

Electronic Supplementary Information

**Regioselective Oxidative Coupling of 2,6-Dimethylphenol to
Tetradiphenoquinone Using Polyamine Dendrimer-encapsulated Cu Catalysts**

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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. (The Netherlands), and fourth and fifth generation PPI dendrimers (G_4 - and $G_5\text{-NH}_2$) were synthesized from the $G_3\text{-NH}_2$ by the divergent method.^{1S} Surface modification of the $G_x\text{-NH}_2$ ($x = 3, 4, \text{ and } 5$) with 3,4,5-triethoxybenzoyl chloride groups was carried out using a previously reported procedure.^{2S} Polyethyleneimine 10000 ($M_w = 10,000$) was purchased from the Junsei Chemical Co., Ltd. All other chemicals were purchased from Wako Pure Chemicals, the Tokyo Kasei Co. and Sigma-Aldrich Inc. and used after appropriate purification.^{3S} ^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. Fourier transformed infrared spectra (FTIR) were acquired on a JASCO FTIR-4100 spectrometer and UV-vis spectra were obtained using a JASCO V-660. Cu K-edge X-ray absorption data were collected in the quick mode and recorded at room temperature in the transmission mode at the BL14B2 station attached to the Si(311) monochromator at SPring-8 (JASRI), Harima, Japan (Proposal No. 2012B1869). Data analysis was carried out using the REX2000 program ver. 2.5.7 (Rigaku). 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 ^{4S} and $\text{Cu}(\text{ImH})_4\text{SO}_4$ ^{5S}.

Preparation of PPI dendrimer-encapsulated Cu complexes

The procedure for the preparation of the $G_4\text{-Cu}^{2+}_{12}$ PPI dendrimer-encapsulated Cu complex, which is typical of all the syntheses, was as follows. CuCl_2 (5 μmol) and $G_4\text{-TEBA}$ (Figure S1, 0.42 μmol) were added to 1.5 mL of $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:2 v/v) and the

mixture was stirred for 2 h under an Ar atmosphere at 25 °C. The resulting solution was evaporated to afford $G_4\text{-Cu}^{2+}_{12}$ as a brown, waxy solid.

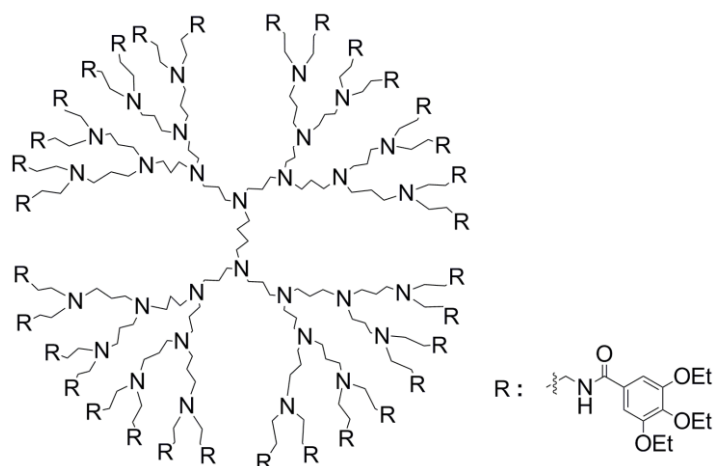


Fig. S1 Structure of the G_4 -PPI dendrimer modified with triethoxybenzamide groups (G_4 -TEBA).

Oxidative coupling of 2,6-dimethylphenol (**1a**) to 3,3',5,5'-tetramethyldiphenoquinone (**2a**) using $G_4\text{-Cu}^{2+}_{12}$

1a (0.5 mmol) was added to 4 mL of a CHCl_3 solution of $G_4\text{-Cu}^{2+}_{12}$ (5 μmol Cu) and the mixture was stirred under O_2 (1 atm) at 50 °C. Following completion of the reaction, hexadecane was added as an internal standard and the mixture was treated with aqueous 6 N HCl, after which the organic phase was separated and characterized by ^1H NMR.

