

Supplementary Materials

General

Third-generation (G_3 , where the subscript denotes the generation) poly(propylene imine) (PPI) dendrimer ($G_3\text{-NH}_2$) was purchased from SyMO-Chem B.V. (Eindhoven, The Netherlands). Polyethyleneimine 10000 ($M_w = 10,000$) was purchased from the Junsei Chemical Co., Ltd (Tokyo, Japan). All other chemicals were purchased from Wako Pure Chemicals (Tokyo, Japan), the Tokyo Kasei Co. (Tokyo, Japan), and Sigma-Aldrich Inc. (St. Louis, MO, USA) and used after appropriate purification. ^1H NMR and ^{13}C NMR spectra were obtained using a JEOL GSX-270 or JNM-ESC400 spectrometer and chemical shifts (δ) were reported in ppm downfield from tetramethylsilane. UV-vis spectra were obtained using a JASCO V-660 (Tokyo, Japan) and Fourier transformed infrared spectra (FTIR) were acquired on a JASCO FTIR-4100 spectrometer (Tokyo, Japan). Electron spin resonance (ESR) spectra were recorded at the Xband using a Bruker EMX-10/12 spectrometer (Kanagawa, Japan). Cu K-edge X-ray absorption data were collected in the quick mode and recorded in the transmission mode at the BL14B2 and BL01B1 stations attached to the Si(311) monochromator at SPring-8 (JASRI), Harima, Japan (Proposal Nos. 2012B1869, 2013B1414, 2014A1513, 2014B1235). The data analysis was carried out using the REX2000 program ver. 2.5.7 (Rigaku, Tokyo, Japan). Powder X-ray diffraction (XRD) patterns were recorded using a Philips X'Pert-MPD (Eindhoven, The Netherlands) with Cu-K α radiation. Elemental analysis was carried out using CHN corder MT-5 (Yanako, Tokyo, Japan) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were performed using ICPS-8100 (Shimadzu, Kyoto, Japan). The continuous flow reactor (column oven and stainless steel column) was purchased from YMC Co., Ltd. (Kyoto, Japan).

Preparation of Cu^{2+} (mono)-Magadiite

Cu^{2+} (mono)-magadiite was prepared in the same manner as reported by Kim *et al.* [1]. A Cu mononuclear complex $\text{Cu}(\text{ethylenediamine})_2(\text{ClO}_4)_2$ was synthesized by addition of ethylenediamine (1.3 mL, 20 mmol) to the MeOH solution containing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mmol), and the resulting solution was refluxed for 4 h. After the reaction, the solution was cooled to room temperature to precipitate the purple solid. The precipitate was filtered and washed with ethanol to afford $\text{Cu}(\text{ethylenediamine})_2(\text{ClO}_4)_2$. Next, $\text{Cu}(\text{ethylenediamine})_2(\text{ClO}_4)_2$ (100 μmol) was dissolved in EtOH (10 mL), and magadiite (0.4 g) was added into the above solution. The resulting mixture was further stirred for 6 h at 313 K. After the reaction, the obtained solid was filtered, washed with EtOH (100 mL), and dried to afford a light purple powder.

Reuse Experiment of $G_4\text{-Cu}^{2+}_{12}$

1a (0.5 mmol) was reacted using fresh $G_4\text{-Cu}^{2+}_{12}$ (Cu: 5 μmol) in 4 mL α,α,α -trifluorotoluene (TFT), after which the synthesized **2a** was removed from the reaction mixture by filtration. **1a** (0.5 mmol) was added to the filtered TFT solution, still containing the original $G_4\text{-Cu}^{2+}_{12}$, and the mixture was vigorously stirred at 323 K for 18 h. By repeating this process, it was determined that the $G_4\text{-Cu}^{2+}_{12}$ catalyst could be reused without significant loss of its activity and selectivity; the yield of **2a** from the first reaction, as determined by ^1H NMR, was 96%, while the isolated yields were 83% (fresh catalyst), and 93% (first reuse).

