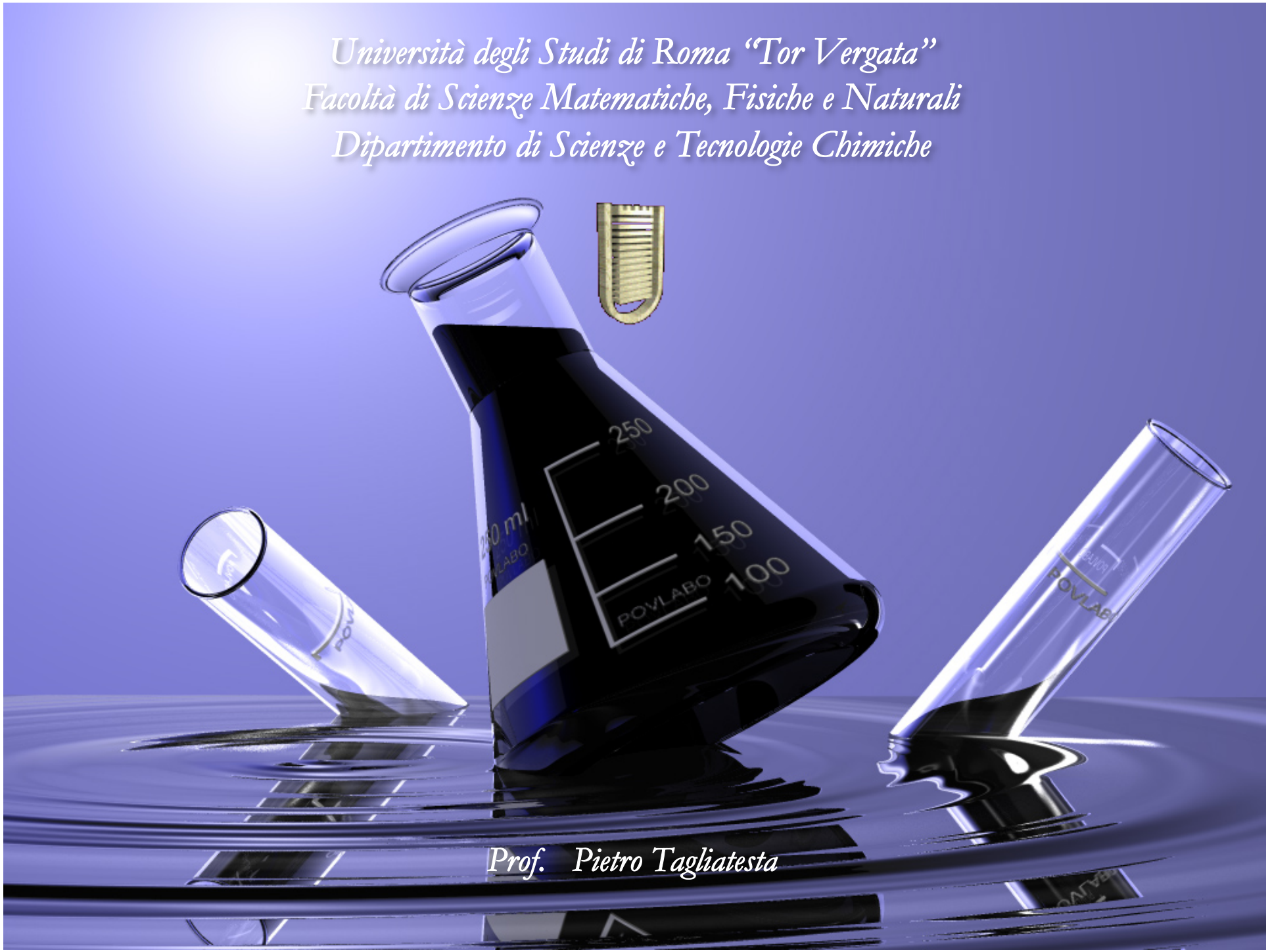
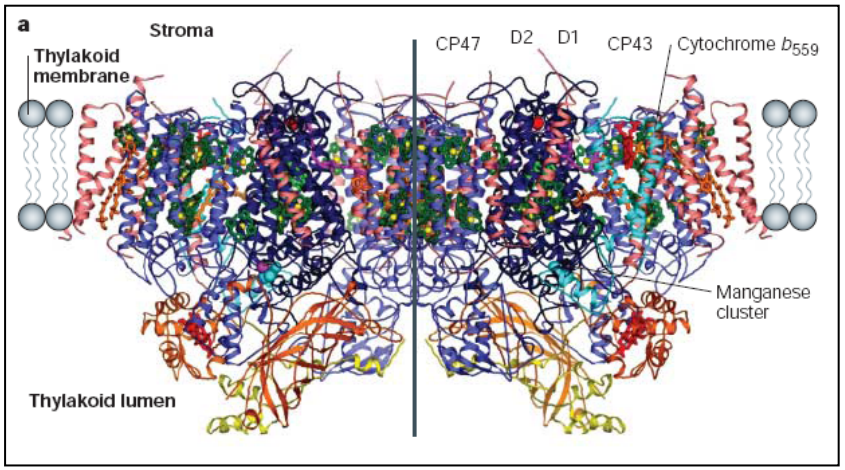
Università degli Studi di Roma "Tor Vergata"
Facoltà di Scienze Matematiche, Fisiche e Naturali
Dipartimento di Scienze e Tecnologie Chimiche

