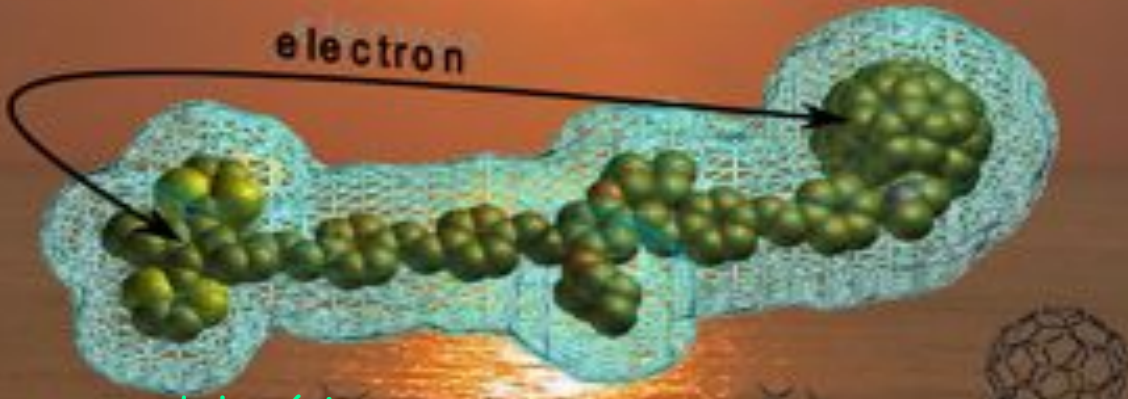




Año Internacional de la  
**QUÍMICA**  
2011

# La Química y la alta tecnología. Materiales inteligentes



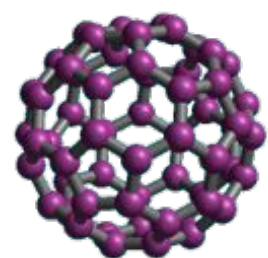
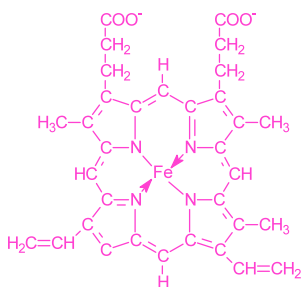
Los avances de la química y su  
impacto en la sociedad  
CSIC, Madrid  
13 de enero de 2011



## ¿Qué opinión tiene la sociedad sobre la Química?

- Aspectos positivos de la Química (tejidos, plásticos, medicamentos, etc)
- Aspectos negativos de la Química (toxicidad, contaminación atmosférica, degradación del entorno, etc)

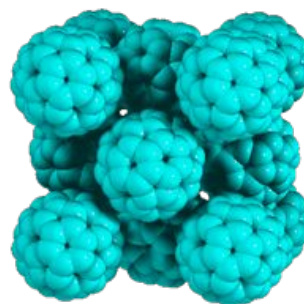
La Química NO es una ciencia popular...  
**pero las moléculas son inteligentes!!!**



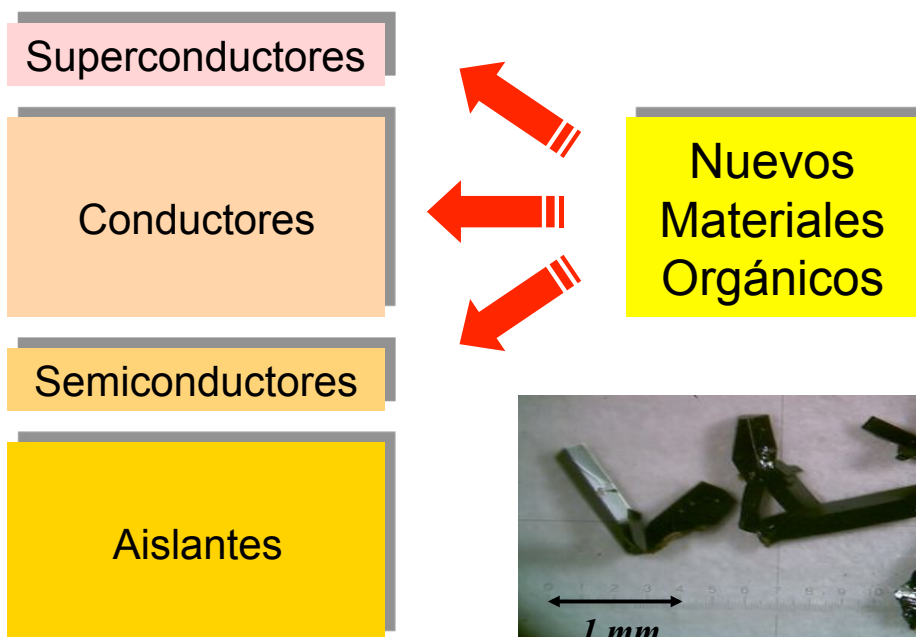


***Las moléculas pueden realizar funciones y dar lugar a propiedades no convencionales (eléctricas, ópticas, magnéticas), en los llamados nuevos materiales***

- **Introducción a los nuevos materiales orgánicos**
- **Compuestos orgánicos eléctricamente conductores**
  - *Polímeros conductores*
- *Fullerenos y nanotubos (nuevos alótropos de carbono)*
- *Células solares de plástico*

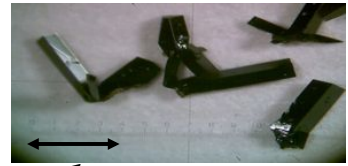
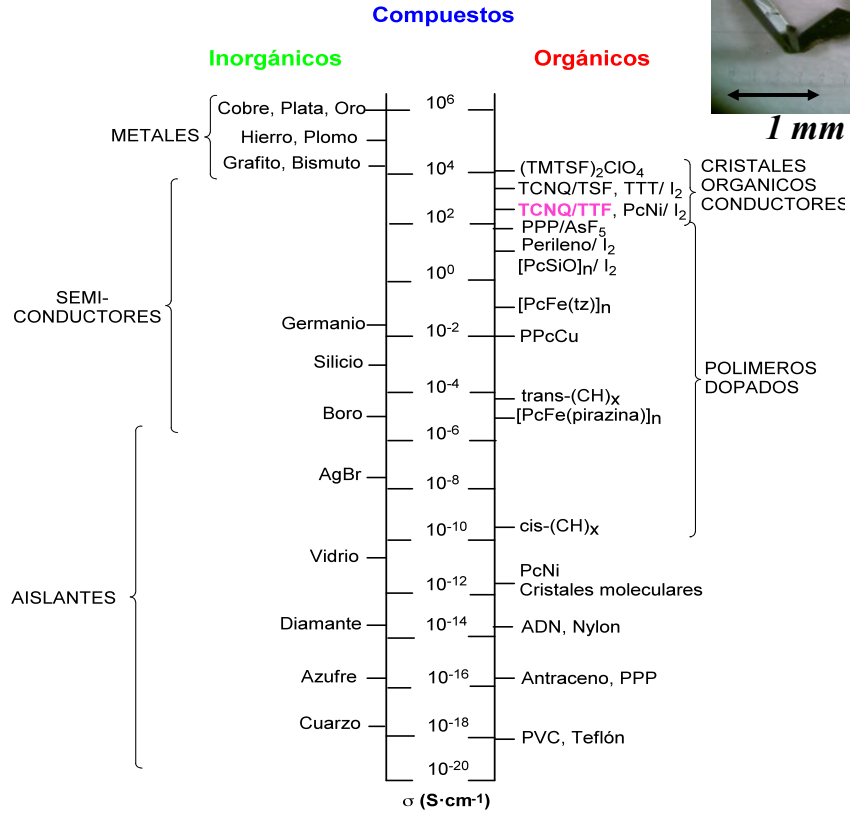


**Materiales orgánicos conductores**

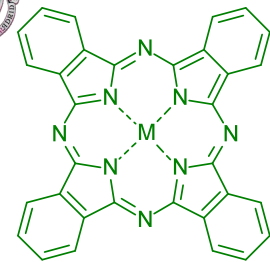




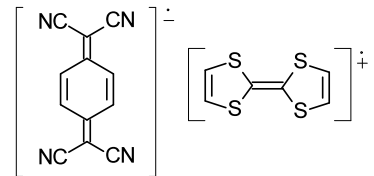
## Valores de la conductividad eléctrica



1 mm

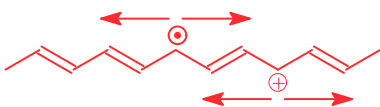


**Metalomacrociclos  
poliméricos**

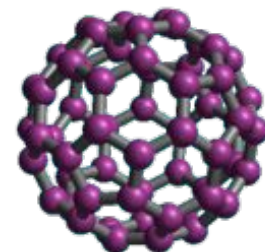


**Complejos de transferencia  
de carga (CTCs)**

**Materiales  
orgánicos  
conductores**



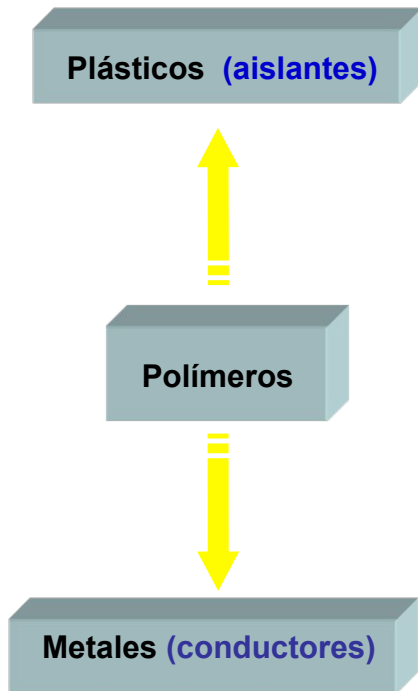
**Polímeros conjugados**



**Fullerenos**



## Polímeros conductores: un descubrimiento sorprendente!!!

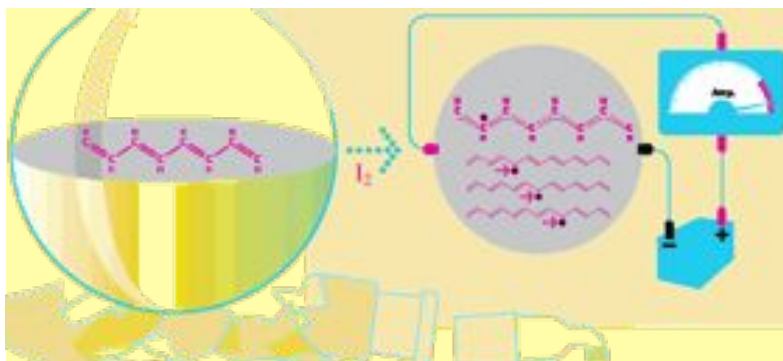


Conductores ligeros, flexibles y moldeables !!!



