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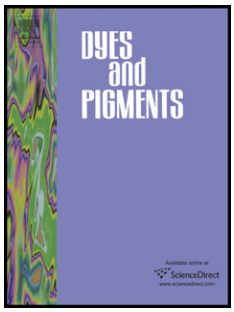

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Synthesis and spectral properties of new hydrazone dyes and their Co(III) azo complexes

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Abstract

A series of six keto-hydrazone dyes was prepared by azo coupling of diazotised substituted 2-aminophenols with pyrrolinone esters. All keto- hydrazone compounds were found as a mixtures of *E* and *Z* isomers by ^{1}H NMR. Irrespective to the position of nitro substituent on the phenol ring, all compounds fluoresce strongly only in solvent glass at 77 K except 4-nitro derivatives which also weakly fluoresce in solution and in solid state at room temperature. Using these hydrazones as tridentate O–N–O´ ligands, six symmetrical 2:1 octahedral Co(III) complexes were prepared. Multinuclear NMR combined with ^{15}N labelled hydrazone derivative proved that the starting mixture of hydrazone isomers was converted exclusively to *E*-azo configuration in complexes with coordinated nitrogen atoms coming solely from phenolic residues. The considerably different effect of 4- and 5-nitrophenol substituents on absorption spectra of the ligands and complexes was ascribed to prevailing azo character of an electronic structure of a ligand in the complex, based on TD DFT calculations.

Keywords:

Hydrazone; Pyrrolinone; Metal-azo complex; Absorption spectra; Fluorescence spectra; DFT.

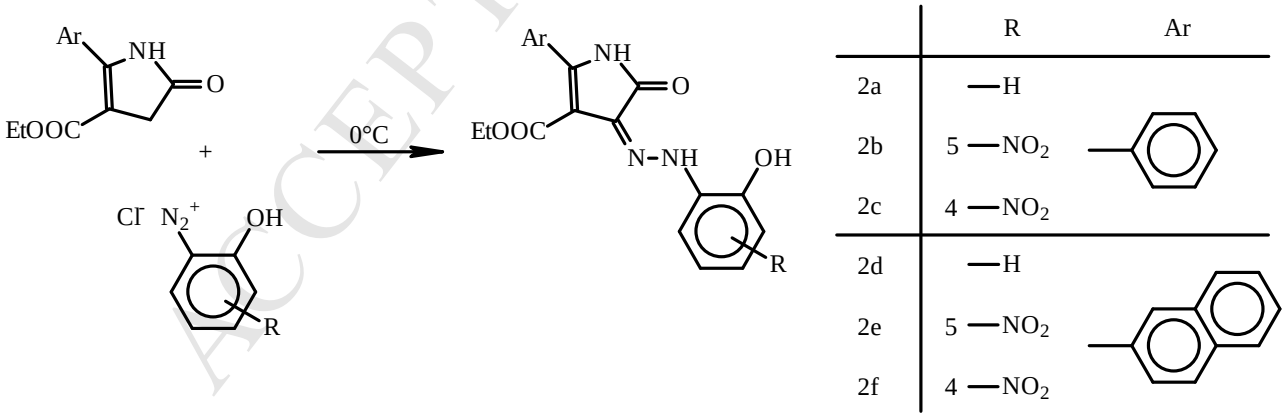
1. Introduction

Azo coupling of diazotized anilines with *β*–diketones, keto-esters and keto-amides (e.g. acetoacetanilides or pyrazolones) forms exclusively keto-hydrazones, i.e. the formal hydroxy-azo / keto-hydrazone equilibrium is strongly shifted towards the latter tautomer [1]. Arising keto-hydrazones can exist as *E* and *Z* isomers with respect to exocyclic C=N bond, both being stabilized by intramolecular hydrogen bonds [2]. Configuration change (switching by isomerization) can be induced by light or heat [3], pH change [2] or coordination-coupled proton transfer [4]. If 2-aminophenols are used as active components, *o*,*o´*-dihydroxy-azo compounds are formal products of azo coupling. Such compounds (either as azo, or hydrazone tautomers) can be used as tridentate ligands forming usually octahedral metal-complex azo dyes mainly in combination with Cr(III) and Co(III) cations in commercial production [1]. Although their application in textile and leather industry becomes problematic, because of health and ecological