Substrate scope of $G_4\text{-Cu}^{2+}_{12}$

The high selectivity for C–C coupling by $G_4\text{-Cu}^{2+}_{12}$ was exemplified in the reaction of other 2,6-disubstituted phenols. $G_4\text{-Cu}^{2+}_{12}$ efficiently catalyzed the C–C selective coupling reaction of a 2,6-substituted phenol incorporating isopropyl groups (**1b**) to afford a 97% yield of 3,3',5,5'-tetraisopropyldiphenoquinone (**2b**). In addition, 6-*t*-butyl-*o*-cresol (**1c**) was also selectively converted to 3,3'-di-*t*-butyl-5,5'-dimethyldiphenoquinone (**2c**) in 95% yield.

$G_4\text{-Cu}^{2+}_{12}$ was not, however, an effective catalyst for the coupling reaction of unsubstituted phenol or for phenol derivatives with electron-withdrawing chlorine atom substituents. Other Cu catalyst systems investigated to date were also unable to promote the oxidative coupling reactions of phenol and 2,6-dichlorophenol.^{6S, 7S}

Product purification following the gram scale synthesis of **2a**

Following the coupling reaction, the supernatant of the reaction mixture was passed through a silica gel column (Wakogel C-200). Byproducts were first removed by elution with hexane/ethyl acetate (3:2) and **2a** was subsequently eluted with hexane/ CH_2Cl_2 (1:3). Evaporation of the solvent gave **2a** in 97% yield (1.04 g).

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

1a (0.5 mmol) was reacted using fresh $G_4\text{-Cu}^{2+}_{12}$ (5 μmol Cu) 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 50 °C 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).

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'-Tetramethyldiphenylquinone (DPQ, **2a**) (CAS-RN 4906-22-3) (Ref. 7S)

3,3',5,5'-Tetramethylbiphenyl-2,2'-diol (TMBP, **3a**) (CAS-RN 2417-04-1) (Ref. 7S)

2,6-Dimethylbenzoquinone (DMQ, **4a**) (CAS-RN 527-61-7) (Ref. 8S)

Poly(2,6-dimethylphenylene ether) (PPE, **5a**) (CAS-RN 42397-25-1) (Ref. 9S)

3,3',5,5'-Tetraisopropyldiphenylquinone (**2b**) (CAS-RN 2178-51-0) (Ref. 7S)

3,3'-Di-*tert*-butyl-5,5'-dimethyldiphenylquinone (**2c**) (CAS-RN 2417-00-1) (Likely a mixture of *cis* and *trans* isomers, Ref. 10S)

UV-vis absorption measurement of $G_x-Cu^{2+}_n$

UV-vis titrations of G_4 -TEBA with $CuCl_2$ were carried out in air at 25 °C. In order to measure the LMCT of the dendrimer- Cu^{2+} species, 2.4 mL of a 0.17 mM solution of G_4 -TEBA in $CH_3CN/CHCl_3$ (1:2 v/v) were added to a quartz cuvette (1 cm optical path) equipped with a cap and a stir bar. A 20 μ L quantity of a 20 mM solution of $CuCl_2$ in $CH_3CN/CHCl_3$ (1:2 v/v), sufficient to give a 1:1 equivalent ratio between Cu and G_4 -TEBA, was then added to the stirred dendrimer solution within the cuvette using a micropipette (Figure S2). When measuring the d-d transition of the Cu^{2+} species, 12 mL of an 4.2 μ M solution of G_4 -TEBA in $CH_3CN/CHCl_3$ (1:2 v/v) in a cuvette with a 5 cm optical path, and 50 μ L of a 1.0 mM solution of $CuCl_2$ (again resulting in a 1:1 Cu to G_4 -TEBA equivalent ratio) in $CH_3CN/CHCl_3$ (1:2 v/v) were used (Figure S3). In processing the resulting UV-vis spectra, the absorption spectrum of a reference sample of G_4 -TEBA was subtracted. Based on titration of G_4 -TEBA with $CuCl_2$ in $CH_3CN/CHCl_3$ solution in this manner, the maximum number of Cu^{2+} ions encapsulated within a G_4 -TEBA dendrimer was estimated to be 32 (Figure S4).^{11S} In the same way, the maximum number of Cu^{2+} ions situated in the

