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Synthesis and Characterization of X-azo Dyes (X = Ni, Cu, Zn) for Digital Versatile Disc-Recordable (DVD-R)

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We have synthesized 5-(diethylamino)-2-[(E)-2-(methoxy-1, 3-benzo thiazole)-1-diazenyl] phenol (DMBTA) azo and DMBTA complexed with Ni, Cu, and Zn for DVD-R fabrication. The structures of the products were characterized by ^{1}H-NMR and FT-IR. The properties of the compounds required for DVD-R fabrication were elucidated by UV-VIS and TGA. From the UV-VIS data, Zn-DMBTA exhibited the best response with 635 nm generally used in a DVD player. Based on the analysis of TGA data, it showed high thermal stability. Accordingly, Zn-DMBTA is the best compound as a recording material for DVD-R fabrication.

Keywords DVD; Optical storage; Recording; Metal complex

INTRODUCTION

A demand for a new storage medium is driven by high storage capacity and a fast data transfer rate. [1] A digital versatile disc is a good storage medium for the requirements since its memory capacity is higher than CD's by 6 times with a fast rate.[2] In order to achieve a better storage capacity in manufacturing a DVD, the following factors should be considered for synthesizing new recording materials. (a) a high refractive index at 635 nm with the most generally used in a recent

DVD player, (b) thermal stability at high temperature up to 250 ℃, and (c) good solubility for spin coating process onto a polycarbonate substrate.[3] Based upon the consideration of the above requirements, X-azo dyes (X = Ni, Zn, and Cu) were designed and synthesized. An azo dye was also synthesized in order to compare its properties with *those of X-azo dyes.*

EXPERIMENTAL

5 -(Diethylamino)- 2 -[(E)-2-(methoxy-1, 3-benzothiaole)-1-diazenyl] phenol (DMBTA) was synthesized by the following procedure. 2.3 g of 2-amino-6-methoxybenzothiazole was dissolved in 17 ml of sulfuric acid at 0 ℃. The diazonium salt was carried out with 0.83 g of sodium nitrite at -10 ℃. 1.65 g of the 3-diethylamino phenol dissolved in 20 ml of methanol was added dropwise into the resulting diazonium liquor at 0 ℃. The product was obtained by filtering and recrystallized with methanol. Zn-DMBTA was synthesized by the following procedure. 1.2 g of DMBTA was dissolved in 28 ml of methanol. 0.51 g of the zinc nitrate dissolved in 5.67 ml of methanol was added to the DMBTA solution in methanol. This solution was diluted with 50 g of water. After filtering, the solid was washed with hot water and dried. Ni-DMBTA and Cu-DMBTA were synthesized by the same procedure. A detail synthetic scheme of the sample compound was shown in Figure 1.

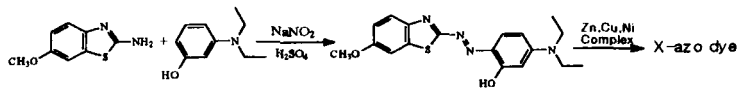


FIGURE 1. A synthetic scheme of DMBTA and X-DMBTA

RESULTS AND DISCUSSION

The structures of DMBTA and X-DMBTA were confirmed by ^{1}H-NMR and FT-IR spectra. The IR spectra of DMBTA and X-DMBTA exhibited

in Figure 2(A) indicates the presence of the coordination sites of X-DMBTA. While a broad hydroxyl (-OH) peak at 3310 cm^{-1} and sharp azyl (-N=N-) peak at 1630 cm^{-1} were observed in the IR spectra of DMBTA, there were no such peaks in the spectra of X-DMBTA. Therefore, the metal was coordinated with hydroxyl and azyl in the DMBTA. The formation of a metal complex was also confirmed by UV-VIS spectra shown in Figure 2(B). In the normalized UV-VIS Spectra, λ_{max} were 510, 528, 531, and 549 nm for DMBTA, Zn-DMBTA, Cu-DMBTA, and Ni-DMBTA, respectively. The spectra of X-DMBTA showed a red shift that is observed in metal complexes. While the UV-VIS spectra of Cu-DMBTA and Ni-DMBTA showed very broad and strong absorption bands at 635 nm, the width of Zn-DMBTA was less broad than those of Cu-DMBTA and Ni- DMBTA. An UV-VIS spectrum of Zn - DMBTA included a steep and weak absorption band at 635 nm. Since a material should be decomposed by 635 nm laser absorption for recording, it should absorb 635 nm light. Also for recording the disc recorded by 635 nm is read by the same laser source. It means that a material should reflect the 635 nm wavelength. Hence, a recording material should have a weak absorption band at 635 nm. Zn-DMBTA is the best material to satisfy these two contradictory factors.

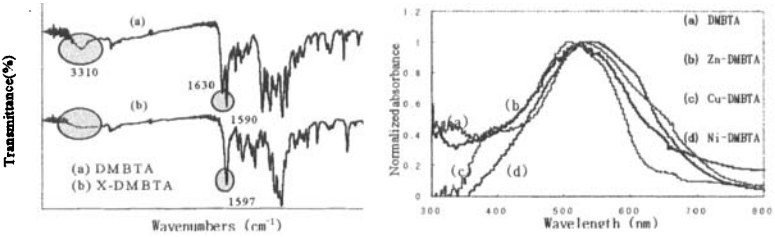
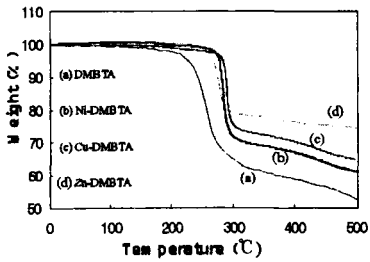


FIGURE 2. (A) IR and (B) UV-VIS spectra of DMBTA and X-DMBTAs

Figure 3 shows thermal decomposition of DMBTA and X-DMBTAs. Decomposition temperatures were 240, 270, 280, and 290 ℃ for DMBTA, Zn-DMBTA, Ni-DMBTA and Cu-DMBTA, respectively. X-



DMBTAs exhibited better stability in the thermal decomposition than DMBTA. A recording material should be stable up to 250 ℃ since the maximum temperature of DVD, while data are written/read, is reached to approximately 250 ℃ or lower.

FIGURE 3. TGA curves of DMBTA and X- DMBTAs.

All of the synthesized dyes had good solubility in the solvent commercially used for a DVD-R. The required characteristics of Zn - DMBTA were satisfied nearly as a recording dye. λ_{max} was 528 nm and the decomposition temperature was 280 ℃ of Zn - DMBTA.

CONCLUSIONS

An Azo compound (DMBTA) and X-DMBTA dyes (X = Zn, Cu, and Ni) were synthesized. The DVD-R disc recording characteristics were evaluated. Zn- DMBTA will be suitable for DVD-R because of good solubility, suitable absorption at 635nm and good thermal stability.

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