Supporting Information

Block copolymer micelles as efficient colloidal photosensitizers in light-driven hydrogen evolution reaction

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S1 General information

Materials

3-Chloro-2-hydroxypropyl methacrylate (≥96.5 %), 2.5 M *n*-butyllithium solution in *n*-hexane, diisopropylamine (≥99.5%) and *cis*-bis(2,2'-bipyridine)dichlororuthenium(II) hydrate (97 %) were purchased from *Sigma-Aldrich* (Steinheim, Germany). 4,4′-Dimethyl-2,2'-bipyridine (99.82%) was purchased from BLD Pharmatech Ltd. (Shanghai, China). 4-(Methoxymethyl)styrene (MMS) and the polystyrene macroinitiator (PS_{375}) were synthesized as reported previously.[1] *N*-*tert*-butyl-*N*-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl-*N*-oxyl nitroxide (SG1) was synthesized in analogy to literature.[2] All chemicals were used as received. The thiomolybdate $(NH_4)_2[Mo_3S_{13}] \times 2H_2O$ was prepared as described elsewhere.[3] Polymerization inhibitor was removed from monomers by passing over a short column of basic aluminum oxide. All polymerization reactions were degassed by gently bubbling argon through the solution for 30 min prior to heating. All deuterated solvents were purchased from Eurisotop or Deutero.

Characterization

Nuclear magnetic resonance (NMR). Nuclear magnetic resonance (NMR) measurements were performed on the 300 MHz *Bruker (Billerica, USA) AC 300/75 MHz* and on the 400 MHz *Bruker DRX 400 MHz* spectrometer. The chemical shift for ^{1}H-NMR experiments is referenced to tetramethylsilane

(TMS). The solvent used is always specified and the spectra were referenced to the solvent signal. The obtained NMR spectra were analyzed with the program *MestReNova*.

Size exclusion chromatography (SEC). Size exclusion chromatography (SEC) was carried out on an *Agilent System (1200 series)*, that was equipped with a *PSS* degasser, a *G1310A* pump, a *G1362A* refractive index detector and a *G1315D* diode array detector. Dimethylacetaminde (DMAc) containing 0.21 wt.% LiCl was used as the eluent at a flow rate of 1 mL/min on a *PSS GRAM guard/30/1,000 Å* (10 µm particle size with a separation range from 400 – 1,000,000 g/mol) as stationary phase. The system was calibrated on a polystyrene standard from *PSS (Mainz, Deutschland)* and the measurement was performed at 40 °C. The analysis of the obtained data was carried out with the program *PSS WinGPC® UniChrom*.

Dynamic light scattering (DLS). Dynamic light scattering was performed with the *ALV/CGS-3 Compact Goniometer System*. The measurement was accomplished under the usage of a laser (λ = 633 nm) at a temperature of 25 °C at a detection angle of 90 °. As correlator the device *ALV/LSE-5004* was utilized. The analysis of the obtained data was carried out with the program *ALV-Correlator 3.0*.

Transmission electron microscopy (TEM). For TEM, copper grids were rendered hydrophilic by Ar plasma cleaning for 30 s (*Diener Electronics*). 10 µL of the respective sample solution were applied to the grid and excess sample was blotted with a filter paper. TEM images were acquired with a 200 kV *FEI Tecnai G2 20* equipped with a 4k x 4k *Eagle HS* CCD and a 1k x 1k *Olympus MegaView* camera for overview images. Data processing as well as the determination of the apparent core radius ($r_{\mathrm{core,app}}$) of micelles (individually measuring area of 40 separated and spherical micelles each sample, while neglecting the contribution of the collapsed shell to the measured radius) was performed with the program *ImageJ*. For determining the aggregation number (N_{agg}) $r_{\mathrm{core,app}}$ was used as basis:

$$N_{agg} = \frac{m_{core}}{m_{PS}^{chain}} = \frac{4\pi N_A \rho_{PS} r_{core}^{\ 3}}{3M_{PS}^{chain}}$$

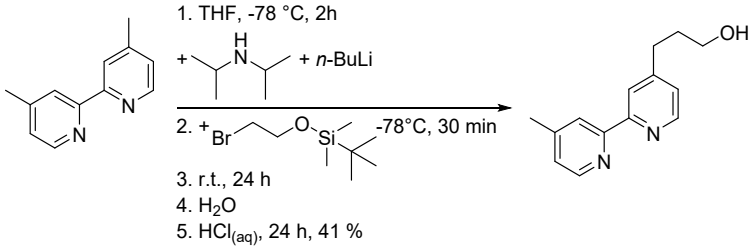
with m_{core}: mass of the micellar core; m_{PS}^{chain} : mass of an individual PS chain; N_A: Avogadro constant; ρ_{PS}: density of polystyrene; $r_{core,app}$: radius of the micellar core according to TEM; M_{PS}^{chain} : molecular weight of an individual PS chain.

UV/vis spectroscopy. Measurements were performed on an *Agilent Cary 60* in a *Hellma* quartz glass cuvette with a pathlength of 10 mm at room temperature in the respective solvent. The absorbance was measured in a range from 200 nm to 800 nm in 1 nm steps.

Gas chromatography (GC). For quantifying hydrogen evolution 100 µL aliquot of the head space from irradiated samples was injected to a Shimadzu Nexis GC-2030 gas chromatograph with molecular sieve Å5 column. Detection is afforded by barrier discharge ionization detector with helium carrier gas.

S2 Synthesis

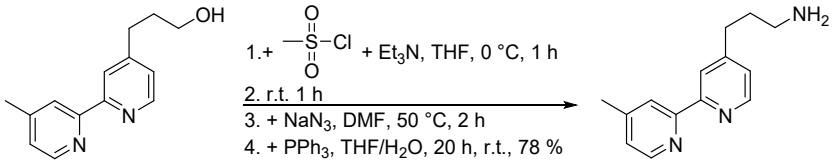
4-(3-Hydroxypropyl)-4-methyl-2,2-bipyridine (bpyOH)



Scheme S1: Synthesis of bpyOH.

The synthesis of 4-(3-Hydroxypropyl)-4-methyl-2,2-bipyridine was carried out according to a modified literature protocol.[4] To a solution of 5.49 g (7.63 mL, 54.28 mmol) diisopropylamine in 30 mL of THF 21.71 mL of a 2.5 M solution of *n*-BuLi in *n*-hexane was added dropwise at -78 °C. The resulting slightly turbid and pale-yellow mixture was stirred for 15 min. Subsequently a mixture of 10.00 g (54.28 mmol) 4,4'-dimethyl-2,2-bipyridine in 250 mL of THF was added within 10 min by a stainless steel cannula to the reaction solution. The dark red-brown solution was further stirred for additional 2 hours at -78 °C. In the next step a solution of 12.98 g (54.28 mmol) (2-bromoethoxy)-*tert*-butyldimethylsilane in 90 mL THF was added *via* a stainless steel cannula. After additional 30 min the low-temperature bath was removed, and the mixture was stirred overnight at room temperature. Subsequently 25 mL of brine were dropped into the green mixture causing a color change to pale yellow. After removing of all volatiles under reduced pressure the orange residue was dissolved in chloroform and washed with water (3 x 100 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and after removal of the solvent the residue was stirred in 50 mL 1 M $HCl_{(aq)}$ overnight at room temperature. Subsequently, the reaction mixture was washed with methyl *tert*-butyl ether (MTBE) (2 x 100 mL), neutralized with 1 M $NaOH_{(aq)}$ and extracted with chloroform (1 x 200 mL). The organic phase was washed with water (2 x 100 mL), afterwards dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the orange, oily residue was recrystallized from ethanol, removing unreacted 4,4'-dimethyl-2,2-bipyridine as precipitate. Further purification was purified by column chromatography (aluminum oxide, neutral, activated, Brockman grade II; ethyl acetate). The purified product was obtained as an orange oil that solidified upon storage at 4 °C. Yield: 5.142 g (41 %). ^{1}H-NMR: ($CDCl_3$, 300.13 MHz, 300.0 K): δ [ppm] 8.53 (d, ^3J(H-H) = 5.0 Hz, 1H, *H*-6, bpy), 8.49 (d, ^3J(H-H) = 5.0 Hz, 1H, *H*-6, bpy), 8.21-8.20 (m, 2H, *H*-3, bpy), 7.14-7.11 (m, 2H, *H*-5), 3.65 (t, ^3J(H-H) = 6.3 Hz, 2H, C_{ar}-CH_2-CH_2-), 2.81-2.76 (m, 2H, -CH_2OH), 2.42 (s, 3H, C_{ar}-CH_3), 1.98-1.88 (m, 2H, -CH_2-CH_2-CH_2-).

