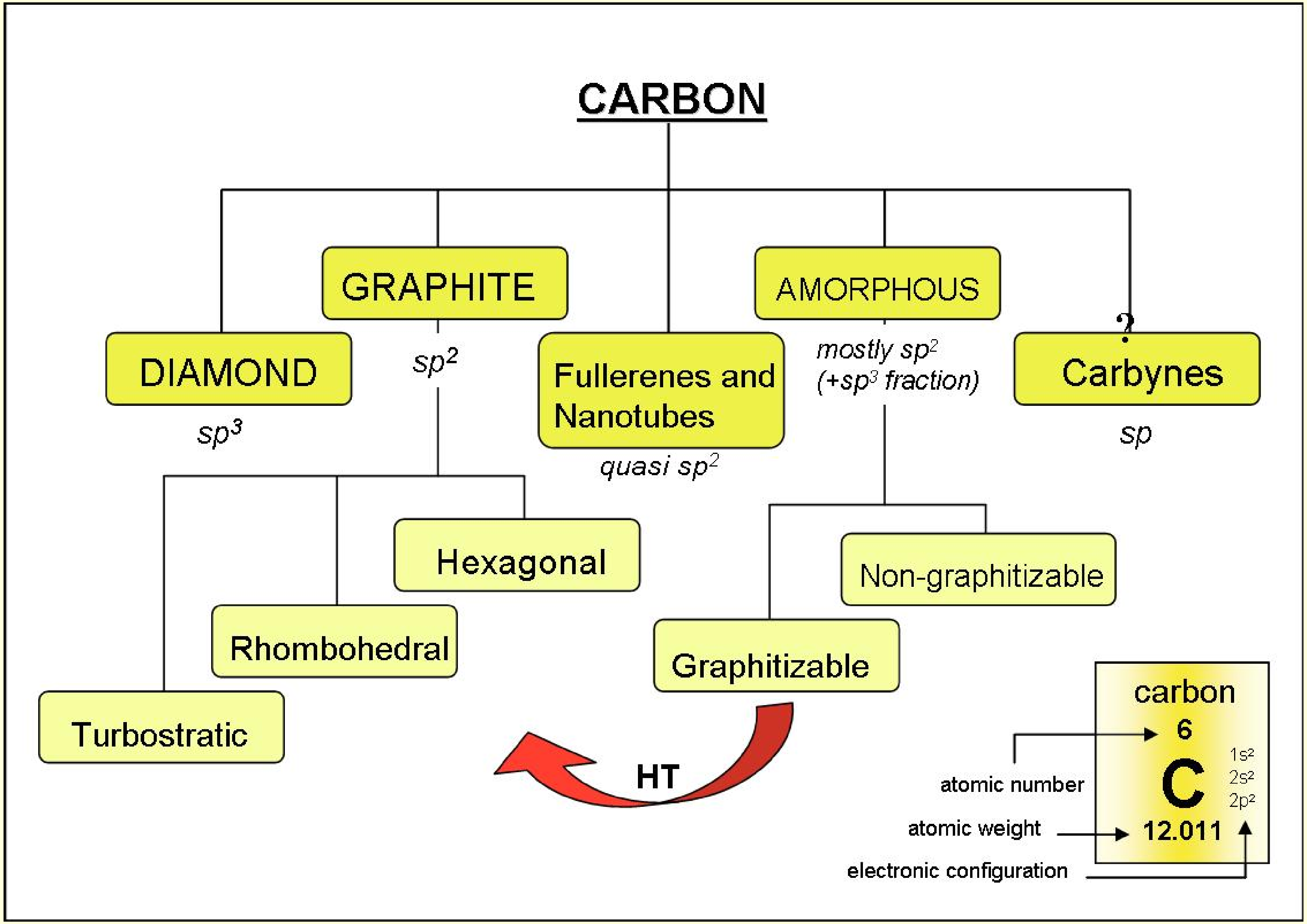
LINZ LECTURES

Lecture 1. The Development of Organic Conductors: Metals, Superconductors and Semiconductors

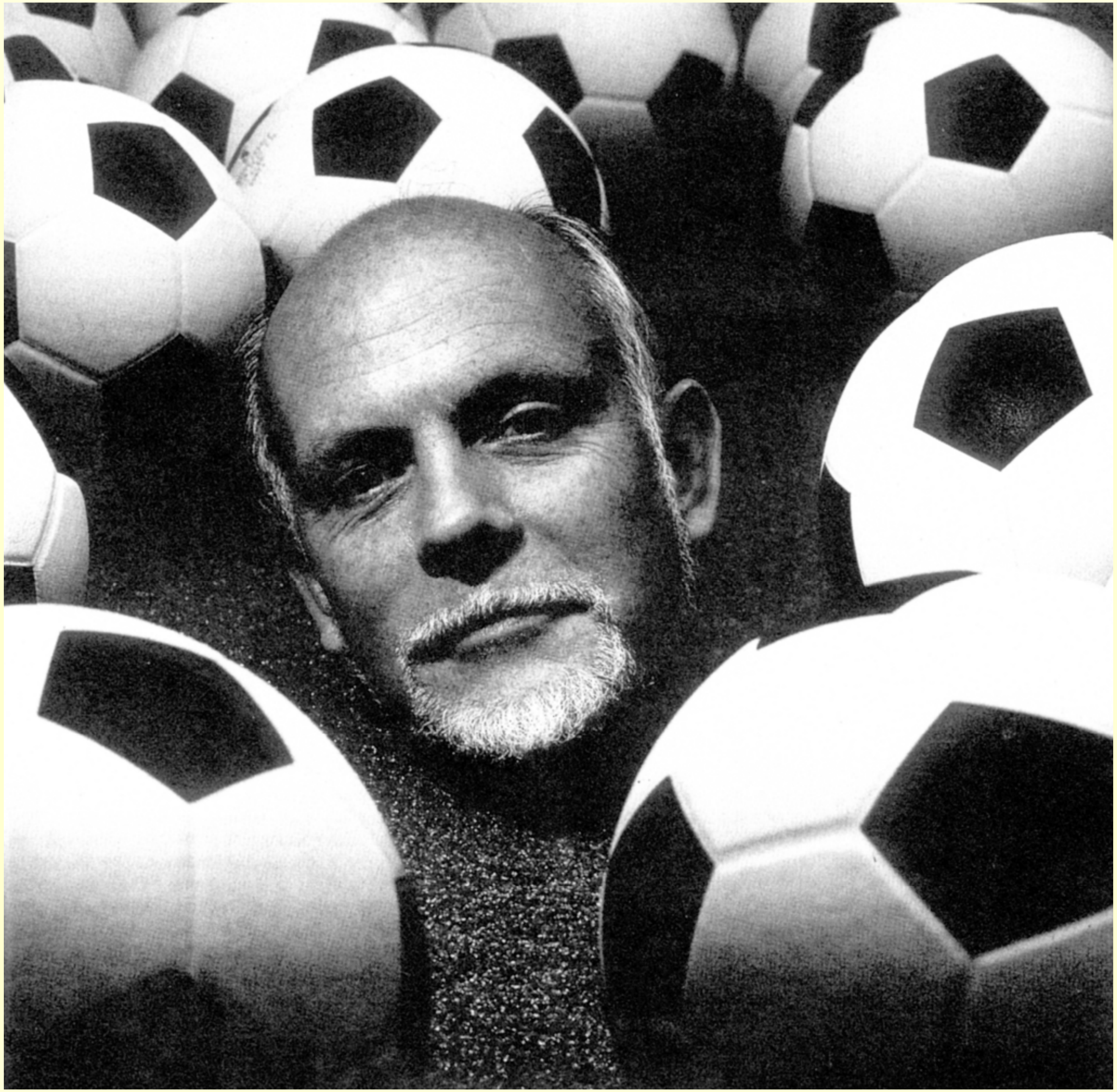
Lecture 2A. Introduction and Synthesis of Important Conjugated Polymers
Lecture 2B. Solid State Polymerization

Lecture 3. Fullerene Chemistry
Lecture 3B. Molecular Engineering

Carbon Allotropes



Falcao EHL, *Carbonaceous materials with exotic morphologies*. PhD Dissertation, University of California, Los Angeles, CA, Ch. 1 (2006)



Popular Science August 1991, p 53

The Arc-Discharge Preparation Method

7500 *J. Am. Chem. Soc., Vol. 113, No. 20, 1991*

Parker et al.

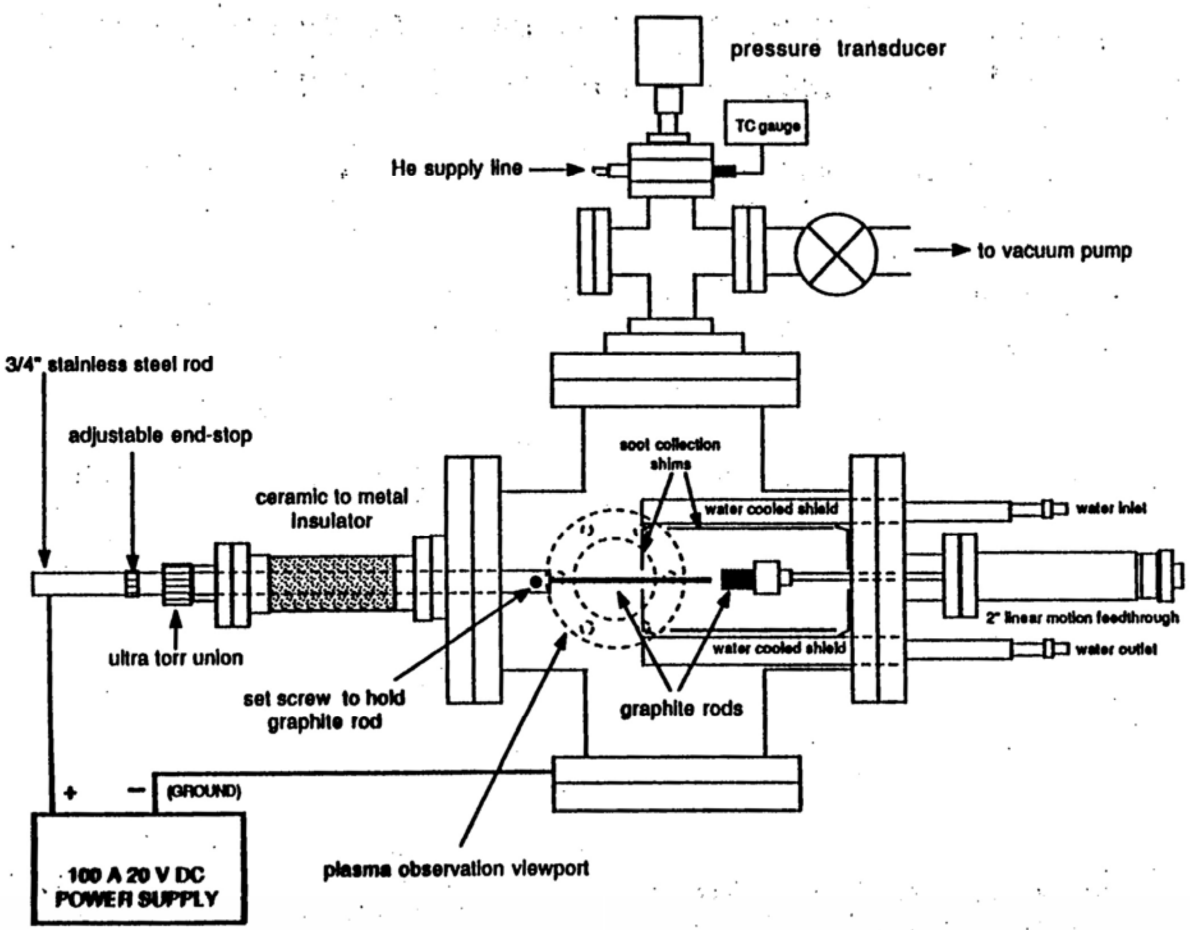


Figure 1. Scale diagram of the apparatus used to produce fullerenes from graphite rods.

The Continuous Process Preparation

HOWARD, J.M., et.al. Carbon, 1992, 30, 1183

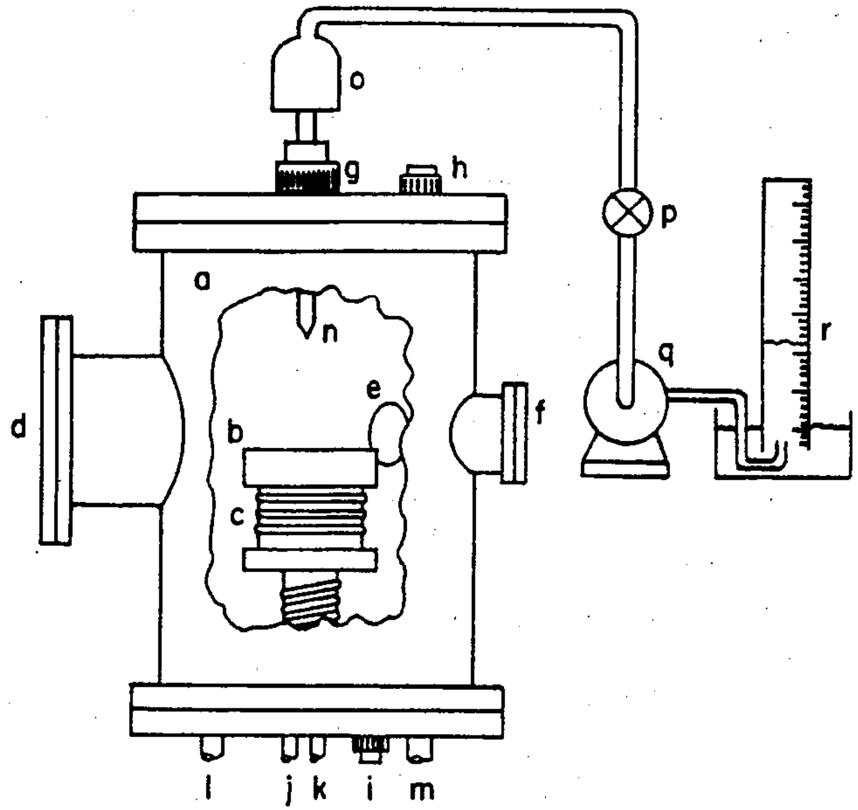
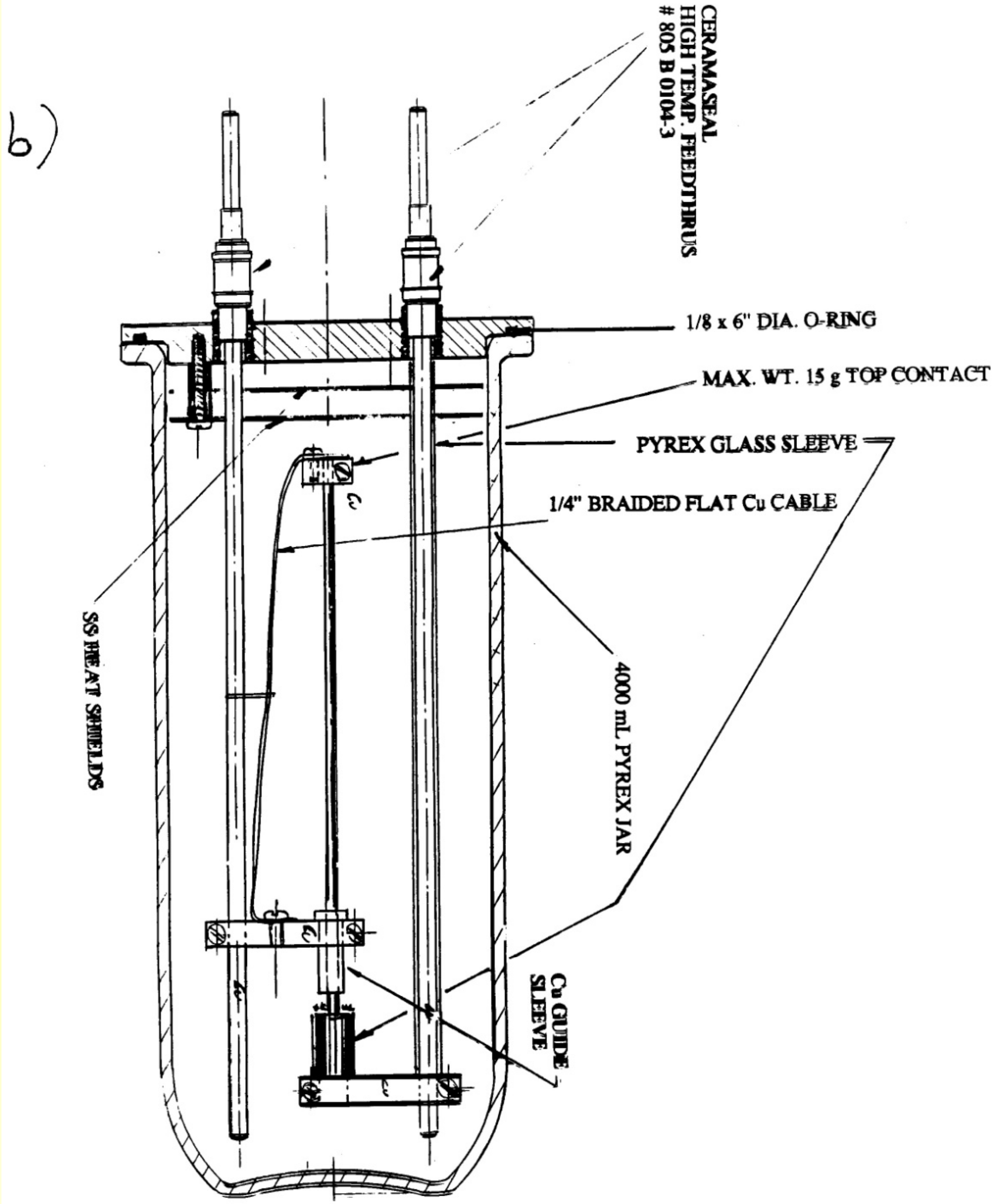


