Supplementary Material (ESI) for *PCCP*

Polymer-microporous Host Interactions Probed by Photoluminescence Spectroscopy

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Supporting information

Contents (14 pages):

I. Analysis of time-resolved luminescence data.

Introduction. For a material made of N non-interacting species its luminescence time-resolved spectra, $D(\nu, t)$ will be given by a sum of the luminescence spectra for each species, S_N, weighted by their contribution at a given time, w_N, as:

$$D(\nu,t)=\sum_{i=1}^{N} w_N(t)S_N(\nu) \tag{S1}$$

For homogeneous species, w_N will be given in general by an exponential decay,

$$w_N=\exp(-t/\tau_N) \tag{S2}$$

where τ_N is the decaying time-constant for species N. For inhomogenous species we should better expect exponentials distributed as B_N,

$$w_N=\int B_N(\tau)\exp(-t/\tau)d\tau \tag{S3}$$

where B_N will be an unimodal function centered about τ_N, which describes how the time constant of decay can vary within a given species due to the inhomegeneties. The narrower B_N, the closer we will be to the homogenous case.

The habitual goal is to estimate from an experimental realization of the luminescence decay, D, the number of species, N, their associated luminescence spectra, S_N, and their time constants, τ_N. In the inhomegenous case, searching for the time constants is replaced by searching for the center value of B_N. Less commonly, and far more challenging, is to aim for an estimate of the width or shape of B_N.

Global exponential nonlinear least-squares. Global exponential nonlinear least-squares (G-ExpNLLS) allows for obtaining estimates of the time constants and the luminescence spectra of the difference species present in the sample. This is done fitting the experimental time-resolved luminescence data to a multiexponential model containing a pre-specified number of discrete exponentials, M:

$$y(\nu,t)=\sum_{i=1}^{M}\exp(-t/\tau_M)A_M(\nu) \tag{S4}$$

Least-squares estimates for τ_M and A_M are obtained minimizing the weighted square discrepancy with the data,

$$\min\left\{\left(\frac{D(\nu,t)-y(\nu,t)}{\sigma(\nu,t)^2}\right)^2\right\}=\min\{\chi^2\} \qquad \text{(S5)}$$

where σ is the standard deviation of the error expected for each data point. The estimated exponential amplitudes dependence on the wavelength, *A*, are often called the decay associated spectra (DAS). DAS relates directly to the least-square estimate of the luminescence spectra for *M* species, although only in the case of independent decaying species, and provided that *M* was adequately chosen. This can be easily seen comparing eq. S2-S3 with eq. S4, setting $M = N$.

Well recognized problems with G-ExpNLLS are: i) how to set *M* value (the number of exponentials), since the obtained time constants and DAS can depend significantly of the value chosen; and ii) difficulties to proof that the least-square (best) estimates for the time constants and the DAS have been obtained, i.e., to be sure that the global minimum of the χ^2 and not a local minimum has been reached. One minor problem of G-ExpNLLS is how it deals with inhomogenous decays. Although eq. S4 can be modified to deal with inhomogenous decays, this requires specifying a priori a parametric model to approximate B_N. Besides, adding extra parameters to be estimated from the minimization of the χ^2 can lead to some serious numerical problems, affecting the solution stability as described next.

A problem not often recognized with G-ExpNLLS is that minimizing the χ^2 can easily become ill-conditioned as the number of parameters to be estimated from the data increases. This is specially the case when parameters to be estimated cannot be uniquely constrained by the experimental data, for instance for parameters controlling the width of distributed exponentials, or for DAS with similar time constants. In these circumstances, small variations from ideality, like errors of different dependence on time or wavelength than assumed, or unexpected errors in the experimental data (spikes, baseline fluctuations, etc), can render the estimated parameters uselessly perturbed from the real ones.

Our approach. Our approach to analyze luminescence the data is as follows. Using the maximum entropy method, described in detail below, we obtain a lifetime distribution from the area of the time-resolved luminescence data. This lifetime distribution is an estimate of the sum of all B_N, weighted by the area of their respective S_N. If the maxima of B_N are enough far a part, and ignoring error effects, the lifetime distribution will contain as many bands as *N*, with maxima located at τ_N. In this approach, in contrast to G-ExpNLLS, there is not need to give *a priori* the number of exponential decays, but this number is determined *a posteriori* from the lifetime distribution obtained. Once we decide the bands of the lifetime distribution representing real components, their time constants and widths are used to construct the decay for each component, and the DAS are obtained from the data by a simple linear least-squares step.

