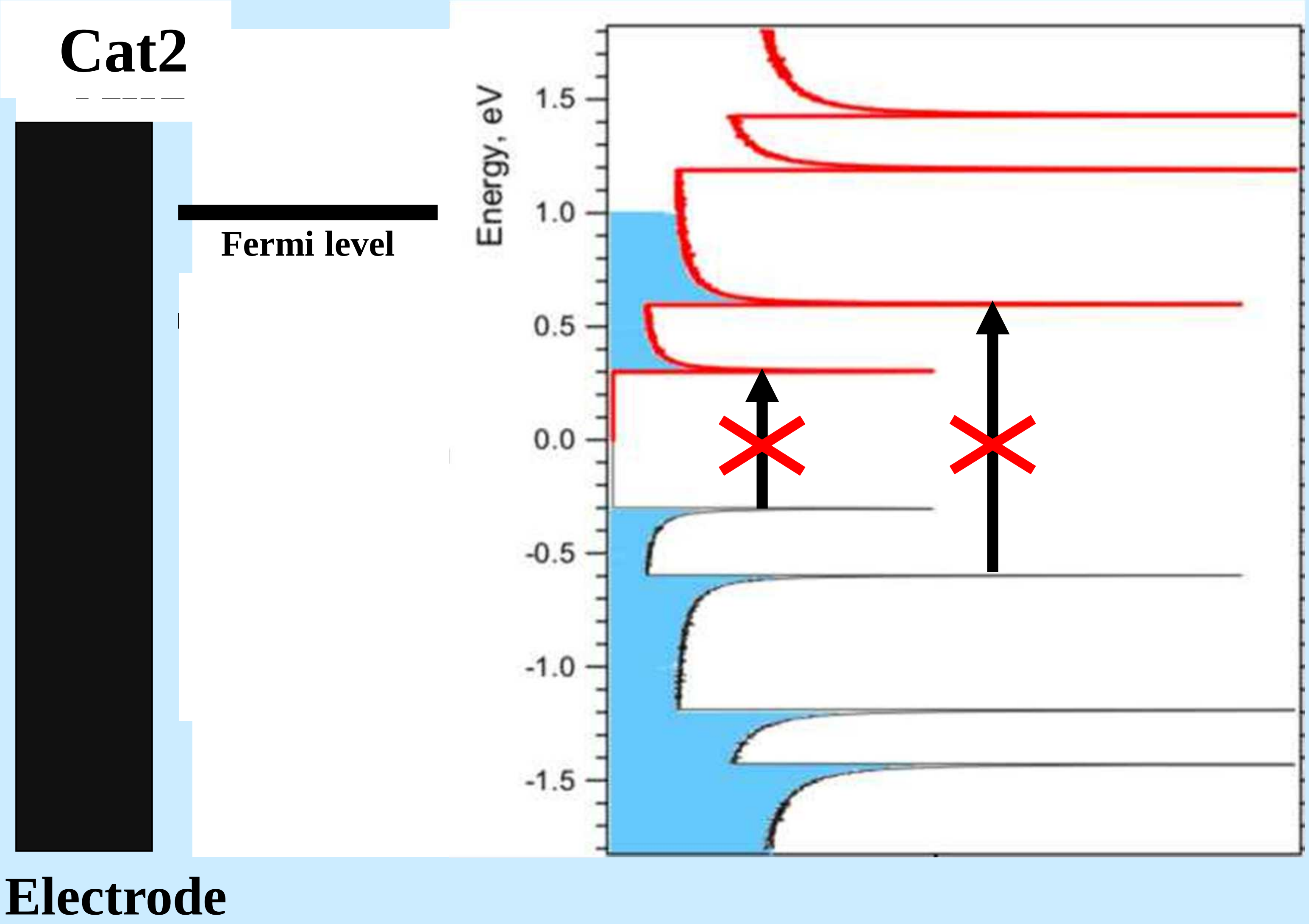
In-situ electrochemical doping of SWCNT

anodic/cathodic= extraction/insertion of e$^-$



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