## Polímeros conductores

Although the polyacetylene film shone like silver, it was not an electrical conductor. Could it perhaps be modified in some way? In the mid-1970s the three Laureates began cooperating to investigate this and results were quick to come. When they caused the films to react with iodine vapour, the conductivity increased by as much as ten million times – a discovery that was eventually to give them a Nobel Prize in Chemistry.



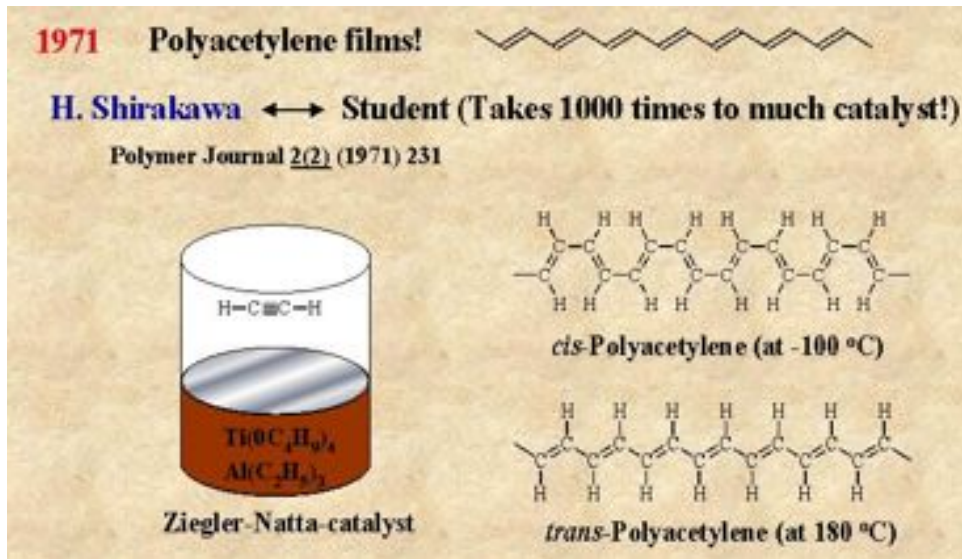
Oxidation with iodine causes the electrons to be jerked out of the polymer, leaving "holes" in the form of positive charges that can move along the chain.



**Serendipia: (serendipity, Horace Walpole, 1754) descubrimientos por accidente y sagacidad de cosas que nunca se habían planteado.**

*“En los campos de la observación, el azar favorece sólo a la mente preparada” (L. Pasteur)*

*“A menos que la mente esté concienzudamente cargada, la proverbial chispa del genio, si se llegara a manifestar, probablemente no encontraría nada que prender” (P. Flory)*

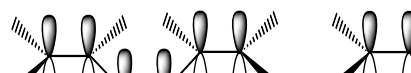
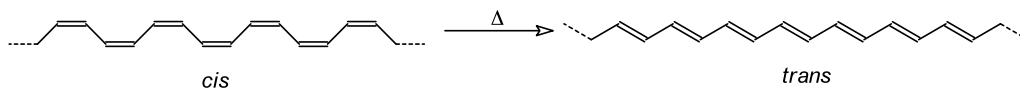


**Estereoisómeros del poliacetileno (cis-trans)**

El poliacetileno ya era conocido en los años 50 como un sólido negro infusible, insoluble e intratable!

1974. Se sintetiza poliacetileno con brillo metálico pero no conductor!!

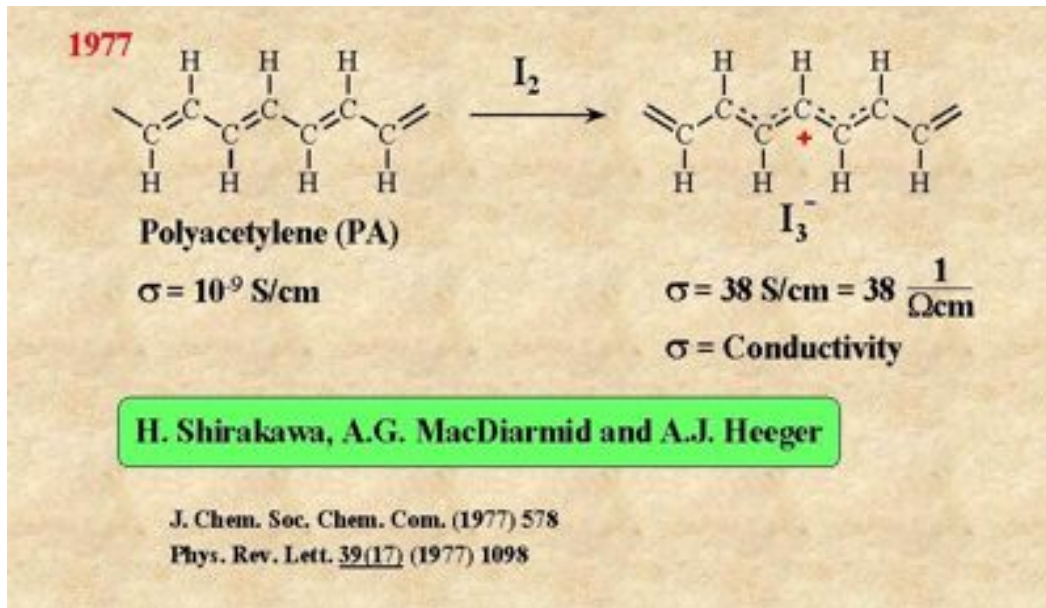
1977. Se sintetiza el primer polímero (poliacetileno) conductor!!!



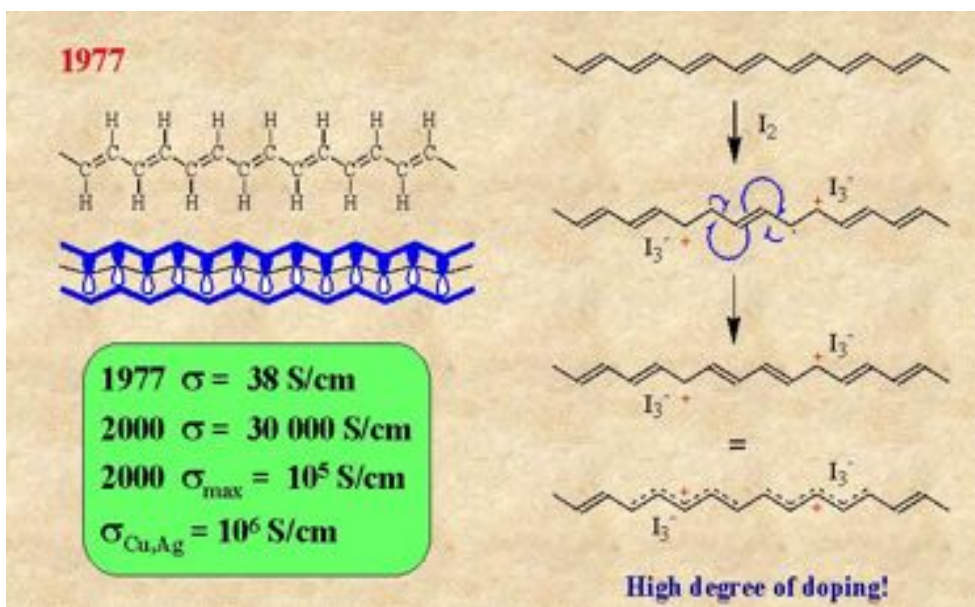




## Desarrollo de los polímeros conductores: Dopado del poliacetileno



### Formación de polarones y bipolarones





## Polímeros con estabilidad mejorada tras el dopado

1977		<b>Poliacetileno (PA)</b>
1979		<b>Poli(p-fenileno) (PPP)</b>
1979		<b>Polipirrol (PPy)</b>
1979		<b>Poli(p-fenilenvinileno) (PPV)</b>
1982		<b>Politiofeno (PT)</b>
1985		<b>Polianilina (PAni)</b>

Valores de conductividad  $10^2$ - $10^4$  S/cm



## Aplicaciones de los polímeros conductores

### Polímeros dopados

- \* Materiales antiestáticos
- \* Cubiertas anticorrosión
- \* Capacitores electrolíticos
- \* Baterías
- \* Ventanas inteligentes
- \* Sensores

### Polímeros no dopados

- \* Diodos emisores de luz
- \* Fotodiodos
- \* Células solares
- \* Láseres
- \* Materiales para ONL
- \* Sensores