In this approach, the problem of local minimum or ill-conditioning can be avoided (as it happens with G-ExpNLLS). Further, there is no need to discriminate between discrete or distributed decays. However, the main difficulty resides in selecting the so-called regularization parameter, which controls the mathematical *resolution* of the estimated lifetime distribution. As the *resolution* increases, not only the details of the lifetime distribution increase (approaching the real one), but so do the errors. A compromise is required, and to select the regularization that best balances both compromises is a key issue. The fact the *resolution* of the lifetime distribution has to be limited causes the broadness of the bands. This arises from the real inhomogeneities in the decays or the limited *resolution* in the recovered lifetime distribution, making difficult to discriminate between the two causes.

Lifetime distribution analysis by the Maximum Entropy inversion of the Laplace Transform (MaxEnt-iLT). Before talking about the Maximum Entropy method it is important to understand how the inversion of the Laplace transform (LT) can help in the analysis of decaying signals. For that, it is useful to compare it with the well-known Fourier transform (FT). The inverse FT (iFT) is able to convert a signal made of an unknown number of sinusoids with unknown frequencies and amplitudes (oscilogram) into a spectrum (distribution of sinusoid amplitudes versus frequencies). On the other hand, the (direct) FT allows for the reverse transformation (from a spectrum to an oscilogram). Although experimentally it may be more conveniently to collected an oscilogram, it is in the spectrum where it is straightforward to determine the number of the sinusoids present, their frequency and amplitude. In a similar way, the inverse (real) Laplace transform (iLT) allows to convert a signal made of an unknown number of decaying exponentials, with unknown rate constants and amplitudes (time-resolved decaying data), into a lifetime distribution (distribution of exponential amplitudes versus the exponential time constant). The (direct) LT codes the reverse transformation i.e. from a lifetime distribution to a time-resolved decaying response. Although, generally, only the time-resolved decaying response of the system is experimental accessible, it is the lifetime distribution which, through the number of bands, and their number, positions, areas and widths, will give us the number of exponentials, their time constants, exponential amplitudes and time constant heterogeneities. Here comes the potential of the iLT in the analysis of experimental data containing an unknown number of exponential decays (discrete or distributed).

Mathematically, the Laplace transform, LT, of a lifetime distribution, *h*, as a function of the exponential rate constant (in decimal logarithm scale) is given by

$$y(t) = LT\{f(\log k)\} = \int_{\log k_{ini}}^{\log k_{fin}} h(\log k)\exp(-kt)d\log k \tag{S6}$$

where $k = 1/\tau$, and it was assumed that $f(\log k) = 0$ for $\log k < \log k_{ini}$ and $\log k > \log k_{fin}$ (i.e., no faster and slower components than k_{ini} and k_{fin} exist in the lifetime distribution). Equation S6 is analogous to the matrix equation y=A×h, where y is a N_t×1 vector (N_t being the number of time points) representing an ideal time-resolved data; h is a N_k×1 matrix (N_k being the number of evaluated rate constants), the lifetime distribution; and A is a $N_t \times N_k$ matrix, which performs the discrete Laplace transform of the y columns, with elements are given by $A_{ij} = \exp(-k_j t_i)$. The vector t (N_t×1) contains the time values of the data, and k is a N_k vector of the rate constant values, which are logarithmically spaced between k_{ini} and k_{fin}. Numerically, the iLT is formaly given by $h=A^{-1}\times y$, or, if A is not a square matrix, by the least-square solution $h=(A^TA)^{-1}\times A^Ty$.

