

Synthesis of Metal-Azo Dyes and Their Optical and Thermal Properties as Recording Materials for DVD-R

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Four kinds of azo dyes and their metal-azo dyes were synthesized in order to obtain a high reflective index and better thermal stability as a recording material for DVD-R. Several kinds of novel azo dyes based on benzoic acid, 6-methoxybenzothiazole, benzothiazole-6-carboxylic acid, and benzimidazole have been synthesized. These azo dyes reacted with metal ions, such as Ni^{2+} , Cu^{2+} , Zn^{2+} , and Co^{2+} , as ligands. All structures of the compounds were confirmed by ^1H -NMR and FT-IR analyses. The optical and thermal properties of azo dyes and their metal-azo dyes were characterized by UV-vis and TGA analyses. In the UV-vis spectra, the absorption maxima of metal-azo dyes show at longer wavelength than those of azo dyes. These spectral shifts are affected by substituent groups, electron-donating or -withdrawing groups, of azo dyes and metal ions. The metal-azo dyes were thermally stable up to 300 °C, which were confirmed by TGA analyses. Particularly, in the case of an azo dye complexed with Zn based on 6-methoxybenzothiazole, good absorption at 635 nm was observed, and its thermal stability was maintained up to 300 °C, with high refractive index of about 2.08.

Optical data storage has become a core technology in the multimedia environment for both the entertainment and computing industries. Rapidly increased information solicits a more convenient and efficient storage method.^{1–2} The structure of a DVD-R (Digital Versatile Disc-Recordable) consists of a polycarbonate substrate, a recording layer, a metal reflective layer, and a protective layer as a kind of optical data storage.³ The recording layer is easily decomposed by laser light with 635 and 650 nm wavelengths.^{4–6} The recording layer has a high refractive index, so it can effectively absorb light and generate heat when the laser beam is focused on the film. The heat is transferred to both the PC substrate and the recording layer. In order to achieve a better storage medium, the following factors should be considered for synthesizing new recording materials: (1) a high refractive index at 635 nm with the most generally used in a recent DVD player, (2) thermal stability at high temperature up to 250 °C, and (3) good solubility for a spin coating process onto a polycarbonate substrate. In general, cyanine dyes, phthalocyanine dyes, and metal-azo complexes dyes are used for DVD-R.^{7–10} As for cyanine dyes, they are unstable against light and not durable for repeated reading use.^{11–13} Phthalocyanine dyes also have demerits, such as a worse solubility and higher cost than cyanine dyes. On the other hand, metal-azo complexes are more stable than cyanine dyes against light, provide easier control of the wavelength according to the substituted groups, and have good thermal stability with a metal complex. Based upon the consideration of the above requirements, we designed and synthesized several azo dyes and their metal-azo dyes. Herein, we report on the syntheses of the compounds. Their optical and thermal properties for DVD-R are discussed while considering substituted

groups of azo dyes and metal ions.

Experimental

Samples. 2-Aminobenzoic acid (**1**), 2-amino-benzothiazole-6-carboxylic acid (**2**), 2-amino-6-methoxy benzothiazole (**3**), 2-aminobenzimidazole (**4**), 3-(diethylamino)phenol (**5**), sodium hydrogen carbonate, sulfuric acid, nitrosyl hydrogensulfate, nickel(II) acetate (**a**), copper(II) acetate (**b**), zinc nitrate (**c**), and cobalt(II) nitrate (**d**) were obtained from Aldrich Chemical Co. and were used without further purification.

Preparation of Azo and Metal Azo Dyes. Figure 1 shows synthetic schemes of azo dyes and metal-azo dyes. To the amine compounds (**1–4**), (1 mmol) in sulfuric acid (17 mL), 35% nitrosyl hydrogensulfate (3.8 g) was slowly added at –20 °C. After stirring for 2 h at the same temperature, 3-(diethylamino)phenol (**5**) (1 mmol) in methanol (20 mL) was added into the resulting diazonium solution at –20 °C. After completion of diazo-coupling, the reaction mixture was neutralized with a saturated sodium hydrogencarbonate solution to pH 6. The product was obtained by filtering and recrystallized with methanol. To the azo dyes (**6–9**), (1 mmol) in methanol (10 mL), metal(II) acetate solution (0.5 mmol) in methanol were added. After completion of complexation, the reaction mixture was diluted with water (50 mL). The precipitated metal azo dyes were filtered, washed with hot water, and dried.

