SUPPORTING INFORMATION

Polyampholyte Graft Copolymers As Unimolecular Matrices For Noble Metal-Free And Visible Light-Driven Hydrogen Evolution By Eosin Y And Molybdenum Phosphide

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EXPERIMENTAL SECTION

Synthesis of tert-butoxycarbonylaminomethylacrylate (*t*BAMA)

N-(*tert*-Butoxycarbonyl)-D-Serine methyl ester (Boc-ester, 10.06 g, 45.6 mmol) was dissolved in dichloromethane (DCM, 200 mL). Methane sulfonyl chloride (6 mL, 77.5 mmol) was added to the solution under vigorous stirring. The reaction mixture was cooled down to 0°C using an ice bath, and triethylamine (TEA, 23 mL, 166 mmol) was added dropwise. At 0°C the solution was stirred for 1 h and further 2 h at room temperature. 1 wt.% $KHSO_4$ solution (200 mL) was prepared and put in the reaction mixture. The organic phase was separated, dried with Na_2SO_4 and filtered. The solvent was removed using a rotary evaporator for approximately 1.5 h. The product was further purified using column chromatography with silica gel (mobile phase: hexane/ethyl acetate: 8/2 v/v). The obtained product was dried under reduced pressure.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.03 (s, 1H, NH), 6.18 (s, 1H, CH_2), 5.74 (d, 1H, CH_2), 3.85 (s, 3H, OCH_3), 1.50 (s, 9H, *t*-butyl).

Yield: 63%.

Synthesis of poly(*tert*-butoxycarbonylaminomethylacrylate) (P*t*BAMA)

*t*BAMA (2 g, 9.94 mmol) with initiator (Bloc builder, 9.56 mg, 24.85 µmol) was dissolved in 4 mL of 1,4-dioxane in a schlenk flask. After 15 min of stirring, three freeze-thaw cycles under vacuum were done. Under argon atmosphere, the sample was placed in an oil bath at 70°C for 10 min. The product was quenched using liquid nitrogen and precipitated in *n*-hexane. The pure product was obtained after ultracentrifugation at 8000 rpm for 4 min followed by vacuum drying.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.60 (s, 1H), 5.52 (s, 1H, NH), 3.72 (s, 3H, CH_3, ester), 1.4 (11H, Boc and –CH_2–).

Yield: 54%.

Synthesis of poly(aminomethylacrylate) (PAMA)

P*t*BAMA (970 mg) was dissolved in 10 mL of TFA/water solution (the volume ratio TFA/H_2O was 77/23) and stirred at room temperature for 20 min to dissolve the polymer. The reaction mixture was heated to 50 °C. The reaction was stopped after 1 h, and the product was precipitated into methanol. The product was collected after centrifugation at 8000 rpm for 5 min, followed by vacuum drying for 45 min.

^{1}H NMR (300 MHz, D_2O+NaOD) δ: 3.22 (s, 3H, OCH_3), 2.48-2.23 (2H, CH_2).

Yield: 60%.

Synthesis of *n*-propyl phosphonic acid acrylamide (*n*PAA)

n-propylamine (1 g) was added to 0.35 mL of water in a round-bottomed flask equipped with a magnetic stir bar and rubber septum. The sample was heated in an oil bath at 45°C. Diethyl vinyl phosphonate (2.36 g) was added dropwise and stirred for 18 h before dichloromethane

(40 mL) was added. Later, the reaction mixture was dried with Na_2SO_4 followed by filtration and solvent evaporation under reduced pressure.

The reaction product was mixed with triethylamine (1 g) and DCM (20 mL) and placed in an ice water bath. Acryloyl chloride (0.8 g) was added dropwise, and the reaction mixture was stirred for 18 h. The sample was washed with 0.1 M NaOH, 0.1 M HCl, and distilled water, and the organic phase was collected. The product was dried using Na_2SO_4 followed by solvent removal under reduced pressure. The final product was obtained after vacuum drying of the sample for 12 h.

For deprotection of the ethyl group, the obtained product was dissolved in anhydrous DCM under Ar atmosphere, and bromotrimethylsilane (TMSBr) was added through a syringe. The reaction mixture was stirred for 24 h at 21°C. TMSBr and DCM were removed via evaporation, and methanol was added. Then the reaction mixture was stirred at 21°C for another 24 h. The product was dried under vacuum for several hours, and an orange, waxy solid was obtained.

