Two-Dimensional Structures

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# Synthesis of Free-Standing, Monolayered Organometallic Sheets at the Air/Water Interface**

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The recent discovery of how to obtain and utilize individual layers of graphite, that is, graphene,[1] and other inorganic monolayered sheets[2] has turned the spotlight brighter than ever on a basically ignored field of chemistry, the rational synthesis of two-dimensional polymers.[3] While there have been numerous reports on the synthesis of monolayered polymer films with irregularly networked internal structures[3] since the pioneering work by Gee in 1935,[4] little is known to date about the synthesis of a free-standing, 2D network with an ordered internal structure.[5] This paucity is contrasted by the richness of fragments of such networks that were obtained by approaches such as iterative organic synthesis,[6] self-assembly,[7,8] or on-surface polymerization.[9] As of now, the lateral dimensions of these fragments are too small to expect sheet-like properties; furthermore, they cannot yet be isolated and manipulated. Considering the huge application potential for structurally well-defined, free-standing 2D networks, which ranges from ultrasensitive membranes, molecular sieves, and devices based on high charge carrier mobility to materials with outstanding mechanical strength and the like, we felt the need to establish a synthesis program aiming at filling the gap between the one-dimensional (linear synthetic and biological polymers, carbon nanotubes, etc.) and the three-dimensional structures (hyperbranched and cross-linked bulk polymers, laminar crystals such as graphite, diamond, etc.) by providing access to structurally defined 2D polymers.[10] Herein we report the synthesis of a free-standing monolayer sheet consisting of the hexafunctional terpyridine (tpy)-based $D_{6h}$-symmetric monomer **1** (Figure 1) which was designed for the present purpose[11,12] and is to be held together by metal ion complexes[13,14] between ideally all six tpy units of one monomer with one of the tpy units of each of the six neighboring monomers. This mode of polymerization is in principle reversible and could allow for dynamic bond formation. It has often been used for construction of complex but well-defined compounds as well as supramolecular assemblies.[7,15,16] Figure 1 shows a targeted network. To avoid any three-dimensional growth of the coordination network during polymerization, monomer **1** was confined to two dimensions prior to polymerization by spreading it at the air/water interface on a Langmuir–Blodgett (LB) trough.[17,18] The main advantages of using the air/water interface for the present synthesis instead of solid substrates include 1) the flat and uniform surface on a large length scale, 2) the availability of the water subphase as a pool of reagents and catalysts, 3) the straightforward preparation and facile isolation of single sheets by transfer onto solid substrates and supports of all sorts,[19,20] 4) the possibility to preset the lateral surface pressure and lateral concentration of monomers prior to the polymerization, and 5) the ease in performing polymerization under ambient conditions.[21]

A sub-monolayer of monomer **1** was spread at the air/water interface from chloroform solution and compressed to a pressure of 30 $mN\,m^{-1}$. The compression process was monitored by Brewster angle microscopy up to 10 $mN\,m^{-1}$ and found to be fully reversible (Figure S1 in the Supporting Information) and to provide thin layers that are homogenous at the resolution of micrometers (Figure S2 in the Supporting Information). The point of inflection of the corresponding surface pressure–area isotherm (Figure 2a) was observed at a pressure of approximately 10 $mN\,m^{-1}$, from which a mean molecular area of approximately 520 $Å^2$ is estimated.[22] This preliminary value is in good agreement with the formation of a dense monolayer in which the monomers lie flat on the interface. This arrangement was supported by AFM contact-mode scratching and tapping-mode imaging experiments after vertical transfer of the compressed monolayer (at 10 $mN\,m^{-1}$) onto a mica substrate. Figure 2b shows the scratched area and the corresponding height profile, providing the apparent height $h_{app} \approx 0.8$ nm.[23] While $h_{app}$ values obtained by ambient-condition AFM are known to not accurately reflect real heights,[24] the value of approximately 0.8 nm nevertheless suggests a monolayer. Not only is it in a reasonable range for a conjugated structure, parts of which may significantly deviate from coplanarity,[25] but also a