# Premio Nobel de Química 2000

Por el descubrimiento y desarrollo de los polímeros conductores



Alan J. Heeger

University of California  
Santa Barbara, USA



Alan G. MacDiarmid

University of Pennsylvania  
Philadelphia, USA

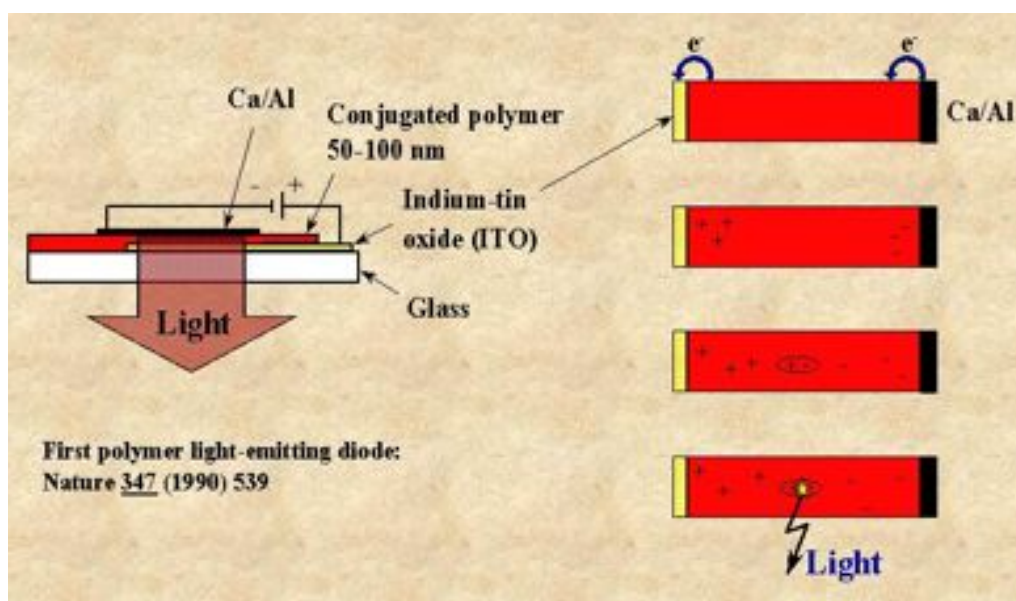


Hideki Shirakawa

University of Tsukuba,  
Japan



Electroluminiscencia

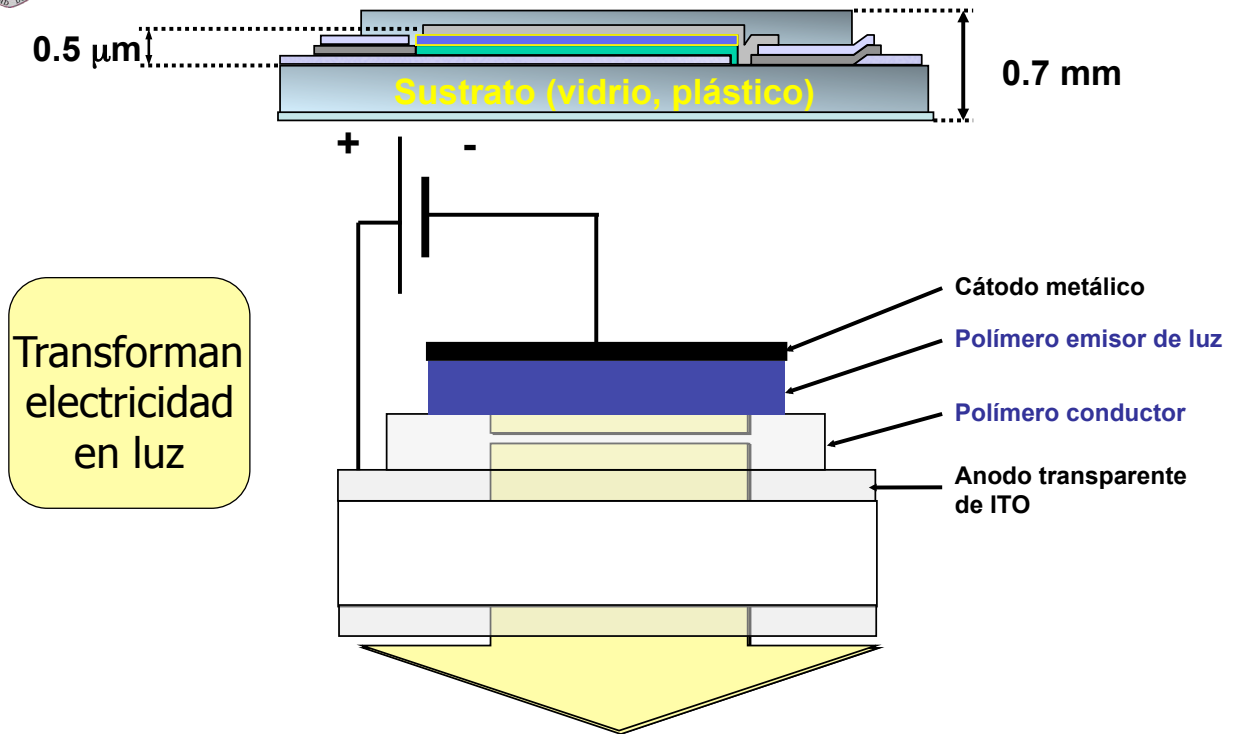


LEDs: Una aplicación de los polímeros orgánicos conductores...



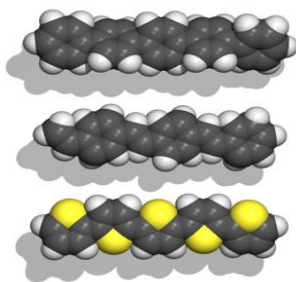


# OLEDs : Polímeros Emisores de Luz

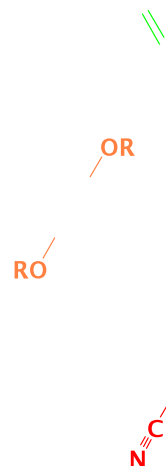


## Posibilidad de modular el color de emisión mediante la modificación de la estructura de los polímeros

Estructura química

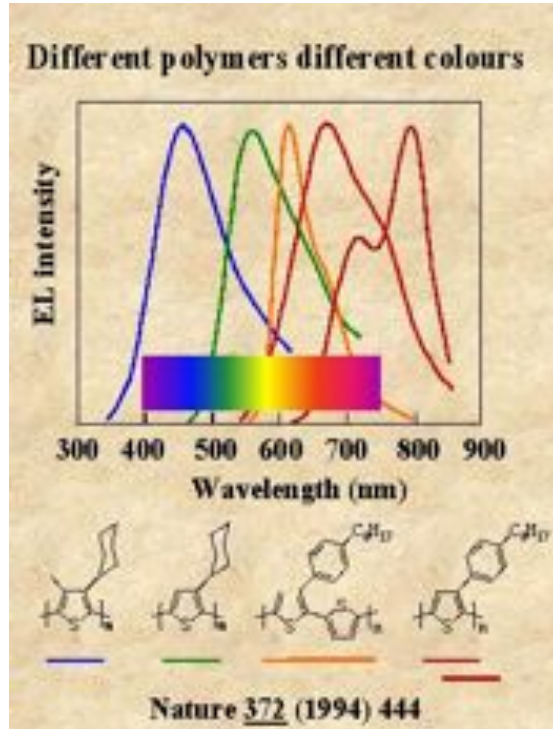


Propiedades del material

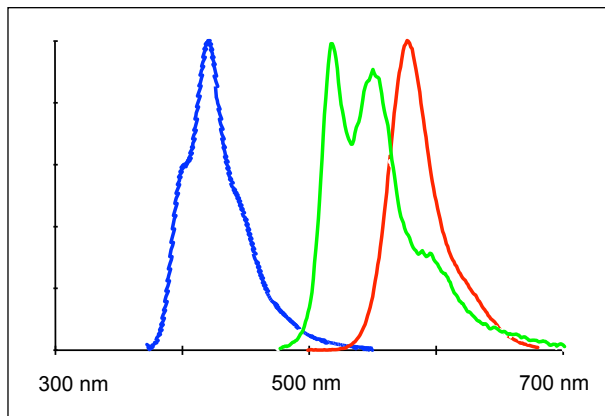




¡¡Se puede modular el color de la emisión variando la naturaleza química!!



**Posibilidad de modular el color de emisión mediante la modificación de la estructura de los polímeros**



# Otras modificaciones en la estructura del polímero emisor



## Síntesis de copolímeros



Monómeros sencillos

Mejorar la solubilidad

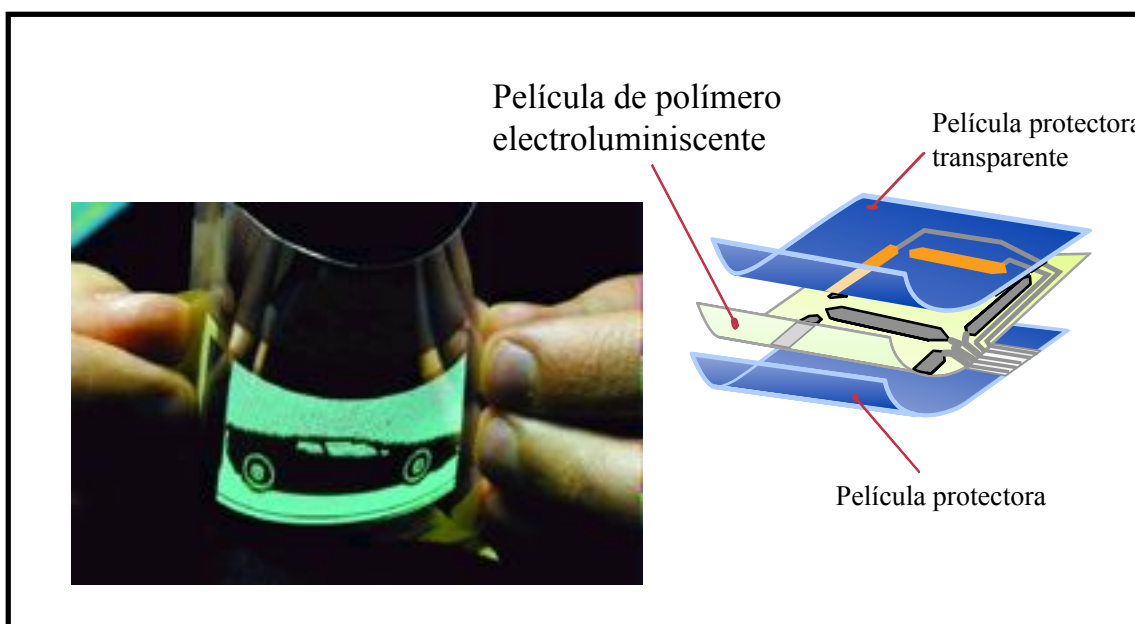
Modificar la inyección de cargas

Modular el color de emisión

## LEDs de tipo plástico



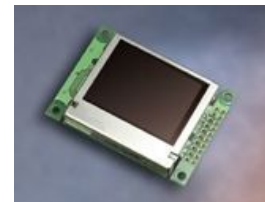
Dado que estos materiales son flexibles y robustos pueden utilizarse para la fabricación de dispositivos no planos





# Presente de los OLEDs

- Pantallas



## Productos y prototipos basados en OLEDs. El Presente



**Pioneer Monochrome OLED display 256x64 pixels (FM radio sold only in Japan)**



**Pioneer Multicolor OLED display in a AM/FM CD changer sold worldwide**



**Pioneer Multicolor OLED display in a cellphone product**

**Sanyo Color AMOLED display - 852x222 pixels (prototype, 2.5" diag.) A 5-inch QVGA has also been shown**



**Sony 13.1-inch SVGA AMOLED Prototype**



# Productos y prototipos basados en OLEDs. El Presente



Demostración de iluminación de una calle  
con OLEDs



# Productos y prototipos basados en OLEDs. El Futuro



Pantallas a todo color plegables?

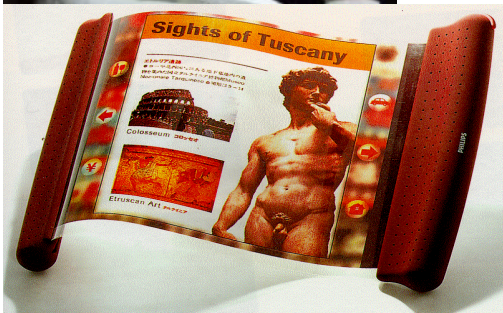






## Productos y prototipos basados en OLEDs. El Futuro

- Luz
- Pantallas



4. Dupont's Olight 4-in. diagonal active-matrix full-color OLED display is

## Productos y prototipos basados en OLEDs. El Futuro



### Philips trabaja en el desarrollo de pantallas OLED transparentes

Philips se encuentra trabajando en el desarrollo de paneles **OLED** transparentes, que podrían ser utilizados en diversas situaciones cotidianas.

