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Synthesis and Photoluminescence Properties of Zinc(II) Complexes with Salicylaldehyde Hetarylhydrazones

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Abstract—New zinc complexes of the salicylaldehyde benzazolyl- and pyrimidinylhydrazones were synthesized. Study of photophysical properties of the hydrazones and their complexes in solution showed that their structure and the luminescence intensities depend on the nature of the heterocyclic fragment included to the molecule.

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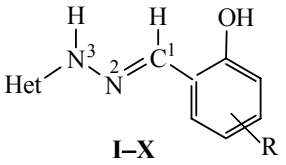
Coordination compounds of transition metals with polyfunctional heterocyclic ligands are widely used as components of the compositions of organic light–emitting diodes [1]. Luminescent properties of complexes based on *o*-hydroxyazomethines [1–3], as well as the monomeric zinc chelates with the organic ligand containing a fragment of azoles, like benzimidazole, have been studied [4]. The hydrazones as molecular systems can combine the structural elements of both oxyazomethines and azoles [5, 6]. Such hydrazones can interact with metal ions as mono- and dianionic bi- and tridentate ligands capable of forming mono– or binuclear metal chelates depending on the nature of the metal [7, 8], which can result in the luminescence of higher intensity.

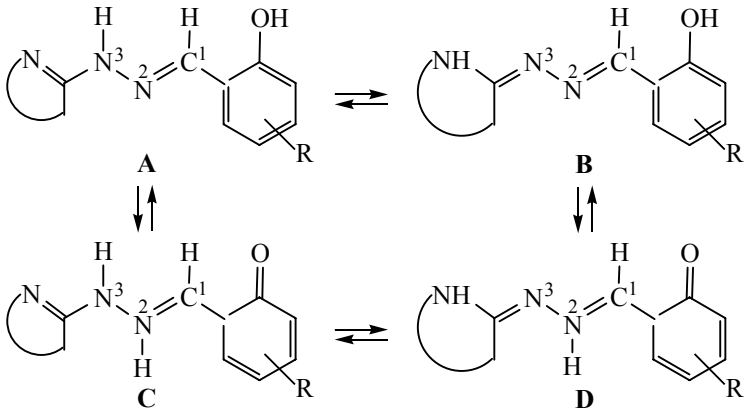
This paper reports the results of studies on the synthesis and photoluminescence properties of zinc(II) complexes based on the salicyl aldehyde benzazolyl- and pyrimidinylhydrazones (Table 1). The luminescent properties of the zinc(II) complexes are determined only by the nature of the organic ligand which has a significant influence on the packing of the molecules in the crystal and the formation of intermolecular contacts, which also affect the luminescence properties. Thus, the variation of the functional properties of the targeted zinc(II) complexes became possible by introducing different substituents in the ligands **I–X**.



I–X

The hydrazones **I–X** can exist in solution as equilibrium mixture of several forms: benzoid amine (**A**), imine (**B**), and the respective quinoid (**C, D**) structures (scheme). It has been shown earlier [9] that in a series of pyrimidinyl → benzothiazole → benzoxazole → benzimidazole → benzylbenzimidazolhydrazones the content of imino tautomer **A** grows. At the same time the introduction of groups R = NO_2, Br into the composition of the aldehyde fragment increases the mobility of the hydrogen of hydroxy group [10], contributing to the predominance of the quinoid form.

It is known that the capability of *o*-oxyazomethines to the ionization of OH bond in the excited singlet state, to the proton transfer on the nitrogen atom and the transition in the quinoid form undelies the fluorescence of these compounds [11]. In the simplest



example of salicylaldehyde hydrazone it was previously shown [12] that under the action of light the formation of quinoid form also occurred. Obviously, in toluene solution the equilibrium of the investigated hydrazones **I**–**X** will be shifted toward the formation of forms **A** and **C**, and the luminescence should be expected by a mechanism similar to that of *o*-oxyazomethines [10].

