

Electronic Supplementary Information for

Extended π -conjugated ruthenium zinc-porphyrin complexes with enhanced nonlinear-optical properties

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Experimental Section:

Instrumentation

¹H NMR spectra were recorded at room temperature on a Varian Inova400 spectrometer. Chemical shifts are reported in ppm vs. TMS. CDCl₃ was used as solvent and internal standard ($\delta = 7.26$ ppm). MALDI-ToF MS analyses were performed in reflector mode on a Bruker Biglex III spectrometer using a solution of dithranol (20 mg/ml in chloroform) as the matrix. Ultraviolet-Visible (UV-Vis) absorbance spectra were recorded on a Cari 50 Conc Varian spectrometer at ambient temperature. The microwave assisted reactions were carried out using a Biotage: Initiator + microwave system **with an optical fiber optic probe to measure the reaction temperature inside the vial**. Dynamic light scattering (DLS) experiments were performed on a Malvern Zetasizer Nano S equipped with a He-Ne (633 nm, 4 mW) laser and an Avalanche photodiode detector at an angle of 173°.

Materials

Zn-Por^{S1} and Ru(DMSO)₄Cl₂^{S2-S4} were synthesised and purified according to literature procedures. ¹H-NMR was used for checking the ratio between *cis*- and *trans*- Ru(DMSO)₄Cl₂. All other chemicals were purchased from commercial sources, Sigma-Aldrich, Acros and Fluka in their higher degree of purity and used as received. Chloroform was purified by distillation from calcium hydride and stored under argon. The toluene used was of spectroscopic grade. Deuterated chloroform for NMR analyses was provided with TMS as a 0 ppm reference. Column chromatography was performed using ACROS silica gel (40 – 60 μ m) and BioRad BioBeads SZ-1 were used for size-exclusion chromatography.

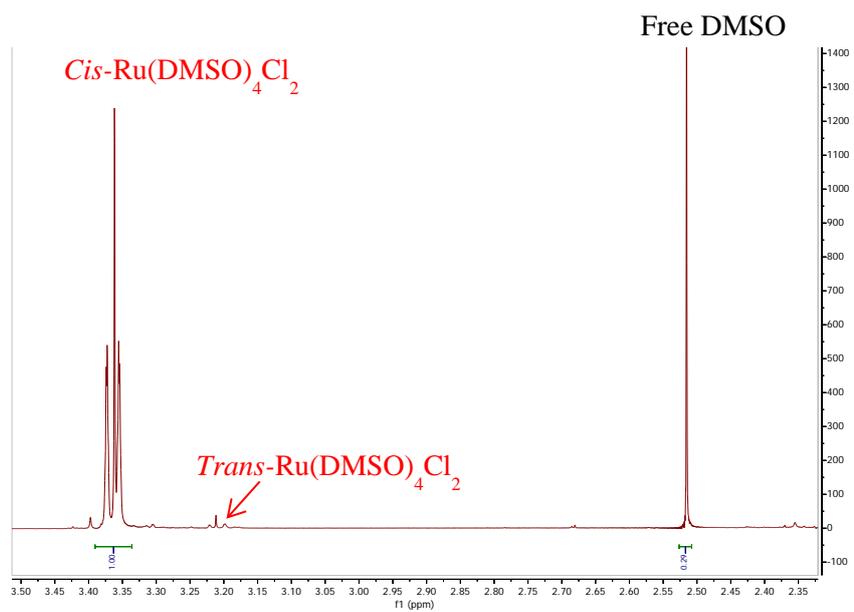


Fig. S1. $^1\text{H-NMR}$ spectrum of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$.

Synthesis of Ru-dimer

ZnP (50 mg, 0.035 mmol) and Ru(DMSO)₄Cl₂ (8.5 mg, 0.0175 mmol) were dissolved in 20 ml of DMF and stirred at 130 °C in argon atmosphere **in the absence of light to prevent the formation of *trans*-Ru-dimer as by-product**. After 3 hours, NH₄SCN (13.3 mg, 0.175 mmol) was added and the mixture was stirred at 130 °C for 2 hours. After cooling and evaporation of the solvent, the residue was purified by column chromatography on silica (eluent: dichloromethane/methanol 20/1, v/v) and size exclusion column chromatography (eluent: toluene), yielding 38 % of Ru-dimer as a dark brown solid. ¹H-NMR (400 MHz, CDCl₃, rt): δ = 10.16 – 10.13 (m, 1H), 9.97 (dd, J = 8.2 Hz, 1.3 Hz, 1H), 9.58 – 9.54 (m, 1H), 9.15 (m, 1H), 9.05 – 8.95 (m, 12H), 8.88 – 8.84 (m, 3H), 8.79 – 8.76 (m, 1H), 8.34 (dd, J = 8.2 Hz, 5.3 Hz, 1H), 8.15 – 7.97 (m, 24H), 7.96 – 7.93 (m, 2H), 7.85 – 7.77 (m, 5H), 1.6 – 1.25 (m, 144H). UV-Vis (CHCl₃): λ = 322.53 nm, 439.72 nm, 532.24 nm. MALDI-TOF: *m/z* = 3083 [M]⁺, 3025 [M-1SCN]⁺.

