Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

New highly brominated Mn-porphyrin: A good catalyst for activation of inert C-H bond

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The free-base porphyrin (H_2T3,5DMPP) (Fig. S1) was characterized by ^{1}H NMR (Fig. S2), which showed that the porphyrin contained two methoxy (-OCH_3) groups in the two *meta-meso*aryl positions of the macrocycle. No chlorin emerged during the synthesis; indeed, integration of the signal relative to the β-pyrrole hydrogens evidenced the presence of eight hydrogen atoms. The signal at 1.55 refers to water in $CDCl_3$.

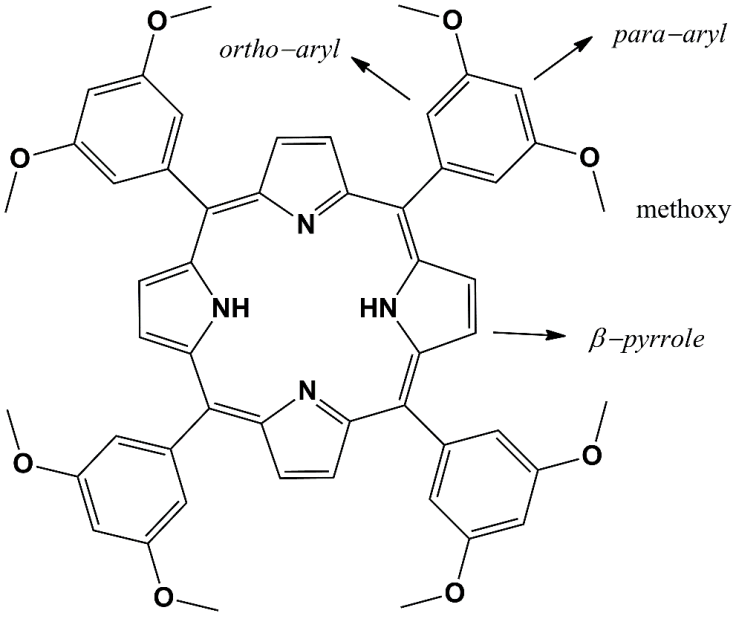

Figure S1. Structural representation of the free-base porphyrin (H_2T3,5DMPP).

