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Self-assembled chiral terpyridine ruthenium complexes

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Abstract—A rigid terpyridine ligand containing chiral alkyl chains has been synthesized, characterized and subsequently complexed with ruthenium(II) ions. The product was characterized by MALDI-TOF-MS, UV–vis and NMR. Circular dichroism showed the appearance of extended helical columnar aggregates.

Spontaneous self-organization of functional molecules into nanostructured assemblies is of growing interest due to their potential application in nanotechnology.[1] Recently, ureidotriazine monomers carrying chiral trialkoxybenzene chains resulted in the formation of dimers via self-complementary quadruple hydrogen bonding, which subsequently assembled to helical columnar aggregates in apolar solvents such as dodecane.[2] It has already been shown that terpyridine complexes bearing biphenyl groups are able to form extended aggregates by π-stacking.[3] For the construction of functional columnar aggregates such as, for example, conducting nanowires,[4] chiral terpyridines are of special interest due to their ability to form stable complexes with a wide range of transition metal ions.[5] The resulting complexes are promising materials due to their interesting electrochemical, photophysical,[6] ferromagnetic[7] and photochemical properties.[8]

In order to design chiral complexes, which could form helical aggregates in apolar solvents, a rigid terpyridine ligand bearing the same chiral trialkoxybenzene units as previously used for the ureidotriazine hydrogen-bonded system, was synthesized by palladium catalyzed cross-coupling between the trialkyloxybenzyl-alkyne **1** and the 4′-bromo-terpyridine **2** in 74% yield (Scheme 1).[‡]

Compound **3** was purified by column chromatography (alumina) and characterized by NMR, UV–vis and MALDI-TOF-MS as well as by elemental analysis. In a second step, the ligand was complexed with ruthenium(II) ions. This metal ion type was chosen due to the

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[‡] Full synthetic details will be given elsewhere. Selected analytical data for compound **3**: ^{1}H NMR (400 MHz, $CDCl_3$): aromatic protons: δ (ppm) 6.81 (s, 2H, H_{phenyl}), 7.33 (ddd, 2H, $J = 5.86, 4.39, 1.47$ Hz, $H_{5,5''}$), 7.85 (dt, 2H, $J = 8.06, 1.47$ Hz, $H_{4,4''}$), 8.56 (s, 2H, $H_{3',5'}$), 8.61 (dd, 2H, $J = 8.06, 1.47$ Hz, $H_{3,3''}$), 8.71 (dd, 2H, $J = 5.86, 2.19$ Hz, $H_{6,6''}$). ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm) 155.6, 155.4, 153.0, 149.1, 139.6, 136.9, 133.5, 123.9, 122.7, 121.2, 116.8, 110.3 (aromatic), 94.4, 86.4 (alkyne), 71.8, 67.4 (OCH_2), 39.3, 39.2, 37.5, 37.3, 37.0 (CH_2), 29.8, 29.6, 28.0 (CH), 24.7 (CH_2), 22.6, 22.7, 19.6 (CH_3). MALDI-TOF-MS: $m/z = 802.59$ ($M+H^+$), 824.56 ($M+Na^+$). Compound **5**: ^{1}H NMR (400 MHz, CD_3CN): aromatic protons: δ (ppm) 7.00 (s, 2H, H_{phenyl}), 7.21 (d, 2H, $J = 6.59$ Hz, $H_{5,5''}$), 7.31 (d, 2H, $J = 5.86$ Hz, $H_{6,6''}$), 7.85 (t, 2H, $J = 7.23$ Hz, $H_{4,4''}$), 8.38 (d, 2H, $J = 8.06$ Hz, $H_{3,3''}$), 8.65 (s, $2H_{3',5'}$). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 158.4, 156.0, 154.2, 153.5, 141.1, 139.1, 131.4, 128.5, 125.9, 125.4, 116.7, 111.4 (aromatic), 98.6, 86.1 (alkyne), 72.4, 68.2 (OCH_2), 40.0, 39.9, 38.1, 38.0, 37.9, 37.1 (CH_2), 30.5, 30.4, 28.7 (CH), 25.5, 25.4 (CH_2), 22.9, 22.8, 20.0, 19.8 (CH_3). ESI-MS: $m/z = 852.73$ $[M{-}2PF_6]^{2+}$, 1850.7 $[M{-}PF_6]^+$. MALDI-TOF-MS: $m/z = 1704.69$ $[M{-}2PF_6]^+$, 1849.75 $[M{-}PF_6]^+$.

