Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 517–519

Fluorimetric detection of Ag$^+$ cations in aqueous solutions using polyvinyl chloride sensor film doped with crown-containing 1,8-naphthalimide

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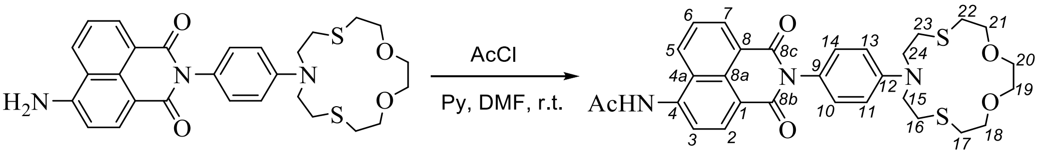
CONTENTS

1. Synthesis of compound **2**

Compound **2** was synthesized by acylation of 4-aminonaphthalimide **3** (Scheme S1) with acetylchloride as described below. Preparation of **3** was reported earlier (for details see ref. 17 in the manuscript text). Melting point of **2** was measured on Melt-temp melting point electrothermal apparatus and was uncorrected. The reaction course and purity of the final product was followed by TLC on silica gel (DC-Alufolien Kieselgel 60 F_{254}, Merck). Column chromatography was conducted over silica gel (Kieselgel 60, particle size 0.063-0.200 mm, Merck). ^{1}H and ^{13}C NMR spectra were recorded on an Avance 300 and Avance 600 spectrometers (Bruker). The chemical shifts (given as δ) were determined with an accuracy of 0.01 ppm relative to the signals corresponding to the residual solvents 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 ^{1}H and ^{13}C signals is based on 2D NMR experiments (HMBC, HSQC, ^{1}H COSY), which were performed using standard pulse sequences from the Bruker library. LC-ESI-MS analyses were performed on a Finnigan LCQ Advantage mass spectrometer equipped with octopole ion-trap mass-analyzer, MS Surveyor pump, Surveyor auto sampler, Schmidlin-Lab nitrogen generator (Germany) and Finnigan X-Calibur 1.3 software for data collecting and processing.



3

2, 60%

Scheme S1

N-(2-(4-(1,4-dioxa-7,13-dithia-10-azacyclopentadecan-10-yl)phenyl)-1,3-dioxo-2,3-dihydro-1H-benzo[d,e]isoquinolin-6-yl)acetamide (**2**). To a stirring mixture of **3** (30 mg, 0.056 mmol) and anhydrous pyridine (0.4 mL) solution of AcCl in DMF (0.1 mL, 9 vol. % AcCl) was added. The reaction mass was stirred for 2 hours at ambient temperature, diluted with ethanol (1.0 mL) and cooled overnight in the fridge. The resulting precipitate was filtered off and chromatographed on silica gel using PhH – EtOH gradient mixture (v/v was changed from 100:1 to 30:1) to yield 19 mg (60%) of **2**. M. p. 244 – 246 ºC. ^{1}H NMR (300.13 MHz, DMSO-d_6, 21 ºC, δ / ppm, J / Hz): 2.30 (s, 3H, CH_3), 2.68 – 2.94 (m, 8H, CH_2(16), CH_2(17), CH_2(22), CH_2(23)), 3.54 – 3.78 (m, 12H, CH_2(15), CH_2(18), CH_2(19), CH_2(20), CH_2(21), CH_2(24)), 6.69 (d, 1H, H(11), H(13), ^{3}J = 8.7), 7.11 (d, 2H, H(10), H(14), ^{3}J = 8.7), 7.85 – 7.96 (m, 1H, H(6)), 8.32 (д, 1H, H(3), ^{3}J = 8.3), 8.47 (d, 1H, H(2), ^{3}J = 8.3), 8.52 (d, 1H, H(7), ^{3}J = 7.3), 8.74 (d, 1H, H(5), ^{3}J = 8.5), 10.43 (br. s, 1H. NHCO). ^{13}C NMR (150.93 MHz, DMSO-d_6, 22 ºC, δ / ppm): 24.11 (CH_3CO), 29.03 (2×CH_2S), 30.58 (2×CH_2S), 51.38 (2×CH_2N), 70.05 (2×CH_2O), 73.01 (2×CH_2O), 111.28 (C(11), C(13)), 118.12 (C(1)), 119.45 (C(3)), 122.96 (C(8)), 123.98 (C(9)), 124.17 (C(4a)), 126.42 (C(6)), 128.73 (C(8a)), 129.26 (C(5)), 129.72 (C(10), C(14)), 130.90 (C(7)), 131.63 (C(2)), 140.29 (C(4)), 146.34 (C(12)), 163.52 (C(8b)), 164.08 (C(8c)), 169.64 (CH_3CO). ESI-mass spectrum, calculated, m/z: 580.19; found: 580.13 ($[M+H]^+$). Elemental analysis, found (%): C, 62.21; H, 5.78; N, 7.16; calculated for $C_{30}H_{33}N_3O_5S_2$ (%): C, 62.15; H, 5.74; N, 7.25.

