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# Synthesis and Photochromic Properties of Ferrocene-Modified Bis(spirobenzopyran)s

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# Synthesis and Photochromic Properties of Ferrocene-Modified Bis(spirobenzopyran)s

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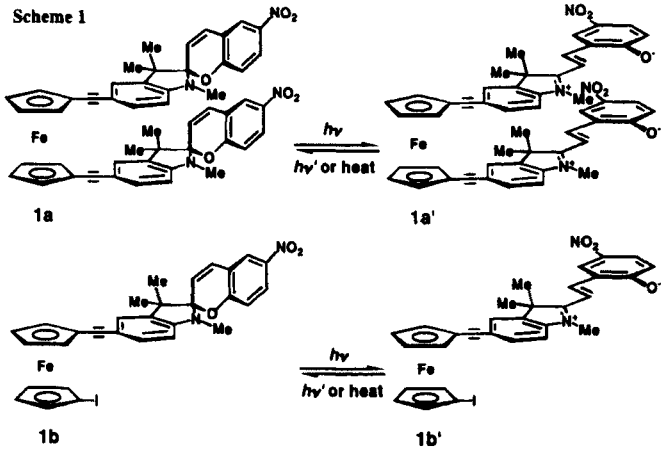
A novel ferrocene-modified bis(spirobenzopyran) was designed and synthesized. The spirobenzopyran possesses two photochromic moieties, which were tethered to two cyclopenta-dienyl rings of ferrocene via ethynediyl spacers. Photochromic properties of the spirobenzopyran were investigated in the absence and presence of various metal cations.

*Keywords:* Spiropyran; Photochromism; Ferrocene; Metal Cation

## Introduction

Transannular π-electron interaction between spatially arranged chromophores is receiving much increased attention from the viewpoints not only of mimic of photosynthetic reaction centers but also of development of new photo-responsive materials [1]. Although several covalently linked bi-chromophoric molecules with well-defined distance and orientation of the chromophores have been investigated [2], designing and synthesizing similar bi-photochromic systems remain to be developed. We recently reported a novel type of artificial receptors possessing a ferrocene skeleton as a modulator for two intermolecular interacting sites [3]. The decision for the use of ferrocene was based on the inter-ring spacing of 0.33 nm between two cyclopentadienyl (Cp) rings in ferrocene. Thus, two flat aromatic planes can interact with each other by π-stacking when both planes are

connected to the Cp rings. As part of our program aimed at the utilization of ferrocene as a useful modulator, we herein report synthesis and photochromic properties of ferrocene-modified bis(spirobenzopyran)s (Scheme 1).



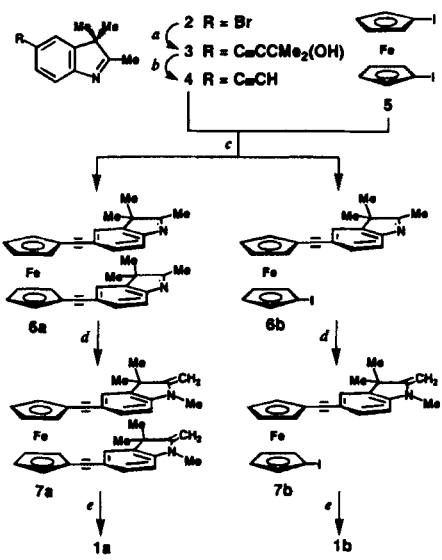

## Synthesis

The bis(spirobenzopyran) **1a** was synthesized from ferrocene-linked bis(3*H*-indole) **6a** and 5-nitrosalicylaldehyde by enamine-passed aldol type cyclization in the final step. The indole **6a** was derived by sequential Sonogashira reactions [4] of 5-bromo-2,3,3,-trimethyl-3*H*-indole [5] (**2**) and 1,1'-diiodoferrocene [6] (**5**) with 2-methyl-3-butyn-2-ol. The referential mono(spirobenzopyran) **1b** was similarly prepared via mono(3*H*-indole) **6b** (Scheme 2).

