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Behavior of UV Sensitive Zinc Complexes Revealed by Using Electrochemistry and Spectroscopy

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Synthesis, electrochemistry and spectroscopic techniques for five zinc(II) coordination complexes with a combination of tetradentate amines 1,4-bis(3-aminopropyl)piperazine (bapi), triethylenetetramine (tet) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (mtet) and thiodiacetic ($tdaH_2$) or 1,3,5-benzenetricarboxylic acid ($btcH_3$) are described. These complexes of general formulas $[Zn_2(L)_2(\mu\text{-tda})](ClO_4)_2$ and $[Zn_3(L)_3(\mu\text{-btc})](ClO_4)_3$, where L = bapi, tet, mtet, have been studied in water solution. Their stability has been studied by electrochemical methods (cyclic voltammetry and differential pulse voltammetry) by using the hanging mercury drop electrode. There were also studied interactions of zinc(II) complexes with UV radiation assessed by fluorescence spectroscopy. It was found out that three complexes ($Zn_3(bapi)_3(\mu\text{-btc})](ClO_4)_3$; $Zn_3(tet)_3(\mu\text{-btc})](ClO_4)_3$; $Zn_3(mtet)_3(\mu\text{-btc})](ClO_4)_3$), after three minutes of UV irradiation became fluorescently active (λ_{Em} = 400 nm) and fluorescence increased after each interval of UV irradiation.

Keywords: Zinc complexes; Thiodiacetic acid; Benzenetricarboxylic acid; Trimesic acid, Voltammetry; Fluorescence; Electrochemistry

1. INTRODUCTION

There is a considerable interest in a study of coordination compounds with mixed ligand donors. The compounds can be also bridged by single atoms as well as by polyatomic bridges. Various kinds of coordination modes can be thus obtained. Some of the complexes can serve as models of biological systems or they are used in medicine as antiviral, antifungal, antibacterial and anticancer agents [1-4]. Spectral and magnetic properties are also of interest as the materials can be used in many applications[5-8].

Thiodiacetic (thiodiglycolic) acid (tda) is a linear chain dicarboxylic acid with sulfur atom in the middle of the chain which can also be used for coordination to central atom. To date, many transition metal complexes involving thiodiglycolic acid were characterized by single-crystal X-ray analysis. From the X-ray study follows that the compounds can be either mononuclear, with one or two coordinated carboxylate groups, or polynuclear with tda mostly forming linear chains having uncoordinated sulfur atom or sulfur atom also involved in order to coordinate central atoms Cd(II) [9], Zn(II) [10,11], Ni(II) [12,13], Co(II) [14,15], Cu(II) [16-18] and Mn(II) [19-21]. The coordination sphere of a central atom in these systems is completed by coordination of water molecules and/or nitrogen-donor ligands.

It was also of our interest to study triangular trinuclear complexes with 1,3,5-benzenetricarboxylic acid (trimesic acid). Potentially six oxygen atoms can be coordinated to the central atoms in different coordination modes. These can be: a) tris-monodentate; b) tris-bidentate; c) chelating bidentate and bis-monodentate; d) chelating bis-bidentate and monodentate; e) chelating tris-bidentate; f) chelating/bridging bidentate and monodentate [9,22-24]. Fluorescence properties of complexes with btc have also been studied, mostly on rare earth metals and in combination with ruthenium [25-27].

In this paper, we present our results on preparation of zinc mixed ligand complexes. They all contain terminal tetradentate nitrogen ligands and carboxylate bridges among central atoms. Binuclear and trinuclear complexes have been prepared and characterized from the point of view of electrochemical and spectral behavior.

2. EXPERIMENTAL PART

2.1. Materials and methods

Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amount of these materials should be handled with great caution. All chemicals and solvents were supplied from Sigma Aldrich and were used as received. Ligands used in the paper are depicted in Fig. 1A.

2.2 Preparation of coordination complexes

2.2.1. $[Zn_2(bapi)_2(\mu\text{-}tda)](ClO_4)_2$ *(1)*

Bapi (0.2 mL, 1 mmol) was added to a stirred solution of $Zn(ClO_4)_2.6H_2O$ (0.36 g, 1 mmol) in water (50 mL). Solution of $tdaH_2$ (0.075 g, 0.5 mmol) neutralized with NaOH (0.04 g, 1 mmol) in water (5 mL) was added. Finally, pH was adjusted to 7 with addition of perchloric acid and solution was diluted with water to final volume of 100 mL.

2.2.2. [$Zn_2(tet)_2(\mu$-tda)]$(ClO_4)_2$ (2)

The preparation was similar to (**1**), only triethylenetetramine hydrate (0.2 g, 1 mmol) was used instead of bapi.

