Electronic Supplementary Information

Insights into the Light-Driven Hydrogen Evolution Reaction of Mesoporous Graphitic Carbon Nitride Decorated with Pt or Ru Nanoparticles

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Figure S1. EDX analyses of freshly prepared a) RuNPs@mpg-CN, b) in-RuPPNPs@mpg-CN, and c) ex-RuPPNPs@mpg-CN

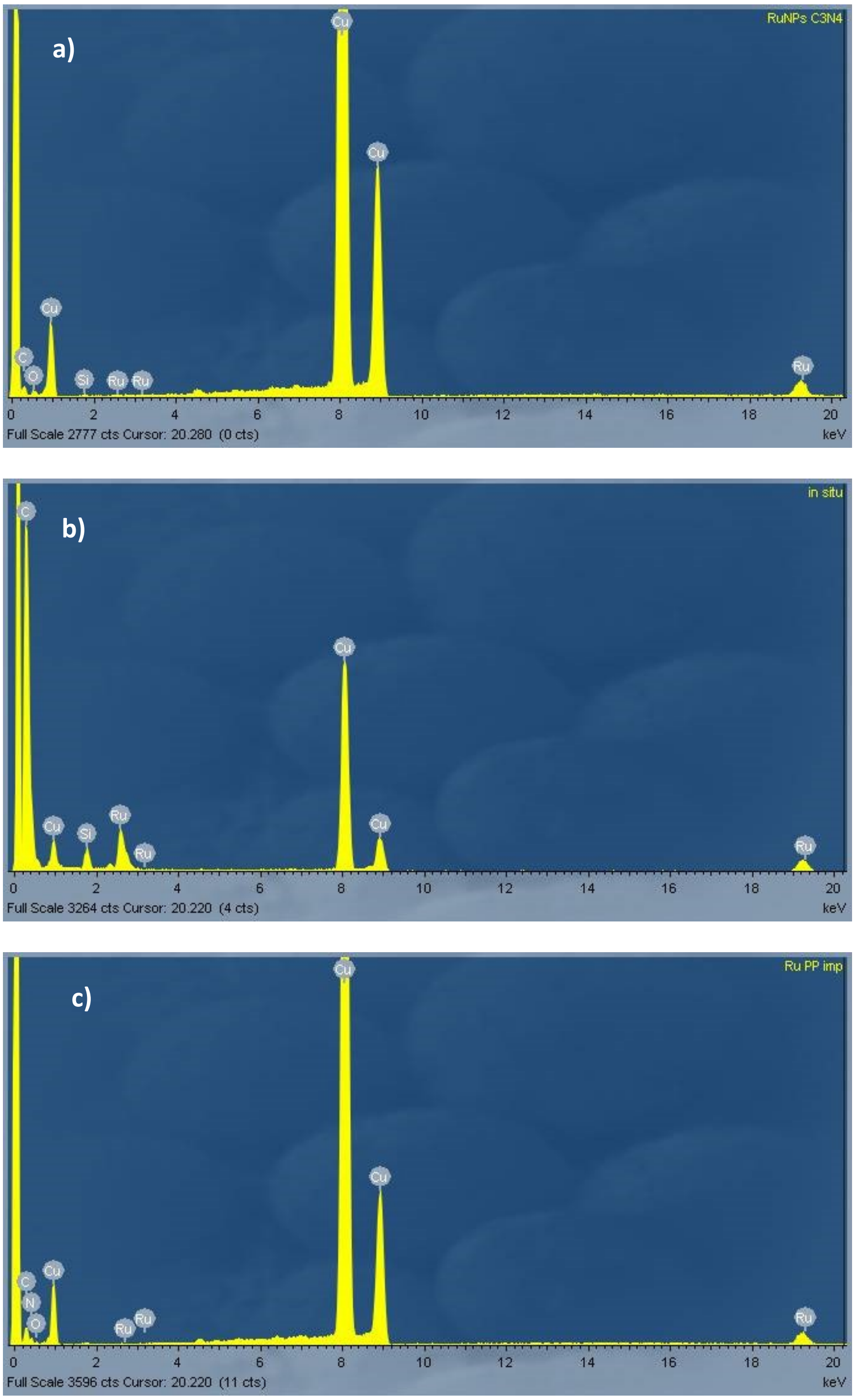

Figure S2. HR-TEM images (left) and high-angle annular dark-field (HAADF)-STEM images (right) of pure mpg-CN.