## Results and Discussion

The bis(spirobenzopyran) **1a** and mono(spirobenzopyran) **1b** showed similar photochromism to those of conventional spirobenzopyrans, i.e., isomerization of **1** to the colored merocyanines **1'** was induced by irradiation of UV-light, and the reverse process by visible-light or heat. The merocyanine forms **1'** were labile in aprotic

solvents, so absorption bands arising from the merocyanines ($\lambda_{max}$ = 585 nm for **1a'** and 583 nm for **1b'** in $CH_3CN$) disappeared within a few minutes even in the dark. Little stabilization of **1'** was observed by addition of metal cations, although the degree of hypsochromic band shifts of **1'** was dependent on the metals, indicating the presence of the electrostatic interactions between the metal cations and *p*-nitrophenolate oxygen of **1'**.




**Scheme 2:** (*a*) 2-Methyl-3-butyn-2-ol, $(Ph_3P)_2PdCl_2$, CuI, $Et_2NH$; (*b*) NaOH, toluene; (*c*) $(Ph_3P)_2PdCl_2$, $Cu(OAc)_2{\cdot}H_2O$, *i*-$Pr_2NH$; (*d*) $CH_3I$, $CH_3CN$, $CHCl_3$, then NaOH; (*e*) 5-nitrosalicylaldehyde, EtOH, $CHCl_3$.

The merocyanine forms were much stable in protic solvents. Thus, intense and long-lived coloration was observed in ethanol after irradiation of UV-light ($\lambda_{max}$ = 567 nm for **1a'** and 565 nm for **1b'**) (Figure 1a). The absorption spectrum of **1a'** revealed a small red shift of the longest wavelength bands compared with that of **1b'**. Negligible changes in the spectra of **1'**, however, occurred upon addition of any of alkali- and alkaline-earth-metal cations, reflecting that the electrostatic interactions seen in aprotic solvents (*vide supra*) are not effective because of the competitive interactions of the cations with the highly polar solvent. On the other hand, transition-metal cations gave interesting perturbation on the electric properties of the merocyanines. When various transition-metal cations (perchlorates of Mn(II), Ni(II), Fe(II), and Zn(II)) were added to the ethanol solution of

**1**, new absorption bands (400–450 nm) appeared in addition to the ordinary merocyanine ones (550–570 nm) after irradiation. Particular interest is in the case of Co(II) perchlorate, in which bis(spirobenzopyran) **1a** and mono(spirobenzopyran) **1b** gave substantially different results (Figure 1b). Although the newly appeared absorption bands still unknown and remain to be assigned, the "ditopic" property of the spatially arranged chromophores of **1a'** as a metal-chelating ligand may play a important role in the different behavior.

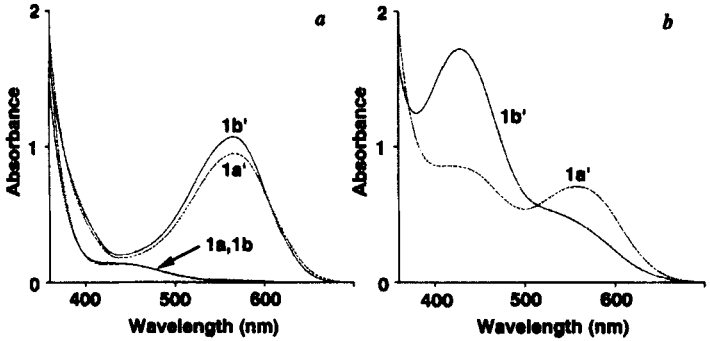



**Figure 1:** Electronic absorption spectra of **1a** (0.1 mM) and **1b** (0.2 mM) in EtOH (*a*) before irradiation of UV-light (360 nm; 3 min) and after the irradiation, and (*b*) in the presence of $Co(ClO_4)_2$ (0.4 mM) after the irradiation.

Further details of these metal-dependent photochromism of the spirobenzopyrans will be reported elesewhere together with results on other systems.

## Experimental

**5-(3-Hydroxy-3-methyl-1-butynyl)-2,3,3-trimethyl-3*H*-indole (3).** To an $Et_2NH$ (150 mL) solution of 5-bromo-2,3,3-trimethyl-3*H*-indole [5] **2** (8.72 g, 36.6 mmol), $(Ph_3P)_2PdCl_2$ (514 mg, 0.732 mmol), and CuI (70 mg, 0.366 mmol) was added 2-methyl-3-butyn-2-ol (6.16 g, 73.2 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 10 h. After removal of the solvent, the residue was poured into water and extracted with $CH_2Cl_2$. The $CH_2Cl_2$ extract was evaporated and chromatographed (silica gel; eluent, hexane/AcOEt 1:1) to give **3**: yield = 89% (7.90 g); oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.24 (s, 6 H), 1.64 (s, 6 H), 2.28 (s, 3 H), 4.51 (s, 1 H), 7.25–7.30 (m, 2 H), 7.50 (d, $J$ = 8.5 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 15.10, 22.65, 31.49, 53.36, 64.82, 81.79, 94.21, 119.46, 119.52, 124.47,

131.21, 145.29, 152.86, 189.01; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 242 ($MH^+$, 100%).

