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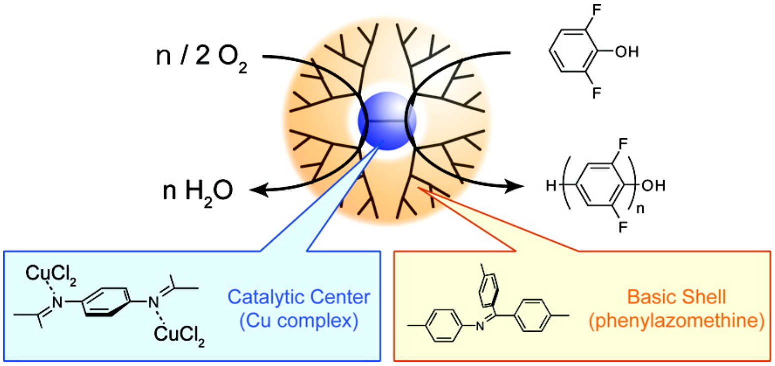

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Additive-Free Synthesis of Poly(phenylene oxide): Aerobic Oxidative Polymerization in a Base-Condensed Dendrimer Capsule

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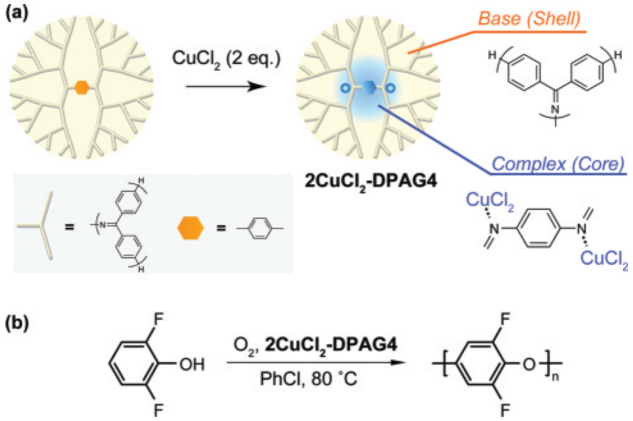
Aerobic oxidation catalyzed by copper complexes is a totally green process for the preparation of various organic products because this procedure only requires the abundant and cheap oxygen in the air.[1] As a prime example, the polymerization of phenols by oxidation produces poly(phenylene oxides) (PPOs) which are well-known and important materials used as engineering plastics.[2] In spite of their convenience for the industrial production of PPOs, catalysts are still required for their improvement from the standpoint of atom economy. Indeed, a large amount of base (e.g., pyridine) is essential for the efficient reaction; therefore, the complete removal of these additives is desired. One of keys for the efficient catalysis is a strong oxidizing power sufficient to oxidize electron-deficient phenols, such as 2,6-difluorophenol,[3] even under very diluted conditions. For this requirement, the transient formation of a dioxygen binding binuclear structure (Cu_2O_2) is very important.[4] In addition, a strong basic condition is indispensable to facilitate the proton removal from the phenol during electron transfer. For the additive-free synthesis, both requirements should be satisfied in a nanoreactor, which contains catalysts, bases, and sufficient space without any external additives.

The dendrimer effect on the catalysis is now regarded not only for shape selectivity or recyclability but also for higher reactivity with the appropriate design.[5] Dendritic phenylazomethines (DPAs)[6] are expected to be specifically suitable as the ligand for the copper catalyst. They have a perfectly monodispersed molecular weight and structure with imine nitrogens (C═N) acting as weak Schiff bases which can coordinate to various metal compounds. Due to its strong gradient property of basicity along the layer-by-layer architecture, metal complexes are forced to bind to the deepest layer.[6a,b] This catalytic center is not completely shielded because the rigid dendrons create a sparse shell through which substrates can pass.[6d] Furthermore, uncoordinated units in the dendrimer can act as super-condensed bases around the catalytic center at which the local concentration of bases is calculated to be 2.7 mol L^{-1}. Herein, we demonstrate the unprecedented additive-free oxidative polymerization of 2,6-difluorophenol under very diluted catalytic conditions.

Preparation of the catalyst was very simple (Scheme 1). A 2 M amount of $CuCl_2$ as the acetonitrile solution was added to the solution containing DPAG4 in chloroform/acetonitrile (1/1). This solution resulted in a quick color change and afforded their 2:1 complex ($2CuCl_2$−DPAG4). We could determine the stoichiometry and fine structure of the dendrimer−copper complexes upon the addition of $CuCl_2$ based on a UV−vis titration analysis (see Supporting Information) similar to that in a previous report.[3] This analysis clearly demonstrated that the copper(II) complex also binds to the dendrimer through a stepwise process that discriminates each layer (generation). Finally, we could determined the fine structure of the catalyst ($2CuCl_2$−DPAG4), in which two copper(II) ions bind to two branch units closest to the core. The crystal structure of a model complex and EXAFS spectra showed that the complexation was centered at the imine nitrogen in each monomer of the dendrimer (Supporting Information). The dendrimer complex solution was evaporated to dryness, and the resulting powder was used for the polymerization of 2,6-difluorophenol.

