Electronic supplementary information

UV-Vis spectra. Fig. S1 shows the UV-Vis spectra observed by the stepwise addition of NaN_3. The Soret band shifts from 393 to 423 nm as revealed by the blue(0.0 equiv) and red(4.0 equiv) lines. In contrast, the broadband characteristic to the porphyrin radical centered at 650 nm exhibits a complicated change as given in the inset of Fig. S1. The signal has gradually increased in intensity by the addition of 0.0(blue) to 1.0(green) equiv of N_3^-. On further addition of N_3^- from 1.0 to 4.0 equiv, it has then decreased as shown by the spectral change from the green to the red line. No further change has been observed even by the addition of 20 equiv of N_3^- (not shown). These results suggest that $[Fe^{III}(TMP^{\cdot})(ClO_4)_2]$ is first converted to radical cationic mono-azide and then to the bis-azide(**2**). The absence of the isosbestic point in Fig. S1 also supports the stepwise formation of **2**. It should be noted that a very broad band ascribed to the porphyrin radical is still observable between 650 and 750 nm even after the addition of 20 equiv of N_3^-, suggesting that **2** maintains some radical character.

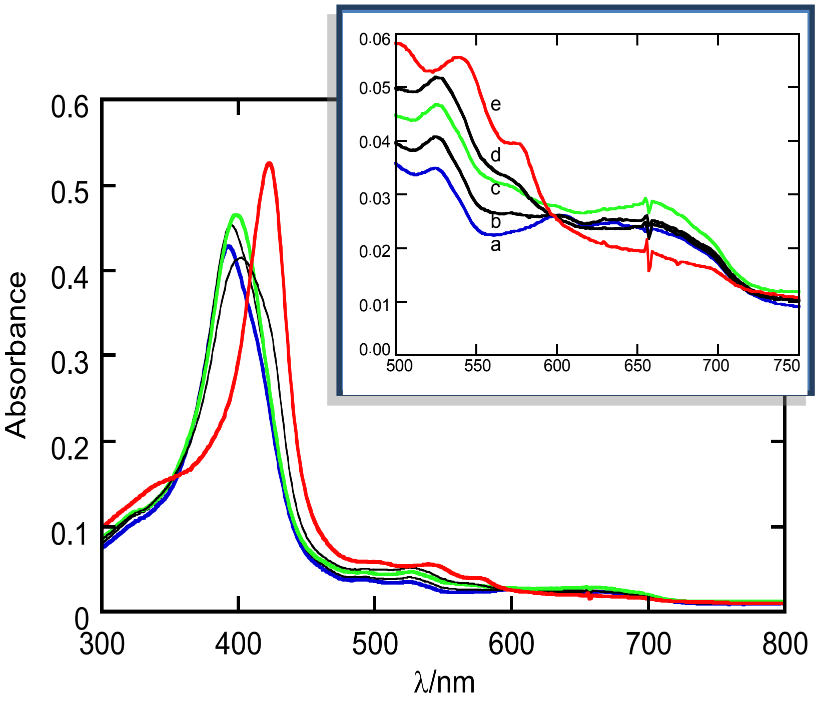

Fig. S1. UV-Vis spectral change of $[Fe^{III}(TMP^{\cdot})(ClO_4)_2]$ observed by the stepwise addition of NaN_3 at 193 K in CH_2Cl_2 solution: (a) 0.0(blue line), (b) 0.5, (c) 1.0(green line), (d) 2.0, and (e) 4.0 equiv (red line). Inset: 500-750 nm region.

^{1}H NMR Spectra

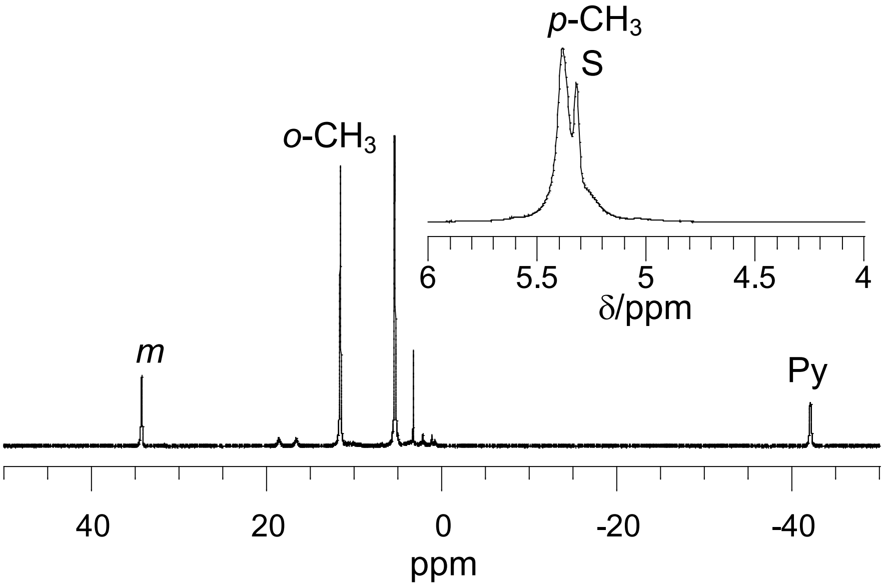

Fig S2. ^{1}H NMR spectra obtained by the addition of 2.0 equiv of NaN_3(in CD_3OD) into the CD_2Cl_2 solution of $[Fe^{III}(TMP^{\cdot})(ClO_4)_2]$ at 193 K. The 4 to 6 ppm region is shown in the inset. Signals labeled as Py, *m*, and S indicate the pyrrole-H, *meta*-H, and solvent signals, respectively. The OH signal of CD_3OH is overlapping with the p-CH_3 signal.