**5-Ethynyl-2,3,3-trimethyl-3*H*-indole (4).** A toluene (160 mL) suspension of **3** (7.90 g, 32.7 mmol) and NaOH (2.62 g, 65.4 mmol) was stirred at 120 °C for 6 h. After filtration, the filtrate was evaporated and chromatographed (silica gel; eluent, hexane/AcOEt 3:1) to give **4**: yield = 92% (5.50 g); mp 63–64 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.30 (s, 6 H), 2.29 (s, 3 H), 3.08 (s, 1 H), 7.41 (s, 1 H), 7.44–7.49 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 15.49, 22.90, 53.68, 76.79, 84.08, 118.54, 119.79, 125.15, 132.08, 145.73, 154.15, 189.56; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 184 ($MH^+$, 100%).

**Bis(3*H*-indole) 6a.** To an *i*-$Pr_2NH$ (7 mL) solution of 1,1'-diiodoferrocene [6] **5** (1.10 g, 2.51 mmol), $(Ph_3P)_2PdCl_2$ (42 mg, 0.060 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (12 mg, 0.060 mmol) was added an *i*-$Pr_2NH$ (7 mL) solution of **4** (1.20 g, 6.28 mmol) at room temperature. The reaction mixture was stirred at 85 °C for 6 h. After removal of the solvent, the residue was poured into water and extracted with $CH_2Cl_2$. The $CH_2Cl_2$ extract was evaporated and chromatographed (silica gel; eluent, AcOEt) to give **6a**: yield = 61% (884 mg); mp >164 °C (dec); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.22 (s, 12 H), 2.23 (s, 6 H), 4.29 (t, $J$ = 1.8 Hz, 4 H), 4.52 (t, $J$ = 1.8 Hz, 4 H), 7.34 (s, 2 H), 7.38 (s, 4 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 15.43, 22.90, 53.57, 66.96, 70.91, 72.90, 86.90, 86.99, 119.67, 120.29, 124.41, 131.26, 145.68, 153.27, 188.89; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 548 ($M^+$, 100%).

**Mono(3*H*-indole) 6b.** This indole was synthesized from **4** (200 mg, 1.09 mmol) and **5** (963 mg, 2.20 mmol) in a manner similar to that described for **6a**. **6b**: yield = 51% (278 mg); oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.28 (s, 6 H), 2.25 (s, 3 H), 4.20 (t, $J$ = 1.8 Hz, 2 H), 4.22 (t, $J$ = 1.8 Hz, 2 H), 4.42 (t, $J$ = 1.8 Hz, 2 H), 4.44 (t, $J$ = 1.8 Hz, 2 H), 7.24 (s, 1 H), 7.40 (s, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 15.49, 22.92, 41.07, 53.71, 70.81, 71.91, 73.85, 76.16, 86.65, 87.24, 119.69, 120.20, 124.40, 131.27, 145.74, 153.34, 189.01; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 493 ($M^+$, 100%).

**Bis(*exo*-methyleneindoline) 7a.** To a $CH_3CN$–$CHCl_3$ (20 + 20 mL) mixed solution of **6a** (884 mg, 1.53 mmol) was added $CH_3I$ (6.52 g, 45.9 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 8 h. After removal of the solvent, the residue was dissolved in water. The aqueous solution was basified to pH 11 with NaOH and extracted with ether. The ether extract was evaporated and chromatographed (silica gel; eluent, hexane/AcOEt/$Et_3N$ 40:10:1) to give **7a**: yield = 90% (794 mg); mp 130–131 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.30 (s, 12 H), 2.99 (s, 6 H), 3.87 (s, 4 H), 4.28 (s, 4 H), 4.51 (s, 4 H), 6.39 (d, $J$ = 8.3 Hz, 2 H), 7.17 (s, 2 H), 7.25 (d, $J$ = 8.3 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 28.67, 29.78, 43.77, 67.61, 70.73, 72.59, 74.28, 84.69, 87.43, 104.64, 112.97, 124.88, 131.65, 137.48, 145.91, 162.16; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 577 ($MH^+$, 100%).

