Multicolored Emitters

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Assembling Micro Crystals through Cooperative Coordinative Interactions**

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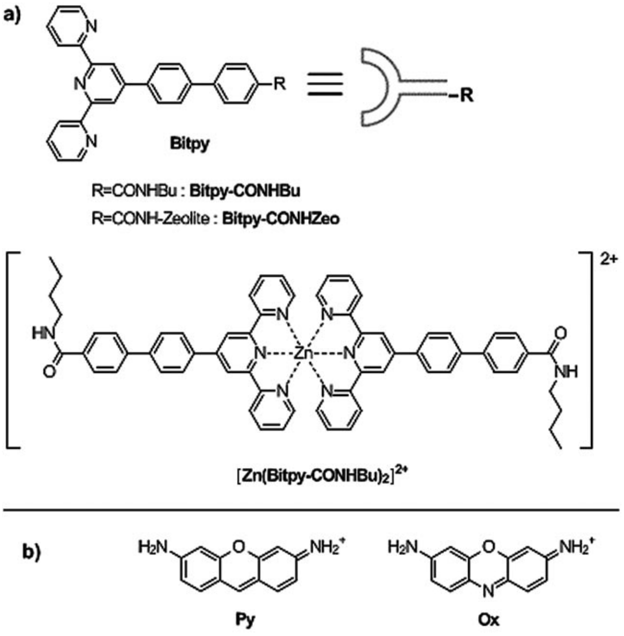
Dedicated to Professor Fritz Vögtle

Self-assembly, as a process to produce complex structures not achievable by standard synthetic techniques, has been largely and successfully explored on molecular level.[1–4] Using molecules as building blocks, chemists realized nanometer-sized architectures that are able to perform functions not present in their molecular components.[5,6] More recently, attention has shifted from molecules to nanoobjects[7]—nanoparticles,[8] -rods,[9] and -plates[10]—with the aim to assemble them into 1D or 2D arrays in analogy to what has been done with molecules. However, control of growth (to achieve large finite structures) and of the geometrical arrangements of the components remains a difficult task. The use of a nanometer-sized objects can easily bridge the gap between the molecular (angstrom-sized) and microscopic (micrometer-sized) worlds.[11,12]

Herein, we report the versatility of zeolite L crystals as components for self-assembly processes through polyvalent interactions. Their choice is dictated by their optical transparency, stiffness, defined morphology, and ease of chemical functionalization. Zeolites are porous materials made of interconnected tetrahedra of SiO_4 and AlO_4, which form a negatively charged channel structure.[13,14] The overall charge neutrality is achieved by exchangeable cations positioned in the channels.

The crystals can be synthesized in size ranges from 30 nm to several micrometers and in different aspect ratios to give disks or cylinders.[15] Various cationic or neutral molecules able to penetrate the 0.71-nm channel openings may intercalate into crystals.[16] The chemical control over zeolite L is further demonstrated by its ability to specifically functionalize the channel entrances,[17] leading to the possibility to self-assemble them in rodlike architectures. Herein, we demonstrate the use of coordinative interactions between Zn^{2+} and the zeolite-functionalized terpyridine derivative (Scheme 1 a) to create one-dimensional zeolite assemblies.



Scheme 1. a) Components employed for the zeolite assembly. b) The fluorescent molecules pyronine (left) and oxonine (right) used for loading of the zeolite L channels.

