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Hybrid sensor materials based on tin(IV) oxide and crown-containing 4-amino-1,8-naphthalimides

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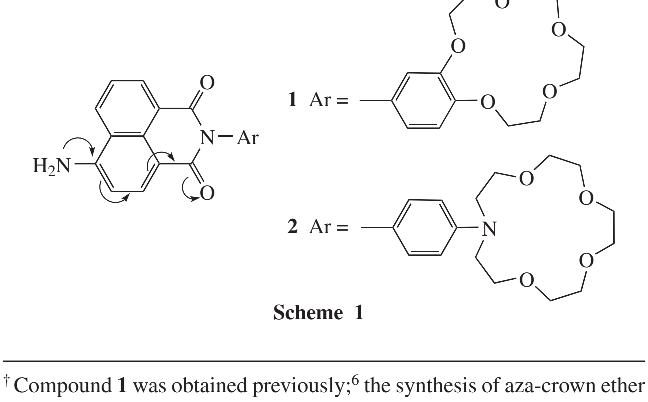
The cation-dependent spectral properties of crown-containing 4-aminonaphthalimide derivatives have been studied in an acetonitrile solution and within hybrid materials based on tin dioxide; these compounds can be of interest for producing fluorescent sensors for metal ions.

The rapid development of nanotechnologies and supramolecular chemistry has led to the creation of hybrid organo-inorganic materials.[1,2] This type of materials is of interest not only for fundamental studies but also for the development of principally new devices because a combination of organic and inorganic compounds expands the functional capabilities of these devices.[3]

Hybrid organo-inorganic materials play an important role in the detection of metal cations in solutions. The operating principle of such materials is based on combining a synthetic receptor (a fluorophore functionalised by an ionophore) and a semiconductor oxide that serves as the support. The binding of cations changes the ability of a fluorophore to undergo photoinduced processes such as electron transfer, charge transfer or energy transfer. A semiconductor oxide modified by a fluorophore also changes its electric characteristics such as electrical conductivity and ability to generate photo-emf, which allows these materials to be integrated in automatic instruments.

The derivatives of naphthalic acid imide (1,8-naphthalimide) are efficient organic luminophores, and they often play a role of signal elements in sensor-type optical molecular devices.[4,5] Here we examined the use of 4-aminonaphthalimide derivatives **1** and **2** containing benzo-15-crown-5 and *N*-phenylaza-15-crown-5 ether substituents, respectively (Scheme 1),[†] as fluoroionophores for hybrid organo-inorganic materials based on quasi-one-dimensional single crystals of tin dioxide. First, the photophysical properties of compounds **1** and **2** were studied in acetonitrile solutions in the presence and absence of alkaline-earth metal cations.



Scheme 1

The spectral characteristics of compounds **1** and **2** and their complexes with magnesium and calcium cations are presented in Table 1.[‡] The long-wavelength band in the absorption spectra of 4-aminonaphthalimides **1** and **2** is due to charge transfer from the electron-donating amino group at the 4-position of the naphthalene ring to the carbonyl groups of the carboxyimide moiety[10] (Scheme 1). As an example, Figure 1 shows the absorption and fluorescence spectra of benzo-crown ether derivative **1**.

Table 1 indicates that the nature of the crown ether substituent does almost not affect the positions of absorption and emission

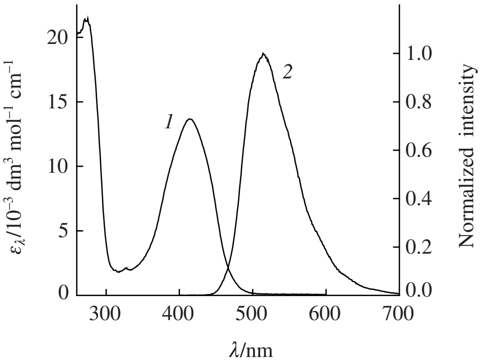


Figure 1 (*1*) Absorption and (*2*) fluorescence spectra of compound **1** in acetonitrile.

