NJC

PAPER

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Cite this: New J. Chem., 2018, 42, 18559

Received 30th July 2018, Accepted 9th October 2018

DOI: 10.1039/c8nj03801e

rsc.li/njc

Introduction

Study of silver(I) complexes with N-donor ligands are of interest due to their unique structural features and potential applications in various fields of science and technology.^{1,2} Silver complexes reveal a large variety of coordination architectures, structural variability correlated with various anions or solvents, and unusual luminescence properties.^{3–8} The dependence between structural architecture and fluorescence properties of mono and multisilver(I) compounds was also studied. The influence of coordination geometry and distance between silver centers was also investigated.^{6,9}

Moreover, silver(1) complexes with benzimidazole derivatives exhibited antimicrobial,¹⁰ antimalarial, antitubercular activity,¹¹ and photoluminescence and catalytic properties.^{11–14} Benzimidazole and anthracene systems found applications in optical

New highly fluorescent silver complexes and their thin films obtained by spin coating method⁺

Magdalena Barwiolek, 💿 * Andrzej Wojtczak, Anna Kozakiewicz, Robert Szczesny, Magdalena Babinska, Lukasz Skowronski^b and Edward Szlyk

New silver complexes with ligands obtained from 2(2-pirydyl)ethylamine (epy) or o-phenylenediamine and series of aldehydes were obtained and characterized by their crystalline, molecular and spectroscopic (UV-Vis, fluorescence, IR, NMR) features. Molecular architecture of the synthesized complexes $[Ag_2(epy(5-Brthca))_2(NO_3)_2]$ **1** and $[Ag(bzim-anthr)_2]^+NO_3^-$ **2** has been determined by X-ray crystal structure analysis. ¹H NMR NOE diff. spectra of Ag complexes reveal different ligand conformations in the solution and the solid state (crystal structure). Thin (13–113 nm average thickness), homogenous layers of the studied silver(i) complexes were obtained by the spin coating method. The new materials were also characterized with AFM, SEM/EDX and ellipsometry. Calculated band-gap energies related to conformational transitions in layers of complexes **3**, **1** and **2** on Si(111) were 2.83 ± 0.02 eV (438 ± 3 nm), 2.90 ± 0.01 eV (428 ± 2 nm) and 2.95 ± 0.02 eV (420 ± 3 nm), respectively. The fluorescence bands of layers observed in the range 470–580 nm revealed significant intensity and were bathochromically shifted in comparison with those observed for the complexes was studied. The highest quantum yield of the fluorescence was achieved in methylene chloride for **2** with $\phi_2 = 0.52$ ($\lambda_{ex} = 335-385$ nm) and is related to the anthracene moiety.

> devices development¹⁵⁻¹⁸ related to their fluorescence properties.^{19,20} Reported benzimidazole derivatives were used in dye syntheses,²¹ or in advanced materials fabrication, such as nonlinear optics (NLO)²² and organic light-emitting diodes (OLED).^{23,24} Amongst the vast range of heterocycles, benzimidazoles were also applied in material science in fuel cell research,²⁵ or in pharmaceutical industry.

> Metallic silver layers and silver(1) compounds are used in the preparation of materials for applications in electronic, photographic and imaging applications.²⁶ Moreover, silver(1) complexes were reported as components of molecular materials with nonlinear optical (NLO) properties.²⁷ Thin layers of metals or metal complexes, including those with Ag(1) ions, are prepared by different deposition techniques, e.g. chemical vapour deposition (CVD), metal-organic chemical vapour deposition (MOCVD), laser ablation, sonication, spin coating, etc.²⁸⁻³⁰ These materials exhibit luminescence and can be used as conductors, semiconductors, in organic light emitting diodes (OLED) and even as drug transporters.^{31,32} The spin coating technique was used for preparation of thin films of silver on TiN-coated oxidized Si wafers, where [(nBu₃P)AgO₂C(CH₂)₂CO₂Ag(nBu₃)] and [(nBu₃P)₂- $AgO_2C(CH_2)_2CO_2Ag(nBu_3)_2$ were used as precursors. For $[(nBu_3P) AgO_2C(CH_2)_2CO_2Ag(nBu_3)$ complex, conductive silver films were obtained with a film resistivity of 3.4 $\mu\Omega$ cm. The film thickness (mean value of about 2.5 μ m) was not homogeneous, and EDX analysis showed traces of oxygen and carbon in the layers.³¹



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^a Faculty of Chemistry, Nicolas Copernicus University in Torun, 87-100 Torun, Poland. E-mail: mbarwiolek@umk.pl; Fax: +48 (56) 611 45 16;

Tel: +48 (56) 611 45 16

^b Institute of Mathematics and Physics, UTP University of Science and Technology, 85-796 Bydgoszcz, Poland

[†] Electronic supplementary information (ESI) available: NMR spectra of complexes, UV-Vis spectra of complexes, details of ligands synthesis, AFM images of layers. CCDC 1504448 and 1834866. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8nj03801e

We have noted that silver(1) complexes derived from 2-thiopheneethylamine with 3-methyl-2-thiophenecarboxaldehyde or 5-bromo-2-thiophenecarboxaldehyde, and thin films prepared from them by spin and dip coating techniques, exhibited significant fluorescence³³ in the range 463–474 nm ($\lambda_{ex} = 361$ nm). Also silver(1) complexes with bis(benzimidazole): [Ag₄(1,3-bis-(benzimidazol-1-ylmethyl)benzene)₂(1,4-ndc)₂]_n, {[Ag(1,3-bis(5,6dimethylbenzimidazole-1-ylmethyl)benzene)]·(1,4-Hndc)·H₂O}_n, and {[Ag(1,4-bis(5,6-dimethylbenzimidazole)butane)·(H₂O)]·(1,4-Hndc)}_n (1,4-H₂ndc = 1,4-naphthalenedicarboxylic acid) obtained under hydrothermal conditions revealed red shifted luminescence.³⁴

The fluorescence properties of silver complexes, the possibility of using the spin coating technique for deposition of silver(1) complexes and the likely fluorescent behaviour of obtained layers prompted us to synthesize a series of silver(1) complexes obtained from different benzimidazoles, and Schiff base synthetized from 2-(2-pirydyl)ethylamine and 5-bromo-2-thiophenecarboxaldehyde. For innovative applications of benzimidazole and anthracene, we planned to synthesize molecules that contain one or both of these units linked at predetermined positions.

