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Organic–Inorganic Composites as Photonic Antenna

Gion Calzaferri*

Abstract: A photonic antenna system is an organized multi-component arrangement in which several chromophoric molecular species absorb the incident light and channel the excitation energy to a common acceptor component. Photonic antenna materials, based on dye–zeolite L composites, collect excitation energy and transport it over large distances. Fine tuning of dye-loaded zeolite L photonic antenna materials in the size range of 30–3000 nm was realized. Stationary and time-resolved luminescence experiments on an ensemble and space and time resolved luminescence measurements on single crystal antenna materials have been carried out. Coupling of the photonic antenna information to an external device is in progress.

Keywords: Energy migration · Energy transfer · Light harvesting · Supramolecular · Zeolite L

Microporous structures containing atoms, clusters, molecules or complexes provide a source of new materials with exciting properties [1–6]. Zeolites are especially appealing crystalline inorganic microporous materials. Some of them occur in nature as a component of the soil. Natural and synthetic zeolites possess a large variety of well-defined internal structures such as uniform cages, cavities or channels [7–10]. A useful feature of zeolites is their ability to host molecular guests [3] and quantum-sized particles [11] within the intravoid space. Chromophore-loaded zeolites have been investigated for different purposes such as interfacial electron transfer, microlasers, second harmonic generation, frequency doubling and optical bistabilities giving rise to persistent spectral hole burning [12–21]. The role of the zeolite framework is to act as a host for realizing the desired geometrical properties and for stabilizing the incorporated molecules. Incorporation of chromophores into the cavities of zeolites can be achieved in different ways, depending on the substances used and on the desired properties: from the gas phase [22–24], by ion exchange if cations are involved [3][25–28] by crystallization inclusion [29] or by performing an *in situ* synthesis inside the zeolite cages[11][30][31].

Plants are masters of the efficient transformation of sunlight into chemical energy. In this process, every plant leaf acts as a light-harvesting device, in which photonic energy is absorbed in the form of sunlight and transported by chlorophyll molecules for the purpose of energy transformation. The light is absorbed by an arrangement consisting of a few hundred chlorophyll molecules in a protein environment. This photonic antenna allows fast energy transfer from an electronically excited molecule to unexcited neighbor molecules in such a way that the excitation energy reaches the reaction center with high probability. Trapping occurs there [32–34]. In this natural device the formation of aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages. A similar approach is possible by enclosing dyes inside a microporous material and by choosing conditions such that the volume of the cages and channels is able to uptake only monomers but not aggregates.

An artificial photonic antenna system is an organized multi-component arrangement in which several chromophoric molecular species absorb the incident light and transport the excitation energy to a common acceptor component. Imaginative attempts to build an artificial antenna different from ours have been presented in the literature [35]. Multinuclear luminescent metal complexes [36–38], multichromophore cyclodextrins [39], Langmuir Blodgett films [40–43], dyes in polymer matrices [44–46], and dendrimers [47] have been investigated. Some sensitization processes in silver halide photographic materials [48] and also the spectral sensitization of polycrystalline titanium dioxide films bear, in some cases, aspects of artificial antenna systems [49–51]. The systems developed by us so far are of bi-directional type, based on zeolite L as a host material, and able to collect and transport excitation over relatively large distances [3][22][26–28][52–55] Light transport is made possible by specifically organized dye molecules which mimic the natural function of chlorophyll. The zeolite L crystal structure consists of a continuous one-dimensional tube system. We have filled each individual tube with successive chains of different joint but non-interacting dye molecules. Light shining on the cylinder is first absorbed and the electronic excitation energy is then transported by the dye molecules inside the tubes to the cylinder ends.