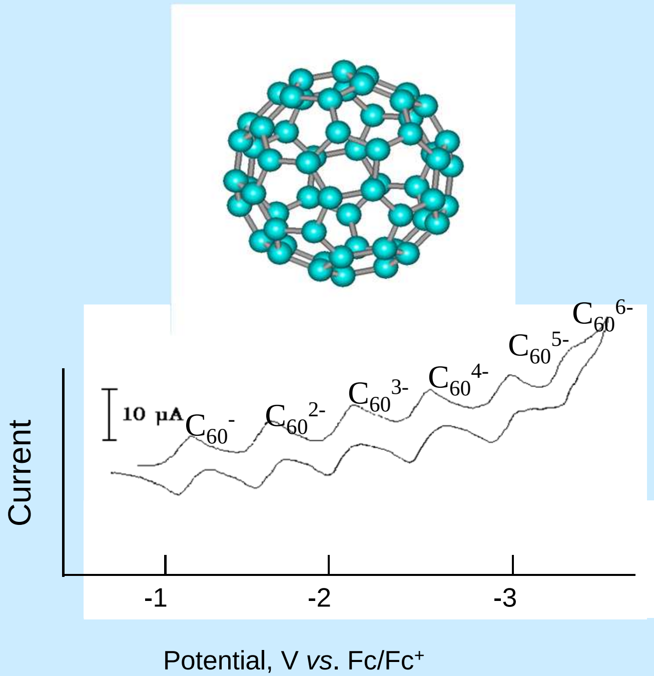
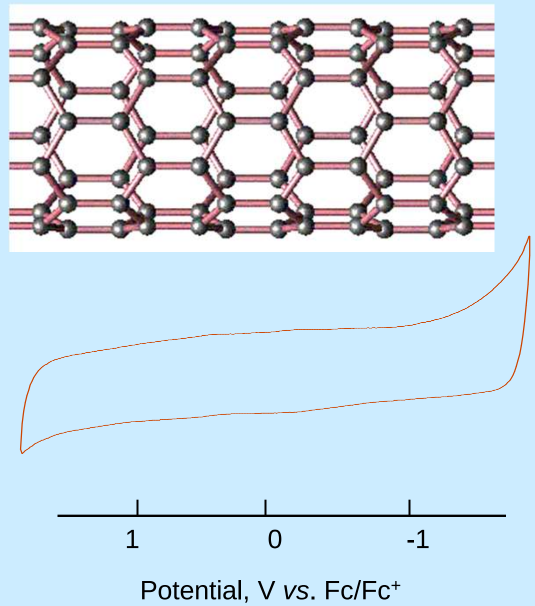
Electrochemistry of C_{60} and SWCNT





C_{60} (solution)……..CH_3CN/toluene + electrolyte solution (at-10°C)