Fourier and Laplace transform differ in a very important aspect though. In the FT the information contained in the data is preserved, and the direct and inverse FT can be reversibly applied to any data without losing any information or perturbing their noise. In contrast, the LT attenuates and practically removes high frequency details in the lifetime distribution h, giving a smooth data vector y. In consequence, in order to undo the process, the iLT must enhance enormously the high frequency components contained in y in order to retrieve h.[1] If we apply the iLT to experimental data vector d the inversion process blows up due to the presence of noise, i.e., high frequency components in d, even if tiny, require enormously huge fluctuations in h to be reproduced. Mathematically, the matrix A^{-1}, or $(A^TA)^{-1}$, is singular or ill-conditioned, and any error in d leads to unbearable big error in the estimated h.

Instead, a solution for the lifetime distribution has to be obtained indirectly, using inverse theory and inference tools.[2, 3] The general approach is to search for a possible solution, i.e., a lifetime distribution h that when Laplace transformed describes the experimental time-resolved data d within the noise level (often measured by the χ^2). From the boundless group of lifetime distributions fulfilling this condition, the most plausible one is considered the less informative/detailed one among this group. In other words, the possible solutions containing more information/details than those essentially required to describe the data within a given level are ruled out. The lack of information, smoothness or simplicity of a solution is measured by a function named entropy, here the term "maximum entropy method" (MaxEnt).

In practice, it is computationally convenient to measure the agreement between d and y can be measured using the χ^2 statistic, even when the errors in d are not strictly expected to follow a Gaussian distribution:

$$\chi^2 = \sum_{j=1}^{N_t}\left[w_j\left(d_j - (\mathbf{A}\times\mathbf{h})_j\right)\right]^2 = \sum_{j=1}^{N_t}\left[w_j\left(d_j - y_j\right)\right]^2 \quad \text{(S7)}$$

where w is here a $N_t\times1$ weight vector, with elements given by the reciprocal of the expected standard deviation for the time-resolved data to a proportionality factor (multiplying w by a scalar is equivalent to multiplying χ^2 by the same scalar). In our case, the noise standard deviation of the time-resolved luminescence was taken to be proportional to data intensity, based on heuristics and inspection of the residuals of the analysis. When required, the w was slightly modified from this initial guess by reanalyzing the residuals.

A solution, besides being feasible, should be plausible, i.e., as simple or non-informative as possible. For a vector that can show both positive and negative values, the lack of information can be measured using the generalized Shannon entropy without sign-restrictions:

$$S = \sum_{i=1}^{N_k}\left[\sqrt{h_i^2 + 4m_i^2} - h_i \ln\left(\frac{\sqrt{h_i^2 + 4m_i^2} + h_i}{2m_i}\right) - 2m_i\right] \quad \text{(S8)}$$

where m represents here the average of the *a priori* solution for the positive and negative components of h in absolute terms. If we do not have any *a priori* knowledge about the solution, a coherent choice is to assign uniform elements of value (*max*(d) − *min*(d)) / N_k to the m vector. This choice for the *a priori* solution has three convenient properties: i) if the time-resolved data does not contain any significant information it would generate a flat featureless lifetime-resolved data; ii) the obtained lifetime-resolved data will become independent of the relative intensity or any scaling of the time-resolved data, d; iii) the obtained lifetime-resolved data area will have minimum bias. In practice, a better choice for the *a priori* vector is $m \times 10^{-NEF}$, where NEF is scalar that we typically set to 4. This modification of the *a priori* solution allows MaxEnt-iLT to be able to reconstruct lifetime distributions with narrow features, while conserving the main desirable properties of the default *a priori* solution, except for the solution area which will be biased (it will tend to be infraestimated).[4]

The numerical problem is therefore to find the lifetime-resolved data with maximum entropy, which at the same time describes the time-resolved data within some tolerance level. This problem can be restated as finding the h vector which minimizes an objective, Q, given by

$$Q = \chi^2 - \lambda \times S \qquad \text{(S9)}$$

where λ (regularization parameter) is a scalar which balances S and χ^2, i.e., the solution multiplicity and the data likelihood. Therefore, strictly speaking, the maximum entropy method does not provide a single solution but a trajectory of solutions, one for each regularization value. The regularization parameter in MaxEnt-iLT has been habitually chosen using the χ^2 or discrepancy criterion,[5-8] which states that λ should be chosen such that at the solution $\chi^2 / N_t \approx 1$. Some of us (as well as other authors) have shown that this estimate for λ is neither objective (requires w to accurately represent the inverse of the noise standard deviation), nor optimum even when the noise variance is accurately known (provides over-smoothed solutions).[9-11] Bayesian inference and the L-curve provide a more objective regularization value (only require w to represent the inverse of the noise standard deviation to a proportionately factor), which more over is close to optimum (the L-curve tends to provide slightly over-smoothed solution). [11-15] On the other hand, the L-curve is more robust to the presence of systematic errors in the data than Bayesian inferences, which in such instances tends to give over-detailed solutions. Details on how to implement these two methods have been given elsewhere.[11]