^{1}H NMR (300 MHz, MeOD) δ: 6.75 (CH_2=CH-), 6.26 (-CH=CH_2), 5.79 (-CH=CH2), 3.78 - 3.54 (m, -N-CH_2), 3.39 – 3.19 (m, -N-CH_2), 2.20 – 1.99 (m, -CH_2-CH_2-CH_3), 1.65 (-CH_2-P=O), 1.08 – 0.87 (m, -CH_2-CH_3) ppm.

Yield: 87%.

Grafting of PAMA and *n*PAA

PAMA (100 mg) and *n*PAA (200 mg) were dissolved in water (5 mL each, pH 13, KOH). Afterwards the clear solutions were mixed and placed in an oil bath at 72°C under stirring. The reaction was terminated after 5 days. The pH of the solution was corrected to 7 using KOH solution. Then, the crude product was dialyzed against deionized water (MWCO = 3.5 kDa) for three days and afterwards freeze-dried to obtain a yellowish polymer powder. During the grafting, PAMA converts to PDha; therefore, the graft copolymer is abbreviated as PDha-*g*-*n*PAA.

^{1}H NMR (300 MHz, D_2O+NaOD) δ: 6.69 – 6.47 (m, 3H, CH_2=CH-), 6.08 – 5.93 (m, 3H, CH=CH_2), 5.71 – 5.56 (m, 3H, -CH=CH_2), 3.67–3.06 (m, (-CH_2-N-C=O- and (-CH_2-N-C=O-)), 2.55-2.41 (C-CH_2-, -NH-CH_2-, -CH_2-CON-), 2.14-1.50 (-CH_2-CH_3 and -CH_2-PO_3H_2), 0.70 (-CH_3) ppm.

Preparation of MoP

0.00165 mol $Na_2MoO_4.2H_2O$ and 0.0066 mol $NaH_2PO_2.H_2O$ were ground well in an agate mortar for 20 min. The obtained white powder was ground and calcined at 400°C in a nitrogen atmosphere for 1.5 h at a heating rate of 5°C . min^{-1}. The resultant product was washed with deionized water and ethanol several times, acid-etched at 50°C for 4 hours, dried in a vacuum at 60°C overnight, and then collected as a HER co-catalyst.

Preparation of photocatalytic dispersions

Each 2.5 mL aqueous colloidal dispersion contained 0.1 g . L^{-1} catalyst and 10 v/v% triethanolamine (TEOA). MoP and graft copolymer concentrations were varied as follows: MoP at 0.005, 0.015, 0.06, and 0.1 g . L^{-1} with a constant graft copolymer concentration of 2 g . L^{-1}; or MoP fixed at 0.1 g/L with graft copolymer concentrations of 0.5, 1, and 2 g . L^{-1}. Each

solution was ultrasonicated at 20% amplitude using a pulsed cycle (60 s on, 30 s off) for 10 min, followed by stirring for 1 h to ensure stability. A control solution without graft copolymer was also prepared under the same conditions.

Photocatalytic system

Each colloidal solution or solution without graft copolymer was purged with argon for 10 min to remove any dissolved oxygen. The solution, along with the magnetic stir bar, was then transferred to a gas chromatography vial in a glove box whose openings were sealed with a silicone rubber septum. The light-driven catalysis experiments were performed at ambient temperature and atmospheric pressure. A Opulent Americas LED (LST1-01F06-GRN1-00) light source with a wavelength λ = 530 nm (with ± 50 nm; 330 mA; 3.1 V) in a 3D-printed irradiation reactor with a fan was used as a visible light source for the catalytic reaction and was positioned 5 cm away from the reactor. After irradiation, 0.1 mL aliquot of the head space was injected to a Shimadzu Nexis GC-2030 with a thermal conductivity detector (TCD) to quantify the evolved hydrogen.

