2-Hydroxybenzaldehyde (2-phenylquinazolin-4-yl)hydrazones and their Zn^{II} complexes: synthesis and photophysical properties*

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N-(2-Phenylquinazolin-4-yl)-*N´*-salicylidenehydrazines and their Zn^{II} complexes were obtained. The structures and luminescent properties of these new quinazoline derivatives were examined.

Key words: salicylidenehydrazine, 4-hydrazino-2-phenylquinazoline, zinc(II) complexes, photoluminescence.

Nitrogen heterocyclic derivatives containing a phenolic OH group are widely known as ligands. For instance, metal complexes with 2-benzimidazolyl-8-hydroxyquinolines have an N,N,O-environment around the central metal atom and exhibit intense luminescence.[1] Systems that combine the structural elements of *o*-hydroxy azomethines and heterocycles are of particular attention because many complexes based on *o*-hydroxy azomethines show luminescent properties.[2] Nitrogen-containing π-deficient heterocycles such as pyridine, pyrimidine, quinoline, quinoxaline, *etc.* have already been used successfully as fragments of electron transport layers in electroluminescent materials.[3] Zinc(II) chelate complexes with ligands of the quinoline series are employed in the design of OLED-oriented materials.[4]

Here we extended the synthesis of fluorine-containing quinazoline derivatives[5—7] to 2-hydroxybenzaldehyde (2-phenylquinazolin-4-yl)hydrazones and their Zn^{II} complexes and studied their photophysical properties. Earlier, complexation reactions of hydrazones prepared from salicylaldehyde and 4-hydrazinoquinazolines have not been examined; nor have the corresponding fluoroquinazoline ligands been documented. We used the phenyl substituent in position 2 because 2-phenylquinazolines containing a long chain of conjugated bonds in a substituent in position 4 are known[8] to exhibit luminescent properties. The presence of a F atom in the ligand enhances both its thermal and chemical stability and its solubility in organic solvents and, consequently, widens the scope of its technical applications (*e.g.*, preparation of superior quality films from materials with unique physicochemical properties[9]). That is why fluorine-containing quinazolines were chosen as objects of our investigations.

5-Fluoro-2-phenylquinazolinone (**1a**) was obtained as described earlier;[6] the same method was employed in the synthesis of its nonfluorinated analog **1b**.

To introduce a hydrazino group into position 4, first we obtained 4-chlorinated derivatives **2a—c** from quinazolinones **1a—c** in boiling $POCl_3$ by analogy with 4-chloro-2-ethylthio-6,7,8-trifluoroquinazoline.[5] Heating of 4-hydrazino-2-phenylquinazolines **3a,b** with appropriate aldehydes in ethanol afforded hydrazones **4a—h** (Scheme 1). To study the photophysical properties of fluorine-containing hydrazones in which the F atom is not hydrogen-bonded to the NH fragment of the substituent in position 4 but can still exert the electronic influence on the system, we obtained 6,7-difluorinated derivatives **4g,h** from earlier[10] described 6,7-difluoro-3*H*-2-phenylquinazolin-4-one (**1c**) (see Scheme 1). The ^{1}H NMR spectra of ligands **4a—h** show multiplets for the fluorobenzene (or benzene), phenyl, and hydroxyphenyl fragments and singlets for the OH and —CH=N groups. The signal for the NH group appears as a doublet for 5-fluorinated derivatives **4a—c** and as a broadened singlet for the other ligands **4**.

Complexes **5a—h** were obtained by heating hydrazones **4a—h** with zinc(II) acetate in methanol (see Scheme 1). The ^{1}H NMR spectra of complexes **5a—h** contain multiplets for the aromatic protons and singlets for the —CH=N group. The spectra of complexes **5a**,**c**,**d**,**f—h** show no signals for the OH groups, while analogous signals in the spectra of complexes **5b**,**e** are fewer by one than for the

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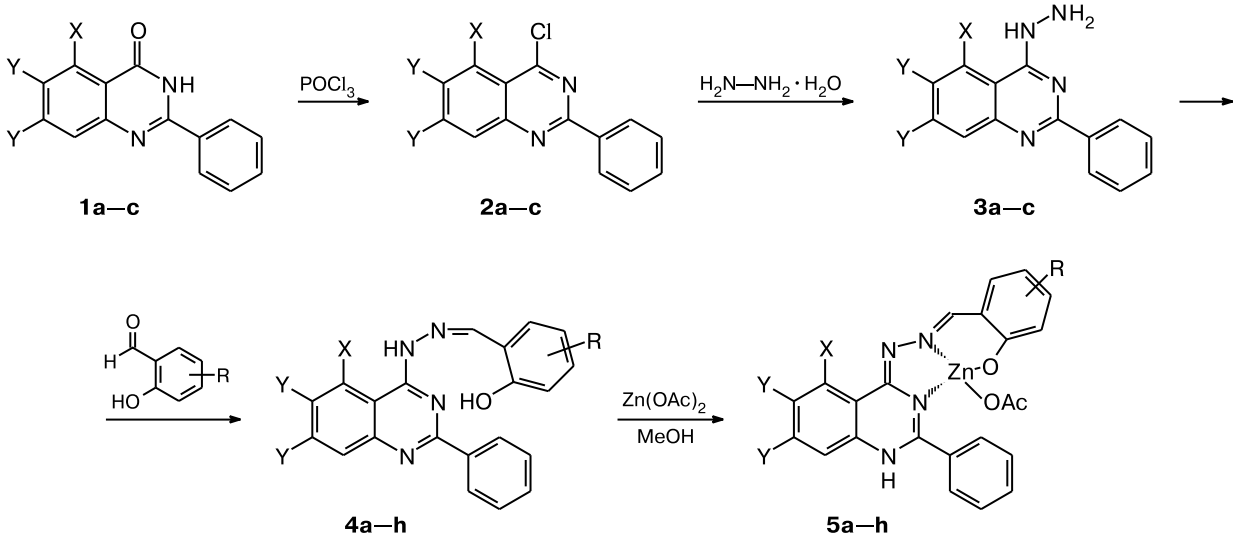
Scheme 1