[†] Compound **1** was obtained previously;[6] the synthesis of aza-crown ether naphthalimide derivative **2** will be published elsewhere.

[‡] Spectroscopic studies were performed using acetonitrile for spectrophotometry (Aldrich). Absorption spectra were measured with a Varian-Cary two-channel spectrophotometer. Fluorescence spectra were recorded using a FluoroMax-3 spectrofluorimeter. The observed fluorescence was detected at right angle relative to the excitation beam. All measured fluorescence spectra were corrected for the nonuniformity of detector spectral sensitivity. Fluorescence quantum yields were determined in air-saturated solutions at 20 ± 1°C with respect to the following standards: quinine sulfate in 1 N sulfuric acid ($\varphi^{\rm fl} = 0.55$)[7] and Rhodamine 6G in ethanol ($\varphi^{\rm fl} = 0.95$).[8] The quantum yields were calculated using the equation[9]

$$\varphi_i^{\rm fl} = \varphi_0^{\rm fl}\frac{(1-10^{-D_0})S_i n_0^2}{(1-10^{-D_i})S_0 n_i^2},$$

where $\varphi_i^{\rm fl}$ and $\varphi_0^{\rm fl}$ are the quantum yields of the test solution and the standard; D_i and D_0 are the absorptions of the test solution and the standard, S_i and S_0 are areas underneath the fluorescence spectrum curves for the test solution and the standard, n_i and n_0 are refraction factors of solvents of the test compound and the standard compound, respectively.

Table 1 Absorption and emission maxima, fluorescence quantum yields and stability constants of compounds **1**, **2** and complexes [**1**]·Mg^{2+}, [**2**]·Ca^{2+} in acetonitrile at 293 K.

Compound	λ^{abs}_{max}/nm (lg ε_λ)	λ^{fl}_{max}/nm	φ^{fl}	lg *K*
1	414 (4.14)	519	0.43	—
[**1**]·Mg^{2+}	417 (4.15)	521	0.59	not determined
2	415 (4.17)	518	0.0024	—
[**2**]·Ca^{2+}	420 (4.16)	520	0.43	4.94 ± 0.02

bands, but it affects considerably the fluorescence quantum yield. Compound **1** demonstrates intense fluorescence, whereas the fluorescence quantum yield of aza-crown ether derivative **2** is a few thousandth.

As noted previously,[6,11] the presence of electron-donating alkoxy or dialkylamino substituents at the *N*-aryl ring results in fluorescence quenching of the naphthalimide chromophore. This effect can be explained by the existence of a nonradiative process related to electron transfer from the *N*-aryl substituent to the naphthalimide residue, which competes with fluorescence. The lower quantum yield of compound **2** is most likely related to the higher electron-donating properties of the nitrogen atom in the aza-crown ether ring in comparison with the oxygen atoms of the crown ether in compound **1**, which are in conjugation with the benzene ring.

The complexation of compounds **1** and **2** with magnesium and calcium cations resulting in a decrease in the electron-donating properties of the oxygen and nitrogen atoms bound to the benzene ring was accompanied by a fluorescence enhancement. These cations were selected because they can form stable complexes of 1:1 stoichiometry upon coordination with 15-crown-5 and aza-15-crown-5. Figure 2 shows changes in the fluorescence spectra of crown-containing derivatives **1** and **2** that occurred upon gradual addition of magnesium perchlorate or calcium perchlorate to their solutions in acetonitrile. As can be seen, spectral changes were most significant in the case of aza-crown derivative **2**.