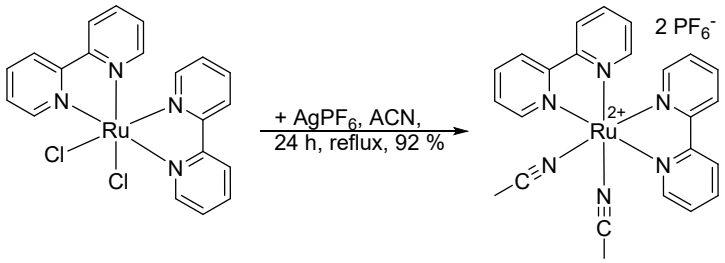
4-aminopropyl-4'-methyl-2,2'-bipyridine ($bpyNH_2$)



Scheme S2: Synthesis of $bpyNH_2$.

To a solution of 1.00 g (4.38 mmol) bpyOH and 0.886 g (1.214 mL, 8.76 mmol) Et_3N in 30 mL anhydrous THF 0.753 g (6.57 mmol) methanesulfonyl chloride was added dropwise at 0 °C. Stirring of the formed suspension was continued at 0 °C for 1 h and subsequently for another hour at room temperature. After that, 120 mL ethyl acetate was added and the mixture was washed with water (1 x 30 mL), saturated $NaHCO_3$ solution (1 x 20 mL), water (30 mL), and brine (60 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtered and all volatiles were removed under reduced pressure. The obtained residue was dissolved in 20 mL anhydrous DMF. To this solution 0.641 g (9.86 mmol) NaN_3 was added and the mixture was stirred for heated at 50 °C for 2 h. After that time, the solution was freed from all volatiles by adding repeatedly *n*-heptane until all DMF residues were removed under reduced pressure by the formed azeotrope. The residue was suspended in 50 mL chloroform and washed with water (3 x 20 mL) and brine (2 x 30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and all volatiles were removed under reduced pressure yielding an orange oil, that was dissolved in a mixture of 20 mL THF and 2 mL water. Afterwards, 1.50 g (5.70 mmol) PPh_3 was added and the mixture was stirred overnight at room temperature until no gas evolution was noted. The solution was freed from all volatiles afterwards, dissolved in 30 mL 1M $HCl_{(aq)}$ and washed with diethyl ether (3 x 100 mL). The aqueous phase was adjusted to pH 10 using 1M $NaOH_{(aq)}$ and extracted with chloroform (3 x 70 mL). The organic phase was washed with saturated $NaHCO_3$ solution (1 x 30 mL) and brine (1 x 50 mL). Afterwards the organic layer was dried over anhydrous Na_2SO_4, and filtered. Removal of all volatiles yielded an orange oil as product, that solidified upon storage at -20 °C. Yield: 0.78 g (78 %). ^{1}H-NMR: ($CDCl_3$, 300.13 MHz, 300.0 K): δ [ppm] 8.54-8.50 (m, 2H, *H*-6, bpy), 8.22-8.20 (m, 2H, *H*-3, bpy), 7.13-7.09 (m, 2H, *H*-5), 2.76-2.70 (m, 4H, C_{ar}-C*H*$_2$-CH$_2$-C*H*$_2$NH$_2$), 2.41 (s, 3H, C_{ar}-C*H*$_3$), 1.88-1.78 (m, 2H, -CH$_2$-C*H*$_2$-CH$_2$-), 1.43 (s, 2H, -NH$_2$).

Bis(2,2'-bipyridine)-bis(acetonitrile)ruthenium-(II) hexafluorophosphate ($[Ru(bpy)_2(ACN)_2](PF_6)_2$)



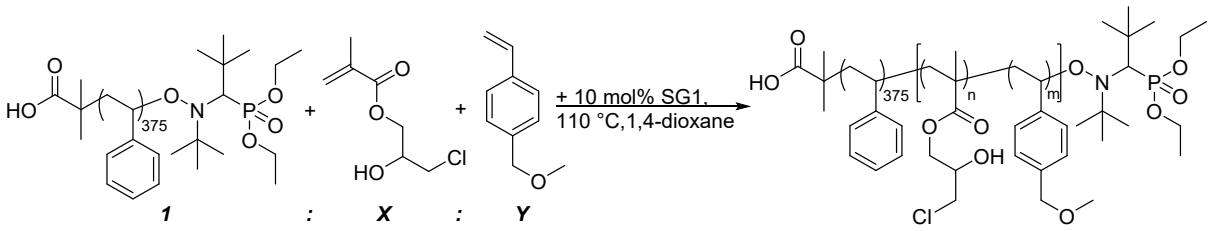
Scheme S3: Synthesis of $[Ru(bpy)_2(ACN)](PF_6)_2$.

$[(bpy)_2RuCl_2]$ was synthesized from $[Ru(COD)Cl_2]_n$ as described previously.[5] The synthesis of the ACN-precursor for the coordination to the polymer is a modified procedure from a previously published method which facilitates removal of chlorido ligands from the complex.[6]

230.6 mg (0.477 mmol, 1 eq.) $[(bpy)_2RuCl_2]$ was suspended with 253.0 mg (1.001 mmol, 2.1 eq) silver hexafluorophosphate in dry acetonitrile. The wine-red solution was heated to reflux for 24 h changing color to orange. The greyish precipitate that formed was removed by decantation of the solution and the solution concentrated *in vacuo* when more grey precipitate occurred. The precipitate was removed by subsequent concentration, cooling to 0 °C and centrifugation or filtration (porosity 4 glass frit with celite filtering bed) until no more precipitate occurred (typically three cycles). After removal of all volatiles the product $[Ru(bpy)_2(ACN)_2](PF_6)_2$ was obtained as an orange solid. Yield: 346 mg (92 %). ^{1}H NMR (400.13 MHz, CD_3CN, 298.0 K): δ [ppm] 9.21 (d, ^3J(H-H) = 5.6 Hz, 2H), 8.41 (d, ^3J(H-H) = 8.1 Hz, 2H), 8.27 (d, ^3J(H-H) = 8.1 Hz, 2H), 8.19 (td, ^3J(H-H) = 8.0 Hz, ^4J(H-H) = 1.5 Hz, 2H), 7.86 (td, ^3J(H-H) = 8.0 Hz, ^4J(H-H) = 1.5 Hz, 2H), 7.78 (ddd, ^3J(H-H) = 7.5, 5.6 Hz, ^4J(H-H) = 1.3 Hz, 2H), 7.47 (d, ^3J(H-H) = 5.7 Hz, 2H), 7.18 (ddd, ^3J(H-H) = 7.2, 5.7 Hz, ^4J(H-H) = 1.3 Hz, 2H), 2.24 (s, 6H).

The secondary signals in the NMR spectrum within the aromatic region (**Figure S4**) arise from the *trans*-$[Ru(bpy)_2(ACN)_2]^{2+}$ species,[7] that forms during the reaction or light activation during workup. This species is not active in following coordinating reactions or can even transform back into the *cis*-isomer, which is why there was no need for further purification.

