High-Throughput Characterisation of Materials by Photoluminescence Spectroscopy

Pedro Atienzar, Avelino Corma,* Hermenegildo García, and José M. Serra[a]

Abstract: An automatic system for high-throughput (HT) characterisation of large libraries of solid materials by photoluminescence spectroscopy is described. The system provides time-resolved transient emission spectra in the microsecond scale and can be employed for characterisation of materials of interest in the fields of catalysis and electroluminescence, amongst others. Here, we present its application to the optimisation of the ship-in-a-bottle synthesis of a novel electroluminescent polymer (PPV) and a photocatalyst (TP+), both encapsulated in large-pore zeolites.

Keywords: combinatorial chemistry · high-throughput screening · luminescence spectroscopy · zeolites

Introduction

The development of chemistry can benefit from high-throughput (HT) techniques that allow the generation, characterisation and determination of the properties of large libraries of compounds and materials.[1–3] More specifically, the development of HT physico-chemical characterisation techniques has been the subject of intense research, as this is normally a tedious, time-consuming step that may cause a bottleneck when a large number of related samples is produced. Gravimetric, thermoanalytical,[4] X-ray diffraction[5–7] and some spectroscopic techniques[8–14] combined with automatic handling, data acquisition and supporting software have been applied to speed up the characterisation of large libraries.

Herein we describe a HT system for characterisation of a library of materials by photoluminescence, which is able to record the emission spectra and to analyse the photoluminescence kinetics. This characterisation system can be applied to a wide range of functional materials, such as those that contain aromatic and other organic compounds, metallic complexes, transition-metal ions and some inorganic oxides and chalcogenides.

An advantage of photoluminescence compared to other spectroscopic techniques is that the samples do not need to be in solution because the emission spectra of opaque powders can also be recorded. Another characteristic of the photoluminescence technique described here is its high sensitivity, in which only very small amounts of sample (less than 20 mg) and very short analysis times (less than 2 s for a single wavelength) are required. In addition, this technique permits different types of information, derived from the study of the spectral and temporal profiles of the emission, to be obtained.

The overall photoluminescence intensity under a given condition is related to the concentration of the lumophore and, consequently, photoluminescence measurements can be used to determine the presence and loading of the emitting species. In addition, photoluminescence through time-resolved measurements is particularly suited to reveal the interaction of the lumophore with the environment or with other molecules. This fact can be of special relevance in host–guest supramolecular systems and in catalysis.

There has been considerable interest in the encapsulation of conducting organic polymers inside porous aluminosilicate matrices to stabilise these highly degradable and labile conducting polymers.[15,16] The preparation of polyaniline, polyacetylenes, polyfuran and other conjugate polymers encapsulated within zeolites and mesoporous matrices has been reported.[17,18] However, as far as is known, the synthesis of poly(*p*-phenylenevinylene) (PPV) oligomers encapsulated within zeolites has never been attempted. In the first part of the present work, the high-throughput system will be described and evaluated by screening a 96-well sample library of the $[Ru(bpy)_3]^{2+}$ encapsulated in different zeolites. In the second part, the potential of the HT technique will be shown through the accelerated optimisation of the synthesis of two host-guest materials with photoluminescent

---

[a] P. Atienzar, Prof. A. Corma, Prof. H. García, Dr. J. M. Serra
Instituto de Tecnología Química CSIC-UPV
Universidad Politécnica de Valencia
Avda. de los Naranjos s/n, 46022-Valencia (Spain)
Fax: (+34) 963-877-809
E-mail: acorma@itq.upv.es

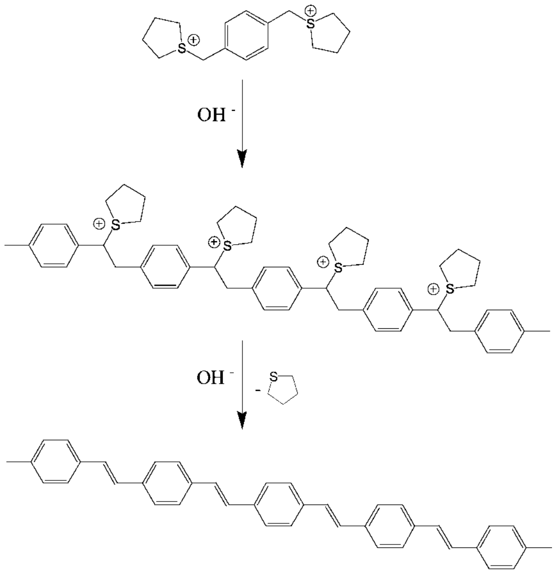
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200400471

properties, which can find application as active components in electroluminescent devices or as photocatalysts.

