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Supporting information

Hybrid Nanoreactors formed by Interpolyelectrolyte Complex Formation: A Colloidal Platform for Light-Driven Catalysis

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Experimental

General

Triethanolamine (≥ 99.7%), Potassium tetrachloroplatinate (≥ 99.9%), 2-Acrylamido-2-methylpropane sulfonic acid, 4,4′-bipyridine (4,4′-bpy), Methanesulfonyl chloride (≥ 99.7%), epichlorhydrin (ECH) (≥ 99%), L-ascorbic acid (99%), Triethanolamine (≥ 98%), NaH (60% dispersion in mineral oil), (3-Acryl amidopropyl) trimethyl ammonium chloride solution and, were purchased from Sigma-Aldrich (St. Louis, USA). TFA (≥ 99.9%) and NaOH (0.1 N) were purchased from Roth (Karlsruhe, Germany), triethyl amine (≥ 99.0%) was purchased from CHEMSOLUTE (Renningen, Germany), and N-(*tert*-butoxycarbonyl)-L-serin methylester (98%) was purchased from Carbolution Chemicals (St. Ingbert, Germany). Organic solvents (Schwerte, Germany) was purchased from TCI chemicals (Tokyo, Japan). HCl (37% solution) was purchased from Fischer Scientific (Hampton, USA). We synthesized the blocbuilder and SG1 according to literature.

Synthesis of 1,1'-bis(2-(oxiran-2-ylmethoxy)ethyl)-[4,4'-bipyridine]-1,1'-diium (viologen modified by 2-(ethoxy methyl)oxirane (VEMO))

Viologen modified with epichlorhydrin (VEMO) was synthesised according to the reported literature with some modifications.[1] Briefly, 1,1'-Bis(2-(oxiran-2-ylmethoxy)ethyl)-[4,4'-bipyridine]-1,1'-diium was prepared by two step. First 1,1'-bis(2-hydroxyethyl)-[4,4'-bipyridine]-1,1'-diium was functionalized with 2-bromoethanol. Hereby, 4,4′-bpy (2.94 g, 0.018 mol) and 2-bromoethanol (4 mL, 0.056 mol) in water (9 mL) was keeping at 80 °C for 3 days. The product was precipitated in methanol and separated by filtration, washed with methanol on the filter, and dried. Yield: 6.23 g (70%). ^{1}H NMR (300 MHz, Deuterium Oxide) 9.20 (4 H, d, *J* 6.9), 8.67 (4 H, d, *J* 6.8), 4.33 – 4.11 (4 H, m).

In second step, epichlorohydrin (ECH) (3.49 mL, 32 mmol) was slowly injected into a flask capped with a rubber septum containing a solution of 1,1'-bis(2-hydroxyethyl)-[4,4'-bipyridine]-1,1'-diium (3.7 g, 7.0 mmol) in dry acetonitrile (40 mL), which had been preheated to 50 °C. After 3 days, the yellow precipitate was collected by filtration of the cooled reaction mixture and washed on the filter with diethyl ether and acetone. Yield: 0.7 g (60%). ^{1}H NMR (400 MHz, Deuterium Oxide) 9.42 – 9.24 (4 H, t, *J* 6.8), 8.89 – 8.72 (4 H, d, *J* 6.3), 5.33 – 4.94 (4 H, dt, *J* 35.2, 5.0), 4.40 – 4.05 (2 H, m), 3.97 – 3.56 (12 H, dtd, *J* 28.3, 16.8, 14.0, 7.0).

Synthesis of *t*BAMA

Boc-Ser-OMe (10.0 g, 45.6 mmol; 1.0 equiv) was dissolved in dichloromethane (200 mL), and MsCl (6 mL; 77.5 mmol; 1.7 equiv) was added. After cooling in an ice bath, triethylamine (23 ml; 165.9 mmol; 3.6 equiv) was slowly added dropwise, and the reaction mixture was stirred for 1 h at 0 °C. After additional 2 h at room temperature, the mixture was afterward washed with potassium bisulfate (1%) to neutrality. The organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was further purified via column chromatography with silica gel (ethyl acetate/*n*-hexane v/v 1/4). After removal of the solvent under reduced pressure, the product was yielded as a colorless oil (8.6 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.01 (s, 1 H, −NH), 6.16 (s, 1 H, $-C{=}CH-$), 5.73 (s, 1 H, $-C{=}CH-$), 3.83 (s, 3 H, $-O-CH_3$), 1.48 (s, 9 H, $-COO-C(CH_3)_3$) ppm.

Synthesis of P*tBAMA*

tBAMA, BlocBuilder and SG1 ([40]/[1]/[0.65]) were dissolved in 1,4-dioxane (66 wt %). The reaction mixture was degassed via four freeze–pump–thaw circles and stirred for 15 min at 80 °C under Ar.

Afterward, the crude product was precipitated in cold *n*-hexane, washed three times with hexane, and dried under vacuum. The product was obtained as a white powder.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.00–5.00 (m, −NH), 4.08–3.37 (m, $-O-CH_3$), 3.32–2.02 (m, $-C-CH_2-$), 1.75–1.16 (m, $-COO-C(CH_3)_3$) ppm.

SEC ($CHCl_3$/*i*-PrOH/NEt_3, PS calibration): M_n = 11,000 g/mol, M_w = 20,790 g/mol, $Đ$ = 1.89.

Deprotection of P*t*BAMA to PAMA

P*t*BAMA was dissolved in TFA (~ 40 equiv per monomer unit) and heated to 50 °C. The reaction was stopped after 1 h, and the product was precipitated in cold methanol. After filtering and washing with methanol and diethyl ether several times, the product was dried under vacuum and obtained as a yellow powder. Yield: 60%

^{1}H NMR (300 MHz, D_2O + NaOD, δ): 3.32 (s, $-COO-CH_3$), 2.78–1.90 (m, $-C-CH_2-$) ppm.