Block extension of PS_{375} with ClHPMA and MMS



Scheme S4: Block extension of PS_{375} with ClHPMA and MMS utilizing different M/I ratios and reaction times; M/I = 400:1, X = 360, Y = 40; M/I = 600:1, X = 540, Y = 60, M/I = 800:1, X = 720, Y = 80, M/I = 1000:1, X = 900, Y = 100, M/I = 1200:1, X = 1080, Y = 120.

In a typical approach the respective amounts (**Table S1**) of PS_{375}, ClHPMA, MMS and SG1 were dissolved in 1,4-dioxane, affording a concentration of ClHPMA of 0.55 M. The mixture was stirred at 110 °C for the specified time and subsequently cooled in a water bath to room temperature. The solution was diluted with 1-2 mL THF and precipitated in *n*-hexane three times affording a white powder after freeze-drying (1,4-dioxane as solvent). For kinetic investigations samples were taken directly from the reaction mixture and precipitated twice in *n*-hexane prior to SEC and NMR analysis.

Table S1: Reaction approaches and batch calculations for the synthesis of PS-*b*-P(ClHPMA-*co*-MMS) block copolymers.

M/I ratio	m (n) PS_{375} / mg (µmol)	m (n) ClHPMA / g (mmol)	m (n) MMS / mg (µmol)	m (n) SG1 / µg (µmol)	V dioxane / mL	Reaction time / min	Yield / mg
1:400	50.00 (1.268)	81.60 (0.457)	7.56 (50.8)	35 (0.13)	0.71	20	70
1:600	50.00 (1.268)	122.4 (0.686)	11.3 (76.2)	35 (0.13)	1.09	20	70
1:800	50.00 (1.268)	163.2 (0.914)	15.0 (102)	35 (0.13)	1.46	20	70
1:1000	50.00 (1.268)	204.2 (1.143)	18.8 (127)	35 (0.13)	1.84	kinetics	-
1:1200	50.00 (1.268)	248.8 (1.371)	22.5 (152)	35 (0.13)	2.214	kinetics	-
1:1000	200.0 (5.071)	816.6 (4.572)	75.2 (508)	150 (0.51)	7.35	30	309

Functionalization of PS-*b*-P(ClHPMA-*co*-MMS) with $bpyNH_2$

In a 5 mL microwave vial a solution of 50 mg (0.82 µmol) PS_{375}-*b*-P($ClHPMA_{97}$-*co*-MMS_{30}) and 27.4 mg (119.0 µmol) $bpyNH_2$ in 0.75 mL THF was degassed by gently bubbling argon through the solution for 30 min before being heated at 70 °C for 48 h. Afterwards, the mixture was diluted with 0.5 mL THF and precipitated three times in diethyl ether affording a white powder after freeze-drying (1,4-dioxane as solvent). Yield: 59.0 mg. ^{1}H-NMR: (300.13 MHz, DMF-d_7, 300.0 K): δ [ppm] 8.66-8.49 (m, br, Ar*H* bpy), 8.40-8.21 (m, br, Ar*H* bpy), 7.44-6.44 (m, br, Ar*H* bpy, Ar*H* styrene and MMS), 4.60-3.08 (m, C_{ar}-C*H*$_2$-CH_2-C*H*$_2$$NH_2^+$-C*H*$_2$-C*H*(OH)-C*H*$_2$-O-), 2.50-2.35 (m, C_{ar}-C*H*$_3$), 2.33-2.12 (m, C_{ar}-CH_2-C*H*$_2$-), 2.10-0.77 (m, backbone, -CH-C*H*$_3$).

Functionalization of PS-*b*-P(bpyHPMA-*co*-MMS) with [Ru]

In a 2 mL microwave vial a solution of 10 mg (0.13 µmol) PS_{375}-*b*-P(bpyHPMA$_{97}$-*co*-MMS_{30}) and 11.4 mg (14.6 µmol) $[Ru(bpy)_2(ACN)_2](PF_6)_2$ in 0.5 mL DMF was degassed by gently bubbling argon through the solution for 30 min before being heated at 90 °C for 48 h. Afterwards, the mixture was diluted with 2 mL DCM, 50 µL Et_3N and purified by size exclusion chromatography (Biobeads SX-1, DCM). The orange colored, high molecular weight fraction was collected. Subsequently, all volatiles were removed under reduced pressure and the residue was dissolved in 1,4-dioxane prior to freeze-drying yielding an orange power as product. Yield: 8.50 mg. ^{1}H-NMR: (300.13 MHz, DMF-d_7, 300.0 K): δ [ppm] 9.22-9.79 (m, br, Ar*H*, [Ru]), 8.61-8.42 (m, br, Ar*H* bpy), 8.40-8.11 (m, br, Ar*H* bpy, Ar*H* [Ru]), 7.98-7.37 (m, br, Ar*H* [Ru]), 7.34-6.44 (m, br, Ar*H* bpy, Ar*H* styrene and MMS), 4.44-3.02 (m, br, C_{ar}-C*H*$_2$-CH$_2$-C*H*$_2$NH-C*H*$_2$-C*H*(OH)-C*H*$_2$-O-), 2.60-2.47 (m, br, C_{ar}-C*H*$_3$ [Ru]), 2.43-2.33 (m, br, C_{ar}-C*H*$_3$ bpy), 2.28-0.77 (m, br, C_{ar}-CH$_2$-C*H*$_2$-, backbone, -CH-C*H*$_3$).

S3 Micellization procedure

The micellization was carried out similarly to our previous report.[1] 2.25 mg of block copolymer was dissolved in 1 mL of DMF. 2 mL of methanol was added under stirring *via* a syringe pump (42 µL/min). Afterwards the turbid mixture was stirred for one hour. After that time 2 mL of methanol was added rapidly and the dispersion was stirred overnight. Subsequently, the mixture was dialyzed against methanol for at least 4 days with minimum 8 changes of the dialysis methanol.

S4 Light-driven catalysis

The preparation of stock solutions and reaction mixtures was conducted in analogy to literature.[3] Therefore, a freshly prepared aqueous 1 M stock solution of ascorbic acid was adjusted to pH 4 using aqueous NH_3. To GC vials (5 mL) the respective amount of the ascorbic acid stock solution (see **Table S2**), MeOH and PS_{375}-*b*-P(bpyHPMA$_{97}$-*co*-MMS_{30}) based micellar solution (c(block copolymer) = 0.42 g/L in MeOH) were added and degassed with argon for 20 min. A $[Mo_3S_{13}]^{2-}$ stock solution was freshly prepared upon dissolving 1 mg of $(NH_4)_2[Mo_3S_{13}]$ in 1 mL DMF. After complete dissolution, 39 mL of MeOH were added, resulting in a final concentration of 32.18 µM (0.025 g/L) $(NH_4)_2[Mo_3S_{13}]$. Under argon atmosphere, the respective amounts of the $[Mo_3]$ stock solution was added to the reaction vials and the rubber septum caps were exchanged by unused ones (avoiding loss of produced hydrogen by pierced septa). Irradiation was started within 1-2 min after adding the catalyst. Illumination time was set to 3 h, except for the kinetic investigation where samples after 5, 10, 20, 30, 60, 180 and 1440 min were removed from the reactor and immediately handled under the exclusion of light to avoid additional ambient light induced activity.

Table S2: Batch calculations for photocatalytic experiments.

[Mo_3]/[Ru]/Asc.[a] (No. of samples)	c([Mo_3]) / µM	c([Ru]) / µM	c(Asc.) / M	V^b ([Mo_3]) / µL	V^b (micelles) / µL	V^b (Asc.) / µL	V^b (MeOH) / µL[c]
1:26:333333 (3)	0.3	7.6	0.1	18.64	73.7	200	1708
1:51:333333 (1)	0.3	15.2	0.1	18.64	147.4	200	1634
1:66:333333 (3)	0.3	20.0	0.1	18.64	191.4	200	1590
1:103:333333 (1)	0.3	30.4	0.1	18.64	294.8	200	1486
2:66:333333 (1)	0.6	20.0	0.1	18.64	95.68	100	785
4:66:333333 (1)	1.2	20.0	0.1	37.28	95.68	100	767
8:66:333333 (1)	2.4	20.0	0.1	74.57	95.68	100	729
1:66:333333 (7) (kinetics)	0.3	20.0	0.1	9.32	95.68	100	795

[a] Asc. = ascorbic acid. [b] Volume of respective stock solution used for sample preparation. [c] Added MeOH for achieving a solvent ratio MeOH/H_2O 9:1.

