



**The Abdus Salam
International Centre for Theoretical Physics**



1938-3

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

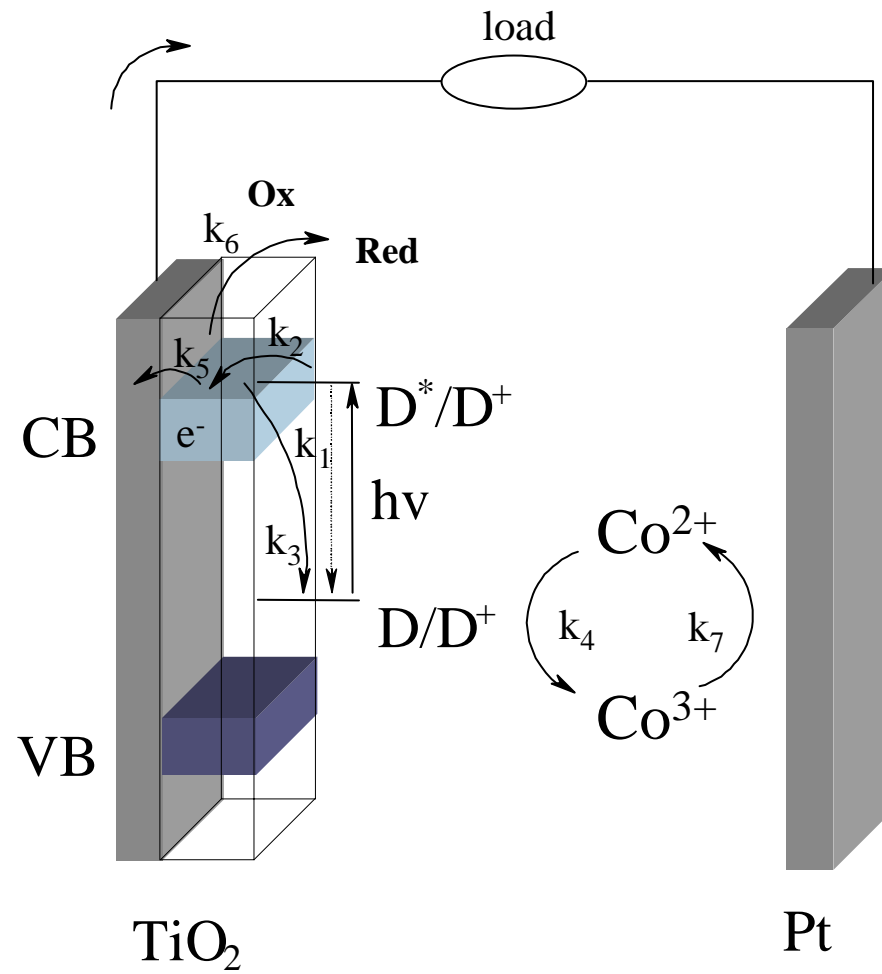
Recent developments in the design of dye sensitized solar cell components

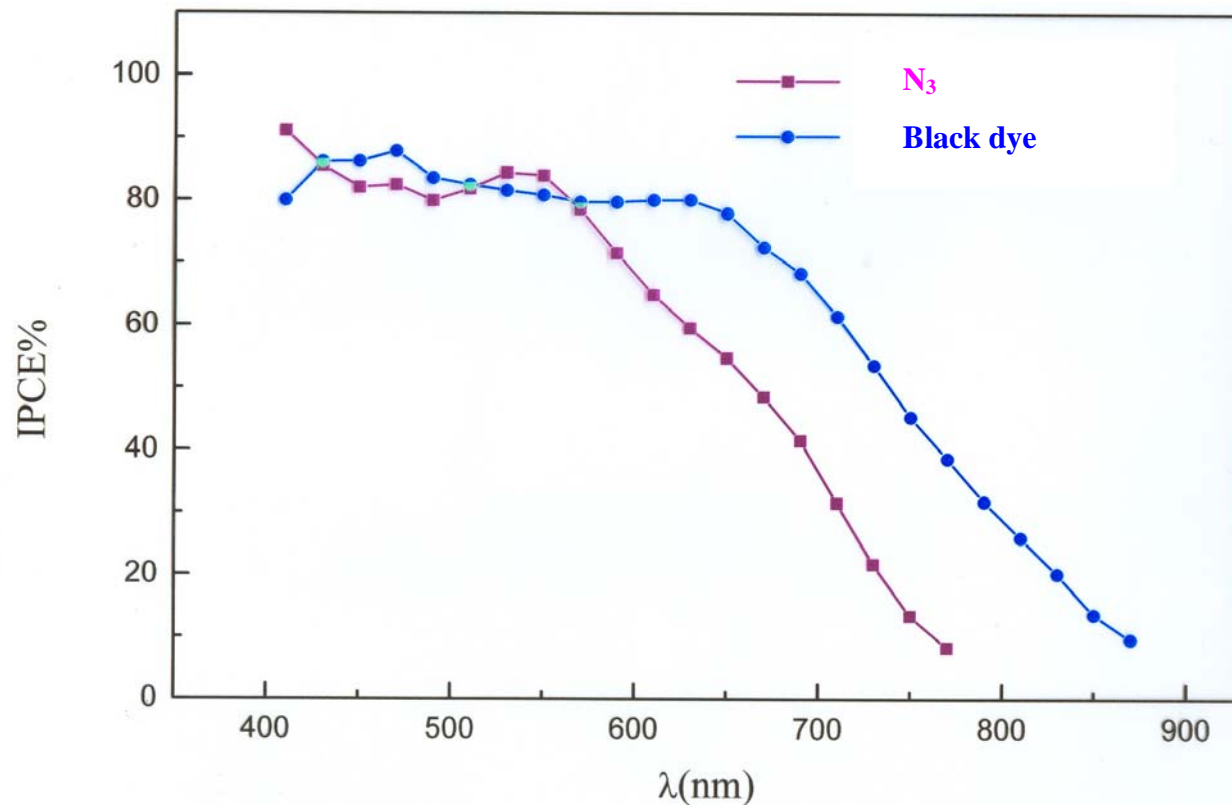
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Italy*

Recent developments in the design of DSSCs components

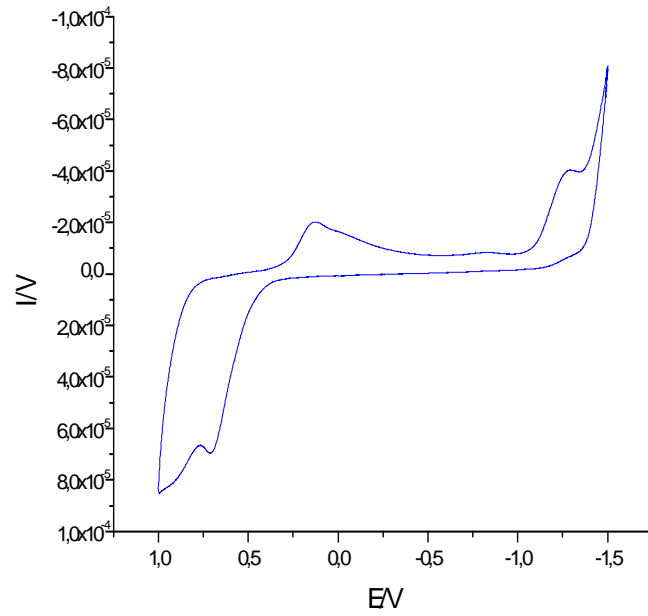
C. A. Bignozzi

**Department of Chemistry
University of Ferrara, Italy**



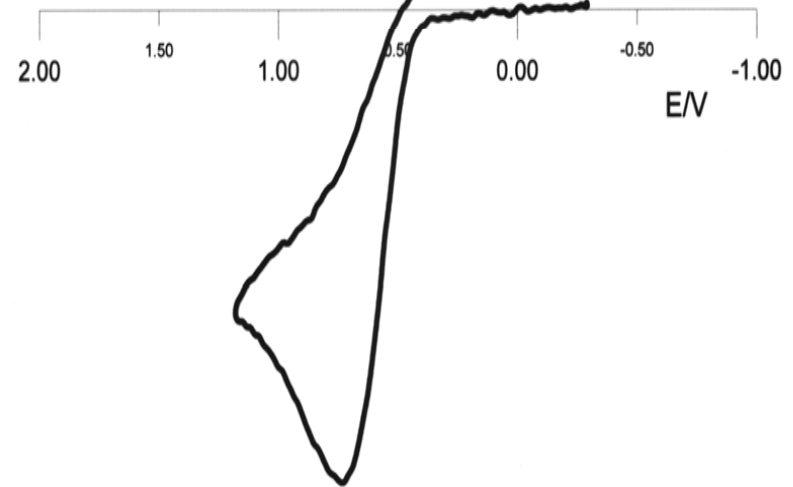


NaNCS in CH₃CN



**Ru(Htcterpy)(NCS)₃(TBA)₃, GC/Pt/SCE
TEATFB 0.1 M in MeOH**

**v = 0.1V/s
T = 25 °C**



Photochemistry in Solution

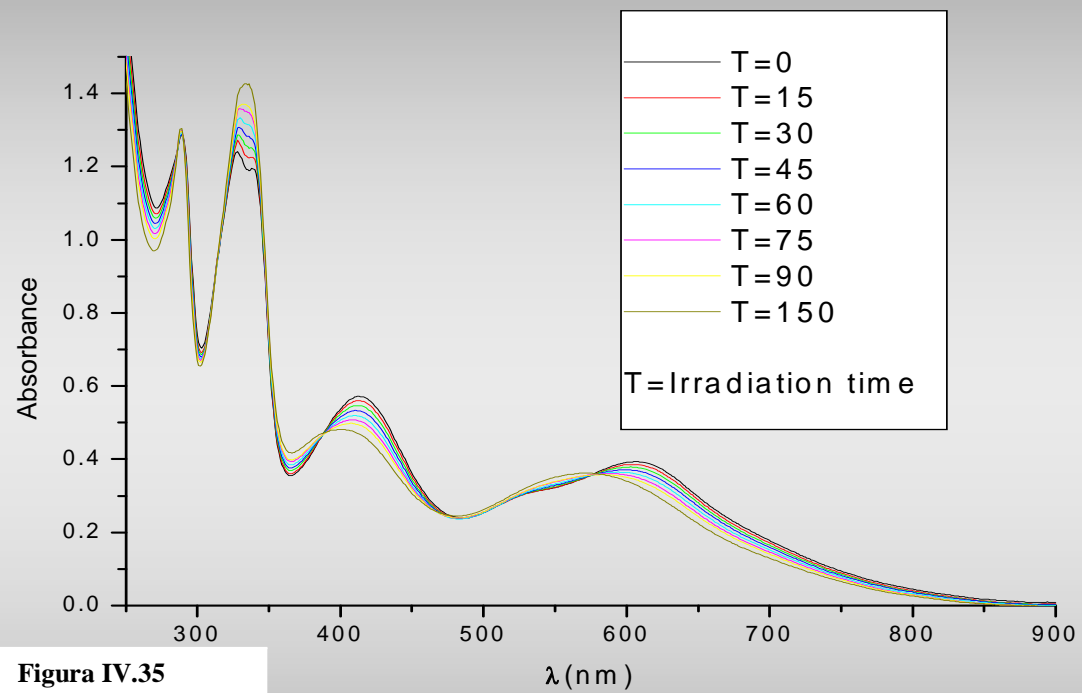


Figura IV.35

$[\text{Ru}(\text{Htcterpy})(\text{NCS})_3] (\text{TBA})_3$ in CH_3OH

Electron mediator

I⁻/I₃⁻ Mediated Solar Cells

Low Cost

Transparency

**Competitive with amorphous
Silicon devices**

Increase of the electron collection efficiency:

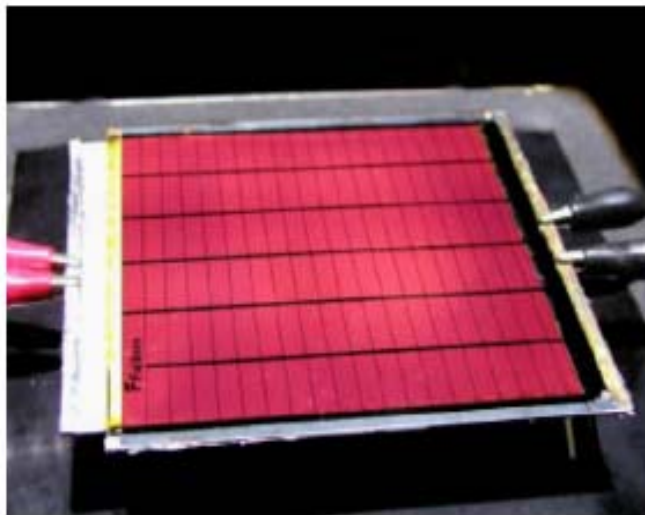


Fig. 8. The Ni grid formed large size DSC.

*****Corrosivity of the I^-/I_3^- redox couple*****

Need for the design of new Electron Mediators

Electron Transfer Mediator Requirements

- 1) Fast oxidized Dye reduction (submicrosecond time scale)
- 2) Slow recombination with photoinjected CB electrons
- 3) Fast reduction at the counter electrode
- 4) Efficient diffusional transport.
- 5) Low extinction coefficient
- 6) Easy to produce in large quantity. Simple Synthetic Chemistry.

Co(II) Complexes as Electron Transfer mediators

- 1) Non corrosive
- 2) Redox tunability
- 3) Low extinction coefficient in the visible region ($10^2 \text{ M}^{-1} \text{ cm}^{-1}$)
- 4) Slow electron transfer on TCO substrates
- 5) Compatibility with metallic grids and plastic materials

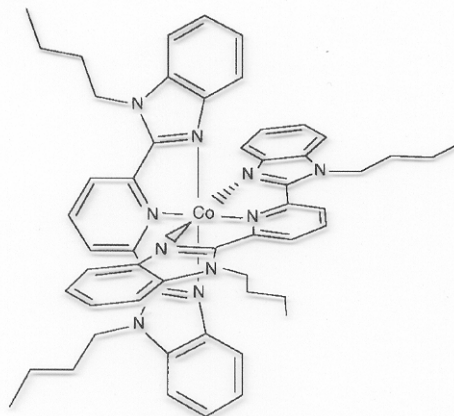
Co^{II}(dbbip)₂²⁺ Complex Rivals Tri-iodide/Iodide Redox Mediator in Dye-Sensitized Photovoltaic Cells

**Hervé Nusbaumer, Jacques-E. Moser,* Shaik M. Zakeeruddin,
Mohammad K. Nazeeruddin, and Michael Grätzel**

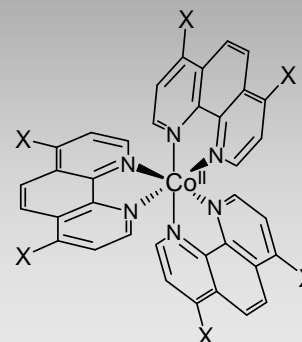
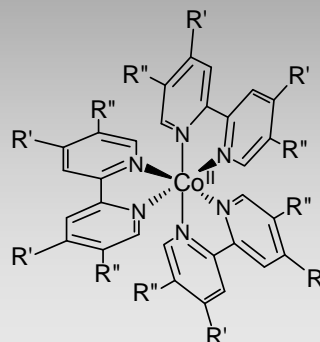
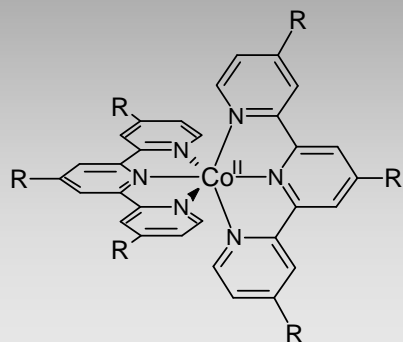
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Received: May 31, 2001; In Final Form: August 6, 2001

CHART 1



Polypyridine Co(II) complexes



R = ethyl (te-terpy)

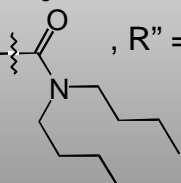
R = *t*-butyl (ttb-terpy)

R' = H, R'' = H (bpy)

R' = CH₃, R'' = H (4,4'-dmb)

R' = H, R'' = CH₃ (5,5'-dmb)

R' = CH₃, R'' = CH₃ (tm-bpy)

R' = , R'' = H (bdb-amd)

R' = *t*-butyl, R'' = H (dtb-bpy)

R' = COO-*t*-butyl, R'' = H (dtb-est)

R' = phenyl, R'' = H (dp-bpy)

R' = 3-pentyl, R'' = H (d3p-bpy)

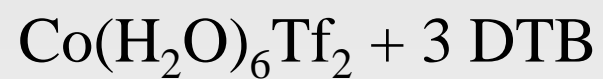
R' = nonyl, R'' = H (dn-bpy)

X = H (phen)

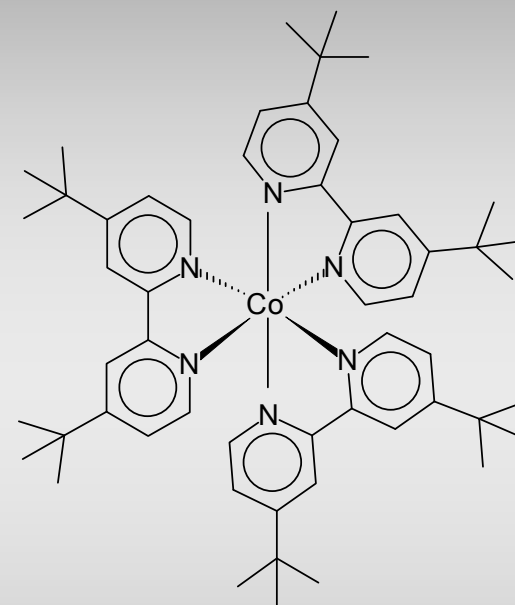
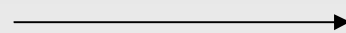
X = phenyl (phen-phen)

J. Am. Chem. Soc. 124, 11215-112122, 2002

PREPARATION



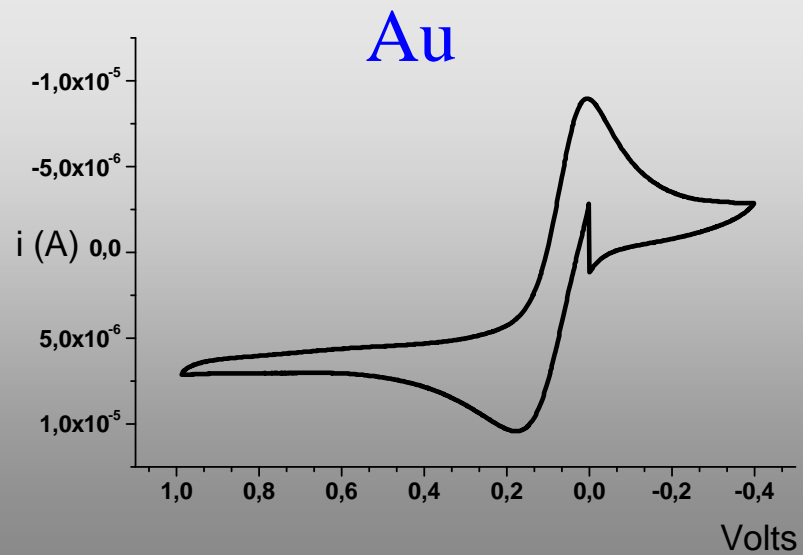
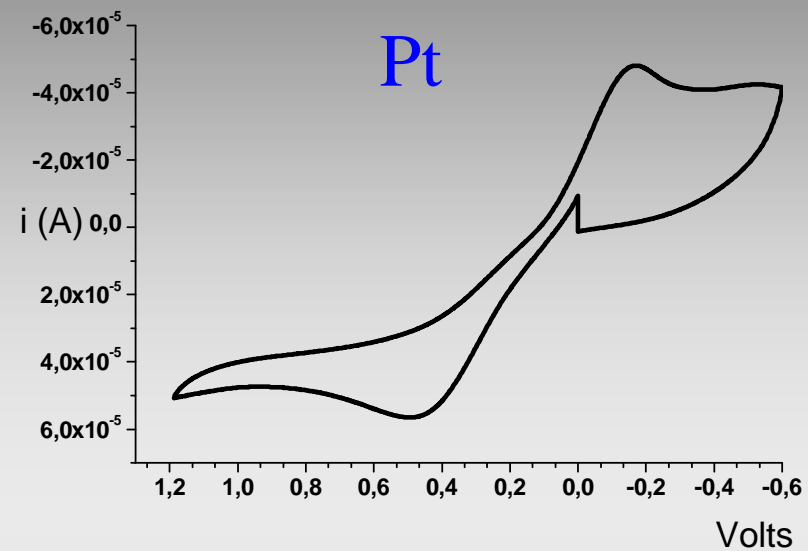
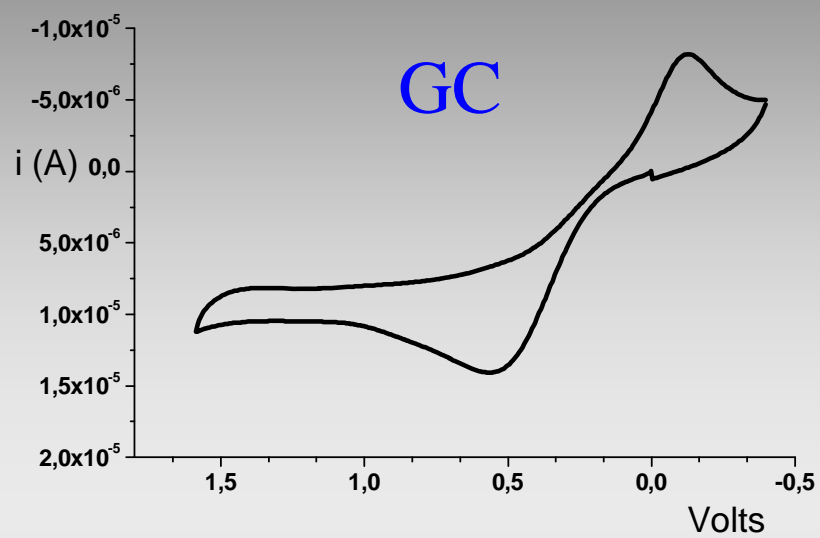
Methanol, r.t



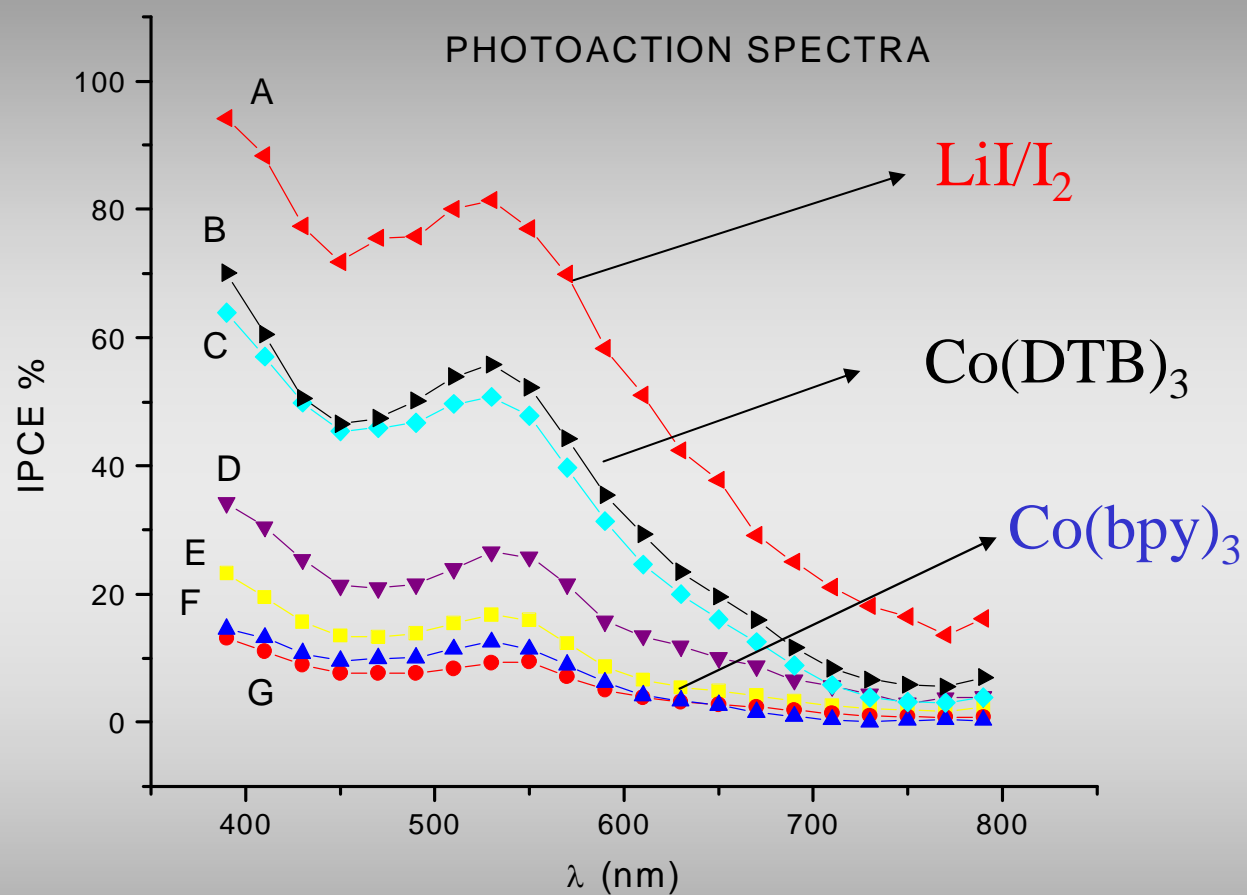
Quantitative one step reaction at r.t.