Analytical Data for Final Compounds (8**, **8a**, and **8c**).** Compound **8**: ^1H NMR (CDCl_3) δ = 1.17 (t, 3H), 3.35–3.59 (m, 2H), 6.15 (s, 1H), 6.42 (d, 1H), 7.1 (d, 1H), 7.5 (d, 1H), 7.82 (d, 1H), and 8.28 (s, 1H); Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$: C, 60.65; H, 5.66; N, 15.72; S, 9.00%. Found: C, 60.63; H, 5.56; N, 15.66; S, 9.02%; IR (KBr pallet) 3428 (OH) and 1630 cm^{-1} (N=N), Compound **8a**: Anal. Calcd for $\text{C}_{38}\text{H}_{44}\text{N}_8\text{NiO}_4\text{S}_2$: C, 57.08; H, 5.55; N,

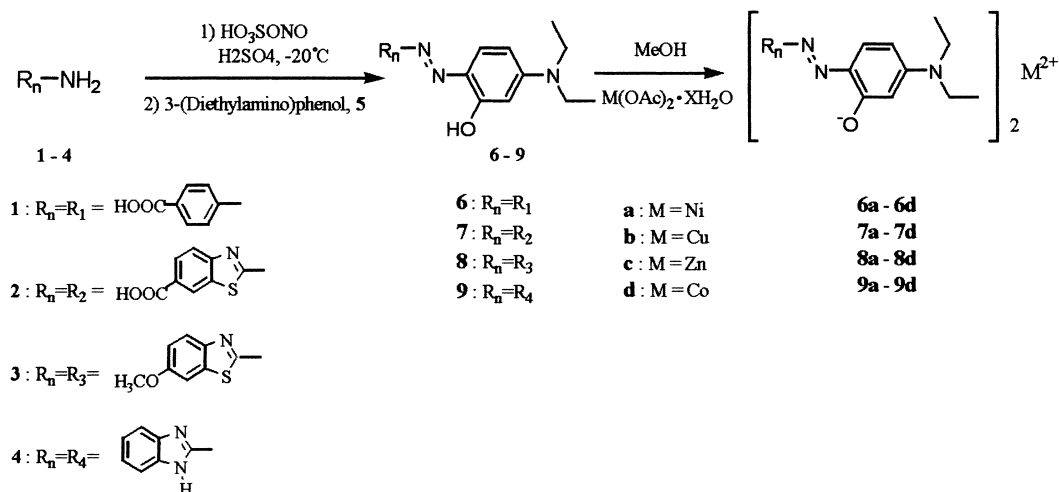


Fig. 1. Synthesis of azo dyes and metal-azo dyes.

14.01; S, 8.02%. Found: C, 52.25; H, 4.62; N, 13.44; S, 8.37%; IR (KBr pallet) 1597 cm^{-1} (N=N), Compound **8c**: Anal. Calcd for $\text{C}_{38}\text{H}_{44}\text{N}_8\text{O}_4\text{S}_2\text{Zn}$: C, 56.60; H, 5.50; N, 13.90; S, 7.95%. Found: C, 57.60; H, 4.27; N, 14.16; S, 9.26%; IR (KBr pallet) 1597 cm^{-1} (N=N).

Instrumentation. FT-IR spectra were recorded as KBr pellets over the range 4000–200 cm^{-1} using a Perkin-Elmer system. The ^1H NMR spectra were obtained on a Varian INOVA (400 MHz) spectrometer. Elemental analyses were performed with an elemental analyzer (EA1110). UV spectra were recorded as PC films coated by 2.0 wt% over the range 300–800 nm using a Scinco spectrophotometer. The refractive indexes were measured by a Rudolph Technologies ellipsometer. Thermal properties were analyzed with a Rheometric Scientific System (TGA1000, DSC PLUS) at a heating rate of 10 $^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

