4. Material aspects of dye loaded zeolite L

4.1 Zeolites, a short introduction

STILBITE: $NaCa_2Al_5Si_{13}O_{36}$ -14H_2O

      NATROLITE: $Na_2Al_2Si_3O_{10}$-2H_2O

           HEULANDITE: $(Ca, Na)_2$ - $3Al_3(Al, Si)_2Si_{13}O_{36}$ - 12H_2O

Natural zeolites are a popular group of minerals for collectors and an important group of minerals for industrial and other purposes. They combine rarity, beauty, complexity and unique crystal habits. Typically forming in the cavities, or vesicles, of volcanic rocks, zeolites are the result of very low grade metamorphism. Zeolites are framework silicates consisting of interlocking tetrahedrons of **SiO_4** and **AlO_4.** In order to be a zeolite the ratio **(Si +Al)/O** must equal 1/2. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Zeolites have large vacant spaces or cages in their structures that allow space for large cations such as sodium, potassium, barium, calcium and even relatively large molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions. In many zeolites, the spaces are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. The large channels explain the consistent low specific gravity of these minerals.

Framework and SEM images of typical crystals of three common zeolites.
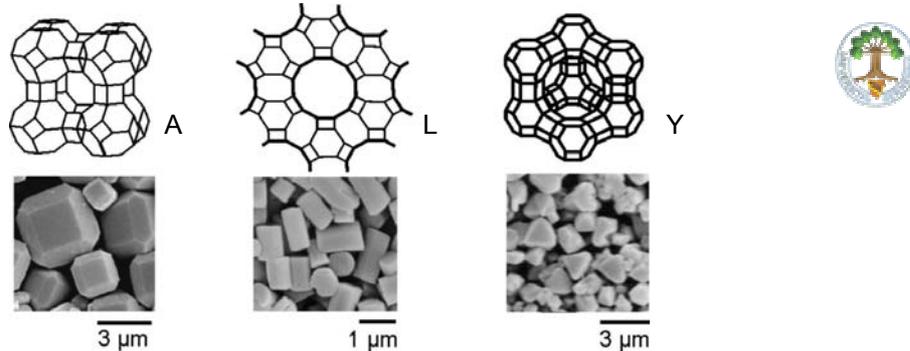
Zeolites are tectosilicates, that is they are formed by the linking together tetrahedral SiO_4 and AlO_4 to give three-dimensional anionic networks in which each oxygen of a given tetrahedron is shared between this tetrahedron and one of the four others. Thus there are no unshared oxygen's in the frameworks. This fact means that in all tectosilicates (Al + Si):O = 1:2. For every Si^{+4} which is replaced in the framework by Al^{+3} a negative charge is created which is neutralized by a charge equivalent of cations. Additionally in zeolites but not in felspars the framework is sufficiently open to accommodate water molecules as well as cations. This openness imparts characteristic zeolite properties, e.g. their ability to lose and absorb water without damage to their crystal structures.

History

🔲 Zeolites have been studied by mineralogists for almost 250 years.

Zeolite	Date	Zeolite	Date
Stilbite	1756	Mordenite	1864
Natrolite	1758	Clinoptilolite	1890
Chabazite	1772	Offretite	1890
Harmotome	1775	Erionite	1890
Analcime	1784	Kehoeite	1893
Laumontite	1785	Gonnardite	1896
Thomsonite	1801	Dachiardite	1905
Scolecite	1801	Stellerite	1909
Heulandite	1801	Ferrierite	1918
Gmelinite	1807	Viseite	1942
Mesolite	1813	Yugawaralite	1952
Gismondine	1816	Wairakite	1955
Brewsterite	1822	Bikitaite	1957
Epistilbite	1823	Paulingite	1960
Phillipsite	1824	Garronite	1962
Levynite	1825	Mazzite	1972
Herschelite	1825	Barrerite	1974
Edingtonite	1825	Merlinoite	1976
Faujasite	1842		

Electronic Excitation Energy Transfer.
Lecture 4
Material aspects of dye loaded zeolite L

History

- 1756: A. F. Cronstedt
  - History of zeolites starts with the discovery of Stilbite.
  - Described behavior under fast heating conditions. The mineral seemed to boil because of the fast water loss.

ζειν = zein = to boil

λιϑος = lithos = stone

➔ **ZEOLITE**

History

- 1784: Barthelemy Faujas de Saint-Fond
  - As a French Professor in geology he formulated a nice formalism based on observations to indentify zeolites in his book ″Mineralogie des Volcans″.
  - In his honor, a well known zeolite is called Faujasite in 1842.

Quels font donc les caractères qui doivent diriger le Naturaliste dans la connaissance de la véritable zéolite? Je crois que ceux que je vais indiquer suffiront.

1°. La zéolite soumise à un feu vif dans un creuset, ou rougie à la lampe d'émailleur, & mieux encore, placée dans un charbon qu'on creuse & qu' on allume, & attaquée avec l' air déphlogistiqué, jette, un instant avant sa fusion complette, un feu vif & brillant qui cesse & n' a plus le même éclat lorsque la matière parfaitement fondue roule en globules dans le creuset de charbon.

2°. La zéolite est fusible sans adition, & donne un beau verre.

3°. Réduite en poudre fine & traitée avec les acides, elle produit bientôt une gelée solide & transparente, sans faire aucune effervescence.

4°. La crystallisation réunie aux autres caractères, sert aussi à la faire reconnoître. Son origine est encore problématique.

History

- Until the early 1940's attempts to synthesize zeolites were made by mineralogists interested in the stability with other minerals.

- Union Carbide pioneered the synthetic molecular sieve zeolite business, initiating research in 1948 on adsorption for purification, separation and catalysis.
  - 1950: Synthesis of pure Zeolite A and X.
  - 1953: Patent filed for Zeolite A and X.
  - 1954: Final structure of Zeolite A and X.
  - 1956: Zeolite X with high silica/alumina ratios ➔ Zeolite Y.
  - 1956: Structure of Zeolite A published.
  - 1958: Structure of Zeolite X published.
  - 1959: Patent granted.

Classical and General Definition

- Classical:
  - Aluminosilicate open network of corner-sharing $[AlO_4]^-$ and $[SiO_4]^-$ tetrahedra (Al, Si ➔ T-atoms build framework).
  - Charge of the framework is compensated by mono or divalent cations or protons within the cavities or channels.
  - Exchange capability of cations.
  - Additional water molecules are present in the cavities.

- General:
  - Three-dimensional framework of tetrahedrally coordinated T-atoms with cavities or channels with the smallest opening larger than six T-atoms.
  - T-atoms: Si, Al, P, As, Ga, Ge, B, Be, etc.

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Application, Examples

- Purification of gaseous and liquid mixtures and solutions by sorption (activation by evacuation and heating).
- Reversible sorption capacity for water.
- Removal of odors and pollutants.
- Ion exchange.
- Softening of water for washing (substituted polyphospates).
- Removal of heavy metal ions in mine wastewater and radioactive fission products (Cs, Sr).
- Natural zeolites used for soil fertilizing purposes (Submit ions of potassium, ammonium, phosphate).
- Catalysis in petrochemical industries (conversion of organic molecules in liquid and gaseous phase).

International Zeolite Association (IZA)

Books from the Structure Commission
http://www.iza-structure.org/databases

Framework Type Code

Three capital letters (IUPAC Commission on Zeolite Nomenclature, 1978),
usually derived from the name of the type materials (Appendix D in the Atlas).

For interrupted frameworks the 3-letter code is preceded by a hyphen (-).
For intergrown materials, the * denotes a framework of a hypothetical end member.

	Code	Abbreviated Name	Full Name
▪	LTA	Linde Type A	Zeolite A (Linde Division, Union Carbide)
▪	LTL	Linde Type L	Zeolite L (Linde Division, Union Carbide)
▪	FAU	Faujasite	
▪	MFI	ZSM-5 (five)	Zeolite Socony Mobil – five
▪	-CLO	Cloverite	Four-leafed clover shaped pore opening
▪	*BEA	Zeolite Beta	

Secondary Building Units (SBU)

- ▪ Zeolite frameworks can be thought to consist of component units:
  - ▪ Finite (i.e. chain-like)
  - ▪ Infinite (i.e. layer-like)

- ▪ The finite units which have been found to occur in tetrahedral frameworks are called Secondary Building Units (SBU)

- ▪ The primary building units are TO_4 tetrahedra

- ▪ SBU are derived assuming that the entire framework is made up of one type of SBU only

- ▪ If more than one SBU is possible, all are listed
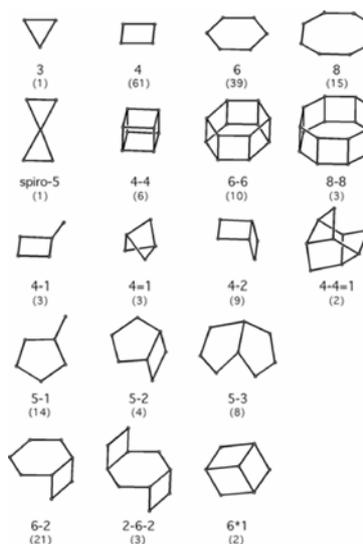
Number in ( ) = frequency of occurrence

Electronic Excitation Energy Transfer.
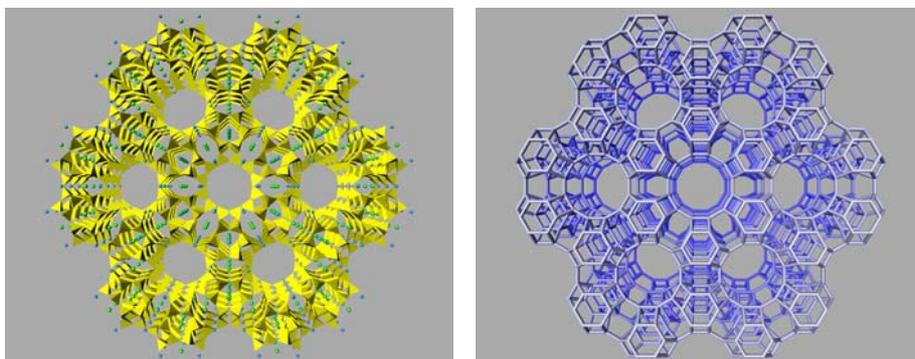Lecture 4
Material aspects of dye loaded zeolite L

4.2 Zeolite A, an illustrative example

LTA Framework: Stereographic Figure
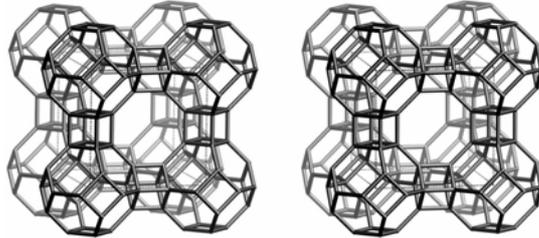
LTA: Channel <1 0 0> **8** 4.1 x 4.1
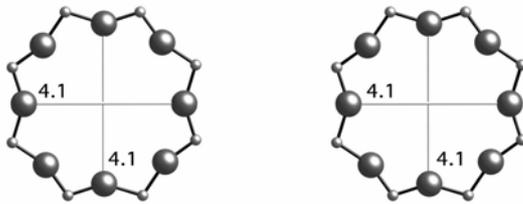
LTA: position of the charge compensating cations