G_3 - and G_5 -TEBA dendrimers was estimated to be 16 and 48, respectively (Figures S5 and S6). Also, each spectrum of $G_x\text{-Cu}^{2+}_n$ ($x = 3-5$) exhibited a sigmoid behavior in the region of smaller ratio of $\text{Cu}/G_x\text{-TEBA}$ ($n \leq 6$ for G_3 , $n \leq 12$ for G_4 , and $n \leq 16$ for G_5 , respectively). It seems that the sigmoid behavior in the titration curve is peculiar to dendrimer-encapsulated metal complex.^{11S} These phenomena might be ascribed to the differences of the environment around Cu^{2+} species within $G_x\text{-Cu}^{2+}_n$.

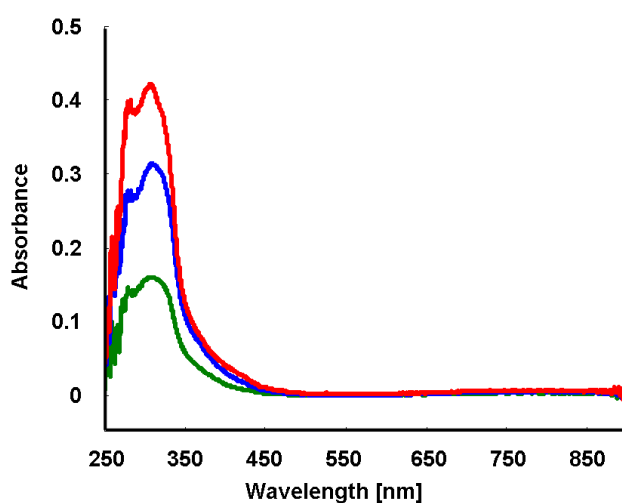


Fig. S2 UV-vis spectra of $G_4\text{-Cu}^{2+}_n$ ($n = 4$ (green), 8 (blue) and 12 (red)). (Note that the absorption spectrum of a G_4 -TEBA reference sample has been subtracted from each of these spectra.)

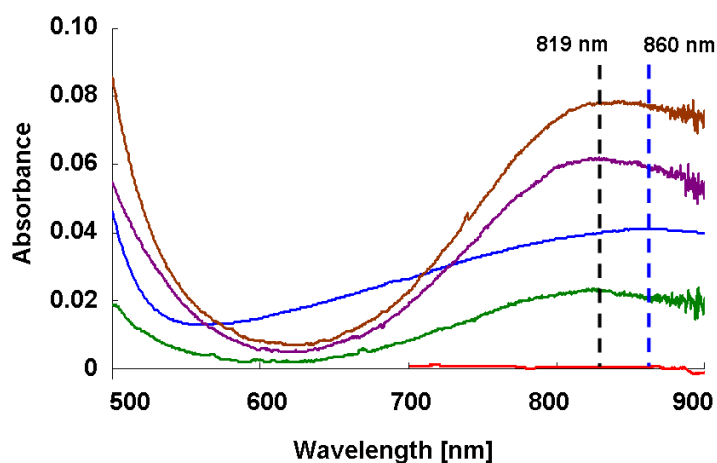


Fig. S3 UV-vis spectra of G_4 -TEBA (red), CuCl_2 (blue), $G_4\text{-Cu}^{2+}_{12}$ (green), $G_4\text{-Cu}^{2+}_{24}$ (purple) and $G_4\text{-Cu}^{2+}_{36}$ (brown). (Note that the absorption spectrum of a G_4 -TEBA reference sample has been subtracted from each of these spectra.)

