Supporting information

Coordination bond as a tool for tuning photoconductance in nanostructured hybrid materials made of molecular antennas and metal nanoparticles

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Supplementary experimental details

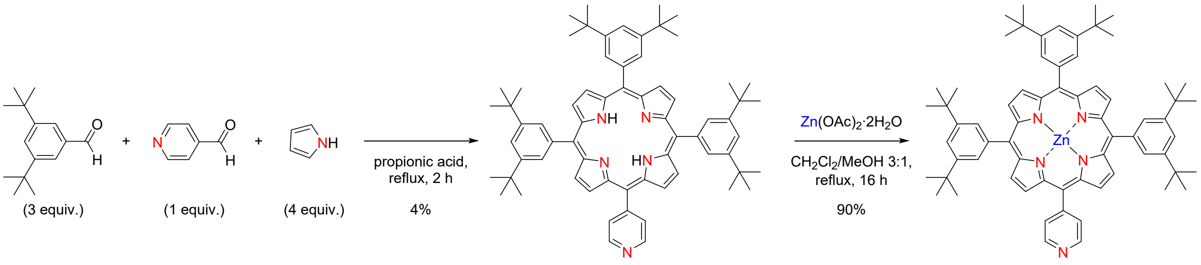
Chemical syntheses

Porphyrins

All chemicals and solvents were purchased from Aldrich, VWR, ABCR, TCI, Acros and Alfa Aesar and used as received, except for pyrrole which was distilled prior to use. Zinc(tetraphenylporphyrin) (**ZTP**) was commercial. 5-(4-Pyridyl)dipyrromethane was synthesized according to a published procedure.[1] All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Column chromatography was carried out on 230-400 mesh silica gel (Aldrich). Thin layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel 60 UV254 plates (Macherey–Nagel) with visualisation effected using ultraviolet irradiation (λ = 254 or 366 nm).

NMR and mass spectra were recorded by the appropriate services of the Toulouse Institute of Chemistry (ICT – UAR 2599). ^{1}H-NMR spectra were recorded on an Avance 300 MHz (probe 5 mm BBO BB-1H Z-GRD) spectrometer. Residual solvent signals were used as internal references; chemical shifts (δ) are reported in ppm; coupling constants (*J*) are given in Hz; the following abbreviations have been used to describe the signals: singlet (s), broad singlet (br. s), doublet (d), triplet (t), multiplet (m). High-resolution mass spectra (HRMS) were performed with a Waters Xevo G2 QTOF spectrometer for electrospray ionization technique.

Synthesis of the A$_3$B-type zinc(II) porphyrin **ZMPy**



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ZMPy

The synthesis of intermediate free-base porphyrin **1** was adapted from a published procedure.[2] In a three-neck round-bottom flask were introduced 3,5-di-*tert*-butylbenzaldehyde (3.5 g, 16 mmol, 3.0 equiv.), 4-pyridinecarboxaldehyde (570 mg, 5.3 mmol, 1.0 equiv.) and pyrrole (1.5 mL, 21.3 mmol, 4.0 equiv.). Propionic acid (60 mL) was added and the mixture was refluxed for 2 h. After cooling to room temperature, the acid was evaporated and the A$_3$B-type free-base porphyrin **1** was isolated by column chromatography (SiO$_2$, CHCl$_3$) as a purple solid in 4% yield (202 mg, 0.21 mmol).