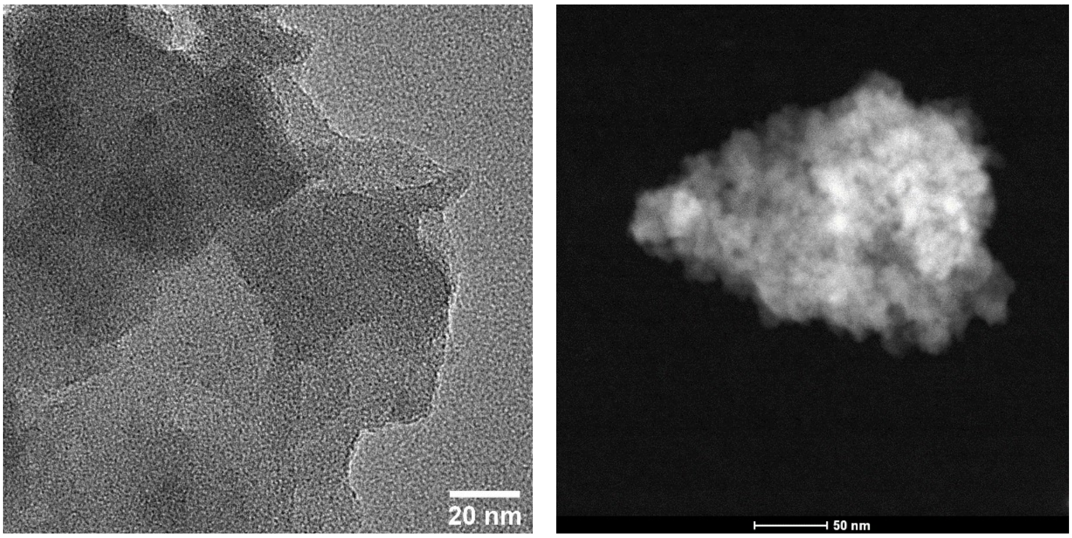

Figure S3. XPS signal of the Ru $3p_{3/2}$ band of RuNP@mpg-CN (left panel) and in-RuPPNP@mpg-CN (right panel). Red lines denote the experimental XPS spectra, black lines the envelope, blue lines the metallic-Ru components and green lines the Ru(IV) components.

