Molecules for plastic electronics:

functionalisation and solubility

Beatrice Saglio

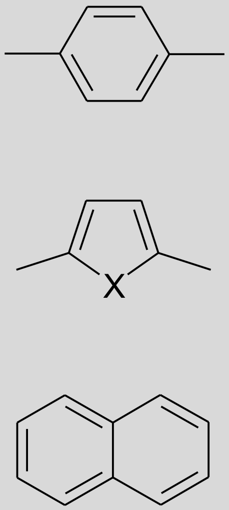
Dipartimento di Chimica, Materiali e Ing. Chimica “G. Natta”

Politecnico di Milano

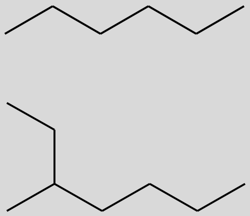
e-mail: beatrice.saglio@polimi.it
tel. 02.2399.3226

Basic ingredients of molecules for organic electronics

Skeleton



Alkyl chains



Functional groups

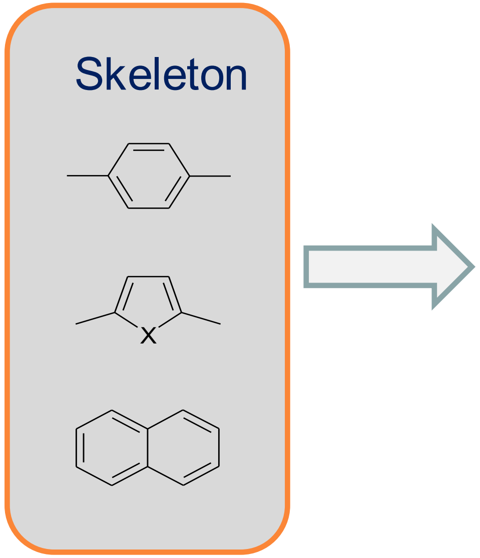
—COOH

—OMe

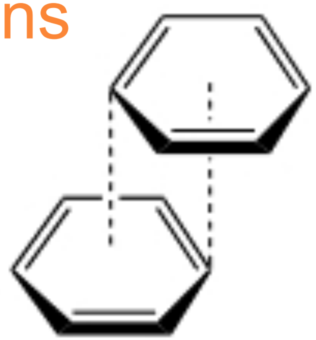
—CN

…

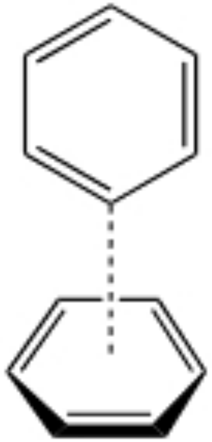
Intermolecular interactions



π stacking



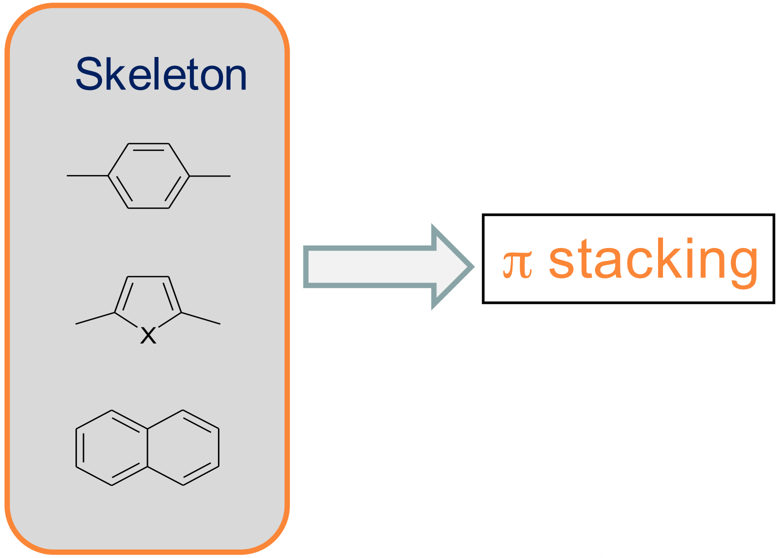
Offset stacking



T-stacking

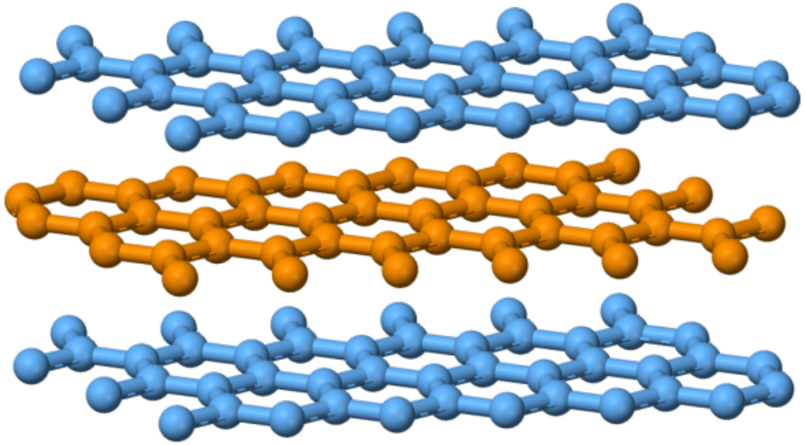
Aromatic-aromatic interaction (aromatic stacking, pi stacking):
A noncovalent attractive force between two aromatic rings.
Alignment of positive electrostatic potential on one ring with negative electrostatic potential on another ring forms:
an offset stack, or
a T-shaped stack.
Also called “pi stacking” but this label is misleading because it implies that stacking might occur in any structure with pi electrons.