It was established that in toluene all investigated hydrazones **I**–**X** with the absorption maximum of λ = 315–365 nm exhibited the photoluminescence excited

Table 1. Composition and characteristics of hetarylhydrazones **I–X** and related zinc complexes **XI–XX**

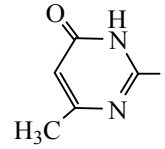
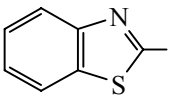
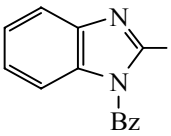
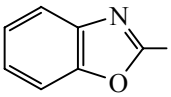
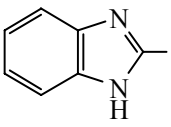
Hydrazone	Het	R	δ_{NH}, ppm	δ_{OH}, ppm	Zn complex	δ_{NH}, ppm
I		H	11.160	9.791	**XI**	11.156
II	″	4-NO_2	11.411	–	**XII**	11.213
III	″	5-Br	1.227	10.026	**XIII**	11.243
IV		H	12.047	10.476	**XIV**	–
V	″	4-NO_2	12.219	–	**XV**	10.08
VI		4-NO_2	12.106	11.411	**XVI**	11.943
VII	″	5-Br	7.867	11.3–11.6 br.s	**XVII**	7.867
VIII		5-Br	8.131	10.2–10.5 br.s	**XVIII**	8.111
IX		H	11.52	10.3–11.2 br.s	**XIX**	11.4–11.6 br.s
X	″	5-Br	11.47	10.34	**XX**	11.52

Table 2. Absorption and emission spectra of hydrazones **I–X** and related zinc complexes **XI–XX**[a]

Comp. no.	λ_A, nm	D_A	λ^{fl}, nm	I^{fl}_{max}, rel. units	Comp. no.	λ_A, nm	D_A	λ^{fl}, nm	I^{fl}_{max}, rel. units
I	345	0.96	505	97	**XI**	360	0.92	496	3
II	330	0.83	512	8	**XII**	350	0.91	506	7
III	315	1.14	495	5	**XIII**	380	1.01	482	6
IV	360	0.96	545	68	**XIV**	405	1.09	545	117
V	362	0.79	523	4	**XV**	413	0.76	515	73
VI	360	1.04	542	7	**XVI**	380	1.18	538	43
VII	365	0.86	548	11	**XVII**	380	0.80	543	9
VIII	350	0.95	501	8	**XVII**	380	1.03	492	5
IX	348	0.76	455	104	**XIX**	405	0.89	409	279
X	347	1.07	468	13	**XX**	372	1.03	440	12

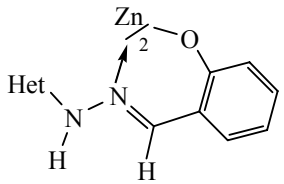
[a] Toluene, c 5×10^{-5} M.

by UV light in toluene, but differing in the position of the emission maxima, and even more by the intensity of the luminescence (Table 2). The position of the emission band is determined mainly by the nature of the heterocycle. The pyrimidinyl- and benzoxazolylhydrazones **I–III, VIII** have a luminescence maximum in the region of 495–512 nm, benzothiazolyl- and benzylbenzimidazolylhydrazones **IV–VII,** at 523–548 nm, and benzimidazolylhydrazones **IX, X**, at 455–468 nm. The highest intensity was observed in the cases of hydrazones **I, IV, IX** with R = H in the aldehyde residue, which contain more quinoid form than the other hydrazones. The introduction of substituents like NO_2, Br leads obviously to the appearance of additional low–lying nπ* levels, which contribute to the nonradiative deactivation of the excited state.

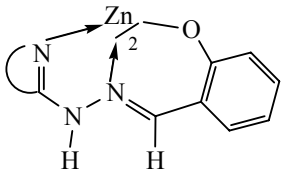
To increase the intensity of the luminophores the complexing with various metals is widely used. A high performance sensitizer of luminescence properties is known to be zinc. In this work we carried out the synthesis of metal complexes **XI–XX** on the basis of the investigated compounds **I–X**.

The complexes were synthesized by reaction of hydrazones **I–X** with zinc acetate in ethanol at heating. According to elemental analysis and mass spectrometry (electrospray), the composition of compounds **XI–XX** is L_2M. ^{1}H NMR spectra of the complexes are characterized by multiplets of aromatic and heterocyclic protons and singlets of the CH=N groups. The OH signals which exist in the spectra of the hydrazones are absent in the spectra of the complexes, but the signals of the NH groups remain (Table 1).

Therefore, in this case, the hydrazones **I–X** in complexes with zinc ions they act as monoanions, most likely as *O,N*-bidentate ligands in which the heterocycle is not involved in the coordination with the metal. The structure of the complexes can be represented by formula **E**, but there is no reason to exclude structure **F**, the choice between them can only be done on the basis of XRD data.

