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> SHORT COMMUNICATIONS

## Fluorescent Chemosensors Based on N-Aminoimidazole and N-Aminobenzimidazole

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Nowadays chemosensors are widely used in express determination of ions and neutral compounds in various samples [1, 2]. Ion-sensitive compounds have found application not only in analytical and environmental chemistry but also in biology. It is very important to design efficient and selective chemosensors for the determination and biovisualization of ions (cations and anions) involved in biological cell processes [3, 4].

We previously demonstrated the possibility of using anthracen-9-ylmethyl-substituted benzimidazol-2amines as efficient pH sensors [5, 6]. In continuation of these studies we have synthesized N-amino derivatives of imidazole and benzimidazole containing an anthracene fluorophore group linked to the NNH group. By reaction of benzimidazole-1,2-diamine (I) and 1-amino-4-phenyl-1*H*-imidazole-2-thiol (II) with anthracene-9-carbaldehyde in acetic acid we synthesized the corresponding Schiff bases which were reduced to diamines III and IV with sodium tetrahydridoborate. In the reaction with diamine I, only the N–NH<sub>2</sub> amino group was involved in the condensation. The <sup>1</sup>H NMR spectrum of **III** contained signals typical of protons in the NH<sub>2</sub>, NH, and CH<sub>2</sub> groups.

Amines III and IV showed anthracene-like fluorescence with an emission maximum at  $\lambda$  414 (415) nm. Their chemosensor properties were studied in acetonitrile ( $c = 5 \times 10^{-6}$  M) by comparing the fluorescence spectra before and after addition of cations  $(H^+, Zn^{2+},$  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Hg^{2+}$ ) and anions (AcO<sup>-</sup>,  $CN^{-}$ ,  $NO_{3}^{-}$ ,  $F^{-}$ ,  $Cl^{-}$ , see table). The results revealed different selectivities of III and IV toward ionic species. The fluorescence intensity of compound III considerably increased in the presence of  $H^+$ ,  $Zn^{2+}$ , and  $Cd^{2+}$  ions and decreased on addition of  $Cu^{2+}$  and  $Hg^{2+}$ . Aminothiol IV turned out to be more sensitive in the determination of anions. It displayed selective increase in the fluorescence intensity in the presence of acetate ions. In all cases, addition of ions to solutions of III and IV did not induce appreciable change in the position of absorption and emission maxima.



Compound	Cations							Anions					
no.	$\mathrm{H}^{+}$	Zn <sup>2+</sup>	$\mathrm{Cd}^{2^+}$	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	$\mathrm{Hg}^{2^+}$	$AcO^{-}$	$\mathrm{CN}^-$	$NO_3^-$	$F^{-}$	Cl	$\mathrm{H}_{2}\mathrm{PO}_{4}^{-}$
III	92.0	30.0	71.0	1.7	0.3	1.7	0.1	1.4	0.6	3.4	0.6	2.8	0.6
IV	18.0	6.7	3.6	0.9	1.6	1.0	0.6	5.0	1.1	1.1	1.2	1.0	1.1

Relative changes in the fluorescence intensities ( $I/I_0$ ) of compounds III and IV ( $c = 5 \times 10^{-6}$  M) in acetonitrile on addition of cations or NBu<sub>4</sub><sup>+</sup> An<sup>-</sup> ( $c = 2.5 \times 10^{-5}$  M)

Thus, 1-(anthracen-9-ylmethylamino)-4-phenyl-1*H*-imidazole-2-thiol is a selective fluorescent chemosensor for acetate ions.

