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Colorimetric and fluorimetric detection of Cu^{2+} ions in aqueous solution using styrylpyridinium dye bearing iminodiacetate receptor group

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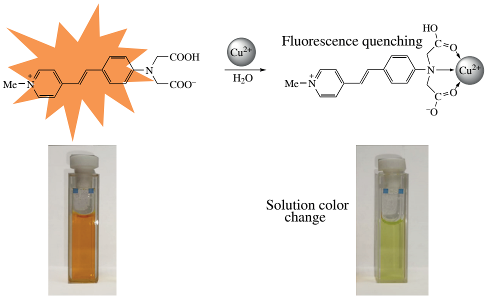
A new 4-styrylpyridinium derivative containing an *N*,*N*-bis(carboxymethyl)amino (iminodiacetate) group as the receptor moiety exhibits a hypsochromic shift and fluorescence quenching when complexed with a copper(II) cation. This compound may be proposed as a fluorescent chemosensory agent for the selective detection of Cu^{2+} in aqueous solutions.

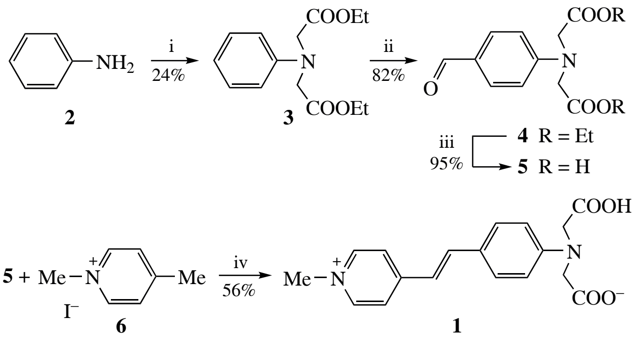


Keywords: sensor, copper(II) cation, fluorescence, complexation, iminodiacetate receptor, bis(carboxymethyl)amino group, intramolecular charge transfer, hypsochromic shift, styryl dye, pyridinium compounds.

The divalent copper cation is involved in many processes occurring in a living organism, such as cellular respiration, iron metabolism, neurotransmitter formation, and connective tissue biosynthesis.[1,2] However, in excessive amounts, copper manifests itself as a toxic element disrupting the functioning of liver, kidneys, and brain.[3–6] Copper(II) compounds are among the most common inorganic pollutants present in many industrial wastewater and can also enter the soil as a result of the use of pesticides.[7,8] For this reason, monitoring the content of Cu^{2+} cation in environmental objects and biological systems is an important analytical task.

Currently, optical chemosensors are widely used to detect low concentrations of metal ions. Sensor molecules consist of a photoactive fragment responsible for the appearance of a spectral response and a receptor group that provides binding of the analyzed cation.[9–12] Since 2010, a fairly large number of highly selective fluoro- and chromoionophore systems based on organic dyes of various classes have been proposed for the determination of Cu^{2+} cations.[11–16] Nevertheless, there is still a high level of interest in Cu^{2+} sensors capable of displaying a fluorescent and/or colorimetric response in the aquatic environment.

In order to obtain a chemosensor for the copper(II) cation, we selected the styryl pyridinium chromophore as a photoactive component in this work, which has proven to be one of the most popular optical platforms for creating molecular devices of various types.[17–20] The *N*,*N*-bis(carboxymethyl)amino group (iminodiacetate group) was used as the receptor, it was introduced into the chromophore as an electron-donating (ED) substituent conjugated to the π-deficient pyridinium core (compound **1**, Scheme 1). Presumably, complexation of sensor **1** with a cation should be accompanied by a decrease in the ED properties of the receptor, which would lead to an increase in the energy of the long wavelength ICT (intramolecular charge transfer) transition from the nitrogen atom of the receptor to the pyridinium residue and, thereby, to a hypsochromic shift in the electronic absorption spectrum. According to the literature data, the selected receptor has the ability to bind Cu^{2+} and Zn^{2+} ions in aqueous solutions.[21–23] It should be noted that a combination of a styrylpyridinium chromophore with an iminodiacetate group has been described earlier,[24] however, that compound similar in structure to sensor **1** was used as a photosensitizer for solar cell production and was not investigated with respect to its sensor properties towards metal cations. Literature also reports on a 4-nitroazobenzene derivative containing a similar receptor in position 4′, but in that case, the spectral response towards Cu^{2+} ion in aqueous solution was absent due to insignificant involvement of nitrogen atom of bis(carboxymethyl)amino group in coordination with cation. To show response, an additional chelation substituent (ethoxy group) had to be introduced in the position 3′ of the azobenzene chromophore.[21,22]



