Electronic Supporting Information for

Photo- and Radio-luminescence of Porphyrin Functionalized ZnO/SiO₂ Nanoparticles

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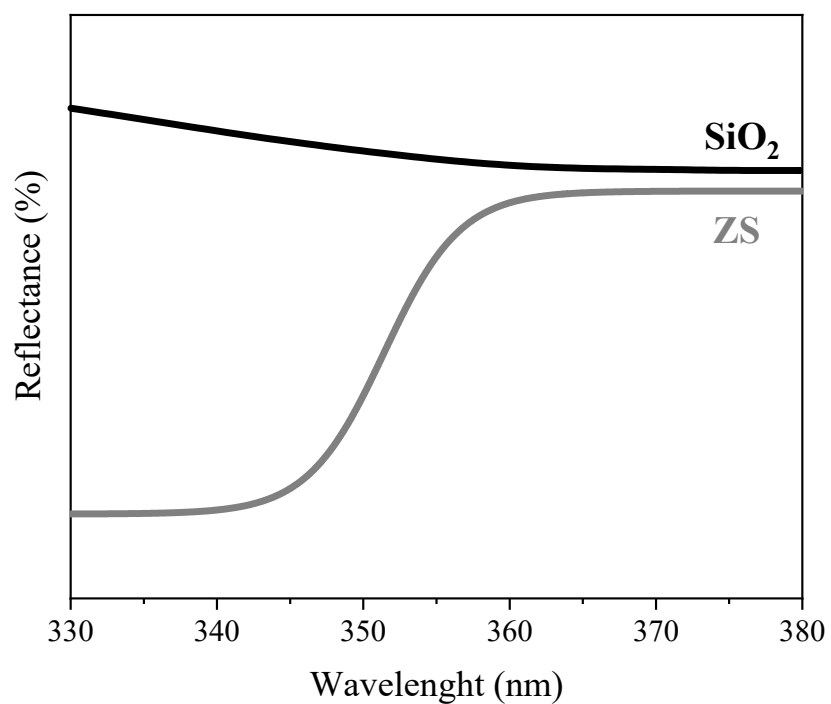
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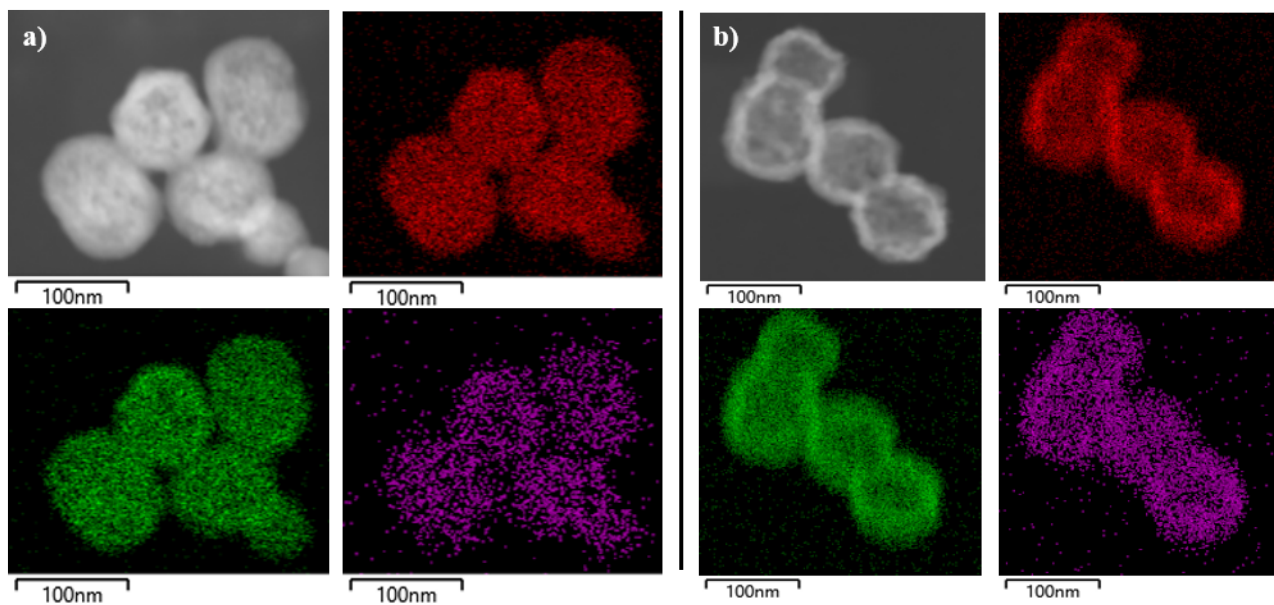[c] FZU Institute of Physics of the Czech Academy of Science, Cukrovarnicka 10/112, 16200 Prague, Czech Republic
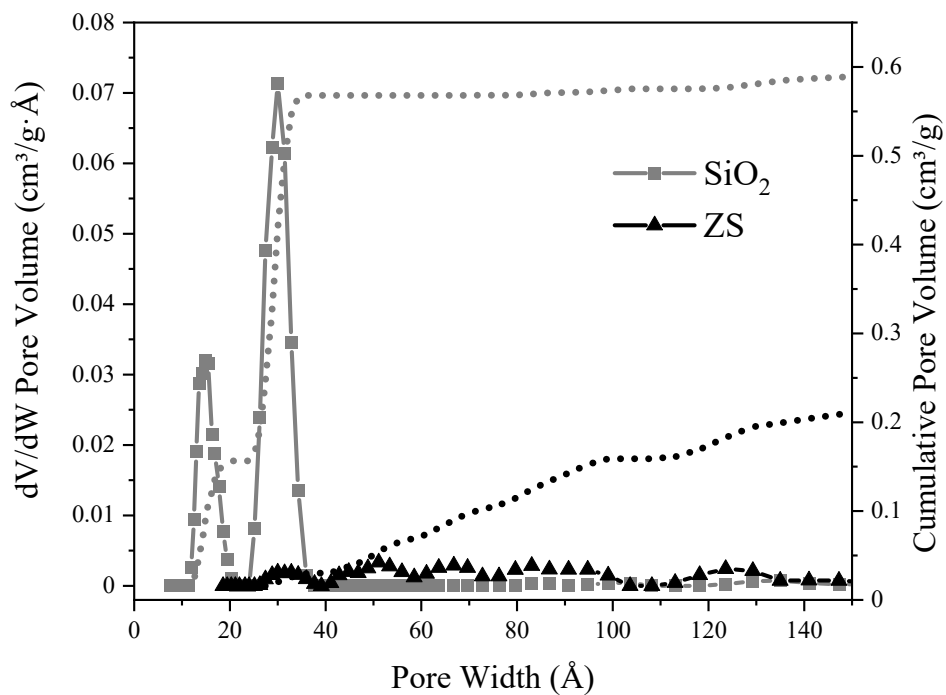
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Figure S1: Spectra of Diffuse Reflectance Spectroscopy (DRS) of ZS.