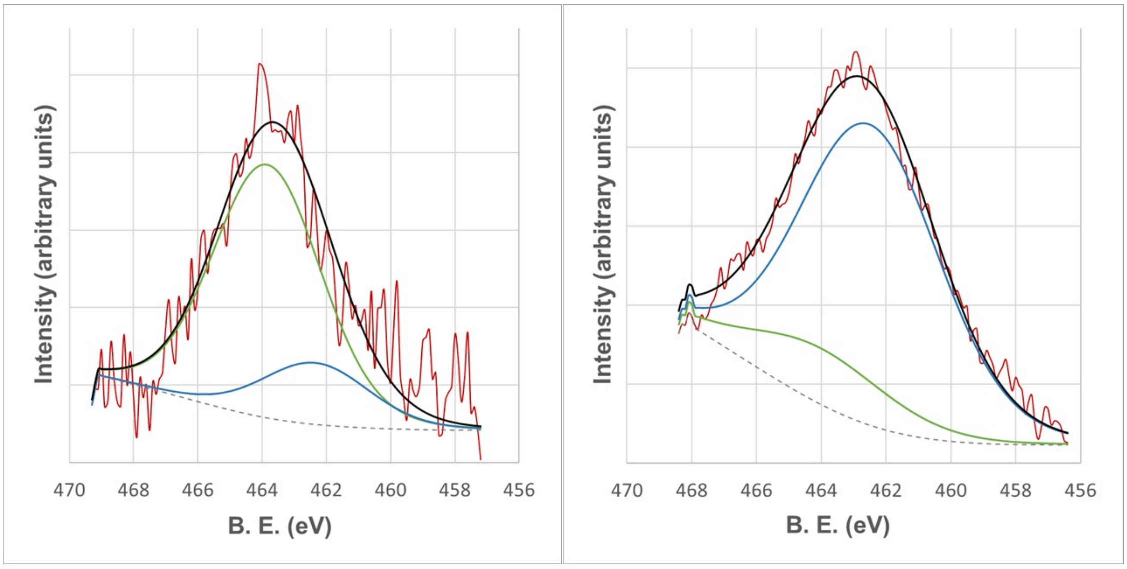

Figure S4. N_2 isotherms of pure mpg-CN, RuNP@mpg-CN, in-RuPPNP@mpg-CN, ex-RuPPNP@mpg-CN, and PtNP@mpg-CN.

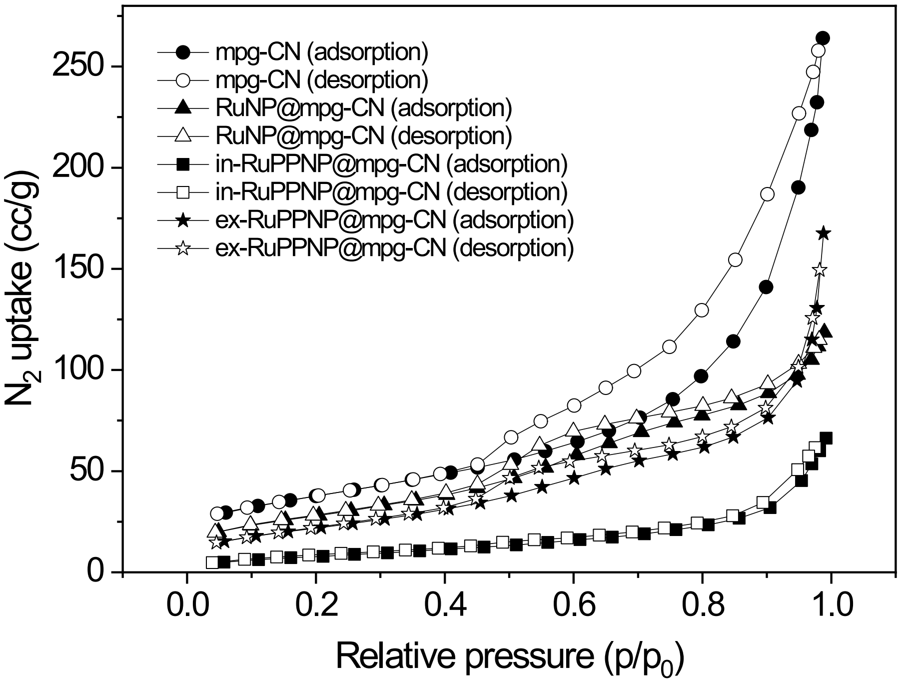

Figure S5. X-ray diffractograms of mpg-CN, RuNPs@mpg-CN, in-RuPPNPs@mpg-CN, and ex-RuPPNPs@mpg-CN