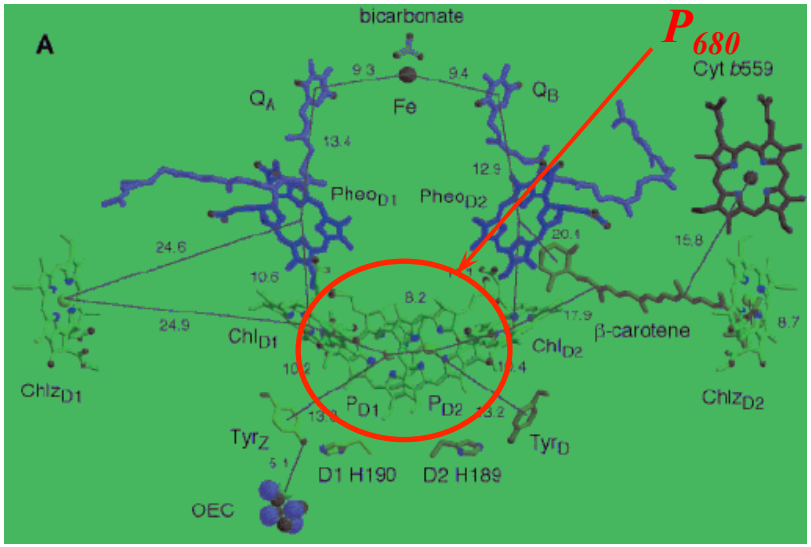


Prof. Pietro Tagliatesta

✓ *Natural Photosystems*



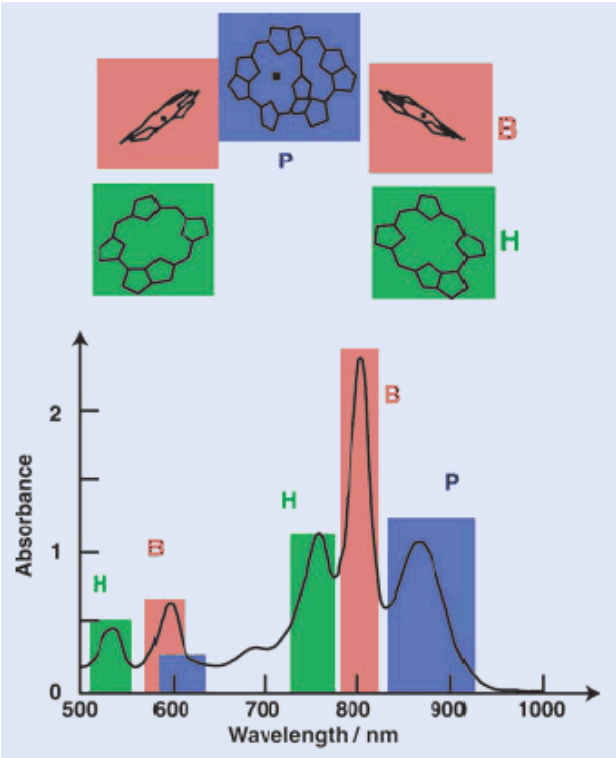
Photosystem II (PSII) from Thermosynecochoccus Elongatus



Reaction center of PSII

K. N. Ferriera; T. M. Iverson and coworkers *Science* **2004**, *303*, 1831

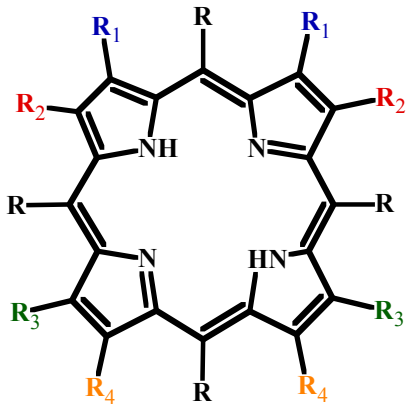
Absorption spectrum of Rhodobacter Sphaeroides reaction center



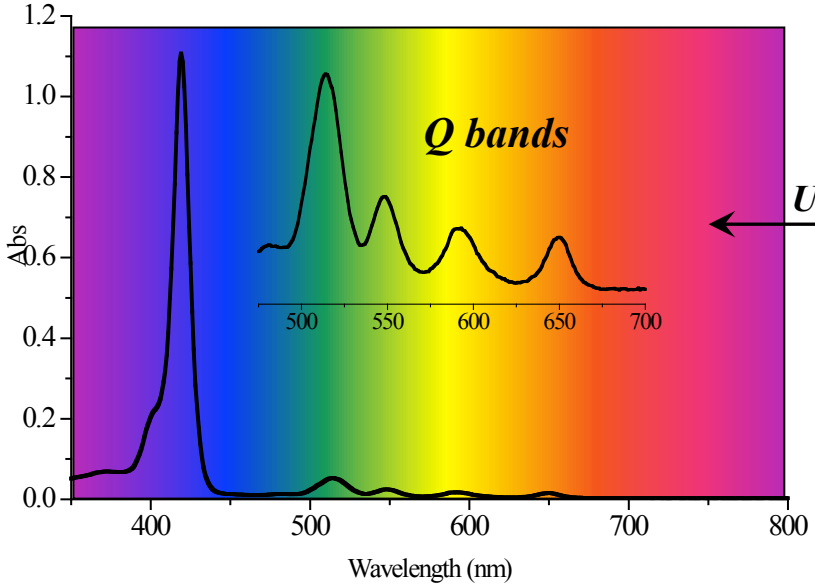
W. Zynth; J. Wachtveitl *ChemPhysChem* **2005**, *6*, 871

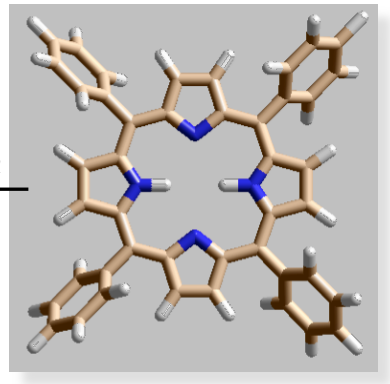
✓ *Natural Pigments*

Tetrapyrrole macrocycle



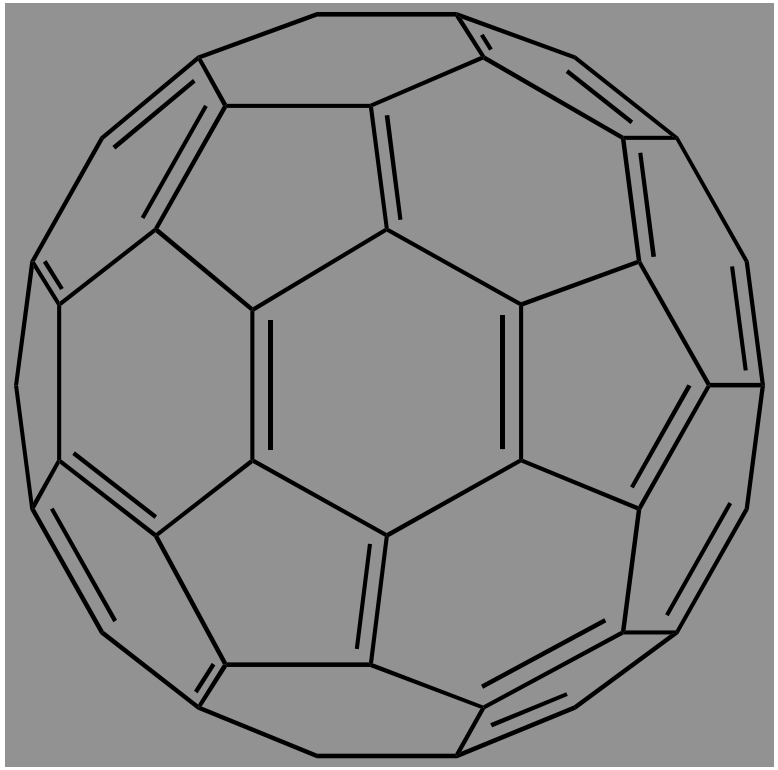
R = aryl, alkyl
R_1, R_2, R_3, R_4 = aryl, alkyl, alogen, nitro group, amino group…



