

Electronic Supplementary Information for

Magnetic iron oxide-porphyrin hybrids as relevant materials synthesised using a cost-efficient method for preparing unsymmetrical meso-aryl porphyrin synthons

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Materials and methods

All chemical materials were purchased from Aldrich having the highest grade available and used as-received. Solvents were purified by standard methods. The MALDI-TOF MS data were acquired using a *Bruker Daltonics flex Analysis* apparatus. ¹H NMR spectra were recorded on a 400 MHz Bruker-Amx. UV-visible absorption spectra were recorded on a *Hitachi U-2010*.

Transmission Electron Microscopy analyses (TEM) were carried out on a Philips CM 200 operating at an accelerating voltage of 200 kV. The TEM samples were prepared in isopropyl alcohol, at room temperature, and then placed onto holey carbon-covered copper grids to dry before analysis. The size distributions were determined through a manual analysis of enlarged micrographs with *Imagetool* software Version 3.0 to obtain a statistical size distribution and a mean diameter by curve fitting using Gaussian function.

The metal content in all MNP@SiO₂-Zn-Trialquil a was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using *Genesis SOP (Spectro)*. Thermogravimetric analyses were made in air using a *TG-DSC Setsys Evo16* instrument (*Setaram*) with a heating rate of 10 °C/min to a maximum temperature of 800 °C.

Nitrogen sorption measurements were carried out with a *Micromeritics ASAP 2010* apparatus. Prior to analysis, all samples were pre-treated for 1 h at 60 °C and then at 110 °C for 4h under vacuum.

The infrared spectra were measured over the range 4000–600 cm^{-1} on a FTIR Nexus 670 Nicolet spectrometer. The samples were pressed into thin wafers (10–20 mg cm^{-2}) and heated in an IR glass cell from room temperature up to 150 $^{\circ}\text{C}$ (heating rate of 5 $^{\circ}\text{C}/\text{min}$) for 1.5 h under vacuum (10^{-3} mbar) before spectra acquisition in transmission mode. Spectra were normalized with the sample weight. 64 scans with a resolution of 4 cm^{-1} were collected for each spectrum. Diffuse reflectance spectra were recorded in a Cary 5000 UV-Vis-NIR spectrophotometer, equipped with a Praying Mantis accessory and using Spectralon as reference.

Absorption and fluorescence spectra were recorded in *N,N*-dimethylformamide (DMF) on a Hitachi U-2010 spectrophotometer and a SPEX Fluorolog 3.22 spectrophotometer, respectively. Fluorescence spectra were corrected for the wavelength response of the system. The absorption of both reference and samples solutions in fluorescence quantum yield measurements were matched at ~ 0.2 at the excitation wavelength of 422 (free-base) or 430 nm (metallated), and then the solutions were diluted by a factor of 10 before collecting fluorescence. Before each measurement with magnetic material, the materials were dispersed on DMF.

~~Highly efficient triplet-triplet energy transfer was observed by a factor of 10.~~
Transient triplet-triplet absorption was obtained with an Applied Photophysics LKS.60 flash photolysis spectrometer with the R928 photomultiplier from Hamamatsu for detection and HP Infinium (500 MHz, 1 GSas $^{-1}$) or Tektronix DPO 7254 (2.5 GHz, 40 GSas $^{-1}$) oscilloscopes. An adaptation of this spectrometer allowed the detection of singlet-oxygen phosphorescence at room temperature. This emission was detected using a Hamamatsu R5509-42 photomultiplier, cooled to 193 K in a liquid nitrogen chamber (Products for research, model PC176TSCE005). Excitation was achieved with the third harmonic of Nd:YAG lasers (spectra-physics Quanta Ray GCR 130, 5–6 ns FWHM, or EKSPILA PL 2143 A, 3 ps pulse width. The modification of the spectrometer for time-resolved singlet-oxygen phosphorescence measurements involved the interposition of a Melles Griot cold mirror (03MCS005), which reflects more than 99% of the incident light in the 400–700 nm range, and of a Scotch RG665 filter. A 600 line diffraction grating was mounted in place of a standard one. This equipment allows spectral identification of the singlet-oxygen phosphorescence and measurement of the singlet-oxygen lifetime in the nanosecond and microsecond ranges. The filters employed are essential for eliminating from the infrared signal all harmonic contributions of the sensitizer emission in the 300–700 nm range.

Singlet oxygen quantum yields in DMF¹ were obtained with a procedure described elsewhere, using phenalene as reference, for which $F_D=1.00$ in acetonitrile.²

Fluorescence decays were measured using a home-built picosecond time-correlated single-photon counting (TCSPC) apparatus described elsewhere in the literature.³ The fluorescence decays and the instrumental response function (IRF) were collected using a timescale of 1024 (or 4096) channels, up to a maximum of 5×10^3 were reached. Deconvolution of the fluorescence decay curves was performed using the modulating function method, as implemented by G. Striker in the SAND program, as previously reported in the literature.⁴

1. Characterization of acidic properties of NaY zeolite

Acidity measurements were performed using pyridine as probe molecule, followed by Infrared spectroscopy (FTIR); a Nicolet Nexus spectrometer was used for the purpose. In a typical experiment, samples were pressed into thin wafers ($10\text{-}20 \text{ mg/cm}^2$) and heated in an IR glass cell from room temperature up to $450 \text{ }^\circ\text{C}$ ($5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) for 3 h under vacuum (10^{-5} mbar). Afterwards, the samples were cooled down to $150 \text{ }^\circ\text{C}$ and left in contact with pyridine for 10 min. Then, excess probe molecule was removed for 30 min under vacuum and the IR spectra were recorded; 64 scans with a resolution of 4 cm^{-1} were collected for each spectrum. The concentrations of Brønsted and Lewis sites able to retain the pyridine at $150 \text{ }^\circ\text{C}$ were determined using the integrated areas of the bands at 1541 cm^{-1} and 1445 cm^{-1} ,⁵ respectively, and the extinction coefficients determined by Emeis (Fig. S1).⁶

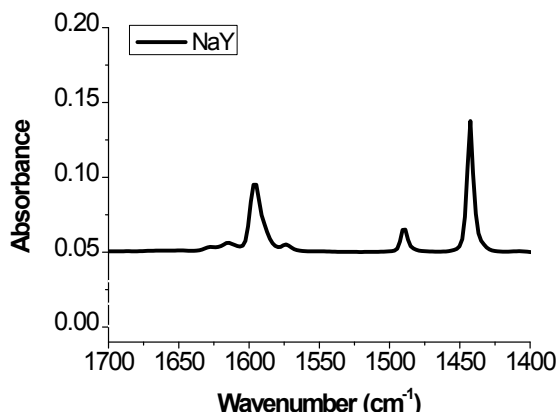


Fig. S1 FTIR spectra of NaY obtained after pyridine contact and subsequent desorption under vacuum at $150 \text{ }^\circ\text{C}$ for 30 min.

