Synthesis of Copper Phthalocyanine-containing Hyperbranched Polymer Starting from 1,2-Bis(3,4-dicyanophenoxy)benzene and CuCl

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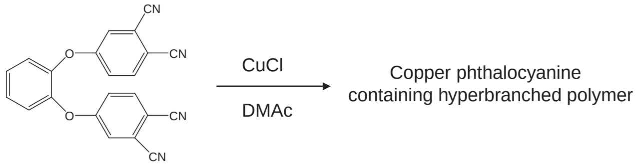
A novel soluble hyperbranched polymer with copper phthalocyanine (CuPc) was successfully prepared by copper fusion technique of 1,2-bis(3,4-dicyanophenoxy)benzene and CuCl. The structure of copper phthalocyanine-containing hyperbranched polymer confirmed by IR, UV–vis absorption spectra. This polymer showed good solubility in DMF, DMAc, and high thermal stability.

Phthalocyanines (Pc) have become one of the most extensively studied classes of materials owing to their unique structure, their extremely high thermal stability, and their potential for commercial exploitation.[1] Copper phthalocyanine (CuPc) is widely used as an hole-transport layer (HTL) and buffer layer in organic light-emitting diodes (OLEDs). One method of some commercial significance for the manufacture of CuPc involves the reaction of phthalonitrile (benzene-1,2-dicarbonitrile) with copper metal or a copper salt at elevated temperatures either in the melt phase or in high boiling solvents. This phthalonitrile route to CuPc reported initially by Linstead and co-workers,[2,3] has been the subject of a number of investigations,[4,5] and attempts have been made to explain the reaction sequence by which the phthalocyanine system is constructed from individual phthalonitrile units.[6] But most CuPc derivatives are used as vapor-deposited thin films, or composite materials dispersed in polymer binder, because of their insufficient solubility in organic solvents. The solubility or processability of the CuPc could be improved by introduction of the flexible units such as phenyl alkyl groups or ether linkages at exterior of CuPc ring system.[7–9] Hyperbranched polymers have received much attention in recent years, because of their unique architecture. These polymers show attractive properties such as low viscosity and excellent solubility in organic solvents,[10–12] and prepared by one-step polymerization of AB*x* monomers, thus seem to be suitable for large scale production. As compared to their linear analogues, various functional groups can be introduced into their structures to create new functional polymeric materials.[13] In this paper, we report the synthesis of a novel soluble copper phthalocyanine containing hyperbranched polymer starting from 1,2-bis(3,4-dicyanophenoxy)benzene and CuCl. The monomer was designed to enhance the solubility of corresponding polymers by not only introduction of flexible ether units in the backbone but also introductions of ortho disubstituted structure. As shown in Ref. 14, catechol and 4-nitrophthalonitrile were allowed to react through nucleophilic substitution in the presence of potassium carbonate to give 1,2-bis(3,4-dicyanophenoxy)benzene in 64% yield. The structure was assigned on the basis of NMR, IR spectra.[15] All of the peaks in the NMR spectra were well-assigned to estimated structure. The IR spectrum showed characteristic absorptions corresponding to the 2230 $\mathrm{cm^{-1}}$ of –CN and no bands at around 1542, 1392 $\mathrm{cm^{-1}}$ assignable to the $-NO_2$ of 4-nitrophthalonitrile and 3400 $\mathrm{cm^{-1}}$ assignable to –OH of catechol. Melting point was 191 °C (measured by DSC, lit. 188–189 °C).[16]

Copper phthalocyanine-containing hyperbranched polymer (**1**) was prepared by copper fusion technique[2,3] as follows (Scheme 1).[17] Structure of **1** was identified by IR, UV–vis absorption spectra. The IR spectrum of **1** showed characteristic absorptions corresponding to the 1771, 746 $\mathrm{cm^{-1}}$ of CuPc and 2231 $\mathrm{cm^{-1}}$ of –CN.[18] At the result of solubility test, **1** was soluble in DMF, DMAc while CuPc itself was not soluble in these solvents. The UV–vis absorption spectra of **1** has peak at 611 and 678 nm which was the same as derivative CuPc peak[8] (Figure 1). It means that CuPc is successfully introduced in hyperbranched polymer chains.