The new silver(i) complexes were used as precursors for thin layer deposition and their fluorescence and optical properties were studied.

Results and discussion

X-ray

Crystal data and structure refinement for complexes 1 and 2 are listed in Table 4, whereas selected bond lengths and angles in are Table 1.

X-ray crystal structure of complex $[Ag_2(epy(5-Brthca))_2(NO_3)_2]$ **1**. The asymmetric unit of **1** consists of half of the dinuclear Ag(i) complex. This unit converts to the dinuclear complex molecule by the inversion symmetry [-x - 1, -y + 2, -z + 2] (Fig. 1). Each Ag ion is bound to imine N9 atom of L1 and pyridine N1 atom of the symmetrically related ligand. In structure **1**, an interaction between Ag and oxygen atom of NO₃⁻ ion is observed, with the Ag1–O1 distance being 2.628(3) Å. Moreover, an interaction between Ag and S atoms of the brominated thiophene is observed, with Ag1–S12 distance of 2.9975(9) Å. Consequently,

Table 1 Selected bond lengths [Å] and angles [°] for 1 and 2				
1		2		
Bond lengths [Å]				
Ag1-N1	2.172(3)	Ag1-N1	2.0995(19)	
Ag1-N9	2.141(3)	Ag1-N21	2.1023(18)	
Ag1-01	2.628(3)	-		
Ag1-S12	2.9975(9)			
Angle [°]				
N9-Ag1-N1	166.91(11)	N1-Ag1-N21	175.27(8)	
N9-Ag1-O1	98.79(10)			
N1-Ag1-O1	94.30(10)			
N9-Ag1-S12	74.77(7)			
N1-Ag1-S12	101.18(8)			
O1-Ag1-S12	107.74(7)			



Fig. 1 A: Asymmetric unit of the crystal structure of dinuclear Ag(i) complex 1. Atoms constituting the asymmetric unit are labeled. Ellipsoids are plotted at 30% probability level. B: Perspective of the complex molecule along the plane of coordination.

each L1 ligand is tridentate. In this architecture, both Ag(I) ions have a distorted tetrahedral coordination environment, and $\tau_4 = 0.6$ is interpreted. The architecture of the molecule might be described as two-stairs system. Each stair is formed by the pyridine moiety and Ag ion of a asymmetric unit and the bromotiophene moiety of the symmetry related ligand. The nitrate ion is positioned on the lower stair of such pairs, limiting the axial access to the Ag ion.

The valence geometry of L1 ligand is typical for such systems. The S12–C11 and S12–C13 distances are 1.723(3) and 1.717(3) Å, respectively. The C13–Br14 bond length of 1.870(4) Å is well matched with those in similar ligands.³³

Analysis of structure **1** revealed the intermolecular C–H···O interactions, between C5–H and C10–H groups of pyridine ring or imine moiety and oxygen atoms of NO₃⁻ ions. The C5···O2[x - 1, y, z] and C10···O3[-x, -y + 2, -z + 2] distances were 3.469(3) and 3.221(3) Å, respectively. The C–H···O interactions were also detected between the C7–H, C8–H and C15–H group and NO₃⁻ ions, with a distances of C7···O1[-x - 1, -y + 2, -z + 2] of 3.415(4) Å, C8···O1[-x - 1, -y + 2, -z + 2] of 3.249(3) Å and C15···O3[x + 1, y - 1, z] of 3.321(3) Å. π ··· π interactions are observed between pyridine rings N1–C6, the π ··· π [-1 - x, 2 - y, 1 - z], with distance between the ring gravity centers being 3.831(2) Å. Also, π ··· π intermolecular interactions between thiophene ring C11–C16 and pyridine ring N1–C6[1 + x, y, z] are found, with a π ··· π distance of 3.755(2) Å.

X-ray crystal structure of complex $[Ag(bzim-anthr)_2]^+NO_3^- 2$. The asymmetric unit in the structure 2 consists of the complex cation $[Ag(bzim-anthr)_2]^+$ and the nitrate anion (Fig. 2).

The coordination sphere of Ag is almost linear, with an N2–Ag–N21 angle of $175.27(8)^{\circ}$ (Fig. 2). There is no statistically significant difference between multiple Ag–N bonds, with Ag1–N1 and Ag1–N21 distances of 2.0995(19) and 2.1023(18) Å, respectively.

The valence geometry of ligands is similar to that found in the structures of free benzimidazole and anthracene moieties. However, the effect of coordination *via* N1 is clearly visible. In the benzimidazole moiety of two ligands, the C11–N2 and C31–N22 distances are 1.345(3) and 1.347(3) Å, respectively, while those involving the coordinated atoms C11–N1 and C31–N21 are significantly shorter (1.325(3) and 1.329(3) Å, respectively). In complex **2**, C11–N1–C12 and C31–N21–C32 angles are 105.87(19) and 106.1(2)°, respectively. In contrast, the C11–N2– C17 and C21–N21–C27 angles on the non-coordinated nitrogen



Fig. 2 Asymmetric unit of the crystal structure of **2**. Ellipsoids are plotted at 30% probability level.

atoms are significantly larger (107.9(2) and 107.84(19)°, respectively). Coordination also affects the relative position of ring moieties in the ligands, with the ligand N1–C11–C9 angle and its equivalents being larger by approximately 3–4° than N2–C11–C9 angles. That difference seems to result from a repulsion between the bulky anthracene moiety and the remaining Ag(bzim-anth) fragment of the complex ion. Meanwhile, the dihedral angle between anthryl and benzimidazolyl moieties in 2 are 61.85(7) and 65.81(7)°. The dihedral angle between two benzimidazolyl rings in 2 is 73.89(8)°, and that between two anthracene moieties is 53.09(6)°.