**Mono(*exo*-methyleneindoline) 7b.** This *exo*-methyleneindoline was synthesized from **6b** (321 mg, 0.65 mmol) and $CH_3I$ (1.85 g, 13.0 mmol) in a manner similar to that described for **7a**. **7b**: yield = 59% (195 mg); oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.34 (s, 6 H), 3.03 (s, 3 H), 3.89 (s, 2 H), 4.21–4.23 (m, 4 H), 4.43–4.45 (m, 4 H), 6.45 (d, $J$ = 8.1 Hz, 1 H), 7.21 (d, $J$ = 1.6 Hz, 1 H), 7.32 (dd, $J$ = 8.1, 1.6 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 28.79, 29.87, 41.13, 43.91, 70.93, 71.82, 73.75, 74.36, 76.19, 82.25, 87.99, 104.75, 112.89, 125.01, 131.73, 137.69, 146.19, 162.32;

FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 508 ($MH^+$, 100%).

**Bis(spirobenzopyran) 1a.** To an EtOH (1.5 mL) solution of 5-nitrosalicylaldehyde (87 mg, 0.52 mmol) was added an $CHCl_3$ (1.5 mL) solution of **7a** (76 mg, 0.13 mmol) dropwise at room temperature over a 10 min period. The reaction mixture was stirred at 60 °C for 1.5 h. After removal of the solvent, the residue was purified by HPLC (GPC; eluent, $CHCl_3$) to give **1a**: yield = 69% (79 mg); mp 134–135 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.19 (s, 6 H), 1.29 (s, 6 H), 2.75 (s, 6 H), 4.31 (t, $J$ = 1.8 Hz, 4 H), 4.52 (t, $J$ = 1.8 Hz, 4 H), 5.84 (d, $J$ = 10.2 Hz, 2 H), 6.48 (d, $J$ = 8.0 Hz, 2 H), 6.76 (d, $J$ = 8.0 Hz, 2 H), 6.94 (d, $J$ = 10.2 Hz, 2 H), 7.21 (s, 2 H), 7.35 (d, $J$ = 8.0 Hz, 2 H), 8.01 (s, 2 H), 8.02 (d, $J$ = 8.0 Hz, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 19.85, 25.75, 28.82, 52.11, 67.33, 70.99, 72.77, 85.15, 87.08, 106.16, 106.87, 114.60, 115.42, 118.53, 121.14, 122.72, 124.87, 125.91, 128.46, 131.87, 136.27, 141.03, 147.39, 159.51; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 874 ($M^+$, 100%).

**Mono(spirobenzopyran) 1b.** This spirobenzopyran was synthesized from **7b** (195 mg, 0.38 mmol) and 5-nitrosalicylaldehyde (127 mg, 0.76 mmol) in a manner similar to that described for **1a**. **1b**: yield = 87% (212 mg); mp 195–196 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.20 (s, 3 H), 1.31 (s, 3 H), 2.76 (s, 3 H), 4.22–4.26 (m, 4 H), 4.44–4.47 (m, 4 H), 5.85 (d, $J$ = 10.5 Hz, 1 H), 6.51 (d, $J$ = 8.0 Hz, 1 H), 6.78 (d, $J$ = 8.0 Hz, 1 H), 6.94 (d, $J$ = 10.5 Hz, 1 H), 7.23 (d, $J$ = 1.7 Hz, 1 H), 7.40 (dd, $J$ = 8.0, 1.7 Hz, 1 H), 8.02 (s, 1 H), 8.01–8.07 (m, 1 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 19.86, 25.79, 28.83, 41.11, 52.12, 70.90, 71.83, 73.83, 73.86, 76.24, 84.57, 87.68, 106.15, 106.90, 114.48, 115.47, 118.52, 121.14, 122.72, 124.87, 125.94, 128.47, 131.91, 136.29, 141.04, 147.50, 159.52; FABMS (in 3-nitrobenzyl alcohol) *m/e* (relative intensity) 656 ($M^+$, 100%).

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