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SYNTHESIS OF NEW SPIROBENZOPYRANS BEARING A MACROCYCLIC DIOXOPOLYAMINE AND THEIR SELECTIVE COLORATION FOR TRANSITION METAL CATIONS

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Three new spirobenzopyrans bearing a macrocyclic dioxipolyamine were synthesized. Sensitive and selective coloration of the spirobenzopyrans for transition metal cations were observed.

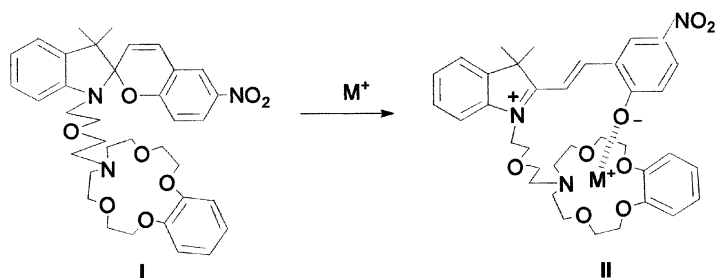
Keywords: macrocyclic dioxipolyamine; selective coloration; spirobenzopyran; transition metal cations

INTRODUCTION

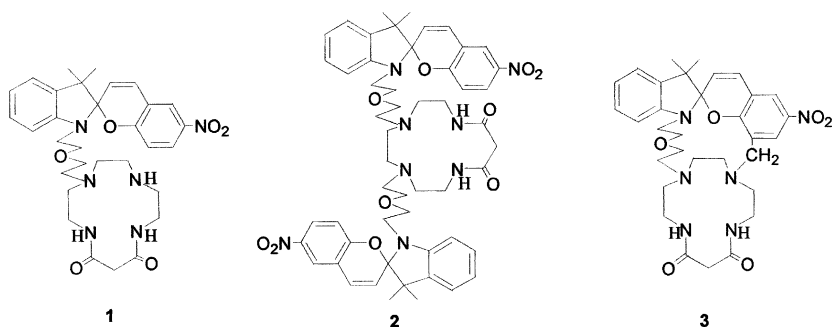
Photochromic properties of recently synthesized compounds have been examined extensively to explore their potential in optical devices [1]. Spirobenzopyrans are well-known photochromic compounds that isomerize from spiropyran to merocyanine forms by UV light and vice versa by visible light or heat [1]. It has been recognized that incorporation of a crown ether moiety into a spirobenzopyran affords ion-responsive photochromic materials, reflecting the metal-ion-binding ability of the crown ether moieties [2]. We previously reported spirobenzopyrans bearing a monoazocrown ether, of which isomerization to the open-colored merocyanines was induced by recognition of alkali metal cations [3]. Here we report three types spirobenzopyran-bearing macrocyclic dioxipolyamine (**1**, **2**, **3**) in which sensitive and selective recognition of the transition metal cation induces the structural change in the spirobenzopyrans to the colored merocyanines.

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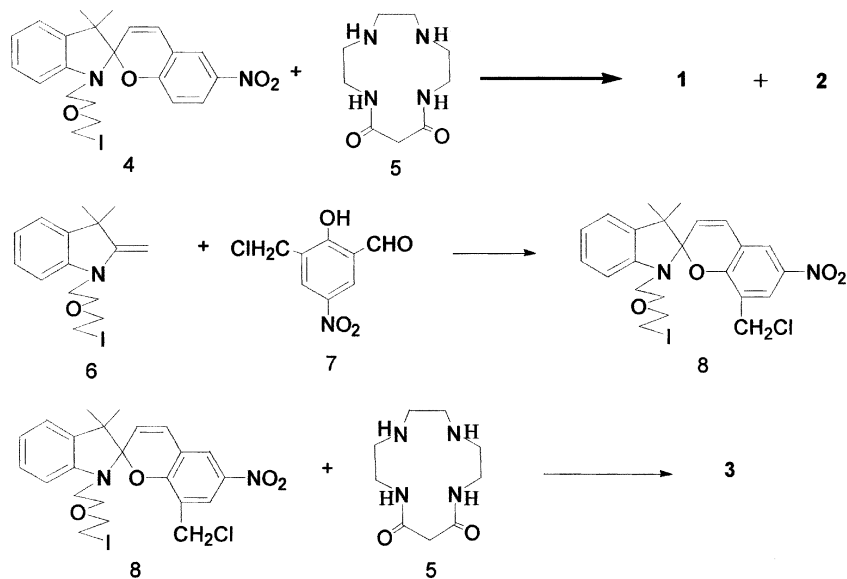
SYNTHESIS