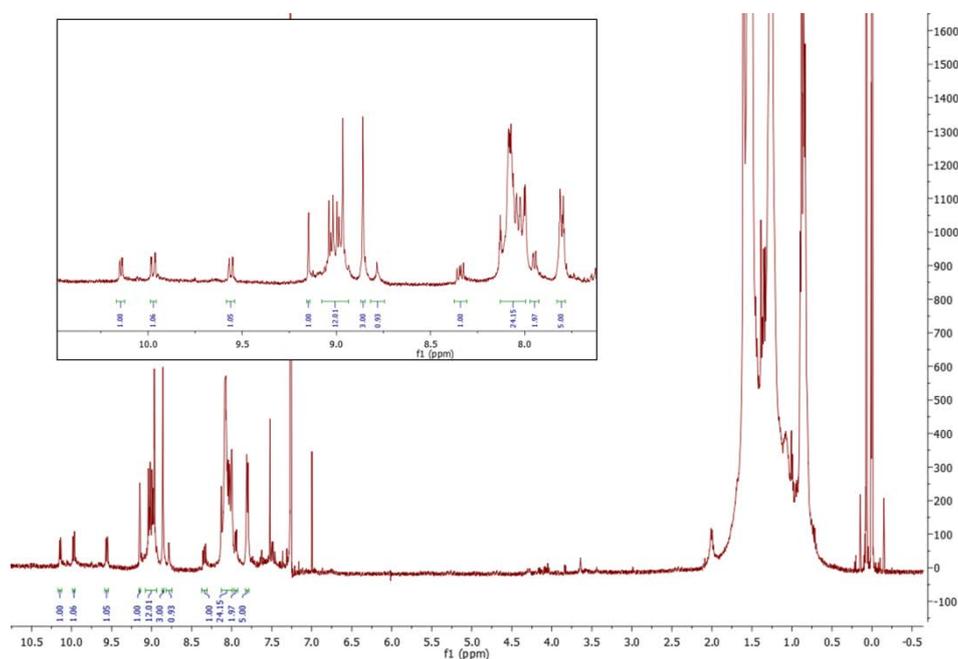


Fig. S2. ¹H-NMR spectrum of the Ru-dimer.

Synthesis of *cis*-Ru-dimer carried out in ambient sunlight resulted in a mixture of *cis* and *trans*-Ru-dimer as by-product which was not possible to remove during the purification steps.

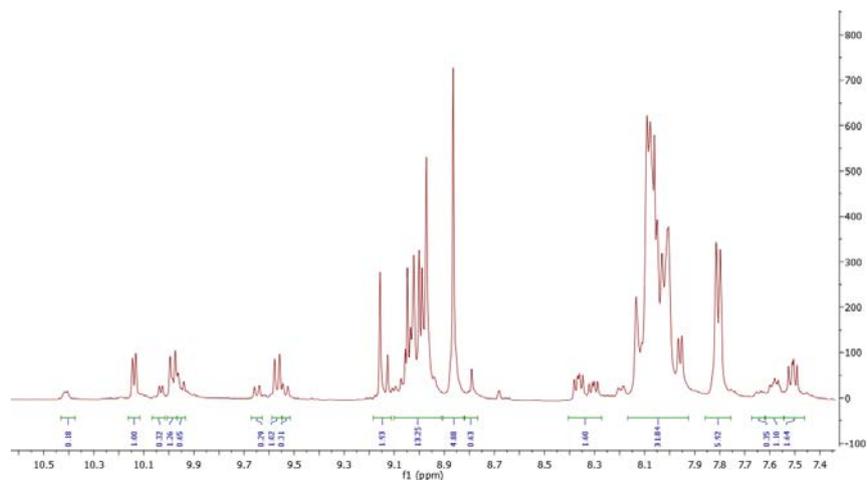


Fig. S3. ¹H-NMR spectrum of the mixture of *cis*- and *trans*-Ru-dimer.

