*Electronic Supplementary Information*

# Charge Transfer in Porphyrin – Calixarene Complexes: Ultrafast Kinetics, Cyclic Voltammetry, and DFT calculations

**Pavel Kubát,[a]* Jakub Šebera,[a] Stanislav Záliš,[a] Jan Langmaier,[a] Marcel Fuciman,[b] Tomáš Polívka,[b] Kamil Lang[c]***

[a] *J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Praha 8, Czech Republic; E-mail: kubat@jh-inst.cas.cz*

[c] *Institute of Physical Biology, University of South Bohemia, Zámek 136, 373 33 Nové Hrady, Czech Republic*

[b] *Institute of Inorganic Chemistry, v.v.i., Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic; E-mail: lang@iic.cas.cz*

**Table S1.** Acido-basic properties of clx*m* and TMPyP*n:* the p$K_a$ values of OH dissociation of clx*m* and protonation of the porphyrin ring in TMPyP*n*.[a]

| clx*m* | p$K_{a1}$ | p$K_{a2}$ | p$K_{a3}$ | p$K_{a4}$ | Ref. | TMPyP*n* | p$K_{a1}$ | p$K_{a2}$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| clx4 | 3.1 | 12.2 | > 13 [a] | > 13 [a] | 1 | TMPyP4 | 1.8 | 0.7 | 3 |
| | 3.2 | - | - | - | 2[c] | | 1.4 | | 4 |
| clx6 | 3.4 | 4.8 | - | - | 5 | TMPyP3 | 1.8 | - | 4 |
| | 2.7 | 5.0 | - | - | 2[c] | | | | |
| clx8 | 3.0 | 4.4 | 8.3 | 10.0 | 2[c] | TMPyP2 | -0.9 | - | 4 |

[a] The sulfonate groups of calixarenes are highly acidic and typically have the p$K_a$ values below 1.0 (p$K_a$ of benzenesulfonic acid is 0.7).
[b] Not measurable.
[c] 0.1M NaCl at 25ºC.

**Table S2.** Absorption spectra of TMPyP*n* in $H_2O$.

| TMPyP*n* | Absorption spectra Band (nm)/ε($10^5 M^{-1}$ $cm^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Soret | $Q_y(1,0)$ | $Q_y(0,0)$ | $Q_x(1,0)$ | $Q_x(0,0)$ |
| TMPyP4 | 421/2.38 | 518/0.154 | 555/0.056 | 585/0.065 | 640/0.016 |
| TMPyP3 | 417/2.56 | 514/0.143 | 547/0.026 | 581/0.052 | 634/0.006 |
| TMPyP2 | 413/2.43 | 511/0.175 | 545/0.041 | 581/0.071 | 634/0.021 |

**Table S3**. Calculated excitation energies in eV (wavelengths in nm in parenthesis), oscillator strengths, main configurations, and comparison with the experimental data (transitions, relative intensity of bands related to $Q_y(1,0)$) for TMPyP*n* in $H_2O$**.** Calculated by TD-DFT (B3LYP/SVP/COSMO).

