Methods and Applications in Fluorescence

PAPER

Non-covalent binding and selective fluorescent sensing of dipyrone with a carbocyanine dye and cetyltrimethylammonium bromide

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Abstract

The work is aimed at the search of selective fluorescent sensors without using specific artificial receptors, antibodies, enzymes etc. With this end in view, methods based on non-covalent binding of target analytes are sought. We observed dramatic changes in the emission spectrum of a carbocyanine dye in a micellar surfactant solution (cetyltrimethylammonium bromide, CTAB) in the presence of dipyrone (metamizol, analgin): the 480 nm band intensity increases with a simultaneous decrease in intensity in near-IR region (720 nm). MALDI and NMR-^{1}H data show the intact molecules of dipyrone and the dye. The detection can be performed in the presence of other organic species and inorganic salts. Dipyrone testing is feasible within 5×10^{-7}–5×10^{-4} M with RSDs of 3.5% by using a visualizer instead of a spectrofluorimeter.

1. Introduction

Many selective fluorimetric sensing methods are based on an interaction of the analyte covalently with the probe or non-covalently with a dedicated supramolecular receptor [1]. However, the development of selective receptors requires significant synthetic efforts. A challenging task to avoid such syntheses evokes interest to selective non-covalent analyte–fluorophore interactions.

Carbocyanines are fluorescent dyes that are useful in non-covalent sensing [2]. These dyes emit in near-infrared (NIR) region, which is valuable for sensing and molecular imaging due to deep penetration of the NIR light into tissues and low interferences from the biological matrices [3]. Most common sensing protocols using carbocyanines are based on covalent interactions with the analytes resulting in strong changes in the emission spectra. Various analytes were determined: tris(2-carboxyethyl)phosphine [4], cysteine [5], carbohydrates (with boronic acid groups) [6], peroxynitrite [7], sulfide [8] and other anions [9–11], transition metal ions [12]. Non-covalent fluorescent tests using carbocyanines are rare (detection of diethylstilbestrol with a heptamethyl indolenine-based dye [13], sensing of organic analytes via metal-ion complexation [2]).

Dipyrone (1-phenyl-2,3-dimethyl-5-pyrazolone-4-methylaminomethane sodium sulfonate, metamizole, analgin, sulpyrine; scheme 1) is a popular non-opioid analgesic, spasmolytic and antipyretic drug, commonly used in human and veterinary medicine. Due to its pharmacological effects and gastrointestinal tolerability it is administered as an alternative to paracetamol and traditional nonsteroidal anti-inflammatory drugs (NSAIDs). Dipyrone (Dip) even can be recommended for the treatment of cancer pain [14]. Its potential harm to liver is not finally established [15]. A well-known (though a rare) serious adverse event of Dip is agranulocytosis, which led to its ban in a number of countries [16]. However, many experts believe that its benefits may outweigh the risks [17]. In practice, Dip is used in many countries, legally or unofficially [15].

Therefore, interest to analytical methods for Dip (table S1 is available online at stacks.iop.org/MAF/9/015001/mmedia) [18–47] has been maintained during the recent years [24, 33–35, 46]. Dip was determined by electrochemical [18–24], chromatographic [25–30, 47] and spectroscopic [31–46]

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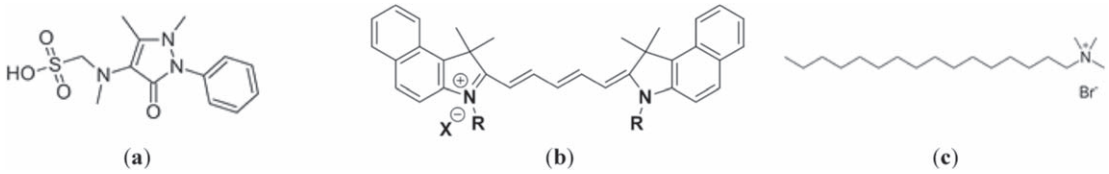


Scheme 1. Structures of the compounds participating in the complex formation: (a) Dipyrone; (b) Dye 1 (R = $(CH_2)_{10}COOH$, X = Br), Dye 2 (R = $(CH_2)_5CH_3$, X = I); (c) CTAB.