SWCNT (solid)..…..CH_3CN + electrolyte solution

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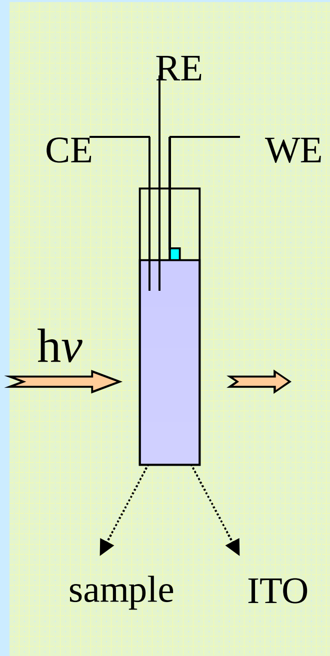
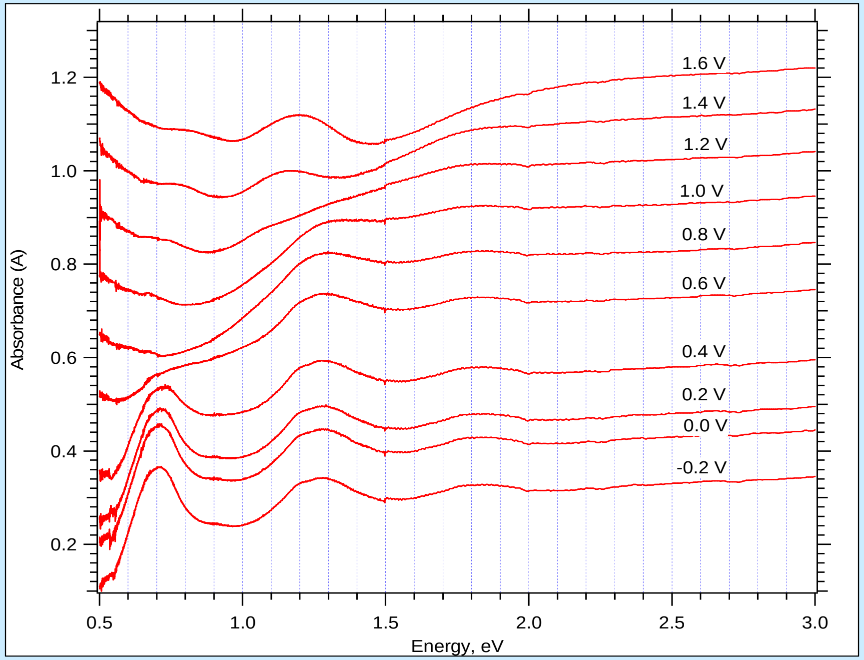
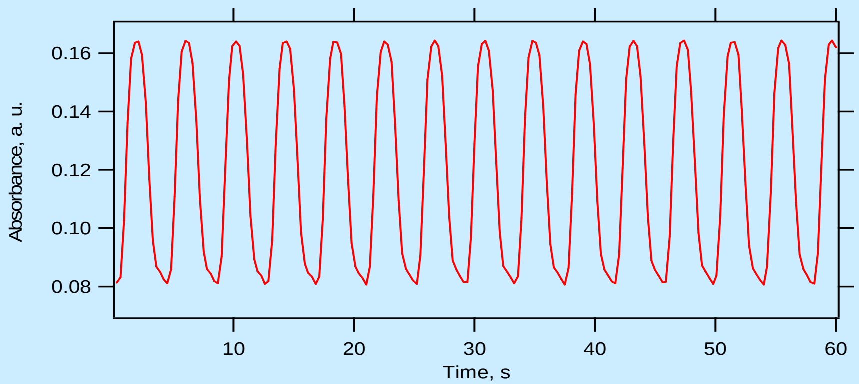
Vis-NIR spectra on ITO electrode of SWCNT

(0.2 M $LiClO_4$ + acetonitrile)



0.7 eV, 1V/s →





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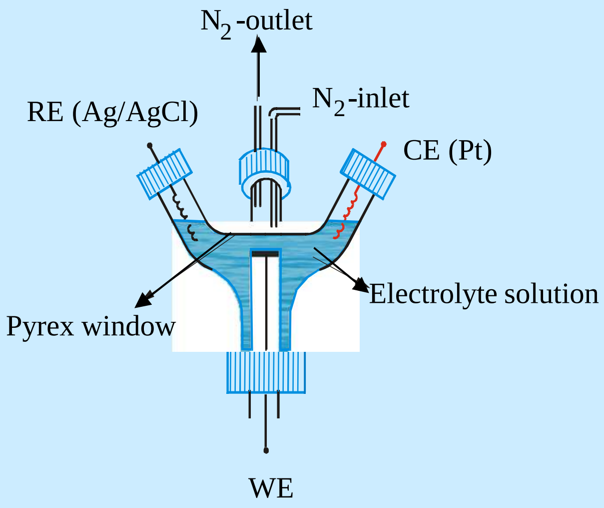
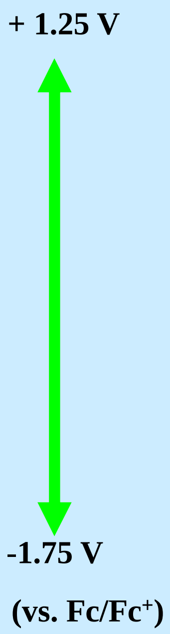
Raman spectra of SWCNT, $h\nu_{exc} = 2.54$ eV