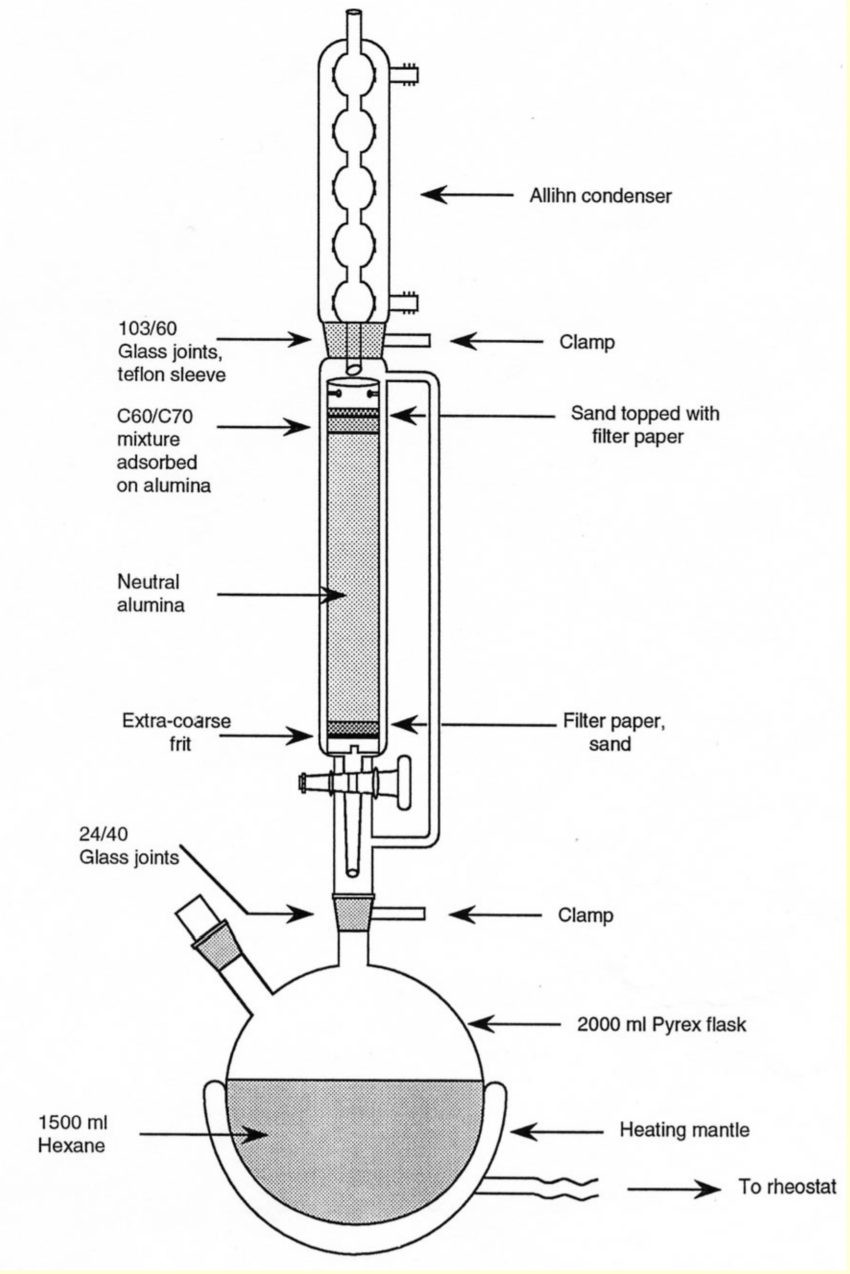
Fig. 1. Burner and associated equipment: a—low-pressure chamber; b—copper-burner plate; c, water cooling coil; d, e, and f—windows; g, h, and i—feedthroughs; j—annular-flame feed tube; k—core-flame feed tube; l and m—exhaust tubes; n—sampling probe; o—filter; p—valve; q—vacuum pump; r—gas meter.

The Fullerene Bench-Top Reactor



Koch, A. et.al. J. Org. Chem. 1991, 56 4543

Soxhlet Chromatography Separation



Physical Properties of Buckminsterfullerene

Hard crystals, red by transmission, black by reflection, yellow in film form

Sublimes above 500 °C @ 10^{-7} Torr

$\Delta H°f$ = 545 kcal/mol, ρ = 1.78 g/mL, $|$ = -260 cgs ppm

Cubic closed packed structure, individual molecules rotate at RT, transition to static Below 250 K

Bond alternation: 1.37 and 1.45 Å

Molecular Orbital Energy Diagram

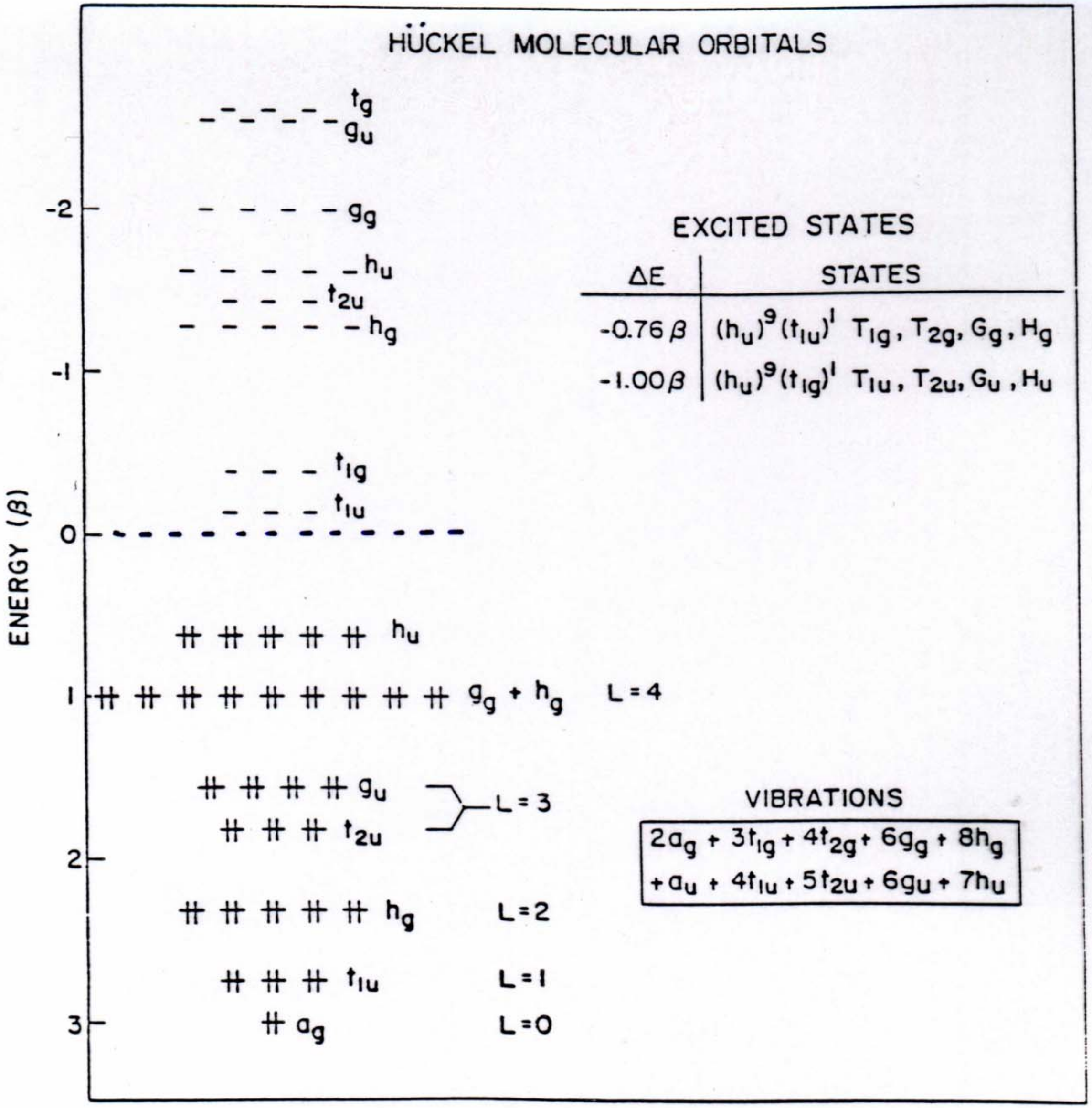
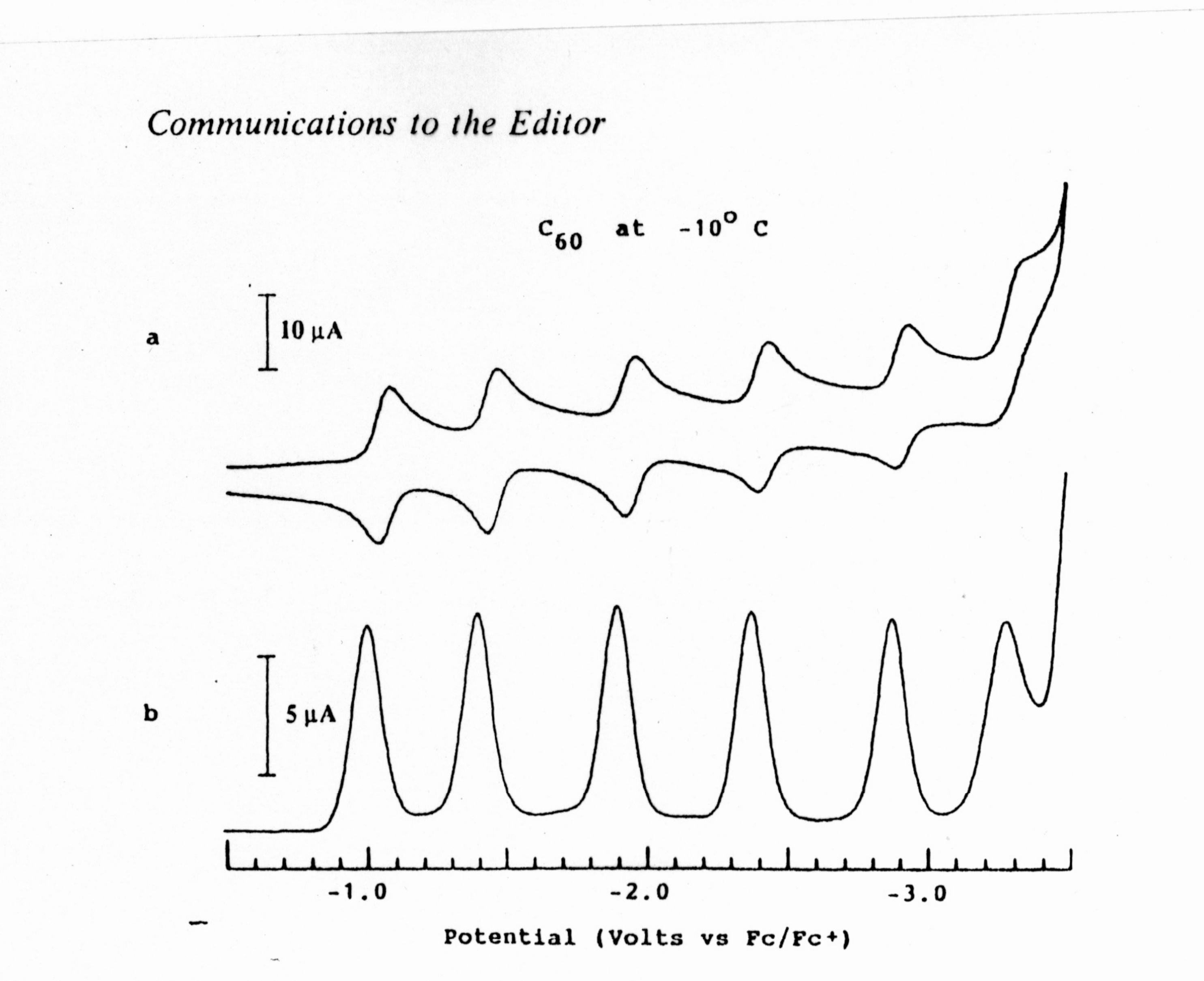


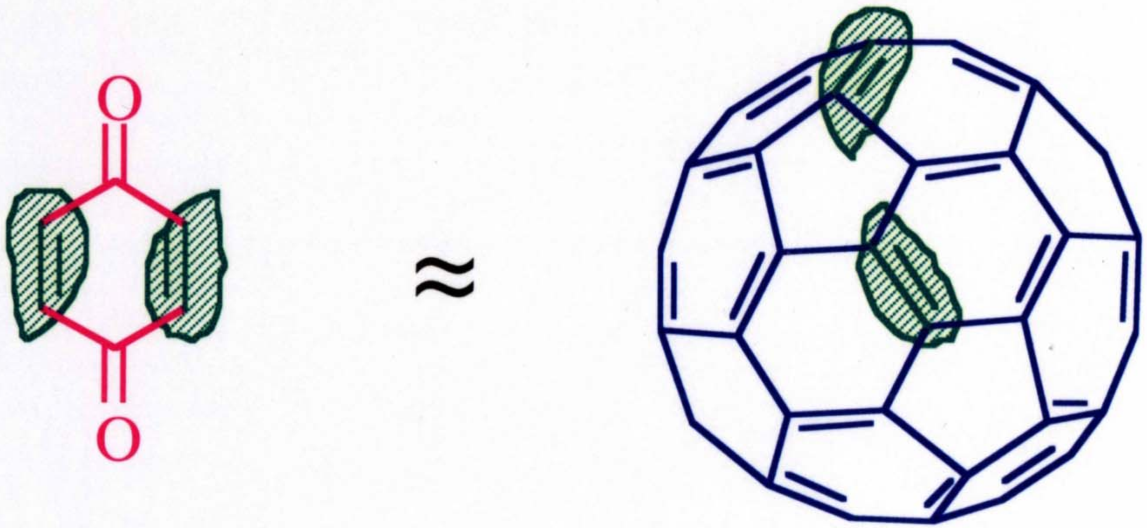
Fig. 2. HMO energy level diagram for C_{60} (unscaled β, see text).

Electrochemical Properties



Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *j. Am. Chem. Soc.* **1992**, *114*, 3978

A Chemical Equivalent



Electron acceptor, dienophile, dipolarophile electrophile

Electron acceptor, dienophile, dipolarophile electrophile

Dipolarophile: the first Crystalline Derivative

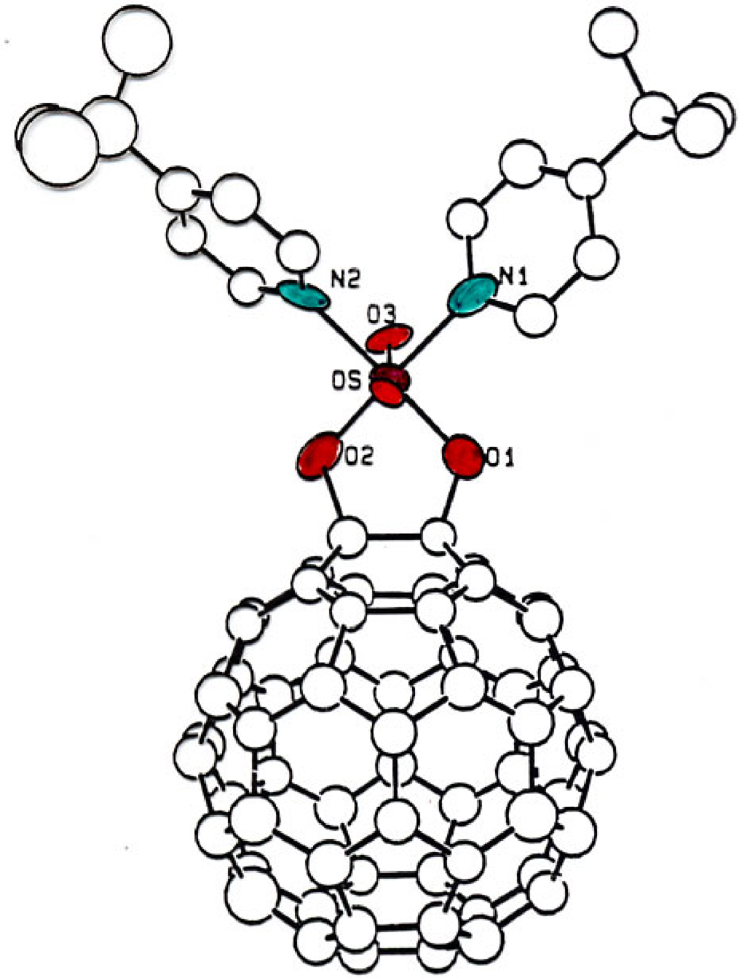


Figure 2. ORTEP drawing (50% ellipsoids) of the 1:1 C_{60}–osmium tetraoxide adduct $C_{60}(OsO_4)$(4-*tert*-butylpyridine)$_2$ (**1**) showing the relationship of the osmyl unit with the carbon cluster. Reprinted with permission from ref 3. Copyright 1991 AAAS.

