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Embedding of a ruthenium(II) water oxidation catalyst into nanofibers by self-assembly

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1. Materials and methods

All chemicals, reagents and solvents were purchased from commercial sources and used without further purification, unless otherwise stated. The starting compound perylene-3,4:9,10-tetracarboxylic acid bisanhydride 1 was obtained from BASF SE. 2,5,8,11,15,18,21,24-octaoxatricosan-13-amine 4,1,2 Ru(bda)(dms)2 precursor complex, 3 and the reference catalyst 7 3 were prepared according to literature known methods.

Ru(II) complex 6 was dissolved in acetonitrile under ultrasound treatment to prepare the nanofibers. Water was added to the acetonitrile solution only after a period of 24 hours.

The catalytic water oxidation reactions were performed under ambient conditions in Schlenk reaction vessels that were connected to pressure sensors from Honeywell (SSCDANN030PAAA5, absolute pressure, 0 to 30 psi). For each measurement 1 g (1.82 mmol) of cerium(IV) ammonium nitrate (CAN) was dissolved in 3 mL of a 1:1 acetonitrile/water mixture (pH = 1, acid: trifluoromethane sulfonic acid) in a Schlenk flask and the catalyst solution (400 µL in acetonitrile/water (pH = 7) 1:1) was injected to it through a septum. After the gas evolution had ceased, 500 µL of the gas head space were taken out with a gas tight Hamilton syringe and injected into the gas chromatograph GC-2010 Plus from Shimadzu applied with a thermal conductivity detector (detector current 30 mA, argon as carrier gas) to determine the gas composition at the end of the reaction.

Melting points were determined on a Büchi Melting Point B-545 system. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured using a Bruker Autoflex II spectrometer in reflector mode with a 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enyldene]malononitrile (DCTB) matrix. High resolution electrospray ionization (HR-ESI) mass spectra were measured using an ESI micrOTOF Focus from Bruker Daltonics. UV/vis absorption spectra were measured in a conventional quartz cell (light pass 10 mm) on a Perkin-Elmer Lambda 40 spectrophotometer. The steady-state fluorescence spectra were recorded under ambient conditions on a PTI QM4-2003 fluorescence spectrometer. Fluorescence quantum yields were determined as the average value of four measurements at different excitation wavelengths using \( N,N'-di(2,6-diisopropylphenyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide \) as reference (\( \Phi_F = 1.00 \) in dichloromethane) by applying high dilution conditions (\( A < 0.05 \)). \(^1\)H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 300 K. Deuterated solvent was used as the lock and residual non-deuterated solvent as the internal reference (CHCl\(_3\): 7.27 ppm for \(^1\)H and 77.00 ppm for \(^13\)C; CHDC\(_2\): 5.32 ppm for \(^1\)H and 54.00 ppm for \(^13\)C). Elemental analyses were performed on a CHNS 932 analyzer (Leco Instruments GmbH, Mönchengladbach, Germany).

AFM measurements were performed under ambient conditions using a Bruker AXS Nanoscope IV system operating in tapping mode in air. Silica cantilevers (OMCL-AC160TS, Olympus) with
a resonance frequency of ~300 kHz and a spring constant of ~40 Nm⁻¹ were used. The samples were prepared by spin-coating a solution of Ru(II) complex 6 in acetonitrile or acetonitrile/water 1:1 mixture ([6] = 10⁻⁵ M) onto highly oriented pyrolytic graphite (HOPG) at 7000 rpm. Cryogenic scanning electron microscopy (cryo-SEM) sample preparation consisted of placing a small drop of the solution of 6 in acetonitrile/water 1:1 ([6] = 10⁻⁵ M) onto copper stub sample holder. Prior to measurement, the specimen was plunged into liquid nitrogen slush at -210 °C. The sample was then transferred under vacuum using the loading transfer rod into the high vacuum cryo-preparation chamber (Quorum PP2000T) at -150 °C and fractured. The specimen transferred into a SEM sample chamber maintained at about -150 °C. Images of the sample were taken using a Zeiss Ultra plus field emission scanning electron microscope operated at 1.7 kV with an aperture size set to 30 μm to avoid excessive charging and radiation damage of the areas imaged.

