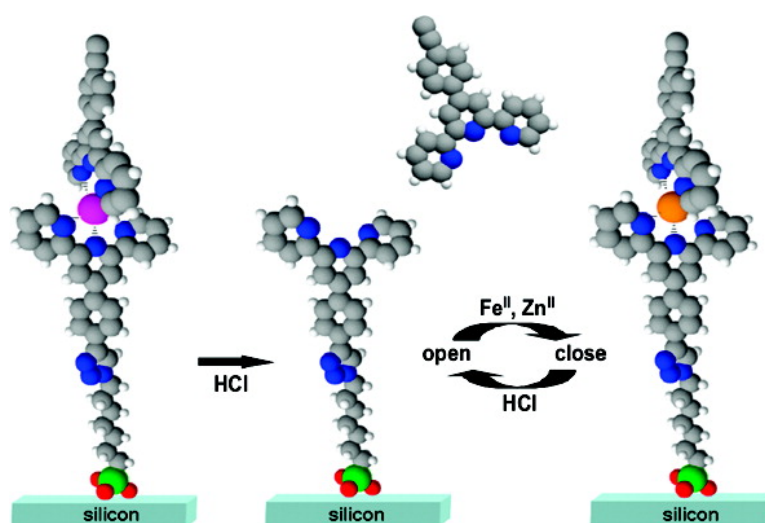Article

Reversible Supramolecular Functionalization of Surfaces: Terpyridine Ligands as Versatile Building Blocks for Noncovalent Architectures

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Reversible Supramolecular Functionalization of Surfaces: Terpyridine Ligands as Versatile Building Blocks for Noncovalent Architectures

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We report on the reversible and selective functionalization of surfaces by utilizing supramolecular building blocks. The reversible formation of terpyridine bis-complexes, based on a terpyridine ligand-functionalized monolayer, is used as a versatile supramolecular binding motif. Thereby, click chemistry was applied to covalently bind an acetylene functionalized Fe(II) bis-complex onto azide-terminated self-assembled monolayers. By decomplexation of the formed supramolecular complex, the ligand modified monolayer could be obtained. These monolayers were subsequently used for additional complexation reactions, resulting in the reversible functionalization of the substrates. The proper choice of the coordinating transition metal ions allows the tuning of the binding strength, as well as the physicochemical properties of the formed complexes and thus an engineering of the surface properties.

Introduction

Responsive surfaces can adapt their physicochemical properties as a result of changes in their environment, i.e., electrical, mechanical, and chemical influences, or changes in pH value or temperature.[1,2] The reason for this responsiveness is mostly related to changes on the molecular level of the structures. The controlled alteration of the surface properties represents an important prerequisite for many applications in microfluidics, microengineering of smart templates for bioseparation or data storage, sensors, as well as for the microfabrication of controlled-release devices. The preparation of such responsive surfaces typically involves self-assembled monolayers (SAMs) or thin polymer films.[3–6] As responsive binding moieties also supramolecular metal complexes are interesting candidates, as the combination of transition metal ions with, e.g., terpyridine ligands offers the possibility to create versatile "switchable" binding motifs.[7–12] In addition to the connection of two or more ligands, the proper choice of the transitional metal ions provides access to the tuning of electrochemical, optical, and magnetic properties as well as

to the binding strength. Under suitable conditions bis-terpyridine metal complexes can be decomplexed ("opened") and subsequently complexed ("closed") by changing external parameters, i.e., temperature, pH, solvents, or by the addition of strong competing ligands; moreover, the alteration of their oxidation state can also be utilized. Therefore, supramolecular systems represent widely applicable building units to fabricate responsive and reversible molecular architectures. 4′-Aryl-substituted 2,2′:6′,2″-terpyridine was used here as a ligand that offers the possibility to obtain a wide range of functionalized metallo-supramolecular building blocks and can, moreover, be used for the assembly of polymer architectures by metallo complexation.[13–17]

