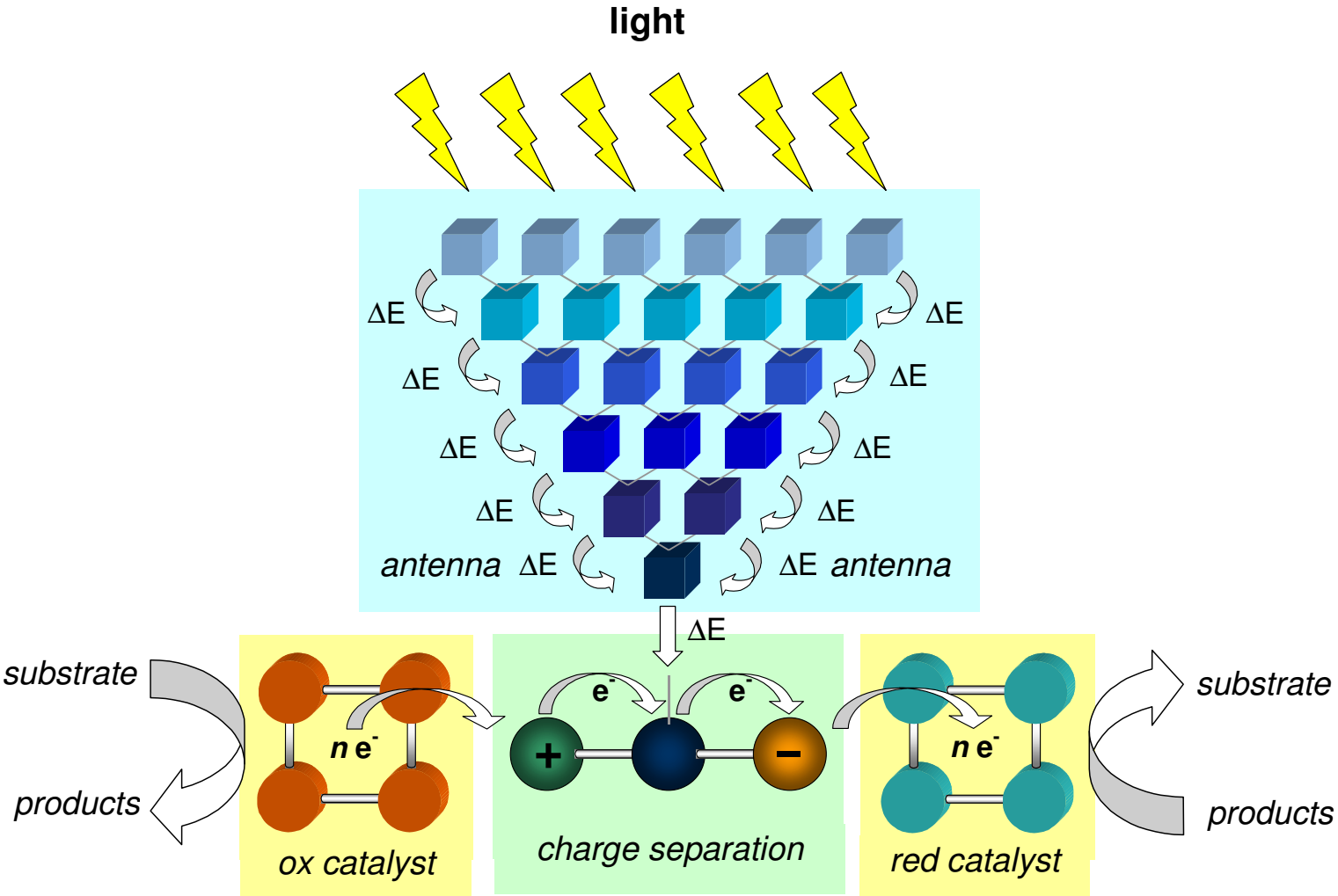
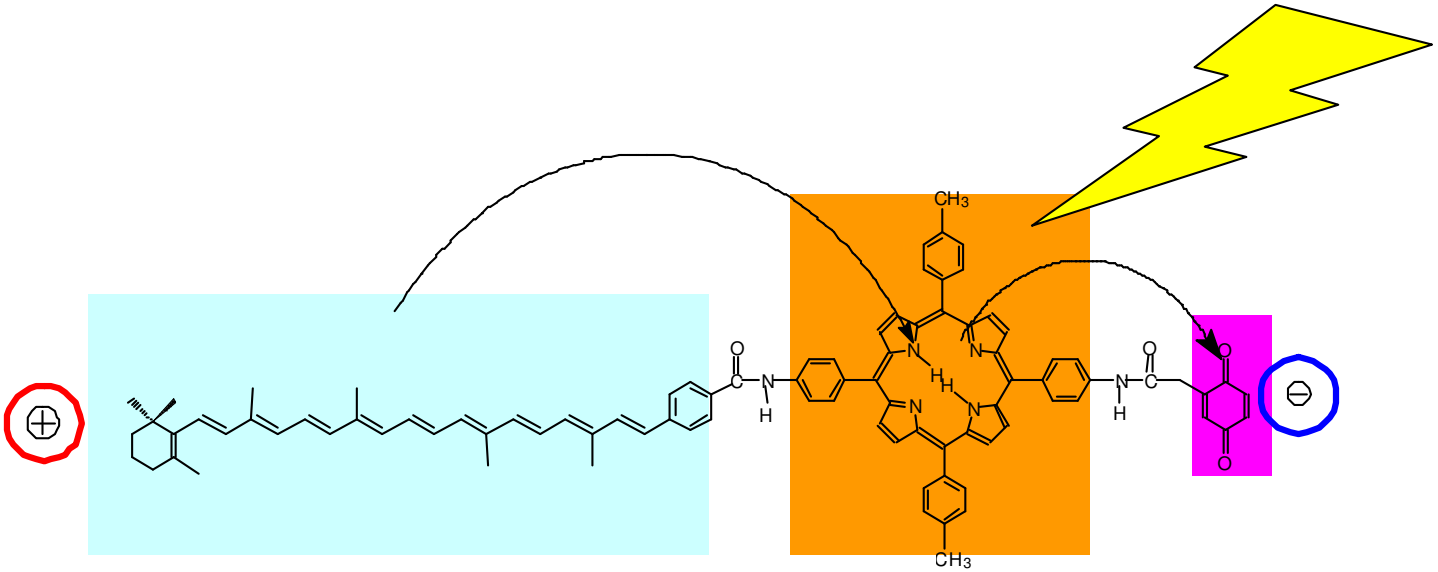
Functional units: require precise organization of molecular components in space and energy



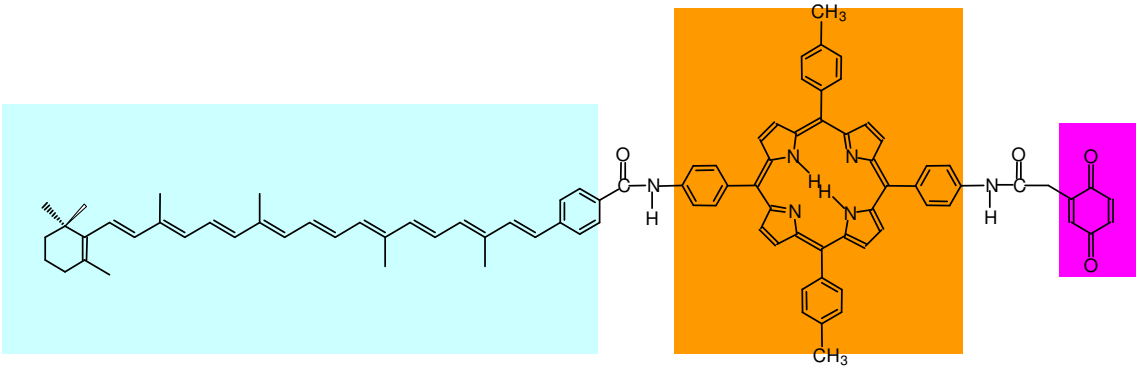
Molecular “Triad”



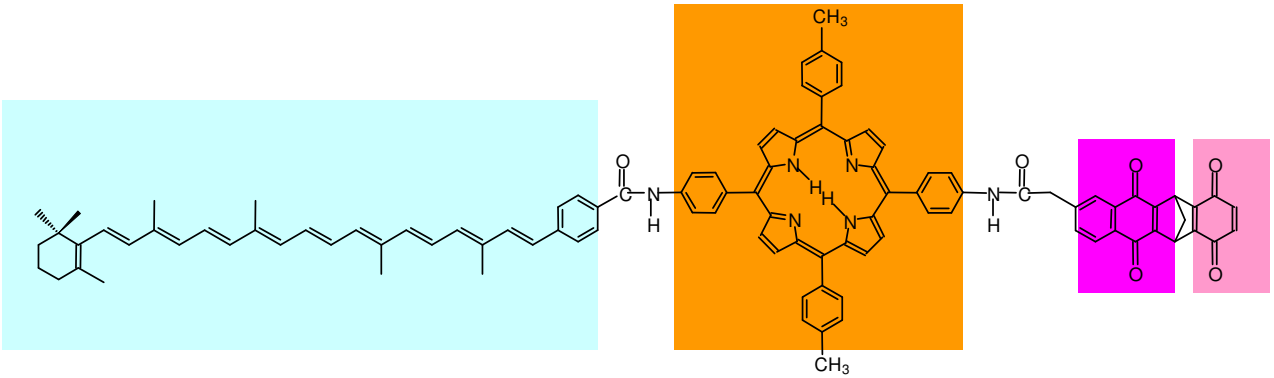
τ = 300 ns Φ = 0.04

Photosynthetic RC
τ = 100 ms Φ = 1.0

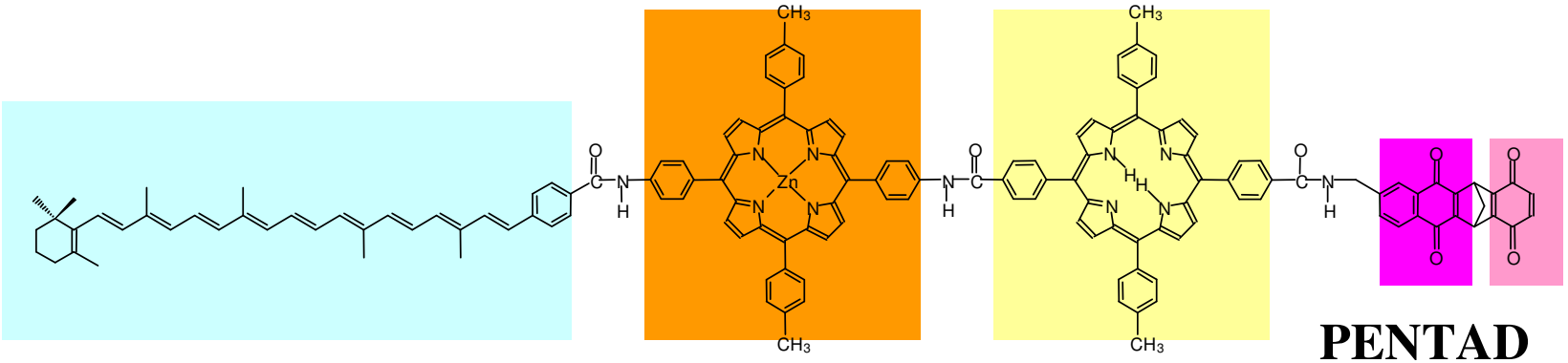
$\Phi = 0.04, \ \tau = 0.3\ \mu s$



TRIAD

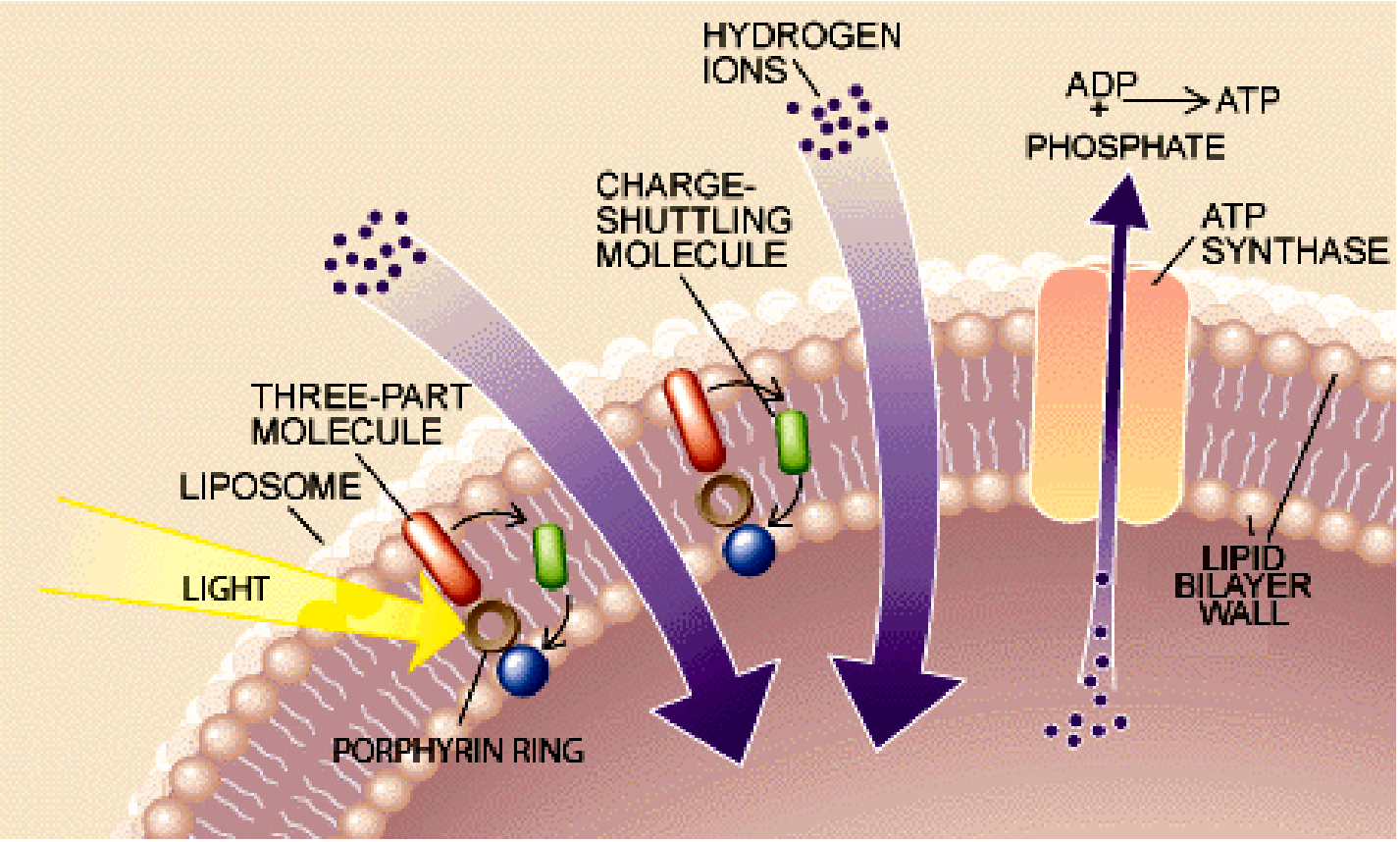


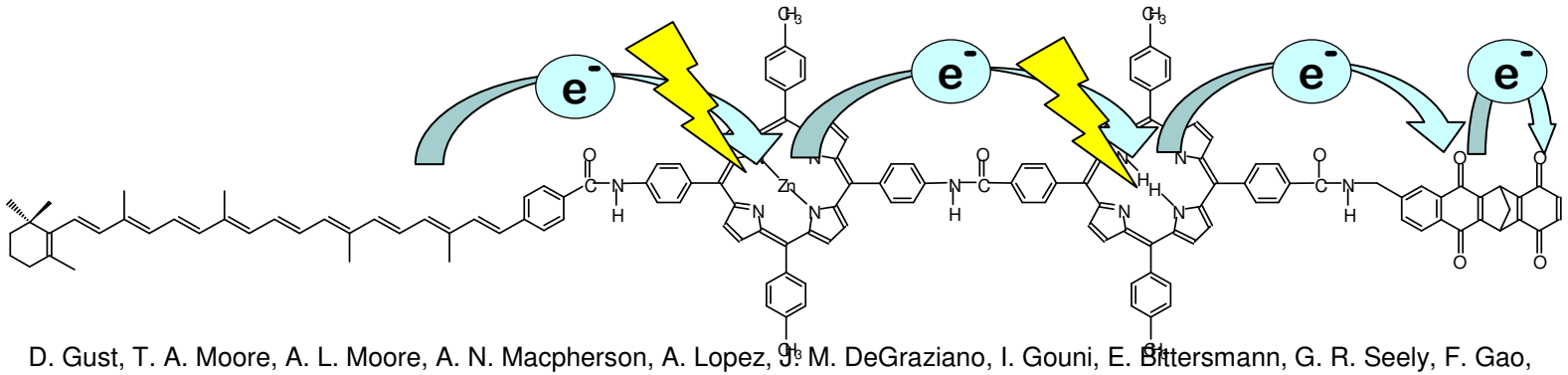
TETRAD



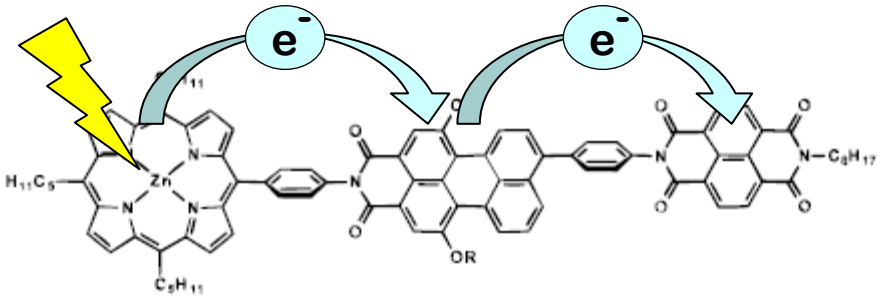
PENTAD

$\Phi = 0.83, \ \tau = 55\ \mu s$

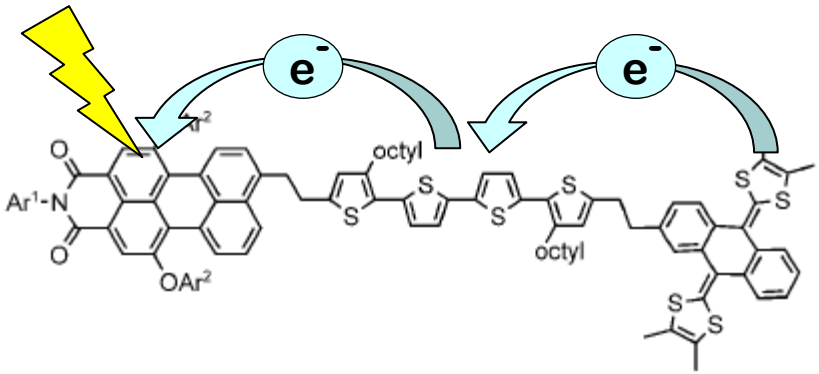

HYDROGEN IONS
ADP + PHOSPHATE → ATP
CHARGE-SHUTTLING MOLECULE
ATP SYNTHASE
THREE-PART MOLECULE
LIPOSOME
LIGHT
LIPID BILAYER WALL
PORPHYRIN RING



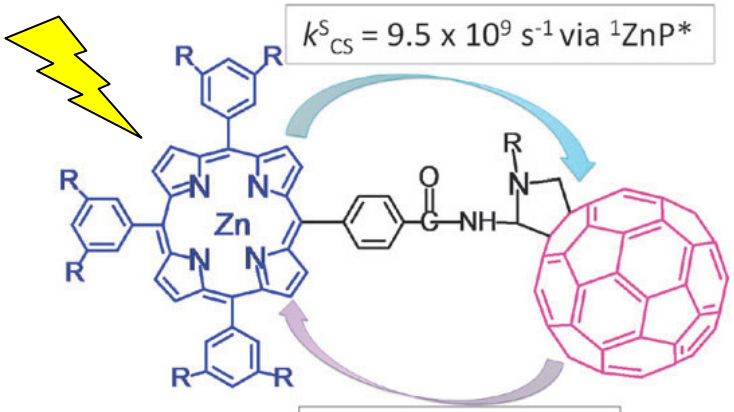
D. Gust, T. A. Moore, A. L. Moore, A. N. Macpherson, A. Lopez, J. M. DeGraziano, I. Gouni, E. Bittersmann, G. R. Seely, F. Gao, R. A. Nieman, X. C. Ma, L. Demanche, D. K. Luttrull, S.-J. Lee and P. K. Kerrigan *J. Am. Chem. Soc.,* **1993**, *115***,** 11141 - 11152 ().

