Laboratorio Sintesi Materiali Organici

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Dr. Mauro Sassi
Dr.ssa Sara Mattiello

2 synthesis labs
1 formulation lab (U28)
1 NMR-GC-MS lab
1 characterization lab

1 Post Doc
9 PhD students
2 Grad Students

PRIN 2017

La^{32}SMO

Materiali organici sostenibili

Materiali

- Molecole e polimeri coniugati
- Coloranti e pigmenti

Metodi

- reazioni in ambienti micro e nanoeterogenei
- reazioni di arilazine diretta

Targets in the 2023-2024 Timeframe

- Heterogenized catalysis in water
- Luminescent radicals
- Materials and inks for edible electronics - IIT
- doping of organic semiconductors
- photon management in organic materials
- photoactive membrane probes - IIT
- hybrid inks for printable solar cells (colloidal quantum dots and wells) - ENI
- Probes for X-ray imaging - Bracco
- Alternative raw materials and formulations for cosmetics - Intercos

Workflow

Describe the problem in chemical and material science terms

Design (based on structure property relationships)

Retrosynthesis (and related operations at the device level)

Synthesis, optimization and scale up

Full characterization(UV-Vis, FTIR, NMR, DSC/TGA, Mass, AE,…)

Field test

Why organics

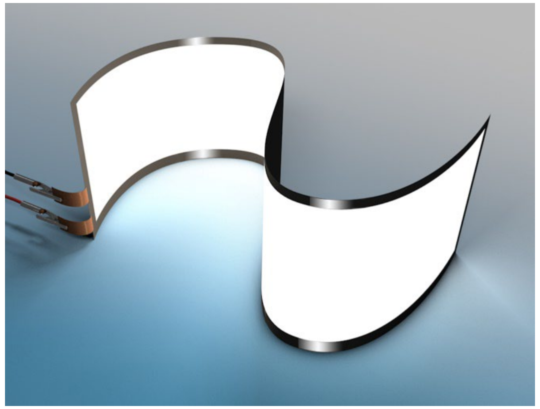
01 Raw Materials

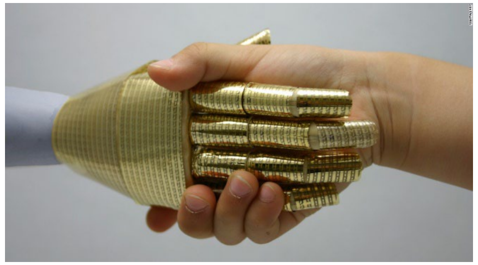
02 Printing technologies

03 Flexleible devices

04 Biodegradable/compatible

05 Low cost/Low energy





Methods

Standard organic chemistry procedures

- Toxic solvents
- Long reaction time
- High temperature
- High palladium loading
- Controlled environment
- Complex purification

Nature's way

- ❑Water
- ❑Fast reactions
- ❑Room temperature
- ❑Traces of metals
- ❑In air
- ❑No purification

The E-factor, processes beyond the yield

$$E - \text{factor} = \frac{\text{Amount } of\ organic\ waste\ (kg)}{Amount\ of\ product\ (kg)}$$

Industry sector	Annual production (t)	E-factor	Waste produced (t)
Oil refining	10^6-10^8	<0.1	10^5 -10^7
Bulk chemicals	10^4-10^6	<1–5	10^4 - 5×10^6
Fine chemicals	10^2–10^4	5–50	5×10^2 – 5×10^5
Pharmaceuticals	10–10^3	25–100	2.5×10^2 –10^5

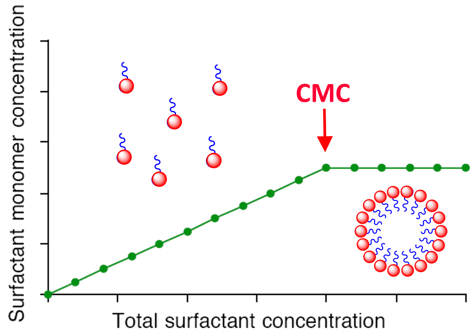
How about organic semiconductors?

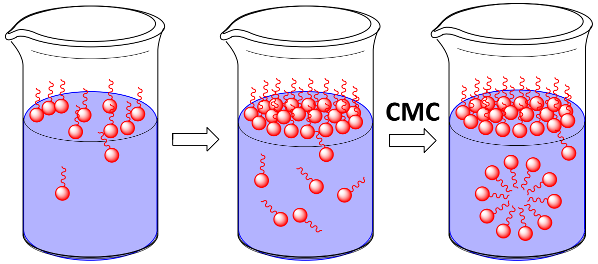
The problem is essentially non debated. Estimates based on experimental procedures hints at numbers in the 10^3-10^4 range!

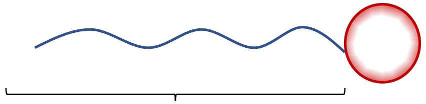
Most of the organic waste is solvents

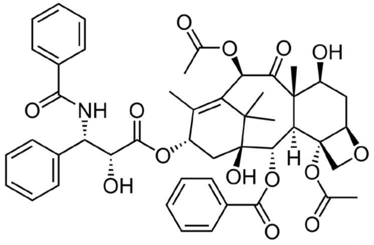
Association colloids, a different way of tackling solubility

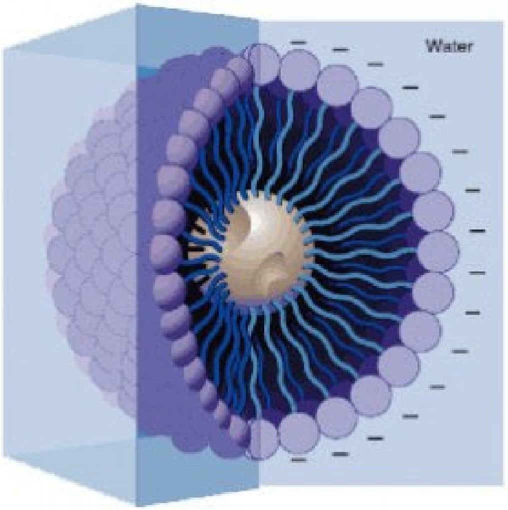
Micellar solutions



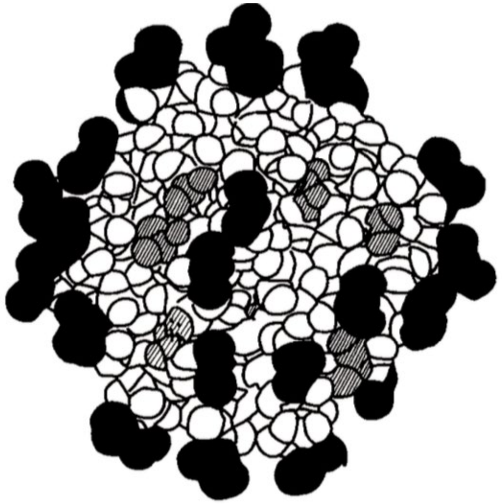








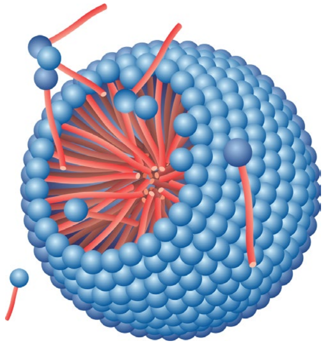
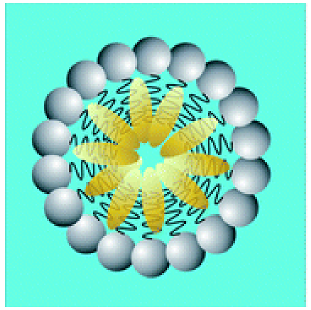
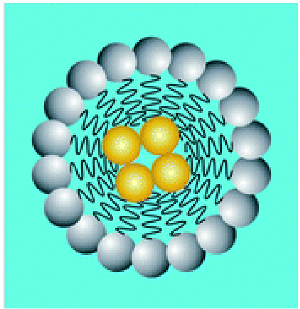
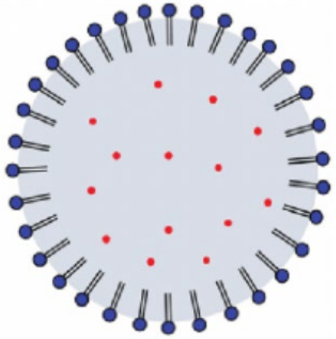
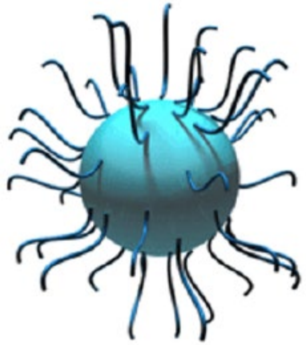
Real structure



