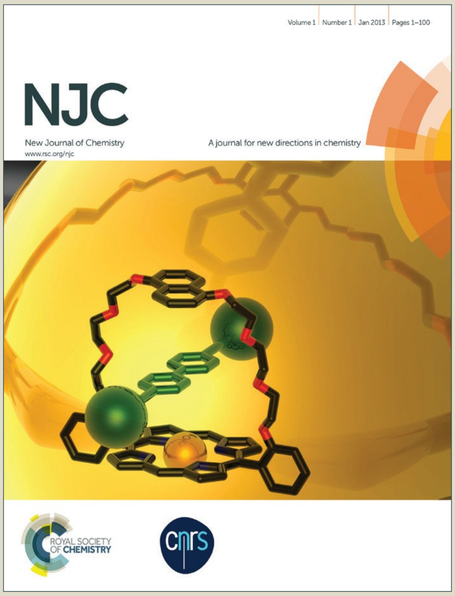
NJC

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Coumarin phenylsemicarbazones: Sensitive colorimetric and fluorescent “turn-on” chemosensors for low-level water content in aprotic organic solvents

Marek Cigáň,[a,]* Jan Gašpar,[a] Katarína Gáplovská,[a] Jana Holekšiová,[a] Klaudia Jakusová,[a] Jana Donovalová,[a] Vladimír Garaj,[b] and Henrieta Stankovičová [a]

The water sensing properties of four new efficient two-component colorimetric and fluorescent “turn-on” chemosensors based on coumarin phenysemicarbazone skeleton bearing different acceptor/donor functional groups on aniline structural subunit were investigated and are discussed in terms of photophysical properties, interaction mechanism, sensitivity and substituent effect. Due to the sensing mechanism based on reversible acid-base keto/enolate (hydrazide/hydrazonolate) equilibrium, all studied coumarin phenylsemicarbazone chemosensors provide rapid and reversible response to low-level water content in polar aprotic solvents. To the best of our knowledge, determined detection limits for water by studied chemosensors are amongst the lowest published detection limits in literature and can compete in sensitivity with chemodosimeters. Their deficiency is, however, the necessity of F^- base presence.

Introduction

A Qualitative and quantitative detection of low-level water as impurities in organic solvents has great significance in several fields of chemistry and industry processes such as pharmaceutical manufacturing, food processing, production of anhydrous solvents and chemical reagents, petroleum fuel industry, paper production and biomedical or environmental monitoring.[1-21] Classic and currently industry-wide methods for the determination of water content are electrical sensors based on electrochemical and electrophysical sensing mechanisms (resistance, capacitance and conductivity change in the presence of water/humidity) and some of them are commercially available.[4] Although they allow a simple sensor calibration and installation procedure, their limitations include mainly insufficient portability/precision and sensitivity to electromagnetic interference. In the laboratory scale, the most broadly used techniques are gas chromatography and particularly the Karl–Fisher titration.[17] However, these methods have the disadvantage of requiring time-consuming sample preparation, inability of real-time monitoring of the water content, skilled personnel, special equipment and interference from other co-existing species.[1-21] Moreover, the Karl–Fisher titration is less sensitive in aprotic and non-alcoholic solvents.[19] Therefore, the development of effective techniques for ultra-sensitive water content determination is urgently required.

Recently, optical (colorimetric and fluorescent) sensors for water sensing have drawn considerable attention due to their flexibility in readout, the possibility of remote and in situ monitoring as well as their easy and low-cost fabrication.[3,4] In particular, low-cost, rapid, simple and sensitive fluorescence methods, including lifetime, intensity and ratiometric wavelength sensing, have been widely investigated. Excellent review related to recent advances in the field of colorimetric and fluorescent sensors for low-level water content, categorized by sensing mechanism, was recently published by Kim *et al*.[22]

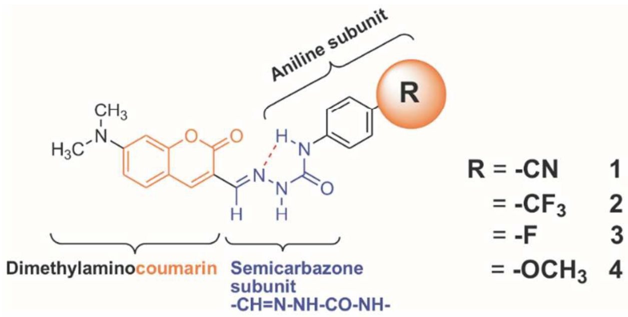
7-Dialkylaminocoumarins (7-dialkylamino-2*H*-chromen-2-ones) are arguably the most important and applicable subset of coumarin fluorescent probes. Their fluorescence is strongly dependent on the polarity, hydrogen bonding ability, pH, the presence of quest anions, various metal ions, biologically important compounds, chemical warfare agents and the micro-viscosity or rotational hindrance in their local environment.[23-48] In our recent two studies, the photophysical properties of 7-(dimethylamino)coumarin-3-carbaldehyde and its five phenylsemicarbazones with various electron-withdrawing substituents in the *para*- position on the phenyl ring in solution and polymer matrix were investigated.[49,50] Although *para*- NO_2 derivative exhibited a strong solvent effect in polar solvents due to the formation of a non-fluorescent TICT state, other *para*- substituted phenylsemicarbazones showed practically solvent polarity independent high fluorescence efficiency (quantum yield) and were often qualified as laser dyes in the given medium. Only recently

---

[a.] Institute of Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH-2, SK-842 15 Bratislava, Slovakia; E-Mails: cigan@fns.uniba.sk (M.C.); gasparjano@gmail.com (J.G.); gaplovska15@gmail.com (K.G.); holeksiova@fns.uniba.sk (J.H.); jakusova@fns.uniba.sk (K.J.); donovalova@fns.uniba.sk (J.D.); stankovh@fns.uniba.sk (H.S.).
[b.] Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, SK-832 32 Bratislava, Slovakia; E-Mail: garajv@fpharm.uniba.sk (V.G.).