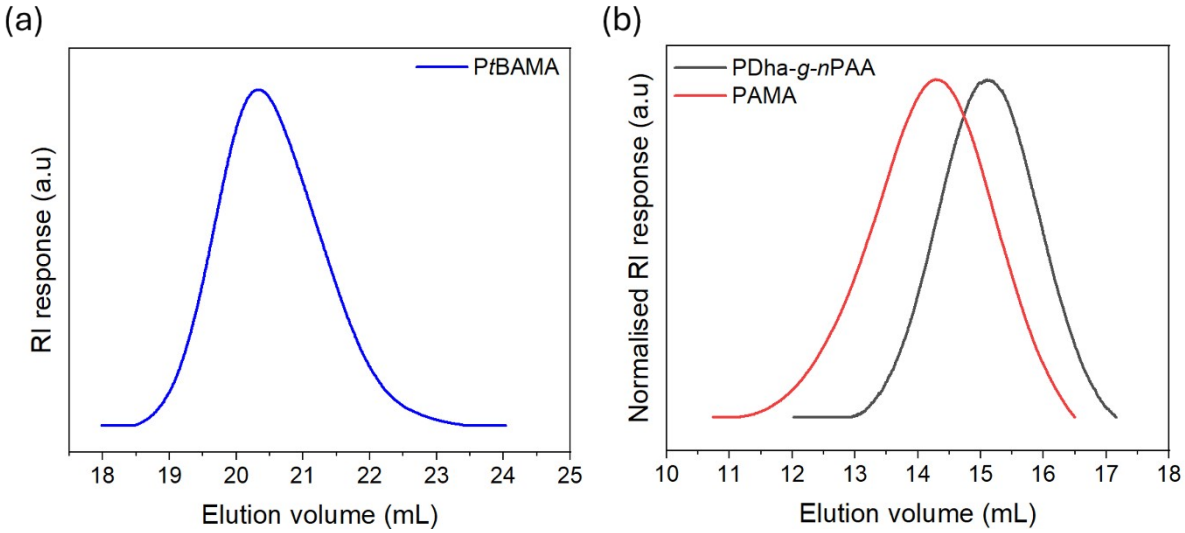

Figure S1: SEC elution traces with RI detector (Refractive Index) for a) PtBAMA (Solvent: $CHCl_3$, Calibration: Polystyrene),b) PAMA (Solvent: DMSO, Calibration: Pullulan), and PDha-g-nPAA (Solvent: DMSO, Calibration: Pullulan). The SEC chromatograms were normalized to the maximum peak intensity to facilitate the comparison of molecular weight distributions, independent of slight variations in sample concentration.