| Band | Main Configurations, % | Excitation Energies, eV (nm) | Oscillator Strengths | Experimental Transitions, eV (nm) | Relative Intensity |
|---|---|---|---|---|---|
| **TMPyP4** ($H_2O$) | | | | | |
| $S_1$‘ | 177-179 58.8 | 2.12 (585) | 0.0142 | | |
| $Q_x(0,0)$ | 176-178 39.5 | | | 1.94 (640) | 0.10 |
| $Q_x(1,0)$ | | | | 2.12 (585) | 0.42 |
| $S_1$“ | 177-178 60.6 | 2.24 (553) | 0.0416 | | |
| $Q_y(0,0)$ | 176-179 38.6 | | | 2.23 (555) | 0.36 |
| $Q_y(1,0)$ | | | | 2.39 (518) | 1.00 |
| | 176-178 34.2 | 2.82 (440) | 0.5543 | 2.94 (421) | |
| $S_2$‘ | 177-182 27.5 | | | | |
| | 177-179 22.8 | | | | |
| | 177-183 34.1 | 2.85 (434) | 0.5373 | | |
| $S_2$“ | 176-179 34.0 | | | | |
| | 177-178 20.5 | | | | |
| **TMPyP3** ($H_2O$) | | | | | |
| $S_1$‘ | 177-178 42.3 | 2.15 (576) | 0.0042 | | |
| | 176-179 26.3 | | | | |
| | 177-179 18.9 | | | | |
| $Q_x(0,0)$ | 176-178 11.3 | | | 1.96 (634) | 0.04 |
| $Q_x(1,0)$ | | | | 2.13 (581) | 0.37 |
| $S_1$“ | 177-179 39.5 | 2.29 (541) | 0.0061 | | |
| | 176-178 29.6 | | | | |
| | 177-178 17.8 | | | | |
| $Q_y(0,0)$ | 176-179 12.5 | | | 2.27 (547) | 0.18 |
| $Q_y(1,0)$ | | | | 2.41 (514) | 1.00 |
| | 177-182 64.3 | 2.85 (435) | 0.1780 | 2.97 (417) | |
| $S_2$‘ | 176-178 10.7 | | | | |
| | 177-183 54.3 | 2.86 (433) | 0.2164 | | |
| $S_2$“ | 176-179 14.2 | | | | |
| **TMPyP2** ($H_2O$) | | | | | |
| $S_1$‘ | 176-179 55.5 | 2.20 (563) | 0.00003 | | |
| $Q_x(0,0)$ | 177-178 43.8 | | | 1.96 (634) | 0.12 |
| $Q_x(1,0)$ | | | | 2.13 (581) | 0.41 |
| $S_1$“ | 176-178 51.2 | 2.35 (527) | 0.00023 | | |
| $Q_y(0,0)$ | 177-179 48.3 | | | 2.27 (545) | 0.23 |
| $Q_y(1,0)$ | | | | 2.43 (511) | 1.00 |
| | 177-178 34.5 | 3.07 (404) | 0.4789 | 3.00 (413) | |
| $S_2$‘ | 174-179 33.6 | | | | |
| | 176-179 22.7 | | | | |
| | 176-183 34.2 | 3.17 (392) | 0.1497 | | |
| $S_2$“ | 175-179 18.2 | | | | |
| | 176-181 16.5 | | | | |
| | 177-180 13.8 | | | | |

**Table S4**. Calculated excitation energies in eV (wavelengths in nm in parenthesis), oscillator strengths, main configurations, and comparison with the experimental data for TMPyP4-clx6 in $H_2O$**.** Calculated by TD-DFT (MPW1B95/6-31G*/COSMO).

| **TMPyP4** ($H_2O$) | | |
|---|---|---|
| Band | Excitation Energies, eV (nm) | Oscillator Strengths |
| $S_1$‘ | 2.20 (565) | 0.0089 |
| $S_1$“ | 2.33 (535) | 0.0639 |
| $S_2$‘ | 2.97 (418) | 1.3914 |
| $S_2$“ | 3.02 (410) | 1.4766 |
| **TMPyP4-clx6** ($H_2O$) | | |
| $S_1$‘ | 2.17 (572) | 0.0126 |
| $S_1$‘ | 2.28 (543) | 0.0883 |
| $S_2$´ | 2.92 (425) | 1.2586 |
| $S_2$“ | 2.97 (417) | 1.3245 |
| **TMPyP4- clx6_O$^-$** ($H_2O$) | | |
| $S_1$‘ | 2.17 (571) | 0.0184 |
| $S_1$“ | 2.30 (540) | 0.0578 |
| $S_2$‘ | 2.93 (423) | 1.0018 |
| $S_2$“ | 2.97 (417) | 0.9311 |
| **TMPyP4- clx6_O$^-$ … Na$^+$** ($H_2O$) | | |
| $S_1$‘ | 2.17 (571) | 0.0198 |
| $S_1$“ | 2.29 (540) | 0.0595 |
| $S_2$‘ | 2.93 (424) | 1.2347 |
| $S_2$“ | 2.97 (417) | 1.3181 |
| **TMPyP4- clx6_$(O)_2^-$** ($H_2O$) | | |
| $S_1$‘ | 2.18 (568) | 0.0161 |
| $S_1$“ | 2.31 (536) | 0.0418 |
| $S_2$‘ | 3.00 (414) | 0.6616 |
| $S_2$“ | 3.04 (408) | 0.8042 |
| **TMPyP4- clx6_$(O)_2^-$ … $(Na)_2^+$** ($H_2O$) | | |
| $S_1$‘ | 2.18 (569) | 0.0223 |
| $S_1$“ | 2.30 (539) | 0.0867 |
| $S_2$‘ | 2.95 (421) | 0.8409 |
| $S_2$“ | 3.01 (412) | 1.1454 |

