# CONFINEMENT OF GUEST MOLECULES IN MICROPOROUS MATERIALS

LARA GIGLI

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, 41121 Modena

## INTRODUCTION AND AIMS

This work focuses on host-guest dye-zeolite L systems, where the photoactive molecules are organized in the one-dimensional channels of the zeolite. The excellent optical properties, chemical stability and biocompatibility of these composites make them key components of artificial antenna systems, sensors, $LED_S$ and bio-nano devices such as markers of tumor cells *in-vivo*. The artificial antenna systems (Calzaferri *et al*., 2005; Brühwiler *et al*., 2007; Lopez-Duarte *et al*., 2011) have been mostly realized using the zeolite L as host because of its high versatility. In fact, the size and shape of its crystallites can be tuned over a wide range; a nanometer sized crystal consists of many thousand one-dimensional channels oriented parallel to the zeolite *c* axis and, as a consequence, strong geometrical constraints are imposed to the encapsulated dye molecules. This leads to a supramolecular organization of a very high concentration of the guests non- or very weakly-interacting in the channels. Owing to the relevance of dye-zeolite L hybrids for environmental sustainability and human health, in this work they have been studied at molecular level detail, to unravel and understand the host-guest interactions that govern the functionality and the optical efficiency of these composites. In order to achieve this aim, three dye- zeolite L (ZL) composites have been synthetized and investigated with an integrated experimental-theoretical strategy, based on the use of *in situ* and *ex situ* X-ray diffraction, with both conventional and non-conventional sources, thermal gravimetric analysis, infrared spectroscopy, UV-Vis and luminescence experiments, and molecular dynamics simulations.

## ZEOLITE L STRUCTURE AND DYE SELECTED

Synthetic ZL used in this research, which has formula $K_{8.76}$ [$Al_{9.21}$ $Si_{26.80}$ $O_{72}$]·17.91($H_2O$), framework type LTL (Baerlocher *et al*., 2007), and space group *P6/mmm* (Fig.1 a, b), is built from columns of cancrinite cages stacked with double six membered rings (D6R) along the *c* axis. These columns are connected to form larger circular 12-ring (12MR) channels and smaller elliptical 8-ring (8MR) channels, all running along the *c* axis (Fig.1 a, b). The main channels are connected to the parallel 8-ring channels by a non-planar boat-shaped 8MR.Since its first synthesis, zeolites with LTL framework type have been reported in various extraframework cationic forms, tetrahedral ion and hydration status, such as: *i*) hydrated (Na, K)-L (Barrer & Villiger, 1969:), *ii*) hydrated (K, Ba)-L (Baerlocher & Barrer, 1972), *iii*) K-GaSi-L (Newsam, 1986), *iv*) Rb-GaSi-L (Lee *et al*., 2007), *v*) AlPO-LTL (Venkatathri, 2002), and *vi*) LZ-212 (Breck & Skeels, 1985). The natural counterpart of zeolite L is perlialite (Artioli & Kvick, 1990).
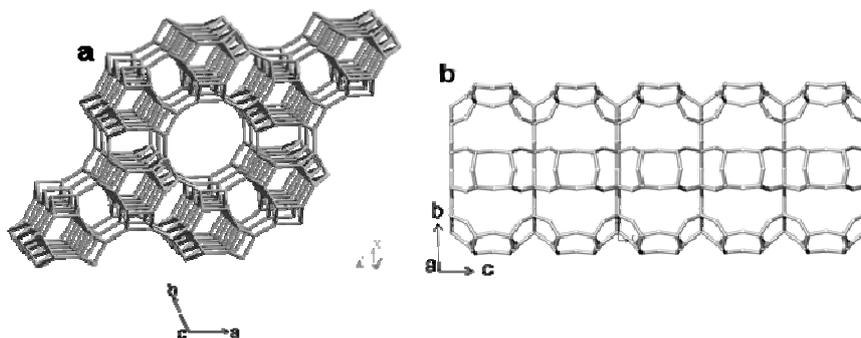


Fig. 1 - Projection along [001] (a); side view (b) of the 12MR channel running along the *c* axis.

A complete structural characterization by Rietveld method was carried out on the as synthetized ZL at RT. Starting structural data were taken from Artioli & Kvick (1990), consisting of two independent tetrahedral sites: T1, in the cancrinite cage and T2 (Fig. 2 a, b), shared between the cancrinite cage and the D6R. The cell parameters determined are: $a$ = 18.3795(4) and $c$ = 7.5281(2) Å.