coumarin-decorated Schiff base hydrolysis as an efficient driving force for the fluorescent detection of water in organic solvents was introduced.[51]

Herein, we report results of a comprehensive investigation of water sensing properties of four donor/acceptor *para*-substituted 7-dimethylaminocoumarin phenylsemicarbazones **1**-**4** as colorimetric and fluorescent chemosensors for low-level water content in aprotic polar organic solvents (Scheme 1). Although the presence of urea moiety in these derivatives designated them to strongly basic anion sensing[52], competition with water in reversible acid-base reaction leads to effective two-component coumarin phenylsemicarbazone/anion optical chemosensors. Despite of the sensing mechanism based on acid-base equilibrium, they can be classified as "competitive ligand-based" chemosensors, similar to fluoride complexes of quinoline or phenolic dyes published by Kim *et al.* and Moon *et al.*, respectively.[10,53] Compared to other "competitive ligand-based" organic chemosensors for water detection, studied two-component sensors exhibit significantly lower detection limits.[22]



Scheme 1. Molecular structure of studied coumarin phenylsemicarbazones **1**-**4**.

Due to relatively high and undefined initial water content in DMSO, quantitative analysis of studied two-component sensors was carried out in acetonitrile (MeCN).

Results and discussion

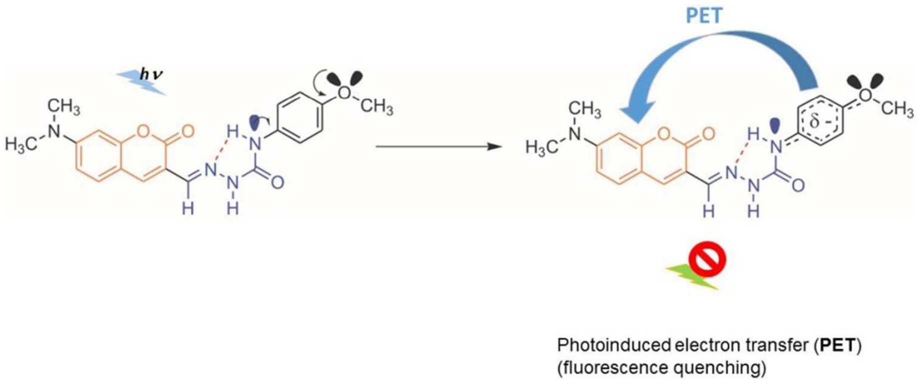
Spectral characteristics

Basic spectral characteristics of acceptor coumarin phenylsemicarbazones **1**-**3** were discussed in our previous paper.[50] It should be only mentioned here that, independently on solvent polarity, all three acceptor coumarin semicarbazones exhibit high fluorescent quantum yields ($\Phi_F > 0.4$). Compared to them, new methoxy derivative **4** shows significantly lower Φ_F values (Table 1). Restricted π-conjugation between coumarin and aniline chromophoric subunits, zero spectral overlap between methoxyaniline and dimethylaminocoumarin subunits and non-sensitivity to solvent viscosity indicate that fluorescence quenching in derivative **4** results from photoinduced electron transfer (PET) from aniline to dimethylaminocoumarin moiety (due to +M mesomeric effect of the $–OCH_3$ group; Scheme 2). The PET manifests itself in rapid fluorescence quenching without the initial fluorescence lifetime (τ) shortening that would indicate a dynamic quenching (Table 1). Moreover, the quantum-chemical calculations of HOMO and LUMO orbital energy of the corresponding chromophoric parts support the PET quenching mechanism (ESI Table S1, ESI Scheme S1). Increased electron density of aniline moiety due to +M effect of $–OCH_3$ leads to HOMO energy increase of this chromophoric subunit.

Table 1. Basic spectral characteristics of studied coumarin derivatives **1**-**4** in MeCN and DMSO.

	R	λ_A (nm)	Log ε_A	λ_F (nm)	Φ_F	τ (ns)	
				MeCN			
1	-CN	433	4.58	504	0.50	$\tau_1 = 2.0$ (32%) $\tau_2 = 3.2$ (68%)	$\chi^2 = 1.135$
2	-F	429	4.56	503	0.69	$\tau_1 = 1.9$ (36%) $\tau_2 = 3.3$ (64%)	$\chi^2 = 1.120$
3	$-CF_3$	432	4.60	504	0.63	$\tau_1 = 1.9$ (28%) $\tau_2 = 3.2$ (72%)	$\chi^2 = 1.160$
4	$-OCH_3$	430	4.48	504	0.14	$\tau_1 = 0.9$ (94%) $\tau_2 = 3.2$ (6%)	$\chi^2 = 1.190$
				DMSO			
1	-CN	441	4.56	514	0.85	$\tau = 3.0$ (100%)	$\chi^2 = 1.100$
2	-F	441	4.53	514	0.89	$\tau = 3.0$ (100%)	$\chi^2 = 1.096$
3	$-CF_3$	441	4.51	514	0.93	$\tau = 3.0$ (100%)	$\chi^2 = 1.123$
4	$-OCH_3$	441	4.49	514	0.28	$\tau_1 = 0.77$ (97%) $\tau_2 = 4.2$ (3%)	$\chi^2 = 1.190$

λ_A – Long-wavelength absorption maximum; Log ε_A – Log of the molar extinction coefficient in λ_A; λ_F – fluorescence maximum; Φ_F – fluorescent quantum yield; τ – fluorescence lifetime; χ^2 – Quality of fluorescence lifetime fitting



Scheme 2. Photoinduced electron transfer (PET) from aniline to dimethylaminocoumarin moiety due to +M mesomeric effect of the $–OCH_3$ group in studied metoxy derivative **4**.

Instead of LUMO-HOMO emissive (fluorescent) deexcitation pathway after photon absorption by coumarin, the electron transfer occurs from aniline HOMO to coumarin LUMO orbital and reduces thus the fluorescence intensity. Although $–OCH_3$ substituent in the *para*- position on the phenyl ring significantly influences sensor brightness $\varepsilon_A \times \Phi_F$ (particularly through Φ_F value), it practically does not affect absorption and fluorescence maxima (λ_A and λ_F, respectively), similar to acceptor substituents. Although studied coumarin phenylsemicarbazones contain C=N double bond in their structure, possible photoisomerization was not observed.

