

Supporting information

Photochemical Upconversion in metal based octaethyl porphyrins diphenylanthracene system

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1 Photochemical Upconversion Yield Determination Method

To determine upconversion quantum yield experimentally a reference sample of neat triplet acceptor molecules was used. Let us assume that in the upconversion experiment, the sample is excited with the wavelength λ_{UC} with power P_{UC} , the optical density of the sample at this wavelength is A_{UC} . The power that is absorbed by the sample according to Beer-Lambert law is equal to

$$P_{UC}^{abs} = P_{UC}(1 - 10^{-A_{UC}}). \quad (1)$$

The sample emits light at the wavelength λ . The intensity measured by the detector is proportional to the number of photons with the wavelength λ that reach the detector, and can be expressed as

$$I_{UC} = \frac{\alpha_{inst}}{n_{UC}^2} P_{UC} (1 - 10^{-A_{UC}}) \frac{\lambda_{UC}}{\lambda} \frac{\Phi_{UC}}{2} \quad (2)$$

where α_{inst} is the instrument factor, n_{UC} is the refractive index of solution, and takes into account the change of solid angle upon refraction on the front surface of the cuvette. The ratio of the wavelengths takes into account the difference in the energies of the photons in the excitation light, and emitted ones. Defining upconversion yield in a traditional way used in literature as equal to 100% when all the input photons are upconverted, we have the upconversion quantum yield equal to $\Phi_{UC}/2$.

If the reference sample that also emits light at the wavelength λ is excited at the wavelength λ_{ref} with excitation power P_{ref} , has optical density A_{ref} at excitation wavelength, and refractive index n_{ref} at emission wavelength, then for the intensity measured by the detector we have:

$$I_{ref} = \frac{\alpha_{inst}}{n_{ref}^2} P_{ref} (1 - 10^{-A_{ref}}) \frac{\lambda_{ref}}{\lambda} \phi_{ref}, \quad (3)$$

where ϕ_{ref} is the luminescence quantum yield of the reference sample.

Dividing eq. 2 over eq. 3, we obtain the following expression to calculate upconversion yield from experimentally measured parameters:

$$\Phi_{UC} = 2 \cdot \phi_{ref} \left(\frac{1 - 10^{-A_{ref}}}{1 - 10^{-A_{UC}}} \right) \left(\frac{\lambda_{ref}}{\lambda_{UC}} \right) \left(\frac{n_{UC}}{n_{ref}} \right)^2 \left(\frac{I_{UC}}{I_{ref}} \right) \left(\frac{P_{ref}}{P_{UC}} \right), \quad (4)$$

in practice typically solutions are diluted, and the same solvent is used, what leads to:

$$\Phi_{UC} = 2 \cdot \phi_{ref} \left(\frac{A_{ref}}{A_{UC}} \right) \left(\frac{\lambda_{ref}}{\lambda_{UC}} \right) \left(\frac{I_{UC}}{I_{ref}} \right) \left(\frac{P_{ref}}{P_{UC}} \right), \quad (5)$$

2 Absorption spectra of triplet sensitizers in the Q-band region

3 Risetime of emission

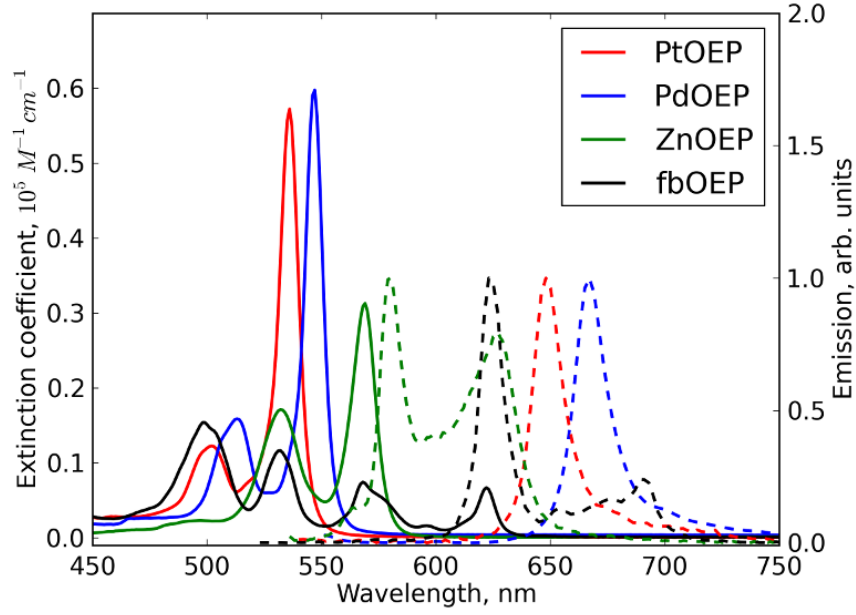


Figure 1: Absorption (solid line) and emission (dashed line) spectra of octaethyl porphyrins, 450-750 spectral range (Q bands of the porphyrins) zoomed in