Simple purification procedures

Electrochemistry $[\text{Co}(\text{Tb}_2\text{bpy})_3](\text{ClO}_4)_2$

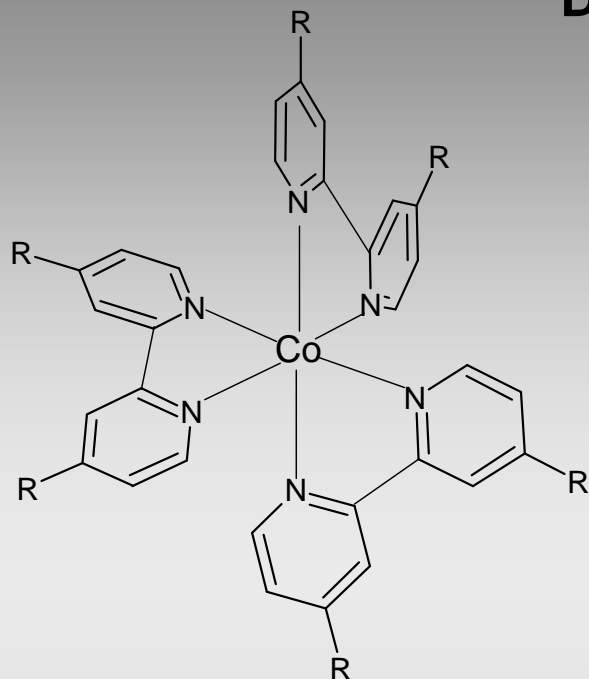


Photoaction Spectra



Dependence of the photovoltaic performances from the chemical structure of the Co(II) complexes, 0.3 M Li⁺

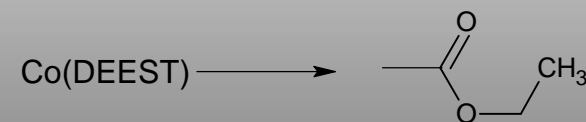
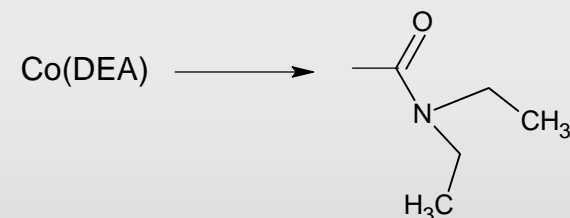
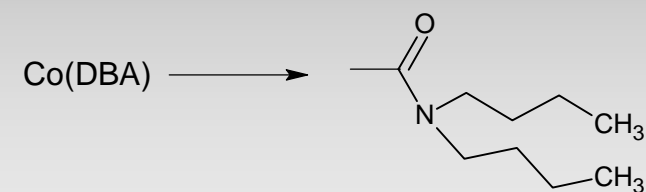
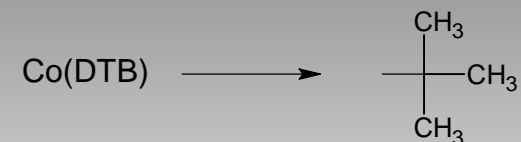
Cobalt trisbipyridyl complexes as electron transfer mediator for DSSC



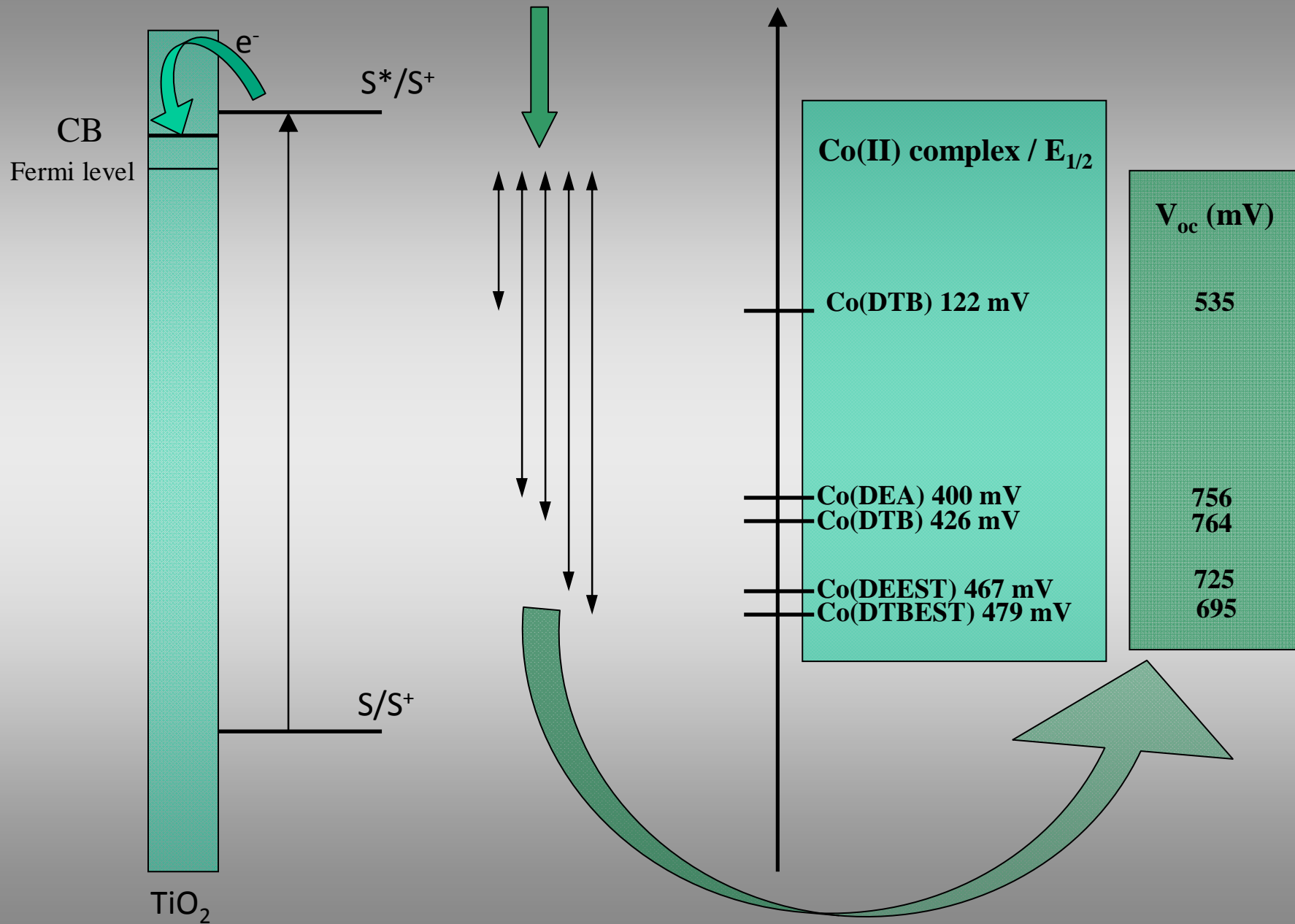
Electrochemistry of trisbipyridyl Co(II) complexes

Pt/GC/SSCE; 100 mV/s; LiClO₄ 0.1 M in acetonitrile

Co(II) complex	E _{pa} (mV)	E _{pc} (mV)	E _{1/2} (mV)	ΔE
Co(DTB) ₃	242	3	122	239
Co(DEA) ₃	465	336	400	129
Co(DBA) ₃	468	385	426	83
Co(DEEST) ₃	517	417	467	100
Co(DTBEST) ₃	548	411	479	137

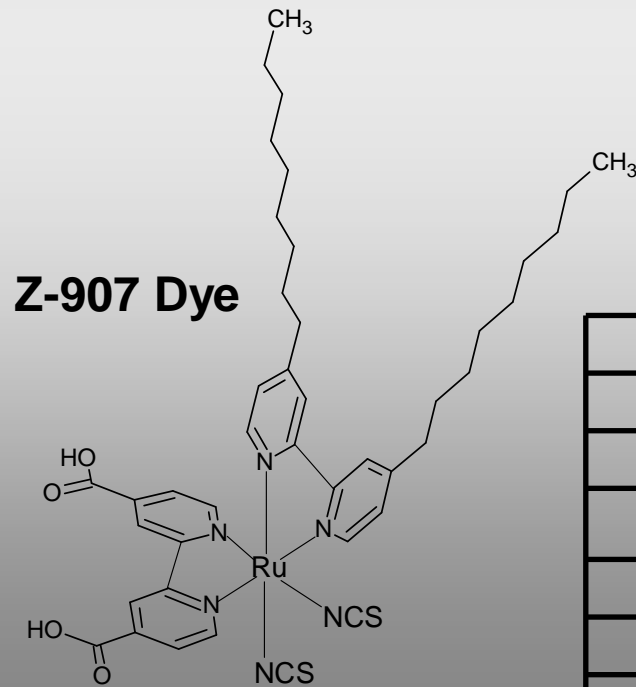
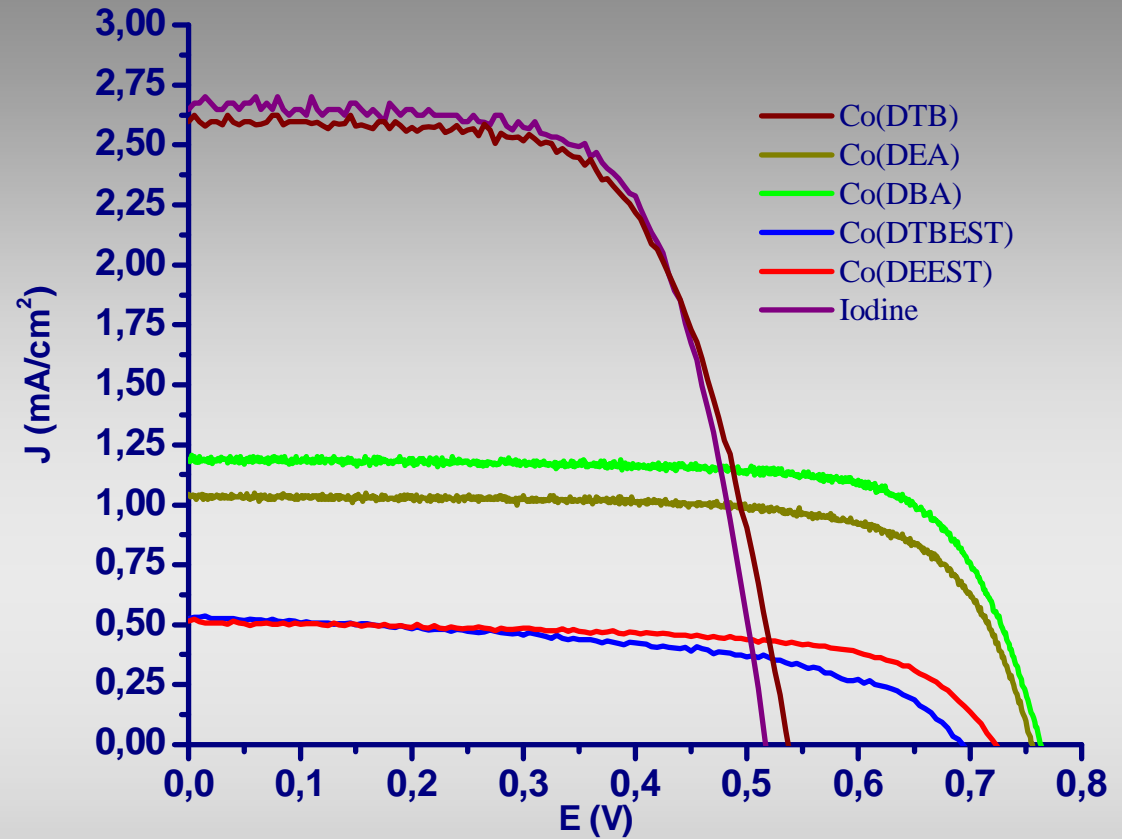


$$V_{oc} = FL(TiO_2) - E_{1/2}(D/D^+)$$



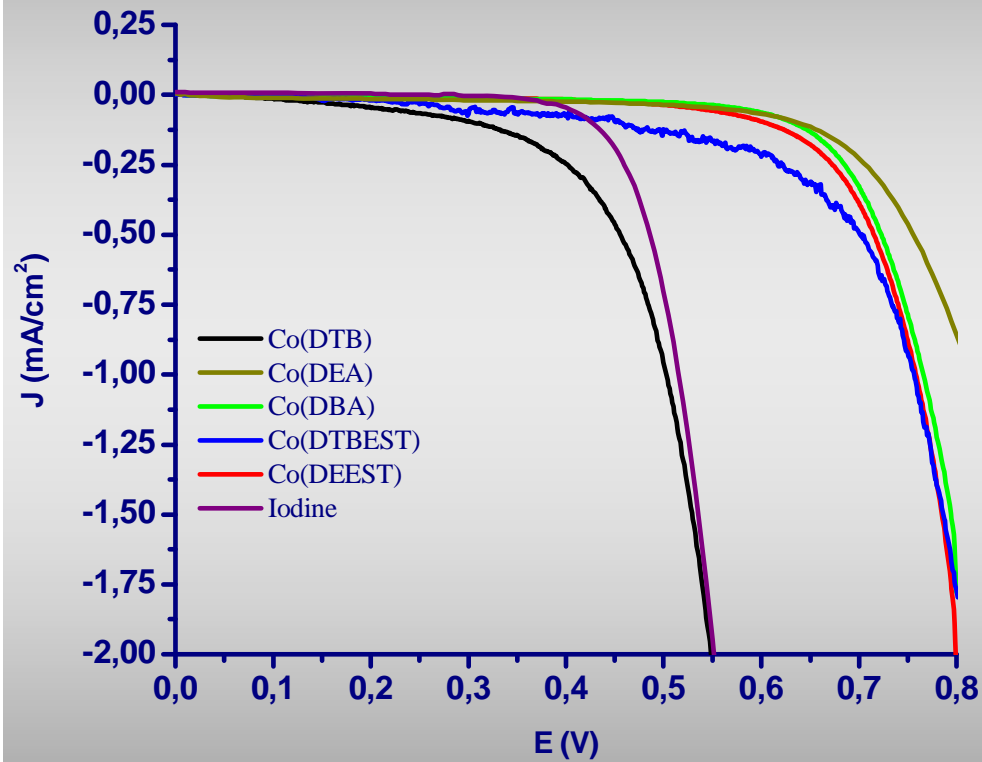
J-V curves of Z-907 SSC. .

0.1 W/cm² of power intensity.
 Gold as counter electrode
 4-tBut-pyridine 0.1 M, LiOTf 0.5 M
 Co(II)/(III) 0.15/ 0.015



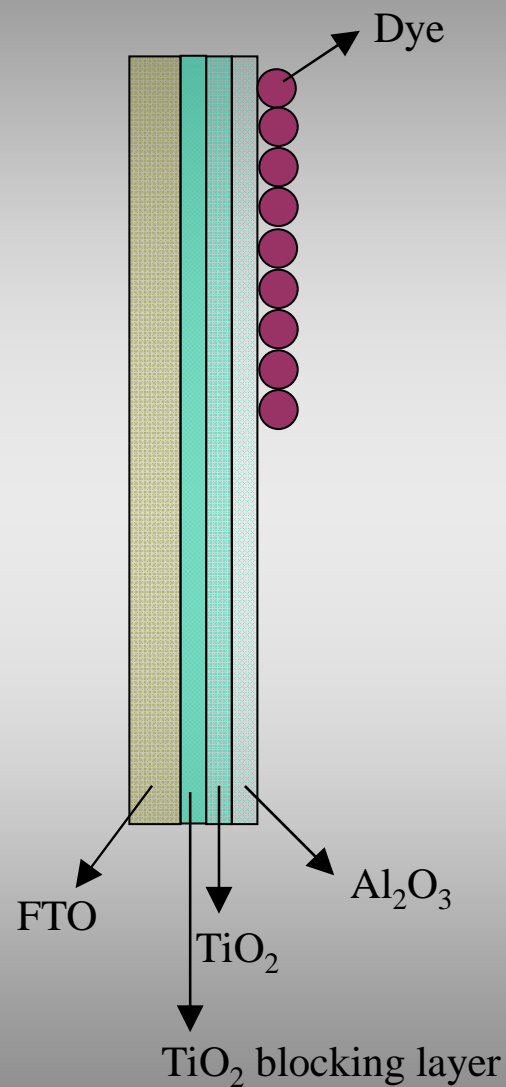
Mediator	J _{sc} (mA cm ⁻²)	V _{oc} (mV)	FF	η %
Iodine	2.65	515	0.63	0.916
Co(DTB) ₃	2.60	535	0.64	0.891
Co(DTBEST) ₃	0.528	695	0.52	0.193
Co(DEEST) ₃	0.515	725	0.63	0.234
Co(DEA) ₃	1.05	756	0.71	0.563
Co(DBA) ₃	1.19	764	0.74	0.67

Back recombination: dark current measurements of Z-907 SSC.

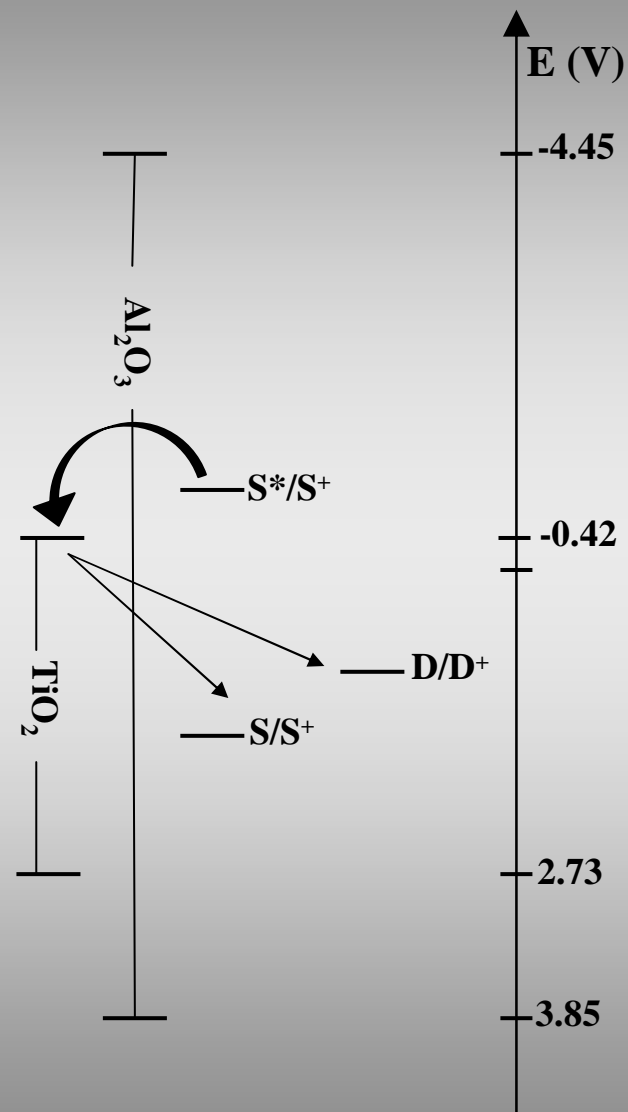


Co(II) complex	V_{oc} (mV) [1 sun]	$E_{1/2}$ (mV)
Co(DTB) ₃	535	122
Co(DEA) ₃	756	400
Co(DBA) ₃	764	426
Co(DEEST) ₃	725	467
Co(DTBEST) ₃	695	479

Al₂O₃ overlayer to block the back recombination reactions

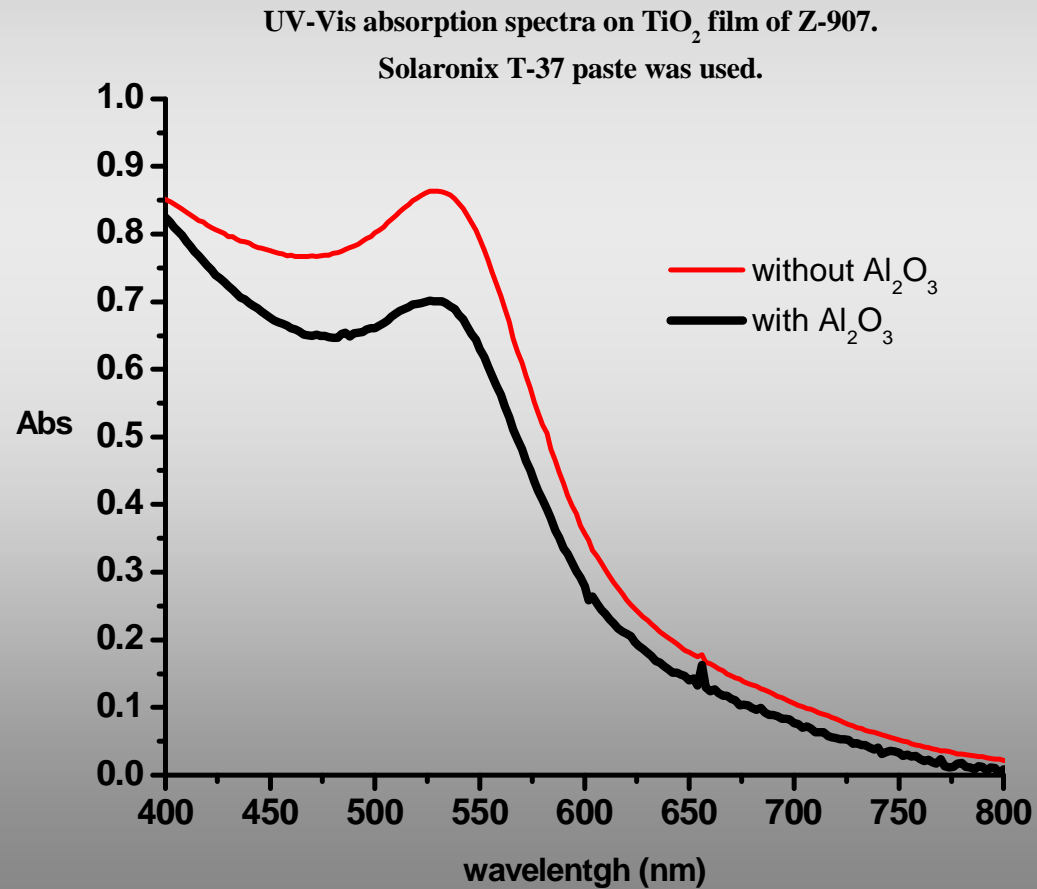


Metal oxide	Band gap (eV)	E _{VB} (V vs SCE)	E _{CB} (V vs SCE)
TiO ₂	3.0-3.3	+2.73	-0.42
Al ₂ O ₃	8.45-9.9	+3.85	-4.45



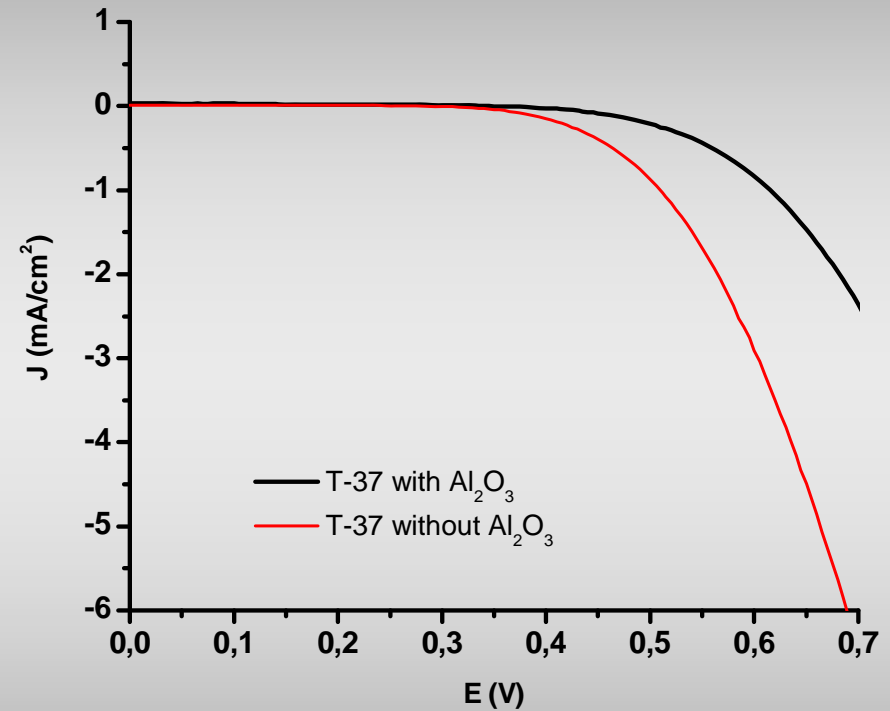
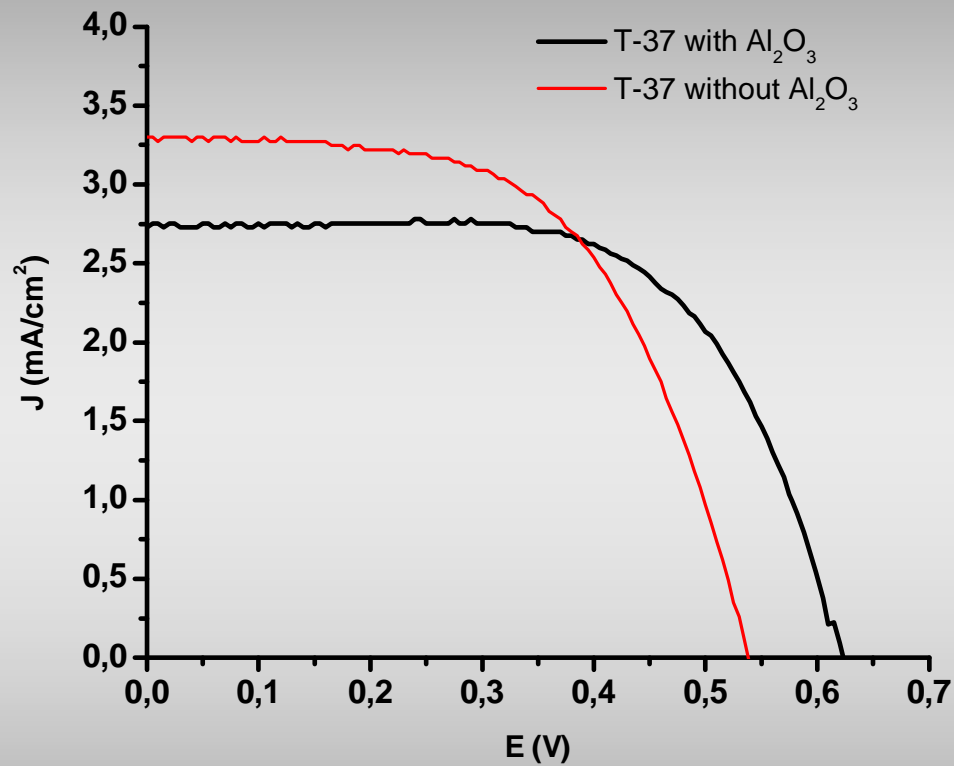
UV-Vis absorption spectra of Z-907 on TiO₂ film.