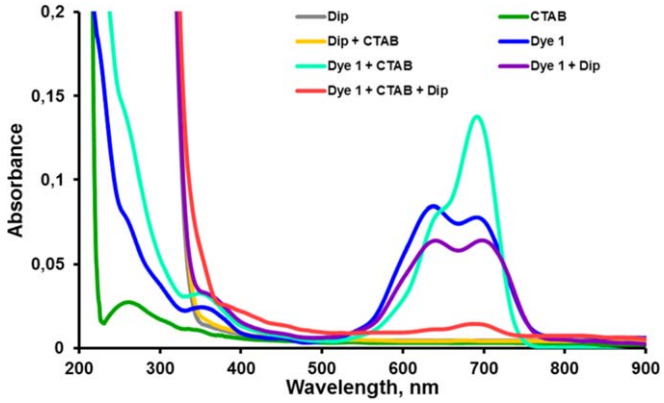


Figure 1. Absorption spectra of dye 1, CTAB, dipyrone (Dip) and their mixtures. Concentrations (shown for the final mixture): 1.5 mM Dip, 0.8 mM CTAB, pH 7.4 (7 mM phosphate buffer), 2 μM dye.

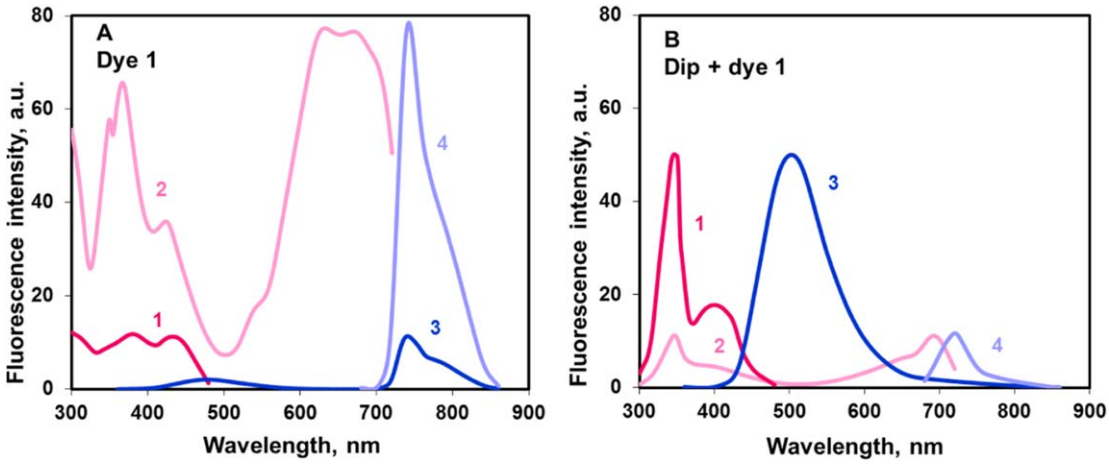
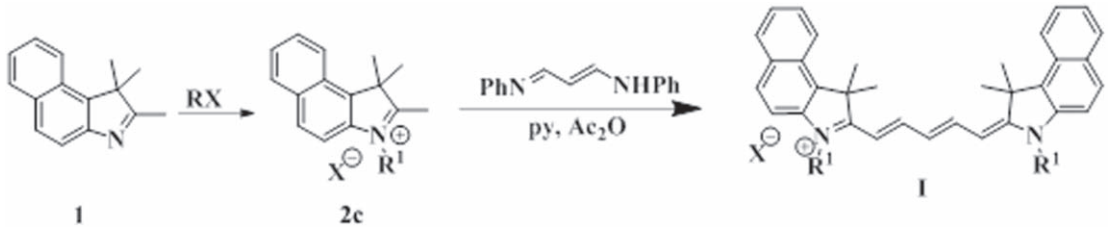


Figure 2. Excitation (1), (2) and emission (3), (4) spectra of dye 1 (A) and dipyrone—dye 1 mixture (B). Registration at 500 nm (1) and 740 nm (2); excitation at 345 nm (3) and 660 nm (4). Conditions: 1.5 mM Dip, 0.8 mM CTAB, pH 7.4 (7 mM phosphate buffer), 2 μM dye.

methods. A number of tests for Dip in single or multi-component pharmaceutical formulations have been developed using intrinsic UV absorption [31–35] or reactions with chemiluminescent [36–38], fluorescent [39], and spectrophotometric detection [40–46]. An immunochromatorgaphic test is offered for the determination of Dip and its metabolites in dairy products [47]. It would be desirable to develop a spectral test for dipyrone not requiring biomolecules [47] or heating with sulfuric acid [36, 37, 39, 41, 42, 46]. If such a method is based on a NIR dye, it would avoid the short-wave background fluorescence of biological samples.