Results and Discussion

Two different libraries aimed at the optimisation of the synthetic preparation of two guests incorporated within zeolite hosts are shown here. The first one was the oligomerisation of 1,4-phenylenemethylene bis-S,S′-(tetrahydrothiophen-1-ium) to form phenylenevinylene oligomers (PPV) according to the process described in Scheme 1. Herein, we wanted to proceed to the in situ synthesis of this polymer by mimicking the solution synthetic route, in which, starting from a bis(tetrahydrothiophenium)phenylenedimethylene, a condensation is performed under strong basic conditions. Photoluminescence measurements are especially suited to characterise PPV samples because the main potential application of this conjugate polymer is as an active component in electroluminescent devices. The main experimental parameters to be controlled during the ship-in-a-bottle synthesis are the strength and population of basic sites, the oligomerisation temperature, monomer loading and the zeolite matrix.



Scheme 1. Oligomerisation of 1,4-phenylenemethylene bis-S,S′-(tetrahydrothiophen-1-ium) to form phenylenevinylene oligomers (PPV).

To demonstrate that PPV can be obtained inside the zeolite pores, as well as to optimise the preparation conditions, a library was prepared based on a factorial design ($2\times3^2\times5$) of the synthesis. The experimental design considers the following preparation factors (level): synthesis temperature (3), ranging from 200 to 300 °C; zeolite structure (3), including three large-pore zeolites (X, Y and Beta); nature of the alkali-metal ion (5) exchanged in the zeolite (H^+, Li^+, Na^+, K^+ and Cs^+); and two different monomer loadings (2), at 4 and 6 wt %. The total number of PPV@zeolite samples synthesised and tested by using this factorial design was 90. A summary of the relative emission intensity obtained by HT photoluminescence screening is shown in Figure 1. Figure 2 shows the surface plots of the emission profiles, in which the global maximum occurs, obtained for a selected building block of the experimental design (250 °C, 6 wt %). It must be noted that self-quenching excimer emission and other photophysical processes can occur at high guest loadings and this can cause a decrease in the overall photoluminescence intensity.[19] However, as the desired outcome of PPV is blue-green emission, our HT photoluminescence technique is still useful to determine the optimum loading. The time required to complete the test of 90 samples was 5 h. As can be seen from Figures 1 and 2, this test shows that the most photoluminescent samples are those in which the highest loading of the monomer was adsorbed in KY, CsY and KX, when the oligomerisation was conducted at 250 °C. In addition to the characteristic PPV photoluminescence, evidence for the formation of PPV inside the channels of KY and KX zeolites was obtained by optical and MAS ^{13}C NMR spectroscopy. Particularly important was the data recorded for a sample prepared independently under the optimum conditions found here. Using MAS ^{13}C NMR spectroscopy to study this sample, we observed sp^2 carbon atoms of the monomer at around 120 ppm, whereas there was a complete absence of sp^3 carbon atoms for those PPV samples that showed the most intense photoluminescence (see Supporting Information). These spectral features indicate the disappearance of the starting material and its transformation into PPV, a process that is accompanied by a strong increase of the photoluminescence.

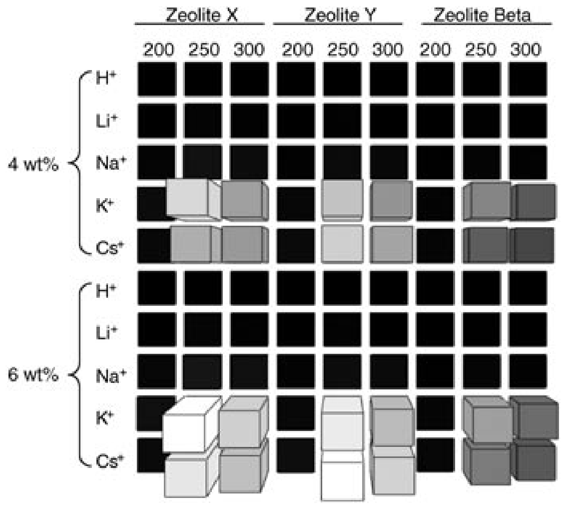


Figure 1. Photoluminescence characterisation results of the PPV@zeolite library. The $2\times3^2\times5$ factorial design shows the influence of synthesis variables on emission performance (time range: 1.2 μs, wavelength: 480–800 nm). The upper block contains 4 wt % monomer content, and the lower block contains 6 wt %. Three temperature values are given: 200, 250 and 300 °C.

