

Article

Zinc(II) Coordination Compounds on Acylhydrazones of 2-Tosylaminobenzaldehyde Basis as Promising Luminescent Agents

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Abstract

Five zinc(II) complexes based on N-[[2-(p-tolylsulfonylamino)-phenyl]-methyleamino]-4R-benzamides were synthesized and characterized by elemental analysis, ESI-MS, FT-IR, ¹H NMR and single-crystal X-ray analysis. Crystallographic studies reveal that the complexes have a polymer structure in the solid state. Acylhydrazones and zinc(II) complexes demonstrate effective photoluminescence in solutions and in the solid state. Preliminary studies have shown that the studied complexes can be used as emitters in OLED devices and for the bioimaging of pathogenic processes at the cellular level.

Keywords: Zn complex; hydrazones; luminescence; OLED; bioimaging

1. Introduction

Luminescence of coordination compounds as a fundamental phenomenon is increasingly used in the most advanced technologies, including the creation of electroluminescent devices and solar panels, switching systems, and biomedical imaging [1–6]. Until recently, most of the luminescent materials described in the literature were obtained based on organic compounds, due to their variable structure [7–11]. At the same time, coordination compounds have a higher potential for enhanced efficiency and broader applications in the field of luminescent materials by combining the possibilities of modifying organic ligands with the electronic features of metals. Most of the complexes used to date are based on heavy transition metals, such as platinum(II), iridium(III), gold (I/III) and lanthanides(III) [12–18]. Unfortunately, these metals are quite rare and expensive, and consequently a crucial aim in this field is the synthesis of luminescent compounds based on less expensive and more-abundant transition metals [19]. However, the use of complexes based on widespread metals (Zn, Al, and so on) as electroluminescent materials demonstrated low-efficient luminescence, so there was a period when these compounds fell out

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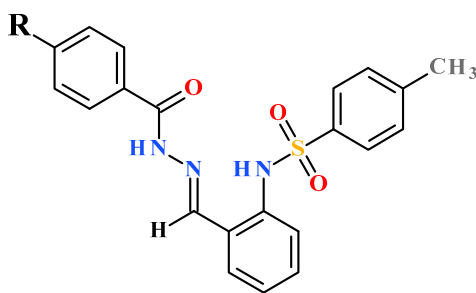
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of the focus of research. However, in the last decade, there has been a qualitative leap in the improvement in electroluminescent devices using zinc(II) complexes as emitters. Devices with high brightness and efficiency comparable to those of phosphorescent and TADF phosphors have been obtained [20,21].

Coordination compounds of zinc(II) with azomethine derivatives are the subject of interest of our group in the construction of electroluminescent architectures and fluorescent probes due to the controllable tuning of the fluorescent properties of zinc(II) complexes based on ligands [22–26]. Most of the previously studied luminescent zinc(II) complexes of azomethine derivatives were derivatives of salicylic aldehyde [27–30]. However, today, the synthetic possibilities of 2-hydroxybenzaldehydes have already been exhausted to a certain extent. Therefore, our current research is based on the use of structural analogues of salicylic aldehyde: 2-(N-tosylamino)benzaldehyde and 4-acylpyrazolone [22–26]. The luminescent properties of azomethine derivatives of these compounds have been poorly studied, but even the available results indicate their great prospects for practical use.

In this paper, we report the synthesis of zinc(II) compounds of N-[[2-(p-tolylsulfonylamino)-phenyl]-methyleneamino]-4R-benzamide (Scheme 1, R is an electron-acceptor substituent) ligands and their structural and optical properties' relationship to utilize this knowledge for the development of efficient emitters. To demonstrate the potential use of the obtained compounds, the possibilities of using the obtained compounds for creating electroluminescent devices and in bioimaging are presented.

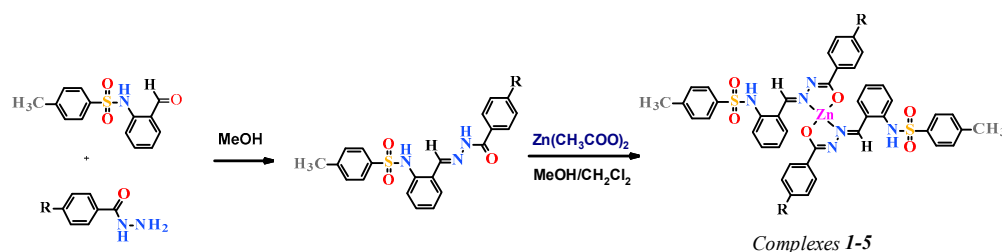


Scheme 1. Structure of N-[[2-(p-tolylsulfonylamino)-phenyl]-methyleneamino]-4R-benzamide ligands (R = H (HL¹), CH₃ (HL²), CH₃O (HL³), F (HL⁴), Cl (HL⁵)).

2. Results

2.1. General Characterization

The five hydrazone ligands (N-[[2-(p-tolylsulfonylamino)-phenyl]-methyleneamino]-4R-benzamide (where R = H (HL¹), CH₃ (HL²), CH₃O (HL³), F (HL⁴), Cl (HL⁵)) were readily prepared in a one-step procedure described yearly in the literature by the condensation of 2-(N-tosylamino)benzaldehyde with the corresponding hydrazides in a 1:1 molar ratio in anhydrous methanol solution [31]. Yields for the five hydrazone ligands varied from 85 to 94%. Target compounds, namely, 1–5 (Scheme 2), were obtained as the products of the reactions between zinc acetate and the corresponding ligands HL^{1–5}. The reactions were performed in MeOH/CH₂Cl₂, followed by recrystallization from MeOH. The elemental analyses and ESI-MS data were consistent with the calculated values and indicate a molar metal–ligand ratio of 1 to 2.



Scheme 2. Structure of zinc(II) compounds **1–5** (R = H (**1**), CH₃ (**2**), CH₃O (**3**), F (**4**), Cl (**5**)).

The complexation is accompanied by the deprotonation of the ligands with the transition to the imidole form, which is consistent with the spectral data. The ¹H NMR spectra of complexes have been recorded in DMSO-d₆ solutions to probe the solution structure (see the Supporting Information, Figures S1–S4). The complexes are stable in solutions and give a set of proton signals characteristic of the deprotonated form of the ligand. Comparison of the ¹H NMR spectra for the pair of HL¹-complex **1** (Figure 1) indicates the chemical shift values of the protons in the complex are slightly different from those observed for the non-coordinated ligand. In particular, the HC=N resonances of the complex are moved downfield (0.12 ppm), which proves the coordination between the imine nitrogen atom of the ligand and the Zn cation. A common trend is the disappearance of the acidic amide proton at 11.3–11.4 ppm in the NMR spectra of **1–5**. At the same time, the signal of the sulfamide proton (12.7–12.9 ppm) is still observed. Summarizing all of the above-mentioned facts, we claim the successful synthesis of the intended Zn(II) compounds.