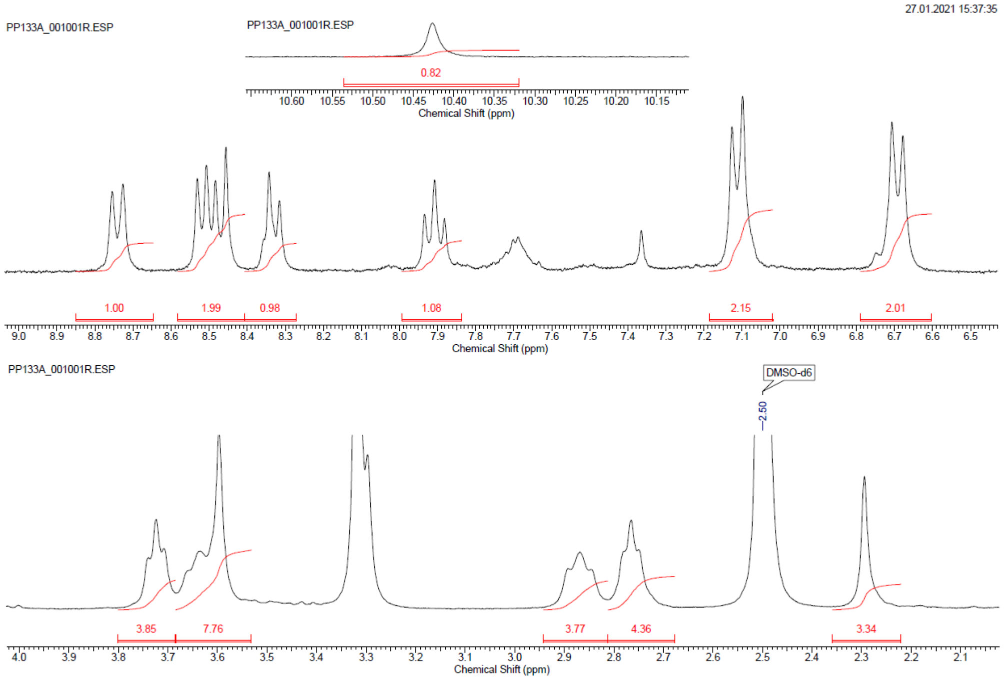


Figure S1. ^{1}H NMR spectrum of compound **2** in DMSO-*d*$_6$

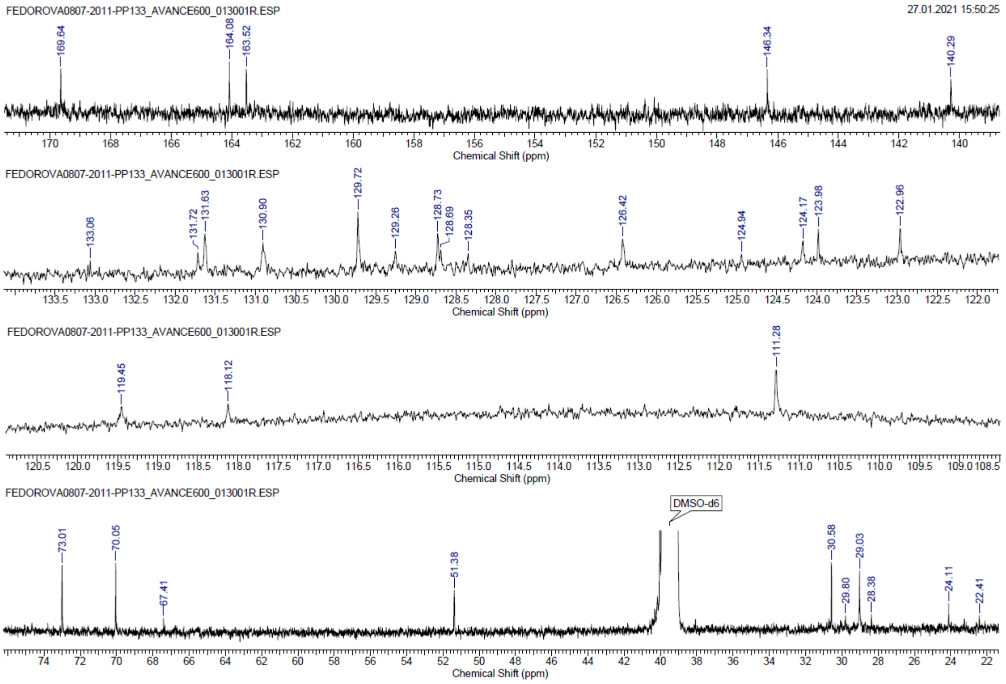


Figure S2. ^{13}C NMR spectrum of compound **2** in DMSO-*d*$_6$

2. Steady-State absorption and emission spectroscopy experiments

Acetonitrile used in spectroscopic studies was of HPLC grade. Acetate and phosphate-citrate buffer solutions were prepared with deionized water (18.2 MΩ·cm).

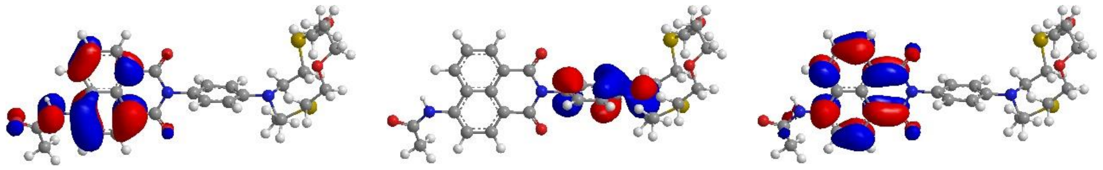
The absorption spectra of **2** in the presence and absence of metal cations were taken on a Cary 300 spectrophotometer (Agilent Technologies). The fluorescence quantum yield measurement for compound **2** was performed using a Cary 300 spectrophotometer and a Fluorolog3-221 spectrofluorimeter (Horiba Jobin Yvon). Spectral measurements were carried out in air-saturated dilute solutions at ambient temperature. All measured fluorescence spectra were corrected for the nonuniformity of detector spectral sensitivity. Coumarin 481 in acetonitrile ($\varphi^{\mathrm{fl}} = 0.08$) [*J. Phys. Chem. A*, 2003, **107**, 4808] was used as a reference for the fluorescence quantum yield measurements. The fluorescence quantum yield was calculated by the Eq. (S1) [*Anal. Chem.*, 1983, **55**, 798],

$$\varphi^{\mathrm{fl}} = \varphi_{\mathrm{R}}^{\mathrm{fl}} \frac{S}{S_{\mathrm{R}}} \cdot \frac{(1 - 10^{-A_{\mathrm{R}}})n^2}{(1 - 10^{-A})n_{\mathrm{R}}^2} \qquad \text{(S1)}$$

wherein φ^{fl} and $\varphi_{\mathrm{R}}^{\mathrm{fl}}$ are the fluorescence quantum yields of the studied solution and the standard compound respectively; A and A_{R} are the absorptions of the studied solution and the standard respectively; S and S_{R} are the areas underneath the curves of the fluorescence spectra of the studied solution and the standard respectively; and n and n_{R} are the refraction indices of the solvents for the substance under study and the standard compound.

The fluorescence spectra of polymer films were recorded on an AvaSpec-2048L portable fiber-optic fluorometer using an LED emitting at 365 nm as an excitation source. The sensor membrane sample was placed into a quartz cell with an 1 cm optical path length filled with 2.5 ml of the test solution. The membrane surface was located along the diagonal of the cell, *i.e.* at an angle of approximately 45° relative to the excitation light beam. The spectra were recorded every 20 s. The spectrum at the time "0 minutes" (see Figures 3, S5) corresponded to the film kept in the solution for about 10–15 s. Since the first registration was carried out at the moment when the sample was placed into the solution (first the measurement program was started, then the sample was fixed in the cell), the collected spectrum had significant distortions and was discarded.