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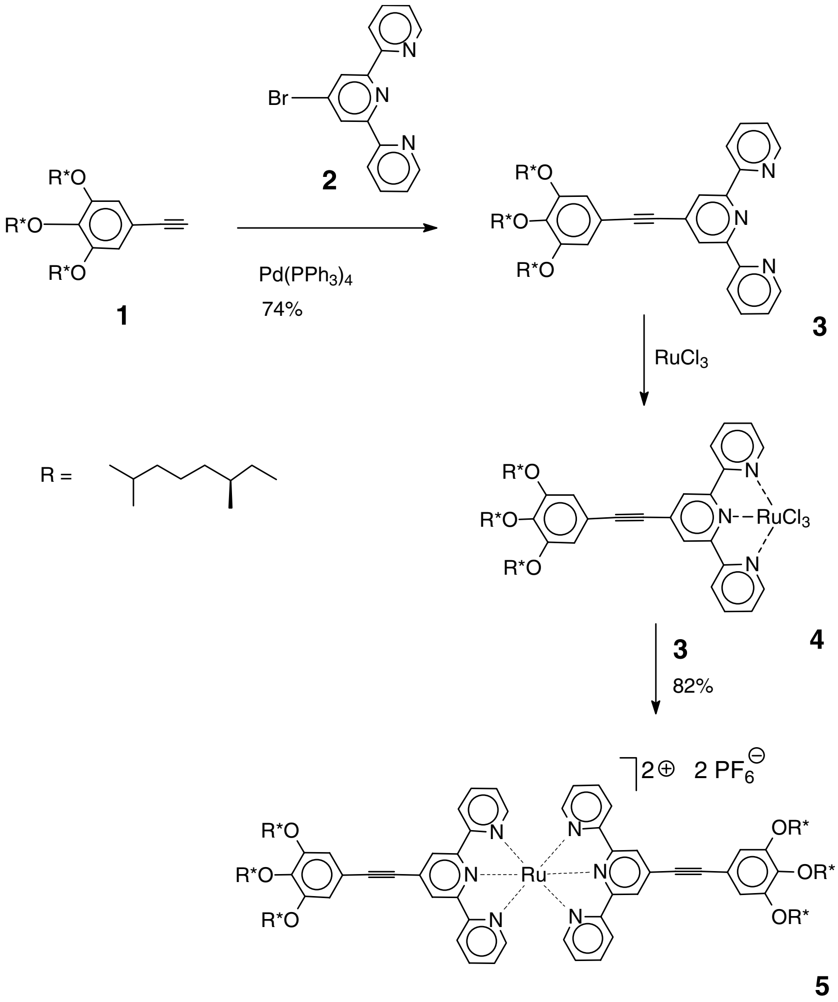

Scheme 1. Schematic representation of the synthesis of complex **5**.

outstanding stability and the interesting photophysical properties of the corresponding ruthenium(II) complexes. A Ru(III) *mono*complex was selectively obtained as an intermediate by reacting ligand **3** with $RuCl_3$. Subsequently, a second equivalent of **3** was added under reductive conditions in refluxing ethanol containing a catalytic amount of *N*-ethylmorpholine. The pure compound **5** was isolated in 82% yield after exchange of the counterions with hexafluorophoshate, followed by preparative size exclusion chromatography on a Bio-Beads column.[‡] The ^1H NMR spectra of compounds **3** and **5** are shown in Figure 1.

The signals for the aromatic protons of the terpyridine rings were found in the region from 7 to 9 ppm. A characteristic upfield shift for the 6,6″-protons was found when comparing the spectrum of the free ligand with the corresponding complex. The OCH_2-signals were located between 4 and 4.5 ppm and the signals of the aliphatic protons between 0.8 and 2.3 ppm. MALDI-TOF mass spectrometry[9,10] showed the molecular mass of the cation at 1704.7. Also ion pairs of the cation with one PF_6-counterion and matrix adducts were observed for **5**. All species detected were singly charged (see e.g., Ref. 9 for this effect). Furthermore, in ESI-MS the singly as well as the doubly charged species was detected. The UV–vis absorption spectrum of the complex (in acetonitrile) is characterized by intense absorption bands attributed to the π–π* transitions associated with the aromatic rings of the ligands. The metal to ligand charge transfer (MLCT) transition of the ruthenium complex **5** was observed at around 500 nm (Fig. 2, top). A UV–vis spectrum of **5** in dodecane revealed a small blue shift of the MLCT absorption band from 505 to 502 nm, which could indicate aggregation.