2.2.3. [$Zn_3(bapi)_3(\mu$-btc)]$(ClO_4)_3$ (3)

Bapi (0.2 mL, 1 mmol) was added to a stirred solution of $Zn(ClO_4)_2.6H_2O$ (0.36 g, 1 mmol) in water (50 mL). Solution of $btcH_3$ (0.07 g, 0.33 mmol) neutralized with NaOH (0.04 g, 1 mmol) in water (5 mL) was added. Finally, pH was adjusted to 7 with addition of perchloric acid and solution was diluted with water to final volume of 100 mL.

2.2.4. [$Zn_3(tet)_3(\mu$-btc)]$(ClO_4)_3$ (4)

The preparation was similar to (**3**), only triethylenetetramine hydrate (0.2 g, 1 mmol) was used instead of bapi.

2.2.5. [$Zn_3(mtet)_3(\mu$-btc)]$(ClO_4)_3$ (5)

The preparation was similar to (**3**), only 1,1,4,7,10,10-hexamethyltriethylenetetramine (mtet) (0.27 mL, 1 mmol) was used instead of bapi.

2.2.6. $Zn(ClO_4)_2$ (6)

Standard of zinc 72 mg $Zn(ClO_4)_2$ was added in water (25 mL)

2.3 Electrochemical analysis

Determination of zinc by differential pulse voltammetry and cyclic voltammetry was performed with 797 VA Computrace instrument (Metrohm, Switzerland), using a standard cell with three electrodes. A hanging mercury drop electrode (HMDE) with a drop area of 0.4 mm^2 was employed as the working electrode. An Ag/AgCl/3M KCl electrode was used as the reference and carbon electrode served as auxiliary. For data processing 797 VA Computrace software by Metrohm CH was employed. The analyzed samples were deoxygenated prior to measurements by purging with argon (99.999%). Acetate buffer (0.2 M CH_3COONa and CH_3COOH, pH 5) as a supporting electrolyte was used. The supporting electrolyte was exchanged after each analysis. The parameters of the measurement by differential pulse voltammetry were as follows: initial potential of -1.7 V, end potential 0.2 V, deoxygenating with argon 90 s, deposition 240 s, time interval 0.04 s, step potential 5 mV, modulation amplitude 25 mV, adsorption potential -1.7 V. Parameters of the measurement by cyclic voltammetry were as follows: initial potential of -1.7 V, first vertex potential 0.2 V, second vertex potential -1.7 V, deoxygenating with argon 90 s, deposition 240 s, voltage step 5 mV, sweep rate 1 $V.s^{-1}$, adsorption potential -1.7 V. For both electrochemical methods the volume of injected sample was 20 μL and volume of measurement cell 2 mL (20 μL of sample + 1980 μl acetate buffer). All measurements were carried out at 25±1°C.

2.4 Fluorescence analysis

Fluorescence was acquired by multifunctional microplate reader Tecan Infinite 200 M PRO (TECAN, Switzerland). Wavelength 245 nm was used as an excitation radiation and the fluorescence scan was measured within the range from 280 to 850 nm per 2-nm steps. The detector gain was set to 100. The samples were placed in UV-transparent 96 well microplate with flat bottom by CoStar (Corning, USA). 50 μL of sample was placed to each well. All measurements were performed at 25°C controlled by Tecan Infinite 200 PRO (TECAN, Switzerland). The complexes were exposed to UV radiation at 254 nm using transilluminator (VilberLourmat, Marne-la-Vallee Cedex, France). The sample area is 20 × 20 cm illuminated by 6 UV emitting tubes with power of 15 Watts each.

2.5 Size measurements analysis

The average complexes size and size distribution was determined by quasielastic laser light scattering with a Malvern Zetasizer (NANO-ZS, Malvern Instruments Ltd., Worcestershire, U.K.). Complexes distilled water solution of 1.5 mL was put into a polystyrene latex cell and measured at a detector angle of 173°, a wavelength of 633 nm, a refractive index of 0.30, a real refractive index of 1.59, and a temperature of 25°C.

3. RESULTS AND DISCUSSION

Binuclear and trinuclear amines and complexes have been prepared by the reaction of zinc perchlorate, tetradentate sodium salts of thiodiacetic or 1,3,5-benzenetricarboxylic acids. The coordination by four nitrogen atoms of used amines is well known and can be demonstrated by complex $[Cu(bapi)(\mu\text{-}NC)Ni(CN)_2(\mu\text{-}CN)Cu(bapi)](ClO_4)_2$, where copper atoms are coordinated by four N atoms of bapi and N atom of bridging cyano group in distorted square-pyramidal geometry [28]. We can expect that in the case of thiodiacetic acid binuclear complexes (**1**) and (**2**) have similar structure (proposed structure is depicted in Fig. 1B) like complexes with solved X-ray structures $[Cu_2(pmdien)_2(H_2O)_2(\mu\text{-}tda)](ClO_4)_2$, [29] and $[Ni_2(pmdien)_2(H_2O)_2(\mu\text{-}tda)](ClO_4)_2\cdot 2H_2O$, where pmdien = N,N,N′,N′′,N′′-pentamethyldiethylenetriamine [30]. In these complexes tda chain forms a bridge between metal centers. The difference between these two complexes is also in the form of coordination of carboxylate groups.

