# SELF-ORGANIZATION, PHOTOLUMINESCENCE AND EMERGENCE IN AMIDE-FUNCTIONALIZED ORGANIC/INORGANIC HYBRIDS


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CENTRO DE QUÍMICA VILA REAL

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# *MAIN GOALS*

- **Hierarchically-structured luminescent hybrid formed by self-direct assembly principles and showing complex behavior.**

- **Thermally actuated photoluminescence memory effect induced by that complexity.**

- **Nanoscopic (~150 nm) sensitivity of the hybrid's light emitted,** in contrast to the customary case for which photoluminescence is determined by the dynamics of the local environment around the emitter probe**. Emergent behavior.**

# I. Organic/Inorganic Hybrids

- **Research supported by the growing interest of physicists, chemists, biologists and materials scientists who are looking to fully exploit the opportunity for creating smart materials that benefit from the best of the three realms: organic, biological and inorganic.**

- ***"Chimie Douce"*: Sol-Gel** method (processing at mild temperatures)

*Hybrid nanostructures*

- self-assembling;
- nanobuilding block approaches;
- integrative and coupled processes;
- bio-inspired strategies;

*"bottom-up" methodology*

C. Sanchez *et al.*, Adv. Mater. 15, 1969 (2003); ***Functional Hybrid Materials***, Gomez-Romero, P.; Sanchez, C. Eds.; Wiley Interscience: New York, 2003; C. Sanchez *et al.*, J. Mater. Chem. 15, 3559 (2005); ***Hybrid Materials, Synthesis, Characterization, and Applications***, Kickelbick, G. Ed.; Wiley Interscience: New York, 2007.

- **E**xtraordinary implications for the design of multifunctional materials induced by the **mixture at the nanosize level of organic (or bio)** and **inorganic components in a single material (not simply physical mistures)**

- That combination of components provides an additional dimension to their properties in becoming part of the hybrid structure (***SYNERGY***).

> *"Synergy refers to the combined (cooperative) effects that are produced by two or more particles, elements, parts or organisms, effects that are not otherwise attainable."*

P. A. Corning, Complexity 7, 18 (2002)

***«The Re-emergence of "Emergence": A Venerable Concept in Search of a Theory»***

- The hybrids' properties are not ***then*** only the sum of the individual contributions of both phases, **but the role of their inner interfaces** could be predominant.

***"The whole is something over and above its parts, and not just the sum of them all..."***

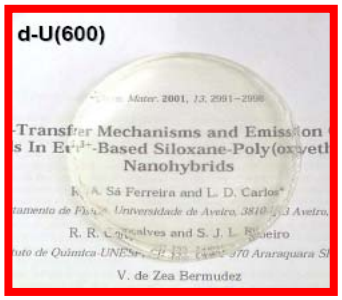
*Aristotle, about the significance of "wholes" in the natural world, more than 2000 years earlier in a philosophical treatise, later renamed the* ***Metaphysics****.*

- **Paramount advantage to facilitate both integration and miniaturization at the nanometer scale (small components and devices and less resources and energy): one of the main challenge of the beginning of this century!**

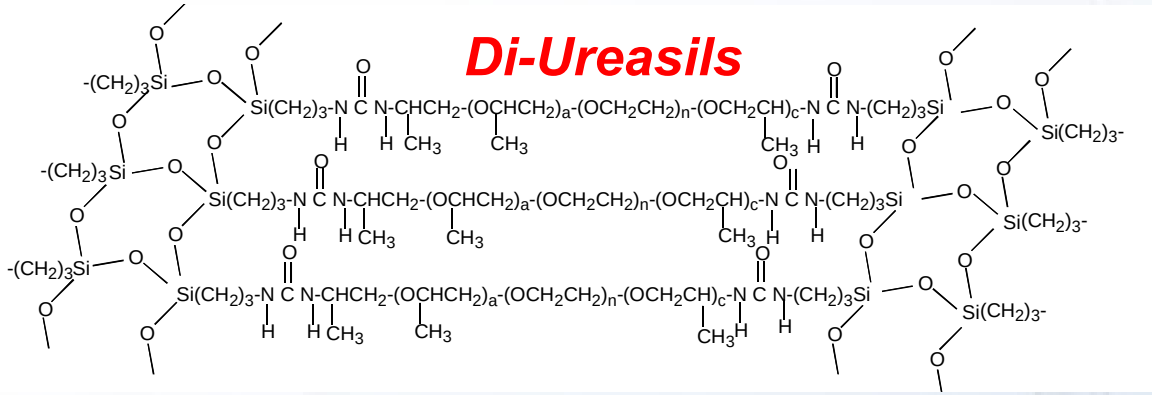
# II. Playing With the Inner Interfaces

## Urea & Urethane OI inner interfaces

- Poly(oxyethylene) chains of variable length grafted to siloxane domains by means of urea:




***Di-Ureasils***

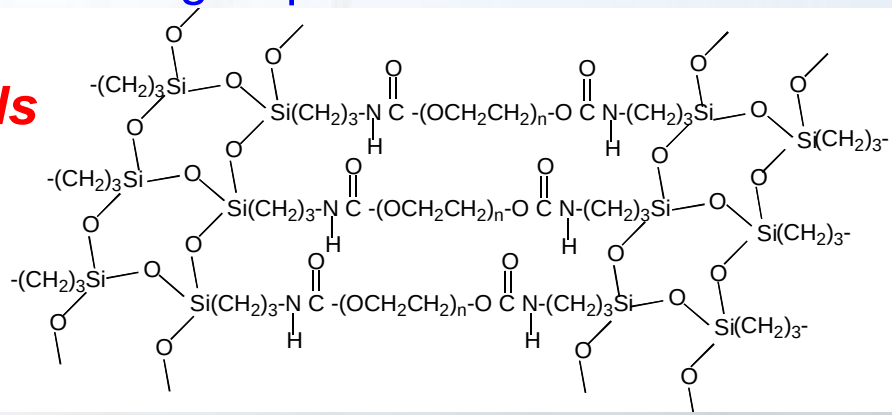


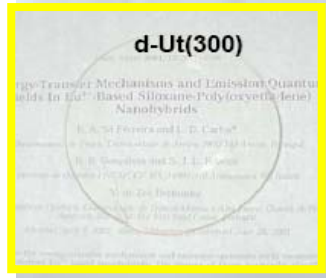
***U(2000)***
***U(900)***
***U(600)***

- or urethane functional groups

***Di-Urethanesils***

***Ut(2000)***
***Ut(300)***





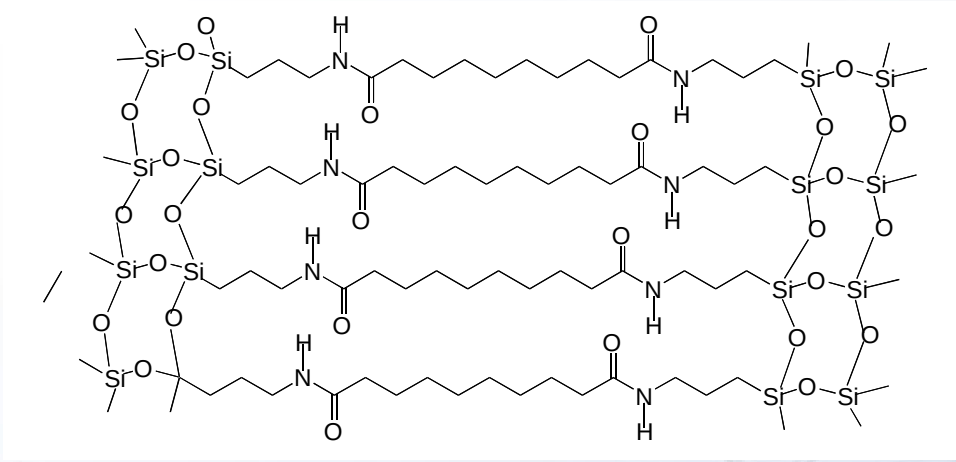

Chem. Mater. 11, 569 (1999); *ibid.* 11, 581 (1999); J. Mater. Chem. 11, 3249 (2001); Adv. Func. Mater. 11, 111 (2001); J. Phys. Chem. B 106, 4377 (2002); *Handbook of Organic-Inorganic Hybrid Materials and Nanocomposites* Vol. 1 (Eds.: H. S. Nalwa), American Sci. Publishers, (2003), pp. 353; Chem. Mater. 16, 1507 (2004); *Phys. Chem. Chem. Phys.* 6, 649 (2004)

