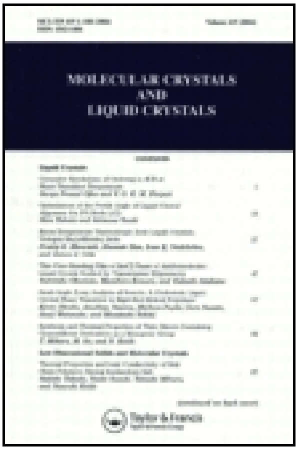

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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# Synthesis of Spirobenzopyrans Bearing Macrocyclic Dioxopolyamine

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Version of record first published: 31 Aug 2006

To cite this article: Weicheng Xiong, Ping Yuan, Jun Yin & Sheng Hua Liu (2005): Synthesis of Spirobenzopyrans Bearing Macrocyclic Dioxopolyamine, Molecular Crystals and Liquid Crystals, 428:1, 127-130

To link to this article: http://dx.doi.org/10.1080/154214090892807

*Mol. Cryst. Liq. Cryst.*, Vol. 428, pp. 127–130, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214090892807

# Synthesis of Spirobenzopyrans Bearing Macrocyclic Dioxopolyamine

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*Six novel spirobenzopyrans bearing macrocyclic dioxopolyamine were synthesized. Their photochromic, transition metal cations–induced photochromic properties were investigated.*

**Keywords:** macrocyclic dioxopolyamine; photochromic; spirobenzopyran; transition metal cations

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 (Scheme l) [2].

We previously reported spirobenzopyrans bearing a monoazocrown ether, of which isomerization to the open colored merocyanines was

The authors acknowledge financial support from National Natural Science Foundation of China (No. 20242010, 20472023), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry and the Hubei Provincial Science Fund for Distinguished Young Scholars (No. 2003ABB006).

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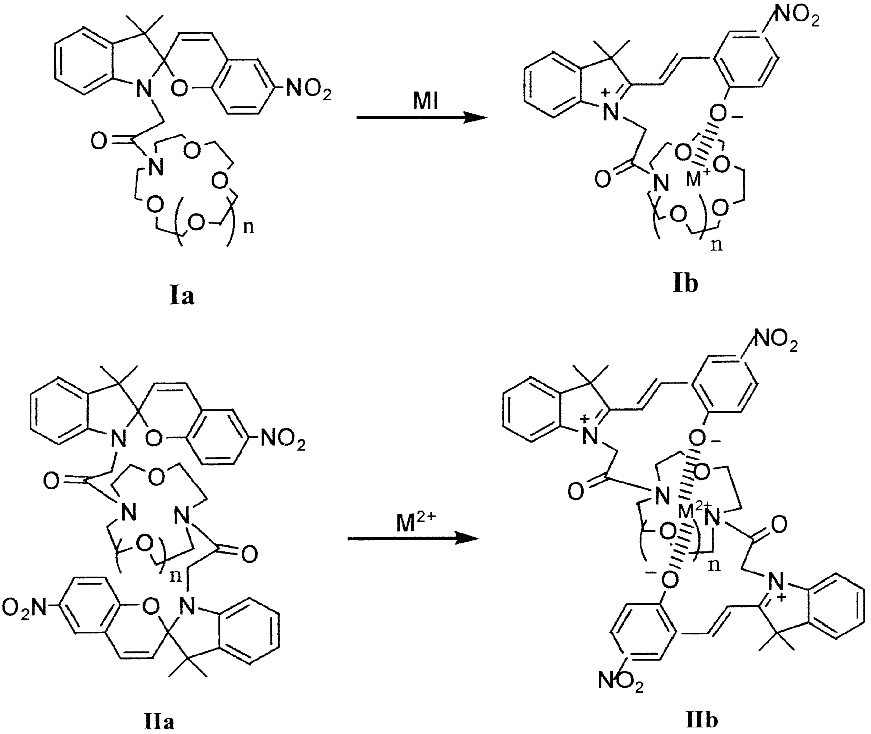
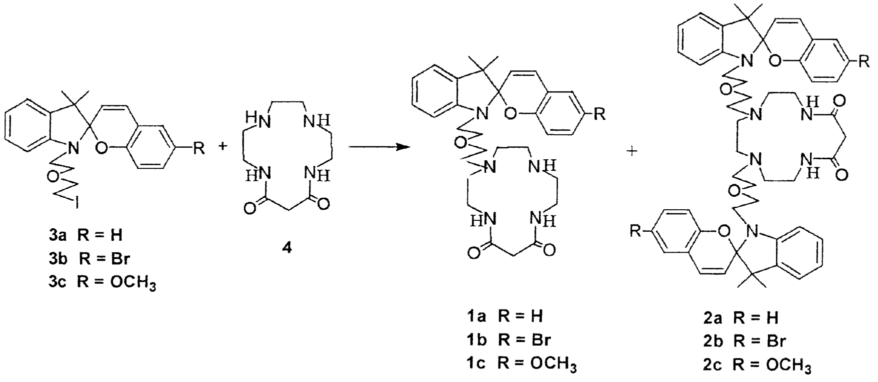