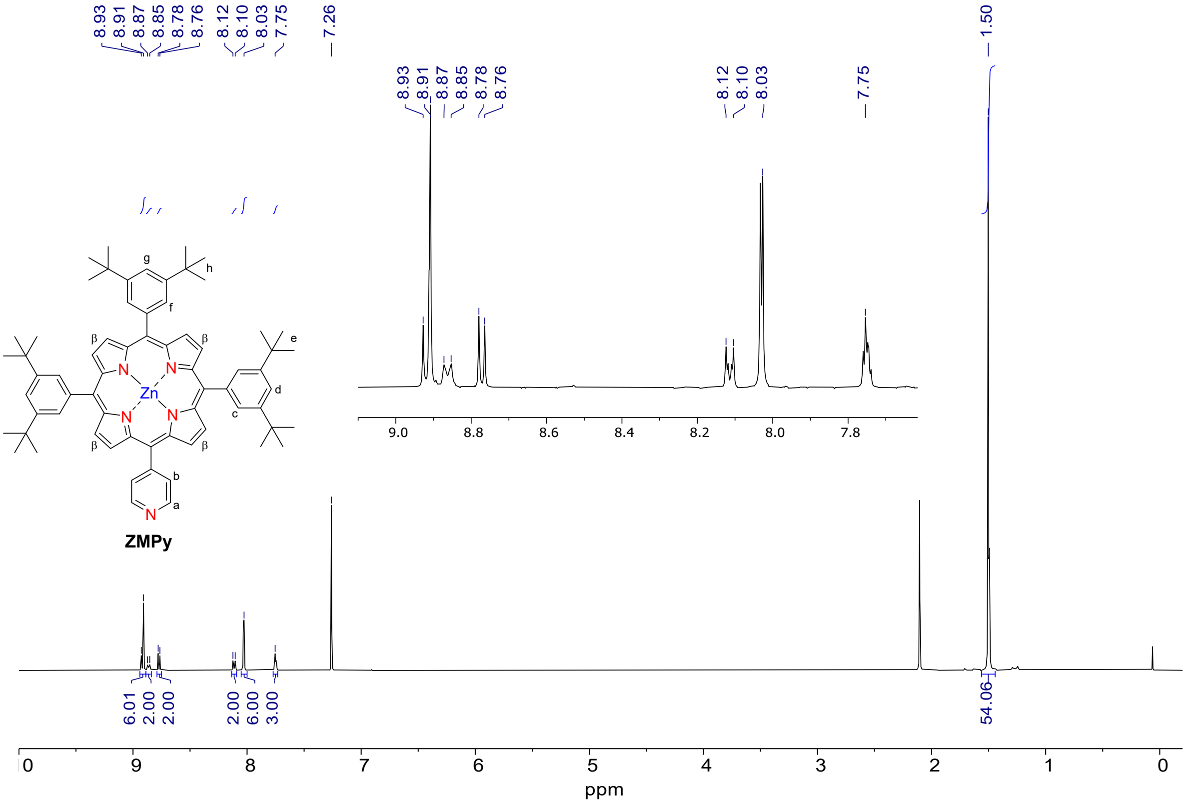
In a dry Schlenk tube under argon, free-base porphyrin **1** (150 mg, 0.16 mmol, 1.0 equiv.) and zinc acetate dihydrate (138 mg, 0.63 mmol, 4.0 equiv.) were dissolved in a mixture of dichloromethane (9 mL) and methanol (3 mL). The solution was refluxed overnight and conversion was monitored by TLC. Volatiles were evaporated and the crude product was dissolved in CH$_2$Cl$_2$, washed with water and dried over magnesium sulphate. The solvent was evaporated and purification by column chromatography

(SiO_2, CH_2Cl_2) gave metalated A_3B-type porphyrin **ZMPy** as a purple solid in 90% yield (144 mg, 0.14 mmol).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.92 (d, ${}^{3}J$ = 4.8 Hz, 2H, H_β), 8.91 (s, 4H, H_β), 8.86 (AA’BB’, ${}^{3}J$ = 5.7 Hz, 2H, H_a), 8.77 (d, ${}^{3}J$ = 4.7 Hz, 2H, H_β), 8.11 (AA’BB’, ${}^{3}J$ = 5.8 Hz, 2H, H_b), 8.03 (d, ${}^{4}J$ = 1.8 Hz, 6H, H_c and H_f), 7.75 (t, ${}^{4}J$ = 1.8 Hz, 2H, H_d), 7.74 (t, ${}^{4}J$ = 1.8 Hz, 1H, H_g), 1.50 (s, 36H, H_e), 1.49 (s, 18H, H_h).