1–3: X = F, Y = H (**a**); X = Y = H (**b**); X = H, Y = F (**c**)

4, **5**	X	Y	R	**4**, **5**	X	Y	R	**4**, **5**	X	Y	R	**4**, **5**	X	Y	R
a	F	H	H	**c**	F	H	3,5-Br_2	**e**	H	H	4-OH	**g**	H	F	H
b	F	H	4-OH	**d**	H	H	H	**f**	H	H	3,5-Br_2	**h**	H	F	5-NO_2

corresponding hydrazones. The broadened singlets for the NH groups are shifted downfield compared to the corresponding signal of the ligand. According to MS data, the ligand-to-metal ratio in the complexes obtained is 1 : 1.

The structure of complex **5c** as an example was examined by X-ray diffraction. Structure **5c** is a chain coordination polymer in which the Zn atoms are bridged by acetate groups; the complex crystallizes as a solvate with two DMF molecules. The Zn atom is five-coordinated to form a distorted trigonal bipyramid with the singly charged quinazoline ligand occupying both the apices and one vertex of the equatorial plane (Fig. 1). The phenyl substituent of quinazoline makes an angle of 55.5° with the plane of the heterocycle. The formation of a conjugated metal chelate structure causes proton transfer from the hydrazone fragment to the N(3) atom of the heterocycle and shortens the C_{Ar}—N bond (N(4)—C(8), 1.309(6) Å), which becomes close in length to the C=N bond (*e.g.*, the N(2)—C(17) bond length in this structure is 1.287(5) Å). The coordination polymer is stacked along the axis 0*c*, the zinc atoms being spaced in the stacks at 5.021(5) Å. The room between the stacks is occupied by solvate DMF molecules. One crystallographically independent DMF molecule is not involved in any specific interactions, while the second molecule forms an intermolecular hydrogen bond between the formyl CO group and the NH group of the quinazoline fragment (N(3)—O(2S) [$x+1, -y+2, z+1/2$], 2.794(6) Å). A fragment of the crystal packing of the polymer chains is shown in Fig. 2; the hydrogen atoms and some solvent molecules are omitted. Selected bond lengths and bond angles in structure **5c** are given in Table 1.

The Cambridge Structural Database[11] contains no data on five-coordinate zinc(II) complexes with tridentate ligands based on hydrazinobenzazines. Their nearest structural analogs are five-coordinate zinc(II) complexes with Schiff bases prepared from salicylaldehyde derivatives and 2-aminomethylpyridine.[12–15] The formation of a seven-coordinate zinc(II) complex with a hydrazonopyridine derivative has been reported.[16]

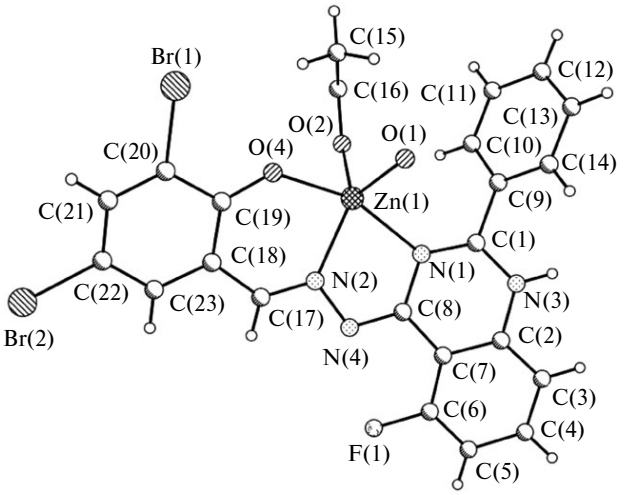


Fig. 1. Fragment of structure **5c**.

Table 1. Selected bond lengths *d* and bond angles ω in complex **5c**

Bond	*d*/Å	Angle	ω/deg
Zn(1)—O(1)	1.940(3)	O(2)—Zn(1)—O(4)	94.39(12)
Zn(1)—O(2)	1.986(3)	O(1)—Zn(1)—O(2)	108.25(13)
Zn(1)—O(4)	2.046(3)	O(1)—Zn(1)—O(4)	92.94(13)
Zn(1)—N(2)	2.049(4)	N(2)—Zn(1)—N(1)	161.02(13)
Zn(1)—N(1)	2.248(4)	O(1)—Zn(1)—N(2)	134.12(14)
N(2)—N(4)	1.400(5)	O(2)—Zn(1)—N(2)	117.50(14)
O(2)—C(16)	1.286(5)	N(4)—N(2)—Zn(1)	120.6(3)
O(4)—C(19)	1.281(5)	C(17)—N(2)—N(4)	111.8(4)
N(4)—C(8)	1.309(6)	C(8)—N(4)—N(2)	113.2(4)
N(2)—C(17)	1.287(5)	C(17)—N(2)—Zn(1)	127.6(4)

The formation of structures **5** suggest that compounds **4** act as monoanionic tridentate ligands in these complexation reactions. In the complex, the ligand is coordinated to the zinc(II) atom through two N atoms and one O atom to form five- and six-membered chelate rings.

