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Sheng Liu [a]

[a] College of Chemistry, Central China Normal University, Wuhan, 430079, China

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

*Sheng Hua Liu**
College of Chemistry, Central China Normal University, Wuhan 430079, China

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

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

INTRODUCTION

Photochromic properties of recently synthesized compounds have been examined extensively to explore their potentiality in optical devices [1]. Spirobenzopyrans are well-known photochromic compounds that isomerize from spiropyran to merocyanine forms by ultraviolet (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 reported three types of spirobenzopyrans bearing macrocyclic dioxopolyamine (**1**, **2**, **3**; Scheme 1), in which sensitive and selective recognition of transition metal cation induces the structural change in the spirobenzopyrans to the colored merocyanines.

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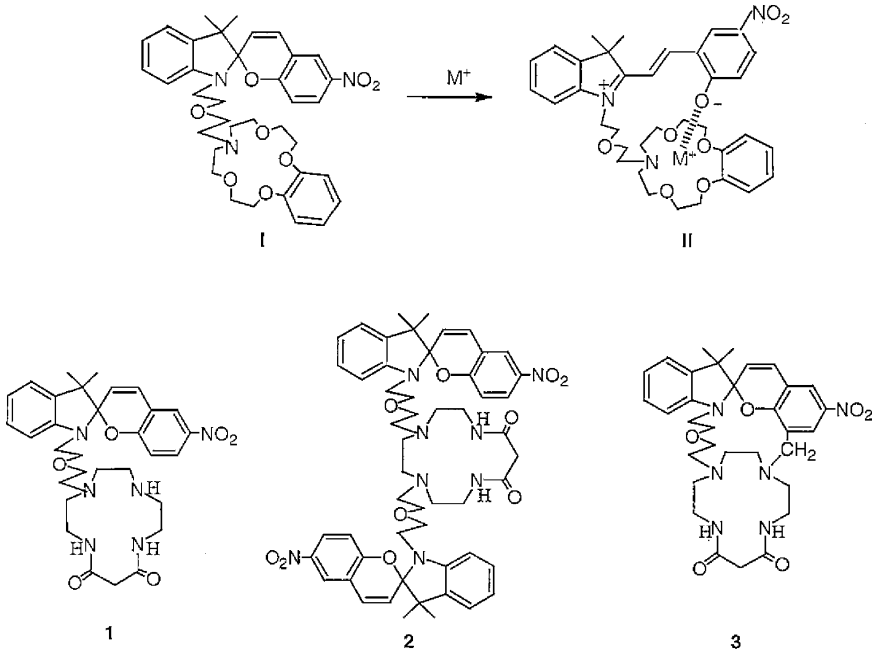
*Corresponding author. E-mail: chshliu65@hotmail.com



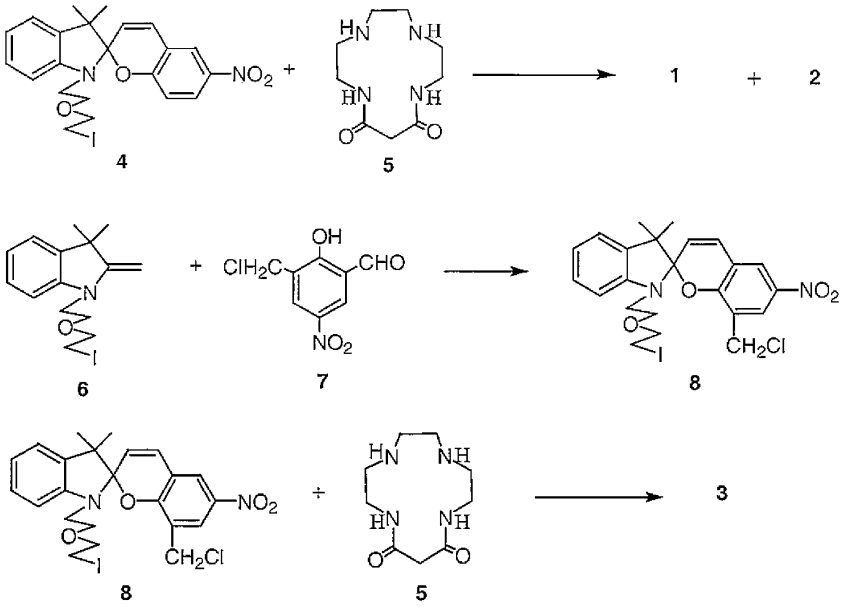
SCHEME 1

Synthesis

The spirobenzopyran **1** and lariat-type spirobenzopyran **2** were synthesized by the condensation of macrocyclic dioxopolyamine **5** with spirobenzopyran **4** [4]. The crytand-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 2).

