Supporting Information

for

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

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1. $^1$H NMR Spectra of NCH$_3$NCTPPs.

NCTPPs and NCH$_3$NCTPPs were characterized by $^1$H NMR.$^1$ Mn(Cl)NCH$_3$NCTPPs have been characterized by HR-MS spectroscopy.$^1$ The $^1$H NMR spectra of NCH$_3$NCTPPs in CDCl$_3$ were recorded by using a Bruker Avance III 400 MHz spectrometer, which are shown in Figs. S1–S6. The $^1$H NMR chemical shifts (δ) were determined with tetramethylsilane (TMS) as the internal reference and reported in parts per million (ppm). The $^1$H NMR assignments for all protons of NCH$_3$NCTPPs are as followed: 1, the inner CH proton; 2, the inner NH proton; 3, three protons of the $N$-CH$_3$ group; 4, seven peripheral pyrrolic C–H protons; 5, sixteen or twenty $meso$ aryl protons; 6, twelve protons of the substituents of $meso$-phenyl rings. Impurity peaks marked with asterisks may be assigned to be the signals of the residual solvents: *, n-hexane; *, water; *, methanol; *, DCM.$^2$

![Fig. S1 $^1$H NMR spectrum of NCH$_3$NCTPP with para-H recorded in CDCl$_3$.](image-url)
Fig. S2 $^1$H NMR spectrum of NCH$_3$NCTPP with para-Cl recorded in CDCl$_3$.

Fig. S3 $^1$H NMR spectrum of NCH$_3$NCTPP with para-CH$_3$ recorded in CDCl$_3$.

Fig. S4 $^1$H NMR spectrum of NCH$_3$NCTPP with para-OCH$_3$ recorded in CDCl$_3$. 
**Fig. S5** $^1$H NMR spectrum of NCH$_3$NCTPP with *meta*-OCH$_3$ recorded in CDCl$_3$.

**Fig. S6** $^1$H NMR spectrum of NCH$_3$NCTPP with *ortho*-OCH$_3$ recorded in CDCl$_3$. 

The triplet state dynamics of Mn(Cl)NCH$_3$NCTPPs and NCTPP with *para*-H were measured using laser flash photolysis apparatus with 532-nm excitation. 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 ($\Phi_T^{(std)} = 0.80$, $\varepsilon_T^{(std)} \approx 35000 \text{ M}^{-1}\text{cm}^{-1}$). The $T_1$-state lifetime of NCTPP with *para*-H in deaerated toluene is fitted to be 47.5 $\mu$s, which is in agreement with the earlier report. Unfortunately, the $^7T_1$-state absorption of Mn(Cl)NCH$_3$NCTPPs in deaerated DCM were not detected by using the same experimental apparatus.

![Figure S7](image-url)

**Fig. S7** Triplet kinetics (a–e) and spectra (f–j) of NCTPP with *para*-H in deaerated toluene and four Mn(Cl)NCH$_3$NCTPPs in deaerated DCM. Sample concentration was about 34 $\mu$M.

Fig. S8 Steady-state absorption spectra of solvents: (a) $n$-hexane, (b) DCM, (c) methanol, and (d) water.
References