Anion addition

Gradual fluoride (F^-) anion addition to coumarin **1**-**4** solutions shifts light absorption to red spectral region (Fig. 1A). Solution colour thus changes from yellow to orange and its fluoresecence almost completely disappears (Fig. 1B). Therefore, all four studied semicarbazone derivatives **1**-**4** could be useful as colorimetric and fluorescent sensors for F^- anions.

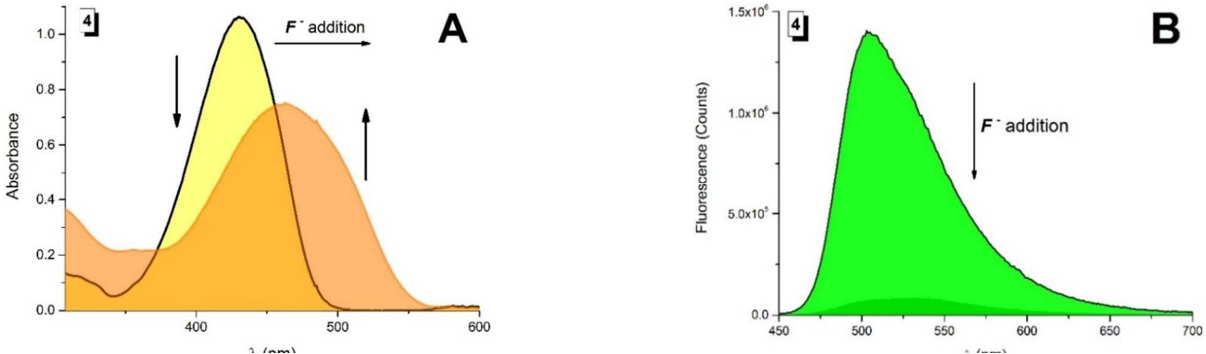


Fig. 1. (A) UV-Vis spectral change of coumarin semicarbazone **4** in MeCN (~3×10^{-5} mol L^{-1}; yellow spectrum) after F^- anion addition (~100 equivalents). (B) Fluorescence change of coumarin semicarbazone **4** in MeCN (~3×10^{-5} mol L^{-1}; greenish spectrum) after F^- anion addition (~100 equivalents; $\lambda_{EX} = \lambda_A$).

Other strongly and/or weakly basic anions such as acetate CH_3COO^-, bisulphate $H_2PO_4^-$ or Cl^- anions do not induce colorimetric response, however, CH_3COO^- anions quench fluorescence quite significantly (probably through hydrogen bonding)(ESI Fig. S1).

However, already air humidity diffusion leads to slow re-colouration of solution to its original colour (from orange to yellow). As expected, the same effect is achieved by gradual low-level water addition (Figs. 2A and 3). Moreover, both result also in initial green fluorescence recovery (Figs. 2B and 4).

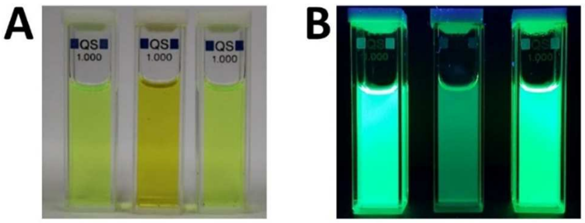


Fig. 2. (A) Yellow-orange colour change of coumarin phenylsemicarbazone **1** in MeCN after F^- anion addition (TBA^+F^-) and reversible colour change due to low-level water addition (< 1 wt%). (B) Fluorescence quenching of coumarin phenylsemicarbazone **1** in MeCN after F^- anion addition (TBA^+F^-) and its fluorescence recovery due to low-level water addition (< 1 wt%) (cuvette photo under commercial UV lamp; ⍰$_{EX}$ = 365 nm).

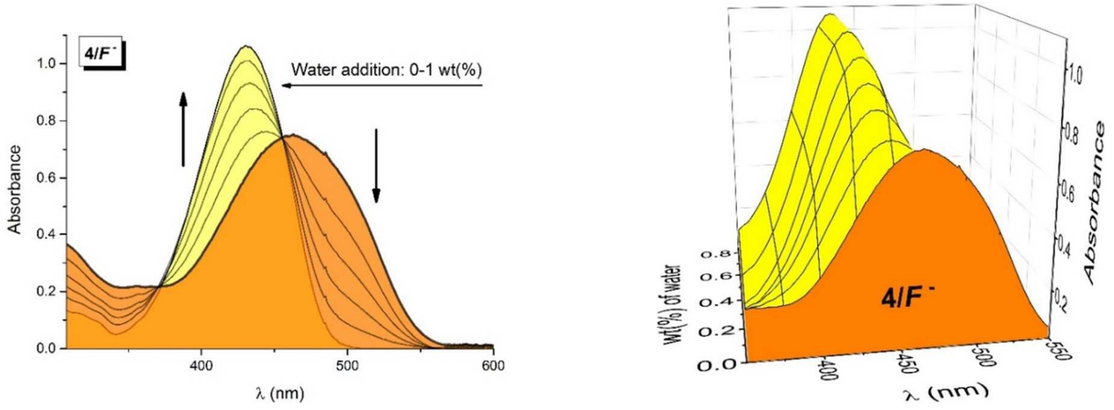


Fig. 3. Evolution of the UV-VIS spectrum of two-component coumarin phenylsemicarbazone **4**/F^- sensor in MeCN during its titration with water (~3×10^{-5} mol L^{-1} **4** + 5×10^{-3} mol L^{-1} *TBA^+F^-*; *T* = 298.15 K) (left) + correspnding 3D graph (right).