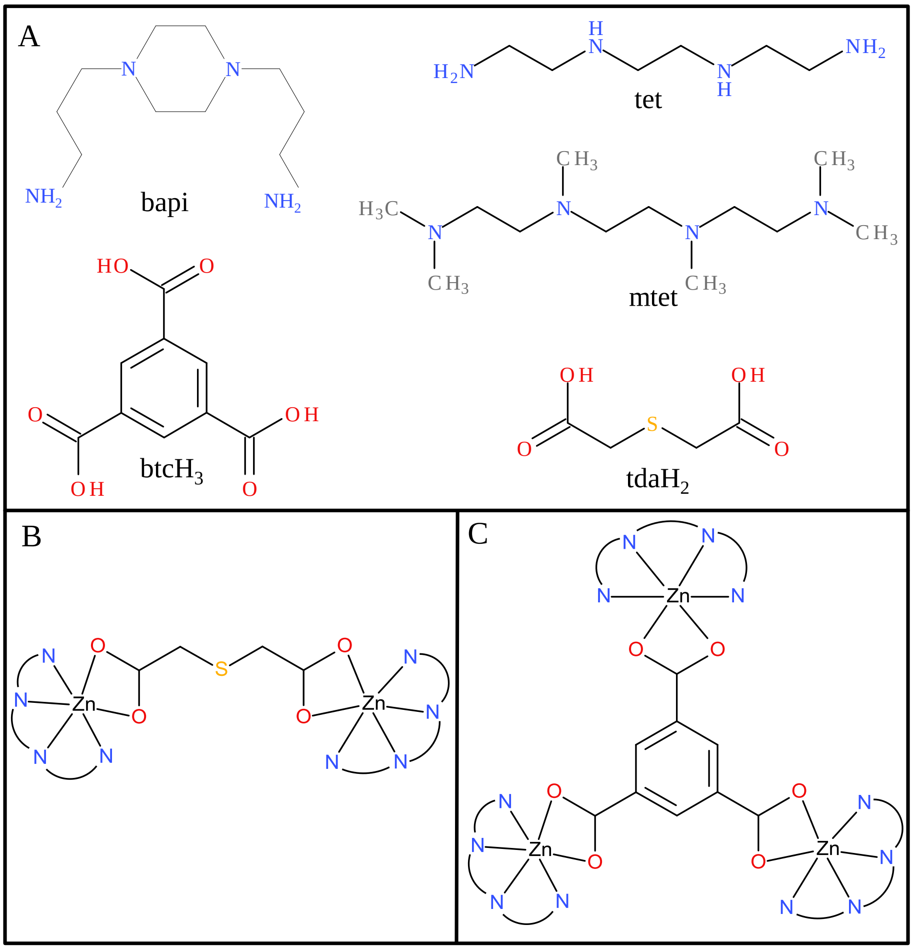

Figure 1. (**A**) Structural formulas of the ligands used. Bapi = 1,4-bis(3-aminopropyl)piperazine, tet = triethylenetetramine, mtet = 1,1,4,7,10,10-hexamethyltriethylenetetramine, $tdaH_2$ = thiodiacetic acid and $btcH_3$ = 1,3,5-benzenetricarboxylic acid. (**B**) Proposed structure of binuclear complexes with tda bridge. (**C**) Proposed structure of trinuclear complexes with btc bridge.

As copper atom prefers lower coordination number (**5**), one oxygen of carboxylate group is coordinated, in contrary to nickel complex, where carboxylate group is in bidentate chelating mode and coordination number of nickel is 6 (octahedral geometry).

Very high diversity in coordination modes for carboxylate groups of $btcH_3$ is well known, but our method of preparation and the use of perchlorate salt probably lead to formation of trinuclear zinc complexes (**3**), (**4**) and (**5**) (proposed structure is depicted in Fig. 1C). Such trinuclear complexes have been prepared and their structures have been unambiguously proved by single crystal X-ray analysis. In the case of $[Cu_3(mdpa)_3(\mu\text{-}btc)](ClO_4)_3{\cdot}4H_2O$, where mdpa = N,N′-bis(3-aminopropyl)methylamine, the three copper centers are bridged by monodentate carboxylate groups and three nitrogens of amine ligand form deformed square arrangement around each copper atom [31].