An important step in this approach is the reliable anchoring of the terpyridine ligands to surfaces, which can be achieved by following a click chemistry approach.[18,19] A currently intensively used click reaction is the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of terminal acetylenes and azides,[20] which already found various applications in surface modification reactions.[21–33] Different approaches have been reported in literature to synthesize

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supramolecular metal complexes and rotaxanes for applications in click chemistry.[34–40] The anchoring of supramolecular systems onto substrates by click chemistry or alternative chemical pathways has been described by different groups.[41–43] Nishimori et al. reported on the fabrication of molecular wires on gold surfaces by combining stepwise coordination reactions of metal ions and bridging ligands.[41] The immobilization of ferrocene and alkyne containing iron porphyrins onto a gold electrode via 1,3-dipolar cycloaddition was investigated by Devaraj et al.[42,43] Hobara et al. reported on the construction of a two-dimensional (2D) network by in situ complex formation between Fe(II) and terpyridine adsorbed on gold nanoparticles.[44] Wang et al. utilized supramolecular binding motifs to introduce a molecular imprinting strategy,[45] and moreover used polymerization/depolymerization reactions of carbon nanotubes[46] to assemble and disassemble nanostructures. To the best of our knowledge, it has not been demonstrated that such supramolecular systems can still be "opened" and "closed" when they are assembled in monolayer systems, thus creating reversible responsive surfaces. This step is, however, an important feature as it opens up new routes in the fabrication of molecular surface architectures.

Experimental Section

All chemicals were purchased from commercial sources. Bicyclohexane (BCH) was freshly distilled over sodium before use. The other reagents were used without further purification. Double-sided polished p-type silicon wafers (100) were obtained from UniversityWafer, and glass substrates were obtained from PGO. The substrates were treated on both sides for 30 min in a UV/ozone chamber before use. Fourier transform infrared (FT-IR) measurements were performed on a Tensor 37 RT from Bruker with a grazing angle setup. Spectra were recorded at 4 cm^{-1} resolution using 500 scans and a clean silicon substrate as reference. UV/vis spectra were recorded on a Perkin-Elmer Lambda-45 spectrometer and a Perkin-Elmer Lambda-900 spectrophotometer. For solutions, a concentration of 10^{-6} M in CH$_2$Cl$_2$ (1 cm cuvette) at 25 °C was used. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα X-ray source and a hemispherical analyzer with a five channeltron detector. Spectra were obtained using a magnesium anode (Mg Kα = 1253.6 eV) operating at 480 W and a constant pass energy of 20 eV with a background pressure of 2 × 10^{-9} mbar; they were referenced to the Si(2p) peak at 103.3 eV of the native SiO$_2$ layer on the substrate.[47]

Bromine and azide terminated monolayers were prepared according to the literature.[48]

Cycloaddition reactions with the iron complex (1) were carried out by immersing the azide functionalized substrate for 48 h in a solution of (1) (5 mg, 6.919 × 10^{-6} mol), dissolved in dimethylformamide (DMF; 20 mL), at 80 °C under argon atmosphere. As catalytic systems, CuSO$_4$ × 5 H$_2$O (5 mol%, in 1 mL of water)/sodium ascorbate (10 mol%, in 1 mL of water) or an excess of CuI were used. Subsequently, the substrates were sonicated in DMF, water, and ethanol for 3 min, and each sample was dried in a stream of air.

The decomplexation of the clicked complex (1) on the surface was performed by immersing the substrate in a solution of concentrated HCl for 24 h at room temperature. Afterward, the substrate was sonicated three times for 5 min in water, followed by drying in a stream of argon.

Complexation of the free terpyridine unit on the surface with (2) was performed by degassing a mixture of MeOH/CH$_2$Cl$_2$ (5:4) for 30 min at room temperature. The Ir(III) precursor (2) (5 mg, 0.003 mmol) and the substrate were added to the solution and heated under reflux conditions for 4 h. Afterward, the solution was cooled to room temperature and treated with an excess of NH$_4$PF$_6$. The mixture was stirred for additional 3 h at room temperature. The substrates were finally sonicated in MeOH and CH$_2$Cl$_2$ for several minutes, followed by drying in a stream of argon.