Correspondence: Prof. Dr. G. Calzaferri
Department of Chemistry and Biochemistry
University of Bern
Freiestrasse 3
CH–3012 Bern
Tel.: +41 31 631 4236
Fax: +41 31 631 3994
E-Mail: Gion.Calzaferri@iac.unibe.ch
http://dcbwww.unibe.ch/groups/calzaferri

A schematic view of the photonic antenna is illustrated in Fig. 1. The monomeric dye molecules are represented by colored rectangles. The dye molecule, which has been excited by absorbing an incident photon, transfers its electronic excitation energy to another one. After a series of such steps the electronic excitation energy reaches a trap, pictured as red rectangles. The energy migration is in competition with spontaneous emission, radiationless decay and photochemically induced degradation. Very fast energy migration is therefore crucial if a trap should be reached before other processes can take place. These conditions impose not only spectroscopic but also decisive geometrical constraints on the material.

Favorable conditions for realizing a photonic antenna are a high concentration of monomeric dye molecules with high luminescence quantum yield, ideal geometrical arrangement of the chromophores and an optimal size of the device. Dyes at high concentration have the tendency to form aggregates which in general show very fast radiationless decay [56][57]. The formation of aggregates can be prevented by fencing dyes inside a microporous material and by choosing conditions such that the volume of the cages and channels is only able to uptake monomers but not aggregates. Linear channels running through crystals allow the formation of highly anisotropic dye assemblies. Our investigations have been concentrated on zeolite L as a host. The reason for this is that neutral dyes as well as cationic dyes can be inserted into the channels of zeolite L and that synthesis procedures for controlling the morphology of zeolite L crystals in the size regime from 30 nm to about 3000 nm are available [53][58–60]. Many results obtained on zeolite L are valid for other nanoporous materials as well. In Fig. 2 we show a scanning electron microscopy picture of a zeolite L material with nice morphology. The hexagonal shape of the crystals can easily be recognized. For simplicity we describe them as crystals of cylinder morphology. A space-filling top view and a side view of the zeolite L framework is illustrated in Fig. 3. The primitive vector ***c*** corresponds to the channel axis while the primitive vectors ***a*** and ***b*** are perpendicular to it, enclosing an angle of 60°.

We distinguish between three types of dye molecules.

i) *Molecules small enough to fit into a single unit cell.* Some examples are biphenyl, hydroxy-TEMPO, fluorenone and methylviologen (MV^{2+}). Structural

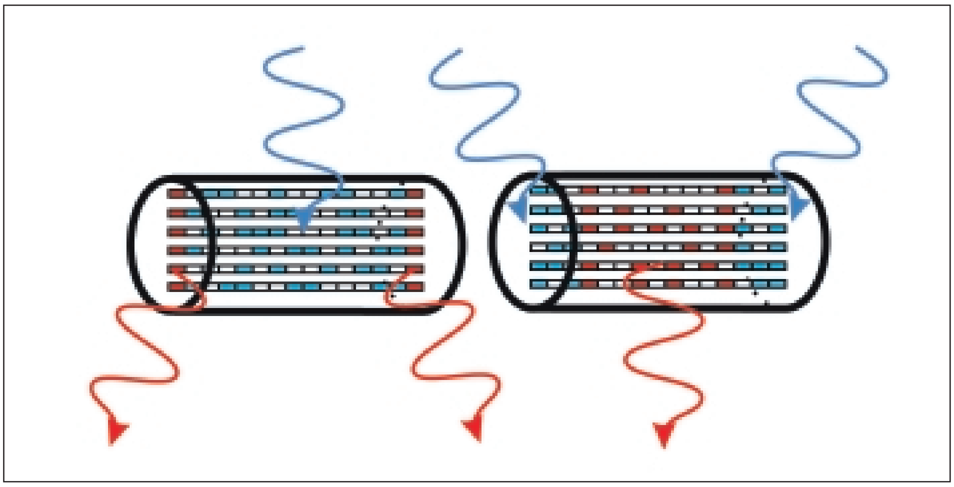


Fig. 1. Representation of a cylindrical nanocrystal consisting of organized dye molecules acting as donors (blue) and acceptors (red) acting as trap. Left: The donors are in the middle part of the crystal and the acceptors at the front and the back of each channel. Right: The donors are at the front and the back of each channel and the acceptors are in the middle part.