The irradiation setup is described in detail in a previous report.[3] In short, photocatalytic experiments were carried out in 4 mL LABSOLUTE 7613421 clear glass screw neck vials (ND13) GC without stirring. As LED source, a 453 nm LED (operating at an electrical current of 0.95 A) was used equipped in the 90×90×100 mm corpus. The sample holder was placed in position 7 with an additional alignment ring holder in position 6 (**Figure S1**). The hydrogen content was measured under exclusion of light *via* head-space GC. For experiments showing error bars in **Figure 3** the reaction was reproduced three times, for the other experiment single determination was performed.

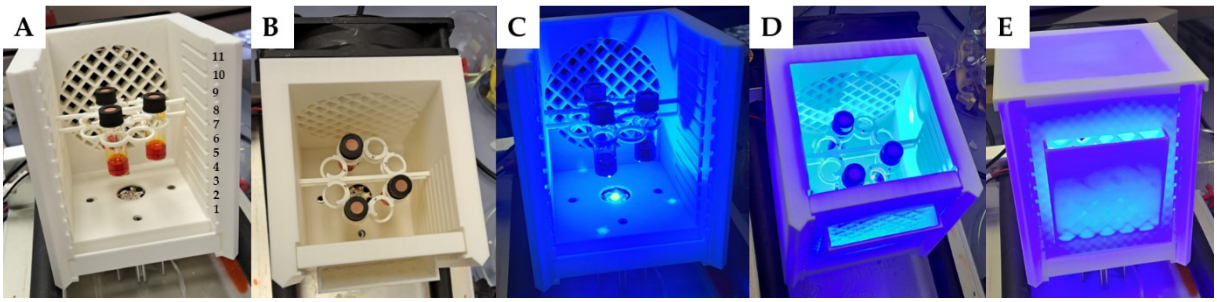


Figure S1: Photoreactor used for hydrogen evolution experiments with 1 mL of aqueous methyl orange solution in three 4 mL LABSOLUTE 7613421 clear glass screw neck vials. (**A**) Side view of reactor including slot position indication. (**B**): Top view of reactor including side shielding. (**C**): Side view of reactor under LED irradiation. (**D**): Top view of reactor under LED irradiation. (**E**): Photoreactor including top- and side shielding under operation.

Turnover numbers (TONs) were calculated from the number of hydrogen molecules produced per molecule $[Mo_3S_{13}]^{2-}$. Therefore, in a first step the volumetric amount V of hydrogen in the head space of the reaction vial was determined by GC. Afterwards, the ideal gas law was solved for the amount of hydrogen n:

$$n_{H_2} = \frac{p * V}{R * T}$$

with p = 101,325 Pa, R = 8.314 J/(mol*K) and T = 298.15 K. Eventually, knowing the amount of substance for produced hydrogen allowed referring it to the amount of substance for [Mo_3] used in the photocatalytic solution to calculate the TON:

$$TON = \frac{n_{H_2}}{n_{[Mo_3]}}$$

Turnover frequencies (TOFs) were calculated by dividing a produced TON to a certain period of time *t*:

$$TOF = \frac{TON}{t}$$

S5 Supplementary figures

NMR spectra

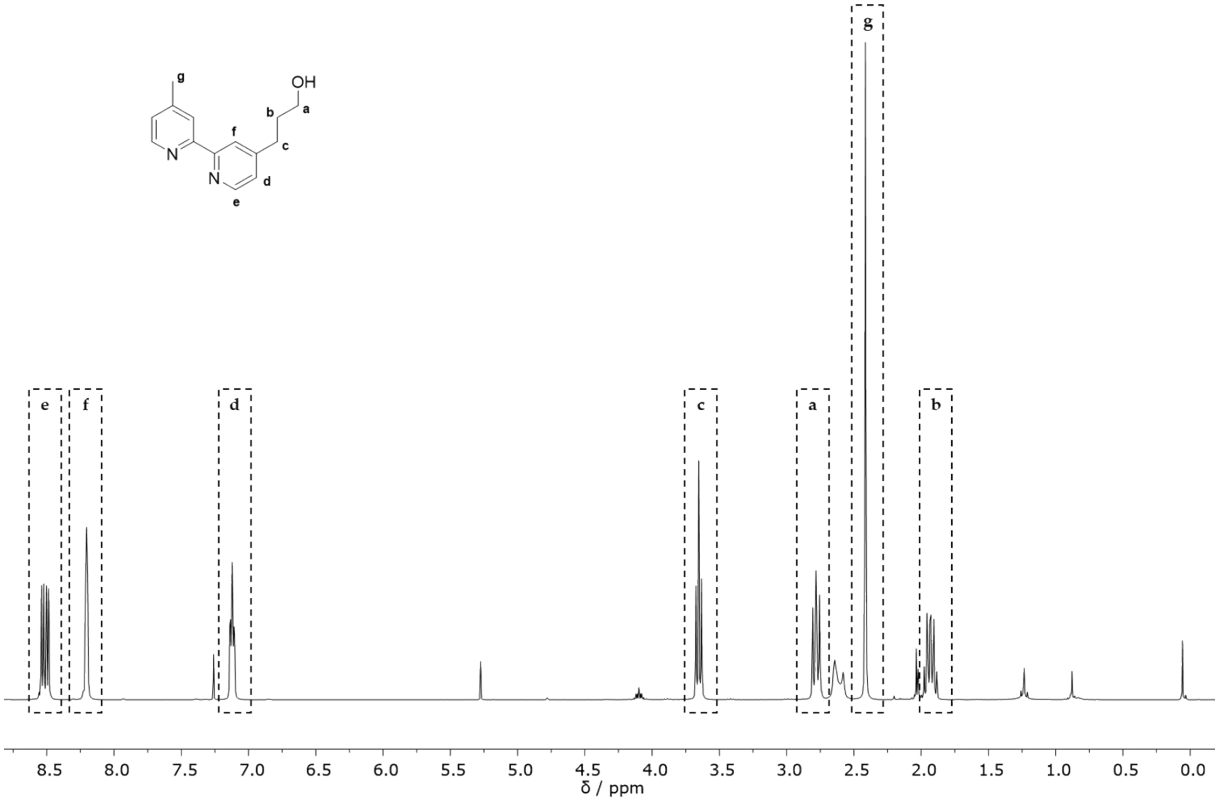


Figure S2: ^{1}H-NMR spectrum of bpyOH (300.13 MHz, $CDCl_3$, 300.0 K) and signal assignment.

