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[13] The site of modification was further proven by enzymatic fragmentation of the duplex **5**·**4** with phosphodiesterase from *Crotalus durissus*, phosphodiesterase from calf spleen, DNase I, and alkaline phosphatase. Reverse-phase HPLC analysis of the digest revealed besides dC, dG, T, dA, and dA^{Me} an additional compound. This was isolated and detected as positively charged ion at *m*/*z* 544.6 in an ESI-MS experiment. The observed mass is identical with the calculated molecular mass of a protonated 2′-deoxyadenosine modified with *N*-adenosylaziridine.

Metallosupramolecular Thin Polyelectrolyte Films**

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The manufacture and investigation of supramolecular devices is an active area of research in chemistry and materials science.[1] Supramolecular devices open new avenues to functional materials with potential applications in electronics, photonics, and catalysis.[2] The realization of such materials will depend on improving existing methods and finding new routes for integrating supramolecular units in ordered, structurally coherent macroscopic assemblies.

Molecular units can be integrated in ordered arrays in Langmuir–Blodgett films or in self-assembled monolayers.[3] Decher et al. developed a versatile approach to assembled multilayer structures by alternating adsorption of oppositely charged polyelectrolytes.[4] This method has been applied to a number of polyelectrolytes (colloids, enzymes, etc.). Mallouck et al. investigated lamellar inorganic structures based, for example, on zirconium phosphates.[5]

Here we present the first integration of metallosupramolecular functional units in structurally coherent, ultrathin polyelectrolyte interfaces.[6] We employed a two-step self-assembly process: first, metal ions react with polytopic ligands to form a charged metallosupramolecular coordination polyelectrolyte,[7] then alternating adsorption with negatively charged polyelectrolytes generates molecular films.[8]

The synthesis of coordination polyelectrolytes is shown in Scheme 1a. Reaction of 1,4-bis(2,2′,6′,2″-terpyrid-4′-yl)benzene (**1**) with metal ions in a 1:1 ratio in solution gives the coordination polyelectrolyte **2**. With most metal ions terpyridine (tpy) forms stereochemically defined octahedral complexes with D_{2d} symmetry.[9] It therefore seems reasonable to assume that **2** has a linear structure in which the positive charge lies along the molecular axis.

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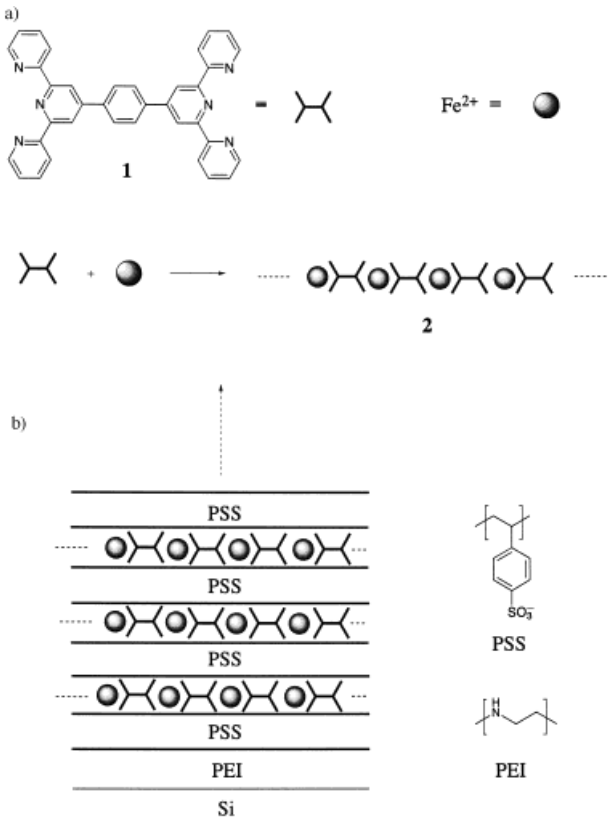

Scheme 1. a) Ligand **1** and metal ions in a 1:1 ratio form the coordination polyelectrolyte **2**. The counterions are omitted for clarity. b) Assembly of multilayers by sequential deposition of oppositely charged polyelectrolytes. PEI = polyethyleneimine, PSS = poly(styrene sulfonate).