The complexation of the free terpyridine unit on the surface with Zn(II) and 4′-(4-ethynyl-phenyl)-2,2′:6′,2″-terpyridine was performed by adding the substrate to a mixture of CH$_3$CN/CHCl$_3$ (2:1) and Zn(OAc)$_2$ (5 mg, 0.026 mmol), followed by stirring under reflux conditions for 12 h. The substrate was sonicated in CH$_3$CN and CHCl$_3$ for several minutes, followed by drying in a stream of Argon. Afterward, the substrate was added to a solution of 4′-(4-ethynyl-phenyl)-2,2′:6′,2″-terpyridine (5 mg, 1.499 × 10^{-5} mmol) in a CH$_3$CN/CHCl$_3$ mixture (2:1) and stirred under reflux for 12 h. The substrate was sonicated in CH$_3$CN and CHCl$_3$ for several minutes, followed by drying in a stream of argon.

The opening of the Zn(II) bis-terpyridine complex on the surface was performed by immersing the substrate in a solution of concentrated HCl for 24 h at room temperature. Afterward, the substrate was sonicated three times in water for 5 min, followed by drying in a stream of argon.

Results and Discussion

In the field of supramolecular chemistry, the 2,2′:6′,2″-terpyridine unit is one of the most interesting and widely used chelating ligand. It can form a large number of different metal complexes with Ru, Fe, Zn, Co, Ni and Cu ions of different oxidations states, which are characterized by a broad range of physicochemical properties and different stabilities. To anchor these ligands on surfaces, a "clickable" precursor, 4′-(4-ethynyl-phenyl)-2,2′:6′,2″-terpyridine, was used, which was synthesized in a one-step procedure starting from 2-acetylpyridine and 4-ethynylbenzaldehyde.[49] The choice of the 1,3-dipolar cy-

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Scheme 1. Schematic Representation of the Synthesis of the Acetylene Functionalized Fe(II) Bis-terpyridine Complex (1) and the Clicking of 1 onto Silicon/Glass Substrates[a]
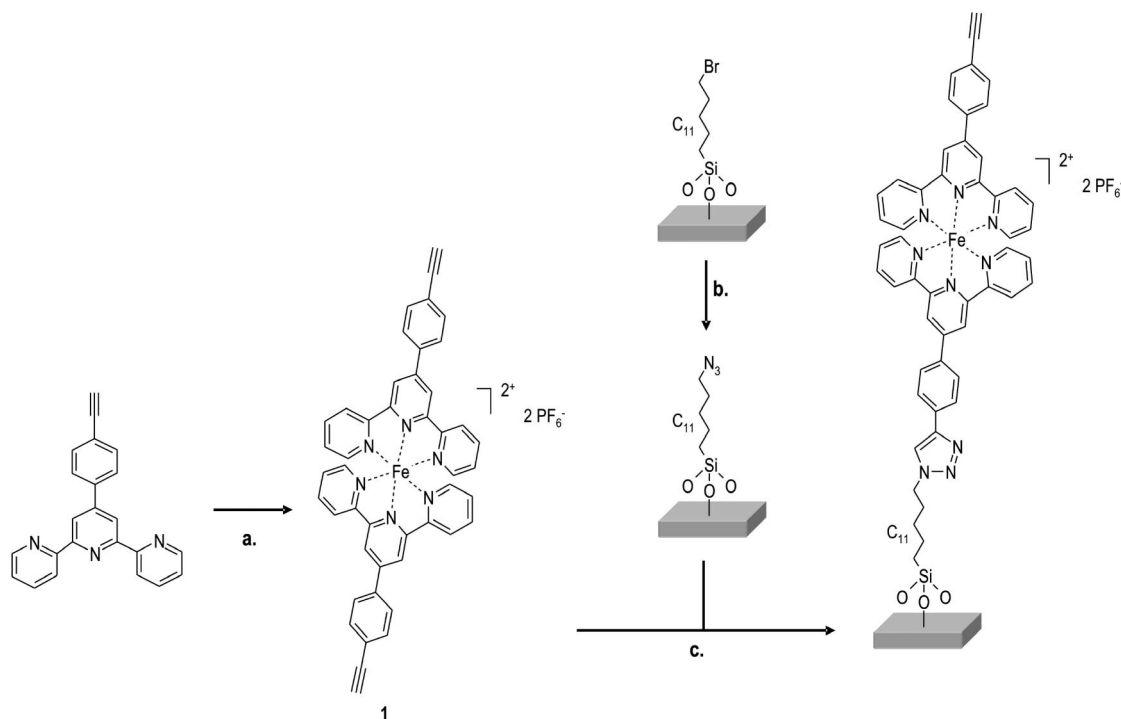
[a] Experimental conditions: (a) Fe(II) acetate; 1. $CH_3CN:CHCl_3$ (2:1), overnight, 80 °C, 2. NH_4PF_6, 3 h at room temperature; (b) NaN_3, 24 h, room temperature; (c) Fe(II) complex (**1**), $CuSO_4 \times 5H_2O$/sodium ascorbate or CuI, 24−48 h, 80 °C.

