Supplementary Materials

General

Third-generation (G₃, where the subscript denotes the generation) poly(propylene imine) (PPI) dendrimer (G₃-NH₂) was purchased from SyMO-Chem B.V. (Eindhoven, The Netherlands). Polyethyleneimine 10000 (Mw = 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 ¹³C 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 X-band 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-Kα 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 Cu²⁺(mono)-Magadiite

Cu²⁺(mono)-magadiite was prepared in the same manner as reported by Kim et al. [1]. A Cu mononuclear complex Cu(ethylenediamine)₂(ClO₄)₂ was synthesized by addition of ethylenediamine (1.3 mL, 20 mmol) to the MeOH solution containing Cu(ClO₄)₂·6H₂O (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 Cu(ethylenediamine)₂(ClO₄)₂. Next, Cu(ethylenediamine)₂(ClO₄)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 G₄-Cu²⁺₁₂

1a (0.5 mmol) was reacted using fresh G₄-Cu²⁺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 G₄-Cu²⁺₁₂, and the mixture was vigorously stirred at 323 K for 18 h. By repeating this process, it was determined that the G₄-Cu²⁺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. G4-Cu$^{2+}$n (n = 2, 8, 12, 16, and 24; Cu: 0.5 µmol) in CHCl₃ (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 µmol) 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 G₄-Cu²⁺₁₂ was recorded in transmission mode at room temperature. Fourier transforms of $k^3$-weighted EXAFS spectra were performed in the 4 Å < $k$ < 12 Å range to obtain radial structural functions. Curve-fitting analysis was performed with the inverse FT of the 1.2 Å < R < 2.4 Å 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 CuCl₂ [2] and Cu(ImH)₄SO₄ [3], respectively. In the case of Cu²⁺-magadiite, the spectrum was recorded at 10 K using a cryostat. Curve-fitting analysis was conducted with the inverse FT of the 1.0 Å < R < 3.3 Å 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 [Cu(OH)TMEDA]₂Cl₂ [4].

Product Identification

The reaction products were identified by $^1$H 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'-Tetraisopropyldiphenoquinone (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](image)

**Scheme S1.** G₄-Cu²⁺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) [Cu(OH)TMEDA]$_2$Cl$_2$, (d) Cu$^{2+}$(mono)-magadiite, (e) CuO, and (f) Cu$_2$O.
Figure S4. Simultaneous in situ UV-vis spectra recorded during \( \text{G}_4\text{-Cu}^{2+}\text{Cu}_{12}\)-catalyzed oxidative coupling of DMP under an Ar atmosphere as shown in Scheme S1.

References

1. Choy, J.-H.; Kim, D.-K.; Park, J.-C.; Choi, S.-N.; Kim, Y.-J. Intracrystalline and electronic structure of copper(II) complexes stabilized in two-dimensional aluminosilicate. *Inorg. Chem.* **1997**, *36*, 189–195.

2. Wells, A.F. 333. The crystal structure of anhydrous cupric chloride, and the stereochemistry of the cupric atom. *J. Chem. Soc.* **1947**, 1670–1675.

3. Fransson, G.; Lundberg, B.K.S. Metal complexes with mixed ligands. 4. The crystal structure of tetrakisimidazole Cu(II) sulphate, \( \text{Cu(C}_3\text{H}_4\text{N}_2)_4\text{SO}_4 \). *Acta Chem. Scand.* **1972**, *26*, 3969–3976.

4. Tromp, M.; van Strijdonck, G.P.F.; van Berkel, S.S.; van den Hoogenband, A.; Feiters, M.C.; de Bruin, B.; Fiddy, S.G.; van der Eerden, A.M.J.; van Bokhoven, J.A.; van Leeuwen, P.W.N.M.; et al. Multitechnique approach to reveal the mechanism of copper(II)-catalyzed arylation reactions. *Organometallics* **2010**, *29*, 3085–3097.

5. Liao, B.-S.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. Efficient oxidative coupling of 2,6-disubstituted phenol catalyzed by a dicopper(II) complex. *Dalton Trans.* **2012**, *41*, 1158–1164.

6. Gui, L.; Wang, H.; Shentu, B.; Weng, Z. Synthesis and characterization of low-molecular-weight poly(2,6-dimethyl-1,4-phenylene oxide) in water. *J. Appl. Poly. Sci.* **2013**, *128*, 2919–2926.

7. Rieker, A.; Kessler, H. Notiz zur rotationsisomerie bei p-diphenochinonen. *Chem. Ber.* **1969**, *102*, 2147–2149.