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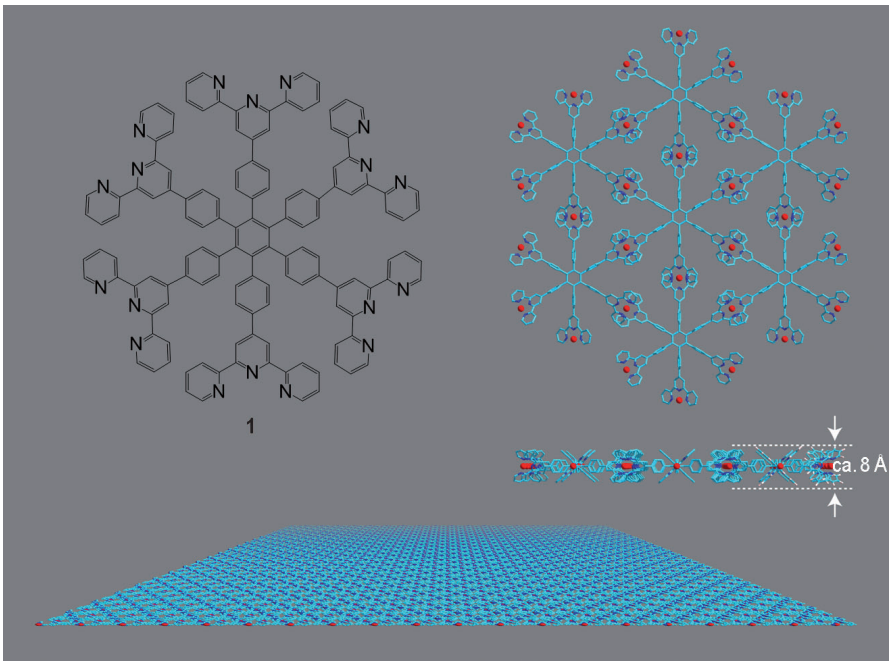


***Figure 1.*** Chemical structure of monomer **1** and small- and large-scale representation of an idealized two-dimensional network obtained from **1** through metal ion complexation between terpyridine units of adjacent monomers (metal ion red, C turquoise, N blue). The center image contains a cross-sectional view to estimate the layer thickness ($h \approx 8$ Å, without counterions).

vertical or tilted packing of monomers should result in much larger $h_{app}$; note $d(\mathbf{1}) = 3.0$ nm. Furthermore, this latter packing would be in contradiction to the mean molecular area. When irradiated with a conventional UV lamp at $\lambda =$ 254 nm, the monolayer at the interface shows a blue fluorescence (Figure S4 in the Supporting Information). There was at no time any fluorescence outside the barriers, indicating that the monomer does not submerge into the subphase. The monomer is arranged at the interface in a 2D manner, which was a prerequisite for the planned polymerization.

Polymerization is based on the complexation between tpy units of adjacent monomers for which appropriate metal salts are supplied from the water subphase, which then diffuse to the monomers at the interface. While the formation of bis(tpy) complexes of metal cations in organic media is well known,[14] the same in water, where protonation of tpy and hydroxylation (and subsequent oxidation) of the metal salts may compete with complexation, has practically not been studied. To get as close as possible to the environment of metal complexes at the air/water interface, the water-soluble tpy derivative **2** (Figure 2c) was synthesized and its complexation with stoichiometric amounts (0.5 equiv) of $Co^{2+}$, $Ru^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Ni^{2+}$, and $Fe^{2+}$ analyzed by UV/Vis spectroscopy in water (Figure 2c,d). Similar to the case with organic media, the mixture of **2** with $Fe^{2+}$ gave rise to a strong metal-to-ligand charge-transfer (MLCT) band[26] around 556 nm. This peak is well separated from all other absorbances and should also appear in complexes involving monomer **1**, yet at a somewhat shifted wavelength (see below). This finding allowed for direct monitoring by UV/Vis spectroscopy of the polymerization in the monolayer, assuming that the intensity of the MLCT band from the complexed monomers is high enough. Therefore, $Fe^{2+}$ was employed for the polymerization study using an LB trough equipped with a quartz glass window in the bottom for in situ UV/Vis spectroscopic monitoring (Figure S5 in the Supporting Information). As all experiments were conducted under ambient conditions, possible oxidation of $Fe^{2+}$ was prevented by using $Fe(NH_4)_2(SO_4)_2$. This iron source ensured a slightly acidic pH value of the subphase ($pH < 6.5$).[27,28] The efficiency of this complexation reaction has an obvious bearing on the polymerization. A titration study showed that the bis(tpy) complex **3** forms quantitatively for the stoichiometric ratio **2**:$Fe^{2+} = 0.5$ and that the complex stays stable even for a large excess of $Fe^{2+}$ (**2**:$Fe^{2+} = 5$, Figure S6