The use of Zn^{2+} as a "chemical glue" for the terpyridine-functionalized zeolite L is desirable for three main reasons: 1) complexation of Zn^{2+} with terpyridine is a dynamic and reversible process;[18–20] 2) complexation is followed by a distinctive change in photophysical properties (i.e., absorption and emission);[21,22] 3) the Zn–terpyridine complexes have either a 1:1[18] or a 1:2 stoichiometry,[23] leading in this latter case to rodlike octahedral complexes. The reversible nature of the binding allows the assembling crystals to maximize their surface-to-surface overlap interactions, and

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the change in emission can be used as a tool for monitoring the progress of the assembly. The synthesis and characterization of the terpyridine-based ligand (Bitpy-CONHBu) and its zinc complex is reported in the Supporting Information. The free ligand Bitpy-CONHBu in ethanol shows a broad absorption band (π-π*)[21] centered at around 296 nm (Figure 1 a). After the ligand coordinates with Zn^{II} ions, the absorption maximum shifts towards lower energy (329 nm, Figure 1 b)[21,22] as a result of perturbation of the lowest-unoccupied molecular orbital (LUMO) upon coordination with the ion. The terpyridine derivative shows an emission band with a maximum at 363 nm, which decays with mono-exponential kinetics ($\tau = 1.2$ ns). The ligand has an emission quantum yield φ_{em} of 0.45. Upon complexation of the ligand with $Zn(ClO_4)_2$ to form $[Zn(Bitpy\text{-}CONHBu)_2](ClO_4)_2$ (Scheme 1 a), the emission is red-shifted to 431 nm and strongly increases in intensity ($\varphi_{em} = 0.84$ and $\tau = 2.1$ ns) (Figure 1 c,d).

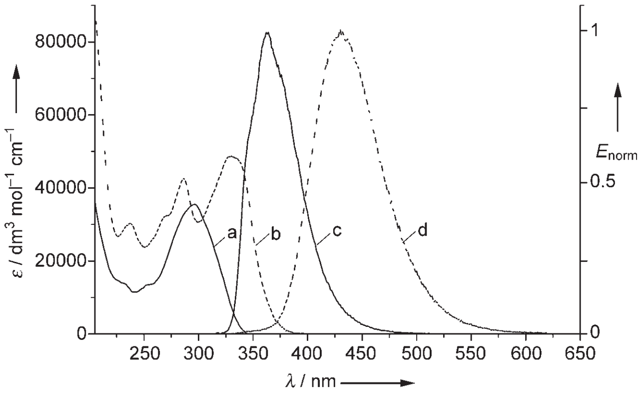

Figure 1. a,b) Absorption spectra of Bitpy-CONHBu (a; ——) and $[Zn(Bitpy\text{-}CONHBu)_2](ClO_4)_2$ (b; -----). c,d) Emission spectra ($\lambda_{ex} = 295$ nm) of Bitpy-CONHBu (c; ——) and $[Zn(Bitpy\text{-}CONHBu)_2]$-$(ClO_4)_2$ (d; -----). All spectra were recorded in air-equilibrated ethanol.

We expect that a similar trend will be followed upon complexation of the Zn^{2+} to the Bitpy-functionalized zeolites. The strong emission of the complex can therefore be used to monitor the reactivity with Zn^{2+} and the assembly process. The strategy followed for the assembly of the zeolite L crystals is depicted in Figure 2 a. Amino-terminated crystals (see the Supporting Information for the synthetic details) were treated with the succinimide-activated ester of the biphenylterpyridine to yield terpyridine-terminated zeolite L crystals Bitpy-CONHZeo. The crystals were then treated in methanol with Zn^{2+} to obtain the bis Bitpy complex, thus assembling the zeolites. The process was monitored by epifluorescence microscopy, whereby the samples were excited in the UV region (Figure 2 b,c). The uncomplexed terpyridine-terminated crystals show weak blue emission (similar to that seen for the ligand in solution) located at the crystal bases, and the crystals are randomly distributed (Figure 2 b). After Zn^{2+} ions are added, organized blue fluorescent structures were observed (Figure 2 c). The emission from the elongated structures is the most intense at the ends and in between the individual segments, indicating the presence of chemically bonded Zn^{2+} complexes. In this case, the emission spectrum corresponds to that of the $[Zn(Bitpy\text{-}CONHBu)_2]^{2+}$ complex, which demonstrates that the species has the same coordination geometry (Figures 1 d and 3 a).