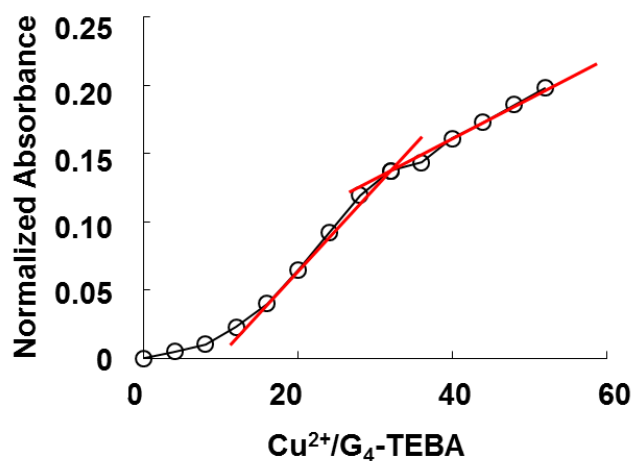


Fig. S4 Titration curve of G₄-Cu²⁺_n at 819 nm. Absorbance values have been normalized to the initial volume of 12 mL.

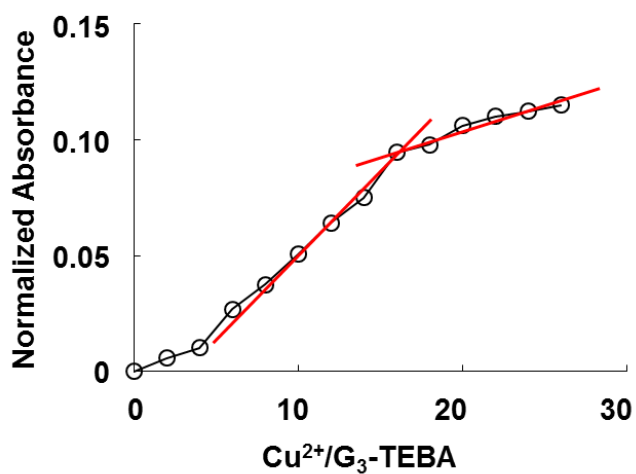


Fig. S5 Titration curve of G₃-Cu²⁺_n at 819 nm. Absorbance values have been normalized to the initial volume of 12 mL.

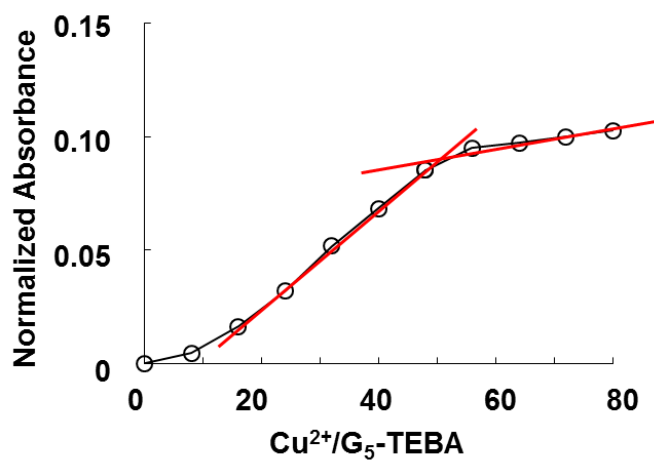


Fig. S6 Titration curve of G₅-Cu²⁺_n at 819 nm. Absorbance values have been normalized to the initial volume of 12 mL.

Cu K-edge XAFS experiments

The X-ray absorption near edge structure (XANES) spectra of $G_4\text{-Cu}^{2+}_{12}$ exhibited an edge peak at 8982 eV, a characteristic feature of the copper(II) ion with nitrogen ligands^{12S} (Figure S7). This peak may be assigned to the shakedown satellite involving a $1s \rightarrow 4p$ transition with simultaneous LMCT.

