

Electronic Supplementary Material (ESI) for New J. Chem.

Deviation from Beer's Law and Relationship of Aggregation with the Effective TPA Coefficient: UV-vis Studies on a Series of Low Symmetry Monophthalocyanines Bearing a Cyclotriphosphazene Substituent

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1. UV-VIS spectra

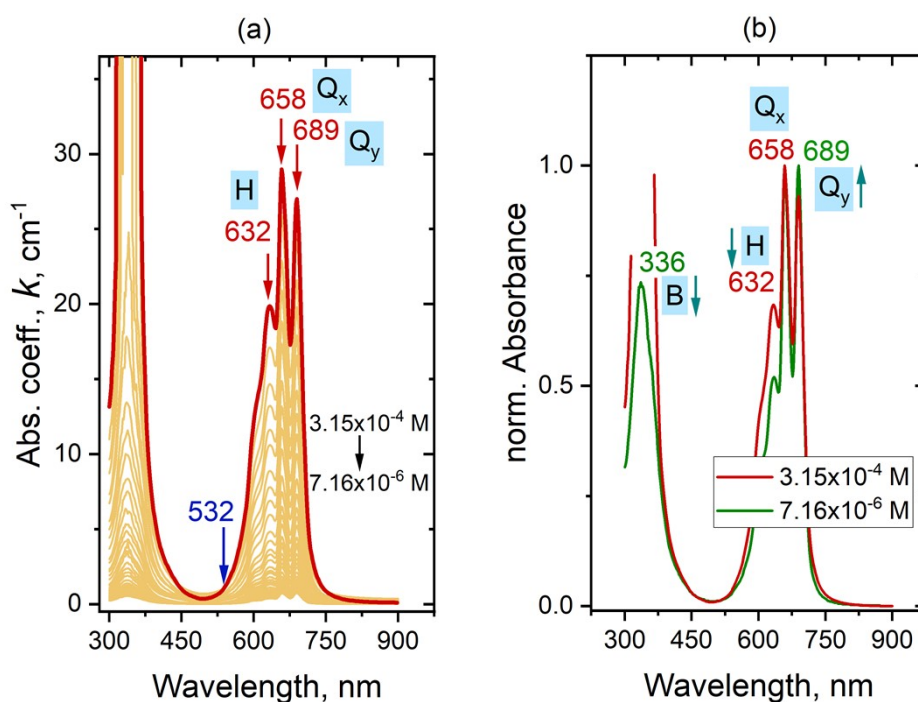


Figure S1. UV-vis spectra of ligand **2a** in THF: (a) sequential dilution and (b) comparison of the most concentrated and most diluted solutions.

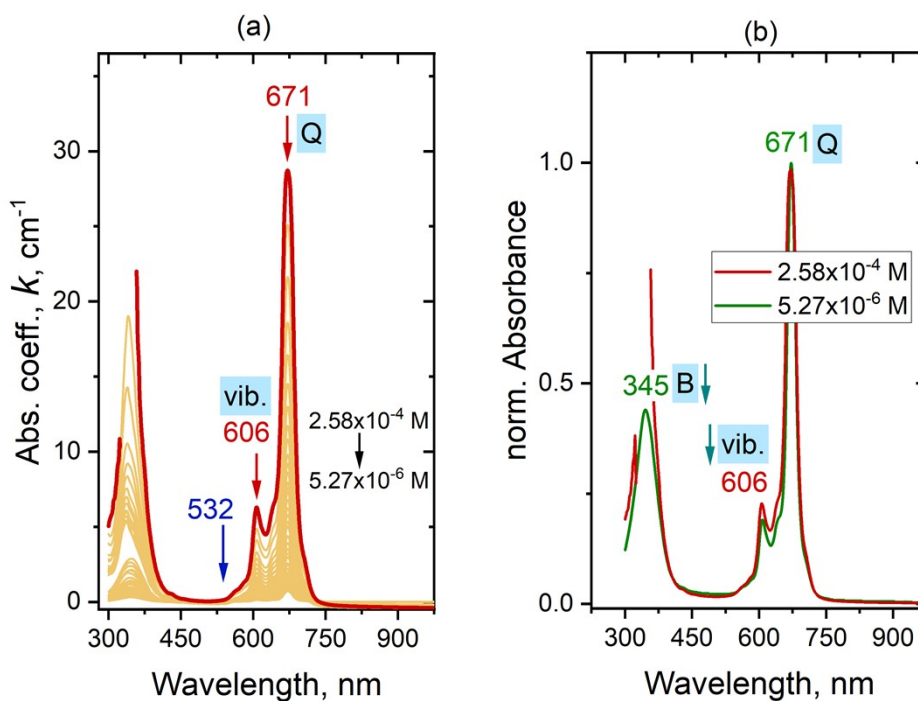


Figure S2. UV-vis spectra of magnesium complex **2b** in THF: (a) sequential dilution and (b) comparison of the most concentrated and most diluted solutions.