The synthesis temperature and the nature of the alkali-metal ion present in the zeolite were identified as the most important experimental parameters to be controlled in the synthesis of PPV@zeolite. The influence of the alkali-metal ion on the formation of PPV can be rationalised by consid-

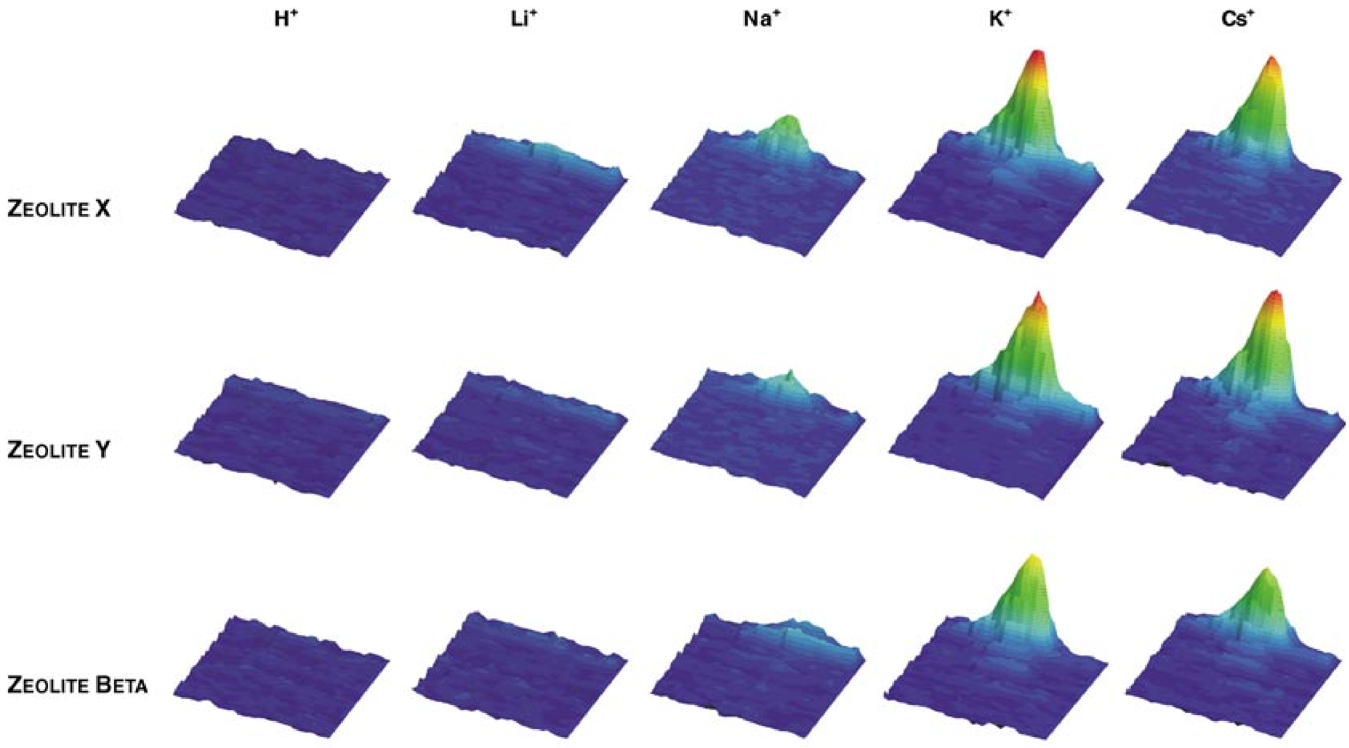


Figure 2. Photoluminescence spectra recorded for the factorial design block of PPV@zeolites in which the maximum emission intensity was achieved (synthesis temperature = 250 °C, monomer loading = 6 wt %).

ering that the charge density of the alkali-metal ion influences the basicity of the framework oxygen atoms. In this regard, it is known that the basicity of the zeolites decreases in the order $Cs^+ > K^+ > Na^+ > Li^+ > H^+$, and zeolites X are more basic than zeolites Y. Therefore, the finding that PPV is formed in the strongest alkali metal ion exchanged zeolites is in agreement with the need for strong bases in the synthesis.