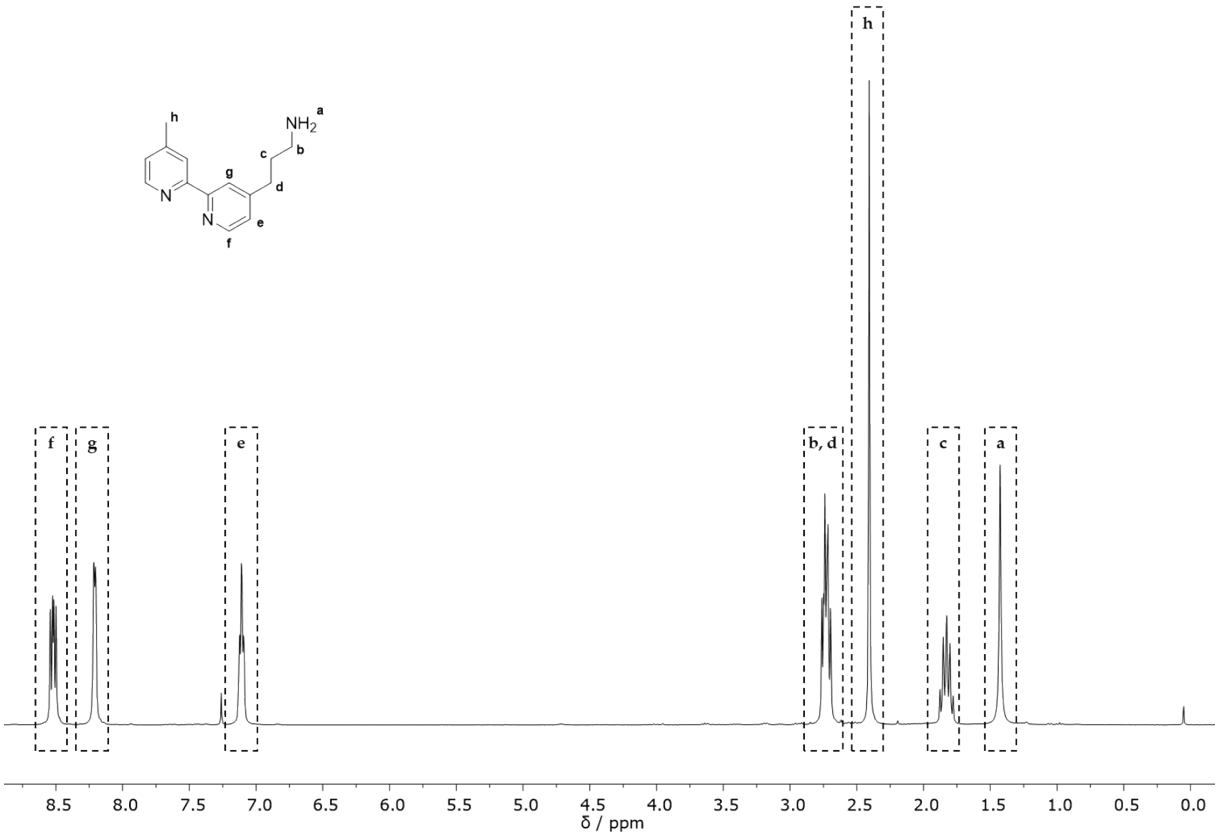


Figure S3: ^{1}H-NMR spectrum of bpyNH_2 (300.13 MHz, $CDCl_3$, 300.0 K) and signal assignment.

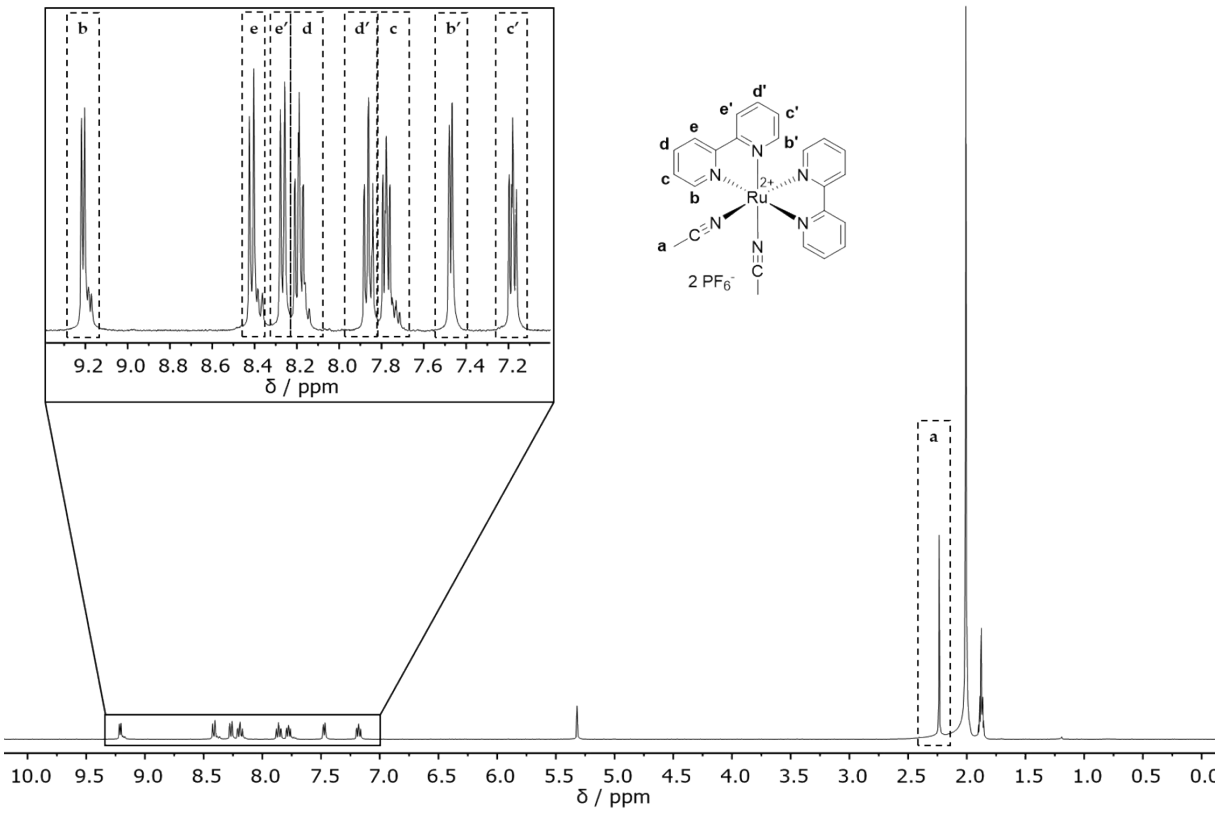


Figure S4: ^{1}H-NMR spectrum of $[Ru(bpy)_2(ACN)](PF_6)_2$ (400.13 MHz, CD_3CN, 298.0 K) and signal assignment.