Intermolecular interactions: π stacking

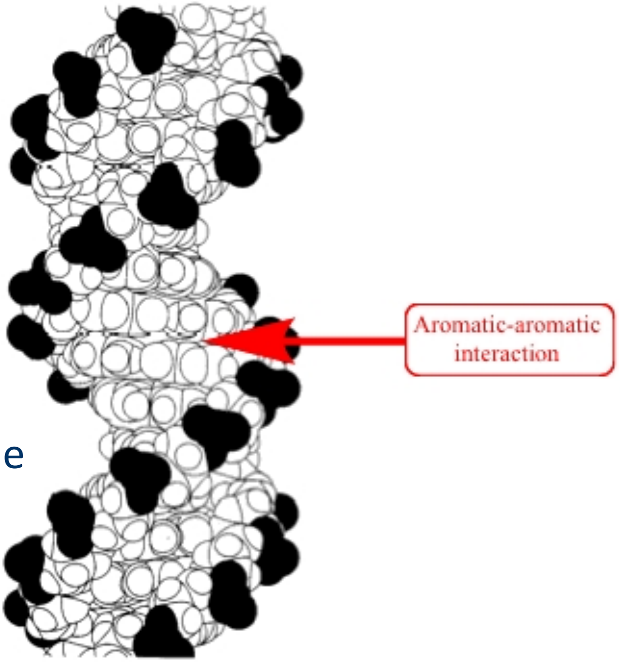


Skeleton

π stacking

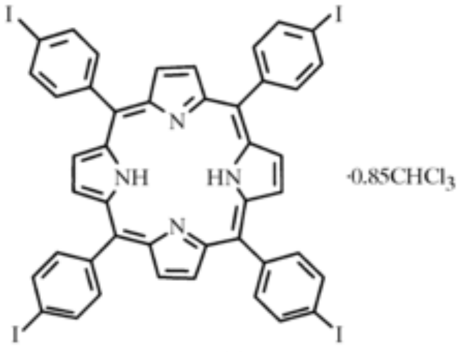


Electrical anisotropy

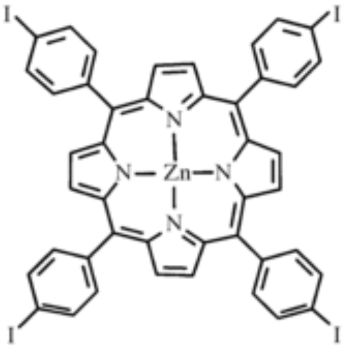


Stacked base pairs cause aromatic-aromatic interactions in DNA

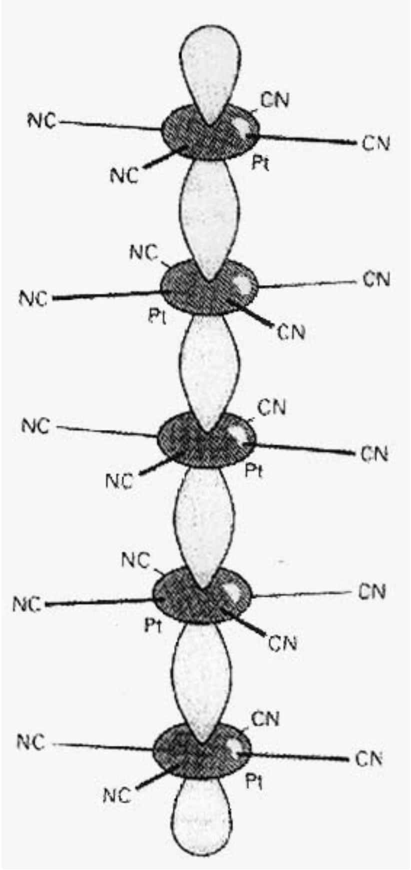
porphyrins

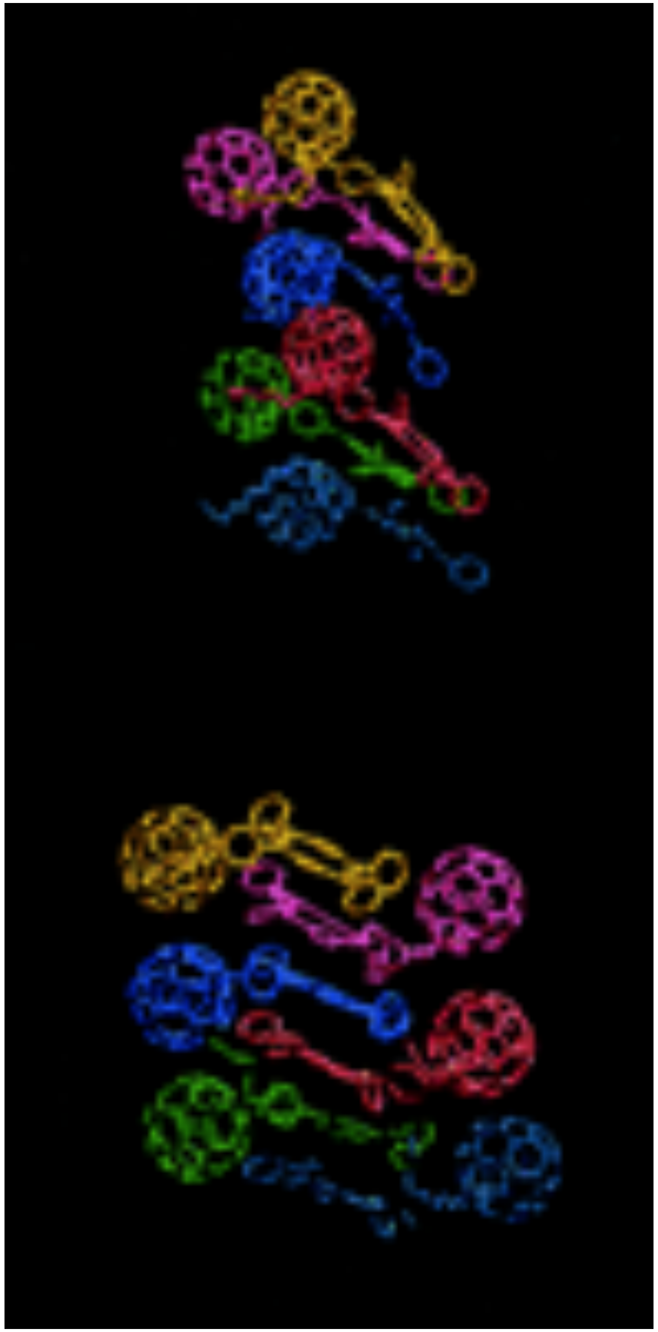


(I)

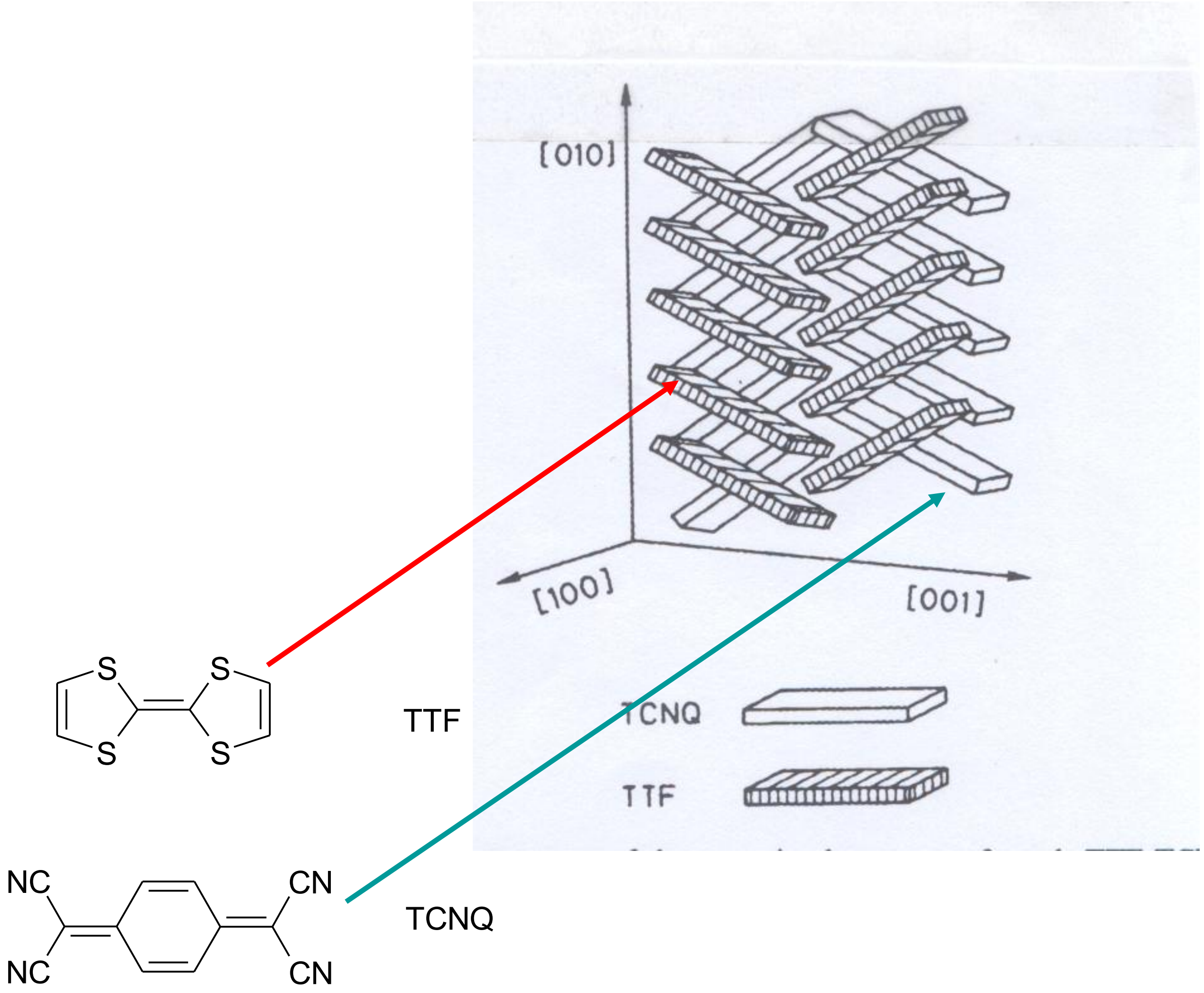


(II)





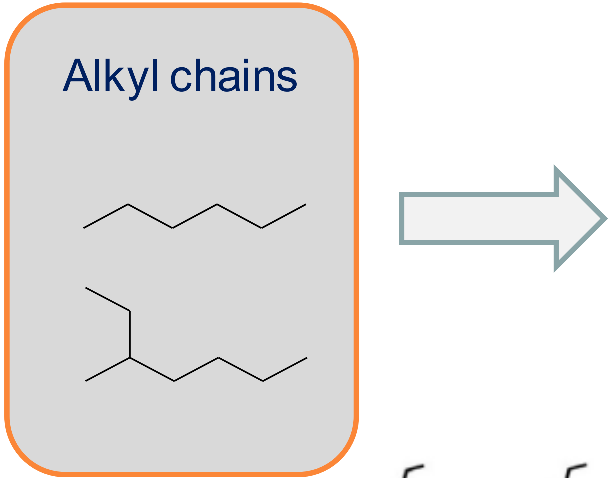
Intermolecular interactions: π stacking



TTF

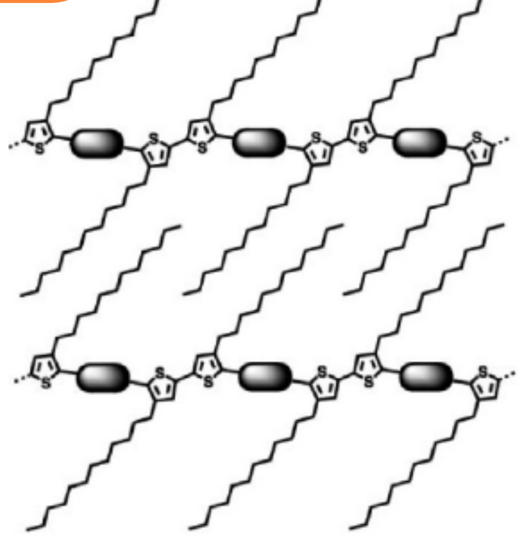
TCNQ

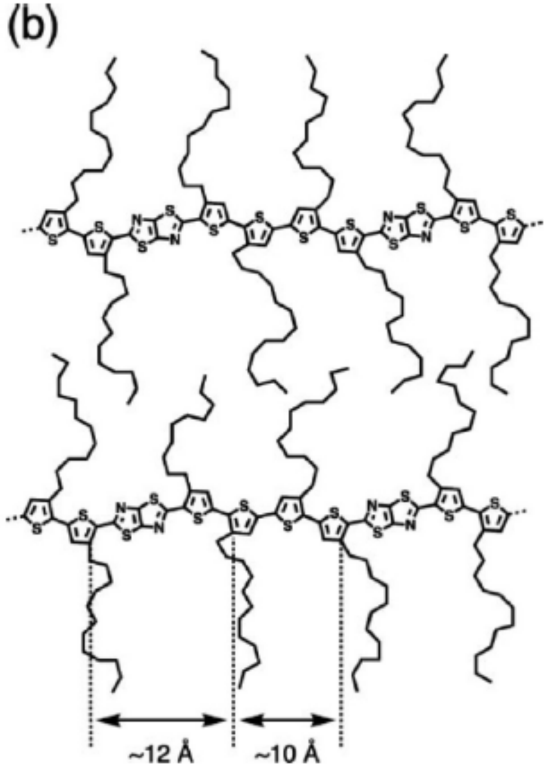
Intermolecular interactions: Van der Waals