Solaronix T-37 → particle size around 35-40 nm



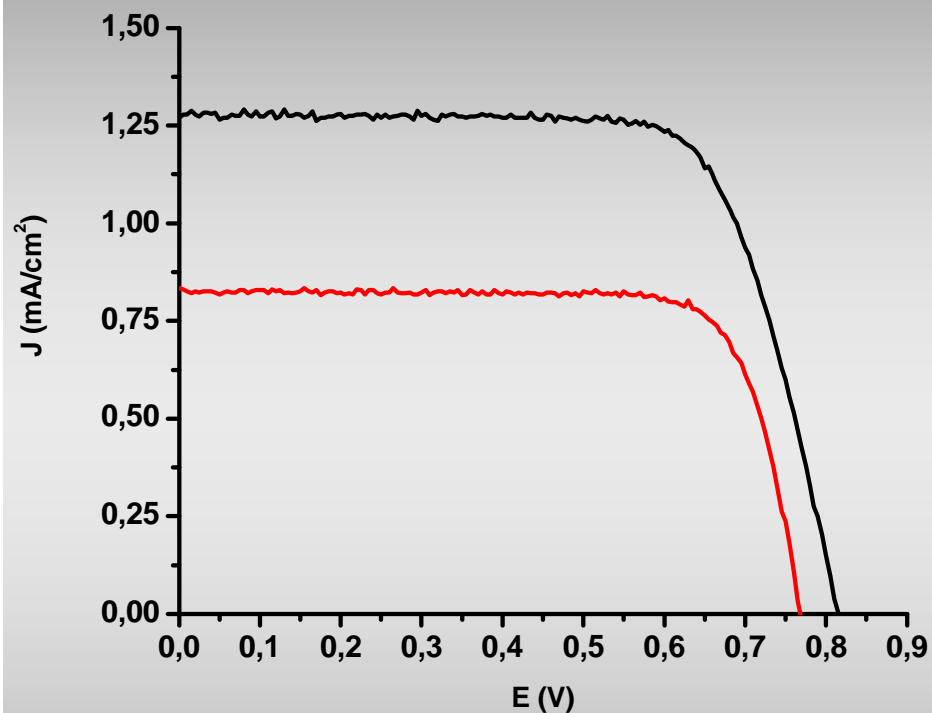
Photoelectrochemical measurements of Z-907 SSC with **Co(DTB)** as electron transfer mediator.

Dark current measurements

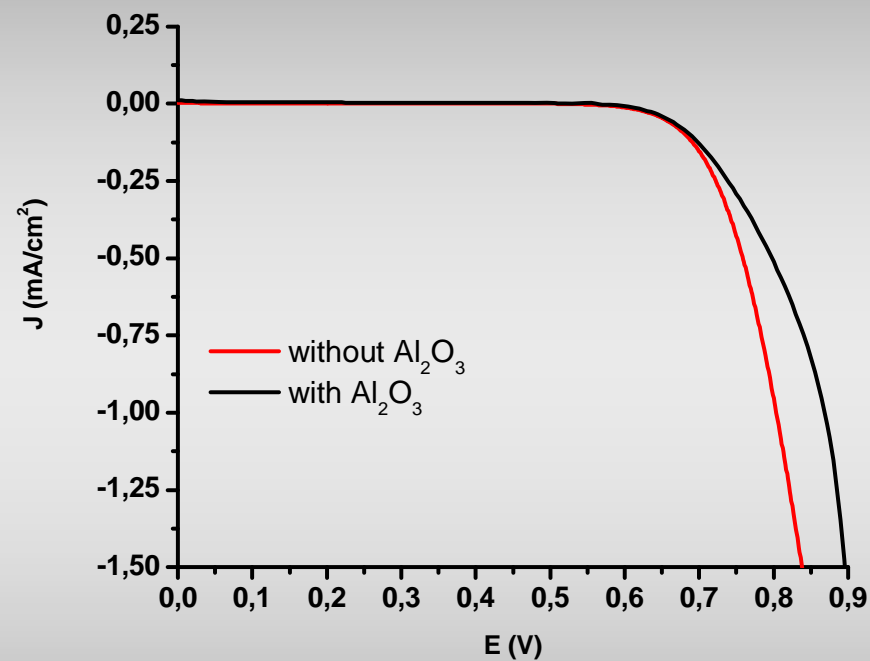


	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η %
TiO ₂ (T-37) w/o Al ₂ O ₃	3.30	540	0.58	1.03
TiO ₂ (T-37) w Al ₂ O ₃	2.74	625	0.64	1.09

Photoelectrochemical measurements of Z-907 SSC with **Co(DBA)** as electron transfer mediator.

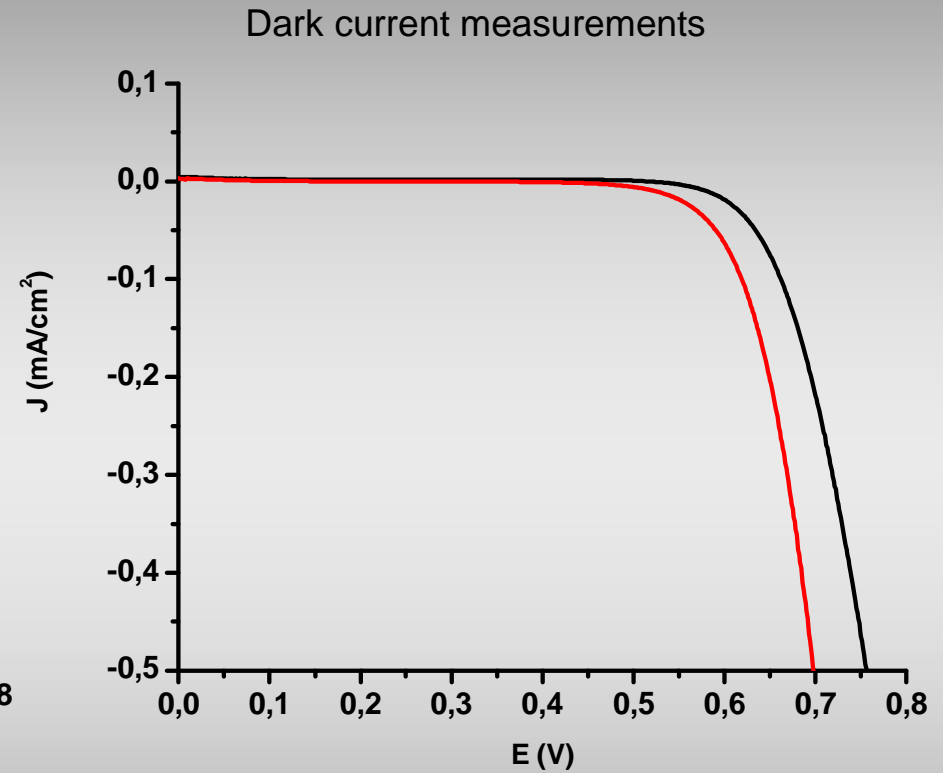
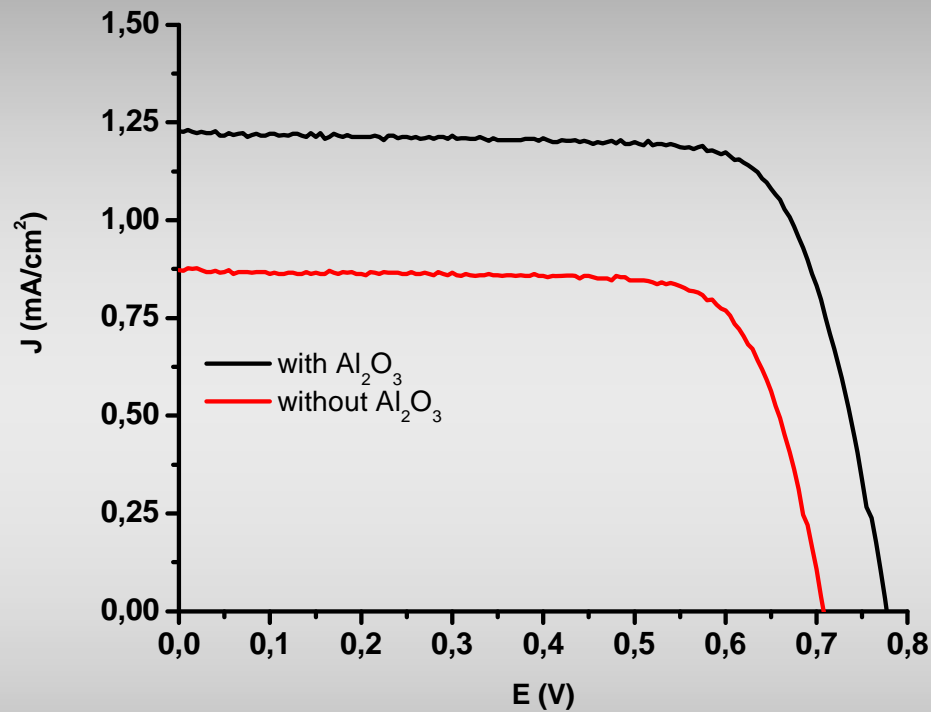


Dark current measurements



	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η %
TiO ₂ (T-37) w/o Al ₂ O ₃	0.834	770	0.79	0.505
TiO ₂ (T-37) w Al ₂ O ₃	1.27	815	0.73	0.758

Photoelectrochemical measurements of Z-907 SSC with **Co(DEA)** as electron transfer mediator.



	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η %
TiO ₂ (T-37) w/o Al ₂ O ₃	0.872	710	0.75	0.467
TiO ₂ (T-37) w Al ₂ O ₃	1.23	775	0.75	0.714

Co(II) mediated cells approach in the best conditions the performances of the I⁻/I₃⁻ couple, but generally suffer from lower Voc and Jsc.

Oxidized dye reduction and recombination with CB electrons are critical in determining the efficiency of the Co(II)/(III) couple in DSSCs.

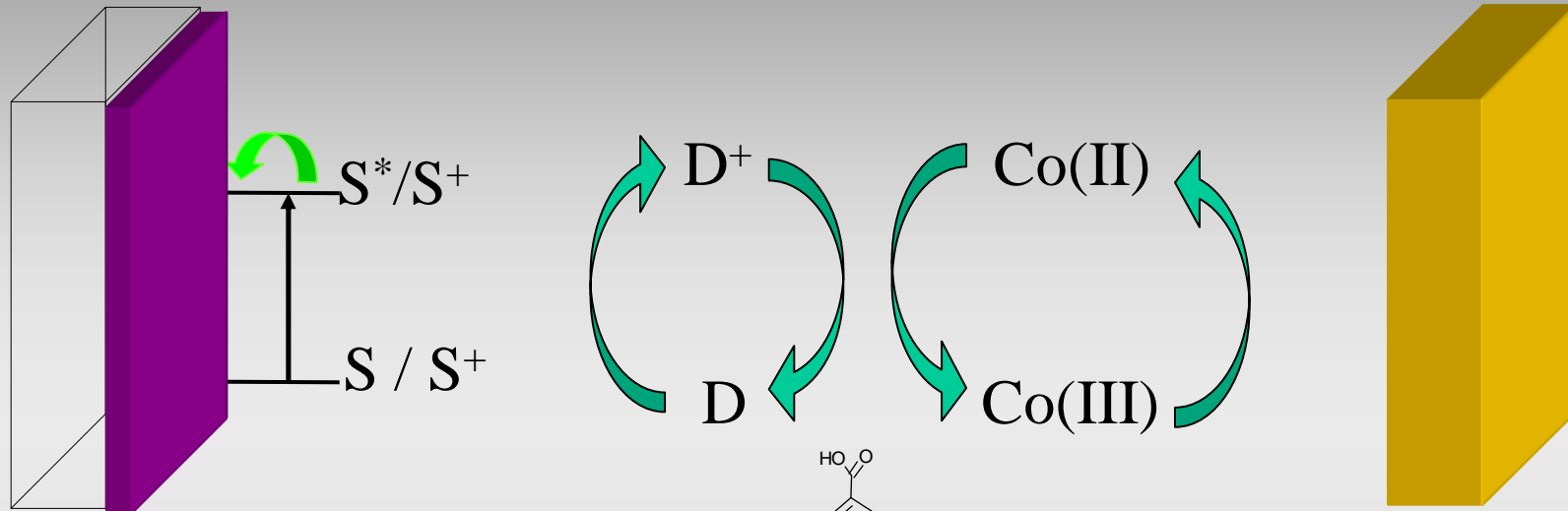
Bulky substituents and high charge density cations reduce the parasitic recombination of CB electrons with the oxidized electron transfer mediator.

Mixtures of Electron Mediators

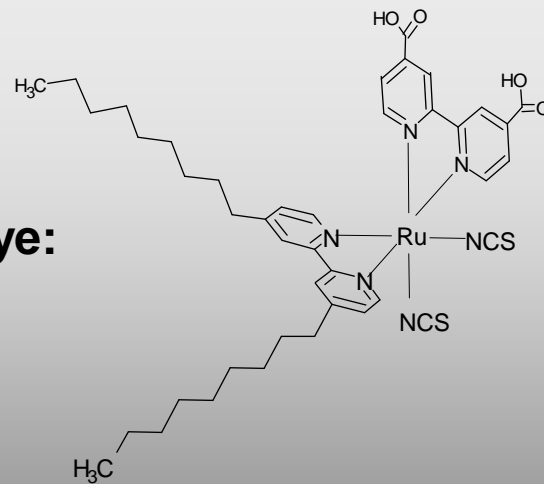
In order to improve dye regeneration a kinetically fast couple D/D^+ can be used in conjunction with the Co(II) mediator

Co(II) should efficiently reduce D^+ before back recombination can occur

MECHANISM



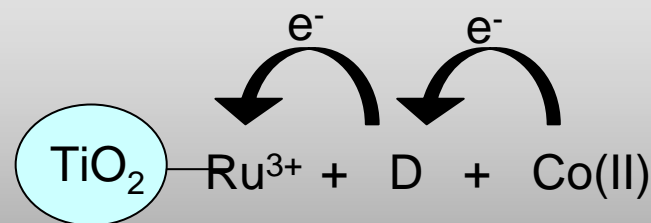
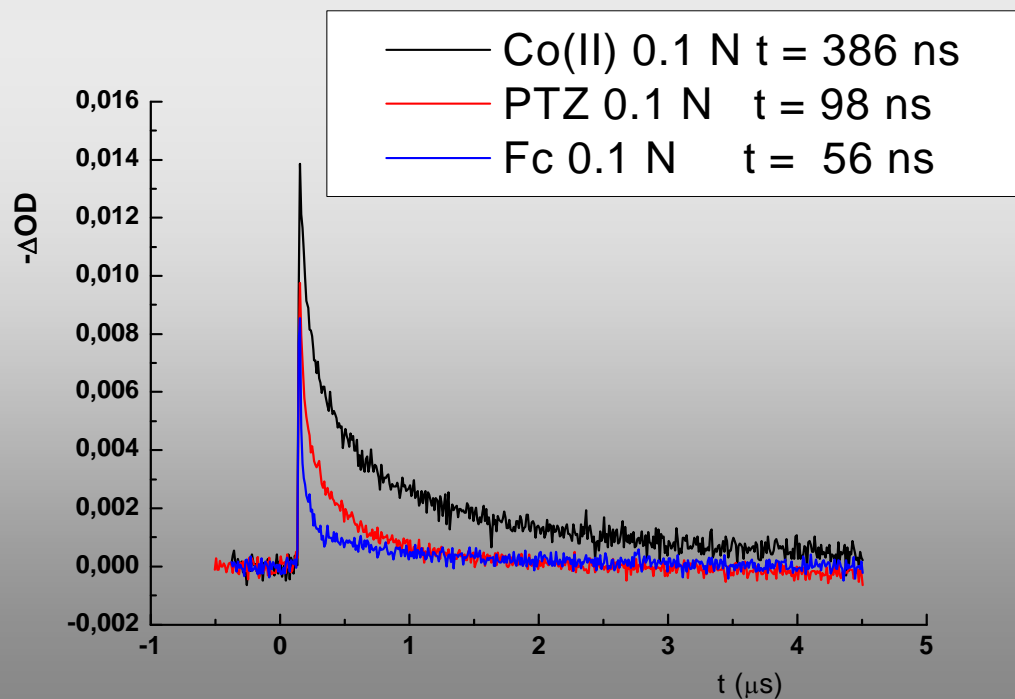
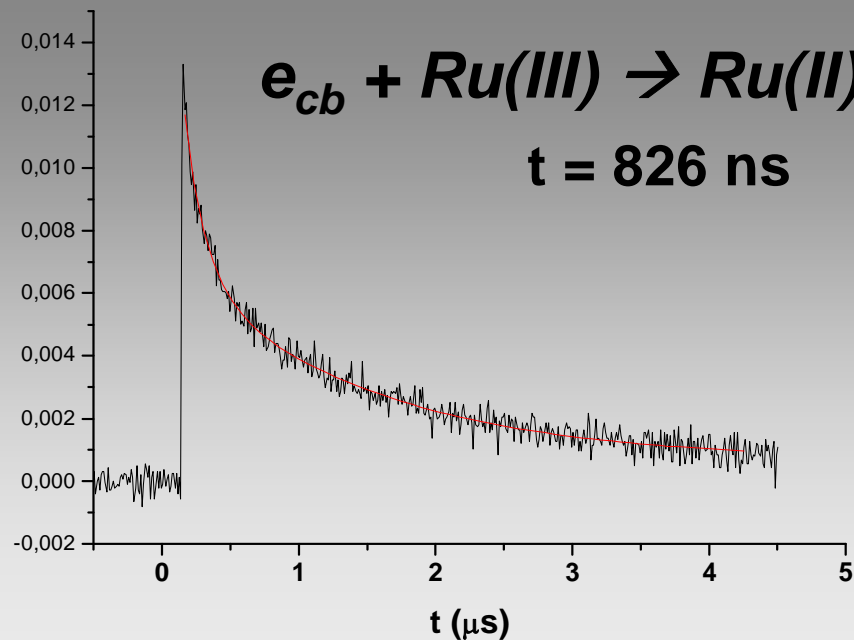
Dye:

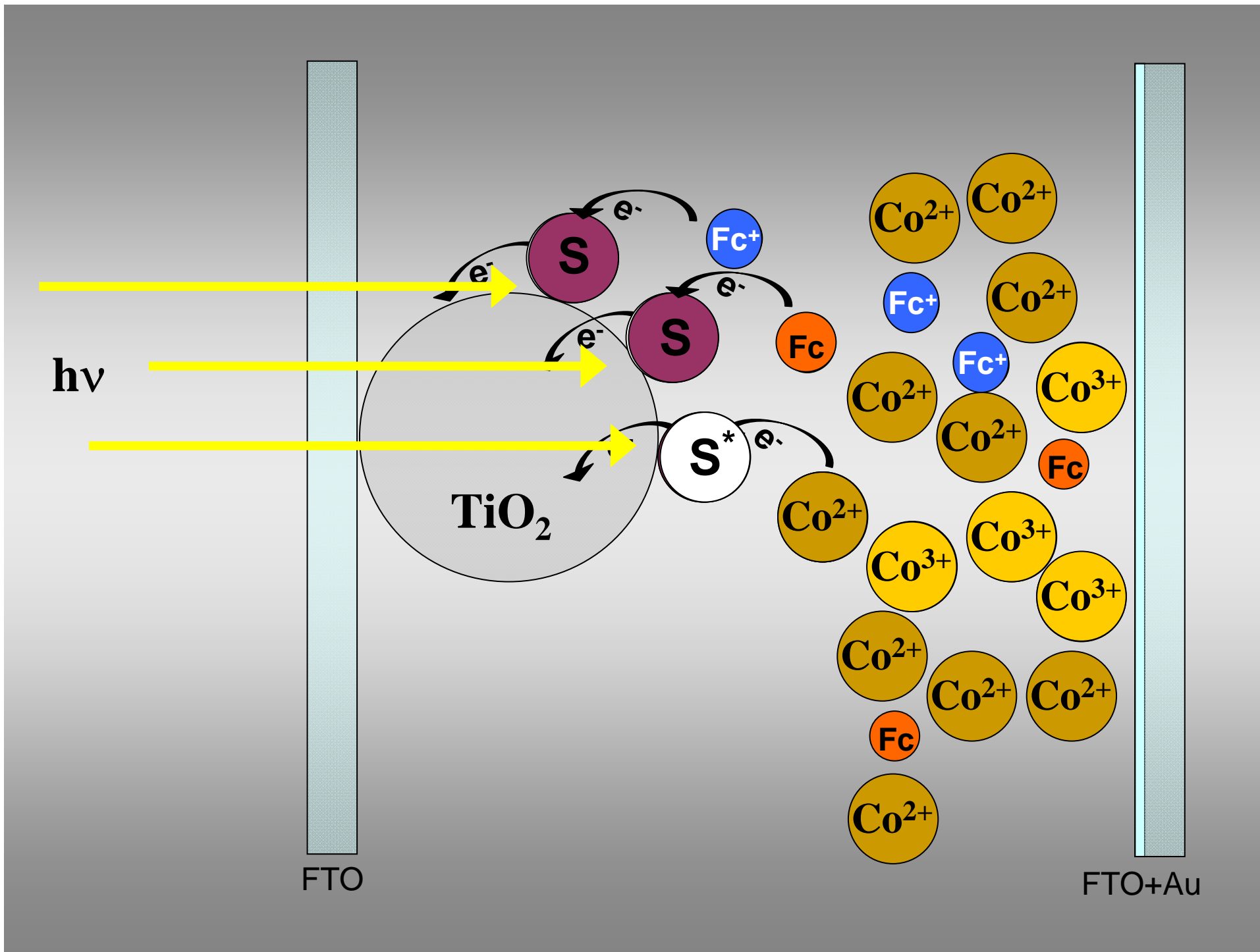


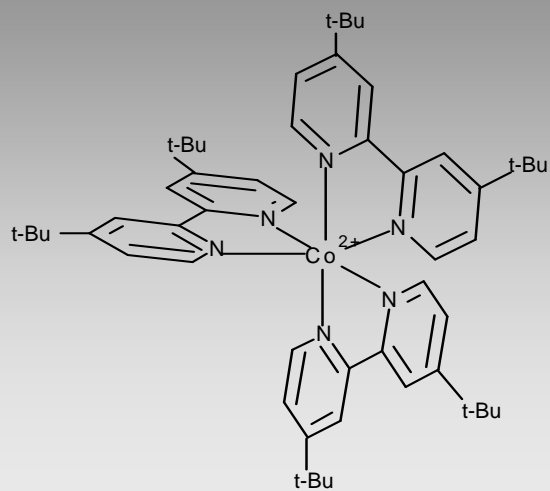
Z 907

D/D^+ : fast reduction of S^+

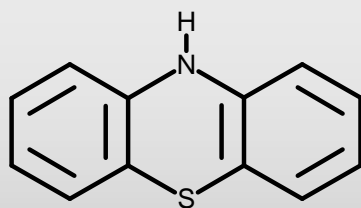
**Z 907 cation regeneration
with the different
electron mediators**



