Supporting Information

Photocatalytic Water Oxidation at Soft Interfaces

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General Methods and Material

For NMR-spectroscopy, a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, T = 300 K) was utilized. All chemical shifts are reported in δ [ppm] (multiplicity, coupling constant J, number of protons, assignment of proton) relative to the solvent residual peak as the internal standard. The coupling constants are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, sep = septet, m = multiplet, p = pseudo. ^{13}C-NMR: (+) = CH, CH_3, (-) = CH_2, q = quaternary carbon. The used solvent is reported for every spectrum.

Absorption spectra were recorded on a Varian Cary BIO 50 UV/VIS/NIR spectrometer. A 10 mm Hellma quartz cuvette was used.

IR-Spectra were measured on a Bio-Rad-FT-IR-Spectrometer Excalibur FTS 3000 equipped with a Golden Gate Diamond Single Reflection ATR System. Signal intensity is abbreviated with s = strong, m= medium and w= weak.

Fluorescence spectroscopy has been carried out on a Varian Cary Eclipse fluorimeter with 10 mm Hellma quartz cuvettes at 25 °C.

Dynamic light scattering was performed on a Malvern Zetasizer Nano at 25 °C using either a disposable Polystyrene or Polymethyl methacrylate cuvette purchased from Kartell.

Mass-spectrometry: ThermoQuest Finnigan TSQ 7000, Finnigan MAT 95 and Finnigan MAT SSQ 710 A.

Melting points were determined on a Stanford Research Systems OptiMelt MPA 100 with a heating rate of 1 °C/min. Elemental analysis was carried out on a Vario EL III. Pre-coated TLC-sheets ALUGRAM Xtra SIL G/UV254 from Macherey-Nagel were used. The detection was done by UV light (254 nm or 366 nm). Two different silica gels were used for column chromatography: Macherey-Nagel silica gel 60 M (230-440 mesh; column chromatography); Macherey-Nagel silica gel 60 (70-230 mesh; flash chromatography). For size exclusion chromatography, Sephadex LH-20 from Sigma was used.

A Fibox 3 fibre optic oxygen sensor purchased from PreSens Precision Sensing GmbH was used for monitoring the amount of oxygen. A Bandelin Sonorex RK 102 H was used for the sonication of vesicular samples. Gas chromatography was performed on a Inficon Micro GC 3000 with a 3 Å mol sieve column, a thermal conductivity detector and Ar as carrier gas.

Synthesis of Photosensitizer 2a

Compounds **14,**[1] **15**[2] and **17**[3] were prepared according to literature procedures. The synthesis of ligand **16**[4] and complex **2a**[5] follows procedures previously reported for similar compounds.

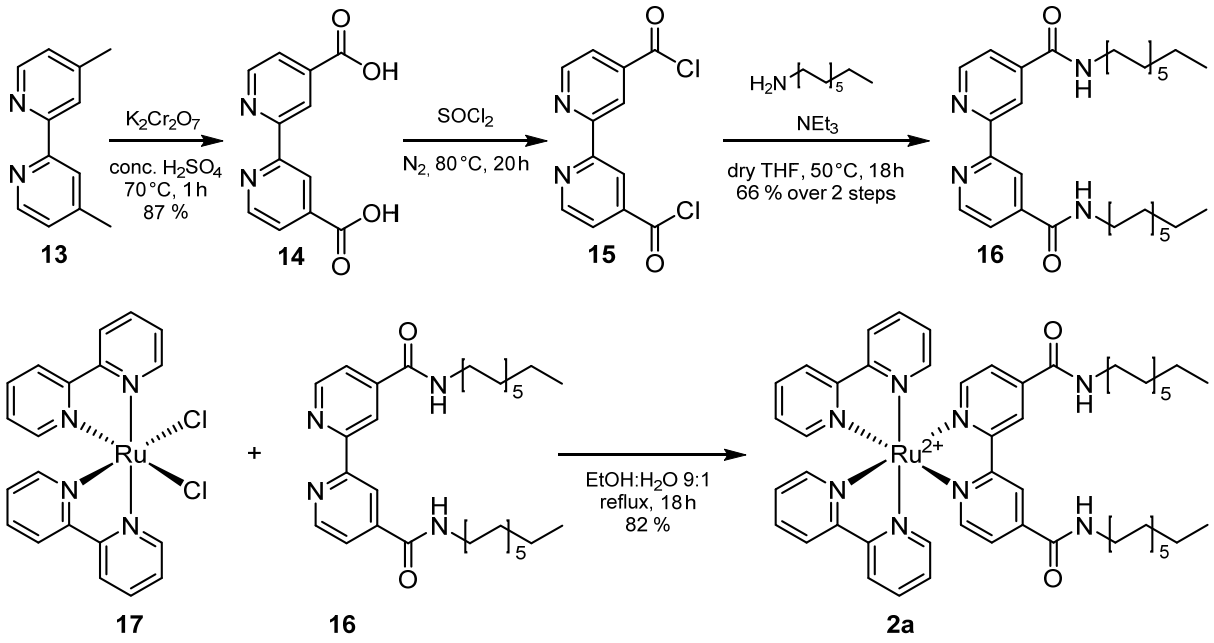


Figure S1: Synthesis of complex **2a**.

