

Excitation Energy Migration in a Photonic Dye-Zeolite Antenna: Computational Techniques

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Abstract: Excitation energy migration between dyes embedded in hexagonal crystals of cylinder morphology is an attractive phenomenon for the construction of photonic antennae [1, 2]. Detailed knowledge of the zeolite structure, the organization and the spectroscopic properties of the dyes and the nature and strength of the host-guest interactions is required to optimize energy migration (EnM). Whether a dye-zeolite antenna efficiently transports excitation energy is mainly determined by the mechanism and rate of energy transfer (EnT) between the dyes embedded in the zeolite channels. The decay of the luminescence of these dyes, which reveals information about the EnT, is measured indirectly using Multi-Frequency Phase Fluorimetry (MFPF). Subsequently a fit of the measured data to a multiexponential decay is performed. A new, user-friendly Windows software has been developed which performs this fit, allowing full control over all fit parameters and providing useful information about the quality of the fit. The software also contains a database capable of storing all the relevant information related to the experiment. It is therefore a highly optimized analysis and managing tool for our experimental method which has greatly improved the efficiency of data analysis. The software is highly flexible and can easily be adapted to other experimental methods.

Keywords: Multi-frequency phase fluorimetry, multiexponential decay, fitting software, nonlinear least-squares method, Levenberg-Marquardt minimization algorithm, chi-square criterion, database management system.

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1 Zeolite L as a host for dye molecules

In plants the energy of the sunlight is transported by chlorophyll molecules for the purpose of energy transformation. We have succeeded in reproducing a similar transport of excitation energy in an artificial antenna system: Zeolite L crystals of cylindrical morphology consist of a continuous one-dimensional channel-system. We fill each individual channel with chains of joined but noninteracting dye molecules. Green emitting pyronine (*Py*) molecules, acting as energy donors, are put in the middle part of each channel, whereas red emitting oxonine (*Ox*) molecules, acting as energy acceptors, are put at both ends of the channels (Fig.1).

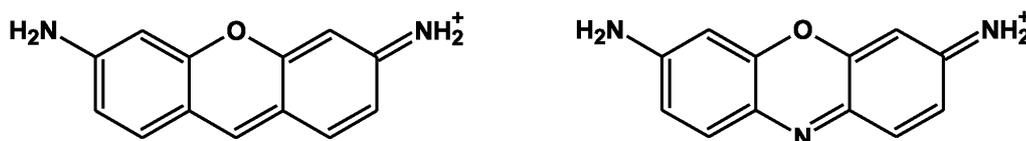


Figure 1: Donor dye pyronine (left) - acceptor dye oxonine (right).

Light of appropriate wavelength shining on the cylinder is absorbed only by *Py*, which transfers its excitation to a neighboring ground-state *Py*. This process is constantly repeated and gives rise to the EnM, which is in competition with spontaneous emission, radiationless decay and photochemically induced degradation [2]. Very fast EnM is therefore crucial if the *Ox* should be reached before other processes take place. If after a series of EnT steps the exciton finally reaches an *Ox* at the end of a channel, it cannot be sent back to *Py*, because the energy of the excited state of *Ox* is too low for reexcitation of *Py*. Instead the exciton is emitted as red light. Hence we have a photonic antenna transporting excitation energy from the middle part to the ends of a zeolite L crystal (Fig.2).

The extremely fast EnM in our system has a great potential in leading to new materials for imaging techniques, dye lasers of extremely small size, probes in biological systems, LED's and thin-layer solar cells. In the latter application the material can be extended to a device in which different dye molecules are arranged so that light of the whole visible spectrum can be absorbed and transported to the ends of the crystal without significant loss. As the absorption of light and the creation of an electron-hole pair are spatially separated, as in the natural antenna system of green plants, this is a fundamental step in the development of a new generation of dye-sensitized solar cells [3].

The decay of the luminescence of the dyes embedded in the zeolite channels reveals information about the mechanism and rate of the EnT and can therefore give an answer to the question how the dye-zeolite antenna transports excitation energy. We have observed that in the presence of *Ox* the *Py*-fluorescence decay becomes much faster with higher *Py*-loading. This is caused by the irreversible EnT to *Ox* which increases parallel to the increase of the EnT between the growing number of *Py*-molecules (Fig. 3A). The *Ox*-time-resolved fluorescence initially increases because of the transport of excitons. It then reaches a maximum before it decays (Fig. 3B).