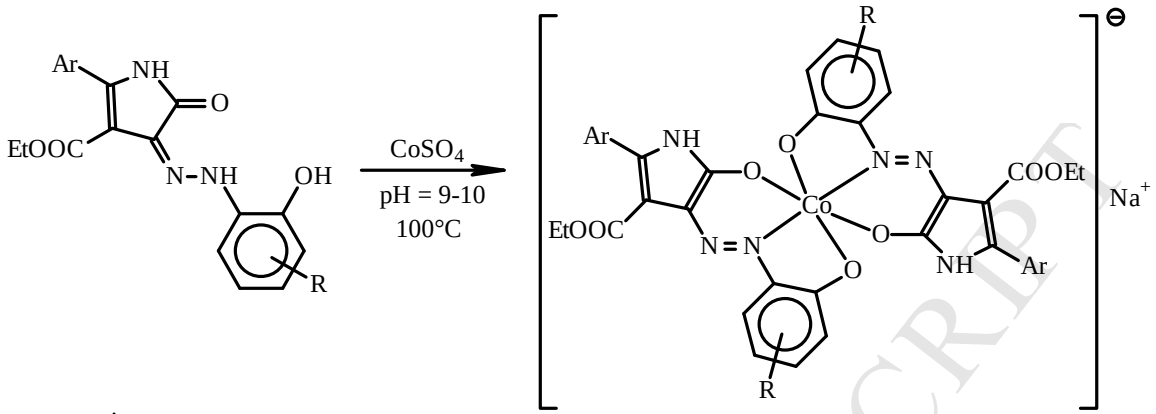
risks [1, 5-6], metal-complex azo dyes remain in the centre of scientific interest, because of their potential applications in technologies like optical data recording [7-8] or catalysis [9].

Hydrazones based on a coupling of *p*-substituted diazonium salts with pyrrolinone esters arise as a mixture of *E* and *Z* isomers, in which the type of hydrogen bonding drives a conformation of side carboxy ester group [10-11]. Their absorption spectra show a moderate bathochromic 'shift, if the aniline contains a *p*-electron donor substituent, while room temperature fluorescence is observed only in the opposite case, i.e. with strong electron-acceptor substituents in the same position. The latter observation was ascribed to the lowering of the competitive excited state photoisomerization rate induced by substituent [12]. The first aim of the presented study was a modification of an aniline part by *o*-hydroxy substituent (Scheme 1) and to study the effect of (potential) second hydrogen bond on an equilibrium composition of the isomers. Furthermore, the hydrogen bonding in the excited state was expected to form a more rigid molecular structure and increase the fluorescence quantum yield.

As these hydrazones contain several oxygen and nitrogen atoms formally able to occupy the coordination positions in octahedral complexes, the synthesis of the metal-azo complexes, their characterization and a study of their spectral properties was the second aim of this study. Among the most frequently used transition metals the Co(III) central cations were chosen, as they are known to be diamagnetic and enable the estimation of the key structural features of metal-azo complexes by multinuclear NMR techniques [13-14].



Scheme 1: Preparation of starting hydrazone dyes



	R	Ar
3a	—H	
3b	5 —NO_2	
3c	4 —NO_2	
3d	—H	
3e	5 —NO_2	
3f	4 —NO_2	

Scheme 2: Preparation of cobalt complexes

2. Experimental and theoretical procedures

2.1 Materials and instruments

Tetrahydrofuran (THF), 1,4-dioxane, dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and 2-methyltetrahydrofuran (MTHF) of spectroscopic grade were purchased from Fluka. Other solvents were purchased from Penta or Lach-Ner s.r.o, Czech Republic. 2-Amino phenol, 2-amino-4-nitrophenol and 2-amino-5-nitrophenol were all purchased from Aldrich Chemical Company and used without further purifications.

The UV/vis absorption spectra were recorded using Perkin-Elmer Lambda 35 spectrophotometer and 1 cm quartz cuvette. The dye solutions in THF were prepared in the dark at concentrations 1×10^{-5} mol/L and measured immediately. A Perkin-Elmer LS55 fluorescence spectrophotometer was used to measure low temperature fluorescence spectra in MTHF. The

fluorescence quantum yields in solution (φ_F) were determined using 4-dicyanomethylene-2-methyl-6-[*p*(dimethylamino)styryl]-4*H*-pyran (DCM) (φ_F = 0.57) in 1-propanol as the standard [15].

An EA 1108 FISONS instrument was used for elemental analysis.

Thin-layer chromatography (TLC) was performed using Kieselgel 60 F254 (Merck, Darmstadt, Germany), for observation of reaction progress and the purity of the prepared intermediates and dyes using different eluents.

Melting points were measured on a Büchi 510 melting point apparatus.