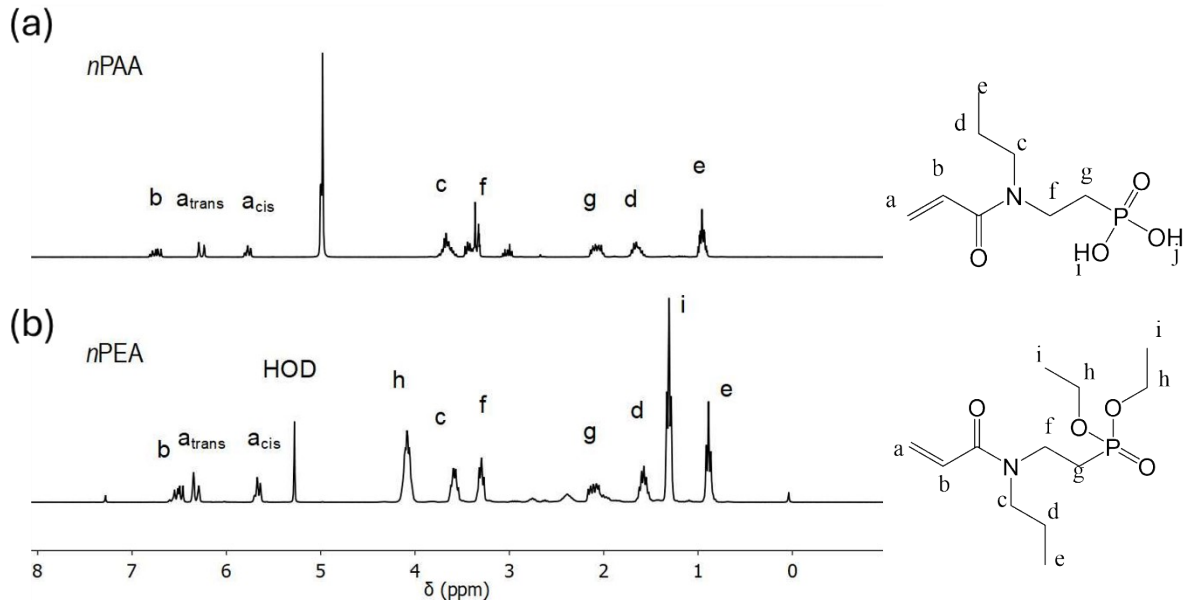

Figure S2: (a) ^{1}H NMR (MeOD, 300 MHz, 27°C) of nPAA and (b) ^{1}H NMR ($CDCl_3$, 300 MHz, 27°C) of nPEA

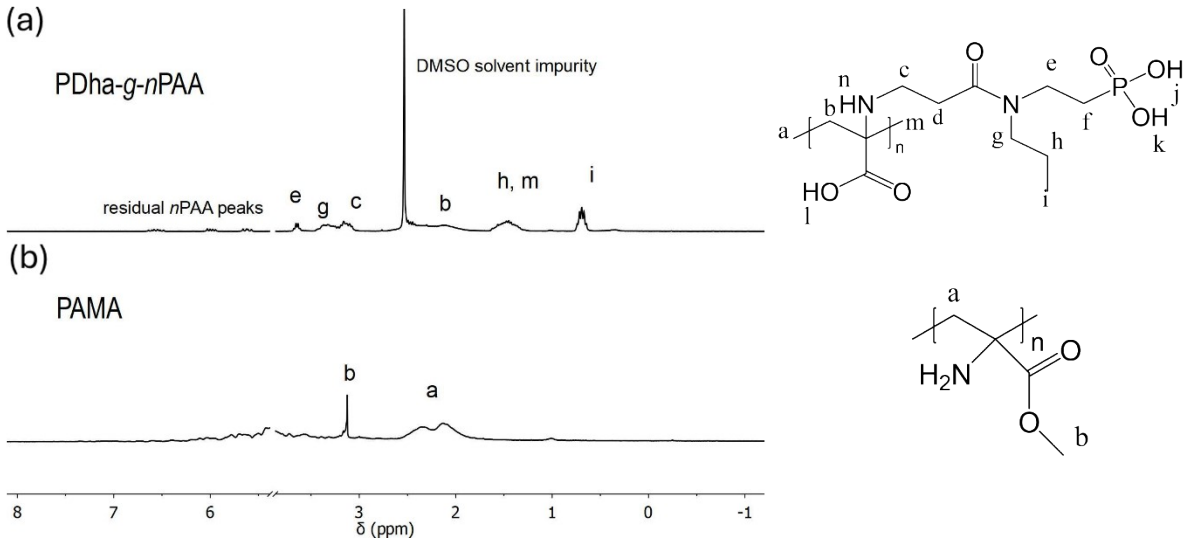

***Figure S3**: (a) ^{1}H NMR (D_2O+NaOD, 300 MHz, 27°C) of PDha-g-nPAA and (b) PAMA. The graft copolymer was used as obtained after dialysis and lyophilization. Purity was determined to be ~76 wt% via ^{1}H NMR integration, and the weight used in subsequent experiments was adjusted accordingly.*