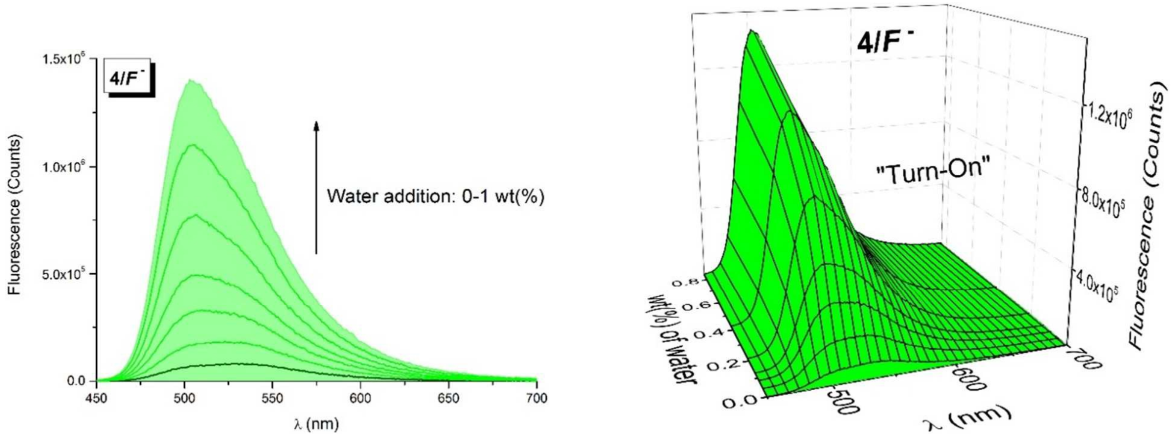


Fig. 4. Evolution of the fluorescence spectrum of two-component coumarin phenylsemicarbazone **4**/F^- sensor in MeCN during its titration with water (~3×10^{-5} mol L^{-1} **4** + 5×10^{-3} mol L^{-1} *TBA^+F^-*; $\lambda_{EX} = \lambda_{A(\text{keto-form})}$; *T* = 298.15 K) (left) + correspnding 3D graph (right).

Observed absorption/emission changes can be rationalized by reversible acid-base keto/enlolate (hydrazide/hydrazonolate) equilibrium (Scheme 3). Addition of strongly basic F^- anion leads to the most acidic NH group deprotonation from initial coumarin phenylsemicarbazone keto form that transforms to corresponding enolate with increased conjugation and results thus in yellow-orange colour change and simultaneous fluorescence quenching (Fig. 5). On the contrary, addition of water as acid transforms the coumarin phenylsemicarbazone enolate base to initial keto form (Figs. 5 and 6). Because the fluorescence decay curve after F^- addition excludes dynamic quenching (Figure 6) and the fluorescence intensity is only slightly sensitive to solution viscosity (ESI Fig. S2), we assume that the fluorescence quenching in the presence of F^- anions results from rapid intersystem crossing.

Reversible process can be observed also in other polar aprotic solvents (DMSO, DMF) (ESI Fig. S3). However, polar protic solvents like MeOH and EtOH compete with water as base and therefore studied two-component coumarin phenylsemicarbazone/F^- chemosensors cannot be use for low-level water content determination in these solvents.

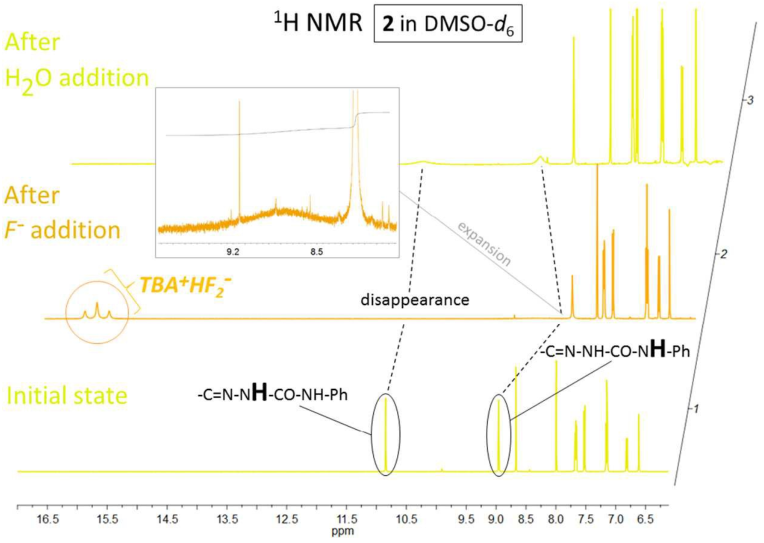


Fig. 5. ^{1}H NMR spectrum of **2** in DMSO-d_6 before and after *TBA*$^+$*F*$^-$ and subsequent water addition (T = 298.15 K).

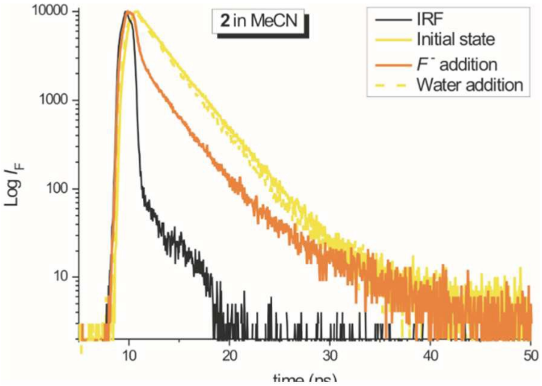
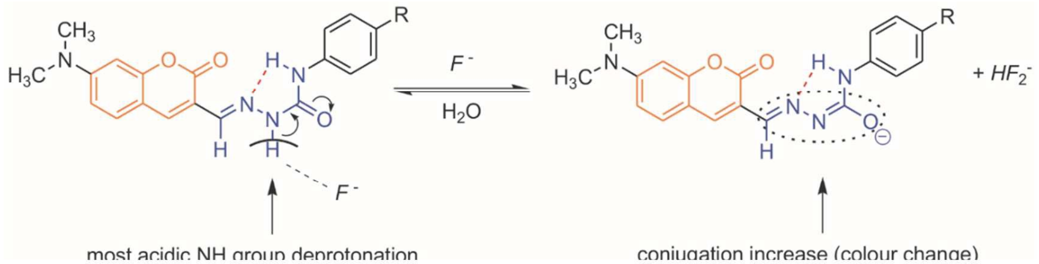


