Sistemas no convencionales para procesos fotoquímicos de oxidación

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1ª Jornada Técnica sobre Oxidación Avanzada en el Tratamiento de Aguas, UJI, 15 enero 2016

1. **Principios de fotocatálisis**
2. **Fotocatálisis con polímeros orgánicos**
3. **Desarrollos en Universitat Jaume I**

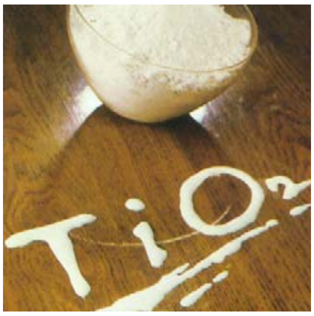
Catálisis

Reactivos + catalizador + energía → Productos + catalizador

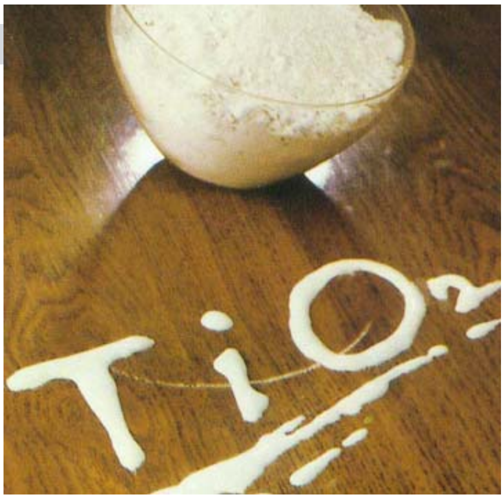
Fotocatálisis

Reactivos + fotocatalizador + luz → Productos + fotocatalizador

⇩



⇦ Perspectiva Inorgánica vs Orgánica ⇨



Semiconductores inorgánicos

Aplicaciones ambientales:

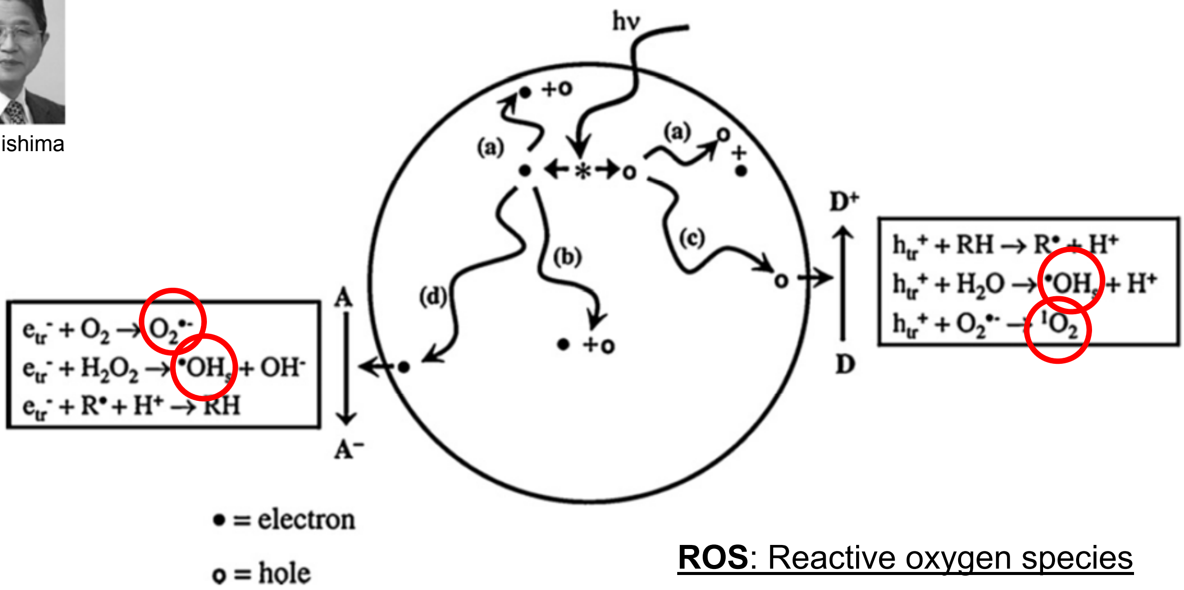
S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco, W. Gernjak. **Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends**. *Catal. Today*, **2009**, *147*, 1-59.

D. Spasiano, R. Marotta, S. Malato, P. Fernandez-Ibañez, I. Di Somma. **Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach**. *Appl. Catal. B: Environmental* **2015**, *170-171*, 90–123.

Aspectos fundamentales:

T. Ochiai, A. Fujishima, **Photoelectrochemical properties of TiO_2 photocatalyst and its applications for environmental purification**, *J. Photochem. Photobiol. C: Photochem. Rev*. **2012**, *13* 247-262.

A. Fujishima



ROS: Reactive oxygen species

Radical hidroxilo **·OH**
Radical-anión superóxido **$O_2^{\cdot -}$**
Oxígeno singlete **$^1O_2$**

T. Ochiai, A. Fujishima / Journal of Photochemistry and Photobiology C: Photochemistry Reviews 13 (2012) 247–262

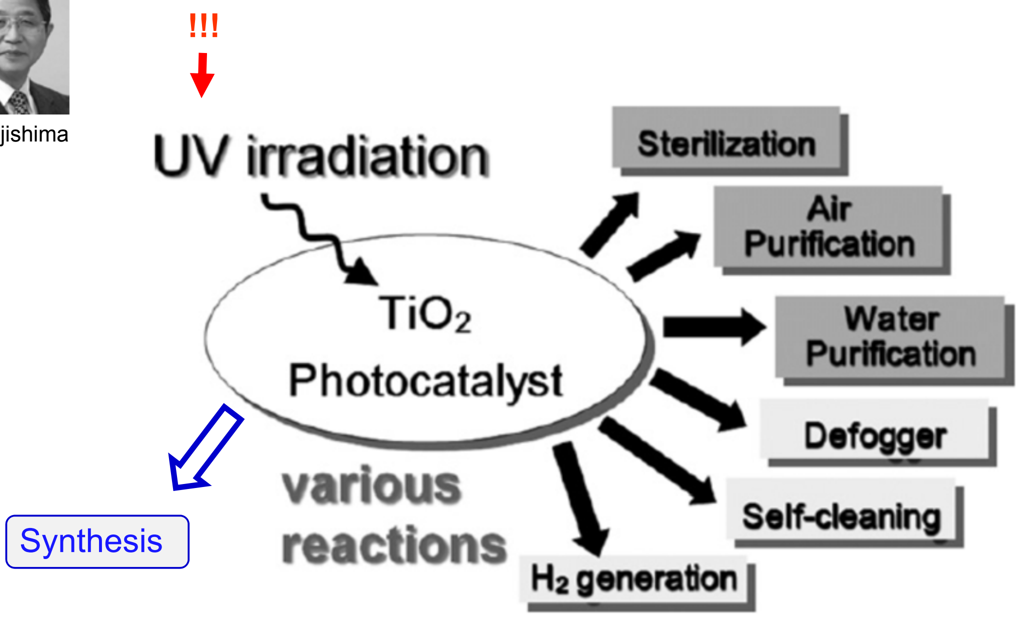
TABLE 1. Average Concentrations of ROS Generated by Different Metal Oxides under UV Irradiation

particles		•OH (μM)	¹O₂ (μM)	$O_2^{\cdot -}$ (μM)	total (μM)
TiO_2	NPs	19.3 ± 0.8	417.3 ± 18.8	8.0 ± 0.4	442.9 ± 20.0
	bulk	4.9 ± 0.2	N.D.[a]	N.D.	4.9 ± 0.2
CeO_2	NPs	N.D.	N.D.	8.4 ± 0.2	8.4 ± 0.2
	bulk	N.D.	N.D.	N.D.	0
SiO_2	NPs	N.D.	56.5 ± 2.5	N.D.	56.5 ± 2.5
	bulk	N.D.	N.D.	N.D.	0
Al_2O_3	NPs	N.D.	158.5 ± 8.0	N.D.	158.5 ± 8.0
	bulk	N.D.	N.D.	N.D.	0
ZnO	NPs	9.5 ± 0.6	100.8 ± 6.4	167 ± 8.6	277.3 ± 15.6
	bulk	1.9 ± 0.1	N.D.	81.8 ± 0.3	83.7 ± 0.4
CuO	NPs	N.D.	N.D.	N.D.	0
	bulk	N.D.	N.D.	N.D.	0
Fe_2O_3	NPs	2.3 ± 0.1	N.D.	18.1 ± 1.1	20.4 ± 1.2
	bulk	N.D.	N.D.	N.D.	0

[a] N.D. indicates that ROS were not detected or were not statistically significant.

