# ORGANIC AND HYBRID MATERIALS FOR SOLAR ENERGY CONVERSION:
## FROM ORGANOMETALLIC METHODS TO BIOTECHNOLOGICAL APPROACHES


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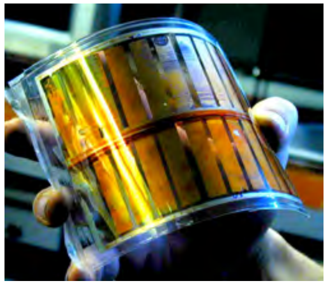
# Outlook

*Routes to organic and hybrid materials for solar energy conversion*

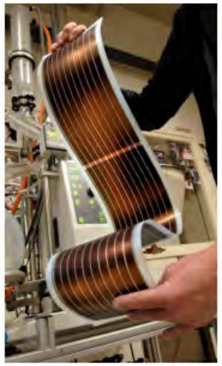
*1) Organometallic routes to conjugated polymers for plastic solar cells*

*2) Photosynthetic enzymes as materials for photoconversion*

# Plastic solar cells



2000



2008

2012

# Plastic solar cells

**Photovoltaic Wi-Fi shelter in San Francisco (konarka.com)**

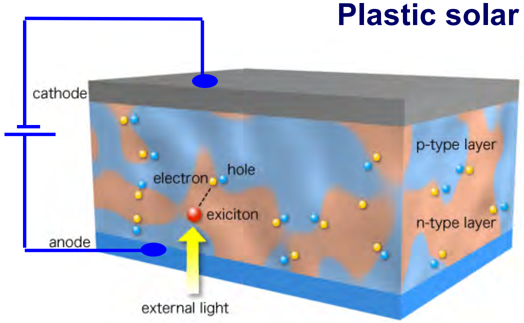
**Roll to roll printable photovoltaics**

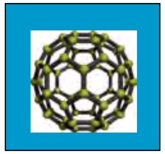
**Photovoltaic ivy (solarivy.com)**

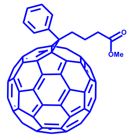
**Photovoltaic textile (tensilesolar.com)**

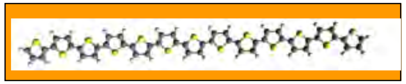
**Portable photovoltaic supplier (solarmer.com)**

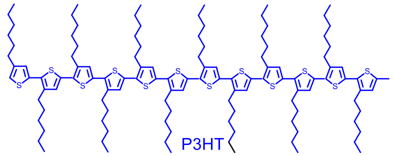
## Plastic solar cells

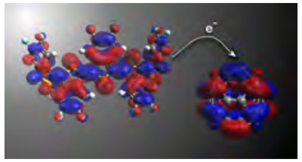




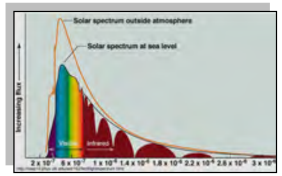


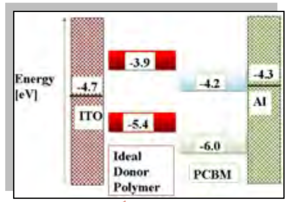
Halls, J.J.M.; Walsh, C.A.; Greenham, N.C.; Marseglia, R.H.; Friend, R.H.; Moratti, S.C.; Holmes, A.B. *Nature*, **1995**, *376*, 498

## Requirements of organic semiconductors

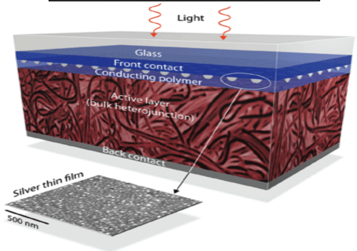
- Good absorption profile in the solar emission spectrum




- Favorable alignment of energy levels with the acceptor

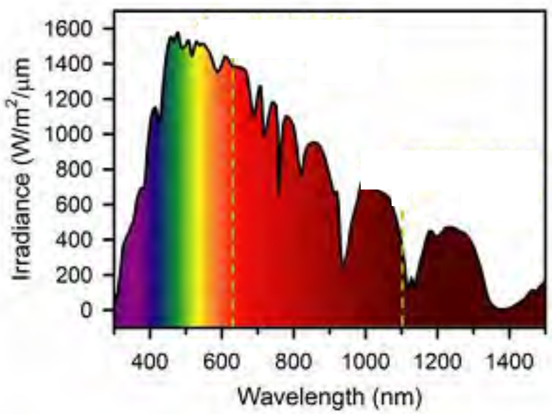


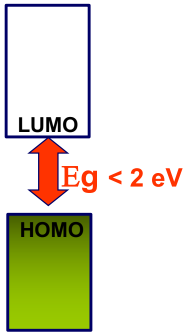

- Appropriate film morphology and stability
  Good charge transport properties



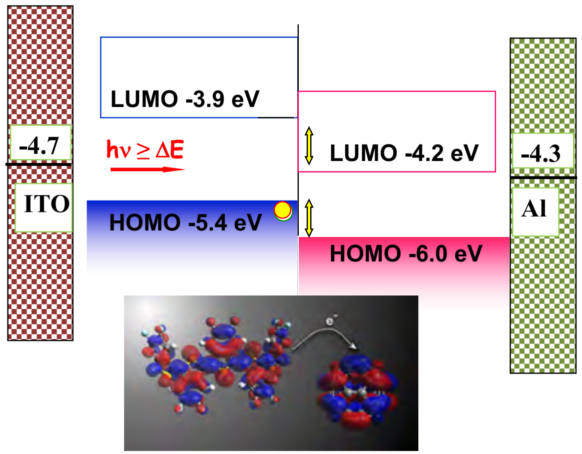

## Properties of organic semiconductors:
*wide absorption in the solar spectrum*

**LOW ENERGY GAP MATERIALS**
**(HOMO – LUMO difference 1.9-1.2 eV)**

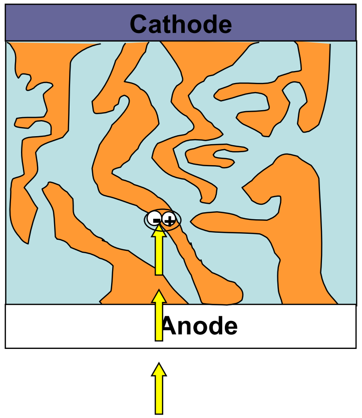


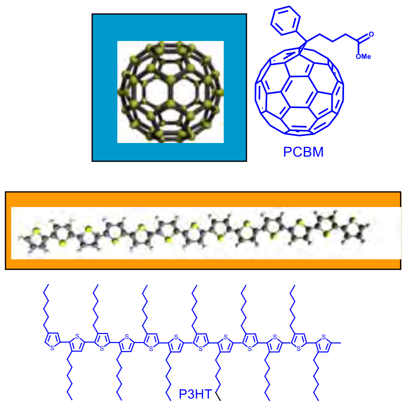




## Properties of organic semiconductors:
*proper alignment of energy levels*



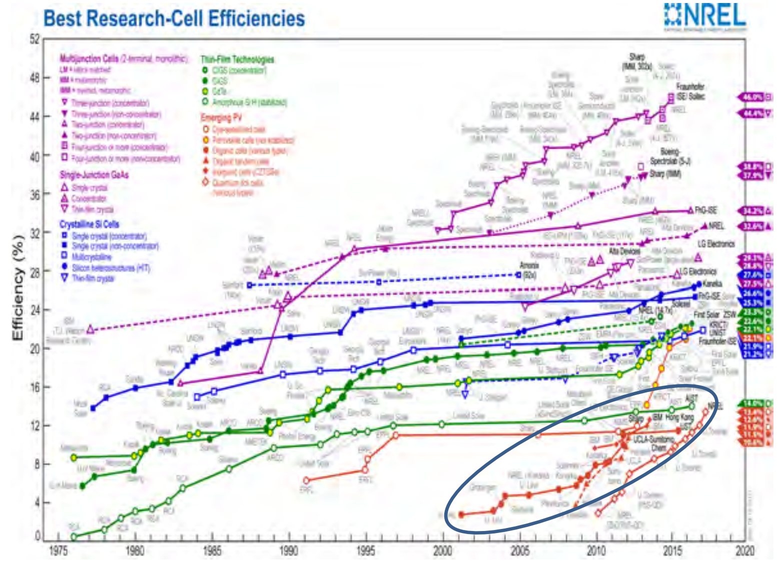
## Properties of organic semiconductors:
*charge transport properties*



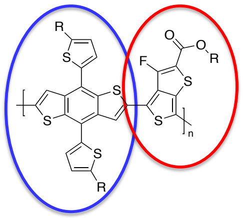




Halls, J.J.M.; Walsh, C.A.; Greenham, N.C.; Marseglia, R.H.; Friend, R.H.; Moratti, S.C.; Holmes, A.B. *Nature,* **1995**, *376*, 498

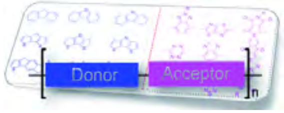
## Common ranking of PV technology:
*The race for maximum efficiency*

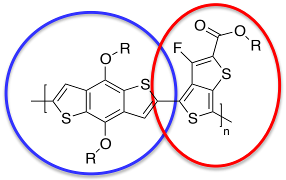



## High efficiency polymers
*the donor-acceptor design*

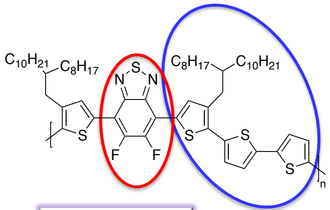


**PDTBDTfTT[1]**
PCE= 9.35%



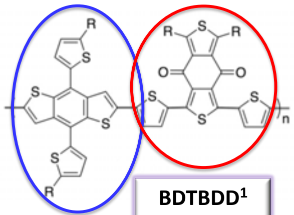
**PBDTfTT[2]**
PCE= 9.21%



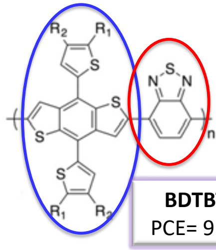
**PffBT4T-2OD[3]**
PCE= 10.8%


1. S. A. Chen et al., *Adv. Mater.* **2013**, *25*, 4766-4771
2. Y. Cao et al., *Nature Photon.* **2012**, *6*, 591-595
3. He Yan et al., *Nat. Commun.* **2014**, *5*,5293-5296

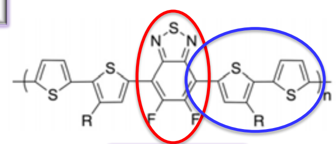

## Donor–acceptor polymers



**BDTBDD[1]**
PCE= 11.2%



**BDTBT[2]**
PCE= 9.5%



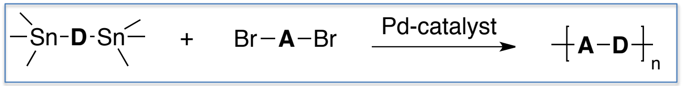
**P3HTTT[3]**
PCE= 11.7%

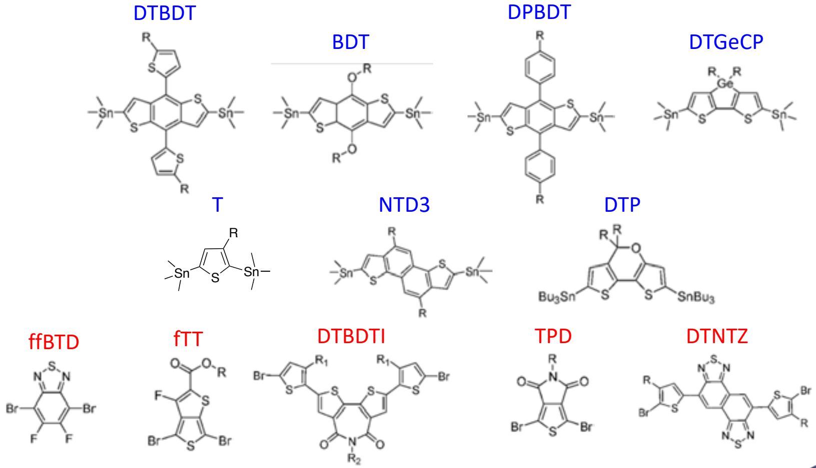

1. Tan Z, Li S, Wang F, Qian D, Lin J, Hou J, et al. *Sci Rep* **2014**, 4, 1–9
2. Gao M, Subbiah J, Geraghty PB, Chen M, Purushothaman B, Chen X, et al. *Chem Mater* **2016,** *28*, 1–7
3. Zhao J, Li Y, Yang G, Jiang K, Lin H, Ade H, et al. *Nat Energy* **2016**, *1*, 1–7.

