New dendritic molecules and branched polymers for molecular nanobatteries (BATMOL)

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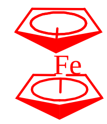
Goals : The design of **star molecular batteries** with a…

- ✓… dendritic,
- ✓… nanoparticular,
- ✓… dendronized,
- ✓… branched and / or hyperbranched core on which electron reservoirs will be grafted.

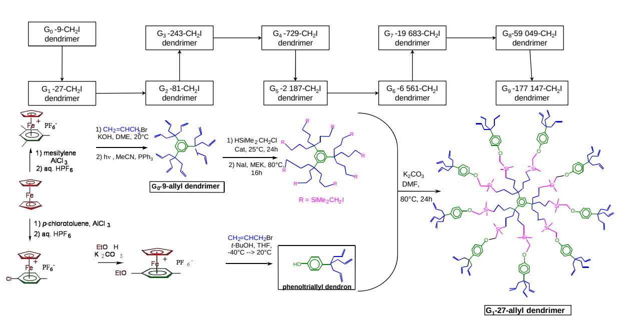


ISM : These electron reservoirs shall be able to undergo redox cycles without decomposition, on dendritic supports. Hence, different sandwich complexes have been synthesised, and their performances have been tested.

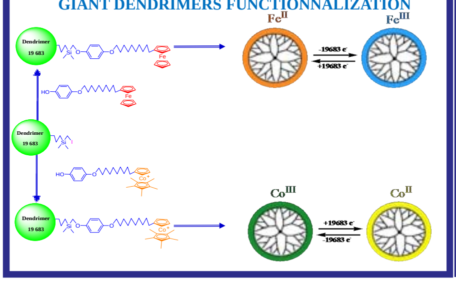
LCPO: The supports for the molecular batteries shall be made up by different polymerization techniques so that a large size scale is scanned. Also they shall be composed of different polymer types (conducting polymer, etc.). The number of synthesis steps shall be minimized.

Those systems will be characterized by classical techniques used in molecular, macromolecular and nanosciences.
The molecular batteries will then be used for molecular recognition, recyclable catalyst, or as such, to check their electric performances.

DIVERGENT CONTRUCTION OF GIANT DENDRIMERS



GIANT DENDRIMERS FUNCTIONNALIZATION



MOLECULAR NANOBATTERY

Publications 2008/2009:

Metallocenyl Dendrimers as Electrocrome Molecular Batteries (Concept article), D. Astruc, C. Ornelas, J. Ruiz, *Chemistry, Eur. J.* 2009, 15, 8936

Giant Cobalticinium Dendrimers. Ornelas, C.; Ruiz, J.; Astruc, D. *Organometallics* ***2009, 28, (9), 2716-2723.***

Towards molecular batteries: coverage of small amino-silica nanoparticles with ferrocenyl and pentamethylferrocenyl groups and their redox properties. T. Kusamoto, J. Ruiz, D. Astruc, New J. Chem. DOI 2009,11**b9nj00481e**

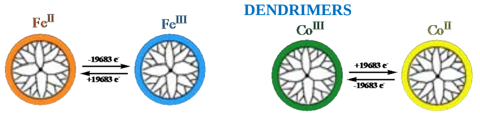
"Click" Dendrimers: Synthesis, Redox Sensing of Pd(OAc) 2, and Remarkable Catalytic Hydrogenation Activity of Precise Pd Nanoparticles Stabilized by 1,2,3-Triazole-Containing Dendrimers., Ornelas, L. Salmon, J. Ruiz Aranzaes, D. Astruc. ***Chem. Eur. J.***, **2008** , 14 (1) 50-64.

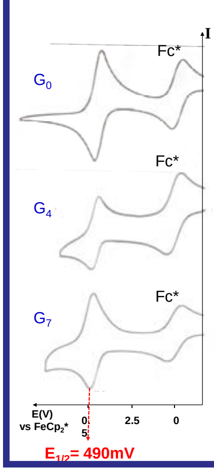
Simple synthesis of organo-iron complexes from iron-sandwich raw materials using visible light., J. Ruiz Aranzaes, D. Astruc. *Inorg. Chim. Acta,* **2008**, 361 (1) 1-4

Ferrocenyl-teminated Dendrimers : Design for Applications in Molecular Electronics, Molecular Recognition and Catalysis, D. Astruc, C. Ornelas, J. Ruiz Aranzaes. *J. Inorg. Organomet. Polym. Mater.*, **2008** , 18 (1) 1-4

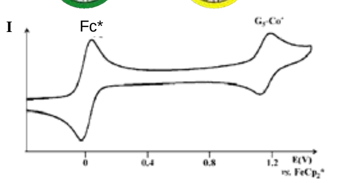
Grafting electron reservoirs at the periphery of core-shell particles: towards new molecular batteries. Costa, M., Mumtaz, M., Cloutet, E., Cramail, H., Ruiz, J., Astruc, D., *J. Mat. Chem,* to be submitted.