Didodecyl-[2,2'-bipyridine]-4,4'-dicarboxamide (16)[4]

Compound **15** (562 mg, 2.0 mmol) was dissolved in 100 mL of dry THF in a Schlenk round bottomed flask under N_2. Dodecyl amine (890 mg, 4.4 mmol) and triethyl amine (520 μL, 2.0 mmol) were added and a white precipitate was observed. The reaction mixture was

heated to 50 °C and stirred overnight. The precipitate was filtered off and washed with water (20 mL), acetone (20 mL) and DCM (20 mL). The white crystalline powder was dried in vacuum yielding 767 mg of **16** (66 %, 1.32 mmol).

m.p.: 232 °C

IR: □ [cm^{-1}]: 3307 (s), 2919 (s), 2849 (s), 1631 (s), 1591 (m), 1524 (s), 1465 (m), 1304 (m), 1099 (m), 1070 (w), 895 (m), 863 (s), 760 (s), 695 (s), 645 (s)

MS: ESI m/z = 579.3 (MH^+)

E.A.: calc. [%] for $C_{36}H_{58}N_4O_2$ M=578.87: C 74.69, H 10.10, N 9.68; found: C 74.18, H 9.97, N 9.30

Ruthenium(II)(didodecyl-(2,2'-bipyridine)-4,4'-dicarboxamide)bis(2,2'-bipyridine)-bis-(hexafluorophosphate) (2a)[5]

Compound **17** (102 mg, 0.19 mmol) and **16** (114 mg, 0.19 mmol) were dissolved in a mixture of EtOH:H_2O (9:1) under N_2 atmosphere, heated to reflux and stirred overnight. The solvent was removed in vacuo and the resulting solid was purified by a size exclusion chromatography with Sephadex LH-20. The column was firstly eluted with MeCN to remove a purple band from the starting material and secondly with a mixture of MeCN:EtOH (9:1) to obtain the dichloride salt of **2a** as a red solid. The solid was dissolved in a minimum amount of water. 5 mL of a saturated NH_4PF_6 solution were added to precipitate **2a** as a dark red solid. After filtration and drying in high vacuum, 200 mg (82 %, 0,16 mmol) of **2a** could be isolated.

^{1}H-NMR (400 MHz, CD_3CN): δ [ppm]: 8.94 (d, J = 1.3 Hz, 2H), 8.51 (m, 4H), 8.07 (m, 4H), 7.87 (d, 2H, J= 5.9 Hz), 7.70 (m, 8H, H3) 7.40 (m, 4H), 3.39 (pq, J= 7.0 Hz, 4H), 1.60 (m, 4H), 1.2-1.4 (m, 36H), 0.87 (t, J= 6.8 Hz, 6H)

^{13}C-NMR (101 MHz, CD3CN): δ [ppm]: 162.6 (q), 157.1 (q), 156.6 (q), 156.5 (q), 152.1 (+), 151.4 (+), 151.3 (+), 142.6 (q), 137.8 (+), 127.4 (+), 127.4 (+), 124.6 (+), 124.0 (+), 121.7 (+), 39.6 (-), 31.3 (-), 29.1 (-), 29.0 (-), 29.0 (-), 29.0 (-), 28.8 (-), 28.7 (-), 28.6 (-), 26.3 (-), 22.0 (-), 13.0 (+)

^{31}P-NMR (162 MHz, CD_3CN): δ [ppm]: -143.26 (sep, J= 706.5 Hz, PF_6)

^{19}F-NMR (162 MHz, CD_3CN): δ [ppm]: 72.89 (d, J= 707.8 Hz, PF_6)

IR: □ [cm^{-1}]: 3419 (w), 2924 (m), 2853 (m), 1666 (m), 1532 (m), 1465 (m), 1446 (m), 1313 (w), 1226 (w), 1162 (w), 1026 (w), 825 (s), 759 (s), 729 (m), 554 (s)

HR-MS: ESI^+ calc. for $C_{56}H_{74}N_8O_2Ru$ (M^{2+}) m/z= 496.2489; found 496.2501

UV/Vis: (in MeCN) λ_{max}=247 nm, λ_{max}=288 nm, λ_{max}=461nm

Synthesis of Catalyst 6b

Compounds **18**[6] and **22**[3] were prepared according to literature procedures. The synthesis of Ligand **21** and its precursors **19** and **20** is described below. Complex **6b**[7] was prepared following the procedure for catalyst **6a.**

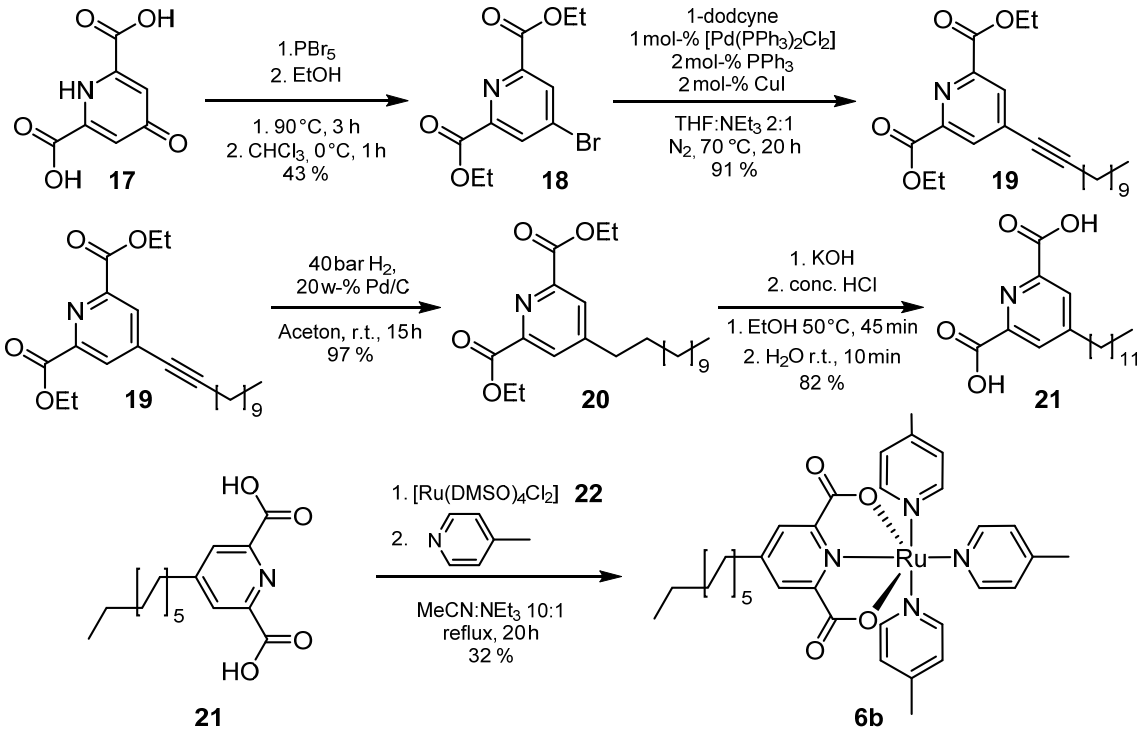


Figure S2: Synthesis of complex **6b**

Diethyl 4-(dodecynyl)pyridine-2,6-dicarboxylate (19)