In this study we explored two new symmetrical polymethine NIR dyes (1, 2) synthesized following simple principles [48] as described earlier [49]; the synthetic scheme is given in ESI (scheme S1). We found that a contact of compounds 1 or 2 with dipyrone resulted in a discoloration of the dye (figure 1) accompanied by sharp changes in the fluorescence spectra (figure 2), which only



Scheme 2. Synthetic route to dye **1**. $R^1 = (CH_2)_{10}COOH$, X = Br.

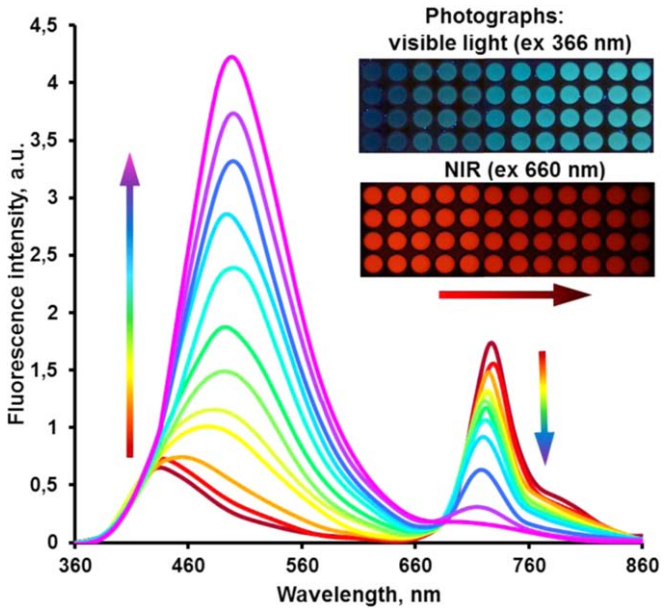


Figure 3. Effect of dipyrone concentration on the emission spectrum of dye 1 in the presence of CTAB. Insert: 96-well plate images with varied concentrations of dipyrone photographed in visible light and in near IR region. Conditions: 0 (dark red)—0.14 μM (red) … 0.14 mM dipyrone (magenta), 0.8 mM CTAB, pH 7.4 (7 mM phosphate buffer), 2 μM dye 1.

occurred in the presence of cetyltrimethylammonium bromide (CTAB) but not anionic surfactants (sodium *n*-dodecyl sulfate).

2. Materials and methods

2.1. Materials and reagents

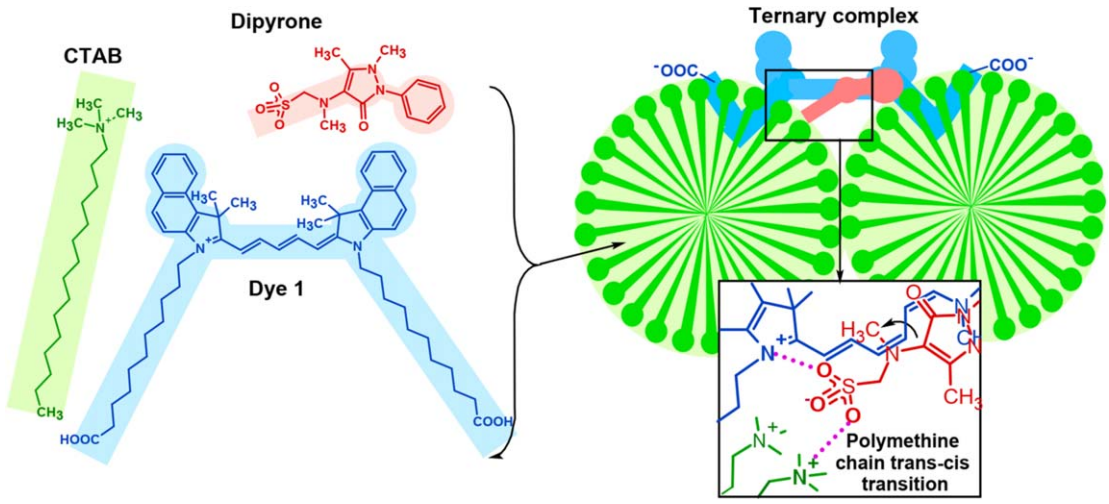
Dipyrone, CTAB, disodium phosphate, monopotassium phosphate, 1,1,2-trimetyl-1H-benzo[e]indole, 11-bromoundecanoic acid, N-((1E,3Z)-3-(phenylimino)prop-1-en-1-yl) aniline hydrochloride, acetic anhydride, diethyl ether, acetonitrile, methanol, dichloromethane and other compounds used in selectivity studies were obtained from Sigma–Aldrich (USA) and used as received. Millipore water (18 mΩ·cm) was used in preparing solutions.