The spirobenzopyran **1** and lariat-type spirobenzopyran **2** were synthesized by the condensation of macrocyclic dioxopolyamine **5** with spirobenzopyran **4** [4]. The cryptand-type spirobenzopyran **3** was prepared by the condensation of macrocyclic dioxopolyamine **5** with spirobenzopyran **8**, which was given by the aldol-type cyclization of the Fischer's base **6** [4] with salicylaldehyde **7** (Scheme 1).

Compound **1**: ^1H NMR (90 MHz, CDCl_3): δ 1.30 (s, 3H, $-\text{CH}_3$), 1.60 (s, 3H, $-\text{CH}_3$), 2.44–2.56 (m, 11H, R_2NH , $\text{R}_2\text{N}-\text{CH}_2$), 2.98–3.68 (m, 12H, OCH_2- , ArNCH_2- , $-\text{CONCH}_2$, $\text{COCH}_2\text{CO}-$), 5.82 (d, $J = 10.8$ Hz, 1H, $\text{HC}=\text{C}-\text{Ar}$), 6.52–7.14 (m, 6H, $\text{Ar}-\text{H}$, $\text{Ar}-\text{CH}=\text{C}-$), 7.85–7.99 (m, 1H, $o-\text{NO}_2-\text{Ar}-\text{H}$), 8.13 (d, $J = 2.7$ Hz, 1H, $o-\text{NO}_2-\text{Ar}-\text{H}$), 8.63 (br, 2H, $\text{HN}-\text{CO}$). MS(m/z): 592 (M^+ , 11%), 593 (MH^+ , 36%). Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{N}_6\text{O}_6$: C, 62.82; H, 6.80; N, 14.18. Found: C, 63.15; H, 7.03; N, 13.93.

Compound **2**: ^1H NMR (90 MHz, CDCl_3): δ 1.35 (s, 6H, $-\text{CH}_3$), 1.62 (s, 6H, $-\text{CH}_3$), 2.40–2.64 (m, 12H, $\text{R}_2\text{N}-\text{CH}_2$), 3.11–3.70 (m, 18H, OCH_2- , ArNCH_2- , $-\text{CONCH}_2$, $\text{COCH}_2\text{CO}-$), 5.81 (d, $J = 10.8$ Hz, 2H, $\text{HC}=\text{C}-\text{Ar}$), 6.46–7.12 (m, 14H, $\text{Ar}-\text{H}$, $\text{Ar}-\text{CH}=\text{C}-$, $-\text{CONH}-$), 7.88–7.95 (m, 2H, $o-\text{NO}_2-\text{Ar}-\text{H}$), 8.18 (d, $J = 2.7$ Hz, 2H, $o-\text{NO}_2-\text{Ar}-\text{H}$). MS(m/z): 970 (M^+ , 35%). Anal. Calcd for $\text{C}_{53}\text{H}_{62}\text{N}_8\text{O}_{10}$: C, 65.55; H, 6.44; N, 11.54. Found: C, 65.20; H, 6.62; N, 11.47.

