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

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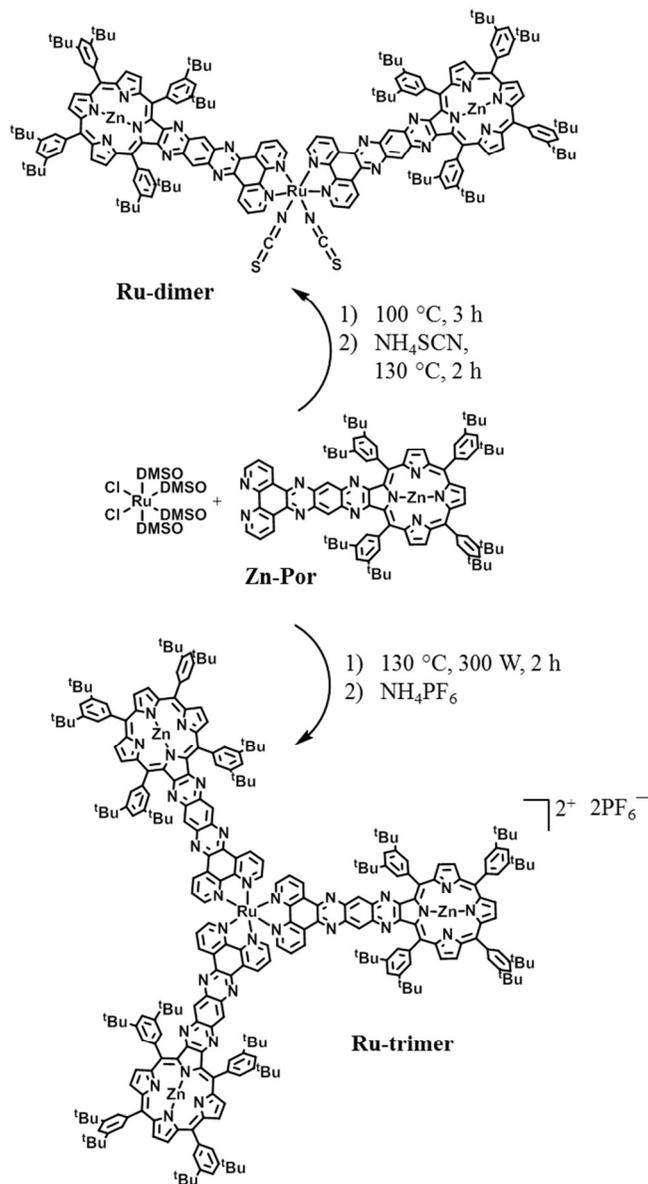
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Zinc porphyrin dimers and trimers, in which the porphyrins are connected via a ruthenium metal core, exhibit large third-order nonlinear optical absorption coefficients and refractive indices. These properties are a result of the presence of the multiple porphyrins, which lead to an extension of the π -conjugated system and the octupolar effect.

The design and synthesis of new materials possessing large nonlinear optical (NLO) responses is an area of increased interest in the domain of photonics.¹ For such applications, π -conjugated organic molecules have received considerable attention because of their high NLO hyperpolarisabilities, fast responses and structural diversities.^{2,3} Organic third-order NLO materials typically require delocalised π -conjugated molecular components, which are substituted by electron donating (D) and accepting (A) groups with an extended π -conjugation.⁴ Porphyrins represent a class of attractive compounds for optoelectronic applications, because they possess an extended π -conjugated system that can be tuned by changing the nature of its substituents.^{2,5} In this context, non-symmetrically substituted porphyrins have more potential for NLO applications than symmetrical ones because of the higher hyperpolarisability of the framework of the former compounds.⁶ Compared to these dipolar molecules, octupolar molecules have shown to display an increase in NLO response. Octupolar molecules have been designed mainly using Fe(II), Ru(II) Zn(II), Cu(I), and Ag(I)-based metal complexes, and organic π -conjugated building blocks.⁷⁻¹⁰ It has recently been reported that Ru(II) complexes with substituted nitrogen-containing heterocyclic ligands exhibit strong third-order NLO responses.^{8,10,11} These complexes might be employed as a scaffold for novel compounds with extended π -conjugated systems. Here, we report the synthesis of a series of three-dimensional (3D) octupolar π -delocalised ruthenium complexes equipped with Zn porphyrin (Zn-Por) pendant groups, which exhibit large third-order nonlinear optical effects.