Trinuclear nickel complex of composition $[Ni_3(pmdien)_3(H_2O)_3(\mu\text{-btc})](ClO_4)_3{\cdot}4H_2O$, has btc bridge with carboxylate groups in bidentate mode [32]. In this case nickel atom is in octahedral arrangement.

3.1. Electrochemical behavior of zinc complexes

The electrochemical behavior and stability of the zinc(II) complexes (**1**, **2**, **3**, **4** and **5**) and standard (**6**) was investigated by means of cyclic voltammetry which is suitable for characterization of zinc(II) complexes and study of their electrochemical behavior (Table 1.) [33,34].

Table 1. Cathodic ($E_{p,c}$), anodic ($E_{p,a}$) potencial peak values and formal reduction potential (E°') and corresponding cathodic ($I_{p,c}$) and anodic ($I_{p,a}$) currents for studied compounds

Compound	**$E_{p,c}$ [V]**	**$E_{p,a}$ [V]**	**E°' [V]**	**ΔE_p [mV]**	**$I_{p,c}$ [nA]**	**$I_{p,a}$ [nA]**
(1)	-1.12	-0.899	-1.01	221	113	230
(2)	-1.11	-0.909	-1.01	201	119	233
(3)	-1.11	-0.899	-1.00	211	113	229
(4)	-1.11	-0.904	-1.00	206	121	246
(5)	-1.11	-0.889	-1.00	221	118	233
(6)	-1.11	-0.914	-1.01	196	126	262

The cyclic voltammetric measurements indicated in all cases one-electron reduction of the zinc(II) complex occurring at approx. -1.1 V (vs. Ag/AgCl). Measurements for Zn(II) complexes were carried out immediately after their synthesis (black single curve) and after 5 days (blue dashed curve). Fig. 2A **1-6** shows no changes in voltammograms and thus confirms the stability of studied compounds. Moreover the resistance of complexes towards UV irradiation (λ = 254 nm) was examined (samples were irradiated 5 times for 3 minutes). No changes in cyclic voltammograms were observed after this procedure (red dashed line). Presented data can be compared to starting compound $Zn(ClO_4)_2$ **(6)**, (Fig. 2-A6). All traces overlap.

Further, dependences of the accumulation time on Zn (II) complexes peak potential were investigated (Fig. 2B). In the range of 0-300 second increasing linear character of dependences can be observed according to the equations:

$E(V) = 0.0214\ t(s) + 1.6681,\ R^2 = 0.9769,\ n = 8$ (compound **1**)

$E(V) = 0.0441\ t(s) + 1.6775,\ R^2 = 0.9944,\ n = 8$ (compound **2**)

$E(V) = 0.0293\ t(s) + 1.7554,\ R^2 = 0.9668,\ n = 8$ (compound **3**)

$E(V) = 0.0387\ t(s) + 1.5957,\ R^2 = 0.9946,\ n = 8$ (compound **4**)

$E(V) = 0.0304\ t(s) + 1.5452,\ R^2 = 0.9949,\ n = 8$ (compound **5**)

$E(V) = 0.0181\ t(s) + 1.5774,\ R^2 = 0.9751,\ n = 8$ (compound **6**)

For determination of Zn(II) complexes calibration curves, the accumulation time of 240 s was chosen due to the most reproducible electrochemical signals (SD = 7.5 nA). Zn(II) complexes concentrations were changed from 0.19 to 50 $\mu g.mL^{-1}$. Linear dependence (Fig. 2C) was observed below the concentration of 6.25 $\mu g{\cdot}mL^{-1}$ where dependences were as follows:

$I(\mathrm{nA}) = 3.1668\ c(\mu g \cdot mL^{-1}) + 0.0459,\ R^2 = 0.9808,\ n = 5$ (compound **1**)
$I(\mathrm{nA}) = 3.6239\ c(\mu g \cdot mL^{-1}) + 0.9087,\ R^2 = 0.9990,\ n = 5$ (compound **2**)
$I(\mathrm{nA}) = 3.6896\ c(\mu g \cdot mL^{-1}) + 0.3279,\ R^2 = 0.9924,\ n = 5$ (compound **3**)
$I(\mathrm{nA}) = 3.4929\ c(\mu g \cdot mL^{-1}) + 0.6198,\ R^2 = 0.9964,\ n = 5$ (compound **4**)
$I(\mathrm{nA}) = 2.8438\ c(\mu g \cdot mL^{-1}) + 1.0026,\ R^2 = 0.9941,\ n = 5$ (compound **5**)
$I(\mathrm{nA}) = 2.9980\ c(\mu g \cdot mL^{-1}) + 0.5605,\ R^2 = 0.9993,\ n = 5$ (compound **6**)