- OI inner interface: amide, -NHC(=O)-, groups

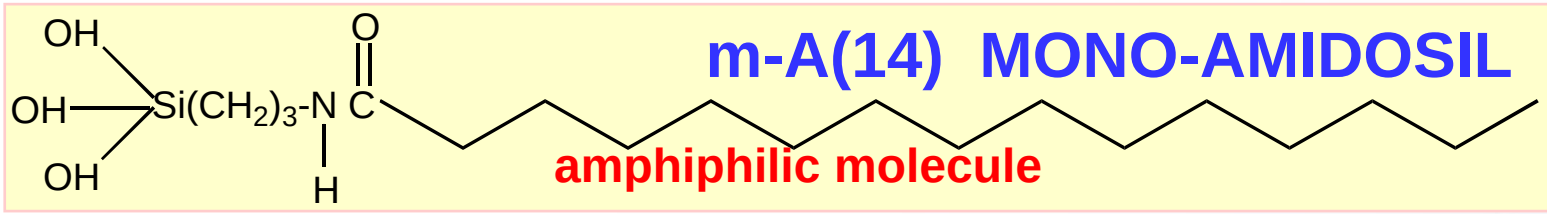
# Di- & Mono-Amidosils

## D-A(8) DI-AMIDOSIL

J. Mater. Chem. 15, 3876 (2005)

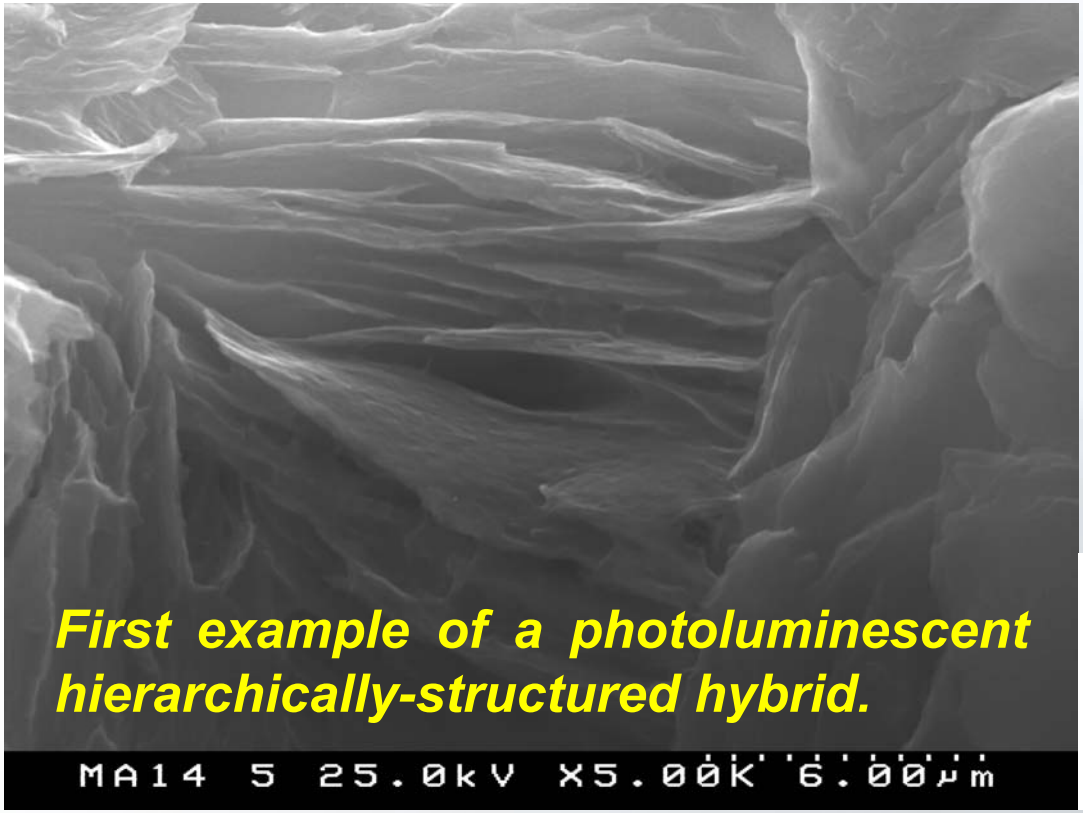


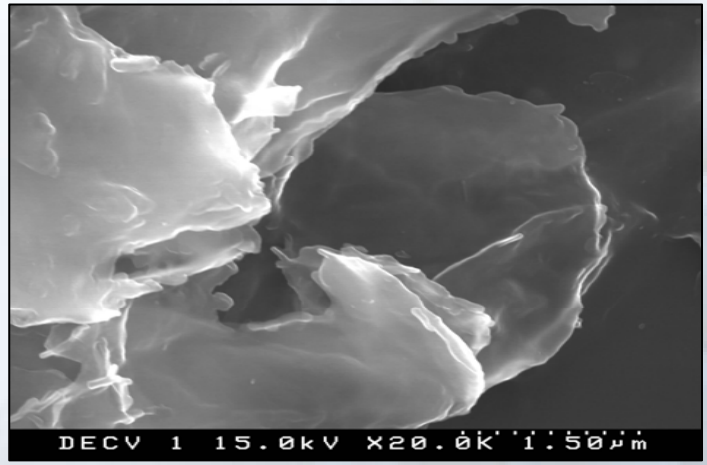
# III. Alkylene/Siloxane Mono-Amidosils



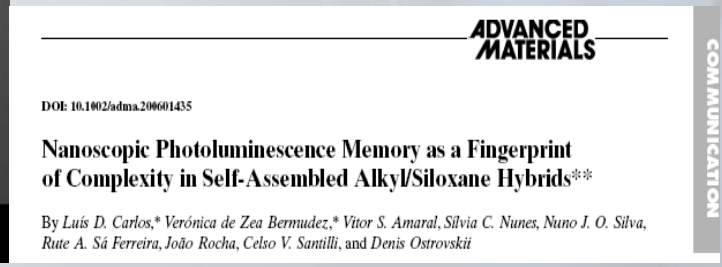

hydrophilic head

hydrophobic tail




*Adv. Mater.* **19**, 341 (2007)



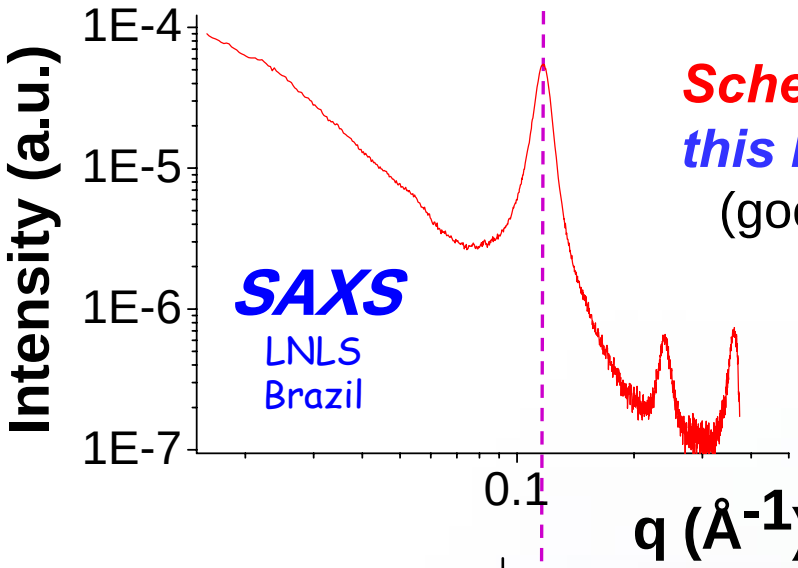
ADVANCED MATERIALS

COMMUNICATION

DOI: 10.1002/adma.200601435

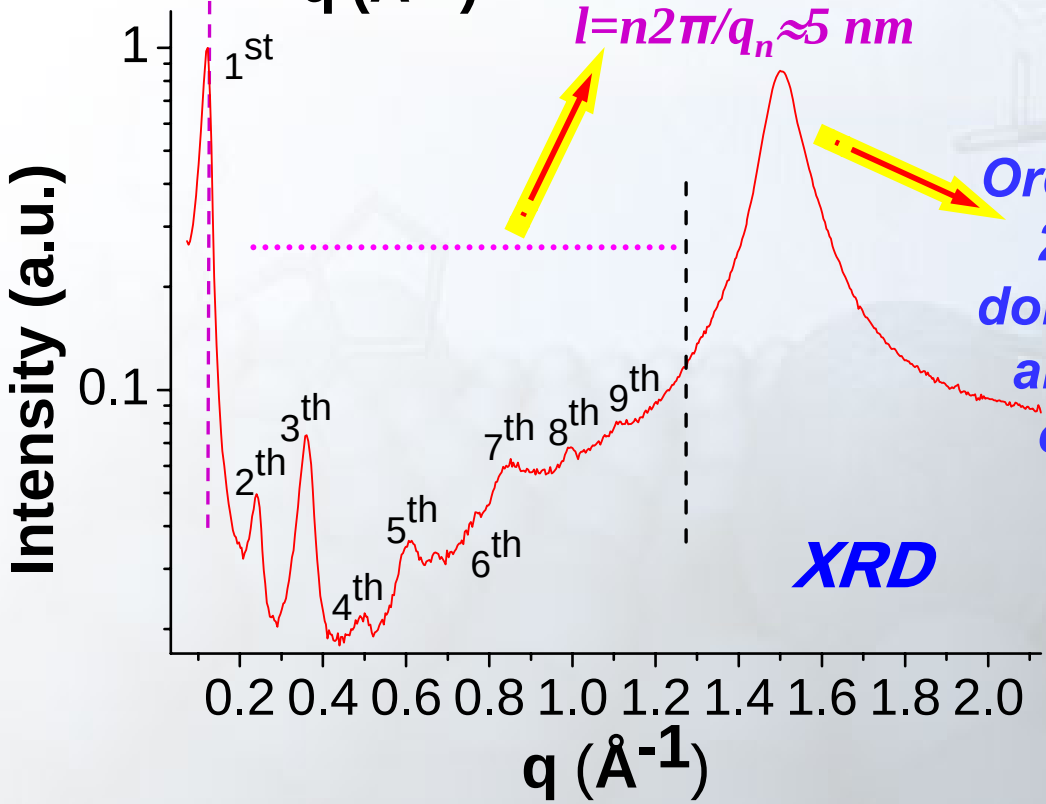
**Nanoscopic Photoluminescence Memory as a Fingerprint of Complexity in Self-Assembled Alkyl/Siloxane Hybrids****