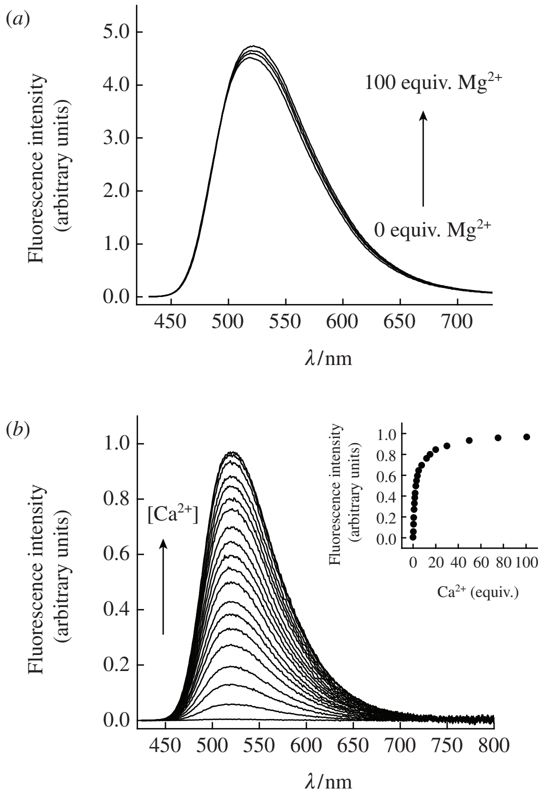
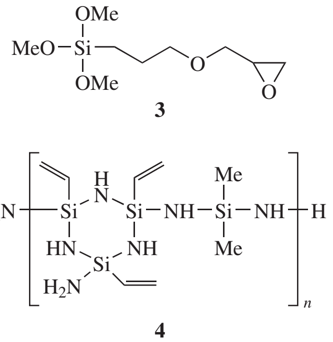


Figure 2 Spectrofluorimetric titration of (*a*) compound **1** with magnesium perchlorate and (*b*) compound **2** with calcium perchlorate in acetonitrile. (*a*) $C_L = 1.3\times10^{-5}$ mol dm^{-3}, $\lambda_{excit} = 365$ nm; (*b*) $C_L = 5.0\times10^{-6}$ mol dm^{-3}, $\lambda_{excit} = 420$ nm; the insert shows the dependence of fluorescence intensity at the maximum on the number of Ca^{2+} equivalents added.

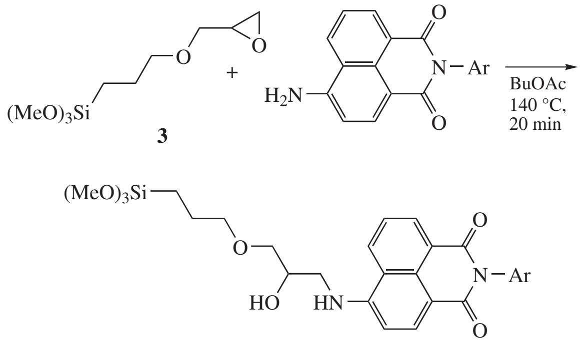
Based on spectrofluorimetric titration data for azacrown derivative **2**, the stability constant of the resulting 1:1 complex was determined (Table 1).[§] In the case of benzocrown-containing naphthalimide **1**, the constant cannot be calculated because of very small changes in the absorption and fluorescence spectra upon complex formation. As reported previously,[11] the stability constant for *N*-acetylamino-substituted analogue of **1** is $\log K = 5.33 \pm 0.02$. Apparently, the value of log *K* for compound **1** will differ only slightly from the above value since changes in the electronic structure of the naphthalimide moiety due to the replacement of an amino group by an acetylamino group should not affect considerably the ionophoric *N*-aryl moiety.

Hybrid sensor materials were obtained using SnO_2 single crystal belts a few micrometers thick (whiskers) that were grown from a gas phase and characterised by IR spectroscopy and X-ray diffraction.[12] To obtain a uniform surface coating on the semiconductor oxide and ensure the maximum bonding of fluorophore molecules to it, organosilicon compounds (3-glycidyloxypropyltrimethoxysilane **3** and polyvinyldimethylsilazane **4**) were used as linkers (Scheme 2).



Scheme 2

The technique of fluorophore immobilization on SnO_2 surfaces involved the following steps. First, a covalent bond was formed between the fluorophore and linker **3** by heating the components in a butyl acetate or toluene solution (Scheme 3). Tin dioxide whiskers previously mounted on the edges of a glass plate were immersed in the resulting solution and then dried in air. To obtain a uniform coating, this operation was repeated several times.



