Supporting Information

for

Photophysical properties of free-base and manganese(III) N-confused porphyrins

Li-Li Wang,1 Su-Hong Peng,2,3 Hui Wang,*,1 Liang-Nian Ji,1,4 and Hai-Yang Liu*,2

1 State Key Laboratory of Optoelectronics Materials and Technologies, Sun Yat-Sen University,
   Guangzhou 510275, China

2 Department of Chemistry, South China University of Technology, Guangzhou 510641, China

3 College of Chemistry and Bioengineering, Yichun University, Yichun 336000, China

4 School of Chemistry and Chemical Engineering/MOE Laboratory of Bioinorganic and Synthetic
   Chemistry, Sun Yat-Sen University, Guangzhou 510275, China
**Fig. S1** EADS of the excited states $S_2$, $S_1^*$, and $S_1$ obtained by SVD-GLF analysis of the TA spectra of TPP in toluene. Dash line represents the steady-state absorption spectrum of TPP in toluene.
Fig. S2 EADS (a–d), SAS (e–h), and kinetics (i–l) of the excited states $^5S_2$, $^5S_1^*$, $^5T_1$, and $^7T_1$ of Mn(Cl)TPP with para-H obtained by SVD-GLF analysis of the TA spectra shown in Fig. 5a.
**Fig. S3** Femtosecond TA spectra of NCTPPs in DCM (a) and DMAc (b) and NCH₃NCTPPs in DCM (c) monitored from 0.1 to 40 ps.
**Fig. S4** SAS of NCTPPs in DCM (a) and DMAc (b) obtained by SVD-GLF analysis of the femtosecond TA spectra shown in Fig. 3a and b. SAS with a lifetime of <0.16 ps has instrumental artifacts and is not shown.
Fig. S5 Time profiles of NCTPPs in DCM (a) and DMAc (b). Solid lines are fits of the experimental data.
Fig. S6 Steady-state absorption (solid lines) and emission (dotted lines) spectra of NCH$_3$NCTPPs and NCTPP with para-H in DMAc.
Fig. S7 SAS of NCH$_3$NCTPPs in DCM obtained by SVD-GLF analysis of the femtosecond TA spectra shown in Fig. 3c.
**Fig. S8** Time profiles of NCH$_3$NCTPPs at four selected detected wavelengths. Solid lines are fits of the experimental data.
**Fig. S9** Steady-state absorption spectra of Mn(Cl)TPP and Mn(Cl)NCH$_3$NCTPP with *para*-H in DCM. Inset shows the molecular structures of Mn(Cl)TPP and Mn(Cl)NCH$_3$NCTPP with *para*-H.
Fig. S10 EADS (a–d), SAS (e–h), and kinetics (i–l) of the excited states $^5S_2$, $^5S_1^*$, $^5T_1$, and $^7T_1$ of Mn(Cl)NCH$_3$NCTPP with para-H obtained by SVD-GLF analysis of the femtosecond TA spectra shown in Fig. 5b.
Fig. S11 EADS (a–d), SAS (e–h), and kinetics (i–l) of the excited states $^5S_2$, $^5S_1^*$, $^5T_1$, and $^7T_1$ of Mn(Cl)NCH$_3$NCTPP with ortho-OCH$_3$ obtained by SVD-GLF analysis of the femtosecond TA spectra shown in Fig. 5c.
**Fig. S12** EADS (a–d), SAS (e–h), and kinetics (i–l) of the excited states $^5S_2$, $^5S_1^*$, $^5T_1$, and $^7T_1$ of Mn(Cl)NCH$_3$NCTPP with *para*-Cl obtained by SVD-GLF analysis of the femtosecond TA spectra shown in Fig. 6b. EADS and SAS of the excited state $^5S_2$ may have instrumental artifact.
**Fig. S13** EADS (a–d), SAS (e–h), and kinetics (i–l) of the excited states $^5S_2$, $^5S_1^*$, $^5T_1$, and $^7T_1$ of Mn(Cl)NCH$_3$NCTPP with para-CH$_3$ obtained by SVD-GLF analysis of the femtosecond TA spectra shown in Fig. 6c. EADS and SAS of the excited state $^5S_2$ have instrumental artifact.
Fig. S14 Time profiles of Mn(Cl)TPP (a) and Mn(Cl)NCH₃NCTPPs (b) at four selected detected wavelengths. Solid lines are fits of the experimental data.
Nanosecond Transient Absorption Measurement of N-confused Porphyrin.

The triplet state dynamics of NCTPP with para-H were measured using laser flash photolysis apparatus with 532-nm excitation.\(^1\) The triplet absorption decay curves were well fitted with a single-exponential function convoluted with a Gaussian response function. The triplet quantum yield of NCTPP with para-H was calculated to be 0.30, using TPP in toluene as a reference (\(\Phi_T^{(\text{std})} = 0.80, \varepsilon_T^{(\text{std})} \approx 35000 \text{ M}^{-1}\text{cm}^{-1}\)).\(^1\)\(^2\) Therefore, the time (\(\tau_{\text{ISC}}\)) of intersystem crossing from the \(S_1\) to the \(T_1\) state of NCTPP with para-H can be determined as about 5.0 ns.\(^1\)\(^3\) The \(T_1\)-state lifetime of NCTPP with para-H in deaerated toluene is fitted to be 47.5 \(\mu\text{s}\), which is in agreement with the earlier report.\(^3\)

![Fig. S15](image)

**Fig. S15** Triplet spectra (a) and kinetic (b) of NCTPP with para-H in deaerated toluene. Sample concentration was about 34 \(\mu\text{M}\).
References