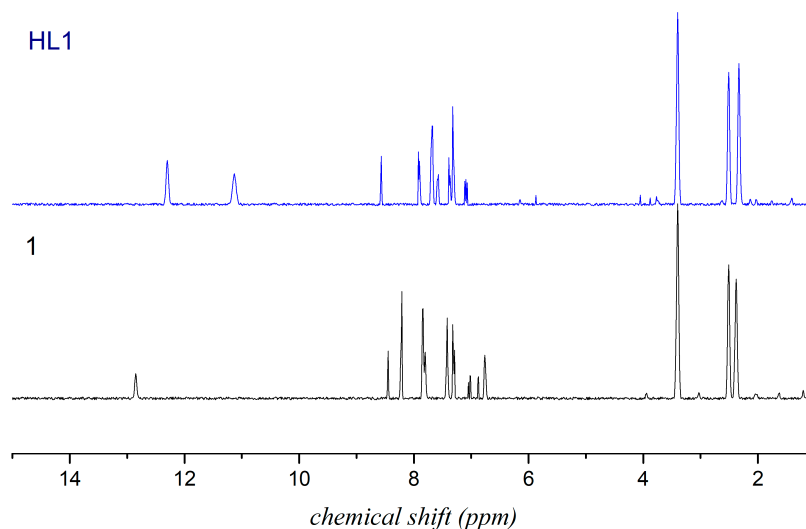


Figure 1. ¹H NMR spectra of HL¹ (**above**) and related compound **1** (**below**).

The IR spectra of compounds **1–5** were compared with those of HL¹–HL⁵ (Figures S5–S9 in the Supporting Information). The most informative bands were selected for further analysis, confirming the coordination mode and tautomeric form of the coordinated ligands. The FT-IR spectra of the ligands and the corresponding zinc(II) compound show the expected signals characteristic for functional groups. The most significant is the disappearance of the Amide-I band, which is observed for free hydrazones at 1640–1645 cm^{−1}. Instead, an intense O=C=N band appears at 1559–1568 cm^{−1}, which is consistent with the ligand transition upon coordination in the deprotonated imidole form. In addition, the C=N azomethine band shifts to a lower-frequency region by 5–9 cm^{−1}, which indicates coordination via this nitrogen atom. It is noteworthy that the valence vibration's bands of

the S=O bond are significantly split into two components at 1129–1133 and 1082–1084 cm⁻¹. The coordination mode and donor set of ligands were further confirmed by single-crystal X-ray diffraction.

The signals of the valence vibrations of C-H and N-H bonds are detected in the long-wavelength region. The No $\nu(\text{OH})$ band was found in the spectra of compounds **1–4**, indicating the absence of the coordinated solvent. At the same time, a broad OH bond vibration signal is observed for the compound **5**, which is consistent with the presence of a methanol molecule in the crystal lattice.

The thermal stability of compounds HL¹-HL⁵ was studied by thermogravimetric analysis (Figures S10–S14 in the Supporting Information). The TGA curves of compounds **1–4** are similar and seem to be independent of the substitution nature. The compounds are stable up to 265 °C (**1**), 255 °C (**2**), 277 °C (**3**), and 279 °C (**4**), corresponding to the 1% weight loss. Upon heating compound **5** in the temperature range of 30–140 °C, a gradual loss of 3.4% mass is observed, corresponding to the removal of one molecule of methanol. The desolvated sample exhibits a constant mass up to a temperature of 286 °C. Further heating of the compounds leads to a two-step decomposition and does not completely end up to temperatures of 700 °C.

2.2. Single-Crystal X-Ray Diffraction Analysis

To further understand the structures of the obtained complexes, single crystals of **1** and **2** were obtained and analyzed by single-crystal X-ray diffraction. Unfortunately, the low quality of the crystals of complexes **3–5** did not allow us to determine the molecular and crystalline structure of these compounds by X-ray diffraction analysis.

Single-crystal X-ray analysis of compounds **1** and **2** revealed that both compounds are coordination polymers. Since the crystal of compound **2** was of poor quality, its structure will not be described in detail, but the key crystal lattice parameters and bond lengths of the resulting model are given in the ESI (Table S1, Figure S15). Importantly, the obtained data indicate that the structural motif of compound **2** is similar to that of compound **1**.

Compound **1** crystallizes in the triclinic $P\bar{1}$ space group (Table S1) and the zinc atom is located at the center of inversion (Figure 2). The monomeric unit is formed by two 5-membered chelate fragments of two HL¹ in the equatorial plane, in which the metal atom coordinates the nitrogen atom of the azomethine group and the deprotonated oxygen atom of the enolate (Zn–O 2.0175(17) Å, Zn–N 2.0522(19) Å, O1–C1 1.272(3) Å, N1–N2 1.381(3) Å, N1–C1 1.344(3) Å, N2–C8 1.290(3) Å), as well as two oxygen atoms of the sulfamide group (S1–O2 1.4399(16) Å, S1–O3 1.4442(17) Å, S1–N3 1.630(2) Å, S1–C15 1.768(2) Å) of adjacent monomer fragments in axial positions (Zn–O 2.4340(17) Å). The environment of the zinc atom (ZnN₂O₄) can be described as an axially elongated octahedron. The shorter distance between Zn atoms in the chain is 7.757 Å. The polymer chain is extended along the *a*-axis. The benzoylhydrazone fragment is almost flat. The torsion angle between the phenyl and chelate cycles (N1–N2–C8–C9) is 1.1(4)°. The tosyl fragments are arranged on both sides of the polymer chain. The crystal structure of **1** is stabilized by intra- and intermolecular non-covalent interactions, including N–H ... N, C–H ... O (see Table S2) and $\pi \dots \pi$ (Cg(C2–C7) ... Cg(C15–C20) 3.9631(15) Å, α = 10.74(12)°, Cg-perp = 3.5349(10) Å) contacts.

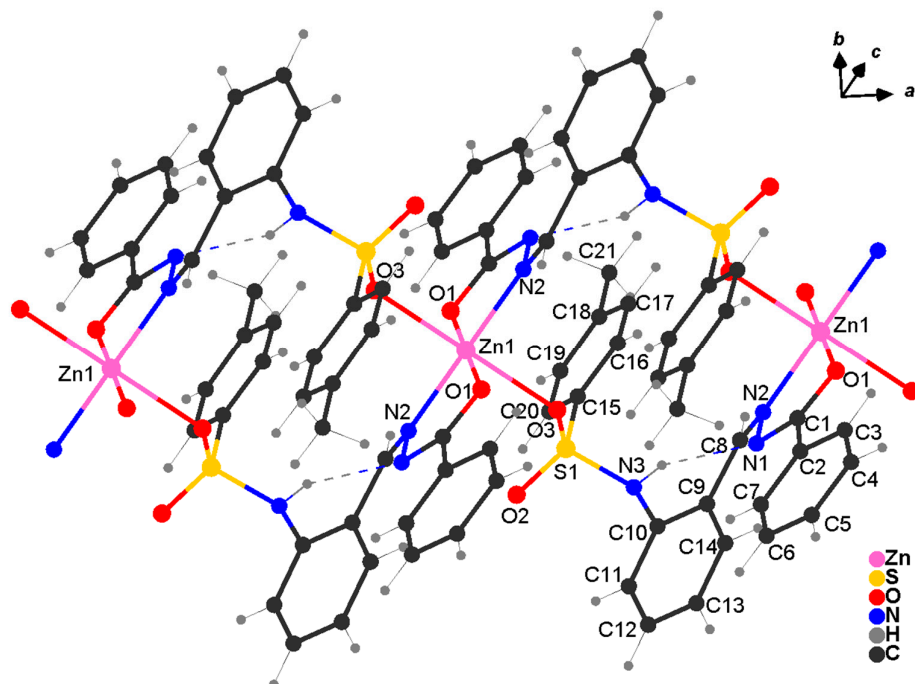


Figure 2. Crystal structure of **1**. Dotted line indicates H-bonds.

