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LETTERS TO THE EDITOR

Fluorescent Chemosensors on the Basis of Naphtho[1,8-*bc*]pyrans

A. V. Tsukanov[a], A. D. Dubonosov[b], O. M. Golyanskaya[a], V. V. Mezheritskii[a], Yu. V. Revinskii[a], V. A. Bren'[a, b], and V. I. Minkin[a, b]

[a]*Institute of Physical and Organic Chemistry, Rostov State University, pr. Stachki 194/2, Rostov-on-Don, 344090, Russia*
e-mail: dubon@ipoc.rsu.ru
[b]*South Research Center, Russian Academy of Sciences, Rostov-on-Don, Russia*

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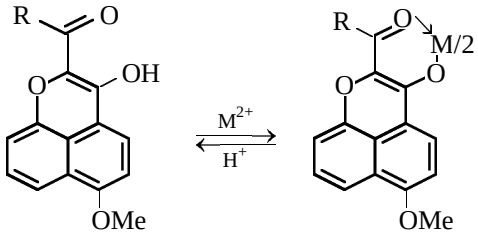
Fluorescent chemosensors for determination of trace amounts of metal cations are important for the environmental chemistry, biology, and medicine [1, 2]. Two main types of sensor molecules capable of chelating metal ions are generally distinguished: CHEF (chelation enhancement of fluorescence) and CHEQ (chelation enhancement of quenching) [3].

We have examined sensor properties of 2-acyl-3-hydroxy-6-methoxynaphtho[1,8-*bc*]pyrans **Ia** and **Ib** in which the coordination center and the fluorophoric group are combined in a single molecule without a bridge necessary for most chemosensors [1].



Ia, Ib **IIa, IIb**

R = Me (**a**), Ph (**b**).

Solutions of compounds **Ia** and **Ib** in propan-2-ol absorb in the long-wave region at λ 438 and 493 nm, respectively, and exhibit a strong fluorescence in the visible region. The fluorescence maxima in propan-2-ol are λ_{max} 532 nm (**Ia**, excitation wavelength λ_{ex} 430 nm) and λ_{max} 571 nm (**Ib**, λ_{ex} 480 nm). The fluorescence quantum yields are fairly high, λ = 0.46 (**Ia**) and 0.52 (**Ib**). Addition of heavy metal salts to solutions of naphthopyrans **Ia** and **Ib**) ($c_{\mathbf{I}} = c_{M^{2+}} = 2.5 \times 10^{-5}$ M) leads to the following results. Complex formation of 2-acetyl derivative **Ia** with Pb^{2+} and Hg^{2+} (complexes **IIa**) induces a blue shift of both absorption and emission maxima by ~20 nm with an appreciable reduction in the fluorescence intensity (I_0/I = 14.0 and 23.6, respectively). Complexes **IIb** derived from 2-benzoyl derivative **Ib** and Co^{2+} or Cu^{2+} cations show almost no fluorescence (I_0/I = 122.4 and 137.7, respectively) as a result of clearly pronounced CHEQ effect. Thus 2-benzoyl-3-hydroxy-6-methoxynaphtho[1,8-*bc*]pyran (**Ib**) can be regarded as a new highly efficient "naked-eye" [4] fluorescent chemosensor for copper and cobalt ions.

2-Acetyl-3-hydroxy-6-methoxynaphtho[1,8-*bc*]-pyran (Ia) was synthesized previously [5]. UV spectrum (propan-2-ol), λ_{max}, nm ($\varepsilon \times 10^{-4}$, l mol^{-1} cm^{-1}): 267 (1.95), 345 (0.54), 360 (0.68), 438 (1.31).

2-Benzoyl-3-hydroxy-6-methoxynaphtho[1,8-*bc*]-pyran (Ib) was synthesized previously [5]. UV spectrum (propan-2-ol), λ_{max}, nm ($\varepsilon \times 10^{-4}$, l mol^{-1} cm^{-1}): 279 (2.50), 348 (0.50), 362 (0.44), 493 (2.04).

The electronic absorption spectra were measured on a Specord M-40 spectrophotometer, and the fluorescence spectra were recorded on a Hitachi 650-60 spectrofluorimeter.

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