The second electroluminescent system studied by means of HT luminescence characterisation was the 2,4,6-triphenylpyrylium (TP^+) incorporated within large-pore zeolite hosts. This study allowed the optimisation of the synthesis conditions for the encapsulation of 2,4,6-triphenylpyrylium inside zeolites. TP^+ is one of the most widely used electron-transfer photosensitisers; this is because of its high oxidation potential in the excited state allowing it to abstract one elec-

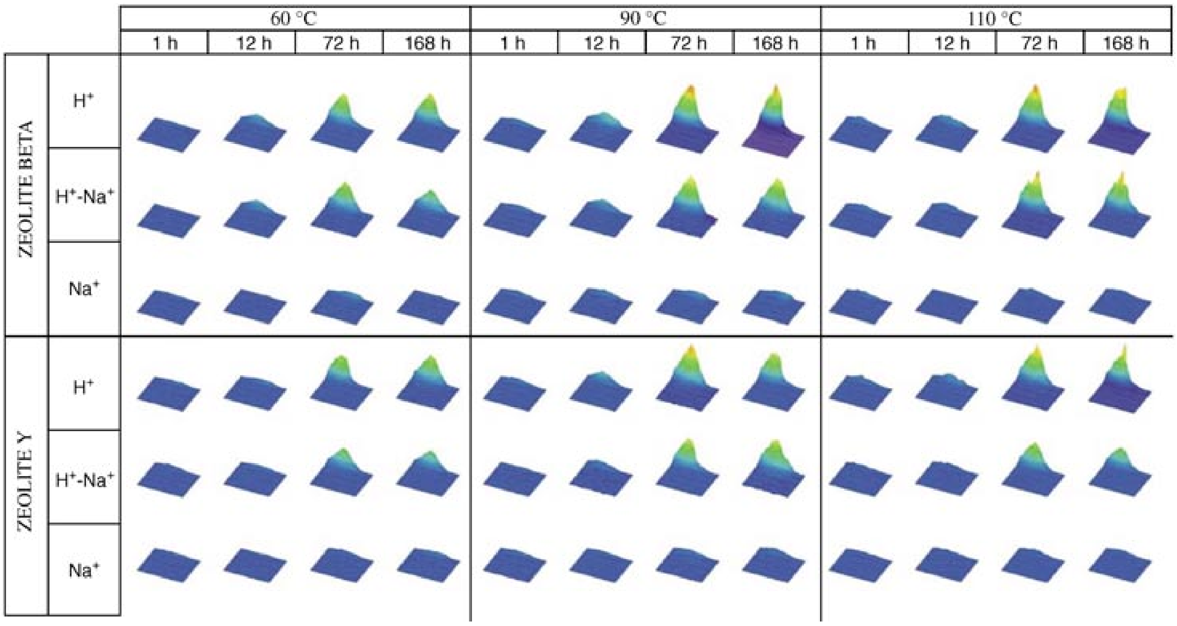


Figure 3. Photoluminescence characterisation results of the TP@zeolite library. The $2 \times 3^2 \times 4$ factorial design shows the influence of synthesis variables on emission performance (time range: 1.2 μs, wavelength: 480–800 nm).

tron from a large number of organic molecules, generating the corresponding radical cation. Although this cation is not stable in water, in which it undergoes a hydrolytic ring opening to 1,3,5-triphenyl-2-penten-1,5-dione, when encapsulated inside zeolites it becomes indefinitely stable due to the spatial constraints imposed by the rigid zeolite framework on hydrolysis. TP@zeolite has been used as an organic photocatalyst for the degradation of pesticides in water by solar light.[20,21] Preparation of TP@zeolite samples under the optimum conditions is crucial to produce samples with the highest photocatalytic activity. The TP@zeolite library was prepared according to a factorial design ($2\times3^2\times4$) for the study and optimisation of the aldol condensation of chalcone with acetophenone. In this case, the following factors (level) were considered for the factorial design: reaction time (4), between 1 h and seven days; reaction temperature (3), between 60 and 110 °C; zeolite acidity (3); and zeolite structure (2). The two last parameters include zeolites Y and Beta in their neutral Na^+ form, as well as H^+-exchanged zeolites at a determined percentage of Na^+-to-H^+ ion exchange. In addition, the library contained some blanks, and the reliability of the system was checked by repeating the same sample in different positions of the sample holder. A description of the TP library and the photoluminescence spectra obtained for each material is shown in Figure 3.