Hydrazones **4** and their complexes **5** absorb at 370—495 nm; the electronic absorption spectra of the fluorinated derivatives and their nonfluorinated analogs are similar. In all the cases but the transformation **4h** → **5h**, the complexation results in a bathochromic shift of the longer-wavelength band in the absorption spectra (Table 2).

In acetonitrile at room temperature, hydrazones **4** and their complexes **5** exhibit dark blue or green photoluminescence with an emission peak at 465—549 nm. The electronic absorption and photoluminescence spectra of ligands **4** and complexes **5** are given in Table 2.

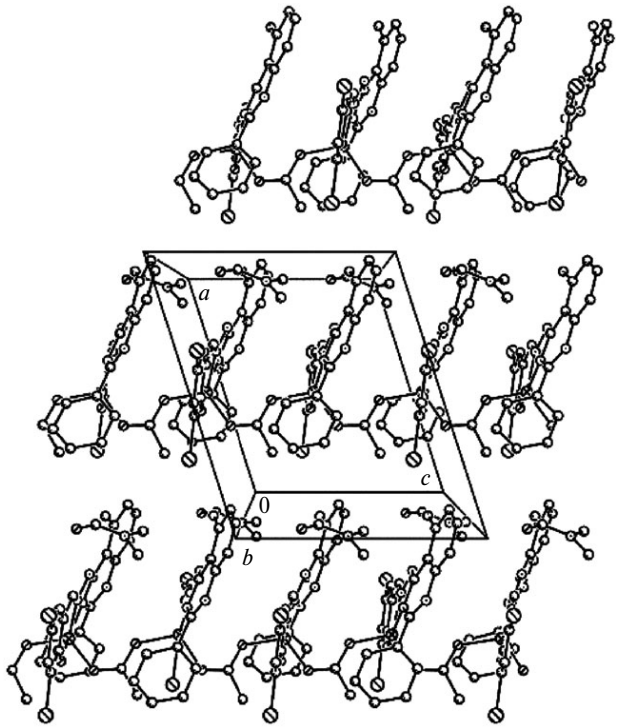


Fig. 2. Fragment of the molecular packing of complex **5c**.

The transformations of hydrazones **4** into complexes **5** result in blue shifts of the emission peaks by 3—41 nm, except for hydrazone **4e** (see Table 2).

It is known[17] that the fluorescence of *o*-hydroxy azomethines is due to the ionization of the OH bond in the

Table 2. Absorption and emission spectra of hydrazones **4** and their complexes **5**

Compound	X	Y	R	λ_{max}/nm		Stokes shift Δλ/nm	Quantum yield
				Absorption	Photoluminescence*		
4a	F	H	H	372, 354	530	158	0.003
4b	F	H	4-OH	377, 362	490	113	<0.001
4c	F	H	3,5-Br_2	375, 359	537	109	0.003
4d	H	H	H	370, 353	492	122	<0.001
4e	H	H	4-OH	375, 360	465	90	<0.001
4f	H	H	3,5-Br_2	374, 358	549	175	0.004
4g	H	F	H	371, 356	522	151	<0.001
4h	H	F	5-NO_2	495, 468, 368	512**	144	0.004
5a	F	H	H	443, 418, 399	489	46	0.092
5b	F	H	4-OH	444, 418, 397	484	40	0.002
5c	F	H	3,5-Br_2	462, 433, 413	510	48	0.01
5d	H	H	H	445, 419, 398	489	44	0.29
5e	H	H	4-OH	444, 418, 397	484	40	0.015
5f	H	H	3,5-Br_2	461, 436	508	47	0.027
5g	H	F	H	448, 422, 401	491	43	0.21
5h	H	F	5-NO_2	445, 420	485	40	0.025

* Excitation at the longer-wavelength absorption band.
** Excitation at 368 nm.

excited singlet state followed by proton transfer to the N atom and the formation of the quinonoid structure. Earlier,[18] it has been illustrated with the simplest salicylaldehyde hydrazone that the formation of a quinonoid structure can be photoinduced as well. It is not unlikely that the luminescence mechanism of hydrazones **4** is similar to that of other *o*-hydroxy azomethines, so the hypsochromic shifts of the emission peak in the spectra of the complexes with respect to its position in the spectra of the starting hydrazones are due to the decomposition of the low-energy quinonoid forms of the ligands during the complexation.

The complexation **4** → **5** considerably lowers the Stokes shift and increases the quantum yield (see Table 2). The more intense fluorescence of zinc complexes with *o*-hydroxy azomethines compared to the ligands themselves (see, *e.g.*, Ref. 19) has been associated with the increased rigidity of the system upon the complexation.

In conclusion, note also that quinazoline-containing hydrazones **4** are promising ligand systems for the design of complexes with other metals.