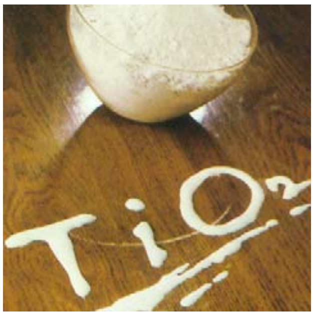
Y. Li, W. Zhang, J. Niu, Y. Chen., *ACS Nano* **2012**, *6*, 5164-5173

A. Fujishima



T. Ochiai, A. Fujishima / Journal of Photochemistry and Photobiology C: Photochemistry Reviews 13 (2012) 247–262

Sistemas no convencionales para oxidación fotoquímica



Perspectiva
⇦ Inorgánica vs Orgánica ⇨

S. Malato (ed.), P. Fernández-Ibáñez (ed), I. Poulios (ed.), D. Mantzavinos (ed.). Número especial, *Catal. Today* **2015**, 252. **8th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, SPEA8, Thessaloniki, 2014**.

D. Mantzavinos (ed.)., I. Poulios (ed.), P. Fernández-Ibáñez (ed), S. Malato (ed.), Número especial, *Catal. Today* **2015**, 240A. **Environmental Applications of Advanced Oxidation Processes – EAAOP3, Almería, 2013.**

¿No hay fotocatalizadores orgánicos?

CHEMICAL REVIEWS

REVIEW

pubs.acs.org/CR

Organic Photocatalysts for the Oxidation of Pollutants and Model Compounds

M. Luisa Marin,[†] Lucas Santos-Juanes,[‡] Antonio Arques,[‡] Ana M. Amat,[‡] and Miguel A. Miranda*[,†]

[†]Instituto Universitario Mixto de Tecnología Química-Departamento de Química (UPV-CSIC), Avda. de los Naranjos s/n, E-46022, Valencia, Spain

[‡]Departamento de Ingeniería Textil y Papelera, Universidad Politécnica de Valencia, Campus de Alcoy, Plaza Ferrándiz y Carbonell s/n, E-03801 Alcoy, Spain

Chem. Rev. 2012, 112, 1710–1750

251 referencias

Ventaja de los fotocatalizadores orgánicos: absorben luz visible

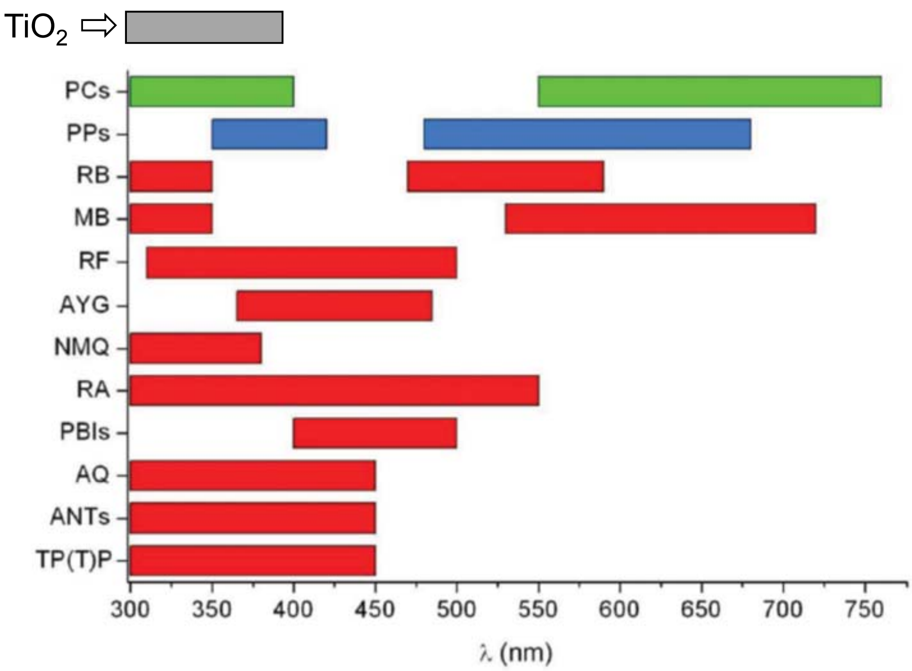


Figure 1. Typical absorption ranges of the organic photocatalysts in the UVB−UVA−vis range.

Chem. Rev. 2012, 112, 1710–1750

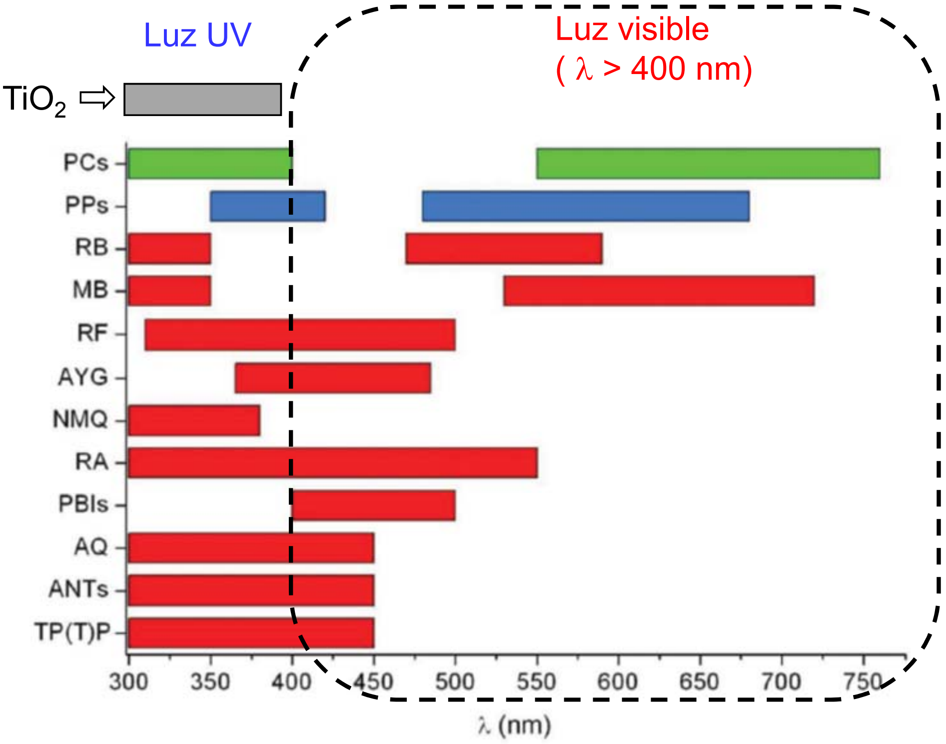
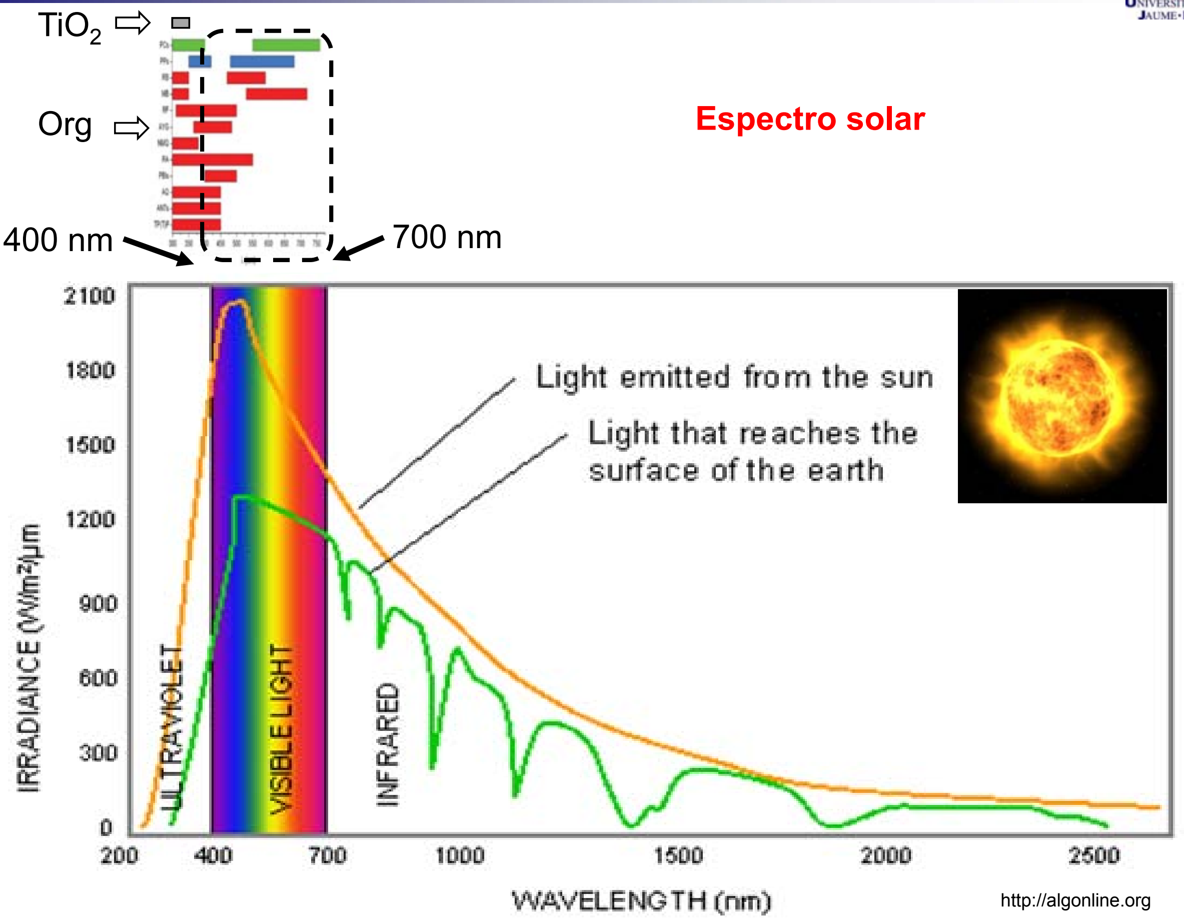