Scanning electron microscopy (SEM) was performed to elucidate the geometric ordering of the crystals. Indeed, the crystals are well aligned in one-dimensional arrays (Figure 2 d–f). The number of the aligned crystals was as high as five although a predominance of two- and three-unit assemblies was observed. The distribution could not be altered by varying the reaction parameters (e.g. temperature, reaction time, reactant ratios, etc.; see the Supporting Information). SEM showed that the adjacent crystals are in contact over the complete base, overruling the possibility that the crystals arranged as a result of the solvent evaporation or other physical processes. This result is further corroborated by the fact that samples without Zn^{2+}, in our experimental con-

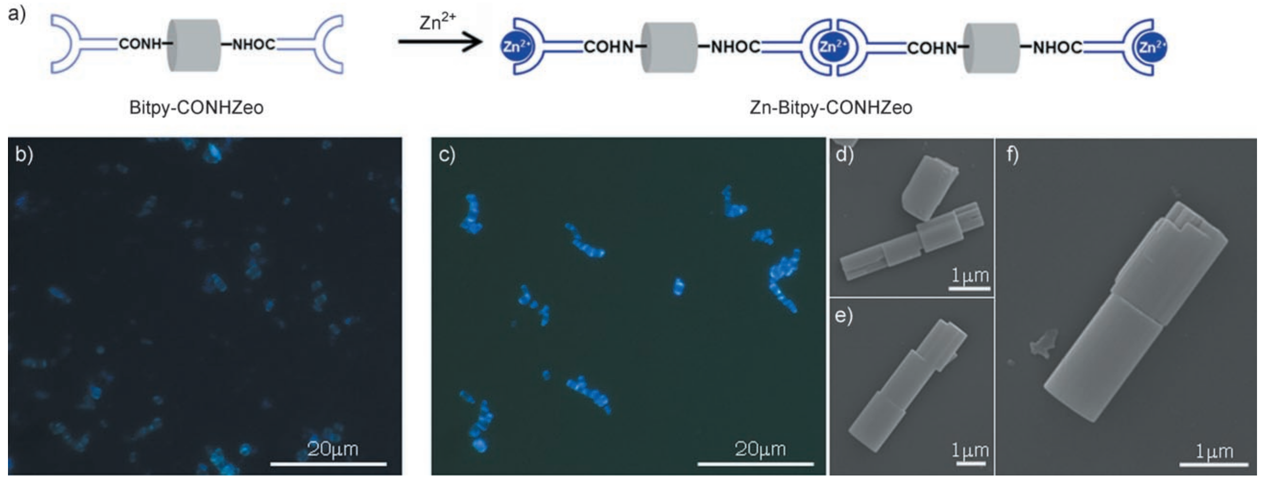

Figure 2. Assembly of zeolite L crystals. a) Terpyridine-terminated zeolite L crystals (Bitpy-CONHZeo) were mixed with Zn^{2+} to induce self-assembly. Each zeolite consists of thousands of channels; thus, thousands of complexes can be formed; for clarity we show only one channel reaction. b) Optical micrograph of unordered Bitpy-CONHZeo crystals. c) Optical micrograph after addition of $ZnCl_2$. d–f) SEM images of the assembled crystals (Zn–Bitpy-CONHZeo).

