Electronic Supplementary Information to:

Origin of the absorption spectra of porphyrin *N*- and dithiaporphyrin *S*-oxides in their neutral and protonated states

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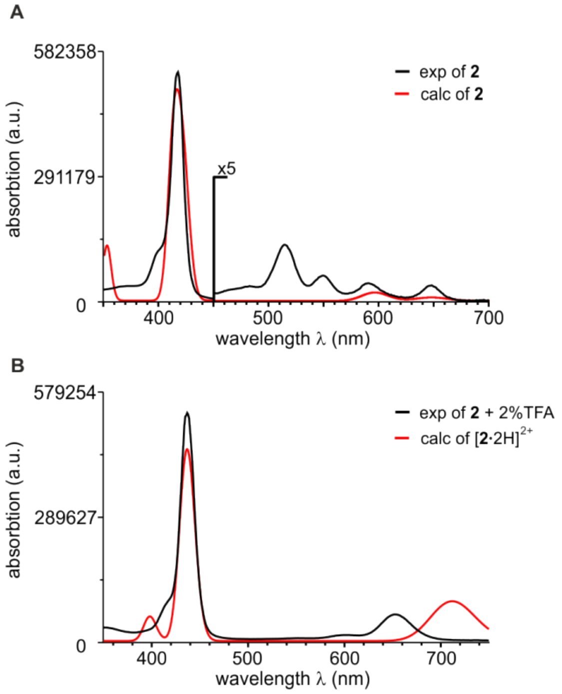

Fig. S1 (A) Comparison of the calculated UV spectra of the TPP **2** with the experimental UV spectrum and (B) of the calculated UV spectra of the diprotonated TPP **2** with the experiment using TD CAM-B3LYP/def2-TZVP. The calculated spectra were corrected by a shift of 47 nm or 42 nm, respectively ($\sigma = 0.07$ or 0.09 eV). Intensities are unscaled.

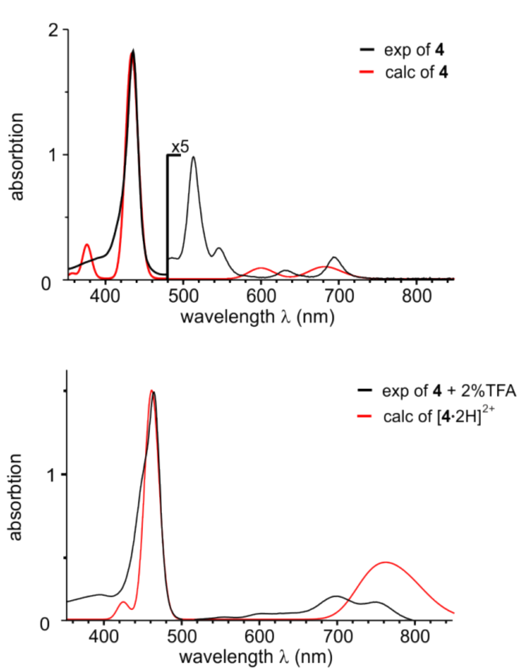

Fig. S2 (A) Comparison of the calculated UV spectra of the dithiaporphyrin **4** with the experimental UV spectrum and (B) of the calculated UV spectra of the diprotonated dithiaporphyrin [**4**·2H]$^{2+}$ with the experiment using TD CAM-B3LYP/def2-TZVP. The calculated spectra were corrected by a shift of 39 nm or 55 nm, respectively ($\sigma = 0.09$ eV).

Table S1 Singlet excitation energies (nm) for the compounds indicated (RI-SCS-CC2/def2-TZVP calculations) and weight of the main single excitations (>5%) in the wavefunction.

State	Excitation energy /nm	Oscillator strength	Main Configuration
N-oxide **1**			
1	686.6	0.0376	55% H–L, 27% H-2–L, 13% H-1–L+1
2	568.1	0.0480	57% H–L+1,18% H-1–L, 18% H-2–L+1
3	486.9	0.0035	60% H-2–L, 26% H-1–L+1, 6% H–L
4	462.0	0.0777	58% H-2–L+1, 33% H-1–L
5	374.6	0.9467	43% H-1–L+1, 18% H–L, 10% H-3–L, 7% H–L+2
6	363.6	1.1209	29% H-1–L, 26% H–L, 18% H-16–L, 11% H-2–L, 6% H-12–L
$[\mathbf{1}\cdot{}^{N}H^{O}H]^{2+}$			
1	642.4	0.2138	74% H–L+1, 22% H-1–L
2	612.6	0.2577	75% H–L, 21% H-1–L+1
3	392.8	1.5535	65% H-1–L, 18% H–L+1, 5% H-9–L+1
4	391.1	1.4217	66% H-1–L+1, 17% H–L, 5% H-3–L+1

Table S2 Orbital energies from CAM-B3LYP/def2-TZVP calculations in eV for the compounds indicated.