Positive-ion and negative-ion atmospheric pressure chemical ionization (APCI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50-1000. The samples were dissolved in acetonitrile and analysed by direct infusion at the flow rate 100 μL.min^{-1}. The selected precursor ions were further analysed by MS/MS analyses under the following conditions: the isolation width m/z= 4, the collision amplitude in the range 0.7-1.0 V depending on the precursor ion stability, the temperature of drying gas was 330°C, the APCI temperature was 400°C, the tuning parameter compound stability was 100%, the flow rate and the pressure of nitrogen were 4 L.min^{-1} and 45 psi, respectively.

Chromatographic apparatus consisted of a LC 1100 Series (Agilent Technologies, USA) and the ion trap mass spectrometer MSD TRAP XCT Plus system (Agilent Technologies, USA) equipped with ESI and APCI probes was used. Negative-ion ESI mass spectra were recorded in mass range 50-1500 m/z in all experiments. The ion trap analyzer was tuned to obtain an optimal response in the range of expected m/z values (target mass was set to m/z = 500). Other ESI ion source parameters were as follows: drying gas flow 8 L.min^{-1}, nebulizer gas pressure 40 psi, drying gas. Samples were dissolved in methanol in appropriate concentrations for MS detection. Injection volumes of 20 μL, a flow-rate of 0.2 mL.min^{-1} and column temperature of 30 °C were used in all analysis. The separation was performed in following chromatographic system: An octadecyl silica cartridge column, Zorbax Eclipse XDB C_{18} (150×2.1 mm i.e. 5 μm particle size) purchased from Agilent (HPST Prague, Czech Republic) was used for the separation of samples. Gradient was employed, with 20 mmol L^{-1} ammonium acetate in water (solvent A, pH 4) and

acetonitrile (solvent B): from 5 % B in 0-3 min, then 5-100% in 3-20 min to 100 % B in 20-30 min.

FT-IR spectra were recorded as KBr pellets over the range 4000–200 cm^{-1} using a Perkin–Elmer system 2000 FT spectrometer.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. The samples were dissolved in hexadeuteriodimethyl sulfoxide. The ^{1}H and ^{13}C NMR chemical shifts were referenced to the central signal of the solvent (δ= 2.55 and 39.6, respectively).

2.2 Synthesis of hydrazones

The procedure of the synthesis of hydrazones is the same as described in our previous study [11] based on corresponding amine in diazotization step and coupling with pyrrolinone ester as a secondary component at 0 °C.

Ethyl-5-oxo-2-phenyl-4-[2-(2-hydroxyphenyl)hydrazono]-4,5-dihydro-1*H*-pyrrole-3-carboxylate (2a).

Preparative yield 86 %; purified by recrystallization from ethanol, mp = 210-212°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.24 (3H, t, ^{3}J = 7.1 Hz, CH_3); 4.19 (2H, q, ^{3}J = 7.1 Hz, CH_2); 10.27 (1H, s, OH); 11.38 (1H, br. s, –CONH–); 13.26 (1H, br. s, –NHN=).

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.91 (3H, t, ^{3}J = 7.1 Hz, CH_3); 4.08 (2H, q, ^{3}J = 7.1 Hz , CH_2); 10.02 (1H, s, OH); 11.23 (1H, br. s, –CONH–); 12.90 (1H, br. s, –NHN=).

6.88-6.99 (m), 7.44-7.53 (m). 7.56-7.61 (m) and 7.62-7.69 (m) aromatic protons of both *E* and *Z* isomers.

IR (KBr), ν_{max}/cm^{-1}: 3439, 3142, 3049, 2994, 1697, 1673, 1569, 1496, 1449, 1420, 1380, 1250, 1206, 1039, 829, 743.

MS analysis M_r= 351 g/mol. Positive-ion MS: m/z 352 $[M+H]^+$, 100%; m/z 306 $[M+H-C_2H_5OH]^+$, Negative-ion MS: m/z 350 $[M-H]^-$,100%; m/z 304 $[M-H-C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{19}H_{17}N_3O_4$): C (64.95%), H (4.88%), N (11.96%). Found: C (64.73 %), H (4.94%), N (11.87%).

Ethyl-5-oxo-2-phenyl-4-[2-(2-hydroxy-5-nitrophenyl)hydrazono]-4,5-dihydro-1*H*-pyrrole-3- carboxylate (2b).

Preparative yield 61 %; purified by recrystalization from ethanol, mp = 256-258°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.33 (3H, t, ^3J = 7.1 Hz, CH_3); 4.21 (2H, q, ^3J = 7.1 Hz, CH_2); 11.30 (1H, s, OH); 11.52 (1H, br. s, –CONH–); 13.14 (1H, br. s, –NHN=).

