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Brno University of Technology

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Novel materials for preparation of active thin layers for organic photonics

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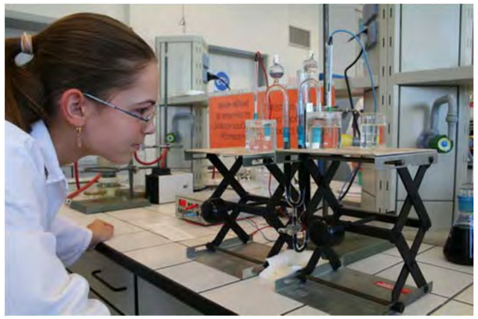


Materials Research Centre

Research focus

- Inorganic silicon based materials (e.g. geopolymers)
- Physical chemistry of colloids
- Advanced organic materials for organic electronics, bioelectronics, photonics and sensors
  - development of new materials (phtalocyanines, diketopyrrolo-pyrroles, pi-conjugated polymers)
  - their complex characterization with focus on stability, processability, optical and electrical properties
  - deposition of multilayered thin organic systems for broad range of applications such organic photovoltaics, sensors, organic photonic devices, etc.

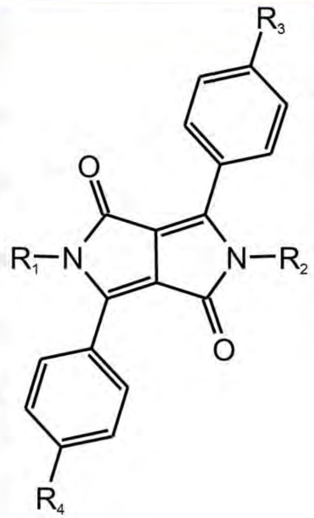
Outline

- Low molecular materials for photonic application - DPPs as an example
- Preparation of soluble materials
- Influence of different substitutions
- Thin film morphology and properties
- Applications
  - Photonics
  - Sensors
  - Photovoltaic textiles

Why DPPs?

One the materials of our interest are small molecular materials called DPPs

- exceptional high thermal and photo stability
- high melting point
- basic molecule extraordinarily bright, stable and resistant to ultraviolet light and extremes of heat and cold



R_1 - R_4 = H:

3,*6*-diphenyl-*2*,*5*-dihydro-pyrrolo[3,4-c]pyrrole-*1*,*4* dione

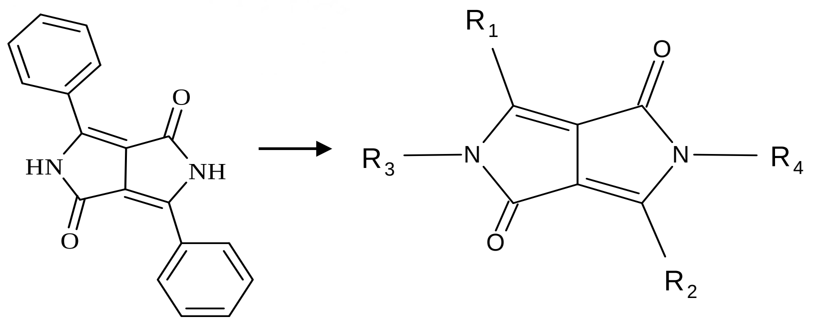
- Pi-conjugated molecule – promising optical and electrical properties (high absorption coefficient, high fluorescence quantum yield)
- The research is driven by cooperation with industrial producer capable of mass production, some materials are currently soled as pigments

Pigment Red 254,
Ciba, Switzerland

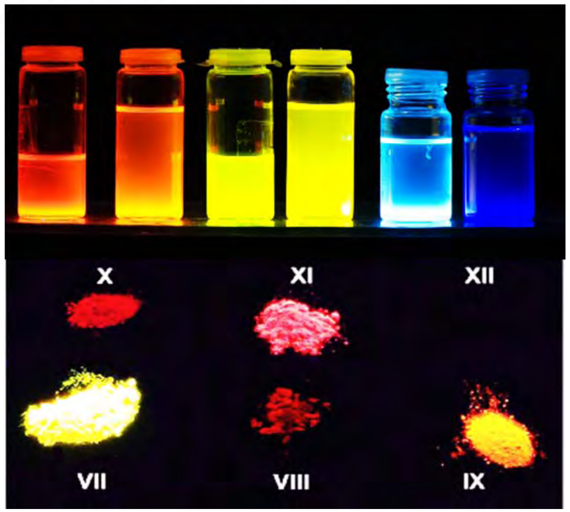
Our approach

- Modification of the molecule by different substitutions to reach desired optical/electrical/sensing properties (based on quantum chemical calculation, which helps us to predict some properties)
- Modification of the solubility: unsoluble derivatives (nanoparticles), soluble derivatives, latent pigments
- Developement of nanoformulations for thin layer deposition (inkjet printing, microdispenzing printing, screen printing, electrophoretic deposition)
- More than 80 derivatives were prepared and characterized, many of them reported for the first time

Pigment Red 254, Ciba, Switzerland



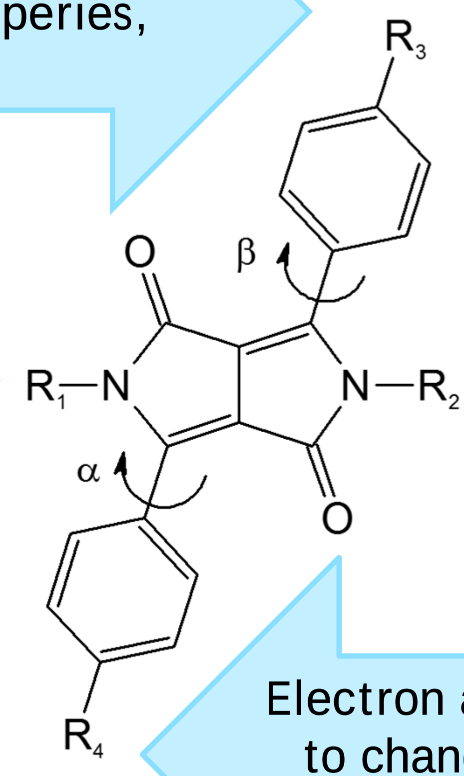
3,6-diphenyl-*2,5*-dihydro-pyrrolo[3,4-c]pyrrole-*1,4* dione



Modification of molecular structure

Electron accepting/withdrawing groups to change the electronic properies, solubilization

Solubilization, polymerization



Solubilization, polymerization

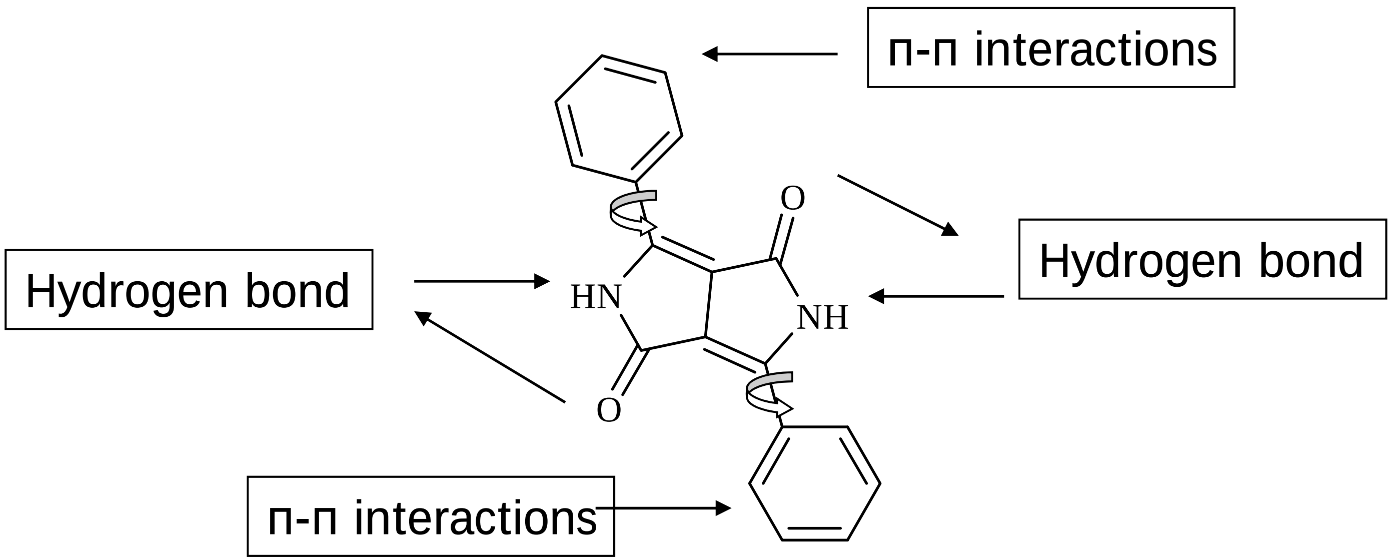
Electron accepting/withdrawing groups to change the electronic properies, solubilization

Solubility

The basic DPP core is perfectly planar

Reason of DPP insolubility is the existence of H-bonds between the -NH group and oxygen and π-π electron overlap in the solid state

Therefoere modified solubility can be achieved either through N-substitution and/or disruption of molecular planarity.

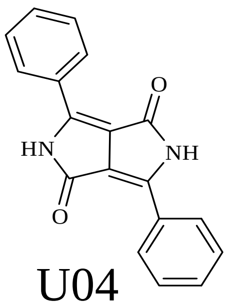


Solubility

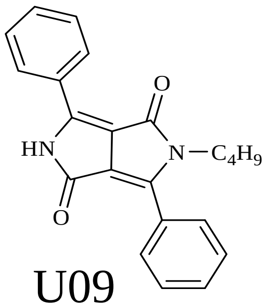
Reason of DPP insolubility is the existence of H-bonds between the -NH group and oxygen because the basic DPP core is perfectly planar and p-p electron overlap occurs in the solid state

Therefoere modified solubility can be achieved either through N-substitution and/or disruption of molecular planarity.