For cyclic voltammetry measurements, a BAS Cell Stand C3 (BAS Epsilon) with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. Acetonitrile was dried over 3 Å molecular sieve and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature⁴ and recrystallized from ethanol/water. The measurements were carried out in dichloromethane or acetonitrile at a concentration of about 2x10⁻⁴ M with ferrocene (Fc) as an internal standard for the calibration of the potential. A Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were applied as working and auxiliary electrodes, respectively.
2. Synthesis and characterization

9,10-Bis(octyloxycarbonyl)-N-(2-(pyridin-4-yl)ethyl)-perylene-3,4-dicarboxylic acid imide (2)

Perylene-3,4:9,10-tetracarboxylic acid bisanhydride 1 (2.0 g, 5.10 mmol, 2 equiv.) was suspended in 20 mL DMF and 1,8-diazabicycloundec-7-ene (3.0 mL, 3.09 g, 20.3 mmol, 8 equiv.) and 1-octanol (6.4 mL, 5.31 g, 40.8 mmol, 16 equiv.) were added. After stirring for one hour at room temperature a homogeneous red solution was obtained. After 24 hours 4-(2-aminoethyl)pyridine (156 mg, d = 1.03 g/mL, 0.151 mL, 1.28 mmol, 1 equiv.) was added and the solution was stirred for 3 days. Then 1-octyl bromide (3.34 g, d = 1.05 g/mL, 3.2 mL, 20.3 mmol, 16 equiv.) was added and the mixture was stirred for further 24 hours. The mixture was poured into 100 mL of deionized water and neutralized with HCl (2N), and subsequently extracted four times with 250 mL dichloromethane each and the organic phase was dried with sodium sulfate. After purification by column chromatography (silica, CH₂Cl₂/CH₃OH 40:1, 32:1) 1.44 g (1.93 mmol, 75%) of the product were obtained as a red solid.

Melting point: 180-182 °C. ¹H NMR (400 MHz, δ, ppm, CDCl₃): 8.55 (dd, J = 4.4, 1.6 Hz, 2H), 8.47 (d, J = 8.0 Hz, 2H), 8.28 (dd, J = 8.2, 3.9 Hz, 4H), 8.05 – 8.01 (m, 2H), 7.31 (dd, J = 4.4, 1.6 Hz, 2H), 4.47 – 4.41 (m, 2H), 4.35 (t, J = 6.9 Hz, 4H), 3.08 (dd, J = 9.0, 6.8 Hz, 2H), 1.87 – 1.77 (m, 4H), 1.52 – 1.25 (m, 20H), 0.92 – 0.86 (t, J = 6.9 Hz, 6H). ¹³C NMR (101 MHz, δ, ppm, CDCl₃): 168.3, 163.5, 150.1, 147.8, 135.8, 132.2, 132.0, 131.5, 130.4, 129.3, 129.2, 129.1, 126.0, 124.5, 122.8, 121.9, 121.8, 66.1, 40.8, 33.7, 32.0, 29.5, 29.4, 28.8, 26.2, 22.8, 14.2. MALDI-MS (matrix: DCTB, pos. mode): calculated for M+H⁺ (C₄₇H₅₁N₂O₆⁺): 739.37, found: 739.38. ESI-MS (from CH₃CN/CHCl₃ 1:1, pos. mode): calculated for M+H⁺ (C₄₇H₅₁N₂O₆⁺): 739.37416, found: 739.37355 (error 0.84 ppm). Elemental analysis (%): calculated for C₄₇H₅₀N₂O₆: C 76.40, H 6.82, N 3.79, found: C 76.54, H 6.93, N 3.91. UV/vis (CH₂Cl₂, 10⁻⁵M): λ_{max} (ε, L mol⁻¹ cm⁻¹) 505 nm (52800), 475 (40325), 446 (18598), 263 (37145). Fluorescence (CH₂Cl₂, λ_{exc} = 470 nm): λ_F = 529, 561 nm.
The diester 2 (1.28 g, 1.73 mmol) was suspended in a mixture of 30 g glacial acetic acid and 1.5 g concentrated sulfuric acid and refluxed for two hours. The mixture was cooled to room temperature and then poured into 100 mL of deionized water. The precipitate was filtered off and washed with water until the filtrate was neutral. After drying the red-brown solid at 80 °C for 12 hours under high vacuum 890 mg (1.79 mmol, 100%) of the monoanhydride 3 were obtained. The product was used without further purification and characterization due to insolubility in all common organic solvents.

Monoanhydride 3 (500 mg, 1.01 mmol, 1 equiv.) and the swallowtail amine 4 (630 mg, 1.64 mmol, 1.6 equiv.) were heated together with 4 g imidazole for 6 hours at 130 °C under a nitrogen atmosphere. Then the reaction mixture was poured into 100 mL of deionized water and neutralized with HCl (2N, 30 mL). The mixture was extracted with dichloromethane (3 x 15 mL). The organic phase was washed with 200 mL saturated potassium carbonate solution and dried with sodium sulfate. The crude product was purified by column chromatography (silica, CH2Cl2/CH3OH 30:1, 20:1, 16:1) to obtain 500 mg (0.580 mmol, 57%) of ligand 5 as a greasy red solid.