Stoichiometrie of sodium zeolite A: $Na_{12}[(SiO_2)_{12}(AlO_2)_{12}]\times 27H_2O$

M^+

H_2O H_2O H_2O H_2O H_2O H_2O

Al^{3+}

O^{2-}

Si^{4+}

α-cage: $\varnothing = 11.4$ Å

opening: $\varnothing = 4.1$ Å
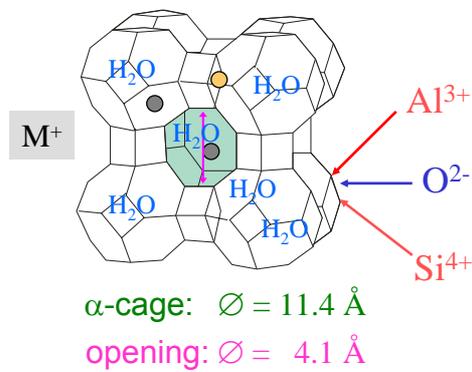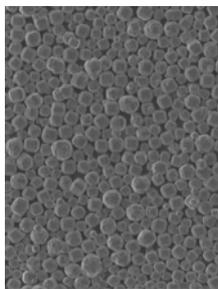
LTA Framework: Example of an ion exchange isotherm

$$bA^{a+}_{sol} + aB^{b+}_{Zeol} \rightleftharpoons bA^{a+}_{Zeol} + aB^{b+}_{sol}$$

Equivalent fraction of exchanging cations A^{a+} in solution $S(A^{a+})$ is defined as:

$$S(A^{a+}) = \frac{a\left[A^{a+}\right]_{sol}}{a\left[A^{a+}\right]_{sol} + b\left[B^{b+}\right]_{sol}}$$

Equivalent fraction of exchanging cations A^{a+} in the zeolite $Z(A^{a+})$:

$$Z(A^{a+}) = \frac{\text{number equivalents of exchanging cations } A^{a+} \text{ in zeolite}}{\text{total equivalents of exchanging cations } A^{a+} \text{ and } B^{b+} \text{ in zeolite}}$$

For zeolite A this can be expressed as follows

$$Z(A^{a+})_{\text{Zeolite A}} = \frac{a \times (\text{number of cations } A^{a+} \text{ per } \alpha - \text{cage})}{12}$$

LTA Framework: Example of ion exchange isotherms

$$Ag^+_{sol} + B^+_{Zeol} \rightleftharpoons Ag^+_{Zeol} + B^+_{sol}$$
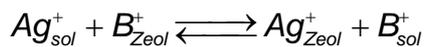
$B^+ = Na^+$ or K^+

$$S_{Ag} = \frac{\left[Ag^+\right]_{sol}}{\left[Ag^+\right]_{sol} + \left[B^+\right]_{sol}}$$

$$Z_{Ag(\text{Zeolite A})} = \frac{Ag^+ \text{ per } \alpha - \text{cage}}{12}$$

B^+	Na^+	K^+
$\Delta G^{\varnothing}$/kJ mol^{-1}	-162	-172
$\Delta H^{\varnothing}$/kJ mol^{-1}	-438	-260
$\Delta S^{\varnothing}$/J mol^{-1} K^{-1}	-925	-297

LTA: position of the charge compensating cations

Rálek 1962
Angew. Chemie
37 (1998) 1521
J. Phys. Chem A,
104 (2000) 7473
Chem. Soc.Rev.
32 (2003) 29

− H_2O

+ H_2O

Ag^+_{aq}

Ag^+

$5s(Ag^+) \leftarrow n(H_2O)$

$5s(Ag^+) \leftarrow n(O)$
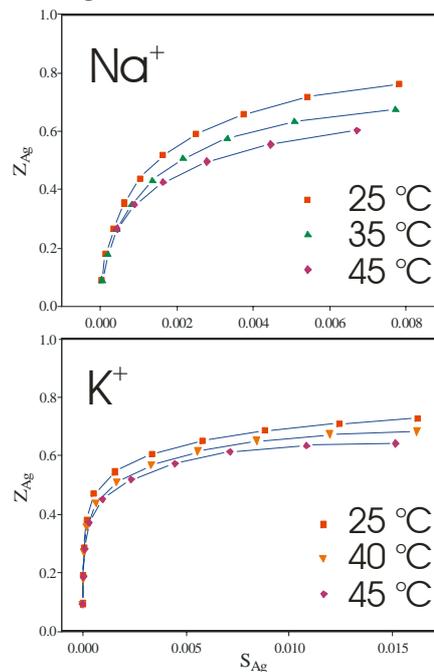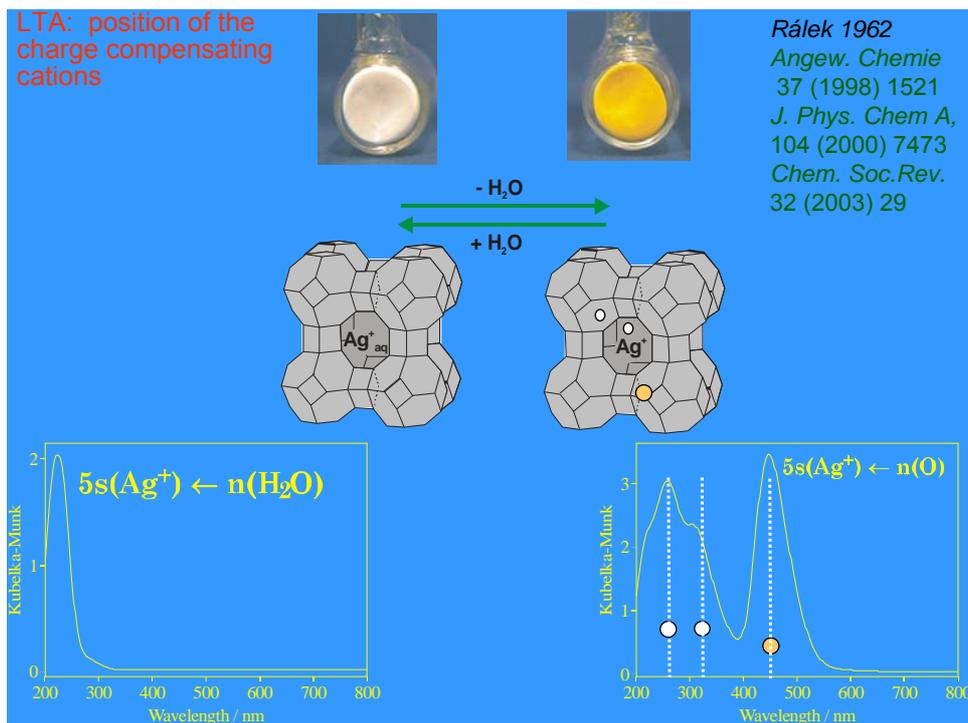
4.3 Structure and morphology of zeolite L

LTL Framework: Stereographic Figure
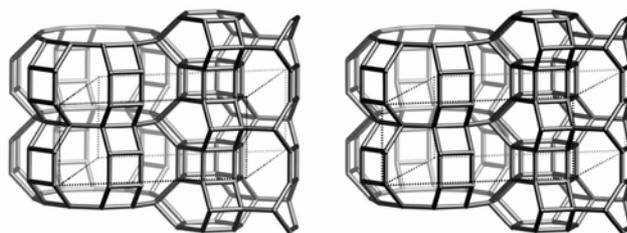
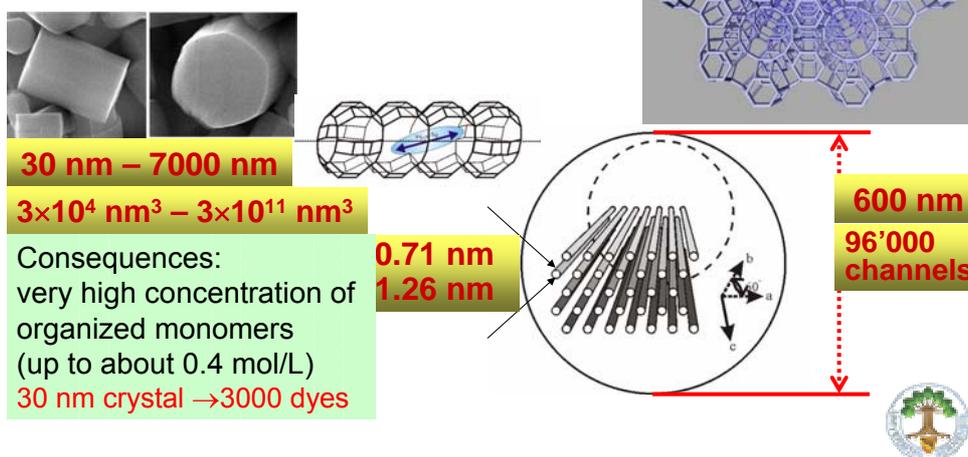LTL: Channel [0 0 1] **12** 7.1 x 7.1 *
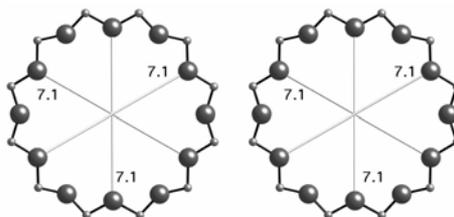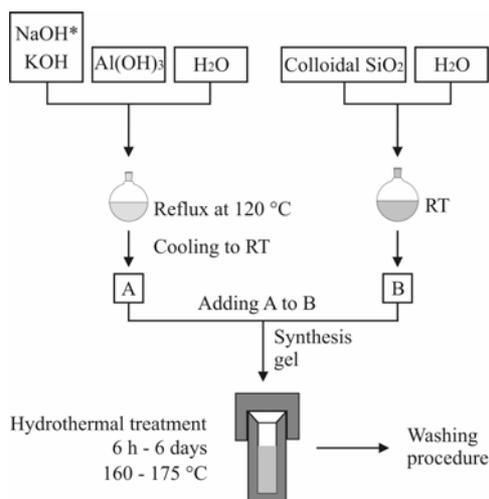
LTL: Structure and framework

LTL: Cation positions

$(M)_{9-\delta}[Al_{9-\delta}Si_{27+\delta}O_{72}] \times nH_2O \quad M=M^+$

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10
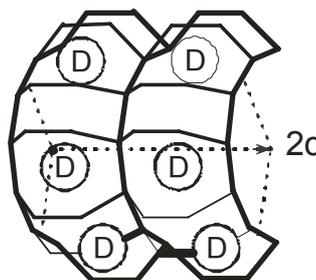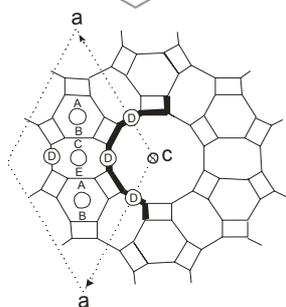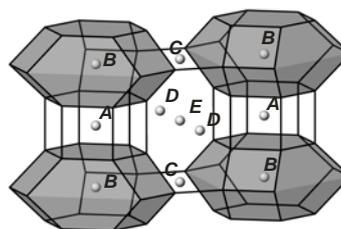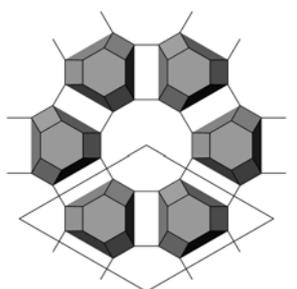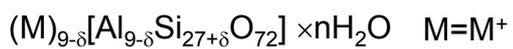
Zeolite L is an ideal host for supramolecular organization of dyes

Its crystals consist of one-dimensional channels.