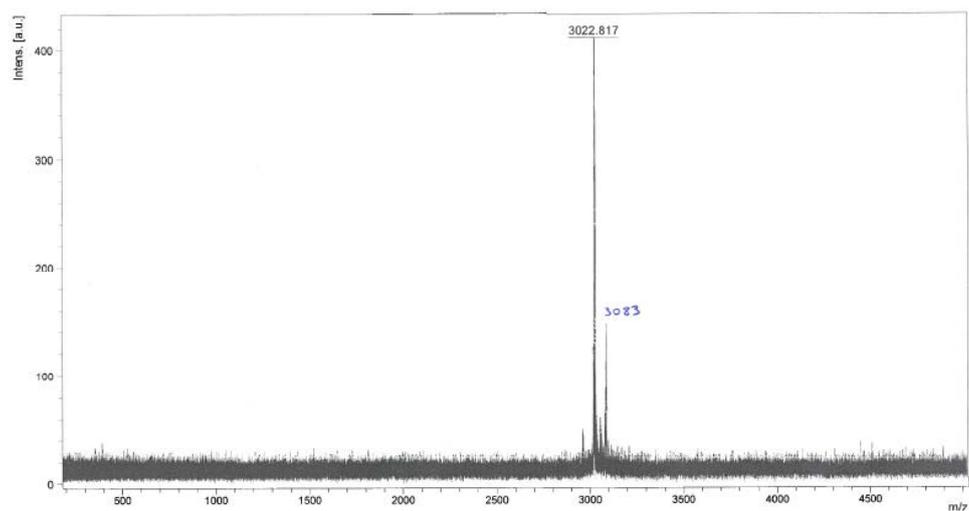


Fig. S4. MALDI-ToF MS spectrum of the Ru-dimer.

Synthesis of Ru-trimer

ZnP (9 mg, 0.0063 mmol), Ru(DMSO)₄Cl₂ (1 mg, 0.0021 mmol), and AgNO₃ (0.5 mg, 0.008 mmol) in 4 ml of DMF were reacted for 2 hours **in a closed vessel** under microwave irradiation (microwave set-up: 300 W, 160 °C, 2h, **with a pressure of 1 atm.**). After cooling and evaporation of the solvent, the residue was purified by size exclusion column chromatography (eluent: toluene). The complex was precipitated as a brown solid from a solution in ethanol by the addition of saturated aqueous NH₄PF₆. The solid was collected by filtration, washed with cold water, and dried under vacuum. Yield: 45 %. ¹H-RMN (400 MHz, CDCl₃, rt): δ = 10.22 – 10.15 (m, 1H), 9.90 – 9.82 (m, 2H), 9.70 – 9.64 (m, 1H), 9.33 – 9.21 (m, 3H), 9.07 – 9.06 (m, 1H), 9.03 – 9.02 (m, 2H), 9.02 – 8.93 (m, 8H), 8.87 – 8.80 (m, 7H), 8.77 – 8.72 (m, 2H), 8.15 – 7.90 (m, 42H), 7.83 – 7.77 (m, 9H), 1.70 – 1.20 (m, 216 H). UV-Vis (CHCl₃): λ = 325.41 nm, 441.80 nm, 540.46 nm. Maldi-TOF: m/z = 4684 [M]⁺, 4539 [M-1PF₆]⁺, 4394 [M-2PF₆]⁺.

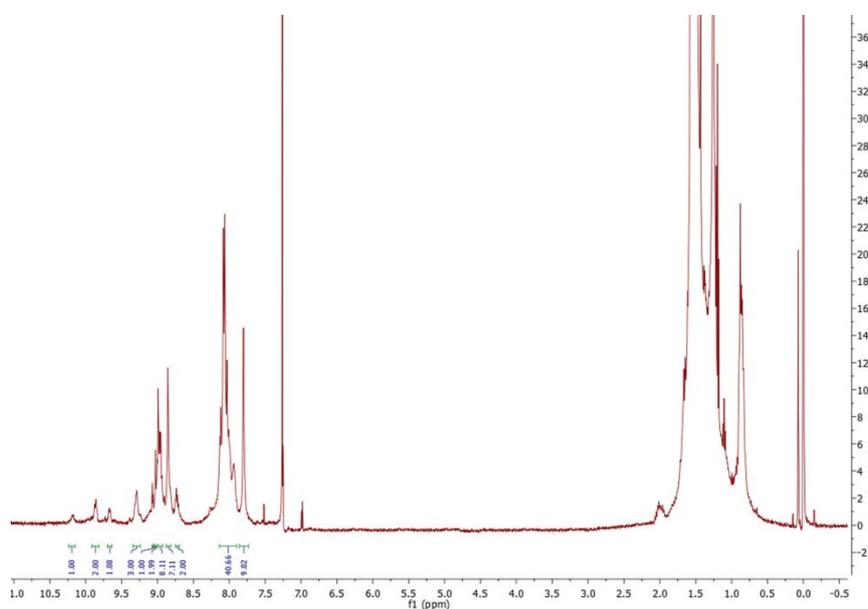


Fig. S5. ¹H-NMR spectrum of the Ru-trimer.