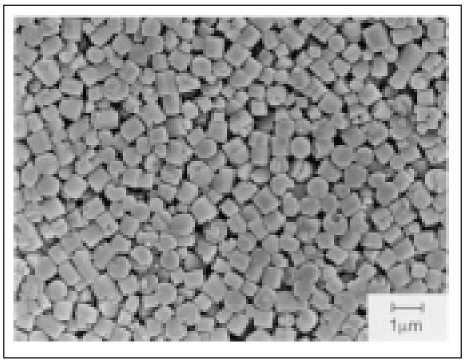


Fig. 2. SEM picture of a zeolite L sample.

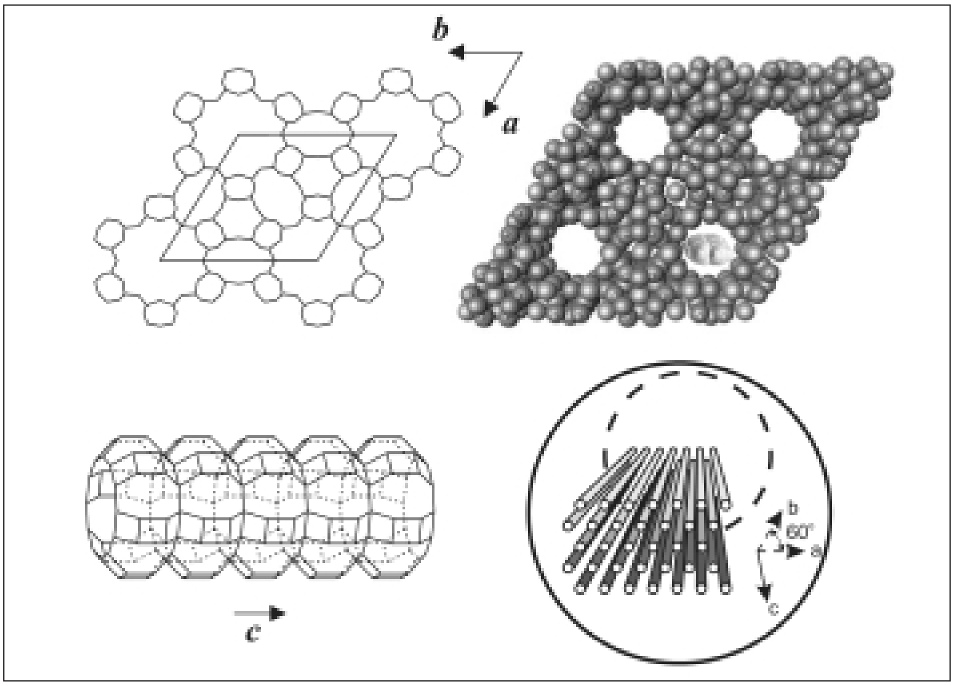


Fig. 3. Framework of zeolite L. Upper*:* top view, perpendicular to the ***c***-axis, displayed as stick- (left) and as Van der Waals- (right) representation with a dye molecule entering the zeolite channel. Lower*:* Side view of a channel along the ***c***-axis, without bridging oxygen atoms (left). Schematic view of some channels in a hexagonal zeolite crystal with cylinder morphology.

details of the latter are known based on vibrational spectroscopy, Rietveld refinement of X-ray data and molecular modeling [25].

ii) *Molecules with a size which makes it hard to guess if they align along the* ***c****-axis or if they find a way to fit into a single unit cell.* Oxonine, pyronine, and thionine are molecules of this type [54].

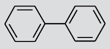
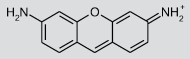
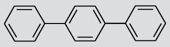
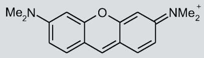
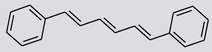
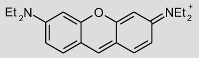
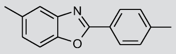
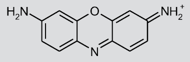
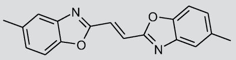
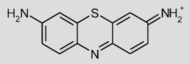
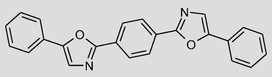
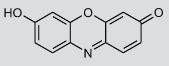
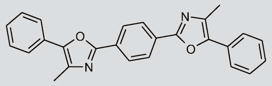
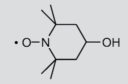
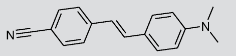
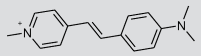
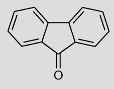
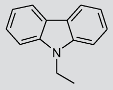
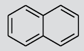
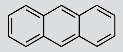
iii) *Molecules which are so large that they have no other choice but to align along the* ***c****-axis.* Many examples fit into this category. It is important to know if molecules can occupy at least part of the same unit cell, so that they can interact *via* their π-system or if they can 'only touch each other' so that their electronic coupling is negligible.