Figure 1. Typical absorption ranges of the organic photocatalysts in the UVB−UVA−vis range.

Chem. Rev. 2012, 112, 1710–1750

Sistemas no convencionales para oxidación fotoquímica



Aprovechamiento luz **VISIBLE** del espectro solar

Nuevos materiales

TiO_2 dopado con metales
Híbridos TiO_2-grafeno
WO_3
$BiVO_4$
$BiWO_6$
Fe_2O_3
Ag_3PO_4
CdS
CdSe
AuNPs
In_2S_3
Fotosensibilizadores orgánicos

Más sobre nuevos materiales inorgánicos para aprovechamiento de luz visible:

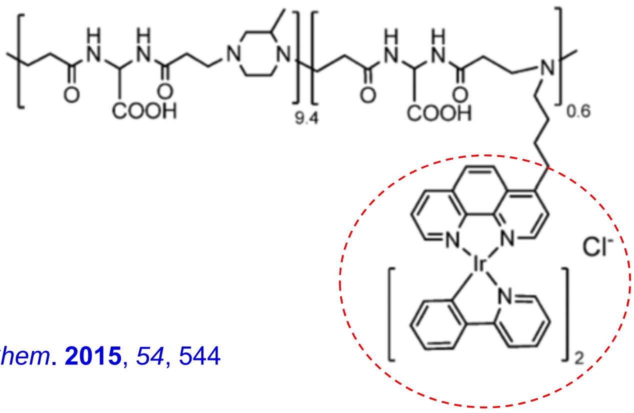
- N. Gao, X. Fang, *Chem. Rev*. **2015**, *115*, 8294-8343
- M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari, D. D. Dionysiou, *Appl. Catal. B: Env*. **2012**, *21*, 331-349
- C. Chatterjee, S. Dasgupta, *J. Photochem. Photobiol.C: Photochem. Rev.* **2005**, *6*, 186-205

Algunos fotosensibilizadores orgánicos SOPORTADOS

Antecedente histórico:
E. C. Blossey, D. C. Neckers (Univ. New Mexico)
A. L. Thayer, A. P. Schaap (Wayne State Univ.)
Polymer-based sensitizers for photooxidations
J. Am. Chem. Soc. **1973**, 95, 5820-5822

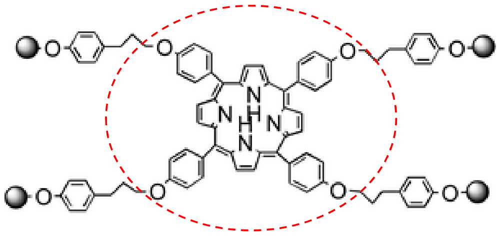
D. C. Neckers

Más recientes:



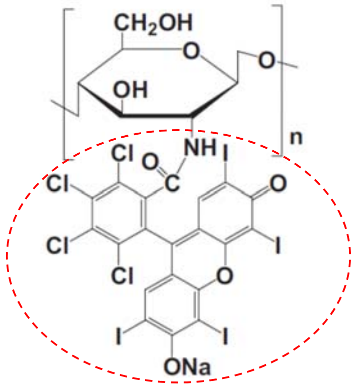
D. Maggioni et al. *Inorg.Chem*. **2015**, *54*, 544