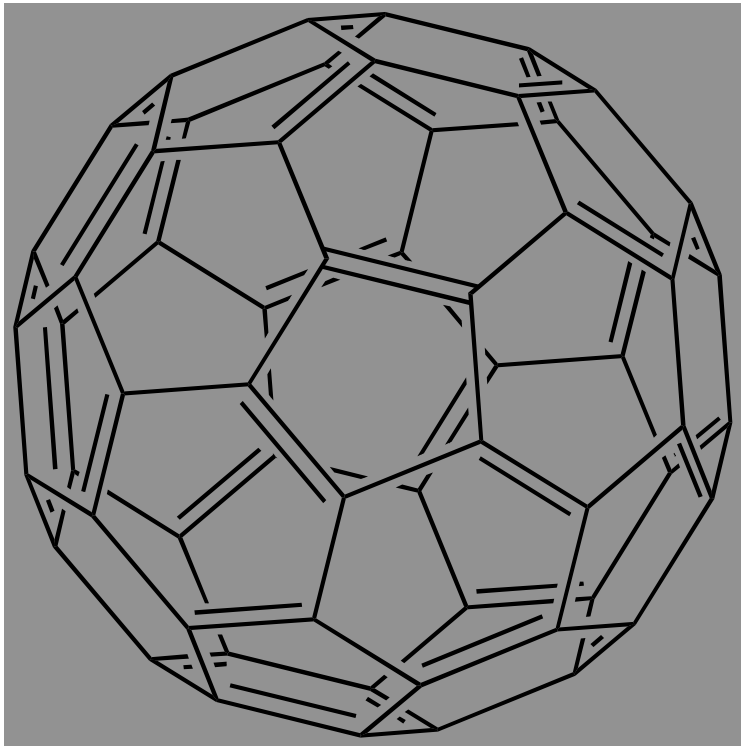


5,10,15,20-Tetraphenylporphyrin

Fullerenes: structures

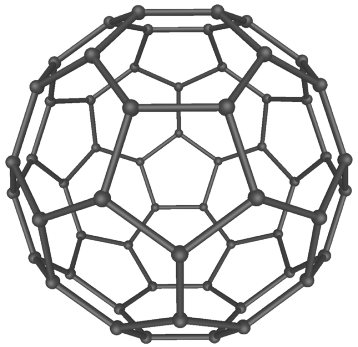


C60



C70

Fullerenes and C60



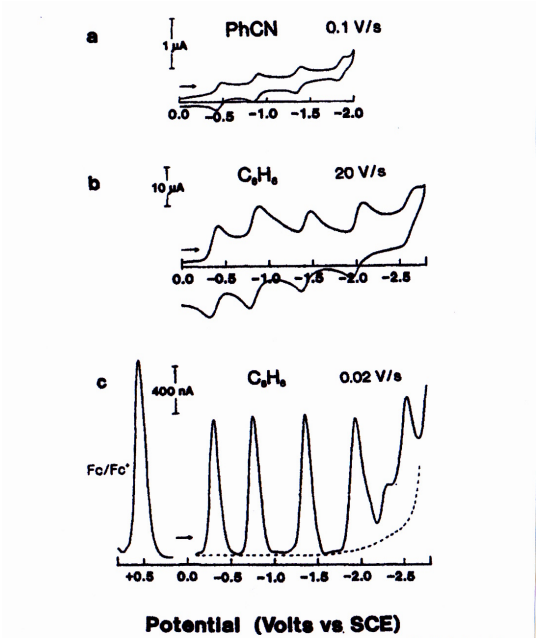
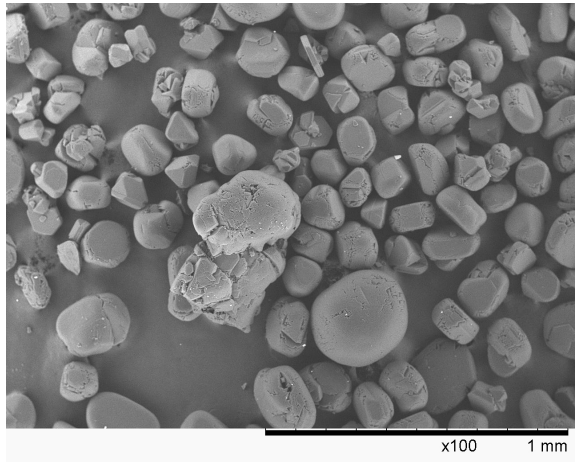
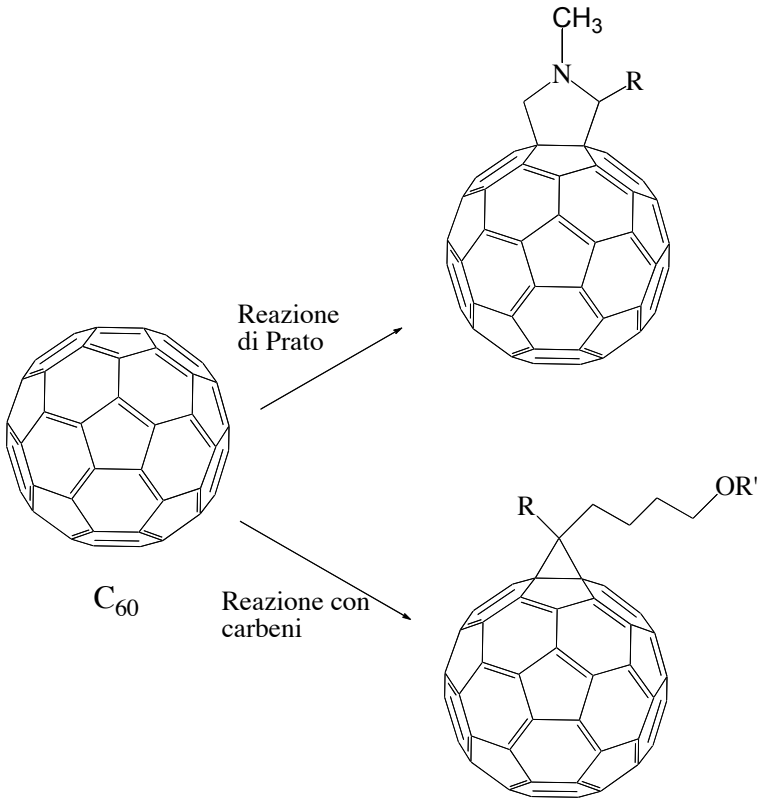


