ORGANIC MATERIALS FOR PHOTONICS

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PLAN OF THE PRESENTATION

- WHY PHOTONICS
- DESIGN OF NLO
- MARDER'S PLOT
- ZWITTERIONICS
  and their characterization
  uv, nmr, β, computations
- QUINOID DYES
- FROM MOLECULES TO MATERIALS
- BULK MATERIALS FOR:
  - ⇨ OPTOELECTRONICS
  - ⇨ CAVITY LASING
  - ⇨ LIMITERS

  as

  - ➢ FILMS
  - ➢ GLASSES
  - ➢ POLYMERS

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MATERIALS FOR ADVANCED APPLICATIONS

- TRADITIONAL MATERIALS (inorganics, organometallics)

⬇

- ORGANIC **MOLECULAR** MATERIALS (benzene derivatives, classic organic functionalities: OR, NR_2, NO_2)

⬇

Our choice

- **ORGANIC MATERIALS FOR PHOTONICS**

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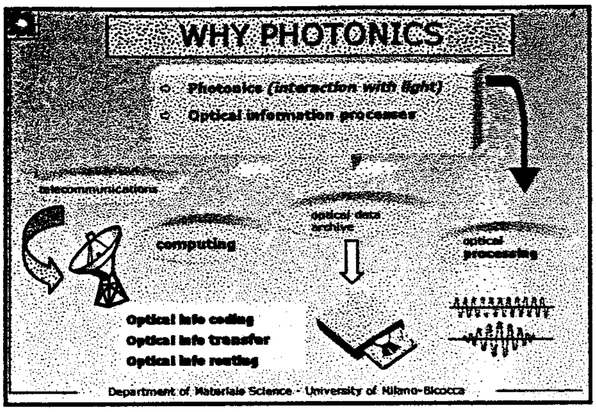
WHY PHOTONICS
Photonics (interaction with light)
Optical information processes
telecommunications
computing
optical data archive
optical processing
Optical info coding
Optical info transfer
Optical info routing
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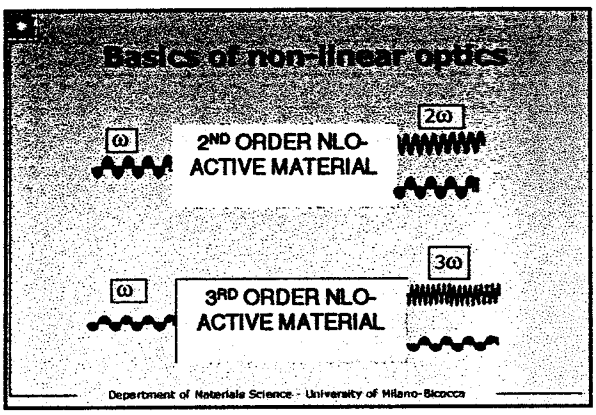
Basics of non-linear optics
ω
2ND ORDER NLO-ACTIVE MATERIAL
2ω
ω
3RD ORDER NLO-ACTIVE MATERIAL
3ω
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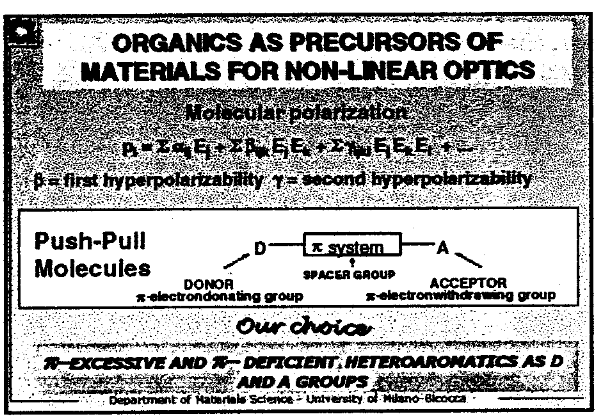
ORGANICS AS PRECURSORS OF MATERIALS FOR NON-LINEAR OPTICS
Molecular polarization
$p_i = \Sigma \alpha_{ij} E_j + \Sigma \beta_{ijk} E_j E_k + \Sigma \gamma_{ijkl} E_j E_k E_l + \dots$
β = first hyperpolarizability γ = second hyperpolarizability
Push-Pull Molecules
D
π system
A
SPACER GROUP
DONOR
π-electrondonating group
ACCEPTOR
π-electronwithdrawing group
Our choice
π–EXCESSIVE AND π– DEFICIENT HETEROAROMATICS AS D AND A GROUPS
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Why heterocycle-based molecular materials?

- non-linear optics, two-photon dyes, optical limiters

π-Electron Donor → Polarizable π-Electron Bridge → π-Electron Acceptor

π-Electron Acceptor ← π-Electronrich Bridge → π-Electron Acceptor

- luminescent materials, emitters, LED

Nitrogen ligand → transition metals, lanthanides

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MESSAGE

Exploit the unique π-excessive and π-deficient properties of heterocycles as **DONORS** and **ACCEPTORS**

This can be done if....

we quantitatively know the π-electron properties of as many heterocycles as possible and their π-electron distribution site by site

method of choice

- ⇨ Shift / π-Charge Relationships by C-13 and N-15 NMR Spectroscopy
- ⇨ Computational (semiempirical and *ab initio*) methods

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From NMR Shift to the π Electron Density

$$\delta^{13}C = 122.8 + \Sigma A_i - 160\,(q^{\pi}_C - 1)$$

$$\delta^{15}N = 345.4 - 366.3\,(q^{\pi}_N - 1)$$

$$\Delta(\delta^{13}C) = -160\,\Delta(q^{\pi}_C)$$

$$\Delta(\delta^{15}N) = -366.3\,\Delta(q^{\pi}_N)$$

Bradamante, Pagani, *J. Org. Chem.* **1984**; Bradamante, Pagani *J. Chem. Soc., Perkin Trans 2* **1986**; Barchiesi, Bradamante, Pagani *Ibid.* **1987**; Berlin, Bradamante, Ferraccioli *Ibid.* **1988**; Abbotto, Alanzo, Bradamante, Pagani *Ibid.* **1991**