While for molecules of type (i) not only translational but also large amplitude modes can be activated, the latter are severely or even fully restricted for molecules of type (ii) and (iii). This has consequences on their stability and also on their luminescence quantum yield which in general increases. An example we have investigated is the very light-sensitive DPH which is dramatically stabilized when inserted into zeolite L [22]. In other cases a dramatic increase of stability is observed because reactive molecules which are too large or anions such as hypochlorite have no access because they cannot enter the negatively charged channels [3]. Representative dyes that we have inserted in zeolite L are listed in the Table. Many of them lead to strongly luminescent materials. Some exceptions are fluorenone, MV^{2+}, ResH, and hydroxy-TEMPO.

We now show an experiment which illustrates the photonic antenna principle of Fig. 1; see [53]. Py$^+$ and Ox$^+$ were found to be very convenient dyes for this purpose. The channels of zeolite L are first loaded with Py$^+$ and then modified at both sides with Ox$^+$. The latter acts as a luminescent trap which gets excited *via* radiationless energy transfer from an excited Py$^+$. If radiationless relaxation is not considered, Ox$^+$ can lose its energy only by fluorescence, as it cannot transfer it back to Py$^+$ because of its lower excitation energy. Fluorescence of excited Py$^+$, internal conversion, and intersystem crossing compete with the energy migration and energy transfer.

We expect that the trapping efficiency decreases with increasing crystal length for otherwise constant parameters, specifically constant Py$^+$ loading, because the excitation energy has to migrate over an increasingly large distance to reach a trap. This can be tested if materials with different average crystal lengths are available. Since we have been able to prepare these materials, experiments with crystals of the following average length were carried out: **1**, 300 nm; **2**, 500 nm; **3**, 850 nm; **4**, 1400 nm; and **5**, 2400 nm. These crystals where loaded with Py$^+$ so that the occupation probability

Table. Dye molecules and abbreviations.

BP			Py$^+$
*p*TP			PyGY$^+$
DPH			PyB$^+$
PBOX			Ox$^+$
MBOXE			Th$^+$
POPOP			ResH
DMPOPOP			Hydroxy-TEMPO
DSC			DMSI$^+$
Fluorenone			N-Ethylcarbazole
Naphtalene			Anthracene

was always the same, namely 0.11. They were then modified with two Ox^+ molecules on average at both ends of the channels. The fluorescence of a thin layer on quartz was measured at room temperature after specific excitation of Py^+ at 460 nm. The fluorescence reported in Fig. 4 is scaled to the same height at the Py^+ emission maximum, as before. It shows a very strong increase of the Ox^+ emission with decreasing crystal length. One can calculate that the front–back trapping efficiency increases from 0.33 up to 0.91. This means that in the 300 nm crystals, 90% of the emitted light is due to energy migration along the Py^+ and transfer to the luminescent traps Ox^+. Interestingly, in these experiments carried out at constant Py^+ loading, there is also a small shift of the Py^+ maximum, from 525 nm for the smallest crystals to 530 nm for the largest ones. The maximum of the Ox^+ emission remains at 605 nm. This wavelength shift is most probably due to self-absorption and re-emission because the absorption depth increases with increasing crystal size despite of the constant Py^+ loading [53]. The measurements were made on thin dye-loaded zeolite L layers on quartz plates. The pronounced increasing trapping efficiency with decreasing length of the zeolite L underlines the interpretation that the antenna behavior is mainly governed by radiationless energy migration [61–65], supported by some self-absorption and re-emission. The latter causes a shift in the maximum of the Py^+ fluorescence spectrum with increasing loading, but also with increasing crystal size at constant loading [3]. Some internal reflection also occurs, especially in the larger crystals [65].