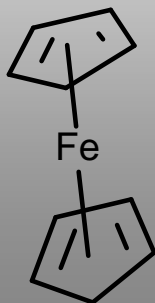




Co(II)

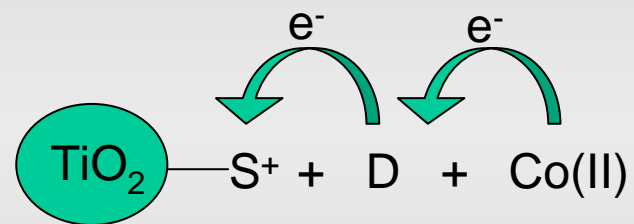


PTZ



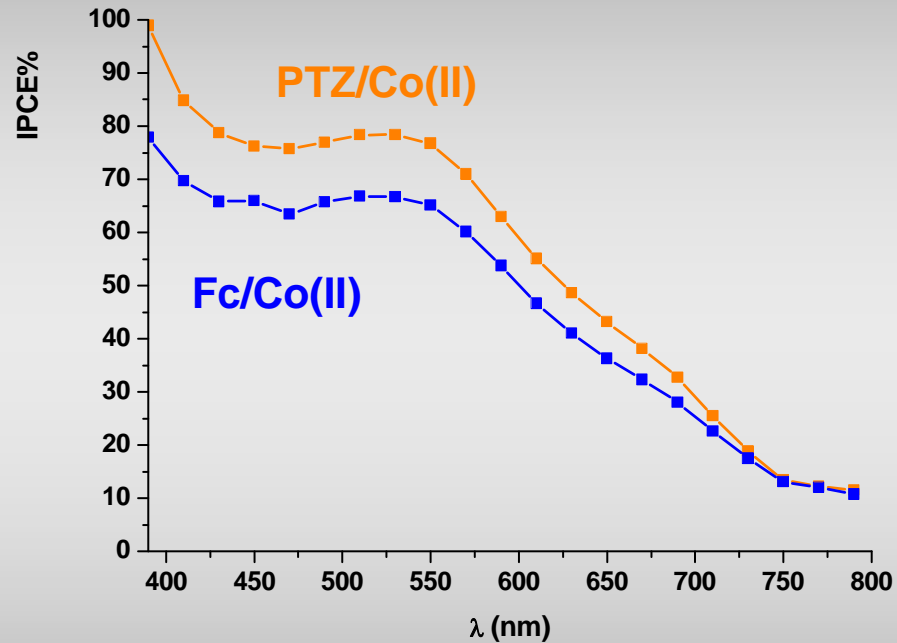
Fc

D

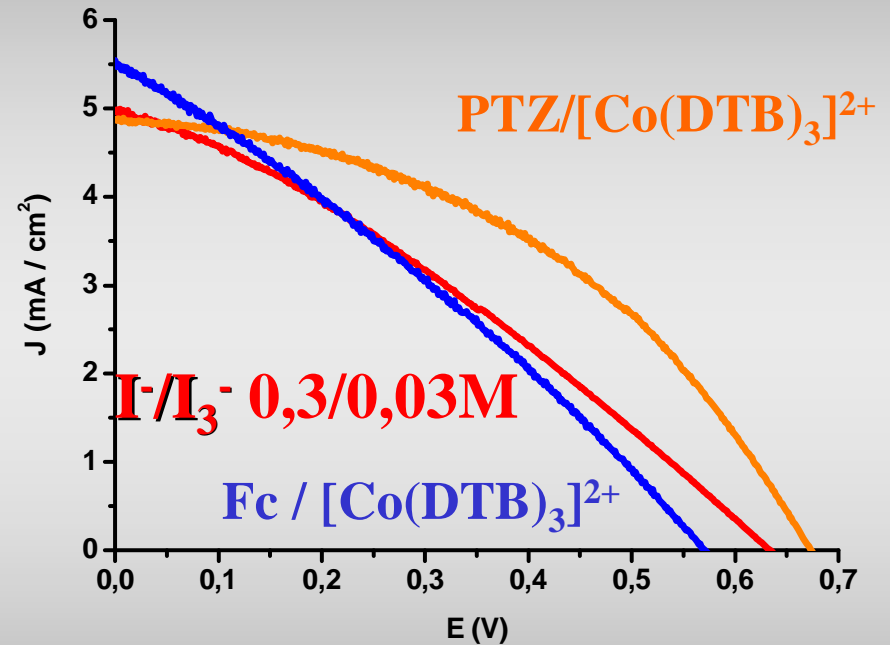


PHOTOELECTROCHEMISTRY

IPCE % Spectra



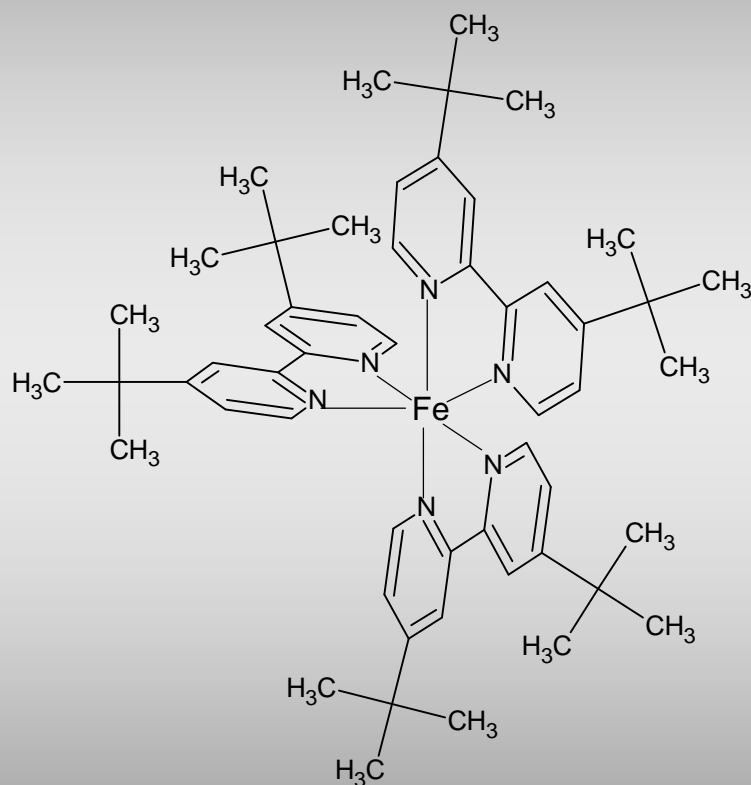
i-V curves



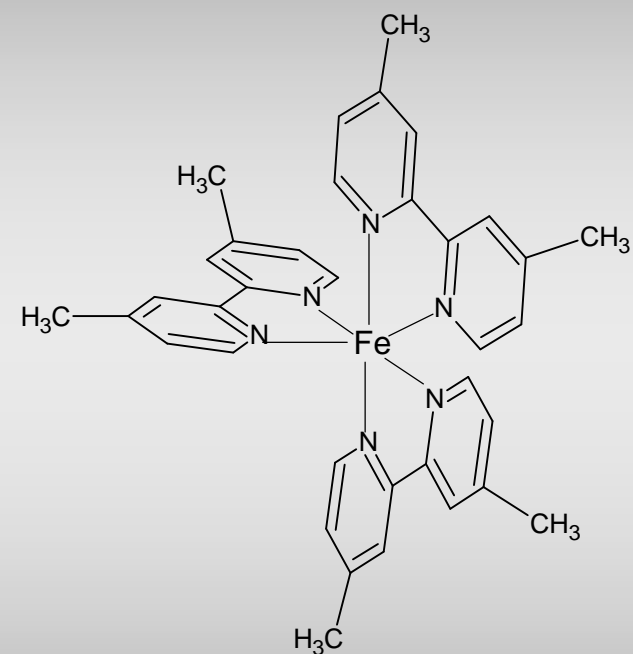
Best results obtained using a 1:2 D/Co(II) ratio

PTZ/Co(II) shows better performances

Iron complexes as co-mediators for DSSC

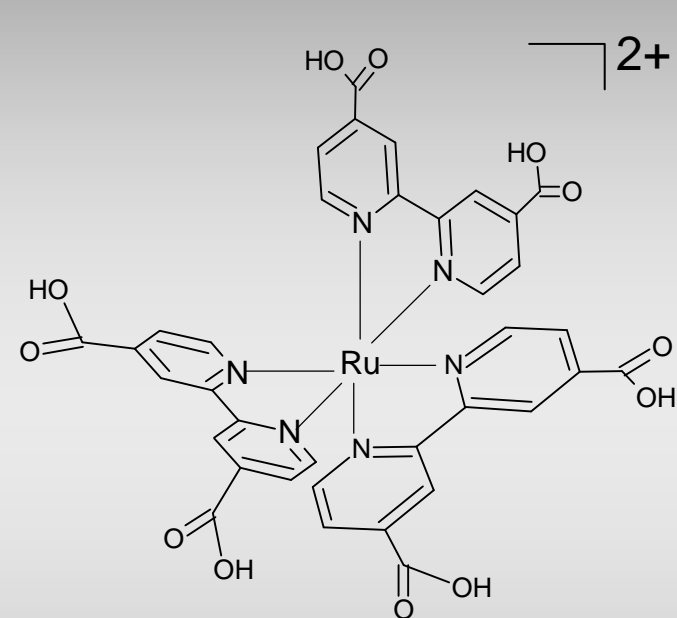
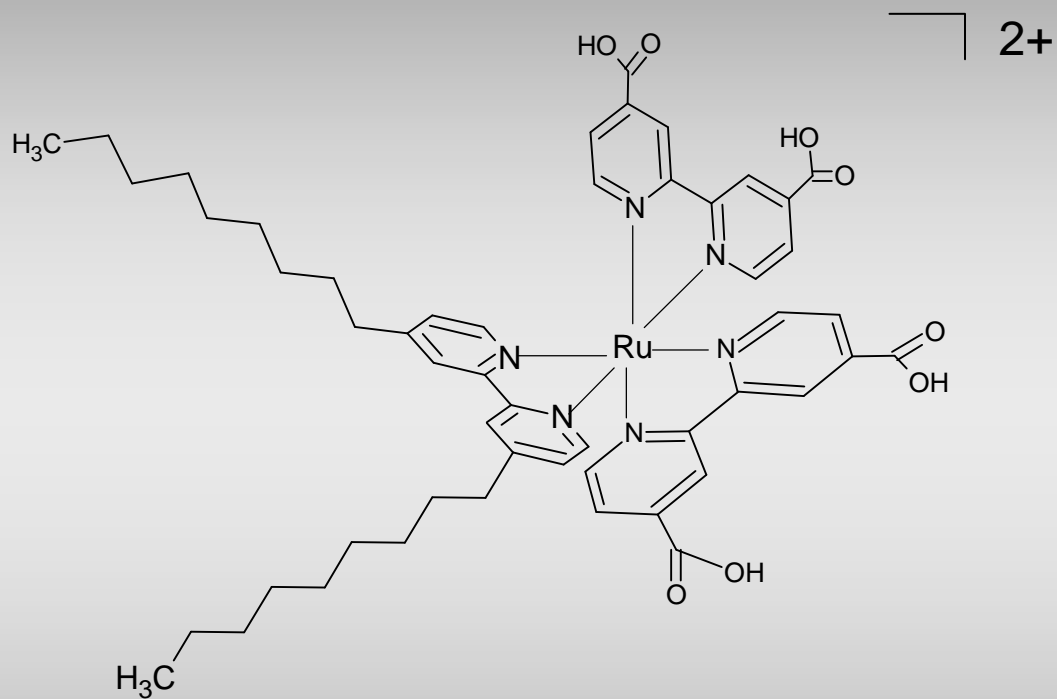


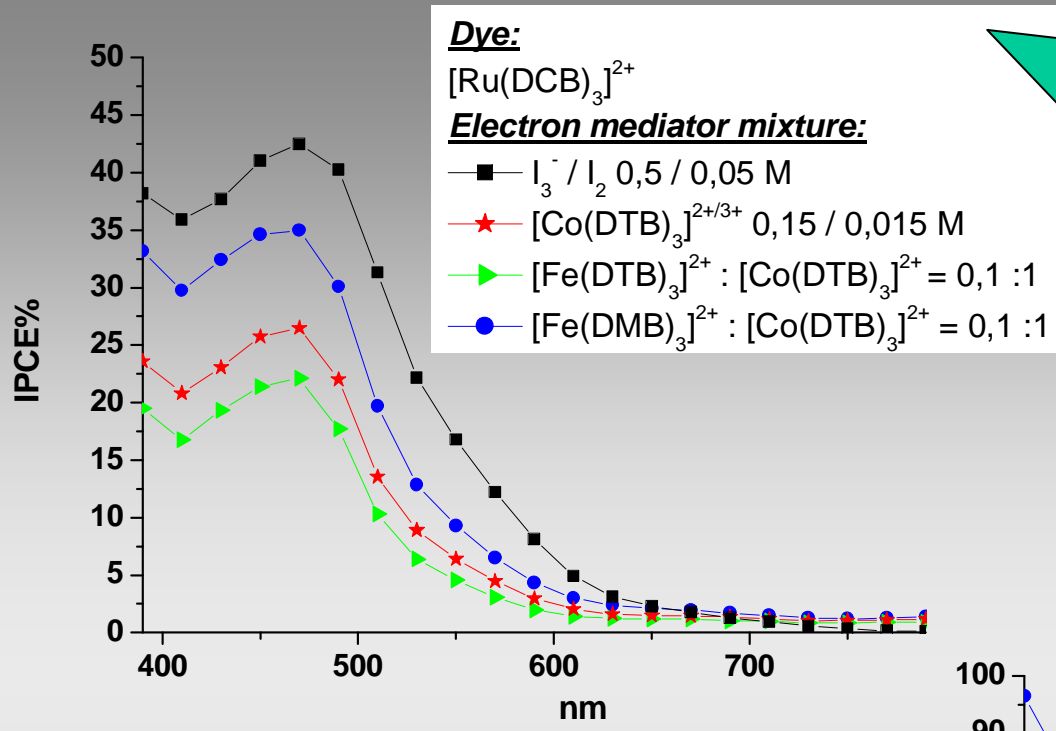
[Fe(DTB)₃]²⁺



[Fe(DMB)₃]²⁺

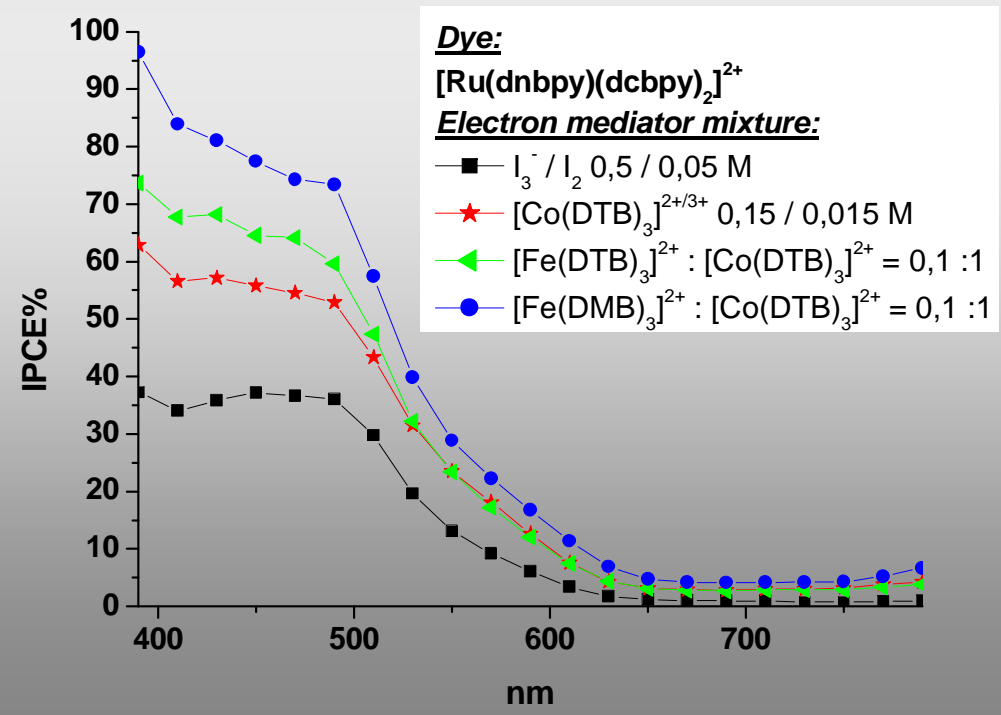
Dyes used in Fe(II)-Co(II) mediated cells



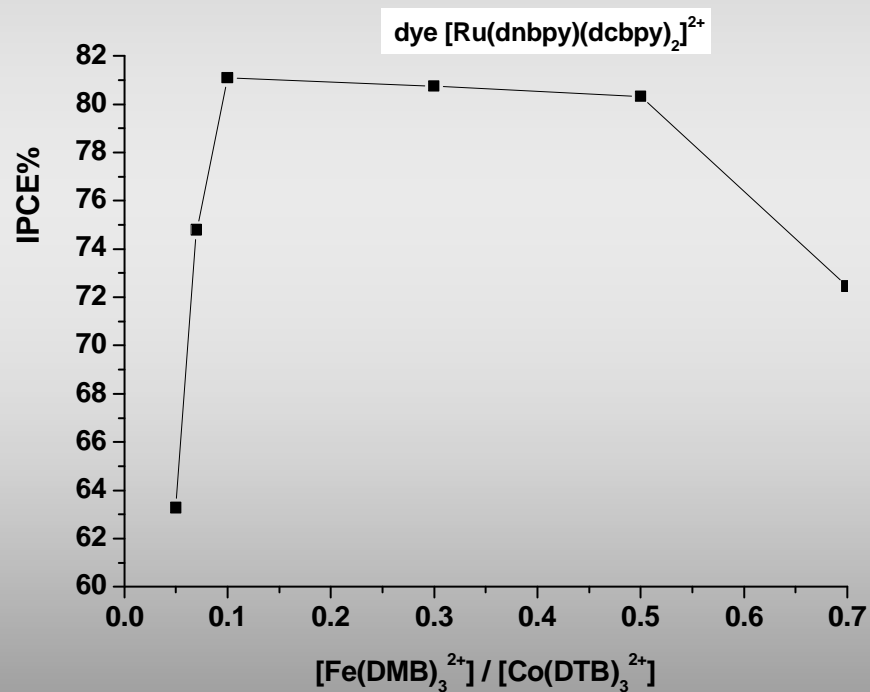


$[\text{Ru}(\text{DCB})_3]^{2+}$

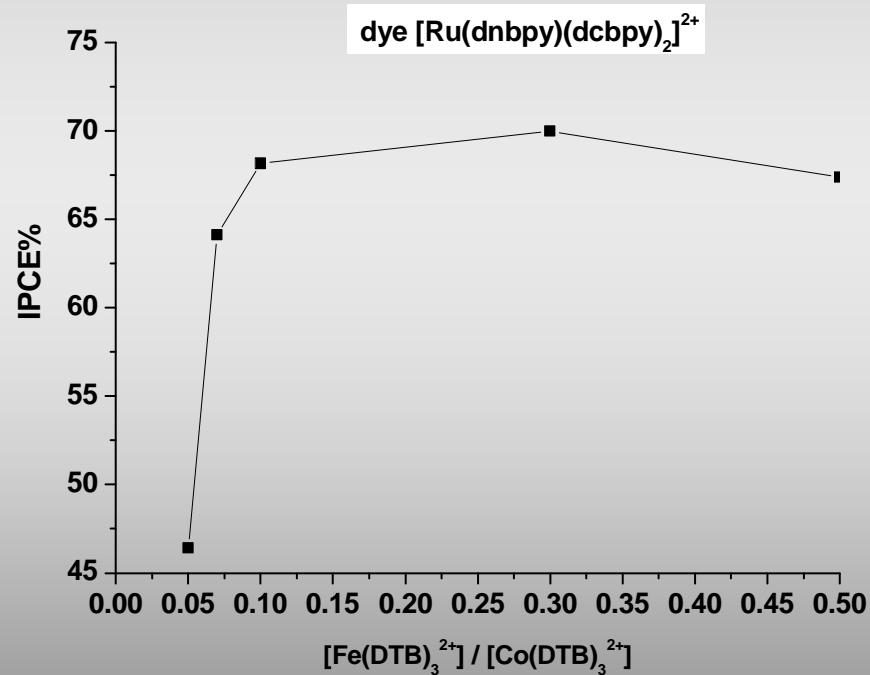
$[\text{Ru}(\text{dnbpy})(\text{dcbpy})_2]^{2+}$



Variation of maximum IPCE%
as function of electron mediator molar ratio, in a
 $[\text{Ru}(\text{dnbpy})(\text{dcbpy})_2]^{2+}$ sensitized SC

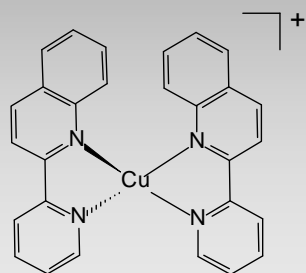


$\text{Fe}(\text{DMB})_3^{2+} / \text{Co}(\text{DTB})_3^{2+}$

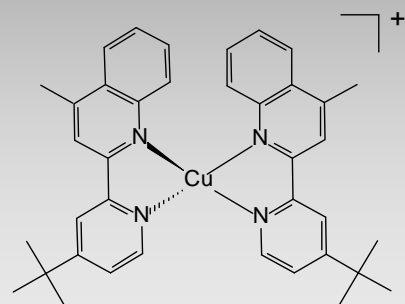


$\text{Fe}(\text{DTB})_3^{2+} / \text{Co}(\text{DTB})_3^{2+}$

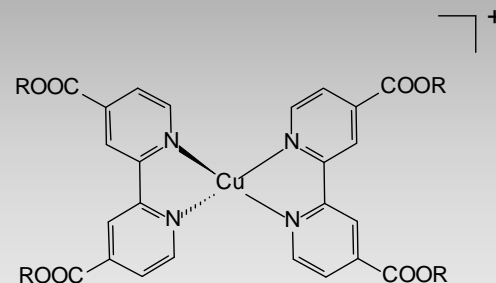
Cu(I) complexes as El. mediators



[Cu(PQ)₂]⁺ (1)



[Cu(MeTbPQ)₂]⁺ (2)



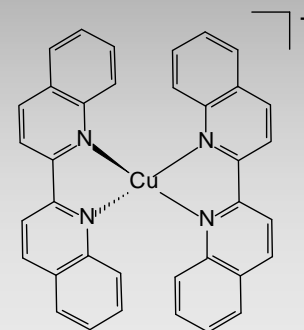
[Cu(bpy-(COOEt)₂)₂]⁺ (3)

[Cu(bpy-(COOnBut)₂)₂]⁺

(4)