Mössbauer Parameters

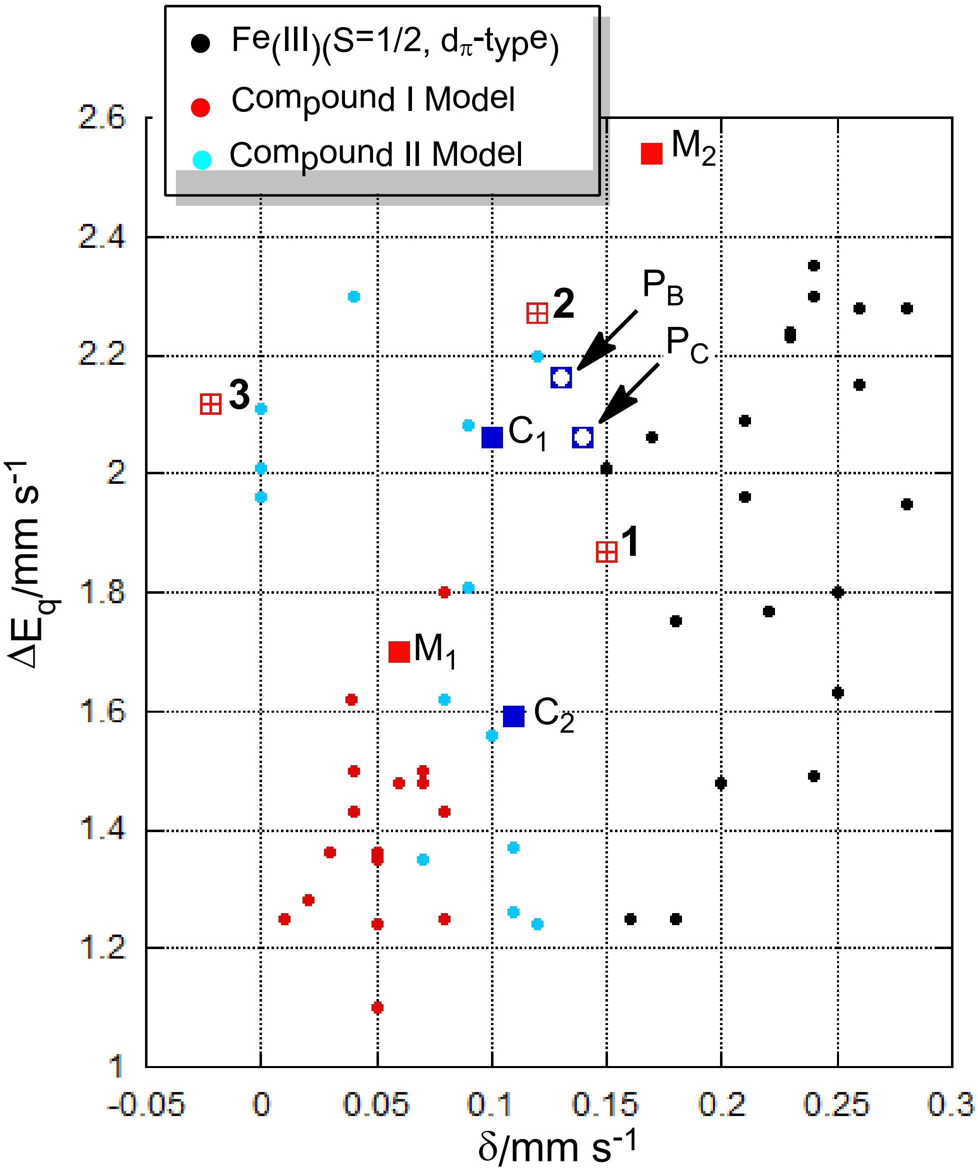

Fig. S3. Correlation between isomer shift(δ) and quadrupole splitting(ΔE_q) in various synthetic low-spin Fe(III)(d_π-type) and Fe(IV) porphyrin complexes. Compound I and II model indicate the Fe^{IV}=O porphyrin radical cation and Fe^{IV}=O porphyrin, respectively. Numbers **1**, **2**, and **3** correspond to $[Fe(TMP)(HIm)_2]^{2+}$, $[Fe(TMP)(N_3)_2]$, and $[Fe(TMP)(OCH_3)_2]$, respectively. M1 and M2 stand for the heme 1 and heme 2 in the reactive intermediates of MauG.[18] C1 and C2 indicate the major and minor components of the ferryl form in CPO.[22] P_B and P_C are the ferryl forms of $P450_{BM3}$ and $P450_{CAM}$, respectively.[23]

References for the Mössbauer parameters of Fe(IV) porphyrin complexes given in Fig. S3:

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