3. Quantum-chemical calculations of frontier orbitals of **2**



	HOMO(–1)	HOMO	LUMO
Energy	–8.91 eV	–8.84 eV	–1.58 eV

Figure S3. Frontier molecular orbitals of compound **2** calculated by the PM6 method

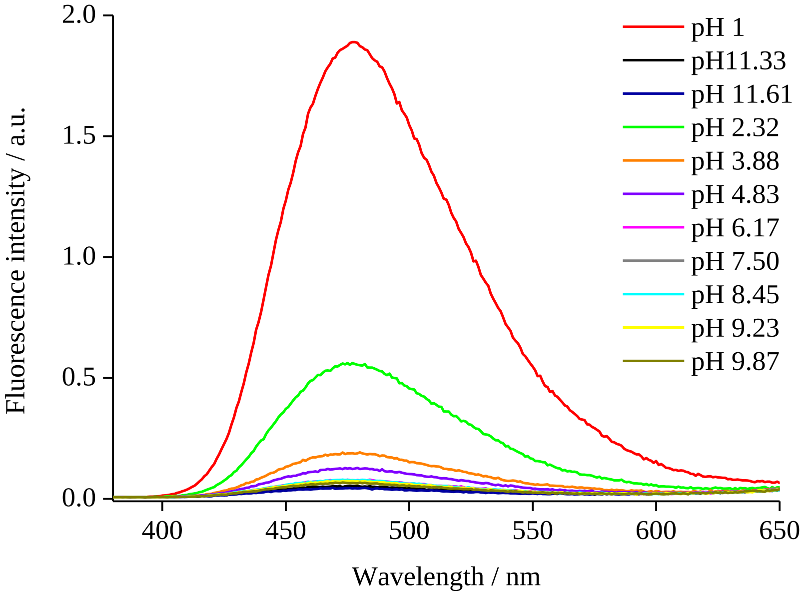
Calculation results show that the highest occupied molecular orbital (HOMO) in the compound **2** is located on the *N*-aryl fragment, whereas HOMO(–1) and LUMO (the lowest unoccupied MO) appear to be naphthalimide local MOs (Figure S3). This means that the photoinduced electron thansfer from the HOMO to half occupied HOMO(–1) of the photoexcited naphthalimide fragment could proceed effectively.

Computational details

Calculations were carried out by the MOPAC 2016 program package using PM6 semiempirical method [*J. Mol. Model.*, 2007, **13**, 1173]. The calculations were performed at optimized geometries, which reached gradient variations less than 0.01 kcal/mol. The solvent effect was included in geometry optimizations following the «COnductorlike Screening Model» (COSMO) implemented in MOPAC. A dielectric constant of $\varepsilon = 40$ and a refraction index of solvent (n) such that $n^2 = 2$ were used.

4. Influence of pH on the emission spectrum of **2**

(*a*)



(*b*)

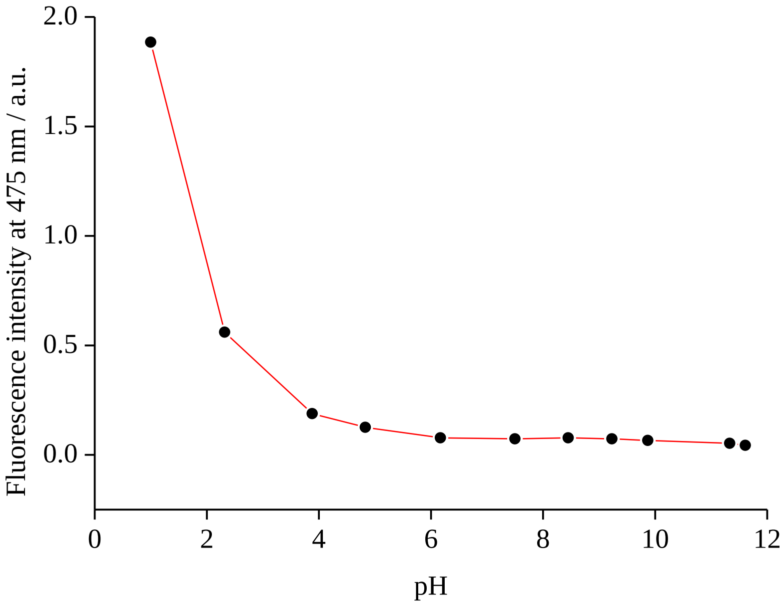


Figure S4. Fluorescence spectra of **2** (5 μM) at different pH (*a*) and fluorescence intensity of **2** at 475 nm versus pH (*b*) in water – methanol mixture (40 vol. % MeOH). Excitation wavelength – 375 nm. pH was maintained by phosphate-citrate buffers (6.7 mM) [see V.A. Rabinovich, Z.Y. Havin, Short Chemical Reference Book (From Russian: Kratkiy Himicheskiy Spravochnik), Second Edition, Himiya Publishing House, St. Petersburg, 1978.].