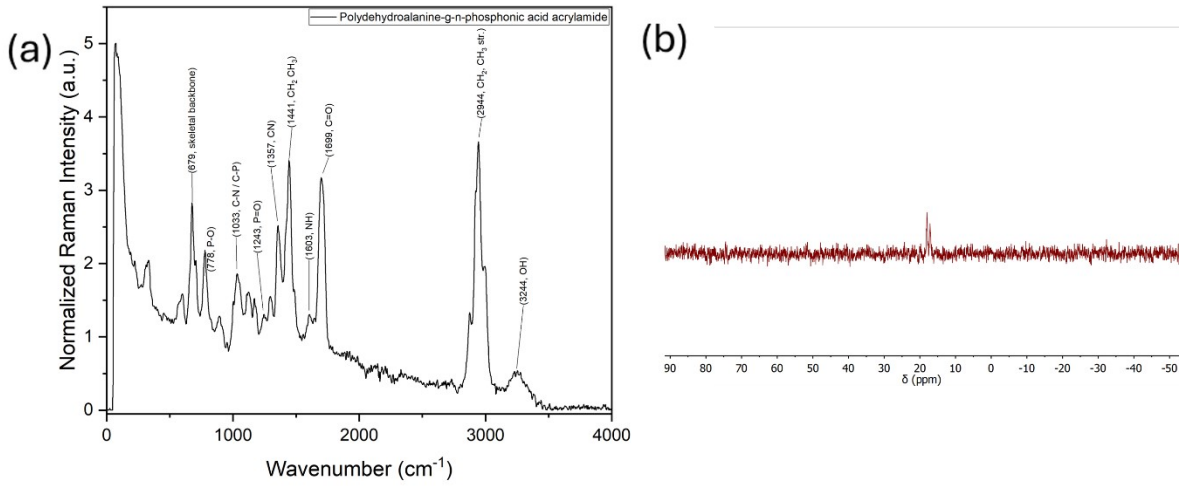

Figure S4: (a) Raman spectrum of graft copolymer and (b) ^{31}P NMR of graft copolymer

