Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Selective Coloration of Cryptand - Type Spirobenzopyran for Alkaline - Earth - Metal Cations

Masahiko Inouye [a] & Yoshiyuki Noguchi [a]

[a] Department of Applied Materials Science, University of Osaka Prefecture, Sakai, Osaka, 593, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Masahiko Inouye & Yoshiyuki Noguchi (1994): Selective Coloration of Cryptand - Type Spirobenzopyran for Alkaline - Earth - Metal Cations, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 187-189

To link to this article: http://dx.doi.org/10.1080/10587259408037811

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 187–189
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

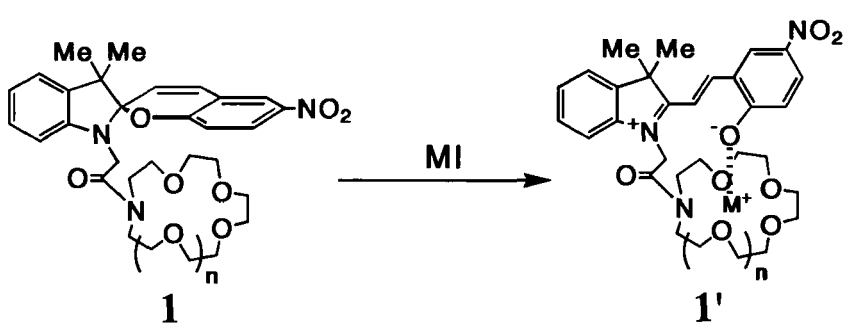
SELECTIVE COLORATION OF CRYPTAND - TYPE SPIROBENZOPYRAN FOR ALKALINE - EARTH - METAL CATIONS

MASAHIKO INOUYE and YOSHIYUKI NOGUCHI
Department of Applied Materials Science
University of Osaka Prefecture, Sakai, Osaka 593, Japan

Abstract Cryptand-type spirobenzopyrans were synthesized. Sensitive and selective colorations of the spirobenzopyrans were observed for alkaline-earth-metal cations.

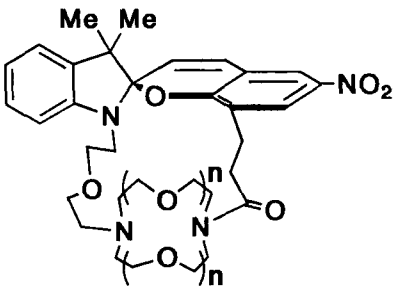
INTRODUCTION

Artificial receptors whose optical properties are significantly perturbed by recognition of cations are of current interest and attracting much attention from the viewpoint of biomimmetic chemistry.[1] These "recognition-structural change-signaling" receptors may also stimulate the investigation of molecular sensors for biologically important alkali-metal cations. We previously introduced a new class of spirobenzopyrans bearing a monoaza-crown ring (**1**) as a recognition site, of which isomerization to the open colored merocyanines (**1'**) was induced by recognition of alkali-metal cations.[2] This new type of chromoionophore is conceptually different from the conventional crown ether dyes thus far synthesized, because in the latter cases, the absorption bands of chromophores are merely shifted by the complexation of cations.



1 **1'**

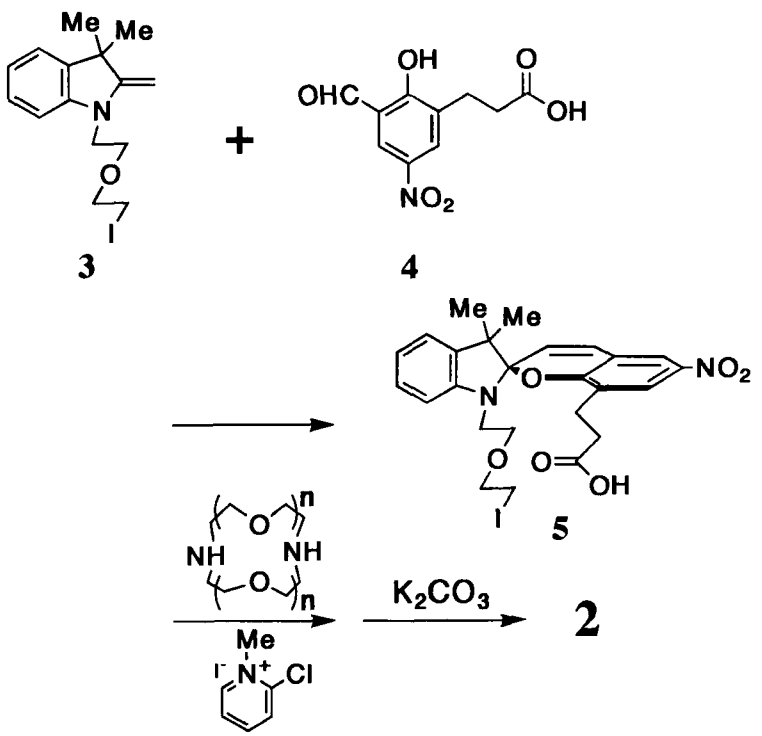
Here we report advanced crowned spirobenzopyrans, cryptand-type spirobenzopyrans **2**, in which sensitive and selective recognition of alkaline-earth-metal cations induces the structural change in the spirobenzopyrans to the colored merocyanines.



2a~2c n=1~3

SYNTHESIS

The cryptand-type spirobenzopyrans **2** were synthesized from two key intermediates, **3** and **4**. The aldol-type cyclization of **3** with **4** gave spirobenzopyran **5** bearing iodoalkyl and carboxyl groups, which was condensed with diaza-crown ether by Mukaiyamas' method, followed by high-dilution cyclization to **2**.



RESULTS AND DISCUSSION

The spirobenzopyran **2b** thus prepared showed no absorption bands above 400nm in nonhydroxylic solvents, indicating the closed spiropyran form. When a equimolar quantity of SrI_2 was added to the CH_3CN solution of **2b**, however, new absorption bands appeared (λmax=528nm, ε=17000), while only small and no changes were observed upon addition of BaI_2 and other alkaline-earth-metal iodide, respectively. While **2a** revealed a significant and selective absorption with CaI_2, **2c** showed little changes in its absorption spectrum in the presence of any alkaline-earth-metal cations. This selective coloration was shown to be unambiguously due to the increasing proportion of the merocyanine form to that of the spiropyran form by recognition of Sr^{2+}(**2b**) and Ca^{2+}(**2a**) on the basis of NMR and FABMS spectra.

REFERENCES

1. (a) H.-G. Löhr and F. Vögtle, *Acc. Chem. Res.*, *18*, 65 (1985). (b) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, *27*, 89 (1988).
2. (a) M. Inouye, M. Ueno, T. Kitao and K. Tsuchiya, *J. Am. Chem. Soc.*, *112*, 8977 (1990). (b) M. Inouye, M. Ueno, K. Tsuchiya, N. Nakayama, T. Konishi and T. Kitao, *J. Org. Chem.*, *57*, 5377 (1992).