ESR Measurement

The spectra were recorded at the Xband using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 10.0 mW. $G_4\text{-Cu}^{2+}_n$ ($n = 2, 8, 12, 16, \text{ and } 24$; Cu: $0.5 \mu\text{mol}$) in CHCl_3 (0.1 mL) was placed in a quartz ESR tube under an Ar atmosphere, and measured at 298 K. In the case of the heterogeneous Cu catalysts, the Cu catalyst (Cu: $0.5 \mu\text{mol}$) was introduced in a quartz ESR tube, evacuated at room temperature, and subjected to analysis at 298 K.

XAFS Measurement

The Cu K-edge XAFS spectrum of $G_4\text{-Cu}^{2+}_{12}$ was recorded in transmission mode at room temperature. Fourier transforms of k^3 -weighted EXAFS spectra were performed in the $4 \text{ \AA} < k < 12 \text{ \AA}$ range to obtain radial structural functions. Curve-fitting analysis was performed with the inverse FT of the $1.2 \text{ \AA} < R < 2.4 \text{ \AA}$ range. The coordination numbers (CN) and interatomic distances (R) were estimated by curve-fitting analysis using Cu-Cl and Cu-N shell parameters obtained from reference samples of CuCl_2 [2] and $\text{Cu}(\text{ImH})_4\text{SO}_4$ [3], respectively. In the case of Cu^{2+} -magadiite, the spectrum was recorded at 10 K using a cryostat. Curve-fitting analysis was conducted with the inverse FT of the $1.0 \text{ \AA} < R < 3.3 \text{ \AA}$ range, and the CN and R were estimated by curve-fitting analysis using Cu-N/O and Cu-Cu shell parameters obtained from a reference sample of $[\text{Cu}(\text{OH})\text{TMEDA}]_2\text{Cl}_2$ [4].

Product Identification

The reaction products were identified by ^1H and ^{13}C NMR and, in each case, the chemical shifts of the products were in agreement with those reported in the literature, as summarized below.

3,3',5,5'-Tetramethyldiphenoquinone (DPQ, **2a**) (CAS-RN 4906-22-3) [5]

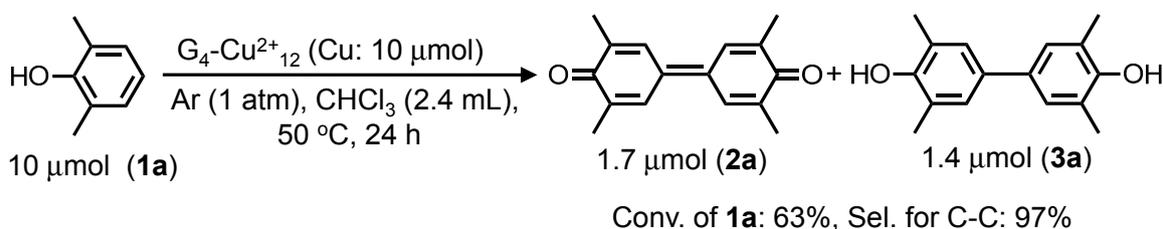
3,3',5,5'-Tetramethylbiphenyl-2,2'-diol (TMBP, **3a**) (CAS-RN 2417-04-1) [5]

Poly(2,6-dimethylphenylene ether) (PPE, **4a**) (CAS-RN 42397-25-1) [6]

3,3',5,5'-Tetraisopropylidiphenoquinone (**2b**) (CAS-RN 2178-51-0) [5]

3,3'-Di-*tert*-butyl-5,5'-dimethyldiphenoquinone (**2c**) (CAS-RN 2417-00-1) [5] (Likely a mixture of *cis* and *trans* isomers [7]).

Scheme and Figures



Scheme S1. $G_4\text{-Cu}^{2+}_{12}$ -catalyzed oxidative coupling of DMP under an Ar atmosphere.

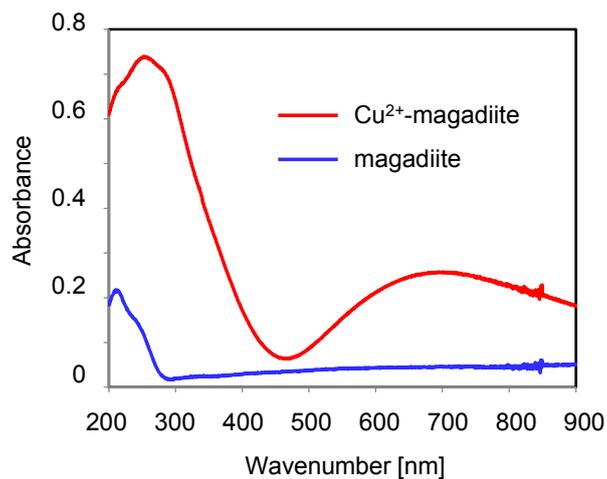


Figure S1. UV spectra of Cu^{2+} -magadiite and magadiite.