Scheme 1 *Reagents and conditions*: i, $BrCH_2COOEt$, NEt_3, CH_2Cl_2, Δ; ii, $POCl_3$, DMF, Δ; iii, KOH, EtOH, H_2O, then HCl, H_2O; iv, piperidine, EtOH, MW, Δ.

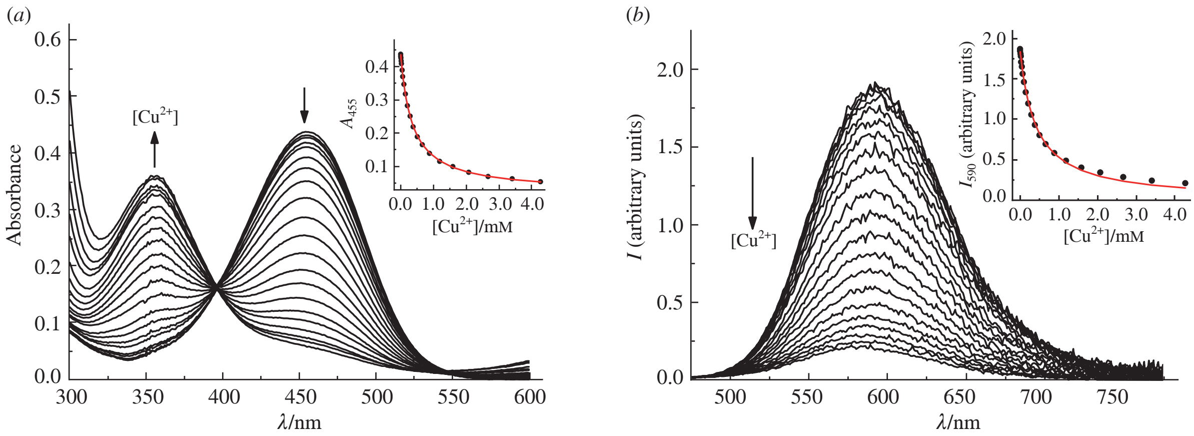


Figure 1 (*a*) Absorption and (*b*) emission spectra of compound **1** (12.5 μM) in water at pH 5.9 (acetate buffer, 0.1 M) upon gradual addition of copper(II) perchlorate. Upper inserts show the plots of absorbance at 455 nm (A_{455}, panel *a*) and fluorescence intensity at 490 nm (I_{490}, panel *b*) *versus* concentration of Cu^{2+} cation. Excitation wavelength was 396 nm.

Compound **1** was synthesized by the condensation of *N*-methyl-γ-picolinium iodide **6** with aldehyde **5** under basic conditions (see Scheme 1). The latter was prepared from aniline **2** and ethyl bromoacetate as described.[24]

The absorption spectrum of styryl dye **1** in water contains a long wavelength ICT transition band with a maximum (λ_{max}^{abs}) at 455 nm [Figure 1(*a*)]. Fluorescence of **1** is observed in the region of 500–700 nm [$\lambda_{max}^{fl} = 593$ nm, see Figure 1(*b*)] and is characterized by a quantum yield φ^{fl} equal to 0.01.