Compound **18** (228 mg, 0.75 mmol), 1-dodecyne (161 μL, 0.75 mmol), [$Pd(PPh_3)2Cl_2$] (5.3 mg, 1 mol%), PPh_3 (4.0 mg, 2 mol%) and CuI (2.9 mg, 2 mol%) were dissolved in a degassed mixture of 16 mL THF and 8 mL triethyl amine under a nitrogen atmosphere. After

stirring for 20 h at 70 °C, the solvents were evaporated under reduced pressure. The residue was dissolved in 15 mL of DCM and washed three times with water (10 mL). The combined aqueous phases were extracted once with 10 mL of DCM. The combined organic phase was dried over $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography (SiO_2, petroleum ether / ethyl acetate 3:1) to yield 264 mg (91 %, 0.68 mmol) of **19** as a white solid.

m.p: 72 °C

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm]: 8.10 (s, 2H), 4.39 (q, J= 7.1 Hz, 4H), 2.37 (t, J= 7.1 Hz, 2H), 1.53 (m, 2H), 1.36 (m, 8H), 1.28-1.13 (m, 12H), 0.78 (t, J= 6.8 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm]: 164.2 (q), 148.6 (q), 135.0 (q), 129.6 (+), 99.0 (q), 77.4 (q), 62.2 (-), 31.8 (-), 29.5 (-), 29.4 (-), 29.2 (-), 29.0 (-), 28.9 (-), 28.1 (-), 22.6 (-), 19.4 (-), 14.1 (+), 14.0 (+)

MS: EI m/z = 387.2 (M^+)

IR: □ [cm^{-1}]: 2916 (s), 2849 (s), 2231 (m), 1714 (s), 1600 (m), 1469 (m), 1408 (m), 1373 (s), 1344 (s), 1246 (s), 1152 (m), 1131 (m), 1020 (m), 782 (s), 580 (m)

E.A.: calc. [%] for $C_{23}H_{33}NO_4$ M=387.51 g/mol: C 71.35, H 8.59, N 3.62; found: C 71.33, H 8.52, N 3.17

Diethyl 4-dodecylpyridine-2,6-dicarboxylate (20)

Compound **19** (200 mg, 0.52 mmol) was dissolved in 5 mL of acetone and Pd/C (20 mg) was added. The solution was stirred overnight in an autoclave at a hydrogen pressure of 3 bar. The catalyst was filtered off over celite and the solvent was evaporated in vacuo to yield 192 mg (94 %, 0.49 mmol) of **20** as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm]: 8.08 (s, 2H, H3,5), 4.46 (q, J= 7.1 Hz, 4H), 2.73 (t, J= 7.1 Hz, 2H), 1.67 (m, 2H), 1.44 (t, J= 7.1 Hz, 6H), 1.37-1.15 (m, 18H), 0.85 (t, J= 6.8 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm]: 165.0 (q), 154.8 (q), 148.6 (q), 128.0 (+), 62.2 (-), 35.3

(-), 31.9 (-), 30.2 (-), 29.6 (-), 29.6 (-), 29.6 (-), 29.5 (-), 29.3 (-), 29.1 (-), 22.7 (-), 14.2 (+), 14.1 (+)

IR: □ [cm^{-1}]: 2924 (s), 2854 (m), 1748 (m), 1717 (s), 1601 (m), 1465 (m), 1375 (m), 1339 (m), 1239 (s), 1204 (s), 1058 (m), 1025 (s), 782 (m)

HR-MS: ESI^+ calc. for $C_{23}H_{37}NO_4$ (MH^+) m/z= 392.2801; found 392.2795

4-Dodecylpyridine-2,6-dicarboxylate (21)

KOH (850 mg), dissolved in 15 mL of ethanol, was added to compound **20** (195 mg, 0.5 mmol). Immediately after the addition, a white solid started to crystallize. The solution was stirred at 50 °C for 45 min. The precipitate was filtered off and dried in high vacuum to give 200 mg (0.48 mmol, 97 %) of the dipotassium salt of **21**. The solid was dissolved in water (ca. 50 mL) and conc. hydrochloric acid was added drop wise, until the pH reached a value of 1. The solution was stirred at room temperature for 10 min and the white precipitate was filtered off. The residue was washed with 10 mL of water and dried in high vacuum to yield 138 mg (82 %, 0.4 mmol) of **21** as a white solid.

m.p.: 143 °C (decomp.)