 $N^{1}$ -(Anthracen-9-ylmethyl)-1*H*-benzimidazole-1,2-diamine (III). A mixture of 0.3 g (2 mmol) of 1H-benzimidazole-1,2-diamine (I) [7] and 0.42 g (2 mmol) of anthracene-9-carbaldehyde in 5 mL of glacial acetic acid was heated for 2 h under reflux. The mixture was cooled and diluted with 25 mL of water, and the pre-cipitate was filtered off, washed with water  $(4 \times 10 \text{ mL})$ , and dried in air. The Schiff base thus obtained was dissolved in 40 mL of ethanol-DMF (2:1), 0.20 g (5 mmol) of NaBH<sub>4</sub> was added, and the mixture was stirred for 30 min, diluted with 100 mL of water, and treated with dilute acetic acid to decompose excess reducing agent. The precipitate was filtered off, washed with water, dried in air, and recrystallized from butan-1-ol. Yield 0.6 g (83%), mp 289-290°C (from butan-1-ol). IR spectrum, v, cm<sup>-1</sup>: 3334, 1665, 1450, 1370. <sup>1</sup>H NMR spectrum, δ, ppm: 4.84 br.s (2H, NH<sub>2</sub>), 5.04 t (1H, NH, J = 5.4 Hz), 5.35 d (2H, CH<sub>2</sub>, J =5.4 Hz), 7.12–7.64 m (8H, H<sub>arom</sub>), 8.05 d (2H, 1-H, 8-H, J = 8.6 Hz), 8.36 d (2H, 4-H, 5-H, J = 8.6 Hz), 8.54 d (2H, 10-H, J = 8.6 Hz). Fluorescence spectrum ( $c = 5 \times 10^{-5}$  M):  $\lambda_{max}$  416 nm. Found, %: C 78.03; H 5.40; N 16.57. m/z 338  $[M]^+$ . C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>. Calculated, %: C 78.08; H 5.36; N 16.56. M 338.15.

1-(Anthracen-9-ylmethylamino)-4-phenyl-1*H*imidazole-2-thiol (IV) was synthesized in a similar way from 1-amino-4-phenyl-1*H*-imidazole-2-thiol (II) [8] and anthracene-9-carbaldehyde. Yield 86%, mp 281–282°C (from butan-1-ol). IR spectrum, v, cm<sup>-1</sup>: 3430, 1664, 1375. <sup>1</sup>H NMR spectrum, δ, ppm: 5.37 s (2H, CH<sub>2</sub>), 6.12 br.s (1H, NH), 6.71 br.s (1H, 5'-H), 7.23–7.43 m (5H, H<sub>arom</sub>), 7.49 t (2H, H<sub>arom</sub>, J =6.4 Hz), 7.49 t (2H, H<sub>arom</sub>, J = 6.4 Hz), 7.58 t (2H, H<sub>arom</sub>, J = 6.4 Hz), 8.03 d (2H, 1-H, 8-H, J = 8.8 Hz), 8.50 s (1H, 10-H), 8.64 d (2H, 5-H, 6-H, J = 8.8 Hz), 10.45 br.s (1H, SH). Fluorescence spectrum (c = $5 \times 10^{-5}$  M):  $\lambda_{max}$  414 nm. Found, %: C 75.51; H 5.07; N 11.07; S 8.35. *m/z* 381 [*M*]<sup>+</sup>. C<sub>24</sub>H<sub>19</sub>N<sub>3</sub>S. Calculated, %: C 75.56; H 5.02; N 11.02; S 8.40. *M* 381.50.

The <sup>1</sup>H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) from solutions in CDCl<sub>3</sub>: the chemical shifts were determined relative to the residual proton signal of the solvent (CHCl<sub>3</sub>,  $\delta$  7.25 ppm). The electronic absorption spectra were measured on a Varian Cary 100 spectrophotometer. The luminescence spectra were recorded on a Varian Eclipse spectrofluorimeter. The IR spectra were taken on a Varian Excalibur FTIR instrument. The mass spectra were obtained on a Shimadzu GCMS-QP2010SE spectrometer. The melting points were determined in glass capillaries using a PTP (M) melting point apparatus. The progress of reactions and the purity of products were monitored by TLC on Silufol UV 254 plates using chloroform as eluent; spots were visualized by treatment with iodine vapor in a moist chamber.

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