Organometallic Superstructures

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Tetrakis(arylisocyanide) Rhodium(I) Salts in Water: NIR Luminescent and Conductive Supramolecular Polymeric Nanowires with Hierarchical Organization**

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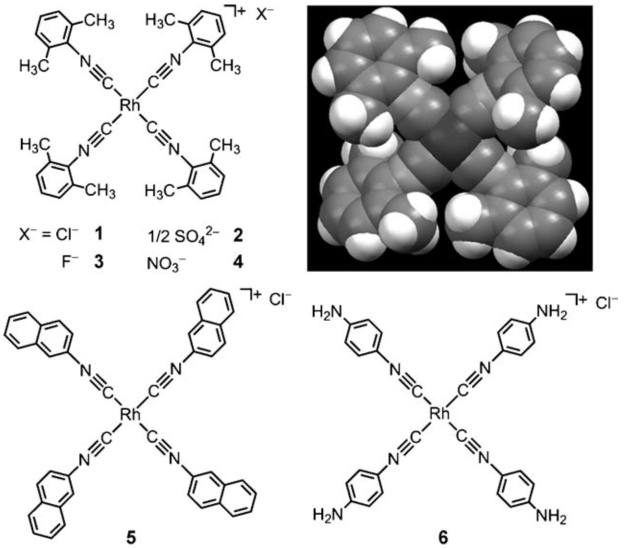
Considerable interest has been focused on functionalized quasi-one-dimensional (quasi-1D) nanostructures self-assembled from organic/organometallic molecular building blocks.[1] Directional intermolecular interactions, typically π–π stacking,[2] hydrogen-bonding,[3] metal–ligand coordination,[4] and metal···metal contacts,[5,6] play a key role in directing the anisotropic growth of supramolecular nanostructures. For nanowires and nanofibers with large aspect ratios, multiple aliphatic chains are introduced covalently to the periphery of the molecular building blocks to enhance their amphiphilic properties and to enable solution processability. This modification could compromise the crystallinity of the nanostructures and sometimes leads to entangled fibrillar networks (gels) with high yield stress, which makes it a formidable task to align the nanowires or to isolate a single nanowire.[7] Herein we report ultralong crystalline nanowires self-assembled from organorhodium(I) salts and their hierarchical organization in water. These nanowires in aqueous dispersions have a strong tendency to bundle and align along a shear force and therefore can be conveniently processed and transferred into electrical devices. In addition, these supramolecular nanowires are luminescent in the near-infrared (NIR) region and are electrically conducting.

We recently reported that organoplatinum(II) complexes bearing an extended π-conjugated ligand and a hydrophilic anion can self-organize, through extended $Pt^{II}\cdots Pt^{II}$ interactions, into viscoelastic chromonic mesophases in water.[6d] The following questions naturally arise: Can this design strategy be applied to other organometallic complexes, and can any differences and advances be achieved by varying the central metal? Both rhodium(I) and platinum(II) ions are in a d^8 electronic configuration, and rhodium(I) complexes homoleptically coordinated with four isocyanide ligands have long been known to self-associate into cofacial oligomers in highly concentrated organic solutions and give characteristic low-energy $4d\sigma^*\rightarrow 5p\sigma$ transitions derived from close $Rh^{I}\cdots Rh^{I}$ contacts.[8] Despite the extensive chemistry of tetrakis(isocyanide) rhodium(I) salts, their aggregation behavior in water remains elusive. Our present study shows that the tetrakis(arylisocyanide) rhodium(I) system is distinct from the previously reported organoplatinum(II) system[6d] in three ways: its self-aggregation mechanism, its long-range order, and the conductivity of the resultant nanostructures.