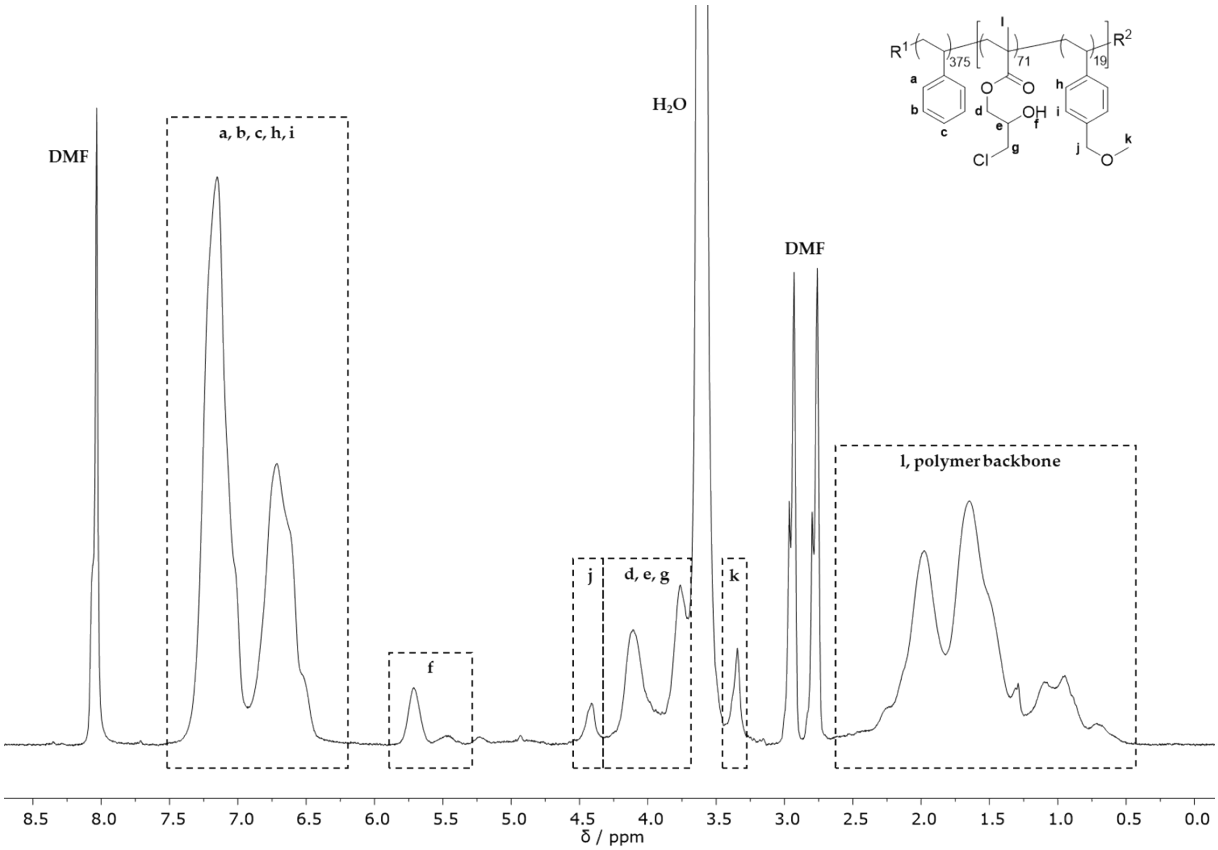


Figure S5: PS_{375}-*b*-P(ClHPMA$_{71}$-*co*-MMS_{19}) (300.13 MHz, DMF-d_7, 300.0 K) and signal assignment, R^1 = 1,1-dimethyl-2-carboxyethyl, R^2 = SG1.

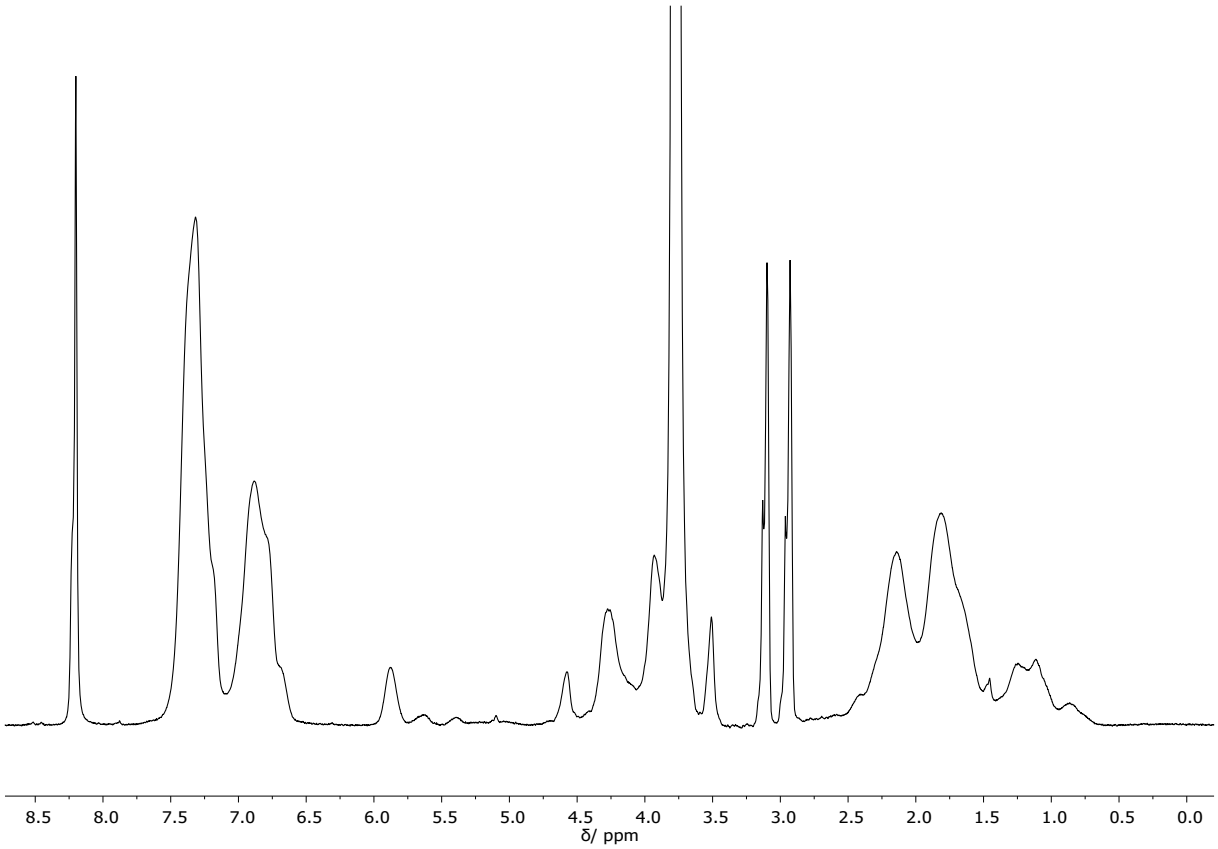


Figure S6: PS_{375}-*b*-P(ClHPMA$_{85}$-*co*-MMS_{26}) (300.13 MHz, DMF-d_7, 300.0 K).

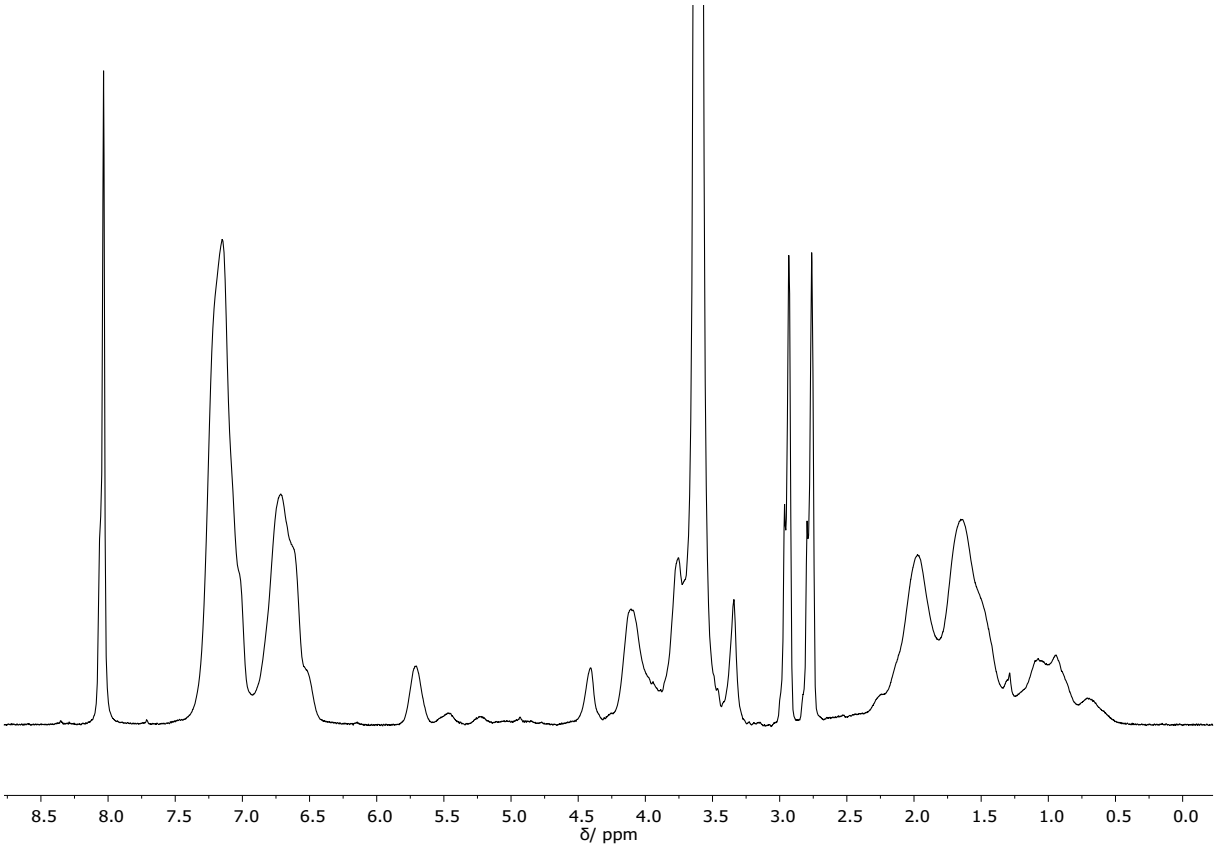


Figure S7: PS_{375}-*b*-P($ClHPMA_{91}$-*co*-MMS_{28}) (300.13 MHz, DMF-d_7, 300.0 K).