**Figure S2:** Elemental mapping images of ZS (a) and ZS-AP-1 (b), reported as an example. Color legend: silicon = green, oxygen = red, zinc = purple.

Figure S3: Pore size distribution (left axis) and cumulative pore volume (right axis) measured through nitrogen physisorption analysis for SiO_2 and ZS.
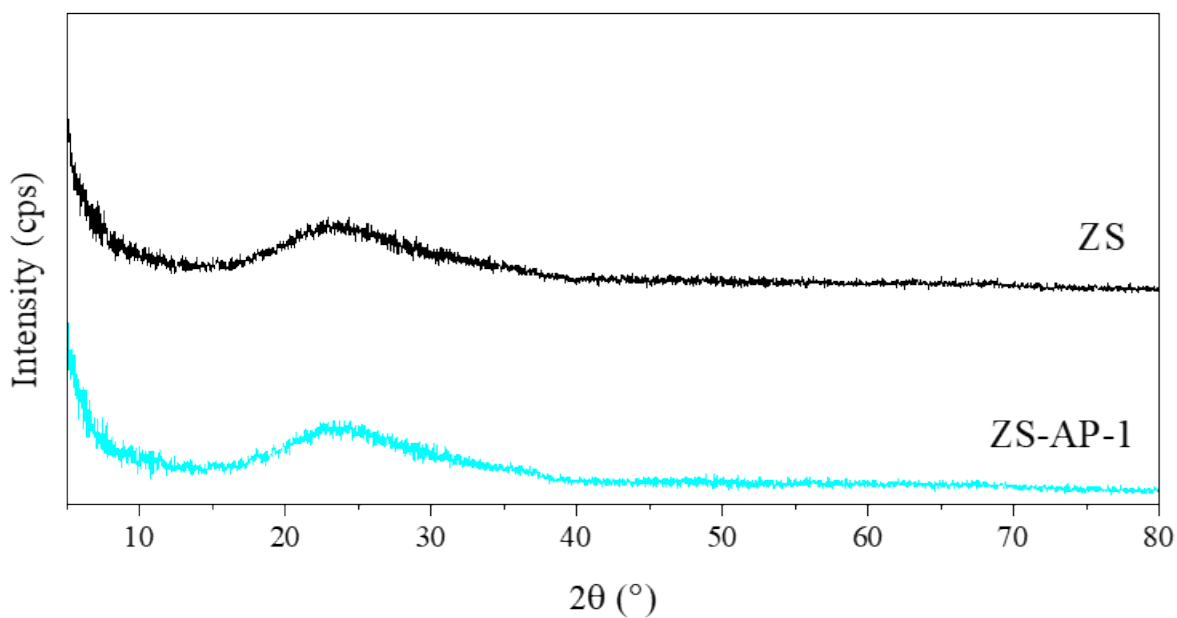
Figure S4: XRPD spectra of ZS (black curve) and ZS-AP-1 (cyan), reported as an example of ZS-AP-Y samples.
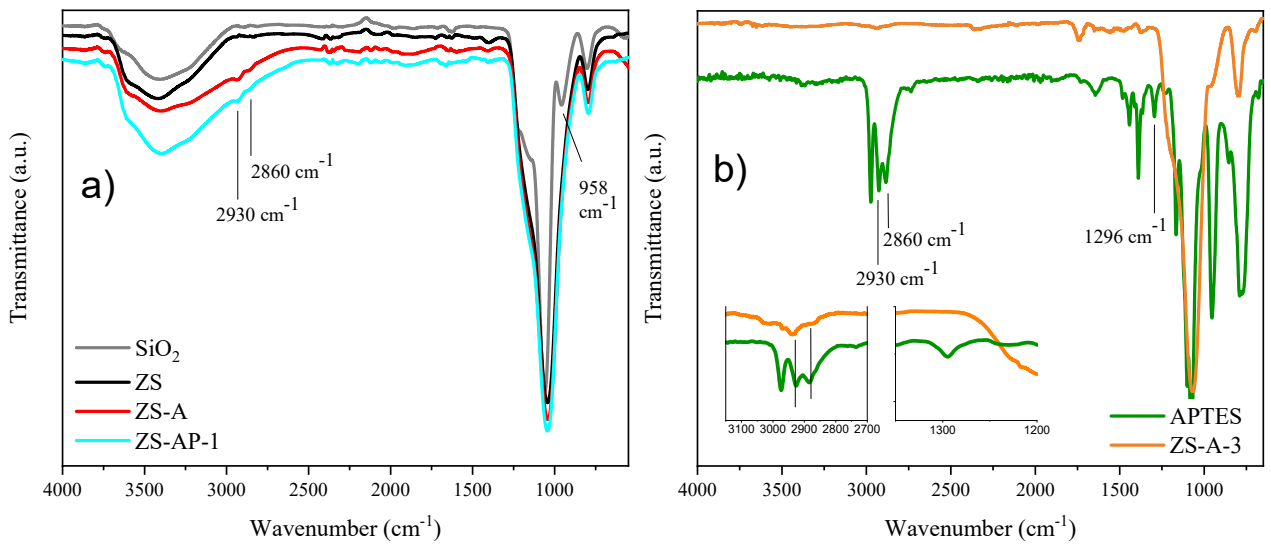
Figure S5: ATR-FTIR spectra of a) SiO_2 (grey line), ZS (black), ZS-A (red) and ZS-AP-1 (cyan); b) APTES (green) and SiO_2 functionalized with APTES (orange, ZS-A-3, APTES amount = 3.0 wt%). In Figure b, the insets show the