Equation S9 can be minimized using different methods. In our approach, minimization of Q to respect h for a given λ value was based on an iterative Newton-Raphson minimization, using line searches to adjust the size of the steps.[4] Whenever a Newton-Raphson iteration failed to reduce Q, the minimization algorithm switched momentarily to a step-descendent method combined with line searches. Convergence was declared only when both the objective function and the second norm of the solution changed less than a 10^{-5} fraction for two consecutive iterations. Given the high dimensionality of the problem false convergence can become an issue. To diagnose false convergence we customarily apply a test function (TEST) introduced by Skilling and Bryan.[16] TEST measures the degree of nonparallelism between the entropy and χ^2 gradients, which is zero for a true maximum entropy solution. At convergence, our algorithm customary obtained TEST values on the order of 10^{-4} (TEST < 0.1–0.001 are often considered proof for true maximum entropy solution).[5, 16, 17]

Even when the regularization parameter has been optimally chosen, the obtained lifetime distribution will contain two types of errors: noise-induced errors and regularization-errors. The presence of noise is the data will be reflected as errors in the position, width and area of band in the lifetime distribution, and more seriously as noise-induced artifactual bands. To identify which bands could be noise-induced, we used a Monte-Carlo re- sampling method. Around 100 realizations of normal noise of the expected magnitude were added to the data, and we evaluate how the MaxEnt lifetime distribution changed in response. This allow us to compute a kind of error bars for the lifetime distribution, and asses which bands where enough significant to be clearly assigned to a real feature present in the data. Regularization errors are more difficult to quantify, but can be easily understood by the concept of the effective resolution function of MaxEnt.[18] Ignoring noise effects, the obtained lifetime distribution will be given by the real lifetime distribution distorted by the effective resolution function of MaxEnt. The most obvious effect is that the bands in the lifetime distribution become broader than they should be. Consequently, the bandwidths in the lifetime distributions provided by MaxEnt-iLT can have a physical or a mathematical origin: the bandwidths could represent the heterogeneity in the time constants (inhomogeneous exponential decays) or just the MaxEnt-iLT limitations to obtain a more resolved lifetime distribution.

Ii. SEM pictures

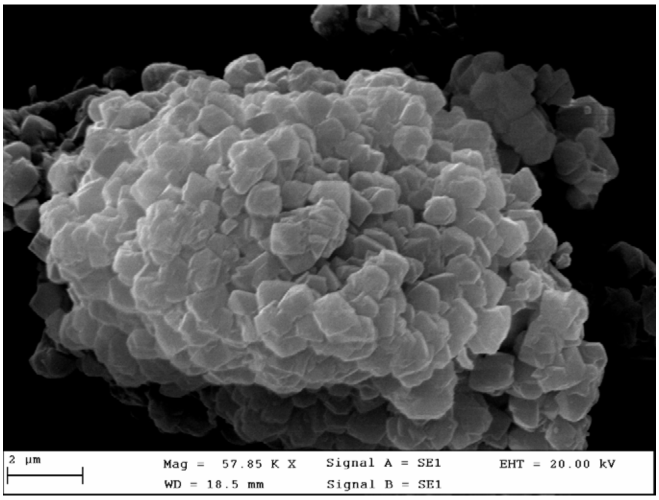

Figure S1 SEM picture of Eu- NaY.