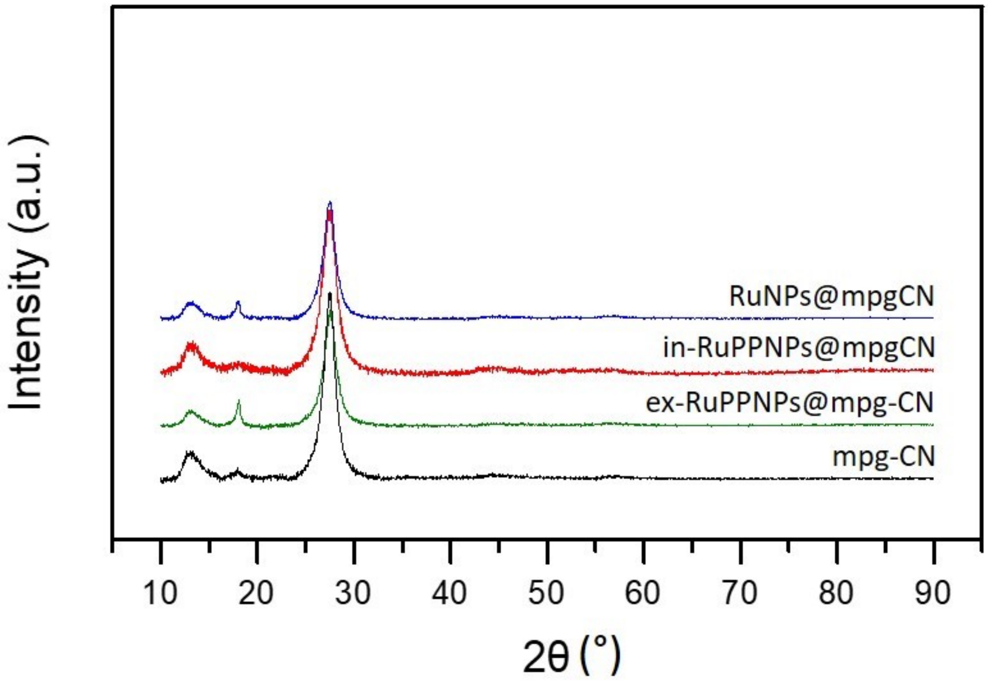

Figure S6. Photocatalytic H_2 evolution with RuNPs@mpg-CN, in-RuPPNPs@mpg-CN, and ex-RuPPNPs@mpg-CN in the presence of visible light irradiation (>395 nm) from 300 W Xe lamp using TEOA as the sacrificial electron donor.