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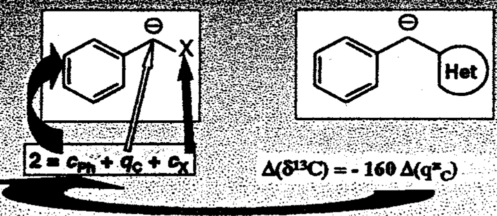
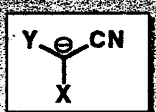
Charge c_X *demands via* ^{13}C NMR



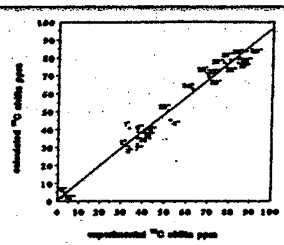
$\Delta(\delta^{13}C) = -160\,\Delta(q^{\pi}_C)$

Bradamente, S.; Pagani, G. A. *J. Org. Chem.* **1984**, *49*, 2863.
Bradamente, S.; Pagani, G. *JAI Press* **1996**, 189-263.

Predictivity Power of chemical shift in di- and tri-substituted carbanionic carbons



X, Y = H, Ph,
EWG (COR, CN, ..)
azines diazines



$\delta^{13}C_{calc} = (0.958 \pm 0.024)\,\delta^{13}C_{exp} + (0.902 + 0.604)(n = 23,\ r = 0.993)$

Abbotto, Bradamante, Pagani *J. Org. Chem.* 1993, 58, 449

Charge Demands of Some Groups

X	c_X
Ph	0.29
CO_2Me	0.40
COMe	0.51
COPh	0.56
CN	0.28
SPh	0.00
Me_3N^+	0.00
2-Pyridyl	0.41
4-Pyridyl	0.41

X	c_X
2-Pyrimidyl	0.43
4-Pyrimidyl	0.50
2-Thiazolyl	0.39
2-Oxazolyl	0.35
2-(*N*-Me)imidazolyl	0.24
2-Benzothiazolyl	0.46
2-Benzoxazolyl	0.44
2-(*N*-Me)benzimidazolyl	0.38

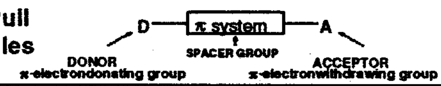
ORGANICS AS PRECURSORS OF MATERIALS FOR NON-LINEAR OPTICS

Molecular polarization

$$p_i = \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_j E_k + \sum \gamma_{ijkl} E_j E_k E_l + \dots$$

β = first hyperpolarizability γ = second hyperpolarizability

Push-Pull Molecules



Question

How β is related to D and A ?

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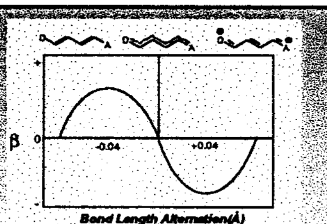
CORRELATION BETWEEN β AND ELECTRONIC STRUCTURE (BOND LENGTH ALTERNATION *Marder, 1993*)



- Optimal combination of donor and acceptor substituents for a given π-bridge spacer (specific strength)
- Specific degree with which the two forms contribute to describe the ground state

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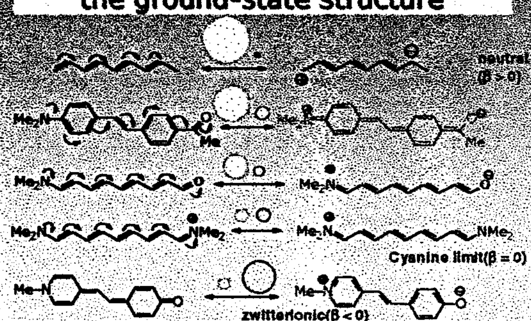
Contribution of resonance forms to the ground-state structure