ELECTROCHEMICAL BEHAVIOR OF METALLOCENE TERMINATED DENDRIMERS

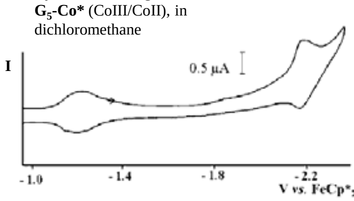




$E_{1/2}$= 490mV



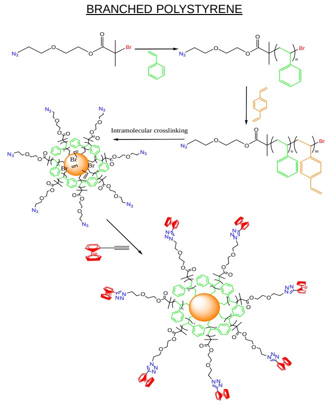
Cyclic voltammogram obtained for the **G_5-Co*** (CoIII/CoII), in dichloromethane



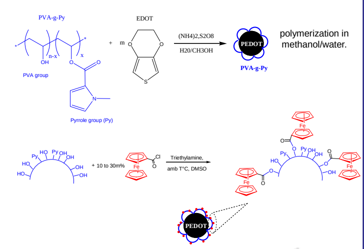
Cyclic voltammogram obtained for the **G_6-Co*** in DMF.
$E_{1/2}$(CoIII/CoII)) = -1.19 V vs FeCp$_2$*
and $E_{1/2}$(CoII/CoI))) = -2.19 V vs FeCp*$_2$.

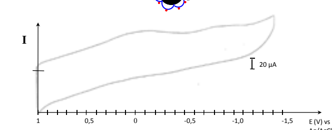
ELECTROCHEMICAL BEHAVIOR OF FERROCENE TERMINATED BRANCHED POLYMERS / PARTICLES

BRANCHED POLYSTYRENE

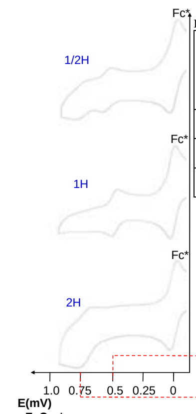


POLY(3,4-ETHYLENEDIOXYTHIOHENE) (PEDOT) PARTICLES





Cyclic voltammogram obtained for PEDOT particles in DMSO.



One wave

Redox potentials of metallic centers extremely close and seem to be even

Microgel	Ferrocene grafting [a] (%) (NMR)	f [b] (N branches)	Ne- exchanged [c] N branches (Cyclic voltammetry)
1/2H	89.00	10	11.4
1H	97.00	6	8.6
2H	72.00	20	8.0

(a) Determined by NMR (peak at δ=7.5 ppm)

(b) $f = \frac{\text{Weight fraction of the macroinitiator}}{(\text{Weight fraction of the macroinitiator} + \text{Weight fraction of DVB})} \times \left(\frac{M_w stars}{M_w arms}\right)$

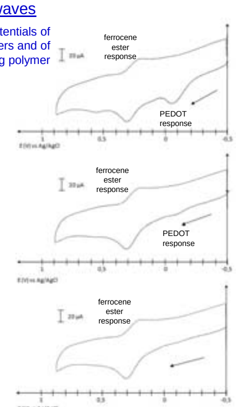
(c) Calculated: $Ne^- = \frac{\left(\frac{I_p}{C_p}\right)}{\left(\frac{I_m}{C_m}\right)} \times \left(\frac{M_p}{M_m}\right)^{0,275}$

$E_{1/2} = E_{1H} = E_{1/2H}$ = 500 mV

$E'_{1/2} = E_{2H}$ = 750 mV

Two waves

Redox potentials of metallic centers and of semi-conducting polymer



Cyclic voltammogram obtained for 10% ferrocene grafted on PEDOT particles in DMSO.

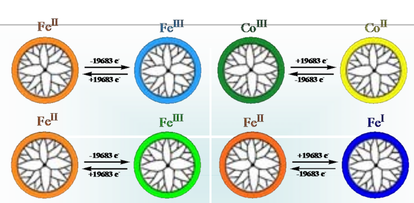
Electrochemically reversible wave
(rapid system)

- ✓ Rapid rotation (in electrochemical time scale)
- ✓ Electron jump mechanism (quantum tunneling)
- ✓Contact between branches which allow electron transfer

Electrochemically quasi-reversible waves

- ✓ Charges diffusion in the polymer matrix
- ✓ Electron jump mechanism (quantum tunneling) for the ferrocene
- ✓Contacts between ferrocenes/polymer which allow electron transfer

CONCLUSIONS AND OUTLOOKS



MOLECULAR NANOBATTERIES

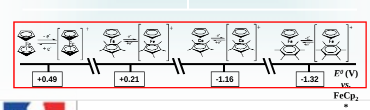
Good redox stability

↓

Molecules able to give and to recieve electrons in reversible/quasi reversible ways

↓

Applications (e. g. photovoltaïsm) by changing the polymer structure and/or the sandwich complex



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