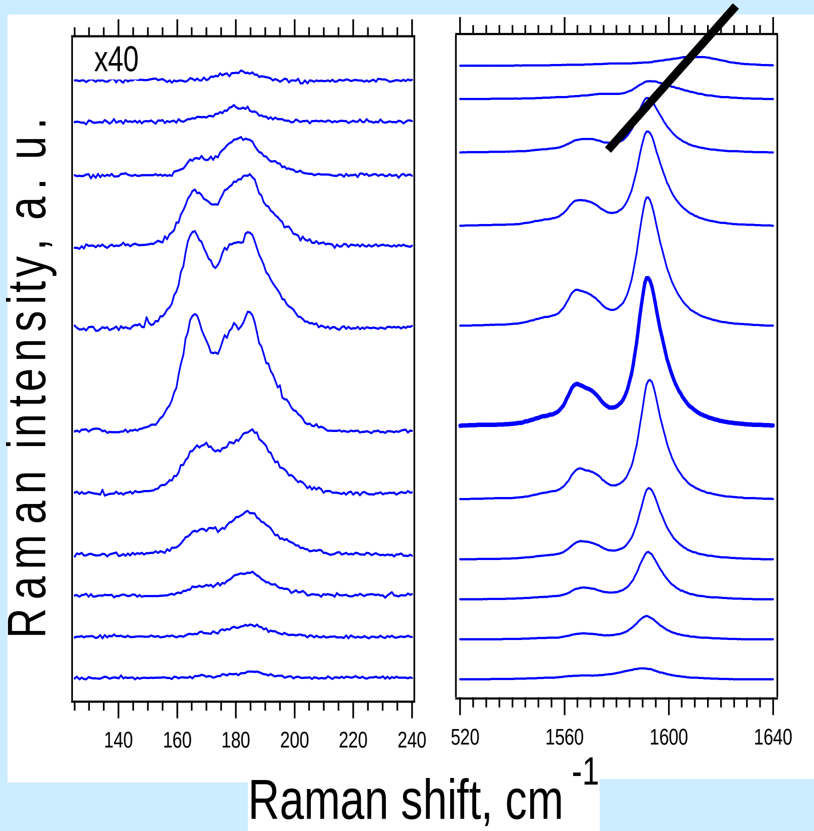
(0.2 M $LiClO_4$ + acetonitrile)

Spectroelectrochemical cell





$$I = \frac{c}{\left|(E_L - E_{ii} - i\gamma)(E_L + E_{ph} - E_{ii} - i\gamma)\right|^2}$$



