

## SUPPORTING INFORMATION

### Ultrafast exciton dynamics after Soret- or Q-band excitation of a directly $\beta,\beta'$ -linked bisporphyrin

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### 1 Experimental Details

Steady-state absorption spectra were recorded with a Hitachi U-  
15 2000 spectrophotometer in a 200  $\mu\text{m}$  flow cell while the fluorescence measurements were done using a 1 mm flow cell in a JASCO FP-6300 spectrofluorometer with diluted solution. Both cells were made of transparent suprasil glass.

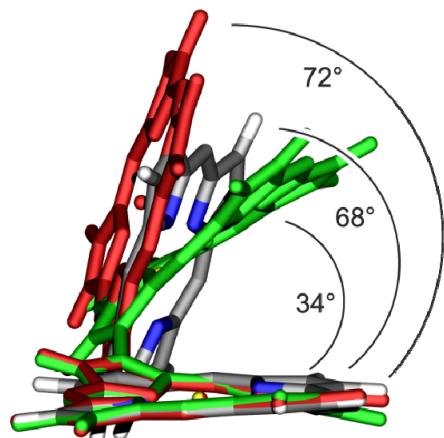
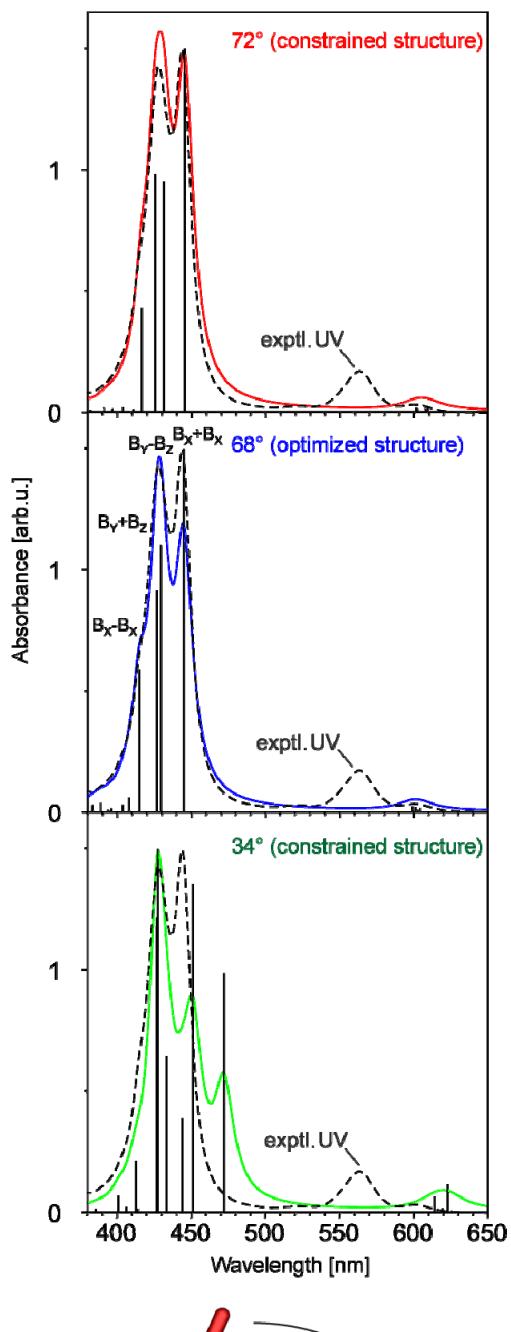
The femtosecond transient-absorption measurements were  
20 performed with a home-built setup consisting of a commercial Ti:sapphire oscillator/amplifier system (Solsice, Spectra Physics) with 800 nm, 100 fs pulses at a repetition rate of 1 kHz, from which three separate beams are generated for further frequency conversion. The 400 nm pump pulses were generated by second  
25 harmonic generation in a  $\beta$ -barium borate crystal after passing a variable motorized delay stage (600 mm) and focussed into the sample down to a width of roughly 200  $\mu\text{m}$ . The visible pump pulses centered at 560 nm were generated with a noncollinear optical parametric amplifier (TOPAS White, Light Conversion),  
30 variably delayed with a second, identical stage, and focussed to 50  $\mu\text{m}$ . The supercontinuum probe pulses were produced by focussing a weak beam into a linearly moving  $\text{CaF}_2$ -plate and focussed by spherical mirrors to a beam width of roughly 40  $\mu\text{m}$  at the sample. The angle between the linearly polarized pump and  
35 probe beams was set to the magic angle of 54.7° by changing the pump polarization direction with a half-wave plate.<sup>51</sup> The signal was measured spectrally resolved and the difference in absorbance was directly calculated by dividing the optical density change induced by two consecutive pulses (shot-to-shot  
40 technique). The optical delay was increased linearly around time zero and exponentially for larger times by variably delaying the pump pulse up to 600 mm with a motorized stage. Averaging was performed by taking multiple data points for one time delay and additionally by combining multiple measurements to account,  
45 respectively, for short-term and long-term noise. A complete setup description can be found in Reference S2.