[Cu(bpy-(COOTbut)₂)₂]⁺

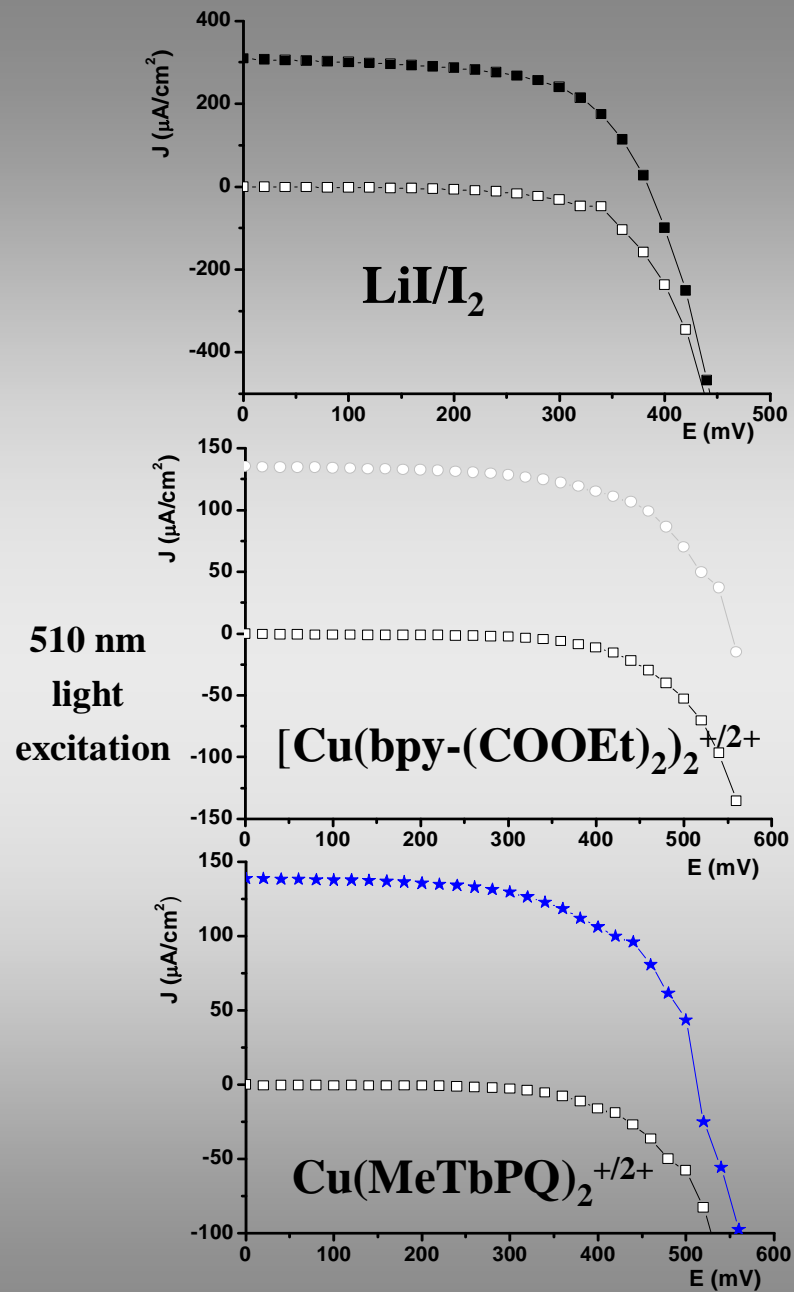
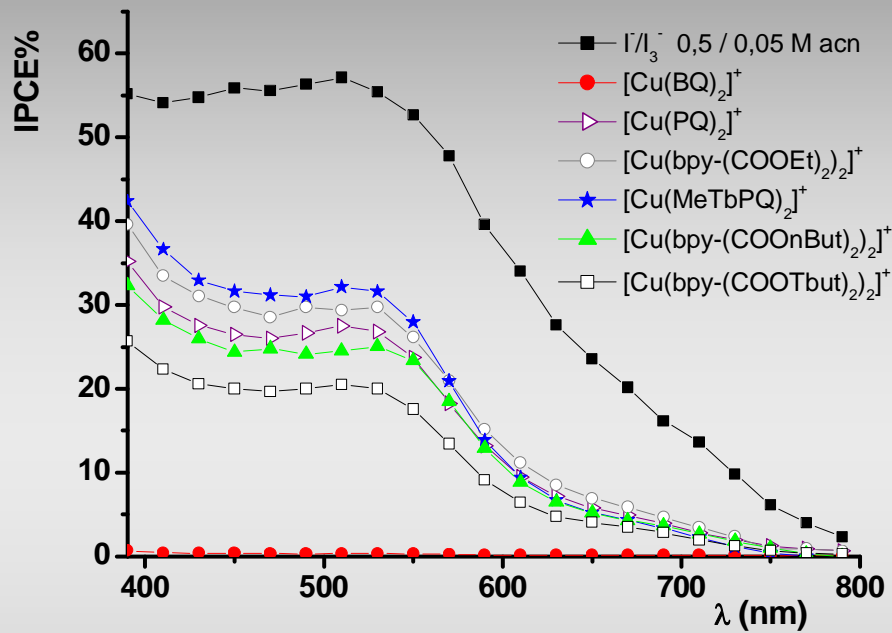
(5)



[Cu(BQ)₂]⁺ (6)

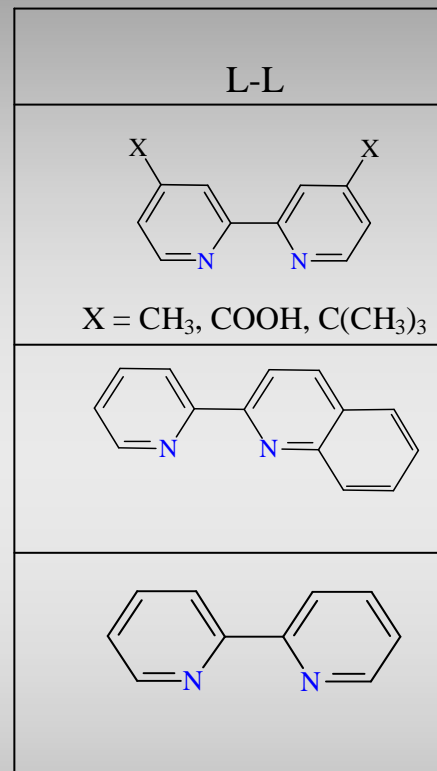
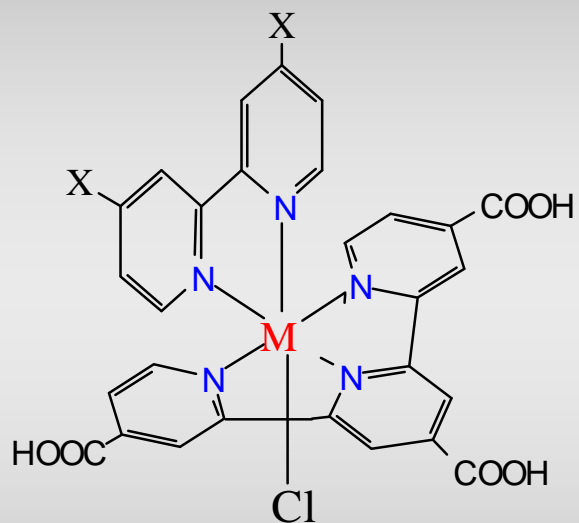
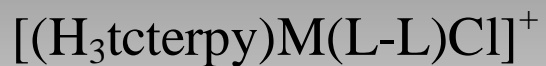
Complex	E _{1/2} (mV Vs SCE)
(1)	350
(2)	280
(3)	445
(4)	350
(5)	350
(6)	688

Z907 Dye



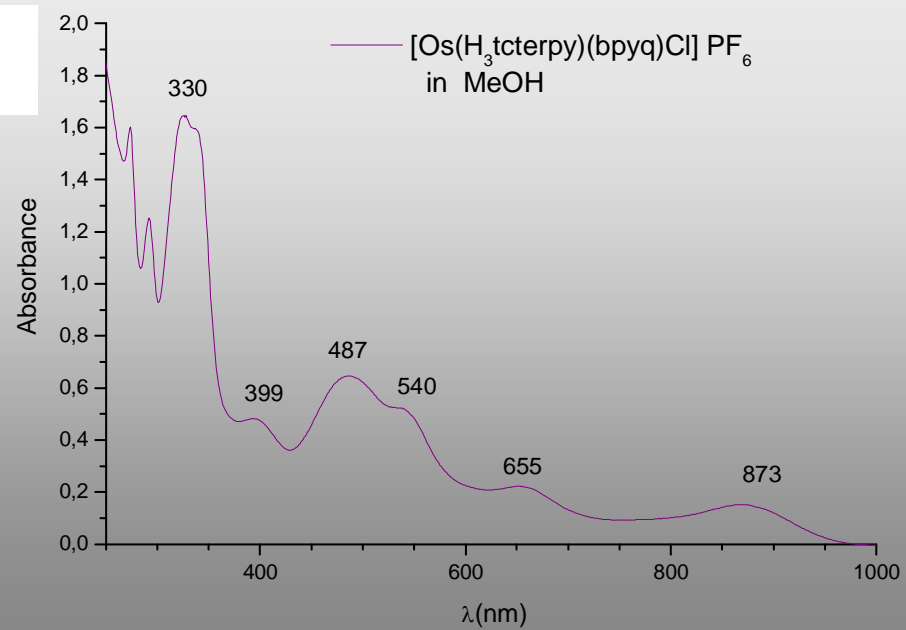
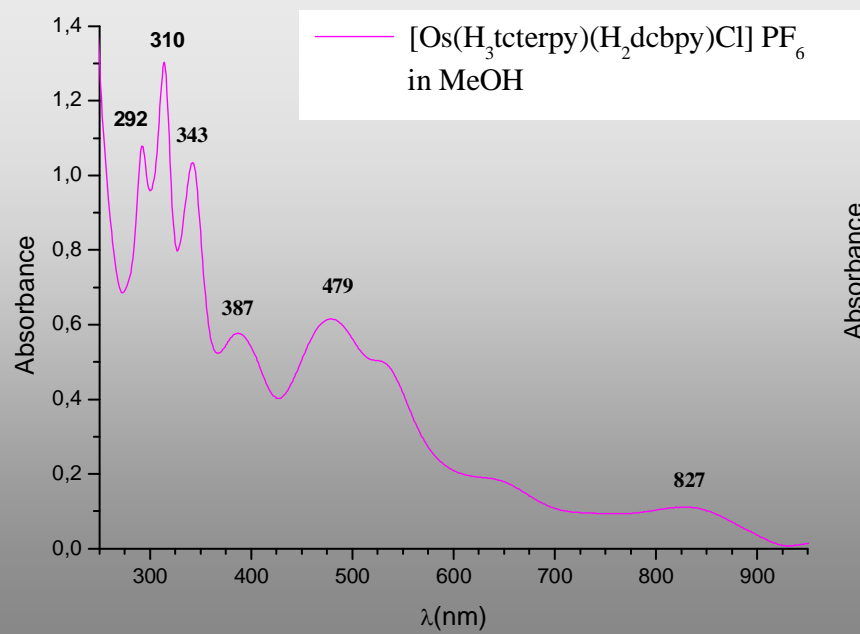
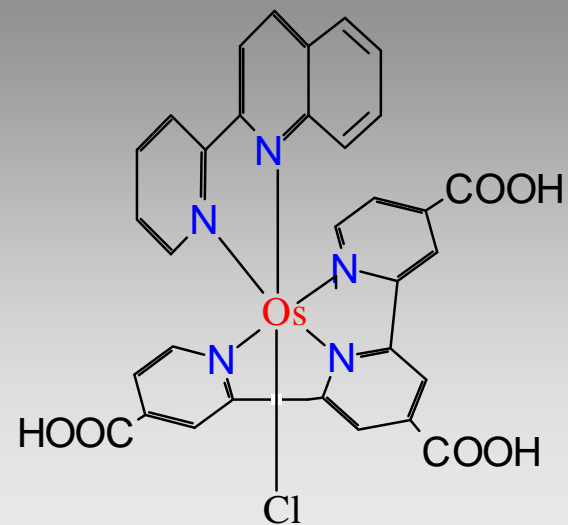
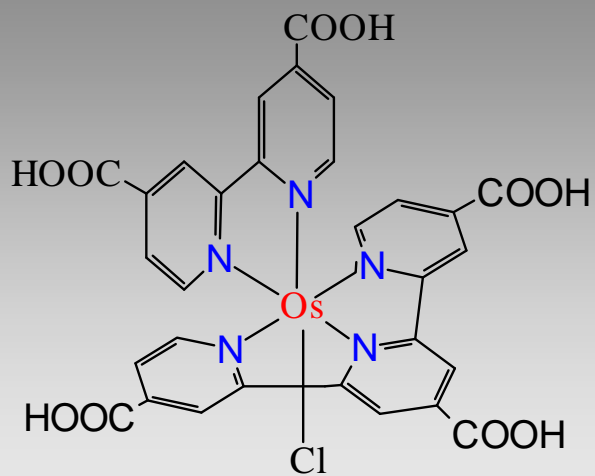
Dyes

Red Sensitive Molecular Sensitizers

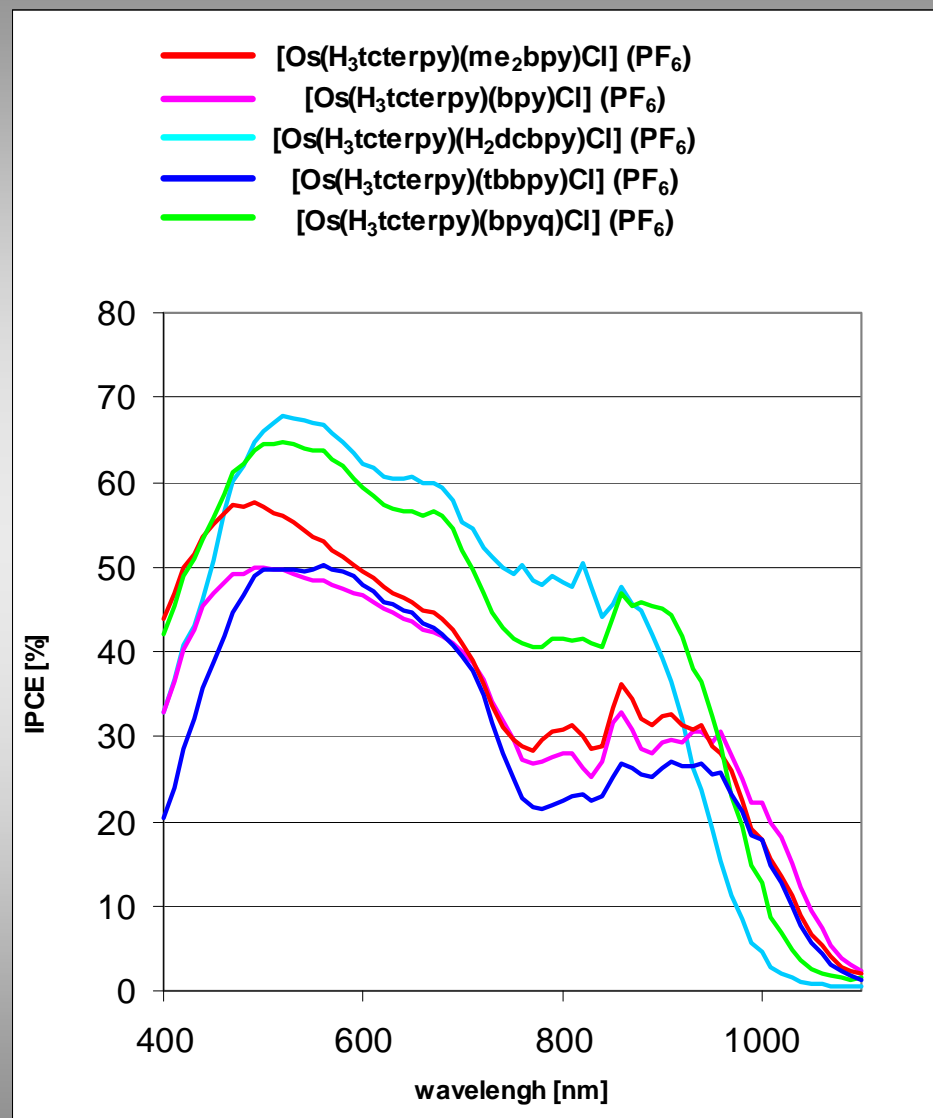


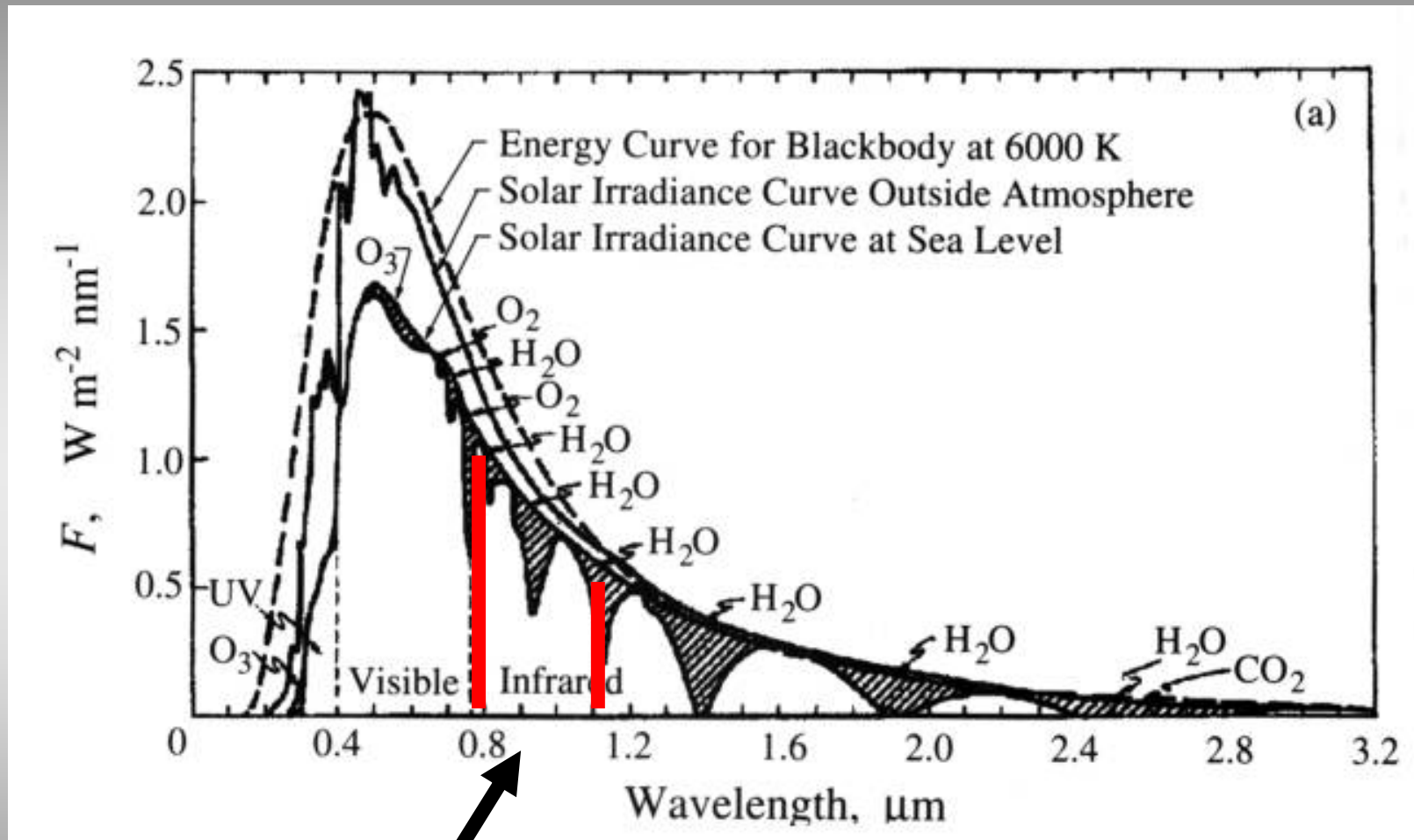
- 1 [Os(H₃tcterpy)(Me₂bpy)Cl] (PF₆)
- 2 [Os(H₃tcterpy)(Bipy)Cl] (PF₆)
- 3 [Os(H₃tcterpy)(H₂dc bpy)Cl] (PF₆)
- 4 [Os(H₃tcterpy)(tbbpy)Cl] (PF₆)

- 5 [Os(H₃tcterpy)(bpyq)Cl] (PF₆)
- 6 [Os(H₂dc bpy)₃]

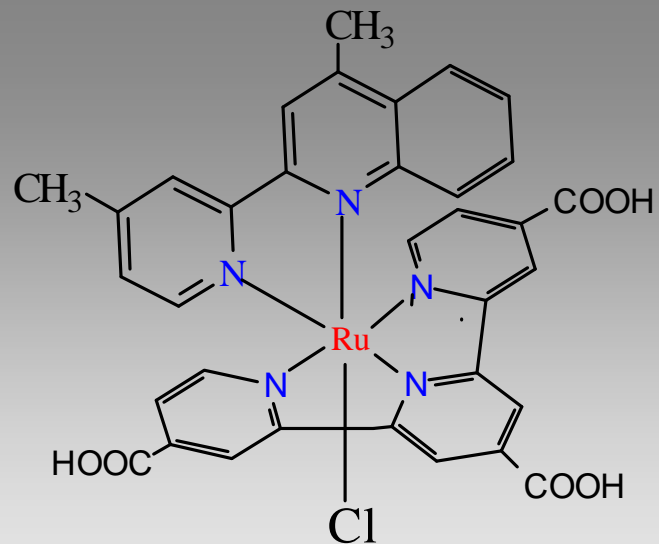


Photoaction Spectra of the New Os Dyes

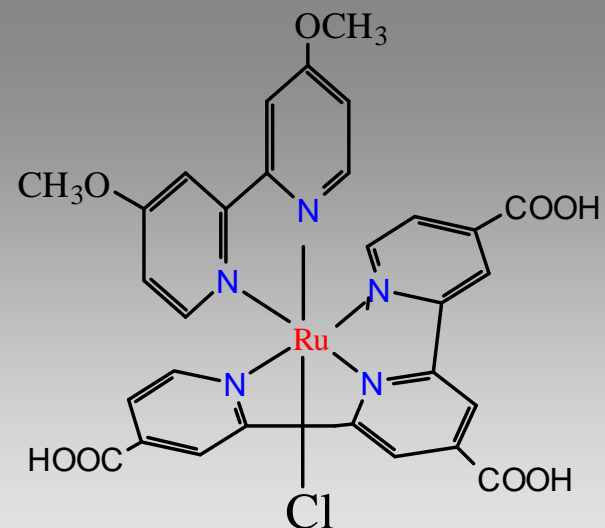




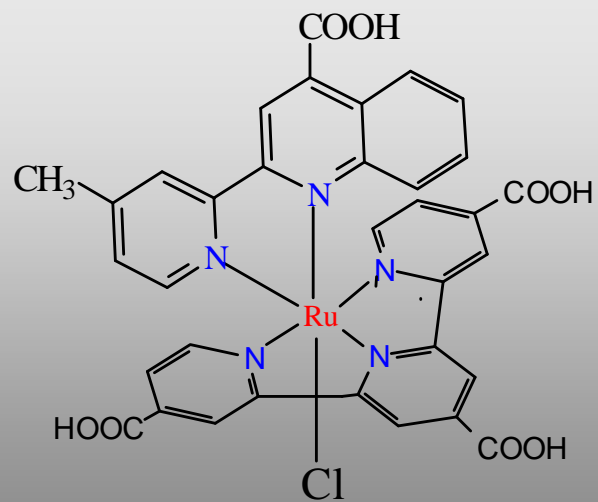
Enhanced red sensitivity by
using Osmium complexes



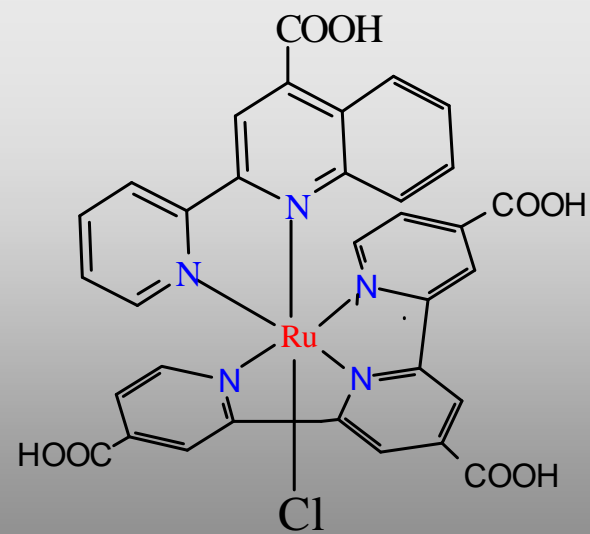
$[\text{Ru}(\text{H}_3\text{tcterpy})(\text{me}_2\text{bpyq})\text{Cl}]^+$