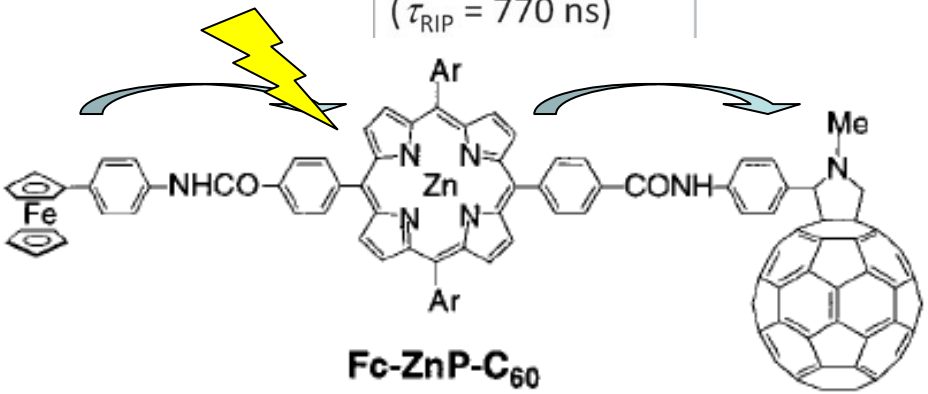


R. T. Hayes, M. R. Wasielewski, D. Gosztola
J. Am. Chem. Soc. **2000,** *122,* 5563-5567



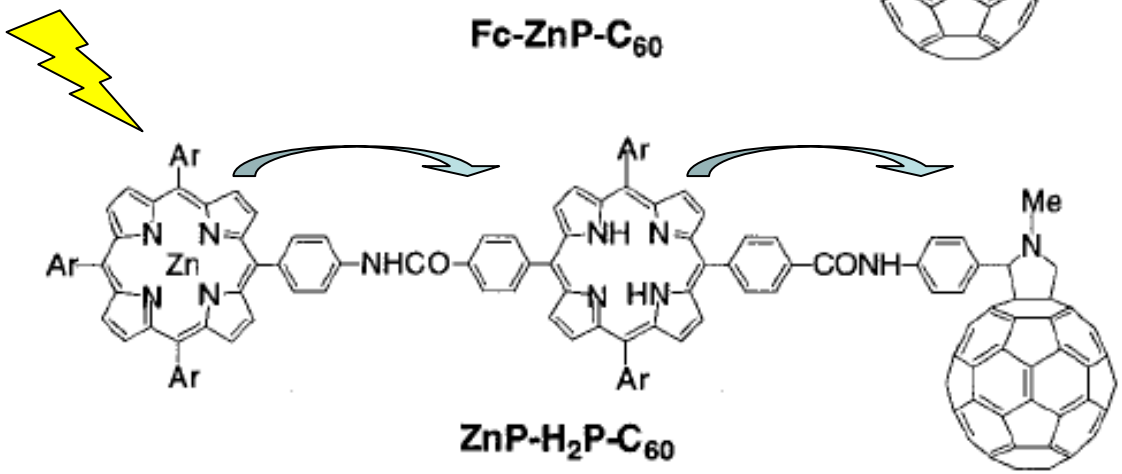
J. Boixel, E. Blart, Y. Pellegrin, F. Odobel, N. Perin, C. Chiorboli, S. Fracasso, M. Ravaglia, F. Scandola
Chem. Eur. J., **2010**, *16*, 9140 – 9153





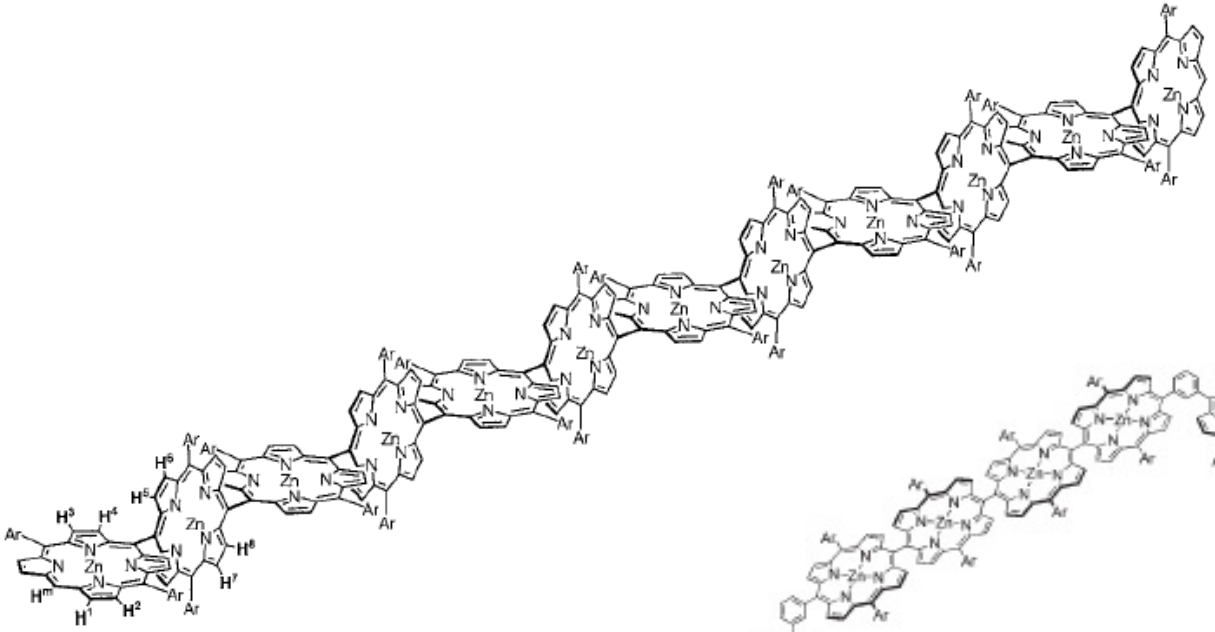
Fc-ZnP-C_{60}

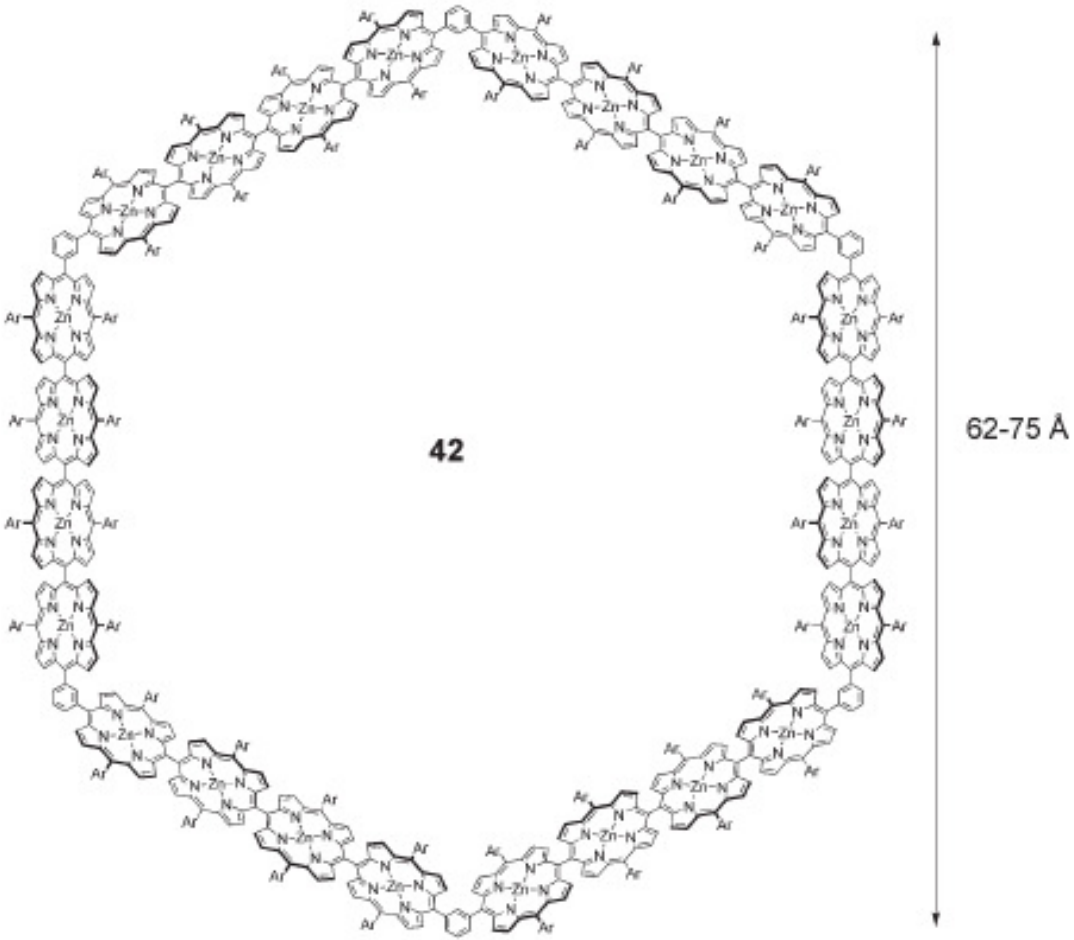
10 µs



ZnP-H_2P-C_{60}

20 µs

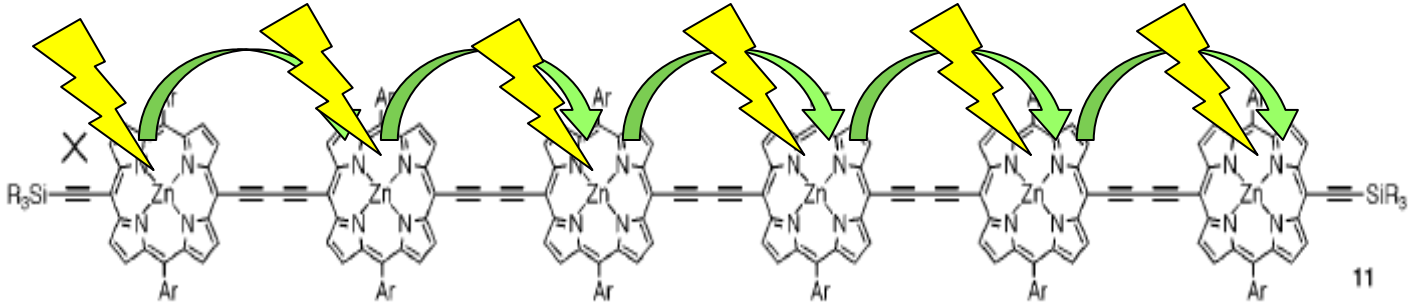




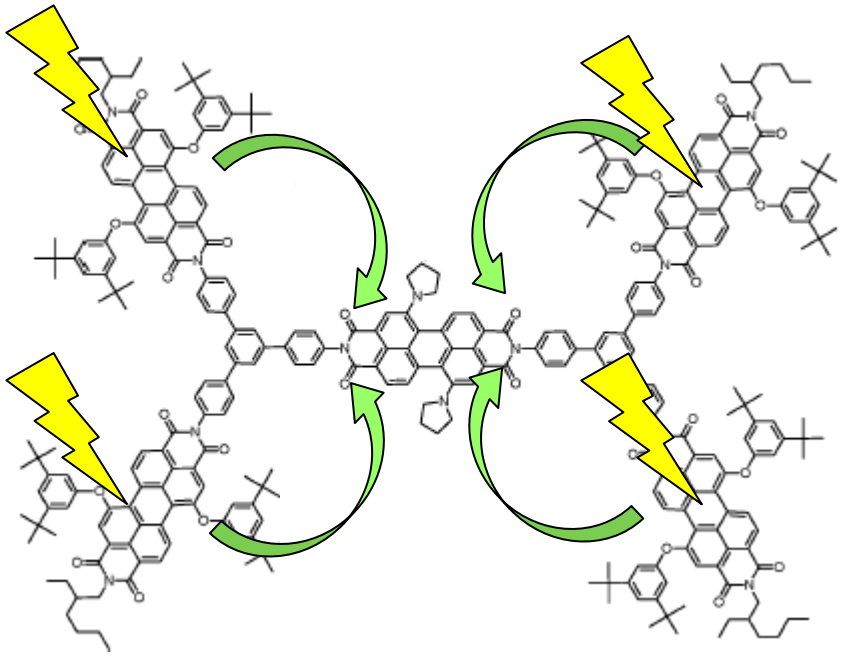
A. Osuka, et al.

Chem. Eur. J. **2005**, *11*, 3389 – 3404

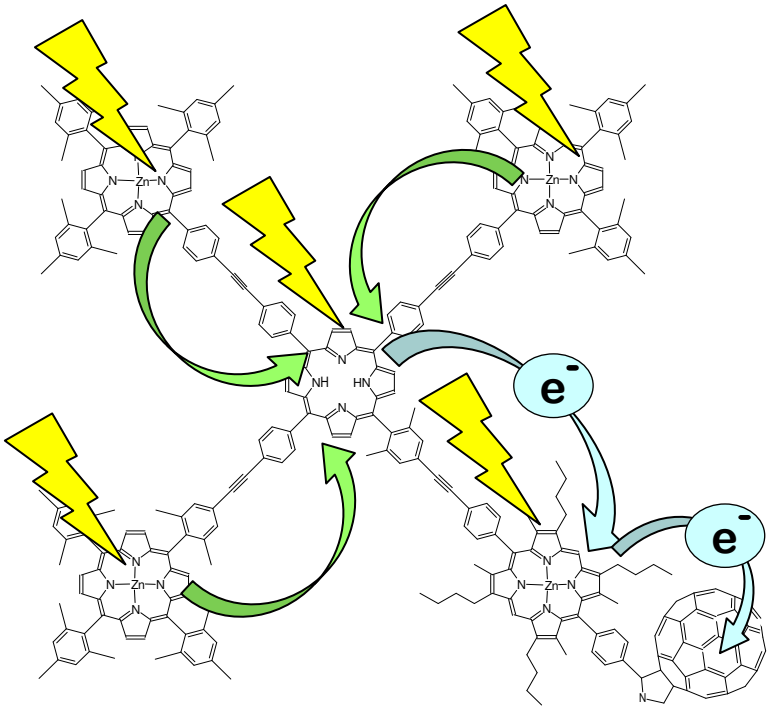
Chem. Soc. Rev., **2007**, *36*, 831–845



C. Anderson

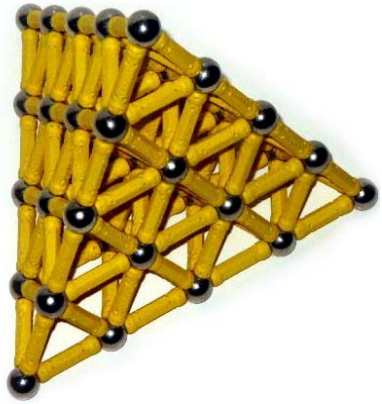


M. R. Wasielewski,



D. Gust, T. A. Moore & A. Moore

Metal-mediated supramolecular approach to Multicomponent systems for artificial photosynthesis



- metal centers to “glue” together molecular units (chromophores, donors, acceptors, etc.)

- linkages: coordinative bonds

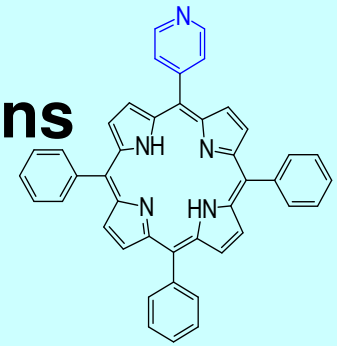
- molecular units carrying peripheral ligands functions

- labile metal centers: thermodynamic control (true self-assembly)

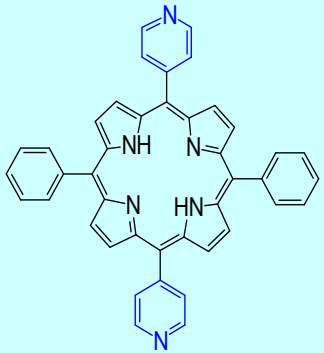
-inert metals: kinetic control (synthesis under mild conditions)

-F. Scandola, C. Chiorboli, A. Prodi, E. Iengo, E. Alessio *Coord. Chem. Rev.*, **2006**, *250*, 1471-1496 .
E. Iengo, F. Scandola, E. Alessio *Struct. Bond.*, **2006** *121*, 105-143 .