M. Benaglia et al. *Org. Lett.* **2002**, *4*, 4229

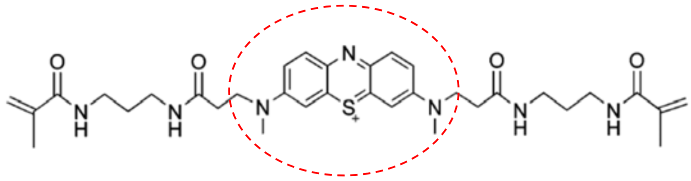


= MeO-$(CH_2CH_2O)_n$-CH_2CH_2, M_w 750 or 2000 daltons

G. V. Ferrari et al. *Photochem. Photobiol.* **2014**, *90*, 1216

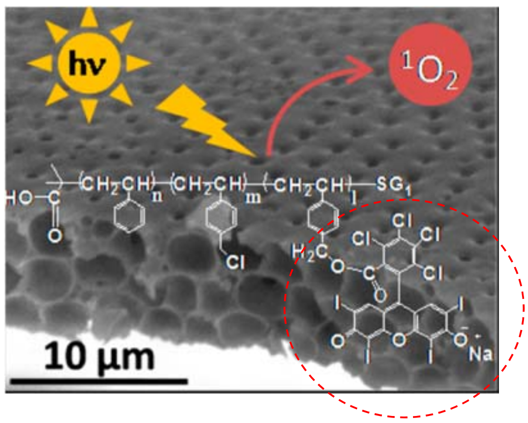


M. Quin et al. *Photochem. Photobiol. Sci.* **2011**, *10*, 832

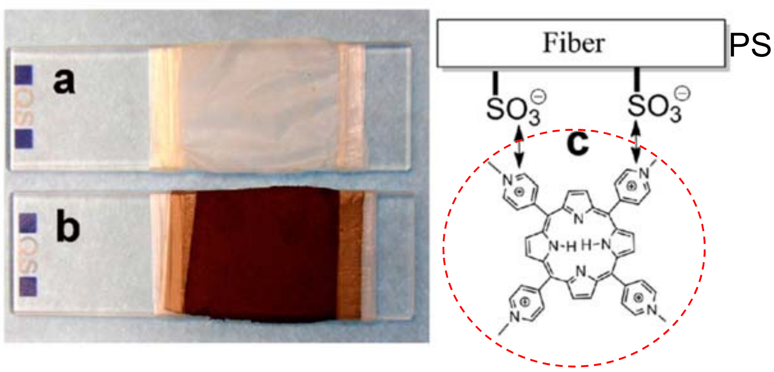


→ Polímero fotoactivo

L. Pessoni et al. *Langmuir* **2013**, *29*, 10264

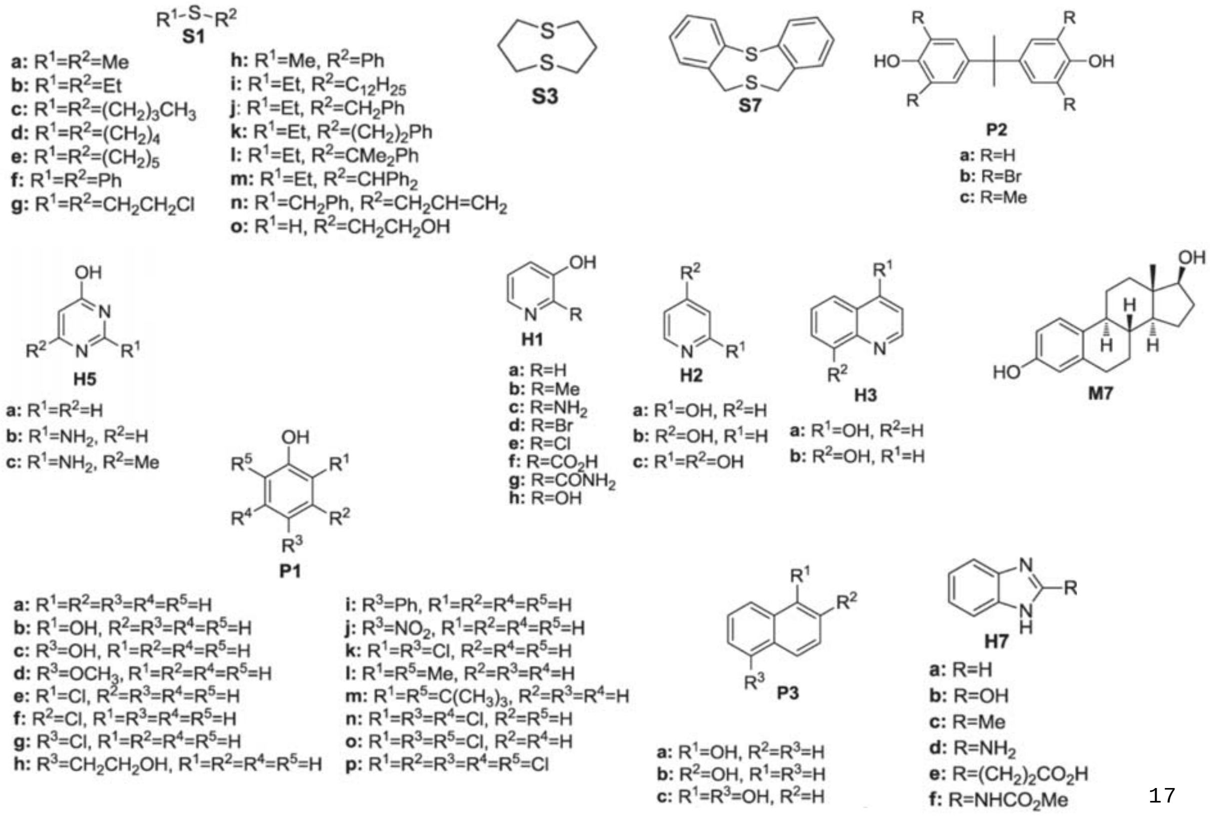


P. Henke et al. *ACS Appl. Mater. Interf.* **2013**, *5*, 3776



Contaminantes degradables por oxígeno singlete ($^1O_2$)

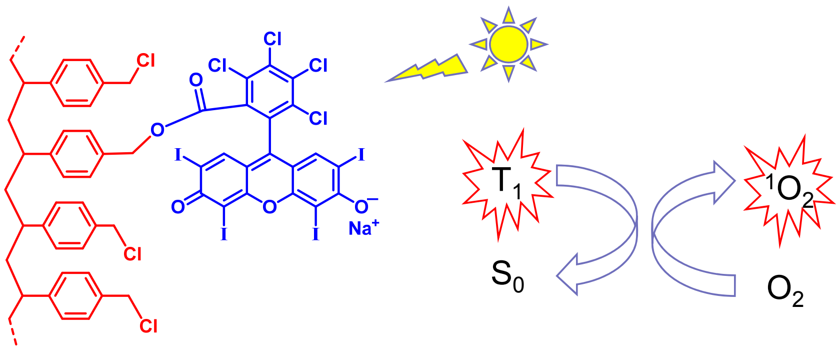
Chem. Rev. **2012**, *112*, 1710-1750

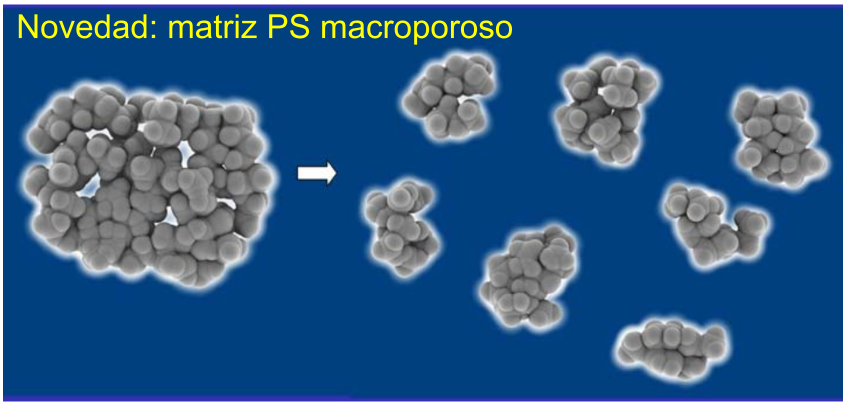


Desarrollos en Universitat Jaume I

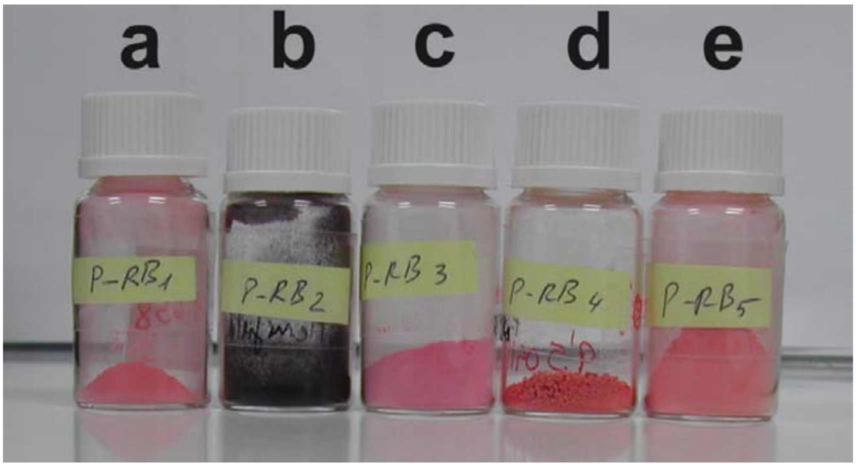
Unión **covalente**

1. PS – Rosa Bengala





M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360
M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1



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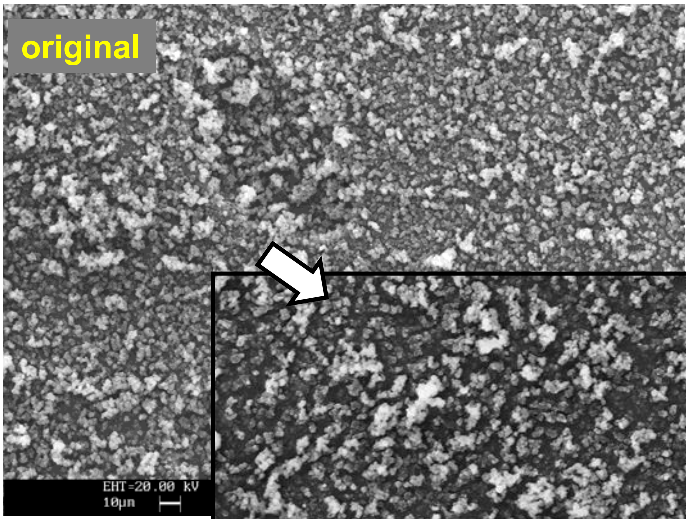
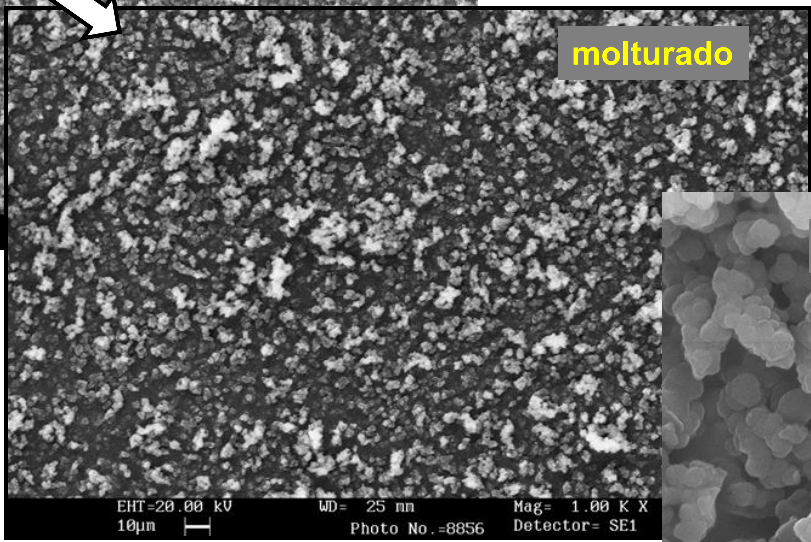
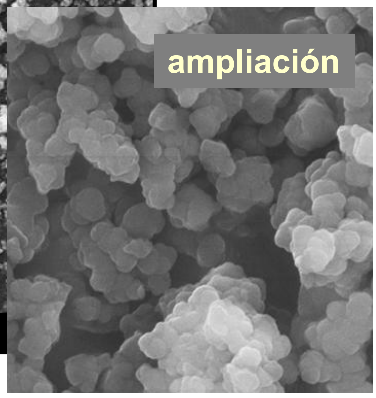