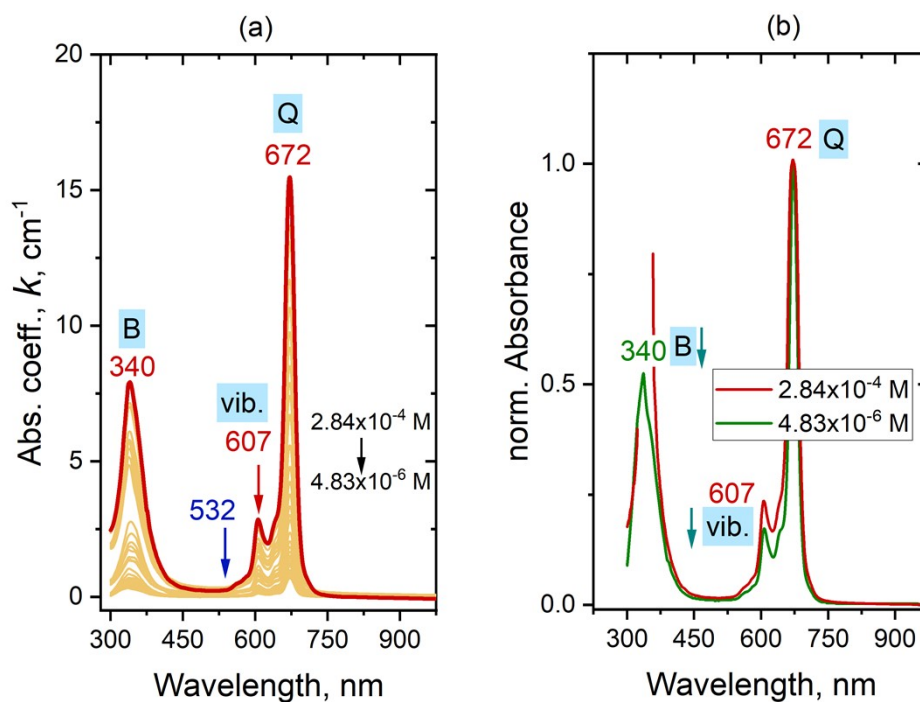


Figure S3. UV-vis spectra of zinc complex **2c** in THF: (a) sequential dilution and (b) comparison of the most concentrated and most diluted solutions.

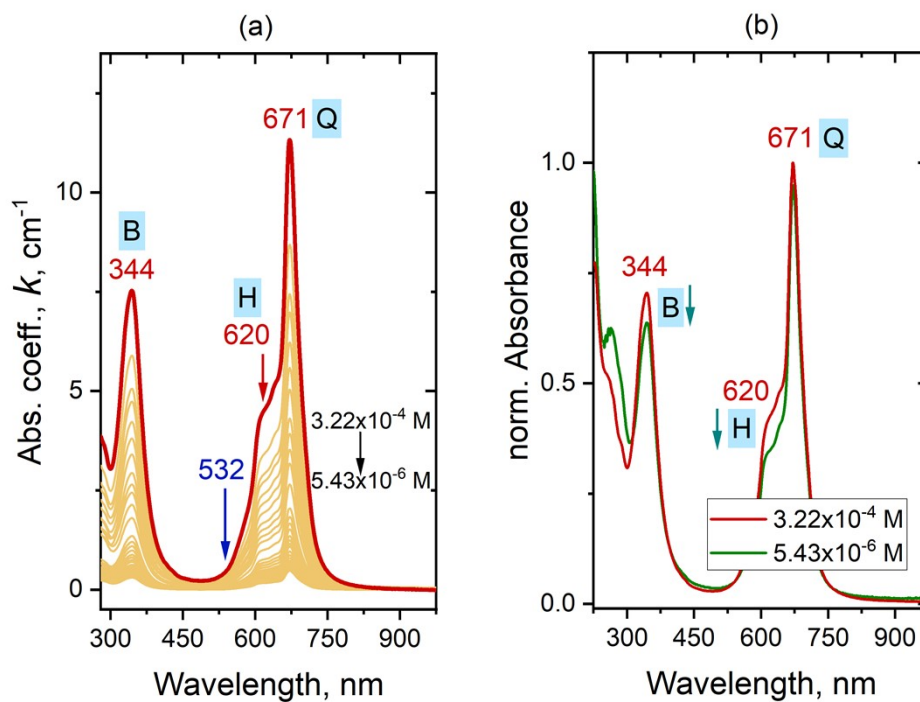


Figure S4. UV-vis spectra of copper complex **2d** in THF: (a) sequential dilution and (b) comparison of the most concentrated and most diluted solutions.