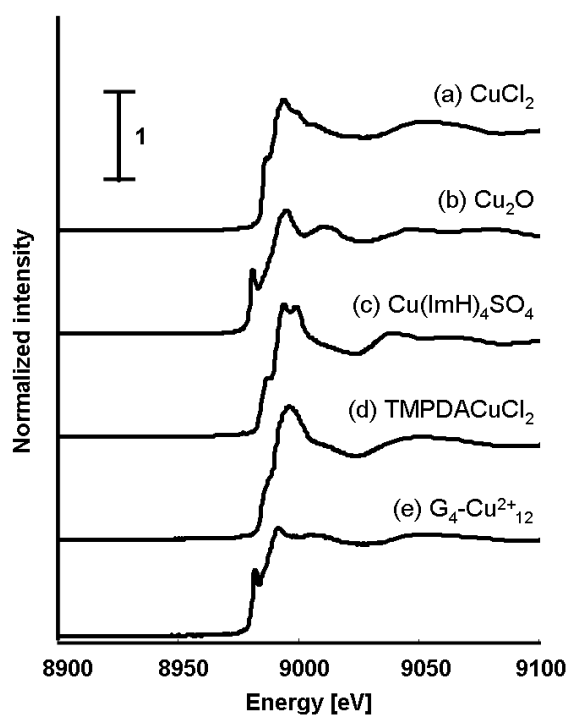


Fig. S7 FT of EXAFS spectra of various Cu complexes.

Table S1 Curve-fitting analysis of Cu K-edge EXAFS data for $G_4\text{-Cu}^{2+}_{12}$ ^[a]

Shell	CN ^[b]	R ^[c] / Å	σ^2 ^[d] / Å ²
Cu-Cl	2.0	2.23	0.0059
Cu-N	2.0	1.98	0.0010

[a] The region of 1.2-2.4 Å in FT of samples was inversely transformed.
[b] Coordination number. [c] Interatomic distance. [d] Debye-Waller factor

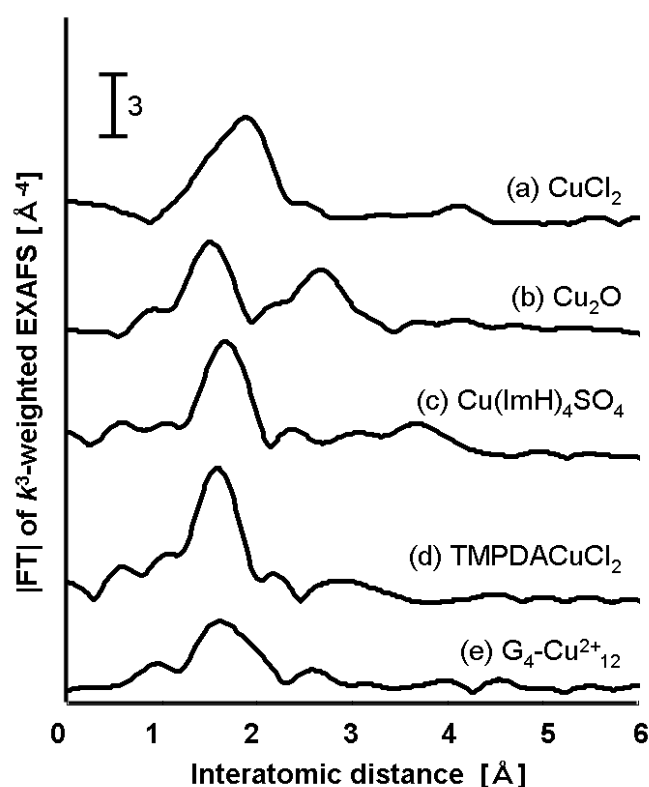


Fig. S8 Cu K-edge XANES spectra of various Cu complexes.