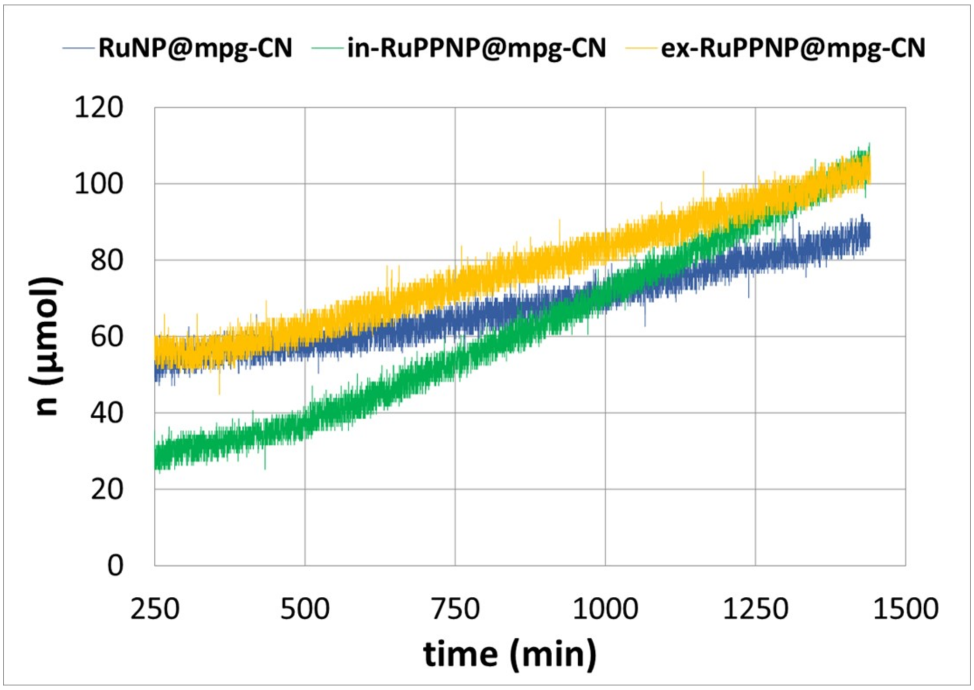

Figure S7. Photocatalytic H_2 evolution with PtNPs@mpg-CN, in the presence of visible light irradiation (>395 nm) from 300 W Xe lamp using TEOA as the sacrificial electron donor.

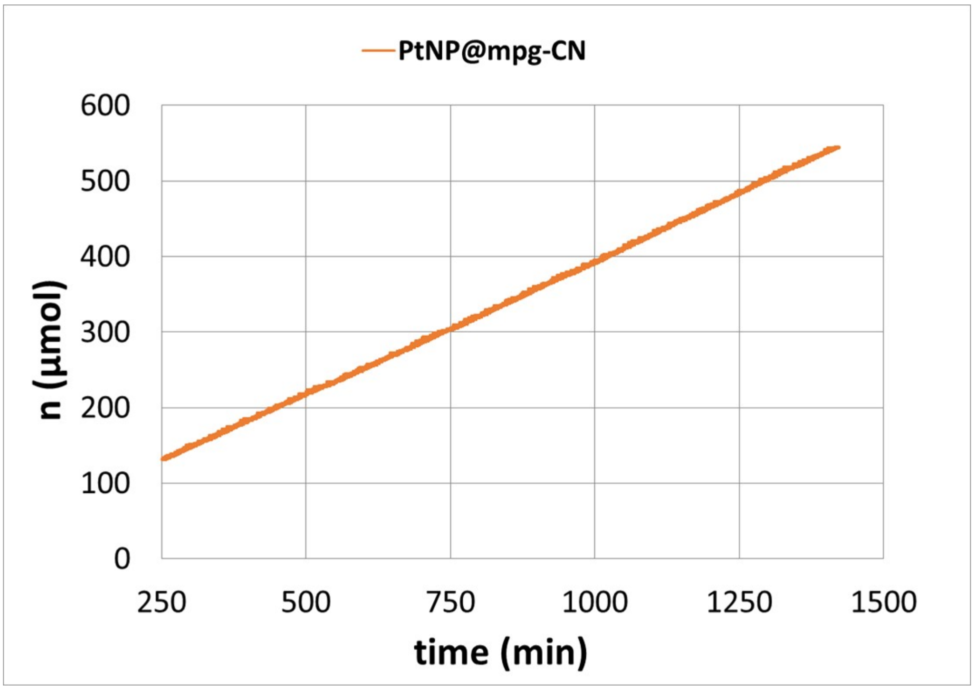

Figure S8. Tauc plot analysis of mpg-CN in water, F(R) is the Kubelka-Munk function.