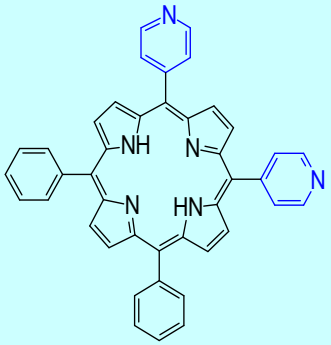
Pyridyl Porphyrins



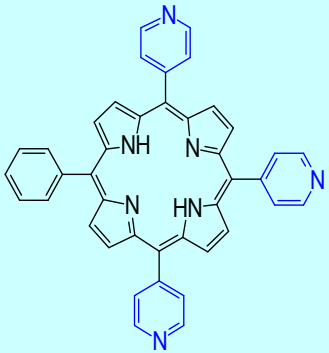
1
MPyP



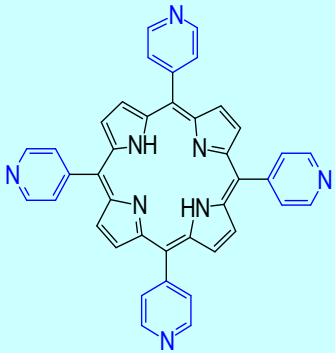
2
t-DPyP



3
c-DPyP

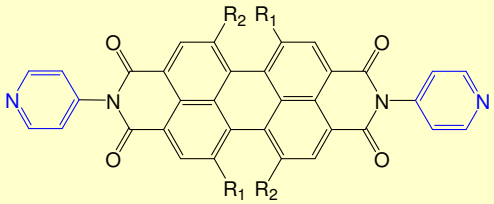


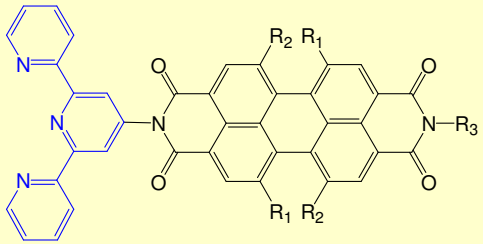
4
TrPyP

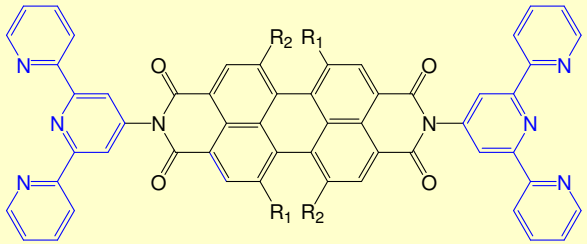


5
TPyP

(poly)Pyridyl Perylenebisimides



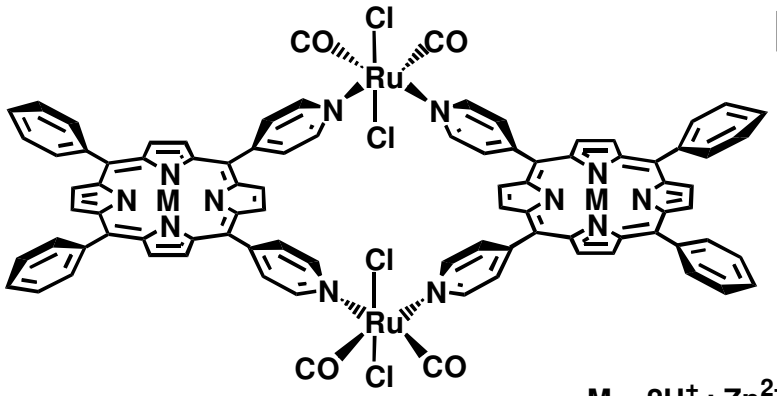




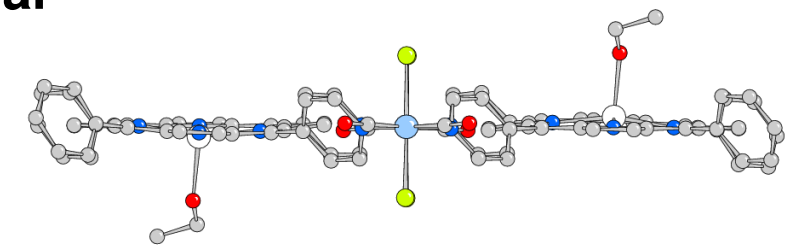
2+2 Molecular squares

with *cis*-D(n)PyP (n=3,4) and *cis*-$Ru(CO)_2Cl_2$ corners

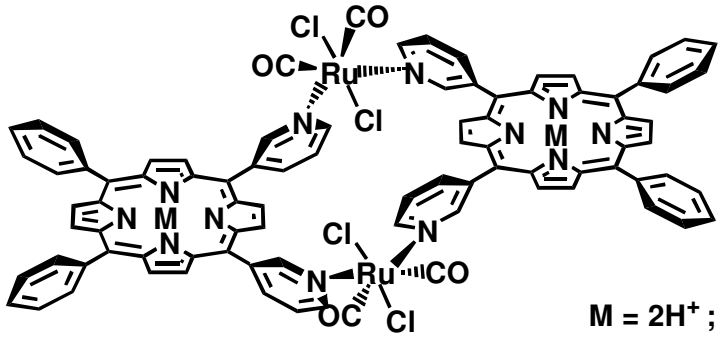
planar



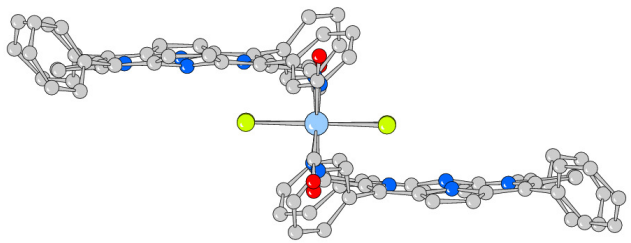
M = $2H^+$; Zn^{2+}



staggered

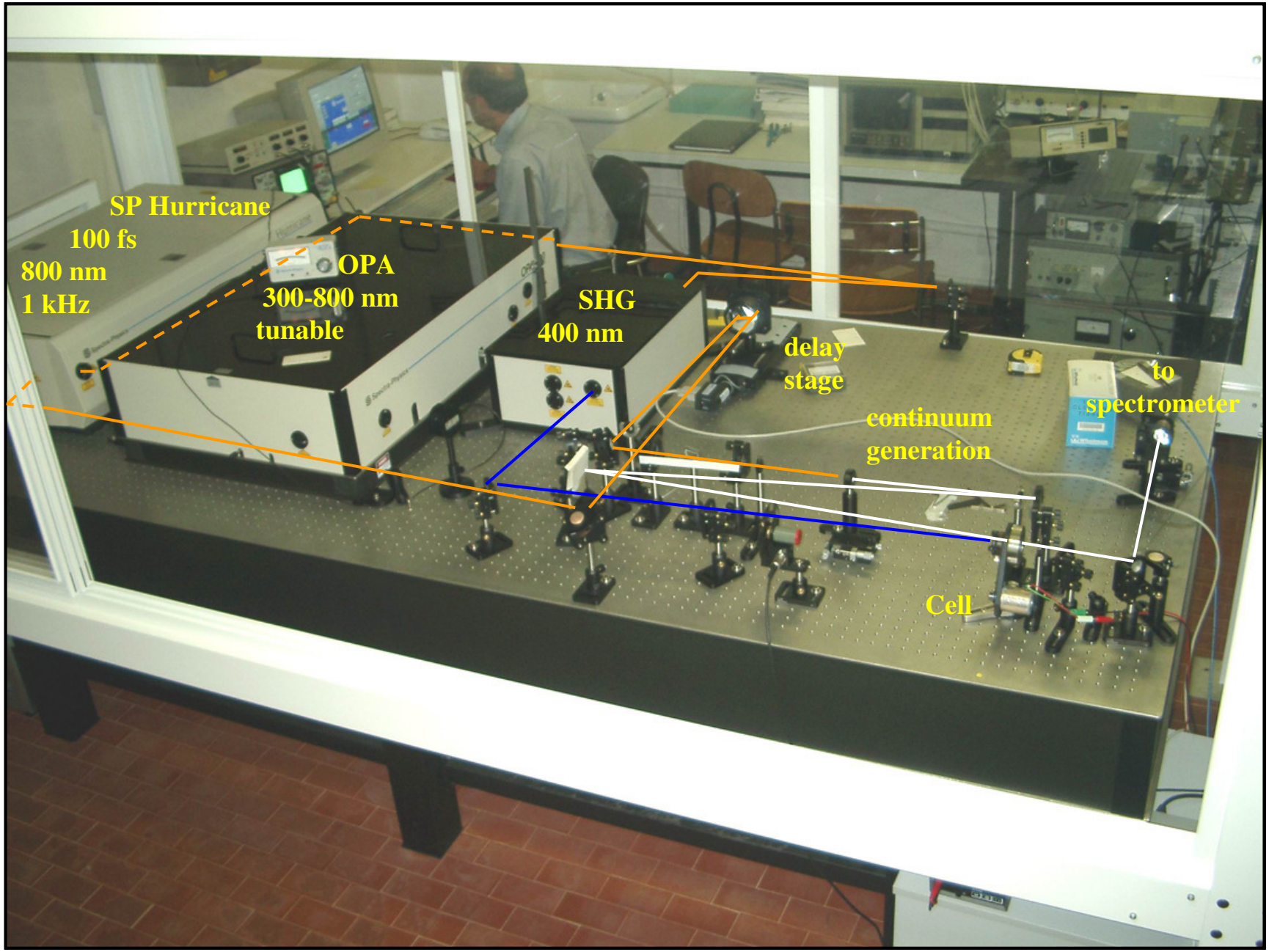


M = $2H^+$; Zn^{2+}



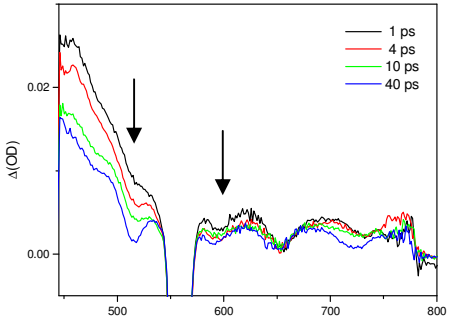
Homonuclear species: Fb-Fb, Zn-Zn **Heteronuclear species: Zn-Fb**

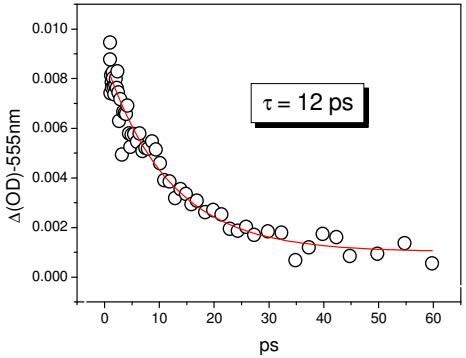
Ultrafast Spectroscopy Setup, Department of Chemistry, University of Ferrara

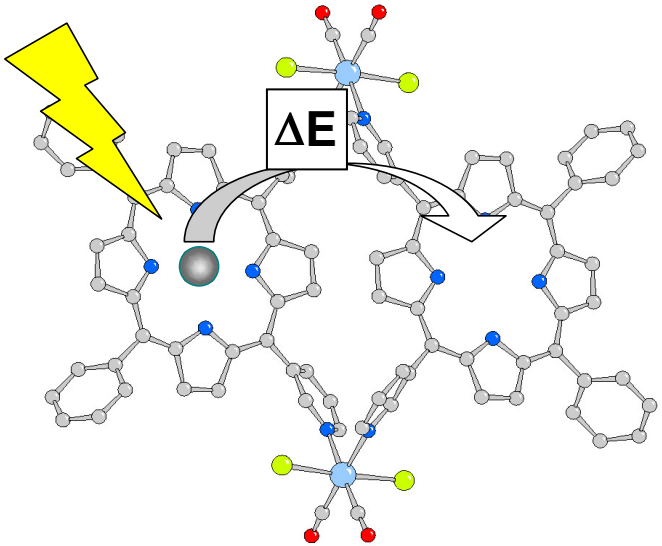


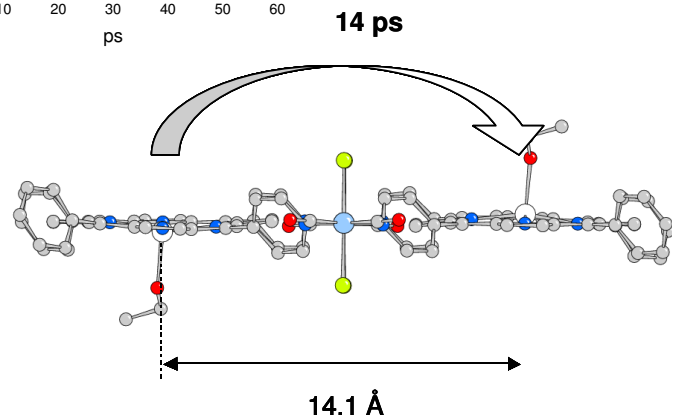
Zn-Fb molecular squares

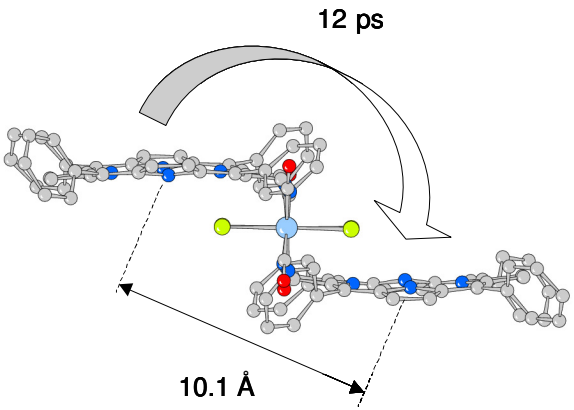
Interporphyrin singlet energy transfer



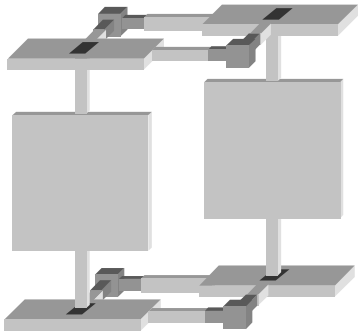




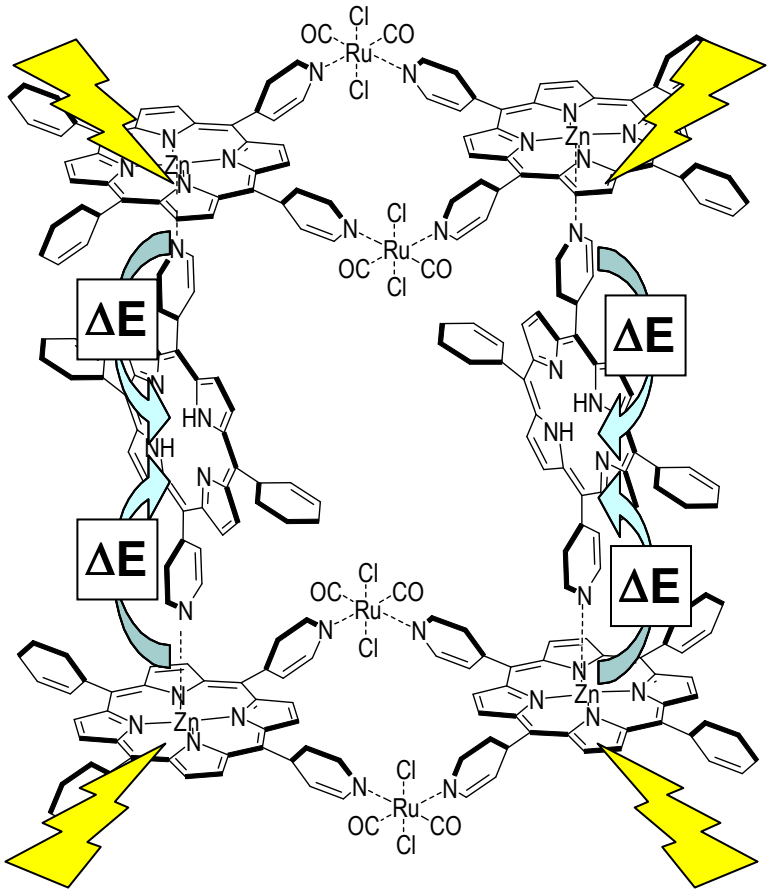




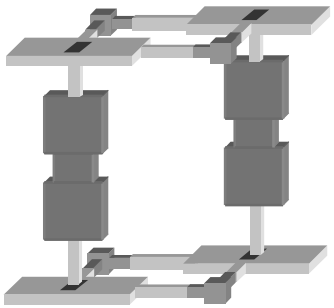
E. Iengo, E. Zangrando, M. Bellini, E. Alessio, A. Prodi, C. Chiorboli, F. Scandola, *Inorg. Chem.* **2005**, 44, 9752 – 9762



