Supporting Information

Thermal isomerization of N-bridged cobalt corrole complexes through transiently formed axial carbenoid

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Figure S1. The magnified $^1$H NMR spectra (in CDCl$_3$) of the purified product obtained by the reaction of 1 with EDA (1 equiv): (a) 9–10 ppm; (b) 1.5–4.5 ppm.
Figure S2. $^{13}$C NMR spectra (in CDCl$_3$) of the purified product obtained by the reaction of 1 with EDA (1 equiv).
Figure S3. $^1$H-$^1$H COSY spectrum (in CDCl$_3$) of the purified product obtained by the reaction of 1 with EDA (1 equiv).
Figure S4. HMQC spectrum of the purified product obtained by the reaction of 1 with EDA (1 equiv).
Figure S5. $^1$H NMR spectrum after photoirradiation of the isolated $N$-bridged complex in benzene-$d_6$ (Xe lamp with a cut filter (< 340 nm), under the air); (a) after 1 h, (b) after 2 h.
Figure S6. All possible structures of the \( N \)-bridged complexes.
**Figure S7.** The aromatic fashions considered in DFT calculations (The axial moieties on Co$^{3+}$ are omitted in the structures shown above). In aromatic fashion A, the nitrogen on A or D ring participates in the aromatic conjugation system, whereas, in aromatic fashion B, the nitrogen atom on B or C ring contributes to the aromatic conjugation system.
Figure S8. Optimized structures (aromatic fashion A) determined by DFT calculation. The left and right figures in each isomer demonstrate top and side view, respectively. For simplification in calculation, the ethyl groups in the framework were omitted and the ethyl ester was replaced with methyl ester. The energy values are normalized at the heat formation energy of Isomer II-4.
Figure S9. Optimized structures (aromatic fashion B) determined by DFT calculation. The left and right figures in each isomer demonstrate top and side view, respectively. For simplification in calculation, the ethyl groups in the framework were omitted and the ethyl ester was replaced with methyl ester. The energy values are normalized at the heat formation energy of Isomer II-4.
Figure S10. The $^1$H NMR spectra for the reaction of 1 with EDA (1 equiv) in benzene-$d_6$: (a) Whole spectrum collected just after addition of EDA; (b) Spectrum in the low field region.
**Figure S11.** HMQC spectrum in the reaction of 1 with EDA (1 equiv) in benzene-$d_6$ (collected after 12 h since the reaction started).