As expected, in view of the previous photoluminescence measurements, the emission from TP^+ encapsulated in zeolites contains a combination of fluorescence ($\lambda_{fl} = 470$ nm; $\tau_{1/2} < 25$ ns) together with phosphorescence ($\lambda_{ph} = 560$ nm; $\tau_{1/2} \gg 800$ ns) in variable proportions. In this work we have considered the total emission intensity as a measurement of the TP^+ content. According to the experimental results of this technique, the optimum synthesis conditions are those using zeolite Y or Beta in their H^+ form, prepared at 110 °C for two or three days. This outcome of the HT technique was used to prepare a batch under the optimum conditions, with the resulting sample showing the spectral features characteristic of TP^+. This sample, having a high TP^+, was tested as a photocatalyst and showed high activity for the degradation of phenol and aniline (see Supporting Information). Controls using a pristine zeolite in the absence of TP^+ did not show significant photocatalytic activity under identical irradiation conditions, as compared to the optimised TP@zeolite.

Conclusions

A new high-throughput characterisation technique for solid materials based on photoluminescence has been described and validated. This novel technique allows the measurement of fluorescence and phosphorescence emission in the range of 350–800 nm; the temporal profile of the emission process (luminescence decay) can also be determined in the microsecond range. As a demonstration of the potential of this technique, two electroluminescence systems based on PPV@zeolite and TP@zeolite have been optimised, and the results have been rationalised. This technique can, therefore, be used as an evaluation assay for optimisation of the preparation conditions of emitting compounds. The high-throughput luminescence characterisation described here can also be applied to other materials, such as catalysts and sensor/probe molecules.

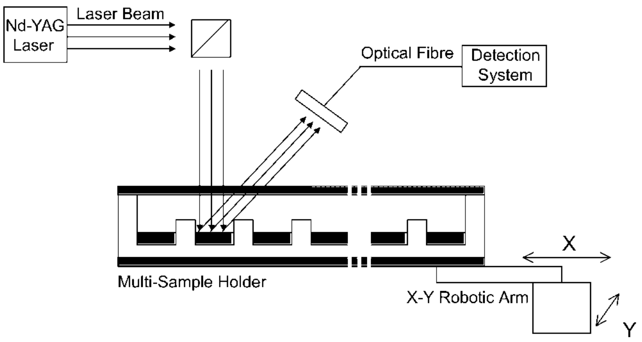


Figure 4. Schematic diagram of the high-throughput assembly for photoluminescence characterisation.[12]

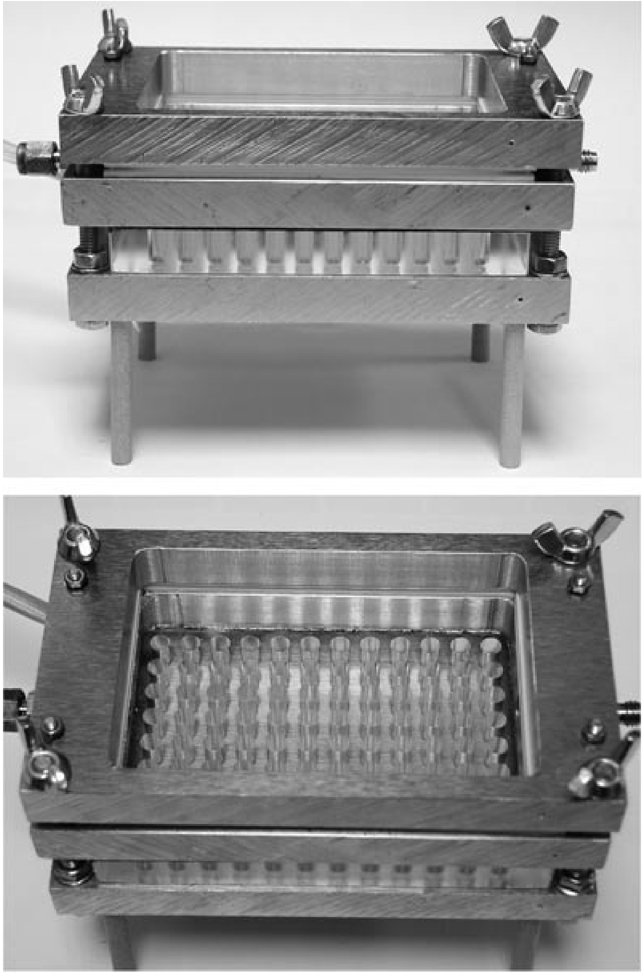


Figure 5. Detailed images of the 96-sample holder.