Post-polymerization modification of PDha-*g*-PAMA with AMPS, VEMO and APTMA

PDha-*g*-PAMA (100 mg) and AMPS, VEMO or APTMA (5 eq per monomer unit) were dissolved in water (5 ml each, pH 13, KOH). Afterwards the clear solutions were mixed and placed in an oil bath at 60 °C for constant stirring. The reaction was terminated after 48 h, by adding aqueous HCl (0.5 M) until a pH of 7 was reached. Then, the crude product was dialyzed against deionized water (MWCO = 3.5 kDa) for 3 days and afterwards freeze-dried to obtain the corresponding polymer powder.

Complex fabrication and catalyst immobilization

Preparation of Pt nanoparticles: PDha-*g*-(APTMA–*co*-VEMO) was dissolved in deionized water (1.0 mg/mL), and a solution of K_2PtCl_4 (0.002 mM, Pt, 1 equivalent) was added. Afterward, the solution was stirred for 30 min for appropriate mixing. Then, light-induced reduction was performed in an UV cube (360 nm) under stirring for 45 minutes.

Sample complexation: The complexes were prepared by mixing solutions of PDha-*g*-AMPS with PDha-*g*-(APTMA-*co*-VEMO) in deionized water. Hereby, the hybrid nanoreactors of polyelectrolyte complexes were prepared using a two-step approach. Firstly, EY was encapsulated by PDha-*g*-AMPS. In this step, a desired amount of PDha-*g*-AMPS solution (with concentration 1 mg/mL) was mixed with an EY solution (0.1 mM) at a ratio of 20:1 in a mixture of deionized water and DMF (1:1). Secondly, a solution of the IPECs nanoparticles with a total concentration of 1 mg/mL was processed by mixing the previous solutions of PDha-*g*-AMPS/EY with a desired amount of PDha-*g*-(APTMA-*co*-VEMO) (1 mg/mL) containing Pt nanoparticles in deionized water under stirring for 30 minutes in order to obtain an IPECs solution with a certain Z ratio. Subsequently, the formed complex was dialyzed against deionized water (MWCO = 1 kDa) for 1 day to remove the excess EY.

Instrumentation

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H- and ^{13}C-NMR spectra were performed on a Bruker AC 300 and 400 MHz using $CDCl_3$ and D_2O/NaOD as solvents at a temperature of 298 K. The spectra were referenced by using the residual signal of the deuterated solvent.

Photocatalytic hydrogen evolution:

Photoreactor: Photocatalytic experiments were carried out in a custom-made, 3D printed photoreactor equipped with a ventilating fan and an Opulent Americas LED(LST1-01F06-GRN1-00) with a maximum wavelength of 450 nm (with ± 50 nm; 281mW; 330 mA; 3.1 V).

Sample preparation:

The photocatalytic hydrogen production experiment was tested in a 5 mL Pyrex flask, the openings of which were sealed with a silicone rubber septum, at ambient temperature in glovebox. In typical experiment, triethanolamine as sacrificial electron donor (1 mM) was added to 500 µl of the respective complex stock solution (1mg/mL, IPECs) which before were deoxygenated by argon stream. Samples were transferred to the glovebox for exchanging the septum and to obtain a total volume of 1000 µl and samples by deoxygenated water. The Samples were irradiated with an Opulent Americas LED (LST1-01F06-GRN1-00) with a maximum wavelength of 450 nm (with ± 50 nm; 281 mW; 330 mA; 3.1 V) in a 3D-printed irradiation reactor with a fan. After irradiation, 100 µL aliquot of the head space was injected to a Shimadzu Nexis GC-2030 to quantify the evolved hydrogen.

Size exclusion chromatography (SEC)

SEC measurements in THF was performed by an Agilent 1260 Infinity System, equipped with a 1260 IsoPump (G1310B), an 1260 ALS (G1310B) autosampler and three consecutive PSS SDV, 5 µm, 8x300mm columns. The flow rate was 1 ml/min and the columns were heated to at 30 °C. The signals were collected using a 1260 DAD VL (GG1329B) and a 1260 RID (G1315D) detector. SEC measurements in water were collected by a Jasco (Groß7Umstedt, Germany) system equipped with a PU7980 and a RI72031 Plus refractive index detector. Water with 0.05 % sodium azide and 0.1 M sodium nitrate and water with 0.3% TFA/ 0.1 M NaCl were used as a solvent at a flow rate of 1 mLCmin71 on a PSS SUPREMA 30 Å at 30 °C.

Dynamic Light Scattering (DLS)

DLS measurements were performed using an ALV laser CGS3 Goniometer equipped with a 633 nm HeNe laser (ALV GmbH, Langen, Germany) at 25 °C and at a detection angle of 90°. The CONTIN analysis of the obtained correlation functions was performed using the ALV 7002 FAST Correlator Software.

Transmission Electron Microscopy (TEM)

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.

ξ-Potential

Zeta-potentials were measured on a ZetaSizer Nano ZS from Malvern via M3-PALS technique with a laser beam at 633 nm. The detection angle was 13°. The samples were prepared by titration of the polymer in 0.1 M NaOH (0.2 g/L) with 0.1 M HCl and 1 mL of the solution was taken at the desired pH values. The titration and pH detection was performed on a Metrohm 765 Dosimat titrator with a Greisinger electronic GMH3539 digital pH-/mV-electrode with a thermometer.

pH measurements

pH measurements were performed with a TitroLine® 7000 titrator equipped a ScienceLine pH combination electrodes with temperature sensor A162 from SI Analytics GmbH.