Zeolite L belongs to the family of classical zeolites which are alumosilicates.

30 nm – 7000 nm

3×10^4 nm^3 – 3×10^{11} nm^3

Consequences: very high concentration of organized monomers (up to about 0.4 mol/L)

30 nm crystal →3000 dyes

0.71 nm
1.26 nm

600 nm

96'000 channels

4.4 Synthesis of zeolite L crystals

NaOH*
KOH | Al(OH)₃ | H₂O   Colloidal SiO₂ | H₂O

Reflux at 120 °C   RT

Cooling to RT

A   B

Adding A to B

Synthesis gel

Hydrothermal treatment
6 h - 6 days
160 - 175 °C   →   Washing procedure

Composition: a K$_2$O-b Na$_2$O-c Al$_2$O$_3$-d SiO$_2$-e H$_2$O

Example: large zeolites 2.21 K$_2$O-0.00 Na$_2$O-1.00 Al$_2$O$_3$-9 SiO$_2$-164.60 H$_2$O

Zabala Ruiz, Brühwiler, Calzaferri Monatshefte für Chemie, 2004, in press
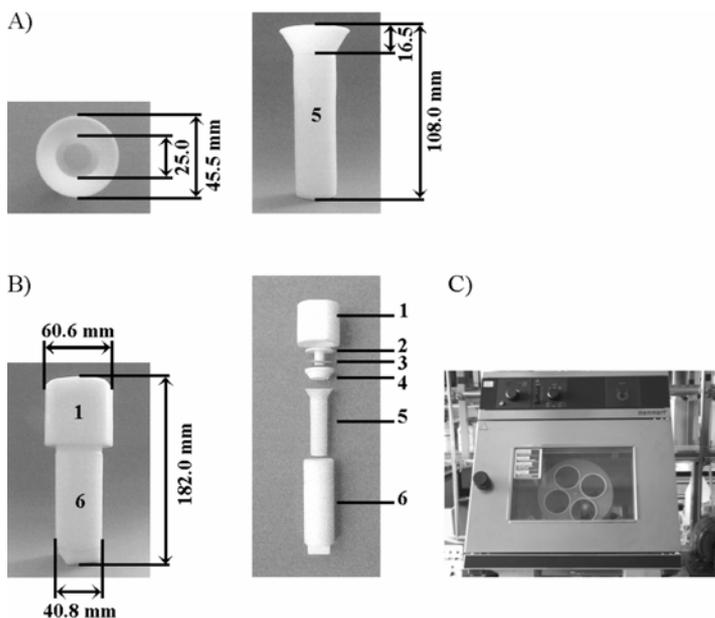
Pressure-tight poly(tetrafluoroethylene) (PTFE) vessel, 175 °C, approximately 9 bar

Zabala Ruiz, Brühwiler, Calzaferri, Monatshefte für Chemie, 2004, in press

Zabala Ruiz, Brühwiler, Calzaferri Monatshefte für Chemie, 2004, in press

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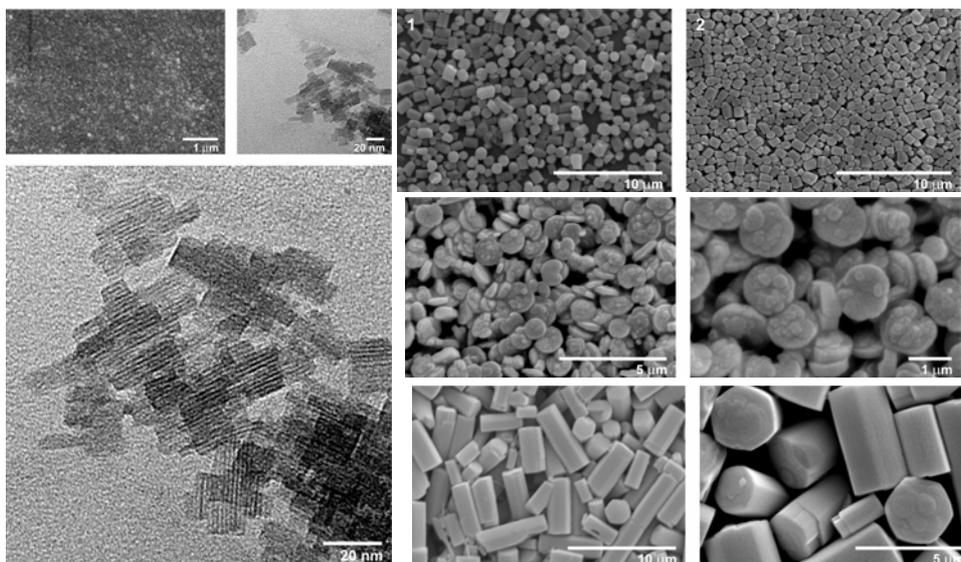
4.5 Inner and outer surface of a zeolite L crystal
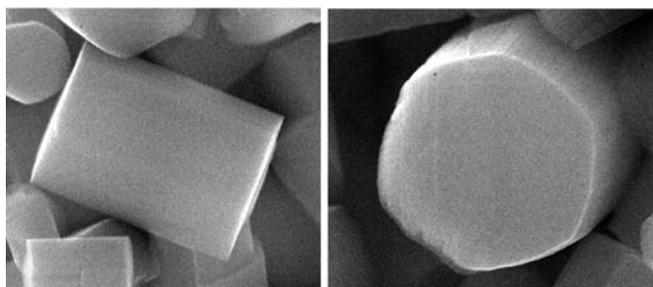
Ratio q between the number of molecules to form a monolayer at the outer surface and number of molecules to fill the channels for a crystal of equal length and diameter d_z (nm).

Number of unit cells n_{uc}: $n_{uc} = 0.357 \cdot d_z^3$

Number of channels n_c: $n_c = 0.268 \cdot d_z^2$

For a molecule of the size of Py$^+$ which occupies two unit cells, we have: $q = \dfrac{d_z}{20}$

$l_Z = d_Z = 60$ nm $n_c = 960$ $n_{uc} = 77 \times 10^3$ q = 3

$l_Z = d_Z = 600$ nm $n_c = 96'000$ $n_{uc} = 77 \times 10^6$ q = 30

Details concerning the calculation of the number of unit cells n_{uc}, the number of channels n_{ch} and the space available at the outer surface.
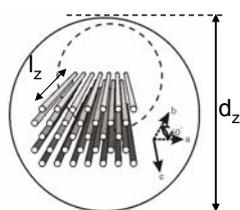
$$n_{ch} = \frac{\pi \cdot \left(\dfrac{d_z}{2}\right)^2}{|a|^2 \sin(60)} = 0.268 \, d_z^2$$

$$n_{uc} = n_{ch} \cdot \frac{l_z}{|c|} = 0.357 \, d_z^2 l_z$$

$|a| = 1.85 \; nm$

$|c| = 0.75 \; nm$

$$n_{D(in)} = n_{uc} \frac{1}{s}$$

$$n_{D(out)} = \frac{1}{A_D} \pi \left(\frac{d_z^2}{2} + d_z l_z\right)$$

$A_D = 1.4 \; nm^2$

s = 2

$$q = \frac{n_{D(in)}}{n_{D(out)}}$$
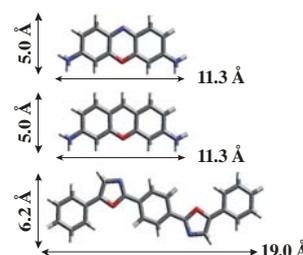
$l_Z = d_Z = 100$ nm $n_{ch} = 2680$ $n_{uc} = 35.7 \times 10^4$

S = 2 $n_{D(in)} = 17.8 \times 10^4$ $n_{D(out)} = 3.36 \times 10^4$ q = 5.3

Inner and outer surface of a zeolite L crystal. A demonstration experiment.
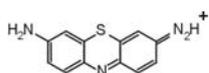
Hypochlorite destroys
only dye molecules at the
outer surface!
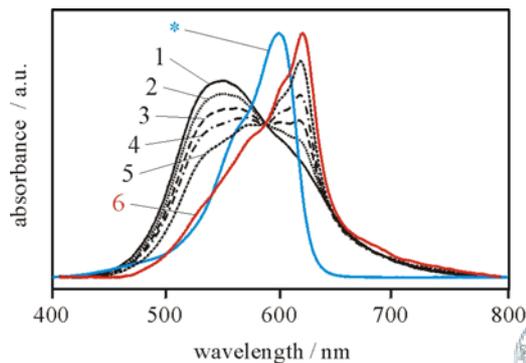
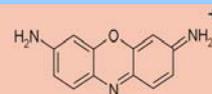Inner and outer surface of a zeolite L crystal. Solvatochromisme.
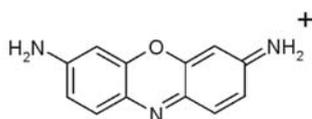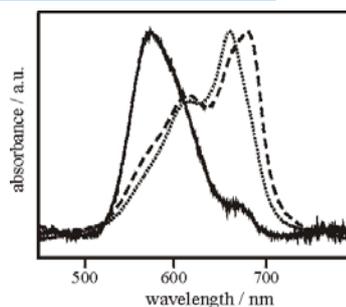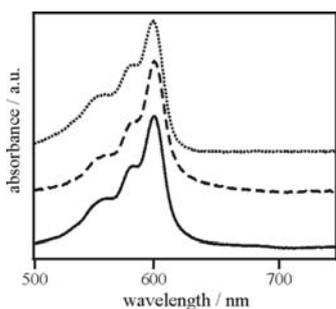
Cyclohexane (dashed)
CH$_2$BrCl   (points)
Water   (solid)
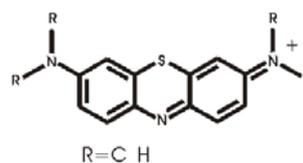
R=C$_2$H$_5$
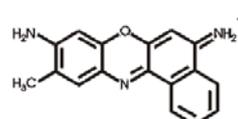
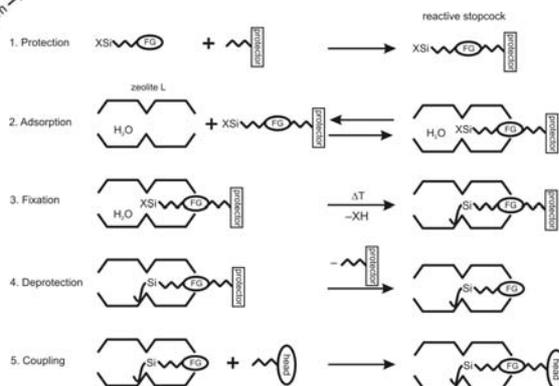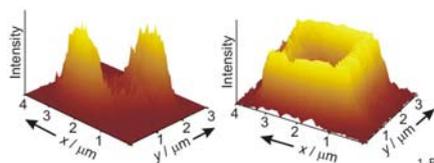Inner and outer surface of a zeolite L crystal. H-aggregates at the outer surface
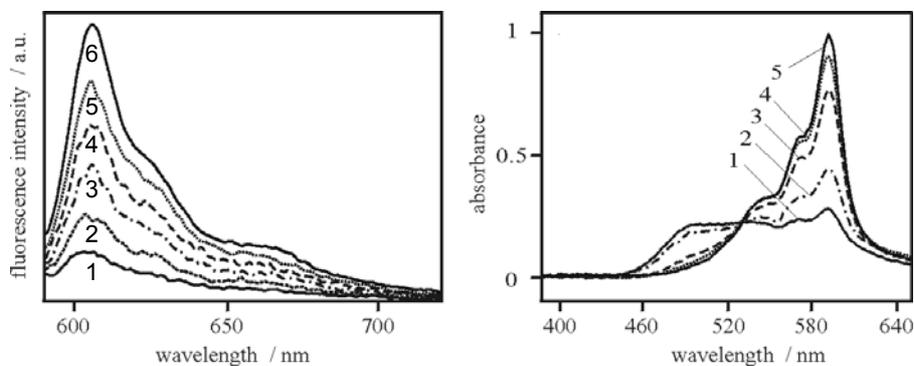
Right: absorption spectra measured under the same conditions at different times after mixing an aqueous zeolite suspension with Ox⁺. **1:** 30 s; **2:** 9 min; **3:** 190 min; **4:** 1 d; **5:** 7 d.
Left: fluorescence spectra of *Ox⁺-zeolite L* dispersions at room temperature measured at different times after mixing an aqueous zeolite suspension with the dye:
1: 10 s; **2:** 30 s; **3:** 90 s; **4:** 4 min; **5:** 4 h; **6:** 18 h. The excitation wavelength was 580 nm.
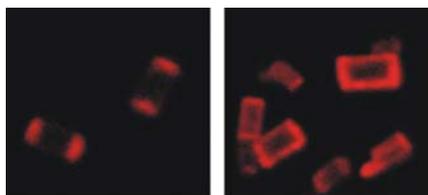
Inner and outer surface of a zeolite L crystal. Selective functionalization