By *Luís D. Carlos,* Verónica de Zea Bermudez,* Vitor S. Amaral, Silvia C. Nunes, Nuno J. O. Silva, Rute A. Sá Ferreira, João Rocha, Celso V. Santilli,* and *Denis Ostrovskii*




***Scherrer equation:*** ***Coherence length of this lamellar order ≈ 150 nm (30 lamellae)***

(good accord with the thickness of the plates observed in SEM)



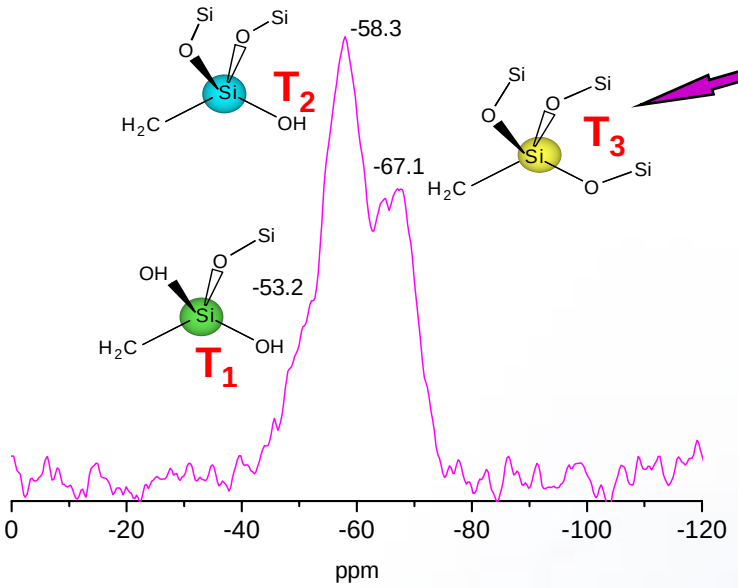

***Inter-layer order***

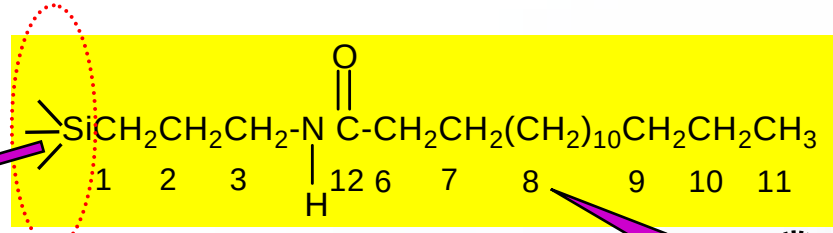
$l = n2\pi/q_n \approx 5$ ***nm***

***Order within the 2D siloxane domains (and/or amide-amide; chain/chain spacing)***

***d=0.42 nm***

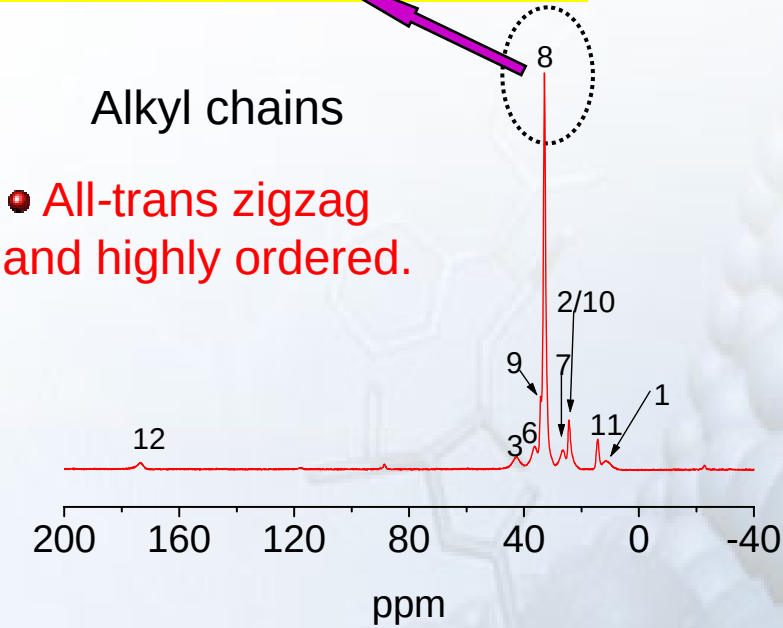
## $^{29}Si$ NMR




Alkyl chains

- All-trans zigzag and highly ordered.



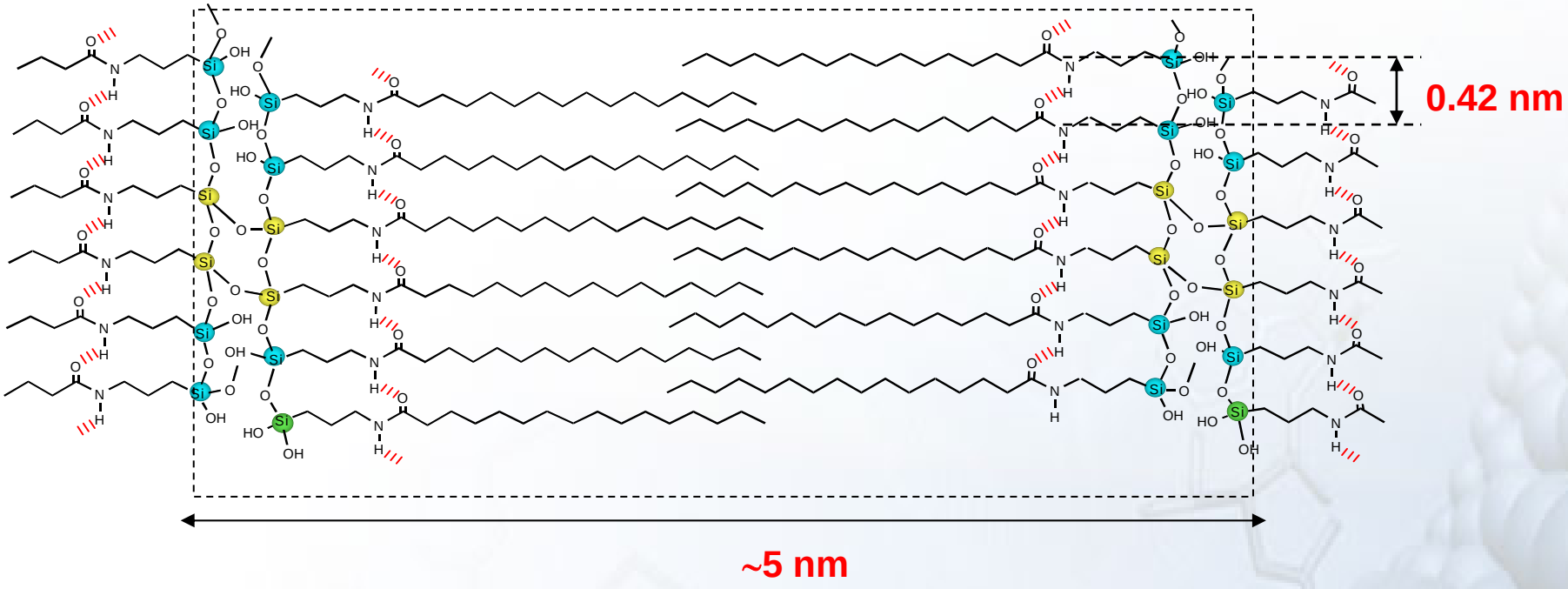

## $^{13}C$ CP/MAS NMR

- Proportion of $T_2$ sites: 2D siloxane network;
- Polycondensation degree=74 %;
- Empirical formula deduced from NMR:
  $CH_3–(CH_2)_{14}C(O)NH(CH_2)_3Si(OH)_{1.1}(O)_{0.8}$

## FT-IR and FT-Raman

The alkylene chains are all-trans zigzag and densely packed (highly ordered).