The nanosecond transient-absorption measurements were also performed with a home-built setup. The excitation was generated with the output of the second harmonic (532 nm) from a Nd:YAG  
50 laser (Quanta-Ray GCR-11, Spectra Physics). Pulse durations of less than 5 ns with energies of up to 7 mJ were selected. The optical detection was based on a pulsed xenon lamp, a monochromator, a photomultiplier tube or a fast silicon

photodiode with a 1 GHz amplification and a 500 MHz digital  
55 oscilloscope. The laser power of every laser pulse was registered using a bypass with a fast silicon photodiode. Several time delays between 2.5 and 150  $\mu\text{s}$  at room temperature were measured with a sample density of 0.1 at the excitation wavelength in argon-saturated ethanol.

### 60 2 Comparison of different conformations of ( $\text{ZnTPP}$ )<sub>2</sub>

As already mentioned in the article, the choice of the correct  
65 density functional is crucial for the optimization of  $\beta,\beta'$ -bisporphyrins. Using B3LYP the porphyrin macrocycles have a nearly orthogonal orientation<sup>S3</sup> while using BLYP-D, a dispersion-corrected functional, the angle between these moieties lowers to only 34°<sup>S4</sup>. Only the combination of long-range and  
70 dispersion corrections in  $\omega\text{B97xD}$  finally gives a conformation that is close to the one found in the X-ray structure of a free-base  $\beta,\beta'$ -bisporphyrin. To compare the effect of the different conformations on the UV spectrum, we tried to get different conformations by constraining the dihedral angle at the porphyrin  
75 axis. In case of the 34° angle a  $\omega\text{B97xD}$ -structure was found that is quite close to the BLYP-D optimized one. However, it was not possible to get a  $\omega\text{B97xD}$  structure that has a 90° angle between the porphyrin macrocycles like within B3LYP. Although the dihedral angle at the axis is fixed to 90°, the porphyrin planes  
80 bend in a way that only an angle of 72° between the monomeric porphyrins could be achieved. Having a look at the UV spectra of these constraint structures, clear differences could be seen between the one of the 34° conformation and the experiment. A much larger Davydov splitting can be found and additional  
85 excited states occur in the Soret region (Figure S1). These additional transitions show charge-transfer character and do not fit to the experiment. Furthermore, the Q band excitations are shifted to the lower energy region as compared to the experiment, hinting at a slightly stronger conjugation between the monomeric  
90 halves in this conformation. Interestingly, the  $\text{S}_2(\text{B}_X\text{-}\text{B}_X)$  state has a much lower intensity than in the minimum conformation, showing the higher symmetry of this geometry by which this transition is again dipole forbidden.



**Fig. S1** Calculated UV spectra of three possible conformations of  $(\text{ZnTPP})_2$ .

The UV spectrum of the  $72^\circ$  conformation is quite similar to that of the minimum conformation ( $68^\circ$ ) which is not surprising due to the small change of the angle between the porphyrin planes. However,  $(\text{B}_Y + \text{B}_Z)$  and  $(\text{B}_Y - \text{B}_Z)$  have a slightly larger distance of 5.8 nm and the oscillator strength of  $(\text{B}_X - \text{B}_X)$  is smaller so that the shoulder in the UV curve nearly vanishes. This lower value shows that the  $\text{B}_X$  transitions are more in-line. Altogether, the best fit with the experimental UV spectrum can be found for the  $\omega\text{B}97\text{xD}$ -minimum conformation with an angle of  $68^\circ$ , clearly showing how important the correct choice of the density functional is here.

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## References

- S1. H. E. Lessing and A. Von Jena, *Chem. Phys. Lett.*, 1976, **42**, 213–217.  
S2. J. Buback, M. Kullmann, F. Langhofer, P. Nuernberger, R. Schmidt, F. Würthner, and T. Brixner, *J. Am. Chem. Soc.*, 2010, **132**, 16510–16519.  
S3. G. Bringmann, S. Rüdenauer, D. C. G. Götz, T. A. M. Gulder, and M. Reichert, *Org. Lett.*, 2006, **8**, 4743–4746.  
S4. G. Bringmann, D. C. G. Götz, T. A. M. Gulder, T. H. Gehrke, T. Bruhn, T. Kupfer, K. Radacki, H. Braunschweig, A. Heckmann, and C. Lambert, *J. Am. Chem. Soc.*, 2008, **130**, 17812–17825.  
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