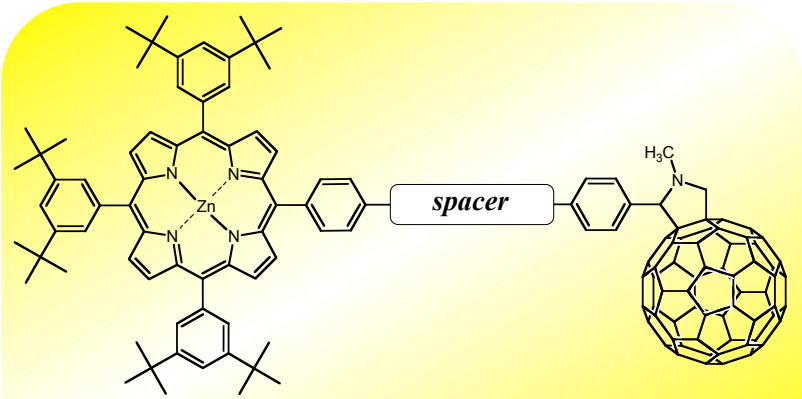
Figure 2. Reduction of C_{60} by (a) cyclic voltammetry in PhCN, 0.1 M $[(n\text{-Bu})_4N](PF_6)$ at 22 °C, and (b) cyclic voltammetry and (c) differential pulse voltammetry (80-mV pulse, 50-ms pulse width, 300-ms period) of C_{60} in C_6H_6 containing $[(n\text{-}C_6H_{13})_4N](ClO_4)$ (0.55 g in 1 cm^3) at 45 °C. The dotted line shows the background current in the absence of C_{60}.



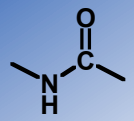
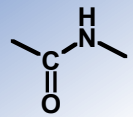
Functionalization of Fullerenes



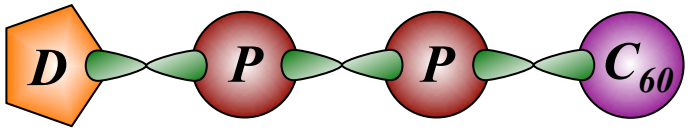
✓ *Porphyrin-fullerene covalent systems:*

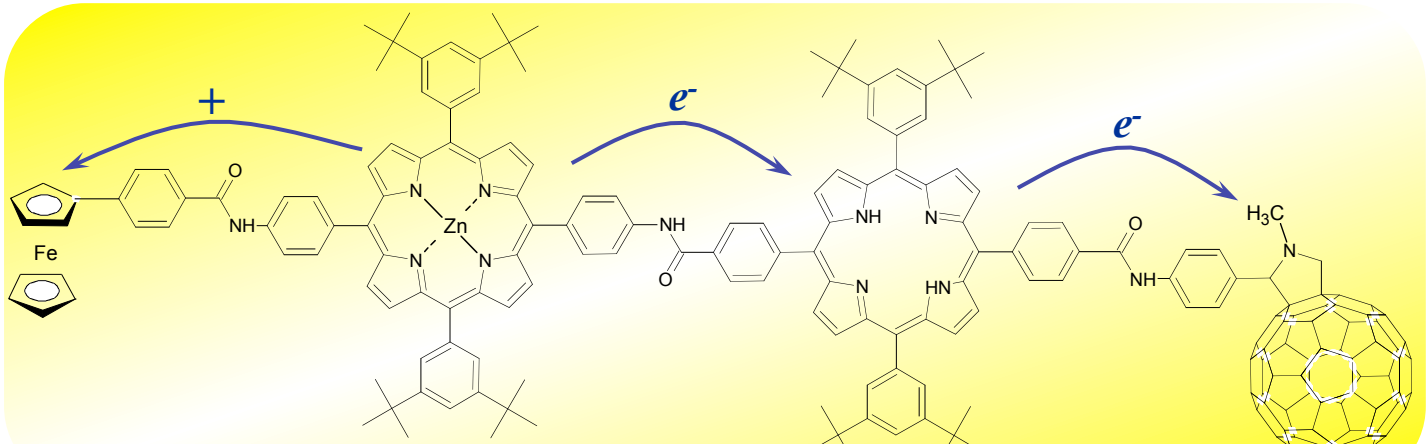


H. Imahori; D. M. Guldi; T. Okada; S. Fukuzumi and coworkers
Angew. Chem. Int. Ed. **2002**, *41*, 2344

Spacer:	k_{ET} (s^{-1})	k_{BET} (s^{-1})	τ
	$2.2 \cdot 10^{10}$	$2.0 \cdot 10^{6}$	500 ns
	$1.3 \cdot 10^{10}$	$3.7 \cdot 10^{5}$	2.7 µs
—C≡C—	$3.7 \cdot 10^{10}$	$1.5 \cdot 10^{6}$	666 ns

✓ *Multichromophoric systems:*





Guldi, D. M.; Imahori, H.; Fukuzumi S. et al. *J. Phys. Chem. A* **2004**, *108*, 541.

$\tau_{RIP} = 0.34$ s
in DMF a 178 K

✓ *Oligomer as spacer: "molecular wires"*

$$k_{ET} = k_0 \exp(-\beta R_{DA})$$

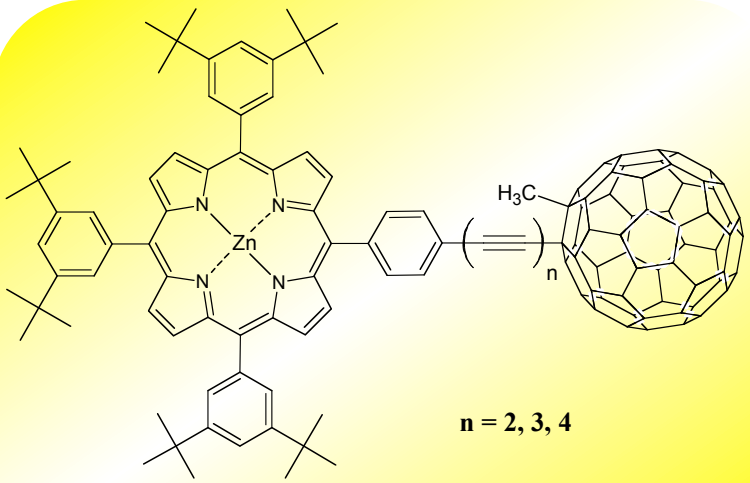
β = *damping factor*

In THF solution:

n	*τ (ns)*
2	*555*
3	*625*
4	*714*

$\beta = 0.06\ Å^{-1}$

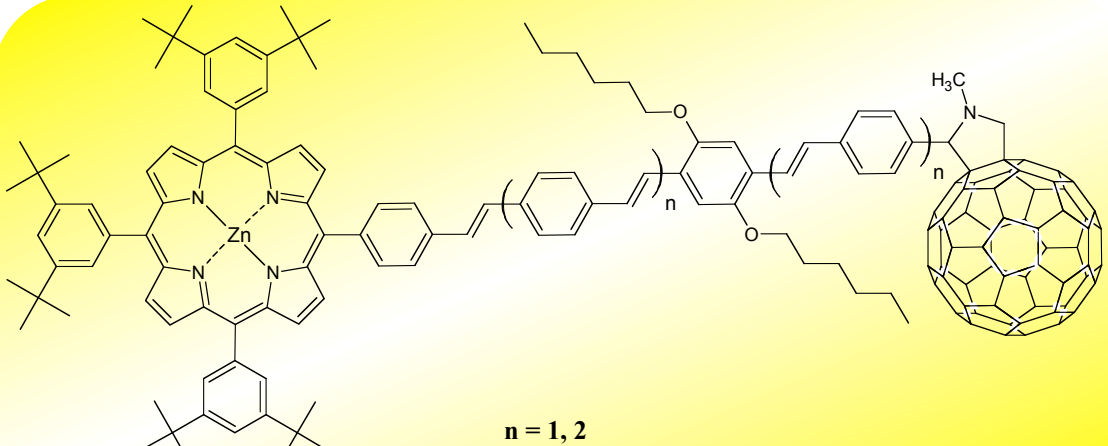
oligo-acetylenes



n = 2, 3, 4

D. I. Schuster; L. Echegoyen; D. M. Guldi; J. P. C. Tomè and coworkers
Chem. Eur. J. **2005**, *11*, 3377

oligo-phenylenevinylenes



n = 1, 2

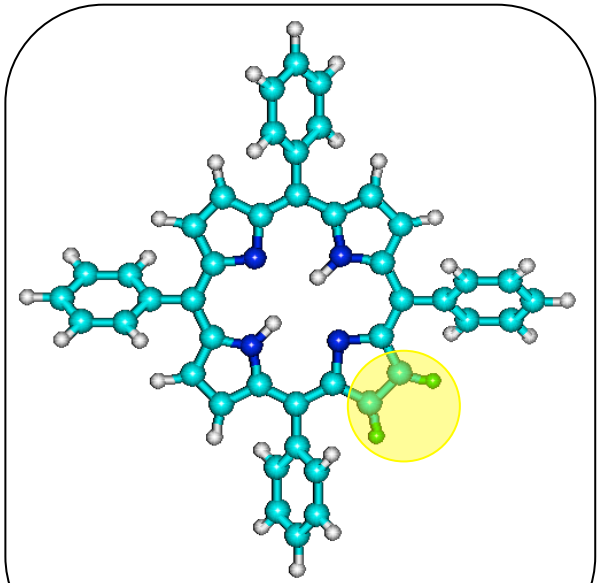
Guldi, D. M.; Martin, N. and coworkers *Chem.Eur.J.* **2005**, *11*, 1267