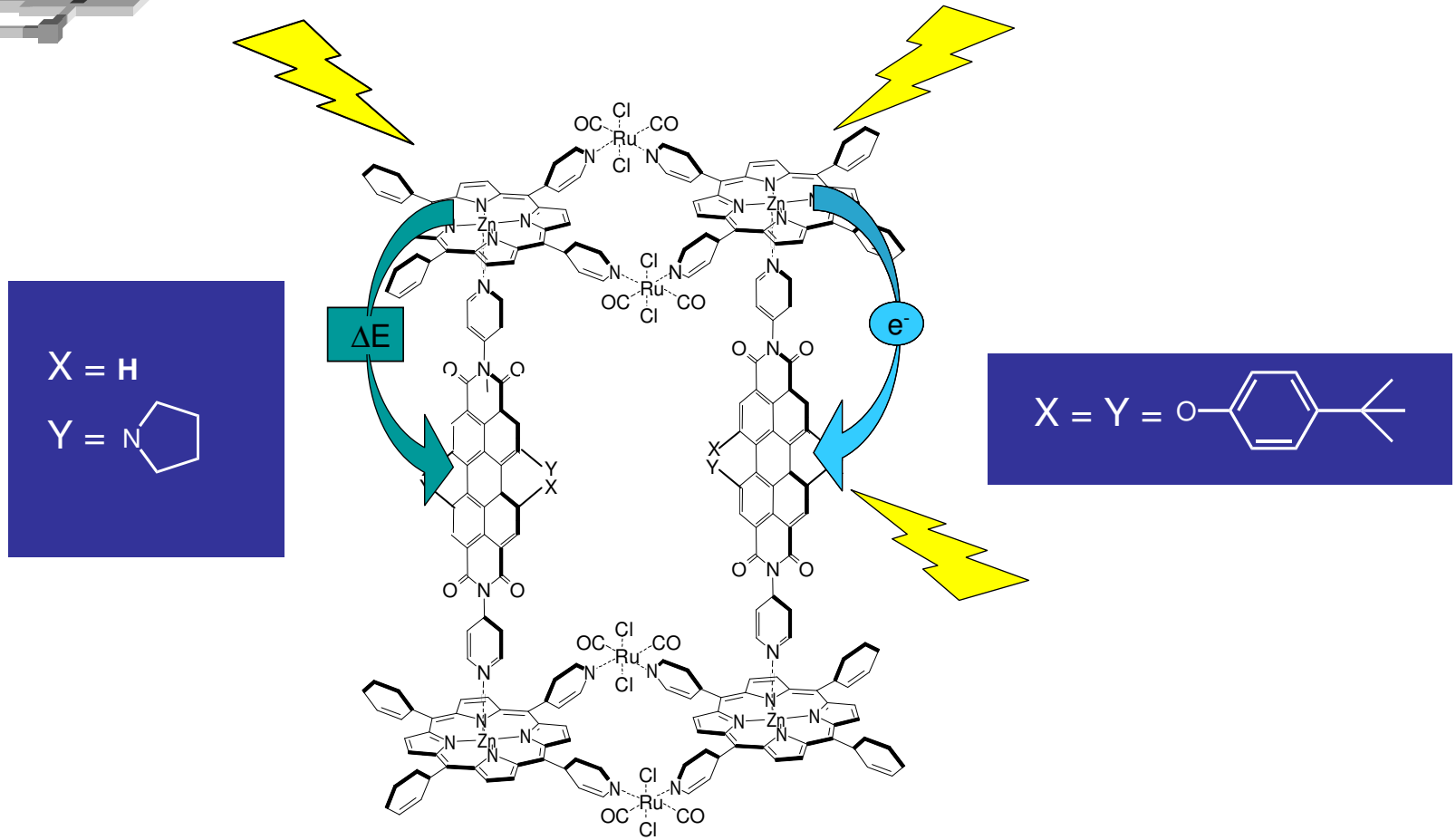
A Fb-Zn molecular sandwich



A. Prodi, C. Chiorboli, F. Scandola, E. Iengo, E. Alessio *Chem. Phys. Chem.* **2006**, *7*, 1514-1519



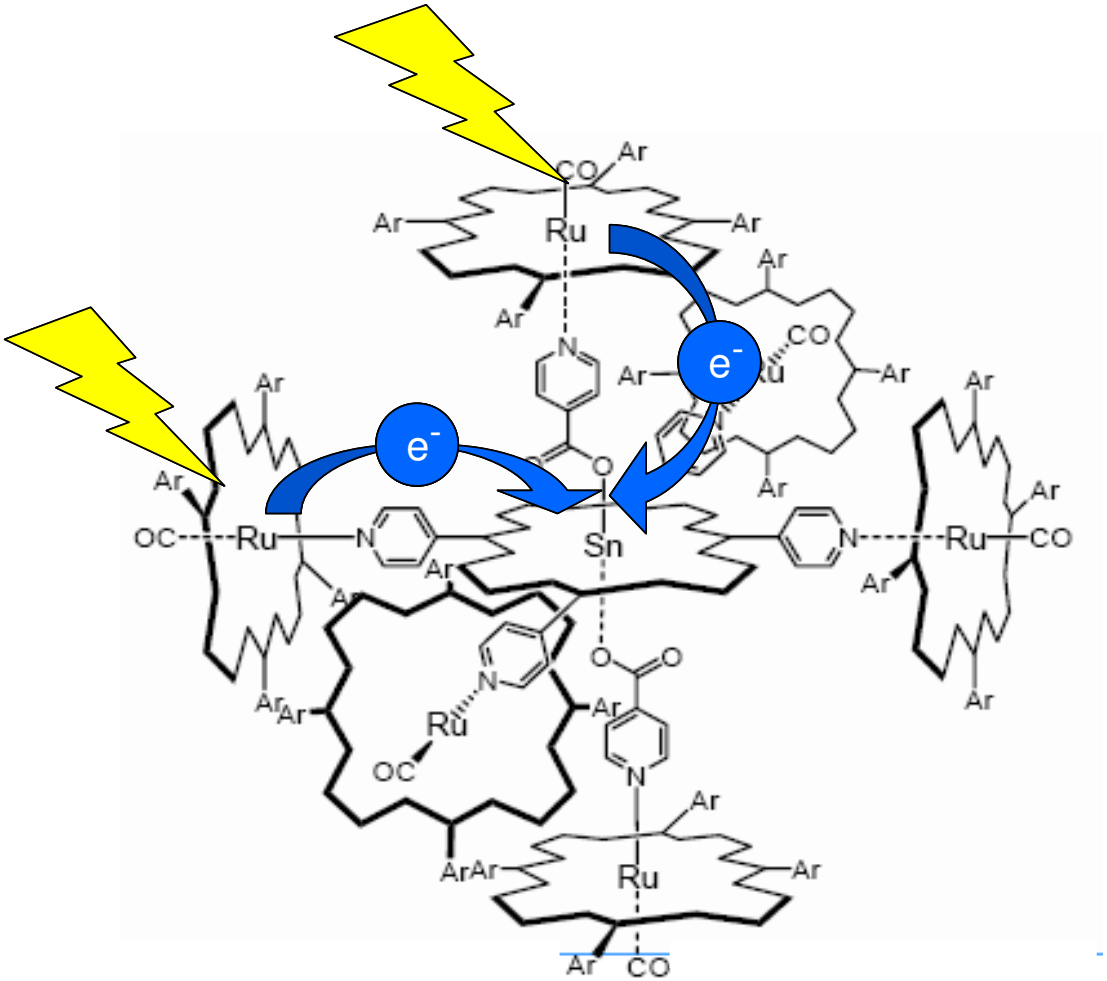
Molecular sandwiches with perylenebisimide pillars

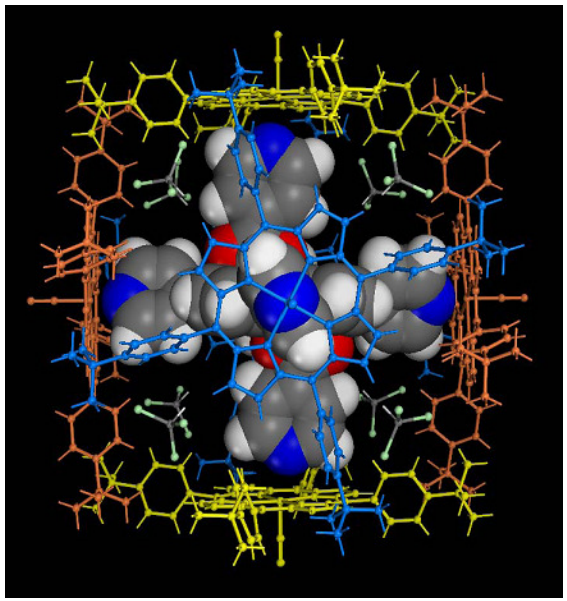


M. T. Indelli, C. Chiorboli, F. Scandola, E. Iengo, P. Osswald, F. Würthner *J. Phys. Chem. B*, **2010,** *114*, 14495–14504.

Side-to-face Sn-Ru porphyrin arrays

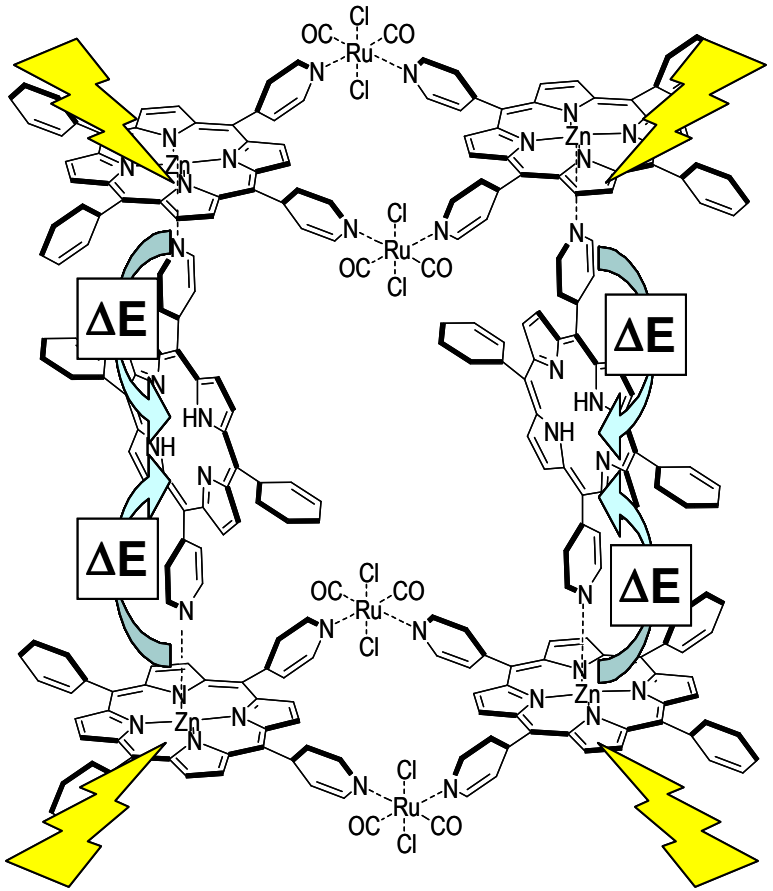
Efficient photoinduced electron transfer from periphery to center

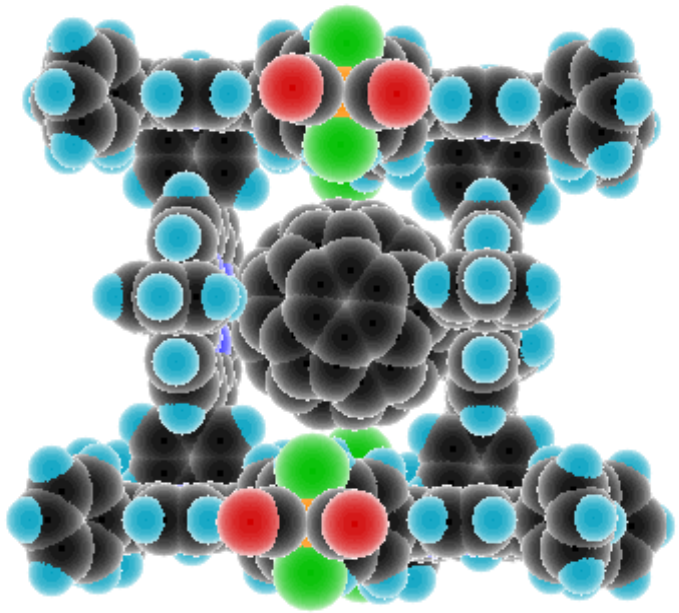




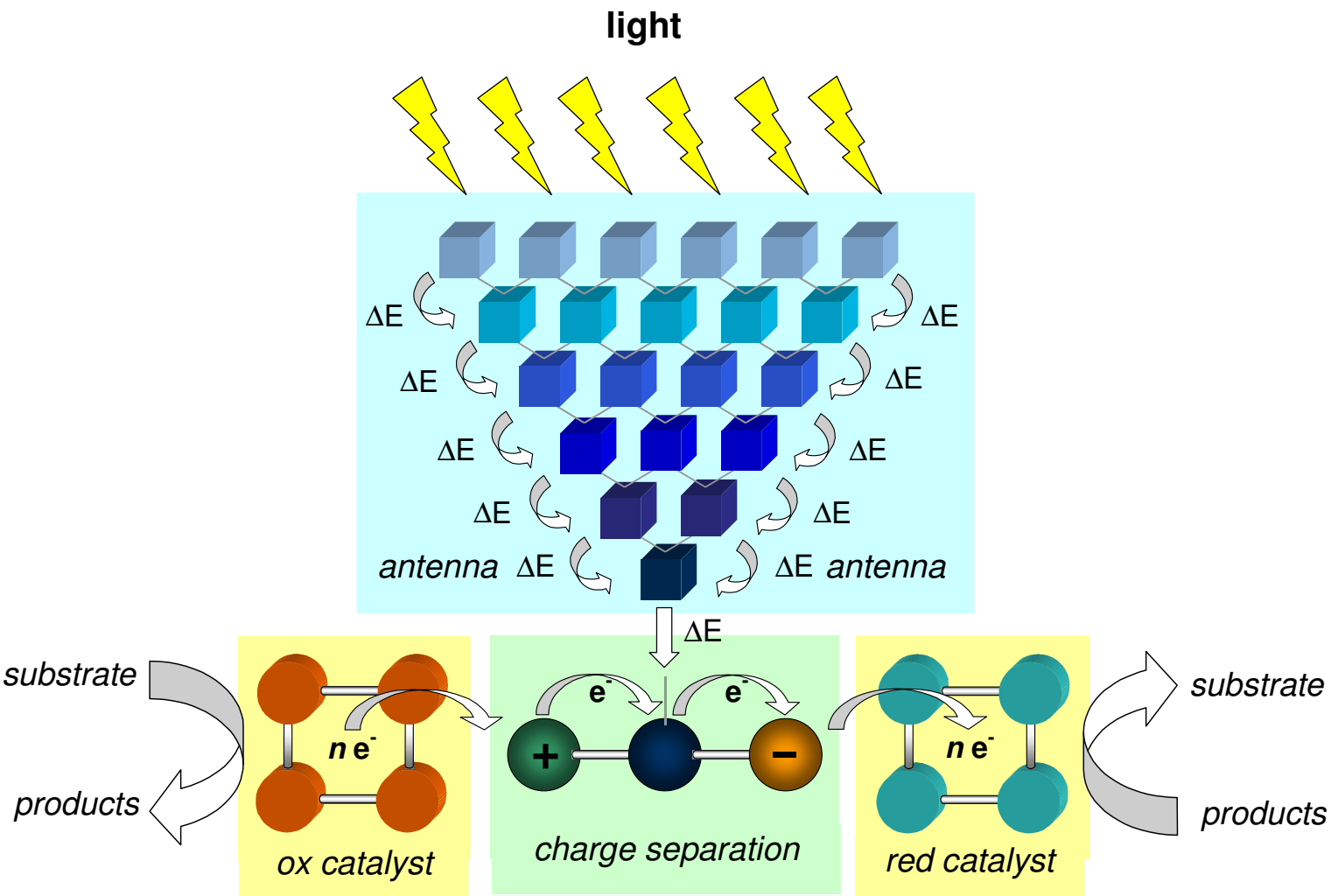
M. T. Indelli, C. Chiorboli, M. Ghirotti, M. Orlandi, F. Scandola, H-J. Kim, *J. Phys. Chem. B*, **2010**, *114*, 14273–14282.

Zn-Fb molecular sandwich: cyclic antenna with host capabilities





E. Iengo, E. Alessio, M. Orlandi, M. T. Indelli, F. Scandola, manuscript in preparation


light
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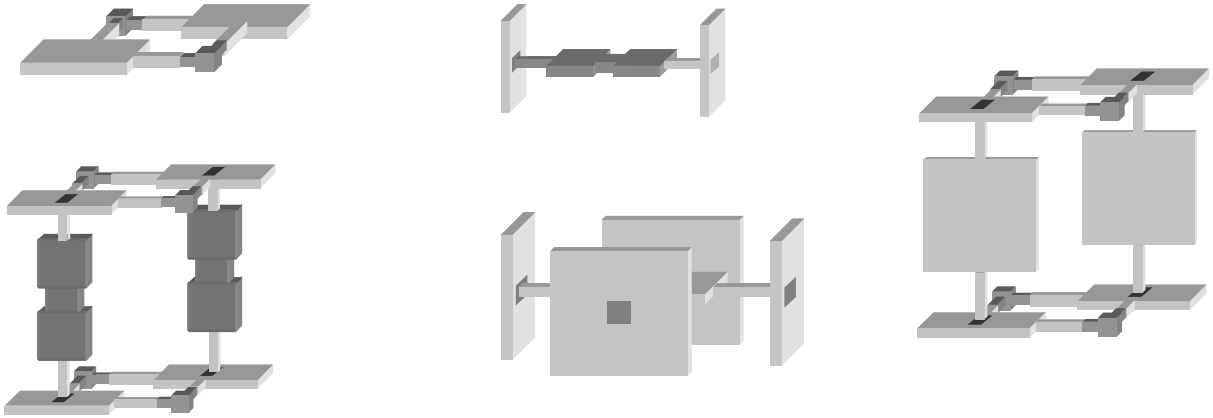
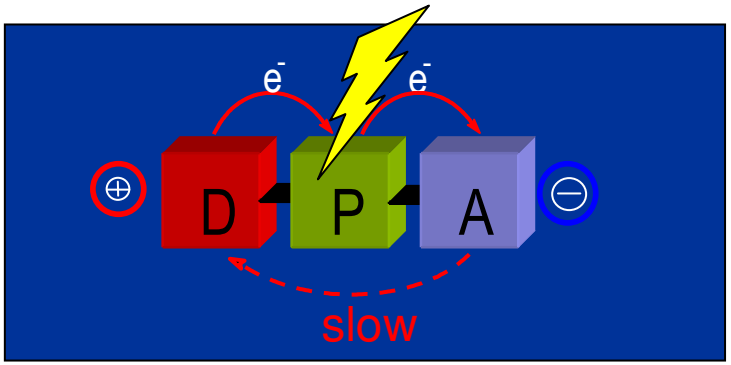
substrate
products
n e-
ox catalyst
e-
e-
+
−
charge separation
n e-
red catalyst
substrate
products

self-assembling of symmetric multi-chromophoric systems relatively easy

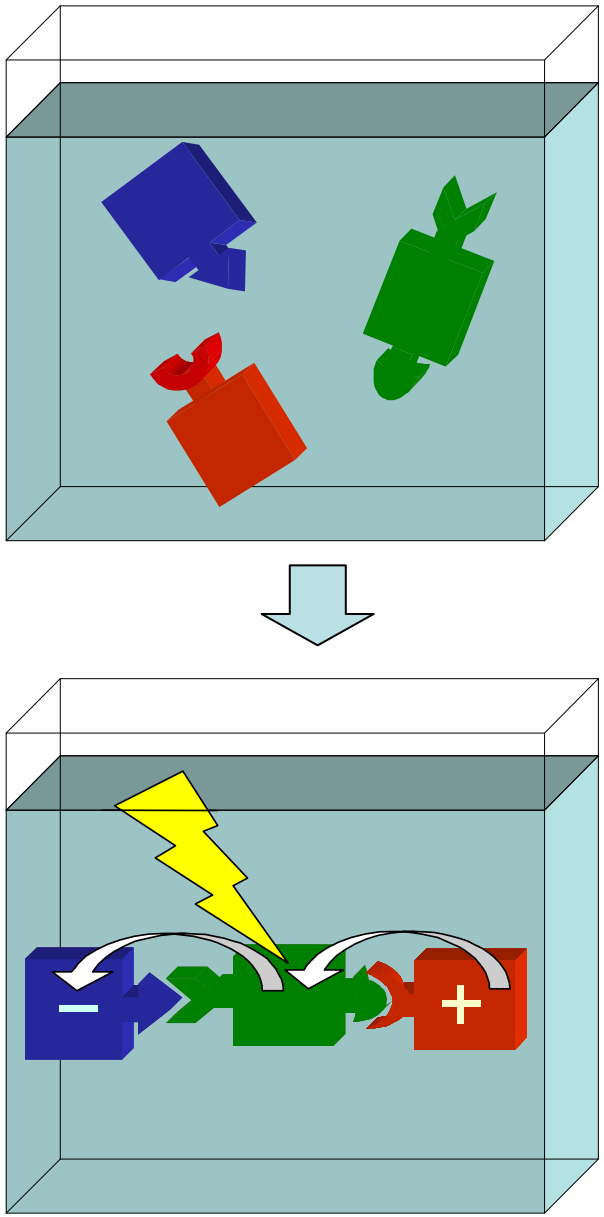


Photoinduced Charge Separation: Triads

Intrinsically asymmetric



Design of a self-assembling system less obvious



Design of self-assembling triads

Requires the use of two different binding motifs at central unit, for selective recognition of terminal units

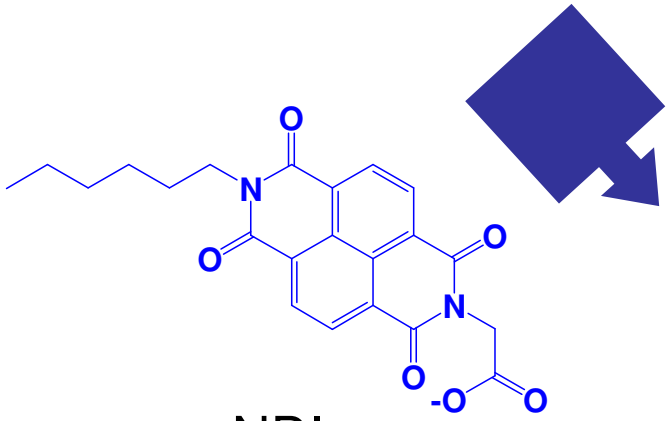
For metal-mediated assemblies, selective coordination based on:

- soft *vs* hard metal-ligand pairs

- ligand-metal coordination geometry matching

- .....