2.2. Instruments and measurements

The fluorescence spectra were obtained on Fluorat-02 Panorama (Lumex, Russia) or Cary Eclipse (Agilent) spectrofluorimeter in 1-cm quartz cells. Visible fluorescence of solutions in 96-well polystyrene plates (Thermo Scientific Nunc F96 MicroWell, white, cat. No 136101) was registered using TLC Visualizer 2 (Camag, Sweden) with excitation at 254 or 366 nm and measured with an embedded digital camera. Near IR fluorescence in 96-well plates was registered using a setup containing a LED source (eleven 3-Wt red LEDs, emission maximum 660 nm; Minifermer, Moscow, Russia) and an NIR digital camera (modernized Nikon D80 with a filter transmitting light with wavelengths above 700 nm). The measurements were taken in 10 min after mixing. ^{1}H NMR spectra were recorded on a Bruker Avance 600 spectrometer with an operating frequency of 600 MHz. MALDI MS spectra were recorded on a Bruker Autoflex spectrometer at 70% of maximum laser energy without using matrix compounds.

2.3. Dye synthesis

1 g (4.78 mM) of 1,1,2-trimetyl-1H-benzo[e]indole and 1.27 g (4.78 mM) of 11-bromoundecanoic acid were heated at 100 °C for 12 h (scheme 2). After cooling to room temperature an excess of diethyl ether was added and the precipitate was filtered off. 2.32 g of



Scheme 3. Suggested structure of the dye—dipyrone—CTAB ensemble.

dark green powder was obtained (yield 92%). Melting point 195 °C–200 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.23 (br.s., 8H), 1.35 (br.s., 2H), 1.47 (br.s., 2H), 1.52–1.58 (m, 2H), 1.85 (s, 6H), 1.97 (br.s., 2H), 2.28 (t, 2H, $^3J_{HH} = 7.3$), 3.18 (s, 3H), 4.81 (br.s., 2H), 7.61–7.82 (m, 3H), 8.07 (m, 3H).

One equivalent of received powder and 1.2 equivalents of N-((1E,3Z)-3-(phenylimino)prop-1-en-1-yl) aniline hydrochloride were dissolved in 1.5 ml acetic anhydride. The reaction mixture was heated at 120°C for 30 min. Then 1.7 equivalents of ammonium salt were dissolved in 1.5 ml of pyridine, added to the reaction mixture and heated for 30 min. After cooling to room temperature an excess of diethyl ether was added and the precipitate was filtered off. The target compound was purified by column chromatography on silica gel (eluent: CH_2Cl_2/MeOH, 30:1 v/v). Carbocyanine dye was obtained as a dark blue powder.

2.4. Experimental procedure for dipyrone determination

Firstly, 100 μl of dipyrone water solutions were prepared at different concentrations (0,14 μM to 0,14 mM). Then Dip was mixed with 30 μl of 0.01 mM CTAB, 30 μl of 70 mM phosphate buffer (pH 7.4) and 170 μl of water. Finally, 25 μl of 0,028 mM dye **1** was added. The final concentrations of CTAB, buffer and dye **1** were 0.8 mM, 7 mM and 2 μM, respectively.

3. Results and discussion

Mixing the dye with dipyrone and CTAB in an aqueous solution resulted in a sharp decrease in absorbance at 600–700 nm (figure 1), which was the stronger, the higher the concentration of dipyrone (figure S1 in ESI). These changes were not observed in the binary systems *dye—dip, dye—CTAB*. In the emission spectra, the band at 720 nm decreased in the ternary system, while the 400–500-nm band became more intense and shifted red with the concentration of dipyrone (figure 3). Dipyrone absorbs at ⩽350 nm (figure S2) and is non-fluorescent itself or in the presence of CTAB. The bands in the spectra were not shifted upon changing conditions, indicating no significant H- or J-aggregation of the dye [50]. Dye 2 showed similar behaviour (its emission spectra with Dip and CTAB are shown in figure S3).

We studied the reaction mixture (dye **1**—dipyrone—CTAB) by MALDI MS (figure S4) and NMR-^{1}H (figures S5(a)–(d), table S3). Surprisingly, both techniques showed the presence of an intact dye **1** (molecular ion of 824 Da in MALDI and virtually non-shifted proton signals in NMR). These results led us to assume that the interaction of dipyrone with the dye is non-covalent, notwithstanding a considerable change in the absorbance and fluorescence spectra.