Experimental

^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400.13 MHz) in DMSO-d_6 with Me_4Si as the internal standard. Mass spectra were measured on a MicrOTOF-Q II mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an ESI source, a six-port valve, and a kd Scientific syringe pump (flow rate 180 μL h^{-1}). The mass spectrometer was controlled with the micrOTOFcontrol 2.3 patch 1 and HyStar 3.2 software (Bruker Daltonics). The operating parameters of the mass spectrometer were as follows: rated resolution 17 500, positive ionization mode for an *m/z* range of 50—800 Da, ion-source capillary voltage 4500 V, glass capillary outlet voltage 166 V, spraying gas pressure 0.8 bar, flow rate of the drying gas 4 L min^{-1}, gas heater temperature 250 °C. Averaging and summation settings were 3 and 5000, respectively, which corresponds to one spectrum per second. The ion travel time was 70 μs; the radio frequency of the hexapole was 100 Vpp. Prior to each measurement, the mass spectrometer was calibrated externally from six reference peaks of lithium formate clusters detected upon the injection of a solution of LiOH (c = 10 mmol L^{-1}) in Pr^{i}OH—0.2% aqueous HCOOH (1 : 1, v/v) into the instrument.

Electronic absorption spectra were recorded on a UV-2401PC spectrophotometer (Shimadzu, Japan) in acetonitrile. Emission spectra were recorded on a Cary Eclipse spectrofluorimeter (Varian, USA) in acetonitrile (c = ~5 · 10^{-6} mol L^{-1}). Relative quantum yields were determined according to a known procedure[20] with quinine bisulfate (φ = 0.546) for compounds **4** and fluorescein (φ = 0.92) as standards. Melting points were determined on a Stuart SMP3 instrument. The course of the reactions was monitored by TLC on silica gel.

Hydrazone **4d** was obtained as described earlier.[21] Compounds **4** and **5** were obtained from 2-amino-6-fluorobenzonitrile (99%), 2-aminobenzonitrile (98%), salicylaldehyde (98%), 2-hydroxy-5-nitrobenzaldehyde (98%), 4-hydroxysalicylaldehyde (98%), and 3,5-dibromosalicylaldehyde (98%) (Alfa Aesar). Reagent-grade solvents (carbinol, DMSO) were used as purchased from Khimmed and Reakhim (Russia).

4-Chloro-5-fluoro-2-phenylquinazoline (2a). Phosphoryl chloride (5 mL) was added to quinazolinone **1a** (1.0 g, 4.2 mmol). The reaction mixture was refluxed for 1.5 h, cooled to room temperature, and poured onto ice. The colorless precipitate that formed was filtered off, washed with water, and dried. The yield was 0.48 g (45%), m.p. 140—142 °C. ^{1}H NMR (DMSO-d_6), δ: 7.15 (dd, 1 H, H(6), $^3J_{H,F}$ = 9.9 Hz, $^3J_{H,H}$ = 8.2 Hz); 7.48—7.57 (m, 3 H, H(3′)—H(5′)); 7.56 (d, 1 H, H(8), ^3J = 8.2 Hz); 7.74 (td, 1 H, H(7), $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,F}$ = 5.5 Hz); 8.19 (dd, 2 H, H(2′), H(6′), ^3J = 7.0 Hz, ^4J = 1.5 Hz). Found (%): C, 64.96; H, 3.09; N, 10.85. $C_{14}H_8ClFN_2$. Calculated (%): C, 65.00; H, 3.12; N, 10.83.

4-Chloro-6,7-difluoro-2-phenylquinazoline (2c) was obtained as described for compound **2a**. Yield 56%, m.p. 94—96 °C. ^{1}H NMR (DMSO-d_6), δ: 7.52—7.60 (m, 3 H, Ph); 8.05 (m, 1 H, H(5)); 8.21 (m, 1 H, H(8)); 8.50 (m, 2 H, Ph). Found (%): C, 60.83; H, 2.59; N, 10.11. $C_{14}H_7ClF_2N_2$. Calculated (%): C, 60.78; H, 2.55; N, 10.13.

5-Fluoro-4-hydrazino-2-phenylquinazoline (3a). Hydrazine hydrate (1.0 mL, 20 mmol) was added to a suspension of 4-chloroquinazoline **2a** (1.0 g, 3.9 mmol) in ethanol (20 mL). The reaction mixture was stirred at 70 °C for 3 h and cooled. The bright yellow precipitate that formed was filtered off, washed with hexane, and recrystallized from acetonitrile. The yield was 0.5 g (50%), m.p. 178—180 °C. ^{1}H NMR (DMSO-d_6), δ: 4.97 (br.s, 2 H, NH); 7.15 (dd, 1 H, H(6), $^3J_{H,F}$ = 11.5 Hz, $^3J_{H,H}$ = = 8.1 Hz); 7.45 (m, 3 H, Ph); 7.53 (d, 1 H, H(8), ^3J = 8.1 Hz); 7.64 (m, 1 H, H(7)); 8.52 (m, 2 H, Ph); 8.72 (br.s, 1 H, NH). Found (%): C, 66.07; H, 4.32; N, 22.09. $C_{14}H_{11}FN_4$. Calculated (%): C, 66.13; H, 4.36; N, 22.03.