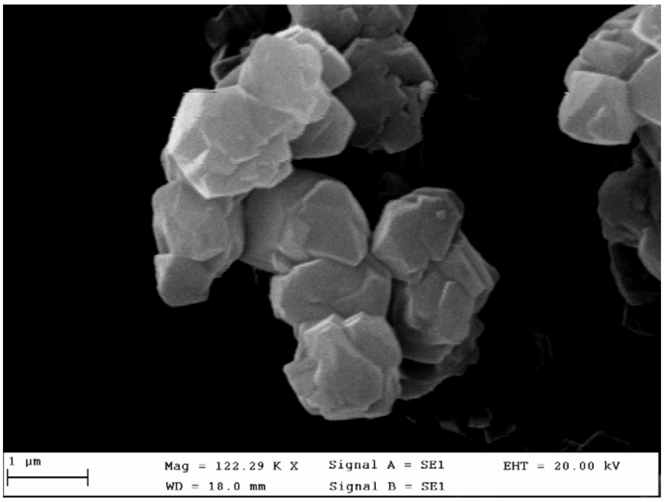

Figure S2. SEM picture of Eu- NaY/PS.

III TGA curves

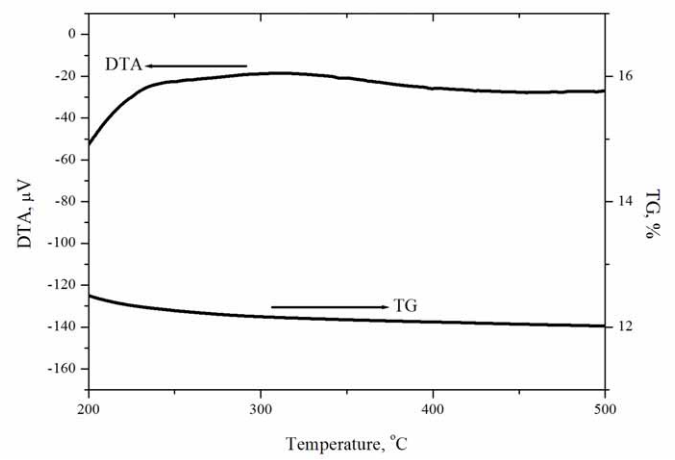

Figure S3 (a). TG-DTA curves of Eu- NaY.

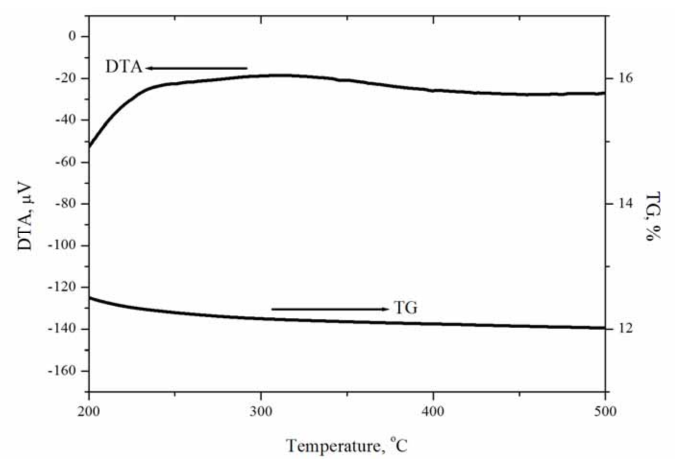

Figure S3 (b). TG-DTA curves of Eu- NaY/PS.

IV. FT- IR spectra

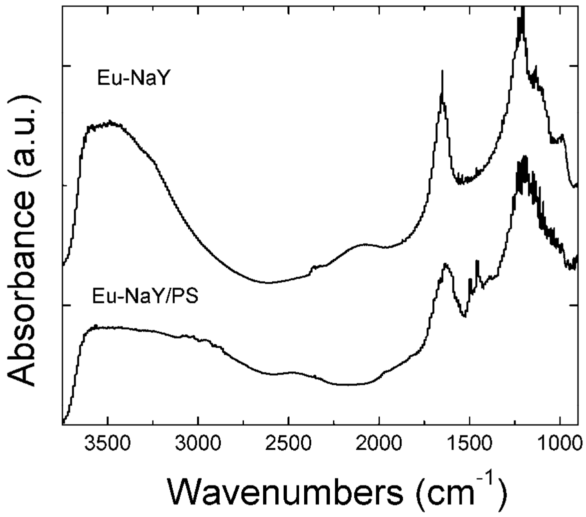

Figure S4. FT-IR spectra of Eu- NaY and Eu- NaY/PS.