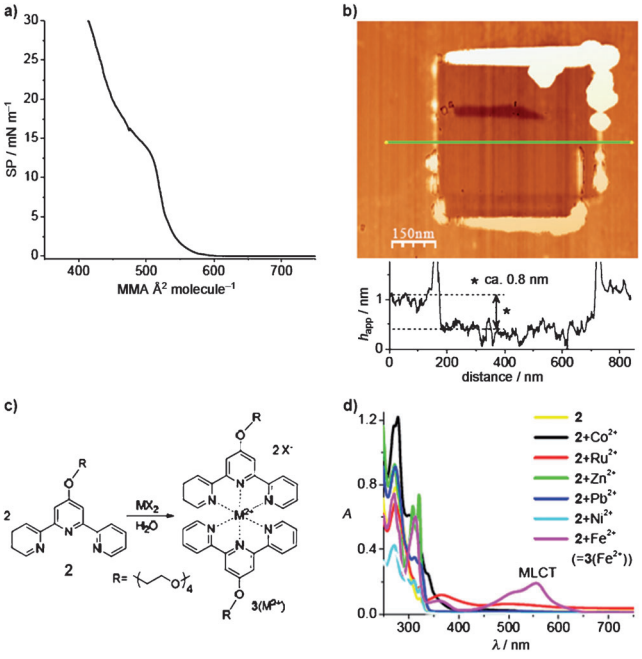


***Figure 2.*** a) Preliminary surface pressure (SP)–mean molecular area (MMA) isotherm of monomer **1** spread at the air/water interface at 20 °C with a compression rate of 2 mm min$^{-1}$. b) AFM scratching experiment of a monomer layer of **1** after vertical transfer onto a mica substrate. The green line indicates where the height profile was recorded. To make sure that the organic layer had been scratched away without part of the substrate, it was shown that a much higher force is needed to scratch the latter (see dark brown area). c) Addition of the transition-metal salts $MX_2$, $M^{2+} = Co^{2+}$, $Ru^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Fe^{2+}$, to aqueous solutions of the tpy derivative **2** for possible bis complexation, and d) the UV/Vis spectra of the resulting solutions in water. The addition of $Fe^{2+}$ was accompanied by the appearance of a strong MLCT band, thus confirming the formation of the complex **3**($Fe^{2+}$), which was used as a convenient read-out of complex formation.

in the Supporting Information).[29] This finding made us hope for the same to happen at the interface.

The experimental variables include choice of metal salt and its concentration, pH value, surface pressure and temperature of the water subphase, and how to deposit the monomer onto the surface and the metal salts into the subphase. For post-polymerization analysis, the choice of the solid support and how to transfer and dry the product sheets are also key issues. Because of this manifold of parameters, the impact of which is only partially understood, the decisions on how to proceed were made with a portion of intuition. Regarding surface pressure, an intermediate value of $2\,mN\,m^{-1}$ was mostly applied.[30] On the one hand, this pressure should be low enough to leave the monomers (on average) sufficient lateral mobility to undergo the substantial structural rearrangements that are required for the complexation to take place. On the other, it should be high enough to keep contraction of the monolayer during complexation to a minimum. Substantial contractions can cause problems with the structural integrity of films.[3] We cannot yet say whether or not the reversibility of the bond formation between tpy and $Fe^{2+}$ has a bearing here. Furthermore, it was decided to first create the monolayer and then add the metal salt to the subphase with a syringe. Though this mode of addition is convenient, it has the disadvantage that, particularly right after the injection, the metal salt concentration in the subphase fluctuates strongly. The polymerization at the interface may even have already started before a homogenous distribution of the salt is reached. Under such non-equilibrium conditions, kinetic studies could not be performed. The final concentration of $Fe^{2+}$ in the subphase was chosen to be approximately 0.1 mM, which represents a considerable excess of metal salt to tpy units. This excess was large enough to ensure a fast complexation but at the same time small enough to prevent formation of a large amount of salt crystallites on the films during transfer and drying. If the salt was injected directly under the optical setup, a low-intensity signal reproducibly appeared at $\lambda = 578$ nm within one minute and reached its final intensity within 10 min (Figure 3). This signal remained unchanged for hours, thus indicating complete conversion but not conclusively demonstrating it. Based on the study using model compound **3**($Fe^{2+}$), this signal was assigned the MLCT of the network $[\mathbf{1}(Fe^{2+})_x]_n$ $(0 < x < 3)$.[31] This film was also transferred onto a quartz glass substrate to get an improved signal-to-noise ratio[32] and to check whether the MCLT would remain. Not only did the ratio improve significantly, but also the MCLT in fact remained (Figure 3). This finding allowed us to conclude that the $Fe^{2+}$–tpy bonds in $[\mathbf{1}(Fe^{2+})_x]_n$ $(0 < x < 3)$ are strong enough to survive the mechanical stress associated with the transfer and that the polymerized monolayer acts largely as an entity. The polymerization of the monolayer was also supported by a complete disappearance of the monomer fluorescence upon addition of the $Fe^{2+}$ salt.[33] The experimental setup for polymerization, in situ spectroscopy, and transfer is shown in Figure S5 in the Supporting Information.