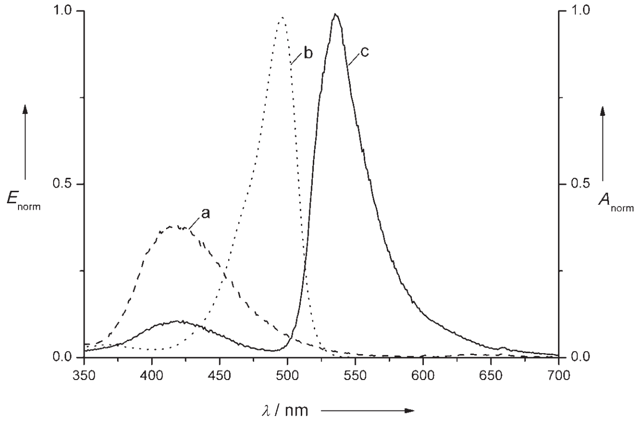

Figure 3. a,c) Emission spectra ($\lambda_{ex}=320$ nm, in ethanol) of Zn-Bitpy-CONHZeo (a; -----) and Zn–Bitpy-CONHZeo(Py) (c; ——). b) Absorption spectrum of pyronine in water.

ditions, do not show any ordered assembly. Furthermore, the observed tumbling of complete assemblies in the microscope immersion oil indicates that the crystals are chemically bound. Base-to-base crystals assembly is thought to depend critically on the flatness of the individual crystals bases because the interaction is on the nanometer scale. For this reason, the use of the high-quality flat-based crystals is desirable, as imperfect zeolites will not assemble.

The crystals shown so far are empty, and the channels contain only solvent molecules and ions. However, as already demonstrated, they can be filled with dye molecules. For example, insertion into zeolite L of the green-emitting dye pyronine (Py; $\lambda_{em}=518$ nm, see the Supporting Information) or the red-emitting oxonine (Ox; $\lambda_{em}=604$ nm) (see Scheme 1 b for chemical formulae), and subsequent functionalization with the terpyridine derivatives results in two building blocks further referred to as Bitpy-CONHZeo(Py) and Bitpy-CONHZeo(Ox), respectively. The addition of Zn^{2+} to either type of filled zeolite leads to highly emitting 1D structures containing red or green repeating units, in the same manner as for the empty zeolites.

Assembly was subsequently repeated using an alternative strategy in an attempt to assemble the different colored crystals in alternating arrays. The Bitpy-CONHZeo(Py) crystals were treated with a 1000-fold excess of Zn^{2+} with respect to the Bitpy groups to obtain the monocoordinated Zn–terpyridine complex. Microscopic analysis indicated that assembly between zeolites had not yet occurred, which indicates the presence of coordinatively unsaturated Zn ions.[18] Excess Zn^{2+} was then removed from the suspension through repeated centrifugations. Equal amounts of Bitpy-CONHZeo(Ox) crystals were added to the coordinatively unsaturated Zn–Bitpy crystals and the samples were allowed to self-assemble. SEM analysis again showed that arrays ranging between two to five crystals had formed; in most cases, two or three zeolites were assembled. Examples of heterochromic arrays are shown in Figure 4. Although the synthesis was planned to lead to only asymmetric assemblies, resulting in alternating red and green emitting zeolites, analysis again presented a 1:1 ratio of homo- (all red or all green) to heterochromic arrays, indicating that the zinc is scrambling between Bitpy groups. SEM analysis of the solution showed that the zeolites are assembled through Bitpy-functionalized bases and that a large number of aggregates are obtained (see the Supporting Information).