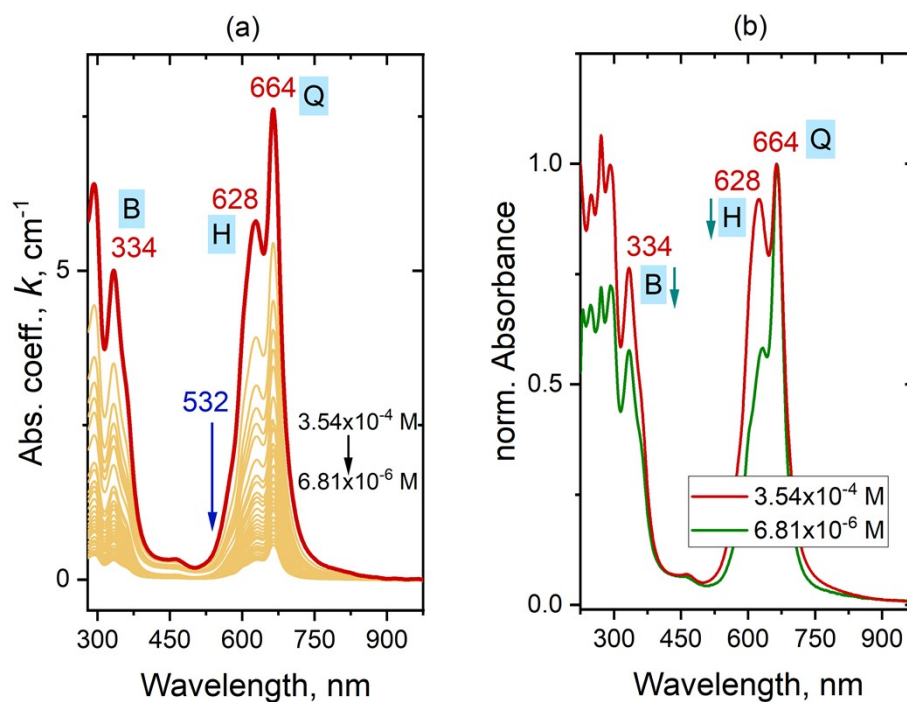


Figure S5. UV-vis spectra of nickel complex **2e** in THF: (a) sequential dilution and (b) comparison of the most concentrated and most diluted solutions.

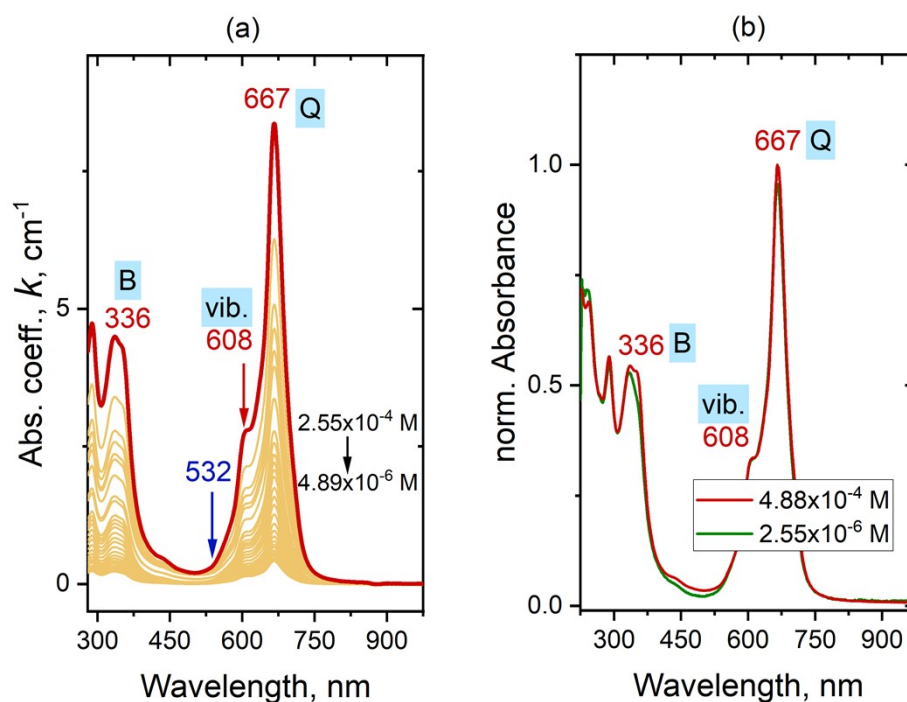
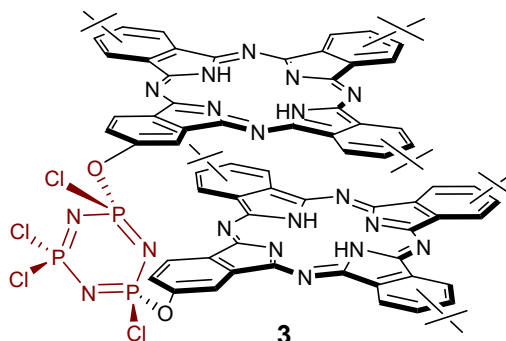