A comparison of the UV/Vis and ^{1}H NMR spectra of **2** and $[Fe(me\text{-}ph\text{-}tpy)_2]Br_2$ (**3**; me-ph-tpy = 4′-*p*-tolyl-2,2′,6′,2″-terpyridine) confirms the presence of a coordination compound. Formation of a metal complex results in a characteristic metal-to-ligand charge-transfer (MLCT) transition in the visible region and a downfield shift of the ^{1}H NMR signals. The polymeric nature of **2** leads to broadening of the ^{1}H NMR signals and a red shift of the MLCT band relative to that of **3**.[10]

The molecular mass and polydispersity of **2** in methanol were determined by analytical ultracentrifugation. The sedimentation coefficient ($s = 1.60$ S) and an estimated diffusion coefficient ($D \leq 5.259 \times 10^{-7}$ cm^2 s^{-1}) were determined from the sedimentation velocity at 25 °C. Since the polydispersity leads to additional broadening of the sedimentation profile, the value of the diffusion coefficient will be too large. From the Swedberg formula, the lower limit of the molecular mass is 14900. For a dissociated polyelectrolyte with a molecular mass per repeat unit of 596.5, this corresponds to 25 repeat units. The width at half height of the particle size distribution function is 40%, that is, coordination polyelectrolytes of different chain length are present in solution. The fragment $[Fe(\mathbf{1})_2]^{2+}$ was observed in the electrospray (ES) mass spectra; oligomeric structures were not detected. Investigations by time-of-flight MS with matrix-assisted laser-desorption ionization (MALDI-TOF-MS) gave no further indications for the molecular weight of **2**.

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Solutions of **2** were used to fabricate multilayer structures (Scheme 1b). A suitable substrate (e.g. quartz, silicon) was treated with polyethyleneimine (PEI) and poly(styrene sulfonate) (PSS) to give a negatively charged interface. In the following steps, alternating adsorption of **2** and PSS generated metallosupramolecular superlattices.

Owing to the intense blue color of **2** and the strong UV absorption of PSS at 185 and 225 nm, the assembly of the multilayers on quartz substrates can be monitored by UV/Vis spectroscopy. Figure 1 shows the absorption spectra of **2** as a function of the number of layers. Since the characteristic

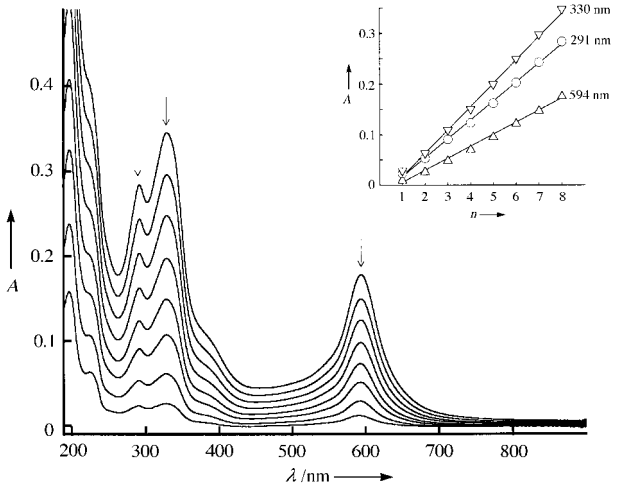

Figure 1. UV/Vis spectra of **2** on quartz glass as a function of the number of layers n. The MLCT band at 594 nm indicates the incorporation of **2** in the multilayer structure. The UV/Vis spectra of the PSS deposition cycle are omitted for clarity. The insert shows the absorption maxima at 291, 330, and 594 nm as a function of the number of layers. The linear increase indicates that equal amounts are deposited in each adsorption cycle.

bands of **2** are retained after deposition of PSS, the removal of **2** during deposition can be ruled out. The insert of Figure 1 shows a linear increase in the characteristic absorption maxima of **2** at 294, 330, and 594 nm. The MLCT transition at 594 nm is shifted by approximately 4 nm to lower energy; this could result from a change of polarity in the film.[11]