Molecular Components

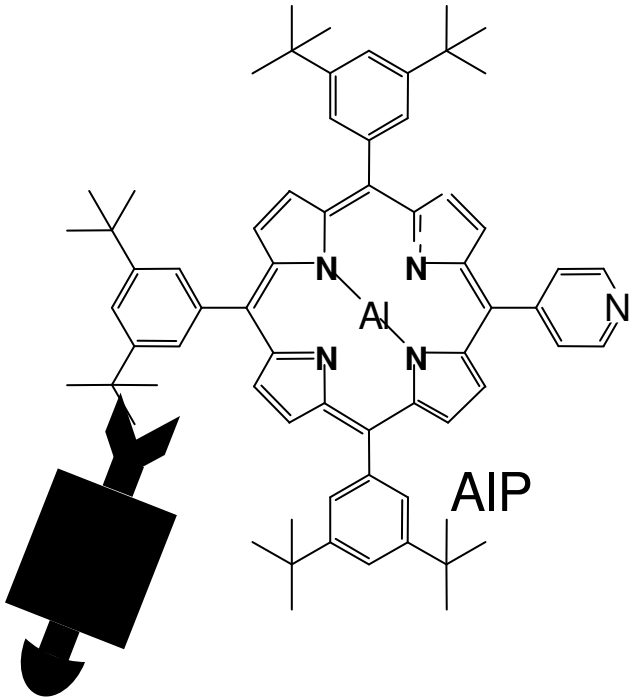


NDI

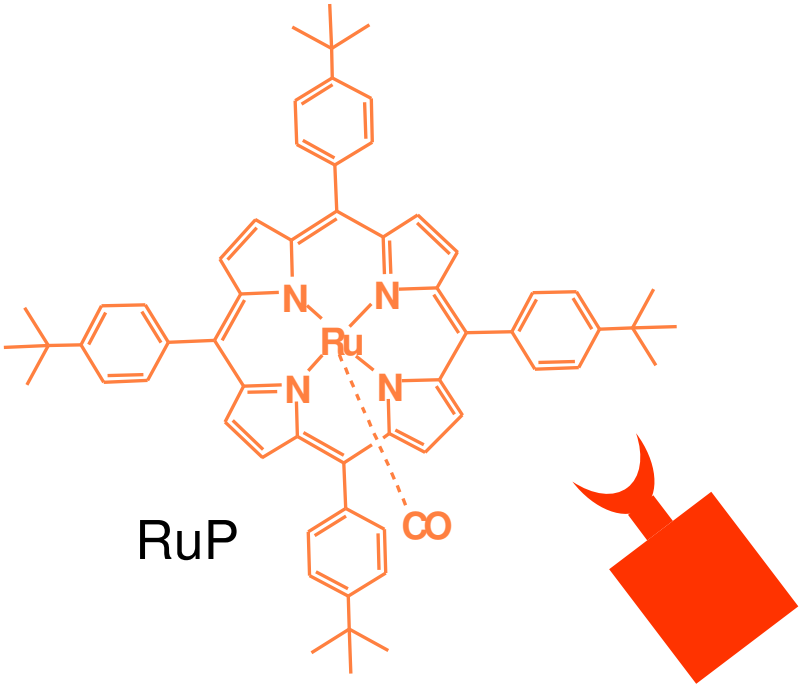
Preferential coordination:

-COO$^-$ ⇨ Al

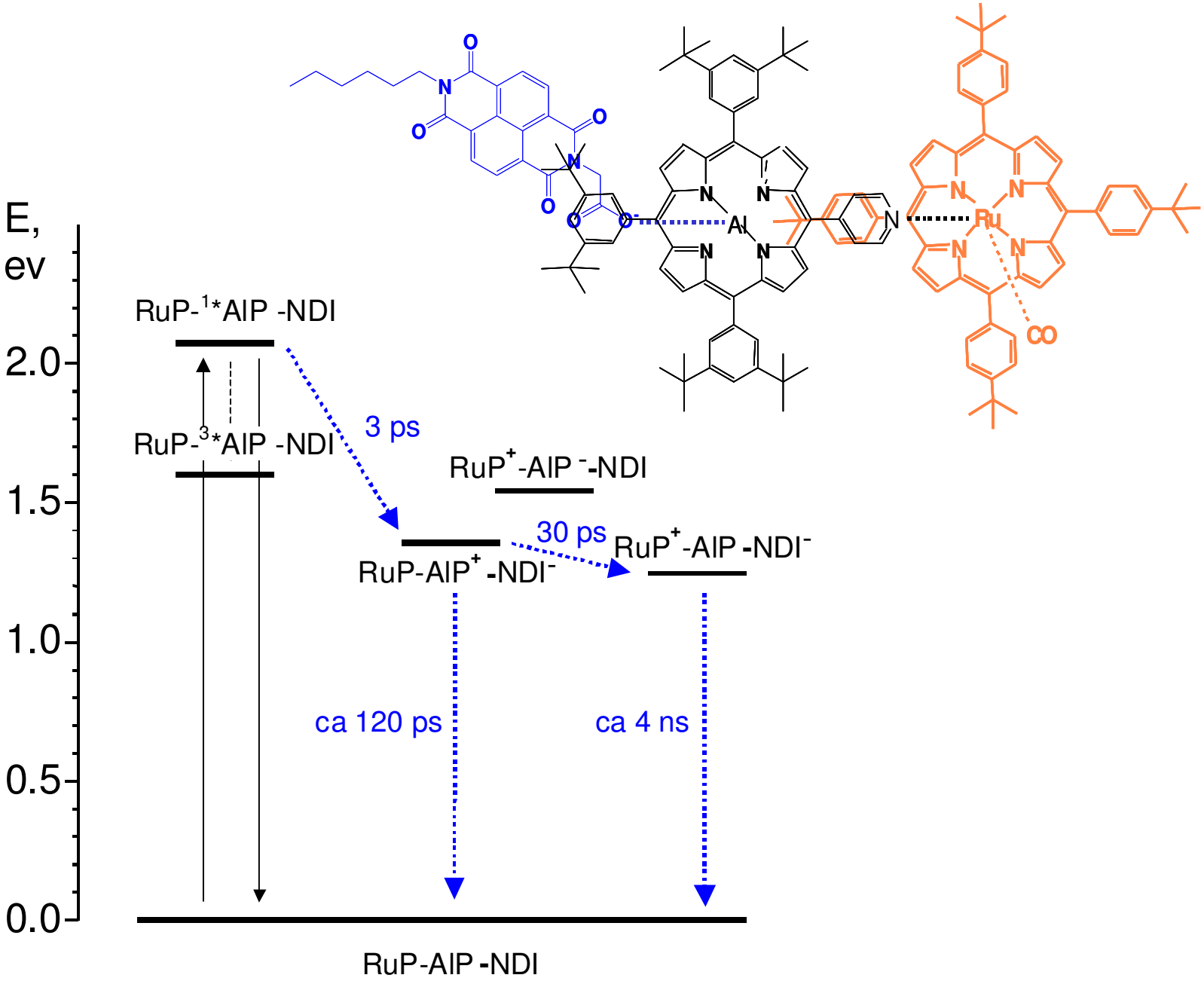
py ⇨ Ru

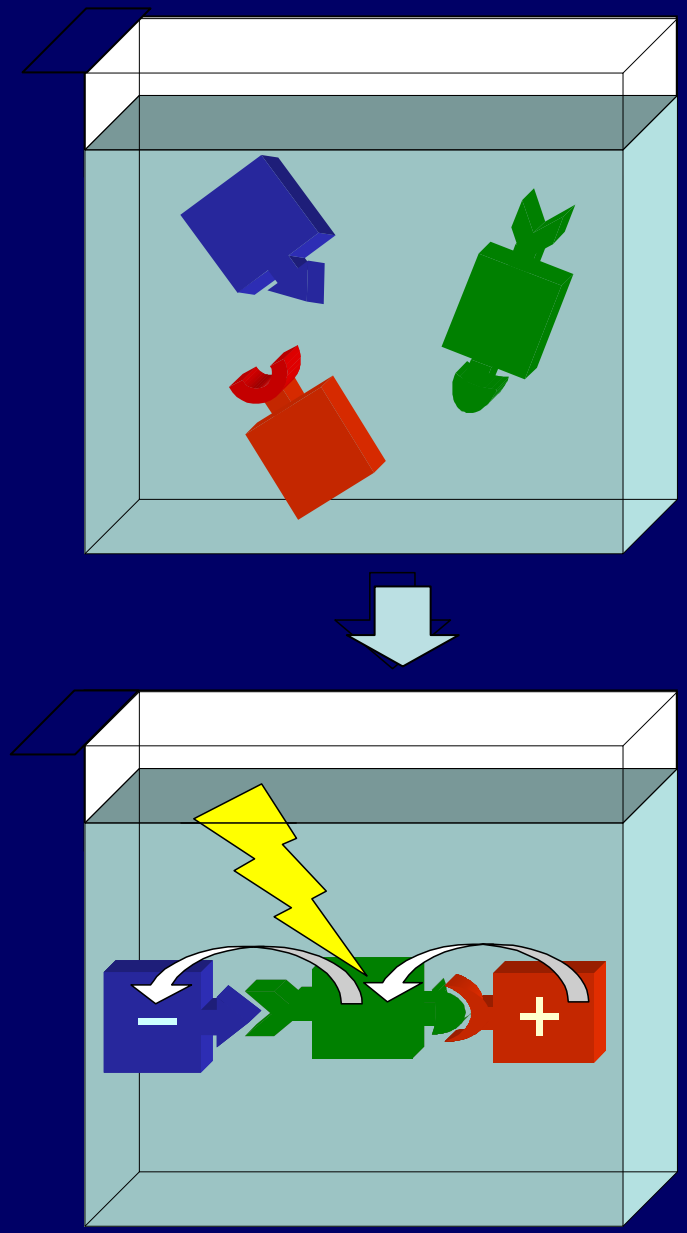


AlP

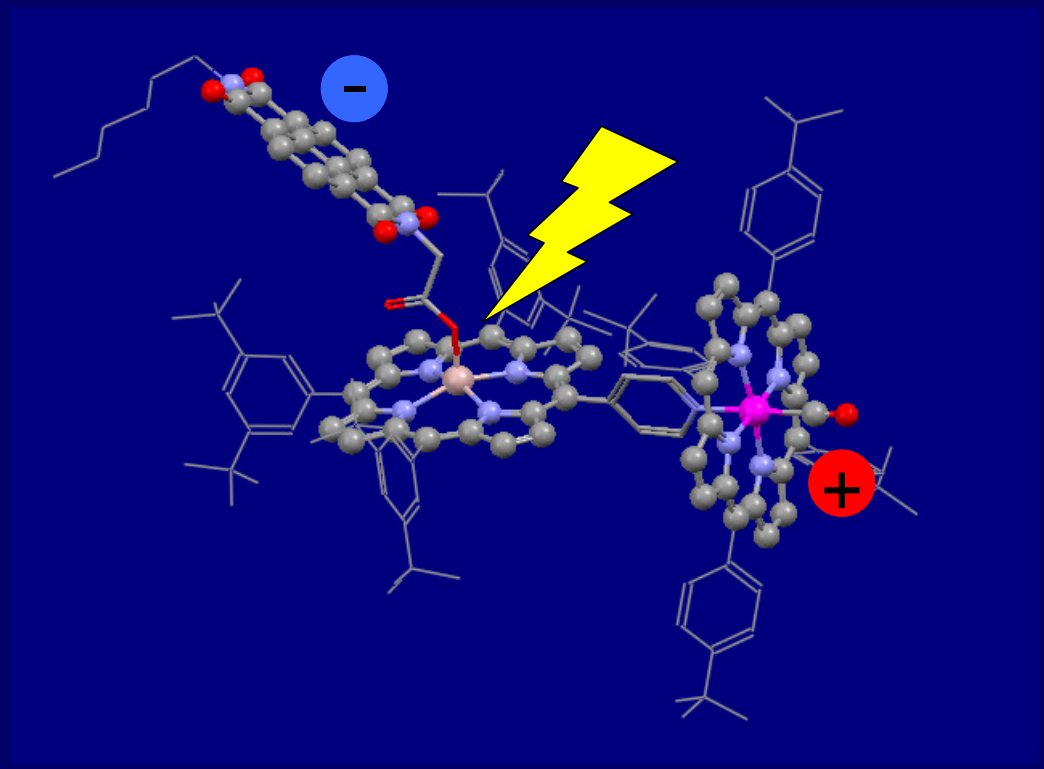


RuP

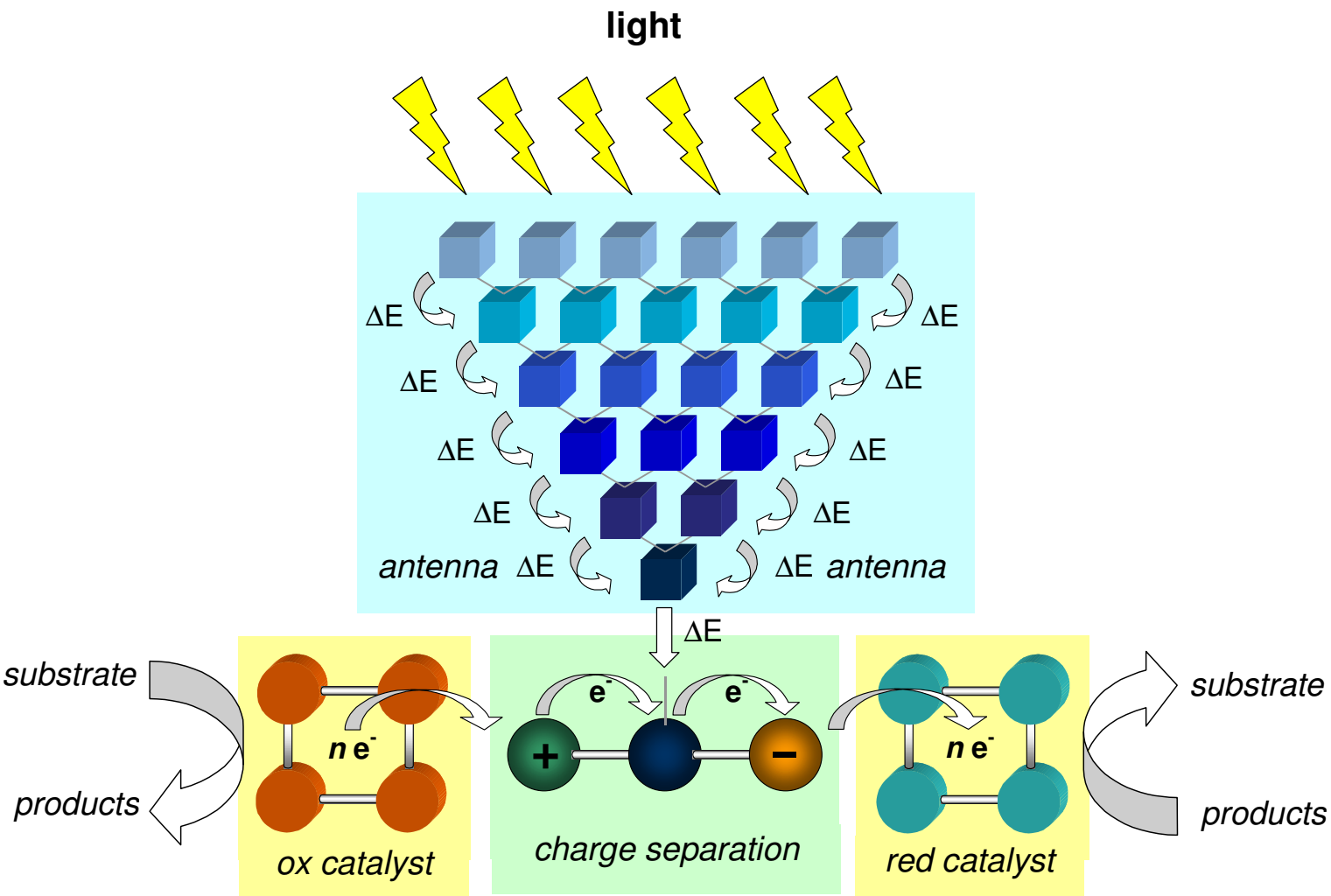

E, ev
2.0
1.5
1.0
0.5
0.0
RuP-1*AIP -NDI
RuP-3*AIP -NDI
3 ps
RuP+-AIP -NDI
30 ps
RuP-AIP+ -NDI-
RuP+-AIP -NDI-
ca 120 ps
ca 4 ns
RuP-AIP -NDI
O
N
O
O
N
O
O
O-
Al
N
N
N
N
N
Ru
N
N
N
CO