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.92 (3H, t, ^3J = 7.1 Hz , CH_3); 4.07 (2H, q, ^3J = 7.1 Hz, CH_2); 11.12(1H, s, OH); 11.39 (1H, br.s, –CONH–); 13.05 (1H, br. s, –NHN=). 7.06 (d, ^3J = 8.8 Hz), 7.11 (d, ^3J = 8.8 Hz), 7.48-7.55 (m), 7.65-7.72 (m), 7.87 (dd, ^4J = 2.7 and ^3J = 8.8 Hz), 7.91 (dd, ^4J = 2.7 and ^3J = 8.8 Hz), 8.26 (d, ^4J = 2.7 Hz) and 8.40 (d, ^4J = 2.7 Hz), aromatic protons of both *E* and *Z* isomers.

IR (KBr), ν_{max}/cm^{-1}: 3386, 3162, 3031, 2984, 1677, 1571, 1529, 1493, 1448, 1421, 1340, 1289, 1250, 1218, 1036, 823, 774, 744.

MS analysis M_r= 396 g/mol. Positive-ion MS: m/z 397 $[M+H]^+$, 100%; m/z 351 $[M+H-C_2H_5OH]^+$, Negative-ion MS: m/z 395 $[M-H]^-$, 100%.

Elemental analysis: calculated ($C_{19}H_{16}N_4O_6$): C (57.58%), H (4.07%), N (14.14%). Found: C (57.29%), H (4.29%), N (14.58%).

Ethyl-5-oxo-2-phenyl-4-[2-(2-hydroxy-4-nitrophenyl)hydrazono]-4,5-dihydro-1*H*-pyrrole-3-carboxylate (2c).

Preparative yield 76 %; purified by recrystallization from ethanol, mp = 266-269°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.20 (3H, t, ^3J = 7.1 Hz, CH_3); 4.18 (2H, q, ^3J = 7.1 Hz, CH_2); 11.25 (1H, s, OH); 11.53 (1H, br. s, –CONH–); 13.21 (1H, br. s, –NHN=).

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.80 (3H, t, ^3J = 7.1 Hz, CH_3); 4.06 (2H, q, ^3J = 7.1 ± 0.2 Hz, CH_2); 11.01 (1H, s, OH); 11.40 (1H, br. s, –CONH–); 13.18 (1H, br. s, –NHN=). 7.48-7.68 (m), 7.69 (d,^4J = 2.5 Hz), 7.74 (d, ^4J = 2.5 Hz), 7.85 (dd, ^4J = 2.5 and ^3J = 8.8 Hz), 7.89 (dd, ^4J = 2.5 and ^3J = 8.8 Hz), aromatic protons of both *E* and *Z* isomers.

IR (KBr), ν_{max}/cm^{-1}: 3404, 3228, 3162, 3057, 2984, 1676, 1581, 1573, 1423, 1384, 1340, 1289, 1254, 1216, 1186, 1033, 821, 763, 747.

MS analysis M_r= 396 g/mol. Positive-ion MS: m/z 397 $[M+H]^+$, 100%; m/z 351 $[M+H-C_2H_5OH]^+$, Negative-ion MS: m/z 395 $[M-H]^-$, 100%.

Elemental analysis: calculated ($C_{19}H_{16}N_4O_6$): C (57.58%), H (4.07%), N (14.14%). Found: C (57.43%), H (4.11%), N (14.19%).

Ethyl-5-oxo-2-(naphthalen-2-yl)-4-[2-(2-hydroxyphenyl)hydrazono]-4,5-dihydro-1*H*-pyrrole-3-carboxylate (2d).

Preparative yield 91 %; purified by re-precipitation from dioxan, cyclohexane, mp=254-256°C. ^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.22 (3H, t, ^3J = 7.1 Hz, CH_3); 4.22 (2H, q, ^3J = 7.1 Hz, CH_2); 10.29 (1H, s, OH); 11.50 (1H, br. s, –CONH–); 13.30 (1H, br. s, –NHN=). ^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.83 (3H, t, ^3J = 7.1 Hz, CH_3); 4.07 (2H, q, ^3J = 7.1 Hz, CH_2); 10.03 (1H, s, OH); 11.34 (1H, br. s, –CONH–); 12.96 (1H, br. s, –NHN=). 6.89 – 6.99 (m), 7.52 – 7.67 (m), 7.68 (dd, ^4J = 2.0 and ^3J = 8.6 Hz), 7.72 (dd, ^4J = 2.0 and ^3J = 8.6 Hz), 8.01 (d, ^3J = 8.6 Hz) and 8.03 (d, ^3J = 8.6 Hz), 8.20 (d, ^4J = 2.0 Hz) and 8.25 (d, ^4J = 2.0 Hz), aromatic protons of both *E* and *Z* isomers.