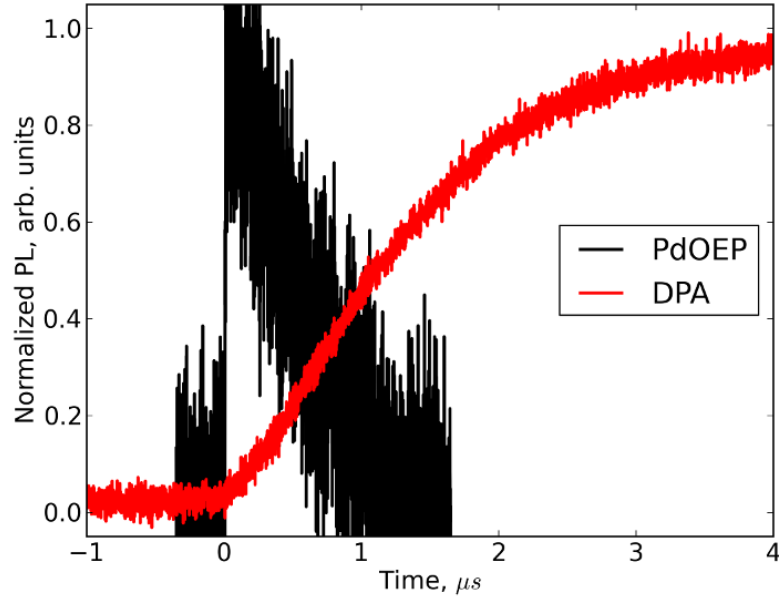


Figure 2: DPA luminescence risetime vs porphyrin phosphorescence quenching in PdOEP:DPA mixture solution

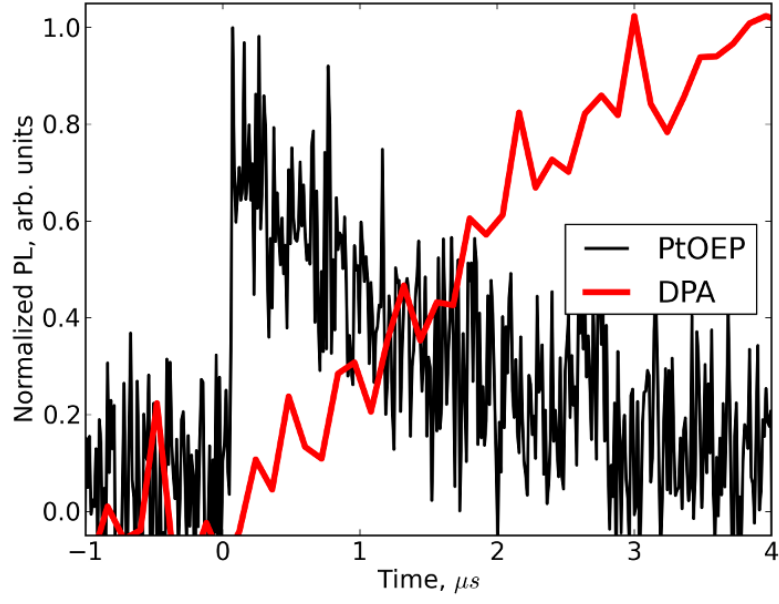


Figure 3: DPA luminescence risetime vs porphyrin phosphorescence quenching in ZnOEP:DPA mixture solution