Concerning the extraframework sites the following species distribution has been found in our ZL sample (Fig. 2 a, b):

site KB - in the center of the cancrinite cage - is fully occupied by K and coordinated to six framework oxygen atoms;

site KC - located in the center of the 8MR channel, midway between the centers of two adjacent cancrinite cages, is fully occupied by K and coordinated to four framework oxygen atoms;

site KD - found in the main 12MR channel - is partially occupied and is coordinated to six framework oxygen atoms and two water molecules.

No extraframework species are found at the center of the D6R, in contrast with that reported in Barrer & Villiger (1969).

The water content corresponds to about 18 molecules, distributed over five extraframework sites located in the main channel, labeled WF, WH, WI, WJ and WK (Fig. 2a). All are partially occupied and weakly bonded to the framework.
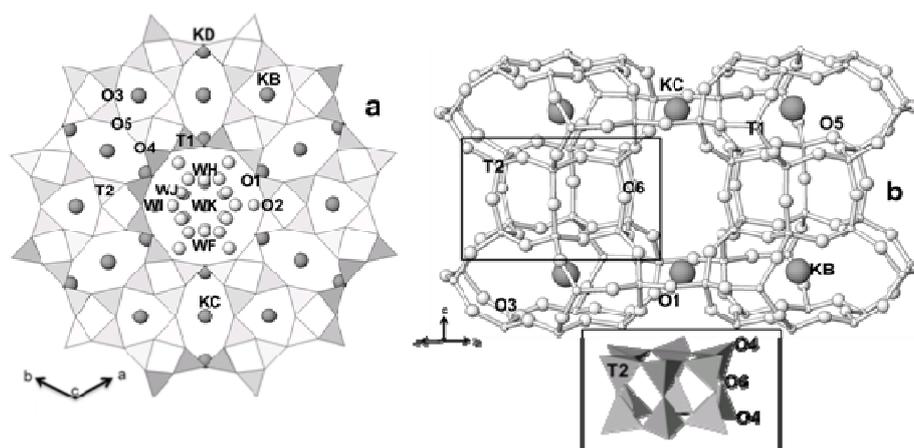


Fig. 2 - Projection along the *c* axis (a) and view from the inside of the 12MR channel (b) of ZL at RT.
Light grey: water sites; dark grey: K sites. The D6R is reported in the inset.

*Dye selected*

The choice of the guests molecules to be encapsulated in the zeolite L was based on the chemical, structural and optical properties. The dyes studied belong to two different species: neutral, 9-fluorenone and tB-DXP and cationic, thionine (Fig. 3 a, b, c).

The 9-fluorenone ($C_{13}H_8O$; Fig. 3a) (Luss & Smith, 1972) belongs to a group of molecules possessing intriguing spectroscopic and photophysical properties (Andrews *et al*., 1978; Arathi Rani *et al*., 1996; Kabayashi & Nagakura, 1976; Murphy *et al*., 1997). Its color originates from the low-lying electronic states, influenced by the bridge joining the carbonyl group (--C=O), which introduces a certain compactness of a closed structure to the molecule skeleton. Experimental and theoretical studies showed the ability of FL in forming stable composites with zeolite L and demonstrated the influence of its orientation and of the water molecules present in the channels on the light harvesting properties. A first model of the host-guest interactions in the system ZL/FL obtained by experimental data is reported in Devaux *et al*. (2004). On the basis of the results obtained by FTIR, Raman spectroscopy, thermal analyses and fluorescence spectroscopy, the authors suggested that a maximum of

