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Selective fluoride chemosensors based on coumarin semicarbazones



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ABSTRACT

Twelve (five new) colorimetric anion sensors based on coumarin semicarbazone were studied for selective sensing of fluoride anion. The distinct colour change (by 44–125 nm) under ambient light observed in the Vis region makes the present sensors suitable for naked eye detection of fluoride anion, with detection limit (LOD) 6.6–8.6 ppm for the most sensitive ones. Whereas significant colorimetric changes are observed in the presence of fluoride anion in Me₂SO, the commonly competing AcO⁻, Cl⁻, Br⁻, HSO₄, NO₂ or NO₃ ions induce none or relatively negligible changes. Deprotonation of the semicarbazone NH group is responsible for the sensing event, albeit the mechanism depends on electron density distribution in the coumarin moiety. Quantum chemical calculations suggest several possible geometries for the semicarbazones; the geometry with a hydrogen bond between the hydrazone nitrogen and the NH hydrogen of all of the aniline, cyclohexylamine and aminopyridine fragments, however, results in the most stable structures.

1. Introduction

Fluoride anion recognition is an area of intensive current research due to the duplicitous nature of fluoride anions. Although several ways of fluoride detection have been elaborated so far, the synthesis and design of new chemosensors and the development of new sensing mechanisms with high selectivity are still intriguing challenges for research in this area [1-7]. With the development of anthropogenic activities, particularly industrial manufacturing of aluminium, semiconductors, pesticides, and food products, the environmental contamination with fluorides becomes a serious problem [8-12]. On the other hand, fluorides are often used in human medicine: low concentrations of fluorides possess significant potential perhaps most notably in the prevention of dental caries or in the treatment of osteoporosis; but fluorides are also contained in anaesthetics and psychiatric drugs. Fluorides are highly soluble in water and therefore interactions with living systems pose a threat especially for water organisms. Nonetheless, fluoride accumulation in living systems has been accused of several pathologies, such as changes in the structure of DNA and interference with metabolic pathways (in the liver and kidneys) or e.g. a loss of mobility in humans and lowering of IQ in children [10–16].

Naked eye (colorimetric) detection of anions is becoming increasingly appreciated because visual detection can – generally quickly – provide both qualitative and quantitative information. Colorimetry does not require any specific equipment and due to its low cost can be widely applied even with low concentration levels of the analyte.

Selective anion sensors containing neutral hydrogen bonding receptor moiety (*e.g.* urea/thiourea) covalently linked to a chromogenic fragment are of considerable interest due to the ease of property tuning in the binding site [17–20]. H-bond induced π -electron delocalization or NH deprotonation are believed to be responsible for signalling the binding event in the (thio)ureas [21–23]. The variations in the physical properties of anions, such as size, shape, charge distribution, the solvation in polar and protic solvents and pH sensitivity are key parameters that govern their selective and sensitive sensing and its mechanism [24–26].

The present study is a part of our current research focused on chemosensors based on coumarin derivatives [27,28]. In our continuing effort to develop novel chromophores/fluorophores leading to sensitive chemosensors we linked coumarin (as a signalling unit) and semicarbazone (as a responding unit) moieties together into one molecule.

Coumarin is a common chromophore/fluorophore known for its ability of significant intramolecular charge transfer (ICT) depending on substitution and surrounding environment. The responding – semicarbazone – fragment as an easily accessible functional group seems to be a proper alternative to urea/thiourea fluoride-recognizing scaffold offering a high degree of tunability of the NH protons acidity by adjacent substituents.

Several coumarin semicarbazones (Fig. 1) were rationally designed and synthesized. Compared to the conventional coumarin dyes, both

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1 : R ¹ = C ₆ H ₅	R ² = H	7 : R ¹ = 2-NO ₂ -C ₆ H ₄ ,	$R^2 = N(CH_3)_2$
2 : R ¹ = 4-F-C ₆ H ₄ ,	$R^2 = N(CH_3)_2$	8 : R ¹ = 4-NO ₂ -C ₆ H ₄ ,	$R^2 = N(CH_3)_2$
3 : R ¹ = 4-Br-C ₆ H ₄ ,	$R^2 = N(CH_3)_2$	9 : R ¹ = 4-CN-C ₆ H ₄ ,	$R^2 = N(CH_3)_2$
4 : R ¹ = 4-CH ₃ -C ₆ H ₄ ,	$R^2 = N(CH_3)_2$	10 : R ¹ = Cyclohexyl,	$R^2 = N(CH_3)_2$
5 : R ¹ = 4-CF ₃ -C ₆ H ₄ ,	$R^2 = N(CH_3)_2$	11 : R ¹ = 2-Py,	$R^2 = H$
$6: R^1 = 4 - OCH_3 - C_6H_4,$	$R^2 = N(CH_3)_2$	1 2 : R ¹ = 2-Py,	$R^2 = N(CH_3)_2$

Fig. 1. Structure of substituted coumarin semicarbazones.

dimethylamino and imine units in the compounds 2-10 and 12 extend the conjugated system of the chromophore. Although some of the investigated semicarbazones are not new compounds [28–31], they have not been previously used as fluoride colorimetric sensors.