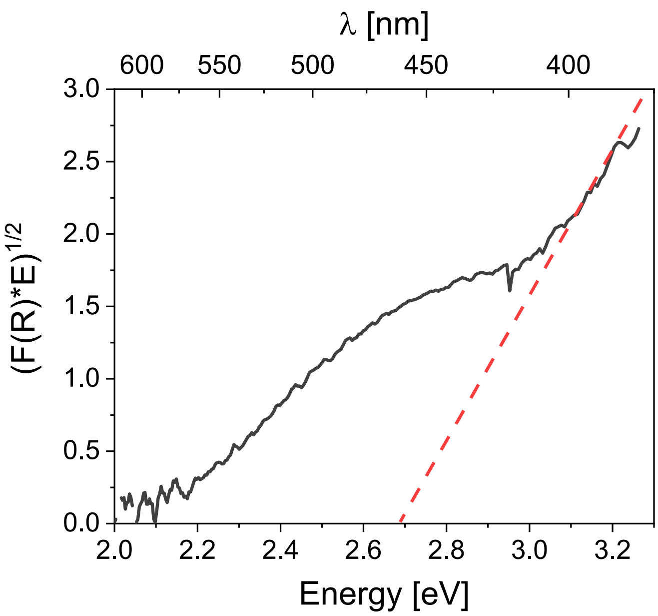

Figure S9. Emission spectrum of mpg-CN in water (excitation at 390 nm). As shown by R. Godin, *et al*., *J. Am. Chem. Soc*., 2017, **139**, 5216 the spectrum can be fitted using two Gaussian functions with relative maxima at 465 and 524 nm (corresponding to energies of 2.7 and 2.4 eV, respectively) and assigned to two different emissive states, both related to electrons and holes at or close to the band edges.

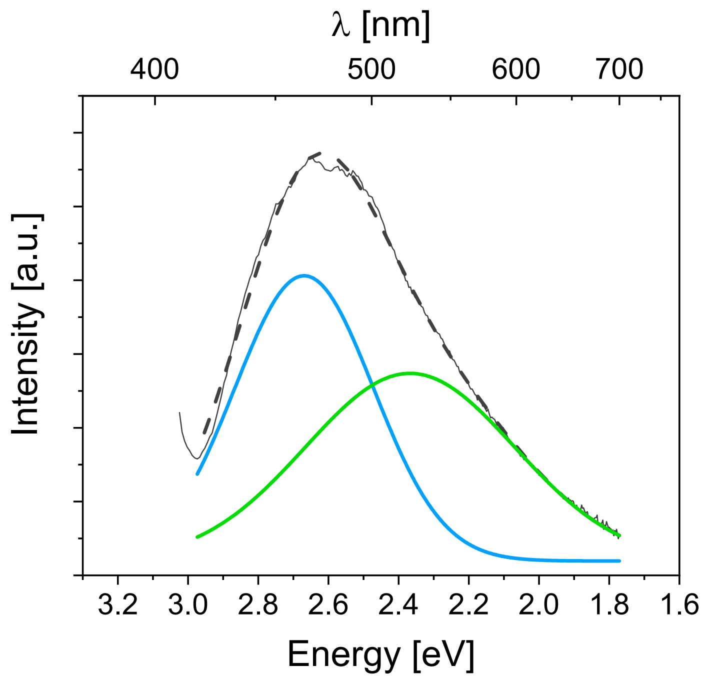

Figure S10. Time-resolved emission decay of mpg-CN in water obtained by TC-SPC (excitation at 380 nm, analysis at 470 nm) and related fitting using a tri-exponential function according to the eq S1.

$$f(t) = A_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + A_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) + A_3 \cdot \exp\left(-\frac{t}{\tau_3}\right) \quad \text{(S1)}$$