Idealized, unrealistic structure

La[32]SM

Interface rich environments

10^{-2}-10^{-3} M — Total organic content — > 0.1 M


Micellar solution

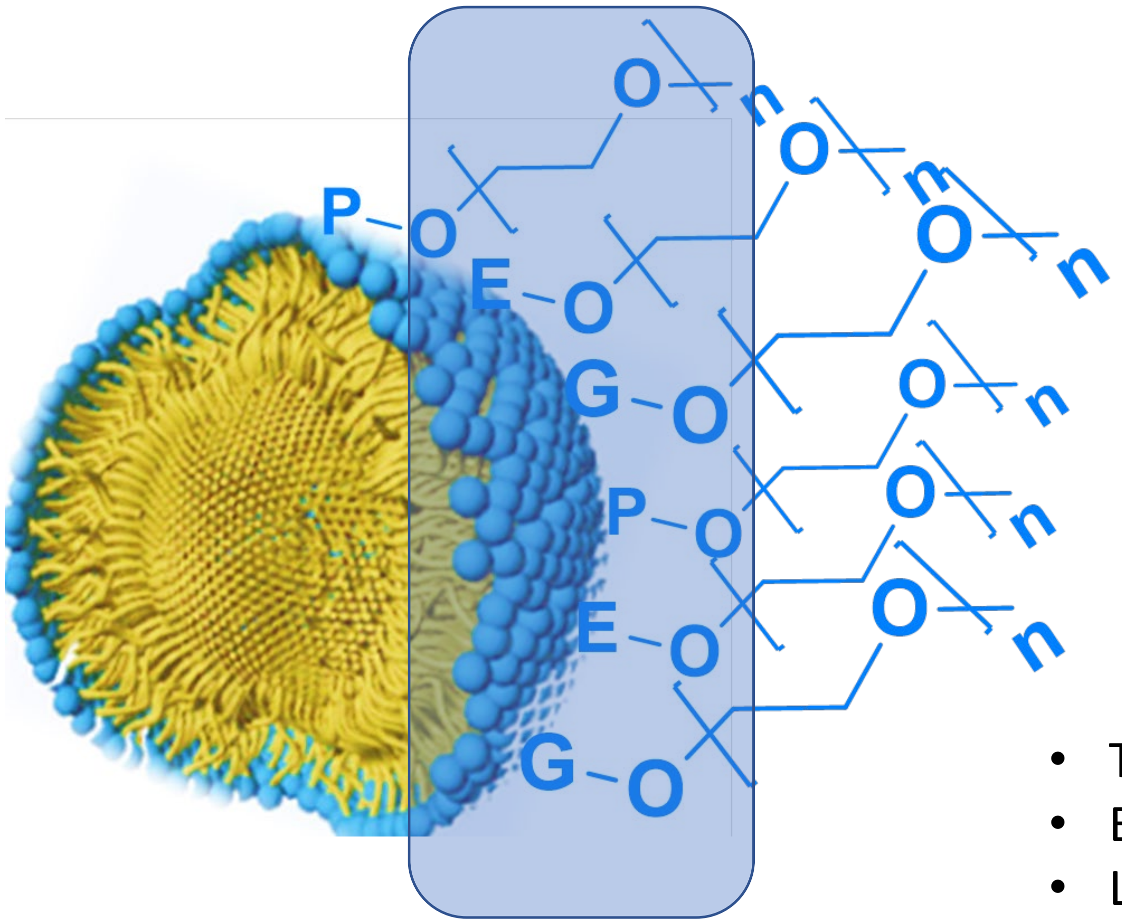

microemulsion

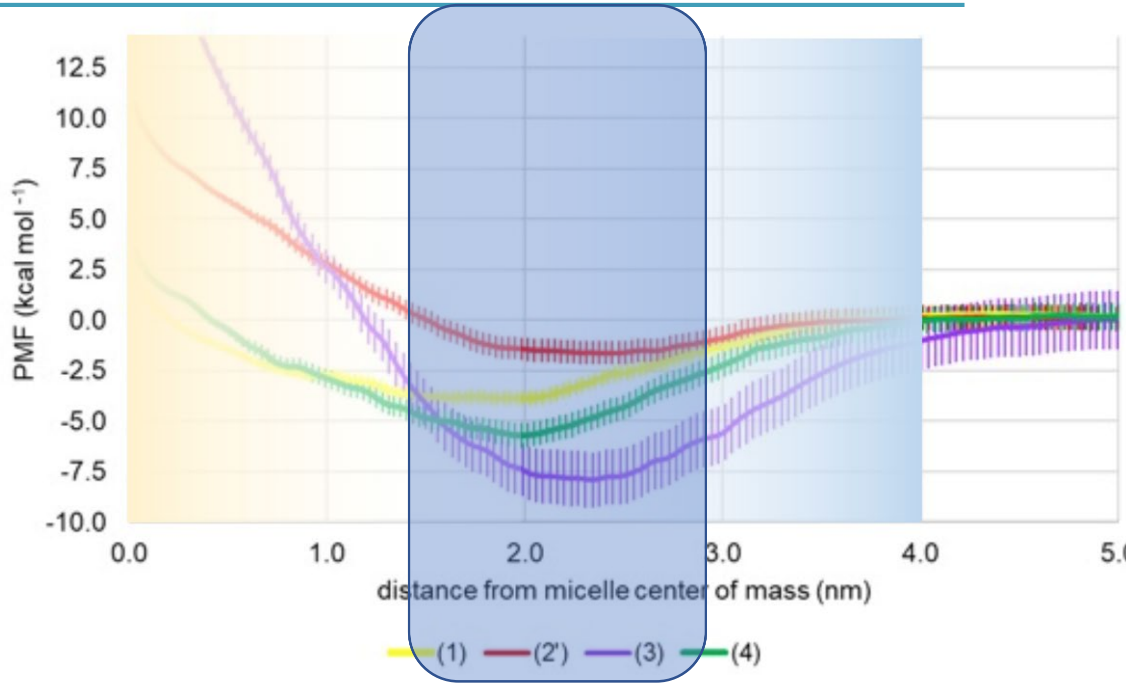

nanoemulsion


emulsion


dispersion

The sweet spot of the association colloid

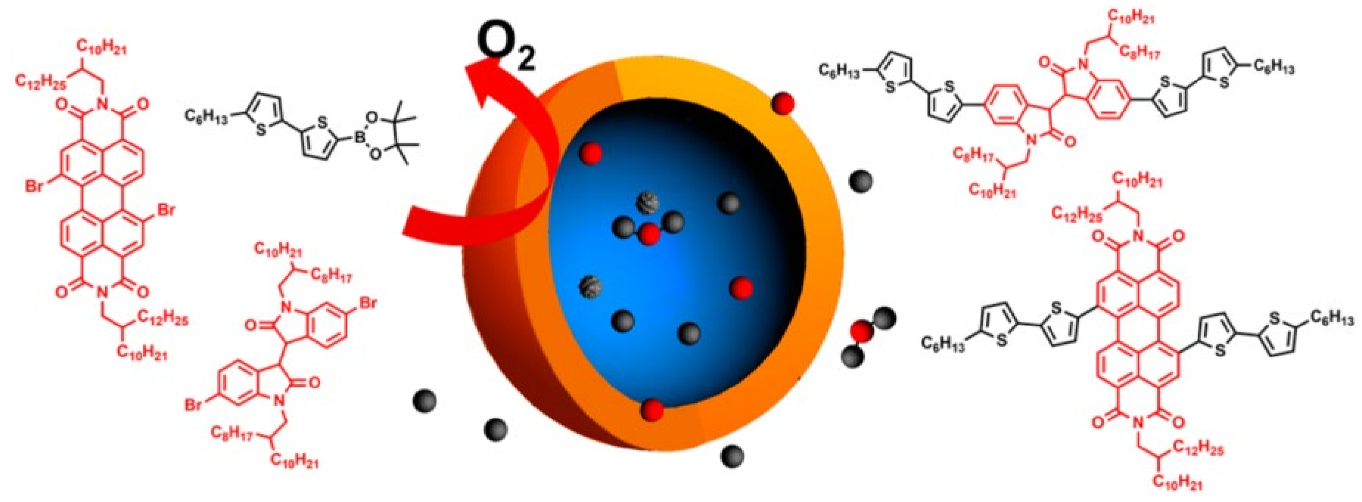


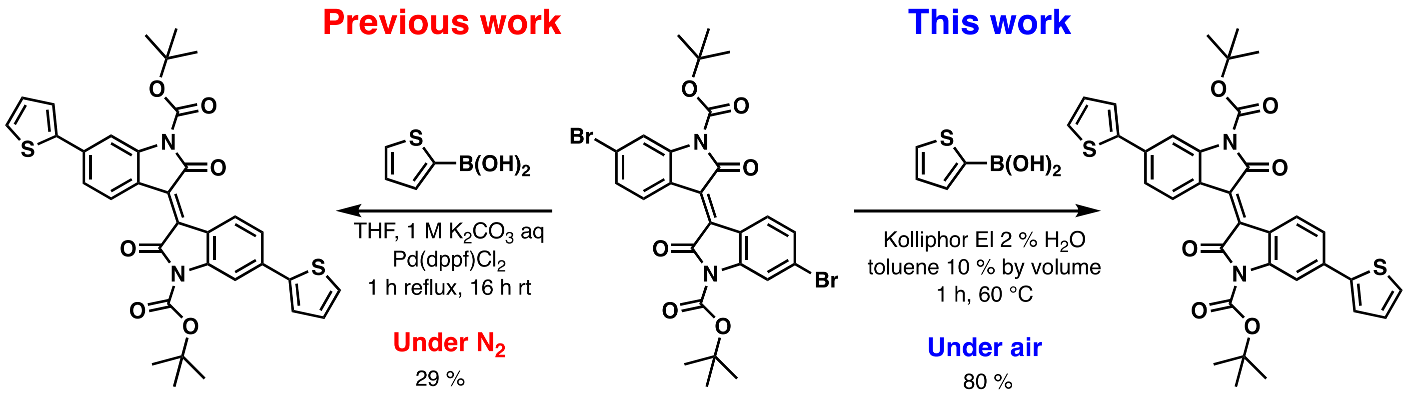


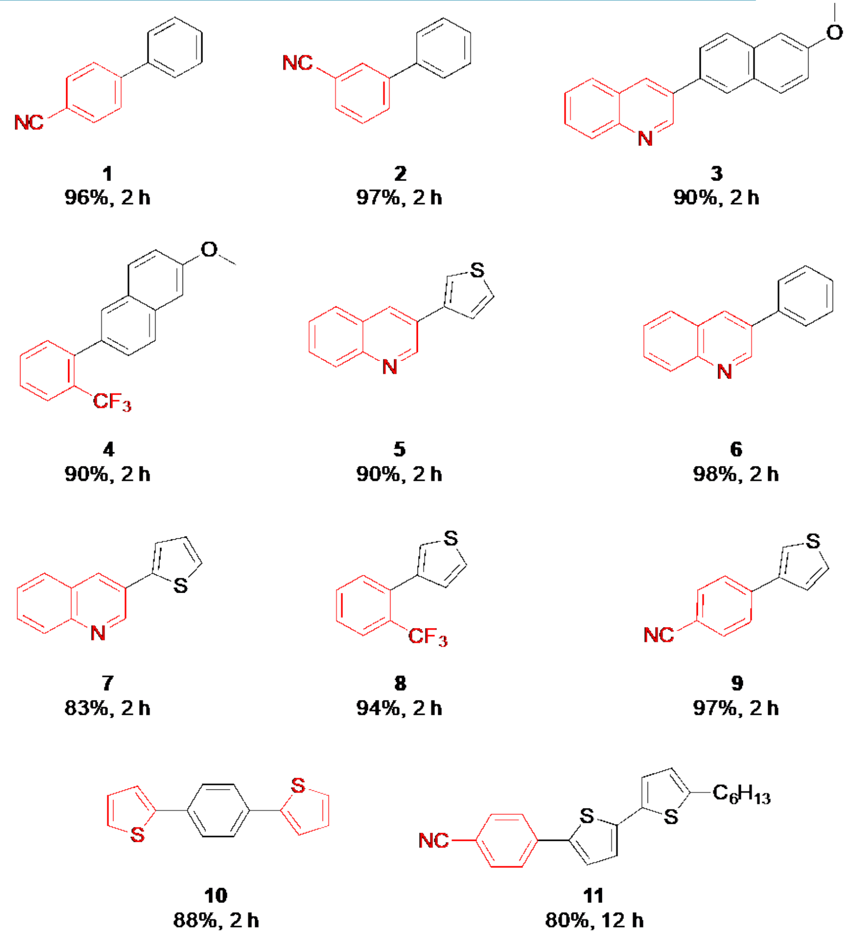
- The organic solvent is not required
- Effective concentration is way higher than nominal one
- Local polarity can reduce the activation energy – Low T reactions
- The external PEG shell prevents oxygen contamination

Reactions can be fast, compatible with aerated environment and efficient at low catalyst loading

Kolliphore EL: one with a secret weapon





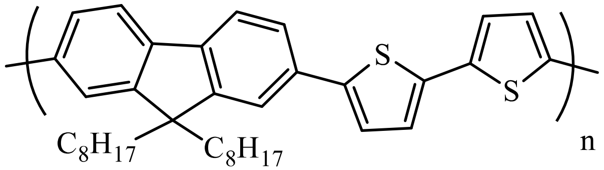
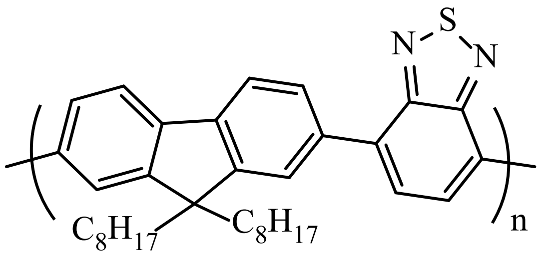