Next, the transfer of the polymerized monolayer was investigated more intensely. A silicon wafer covered with 300 nm $SiO_2$ and holey solid supports (regular Cu and lacey carbon TEM grids) were used to address the following questions: Do the products remain monolayers during polymerization and transfer? Which lateral sizes do the sheets have after transfer? Are the networks mechanically stable enough to span holes? These issues were addressed by 1) vertical transfer onto $SiO_2$/Si, 2) vertical transfer onto quartz glass, and 3) horizontal transfer either from top onto a TEM Cu grid or from the subphase onto a lacey carbon grid. AFM, optical microscopy (OM), and TEM images corresponding to (1) and (3) are displayed in Figure 4.

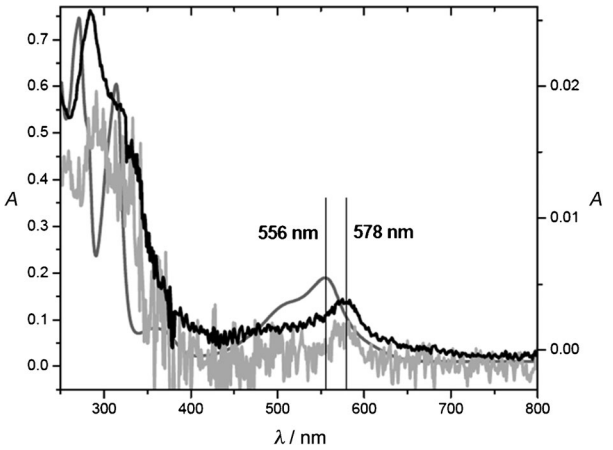


***Figure 3.*** UV spectra with absorbance of model complex **3**($Fe^{2+}$) (dark gray, left *y* axis) and the monolayer network $[\mathbf{1}(Fe^{2+})_x]_n$ $(0 < x < 3)$ before (light gray line, right *y* axis) and after transfer onto quartz glass (black line, right *y* axis). The intensities of the two polymer spectra cannot easily be compared. Though the pre-set lateral pressure at transfer was the same as when recording the in situ spectrum, there may be several effects operative that can impact the measured intensities in both directions. These effects include incomplete transfer and tablecloth effects; also note that the glass plate was covered on both sides during vertical transfer.

The AFM image in Figure 4a shows homogeneous, partially folded sheets after a brief and mild thermal annealing. Height profiles were recorded at several sites and give $h_{app} \approx (1.3 \pm 0.1)$ nm for the height of a sheet on the substrate and $h_{app} \approx (1.4 \pm 0.1)$ nm when a fold is involved (Figure S7 in the Supporting Information). The section analysis indicated in Figure 4a by a white line reveals a monolayer and a triple layer, whereby the latter can be attributed to tablecloth-like folding of the sheet. These heights agree reasonably well to the cross-sectional height $h = 0.8$ nm of one sheet obtained from the model in Figure 1 considering counter ions ($SO_4^{2-}$) and possibly a water layer. The optical micrograph in Figure 4b has a scale bar of 200 μm, showing that the sheets reach truly macroscopic dimensions. The TEM image in Figure 4c demonstrates that they are stable enough to span over $20 \times 20\ \mu m^2$-sized holes (ca. $5 \times 10^7$ monomers per hole), despite the obvious ruptures. It is difficult to differentiate whether rupture and crumpling events happen during transfer or during drying. Note that the sheets are sensitive to an electron beam (100 kV, 20 °C). Upon focusing, they rupture almost instantaneously. Considering the charged nature of the sheets, the removal of the last water molecules may play a critical role and exert substantial

  

forces. If the sheets do not strongly adsorb on the substrate during drying, they contract and shrivel up such that sharp ridges are formed (Figure 4d). It should be noted that all features shown in Figure 4 are tightly connected to the action of $Fe^{2+}$. Monolayers of **1** alone do not span holes at all.