Earlier, we discussed the fluorescence of the compounds **2**, **5**, **6**, and **9** [29]. It should be only mentioned here that, independently on solvent polarity, all EWG (on aniline ring) substituted coumarin semicarbazones exhibit high fluorescent quantum yields ($\Phi_F = 0.5-0.93$). In comparison, EDG (on aniline ring) substituted derivatives show significantly lower Φ_F values (about 0.14–0.28) [28,29,31]. We reported their use as fluorescent sensors for traces of water in organic solvents in the presence of fluoride anions [28]. Dimethylamino derivatives **2**, **5**, **6**, and **9** behave as turn off fluorometric sensors for fluoride anion, the fluorescence of semicarbazones decreases/quenches upon interaction with fluoride anion. However, no more than air humidity diffusion as well as low-level water addition (< 1 wt%) leads to fluorescence recovery [28].

Despite the fluorescent sensing being highly accurate it requires sophisticated instrumentation. For studied derivatives 1 and 11 unsubstituted on coumarin moiety, the fluorescent sensing is not applicable because they exhibit very low fluorescent quantum yields (e.g for 1 $\Phi_F < 0.001$ in methanol [31]). Even though the possibility of the applicability of the aforementioned compounds as sensors led us to the study of practical colorimetric detection of interaction of the substances 1-12 with an analyte. Substitution effect as well as interaction with different ions were studied to delineate the complex picture of analyte – receptor interaction. It was revealed that only the fluoride anion could be detected without interference from other anions. Derivatives 1 and 11 that do not have suitable fluorescence properties have proven to be ones with the most sensitive colorimetric abilities among the studied chemosensors.

2. Materials and methods

2.1. Synthesis

2.1.1. General

Melting points were measured on a Kofler hot stage and are uncorrected. The ¹H and ¹³C NMR spectra were recorded at 300 MHz and at 75 MHz, respectively, in a 5 mm NMR tube on a Varian VNMRS 300 MHz spectrometer (Agilent, Santa Clara, CA, USA) in CDCl3 or Me2SO-d6 with tetramethylsilane as internal standard. Chemical shift values are recorded in δ units (ppm) and coupling constants (J) are expressed in Hertz (Hz). IR spectra were recorded on a Nicolet FT-IR-ATR 6700 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using the ATR technique and ν are given in wavenumbers (cm⁻¹). Elemental analyses were performed on a Carlo Erba Strumentacione 1106 apparatus. HRMS spectra were recorded on a Thermo Scientific Orbitrap Velos Pro Mass Spectrometer (ThermoFisher Scientific, Waltham, MA, USA), HESI (heated electrospray), MeOH, analyzer: FTMS, resolution 120000, capillary temperature 275 °C, direct injection to MS. Chemicals and solvents were purchased from the major chemical suppliers (Merck, Darmstadt, Germany; Acros Organics, Geel, Belgium) as the highest purity grade and all solvents were dried by standard methods and distilled prior to use. 2-Oxo-2H-chromene-3-carbaldehyde (13) [32], 7-(N,N-dimethylamino)-2-oxo-2H-chromene-3-carbaldehyde (14) [33], semicarbazides (15-18) [29, ESI S12], semicarbazones 1-3, 5, 8, 9 [29], 6 [28] were prepared according to literature procedures. The structures of the prepared compounds were proven by ¹H NMR spectra.

2.1.2. General procedure for the synthesis of substituted (E)-1-[(2-oxo-2H-chromen-3-yl)methylidene]semicarbazones

A solution of semicarbazide (1 eq) in hot absolute ethanol (10 mL) was added to a solution of aldehyde (1 eq) in hot absolute ethanol



Scheme 1. Reaction scheme of the synthesis of semicarbazones 1 - 12.

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(10 mL). The reaction mixture was refluxed for 15 min and the desired product precipitated. The precipitate was filtered off, washed with cold ethanol, dried and recrystallized from ethanol, crystalline solid products obtained in 62–98 % yields. (Scheme 1)

(E)-1-{[7-(N,N-Dimethylamino)-2-oxo-2H-chromen-3-yl]methylidene}-4-(4-methylphenyl)semicarbazone (4): Obtained from 100 mg (0.46 mmol) of aldehyde 14 and 76 mg (0.46 mmol) of 4-(4-methylphenyl)semicarbazide (15) in 93 % yield (155 mg), orange powder: mp (ethanol) 262-265 °C (decomp.); UV-Vis (Me₂SO): 440 nm; IR (ATR) ν/cm^{-1} : 3340 (s, br), 2956 (s, br) and 1522 (m) amine, 1686 (s) and 1137 (s) ester, 1601 (m) imine; ¹H-NMR (Me₂SO-d₆): δ (ppm) 2.26 (s, 3H, CH₃), 3.07 (s, 6H, N(CH₃)₂), 6.61 (d, ${}^{1}J = 2.4$ Hz, 1H, H-8), 6.81 (dd, $^{2}J = 8.9$ Hz, $^{1}J = 2.4$ Hz, 1H, H-6), 7.11 (d, $^{3}J = 8.3$ Hz, 2H, H-2', H-6'), 7.53 (d, ${}^{2}J = 9$ Hz, 1H, H-5), 7.54 (d, ${}^{3}J = 8.3$ Hz, H-3', H-5'), 7.98 (s, 1H, H-4), 8.68 (s, 1H, HC = N), 8.81 (brs, 1H, NH), 10.80 (brs, 1H, NH); ¹³C-NMR (Me₂SO-d₆): δ (ppm) 20.37, 38.67, 97.15, 108.48, 110.02, 113.48, 119.91, 128.84, 129.80, 131.33, 134.80, 136.41, 138.37, 152.85, 153.20, 155.77, 160.71. MS: *m/z* [M+H]⁺ 365.16077 (theoretical value: 365.1569). Anal. calcd for C₂₀H₂₀N₄O₃ (364.40): C, 65.92; H, 5.53; N, 15.38; found C, 65.94; H, 5.51; N, 15.40.