Fig. 6. Fluorescence lifetime of **2** in MeCN before and after *TBA*$^+$*F*$^-$ and subsequent low-level water addition (T = 298.15 K; $\lambda_{EX} = \lambda_{A(keto\text{-}form)}$); results of fitting: Initial state: τ_1 = 2.0 ns (27%), τ_2 = 3.3 ns (73%), χ^2 = 1.082; F^- addition: τ_1 = 0.2 ns (47%), τ_2 = 2.4 ns (45%), τ_3 = 6.4 ns (8%), χ^2 = 1.154; Water addition: τ_1 = 1.7 ns (20%), τ_2 = 3.0 ns (82%), χ^2 = 1.191).

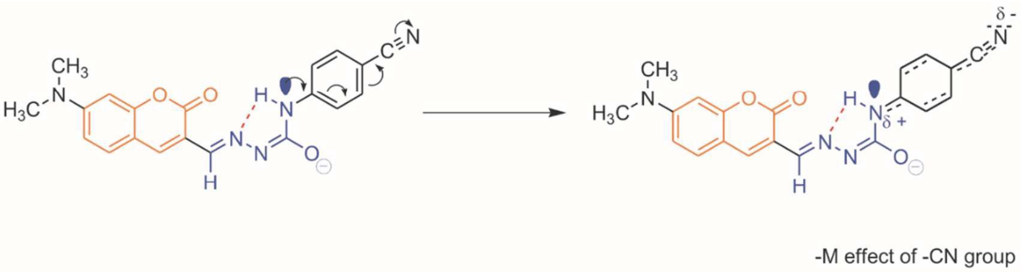


Scheme 3. Acid-base keto/enolate (hydrazide/hydrazonolate) equilibrium in two-component coumarin phenylsemicarbazone/F^- chemosensors **1**-**4**/F^- for low-level water content determination in polar aprotic solvents.

Detection limit (3σ/S) is the lowest concentration level determined statistically different from a blank with 99% confidence and quantification limit (10σ/S) is the level above which quantitative results are obtained with a specified degree of confidence. The calculated detection and quantification limits for water using studied two-component colorimetric and fluorescence "turn-on" coumarin phenylsemicarbazone/F^- chemosensors **1**-**4**/F^- are summarized in Table 2 and ESI Table S2. The determined 3σ/S for water by chemosensors **1**-**4**/F^- are amongst the lowest published detection limits for this molecule in MeCN and can compete in sensitivity with chemodosimeters.[22] Compared to other "competitive ligand-based" chemosensors for water detection, determined 3σ/S are practically equal to the most sensitive Eu^{3+} luminiscent chemosensor published by Song *et al*.[54]

Although *para*- phenyl substitution does not significantly affect the water detection limit of **1**-**4**/F^-, the difference in 3σ/S can be noticed, almost for derivatives with mesomeric effect of *para*- substituent (Table 2 and ESI Table S2). It should be mentioned here that, instead of a typical Y-shaped urea –NH-CO-NH- moiety conformation (*s-trans*, *s-trans*), quantum chemical calculations confirm the presence of relatively strong intramolecular hydrogen bonding in coumarin phenylsemicarbazones (*s-cis*, *s-trans* conformation of urea structural fragment)(ESI Table S3), similar to isatin phenylsemicarbzones.[55]

3σ/S order correlates well with the determined association constant (K_{ass}) order for apparent coumarin phenylsemicarbazone:F^- 1:1 complex (ESI Table S4 and Fig. S4; ESI Association constant determinations†). As is evident from K_{ass} order, lower amount of for F^- in coumarin **1** solution with the highest K_{ass} value is necessary to achieve the same enolate concentration in solution compared to coumarin **4** with the lowest K_{ass} value. Therefore, the presence of –CN substituent with –M effect stabilizes enolate form by π-conjugation enlargement and intramolecular hydrogen bond strengthening, similar to corresponding enol form stabilization by strong electron-accepting –NO_2 substituent in unsubstituted coumarin phenylsemicarbazone (Scheme 4).[50] Consequently, lower amount of water is necessary to solvate the present inorganic salts in solution and to initiate simultaneously back acid-base (enolate/keto) reaction. This leads to slight decrease in 3σ/S for **1**/F^-, contrary to other three chemosensors and almost **4**/F^- sensor with +M effect and the highest 3σ/S value. However, the **4**/F^- sensor fluorescent sensitivity can be largely affected (reduced) by significantly lower Φ_F due to PET.



Scheme 4. Stabilization of enolate form of coumarin cyano (CN) derivative **1** due to –M mesomeric effect of –CN group. –M effect leads to π-conjugation enlargement, intramolecular hydrogen bond streightening and thus to enolate form stabilization.

Water detection range valid for chemosensors **1**-**4**/F^- in MeCN using fluorescence spectroscopy lies in the interval of 0-2 wt% (0-1.6 v/v%) and shows an excellent linearity in the range of 0-0.46 wt% (0-0.36 v/v%)(ESI Fig. S5). It is only natural that the detection range can be enlarged by a suitable coumarin phenylsemicarbazone increase and simultaneous optical path length decrease.[55] Detection range for studied chemosensors is slightly larger for fluorescent than for colorimetric determination and results probably from later emissive "keto" excited state recovery in the presence of salts.

Table 2. Detection limit (LOD) and quantification limit (LOQ) for water in MeCN using studied two-component coumarin phenylsemicarbazone/F^- chemosensors (determined by fluorescence spectroscopy; *T* = 298.16 *K*).