2.3. Absorption and Photoluminescent Studies

The HL¹–HL⁵ and corresponding compounds **1**–**5** were investigated via their UV–vis absorption spectra in dichloromethane solution (2.0×10^{-5} M). In the UV–vis spectra (Figure 3) of the hydrazones, a higher-energy band at 297–301 nm and lower-energy band at 324–330 nm are displayed. The spectra of compounds **1**–**5** show similar absorption profiles, that is, broad bands with a maximum absorption wavelength at 304–306 nm, and two satellite maxima at 293–294 and 321–323 nm as shoulders. The position of the absorption maximum slightly depends on the electronic nature of the substituents. Experimental absorption spectra of complexes **1**–**5** in DMSO are provided in Figure S16 (see Supporting Information). They show a profile similar to that in CH₂Cl₂ solutions, with a maximum in the 300–310 nm range, thereby validating the use of the PCM–DMSO model for the theoretical calculations on complex **1** (see Section 2.4).

Figure 3. UV–vis absorption spectra of HL¹–HL⁵ (left) and compounds **1**–**5** (right) in CH₂Cl₂ solution at 2×10^{-5} M at room temperature.

Following the absorption studies of HL¹–HL⁵ and **1**–**5**, their emission spectra were recorded in solution and in the solid state (Figures 4–6). Photoexcitation of HL¹–HL⁵ in dichloromethane at the lowest energy band (350 nm) leads to a dual emission in the visible

spectrum with peaks around 419–424 nm and 547–595 nm (Figure 4b). The low-energy emission band, exhibiting an unusually large Stokes shift, was attributed to the emission from the excited phototautomer, specifically to the radiative transition of the keto-amine form. In contrast, the high-energy band at 419–424 nm, with a smaller Stokes shift, can be assigned to the emission from the locally excited state of the enol-imine form of the ligand. Proton transfer occurs from the NH sulfamide group to the imine nitrogen along the intramolecular six-membered H-bonded ring. The emission decay profiles were fitted with a biexponential curve, indicating short (>1 ns) and long (3.3–5.8 ns) components (Table 1).

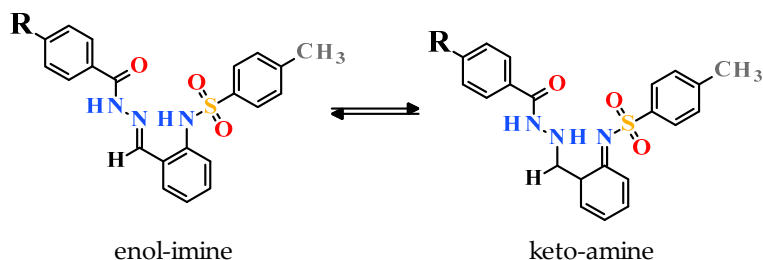
It should be noted that the high-energy band is insensitive to the nature of the substituent in the benzene ring. At the same time, the maximum of the low-energy emission band depends on the substituent. In all cases, the introduction of substituents leads to a bathochromic shift in the emission maxima; meanwhile, electron-donating substituents ($-\text{CH}_3$ and $-\text{CH}_3\text{O}$) lead to a greater shift compared to halogen substituents.

Table 1. Photophysical properties of acylhydrazones HL^1 – HL^5 and related **1**–**5** complexes.

	Absorbance (CH_2Cl_2)	Emission (Solution)						Emission (Solid)			
		CH_2Cl_2			$\text{DMSO}/\text{H}_2\text{O}$						
		λ_{max}	QY	τ	λ_{max}	QY	τ	λ_{max}	QY	τ	CIE
HL^1 R-H	297, 325	421, 593	1.1	0.81 4.31	462	3.3	3.84	437, 552	6.5	2.15 *	0.37; 0.44
1 R-H	295, 305, 317	472	6.8	5.49	453	12.5	4.42	474	33.7	5.29	0.15; 0.24
HL^2 R- CH_3	298, 322, 330	420, 548	1.0	0.98 4.63	463	3.0	3.58	563	5.1	2.88 *	0.45; 0.42
2 R- CH_3	296, 306, 317	468	7.1	5.63	456	11.2	4.81	470	22.9	5.25	0.15; 0.25
HL^3 R- OCH_3	301, 330	420, 584	2.8	0.85 4.27	463	5.6	3.18	441, 468, 566	8.3	2.99 *	0.32; 0.39
3 R- OCH_3	297, 306, 320	457	8.7	6.06	446	14.4	4.75	461	21.1	5.52	0.15; 0.17
HL^4 R-Cl	290, 299, 322	421, 544	2.6	0.88 4.93	463	4.2	4.02	438 546	6.2	2.49 *	0.34; 0.42
4 R-Cl	294, 304, 320	469	7.9	5.73	446	10.8	4.34	477	25.8	4.65	0.16; 0.26
HL^5 R-F	301, 322, 330	422, 588	1.8	0.77 4.85	462	2.8	3.44	441 467 566	3.9	2.69 *	0.37; 0.43
5 R-F	295, 304, 318	467	6.3	5.80	447	8.0	4.21	477	24.8	4.85	0.16; 0.28

* Average lifetime (τ_{av}) calculated by using the following equation $\tau_{\text{av}} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$.

It should be noted that the transition from nonpolar methylene chloride to the polar DMSO–water medium leads to the realization of single-band fluorescence with a maximum at 462–463 nm (Figure 4a). It is obvious that the polar solvent stabilizes only the enol-imine form (Scheme 3), which leads to the observation of only one band in the spectrum.



Scheme 3. Keto-enol tautomerism.

The keto-amine form can be stabilized by changing the pH of the solution. Thus, in the weakly acidic medium, the enol-imine form dominates with a maximum at 465 nm, while in a weakly alkaline medium, a bathochromic shift in the emission maximum to 511 nm is observed due to the transition of the acylhydrazone to the keto-amine form [31].

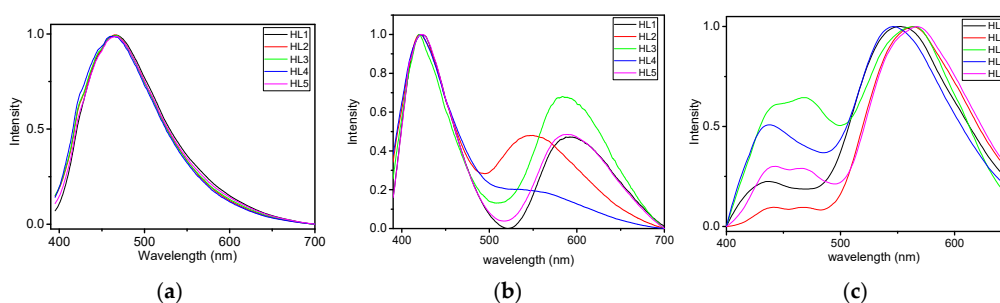


Figure 4. The luminescent emission spectra of HL¹–HL⁵ in DMSO–H₂O solution (a); CH₂Cl₂ solution (b); and solid state (c).