The observed phenomena may be due to the formation of a stable complex between the dye and dipyrone, in which the conformation of the fluorophore is substantially changed. Supposing a 1:1 complex composition, the binding constant

$$K = \frac{[Complex]}{[Dye][Dip]} = (9 \pm 3) \times 10^4$$

was estimated from the emission data (figure 3) by using standard methods [51] (see ESI for the calculations). Judging by the disappearance of the red absorption and NIR fluorescence bands, the polymethine chain of the complexed dye is driven out of conjugation state. Polymethine chain emits in trans-state, while cis-conformation is non-emissive [52]. The trans–cis transition can occur as a consequence of multi-point dye binding with dipyrone. The concrete structure of this complex is unknown, but we can hypothesize that it could involve π-π stacking of the aromatic moieties of Dip and the dye and ionic interaction of the sulfonic group with the quaternized nitrogen; an additional interaction is possible between the carbonyl carbon atom with the π-electrons of the polymethine chain (scheme 3). If such a complex

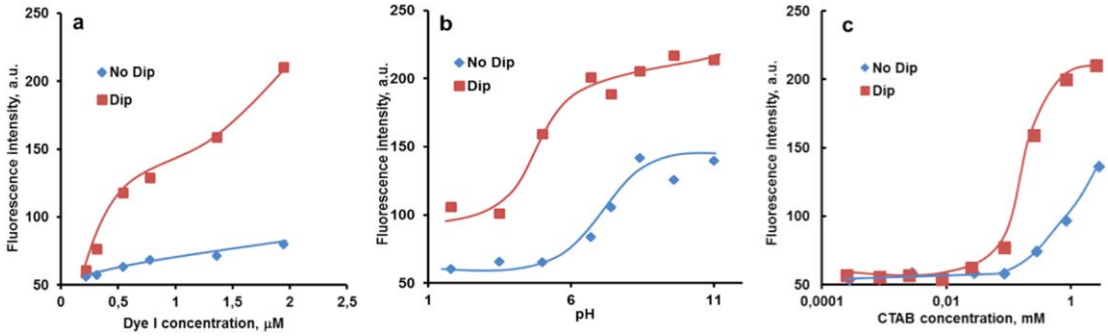
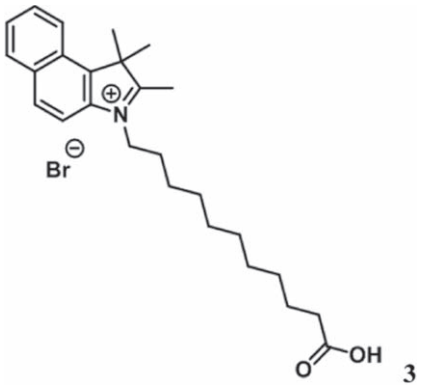


Figure 4. Fluorescent intensity* as a function of (a) concentration of dye **1**, (b) pH, and (c) CTAB concentration. General conditions: pH 7.4 (7 mM phosphate buffer), 0.8 mM CTAB, 1.9 μM dye **1**, 0.14 mM dipyrone. In varying pH, the following buffers were used in 7 mM concentrations (by anion): borate (pH 9.6–11.0), phosphate (pH 7.4–8.4), citrate (pH 6.7), acetate (pH 3.5–5.0), and HCl (pH 1.8).

stabilizes the cis-conformation, the NIR fluorescence will be quenched, while the short-wavelength emission band, caused mainly by benzoindolenine fragments, will be enhanced. Since the spectral changes are only observed with a sufficient amount of CTAB close to micellar concentration (figures S6 and 4(c)), the surfactant role can involve additional stabilization of the complex by including the methylene chains of the dyes into the micelle, on the one hand, and ionic binding of the CTAB cation with the sulfonic group of Dip, on the other (scheme 3). Dye **2** has no carboxylic groups and still shows a similar behavior (figure S3), which implies that COOH groups of dye **1** are not directly involved in complexation.

Competitive binding was carried out by adding an oppositely charged surfactant (sodium dodecyl sulfate SDS) to the dye **1**—CTAB—dipyrone system. SDS efficiently decomposes the complex, regaining the visible spectrum of the initial dye **1** and its long-wave emission with a decrease in short-wave emission (figure S7). Subsequent addition of more Dip to the system reversed the situation, regaining the short-wave peak and reducing long-wave absorbance, the reverse change was incomplete due to an interference from SDS. These phenomena confirm the reversibility of binding and allow considering covalent complexation as less probable.