We conclude that zeolite L is a very suitable framework for organizing a wide variety of chromophores. Its structure is such that the formation of non-fluorescent dimers inside the channels can be prohibited and chromophores can be aligned in a certain direction. We have shown that this host/guest system can be used to make very efficient nanoscale bidirectional photonic antenna materials. A broad spectral absorption range can be achieved by using several different cationic and neutral dyes. We were interested in reversing the scheme in Fig. 1 (left) and to have an acceptor dye in the center, and the donors at both ends, Fig. 1 (right), because such systems could be useful for analytical purposes or to develop a new generation of LEDs. It turned out that it is indeed possible to prepare such materials and to perform stationary energy migration experiments on an ensemble and space and time resolved measurements on single crystals [63–65]. It is a challenge to couple the antenna material to a device, *e.g.* a semiconductor. Preparation of organized zeolite monolayers on flat surfaces has been reported [66][67]. The interface between the chromophore-loaded zeolite and the semiconductor becomes very important for the coupling purpose. We expect that 'stopcock molecules' could function as a bridge between the chromophores in the zeolite L channels and the device surface (Fig. 5) [65]. This opens a whole new exciting research area.

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[1] R.F. Cracknell, K.E. Gubbins, M. Maddox, D. Nicholson, *Acc. Chem. Res.* **1995**, *28*, 281.

[2] J.M. Thomas, *Angew. Chem.* **1999**, *111*, 3800.

[3] G. Calzaferri, D. Brühwiler, S. Megelski, M. Pfenniger, M. Pauchard, B. Hennessy, H. Maas, A. Devaux, U. Graf, *Solid State Sciences* **2000**, *2*, 421; G. Calzaferri, *Chimia* **1998**, *52*, 525.

[4] J.P. Langley, J. Hulliger *Chem. Soc. Revs.* **1999**, *28*, 279.