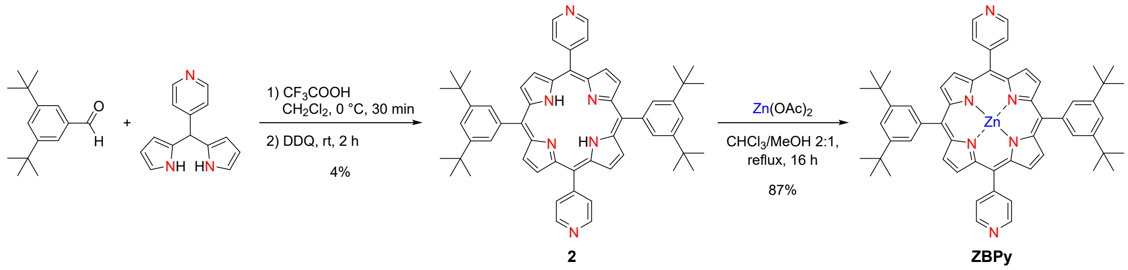
^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 9.00 (AA’BB’, ${}^{3}J$ = 6.0 Hz, 2H, H_a), 8.82 – 8.77 (m, 8H, H_β), 8.21 (AA’BB’, ${}^{3}J$ = 5.9 Hz, 2H, H_b), 8.01 (d, ${}^{4}J$ = 1.8 Hz, 4H, H_c), 7.99 (d, ${}^{4}J$ = 1.9 Hz, 2H, H_f), 7.83 – 7.81 (m, 3H, H_d and H_g), 1.50 (br. s, 54H, H_e and H_h).

HRMS (ESI+): calcd. for $C_{67}H_{76}N_5Zn$ $[M+H]^+$: 1014.5392, found 1014.5363.



^{1}H-NMR spectrum of porphyrin **ZMPy** (300 MHz, $CDCl_3$, 25°C).