n = 1
PhCN $\tau_{RIP} = 230$ ***ns***
THF $\tau_{RIP} = 830$ ***ns***

n = 2
PhCN $\tau_{RIP} = 370$ ***ns***
THF $\tau_{RIP} = 1000$ ***ns***

$\beta = 0.03\ Å^{-1}$

✓ ***In our laboratory***

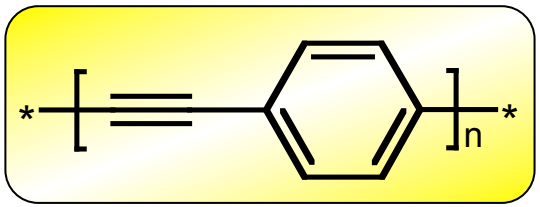


H_2-TPP

✓ ***New β-substituted porphyrins***

✓ ***Molecular wires directly linked to the β-pyrrole position***

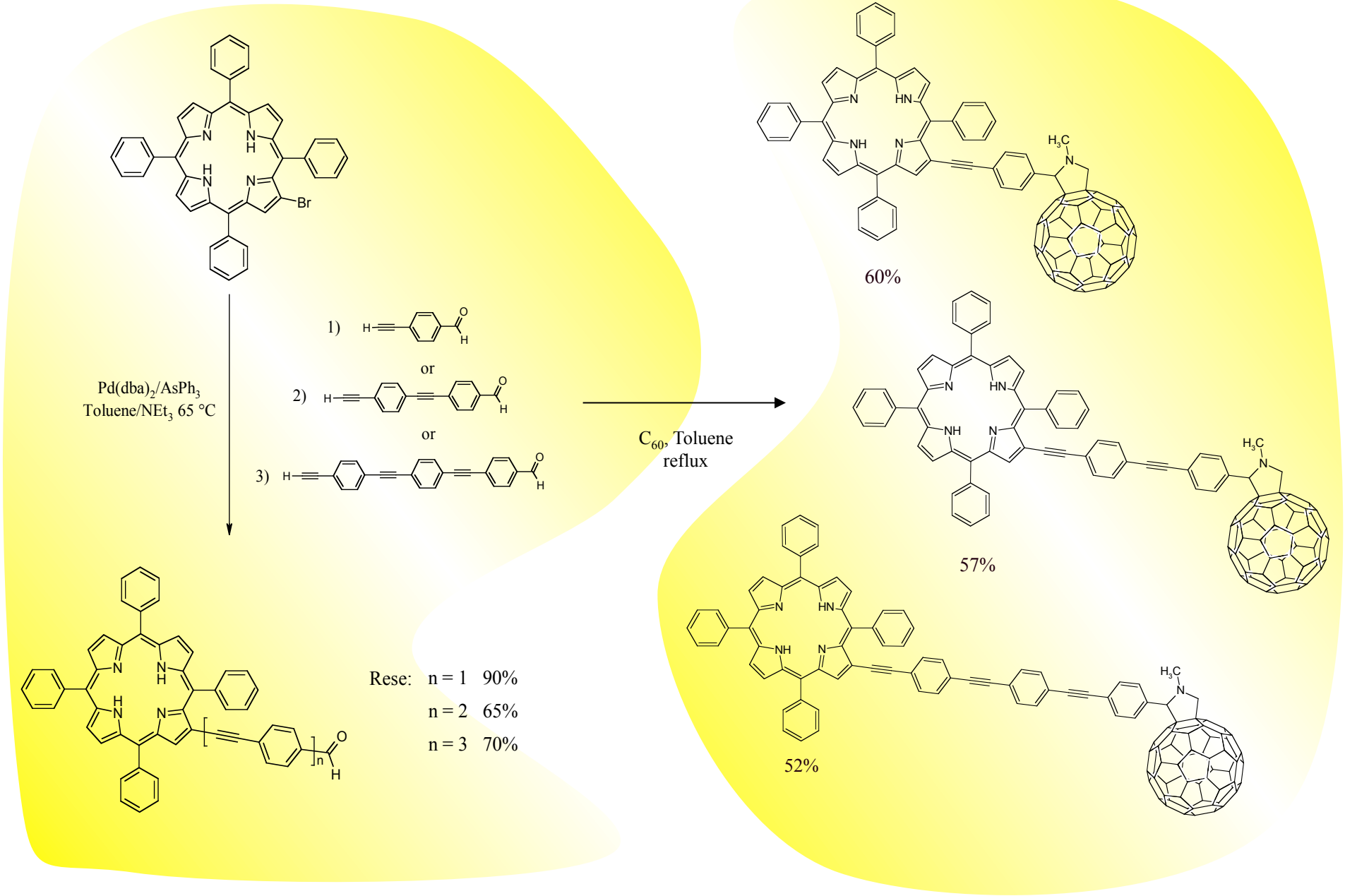
✓ ***Use of oligo-phenyleneethynylenes as molecular wire***



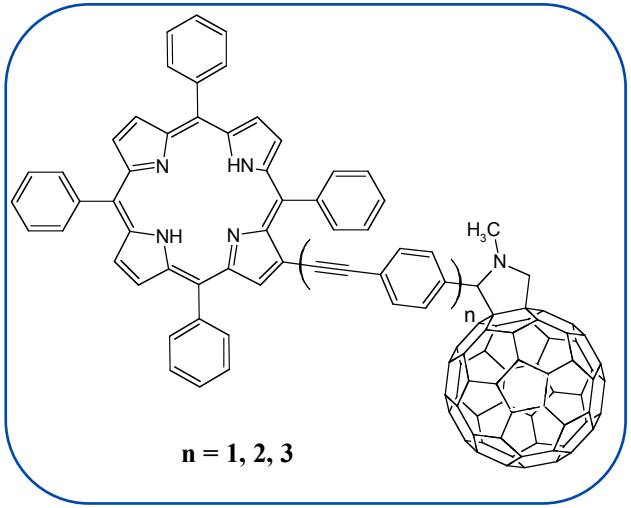
✓ ***Rigid structure between the chromophores***

✓ ***Extended π delocalization along the linker***

✓ *Synthesis of new porphyrin-"wire"-fullerene systems*



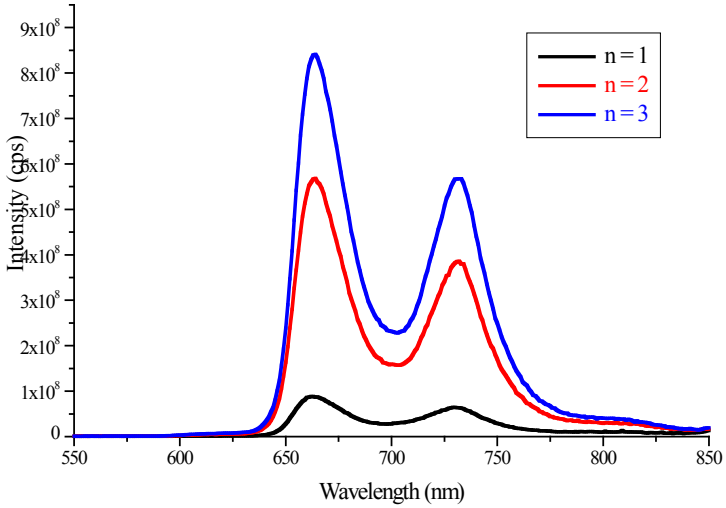
✓ *Steady state fluorescence studies*



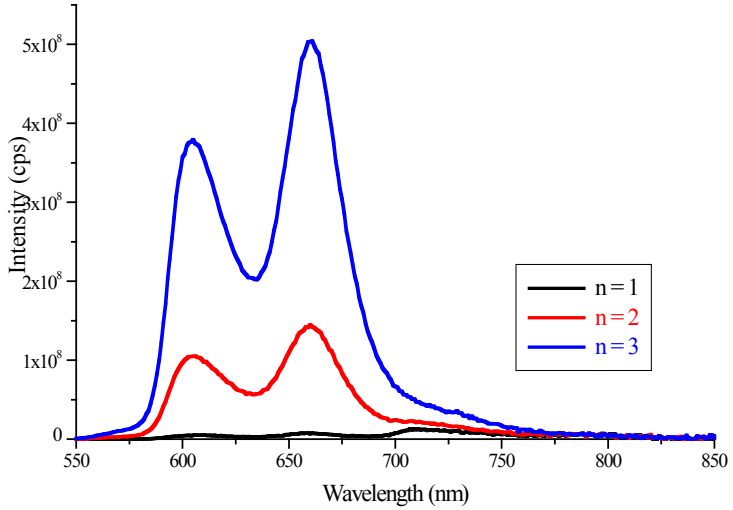
The fluorescence quencing efficiency is distance dependent

Compound	Quencing efficiency		
	Toluene	THF	Benzonitrile
$H_2P\text{-}EP_1\text{-}C_{60}$	93%	>99%	>99%
$ZnP\text{-}EP_1\text{-}C_{60}$	98%	>99%	>99%
$H_2P\text{-}EP_2\text{-}C_{60}$	47%	60%	71%
$ZnP\text{-}EP_2\text{-}C_{60}$	81%	94%	95%
$H_2P\text{-}EP_3\text{-}C_{60}$	20%	23%	24%
$ZnP\text{-}EP_3\text{-}C_{60}$	45%	58%	66%