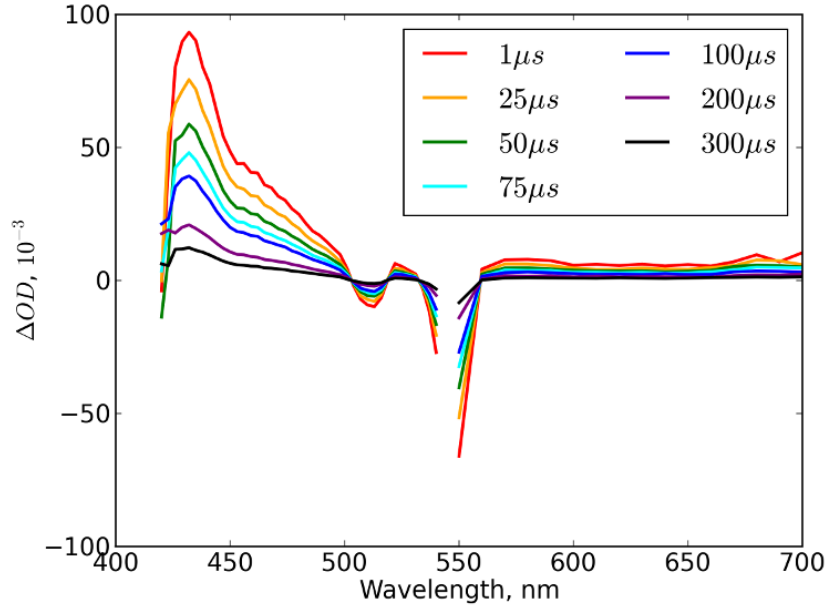


Figure 4: Transient absorption spectra of neat PdOEP sample

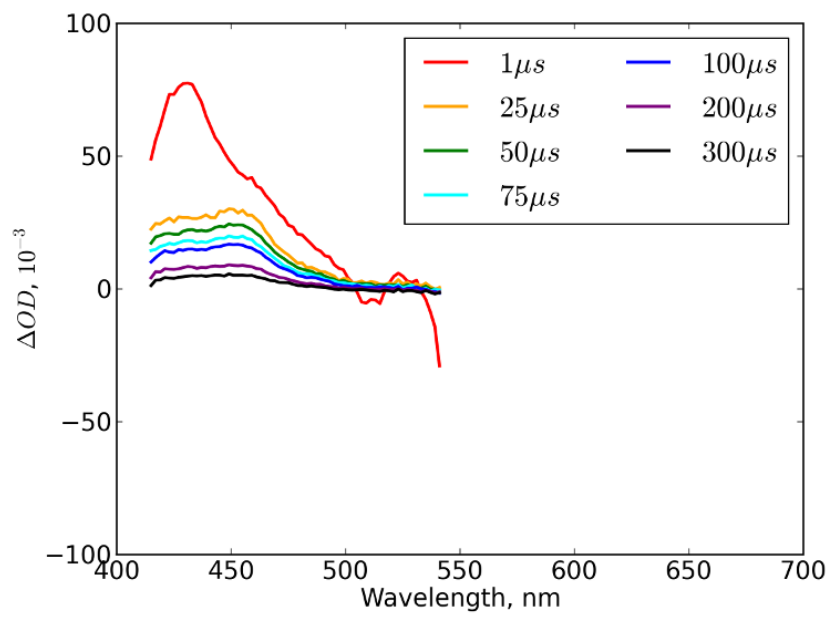


Figure 5: Transient absorption spectra of PdOEP:DPA mixture

4 Transient absorption spectra

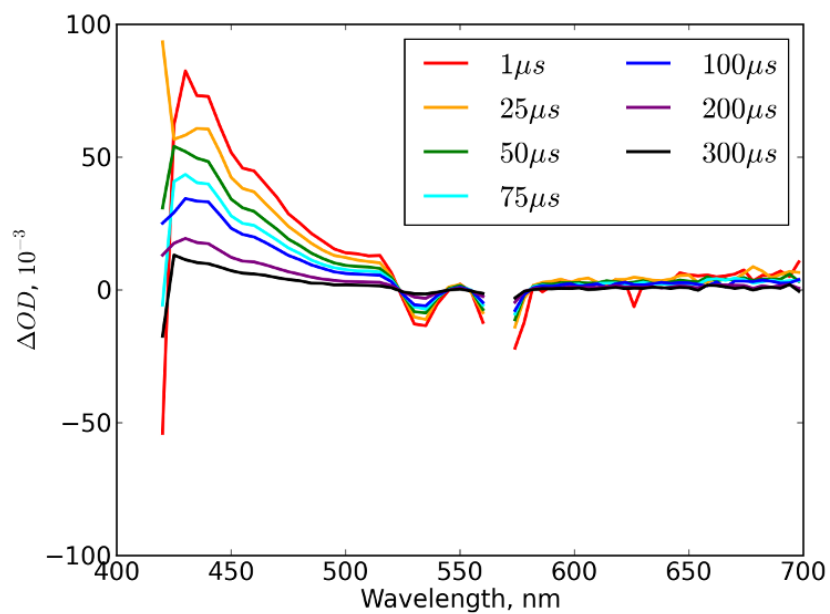


Figure 6: Transient absorption spectra of neat ZnOEP solution