To reveal the origin of the spectral changes, we studied the UV–vis and fluorescence spectra of compounds **3** and **4** as parts of dye **1**:



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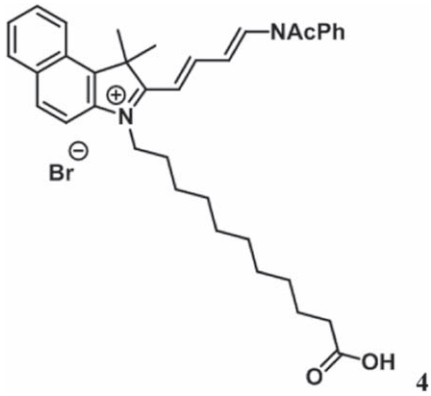
As can be noticed from figure S8, 400–500-nm emission band intensity changes in the following order (for 2 μM compounds in 0.8 mM CTAB):

compound **3** $\gg$ compound**4** $\gg$ dye**1**.

This implies that non-conjugated benzoindolenine moiety



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(as in **3**) displays more intense short-wave fluorescence than the same moiety conjugated to a polymethine chain (as in **4** or dye **1**). Accordingly, the increase in the 500-nm emission intensity of dye **1** in the presence of Dip (figure 3) is probably due to benzoindolenine fragments pull-out of conjugation with the polymethine chain.

The fluorescence signal in this system can be measured by a number of ways: by intensities in the emission spectrum, by the ratio of intensities of the short-wave and long-wave bands, or using the digital photographs in visible and near-IR ranges (excitation with a UV lamp of red LED, respectively). To compare these variants, the determination coefficients of the corresponding linear calibration graphs were calculated (Table S4). Since the signal was obtained in a wide range of concentrations (1.4×10^{-7}…1.4×10^{-4} M), two linear portions were constructed for each type of graph (figure S9). Higher determination coefficients were obtained for the logarithmic rather than linear dipyrone concentration scale. The short-wave emission band is more sensitive to the lower concentrations of Dip (log c = –6.9 … –5.8), while the NIR emission band should be used for its

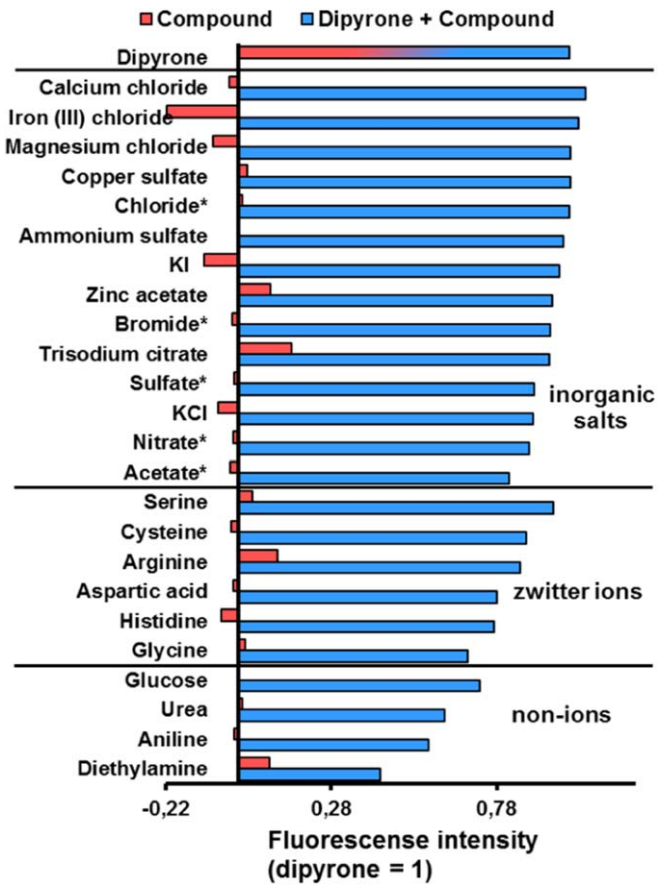

Figure 5. Selectivity and interferences: blue bars—dipyrone and diverse species in the same concentration; red bars—diverse species without dipyrone. Conditions: 1.4 mM dipyrone, 0.8 mM CTAB, pH 7.4 (7 mM phosphate buffer), 2 μM dye 1, 1.5 mM diverse compounds. The fluorescence intensities were measured using visualizer images, as shown in figure 4. The signals of diverse compounds (red bars) were obtained by subtracting the blank signal (without the compound) from the raw signal. All signals were normalized to dipyrone.

higher concentrations (log c = –5.8 … –3.9). When using emission spectra, the most efficient is using ratiometry, while photographic registration is more precise when using two different conditions for obtaining calibration graphs: UV excitation for low concentrations of Dip (log c = –6.9 … –5.8, obtaining visible images) and red LED excitation for the higher concentrations (log c = –5.8 … –3.9, obtaining NIR images).