magnifications in the region 3200-2700 cm^{-1} and 1350-1200 cm^{-1}, to highlight the peaks due to CH_2 groups and ethoxy groups of APTES, respectively. The FTIR of ZS-A-high was registered to monitor the intensity of the peaks of CH_2 groups at higher APTES amount (2930 and 2860 cm^{-1}) and the disappearance of the peak due to ethoxy groups (1296 cm^{-1}) after the reaction with the surface OH groups of SiO_2.
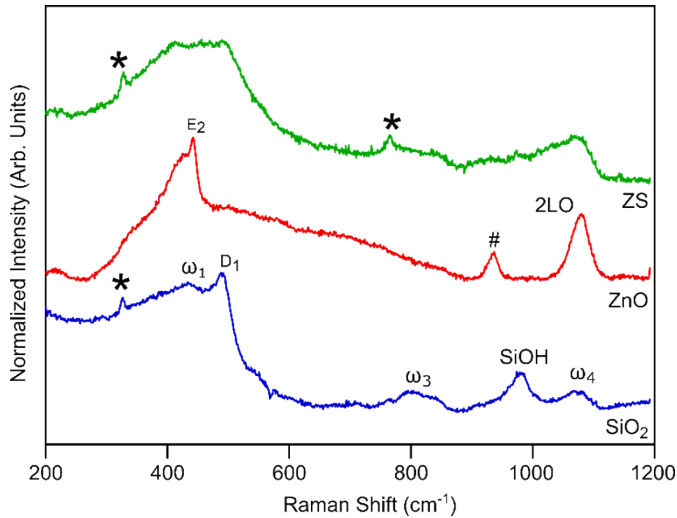
Figure S6: Raman spectra of ZS (green line), bare ZnO (red line), and bare SiO_2 (blue line) prepared in the same reaction conditions of ZS. Peaks marked with asterisks (*) and hash (#) are related to minor impurities of CTAB and zinc acetate, respectively.