The anthracene moieties are bent along the C1A–C4A and C5A–C8A bonds, with the respective dihedral angles between neighboring six-membered rings being 2.33(13) and $2.37(12)^{\circ}$, and the resulting angle between the peripheral rings is $4.11(13)^{\circ}$. For the second ligand, the analogous bend along C21A–C24A and C25A–C28A results in the corresponding dihedral angles of 1.87(12), 3.53(12) and $4.55(13)^{\circ}$.

In the crystal packing, $\pi \cdots \pi$ interaction is found between the anthryl six-membered rings C1A-C9 and C5-C6[-x, 1 - y, -z] with the distance between the ring gravity centers of 3.9478(15) Å. C-H··· π interactions are found between C7-H7A and C21-C22 fragment, C16-H16A and benzimidazole C33-C37[1/2 + x, 3/2 - y, 1/2 + z], C30-H30A and C1A-C9[1 + x, y, z], and C33-H33A and C25-C26[-1 + x, y, z], with H distances to the ring gravity centers being 2.82, 2.81, 2.75 and 2.86 Å, respectively. The H-bonds between benzimidazolyl N-H and nitrates are detected N2-H2B···O52[x - 1/2, -y + 3/2, z + 1/2] and N2-H2B···O54[x - 1/2, -y + 3/2, z + 1/2] and N2-H2B···O54[x - 1/2, -y + 3/2, z + 1/2], as well as in N22-H22N···O52 and N22-H22N···O53, with the N···O distances being 2.986(3), 2.930(3), 2.721(3) and 3.227(3) Å, respectively.

NMR analysis

NOE experiment

To determine the impact of substituents on deformation of the coordination plane and position of the neighboring atoms, NOE difference spectra of the studied complexes (2-4) were measured. Because of the low solubility of complex 1 in common solvents the NOE spectra of 1 were not registered.



L3 R₃=OCH₃, R₂=Br, R₁=OH, R₄=H **L4** R₂= R₄= OCH₃, R₁= R₃ =H



In a series of NOE experiments, H–N protons at 9.11 ppm H(3b) in 2, 10.43 ppm H(3) in 3 and at 12.50 ppm H(3) in 4 were saturated (cods of ligands correspond to Fig. 3). Surprisingly, there was no NOE effect observed in spectra of complexes 2 and 3 when N-H(3) protons at 9.11 ppm 2, at 13.63 ppm 3 were saturated, possibly because the nearest protons H8 and H7 in anthracene moiety and H5b in phenyl ring are most probably out of sp³ nitrogen–H distance. In the benzimidazole moiety of two ligands, the C11-N2 and C31-N22 distances were 1.345(3) and 1.347(3) Å, respectively. That resulted in the increased distances between N-H bond and hydrogens H8, H7 and H5b hydrogens, leading to the lack of NOE effect. Moreover, the NOE results of 2 suggest identical conformations of the complex in solution and in solid state. X-ray analysis confirmed the lack of H ··· H interaction between N-H and other H atoms in solid state as well. In 4, the enhancement of 7,8 protons signals after irradiation of N-H(3) protons (10.60%) was noted. Additionally, the saturation of H7,8 protons in 4 led to the enhancement of H6,9 (21%) signals; moreover, an interaction between H15 and H13 protons (74%) was observed as well. The latter can be related to the deformation of the three hydrogen atoms below or above the two phenyl rings, and to the experiment with OCH₃ signal saturation, where the interaction with H(13) and H(7,8) was registered.

The NOE analyses of the silver complexes show that the ligands adopt different conformations in the solution in comparison to the crystal structures. Since such changes would include breaking of intramolecular $H \cdots H$ interactions and overcoming the rotational energy barriers, the energy necessary for such transitions should not exceed 100 kcal mol⁻¹. This is consistent with our results of ellipsometry discussed further in the text.

Fluorescence and UV-Vis studies

UV-Vis absorption and emission spectra of the reported Ag(1) complexes were studied at room temperature in acetonitrile (Fig. S1, ESI†) and methylene chloride solutions. In case of complex **1**, the UV-Vis and fluorescence spectra were measured only in acetonitrile because of low solubility in methylene chloride. UV-Vis spectra revealed the emission bands for **1** at: 371, 302 and 230 nm, **2** at: 283, 347, 383, 364 nm, **3** at: 328, 303 and 291 nm and **4** at: 498, 326, 301 nm (MeCN). The bands registered in the region 230–303 nm are related to intra-ligand $\pi \rightarrow \pi^*$ transitions in aromatic rings, while those between 326–371 nm are related with $\pi \rightarrow \pi^*$ transitions in -C—N– group.

Complex 1 exhibits emission at 460 nm (λ_{ex} =355 nm, MeCN), and complex 2 gives strong luminescence at λ_{em} = 476 nm (λ_{ex} = 355 nm), whereas in the spectrum of 3, an intense band at λ_{em} = 490 nm was noted (λ_{ex} = 350 nm) (Fig. 4). Complex 4 exhibits strong emission band at 410 nm after excitation at 370 nm, and a band at 370 nm when λ_{ex} = 335 nm. The intensity of luminescence for complex 1 is relatively low in comparison to other complexes. This may be due to the ligand conformation in 1 and the distance between Ag···Ag centers of 4.356(2) Å. The architecture of molecule 1 was described as a two-stairs system. As a stair is formed by the pyridine moiety and Ag ion of one asymmetric unit and another by the bromotiophene moiety of the symmetrical unit ligand, any interactions between silver ions were not detected. The long distance between silver centers and the lack of intermolecular interactions prevents the Ag· · · Ag interactions enhanced emission as observed previously.¹⁶ The influence of coordination of the ligand on the fluorescence properties of disilver complexes has been already observed.^{6,24} Photoluminescence properties were closely associated with the local environments around metal ions. Moreover, the presence of $\pi \cdots \pi$ intermolecular interactions between thiophene and pyridine rings enhanced the luminescence properties of 1, as emission mostly results from ligand charge transfer transitions. The oxidation state of silver ions has minor influence on the fluorescence properties of studied compounds. Additionally, the quantum yield of fluorescence for complex 1 is the lowest in comparison to those of 2-4 silver compounds. This can be a result of the presence of two silver ions, which are known to quench the fluorescence, or conformational changes around Ag central ions in molecule 1 leading to flattening of the molecule. Yet another possibility could be weak coupling between the ring



systems in the ligand due to the presence of ethylene spacer. This hypothesis is further supported by our unpublished results, which show that in complexes 2 and 4, fluorescence bands originate from transitions: benzimidazole to phenyl ring, benzimidazole to benzimidazole and phenyl to phenyl ring. In contrast, in 3, the fluorescence bands could be from charge transfer transitions from the benzimidazole to the phenyl group and from bromine towards the benzimidazole.