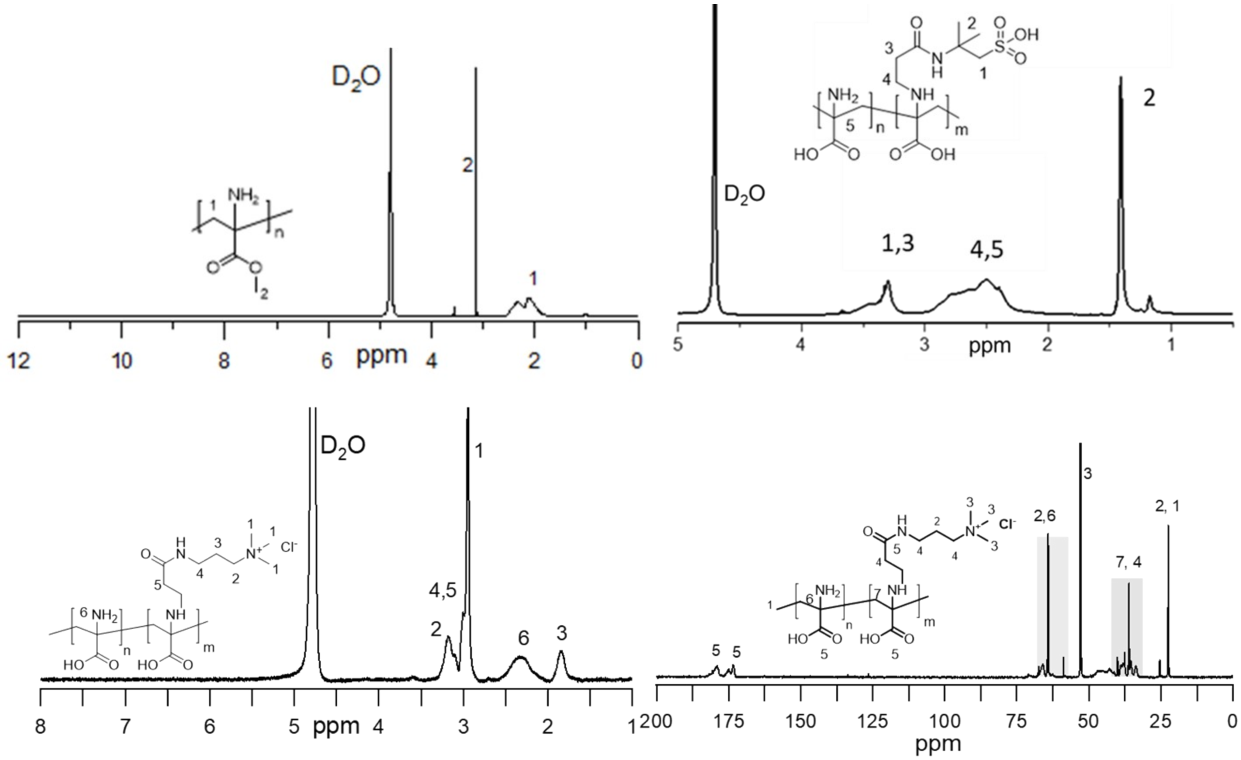

Figure S1: ^{1}H and ^{13}C NMR characterization of PDha, PDha-*g*-AMPS$_{35}$, and PDha-*g*-APTMA$_{40}$ graft hydrophilic graft copolymer, respectively.

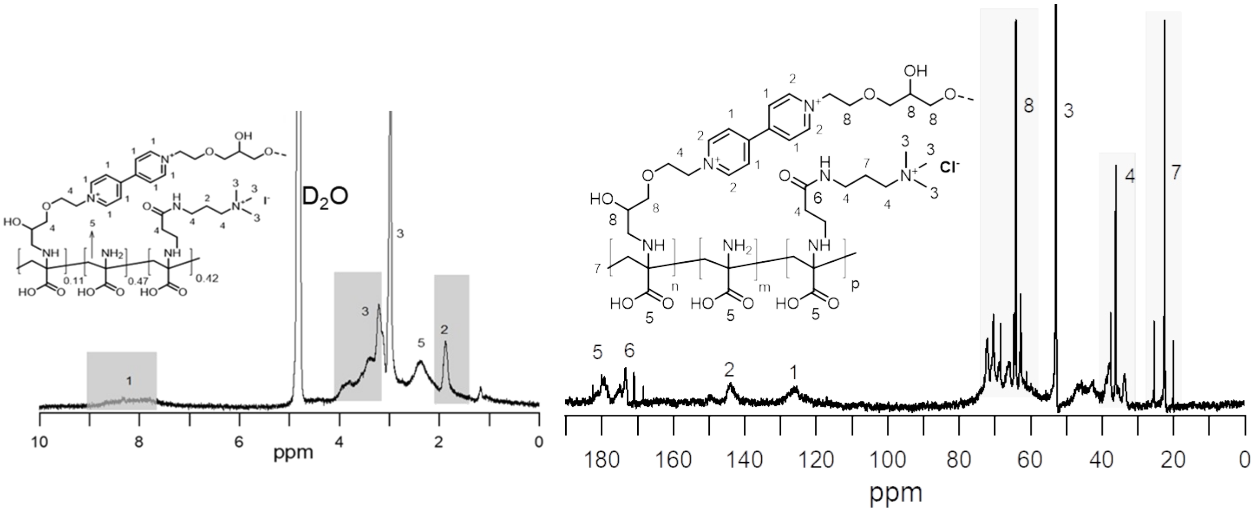

Figure S2: ^{1}H and ^{13}C NMR characterization of PDha-*g*-(APTMA$_{40}$-*co*-VEMO$_{11}$) multi hydrophilic graft copolymer.