Complexation of sensor **1** with copper(II) cation was studied at pH 5.9 in acetate buffer solution. On the one hand, at the specified pH value, the nitrogen atom of the receptor group conjugated with the pyridinium ring is not subjected to protonation,[25] and on the other hand, the weakly acidic medium suppresses hydrolysis of the Cu^{2+} cation in salt $Cu(ClO_4)_2$, which should increase the stability of the resulting complexes. In the electronic absorption spectrum, the addition of Cu^{2+} led to a decrease in the intensity of the ICT band with the simultaneous appearance of a peak with $\lambda_{max}^{abs} = 355$ nm, while the color of the solution changed from orange to pale yellow. The isosbestic point was observed at 396 nm.

It was found that the experimental data on the dependence of the optical density of the solution at a wavelength of 455 nm on the concentration of Cu^{2+} [shown as dots in Figure 1(*a*)] are in the best agreement with the calculation in the SPECFIT/32 program (shown as a solid curve therein) taking into account the formation of only one metal–ligand 1 : 1 complex according to the equilibrium:

$$L + Cu^{2+} \rightleftarrows [CuL]^{2+},$$

where the designation L corresponds to the ligand (compound **1**). Based on spectrophotometric titration data, the value of the logarithm of the stability constant (log*K*) of the $[CuL]^{2+}$ complex was determined to be 3.46 ± 0.01.

In the fluorescence spectrum recorded using excitation at the isosbestic point (396 nm), the addition of aliquots of copper(II) perchlorate solution caused a decrease in the intensity of the emission band [see Figure 1(*b*)]. The observed spectral changes corresponded to the formation of a non-fluorescent complex $[CuL]^{2+}$, the log*K* value for which, obtained as a result of processing the spectrofluorometric titration data, was very close to the one obtained in the spectrophotometric experiment and was 3.39 ± 0.02. In all likelihood, the suppression of the radiative deactivation of the chromophore in the $[CuL]^{2+}$ complex is due to the paramagnetic nature of the Cu^{2+} cation. Such fluorescence quenching during complex formation is a characteristic feature of many optical chemosensors for the Cu^{2+} cation.[15,16,26]

The fluorescent and colorimetric response of chemosensor **1** to the Cu^{2+} cation was selective: the presence of 40 equiv. of other metal perchlorates (Ag^+, Ni^{2+}, Hg^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, Fe^{2+}) did not cause a significant change in the shape and intensity of the spectral bands. As an example, Figure 2 shows the ratio of the fluorescence intensity of a solution of free ligand **1** before addition of the cation (I_0) to the intensity after addition (*I*). The exception was the Zn^{2+} cation when a slight increase in the intensity of the emission band was noted. In the course of the work, the possibility of detecting Cu^{2+} in the presence of competing ions was also tested. In a typical experiment, the emission (or absorption) spectrum was recorded before and after the addition of 40 equiv. of Ag^+, Ni^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, and Fe^{2+} to a solution containing chemosensor **1** and 40 equiv. of Cu^{2+}. As can be seen from the data presented in Figure 2, all cations except Zn^{2+} did not cause a significant decrease in the analytical signal. Presumably, the Zn^{2+} cation forms a fluorescent complex with ligand **1** and interferes with the determination of Cu^{2+}. The coordination of Zn^{2+} in aqueous solution with the bis(carboxymethyl)amino group is known.[23]

The dependence of the fluorescence intensity of sensor **1** at 590 nm (I_{590}) and the optical density at 455 nm (A_{455}) showed a good linear correlation (correlation coefficients in both cases were 0.993) with the Cu^{2+} concentration in the range of 3–40 μM (see Online Supplementary Materials, Figures S1 and S2). By the tangents of the slope angles *r* of the corresponding calibration lines and the standard deviation of the analytical signal *s* (obtained in blank experiment) according to equation (1),[27] it was found that the values of the detection limits (C_{DL}) of Cu^{2+} cations using sensor **1** under specified conditions were 27 μM