Un ejemplo práctico en el que se podrían utilizar es en las ventanas de una casa, donde se podría regular la entrada de la luz solar según el grado de transparencia que tenga el panel.

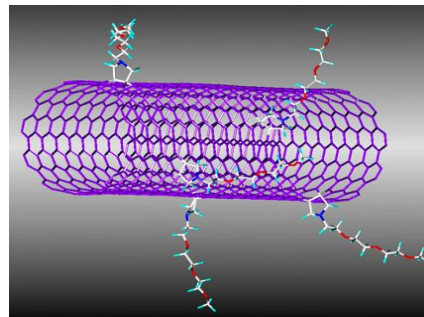
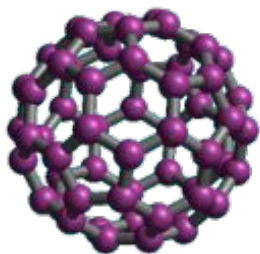
Una de las gracias que tienen estos paneles, es que poseen un bajo consumo y un alto contraste, por lo que podrían ser utilizados incluso como un nuevo sistema de iluminación.

Se espera que este tipo de paneles puedan ser utilizados en unos 3 a 5 años, tiempo en el que los investigadores deberán ir puliendo la tecnología.

## **Fullerenos para células fotovoltaicas**



## **¿Qué son los Fullerenos?**

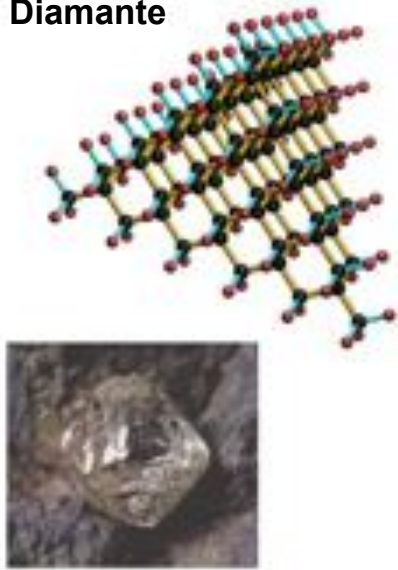


**Los Fullerenos constituyen la tercera forma  
alotrópica conocida del elemento carbono**

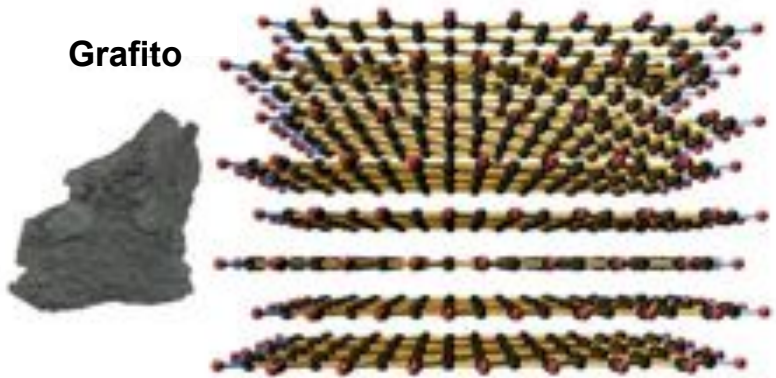


# Alótropos de carbono

**Diamante**



**Grafito**



**Buckminster Fullerenos C<sub>60</sub>**

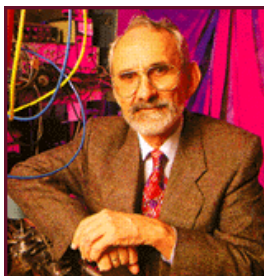


Estrictamente hablando, solo los Fullerenos están constituidos exclusivamente por carbono

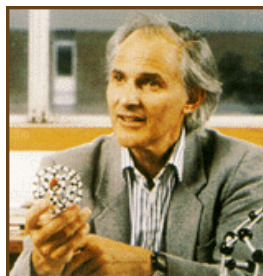


Fullerenos

**PREMIO NOBEL DE QUÍMICA 1996**  
(por el descubrimiento de los Fullerenos)



**Prof. Robert F. Curl**



**Prof. Sir Harold W. Kroto**

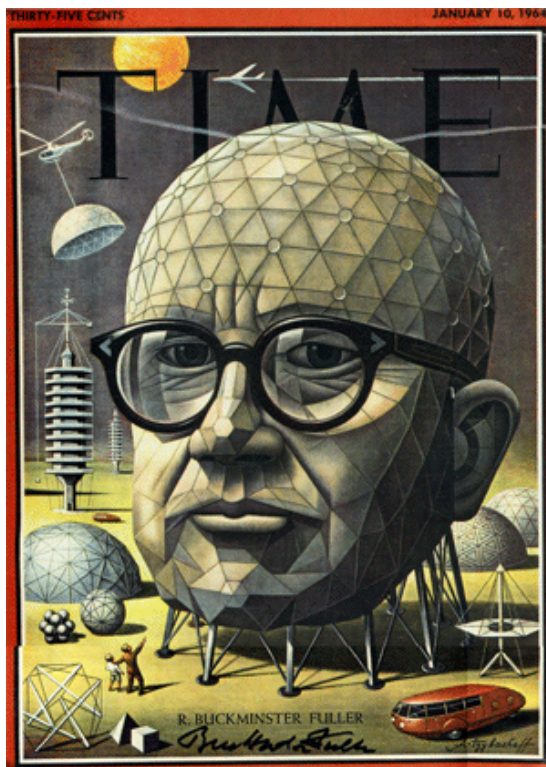


**Prof. Richard E. Smalley**



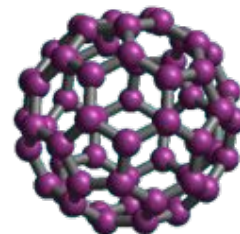


## Geodesic Dome in Montreal



*Time Magazine, Vol.83 no.2, January 10, 1964*

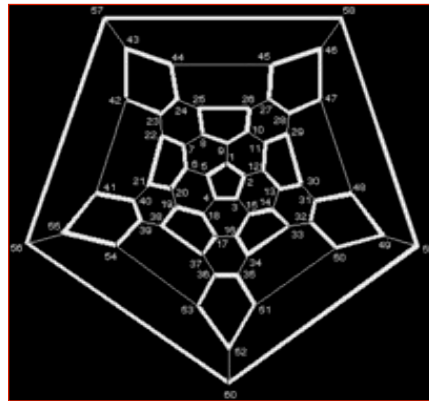
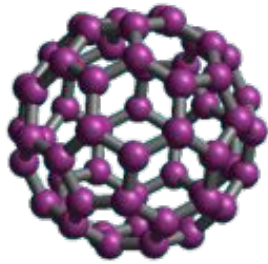
*He has been called “the first poet of technology,” “the greatest living genius of industrial-technical realization in building,” “an anticipator of the world to come, which is different from being a prophet,” “a seminal thinker,” and “an inspired child.” But all these encomiums are fairly recent. For most of his life, R. Buckminster Fuller was known simply as a crackpot.*



***He proposed that only an understanding of technology in the deepest sense would afford humans a proper guide to individual conduct and the eventual salvation of society.***



IUPAC name of [60]Fullerene

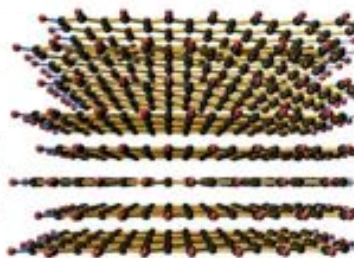


*Hentriacontacycle* [29.29.0.0.0<sup>2,14</sup>.0<sup>3,12</sup>.0<sup>4,59</sup>.0<sup>5,10</sup>.0<sup>6,59</sup>.0<sup>7,55</sup>.0<sup>8,53</sup>.0<sup>9,21</sup>.0<sup>11,20</sup>.0<sup>13,18</sup>.0<sup>15,30</sup>.0<sup>16,28</sup>.0<sup>17,25</sup>.0<sup>19,24</sup>.0<sup>22,52</sup>.0<sup>23,50</sup>.0<sup>26,49</sup>.0<sup>27,47</sup>.0<sup>29,45</sup>.0<sup>32,44</sup>.0<sup>33,60</sup>.0<sup>34,57</sup>.0<sup>35,43</sup>.0<sup>36,56</sup>.0<sup>37,41</sup>.0<sup>38,54</sup>.0<sup>39,51</sup>.0<sup>40,48</sup>.0<sup>42,46</sup>]hexaconta-1,3,5(10),6,8,11,13(18),14,16,19,21,23,25,27,29(45),30,32(44),33,35(43),36,38(54),39(51),40(48),41,46,49,52,55,57,59-triacontaene

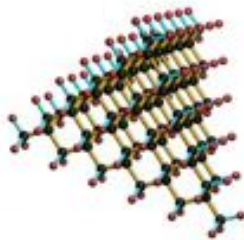
### [5,6]-Fullerene-60-I<sub>h</sub>



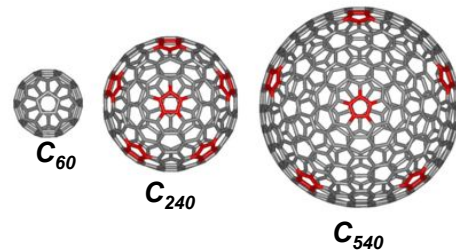
### The fascinating forms of carbon



Graphite



Diamond



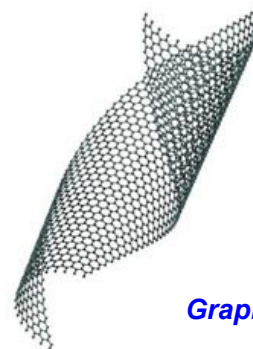
Fullerenes (1985)



Multiwall carbon Nanotubes (MWNTs; 1991)



Singlewall carbon Nanotubes (SWNTs; 1993)



Graphenes

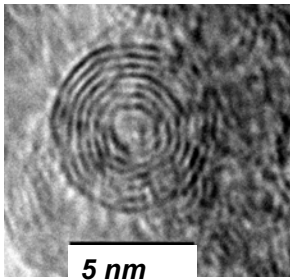
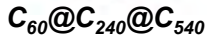
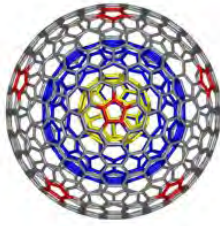
*J. Mater. Chem.* 2008, 18, 1415-1592  
Special issue on Carbon Nanostructures