Scheme 1. (a) Preparation of the Catalyst by the Complexation between DPAG4 and $CuCl_2$ and (b) Aerobic Oxidation of 2,6-Difluorophenol Producing F_2PPO



The oxidative polymerization was performed in the presence of the catalyst (1/140 molar amount based on the monomer) in chlorobenzene (2 mL) under an O_2 atmosphere (1 atm) at 80 °C. During the reaction, the conversion ratio was monitored by GC, showing the steady consumption of the monomer. At 72 h, the polymerization was terminated and the reaction mixture was poured into excess methanol containing 5% HCl. After washing with methanol, the precipitate of poly[2,6-difluorophenylene oxide] (F_2-PPO) was produced. The product was characterized by ^{1}H, ^{13}C, and ^{19}F NMR measurements in which the head (OH terminal), intermediate, and tail (Ph terminal) monomers were individually recognized. The weight-average molecular weight (M_w) of the obtained polymer was estimated to be 32 000 by a triple-detection analysis based on size exclusion chromatography (TriSEC). We isolated the polymers of relatively low molecular weights using preparative SEC and analyzed by ^{19}F NMR. The ratio of the integrals between each ^{19}F signal (F_1, head; F_2, intermediate; F_3, tail) gave information about the averaged molecular weight of the polymer. The calculated value of the molecular weight ($M_n = 4000$) from the NMR result was in good agreement with that estimated from the TriSEC analysis ($M_n = 4500$, $M_w = 4600$).

The generation number of the dendrimer strongly affects the catalytic performance. Under the same conditions ([Cu]/[monomer] = 1/140 without any bases), DPAG1, G2, and G3 did not afford the PPO products (Figure 1a). Similarly, the PPO synthesis using conventional catalysts was also performed under the same conditions (atmosphere, temperature, and concentration of monomers). Indeed, the copper(I)−pyridine complex (CuCl−Py) did not afford any polymerized products when it was used under dilute conditions (1/140 molar amount for the monomer). Even if a large amount of the catalyst was used, the yield at 72 h was still low (46%).

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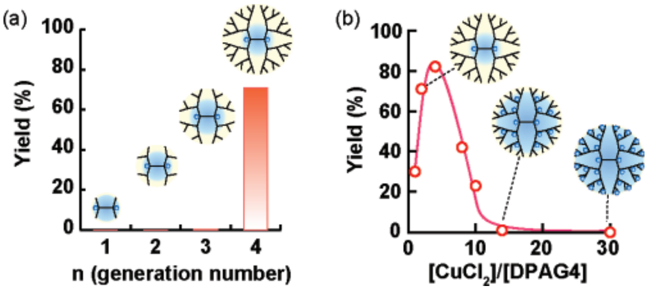

Figure 1. (a) Generation number dependence of the PPO yields using 2CuCl$_2$−DPAG*n* catalysts. (b) Dependence of the yields on the stoichiometry ([CuCl$_2$]/[DPAG4]). Each experiment was performed using the same amount of CuCl$_2$ (1/140 for the monomer).

Table 1. Aerobic Oxidative Polymerization of 2,6-Difluorophenol

entry	catalyst	[Cu]^a	base	yield^b (%)	additive^c (g)
1	2CuCl$_2$−DPAG4	1/140		71	0.22
2	4CuCl$_2$−DPAG4	1/140		82	0.11
3	2CuCl$_2$−PAMAM	1/140		0	
4	CuCl−Py	1/20	Py	46	11.5
5	CuCl−Py	1/140	Py	0	
6	CuCl$_2$−TMED	1/20	Ph$_2$Py^d	71	1.40
7	CuCl$_2$−TMED	1/140	Ph$_2$Py^d	0	
8	CuCl$_2$−TMED	1/140		0	

[a] Molar ratio of the copper complexes vs monomers. [b] Total yield of the polymers obtained as methanol-insoluble part. [c] Total amount of catalysts and bases (except for monomers) to obtain 1 g of polymer product. [d] Concentration of the 2,6-diphenylpyridine was 0.25 mol L^{-1}.

Although the copper(II)−TMED (CuCl$_2$−TMED) complex acted as a better catalyst than CuCl−Py, it required a large excess amount of 2,6-diphenylpyridine (0.25 mol L^{-1} Ph$_2$Py, 115 mg in 2 mL of PhCl) as a proton-removing reagent for its efficient operation. In sharp contrast to these conventional catalysts, 2CuCl$_2$−DPAG4 showed a higher catalytic activity even in the absence of any additive (pyridines). This catalyst efficiently polymerizes the monomer with molecular oxygen (O$_2$) by itself. It should be noted that 1/140 amount of the catalyst is sufficient to complete the polymerization within 72 h. Actually, we determined a higher turnover frequency (TOF) of the dendrimer catalyst (2CuCl$_2$−DPAG4) than that of CuCl$_2$−TMED at the beginning of the polymerization. This advantage was emphasized when the catalyst concentration decreased to 1/140. The dendrimer complex retained their catalytic activity even at a very low concentration, while the conventional catalyst lost it (Supporting Information). These results strongly suggest a concentration effect of the dendritic capsule, in which the copper complexes and bases (imines) are filled with a fine nanostructure. A rough estimation of the nanoenvironment inside the dendrimer based on its hydrodynamic volume suggested a very high local concentration of the copper complex (180 mM) and base (2.7 mol L^{-1}), which is about 10 times greater than the typical condition for the conventional catalysis (0.25 mol L^{-1}). The yields obtained under the various conditions of stoichiometry ([CuCl$_2$]/[DPAG4]) clearly demonstrated that the peripheral base capsule around the catalytic center is also indispensable for its efficient catalysis (Figure 1b). Because the rigid dendritic shell prevents its deformation,[7] two copper cores and monodentate ligands, which are necessary for the efficient reaction,[1,4] are closely arranged in the nanoreactor. Such a catalytic activity was not achieved using a similar copper-containing dendrimer based on the PAMAM (polyamidoamine) architecture.[8] The low activity should originate from the local flexibility and ligand structure of PAMAM, resulting in capturing the copper ions through a multisite complexation.