In sum, this work demonstrates the synthesis of the first monolayered, metal-complexed, large sheet ($>500\times500\ \mu m^2$) that has sufficient mechanical strength to be free-standing over $20\times20\ \mu m^2$-sized holes. It is a straightforward approach to a 2D structure, which is based on monomer pre-orientation at the air/water interface and supply of connector units from the subphase. This approach has the potential for structure self-correction owing to the reversible nature of the bond between monomer and connector and avoids potential complications associated with exfoliation of sheets from laminar crystals or isolation of sheets from solid substrates. While according to AFM, OM, and TEM the sheets are homogeneous, their molecular structure still requires proof before they may qualify as 2D polymers according to a recent definition by our laboratory.[3] In this context, it should be noted that the intensity of the MLCT band does converge,[34] and the model complexation of **2** to **3** yields virtually 100% conversion even with the stoichiometric amount of $Fe^{2+}$; moreover, complex **3** withstands even a high excess of $Fe^{2+}$. Though other metal cations may not provide a convenient MLCT probe for complexation as $Fe^{2+}$ does, they offer interesting options, including a better healing capability based on reversible complexation with weakly binding cations such as $Zn^{2+}$ and generation of even more stable networks by the use of more strongly binding cations such as $Ru^{2+}$.[35] Furthermore, the monomer structure can be easily altered in terms of spacer lengths between tpy and central benzene ring as well as the number of arms. Such modification will eventually allow for control of mesh size. We thus foresee a bright future for this approach to synthetic 2D polymers with interesting mechanical, optical, and redox properties.[36]

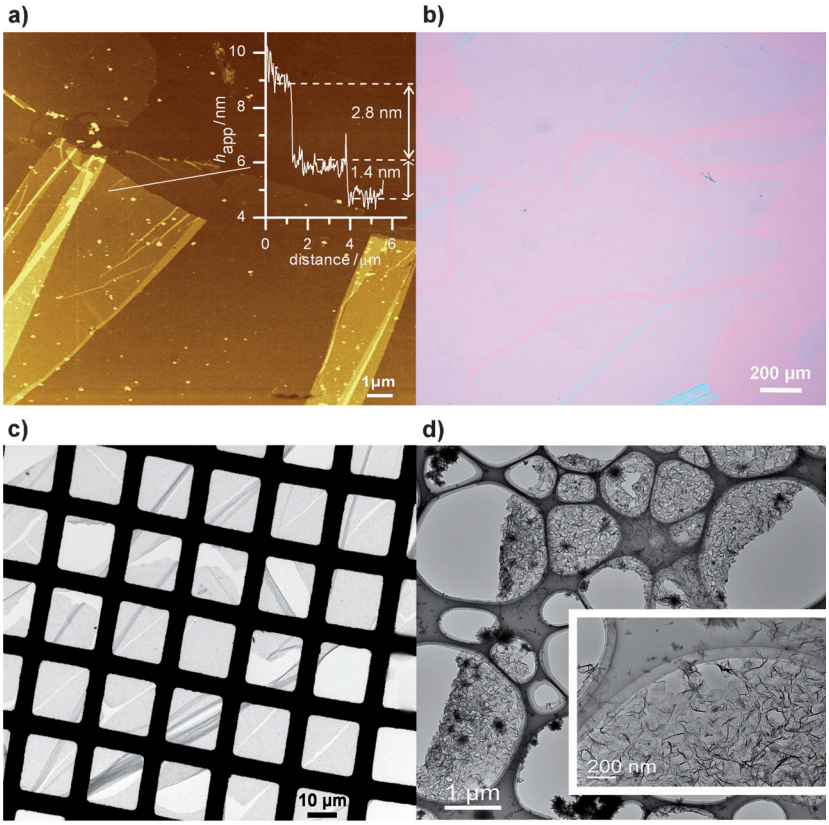


***Figure 4.*** Microscopy images of the sheet $[\mathbf{1}(Fe^{2+})_x]_n$ ($0<x<3$). a) Tapping-mode AFM image with height profile measured along the white line and b) OM image after vertical transfer onto 300 nm $SiO_2$/Si and annealing for 2 min at approximately 80 °C. c) TEM image after horizontal transfer from top onto a Cu grid with $20\times20\ \mu m^2$ sized holes. d) TEM images at two different magnifications after horizontal transfer from the subphase onto a lacey carbon grid. The white spots in (a) likely stem from small crystals of excess iron salt. The color contrast in the OM image (b) is caused by optical interference. The film in (c) was obtained at 10 mN m$^{-1}$. For a large-scale representation of these four images, see Figure S7 in the Supporting Information.