RESULTS AND DISCUSSION

The spirobenzopyran **1**, **2**, **3** prepared showed no absorption bands above 400 nm in EtOH, indicating the closed spiropyran forms. When transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}) were added to the solution above and set in the dark for 1 h, however, new absorption bands appeared. These results indicated 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 1) because the complexed cations in **2** could interact with



SCHEME 2

the two phenolate oxygens of the open merocyanines at the up and down areas perpendicular to the rings. The crytand 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 phonolate oxygen in the crytand spirobenzopyran **3** than that in **1**, **2**, and Cu^{2+} chelates more intensely with the macrocyclic dioxopolyamine **5** than Co^{2+}, Ni^{2+} [5].

Compound **1**: ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.30 (s, 3H, -CH_3), 1.60 (s, 3H, -CH_3), 2.44–2.56 (m, 11H, R_2NH, R_2N-CH_2), 2.98–3.68 (m, 12H, OCH_2-, $ArNCH_2$-, -$CONCH_2$, $COCH_2CO$-), 5.82 (d, $J = 10.8$ Hz, 1H,

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

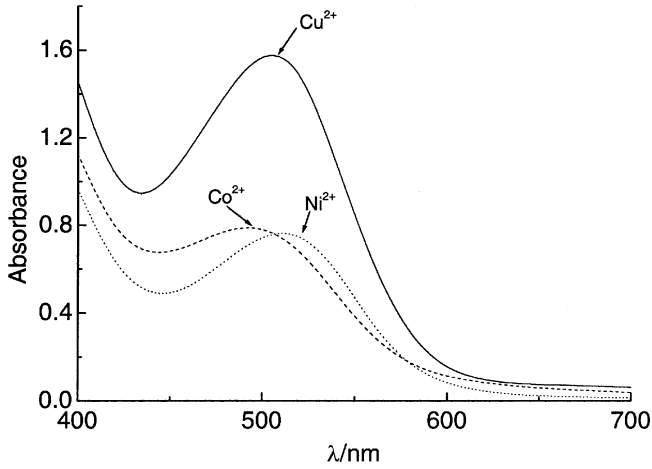


FIGURE 1 UV-Vis spectra of compound **3** set in the dark for 1 h.

HC=C-Ar), 6.52–7.14 (m, 6H, Ar-H, Ar-CH=C-), 7.85–7.99 (m, 1H, o-NO_2-Ar-H), 8.13 (d, $J = 2.7$ Hz, 1H, o-NO_2-Ar-H), 8.63 (br, 2H, HN-CO). MS (m/z): 592 (M+, 11%), 593 (MH+, 36%). Anal. Calcd for $C_{31}H_{40}N_6O_6$: C, 62.82; H, 6.80; N, 14.18. Found: C, 63.15; H, 7.03; N, 13.93. Compound **2**: ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.35(s, 6H, -CH_3), 1.62 (s, 6H, -CH_3), 2.40–2.64 (m, 12H, R_2N-CH_2), 3.11–3.70 (m, 18H, OCH_2-, $ArNCH_2$-, -$CONCH_2$, $COCH_2CO$-), 5.81 (d, $J = 10.8$ Hz, 2H, HC=C-Ar), 6.46–7.12 (m, 14H, Ar-H, Ar-CH=C-, -CONH-), 7.88–7.95 (m, 2H, o-NO_2-Ar-H), 8.18 (d, $J = 2.7$ Hz, 2H, o-NO_2-Ar-H). MS(m/z): 970 (M+, 35%). Anal. Calcd for $C_{53}H_{62}N_8O_{10}$: C, 65.55; H, 6.44; N, 11.54. Found: C, 65.20; H, 6.62; N, 11.47. Compound **3**: ^{1}H 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, HC=C-Ar); 6.50–7.10 (m, 9H, ArH, C=CH-Ar); 7.85 (d, 1H, o-NO_2-Ar-H); 8.00 (d, 1H, o-NO_2-Ar-H). MS (m/z): 605 (MH^+, 28%). Anal. Calcd for $C_{32}H_{40}N_6O_6$: C, 63.56; H, 6.67; N, 13.90. Found: C, 63.28; H, 6.74; N, 13.78.

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