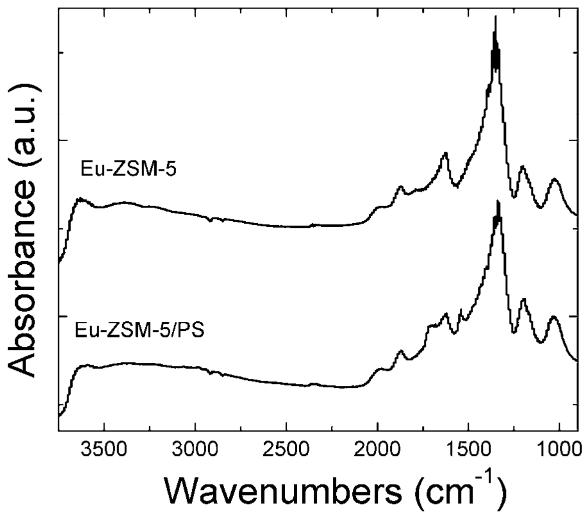

Figure S5. FT-IR spectra of Eu- NaY and Eu- NaY/PS.

V. Excitation spectra of europium luminescence

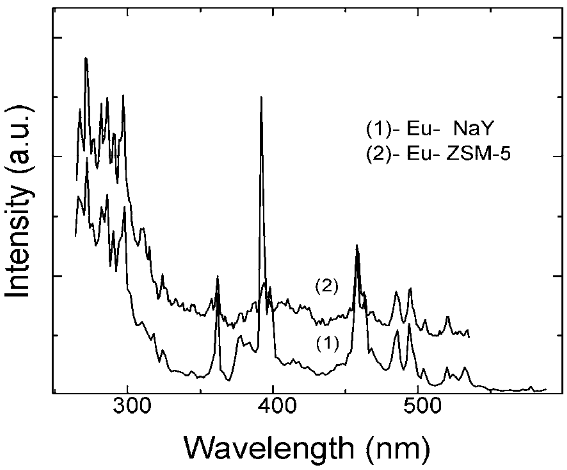

Figure S6. PL excitation spectra of europium emission in NaY (1) and ZSM-5 (2) zeolites measured at λ_{em}= 614 nm.

VI. Lifetimes distribution analysis by using Maximum Entropy Method

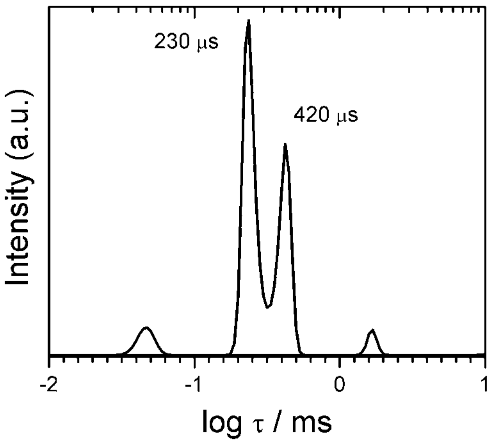

Figure S7. Lifetime distribution recovered by MaxEnt for Eu- NaY.

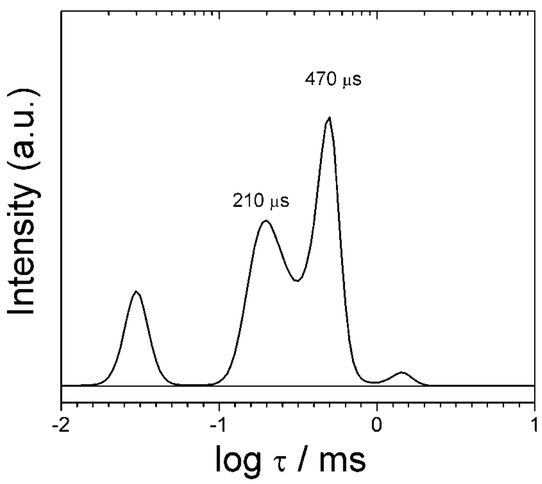

Figure S8. Lifetime distribution recovered by MaxEnt for Eu- NaY/PS.

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