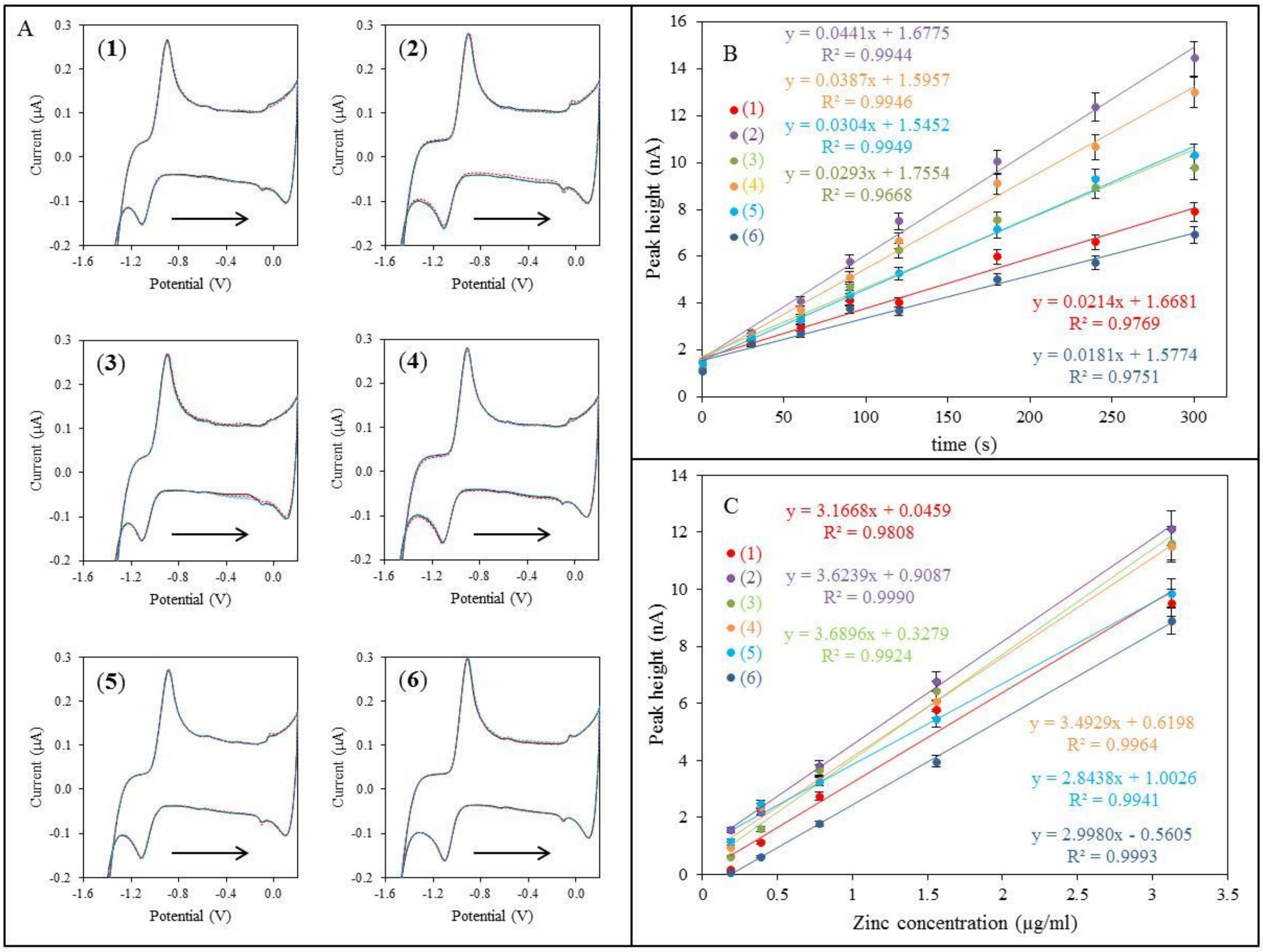

Figure 2. (A) Cyclic voltammograms of Zn(II) compounds (**1-6**) (3.125 μg.mL^{-1}) in acetate buffer pH 5.0 and 1000 mV/s scan rate using Ag/AgCl reference electrode. Black curve – measured immediately after synthesis; the dashed blue curve – measured after 5 day; the dashed red curve – measured after irradiation by UV (all curves overlap). Deposition time dependence on peak height (**B**) – 0, 30, 60, 90, 120, 180, 240 and 300 s. Calibration curves for Zn(II) compounds (**C**), measured by DPV, deposition potential of -1.7 V, accumulation time 240 s.