TGA data elaboration

The weight loss of ZS-A and ZS-AP-Y in the range 150-1000°C ($\Delta W_{150-1000°C}$) was used to estimate the amount of APTES covalently bonded to the surface silanol groups on silica and TCPP, respectively. In ZS-A, $\Delta W_{150-1000°C}$ was attributed to two main components by using a simplified model where APTES is bonded to SiO_2 through three covalent bonds <u>at low APTES loadings</u>: i) combustion of the $-CH_2CH_2CH_2NH_2$ groups anchored to SiO_2 NPs after the reaction with APTES; ii) water desorption from the residual surface silanol groups, assuming that three surface OH groups have been replaced by each APTES bonded to SiO_2. In ZS-AP-Y samples an additional contribution due to TCPP has to be considered. The contributions to the weight loss $\Delta W_{150-1000°C}$ in ZS-AP-Y are reported in the following equation:

$$\Delta W_{150-1000°C} = n_{APTES} \cdot MW_{APTES} + \frac{1}{2} \cdot \left(n_{OH} \cdot w_{SiO_2(1000°C)} - 3n_R \right) \cdot MW_{H_2O} + n_{TCPP} \cdot MW_{TCPP}$$

(Eq. S1)

where n_{APTES} and n_{TCPP} represent the APTES and TCPP moles on SiO_2, respectively; MW is the molecular weight (APTES: $-CH_2CH_2CH_2NH_2$ groups = 58.0 g mol^{-1}; TCPP = 790.8 g mol^{-1}); n_{OH} is the moles number of OH surface groups of bare SiO_2; $w_{SiO2(1000°C)}$ is the weight of residual SiO_2 at 1000°C. In ZS-A the APTES amount (wt%) was calculated by deriving n_R from Eq. S1. In ZS-AP-Y, considering that the APTES amount is very small and remains constant from ZS-A to ZS-AP-Y, the only difference in the measured $\Delta W_{150-1000°C}$ came from the TCPP contributions. Thus, from Eq. S1 the TCPP amount (wt%) can be calculated using the following equation:

$$TCPP\ amount = \Delta w_{150-1000°C}(ZS-AP-Y) - \Delta w_{150-1000°C}(ZS-A)$$

(Eq. S2)

and compared to the nominal TCPP amounts. From the obtained TCPP amounts (wt%) and APTES amount (wt%), the number of TCPP and APTES molecules anchored onto SiO_2 surface was calculated:

$$\frac{n.molecules}{surface(nm^2)} = \frac{m_{species}}{1g_{SiO2}} \frac{N_A}{MW_{species} \cdot SSA_{BET} * 10^{18}}$$

(Eq. S3)

where $m_{species}/1g_{SiO2}$ is the mass of TCPP or APTES anchored on 1.0 gram of SiO_2 (calculated from TCPP or APTES amount), N_A the Avogadro number, SSA is the specific surface area of SiO_2 (reported equal to 1100 m^2 g^{-1}).

