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Paper
Статья

Synthesis, Optical Characteristics and Complex Formation of Molecular Receptors Based on 1,8−Naphthalimide Derivatives in Solution and in Composition of Hybrid Tin Dioxide Nanoparticles

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In the present work the synthesis of N-alkyl- and N-phenyl-1,8-naphthalimides containing dithiacrown ether, carboxyl group or both of these substituents has been developed. Molecular receptor 4-methoxy-N-benzodithiacrown-1,8-naphthalimide was synthesized from anhydride of 4-nitro-1,8-naphthalene dicarboxylic acid by acylation of crown-containing aniline and the replacement of nitro group onto methoxy one. Carboxylic derivatives of 1,8-naphthalimide with or without thiacrown ether moiety were prepared and the method of their covalent attachment to the SnO_2 surface has been proposed. Molecular receptor 4-methoxy-N-benzodithiacrown-1,8-naphthalimide demonstrates selectivity towards Hg^{2+} and Pb^{2+} cations in acetonintrile solution and towards Hg^{2+} in aqueous media. Due to its structure this receptor shows low fluorescence intensity in the free state and substantial increase of fluorescence in the presence of Hg^{2+} and Pb^{2+} is observed. This phenomenon is explained by the fact that an efficient photoinduced electron transfer takes place between fluorophore and receptor parts of the molecule in the absence of metal ions, resulting in fluorescence quenching. Electron transfer process is blocked in the presence of metal ions because the lone pair of electrons originally involved in the electron transfer process is engaged in metal ion binding. As a result the fluorescence enhancement is observed upon complexation with metal ions. 1,8-Naphthalimide derivatives in the composition of hybrid SnO_2 sol demonstrate optical characteristics similar to those of molecular fluorophores. However, the binding of metal ions by hybrid nanoreceptor was not observed. It should be due to effective interaction of crown-containing molecule with SnO_2 surface.

Keywords: 1,8-Naphthalimide, dithiacrown ether, tin dioxide, complex formation, fluorescence, nanoparticle.

Синтез, оптические свойства и комплексообразование молекулярных рецепторов на основе производных 1,8−нафталимида в растворе и в составе гибридных наночастиц диоксида олова

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В настоящем исследовании синтезированы производные 1,8-нафталимида, содержащие в качестве заместителей дитиакраун-эфир фрагмент и карбоксильные группы. Наличие карбоксильных групп позволило осуществить пришивку нафталимида на поверхность наночастиц диоксида олова. Изучено комплексообразование краун-содержащих молекулярных 1,8-нафталимидов в растворе и в составе наночастиц.

Ключевые слова: 1,8-Нафталимид, тиакраун-эфир, диоксид олова, комплексообразование, флуоресценция, наночастицы.

Introduction

Determination of metal cations and hydrogen ions in the environment and biological systems is a major technical challenge for industry, medicine, ecology, as well as for chemical and biochemical research. Among the large arsenal of modern physical and chemical methods of analysis the optical spectroscopy has huge popularity,[1] which is primarily due to the relative simplicity of the experiment coupled with a high sensitivity with respect to detectable substrates. In the past two decades, much progress has been achieved due to the development of optical chemosensors containing a selective receptor, and a signaling moiety capable of changing its spectral characteristics as a result of complex formation.[2]

The functionalization of nanostructured solids with specific groups to enhance active functions, such as the recognition of guests or to switch surface properties, is particularly interesting. Such materials with a high and readily accessible specific surface can amplify certain functional chemical processes. The step from a one-dimensional molecule to a two-dimensional arrangement – the hetero-supramolecular ensemble – leads to unique properties which are not simply an extrapolation of the solution conduct to the surface. Hybrid semiconductor organic-inorganic materials are promising for the creation of sensor materials. They combine the inorganic semiconductor basis providing an electrical detection of the analyte and the organic modifier responsible for chemical reaction with the analyte.[3] A critical step is the rational choice and preparation of the sensing material, because most of the important properties of a sensor, such as, for example, sensitivity and selectivity, strongly depend on the characteristics of the sensing material. For this reason a large effort has been done from one side to prepare materials having promising characteristics for sensor applications and from the other side to understand their sensing mechanisms, with the aim to improve their sensing performances, in terms of stability, selectivity, sensitivity.

Following this idea, the aim of the work presented here is to study the possibility to develop hybrid materials composed by SnO_2 and di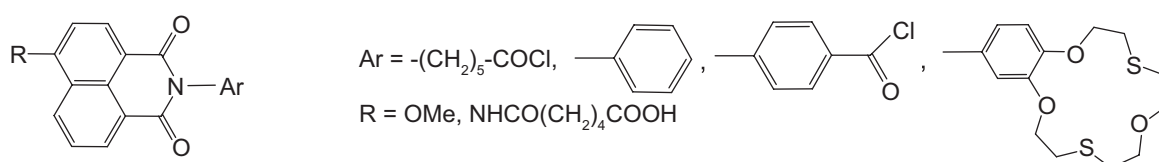thiacrown ether containing 1,8-naph-thalimides (Scheme 1). Nanoscale particles of tin dioxide are of great scientific and practical interest. Such characteristics as transparency, semiconducting properties and relatively low cost, provide the application of the tin dioxide as components of optoelectronic devices and materials. Thus, the tin dioxide is widely used as an electrode material in solar cells, component of light-emitting diodes, liquid crystal displays, transistors and so-called "smart windows" as well as an active material in gas sensor equipment.[4]

One of the most popular platforms for the creating of optical molecular sensor device is the imide of naphthalic acid (1,8-naphthalimide). Derivatives of 1,8-naphthalimide are an important class of organic luminophores, which are widely used as optical brighteners,[5] laser dyes,[6] solar cells elements,[7] fluorescent markers in biology,[8] electroluminescent materials,[9] anticancer drugs,[10] fluoroscent crack detection reagents.[11] The 1,8-naphthalimide derivatives demonstrate a large variety of photophysical properties and can act as the photoactive components of the optical chemosensors. Furthermore, the 1,8-naphthalimide derivatives containing dithiacrown ether moieties are capable of binding with heavy and transition metals cations in organic solvents and in aqueous medium.[12]

Previously we have carried out the attachment of crown ether containing 1,8-naphthalimides to the surface of SnO_2 through the silicon-organic linker.[13] The obtained hybrid material showed a fluorescence enhancement upon the binding with magnesium cations. In the present paper the attachment of 1,8-naphthalimide derivatives to the surface of SnO_2 nanoparticles have been done by applying of carboxylic group or chloro anhydride groups incorporated in the *N*-imide fragment of studied compounds (Scheme 1) and superficial OH groups of tin dioxide. In literature there are only a few examples of the organic-inorganic material composed by SnO_2.[13-15]

Experimental

NMR spectra were recorded on a Bruker Avance 300, 400 and 600 MHz instruments operating at 300.13, 400.13, 600.22 MHz (for ^{1}H) and 75.47, 100.61, 150.93 MHz (for ^{13}C) respectively.

Ar = -$(CH_2)_5$-COCl, R = OMe, NHCO$(CH_2)_4$COOH

Scheme 1.

Molecular Receptors Based on 1,8-Naphthalimide Derivatives

The measurements were performed in CD_3COCD_3, CD_3SOCD_3 and CD_3CN; δ values are given in ppm, coupling constants are presented in Hz. The chemical shifts were determined with an accuracy of 0.01 ppm relative to the signals corresponding to the residual solvent and recalculated to the internal standard (TMS); the spin–spin coupling constants (J) were measured with an accuracy of 0.1 Hz. The assignment of ^{13}C signals is based on the data of two-dimensional NMR spectra (HMBC and HSQC). The numbering of carbon atoms in the naphthalimide moiety, N-aryl ring and crown ether fragment of compounds commonly used by us for the description of ^1H and ^{13}C NMR spectra is shown on Figures 3, 4.

Melting points were determined in capillaries using Meltemp instrument and were not corrected. Elemental analysis was performed in the microanalysis laboratory of A.N. Nesmeyanov Institute of Organoelement compounds of RAS. The reaction course and purity of the final products was followed by TLC on silica gel DC-Alufolien Kieselgel 60 F254 plates (Merck). Column chromatography was carried out using silica gel Kieselgel 60 (particle size 0.063–0.200 mm, Merck) and benzene-ethanol mixture as an eluent.