Synthesis of the *trans* A_2B_2-type zinc(II) porphyrin **ZBPy**

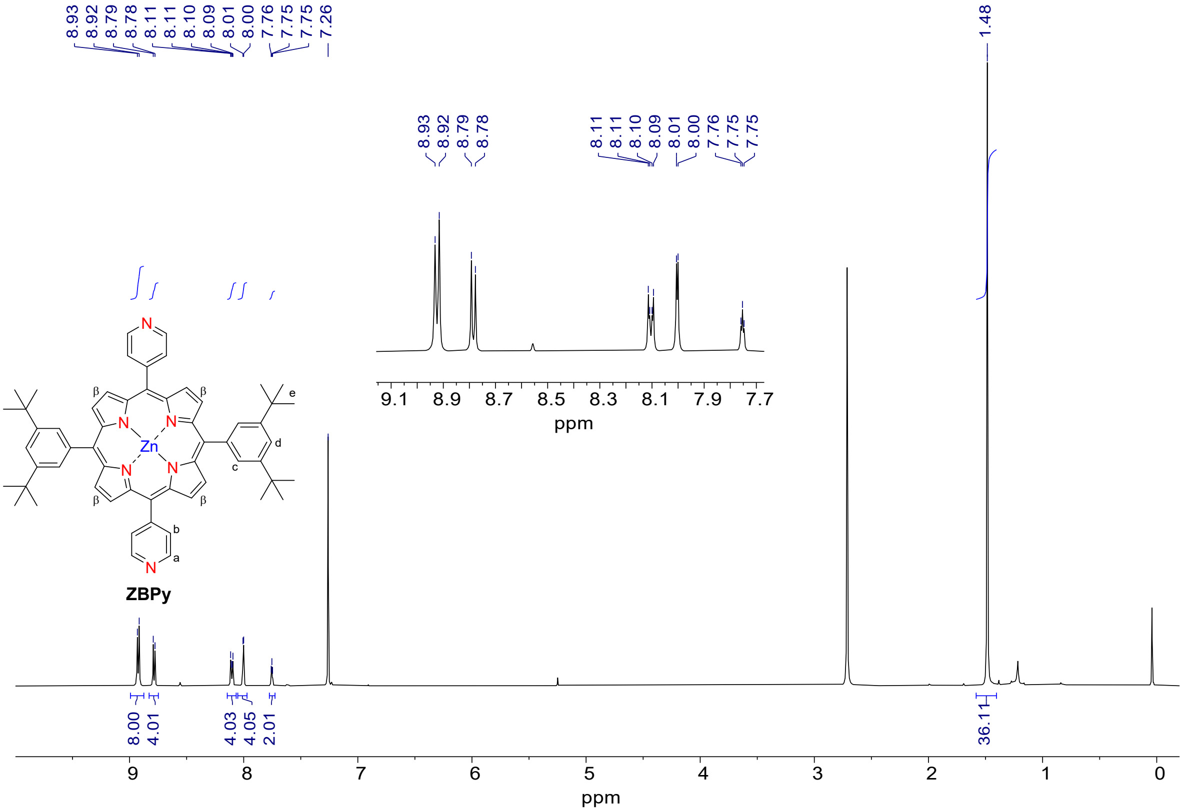


The synthesis of intermediate free-base porphyrin **2** was adapted from a published procedure.[1] In a three-neck round-bottom flask under argon and protected from light, 5-(4-pyridyl)dipyrromethane (1.0 g, 4.5 mmol, 1.0 equiv.) and 3,5-di-*tert*-butylbenzaldehyde (0.98 g, 4.5 mmol, 1.0 equiv.) were dissolved in 600 mL of anhydrous dichloromethane. The solution was stirred in an ice bath and trifluoroacetic acid (26.6 mL, 358 mmol, 80.0 equiv.) was added dropwise. After 30 minutes, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.0 g, 9.0 mmol, 2.0 equiv.) was added and the mixture was stirred at room temperature for another 2h. The organic phase was washed with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous magnesium sulphate and filtered. The solvent was then evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH gradient from 100:0 to 90:10) to give the *trans*-A_2B_2 free-base porphyrin **2** as a purple solid in 4% yield (73 mg, 0.087 mmol).

In a dry Schlenk tube under argon, free base porphyrin **2** (80 mg, 0.095 mmol, 1.0 equiv.) was dissolved in a mixture of chloroform (40 mL) and methanol (20 mL). Then, a large excess of zinc diacetate (175 mg, 0.95 mmol, 10.0 equiv.) was added and the mixture was refluxed overnight. The solution was concentrated to the half and filtered through a silica pad to remove the excess of metal salt. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) and the resulting product was then precipitated from a mixture of CH_2Cl_2 and MeOH to give metalated *trans*-A_2B_2 porphyrin **ZBPy** as a purple solid in 87% yield (75 mg, 0.083 mmol).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.95 – 8.90 (m, 8H, H_β and H_a), 8.78 (d, ^3J = 4.6 Hz, 4H, H_β), 8.10 (AA'BB', ^3J = 5.9 Hz, 4H, H_b), 8.00 (d, ^4J = 1.8 Hz, 4H, H_c), 7.75 (t, ^3J = 1.8 Hz, 2H, H_d), 1.48 (s, 36H, H_e).

HRMS (ESI+): calcd. for $C_{58}H_{59}N_6Zn$ $[M+H]^+$: 903.4093, found 903.4071.



^{1}H-NMR spectrum of porphyrin **ZBPy** (300 MHz, $CDCl_3$, 25°C).

Platinum nanoparticles. The Pt NPs have been synthesized as followed.[3,4] All operations were carried out using Fischer-Porter bottle techniques under argon. A solution of $Pt_2(dba)_3$ (90 mg; 0.165 mmol of Pt) in 20 mL of freshly distilled and deoxygenated THF was pressurized in a Fischer-Porter bottle with 1 bar of CO during 30 minutes at room temperature under vigorous stirring. During this time, the solution color changed from violet to brown (attesting the formation of the NPs). The mixture was evaporated and washed with pentane to eliminate the dba (3 x 20 mL), and to obtain native NPs. The colloid was then redissolved in 20 mL of THF.

Self-assembly. 1 mL of a solution of porphyrins (at 6.10^{-3} $mol.L^{-1}$ in THF) was added to 4 mL of the native NP mixture under vigorous mixing. The precursor concentrations were adapted to obtain the desired equivalent number of porphyrins per introduced Pt. The brown solution was agitated for 2 hours. Drops of the crude solution were deposited on specific substrates for each characterization (see below). The remaining solution was evaporated to dryness and was isolated as dark-brown powder. For each series of measurements, the size of the Pt NPs was determined by TEM imaging.

Structural characterization of nanoparticles and self-assemblies

Transmission Electron Microscopy. Samples for TEM were prepared by deposition of one drop of the crude solution on a carbon covered holey copper grid. TEM analyses were performed at the "centre de microcaractérisation Raimond Castaing" using a JEOL JEM 1400 electron microscope operating at 120 kV. The mean size of the particles was determined by image analysis on a large number of particles (~300) using the ImageJ software. The size of the NPs was found to be 1.4 ± 0.3 nm.