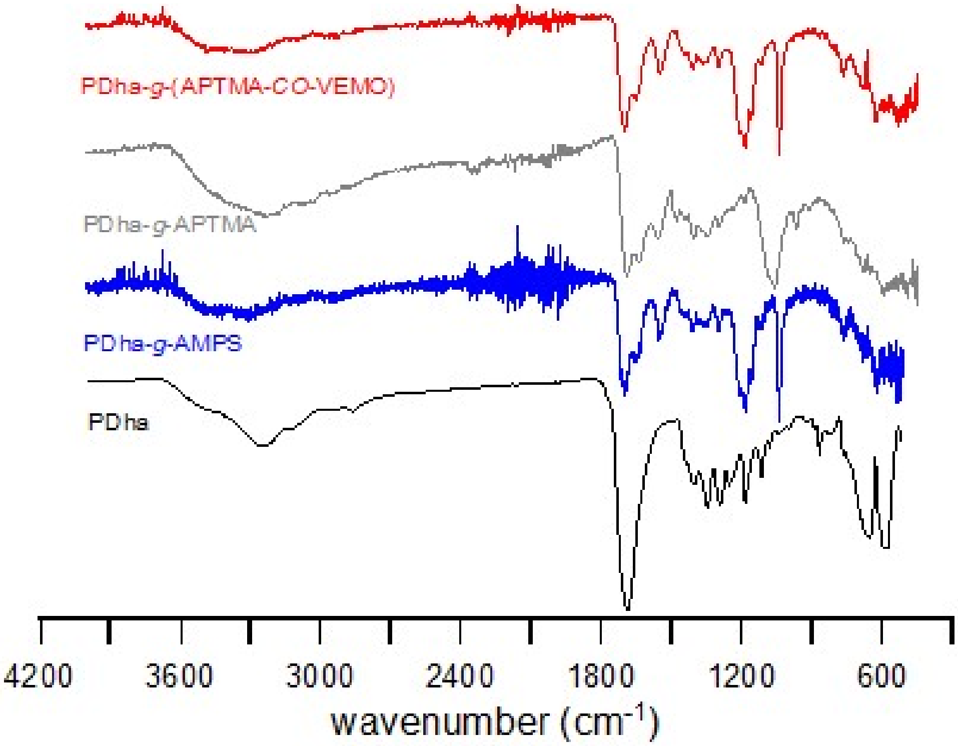

Figure S3: Characterization of PDha, PDha-*g*-AMPS$_{35,}$ PDha-*g*-APTMA$_{40'}$ $^{\text{and}}$ PDha-*g*-(APTMA$_{40}$-*co*-VEMO$_{11}$) multi hydrophilic graft copolymer using FT-IR spectroscopy.

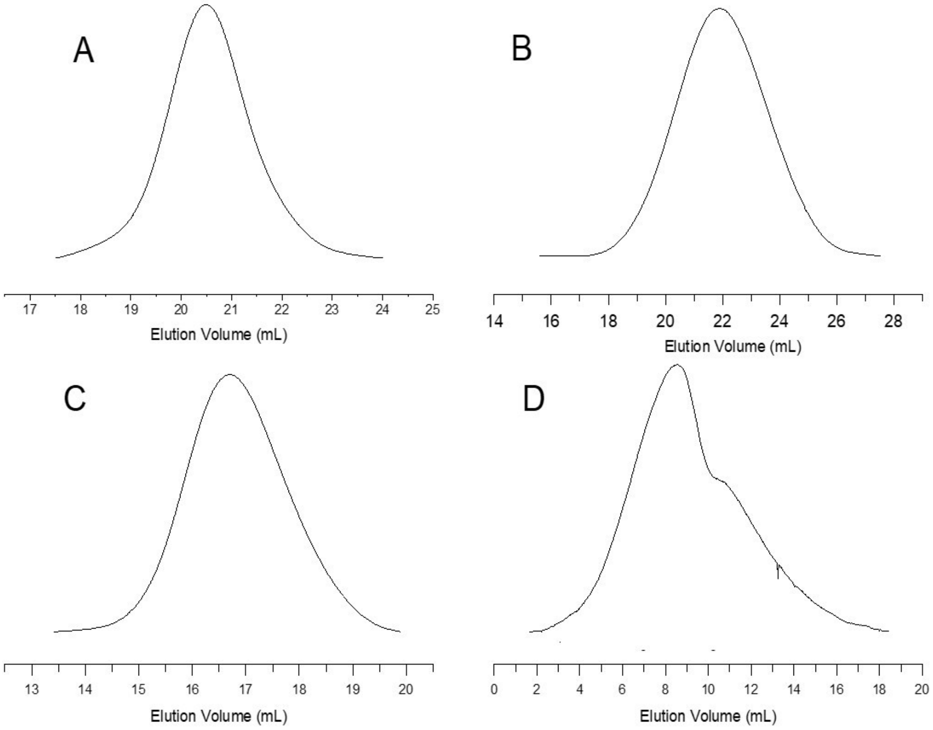

Figure S4: SEC traces of A: P*t*BAMA (THF), B: PDha-*g*-APTMA (water with 0.3% TFA/ 0.1 M NaCl [pH < 2]), C: PDha-*g*-AMPS (0.08 M Na_2HPO_4, 0.05% NaN_3 pH 9), and D: (PDha-*g*-($APTMA_{40}$-*co*-$VEMO_{11}$) (water with 0.3% TFA/ 0.1 M NaCl [pH < 2).