We focus on the salts $[Rh(C{\equiv}N\text{-}2,6\text{-xylyl})_4]X$ (Scheme 1, $X = Cl$,[9] $\frac{1}{2}SO_4$, and F for **1**–**3**, respectively; see the Supporting Information for preparation details). The bulky 2,6-xylylisocyanide ligand is anticipated to render the planar four-coordinate rhodium(I) cation hydrophobic. The chloride, sulfate, and fluoride anions were chosen to increase the hydrophilicity of the salts, in view of the excellent hydrating capability of these anions in the lyotropic series.[10] Regarding amphiphilicity, these organorhodium(I) salts are distinct from conventional surfactants that integrate aliphatic chains with ionic heads, but are similar to chromonic mesogens, which possess a rigid molecular plane surrounded by peripheral ionic groups.[11] For comparison, complex **4** with a nitrate



Scheme 1. Chemical structures of the rhodium(I) complexes **1**–**6** and a space-filling drawing[9] of the cation in complexes **1**–**4**.

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anion, and complexes **5** and **6** homoleptically coordinated with a hydrophobic naphthyl-2-isocyanide and a hydrophilic (4-aminophenyl)isocyanide, respectively, were prepared and studied.

Complexes **1**–**3** self-aggregate even in dilute aqueous solutions. Methanolic solutions of **1**–**3** at concentrations ranging from 5.0×10^{-5} to $5.0\times10^{-4}\,\mathrm{mol\,dm^{-3}}$ are yellow. In contrast, complexes **1**–**3** at these concentrations are soluble in boiling water to give wine-red solutions with a low-energy absorption band at $\lambda_{max}=530$ nm (Figure 1 a), indicating a dimeric aggregate with a $Rh^{I}\cdots Rh^{I}$ interaction.[8b] Upon cooling from 80 to 20 °C, these aqueous solutions become blue and display a lower-energy absorption band at $\lambda_{max}\approx625$ nm, which is attributable to trimeric or even higher aggregates.[8b] The temperature-dependent spectral traces are fully reversible. These findings imply that complexes **1**–**3** are oligomerized in their aqueous solutions at a concentration lower than $5.0\times10^{-5}\,\mathrm{mol\,dm^{-3}}$ and at a temperature higher than 80 °C (Figure 1 a). It is notable that complex **1** is stable in the solid state and in methanol, but in ethanolic solution it transforms into neutral $[Rh(C{\equiv}N\text{-}2,6\text{-xylyl})_3Cl]$ complex, as a result of a competitive ligand-exchange reaction between isocyanide and chloride anion.[12] Complexes **2** and **3** do not reveal such an instability problem. In contrast, complexes **4** and **5** are soluble but quickly decompose in hot water. Complex **6** is soluble in cold water to form a brown solution that exhibits birefringence between two crossed polarizers (see the Supporting Information).

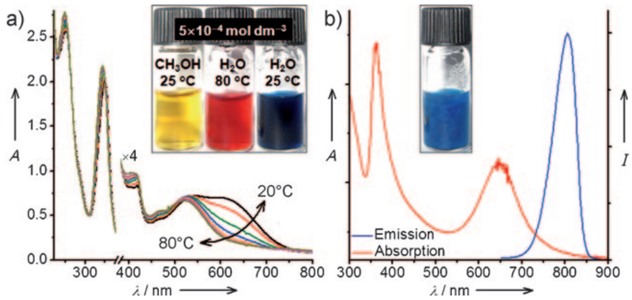

Figure 1. a) UV/Vis absorption traces of **2** in water (concentration ca. $5.0\times10^{-5}\,\mathrm{mol\,dm^{-3}}$) upon varying the temperature from 20 to 80 °C. The inset shows complex **2** in methanolic and aqueous solutions at a concentration of $5.0\times10^{-4}\,\mathrm{mol\,dm^{-3}}$. b) UV/Vis absorption and emission spectra of an aqueous dispersion of nanowires of **2** at 298 K. The inset shows the nanowire dispersion at a concentration of $5.0\times10^{-4}\,\mathrm{mol\,dm^{-3}}$, prepared by aging the aqueous solution shown in (a).