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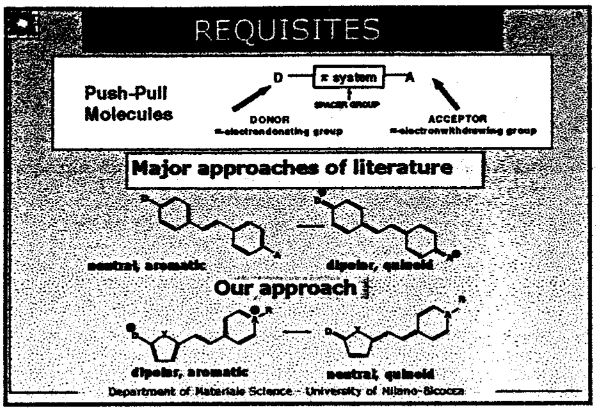
REQUISITES
Push-Pull Molecules
D
π system
A
DONOR
ACCEPTOR
Major approaches of literature
neutral, aromatic
dipolar, quinoid
Our approach
dipolar, aromatic
neutral, quinoid
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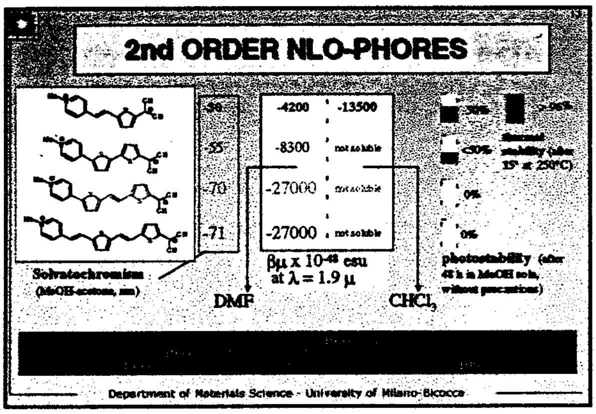
2nd ORDER NLO-PHORES
-30
-55
-70
-71
-4200
-13500
-8300
not soluble
-27000
not soluble
-27000
not soluble
βμ x 10-48 esu
at λ = 1.9 μ
DMF
CHCl3
Solvatochromism
0%
0%
photostability
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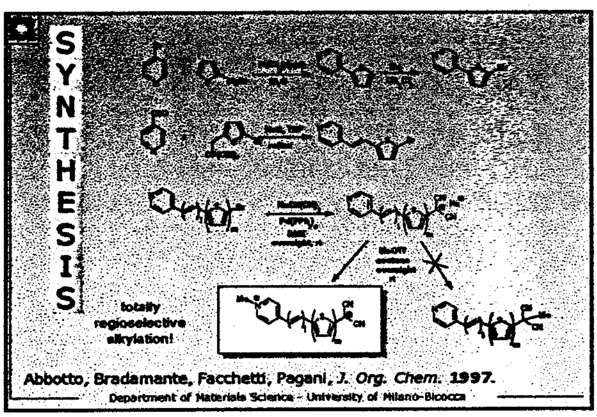
SYNTHESIS
totally regioselective alkylation!
Abbotto, Bradamante, Facchetti, Pagani, J. Org. Chem. 1997.
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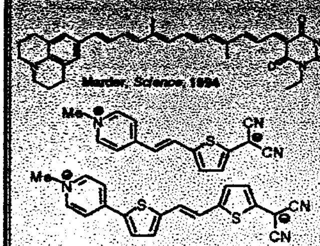
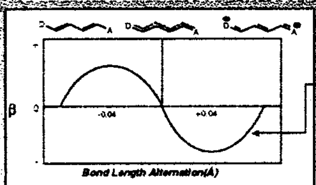
A figure of merit: hyperpolarizability β per unit of MW



	MW	$\beta\mu(0)$	$\beta\mu$ / M
Marder, Science, 1994	567	14920	26.3
2	265	6990	26.4
3	347	11000	31.7

Gazz. Chim. Ital. **1997**, *127*, 165; *J. Org. Chem.* **1997**, *62*, 5755; *Mat. Res. Soc. Symp. Proc.* **1998**, *488*, 819

Where are we on Marder's plot?



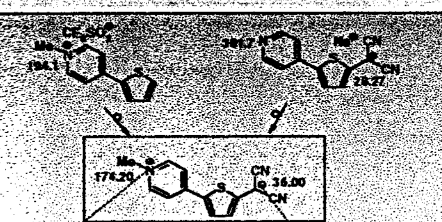
Are we about here?

Yes!

Evidence

- NMR
- Solvatochromism
- Computations

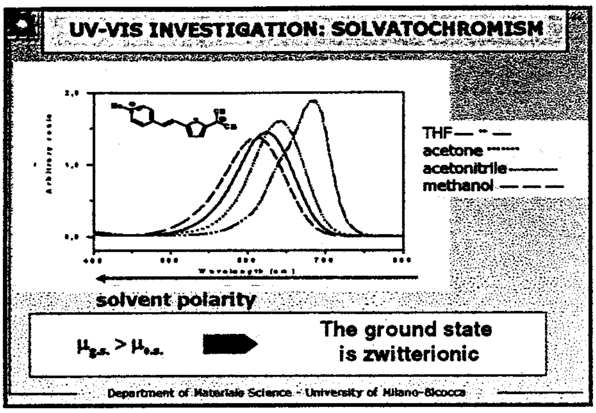
N-15 and C-13 NMR: Mapping of the ACCEPTOR and DONOR site



Pyridinium nitrogen: increase by 0.05 π electrons

Carbanionic carbon: decrease by 0.05 π electrons

The negative and positive charges are highly LOCALIZED!