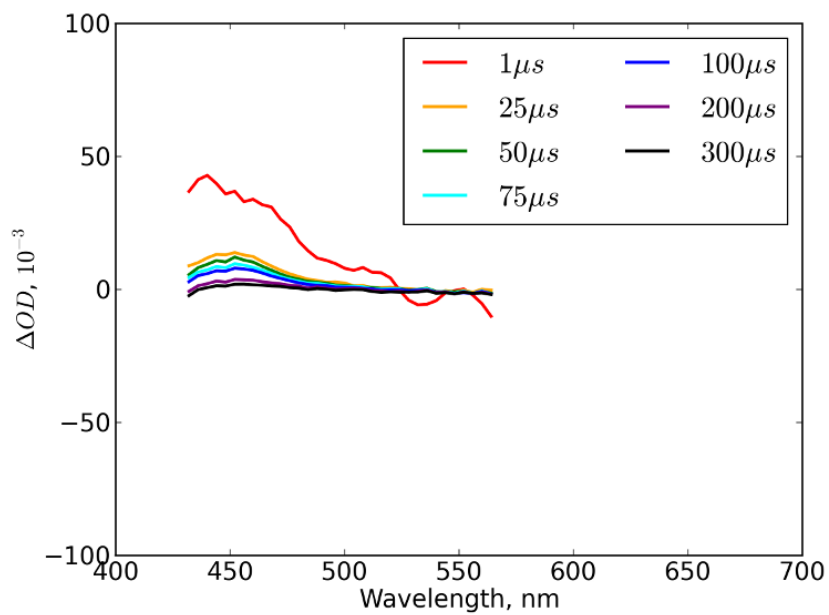


Figure 7: Transient absorption spectra of ZnOEP:DPA mixture in solution

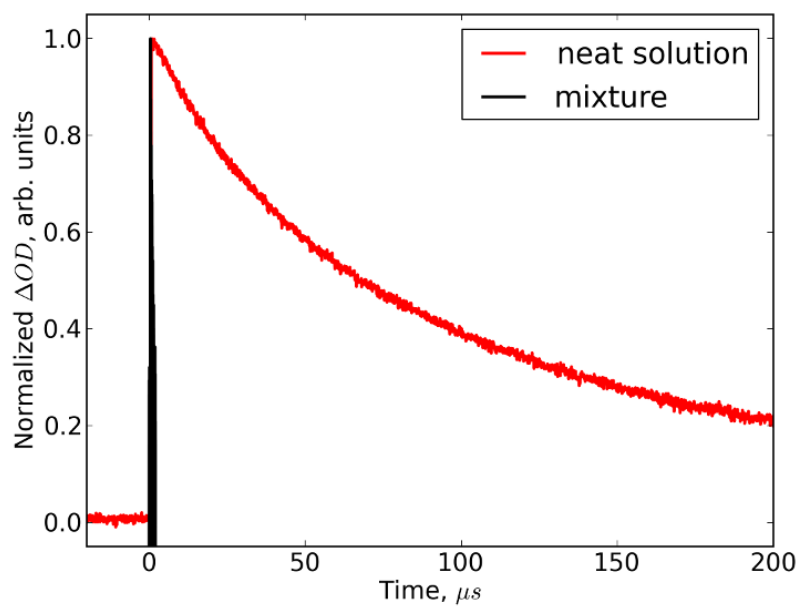


Figure 8: Quenching of PdOEP triplets in mixture with DPA versus neat solution

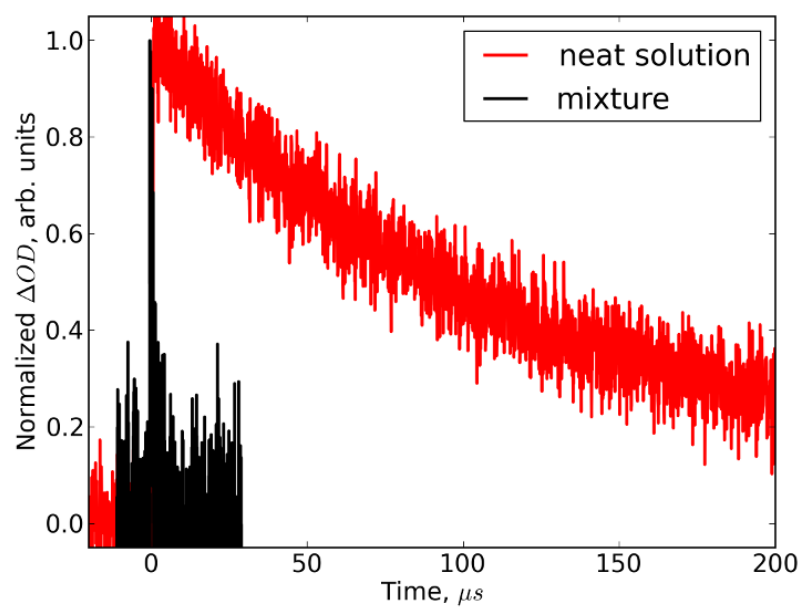


Figure 9: Quenching of ZnOEP triplets in mixture with DPA versus neat solution