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm]: 8.08 (s, 2H), 2.77 (t, J= 7.6 Hz, 2H), 1.61 (m, 2H), 1.32-1.12 (m, 18H), 0.84 (t, J= 6.7 Hz, 3H)

^{13}C-NMR (101 MHz, DMSO-d_6): δ [ppm]: 165.6 (q), 154.5 (q), 148.1 (q), 127.3 (+), 34.1 (-), 31.3 (-), 29.7 (-), 29.0 (-), 29.00 (-), 29.0 (-), 28.9 (-), 28.7 (-), 28.4 (-), 22.1 (-), 14.0 (+)

IR: □ [cm^{-1}]: 3473 (w), 2915 (s), 2849 (s), 1745 (s), 1681 (m), 1605 (m), 1471 (m), 1328 (m), 1172 (s), 1002 (m), 904 (m), 681 (s), 511 (m)

E.A.: calc. [%] for $C_{19}H_{29}NO_4$*H_2O M=353.45 g/mol: C 64.56, H 8.84, N 3.96; found: C 63.58, H 8.89, N 3.72

Ruthenium(II) (4-dodecylpyridine-2,6-dicarboxylate) tris (4-metyhlpyridine) (6b)[7]

A mixture of MeCN (10 mL) and triethyl amine (1 mL) was degassed by the freeze-pump-thaw method. Compound **21** (130 mg, 0.37 mmol) and **22** (180 mg, 0.37 mmol) were added

to the solvent under nitrogen. The solution was heated to reflux and stirred overnight. The colour changed from light yellow to red. 4-Methylpyridine (Pic, 5 mL, 56.2 mmol) was added and the solution was stirred for additional 4.5 h under reflux. After cooling to room temperature, the solvent was removed in vacuo and the 4-metylpyridine was removed in high vacuum at 40 °C. The residue was dissolved in DCM (15 mL) and washed with water (3 x 10 mL). After removal of the solvent, the crude product was purified by column chromatography (SiO_2, EtOH:Et_2O 8:1). The second fraction was collected and dissolved in a mixture of 5 mL of MeCN, 0.5 mL of triethyl amine and 5 mL (56.2 mmol) of 4-methylpyridine, degassed by nitrogen and heated to reflux for 5 h. After removal of the solvent in vacuo, the crude product was purified by flash column chromatography (SiO_2, EtOH:Et_2O 10:1). The second fraction was collected and yielded 87 mg (32 %, 0.12 mmol) of **6b** as a dark red-brownish solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm]: 8.74 (d, J= 6.3 Hz, 2H), 8.12 (d, J= 6.5 Hz, 4H), 7.82 (s, 2H), 7.04 (d, J= 5.8 Hz, 2H), 6.85 (d, J= 6.1 Hz, 4H), 2.64 (t, J= 7.8 Hz, 2H), 2.34 (s, 3H), 2.19 (s, 6H), 1.64 (m, 2H) 1.32-1.16 (m, 18H), 0.88 (t, J= 6.9 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm]: 174.8 (q), 154.4 (q), 153.1 (+), 152.7 (+), 147.8 (q), 147.4 (q), 146.6 (q), 127.3 (+), 125.4 (+), 125.1 (+), 35.9 (-), 31.9 (-), 30.1 (-), 29.7 (-), 29.6 (-), 29.5 (-), 29.4 (-), 29.4 (-), 29.3 (-), 22.7 (-), 21.1 (+), 20.8 (+), 14.1 (+)

HR-MS: ESI^+ calc. for $C_{37}H_{49}N_4O_4Ru$ (MH^+) m/z= 715.2797; found 715.2806

IR: □ [cm^{-1}]: 2923 (m), 2851 (m), 1630 (s), 1496 (m), 1414 (m), 1315 (w), 1206 (m), 1033 (w), 920 (w), 819 (s), 735 (m), 506 (m)

Synthesis of Catalyst 3 and 7

Compounds **23**, **24** and **25** were prepared according the previously reported procedure.[8] The synthesis of catalysts **3** and **7** is described below.

