

Monolayer of metallo-supramolecular complexes

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Self-assembled thin films of metallo-supramolecular complexes were prepared and characterized by synchrotron based X-ray reflectivity and fluorescence techniques.

In recent years, layer-by-layer self-assembly has become a very useful technique as an easy and inexpensive method for the preparation of functional thin films.¹ Monolayers and multilayers containing *e.g.* organics, polymers or nanoparticles have been prepared providing a potential approach towards advanced materials or devices with molecularly engineered properties.² However, to date, this method has not been used for the defined arrangement of special functional supramolecular units with nanometer dimensions into ordered molecular architectures on surfaces.³ Here, we report the successful extension of the self-assembly technique to such metallo-supramolecular systems.

We used metal–ligand interactions as non-covalent forces to assemble well-ordered metallo-supramolecular architectures. Such metal coordination arrays ($[1 \times 1]$ or $[2 \times 2]$ grid-type architectures) based on transition metal ions with octahedral coordination and terpyridine or 4,6-bis(6'-(2',2''-bipyridyl))-pyrimidine ligands were found to present interesting electronic, magnetic, and structural properties, such as electronic interactions between the metal centers and antiferromagnetic transitions at low temperatures.^{4,5} These complexes are formed by spontaneous self-assembly of the corresponding ligands and suitable metal ions such as Co(II), Cd(II), Zn(II) or Hg(II) (see Fig. 1 for $[2 \times 2]$ grids). Besides the design and synthesis of 'isolated' grid units, the ordered and stable arrangement of such metallo-supramolecular architectures on surfaces or thin films is of special interest. Two approaches were recently described: (a) hydroxy-terminated grids could be organized on a water trough using the Langmuir–Blodgett (LB) technique and transferred onto substrates;⁶ (b) unfunctionalized ligands were self-assembled in the presence of metal ions at the air–water interface.⁷ However, both methods are rather complicated and

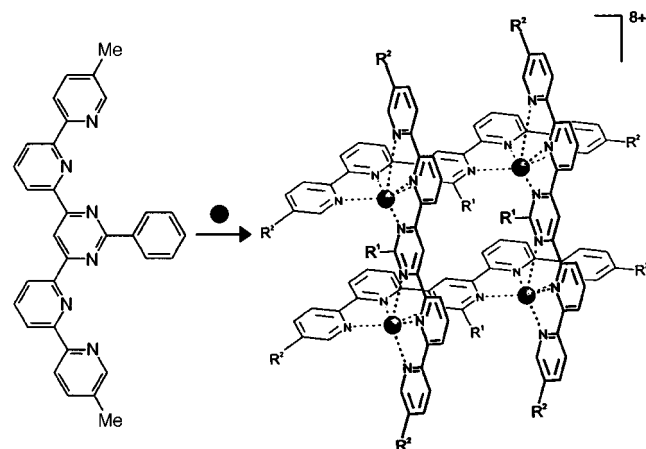


Fig. 1 Schematic representation of the bis-terdentate ligands leading to the formation of the $[2 \times 2]$ grid type complexes $[Cd_4L_4]^{8+}$ ($R^1 = Ph$, $R^2 = Me$). The terpyridine ligand (5,5''-dimethyl-2,2':6',2''-terpyridine) and the complexes are not shown.

not applicable for larger areas. We used the self-assembly into thin monomolecular films by adsorption onto polyelectrolyte covered substrates. As model systems for the film growth we chose the $[1 \times 1]$ Zn(II) and $[2 \times 2]$ Cd(II) complexes (Fig. 1).[†]

First we prepared a thin cushion of polyelectrolytes onto a glass or silicon substrate using poly(ethyleneimine) hydrochloride (PEI) followed by the adsorption of a layer of poly(styrenesulfonate) (PSS) which reversed the surface density (Fig. 2).[‡] In the next step the supramolecular units were adsorbed on the PSS layer. Owing to the counterions used the complexes were not soluble in water. However, the procedure could be also performed in acetone.[§]