5. Preparation of polymer films

Optically transparent membranes were obtained by slow evaporation of tetrahydrofuran (the samples were dried for 1 hour in a closed Petri dish at room temperature, then for 1 hour in air). The composition of solutions for the preparation of membranes is given in Table S1. The solution used to obtain the films (solution *B*, Table S1) was prepared by adding to solution *A* certain amounts of a fluoroionophore (**1** or **2**) solution in benzene and solution of potassium tetra(*p*-chlorophenyl)borate ($K[B(p\text{-}C_6H_4Cl)_4]$) in tetrahydrofuran. When preparing solution *A*, polyvinylchloride was first mixed with dioctyl sebacic acid ester ($C_8H_{16}OOC(CH_2)_8COOC_8H_{16}$), and tetrahydrofuran was added to the resulting suspension. To prepare samples of sensor membranes, 200 μL of solution *B* was uniformly applied onto a substrate (polyester film for laser printers 35 × 11 mm in size) with an area of 3 cm^2. The calculated thickness of the obtained membranes was 40 μm.

Table S1. Composition of solutions for the preparation of sensor films

Solution *A*		Solution *B*	
Component	Quantity	Component	Quantity
Polyvinylchloride	400 mg	Solution A	800 μL
Dioctyl sebacate (plasticizer)	0.87 mL	Solution of fluoroionophore in benzene, 0.2 wt.%	40 μL
Tetrahydrofuran	8 mL	Solution of $K[B(p\text{-}C_6H_4Cl)_4]$ in tetrahydrofuran, 0.23 wt.%	40 μL

6. Emission spectra of polymer films

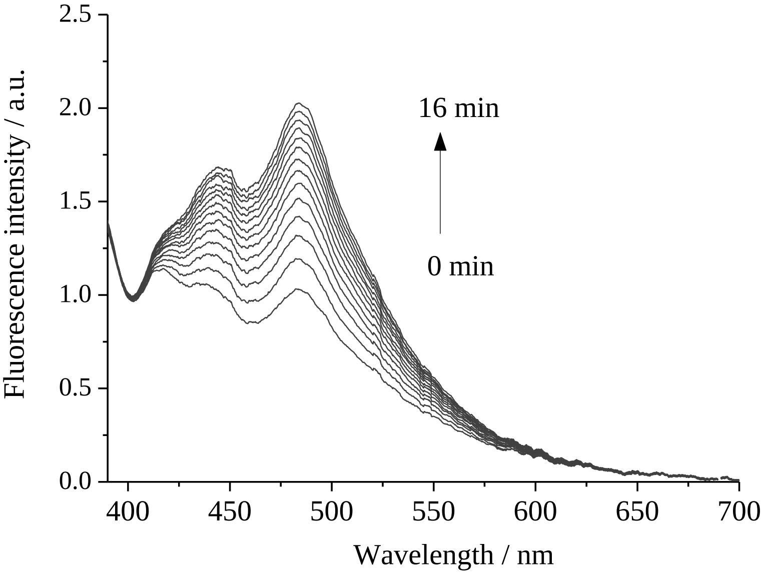


Figure S5. Changes in the emission spectrum of sensor film doped with compound **1** upon exposure to acetate buffer solution with pH 4.8. Excitation wavelength 365 nm.

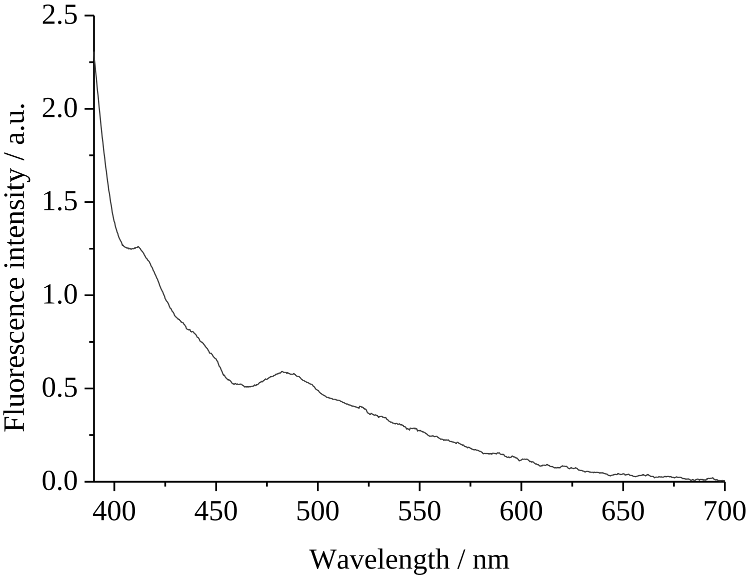


Figure S6. Emission spectrum of sensor film not containing compound **1** measured after 16 min exposure to acetate buffer solution with pH 6.0. Excitation wavelength 365 nm.