S. Huber, Gion Calzaferri,
Angew.Chemie 2004, in press

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4.6 Insertion of molecules into the channels

Neutral and cationic molecules which can pass the 0.71 nm opening of zeolite L can be inserted. Negatively charged dyes can not be inserted because of the negative charge of the channels unless very special conditions are met.
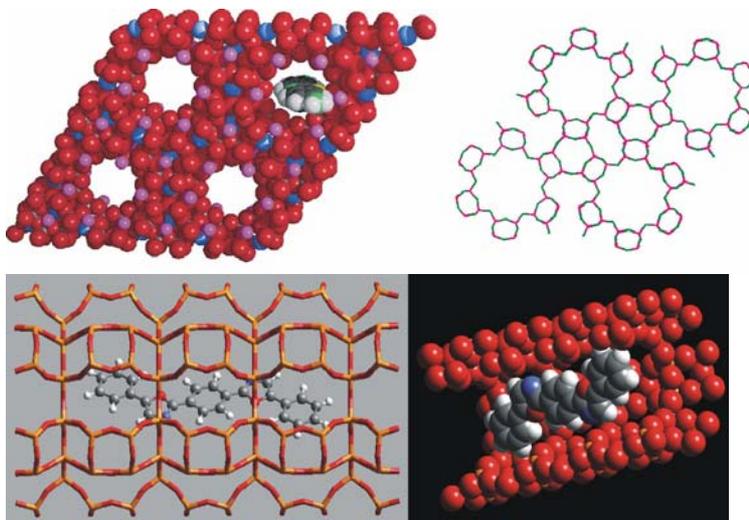
Incorporation of chromophores into the cavities of zeolites can be achieved in different ways:
from the gas phase,
by ion exchange if cations are involved,
by crystallization inclusion,
by performing an *in situ* synthesis inside the zeolite cages (ship-in-a-bottle synthesis).
Many interesting materials have been prepared by means of the ship-in-a-bottle and the crystallization inclusion syntheses.
For the purpose of this work, the reversible methods which are ion exchange, insertion from the gas phase, and insertion from a solution in a solvent where the solvent molecules are too large to enter the channels, are more important. We therefore focus on these methods.

Solid-gas-, displacement-, ion exchange-, and adsorption equilibria play the most important role in the reversible methods.

Solid-gas equilibrium: Molecules *D* in the gas phase *(g)* are in equilibrium with molecules in the channels of zeolite L.

$$ZD_{r-1} + D(g) \rightleftharpoons ZD_r \qquad\qquad K_r^{SG} = \frac{[ZD_r]}{[ZD_{r-1}][D(g)]}$$

r   = number of sites occupied by dye molecules. $0 \le r \le nbox$.

n_{box} = number of sites in one channel. Example, *nbox* is equal to 200 in a 300 nm long zeolite and a 1.5 nm long dye which occupies two unit cells.

ZD_r = denotes the number of channels which contain *r* dye molecules *D*.

SG   = solid-gas
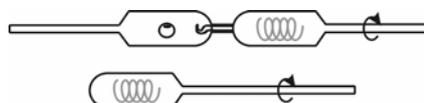
Displacement equilibrium:

Molecules *X* can sometimes displace molecules *D* located inside of the zeolite. In a zeolite ZD_rX_{p-x} a dye can also displace *x* molecules of *X*. *D(out)* and *X(out)* refer to dyes and molecules at the outside. The state of these species has in general to be specified.

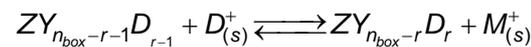$$ZD_{r-1}X + D(out) \rightleftharpoons ZD_rX_{p-x} + xX(out) \qquad K_r^{DI} = \frac{[ZD_rX_{p-x}]}{[ZD_{r-1}X_p][D(out)]}[X(out)]^x$$
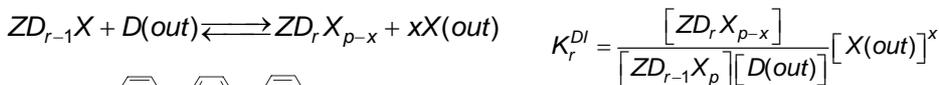
D = pTP ⬡—⬡—⬡   X=H_2O
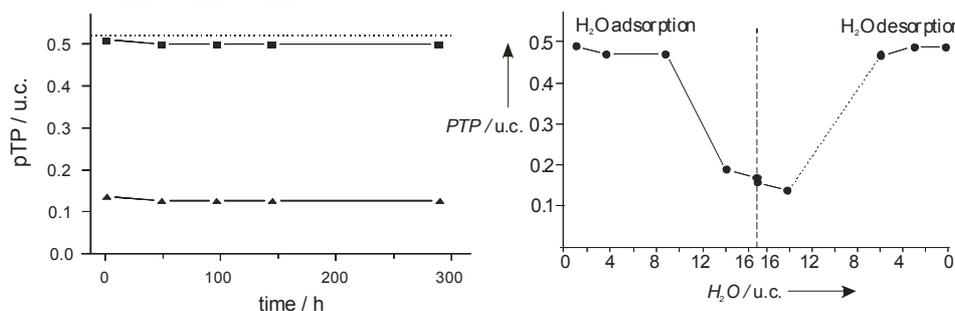
Left: Amount of *p*TP/u.c. staying inside the channels when dry (■) and wet (▲) pTp-Zeolite L with originally the same loading (dotted line) is dispersed in 1-butanol.

Right: Amount of *p*TP/u.c. located inside the zeolite depending on the amount of coadsorbed H_2O/u.c. The water content of the sample was varied either by adsorption of water on the dry *pTP-zeolite L* sample or desorption of water from a wet *pTP-zeolite L*

Ion exchange equilibrium: In most ion exchange experiments monovalent cationic dyes have been used. *DS+* and *MS+* denote the dye and the alkali metal cations in solution. *Y* describes the cation concentration inside the zeolite. For monovalent cations and dyes which occupy two unit cells in zeolite L (e.g. pyronine, Py+, or oxonine, Ox+) we must use

$$Y_{n_{box}-r-1} = \left[M_{18}^+\right]_{n_{box}-r}\left[M_{17}^+\right]_r$$

to describe the state of a given channel. An empty site contains 18 cations *M+*. Only one of them can be exchanged by a singly charged dye *D+* cation. By the exchange of *rD+* molecules the number of sites containing 18 cations is reduced by *r*, and *r* sites containing only 17 alkali cations are formed. In the following (s) means "in solution".

$$ZY_{n_{box}-r-1}D_{r-1} + D_{(s)}^+ \rightleftharpoons ZY_{n_{box}-r}D_r + M_{(s)}^+$$

$$K_r^{DI} = \frac{[ZY_{n_{box}-r}D_r]}{[ZY_{n_{box}-r-1}D_{r-1}][D^+]_{(s)}}[M^+]_{(s)}$$

Example:

$$ZY_{n_{box}-r-2}MV_r^{2+} + MV_{(s)}^{2+} \rightleftharpoons ZY_{n_{box}-r}MV_{r+1}^{2+} + 2M_{(s)}^+$$

Electronic Excitation Energy Transfer.
Lecture 4
Material aspects of dye loaded zeolite L
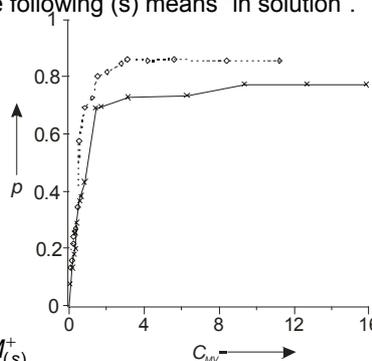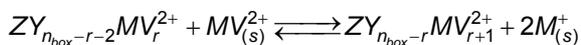
Influencing the ion exchange equilibrium:
The exchange equilibrium can be shifted to higher D⁺ loading by (a) choosing a
solvent in which the dye cations that have to be inserted are only poorly
soluble so that they prefer to enter the channels, by (b) working in a solvent in
which the exchanged potassium cations precipitate with the corresponding
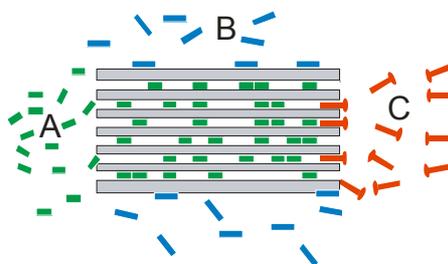anions originally belonging to the dye or by by means of an ionophore *crypt*.
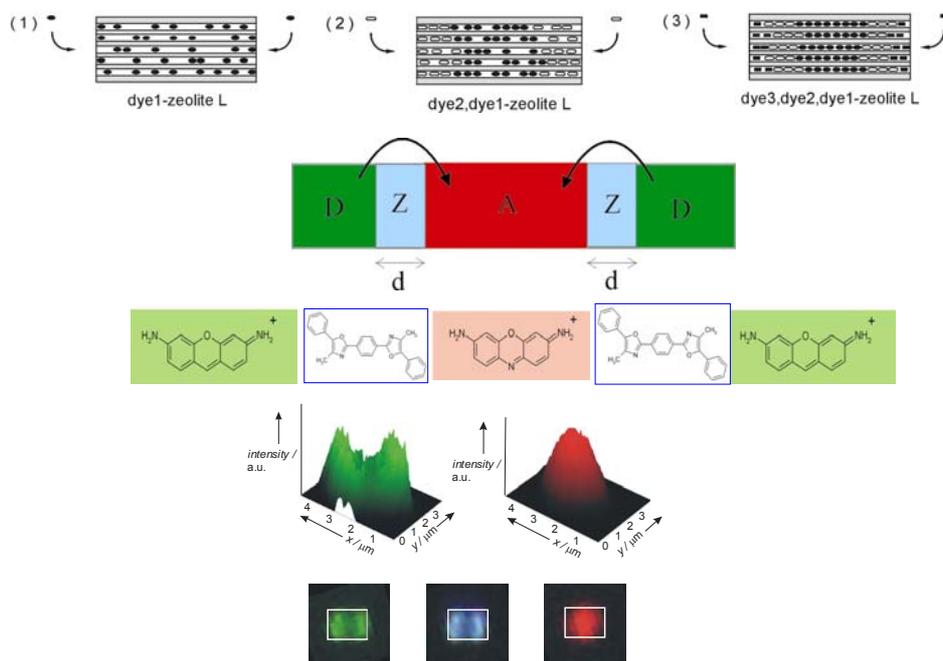
For potassium zeolites, cryptofix 222 can be used.