2 Experimental method

The data of figure 3 were measured using the MFPPF method [4, 5]. With this method the phase shift of amplitude modulated laser light between an unloaded zeolite layer and a dye-loaded zeolite layer is measured for different modulation frequencies. The unloaded zeolite layer acts as a scatterer, whereas in the dye-loaded zeolite layer the incident light is partially absorbed and emitted with a

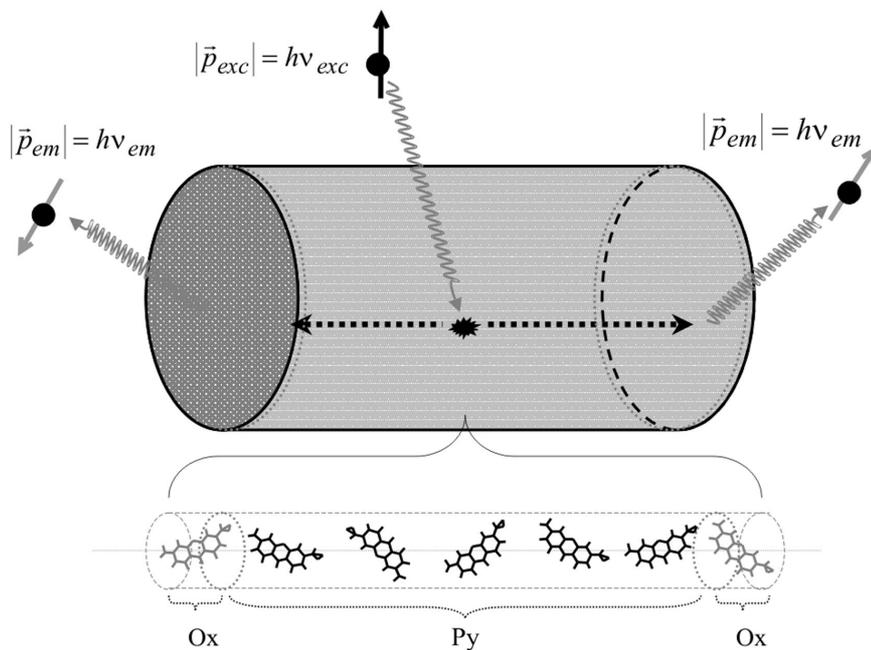


Figure 2: Photonic Ox,Py-zeolite L antenna and corresponding energy migration pathways.

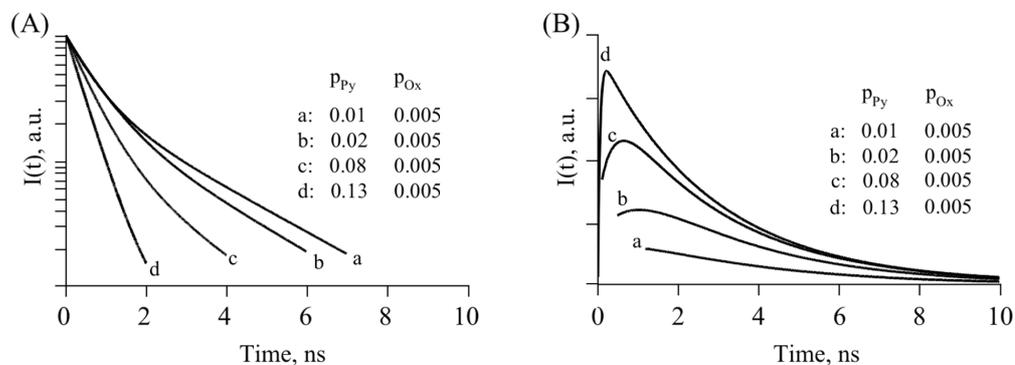


Figure 3: Experimentally observed fluorescence decay of Py (A) and Ox (B) after specific excitation of Py. Traces a to d differ in the loading composition of the zeolite. Unity corresponds to a fully dye-loaded crystal.