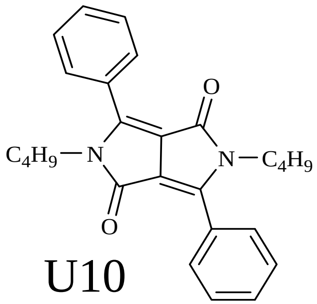
The disruption of molecular planarity was confirmed by quantum chemical calculation



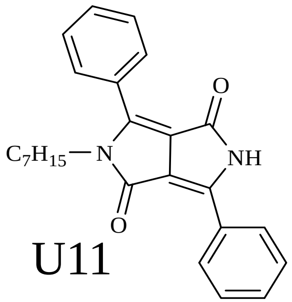
U04



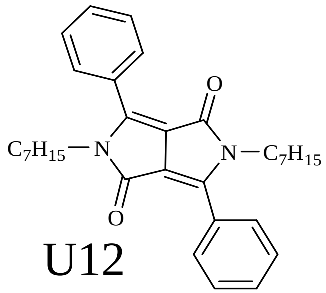
U09



U10

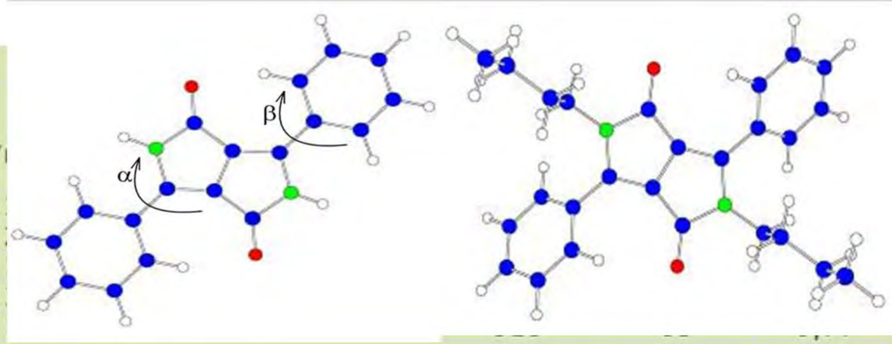


U11



U12

	Calculated						
Derivative	α [°]	β [°]	E_{S0-S1} [eV]	E_{lum} [eV]	ΔE_{Stokes} [eV]	E_{def} [eV]	[I/
DPP U4	0,0	0,0	2,84	2,43	0,41	0,34	
DPP U9	16,9	46,9	2,94	2,42	0,51	0,44	
DPP U10	46,1	46,1	3,01	2,44	0,57	0,48	
DPP U11	46,9	16,9	2,93	2,42	0,51	0,44	
DPP U12	46,0	46,0	3,01	2,44	0,57	0,48	



Vala, M.; Weiter, M. et al., *Journal of Fluorescence* **2008**, *18*, 1181

Solubility

Unsoluble derivatives

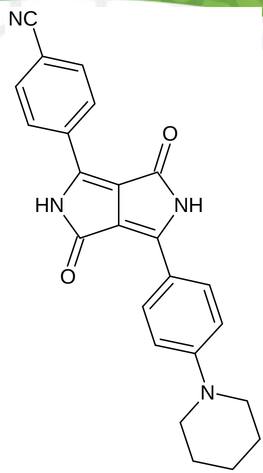
- Nanoparticles, clusters

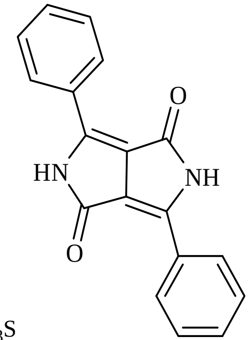
Soluble derivatives

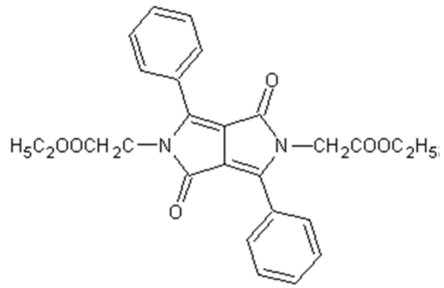
- Symetrically and unsymetrically substituted by different groups; polar and organic solvents

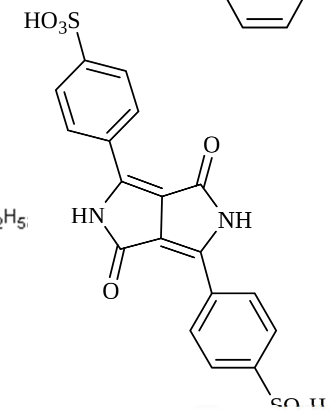
Latent derivatives

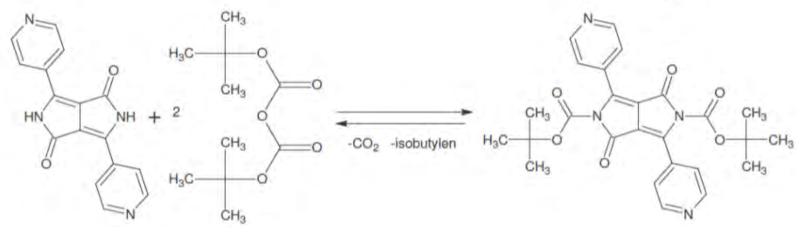
- Irreversible change from soluble to unsoluble material





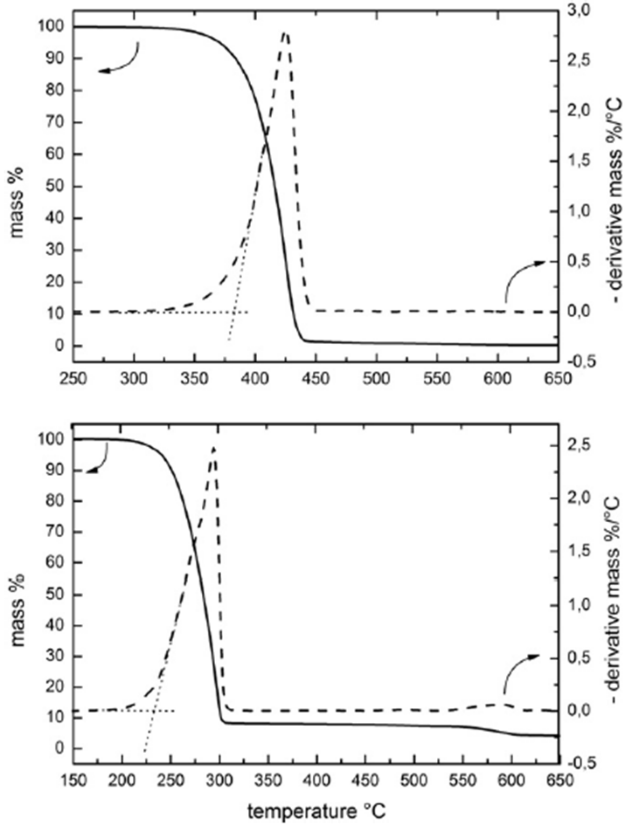




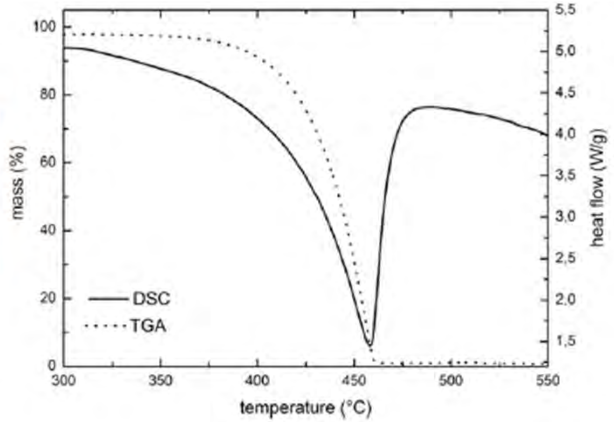


Vala, M.; Weiter, M. et al., *Journal of Fluorescence* **2008**, *18*, 1181
Luňák Jr, S.; Vyňuchal, J.; Vala, M. et al. *Dyes and Pigments* **2009**, *82*, 102
Vala, M.; Vyňuchal, J.; Toman, P.; Weiter, M.; Luňák Jr, S. *Dyes and Pigments* **2010**, *84*, 176
Luňák Jr, S.; Vala, M. ; Vyňuchal, J. , Weiter, M . *Dyes and Pigments* **2011**, *91*, 269

Thermal stability

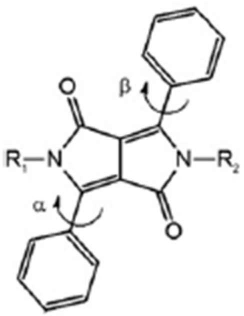


TGA for the DPP-alkyl derivate in the nitrogen and oxygen atmosphere.



Thermogravimetric analyses results.

The onset1 suggests the temperature of evaporation, the onset2 indicates possible beginning of degradation.



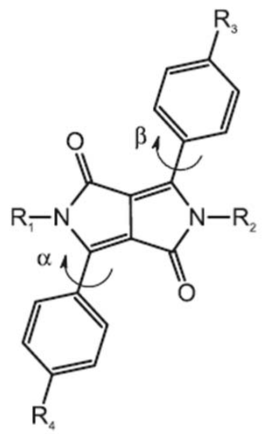
	R_1	R_2
DPP	H	H
DPP-MM	CH_3	CH_3
DPP-B	C_4H_9	H
DPP-BB	C_4H_9	C_4H_9
DPP-H	C_7H_{15}	H
DPP-HH	C_7H_{15}	C_7H_{15}

Sample	Purge gas	$Onset_1$ [°C]	$Onset_2$ [°C]	Char [%wt]	Steps
DPP	N_2	383	396	0.4	1
DPP	air		356	0	1
DPP-MM	N_2	238	262	3.8	2
DPP-MM	air		237	0	2
DPP-B	N_2	269	281	0.1	1
DPP-B	air		267	0	2
DPP-BB	N_2	241	246	0	1
DPP-BB	air		234	0	2
DPP-H	N_2	290	E	0	1
DPP-H	air		267	0	2
DPP-HH	N_2	282	290	0	1
DPP-HH	air		271	0	1

David, J., Weiter, M. et al. *Dyes and Pigments* **2011**, *89*, 137

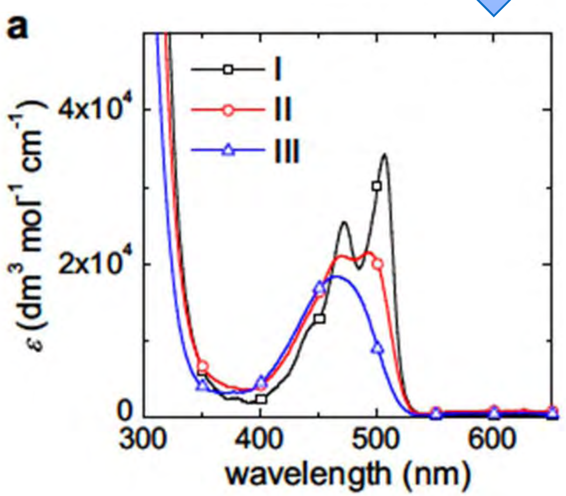
Influence of N-alkylation

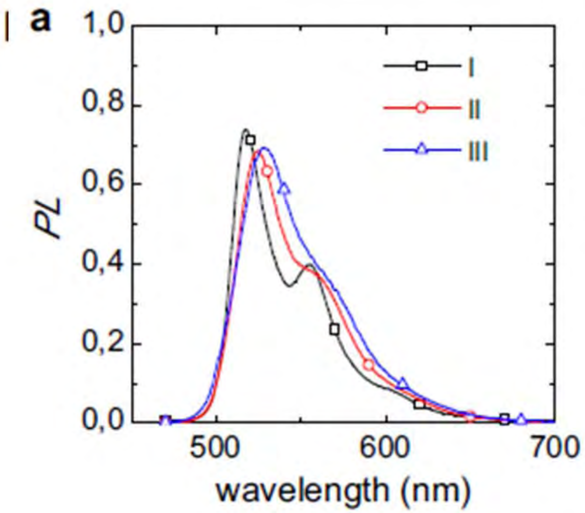
	R_1	R_2	R_3	R_4
I	H	H	H	H
II	C_4H_9	H	H	H
III	C_4H_9	C_4H_9	H	H



The Influence of N-substitution on optical spectra

- insertion of an alkyl group decreases molar absorption coefficient (hypochromic shift)
- simultaneously the longer wavelength maximum is shifted towards higher energy region (hypsochromic)
- the vibration structure is less pronounced





This is caused by torsion between pyrrolinone central part and phenyl adjacent to the alkyl group and consequently, is caused by loss of molecule planarity which is in turn responsible for loss of effective conjugation.