2. Preparation of 5-(4-hydroxyphenyl)-10,15,20-tris(4-ethylhexyloxyphenyl) porphyrin (**1**)

2.1. NaY method

An amount of 1.0 g of NaY zeolite (0.08 mmol) was introduced into a 50 mL round flask, containing a mixture of 4-hydroxybenzaldehyde (0.625 mmol, 76.3 mg), 4-(ethylhexyloxy)benzaldehyde (1.875 mmol, 439 mg) in a glacial acetic acid/nitrobenzene mixture (7 mL/5 mL). Addition of equimolar amount of pyrrole (2.5 mmol, 0.17 mL) was carried out dropwise under stirring and heating (≈ 120 °C). After complete addition (ca. 3 min), the suspension was heated further till reflux temperature (≈ 130 °C) and maintained at this temperature for ca. 2 hours. The hot suspension was filtered and the resulting solid material washed with tetrahydrofuran (THF) until no coloured material was collected on the supernatant (250 mL). As alternative Soxhlet extraction with THF can be performed, but in our case we found washing sufficient. The volume of solution was then reduced by rotoevaporation (enough volume to remove the added washing solvent). To induce precipitation, *n*-hexane (ca. 50 mL) was added. The Erlenmeyer flask containing the statistical porphyrin mixture was left overnight in the refrigerator and the deposited solid was collected by filtration and then purified by column chromatography using silica gel as stationary phase, starting with *n*-hexane:CH₂Cl₂ (1:3) to collect the first fraction and then with CH₂Cl₂ to collect the second band. As this fraction was identified as the porphyrin **1**, other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 95 mg (0.0938 mmol) of **1** (16% yield). Characterisation data is in accordance with the literature⁷

2.2. Adler-Longo method⁸

A mixture of 4-hydroxybenzaldehyde (3.75 mmol, 0.458 g) and 4-(ethylhexyloxy)benzaldehyde (11.25 mmol, 2.63 g) was introduced into a 100 mL round flask containing propionic acid (50 mL/25 mL). Addition of equimolar amount of pyrrole (15 mmol, 1.03 mL) was carried out dropwise under stirring and heating (≈ 130 °C). After complete addition (ca. 10-12 min), the suspension was heated further till reflux temperature (≈ 150 °C) and maintained at this temperature for ca. 2 hours. The flask condenser was substituted by a distillation apparatus and the solvent mixture was removed by vacuum, under heating. The obtained solid was redissolved in CH₂Cl₂ (30

mL) and the solution washed with saturated NaHCO₃ solution (3 x 25 mL). The solution was concentrated to dryness in a rotoevaporator and purified by column chromatography using silica gel as stationary phase, starting with *n*-hexane:CH₂Cl₂ (1:3) to collect the first fraction and finally with CH₂Cl₂ to collect the second band, contaminated with the corresponding chlorin (close R_f). Other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 304 mg (0.3 mmol) of **1** plus its corresponding chlorin (~10%), in an approximated 8% yield.

2.3. Gonsalves-Pereira method⁹

A mixture of 4-hydroxybenzaldehyde (3.75 mmol, 0.458 g) and 4-(ethylhexyloxy)benzaldehyde (11.25 mmol, 2.63 g) was introduced into a 100 mL round flask containing a glacial acetic acid/nitrobenzene mixture (50 mL/25 mL). Addition of equimolar amount of pyrrole (15 mmol, 1.03 mL) was carried out dropwise under stirring and heating (≈120 °C). After complete addition (ca. 10-12 min), the suspension was heated further till reflux temperature (≈130 °C) and maintained at this temperature for *ca.* 1 hour. The flask condenser was substituted by a distillation apparatus and the solvent mixture was removed by vacuum, under heating. The deposited solid was purified by column chromatography using silica gel as stationary phase, starting with *n*-hexane to remove nitrobenzene traces, then *n*-hexane:CH₂Cl₂ (1:3) to collect the first fraction and finally with CH₂Cl₂ to collect the second band. As this fraction was identified as the porphyrin **1**, other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 304 mg (0.3 mmol) of **1** (8% yield).

2.4. Lindsey method¹⁰

A mixture of pyrrole (0.25 mL, 3.75 mmol), 4-hydroxybenzaldehyde (114 mg, 0.938 mmol) and 4-(ethylhexyloxy)benzaldehyde (644 mg, 2.75 mmol) in CH₂Cl₂ (250 ml) was bubbled with N₂ for 30 min, and TFA (0.13 mL, 2.0 mmol) was added. The mixture was stirred at room temperature under N₂ for 1 hr. DDQ (625 mg, 3.75 mmol) was added and the mixture was stirred for 12 hr with protection from light. Triethylamine (2.5 ml, 19 mmol) was added and stirred for 30 min, and the solvent was removed by rotary evaporation. The residue was then suspended in CH₂Cl₂, placed on the top of a

dry column of Al₂O₃, and eluted with CH₂Cl₂. The eluted solution was evaporated and then purified by chromatography on silica gel, starting with *n*-hexane:CH₂Cl₂ (1:4) to collect the first fraction and finally with CH₂Cl₂ to collect the second band. As this fraction was identified as the porphyrin **1**, other following bands were discarded. Fraction 2 was evaporated to dryness and the resulting solid was dried under vacuum and weighed to give 101 mg (0.1 mmol) of **1** (11% yield).

Table S1. Synthesis of 5-(4-hydroxyphenyl)-10,15,20-tris(4-ethylhexyloxyphenyl) porphyrin (**1**) using Adler-Longo, Gonsalves-Pereira, Lindsey and “NaY method”.

Method	Reagents (exc. aldehydes and pyrrole)	Conditions	Concentration (M)	Yield (%)
Adler-Longo	propionic acid	140°C	0.30	8
Gonsalves-Pereira	acetic acid/nitrobenzene	130°C	0.40	8
Lindsey	dichloromethane trifluoroacetic acid DDQ, triethylamine	25°C, then 45 °C	0.03	11
This work (NaY method)	acetic acid/ nitrobenzene NaY zeolite	130°C	0.42	16

3. Porphyrin yield as function of the amount of zeolite NaY used

Ratio was calculated as the quotient between the number of moles of NaY used per sum of moles of pyrrole and aldehydes (reagents). For instance, when the reaction (see above, point **2**) was performed using 1 g NaY (0.08 mmol) per 5 mmol reagents, the ratio was 0.032 *i.e.*, NaY was present in 3.2% of all reagents. When ratio was 0.032, the yield obtained was *ca.* 16 %. The yields obtained using different ratios of NaY per amount of reagents is presented in Table S2 and Fig. S2.