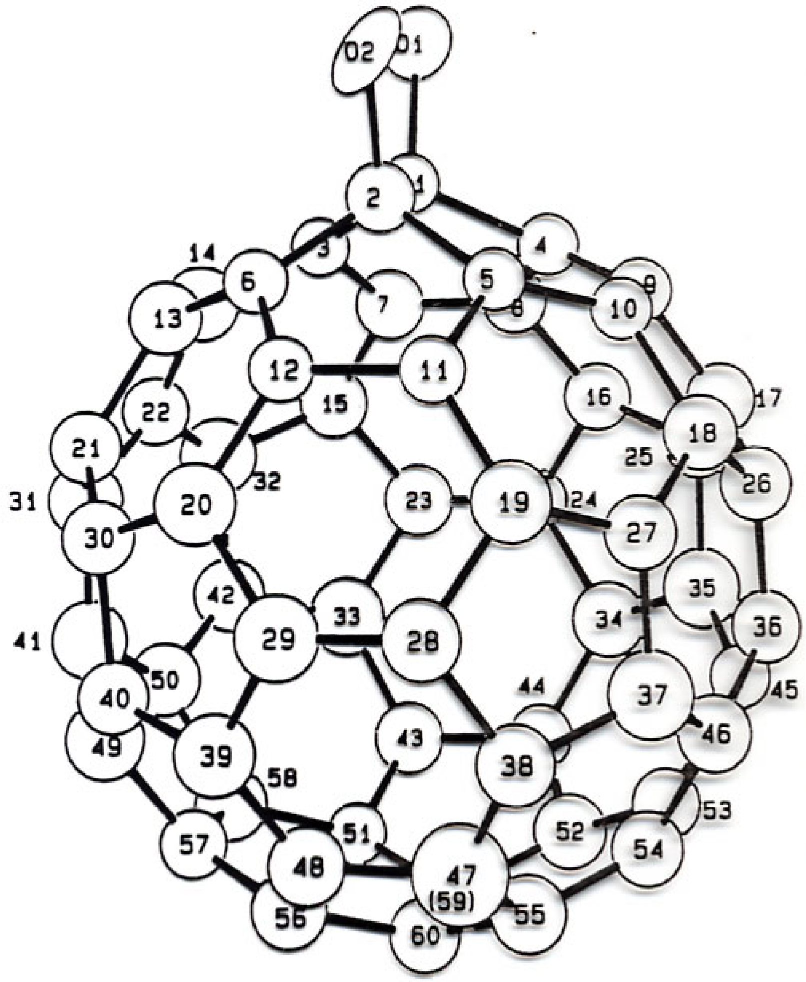
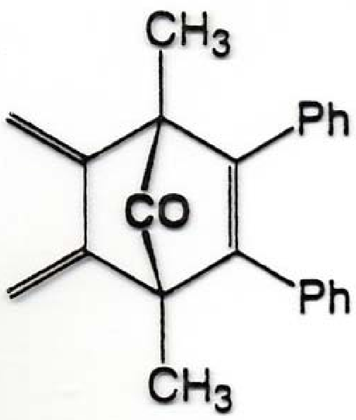
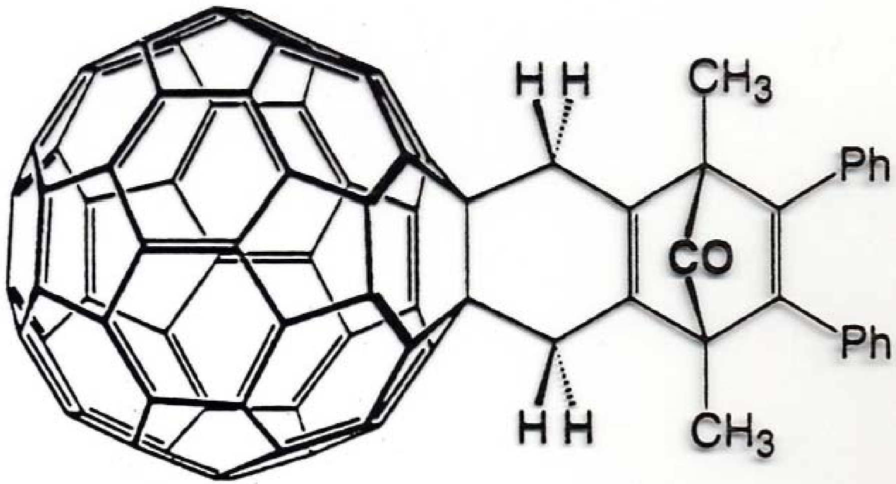


Figure 3. ORTEP drawing (50% ellipsoids) of **1** showing the geometry of the $C_{60}O_2$ unit and the numbering scheme. Reprinted with permission from ref 3. Copyright 1991 AAAS.

Dienophile: Crystalline Diels Alder Adduct



2



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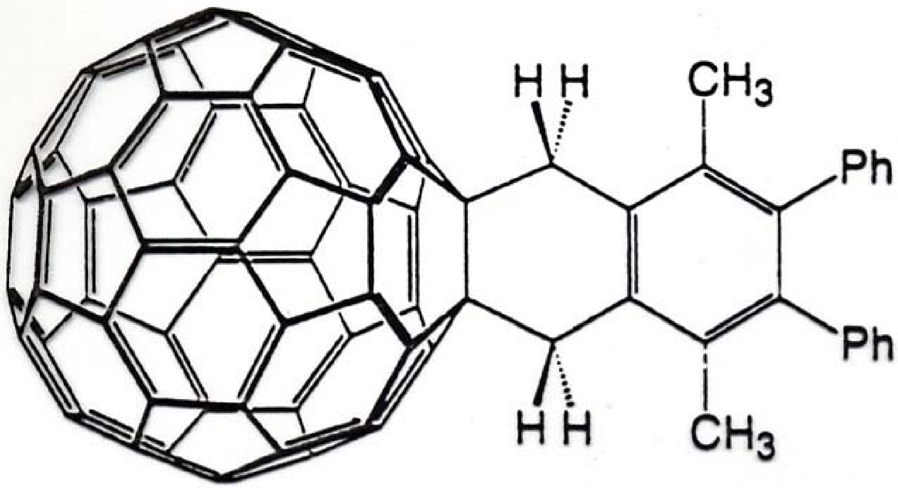
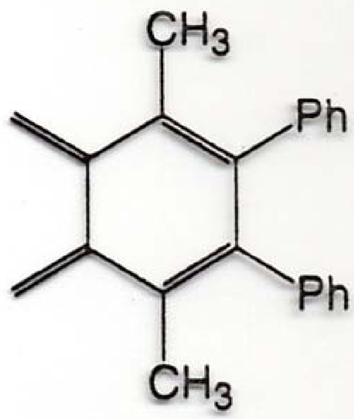


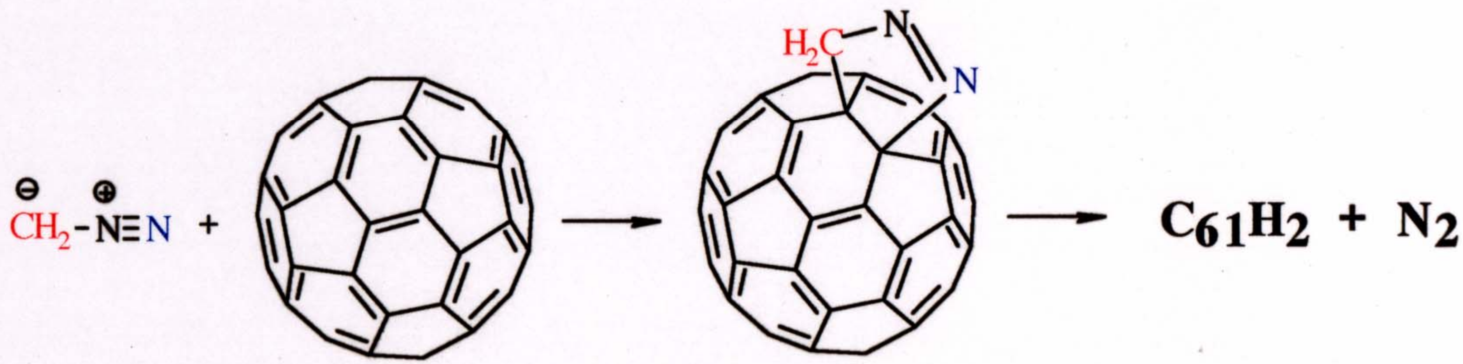
1



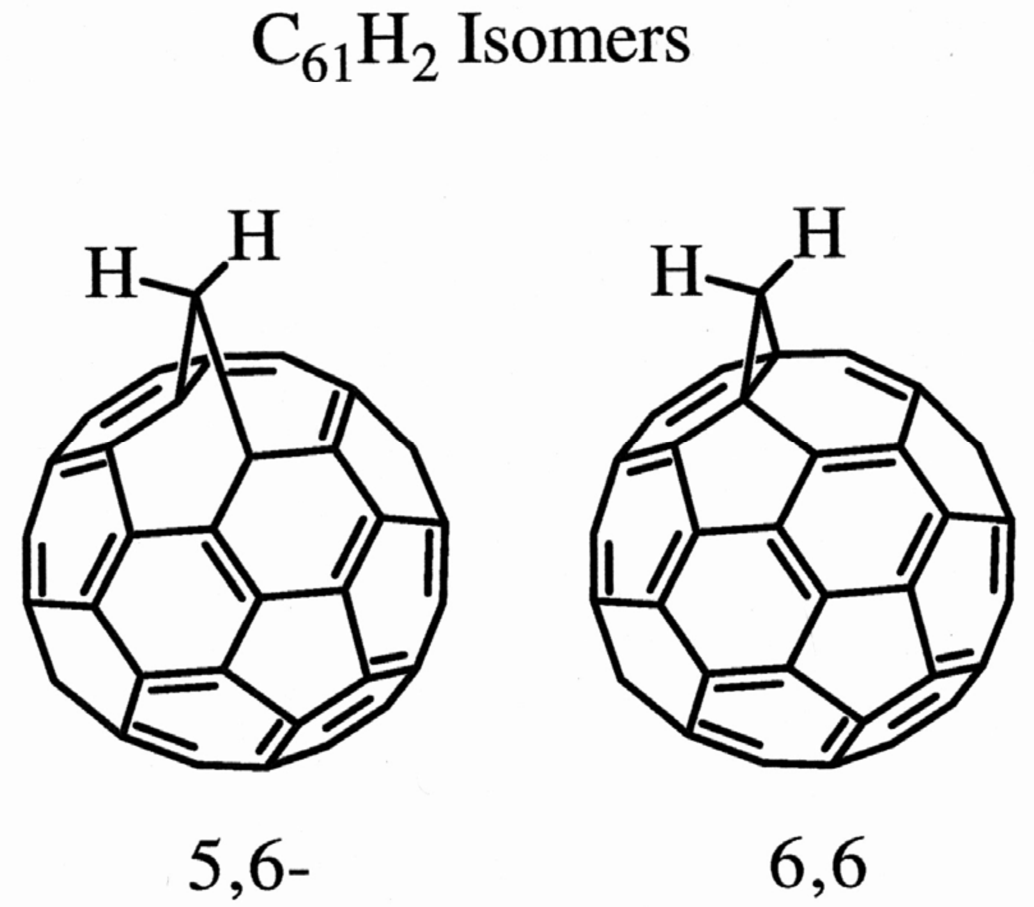
4

Y. Rubin, et al. J. Am. Chem. Soc. 1993, 115, 344.

Dipolarophile: the first C_{61}, 60-π Electron Derivative

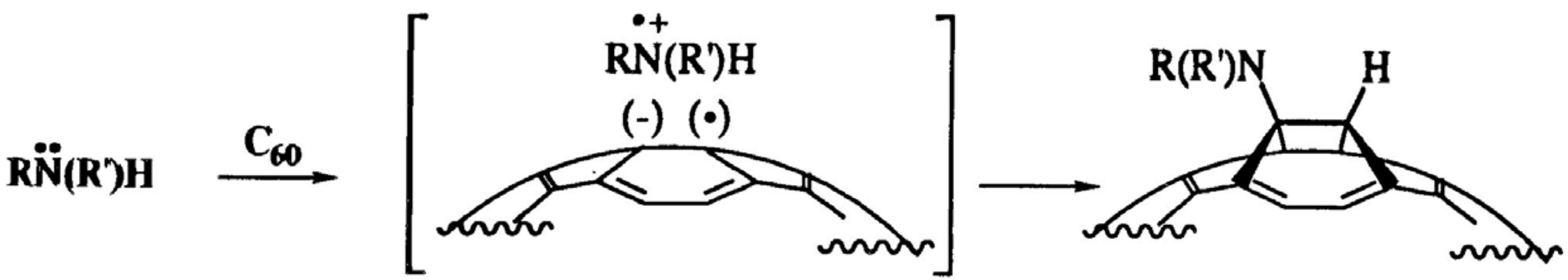


Dipolarophile: the first C_{61}, 60-π Electron Derivative

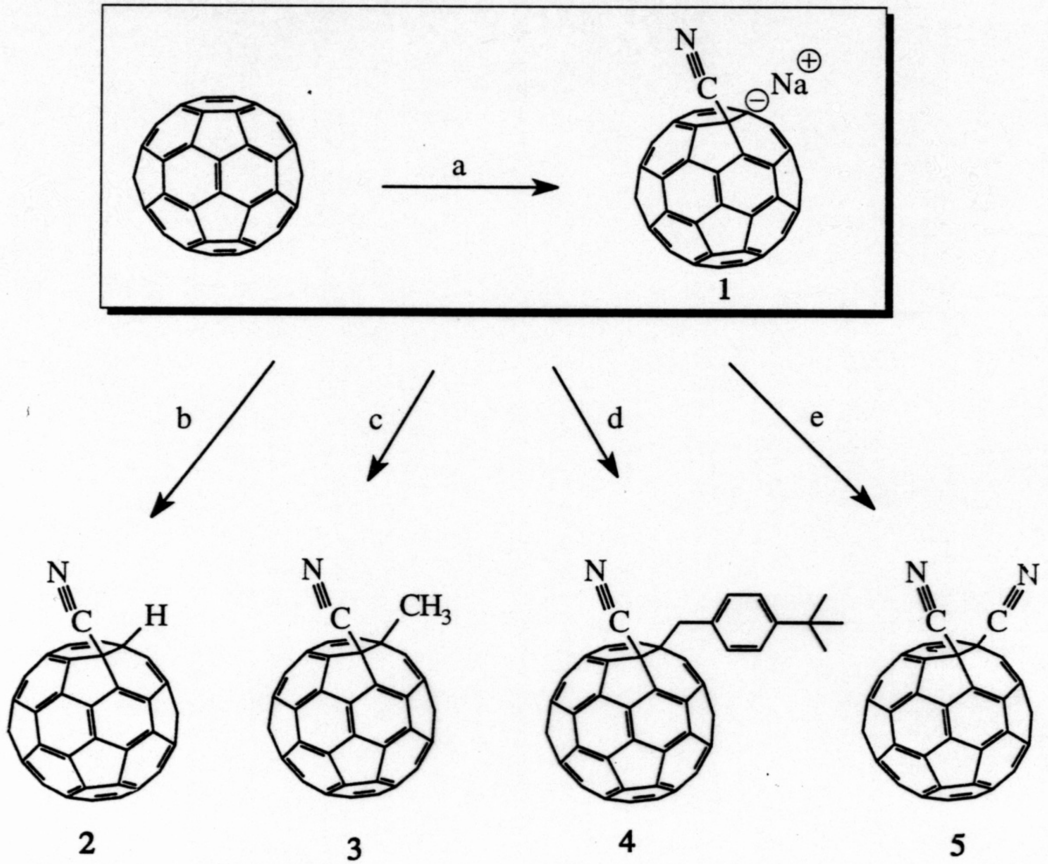


60-π Electron   58-π Electron

Electrophile: Nucleophilic Additions



Cyanide Addition



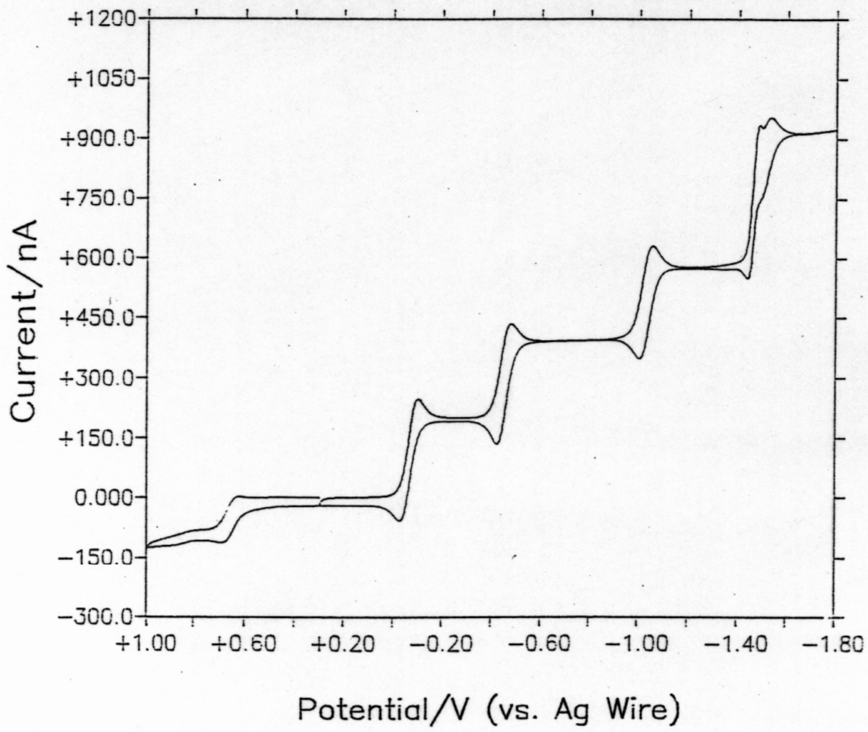
Reagents and Conditions:

(a) NaCN, ODCB/DMF, RT; (b) Trifluoroacetic acid, RT, 29%;

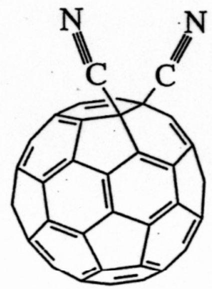
(c) Methyl trifluoromethanesulfonate, RT,10%; (d) 4-(*tert*-Butyl)benzyl bromide, 70 ^{o}C, 11%;

(e) *p*-Toluenesulfonyl cyanide, RT, 61%.