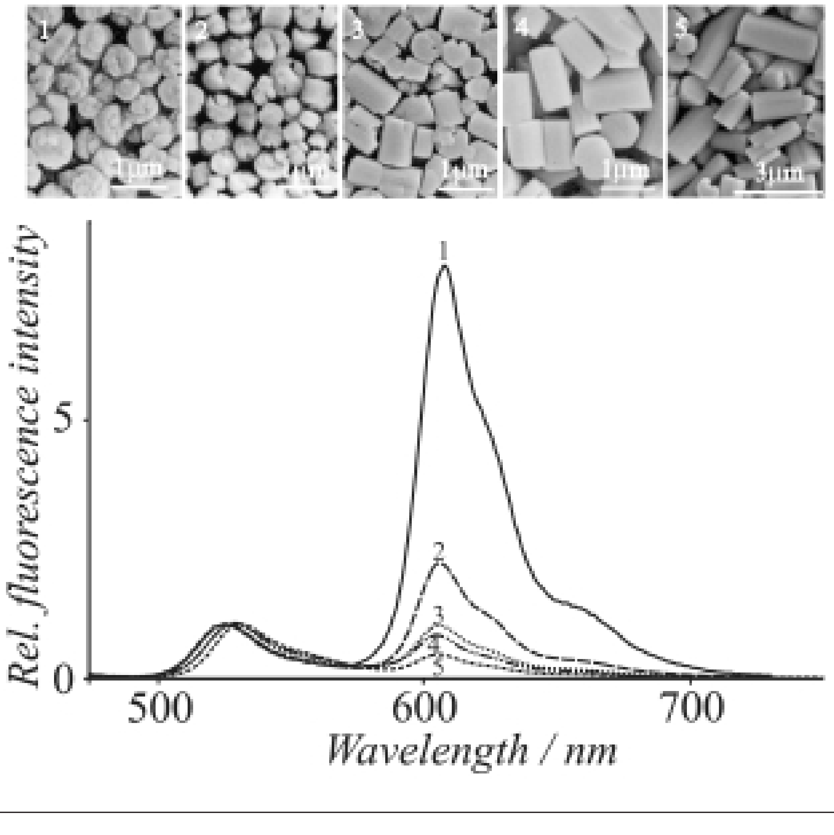

Fig. 4. Upper: SEM pictures of the investigated zeolite L samples with different crystal length: **1**, 300 nm; **2**, 500 nm; **3**, 850 nm; **4**, 1400 nm; **5**, 2400 nm. Lower: Fluorescence intensity, after specific excitation of only Py^+ at 460 nm (scaled to the same height at the maximum of the Py^+ emission) of Py^+ loaded and Ox^+ modified zeolite L crystals with constant Py^+ loading, for different crystal lengths. The Ox^+ modification was two molecules at both ends of the channel, on average.

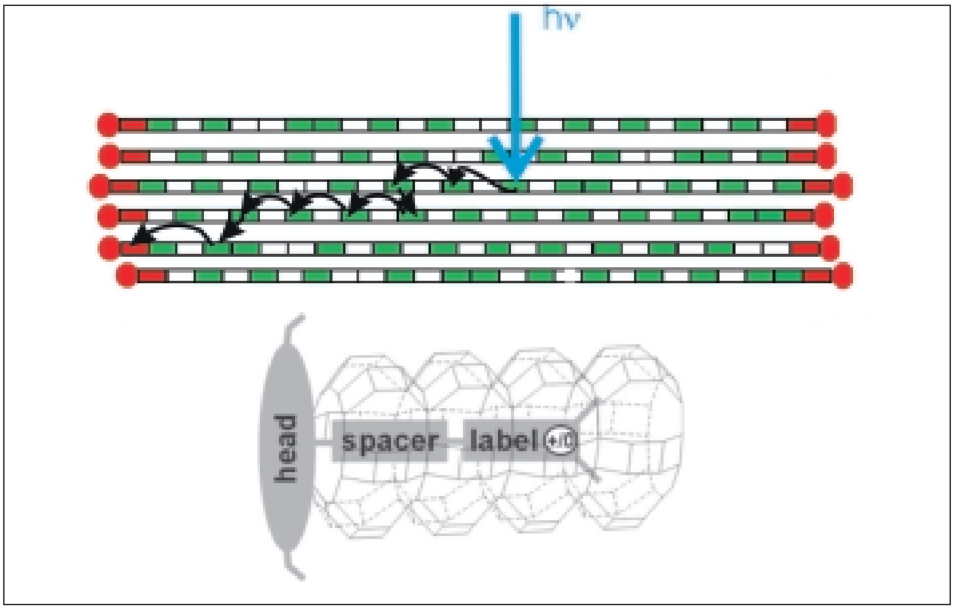

Fig. 5. Principle of the stopcock approach. Some channels of a zeolite filled with dye molecules (green rectangles) which are closed with a stopcock molecule, consisting of a head, a spacer, and a label.

[5] A. Douhal, T. Fiebig, M. Chachisvilis, AH. Zewail, *J. Phys. Chem. A* **1998**, *102*, 1657.

[6] Y.S. Park, S.Y. Um, K.B. Yoon, *J. Am. Chem. Soc.* **1999**, *121*, 3193.

[7] D.W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons, New York, **1974**.

[8] W.M. Meier, D.H. Olson, C. Baerlocher, 'Atlas of Zeolite Structure Types', Elsevier, London, **1996**.

[9] S.L. Suib, *Chem. Rev.* **1993**, *93*, 803.

[10] F. Schüth, *Chemie in unserer Zeit* **1995**, *29*, 42.

[11] G. Calzaferri, D. Brühwiler, S. Glaus, D. Schürch, A. Currao, C. Leiggener, *J. Imaging Sci. Technol.* **2001**, *45*, 331.

[12] G. Calzaferri, M. Lanz, J. Li, *J. Chem. Soc., Chem. Commun.* **1995**, 1313.

[13] K.B. Yoon, Y.S. Park, J.K. Kochi, *J. Am. Chem. Soc.* **1996**, *118*, 12710.