To characterize the obtained layers we performed both specular and non-specular X-ray reflectivity measurements.[¶] Examples of the reflectivity profiles are displayed in Fig. 3 as a function of vertical momentum transfer q_z after normalization by the Fresnel reflectivity $R_F(q_z)$. The response is proportional to the squared Fourier transform of the density gradient along the interface normal⁸ and hence reflects the vertical film structure. The three data sets are shifted by arbitrary factors for clarity and correspond to films composed of the polyelectrolyte layers PSS/PEI/Si (a) without any metal complexes, (b) with $[1 \times 1]$ Zn complexes, and (c) with $[2 \times 2]$ Cd complexes adsorbed on top. The spacing of the minima is given by the inverse $2\pi/d$ of the total layer thickness d , yielding (a) $d = 30$ Å, (b) 46 Å and (c) 66 Å, respectively. Note the large thickness increase when $[2 \times 2]$ Cd grids are adsorbed, indicating an upright position of the grids (see Fig. 2). The observed differences in the oscillation amplitude reflects the different density contrasts and interfacial widths. The most pronounced fringes in Fig. 3(b) indicate particularly well defined interfaces for the adsorbed $[1 \times 1]$ Zn complexes. A more complete data analysis will be presented elsewhere.⁹ Similar curves have been measured with $[1 \times 1]$ Cu(II), $[1 \times 1]$ Hg(II) and $[1 \times 1]$ Cd(II) adsorbed onto the polyelectrolytes. From the typical mass densities of the adsorbed $[1 \times 1]$ metal complexes, molecular

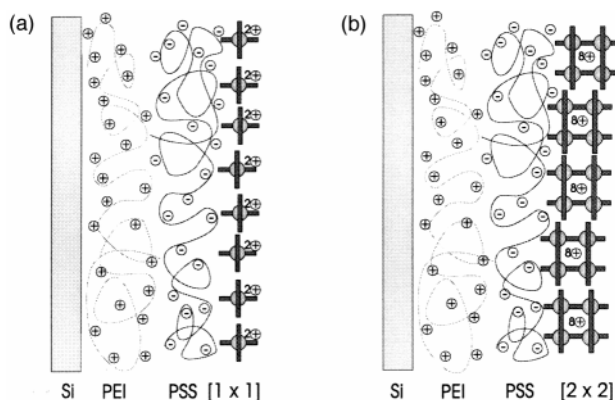


Fig. 2 Schematic drawing illustrating the build-up of the complex layers: (a) $[1 \times 1]$ metal grids; (b) $[2 \times 2]$ metal grids. Si, PEI and PSS refer to silicon substrate, poly(ethyleneimine) and poly(styrene-4-sulfonate), respectively. The filled circles denote the metal ions.

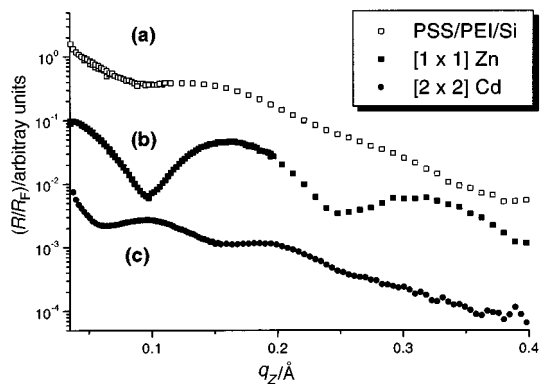


Fig. 3 Typical X-ray reflectivity profiles $R(q_z)/R_F(q_z)$ of the self-assembled films after normalization by the Fresnel reflectivity $R_F(q_z)$. The three data sets are shifted by arbitrary factors for clarity and correspond to films composed of the polyelectrolyte layers PSS/PEI/Si (a) without any metal complexes, (b) with $[1 \times 1]$ Zn complexes, and (c) with $[2 \times 2]$ Cd complexes adsorbed on top. The curves reflect the laterally averaged density profiles of the film along the interface normal (see text). The total film thickness can be derived directly from the spacing of the minima.