Electrochemistry of the Dicyano Derivative



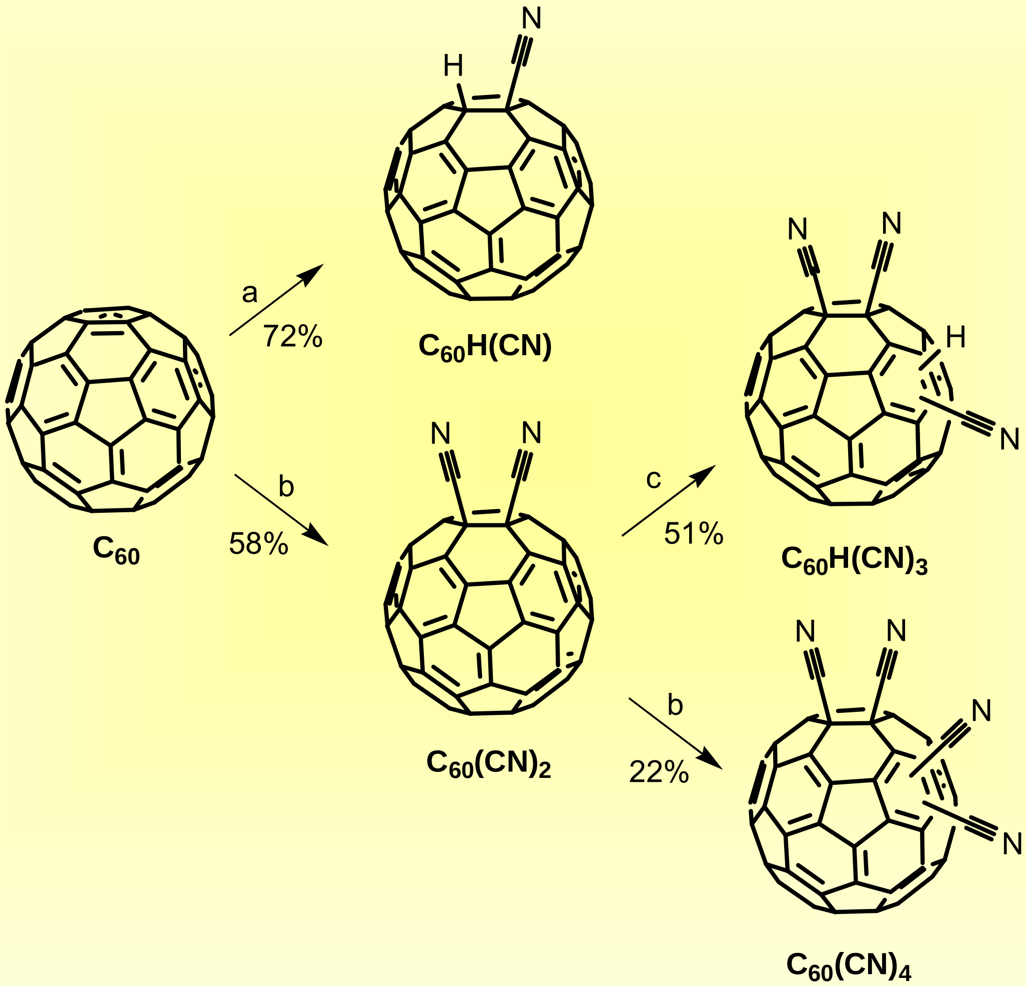
The CV of



at -72°C.

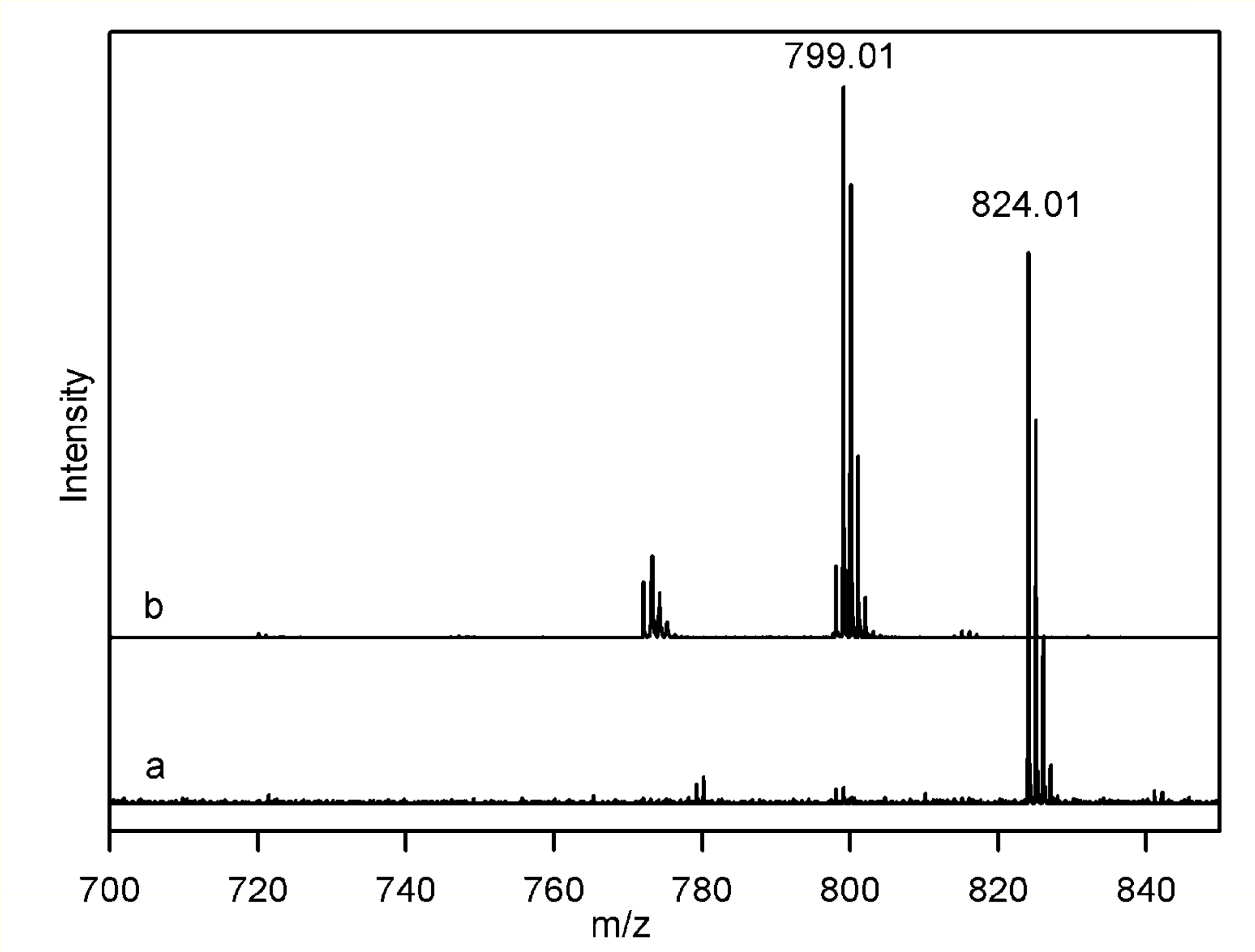
Ferrocene is at the left.

Multi-cyanation of C_{60}

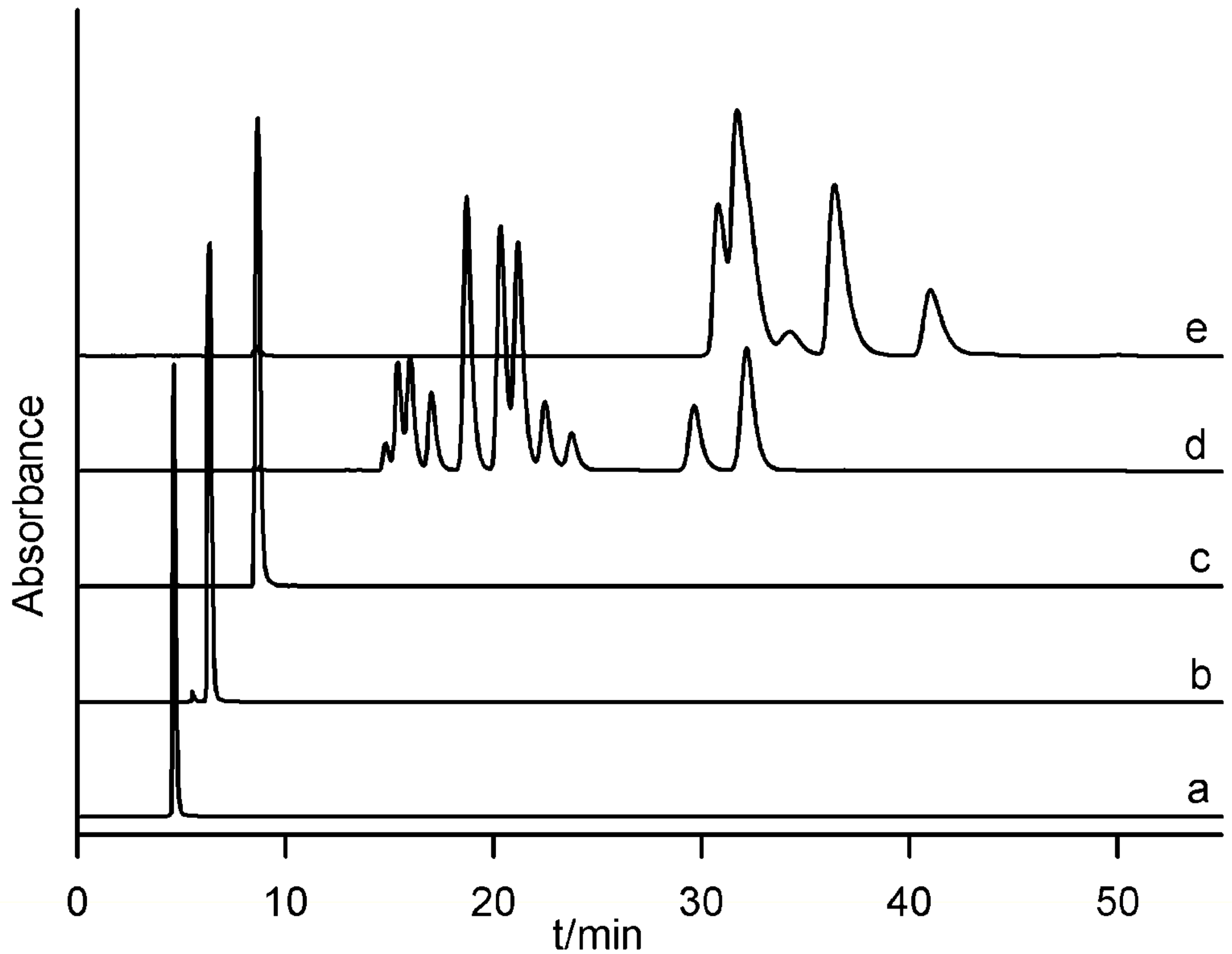


Jousselme, B.; Sonmez, G.; Wudl, F. *J. Mater. Chem.*, **2006**, *16*, 3478 - 3482

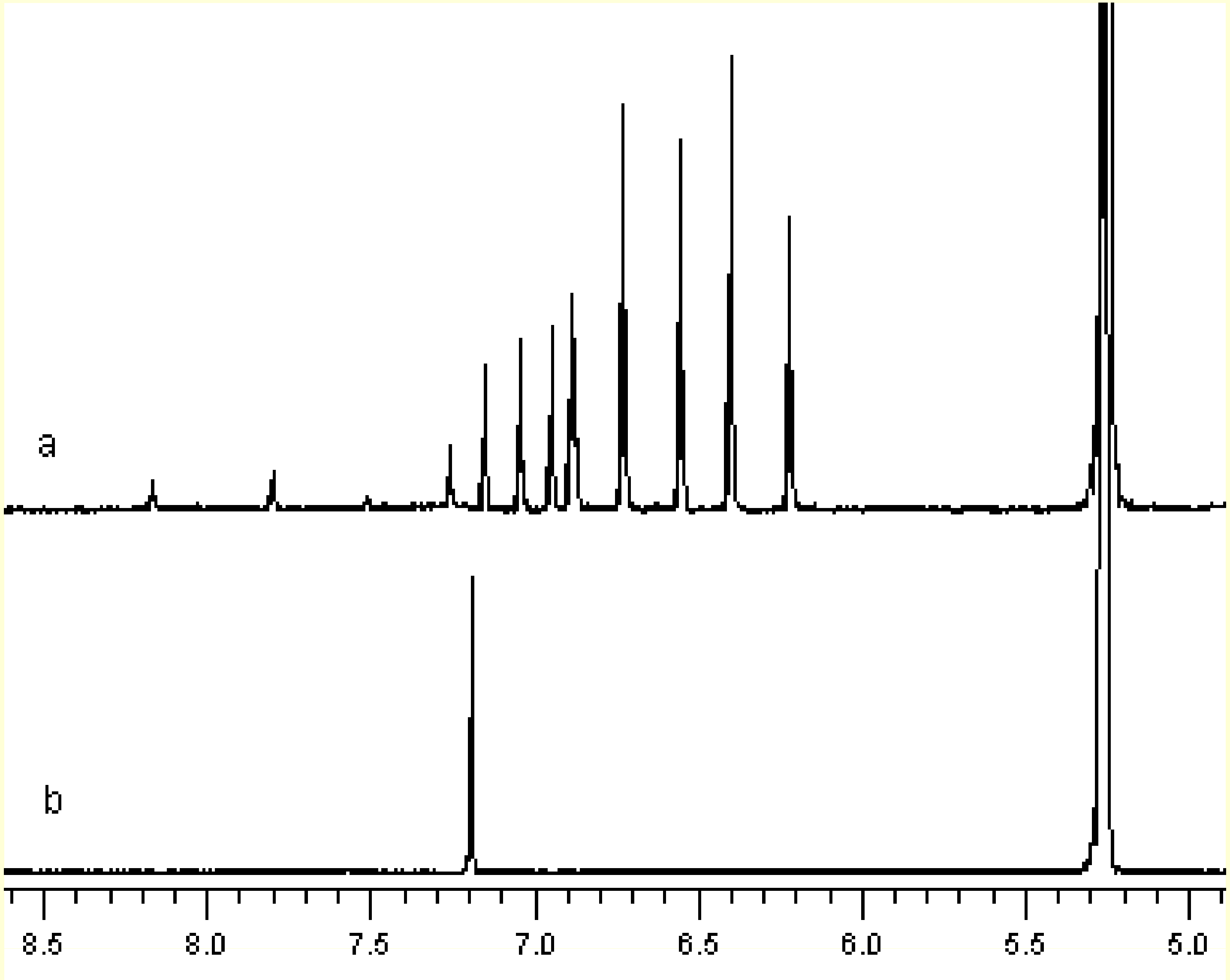
Negative MALDI-TOF spectra of $C_{60}H(CN)_3$ (a) and $C_{60}(CN)_4$ (b).



HPLC profile of (a) C_{60}, (b) $C_{60}H(CN)$, (c) $C_{60}(CN)_2$, (d) $C_{60}H(CN)_3$, (e) $C_{60}(CN)_4$

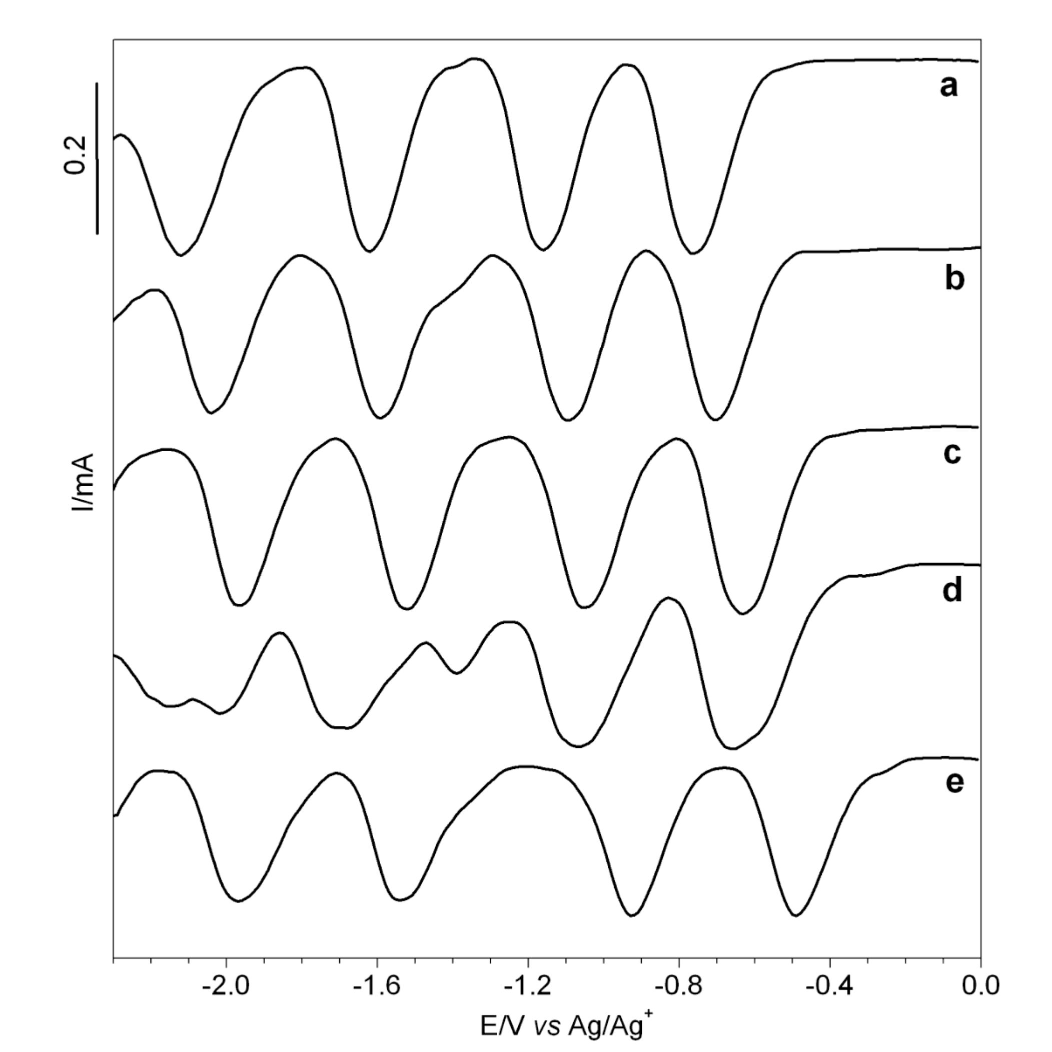


Non-Regiospecific Addition of $CN^{(-)}$



Aromatic part spectrum ^{1}H NMR of (a) **$C_{60}H(CN)_3$** and (b) **$C_{60}H(CN)$,** in CD_2Cl_2**.**