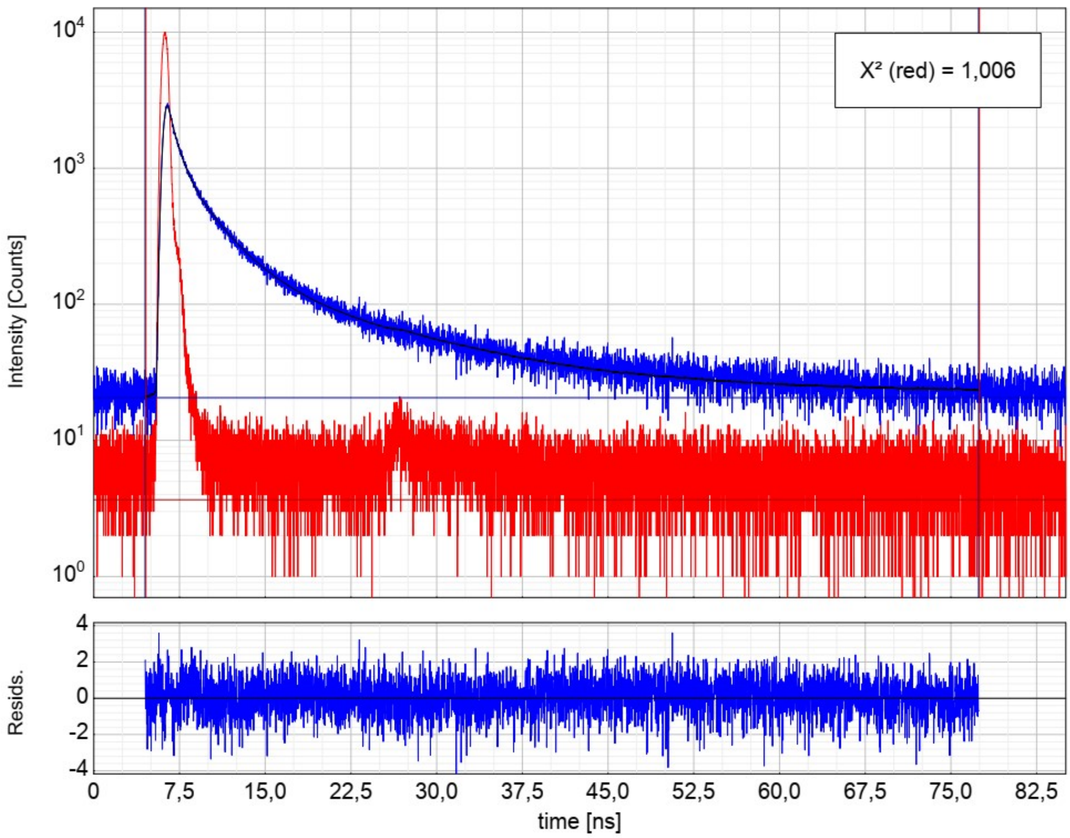

Table S1. Summary of the lifetimes of the different mpg-CN samples in water obtained by TC-SPC (excitation at 380 nm, analysis at 470 nm). All the decays have been fitted using triexponential functions according to eq S1, the percentages represent the weight of the *i*-th time component, according to eq. S2.

$$W\,\% = \frac{A_i}{A_1 + A_2 + A_3} \cdot 100 \tag{S2}$$

	τ_1 [ns]	τ_2 [ns]	τ_3 [ns]	$\langle\tau\rangle$ [ns]
mpg-CN	0.75 (68%)	3.28 (28%)	14.92 (4%)	2.04
mpg-CN + TEOA	0.75 (69%)	3.27 (27%)	14.00 (4%)	1.97
PtNP@mpg-CN	0.72 (69%)	3.17 (27%)	13.78 (4%)	1.95
PtNP@mpg-CN + TEOA	0.67 (68%)	2.94 (28%)	13.30 (4%)	1.81
RuNP@mpg-CN	0.70 (66%)	3.14 (29%)	14.00 (5%)	2.02
RuNP@mpg-CN + TEOA	0.71 (68%)	3.17 (28%)	14.30 (4%)	1.94
in-RuPPNP@mpg-CN	0.74 (65%)	3.17 (30%)	13.26 (5%)	2.09
in-RuPPNP@mpg-CN + TEOA	0.75 (68%)	3.19 (28%)	14.23 (4%)	2.00
ex-RuPPNP@mpg-CN	0.62 (68%)	2.87 (28%)	13.22 (4%)	1.76
ex-RuPPNP@mpg-CN + TEOA	0.61 (69%)	2.77 (27%)	12.01 (4%)	1.67

Figure S11. a) Transient absorption spectra at 100 μs time-delay obtained by laser flash photolysis (excitation at 355 nm) of mpg-CN in water in the absence/presence of 10% TEOA (dots are experimental data, lines are the best fits using gaussian functions); b) kinetic analysis at 750 nm.