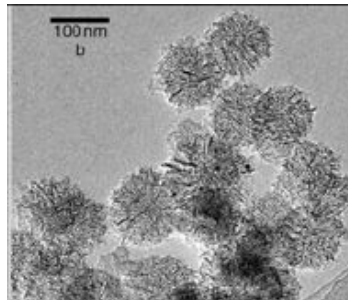


# The fascinating forms of carbon

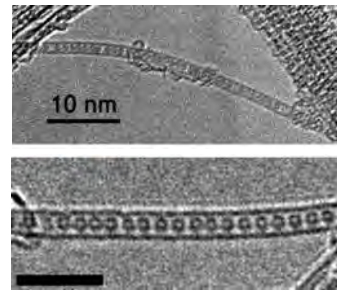
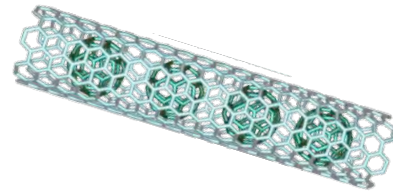
## Carbon nanonions



## Nanohorns



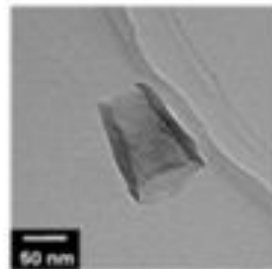
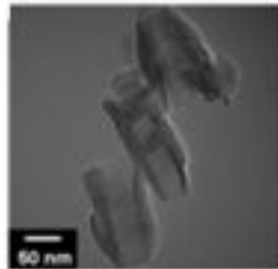
## Peapods



*"The Nanoforms of Carbon"*  
*J. Mater. Chem. 2008, 18, 1417 - 1426*



# The fascinating forms of carbon



## Nanocups

Figure 11 TEM images of reduced CSCNTs (Reprinted with permission from ref. [54b]. Copyright (2007) American Chemical Society).

## Nanotorus

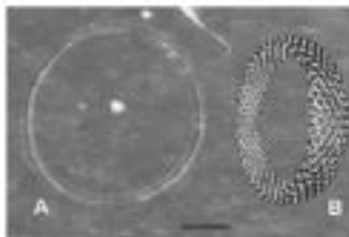


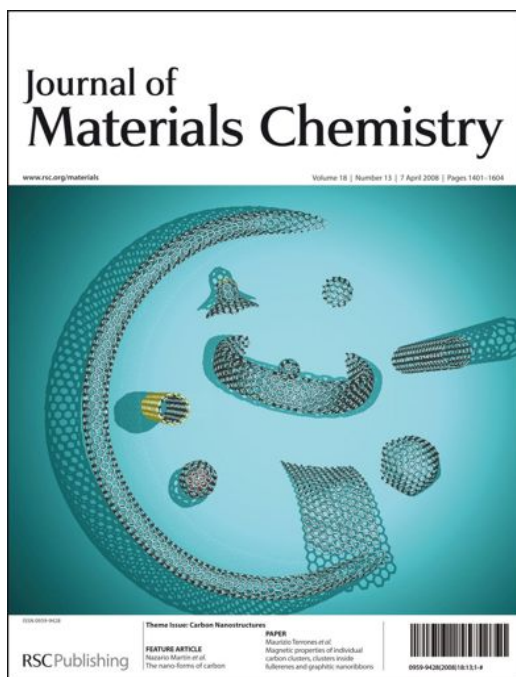
Figure 13 (A) Scanning probe micrograph of a carbon nanotorus (Reproduced from ref. 57 with permission from the Nature publishing group). (B) Computer generated image of a carbon nanotorus built without introducing the pairs of pentagons and heptagons.

## Nanobuds



Figure 14 (A) TEM observation of a Nanobud structure, with a fullerene linked to the SWCNT (Reproduced from ref. 58 with permission from the Nature publishing group). (B) Computer generated image of a [50]fullerene linked to the outer surface of the SWCNT by [2-2] cycloaddition.

*J. Mater. Chem. 2008, 18, 1417 - 1426*



Dirk M. Guldi



Nazario Martin



Maurizio Prato

Journal of  
Materials Chemistry

**Theme issue: Carbon Nanostructures J. Mater. Chem. 2008, 18, 1415-1592**



## Producción de Fullerenos

- Vaporización con láser y expansión supersónica
- Descarga de arco eléctrico en atmósfera inerte
- Síntesis de Fullerenos en combustiones
- Fullerenos formados naturalmente

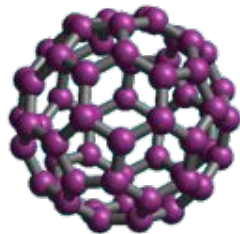


Becker et al. Science 265 (1994) 642





¿Qué propiedades tienen los fullerenos?



**Fullerenes: Superbencenos o superpolienos?**





# Isolated Pentagon Rule

In all of the fullerenes synthesized so far, each pentagon is surrounded by hexagonal rings. Indeed, this has been proposed as a criterion for fullerene stability-the 'isolated-pentagon rule'-on the basis that adjacent pentagons are expected to be chemically reactive.

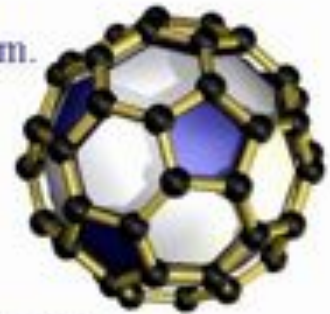
$C_{60}$  is the smallest fullerene that fulfills the IPR

$C_{70}$  is the next larger one

For both molecules exists only one isomeric IPR form.

Larger fullerenes exhibit several IPR isomers:

$C_{78} : 4, C_{80} : 7, C_{82} : 9, C_{88} : 35$

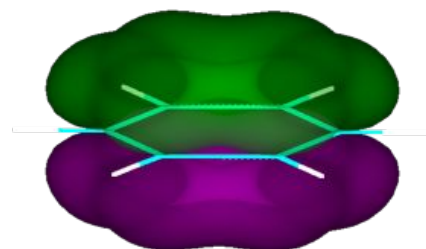
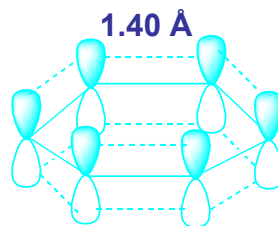
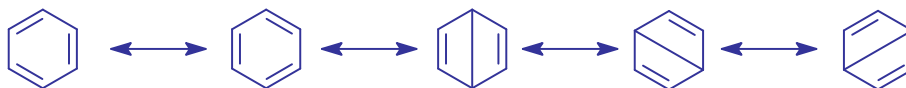


Petrie et al. *Nature* **365** (1993) 426

Fowler et al. *The Fullerenes* (eds. H. Kroto et al.) Pergamon Press, Oxford (1993) 97

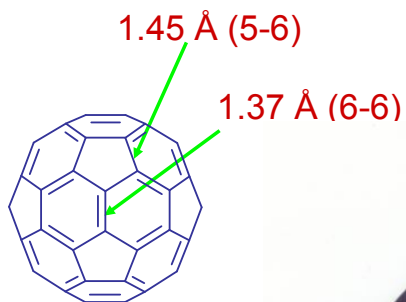
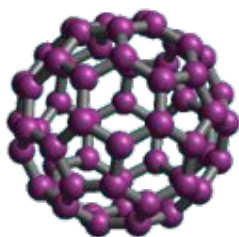


## Aromaticidad en el Benceno





## Propiedades físicas del C<sub>60</sub>



$$\Delta H_f^\circ = 545 \text{ Kcal/mol}$$

$$\rho = 1.78 \text{ g/cc}$$

$$\chi = -260 \text{ cgs ppm}$$

Sublima por encima de 500 °C a  $10^{-7}$  torr

Alternancia de enlaces: 1.37 y 1.45 Å



The beginning ...  
(Resembling the attitude of a scientist in front of the new Fullerene ball)

Today...  
(A good control on the basic concepts)







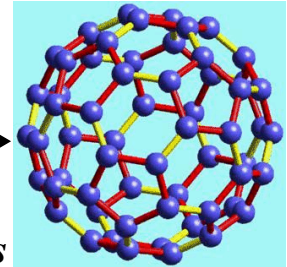
Size



→  
*100  
millions*



→  
*100  
millions*



*d ~ 1 nm*

*An appropriate molecule for the development of nanoscience and nanotechnology but still looking for real applications...*

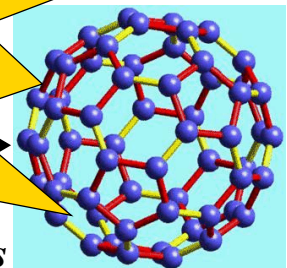


Size



**Photovoltaics  
represents one of the  
most realistic  
applications of  
Fullerenes !!!**

→  
*100  
millions*



*d ~ 1 nm*

*An appropriate molecule for the development of nanoscience and nanotechnology but still looking for real applications...*



## Renewable Energies

**elmundo.es** Ciencia y ecología

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**S.O.S. Cambio climático**

La UE acuerda que el 20% de su consumo en 2020 proceda de energía renovable

**ABC.es**

La UE acuerda que el 20% del consumo en 2020 proceda de energías renovables

**TIMESONLINE**

Europe agrees to embrace nuclear option in battle to save the planet

EU agrees renewable energy target

European Union leaders have agreed to adopt a binding target on the use of renewable energy, such as wind and solar power, officials say.

**la Repubblica.it** Ambiente

**DAL 27 APRILE AL CINEMA**

**Intesa europea su energia e clima rinnovabili obbligatorie, si al nucleare**

**LE FIGARO.fr**

L'Europe se met à l'énergie renouvelable

Les États membres s'engagent à réduire de 20 % leurs émissions de gaz à effet de serre d'ici à 2020.