**SCHEME 1**

induced by recognition of alkali metal cations [3]. It is well known that oxygen atoms prefer hard metal ions such as alkali and alkali-earth metal ions, whereas nitrogen atoms tend to bind with transition metal ions. Therefore, we designed a new type of spirobenzopyran bearing macrocyclic dioxopolyamine (**1**, **2**), in which sensitive and selective recognition of transition metal cation induces the structural change in the spirobenzopyrans to the colored merocyanines.

Spirobenzopyran **3** [3d] and macrocyclic dioxopolyamine **4** [4] were prepared according to literature procedures.

Spirobenzopyran **1** and lariat-type spirobenzopyran **2** (exemplified with la and 2a): A mixture of macrocyclic dioxopolyamine **4**, spirobenzopyran **3a**, and $K_2CO_3$ in dry acetonitrile was refluxed for 48 h. The product was purified by column chromatography (silica gel; eluent, $AcOEt:Et_3N = 20:1$ and $AcOEt:Et_3N:NH_3 \cdot H_2O = 10:1:0.4$) to give lariat-type spirobenzopyran **2a** and spirobenzopyran **la** (Scheme 2), respectively [4].



**SCHEME 2**

The spirobenzopyrans prepared (**1** and **2**) snowed positive photochromism, and the spirobenzopyrans **2** showed selective coloration with transition metal ions. When transition metal ions ($Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$) were added to the spirobenzopyrans **1** and **2** in EtOH and set in the dark for 1 h, new absorption bands at about 500 nm appeared in absorption spectra of **2**. However, no influence in absorption spectra of **1** was observed. These results indicate that transition metal ions ($Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$) induce a structural change in the spirobenzopyrans **2** to the colored merocyanines. Spirobenzopyran **2** showed transition metal cations induced photochromism 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 [2h].

Compound **1a**: Yield 52.3%. $^1$H NMR ($CDCl_3$, 90 MHz): $\delta$1.16 (3H, s, $CH_3$); 1.32 (3H, s, $CH_3$); 2.60–2.95 (10H, m, $NCH_2$); 3.10–3.60 (13H, m, $ArNCH_2$, $OCH_2$, $CH_2NCO$, $COCH_2CO$, NH); 5.60 (1H, d, HC=C-Ar); 6.50–7.15 (9H, m, ArH, C=CH-Ar); 8.00 (2H, br, HNCO). IR($\nu_{max}$): 3260, 2958, 2927, 2865, 1681, 1606, 1552, 1484, 1457, 1311, 1253, 1111, 966, 751 $cm^{-1}$. MS (m/z): 549 ($MH^+$, 100%). Anal. calcd. for $C_{31}H_{41}N_5O_4$: C, 67.98; H, 7.55; N, 12.79. Found: C, 68.21; H, 7.50; N, 12.88. Compound **2a**: Yield 10.2%. $^1$H NMR ($CDCl_3$, 90 MHz): $\delta$ 1.12 (6H, s, $CH_3$); 1.30 (6H, s, $CH_3$); 2.40–2.60 (12H, m, $NCH_2$); 3.10–3.60 (18H, m, $ArNCH_2$, $OCH_2$, $CH_2NCO$, $COCH_2CO$); 5.64 (2H, d, HC=C-Ar); 6.50–7.15 (18H, m, ArH, C=CH-Ar); 7.28–7.45 (2H, br, HNCO). IR($\nu_{max}$): 3293, 2981, 2926, 2867, 1654, 1608, 1550, 1484, 1456, 1311, 1255, 1111, 967, 747 $cm^{-1}$. MS (m/z): 882 ($MH^+$, 100%). Anal, calcd. for $C_{31}H_{41}N_5O_4$: C, 72.25; H, 7.32; N, 9.54. Found: C, 72.46; H, 7.27; N, 9.62.

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