6,7-Difluoro-4-hydrazino-2-phenylquinazoline (3c) was obtained as described for compound **3a**. Yield 56%, m.p. 240—243 °C. ^{1}H NMR (DMSO-d_6), δ: 4.76 (br.s, 2 H, NH); 7.44 (m, 3 H, Ph); 7.56 (dd, 1 H, H(5), ^3J = 11.6 Hz, ^4J = 8.0 Hz); 8.21 (dd, 1 H, H(8), ^3J = 11.6 Hz, ^4J = 9.2 Hz); 8.52 (d, 2 H, Ph); 9.61 (br.s, 1 H, NH). Found (%): C, 61.73; H, 3.65; N, 20.61. $C_{14}H_{10}F_2N_4$. Calculated (%): C, 61.76; H, 3.70; N, 20.58.

***N*-(5-Fluoro-2-phenylquinazolin-4-yl)-*N*′-salicylidenehydrazine (4a).** Salicylaldehyde (0.5 mL, 4.77 mmol) was added to a solution of hydrazine **3a** (0.45 g, 1.77 mmol) in ethanol (15 mL). The reaction mixture was refluxed for 1.5 h and cooled. The yellow precipitate that formed was filtered off and recrystallized from acetonitrile. The yield was 0.4 g (63%), m.p. 202—204 °C. ^{1}H NMR (DMSO-d_6), δ: 6.92 (t, 1 H, H(5″), ^3J = 7.4 Hz); 7.00 (d, 1 H, H(3″), ^3J = 8.1 Hz); 7.28 (m, 2 H, H(6), H(4″)); 7.38 (dd, 1 H, H(6″), ^3J = 7.6 Hz, ^4J = 1.5 Hz); 7.53 (m, 3 H, H(3′)—H(5′)); 7.69 (d, 1 H, H(8), ^3J = 8.4 Hz); 7.78 (td, 1 H, H(7), $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,F}$ = 6.0 Hz); 8.60 (dd, 2 H, H(2′), H(6′), ^3J = 7.93 Hz, ^4J = 2.1 Hz); 8.81 (s, 1 H, CH=N); 11.12 (d, 1 H, NH, $^5J_{H,F}$ = 9.2 Hz); 12.34 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 359 [M + H] (100). Found (%): C, 70.43; H, 4.18; N, 15.58. $C_{21}H_{15}FN_4O$. Calculated (%): C, 70.38; H, 4.22; N, 15.63.

***N*-(5-Fluoro-2-phenylquinazolin-4-yl)-*N*′-(4-hydroxysalicylidene)hydrazine (4b)** was obtained from 4-hydroxysalicylaldehyde and hydrazine **3a** as described for compound **4a**. Yield 56%, m.p. 271—273 °C. ^{1}H NMR (DMSO-d_6), δ: 5.90 (d, 1 H, H(4″), ^3J = 8.3 Hz); 5.92 (s, 1 H, H(3″)); 6.69 (d, 1 H, H(5″), ^3J = 8.3 Hz); 6.80 (dd, 1 H, H(6), $^3J_{H,F}$ = 11.5 Hz, ^4J = 7.9 Hz);

7.00—7.05 (m, 3 H, H(3′)—H(5′)); 7.20 (d, 1 H, H(8), ^3J = 8.2 Hz); 7.29 (td, 1 H, H(7), $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,F}$ = 7.9 Hz); 8.13 (dd, 2 H, H(2′), H(6′), ^3J = 7.8 Hz, ^4J = 1.7 Hz); 8.23 (s, 1 H, CH=N); 9.30 (br.s, 1 H, OH); 10.4 (d, 1 H, NH, $^3J_{H,F}$ = 10.0 Hz); 11.9 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 375 [M + H] (100). Found (%): C, 67.33; H, 4.07; N, 14.93. $C_{21}H_{15}FN_4O_2$. Calculated (%): C, 67.37; H, 4.04; N, 14.97.

***N*-(3,5-Dibromosalicylidene)-*N′*-(5-fluoro-2-phenylquinazolin-4-yl)hydrazine (4c)** was obtained from 3,5-dibromosalicylaldehyde and hydrazine **3a** as described for compound **4a**. Yield 43%, m.p. 269—271 °C. ^{1}H NMR (DMSO-d_6), δ: 7.27 (dd, 1 H, H(6), $^3J_{H,F}$ = 11.3 Hz, ^4J = 8.2 Hz); 7.51 (m, 3 H, H(3′)—H(5′)); 7.56 (d, 1 H, H(4″), ^3J = 1.7 Hz); 7.66 (d, 1 H, H(6″), ^3J = 1.7 Hz); 7.69 (d, 1 H, H(8), ^3J = 8.3 Hz); 7.79 (m, 1 H, H(7)); 8.62 (d, 2 H, H(2′), H(6′), ^3J = 3.8 Hz); 8.74 (s, 1 H, CH=N); 11.45 (d, 1 H, NH, $^3J_{H,F}$ = 6.5 Hz); 13.6 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 517 [M + H] (100). Found (%): C, 48.89; H, 2.52; N, 10.81. $C_{21}H_{13}Br_2FN_4O$. Calculated (%): C, 48.87; H, 2.54; N, 10.85.