[14] U. Vietze, O. Krauss, F. Laeri, G. Ihlein, F. Schüth, B. Limburg, M. Abraham, *Phys. Rev. Lett.* **1998**, *81*, 4628.

[15] S.D. Cox, T.E. Gier, G.D. Stucky, J. Bierlein, *J. Am. Chem. Soc.* **1988**, *110***,** 2986.

[16] G. Schulz-Ekloff, in 'Advanced Zeolite Science and Applications, Studies in Surface Science and Catalysis', Eds. J.C. Jansen, M. Stöcker, H.G. Karge, J. Weitkamp, Elsevier; Amsterdam, **1994**, Vol. 85, p. 145.

[17] M. Ehrl, F.W. Deeg, C. Bräuchle, O. Franke, A. Sobbi, G. Schulz-Ekloff, D. Wöhrle, *J. Phys. Chem.* **1994**, *98*, 47.

[18] R. Hoppe, G. Schulz-Ekloff, D. Wöhrle, C. Kirschhock, H. Fuess, in 'Zeolites and Related Microporous Materials: State of the Art 1994. Studies in Surface Science and Catalysis', Eds. J. Weitkamp, H.G. Karge, H. Pfeifer, W. Hölderich, Elsevier, Amsterdam, **1994**, Vol. 84, pp. 821.

[19] J. Caro, F. Marlow, M. Wübbenhorst, *Adv. Mater.* **1994**, *6*, 413.

[20] D. Wöhrle, G. Schulz-Ekloff, *Adv. Mater.* **1994**, *6*, 875.

[21] V. Ramamurthy, D.R. Sanderson, D.F. Eaton, *J. Am. Chem. Soc.* **1993**, *115*, 10438.

[22] M. Pauchard, A. Devaux, G. Calzaferri, *Chem. Eur. J.* **2000**, *6*, 3556.

[23] D. Brühwiler, N. Gfeller, G. Calzaferri, *J. Phys. Chem. B* **1998**, *102*, 2923.

[24] B. Müller, G. Calzaferri, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1633.

[25] B. Hennessy, S. Megelski, C. Marcolli, V. Shklover, C. Bärlocher, G. Calzaferri, *J. Phys. Chem. B* **1999**, *103*, 3340.

[26] G. Calzaferri, N. Gfeller, *J. Phys. Chem.* **1992**, *96*, 3428.

[27] F. Binder, G. Calzaferri, N. Gfeller, *Solar Energy Mat. and Sol. Cells* **1995**, *38*, 175.

[28] F. Binder, G. Calzaferri, N. Gfeller, N. *Proc. Ind. Acad. Sci.* **1995**, *107*, 753.

[29] M. Bockstette, D. Wöhrle, I. Braun, G. Schulz-Ekloff, *Microp. Mesop. Mater.* **1998**, *23*, 83.

[30] P. Lainé, M. Lanz, G. Calzaferri, *Inorg. Chem.* **1996**, *35*, 3514.

[31] D. Brühwiler, R. Seifert, G. Calzaferri, *J. Phys. Chem B* **1999**, *103*, 6397.

[32] Z.G. Fetisova, A.M. Freiberg, K.E. Timpmann, *Nature* **1988**, *334*, 633.

[33] X. Hu, K. Schulten, *Phys. Tod.* **1997**, *50*, 28.

[34] W. Kühlbrandt, D.N. Wang, *Nature* **1991**, *350*, 130.

[35] H.R. Kerp, H. Donker, R.B.M. Koehorst, T.J. Schaafsma, E.E. van Faassen, *Chem. Phys. Lett.* **1998**, *298*, 302.

[36] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Sol. Ener. Mat. Sol. Cells* **1995**, *38*, 159.

[37] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Coord. Chem. Rev.* **1994**, *132*, 1.

[38] C.V. Kumar, A. Chaudhary, *Microp. Mesop. Mater.* **1999**, *32*, 75.

[39] L. Jullien, J. Canceill, B. Valeur, E. Bardez, J.-M. Lehn, *Angew. Chem.* **1994**, *106*, 2582.

[40] H. Bücher, K.H. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F.P. Schäfer, J. Sondermann, W. Sperling, P. Tillmann, J. Wiegand, *Mol. Crystals* **1967**, *2*, 199.