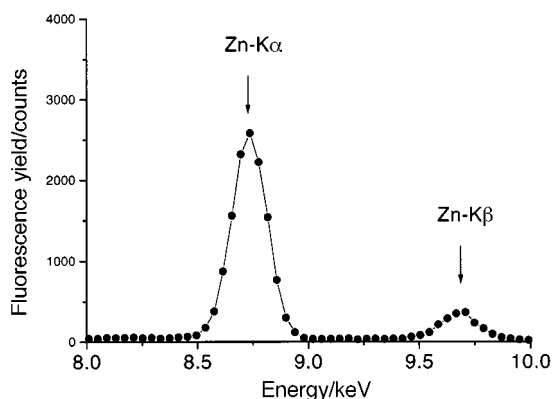


Fig. 4 The successful adsorption of complexes is evidenced most directly by the measured X-ray fluorescence. Typical spectra of monomolecular layers are collected on the time scale of a few min. For the case of $[1 \times 1]$ Zn the corresponding $K\alpha$ and $K\beta$ emission lines are observed.

volumes of *ca.* 1700 \AA^3 can be inferred, yielding a mean intermolecular distance of *ca.* 11 \AA . This value is in good agreement with the metal-metal distance in the crystals indicating an essentially closed packed complex layer.¹⁰ Furthermore, to investigate the lateral structural parameters of the complex layer (two-dimensional order) we performed grazing incidence X-ray diffraction on the $[2 \times 2]$ Cd complexes. However, as yet, we could not find a long-range ordering within the layer.¶

Simultaneously to the specular reflectivity, the X-ray fluorescence of the metal ions in the complexes adsorbed on the surface has been measured.** X-Ray fluorescence under grazing incidence has been shown to be a very powerful tool of surface chemical analysis. By means of the characteristic fluorescence energies ($K\alpha$ and $K\beta$ lines for Co, Cu, Zn, $L\alpha$ for Hg) excitable at an incident energy of 12.5 keV , this provides the most direct proof of the complex adsorption. Moreover, the variation of the fluorescence yield with α_i contains quantitative information on the position and width of the metal distribution with respect to the substrate. A typical curve of the energy dispersive spectrum for the $[1 \times 1]$ Zn complex is shown in Fig. 4.

At this stage, we use the data as additional, unequivocal proof that the complexes of different types have been adsorbed. Except for the peaks of the corresponding elements the spectra were clean, indicating no contamination of other transition metals or cross-contamination in sample preparation.

The present results demonstrate a simple entry to an ordered arrangement of metallo-supramolecular systems on surfaces. Using X-ray reflectivity we could establish the controlled

adsorption of one layer of metal complexes onto a PSS/PEI substrate. Furthermore, the structures of the films have been characterized by synchrotron based X-ray reflectivity and fluorescence techniques. The layer-by-layer adsorption method together with the described analytical techniques opens new avenues for the construction of novel metallo-supramolecular thin film materials which could find potential applications in the preparation of various optical, electronic, or magnetic devices.

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Notes and references

† The ligands were synthesized and characterized as described elsewhere.⁴⁻⁶ The reaction of suitable quantities of the ligands and the corresponding metal acetates in refluxing methanol or water exclusively leads to the formation of the monomolecular or tetranuclear complexes (isolated as PF_6 salts and recrystallized twice from acetone-ether).

‡ The silicon or glass substrates were washed extensively in trichloroethylene, methanol, and Millipore water followed by treatment with 5 M KOH (glass) and a saturated KOH solution in ethanol (silicon), respectively, for 1 min. Subsequently, they were washed with water. All samples were then kept in a 0.5% solution of poly(ethyleneimine) hydrochloride (PEI) for 20 min. Then the samples were rinsed in water followed by adsorption of a layer of poly(styrenesulfonate) (PSS) in a 3 mg ml^{-1} solution of PSS in water. The samples were again washed with water.

§ The metal complexes were adsorbed on the PSS layer by immersing the samples in 0.5 mg ml^{-1} solutions of the complexes in acetone for *ca.* 20 min and subsequent rinsing in acetone and water before drying (acetone did not destroy the polyelectrolyte layers, as shown by *ex situ* and *in situ* measurements).

¶ X-Ray experiments were carried out at the D4 bending magnet station of the storage ring DORIS at HASYLAB/DESY with a monochromatic X-ray beam of 12.5 keV . Typically, the reflectivity can be recorded over eight orders of magnitude, after correction for diffuse scattering background.

|| The surface diffuse scattering (non-specular scattering) has been measured both in the plane of incidence and out of the plane of incidence.

** The X-ray fluorescence under grazing angles was recorded simultaneously with the reflectivity measurements. The detector was placed at 90° opposite the sample surface at a distance of a few centimeters.

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