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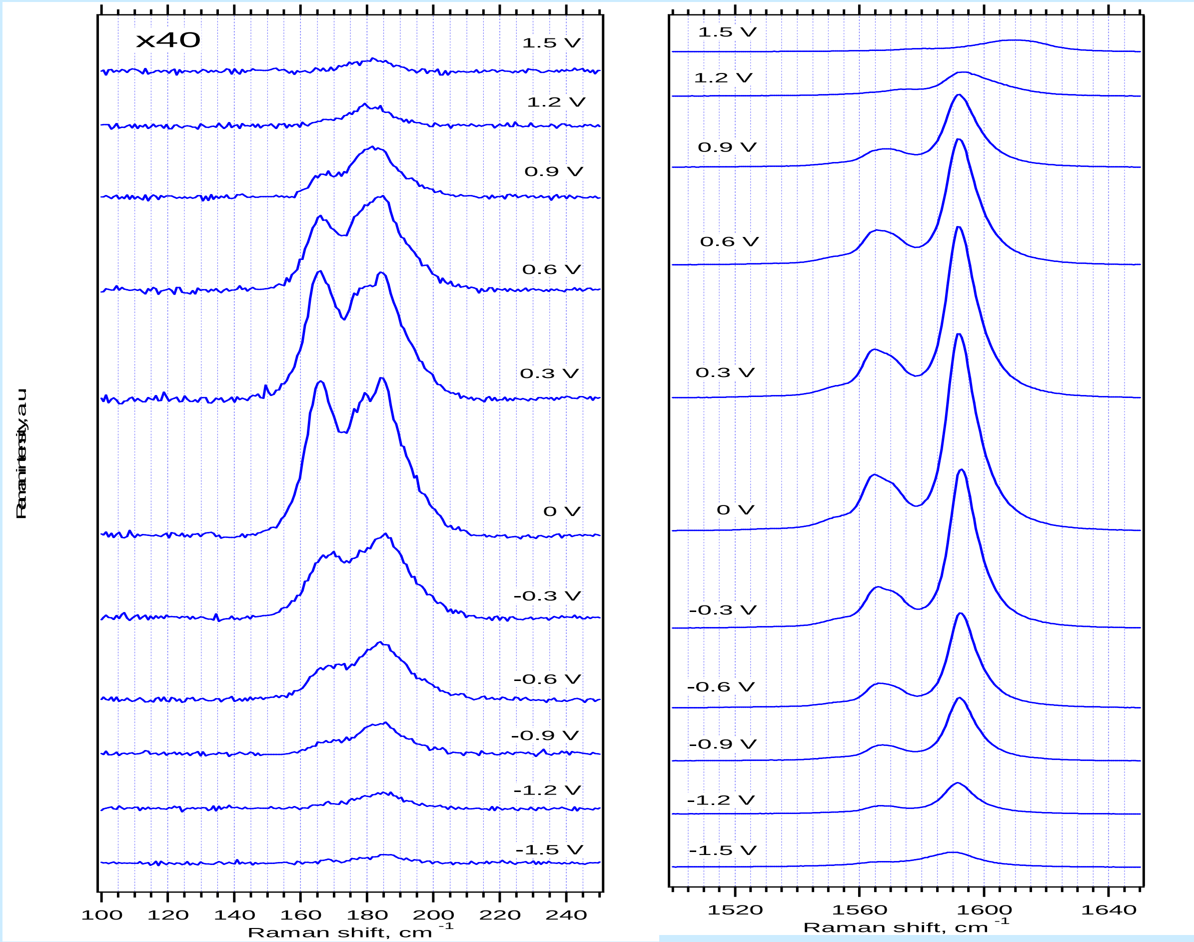
Raman spectra of SWCNT, hν_{exc}= 2.54 eV

(0.2 M $LiClO_4$ + acetonitrile)



A Faradaic process at the cathodic and anodic scale

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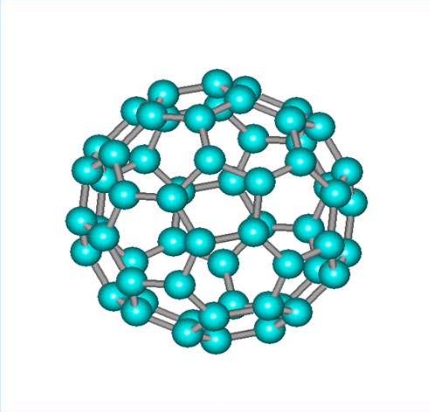
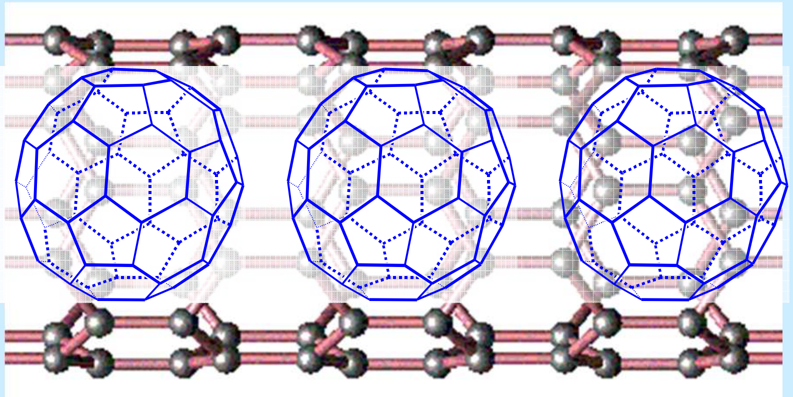
Formation of fullerene peapod C_{60}@SWCNT
An endohedral nanotube





C_{60} (g)