| Sample	TGA results				CHNS results	
	$\Delta W_{150\text{-}1000}$ (%)	TCPP amount (wt%)	Nominal TCPP (wt%)	Ratio n molecules TCPP/APTES	N% nominal	N% measured
ZS	6.4	-	-	-	-	0.15
ZS-A	6.7	-	-	-	0.05	0.21
ZS-AP-0.1	7.7	1.0	0.3	0.3	0.07 (+0.02)	0.24 (+0.03)
ZS-AP-0.25	7.8	1.1	0.7	0.4	0.10 (+0.05)	0.30 (+0.09)
ZS-AP-0.5	8.5	1.8	1.4	0.6	0.15 (+0.10)	0.36 (+0.15)
ZS-AP-1	9.6	2.9	2.7	1.1	0.24 (+0.19)	0.41 (+0.20)

Table S1: Amount of APTES and TCPP anchored over SiO_2 calculated from TGA results (according to Equation S1-S3) and nitrogen content (CHNS analysis) of ZS-A and ZS-A-PY compared to bare ZS. For CHNS: in the brackets the additional N% due to TCPP compared to ZS-A.

Absorption measurements (Lambert-Beer elaboration)

TCPP concentration in ZS-AP-Y was calculated from absorbance measurements by using the Lambert-Beer equation:

$$Abs_\lambda = \varepsilon_\lambda \times d \times C$$

(Eq. S4)

where Abs_λ is the absorbance at a given wavelength, ε_λ is molar extinction coefficient at a given wavelength, *d* the optical path length, and *C* the concentration[1]. ε_λ was derived from a calibration procedure by measuring the Abs values of TCPP solutions at different concentration in DMF (10^{-6} M – $7\cdot10^{-5}$ M, data not shown). The best liner regression for ε was obtained at 520 nm, that is the first peak of the TCPP Q-bands (data not shown). In fact, since the Soret band shape is distorted at high concentration, the calibration is not reliable. ε_{520} results about 8900 M^{-1} cm^{-1} and the used optical path length is 0.1 cm.
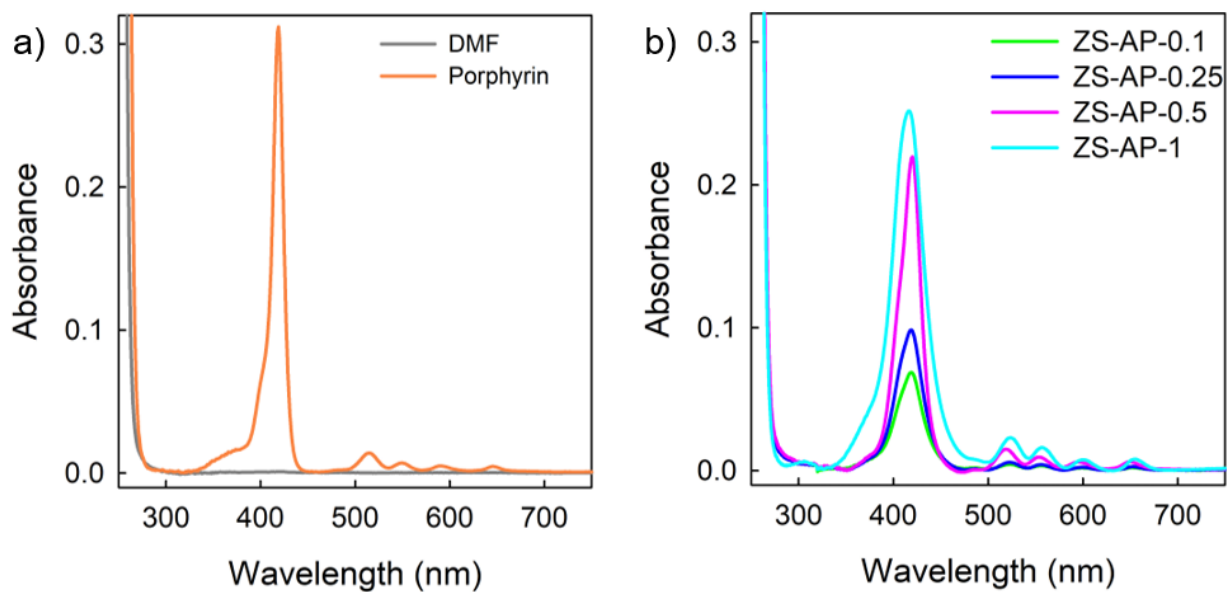
Figure S7: Absorption spectra of a) TCPP in DMF solution (10^{-5} M) compared to DMF and b) ZS-AP-Y in DMF (ZnO concentration of 10^{-3} M).