**EL PAIS plus**

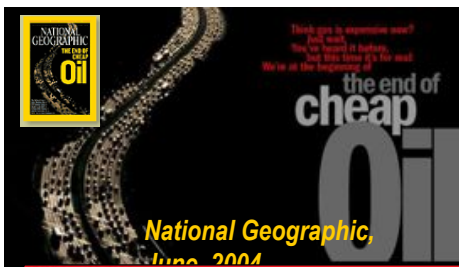
La UE logra un acuerdo histórico que fija el uso de energías limpias en un 20% en 2020

**BBC NEWS**

EU agrees renewable energy target

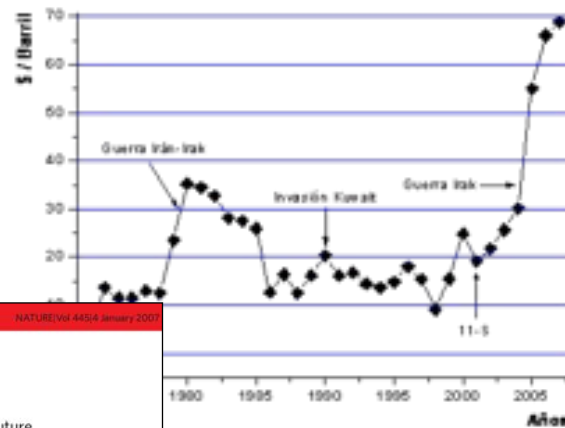


## Renewable Energies



**That's oil, folks...**

Optimists see oil gushing for decades; pessimists see the planet's energy future already drying up. **Alexandra Witze** reports.







# Renewable Energies



**Biomass**



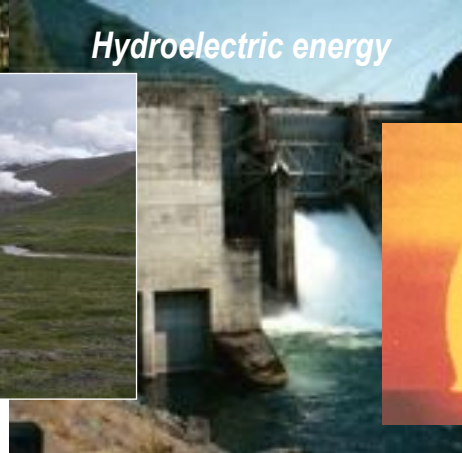
**Eolic energy**



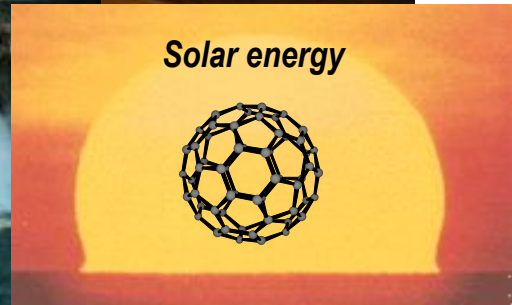
**Hydroelectric energy**



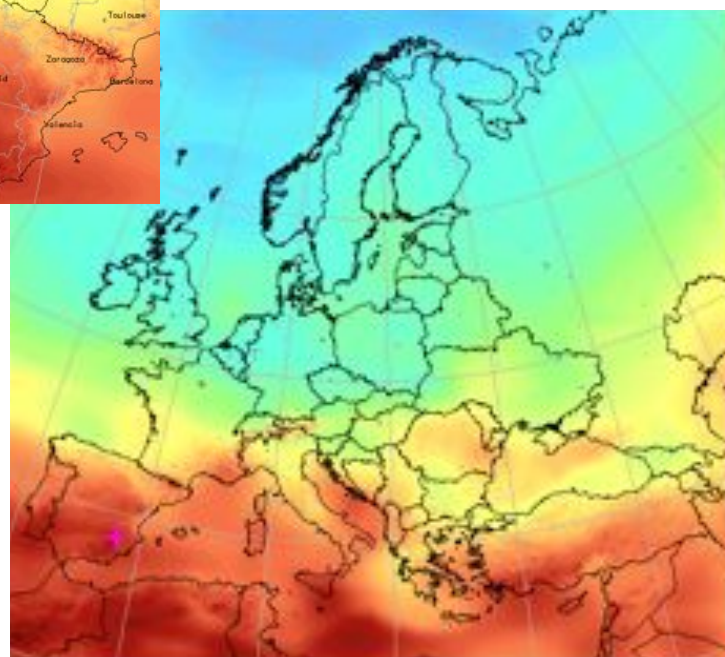
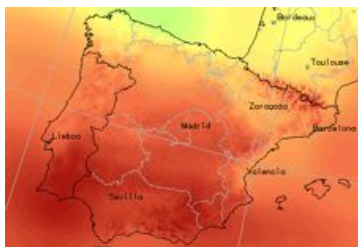
**Geothermal energy**



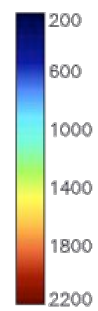
**Solar energy**



**Solar Map**

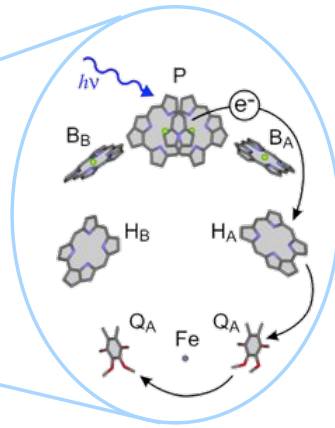
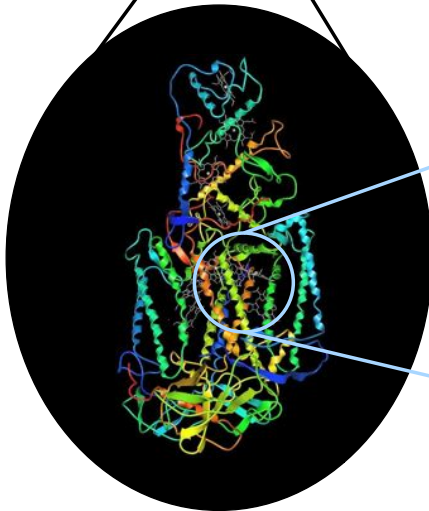
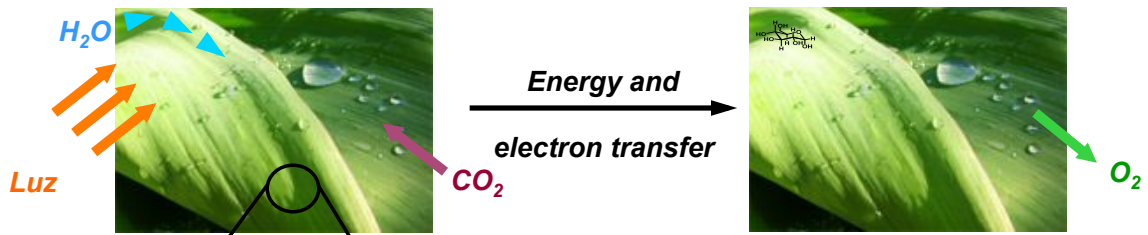


Yearly global irradiation [kWh/m<sup>2</sup>]

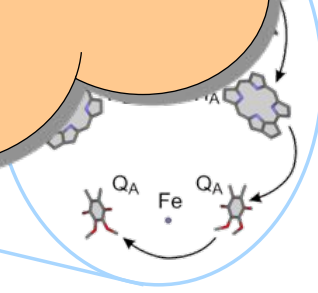
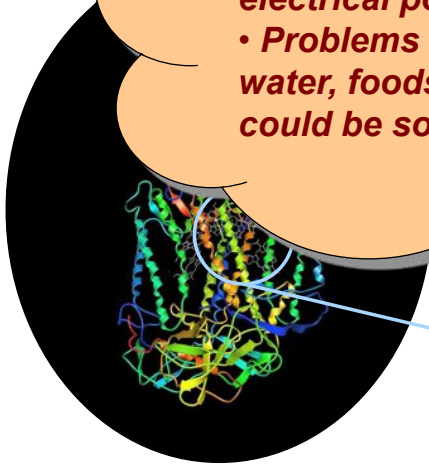
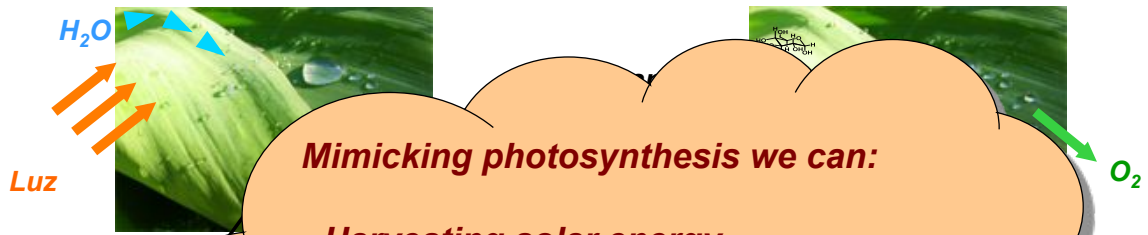