Experimental Section

The HT photoluminescence assembly[12] consists of: 1) a pulsed Nd-YAG laser (7 ns pulse width, 1–5 mJ $pulse^{-1}$), which can operate at wavelengths of 266, 355 or 532 nm; 2) a 96-sample holder made of a material transpar-

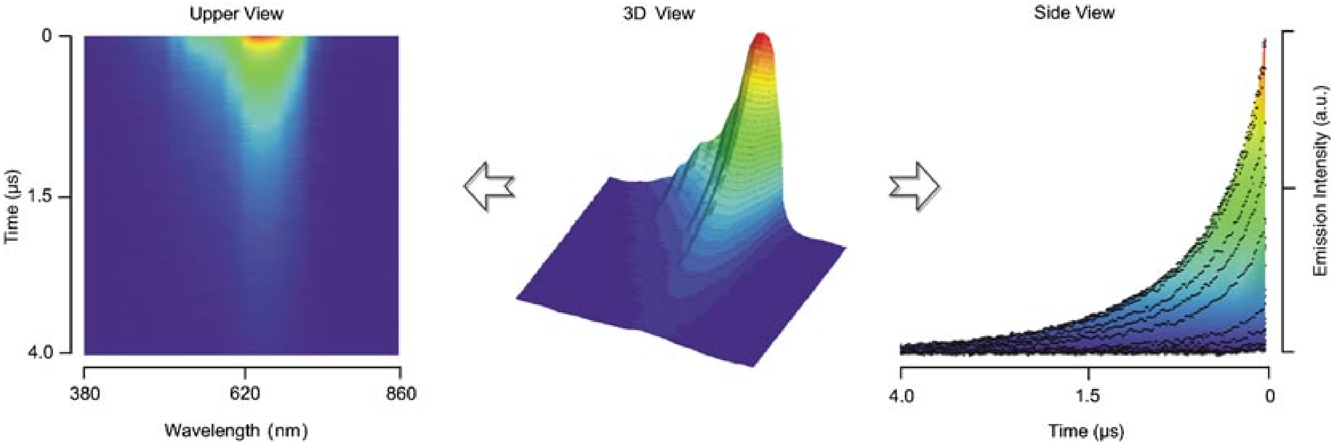


Figure 6. Representation of the three-dimensional data acquired by HT-photoluminescence for a single sample, $[Ru(bpy)_3]^{2+}$@beta (time range: 4 µs, wavelength: 380–860 nm).

ent to the laser beam; 3) an X-Y linear robotic system with a repeatability of ±10 µm, which controls the positioning of the library holder; 4) an optical fibre to transfer the photoluminescence from the emitting sample to the detector; and 5) the detection module containing a monochromator, a photomultiplier and an oscilloscope to digitalise the signal that is finally transferred to a computer. The system also contains the appropriate set of prisms, lens, mirrors and filters. The system is fully automated and controlled by a PC. Data management and analysis is carried out using in-house developed software. A schematic diagram of the HT assembly and its working principle is provided in Figure 4.

The sample-holder geometry is similar to the 96-well microtiter plate currently used in biochemistry. Therefore, this holder can be handled by commercial robotic liquid/solid handling systems for its automated loading, or even the library preparation can be carried out in the same holder. The amount of solid required for the characterisation is 10 to 20 mg, and samples are deposited as a powder without any pre-treatment. For the examples illustrated below, the holder used was made of polymethacrylate or glass (Pyrex), but quartz may be necessary when using a 266-nm laser as the excitation source. The sample holder is covered with an optical-quartz lid to isolate the samples from the ambient and, when required, it is possible to expose the samples to a controlled atmosphere or mild vacuum. In addition, the glass or quartz holder can be heated, allowing thermal pre-treatments such as drying or calcinations to be carried out. Thus, the system enables the performance of *operando* photoluminescence spectroscopy during adsorption or catalytic processes with different probe molecules. Figure 5 gives a detailed image of the 96-well sample holder. For convenient operation and loading or unloading, the sample holder can be easily removed from the zone exposed to the laser beam. The holder is placed horizontally and excitation and emission detection is carried out from the top of the holder. Problems arising from laser scattering reaching the detector are minimised by the geometry of the system focusing the optical fibre out of the laser reflection angle and by placing a cut-off filter on the optical fibre. (The details of the operation of the system, its validation and control software are given in the Supporting Information.)