	LOD (3σ/S)	
	wt%	v/v%
1/F^-	0.0015	0.0019
2/F^-	0.0019	0.0024
3/F^-	0.0019	0.0024
4/F^-	0.0026	0.0033
	LOQ (10σ/S)	
	wt%	v/v%
1/F^-	0.0064	0.0050
2/F^-	0.0080	0.0063
3/F^-	0.0082	0.0064
4/F^-	0.0109	0.0085

wt (%) – weight of water/weight of solution in %; v/v (%) – volume of water/volume of solution in %

Conclusion

This paper investigated the mechanism, sensitivity and effect of substituent on water sensing of four two-component coumarin phenylsemicarbazone/fluoride water chemosensors **1**-**4/**F^-. Addition of water transforms the coumarin phenylsemicarbazone enolate form to less conjugated keto form and results in naked-eye orange-yellow colour change and simultaneous fluorescence increase in polar aprotic solvents. Polar protic solvents compete with water as base in acid-base enolate/keto (hydrazonolate/hydrazide) equilibrium and studied chemosensors therefore cannot be used for low-level water content determination in these solvents. Determined detection and quantification limits for water are amongst the lowest published detection limits water in MeCN and quite reasonably correlate with apparent association constants between coumarin phenylsemicarbazones and fluoride anion.

Experimental Section

Synthesis

Synthesis of acceptor coumarin phenylsemicarbazones **1**-**3** was published by Cigáň *et al.*, 2014.[50] For data on the synthesis and characterization of donor coumarin phenylsemicarbazone **4**, please see ESI Synthesis†.

Spectroscopic measurements

Electronic absorption spectra were obtained on a HP 8452A diode array spectrophotometer (Hewlett Packard, USA). Used solvents (MeCN, DMSO, DMF) were HPLC (MeCN; LiChrosolv®, Merck, Germany) or UV-spectroscopy grade (DMSO and DMF; Uvasol®, Merck, Germany) and were used without further purification. Solution fluorescence was measured in a 1 cm cuvette with a FSP 920 (Edinburgh Instruments, UK) spectrofluorimeter in a right-angle or front/face arrangement (to exclude solution self-absorption). The fluorescent quantum yield (Φ_F) of studied compounds in DMSO and MeCN was determined by equations (1) and (2) using integrating sphere (Edinburgh Instruments):

$$\Phi_{\mathrm{F}}^{X} = \frac{L_{\mathrm{Sam}}}{E_{\mathrm{Ref}} - E_{\mathrm{Sam}}}\,(\%) \qquad (1)$$

corrected to re-absorption by:

$$\Phi_{\mathrm{F}} = \frac{\Phi_{\mathrm{F}}^{X}}{1 - a + a\,\Phi_{\mathrm{F}}^{X}/100}\,(\%) \qquad (2)$$

where L_{Sam} is the area under the detected spectrum in the part of the spectrum where sample emission occurs, E_{Ref} is area under the reflection part of the detected spectrum using pure solvent as reference material (diffuse reflectance), E_{Sam} is area under the reflection part of the detected spectrum after absorption by sample and a is reabsorbed area. The time-resolved fluorescence measurements were performed on a FSP 920 (Edinburgh Instruments, UK) spectrofluorimeter with a time-correlated single-photon counting (TCSPC) module and a red sensitive high speed photomultiplier in peltier housing, featuring Hamamatsu H5773-04 detector (R928P detector; Edinburgh Photonics, UK). Excitation source was 402.8 nm picosecond pulsed diode laser (Model EPL-405; Pulse Width: 60.5 ps; Edinburgh Photonics, UK). Reconvolution fit analysis software (F900, Edinburgh Instruments) was used for lifetime data analysis.

Titration experiments

Materials

All four F^-, CH_3COO^-, $H_2PO_4^-$ and Cl^- anions in titration experiments were added in the form of tetrabutylammonium (TBA^+) salts purchased from Sigma-Aldrich (USA), and used without further purification. Distilled water was used in all H_2O titration experiments.

General method

All titration experiments were carried out in MeCN (or in DMSO, DMF) at 298.16 K. The coumarin phenylsemicarbazone solutions were titrated with the corresponding anion solutions to obtain 3×10^{-5} mol.dm^{-3} overall coumarin phenylsemicarbazone concentration of the resultant solution. The titration process in 1×10^{-5} mol.dm^{-3} to 1×10^{-2} mol.dm^{-3} anion concentration range was monitored by UV-Vis and fluorescence spectroscopy (in a 1 cm cuvette).

Detection and quantification limits

Detection limit ($3\sigma/S$) and quantification limit ($10\sigma/S$) for water using studied two-component chemosensors were determined by the following equations:

$$3\sigma/\mathrm{S} = 3\frac{\sqrt{\dfrac{\sum (F-\bar{F})^2}{\mathrm{n}-1}}}{\mathrm{S}}; \qquad (4)$$

$$10\sigma/\mathrm{S} = 10\frac{\sqrt{\dfrac{\sum (F-\bar{F})^2}{\mathrm{n}-1}}}{\mathrm{S}}, \qquad (5)$$

where: σ is the standard deviation, F is the area under the fluorescence emission curve of coumarin phenylsemicarbazone and S is the slope of the $F = f$(wt%) or $F = f$(v/v%) plot in the initial linear portion of the curve; in all cases n = 10.

Quantum-chemical calculations

The Gibbs free energy of coumarinphenylsemicarbazone conformers were investigated using quantum-chemical calculations at the M06-2x/6-311++G(dp) level of theory. Stationary points were characterized as minima by computation of harmonic vibrational frequencies. All calculations were performed by Gaussian 09 program package.[56]

NMR spectroscopy

NMR experiments were recorded on Varian VNMRS 600MHz spectrometer in 5mm NMR tube.

Acknowledgements

This contribution is the result of the project implementation (ITMS 26240220086), supported by ERDF funded OPRaD.