The donor atoms of acylhydrazones involved in proton transfer are also involved in the coordination of the zinc atom, causing the destruction of the hydrogen bond network, which, in turn, leads to the frustration of proton transfer in the emission spectra of the complexes. The changes in the fluorescence emission spectra of HL¹ at pH ~7.5 induced by the addition of Zn(NO₃)₂ in DMSO-H₂O (3:1, *v/v*, λ_{ex} = 390 nm) are depicted in Figure 5b. The maximum of the fluorescence emission band of HL¹ shifts from 511 nm in an ion-free solution to 462 nm in the presence of Zn²⁺ and is accompanied by a 4-fold increase in intensity (Figure 5b). Under UV light, bright luminescence changes after the addition of zinc ions are easily observed with the naked eye. The emission response of HL¹ in the presence of other metal ions (Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Fe³⁺, Ni²⁺, Co²⁺, Pb²⁺, Mn²⁺) leads either to the quenching of luminescence or does not induce noticeable spectral change. This indicated that the obtained acylhydrazones HL¹⁻⁵ could serve as a promising fluorescent probe for Zn²⁺.

A nonlinear curve fitting the fluorescence intensity data using the equation [32]

$$I = \frac{I_{max}[Zn^{2+}]^n + I_{min}K_d}{[Zn^{2+}]^n + K_d}$$

recorded as a function of $[\text{Zn}^{2+}]$ yields values of K_d of $6.8 \cdot 10^4 \text{ M}^{-1}$ and $n = 0.57$. Job's plots [33] gave an n value close to 0.5, similar to the titration fitting data, which indicated a 2:1 stoichiometry between HL¹ and Zn^{2+} .

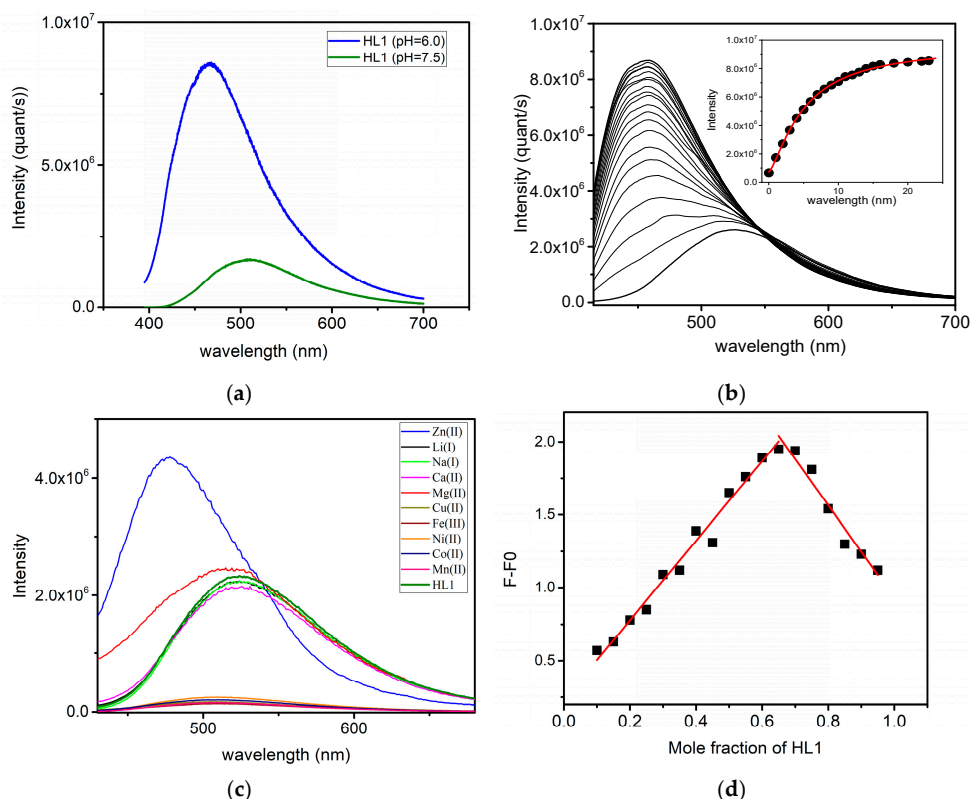


Figure 5. (a) Emission spectra of HL¹ at different pH; (b) the Fluorescence spectra of HL¹ (20 μM) in the absence and presence of Zn(NO₃)₂ (0–12 μM) in DMSO-H₂O (3:1, v/v) HEPES 10 mM, pH = 7.5). Inset: Emission intensity vs. Zn²⁺ concentration; (c) emission spectra of HL¹ (50 μM) in the presence of various metal ions; (d) Job's plot for HL¹ with Zn²⁺ in DMSO-H₂O (3:1, v/v) HEPES 10 mM, pH = 7.5).

In DMSO solution, the single emission bands are observed at 446–457 nm for complexes **1–5** (Figure 6b), respectively. Due to the similarity in the emission bands with that of the corresponding ligand, the emissions of these zinc(II) complexes may be attributed to the π - π^* intraligand transitions. In solution, the maxima emission peaks are blue-shifted 6–16 nm compared to those of the corresponding ligand, which may be attributed to the coordination of hydrazone to the metal centers [34]. A trend is observed in λ_{em} with $2 < 1 < 3 \approx 4 \approx 5$, which is consistent with the electron-donating ability ($-\text{CH}_3 < \text{H} < -\text{OCH}_3 \approx \text{F} \approx \text{Cl}$). The electron-donating effect descended the energy difference between HOMO and LUMO, leading to λ_{em} shifting. The luminescence decay profiles of the zinc(II) complexes **1–5** were measured at their optimal excitation wavelengths. A general trend is that the luminescence lifetimes for complexes **1–5** in solution at 298 K are longer than those of the corresponding hydrazones HL¹–HL⁵. The most obvious observation is that the lifetime of complex **1** ($\tau = 4.75 \mu\text{s}$) is 1.5-fold to the corresponding ligand HL¹ ($\tau = 3.18 \mu\text{s}$) in DMSO solution. This is attributed to the more stable structure and interaction upon coordination.

Further studies were focused on the photoluminescence in the solid state. Figure 4c shows the normalized luminescence spectra of the crystalline solids of HL¹–HL⁵ at ambient temperature. Upon excitation at 365 nm, the studied hydrazones showed weak dual fluorescence (quantum yield 3.9–8.3%) in the visible region, i.e., blue fluorescence at 440–470 nm and yellow fluorescence at 545–565 nm (Table 1) as a result of the keto-amine and enol-imine forms' emission.

Excitation at 360–380 nm of the polycrystalline samples of **1–5** leads to brilliant blue emissions. The emission wavelengths are blue-shifted compared with those in solution

(Figure 6c). In contrast to the luminescence of acylhydrazones, the spectra of the compounds contain a single maximum located at 461–477 nm with CIE coordinates of (0.15–0.16; 0.17–0.24). The absolute fluorescence quantum yields a range from 21.1 to 33.7%. The highest quantum yield in the series is exhibited by compound 1.