1.1 FL molecules can be hosted in ZL channels. They located the dye close to the channel walls and justified the high stability in air conditions of ZL/FL composite on the basis of two molecule-framework interactions: 1) FL carbonyl group with an $Al^{3+}$ of the zeolite framework, and 2) FL aromatic ring with $K^+$. On the contrary, a further paper based on first principle molecular dynamics simulations (Fois *et al.*, 2010) established, that the stability of the ZL/FL material, both in dehydrated and hydrated forms, is due to the strong interaction between the oxygen of the carbonyl group with the extraframework potassium cation. Recently Zhou *et al.* (2013) reported the comparison between the simulated and measured UV-Vis absorption spectra of fluorenone both in hydrated and dehydrated zeolite L. The authors confirmed the K---O=C motif and stated that the shape of the absorption spectra is affected by the fluorenone's orientation, which is in turn strongly affected by the presence of water, although the interactions between the fluorenone and water molecules are negligible. The dye named tB-DXP N,N'-bis(4-tert-butyl-2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylicdiimide ($C_{48}H_{42}N_2O_4$; Fig. 3b) belongs to the perylene family.
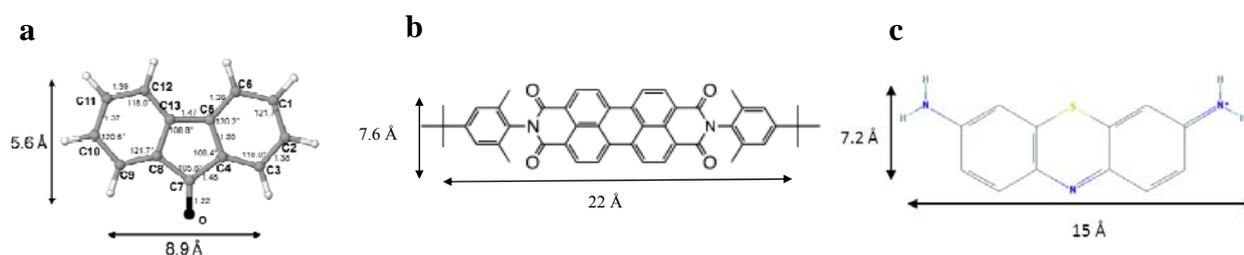


Fig. 3 - a) Molecular structure (in light grey, C atoms; in black O atom and in white H atoms), dimensions, bonds lengths and angles of 9-fluorenone; b) molecular structure and dimensions of tB-DXP, c) molecular structure and dimensions of thionine.

Perylene dyes and their derivatives are promising compounds for their intense visible light absorption, high stability, electron accepting ability, and high quantum yield (Huang *et al.*, 2011). Due to these properties, these are actually studied for optoelectronic and photovoltaic devices, energy-transfer cascades, light-emitting diodes, and near-infrared-absorbing systems. The tB-DXP compound, in particular, was recently synthesized (Devaux *et al.*, 2013) according to newly developed procedures based on previously published works (Rademacher *et al.*, 1982), in the laboratory of the Department of Chemistry at the University of Fribourg. Given its large size tB-DXP it is expected that it aligns parallel to the *c* axis of ZL and that the formation of aggregates is avoided for the geometric inability of the molecules to slide over each other (Busby *et al.*, 2011). Moreover, the presence of substituents in the para positions, acting as spacers, leads to an increase of the minimum contact distances and hence to a decrease of the interaction with the neighbor molecule, that would entail to J-coupling when the dyes are densely packed inside the ZL channels.

The cationic dye, Thionine (Th) (3,7-Diamino-5-phenothiazinium acetate) ($C_{12}H_9N_3S \cdot C_2H_4O_2$; Fig. 3c) was chosen because ZL cannot accommodate thionine dimers such as H-aggregates due to space filling effect, so the composites show intense fluorescence within the zeolite channels (Ramamurthy *et al.*, 1993). Moreover Th contains a sulfur atom, a relatively heavy atom, that can be more easily located by X-ray diffraction study respect to other dye molecules consisting of only light atoms (C, N and O), more difficult to localize in the zeolite framework. A single crystal X-ray study of Th incorporated into a mordenite -Na (Simoncic *et al.*, 2004) reported strong host-guest interactions through short C-O, N-O and S-O distances favored by a slight tilted arrangement of the molecule inside the 12 member ring of the mordenite.

THE THERMAL BEHAVIOUR OF ZEOLITE L

The insertion of neutral chromophores, requires high temperature and a preceding dehydration of the zeolite because the $H_2O$ molecules block the molecule pathway. This implies that the thermal behaviour of ZL has to be preliminary investigated.