Alkyl chains

Van der Waals

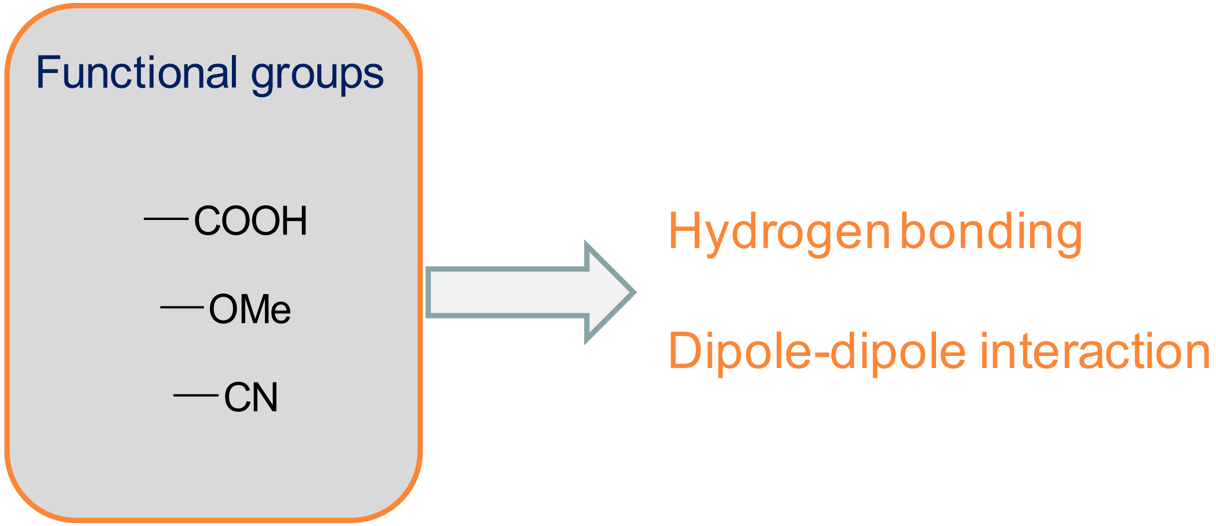
- ✓ Weak secondary bond
- ✓ Strong effect in intermolecular packing
- ✓ Short range interaction





Schematic illustrations for (a) the packing structure of PQT (P2) and PBTTT (P3) with dodecyl side chain with uniform side chain interdigitation and (b) proposed packing structure for P30 with disordered side chains. Reprinted with permission from ref 52. Copyright 2009 American Chemical Society.

Intermolecular interactions



Functional groups

—COOH

—OMe

—CN

Hydrogen bonding

Dipole-dipole interaction

Intermolecular interactions

Functional groups

—COOH

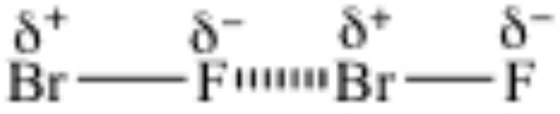
—OMe

—CN

Hydrogen bonding

Dipole-dipole interaction

A noncovalent (van der Waals) attractive force caused by alignment of bond dipoles with opposite charges.



$$\overset{\delta^+}{Br}-\overset{\delta^-}{F}\cdots\overset{\delta^+}{Br}-\overset{\delta^-}{F}$$

Intermolecular interactions

Functional groups

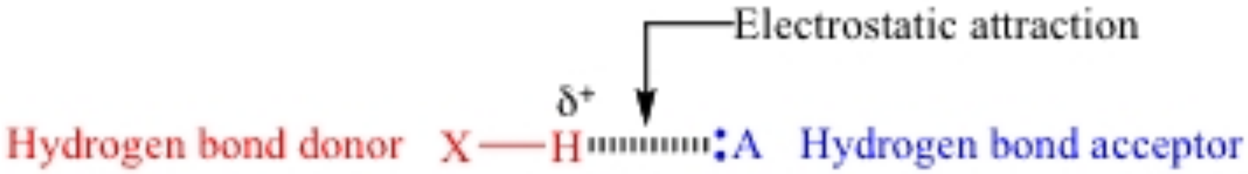
—COOH

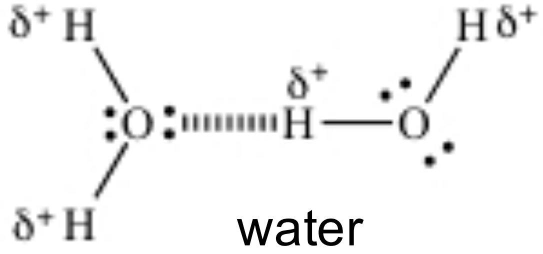
—OMe

—CN

Hydrogen bonding

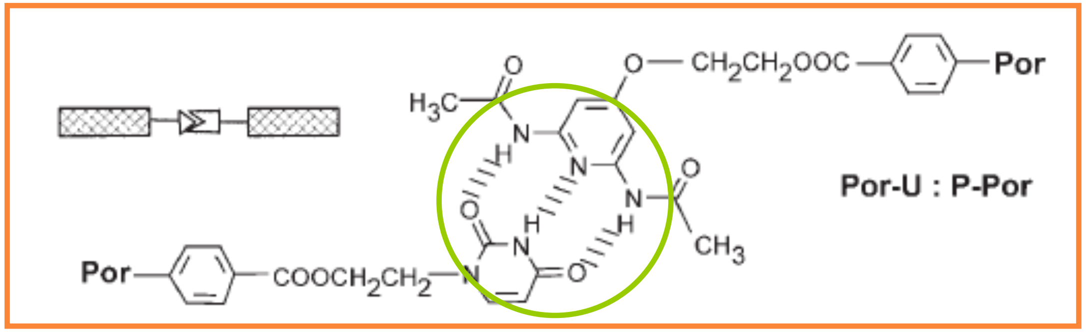
A non covalent attractive force caused by electrostatic attraction of a hydrogen atom with a lone pair of another atom. The hydrogen bond donor must have a sufficiently large δ+ charge caused by bonding to a highly electronegative element (O, N, or F). The hydrogen bond acceptor must have a lone pair, and sufficiently high electron density .