The advantages of combining porphyrins and ruthenium complexes are manifold.¹¹⁻¹⁴ Depending on their structure, both building blocks can be optimised to be chemically stable with rich redox chemistry and strong optical absorption, over a wide spectral range, which makes them efficient light-harvesting systems. The octahedral ruthenium complex is able to organise the porphyrin ligands in a 3D geometry, resulting in a long π -pathway for high degrees of electron delocalisation which facilitates their NLO responses.^{7,9,10} The conjugated system is enlarged by using quinoxaline-phenanthroline-type ligands, which act as aromatic bridges to the porphyrins. The incorporation of these ligands allows a higher electron mobility in comparison to the Ru core and also a stable connection between the ruthenium core and the porphyrins.⁹

We have synthesised two Ru-Zn-porphyrin complexes by reacting *cis*-Ru(DMSO)₄Cl₂ with Zn-Por in dimethylformamide (DMF), as shown in Scheme 1. The Ru-dimer was readily obtained by heating the reactants in a 1:2 ratio at 100 °C for 3 h, followed by the addition of NH₄SCN at 130 °C over a period of 2 h, with a final yield of 38%. However, even long reaction times (up to 72 h) at high temperatures (130 °C) failed to afford any Ru-trimer. Only with the assistance of microwave irradiation (300 W),¹⁵ the Ru-trimer was finally synthesised by mixing the reactants in a 1:3 ratio in DMF at 130 °C for 2 h. After removing the solvent by rotary evaporation, the obtained solid residue was redissolved in ethanol. The product was then precipitated by adding a saturated aqueous solution of NH₄PF₆, filtered and dried under vacuum (yield: 45%). It has previously been reported that *cis*-Ru(DMSO)₄Cl₂ and *trans*-Ru(DMSO)₄Cl₂ are in equilibrium in solution, with the *trans*-isomer mostly being formed under irradiation and the *cis*-isomer by heating to high temperatures.¹⁶ In this case, the reaction conditions for the synthesis of Ru-dimer were chosen such that only the *cis*-isomer was obtained (ESI,†, Fig. S1-S3).



Scheme 1. Synthesis and molecular structures of the ruthenium (II) zinc porphyrin complexes.

The compounds were characterised by ¹H NMR, mass spectrometry (ESI,†, Fig. S1-S6), and UV/Vis absorption spectroscopy (Fig. 1). The signals of the protons in the ¹H NMR spectrum of Ru-trimer are broad compared to those of the Ru-dimer. Nevertheless, the integration values of the assignable signals were in good agreement with the expected values. Mass spectrometric analysis of the complexes by MALDI-TOF showed the expected molecular peak associated with the correct isotopic pattern. For the Ru-trimer, the laser power of the MALDI-TOF instrument had to be increased and therefore signals corresponding to the loss of one and two porphyrin units were also observed. A loss of one thiocyanate group was detected in the case of the Ru-dimer.

The UV/vis absorption spectra of the Ru-dimer and Ru-trimer (Fig. 1) showed the characteristic Soret bands of the

porphyrin units at 440 nm and 443 nm, respectively, both being red-shifted with respect to the Soret band of Zn-Por (436 nm). These shifts suggest the presence of electronic interactions between the porphyrin moieties and the Ru(II) core. Furthermore, the Soret band of the Ru-trimer was broadened, which indicates the presence of stronger electronic interactions.¹¹ Upon excitation at the Soret band, the fluorescence emission of both complexes was totally quenched, which is in line with the known energy transfer processes between the Ru core and the Zn-Por moieties.¹⁷

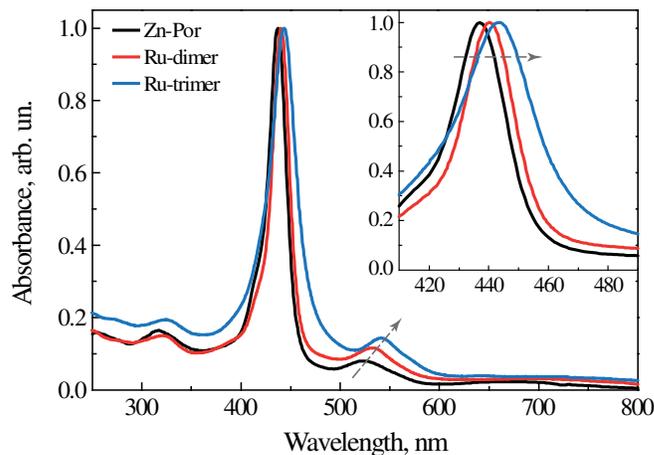


Fig. 1 Normalized absorption spectra of Zn-Por, Ru-dimer and Ru-trimer solutions in CHCl₃.