High resolution STEM HAADF tomography was performed at the Advanced Microscopy Laboratory (LMA), Instituto Universitario de Nanociencia de Aragon (INA), Zaragoza, Spain, by a FEI Tecnai field emission gun operated at 300 kV. 3D reconstruction was carried out with FEI tomography acquisition software, Inspect 3D and Amira 3D reconstruction software after the acquisition of 140 images.

Infrared spectroscopy. FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the range 4000-700 cm-1, using a Smart Orbit ATR platform. The sample deposition was performed by drop casting of the crude solution on the germanium crystal of the platform; the measurement was acquired after evaporation of the THF solvent.

Small angle X-ray scattering. SAXS patterns were recorded on a PANalytical Empyrean diffractometer using the Co Kα radiation. Small angle measurements were performed on a microscopy glass, on which the crude solution was drop casted. An advantage of working with particles smaller than 2 nm is that the inter-particle distance is sufficiently small to observe correlation distances between two particles with a regular XRD diffractometer without the need of any dedicated SAXS facilities.

Visible light spectroscopy measurements

UV–Visible absorption measurements. Absorbance spectra were measured in solution by using a Agilent Cary 5000 scanning spectrometer with 2 mm-wide cells.

Photoluminescence (PL) measurements. Continuous wave cw-PL spectra were recorded in solution using a xenon lamp as excitation source. The white light is dispersed by a monochromator and filtered at 500 nm. The PL emission is collected at 90° with respect to the excitation beam, dispersed by a monochromator and recorded using a UV–vis Hamamatsu photomultiplier tube. Acquisition is performed by the FelixGX software and all the spectra were recorded with the same parameters. Stern-Volmer plots were calculated from the full intensity of the absorption band.

Time-resolved photoluminescence (TRPL) experiments. TRPL spectra were performed at room temperature using a mode-locked frequency-doubled Ti-sapphire laser with a 1.5 ps pulse width and a wavelength of 430 nm. A pulsepicker was used to reduce the repetition rate from 80 MHz to 0.4 MHz. The non-resonant TRPL is dispersed by a spectrometer and then recorded using a Hamamatsu S20 photocathode streak camera with an overall temporal resolution of ~50 ns. The excitation average power is kept at ~20 µW @ 0.4 MHz with a laser spot diameter of ~2 mm.

Charge transport measurements

I-V curve measurements. Conductive AFM measurements were performed with an AIST-NT SmartSPM 1000 microscope, equipped with a conductive AFM unit. The samples were prepared by drop casting of one drop of the crude solution on silicon wafers covered by a ~50 nm layer of gold (with a ~5 nm chromium anchoring layer). We used conductive silicon tips covered by platinum (Mikromash HQ-NSC15/Pt). Typical measurements consisted in first performing a topography image of the sample and then going in contact on zones with individual assemblies to measure their *I-V* characteristics. Measurements were performed on several objects per zone and several zones of the substrates. Our system allows current measurements between 10 pA and 100 nA, the amplitude of the current decreasing with the size of the objects.

Data analysis. The *I-V* characteristics were normalized at 2 V. We then averaged the characteristics on 50 curves (error bars on the graphs are 95% confidence intervals). In order to fit the $I \alpha V^{\xi}$ behavior, the linear component determined at low *I* values was subtracted and data were fitted for positive *I* values by the formula $I/I(2V) = (V/2)^{\xi}$. The charging energies were calculated by the formula given in the main text; all the experimental data necessary to calculate the charging energies are available in Table S1.

Measurements under light irradiation. For measurements under light irradiation, a green laser at 532 nm was focalized at the interface between the AFM tip and the substrate, thanks to a HORIBA coupled system, initially conceived for Raman cartography. The laser power was measured at 10 mW at the location of the surface. The variation of current was measured at a voltage of 2 V whereas light was successively switched on and off every 10 s. The variation of current was calculated as the ratio between the current value before and after the light switching, and averaged on 60 on-off switches to estimate the response of the different samples.

