Appendix A. Supplementary data

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A Zinc(II) Tetraphenylporphyrin Peripherally Functionalized with Redox-Active "*trans*-[(η^5-C_5H_5)Fe(η^5-C_5H_4)C≡C](κ^2-dppe)$_2$Ru(C≡C)-" Substituents: Linear Electrochromism and Third-Order Nonlinear Optics

Including:

1. Labelling Scheme in NMR Spectral Assignments and ^{13}C NMR Spectrum

^{13}C{^{1}H} NMR (δ, 125 MHz, CD_2Cl_2): 150.6 (s, $C_{\alpha\text{-pyrrolic}}$), 137.7 (m, 2 $C_{ipso/dppe}$), 134.8 (m, 2 $CH_{ortho/Ph/dppe}$), 134.6 (s, $CH_{Ar}[C_b]$), 132.2 (s, $C_{\beta\text{-pyrrolic}}$), 130.1 (s, $C_{Ar}[C_d]$), 129.1 & 129.0 (s, $CH_{para/Ph/dppe}$), 128.5 (s, $CH_{Ar}[C_c]$), 127.5 & 127.3 (s, $CH_{meta/Ph/dppe}$), 123.0 (s, C_{meso}), 116.9 (s, RuC≡C[C_e]), 112.6 (s, RuC≡C[C_h]), 78.3 (s, $C_{CpC\equiv C}$), 70.2 (s, $CH_{CpC\equiv C}$), 70.0 (s, C_5H_5), 67.5 (s, $CH_{CpC\equiv C}$), 33.1 (m, $CH_{2/dppe}$); 2 RuC≡C [$C_{f\text{-}g}$] and 1 $C_{Ar}[C_a]$ not observed, possibly overlapped. Proposed attribution based on HMBC and HMQC-type polarization transfer.