Scheme 3

Afterwards, the plate with the whiskers was dried for 1.5 h at 100 °C. At this step, the linkers were bound to the SnO_2 surface *via* the OH groups located on it (Scheme 4). Note that the addi-

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[§] The stability constant of the complex [**2**]·Ca^{2+} was determined according to the general procedure used previously for benzocrown-containing naphthalimide derivatives.[11]

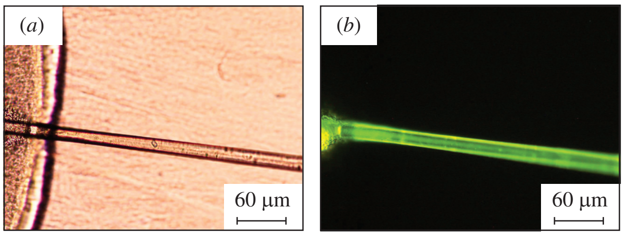
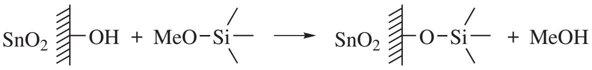


Figure 3 Micrographs of band-shaped SnO_2 crystals: (*a*) clean specimen (optical micrograph); (*b*) specimen coated with a polymeric organosilicon film containing functionalized fluorophore **1** (fluorescent micrograph).

tion of silazane **4** to the working solution favoured the formation of a cross-linked polymeric coating and improved the binding quality of the fluorophore with the surface.



Scheme 4

The materials obtained by this procedure were analysed using a Nikon Digital Eclipse C1 laser scanning confocal microscope connected to an Avantes 2040 fibre-optic spectrofluorimeter. Figure 3 exhibits the micrographs of SnO_2 whiskers modified by benzocrown-containing derivative **1**.

The treatment of surfaces of the hybrid materials modified by fluorophores **1** and **2** with a 0.1 M solution of magnesium or calcium perchlorate in acetonitrile was accompanied by a fluorescence enhancement (Figures 4 and 5). The subsequent water treatment of the surface led to the cation wash-out from the crown ether cavity resulting in a fluorescence intensity decrease to the original level [Figure 4(*c*)].

Thus, we found that crown-containing naphthalimide derivatives **1** and **2** are fluorescent sensors for metal cations in acetonitrile solutions and in composite hybrid materials. The covalent binding of fluorophores to the surface of single crystal SnO_2 whiskers does not result in a loss of their sensor properties. Since the interaction of metal ions with the crown ether moiety is reversible, the materials can be used for creation of sensitive optical sensors selective for Mg^{2+} and Ca^{2+} cations.

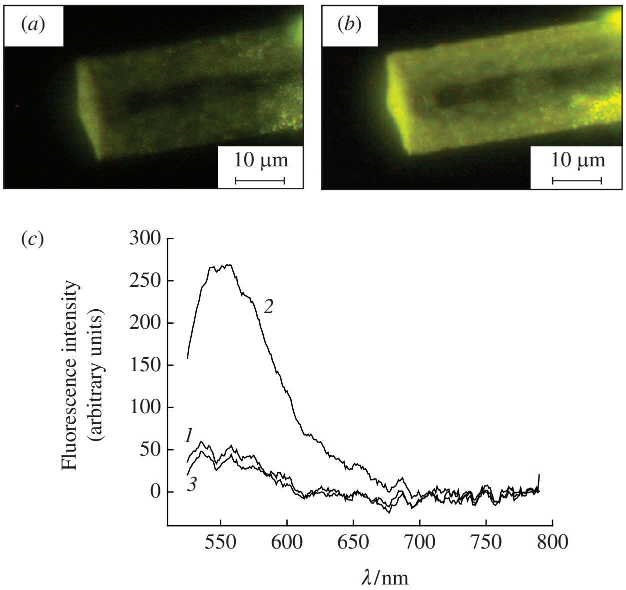


Figure 4 Sensor properties of single crystal SnO_2 whiskers modified by fluorophore **1**. Fluorescent micrographs of the hybrid material (*a*) before and (*b*) after treatment with a 0.1 M solution of $Mg(ClO_4)_2$ in acetonitrile. (*c*) Fluorescence spectra of the specimen surface: (*1*) original specimen and (*2*), (*3*) specimens treated with 0.1 M solution of $Mg(ClO_4)_2$ in acetonitrile and then with water.