cloaddition click chemistry approach to attach the ligand on surfaces requires the use of copper(I) species as a catalytic system. As a consequence, a direct functionalization of surfaces with the uncomplexed acetylene functionalized ligand is not possible, because of the preferential formation of a bis-complex between the terpyridine ligand and the originally added Cu(II) ions. Therefore, an alternative route had to be developed, making use of the fact that Fe(II) bis-terpyridine complexes can be uncomplexed under suitable reaction conditions.[50−53] Thus, the synthesis of an acetylene functionalized Fe(II) bis-terpyridine complex (**1**) was identified as a possible route to finally obtain a surface functionalized with free ligands, with the Fe(II) ions functioning here as a kind of protection group. The protected supramolecular ligand (the iron(II) complex **1**) was clicked onto azide terminated monolayers, which were fabricated starting from 11-bromoundecyltrichlorosilane monolayers following a procedure described elsewhere.[48] An overview of the functionalization steps is displayed in Scheme 1.

These azide terminated monolayers were used for the 1,3-dipolar cycloaddition of the acetylene-functionalized complex. The click reaction of the Fe(II) complex (**1**) requires careful optimization of the reaction conditions (see Supporting Information). An excess of Cu(I) iodide, the increase of the reaction time to 48 h, and a reaction temperature of 80 °C resulted in the full conversion of the azide moieties. This conversion could be followed by IR spectroscopy. The corresponding spectra are depicted in Figure 1 (for the full characterizations of the whole reaction sequence see the Supporting Information). It is observed
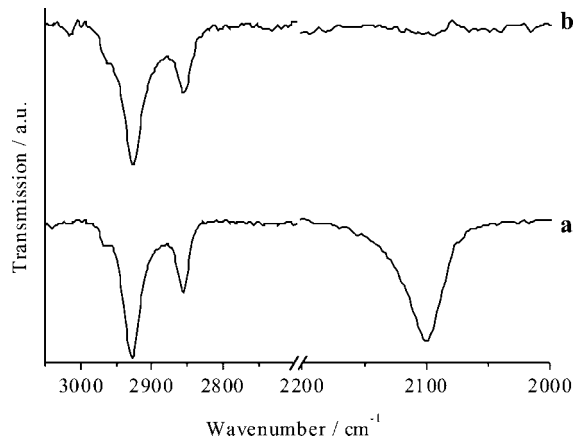
Figure 1. IR spectra of (a) the azide and (b) the clicked SAM with **1**.

that the absorption peak of the azide moiety at $2100\ cm^{-1}$ (Figure 1a) is not present anymore after the cycloaddition of the acetylene-modified Fe(II) complex (Figure 1b), indicating that the reaction was quantitative. However, the −CH_2 vibrations remain identical, which allows the conclusion that the monolayer is not significantly degraded during the reaction.