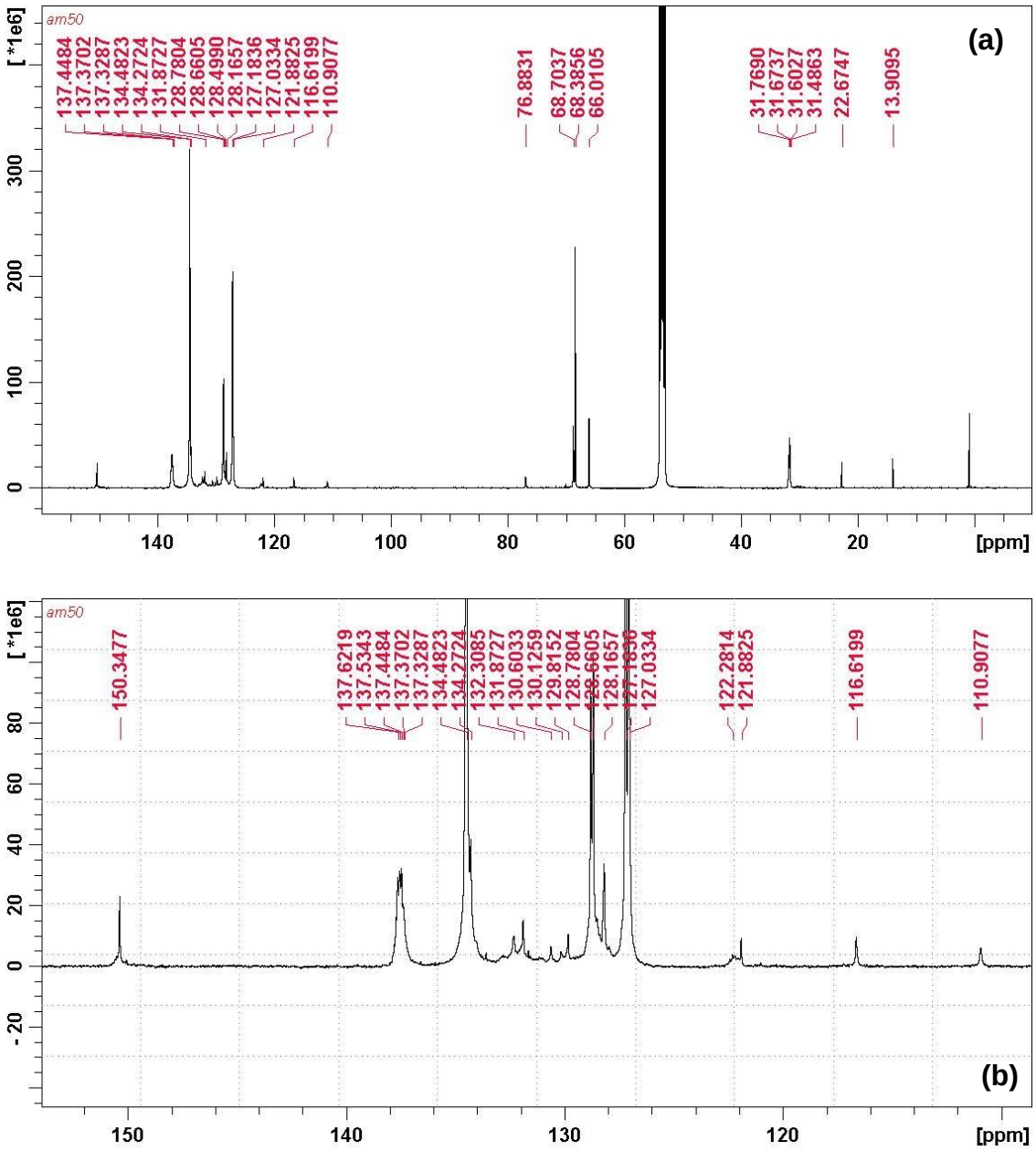

Fig. S1. (a) Full ^{13}C NMR spectrum of **4** in CD_2Cl_2 at 300 K. (b) Expanded part of spectrum (a).

2. Cyclic Voltammogram of 4

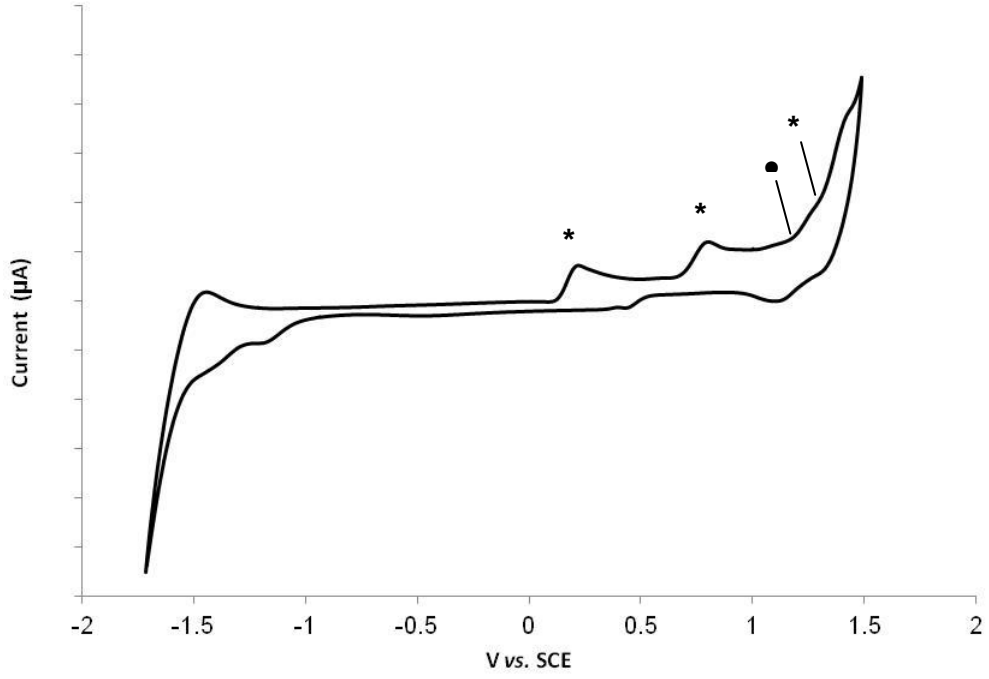

Fig. S2. Cyclic voltammogram of compounds **4** in the -1.8 V/1.6 V range, showing the Fe- and Ru-centered redox processes and another intense redox event (*). The second oxidation of the ZnTPP core is indicated by a dot (●). Conditions: CH_2Cl_2, 20 °C, [*n*-Bu_4N][PF_6] 0.1 M, scan rate: 0.1 V/s. Potential values given *vs.* SCE.