These results indicate that complexes **1–5** exhibit an excellent luminescence emission in the solid state; at the same time, they are a poor emitter in dilute solution, which is close to the properties described by the aggregation-induced emission concept that arose from the restriction of intramolecular rotation in crystals [35–37].

The lifetime decay curves of **1–5** in solid can be well-fitted into a monoexponential function while the luminescence decay of ligands is described by a biexponential function state (Figures S17–S21). The luminescence lifetimes of the ligand and corresponding complexes **1–5** in the solid state ($\tau_{av} = 2.15$ – 2.99 ns for HL¹–HL⁵; $\tau = 4.65$ – 5.52 ns for Zn complexes **1–5**) are longer than those in solution, which might be explained by the fact that there is a less polar nature in the solid-state environment.

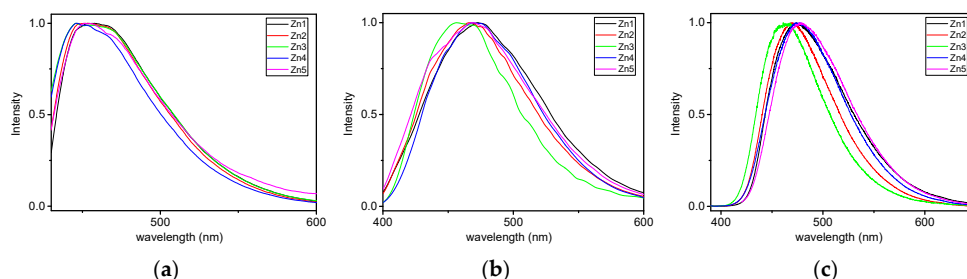


Figure 6. The luminescent emission spectra of **1–5** in DMSO–H₂O solution (a); CH₂Cl₂ solution (b) and solid state (c).

2.4. Computational Studies

TD-DFT calculations (B3LYP/6-31G(d,p)) provide a detailed interpretation of the nature of the electronic transitions responsible for the formation of the long-wavelength absorption band in the UV–vis spectrum of **1**. Each of the two symmetrical ligands in **1** can be conditionally divided into two fragments: diazenyl(phenyl)methanol (named DP) and 4-methyl-N-(o-tolyl)benzenesulfonamide (named MB). An analysis of the electron density localization on the frontier molecular orbitals reveals the following.

The HOMO-1 ($E = -6.132$ eV) is a π -orbital delocalized between the DP (63%) and MB (30%) fragments of ligand **1**. The HOMO ($E = -6.120$ eV) is a π -orbital with a similar energy, also delocalized between the DP (63%) and MB (31%) fragments of ligand **2** (Figure 7). Thus, the HOMO and HOMO-1 are practically degenerate in energy but are spatially localized on different, symmetrically equivalent ligands (denoted as π_1 and π_2 , respectively). The LUMO ($E = -1.889$ eV) and LUMO + 1 ($E = -1.862$ eV) also form a close-energy pair of π^* -orbitals. The LUMO is delocalized between the MB (52%) and DP (43%) fragments of ligand **1** (π_1^*), while the LUMO + 1 is delocalized between the corresponding fragments of ligand **2** (π_2^*).

Based on this analysis, the character of the four low-energy electronic transitions responsible for the appearance of the absorption band with a maximum at ~ 300 nm (Table 2) can be precisely described. The transitions $\pi_1 \rightarrow \pi_1^*$ ($H-1 \rightarrow L$) and $\pi_2 \rightarrow \pi_2^*$ ($H \rightarrow L + 1$) exhibit an intraligand ($\pi \rightarrow \pi^*$) character (ILCT), as the electron density is redistributed within the same ligand. The transitions $\pi_2 \rightarrow \pi_1^*$ ($H \rightarrow L$) and $\pi_1 \rightarrow \pi_2^*$ ($H-1 \rightarrow L + 1$) correspond to ligand-to-ligand charge transfer (LLCT), since the electron moves from the π -orbital of one ligand to the π^* -orbital of the other. The results of the TD-DFT calculations (Table 2) show that the observed band results from strong configuration interaction between these transitions, caused by the near-degeneracy of the orbital pairs π_1/π_2 and

π_1^*/π_2^* . The excited states S_1 and S_2 represent a mixture of ILCT and LLCT transitions, which accounts for their high intensity (large oscillator strength f values). In contrast, the S_3 and S_4 states are characterized by a predominant LLCT character (dominating contributions from the $\pi_2 \rightarrow \pi_1^*$ and $\pi_1 \rightarrow \pi_2^*$ transitions, respectively) and are weak in intensity. It should be noted that the calculated UV–vis spectrum for **1** agrees well with the experimental absorption spectrum measured in DMSO solution (Figure 7a), confirming the adequacy of the chosen model.

Table 2. Calculated absorption wavelengths (λ), energies (E), oscillator strengths (f), involved molecular orbitals and their contributions for different electronic transitions in complex **1** according to TD-DFT calculations. Calculations were performed including solvent effects (DMSO) using the polarizable continuum model (PCM).

State	$\lambda_{\text{cal}}, \text{nm}$	E, eV	Electronic Transitions, (Contribution, %) ^a	f	Character (Assignment)
S_1	307.5	4.033	$\pi_1 \rightarrow \pi_1^*$ (ILCT, 69%) + $\pi_2 \rightarrow \pi_2^*$ (ILCT, 22%) + $\pi_2 \rightarrow \pi_1^*$ (LLCT, 8%)	0.48	Mixed ILCT/LLCT
S_2	305.4	4.060	$\pi_2 \rightarrow \pi_2^*$ (ILCT, 64%) + $\pi_2 \rightarrow \pi_1^*$ (LLCT, 15%) + $\pi_1 \rightarrow \pi_1^*$ (ILCT, 11%)	0.42	Mixed ILCT/LLCT
S_3	299.5	4.140	$\pi_2 \rightarrow \pi_1^*$ (LLCT, 79%) + $\pi_1 \rightarrow \pi_1^*$ (ILCT, 17%)	0.05	Dominant LLCT [$\pi_2 \rightarrow \pi_1^*$]
S_4	297.2	4.172	$\pi_1 \rightarrow \pi_2^*$ (LLCT, 79%) + $\pi_2 \rightarrow \pi_2^*$ (ILCT, 17%)	0.01	Dominant LLCT [$\pi_1 \rightarrow \pi_2^*$]

^a π_1/π_1^* : π - and π^* -orbitals localized on ligand 1 (corresponding to the HOMO-1 and LUMO orbitals), π_2/π_2^* : π - and π^* -orbitals localized on ligand 2 (corresponding to the HOMO and LUMO + 1 orbitals).