Melting point: 163-165 °C. 1H NMR (400 MHz, δ, ppm, CDCl3): 8.62 (d, J = 8.0 Hz, 2H), 8.59 – 8.53 (m, 4H), 8.53 – 8.48 (m, J = 8.2, 6.6 Hz, 4H), 7.31 (dd, J = 4.4, 1.6 Hz, 2H), 5.74 – 5.66 (m, 1H), 4.50 – 4.43 (m, 2H), 4.20 (dd, J = 10.6, 7.8 Hz, 2H), 3.98 (dd, J = 10.6, 5.9 Hz, 2H), 3.76 – 3.69 (m, 2H), 3.67 – 3.50 (m, 18H), 3.49 – 3.45 (m, 4H), 3.32 (s, 6H), 3.13 – 3.06 (m, 2H). 13C NMR (101 MHz, δ, ppm, CDCl3): 163.9, 163.3, 150.1, 147.6, 135.0, 134.4, 131.6, 131.5, 129.6, 129.4, 126.6, 126.3, 124.5, 123.7, 123.3, 123.2, 123.0, 72.0, 70.7, 70.7, 70.6, 70.6, 70.5, 69.5, 59.1, 52.3, 40.9, 33.7. MALDI-MS (matrix: DCTB, pos. mode): calculated for M+H+ (C48H52N3O12+): 862.35, found: 862.23. ESI-MS (DCM/CH3CN 1:1, pos. mode): calculated for M+H+ (C48H52N3O12+): 884.35455, found: 884.35200 (error 2.96 ppm). Elemental analysis (%): calculated for C48H52N3O12: C 66.89, H 5.96, N 4.88; found: C 66.72, H 6.12, 5.04. UV/vis (CH2Cl2, 10−5M): λmax (ε, L mol−1 cm−1) 525 nm (85700), 489 (51520), 457 (18570), 429 (5000), 260 (34790); (CH3CN, 10−5M): λmax (ε, L mol−1 cm−1) 521 nm (74336), 486 (47946), 455 (18089), 261 (30650). Fluorescence (CH2Cl2, λexc = 490 nm): λF = 539, 577, 624 nm; ΦF = 1.00 ± 0.04.
[Ru(bda)(PBI)₂] complex 6

Ru(bda)(dmso)₂ precursor (30.2 mg, 0.0604 mmol, 1 equiv.) and PBI ligand 5 (130 mg, 0.151 mmol, 2.5 equiv.) were dissolved in a degassed 1:1 mixture of chloroform and methanol under a nitrogen atmosphere and heated at 60 °C for 6 hours. Then the solvent was removed under reduced pressure and the product was purified by column chromatography (Al₂O₃ deactivated with 15% H₂O w/w, CH₂Cl₂/CH₃OH 100:1, 50:1, 30:1). Complex 6 was obtained as a dark red solid (106 mg, 0.051 mmol, 85%).

Melting point: 239-241 °C. ¹H NMR (400 MHz, δ, ppm, CD₂Cl₂/MeOD 5:1): 8.49 (d, J = 8.0 Hz, 2H), 8.33 – 8.06 (m, 18H), 7.85 (t, J = 8.0 Hz, 2H), 7.76, (d, J = 4.9 Hz, 4H), 7.20 (d, J = 5.4 Hz, 4H), 5.58 (m, 2H), 4.25 (m, 4H), 4.17 (m, 4H), 3.96 (m, 4H), 3.76 - 3.39 (m, 48H), 3.25 (s, 12H), 2.99 (m, 4H). ¹³C NMR (400 MHz, δ, ppm, CD₂Cl₂/MeOD 5:1): 174.2, 164.2, 163.5, 160.7, 157.7, 152.3, 150.1, 134.7, 134.2, 132.1, 131.5, 131.4, 129.3, 129.1, 126.7, 126.4, 126.0, 125.9, 125.1, 123.7, 123.6, 123.5, 122.8, 72.4, 71.0, 71.0, 71.0, 70.9, 70.0, 59.1, 53.0, 40.7, 33.7. MALDI-MS (matrix: DCTB, pos. mode): calculated for M⁺ (C₁₀₈H₁₀₈N₈O₂₈Ru⁺): 2066.63, found: 2066.76. ESI-MS (CHCl₃/CH₃CN 1:1, pos. mode): calculated for M+H⁺ (C₁₀₈H₁₀₉N₈O₂₈Ru⁺): 2067.63893, found: 2067.64021 (error 0.62 ppm). Elemental analysis (%): calculated for C₁₀₈H₁₀₉N₈O₂₈Ru·2H₂O: C 61.68, H 5.37, N 5.33, found: C 61.45, H 5.40, N 5.44. UV/vis (CH₂Cl₂, 10⁻⁵M): λ_max (ε, L mol⁻¹ cm⁻¹) 526 nm (166066), 489 (103044), 458 (40592), 429 (17405), 301 (32915), 260 (76161); (CH₃CN, 10⁻⁵M): λ_max (ε, L mol⁻¹ cm⁻¹) 547 nm (19058), 495 (39929), 375 (12650), 312 (22167), 304 (21608). Fluorescence (CH₂Cl₂, λ_exc = 490 nm): λ_F = 539, 577, 625 nm; Φ_F = 0.04 ± 0.01.
3. NMR and mass spectra