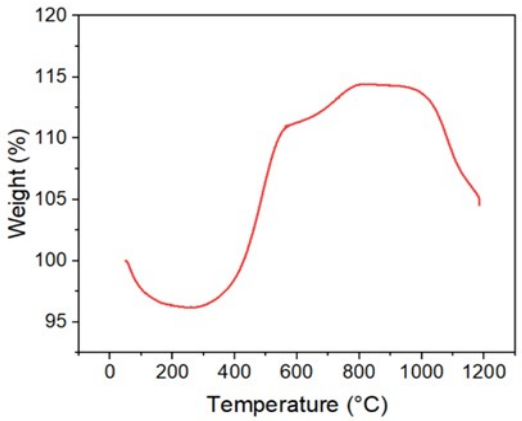

Figure S5: (a) Thermogram of MoP in air flow

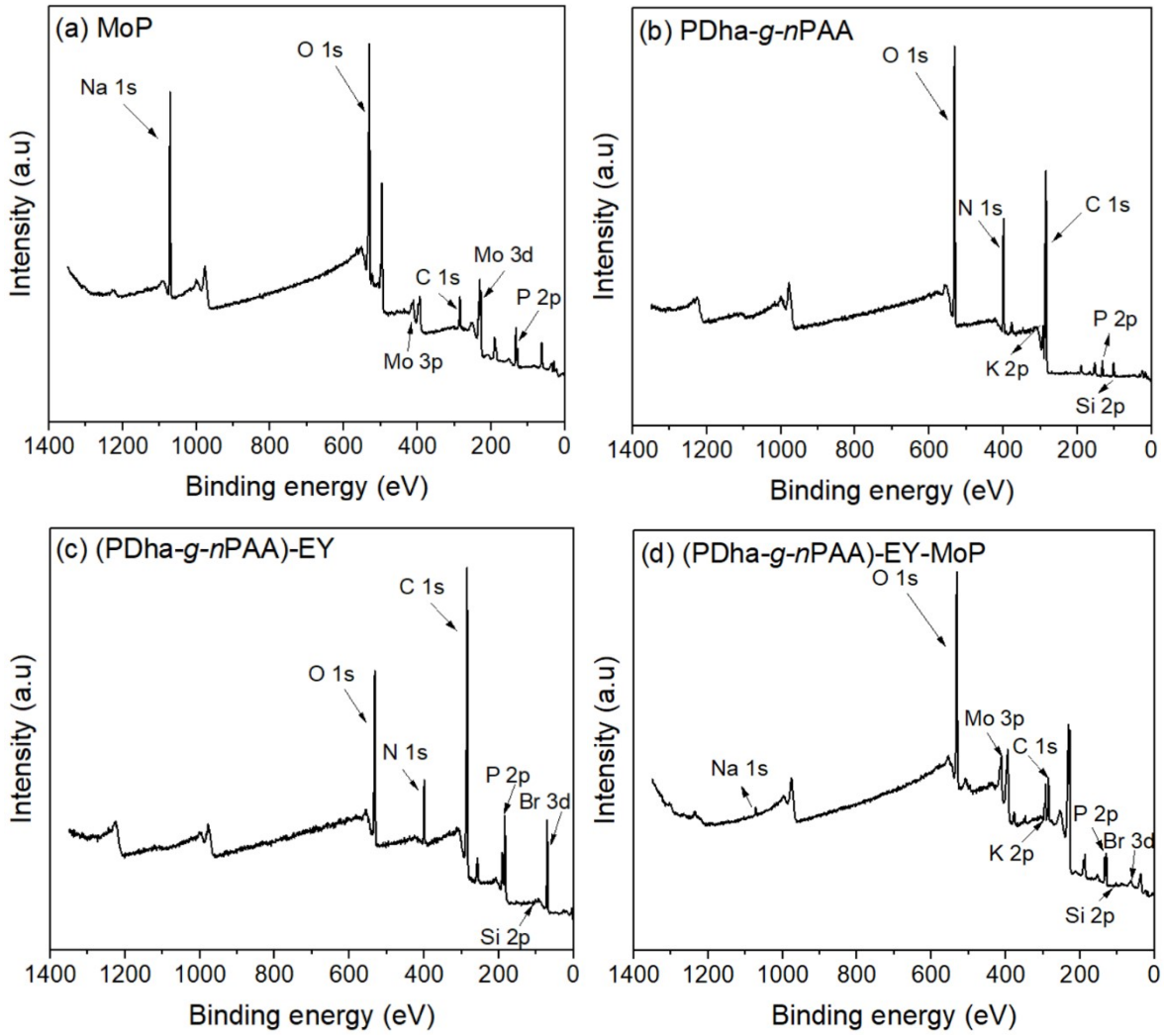

Figure S6: XPS spectra of (a) bare graft copolymer; (b) EY immobilised within graft copolymer and (c) EY and MoP immobilised within graft copolymer (0.1 g/L EY, 0.06 g/L MoP, 2g/L of graft copolymer)

Table S1: *Surface atomic compositions (at%) obtained from quantitative XPS survey spectra of EY, MoP, PDha-g-nPAA, (PDha-g-nPAA)–EY, and (PDha-g-nPAA)–EY–MoP. Atomic percentages were calculated from the integrated core-level peak areas using appropriate sensitivity factors; values below the quantitative detection*

Material	C 1s	N 1s	O 1s	P 2p	Br 3d	Mo 3d/3p	K 2p/2s	Si 2p/2s	Na 1s
EY	74.5	-	19.4	-	6.13	-	-	-	-
MoP	15.5	-	48.6	15	-	5.11	-		15.8
Pdha-*g*-*n*PAA	57.4	11.2	24.5	1.9	-	-	1.9	3	
(Pdha-*g*-*n*PAA)-EY	69.3	6.9	17.5	-	5.3	-	-	0.8	
(Pdha-*g*-*n*PAA)-EY-MoP	19.13	6.7	46.3	15.3	-	7.3	3.6	1.1	0.6