(E)-1-{[7-(N,N-Dimethylamino)-2-oxo-2H-chromen-3-yl]methylidene}-4-(2-nitrophenyl)semicarbazone (7): Obtained from 100 mg (0.46 mmol) of aldehyde **14** and 90 mg (0.46 mmol) of 4-(2-nitrophenyl)semicarbazide (**16**) in 91 % yield (163 mg), orange powder: mp (ethanol) 269–271 °C (decomp.); UV–Vis (Me₂SO): 446 nm; IR (ATR) ν/cm^{-1} : 3270 (s, br), 1712 (s) and 1139 (s) ester, 1621 (m) imine, 1607 (m) amine, 1505 (s) and 1344 (s) nitro; ¹H-NMR (Me₂SO-d₆): δ (ppm) 3.08 (s, 6H, N(CH₃)₂), 6.63 (d, ¹J = 2.2 Hz, 1H, H-8), 6.83 (dd, ²J = 8.9 Hz, ¹J = 2.1 Hz, 1H, H-6), 7.24 (ddd, ³J = 8.6 Hz, ⁴J = 7.5 Hz, ⁵J = 1.6 Hz, 1H, H-4'), 7.47 (d, ²J = 9 Hz, 1H, H-5), 7.73–7.79 (m, 2H, H-4, H-5'), 8.06 (brs, 1H, NH), 8.21 (dd, ⁶J = 8.3 Hz, ⁵J = 1.6 Hz, 1H, H-6'), 8.41 (s, 1H, CH = N), 8.59 (d, ³J = 8.6 Hz, 1H, H-3'), 11.34 (brs, 1H, NH); ¹³C-NMR (Me₂SO-d₆): due to low solubility in Me₂SO-d₆ ndt. MS: *m*/z [M+H]⁺ 396.13006 (theoretical value: 396.1263). Anal. calcd for C₁₉H₁₇N₅O₅ (395.37): C, 57.72; H, 4.33; N, 17.71; found C, 57.71; H, 4.34; N, 17.70.

(E)-4-Cyclohexyl-1-{[7-(N,N-dimethylamino)-2-oxo-2H-chromen-3-yl] methylidene}semicarbazone (10): Obtained from 150 mg (0.69 mmol) of aldehyde 14 and 108 mg (0.69 mmol) of 4-cyclohexylsemicarbazide (17) in 87 % yield (210 mg), yellow powder: mp (ethanol) 256-258 °C; UV-Vis (Me₂SO): 439 nm; IR (ATR) v/cm⁻¹: 3410 (s, br), 2846 (s, br) and 1526 (m) amine, 1714 (s) and 1138 (s) ester, 1667 (m) imine, 1440 (m) alkane (cyclohexyl); ¹H-NMR (CDCl₃): δ (ppm) 1.16-1.48 (m, 4H, CH2-CH2-CH2-CH2-CH2), 1.61-1.81 (m, 4H, CH2-CH2-CH2-CH2-CH2), 2.01-2.06 (m, 2H, CH2-CH2-CH2-CH2-CH2), 3.11 (s, 6H, N(CH₃)₂), 3.70-3.78 (m, 1H, CH₂-<u>CH</u>-CH₂), 5.91-5.95 (m, 1H, NH), 6.51 (d, ${}^{1}J$ =2.5 Hz, 1H, H-8), 6.65 (dd, ${}^{2}J$ =9 Hz, ${}^{1}J$ =2.5 Hz, 1H, H-6), 7.39 (d, ${}^{2}J$ =8.9 Hz, 1H, H-5), 7.70 (brs, 1H, NH), 7.81 (s, 1H, H-4), 8.08 (s, 1H, CH = N); 13 C-NMR (CDCl₃): δ (ppm) 25.07, 25.61, 33.78, 40.24, 48.74, 97.75, 108.91, 109.73, 113.97, 129.62, 135.15, 137.97, 153.34, 154.39, 156.27, 161.46. MS: *m/z* [M+H]⁺ 357.19202 (theoretical value: 357.1882). Anal. calcd for C₁₉H₂₄N₄O₃ (356.42): C, 64.03; H, 6.79; N, 15.72; found C, 64.06; H, 6.80; N, 15.75.

(*E*)-1-[(2-Oxo-2H-chromen-3-yl)methylidene]-4-(pyridine-2-yl)semicarbazone (11): Obtained from 50 mg (0.287 mmol) of aldehyde 13 and 43 mg (0.287 mmol) of 4-(pyridine-2-yl)semicarbazide (18) in 62 % yield (55 mg), light yellow powder: mp (ethanol) 215 °C (decomp.); UV–Vis (Me₂SO): 362 nm; IR (ATR) ν /cm⁻¹: 3351 (s, br), 2948 (s, br) and 1576 (m) amine, 1699 (s) and 1149 (s) ester, 1620 (m) imine; ¹H-NMR (Me₂SO-d₆): δ (ppm) 7.09 (ddd, ¹J = 7.5 Hz, ²J = 5.0 Hz, ³J =0.7 Hz, 1H, H_{py}-5), 7.40–7.46 (m, 2H, H_{py}-4, H-8), 7.65 (dd, ⁴J = 7.1 Hz, ⁵J = 1.4 Hz, 1H, H-7), 7.79 (ddd, ⁶J = 8.4 Hz, ⁴J = 7.0 Hz, ⁷J =1.8 Hz, 1H, H-6), 7.89 (dd, ¹J = 7.6 Hz, ⁵J = 1.3 Hz, 1H, H_{py}-3), 7.98 (d, ⁶J = 8.4 Hz, 1H, H-5), 8.10 (s, 1H, H-4), 8.32 (d, ²J = 4.9 Hz, 1H, H_{py}-6), 8.77 (s, 1H, HC = N), 9.13 (brs, 1H, NH), 11.35 (brs, 1H, NH); ¹³C-NMR (Me₂SO-d₆): δ (ppm) 112.76, 116.11, 118.74, 119.08, 120.97, 124.88, 129.22, 132.29, 135.44, 137.74, 138.14, 147.67, 151.64, 152.02, 153.09, 159.61. MS: m/z [M+H]⁺ 309.09836 (theoretical value: 309.0943). Anal. calcd for C₁₆H₁₂N₄O₃ (308.29): C, 62.33; H, 3.92; N, 18.17; found C, 62.35; H, 3.84; N, 17.99.