Mass spectra were obtained on an Agilent 1100 Series LC/MSD trap interface operated in positive-ion mode. The analyte solution was injected directly into the device. The flow rate was 400 μl/h, the drying gas temperature was 350 °C and the pressure was 10 psi. The nebulizer needle voltage was 4.5–5.5 kV. The isotope distribution was calculated using the Molecular Weight Calculator software, version 6.73.

Electronic absorption spectra were measured on a two-channel spectrophotometer Varian-Cary 100, fluorescence spectra were recorded on spectrofluorimeter FluoroLog-3-221 at 20±1 °C. The observed fluorescence was detected at a direct angle relative to the excitation beam in the case of determining the quantum yields of compounds and frontally relative to the exciting beam in the case of measuring sol fluorescence. The fluorescence spectra were corrected for the nonuniformity of detector spectral sensitivity. Spectroscopic grade solvents (Aldrich, Acros) were used for recording of the absorption and fluorescence spectra.

A study by FTIR absorption spectroscopy was performed on a spectrometer Perkin Elmer Spectrum One. The spectra were recorded in transmission mode in wavenumber range 4000–370 cm^{-1} in steps of 1 cm^{-1}. Samples (dried powders sols) weighing 5 mg were grinded with 100 mg of potassium bromide (Aldrich, «for FTIR analysis») and pressed into tablets of about 0.5 mm thick and 12 mm diameter.

General Procedure for acylation of aromatic amines by 4-substituted 1,8-naphthalic anhydride. To a suspension of 10.0 mol of 4-bromo- or 4-nitronaphthalic anhydride in 30 ml of glacial acetic acid or ethyl alcohol 10.0–20.0 mmol of the appropriate amine was added. The reaction mixture was refluxed for 6 hours, cooled to room temperature. The precipitate of N-substituted naphthalimide was filtered off, washed with 5 % hydrochloric acid, then with 10 % aqueous Na_2CO_3, water and ethanol. The product was dried at 80 °C.

6-Nitro-2-phenyl-1H-benzo[d,e]isoquinoline-1,3(2H)-dione (4-nitro-N-phenyl-naphthalimide) (1a). According to the general procedure for acylation of aromatic amines 1.2 g (91 % yield) of 4-nitro-N-phenylnaphthalimide **2a** was obtained from 1.0 g (4.1 mmol) of 4-nitronaphthalic anhydride, 0.75 ml (8.2 mmol) of aniline and 12 ml of acetic acid. M.p. 291–293 °C (lit.[16] 280–282 °C). ^1H NMR (300.13 MHz, [D_6]DMSO, 21 °C) δ ppm (J/Hz): 7.38–7.45 (m, 2H, H(10), H(14)), 7.45–7.59 (m, 3H, H(11), H(12), H(13)), 8.13 (dd, 1H, H(6), J=7.2, J=8.6), 8.59 (d, 1H, H(3), J=8.0), 8.62 (d, 1H, H(2), J=8.0), 8.65 (d, 1H, H(7), J=7.2), 8.77 (d, 1H, H(5), J=8.6). MS, m/z (I, %): 318 ([M]+) (76), 317 (100), 287 (25), 271 (42), 227 (21), 214 (8), 195 (9), 179 (11), 151 (9), 125 (9).

6-Nitro-2-(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,10,7,13] trioxadithiacyclopentadecyn-15-yl)-1H-benzo[d,e]isoquinoline-1,3(2H)-dione (1b). According to the general procedure for

acylation of aromatic amines 460 mg (yield 71 %) of 4-nitro-N-arylnaphthalimide **2b** was obtained from 300 mg (1.2 mmol) of 4-nitronaphthalic anhydride, 650 mg (1.8 mmol) of the aniline hydrochloride salt containing dithiacrown-ether, 160 mg (2.0 mmol) of sodium acetate and 10 ml of acetic acid. M.p. 228–230 °C (lit.[17] 228–230 °C). ^1H NMR (300.13 MHz, [D_6]DMSO, 23 °C) δ ppm (J/Hz): 2.85–3.11 (m, 8H, CH_2(16), CH_2(17), CH_2(20), CH_2(21)), 3.68–3.78 (m, 4H, CH_2(18), CH_2(19)), CH_2(15)), 4.22–4.30 (m, 2H, CH_2(22)), 6.95 (dd, 1H, H(14), J=2.2, J=8.6), 7.08 (d, 1H, H(10), J=2.2), 7.11 (d, 1H, H(13), J=8.6), 8.13 (dd, 1H, H(6), J=7.4, J=8.6), 8.58 (d, 1H, H(3), J=8.0), 8.62 (d, 1H, H(2), J=8.0), 8.64 (d, 1H, H(7), J=7.4), 8.76 (d, 1H, H(5), J=8.6). Found (%): C, 57.79; H, 4.46; N, 5.14; S, 11.62. $C_{26}H_{24}N_2O_7S_2$. Calculated (%): C, 57.76; H, 4.47; N, 5.18; S, 11.84.

6-Methoxy-2-phenyl-1H-benzo[d,e]isoquinoline-1,3(2H)-dione (4-methoxy-N-phenyl-naphthalimide) (2a). 4-Nitro-N-phenylnaphthalimide **1a** (50 mg, 0.16 mmol) and 32 mg (0.32 mmol) of potassium carbonate were dissolved in 4 ml of methanol. The mixture was refluxed for 6 h, then it was poured into 8 ml of water and acidified with 4 ml of acetic acid. The resulting precipitate was filtered off, washed with water and dried to yield 39 mg (80 %) of 4-methoxy-N- phenylnaphthalimide **2a**. M.p. 234–238 °C (lit.[18]: 235–239 °C). ^1H NMR (300.13 MHz, [D_6]acetone, 21 °C) δ ppm (J/Hz): 4.22 (s, 3H, OCH_3), 7.32–7.42 (m, 3H, H(11), H(12), H(13)), 7.45 (d, 1H, H(3), J=8.0), 7.48–7.56 (m, 2H, H(10), H(14)), 7.85 (dd, 1H, H(6), J=7.3, J=8.6), 8.50–8.58 (m, 2H, H(5), H(7)), 8.64 (d, 1H, H(2), J=8.0). Found (%): C, 75.19; H, 4.30; N, 4.59. $C_{19}H_{13}NO_3$. Calculated (%): C, 75.22; H, 4.32; N, 4.62.

6-Methoxy-2-(2,3,5,6,8,9,11,12-octahydrobenzo[b] [1,4,10,7,13]trioxadithiacyclopentadecyn-15-yl)-1H-benzo[d,e] isoquinoline-1,3(2H)-dione (2b). A solution containing 138 mg (2.55 mmol) of sodium methylate and 7 ml of methanol was added to a suspension of 100 mg (0.17 mmol) of 4-nitronaphthalimide **1b** in 10 ml of methanol. The reaction mixture was refluxed for 10 h and then cooled to room temperature. Methanol was removed in vacuum, 10 ml of water was added to the residue. The precipitate of 4-methoxy-N-arylnaphthalimide **2b** was filtered off, washed with water and ethanol to yield 73 mg (90 %) of **2b**. M.p. 233–235 °C. ^1H NMR (600.22 MHz, [D_6]DMSO, 20 °C) δ ppm (J/Hz): 2.84–3.11 (m, 8H, CH_2(16), CH_2(17), CH_2(20), CH_2(21)), 3.65–3.81 (m, 4H, CH_2(18), CH_2(19)), 4.06–4.14 (m, 2H, CH_2(15)), 4.16 (s, 3H, OCH_3), 4.22–4.31 (m, 2H, CH_2(22)), 6.89 (dd, 1H, H(14), J=1.8, J=8.6), 7.04 (d, 1H, H(10), J=1.8), 7.08 (d, 1H, H(13), J=8.6), 7.35 (d, 1H, H(3), J=8.2), 7.81–7.90 (m, 1H, H(6)), 8.47 (d, 1H, H(2), J=8.2), 8.52 (d, 1H, H(7), J=7.3), 8.58 (d, 1H, H(5), J=8.5). ^{13}C NMR (150.93 MHz, [D_6]DMSO, 20 °C) δ ppm: 32.30 (CH_2S), 32.40 (CH_2S), 32.73 (CH_2S), 32.75 (CH_2S), 57.02 (OCH_3), 71.64 (CH_2O), 71.69 (CH_2O), 71.95 (CH_2O), 71.97 (CH_2O), 106.88 (C(3)), 113.86 (C(13)), 115.05 (C(10)), 115.50 (C(1)), 122.01 (C(14)), 123.00 (C(8)), 123.14 (C(4a)), 127.01 (C(6)), 129.21 (C(5)), 129.97 (C(8a)), 130.02 (C(9)), 131.97 (C(7)), 133.98 (C(2)), 147.52 (C(12)), 147.99 (C(11)), 160.06 (C(4)), 163.03 (C(8b)), 163.57 (C(8c)). MS (IES), calculated, m/z: 580.19; found: 580.13 ([M+H]⁺). Found (%): C, 62.21; H, 5.78; N, 7.16. $C_{30}H_{33}N_3O_5S_2$. Calculated (%): C, 62.15; H, 5.74; N, 7.25.