UV-VIS INVESTIGATION: SOLVATOCHROMISM
THF
acetone
acetonitrile
methanol
solvent polarity
$\mu_{g.s.} > \mu_{e.s.}$
The ground state is zwitterionic
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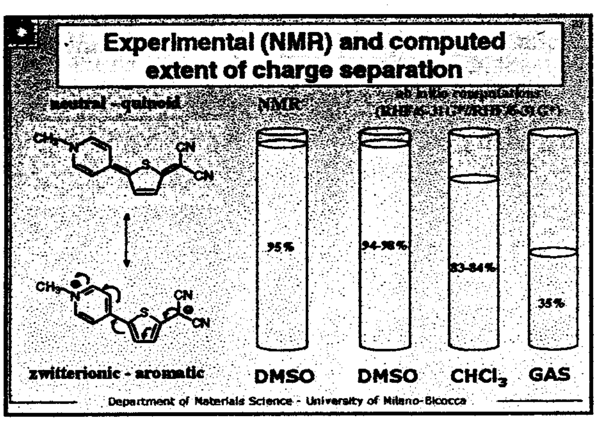
Experimental (NMR) and computed extent of charge separation
NMR
95%
94-98%
83-84%
35%
zwitterionic - aromatic
DMSO
DMSO
$CHCl_3$
GAS
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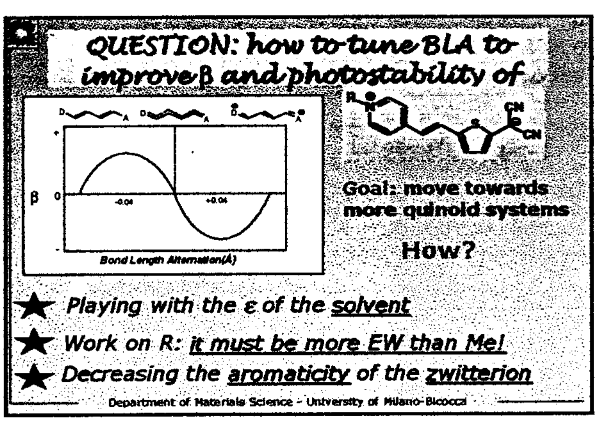
QUESTION: how to tune BLA to improve β and photostability of
β
Bond Length Alternation(Å)
Goal: move towards more quinoid systems
How?
Playing with the ε of the solvent
Work on R: it must be more EW than MeI
Decreasing the aromaticity of the zwitterion
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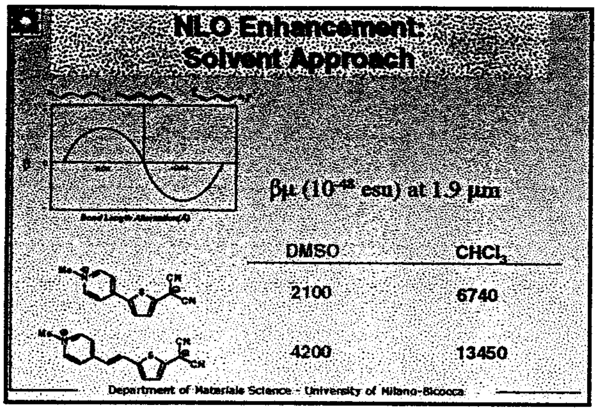
NLO Enhancement:
Solvent Approach
βμ (10-48 esu) at 1.9 μm
DMSO
CHCl3
2100
6740
4200
13450
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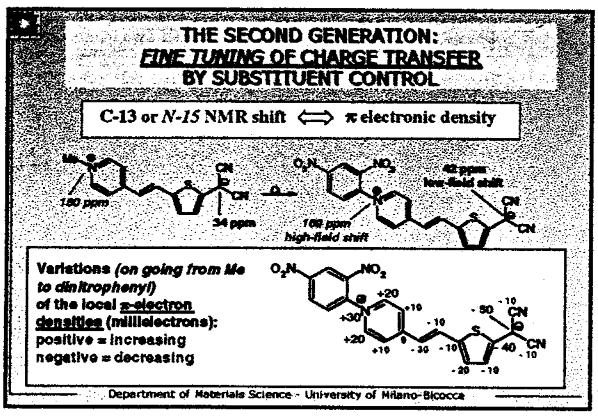
THE SECOND GENERATION:
FINE TUNING OF CHARGE TRANSFER
BY SUBSTITUENT CONTROL
C-13 or N-15 NMR shift ⟺ π electronic density
180 ppm
34 ppm
42 ppm
low-field shift
169 ppm
high-field shift
Variations (on going from Me to dinitrophenyl) of the local π-electron densities (millielectrons):
positive = increasing
negative = decreasing
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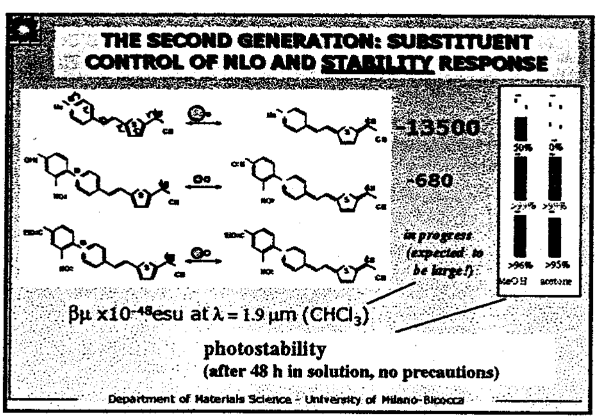
THE SECOND GENERATION: SUBSTITUENT CONTROL OF NLO AND STABILITY RESPONSE
-13500
-680
in progress (expected to be large!)
50%
0%
>96%
>95%
MeOH
acetone
βμ x10-48esu at λ = 1.9 μm (CHCl3)
photostability
(after 48 h in solution, no precautions)
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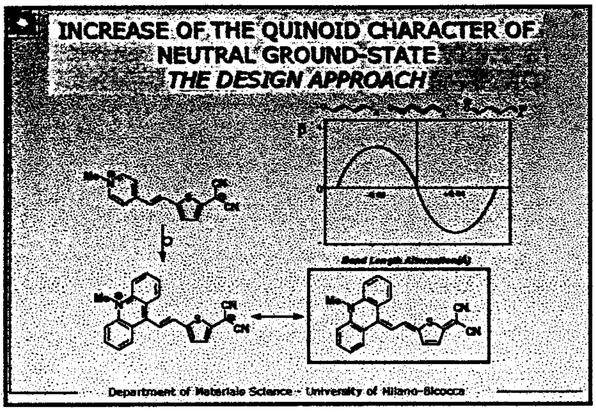
INCREASE OF THE QUINOID CHARACTER OF
NEUTRAL GROUND-STATE
THE DESIGN APPROACH
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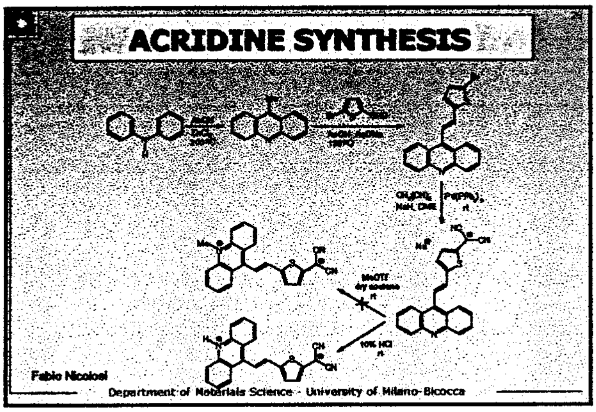
ACRIDINE SYNTHESIS
Fabio Nicoloi
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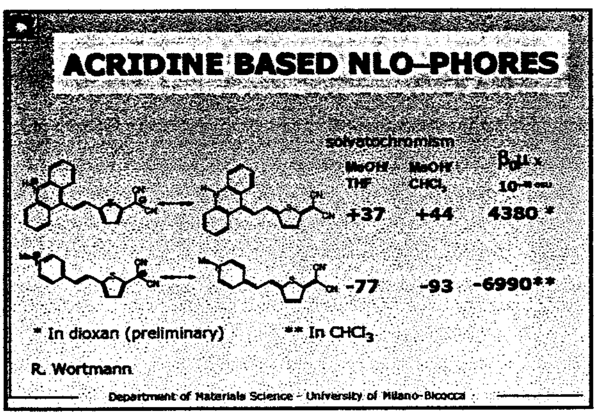
ACRIDINE BASED NLO-PHORES
solvatochromism
MeOH-THF
MeOH-CHCl3
+37
+44
4380 *
-77
-93
-6990**
* In dioxan (preliminary)
** In CHCl3
R. Wortmann
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From molecules to bulk materials