Notes and references

1 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515-1566, DOI: 10.1021/cr960386p.
2 M. M. F. Choi and O. L. Tse, *Anal. Chim. Acta*, 1999, **378**, 127-134, DOI:10.1016/S0003-2670(98)00614-X.
3 D. Citterio, K. Minamihashi, Y. Kuniyoshi, H. Hisamoto, S. Sasaki and K. Suzuki, *Anal. Chem.,* 2001, **73**, 5339-5345, DOI: 10.1021/ac010535q.
4 C.-G. Niu, A.-L. Guan, G.-M. Zeng, Y.-G. Liu and Z.-W. Li, *Anal. Chim. Acta*, 2006, **577**, 264–270, DOI: 10.1016/j.aca.2006.06.046.
5 A. P. de Silva, T. S. Moody and G. D. Wright, *Analyst*, 2009, **134**, 2385-2393, DOI: 10.1039/B912527M.
6 F. Gao, F. Luo, X. Chen, W. Yao, J. Yin, Z. Yao and L. Wang, *Microchim. Acta*, 2009, **166**, 163-167, DOI: 10.1007/s00604-009-0180-0.
7 C. Niu, L. Li, P. Qin, G. Zeng and Y. Zhang, *Anal. Sci.*, 2010, **26**, 671-674, DOI: 10.2116/analsci.26.671.
8 V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189-227, DOI: 10.1039/B905604C.
9 X. Chen, Y. Zhou, X. Peng and J. Yoon, *Chem. Soc. Rev.*, 2010, **39**, 2120-2135, DOI: 10.1039/B925092A.
10 Y.-H. Kim, Y. K. Han and J. Kang, *Bull. Korean Chem. Soc.*, 2011, **32**, 4244-4246, DOI: 10.5012/bkcs.2011.32.12.4244.
11 J. Wu, W. Liu, J. Ge, H. Zhang and P. Wang, *Chem. Soc. Rev.*, 2011, **40**, 3483-3495, DOI: 10.1039/C0CS00224K.
12 S. Karuppannan and J.-C. Chambron, *Chem. Asian J.*, 2011, **6**, 964-984, DOI: 10.1002/asia.201000724.
13 Q. Deng, Y. Li, J. Wu, Y. Liu, G. Fang, S. Wang and Y. Zhang, *Chem. Commun.*, 2012, **48**, 3009-3011, DOI: 10.1039/C2CC17856G.
14 J. Zhao, S. Ji, Y. Chen, H. Guo and P. Yang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8803-8817, DOI: 10.1039/C2CP23144A.
15 Y. H. Kim, M. G. Choi, H. G. Im, S. Ahn, I. W. Shim and. S. K. Chang, *Dyes Pigm.*, 2012, **92**, 1199-1203, DOI:10.1016/j.dyepig.2011.07.019.
16 K. Zhao, T. Liu, G. Wang, X. Chang, D. Xue, K. D. Belfield and Y. Fang, *J. Phys. Chem. B*, 2013, **117**, 5659-5667, DOI: 10.1021/jp312318b.
17 K.-H. Kim, W.-J. Lee, J. N. Kim, and H. J. Kim, *Bull. Korean Chem. Soc.*, 2013, **34**, 2261-2266, DOI: 10.5012/bkcs.2013.34.8.2261.
18 W. Chen, Z. Zhang, X. Li, H. Ågren and J. Su, *RSC Adv.*, 2015, **5**, 12191-12201, DOI: 10.1039/c4ra15199b.
19 D. Huang, Y. Bing, H., W. Hong, C. Lai, Q. Guo and C. Niu, *Anal. Methods*, 2015, **7**, 4621-4628, DOI: 10.1039/c5ay00110b.
20 M. H. Lee, J. S. Kim and J. L. Sessler, *Chem. Soc. Rev.*, 2015, **44**, 4185-4194, DOI: 10.1039/C4CS00280F.
21 P. Shen, M. Li, C. Liu, W. Yang, S. Liu and C. Yang, *J. Fluoresc.*, 2016, **26**, 363-369, DOI: 10.1007/s10895-015-1722-y.
22 H. S. Jung, P. Verwilst, W. Y. Kim and J. S. Kim, *Chem Soc. Rev.*, 2016, **45**, 1242-1256, DOI: 10.1039/C5CS00494B.
23 G. Jones, W. R. Jackson, S. Kanoktanaporn and A. M. Halpern, *Opt. Commun.*, 1980, **33**, 315-320, DOI: 10.1016/0030-4018(80)90252-7.
24 G. Jones, W. R. Jackson, C. Choi and W. R. Bergmark, *J. Phys. Chem.,* 1985, **89**, 294-300, DOI: 10.1021/j100248a024.
25 A. Nag and K. Bhattacharyya, *Chem. Phys. Lett.,* 1990, **169**, 12-16, DOI: 10.1016/0009-2614(90)85156-7.
26 M. S. A. Abdel-Mottaleb, M. S. Antonious, M. M. A. Ali, L. F. M. Ismail, B. A. El-Sayed and A. M. K. Aherief, *Proc. Indian Acad. Sci.*, 1992, **104**, 185-196, DOI: 10.1007/BF02863363.
27 R. B. Bangar and T. S. Varandajaran, *J. Phys. Chem.*, 1994, **98**, 8903–8905, DOI: 10.1021/j100087a014.
28 S. Nad and H. Pal, *J. Phys. Chem. A*, 2001, 105, 1097-1106, DOI: 10.1021/jp003157m.
29 R. Królicki, W. Jarzęba, M. Mostafavi and I. Lampre, *J. Phys. Chem. A*, 2002, **106**, 1708-1713, DOI: 10.1021/jp013916g.
30 S. Nad, M. Kumbhakar and H. Pal, *J. Phys. Chem. A*, 2003, **107**, 4808-4816, DOI: 10.1021/jp021543t.
31 P. Dahiya, M. Kumbhakar, T. Mukherjee and H. Pal, *Chem. Phys. Lett.*, 2005, **414**, 148-154, DOI: 10.1016/j.cplett.2005.08.051.
32 A. K. Satpati, S. Senthilkumar, M. Kumbhakar, S. Nath, D. K. Maity and H. Pal, *Photochem. Photobiol.*, 2005, **81**, 270-278, DOI: 10.1111/j.1751-1097.2005.tb00184.x.
33 U. S. Raikar, C. G. Renuka, Y. F. Nadaf, B. G. Mulimani, A. M. Karguppikar and M. K. Soudagar, *Spectrochim. Acta Part A*, 2006, **65**, 673-677, DOI: 10.1016/j.saa.2005.12.028.
34 A. S. Satpati, M. Kumbhakar, S. Nath and H. Pal, *Photochem. Photobiol.*, 2009, **85**, 119-129, DOI: 10.1111/j.1751-1097.2008.00405.x.
35 B. D. Wagner, *Molecules*, 2009, **14**, 210-237, DOI: 10.3390/molecules14010210.
36 P. Verma and H. Pal, *J. Phys. Chem. A*, 2012, **116**, 4473-4484, DOI: 10.1021/jp210433f.
37 J. Donovalová, M. Cigáň, H. Stankovičová, J. Gašpar, M. Danko, A. Gaplovský and P. Hrdlovič, *Molecules*, 2012, **17**, 3259–3276, DOI: 10.3390/molecules17033259.
38 A. Chatterjee, B. Maity and D. Seth, *Phys. Chem. Chem. Phys.*, 2013, **15**, 1894-1906, DOI: 10.1039/C2CP43483K.
39 H. Li, L. Cai and Z. Chen, Coumarin-Derived Fluorescent Chemosensors. Advances in Chemical Sensors, Prof. Wen Wang (Ed.), ISBN: 978-953-307-792-5, InTech, 2012. Available from: http://www.intechopen.com/books/advances-in-chemical-sensors/coumarin-derived-fluorescent-chemosensors
40 A. P. de Silva, H. Q. N. Gunaratante, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515-1566, DOI: 10.1021/cr960386p.
41 J. Wu, W. Liu, J. Ge, H. Zhang and P. Wang, *Chem. Soc. Rev.*, 2011, **40**, 3483-3495, DOI: 10.1039/C0CS00224K.
42 S. Park and H.-J. Kim, *Sensor Actuat. B-Chem.,* 2012, **161**, 317-321, DOI: 10.1016/j.snb.2011.10.038.
43 H. Kwon, K. Lee and H.-J. Kim, *Chem. Commun.*, 2011, **47**, 1773-1775, DOI: 10.1039/C0CC04092D.
44 T.-K. Kim, D.-N. Lee and H.-J. Kim, *Tetrahedron Lett.*, 2008, **49**, 4879-4881, DOI: 10.1016/j.tetlet.2008.06.003.
45 G.-J. Kim and H.-J. Kim, *Tetrahedron Lett.*, 2010, **51**, 4670-4672, DOI: 10.1016/j.tetlet.2010.07.003.
46 J. Li, C.-F. Zhang, S.-H. Yang, W.-C. Yang and G.-F. Yang, *Anal. Chem.*, 2014, **86**, 3037-3042, DOI: 10.1021/ac403885n.
47 L. He, Q. Xu, Y. Liu, H. Wei, Y. Tang and W. Lin, *ACS Appl. Mater. Interfaces*, 2015, **7**, 12809-12813, DOI: 10.1021/acsami.5b01934.
48 G. He, J. Li, L. Yang, C. Hou, T. Ni, Z. Yang, X. Qian and C. Li, PLoS ONE, 2016, **11**, e0148026. DOI:10.1371/journal.pone.0148026.