3.2. Fluorescence analysis

Fluorescence spectroscopy was employed for monitoring the interaction of UV radiation with five different zinc complexes (**1**, **2**, **3**, **4** and **5**) and with Zn standard solution (**6**) as control sample.

Emission spectra in the range of 300 – 800 nm with excitation wavelength λ_{Ex} = 254 nm at temperature (Fig. 3 A, D, G, J, M, P; a-before irradiation, b-after irradiation) 25°C of all five examined complexes and Zn control sample were obtained.

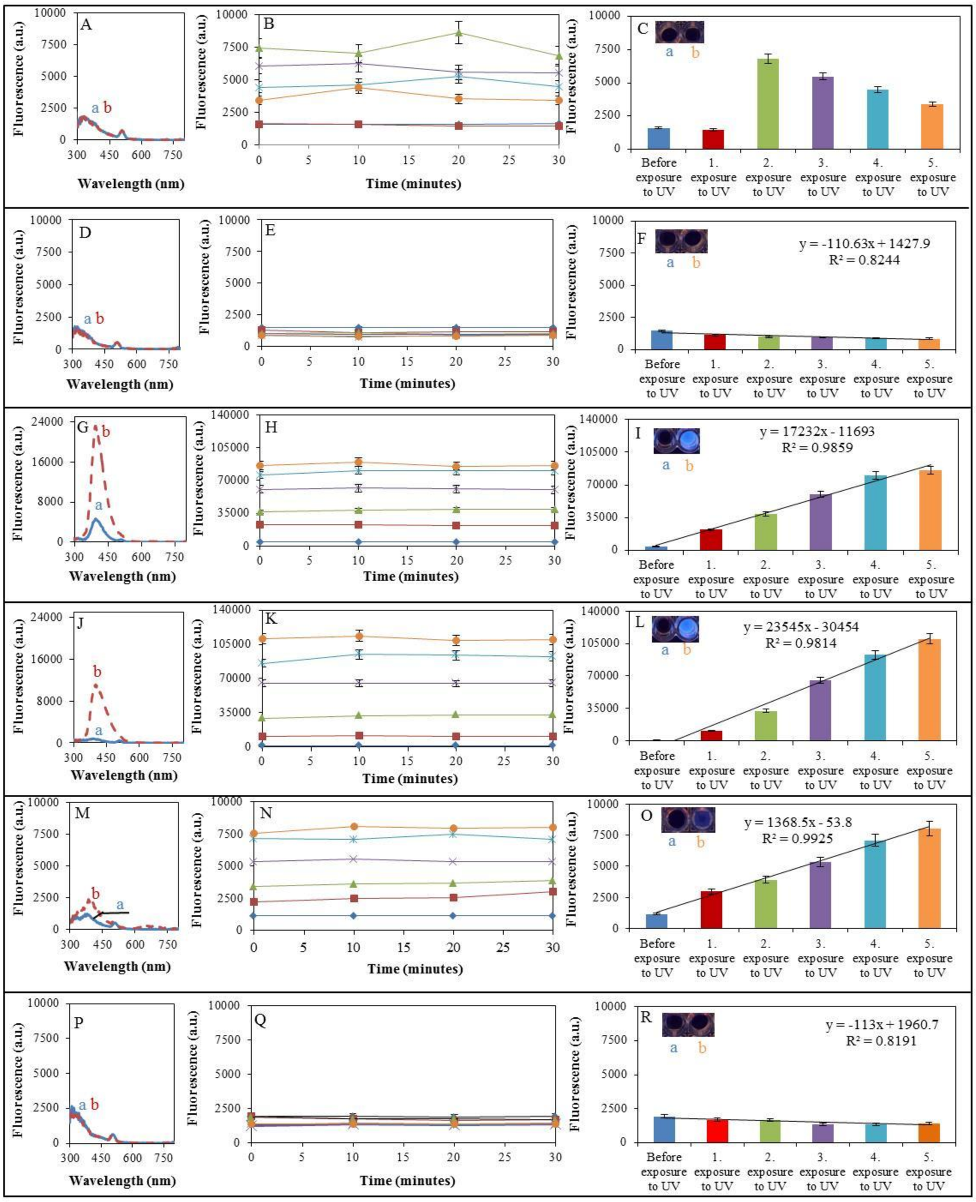

Figure 3. Emission spectra in the range of 300 – 800 nm with excitation wavelength λ_{Ex} = 254 nm of all five examined complexes and Zn control sample were obtained. **A, D, G, J, M, P)** Emission spectra of complexes (**1, 2, 3, 4, 5**) and standard (**6**), a = before UV exposure, b = after 3 minutes of UV exposure. **B, E, H, K, N, Q)** The fluorescence intensity of the complexes (**1, 2, 3, 4, 5**) and standard (**6**) recorded in time 0, 10, 20 and 30 minutes, blue line = before UV exposure, red line = after the first UV exposure, green line = after the second UV exposure, purple line = after the third UV exposure, light blue line = after fourth UV exposure and orange line = after the fifth UV exposure. **C,F,I,L,O,R)** Fluorescence intensity of the complexes (**1, 2, 3 ,4, 5**) and standard (**6**) after the 5th UV exposure and 30 minutes of waiting, real photos of complexes in transilluminator (left corner of the graphs), **a** = before UV exposure, **b** = after the 5th UV exposure. For all measurements λ_{ex} = 254 nm and λ_{em} = 400 nm was used.