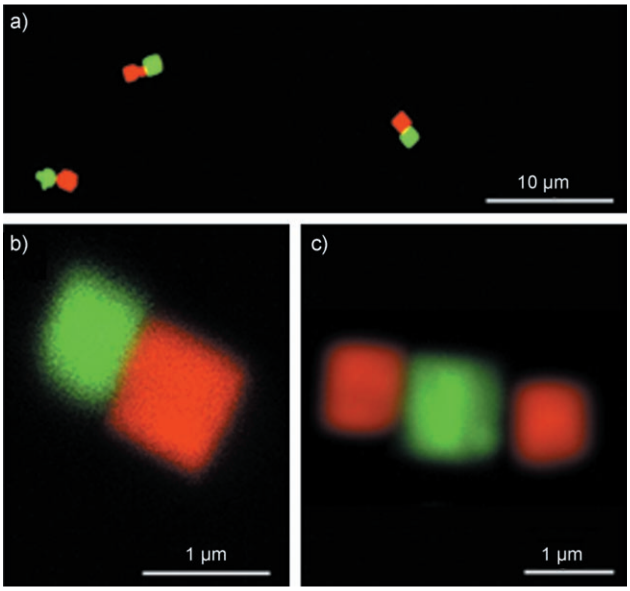

Figure 4. Confocal micrographs of mixed Bitpy-CONHZeo(Ox)–Bitpy-CONHZeo(Py) pairs. b) Magnified image of a Py–Ox zeolite pair. c) Magnified image of an Ox–Py–Ox zeolite array.

In view of the spectral overlap and close proximity of the blue-emitting Zn–Bitpy donor and the green (Py) dye molecules inserted into the zeolites, we also investigated the possibility of electronic energy transfer upon excitation of the complex. Samples of Zn–Bitpy-CONHZeo(Py) and Zn–Bitpy-CONHZeo, prepared under identical conditions with an equal number of Zn–Bitpy-CONHZeo groups, were excited at 320 nm, and both showed the blue Zn–Bitpy emission at around 420 nm. In the case of the Zn–Bitpy-CONHZeo(Py) system, also the intense emission of pyronine was observed at 535 nm (Figure 3 a,c), This green emission was also present in a control sample of Py-loaded zeolite under identical excitation conditions, which indicates that specific excitation of the donor was not possible. The weaker intensity of the Zn–Bitpy emission in the Py-containing zeolite is indicative of partial energy transfer resulting in at least a 75 % quenching of the Bitpy excited state.

As the emission spectra cannot give quantitative information because we cannot rule out emission of the Zn complex in single, non-assembled, zeolites, time-resolved emission measurements were performed ($\lambda_{ex}=295$ nm, $\lambda_{em}=420$ nm). The empty Zn–Bitpy zeolite system can be fitted satisfactorily to a monoexponential function to afford a lifetime of 1.8 ns. This value is very similar to the lifetime observed for the free $[Zn(Bitpy\text{-}CONHBu)_2](ClO_4)_2$ model system in solution. The fitted decay of Zn–Bitpy-Zeo(Py) was measured under identical conditions and gives a biexponential decay with a major component of 2.6 ns (65 %) and a second shorter component of 670 ps (35 %). We attribute the shorter decay component to the decay of the quenched Zn–

Bitpy excited state. This sub-nanosecond decay component is most likely due to a Förster-type energy-transfer process from the excited Zn–Bitpy groups at the channel entrances to the closest pyronine molecules entrapped in the channels of the zeolite crystal.[16]

Herein we have shown how geometric control, inherent to the chemical functionalization of zeolite L crystals, can be taken beyond the realm of single-crystal modification. We have created one-dimensional arrays of zeolite L crystals which are held together through multiple coordinative interactions. The reversible nature of the coordinative bond allows the arrays to maximize the overlap between crystals. Furthermore, these novel arrays have been intercalated with different fluorophores to create a multicolor system that upon assembly may alter the properties of the single crystals. This phenomenon has been investigated through energy-transfer quenching of the Zn–Bitpy unit. Applications for the systems range from microbarcodes used for bioimaging and tagging purposes[24] to the creation of unidirectional light-harvesting systems.[16,25] So far we have demonstrated the applications of coordinative bonds for interzeolite connection, but other types of connective interactions as well as assemblies of different objects[27] can be envisaged.