Additional evidence of the 1,2,3-triazole formation on the azide terminated monolayer was obtained from high-resolution XPS investigations of the N(1s) spectral region, which displayed only a single peak at 401 eV in contrast to a characteristic split-peak that was observed on the azide terminated monolayer (Figure 2a-b), thus confirming the conversion of the azide functions. The presence of the Fe(II) bis-terpyridine complex is, moreover, confirmed by the investigation of the Fe(2p) region of the XPS spectrum (Figure 2c). The clicked Fe(II) complex shows a characteristic splitting of the 2p orbital at 709.9 and 722.8 eV.
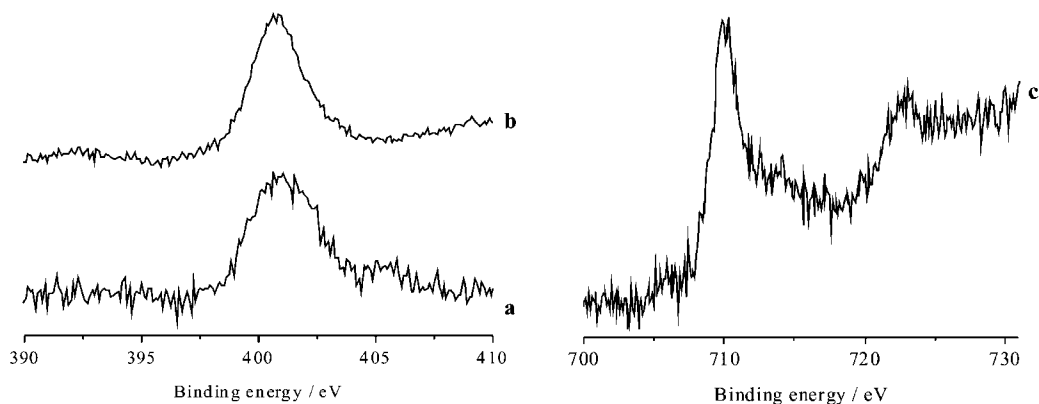
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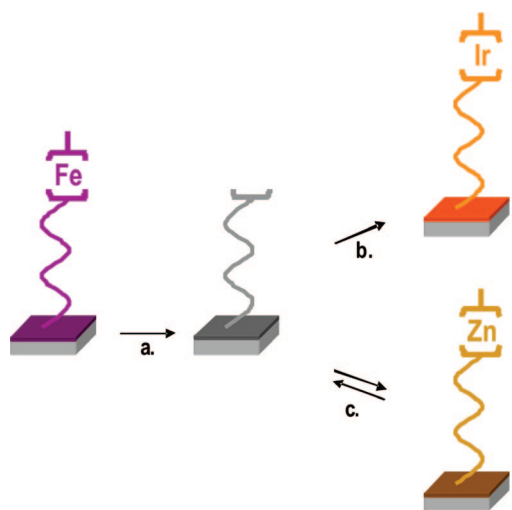(52) Hofmeier, H.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 1391–1397.

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Figure 2. Left: XPS spectra of the N(1s) region of (a) the azide and (b) the clicked SAM with (**1**). Right: XPS spectrum of the Fe(2p) region of (c) the clicked SAM with **1**.

Scheme 2[a]

[a] The attached Fe(II) complex was uncomplexed to obtain the free terpyridine ligands on the substrates (a). These units can be used for the subsequent complexation with an iridium precursor (b) or with Zn(II) ions; the latter system can be reversibly opened and closed (c).

The free ligand on the surface can be obtained by a subsequent decomplexation step (Scheme 2a). This can be performed by the addition of a strong competing ligand, i.e., hydroxyethyl ethylenediamine triacetic acid (HEDTA).[52,53] However, the limited stability of the silane monolayers with respect to basic environments does not allow this approach. Therefore, the decomplexation of the clicked Fe(II) complex was achieved by immersing the substrate in concentrated hydrochloric acid.