The dehydration and re-hydration dynamics and the thermal stability have been investigated, at a fine temperature scale, in the RT-814 °C thermal range by *in situ* Synchrotron X-ray powder diffraction (Gigli *et al.*, 2013). In the investigated temperature range, the cell parameter variations, although very small, are rather discontinuous and the total variations of the *a*, *c*, and *V* parameters are 0.2%, 0.3% and 0.7%, respectively (Fig. 4). ZL is stable up to 814 °C and no structural breakdown is observed.
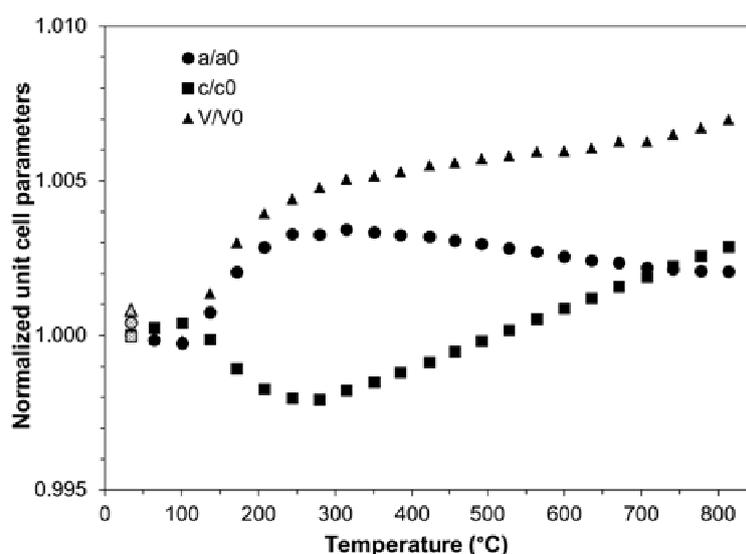


Fig. 4 - Normalized unit cell parameters *vs.* temperature. The grating symbols correspond to the rehydrated phase.

*Framework modifications*

The main framework modifications can be resume as following:

*i*) the main 12MR channel, and the 8MR channel parallel to the *c* axis (Fig. 2a), becomes more circular upon heating; *ii*) during water release, between 101 and 244 °C, the 8MR apertures surrounding the main 12MR channel become more circular, in contrast, after complete dehydration, above 244 °C, the trend inverts and the rings become more elliptic; *iii*) the D6R (Fig. 2b) becomes less di-trigonal and also its thickness tends to decrease.

*Extrafaramework changes*

Upon heating, KD slightly shifts from its original position and the potassium distribution on KC and KD sites (Fig. 2a) undergoes a slight reassessment. The KB site maintains the same occupancy factor in all the studied T range, while the occupancy of KD and KC sites decreases and increases, respectively, indicating a partial migration of potassium from the main channel to the inner KC site. This migration, induced by the necessity of KD to restore its coordination requirements after the loss of the previously coordinated water molecules, ends when the KC site is full. The further decrease in the occupancy of KD, between 244 and 707 °C, can be ascribed to the presence of some water in KD, which is lost above 244 °C. Concerning the water molecules most of them are released above 101 °C, and at 244 °C the zeolite is completely dehydrated.

In particular: *i*) water WI, the most occupied site and the only water molecule bonded to potassium KD, is the last to be completely removed; *ii*) water WF, initially not bonded either to the framework or to the cations,

upon heating moves closer to KD and, as a consequence, it is one of the last water molecules to be released; *iii*) water WH, initially coordinated to the oxygen atom O1, drifts away during dehydration, hence allowing the relaxation of the 12MR aperture along the O1–O1 direction (Fig. 2a); *iv*) water WJ, on the contrary, moves closer to the framework oxygen O2 and its release is slower compared to WH. This could explain the almost constant value of the O2–O2 diameter of the 12MR aperture (Fig. 2a); *v*) water WK, bonded only to other water sites, is the freest water molecule and its release begins already at 65 °C.

*Re-hydration process*

The results of the study of the re-hydration process can be summarized as follows: *i*) the cell parameters are almost perfectly recovered (Fig. 4); *ii*) the original framework structure of the hydrated phase is almost completely regained although a slight hysteresis is observed; *iii*) the potassium cations regain the original distribution on KC and KD (Fig. 2a); *iv*) the WF and WJ sites do not return exactly to the original positions and, more importantly, the original water content is not completely regained (upon rehydration only 16.7 water molecules are found instead of the original 18). In particular, compared to the original zeolite L, the WK site is empty, WF and WI and WJ show a lower occupancy, while WH is slightly more occupied (Fig. 2a).

SYNTHESIS OF THE ZL/DYE COMPOSITES

The neutral dyes Fluorenone and tB-DXP were inserted into the channels of ZL by using gas-phase adsorption.