(E)-1-{[7-(N,N-Dimethylamino)-2-oxo-2H-chromen-3-yl]methylidene}-4-(pyridine-2-yl)semicarbazone (12): Obtained from 50 mg (0.23 mmol) of aldehyde 14 and 35 mg (0.23 mmol) of 4-(pyridine-2-yl)semicarbazide (18) in 81 % yield (65 mg), orange powder: mp (ethanol) 230–233 °C (decomp.); UV–Vis (Me₂SO): 440 nm; IR (ATR) ν/cm^{-1} : 28310 (s, br) and 1606 (m) amine, 1704 (s) and 1141 (s) ester, 1621 (m) imine; ¹H-NMR (Me₂SO-d₆): δ (ppm) 3.07 (s, 6H, N(CH₃)₂), 6.61 (d, ¹J =2.3 Hz, 1H, H-8), 6.80 (dd, ${}^{2}J$ =8.4 Hz, ${}^{1}J$ =2.3 Hz, 1H, H-6), 7.08 (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 5.4$ Hz, 1H, H_{py}-5), 7.65 (d, ${}^{5}J = 9$ Hz, 1H, H_{py}-3), 7.78 (ddd, ${}^{5}J$ =8.9 Hz, ${}^{3}J$ = 7.2 Hz, ${}^{6}J$ =1.8 Hz, 1H, H_{pv}-4), 7.98 (d, ${}^{2}J$ =8.4 Hz, 1H, H-5), 8.05 (s, 1H, H-4), 8.30 (dd, ${}^{4}J = 5.5$ Hz, ${}^{6}J = 1.9$ Hz, 1H, H_{pv}-6), 8.55 (s, 1H, HC = N), 9.00 (brs, 1H, NH), 11.11 (brs, 1H, NH); ¹³C-NMR (Me₂SO-d₆): δ (ppm) 39.72, 96.96, 108.39, 109.93, 112.52, 113.00, 118.56, 130.17, 136.72, 138.08, 138.73, 147.65. 151.71, 152.02, 153.31, 155.81, 160.46. MS: *m*/*z* [M+H]⁺ 352.14021 (theoretical value: 352.1365). Anal. calcd for C18H17N5O3 (351.13): C, 61.53; H, 4.88; N, 19.93; found C, 61.22; H, 4.81; N, 19.59.

2.2. Spectroscopic measurements

UV–Vis absorption spectra were recorded on a HP 8452A (Hewlett Packard, USA) diode array spectrophotometer. All measurements were performed in a 1 cm cuvette.

Both anions in the titration experiments were added in the form of tetrabutylammonium salts purchased from Sigma–Aldrich (USA), and used without further purification. The anhydrous dimethyl sulfoxide (Me₂SO) solvent was of UV-spectroscopy grade (Uvasol®, Merck, Darmstadt, Germany).

All titration experiments were carried out at 298.16 K. The receptor solutions were titrated with the corresponding anion solutions (F⁻, AcO⁻) to obtain receptor concentration of the resultant solution as indicated in ESI Figs. S1–S12. The titration process in the anion concentration range of 1.43×10^{-5} mol/L to 1×10^{-2} mol/L was monitored by UV–Vis spectroscopy (in a 1 cm cuvette).

2.3. Association constant determination

Association constants K_{ass} for apparent coumarin semicarbazone: anion 1:1 complex formation were determined by the acknowledged formula describing complex anion concentration [34]:

$$A = A_0 + \frac{A_{\rm lim} - A_0}{2c_0} \left[c_0 + c_{\rm A^-} + 1/K_{\rm ass} - \left[(c_0 + c_{\rm A^-} + 1/K_{\rm ass})^2 - 4c_0 c_{\rm A^-} \right]^{1/2} \right]$$
(1)

where: A_0 is the absorbance of free coumarin semicarbazone, A is the coumarin semicarbazone absorbance measured after anion addition, A_{lim} is the coumarin semicarbazone absorbance measured with excess of the particular anion, c_0 is the overall concentration of coumarin semicarbazone and c_{A^-} is the overall concentration of the added anion A^- .

Eq. (1) was rewritten to the following form for nonlinear fit in OriginPro8.1 software:

$$A = A_0 + c_1 * (P1-A_0) * \left(c_0 + x + 1/P2 \cdot \sqrt{(c_0 + x + 1/P2)^2 \cdot 2 \cdot 4 * c_0 * x} \right)$$
(2)

where: $c_0 = 1 \times 10^{-4}$, $c_1 = 1/2c_0 = 5 \times 10^3$, parameter P1 = A_{lim} , parameter P2 = K_{ass} and x = c_{F} . The A_0 value was fixed to the absorbance A value for x = 0.