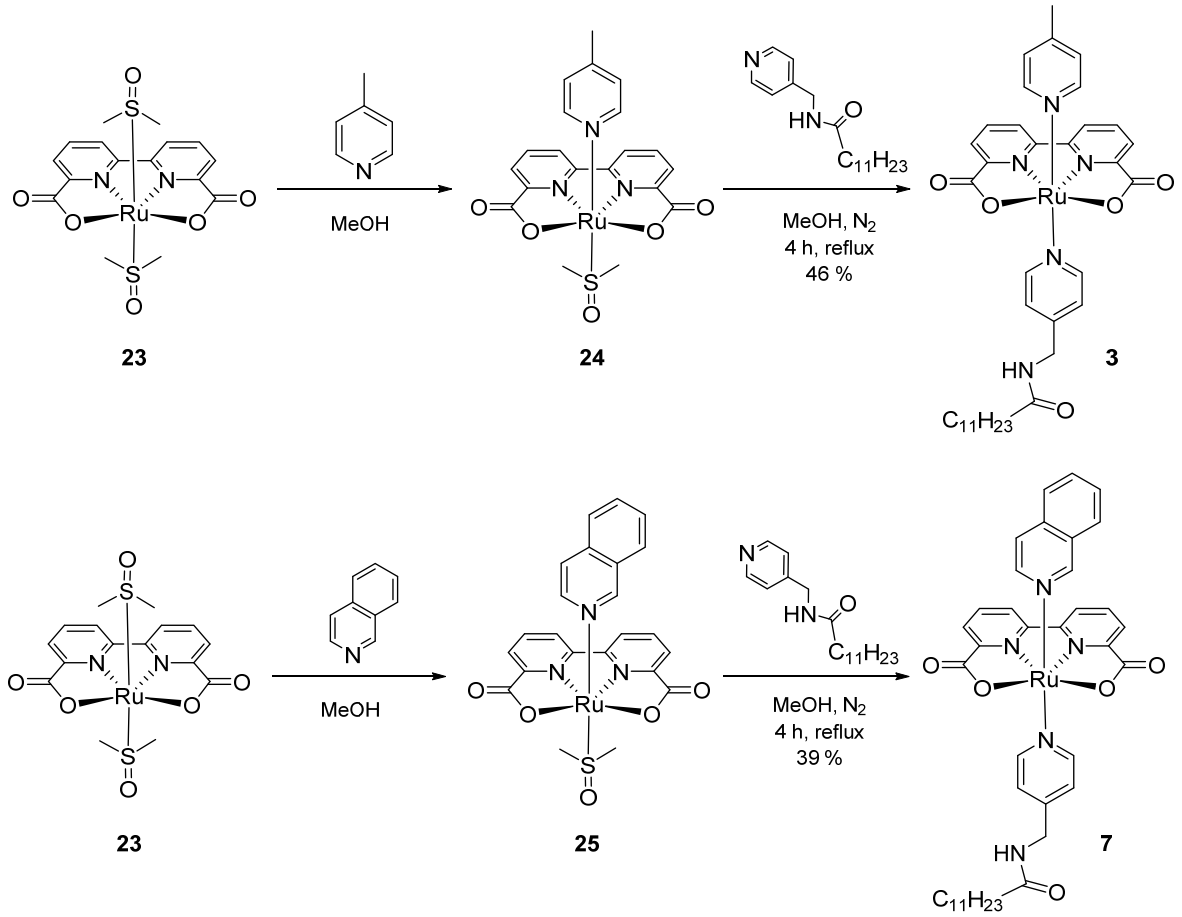


Figure S3: Synthesis of Catalysts **3** and **7**.

Ruthenium(II)([2,2'-bipyridine]-6,6'-dicarboxylate)(*N*-(pyridin-4-ylmethyl)dodecanamide) (4-methylpyridine) (3)

A mixture of **24** (310 mg, 0.6 mmol) and N-(pyridin-4-ylmethyl) dodecanamide (140 mg, 0.6 mmol) in methanol (30 ml) was degassed by N_2 and refluxed for 4 h. The solvent was removed under reduced pressure and the dark red solid obtained was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ 1:5) to give 200 mg of catalyst **3** (46 %, 0.28 mmol).

^{1}H-NMR (400 MHz, CD_3OD): δ[ppm]: 8.02 (s, 2H), 7.89 (t, J = 8 Hz, 2H), 7.75 (d, 2H, J = 8 Hz), 7.65 (d, 2H, J = 8 Hz), 7.09 (d, 2H, J = 8 Hz), 7.04 (d, 2H, J = 4 Hz), 4.26 (s, 2H), 2.26 (s, 3H), 2.19 (t, 2H, J = 8 Hz) 1.56 (m, 2H), 1.28 (m, 16H), 0.90 (t, J = 8 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ[ppm]: 176.44, 157.25, 152.96, 152.37, 152.35, 151.35, 150.81, 133.09, 127.15, 126.85, 126.40, 124.57, 42.46, 36.83, 33.06, 30.70, 30.56, 30.46, 30.34, 30.31, 26.82, 23.73, 20.67, 14.45

HR-MS: ESI^+ calc. for $C_{36}H_{43}N_5O_5Ru$ (MH^+) m/z= 728.2386; found 728.2398

UV/Vis: (in methanol) λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 250 (20900), 300 (31900), 370 (12200), 480 (4833), 530 (4200)

Ruthenium(II)([2,2'-bipyridine]-6,6'-dicarboxylate)(*N*-(pyridin-4-ylmethyl)dodecanamide) (isoquinoline) (7)

A mixture of **25** (330 mg, 0.6 mmol) and N-(pyridin-4-ylmethyl)dodecanamide (140 mg, 0.6 mmol) in methanol (30 ml) was degassed with N_2 and refluxed for 4 h. The solvent was removed under reduced pressure and the dark red solid obtained was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ 1:5) to yield 180 mg of catalyst **7** (39 %, 0.23 mmol).

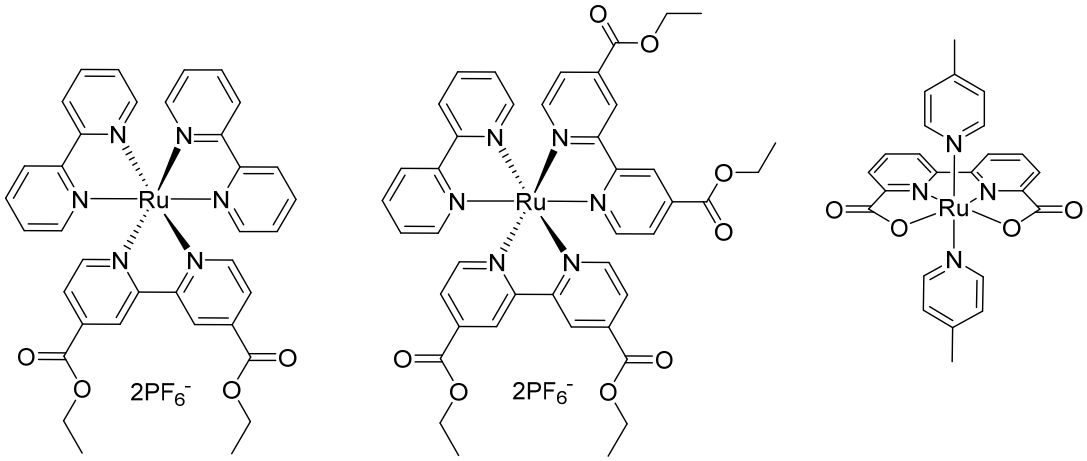
^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm]: 8.64 (t, J= 8 Hz, 3H), 8.04 (m, 2H), 7.93 (m, 2H), 7.93-7.76 (m, 4H), 7.73 (m, 1H), 7.64-7.56 (m, 3H), 7.12 (d, J= 4 Hz, 2H), 4.28 (s, 2H), 2.19 (t, 2H, J= 8 Hz) 1.56 (m, 2H), 1.28 (m, 16H), 0.90 (t, J= 8 Hz, 3H)

^{13}C-NMR (101 MHz, $CDCl_3$): δ[ppm]: 175.08, 156.12, 151.60, 150.08, 142.47, 134.77, 132.03, 128.52, 126.17, 125.24, 123.25, 121.74, 41.09, 35.44, 31.66, 29.30, 29.16, 29.07, 28.92, 25.42, 22.34, 13.06

HR-MS: ESI^+ calc. for $C_{39}H_{43}N_5O_5Ru$ (MH^+) m/z= 764.2386; found 764.2396

UV/Vis: (in methanol) λ_{max} / nm (ε / $M^{-1}cm^{-1}$): 250 (23100), 300 (36600), 395 (14900), 530 (4700)

Photosensitizers **2b,**[9] **2c**[10] and catalyst **5**[11] were prepared according to literature procedures.