This process can be followed by UV/vis spectroscopy. The Fe(II) bis-complex exhibits a characteristic metal-to-ligand charge-transfer (MLCT) absorption band at 580 nm and a ligand-centered (LC) absorption at 350 nm, respectively (Figure 3a). Both absorption peaks are in good correlation with measurements of the synthesized complex in solution (**1**, see Supporting Information), where the MLCT band is observed at 570 nm and the LC band is detected at 320 nm.

After the decomplexation step, only a small MLCT absorption peak is observed at 576 nm in the corresponding UV/vis spectrum, whereas the absorption band for the terpyridine ligand remains at 322 nm (Figure 3b). This indicates that only a small percentage of the Fe(II) bis-terpyridine is remaining on the surface.

The uncomplexed terpyridine, covalently attached onto the surface, can be used for further complexation reactions with different metal ions. Thereby, the choice of the coordinating ion
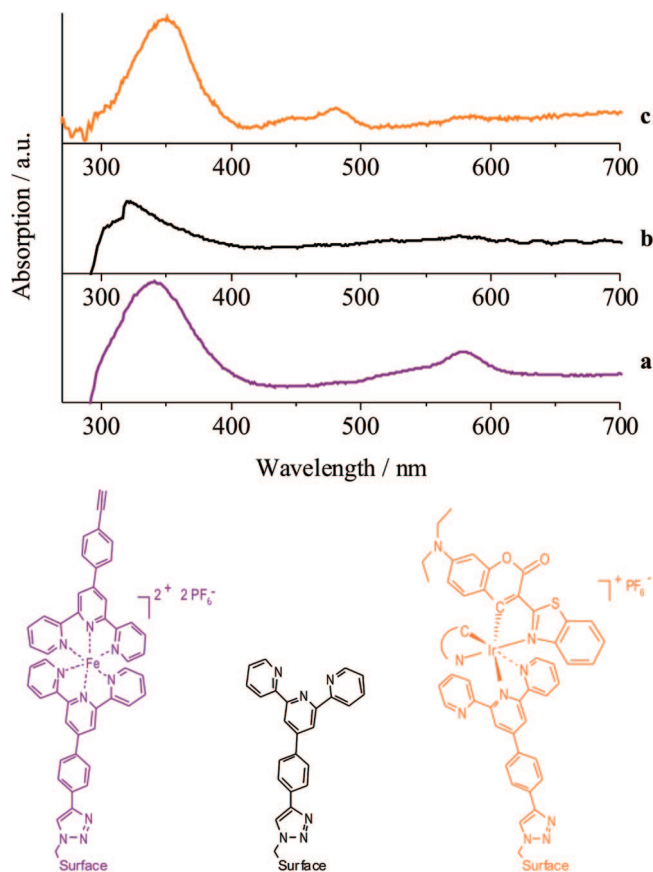

Figure 3. UV/vis spectra of (a) the clicked Fe(II) complex (**1**), (b) the free terpyridine units, and (c) the closed complex with iridium (**2**) onto glass.

determines the stability of the terpyridine complexes formed on the surfaces. While, e.g., Zn(II) or Fe(II) ions lead to a reversible complex formation (Scheme 2c), other coordinating metal ions, i.e., Ir(III) (Scheme 2b), will result in the formation of complexes with interesting optical properties.[54] To test the versatility of this approach, different reaction sequences have been performed. The substrates were characterized by means of UV/vis and XPS spectroscopy.