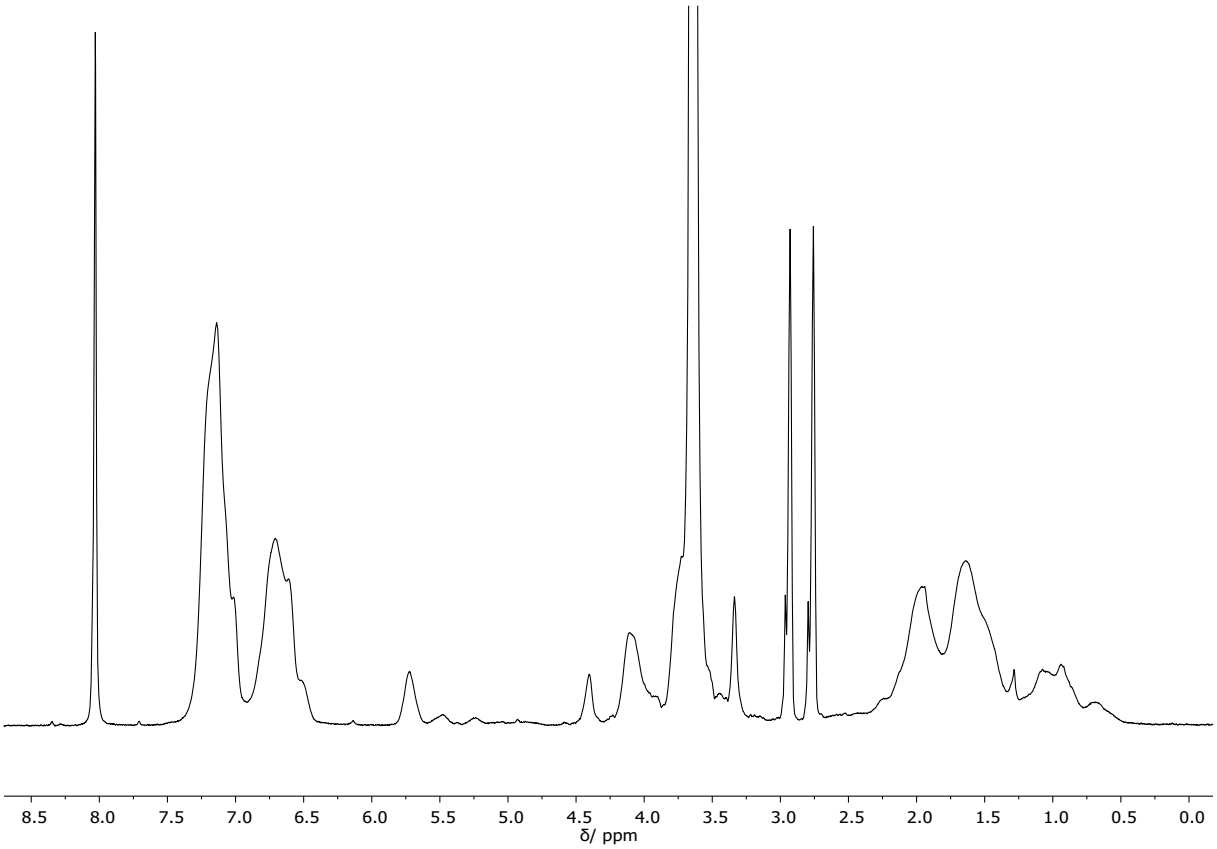


Figure S8: ^{1}H-NMR spectrum of PS_{375}-*b*-P($ClHPMA_{97}$-*co*-MMS_{30}) (300.13 MHz, DMF-d_7, 300.0 K).

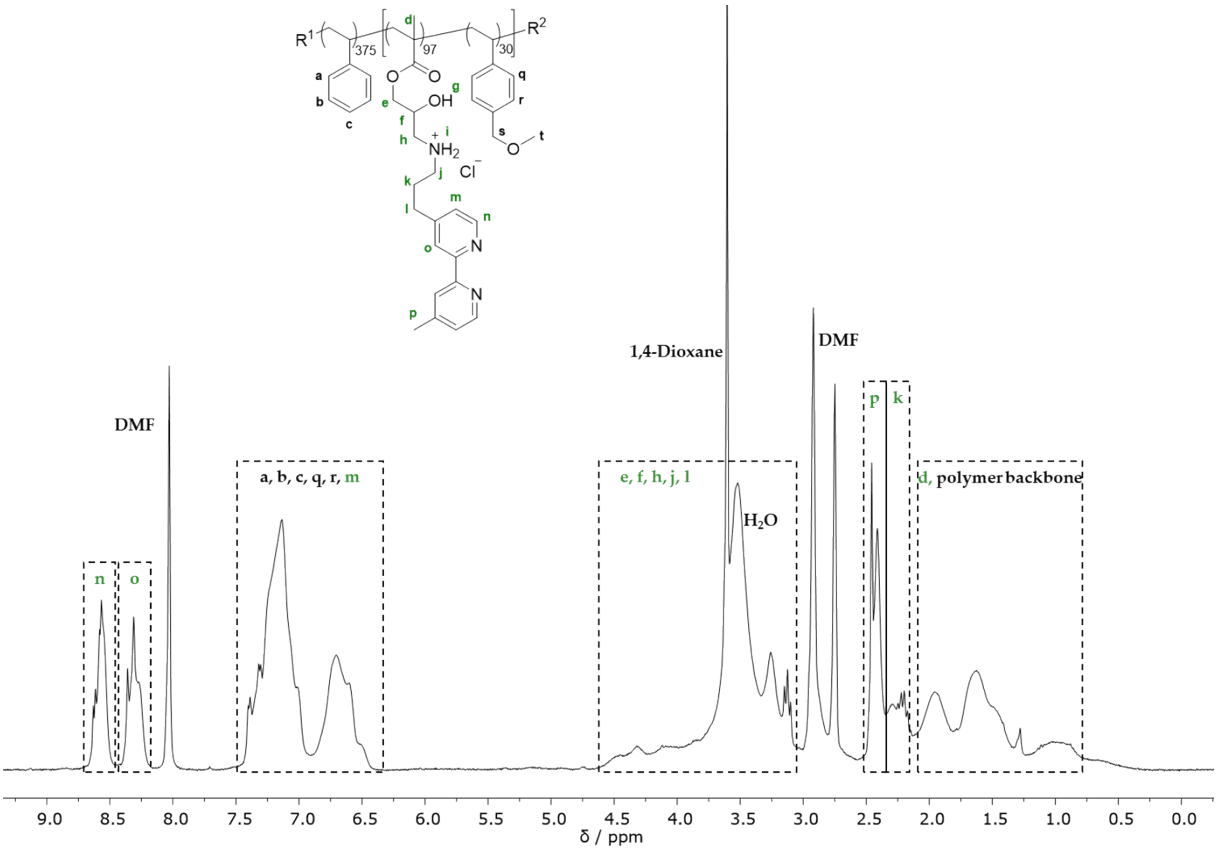


Figure S9: ^{1}H-NMR spectrum of PS_{375}-*b*-P(bpyHPMA$_{97}$-*co*-MMS$_{30}$) (300.13 MHz, DMF-d_7, 300.0 K) and signal assignment.