Microscopía electrónica de barrido (SEM)





M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

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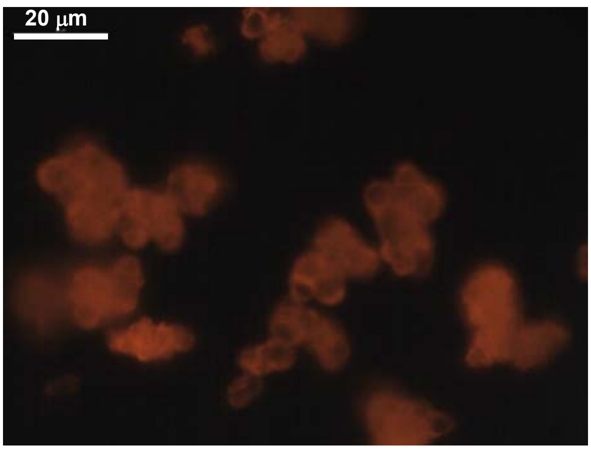
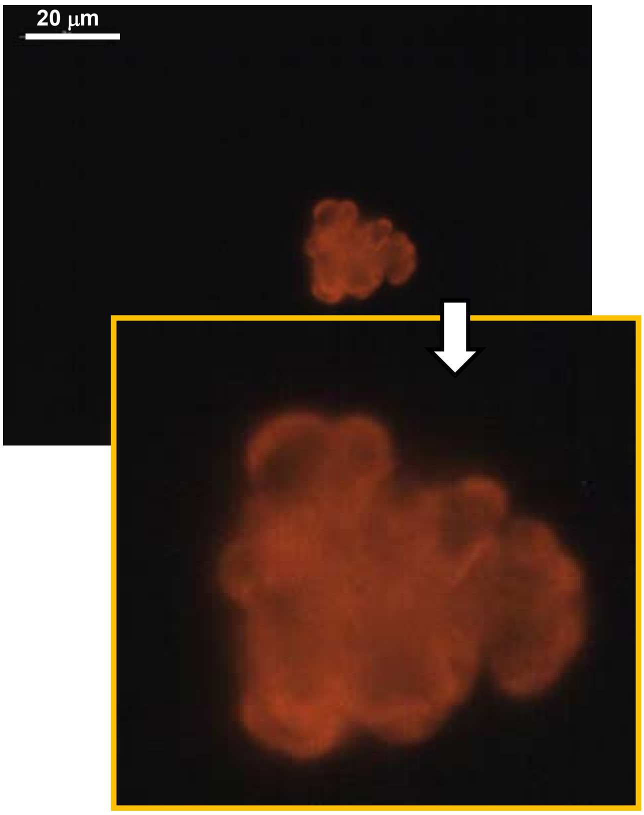
Sistemas no convencionales para oxidación fotoquímica



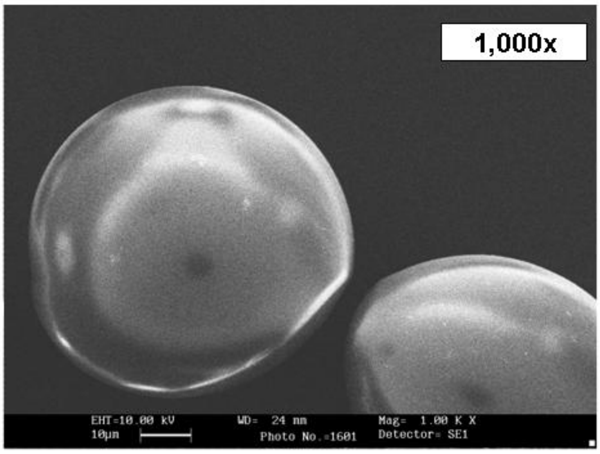


Microscopía de fluorescencia

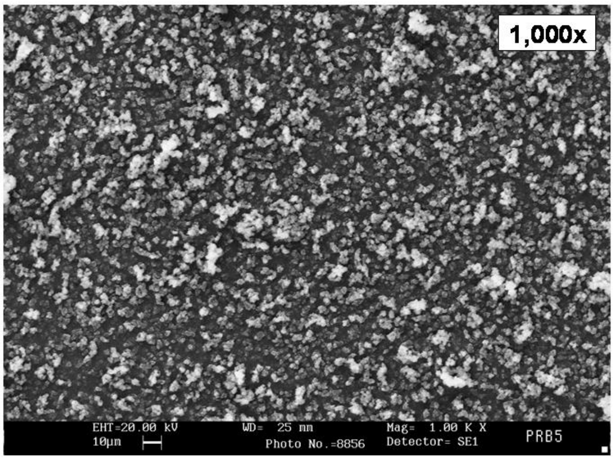
M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1

Microscopía electrónica de barrido (SEM)



Polímero clásico (tipo Neckers)

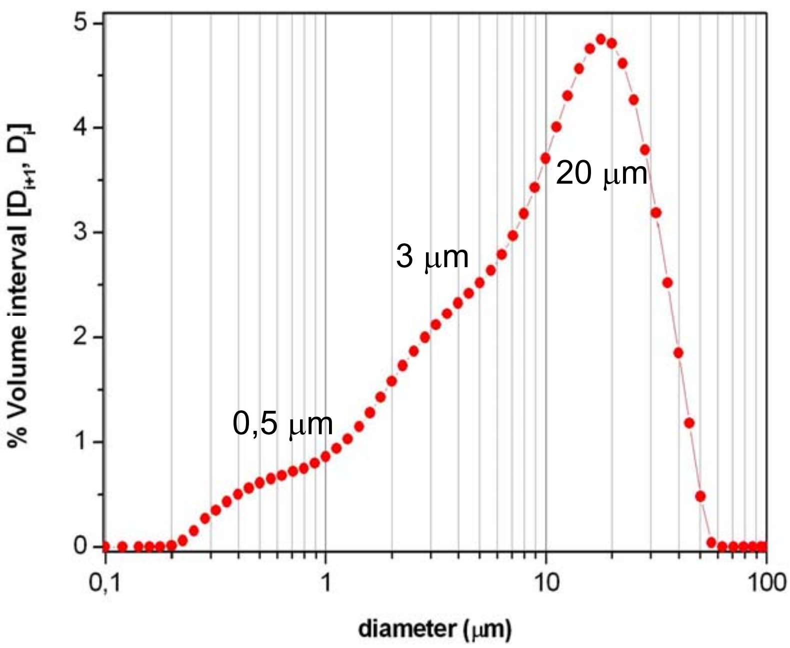


Polímero macroporoso

M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1

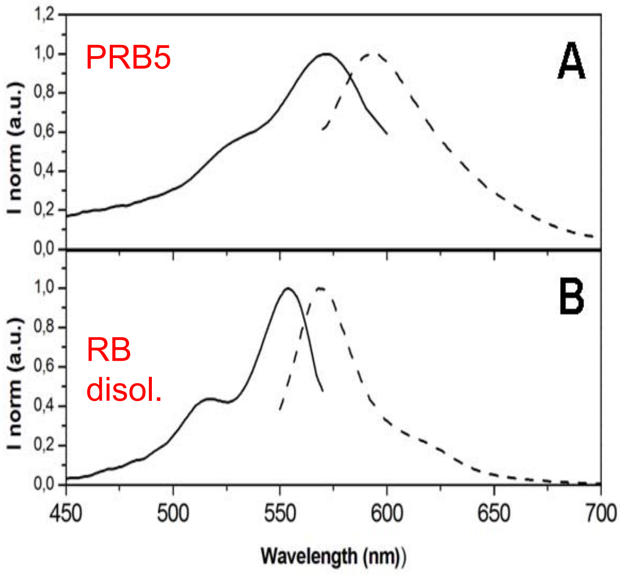
Dispersión de luz (determinación tamaño partícula)