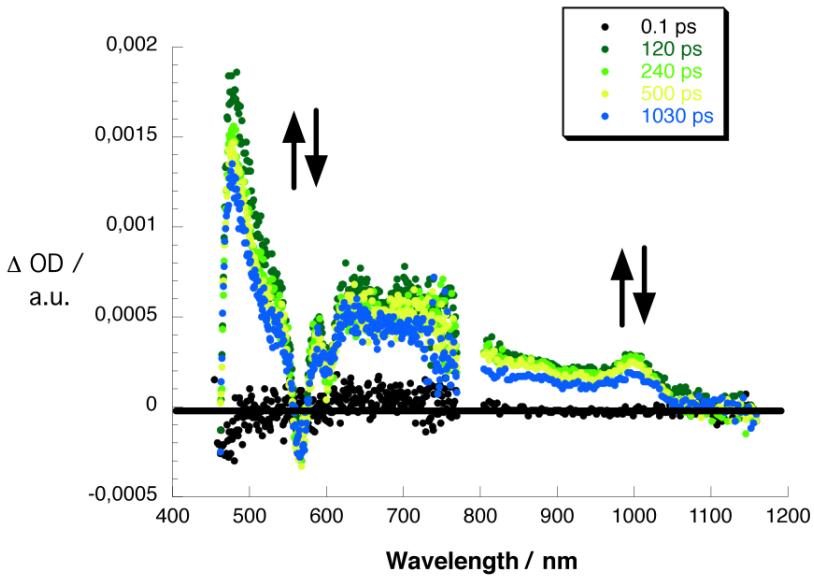
Free base



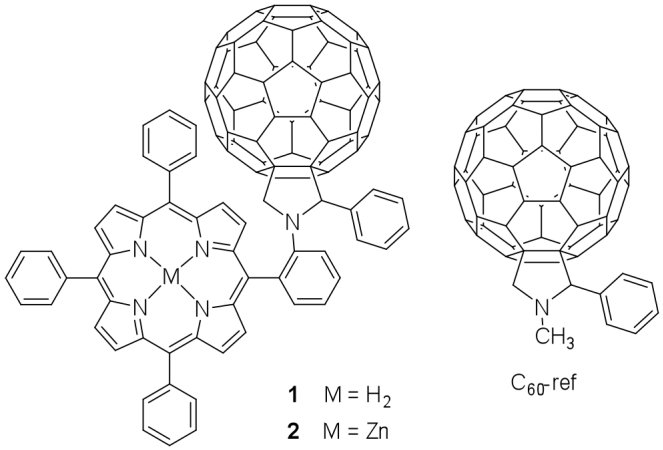
Zinc complex

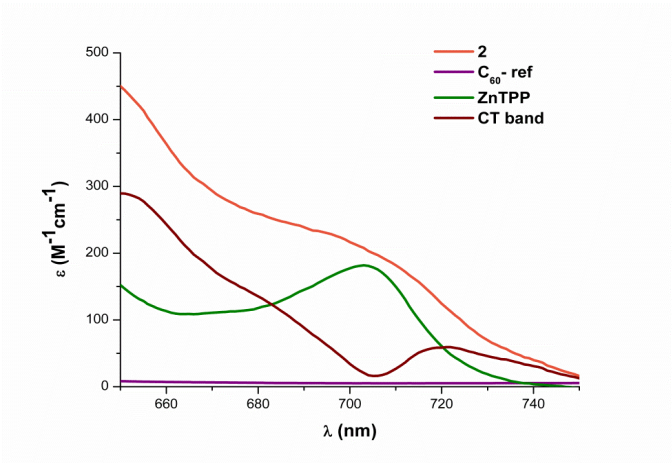


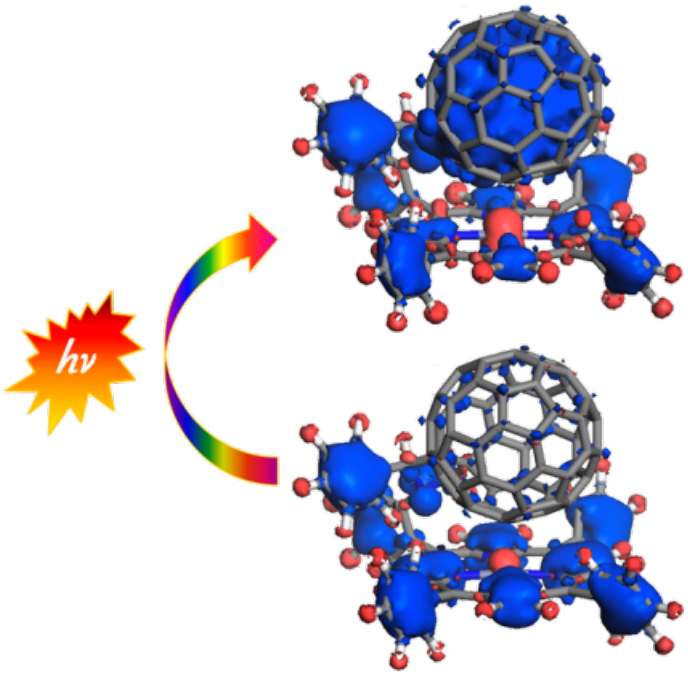
Transient spectroscopy



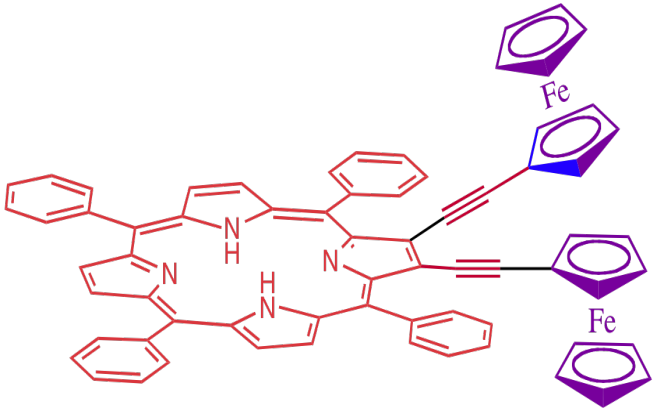
