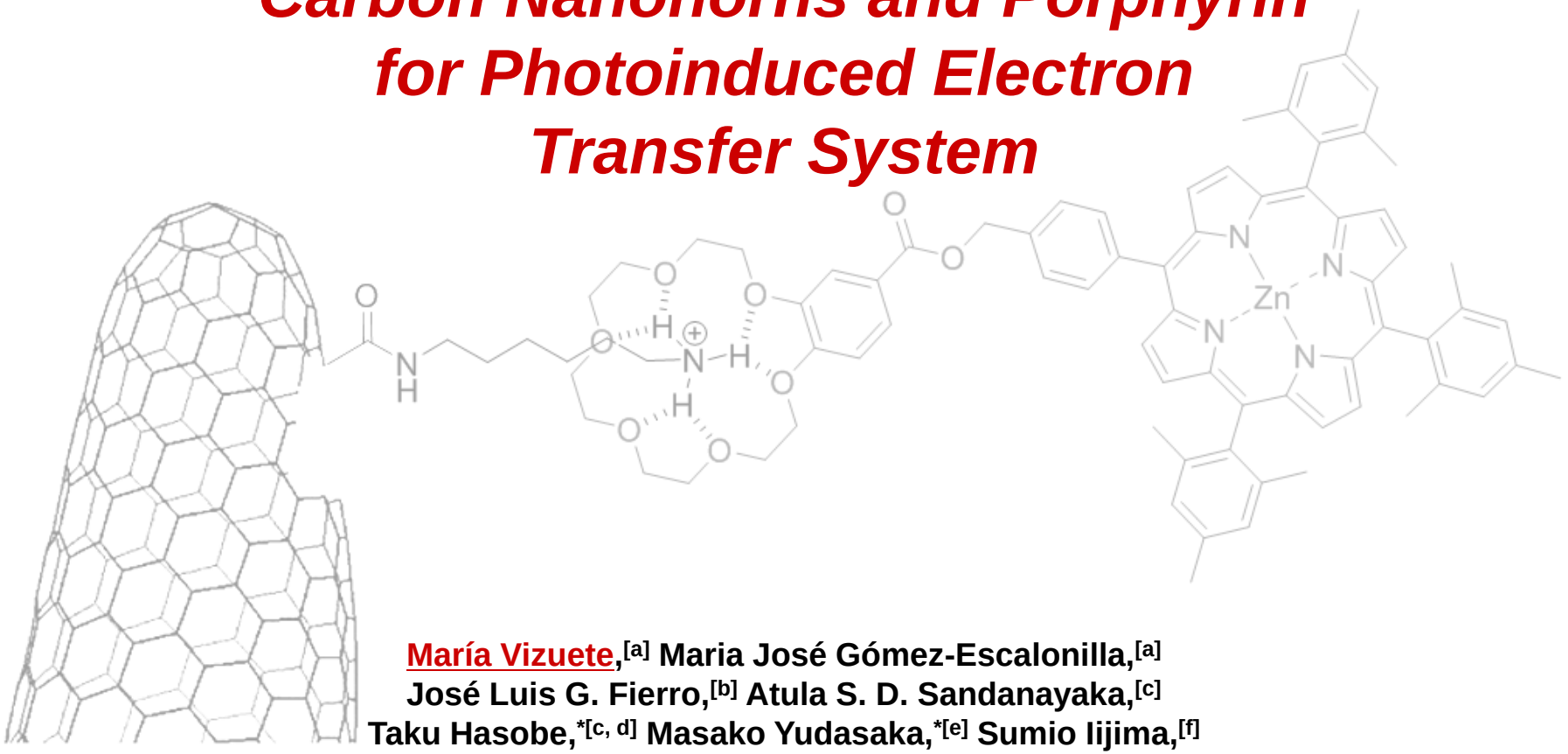
Supramolecular Assembles of Carbon Nanohorns and Porphyrin for Photoinduced Electron Transfer System