Orbital	*S*-oxide (**3**)	Dithiaporphyrin (**4**)	$[\mathbf{4}\cdot 2H]^{2+}$	$[\mathbf{3}\cdot{}^{N}H]^{+}$	$[3\cdot 2^{N}H]^{2+}$
LUMO+2	0.001	0.06	-6.00	-3.15	-6.10
LUMO+1	-1.90	-1.88	-8.11	-5.03	-8.05
LUMO	-2.35	-1.99	-8.14	-5.40	-8.35
HOMO	-6.54	-6.27	-11.64	-9.23	-11.79
HOMO-1	-6.67	-6.58	-12.90	-9.83	-12.93
HOMO-2	-7.25	-8.00	-13.15	-10.57	-13.10
HOMO-3	-8.08	-8.07	-13.20	-10.70	-13.21

Table S3 Singlet excitation energies (nm) for the compounds indicated (RI-SCS-CC2/def2-SVP calculations) and weight of the main single excitations in the wavefunction(>5%).

State	Excitation energy [nm]	Oscillator strength	Main Configuration
S-oxide **3**			
1	635.6	0.0164	62% H-1–L, 31% H–L+1
2	590.9	0.0002	61% H-2–L, 19% H-4–L, 6% H-13–L
3	514.9	0.0017	55% H-2–L+1, 16% H-4–L+1, 7% H–L
4	510.4	0.0393	61% H–L, 23% H-1–L+1, 7% H-1–L+1
5	418.9	0.1188	52% H-14–L, 25% H-1–L+1, 5% H-18–L, 5% H-17–L
6	393.6	0.3698	46% H-16–L, 27% H–L+1, 7% H-1–L, 5% H-3–L
7	386.9	0.4340	40% H-16–L, 19% H–L+1,12% H-1–L, 8% H-14–L+1, 5% H-13–L
8	373.8	1.0953	43% H-1–L+1, 22% H-14–L, 21% H–L
$[\mathbf{3}\cdot{}^{N}\mathrm{H}]^{+}$			
1	679.4	0.1307	70% H–L+1, 20% H-1–L+1
2	559.0	0.0159	42% H–L+1, 40% H-1–L
3	537.3	0.0096	44% H-10–L, 19% H-12–L, 10% H-1–L+1, 8% H-11–L, 5% H-1–L
4	469.3	0.0521	45% H-10–L+1, 24% H-12–L+1, 11% H-1–L, 9% H-11–L+1
5	418.5	0.7799	35% H–L+1, 23% H-1–L, 7% H-8–L, 6% H-15–L, 6% H-12–L+1
6	395.1	-0.141	33% H-8–L, 16% H-1–L+1, 11% H-15–L, 9% H-11–L, 5% H-4–L, 5% H-17–L
7	393.3	0.9156	52% H-1–L+1, 12% H-8–L, 8% H–L, 5% H-1–L
$[\mathbf{3}\cdot 2{}^{N}\mathrm{H}]^{2+}$			
1	701.6	0.3157	81% H–L, 9% H-1–L+1
2	599.7	0.1929	73% H–L+1, 19% H-1–L
3	528.6	0.0166	59% H-10–L, 12% H-11–L, 9% H-9–L, 5% H-14–L
4	473.9	0.0630	49% H-10–L+1, 19% H-1–L, 12% H-11–L+1, 7% H-9–L+1
5	448.5	0.3936	32% H-1–L, 15% H-10–L+1, 13% H-3–L, 12% H–L+1, 11% H-15–L
6	416.6	0.3688	35% H-3–L, 18% H-1–L, 13% H-4–L, 9% H–L+1
7	407.7	0.3295	62% H-1–L+1, 9% H-3–L+1, 8% H–L, 7% H-15–L+1
8	399.2	0.4914	43% H-5–L, 15% H-2–L, 14% H-1–L+1, 9% H-9–L

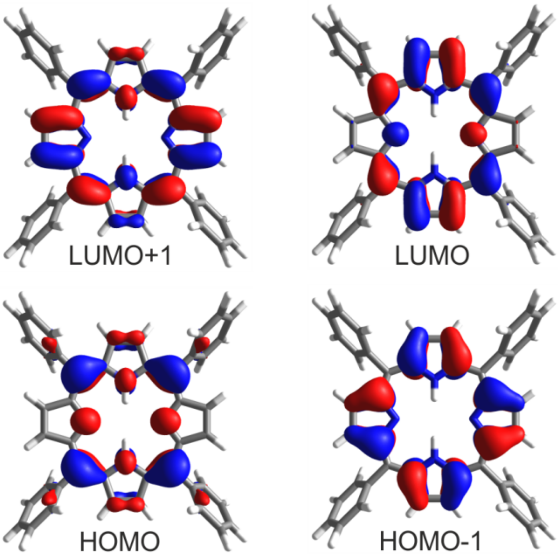

Fig. S3 Frontier orbitals (CAM-B3LYP/def2-TZVP) of TPP **2** that mainly contribute to the first four excitations.