3. ^{1}H NMR Spectrum of 2[PF_6]$_4$

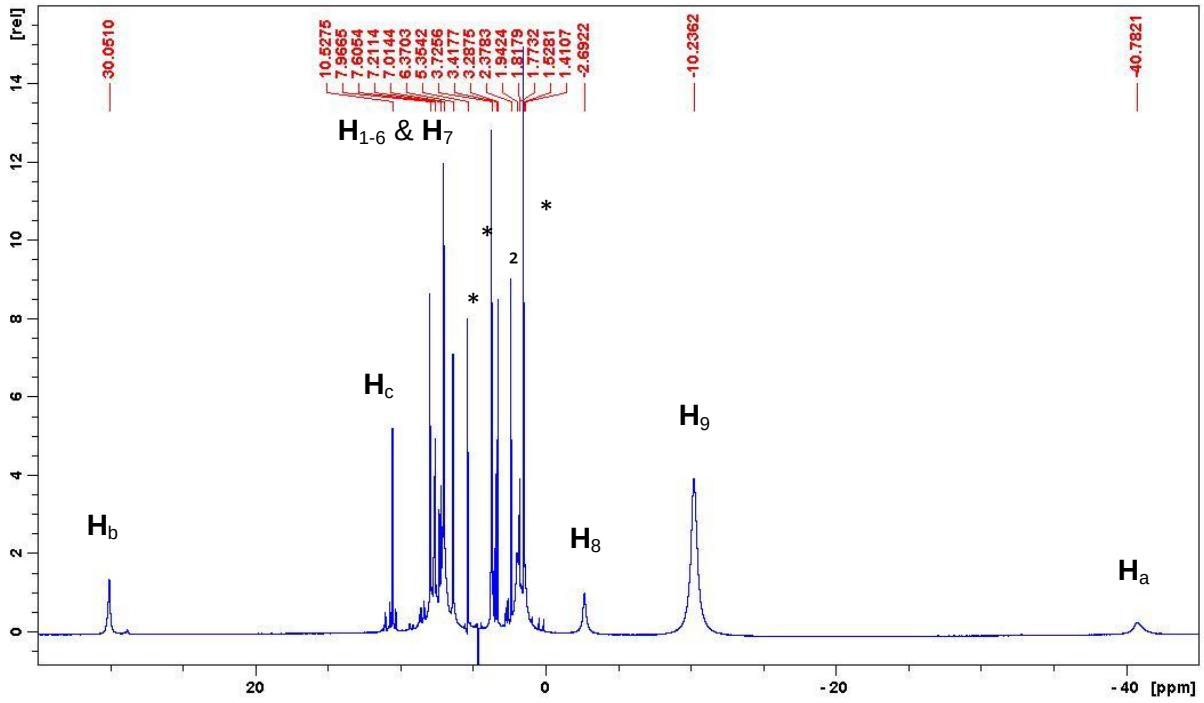

Fig. S3. ^{1}H NMR spectrum of **2**[PF_6]$_4$ in CD_2Cl_2 at 300 K. Numbering of selected protons according to Chart S1 (below). Signals corresponding to solvents are designated by asterisks (*).

Chart S1. ^{1}H nuclei numbering corresponding to the proposed assignment for **2**[PF_6]$_4$.

4. Spectroelectrochemistry of 3

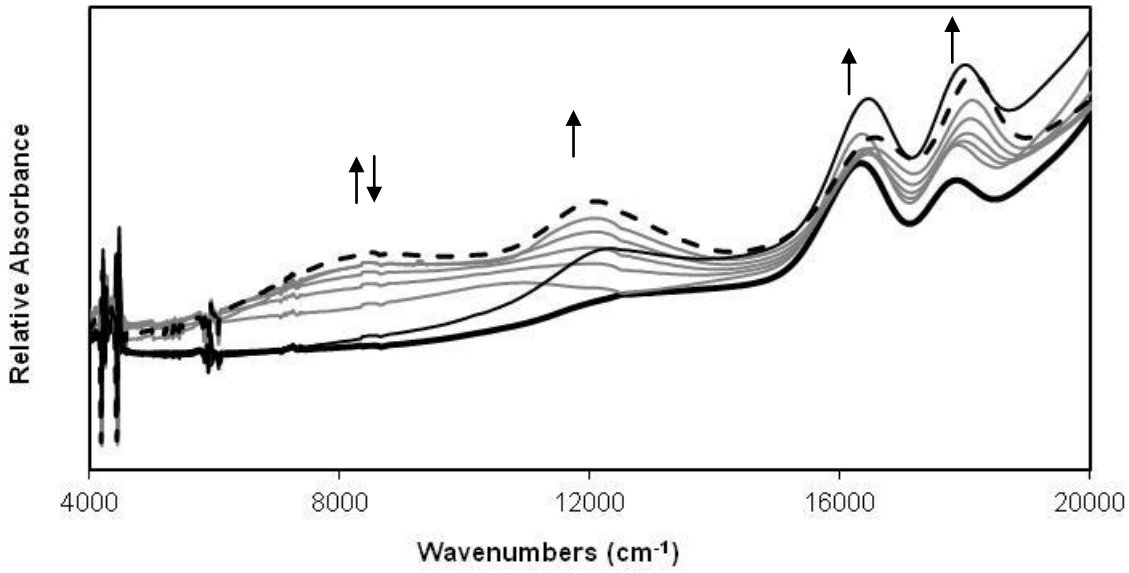

Fig. S4. Spectroelectrochemistry of compound **3**. The oxidized state is shown with a dotted line and the state recovered after back-reduction is given with a thin black line. Conditions: CH_2Cl_2, 20 °C, [*n*-Bu_4N][PF_6] 0.3 M, starting potential: -0.6 V, applied potential: 0.9 V *vs.* SCE. The region of the spectrum to higher energy of 20,000 cm^{-1} is only marginally affected by redox changes.