Experimental Section

All reagents were purchased from commercial suppliers and used without purification unless otherwise indicated. Instrumentation: Absorption spectra were measured on a Varian Cary 5000 double-beam UV/Vis/NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450-W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm mm^{-1} dispersion; 1200 grooves mm^{-1}), and a TBX-4-X single-photon-counting detector. Emission spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements were performed by using the time-correlated single-photon-counting (TCSPC) option on the Fluorolog 3. NanoLEDs (295 or 431 nm; FWHM $<$ 750 ps) with repetition rates between 10 kHz and 1 MHz were used to excite the sample. The excitation sources were mounted directly on the sample chamber at 90° to a double grating emission monochromator (2.1 nm mm^{-1} dispersion; 1200 grooves mm^{-1}) and collected by a TBX-4-X single-photon-counting detector. The photons collected at the detector were correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected by using an IBH DataStation Hub photon-counting module, and data analysis was performed with the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The goodness of fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals. Luminescence quantum yields (Φ_{em}) were measured in optically dilute solutions (OD $<$ 0.1 at excitation wavelength: 293 nm for Bitpy-CONHBu and 310 nm for [Zn(Bitpy-CONHBu)$_2$](ClO$_4$)$_2$) and calculated relative to quinine sulphate in 0.5 M H_2SO_4.[26] Epifluorescence microscopy images were measured with an Olympus BX60 microscope equipped with excitation and emission filters and a color CC-12 high-sensitivity CCD camera (SiS). Confocal microscopy was performed on a Leica TCS SPE with a 100 × 1.30 NA oil-immersion objective. Pyronine was excited with a laser at 488 nm, and emission was detected between 510 and 540 nm through a DD 488/635 filter. Oxonine was excited with a laser at 532 nm, and emission was detected between 600 and 625 nm through a DD 405/532 filter. The pinhole was set to one Airy.

Zeolite assembly: The cylindrical Zeolite L crystals used in this work had a mean length of 2.2 μm and a mean diameter of 1.2 μm. Crystals used for the asymmetric study were 1 μm long and 800 nm wide. Amino-terminated Zeolite L crystals (ca. 40 mg, empty or intercalated with oxonine or pyronine)[16,17] were suspended in dry DMF (2 mL) and mixed with triethanolamine (10 μL). The suspension was heated to 65 °C in a sealed glass tube. Activated terpyridine ligand (Bitpy-COOSu, see the Supporting Information) (100-fold excess with respect to the number of Zeolite L channel entrances $n_e = (X_z/l_z) \times 5.21 \times 10^{-7}$; X_z: mass of zeolite in mg, l_z: average length of zeolite in nm) was suspended in dry DMF (1 mL), and half the solution was added to the warm suspension. The solution was stirred for 15 min, the remaining amount was added, and the solution was stirred for an additional 2 h. The solution was centrifuged in DMF and methanol to yield the ligand-terminated zeolite L crystals Bitpy-CONHZeo, which were further dried at 60 °C in an oven for 12 h.

Zeolite L crystals assembly with Zn^{2+}: Method 1: Bitpy-CONHZeo (ca. 10 mg) or pyronine- and oxonine-loaded Bitpy-CONHZeo (5 mg each) were suspended in methanol (1 mL) and warmed to 60 °C. A calculated amount (1 equiv of ZnCl to 2 equiv of zeolite L channel entrances) of the standard solution of $ZnCl_2$ in methanol was added slowly to the stirred suspensions. The reaction mixture was sonicated for 1 min and stirred for 1.5 days. Centrifugation was performed in methanol to yield assembled zeolite L crystals, which were further dried at 60 °C in oven for 2 h. Method 2: Bitpy-CONHZeo(Py) (ca. 10 mg) was suspended in methanol (1 mL), and the mixture was warmed to 60 °C. A calculated amount (1000 equiv of $ZnCl_2$ to 1 equiv of zeolite L channel entrances) of the standard solution of $ZnCl_2$ in methanol was added slowly to the stirred suspension. The reaction mixture was sonicated for 20 min. Centrifugation was performed in methanol. An equal amount of Bitpy-CONHZeo(Ox) was added and the reaction mixture was sonicated for 1 min and stirred for 1.5 days. Centrifugation was performed in methanol to yield the assembled zeolite L crystals, which were further dried at 60 °C in oven for 2 h.

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