Li, Gang & Chang, Wei-Hsuan & Yang, Yang *Nature Reviews Materials* **2017**. 2. 17043

## Common syntheses of donor-acceptor copolymers

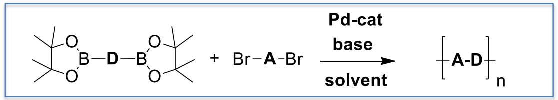

## The Stille coupling

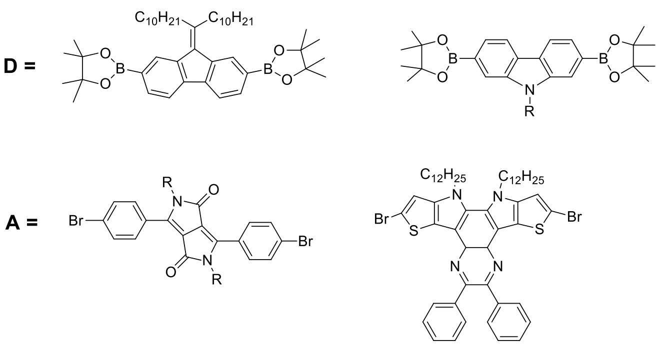


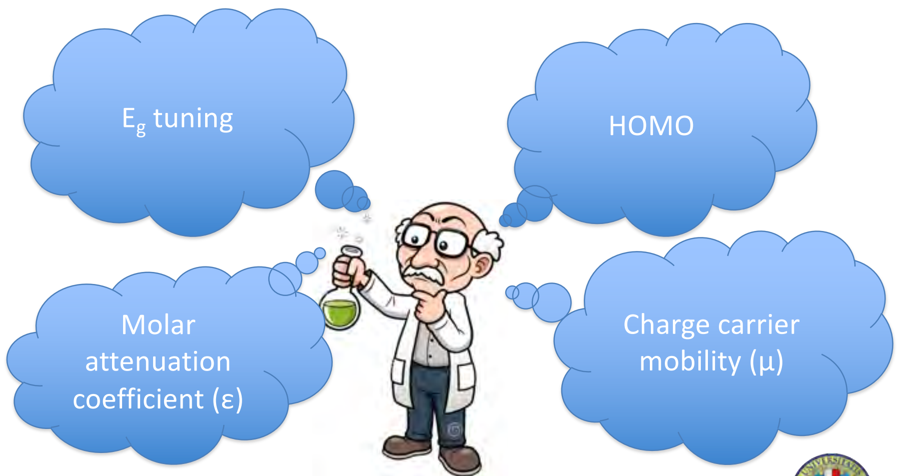

G. Marzano, G.M. Farinola et al. *Eur. J. Org. Chem.* **2014**, *30*, 6583

## The Suzuki-Miyaura coupling

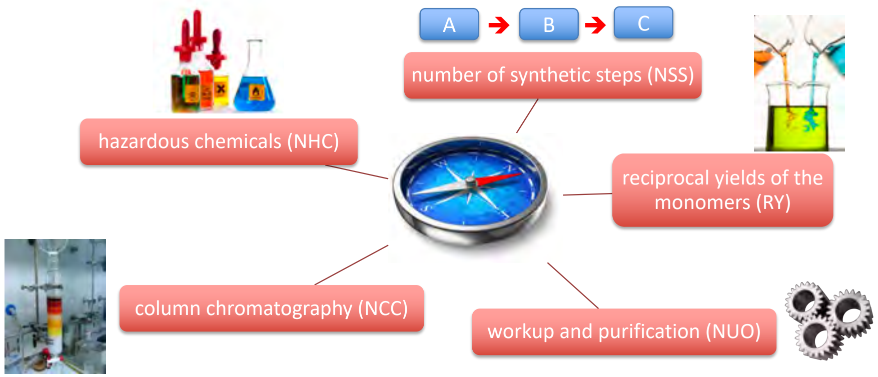



## Traditional guidelines for performance improvement



## Synthetic Complexity (SC)

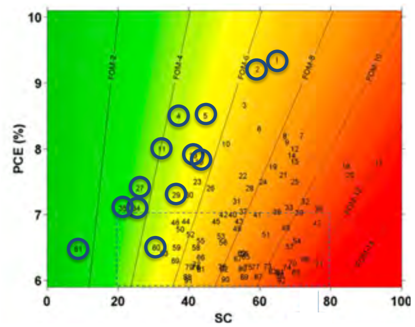


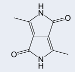
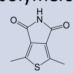
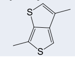

$$SC = 35\frac{NSS}{NSS_{max}} + 25\frac{logRY}{logRY_{max}} + 15\frac{NUO}{NUO_{max}} + 15\frac{NCC}{NCC_{max}} + 10\frac{NHC}{NHC_{max}}$$

$$FoM = \frac{SC}{PCE}$$

R. Po, G. Bianchi, C. Carbonera, A. Pellegrino *Macromolecules*, **2015**, *48*, 453
G. Marzano, G.M. Farinola et al. *Eur. J. Org. Chem.* **2014**, *30*, 6583

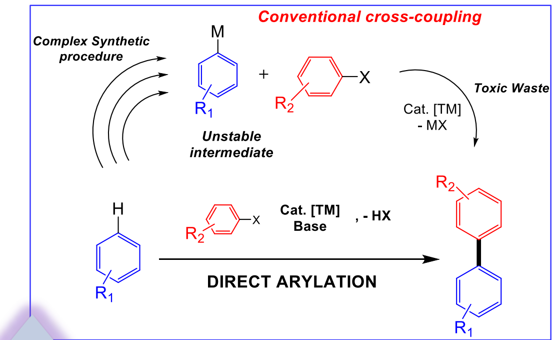
## Synthetic complexity (SC) *vs* efficiency (PCE)




| entry | type | SC | PCE |
|---|---|---|---|
| ***p61*** | P3HT | <10 | 6.48% |
| ***p11 p27 p34 p35 p60*** | DPP polymers  | <32 | 6.5%-8.0% |
| ***p4 p5 p13 p16 p29*** | TPD polymers  | 20<SC<40 | 7.2%-8.5% |
| ***p1 p2*** | TT polymers  | 20<SC<40 | >9% |

G. Marzano, G.M. Farinola et al. *Eur. J. Org. Chem.* **2014**, *30*, 6583
R. Po, G. Bianchi, C. Carbonera, A. Pellegrino *Macromolecules*, **2015**, *48*, 453

## Conventional cross-coupling reactions *vs* direct arylation

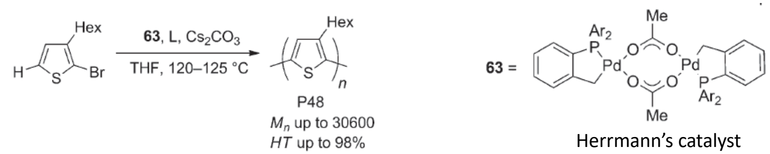



**Advantages**

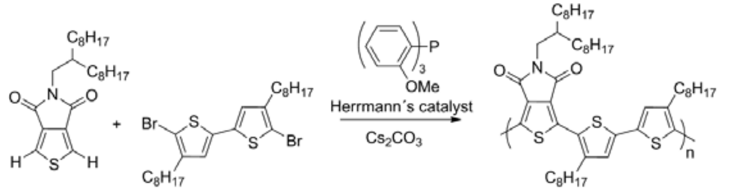
- *Reduction of the synthetic steps*
- *Prevents the use of highly toxic organometallic reagents*

T. Bura, T. Blaskovits, M. Leclerc, *J. Am. Chem. Soc.*, **2016**, *138*, 10056-10071
J. Pouliot, F. Grenier, J. .e Blaskovits, S. Beaupré, M. Leclerc, *Chem. Rev.* **2016**, *116* , 14225
A. S. Dudnik, T. J Aldrich, A. Facchetti, et al T. J. Marks, *J. Am. Chem. Soc.* **2016**

## Direct Heteroarylation Polymerization (DHAP)

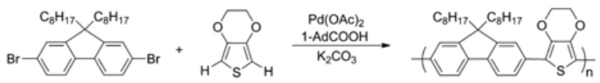



Q. Wang, R. Takita, Y. Kikuzaki, F. Ozawa, *J. Am. Chem. Soc.* **2010**, 132, 11420–11421

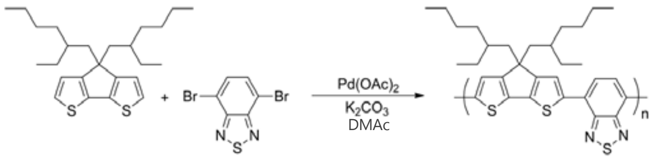



P. Berrouard, A. Najari, P. O. Morin, M. Leclerc et al, *Angew. Chem. Int. Ed.* **2012**, *51*, 2068–2071

## Direct Heteroarylation Polymerization (DHAP)

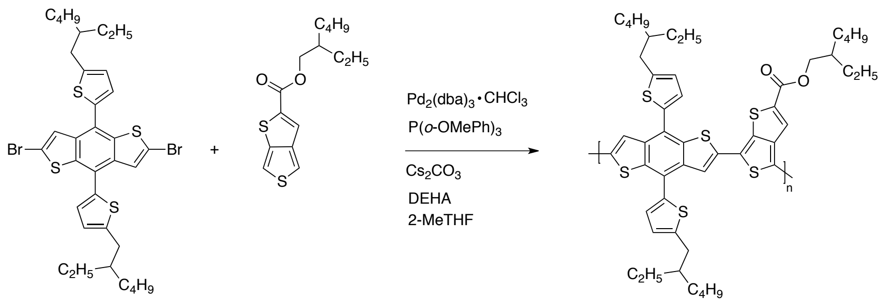



K. Yamazaki J. Kuwabara , T. Kanbara *Macromol Rapid Commun* **2012,** *34,* 69




S. Kowalski, S. Allard, K. Zilberberg, T. Riedl, U. Scherf, *Progress in Polymer Science,* **2013**, *38,* 1805

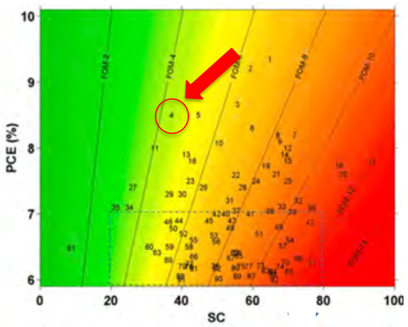
## Direct Heteroarylation Polymerization (DHAP)