$$ZY_{n_{box}-r-1}D_{r-1} + D^+_{(s)} \rightleftharpoons ZY_{n_{box}-r}D_r + K^+_{(s)}$$

$$K^+_{(s)} + crypt_{222} \rightleftharpoons K^+crypt_{222}$$
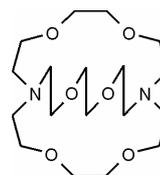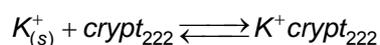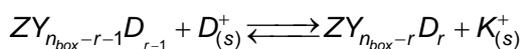
Adsorption equilibria at the outer surface play an important role.
As the zeolite L crystals have a more or less cylindrical shape, we must
distinguish between two external surfaces: the coat and the base. The coat is
round and lacks channel entrances, whereas the base is flat and contains the
channel openings.
These chemical differences strongly influence the adsorption affinity of
molecules with respect to these surfaces. They can be used for developing
very specific synthesis strategies.

4.6.1. Preparation of Sandwich materials

Preparation of sandwich materials

M. Pauchard,
A. Devaux,
G. Calzaferri
Chem. Eur. J.
2000, *6*, 3456

Electronic Excitation Energy Transfer.
Lecture 4
Material aspects of dye loaded zeolite L
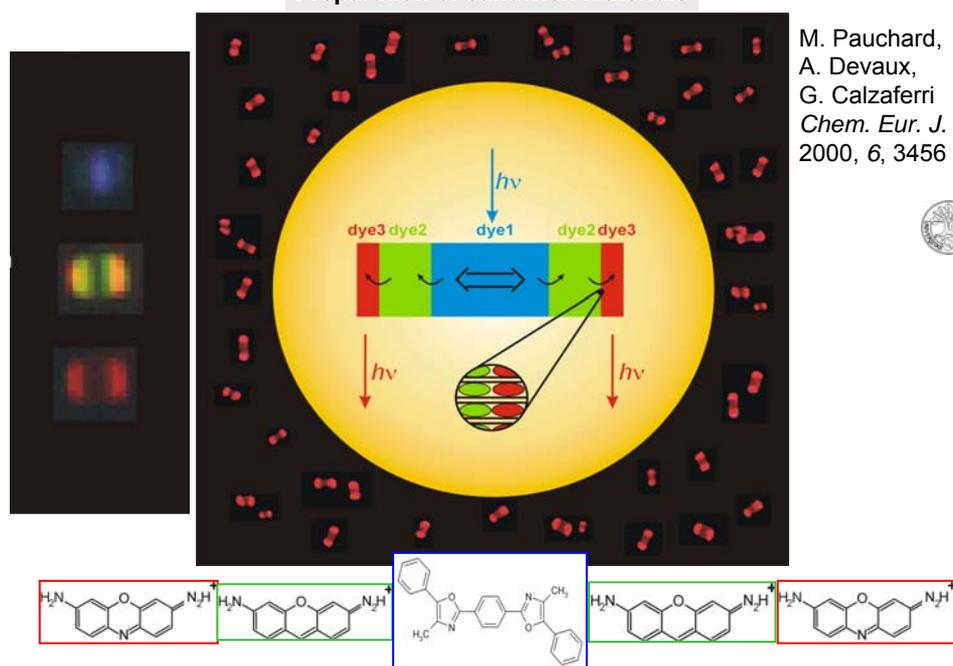
4.7 Kinetics of the insertion process

A way to study the insertion kinetics of dyes in an ion exchange reaction is to make use of the fact that cationic dyes usually adsorb very fast at the outer surface of the crystals, as can be seen by the formation of typical H-aggregat bands in the elctronic spectra which disappear when the dyes slipp into the channels.
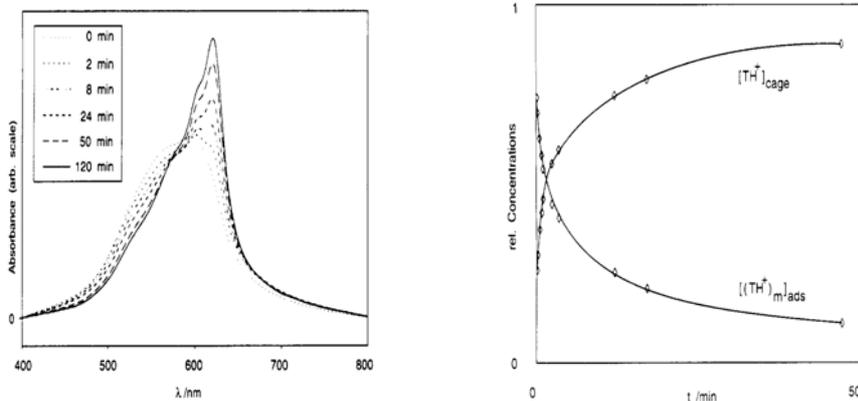
Spectra of a thionine-zeolite L dispersion at *70 °C* measured at different times after mixing of an aqueous zeolite dispersion with the dye. Right: kinetics of insertion of the aggregates formed in the first step into the main channel at *70 °C*

4.7.1 Kinetics of the insertion of two randomly mixed luminescent dyes, monitored by EnT
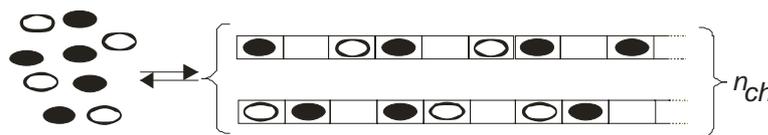
A) Principle of the EnT measurement: a demonstration experiment
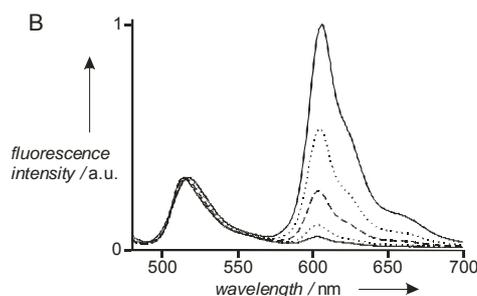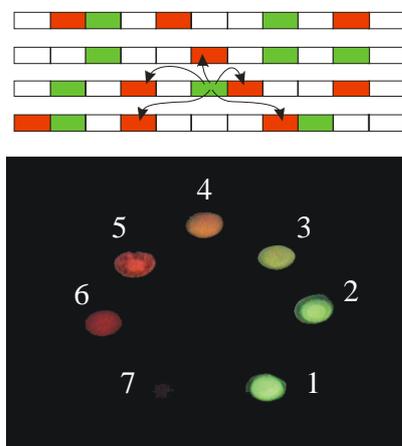
A) Principle of the EnT measurement: a demonstration experiment
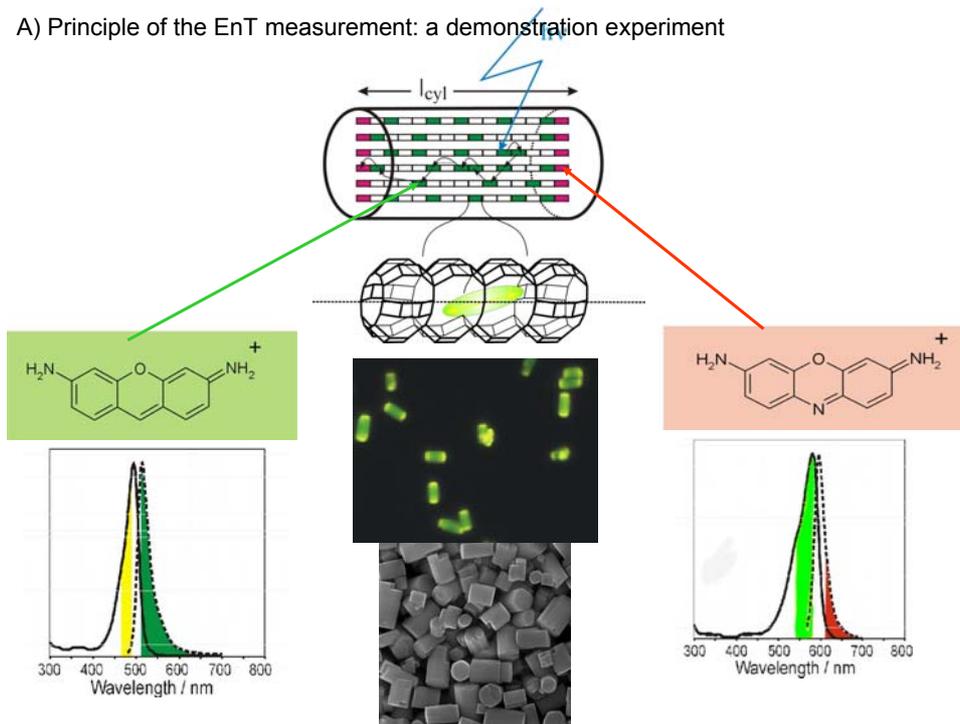
A) Principle of the EnT measurement: kinetics
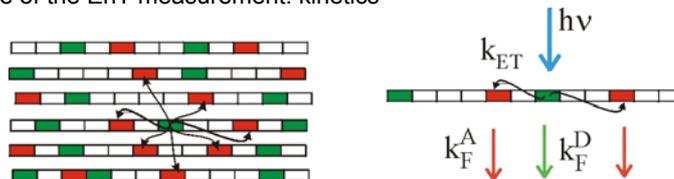
$$\frac{d\left[D_{S_1}\right]}{dt} = j_{abs} - \left[D_{S_1}\right]\sum_d k_d^D$$

$$\frac{d\left[A_{S_1}\right]}{dt} = k_{EnT}\left[D_{S_1}\right] - \left[A_{S_1}\right]\sum_a k_a^A$$

$$\Phi_F^D = \frac{k_F^D}{\sum_d k_d^D}$$

$$\Phi_F^A = \frac{k_{EnT}}{\sum_d k_d^D}\frac{k_F^A}{\sum_a k_a^A}$$

$$\frac{\Phi_F^A}{\Phi_F^D} = k_{EnT}\frac{k_F^A}{k_F^D \sum_a k_a^A}$$

$$k_{EnT} \propto p_a$$

$$\frac{\Phi_F^A}{\Phi_F^D} = Cp_a$$

Electronic Excitation Energy Transfer.
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Material aspects of dye loaded zeolite L