2.4. Theoretical calculations

The relative stability of the coumarin semicarbazones was

Table 1

Absorption maxima, extinction coefficients and equilibrium constant K_W (of protonation of formed anion after interaction with fluoride) for the semicarbazones 1 - 12 in Me₂SO.

Sensor	\mathbb{R}^1	R ²	without F ⁻ ions	with F ⁻ ions		K _W
#			$\lambda^1_{\max}[nm]/log(\varepsilon)$	$\lambda^2_{\text{max}}[nm]/\log(\varepsilon)$	$(\lambda^2_{\text{max}}, \lambda^1_{\text{max}})[nm]$	mol^{-1}
1	C ₆ H ₅	Н	368/4.25	493/4.37	125	4.01
2	4-F-C ₆ H ₄	$N(CH_3)_2$	441/4.45	493/4.43	53	2.58
3	4-Br-C ₆ H ₄	$N(CH_3)_2$	442/4.55	491/4.50	49	2.58
4	4-CH ₃ -C ₆ H ₄	$N(CH_3)_2$	440/4.50	495/4.40	53	2.17
5	4-CF3-C6H4	$N(CH_3)_2$	442/4.47	487/4.44	44	1.73
6	4-OCH3-C6H4	N(CH ₃) ₂	439/4.52	496/4.47	60	1.64
7	2-NO2-C6H4	$N(CH_3)_2$	446/4.50	469/overlap	22	2.20
8	4-NO2-C6H4	$N(CH_3)_2$	444/4.74	507/4.83	66	1.53
9	4-CN-C ₆ H ₄	$N(CH_3)_2$	443/4.68	486/4.65	44	1.63
10	Cyclohexyl	$N(CH_3)_2$	437/4.49	504/4.45	67	2.73
11	2-Py	Н	362/4.30	478/4.43	116	2.50
12	2-Py	N(CH ₃) ₂	440/4.30	478/4.43	38	2.51



Fig. 2. Charge distribution in the 7-N,N-dimethylaminocoumarin fragment of the compounds 2 - 10, 12.

investigated using quantum chemical calculations. Structural geometries were optimized at the semiempirical PM6 level. Stationary points were characterized as minima by computations of harmonic vibration frequencies at the same theoretical level as the geometric optimization. Single point energies were calculated at the M062X/6-311++G(d,p) level. All calculations were performed by the Gaussian 09 program package [35].

3. Results and discussion

3.1. Spectral characteristics and optimal geometry

3.1.1. Spectral characteristics

Absorption spectral characteristics of the studied semicarbazones **1** – **12** in dimethyl sulfoxide, such as the absorption maxima (λ^{1}_{max}) and the molar extinction coefficients (ϵ) are presented in Table 1. The absorption

spectra of all studied derivatives exhibit one intense long-wavelength absorption band without vibrational structure. Electronic transitions corresponding to these bands are proposed to be $n-\pi^*$ transitions and are related to the charge transfer within the coumarin moiety [36]. Measured and calculated data suggest that electron donating substituent at C-7 of the coumarin skeleton has crucial effect on the position of the absorption maxima. In the substances containing the dimethylamino group (2 – 10 and 12), compared to the ones with unsubstituted coumarin skeleton (1, 11), the long wave absorption maximum is bathochromically shifted by approx. 80 nm indicating significant influence of the substitution on excitation.

The dimethylamino group as an electron donating group (EDG) contributes to the high degree of ICT in the coumarin fragment. During the charge transfer either enolization of the coumarin carboxyl C=O group can occur or an enamine-like structure can be formed (Fig. 2). The degree of enolization/"enamine" formation depends on the electron



Fig. 3. Correlation of the absorption maxima of the compounds $2-6,\,8,\,9$ with σ_p in Me_2SO.



Fig. 4. Effect of solvent polarity on the position of the absorption maxima of the methyl substituted derivative 4, $c = 1 \times 10^{-5}$ M.

Table 2

Calculated relative energies of selected isomeric forms of the compound 1.





Fig. 5. Interaction of compound 11 with AcO^- and F^- in Me_2SO .

donating power of substituent in the C-7 position – in accordance with ¹H NMR spectra of the compounds. The chemical shift (δ) of imine H (<u>H</u>C=N) shifts upfield with the introduction of the EDG, *e.g.* for the compound **11** <u>H</u>CN δ is 8.77 ppm and for **12** <u>H</u>CN δ is 8.54 ppm. Resultantly, the contribution of the enamine-like structure to the charge distribution is non-negligible for the EDG substituted derivatives.

The influence of aromatic, aliphatic and heterocyclic substitution on the semicarbazone fragment on absorption spectra is demonstrated in the differences in the absorption maxima. All derivatives with the same coumarin substitution (2 – 9, 11, 12) exhibit absorption maxima at 441 \pm 5 nm. Thus the aniline ring of the semicarbazone moiety together with its substitution have minor effect on S₀-S₁ transition as the substituents do not affect the position of the absorption maxima significantly (Table 1). The insignificance is supposedly caused by cross conjugation of this fragment with the coumarin chromophore through the HN—C=O bridge.

Nevertheless, a linear correlation of the absorption maxima (reciprocal) with the Hammett σ_p constants can be observed within the series

of the compounds 2 - 6, 8, 9 (Fig. 3). The correlation indicates a considerable interconnection between the two π -systems (the coumarin moiety and the aniline ring), presumably a result of variation of the strength of intramolecular H-bond.

