Two-Photon Absorption of Metal-Organic DNA Probes

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Supporting information

Ruthenium (II) complexes were synthesized according to the protocol described elsewhere [1] . The NLO measurements of ruthenium based metal-organic DNA probes were carried out as described previously[2] with some modifications. The present experiments were carried out using a laser system consisting of a Quantronix Integra-C regenerative amplifier operating as an 800 nm pump and a Quantronix-Palitra-FS BIBO crystal-based optical parametric amplifier. This system delivers wavelength tunable pulses of ~130 fs length and was operated at the repetition rate of 1 kHz. Ruthenium complexes were dissolved in MQ water at the concentration ~ (**1** and **3**) 0.8% and (**2**) 0.7% w/w. For the NLO experiment the solutions were placed in 1 mm path length Starna quartz glass cuvettes, stoppered, and sealed with Teflon tape. Results obtained on the cells with solutions were calibrated against Z-scan measurements on a fused silica plate (4.66 mm thick) and compared with the measurements on an identical glass cell filled with the solvent alone. The output from the Palitra in the range from 460 nm to 1100 nm was appropriately filtered using wavelength separators and colour glass filters to remove unwanted wavelength components, attenuated to μJ/pulse range and used as excitation source for simultaneous recording of standard open-aperture (OA) and closed-aperture (CA) Z-scan traces. The beam was focused so as to provide a focal spot in the range $w_0 \approx$ 25 - 50 μm (giving the Rayleigh range which was always taken well in excess of the total thickness of the cell and the reference silica plate) and the cuvette was made to travel in the Z- direction, typically from -20 to 20 mm. The data were collected using three InGaAs photodiodes (Thor Labs Inc.) that monitored the laser input, the OA signal and the CA signal, respectively. The outputs were fed into three channels of a digital oscilloscope and the data were collected by a computer using custom LabWIEV software. The traces of the CA and OA scans obtained by dividing each of them by the laser input reference were analyzed with the help of a custom fitting program that used equations derived by Sheik-Bahae et al.[3] The real and imaginary parts of the second hyperpolarizability, γ, of the solutes were computed assuming additivity of the nonlinear contributions of the solvent and the solute and the applicability of the Lorentz local field approximation[4]. The values of the imaginary part of γ were also converted into values of the two-photon cross section σ_2 and, where the shapes of the Z-scans indicated predominance of the three-photon absorption process, into values of the three-photon cross sections σ_3. The two-photon absorption cross sections were scaled using the molecular weight M, i.e. by comparing σ_2/M values as discussed recently[5].
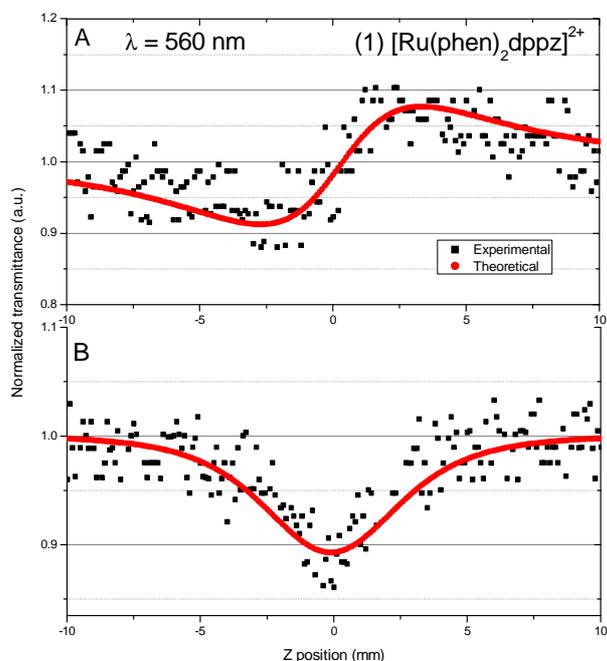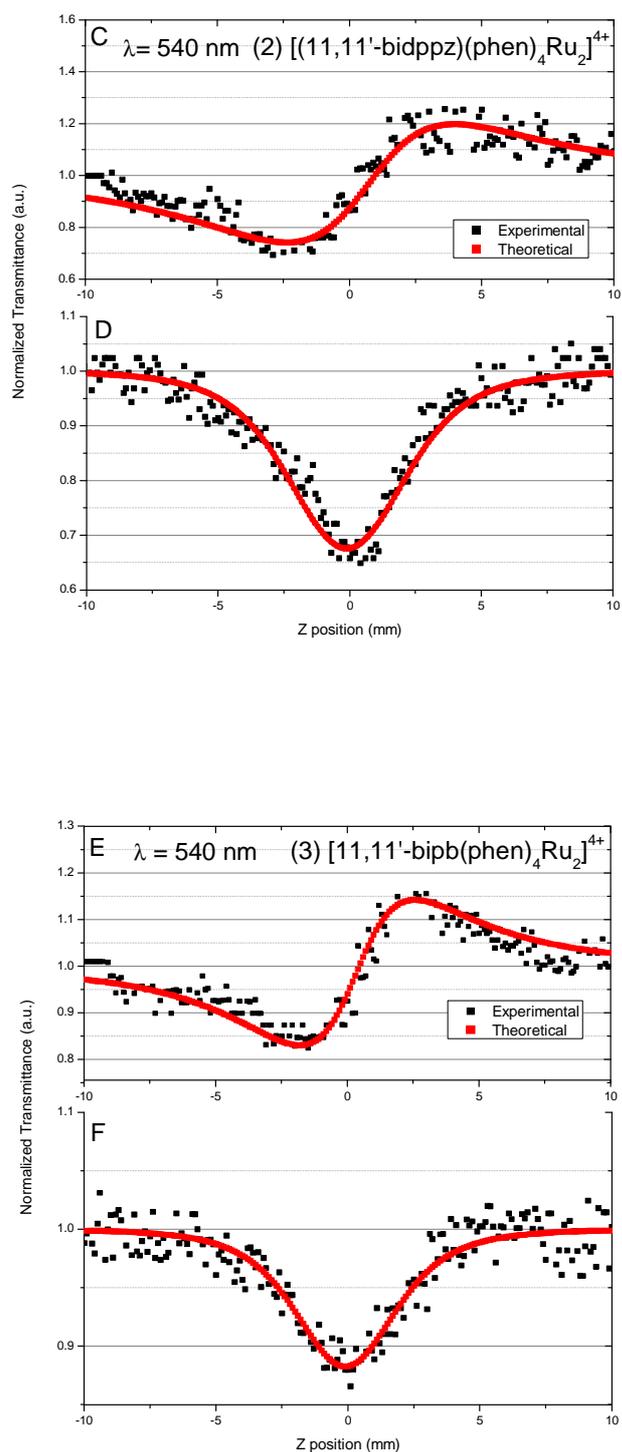
Fig. S1 Representative open (a, c, e) and closed aperture (b, d, f) Z-Scans and the theoretical fits for ruthenium complexes at 560 nm (**1**) $[Ru(phen)_2dppz]^{2+}$(a,b) and at 540 nm(**2**) $[(11,11'-bidppz)(phen)_4Ru_2]^{4+}$and (**3**) $[11,11'-bipb(phen)_4Ru_2]^{4+}$ (c, d e, f); respectively.

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