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[21] Neither pyrolytic nor ultra-high-vacuum conditions are necessary.

[22] Because of the considerable uncertainties associated with the determination of the mean molecular area, we wish to compare this value with those we consider the extremes. The smallest area is derived from a single crystal structure of **1** (see Figure S3 in the Supporting Information) in which the monomer is layered and strongly interdigitated. The largest area is derived from a simple model consideration taking the monomers as discs with the realistic diameter of $d = 3.0$ nm in a hexagonal dense packing. The corresponding mean molecular areas are 340 and 780 $Å^2$, respectively.

[23] If the same experiment was repeated at 2 $mN\,m^{-1}$, $h_{app} = 0.6$–0.7 nm.

[24] a) D. Beaglehole, H. K. Christenson, *J. Phys. Chem.* **1992**, *96*, 3395 – 3403; b) G. Yang, J. P. Vesenka, C. J. Bustamante, *Scanning* **1996**, *18*, 344 – 350; c) S. J. T. Van Noort, K. O. Van der Werf, B. G. De Grooth, N. F. Van Hulst, J. Greve, *Ultramicroscopy* **1997**, *69*, 117 – 127; d) W. Zhuang, C. Ecker, G. A. Metselaar, A. E. Rowan, R. J. M. Nolte, P. Samori, J. P. Rabe, *Macromolecules* **2005**, *38*, 473 – 480.

[25] The extremes of monomer thickness are approximately 0.34 and 0.8 nm. They refer to the fully coplanar conformation, which should result in a similar thickness as a sheet in graphite, and the conformation in which at least one of the tpy units stays orthogonal to the rest, respectively. We consider the fully coplanar conformation unlikely. See Figure S3 in the Supporting Information.

[26] See for example: a) M. L. Stone, G. A. Crosby, *Chem. Phys. Lett.* **1981**, *79*, 169 – 173; b) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993 – 1019.

[27] The pH values of bulk solution can differ from those near interfaces: a) P. B. Petersen, R. J. Saykally, *Chem. Phys. Lett.* **2008**, *458*, 255 – 261. Moreover, interfacial acid – base equilibria of molecular assemblies depend on their inner structures: b) J. G. Petrov, D. Möbius, *Langmuir* **1993**, *9*, 756 – 759.

[28] A thorough study on the influence of pH value upon the complexation in water is underway.

[29] Neither the spectrum as such nor the intensity of the MLCT absorption changed upon addition of this excess. This result makes formation of mono(tpy) complexes unlikely.

[30] Though this value was formally kept constant during polymerization, physically this is not meaningful. Surface pressure measurements depend on the reversible interaction between Wilhelmy plate and monolayer. Upon polymerization the reversible situation is gradually converted into an irreversible one, which eventually will result in the plate "frozen in" into the polymer.

[31] While the tpy units in **3** have a donor substituent (the oligo(ethylene glycol) chain), those in **1** are acceptor-substituted. This

  

situation should render the charge transfer from metal to ligand easier for the complexes in the monolayer and thus provides an explanation for the red shift. It should be noted that intramolecular complexes between $Fe^{2+}$ and two tpy units of the same monomer are considered unlikely because of the rigidity of the monomer skeleton.

[32] There are substantial intensity losses associated with the use of fiber optics in the in situ experiment.

[33] This disappearance does not necessarily indicate full monomer conversion because of a possible energy transfer from unreacted monomers to complexed sites and subsequent non-irradiative deactivation.

[34] Preliminary XPS investigations suggest conversions of approximately 65%: Z. Zheng, T. Bauer, J. Sakamoto, A. D. Schlüter, unpublished results.

[35] A $Ru^{2+}$ source that can be used under ambient conditions has been reported: V. Grosshenny, R. Ziessel, *J. Organomet. Chem.* **1993**, *453*, C19–C22.

[36] See for example: V. Balzani, A. Juris, M. Venturi, *Chem. Rev.* **1996**, *96*, 759–834.

  