The assembly of multilayers was confirmed by X-ray reflectivity measurements. Figure 2 shows the interference curves of a PEI/(PSS/**2**)$_n$/(PSS)$_m$ ($n = 3,4$; $m = 0,1$) multilayer. The presence of fringes is consistent with a smooth, plano-parallel interface. An increase of the film thickness results in closer interference fringes. Curve fitting of the reflectivity data for a PEI/(PSS/**2**)$_3$/PSS film gives a total film thickness of 99 Å. Deposition of an additional layer of **2** increases the thickness by 17 Å to 116 Å; adsorption of PSS increases the thickness by 7 Å to 123 Å. The film thickness approximately corresponds to the molecular dimension of **2** perpendicular to the molecular axis. The roughness of the interfacial surface was determined from the XRR data to be less than 8 Å.

The elemental composition of the film was investigated by X-ray photoelectron spectroscopy (XPS). The XPS data confirm the presence of the expected elements. Quantitative analysis of the XPS bands gives an Fe:N atomic ratio of 0.96:6 (estimated error ± 10 %), which is in agreement with octahedrally coordinated Fe^{II}.

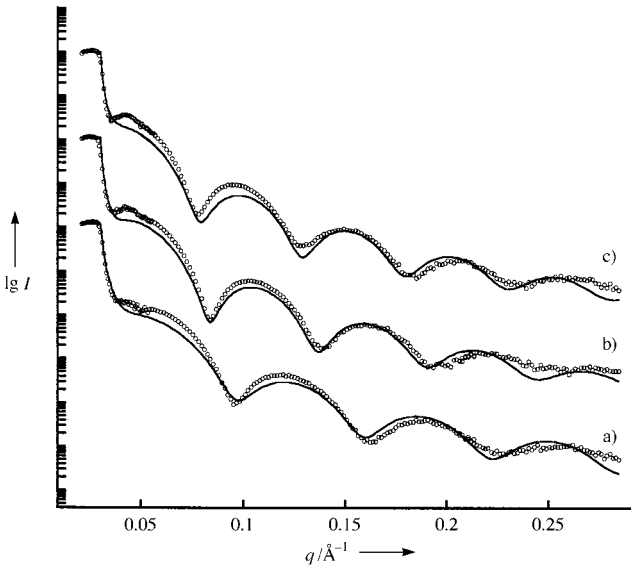

Figure 2. Experimental (dots) and calculated (lines) X-ray reflection interference curves for multilayers with the following compositions: a) PEI/(PSS/**2**)$_3$/PSS (thickness: 99 Å), b) PEI/(PSS/**2**)$_4$ (116 Å), c) PEI/(PSS/**2**)$_4$/PSS (123 Å). q = scattering vector.

Our results open a novel route for the integration of functional supramolecular units in ultrathin multilayers. The combination of two principles of supramolecular chemistry (molecular recognition by coordination of metal ions and electrostatic interactions) permits assembly of a wide variety of multilayered structures with intriguing properties.

Experimental Section

Ligand **1** was synthesized by literature procedures.[12]

2: A solution of Fe(OAc)$_2$ (16.5 mg, 0.092 mmol) in methanol (30 mL) was added to a solution of **1** (51.9 mg, 0.093 mmol) in refluxing toluene (100 mL) under an inert atmosphere. After 30 min the deep blue solution was concentrated under vacuum until **2** precipitated. The precipitate was washed with hot toluene and dried under vacuum (yield: 18 %). Compound **2** is soluble in methanol and ethanol. For the elemental analysis, **2** was isolated as the bromide by precipitation from aqueous solution. ^{1}H NMR (CD_3OD, room temperature): $\delta = 9.74$ (H3′), 8.95 (H3), 8.75 (HAr), 8.10 (H4), 7.44 (H6), 7.31(H5); UV/Vis (ethanol): MLCT band at 579 nm; IR (KBr): 1602, 1462, 1433, 1403, 1160, 831, 786, 731 cm^{-1}; elemental analysis calcd for $C_{36}H_{24}N_6FeBr_2 \cdot 6H_2O$: C 50.0, H 4.2, N 9.7, found: C 49.9, H 3.2, N 9.9.