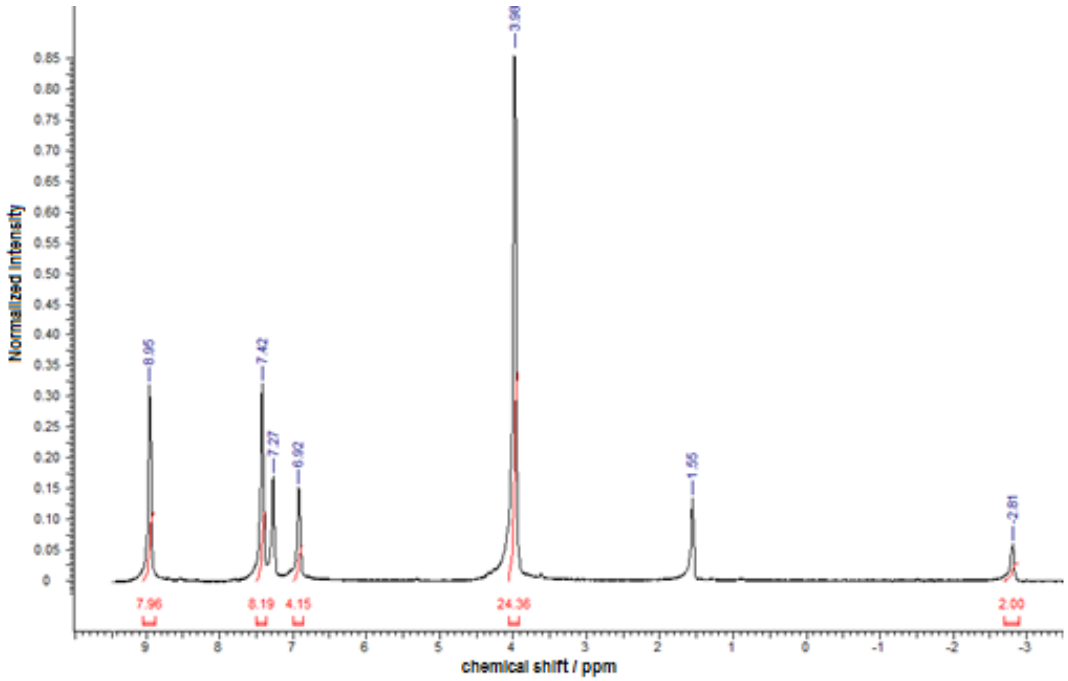

Figure S21. ^{1}H NMR spectrum of H_2T3,5DMPP recorded at 200 MHz, in $CDCl_3$. δ 8.95 (s, 8H, β-pyrrole), 7.42 (s, 8H, *ortho*-aryl), 6.92 (s, 4H, *para*-aryl), 3.98 (s, 24H,methoxy), -2.81 (s, 2H, pyrrole NH).

The UV-vis spectrum of Cat.2 in DMF (Fig. S3) is typical of a brominated MnP bearing Mn(II).

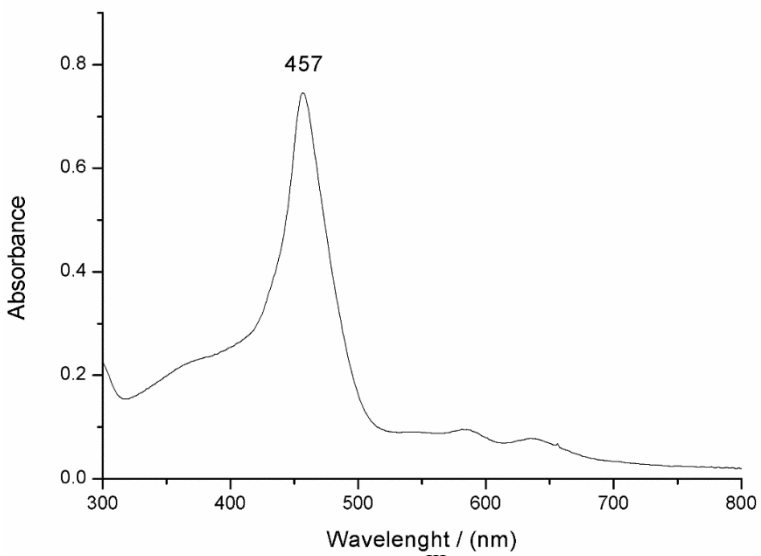

Figure S3. UV-vis spectrum of [$Mn^{III}Br_{12}$T3,5DMPP]Cl in DMF.

FTIR results confirmed formation of the free-base porphyrin, Cat.1, and Cat.2 (Figure S4).

[Mn^{III}T3,5DMPP]Cl: FTIR in KBr (cm^{-1}): (1593) δ C=C; (1206) ν C-O-C; (1155) ν OCH_3; (1009) δ Mn-N (pyrrole).

[$Mn^{III}Br_{12}$T3,5DMPP]Cl: FTIR in KBr (cm^{-1}): (1569) δ C=C; (1277) δ C_{β}-Br; (1210) ν C-O-C, (1155) ν OCH_3; (1022) δ Mn-N(pyrrole).