An advantage using the DPA nanocapsule is the high concentration of these chemical elements without deformation and deactivation. Furthermore, the weak basicity of the ligands is one of the reasons for the strong oxidizing power. Although the phenylazomethine−copper complex is labile in solution, we could manage this problem using the rigid dendritic architecture. This may provide the facile electron transfer between the copper and phenols which is known to be the rate-limiting process during conventional catalysis (Supporting Information).[9] It should be noted that the additive-free catalysis is enabled only when the condensed catalytic center is encapsulated in a highly condensed base capsule.

In summary, we could build a well-defined molecular nanoreactor based on a dendrimer structure. The copper complexes and base units are packed in the dendrimer with a core−shell configuration. It is important that the hybrid structure should be designed with a rigid architecture so as not to deactivate the catalytic center. Due to the rigid π-conjugating structure of the phenylazomethine dendrimer,[4] the metal center can retain its fine conformation. The additive-free aerobic oxidation using the dendrimer catalysts drastically decreased the total waste required to produce the PPO derivatives. Finally, the total mass of additives to obtain 1 g of polymer using the dendrimer catalyst could be decreased to 1/100 because it does not need any bases.

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Supporting Information Available: Additional data and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Gamez, P.; Aubel, P. G.; Driessen, W. L.; Reedijk, J. *Chem. Soc. Rev.* **2001**, *30*, 376−385.

(2) (a) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 6335−6336. (b) Hay, A. S. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 505−517. (c) Higashimura, H.; Fujisawa, K.; Kubota, M.; Kobayashi, S. *J. Polym. Sci. A: Polym. Chem.* **2005**, *43*, 1955−1962.

(3) (a) Oyaidzu, K.; Kumaki, Y.; Saito, K.; Tsuchida, E. *Macromolecules* **2000**, *33*, 5766−5769. (b) Ikeda, R.; Tanaka, H.; Uyama, H.; Kobayashi, S. *Macromolecules* **2000**, *33*, 6648−6652. (c) Ikeda, R.; Maruichi, N.; Tonami, H.; Tanaka, H.; Uyama, H.; Kobayashi, S. *J. Macromol. Sci., Pure Appl. Chem.* **2000**, *37*, 983−995.

(4) (a) Karlin, K. D.; Kaderli, S.; Zuberbühler, A. D. *Acc. Chem. Res.* **1997**, *30*, 139−147. (b) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047−1076.

(5) (a) Helms, B.; Fréchet, J. M. J. *Adv. Synth. Catal.* **2006**, *348*, 1125−1148. (b) Zhang, X.; Xu, H.; Dong, Z.; Wang, Y.; Liu, J.; Shen, J. *J. Am. Chem. Soc.* **2004**, *126*, 10556−10557. (c) Fujihara, T.; Obora, Y.; Tokunaga, M.; Sato, H.; Tsuji, Y. *Chem. Commun.* **2005**, 4526−4528.

(6) (a) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509−511. (b) Yamamoto, K.; Imaoka, T. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 621−626. (c) Higuchi, M.; Shiki, S.; Ariga, K.; Yamamoto, K. *J. Am. Chem. Soc.* **2001**, *123*, 4414−4420. (d) Imaoka, T.; Tanaka, R.; Yamamoto, K. *Chem.*−*Eur. J.* **2006**, *12*, 7328−7336. (e) Satoh, N.; Cho, J-S.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104.

(7) (a) Ballauff, M.; Likos, C. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 2998−3020. (b) Rosenfeldt, S.; Dingenouts, N.; Pötschke, D.; Ballauff, M.; Berresheim, A. J.; Müllen, K.; Lindner, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 109−112. (c) Wind, M.; Saalwächter, K.; Wiesler, U. M.; Müllen, K.; Spiess, H. W. *Macromolecules* **2002**, *35*, 10071−10086.

(8) (a) Ottaviani, M. F.; Bossmann, S.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 661−671. (b) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355−7356. (c) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877.

(9) Tsuchida, E.; Nishide, H.; Nishiyama, T. *Makromol. Chem.* **1975**, *176*, 1349−1358.

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