Electrochemistry of (Cyano)C_{60}



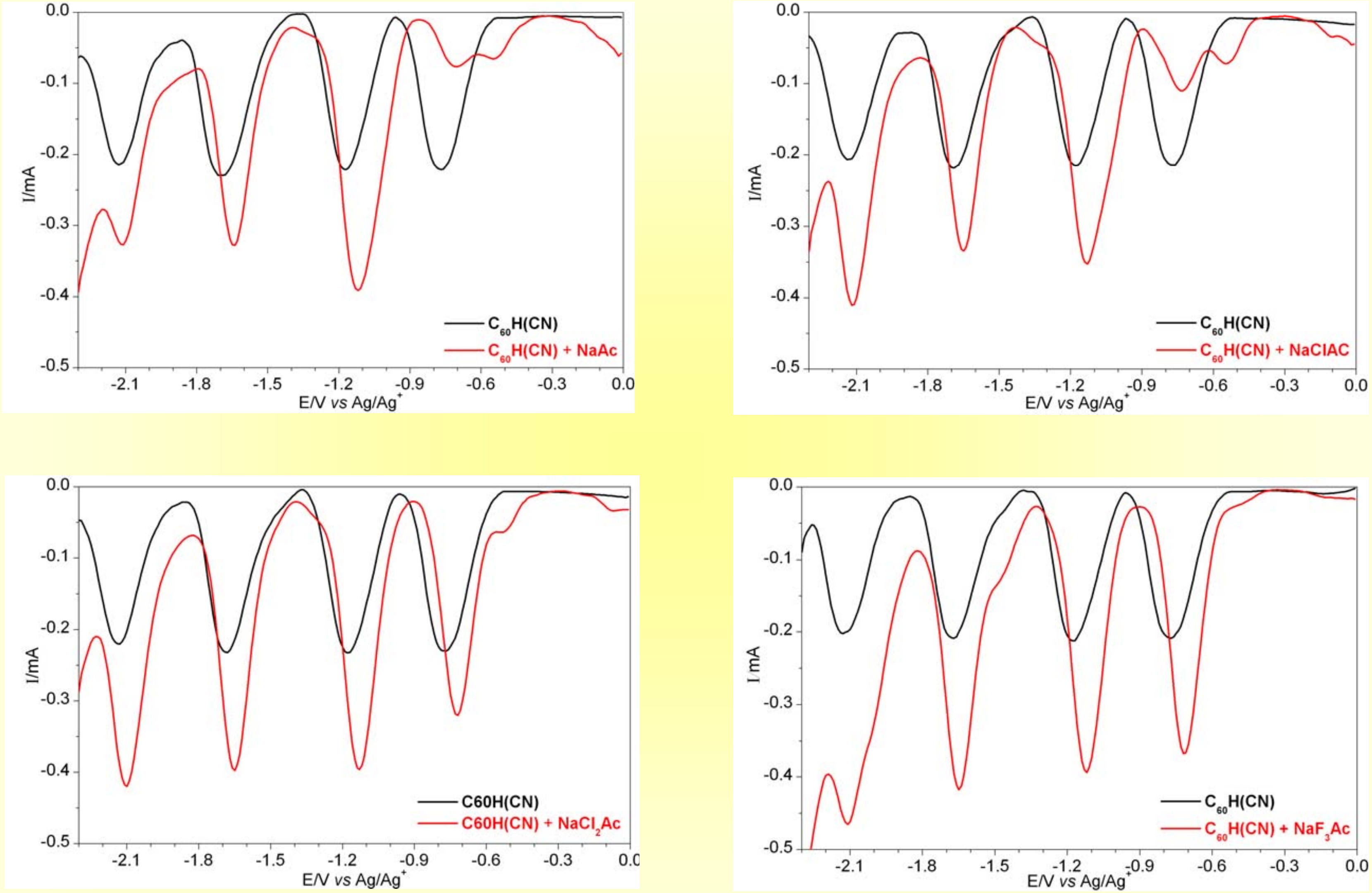
Differential Pulse Voltammetry of (a) C_{60}, (b) **$C_{60}H(CN)$**, (c) **$C_{60}(CN)_2$**, (d) **$C_{60}H(CN)_3$**, (e) **$C_{60}(CN)_4$** in 0.1 M TBAP/ODCB

Reduction Potentials of Cyano-Fullerenes

	Reduction potentials (V vs Ag/Ag^+)			
Compound	E_1	E_2	E_3	E_4
C_{60}	- 0.77	- 1.16	- 1.62	- 2.12
$C_{60}H(CN)$	- 0.70	- 1.09	- 1.59	- 2.04
$C_{60}(CN)_2$	- 0.63	- 1.05	- 1.52	- 1.97
$C_{60}H(CN)_3$	- 0.65	- 1.06	- 1.69	- 2.02
$C_{60}(CN)_4$	- 0.49	- 0.93	- 1.54	- 1.97

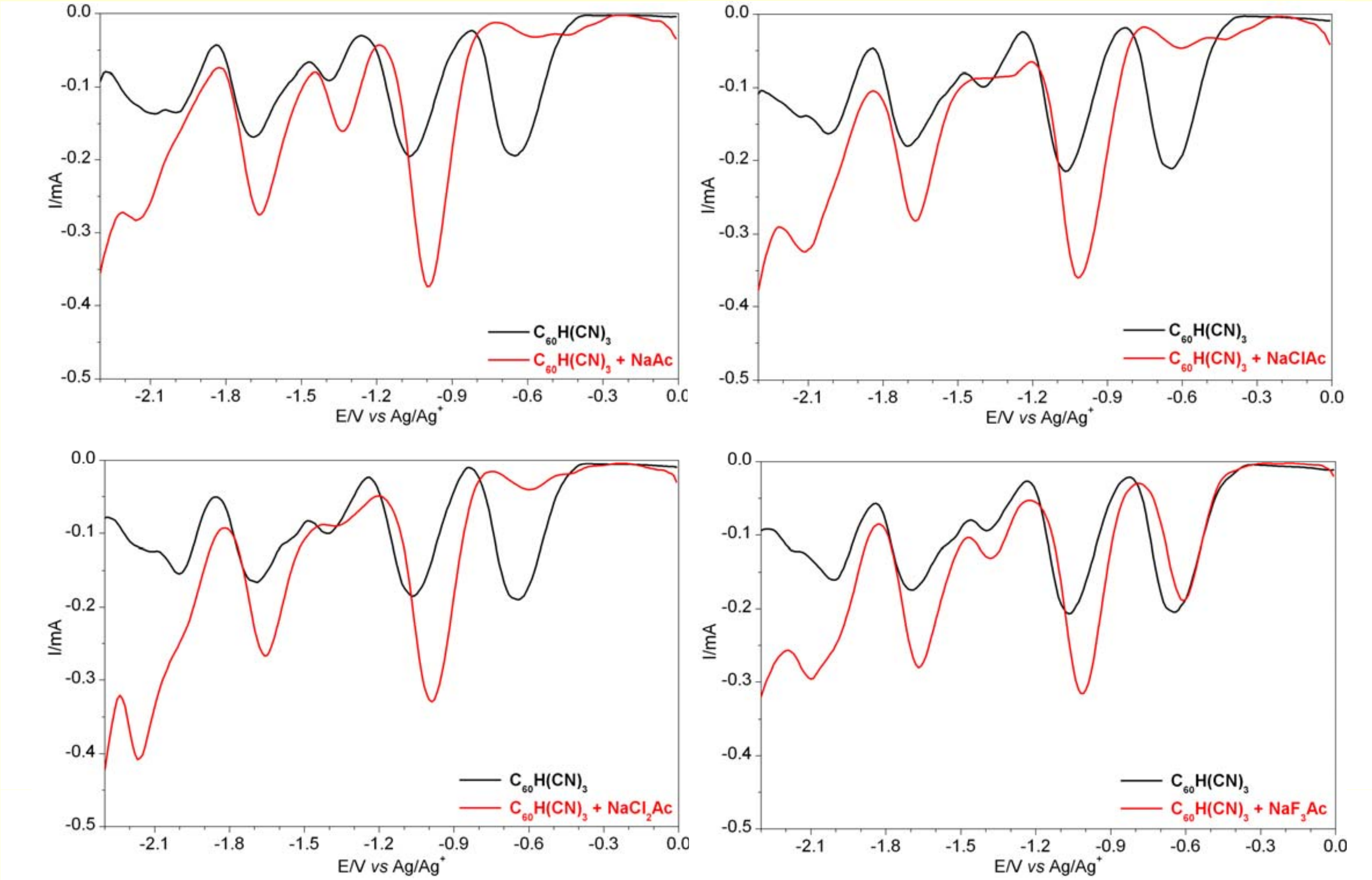
Electrochemical pKa Determination

M. Niyazymbetov, D. Evans, S. Lerke, P. Cahill, C. Henderson, *J. Phys. Chem.*, **1994**, *98*, 13093



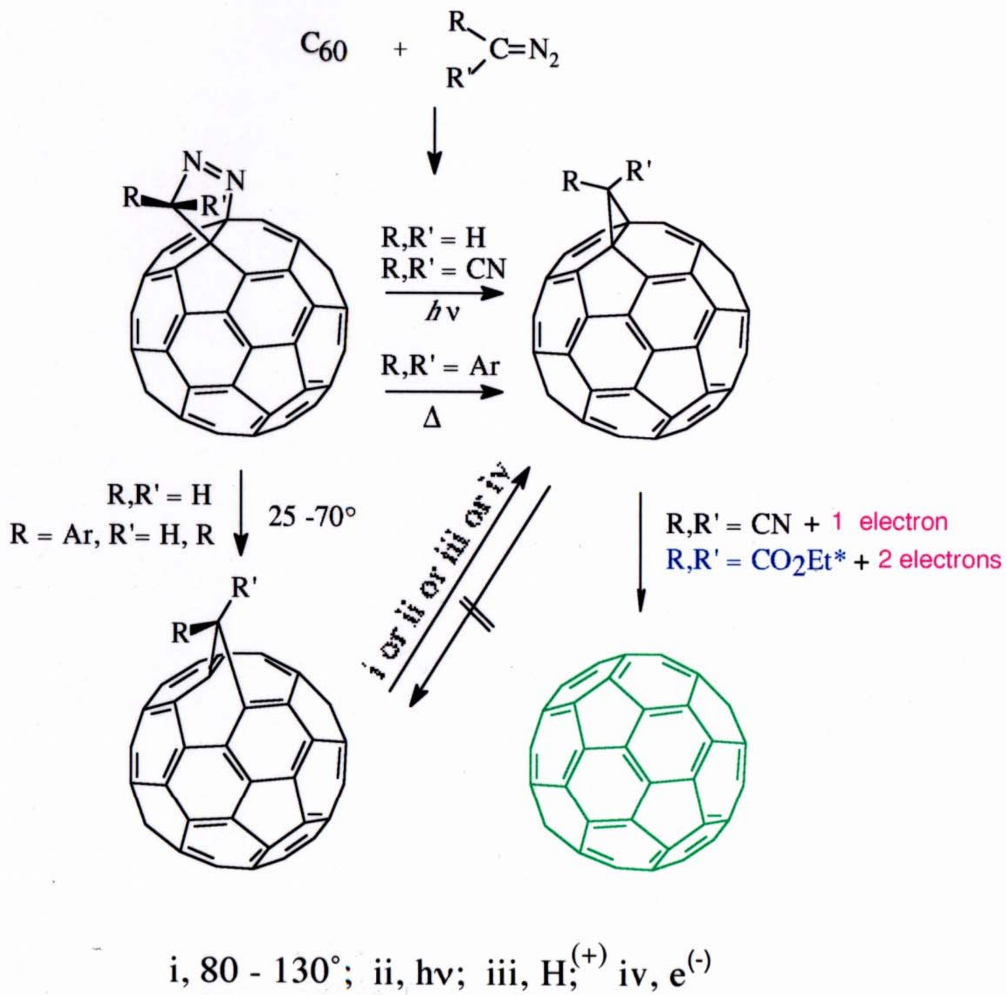
DPV of $C_{60}H(CN)$ (black) with one equivalent of sodium salt (red). (Top left, sodium acetate; top right, sodium chloroacetate. Bottom left, sodium dichloroacetate; bottom right, sodium trifluoroacetate).

Electrochemical pKa Determination



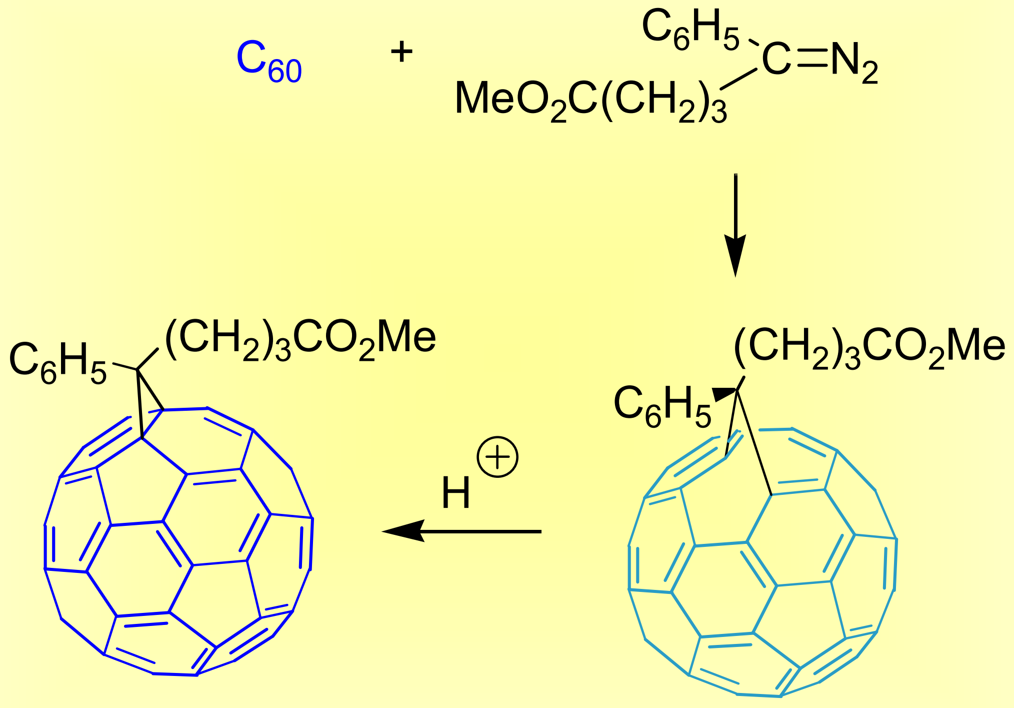
DPV of $C_{60}H(CN)_3$ (black) with one equivalent of sodium salt (red). (Top left, sodium acetate; top right, sodium chloroacetate. Bottom left, sodium dichloroacetate; bottom right, sodium trifluoroacetate).

Isomer Interconversions, Including Reversion to C_{60}



*Echegoyen, L.; Diederich, F., et al, *Angew. Chem. Int. Ed. English* 1998, *37*, 1919.
Keshavarz-K., M; Knight, B.; Haddon, R. C.; Wudl, F. *Tetrahedron* 1996, *52*, 5149.