Solvent polarity affects the position of the absorption maxima only slightly (Fig. 4). This behaviour comes to an agreement with the nature of the corresponding aldehydes [30,31]. Furthermore, in respect to the effect of aniline (or substituted aniline) ring addition on UV-Vis spectra – compared with the UV-Vis spectra of the corresponding aldehydes – it is the coumarin subunit which is the one responsible for the long wave absorption maximum (chromogenic unit). This is also supported by the fact that coumarin substituents significantly affect the S₀-S₁ electronic transition of the semicarbazones **1** – **12**.

3.1.2. Optimal geometry

To confirm that the UV-Vis spectra were in accordance with the proposed charge distribution in the semicarbazones 1 - 12, we performed quantum chemical calculations of the relative energies for the most probable isomeric forms of the compounds. As an illustration, the selected isomeric forms of the compound **1** are shown in the Table 2 (for the corresponding cartesian coordinates see ESI S17-S25). The intramolecular hydrogen bond between the hydrazone nitrogen and the NH hydrogen of the aniline fragment together with small electronic repulsion contribute to the stabilization of the structure **C** with the lowest energy amongst all studied isomers. The (*E*)-geometric isomer **C5** (Table 2) is approximately 14 kJ/mol more stable than the corresponding (*Z*)-isomer **C4**. It is a relatively small difference in order to photochemically prepare single isomer, or to work with a single isomer in solution at room temperature.

Tautomerism as well as double bonds configuration (-C=C-C=N- – whether *s-cis* or *s-trans*) are another important factors in isomers' stability. As the Table 2 shows, enolization of the semicarbazone carbonyl leads to less stable structures (**C2**, **C3**, **C6**, **C8**). Even if a structure can be stabilized by an intramolecular H-bond, its contribution to the over-all energy cannot compete with the stability of the C=O bond.

3.2. Effect of anions on UV-Vis spectra of the substituted coumarin semicarbazones

3.2.1. Effect of fluoride anion

Despite the small effect of solvent or substitution pattern on the aniline ring on the UV-Vis spectra of the studied semicarbazones, the presence of anions in Me₂SO solution affects the spectra considerably. Ions AcO⁻, Cl⁻, Br⁻, HSO₄, NO₂ and NO₃ induce none or relatively negligible changes, whereas substantial naked eye colorimetric changes are almost immediately observed (within few seconds) in the presence of fluoride anion.

The most significant colour change after the addition of $(Bu_4N)F$ (TBAF) to Me₂SO solutions of semicarbazones was detected for the derivatives **1** and **11** – substances unsubstituted at the coumarin C-7 position. The magnitude of these changes was dependent on the concentration of anions in the solution. Fluoride anion produces an appreciable visual colour change upon interaction with the semicarbarbazone **11** leading to an immediate orange colour (Fig. 5). For dimethylamino derivatives, we did not observe such a distinct colour change as their solutions are yellow to orange and, after adding fluorides, their colour only deepens so the difference between the colour before and after the addition of anions is not so intense.

To check the anion sensing capability of semicarbazones 1-12 against fluoride, UV–Vis spectrophotometric titrations were carried out at 298.16 K. Solutions of compounds (concentrations are indicated in ESI, Figs. S1–S12) in Me₂SO were prepared followed by the addition of TBAF in different concentrations (for all samples from 1.43×10^{-6} mol/L and its folds to 1×10^{-2} mol/L). Aprotic, polar and water miscible Me₂SO was chosen as the solvent for anion titrations in order to avoid

anion-solvent interactions and also because of the low solubility of semicarbazones (in particular nitroderivatives) in other solvents. We found out that increasing concentration of F^- anions in a solution of semicarbazone resulted in a decrease of absorbance at the absorption maximum at around 440 nm and simultaneously the formation of a new absorption band with an absorption maximum at around 500 nm occurred (Table 1). Correspondingly, the absorption red-shift of 53–125 nm resulted in the solution distinct colour change, which can be directly observed by naked eyes. As an example, UV-Vis titration of derivatives 6 and 8 in Me₂SO with TBAF is displayed in the Figs. 6 and 7. Similar changes in the UV–Vis spectra in the presence of F^- anions were observed in all studied semicarbazones (Table 1, ESI Figs. S1–S12).

The detection and quantification limits were calculated on the basis of absorption titrations (see ESI S26-S30). We compared the estimated detection limits to other fluoride sensors with coumarin moiety with same sensing mechanism, specifically H-bond induced deprotonation, as well as with few recently reported sensors containing neutral hydrogen bonding receptor moiety (Tables 3 and S1) operating primarily in Me₂SO. As resulted from Tables 3 and S1, the studied semicarbazones exhibit good (semicarbazones 1, 3, 9, 11) to moderate (other semicarbazones investigated) colorimetric fluoride anion sensing abilities.

It is well known, that coumarins are compounds with interesting fluorescent properties. Recently, a variety of fluorescent turn off fluoride anion sensors with coumarin moiety have been developed [4], but majority of them involves a EDG group substituted coumarin skeleton which has suitable fluorescence properties and their detection limits are



Fig. 6. Effect of F^- anions on UV–Vis spectra of the methoxy derivative 6 in Me_2SO, $c=2.9\times 10^{-5}$ M.



Fig. 7. Effect of F^- anions on UV–Vis spectra of the nitro derivative 8 in Me₂SO, $c=2.9\times 10^{-5}$ M.

Table 3

The analytical performance of studied semicarbazones compared with similar type of fluoride sensors ^{***}.