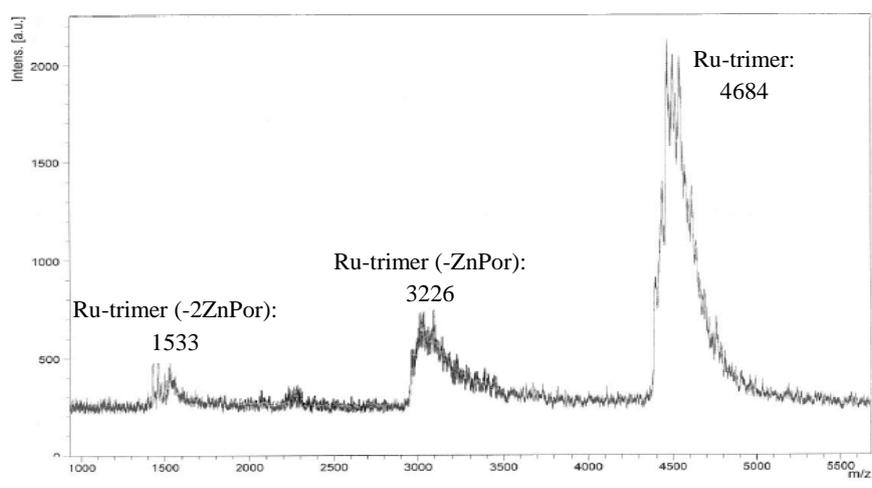


Fig. S6. MALDI-ToF MS spectrum of the Ru-trimer.

Table S1: DLS measurements on the Ru-dimer and Ru-trimer in toluene and CHCl₃ at different concentrations. Three measurements were performed for each sample to make an average.

	Concentration (M)	Toluene	CHCl ₃
		Z-average (nm)	Z-average (nm)
Rudimer	10 ⁻³	3.5	3.8
	5 × 10 ⁻⁴	3.6	
Rutrimer	10 ⁻³	4.5	4.8
	10 ⁻⁴	4.0	

The role of two-photon absorption

Two-photon absorption is known to modify the (otherwise purely antisymmetric) closed-aperture z-scan curve shapes. In order to take this effect into account, a series of open-aperture z-scan measurements were performed under experimental conditions similar to those of the closed-aperture measurements. Fig. S5 illustrates the typical data obtained for the closed-aperture (a) and open-aperture (b) z-scan. Note the difference in laser power used in these experiments. It is seen that the relative size of the effect (deviation of normalised transmission from unity) in the open-aperture measurements is about one order of magnitude smaller than that seen in the closed-aperture z-scan with the aperture transmission S of about 10%. Taking into account the different laser power, we can conclude that the effects from two-photon absorption, which are seen in the open-aperture setup, contribute to about 1% to the total signal observed in the closed-aperture experiments and thus can be excluded from consideration as being negligible.

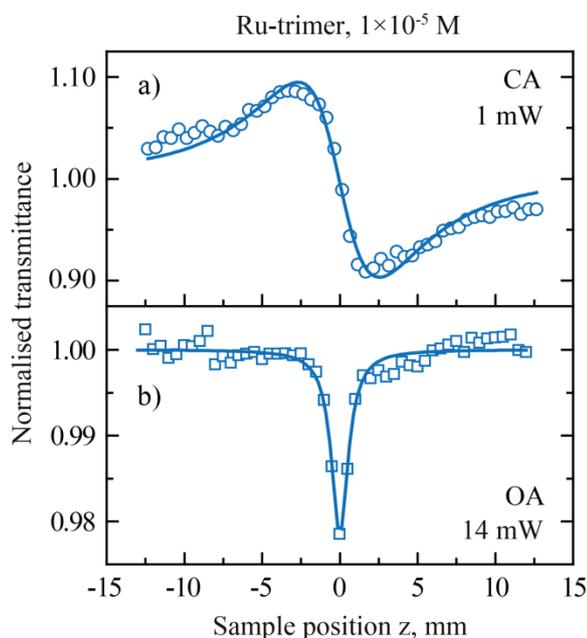


Fig. S7: a) Closed-aperture and b) open-aperture z-scan data for the Ru-trimer at 10^{-5} M concentration, laser wavelength 800 nm. The solid lines in both panels are fits to the experimental data according to Ref.[5].