# Highly-organized bilayer hybrid

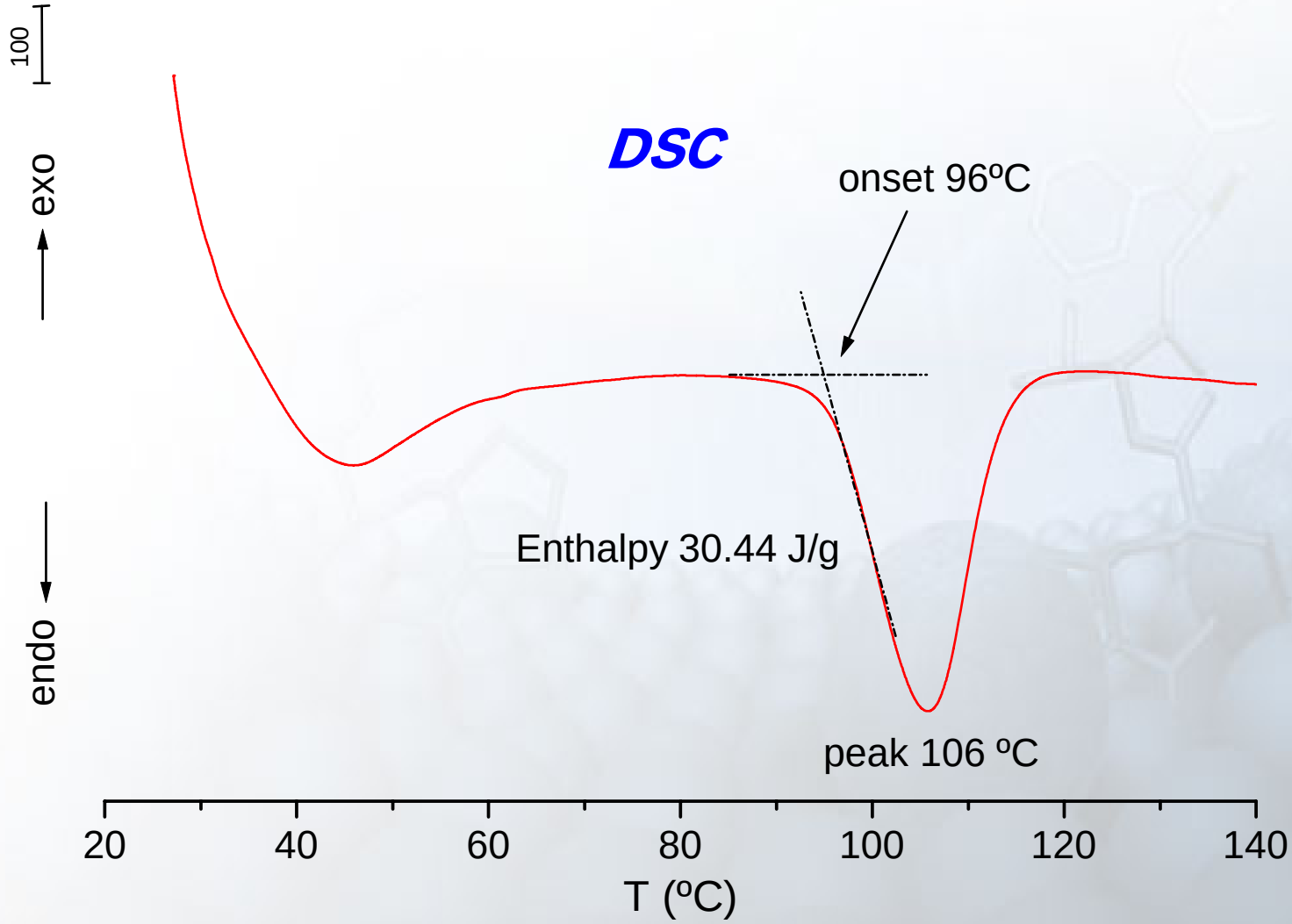



***Hierarchical structure*** (combines self-assembly at different length scales) induced by:

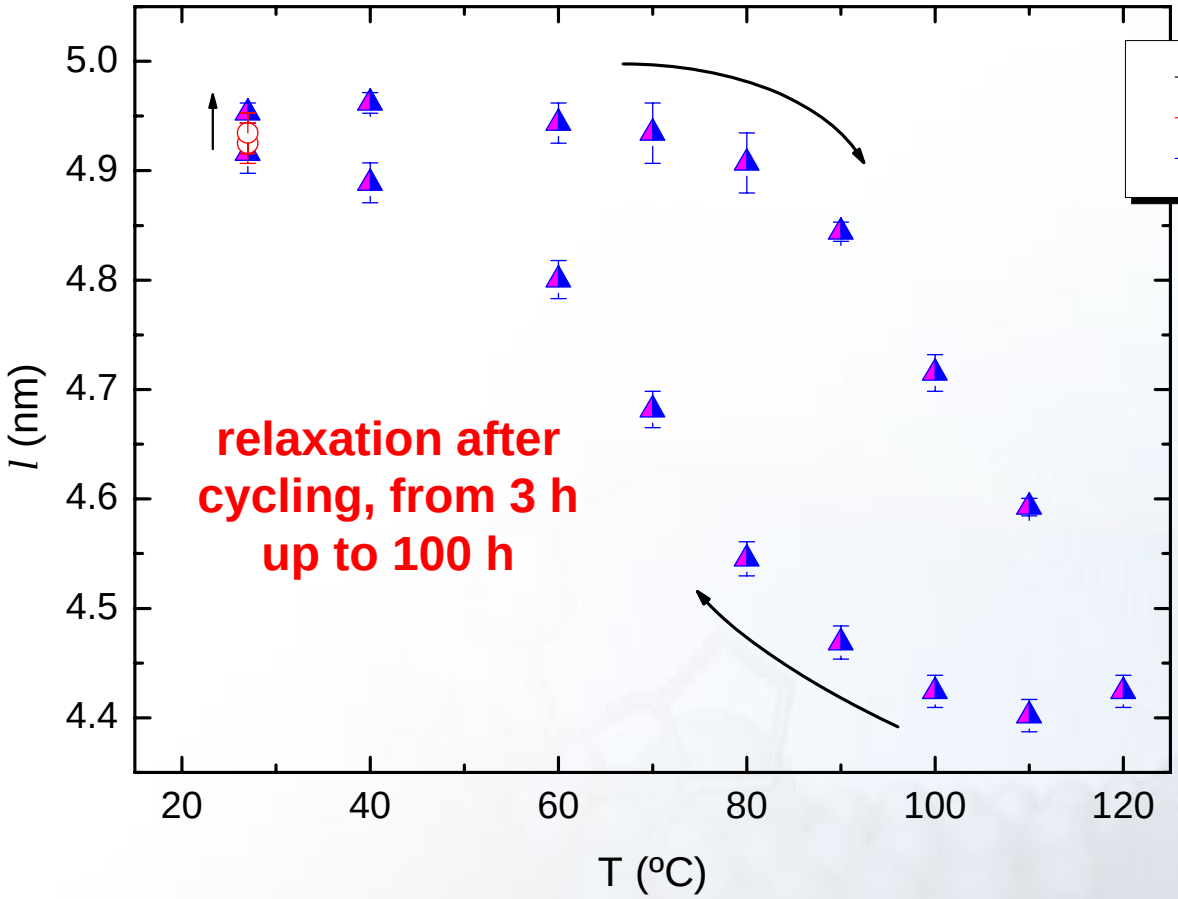
- **Hydrophobic tail-to-tail van der Waals interactions** between the alkylene chains.
- **Intermolecular hydrogen bonds** between amide groups.
- **Entropic term** related to the phase separation between the alkyl chains and the siloxane nanodomains.

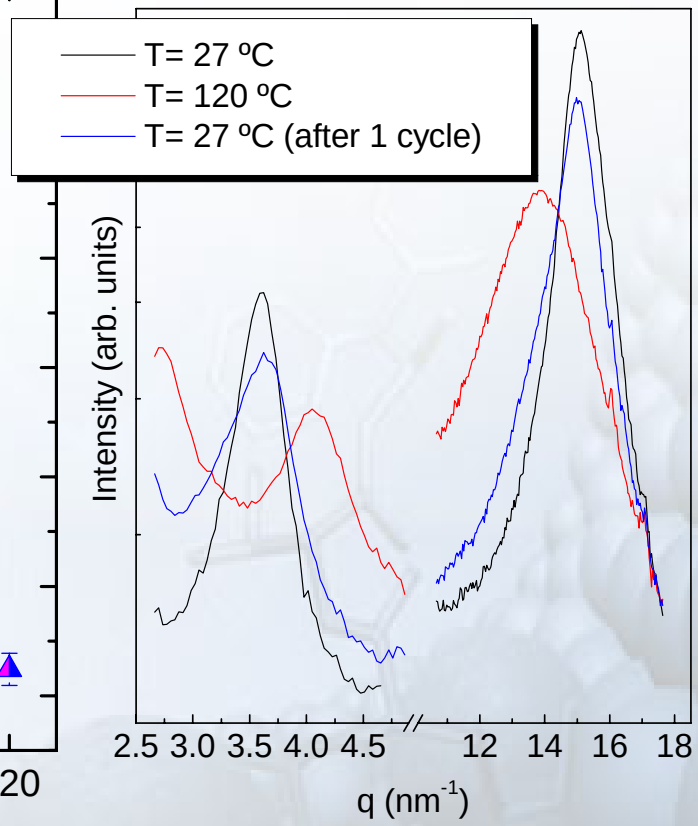
# III.1 Structure Temperature Dependence