Four ZL/FL samples (named ZL/0.5FL, ZL/1.0FL, ZL/1.5FL, and ZL/2.25FL) were synthesized with nominal loadings of 0.5, 1.0, 1.5, and 2.25 molecules p.u.c, following the experimental set up reported in (Devaux *et al.*, 2004). Zeolite L was preliminary dehydrated at 200 °C for 4 h under vacuum ($10^{-4}$ mbar) on the basis of the results of the dehydration and rehydration study reported in (Gigli *et al.*, 2013). Dehydrated ZL was mixed, in inert atmosphere, with FL powder, in ratios corresponding to the desired loadings, and placed in a rotating oven. The mixture was kept at 120 °C for 24 h in order to assure the encapsulation of the dye and its homogenous distribution in the zeolite channels.

Several samples at different tB-DXP nominal loadings were prepared and only the high loaded composite was investigated in this work because the most suitable for XRPD structure refinement. In a typical experiment, the powder of ZL and the desired amount of tB-DXP were mixed with dichloromethane to dissolve the dye and ensure a good dispersion of the zeolite. The solvent was then evaporated thus leading to a homogeneous coating of the zeolite surface with tB-DXP. The coated zeolite was then put into a small glass ampule and dried on a vacuum line for 24 h at a pressure of $2\times10^{-2}$ mbar. The ampule was then sealed off under vacuum and put into a rotating oven. The gas phase insertion process took place over 4 days at 260 °C. Once this process was completed, the ampule was removed from the heating source and cooled to RT. The ampule was then opened and the colored powder was washed three times with dichloromethane until the supernatant was colorless.

The thionine incorporation was carried out by ion exchange (Simoncic & Armbruster, 2005; Calzaferri & Gfeller, 1992). An amount of ZL powder was treated in high concentrated aqueous thionine acetate solution ($C_{12}H_9N_3S \cdot C_2H_4O_2$, Aldrich, 90%) at 80 °C for 3 days in a sealed ampule. After ion exchange, the blue colored powder was extensively washed, with distilled water and ethanol, to remove possible adsorbed molecules on the ZL surface. Following this procedure two composites with different Th loading were synthetized named ZL/Th20 and ZL/Th50.

CHARACHTERIZATION OF THE ZL/DYE COMPOSITES

*ZL/FL composites*

Results of thermogravimetric and X-ray structural refinements established that the maximum degree of FL loading corresponds to 1.5 FL molecules per ZL unit cell. The infrared measurement clearly demonstrated the encapsulation of the dye, the strong interaction of the carbonyl group of FL with the $K^+$ cations and that

water molecules do not play a role in the organization of the FL molecules inside the channel. A thorough characterization of structural properties and energetics of this dye-zeolite system has been accomplished by DFT-based modeling, which, besides supporting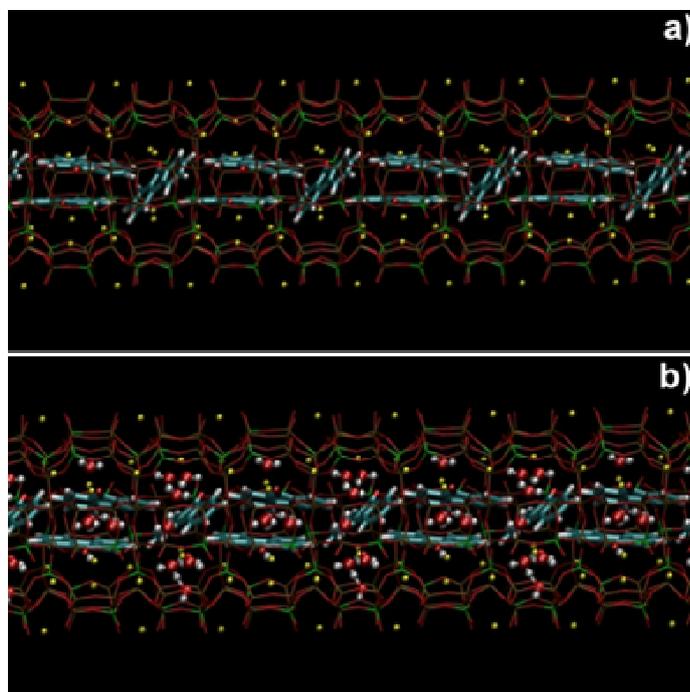 and strengthening experimental evidences, highlight the key role of the ZL channels in providing spatial, directional and morphological control of the photoactive species and stress the relevance of extraframework $K^+$ cations in stabilizing carbonyl-functionalized species inside ZL and in fine tuning their organization (Fig. 5).