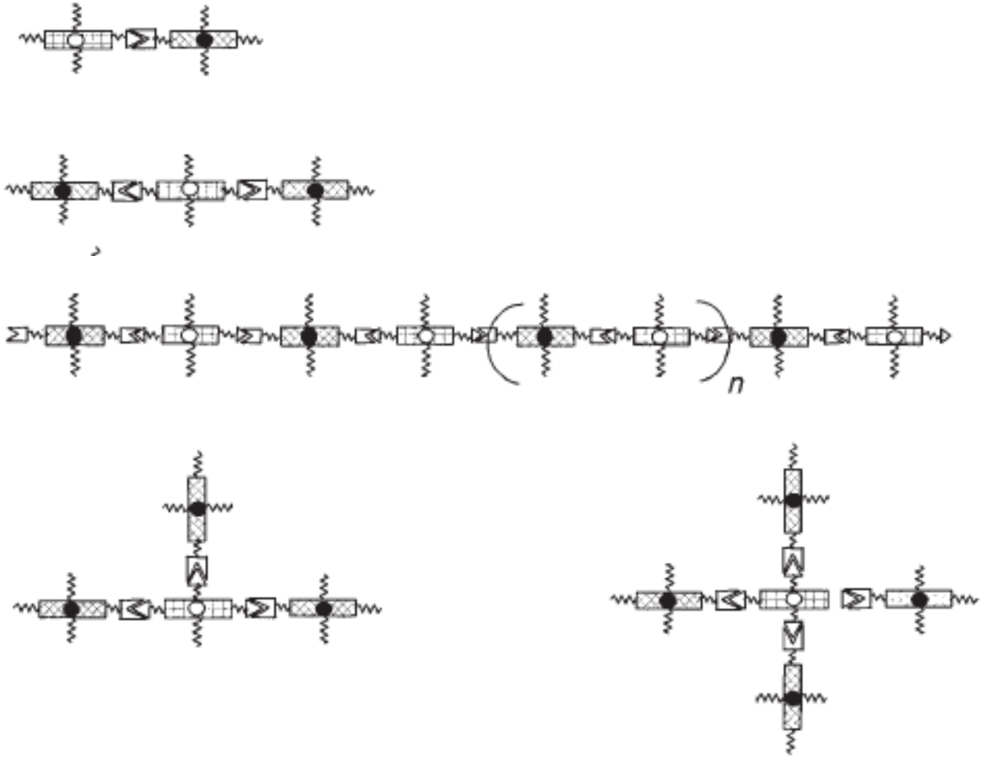




water

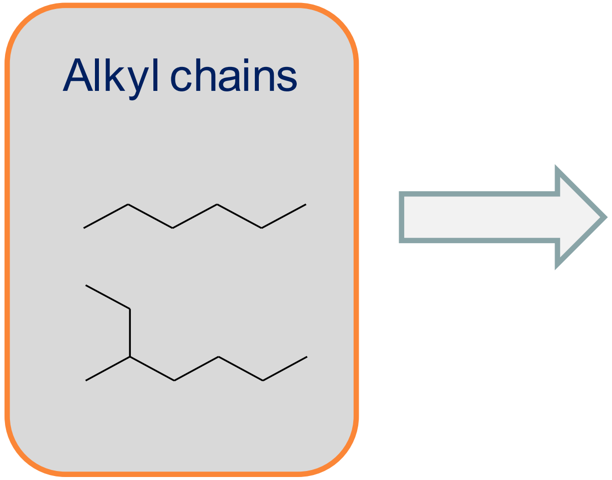
Supramolecular organization





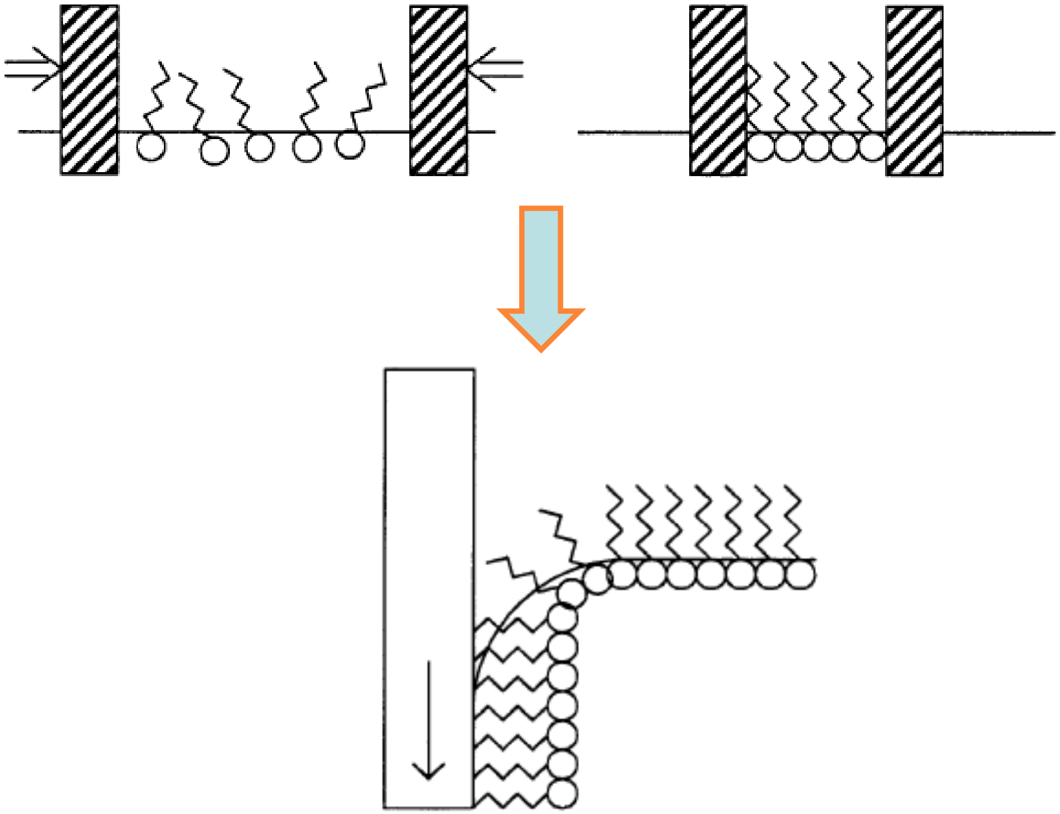
J.-M. Lehn, *Chem. Eur. J.* 2007, 13, 8411 – 8427

Intermolecular interactions: Van der Waals

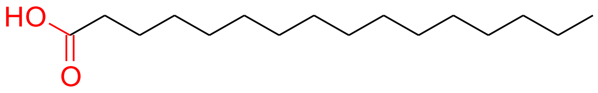


Van der Waals

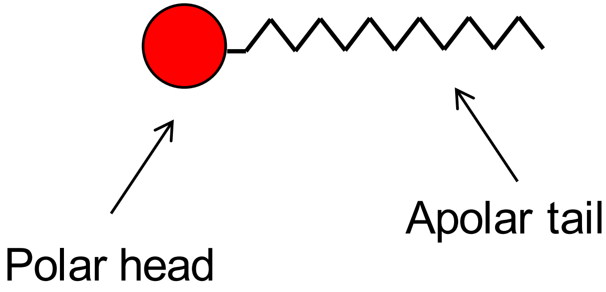
- ✓ Weak secondary bond
- ✓ Strong effect in intermolecular packing
- ✓ Short range interaction



Example #1: amphiphiles

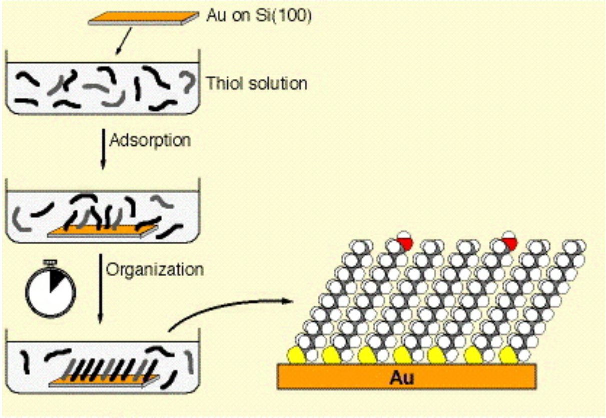


stearic acid



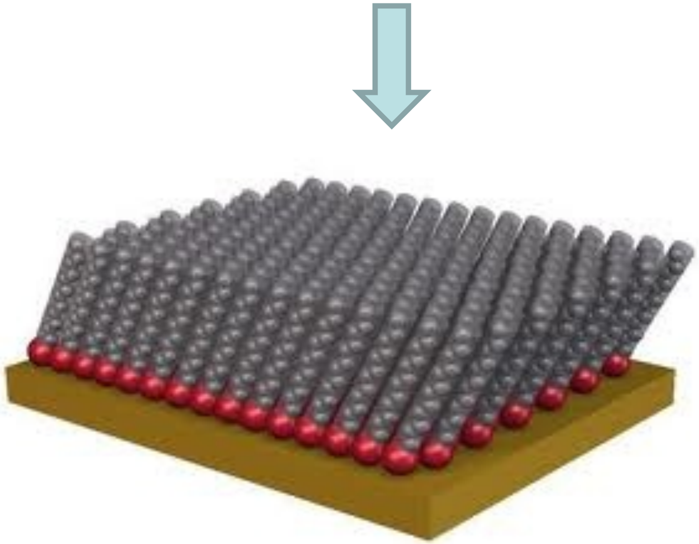
SAMs (self-assembled monolayers): alkanethiols onto gold

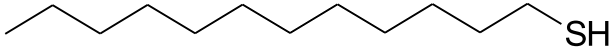
Upon immersion of a clean gold surface into a dilute solution (typically 1mM) of an alkanethiol derivative, the thiol molecules are chemisorbed via the formation of dative gold-sulfur bonds.



- Gold has specific interaction with sulfur

- Long-chain alkanethiols form densely packed, crystalline or liquid-crystalline monolayers due to strong molecular interactions (van der Waals forces) between long carbon chains.





#3: Alkyl chains onto well-packed aromatic moieties: liquid crystals

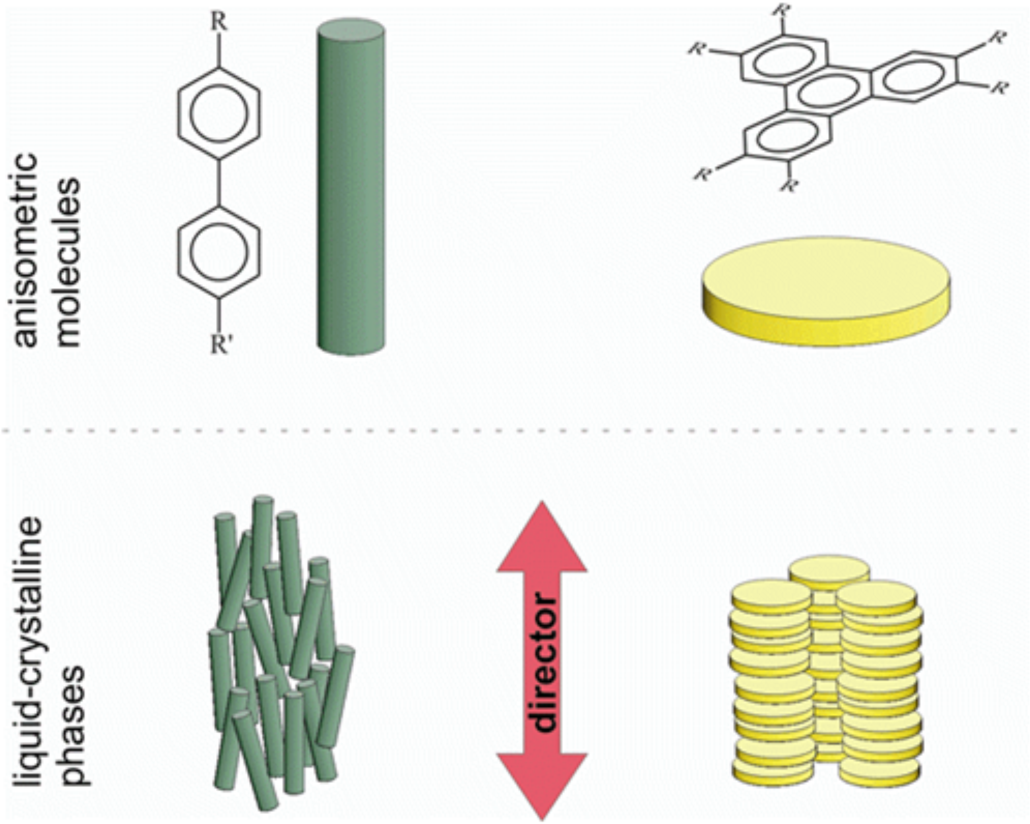
✓Liquid crystals are examples of self-assembling structures, as a result of intermolecular interactions: SECONDARY STRUCTURE

✓These structures are characterized by a some degree of long-range molecular order.

✓The particular intermolecular interactions define the specific secondary structure, that is the liquid crystal phase.

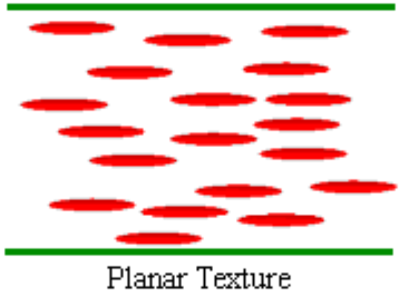
✓Liquid crystals are fluid, so they form continuous structures without interfaces.