specific time delay according to the physical processes described above. The resulting phase shift φ is a function of the circular modulation frequency ω , and the underlying time dependent decay is represented as a multiexponential function:

$$I_{par}(t) = \sum_{j=1}^{n_{\tau}} p_j e^{-\frac{t}{\tau_j}} \quad (1)$$

par represents the parameters of the decay function that contain the desired information about the mechanism and rate of the energy transfer in the zeolite channels: n_τ is the number of exponentials, p_1, \dots, p_{n_τ} are the pre-exponential factors, and $\tau_1, \dots, \tau_{n_\tau}$ are the lifetimes. The decay of the luminescence of a dye in a zeolite channel can be multiexponential if, for example, there is a heterogeneity of the absorbing molecules, e.g. if they have different environments, or if radiationless relaxation or photochemically induced degradation occur parallel to luminescence. The relation between the decay function and the phase shift is given as:

$$\tan(\varphi(\omega)) = \frac{N(\omega)}{D(\omega)} \quad (2)$$

$N(\omega)$ and $D(\omega)$ are the sine and cosine transforms of $I(t)$:

$$N(\omega) = \frac{\int_0^\infty I(t) \sin(\omega t) dt}{\int_0^\infty I(t) dt} \quad (3)$$

$$D(\omega) = \frac{\int_0^\infty I(t) \cos(\omega t) dt}{\int_0^\infty I(t) dt} \quad (4)$$

For a sum of exponentials the transforms are

$$N_{par}(\omega) = \frac{\sum_{j=1}^{n_\tau} \frac{\omega p_j \tau_j^2}{1 + \omega^2 \tau_j^2}}{\sum_{j=1}^{n_\tau} p_j \tau_j} \quad (5)$$

$$D_{par}(\omega) = \frac{\sum_{j=1}^{n_\tau} \frac{p_j \tau_j}{1 + \omega^2 \tau_j^2}}{\sum_{j=1}^{n_\tau} p_j \tau_j} \quad (6)$$

For a set of measurement points (ω, φ) the parameters p_j and τ_j can be fitted for any needed number of exponentials according to equations (2), (5) and (6).

3 Time Resolved Frequency Domain (TRFD) Fitting Software

A successful approach to fit the parameters p_j and τ_j is least-squares estimation in combination with the Levenberg-Marquardt minimization algorithm [6]. Although numerous software packages are available for fitting purposes, there has been no professional Windows-based software so far which meets all the needs arising from our experimental method. For this reason we have developed a fast and user-friendly software for the purpose of data analysis, the Time Resolved Frequency Domain (TRFD) Fitting Software.

General description The TRFD Fitting Software (Fig. 4) allows to perform parameter fits based on the multiexponential representation using any number of exponentials from 1 to 10. This covers all systems that ever might be analyzed based on a multiexponential decay.