	C_{TCPP} (A_{520} nm) [M]
ZS-AP-1	$2.6*10^{-5}$
ZS-AP-0.5	$1.5*10^{-5}$
ZS-AP-0.25	$6.5*10^{-6}$
ZS-AP-0.1	$4.9*10^{-6}$

Table S2: TCPP concentration in functionalized nanoscintillators calculated from the absorption spectra with Eq. S4.
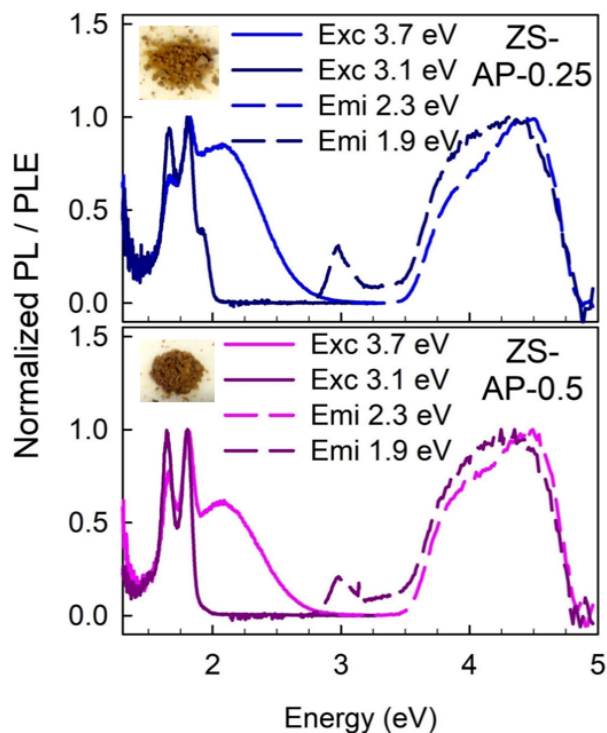
Figure S8: Normalized steady-state photoluminescence (PL, solid lines) and excitation photoluminescence (PLE, dashed lines) extrapolated from PL/PLE contour plots recorded under continuous CW excitation of ZS-AP-0.25 (top) and ZS-AP-0.5 (bottom) in DMF. Insets are digital pictures of the materials as synthesized.
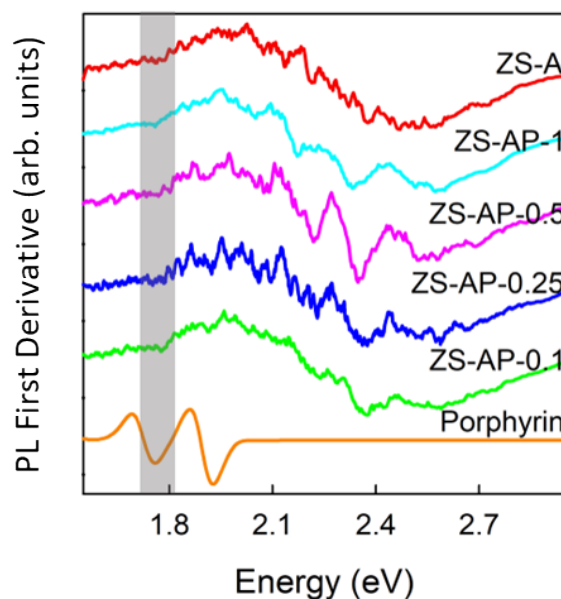