Virtually homogeneous blue dispersions with silky sheen were obtained when the above-mentioned aqueous solutions of **1**–**3** were aged at room temperature for over 12 h (Figure 1 b, inset). UV/Vis absorption and emission spectra of the as-prepared dispersions showed a distinct low-energy band at $\lambda=645$ nm and a structureless NIR transition at $\lambda=806$ nm, respectively (Figure 1 b). These spectroscopic characters could be attributed to a typical $4d\sigma^{*}\rightarrow5p\sigma$ excited state associated with extended $Rh^{I}\cdots Rh^{I}$ interactions.[8b] The incipient red and blue solutions were regenerated by boiling the dispersion and subsequently cooling to room temperature. Dispersions of **2** and **3** were stable for months, whereas a small amount of $[Rh(C{\equiv}N\text{-}2,6\text{-xylyl})_3Cl]$ (isolated and characterized by its NMR spectrum) precipitated out as a yellow solid from the dispersion of **1** within several days. The self-aggregation of the organorhodium(I) salts in water is evidently a nucleation–elongation process,[13] which is distinct from the chromonic mesophases of organoplatinum(II) complexes formed through an isodesmic mechanism.[6d]

Microscopic observations revealed randomly distributed ultralong crystalline nanowires in the blue aqueous dispersions of **1**–**3** with a concentration of $5.0\times10^{-4}\,\mathrm{mol\,dm^{-3}}$. We take complex **2** as a representative example. These nanowires exhibited birefringence typical for anisotropic crystals under polarized optical microscopy (POM) (Figure 2 a). Scanning (Figure 2 b) and transmission (Figure 2 c) electron microscopy revealed the diameters and lengths of these nanowires to be down to 50 nm and up to millimeters, respectively. Some of these nanowires were bundled to form thicker fibers with diameters in the submicrometer scale. The selected-area electron-diffraction pattern (Figure 2 c, inset) of a single nanowire showed sharp and ordered spots with a d space of 16.9 Å in the transverse direction and elongated streaks with a d space of 4.0 Å along the longitudinal direction. We successfully indexed most of the low-angle peaks in the X-ray diffraction pattern (Figure 2 d) of nanowires of **2** based on a primitive monoclinic lattice with $a=16.9$ Å, $b=15.3$ Å, $c=14.5$ Å, and $\beta=102°$. The value of 16.9 Å is close to the diagonal dimension (ca. 15.8 Å) of the $[Rh(C{\equiv}N\text{-}2,6\text{-xylyl})_4]^{+}$

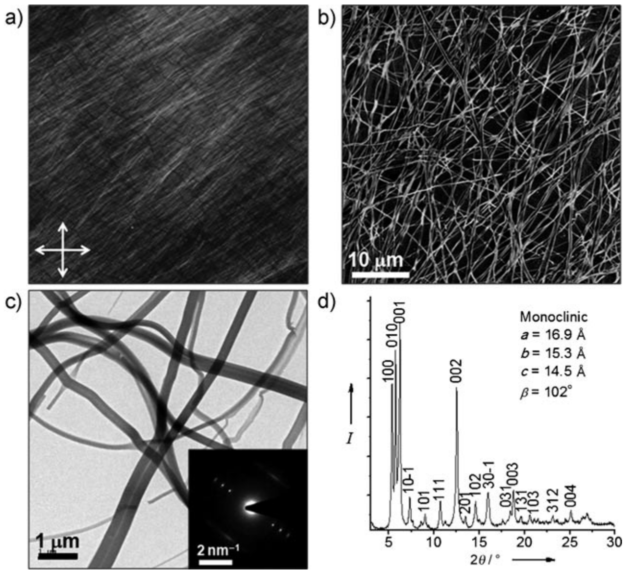

Figure 2. Microscopic and X-ray diffraction studies on nanowires of complex **2**. a) Optical micrograph of the nanowires in a drop of the aqueous dispersion sandwiched between two crossed polarizers. The double arrows indicate the configuration of the polarizers. b) Scanning and c) transmission (Inset: SAED pattern of a single nanowire) electron micrographs of the nanowires. d) Powder X-ray diffraction pattern of the nanowires drop-cast on a glass slide.

plane. We therefore infer that the nanowires grew along the *b* axis, which is also likely the direction of the propagated $Rh^I \cdots Rh^I$ interactions.