In methylene chloride, the emission bands of 3 and 4 were detected at 430 nm and 410 nm (λ_{ex} = 360 nm), respectively, while in the spectrum of complex 2, two strong emission bands were registered at 420 nm and 550 nm (λ_{ex} = 380 nm) (Fig. 5). Spectra of complexes exhibit an increase in the fluorescence intensity and bathochromic shifts, which is rarely noted for Ag(1) complexes and is important for their future applications as fluorescence probes. In complex 2, interactions occur between the anthracene π electrons system and the imidazole nitrogen atoms or the C-N carbon atoms. Moreover, in 2, Ag(I) is coordinated to the imine N atom adjacent to the anthracene moiety, which suggests that the electron density redistribution might be responsible for the observed high fluorescence quantum yield and the splitting of fluorescence band. The shift in emission bands towards higher wavelengths in methylene chloride can correlate with the changes in molecular geometry of the excited state, which implies a decrease in the resonance energy and a red shift of the fluorescence band.³⁵ For complex 3, the opposite effect was noted, which can be caused by the presence of methoxy groups and bromine atoms in the structure. The fluorescence of all complexes depends on solvent polarity, which is important because tailored emission of materials can lead to potential application as optical sensors. Similar behavior was observed for 2-(phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenol.³⁵

The enhancement of luminescence for silver complexes relative to the free ligand (paper in preparation) can be related to the ligand coordination (N–Ag–N bonds) resulting in conformational rigidity and reduction of the non-radiative transitions of the excited state.³⁶ The same bathochromic shift was previously observed by us in case of $[Ag(thet(9-anthraceneca))_2]NO_3$, where thet = 2-thiopheneethylamine.³⁷ Very high intensity of the fluorescence bands, observed at room temperature, is an important and unusual phenomenon for silver(1) compounds. It should be



Fig. 5 Fluorescence spectra of complexes in methylene chloride solutions, $\lambda_{ex} = 380$ nm for **2**, 360 nm for **3** and for **4**.

Table 2Relevant photophysical data of studied compounds, ($\lambda_{\rm em}$, $\lambda_{\rm ex}$ in nm, ϕ total fluorescence quantum yield)

Compound	Solvent	λ_{ex}	$\lambda_{ m em}$	ϕ
1	Acetonitrile	385	460	0.1
2	Acetonitrile	355	476	0.53
	Methylene chloride	380	470, 560	0.78
3	Acetonitrile	350	490	0.71
	Methylene chloride	360	430	0.61
4	Acetonitrile	360	410	0.56
		335	370	0.50
	Methylene chloride	335	370	0.62

noted that luminescent silver(1) compounds usually exhibit emission at low temperature, ^{38,39} and only a few monomeric^{40–43} and polymeric^{44,45} silver(1) complexes have been reported to date, which exhibit luminescent properties at room temperature.

Quantum yields of the fluorescence in acetonitrile and methylene chloride are high for all complexes except for 1 ($\phi_{(MeCN)} = 0.50-0.71$ and $\phi_{(CH_2Cl_2)} = 0.61-0.78$)⁴⁶⁻⁴⁸ (Table 2). The highest quantum yield of fluorescence was observed for complex 2 due to the presence of anthracene ring in the structure. Generally, the quantum yields of studied ligands have decreased along with a decrease in solvent polarity. For complexes 2 and 4, the yield of fluorescence increased in methylene chloride. The polarity of solvent influences the redistribution of electrons and consequently, stabilization of the excited state in MeCN. The opposite effect was found for 3.

Fluorescence properties of the obtained materials were also studied. Upon excitation between 228 and 320 nm, the emission band between 470 and 580 nm from intraligand $\pi \rightarrow \pi^*$ transitions was noted. Bathochromic shifts in the fluorescence bands of layers in comparison to those for the compound solutions were noted (Fig. 6).

This can be a result of different pathways of non-radiative transitions and may be due to the reduced conformational flexibility of ligand in the complex. This reduction results from the restraints imposed by the substrate surface. During comparison of fluorescence properties of the new layers with our previously obtained data,³³ shifts in emission bands towards longer wavelengths is noted. This can be connected with the presence of benzimidazole rings in complexes structures. Highest intensity of



Fig. 6 Fluorescence spectra of thin layers of complexes 1, 2 and 3 on Si, λ_{ex} = 282 nm.

the emission band was observed for the layers of complex 3, compared to complex 2 ($\lambda_{ex} = 282 \text{ nm}$). This is opposite to our observations for the solutions of complexes, and can be attributed to the thickness of these layers. The film of 3, PMMA/Si is thicker than that of 2, PMMA/Si, which causes a higher concentration of the silver complex in the layer, and consequently, higher fluorescence intensity. The least intense fluorescence bands were registered for the layers of 1 and is compatible with the fluorescence emission observed for these compounds in solutions. All these layers displayed even distributions of the complexes over the silicon surface. The highest intensity band was registered for the layer obtained at 2500 rpm spin speed, with coating time of 30 s.

Thin layers of complexes

The morphology and the surface roughness of these thin films have been investigated by SEM and AFM techniques. To study the chemical composition of the films, EDS analyses were conducted for all samples.