$Ar\text{-}B(OH)_2$ + Ar'-Br

In water, at r.t. and in the air

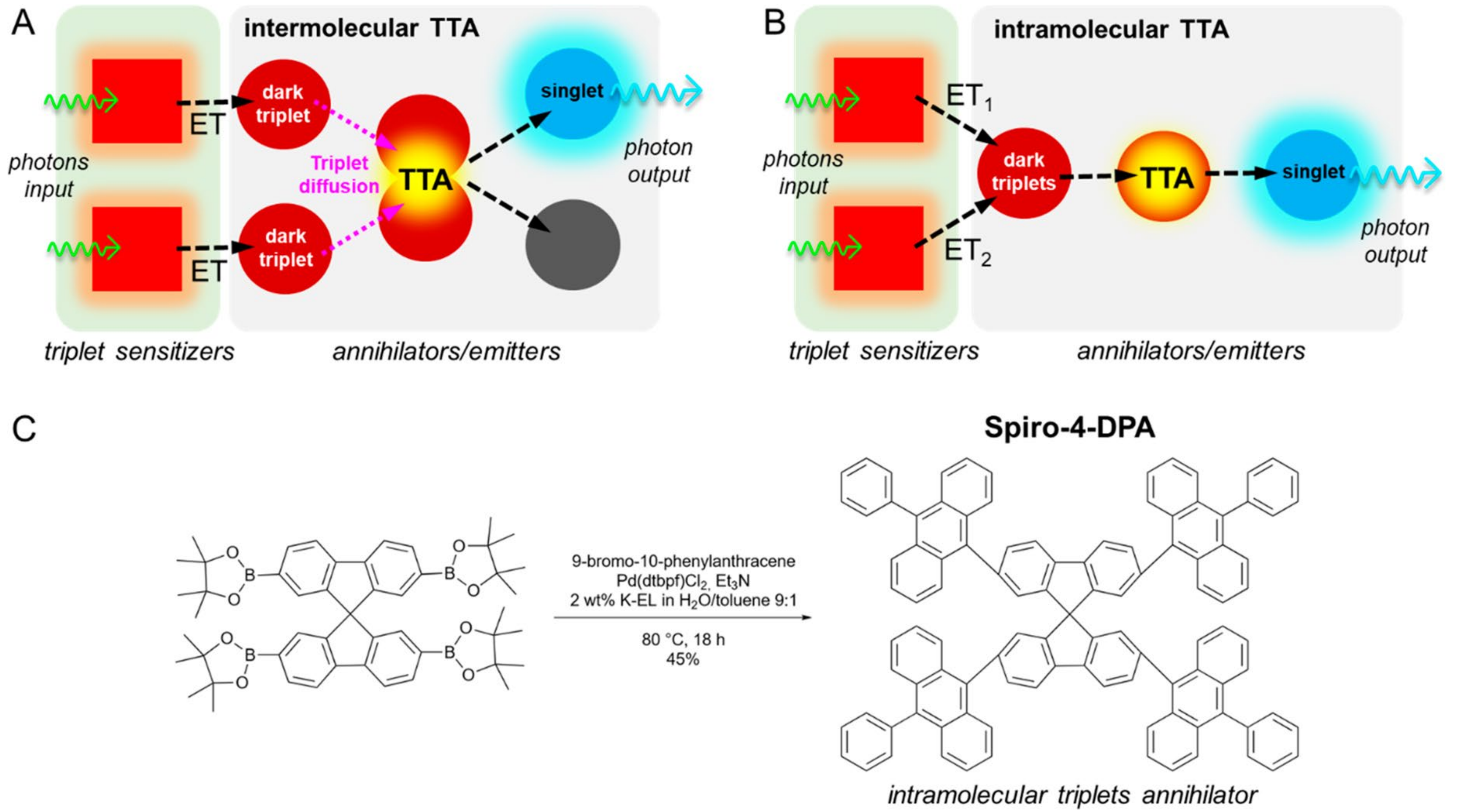
S. Mattiello, M. Rooney, A. Sanzone, P. Brazzo, M. Sassi and L. Beverina, *Org. Lett.*, 2017, **19**, 654–657
Rooney, M.; Mattiello, S.; Stara, R.; Sanzone, A.; Brazzo, P.; Sassi, M.; Beverina, L. Dyes and Pigments 2018, 149, 893–901.

Dispersion polymerizations – Green, efficient and food grade!

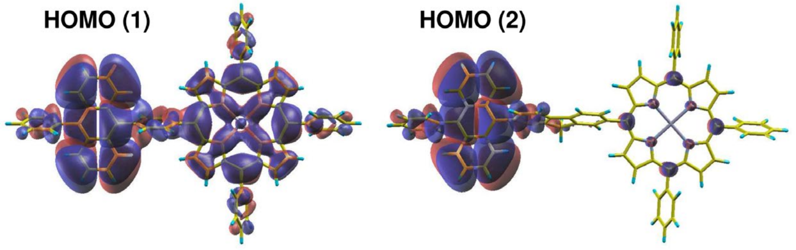
	Literature conditions	Micellar conditions	Dispersion (2 wt% lecithin/Tween80)
 PF8T2	<u>**Mn = 19698 g/mol**</u> **Mw = 38997 g/mol** <u>**PDI = 1.98**</u>	**Mn = 11960 g/mol** **Mw = 25130 g/mol** **PDI = 2.10**	<u>**Mn = 18100 g/mol**</u> **Mw = 33300 g/mol** <u>**PDI = 1.84**</u>
 PF8BT	**Yield: 91%** <u>**Mn = 19891 g/mol**</u> **Mw = 41771 g/mol** <u>**PDI = 2.10**</u>	**Yield: 88%** **Mn = 9923 g/mol** **Mw = 22029 g/mol** **PDI = 2.22**	**Yield: 95%** <u>**Mn = 23500 g/mol**</u> **Mw = 40655 g/mol** <u>**PDI = 1.73**</u>
	<u>***E-factor = 302***</u>	<u>**E-factor = 53**</u>	<u>***E-factor = 41***</u>

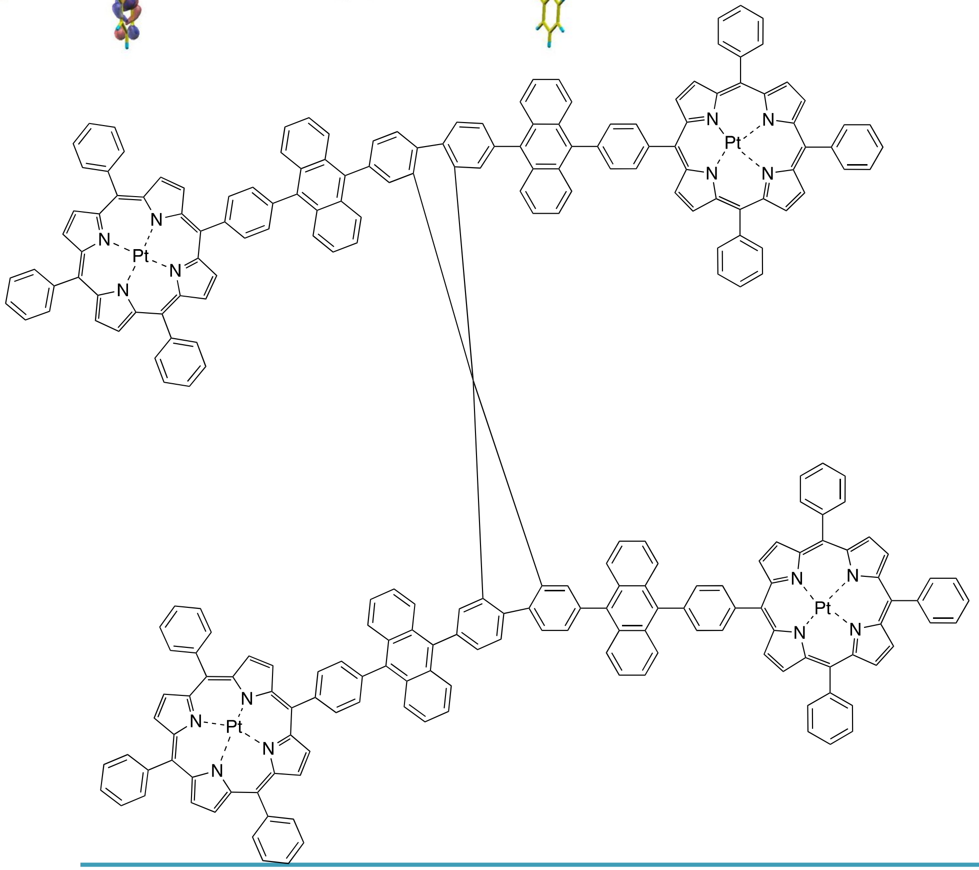
A. Sanzone, A. Calascibetta, M. Monti, S. Mattiello, M. Sassi, F. Corsini, G. Griffini, M. Sommer and L. Beverina, *ACS Macro Lett.*, 2020, **9**, 1167–1171.
Chiara Ceriani, Mattia Scagliotti, Tommaso Losi, Alessandro Luzio, Sara Mattiello, Mauro Sassi, Matteo Rapisarda, Luigi Mariucci, Mario Caironi, and Luca Beverina. Manuscript in preparation