Depending on the concentrations of complex and processing protocols, nanowires of **1**–**3** exhibited a variety of hierarchically organized superstructures that can be discerned by the naked eye. Again we take complex **2** as a representative example. Discrete spherulites with diameters in the millimeter scale were found in aqueous dispersions at concentrations of 5.0×10^{-5} mol dm^{-3} or lower. The well-defined sphere-like shape and radially distributed nanowires in such a spherulite suspended in water are shown in Figure 3a. The POM image of the spherulite (Figure 3b) exhibited birefringence with a Maltese cross pattern, indicating a highly ordered arrangement of the self-organized nanowires. These spherulites could be readily transferred with a pipette to other containers or surfaces. SEM observations (see the Supporting Information) of a spherulite dried on a silicon wafer revealed radially distributed nanowires from a collapsed center. This could be a rare example of a macroscopically ordered superstructure self-organized from small organometallic molecules.

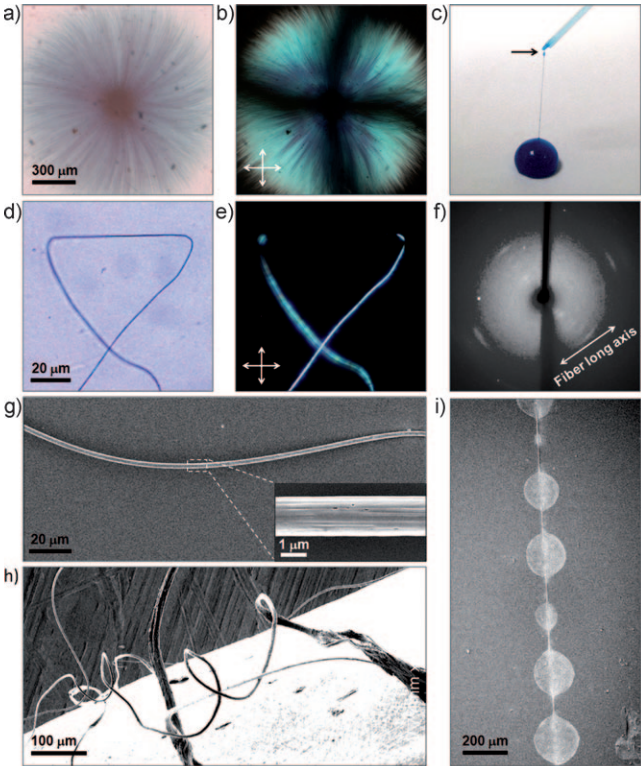

Figure 3. Hierarchical organization of the nanowires of **2**. a) Bright-field image and b) polarized optical microscopy (POM) image of a spherulite suspended in water. The double arrows indicate the configuration of the polarizers. c) Snapshot of a microfiber being fished out by a capillary (inner diameter 0.3 mm) from an aqueous dispersion of nanowires. The arrow refers to a small drop of water sticking to the microfiber. d) Bright-field image, e) POM image, f) 2D X-ray diffraction pattern, and g) SEM image of such a single microfiber. SEM images of h) a helical microfiber and i) a series of spheres threaded by a microfiber. All these superstructures were prepared by drawing from the aqueous dispersion of nanowires and dried in air before SEM observations.

Microfibers with optical uniaxiality and crystalline order can be readily fished out (Figure 3c) with a capillary from the aqueous dispersions of complexes **1**–**3**. This process resembles the silk reeling process from a hot soup of cocoons,[14] but differs from the previously reported organoplatinum(II) fiber-drawing system,[6d] which is similar to the extruding process of a dragline from the stock solution inside a silkworm. The diameters and lengths of the as-prepared organorhodium(I) microfibers were down to one micrometer and up to 10 cm, respectively, leading to an aspect ratio up to 10^4. These microfibers were flexible and could be folded (Figure 3d) without sacrificing their optical uniaxiality. This was confirmed by POM observations (Figure 3e). For a curved single microfiber, only the segments oriented approximately 45° to both of the polarizers have the maximized birefringence, whereas those parallel to either of the polarizers appeared dark. The 2D X-ray diffraction pattern (Figure 3 f) of such a single microfiber exhibited characteristic *d* spaces (16.5 and 4.1 Å) close to those orientations derived from the SAED result recorded with a single nanowire (Figure 2d). This result is consistent with SEM observations (Figure 3g) that the single microfibers were formed by nanowires well-aligned along the shear direction.