FULLERENE PEAPOD

ΔE = 49 kJ/mol

Raman spectra of C_{60} (single crystal) and SWCNT

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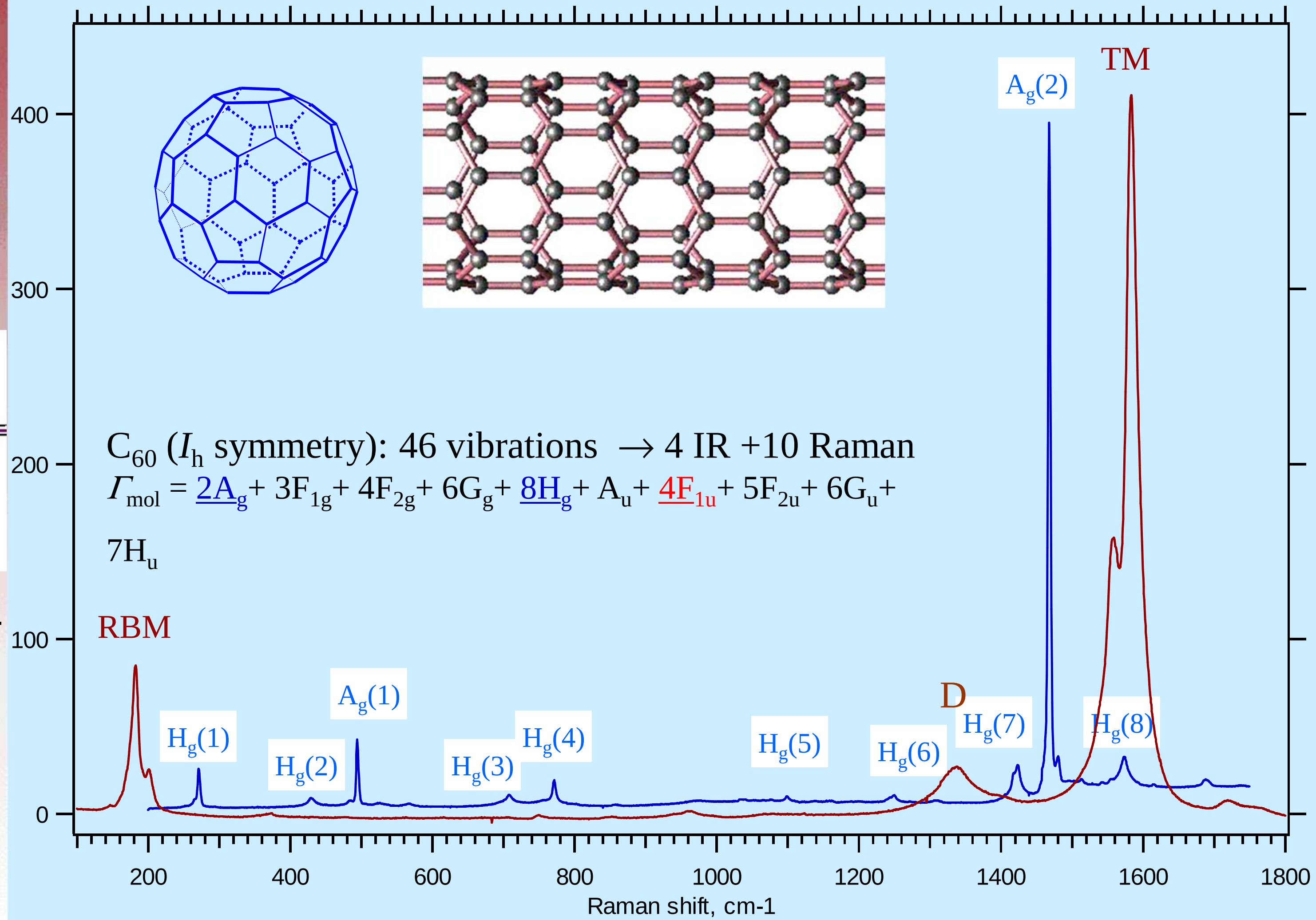