Results and Discussion

The diazonium salt was easily obtained by using sodium nitrite. Azo dyes were synthesized by azo coupling. These products were confirmed by the ^1H NMR and FT-IR spectra. FT-IR spectra indicate the presence of coordination sites of metal-azo dyes. A strong band at around 3310 cm^{-1} corresponding to OH in the azo ligand was very weak, and a sharp single band around 1630 cm^{-1} corresponding to $\text{N}=\text{N}$ in the azo ligand was shifted to 1597 cm^{-1} in the spectra of the metal complex.^{14–16} The peak of carbonyl and other peaks were almost identical. Therefore, strong coordinations between metal ions and hydroxy and azo groups were formed.¹⁴

Optical characterization of the products was accomplished using a UV-vis. spectra. Figure 2 shows the optical properties of azo and their metal-azo dyes. The recording material should be decomposed by 635 nm laser absorption; for recording it should absorb a 635 nm wavelength. Also, for reading the disc recorded by 635 nm, the same laser source is used. This means that a material should reflect a little light at 635 nm. Therefore the value of the absorbance for the recording material is good at about 0.4–0.5 in the normalized UV-vis. spectrum. The $\pi-\pi^*$ transitions were observed in the spectra of azo dyes.¹⁸ Their $\pi-\pi^*$ transitions were exhibited by the absorption with the maximum absorbances ($\lambda_{\max}$) at around 427 (6), 512 (7),

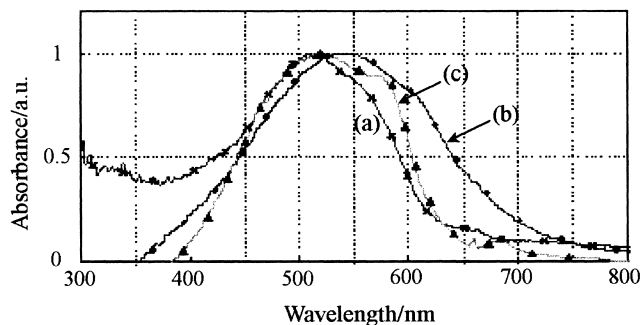


Fig. 2. UV spectra of MBT-A-X dyes: (a) **8**; (b) **8a**; (c) **8c**.

516 (**8**), and 489 nm (**9**), respectively. These spectral shifts are affected by the substituent groups of the azo dye and metal ions.¹⁶ The longer double bond in the azo dye caused longer λ_{max} wavelength from the shorter double bond in the normalized UV-vis. spectrum. Also a λ_{max} of **7** was observed to be almost identical to that of **8**. The $\pi-\pi^*$ transitions of an azo containing benzothiazole moiety were not affected by the substituent group ($-\text{COOH}$, $-\text{OCH}_3$). However, a λ_{max} of **7** was observed at a longer wavelength than that of **9** due to a sulfur atom. In the normalized UV-vis Spectra, the λ_{max} were observed at 476 (**6a**), 537 (**7a**), 541 (**8a**), and 522 nm (**9a**), respectively. **6a** and **9a** showed a slight absorption shoulder near 635 nm. In contrast, **8a** showed a very broad absorption band at 635 nm; **7a** showed a sharp absorption band at 635 nm.

Thermal characterizations of the products were accomplished by TGA and DSC analyses (Figs. 3 and 4). The onset temperatures of weight loss were 240 (**6**), 220 (**7**), and 243 °C (**8**), respectively. The decomposition temperatures were 300 (**8a**), 310 (**8b**), 300 (**8c**), and 280 °C (**8d**), respectively. Metal-azo dyes were more thermally stable at about 50 °C higher than that of the azo dyes. Also, the metal-azo dyes showed crystallization temperatures as shown in Fig. 4. The melting temperatures were 179 (**8**), 187 (**8a**), and 177 (**8c**), respectively.

The recording dye must be soluble in specific organic solvents, such as 2,2,3,3-tetrafluoro-1-propanol (TFP) or diacetone alcohol (DAA), 4-hydroxy-4-methyl-2-pentane, because