[41] F. Willig, in 'Photochemical Conversion and Storage of Solar Energy', Eds. E. Pelizzetti, M. Schiavello, Kluwer Academic Publishers, Dordrecht, **1991**, pp. 235-249.

[42] N. Tamai, T. Yamazaki, I. Yamazaki, *J. Phys. Chem.* **1987**, *91*, 841.

[43] J.A. Pescatore, Jr., I. Yamazaki, *J. Phys. Chem.*, **1996**, *100*, 13333.

[44] B.A. Gregg, U. Resch, *J. Photochem. Photobiol., A: Chem.*, **1995,** *87*, 157.

[45] S.E. Webber, *Chem. Rev.* **1990**, *90*, 1469.

[46] D.M. Watkins, M.A. Fox, *J. Am. Chem. Soc.* **1996**, *118*, 4344.

[47] V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann, M. Maestri, F. Vögtle, *ChemPhysChem* **2000**, *4*, 224.

[48] D.M. Sturmer, D.W. Heseltine, in 'The Theory of the Photographic Process', Ed. T.H. James, Macmillan Publishing Co., New York, **1977**, pp. 194-234.

[49] C.A. Bignozzi, R. Argazzi, J.R. Schoonover, G.J. Meyer, F. Scandola, *Solar Energy Mater. Sol. Cells* **1995**, *38*, 187.

[50] H. Tributsch, 'Proc. IPS-10', Eds. Z.W. Tian, Y. Cao, Intern. Academic Publishers, Beijing, **1993**, pp. 235-247.

[51] R. Memming, H. Tributsch, *J. Phys. Chem.* **1971**, *75*, 562.

[52] N. Gfeller, S. Megelski, G. Calzaferri, *J. Phys. Chem.* B **1999**, *103*, 1250.

[53] S. Megelski, G. Calzaferri, *Adv. Function. Mater.* **2001**, *11*, 277.

[54] S. Megelski, A. Lieb, M. Pauchard, A. Drechsler, S. Glaus, C. Debus, A. J. Meixner, G. Calzaferri, *J. Phys. Chem.* B **2001**, *105*, 25.

[55] N. Gfeller, S. Megelski, G. Calzaferri, *J. Phys. Chem. B* **1998**, ***102***, 2433.

[56] M. Kasha, H.R. Rawls, M. Ashraf El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371.

[57] E.G. McRae, M. Kasha, *J. Chem. Phys.* **1958**, *28*, 721.

[58] M. Tsapatsis, T. Okubo, M. Lovallo, M.E. Davis, *Mat. Res. Soc. Symp. Proc.* **1995**, *371*, 21.

[59] S. Ernst, J. Weitkamp, *Catal. Today* **1994**, *19*, 27.

[60] P.A. Anderson, A.R. Armstrong, A. Porch, P.P. Edwards, L.J. Woodall, *J. Phys. Chem. B* **1997**, *101*, 9892.

[61] N. Gfeller, G. Calzaferri, *J. Phys. Chem. B* **1997**, *101*, 1396.

[62] M. Pfenniger, G. Calzaferri, *ChemPhys Chem* **2000**, *1*, 211.

[63] M. Pauchard, S. Huber, R. Méallet-Renault, H. Maas, R. Pansu, G. Calzaferri, *Angew. Chem. Int. Ed.* **2001**, 40, 2839.

[64] G. Calzaferri, H. Maas, M. Pauchard, M. Pfenniger, A. Dévaux, *Advances in Photochemistry*, **2002**, Vol 27, in press.

[65] G. Calzaferri, M. Pauchard, H. Maas, S. Huber, A. Khatyr, T. Schaafsma, *J. Mater. Chem.* **2002**, in press.

[66] P. Lainé, R. Seifert, R. Giovanoli, G. Calzaferri, *New J. Chem.* **1997**, *21*, 453.

[67] K. Ha, Y.-J. Lee, D.-Y. Jung, H.J. Lee, K.B. Yoon, *Adv. Mater.* **2000**, *12*, 1114.