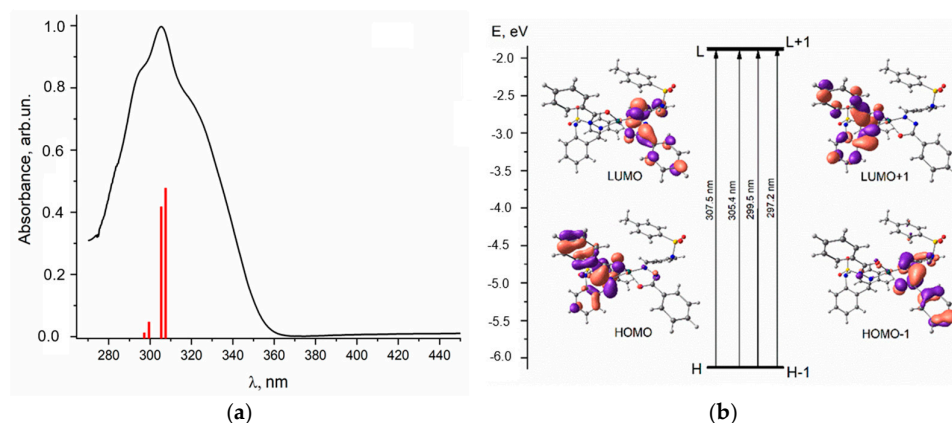


Figure 7. (a) Comparison of experimental (solid black line) and theoretical (vertical red bars) UV–vis spectra of **1**. The red bars represent the positions and relative intensities (oscillator strengths) of electronic transitions obtained from TD-DFT calculations. (b) Schematic representation of the frontier molecular orbitals involved in the low-energy transitions. The diagram shows the orbital energies and isosurfaces, with arrows indicating the primary electronic transitions and their corresponding calculated wavelengths.

2.5. Electroluminescence Studies

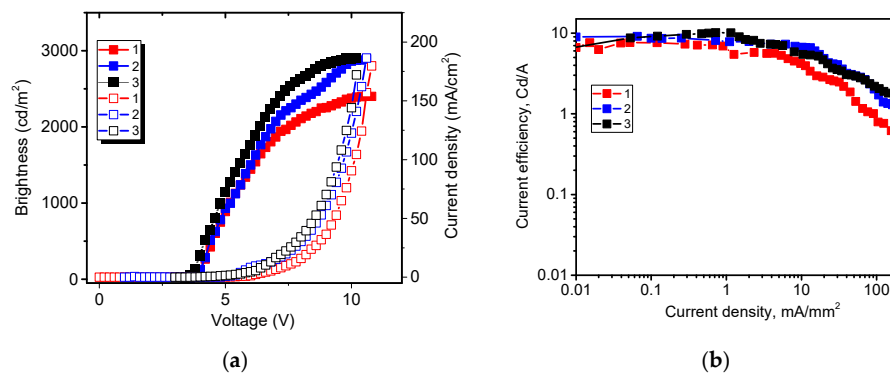
To evaluate and compare the EL properties of these compounds, compounds **1**, **2**, and **4** were selected as emitting dopants for OLED fabrication due to their favorable processing characteristics and high emission efficiency. The device architecture was ITO/MoO₃/TAPC/(compound + host matrix)/TSPO1/TPBi/LiF/Al. Here, a combination of ITO/MoO₃/TAPC (TAPC-1,1-bis[(di-4-tolylamino)phenyl]cyclohexane) was utilized as

the hole injection layer. TSP01 (diphenyl [4-(triphenylsilyl)phenyl]phosphine oxide), TPBi (2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) and LiF were used as hole-blocking, electron transport layers and electron injection material, respectively, to ensure an optimal balance of charge carriers in the emissive layer. The non-doped device exhibited poor electroluminescent brightness, likely due to imbalanced charge carrier injection and transport in the emissive layer [38]. Therefore, the synthesized compounds were used as emitting dopants at 20 wt% concentration in mCp-1,3-bis(carbazol-9-yl)benzene as the host matrix [39]. The choice of host matrix was based on the alignment of HOMO-LUMO energy levels with those of the adjacent layers and the emitter molecules, ensuring efficient charge transport, good film-forming properties, and high thermal stability. Following the literature procedures [40], the frontier orbital energies of the compounds were estimated from electrochemical potentials and UV-vis data. The HOMO/LUMO levels were determined as 5.42/2.33 eV for **1**, 5.41/2.32 eV for **2**, and 5.42/2.33 eV for **4**. The frontier orbital energy levels of the others used in the devices are referenced to the literature [39]. The schematic energy-level diagram in eV of OLED devices fabricated in this work is shown in Figure 8c.

The electroluminescence spectra of the devices A, B and C and their characteristics are shown in Figure 8a,b and summarized in Table 3. The excitons in three devices are recombined and confined within the emitting layer, exhibiting similarly strong sky-blue emissions with peak wavelengths at 473 nm for device A (**1**), 472 nm for device B (**2**), and 475 nm for device C (**4**). The EL spectra do not contain signals from the host or other layers [41,42], indicating that the emission originates entirely from the in situ formed zinc(II) complexes. Moreover, the observed peak position of the emitted light is independent of the applied voltage.

A maximum brightness above 2400 cd m⁻² was observed for all OLEDs. As shown in Figure 8a, the current density and luminance increase with the applied voltage. Among the three devices, device C achieved the highest efficiency with a low turn-on voltage of 3.4 V, maximum CE of 10.1 cd/A, an external quantum efficiency (EQE) of 3.1%, and a power efficiency (PE) of 2.1 lm W⁻¹, highlighting the influence of the compound structure on electroluminescent performance.

Although the data obtained are not record-breaking for zinc(II) complexes [23], due to the simplicity of the emitter synthesis and the possibility of increasing the efficiency by varying the structure of the compounds, **1–5** are promising materials for creating OLED devices.



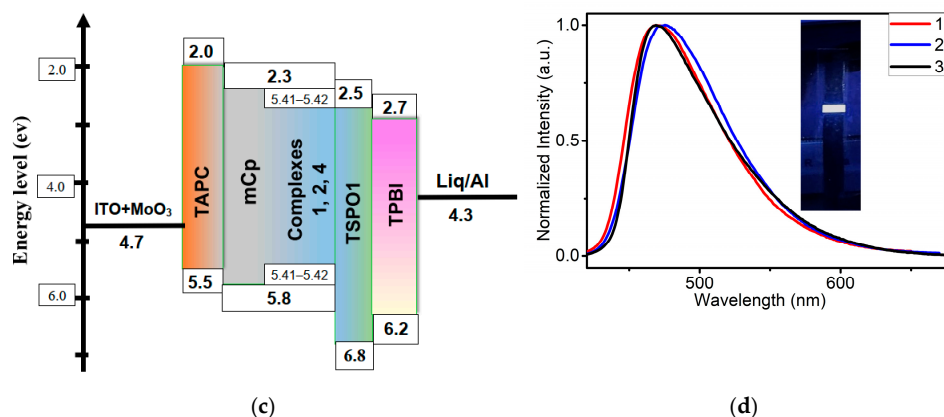


Figure 8. (a) Brightness and current density as a function of applied voltage of devices; (b) CE as a function of luminance; (c) energy diagram of the multilayer devices architecture; (d) electroluminescence spectra of OLED devices.

Table 3. Electroluminescence characteristics of devices A–C.