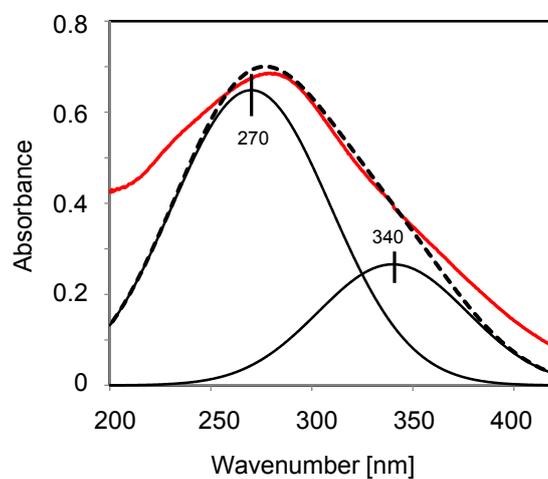


Figure S2. UV-vis spectrum of LMCT band of Cu^{2+} -magadiite.

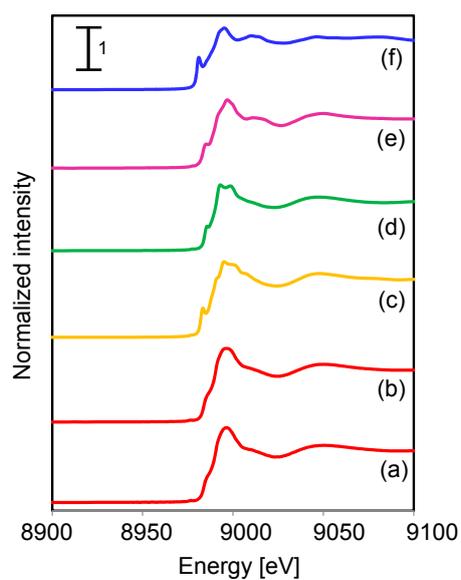


Figure S3. Cu K-edge XANES spectra of (a) Cu^{2+} -magadiite, (b) Cu^{2+} -magadiite (used), (c) $[\text{Cu}(\text{OH})\text{TMEDA}]_2\text{Cl}_2$, (d) Cu^{2+} (mono)-magadiite, (e) CuO , and (f) Cu_2O .

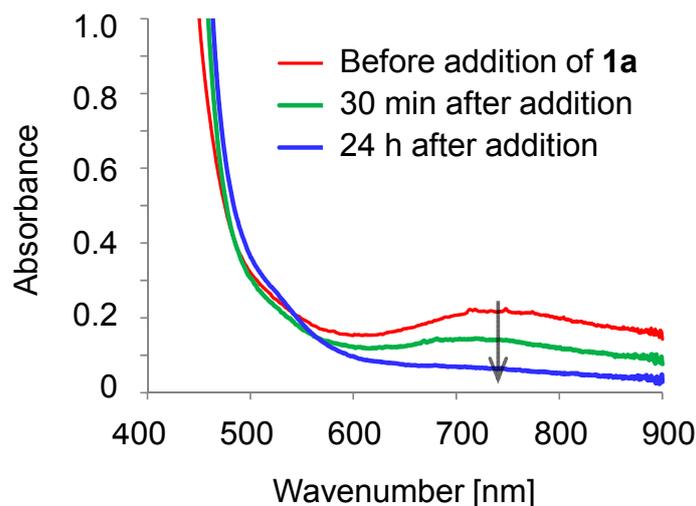


Figure S4. Simultaneous *in situ* UV-vis spectra recorded during $G_4\text{-Cu}^{2+}_{12}$ -catalyzed oxidative coupling of DMP under an Ar atmosphere as shown in Scheme S1.

References

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