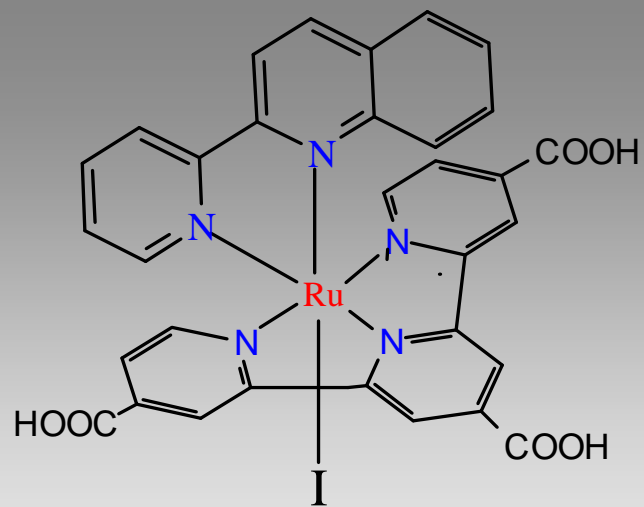
$[\text{Ru}(\text{H}_3\text{tcterpy})((\text{meO})_2\text{bpy})\text{Cl}]^+$



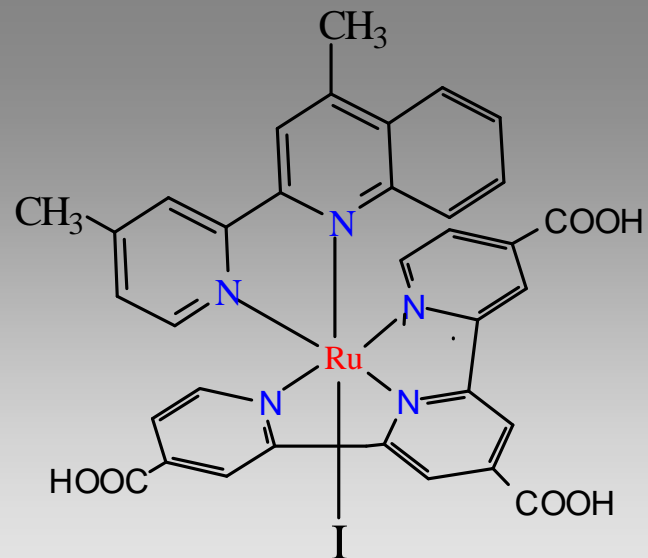
$[\text{Ru}(\text{H}_3\text{tcterpy})(\text{mebpyqCOOH})\text{Cl}]^+$



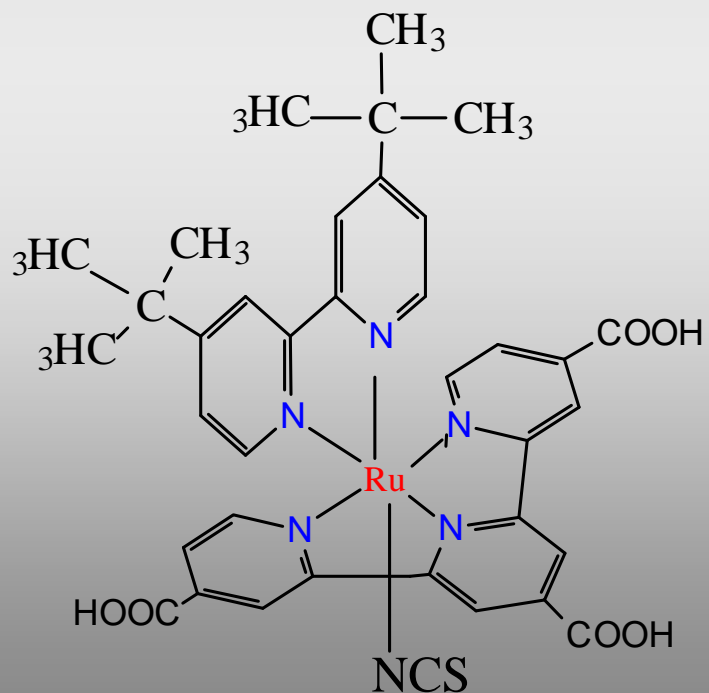
$[\text{Ru}(\text{H}_3\text{tcterpy})(\text{Hcbpyq})\text{Cl}]^+$



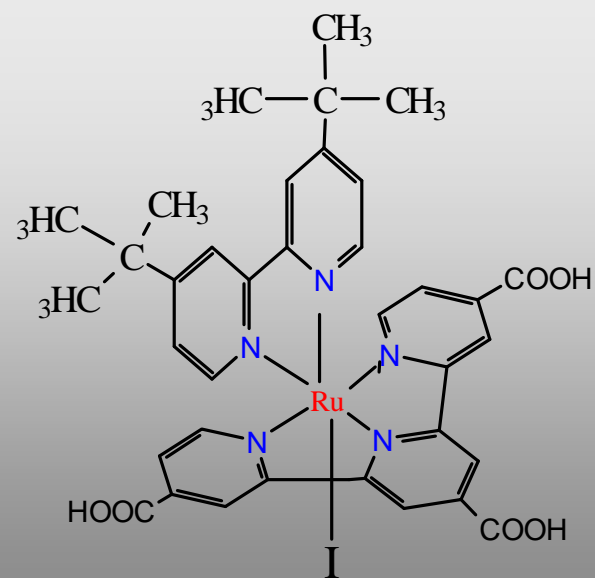
$[\text{Ru}(\text{H}_3\text{tcterpy})(\text{bpyq})\text{I}]^+$



$[\text{Ru}(\text{H}_3\text{tcterpy})(\text{me}_2\text{bpyq})\text{I}]^+$

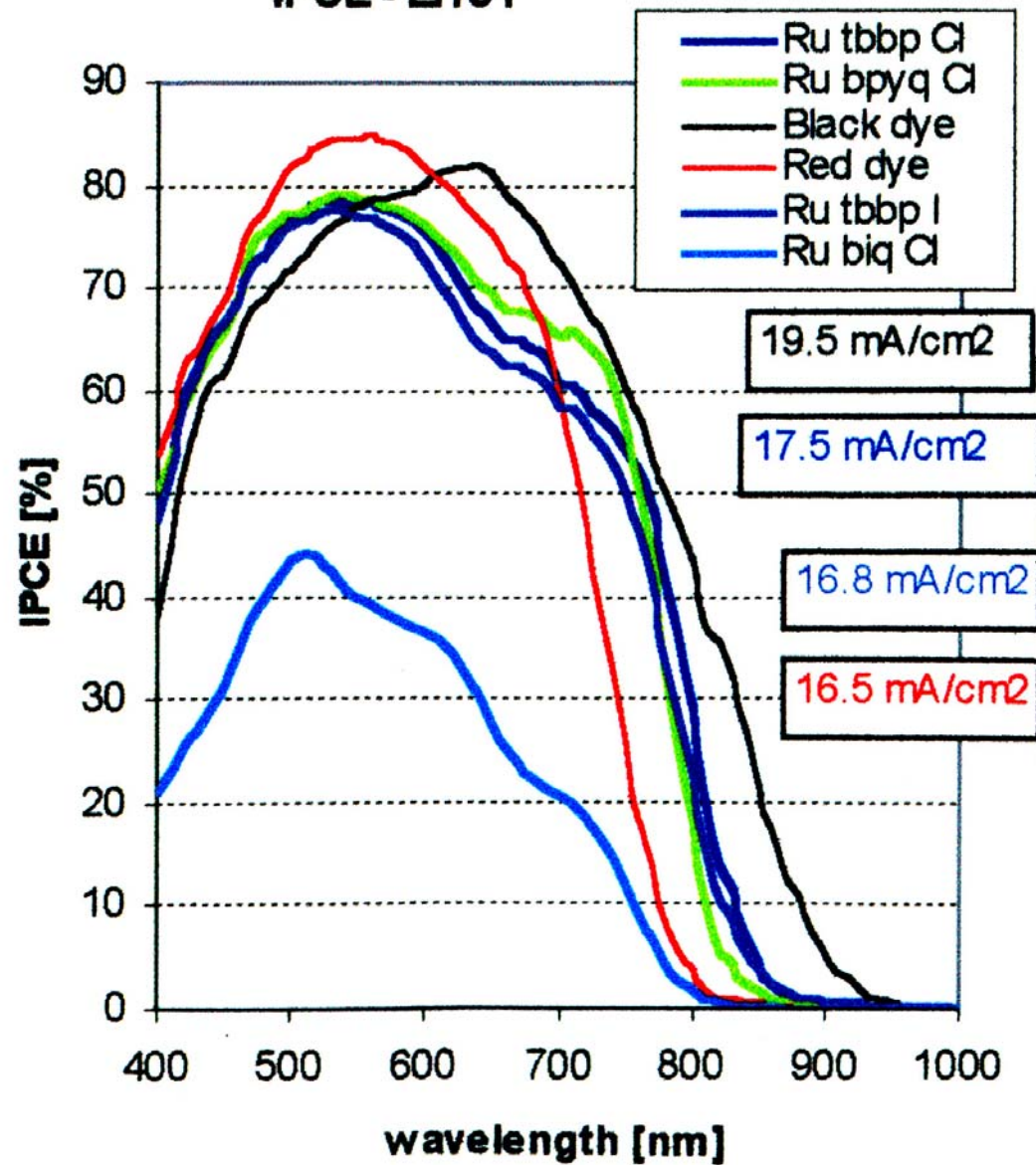


$[\text{Ru}(\text{H}_3\text{tctery})(\text{tb}_2\text{bpy})\text{NCS}]^+$



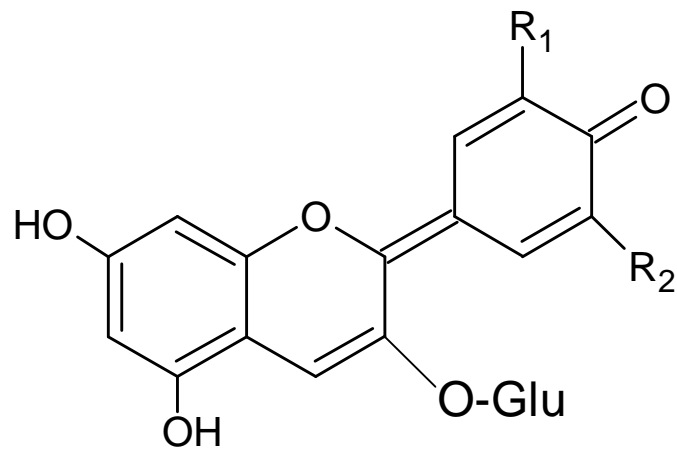
$[\text{Ru}(\text{H}_3\text{tctery})(\text{tb}_2\text{bpy})\text{I}]^+$

IPCE - E151



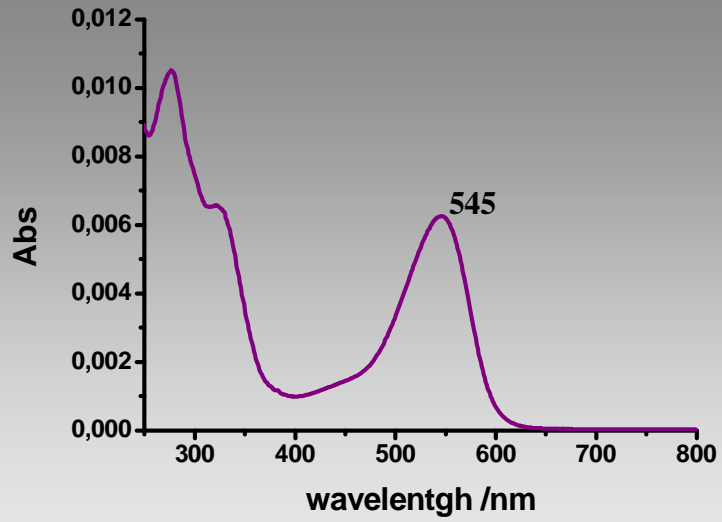
Natural Dyes

Anthocyanin dyes extracted from eggplants, radicchio and red grapes.

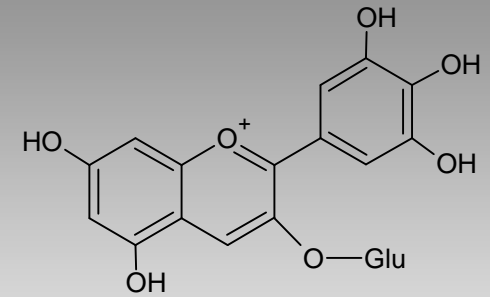


	R_1	R_2
Delfidina 3-glucoside	OH	OH
Malvidina 3-glucoside	OCH_3	OCH_3
Cianidina 3-glucoside	OH	H

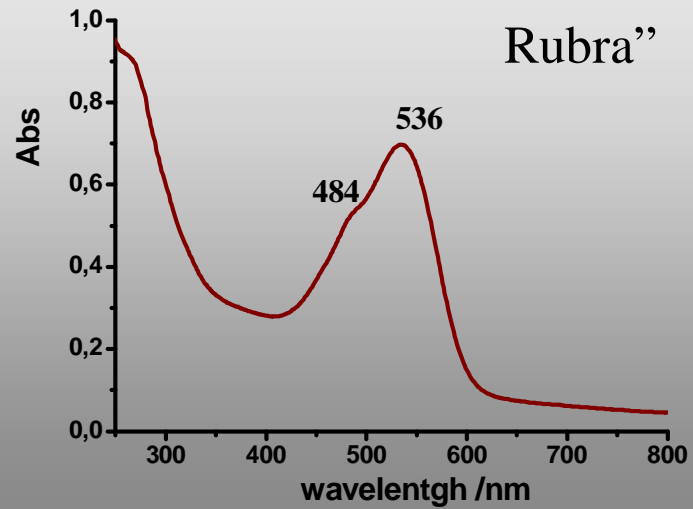




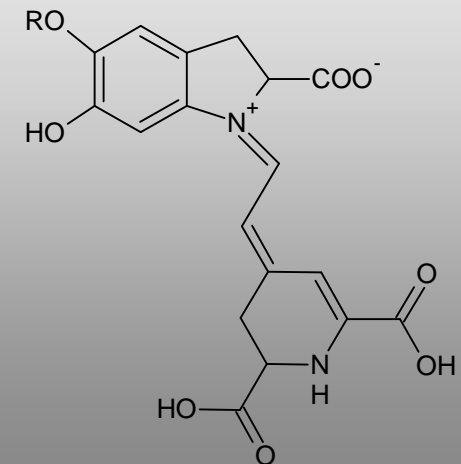
Anthocyanins



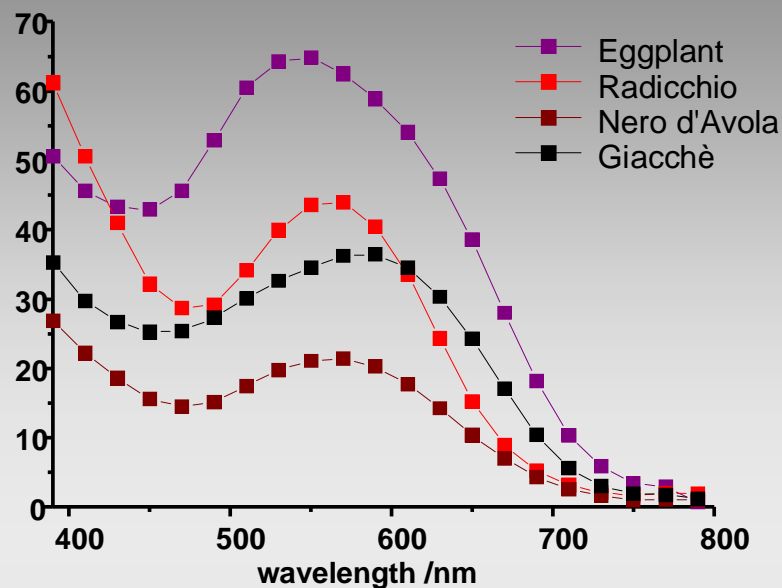
Red Turnip "Beta Vulgaris Rubra"



Betalains



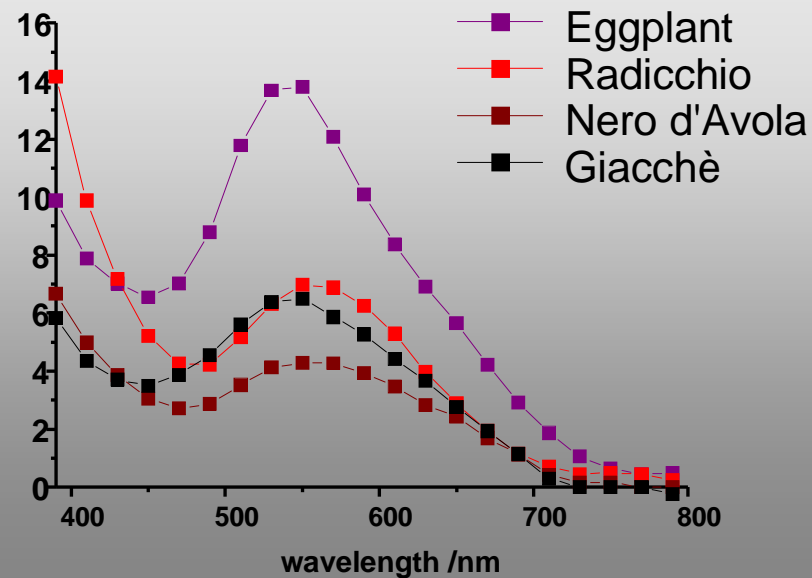
IPCE%



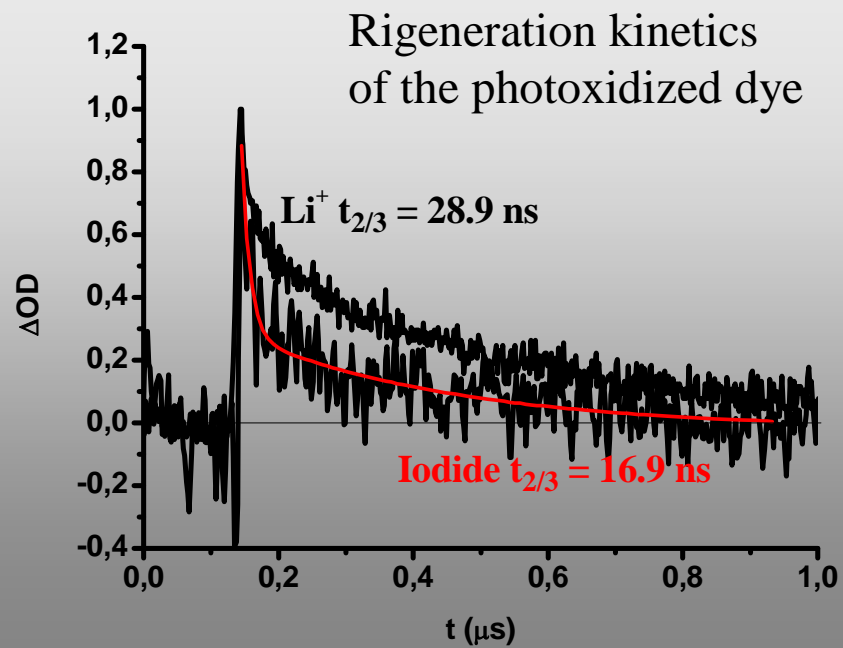
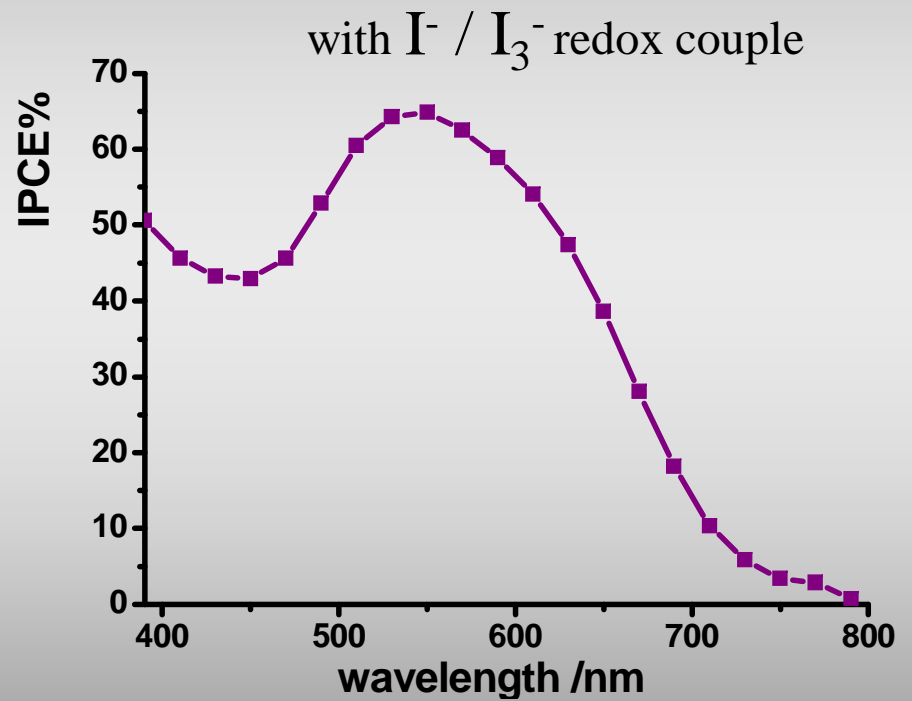
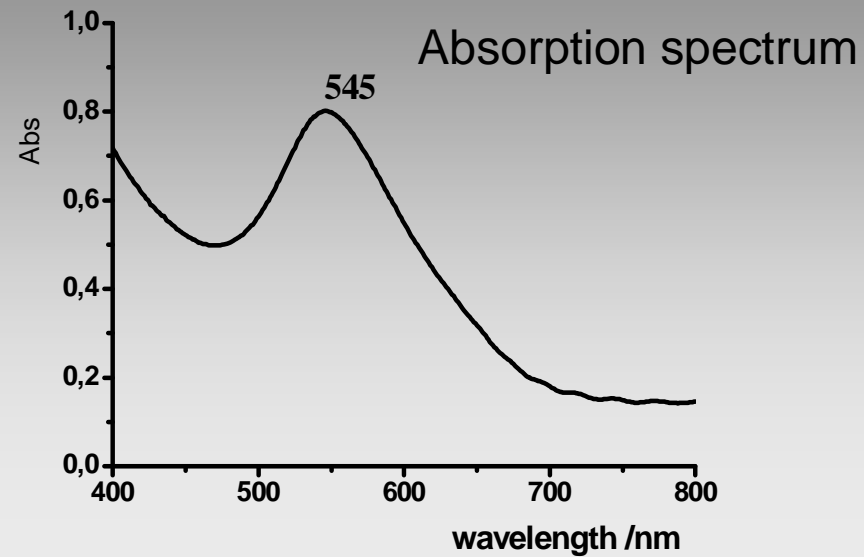
IPCE%
LiI/I₂ 0,5/ 0,05 M in ACN