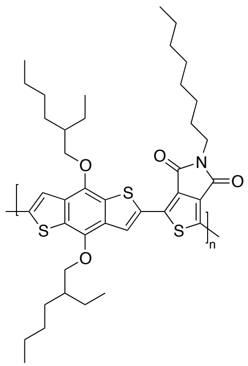



PCE= 8.4%

Dudnik, A.S.; Aldrich, T.J.; Eastham, N.D.; Chang, R.P.H.; Facchetti, A.; Marks, T.J. *J. Am. Chem. Soc*. **2016**, *138*, 15699-15709

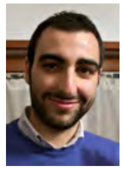
## PBDTTPD: a good trade-off



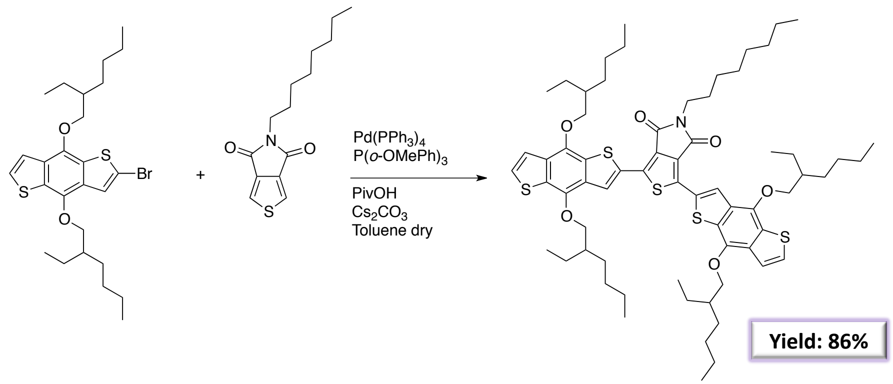



S. Beauprè, A. Pron, S. H. Drouin, L. G. Mercier, A. Robitaille and M. Leclerc, *Macromolecules*,**2012**, *45,* 6906.
M. Wakioka, N. Ichihara, Y. Kitano and F. Ozawa, *Macromolecules* **2014**, 47, 626.
T. L. D. Tam and T. T. Lin, *Macromolecules* **2016**, 49, 1648.

## PBDTTPD synthesis via DHAP: model reaction



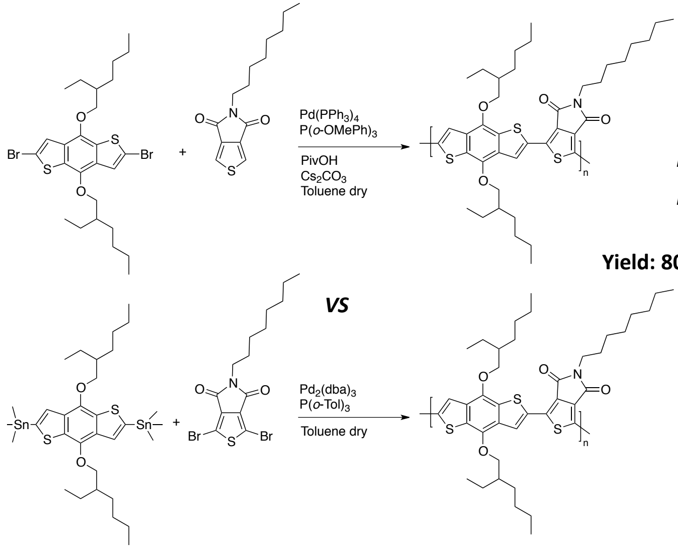
Giuseppe Marzano




**Yield: 86%**

G. Marzano, F. Carulli, F. Babudri, A. Pellegrino, R. Po, S. Luzzati G. M. Farinola, *J. Mater. Chem. A*, **2016**, *4*, 17163

## DHAP vs Stille polymerization




$P_{DHAP}$

$M_w$= 72 KDa

$M_n$= 12 KDa

**Yield: 80%**

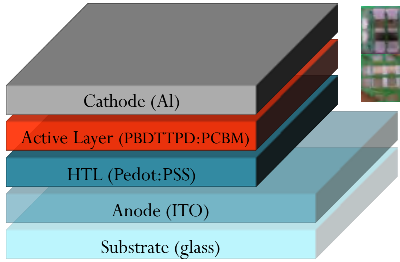
$P_{STILLE}$

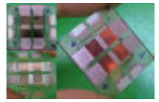
$M_w$= 34 KDa

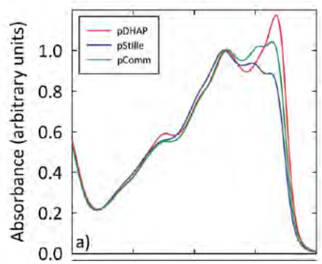
$M_n$= 10 KDa

G. Marzano, F. Carulli, F. Babudri, A. Pellegrino, R. Po, S. Luzzati G. M. Farinola, *J. Mater. Chem. A*, **2016**, *4*, 17163

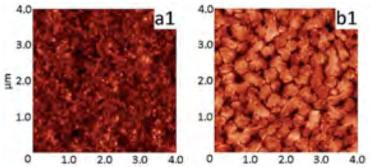
## DHAP vs Stille polymerization



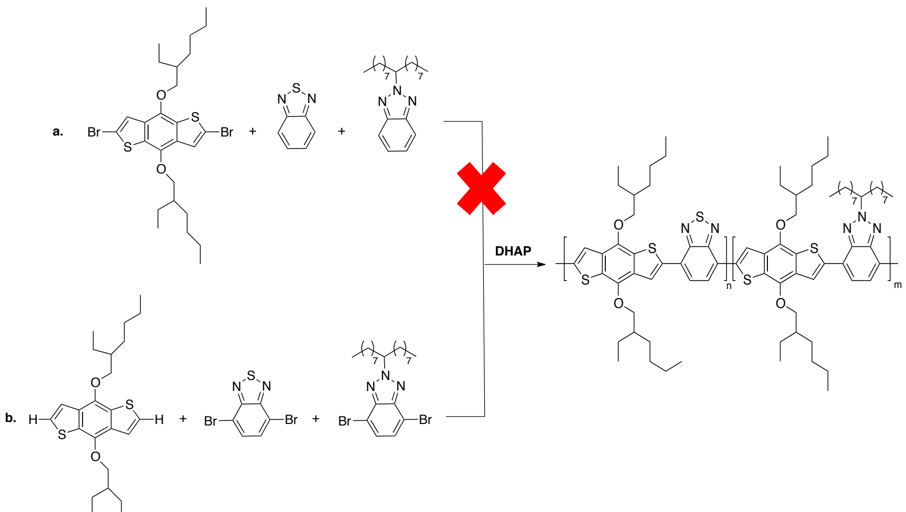



| PBDTTPD | Solvent | Efficiency [%] |
|---|---|---|
| $P_{STILLE}$ | CB | 2.70% (2.80%) |
| | CB + 4% CN* | 4.65% (4.82%) |
| $P_{DHAP}$ | CB | 3.09% (3.27%) |
| | CB + 4% CN* | 5.14% (5.31%) |



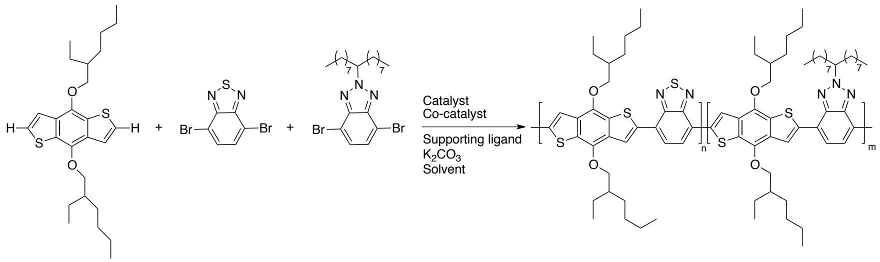

**FoM (improved) = SC (Reduced)**
**PCE (Increased)**

## A double acceptor/donor random copolymer via DHAP



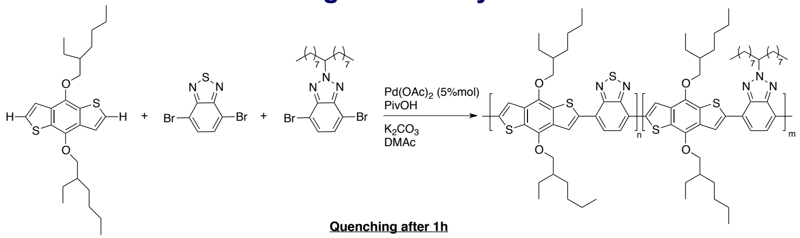

G. Marzano, D. Kotowski, F. Babudri, R. Musio, A. Pellegrino, S. Luzzati, R. Po, G. M. Farinola
*Macromolecules* **2015**, *48*, 7039

## Double acceptor/donor random copolymer

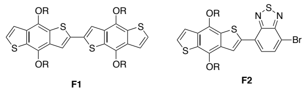



| Polymer | Catalyst | Co-catalyst | Supporting ligand | Solvent | Yield | $M_w(M_n)$ KDa |
|---|---|---|---|---|---|---|
| $P_{STILLE}$ | $Pd(PPh_3)_4$ | / | / | Toluene | 85% | 61(20) |
| / | $Pd(OAc)_2$ | PivOH | / | NMP | / | / |
| / | $Pd(OAc)_2$ | PivOH | / | NMP/Toluene | / | / |
| / | $Pd(OAc)_2$ | PivOH | / | NMP, MW assisted | / | / |
| $P_{DA}$1 | $Pd(OAc)_2$ 10% | PivOH | / | DMAc | 50% | 64 (9) |
| $P_{DA}$2 | $Pd(OAc)_2$ 5% | PivOH | / | DMAc | 70% | 73 (10.4) |
| $P_{DA}$3 | $Pd(OAc)_2$ 5% | PivOH | $PCy_3$. | DMAc | 70% | 78 (10.3) |
| $P_{DA}$4 | $Pd(OAc)_2$ 1% | PivOH | / | DMAc | 40% | 18 (4.8) |
| $P_{DA}$5 | $Pd_2(dba)_3$ | PivOH | $P(o-MeOPh)_3$ | THF | 40% | 14 (5.2) |

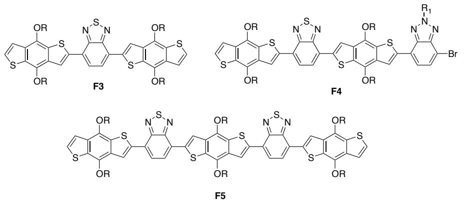
## Regiochemistry




**Quenching after 1h**




**Quenching after 2h**

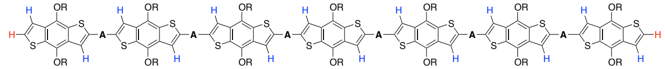



G. Marzano, D. Kotowski, F. Babudri, R. Musio, A. Pellegrino, S. Luzzati, R. Po, G. M. Farinola, *Macromolecules* **2015**, *48*, 7039