Table S2 Isolated yields of 5-(4-hydroxyphenyl)-10,15,20-tris(4-ethylhexyloxyphenyl) (1) vs amount of NaY used.

NaY ratio	Isolated yield (%)
0	7
0.013	9
0.021	11
0.032	16
0.043	16

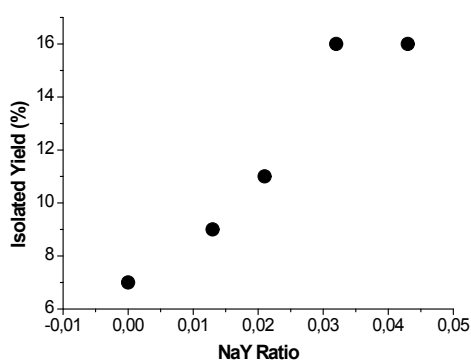


Fig. S2 Isolated yields of TDFPP vs NaY amount. Note: when amount NaY = 0, it represents the isolated yields using the nitrobenzene method.

4. Catalyst recycling

The catalyst zeolite NaY was tested in successive cycles to evaluate the reutilisation process in the synthesis of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin **1**. Using the best determined conditions, after the first cycle, the selected catalyst was collected by filtration and washed with chloroform and tetrahydrofuran, following drying of the solid overnight, at 150 °C under vacuum. The second, third, fourth and fifth and sixth cycles were carried out with the recovered solid and reactivation procedure was followed for each reutilisation.

Table S3 Reutilisation of NaY on the synthesis of porphyrin **1**

Number of cycles in NaY reutilisation	Isolated yields of porphyrin 1 (%)
1	16
2	15
3	16
4	16
5	15

5. Calculation of sustainability E Factors

Density of liquid chemicals used for the calculation of residues (d = density)

Propionic acid d= 990 g/L

Nitrobenzene d= 1200 g/L

Acetic acid d= 1050 g/L

Dichloromethane d= 1330 g/L

Chloroform d= 1489 g/L

Trifluoroacetic acid d= 1489 g/L

n-Hexane d= 655 g/L

Water d= 1000g/L

Triethylamine d= 725.5 g/L

Saturated sodium bicarbonate solution d= 2200 g/L

5.1. Calculation of E Factor for the preparation of 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin **1**, considering the preparation of 10 mmol of end product

Adler-Longo method

$E = (4356 \text{ g propionic acid} + 1771.6 \text{ g dichloromethane} + 7392.6 \text{ g sodium bicarbonate} + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane}) / 11.3 \text{ g porphyrin}$

$E = 3787$

Gonsalves-Pereira method

$E = (1995 \text{ g nitrobenzene} + 1140 \text{ g acetic acid} + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane}) / 11.3 \text{ g porphyrin}$

$E = 2360$

Lindsey method

$E = (29184.4 \text{ g chloroform} + 15.2 \text{ g TFA} + 142.2 \text{ g triethylamine} + 49 \text{ g DDQ} + 2000 \text{ g Al}_2\text{O}_3 + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane})/11.3 \text{ g porphyrin}$
 $E = 3953$

NaY method

$784 \text{ g nitrobenzene} + 640.1 \text{ g acetic acid} + 106.7 \text{ g NaY} + 2000 \text{ g silica} + 9310 \text{ g dichloromethane} + 1965 \text{ g n-hexane})/ 11.3 \text{ g porphyrin}$
 $E = 1310$

6. Price evaluation related to the synthesis of porphyrin 1

Notes: Market prices were calculated on basis of laboratory scale acquisition at Sigma-Aldrich company and available at www.sigmaaldrich.com, excluding NaY, whose prices were calculated from Zeolyst International company. Prices do not reflect reagents and solvents acquisitions on a large scale, but at a laboratory scale, just following Sigma-Aldrich website prices. Amounts of solvents and reagents used for the preparation of 10 mmol product were calculated simply by multiplying the amounts used in preparations according to the experimental above, considering obtained yields. Prices are given in Euro (€) and converted to US dollar (\$), British pound (£) and Chinese Yuan Renminbi (¥) using an online currency converter considering values at the end of May 2016.

Table S4 Price calculation for the preparation of porphyrin **1** using Adler-Longo method.

Solvents/Reagents	CAS Number	Market Prices ^a (€)	Amount used (10 mmol product)	Price (10 mmol product)
Propionic acid	79-09-4	1L = 69 €	4.44 L	306.36 €
4-hydroxybenzaldehyde	123-08-0	50g = 34.7 €	20.34 g	14.12 €
4-ethylhexyloxy-benzaldehyde		100mL = 60 €	50.17 mL	30.06 €
pyrrole	109-97-7	100mL = 64.7 €	45.73 mL	29.59 €
NaHCO ₃	144-55-8	500g = 39.1 €	130 g	10.17 €
Silica gel	112926-00-8	1Kg = 143 €	2 Kg	286 €
n-hexane	110-54-3	2.5L = 84 €	3 L	100.8 €
dichloromethane	75-09-2	2.5L = 104 €	7 L	291.2 €
Total				1068.3 €

Table S5 Price calculation for the preparation of 10 mmol of porphyrin **1** using Gonsalves-Pereira method.

Solvents/Reagents	CAS	Market Prices (€)	Amount used (10 mmol product)	Price (10 mmol product)
acetic acid	64-19-7	1 L = 69 €	1.9 L	131.1 €
nitrobenzene	98-95-3	0.5 L = 73.0 €	0.95 L	138.7 €
4-hydroxybenzaldehyde	123-08-0	50 g = 34.7 €	17.40 g	12.08 €
4-ethylhexyloxy-benzaldehyde	100-52-7	100 mL = 60 €	42.94 mL	25.76 €
pyrrole	109-97-7	100 mL = 64.7 €	39.14 mL	25.32 €
Silica gel	112926-00-8	1 Kg = 143 €	2 Kg	286 €
n-hexane	110-54-3	2.5 L = 84 €	3 L	100.8 €
dichloromethane	75-09-2	2.5 L = 104 €	7 L	291.2 €
Total				1010.96 €

Table S6 Price calculation for the preparation of porphyrin **1** using Lindsey method.