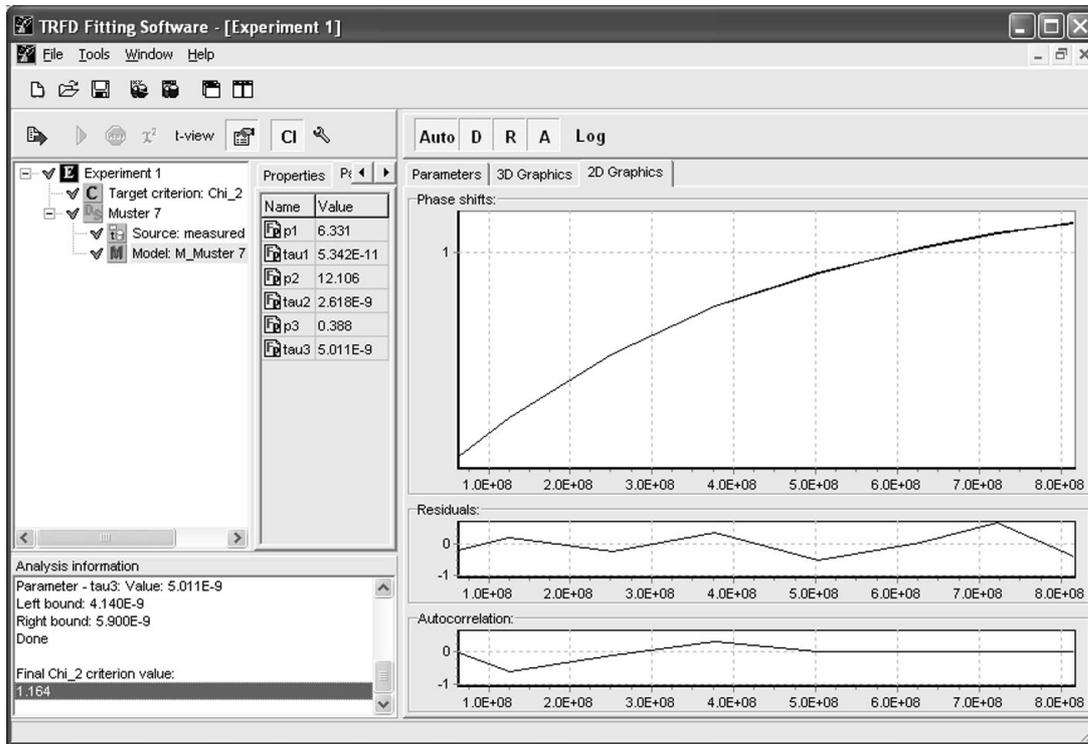


Figure 4: Analysis interface of the TRFD Fitting Software.

Each parameter p_j and τ_j can be fixed to a predefined value or to an interval of allowed values by defining the minimum and maximum value. The software also allows to link parameters in user-definable groups. That forces the fit algorithm to assign the same value to all members of the group. This feature is especially useful, if the contribution of different lifetimes to the decay function is assumed to be equal. Apart from analysis of single phase vs. frequency traces, the software also allows to perform global analysis of multiple phase vs. frequency traces. In global analysis several experimentally obtained data traces are combined and simultaneously fitted. Such a simultaneous analysis of several experiments is more accurate and reliable in the analysis of complicated photophysical phenomena [4].

Minimization method The software uses the Nonlinear Least-Squares method to compare the experimental data with the values calculated from the fitted parameters. The method is based on the following equation:

$$\chi^2 = \frac{1}{\nu} \sum_{k=1}^{n_\omega} \frac{(\varphi_{meas}(\omega_k) - \varphi_{par}(\omega_k))^2}{w_k} \quad (7)$$

where

$$w_k = s^2[\varphi_{meas}(\omega_k)] \quad (8)$$

are weighting factors. The value of each weighting factor is the variance (s^2) of all phase shifts measured for the corresponding circular modulation frequency. (For every circular modulation frequency the phase shift is measured at least 100 times.)

The degrees of freedom are defined as the number of measurement points minus the number of fit parameters minus 1:

$$\nu = n_{\omega} - 2n_{\tau} - 1 \quad (9)$$

The Levenberg-Marquardt algorithm is used as the standard minimization algorithm for the Least-Squares method.

Fit judgement The following criteria [4, 7] for judging the quality of the fit are provided:

- The value of the χ^2 criterion
- The frequency dependence of the weighted residuals, which is calculated according to the following equation:

$$R(\omega_k) = \frac{\varphi_{meas}(\omega_k) - \varphi_{par}(\omega_k)}{\sqrt{w_k}} \quad (10)$$

- The frequency dependence of the autocorrelation function of the weighted residuals
- The confidence intervals for the estimated parameters

Software structure and interface features The software package consists of an analysis application and a database management system.

The analysis application is responsible for data fitting and can communicate with the attached databases. It includes an interface allowing to load the measurements database and the analysis database, to visually configure the analysis, to execute the parameters fit and to view the analysis results. Some data are shown in text form (value of χ^2 , values of the fitted parameters), others in graphical form (2D- and 3D-graphical views of the experimental and fitted curves, of the weighted residuals and of the autocorrelation function of the weighted residuals in the frequency domain; 2D-graphical view of the fitted decay function in the time domain) (Fig. 4).

The database management system provides capabilities to import, store, search and manage both experimental data and analysis results. The system consists of two databases, a measurements database (Fig. 5) and an analysis database.

Features of the databases:

- Import wizard (measurements database only) for the loading of raw experimental data from text files.
- Convenient representation of all stored information.
Measurements database: Information about the experiment, such as the experimental parameters, information about the sample a.s.o., are displayed.
Analysis database: Parameter linkage configurations, the values of the fitted parameters and the fit quality values are displayed.
- Built-in 2D-graphical previewer for the data stored in the database.
- Facilities to find, sort and filter stored information in any field of any table using complex user-generated filter conditions.
- Communication with the analysis application.
- Facility to create user-defined reports for convenient representation of the data on the basis of selected records.
- Export of the stored data to the ASCII file format.