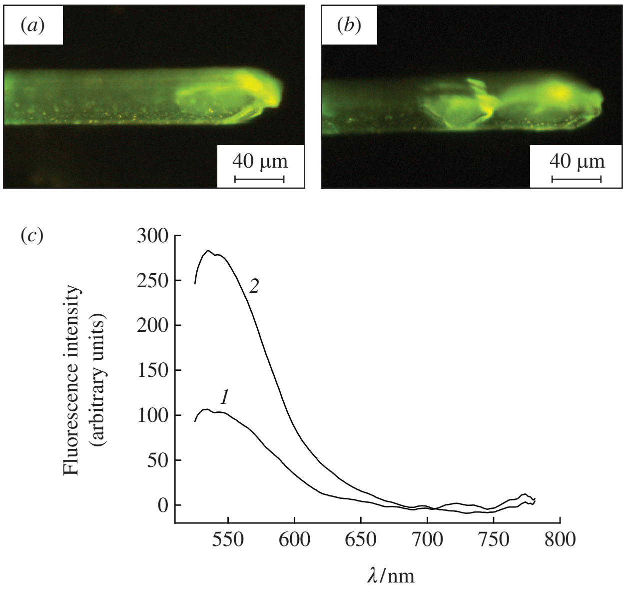


Figure 5 Sensor properties of single crystal whiskers of SnO_2 modified by fluorophore **2**. Fluorescent micrographs of the hybrid material (*a*) before and (*b*) after treatment with 0.1 M solution of $Ca(ClO_4)_2$ in acetonitrile. (*c*) Fluorescence spectra of the specimen surface: (*1*) original specimen and (*2*) specimen treated with 0.1 M solution of $Ca(ClO_4)_2$ in acetonitrile.

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References

1 E. Bescher and J. D. Mackenzie, *Mat. Sci. Eng. C*, 1998, **6**, 145.
2 A. B. Descalzo, R. Martínez-Máñez, F. Sancenón, K. Hoffmann and K. Rurack, *Angew. Chem. Int. Ed.*, 2006, **45**, 5924.
3 C. Sanchez, B. Julián, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559.
4 J. Gan, K. Chen, C.-P. Chang and H. Tian, *Dyes Pigm.*, 2003, **57**, 21.
5 K. Rurack, U. Resch-Genger, J. L. Bricks and M. Spieles, *Chem. Commun.*, 2000, 2103.
6 P. A. Panchenko, Yu. V. Fedorov, O. A. Fedorova, V. P. Perevalov and G. Jonusauskas, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 1199 (*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1233).
7 J. N. Demas, *Optical Radiation Measurements. Measurement of Photon Yields*, Academic Press, Virginia, 1982, vol. 3.
8 J. R. Lakowicz, *Principles of Fluorescent Spectroscopy*, Kluwer Academic, Plenum Publishers, New York, 1999, p. 53.
9 C.L. Renschler and L.A. Harrah, *Anal. Chem.*, 1983, **55**, 798.
10 B. M. Krasovitsky and B. M. Bolotin, *Organicheskie lyuminofory* (*Organic Luminophors*), Khimiya, Moscow, 1984 (in Russian).
11 P. A. Panchenko, Yu. V. Fedorov, V. P. Perevalov, G. Jonusauskas and O. A. Fedorova, *J. Phys. Chem. A*, 2010, **114**, 4118.
12 M. N. Rumyantseva, A. A. Zhukova, F. M. Spiridonov and A. M. Gas'kov, *Neorg. Mater.*, 2007, **43**, 1076 [*Inorg. Mater.* (*Engl. Transl.*), 2007, **43**, 964].

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