Compound **3** was synthesized according to literature procedures.[13] ^{1}H NMR (CD_3OD, room temperature): $\delta = 9.43$ (H3′), 8.85 (H3), 8.32 (HAr), 7.96 (H4), 7.61 (HAr), 7.30 (H6), 7.18 (H5), 2.56 (HMe); UV/Vis (ethanol): MLCT band at 567 nm; IR (KBr): 3050, 3015, 2915, 1605, 1465, 1430, 1410, 1160, 820, 790, 730 cm^{-1}.

Multilayers were prepared by the method developed by Decher et al.[14] The following solutions were used: 10^{-2} M polyethylenimine in water, 10^{-3} M sodium poly(styrene sulfonate) in 1 M NaCl, $0.03 \cdot 10^{-3}$ M solution of **2** in water/methanol (90/10). The substrate for the UV/Vis spectroscopic investigations was quartz glass (Hellma Optik, Jena, Germany). For the XRR measurements, polished (100) silicon wafers (Silchem, Dresden, Germany) were employed. XRR measurements were made on a unit from the company STOE&CIE (Darmstadt, Germany); $U = 40$ kV, $I = 50$ mA, $\lambda = 1.54$ Å (CuK_α). The XRR data was analyzed according to a published procedure.[15]

The molecular mass was measured with a Beckman Optima XL-I ultracentrifuge (Beckman Instruments, Palo Alto, USA) with integrated UV/Vis absorption and Rayleigh interference optics. The samples were

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measured in 0.1N KOAc/methanol and 1.0N NH_4OAc/methanol solutions at 25 °C and 60000 rpm; both protocols gave similar results. In pure methanol the sample sedimented very slowly as a result of electrostatic repulsion. The partial specific volume of 0.6305 $mL\,g^{-1}$ was used.[16]

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Efficient Sialyltransferase Inhibitors Based on Transition-State Analogues of the Sialyl Donor**

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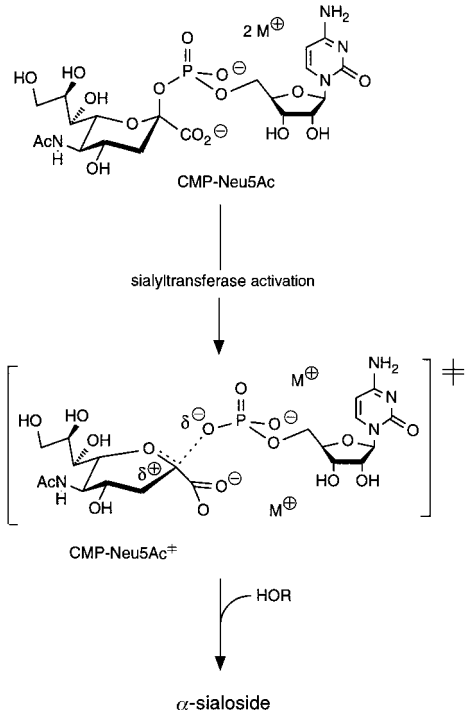
Sialic acid containing epitopes are involved in important biological processes, such as cell adhesion and inflammation.[1] There is also a correlation between the sialyl content of glycoconjugates and the malignancy of tumor cells.[2] Furthermore, differences in sialylation type between tumor cells and normal cells were found;[3, 4] for instance, although *N*-glycolylneuraminic acid has not been observed thus far on the surface of normal human cells, 30–50% of tumor cells of different origin contain this compound in small amounts.[3] Recently, an interesting correlation between α(2-6)-sialylation of *N*-acetyllactosamine and B lymphocyte activation and immune function was reported, which could find medicinal application.[5] Therefore, to study the influence of sialyl residues in biological systems it is highly desirable to develop efficient inhibitors for sialyltransferases.

The various sialyltransferases employ, independent of their source and their acceptor specificity, cytidine monophosphate *N*-acetylneuraminic acid (CMP-Neu5Ac, Scheme 1) as sialyl



Scheme 1. Mechanism of the sialylation.

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