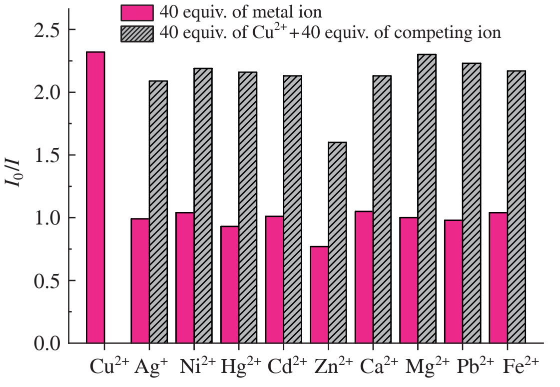


Figure 2 Selectivity of fluorescent response of sensor **1** (12.5 μM) to the presense of copper(II) cations in water at pH 5.9 (acetate buffer, 0.1 M). Excitation wavelength 396 nm.

(spectrofluorometry) and 12 μM (spectrophotometry). The higher C_{DL} value in the former case can be explained by a rather low fluorescence intensity of sensor **1** and a relatively high s as a result. However, both calculated C_{DL} values are close to the maximum allowable concentrations of copper(II) ions in drinking water (31.5 μM).[16]

$$C_{DL} = \frac{3s}{r} \qquad (1)$$

In summary, we have synthesized a new fluorescent ICT chemosensor capable of detecting copper(II) cations in an aqueous solution at the level of their maximum permissible concentration by changes in the absorption and fluorescence spectra. The presented results of the study of sensory properties of **1** are of interest for the development of fluorescent receptors for heavy and transition metal cations based on styryl dyes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7718.

References

1 T. Tsang, C. I. Davis and D. C. Brady, *Curr. Biol.*, 2021, **31**, R421; https://doi.org/10.1016/j.cub.2021.03.054.

2 L. Chen, J. Min and F. Wang, *Signal Transduction Targeted Ther.*, 2022, **7**, 378; https://doi.org/10.1038/s41392-022-01229-y.

3 M. Araya, M. Olivares and F. Pizarro, *Int. J. Environ. Health*, 2007, **1**, 608; https://doi.org/10.1504/IJENVH.2007.018578.

4 H. Tapiero, D. M. Townsend and K. D. Tew, *Biomed. Pharmacother.*, 2003, **57**, 386; https://doi.org/10.1016/S0753-3322(03)00012-X.

5 J. J. DiNicolantonio, D. Mangan and J. H. O'Keefe, *Open Heart*, 2018, **5**, e000784; https://doi.org/10.1136/openhrt-2018-000784.

6 A. A. Taylor, J. S. Tsuji, M. R. Garry, M. E. McArdle, W. L. Goodfellow, Jr., W. J. Adams and C. A. Menzie, *Environ. Manage.*, 2020, **65**, 131; https://doi.org/10.1007/s00267-019-01234-y.

7 A. M. Elkhatat, M. Soliman, R. Ismail, S. Ahmed, N. Abounahia, S. Mubashir, S. Fouladi and M. Khraisheh, *Bull. Natl. Res. Cent.*, 2021, **45**, 218; https://doi.org/10.1186/s42269-021-00677-w.

8 C. Hadjipanagiotou, A. Christou, A. M. Zissimos, E. Chatzitheodoridis and S. P. Varnavas, *Environ. Sci. Pollut. Res.*, 2020, **27**, 41279; https://doi.org/10.1007/s11356-020-10098-3.

9 P. A. Panchenko, Yu. V. Fedorov, O. A. Fedorova, B. A. Izmailov, V. A. Vasnev, V. V. Istratov, E. A. Makeeva, M. N. Rumyantseva and A. M. Gaskov, *Mendeleev Commun.*, 2011, **21**, 12; https://doi.org/10.1016/j.mencom.2011.01.005.

10 P. A. Panchenko, P. A. Ignatov, M. A. Zakharko, Yu. V. Fedorov and O. A. Fedorova, *Mendeleev Commun.*, 2020, **30**, 55; https://doi.org/10.1016/j.mencom.2020.01.018.