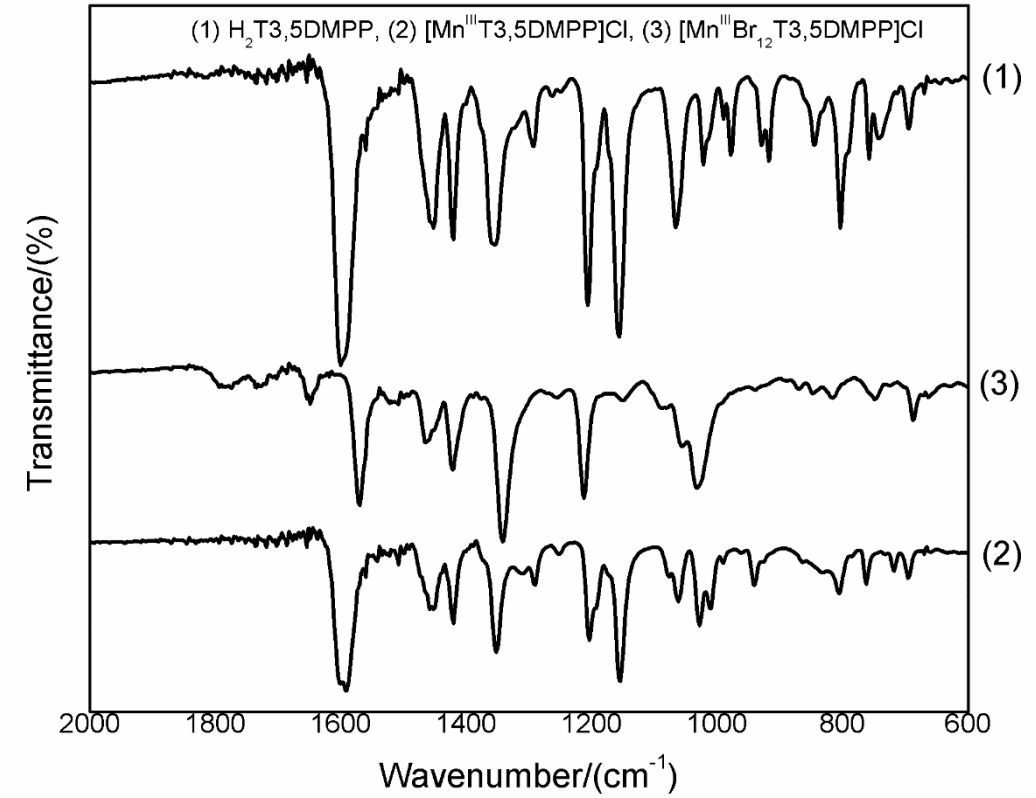

Figure S4. FTIR spectrum of H_2T3,5DMPP (1), [Mn^{III}T3,5DMPP]Cl (2); and [$Mn^{III}Br_{12}$T3,5DMPP]Cl (3) in KBr pallets.

The mass spectrum obtained for Cat.2 by electrospray ionization (ESI) in the positive mode revealed a peak at m/z 1886.02, with 100% relative intensity (Figure S5).

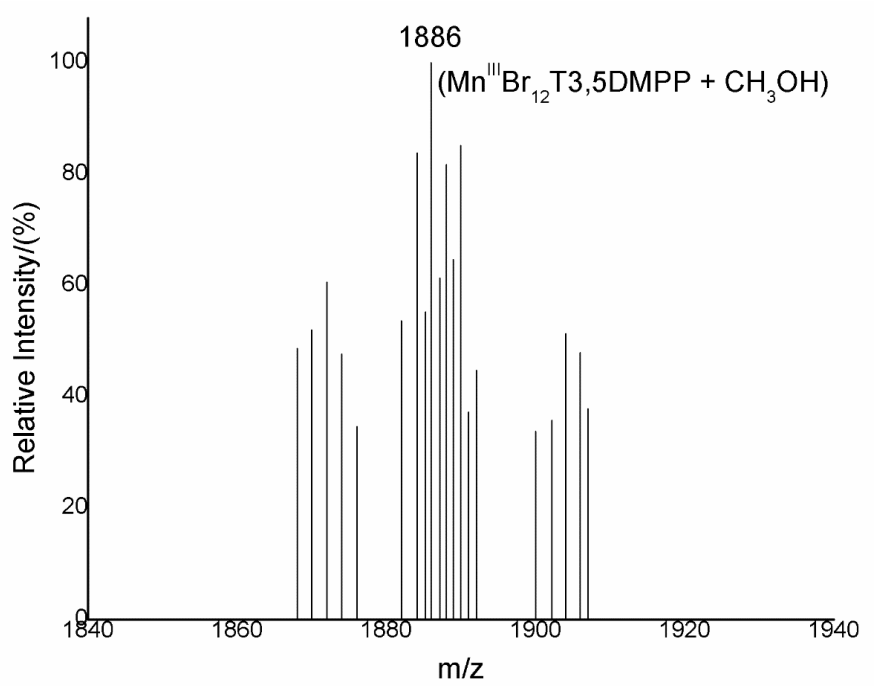

Figure S5. (a) Mass spectrum of [$Mn^{III}Br_{12}$T3,5DMPP]Cl. Analysis conducted in CH_3OH with the ESI-MS operating in the positive mode.