Vala, M.; Weiter, M. et al., *Journal of Fluorescence* **2008**, *18*, 1181

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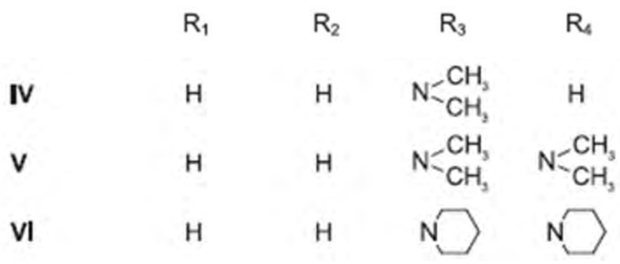
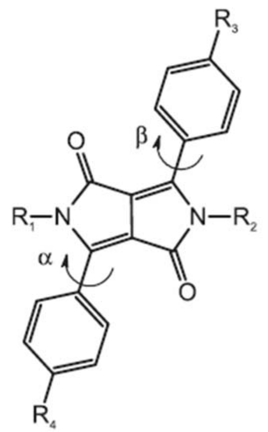
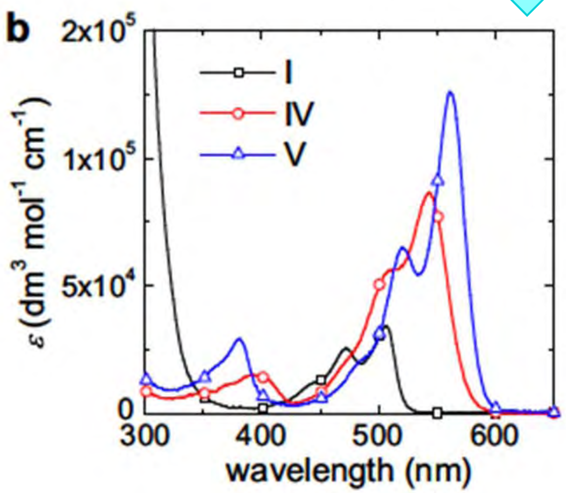
Influence of electron-donating groups

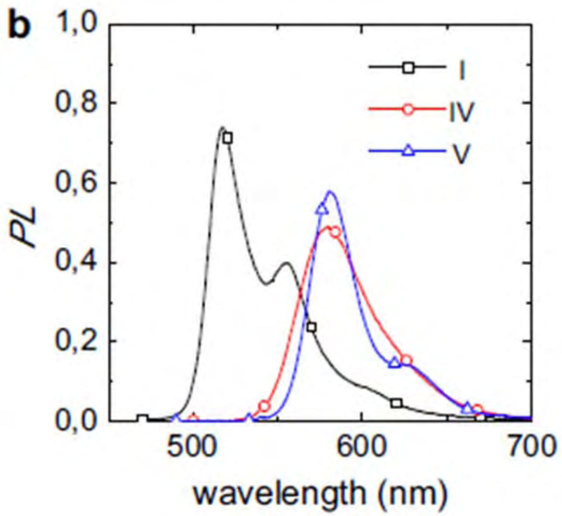




The Influence of electron-donors

- Increase of the molar absorption coeficient of the parent compound I accompanied with strong bathochromic shift (up to 55 nm)
- This behaviour implies that charge separation occurs via electron delocalization leading to creation of permanent dipole moment.





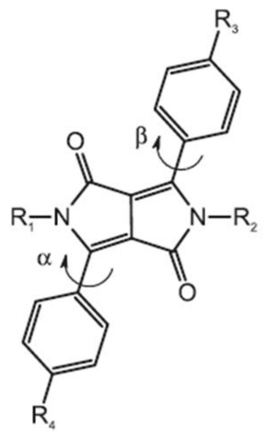
The central part composed of H-chromophores behaves as an electron-accepting group.

Vala, M.; Vyňuchal, J.; Toman, P.; Weiter, M.; Luňák Jr, S. *Dyes and Pigments* **2010**, *84*, 176

Luňák Jr, S.; Vala, M. ; Vyňuchal, J. , Weiter, M . *Dyes and Pigments* **2011**, *91*, 269

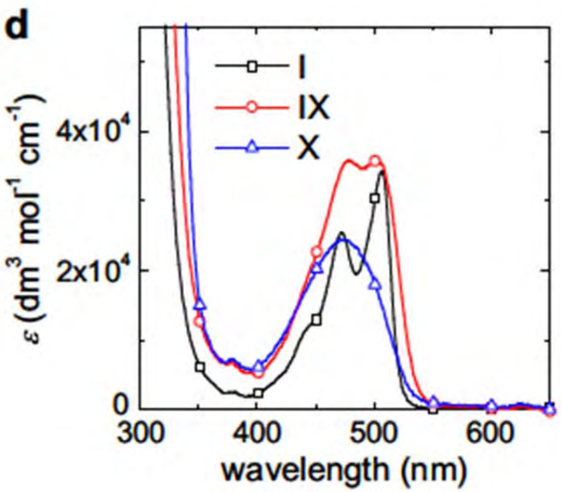
Influence of electron-withdrawing groups

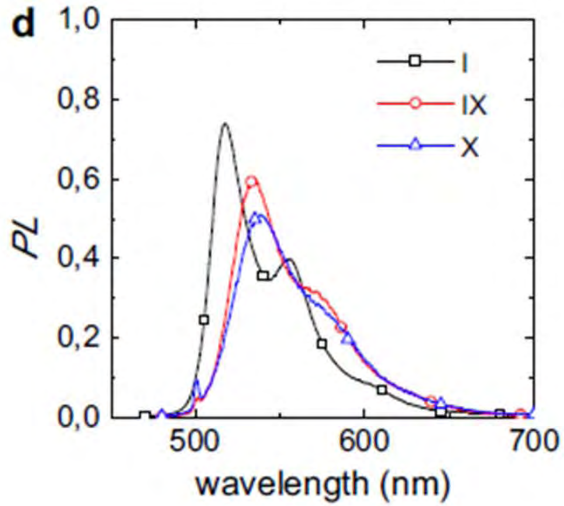
	R_1	R_2	R_3	R_4
I	H	H	H	H
IX	C_4H_9	H	Cl	Cl
X	C_4H_9	C_4H_9	Cl	Cl



The Influence of electron-acceptors

- The introduction of the electron-acceptors did not caused increase of absorption
- This is further evidence for the electron-accepting character of the central part.
- For the alkylated derivatives we observed hypso- and hypochromic shift with the loss of vibration structure again.





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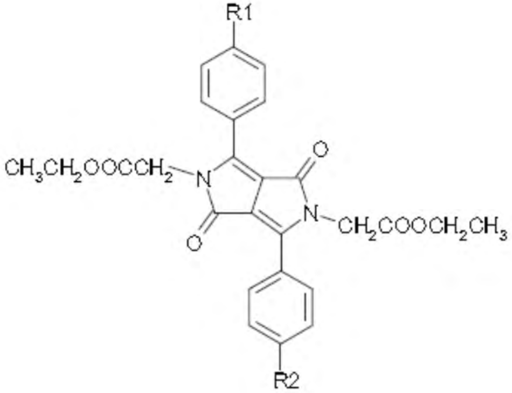
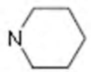
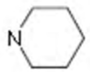
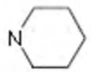
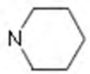
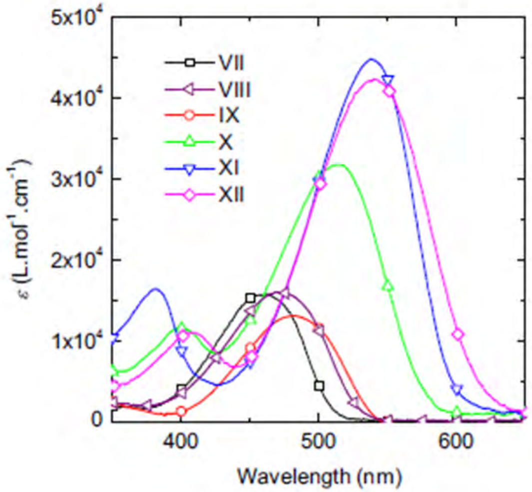
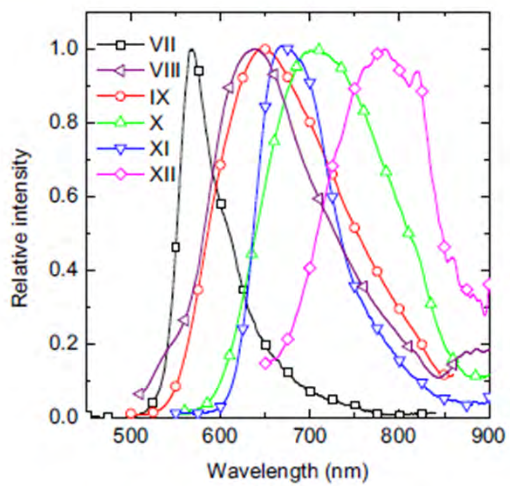
Luňák Jr, S.; Vala, M. ; Vyňuchal, J. , Weiter, M . *Dyes and Pigments* **2011**, *91*, 269