The third-order optical nonlinearities of the prepared complexes were measured by a closed-aperture (CA) z-scan technique using a home-built setup with a femtosecond laser as the light source (pulse width 100 fs, repetition rate 82 MHz). The method is based on measuring the nonlinear refractive index n_2 in $n = n_0 + \Delta n = n_0 + n_2 I$; details are described elsewhere.¹⁸ A 1 mm-thick quartz cuvette containing a chloroform solution of the sample was moved along the beam direction by means of a motorised stage. The transmitted radiation was cut off by an on-axis aperture (transmittance $S = 0.1$) and registered by a photodiode. Two-photon absorption effects were taken into account by performing the open-aperture (OA) z-scan measurements.¹⁸ It was found that the contribution of two-photon absorption to the CA z-scan results did not exceed 1-2% (see ESI,† for details), which is why we excluded this from further considerations. The system was calibrated using CS₂ as a reference.¹⁹ Fig. 2 shows typical dependences of the normalised transmission on the position of the sample with respect to the focal point of the lens (corresponding to $z = 0$) for an incident laser power of 2 mW.

The data were normalised over the transmission values far away from the focus (at large $|z|$). The clear antisymmetric shape of the curves indicates prominent self-defocusing of the light in all the studied samples. The experimental data were fitted with the following equation:²⁰

$$T(z) \approx 1 - \frac{4\Delta\Phi_0\left(\frac{z}{z_0}\right)}{\left(\frac{z^2}{z_0^2} + 9\right)\left(\frac{z^2}{z_0^2} + 1\right)} \quad (1)$$

in which z_0 is the Rayleigh length, $z_0 = ka_0^2/2$, k is the wavenumber of the light and a_0 is the beam waist. The fitting parameter $\Delta\Phi_0$ is the phase in the case of on-axis transmission (small S), which is related to the nonlinear refractive index in the following way: $\Delta\Phi_0 = k\Delta n L_{\text{eff}}$, where L_{eff} is the effective thickness of the nonlinear media, $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, and L is the physical thickness. Due to the low absorption of the samples, L was used instead of L_{eff} , which introduced no significant experimental error. For each sample, several measurements were carried out at different light intensities, and the slope of the intensity dependence was used in the aforementioned calculations. Various concentrations of both Ru-trimer and Ru-dimer complexes were used (Fig. 2) in order to negate the effects of higher-order nonlinearities, which can modify the shape of the normalised transmission dependence.

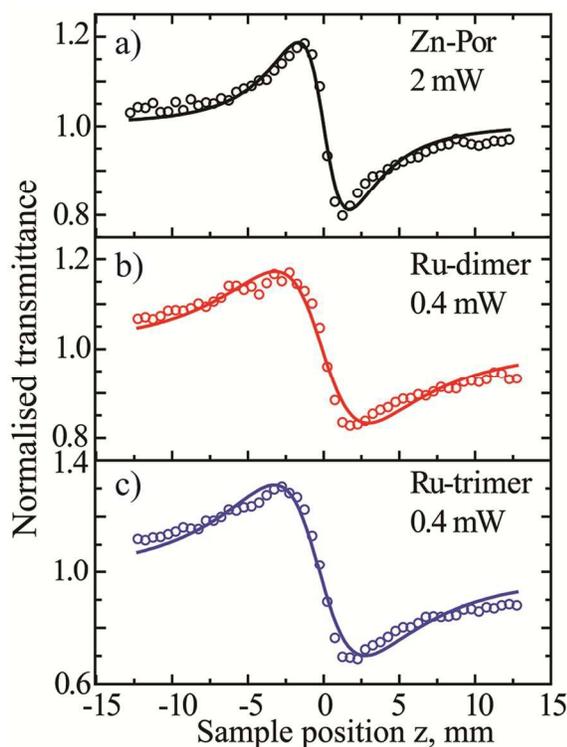


Fig. 2 CA z-scan curves of normalised transmittance of Zn-Por, Ru-dimer, and Ru-trimer, respectively, as a function of the sample position with respect to the focus of the lens ($z = 0$). The solid lines show the fits to the experimental data, see Eq. (1). Solutions: 10^{-4} M in chloroform; laser wavelength: 800 nm. Note that the power of the laser needs to be decreased (to 0.4 mW) when measuring Ru-dimer and Ru-trimer in order to obtain proper curves with suitable amplitudes due to the enhanced NLO effects.

When using the laser at 800 nm, the n_2 values were deduced to be -4.8×10^{-11} cm²/W and -9.2×10^{-11} cm²/W for the Ru-dimer and Ru-trimer, respectively, in contrast to that of -6.4×10^{-12} cm²/W for the Zn-Por, at a concentration as low as 10^{-4} M in CHCl₃. The observed nonlinear refraction indices are among the highest values of the porphyrins studied so far.⁵ When compared to Zn-Por, enhancements of the nonlinear refraction

index of approximately one order of magnitude are observed for both Ru-complexes (Table 1). A “cooperative effect” of incorporating Zn-Por into the Ru-dimer and Ru-trimer is clearly seen in Table 1, where the normalised n_2 values of the three samples are presented for the concentration of 1×10^{-4} M. At the same time, the nonlinear absorption coefficients β measured at the same concentrations were found to be 3.7 and 5.9×10^{-9} cm/W for the Ru-dimer and Ru-trimer, respectively (ESI,† Fig. S7).