Figure S9: Normalized first derivate of PL spectra of ZS-A and ZS-AP-Y recorded with 0.2 ms delay with respect to the 3.7 eV excitation pulse (reported in Figure 4c bottom panel) compared to TCPP.
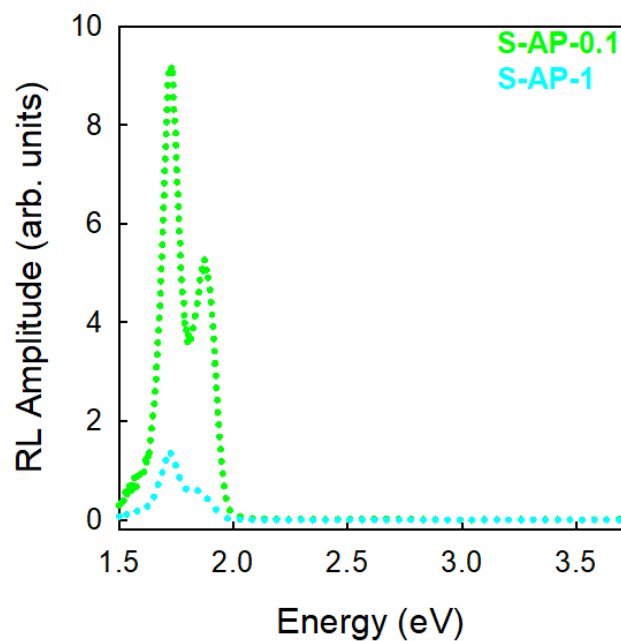
Figure S10: RL intensities of SiO_2 NPs functionalized with 0.1 (S-AP-0.1) and 1 (S-AP-1) wt% of TCPP, both normalized to their dye content.
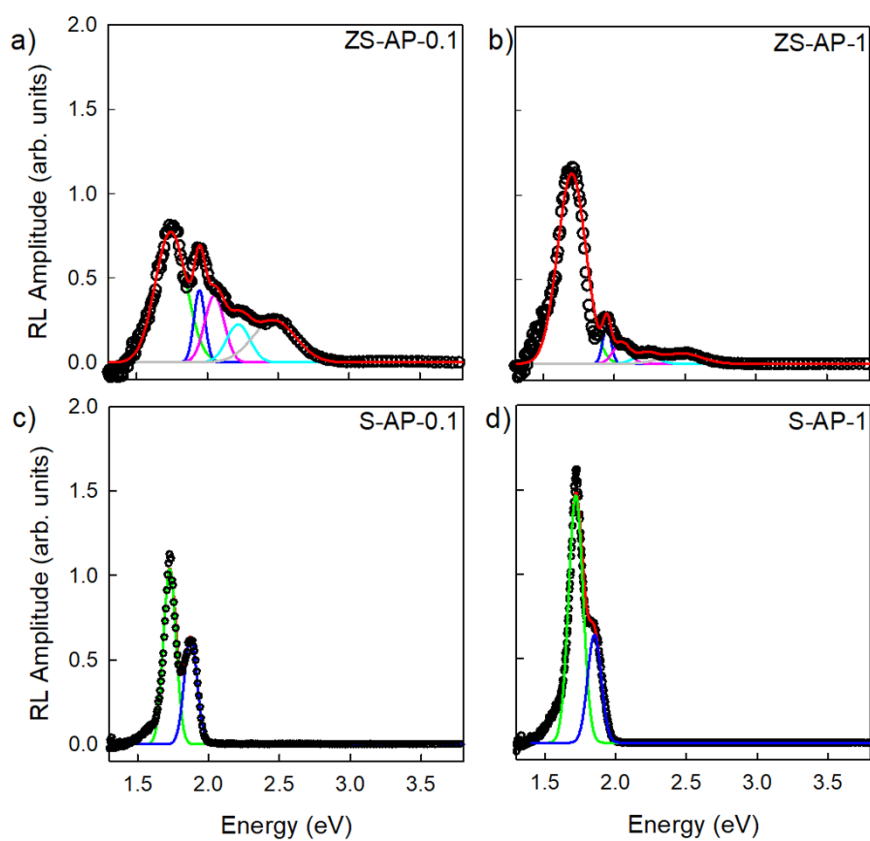
Figure S11: Gaussian deconvolution of the RL spectra of ZS-AP-0.1 and ZS-AP-1 (a,b) and bare SiO_2 NPs (c,d) functionalized with 0.1 and 1 wt% of porphyrin (S-AP-0.1 and S-AP-1, respectively).