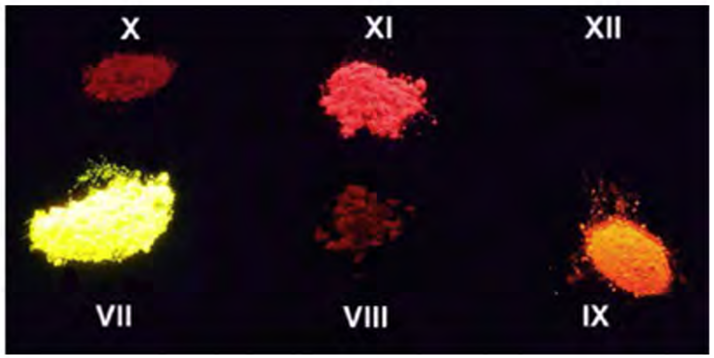
Influence of conjugation



Symbol	R_1	R_2
VII	H	H
VIII	CN	H
IX	CN	CN
X	H	
XI		
XII	CN	

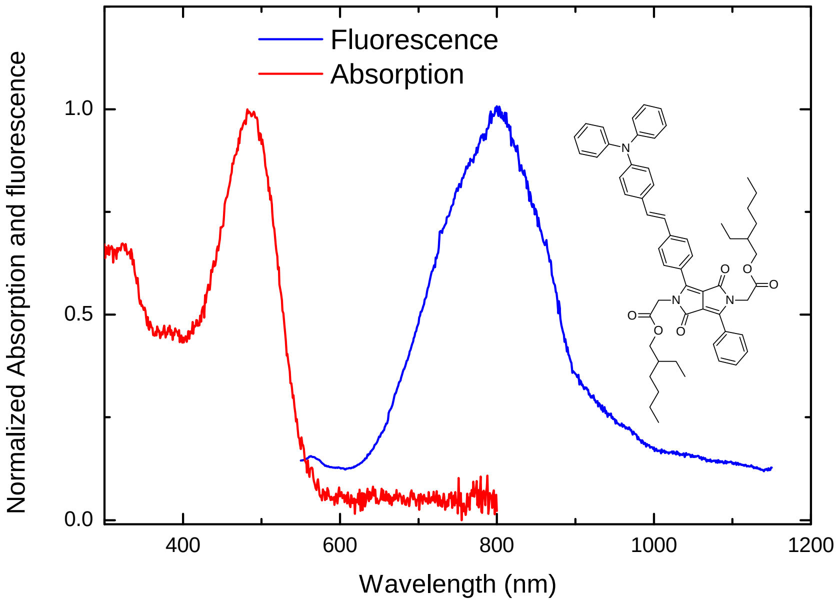


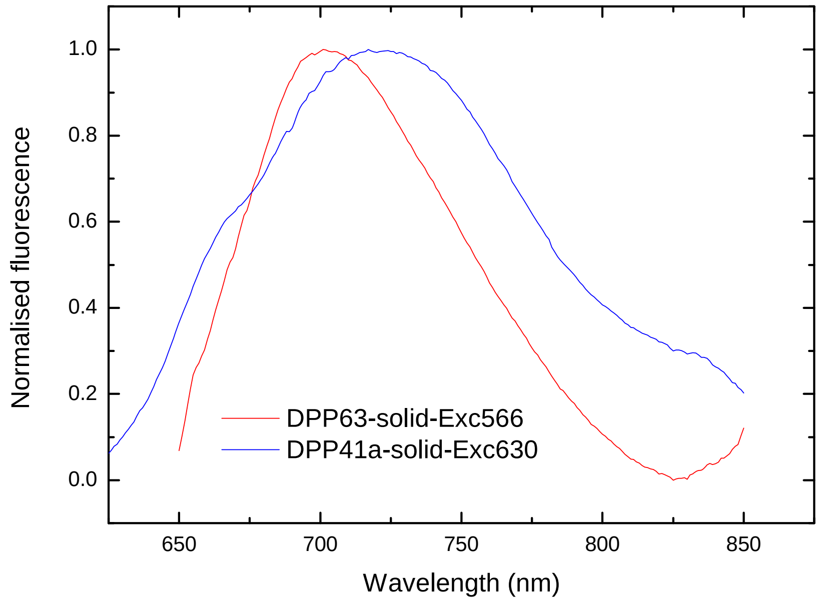


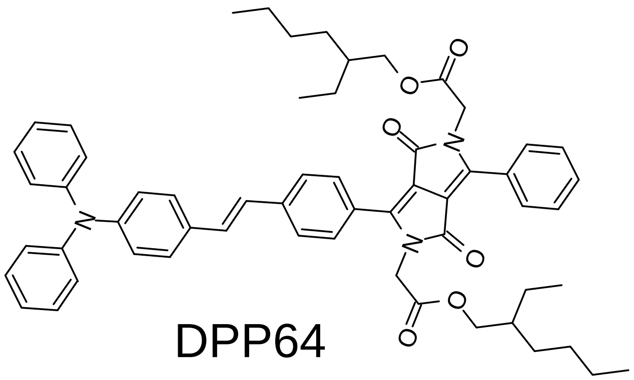


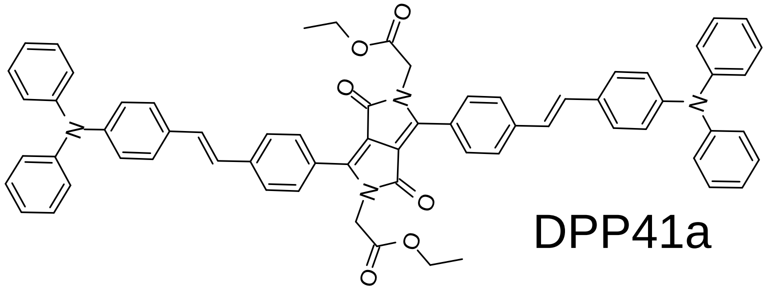
Luňák Jr, S.; Vala, M. ; Vyňuchal, J. , Weiter, M., *Dyes and Pigments* **2011**, *91*

Influence of conjugation

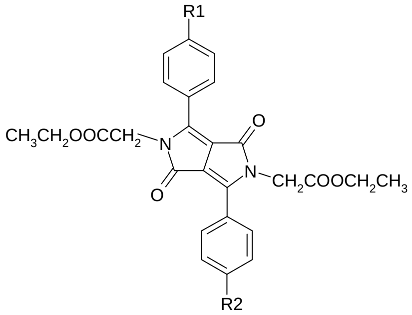





DPP64


DPP41a

Two photon absorption - TPA



Symbol	R_1	R_2
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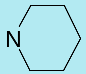
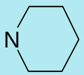
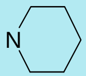
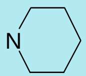
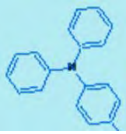
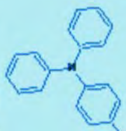
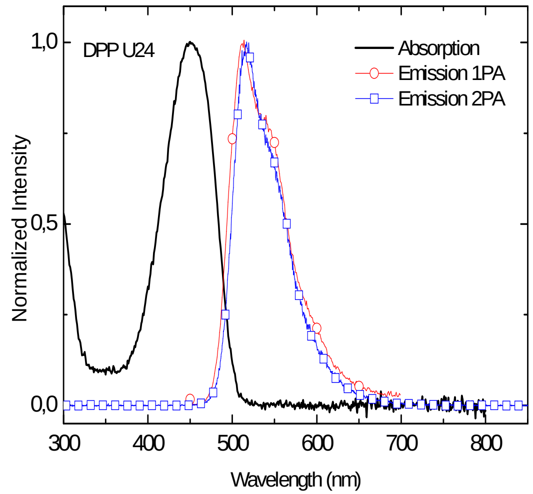
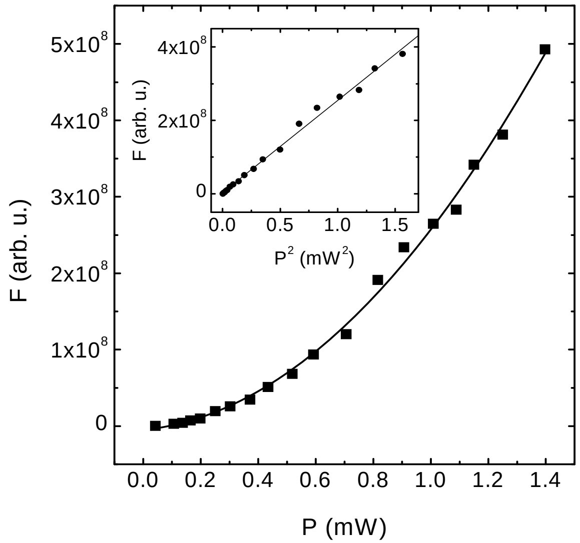
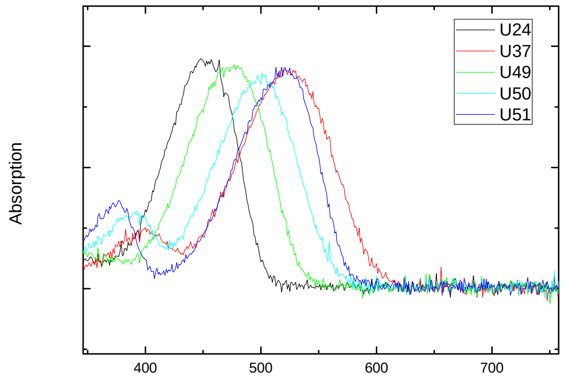
VII	CN	CN
VIII	H	
IX		
X	CN	
XI		

TPA is the simultaneous absorption of two photons. Applications in **Imaging methods in medical diagnostics or in Photodynamic therapy** (if the molecule posses triplet quantum yield).

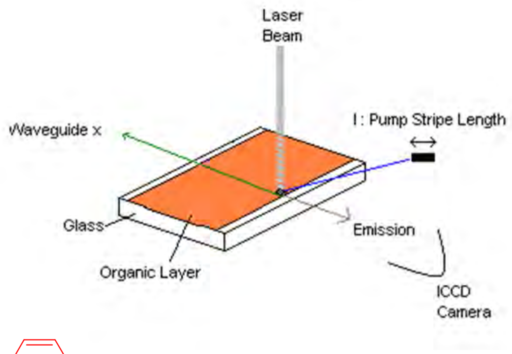




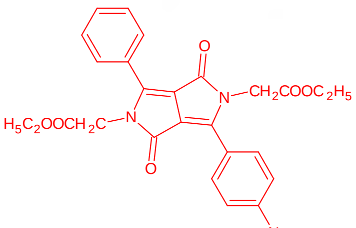
Molecule	λ_{TPF} (nm)	σ_{TPA} (GM)[a]	ε (532 nm) (dm^{-3} mol^{-1} cm^{-1})	σ_{TPE} (GM)[a]
VI	520	2,1±0,4	320	1,7±0,3
VII	555	2,4±0,5	3500	1,7±0,3
VIII	**594**	**1400±300**	**26000**	**170±30**
IX	598	44±9	45000	20±4
X	650	9.3±1.5	44000	0.093±0.029
XI	**595**	**1100±200**	**41500**	**490±100**



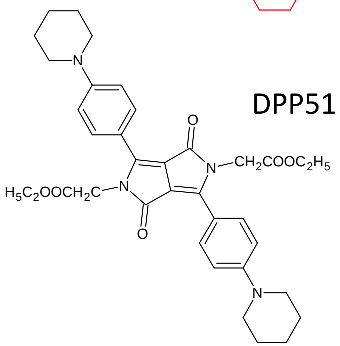
Amplified spontaneous emission - ASE



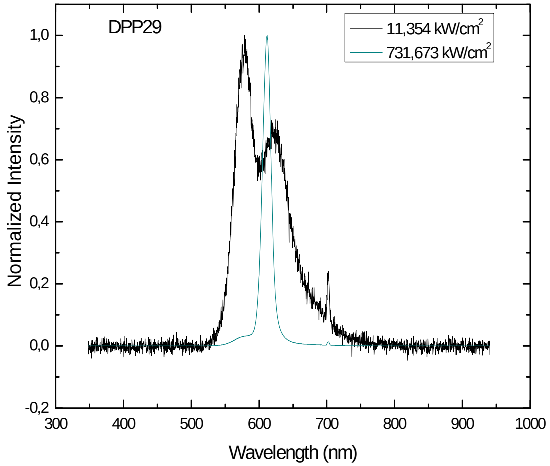
ASE or superluminescence is light, produced by spontaneous emission, that has been optically amplified by the process of stimulated emission in a gain medium. DPP has to be mixed with polymers (PMMA, PS) to create nanostrucured photonic layers.