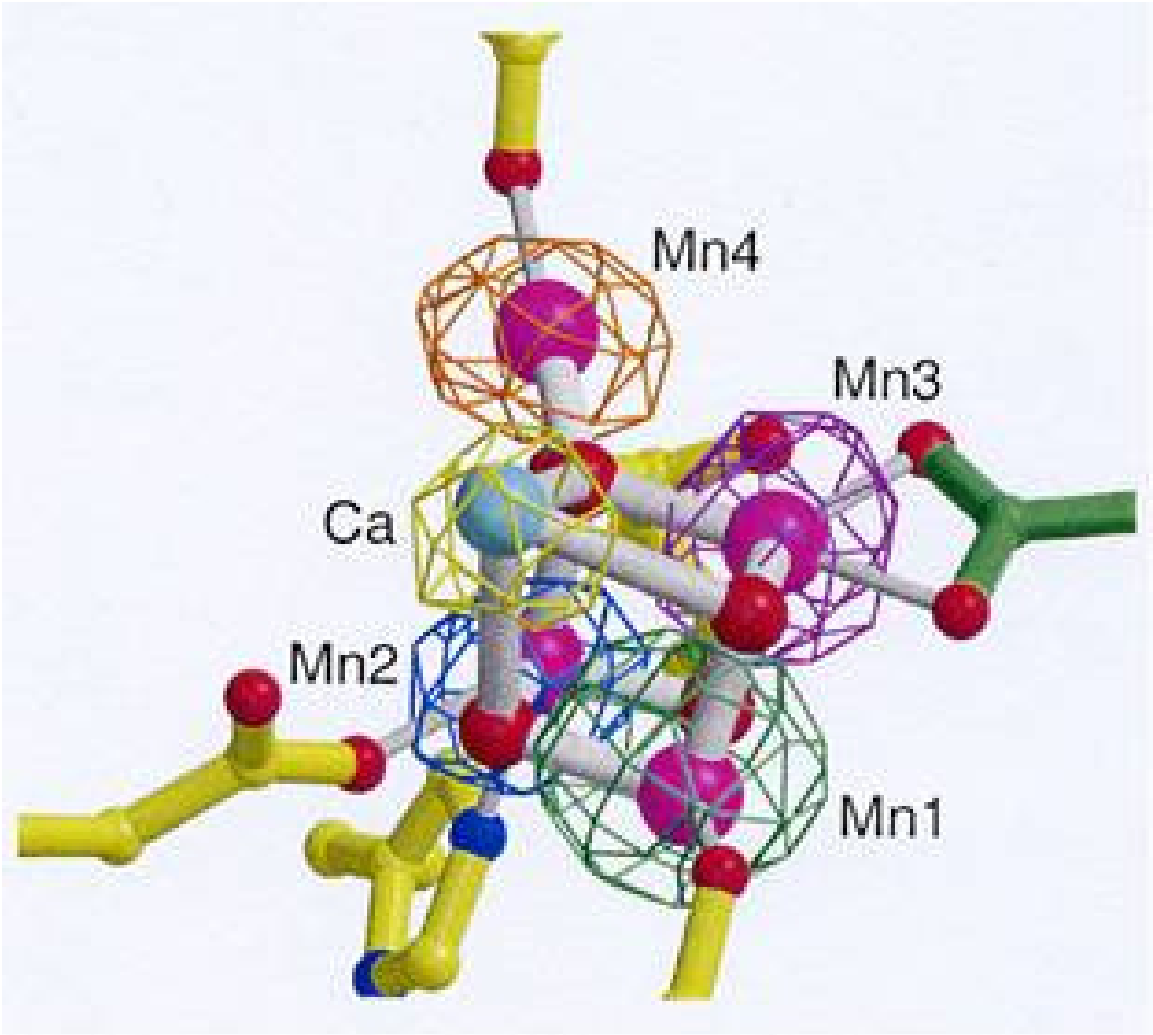


proof-of-principle self-assembling triad for photoinduced charge separation

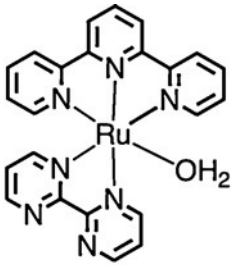


must be improved (energetics, geometry)

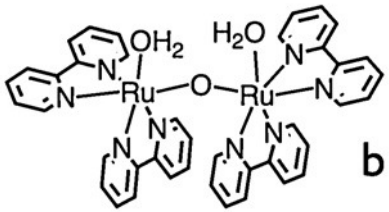

light
ΔE
ΔE
ΔE
ΔE
ΔE
ΔE
ΔE
ΔE
ΔE
ΔE
antenna
antenna
ΔE
substrate
products
n e-
ox catalyst
e-
e-
+
−
charge separation
n e-
red catalyst
substrate
products


Mn4
Mn3
Ca
Mn2
Mn1

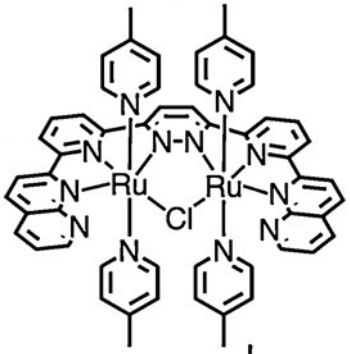
a



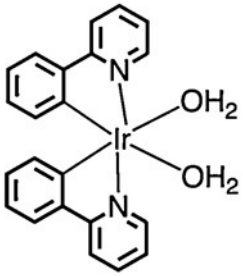
b

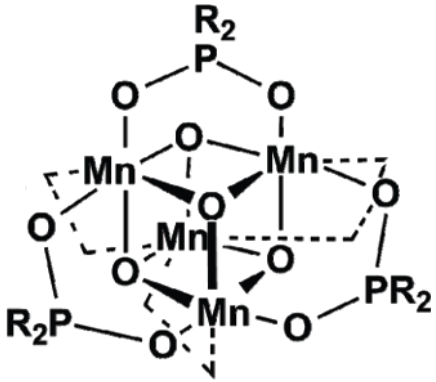


c



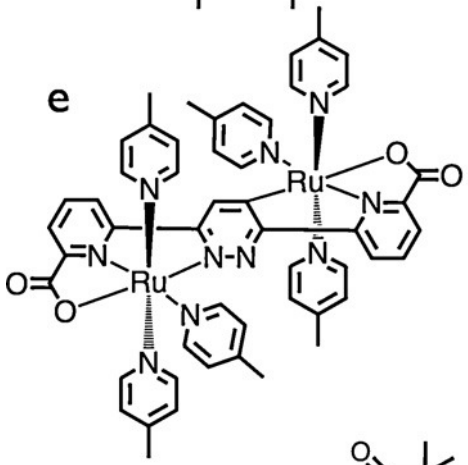
d

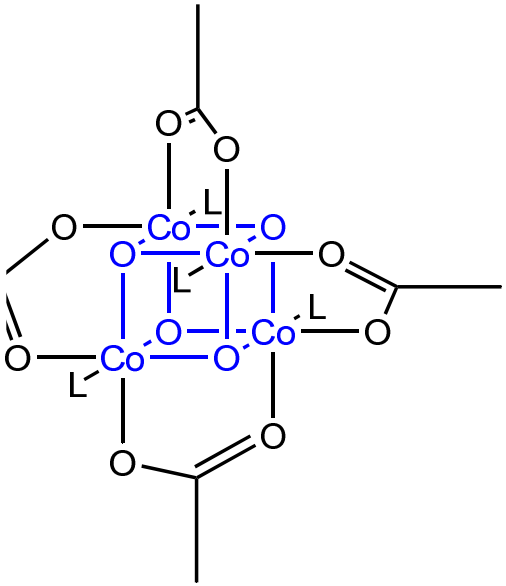




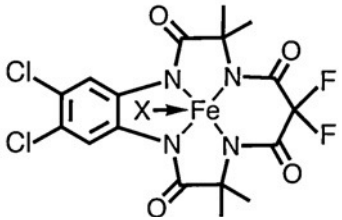
1a: R = Ph
1b: R = (*p*-MeO-Ph)
1c: R = (*p*-Me-Ph)
1d: R = (*p*-I-Ph)

e



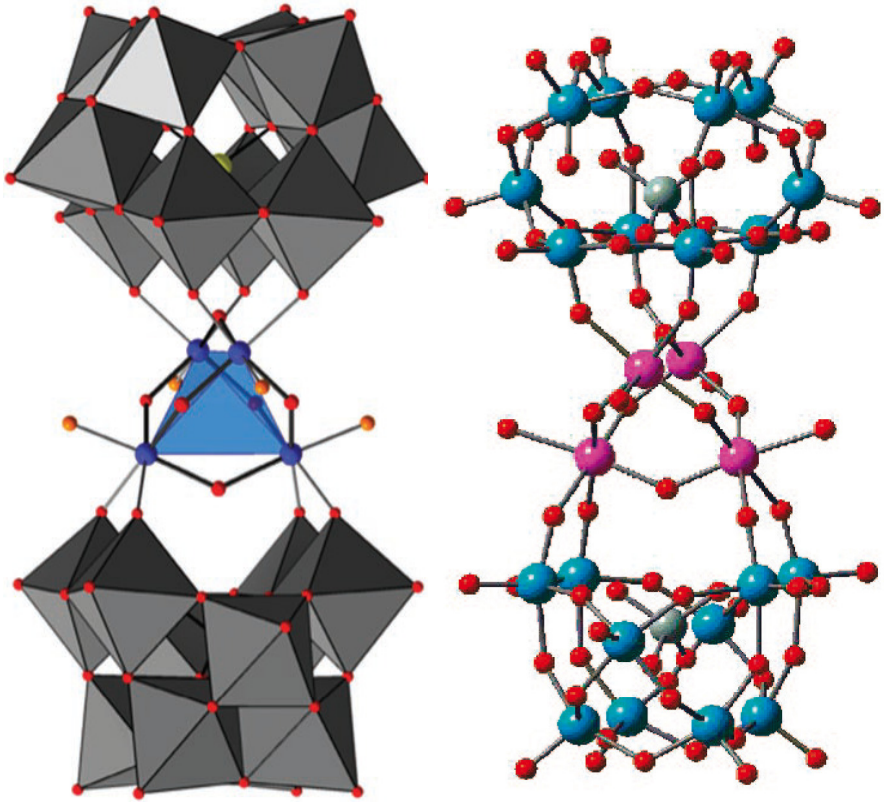


g



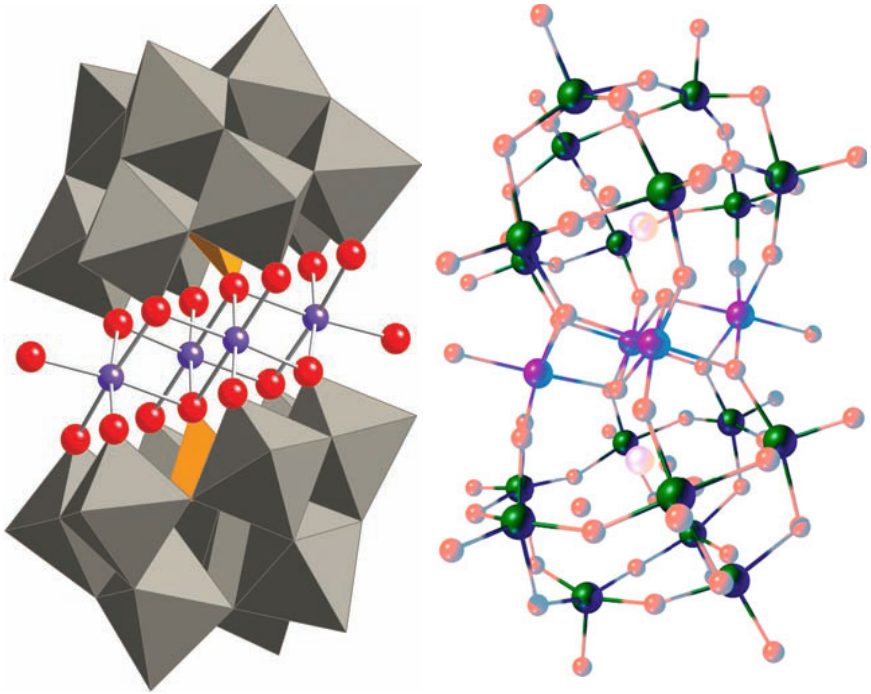
X = H_2O

All-Inorganic Molecular Catalysts: Tetrametallic Polyoxometalates



$[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$

(a) Sartorel, A.; Carraro, M.; Scorrano, G.; De Zorzi, R.; Geremia, S.; McDaniel, N. D.; Bernhard, S.; Bonchio, M. *J. Am. Chem. Soc.,* **2008**, *130*, 5006. (b) Geletii, Y. V.; Botar, B.; Köegerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. *Angew. Chem. Int. Ed.*, **2008**, *47*, 3896.



$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$

(a) Weakley, T. J. R.; Evans, H. T.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.*, **1973**, 139-140. (b) Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. *Science*, **2010**, *328*, 342.

Ruthenium Polyoxometalates as oxidation catalysts

Redox properties

CV at pH = 0.6
vs. SSCE (+ 0.24 vs. NHE)

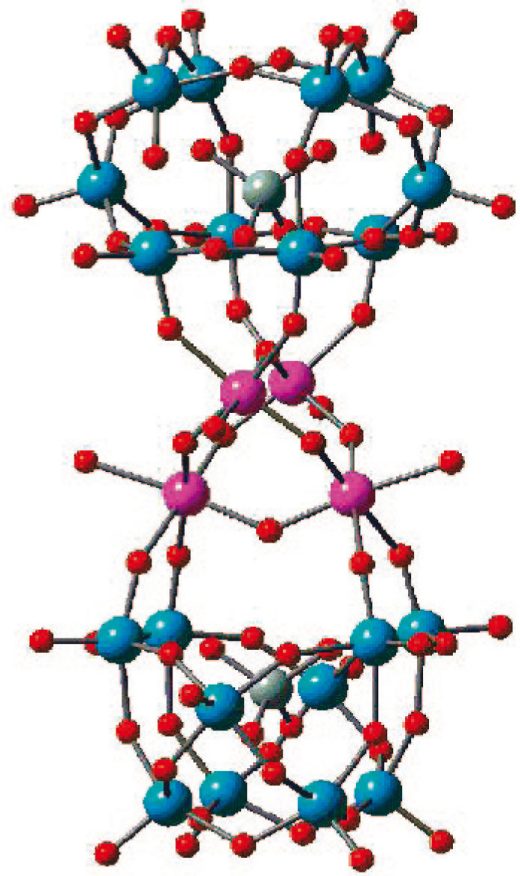
$E_{1/2}$ = + 0.48 V

$E_{1/2}$ = + 0.61 V

$E_{1/2}$ = + 0.86 V

E_{pA} = + 1.06 V

	$S_{0\text{-}4}$	Ru_4POM
$SnCl_2$ ↑ native state in air	S_0	Ru_4 {4, 4, 4, 4}
	S_1	Ru_4 {4, 4, 4, 5}
	S_2	Ru_4 {4, 4, 5, 5}
Ce(IV) ↓	S_3	Ru_4 {4, 5, 5, 5}
	S_4	Ru_4 {5, 5, 5, 5}

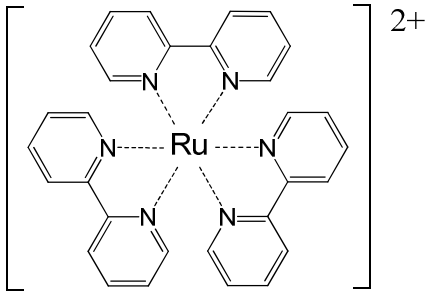


$[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{–}SiW_{10}O_{36})_2]^{10-}$

A. Sartorel, P. Miro´ , E. Salvadori, S. Romain, M. Carraro, G. Scorrano, M. Di Valentin, A. Llobet, C. Bo, M. Bonchio
J. Am. Chem. Soc., 2009, *131*, 16051–16053.

Oxygen evolution from a light-driven catalytic cycle in solution

Photosensitizer = **RuB^{2+}**

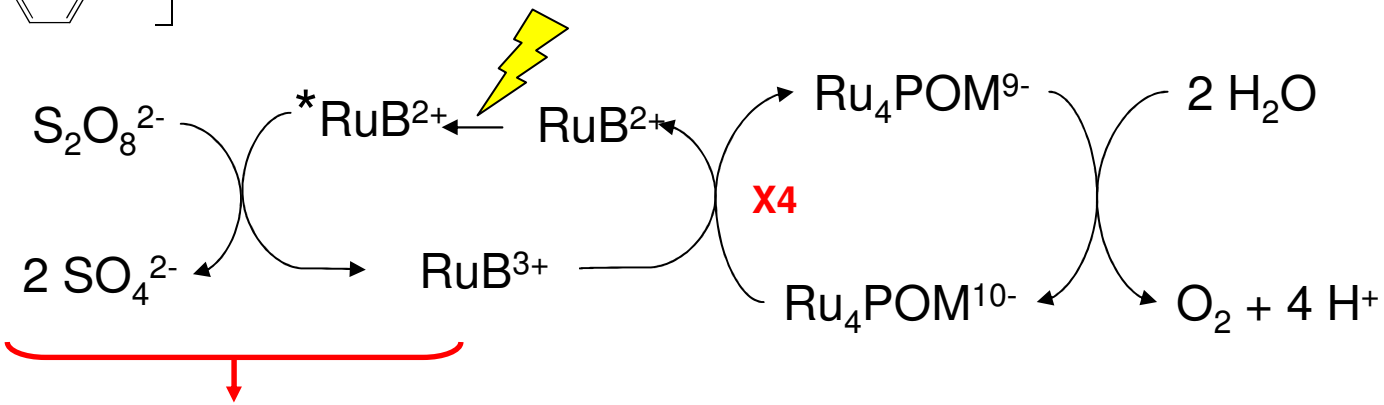


Catalyst = **Ru_4POM**

$Li_{10}[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]$

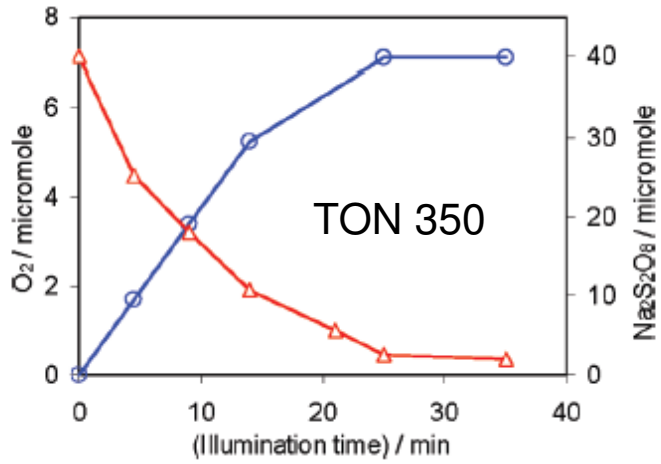
Sacrificial donor

$Na_2S_2O_8$



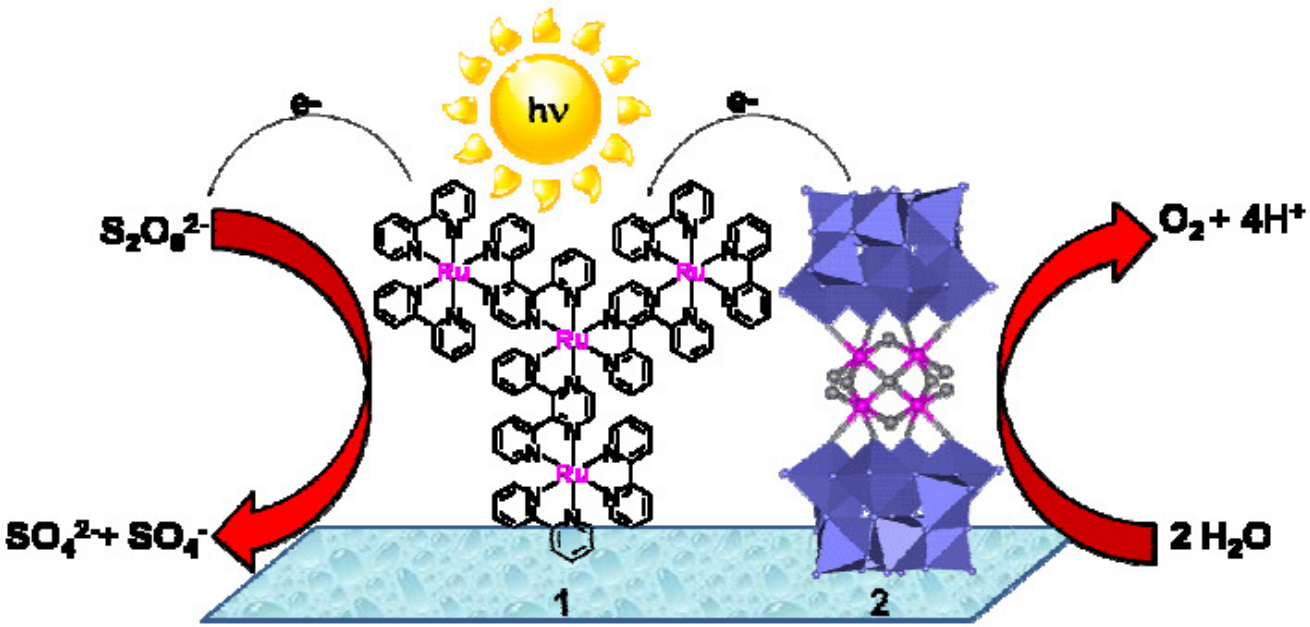
$$^*Ru(bpy)_3^{2+} + S_2O_8^{2-} \longrightarrow Ru(bpy)_3^{3+} + SO_4^{2-} + SO_4^{\cdot-}$$