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Toledo, Spain

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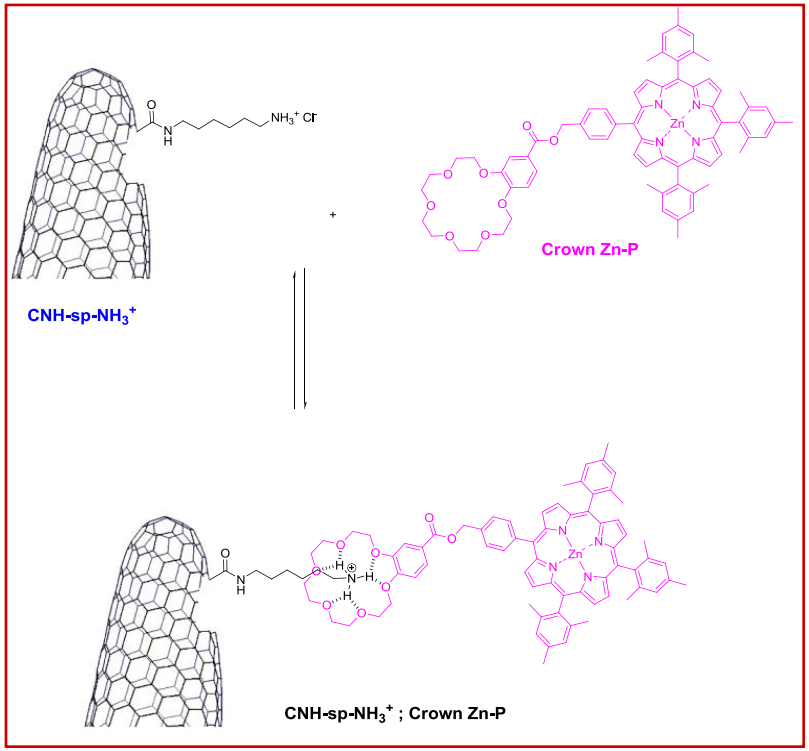
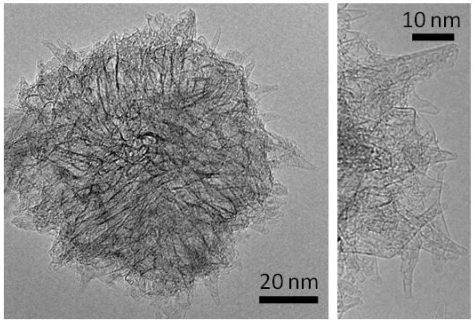
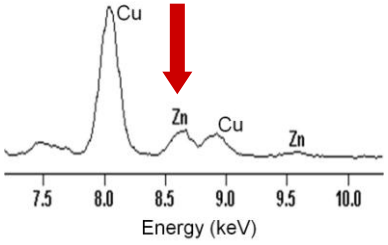
Preparation of Nanohybrid **CNH-sp-NH_3^+; Crown-ZnP**

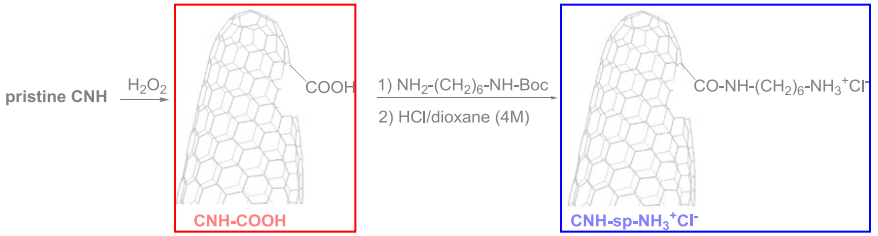


HR-TEM image of **CNH-sp-NH_3^+; Crown-ZnP**

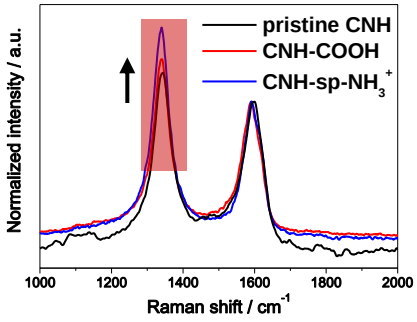




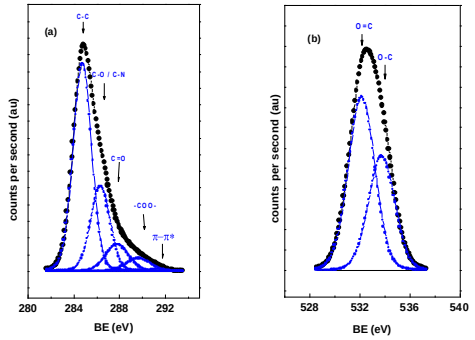
Synthesis and characterization of **CNH-sp-NH_3^+ Cl^-**