## Regiochemistry

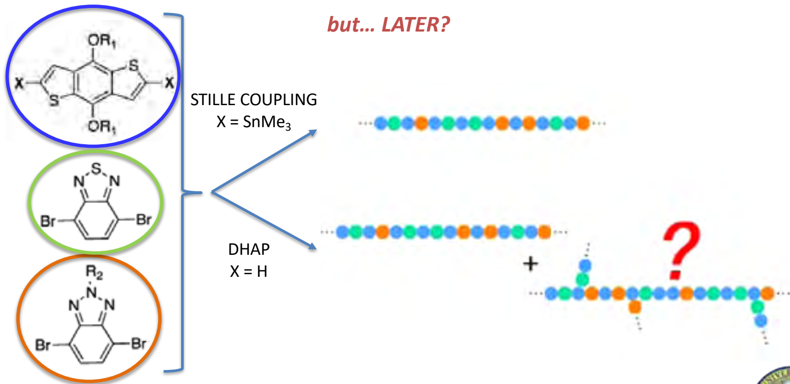
*Regioregular in the early stages of the process*

Free alpha positions
Free beta positions

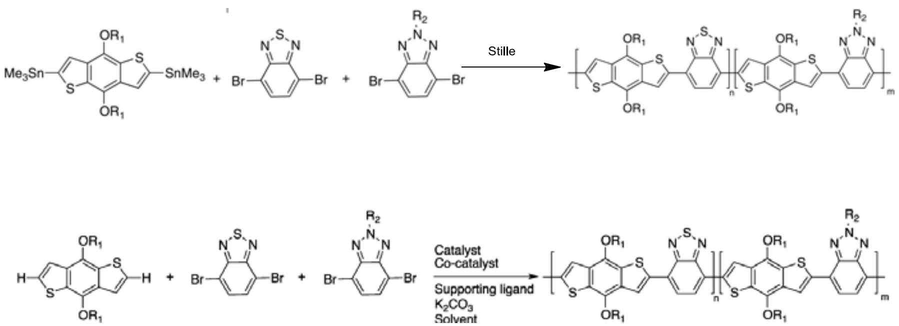


A= electron accepting unit

*but… LATER?*

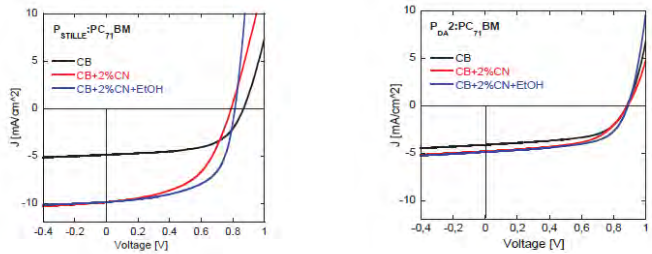



## DHAP vs Stille polymerization



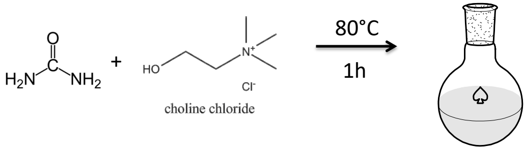

## Photovoltaic performances

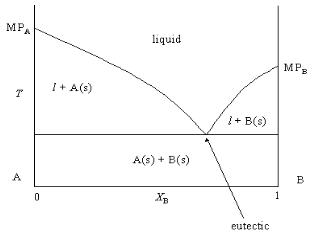
| polymer/PC$_{71}$BM (1:3) | without CN processing $V_{oc}$ [V] | FF [–] | $J_{sc}$ [mA/cm$^2$] | PCE [%][a,b] |
|---|---|---|---|---|
| P$_{STILLE}$ | 0.87 | 0.60 | 4.88 | 2.5 |
| P$_{DA}$1 | 0.86 | 0.54 | 3.91 | 1.8 |
| P$_{DA}$2 | 0.88 | 0.58 | 4.13 | 2.1 |
| P$_{DA}$3 | 0.87 | 0.53 | 4.10 | 1.9 |
| P$_{DA}$4 | 0.79 | 0.46 | 2.68 | 1.0 |
| P$_{DA}$5 | 0.72 | 0.44 | 3.60 | 1.1 |

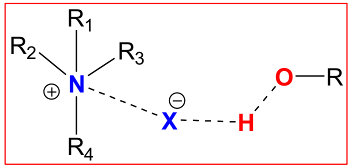



G. Marzano, D. Kotowski, F. Babudri, R. Musio, A. Pellegrino, S. Luzzati, R. Po, G. M. Farinola *Macromolecules* **2015**, *48*, 7039 and the solvent

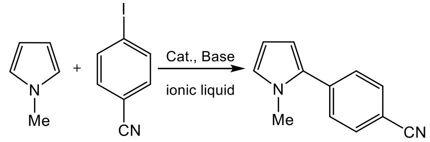
## Deep Eutectic Solvents (DES)

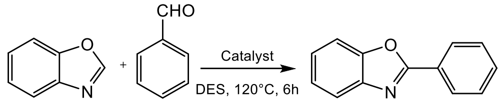



## DES and ionic liquids as reaction media for direct arylation reactions



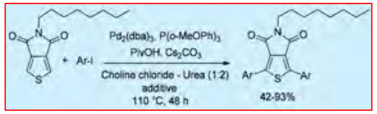
O. Vakuliukand, D. T. Gryko, *Eur. J. Org. Chem*. **2011**, 2854–2859

Ya Zhou, Z. Liu, T. Yuan, J. Huang and C. Liu, *Molecules*, **2017**, *22(4)*, 576

D. J. Ramón, G. Guillena, and X. Marset, *J. Eur. J. Org. Chem*, **2017**

P.H.Tran and A.H. Thi Hang, *RSC Adv*., **2018**, *8*, 11127

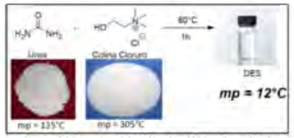

## Pd-catalyzed thiophene–aryl coupling reaction via C–H bond activation

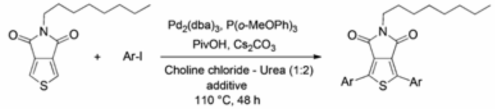


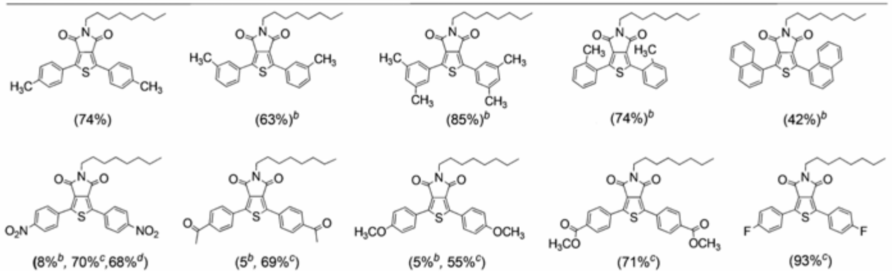

Angela Punzi

| entry | additive | halide | catalyst | ligand | solvent | yield (%)[b] |
|---|---|---|---|---|---|---|
| 1[c] | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | toluene | 82 |
| 2 | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | decanoic acid/tetraoctylammonium bromide (2:1) | 50 |
| 3 | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | α-CD (30% w/w)/DMU (70% w/w) | traces |
| 4 | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | choline chloride/glycerol (1:2) | 23 |
| 5 | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | choline chloride/ethylene glycol (1:2) | 24 |
| 6 | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | choline chloride/1,4-butanediol (1:2) | 6 |
| 7 | PivOH | 2a | Herrmann–Beller | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 35 |
| 8 | PivOH | 2a | $Pd(OAc)_2$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 6 |
| 9 | PivOH | 2a | $PdCl_2(PPh_3)_2$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 55 |
| 10 | PivOH | 2a | $PdCl_2(CH_3CN)_2$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | traces |
| 11 | PivOH | 2a | $Pd(PPh_3)_4$ | none | choline chloride/urea (1:2) | traces |
| 12 | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 82 |
| 13[d] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 79 |
| 14[e] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 16 |
| 15[f] | none | 2a | $CuCl_2$ | phenanthroline | choline chloride/urea (1:2) | 5 |
| 16 | PivOH | 2a | $Pd_2(dba)_3$ | none | choline chloride/urea (1:2) | 0 |
| 17 | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MePh)_3$ | choline chloride/urea (1:2) | 24 |
| 18 | PivOH | 2a | $Pd_2(dba)_3$ | $PPh_3$ | choline chloride/urea (1:2) | 55 |
| 19 | PivOH | 2a | $Pd_2(dba)_3$ | S-Phos | choline chloride/urea (1:2) | 24 |
| 20 | PivOH | 2b | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 13 |
| 21[g] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 43 |
| 22[h] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 30 |
| 23[i] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/urea (1:2) | 20[j] |
| 24[k] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/glycerol (1:2) | 25 |
| 25[l] | PivOH | 2a | $Pd_2(dba)_3$ | $P(o\text{-}MeOPh)_3$ | choline chloride/ethylene glycol (1:2) | 6 |

## Pd-catalyzed thiophene–aryl coupling reaction via C–H bond activation



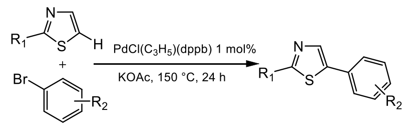



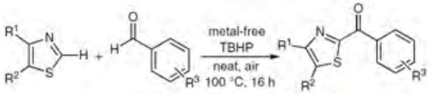

The first demonstration of a thiophene–aryl coupling via direct arylation in **deep eutectic solvents**


A. Punzi, D. I. Coppi, S. Matera, G.M. Farinola, *Org. Lett*., **2017**, *19*, 4754–4757

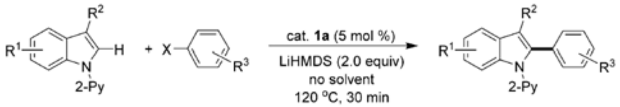
## Solvent-Free direct arylation reactions