Zinc complexes were exposed to UV radiation with wavelength λ_{Ex} = 254 nm for 3 minutes in the transilluminator and emission spectra of all samples were measured in time of 10, 20 and 30 minutes after irradiation to monitor the stability of the fluorescence intensity. This process was repeated five times to observe the UV dose dependency on fluorescence intensity of complexes. It was found out that the complex (**1**) does not become fluorescent after first exposition, however already second dose of the radiation caused significant increase of fluorescence. Unlike other complexes, in case of complex **(1)** was observed decreasing trend of fluorescence intensity after repeated UV doses. The signal after 2nd exposition was 4.7 times higher compared to the signal after 1st exposition. The linear decrease of the signal was observed reaching 50% after five exposition cycles. However, the acquired fluorescence was stable in time as shown in Fig. 3B. In case of complex (**2**) no effect of UV radiation was observed (Fig 3D, 3E, 3F). Nevertheless the complex (**3**) achieved very significant increase of fluorescent intensity even after the first UV exposition (Fig. 3G-a before UV, 3G-b after UV irradiation). Every other exposition caused further intensity increase (Fig. 3H, 3I). The complex (**4**) showed similar results, every exposure to UV radiation also led to the increase of fluorescent intensity (Fig. 3J-a before UV, 3J-b after UV). Every other exposition caused further intensity increase, which was stable in time (Fig. 3K, 3L). After first UV dose showed the complex (**4**) about approximately 50% lower intensity of fluorescence in comparison with complex (**3**), after the second dose has been decreased only by 18% and after the third one was the intensity of complex (**4**) already higher than of complex (**3**). An increase of fluorescence intensity after UV exposition on the complex (**5**) was also observed and every other exposure caused an increase (Fig. 3M, 3N, 3O) however in comparison with complexes (**3**) and (**4**) the signal increase was significantly lower. As expected the Zn standard control sample (**6**) did not change the fluorescent intensity after none of UV expositions (Fig. 3P, 3Q and 3R).

3.3. Size measurements analysis

The interaction of complexes (**1**, **2**, **3**, **4**, **5**) and the Zn standard (**6**) with UV radiation was subsequently monitored by size analysis. Samples were processed in the same way as in previous case (see *Fluorescence analysis*). For the measurement only final complexes after five UV doses were chosen. The particle size of the complex (**1**) was determined to 0.6 nm (±0.3 nm), Fig. 4A-a. The UV radiation probably induced an agglomeration of the complex into the higher order and the size significantly increased (Fig. 4B-b). The size of the other complexes (**2**, **3**, **4** and **5**) was determined to 0.6 nm (±0.3 nm) but only the complex (**2**) increased its size similarly like the complex (**1**) after irradiation (Fig 4B-a, 4C-a, 4D-a and 4E-a). The observed size increase in complex solution can be connected with generally known fact that Zn complexes willingly create coordination polymer structures with nonbinding interaction or reversible donor-acceptor bond [35]. It can be also given by structure flexibility of used ligands and/or by different sensitivity of groups to pH. There were no changes in electrochemical signal during electrochemical observation (cyclic voltammetry) of UV exposed complexes and thus it can be stated that so created bonds are not much strong. These results confirm the previously described expectation. On the other hand, there was completely different effect of UV radiation on complexes (**3**, **4** and **5**). The UV exposition on complexes (**3**) and (**4**) induce the shift to smaller size diameters of the particles, Fig. 4C-b and 4D-b. We assume that the reason of this shift is the separation of Zn atoms from the complex which leads to conjugation of the ligands ($btcH_3$) a subsequent fluorescent activity. The ligand ($btcH_3$) in the form of solution does not show fluorescent activity while in the solid (crystal) form does. Solid-state emission spectrum of the free $btcH_3$ ligand shows the strongest emission peak centers at λ = 370 nm [36]. Emission spectrum of complexes (**3**, **4**) shows the strongest emission peak centers at λ = 400 nm (see Fluorescence analysis). This 30 nm wide shift could be induced by Zn(II) and ligand $btcH_3$ conjugation. There is also interesting shift of most complex (**5**) particles to bigger size diameters (1 nm ±0.3nm) (**Fig. 4E-b**) but about 20% stay in original size diameter around 0.6 nm. The fluorescent intensity was then much lower in comparison with fluorescent intensity of complexes (**3**) and (**4**). The Zn standard solution (**6**) as control sample was measured (**Fig. 4F**).