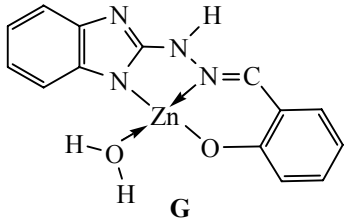


E



F

Earlier [6] the zinc complex of the salicylic aldehyde benzimidazolylhydrazone was synthesized of LM composition and structure **G** was attributed to it only on the basis of the IR spectra: metal chelate presumably formed through deprotonation of both the phenolic OH and imidazole NH groups.



G

Complexes of hydrazones **XI–XX** also show luminescence. The emission band suffered a blue shift relative to that of hydrazones (Table 2) due to the destruction of low-energy quinoid forms of the ligands at the complex formation. The position of the emission

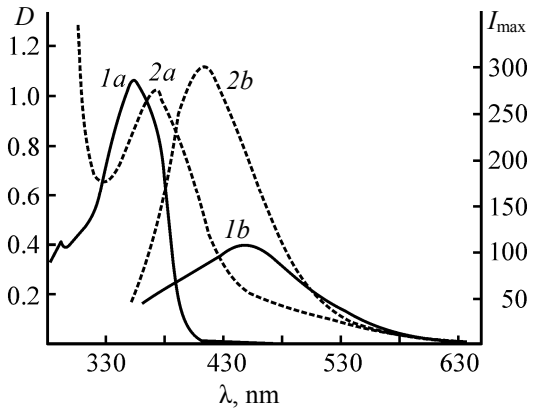


Fig. 1. Electron absorption (*a*) and emission (*b*) spectra of benzimidazolylhydrazone **IX** (*1*) and its zinc complex (*2*).

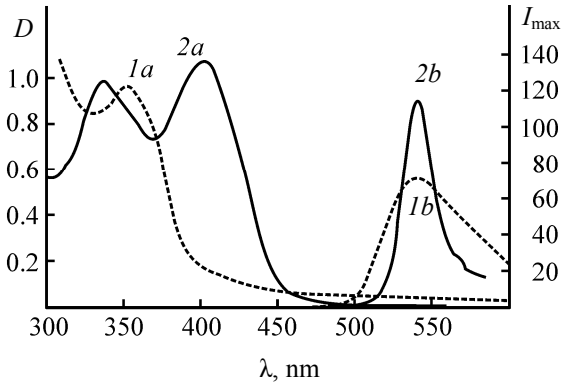


Fig. 2. Electron absorption (*a*) and emission (*b*) spectra of benzothiazolylhydrazone **IV** (*1*) and its zinc complex (*2*).

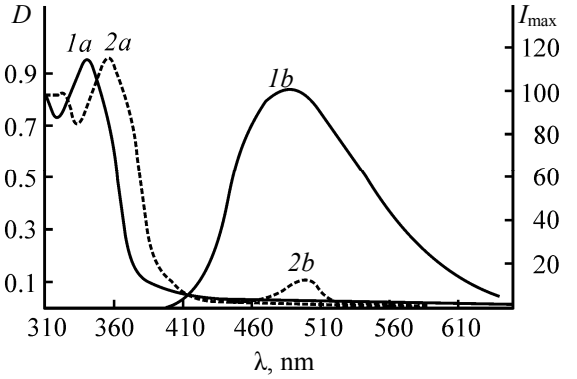


Fig. 3. Electron absorption (*a*) and emission (*b*) spectra of pyrimidinylhydrazone **I** (*1*) and its zinc complex (*2*).

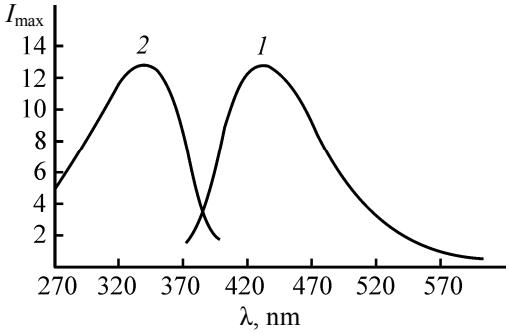


Fig. 4. Emission (*1*) at l 350 nm and excitation (*2*) spectra of the polymer composition containing zinc complex **XIX**.

band and the luminescence intensity of the zinc complexes are defined by the nature of the heterocycle. The highest intensity of luminescence exhibit the complexes based on benzothiazolyl- (**IV**) and benzimidazolylhydrazones (**IX**), a three-fold increase in the intensity of the emission was registered for the latter (Fig. 1).