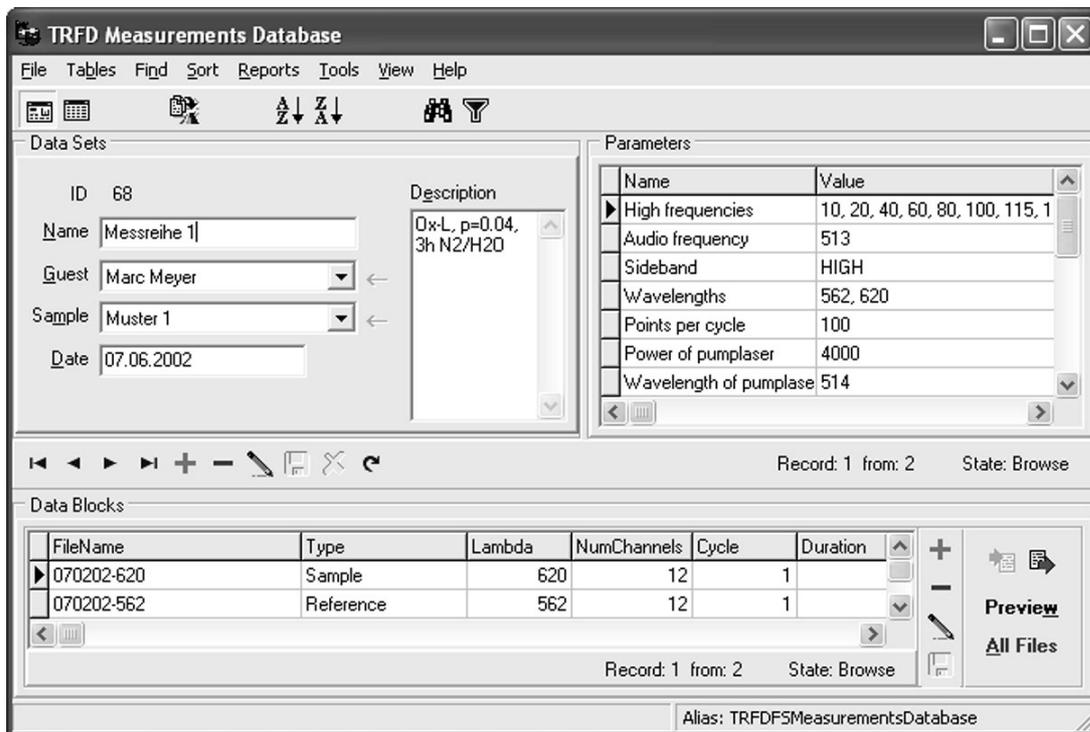


Figure 5: Screenshot of the measurements database interface.

- Packing, emptying and repairing of the tables.
- Support of data integrity and validity.

Future plans The TRFD Fitting Software is currently being developed further. Projects include the implementation of:

- Additional representations of the time dependent decay.
- Graphical representation of the fitted parameters and the corresponding confidence intervals.
- Calculation and representation of the error corridor for the fluorescence decay in the time domain.
- Various formatting and exporting facilities for the graphical representations.
- Additional fit quality criteria, such as the normal probability function of the weighted residuals.
- Client-server database architecture.
- Wizards for the import of other file formats to the measurements database.
- A templates database for storing and managing often-used analysis schemes.
- A help system and facilities to simulate measurements allowing new users to train data analysis on the basis of computer-generated data.

4 Conclusion

If data analysis software is used which is not optimized for the applied experimental method, a loss of valuable information can be the result. The TRFD Fitting Software, providing a modern, intuitive and user-friendly environment, has shown to be an appropriate and reliable instrument for the analysis of the experimental data resulting from our MFPPF experiments.

Using this software we can efficiently investigate the mechanism and rate of the energy transfer between dyes embedded in zeolite channels, for the following reasons: First, less time is used to evaluate a measurement. Secondly, the software allows to partially evaluate an experiment under operating conditions. This, in return, makes it possible to change the parameters of an experiment or to abort it, if necessary, before it has been completed and therefore to save time and resources. The facilities of the database management system give rise to a highly improved data management. Experimental results can be compared or reevaluated in a comfortable way, and the storage of the data in a database provides a compact, clear and safe way to collect and keep the experimental results. The flexibility of the TRFD, which allows to adapt it to other experimental methods, makes it an excellent tool for many applications.

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