Novel phthalocyanine-based stopcock for zeolite L

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We report the first phthalocyanine-based stopcock for selective adsorption to the channel entrances of zeolite L and realisation of a new electronic dipole moment coupling situation.

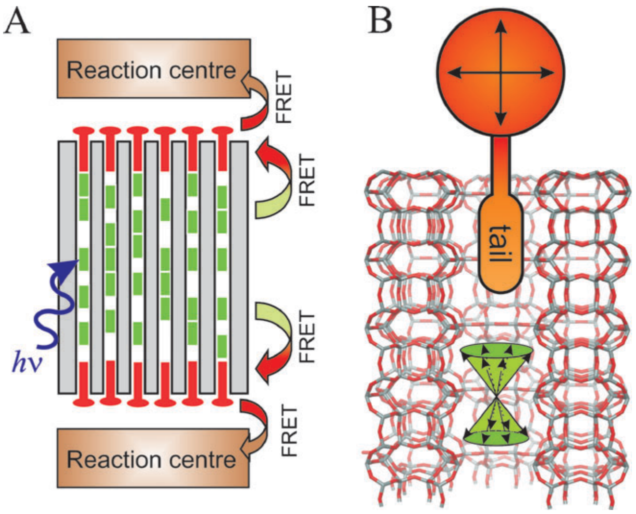
The supramolecular organisation of guests species inside a well-defined host material is a highly versatile principle for preparing systems exhibiting macroscopic properties.[1] Zeolite L has been shown to be an ideal host for the realisation of such systems.[2] It is a cylindrically shaped, microporous aluminosilicate with hexagonal symmetry and a one-dimensional channel system running parallel to the cylinder axis. Due to the geometric constraints imposed by the channel structure, it is possible to obtain materials with very high concentrations of monomeric dyes. The orientation of the electronic transition dipole moments can, in some cases, be described by assuming a cone shaped distribution.[3] Energy transfer materials, as illustrated in Scheme 1(A), can be prepared by sequentially incorporating different types of organic dyes.[2] The channel entrances are plugged with specific types of molecules called *stopcocks*.[4] These are composed of a rigid tail that can enter the channel and a head group that is too bulky to pass the pore opening.

The spectral properties of dyes and stopcocks are precisely tuned to each other so that, upon selective excitation of the dyes inside, the energy travels *via* Förster Resonance Energy Transfer (FRET) to the stopcocks at the edges, but not back.[2] These can now either re-emit this energy as luminescence from the crystal surface, or transfer it radiationlessly to a photoelectronic or a photochemical device, labelled as "Reaction centre" in Scheme 1(A). Such artificial antenna materials are of particular interest in the design of sensitised organic solar cells or fluorescent concentrators.[5] Since the role of the stopcock head also includes the mediation of communication between molecules inside and outside of the zeolite crystals, it is additionally required to be fluorescent in order to extract or inject electronic excitation energy from or into the zeolite L crystals.

Considering their strong absorption and near-infrared emission, as well as their rich electrochemical properties, phthalocyanines are among the most appealing chromophores for functional energy and electron transfer materials and photovoltaic applications.[6,7]

The efficiency of the FRET process depends on several parameters, among them the spectral overlap integral between the emission and absorption band, as well as the distance and relative orientation of the electronic transition dipole moments of the donor–acceptor pair. FRET will be most efficient when both electronic transition dipole moments are parallel to each other. We will focus in this communication on the specifically designed novel phthalocyanine-based stopcock **IL-1**. Its structural formula is shown in Fig. 1(A) and consists of a phthalocyanine head bearing three *tert*-butyl groups as well as one rigid tetraphenylene tail. It is of great interest because it allows for the first time to realise the situation depicted in Scheme 1(B) and because the *tert*-butyl groups bound to the Zn-phthalocyanine head can act as an intrinsic "insulating" layer between the stopcocks and the active layer, *e.g.*, in an organic solar cell.[5]

A top and side view of a van der Waals model of **IL-1** adsorbed to the channel entrances of zeolite L is given in Fig. 1(B) and (C), respectively. The tetraphenylene tail enters the zeolite L channels if the adsorption is carried out in an appropriate solvent.[8,9]



Scheme 1 Schematic representation of an energy transfer material (A) and a possible arrangement of electronic transition dipole moments for a stopcock molecule parallel to the channel axis in two dimensions (B). The green double cone describes the orientation of the transition dipole moments of a dye incorporated into zeolite L.[3]

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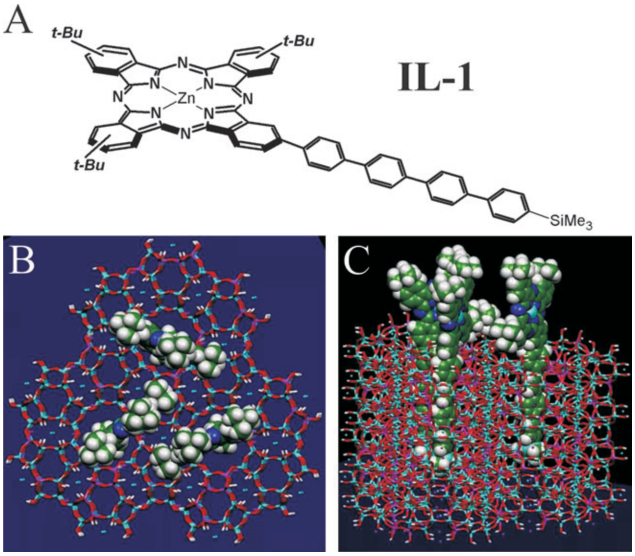

Fig. 1 Structural formula of stopcock molecule **IL-1** (A) as well as top (B) and side (C) views of the phthalocyanine adsorbed to the channel entrances of zeolite L (van der Waals model).