IPCE%
Co(DTB)₃²⁺ 0,15 M in acetonitrile

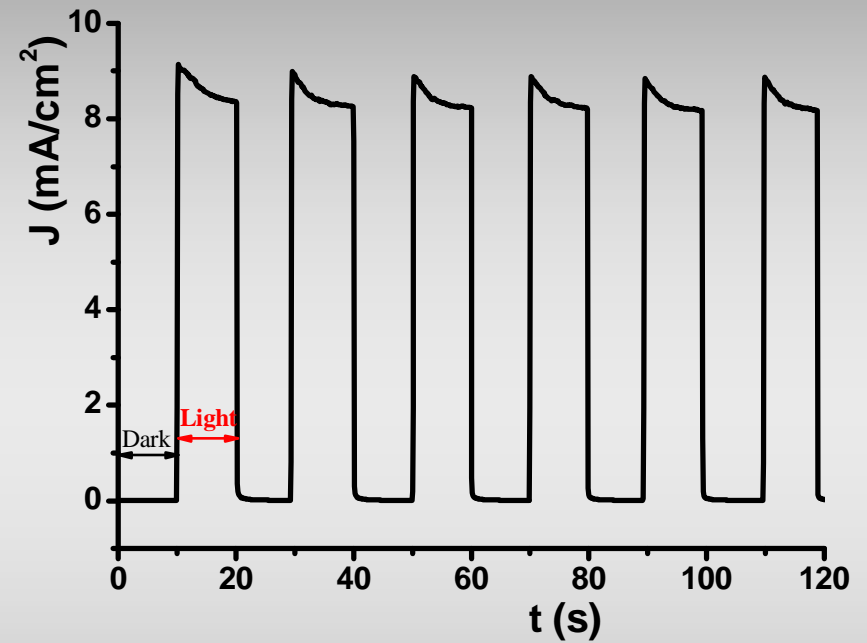
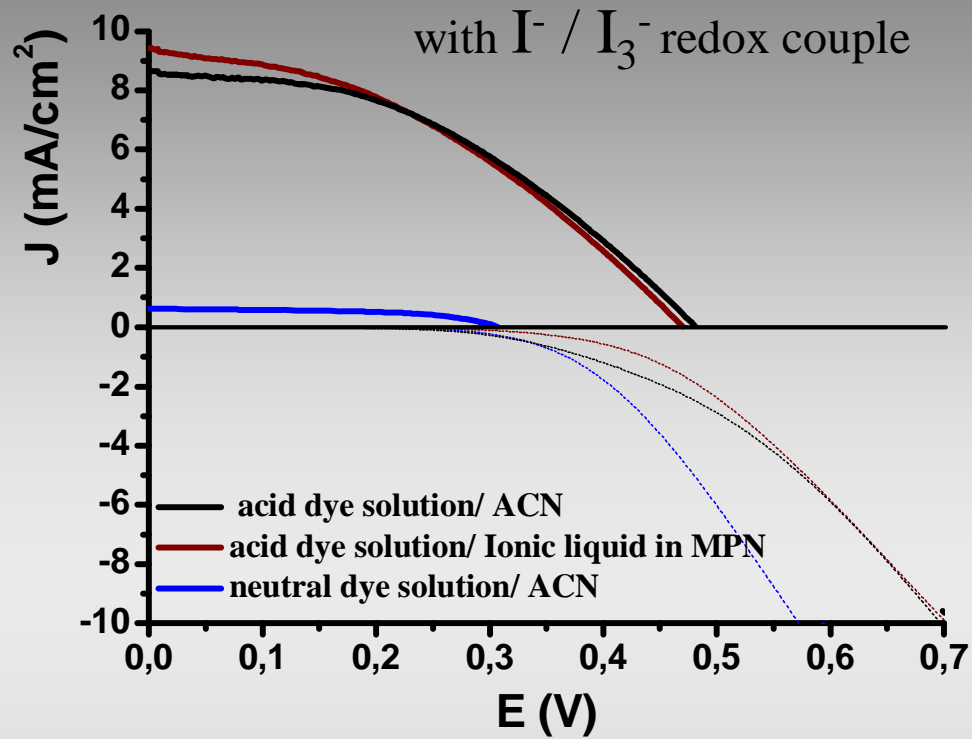
IPCE%



Eggplant



Red Turnip



	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	$\eta\%$
w block	8.66	480	0.42	1.74

N-719

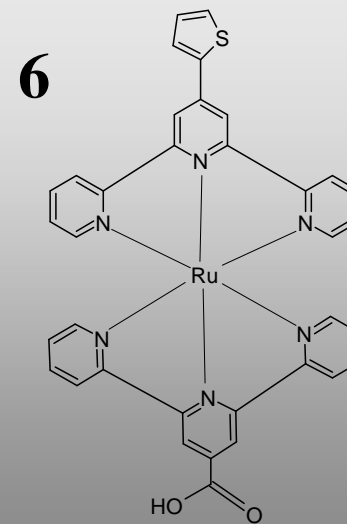
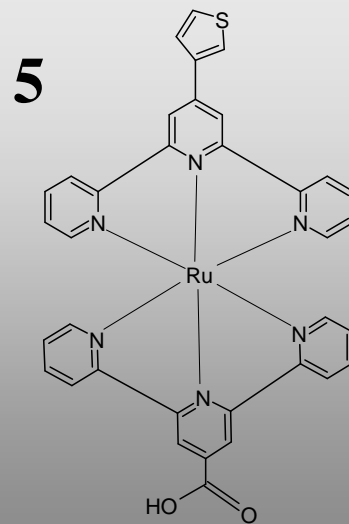
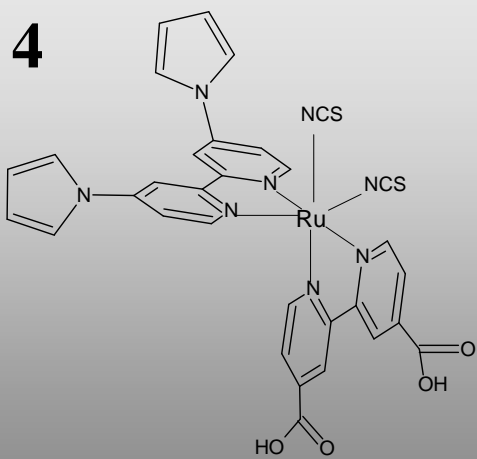
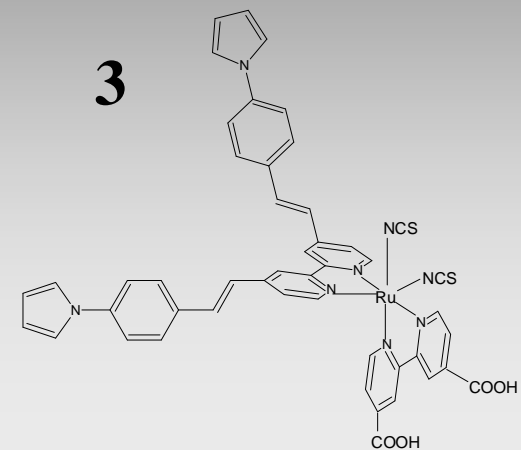
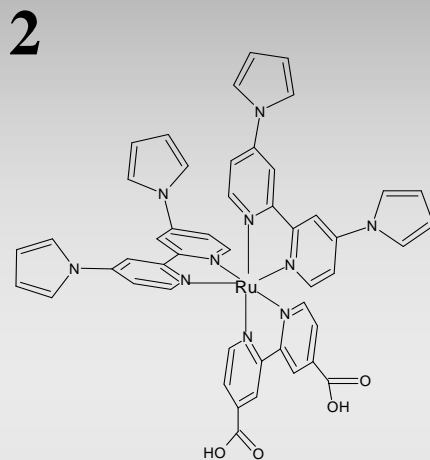
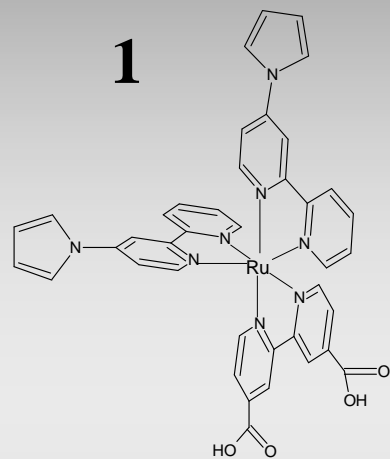
$$J_{sc} = 17.73 \text{ mA/cm}^2$$

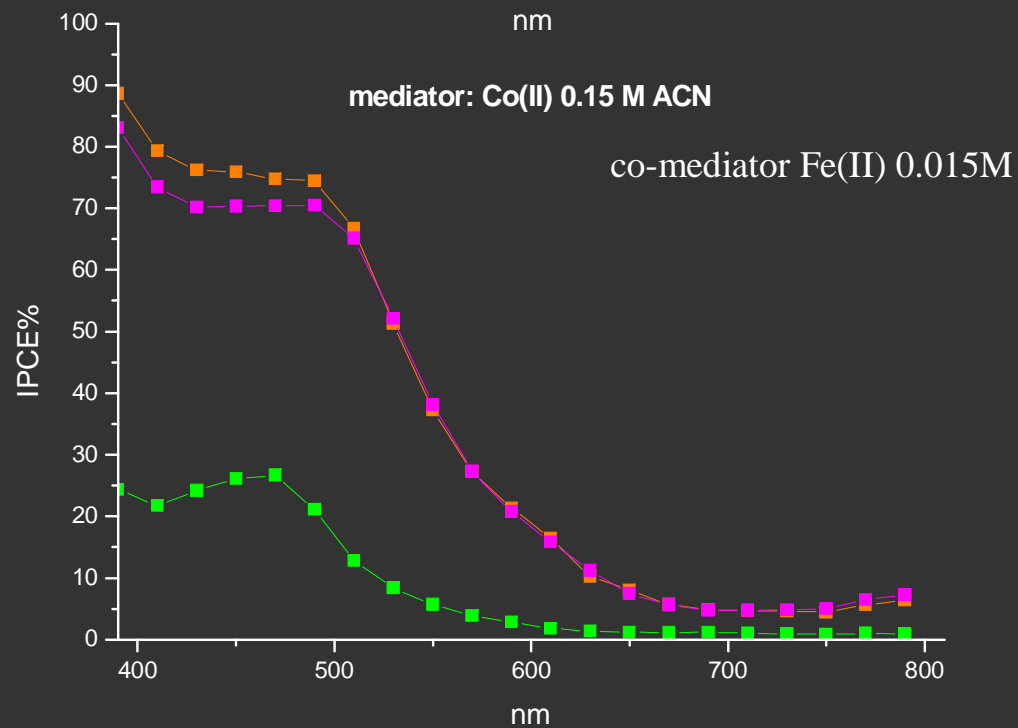
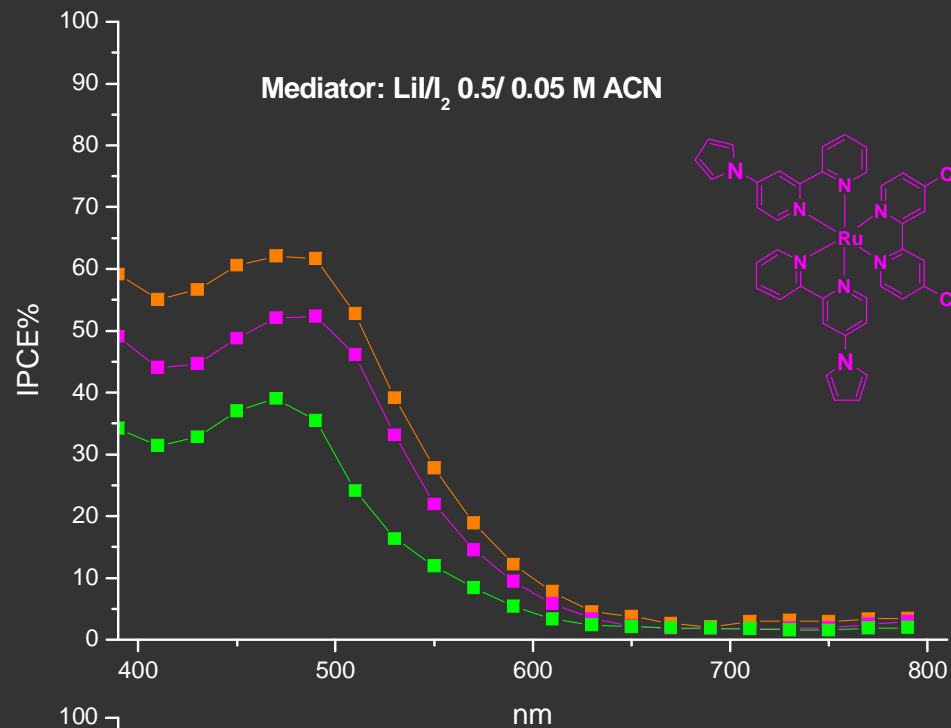
$$V_{oc} = 532 \text{ mV}$$

$$\eta = 3.3\%$$

- Polymerizable Dyes
- Towards Solid State Devices

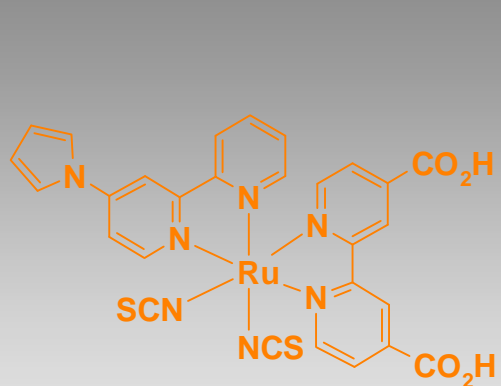
Polipyridyl Ru(II) complexes



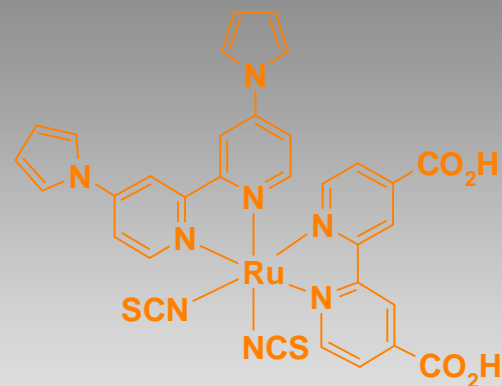


Strong influence of Redox mediator

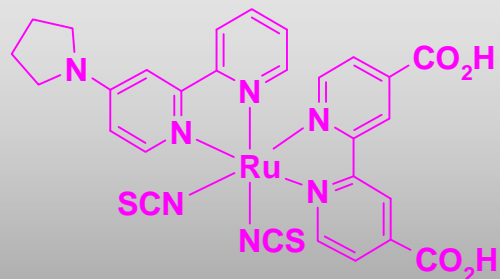
tris-heteroleptic complexes



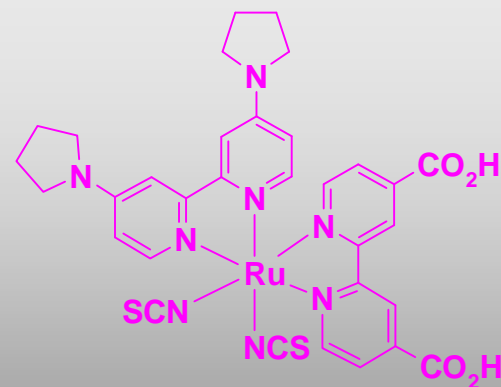
λ_{max} (nm) : 385 (7300) et 532 (7200)
E1/2 ox (V/ECS) : 0.62



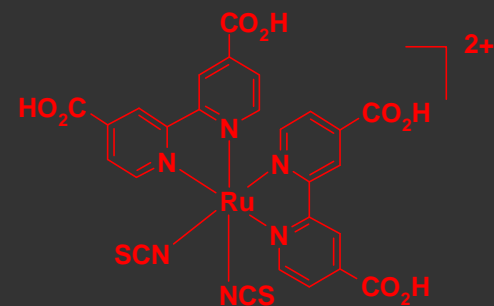
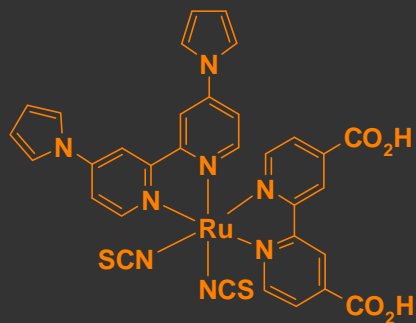
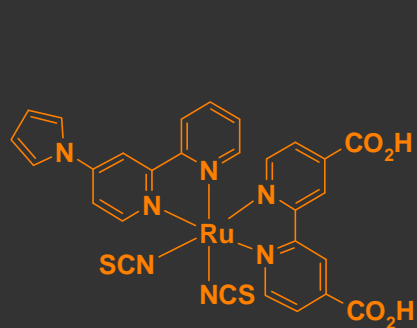
λ_{max} (nm) : 379 (10200) et 534 (8700)
E1/2 ox (V/ECS) : 0.61



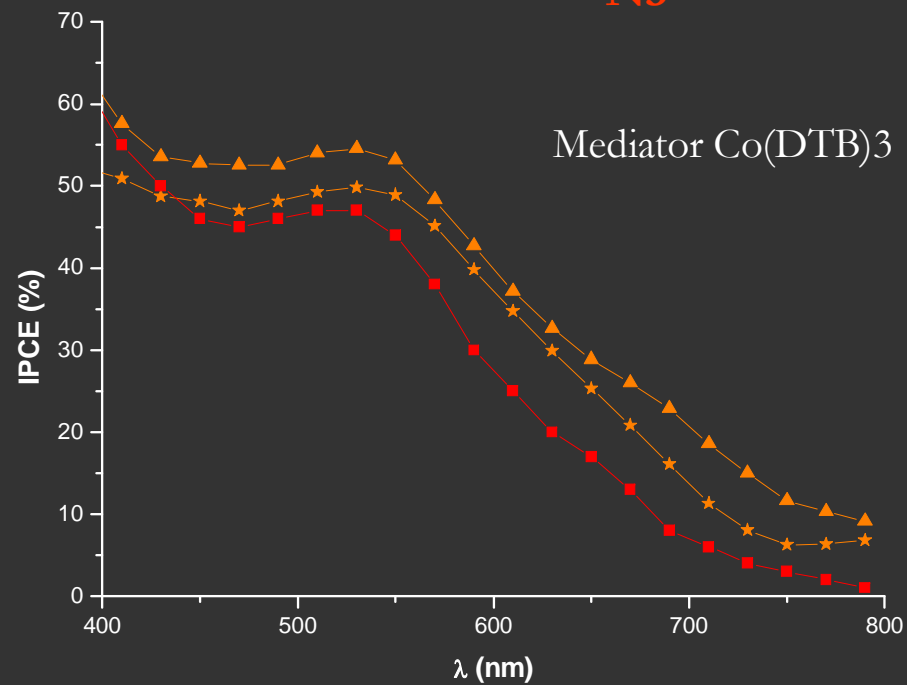
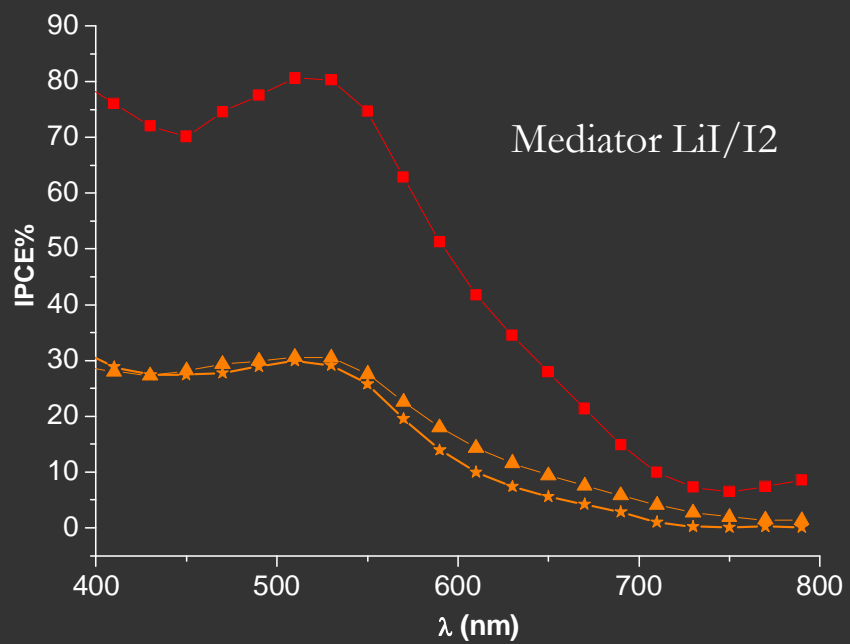
λ_{max} (nm) : 385 (7200) et 538 (7600)
E1/2 ox (V/ECS) : 0.50



λ_{max} (nm) : 424 (7700) et 542 (6500)
E1/2 ox (V/ECS) : 0.37

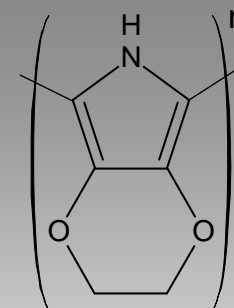


N3

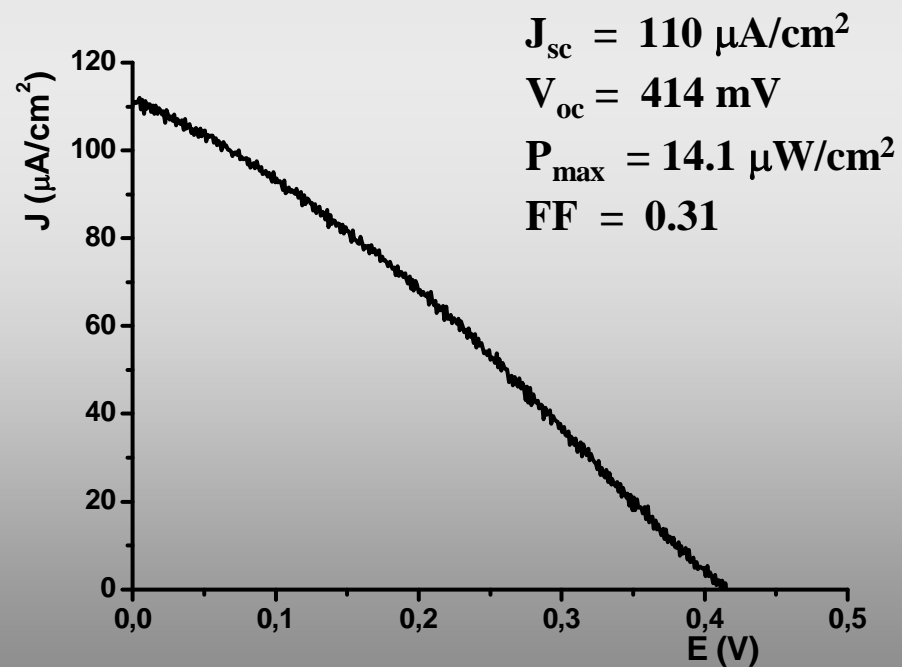
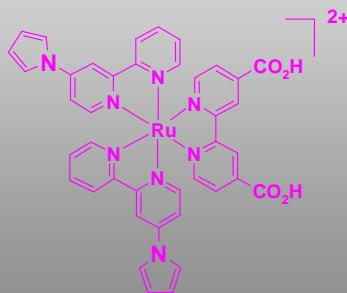
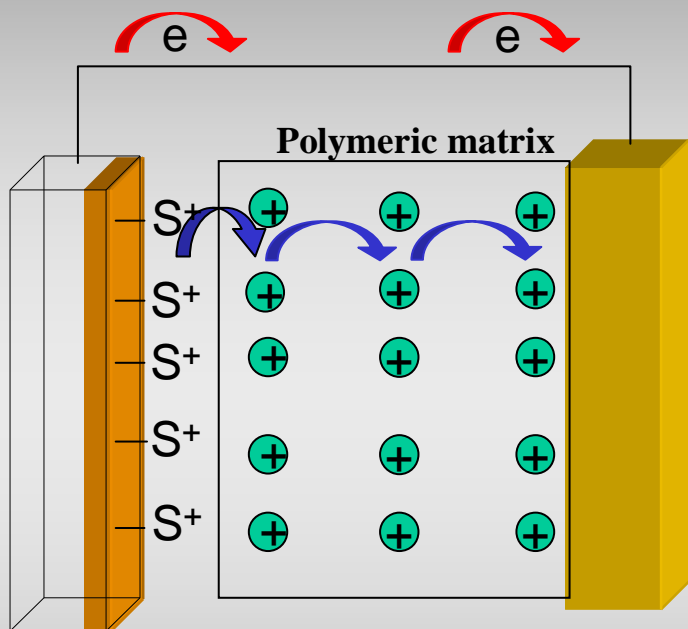