11 Y. Jeong and J. Yoon, *Inorg. Chim. Acta*, 2012, **381**, 2; https://doi.org/10.1016/j.ica.2011.09.011.

12 L. Li, J. Wang, S. Xu, C. Li and B. Dong, *Front. Chem.*, 2022, **10**, 875241; https://doi.org/10.3389/fchem.2022.875241.

13 G. Sivaraman, M. Iniya, T. Anand, N. G. Kotla, O. Sunnapu, S. Singaravadivel, A. Gulyani and D. Chellappa, *Coord. Chem. Rev.*, 2018, **357**, 50; https://doi.org/10.1016/j.ccr.2017.11.020.

14 M. Saleem, M. Rafiq, M. Hanif, M. A. Shaheen and S.-Y. Seo, *J. Fluoresc.*, 2018, **28**, 97; https://doi.org/10.1007/s10895-017-2178-z.

15 T. Chopra, S. Sasan, L. Dev, R. Parkesh and K. K. Kapoor, *Coord. Chem. Rev.*, 2022, **470**, 214704; https://doi.org/10.1016/j.ccr.2022.214704.

16 K. M. Trevino, C. R. Wagner, E. K. Tamura, J. Garcia and A. Y. Louie, *Dyes Pigm.*, 2023, **214**, 110881; https://doi.org/10.1016/j.dyepig.2022.110881.

17 E. Yu. Chernikova, A. I. Grachev, A. S. Peregudov, O. A. Fedorova and Yu. V. Fedorov, *Dyes Pigm.*, 2021, **189**, 109194; https://doi.org/10.1016/j.dyepig.2021.109194.

18 P. A. Panchenko, A. V. Efremenko, A. S. Polyakova, A. V. Feofanov, M. A. Ustimova, Yu. V. Fedorov and O. A. Fedorova, *Biosensors*, 2022, **12**, 770; https://doi.org/10.3390/bios12090770.

19 A. S. Efimova, M. A. Ustimova, N. S. Chmelyuk, M. A. Abakumov, Yu. V. Fedorov and O. A. Fedorova, *Biosensors*, 2023, **13**,734; https://doi.org/10.3390/bios13070734.

20 A. S. Efimova, M. A. Ustimova, M. A. Maksimova, A. Yu. Frolova, V. I. Martynov, S. M. Deyev, A. A. Pakhomov, Yu. V. Fedorov and O. A. Fedorova, *Mendeleev Commun.*, 2023, **33**, 384; https://doi.org/10.1016/j.mencom.2023.04.027.

21 T. Gunnlaugsson, J. P. Leonard and N. S. Murray, *Org. Lett.*, 2004, **6**, 1557; https://doi.org/10.1021/ol0498951.

22 J. Pang, L. Shi, M. Li and X. Hu, *RSC Adv.*, 2020, **10**, 23196; https://doi.org/10.1039/d0ra02468f.

23 J. H. Lee, J. H. Lee, S. H. Jung, T. K. Hyun, M. Feng, J.-Y. Kim, J.-H. Lee, H. Lee, J. S. Kim, C. Kang, K.-Y. Kwon and J. H. Jung, *Chem. Commun.*, 2015, **51**, 7463; https://doi.org/10.1039/c5cc01364j.

24 E. Stathatos, P. Lianos, A. Laschewsky, O. Quari and P. van Cleuvenbergen, *Chem. Mater.*, 2001, **13**, 3888; https://doi.org/10.1021/cm0012217.

25 P. A. Panchenko, A. V. Efremenko, A. V. Feofanov, M. A. Ustimova, Yu. V. Fedorov and O. A. Fedorova, *Sensors*, 2021, **21**, 470; https://doi.org/10.3390/s21020470.

26 M. A. Pavlova, P. A. Panchenko and O. A. Fedorova, *Mendeleev Commun.*, 2024, **34**, 335; https://doi.org/10.1016/j.mencom.2024.04.008.

27 H.-P. Loock and P. D. Wentzell, *Sens. Actuators, B*, 2012, **173**, 157; https://doi.org/10.1016/j.snb.2012.06.071.

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