Solvents/Reagents	CAS Number	Market Prices (€)	Amount used (10 mmol product)	Price (10 mmol product)
chloroform	67-66-3	2.5 L = 104 €	19.6 L	815.36 €
4-hydroxybenzaldehyde	123-08-0	50 g = 34.7 €	8.94 g	6.2 €
4-ethylhexyloxy-benzaldehyde	100-52-7	100 mL = 60 €	21.56 mL	12.94 €
pyrrole	109-97-7	100 mL = 64.7 €	19.6 mL	12.68€
Trifluoroacetic acid	76-05-1	100 mL = 58.1 €	10.19 mL	5.92 €
2,3-Dichloro-5,6-dicyano-p-benzoquinone	84-58-2	10 g = 30.2 €	49 g	147.98 €
triethylamine	121-44-8	1 L = 52 €	196 mL	10.19 €
Al ₂ O ₃	1344-28-1	1 Kg = 94 €	2 Kg	188.0 €
Silica gel	112926-00-8	1 Kg = 143 €	2 Kg	286.0 €
n-hexane	110-54-3	2.5 L = 84 €	3 L	100.8 €
dichloromethane	75-09-2	2.5 L = 104 €	10 L	416.0 €
			Total	2002.07 €

Table S7 Price calculation for the preparation porphyrin **1** using “NaY” method.

Solvents/Reagents	CAS	Market Prices (€)	Amount used (10 mmol product)	Price (10 mmol product)
acetic acid	64-19-7	1 L = 69 €	746.7 mL	51.52 €
nitrobenzene	98-95-3	0.5 L = 73.0 €	533.4 mL	38.94 €
4-hydroxybenzaldehyde	123-08-0	50 g = 34.7 €	8.14 g	5.65 €
4-ethylhexyloxy-benzaldehyde	100-52-7	100 mL = 60 €	20.05 mL	12.03 €
pyrrole	109-97-7	100 mL = 64.7 €	18.13 mL	11.73 €
NaY	1318-02-1	0.5 Kg = 220 €	106.7 g	46.95 €
Silica gel	112926-00-8	1 Kg = 143 €	1.75 Kg	250.2 €
n-hexane	110-54-3	2.5 L = 84 €	2,5 L	84 €
dichloromethane	75-09-2	2.5 L = 104 €	6 L	249.6 €
			Total	750.62 €

Table S8 E Factors and prices (€) calculated for the synthesis of porphyrin **1** using several methods

Method	E Factor	Price (10 mmol product)
Adler-Longo	6793	1068.30 €
Gonsalves-Pereira	4233	1010.96 €
Lindsey	7090	2002.07 €
NaY	2350	750.62 €

7. UV-Vis Spectrum of compound 1

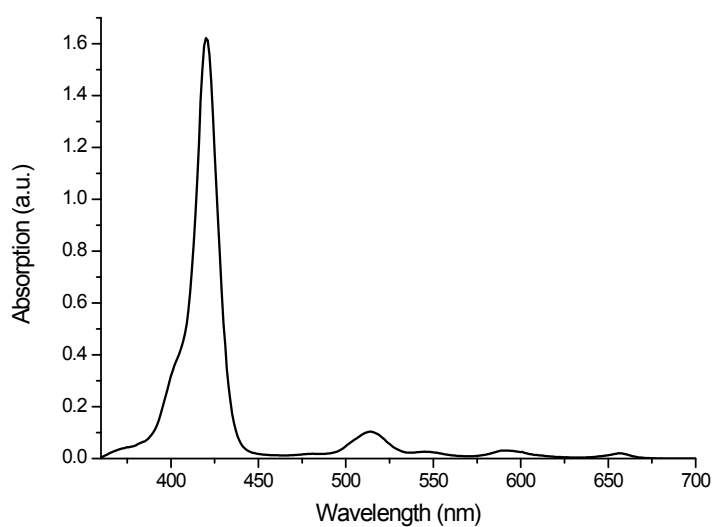
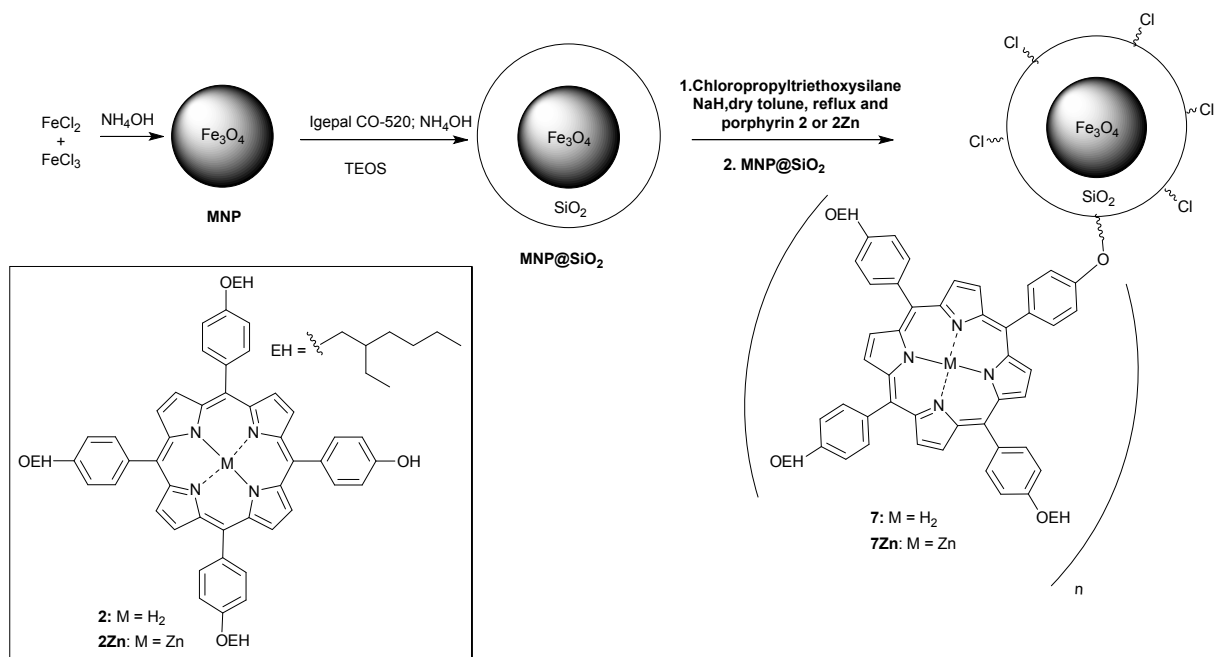


Fig. S3. Absorption spectrum of compound **1**, recorded in toluene.

8. Synthesis of porphyrin based magnetic nanohybrids **2** and **2Zn**

Compound 5-(4-hydroxyphenyl)-10,15,20-tris-(4-(2-ethyl-hexyloxy)phenyl) porphyrinato zinc(II) (**2Zn**) was synthesized, purified and characterized following our recent developments described in literature.^{11,12}



Scheme S2: Preparation and functionalization of magnetic nanoparticles by covalent linking.