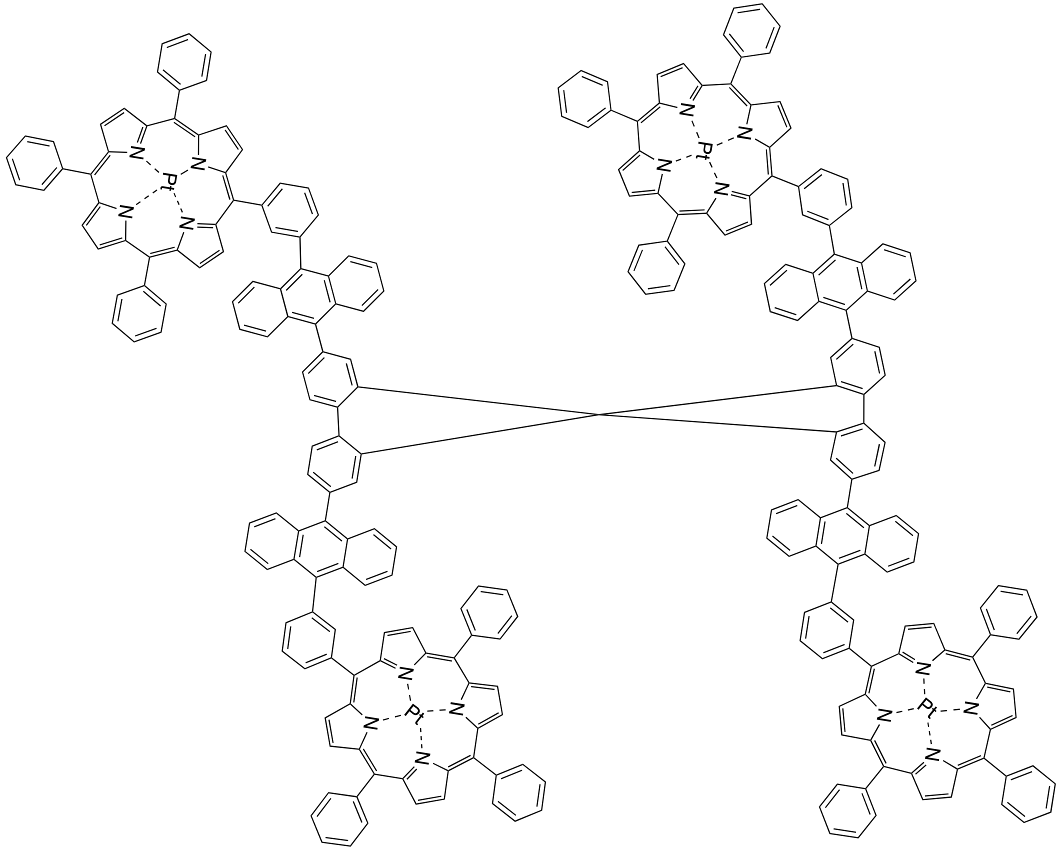
Photon management



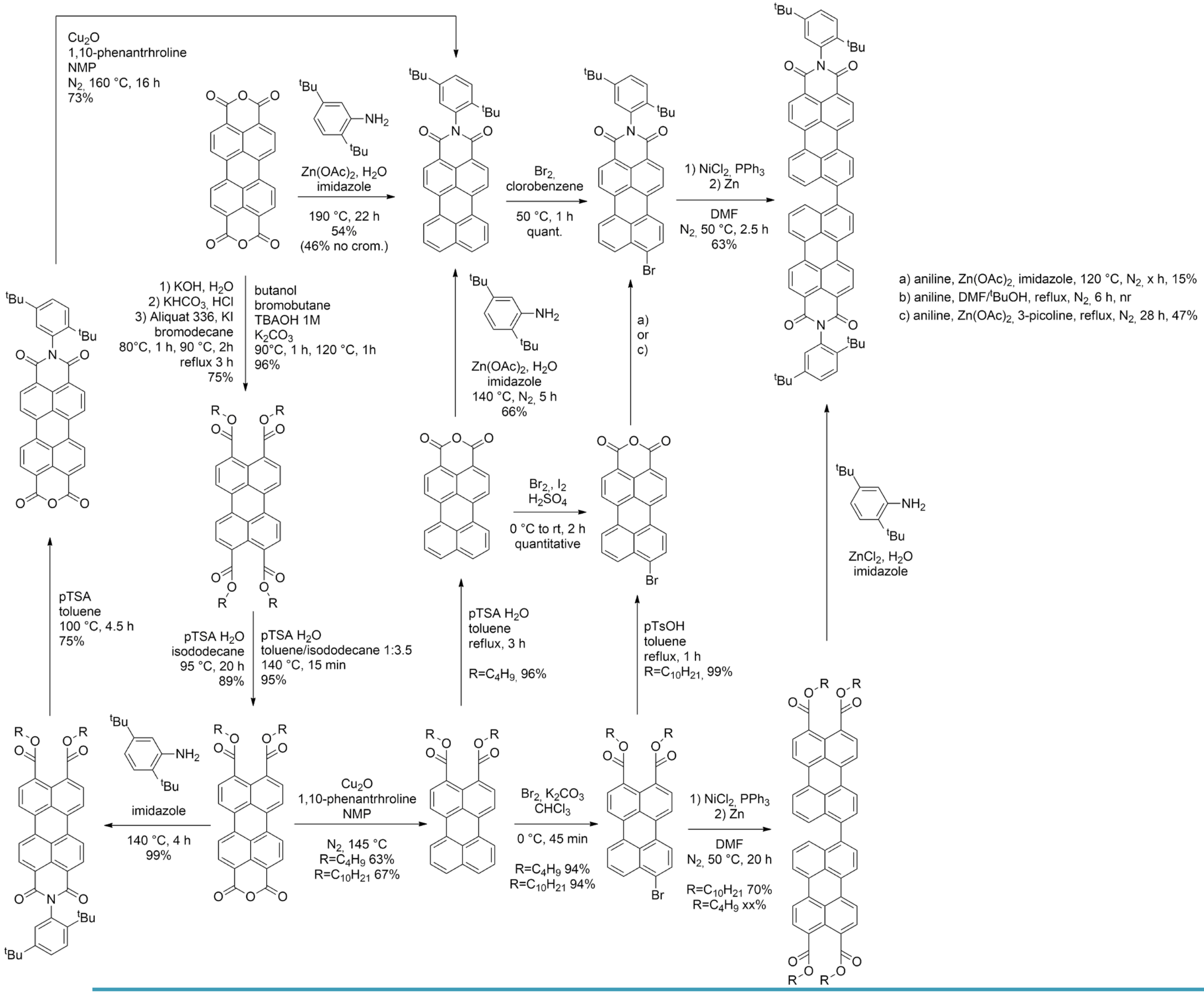
Multifunctional architectures

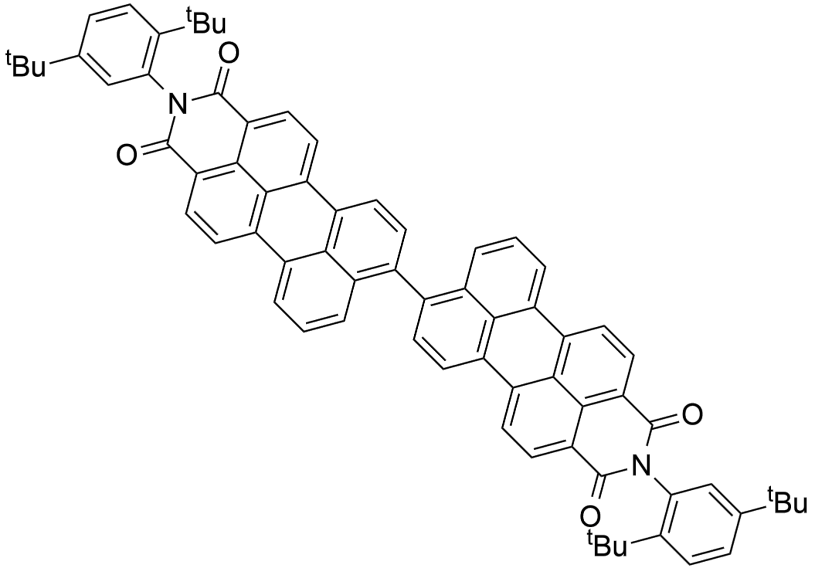


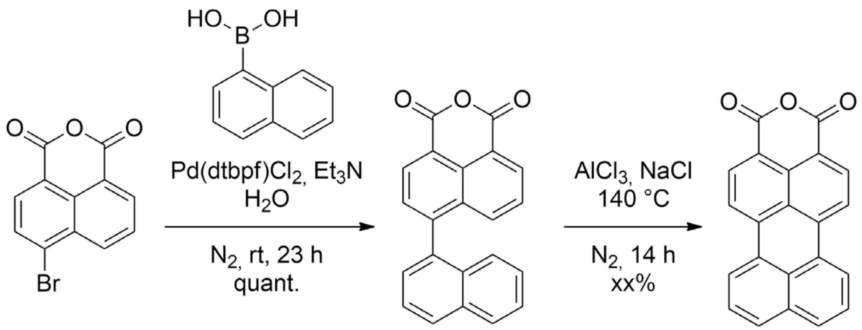




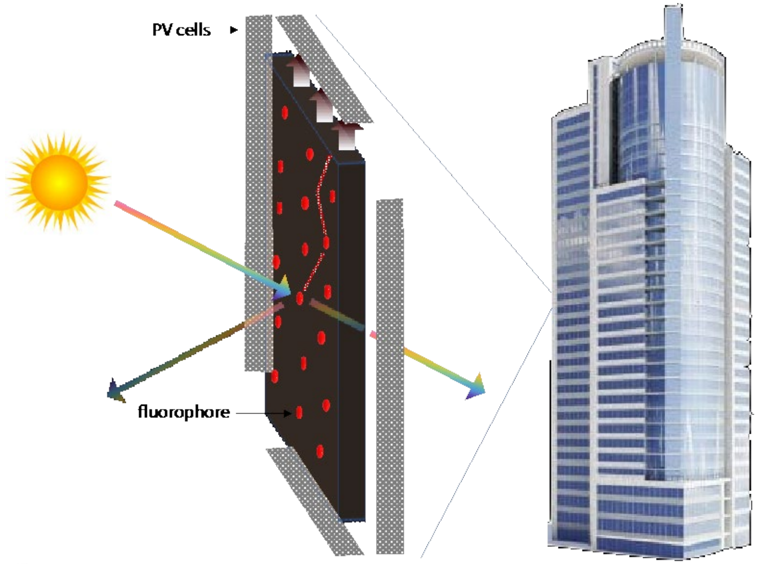
Perylene dyes

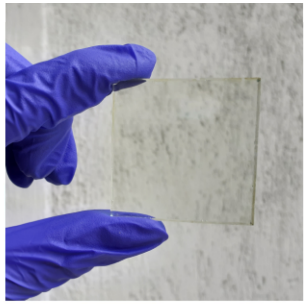


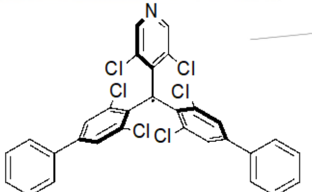




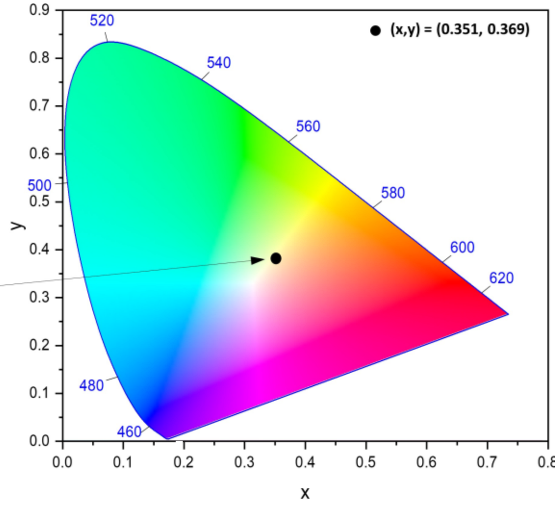
Luminescent radicals for LSC