B) Intrazeolite diffusion kinetics monitored by energy transfer

$$\frac{I_F^A}{I_F^D}(t) = C\frac{(p^0)^2}{\sqrt{8\pi}}\frac{1}{\sqrt{Dt}}$$
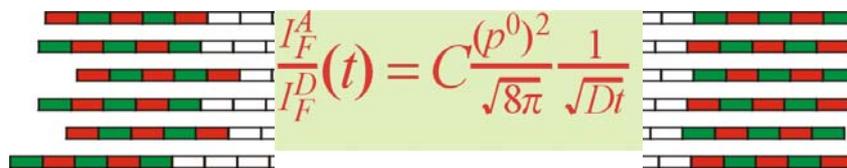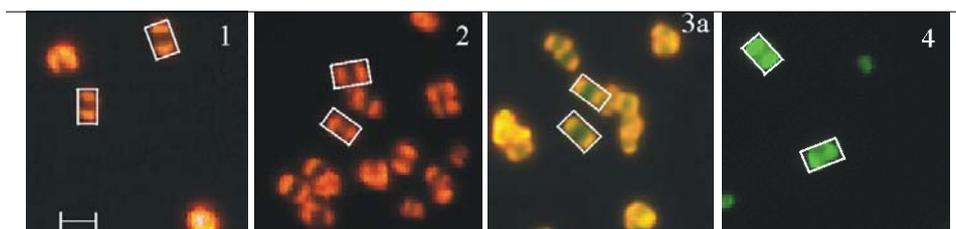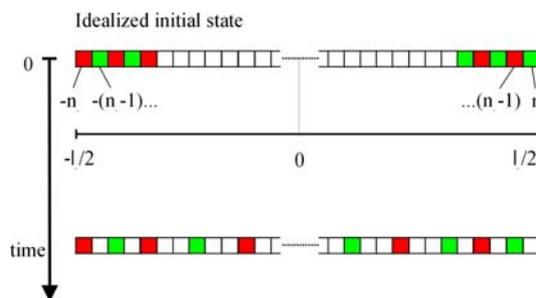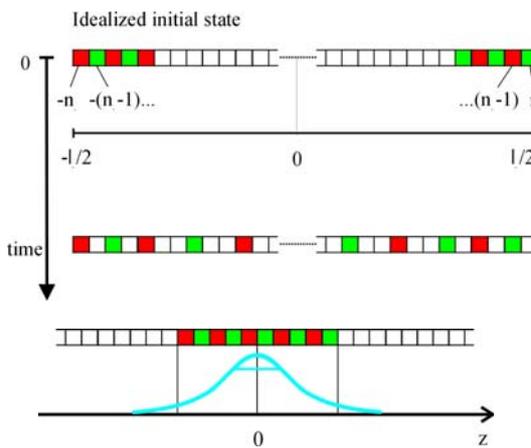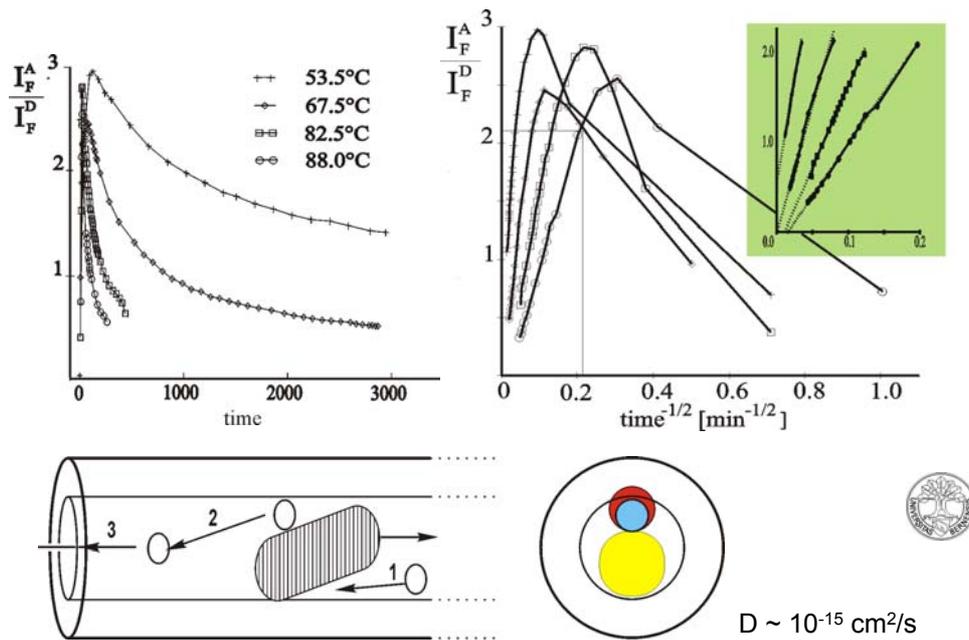
Intrazeolite Diffusion Kinetics of Dye Molecules in the Nano Channels of Zeolite L monitored by Energy Transfer. Michel Pfenniger and Gion Calzaferri, *ChemPhysChem*, 1, 2000, 211-216

4.7.2 Exit kinetics and reversible insertion and release of molecules

Displacement equilibrium: $Z(pTp)_r(H_2O)_{p-x} + xH_2O \rightleftharpoons Z(pTp)_{r-1}(H_2O)_p + pTp$
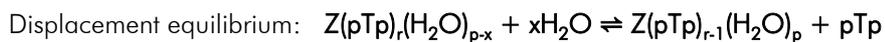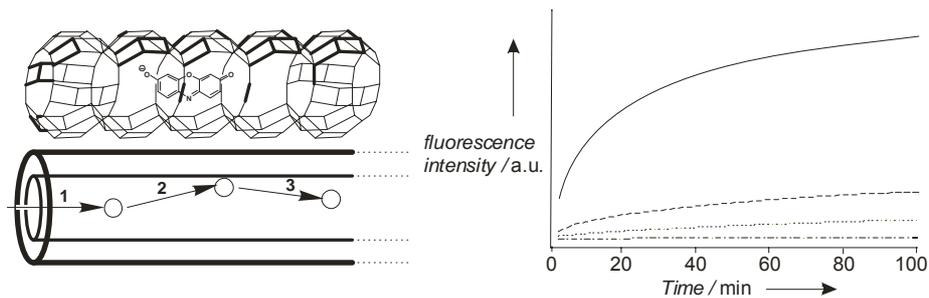
Exit kinetics depends on Interactions of the dyes with the zeolite

Fluorenon is hardly displaced by water molecules when the zeolite is held in air,
in contrast to pTP. The main difference between the two molecules is the C=O group.
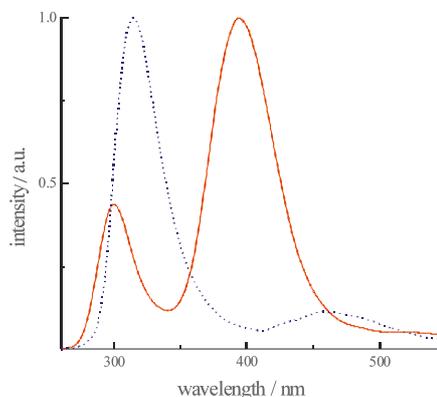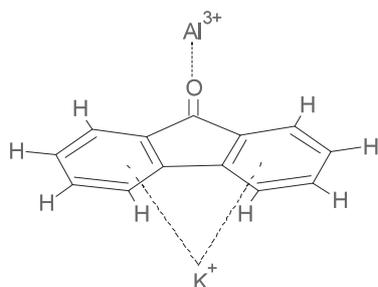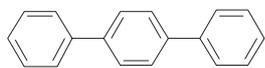
Fluorenon shows unusual luminescence behaviour in that it emits from two states.
Right: Luminescense spectra in c-hexane (doted) and in zeolite L (solid), measured at r.t.
and excited at 270 nm.

Electronic and Vibrational Properties of Fluorenone in the Channels of Zeolite L
André Devaux, Claudia Minkowski, Gion Calzaferri, *Chem. Eur. J.* 2004, *10*, 2391

Fluorenon shows unusual luminescence
behavior in that it emits from two states.
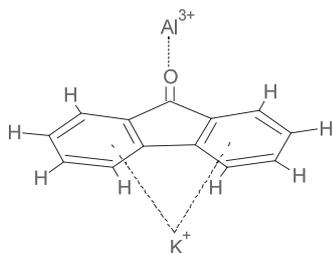
Energy states diagram for fluorenone-
zeolite L.
Left: calculated energy levels and
oscillator strengths.
Right: observed luminescence (ST_1,
ST_2), excitations (L_1, L_2), and lifetimes.
Excitation spectra are depicted as boxes
and the shading corresponds to the
spectral intensity. Darker shading
represents a stronger signal.
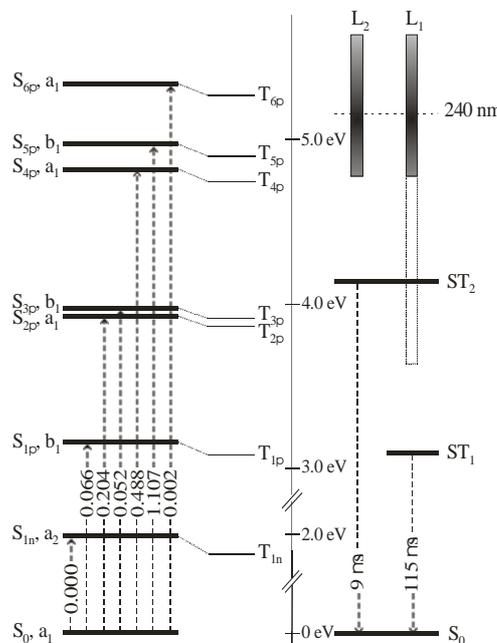
Electronic and Vibrational Properties of Fluorenone in the Channels of Zeolite L
André Devaux, Claudia Minkowski, Gion Calzaferri, *Chem. Eur. J.* 2004, *10*, 2391

Electronic Excitation Energy Transfer.
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Material aspects of dye loaded zeolite L
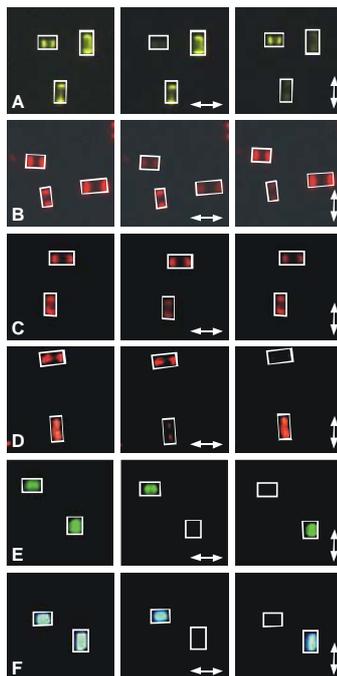
24