2b **2c** **5**

Figure S4: Structure of photosensitizers **2b**, **2c** and water oxidation catalyst **5**.

Vesicle Preparation and Characterisation

Preparation of Vesicles with Catalyst 6b:

Appropriate volumes of stock solutions of amphiphiles in chloroform or acetonitrile were mixed in a 10 mL crimp-top vial to obtain a total amphiphile concentration of 1 mM and the solvent was removed at 85 °C and under reduced pressure. 4.5 mL of aqueous phosphate buffer (50 mM, pH = 7.0) containing 2.5 mM sodium persulfate were added and the vial was closed with a septum-cap. Sonication in an ultrasonic bath at 20 °C above the main phase transition temperature for 20 min yielded a vesicular solution with a narrow size distribution.

Table S1: Composition of a typical vesicular sample containing catalyst **6b**.

Entry	V_{6b}[a] / μL	V_{2a}[b] / μL	V_{lipid}[c] / μL	C_{6b} / μM	C_{2a} / μM	c_{lipid} / μM	$c_{S_2O_8^{2-}}$ / μM	V_{buffer} / mL
1	56.3	281	388	12.5	125	863	2.5	4.5

[a] c (stock solution) = 1 mM [b] c (stock solution) = 2 mM [c] c (stock solution) = 10 mM

Preparation of Vesicles with Catalyst 3 or 7:

Appropriate volumes of stock solutions of amphiphiles in chloroform or acetonitrile were mixed in a 25 mL round bottom flask to obtain a total amphiphile concentration of 1 mM and the solvent was removed at the rotatory evaporator and in high vacuum. 8.5 mL of aqueous phosphate buffer (50 mM, pH = 7.0) containing 2.5 mM sodium persulfate were added and the vial was closed. Sonication in an ultrasonic bath at 20 °C above the main phase transition temperature for 20 min yielded a vesicular solution with a narrow size distribution.

Table S2: Composition of a typical vesicular sample containing catalyst **3** or **7**.

Entry	V_{cat}[a] / μL	V_{2a}[b] / μL	V_{lipid}[c] / μL	c_{cat} / μM	c_{2a} / μM	c_{lipid} / μM	$c_{S_2O_8^{2-}}$ / μM	V_{buffer} / mL
1	21	531	742	2.5	125	863	2.5	8.5

[a] c (stock solution) = 1 mM [b] c (stock solution) = 2 mM [c] c (stock solution) = 10 mM

Size Distribution:

The size distribution of the vesicular dispersion was determined by dynamic light scattering.

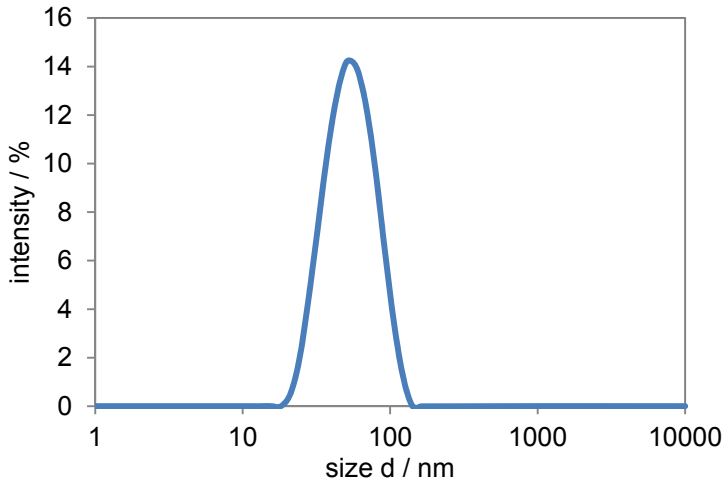


Figure S5: Typical size distribution of DMPC (**9**) vesicles containing 12.5 mol% **2a** and 1.25 mol% **6b** with a poly dispersity index of 0.25 and an average diameter of 57 nm.

UV Spectra:

UV Spectra of all samples were measured in a 10 mm cuvette at a 62.5 μM concentration of the photosensitizer. All samples showed UV spectra comparable to the homogeneous solution.

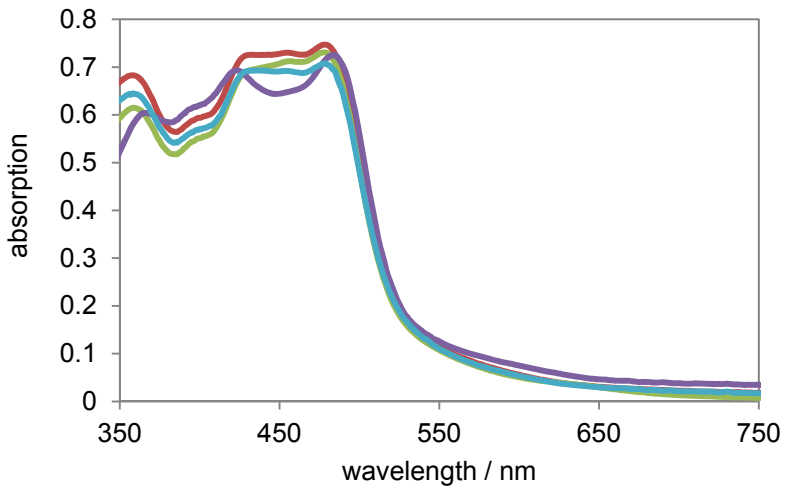


Figure S6: UV-Vis spectra of DMPC (**9**) vesicles (blue trace), SMPC (**10**) vesicles (green trace), DOPC (**11**) vesicles (red trace) containing 12.5 mol% **2a** and of aequimolar homogeneous solution of **6b** (purple trace). All samples had a photosensitizer concentration of 62.5 μM and were measured in phosphate buffer (pH 7.0, 50 mM).