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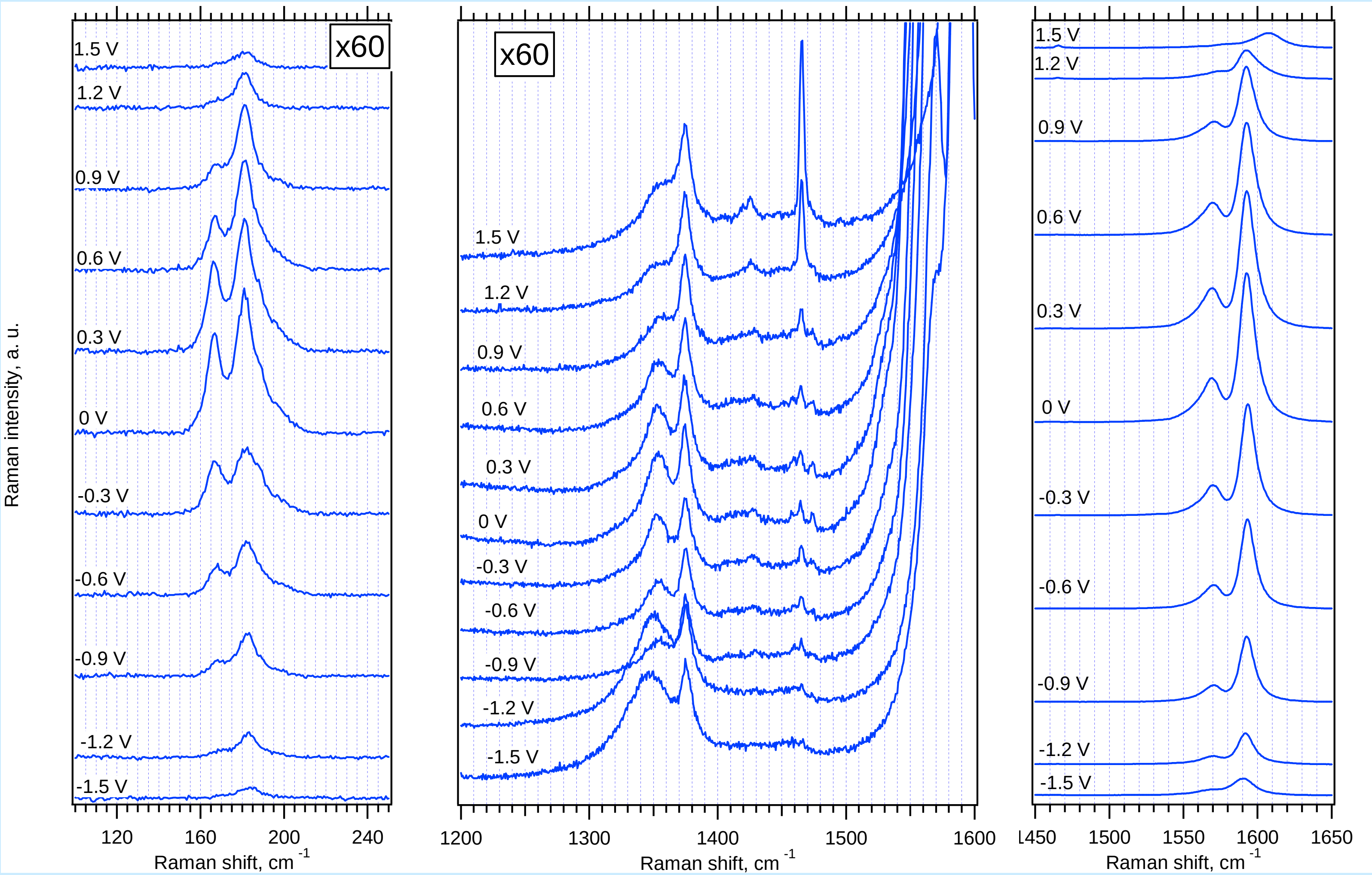
Raman spectroelectrochemistry C_{60}@SWCNT ($h\nu_{exc}$= 2.54 eV)

(0.2 M $LiClO_4$ + acetonitrile)



Raman spectroelectrochemistry C_{70}@SWCNT ($h\nu_{exc}$= 2.41 eV)

(0.2 M $LiClO_4$ + acetonitrile)