The maximum of luminescence band of the benzothiazolyl-containing zinc complex **XIV** coincides with the emission band of the original ligand (Fig. 2).

In the case of the pyrimidinyl-containing hydrazone at the complexation with zinc(II) ions the ability of the complex to emission under irradiation disappeared almost completely (Fig. 3).

Typically, in the modern technologies the functional (including luminescent) materials are used in the convenient form of polymeric compositions or as thin films produced by sputter deposition. To determine the behavior of zinc complexes of hydrazones in a polymer layer, we prepared compositions based on polymethyl methacrylate. The thin polymer films were deposited on the surface of the optically transparent glass by sequential deposition of the layers of polymer–complex–polymer. The uniform distribution of layers on the glass surface was achieved using centrifugation. As a result, on the glass surface formed a polymer composition with the film thickness $d = 0.01$ μm, the concentration of the complex $6–9\times10^{-6}$ M.

The absorption band of compounds **XIV** and **XIX** in the polymer remained unchanged, but the emission band of the polymer composites were shifted slightly to longer wavelengths (560 and 428 nm, respectively). The luminescence spectrum of the polymer composition comprising the complex **XIX** is shown in Fig. 4.

Thus, the luminescence of the zinc complexes of hydrazones in the film is recorded in the same area, but the emission intensities are incomparable since the concentrations of the compounds in toluene and in the polymer composition differ by an order of magnitude.

EXPERIMENTAL

Mass spectrometric study was carried out on a Bruker Daltonics mass spectrometer MicrOTOF-Q II series equipped with electrospray ionization source, six port valve and a KD Scientific multi syringe infusion pump (flow rate 180 ml h^{-1}). The mass spectrometer operates under control of the micrOTOFcontrol 2.3 patch 1 and HyStar 3.2 softwares (Bruker Daltonics). The nominal resolution of the instrument 17500. The mass spectrometer operated in a positive mode of ionization in the mass range *m/z* 50–800 Da. The voltage on the ionization source capillary 4500 V, on the glass capillary output 166 V. The pressure of atomizing gas 0.8 bar, the gas-dryer flow rate 4 l min^{-1}, the gas heater temperature 250°C. Averaging option 3, summation value 5000, which corresponds to one spectrum per second. Ion transit time 70 μs, the hexapole ion guide 100 Vpp. The instrument was calibrated externally by 6 points before registration of a sample. As reference points were used the peaks of lithium formate clusters obtained by the introduction into the instrument of 10 mM solution of LiOH in a mixture 2-pro–panol/0.2% aqueous formic acid (1:1 by volume).

^{1}H NMR spectra were taken on a Bruker DRX-400 spectrometer with operating frequency 400.13 MHz, from solutions in DMSO-d_6, internal reference TMS. The mass spectra of hydrazones were recorded on a liquid chromato-mass spectrometer Shimadzu LCMS-2010 (registration of positive and negative ions, recording mode was scanning within a given mass range, SIM, profile scans, APSI (atmospheric pressure chemical ionization).

The luminescence spectra were recorded on a Varian B. V. Cary Eclipse instrument. The light source was a pulsing Xe lamp, pulse width 2 μs, equivalent power 75 kW, the monochromators a Czerny–Turner, 0.125 m, and a diffraction grating 30×35 mm, 1200 lines mm^{-1}. The optical range of excitation 200–900 nm, of emission 200–900 nm. For the measurements toluene solutions were used of concentration 5×10^{-5} M, in quartz cells with the layer thickness 1.01 cm.

General method of synthesis of the hetaryl-hydrazone zinc complexes. To a hot solution of 0.00068 mol of a hetarylhydrazone of the corresponding aldehyde in 15 ml of ethanol was poured a solution of 0.00034 mol of zinc(II) acetate in 25 ml of ethanol. The mixture was heated on a water bath for 30 min and then kept at room temperature for 24 h. The precipitated crystals of the complex were filtered off, washed with cold ethanol, and dried in air.