- Langmuir-Blodgett Films
- Surface Functionalization
- Sol-Gel materials
- Polymeric materials

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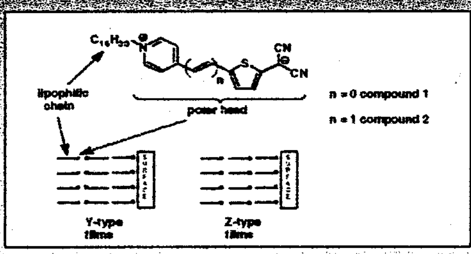
LANGMUIR-BLODGETT FILMS



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From molecules to bulk materials

- Langmuir-Blodgett Films
- Surface Functionalization
- Sol-Gel materials
- Polymeric materials

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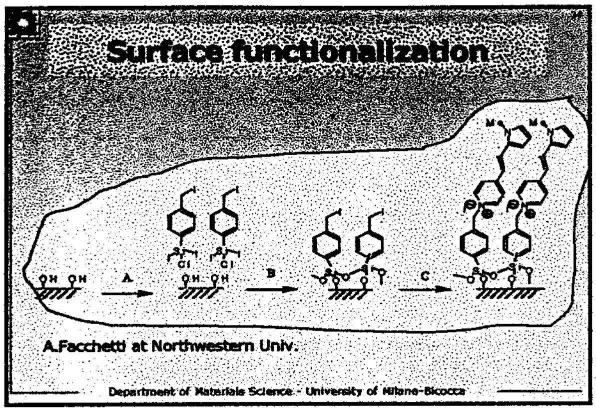
Surface functionalization
A.Facchetti at Northwestern Univ.
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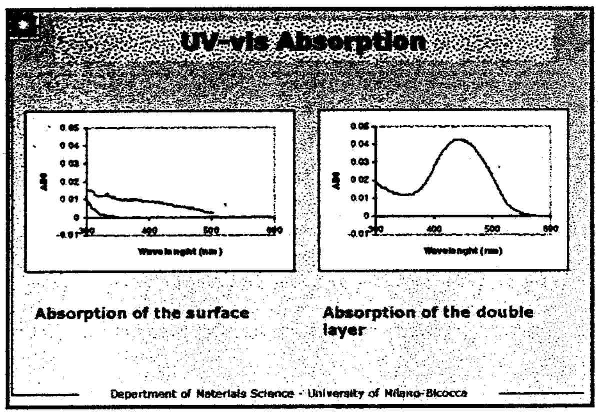
UV-vis Absorption
Absorption of the surface
Absorption of the double layer
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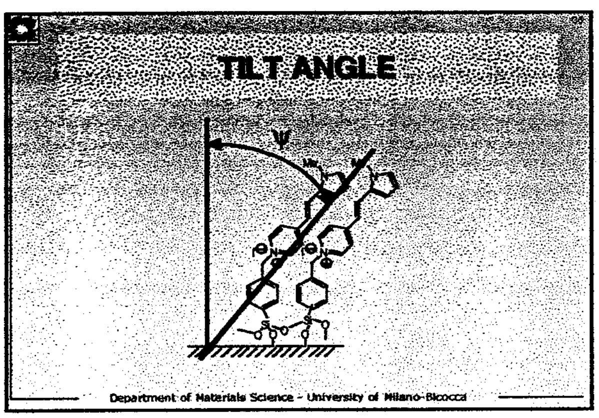
TILT ANGLE
Ψ
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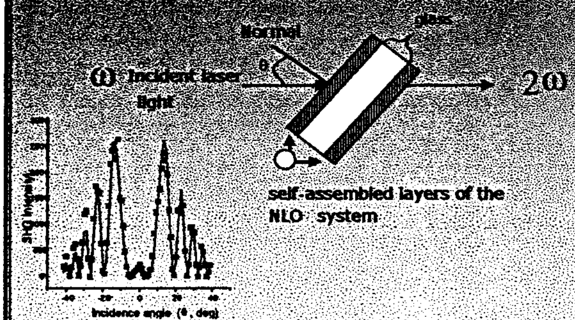
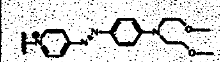
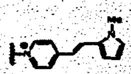
Second harmonic generation