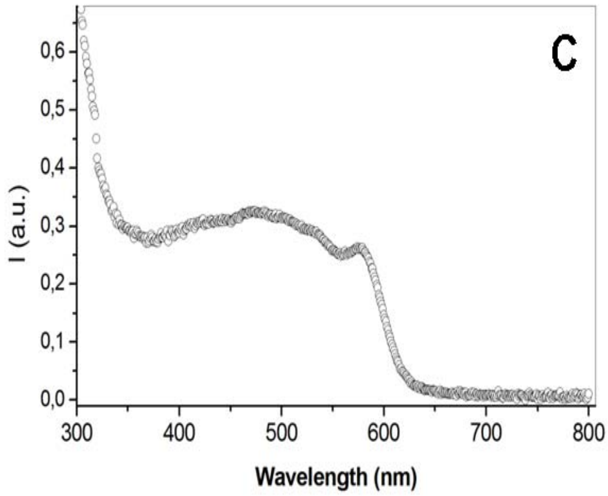
M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1

Espectroscopía de fluorescencia



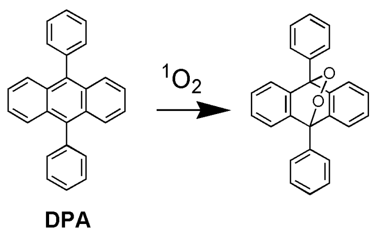
Espectroscopía de reflectancia difusa

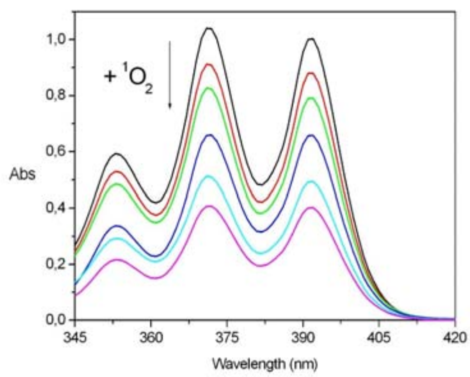


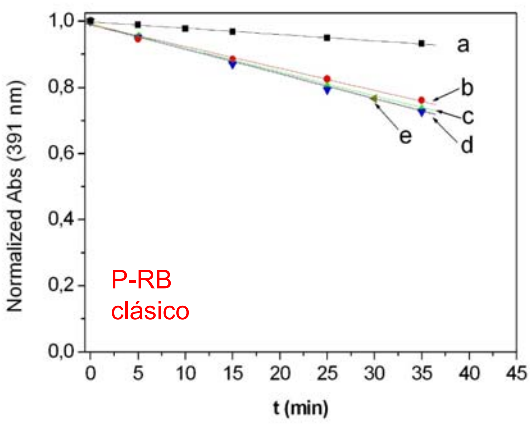
M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

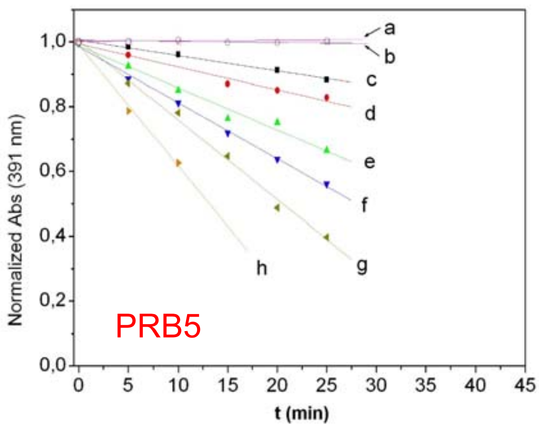
M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1

Test DPA









M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1

Test DPA

Photosensitizer	Conc. Polymer/mg ml^{-1}	Conc. RB/M^{a}	$k/10^{-3}$ min^{-1}
RB *disolución*	—	1.67×10^{-6}	1.9
	—	6.64×10^{-6}	6.6
	—	1.44×10^{-5}	7.2
	—	2.93×10^{-5}	7.5
	—	5.86×10^{-5}	7.4
P_m-RB *(PRB5)*	0.67	1.34×10^{-6}	4.8
	1.33	2.66×10^{-6}	7.1
	2.67	5.34×10^{-6}	13.0
	4.00	8.00×10^{-6}	17.3
	6.65	1.33×10^{-5}	24.6
	13.30	2.66×10^{-5}	37.3
P_g-RB *Polim. como Neckers*	4.33	6.90×10^{-4}	2.9
	8.33	1.33×10^{-3}	4.2
	16.67	2.67×10^{-3}	6.3
	33.33	5.33×10^{-3}	5.8

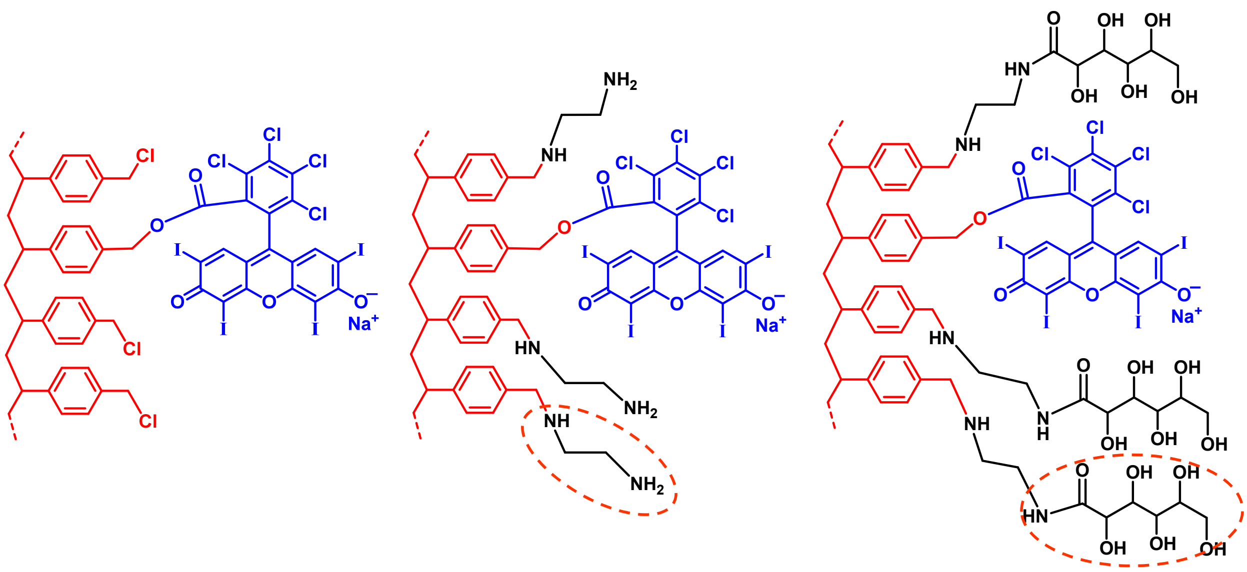
M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Tetrahedron Lett.* **2010**, *51*, 3360

M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas, D. A. Russell, *Photochem. Photobiol. Sci*. **2009**, *8*, 1