Table 1. Summary of Physical and Optical Properties for Azo and Metal-Azo Dyes

Product number	Solubility ^{a)}	Refractive index at 632 nm ^{b)}	$\lambda_{\max}$ ^{c)} /nm	Abs. ^{c)} at 635 nm	T_d /°C ^{d)}
6	O	—	427	0.0	240
7	O	—	512	0.19	220
8	O	1.66	516	0.21	243
9	O	—	489	0.02	—
6a	X	—	476	0.02	290
7a	O	—	537	0.11	250
8a	O	1.87	541	0.20	292
9a	O	—	522	0.05	220
8c	O	2.08	517	0.54	284

a) in TFP solvent (O: good, X: bad), b) on Si-substrate,

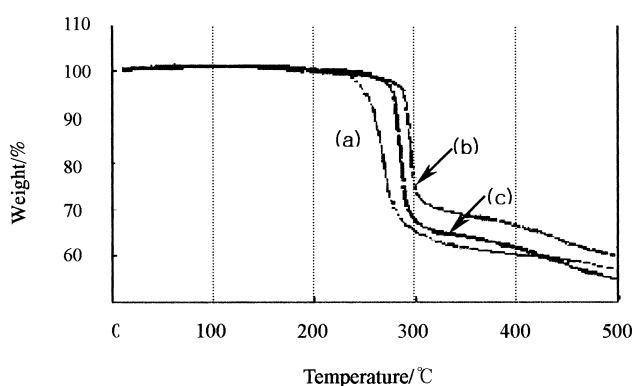
c) on PC substrate with TFP solvent, d) 10 °C/min under N₂ gas

Fig. 3. TGA curves of MBT-A-X dyes: (a) 8; (b) 8a; (c) 8c.

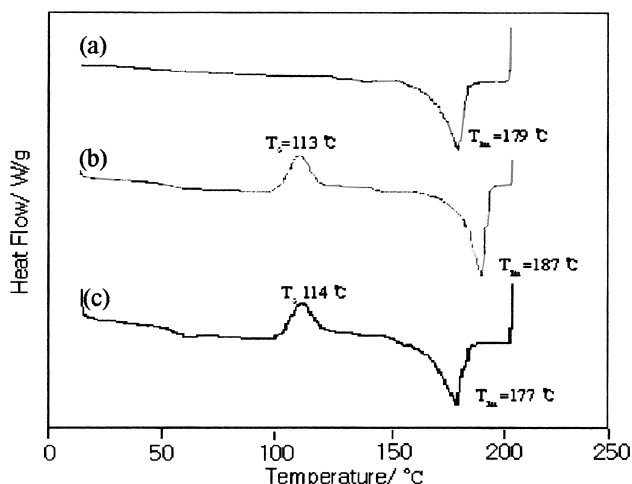


Fig. 4. DSC curves of MBT-A-X dyes: (a) 8; (b) 8a; (c) 8c.

the recording layer is applied on a polycarbonate substrate by the spin-coating method. In general, more than 2.0 wt% solubility is necessary. All of the synthesized materials were soluble in TFP solvent except for **6a**. Although the optical property of **6a** was good, disc fabrication will be hard due to poor solubility. DVD-R dye has an absorption maximum at 590–610 nm and an absorption edge at the recording or reading wavelength (635–650 nm), the refractive index (n) value of the dye is maximized at 650 nm. This high refractive index results in a

high-modulated amplitude of the recording signal.^{16–18} To improve the recording sensitivity with high refraction and a high signal amplitude, the recording materials should have high n values. The n values of the products were measured by an ellipsometer with the optimized thickness and optical constant (k) at 632 nm. The k value means the absorbance at 632 nm, it was obtained from the UV-vis spectrum. The n values of metal-azo dyes are higher than those of azo dyes because the n value is enhanced by metal. Table 1 gives a summary of the physical and optical properties for the azo and metal-azo dyes.

Conclusion

In summary, we synthesized four kinds of azo dyes and their metal-azo dyes in order to obtain a high reflective index and better thermal stability as a recording material. Almost all of the metal-azo dyes had good thermal stability up to 300 °C. From the UV-vis spectrum, it could be seen that the azo dye complexed with Ni based on 2-amino-benzothiazole-6-carboxylic acid (**7a**) had good optical property, but its solubility was very poor. The azo dye complexed with Zn based on 2-amino-6-methoxy benzothiazole (**8c**) showed good optical, thermal, and solubility properties compared to other metal-azo dyes. The absorption maximum of **8c** was observed at 517 nm and the decomposition temperature was 280 °C. The UV-vis spectrum of **8c** included a steep and weak absorption band at 635 nm. Also, the refractive index of **8c** was 2.08 at 632 nm wavelength. Because of the optical and thermal characteristics of **8c** were nearly satisfied, it will be suitable as a recording dye for DVD-R.

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