Interestingly, because the freshly fished microfibers were wetted by water, the morphology of the microfibers could be manipulated at will before the water completely evaporated. Figure 3h,i shows SEM images of a helixlike microfiber and a straight microfiber with threaded nanowire knots, respectively. The former was prepared by swirling the capillary during the fishing process and the latter by drawing the microfiber at a relatively slow velocity. Small drops of water sticking to the microfiber during the slow drawing process are responsible for the formation of the threaded knots shown in Figure 3i. SEM images at a higher magnitude (see the Supporting Information) reveal randomly distributed and well aligned nanowires in the knot and the thread regions, respectively. This finding is reminiscent of the nanostructures of spider silks that can harvest water drops at spindle-knots on the hydrophilic protein fiber threads.[15] Thus, we envisage that the organorhodium(I) superstructures could be a biomimetic venue for such a natural system of water collection.

The well-defined molecular and hierarchical order in the aligned nanowires of complexes **1**–**3** led us to study their electrical conductivity. A bundle of nanowires was fished out from an aqueous dispersion of complex **2** and oriented across the 50 µm channel of prefabricated gold electrodes (Figure 4a). The device showed a current of 80 and 55 nA upon a +40 and −40 V bias voltage, respectively (Figure 4b). Although the *I*–*V* profile upon bias voltage sweeping from −40 to +40 V deviated slightly from a straight ohmic line, the conductivity of the aligned nanowires was estimated to be in the order of 10^{-3} S cm^{-1} by assuming a cross-sectional area of 10^{-8} cm^2. This conductivity can be enhanced to 10^{-2} S cm^{-1} by iodine doping (Figure 4b). In IR spectra, the C≡N stretching frequency was changed from a single peak at 2136 cm^{-1} for pristine nanowires to dual peaks at 2179 and 2210 cm^{-1} for the sample treated with iodine vapor. This behavior is a signature of partial oxidation of the organorhodium(I) complex[8e] by iodine doping. The electrical conductivity of our solution-

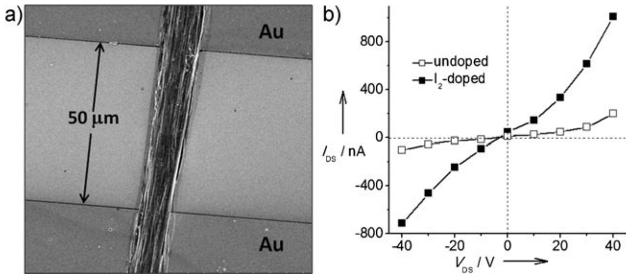

Figure 4. a) SEM image of a bundle of aligned nanowires of complex **2** bridging two gold electrodes with a channel length of 50 µm. b) *I–V* profiles of the aligned nanowires in pristine and iodine-doped states.

processable organometallic nanowires is several orders higher than those recorded (ca. $10^{-11}\,\mathrm{S\,cm^{-1}}$) with compressed powder cakes of tetrakis(isocyanide) rhodium(I) complexes, and comparable with those recorded (ca. $10^{-2}\,\mathrm{S\,cm^{-1}}$) with single crystals containing crystallographically characterized extended $\mathrm{Rh^I\cdots Rh^I}$ interactions.[16]

In summary, the amphiphilic tetrakis(2,6-xylylisocyanide)rhodium(I) complexes with a hydrating counterion can self-assemble in water into ultralong crystalline nanowires and in turn hierarchically organize into a variety of micro- and macrostructures. This type of solution-processable and electronically active nanomaterial from small molecular complexes deserves further research endeavors.

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