It can be concluded that Zn complex cations $[Zn(H_2O)_6]^{2+}$ present in the solution creates due to hydrolytic reaction an agglomerates with the size of 250 nm (±6nm) which is in accordance with general theory. It was described that formation of polynuclear cations can be associated with a formation of hydroxide bridges [37].

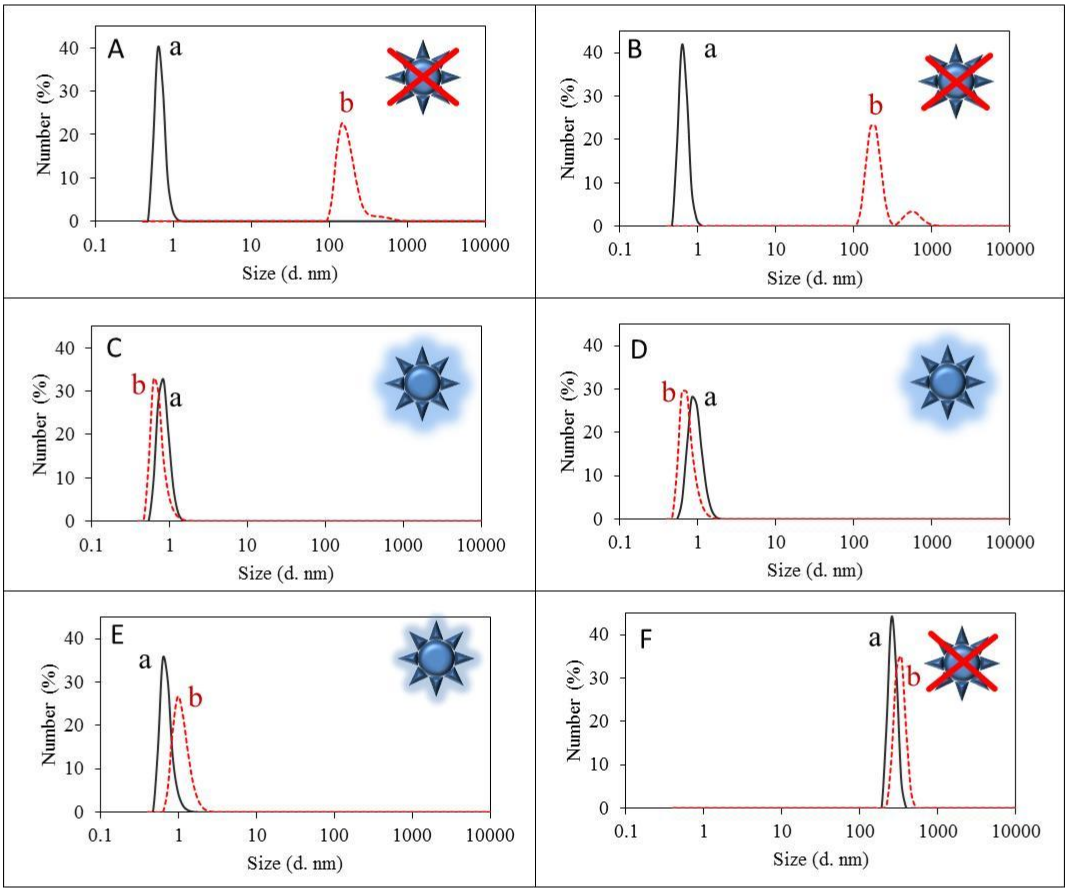

Figure 4. A, B, C, D, E and F show the size distribution of complexes (**1, 2, 3, 4, 5**) and Zn standard (**6**) measured by Zetasizer, **a** = before UV exposure, **b** = after UV exposure.

4. CONCLUSIONS

Synthesis, electrochemistry and spectroscopic techniques for five Zn(II) coordination complexes are described. It has been shown that complexes (**3** and **4**) exhibit high fluorescence activity after exposure of UV radiation. Fluorescence intensity of complex (**5**) after UV exposition was negligible in comparison with complexes (**3** and **4**). Finally in complexes (**1 and 2**) and Zn(II) standard (**3**) were not these properties observed. The ability of the complexes to change their fluorescence properties upon exposure to UV radiation can be used for constructing the UV-sensitive biosensors.

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Conflict of interest:
The authors have declared no conflict of interest.

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