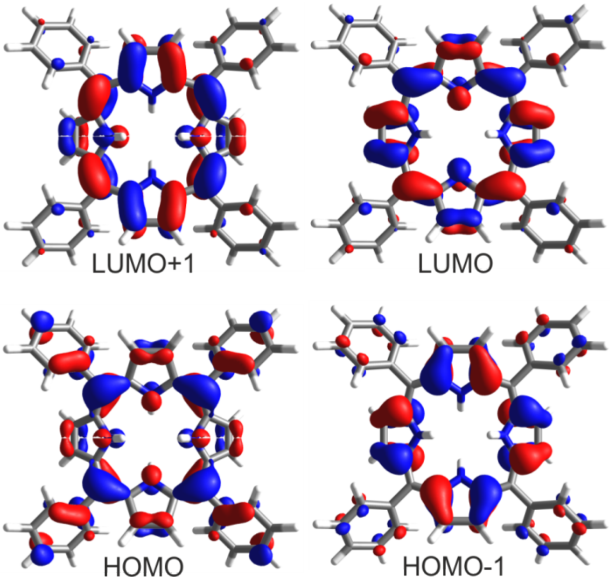

Fig. S4 Frontier orbitals (CAM-B3LYP/def2-TZVP) of diprotonated TPP that mainly contribute to the first four excitations.

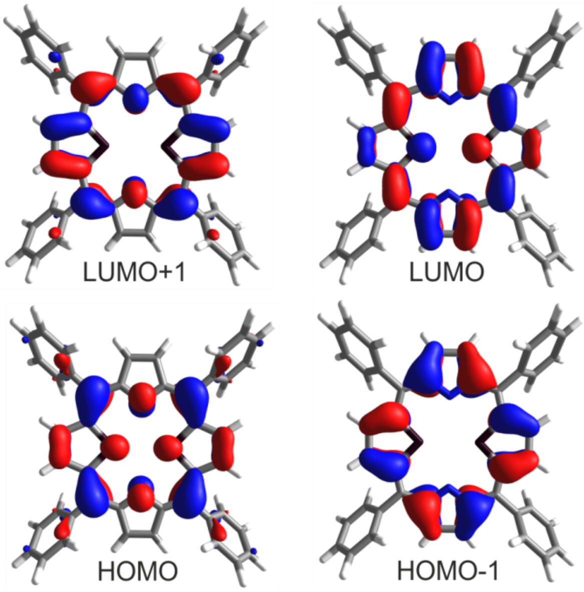

Fig. S5 Frontier orbitals (CAM-B3LYP/TZVP) of dithiaporphyrin **4** that mainly contribute to the first four excitations.

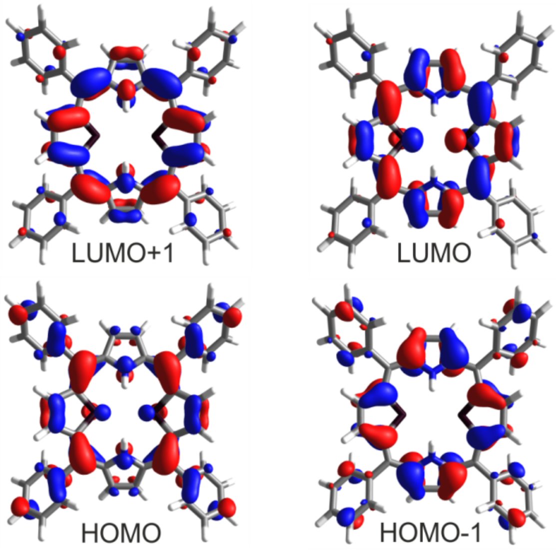

Fig. S6 Frontier orbitals (CAM-B3LYP/TZVP) of the diprotonated dithiaporphyrin [**4**·2H]$^{2+}$ that mainly contribute to the first four excitations.