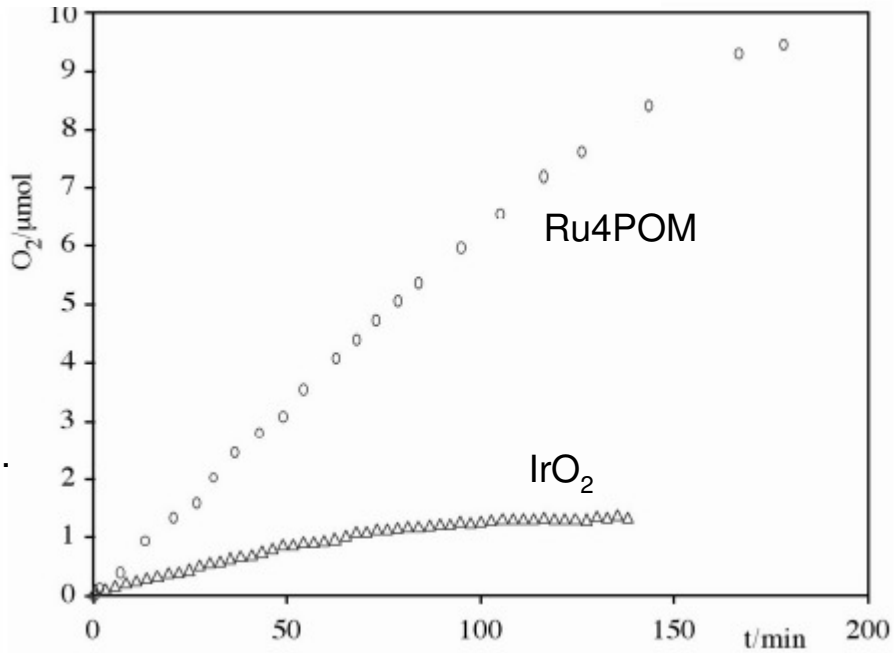
$$Ru(bpy)_3^{2+} + SO_4^{\cdot-} \longrightarrow Ru(bpy)_3^{3+} + SO_4^{2-}$$



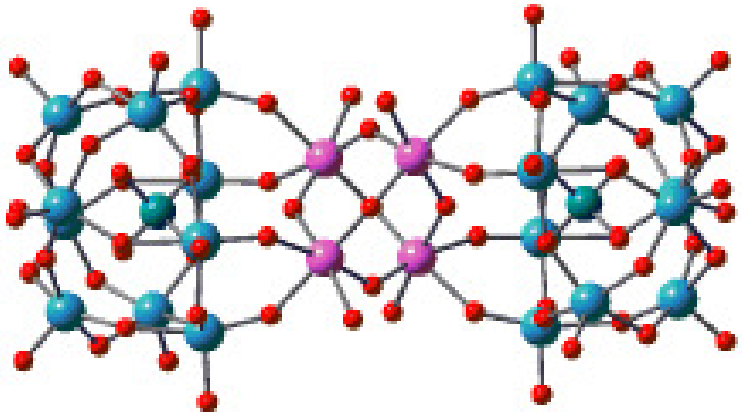
C. L. Hill, JACS 2009

M. Bonchio, Chem Comm 2010





F. Puntoriero, G. La Ganga, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio, S. Campagna, *Chem. Commun.* **2010,** *46*, 4725.

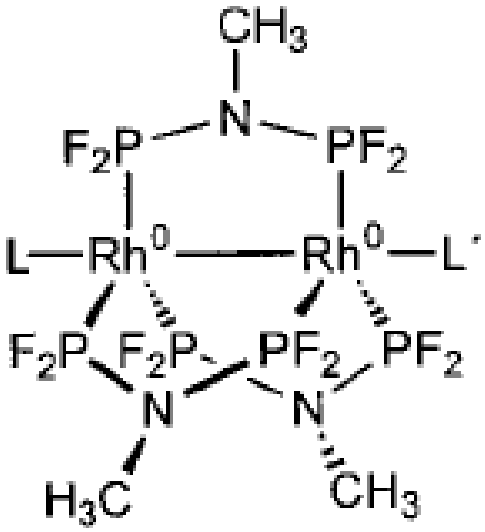


The Ru_4POM catalyst is able to give very fast hole scavenging from photogenerated Ru(III) species, both in 140 homogeneous solution and at a sensitized semiconductor surface.

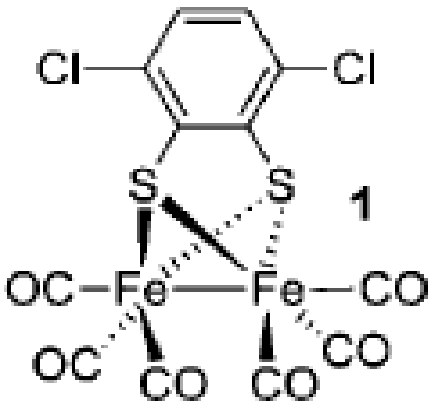
This fast behavior is likely related to a combination of favorable features of Ru_4POM : the high negative charge, that facilitates intimate contact with positively charged oxidants; the low reorganizational energy brought about by the POM ligands that firmly hold and effectively shield from solvent the redox active Ru_4 core.

The fast rates of hole scavengling are an excellent premise for the use of the new catalyst in practical water splitting photochemical devices.

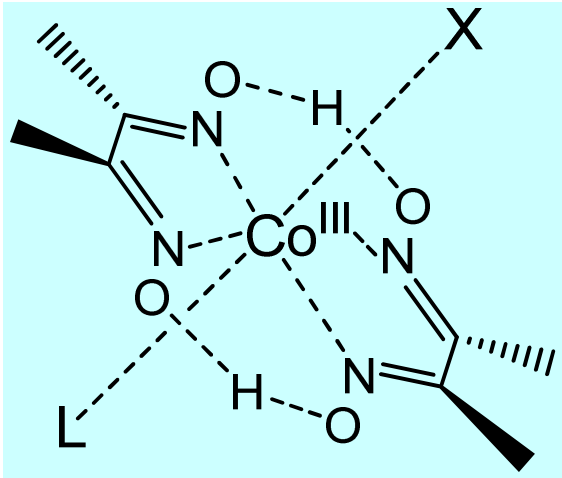
homogeneous catalysts for Hydrogen production

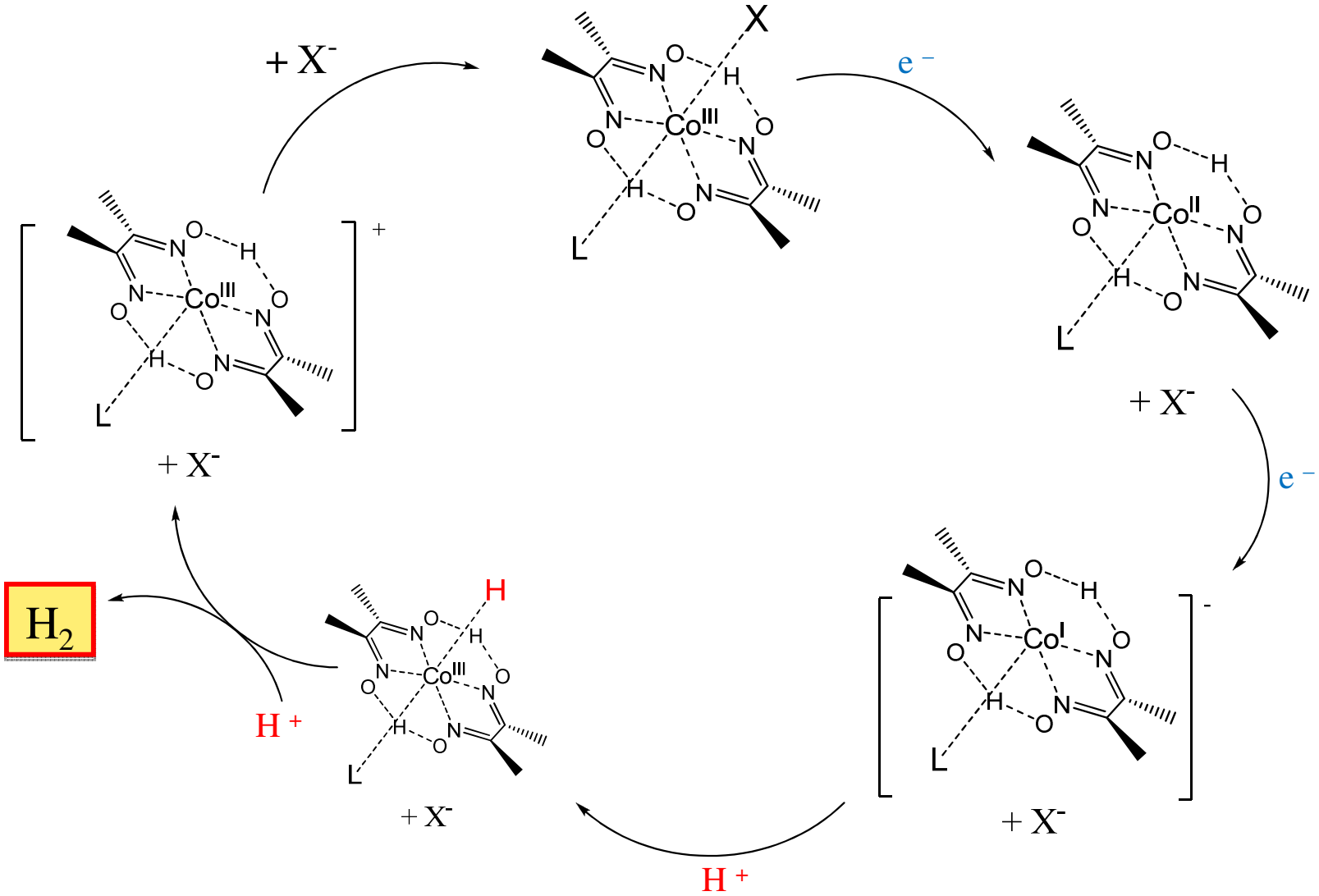


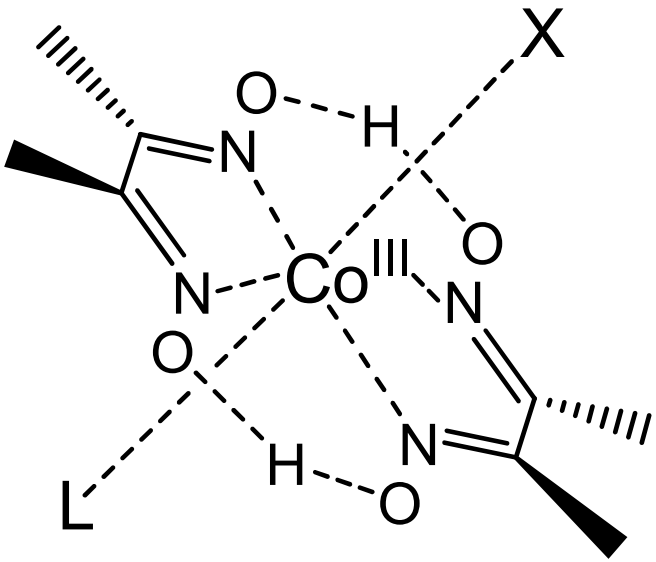
2



1




+ X-
X
e −
+ X-
e −
+ X-
+ X-
H
H +
H2
+ X-
H +



➢ Active in electrocatalysis (DMF, ACN, acetone, H_2O mixed solvents;

P. Connolly, J. Espenson, *Inorg. Chem.* **1986**, *25*, 2684–2688;

- M. Razavet, V. Artero, M. Fontecave, *Inorg. Chem.*, **2005**, 44 (13), 4786-4795;

- X. Hu, B.S. Brunschwig, J.C. Peters, *J.Am.Chem.Soc.*, **2007**, *129*, 8988-8998.

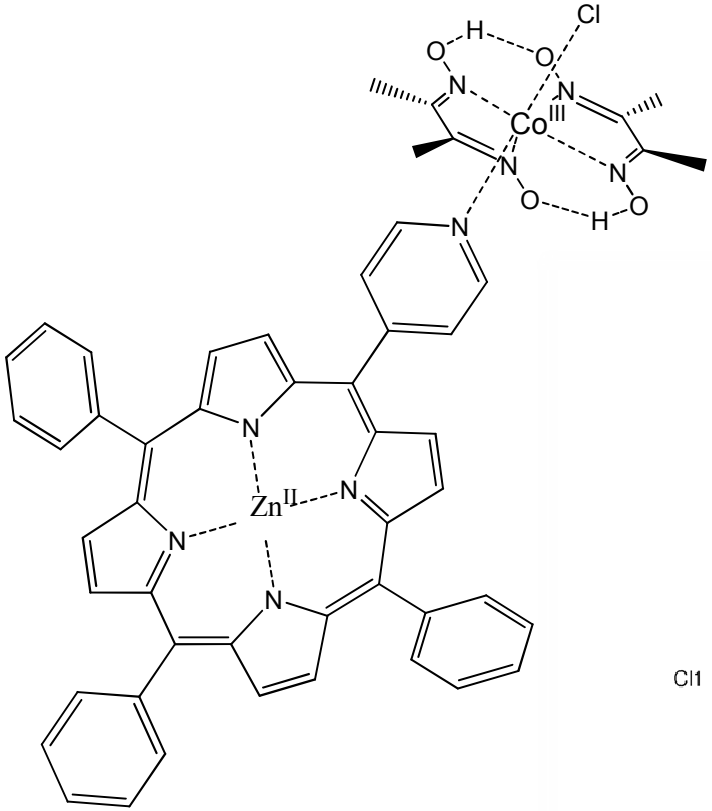
➢ Active in photocatalysis with chromphores such as $Ru(bpy)_3^{2+}$, $Ir(ppy)_2(phen)^+$ e Pt (II) complexes.

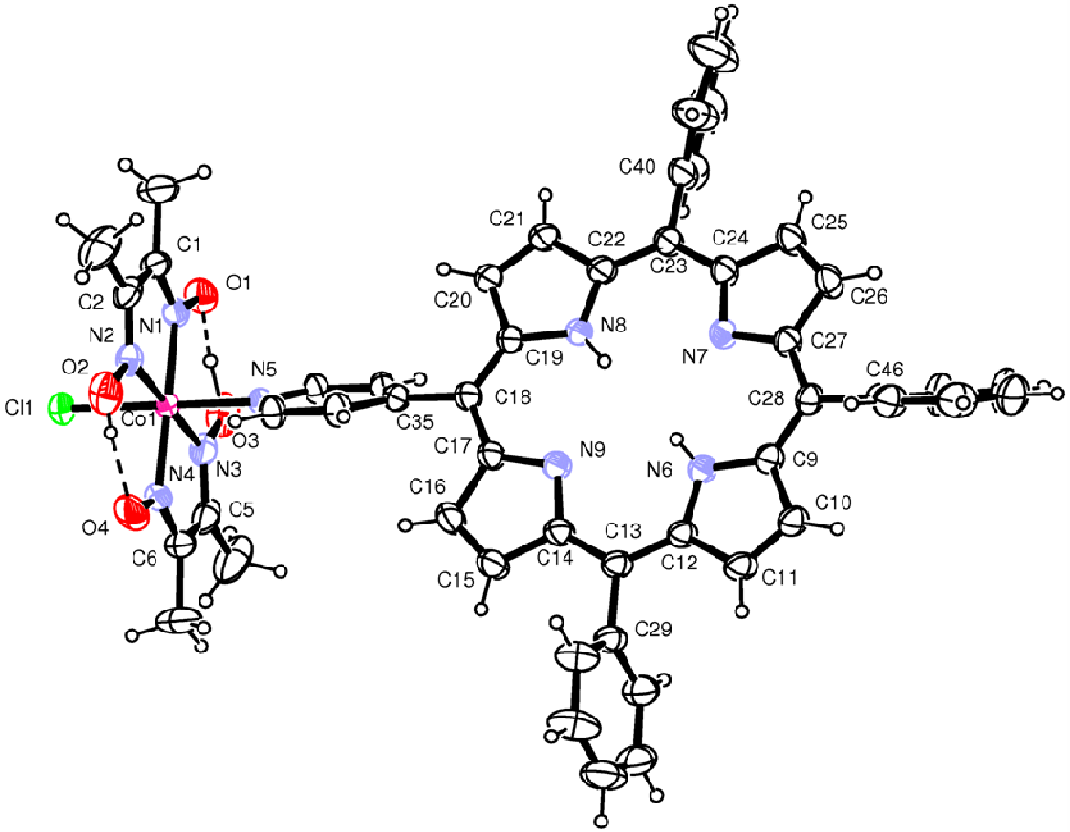
- J. Hawecker, J. Lehn, R. Ziessel, *New J. Chem.* **1983**, *7*, 271–277;

- A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem. Int. Ed.*, **2008**, *47*, 564-567;