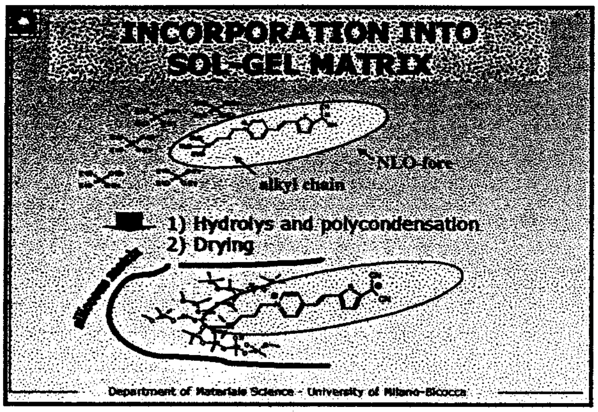


TABLE

CHROMOPHORE	β $10^{-30}cm^5esu^{-1}$	film χ^2 pm/V	ψ deg	footprint Å
	180	210	37	95
	178	150	40	49
	-	140	41	-

From molecules to bulk materials

- ➪ Langmuir-Blodgett Films
- ➪ Surface Functionalization
- ➪ Sol-Gel materials
- ➪ Polymeric materials


INCORPORATION INTO SOL-GEL MATRIX
NLO-fore
alkyl chain
1) Hydrolys and polycondensation
2) Drying
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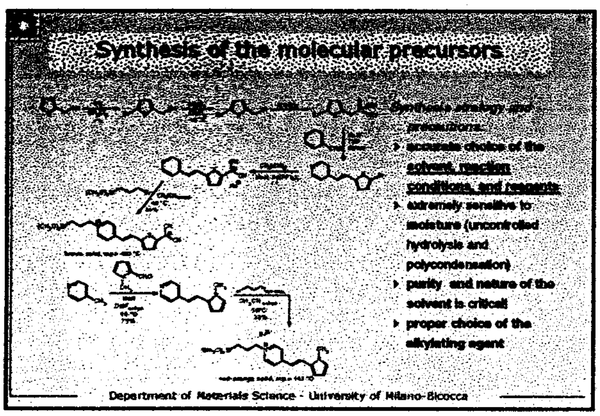
Synthesis of the molecular precursors
Synthesis strategy and precautions:
accurate choice of the solvent, reaction conditions, and reagents
extremely sensitive to moisture (uncontrolled hydrolysis and polycondensation)
purity and nature of the solvent is critical
proper choice of the alkylating agent
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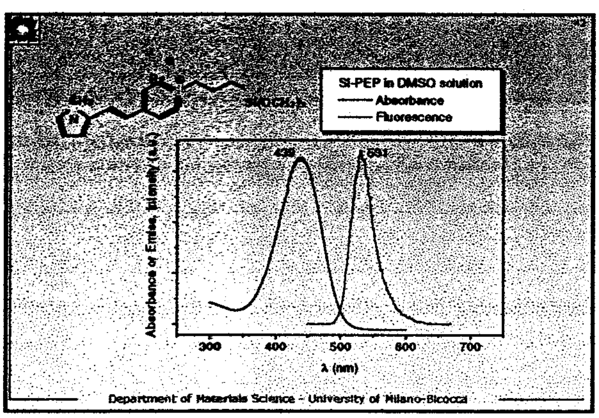
SI-PEP in DMSO solution
Absorbance
Fluorescence
Absorbance or Emiss. Intensity (a.u.)
300
400
500
600
700
λ (nm)
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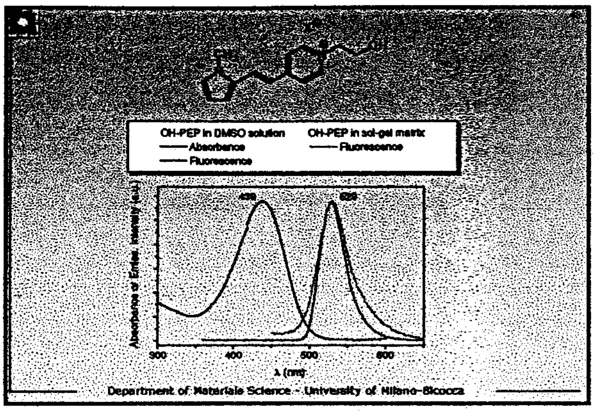
OH-PEP in DMSO solution
Absorbance
Fluorescence
OH-PEP in sol-gel matrix
Fluorescence
Absorbance or Emiss. Intensity (a.u.)
λ (nm)
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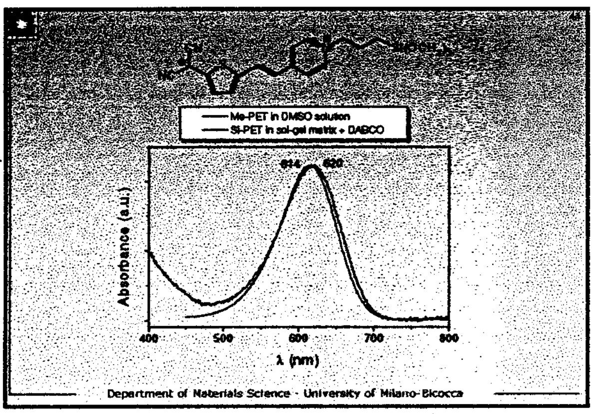
Me-PET in DMSO solution
Si-PET in sol-gel matrix + DABCO
614
620
Absorbance (a.u.)
400
500
600
700
800
λ (nm)
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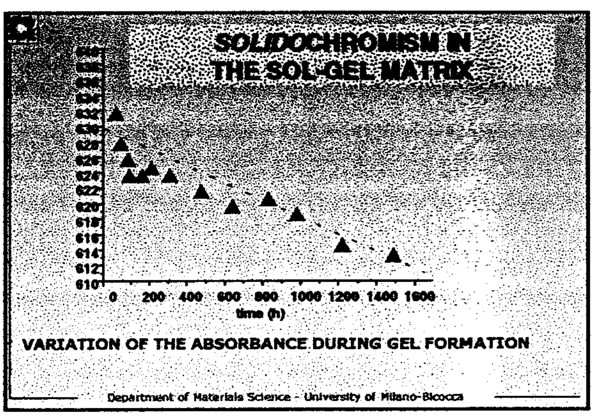