The thin layers of complex 1 were obtained on the activated silicon substrate (first covered with one drop of PMMA). (Fig. 7), after which the silver solvent was spun on the Si(111) surface (the procedure was repeated four times). In case of complexes 2 and 3, mixtures of toluene and 2 or 3 compound were used. EDS results confirmed the presence of silver, nitrogen and carbon from silver complexes in the layers. Mappings of the films indicate uniformly distributed Ag(1) complexes over the Si(111) surface (Fig. 8c). The layers are homogenous, and the discontinuity of the surface was only sporadically noted. This was confirmed by covering the 1/PMMA/Si(111), 2/PMMA/Si(111) and 3/PMMA/Si(111) materials with a gold layer (Fig. 8a and b).



Fig. 7 SEM image of 1/PMMA/Si(111) layer. (1 in PMMA: 4.0 mg of 1 dissolved in 10 cm³ toluene, + 100 μ L 5% PMMA, at 2500 rpm for 30 s, and 3000 rpm for 10 s. The sequence was repeated 4 times).



Fig. 8 SEM image after application of a nanometer gold with palladium layer of (a) **1**, PMMA/Si layer covered with gold, and (b) **3**, PMMA/Si, magn. 100 000. (c and d) EDS mappings of **3**, PMMA/Si Ag-2.65, Br 1.58%.



Fig. 9 AFM image of 1, PMMA/Si(111), 2500 rpm 30 s, 5000 rpm 20 s \times 4.

Two dimensional (2D) and three dimensional (3D) AFM images scanned over a surface area of $1 \times 1 \mu m^2$ show a uniform and dense morphology (Fig. 9 and Fig. S6, ESI[†]). The phase images indicated a single compound covers Si(111) surface in all cases. The root-mean square (RMS) parameters were calculated from AFM images. The average roughness parameters equaled $R_q = 1.59$ nm and $R_a = 1.22$ nm for 1, PMMA/Si, and $R_q = 2.24$ nm and $R_a = 1.25$ nm for 2, PMMA/Si, which indicated smooth layers of materials. This smooth morphology reveals that the organic–inorganic hybrid coatings are well deposited on Si substrates by spin-coating method.

The average depth of the layer equals 13.23 nm for **1**, PMMA/Si and 51 nm for **2**, PMMA/Si (Fig. 9 and Fig. S6, ESI[†]).

In case of 3, PMMA/Si(111), the roughness parameters are $R_{\rm q}$ = 3.76 nm and $R_{\rm a}$ = 2.45 nm, whereas the average depth of the layer equaled 113 nm. This material also displays homogeneity of the thin, smooth layers and equally distributed compound over the silicon surface. The new layers are thinner than those previously obtained by us ([Ag(thet(3-methca))₂(NO₃)]/Si, [Ag(thet(5-Brthca))₂-(NO₃)]/Si), thickness (150-400 nm).³³ Also, the values of roughness parameters of the new materials are lower in comparison with previously observed roughness parameters of [Ag(thet(3-methca))2-(NO₃)]/Si, [Ag(thet(5-Brthca))₂(NO₃)]/Si layers (8.17-21.7 nm). Concluding from the presented results, the spin-coating procedure provides thin, homogeneous films with the complexes uniformly spread over the substrate surface. The best coverage results were obtained for the following spin coating parameters: Spin speed of 2500 rpm, time of covering at 30 s, and 3000 rpm for 30 s. Any further increase in deposition time or spin speed leads to formation of heterogeneous films, in which crystallites appear. The layers exhibit fluorescence, which in conjunction with their homogeneity, make them promising candidates for use in solar cells.

Ellipsometric analysis of the thin films

To determine the complex refractive index (\hat{n}) and thickness of the deposited films, the four phase optical model of sample was considered: Si (substrate)/SiO₂ (native oxide)/Ag complex layer. The complex refractive index is then,

$$\tilde{n} = n + \mathrm{i}k,\tag{1}$$

where, *n* is the real part of the complex refractive index and *k* is the extinction coefficient directly associated with the complex dielectric function $(\tilde{\varepsilon})$ of a material:

$$\tilde{\varepsilon} = \tilde{n}^2$$
. (2)

Optical constants of Si and SiO_2 were taken from the database of optical constants.⁴⁹ To provide the Kramers–Kronig

consistency to the optical constants, the complex dielectric functions of Ag complex layers were parameterized using a sum of Gaussian oscillators:^{49,50}

$$\tilde{\varepsilon} = \varepsilon_{\infty} + \sum_{j=1}^{m} \text{Gauss}(A_j, E_j, \text{Br}_j),$$
 (3)

where, ε_{∞} is the high frequency dielectric constant, A_j , E_j and Br_j are the amplitude, energy and broadening of the *j*-th absorption band, respectively.

Fig. 10 shows the experimental Ψ and Δ azimuths for the 2, PMMA/Si. Results for the two other samples also exhibit a very good agreement between the raw and calculated data. Thicknesses for the examined films are 15.8 ± 0.1 nm, 3.8 ± 0.1 nm and 10.4 ± 0.1 nm for layers of **1**, **2** and **3** complexes on Si, respectively.

The real components of the complex refractive indexes and extinction coefficients determined for the samples are presented in Fig. 11, where the optical constants of PMMA (taken from ref. 49) are presented for a comparison. The value of n for PMMA (a matrix material for the new samples) is about 1.5 in the non-absorbing spectral range ($\lambda > 300$ nm) and exhibits a normal dispersion in the presenting spectral range. At wavelengths longer than 500 nm, the refractive index of Ag complex layers is higher than that for PMMA, and the highest value (about 1.65) is for the sample 3, while the lowest (about 1.52) is for the sample 1. At shorter wavelengths (<500 nm), the absorption bands are visible. These features were reproduced using a sum of Gaussian oscillators. Energies (and wavelengths) of particular oscillators are summarized in Table 3. The extinction coefficient spectra of Ag complex films presented in Fig. 11b show two regions of absorption bands (300-400 nm and <300 nm) associated with $\pi \to \pi^*$ and $n \to \pi^*$ transitions in the aromatic rings and C=N group, respectively. To determine the band



Fig. 10 Experimental (dashed lines) and model based (solid lines) plots for (a) Ψ and (b) \varDelta azimuths for the **2**/Si ($\chi^2 = 2.6$).