#	Sensor	Medium	λ [nm]	LOD [µmol/L]	Approach	Ref.
1		Me ₂ SO	493	8.59	colorimetric	this work
3		Me ₂ SO	490	6.61	colorimetric	this work
9		Me ₂ SO	486	7.39	colorimetric	this work
11		Me ₂ SO	476	7.13	colorimetric	this work
Α		Me ₂ SO/CH ₃ CN	448	9.2	colorimetric/ fluorescent	[37]
В		THF	504	0.21	colorimetric/ fluorescent	[38]
C		Me ₂ SO	458	not specified	colorimetric/ fluorescent	[39]
D		CH ₃ CN (0.08% Me ₂ SO)	455	not specified	colorimetric/fluorescent	[40]
Е	$\sim \sim $	CH ₃ CN	620	not specified	colorimetric	[41]
F	OH NH NH	Me ₂ SO	422	not specified	colorimetric/fluorescent	[42]
G		Me ₂ SO:H ₂ O 1:1	490	0.95	colorimetric	[43]
	N-N					
н	HO N	CH ₃ CN	494	0.72	colorimetric/ fluorescent	[44]
I		Me ₂ SO	485	15	colorimetric	[45]
J		Me ₂ SO	391	5	colorimetric	[46]

* Coumarin derivatives with different F⁻ sensing mechanism are not listed (e.g. silyl capped coumarins [4]).

** For comparison with other types of fluoride sensors see review article [4].

lower than for colorimetric ones as fluorometry is more sensitive compared to colorimetry. However, many of the currently known fluoride sensors show less preferable turn-off fluorescence response, contrary to the turn-on fluorescence response. Indeed, the turn-off probes may exhibit an undesirable false positive response with high probability because number of other factors instead of the target analyte alone can be responsible for fluorescence quenching of the sensor molecule [47, 48]. Considerably less attention has been paid to the development of colorimetric sensors with coumarin moiety capable of operating without undesirable false positive responses in many applications. Semicarbazones listed in Table 3 with the major shift of absorption maxima (116–125 nm) found in the absorption spectra in the presence of F^-

together with the distinct colour change under ambient light are highly suitable for naked eye detection of F^- with good detection limit 7.13 μ M for derivative **11** resp. 8.59 μ M for semicarbazone **1**. These detection limits are below the detection limit determined by fluorescent approach for coumarin derivative **A** with similar structural motive [37].

3.2.2. Effect of commonly competing anions

According to visual inspection of the solutions of the semicarbazones $(1 \times 10^{-4} \text{ M} \text{ in Me}_2\text{SO})$ before and after the addition of commonly competing anions, the addition of either AcO⁻, Cl⁻, Br⁻, HSO₄, NO₂⁻ or NO₃⁻ does not result in appreciable changes in colour. Additionally, binding properties of the semicarbazones were investigated by ¹H NMR



Fig. 8. Effect of CH₃COO⁻ TBA⁺ (TBAOAc) on UV-Vis spectra of the cyano derivative 9 in Me₂SO, $c = 7 \times 10^{-4}$ M.



Fig. 9. 1 H NMR spectra of the cyano derivative 9 in Me₂SO 1) without TBAF, 2) with 20 eq of TBAF, 3) with 20 eq of TBAOAc.

and UV-Vis spectroscopy in Me₂SO using tetra-*n*-buthylammonium salts of the anions (TBA-X: $X = AcO^-$, CI^- , Br^- , HSO_4^- , NO_2^- , NO_3^-). Absorption spectra were recorded after 5 min upon addition of 1 eq of each of these anions. Only one of the studied analytes, AcO^- , did affect the spectra. Another one $-OH^-$ – might interfered with the analysis. Nevertheless, detailed studies with this anion could not be carried out – in required concentrations the strong basic/nucleophilic properties of hydroxide anions led to fast destruction of the semicarbazones.

As highly basic anions, though different in shape, fluoride and acetate generally engage in hydrogen bond interactions with a variety of Hbond donors. The selectivity of AcO^- and F^- chemosensors is typically



related either to the ability to form H-bonds or to the possibility of deprotonation of the probe by the anion.

We carried out detailed studies to gain further insight into the anion sensing capability of the coumarin semicarbazones for F^- and AcO⁻, as well as to check the possibility of the detection of the fluoride anion in the presence of acetate.

As expected from the visual inspection, the UV-Vis spectra show remarkable difference between interaction of the compounds 1 - 12 with F⁻ and AcO⁻ (Figs. 5, 8, shown for the cyano compound 9). An addition of more than 20 equivalents of TBAOAc to the solutions of semicarbazones results in a slight increase of band intensity at 440 nm instead of the bathochromic shift of the long wave absorption maximum observed for fluoride interaction with the chemosensors (as shown in Figs. 5, 6). Furthermore, an appearance of a new band at around 350 nm can be used for the distinction of F⁻ in the presence of AcO⁻.

Contrary to the UV-Vis spectra, in our ¹H NMR spectral study we observe the complete disappearance of the signal of the most acidic hydrogen from the spectra after the addition of the excess amount of F^- as well as AcO⁻ to the Me₂SO solutions of the semicarbazones (the cyano derivative **9** displayed in Fig. 9 as an example).