6-Amino-2-phenyl-1H-benzo[d,e]isoquinoline-1,3(2H)-dione (4-amino-N-phenylnaphthalimide) (3a). To a stirred suspension of 2.30 g (7.2 mmol) of 4-nitro-N-phenylnaphthalimide **1a** in 34 ml of ethanol at 50 °C a solution of 11.24 g of $SnCl_2 \cdot 2H_2O$ in 8.0 ml of concentrated hydrochloric acid (ρ=1.18 g/ml) was added dropwise. The mixture was refluxed for 1.5 hours. The reaction mixture was poured into 50 ml of water, the precipitate was filtered off, washed with water, 1 % aqueous NaOH (to remove tin compounds), then again with water and ethanol. The product was dried at 80 °C to give 1.90 g (92 % yield) of **3a**. M.p. 310–312 °C (lit.[19]: 302–304 °C). ^1H NMR (300.13 MHz, [D_6]DMSO, 23 °C) δ ppm (J/Hz): 6.87 (d, 1H, H(3), ^3J=8.5), 7.26–7.35 (m, 2H, H(10), H(14)), 7.37–7.57 (m, 5H, H(11), H(12), H(13), NH_2), 7.63–7.72 (m, 1H, H(6)), 8.19 (d, 1H,

H(2), ^3J=8.5), 8.42 (d, 1H, H(7), ^3J=7.2), 8.66 (d, 1H, H(5), ^3J=8.5). UV-Vis (CH$_3$CN) λ_{max} nm (lg ε): 417 (4.11). MS, *m/z* (*I*, %): 289 (16), 288 ([M]$^+$) (81), 287 (100), 244 (9), 243 (29), 242 (9), 216 (6), 195 (18), 167 (6), 140 (11).

6-Amino-2-(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,10,7,13] trioxadithiacyclopentadecyn-15-yl)-1H-benzo[d,e]isoquinoline-1,3(2H)-dione (3b). To a solution of 150 mg (0.278 mmol) of 4-nitronaphthalimide **1b** in 4 ml of DMF warmed to 90 °C 1.2 ml of 100 % hydrazine hydrate was added.[20] Raney nickel catalyst prepared from 0.7 g of nickel aluminum alloy (50 weight % of Ni) was added portionwise to the reaction mass at vigorous stirring over a period of 30 min. The reaction mixture was kept at 90 °C for 1 hour, the presence of starting nitro compound was monitored by TLC (SiO$_2$ plates, eluting with PhH–EtOH, 5 : 1). After the reaction mixture was cooled to room temperature, the catalyst was filtered off, the filtrate was evaporated in vacuo. The residue was purified by column chromatography (silica gel, eluent PhH–EtOH, gradient elution) to yield 23 mg (16 %) of **3b**. M.p. 249–250 °C. ^{1}H NMR (300.13 MHz, [D$_6$]DMSO, 23 °C) δ ppm (*J*/Hz): 2.85–3.10 (m, 8H, CH$_2$(16), CH$_2$(17), CH$_2$(20), CH$_2$(21)), 3.67–3.79 (m, 4H, CH$_2$(18), CH$_2$(19)), 4.07–4.17 (m, 2H, CH$_2$(15)), 4.19–4.29 (m, 2H, CH$_2$(22)), 6.82 (dd, 1H, H(14), ^4J=2.2, ^3J=8.6), 6.86 (d, 1H, H(3), ^3J=8.4), 6.95 (d, 1H, H(10), ^4J=2.2), 7.05 (d, 1H, H(13), ^3J=8.6), 7.49 (br. s, 2H, NH$_2$), 7.63–7.72 (m, 1H, H(6)), 8.18 (d, 1H, H(2), ^3J=8.4), 8.42 (d, 1H, H(7), ^3J=7.3), 8.65 (d, 1H, H(5), ^3J=8.5). ^{13}C NMR (100.62 MHz, [D$_6$]DMSO, 27 °C) δ ppm: 30.31 (CH$_2$S), 30.40 (CH$_2$S), 30.72 (2×CH$_2$S), 70.66 (CH$_2$O), 70.69 (CH$_2$O), 70.94 (CH$_2$O), 70.98 (CH$_2$O), 107.92 (C(1)), 108.20 (C(3)), 112.95 (C(13)), 114.48 (C(10)), 119.48 (C(4a)), 121.67 (C(14)), 122.33 (C(8)), 124.03 (C(6)), 129.43 (C(9)), 129.66 (C(5)), 130.17 (C(8a)), 131.10 (C(7)), 133.99 (C(2)), 147.64 (C(12)), 148.16 (C(11)), 152.76 (C(4)), 163.29 (C(8b)), 164.15 (C(8c)). UV-Vis (CH$_3$CN) λ_{max} nm (lgε): 417 (4.13). MS (IES), calculated, *m/z* (*I*, %): 617.03 ([M+Ag]$^+$) (92), 619.02 ([M+Ag+2]$^+$) (100); found: 617.08 ([M+Ag]$^+$) (92), 618.97 ([M+Ag+2]$^+$) (100). Found (%): C, 61.32; H, 5.18; N, 5.45. C$_{26}$H$_{26}$N$_2$O$_5$S$_2$. Calculated (%): C, 61.16; H, 5.13; N, 5.49.

6-(1,3-Dioxo-2-phenyl-2,3-dihydro-1H-benzo[d,e]isoquino-lin-6-yl-amino)-6-adipic acid (4a). To a stirring suspension of 80 mg (0.28 mmol) of 4-aminonaphthalimide **3a** in 0.8 ml of pyridine at room temperature a solution of 0.19 g of monochloroanhydride of adipic acid in 0.8 ml of DMF was added dropwise. The reaction mixture was stirred for 4 hours at 40–60 °C, then the precipitate was filtered off, washed with water, 5 % hydrochloric acid, again with water and hot ethanol. The product was dried in air to yield 69 mg (60 %) of **4a**. M.p. 210–213 °C. ^{1}H NMR (400.22 MHz, [D$_6$] DMSO, 21 °C) δ ppm (*J*/Hz): 1.57–1.72 (m, 4H, CH$_2$(25,26)), 2.29 (t, 2H, CH$_2$(24), *J*=7.5), 2.61 (t, 2H, CH$_2$(23), *J*=7.5), 7.35–7.41 (m, 2H, H(10), H(14)), 7.42–7.56 (m, 3H, H(11), H(12), H(13)), 7.93 (dd, 1H, H(6), *J*=8.5, *J*=7.2), 8.33 (d, 1H, H(3), *J* = 8.3), 8.49 (d, 1H, H(2), *J*=8.3), 8.54 (d, 1H, H(7), *J*=7.2), 8.74 (d, 1H, H(5), *J*=8.5), 10.40 (br. s, 1H, NHCO), 12.10 (br. s, 1H, COOH). Found (%): C, 69.28; H, 4.79; N, 6.71. C$_{24}$H$_{20}$N$_2$O$_5$. Calculated (%): C, 69.22; H, 4.84; N, 6.73.