## *heating-cooling cycle (24-120 °C)*



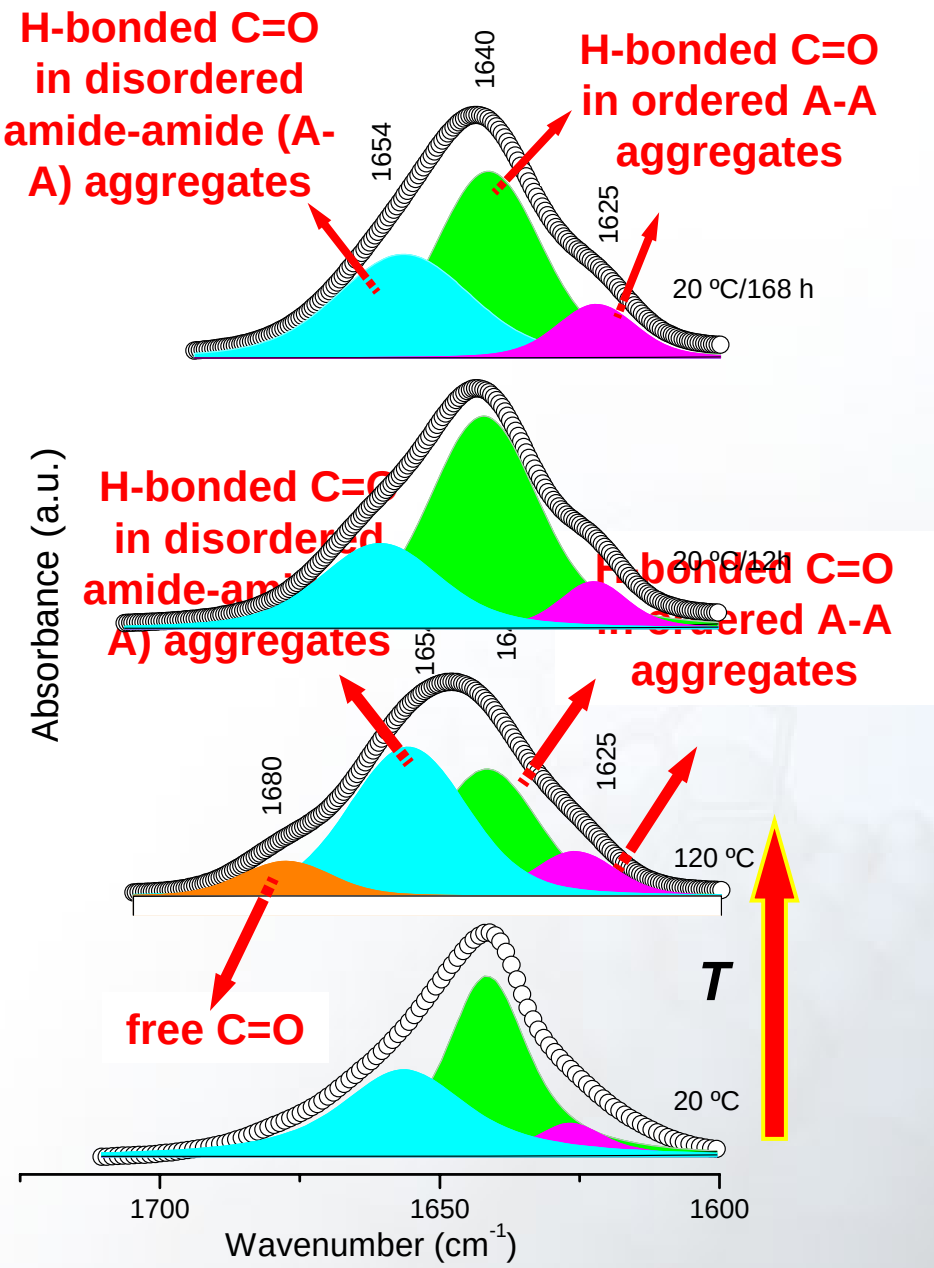
# -XRD: inter-layer distance dependence




- **The layers become closer as temperature increases!**
- **The inter-layer distance is restored after ~100 h, following a logarithmic time dependence.**

# -FT-IR: amide I region



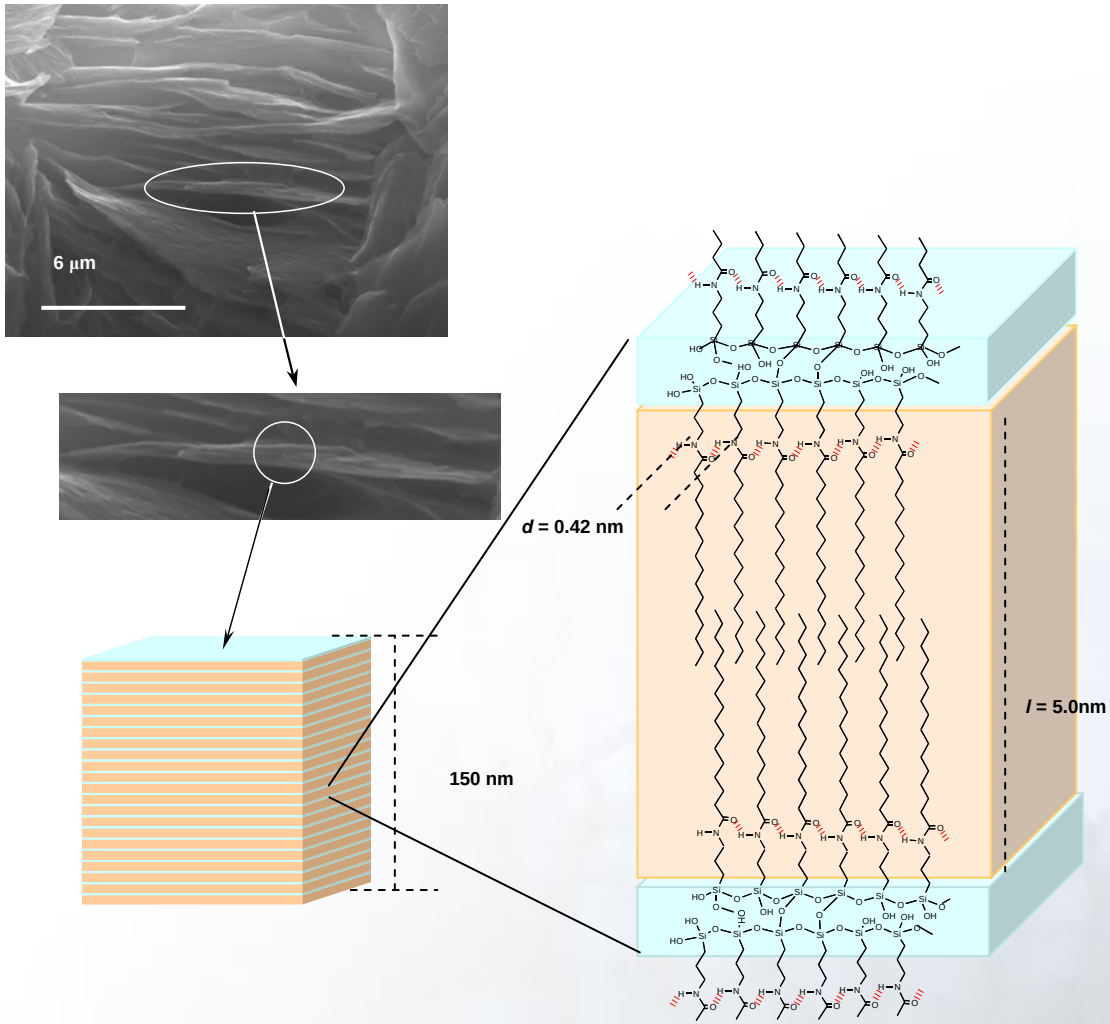

## *On cooling*

- **Slow formation rate of the H-bonds that regenerate the A-A array (metastable state).**
- **After ~168 h the reversibility is not complete (rate of conformational recovery of the polymer chains is much faster than the rate of rebuilding the H-bonded A-A network).**

## *24-120 °C*

- **H-bonded A-A network partly destroyed (freeing C=O groups).**
- **Increase of the amount of disordered A-A structures at the expense of the breakdown of the ordered A-A ones (redistribution of the proportion of H-bonded associations).**