Sistemas no convencionales para oxidación fotoquímica

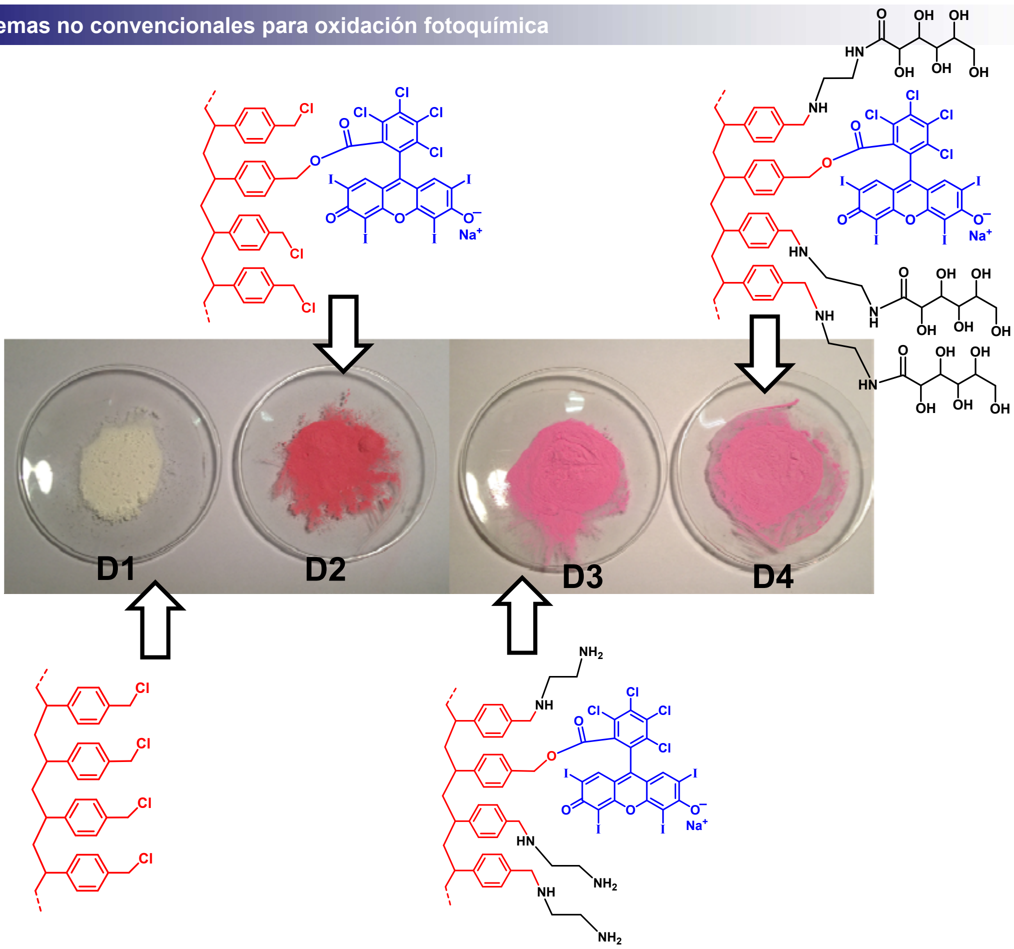
Unión **covalente**

2.- PS – (Rosa Bengala)(gluconolactona)

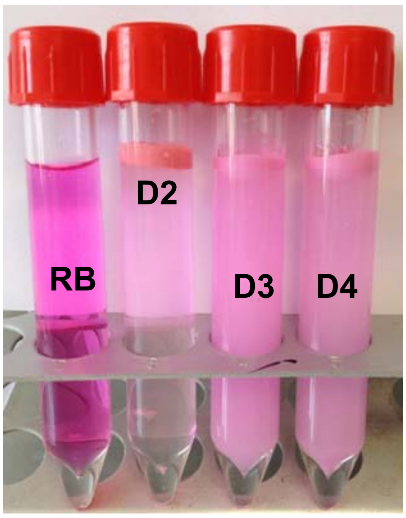


D2 **D3** **D4**

V. Fabregat, M. I. Burguete, F. Galindo, S. V. Luis, *Env. Sci. Pollut. Res*. **2014**, *21*, 11884

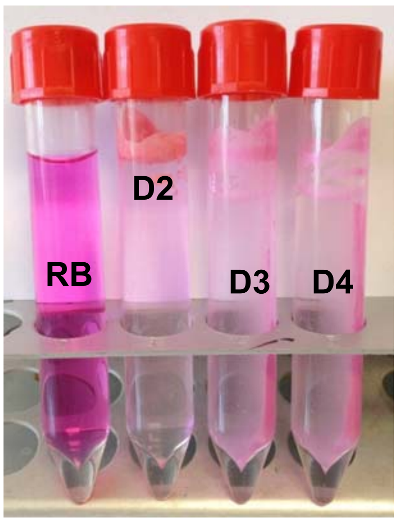


Polímeros hidrofílicos quedan en **suspensión**



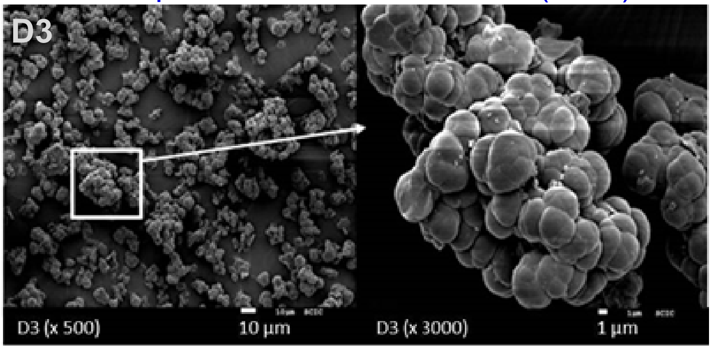
Centrifug. ⇨

Polímeros hidrofílicos pueden **recuperarse**

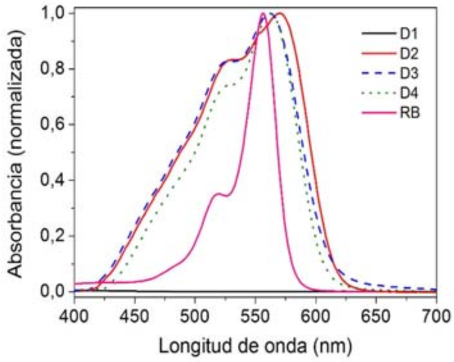


V. Fabregat, M. I. Burguete, F. Galindo, S. V. Luis, *Env. Sci. Pollut. Res*. **2014**, *21*, 11884

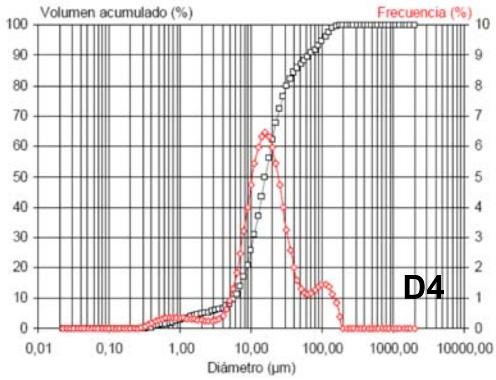
Microscopía electrónica de barrido (SEM)



Absorción & Reflect. Difusa

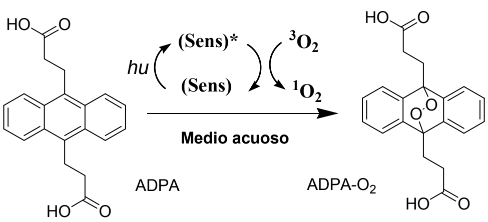


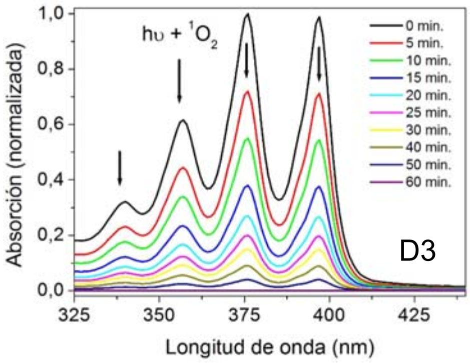
Dispersión de luz

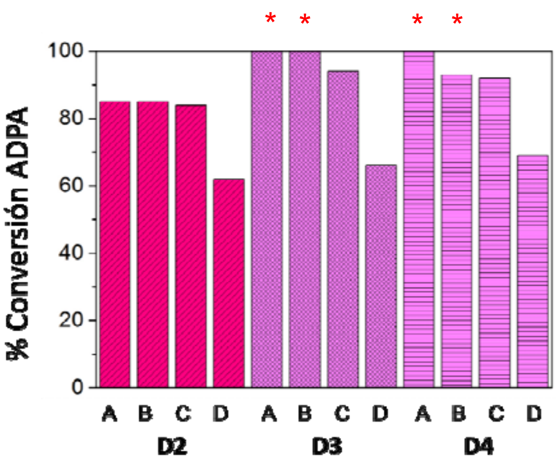


V. Fabregat, M. I. Burguete, F. Galindo, S. V. Luis, *Env. Sci. Pollut. Res.* **2014**, *21*, 11884

Test ADPA







* Polímeros hidrofílicos (D3, D4) mejor rendimiento que hidrofóbico (D2)