S. Bensaid and H. Doucet, *ChemSusChem* **2012**, *5*, 1559 – 1567



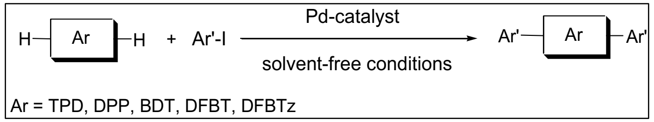

A. B. Khemnar, B. M. Bhanage, Synlett **2014**, *25*, 110–114



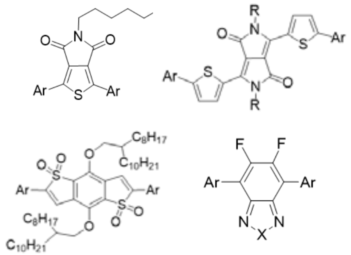

R. A. Jagtap, V. Soni and B. Punji, *ChemSusChem* **2017**, *10*, 2242 – 2248

## Solvent-free heteroaryl-aryl coupling via C−H bond activation for the synthesis of extended conjugated molecules

Nicola Zappimbulso

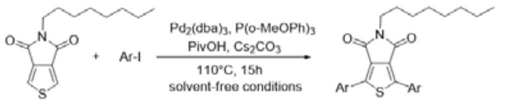


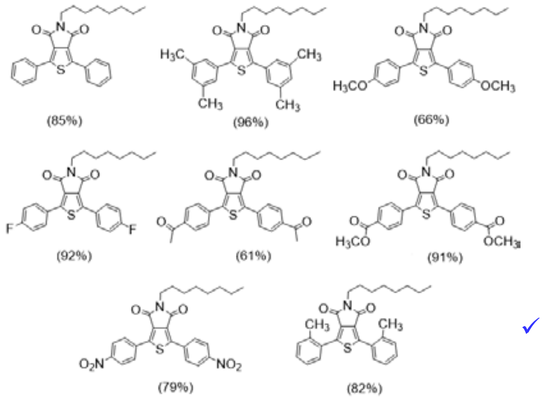

- *Green reaction protocols*
- *Step-economy*
- *Scalable processes*



A. Punzi, M. A. M. Capozzi, S. Di Noja, R. Ragni, N. Zappimbulso, G. M. Farinola, *J. Org. Chem*, **2018**, *83*, 9312

## Synthesis of TPD-based compounds

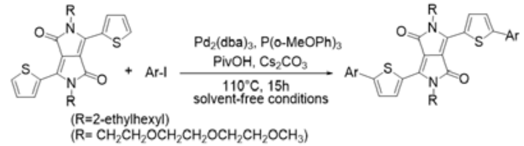


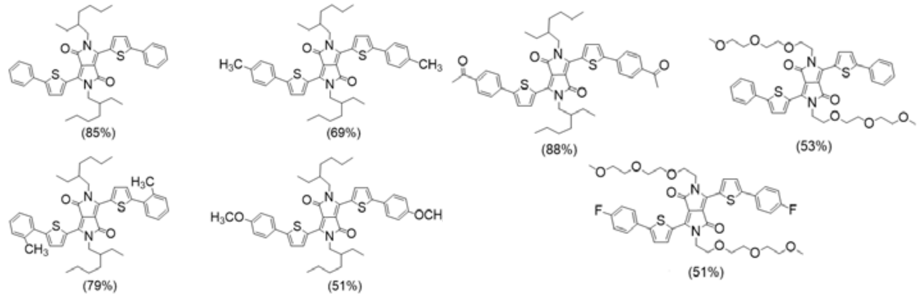




- ✓ Solvent-free
- ✓ Non-anhydrous Conditions
- ✓ Without exclusion of air

A. Punzi, M. A. M. Capozzi, S. Di Noja, R. Ragni, N. Zappimbulso, G. M. Farinola, *J. Org. Chem*, **2018**, *83*, 9312

## Synthesis of DPP-based compounds

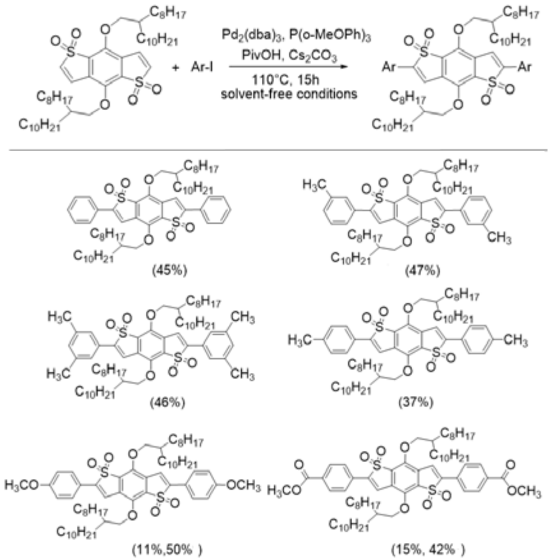



A. Punzi, M. A. M. Capozzi, S. Di Noja, R. Ragni, N. Zappimbulso, G. M. Farinola, *J. Org. Chem*, **2018**, *83*, 9312

See also: G. Farinola, I. Ratera, N. Ventosa, J. Veciana et. Al. Chem. Eur. J. **2018**, |*https://doi.org/10.1002/chem.201801444*

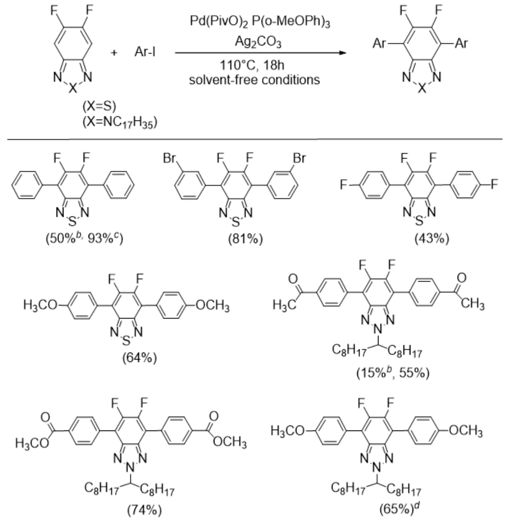
## Synthesis of BDT-based compounds




A. Punzi, M. A. M. Capozzi, S. Di Noja, R. Ragni, N. Zappimbulso, G. M. Farinola, *J. Org. Chem*, **2018**, *83*, 9312

## Direct arylation reactions on fluorinated benzothiadiazole and benzotriazole

Simone Di Noja




A. Punzi, M. A. M. Capozzi, S. Di Noja, R. Ragni, N. Zappimbulso, G. M. Farinola, *J. Org. Chem*, **2018**, *83*, 9312

## DHAP in the synthesis of organic semiconductors

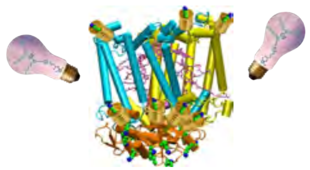
- *REDUCED NUMBER OF SYNTHETIC STEPS*
- *REDUCTION OF TOXIC TIN REAGENTS*
- *GREEN SOLVENTS*
- *SOLVENT-FREE CONDITIONS*

# Outlook

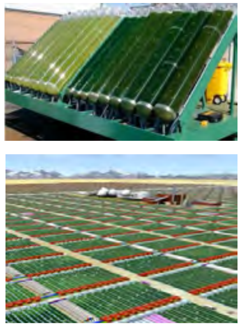
## *Routes to organic and hybrid materials for solar energy conversion*

*1) Organometallic routes to conjugated polymers for plastic solar cells*

*2) Photosynthetic enzymes as materials for photoconversion*



## Can we envisage general biotechnological routes to molecular and nano-materials for photoconversion of solar energy?



## Smart materials for optoelectronics from photosynthetic microorganisms: a mixed chemical biotechnological approach

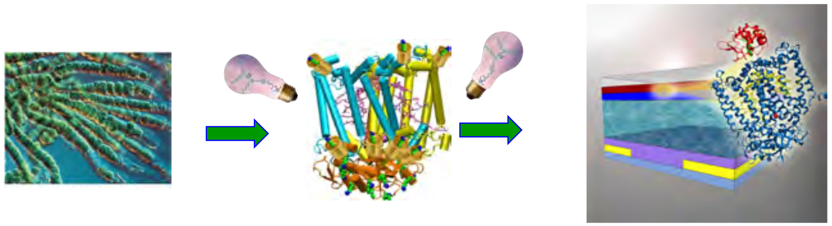
**PHOTOSYNTHETIC BACTERIA**

## Bacterial photoenzymes as photoconverters

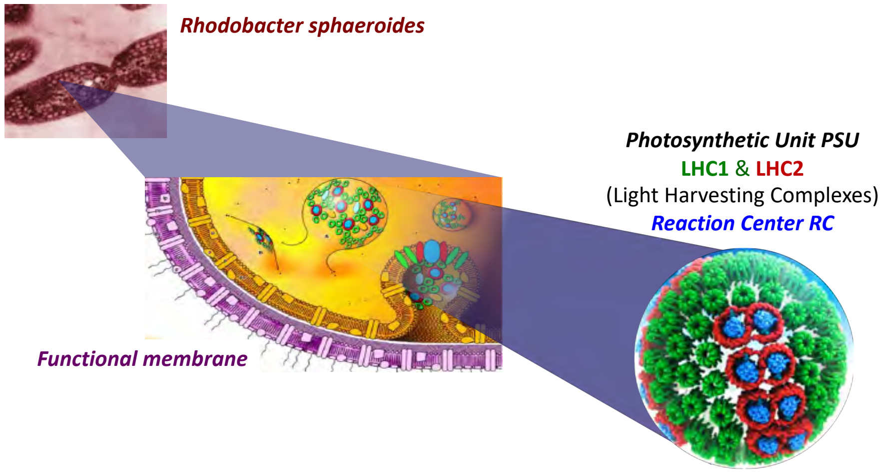
*1) Functionalization with photoactive molecules*

*2) Supramolecular architectures*

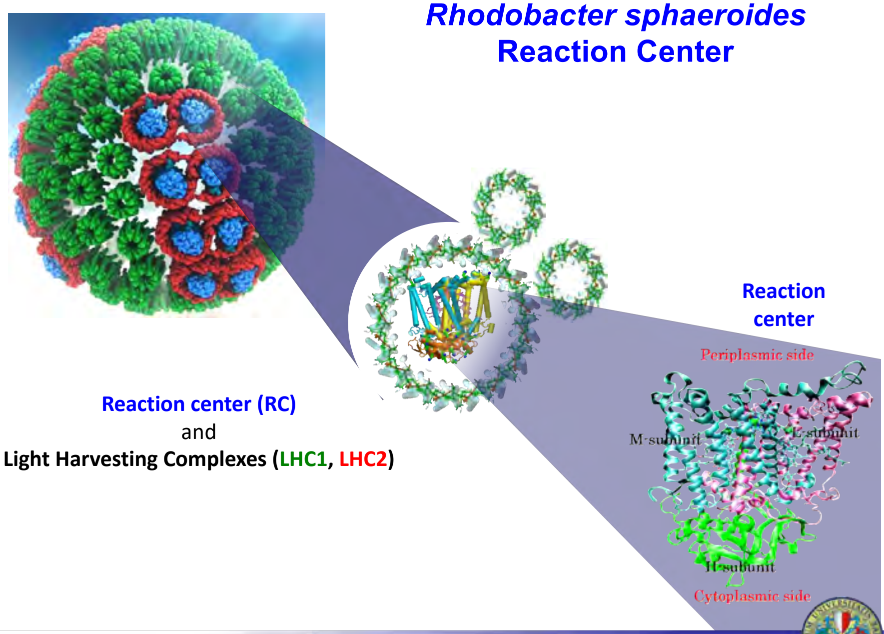
*3) Photoresponsive devices*



## *Rhodobacter sphaeroides*

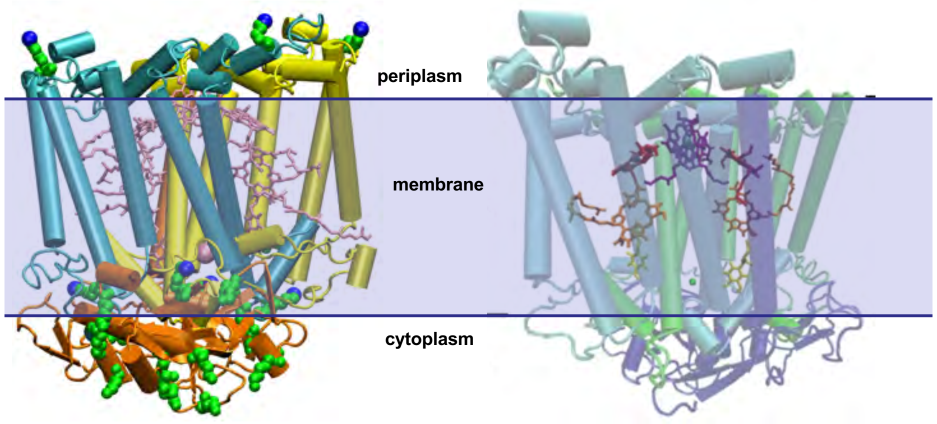


## *Rhodobacter sphaeroides* Reaction Center



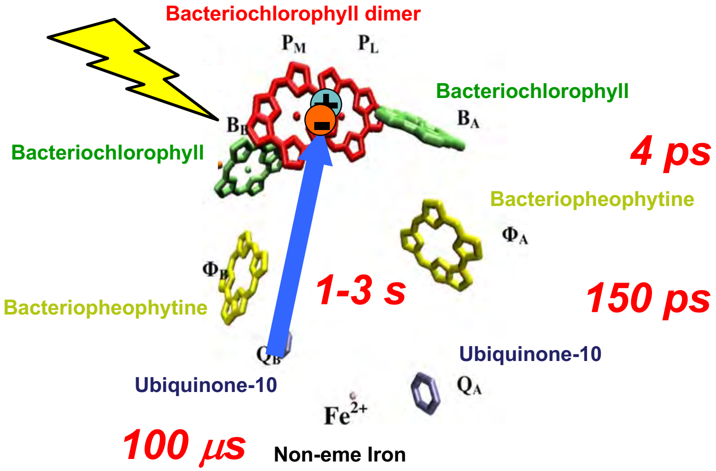

Reaction center (RC)
and
Light Harvesting Complexes (LHC1, LHC2)