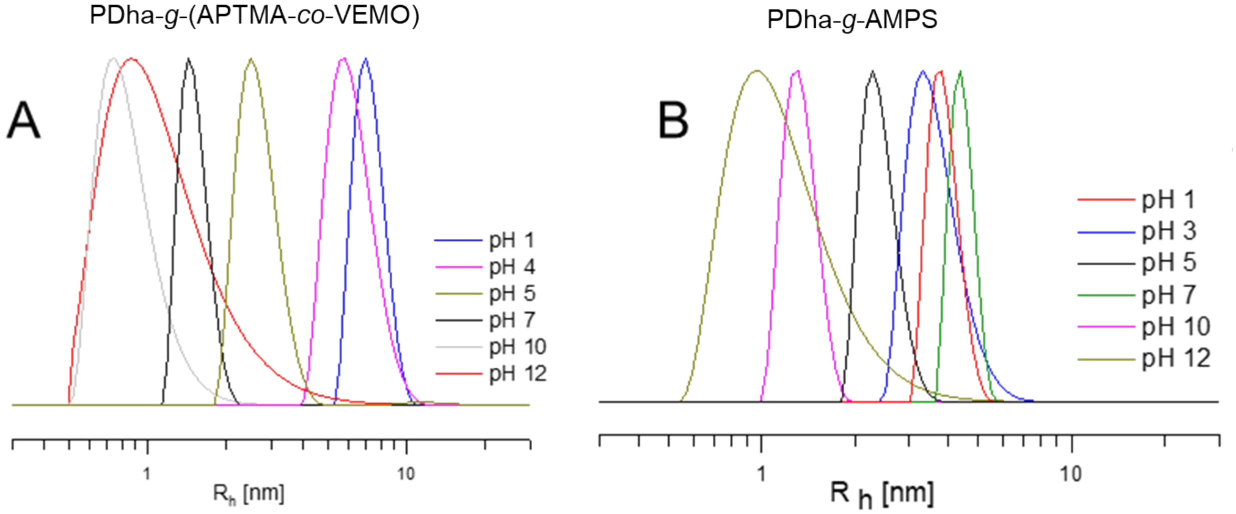

Figure S5: DLS measurements of graft copolymers in different pH range (A): PDha-*g*-(APTMA-*co*-VEMO) and (B): PDha-*g*-AMPS.

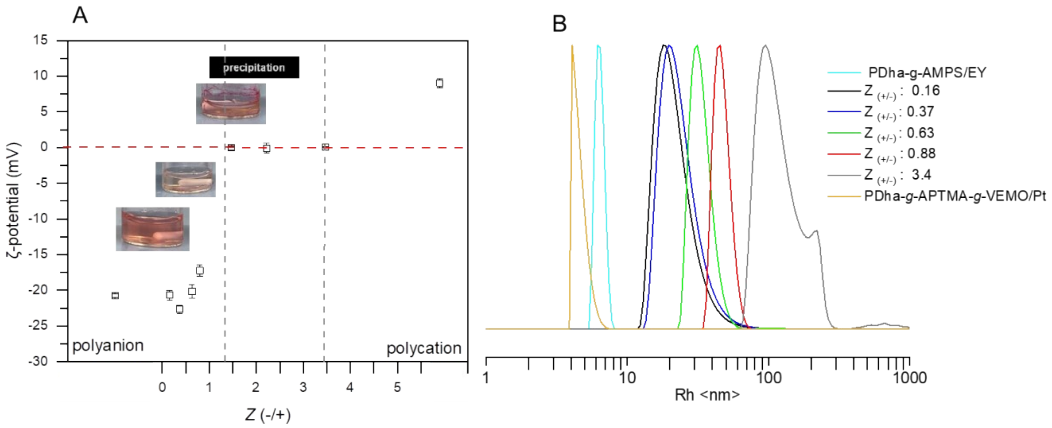

Figure S6: ζ-potential (A)Hydrodynamic radii (R_h) (B) of IPEC micelles formed in mixtures with constant concentration of the parent micelle-forming component, c = 1 mg/mL and an increasing charge ratio, Z.