6-(2-(2,3,5,6,8,9,11,12-Octahydrobenzo[b][1,4,10,7,13] trioxadithiacyclopentadecyn-15-yl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl-amino)-6-adipic acid (4b). To a stirring suspension of 85 mg (1.67 mmol) of 4-aminonaphthalimide **3b** in 1.0 ml of pyridine at room temperature a solution of 0.20 g of monochloro anhydride of adipic acid in 1.0 ml of DMF was added dropwise. The reaction mixture was stirred for 4 hours at 40–60 °C, then diluted with water, the precipitate was filtered off, washed with 5 % hydrochloric acid, again with water and ethanol several times. The product was dried in air to yield 71 mg (67 %) of **4b**. M.p. 183–186 °C. ^{1}H NMR (400.22 MHz, [D$_1$]CDCl$_3$, 22 °C) δ ppm (*J*/Hz): 1.58–1.75 (m, 4H, CH$_2$(25,26)), 2.29 (t, 2H, CH$_2$(24), *J*=7.5), 2.60 (t, 2H, CH$_2$(23), *J*=7.5), 2.85–3.09 (m, 8H, CH$_2$(16,17,20,21)), 3.68–3.79 (m, 4H, CH$_2$(18,19)), 4.07–4.18 (m, 2H, CH$_2$(15)), 4.19–4.33 (m, 2H, CH$_2$(22)), 6.67 (d, 1H, H(13), *J*=8.8), 7.01–7.11 (m,

2H, H(10), H(14)), 7.92 (dd, 1H, H(6), *J*=8.8, *J*=7.2), 8.32 (d, 1H, H(3), ^3J=8.4), 8.47 (d, 1H, H(2), *J*=8.4), 8.53 (d, 1H, H(7), *J*=7.2), 8.73 (d, 1H, H(5), *J*=8.8), 10.39 (br.s, 1H, NHCO), 12.04 (br.s, 1H, COOH). Found (%): C, 60.15; H, 5.24; N, 4.35. C$_{32}$H$_{34}$N$_2$O$_8$S$_2$. Calculated (%): C, 60.17; H, 5.37; N, 4.39.

6-(6-Nitro-1,3-dioxo-1H-benzo[d,e]isoquinoline-2-(3H)-yl) hexanoic acid (5). To a suspension of 0.08 g (0.3 mmol) of 4-nitro-1,8-naphthalic anhydride **1** in 2 ml of ethanol 0.04 g (0.3 mmol) of 6-aminocaproic acid was added. The reaction mixture was refluxed for 2 h, cooled to room temperature. The precipitate was filtered off, washed with 5 % hydrochloric acid, water and ethanol to yield 0.04 g (53 %) of **5**. M.p. 168–170 °C. ^{1}H NMR (300.13 MHz, [D$_6$] DMSO, 23 °C) δ ppm (*J*/Hz): 1.30–1.40, 1.50–1.60, 1.67–1.70 (m, 6H, CH$_2$(10), CH$_2$(11), CH$_2$(12)), 2.22 (t, 2H, H(9), ^3J=7.3), 4.03 (t, 2H, CH$_2$(13), ^3J=7.3), 8.09 (dd, 1H, H(6), ^3J=7.5, ^3J=8.6), 8.56 (d, 1H, H(2), ^3J=8.0), 8.58–8.65 (m, 2H, H(5), H(7)), 8.71 (d, 1H, H(3), ^3J=8.7). Found (%): C, 60.65; H, 4.47; N, 7.88. C$_{18}$H$_{16}$N$_2$O$_6$. Calculated (%): C, 60.67; H, 4.53; N, 7.86.

6-(6-Methoxy-1,3-dioxo-1H-benzo[d,e]isoquinoline-2-(3H)-yl)hexanoic acid (6). 0.25 g (1.1 mmol) of 4-nitro-1,8-naphthalimido-*N*-hexanoic acid **5** and 0.55 mg (10.2 mmol) of sodium methylate were dissolved in 10 ml of methanol. The reaction mixture was refluxed for 4 h, cooled to room temperature, and 1 ml of acetic acid was added to the reaction mixture, then the resulting solution was evaporated in vacuum. To the crude product water and 125 ml of concentrated hydrochloric acid were added. The precipitate was filtered off and washed with water to yield 210 mg (60 %) of **6**. M.p. 160–162 °C. ^{1}H NMR (300.13 MHz, [D$_6$]DMSO, 21 °C) δ ppm (*J*/Hz): 1.28–1.39 (m, 2H, CH$_2$(11)), 1.48–1.68 (m, 4H, CH$_2$(10), CH$_2$(12)), 2.21 (t, 2H, CH$_2$(13), ^3J=7.4), 4.02 (t, 2H, CH$_2$(9), ^3J=7.4), 4.13 (s, 3H, OCH$_3$), 7.34 (d, 1H, H(3), ^3J=8.3), 7.83 (dd, 1H, H(6), ^3J=7.5, ^3J=7.7), 8.48 (d, 1H, H(2), ^3J=8.3), 8.51 (d, 1H, H(7), ^3J=7.2), 8.55 (d, 1H, H(5), ^3J=7.2), 11.99 (s, 1H, COOH). ^{13}C NMR (100.61 MHz, [D$_6$]DMSO, 27 °C) δ ppm: 24.23 (CH$_2$), 27.33 (CH$_2$), 33.48 (CH$_2$), 41.25 (CH$_2$), 56.67 (–OCH$_3$), 106.36 (C(3)), 114.31 (C(1)), 121.98 (C(8)), 122.82 (C(4a)), 126.49 (C(6)), 128.33 (C(5)), 128.62 (C(8a)), 131.12 (C(7)), 133.38 (C(2)), 160.38 (C(4)), 162.99 (C(8b)), 163.61 (C(8c)), 174.45 (–COOH). Found (%): C, 66.80; H, 5.62; N, 4.14; O, 23.43. C$_{19}$H$_{19}$NO$_5$. Calculated (%): C, 66.85; H, 7.61; N, 4.10; O, 23.43.

6-(6-Methoxy-1,3-dioxo-1H-benzo[d,e]isoquinoline-2-(3H)-yl)hexyl chloride (7). 4-Methoxynaphthalimide **6** (0.1 g, 0.3 mmol) and 200 µl (2.3 mmol) of oxalyl chloride were refluxed in 5 ml of dichloromethane for 3 hours. The solvent was evaporated in vacuo. The obtained product (0.14 g) was used in the next step of synthesis without further purification.

2-(4-(Bromo-1,3-dioxo-1H-benzo[d,e]isoquinoline-2-(3H)-yl)-phenyl) acetic acid (8). According to the general procedure for acylation of aromatic amines 980 mg (69 %) of 4-bromo-*N*-arylnaphthalimide **8** was obtained from 970 mg (3.5 mmol) of 4-bromonaphthalic anhydride, 795 mg (5.3 mmol) of 4-amino-phenylacetic acid and 27 ml of acetic acid. M.p. 261–264 °C. ^{1}H NMR (600.22 MHz, [D$_6$]DMSO, 23 °C) δ ppm (*J*/Hz): 3.69 (s, 2H, CH$_2$(15)), 7.29–7.35 (m, 2H, H(10), H(14)), 7.37–7.44 (m, 2H, H(11), H(13)), 8.01 (dd, 1H, H(6), *J*=7.9, *J*=8.7), 8.21 (d, 1H, H(3), *J*=8.1), 8.32 (d, 1H, H(2), *J*=8.1), 8.57–8.58 (m, 2H, H(7),H(5)). ^{13}C NMR (150.93 MHz, [D$_6$]DMSO, 23 °C) δ ppm: 41.25 (CH$_2$), 106.56 (C(3)), 114.91 (C(1)), 122.98 (C(8)), 123.02 (C(4a)), 126.49 (C(6)), 128.13 (C(5)), 128.89 (C(10), C(14)), 129.62 (C(8a)), 130.56 (C(11), C(13)), 132.91 (C(7)), 133.78 (C(2)), 134.72 (C(9)), 135.81 (C(12)), 161.38 (C(4)), 162.99 (C(8b)), 163.61 (C(8c)), 174.45 (–COOH). MS (IES), calculated, *m/z*: 433.1233; found: 433.1235 ([M+Na]$^+$). Found (%): C, 56.61; H, 3.34; N, 3.06; C$_{20}$H$_{12}$BrNO$_4$×0.8CH$_3$COOH. Calculated (%): C, 58.56; H, 2.95; N, 3.41.