# THE STRUCTURAL MODEL




**$\nu_a CH_2$ and $\nu_s CH_2$:**
trans-to-gauche
conformation change.

**Reversible order-disorder phase transition!**

# III.2 Self-Organization & Emergence

## *Self-Organization*

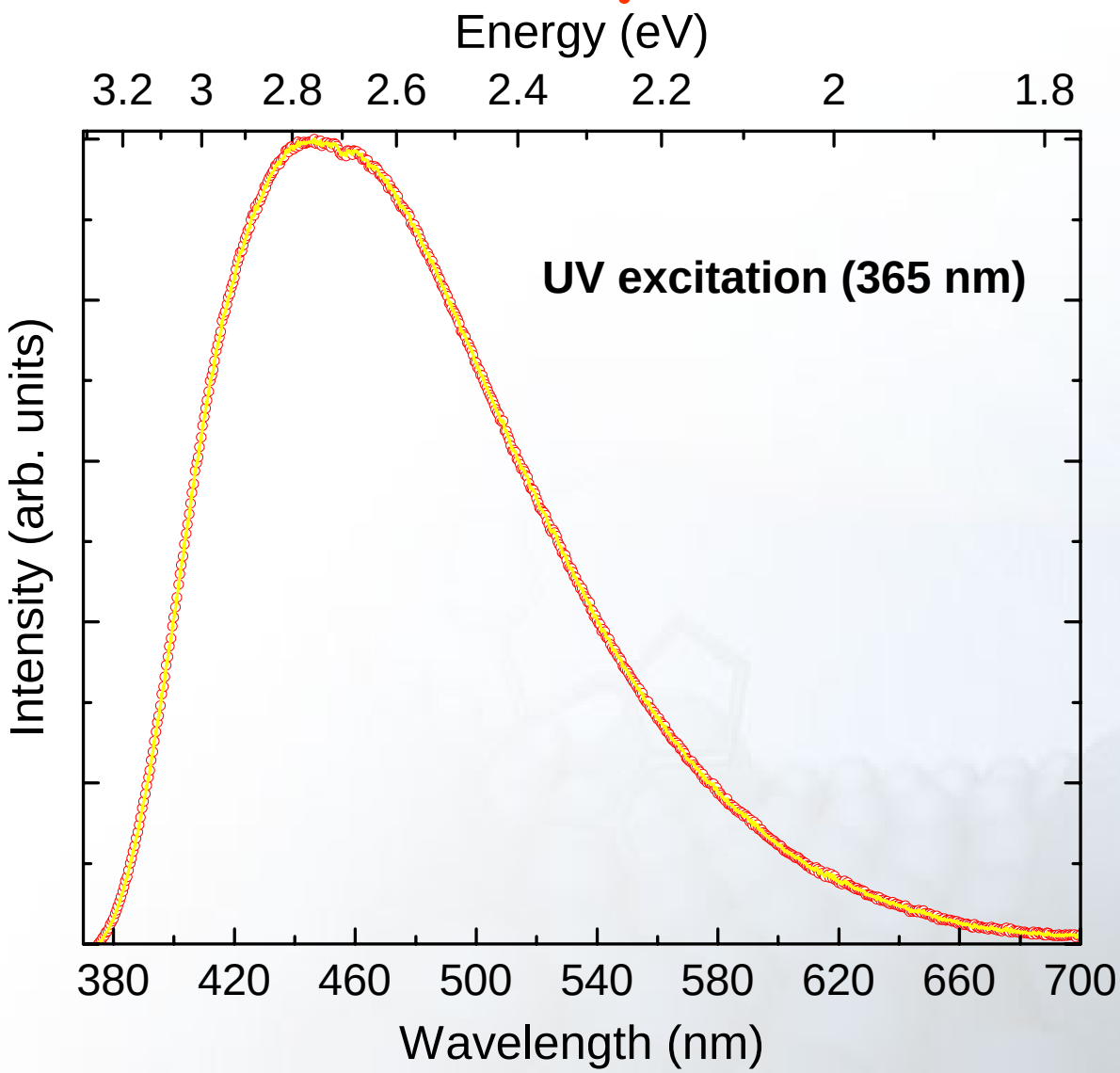
**A process in which the internal organization of a system increases in complexity without being guided or managed by an outside source.**

- Self-organization includes intramolecular self-assembly (or folding) and intermolecular self-assembly
- Supramolecular systems
- Biological systems
- Materials self-assembly (nanotecnology)

***Self-organizing systems typically (though not always) display emergent properties!***

P. A. Corning *Complexity.* 7 18 (2002); T. De Wolf & T. Holvoet, *ESOA* 3464 1 (2005); C. Fuchs, Nature, Society, and Thought 16, 281 (2003).

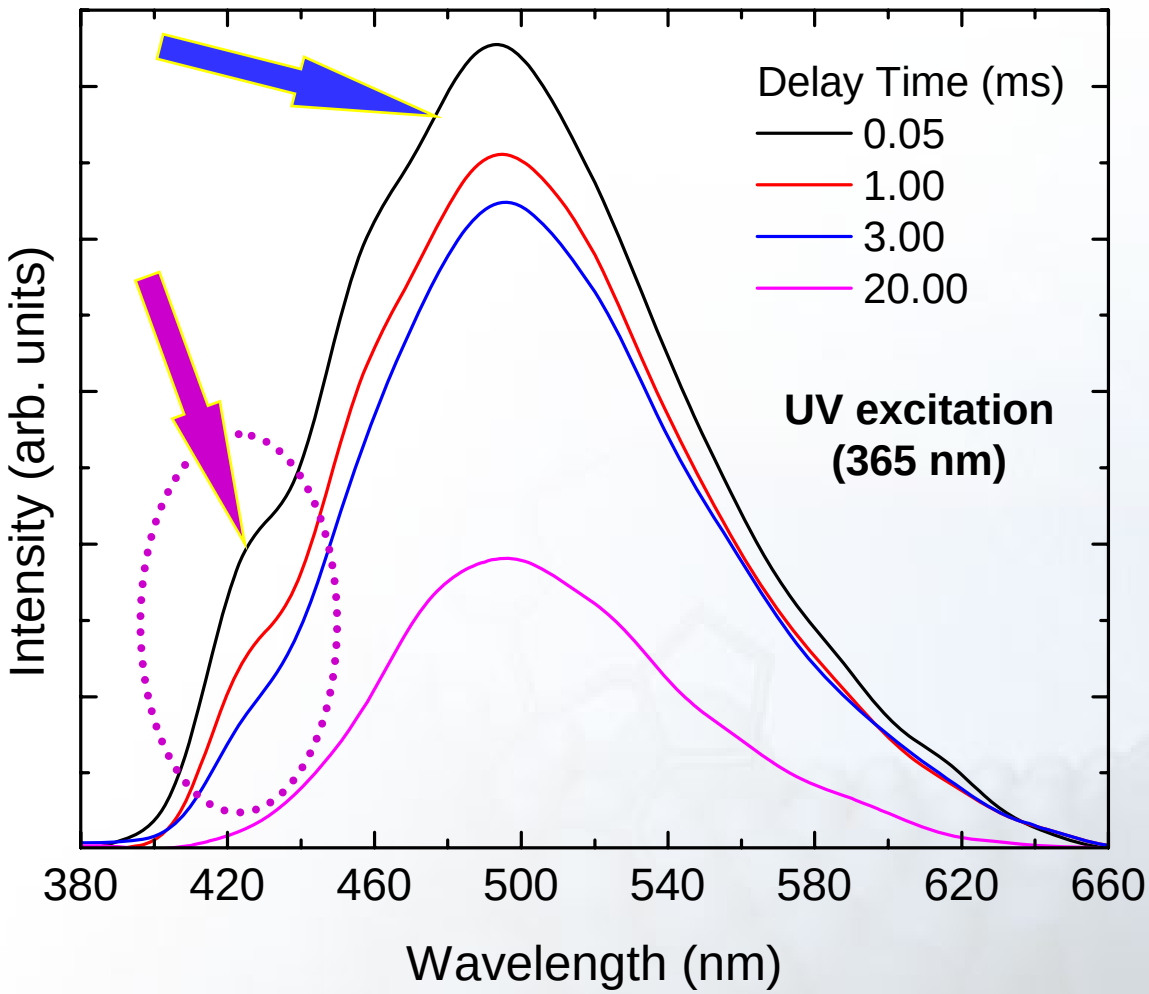
# III.3 Nanoscopic Photoluminescence




- White- light emitter.
- Broad emission analogous to those reported for other similar hybrids, ***di-ureasils***, ***di/mono-urethanesils***, ***amino-sils***, and ***di-amido-sils***.
- External Quantum yield of 3.0%.

*Chem. Mater.* **11**, 581 (1999); *Thin Solid Films* **343**, 746 (1999); *Adv. Func. Mater.* **11**, 111 (2001); *Chem. Mater.* **13**, 2991 (2001); *Chem. Mater.* **16**, 1507 (2004); J. Mater. Chem. **15**, 3876 (2005); Eur. Phys. J. B **50**, 371 (2006); Adv. Mater. **19**, 341 (2007).

# -Time-Resolved Spectroscopy (14 K)




- Two bands: ***Purplish-Blue*** and ***Blue*** spectral regions.
- Different lifetimes: **$10^{-1}$ s**, **Blue** band, **$10^{-3}$ s** **Purplish-blue** one (14 K).
- Distinct dependence with the excitation energy.
- **Purplish-blue** to **Blue** energy transfer.