49 M. Cigáň, J. Donovalová, V. Szöcs, J. Gašpar, K. Jakusová and A. Gaplovský, *J. Phys. Chem. A*, 2013, **117**, 4870-4883, DOI: 10.1021/jp402627a.

50 M. Cigáň, M. Danko, J. Donovalová, J. Gašpar, H. Stankovičová, A. Gaplovský and P. Hrdlovič, *Spectrochim. Acta Part A*, 2014, **126**, 36-45, DOI: 10.1016/j.saa.2014.01.127.

51 W. Y. Kim, H. Shi, H. S. Jung, D. Cho, P. Verwilst, J. Y. Lee and J. S. Kim, *Chem. Comm.*, 2016, **52**, 8675-8678. DOI: 10.1039/C6CC04285F.

52 P. A. Gale, N. Busschaert, C. J. E.Haynes, L. E. Karagiannidis and I. L. Kirby, *Chem. Soc. Rev.*, 2014, **43**, 205-241. DOI: 10.1039/C3CS60316D.

53 J. O. Moon, Y. H. Kim, M. G. Choi and S.-K. Chang, *Bull. Korean Chem. Soc.*, 2011, **32**, 3517-3520, DOI: 10.5012/bkcs.2011.32.9.3517.

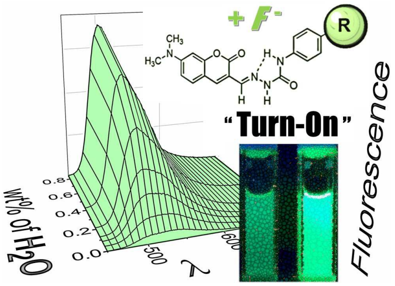
54 L. Song, Y.-W. Wu, W.-X. Chai, Y.-S. Tao, C. Jiang and Q.-H. Wang, *Eur. J. Inorg. Chem.*, 2015, 2264-2271, DOI: 10.1002/ejic.201500062.

55 M. Cigáň, K. Jakusová, J. Donovalová, V. Szöcs and A. Gáplovský, *RSC Adv.*, 2014, **4**, 54072-54079, DOI: 10.1039/c4ra04847d.

56 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision A.1, Gaussian, Inc., Wallingford CT, 2009.

Coumarin phenylsemicarbazones: Sensitive colorimetric and fluorescent “turn-on” chemosensors for low-level water content in aprotic organic solvents

Marek Cigáň, Jan Gašpar, Katarína Gáplovská, Jana Holekšiová, Klaudia Jakusová, Jana Donovalová, Vladimír Garaj and Henrieta Stankovičová



Highly-sensitive two-component colorimetric and fluorescent “turn-on” coumarin phenysemicarbazone/anion chemosensors for water detection in aprotic organic solvents: Reversible keto/enolate equilibrium