4.7.3 Photochromism
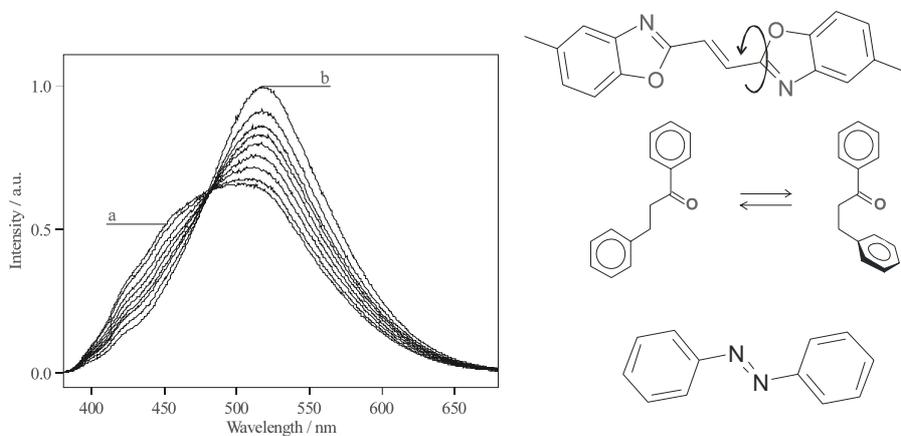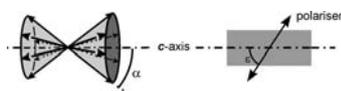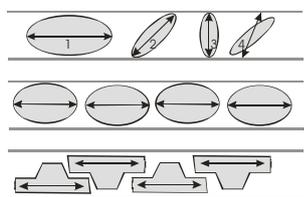

D. Brühwiler, G. Calzaferri, Microp. Mesop. Mat. 2004, *72*, 1-23

4.8 Orientation and organization of the dye molecules in the channels

exciting light

anisotropically arranged
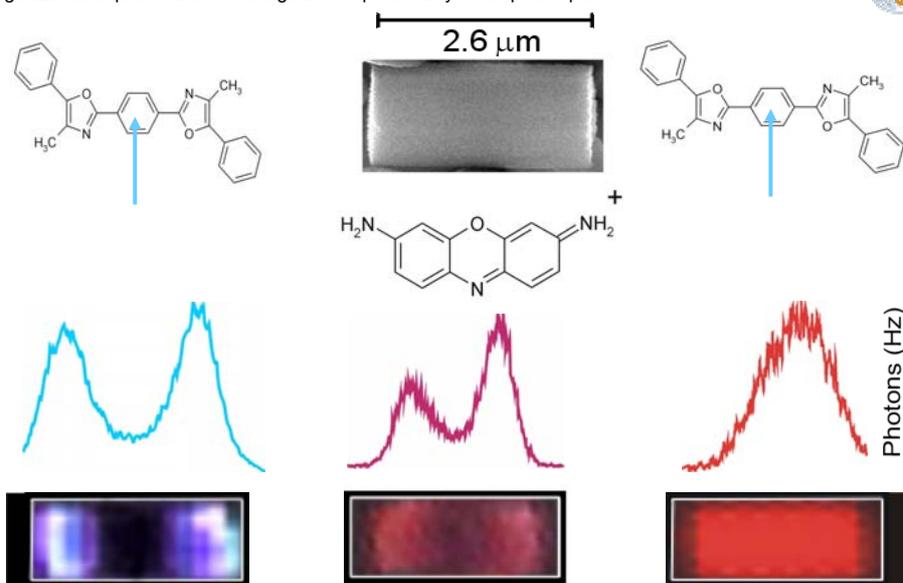
electronic transition moments

300 – 3000 nm
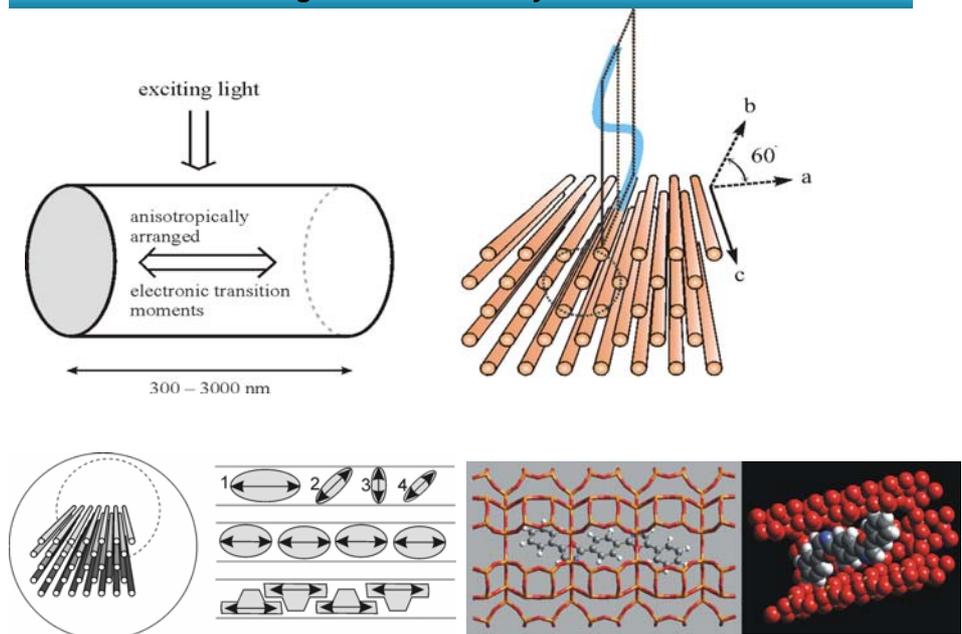
Orientation of the dyes
in the channels.
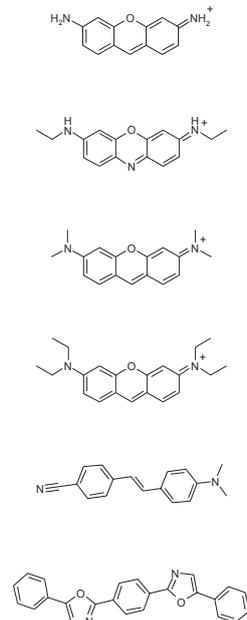
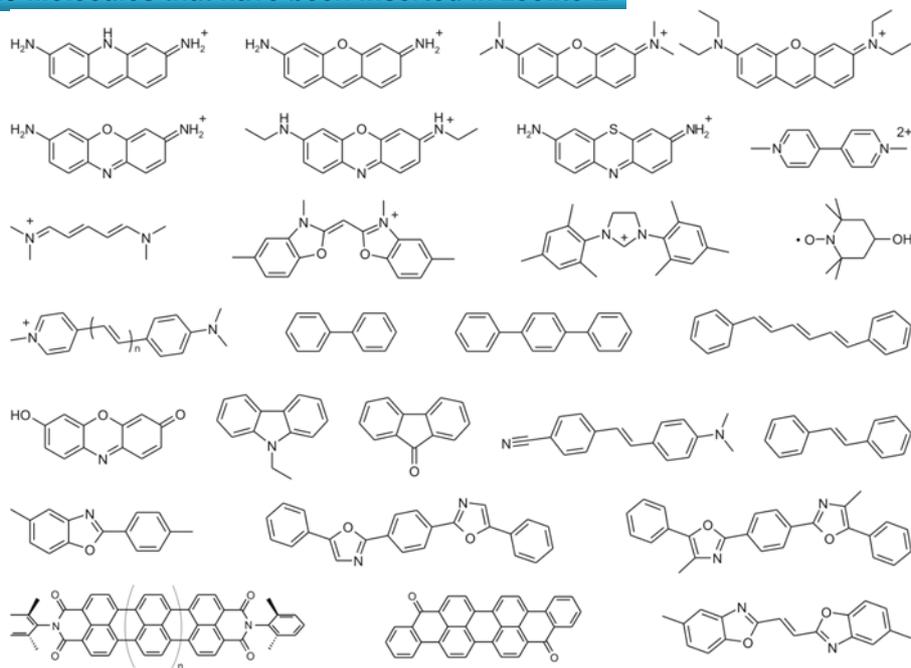### 4.8.1 Organization of the dye molecules in the channels.

*Organization* implies transfer of a signal in a specific way to a specific place.   see also 4.6.1

2.6 μm

Photons (Hz)

Pauchard, Huber, Méallet, Maas, Pansu, Calzaferri, Angew. Chem. Int. Ed. 40 (2001) 2839

4.9 Molecules that have been inserted in zeolite L
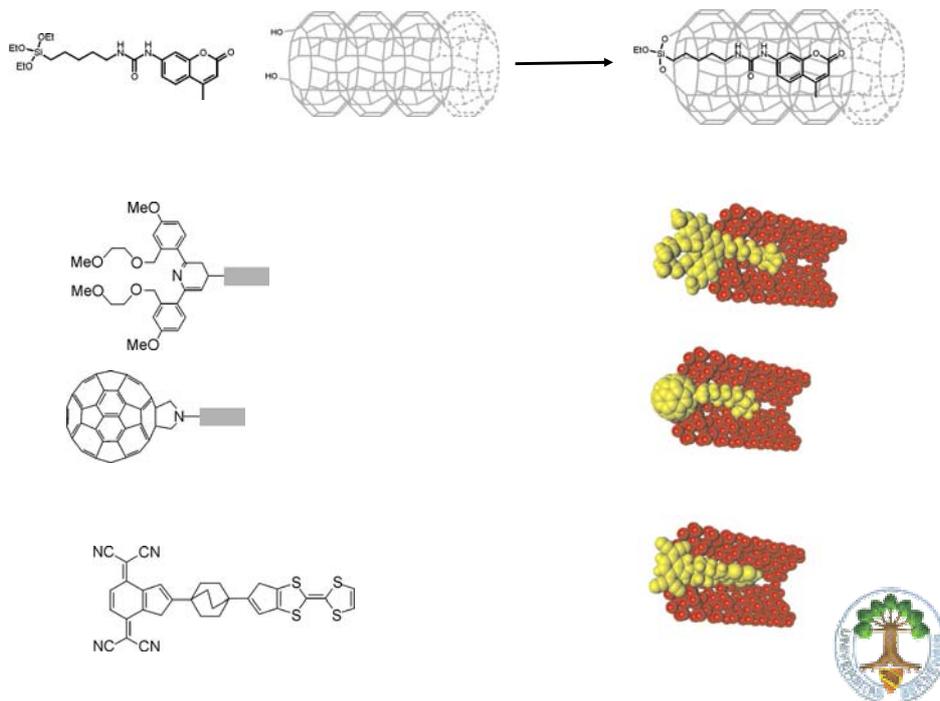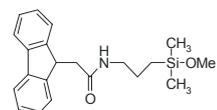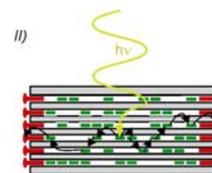
4.10 Addition of stopcock molecules