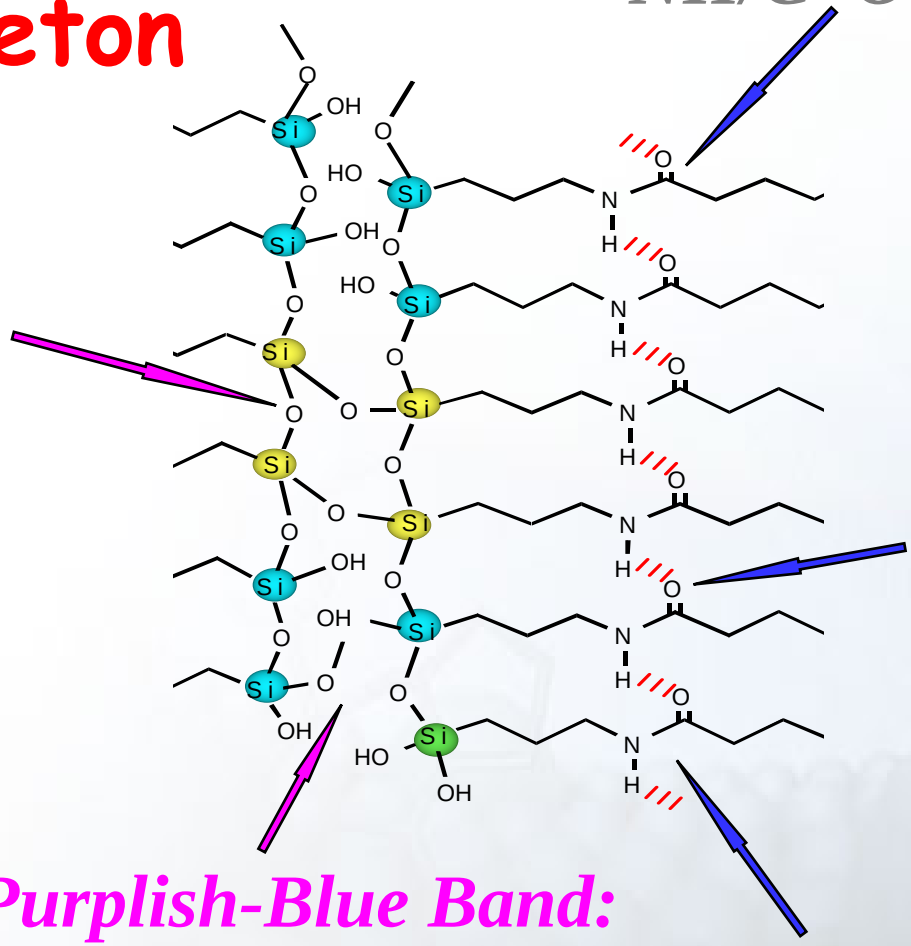
*J. Phys. Chem. C* **111**, 3275 (2007)

*Adv. Func. Mater.* **11**, 111 (2001); *J. Phys. Chem. B* **108**, 14924 (2004

# m-A(14) skeleton

**Blue Band:**

*NH/C=O groups*



***Blue Band** sensitive to the H-bonded associations of the AA array!!!*

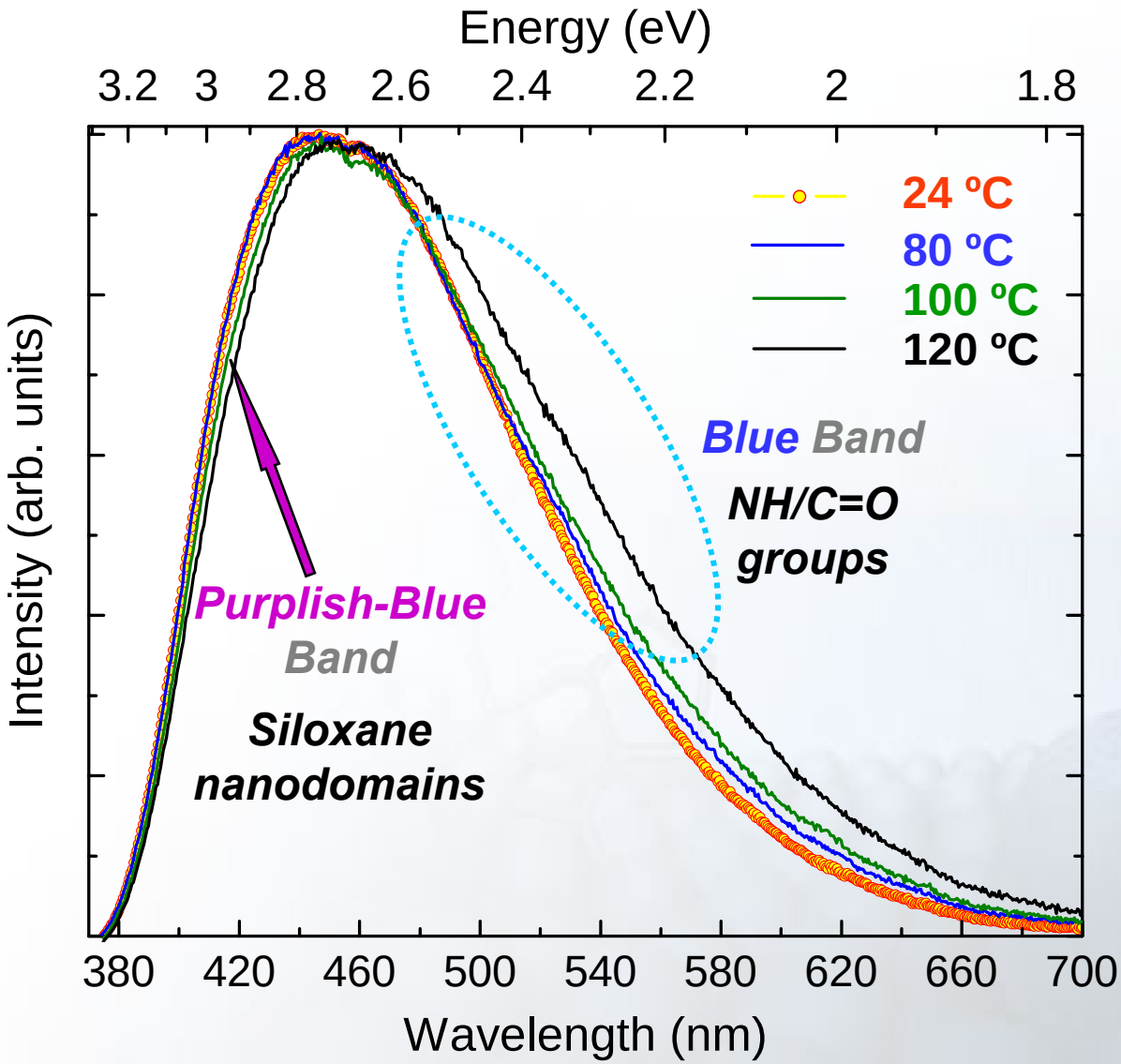
***Purplish-Blue Band:***

*siloxane nanodomains*

*oxygen-related defects (EPR)*

*Adv. Func. Mater.* **11**, 111 (2001); *J. Phys. Chem. B* **108**, 14924 (2004); J. *Phys. Chem. C* 111, 3275 (2007); Adv. Mater. **19**, 341 (2007).