Salicylaldehyde 4-methyl-6-hydroxypyrimidinyl-hydraxone zinc complex (XI). Yield 84%, mp 243°C. Found, %: C 52.19, H 3.98, N 20.35, Zn 11.80. $C_{24}H_{22}N_8O_4Zn$. Calculated, %: C 52.24, H 4.02, N 20.30, Zn 11.85. *M* 551.86. Mass spectrum (ESI), *m/z* (I_{rel}, %): 551.13 [M^+] (100), 498.20 (47). ^{1}H NMR spectrum (DMSO), δ, ppm: 11.16 br.s (4H, NH pyrimidinyl), 8.31 s (2H, N=CH), 7.76 m (2H, phenyl), 7.15 m (2H, phenyl), 7.03 m (2H, phenyl), 6.83 m (2H, phenyl), 5.45 s (2H, pyrimidinyl), 2.10 m (6H, CH_3 pyrimidinyl).

2-Hydroxy-5-nitrocarboxaldehyde 4-methyl-6-hydroxypyrimidinylhydrazone zinc complex (XII). Yield 82%, mp 296°C. Found, %: C 44.97, H 3.10, N 21.86, Zn 10.21. $C_{24}H_{20}N_{10}O_8Zn$. Calculated, %: C 44.91, H 3.14, N 21.82, Zn 10.18. *M* 641.86. Mass spectrum (ESI), *m/z* (I_{rel}, %): 641.0 [M^+] (67), 430.0 (100), 352.0 (100). ^{1}H NMR (DMSO), δ, ppm: 11.2 br.s (2H, NH pyrimidinyl), 8.32 s (2H, N=CH), 5.8 m (2H, phenyl), 7.85 m (2H, phenyl), 6.63 m (2H, phenyl), 5.25 s (2H, pyrimidinyl), 2.08 m (6H, CH_3 pyrimidinyl).

2-Hydroxy-5–bromocarboxaldehyde 4-methyl-6-hydroxypyrimidinylhydraxone zinc complex (XIII). Yield 91%, mp 314°C. Found, %: C 40.66, H 2.83, N 15.71, Zn 9.19 $C_{24}H_{20}Br_2N_8O_4Zn$. Calculated, %: C 40.62, H 2.84, N 15.79, Zn 9.21. *M* 709.66 Mass spectrum (ESI), *m/z* (I_{rel}, %): 708.9 [M^+] (31), 647.0 (27), 464.9 (11), 323.0 (100). ^{1}H NMR spectrum (DMSO), δ, ppm: 11.24 br.s (4H, NH pyrimidinyl), 8.31 c (2N, N = CH), 7.25 m (2H, phenyl), 6.79 m (2H, phenyl), 6.56 m (2H, phenyl), 5.47 s (2H, pyrimidinyl), 2.09 m (6H, CH_3 pyrimidinyl).

Salicylaldehyde benzothiazolyl-2-hydrazone zinc complex (XIV). Yield 72%, mp 314°C. Found, %: C 55.85, H 3.36, N 13.97, Zn 10.88. $C_{28}H_{20}N_6O_2S_2Zn$. Calculated, %: C 55.86, H 3.35, N 13.96, Zn 10.85. *M* 602.0 Mass spectrum (ESI), *m/z* (I_{rel}, %): 601.0 [M^+] (80). ^{1}H NMR spectrum (DMSO), δ, ppm: 8.20 s (2N, N=CH). 7.37 m (2H, benzothiazole), 7.25 m (2H, benzothiazole), 6.7 m (4H, benzothiazole), 6.79 m (8H, phenyl).

2-Hydroxy-5-nitrocarboxaldehyde benzothiazolyl-2-hydrazone zinc complex (XV). Yield 76%, mp >330°C. Found%: C 55.18, H 3.12, N 18.94, Zn 10.80.

$C_{28}H_{18}N_8O_6S_2Zn$. Calculated, %: C 55.28, H 3.02, N 18.64, Zn 10.87. *M* 691. Mass spectrum (ESI), *m/z* (I_{rel}, %): 691.0 [M^+] (11), 376.9 (61), 315 (100). ^{1}H NMR spectrum (DMSO), δ, ppm: 9.02 s (2H, N=CH),), 7.52 m (4H, phenyl). 6.80 m (4H, benzothiazole), 6.63 m (2H, benzothiazole), 8.61 m (2H, benzothiazole), 8.60 m (2H, phenyl).