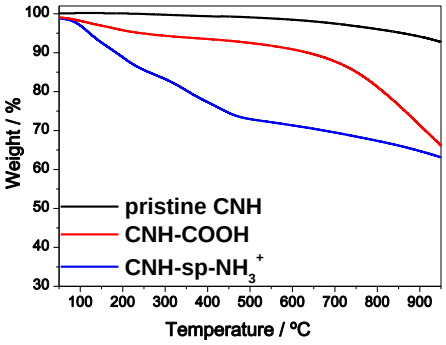
FT-Raman Spectra

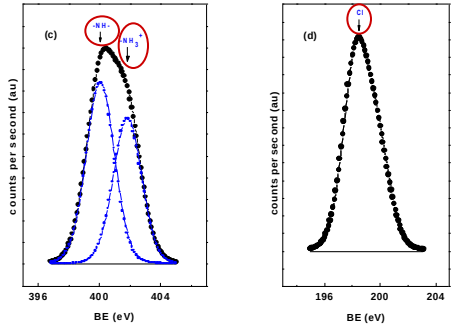


HR-XPS



TGA Curves



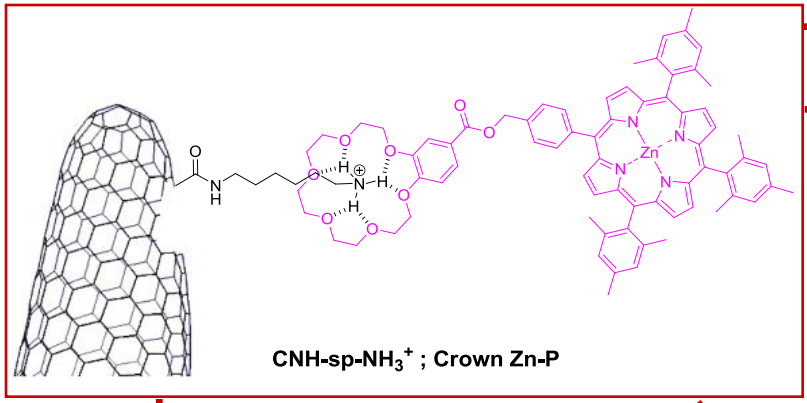


Degree of functionalization for **CNH-COOH** and **CNH-sp-$NH_3^+Cl^-$** is 1 functional group *per around* 40 C atoms (6-7 benzene rings)

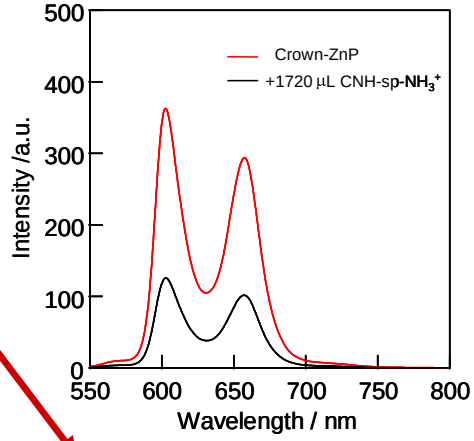
Atomic percentages (% atom) of **CNH-sp-$NH_3^+Cl^-$** evaluated from XPS

	C	O	N	Cl
CNH-sp-NH_3+Cl^-	85.7	11.5	1.8	1.0

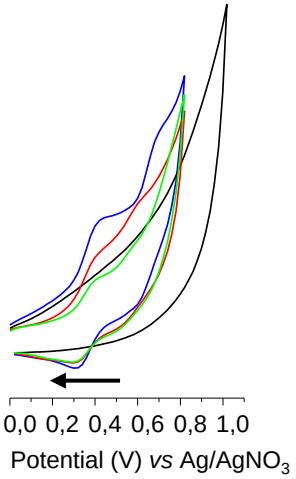
Proofs for the formation of the Supramolecular Complex

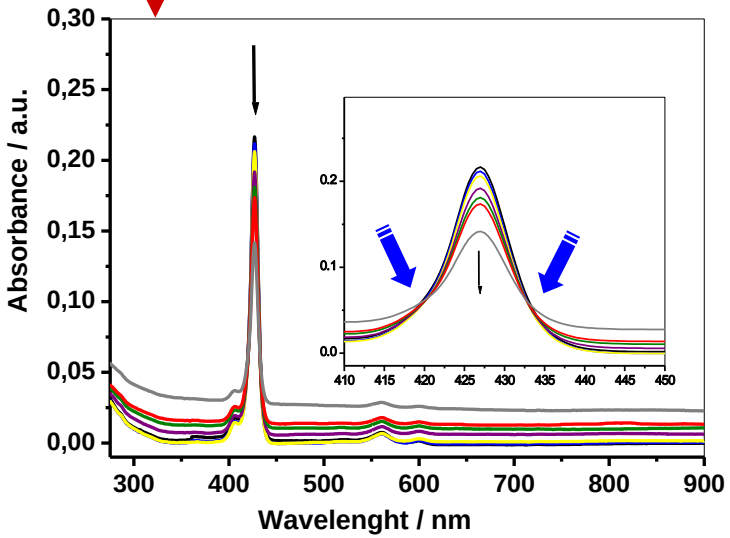


Fluorescence spectra of Crown-ZnP (4.27×10^{-7} M; 2 mL) before and after addition of **CNH**-sp-NH_3^+ (0.5 mg/100 mL 1720 μL) in DMF; λex=433 nm (isosbestic point).