8.1. Synthesis of magnetic nanoparticles (MNP)

Magnetite nanoparticles were prepared, according to a previously reported procedure.¹² A mixture of aqueous solutions of 10 mL FeCl₃ (1 mol L⁻¹) and 2.5 mL FeCl₂ (2 mol L⁻¹) in hydrochloric acid (2 mol L⁻¹) was added to 250 mL NH₄OH (1 mol L⁻¹) under mechanical stirring (10000 rpm, Ultra-Turraz T18 Homogenizer, IKA Works). After 30 minutes the MNP were magnetically recovered and washed 3 times with 250 mL of distilled water. Then, the MNP were dispersed again in 250 mL of distilled water and oleic acid (2 mL; 7 mmol) diluted in acetone (5 mL) was added dropwise under vigorous mechanical stirring for 30 min. The resulting precipitate was magnetically separated, washed with acetone (3 times, 25 mL) and redissolved in cyclohexane (15 mL). The final solution was centrifuged (2000 rpm, 30 min) to remove the non-stabilized particles and was stocked under air. After solvent evaporation a stock solution containing 72 mg of MNP/ml of cyclohexane was obtained.

8.2. Coating magnetic nanoparticles with silica (MNP@SiO₂)

The silica coating was obtained by means of reverse microemulsion process.¹³ Igepal CO-520 (178.4 g), magnetite (800 mg; 11.1 mL of stock solution in cyclohexane) and ammonium hydroxide (29%; 38 mL) were dispersed in cyclohexane (2.8 L). Then, tetraethyl orthosilicate (TEOS; 30.8 mL) was added dropwise and the mixture was kept under slow mechanical stirring along 16h. The solid was precipitated with methanol (~250mL), recovered by centrifugation (7000 rpm, 30 min) and washed with ethanol (3 times). Finally, the solid material was dried open air for 24 hours, at room temperature, and then calcined in the oven at 500°C for 2 hours. Typically, 5.40 g of magnetic nanoparticles coated with silica (MNP@SiO₂) were obtained.

8.3. General procedure for anchoring of tetrapyrrolic macrocycles to MNP@SiO₂

The 3-chloropropyltriethoxysilane was mixed with tetrapyrrolic macrocycle and NaH (60% dispersion in mineral oil) in dry toluene and heated at reflux temperature for 24 hours. Then, the MNP@SiO₂ was added and the mixture was refluxed for more 24 hours. The products were magnetically collected and washed several times with acetonitrile, ethyl acetate and dichloromethane to rinse away excess of unreacted porphyrin. The absence of porphyrin or metalloporphyrin in the washing solvents was confirmed by UV-Vis. The final materials **2** and **2Zn** were dried under vacuum for 24 hours.

For **2**: were used 0.125 g (0.123 mmol) of 5-(4-hydroxyphenyl)-10,15,20-tri-(4-(2-ethyl-hexyloxy)phenyl)porphyrin **1**, 3-chloropropyltriethoxysilane (0.24 mmol; 0.5 ml), NaH (60% dispersion in mineral oil) (0.24 mmol; 9.4 mg) and 1g of MNP@SiO₂ in 25 mL of dry toluene.

For **2Zn**: were used 0.200 g (0.185 mmol) of 5-(4-hydroxyphenyl)-10,15,20-tris-(4-(2-ethyl-hexyloxy)phenyl)porphyrinato zinc(II) **1Zn**, 3-chloropropyltriethoxysilane (0.37 mmol; 0.7 ml), NaH (60% dispersion in mineral oil) (0.37 mmol; 14 mg) and 1.5 g of MNP@SiO₂ in 40 mL of dry toluene.

8.4. Functionalization of MNP@SiO_2 with 3-chloropropyltriethoxysilane

MNP@SiO_2 (1 g) was mixed with 3-chloropropyltriethoxysilane (0.5 mL) in dry toluene and the mixture was refluxed for 2 hours. Then, the chlorine-functionalized solid ($\text{MNP@SiO}_2\text{-Cl}$) was washed with toluene, separated by centrifugation, and dried at 100 °C for 20 hours.

9. Characterisation of MNP hybrids

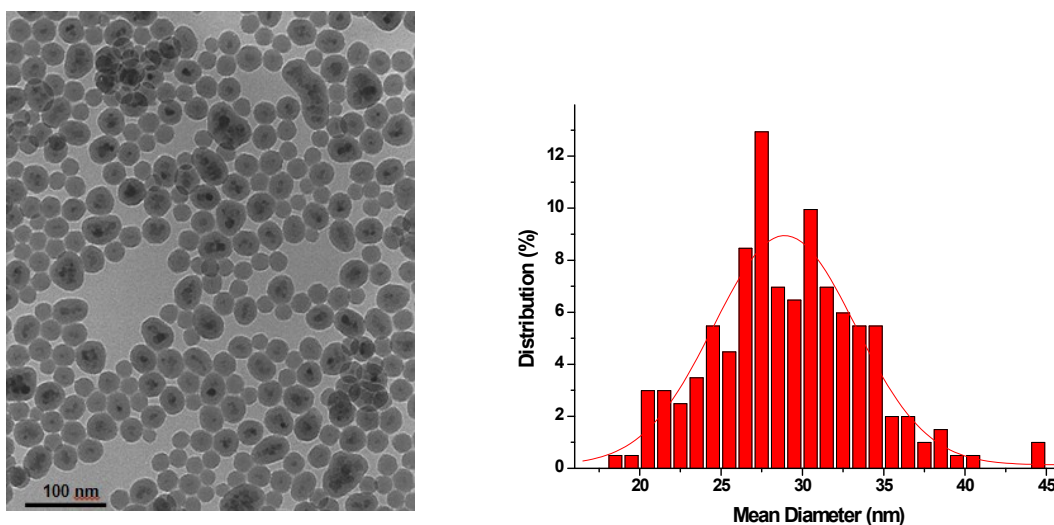


Fig. S4: Transmission electron microscopy (TEM) image of MNP@SiO_2 and particle diameter histogram (D_{TEM} : average diameter) fitted by a Gaussian function.