# -Temperature Dependence (24-120 °C)

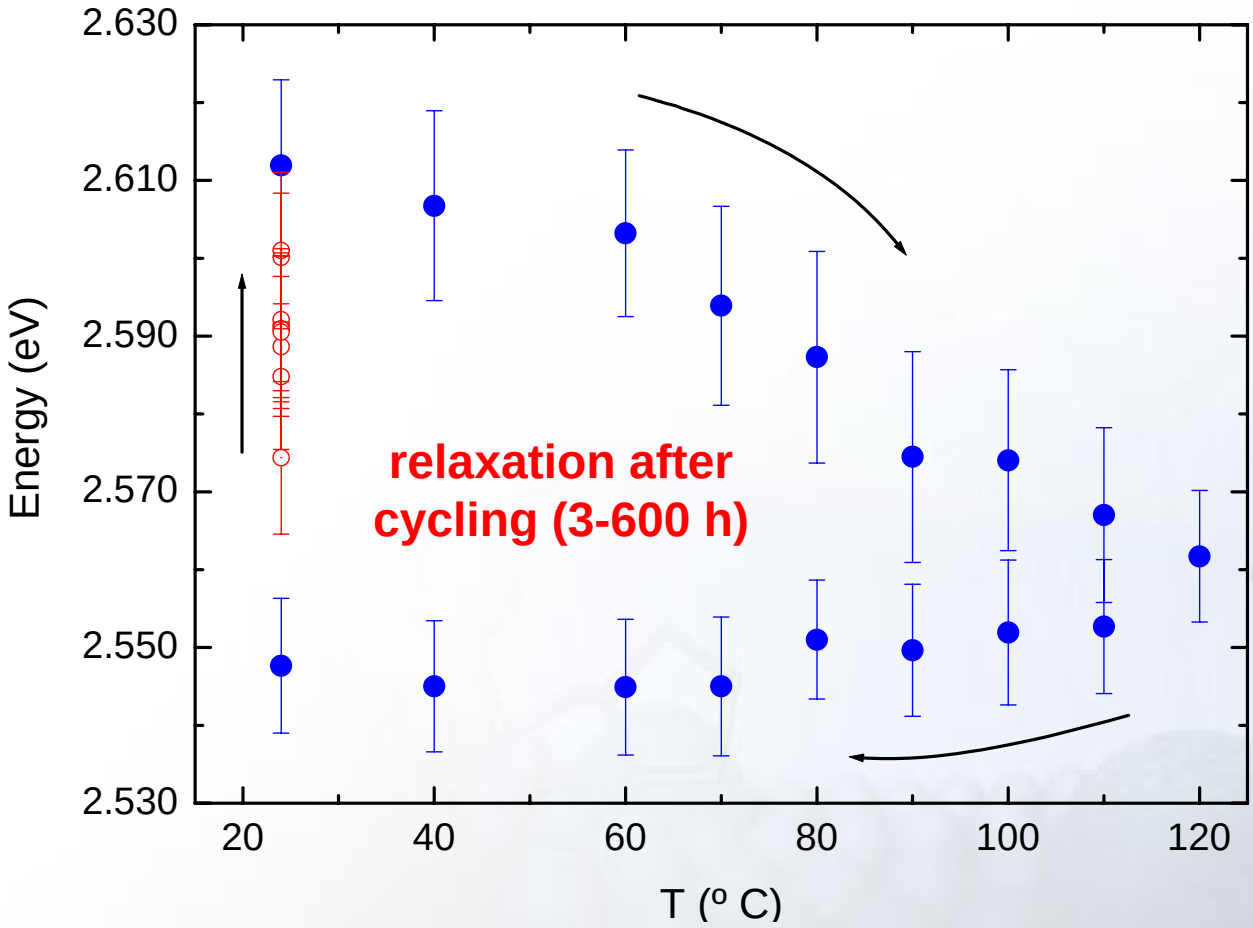


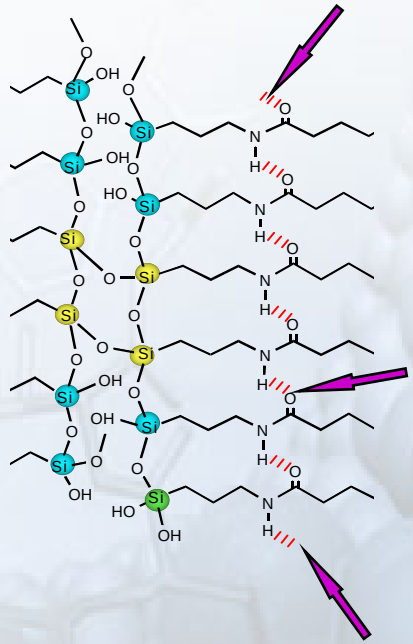

- The emission spectra were fitted by two Gaussian functions following a procedure already reported.

*J. Phys. Chem. B* **108**, 14924 (2004)

- Negligible temperature dependence of the Purplish-blue band energy!

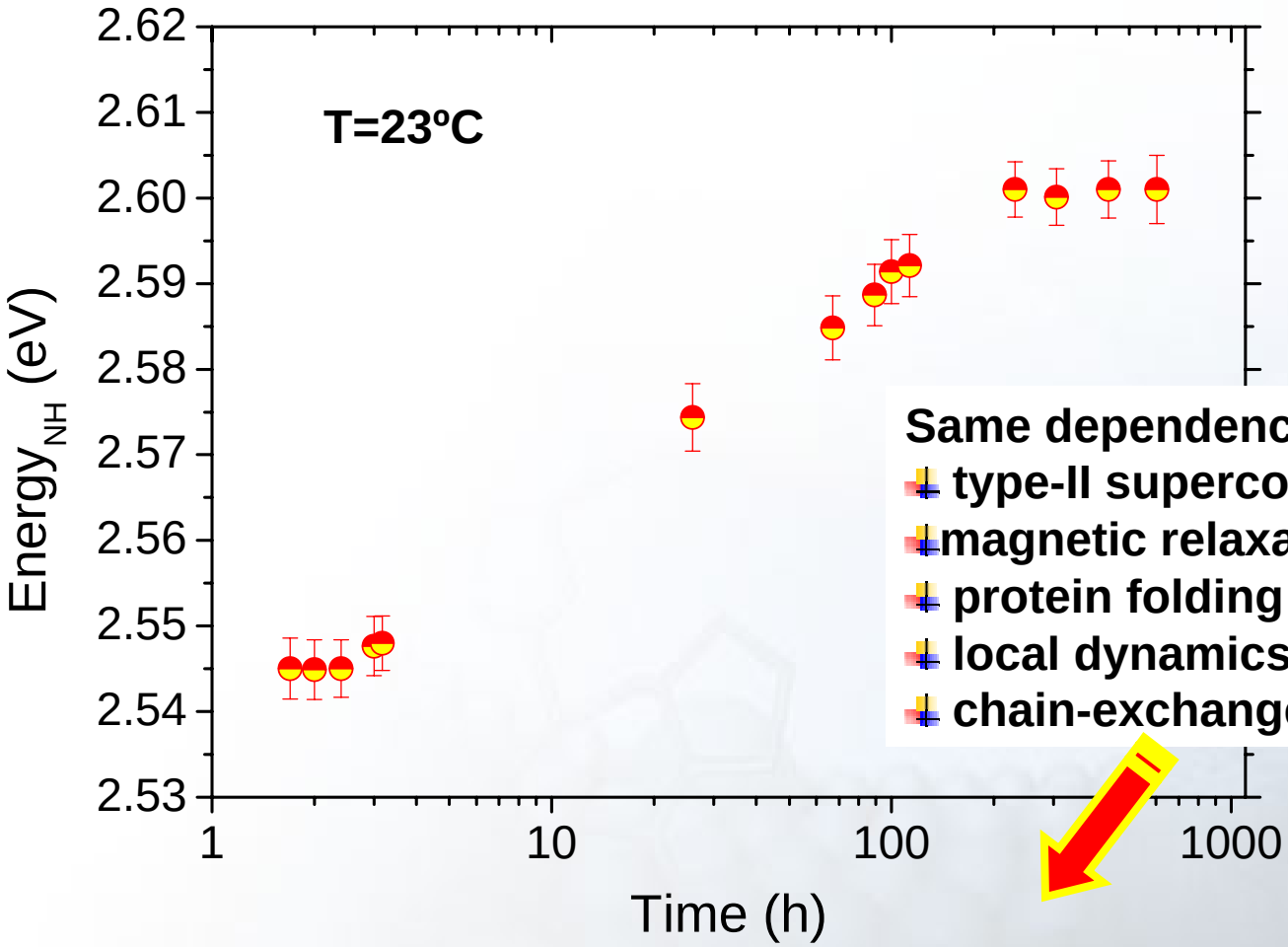
# NH/C=O-related emission energy



- The slow kinetics (energy reversing only achieved after ~300 h) being the result of the metastable state of the amide-amide array.
- Increase of the integrated intensity and quantum yield (3.0-7.2%) after cycling.

- **Relaxation after cycling follows a logarithmic time dependence:**




**Same dependence found in:**

- **type-II superconductors**
- **magnetic relaxation in spin glasses**
- **protein folding**
- **local dynamics of DNA**
- **chain-exchange kinetics of micelles**

***Hierarchically constrained dynamics without any characteristic microscopic time***

J. J. Brey & A. Prados, *Phys. Rev. E* **63**, 021108-1 (2001); E. B. Brauns *et al.*, *Phys. Rev. Lett.* **88**, 158101-1 (2002); P. E. Anderson *et al. Complexity* **10**, 49, (2004); R. Lund *et al. Phys. Rev. Lett.* **96**, 068302-1 (2006).

- **The time dependence of the NH-C=O emission after cycling is an *emergent phenomenon*, induced by the self-organization of the hybrid, namely by the rebuilding of the H-bonded A-A network.**

such as, for instance:

- *Colour*

*Elementary particles have no color; it is only when they are arranged in atoms that they absorb or emit specific wavelengths of light and can thus be said to have a color.*

- World Wide Web (WWW). The WWW is an example of a decentralized system exhibiting emergent properties. There is no central organization rationing the number of links, yet the number of links pointing to each page follows a power law in which a few pages are linked to many times and most pages are seldom linked to.

- Stock market (emergence on a grand scale).

# How this can be realised?

*"If complexity is currently the buzzword of choice for our newly minted millennium, as many theorists proclaim, emergence seems to be explication of the hour for how complexity has evolved."...*

**P. A. Corning**

*Emergence* **is widely recognized as the core principle behind** *self-organization*.

***But what is emergence? What doest it explain really? As the physicist Doyne Farmer observed, "It´s not magic...but feels like magic".***

P. A. Corning Complexity. 7 18 (2002); T. De Wolf & T. Holvoet, ESOA 3464 1 (2005); J. Goldstein Emergence, 1, 49 (1999).

A termite "cathedral" mound produced by a termite colony: a classic example of emergence in nature.

***"Emergence refers to the arising of novel and coherent structures, patterns and properties during the process of self-organization in complex systems."***

*J.Goldstein* in the inaugural issue of *Emergence*.

The common characteristics are:

- **Radical** novelty (features not previously observed in systems);
- **Coherence** or correlation (meaning integrated wholes that maintain themselves over some period of time);
- **A global** or macro "level" (i.e. there is some property of "wholeness");
- It is the product of a **dynamical process** (it evolves); and it is "ostensive" - it can be perceived.

J. Goldstein *Emergence*, **1** 49 (1999)

# V. Conclusions

- *Highly organized bilayer hybrid formed by 2D siliceous domains separated by perpendicularly-oriented alkylene chains.*
- *Self-assembly through tail-to-tail van der Waals packing, inter-molecular hydrogen bonds and alkyl chains-siloxane phase separation*
- *Reversible order-disorder phase transition (heating/cooling cycles, 30-120 ºC) and hysteretic behaviour in the emission energy*
- *Slow kinetics of the formation of the hydrogen-bonded amide-amide network on cooling; total energy reversing only achieved after ~300 h follows a logarithmic time dependence*
- *PL susceptible to the annihilation/formation of the hydrogen-bonded amide-amide array*
- *Sensitivity with a quite unique nanoscopic nature (~150 nm)*
- *The logarithmic time dependence reflects hierarchically constrained dynamics without any characteristic microscopic (Emergence)*

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