Interazioni π−π tra porfirine e C60

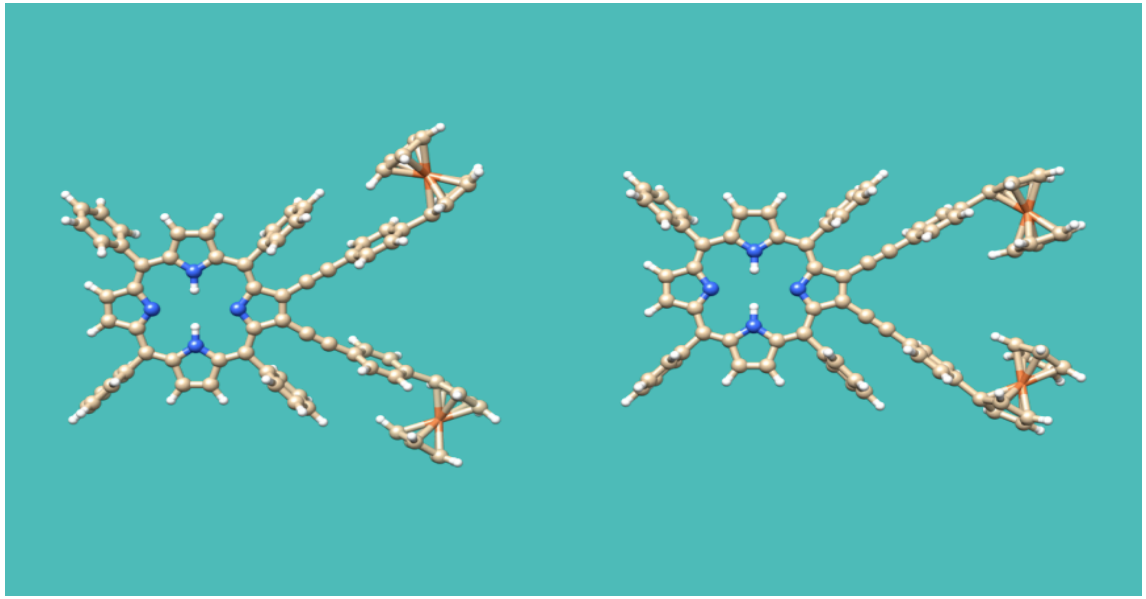




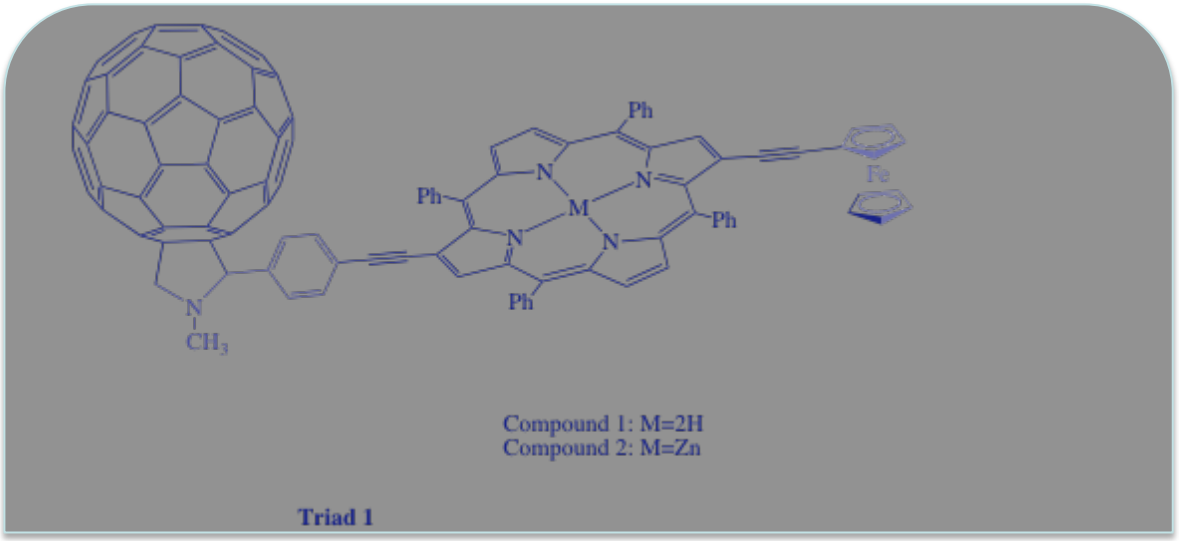


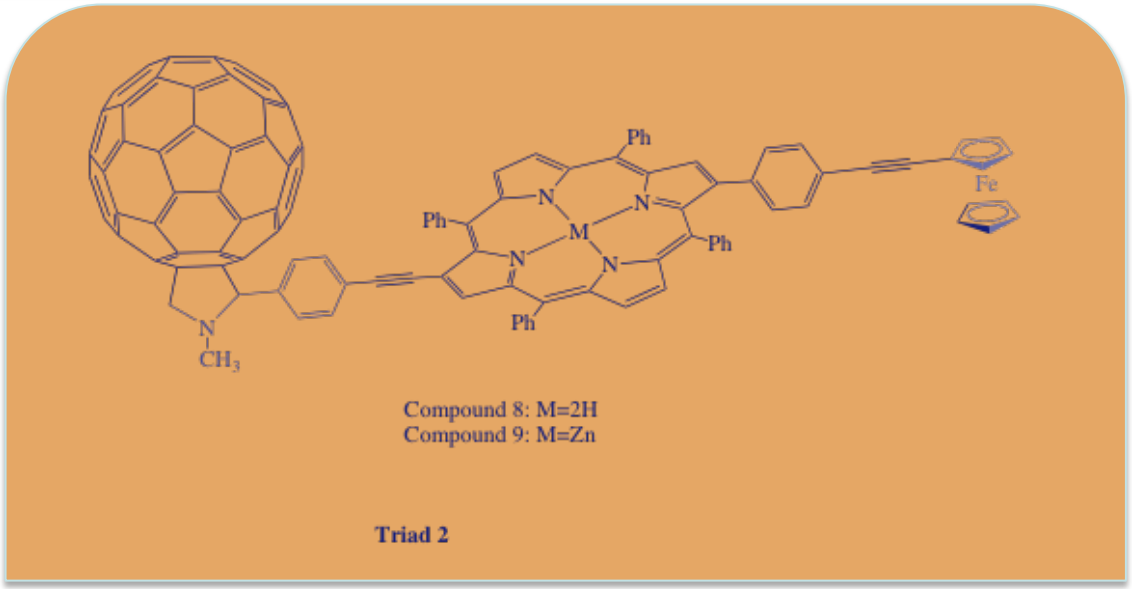
Structures of ferrocene-porphyrin





Structures of the triads





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