Supplementary Information for:

Weak forces at work in dye-loaded zeolite materials: spectroscopic investigation on cation-sulfur interactions

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Supplementary Experimental:

Accordingly to the recipe described in the paper, DM4T has been loaded into LTL (DM4T-LTL-0) with nominal percentage of ~ 0.9 % (zeolite outgassed in ~ 3 x 10^{-2} torr @ 673 K for 1 night, inclusion @ 523 K for 2 days). The washing procedure was extended: the removing of included chromophores (not only the molecules adsorbed on the outer surfaces of LTL crystals) was in this case preferred, lowering the overall loading of DM4T.

Microscope fluorescence images were collected by an 80i Eclipse NIKON microscope, equipped with a 100X oil-immersion objective and an Hg lamp as excitation source.

Micro-PL spectra were collected by an home-made, fiber optic-based setup consisting of a Ti:Sapphire laser (Coherent MIRA) pumped by a Nd:YAG laser (VERDI) as excitation source, an 80i Eclipse NIKON microscope, equipped with a confocal head. The light emitted by the sample is collected through an optical fiber by an Hamamatsu Photonics Mini Spectrometer. Reference PL emission of DM4T dilute solution in CH_2Cl_2 was obtained by coupling the detector with an high-resolution (small core) optical fiber.

Supplementary Results and discussion:

Time-resolved spectra:

Two-dimensional PL profile (Fig. S1(a)) of DM4T-LTL-H (400 nm laser excitation) provided detailed information on both time-dependent intensity and spectral features. PL spectra have been extracted (Fig. S1(b)) and integrated over 40 ps-wide regions. The overall position and shape of DM4T-LTL-H emission band immediately after laser pulse remain unchanged as time passes, demonstrating that migration of excitation is negligible. PL decay traces (Fig. S1(c)) have been extracted and integrated over 10 nm-wide regions centered at PL maximum and in the long-wavelength tail. Both the curves are mainly single-exponential and lye parallel to each other (100 ps decay lifetime), demonstrating that in DM4T-LTL-H sample there is only one emitting species. As a reference, PL decay measurements on DM4T dilute solution in CH_2Cl_2 have been performed (Fig. S1(d)).

Micro-PL analysis of DM4T-LTL-0 sample:

Being the resolution of the PL detection apparatus (coupled with microscope) lower than usual, we have firstly compared PL emission of DM4T dilute solution in CH_2Cl_2 collected with the microscope setup with that collected by the standard setup (same excitation source). The data obtained (Fig. S2) show that, in the first case, even if the spectrum lacks the details of vibronic progression, it is indeed the convolution of the second one, maintaining both the overall shape and position.

Fluorescence microscope image of DM4T-LTL-0 sample under UV excitation (Fig. S2 inset) shows a distribution of PL intensity emitted by single LTL crystals, with many weakly emitting cylinders and few bright ones. Taking into account the nominal loading in the material preparation and the following washing procedure, we can infer that low-emitting LTL crystals do not have a loading higher than the nominal one, *i.e.* 0.9 % (nothing can be said for what it concerns the loading of strongly emitting crystals, which should be indeed higher). Micro-PL measurements were then performed over a rather big collection of differently-loaded crystals (Fig. S2). Although the lack of details concerning vibronic progression prevents an accurate estimation of peaks positions, both the PL of low- and high- loaded crystals are indeed red-shifted with respect to DM4T dilute solution in CH_2Cl_2 . For what it concerns the PL spectrum of high-loaded LTL crystal, it should be noted that also a low-energy tail is present. This may be related with some kind of interaction between DM4T

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molecules, but may be also an experimental artefact (in these high-loaded objects the selfabsorption can affect the PL onset and therefore lead to a small increasing of the low-energy tail after the normalization of the spectrum). These findings demonstrate that the shift of the main emission band is independent of dye loading and must therefore be related to the interaction of the chromophores with the framework (namely, the charges). Intermolecular interactions, if present, may increase the low-energy tail of the PL, but cannot explain the rigid shift of the vibronic progression.

PLE spectra of DM4T-LTL samples:

In Fig. S3, optical absorption and PL spectra of DM4T dilute solution in CH_2Cl_2 are compared with PLE and emission spectra of DM4T-LTL samples. The red-shift of vibronic progression in the main emission band is extensively discussed in the paper.

PLE spectra of DM4T-LTL-L and -H show an almost unstructured band centered just below 400 nm, reproducing quite well the absorption spectra of the dye in dilute solution. A low-energy shoulder close to PLE onset is also observed, its increasing with sample loading. Its occurrence could be ascribed to the fraction of interacting molecules inside LTL channels which statistically increases along with dye concentration.

Supplementary Figures:



Figure S1. (a) two-dimensional PL intensity profile of DM4T-LTL-H emission excited at 400 nm (white boxes depict integration regions for PL and decay spectra in (b) and (c)). (b) emission spectra (extracted from (a)) of DM4T-LTL-H sample collected (from top to bottom) in a 40 ps-windows immediately, 300 ps and 600 ps after laser pulse respectively (dashed vertical line is a guide for the eye to highlight the position of the spectrum). (c) PL decay traces of DM4T-LTL-H detected at PL maximum (\circ) and in the long-wavelength region of emission band (**x**), extracted from (a). (d) PL decay traces of DM4T dilute solution in CH₂Cl₂ detected at PL maximum (\circ) and in the long-wavelength region of emission band (**x**), excited at 400 nm.

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Figure S2. Comparison of PL spectra of DM4T dilute solution in CH_2Cl_2 collected with highresolution setup (solid line) and micro-PL setup (dashed line), along with micro-PL emission of weakly- (\circ) and brightly-emitting (**x**) zeolite crystals in DM4T-LTL-0 sample (395 nm laser excitation). Inset: collection of zeolite crystals imaged by fluorescence microscope (330 – 380 nm excitation, 100X magnification). Vertical arrows are guides to highlight the shift of PL maxima.

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Figure S3. Comparison between optical absorption/PLE (solid lines) and PL spectra (dashed lines) of DM4T dilute solution in CH_2Cl_2 (top), DM4T-LTL-L (middle) and DM4T-LTL-H (bottom). Excitation wavelength is always 355 nm. Vertical dotted line is a guide to highlight the shift in PL emission.