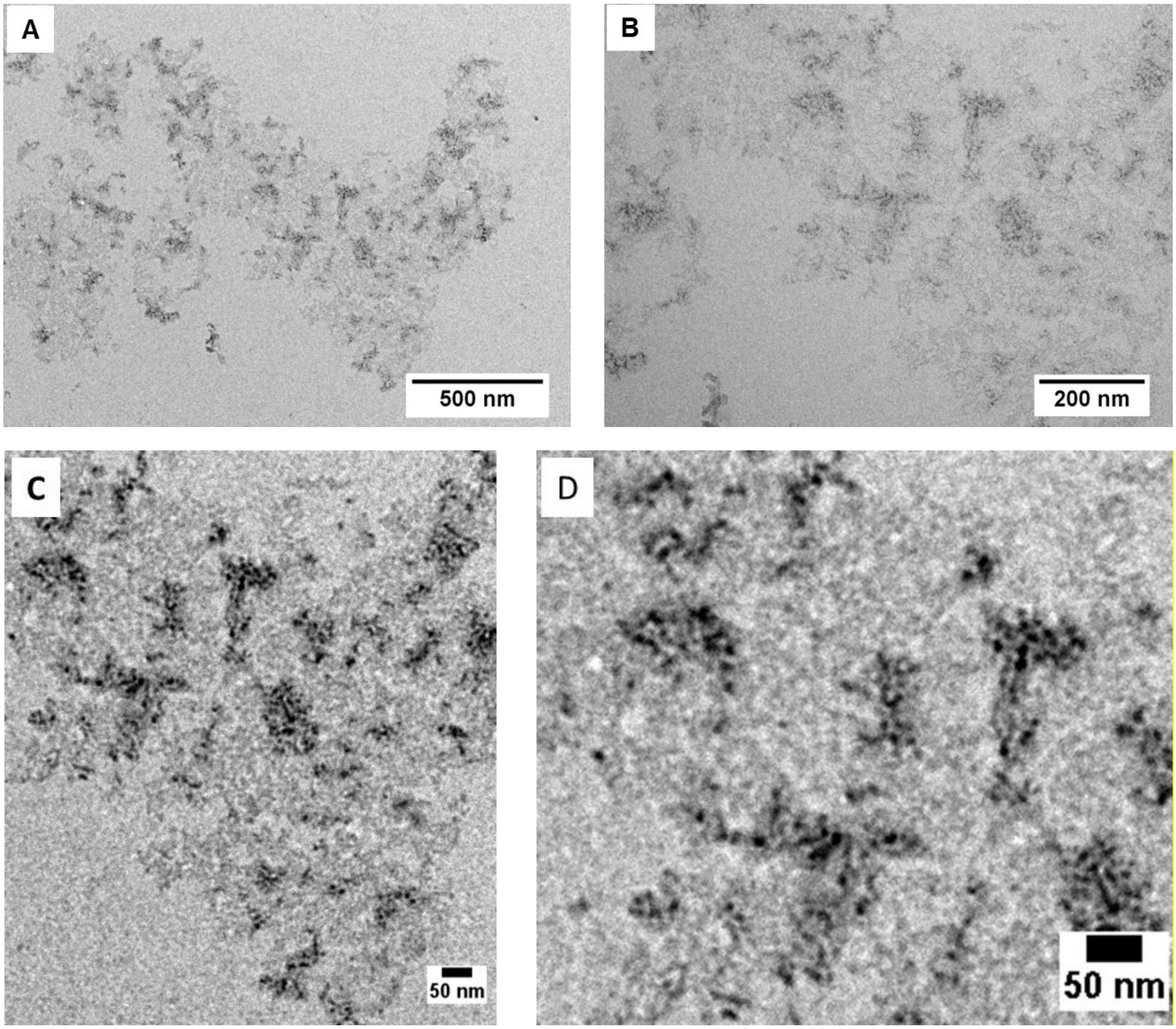

Figure S7: TEM micrographs of Pt@ PDha-*g*-(APTMA-*co*-VEMO).

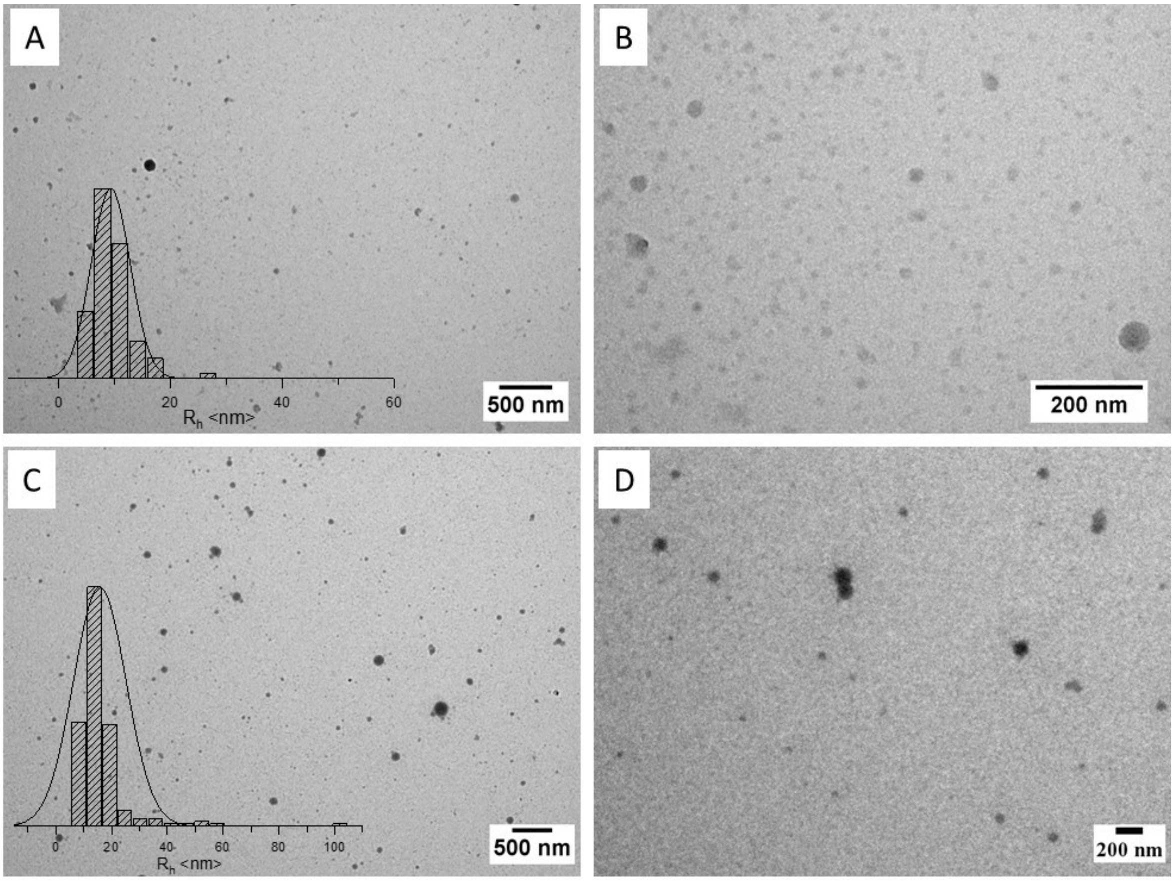

Figure S8: TEM micrographs of the IPECs micelles (A-B) and Pt@IPECs micelles (C-D) with Z= 0.6.