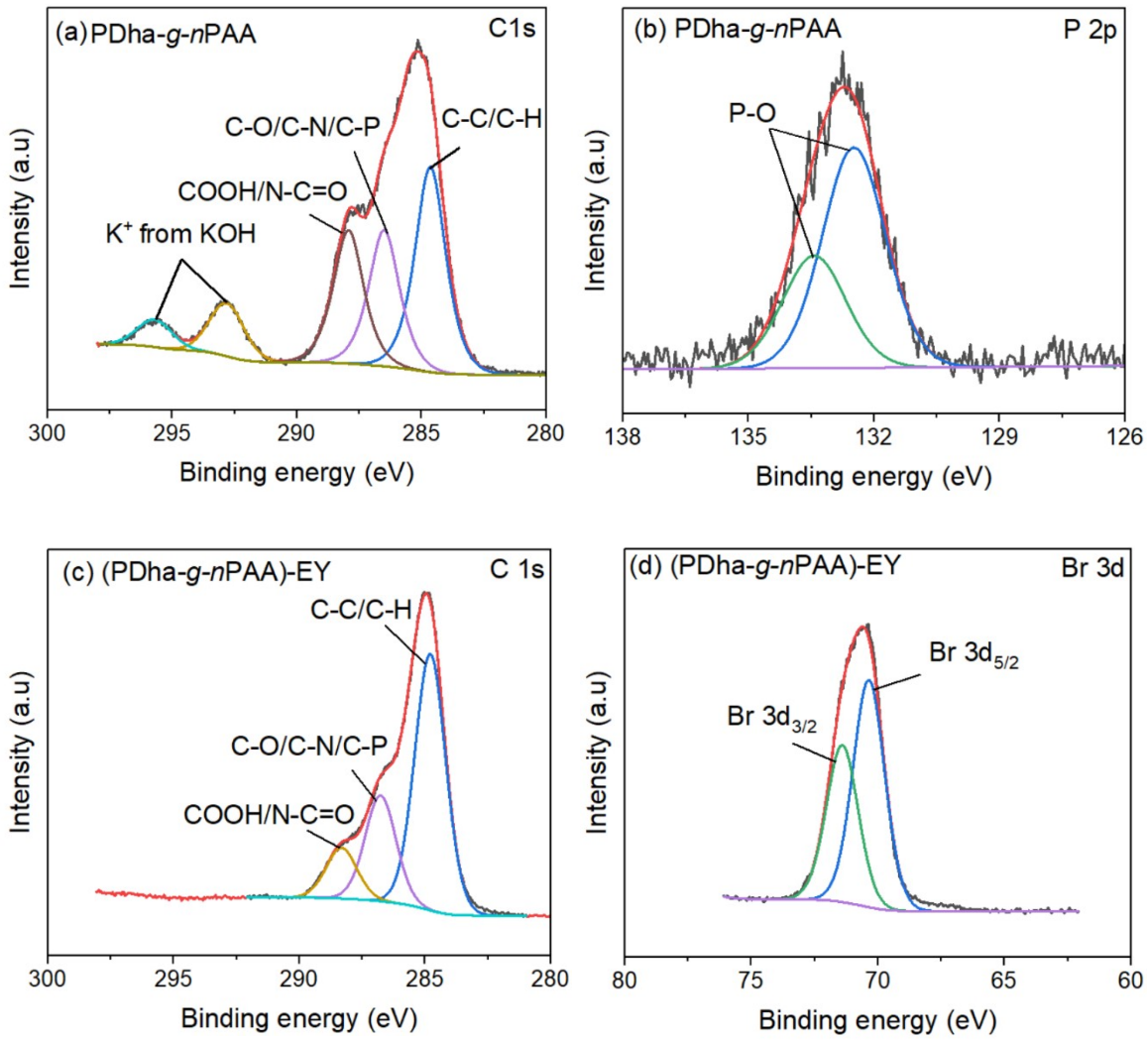

Figure S7: High-resolution XPS spectra of the graft copolymer and dye-modified hybrid. (A) C 1s and (B) P 2p regions of PDha-g-nPAA, showing contributions from the polymer backbone and phosphonate groups. (C) C 1s and (D) Br 3d regions of (PDha-g-nPAA)–EY, evidencing incorporation of the brominated EY dye into the graft-copolymer surface.

***Table S2**: Parameters obtained from the segmented fitting of time-resolved fluorescence decay curves for Eosin Y (EY) in the presence of TEOA and MoP at varying graft copolymer concentrations. The early-phase decay (t < 300 ps) was analyzed using a mono-exponential model to determine the fitting time constants. The late-phase decay (300 < t < 1200 ps) was fitted using a power-law function of the form $f(x) = Ax^{-b}$, where A is the amplitude factor and b is the power-law exponent. All measurements were conducted at an excitation wavelength of 470 nm.*

EY ($g \cdot L^{-1}$)	**TEOA (vol%)**	**MoP ($g \cdot L^{-1}$)**	**Graft copolymer ($g \cdot L^{-1}$)**	**Exponential fitting time constants (ps)**	**b value**	**A value**
$1*10^{-3}$	10	$6*10^{-4}$	0	194	4.91	1.104
			0.5	254.5	3.81	0.005
			1	205.2	4.64	0.271
			1.5	499.2	3.98	0.017
			2	463.1	4.37	0.127