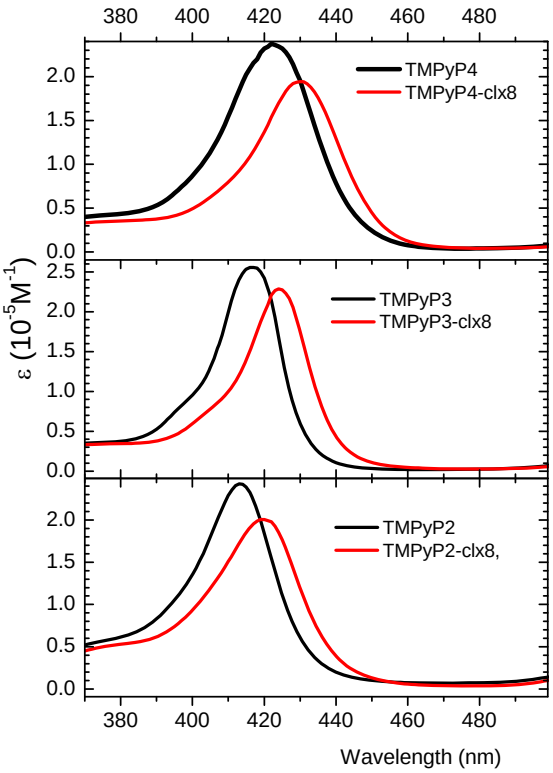


**Figure S1**. Soret bands of TMPyP*n* and corresponding complexes TMPyP*n*-clx8.

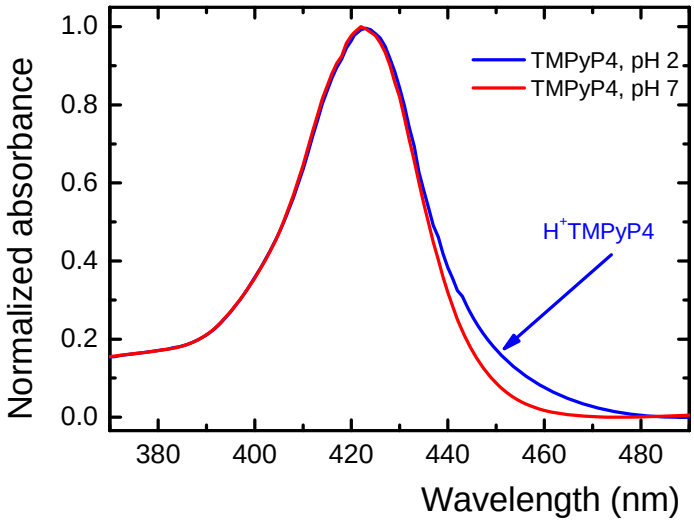


**Figure S2**. Normalized Soret band of TMPyP4 at pH 7 and pH 2, blue arrow shows the partial protonation of TMPyP4 (p$K_{a1}$~1.4) at pH 2.