Table 1 Analysis of the nonlinear coefficients (n_2) in terms of the number of porphyrins and normalised by the n_2 of Zn-Por.^a

Compound	n_2 (cm ² /W)	n_2 normalized by porphyrin (cm ² /W)	n_2 normalized by n_2 of Zn-Por
Zn-Por	-6.4×10^{-12}	-6.4×10^{-12}	1
Ru-dimer	-4.8×10^{-11}	-2.4×10^{-11}	7.5
Ru-trimer	-9.2×10^{-11}	-3.1×10^{-11}	14.3

^aSolutions: 10^{-4} M in chloroform. Laser wavelength: 800 nm.

It is worth noticing that Zn-Por itself displays a relative high third-order nonlinear optical susceptibility because of the presence of the quinoxaline-phenanthroline ligand, which is an electron acceptor group that increases the hyperpolarisability of the porphyrin.⁹ However, it is found that the specific nonlinear refractive indices of the porphyrins (normalised by the number of porphyrins: 2 or 3 in the case of the Ru-dimer and Ru-trimer, respectively) are increased by a factor of 4 in the case of the Ru complexes as compared to Zn-Por. We can conclude that the higher n_2 value in the case of the ruthenium complexes is not only a result of the presence of two or three Zn-Por moieties instead of a single one, but rather related to the extended π -conjugation which leads to a strong induced optical hyperpolarisability.

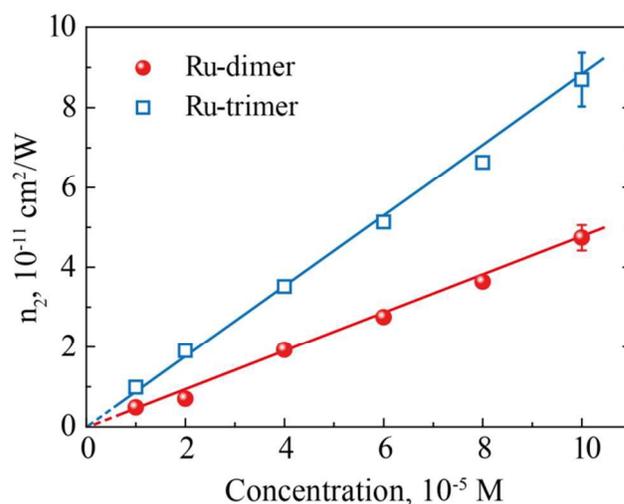


Fig. 3 Concentration dependence of the nonlinear refractive index (absolute value) of the Ru-dimer (red circles) and the Ru-trimer (blue open squares) in chloroform. The solid lines are linear fits to the experimental data.

The effects of possible aggregation of the complexes on the nonlinear optical properties were studied by the concentration dependence of the nonlinear refraction indices (Fig. 3). It was found that the n_2 of Ru-trimer and Ru-dimer scales linearly with the concentration, which indicates the absence of aggregation or other strong supramolecular interactions between both Ru-dimer and Ru-trimer complexes. These findings are in line with dynamic light scattering (DLS) analyses of solutions of the Ru-dimer and Ru-trimer, which showed that within the concentration range of 10^{-4} M – 10^{-3} M the average sizes of these complexes are about 4 nm and 5 nm in toluene and dichloromethane, respectively (ESI,† Table S1). These sizes are in agreement with estimated values of the diameters of the complexes, obtained by Molecular Modelling studies (ESI,† Fig. S8).

In conclusion, we have synthesised two new complexes based on Zn-porphyrins that are attached to a ruthenium (II) core and investigated their third-order nonlinear optical properties. The nonlinear refractive coefficient of these ruthenium complexes was found to be in the order of 10^{-11} cm²/W at a concentration as low as 10^{-4} M. This large optical nonlinearity is in line with an extended electron delocalisation over the ruthenium central core and the porphyrins. Ongoing studies are directed at the investigation of the relationship between the supramolecular architectures of the extended π -conjugated porphyrin complexes and their nonlinear optical responses.

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Notes and references

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†The nonlinear-optical response of the quartz cuvette itself and the solvent (CHCl₃) was measured to be less than 0.1% of that of all the samples.

Electronic Supplementary Information (ESI) available: Experimental Section, synthesis and characterisations of the complexes; additional figures. See DOI: 10.1039/c000000x/

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