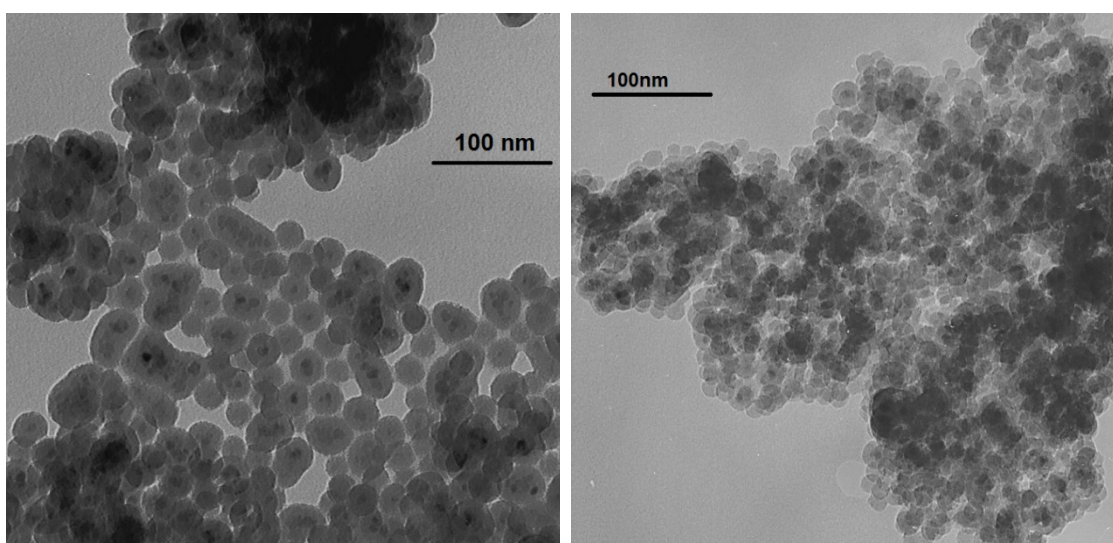


Fig. S5: Transmission electron microscopy (TEM) image of **2** (left) and **2Zn** (right).

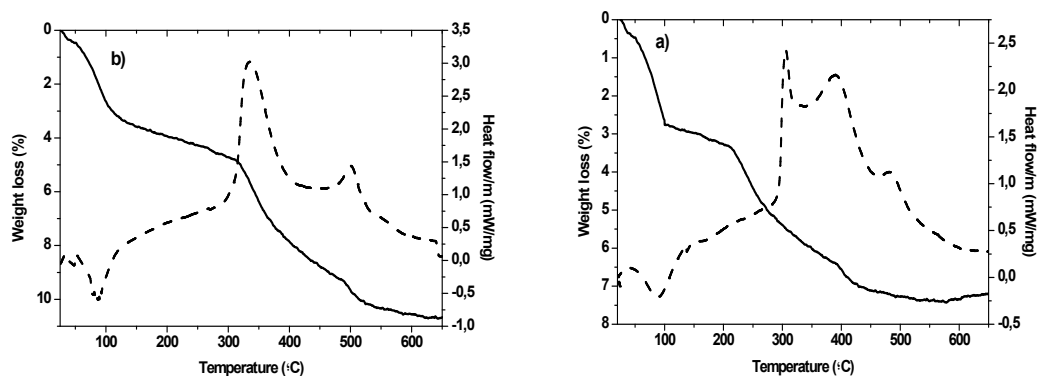


Fig. S6: TG/DSC curves: a) blank of **2** and b) blank **2Zn**.

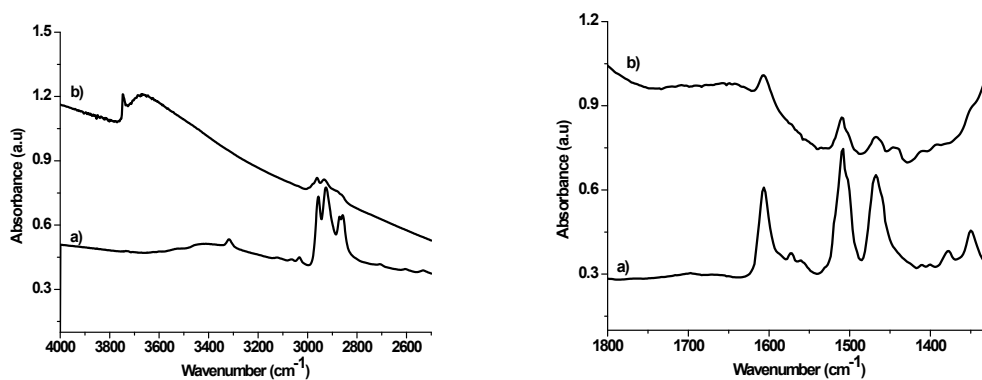


Fig. S7: Infrared spectra of **1** (a), **2** (b) samples in the zones 4000-2500 (left) and 1800-1325 cm^{-1} (right), respectively.

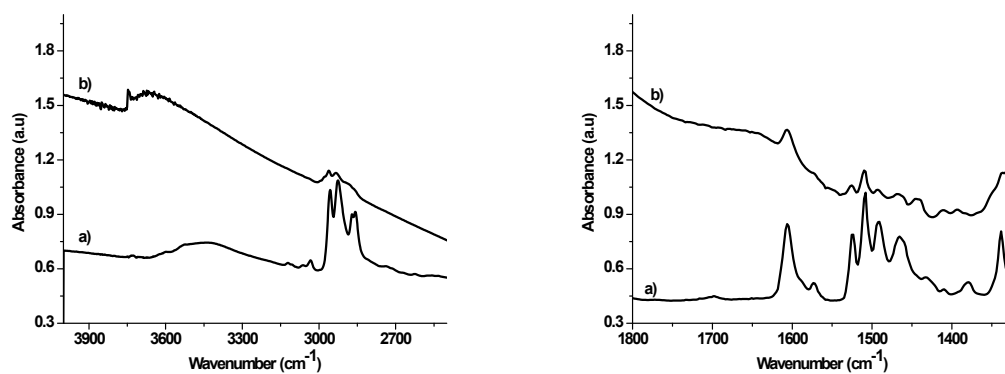


Fig. S8 Infrared spectra of **1Zn** (a), **2Zn** (b) samples in the zones 4000-2500 (left) and 1800-1325 cm^{-1} (right), respectively.