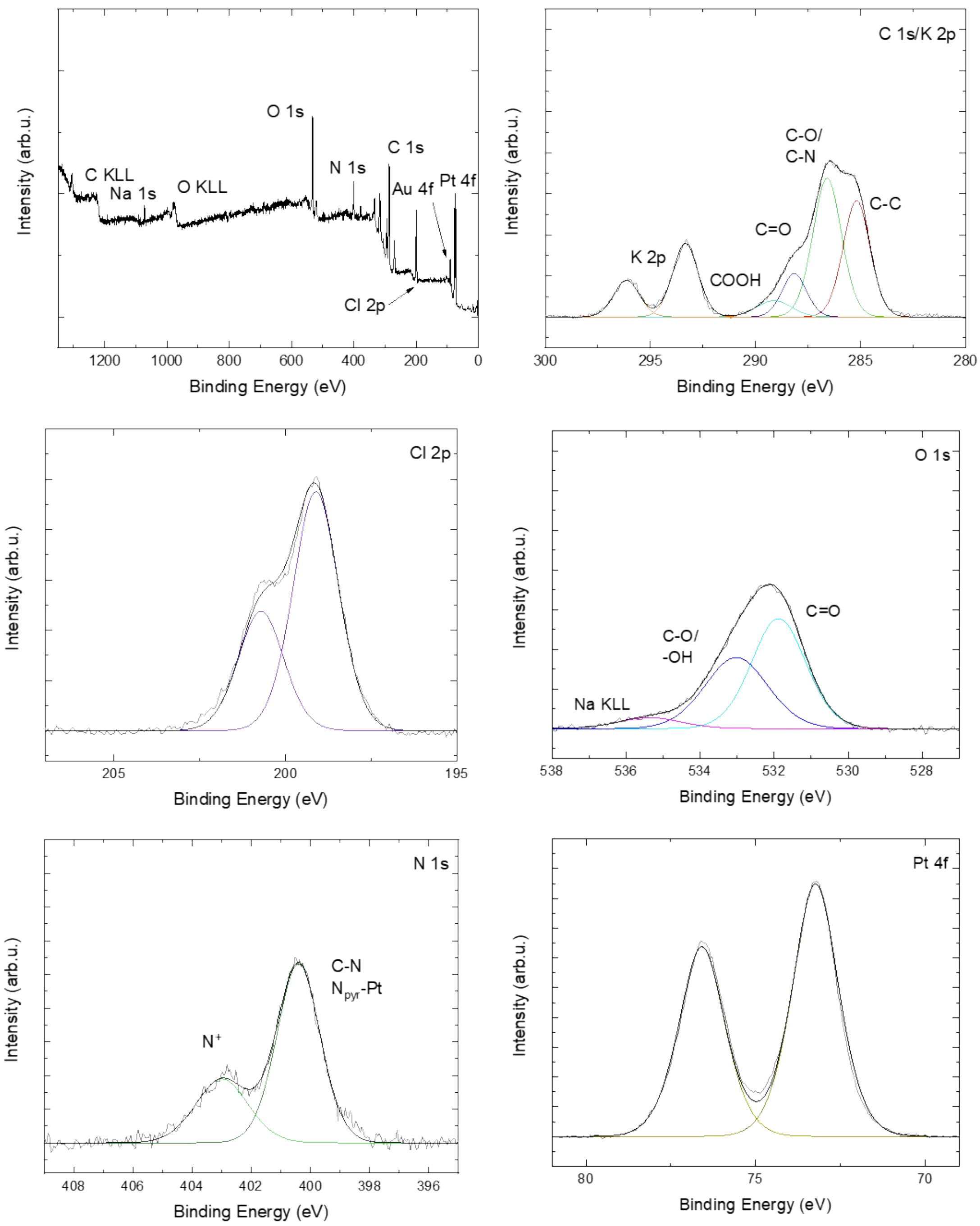

Figure S9: XP spectra of O 1s, N 1s, C 1s, Cl 2p, and Pt4f of Pt@PDha-*g*-(APTMA-*co*-VEMO).