## *Rhodobacter sphaeroides* Reaction Center

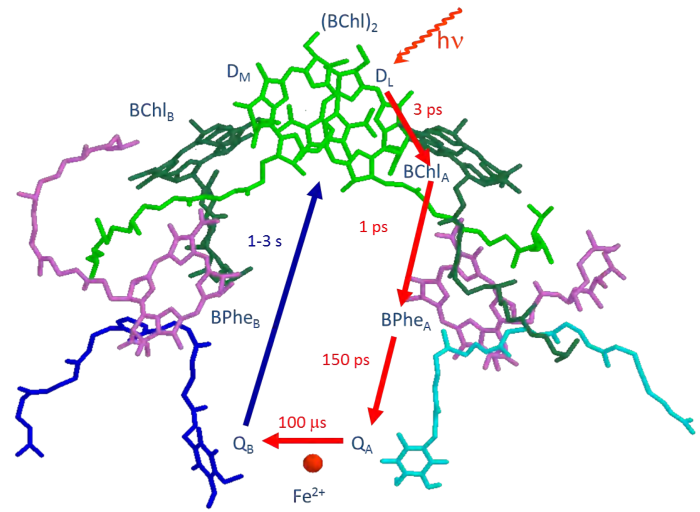



G. Feher, J.P. Allen, M.Y. Okamura, D.C. Rees *Nature* **1989**, *339*, 111

## *Rhodobacter sphaeroides* Reaction Center

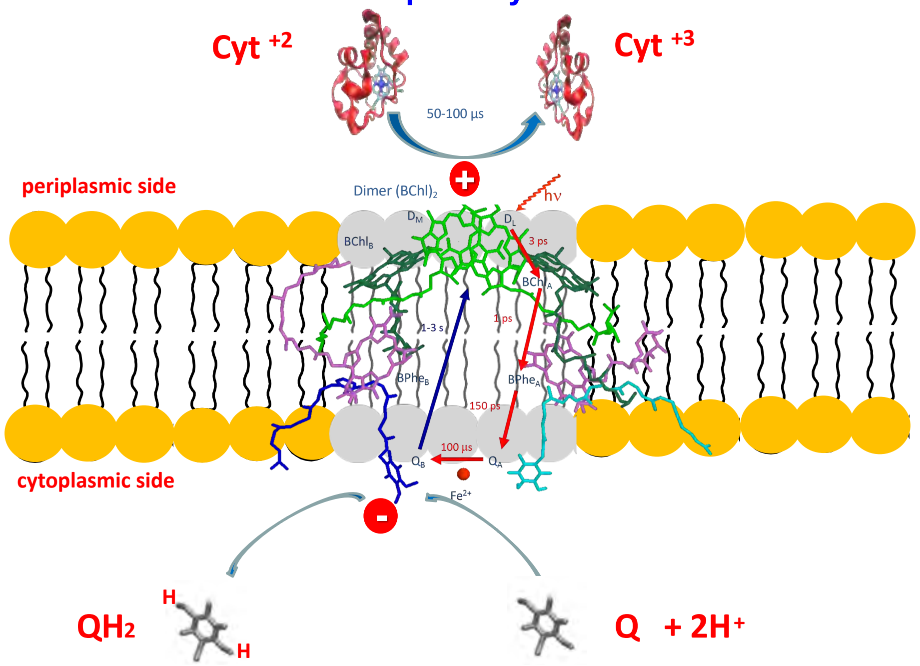



## *Rhodobacter sphaeroides* Reaction Center

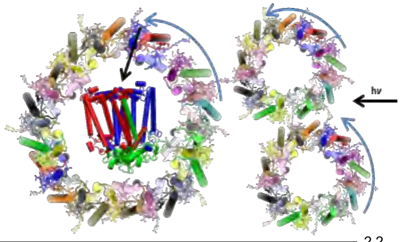


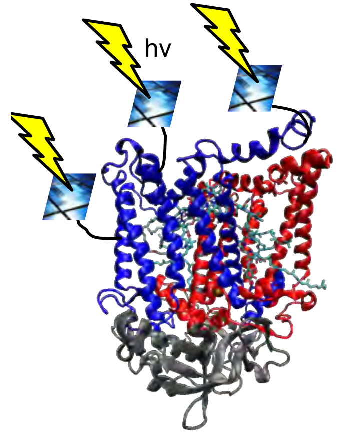

G. Feher, J.P. Allen, M.Y. Okamura, D.C. Rees *Nature* **1989**, *339*, 111

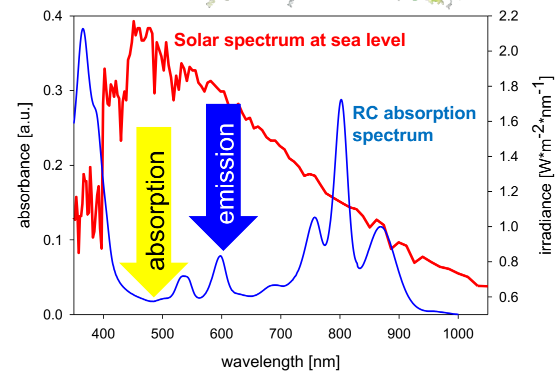
## The photocycle




## Bio-organic hybrid photoconverter

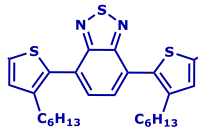


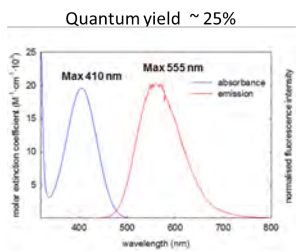



R. R. Tangorra, A. Antonucci, F. Milano, S. la Gatta, G. M. Farinola, A. Agostiano, R. Ragni, M. Trotta, *CRC Handbook of Photosynthesis*, CRC press, Boca Raton, **2016**, 201-219.

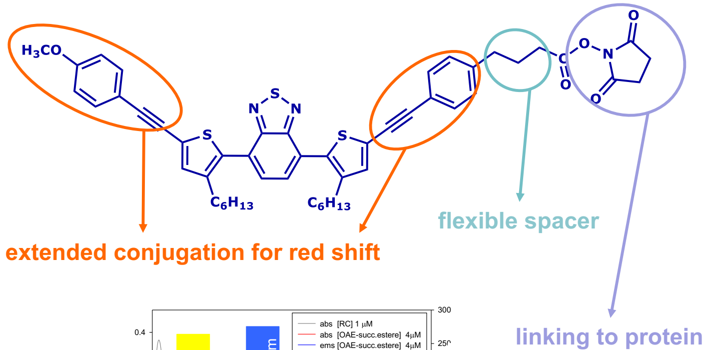
## Antenna design



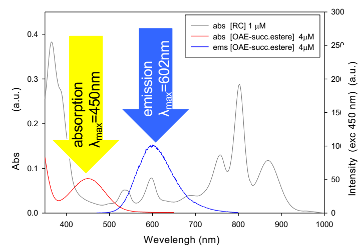




*G. M. Farinola, A Operamolla, F. Babudri et al. Sol. Energy Mater. and Sol. Cells* **2011**, *95*, 3490