Irradiation and Gas Chromatography

Samples Containing Catalyst 6b:

After the sonication all samples were degased by blubbling argon through the solution for 5 min. The degassed samples were then stirred with a magnetic stirrer and irradiated with high power OSRAM Oslon SSL 80 royal-blue LEDs for 20 min. For temperature control a aluminium cooling block connected to a thermostat was used (Figure S7). After irradiation the amount of evolved oxygen in the gas phase was determined by directly connecting the sample vial to a Inficon micro GC 3000 equipped with a 5 Å mol sieve column, a thermal conductivity detector and Ar as carrier gas. For monitoring the oxygen concentration during the reaction a vial equipped with a oxygen sensor spot and a Fibox 3 oxygen sensor purchased from PreSens Precision Sensing was used.

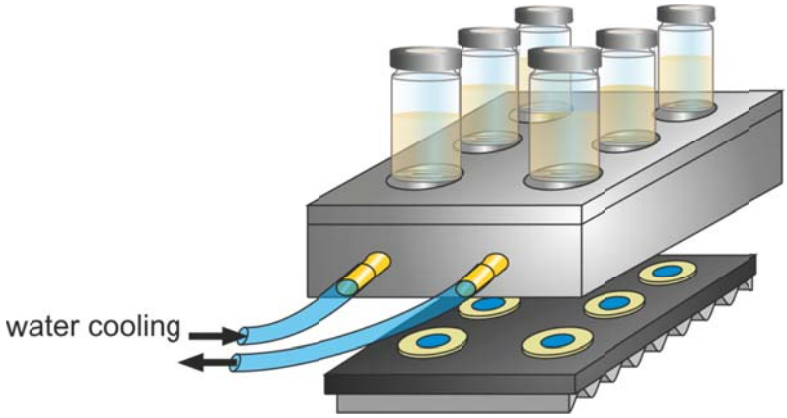


Figure S7: Schematic setup of the irradiation device for samples containing catalysts **6**.

Samples Containing Catalyst 3 or 7:

For the irradiation 8 mL of the vesicular solution were filled in a 25 mL vial. The vial was closed with a septum and the solution was degassed with argon for 10 min. This solution was stirred magnetically and irradiated for 20 min with a 500 W Xenon lamp (cut off filter, λ > 400 nm; 450 mW light intensity) under water cooling at 25 °C (Figure S8). After irradiation a 500 μL sample of the gaseous phase above the reaction solution was injected into a Techcomp GC 7890T gas chromatograph, with a 5 Å mol sieve column, a thermal conductivity detector and Ar as carrier gas.

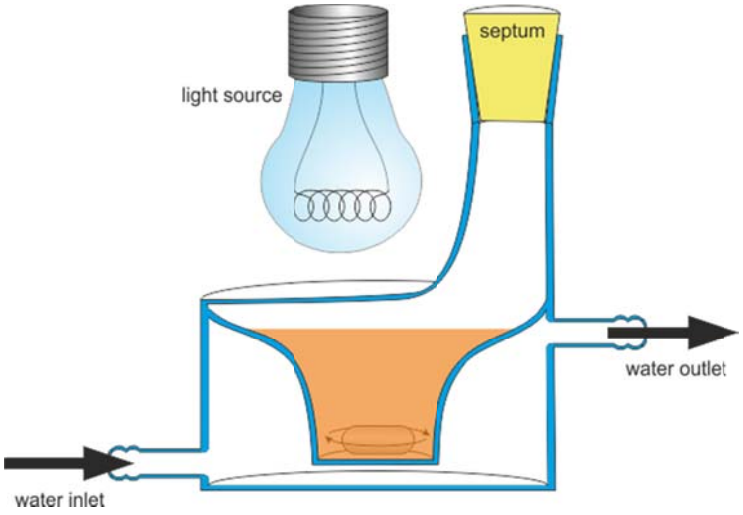


Figure S8: Schematic setup of the irradiation device for samples containing catalyst **3** and **7**

Influence of Solution Turbidity on Oxygen Evolution

To determine the influence of the turbidity of a vesicular solution on oxygen evolution three vesicular samples were prepared by different techniques. A vesicular stock solution was prepared by creating a lipid film composed of appropriate amounts of DMPC (**9**) (863 µM), catalyst **6b** (12.5 µM) and photosensitizer **2b** (125 µM). This film was hydrated with phosphate buffer (pH = 7.0, 50 mM) creating a polydisperse vesicular solution. Two aliquots of this solution were homogenised by extrusion through a polycarbonate membrane (pore size 100 nm), using a LiposoFast extruder (Avestin), and ultrasound, respectively. The third aliquot was used directly. The size distributions are shown in Figure S9. The oxygen evolution in the liquid phase was monitored (Figure S10) using the Fibox 3 system. The difference in oxygen evolution for all three samples is within the typical experimental error, which indicates that size and polydispersity do no change the catalytic performance significantly.

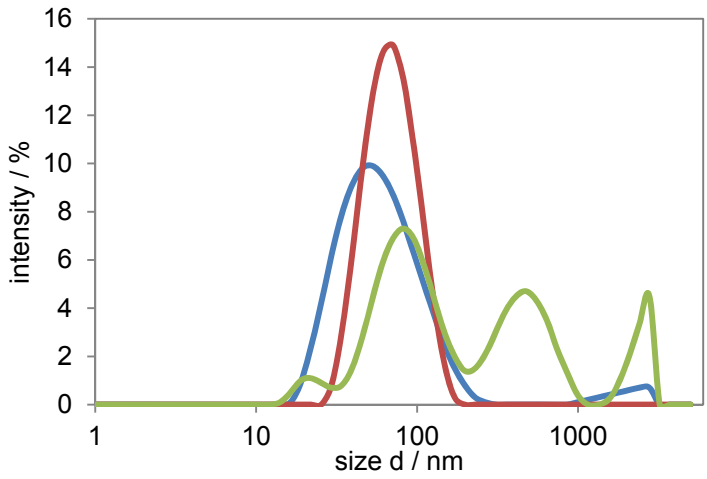


Figure S9: Size distribution of the extruded (red), sonicated (blue) and polydisperse (green) vesicular samples.