5. Z-Scan Plots for 4

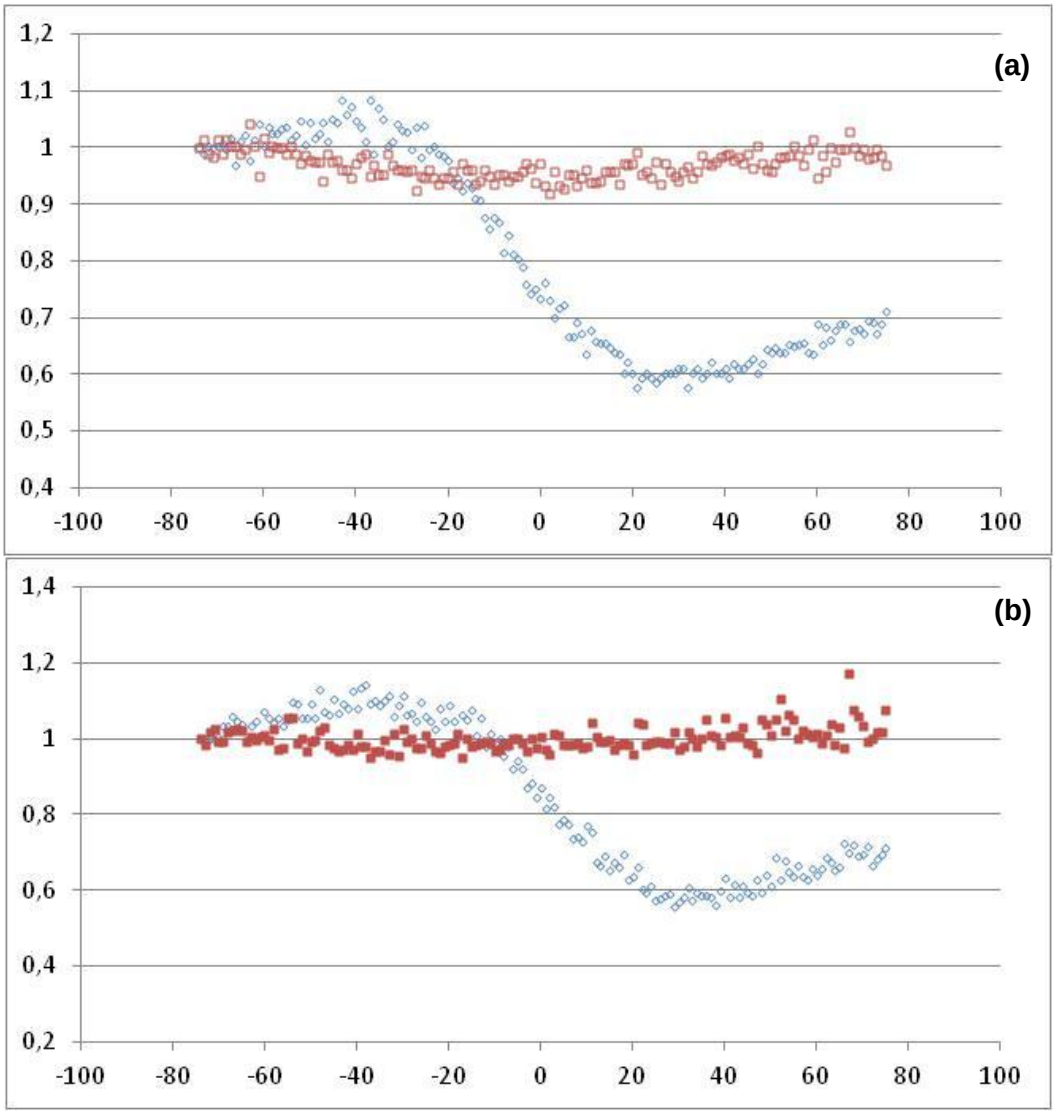

Fig. S4. Z-scan plots obtained for compound **4** at 560 nm (a) and 630 nm (b). Blue: closed-aperture traces. Red: open-aperture traces.