* The signals were obtained as the sum of the intensities of R, G, and B channels of the 96-well plate images obtained by visualizer camera under 366 nm excitation, averaged over each well.

Notwithstanding the non-covalent character of binding, sensing of dipyrone is relatively selective (figure 5). Without dipyrone, a number of organic species and inorganic salts do not exert any considerable effect on the emission spectrum of the carbocyanine; the highest signals are observed for Cu(2+) and citrate (figure 4, red bars). Interferences with the signal of Dip are observed from a number of organic species (amines, urea, glucose and amino acids, figure 4, blue bars), probably due to breakdown of the ternary complex. Proteins interfere as they enhance the fluorescence of carbocyanines [53]. Bovine serum albumin used as an example of protein does not significantly change Dip signal in concentrations less than 0.5 g l^{-1}; a calibration plot for Dip can be constructed in the presence of that amount of BSA (figure S10).

4. Conclusion

Non-covalent binding between low-molecular compounds are used for drug sensing. The strong spectral changes are only observed in the presence of a micellar surfactant as the third party of the forming ensemble. Similar non-covalent complexes involving carbocyanines should be sought for to gain an insight into the origin of selective interactions with analytes.

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References

[1] Demchenko A P 2015 *Introduction to Fluorescence Sensing* 2nd edn (Switzerland: Springer) p 818
[2] Sun W, Guo S, Hu C, Fan J and Peng X 2016 *Chem. Rev.* **116** 7768–817
[3] Hong G, Antaris A L and Dai H 2017 *Nat. Biomed. Eng.* **1** 0010
[4] Guo H, Tanga W and Duan X 2018 *Anal. Methods* **10** 5823–6
[5] Ernst L A, Gupta R K, Mujumdar R B and Waggoner A S 1989 *Cytometry* **10** 3–10
[6] Takeuchi M, Mizuno T, Shinmori H, Nakashima M and Shinkai S 1996 *Tetrahedron* **52** 1195–204
[7] Hou T *et al* 2019 *Talanta* **196** 345–51
[8] Xiong J, Xia L, Huang Q, Huang J, Gu Y and Wang P 2018 *Talanta* **184** 109–14
[9] Liu Y, Qui D, Pan H, Li M, Chen H and Li H 2018 *J. Photochem. Photobiol.* A **364** 151–8
[10] Xiang K, Chang S, Feng J, Li C, Ming W, Liu Z, Liu Y, Tian B and Zhang J 2016 *Dyes Pigm.* **134** 190–7
[11] Sun Y, Fan S, Zhang S, Zhao D, Duan L and Li R 2014 *Sens. Actuat.* B **193** 173–7
[12] Shi Y, Wang R, Yuan W, Liu Q, Shi M, Feng W, Wu Z H, Hu K and Li F 2018 *ACS Appl. Mater. Interf.* **10** 20377–86
[13] Yin K, Yu F, Liu D, Xie Z and Chen L 2016 *Sens. Actuat.* B **223** 799–805
[14] Gaertner J *et al* 2017 *Palliat. Med.* **31** 26–34
[15] Lutz M 2019 *J. Clin. Pharmacol.* **59** 1433–42
[16] Blaser L S, Hassna H, Hofmann S, Holbro A, Haschke M, Rätz Bravo A E, Zeller A, Krähenbühl S and Taegtmeyer A B 2017 *Swiss Med Wkly* **147** w14438
[17] Stamer U M *et al* 2019 *Der Chirurg* **90** 652–9
[18] Teixeira M F S and Dadamos T R L 2009 *Procedia Chem.* **1** 297–300
[19] Dos Santos W T P, Gimenes D T, de Almeida E G N, Sebastião de P E, Albuquerque Y D T and Richter E M 2009 *J. Braz. Chem. Soc.* **20** 1249–55
[20] Teixeira M F S, Marcolino-Junior L H, Fatibello-Filho O, Moraes F C and Nunes R S 2009 *Curr. Anal. Chem.* **5** 303–10
[21] Ghica M E, Ferreira G M and Brett C M A 2015 *J. Solid State Electrochem.* **19** 2869–81