### Photosynthesis



### Photosynthesis

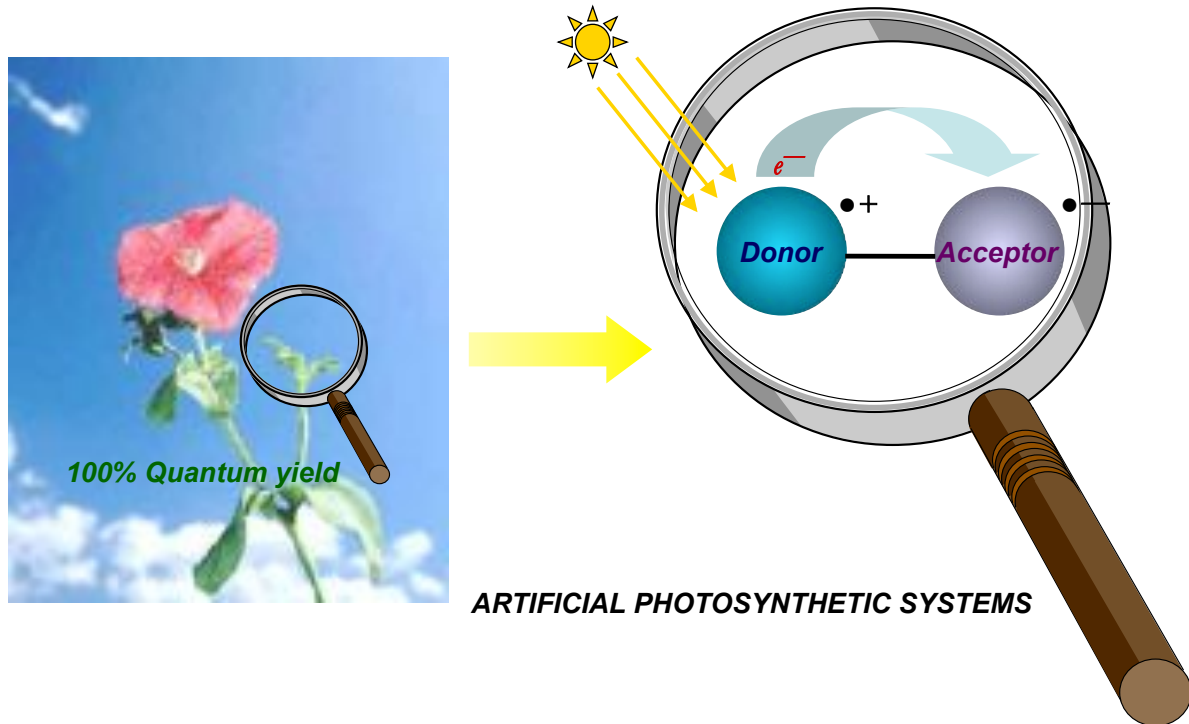


**Mimicking photosynthesis we can:**

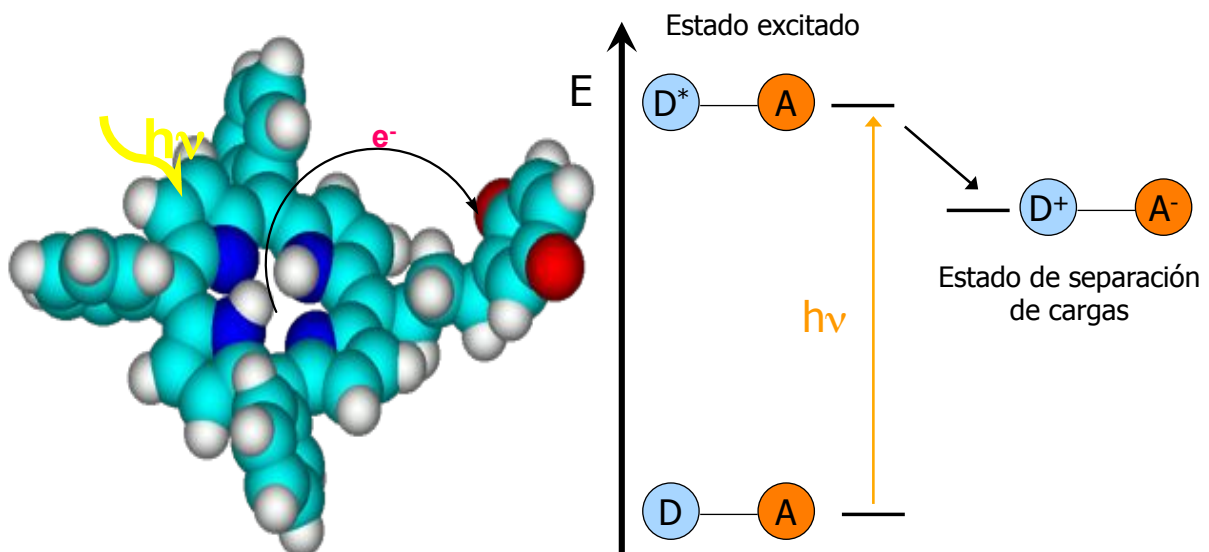
- Harvesting solar energy
- Transform it into chemical or electrical power
- Problems such as lack of energy, water, foods, environment etc could be solved...



## Photoinduced Electron Transfer (PET)



## Las molécula imitan el proceso de la Fotosíntesis. Transferencia electrónica fotoinducida

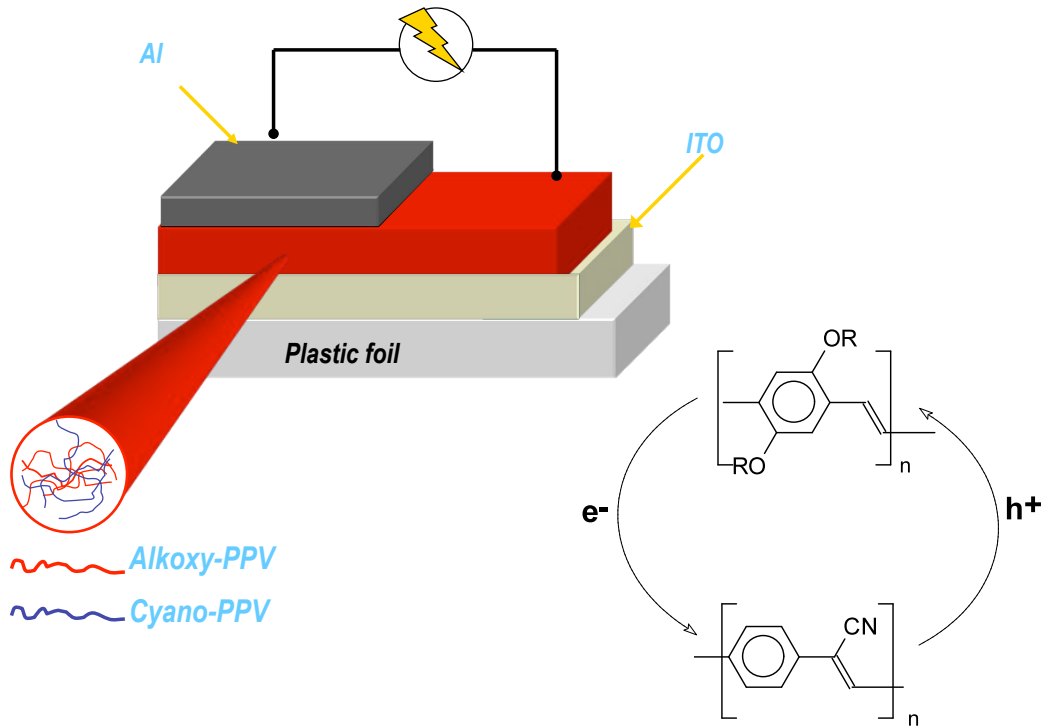






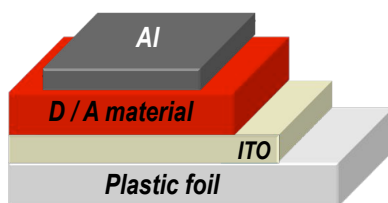
## Types of organic solar cells (II)

### d) Bulk heterojunction. Conducting polymers

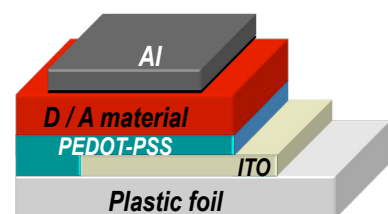


## Fabrication of PV devices (I)

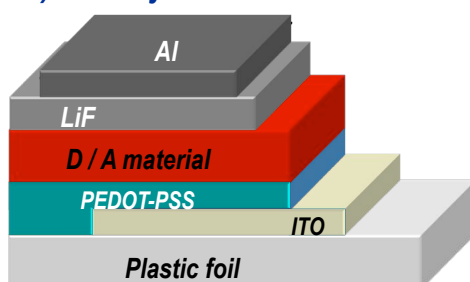
### a) Three layers



### b) Four layers



### c) Five layers

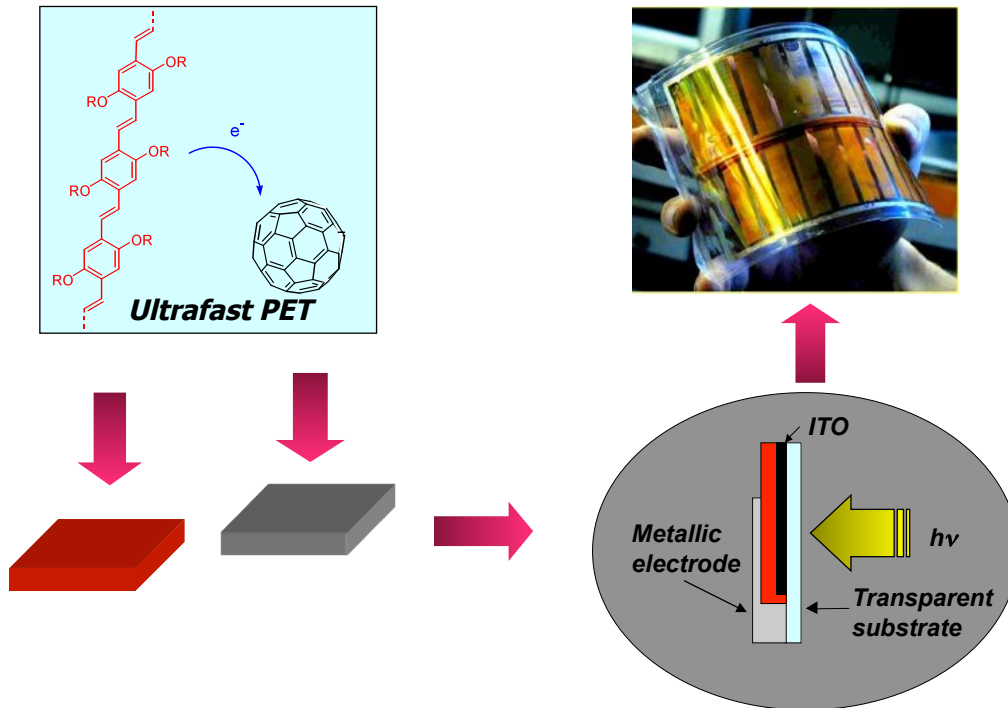


- PEDOT:PSS. Improves the contact in the interface between the active phase and the ITO electrode