Strong influence of the mediator

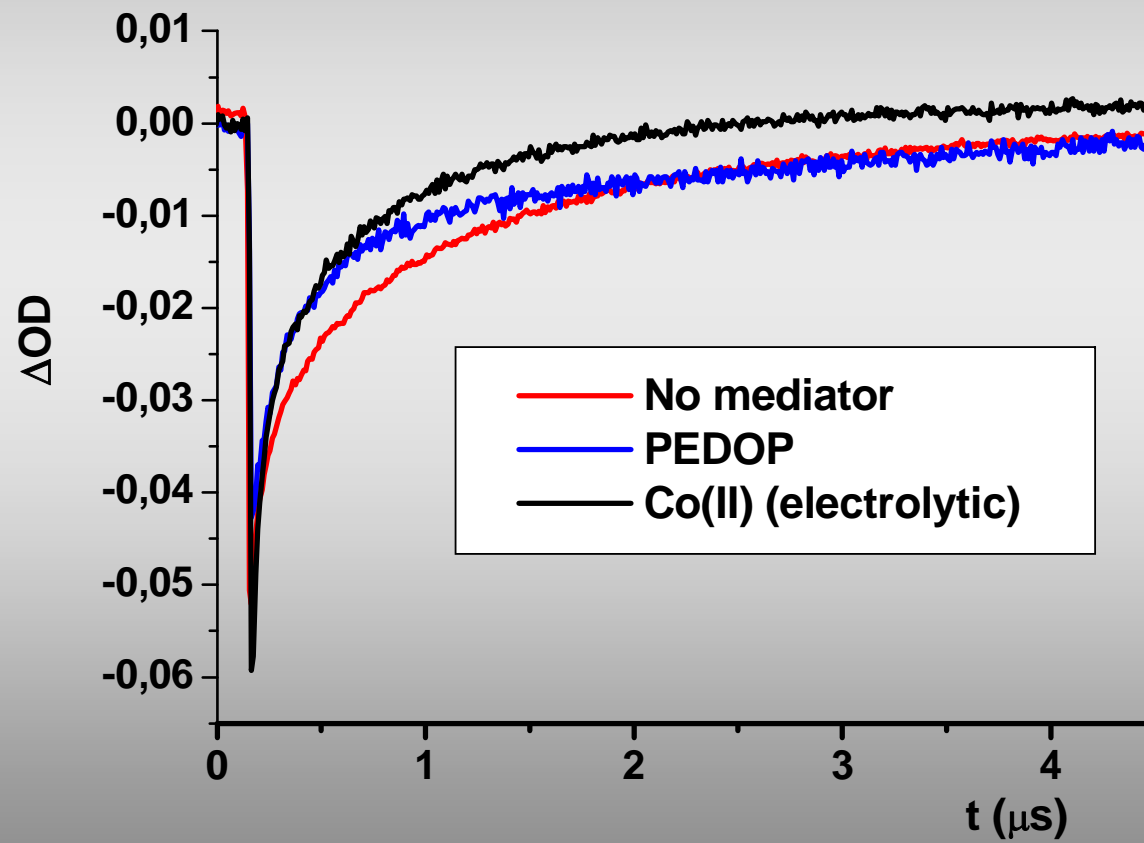
Solid state device poly(3,4-ethyldioxypyrrole) as hole-transporter



(PEDOP)

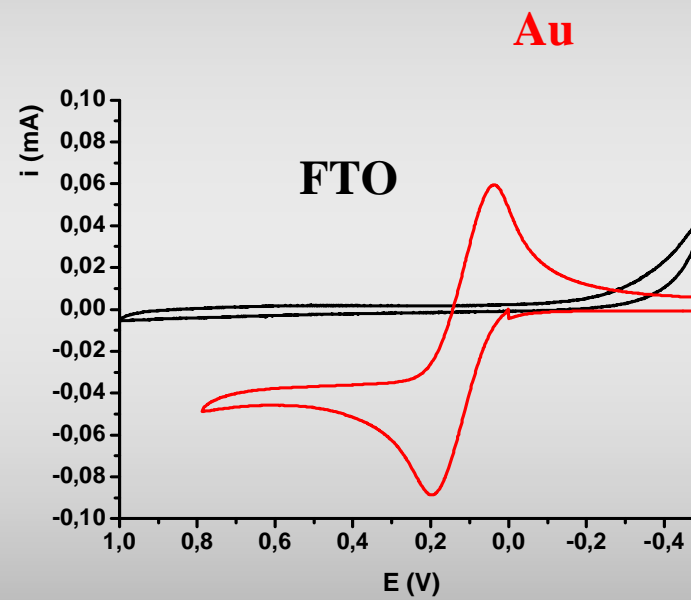
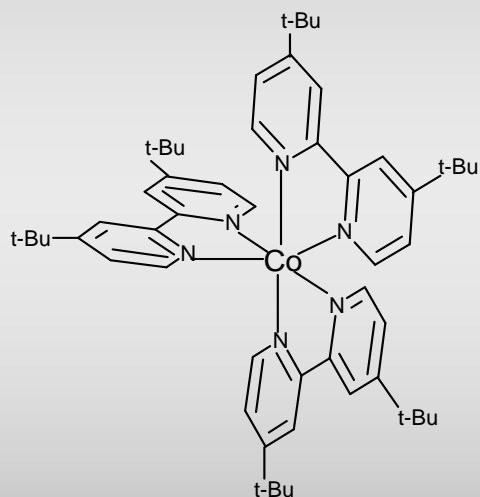


Ru(II) recovery @ 450 nm



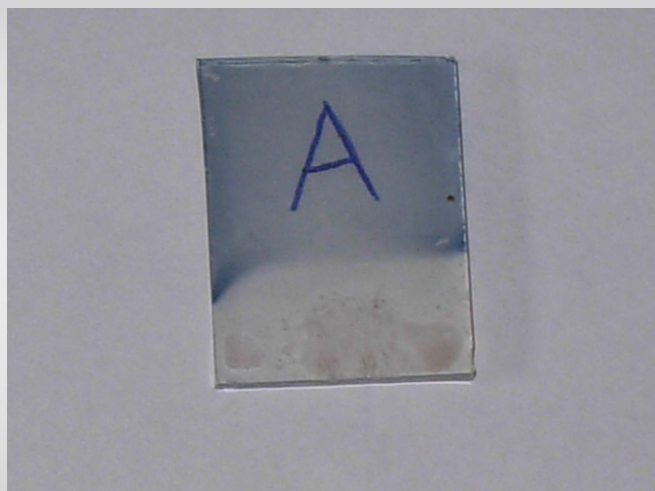
Counterelectrode

Electrochemistry of Co(II) on FTO.

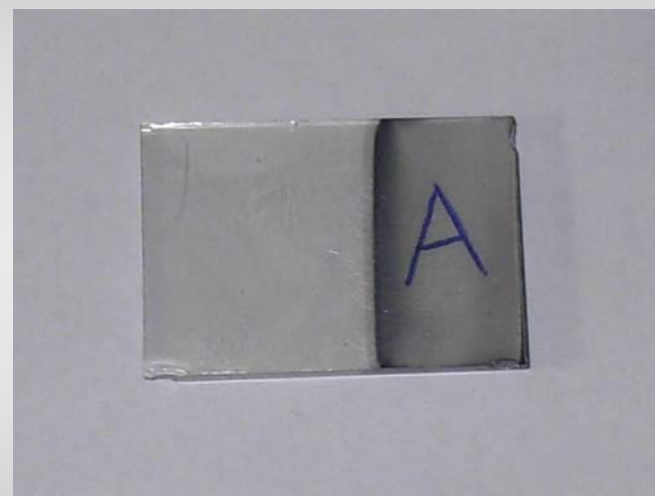


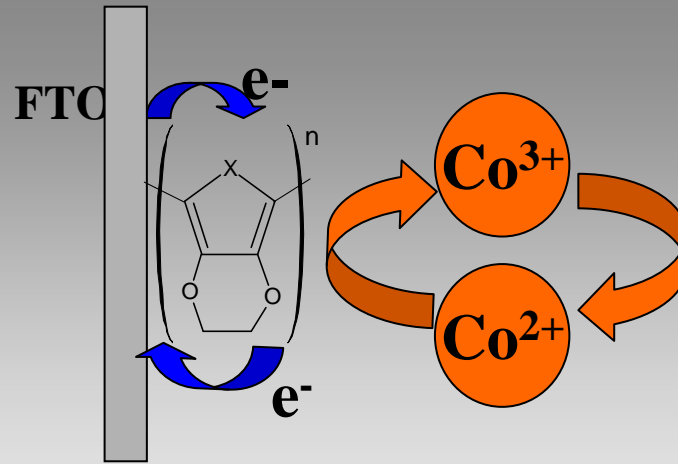
Polymer modified CE

PEDOT

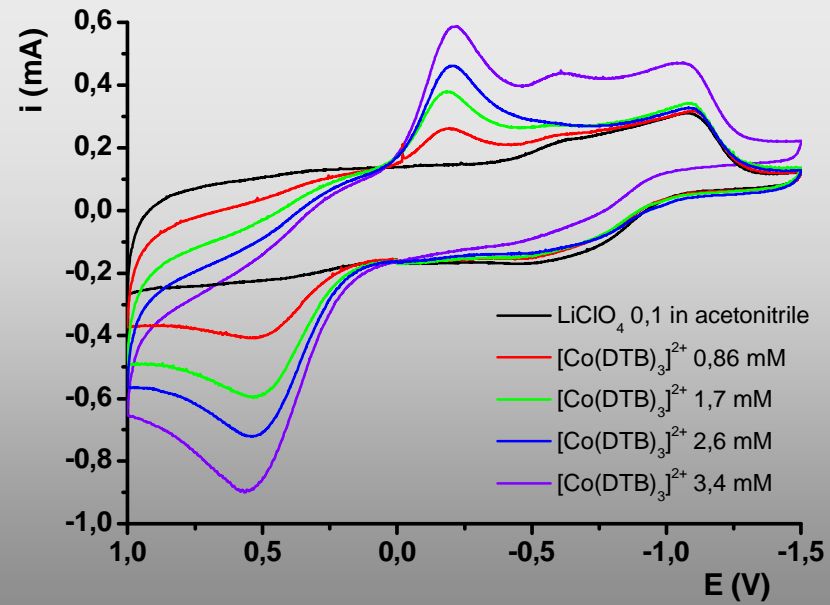


PEDOP

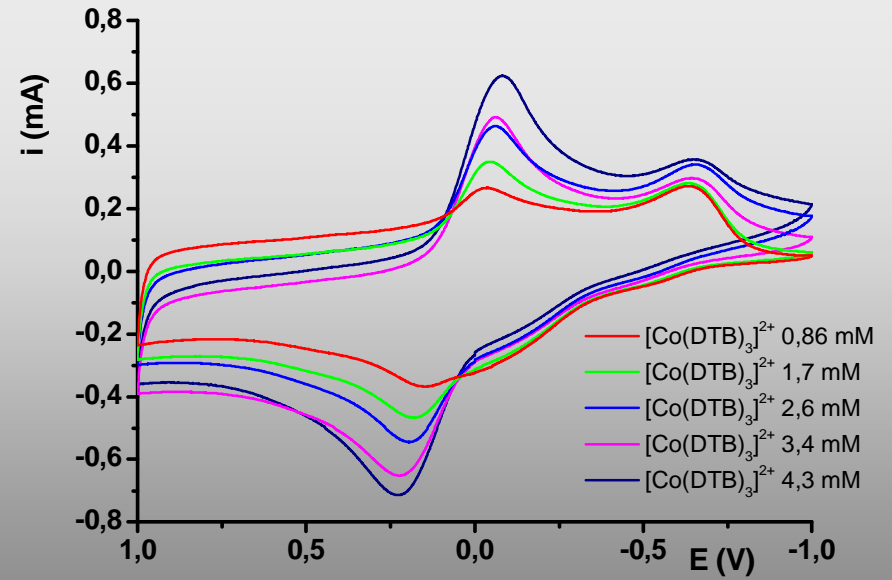


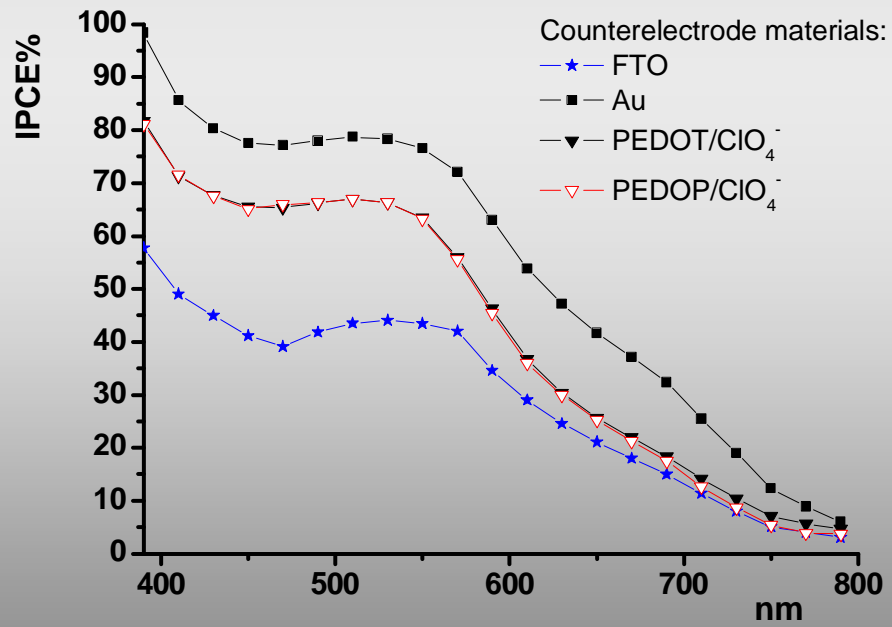
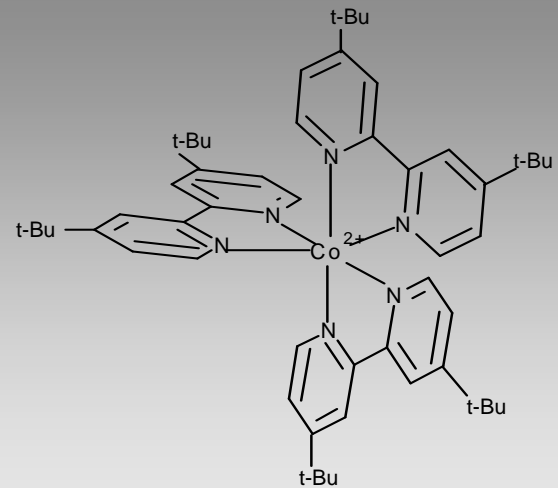
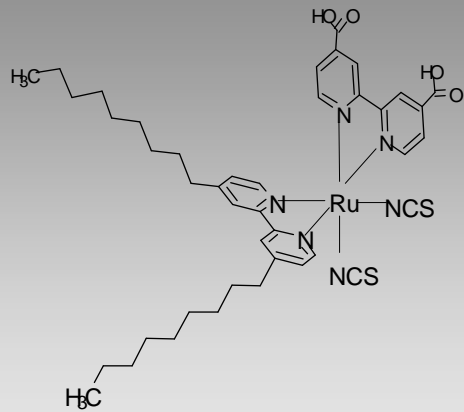


PEDOP/ ClO_4^-

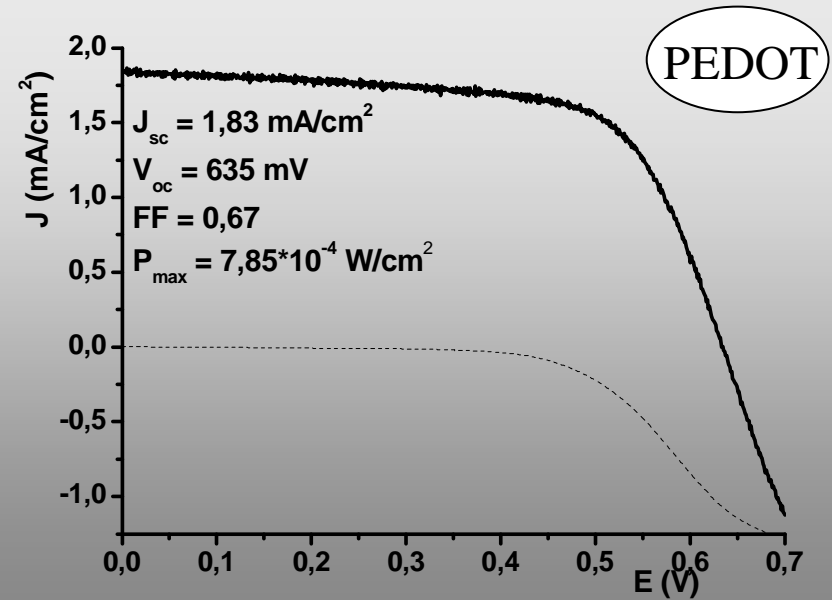
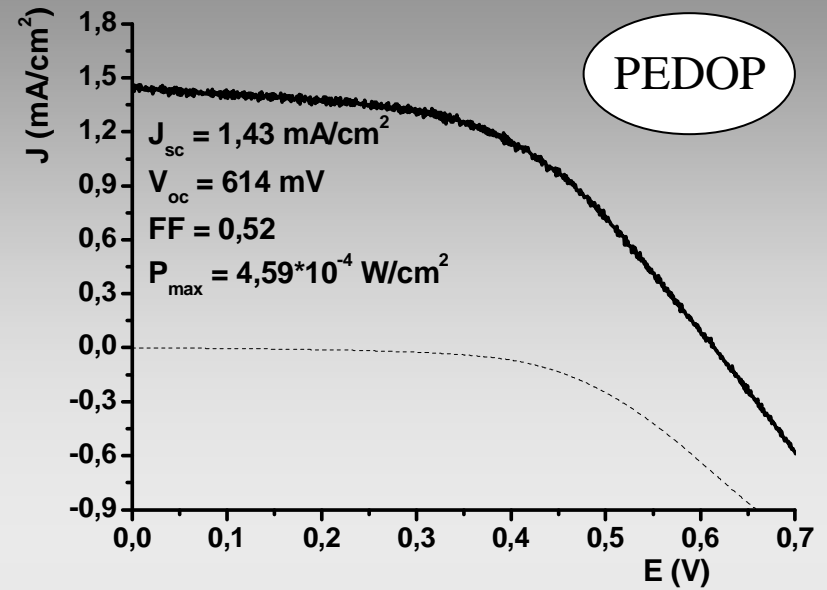
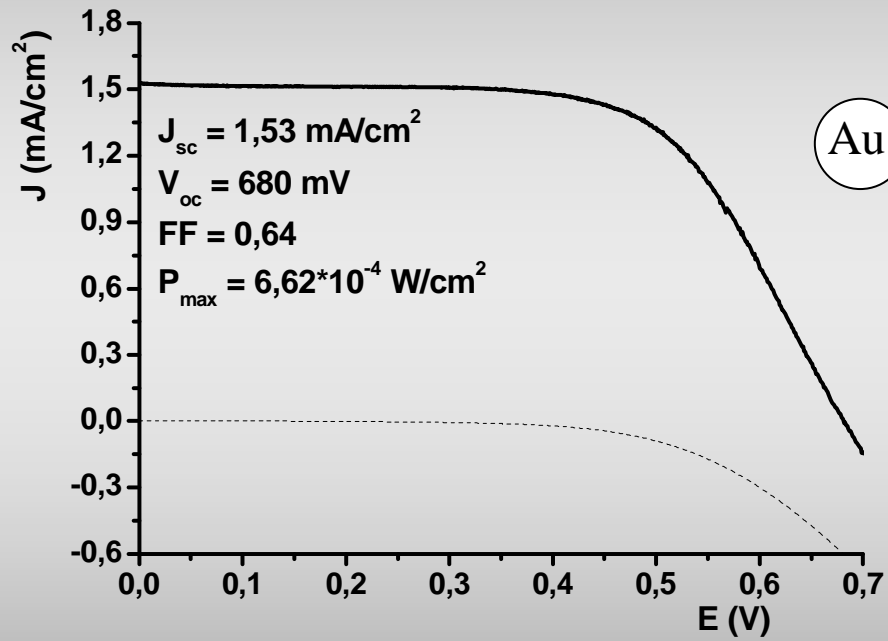


PEDOT/ ClO_4^-

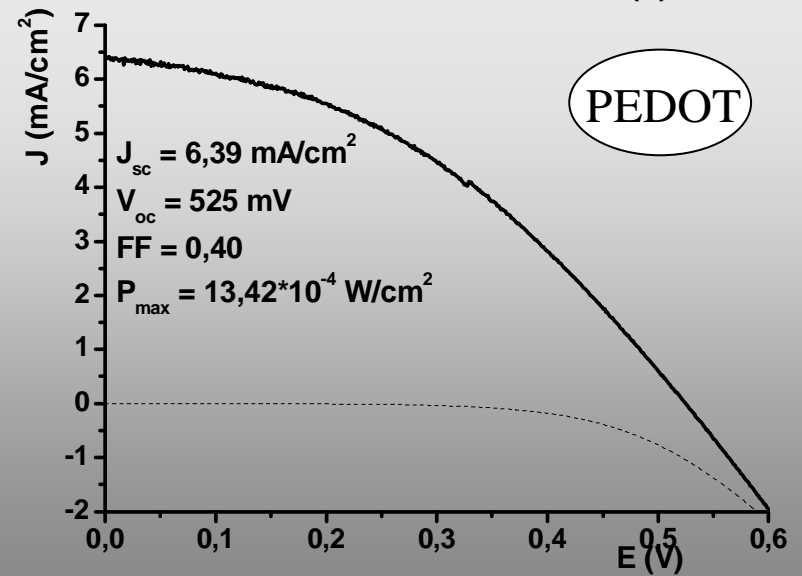
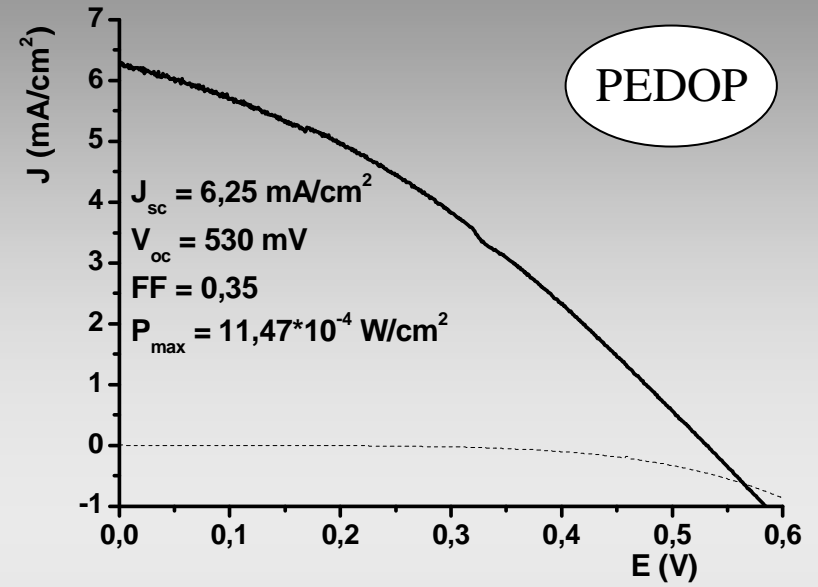
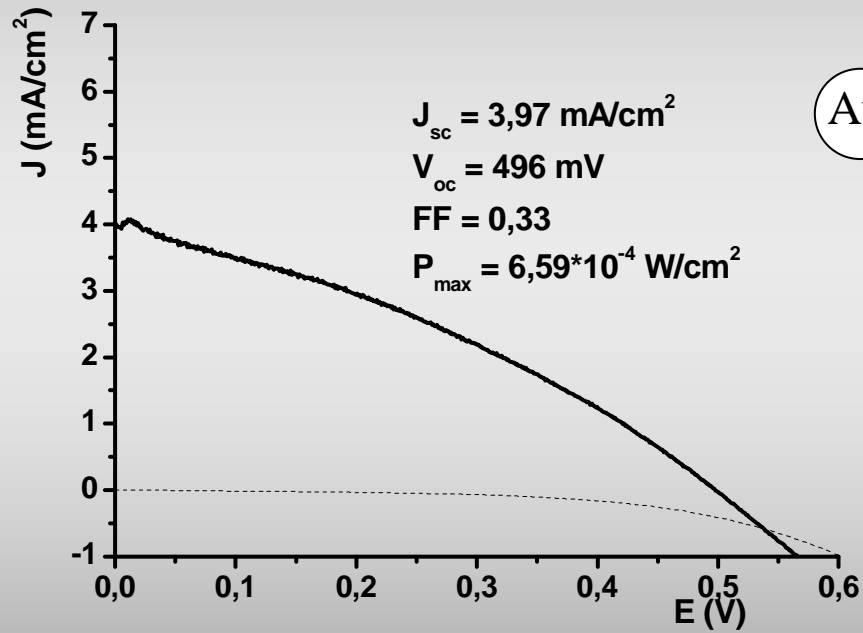




120 μ spacer



without spacer



Conclusions

- The electrochemical properties of Co(II) offer the chance of studying new electrodes and cell configurations.
- Conductive polymers may find interesting application in photoelectrochemical cells as catalytic coatings or solid state electron mediators
- Solid state devices based on polymeric materials needs the optimization of the electronic properties of the conductive polymer and of the electronic contact with the counter electrode

ACKNOWLEDGEMENTS

Aldo Di Carlo
Polo Solare CHOSE

R. Argazzi; UNIFE

S. Caramori; UNIFE

V. Dissette; UNIFE

S. Cazzanti; UNIFE

L. Marchini; UNIFE

V. Cristino; UNIFE

P. Calogero; CNR Messina

G. Di Marco; CNR Messina

C. M Elliott, Fort Collins, USA

P. Gros, Univ. Poincarè, France

M. Beley, Univ. Poincarè, France