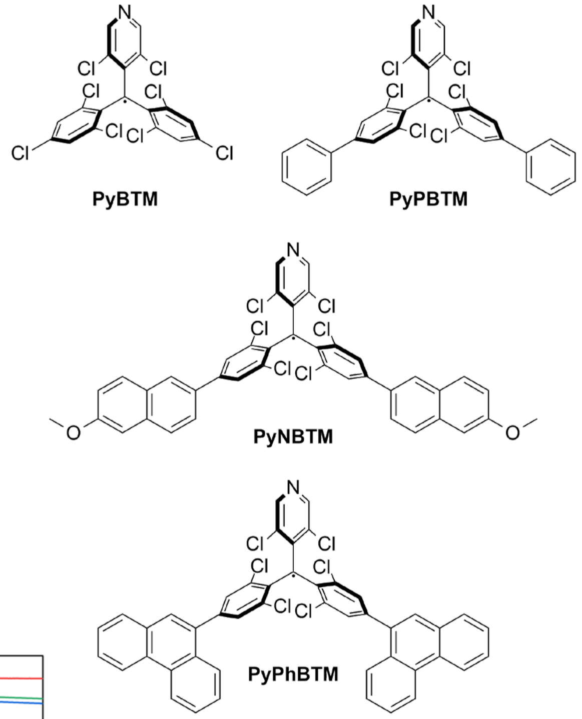


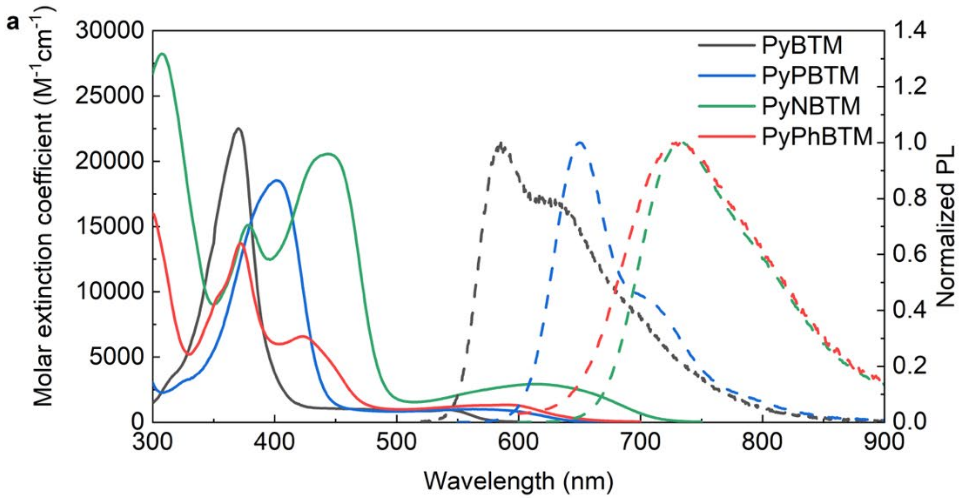


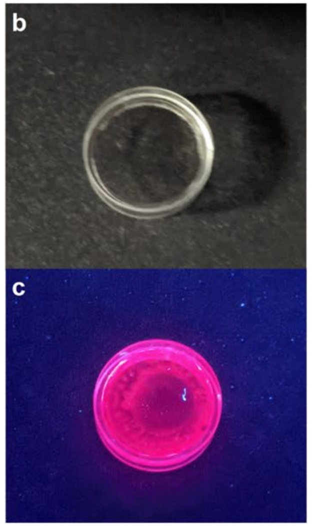


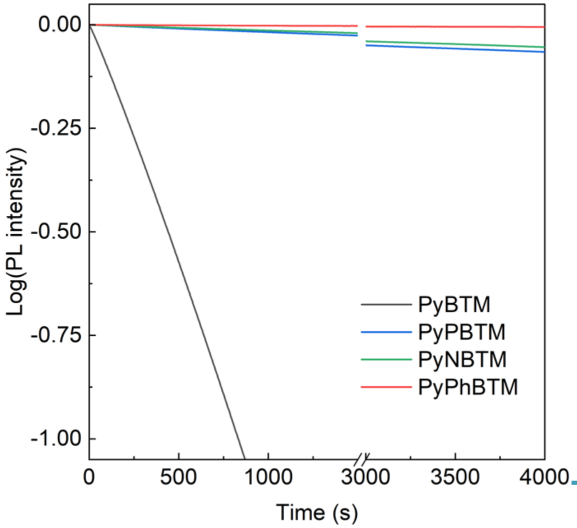
PyPBTM







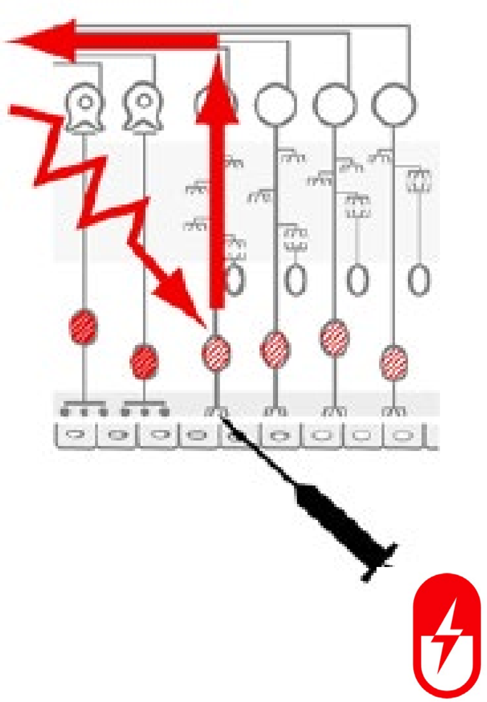


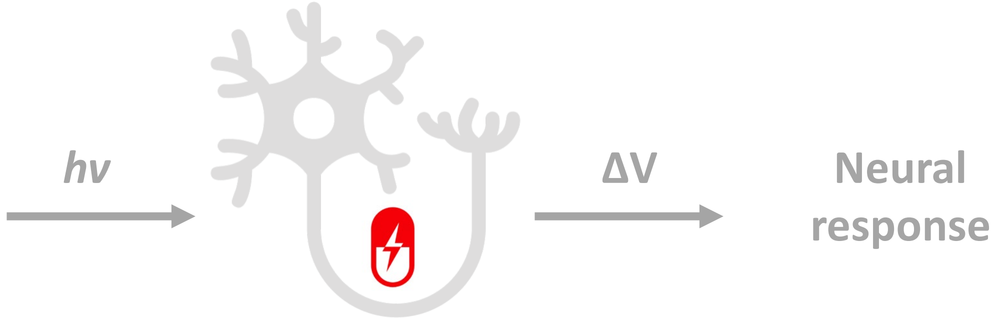


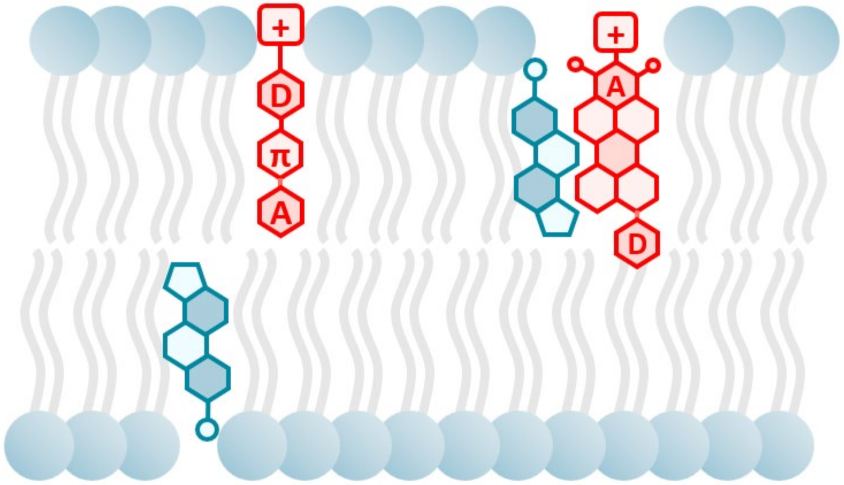
ASAP, Materials Advances

Photoactive membrane probes

Photosensitization of neural retinal cells with engineered **PUSH-PULL MOLECULES**