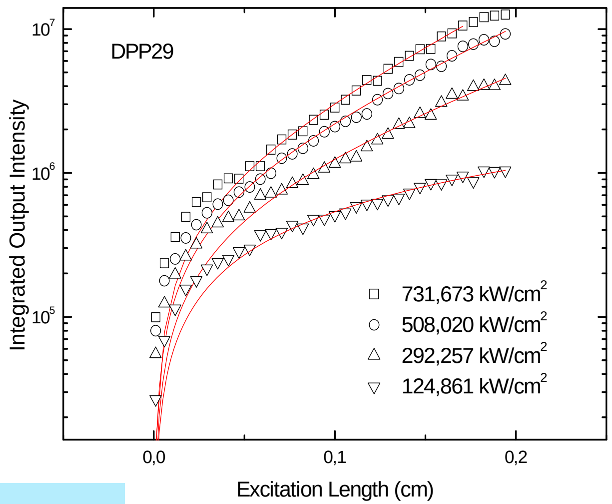


DPP50



DPP51

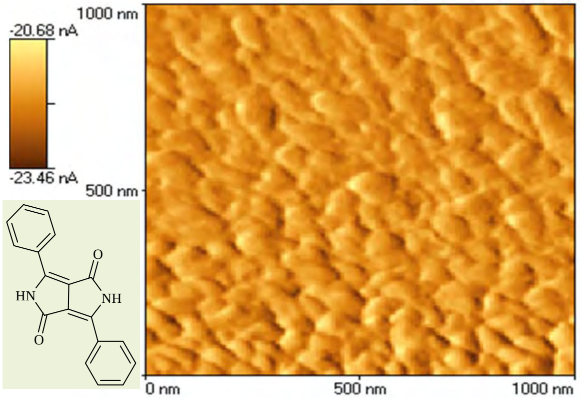


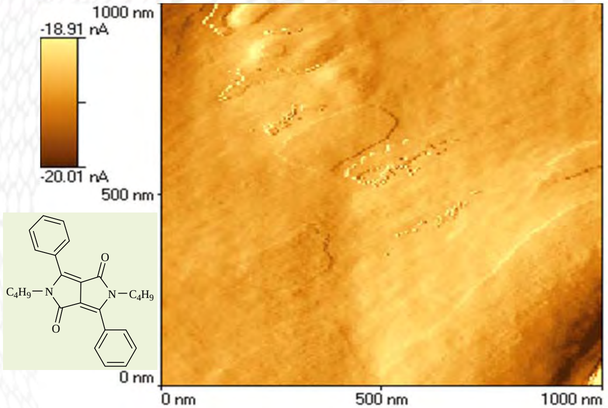


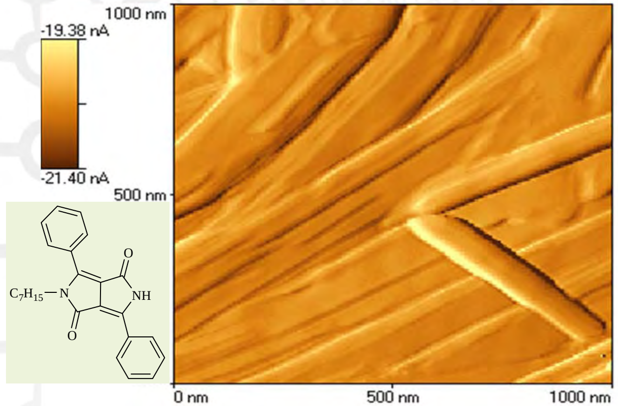
Compound	λ_{ABS} (nm)	λ_{Em} (nm)	E_{th} (kW/cm^2)	λ_{Fl} (nm)	$\lambda_{ASE\text{-}CE}$ (nm)	Φ_{FL}
U29	384	601	257,833	595	631	0.41
U50	398	595	1008,890	567	579	0.12
U51	537	601	298,033	583	612	0.45
U65	404	606	1025,073	574	594	x
U12	301	533	1095,674	525	558	0.77

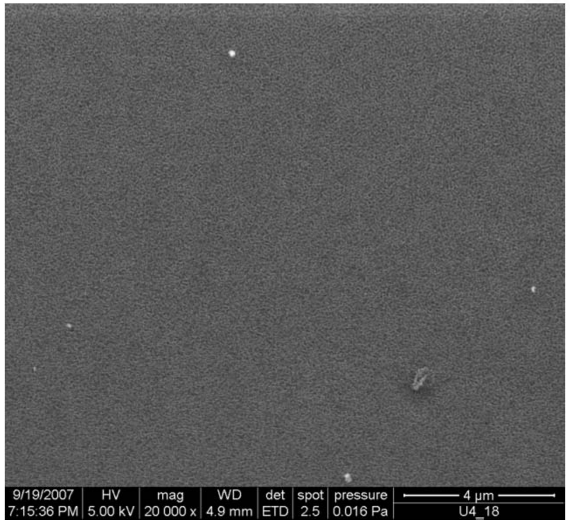
Energy (kW/cm2)	Gain
124,861	4,53
292,257	10,73
508,02	13,26
731,673	15,23

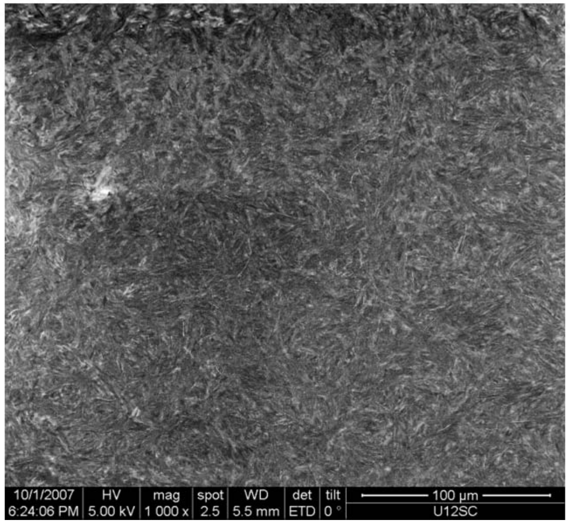
Morphology of thin layers

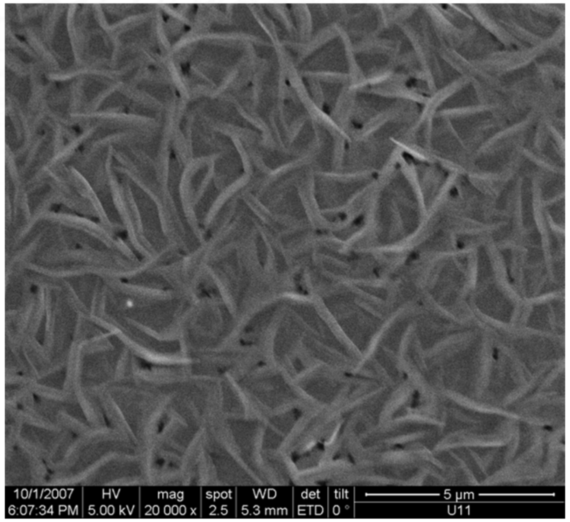








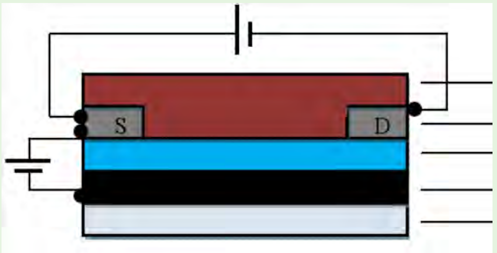




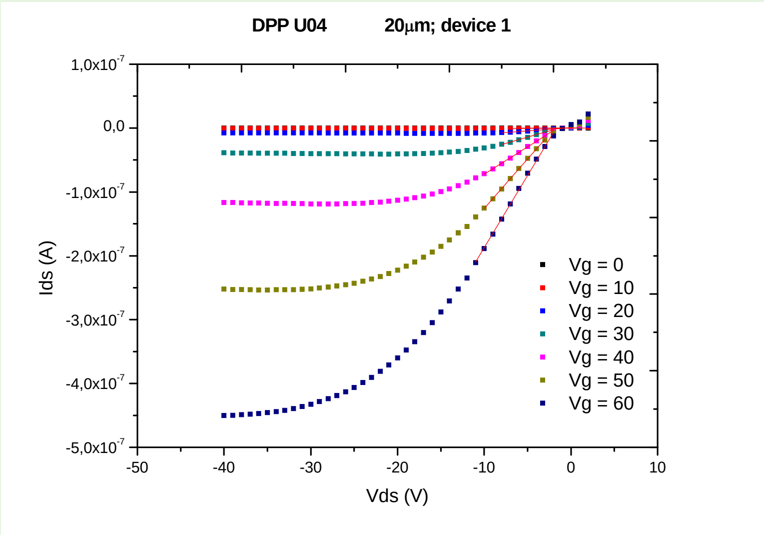
Charge carrier mobility - holes

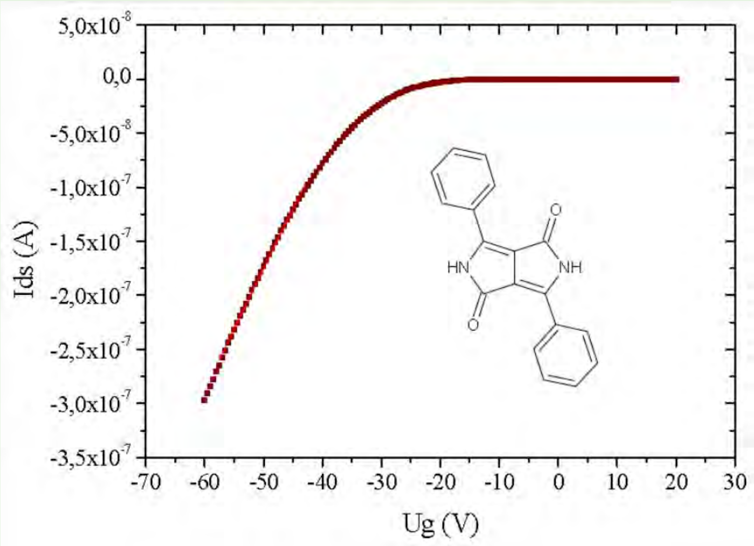
Organic Field Effect Transistors based on different derivatives of DPP were prepared