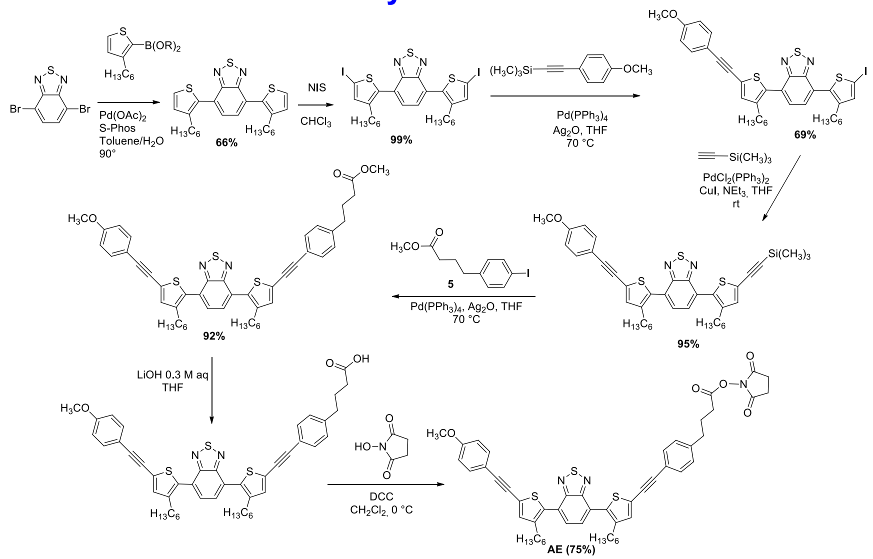
## Antenna design




In TRITON-X-100 solution
Fluorescence QY= 23%
ε(450)=19300 L mol⁻¹cm⁻¹

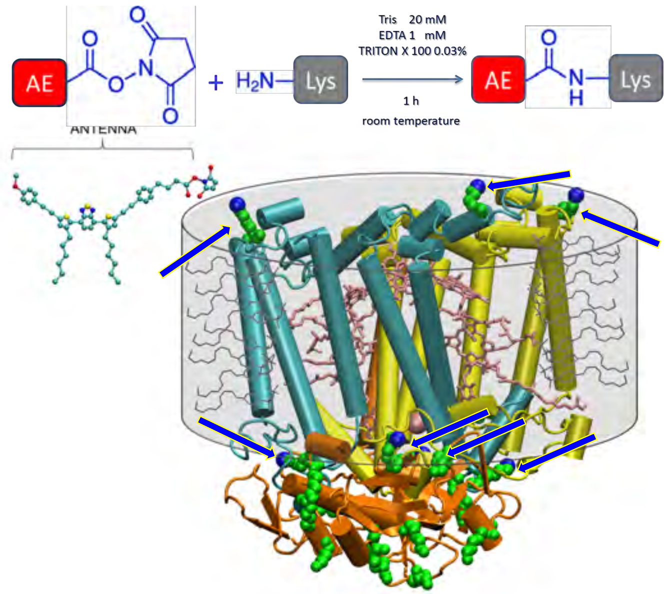


## Synthesis




R. Tangorra, A Operamolla, M. Trotta, G.M. Farinola et al. *Angew. Chem. Int. Ed.* **2012**, *51*, 11019

## Selective bio-conjugation

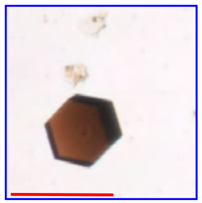



## Bio-conjugate crystallization

**Native RC photoenzime**

200 µm

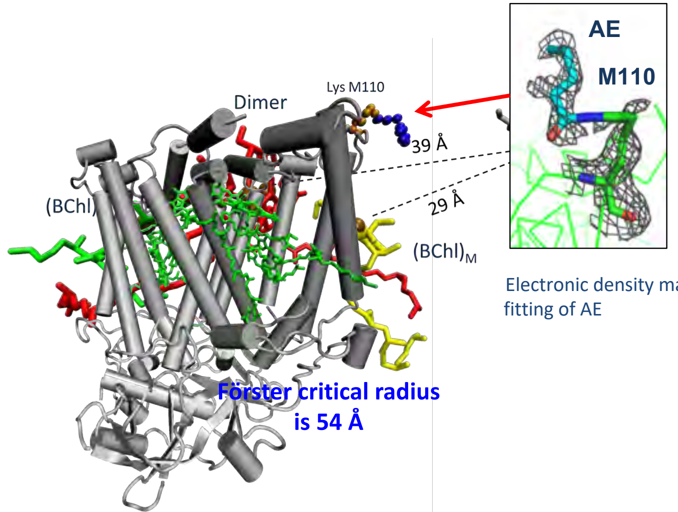
**Bio-conjugate AE-RC**



100 µm

European Synchrotron Radiation Facility - Grenoble

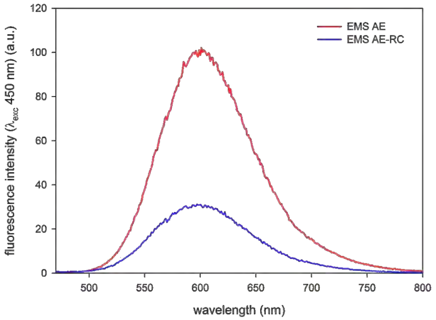
## X-ray structure



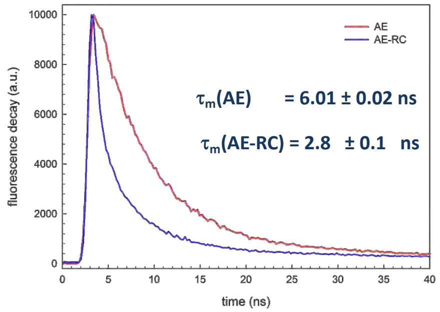

Electronic density map
fitting of AE

# Energy transfer

**ISOLATED & CONJUGATED ANTENNA EMISSION SPECTRA**



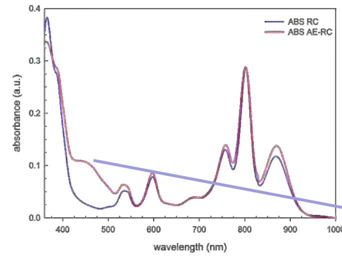

**FLUORESCENCE DECAY**



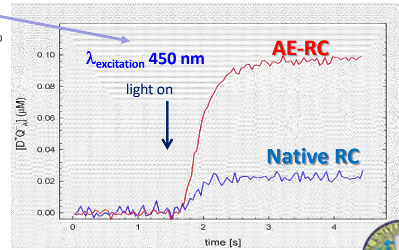

# Enhanced activity of the RC

***Generation of the charge separated state under continuous illumination***

$$DQ_A \xrightarrow{h\nu} D^+Q_A^-$$



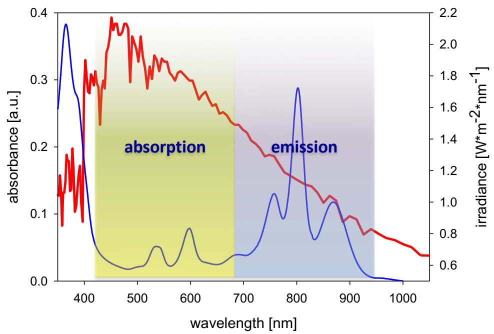

**Five times increase**

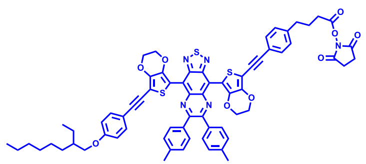



*Angew. Chem. Int. Ed.* **2012**, *51*, 11019

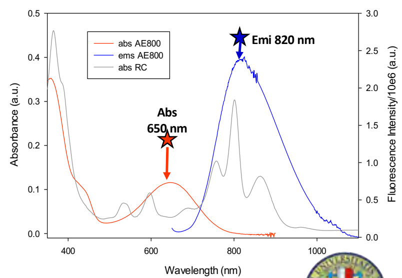
# Antenna with extended absorption

- ✓ *Absorption in the visible spectral range*
- ✓ *Emission with high quantum yield in the NIR region*

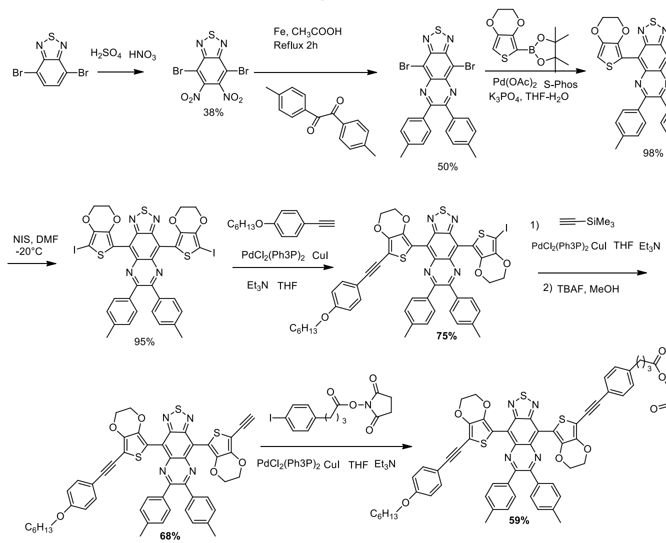


**AE800**

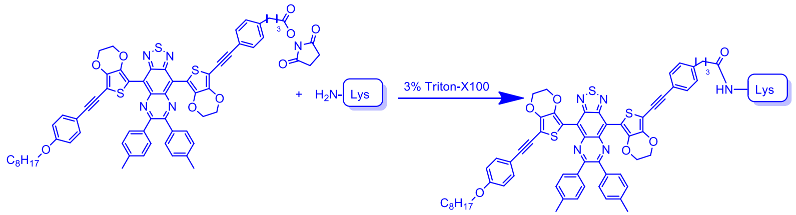



# Synthesis




O. Hassan Omar, S. la Gatta, R. R. Tangorra, F. Milano, R. Ragni, A. Operamolla, R. Argazzi, C. Chiorboli, A. Agostiano, M. Trotta, G. M. Farinola, *Bioconjugate Chem.* **2016**, 27, 1614–1623.

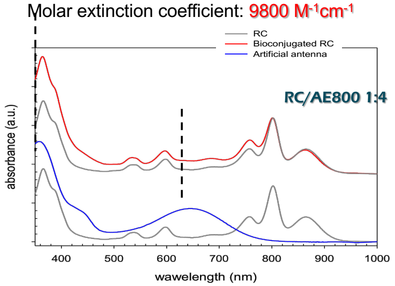
# Bio-conjugation



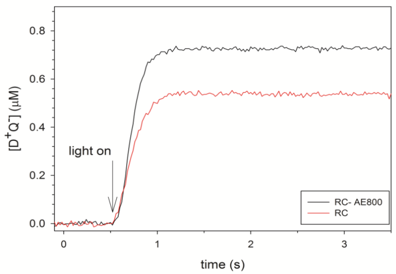

Fluorescence QY: 5.6%

Fluorescence lifetime: 1.2 ns

Molar extinction coefficient: 9800 $M^{-1}cm^{-1}$

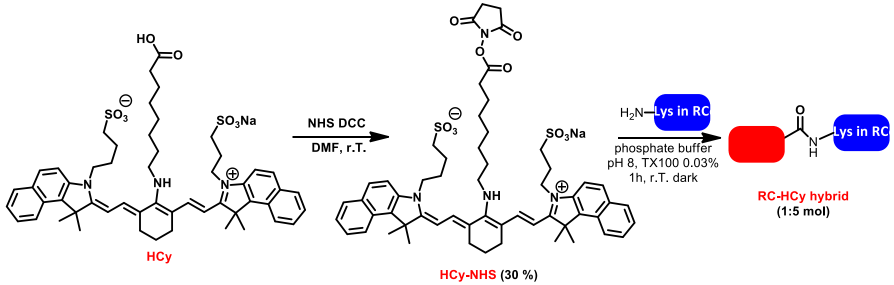


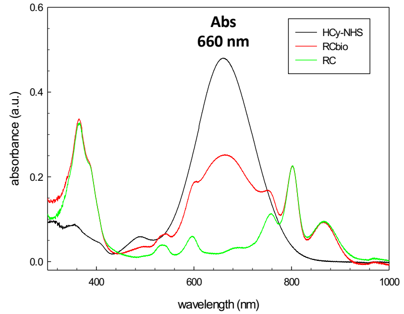

*White light: 30% activity increase*



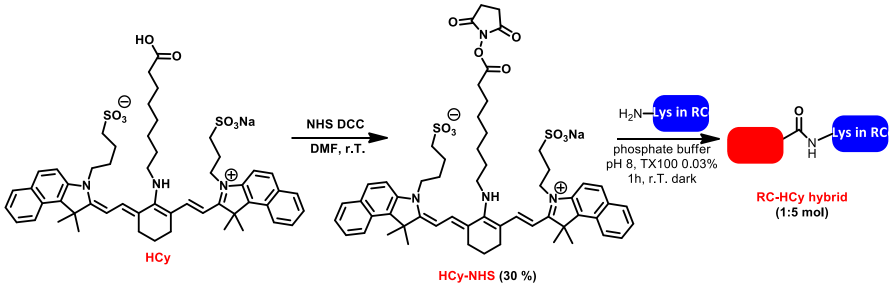

O. Hassan Omar, S. la Gatta, R. R. Tangorra, F. Milano, R. Ragni, A. Operamolla, R. Argazzi, C. Chiorboli, A. Agostiano, M. Trotta, G. M. Farinola, *Bioconjugate Chem.* **2016**, 27, 1614–1623.