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Center for Spectro-electrochemistry at IFW Dresden

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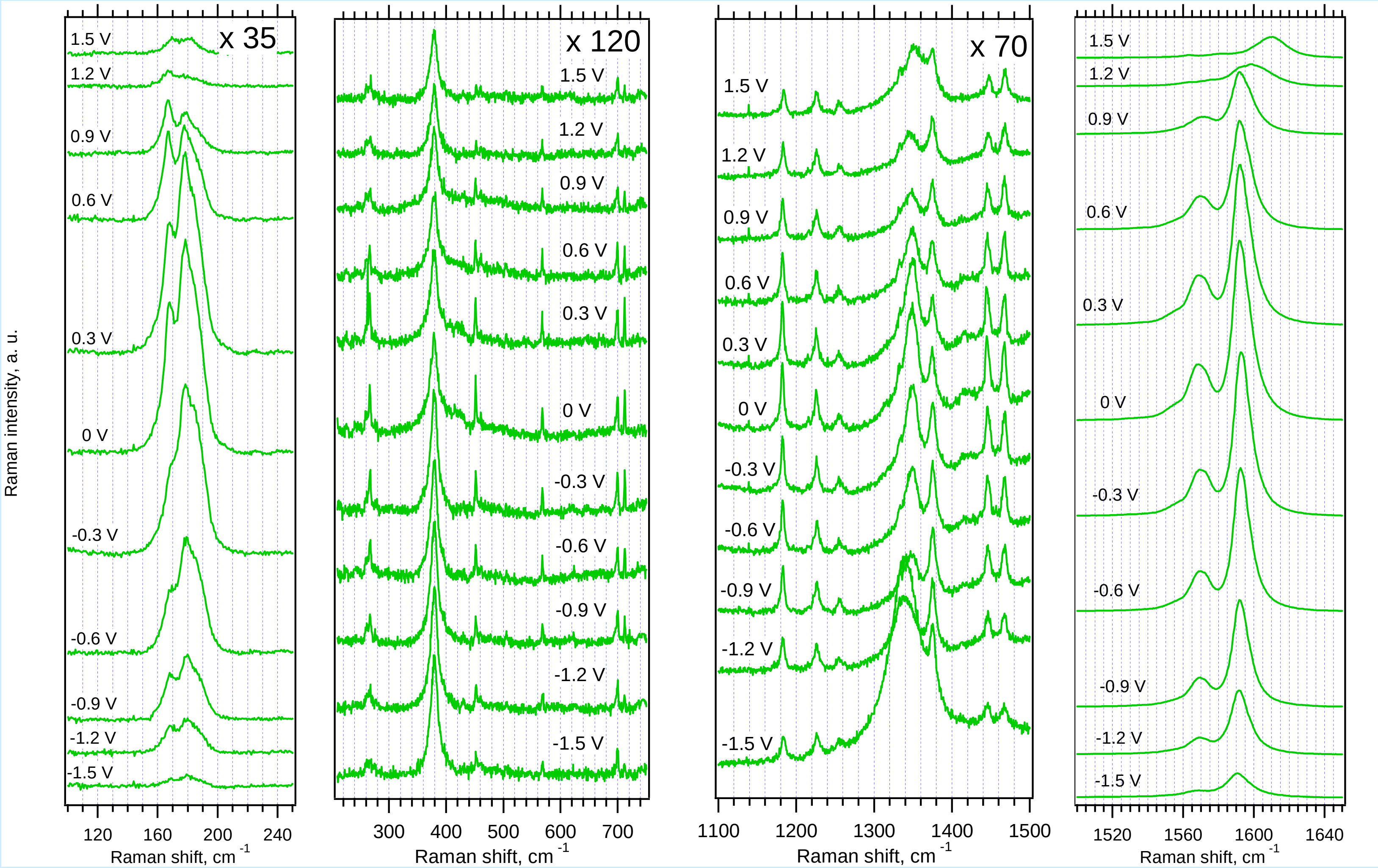

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Mögliche Anwendungen

Batterien

Supercaps

Transistoren

Feldemitter

Displays

Datenspeicher

Aktoren

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