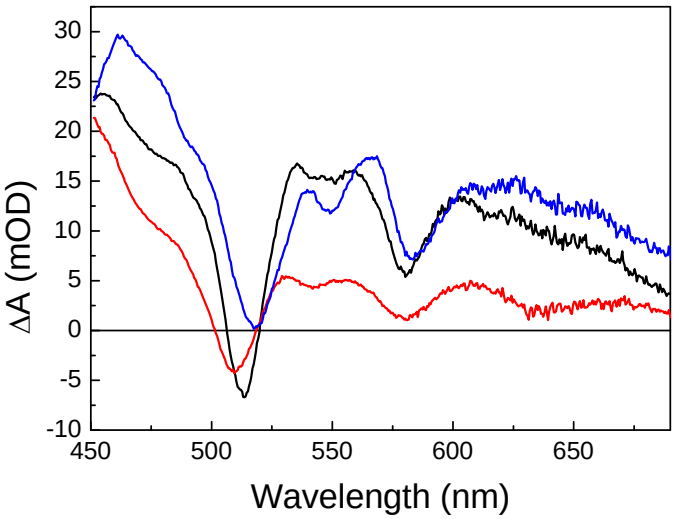


**Figure S3**. Comparison of the transient absorption spectra of TMPyP4 (blue), TMPyP3 (black), and TMPyP2 (red) in $H_2O$, pH 7. Spectra were measured 30 ps after excitation at 395 nm and correspond to the relaxed $S_1$ state of TMPyP*n* molecules.

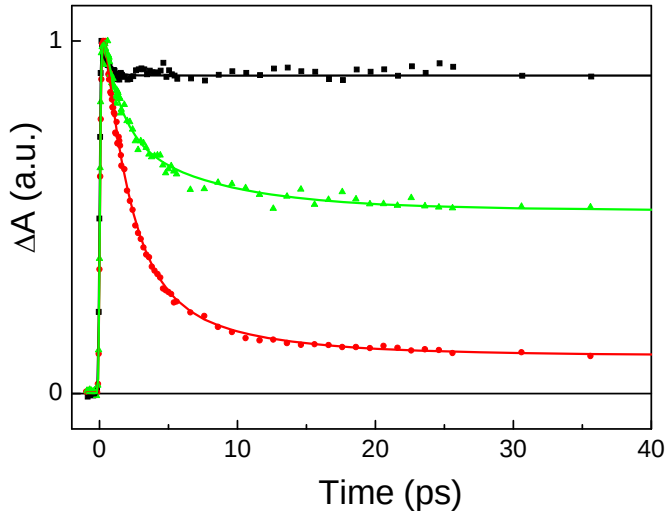


**Figure S4**. Kinetics of TMPyP2-clx8 measured in $H_2O$ at pH 2 (green), and pH 7 (red). Kinetic curves were measured at 470 nm after 395 nm excitation. Kinetic of TMPyP2 in $H_2O$ at pH 7 is shown for comparison (black). All kinetics are normalized at maximum.

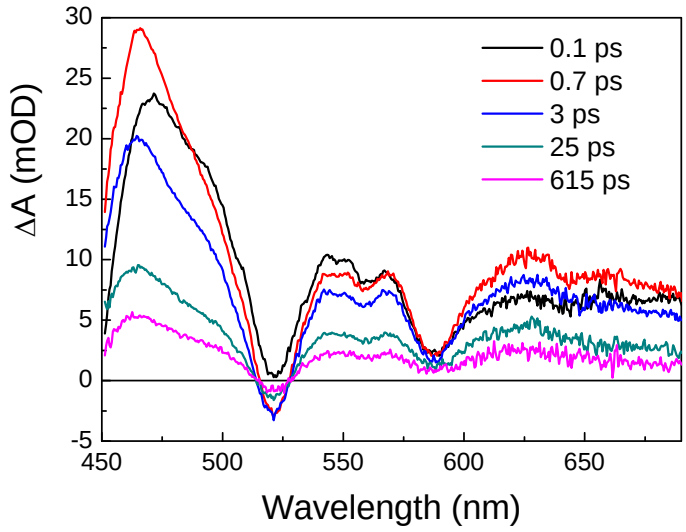


**Figure S5**. Transient absorption spectra of TMPyP4-clx8 complex in $H_2O$ at pH 7 measured at different delay times after excitation at 395 nm.

**References**

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