Circular dichroism (CD) spectroscopy was used in order to probe the helical order of the assemblies formed by complex **5**. In chloroform, no Cotton effect was detected, indicating that complex **5** was molecularly dissolved.[2] However, circular dichroism studies of **5** in dodecane showed a bisignate CD effect in the MLCT absorption band exhibiting a positive Cotton effect at lower ($\lambda = 512$ nm) and a negative Cotton effect at higher energy ($\lambda = 499$ nm, Fig. 2, bottom). A similar bisignated CD effect was found in the π–π* transition region. The zero crossing in both cases is close to the absorption maximum of the chromophore, indicating

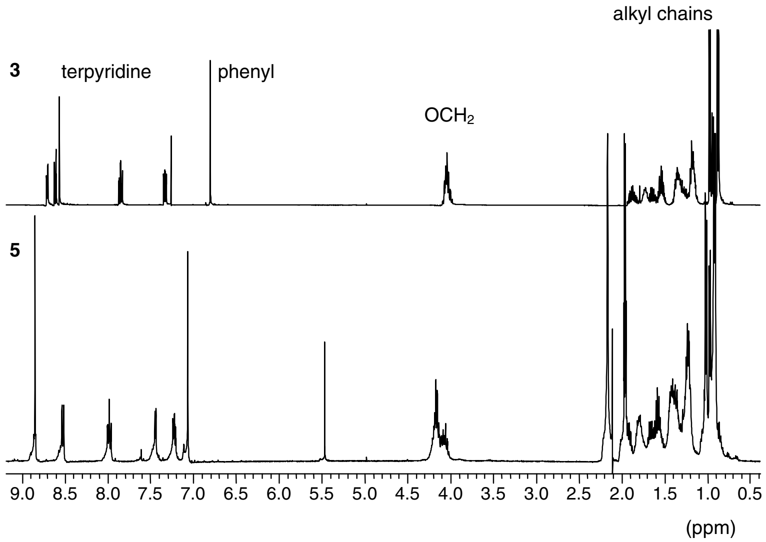

Figure 1. ^{1}H NMR spectra of ligand **3** (in chloroform) and complex **5** (in acetonitrile).

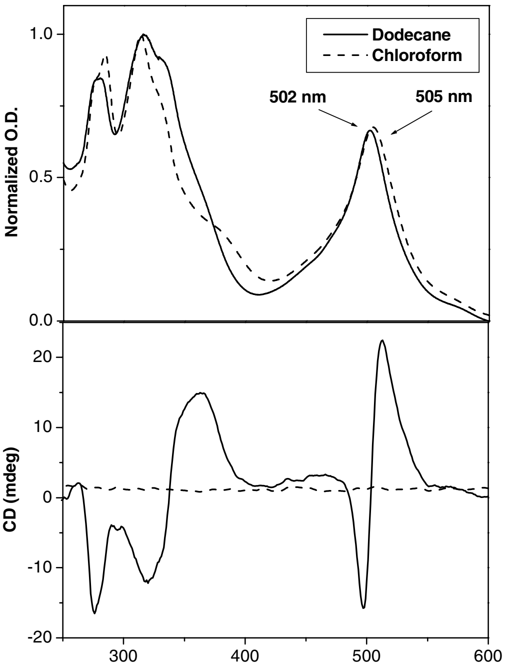

Figure 2. UV–vis (top) and CD (bottom) spectra of **5** (chloroform and dodecane).

exciton coupling due to aggregated terpyridine ruthenium rods forming a chiral superstructure.[11] CD spectroscopy at elevated temperatures revealed that the resulting aggregates were stable up to 110 °C.

Dynamic light scattering (DLS) also confirmed the formation of aggregates. In chloroform solution, no light scattering was present, whereas in the dodecane solutions scattering was observed, revealing aggregates of an average size of approximately 100 nm.

In conclusion, we have synthesized a chiral ruthenium complex that shows unprecedented aggregation in solution, leading to extended rods. The chirality in these stacks was proven by circular dichroism. The compound presented opens avenues to new electrooptical supramolecular materials. In particular the selective Ru(III)/Ru(II) chemistry can be utilized to construct a variety of novel compounds with the ability to assemble into ordered supramolecular architectures. In future, the morphology of the rods will be investigated utilizing microscopic techniques.

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