Supplementary characterization data

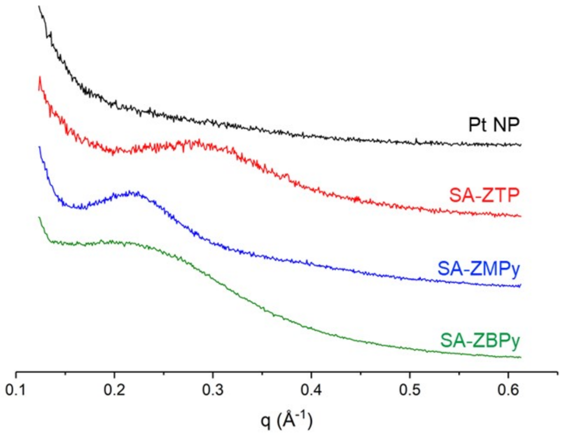


Fig. S1 Small angle X-ray scattering (SAXS) patterns for **Pt NP**, and for the **SA-ZTP**, **SA-ZMPy** and **SA-ZBPy** self-assemblies. The reference **Pt NP** does not show any specific pattern, whereas the self-assemblies show supplementary broad peaks, which correspond to a specific correlation distance between the nanoparticles. Estimation of the correlation distances ($s = 2\pi / q_{max}$): **SA-ZTP**: $q_{max} = 0.29$ Å^{-1}, $s = 2.2$ nm; **SA-ZMPy**: $q_{max} = 0.22$ Å^{-1}, $s = 2.9$ nm; and **SA-ZBPy**: $q_{max} = 0.23$ Å^{-1}, $s = 2.7$ nm.

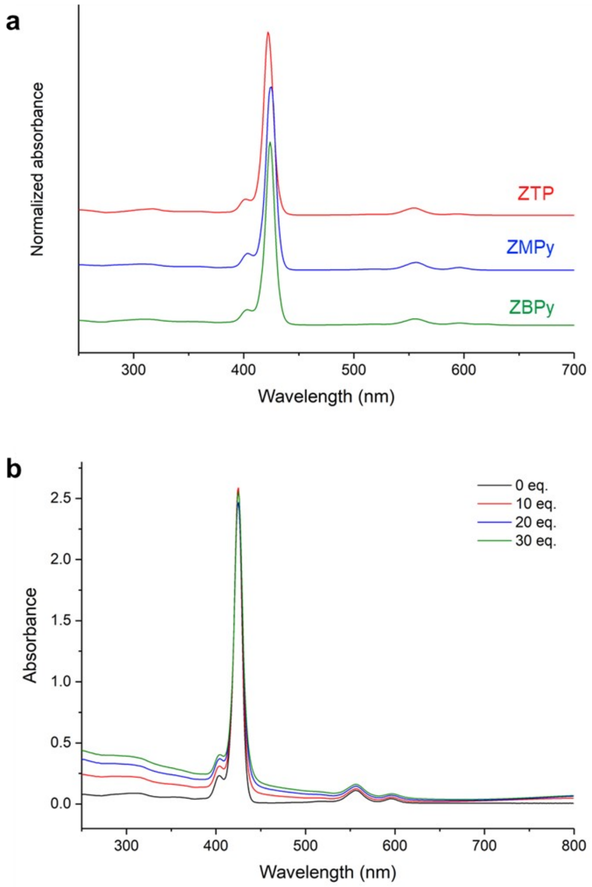


Fig. S2 UV-Vis spectra (a) of the **ZTP**, **ZMPy** and **ZBPy** porphyrins and (b) of the **SA-ZMPy** self-assemblies in the presence of different amounts of **Pt NP**; *eq.* corresponds to the equivalent number of platinum atoms per porphyrin molecule.