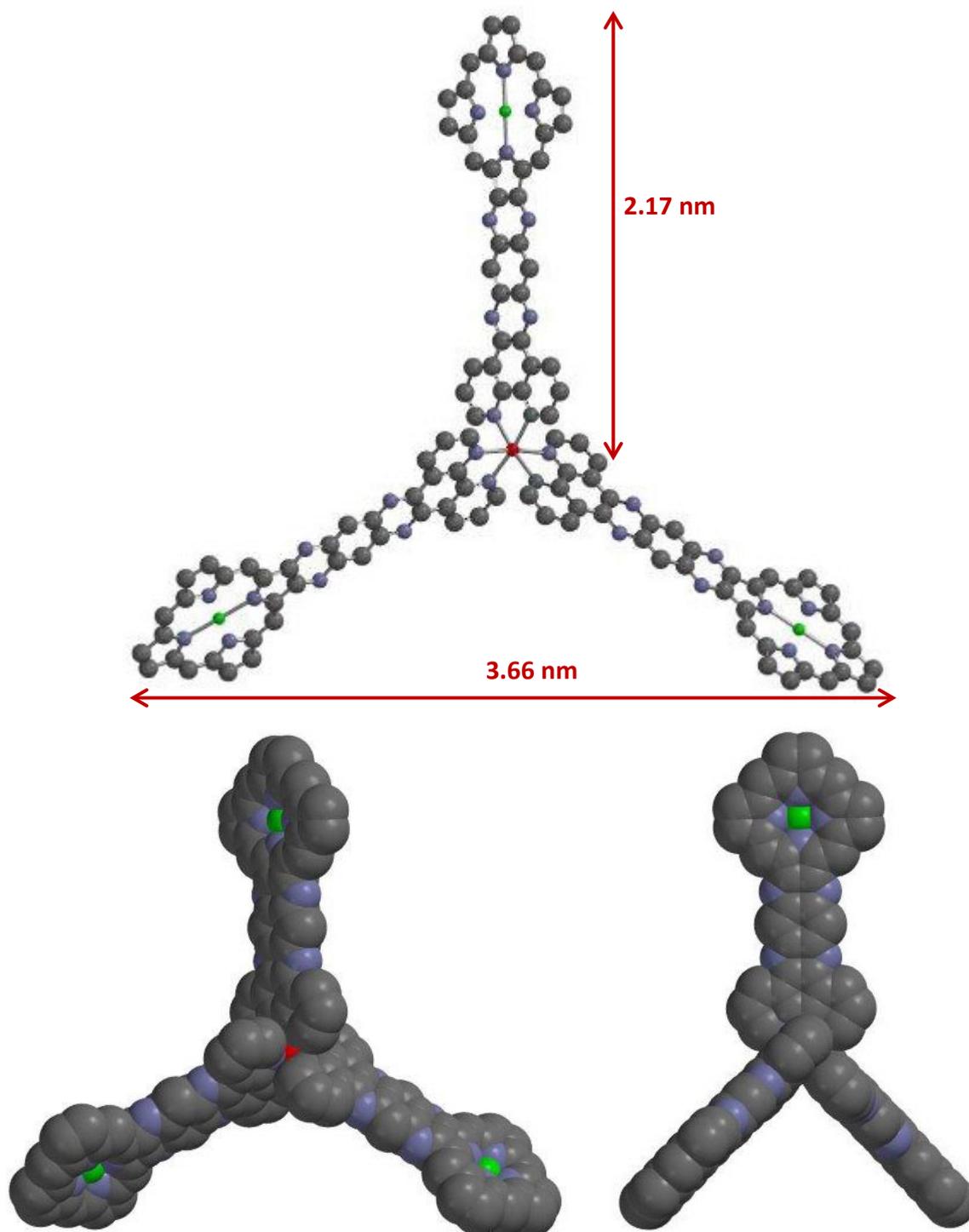


Fig. S8: Computer generated model of Ru-trimer by Spartan. Top: front view; bottom: side view. The *t*-Butyl groups have been replaced by hydrogen atoms to reduce the calculation time. The geometry optimization was obtained from SCF calculations using a 3-21G(*) basis set. The estimated diameter of this molecule is 3.66 nm. Hydrogen atoms are omitted for clarity.

Supporting references

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