The result of gel permeation chromatography (GPC) measurement of **1** showed that weight-average molecular weight (M_w) was 12.8×10^3, and M_w/M_n was 1.37 with detector (Refractive Index) against PS standard. The thermal properties of **1** was examined by thermogravimetry analysis (TGA). It showed excellent thermal stability, the 10% weight loss was at 371 °C (Figure 2).

Contents of CuPc unit in **1** was calculated based on the following observation. Quantitative analysis is based on the application of the BEER-LAMBERT LAW, which is given by



Scheme 1. Synthesis of copper phthalocyanine-containing hyperbranched polymer.

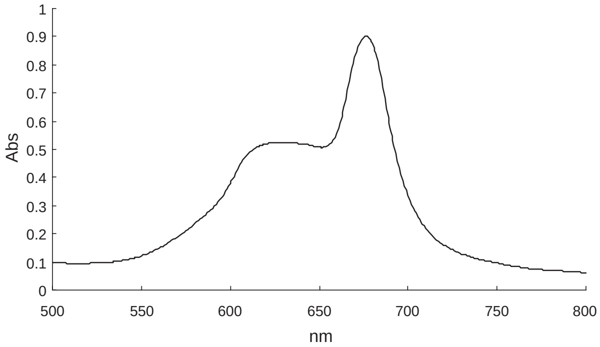


Figure 1. UV–vis absorption spectra of copper phthalocyanine-containing hyperbranched polymer.

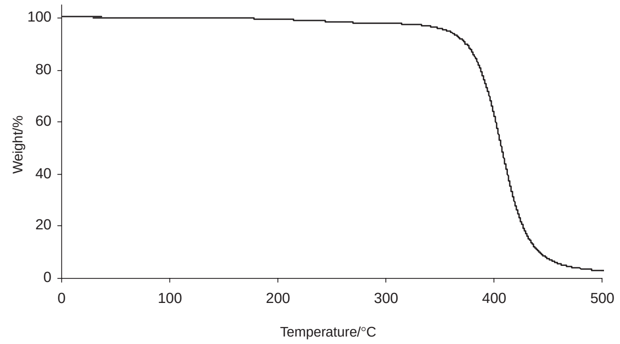


Figure 2. TGA spectrum of copper phthalocyanine-containing hyperbranched polymer in air.

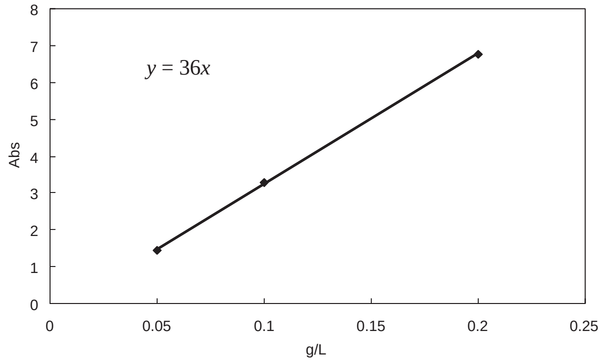
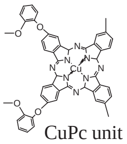


Figure 3. *a* of copper phthalocyanine-containing hyperbranched polymer.

$$A = acl \tag{1}$$

where A is absorbance, a is absorption coefficient ($\mathrm{L\,g^{-1}\,cm^{-1}}$), c is the concentration of the solute (g/L), l is the path length of the sample (cm).

If the monomer ideally reacted with CuCl, the structure of the repeating unit is shown as below (CuPc unit). *a* value of CuPc unit in this structure was calculated as $a = 205$ using molecular weight of CuPc unit and CuPc *a* (281 at 678 nm[19]). Hyperbranched polymer *a* obtained in this study was found as $a = 36$ at 678 nm (Figure 3). CuPc unit contents in hyperbranched polymer calculated using the equation bellow. We have approximated disassociated CuPc at about 17%, in all about 20% or more of CuPc is contained in the hyperbranched polymer.