From the OFET characteristics the **hole mobility** in range from 1×10^{-4} to 1×10^{-9} $cm^2s^{-1}V^{-1}$ were evaluated



Organic semicondutor (e.g. DPP)
Soure and Drain electrodes
Dielectric layer
Gate electrode
Substrate

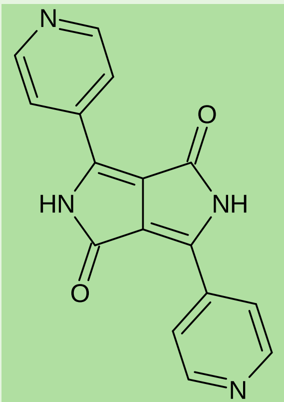


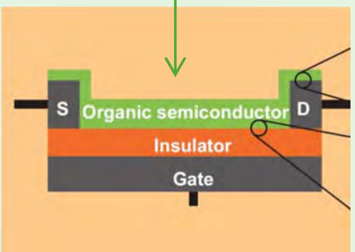


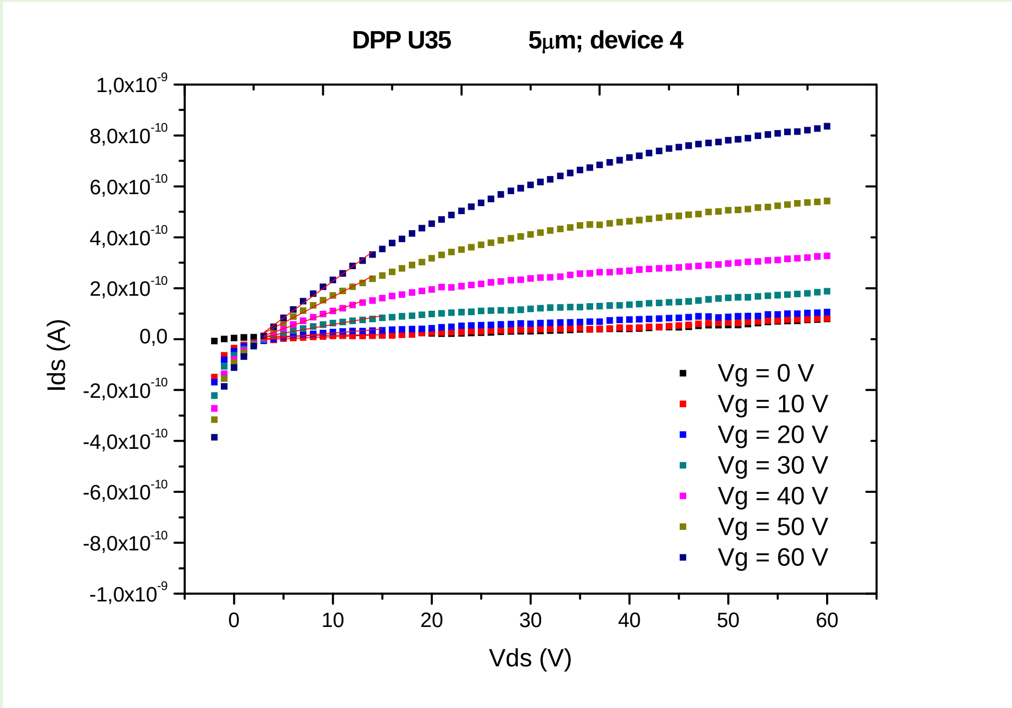
Charge carrier mobility - electrones

Some derivatives exhibit also electron conductivity with **electron mobility** range from 1×10^{-6} to 1×10^{-8} $cm^2s^{-1}V^{-1}$

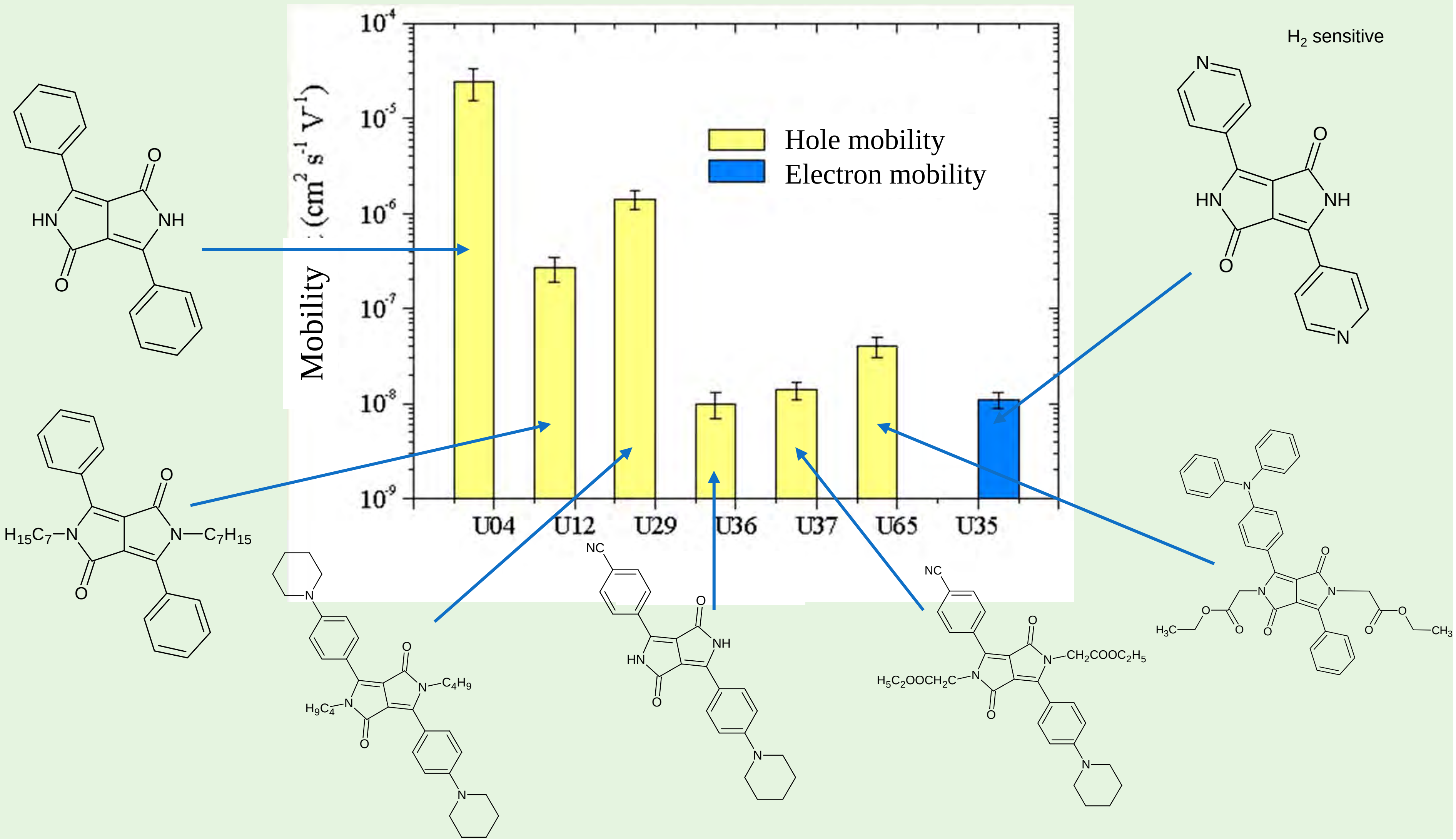
DPP derivatives allow us to prepare both p-type and n-type organic semiconductors



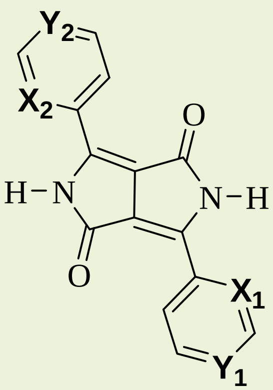




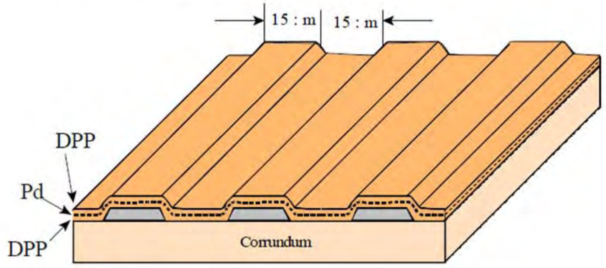
Charge carrier mobility

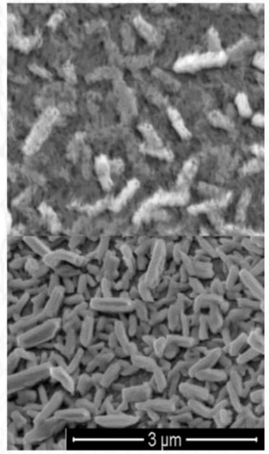


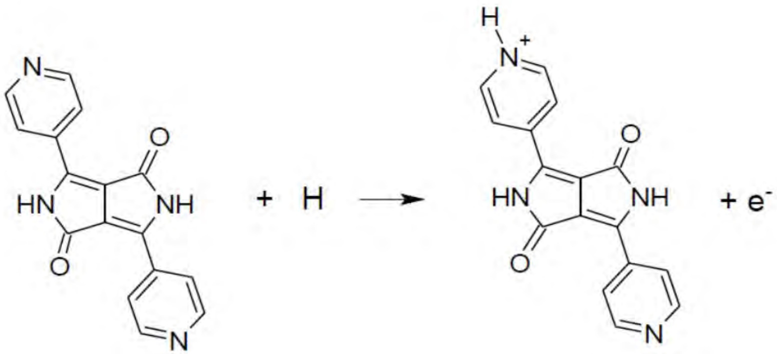
Application: hydrogen sensor



BPPB	$X_1=X_2=Y_1=Y_2=CH$
2PyPPB	$X_1=N$, $X_2=Y_1=Y_2=CH$
2PyPP2Py	$X_1=X_2=N$, $Y_1=Y_2=CH$
4PyPPB	$X_1=X_2=CH$, $Y_1=N$, $Y_2=CH$
4PyPP4Py (DPPP)	$\mathbf{X_1}=\mathbf{X_2}=CH$, $\mathbf{Y_1}=\mathbf{Y_2}=N$







Family of some DPP analogues with pyridyl group can be used for construction of hydrogen sensor wich is sensitive to hydrogen.

