## **Supporting Information**

for

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

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#### 1. <sup>1</sup>H NMR Spectra of NCH<sub>3</sub>NCTPPs.

NCTPPs and NCH<sub>3</sub>NCTPPs were characterized by <sup>1</sup>H NMR.<sup>1</sup> Mn(Cl)NCH<sub>3</sub>NCTPPs have been characterized by HR-MS spectroscopy.<sup>1</sup> The <sup>1</sup>H NMR spectra of NCH<sub>3</sub>NCTPPs in CDCl<sub>3</sub> were recorded by using a Bruker Avance III 400 MHz spectrometer, which are shown in Figs. S1–S6. The <sup>1</sup>H NMR chemical shifts ( $\delta$ ) were determined with tetramethylsilane (TMS) as the internal reference and reported in parts per million (ppm). The <sup>1</sup>H NMR assignments for all protons of NCH<sub>3</sub>NCTPPs are as followed: 1, the inner CH proton; 2, the inner NH proton; 3, three protons of the *N*-CH<sub>3</sub> 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.<sup>2</sup>



Fig. S1 <sup>1</sup>H NMR spectrum of NCH<sub>3</sub>NCTPP with *para*-H recorded in CDCl<sub>3</sub>.



Fig. S2 <sup>1</sup>H NMR spectrum of NCH<sub>3</sub>NCTPP with *para*-Cl recorded in CDCl<sub>3</sub>.



Fig. S3 <sup>1</sup>H NMR spectrum of NCH<sub>3</sub>NCTPP with *para*-CH<sub>3</sub> recorded in CDCl<sub>3</sub>.



Fig. S4 <sup>1</sup>H NMR spectrum of NCH<sub>3</sub>NCTPP with *para*-OCH<sub>3</sub> recorded in CDCl<sub>3</sub>.



Fig. S5 <sup>1</sup>H NMR spectrum of NCH<sub>3</sub>NCTPP with *meta*-OCH<sub>3</sub> recorded in CDCl<sub>3</sub>.



Fig. S6 <sup>1</sup>H NMR spectrum of NCH<sub>3</sub>NCTPP with ortho-OCH<sub>3</sub> recorded in CDCl<sub>3</sub>.

#### 2. Nanosecond Transient Absorption Measurement of N-confused Porphyrins.

The triplet state dynamics of Mn(Cl)NCH<sub>3</sub>NCTPPs and NCTPP with *para*-H were measured using laser flash photolysis apparatus with 532-nm excitation.<sup>3</sup> 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  $(\Phi_{T(std)} = 0.80, \varepsilon_{T(std)} \approx 35000 \text{ M}^{-1}\text{cm}^{-1})$ .<sup>3, 4</sup> The T<sub>1</sub>-state lifetime of NCTPP with *para*-H in deaerated toluene is fitted to be 47.5 µs, which is in agreement with the earlier report.<sup>5</sup> Unfortunately, the <sup>7</sup>T<sub>1</sub>-state absorption of Mn(Cl)NCH<sub>3</sub>NCTPPs in deaerated DCM were not detected by using the same experimental apparatus.



**Fig. S7** Triplet kinetics (a–e) and spectra (f–j) of NCTPP with *para*-H in deaerated toluene and four Mn(Cl)NCH<sub>3</sub>NCTPPs in deaerated DCM. Sample concentration was about 34 μM.

## 3. Steady-state Absorption Spectra of Solvents.



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

## References

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