CuPc unit

$$\text{CuPc unit contents in hyperbranched polymer /\%} = \frac{\text{Hyperbranched polymer } a}{\text{CuPc unit } a} \times 100 \tag{2}$$

In conclusions, copper phthalocyanine-containing hyperbranched polymer was synthesized starting from 1,2-bis(3,4-dicyanophenoxy)benzene and CuCl. This polymer showed high thermal stability and good solubility in DMF, DMAc. This polymer is expected as good solution processable materials for hole-transport materials and buffer layers in OLEDs as well as other microelectronics fields.

References and Notes

1 R. M. Christie, D. D. Deans, *J. Chem. Soc., Perkin Trans II*, **1989**, 193.

2 R. P. Linstead, A. R. Lowe, *J. Chem. Soc.* **1934**, 1022.

3 C. E. Dent, R. P. Linstead, *J. Chem. Soc.* **1934**, 1027.

4 M. T. Reetz, N. Jiao, *Angew. Chem.* **2006**, *118*, 2476.

5 H. Z. Lecher, H. T. Lacey, H. P. Orem, *J. Am. Chem. Soc.* **1941**, *63*, 1326.

6 F. Baumann, B. Bienert, G. Rösch, H. Vollmann, W. Wolf, *Angew. Chem.* **1956**, *68*, 133.

7 N. B. McKeown, *Adv. Mater.* **1999**, *11*, 67.

8 J. J. Burack, J. D. LeGrange, J. L. Markham, W. Rockward, *Langmuir* **1992**, *8*, 613.

9 G. J. Clarkson, N. B. Mckeown, K. E. Treacher, *J. Chem. Soc., Perkin Trans. 1* **1995**, 1817.

10 C. S. Hong, M. Jikei, R. Kikuchi, M. Kakimoto, *Macromolecules* **2003**, *36*, 3174.

11 Y. H. Kim, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

12 G. Yang, M. Jikei, M. Kakimoto, *Macromolecules* **1999**, *32*, 2215.

13 K. Yamanaka, M. Jikei, M. Kakimoto, *Macromolecules* **2000**, *33*, 1111.

14 J. Hao, M. Jikei, M. Kakimoto, *Macromolecules* **2002**, *35*, 5372.

15 ^{1}H NMR (DMSO-d_6, ppm) 8.02 (dd, 2H, $J = 9$ Hz, $J = 0.9$ Hz), 7.75 (dd, 2H, $J = 2.7$ Hz, $J = 0.9$ Hz), 7.47–7.40 (m, 4H), 7.37–7.33 (m, 2H). ^{13}C NMR (DMSO-d_6, ppm) 160.1, 144.6, 136.1, 127.8, 123.3, 121.8, 121.5, 116.6, 115.8, 115.2, 108.6. IR (KBr, cm^{-1}): 3433, 3082, 2923, 2852, 2360, 2239, 2230, 1587, 1566, 1486, 1455, 1416, 1384, 1286, 1257, 1244, 1180, 1103, 951, 901, 873, 852, 795, 775, 669, 525.

16 S.-H. Hsiao, C.-P. Yang, K.-Y. Chu, *Macromolecules* **1997**, *30*, 165.

17 1.08 g (3 mmol) of 1,2-bis(3,4-dicyanophenoxy)benzene and 0.09 g (1 mmol) of CuCl were dissolved in 40 mL of dimethylacetamide (DMAc) and then the mixture was stirred at 160 °C for 24 h. The reaction mixture was poured into 800 mL of water. The crude product was collected by filtration, washed with water, and dried in vacuo. After refluxing in methanol twice, the product was filtrated and washed using cold methanol for three times. The dark blue powdery product was dried in vacuo, affording 0.98 g of copper phthalocyanine-containing hyperbranched polymer.

18 IR (KBr, cm^{-1}): 3222, 3065, 2231, 1771, 1717, 1607, 1588, 1565, 1489, 1454, 1402, 1361, 1309, 1255, 1217, 1183, 1092, 1049, 950, 881, 838, 770, 746, 674, 643, 553, 524.

19 M. Whalley, *J. Chem. Soc.* **1961**, 866.

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