2-(4-(6-Methoxy-1,3-dioxo-1H-benzo[d,e]isoquinoline-2-(3H)-yl)-phenyl) acetic acid (9). 240 mg (0.6 mmol) of 4-bromo-*N*-phenylnaphthalimide **8** and 70 mg (1.2 mmol) of potassium

carbonate were dissolved in 7 ml of methanol. The reaction mixture was refluxed for 6 hours, then poured into 15 ml of water and acidified with 7 ml of acetic acid. The resulting precipitate was filtered off, washed with water and dried to yield 190 mg (63 %) of **9**. M.p. 257–260 °C. ^{1}H NMR (600.22 MHz, [D$_3$]CD$_3$CN, 25 °C) δ ppm (J/Hz): 3.69 (s, 2H, CH$_2$), 4.13 (s, 3H, CH$_3$), 7.21–7.30 (m, 3H, H(10), H(14), H(3)), 7.43 (d, 2H, H(11), H(13)), 7.80 (dd, 1H, H(6), J=7.9, J=8.7), 8.47–8.56 (m, 2H, H(7), H(2)), 8.61 (d, 1H, H(5), J = 7.9). ^{1}H-NMR (600.22 MHz, [D$_6$]DMSO, 24 °C, δ/ppm, J/Hz): 3.35 (s, 2H, CH$_2$), 4.14 (s, 3H, CH$_3$), 7.10–7.16 (m, 2H, H(10), H(14)), 7.27–7.38 (m, 3H, H(11), H(13), H(3)), 7.84 (dd, 1H, H(6), J = 7.9, J = 8.7), 8.44–8.55 (m, 2H, H(7), H(2)), 8.58 (d, 1H, H(5), J=7.9). ^{13}C NMR (150.93 MHz, [D$_6$]DMSO, 24 °C) δ ppm: 41.25 (CH$_2$), 56.67 (–OCH$_3$), 106.56 (C(3)), 114.91 (C(1)), 122.98 (C(8)), 123.02 (C(4a)), 126.49 (C(6)), 128.13 (C(5)), 128.89 (C(10), C(14)), 129.62 (C(8a)), 130.56 (C(11), C(13)), 132.91 (C(7)), 133.78 (C(2)), 134.72 (C(9)), 135.81 (C(12)), 161.38 (C(4)), 162.99 (C(8b)), 163.61 (C(8c)), 174.45 (–COOH). MS (IES), calculated, m/z: 384.0847; found: 384.0842 ([M+Na]$^+$). Found (%): C, 61.52; H, 5.07; N, 3.51. C$_{21}$H$_{15}$NO$_5$×2.7H$_2$O. Calculated (%): C, 61.50; H, 5.02; N, 3.42.

2-(4-(6-Methoxy-1,3-dioxo-1H-benzo[de]isoquinoline-2-(3H)-yl)-phenyl) acetyl chloride (10). 0.1 g (0.3 mmol) of 4-methoxynaphthalimide **9** was refluxed in 5 ml of thionyl chloride for 3 hours. The excess of thionyl chloride was removed in vacuo. The obtained product (0.15 g) was used in the subsequent step without further purification.

Synthesis of SnO$_2$ nanoparticles sols, modified by naphthalimide derivatives. All investigated sols based on SnO$_2$ nanoparticles and naphthalimide were obtained by the following procedure. To the 100 ml of SnO$_2$ nanoparticles water sol in a dark flask 200 ml of naphthalimide solution in DMSO with concentration of 5·10^{-3} mol/l of naphthalimide dye was added. The reaction mixture was stirred and kept at 60 °C for 1 hour, and

then cooled to room temperature. Partly the obtained solution of modified sol was applied for further study of optical properties, and the remainder one was evaporated to dryness to carry out the study by IR spectroscopy. Samples were stored in a dark to avoid the naphthalimide degradation on the surface of SnO$_2$ nanoparticles.

Results and Discussion

Synthesis of 1,8-naphthalimide derivatives 2a,b

Synthesis of 4-methoxynaphthalimide derivatives containing N-phenyl (**2a**) and N-benzoditiacrown ether (**2b**) fragments is presented in Scheme 2. Compound **2a** possesses the optical characteristics similar to those of **2b** but is not able to coordinate with metal ions. The starting compound in the synthesis of **2a,b** is commercially available 4-nitronaphthalic anhydride which is used to acylate the aromatic amines. For introduction of the donor methoxy group to the 4th position of naphthalimide residue of **2a,b** known procedures were applied.[21]

Two-step synthesis was carried out to obtain **4a,b**. The first step was reduction of nitro groups of **1a,b** giving **3a,b**. The second one was the interaction of amino derivatives **3a,b** with monochloro anhydride of adipic acid resulting in crown-free (**4a**) and dithiacrown-containing (**4b**) derivatives.
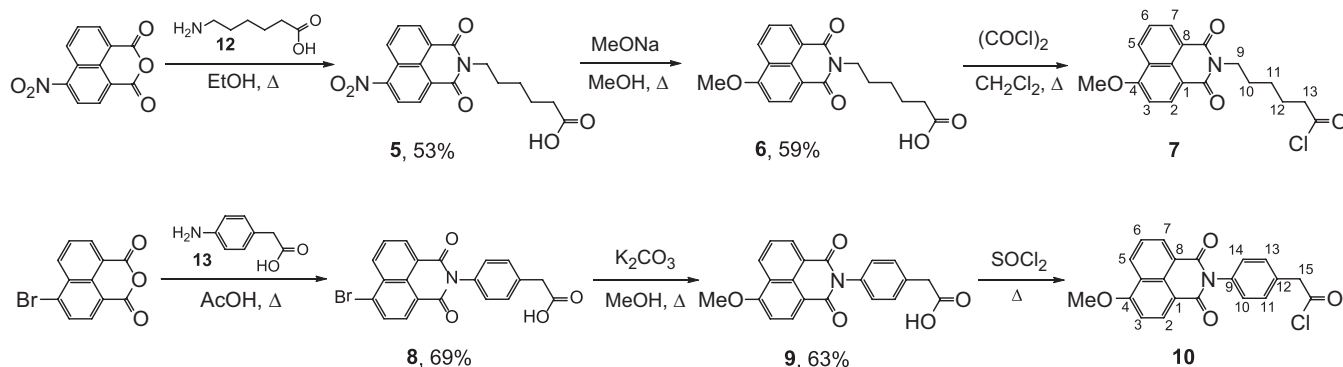
Synthesis of 4-methoxynaphthalimide derivatives **6** and **9** containing a carboxyl group in N-phenyl or N-alkyl substituent was carried out based on the 4-nitro- and 4-bromnaphthalic anhydride according to Scheme 4 (see
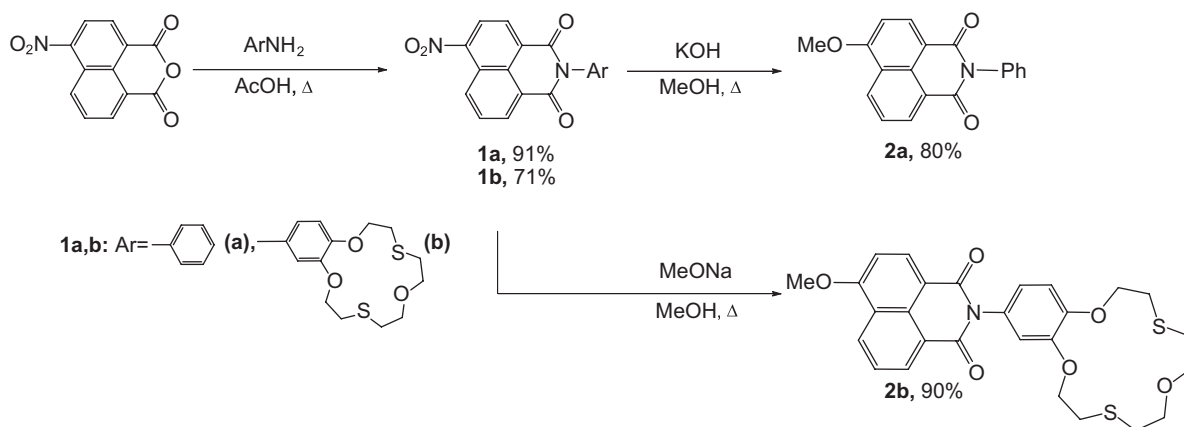
Scheme 2.
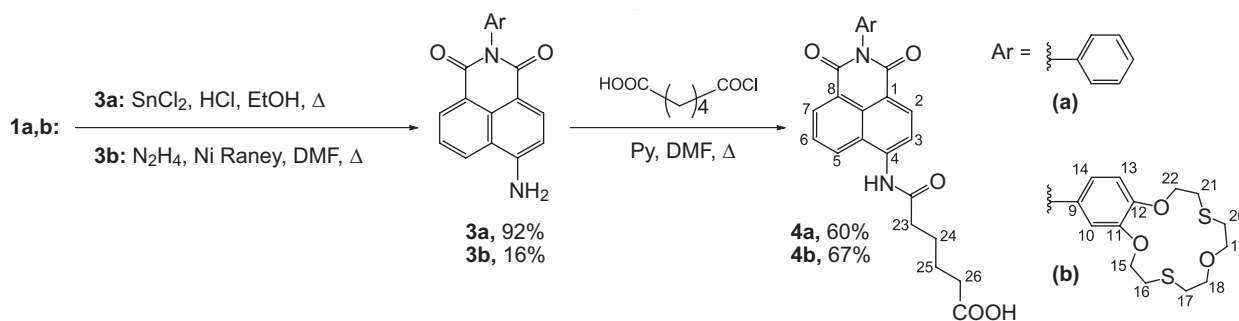
Scheme 3.