Fig. 11 (a) Real component of the complex refractive index and (b) the extinction coefficients of the layers.

Table 3The band-gap energy (E_g) and energies of Gaussian oscillators

Sample	$E_{\rm g} ({\rm eV} {\rm nm}^{-1})$	E_1 (eV nm ⁻¹)	E_2 (eV nm ⁻¹)	E_3 (eV nm ⁻¹)	E_4 (eV nm ⁻¹)	$E_5 (\text{eV nm}^{-1})$
1/Si	$2.90 \pm 0.01/428 \pm 2$	$3.04 \pm 0.08 / 408 \pm 11$	$3.25 \pm 0.11/381 \pm 13$	$3.59 \pm 0.24 / 345 \pm 23$	$4.15 \pm 0.15/299 \pm 11$	$7.99 \pm 0.55 / \\ 155 \pm 11$
2/Si 3/Si	$\begin{array}{c} 2.95 \pm 0.02/420 \pm 3 \\ 2.83 \pm 0.02/438 \pm 3 \end{array}$	$\begin{array}{c} 3.19 \pm 0.01/389 \pm 1 \\ 3.14 \pm 0.13/395 \pm 16 \end{array}$	$\begin{array}{c} 4.87 \pm 0.02/255 \pm 1 \\ 3.32 \pm 0.17/373 \pm 17 \end{array}$	$\begin{array}{c} 13^{*} \\ 3.82 \pm 0.12 / 325 \pm 10 \end{array}$	$\frac{-}{6.52 \pm 0.33/190 \pm 10}$	



Fig. 12 The Tauc plot of Ag complex layers (1, 2, 3 means films of complexes 1, 2 and 3, respectively, deposited on Si(111)).

gap-energy of the examined specimens, the Tauc method was used.⁵¹ To extract value of the band gap-energy, the relation $(\alpha h\nu)^m$ versus $h\nu$ should be plotted, where α is the absorption coefficient, $h\nu$ is the photon energy and m is a parameter associated with the type of transition: m = 1/2 for a direct allowed transition, m = 3/2 for a direct forbidden transition, m = 2 for an indirect allowed transition and m = 3 for an indirect forbidden transition. For the prepared films, m = 1/2 was chosen. The Tauc plot for the Ag complex layers is presented in Fig. 12. The band-gap energies are 2.83 ± 0.02 eV (438 ± 3 nm), 2.90 ± 0.01 eV (428 ± 2 nm) and 2.95 ± 0.02 eV (420 ± 3 nm) for compounds 3, 1 and 2 on Si(111), respectively.

Experimental

Materials

o-Phenylenediamine (96%), 2-(2-pirydyl)ethylamine (epy) (95%), 9-anthracenecarboxaldehyde (anthr) (97%), 5-bromo-2-hydroxy-3-methoxybenzaldehyde (97%), 2,5-dimethoxybenzaldehyde (99%), 5-bromo-2-thiophenecarboxaldehyde (5-Brthca) (95%), AgNO₃ > 99.0% were purchased from Aldrich and used without further purification.

Methods and instrumentation

IR spectra were captured on a Bruker instrument using ATR technique in the range 70–4000 cm⁻¹. ¹H, ¹³C NMR spectra were collected with a Bruker AMX-400 spectrometer (400 MHz) in DMSO-d₆ against TMS. UV-Vis absorption spectra were recorded using a Hitachi spectrophotometer, in CH₃CN or CH₂Cl₂ (1×10^{-5} M) solution. The fluorescence spectra were recorded on a spectrofluorometer Gilden photonics 700 in the range 900–200 nm (at 5×10^{-4} mol dm⁻³ in MeCN or CH₂Cl₂ solution or silicon slides). Elemental analyses were carried out

using Vario EL III Elemental analyzer. Layers of complexes were deposited on Si(111) wafers (2 cm \times 2 cm), \sim 500 nm thick, using spin coating technique. Precursors were dissolved in toluene with 5% solution of PMMA and deposited on Si(111) using a spin coater (Laurell 650 SZ). The morphology and composition of obtained materials were analysed with a scanning electron microscope, (SEM) LEO Electron Microscopy Ltd, England, model 21430 VP equipped with secondary electrons (SE) detectors and an energy dispersive X-ray spectrometer (EDX) Quantax with a detector XFlash 4010 (Bruker AXS microanalysis GmbH). Morphology of the layers was also studied using SEM/FIB (scanning electron microscope/focused ion beam) Quanta 3D FEG equipped with gold and palladium sputter SC7620. Atomic force microscopy (AFM) images were captured in the tapping mode with a Multi Mode Nano Scope IIIa (Veeco Digital Instrument) microscope.

The ellipsometric azimuths Ψ and Δ were measured for three angles of incidence (65°, 70° and 75°) by means of the V-VASE device (J.A. Woollam Co., Inc.) in the spectral range from 0.62 eV to 6.5 eV (191–2000 nm).

Model quantities were varied to minimize the reduced mean squared error (χ^2) defined as:^{49,50}

$$\chi^2 = \frac{1}{N-P} \sum_j \left[\left(\frac{\Psi_j^{\text{mod}} - \Psi_j^{\text{exp}}}{\sigma_j^{\Psi}} \right)^2 + \left(\frac{\Delta_j^{\text{mod}} - \Delta_j^{\text{exp}}}{\sigma_j^{\Delta}} \right)^2 \right], \quad (4)$$

where, *N* and *P* are the total number of data points and the number of fitted model parameters, respectively. Ψ_j^{exp} and Δ_j^{exp} are experimental data, while Ψ_j^{mod} and Δ_j^{mod} correspond to the values obtained during the fitting procedure. σ_j^{Ψ} and σ_j^A are standard deviations of Ψ and Δ data. The fit procedure was performed using WASE32 software (J. A. Woollam Co., Inc.).⁴⁹

X-ray crystallography

Crystal structures of $[Ag_2(epy(5-Brthca))_2(NO_3)_2]$ 1 and $[Ag(bzim-anthr)_2]^+NO_3^-$ 2. Crystals of 1 and 2 were obtained from ethanol solution after slow evaporation. X-ray diffraction data were collected at 293(2) K with an Oxford Sapphire CCD diffractometer using Mo K α radiation $\lambda = 0.71073$ Å and $\omega - 2\theta$ method. Structures were solved by the Patterson method and refined with the full-matrix least-squares method on F^2 with the use of SHELX2014 and SHELX2017 program packages.⁵² Analytical absorption corrections were applied (CrysAlis version 171.38.43 package of programs Rigaku OD, 2015⁵³). Hydrogen atoms were located from the difference electron density maps and their positions were constrained in the refinement with appropriate AFIX commands as implemented in SHELX. Data collection and refinement processes are summarized in Table 4.

