Supporting Information

Highlight on the solution processes occurring on silver(I)-assembling porphyrins in presence of an excess of silver salt

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Contents

NMR Spectra	S2
Additional spectroscopic and photophysical data	S5
Additional electrochemical data	S7
References	S9

NMR Spectra



Fig. SI1. ¹H NMR (CDCl₃, 400 MHz) spectrum of *meso*-tetrakis(2,6-dimethyl-4-methoxyphenyl)porphyrin.



Fig. SI2. ¹H-¹³C HMBC NMR (CDCl₃, 100 MHz, 223 K) spectrum of *meso*-tetrakis(2,6-dimethyl-4-methoxyphenyl)porphyrin.



Fig. SI3. ¹H-¹³C HSQC NMR (CDCl₃, 100 MHz, 223 K) spectrum of *meso*-tetrakis(2,6-dimethyl-4-methoxyphenyl)porphyrin.



Fig. SI4. ¹H NMR (CD₂Cl₂, 400 MHz) spectrum of **Zn-Ref**.



Fig. SI5. ¹³C NMR (CD₂Cl₂, 126 MHz) spectrum of **Zn-Ref**.

Additional spectroscopic and photophysical data

	λ_{\max} / nm ^a	$\phi_{fl}{}^{b}$	τ / ns ^c
2H-Ref	654, 716	0.11	10.2
Zn-Ref	594, 646	0.036	2.2

Table SI1. Luminescence data of reference compounds 2H-Ref and Zn-Ref in CH₂Cl₂ at room temperature.

^a From corrected spectra. ^b Fluorescence quantum yields determined using tetraphenyl-porphyrin in aerated toluene as a standard ($\phi_{fi}=0.11$).^{1 c} Fluorescence lifetimes, excitation at 465 nm.



Fig. SI6. Corrected excitation spectra (green line $\lambda_{em} = 642$ nm, red line $\lambda_{em} = 692$ nm) and arbitrarily scaled absorption spectrum (black line) of the final species formed upon titration of **2H-TPyP** with [Ag(SbF₆)].



Fig. SI7. Absorption spectrum of a solution of **Zn-TPyP** in CH_2Cl_2 (1.1 × 10⁻⁵ M) upon addition of 15 equivalents of [Ag(SbF₆)], collected with a UV-VIS-NIR spectrophotometer.



Fig. SI8. Corrected excitation spectra (green line λ_{em} = 630 nm, red line λ_{em} = 690 nm) and arbitrarily scaled absorption spectrum (black line) of the final species formed upon titration of **2H-Ref** with [Ag(SbF₆)].



Fig. SI9. Absorption spectrum of a solution of **Zn-Ref** in CH_2Cl_2 (1.1 × 10⁻⁵ M) upon addition of 15 equivalents of [Ag(SbF₆)], collected with a UV-VIS-NIR spectrophotometer.



Fig. SI10. Cyclic (top panel) and square wave (bottom panel) voltammetry scans of 2H-TPP and Zn-TPP in CH_2Cl_2 solution.



Fig. SI11. Cyclic (top panel) and square wave (bottom panel) voltammetry scans of 2H-TPyP and Zn-TPyP in CH_2Cl_2 solution.



Fig. SI12. Cyclic (top panel) and square wave (bottom panel) voltammetry scans of 2H-Ref and Zn-Ref in CH_2Cl_2 solution.

E (V)

References

1. P. G. Seybold and M. Gouterman, J. Mol. Spectrosc., 1969, **31**, 1-13.