SOLIDOCHROMISM IN THE SOL-GEL MATRIX
0
200
400
600
800
1000
1200
1400
1600
time (h)
VARIATION OF THE ABSORBANCE DURING GEL FORMATION
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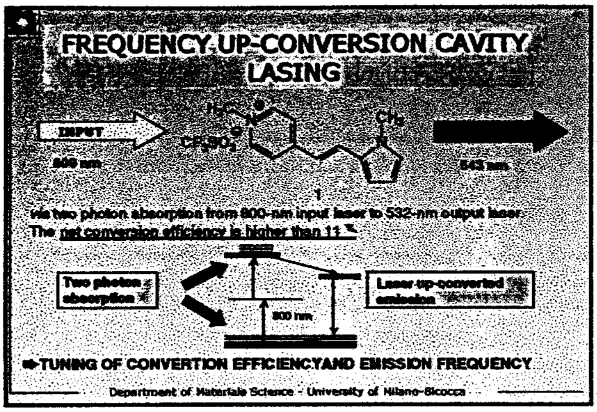
FREQUENCY UP-CONVERSION CAVITY LASING
INPUT
CF3SO3
1
via two photon absorption from 800-nm input laser to 532-nm output laser
The net conversion efficiency is higher than 11 %
Two photon absorption
800 nm
Laser up-converted emission
TUNING OF CONVERTION EFFICIENCYAND EMISSION FREQUENCY
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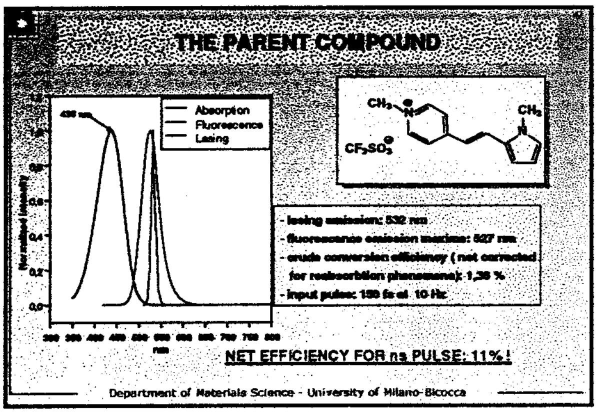
THE PARENT COMPOUND
Absorption
Fluorescence
Lasing
CH3
CH3
CF3SO3
- lasing emission: 532 nm
- fluorescence emission maxima: 527 nm
- crude conversion efficiency (not corrected for reabsorbtion phenomena): 1,38 %
- input pulse: 150 fs at 10 Hz
NET EFFICIENCY FOR ns PULSE: 11% !
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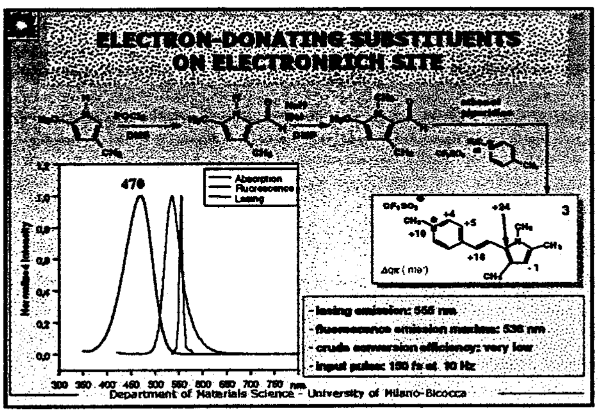
ELECTRON-DONATING SUBSTITUENTS ON ELECTRONRICH SITE
470
Absorption
Fluorescence
Lasing
3
+4
+5
+24
+10
+16
-1
Δqπ (me⁻)
- lasing emission: 555 nm
- fluorescence emission maxima: 536 nm
- crude conversion efficiency: very low
- input pulse: 150 fs at 10 Hz
300 350 400 450 500 550 600 650 700 750 nm
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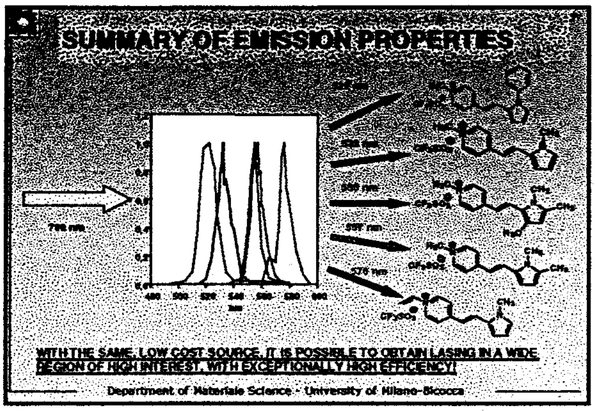

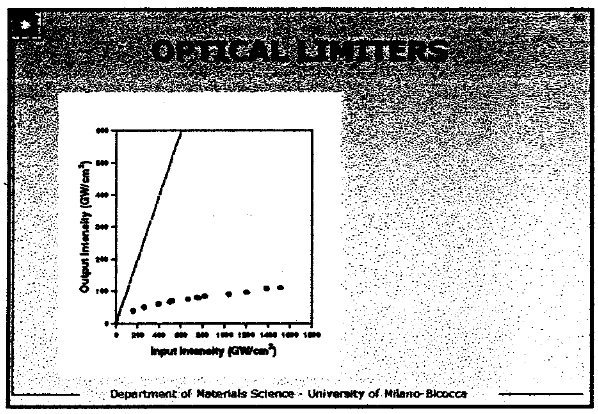

From molecules to bulk materials

- Langmuir-Blodgett Films
- Surface Functionalization
- Sol-Gel materials
- Polymeric materials