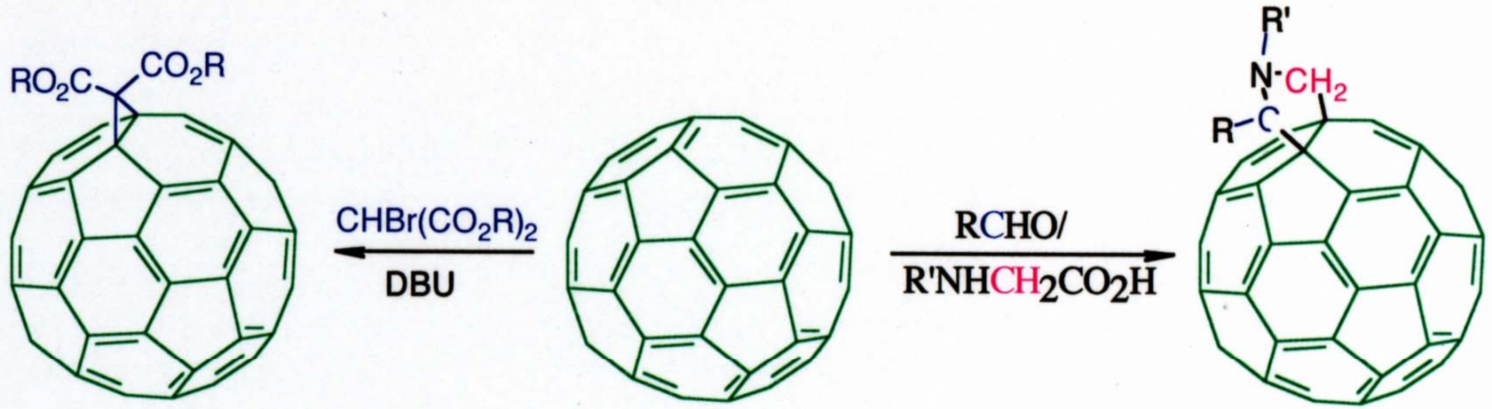
An Important Example, PCBM



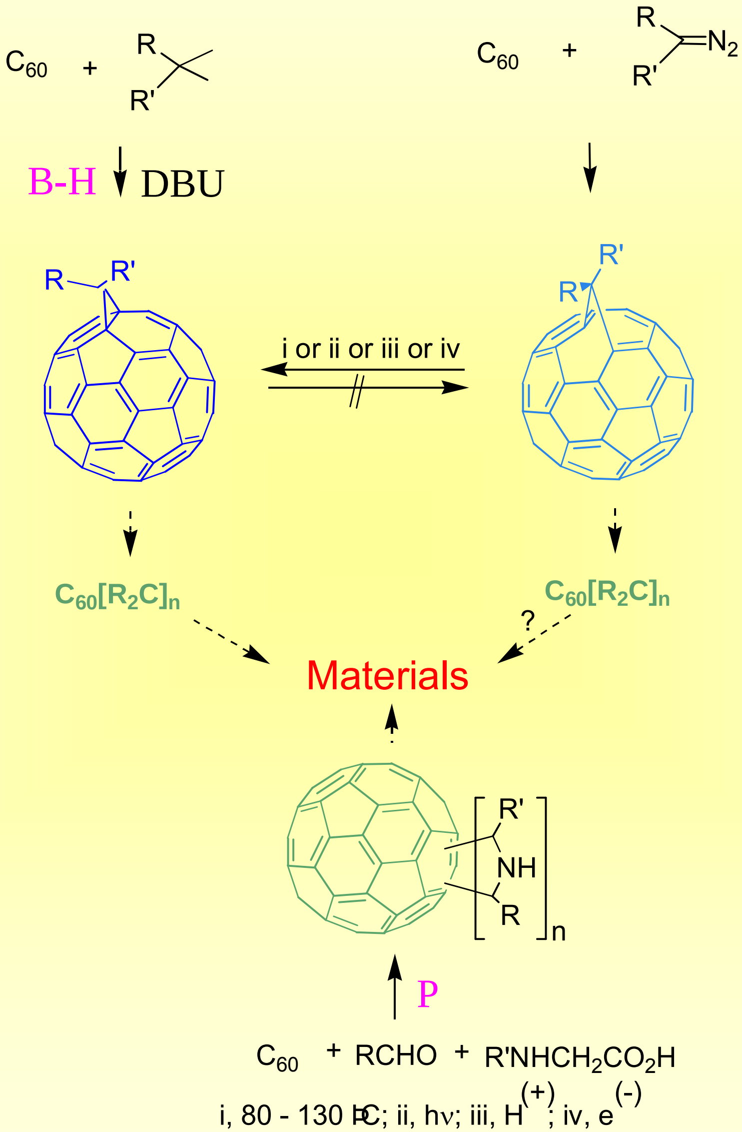
PCBM

Preparation and Characterization of Fulleroid and Methanofullerene Derivatives. Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60,* 532–538.

Dipolarophile: The Most Efficient Derivatizations

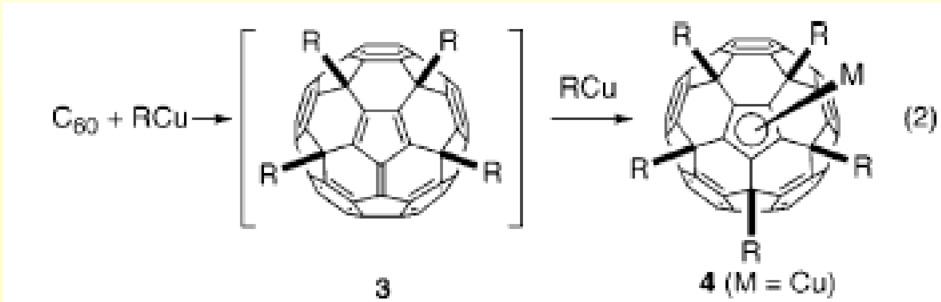


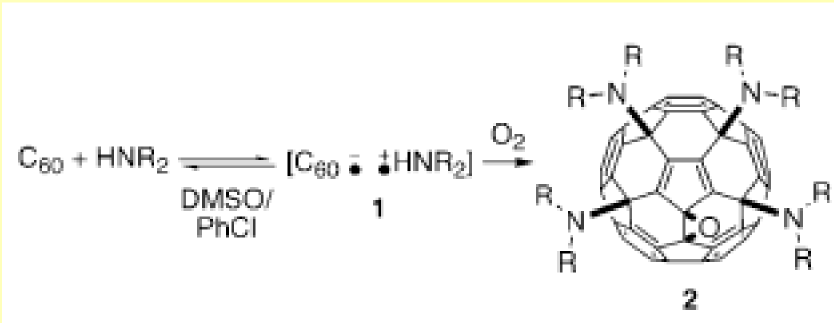
Synthetic Reactions Applicable to Fullerene Materials



Prato, M. Fullerene Materials. *Topics in Current Chemistry* **1999**, *199*, 173-188.zz

High Yield Regioselective Additions



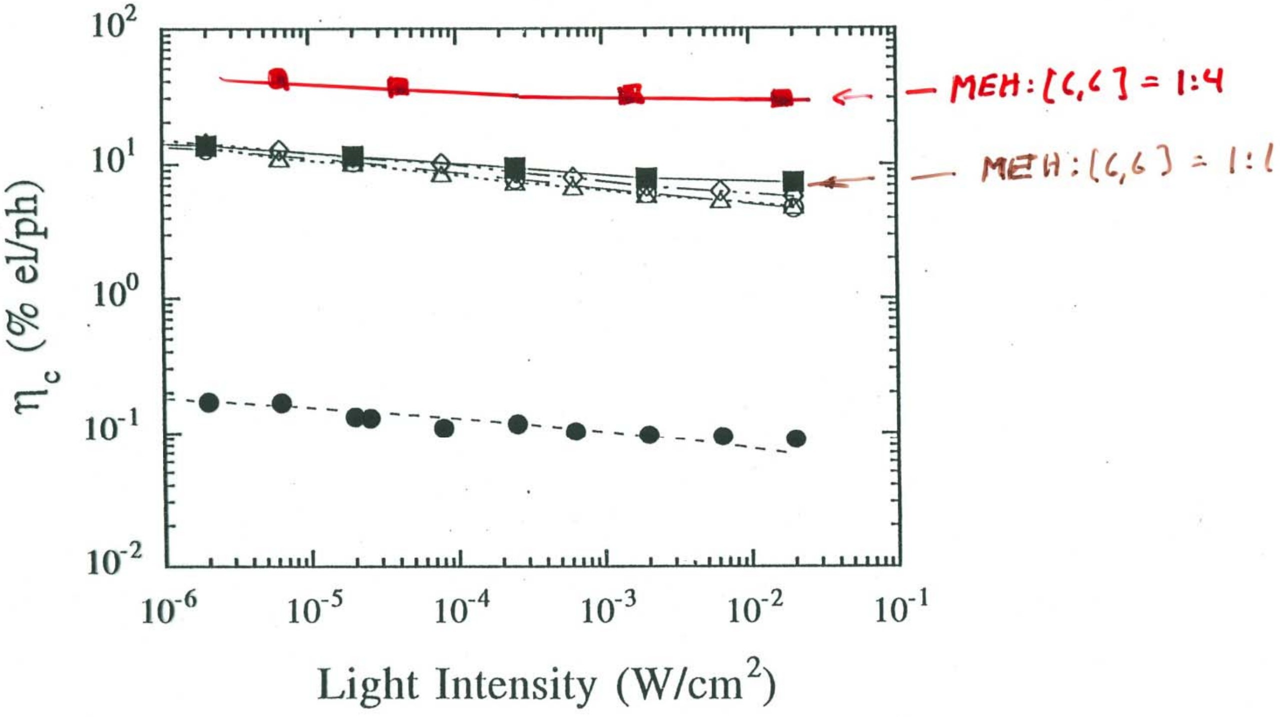


Murata, Y.; Shiro, M.; Komatsu, K. *J. Am. Chem. Soc.* **1997**, *119*, 8117-8118.

Sawamura, M.; Ilkura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850-12851.
Nakamura, E. *Pure and Appl. Chem.* **2003**, *75*, 427-434.

Isobe, H.; Tanaka, T.; Nakanishi, W.; Lemiegre, L.; Nakamura, E. *J. Org. Chem.* **2005,** *70*, 4826

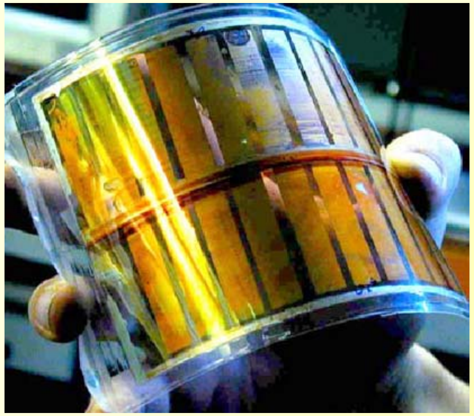
Applications ?

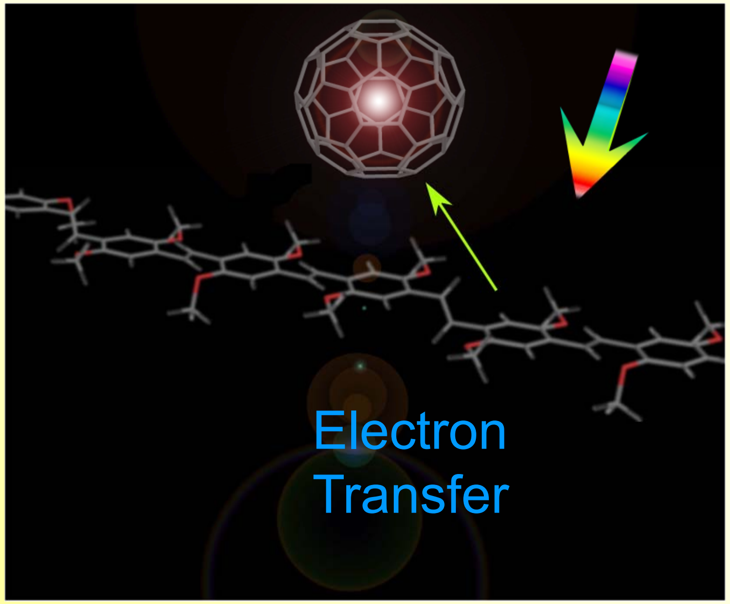


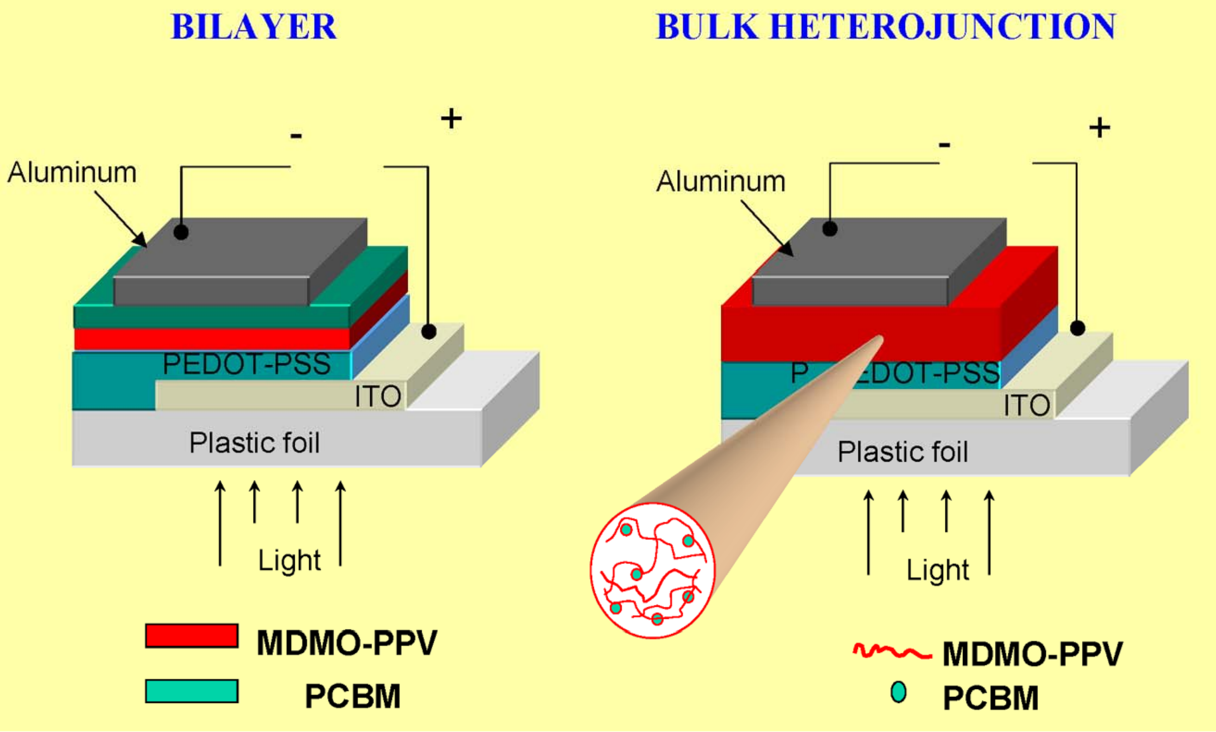
3. Carrier collection efficiencies, η_c, of Ca/MEH-PPV:[6,6]PCBM /ITC (solid 1:4 squares), Al/MEH-PPV:[6,6]PCBM/ITO (open diamonds), Ca/MEH-PPV:[5,6]PCBM/ITO (open circles), Ca/MEH-PPV:C_{60} /ITO (open triangles) and Ca/MEH-PPV/ITO (solid circles).

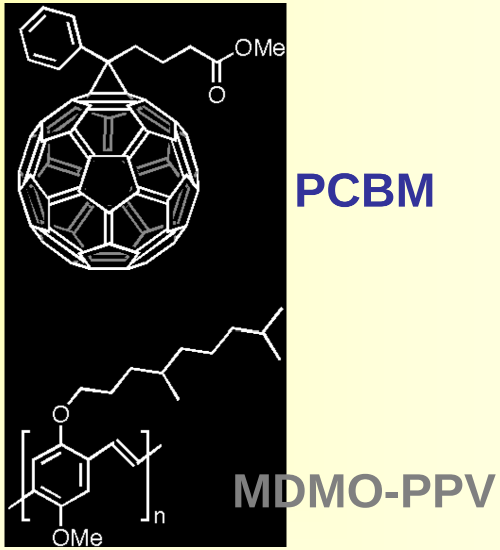
G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger Science, 1995, 270, 1789

Fullerene-PPV Plastic Solar Cell





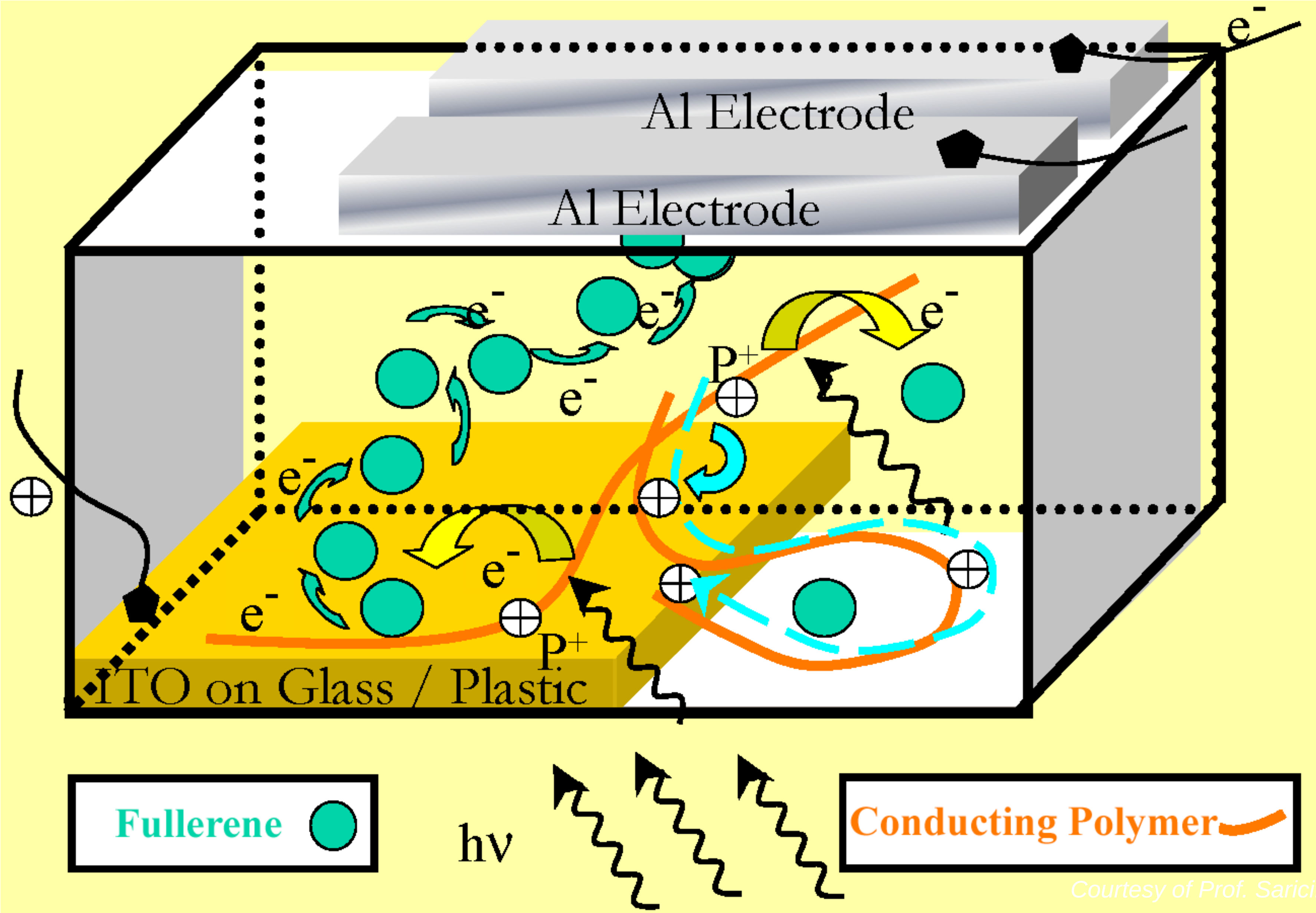




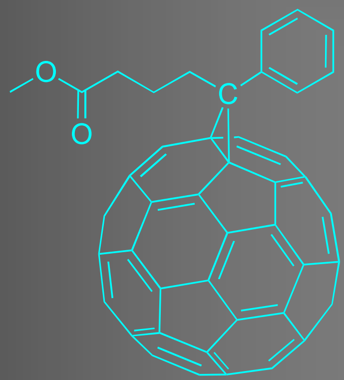
http://www.ipc.uni-linz.ac.at/publ/homecol.pdf