In a first step it was tested whether the terpyridine units are still accessible after the decomplexation cycle and can be used in further complexation reactions. Therefore, an Ir(III) precursor

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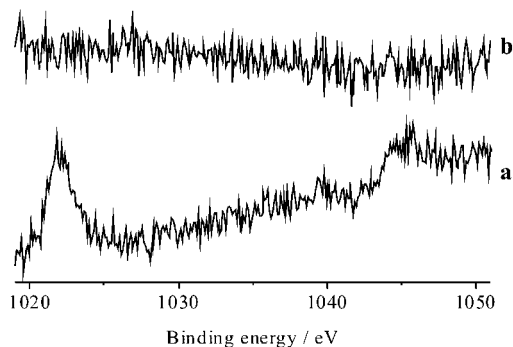
Figure 4. High-resolution XPS spectra of the Zn(2p) region of (a) the Zn(II) complex and (b) the uncomplexed terpyridine unit on the surface.

was used to form stable complexes on the ligand-functionalized surface. Additional luminescent properties were introduced by using coumarin-6 as a ligand in the iridium(III) precursor. Figure 3c displays the UV/vis spectrum of the corresponding functionalized glass substrate. The MLCT absorption arises at 480 nm, and the LC absorption is found at 340 nm. At 580 nm, a small absorption peak is still visible for the Fe(II) bis-terpyridine complex on the surface, which could not be completely uncomplexed. For comparison, the corresponding iridium model complex (**3**, see Supporting Information) was synthesized and revealed in solution an MLCT absorption at 486 nm and an LC absorption at 309 nm, which correlates to the obtained values on the substrate. The difference in the measured values for the LC absorption is attributed to the different environment of the molecules in solution compared to the surface. This indicates that the terpyridine units on the surface were successfully complexed with the Ir(III) precursor.

As an alternative to the complexation with Ir(III) ions, Zn(II) ions can be utilized to complex the terpyridine units on the surface to demonstrate the reversibility of the functionalization route. Compared to Fe(II) ions, Zn(II) bis-terpyridine complexes are also well-known to assemble and disassemble by changing, e.g., the pH value or the temperature.[52] Therefore, the terpyridine ligand-functionalized surface was treated with zinc(II) acetate and 4′-(4-ethynyl-phenyl)-2,2′:6′,2″-terpyridine in a two-step procedure to obtain a Zn(II) bis-terpyridine complex. The investigation with UV/vis spectroscopy is in this case not a suitable characterization tool, as the intraligand charge-transfer (ILCT) band for the Zn(II) complex does not differ significantly from the absorption band of the terpyridine ligand on the surface. Therefore, high-resolution XPS measurements, analyzing the Zn(2p) region, have been used as an alternative investigation

method. Figure 4 displays the XPS spectra for the complexed terpyridine units with Zn(II) and the subsequently uncomplexed Zn(II) complex on a glass substrate. The spectrum of the complexed terpyridine unit shows at 1022 and 1045 eV the 2p peaks for the zinc (Figure 4a). The splitting of the peaks is 23 eV, which is in accordance to literature values.[55] XPS investigations of the Zn(II) bis-terpyridine model complex (**4**, see Supporting Information), which was synthesized in solution, revealed the same peaks at 1022 and 1045 eV for the complex, indicating a successful complexation of the terpyridine units on the surface. After decomplexation ("opening") of the formed Zn(II) bis-complex on the surface with concentrated HCl, no peaks were found in the corresponding range of the XPS spectrum (Figure 4b).

Conclusions

Supramolecular terpyridine binding motifs have been used to reversibly functionalize surfaces. The controlled formation of complexes tethered to a monolayer of terpyridine precursors has been demonstrated. By the choice of the coordinating metal ion, the optical surface properties could be tuned. The introduction of suitable coordinating transition metal ions allows the reversible formation and disassembly of the surface bounded complexes. The results encourage future work to obtain highly selective surface functionalizations that can change their physicochemical properties as a result of the influence of external triggers. The present study demonstrates a first example of a reversible cycle that can be expanded and modified in a versatile and creative fashion to design surfaces with desired properties for the microfabrication of devices or for use in sensors.

Supporting Information Available: Instrumentation, synthesis of the supramolecular units and complexes, characterization of the surfaces, and table of the reaction conditions for the 1,3-dipolar cycloaddition of azide terminated substrates and the iron complex (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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