Scheme 4.

the details in the Experimental Part). The variation of the carboxylic derivative structure was done aimed to find the better modification agent for SnO$_2$.

*Preparation of the modified SnO$_2$ nanoparticles*

An aqueous sol of SnO$_2$ nanoparticles modified by naphthalimide derivatives were obtained and used for physico-chemical study. IR spectra of unmodified SnO$_2$ nanoparticles and nanoparticles modified by organic components and starting naphthalimides **5a,b**, **7** and **9** were recorded to confirm the covalent binding of compounds. Figures 1–3 show the IR spectra of SnO$_2$, compound **9** and SnO$_2$ nanoparticles modified by naphthalimide **9**. The IR spectra of **5a,b**, **7** and SnO$_2$ nanoparticles modified by these compounds are presented in Supporting Information (SI, Figs. S2–S6). In the IR-spectrum of SnO$_2$ nanoparticles the band of O–H stretching in the region 3440–2500 cm^{-1} is observed (Figure 1). In IR spectrum of **9** there are bands belonging to carboxylate anion. There are intense band

of antisymmetric stretching at 1650–1550 cm^{-1} and less intense symmetric one band at 1400 cm^{-1} (Figure 2).[22] The broad band at 3400 cm^{-1} which is characteristic for the stretching of O–H group is observed in the IR spectrum of molecular naphthalimide **9** (Figure 2). In the SnO$_2$×**9** hybrid material the stretching of O–H group was disappeared, but there are intense bands characteristic for carboxylate anion (Figure 3). The IR spectroscopy data confirm the covalent binding of naphthalimide **9** to SnO$_2$ nanoparticles.

Investigation of the complex formation of 4-methoxynaphthalimide 2b containing dithiacrown ether with heavy metal ions

Complex formation of dithiacrown-containing derivative **2b** with Cu(ClO$_4$)$_2$, AgClO$_4$, Hg(ClO$_4$)$_2$, Ni(ClO$_4$)$_2$, Fe(ClO$_4$)$_2$, Zn(ClO$_4$)$_2$, Cd(ClO$_4$)$_2$, Mg(ClO$_4$)$_2$, Ca(ClO$_4$)$_2$ was studied in acetonitrile solution and in water. The former observation of naphthalimide containing oxocrown ether in *N*-aryl moiety[23] by X-ray crystallography method showed
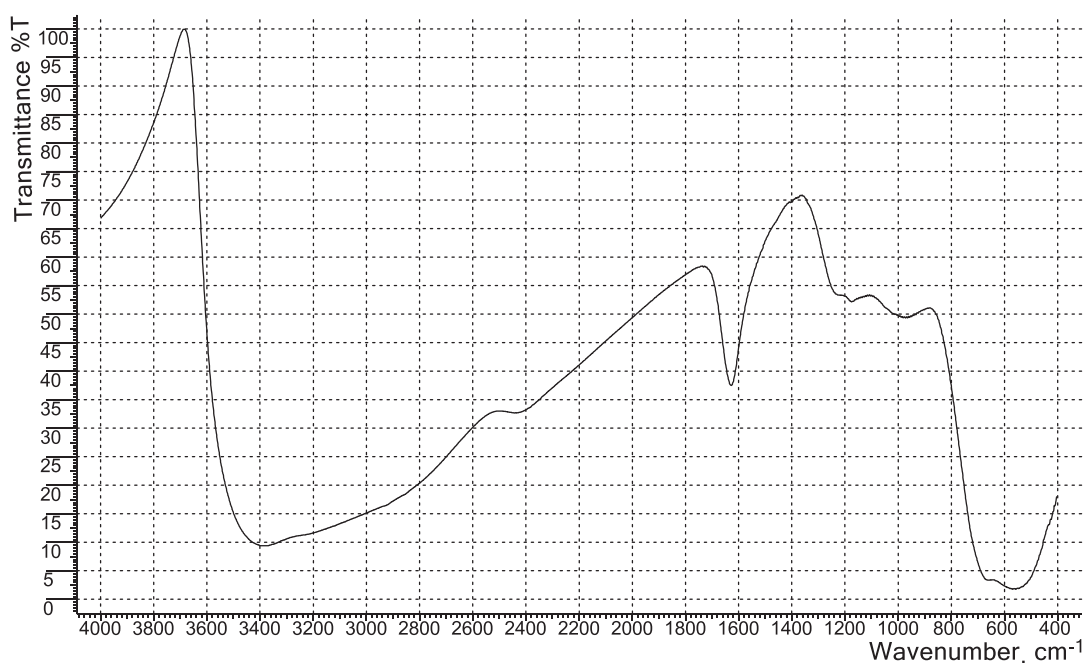
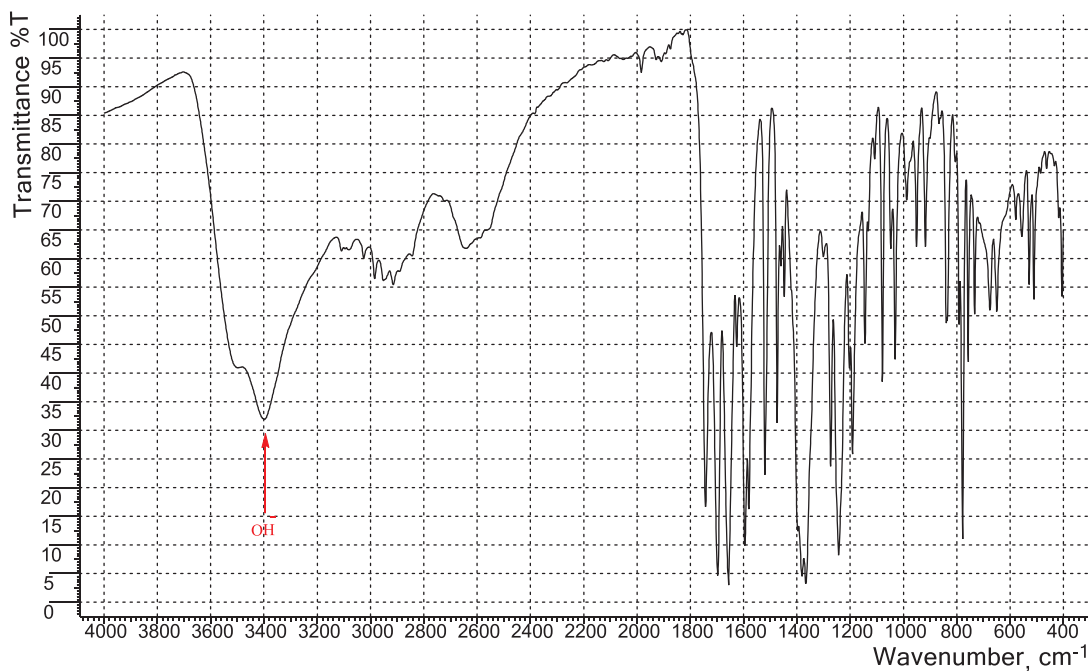**Figure 1**. IR spectrum of unmodified SnO$_2$ nanoparticles.