Figure 6 shows different representations of the three-dimensional data acquired for a single sample of $[Ru(bpy)_3]^{2+}$@zeolite ITQ-2, used in the validation of the system, to provide a fast visualisation of emission spectra and the photoluminescence kinetics of each sample.

Acknowledgements

The authors are thankful for the financial support of MAT 2003–07945-C02–01.

[1] B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111* 2648–2689; *Angew. Chem. Int. Ed.* **1999**, *38*, 2494–2532.
[2] X. D. Xiang, X. D. Sun, G. Briceño, Y. L. Lou, K. A. Wang, H. Y. Chang, W. G. Wallacefreedman, S. W. Chen, P. G. Schultz, *Science* **1995**, *268* 1738–1740.
[3] A. Corma, J. M. Serra, E. Argente, S. Valero, V. Botti, *ChemPhysChem* **2002**, *3*, 939–945.
[4] H. Wang, Z. Liu, J. Shen, H. Liu, *Catal. Commun.* **2004**, *5*, 55–58.
[5] J. Holmgren, D. Bem, M. Bricker, R. Gillespie, G. Lewis, D. Akporiaye, I. Dahl, A. Karlsson, M. Plasser, R. Wendelbo, *Stud. Surf. Sci. Catal.* **2001**, *135*, 461–470.
[6] V. W. Rosso, G. Young, J. Nolfo, I. M. Vitez, J. J. Venit, WO2003/087796, **2003**.
[7] H. Lieberman, *Am. Pharm. Rev.* **2003**, *6*, 74.
[8] A. Tuchbreiter, J. Marquardt, J. Zimmermann, P. Walter, R. Muelhaupt, B. Kappler, D. Faller, T. Rohts, J. Honnerkaup, *J. Comb. Chem.* **2001**, *3*, 598–603.
[9] J. Hochlowski, D. Whittern, J. Pan, R. Swenson, *Drugs Future* **1999**, *24*, 539–554.
[10] T. Makino, C. H. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, Y. Matsumoto, H. Koinuma, *Appl. Surf. Sci.* **2002**, *189*, 277–283.
[11] A. Corma, J. M. Serra, *WO Patent* App. N° ES03/00365, **2003**.
[12] A. Corma, H. García, J. M. Serra, *ES Patent* App. N° P200301935, **2003**.
[13] A. Holzwarth, P. Denton, H. Zanthoff, C. Mirodatos, *Catal. Today* **2001**, *67*, 309–318.
[14] C. Kiener, M. Kurtz, H. Wilmer, C. Hoffmann, H.-W. Schmidt, J.-D. Grunwaldt, M. Muhler, F. Schuth, *J. Catal.* **2003**, *216*, 110–119.
[15] M. Murasko, P. Kinlen, B. St. John, (Lumimove Inc.) WO2002/087308, **2002**.
[16] P. Enzel, T. Bein, *NATO ASI Ser., Ser. B* **1990**, *248*, 421–426.
[17] T. Bein, P. Enzel, *Synth. Met.* **1989**, *29(1)*, E163–E168.
[18] M. Alvaro, B. Ferrer, H. García, A. Lay, F. Trinidad, J. Valenciano, *Chem. Phys. Lett.* **2002**, *356*, 577–584.
[19] P. L. Burn, D. D. C. Bradley, R. H. Friend, D. A. Halliday, A. B. Holmes, R. W. Jackson, A. Kraft, *J. Chem. Soc. Perkin Trans. 1* **1992**, 3225–3232.
[20] A. Sanjuan, G. Aguirre, M. Alvaro, H. García, *Water Res.* **1999**, *34*, 320–326.
[21] A. Sanjuan, G. Aguirre, M. Alvaro, H. García, *Appl. Catal. B* **1998**, *15*, 247–257.

Received: May 13, 2004