Figure S6. UV-vis spectra of cobalt complex **2f** in THF: (a) sequential dilution and (b) comparison of the most concentrated and most diluted solutions.

2. Predictive power of the correlation model

Below is a demonstration of a qualitative assessment of the aggregation effect on the effective two-photon absorption coefficient in THF for dye **3**, which did not participate in the construction of the primary correlation diagram (Fig. 5, main text). Figure S8 shows the change in extinction with increasing concentration for bis-phthalocyanine, in which macrocycles are strapped through a cyclotriphosphazene spacer.¹



The nonlinear response for this phthalocyanine was investigated in Ref.,² and the aggregation and thermodynamic parameters were calculated from the UV-vis spectra (Fig. S7) using Eqns. 4,6 (see main text). The final result is shown in Fig. S9.

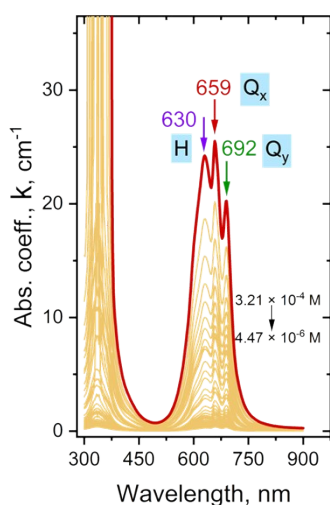


Figure S7. UV-vis spectra of phthalocyanine **3** in THF. Concentrations were varied in the ranges of 3.21×10^{-4} – 4.47×10^{-6} M.

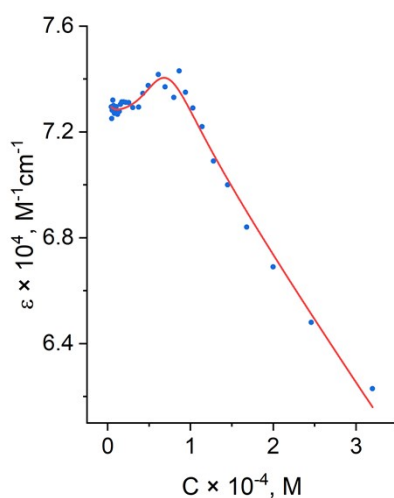


Figure S8. Change in the extinction of dye **3** with increasing the concentration (THF) at a wavelength of 692 nm. Fitting is accomplished on the Extinction model (Eqns. 4,6).

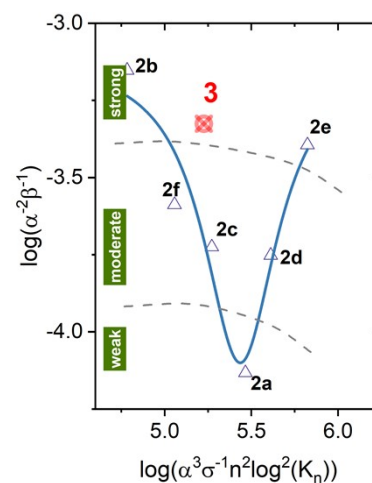


Figure S9. The influence of aggregation on the nonlinear response of dye **3** in THF at a wavelength of 532 nm (Nd:YAG laser, 16 ns).

As seen from Fig. S9, the position of dye **3** is far outside the function (blue line), however, it falls into the “strong” zone, i.e. aggregation has the most negative impact on the NLO response. But here it is to be emphasized that we are comparing bis-phthalocyanine **3** with related monomers **2a-f**, using the latter as standards. Variations of the standard will give a different result.

3. References

1. A. Y. Tolbin, B. N. Tarasevich, M. K. Beklemishev, V. K. Brel and V. E. Pushkarev, *ChemistrySelect*, 2022, **7**, e202201065.
2. A. Y. Tolbin, M. S. Savelyev, A. Y. Gerasimenko, M. V. Sedova, S. S. Maklakov and V. E. Pushkarev, *Journal of Porphyrins and Phthalocyanines* 2022, in press.