Fig. 5 - Graphical representation of the minimum energy structure calculated for the: a) dry ZL/1.5FL model, b) hydrated ZL/1.5FL model (with 13 $H_2O$ in the simulation cell). Atom color codes brown: Si, green: Al, red: O), $K^+$ as yellow spheres. FL atoms are in van-der-Waals representation (cyan: C, red: O, white: H).
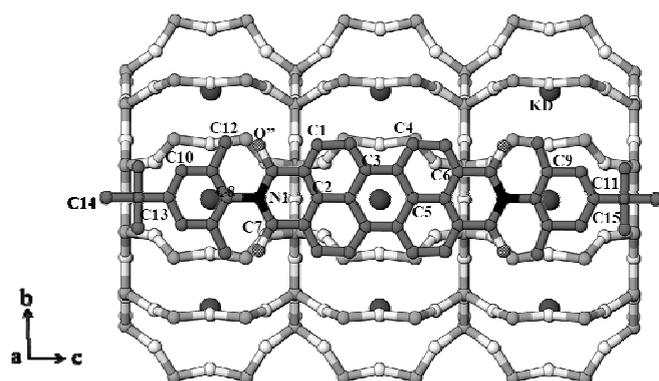


Fig. 6 - Projection of three unit cells of the ZL/tB-DXP composite structure along [100]. Only one dye molecule is shown for sake of clarity.

### ZL/tB-DXP composites

The successful encapsulation of the dye and its maximum possible loading, equal to 0.23 molecules p.u.c., was determinated by the thermogravimetric analysis.

Infrared measurement performed on the hydrate and de-hydrathed form of the ZL/tB-DXP composite has evidenced that the dye vibrational signals are strongly perturbed during the water removal, suggesting the presence of some interaction between the dye and the water molecules inside the ZL channel. The structural refinements revealed the presence of 0.25 molecules per unit cell. Three symmetrically equivalent, partially occupied, sites were found for the atoms of tB-DXP. These sites are placed at the center of the channel and lie on the mirror planes parallel to *c* axis (Fig. 6). Various models of the tB-DXP distribution based on our structural data are possible due to the presence of the t- butyl functional end-substituents group of the molecule that can rotate respect to rigid central part of the molecule contributing to increase the disorder of this final part of the molecule. The host-gust interactions evidenced by the structural refinement indicated a CH--O hydrogen bond between the dye molecules and the ZL framework and a second interaction between a carbon site of tB-DXP and the $K^+$ mediated by a water molecule.

### ZL/Th composites

Even in the case of the ZL/Th composites a multidisciplinary approach was essential to verify the insertion of the Th in the channels of zeolite. The thermogravimetric analysis showed that the two samples have different thionine contents and that the

sample ZL/Th50 presents the maximum Th loading for ZL, equal to 0.27 molecules, confirming the data of literature reported by Calzaferri & Gfeller (1992).

The IR spectroscopy revealed a blue shift of all the Th peaks once trapped in the zeolite, with respect to the pure dye. This effect could be interpreted as due to an interaction of Th with the zeolite framework. The structure refinement indicated high disorder around the 6-fold axis, within the 12MR channel, that led to the localization of the only thiazine ring, bearing the sulfur atom. The presence of short distances between the thiazine ring and a water molecules site bonded to the framework oxygen of the 12 MR suggested a water-mediated thionine-ZL interaction.

OPTICAL PROPERTIES

The optical properties, studied by means of UV-Vis absorption and photoluminescence spectroscopy for all the synthetized composites showed that the absorption and the emission properties of the systems are in general independent on the dye loading and on its orientation or packing inside the ZL channel. In particular, a very interesting result in the case of ZL/FL composite is that no emission intensity decrease in the ZL/1.5FL is observed, as could be expected as a consequence of the high amount and packing of the fluorenone molecules. Another important result is that, in the emission spectrum of the ZL/tB-DXP composite, the formation of aggregates are negligible, notwithstanding the high loading of the tB-DXP, suggesting that the t-butyl end-substituents in the molecule act as spacers. Also the absorption spectra of the ZL/Th composites show the presence of only monomeric thionine caged the ZL channel excluding the formation of aggregates on the zeolite surface also at so high Th concentration.

CONCLUSIONS

This work dealt, for the first time, with the organization of very high concentrated dye molecules inside ZL channels. In a broader perspective, the fundamental-level understanding of the interplay of host-guest/guest-guest interactions, which underlies supramolecular organization at high packing conditions, holds the promise to disclose alternative routes for the design of dye-ZL composites as building blocks for innovative optical devices.

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