SEC data

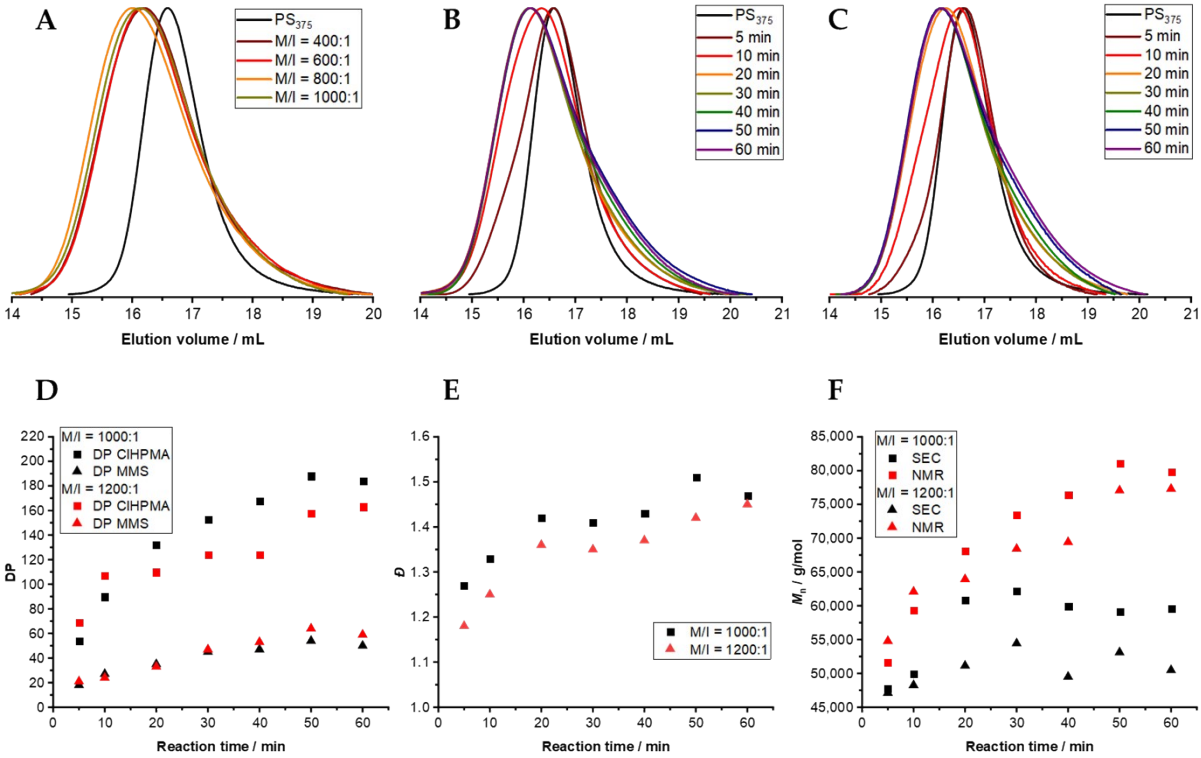


Figure S10: (**A**): Normalized RI SEC elution trace of PS-*b*-P(ClHPMA-*co*-MMS) block copolymers for different M/I ratios, 20 min reaction time for M/I = 400:1-800:1, 30 min reaction time for M/I = 1000:1; (**B**): Normalized RI SEC elution trace of PS-*b*-P(ClHPMA-*co*-MMS) block copolymers for different reaction times, M/I = 1000:1; (**C**): Normalized RI SEC elution trace of PS-*b*-P(ClHPMA-*co*-MMS) block copolymers for different reaction times, M/I = 1200:1.; (**D**): DP of ClHPMA and MMS obtained from kinetics shown in (B) and (C); (**E**) Obtained dispersities of PS-*b*-P(ClHPMA-*co*-MMS) copolymers from kinetics shown in (B) and (C); (**F**): Apparent average molar mass of PS-*b*-P(ClHPMA-*co*-MMS) copolymers determined by SEC analysis, DMAc + 0.21 % LiCl as eluent and NMR analysis. Reaction and analysis parameter for shown results (**A**)-(**F**): c(ClHPMA) = 0.55 M, 10 mol% MMS, SEC and NMR after purification.

SEC traces in **Figure S10A** indicate no significant difference in M_n. This leads to the conclusion, that the change of DP is underrepresented by the change of size for the block copolymer coil. Note that M_n determined by SEC and NMR show a strong discrepancy and incoherent trends (**Figure S10F**). A suitable explanation may be intramolecular hydrogen bonding in PClHPMA *via* hydroxyl groups resulting in a rather collapsed PClHPMA block in the SEC solvent. Experiments with M/I-ratios of 400-800:1 were not successful to achieve an average DP of ClHPMA in the second block close to 100 units per chain. In the following steps the M/I ratio was further increased to 1000:1 and 1200:1. The kinetic investigations in **Figure S10B-F** revealed best results for a M/I ratio of 1000:1 (compromise of DP and *Đ*). For the synthesis of a larger batch of PS-*b*-P(ClHPMA-*co*-MMS) with a relatively high DP in the second segment, the latter conditions were used (corresponding SEC trace in **Figure S10A**), but a lower DP compared to the kinetic trial was observed (*Đ* =1.37). It can be assumed, that upscaling effects took place due to a four-fold increase of the batch size.

TEM data

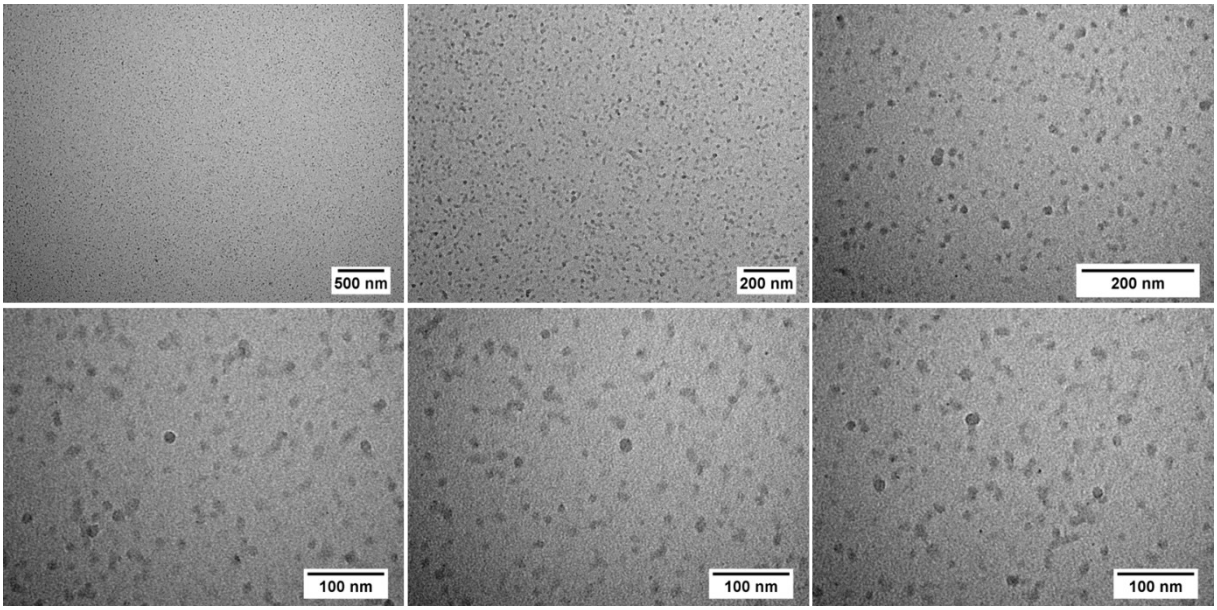


Figure S11: TEM images of PS_{375}-*b*-P([Ru]$_{61}$-*co*-bpyHPMA$_{36}$-*co*-MMS_{30}) block copolymer micelles in MeOH, c(block copolymer) = 0.42 g/L.

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