(A) Agua
(B) Tampón PBS
(C) Metanol
(D) Cloroformo

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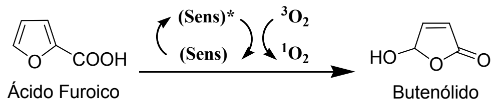
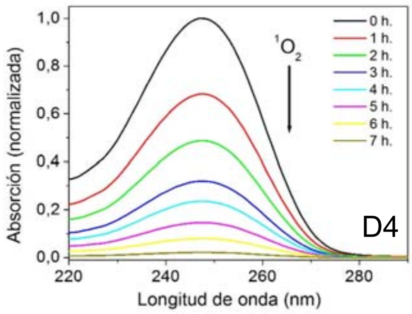
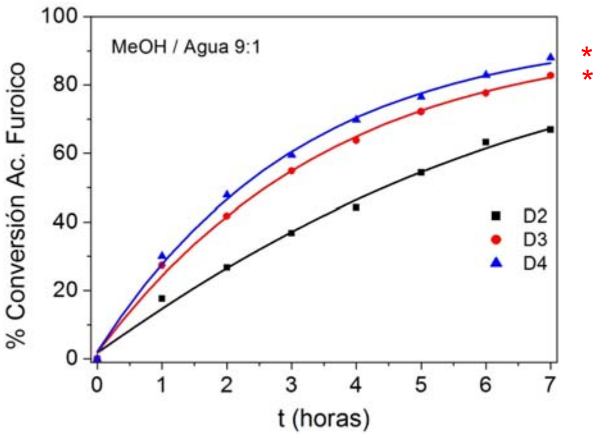
Test Ac. Furoico







* Polímeros hidrofílicos (D3, D4) mejor rendimiento que hidrofóbico (D2)

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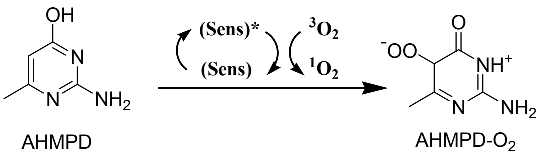
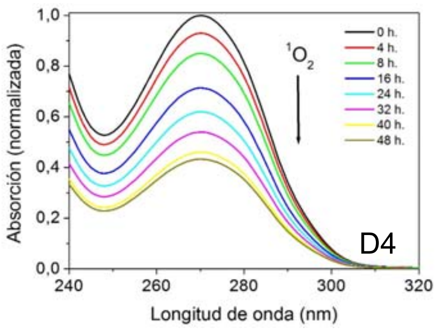
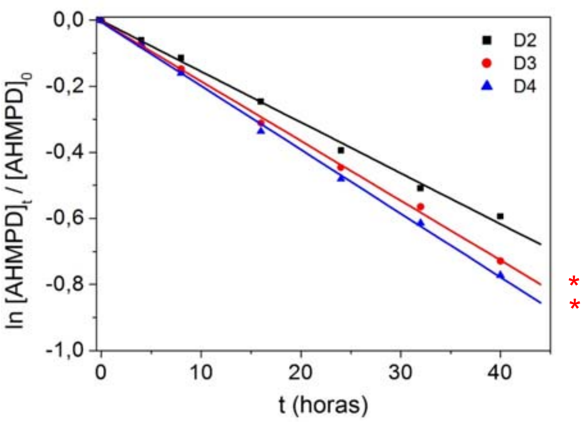
Fungicida AHMPD (2-amino-4-hydroxy-6-methylpyrimidine)







* Polímeros hidrofílicos (D3, D4) mayor velocidad que hidrofóbico (D2)

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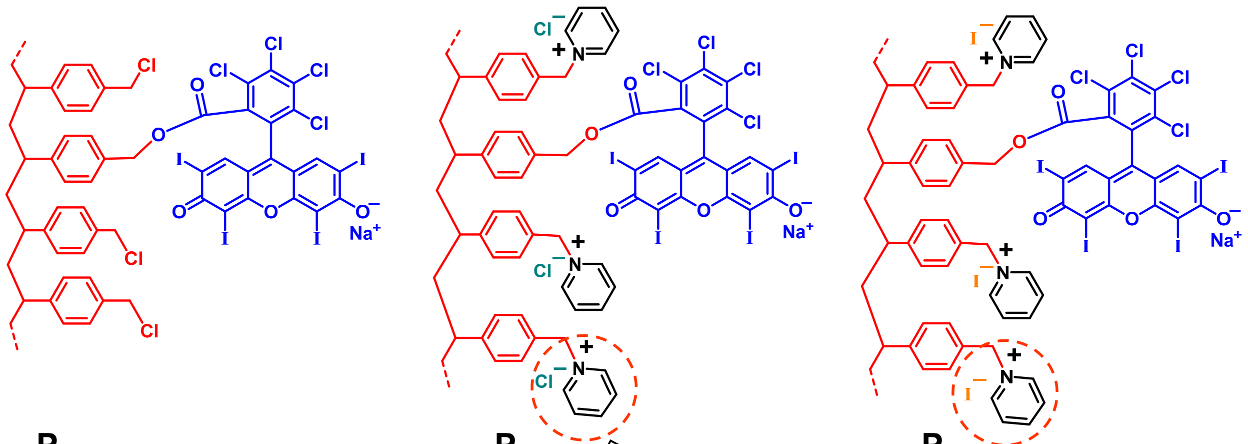
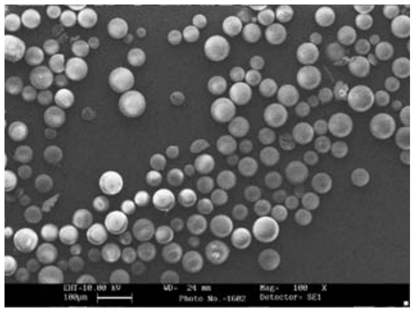
Unión **covalente**

3.- PS – (Rosa Bengala)(piridina)



P_A P_B P_C

Introducción de grupos iónicos (permanentes)



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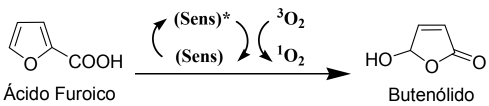
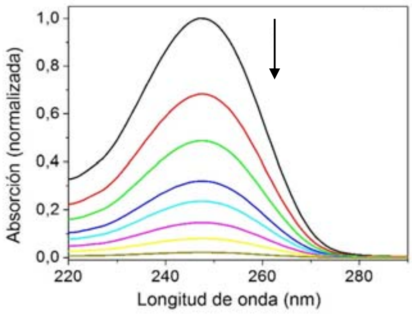
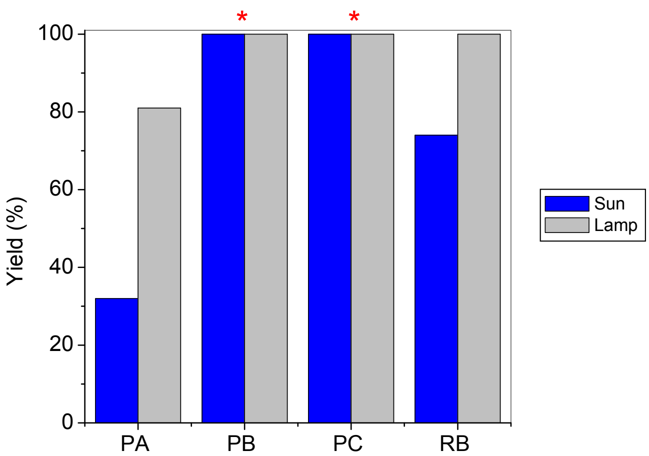
Test Ac. Furoico

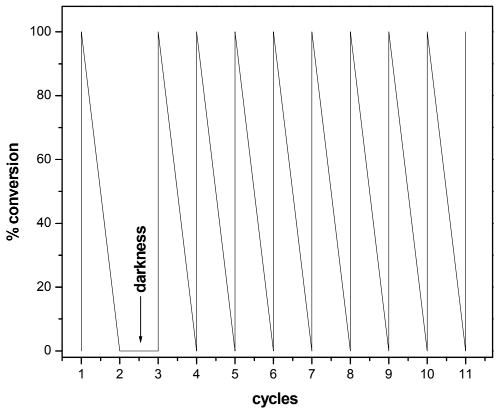




* Polímeros hidrofílicos (PB, PC) mayor velocidad que hidrofóbico (PA)



Reciclabilidad: hasta 11 ciclos



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- Generalitat Valenciana
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Sistemas no convencionales para procesos fotoquímicos de oxidación

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