[22] Rumin M, Smajdor J, Paczosa-Bator B and Piech R 2016 *ECS J. Solid State Sci. Technol.* **5** M3005
[23] Abd El Rahman M K, Elzanfaly E S, Ibrahim M M, Kelani K M and Ramadan N K 2017 *Anal. Bioanal. Electrochem.* **9** 1–14
[24] De Faria L V, Lisboa T P, Azevedo G C, Sousa R A, Matos M A C, Muñoz R A A and Matos R C 2019 *Electroanal.* **31** 646–51
[25] Aburjai T, Amro B I, Aiedeh K, Abuirjeie M and Al-Khalil S 2010 *Pharmazie* **55** 751–4
[26] Altun M L 2002 *Turk. J. Chem.* **26** 521–8 (https://journals.tubitak.gov.tr/chem/issues/kim-02-26-4/kim-26-4-8-0106-13.pdf)
[27] Salmerón-García A, Navas N, Martin A, Román E, Cabeza J and Capitán-Vallvey L F 2009 *J. Chromatogr. Sci.* **47** 231–7
[28] Senyuva H Z, Aksahin I, Ozcan S and Kabasakal B V 2005 *Anal. Chim. Acta* **547** 73–7
[29] Penney L, Bergeron C and Wijewickreme A 2005 *J. AOAC Int.* **88** 496–504
[30] Vieira J C, Sversut R A, Maciel I T, Carollo A R H, do Amaral M S and Kassab N M 2017 *Chromatographia* **80** 489–95
[31] Erk N and Onur F 1997 *Anal. Lett.* **30** 1201–10
[32] Aburjai T, Amro B I, Aiedeh K, Abuirjeie M and Al-Khalil S 2000 *Pharmazie* **55** 751–4
[33] da Costa Lopes F C, Fonseca L, Moita G C and Ribeiro M V M 2018 *Int. J. Pharm. Sci. Res.* **7** 2201–10
[34] Ribeiro P C *et al* 2019 *Intern. J. Adv. EnG Res. Sci.* **6** 720–4
[35] Savic I M, Gajic I M S and Sibinovic P S 2020 *Anal. Lett.* **53** 1956–69
[36] Huang Y-M, Zhang C, Zhang X-R and Zhang Z-J 1999 *J. Anal. Chem.* **365** 381–3
[37] Huang Y, Zhang C, Zhang X and Zhang Z 1999 *Anal. Lett.* **32** 933–43
[38] Zhao L, Li B, Zhang Z H and Lin J-M 2004 *Sens. Actuat.* B **97** 266–71
[39] Uno T and Yamamoto M 1973 *Bunseki Kagaku* **22** 1420–3
[40] Qureshi S Z, Saeed A and Hasan T 1989 *Talanta* **36** 869–71
[41] Sakiara K A, Pezza L, Melios C B, Pezza H R and Moraes M 1999 *Il Farmaco* **54** 629–35
[42] Pezza L, Tubino M, Melios C B and Pezza H R 2000 *Anal. Sci.* **16** 313–5
[43] Lima J L F C, Sá S M O, Santos J L M and Zagatto E A G 2003 *J. Pharm. Biomed. Anal.* **32** 1011–7
[44] Marcolino-Júnior L H, Sousa R A, Fatibello-Filho O, Moraes F C and Teixeira M F S 2005 *Anal. Lett.* **38** 2315–26
[45] Suarez W T, Pessoa-Neto O D, Vicentini F C, Janegitz B C, Faria R C and Fatibello-Filho O 2011 *Anal. Lett.* **44** 340–8
[46] Gavat C C, Vasilescu L V and Marculescu A D 2019 *Revista de Chimie* **70** 475–82
[47] Sulpyrine/Dipyrone/Metamizole rapid test for milk based on the colloidal gold immunochromatography technology (http://en.bioeasy.com.tr/sulpyrine-dipyrone-metamizole-rapid-test-for-milk/)
[48] Kvach M V, Ustinov A V, Stepanova I A, Malakhov A D, Skorobogatyi M V, Shmanai V V and Korshun V A 2008 *Eur. J. Org. Chem.* **12** 2107–17
[49] Zakharenkova S A, Katkova E A, Doroshenko I A, Kriveleva A S, Lebedeva A N, Vidinchuk T A, Shik A V, Abramchuk S S, Podrugina T A and Beklemishev M K 2021 *Spectr. Acta* A, A, **247** In Press
[50] Bricks J L, Slominskii Y U L, Panas I D and Demchenko A P 2018 *Methods Appl. Fluoresc.* **6** 012001
[51] Hirose K A 2001 *J. Inclus. Phenom. Macroc. Chem.* **39** 193–209
[52] Razumov V F and Ivanchenko A G 1995 *Opt. Spectrosc.* **79** 568–73
[53] Kuzmin V A, Nekipelova T D, Podrugina T A, Golovina G V, Kostyukov A A, Temnov V V, Doroshenko I A, Radchenko E V, Palyulin V A and Zefirov N S 2016 *Photochem. Photobiol. Sci.* **15** 1377–84