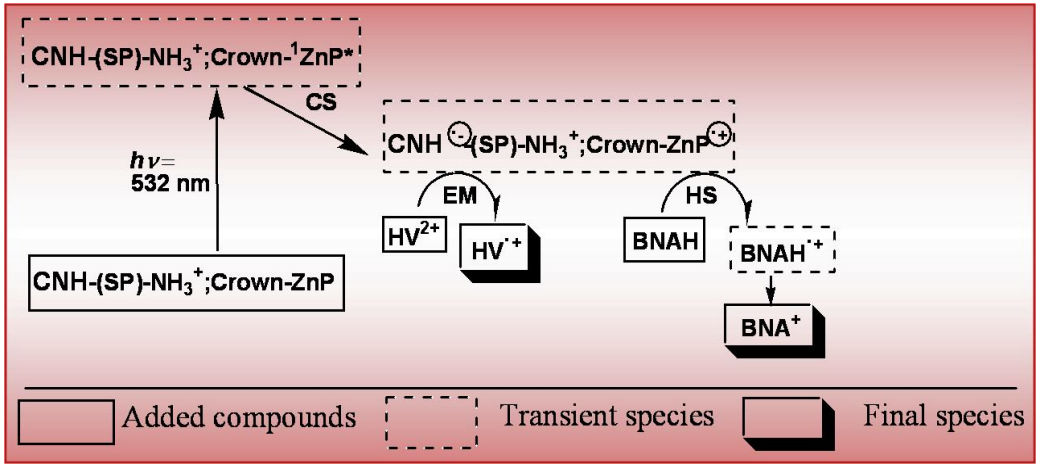
Electrochemistry: Additions of **CNH-sp-NH_3^+** resulted in a small cathodic shift of the oxidation wave (~20 mV) of the Crown-ZnP moiety due to the interaction with CNH moiety, supporting the formation of the inclusion complex **CNH-sp-NH_3^+; Crown-ZnP**



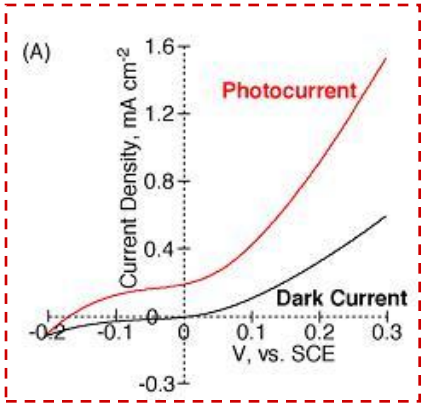


Absorption spectra for a solution of Crown-ZnP (10^{-7} M in DMF) upon addition of increasing amounts of **CNH-sp-NH_3^+** (0.5 mg/100 mL) shows a decrease of the intensity in the Soret band (λ = 420 nm) of the porphyrin and the formation of *two isosbestic points* at 420 and 433 nm

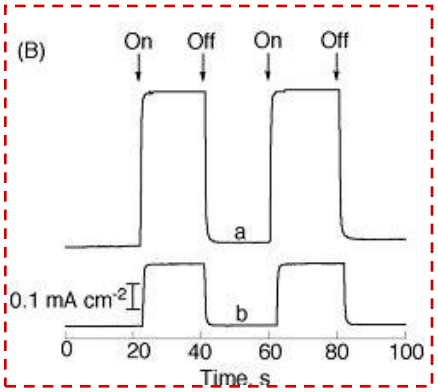
Studies of Transient Absorption Spectroscopy: demostrate the existence of photoinduced electron-transfer



I-V Curves

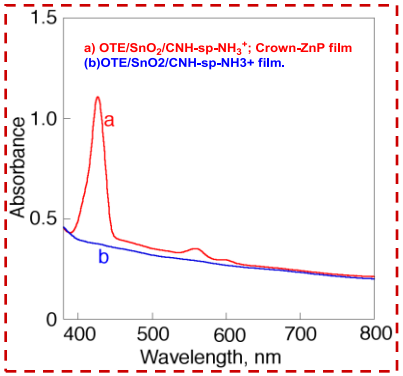


(A) I-V characteristics of OTE/SnO_2/**CNH-sp-NH_3^+;Crown-ZnP** electrode under white light illumination (red curve; AM 1.5 condition; input power = 100 mW cm^{-2}) and in the dark (black curve).