***N*-(2-Phenylquinazolin-4-yl)-*N′*-salicylidenehydrazine (4d)** was obtained from salicylaldehyde and hydrazine **3b** as described for compound **4a**. Yield 65%, m.p. 178—180 °C. ^{1}H NMR (DMSO-d_6), δ: 6.91 (m, 1 H, H(5″)); 7.10 (m, 1 H, H(3″)); 7.31 (m, 1 H, H(6)); 7.45—7.65 (m, 5 H, H(3′)—H(5′), H(4″), (6″)); 7.80—7.90 (m, 2 H, H(5), H(7)); 8.37 (m, 1 H, H(8)); 8.62 (m, 2 H, H(2′), H(6′)); 8.66 (s, 1 H, CH=N); 11.9 (br.s, 1 H, NH); 12.3 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 341 [M + H] (100). Found (%): C, 74.15; H, 4.78; N, 16.43. $C_{21}H_{16}N_4O$. Calculated (%): C, 74.10; H, 4.74; N, 16.46.

***N*-(4-Hydroxysalicylidene)-*N′*-(2-phenylquinazolin-4-yl)hydrazine (4e)** was obtained from 4-hydroxysalicylaldehyde and hydrazine **3b** as described for compound **4a**. The reaction time was 3 h. The reaction product was recrystallized from DMSO. Yield 59%, m.p. 275—277 °C. ^{1}H NMR (DMSO-d_6), δ: 6.33 (m, 2 H, H(3″), H(5″)); 7.21 (d, 1 H, H(6″), ^3J = 8.4 Hz); 7.45—7.65 (m, 4 H, H(3′)—H(5′), H(6)); 7.75—7.85 (m, 2 H, H(5), H(7)); 8.32 (m, 1 H, H(8)); 8.54 (s, 1 H, CH=N); 8.60 (m, 2 H, H(2′), H(6′)); 9.70 (br.s, 1 H, OH); 11.7 (br.s, 1 H, NH); 12.30 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 357 [M + H] (100). Found (%): C, 70.82; H, 4.56; N, 15.70. $C_{21}H_{16}N_4O_2$. Calculated (%): C, 70.78; H, 4.53; N, 15.72.

***N*-(3,5-Dibromosalicylidene)-*N′*-(2-phenylquinazolin-4-yl)hydrazine (4f)** was obtained from 3,5-dibromosalicylaldehyde and hydrazine **3b** as described for compound **4a**. The reaction time was 3 h. Yield 57%, m.p. 255—257 °C. ^{1}H NMR (DMSO-d_6), δ: 7.50—7.80 (m, 5 H, H(3′)—H(5′), H(6), H(4″), H(6″)); 7.86 (m, 2 H, H(2′), H(6′)); 8.34 (m, 1 H, H(5) or H(7)); 8.61 (m, 1 H, H(7) or H(5)); 8.64 (m, 1 H, H(8)); 9.06 (s, 1 H, CH=N); 12.0 (br.s, 1 H, NH); 13.5 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 499 [M + H] (100). Found (%): C, 50.68; H, 2.87; N, 11.21. $C_{21}H_{14}Br_2N_4O$. Calculated (%): C, 50.63; H, 2.83; N, 11.25.

***N*-(6,7-Difluoro-2-phenylquinazolin-4-yl)-*N′*-salicylidenehydrazine (4g)** was obtained from salicylaldehyde and hydrazine **3c** as described for compound **4a**. Yield 74%, m.p. 195—197 °C. ^{1}H NMR (DMSO-d_6), δ: 6.93 (m, 1 H, H(5″)); 6.99 (m, 1 H, H(3″)); 7.29 (m, 1 H, H(4″)); 7.45—7.55 (m, 4 H, H(3′)—H(5′), H(6″)); 7.71 (dd, 1 H, H(5), ^3J = 11.4 Hz, ^5J = 7.5 Hz); 8.44 (m, 1 H, H(8)); 8.58 (m, 2 H, H(2′), H(6′)); 8.61 (s, 1 H, CH=N); 11.90 (br.s, 1 H, NH); 12.10 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 377 [M + H] (100). Found (%): C, 66.98; H, 3.70; N, 14.92. $C_{21}H_{14}F_2N_4O$. Calculated (%): C, 67.02; H, 3.75; N, 14.89.

***N*-(6,7-Difluoro-2-phenylquinazolin-4-yl)-*N′*-(5-nitrosalicylidene)hydrazine (4h)** was obtained from 5-nitrosalicylaldehyde and hydrazine **3c** as described for compound **4a**. Yield 71%, m.p. 223—225 °C. ^{1}H NMR (DMSO-d_6), δ: 7.17 (m, 1 H, H(3″)); 7.51 (m, 3 H, H(3′)—H(5′)); 7.73 (m, 1 H, H(5)); 8.17 (m, 1 H, H(8)); 7.40—7.60 (m, 4 H, H(2′), H(6′), H(4″), H(6″)); 8.71 (s, 1 H, CH=N); 12.20 (br.s, 1 H, NH); 13.30 (br.s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 422 [M + H] (100). Found (%): C, 59.90; H, 3.16; N, 16.59. $C_{21}H_{13}F_2N_5O_3$. Calculated (%): C, 59.86; H, 3.11; N, 16.62.