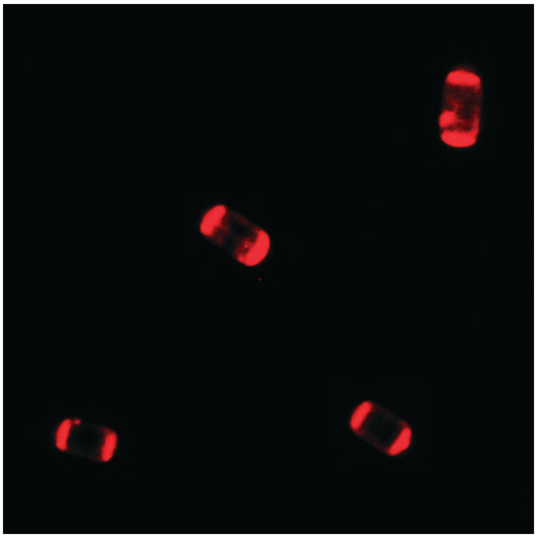

Fig. 2 Fluorescence microscopy image of four 4.5 μm long zeolite L crystals with stopcock **IL-1** adsorbed at the channel entrances.

The convergent strategy used to synthesise compound **IL-1** is laid out in Scheme 2. The first step implies the preparation of a "reactive" phthalonitrile precursor **2** by Suzuki coupling between 4-iodophthalonitrile[10] and 4′-(4,4,5,5-tetramethyl)-1,3,2-dioxaborolyl)-4-trimethylsilylbiphenyl,[8] followed by the transformation of the TMS into a iodo functional group using the ICl reagent. The statistical cross-condensation of phthalonitriles **2** and 4-*tert*-butylphthalonitrile in the presence of $ZnCl_2$ yielded phthalocyanine **3** in 30% yield. The subsequent palladium mediated cross coupling of **2** with the above mentioned boronic ester gave the desired compound **IL-1** in 73% yield. All new compounds were spectroscopically characterized.†

An adsorption procedure from a *n*-hexane–CH_2Cl_2 suspension was found to be appropriate for the attachment of **IL-1** to zeolite L. The fluorescence microscopy image in Fig. 2 shows the result of such an experiment at room temperature. The luminescence is concentrated at the bases of the crystals and, as expected for the arrangement shown in Scheme 1(B), it is not polarised. These results prove that the stopcocks are located at the channel entrances.

Emission (solid) and absorption (dashed) spectra of **IL-1** in THF (black) and of the potential donor molecule oxonine (**Ox**) (light grey) are collected in Fig. 3. The dye **Ox** has been chosen since it has often been used successfully for synthesising energy transfer materials.[2] It is well suited as donor for FRET experiments, as it can be excited in a spectral range where the stopcock **IL-1** has a very weak absorption (around 550 nm). The spectral overlap integral between the emission band of **Ox** and the absorption band of **IL-1** in THF has been determined from the spectra shown in Fig. 3(B) to be J_{DA} = 9.76 × 10^{-13} cm^3 M^{-1}. Experiments with different **IL-1**,**Ox**-zeolite L samples have been made and show considerable energy transfer from **Ox** to **IL-1**.

From this we conclude that **IL-1** stopcock based energy transfer materials can be made, for which a wide range of donor or acceptor dyes is available.[2] The combination of channel entrance functionalised zeolite L[11] with **IL-1** derivatives bearing a reactive tail end group is expected to lead to more robust materials for optoelectronic applications by providing covalent stopcock attachment.

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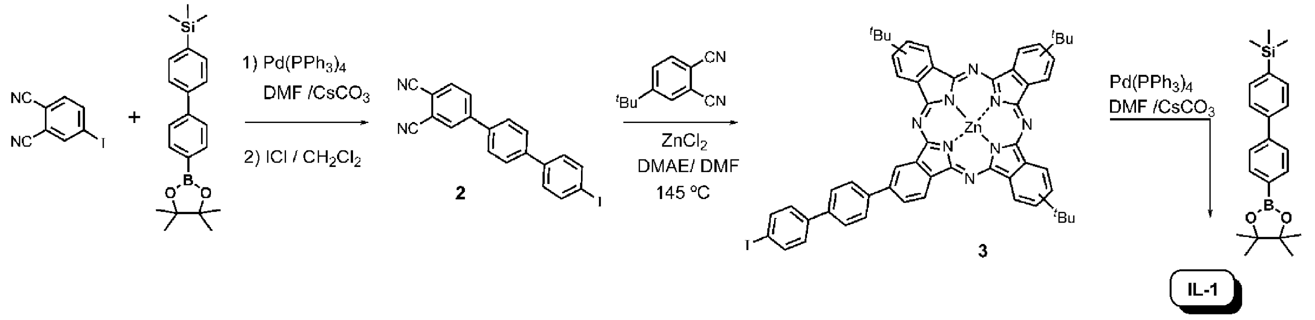

Scheme 2 Synthesis of the Zn(II)-phthalocyanine stopcock molecule **IL-1**.