- LiF. Makes unlikely that recombination of charges happen after charge transfer



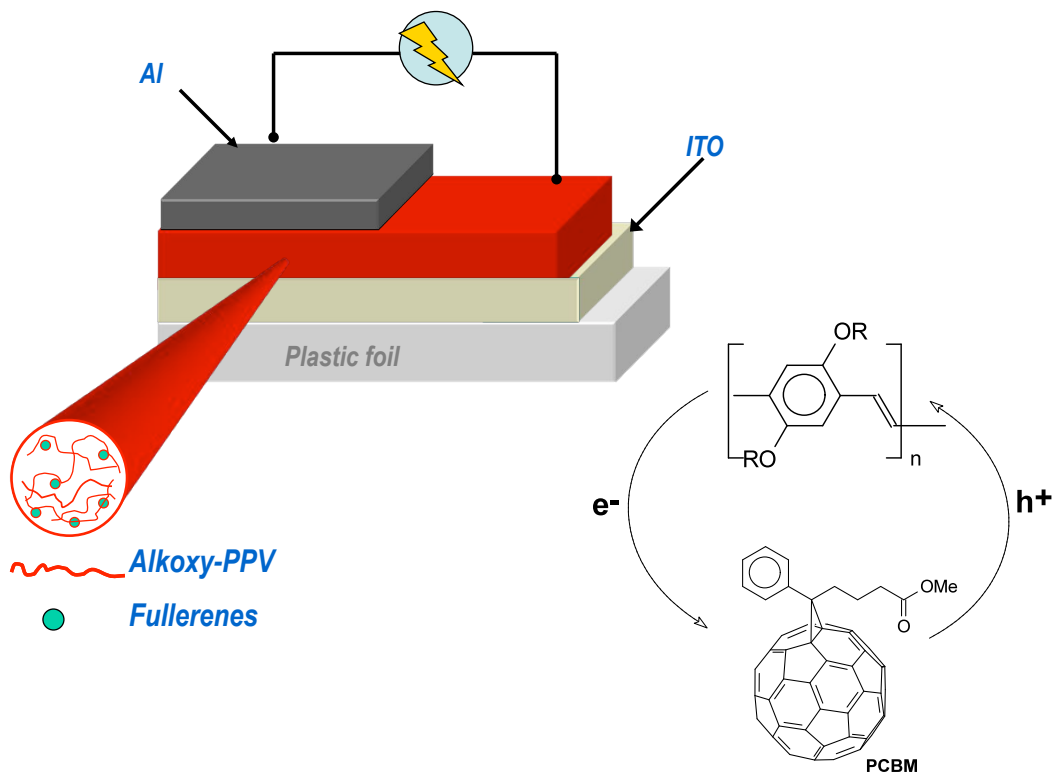
## Plastic Organic Solar Cells



F. Wudl, A. Heeger et al. *Science*, 1992



### Bulk heterojunction. Conducting polymer as donor and C<sub>60</sub> as acceptor



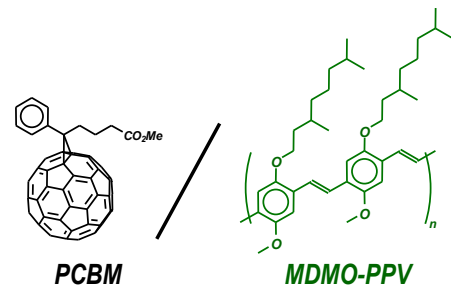


## Bulk heterojunction. Conducting polymer as donor and C<sub>60</sub> as acceptor

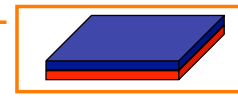
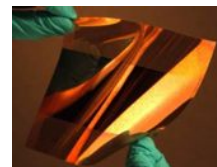


- Inorganic PV devices show  $\eta$  of around 30 %
- Organic PVs show a better mechanic flexibility and lower production costs.

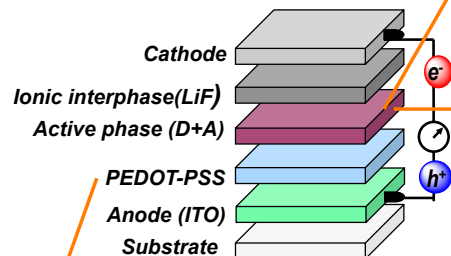
$\eta = 2.5 \%$



## Architecture of an organic solar cell



p-n heterounion



Transparent by doping and  $E_{HOMO} - E_{HOMO(D)}$



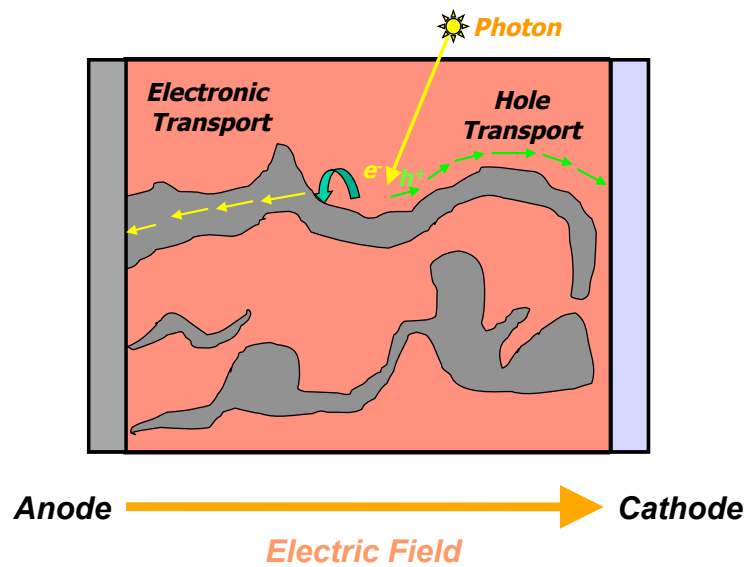
Bulk heterojunction (BHJ)

C. J. Brabec et al. *Adv. Funct. Mater.* 2001, 11, 15;  
S. Günes et al. *Chem. Rev.* 2007, 107, 1324

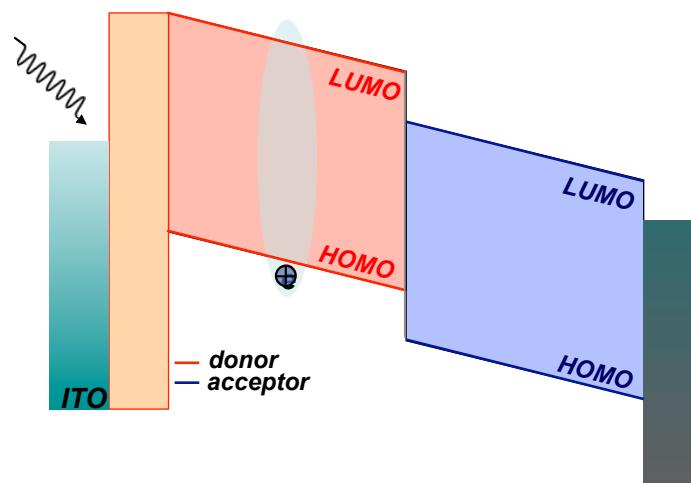


# Organic Solar Cells: How does it work?

## Bulk-Heterojunction Diodes



## Efecto PV en heterounión



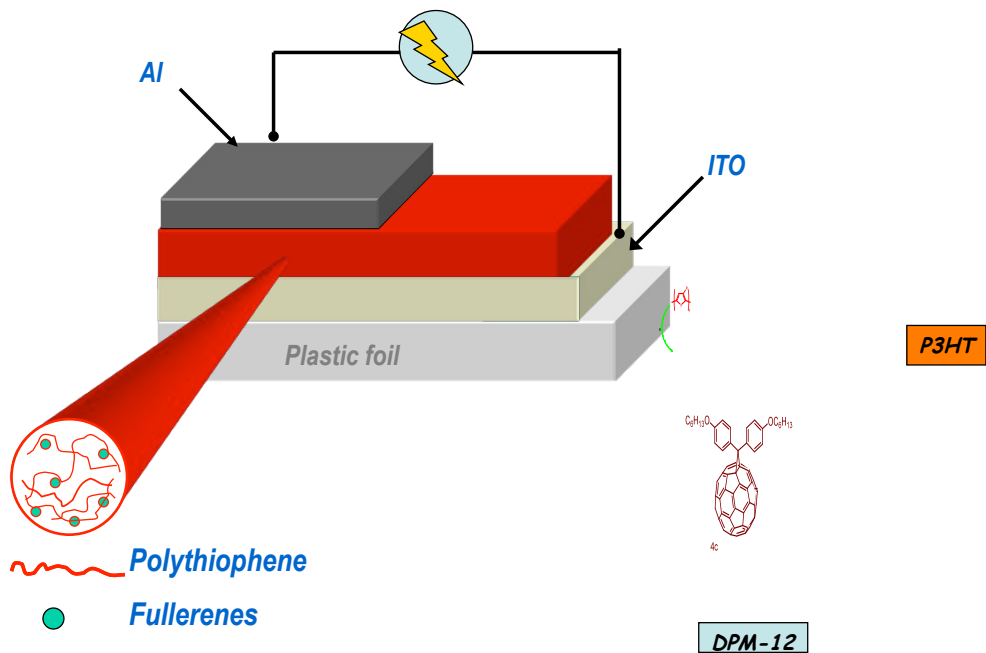
### ✦ Efecto fotovoltaico en heterounión p-n

- Absorción de luz
- Formación del excitón y transferencia electrónica
- Movilidad de los transportadores de carga





## Bulk heterojunction. Conducting polymer as donor and C<sub>60</sub> as acceptor



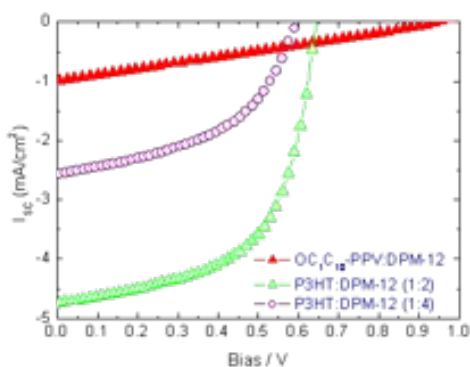
Adv. Funct. Mater. 2005, 15, 1979



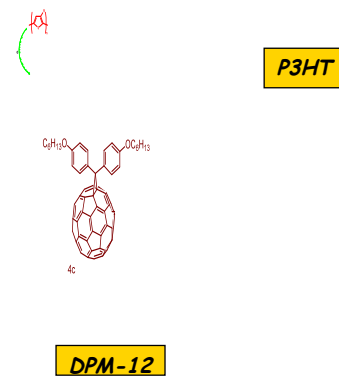
## Photovoltaic cells from DPM-12: Optimization studies

Material	$J_{SC}$ [mA cm <sup>-2</sup> ]	$V_{OC}$ [V]	FF	$\eta_{AM1.5}$ [%] <sup>a</sup>
MDMO-PPV:DPM12 (1:4)	1.3	0.96	0.28	0.3
MDMO-PPV/PCBM (1:4)	4.17	0.83	0.52	2.28
P3HT:DPM-12 (1:4)	2.55	0.60	0.49	0.95
<b>P3HT:DPM-12 (1:2)</b>	<b>4.74</b>	<b>0.65</b>	<b>0.58</b>	<b>2.3</b>
P3HT/PCBM (1:2)	6.5	0.55	0.50	2.2

<sup>a</sup> at 78 mW/cm<sup>2</sup> white light intensity



Energy Conversion Efficiency of 2.3%



Adv. Funct. Mater. 2005, 15, 1979



**The future of organic solar cells?**

**Silicon photovoltaic solar cells**





*Physicist who works with chemicals, at the end of the day*

*Synthetic chemists at the end of the day*





*En cualquier caso, las moléculas son las protagonistas. Cuando sean consideradas por la sociedad en su justa medida, la química perderá su mala imagen y podrá ser reconocida como una forma más de expresión de la creatividad humana.*