**SCHEME 1** Preparation of Compound 1, 2, and 3.

Compound **3**: ^1H NMR (90 MHz, CDCl_3): δ 1.12 (s, 3H, CH_3); 1.30 (s, 3H, CH_3); 2.20–2.60 (m, 10H, NCH_2); 3.05–3.70 (m, 14H, ArNCH_2 , ArCH_2N , OCH_2 , CH_2NCO , COCH_2CO); 5.70 (d, 1H, $\text{HC}=\text{C}-\text{Ar}$); 6.50–7.10 (m, 9H, ArH , $\text{C}=\text{CH}-\text{Ar}$); 7.85 (d, 1H, $\text{o}-\text{NO}_2-\text{Ar}-\text{H}$); 8.00 (d, 1H, $\text{o}-\text{NO}_2-\text{Ar}-\text{H}$). MS(m/z): 605 (MH^+ , 28%). Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_6\text{O}_6$: C, 63.56; H, 6.67; N, 13.90. Found: C, 63.28; H, 6.74; N, 13.78.

RESULTS AND DISCUSSION

The spirobenzopyran **1**, **2**, **3** prepared showed no absorption bands above 400 nm in EtOH, indicating the closed spiropyran forms. When a

TABLE 1 λ_{max} and ϵ of Compound **1**, **2**, **3** in EtOH Set in the Dark for 1 h

		1	2	3
Cu^{2+}	$\lambda_{\text{max}}/\text{nm}$	548	546	507
	$\epsilon/10^3$	0.37	0.62	1.58
Co^{2+}	$\lambda_{\text{max}}/\text{nm}$	548	546	493
	$\epsilon/10^3$	0.39	0.78	0.79
Ni^{2+}	$\lambda_{\text{max}}/\text{nm}$	545	542	513
	$\epsilon/10^3$	0.18	0.51	0.77

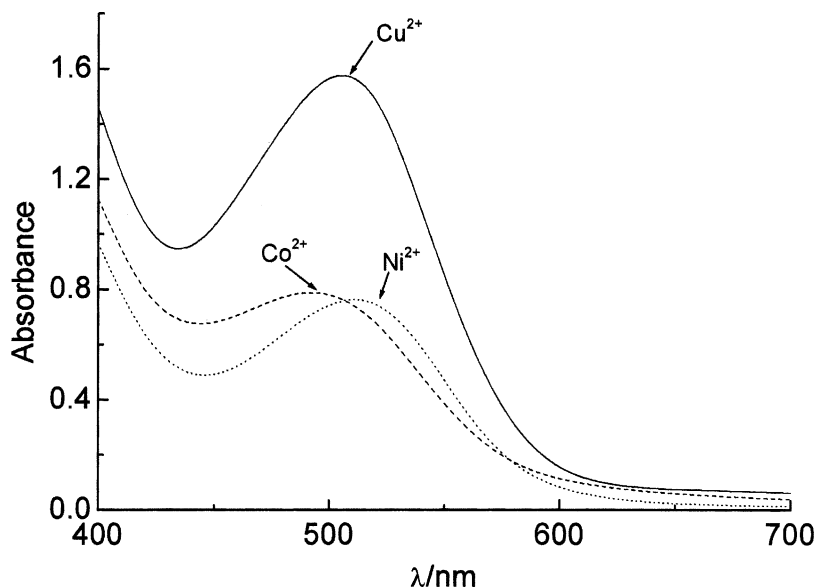


FIGURE 1 UV-Vis spectra of compound **3** set in the dark for 1 h.

transition metal ion (Cu^{2+} , Co^{2+} , Ni^{2+}) was added to the solution above and set in the dark for 1 h, however, new absorption bands appeared. These results indicate that transition metal ions (Cu^{2+} , Co^{2+} , Ni^{2+}) induced the structural change in the spirobenzopyrans to the colored merocyanines. Spirobenzopyran **2** showed a higher coloring efficiency when compared to those of **1** (Table I) because the complexed cations in **2** could interact with the two phenolate oxygens of the open merocyanines at the up and down areas perpendicular to the rings. The cryptand spirobenzopyran **3** gave the most intense coloration for transition metal ions and showed a high selective coloration for Cu^{2+} (Table 1, Figure 1). This may be because the crown-bound cations are nearer to the phenolate oxygen in the cryptand spirobenzopyran **3** than that in **1** and **2**, and Cu^{2+} chelates more intensely with the macrocyclic dioxopolyamine **5** than Co^{2+} , Ni^{2+} [5].

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