Table 4 Crystal data, structure refinement and CCDC deposition numbers for 1 and 2

	1	2
CCDC	1504448	1834866
Empirical formula	C ₁₂ H ₁₁ AgBrN ₃ O ₃ S	$C_{42}H_{28}AgN_5O_3$
Formula weight	465.08	758.56
Temperature, K	293(2)	293(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	8.7498(4)	8.7674(5)
<i>b</i> , Å	9.3160(6)	18.6110(11)
<i>c</i> , Å	10.2463(6)	20.4404(10)
α, deg	70.602(6)	90
β , deg	84.715(4)	94.806(4)
γ, deg	68.444(6)	90
Volume, Å	732.27(8)	3323.5(3)
Z	2	4
Density (calculated), Mg m^{-3}	2.109	1.516
Absorption coefficient, mm ⁻¹	4.259	0.657
F(000)	452	1544
Theta range for data collection, deg	2.483 to 28.123	2.189 to 28.527
Reflections collected	4369	23 871
Independent reflections	3185 [R(int) = 0.0256]	7662 [R(int) = 0.0554]
Completeness to theta	25.000°	25.242°
•	100.0%	100.0%
Max./min. transmission	1.000/0.4075	0.811/0.409
Data/restraints/parameters	3185/0/190	7662/0/460
Goodness-of-fit on F^2	1.010	0.814
Final R indices $[I > 2 \operatorname{sigma}(I)]$	$R_1 = 0.0393, wR_2 = 0.1079$	$R_1 = 0.0347, wR_2 = 0.0533$
R indices (all data)	$R_1 = 0.0449, WR_2 = 0.1106$	$R_1 = 0.0920, WR_2 = 0.0608$
Largest diff. peak/hole, e Å ⁻³	1.055/-1.025	0.257/-0.354

The structural data of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, and the CCDC numbers are 1504448 for **1** and 1834866 for **2**.†

Synthesis of the ligands and complexes

Details of ligands syntheses are found in ESI.†

Synthesis of complexes

 $AgNO_3 + L1 \rightarrow Ag_2L1_2(NO_3)_2$

 $AgNO_3 + L \rightarrow AgL_2NO_3$

L = L2-L4

 $[Ag_2(L1)_2](NO_3)_2$ 1. The dinuclear complex of Ag 1 was synthesized in the following manner: 0.2738 g (1.6118 mmol) AgNO₃ was added to 0.4758 g (1.6118 mmol) of ligand L1 dissolved in ethanol. Synthesis was carried out for 3 hours under reflux. Yellow crystals suitable for X-ray data collection were obtained from ethanol solution. Calc. elemental composition for C₂₄H₂₂N₈O₁₂S₂Br₂Ag₂: C 27.34, H 2.10, N 10.63, Ag 20.47%. Observed composition was: C 27.19, H 2.20, N 10.46, Ag 20.45%. Yield = 48%.

¹H NMR (400 MHz, DMSO-d₆) δ 8.37 (d, HC=N, 1H), 8.27 (HC=N, 1H), 7.21 (m, 2H), 7.16 (m, 2H), 3.77 (t, *J* = 7.0 Hz, 2H), 3.21 (t, *J* = 14.7 Hz, 2H) [ppm]; IR (KBr): 3008, 2924 ν (C-H_{Ar}), 2851 ν CH₂, 1631 ν (C=N), 1477, 1385 ν (C=C) [cm⁻¹]. UV-Vis λ (Å) [nm] in MeCN: 371(0.08), 302(0.05), 230(0.22).

 $[Ag(L2)_2]NO_3$ 2. A solution of AgNO₃ (0.030 g, 0.17 mmol) in 5 mL of ethanol was added to a solution of L2 (0.050 g, 0.17 mmol) in the same solvent and stirred at 78 °C in the dark for 2 days. The light yellow precipitate was filtered off and the resultant yellow filtrate was slowly evaporated to dryness. Yellow crystals suitable for X-ray data collection were obtained from the ethanol solution. Yield = 61%. M.p. = 240-270 °C.

[Ag(L2)₂]NO₃ 2. Calc. elemental composition for C₄₂H₂₈AgN₅O₃: C 66.49, H 3.72, N 9.23, Ag 14.21%. Found composition: C 66.12, H 4.02, N 9.29, Ag 14.19%. ¹H NMR (400 MHz, DMSO-d₆) δ 9.11 (s, 1H, H3b), 8.35 (d, *J* = 7.7 Hz, 2H), 7.98 (m, 2H), 7.74 (m, 2H), 7.71 (m, 6H); ¹³C NMR (400 MHz, DMSO-d₆) δ 149.6 C2, 136.1 C9, 134.7 C4b, 9b, 133.4 C1A, 132.3 C8A, 131.8 C10, 131.5 C4,5, 130.4 C1, 130.0 C8, 128.2 C4A, 127.7 C5A, 127.2 C3.6, 125.8 C2,7, 122.5 C8b, 122.2 C5b [ppm]. (Fig. 3) ATR IR: 2936 ν(C-H_{Ar}), 1667 ν(C=C), 1488 ν(C=N), 1464, 1334 ν(C=C), 1283, 1259 ν(C-N), 1178 [cm⁻¹]. UV-Vis λ (Å) [nm]: 383(0.357), 364(0.379), 347(0.271), 283(2.53). CH₂Cl₂: 255(2.67), 349(0.26), 366(0.32), 385(0.30).