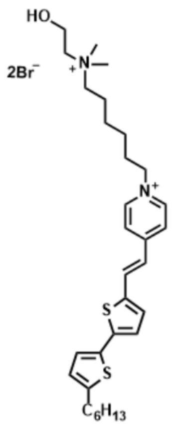




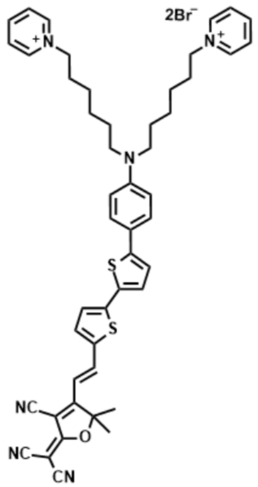
SYNTHETICS TARGETS

Traditional linear push-pull systems

BV1

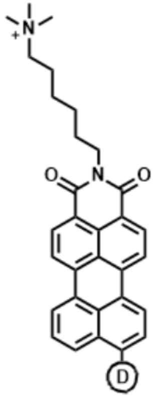


A

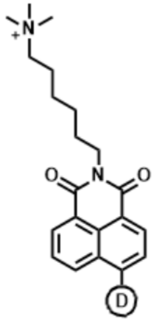


Rylenic twisted push-pull systems

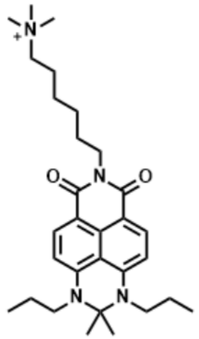
B



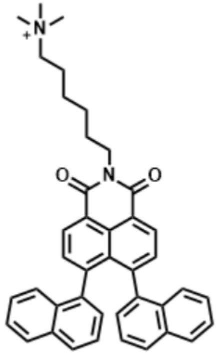
C

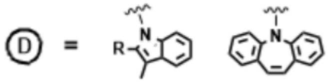


D



E





R= CH_3, Ph

Tests in vitro

Localization in the cell:

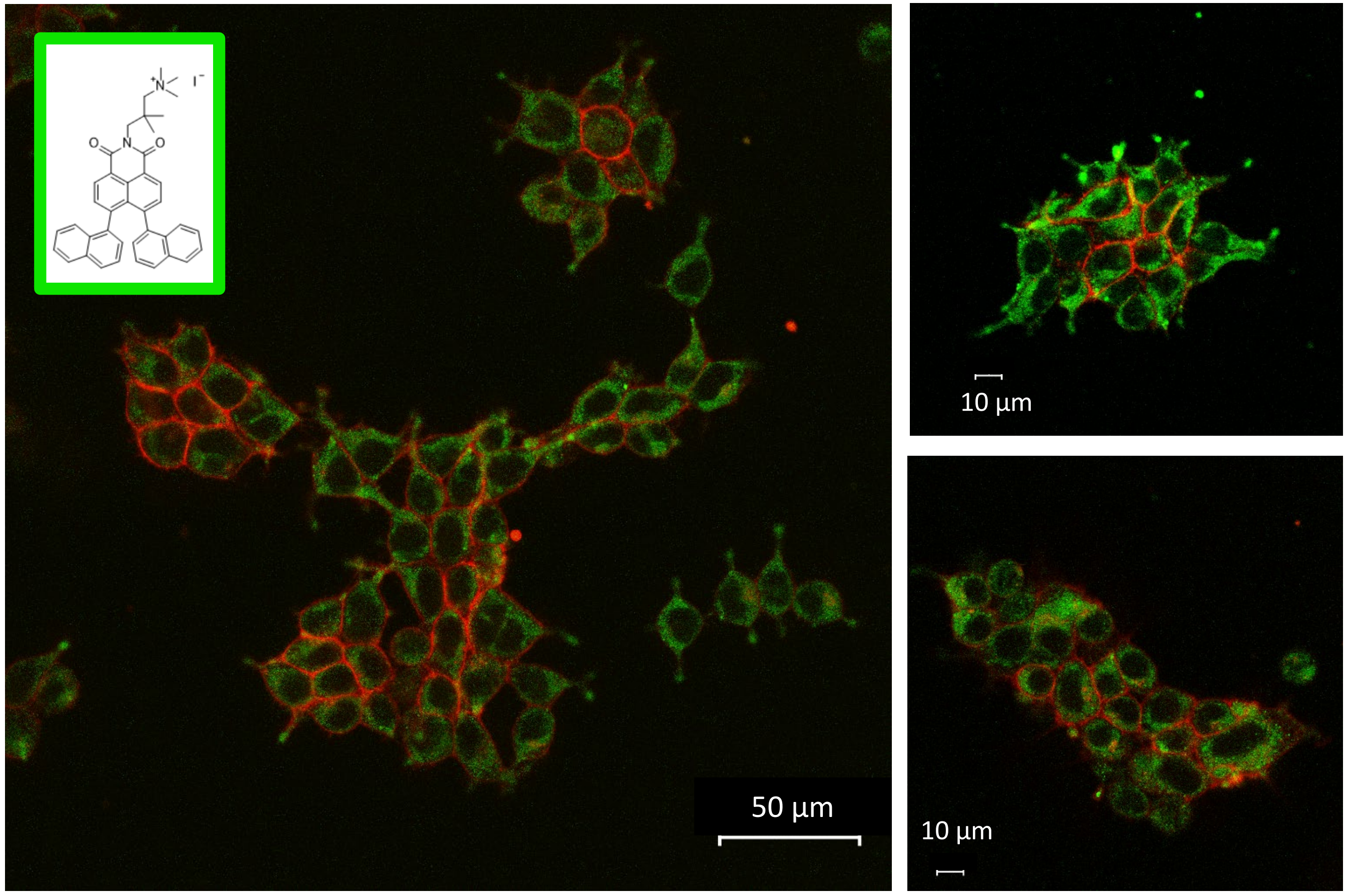
- Localization in cytosol
- Inappropriate hydrophilic/lipophilic balance

Electrophysiology:

- No photoinduced effect recorded
- Not suitable for optopharmaceutics

Imaging:

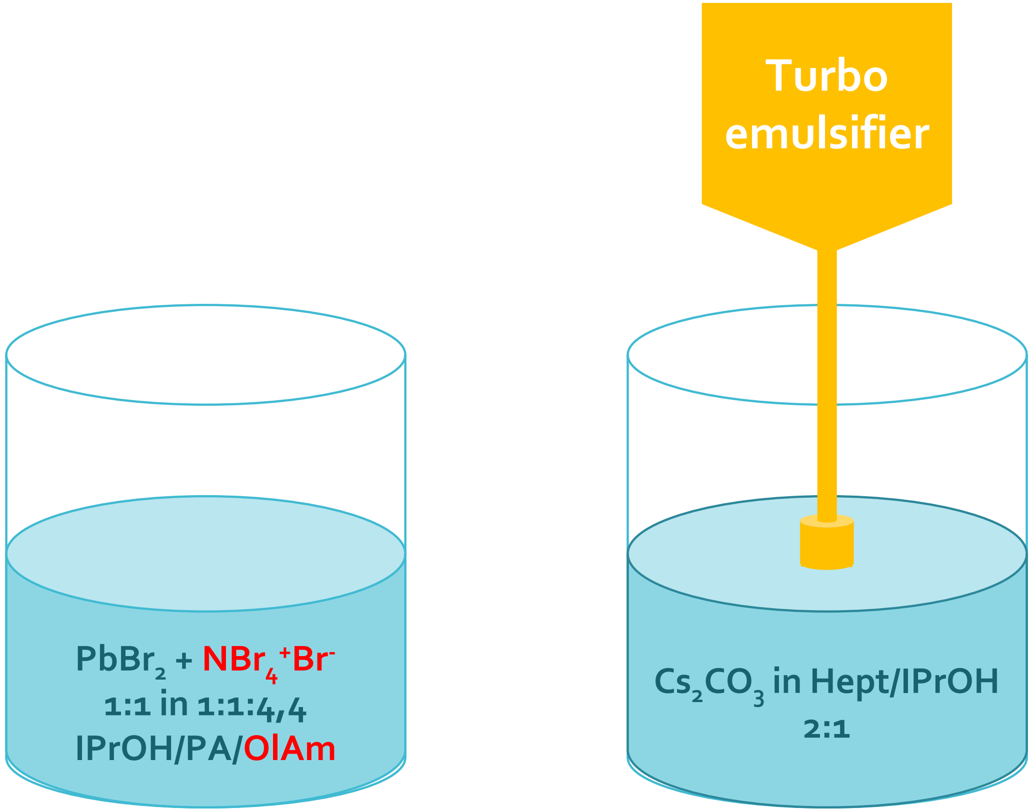
- No evident cytotoxic effects
- Broad Stokes shift
- Good cytoplasmatic probe



HEK-293 cells live-stained with CellMask™ after removal of the unbound AZ36 , 3D z-stack confocal imaging
A. Magni, PhD – Prof . G. Lanzani

Colloidal $CsPbBr_{3-x}I_x$ perovskites

- Up to 2.6 g of nanocrystals in 30 min, working at room temperature and under standard aerated lab environment

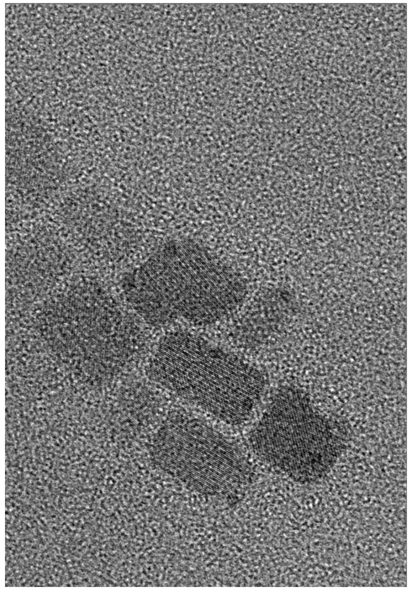


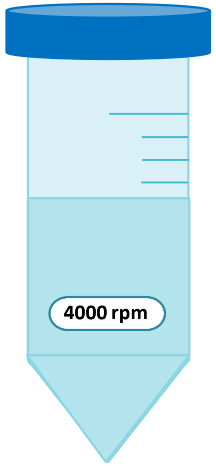
SOLUTION A

SOLUTION B

10 s

Reprecipitated with IPrOH





Dryed

Fresh toluene

Just solar illumination

Under 365 nm illumination

03

Characterizations: SEM-EDS

Pd% (ICP-OES) = 1,90 %