These changes in spectra (UV-Vis, ¹H NMR) can be explained by the proposed structures of the formed species (Fig. 10). As F^- is a stronger base than AcO⁻ in Me₂SO (HF pK_a(Me₂SO) = 15, AcOH pK_a(-Me₂SO) = 12.3 [49]; and in particular the HF₂⁻ anion formed in an excess amount of F^- [21]), it is more likely for deprotonation – accompanied by an elongation of the conjugated system resulting in the colour change – to occur in comparison to acetate with weaker basic properties. Besides, acetate can also act as a bifurcate H-bond acceptor capable of interacting with the two acidic hydrogens of the semicarbazone substructures forming a cyclic bimolecular structure, *e.g.* **9A**. This interaction can explain the disappearance of the signal of the more acidic hydrogen from the ¹H NMR spectra, the different shift of the aromatic protons in ¹H



Fig. 11. Effect of CH_3COO^ TBA^+ (TBAOAc) on UV–Vis spectra of 1 in Me_2SO, $c=7\times 10^{-4}$ M.



Fig. 10. Proposed structures: coordination of the cyano derivative 9 with TBAOAc (9A) and the deprotonated cyano derivative 9 (9B) with TBAF.



Fig. 12. Correlation of the absorption maxima of the compounds 2 – $6,\,8,\,9$ with σ_p in Me_2SO in the presence of F⁻.

NMR and also the differences in the UV-Vis spectra.

Similar behaviour in the presence of AcO^- is observed in all studied substances except the unsubstituted derivative **1** (Fig. 11). After the addition of acetate, a slight bathochromic shift of the long wave absorption maximum (by 11 nm) can be observed in the UV-Vis spectrum in this case. The aforementioned indicates an effect of the electron density distribution in the coumarin scaffold on the character of interaction because the hydrogens on the semicarbazone substructure become less acidic with the presence of EDG on the coumarin skeleton.

Correlation of the absorption maxima (reciprocal) with Hammett σ_p constants of the series of the compounds **2** – **6**, **8** and **9** is observed after the addition of fluoride as well as without fluorides (Fig. 12). It shows that even though the effect of substitution on the absorption maxima is small, it has a remarkable impact on the stabilization and the spectral properties of the species formed by deprotonation, as the two π -systems are interconnected.

The nitro derivative 8 does not fit in the correlation in the Fig. 12,



Fig. 13. Effect of H₂O addition on UV-Vis spectra of the pyridine derivative 12, $c = 5 \times 10^{-5}$ M, in excess of TBAF in anhydrous Me₂SO.

and thus we expect an interaction of a different kind. For instance, the deprotonation may partially occur from the aniline NH group instead of the hydrazone NH group (being more acidic in the other derivatives; similar to **9B** in Fig. 10).

For further understanding of the sensing mechanism, after the deprotonation of the semicarbazones with F^- in Me₂SO we performed a study of protonation of the formed anion by a spectrophotometric titration with water in anhydrous Me₂SO. For demonstration we chose titration of the derivative **12** (Fig. 13).

According to the equilibrium showed in Scheme 2, we calculated equilibrium constants K_w of this reaction for all compounds (Table 1). In all cases we observed a higher rate constant for the forward reaction (K_w was always higher than 1).

The most plausible explanation of the K_w trend is that the anions are of low stability (high energy) because the negative charge cannot be distributed throughout the whole molecule and is localized in a 3 atom region (the hydrazide part of the semicarbazone moieties). Because of this the compounds 1 - 12 are not acidic, which is confirmed by that the interaction with mildly basic acetate anion is based more on coordination/H-bonding than on deprotonation.

4. Conclusions

Colorimetric naked eye detection without the need for any sophisticated instrumentation as the semicarbazones presented in this article offer is attractive especially for applied fields of chemistry such as environmental analysis or waste water treatment. For these fields it is highly important to detect fluoride anions, as F^- can cause severe damage to water organisms. As such, the chemosensors based on coumarin semicarbazone moiety designed by our research group may be potentially utilizable for the aforementioned applications.

Our results offer a complex view of coumarin semicarbazones with aryl, hetaryl and alkyl substituents on the semicarbazone scaffold as potential colorimetric sensors for fluoride anions. The interaction of F^- with the sensors is, according to the reported results, based on deprotonation, however the exact mechanism depends on the electron density distribution in the coumarin moiety.

The described sensing of fluorides is highly selective with to $10 \,\mu$ M detection limits, with short response time even in the presence of acetate anions, which is confirmed by the appearance of a red shifted high energy absorption band only upon interaction with fluoride. This considerable competitor – acetate – exhibits another type of interaction with the semicarbazones. The pK_a of conjugated acid is not as different as it is for some of the other anions (HF pK_a(Me₂SO) = 15; AcOH pK_a(Me₂SO) = 12.3; HCl pK_a(Me₂SO) = 1.8; HBr pK_a(Me₂SO) = 0.9), nevertheless these two anions (F⁻ and AcO⁻) are the only studied ones affecting UV-Vis and ¹H NMR spectra of the compounds. We assume this interaction is selective for fluorides in the presence of majority of anions.

The colour change observed for the dimethylamino derivatives in the Vis region (by approx. 50 nm) is sufficient for naked eye detection. The highest shift in the UV-Vis spectra for the sensor – analyte interaction is observed for the derivatives unsubstituted on the coumarin scaffold. In these cases the colour of the solution changes from colourless (absorption in the "invisible" UV region) to yellow (in the Vis region), thus these sensors can be used for detection without sophisticated instrumentation as the colour difference is significant.



Scheme 2. Reaction of 12 with H₂O and F⁻ respectively.

CRediT authorship contribution statement

Hana Janeková: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - review & editing, Visualization. Jan Gašpar: Methodology, Validation, Investigation. Anton Gáplovský: Conceptualization, Methodology, Software, Data curation, Writing original draft, Visualization, Supervision, Funding acquisition. Henrieta Stankovičová: Conceptualization, Validation, Resources, Writing original draft, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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