Proposed Interaction between Polymer and Fullerene Derivativ

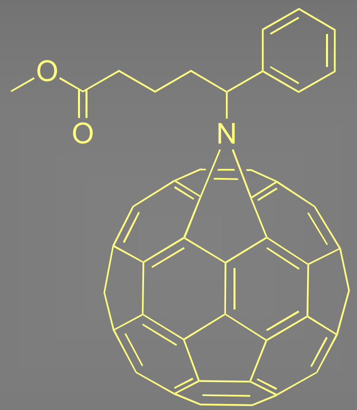
http://www.ipc.uni-linz.ac.at/publ/homecol.pdf



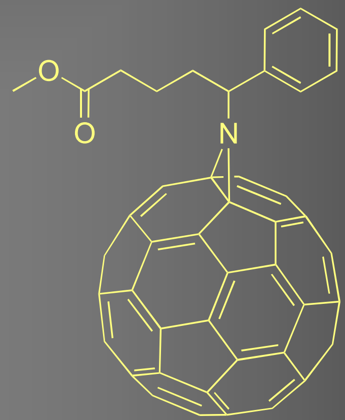
Dipolar Cycloaddition of Azide: Synthesis of a PCBM Nitrogen Analog



PCBM



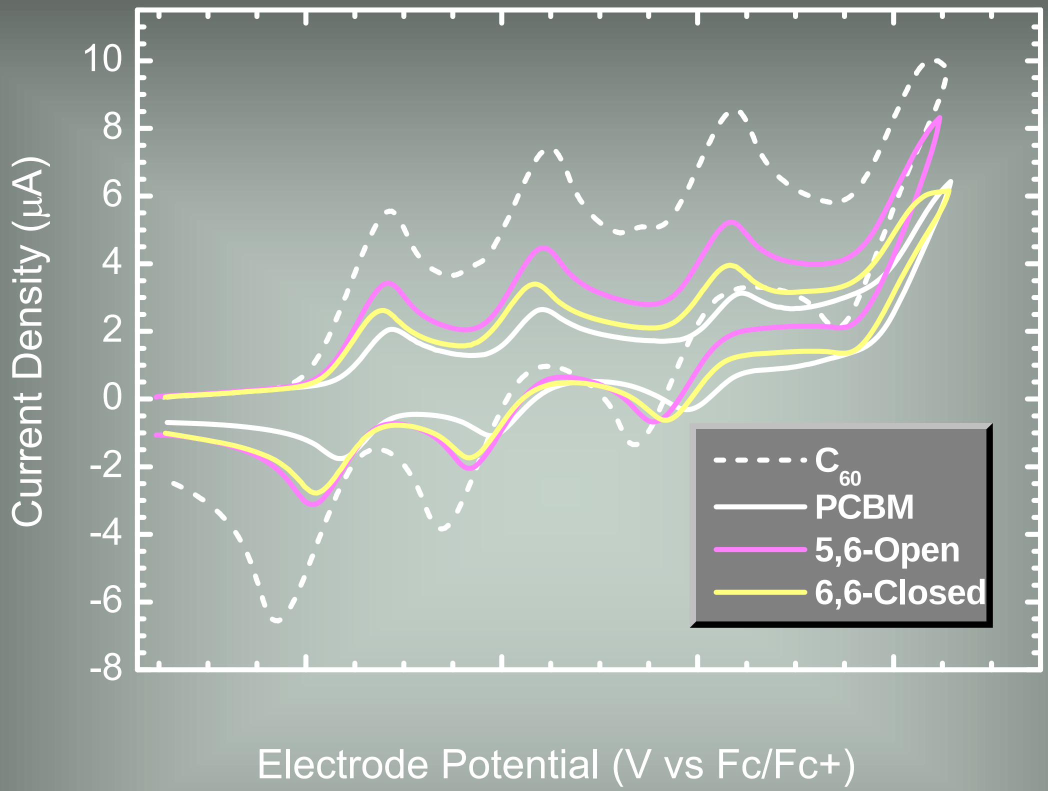
5,6-Open
5,6 APCBM



6,6-Closed
6,6 APCBM

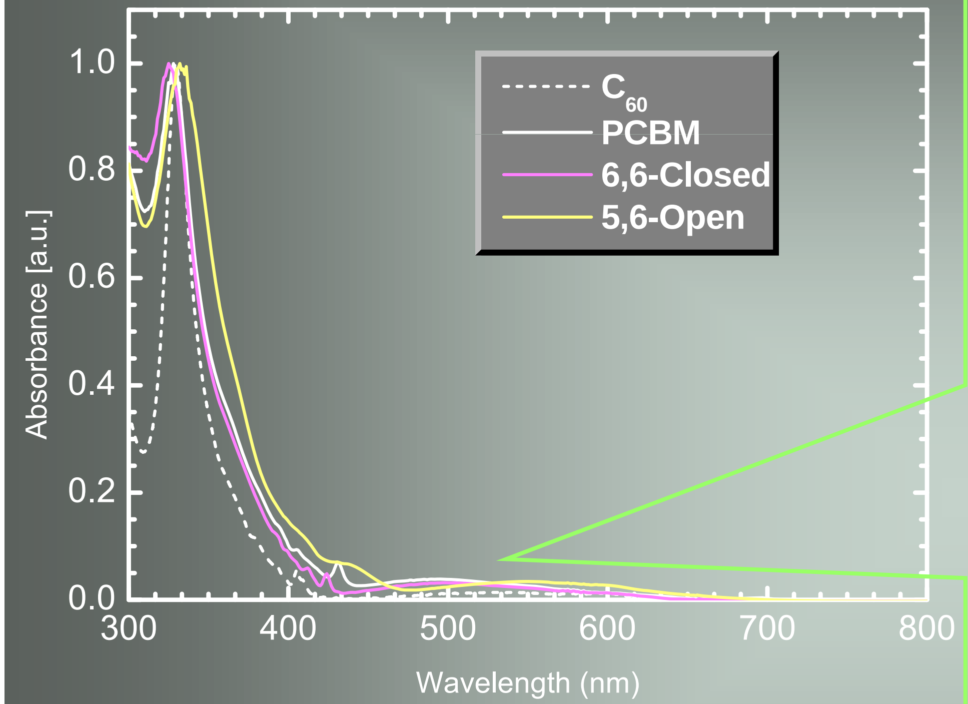
Changduk Yang

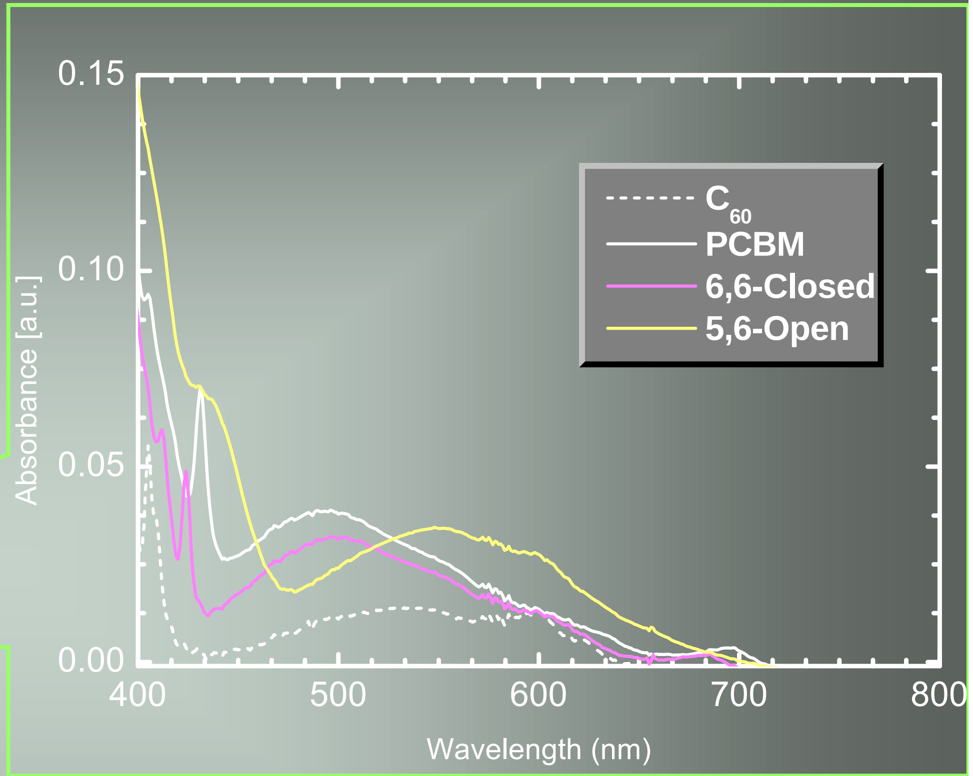
Electrochemical Data



compound	E^1_{red}	E^2_{red}	E^3_{red}
5,6-Open	-1.114	-1.512	-1.984
6,6-Closed	-1.110	-1.504	-2.000
PCBM	-1.158	-1.540	-2.039
C_{60}	-1.071	-1.484	-1.969

Optical Data

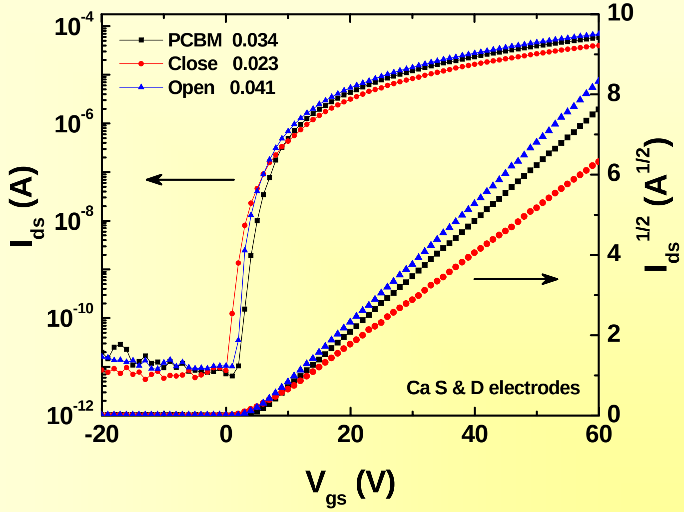


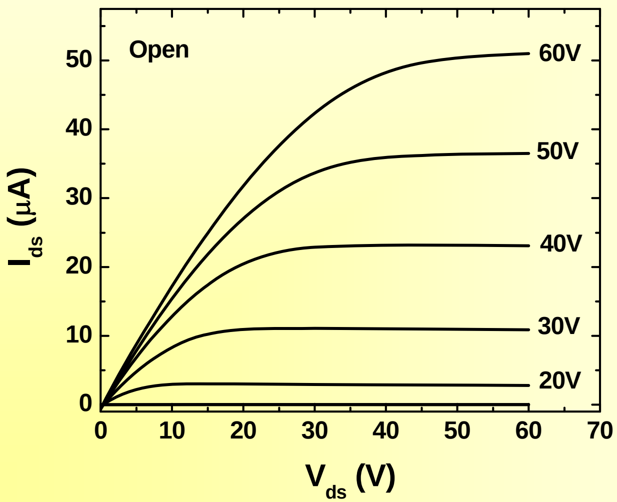


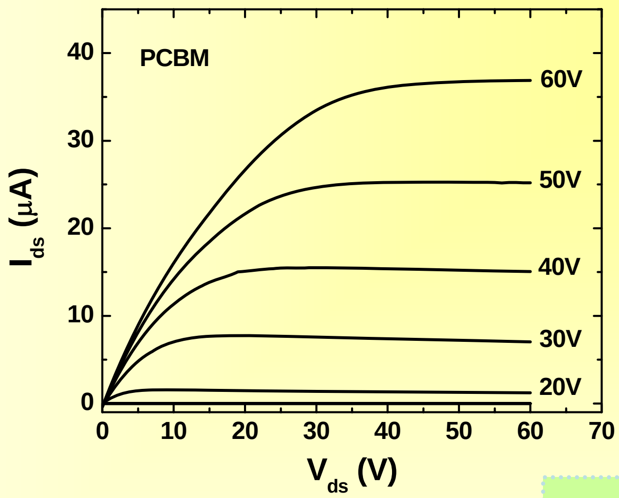
UV-Vis absorption in $CHCl_3$ solution.

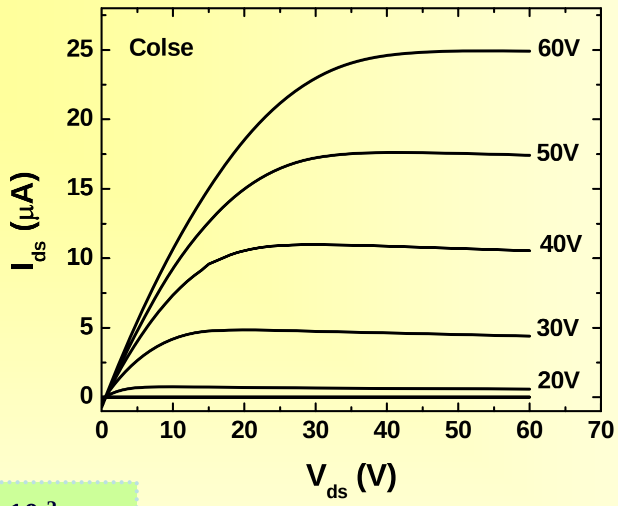
compound	Absorption (nm)
5,6-Open	332, 435(sh), 547, 602(sh)
6,6-Closed	326, 423, 495, 607(sh), 685
PCBM	328, 430, 490, 603(sh), 695
C_{60}	330, 405, 540, 600, 623(sh)