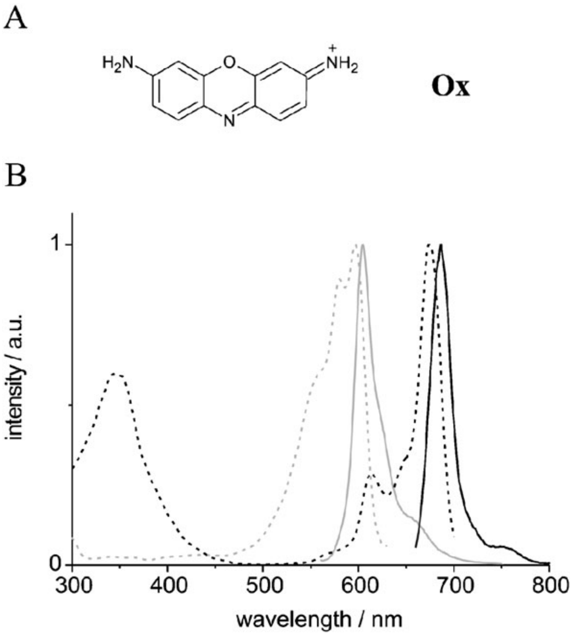

Fig. 3 (A) Structural formula of oxonine (**Ox**) and (B) emission (solid) and absorption (dashed) spectra of a 7×10^{-7} M **IL-1** solution in THF (black) and of oxonine (**Ox**) in zeolite L (0.025 molecules per unit cell, light grey).

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Notes and references

† *Phthalonitrile* **2**: H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (d, J = 1.6 Hz, 1H), 7.97 (dd, J = 8.3 Hz, 1.6 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.7 Hz, 2H), 7.69 (m, 4H), 7.37 (d, J = 8.7 Hz, 2H); C NMR (75 MHz, $CDCl_3$): δ (ppm) 145.82, 141.61, 139.23, 138.14, 136.10, 134.08, 131.83, 131.24, 128.91, 127.95, 127.78, 116.62, 115.50, 115.39, 114.08, 94.06; HR-EI: calc. for $C_{20}H_{11}IN_2$: $[M]^+$: m/z 405.9967, found: 405.9960.
Phthalocyanine **3**: H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.4 (br, 4H), 7.6 (br, 16H), 1.6 (br, 27H, $C(CH_3)_3$); HR-MALDI (dithranol): calc. for $C_{56}H_{47}IN_8Zn$: $[M]^+$: m/z 1022.2260, found: 1022.2275; UV/Vis ($CHCl_3$): λ_{max}/nm (log ε)) = 351 (4.9), 610 (4.4), 676 nm (5.2).
Phthalocyanine **IL-1**: H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.0 (br, 28H), 1.6 (br, 27H, $C(CH_3)_3$), 0.3 (br, 9H, $Si(CH_3)_3$); HR-MALDI (dithranol): calc. for $C_{71}H_{64}N_8SiZn$: $[M]^+$: m/z 1120.4315, found: 1120.4326; UV/Vis ($CHCl_3$): λ_{max}/nm (log ε) = 347 (4.9), 610 (4.5), 676 nm (5.2).
Zeolite L crystals were synthesised and characterised as described previously.[12] The potassium-exchanged form was used. Oxonine (**Ox**) was synthesised and purified according to a published procedure.[13] **Ox** was inserted into zeolite L by ion exchange out of H_2O. A weighed amount of zeolite L crystals (typically 20 mg) was suspended in 1 ml of H_2O. The desired amount of **Ox** was added to the suspension while vigorously stirring. The mixture was first sonicated for 15 min and then refluxed and stirred for 16 h. Afterwards the dye-loaded crystals were washed with methanol in order to remove dye molecules adsorbed on the outer surface of the crystals.
For the adsorption of the phthalocyanine **IL-1** to the channel ends, 10 mg of zeolite L was dispersed in 2 ml of n-hexane and sonicated for 15 min. A solution of **IL-1** in CH_2Cl_2, containing a molar equivalent of **IL-1** to the number of channel entrances, was added. The suspension was sonicated for 15 min and then stirred overnight at room temperature.
Fluorescence spectra were measured with a Perkin Elmer LS 50B fluorescence spectrometer using suitable cut-off filters. Absorption spectra were recorded on a Cary 1E spectrophotometer. Fluorescence microscopy images were recorded with an Olympus BX 60 microscope equipped with a SiS CC-12 high-sensitivity CCD camera and a 100× magnification objective.

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