To reach this goal it is necessary to prepare some nanostructured layer with DPP and Palladium which enable the dissociation of the hydrogen.

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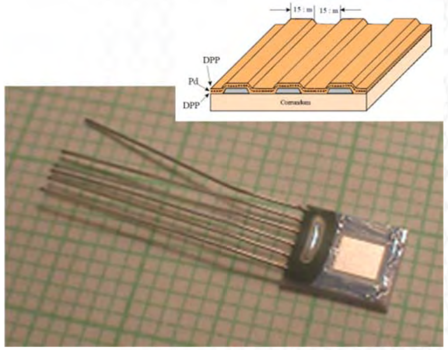
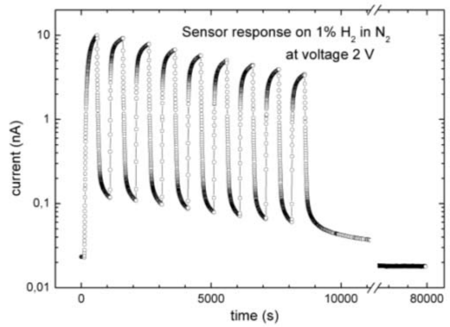
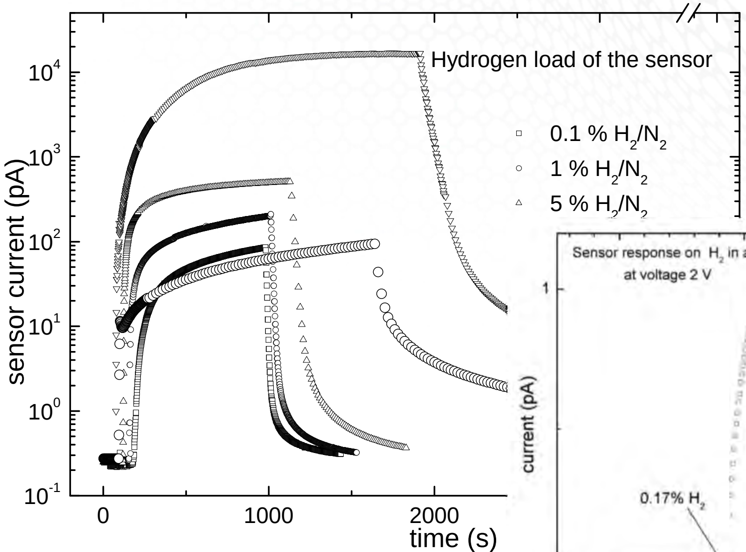
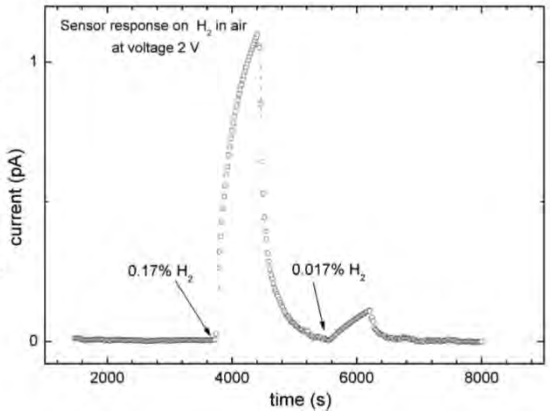
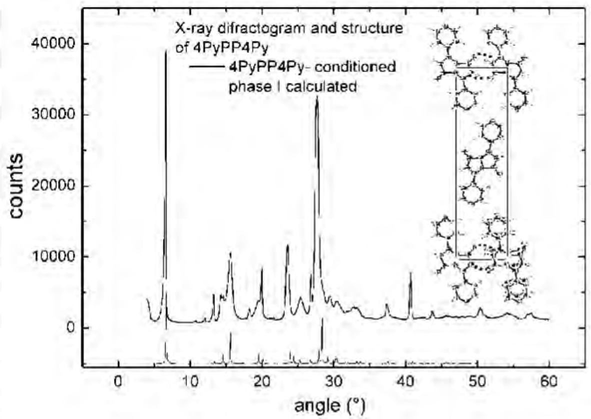
Application: hydrogen sensor

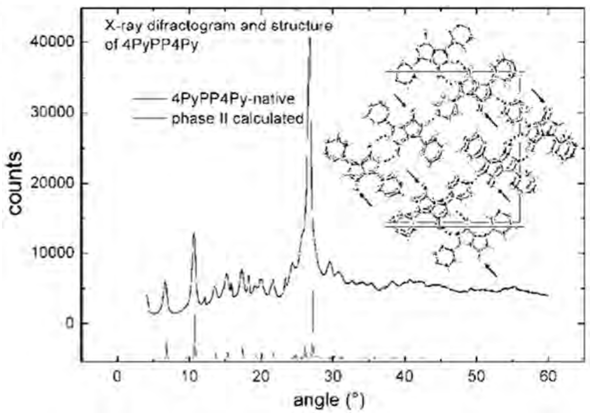












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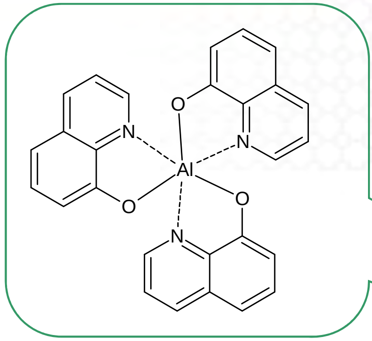
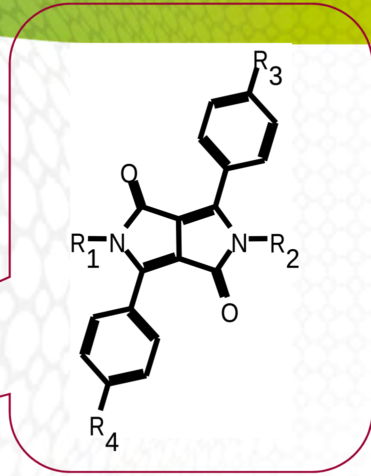
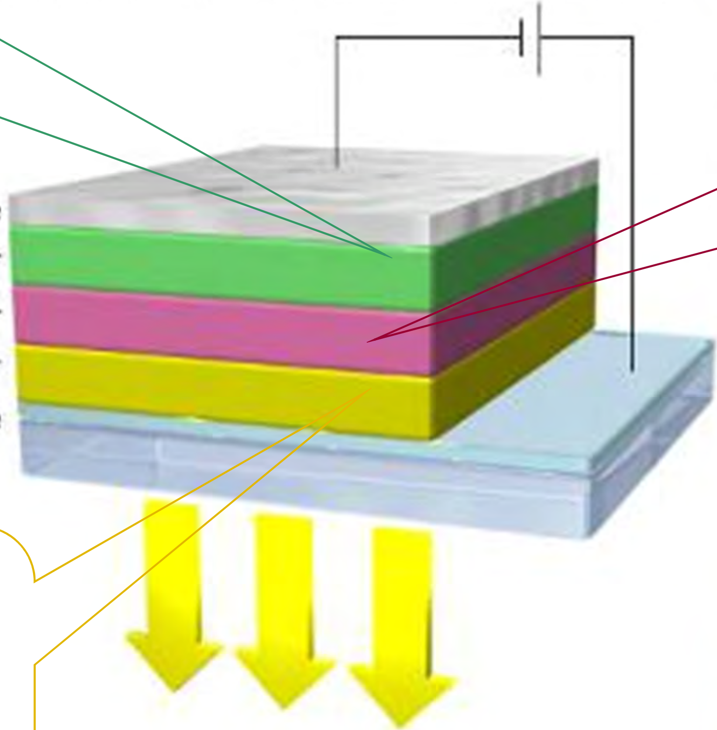
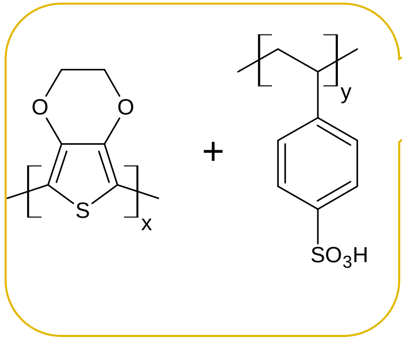
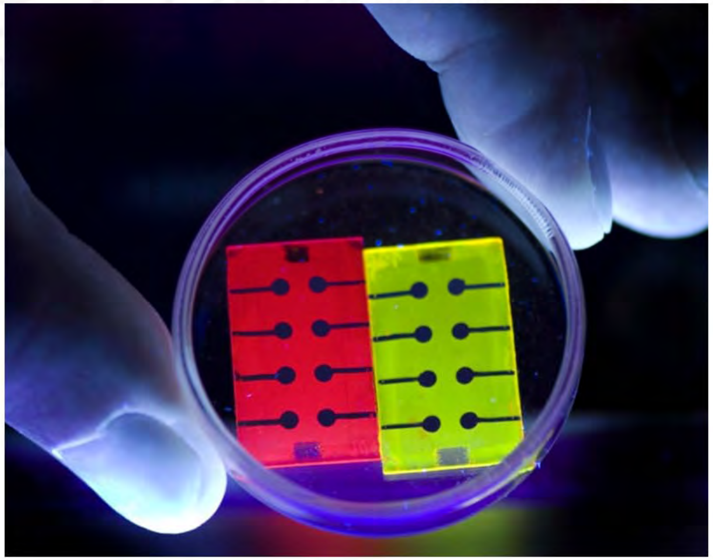
Application: DPPs in OLED











Vala, M.; Weiter, M.; Vyňuchal, J.; Toman, P.; Luňák, S. *Journal of Fluorescence* **2008**, *18*, 1181–1185.