2-[(5-Fluoro-2-phenylquinazolin-4-ylidene)hydrazonomethyl]phenyloxidozinc(II) acetate (5a). Potassium hydroxide (0.05 g, 1.25 mmol) and zinc acetate (0.2 g, 1.08 mmol) were successively added to a stirred suspension of hydrazone **4a** (0.20 g, 0.56 mmol) in methanol (20 mL). The reaction mixture was stirred at room temperature for 48 h. The precipitate of complex **5a** that formed was filtered off, washed with water, and dried *in vacuo*. The yield was 0.23 g (82%), m.p. >320 °C. ^{1}H NMR (DMSO-d_6), δ: 1.79 (s, 3 H, MeCO); 6.93 (t, 1 H, H(5″), ^3J = 7.5 Hz); 7.02 (d, 1 H, H(3″), ^3J = 8.0 Hz); 7.25—7.35 (m, 2 H, H(6), H(4″)); 7.44 (dd, 1 H, H(6″), ^3J = 7.3 Hz, ^4J = 1.5 Hz); 7.54 (m, 3 H, H(3′)—H(5′)); 7.69 (d, 1 H, H(8), ^3J = 8.2 Hz); 7.79 (m, 1 H, H(7)); 8.54 (m, 2 H, H(2′), H(6′)); 8.88 (s, 1 H, CH=N); 12.00—12.10 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 421 [M – HOAc] (100). Found (%): C, 57.32; H, 3.33; N, 11.54. $C_{23}H_{17}FN_4O_3Zn$. Calculated (%): C, 57.38; H, 3.54; N, 11.64.

2-[(5-Fluoro-2-phenylquinazolin-4-ylidene)hydrazonomethyl]-4-hydroxyphenyloxidozinc(II) acetate (5b) was obtained from zinc acetate and hydrazone **4b** as described for complex **5a**. Yield 77%, m.p. >300 °C. ^{1}H NMR (DMSO-d_6), δ: 3.18 (s, 3 H, MeCO); 6.05 (m, 1 H, H(4″)); 6.10—6.20 (m, 1 H, H(3″)); 6.96 (m, 1 H, H(5″)); 7.02 (m, 1 H, H(6)); 7.18 (m, 3 H, Ph); 7.30—7.40 (m, 1 H, H(8)); 7.43 (m, 1 H, H(7)); 7.91 (m, 2 H, H(2′), H(6′)); 8.45 (s, 1 H, CH=N); 9.60 (br.s, 1 H, OH); 12.00—13.00 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 437 [M – HOAc] (100). Found (%): C, 55.55; H, 3.41; N, 11.32. $C_{23}H_{17}FN_4O_4Zn$. Calculated (%): C, 55.53; H, 3.40; N, 11.26.

3,5-Dibromo-2-[(5-fluoro-2-phenylquinazolin-4-ylidene)hydrazonomethyl]phenyloxidozinc(II) acetate (5c) was obtained from zinc acetate and hydrazone **4c** as described for complex **5a**. Yield 74%, m.p. >330 °C. ^{1}H NMR (DMSO-d_6), δ: 1.84 (s, 3 H, MeCO); 6.87 (dd, 1 H, H(6), $^3J_{H,F}$ = 10.4 Hz, ^4J = 8.4 Hz); 7.14 (d, 1 H, H(8), ^3J = 8.1 Hz); 7.35 (d, 1 H, H(4″), ^3J = 1.9 Hz); 7.40 (m, 4 H, H(3′)—H(5′), H(7)); 7.46 (d, 1 H, H(6″), ^3J = 1.9 Hz); 7.86 (m, 2 H, H(2′), H(6′)); 8.45 (s, 1 H, CH=N); 12.00—13.00 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 579 [M – HOAc] (100). Found (%): C, 43.21; H, 2.28; N, 8.73. $C_{23}H_{15}Br_2FN_4O_3Zn$. Calculated (%): C, 43.19; H, 2.34; N, 8.76.

2-[(2-Phenylquinazolin-4-ylidene)hydrazonomethyl]phenyloxidozinc(II) acetate (5d) was obtained from zinc acetate and hydrazone **4d** as described for complex **5a**. Yield 80%, m.p. >300 °C. ^{1}H NMR (DMSO-d_6), δ: 1.78 (s, 3 H, MeCO); 6.65 (m, 1 H, H(5″)); 6.89 (m, 1 H, H(3″)); 7.14 (m, 1 H, H(6)); 7.29 (m, 1 H, H(6″)); 7.38 (m, 1 H, H(7) or H(5)); 7.40—7.55 (m, 4 H, H(3′)—H(5′), H(4″)); 7.61 (m, 1 H, H(5) or H(7)); 7.87 (m, 2 H, H(2′), H(6′)); 8.25 (m, 1 H, H(8)); 8.66 (s, 1 H, CH=N); 12.10—12.40 (br.s, 1, NH). MS, *m/z* (I_{rel} (%)): 403 [M – HOAc] (100). Found (%): C, 59.63; H, 3.82; N, 12.07. $C_{23}H_{18}N_4O_3Zn$. Calculated (%): C, 59.61; H, 3.88; N, 12.09.

4-Hydroxy-2-[(2-phenylquinazolin-4-ylidene)hydrazonomethyl]phenyloxidozinc(II) acetate (5e) was obtained from zinc acetate and hydrazone **4e** as described for complex **5a**. Yield 76%, m.p. >340 °C. ^{1}H NMR (DMSO-d_6), δ: 1.78 (s, 3 H, MeCO); 6.13 (m, 2 H, H(3″), H(5″)); 7.04 (d, 1 H, H(6″), ^3J = 8.0 Hz); 7.30—7.55 (m, 6 H, H(3′)—H(5′), H(5)—H(7)); 7.85—8.10 (m, 2 H, H(2′), H(6′)); 8.18 (m, 1 H, H(8)); 8.49 (s, 1 H, CH=N); 9.60 (br.s, 1 H, OH); 12.00—13.00 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 419 [M – HOAc] (100). Found (%): C, 57.65; H, 3.74; N, 11.63. $C_{23}H_{18}N_4O_4Zn$. Calculated (%): C, 57.62; H, 3.75; N, 11.69.