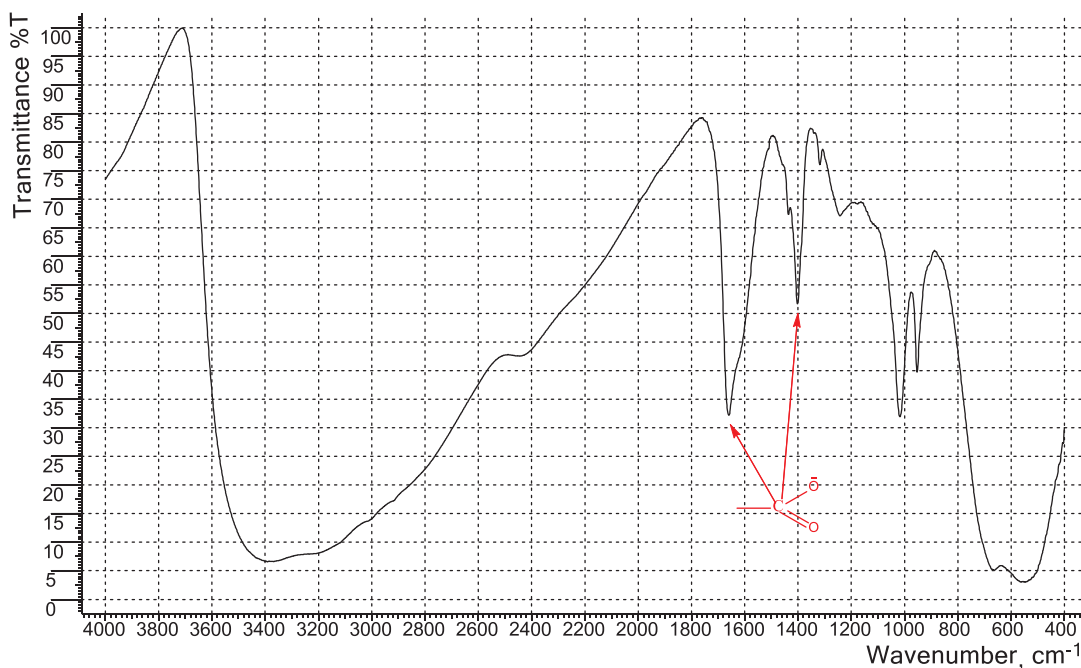**Figure 2**. IR spectrum of molecular naphthalimide **9**.

Figure 3. IR spectrum of SnO$_2$ nanoparticles modified by naphthalimide **9**.

the dihedral angle between the naphthalimide moiety and *N*-aryl group to be close to 90°. Thus, one can conclude that the π-electronic interaction between these two fragments is very weak and negligible in the ground state. As a result, the complex formation through interaction of metal ions with crown ether macrocycle does not lead to significant changes in the positions of absorption and fluorescence bands. It was shown also that the presence of crown ether group in the *N*-aryl moiety of naphthalimide leads to dramatic decrease of emission intensity with respect

to crown free *N*-phenylnaphthalimide due to efficient electron transfer between naphthalimide chromophore and receptor unit.[23,24] Upon the addition of metal ions the lone pair of electrons of crown ether receptor's heteroatoms are engaged in cation binding, this suppresses PET process and causes fluorescence enhancement (Scheme 5).

As expected the addition of metals salts (Cu(ClO$_4$)$_2$, AgClO$_4$, Hg(ClO$_4$)$_2$, Ni(ClO$_4$)$_2$, Fe(ClO$_4$)$_2$, Zn(ClO$_4$)$_2$, Cd(ClO$_4$)$_2$, Mg(ClO$_4$)$_2$, Ca(ClO$_4$)$_2$) into solution of **2b** does not cause

Electron transfer (PET)
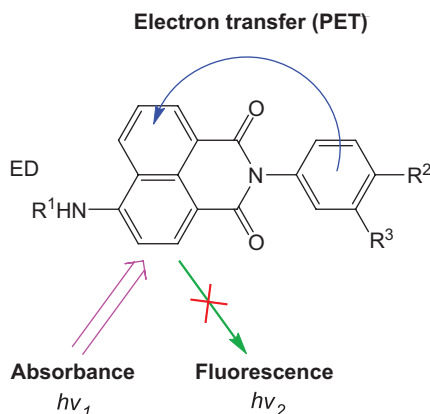
Scheme 5.

remarkable changes in position of the long wavelength bands in the absorption and fluorescence spectra, but in the case of Hg^{2+}, Pb^{2+} and Cu^{2+} fluorescence enhancement associated with inhibition of photoinduced electron transfer process was observed. Figures 4a,b show the change in absorption and fluorescence spectra of compound **2b** in acetonitrile by adding of 10 equivalents of Hg^{2+}, Pb^{2+} and Cu^{2+} cations. Other studied metal ions did not give rise to remarkable changes in the fluorescence emission even at high concentration. These

results are presumably due to well-known high affinity of thiacrown ethers towards the Hg^{2+}, Pb^{2+} and Cu^{2+} cations.[12]

The degree of fluorescence enhancement (FE) of **2b** in the presence of tenfold excess of various metal cations is shown in Figure 5. FE value represents the ratio of the integrated fluorescence intensities of the ligand solution in the presence and absence of the cation, respectively. Fluorescent receptor **2b** in acetonitrile solution showed fluorescence enhancement upon addition of Pb^{2+} cations in 45 times and to a less extent in the presence of Hg^{2+} (in twenty two times) and Cu^{2+} (in five times) (Figure 5a). In water compound **2b** showed selectivity towards Hg^{2+} only. The degree of fluorescence enhancement in this case was in eighteen times (Figure 5b).

Studies have shown that the introduction of the two sulfur atoms in the crown ether receptor leads to ligands selective towards the Hg^{2+} and Pb^{2+} cations in the presence of alkali, alkaline earth and some heavy metal ions ($AgClO_4$, $Ni(ClO_4)_2$, $Fe(ClO_4)_2$, $Zn(ClO_4)_2$, $Cd(ClO_4)_2$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$).

Optical properties of *4a,b, 6* and *9* and nanoparticles of SnO_2 modified by *4a,b, 6* and *9*

Compounds **4a,b**, **6** and **9** demonstrate the long-wavelength absorption band with a maximum at 350–360 nm in acetonitrile and 360–375 nm in water (Figure S7
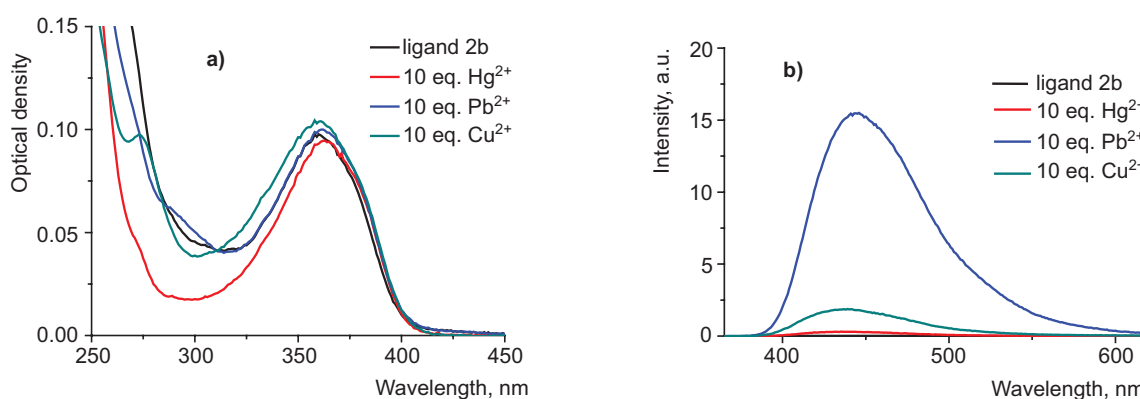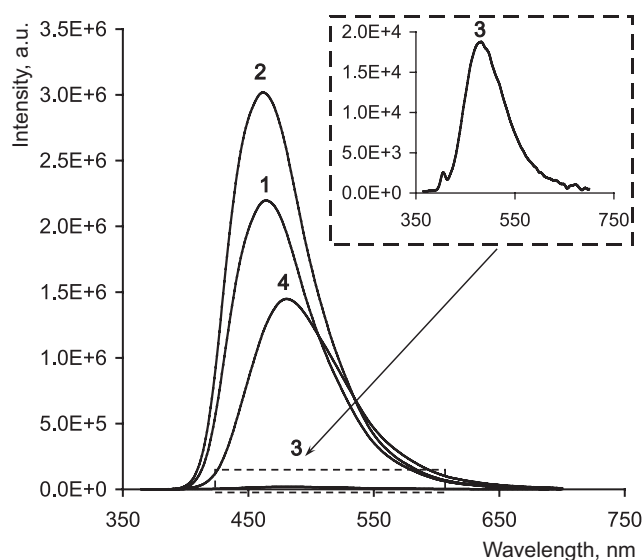