# Cyanine dyes for white light harvesting



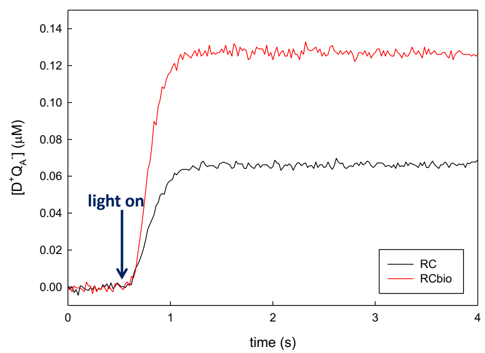




# Cyanine dyes for white light harvesting

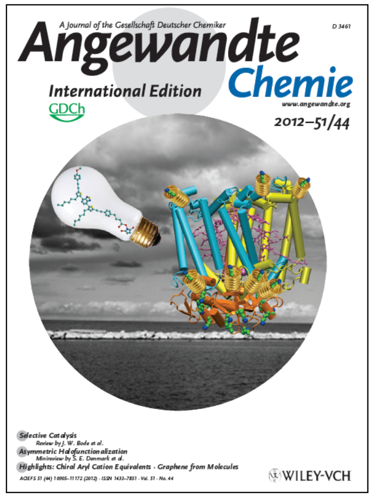



**90% INCREASE under continous illumination**

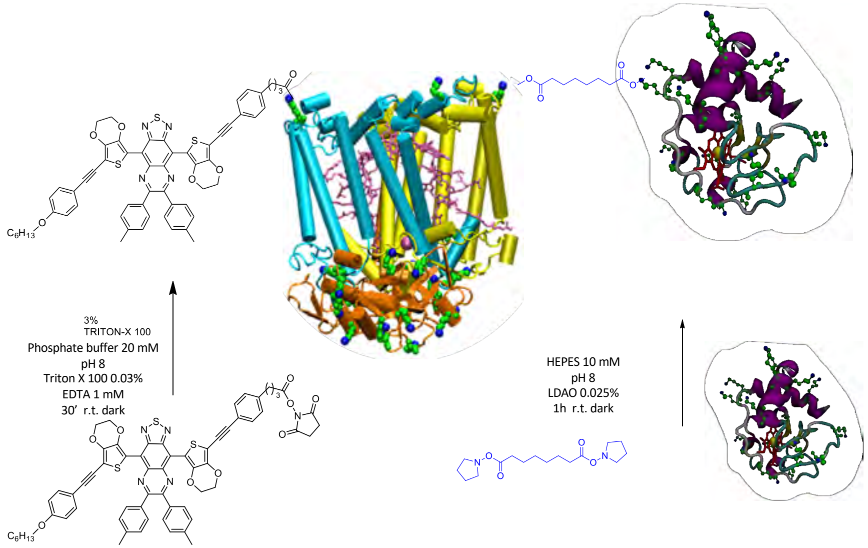
**λexc = 380-668 nm**



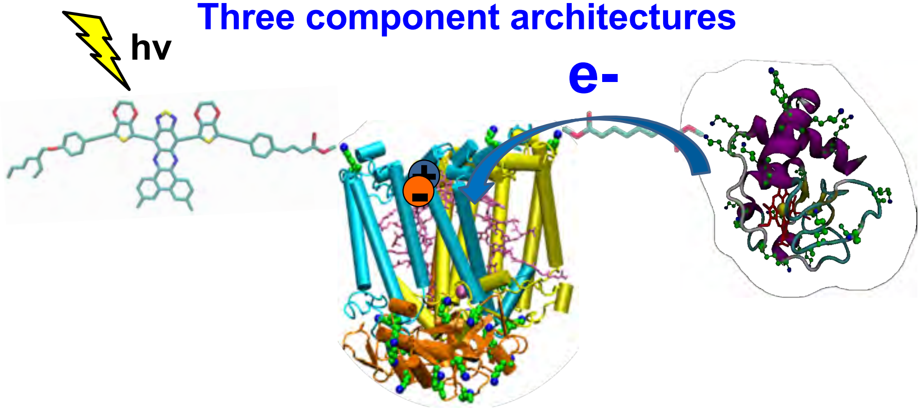

# Enhancing the light harvesting capability of a photosynthetic reaction center by tailored molecular fluorophores

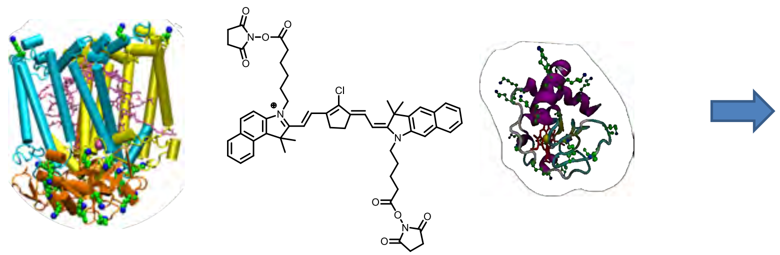
# Three component architectures

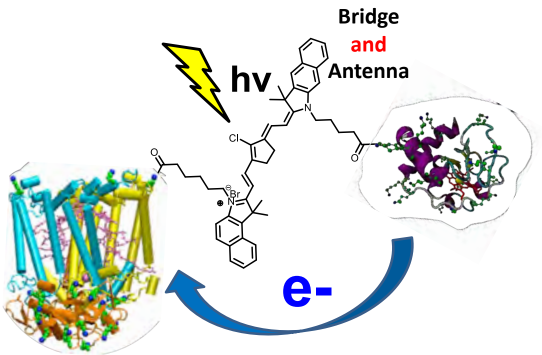


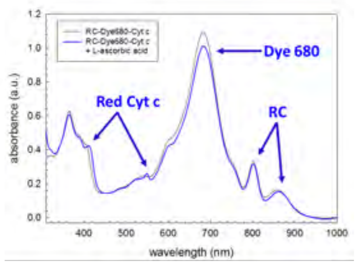

# Three component architectures



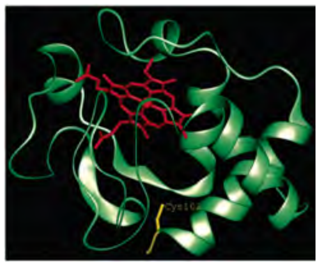

# Three component architectures






# …and genetic modification…



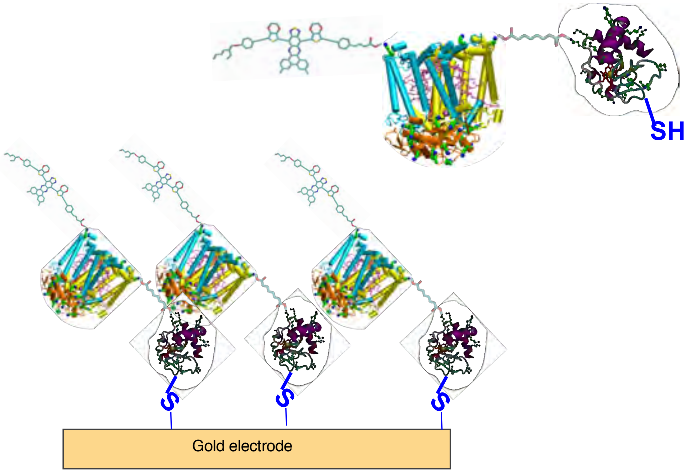
NATIVE

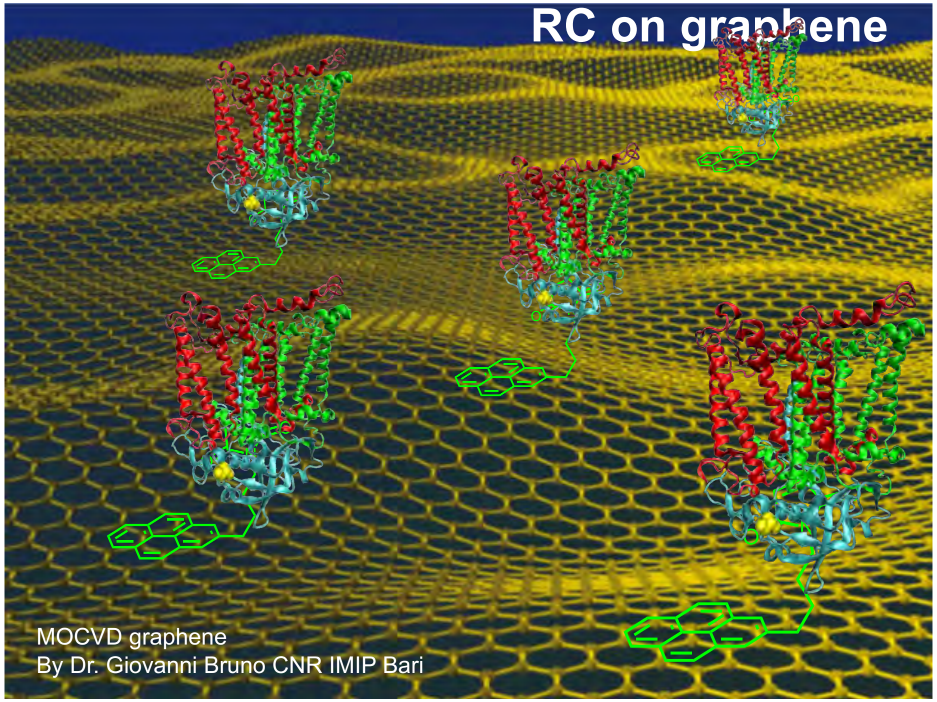

MUTANT:

1) BETTER ORIENTATION FOR ELECTRON TRANSFER
2) SH FOR ASSEMBLY ON GOLD ELECTRODE

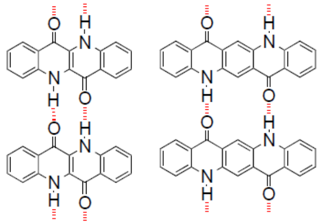
C. Augusto Bortolotti, G. Battistuzzi, M. Borsari, P. Facci, A. Ranieri, M. Sola *J. Am. Chem. Soc.* **2006**, *128*, 5444

## Funtionalization via protein mutation



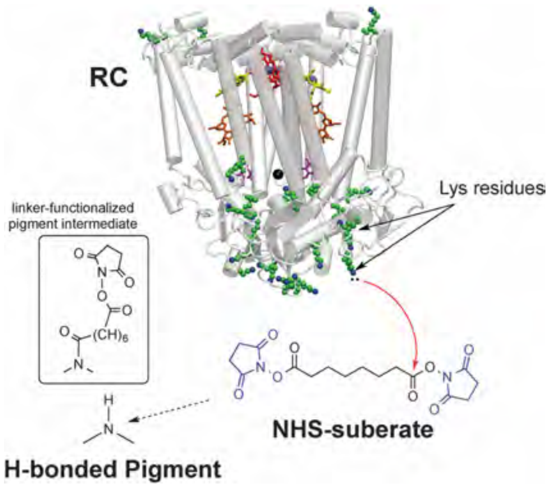




## RC and H-bonded organic semiconductors

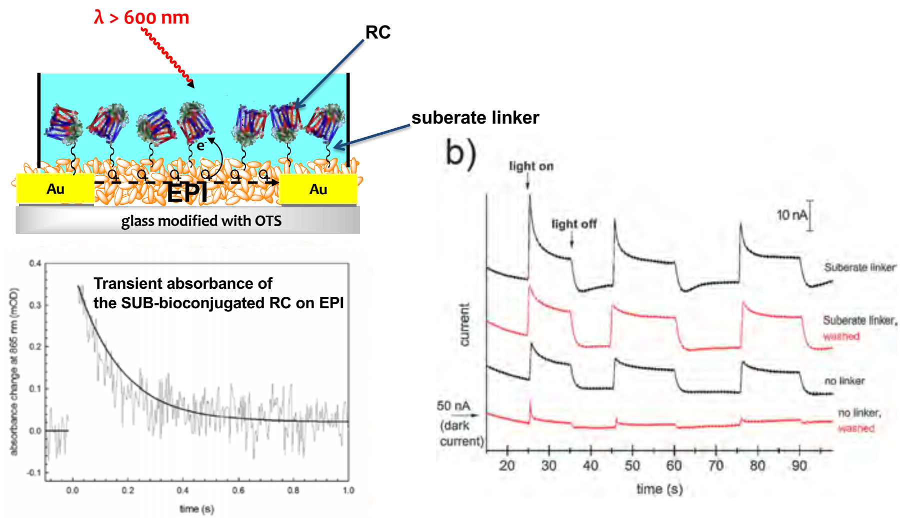


EPI QNC

E. D. Glowacki, N. S. Sariciftci, et al.
*Adv. Mater.* **2013**, *25*, 6783




## RC-sensitized photoconductor device




E. Głowacki, R. Tangorra, H. Coskun, D. Farka, A. Operamolla, Y. Kanbur, F. Milano, L. Giotta, G. M. Farinola and N. S. Sariciftci *J. Mater. Chem. C*, **2015**, *3*, 6554-6564

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Rhodobacter sphaeroides


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*PRIN (Italian MIUR)*
AQUA-SOL

**FET OPEN: HYPHOE (2018)**
**Hybrid electronics based on photosynthetic organisms**

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