3,5-Dibromo-2-[(2-phenylquinazolin-4-ylidene)hydrazonomethyl]phenyloxidozinc(II) acetate (5f) was obtained from zinc acetate and hydrazone **4f** as described for complex **5a**. Yield 73%, m.p. >340 °C. ^{1}H NMR (DMSO-d_6), δ: 2.53 (s, 3 H, MeCO); 7.24 (m, 1 H, H(6″)); 7.32 (s, 1 H, H(4″)); 7.35—7.50 (m, 5 H, H(3′)—H(5′), H(6), H(5) or H(7)); 7.52 (m, 1 H, H(7) or H(5)); 7.89 (m, 1 H, H(8)); 7.91 (s, 1 H, CH=N); 8.21 (m, 1 H, H(2′)); 8.43 (m, 1 H, H(6′)); 12.00—13.00 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 561 [M – HOAc] (100). Found (%): C, 44.48; H, 2.53; N, 9.08. $C_{23}H_{16}Br_2N_4O_3Zn$. Calculated (%): C, 44.44; H, 2.57; N, 9.01.

2-[(6,7-Difluoro-2-phenylquinazolin-4-ylidene)hydrazonomethyl]phenyloxidozinc(II) acetate (5g) was obtained from zinc acetate and hydrazone **4g** as described for complex **5a**. Yield 83%, m.p. >340 °C. ^{1}H NMR (DMSO-d_6), δ: 2.53 (s, 3 H, MeCO); 6.42 (m, 1 H, H(5″)); 6.57 (m, 1 H, H(3″)); 7.03 (m, 1 H, H(4″)); 7.12 (m, 1 H, H(5)); 7.19 (m, 1 H, H(6″)); 7.40 (m, 3 H, H(3′)—H(5′)); 7.87 (m, 2 H, H(2′), H(6′)); 7.96 (m, 1 H, H(8)); 8.42 (s, 1 H, CH=N); 12.00—13.00 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 439 [M – HOAc] (100). Found (%): C, 55.33; H, 3.18; N, 11.27. $C_{23}H_{16}F_2N_4O_3Zn$. Calculated (%): C, 55.31; H, 3.20; N, 11.22.

2-[(6,7-Difluoro-2-phenylquinazolin-4-ylidene)hydrazonomethyl]-6-nitrophenyloxidozinc(II) acetate (5h) was obtained from zinc acetate and hydrazone **4h** as described for complex **5a**. Yield 85%, m.p. >320 °C. ^{1}H NMR (DMSO-d_6), δ: 2.54 (s, 3 H, MeCO); 6.60 (m, 1 H, H(3″)); 7.27 (m, 1 H, H(5)); 7.43 (m, 3 H, H(3′)—H(5′)); 7.87 (m, 2 H, H(2′), H(6′)); 7.95 (m, 1 H, H(4″)); 8.01 (m, 1 H, H(6″)); 8.24 (m, 1 H, H(8)); 8.57 (s, 1 H, CH=N); 12.00—13.00 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 484 [M – HOAc] (100). Found (%): C, 50.74; H, 2.71; N, 12.91. $C_{23}H_{15}F_2N_5O_5Zn$. Calculated (%): C, 50.73; H, 2.75; N, 12.86.

X-ray diffraction study of complex 5c was carried out for a yellow crystal stub (0.29×0.16×0.09 mm) on an Xcalibur 3 automatic four-circle diffractometer equipped with a CCD detector according to a standard procedure (Mo-Kα radiation, graphite monochromator, ωscan mode, scan step 1°, T = 295(2) K). An absorption correction was applied analytically using a multifaceted crystal model.[22] The crystal is monoclinic, space group *Cc*; the unit cell parameters are a = 11.4604(8) Å, b = 31.4795(19) Å, c = 9.5863(5) Å, β = 107.754(5)°, V = 3293.7(3) Å^3; Z = 4 for the molecular formula $C_{29}H_{29}Br_2FN_6O_5Zn$, d_{calc} = 1.585 g cm^{-3}, μ = 3.223 mm^{-1}, F(000) = 1576, scan range 3.11° < θ < 26.37°. The measured 6914 reflections included 4666 independent ones (R_{int} = 0.0357); the number of reflections with $I > 2\sigma(I)$ was 2698. The completeness of the data set was 95.7%. The structure was solved by the direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXTL program package.[23] All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located geometrically and refined using a riding model with dependent thermal parameters. The final R factors are R_1 = 0.0366 and wR_2 = 0.0400 for reflections with $I > 2\sigma(I)$ and R_1 = 0.0762 and wR_2 = 0.0420 for all reflections; S = 1.001. The maximum and minimum peaks of the residual electron density are 0.444 and –0.337 e Å^{-3}, respectively.

The X-ray diffraction data for structure **5c** have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 841489) and can be retrieved free of charge from www.ccdc.cam.ac.uk/data_request/cif.

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