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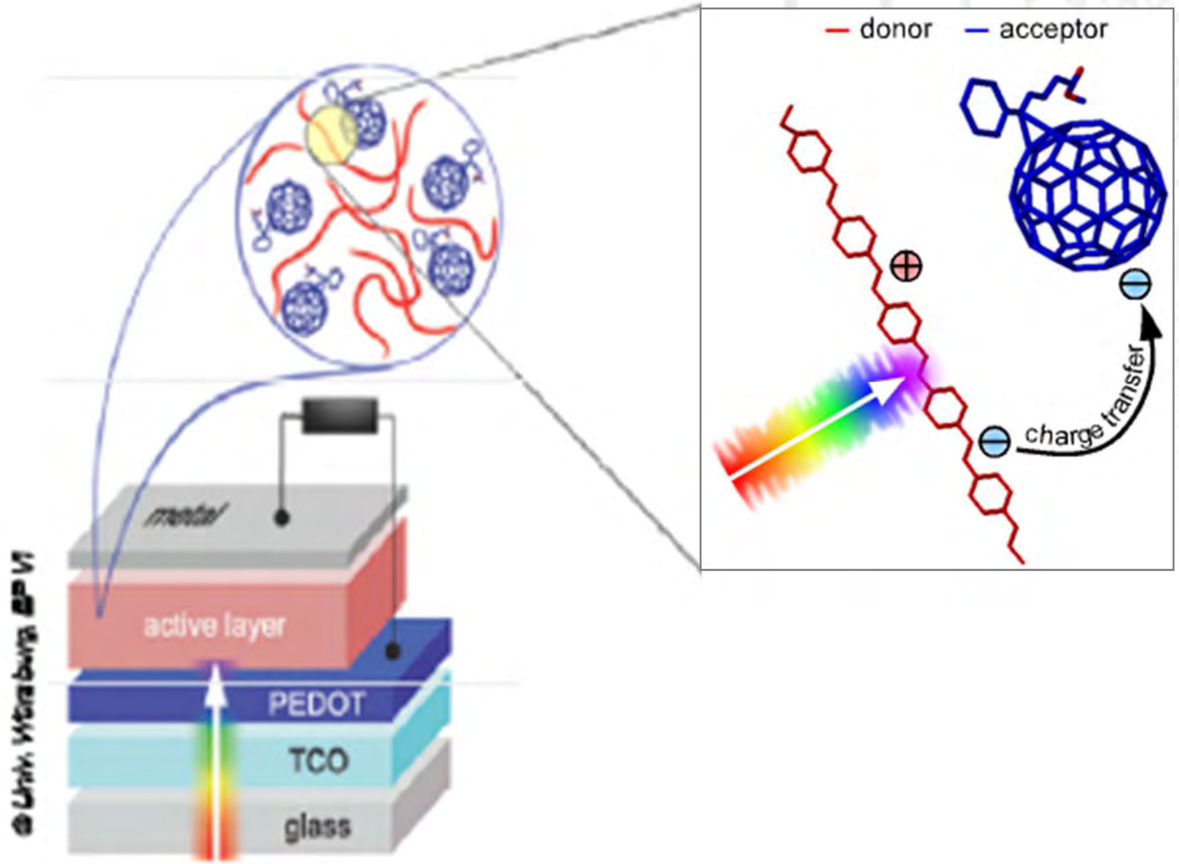
Application: organic photovoltaics

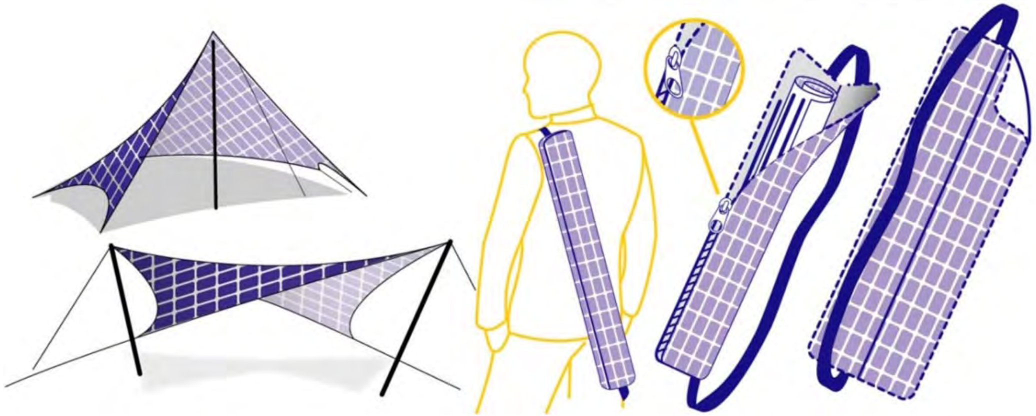


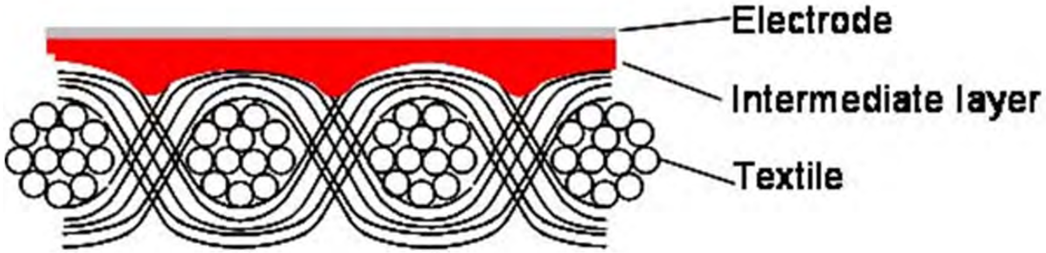
Textile solar cells

FP7-NMP-SME

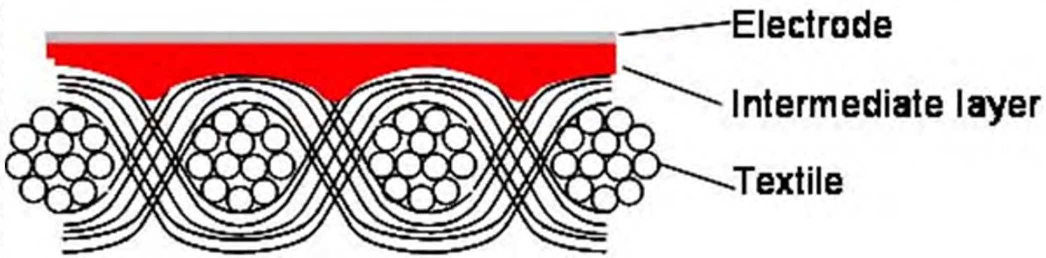
Developement of photovoltaic textiles based on novel fibres

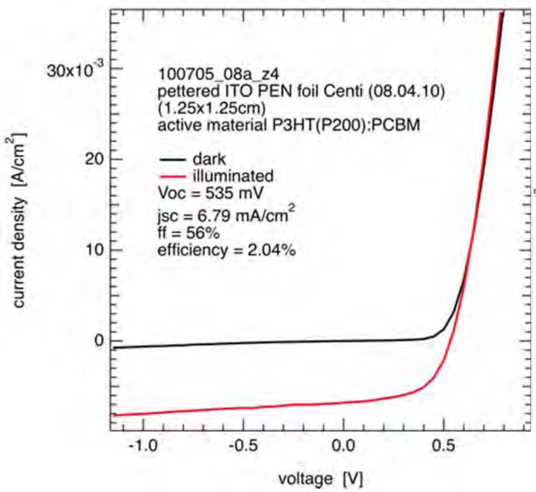
www.dephotex.com

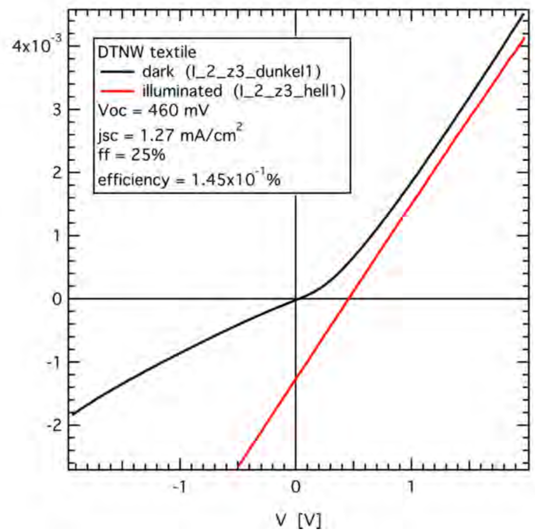


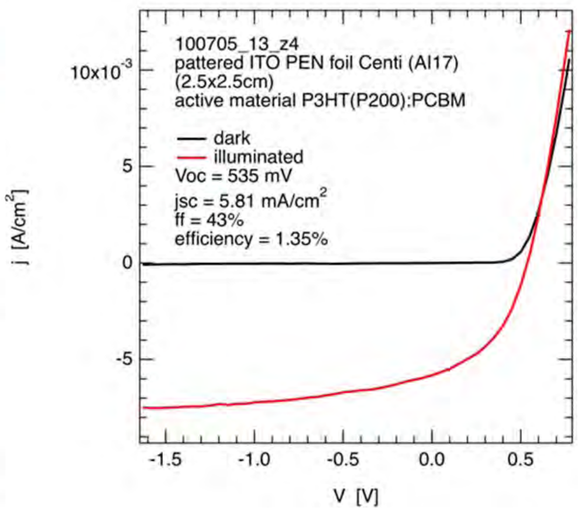


Textile solar cells









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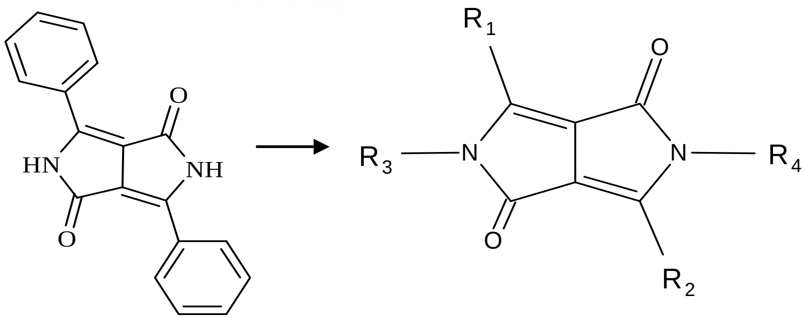
Summary

Unsoluble derivatives	• Nanoparticles, clusters
Soluble derivatives	• Symetrically and unsymetrically substituted by different groups; polar and organic solvents
Latent derivatives	• Irreversible change from soluble to unsoluble material

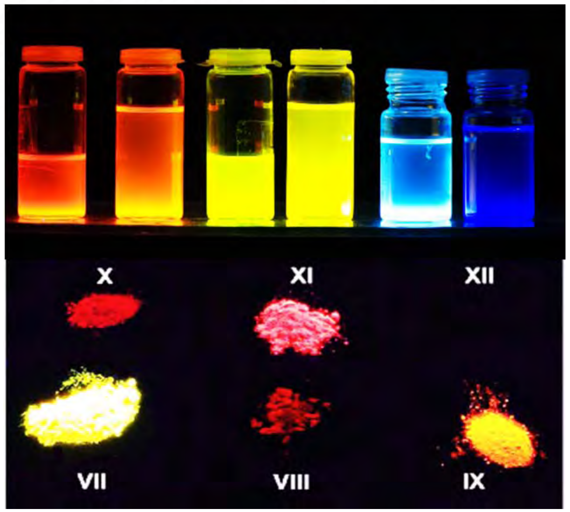
DPP based materials enable us to create the diverse electrical and optical components or subsystems needed for tomorrow's electronics applications:

- ✓ optical devices and components
- ✓ organic field effect transistors
- ✓ organic light emmiting diodes
- ✓ organic solar cells
- ✓ humidity and hydrogen sensors

Pigment Red 254,
Ciba, Switzerland



3,6-diphenyl-*2,5*-dihydro-pyrrolo[3,4-c]pyrrole-*1,4* dione



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