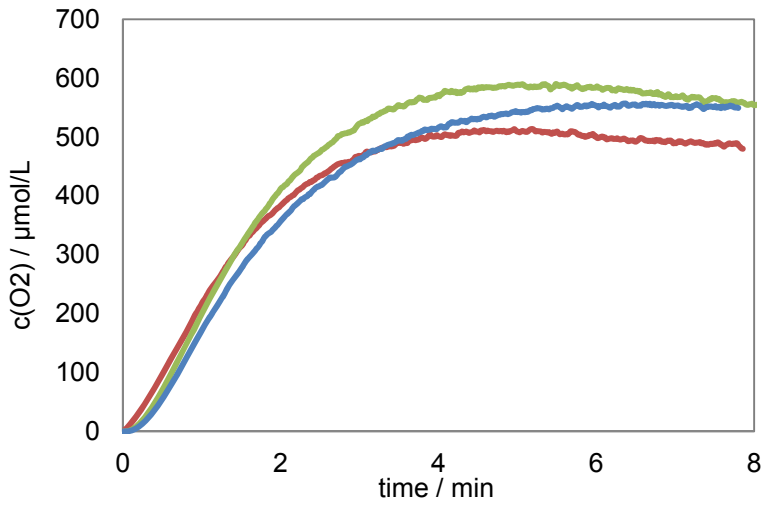


Figure S10: Oxygen evolution of the extruded (red), sonicated (blue) and the polydisperse (green) vesicular samples

Regeneration of the Catalytic Activity

It is known in literature that the activity of a water photooxidizing system is often limited by the stability of the photosensitizer.[12] We could regain about 60 % of the initial TON by embedding new photosensitizer to the membrane and adding new sacrificial electron acceptor (Table 2). A vesicular solution containing DMPC (**9**), **2a** and **7** was prepared and irradiated as described above. A lipid film of photosensitizer **2a** was prepared by adding 470 µL of a 2 mM stock solution to a round bottom flask and evaporating the solvent. 7.5 mL of the vesicular solution after irradiation were added to the lipid film and the mixture was stirred for 2 h at 60 °C. Sodium persulfate was added to this solution and the sample was degassed by Ar. After 20 min of illumination the amount of evolved oxygen was determined by gas chromatography.

Polarity at the Membrane Interface:

The dansyl dye **12** (Figure S11) was synthesized according to a literature known procedure.[13] The polarity at the interface was determined by embedding **6** into DMPC (**9**), SMPC (**10**) or DOPC (**11**) bilayer membranes (5 mol%) and exiting the dye at a wavelength

of 335 nm.[14] The emission maximum wavelength was measured and no significant difference was obtained (Figure S12).

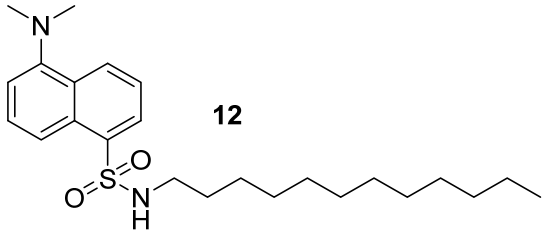


Figure S11: Structure of amphiphilic dansyl dye **12**.

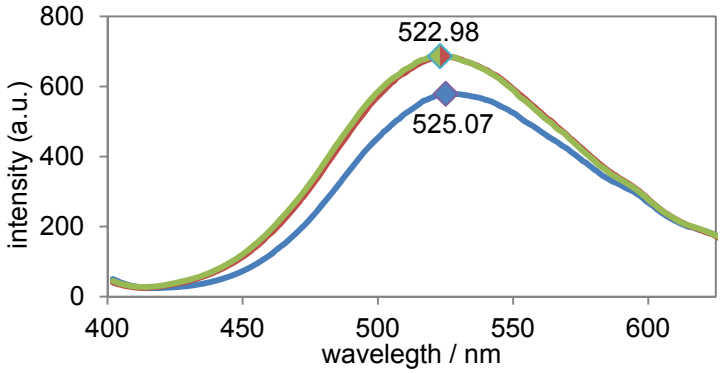


Figure S12: Emission spectra of dansyl dye **12** embedded in DOPC (**11**) (blue trace), DMPC (**9**) (red trace) and SMPC (**10**) (green trace) vesicles.

Determination of the Quantum Efficiency

The quantum efficiency φ for the oxidant generation between $Ru(bpy)_3$ and sodium persulfate can be determined by measuring the the emission intensity of the $Ru(bpy)_3^{2+}$ in the absence and presence of persulfate under the same condiaitons used in the reaction.[15] This was done by preparing vesicular samples as described in Table S1 without sodium persulfate. After degassing with Ar the emission intensity of **2a** at 665 nm was measured. Then sodium persulfate was added and the emission intensity was determined again (

Table S3). With this data the qauntum efficiency $\varphi = 1\text{-}I/I_0$ was calculated.

Table S3: Determined emission intensities at 665 nm of vesicular samples containing 125 μM **2a**, 12.5 μM **6b** and 863 μM phospholipid and calculated quantum efficiencies φ.

entry	phospholipid	I_o (without $S_2O_8^{2-}$)	I (with $S_2O_8^{2-}$)	φ ($1-I/I_0$) / %
1	DMPC (**9**)	699	454	35
2	SMPC (**10**)	633	445	30
3	DOPC (**11**)	758	685	10

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