![NMR spectrum of 2](image1)

**Fig. S1** $^1$H NMR spectrum of 2 (CDCl$_3$, 400 MHz, 300 K).

![13C NMR spectrum of 2](image2)

**Fig. S2** $^{13}$C NMR spectrum of 2 (CDCl$_3$, 101 MHz, 300 K).
**Fig. S3** MALDI mass spectrum of 2 (matrix: DCTB in chloroform, positive mode).

**Fig. S4** HR-ESI mass spectrum of 2 measured from chloroform/acetonitrile (positive mode). The inset shows the isotopic distribution of the $[\text{M+H}]^+$ peak (black = measured, red = calculated).
Fig. S5 $^1$H NMR spectrum of 5 (CDCl$_3$, 400 MHz, 300 K).

Fig. S6 $^{13}$C NMR spectrum of 5 (CDCl$_3$, 101 MHz, 300 K).
Fig. S7 MALDI mass spectrum of 5 (matrix: DCTB in chloroform, positive mode).

Fig. S8 HR-ESI mass spectrum of 5 measured from chloroform/acetonitrile (positive mode). The inset shows the isotopic distribution of the $[\text{M+H}]^+$ peak (black = measured, red = calculated).
Fig. S9 $^1$H NMR spectrum of 6 (CD$_2$Cl$_2$/MeOD 5:1, 400 MHz, 300 K). Peaks labelled with * derive from the solvent.

Fig. S10 $^{13}$C NMR spectrum of 6 (CD$_2$Cl$_2$/MeOD 5:1, 101 MHz, 300 K).
**Fig. S11** MALDI mass spectrum of 6 (matrix: DCTB in chloroform, positive mode).

**Fig. S12** HR-ESI mass spectrum of 6 measured from chloroform/acetonitrile (positive mode). The inset shows the isotopic distribution of the [M+H]$^+$ peak (black = measured, red = calculated).
4. Additional UV/vis spectra

Fig. S13 UV/vis absorption spectrum of 5 in acetonitrile at a concentration of $10^{-5}$ M.

Fig. S14 UV/vis absorption (solid) and emission (dotted) spectrum of 2 in dichloromethane at a concentration of $10^{-5}$ M.
5. Electrochemistry

Fig. S15 Left: Differential pulse voltammograms of 5 and 6 in dichloromethane and acetonitrile, respectively. Right: Cyclovoltammograms for 5 and 6 in dichloromethane and acetonitrile, respectively. The concentration of 5 and 6 for all measurements was 2x10^-4 M and the scan rate 100 mV/s. TBAHFP was used in all cases as supporting electrolyte at a concentration of 0.1 M.
6. Additional AFM images

Fig. S16 AFM height images of a sample obtained by spin-coating a solution of 6 in acetonitrile/water 1:1 with a concentration of $10^{-3}$ M onto mica.
7. Cryo-SEM images

[Images of Cryo-SEM images showing a solution of 6 in an acetonitrile/water 1:1 mixture (c = 10^{-5} M).]

Fig. S17 Cryo-SEM images of a solution of 6 in an acetonitrile/water 1:1 mixture (c = 10^{-5} M).
8. Influence of acetonitrile content on the catalytic activity

![Graph showing the influence of acetonitrile content on catalytic activity.](image)

**Fig. S18** Catalytic activity of reference 7 (c = 75.5 µM) depending on the acetonitrile content in the reaction mixture. With increased acetonitrile content the oxygen evolution is significantly slowed down. The catalyst solution (400 µL, acetonitrile/water (pH 7) 1:9) was injected into a reaction vial filled with 1 g (1.82 mmol) CAN dissolved in 3 mL of the corresponding acetonitrile/water (pH 1) mixture.
9. Gas chromatography

**Fig. S19** Gas chromatography calibration curve for different oxygen/nitrogen mixtures (red square marks the natural composition of air).

**Fig. S20** Exemplary gas chromatogram measured via injection of 500 µL of the gas head space after the water oxidation using 6 a catalyst at a concentration of 96 µM.
10. References