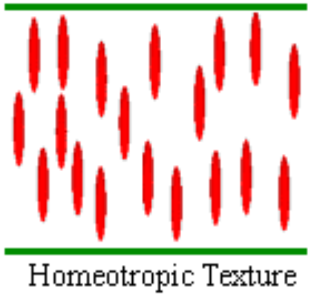
✓Liquid crystal phases differ from a liquid phase due to the peculiar anisotropy

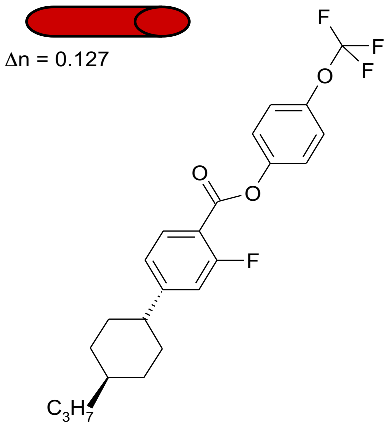


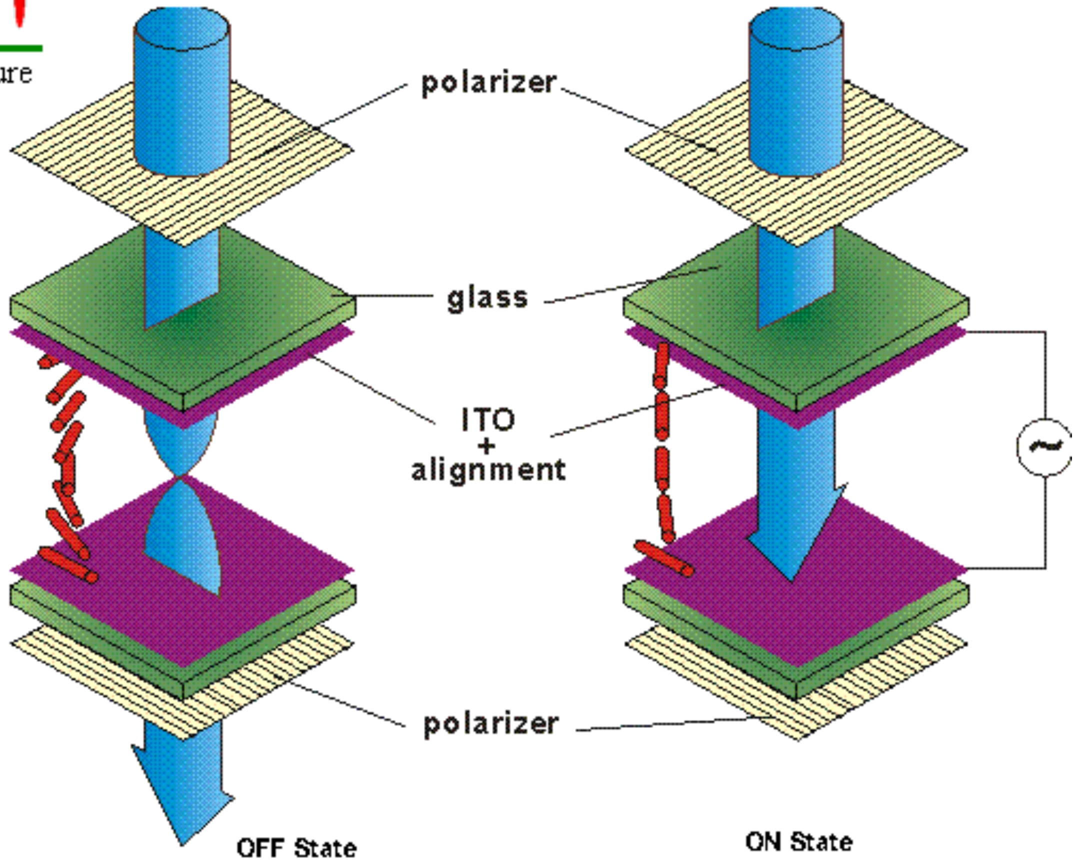
R= long alkyl (or perfluorinated alkyl) chain

Adding a strong polar group: large dipole moment









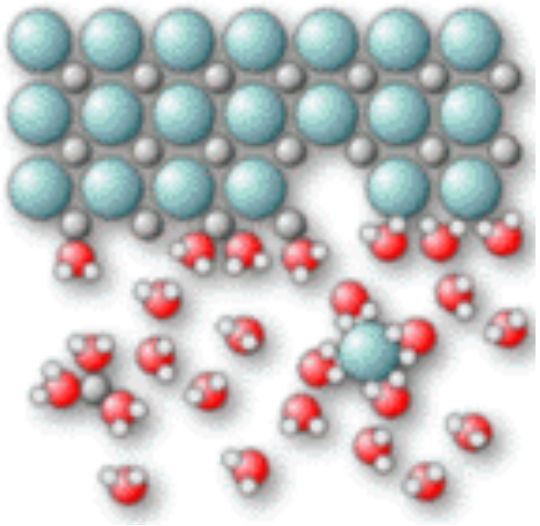
Secondary structure

Tertiary structure

From solid state to solution: solubility

✓ dissolution: the structural units (ions or molecules) gets separated

✓ energy has to be provided to overcome the interionic or intermolecular forces



Dissolving salt

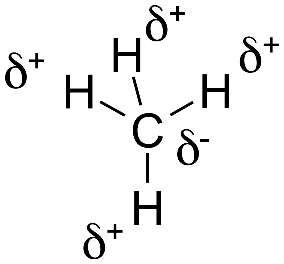
✓ energy required to break the bonds between particles is recovered by formation of new bonds between solute and solvents molecules

✓ the variation of entropy due to dissolution is positive (as disorder increases)

From solid state to solution: solubility

Main statement: similar likes similar

Substance: methane



→

Solubility in water: zero

Solubility in CCl_4: high

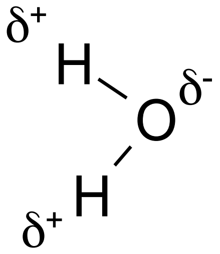
NaCl

→

Solubility in water: high

Solubility in CCl_4: zero

From solid state to solution: solubility

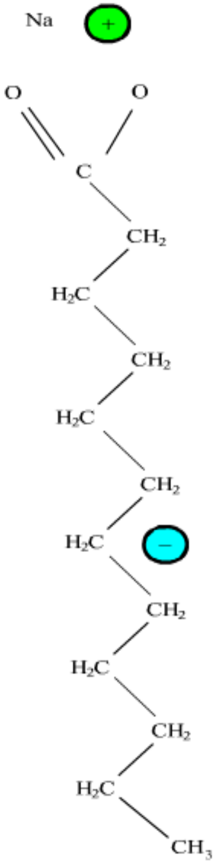


Solubility of alcohols into water

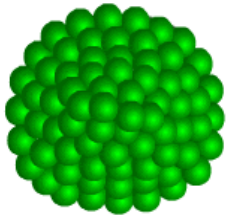
Alcohol	solubility g/100g H_2O
CH_3OH	∞
CH_3CH_2OH	∞
$CH_3CH_2CH_2OH$	∞
$CH_3CH_2CH_2CH_2OH$	7.9
$CH_3CH_2CH_2CH_2CH_2OH$	2.3
$CH_3CH_2CH_2CH_2CH_2CH_2OH$	0.6
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	0.2
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$	0.05

Solubility: amphiphiles

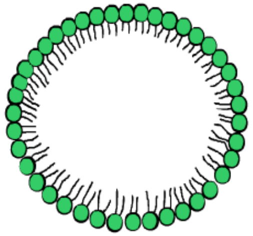
✓ if molecules are large enough and bear an apolar moiety and a polar group, this double nature influences solubilization, thus showing an amphiphilic behaviour



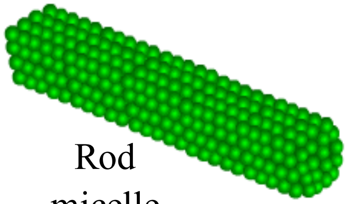
Sodio laurato



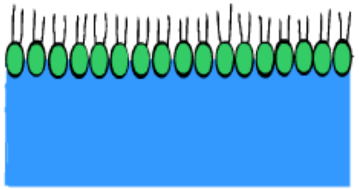
Spherical micelle

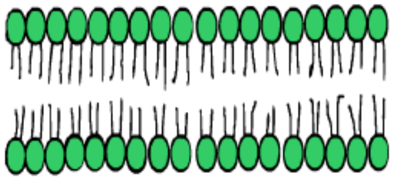


Cross-section



Rod micelle close-up



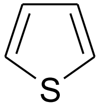


Solubility: the conjugated systems

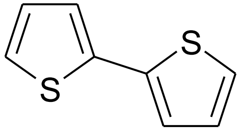
✓ solubility is usually a basic requirement to process materials into thin films by means of easy-handling solution techniques (spin coating, casting).

✓At the solid state, conjugated systems and specifically oligo- /poly-aromatic systems are characterized by interactions π-π

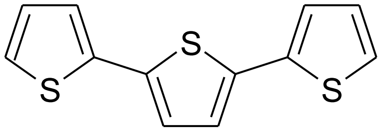
✓ the longer the oligomer, the poorer the solubility



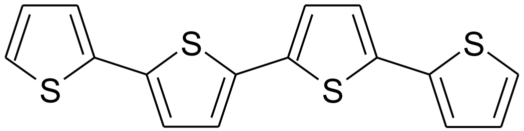
T



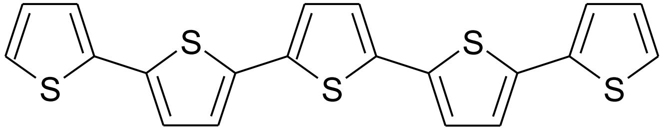
2T



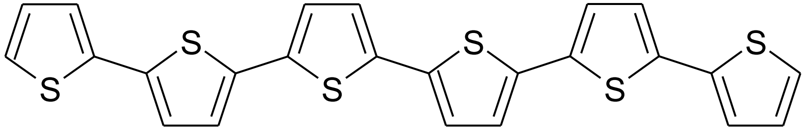
3T



4T



5T

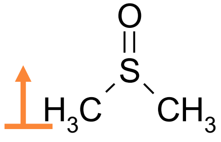


6T

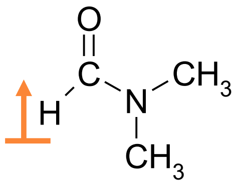
Solubility: the conjugated systems

✓ the use of polar solvents having relatively high dielectric constant, but with no acid proton, can favour solubilization of conjugated systems