10. Photophysical characterisation of hybrid materials

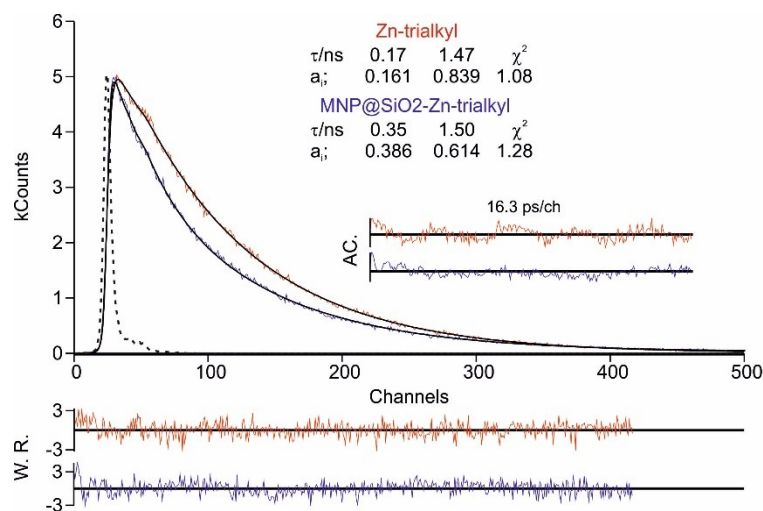


Fig. S9 Room-temperature fluorescence decays for Zn-trialkyl (**1Zn**) and MNP@SiO₂-Zn-trialkyl (**2Zn**) in DMF solution collected with $\lambda_{\text{exc}} = 451$ nm and $\lambda_{\text{em}} = 655$ nm. For a better judgment of the quality of the fit, weighted residuals (W.R.), autocorrelation function (A.C.) and χ^2 values are also presented. The dashed line in the decay is the instrumental response function.

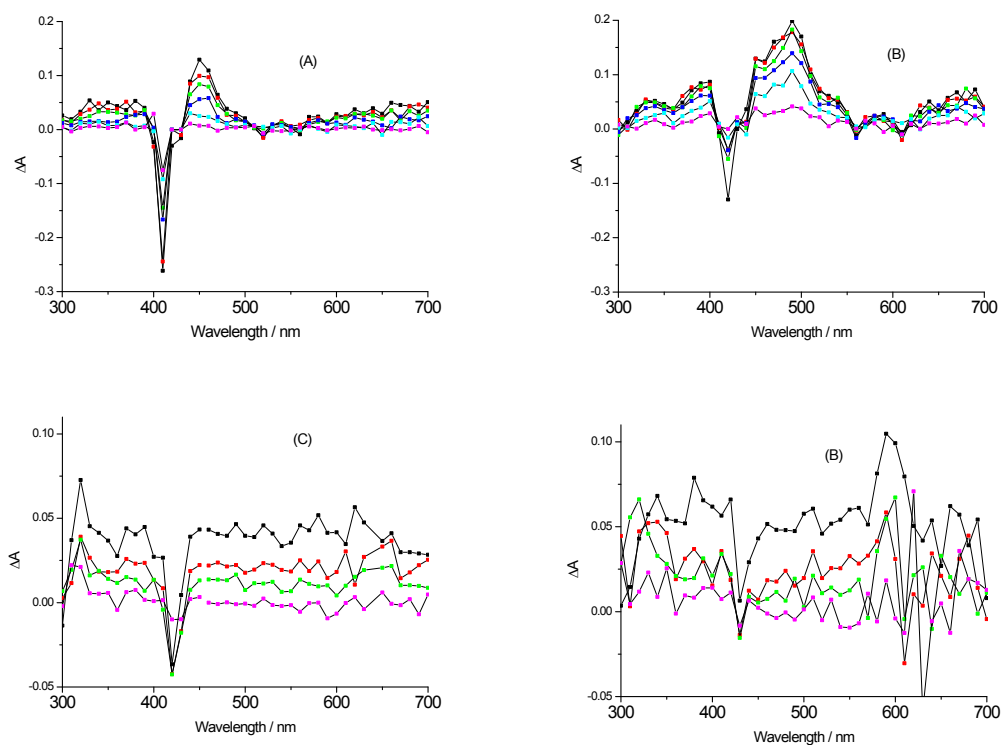


Fig. S10 Transient absorption spectra of (A) **1** (B) **1Zn** (C) **2** and (D) **2Zn** in DMF following excitation with 355 nm. Traces correspond to 240 ns, 400 ns, 560 ns, 800 ns, 1.2 μ s and 2 μ s after laser pulse.

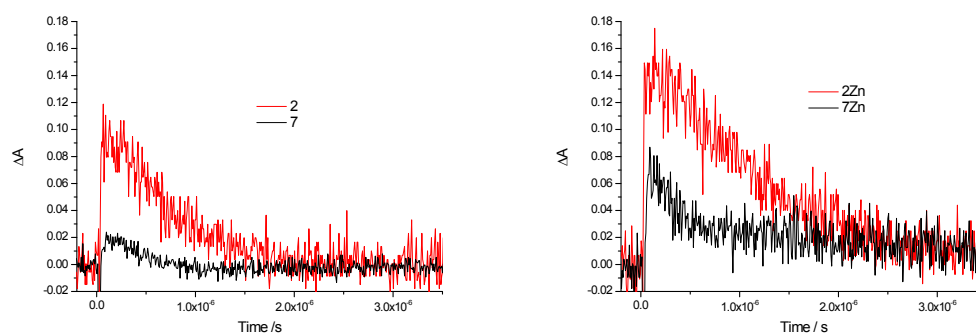


Fig. S11: Transient absorption spectra and triplet decay profile of **1** and **2** (left) and **1Zn** and **2Zn** (right) in DMF (in absence of oxygen) following excitation at 355 nm.