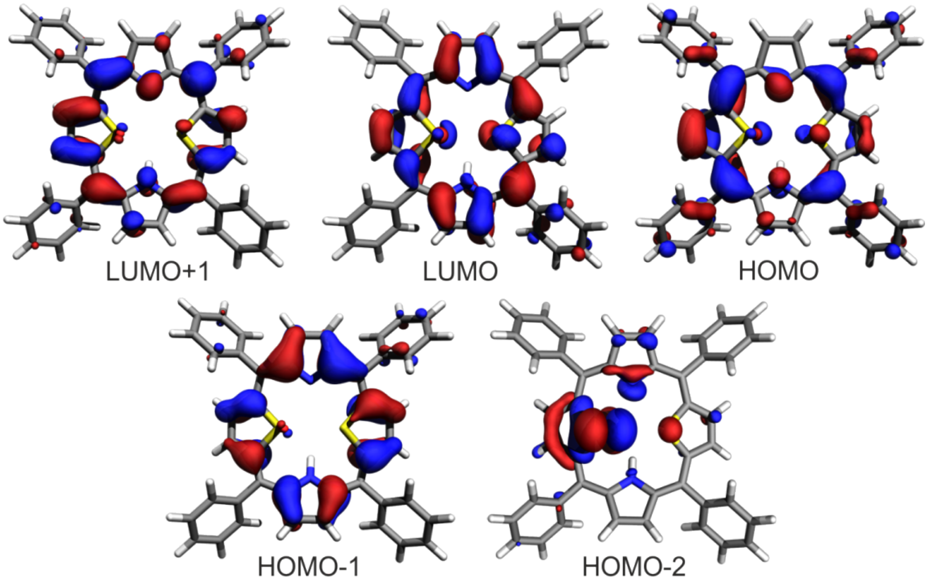

Fig. S7 Frontier orbitals (CAM-B3LYP/TZVP) of the monoprotonated *S*-oxide $[\mathbf{3}\cdot{}^{\mathrm{N}}\mathrm{H}]^{+}$ that mainly contribute to the first six excitations.

Table S4 Singlet excitation energies in nm of the S-oxide compounds indicated calculated with TDB3LYP/TZVP, TDPBE0/TZVP, TDCAM-B3LYP/def2-TZVP, and SCS-CC2/def2-TZVP.

State	B3LYP	PBE0	CAM-B3LYP	SCS-CC2
N-oxide **1**				
1	682.1	662.0	653.50	686.6
2	585.8	571.7	574.82	568.1
3	511.4	496.2	459.57	486.9
4	475.3	459.3	418.49	462.0
5	402.7	392.1	373.19	374.6
6	390.1	380.32	357.46	363.6
7	380.18	364.9		
8	377.6	361.1		
$[\mathbf{1}\cdot{}^{\mathrm{N}}\mathbf{H}]^{+}$				
1	626.8	611.6	618.43	613.1
2	589.7	585.5	598.64	577.6
3	505.1	486.5	433.95	458.0
4	476.8	457.8	409.77	451.3
5	412.9	399.7	370.32	365.6
6	406.7	393.9	365.49	365.4
7	398.5			
8	395.9			
$[\mathbf{1}\cdot{}^{\mathrm{N}}\mathbf{H}^{\mathrm{O}}\mathbf{H}]^{2+}$				
1	687.7	670.6	682.40	642.4
2	667.9	652.3	661.04	612.6
3	480.5	455.9	396.53	392.8
4	479.2	454.2	395.62	391.1
5	472.3	447.9		
6	469.9	445.4		
7	467.1	440.6		
8	465.4	439.0		
9	460.6	434.8		
10	458.2	432.9		

Table S5 Singlet excitation energies in nm of the S-oxide compounds indicated calculated with TDB3LYP/TZVP, TDPBE0/TZVP, TDCAM-B3LYP/def2-TZVP, and SCS-CC2/def2-SVP.

State	B3LYP	PBE0	CAM-B3LYP	SCS-CC2
S-oxide **3**				
1	696.4	662.4	649.70	635.6
2	659.8	647.4	582.92	590.9
3	585.2	568.4	523.70	514.9
4	580.7	559.3	454.13	510.4
5	480.2	460.9	411.79	418.9
6	443.5	429.1	405.31	393.6
7	432.6	417.7		386.9
8	421.1	408.4		
9	418.2	406.1		
10	415.6	401.3		
$[3{\cdot}{}^{N}H]^{+}$				
1	697.6	683.6	685.98	679.4
2	619.9	606.0	609.49	559.0
3	588.3	562.3	461.71	537.3
4	524.7	503.5	435.77	469.3
5	486.9	467.9	418.83	418.5
6	467.4	447.8	397.19	395.1
7	459.0	437.2	387.8	393.3
8	440.1	426.2		
$[3{\cdot}2{}^{N}H]^{2+}$				
1	778.2	757.7	729.5	701.6
2	692.3	674.7	659.5	599.7
3	555.3	524.2	433.1	528.6
4	551.2	521.5	425.0	473.9
5	549.6	514.9	405.0	448.5
6	547.6	514.5	403.1	416.6
7	508.3	481.4	390.2	407.7
8	506.0	480.5	388.4	399.2
9	505.4	478.0		
10	500.6	474.9		
11	496.8	470.8		
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18	437.9	422.9		
19	431.4	417.0		