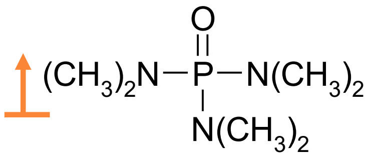
✓ aromatic solvents can contribute to solubilization as they can interact trough the π electronic cloud



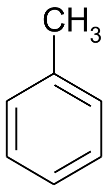
dimetilsolfossido (DMSO)



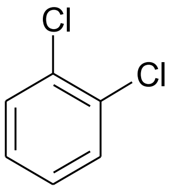
N,N-dimetilformamide (DMF)



esametilfosforotriammide (HMPT)



toluene



o-diclorobenzene

✓ in case of planar systems and with very effective π stacking mixture of different solvent can help in solubilizing. Strong acids plus aprotic solvents with high dielectric constant are typical examples

Solubility of the conjugated systems:

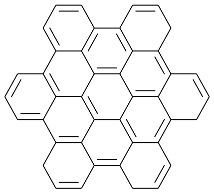
The effect of alkyl chains

- ✓Alkyl chains are characterized by high conformational freedom
- ✓ their electronic effect on conjugation is very weak (weak donor)
- ✓Usually they force a distortion of inter ring bonds (steric hindrance)
- ✓ if they are placed in a regular way, crystallinity is favoured

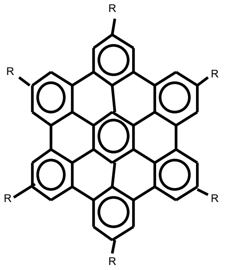
Solubility of the conjugated systems:

The effect of alkyl chains

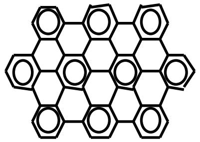
CORONENE



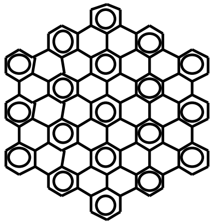
ESABENZOCORONENE



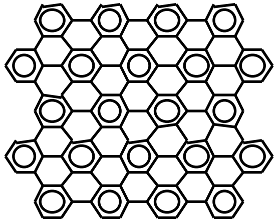
ESABENZOCORONENE R=C12H25



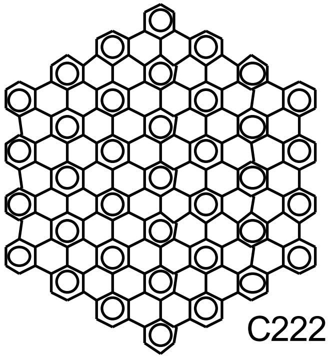
C60



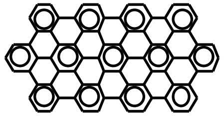
C114



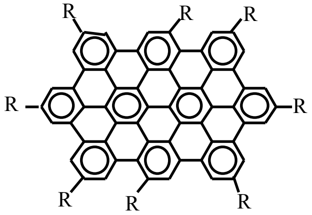
C132



C222



C78



C60 R=C12H25

CORONENE: SOLUBLE IN ACETONE, TOLUENE, CLOROFORM

HEXABENZOCORONENE: ALMOST INSOLUBLE

SUBSTITUTED HEXABENZOCORONENE: SOLUBLE IN CLOROFORM

C60,78,114,132,222: INSOLUBLE

SUBSTITUTED C60 : SOLUBLE IN CLOROFORM

Solvatochromism

✓ solvatochromic and/or thermochromic phenomena are commonly occurring in conjugated systems

✓ these phenomena are often related to the formation of aggregates (p-stacking) which occurs in presence of bad solvents or in mixtures of good and bad solvents

✓ techniques: light scattering, circular dichroism, UV-vis absorption spectra, photoluminescence, microfiltration, etc.

A case study:

The effect of the casting solvent in P3HT performance

M. Dang *et al.* Solar Energy Mater.& Solar Cells 95 (2011) 3408

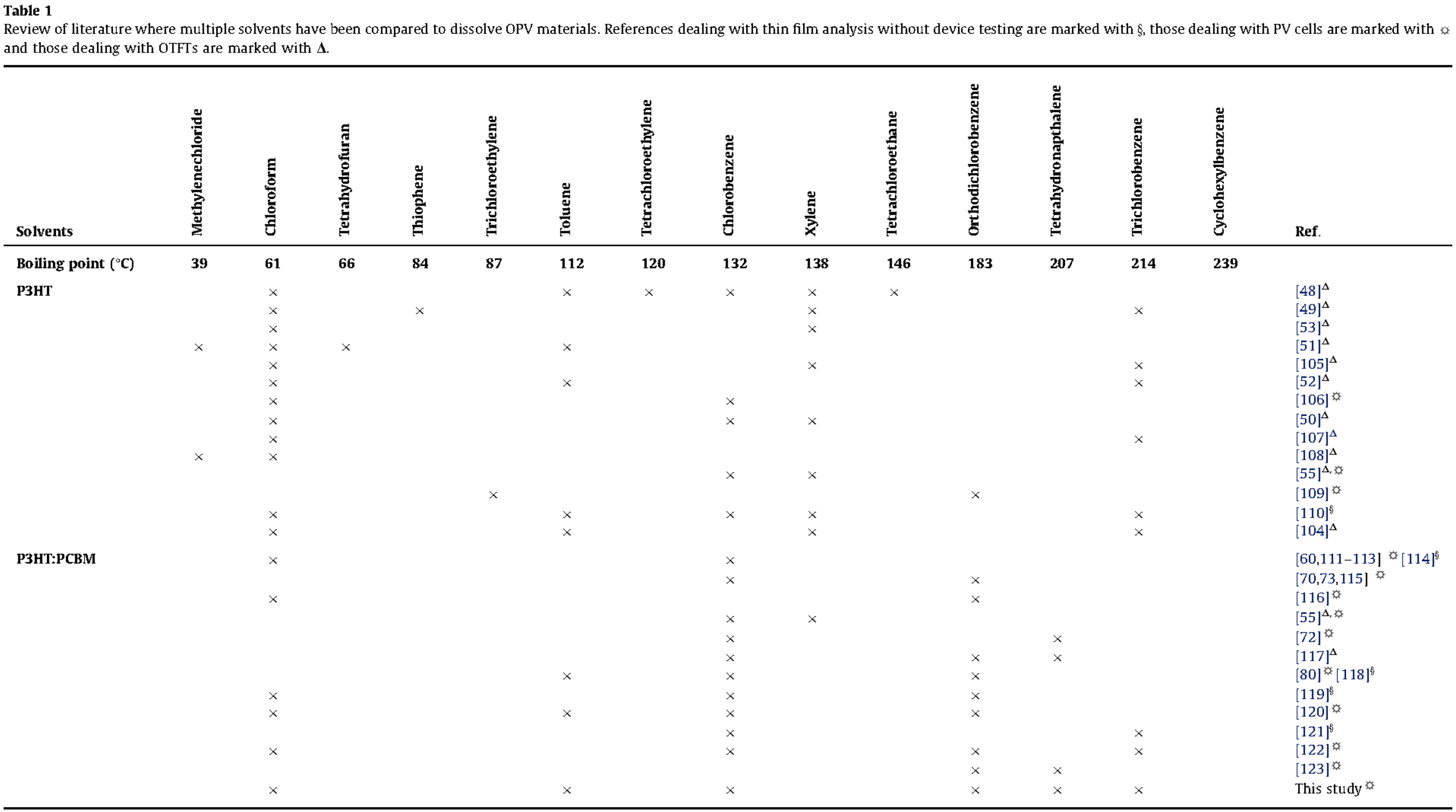


Table 1
Review of literature where multiple solvents have been compared to dissolve OPV materials. References dealing with thin film analysis without device testing are marked with §, those dealing with PV cells are marked with ☼ and those dealing with OTFTs are marked with Δ.

Solvents	Methylenechloride	Chloroform	Tetrahydrofuran	Thiophene	Trichloroethylene	Toluene	Tetrachloroethylene	Chlorobenzene	Xylene	Tetrachloroethane	Orthodichlorobenzene	Tetrahydronapthalene	Trichlorobenzene	Cyclohexylbenzene	Ref.
Boiling point (°C)	**39**	**61**	**66**	**84**	**87**	**112**	**120**	**132**	**138**	**146**	**183**	**207**	**214**	**239**	
P3HT		×				×	×	×	×	×					[48]Δ
		×		×					×				×		[49]Δ
		×							×						[53]Δ
	×	×	×			×									[51]Δ
		×							×				×		[105]Δ
		×				×							×		[52]Δ
		×						×							[106]☼
		×						×	×						[50]Δ
		×											×		[107]Δ
	×	×													[108]Δ
								×	×						[55]Δ,☼
					×						×				[109]☼
		×				×		×	×				×		[110]§
		×				×			×				×		[104]Δ
P3HT:PCBM		×						×							[60,111–113]☼ [114]§
								×			×				[70,73,115]☼
		×									×				[116]☼
								×	×						[55]Δ,☼
								×				×			[72]☼
								×			×	×			[117]Δ
						×		×			×				[80]☼ [118]§
		×						×			×				[119]§
		×				×		×			×				[120]☼
								×					×		[121]§
		×						×			×		×		[122]☼
											×	×			[123]☼
		×				×		×			×	×	×		This study☼

A case study:

The effect of the casting solvent in P3HT performance

M. Dang *et al.* Solar Energy Mater.& Solar Cells 95 (2011) 3408

Yang at al.

$\mu_{CHCl3} > \mu_{THF} > \mu_{toluene} > \mu_{CH2Cl2}$

No obvious correlation between boiling point and measured mobilities

Sethuraman et al.

$\mu_{CHCl3} \approx \mu_{TCB}$ (0.084-0.073)

Morana et al.

$\mu_{o\text{-}xylene} > \mu_{CB}$

μ_{TCB}=0.12 cm^2/Vs

Do high boiling point solvents enable polymer chains to self-organize during the slow drying?