Device	Turn-on Voltage (V)	Luminance (cd/m ²)	CIE Coordinates	CE (cd/A)	EQE (%)	PE lm/W
A (1)	3.6	2400	0.15, 0.22	7.6	2.4	1.6
B (2)	3.6	2890	0.16, 0.22	9.0	2.8	1.9
C (4)	3.3	2910	0.15, 0.23	10.1	3.1	2.1

2.6. Bioimaging Studies

High fluorescence activity combined with high solubility in polar solvents allows the use of synthesized compounds for bioimaging. It is known that one of the markers of cancer cells is a significant decrease in the concentration of zinc(II) cations [43–45]. Given the high sensitivity of the HL/ZnL₂ pair to the zinc content, we counted on the possibility of the visual control of the ratio of cancer and healthy cells. PC-3 cells, which are often used as test systems for oncological prostate diseases, were used as an object. The experiment used visual monitoring of the fluorescent signal of cancer and healthy (normal) human prostate cells. During the experiment, the cells were incubated with a solution of HL¹ (5 μM) in a HEPES buffer and further treated by ZnCl₂ (1 μM) solution. Confocal images of normal and tumor cells after treatment with the test system are shown in Figure 9. It turned out that the color and intensity of the fluorescence of normal and tumor cells differ significantly, i.e., intracellular emission of normal cells is blue-shifted compared with PC-3 cells, reflecting reduced intracellular zinc content in tumor cells. This fact indicates that the proposed probe system reacts effectively to the intracellular zinc levels and can be used for cancer diagnostics after more detailed investigations.

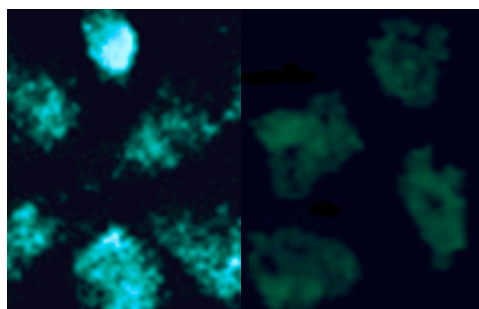


Figure 9. Fluorescence colocalization images of healthy (normal) human prostate cells (left) and PC-3 cells (right) incubated with HL¹ and Zn²⁺ probes.

In addition, an urgent promising area of use of luminescent compounds is the diagnosis of heart diseases, in particular, the visualization of ischemic (necrotic) myocardial tissues. To assess the suitability of zinc(II) compounds as an imaging agent using luminescent microscopy, sections of ischemic myocardium were used, with the capture of tissues undamaged by ischemia (positive control) (Figure 10). Histological sections of ischemic myocardium with a thickness of 10 microns were treated with 1 μ M of **3** solution and kept for staining for 24 h at room temperature. The luminescence of the fixed material after interaction with the substance was evaluated using a luminescent microscope using a digital camera "MC-6.3". As the conducted studies have shown, the studied substances make it possible to clearly visualize ischemic (necrotic) and living myocardial tissues. At the histochemical level, there is a clear differentiation in myocardial cells in the ischemic myocardium: living and necrotic cells are clearly visually and instrumentally differentiated by the intensity of the glow. Thus, further research can formulate clear methodological recommendations for use in biological and medical practice.

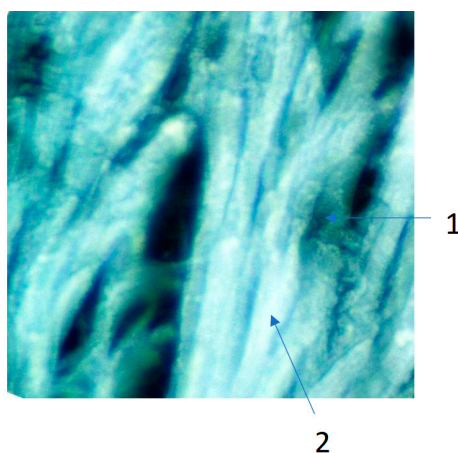


Figure 10. Histological sections (myocardial infarction) under a fluorescent microscope demonstrating the differentiating ability of **3**. 1—alive cardiomyocytes, 2—dead cardiomyocytes.

3. Materials and Methods

All the reagents and solvents were commercially available and used as received without further purification. 2-(tosylamino)-benzylidene-N-benzoylhydrazones (HL¹–HL⁵) were prepared according to the literature method [31].

Elemental analyses of C, H, and N were performed with the EuroEA 3000 analyzer. The IR spectra were measured by the FSM 2202 spectrometer in the range of 4000–400 cm^{-1} . UV–vis spectra were recorded with a Cintra-3000 spectrophotometer for the solid-state samples. ¹H NMR spectra were recorded on a Bruker VXR-400 spectrometer at 400 MHz using the DMSO-*d*₆ solutions. Photoluminescence and excitation spectra were recorded on the FluoroMax-4 spectrofluorometer. Luminescence decays were measured using the same spectrometer equipped with a xenon flash lamp. The luminescence quantum yields of the solid samples were determined by the absolute method using an integrating sphere. The thermal behavior of the compound was studied using the simultaneous thermal analysis (STA) technique for the parallel recording of TG (thermogravimetry) and DSC (differential scanning calorimetry) curves.

3.1. Synthetic Procedures

Related ligands (HL¹–HL⁵) 2 mmol and Zn(CH₃COO)₂·2H₂O (219 mg, 1 mmol) were dissolved in 40 mL CH₂Cl₂ and 10 mL CH₃OH respectively, and then these two solutions were mixed together. After stirring for about 2 h at 60 °C, the reaction mixture was cooled

and crude compounds were collected by filtration. Pure crystalline samples were obtained by the recrystallization of crude products from MeOH.

$\text{Zn}(\text{L}^1)_2$ (**1**) Yield 72%. Anal. calc. (%) for $\text{C}_{42}\text{H}_{36}\text{N}_6\text{O}_8\text{S}_2\text{Zn}$: C, 59.32; H, 4.27; N, 9.88. Found (%): C, 59.21; H, 4.25; N, 9.75. ESI-MS: 851.33 $[\text{M} + \text{H}]^+$ (calcd: 851.29). IR (cm^{-1}): 3231 w, 3090 w, 3057 w, 2976 w, 1645 s, 1621 s 1600 m, 1560 s, 1490 m, 1414 m, 1292 m, 1250 m, 1131 vs, 1084 vs, 948 s, 859 s, 688 s, 541 s, 508 m.

$\text{Zn}(\text{L}^2)_2$ (**2**) Yield 73%. Anal. calc. (%) for $\text{C}_{44}\text{H}_{40}\text{N}_6\text{O}_8\text{S}_2\text{Zn}$: C, 60.17; H, 4.59; N, 9.57. Found (%): C, 60.31; H, 4.53; N, 9.48. ESI-MS: 879.39 $[\text{M} + \text{H}]^+$ (calcd: 879.34). IR (cm^{-1}): 3231 w, 3090 w, 3057 w, 2976 w, 1645 s, 1619 s 1600 m, 1559 s, 1490 m, 1414 m, 1292 m, 1250 m, 1131 vs, 1084 vs, 948 s, 859 s, 688 s, 541 s, 508 m.