Figure 4. Changes in the absorption spectra (a) and fluorescence (b) of the compound **2b** caused by addition of Pb^{2+}, Hg^{2+} and Cu^{2+} perchlorates in acetonitrile (C_L=6.4·10^{-6} mol/l).
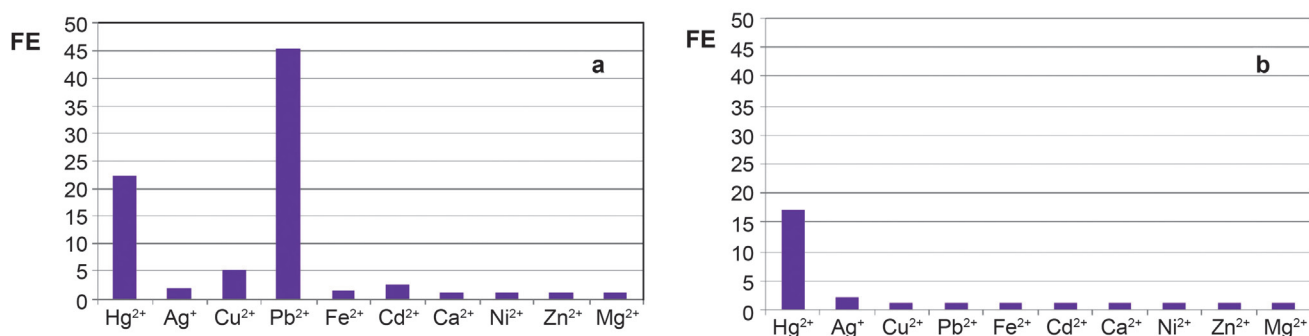
Figure 5. A fluorescence enhancement (FE) of compound **2b** upon addition a tenfold excess of metal perchlorates in acetonitrile (a) and water (b) (C_L=6.4·10^{-6} mol/l).
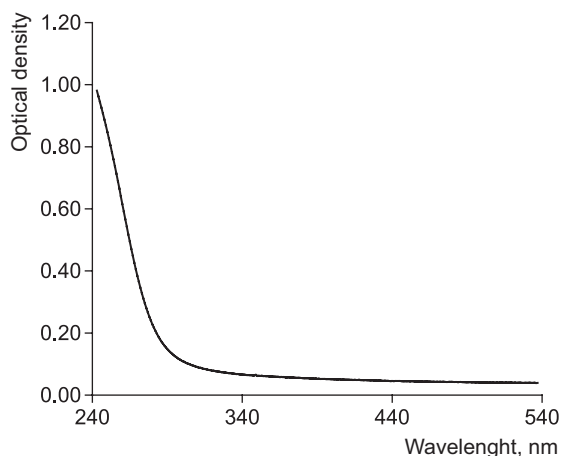
Figure 6. The fluorescence spectra of the compounds **6** (1), **9** (2), **4b** (3), **4a** (4) in water (C_L=6.4·10^{-6} mol/l, excitation wavelength: 375, 375, 355, 355 nm, respectively).

Figure 8. Electronic absorption spectra of compound **6** (1) and modified by it sol $SnO_2×\mathbf{6}$ (2) in water.

in SI). Similar to compound **2b** crown containing carboxyl derivative **4b** shows a low level of fluorescence due to the concurrent efficient photoinduced electron transfer process (Figure 6).
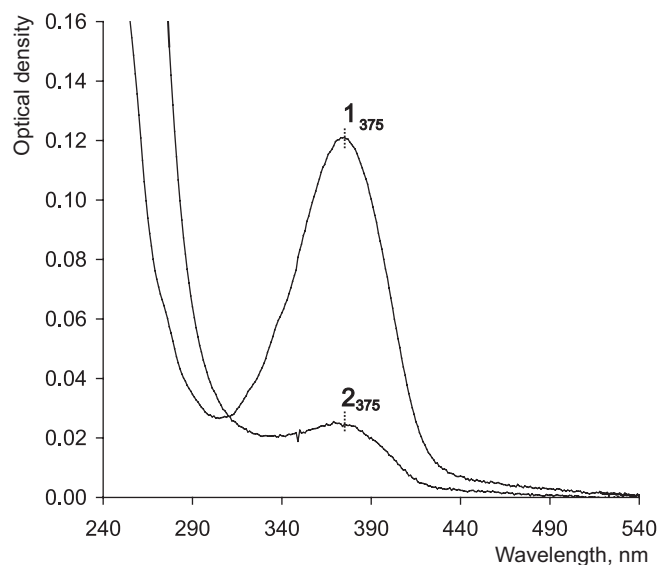
It should be noted that the sol of SnO_2 nanoparticles does not absorb or emit the light (Figure 7). Analysis of the absorption spectra of SnO_2 nanoparticles modified by naphthalimide derivatives shows the absorption in the region 350–360 nm similar to that observed for **4a,b**, **6** and **9** but of lower intensity (Figures 8 and S8-S10 in SI).

It is important that position and intensity of the fluorescence bands of free **4a,b**, **6**, **9** are the same as for those of the compounds in the composition of SnO_2 nanoparticles (Figure 9).
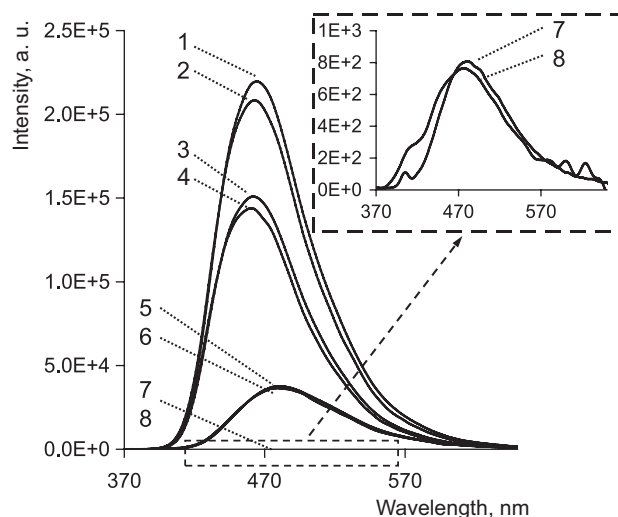
The addition of metal salts to the sol $SnO_2×\mathbf{4b}$ did not lead to the fluorescence enhancement as observed for molecular ligand **2b**. A possible explanation for the observed effect is the assumption that due to considerable length and

Figure 9. Fluorescence spectra of starting compounds **6** (1), **9** (3), **4a** (5), **4b** (7) and fluorescence spectra (normalized) of modified sols $SnO_2×\mathbf{6}$ (2), $SnO_2×\mathbf{9}$ (4), $SnO_2×\mathbf{4a}$ (6), $SnO_2×\mathbf{4b}$ (8) in water (T=294 °K, excitation wavelength: 375 nm for (1)–(4) and 355 nm for (5)–(8)).

flexibility of the carboxyl-containing spacer the molecule may be placed on the surface of nanoparticles making inaccessible crown ether cavity for the coordination with the metal cations (Scheme 4).

Figure 7. The electronic absorption spectra of unmodified sol of SnO_2 nanoparticles in water.
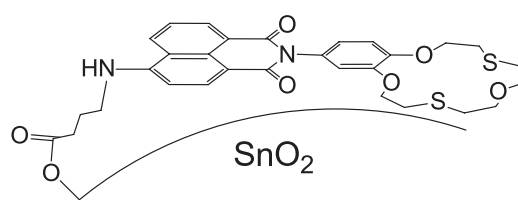
Scheme 4.

Conclusion

In this paper the synthesis of a number of *N*-alkyl- or *N*-phenyl-1,8-naphthalimide derivatives having in its structure a carboxylic group and dithiacrown ether as substituents or two substituents of this type simultaneously was represented. Complex formation study of the molecular naphthalimide-containing dithiacrown ether showed selectivity towards Hg^{2+} and Pb^{2+} cations in acetonitrile and Hg^{2+} cations in the water. Influence of the solvent on the ligand selectivity upon complexation is well explained if we take into account the fact that there is a metal cation removing from the solvation shell to the macrocyclic cavity in the process of complex formation. Due to the photoinduced electron transfer process between benzodithiacrown ether receptor and naphthalimide residue in the excited state, free ligands **2b**, **4b** have a low fluorescence intensity and show a significant fluorescence enhancement upon the binding with Pb^{2+} and Hg^{2+} cations.

The paper also proposed a method for naphthalimide covalent binding with SnO_2 surface. It is shown that carboxyl derivatives as well as acyl chlorides are suitable for this purpose. In the composition of modified SnO_2 sols 1,8-naphthalimide derivatives exhibit optical characteristics similar to molecular ones. However, in the case of SnO_2 modified by crown-containing naphthalimide complex formation with metal ions has not been observed. It was assumed that due to considerable length and flexibility of the carboxyl-containing spacer the molecule may be placed on the surface of nanoparticles to prevent the coordination of crown ether's cavity with metal cations. Obviously to obtain nanoparticles capable for coordination of cations it is necessary to modify a spacer between the fluorescent receptor and the nanoparticle surface so that the adsorption of the fluorophore on the surface could be impossible.

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