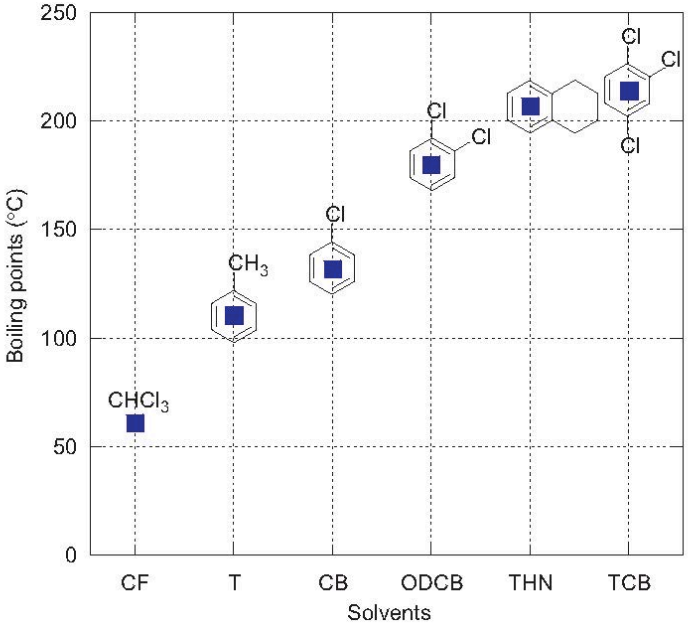


Fig. 2. Chemical structures and boiling points of the different solvents used in this study: chloroform, toluene (T), chlorobenzene (CB), ortho-dichlorobenzene (ODCB), tetrahydronaphthalene (THN) and trichlorobenzene (TCB).

A case study:

The effect of the casting solvent in P3HT:PCBM

M. Dang *et al.* Solar Energy Mater.& Solar Cells 95 (2011) 3408

Al-Ibrahim at al.

CB better tan CHCl3 (not annealed)

The CHCl3 film is thicker

Kim et al.

ODCB better than CB

Higher boiling point – phase separation – vertical segregation

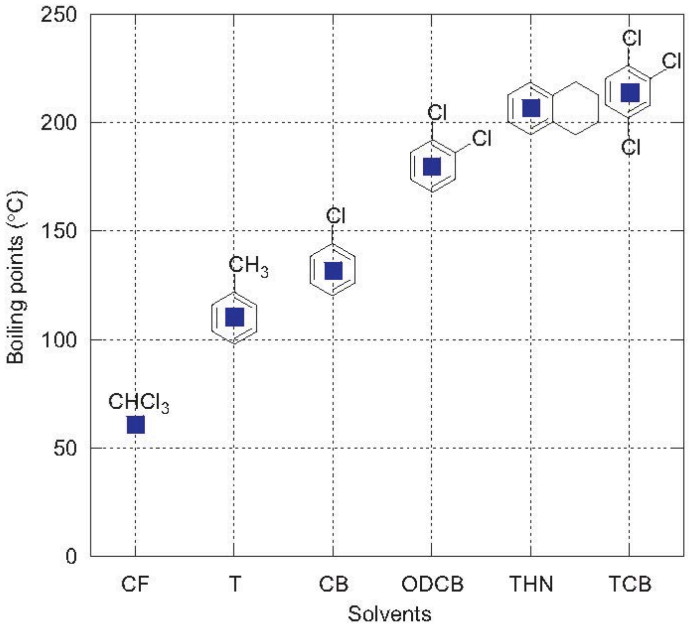
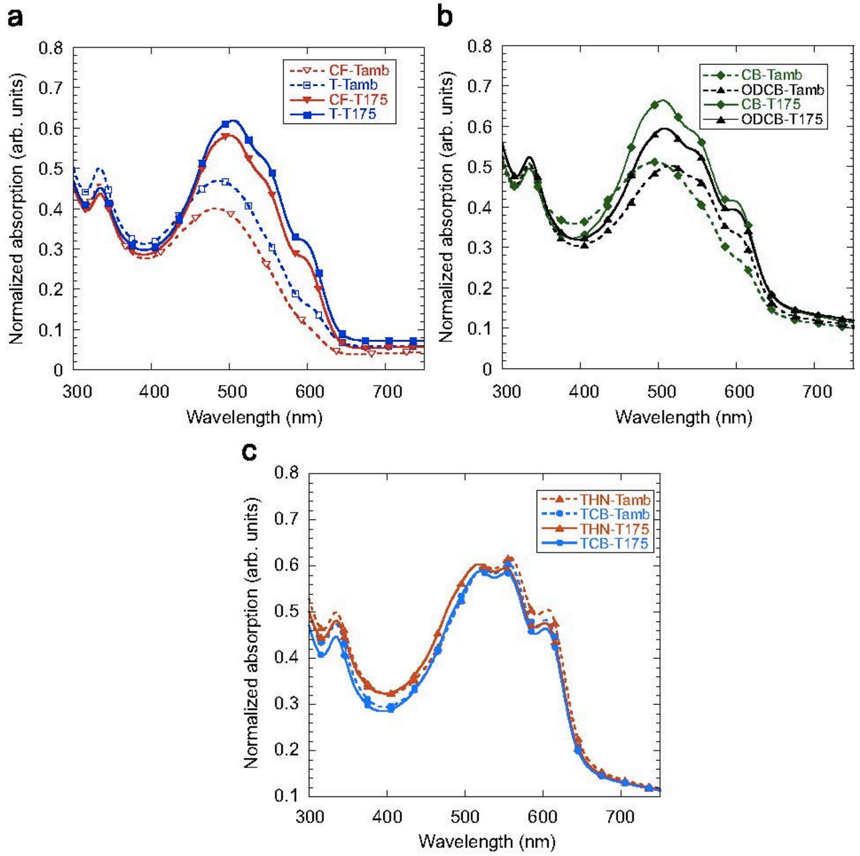


Fig. 2. Chemical structures and boiling points of the different solvents used in this study: chloroform, toluene (T), chlorobenzene (CB), ortho-dichlorobenzene (ODCB), tetrahydronaphthalene (THN) and trichlorobenzene (TCB).

A case study:

The effect of the casting solvent in P3HT:PCBM

M. Dang *et al.* Solar Energy Mater.& Solar Cells 95 (2011) 3408



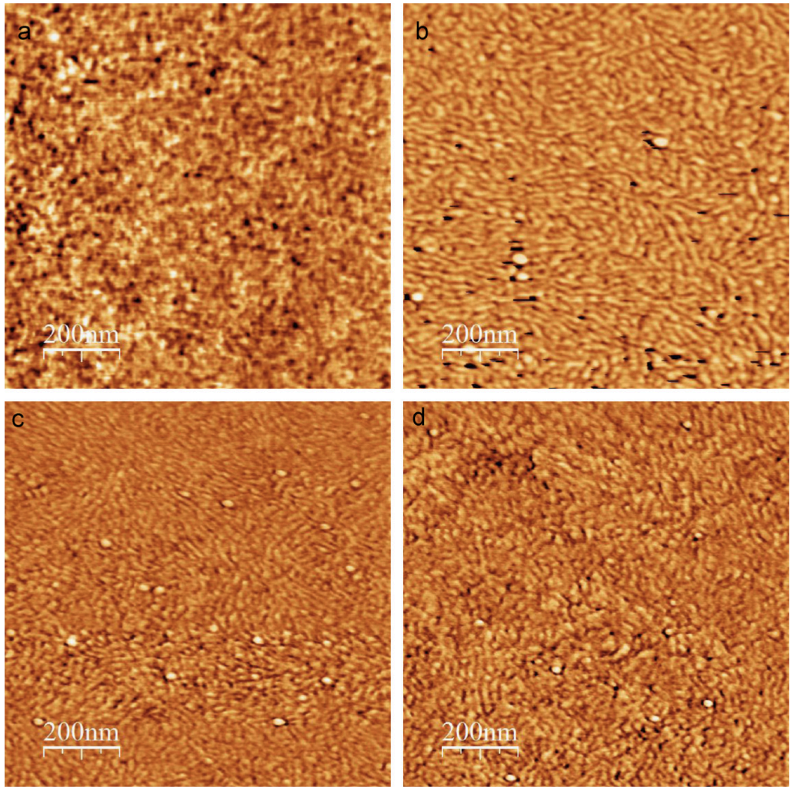
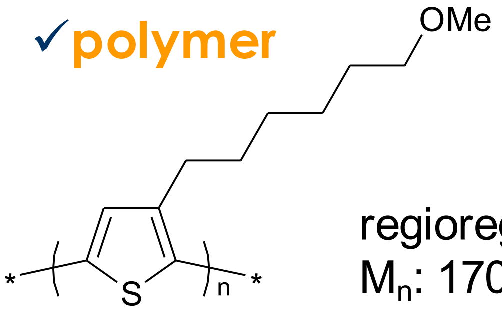


Fig. 4. AFM phase images of pristine and thermally annealed films coated from chlorobenzene CB (a) and (b) and from tetrahydronaphthalene THN (c) and (d).

Prediction in OPV: not straightforward

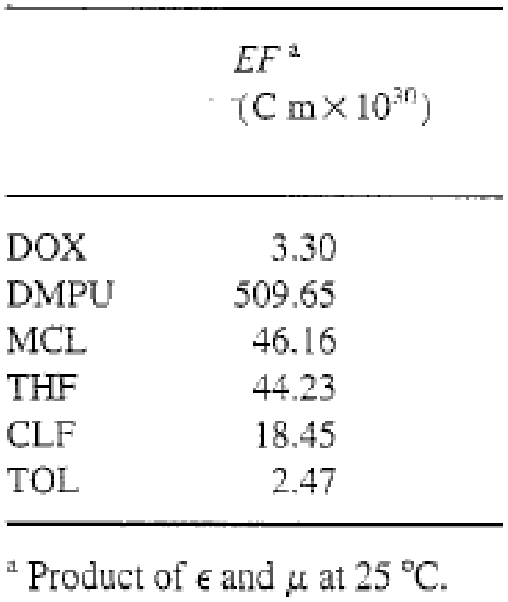
Solvatochromism

✓**polymer**



regioregularity: 74-78 %
M_n: 17000-32000

✓**solvents**



	EF [a] ($C\,m \times 10^{30}$)
DOX	3.30
DMPU	509.65
MCL	46.16
THF	44.23
CLF	18.45
TOL	2.47

[a] Product of ϵ and μ at 25 °C.