2-Hydroxy-5-nitrocarboxaldehyde benzylbenzimidazolyl-2-hydrazone zinc complex (XVI). Yield 86%, mp 295°C. Found, %: C 60.22, H 3.83, N 16.72, Zn 7.78. $C_{42}H_{32}N_{10}O_6Zn$. Calculated, %: C 60.19, H 3.85, N 16.71, Zn 7.80. *M* 838.16 Mass spectrum (ESI), *m/z* (I_{rel}, %): 837.2 [M^+] (9), 528.0 (13), 450.0 (17), 388.0 (100). ^{1}H NMR spectrum (DMSO), δ, ppm: 11.94 s (2H, NH), 9.03 s (2H, N=CH),), 8.62 m (6H, phenyl), 7.96 m (10H, benzimidazole), 7.12 m (8H, benzimidazole), 5.38 d (4H, CH_2).

2-Hydroxy-5-bromocarboxaldehyde benzylbenzimidazolyl–2–hydrazone zinc complex (XVII). Yield 83%, mp 276°C. Found, %: C 54.63, H 3.76, N 12.10, Zn 7.05. $C_{42}H_{32}Br_2N_8O_2Zn{\cdot}H_2O$. Calculated, %: C 54.59, H 3.72, N 12.13, Zn 7.08 *M* 924.03. Mass spectrum (ESI), *m/z* (I_{rel}, %): 907.0 [M^+] (17), 423 (100). ^{1}H NMR spectrum (DMSO), δ, ppm: 8.91 s (2N, N=CH), 7.89 m (2H, phenyl), 7.34 m (4H, phenyl), 7.31 m (10H, benzimidazole), 6.98 m (8H, benzimidazole), 5.17 d (4H, CH_2).

2-Hydroxy-5-bromocarboxaldehyde 2-benzoxazolylhydrazone zinc complex (XVIII). Yield 72%, mp 306°C. Found, %: C 46.28, H 2.47, N 21.67, Zn 8.98. $C_{28}H_{18}Br_2N_6O_4Zn$. Calculated, %: C 46.22, H 2.49, N 21.96, Zn 8.98. *M* 727.67 Mass spectrum (ESI), *m/z* (I_{rel}, %): 728.9 [M^+] (24), 473.92 (20), 395.9 (18), 334.0 (100). ^{1}H NMR spectrum (DMSO), δ, ppm: 8.36 s (2N, N=CH), 7.76 m (2H, phenyl), 7.52 m (2H, phenyl), 7.36 m (2H, benzoxazolyl), 7.32 m (2H, benzoxazolyl), 6.86 m (2H, benzoxazolyl), 6.78 m (2H, phenyl), 6.59 m (2H, benzoxazolyl).

Salicylaldehyde benzimidazolyl-2-hydrazone zinc complex (XIX). Yield 94%, mp > 330°C. Found, %: C 60.02, H 3.93, N 18.69, Zn 11.48. $C_{28}H_{22}N_8O_2Zn$. Calculated, %: C 59.22, H 3.90, N 19.73, Zn 11.51. *M* 567.91 Mass spectrum (ESI), *m/z* (I_{rel}, %): 569.1 (41.2), 567.1 [M^+] (65.2), 413.4 (99) 315.0 (53.2). ^{1}H NMR spectrum (DMSO), δ, ppm: 8.46, 8.28 s (2H, N=CH), 11.4–11.6 br.s, m (2H, N–NH), 7.59 m (2H, NH of benzimidazole), 7.14 m (4H, benzimidazole, 4H, phenyl), 6.87 m (4H, benzimidazole, 2H, phenyl), 6.53 m (2H, phenyl).

2-Hydroxy-5-bromocarboxaldehyde benzimidazolyl-2-hydrazone zinc complex (XX). Yield 89%, mp 328°C. Found, %: C 46.55, H 3.33, N 14.13, Zn 9.07. $C_{28}H_{20}Br_2N_8O_2Zn$. Calculated, %: C 46.59, H 3.61, N 14.52, Zn 9.01. *M* 725,70 Mass spectrum (ESI), *m/z* (I_{rel}, %): 724.9 [M^+] (70.1), 725.94 (72.1), 726.94 (66.6), 728.93 (71.5). ^{1}H NMR spectrum (DMSO), δ, ppm: 8.23 s (2N, N=CH), 11.48 m (2H, N–NH), 7.91 m (2H, NH benzimidazole), 7.15 m (4H, benzimidazole, 2H, phenyl), 6.87 m (4H, benzimidazole, 2H, phenyl), 6.81 m (2H, phenyl).

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