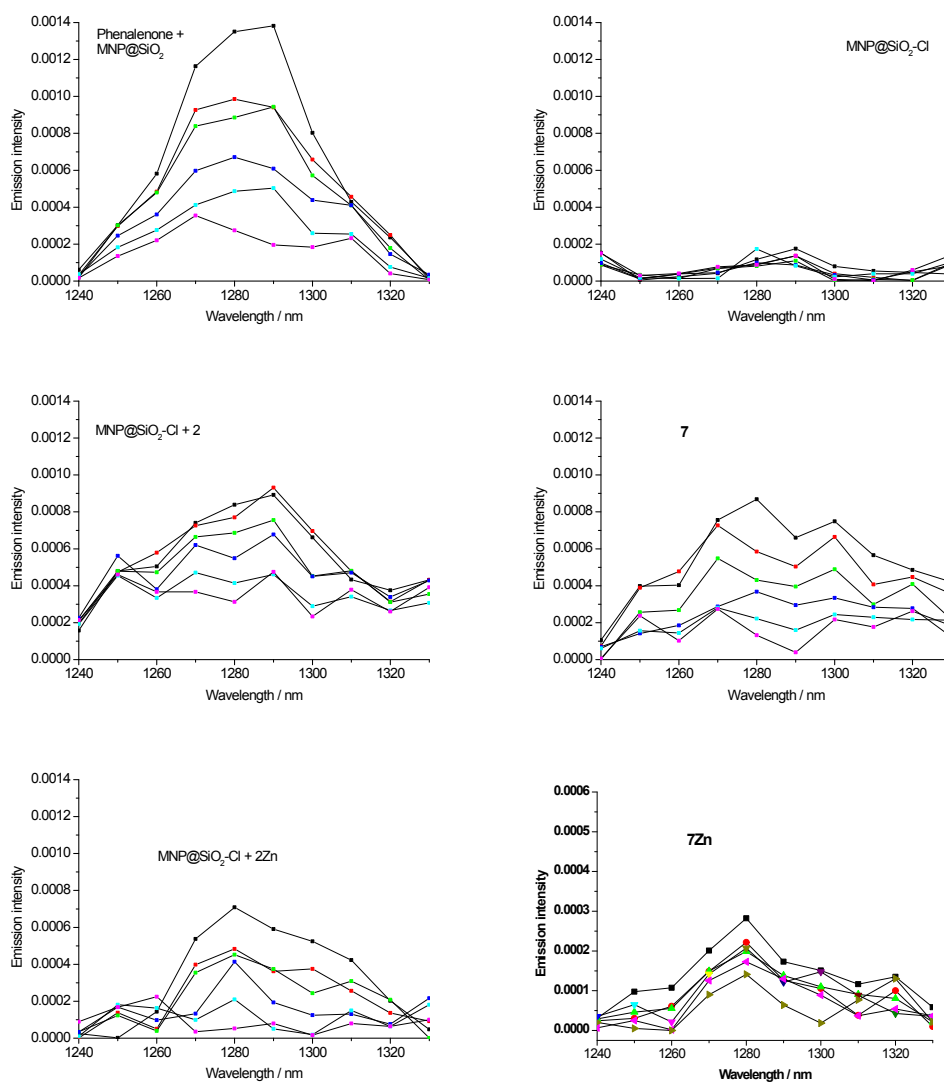


Fig. S12 Singlet oxygen phosphorescence spectra sensitized by **MNP@SiO₂-Cl** + phenalene, **MNP@SiO₂**, **MNP@SiO₂-Cl** + **1**, **2**, **MNP@SiO₂-Cl** + **1Zn**, **2Zn** (spectrum taken at distinct experimental conditions) in DMF following excitation at 355

nm. Traces correspond to phosphorescence 6 μ s, 10 μ s, 14 μ s, 20 μ s, 30 μ s and 50 μ s after laser pulse.

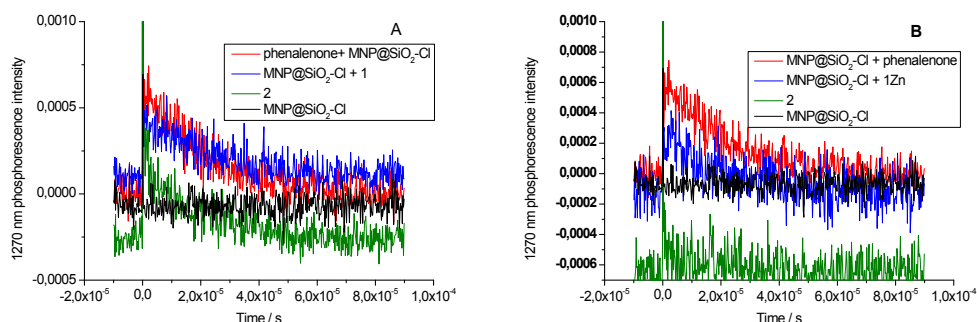


Fig. S13: Phosphorescence decays obtained at 1270 nm following excitation at 355 nm. (A) $\text{MNP@SiO}_2\text{-Cl}$ + phenalenone, $\text{MNP@SiO}_2\text{-Cl}$ + **1**, **2**, and $\text{MNP@SiO}_2\text{-Cl}$; (B) $\text{MNP@SiO}_2\text{-Cl}$ + phenalenone, $\text{MNP@SiO}_2\text{-Cl}$ + **1Zn**, **2Zn** and $\text{MNP@SiO}_2\text{-Cl}$; in DMF. (Laser energy=11; within linearity).

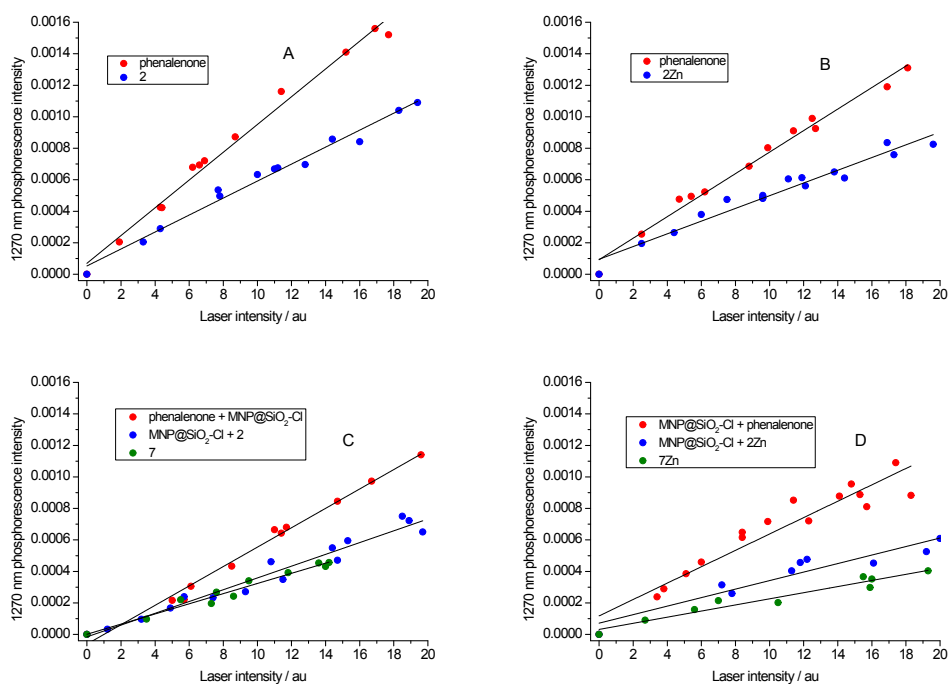


Fig. S14 Relation between phosphorescence intensity at 1270 nm (singlet oxygen) and sensitizer excitation light intensity (355 nm). (A) phenalenone and **1**; (B) phenalenone and **1Zn**; (C) $\text{MNP@SiO}_2\text{-Cl}$ + phenalenone, $\text{MNP@SiO}_2\text{-Cl}$ + **1** and **2**, (D) $\text{MNP@SiO}_2\text{-Cl}$ + phenalenone, $\text{MNP@SiO}_2\text{-Cl}$ + **1Zn** and **2Zn**, in DMF.

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