✓**Bad solvent: MeOH**

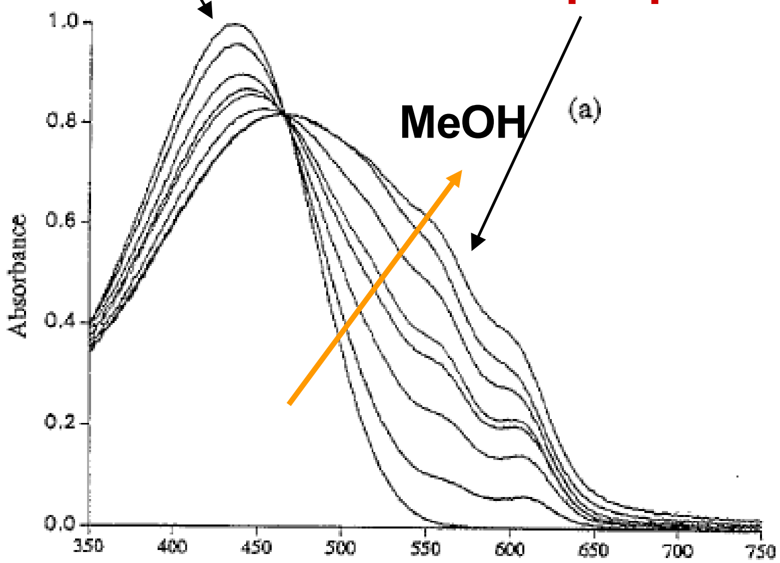
M. Lanzi, P. Costa-Bizzarri, C. Della Casa, Synth Metals, ***89*** *(1997) 181*

Solvatochromism

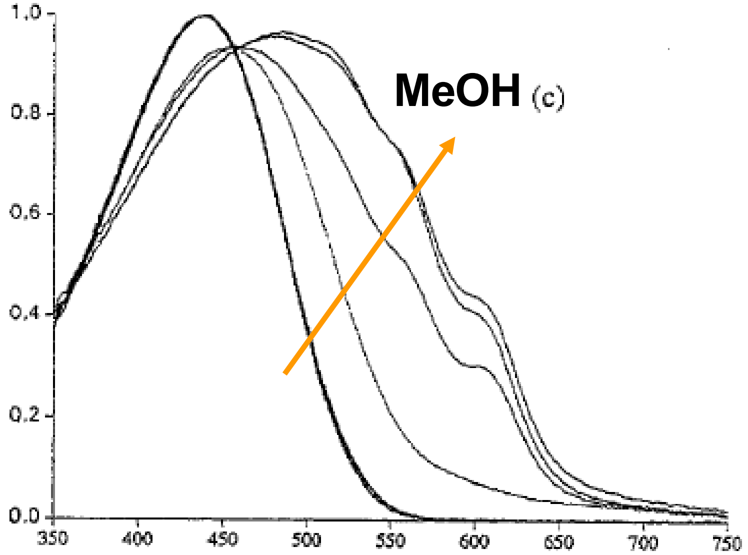
Yellow-orange

✓**dioxane**

Red-purple



toluene



✓ **polar solvent**

✓ site of solvatation: **end group**

✓**Non-solvent effect: relatively high**

✓ **less polar solvent**

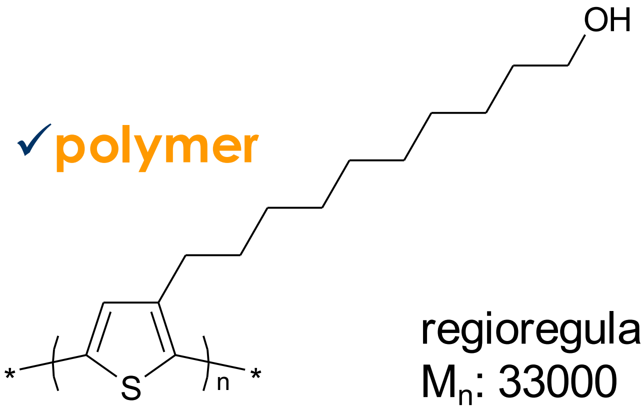
✓ site of solvatation: **backbone**

✓**Non-solvent effect: weak (at low molar concentration)**

M. Lanzi, P. Costa-Bizzarri, C. Della Casa, Synth Metals, ***89*** *(1997) 181*

Solvatochromism/thermochromism

✓**polymer**



regioregularity: 75%
M_n: 33000

✓**solvents**

solubility

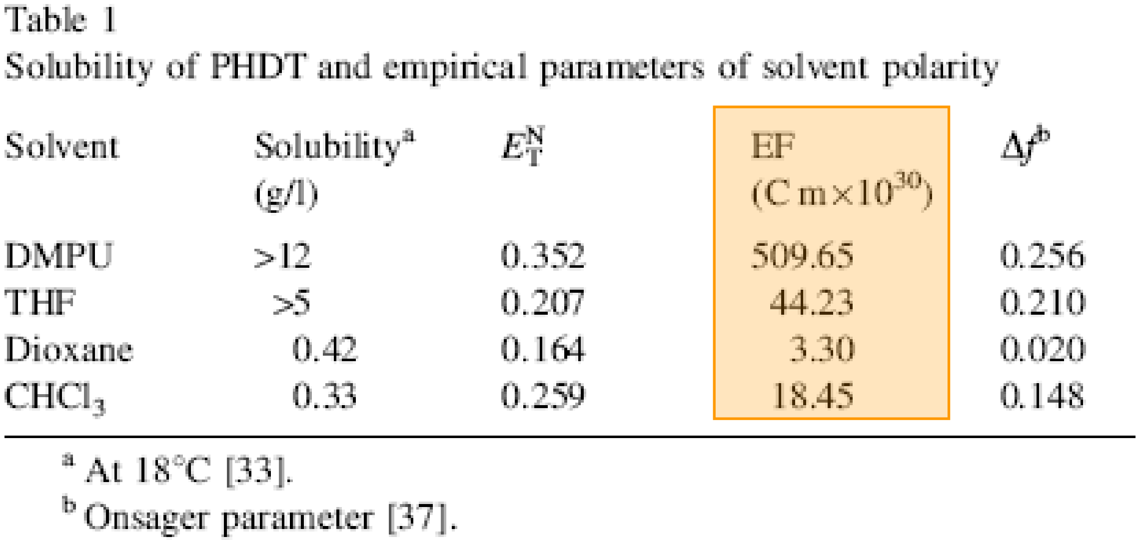


Table 1
Solubility of PHDT and empirical parameters of solvent polarity

Solvent	Solubility[a] (g/l)	E_T^N	EF ($C\,m \times 10^{30}$)	Δf[b]
DMPU	>12	0.352	509.65	0.256
THF	>5	0.207	44.23	0.210
Dioxane	0.42	0.164	3.30	0.020
$CHCl_3$	0.33	0.259	18.45	0.148

[a] At 18°C [33].
[b] Onsager parameter [37].

✓**Bad solvent: MeOH**

F. Bertinelli, P. Costa-Bizzarri, C. Della Casa, M. Lanzi, Synth Metals, ***122*** *(2001) 267*

Solvatochromism

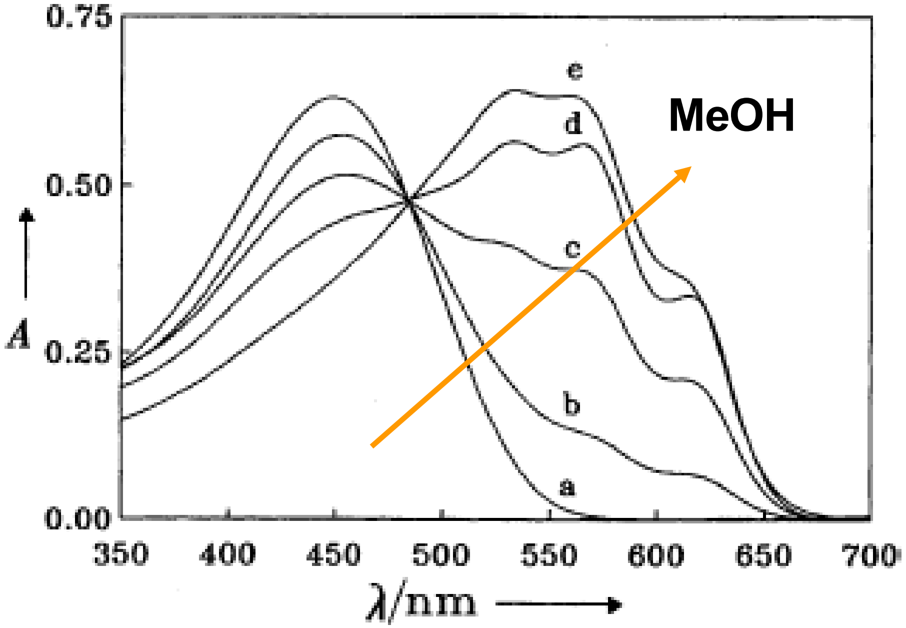


Fig. 2. Absorption spectrum in DMPU/MeOH solutions at −30°C with different m.f. of MeOH: (a) 0.00; (b) 0.093; (c) 0.23; (d) 0.37; (e) 0.75. The reference (a) spectrum in pure DMPU was taken at −16°C.

F. Bertinelli, P. Costa-Bizzarri, C. Della Casa, M. Lanzi, Synth Metals, ***122*** *(2001) 267*