Preparation and FTIR studies of G₄-Cu²⁺_n(N₃)

G₄-TEBA encapsulated-Cu azide complexes (G₄-Cu²⁺_n(N₃)) were prepared as follows. A 200 μL quantity of a 5.0 × 10⁻⁵ mM MeOH solution of NaN₃ was added to 1 mL of a MeOH solution of G₄-Cu²⁺_n (10 μmol Cu) at 40 °C and the mixture stirred for 4 h. Next, 1 mL of *n*-BuOH was added and the MeOH was evaporated under reduced pressure. The residue was diluted with 10 mL CH₂Cl₂ and filtered using a disk membrane filter (0.20 μm PTFE membrane, 25 mm diameter), after which the solution was concentrated under reduced pressure to afford G₄-Cu²⁺_n(N₃). FTIR spectra of the G₄-Cu²⁺_n(N₃) complexes were acquired at room temperature in CHCl₃ using a 0.1 mm liquid cell with NaCl windows. Spectra were recorded at a resolution of 1 cm⁻¹ and 32 scans were summed for each spectrum.

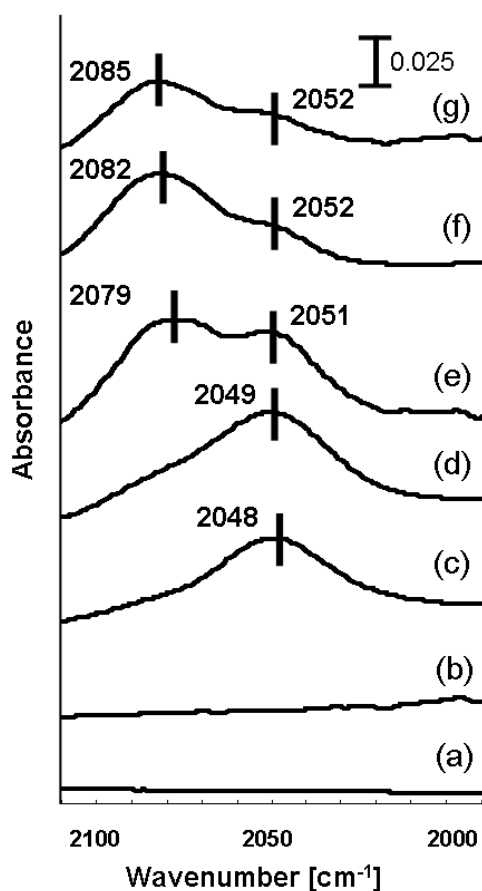
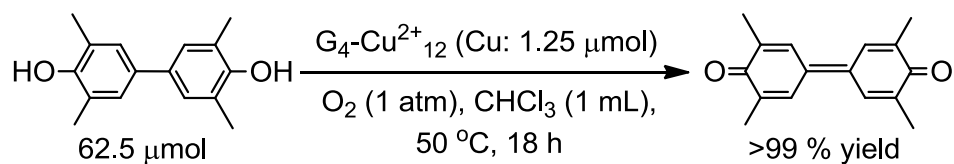


Fig. S9 FTIR spectra of (a) G₄-TEBA, (b) G₄-Cu²⁺₁₂, (c) G₄-Cu²⁺₂(N₃), (d) G₄-Cu²⁺₆(N₃), (e) G₄-Cu²⁺₁₂(N₃), (f) G₄-Cu²⁺₁₆(N₃) and (g) G₄-Cu²⁺₂₄(N₃).

Oxidation of TMBP to DPQ catalyzed by G₄-Cu²⁺₁₂

The oxidation of TMBP was performed using G₄-Cu²⁺₁₂ as the catalyst and it was found that G₄-Cu²⁺₁₂ produced the desired product DPQ in quantitative yield (Scheme S1). This result supports our theory that TMBP is a plausible reaction intermediate in the C–C coupling of DMP to DPQ.



Scheme S1 Oxidation of TMBP catalyzed by G₄-Cu²⁺₁₂.

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