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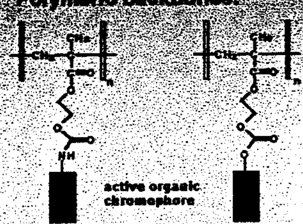
Constraints

- high loading of chromophore in the active material
- high temporal stability
- low dielectric constants are preferable to possibly increase the nlo response
- low poling temperatures mimicking the *sol-gel procedure* but assuring lack of randomization of nlo-phore dipoles
- presence of tertiary amines as oxygen scavengers: photostability

POLYMERIC MATERIALS

Polymeric backbones:

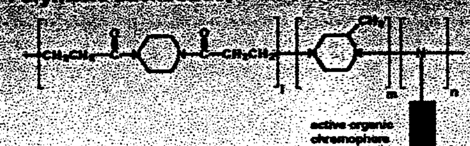


Tuning of:
- linking reaction approach
- chromophore number density
- cross-linking ratio
- thermal properties
- optical properties

Functionalized poly-methacrylate materials

POLYMERIC MATERIALS

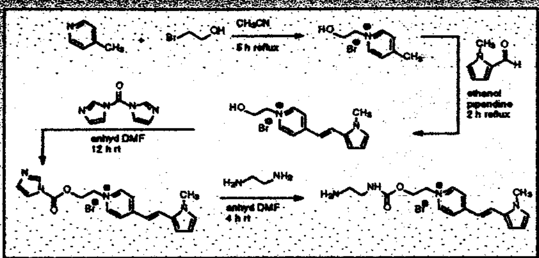
Polymeric backbones:



Functionalized poly-amidoamines

- facile preparation
- linear, soluble
- highly crosslinked
- 5-40% by weight of chromophore

Functionalization for matrix grafting



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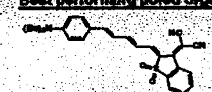
Target for electro-optics applications

Figure of Merit: electro-optic coefficient r_{33}
(Mach-Zender Modulator: info-coding in fiber-optic transmission)

Present technology

$LiNbO_3$ $r_{33} = 31$ pm V^{-1}

Best performing poled organic NLO polymer to date



$r_{33} = 55$ pm V^{-1}

polycarbonate matrix
20% wt% loading

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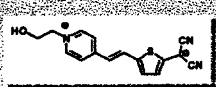
Our materials: electro-optic coefficient guess

[illegible] Two state model



$\beta\mu = -13500 \cdot 10^{-48}$ esu
As dopant in PHEMA-im matrix

Wt % loading	Estimated r_{33} (pm*V^{-1})
0.1	1.43
1	14.3
10	143

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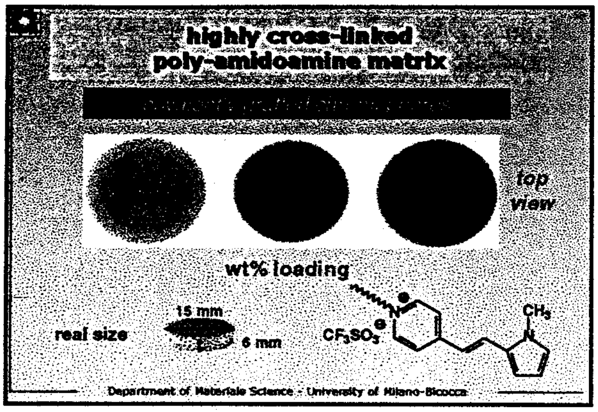
highly cross-linked
poly-amidoamine matrix
top view
wt% loading
real size
15 mm
6 mm
CF3SO3
CH3
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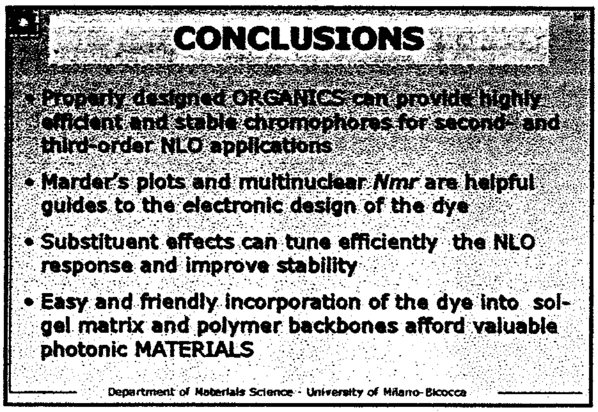
CONCLUSIONS
• Properly designed ORGANICS can provide highly efficient and stable chromophores for second- and third-order NLO applications
• Marder's plots and multinuclear Nmr are helpful guides to the electronic design of the dye
• Substituent effects can tune efficiently the NLO response and improve stability
• Easy and friendly incorporation of the dye into sol-gel matrix and polymer backbones afford valuable photonic MATERIALS
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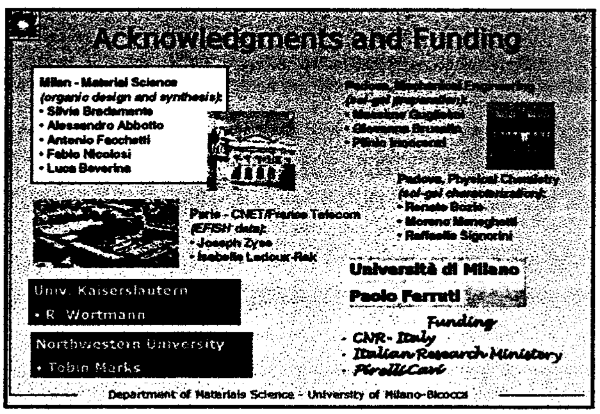
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