OFET Results



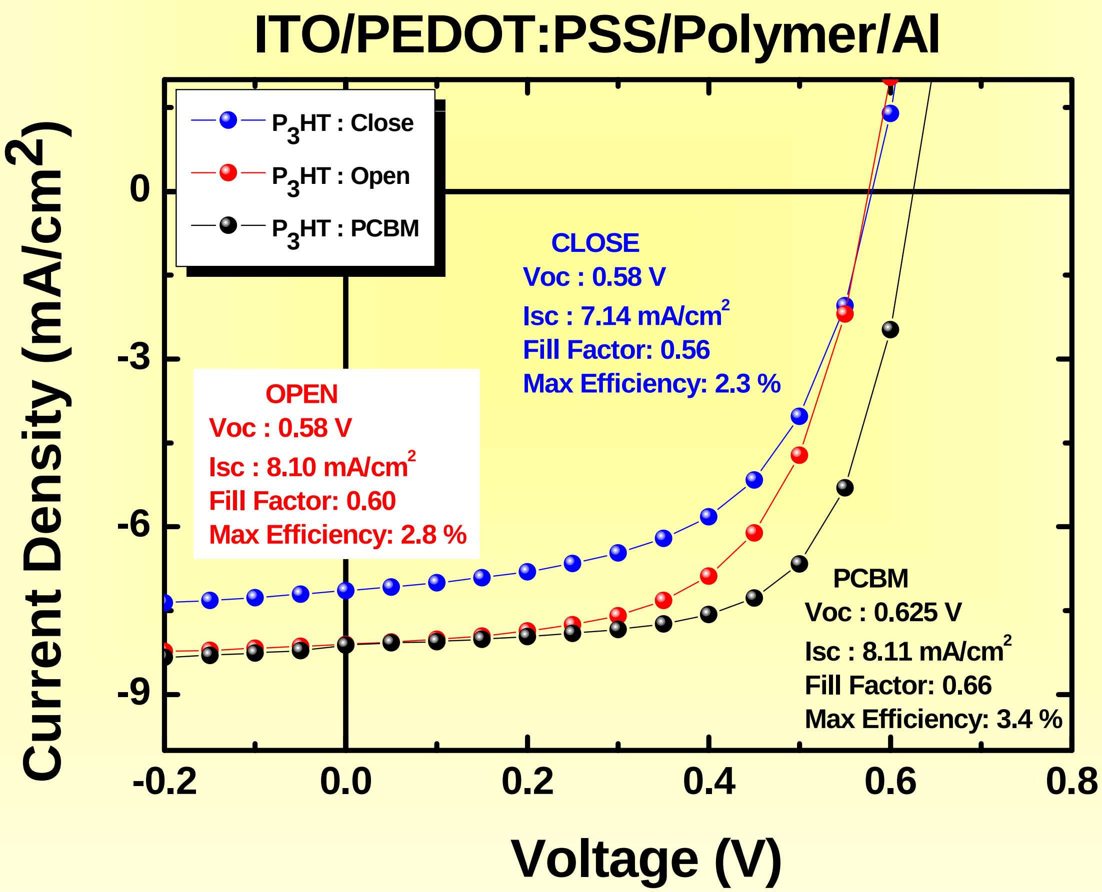




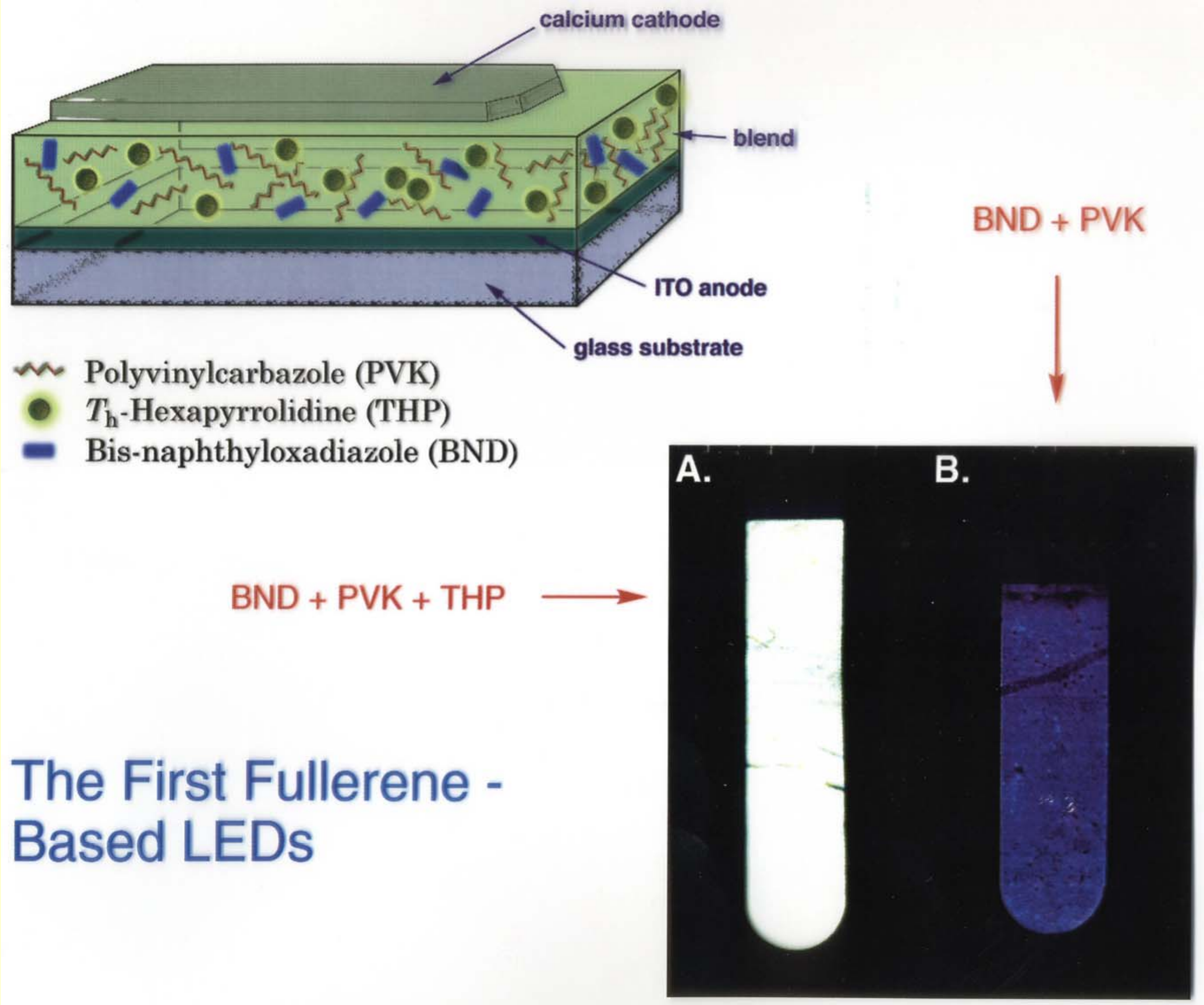


PCBM: $\mu = 3.4 \times 10^{-2}$
6,6-Closed: $\mu = 2.8 \times 10^{-2}$
5,6-Open : $\mu = 4.1 \times 10^{-2}$

Bulk Heterojunction Solar Cell Device

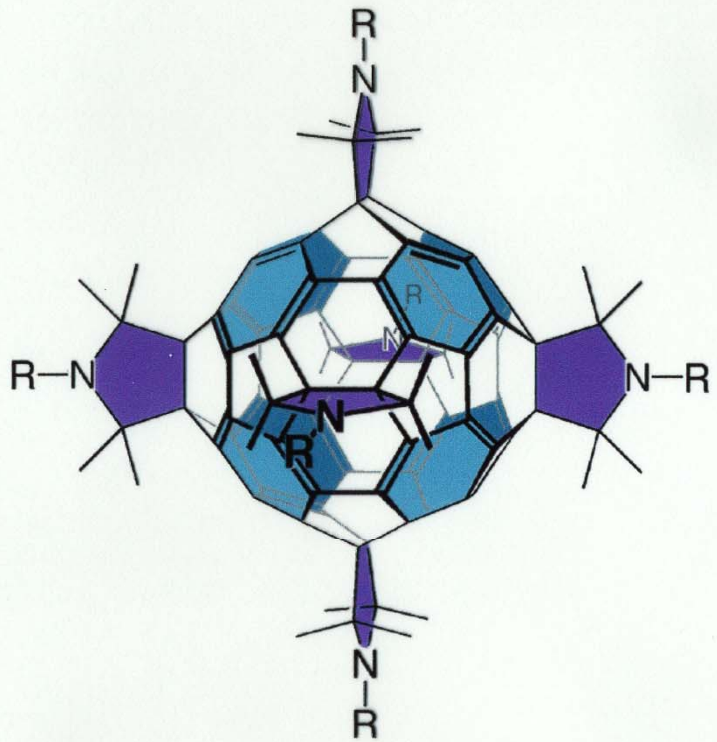


White Light LED

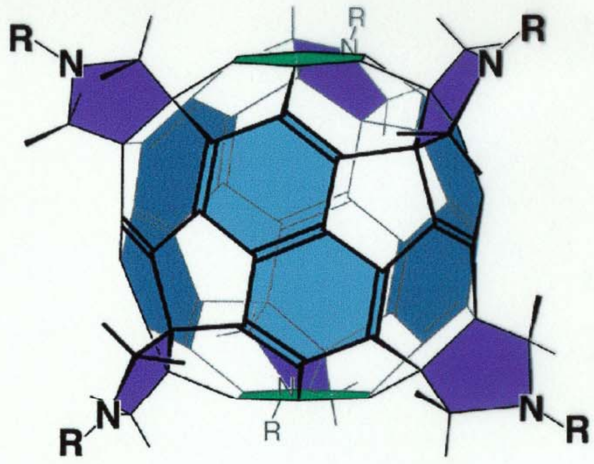


Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *Journal of the American Chemical Society* **1999**, *121*, *23,* 5611-5612.

Addition Patterns for the T_h and D_3-Hexaadducts



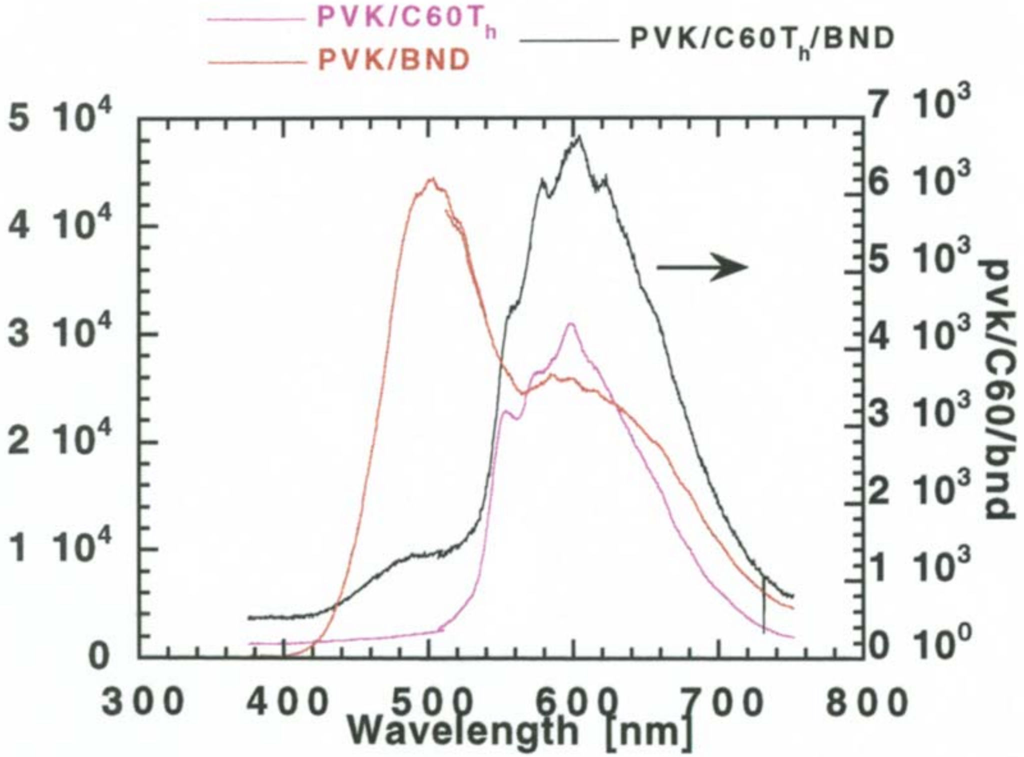
T_h-Hexaadduct
("meso")



D_3-Hexaadduct
(chiral)

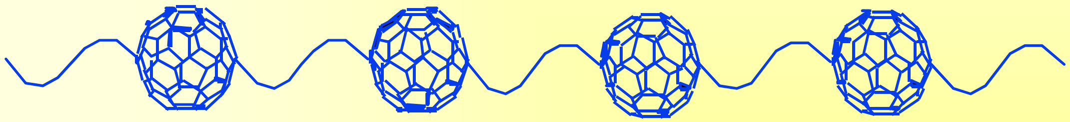
Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *Journal of the American Chemical Society* **1999**, *121*, *23,* 5611-5612.

Electroluminescens Spectra

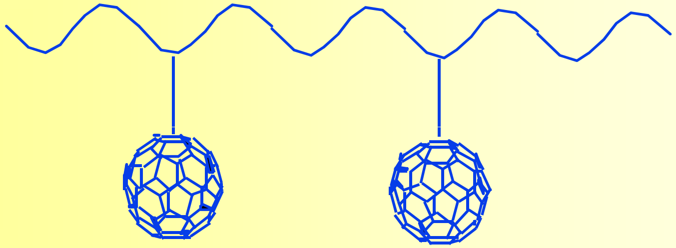


Bucky Light Bulbs: White Light Electroluminescence from a Fluorescent C_{60} Adduct-Single Layer Organic LED. Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *Journal of the American Chemical Society* **1999**, *121*, *23,* 5611-

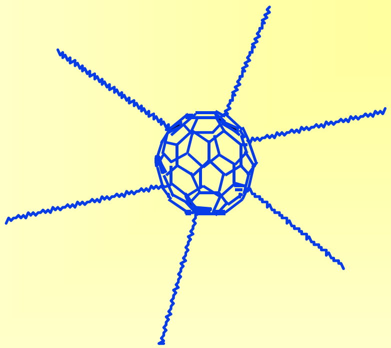
C_{60} POLYMERS



pearl necklace polymer



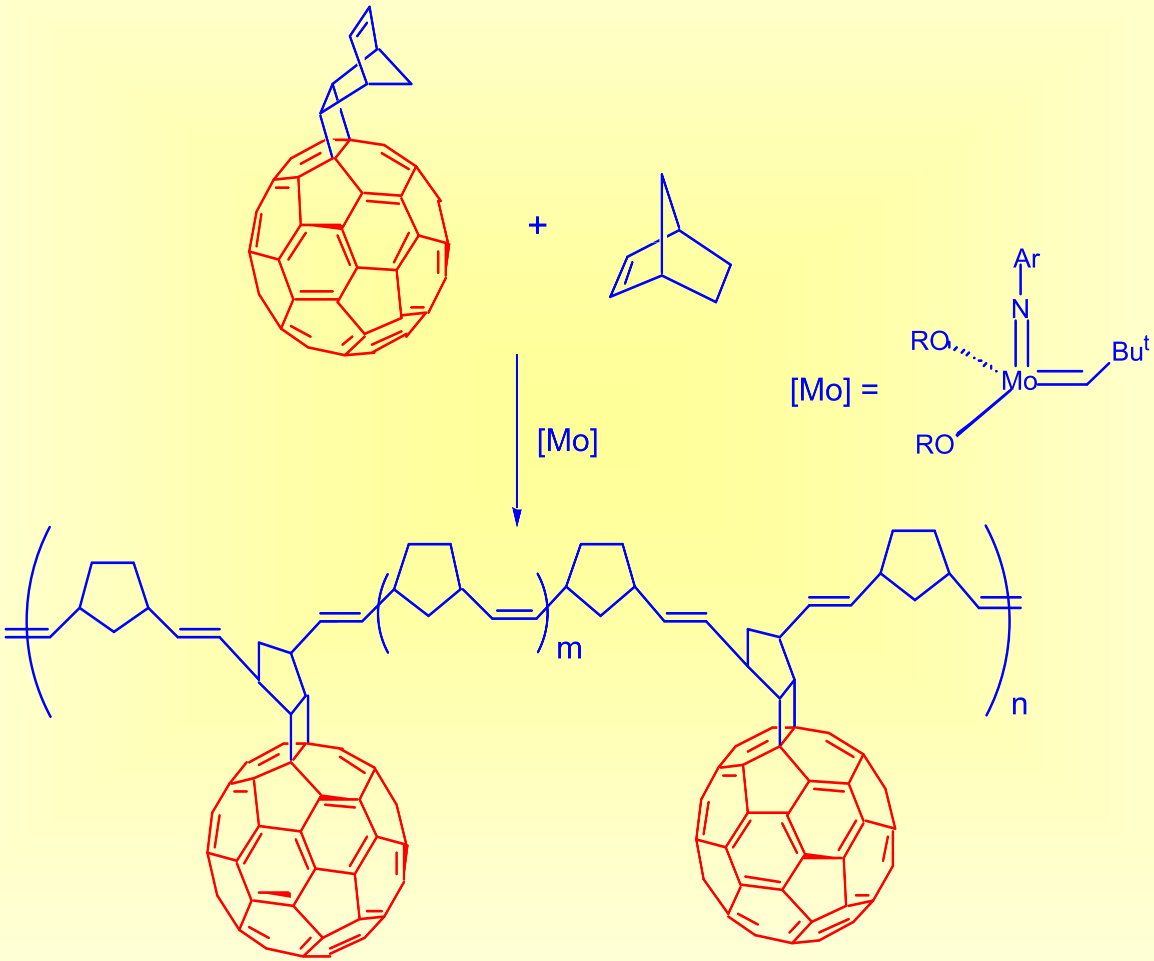
charm bracelet polymer



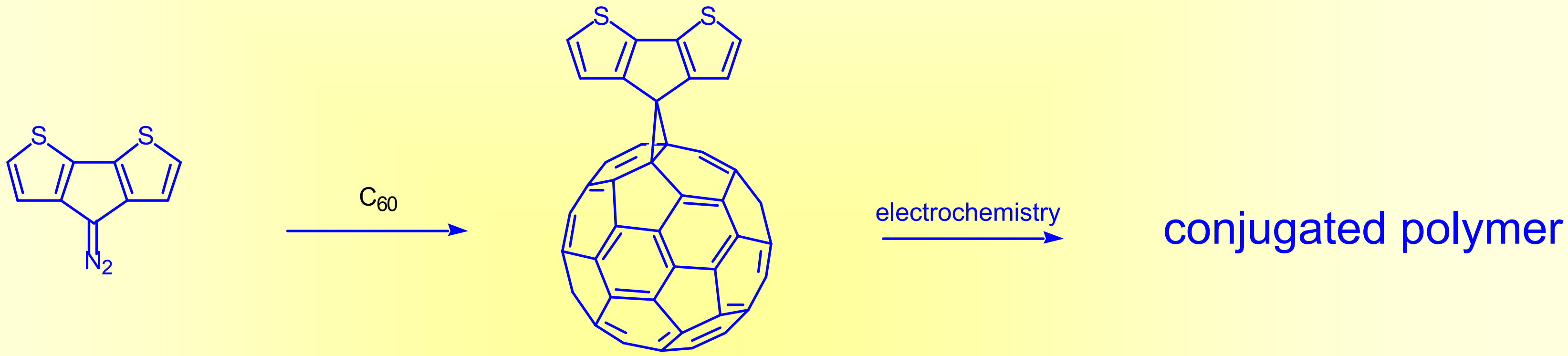
star-like polymer

Prato, M. Fullerene Materials in *Topics in Current Chemistry* **1999**, *199*, 173-188.

C_{60} POLYMERS



Wudl, F.; Prato, M. et al. *Chem. Mater*. **1995**, *7*, 441-442



Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Zotti, G. et al. The First "Charm Bracelet" Conjugated Polymer: An Electroconducting polythiophene with covalently bound fullerene moieties. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 648-651

Summary

Though Buckminsterfullerene C_{60} is easily derivatized through cycloaddition/nucleophilic addition, there are still major applications waiting to be invented/discovered

Though Buckminsterfullerene C_{60} is easily derivatized, most derivatization reactions occur in moderate-to-low yield

The End

Thanks!