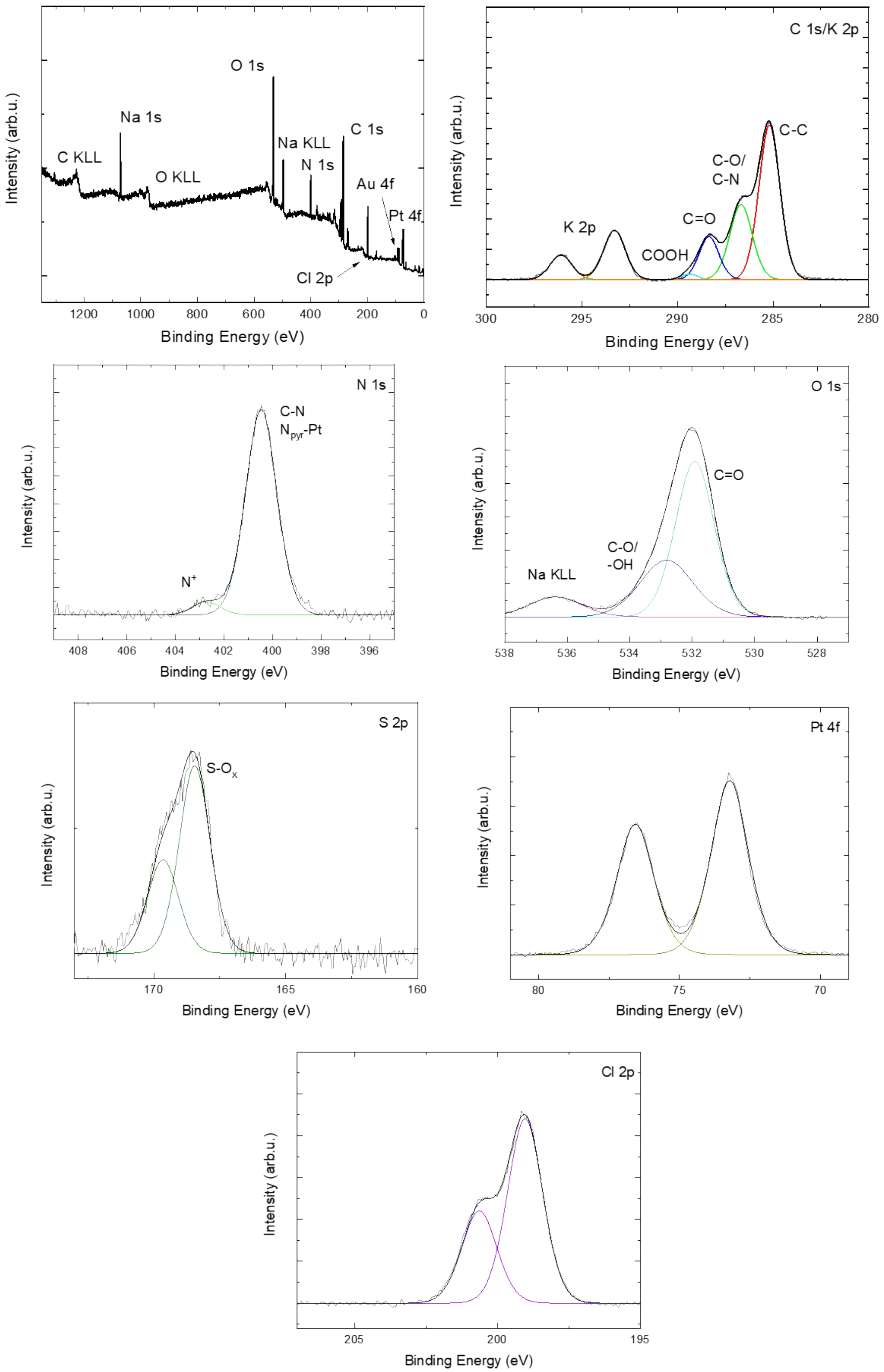

Figure S10: XP spectra of O 1s, N 1s, C 1s, Cl 2p, and Pt4f of IPEC micelles of (PDha-*g*-AMPS) and (Pt@PDha-*g*-(APTMA-*co*-VEMO)) polyelectrolyte graft copolymers.

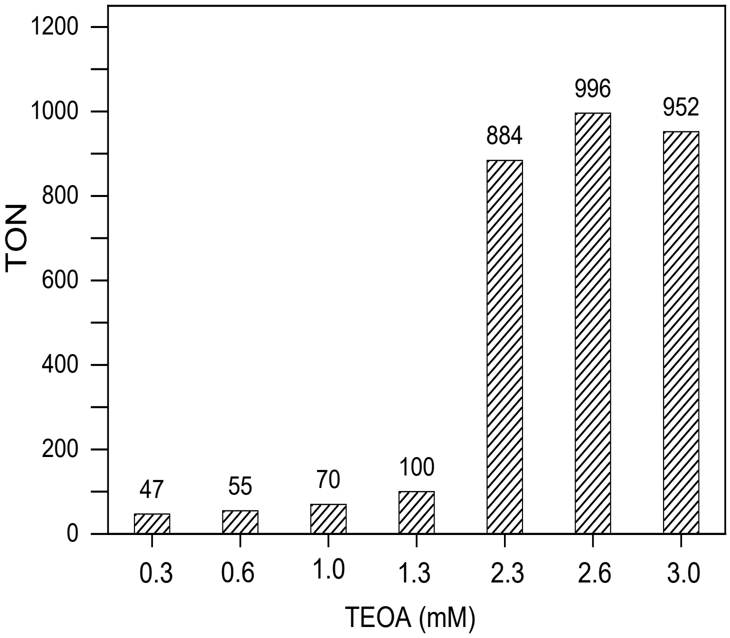

Figure S11: Optimization of TEOA concentration (mg/mL). Measured under illumination of LED light with λ>450, Z=0.37, total micellar concentration 1mg/mL, EY 0.05 mM, K_2PtCl_4 0.002 mM, and the turnover number The turnover number (TON) is defined as the ratio of the moles of hydrogen produced to the moles of the Pt precursor initially introduced during the micellar formation from a fresh aqueous solution of K_2PtCl_4.

Table 1: Brief survey of photocatalytic systems using EY as photosensitizer reported in literature.

photocatalyst	Sacrificial reagent/h*v*	H_2 production activity a	Reference
IPECs, Z=0.16	TEOA, λ ≥ 450 nm	[b]TON: 1096 216 μmol.mg^{-1}.h^{-1}	This work
mpg-C_3N_4/Pt (1 wt %)	TEOA, λ ≥ 420 nm	385.0 μmol.mg^{-1}.h^{-1}	[2]
Pt colloid	TEOA, λ >, 300 W Xe	[d]54.1 μmol·mg^{-1}·h^{-1}	[3]
CuO/TiO_2	TEA, λ ≥ 420 nm	0.127 μmol.mg^{-1}.h^{-1}	[4]
$AlSiW_{11}$-H_2PtCl_6	TEOA, λ > 420 nm	[c]TON: 473, [d]74.6 μmol.mg^{-1}.h^{-1}	[5]
GO/Pt-0.5%	TEOA, λ > 420 nm	0.5 mmol·g^{-1}·h^{-1}	[6]
g-C_3N_4/Pt-0.5%	TEOA, λ > 420 nm	1.81 mmol·g^{-1}·h^{-1}	[6]
g-C_3N_4/Pt/GO-0.5%	TEOA, λ > 420 nm	[e]TON: 302, 3.82 mmol·g^{-1}·h^{-1}	[6]
MWNTs-5.7 wt% CuO/NiO	TEOA, λ > 420 nm	1.0 mmol g^{-1} h^{-1}	[7]

[a] Rate was converted based on mg of catalyst that used for photocatalysis reaction. [b] TON was calculated based on mmol of Pt nanoparticles that used in beginning of micellar formation. [c] TON was calculated based on EY activity. [c] Rate was converted based on mg of Pt colloid with concentration of 6.0×10^{-5} M as catalyst that used for photocatalysis reaction. [d] Rate was converted based on 80 mL catalytic solution with initial concentrations H_2PtCl_6 as active centers for hydrogen evolution (2.4×10^{-5} mol L^{-1}). [e] TON H_2 *vs* EY.

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