Gaussian components (green, blue, pink, cyan, and grey) obtained by numerical fit are shown together with experimental curves (black empty circle lines). The curve representing the whole numerical fit (red solid line) is superimposed to the experimental data. The sets of all parameters of the deconvolutions are listed in Table S3.

Gaussian deconvolution parameters		ZS-AP-0.1	ZS-AP-1	S-AP-0.1	S-AP-1
Band A (green line)	Energy (eV)	1.74 ± 0.01	1.70 ± 0.01	1.73 ± 0.01	1.72 ± 0.01
	FWHM (eV)	0.26 ± 0.01	0.23 ± 0.01	0.10 ± 0.01	0.11 ± 0.01
	Integral (arb. units)	0.21 ± 0.01	0.28 ± 0.01	0.12± 0.01	0.18 ± 0.01
Band B (blue line)	Energy (eV)	1.94 ± 0.01	1.95 ± 0.01	1.87 ± 0.01	1.85 ± 0.01
	FWHM (eV)	0.09 ± 0.01	0.07 ± 0.01	0.11 ± 0.01	0.12 ± 0.01
	Integral (arb. units)	0.04 ± 0.01	0.02 ± 0.01	0.07 ± 0.01	0.07 ± 0.01
Band C (pink line)	Energy (eV)	2.05 ± 0.01	2.05 ± 0.02	-	-
	FWHM (eV)	0.16 ± 0.05	0.14 ± 0.09	-	-
	Integral (arb. units)	0.07 ± 0.03	0.018 ± 0.003	-	-
Band D (cyan line)	Energy (eV)	2.22 ± 0.03	2.22 ± 0.07	-	-
	FWHM (eV)	0.19 ± 0.06	0.20 ± 0.10	-	-
	Integral (arb. units)	0.05 ± 0.01	0.012 ± 0.004	-	-
Band E (grey line)	Energy (eV)	2.47 ± 0.02	2.50 ± 0.10	-	-
	FWHM (eV)	0.36 ± 0.03	0.32 ± 0.09	-	-
	Integral (arb. units)	0.10 ± 0.02	0.02 ± 0.01	-	-

Table S3: Fit parameters of the Gaussian deconvolution of the RL spectra of ZS (a,b) and SiO2 NPs (c,d) functionalized with 0.1 and 1 wt% of TCPP. The boxes in blue remark the integral of the porphyrin luminescence.

TRPL data analysis

The time resolved PL spectra reported in Figure 5 of the manuscript show a complex behaviour. The signal decay has been reproduced with an analytically multi-exponential function[2]:

$$I_{PL} \propto \sum_{1}^{i} A_i e^{-t/\tau_i}$$

(Eq. S5)

The parameters used for the fit procedure are reported below in Table S3 and S4. The weight of each component of the TRPL decay, that represents the fractional contribution, has been computed using:

$$w_i = \frac{A_i \tau_i}{\sum_{1}^{i} A_i \tau_i}$$

(Eq. S6)

where the terms $A_i\tau_i$ are proportional to the area under the decay curve for each decay time. Then, the average PL lifetime $\bar{\tau}$ has been calculated as the weighted average of the characteristic decay time for each exponential function i using:

$$\bar{\tau} = \frac{\sum_{1}^{i} w_i \tau_i}{\sum_{1}^{i} w_i}$$

(Eq. S7)

	ZS	ZS-A	ZS-AP-0.1	ZS-AP-0.25	ZS-AP-0.5	ZS-AP-1
τ_1 (ns)	26 ± 1	23 ± 1	25 ± 1	27 ± 1	27 ± 1	27 ± 2
Weight$_1$ (%)	15	12	12	14	13	14
τ_2 (ns)	190 ± 20	180 ± 20	180 ± 20	200 ± 40	200 ± 30	180 ± 40
Weight$_2$ (%)	16	19	14	13	12	13
τ_3 (ns)	1000 ± 40	1030 ± 40	1000 ± 30	990 ± 50	1020 ± 40	1000 ± 50
Weight$_3$ (%)	69	69	74	73	75	73

Table S4: TRPL fit parameters of the emission recorded at 2.3 eV under pulsed excitation at 3.6 eV.

	TCPP	ZS-AP-0.1	ZS-AP-0.25	ZS-AP-0.5	ZS-AP-1
τ_1 (ns)	-	2.4 ± 0.1	2.5 ± 0.1	2.4 ± 0.1	2.4 ± 0.1
Weight$_1$ (%)	-	63	70	77	82
τ_2 (ns)	11.0 ± 0.1	11.5 ± 0.2	11.5 ± 0.2	12.0 ± 0.4	12 ± 0.7
Weight$_2$ (%)	100	37	30	23	18

Table S5: TRPL fit parameters of TCPP and ZS-AP-Y emission recorded at 1.9 eV under pulsed excitation at 2.4 eV.

REFERENCES

1   J. G. Solé, L. E. Bausá and D. Jaque, *An Introduction to the Optical Spectroscopy of Inorganic Solids*, John Wiley & Sons, Ltd, Chichester, UK, 2005.

2   J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer US, Boston, MA, 3th edn., 2006.