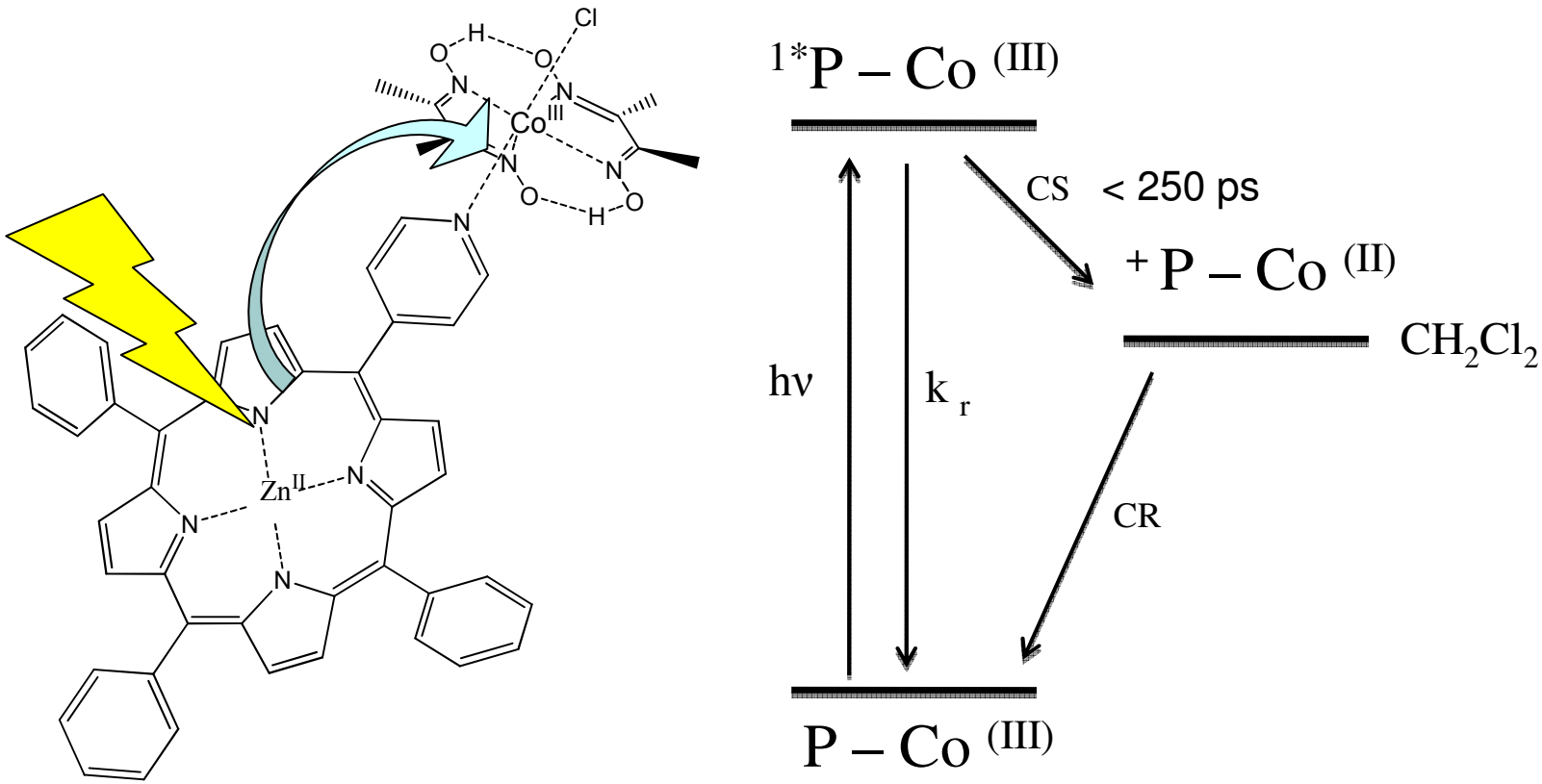
- A. Fihri, V. Artero, A. Pereira, M. Fontecave, *Dalton Trans.* **2008**, 5567–5569;

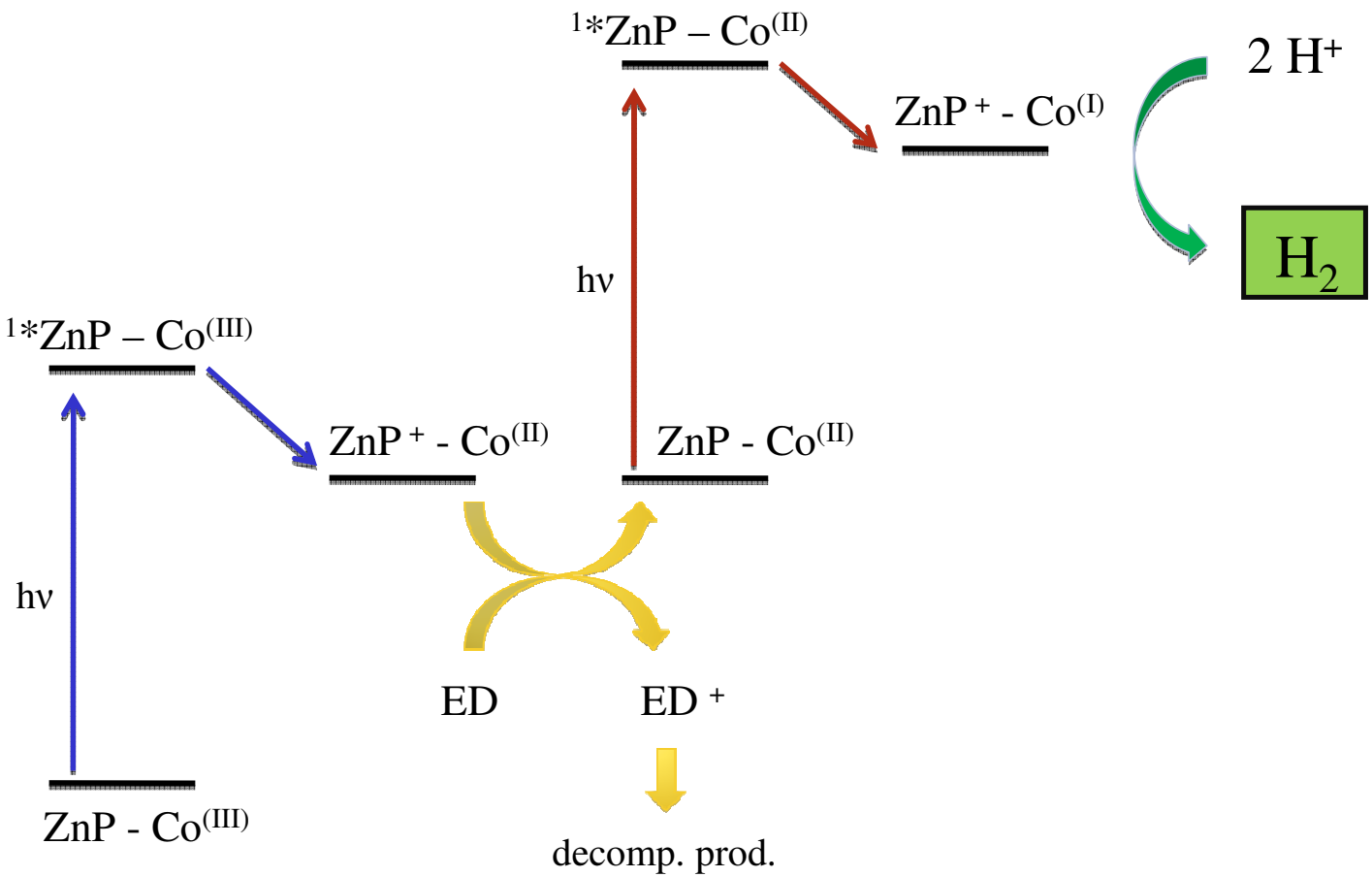
- P. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.*, **2008**, *130* (38), 12576-12577.

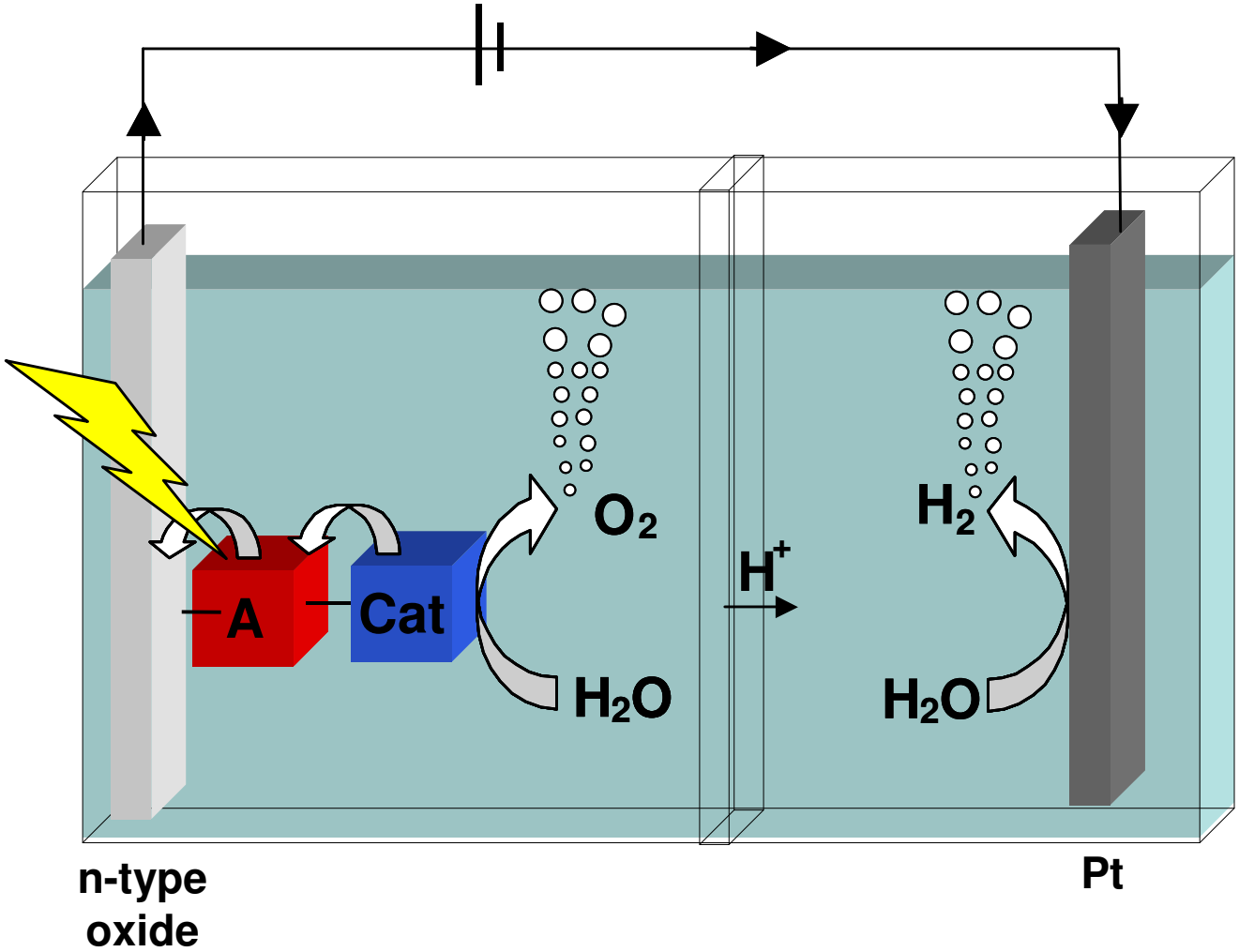


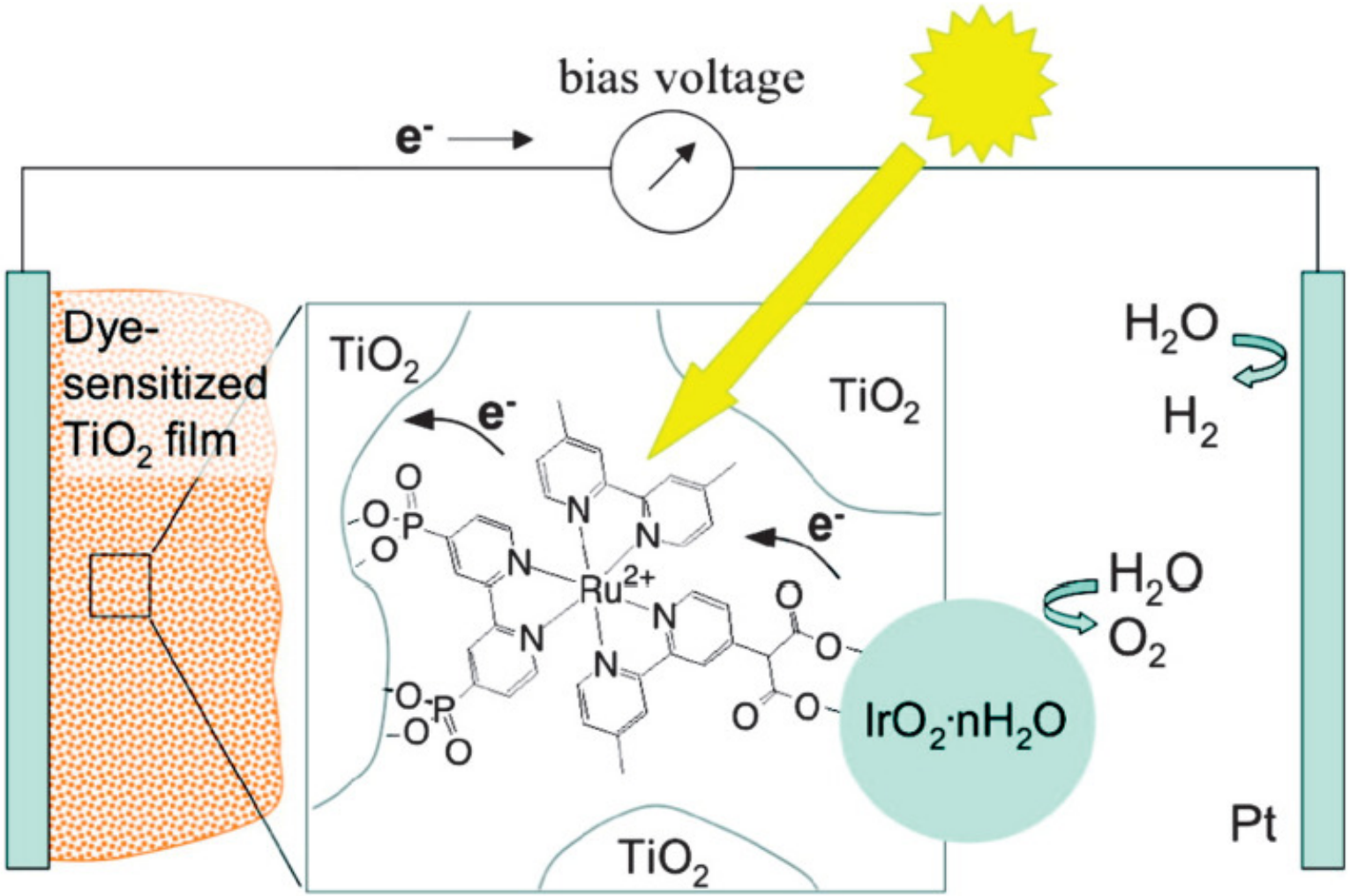


$Co(dmgH)_2Cl$ (4’-MPyZ


Cl
H
O
O
N
N
Co^III
N
N
O
H
O
N
N
N
Zn^II
N
N
1*P – Co (III)
CS < 250 ps
+P – Co (II)
CH2Cl2
hν
k r
CR
P – Co (III)


1*ZnP – Co(II)
2 H+
ZnP + - Co(I)
H2
hν
1*ZnP – Co(III)
ZnP + - Co(II)
ZnP - Co(II)
hν
ED
ED +
ZnP - Co(III)
decomp. prod.

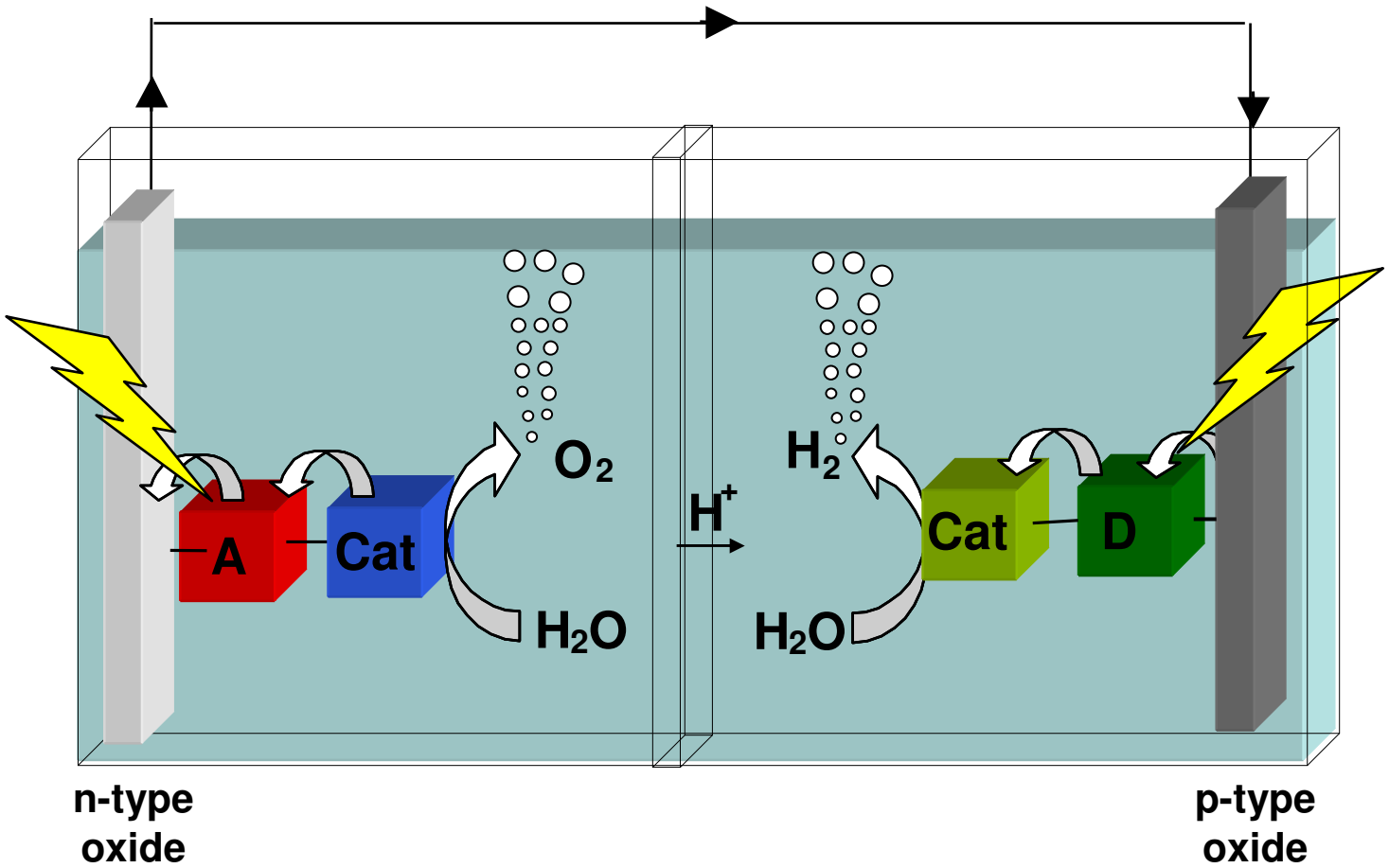

A
Cat
O_2
H_2O
H^+
H_2
H_2O
n-type
oxide
Pt


bias voltage
e-
Dye-
sensitized
TiO2 film
TiO2
TiO2
TiO2
e-
e-
Ru2+
IrO2·nH2O
H2O
H2
H2O
O2
Pt

Real artificial photosynthetic devices will likely be heterogeneous in nature:

-interfacial charge separation at semiconductor electrodes

-electron transfer + electric connections



“Artificial Leaf”