Electronic Excitation Energy Transfer.
Lecture 4
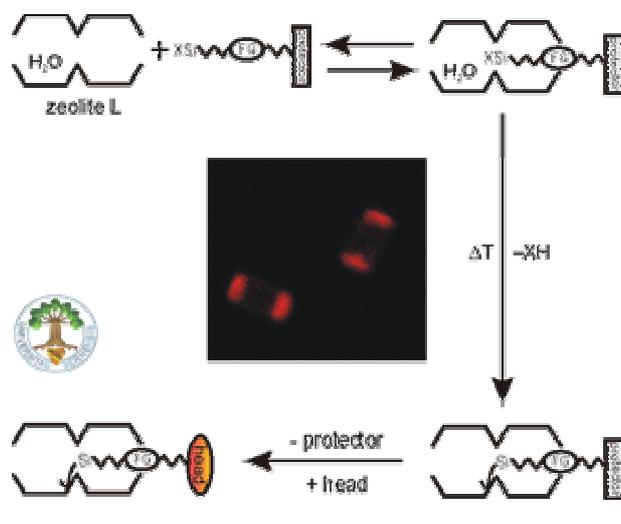Material aspects of dye loaded zeolite L
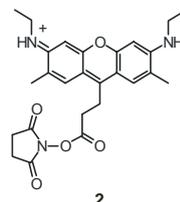
27
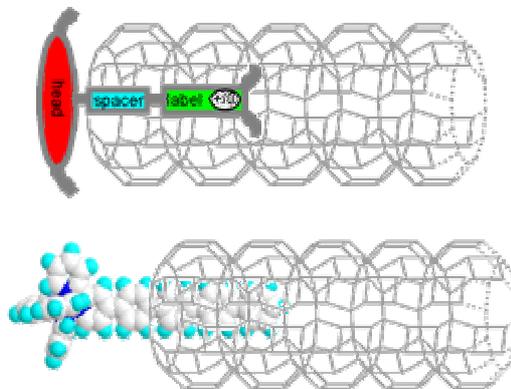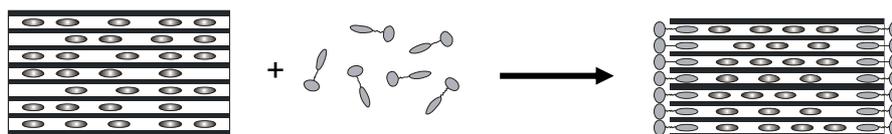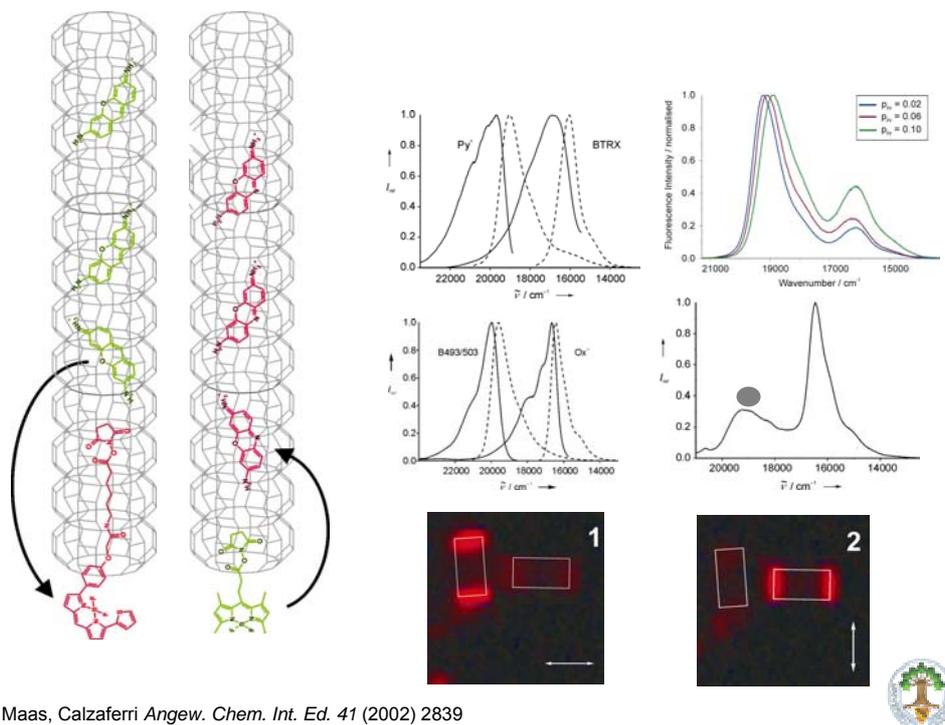
Maas, Calzaferri *Angew. Chem. Int. Ed. 41* (2002) 2839
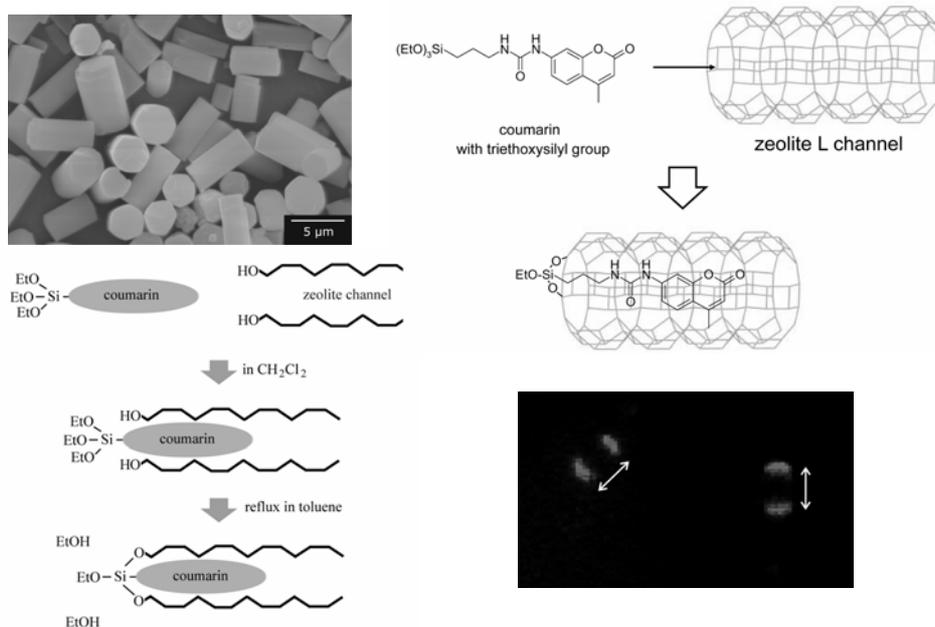
Takayuki Ban, Dominik Brühwiler, Gion Calzaferri, *J. Phys. Chem. B*, **2004**, *108*, 16348.

Electronic Excitation Energy Transfer.
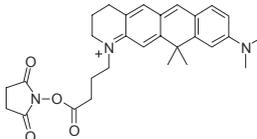Lecture 4
Material aspects of dye loaded zeolite L

Sequential Functionalization of the Channel Entrances
of Zeolite L Crystals
S. Huber, G. Calzaferri, Angew. Chemie, 2004, …

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Electronic Excitation Energy Transfer.
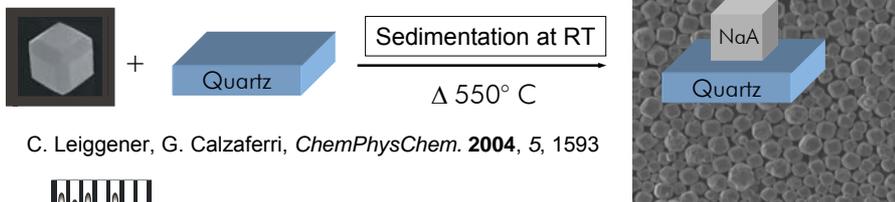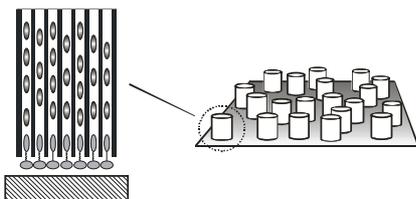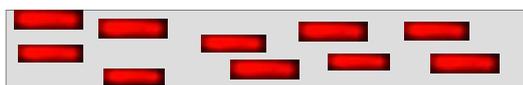Lecture 4
Material aspects of dye loaded zeolite L

4.11 Organization of the individual crystals

C. Leiggener, G. Calzaferri, *ChemPhysChem.* **2004**, *5*, 1593
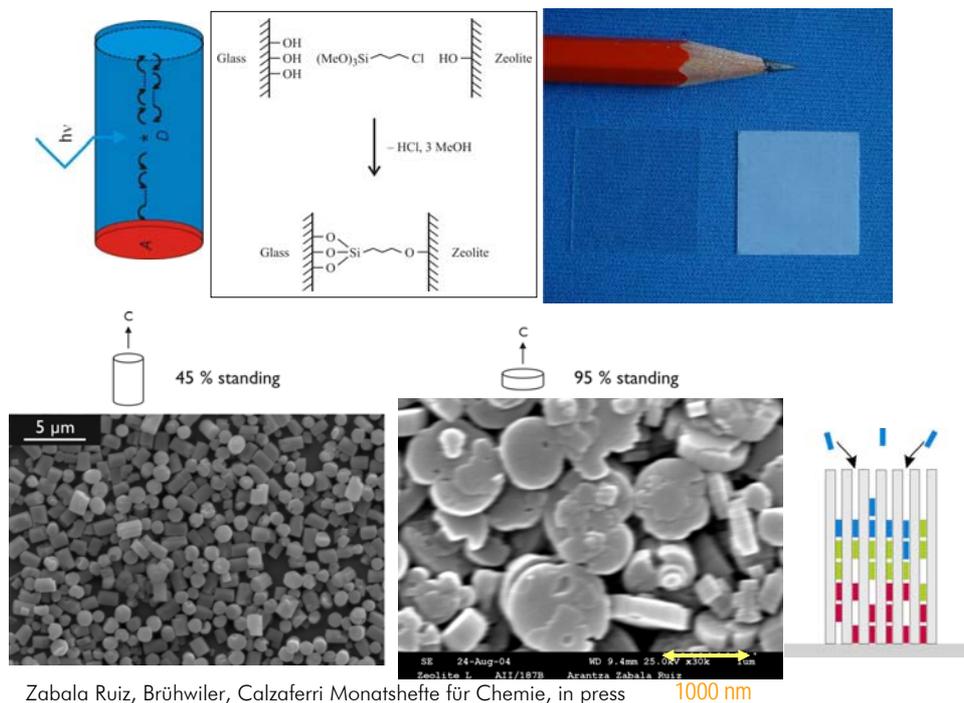

Alignment in a polymer:

Electronic Excitation Energy Transfer.
Lecture 4
Material aspects of dye loaded zeolite L

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Zabala Ruiz, Brühwiler, Calzaferri Monatshefte für Chemie, in press   1000 nm

4.12 Monodirectional materials