$\text{Zn}(\text{L}^3)_2$ (**3**) Yield 68%. Anal. calc. (%) for $\text{C}_{44}\text{H}_{40}\text{N}_6\text{O}_8\text{S}_2\text{Zn}$: C, 58.05; H, 4.43; N, 9.23. Found (%): C, 58.16; H, 4.60; N, 9.12. ESI-MS: 911.40 $[\text{M} + \text{H}]^+$ (calcd: 911.34). IR (cm^{-1}): 3240 w, 3060 w, 1624 s, 1607 m 1563 s, 1510 s, 1489 m, 1407 m, 1294 m, 1252 m, 1130 vs, 1082 vs, 947 m, 859 s, 751 m, 578 w, 542 m.

$\text{Zn}(\text{L}^4)_2$ (**4**) Yield 68%. Anal. calc. (%) for $\text{C}_{42}\text{H}_{34}\text{F}_2\text{N}_6\text{O}_8\text{S}_2\text{Zn}$: C, 56.92; H, 3.87; N, 9.48. Found (%): C, 57.03; H, 3.70; N, 9.42. ESI-MS: 887.18 $[\text{M} + \text{H}]^+$ (calcd: 887.27). IR (cm^{-1}): 3237 w, 3102 w, 3060 w, 1647 s, 1623 m 1603 s, 1568 s, 1508 m, 1489 s, 1418 m, 1289 s, 1248 s, 1249 m, 1130 vs, 1083 vs, 948 s, 862 m, 576 m, 541 m.

$\text{Zn}(\text{L}^5)_2 \cdot \text{MeOH}$ (**5**) Yield 74%. Anal. calc. (%) for $\text{C}_{43}\text{H}_{38}\text{Cl}_2\text{N}_6\text{O}_7\text{S}_2\text{Zn}$: C, 54.29; H, 4.03; N, 8.83. Found (%): C, 54.43; H, 3.82; N, 9.01. ESI-MS: 920.04 $[\text{M} + \text{H}]^+$ (calcd: 920.17). IR (cm^{-1}): 3235 w, 3096 w, 1643 s, 1625 m 1600 s, 1563 s, 1489 s, 1415 m, 1370 m, 1315 m, 1285 m, 1248 m, 1207 m, 1129 s, 1105 s, 1083 s, 948 m, 859 s, 746 m, 544 m.

The single-crystal X-ray diffraction data for **1** and **2** were collected using the Bruker D8 Venture diffractometer equipped with a CCD detector and a micro-focus MoK α radiation source ($\lambda = 0.71073 \text{ \AA}$). Semi-empirical absorption correction was applied for both samples [46]. The structure was solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. The hydrogen atom of the NH-group was found in differential Fourier maps. The hydrogen atoms of the carbon-containing ligand were positioned geometrically and refined by using a riding model. All the calculations were performed by direct methods and used the SHELX-2014 and OLEX-2 program package [47,48]. The crystallographic parameters and the structure refinement statistics are shown in Table S1. CCDC numbers 2519321 for **1** contain the supplementary crystallographic data for the reported compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif (accessed on 29 December 2025).

3.2. Electroluminescence

Creation of OLED structures: glass substrates coated with a transparent layer of a mixture of indium and tin oxides (ITO) with a resistance of $10 \Omega/\text{sq}$ were used. Preliminary preparation of substrates was carried out according to the established procedure: thorough purification in organic solvents followed by etching in oxygen plasma. The application of the layers to the prepared substrate was carried out in a glove box under a dry N_2 atmosphere. Thermal vacuum deposition (TVD) was performed on a BOC Edwards Auto 306 equipment using shadow masks at a residual pressure of $\sim 10^{-5}$ mbar and with deposition rates of 0.2 nm/s for organic layers and 1 nm/s for metals. The emission areas were $2 \times 6 \text{ mm}^2$. The layers of organic substances and cathode metals were formed without a depressurizing chamber. A quartz detector SQM 160 controlled the evaporation speed and thickness of the deposited layers. The voltage–current, voltage–brightness, and spectral characteristics of the obtained OLED structures were studied on a measuring compound consisting of a voltage analyzer source (Keithley 237, KEITHLEY, Cleveland, OH, USA) and a fiber spectrometer.

3.3. Computational Details

The density functional theory (DFT) calculations in this work were carried out using the GAUSSIAN 09 software package [49]. The ground-state geometry of the isolated complex molecule **1** was optimized using the hybrid B3LYP exchange–correlation functional [50,51] and the standard split-valence polarized 6-31G(d,p) basis set [52,53]. To ensure that the optimized structure corresponds to a true energy minimum and not a transition state, the absence of imaginary frequencies was confirmed by normal mode analysis. The TD-DFT formalism was employed to calculate the UV absorption spectrum for complex **1** using its optimized geometry, accounting for solvent effects (DMSO) via the polarizable continuum model (PCM) [54]. Complex **1** was chosen as a representative model because all synthesized compounds (**1–5**) share the same coordination core (ZnN_2O_4) and polymeric architecture in the solid state (confirmed for **1** and **2**), and exhibit similar photoluminescent properties; complex **1** was chosen as a representative model for investigating the nature of electronic transitions. Full geometry optimization and absorption spectrum calculations were not performed for the remaining complexes (**2–5**), because the introduction of different substituents (CH_3 , OCH_3 , F, Cl) at the para-position of the benzoylhydrazone fragment has a negligible effect on the energy and localization of the frontier molecular orbitals, as evidenced by the similarity of the experimental UV–vis spectra of all complexes.

3.4. Procedures for Bioimaging

The castration-resistant prostate cancer cell model (PC-3) was cultured in F12K medium; prostate healthy epithelial cells (RWPE-1) were cultured in DMEM (37 °C, 5% CO_2). All cultures were cultured for 24 h with serum-free medium. Title cells had been washed and replaced with a fresh medium before imaging.

In the study of the biovisualization of ischemic heart areas, materials from male rats were used. All applicable international, national and/or institutional principles of animal care and use have been followed. All procedures performed in animal studies complied with ethical standards approved by the legal acts of the Russian Federation and the principles of the Basel Declaration [55].

Microscopy was performed using a MICMED-2 var. 26 microscope (Lomo-Microsystems, Saint Petersburg, Russia) with planachromatic lenses. The photofixation was carried out using a digital camera “MC-6.3” (LOMO-Microsystems, Russia) integrated with the software “ToupView” version 4.11 (ToupTek Photonics, China).

4. Conclusions

In summary, we have successfully synthesized and characterized five new coordination compounds of zinc(II) with aroylhydrazones of 2-tosylaminobenzaldehyde. The compounds demonstrate effective photoluminescence in the solid state and in solutions. Moreover, studies demonstrating the prospects of using the obtained compounds as optical materials have been carried out. Three of the compounds were employed as a dopant in electroluminescent devices. The maximum current efficiency of 7.6–10.11 Cd/A and maximum luminance of 2400–2900 cd/m^2 were achieved. Moreover, the compounds can be used for bioimaging in the study of biological pathologies at the cellular and tissue levels.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijms27041718/s1>.

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K.M. and M.R.; writing—original draft preparation, A.G.; writing—review and editing, M.K. and W.L.; supervision, A.G. and W.L.; project administration W.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Samples of the compounds are available from the authors.

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