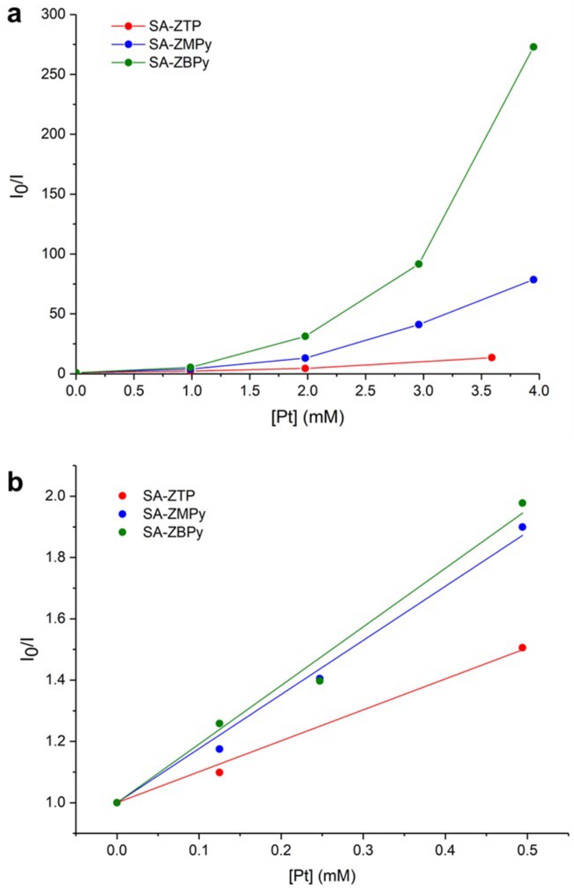


Fig. S3 Stern-Volmer plots of the **SA-ZTP**, **SA-ZMPy** and **SA-ZBPy** self-assemblies with a gradual increase of Pt concentration. (a) general curve; (b) zoom on the small Pt concentrations, with linear fitting. Estimation of the static quenching constants: **SA-ZTP**: $K_a = 0.9 \pm 0.2$ mM^{-1}; **SA-ZMPy**: $K_a = 1.8 \pm 0.1$ mM^{-1}; and **SA-ZBPy**: $K_a = 1.9 \pm 0.1$ mM^{-1}.

	d (± 0.05 nm)	s (± 0.05 nm)	ε_r (± 0.05)	Ec (eV)	ξ
SA-ZTP	1.4	2.2	2.50	0.81 ± 0.07	2.79 ± 0.06
SA-ZMPy	1.4	2.9	2.25	1.39 ± 0.12	4.13 ± 0.07
SA-ZBPy	1.4	2.7	2.30	1.22 ± 0.11	4.23 ± 0.07

Table S1. Nanoparticle size d, inter-particle distance s, dielectric constant of the porphyrins ε_r, charging energy Ec, and power exponent ξ of the self-assemblies considered in the manuscript. d, s and ε_r are determined experimentally; Ec is calculated from these values with the equation given in the main text; and ξ is fitted from the *I-V* curves.

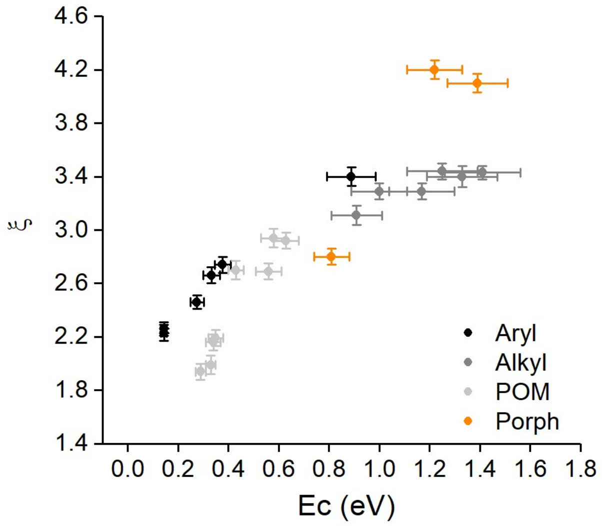


Fig. S4 Evolution of the power exponent ξ (fitted from the I–V characteristics) as a function of the corresponding charging energies. Charging energies are calculated from experiments characterization, using the expression $E_C = e^2/(2\pi\, \varepsilon_r\, \varepsilon_0\, d\, ln(s/(s-d)))$, where e is the charge of the electron, ε_0 the permittivity of vacuum, ε_r the dielectric constant of the medium surrounding the particles, d the particle diameter, and s the center-to-center distance between two particles. Data from this study are in orange and data from previous studies are in black and grey – aryl: thiols with functionalized aromatic groups; alkyl: thiols with alkyl chains of different lengths; POM: thiols with polyoxometalate moieties.[4,5]

References

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