 $[Ag(L3)_2]NO_3$ 3 and $[Ag(L4)_2]NO_3$ 4 were synthesized in the same manner as 2.

[Ag(L3)₂]NO₃ 3. Calc. composition for C₂₈H₂₂N₅O₇Br₂Ag: C 41.61, H 2.74, N 8.66, Ag 13.35%. Found composition: C 41.18, H 2.44, N 8.39, Ag 13.25%. (48% yield), m.p. = 115 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 13.63 (s, 2H, OH, NH), 7.86 (d, *J* = 2.4 Hz, 1H, H13), 7.77 (m, 2H, H6,9), 7.44 (m, 2H, H7, H8), 7.37 (d, *J* = 2 Hz, 1H, H15), 3.99 (s, OCH₃); ¹³C NMR (400 MHz, DMSO-d₆) δ 150.1 C2, 147.4 C(12, 14), 125.0 C(8,7), 121.3 C(13), 117.9 C(11), 115.0 C(6,9), 113.0 C(5), 112.10 C(4), 110.7 C(10), 57.0 OCH [ppm]. (Fig. 3). FT-IR (KBr): 3085 ν(C=H)_{Ar}, 1623 ν(C=C), 1557, 1504, 1457 ν(C=N), 1445, 1341, 1308, 1267 ν(C-N), 1250, 1237, 1215 ν(C-N), 876[cm⁻¹]. UV-Vis λ (Å) [nm]: In MeCN: 328(0.147), 291(0.200), 303(0.229) nm, in CH₂Cl₂: 229(0.26), 305(0.154) nm. [Ag(L4)₂]NO₃ 4. Calc. composition for C₃₀H₂₈N₅O₇Ag: C 53.11, H 4.15, N 10.32, Ag 15.89%. Found composition: C 53.09, H 4.20, N 10.46, Ag 15.45%. (48% yield), m.p. = 195 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.50 (s, 1H, NH), 7.77 (d, J = 3.2 Hz, 1H, H(9)), 7.72 (m, 2H, H6,8), 7.33 (m, 2H, H7, 12), 7.23 (d, J = 3.2 Hz, 1H, H15), 7.15 (m, 1H, H13), 3.94 (s, OCH₃), 3.81 (s, OCH₃). ¹³C NMR (400 MHz, DMSO-d₆) δ 153.6 C2, 151.7 C12, 149.18 C14, 132.0 C(10), 128.0 C(15), 122.8 C(7), 123.5 C7, 118.5 C8, 114.7 C11, 114.1 C12, 112.4 C6, 56.7 OCH₃, 56.1 OCH₃ [ppm]. (Fig. 3) FT-IR (ATR): 3074 ν(C-H_{AT}), 1627 ν(C=C), 1574, 1528, 1494 ν(C=N), 1452, 1360 ν(C=C_{AT}), 1337, 1307, 1276 ν(C-N), 1225, 1200, 1187, 1043 ν(C-N), 1020 [cm⁻¹]. UV-Vis λ (Å) [nm]: In MeCN: 498(0.05), 326(0.21), 301(0.22) nm, in CH₂Cl₂: 228(0.20), 303(0.21), 328(0.18) nm.

Thin films preparation

Thin layers of complexes were deposited by a spin coating technique, using rotation speeds ranging from 2000 to 5000 rpm, to modify film thickness, homogeneity and optical properties. The obtained materials were characterized with SEM/EDX, AFM, spectroscopic ellipsometry and fluorescence spectroscopy.

Two different procedures of spin-coating were carried out. In the first procedure, silicon was covered with PMMA (polymethyl methacrylate) solution, and then, the complex solution was dosed onto the PMMA/Si surface. In the second procedure, a mixture of PMMA and silver solution was applied on the silicon surface. 5% PMMA solution in toluene was used to increase adhesion of the complex solution to the silicon surface.

Conclusions

New silver(1) complexes with benzimidazole derivatives or ligand derived from 2-(2-pyridyl)ethylamine and 5-bromo-2-thiophenecarboxaldehyde were synthetized.

Structural analysis of **1** revealed a distorted tetrahedral environment of Ag with linear N–Ag–N coordination. Stairs architecture of the dinuclear molecule is observed with the benzimidazole and thiophene moieties occupying different levels. In **2**, silver(1) is linearly coordinated *via* two azomethine nitrogen atoms of two different 2-anthracene benzimidazole molecules. A dihedral angle between the two ring system of close to 70° prevents the system from global electron coupling. Therefore, the low quantum yield of **1** can be attributed to the lack of interactions between thiophene and benzimidazole. In contrast, for **2**, the high quantum yield can be related to an excited state concentrated on the anthracene moiety. In **3** and **4**, the ligands are flat and fluorescence can be caused by a transition involving both benzimidazole and substituted phenyl moieties.

High quantum yields of fluorescence for complexes in both acetonitrile and methylene chloride solvents were registered. In methylene chloride, shifts in emission towards higher wavelengths were noted and can be related to changes in the molecular geometry in the excited state, which implies decreased resonance energy; the fluorescence band is bathochromically shifted to a larger extent. Using a spin coating process thin layers of the silver complexes were obtained. The band-gap energies were 2.83 ± 0.02 eV (438 ± 3 nm), 2.90 ± 0.01 eV (428 ± 2 nm) and 2.95 ± 0.02 eV (420 ± 3 nm) for compounds 3, 1 and 2, respectively, with PMMA on Si(111). Such gaps might be due to conformational changes and breaking of the intramolecular interactions during non-radiative transitions of the excited state. This is consistent with our results from NOE experiments. The new materials exhibited fluorescence in the range 470 to 580 nm after excitation between 228 and 368 nm. This is important as it indicates the possibility of applying these materials in solar cells.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank the National Science Centre Poland for financial support (grant no 2013/09/B/ST5/03509).

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