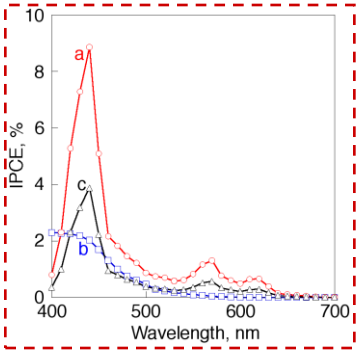
(B) Photocurrent generation responses of (a) **OTE/SnO_2/CNH-sp-NH_3^+;Crown-ZnP** and (b) OTE/SnO_2/**CNH-sp-NH_3^+** at an applied bias voltage of 0.2 V *vs* SCE. Electrolyte: LiI 0.5 M, I_2 0.01 M in acetonitrile; input power = 100 mW cm^{-2}.

Absorption Spectra



(drop-cast method)

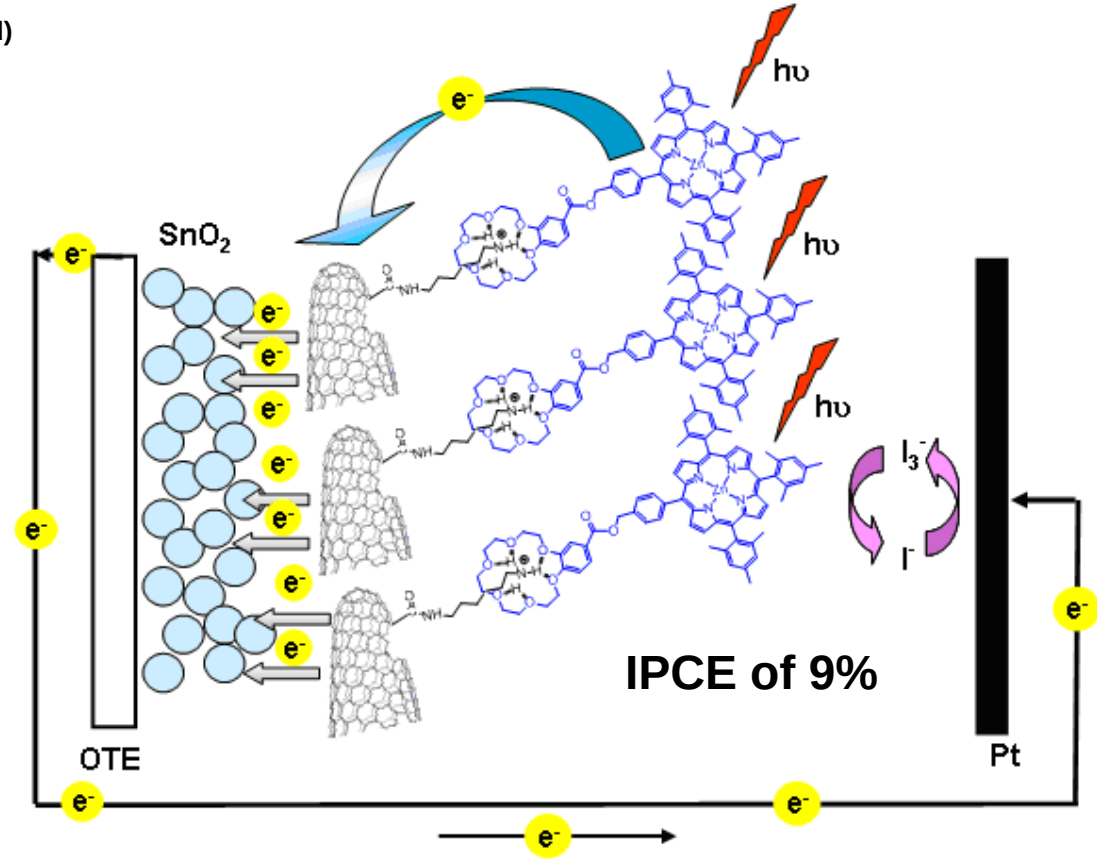
Photocurrent action spectra of IPCE



(a) OTE/SnO_2/CNH-sp-NH_3^+;Crown-Zn
(b) OTE/SnO_2/CNH-sp-NH_3^+
(c) OTE/SnO_2/Crown-ZnP

Applied bias potential: 0.2 V *vs*. SCE.
Electrolyte: LiI 0.5 M,I_2 0.01 M in CH_3CN

CNH-BASED PHOTOVOLTAIC CELL



OTE: Optically Transparent Electrode

OTE/SnO_2/CNH-sp-NH_3^+;Crown-ZnP