IR (KBr), ν_{max}/cm^{-1}: 3431, 3177, 3061, 2982, 1671, 1601, 1565, 1423, 1310, 1261, 1242, 1226, 1210, 1184, 824, 761, 739.

MS analysis M_r= 401 g/mol. Positive-ion MS: m/z 402 $[M+H]^+$, m/z 356 $[M+H-C_2H_5OH]^+$, 100 %, Negative-ion MS: m/z 400 $[M-H]^-$, 100 %.

Elemental analysis: calculated ($C_{23}H_{19}N_3O_4$): C (68.82%), H (4.77%), N (10.47%). Found: C (68.50%), H (4.45%), N (10.40%).

Ethyl-5-oxo-2-(naphthalen-2-yl)-4-[2-(2-hydroxy-5-nitrophenyl)hydrazono]-4,5-dihydro-1*H*-pyrrole-3-carboxylate (2e).

Preparative yield 80 %; purified by re-precipitation from dioxan, cyclohexane, mp =217-219°C. ^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.31 (3H, t, ^3J = 7.1 Hz, CH_3); 4.23 (2H, q, ^3J = 7.1 Hz, CH_2); 11.31 (1H, s, OH); 11.62 (1H, br. s, –CONH–); 13.19 (1H, br. s, –NHN=). ^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.82 (3H, t, ^3J = 7.1 Hz, CH_3); 4.08 (2H, q, ^3J = 7.1 Hz, CH_2); 11.16 (1H, s, OH); 11.50 (1H, br. s, –CONH–); 13.10 (1H, br. s, –NHN=). 7.07 (d, ^3J = 8.5 Hz), 7.12 (d, ^3J = 8.5 Hz), 7.61-7.78 (m), 7.89 (dd, ^4J = 2.9 and ^3J = 8.5 Hz), 7.95 (dd, ^4J = 2.9 and ^3J = 8.5 Hz), 7.99-8.11 (m), 8.24 (d, ^4J = 2.9 Hz) and 8.40 (d, ^4J = 2.9 Hz), aromatic protons of both *E* and *Z* isomers.

IR (KBr), ν_{max}/cm^{-1}: 3385, 3168, 3039, 2985, 1679, 1628, 1587, 1438, 1401, 1340, 1268, 1252, 1211, 1186, 821, 774, 742.

MS analysis M_r= 446 g/mol. Positive-ion MS: m/z 447 $[M+H]^+$, 100 %; m/z 401 $[M+H-C_2H_5OH]^+$, Negative-ion MS: m/z 445 $[M-H]^-$, 100 %.

Elemental analysis: calculated ($C_{23}H_{18}N_4O_6$): C (61.88%), H (4.06%), N (12.55%). Found: C (61.63%), H (4.28%), N (12.50%).

Ethyl-5-oxo-2-(naphthalen-2-yl)-4-[2-(2-hydroxy-4-nitrophenyl)hydrazono]-4,5-dihydro-1*H*-pyrrole-3-carboxylate (2f).

Preparative yield 73 %; purified by re-precipitation from dioxan, cyclohexane, mp =274-277°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.22 (3H, t, ^3J = 7.1 Hz, CH_3); 4.21 (2H, q, ^3J = 7.1 Hz, CH_2); 11.28 (1H, s, OH); 11.65 (1H, br. s, -CONH-); 13.27 (1H, br. s, -NHN=).

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.81 (3H, t, ^3J = 7.1 Hz, CH_3); 4.06 (2H, q, ^3J = 7.1 Hz, CH_2); 11.05 (1H, s, OH); 11.52 (1H, br. s, -CONH-); 13.24 (1H, br. s, -NHN=). 7.58 – 7.78 (m), 7.81 – 7.92 (m), 7.97 - 8.09 (m), 8.20-8.26 (m), aromatic protons of both *E* and *Z* isomers.

IR (KBr), ν_{max}/cm^{-1}: 3411, 3230, 3168, 3059, 2988, 1677, 1626, 1583, 1429, 1382, 1340, 1281, 1244, 1214, 1180, 821, 763, 747.

MS analysis M_r= 446 g/mol. Positive-ion MS: m/z 447 $[M+H]^+$, 100 %; m/z 401 $[M+H-C_2H_5OH]^+$, Negative-ion MS: m/z 445 $[M-H]^-$, 100 %.

Elemental analysis: calculated ($C_{23}H_{18}N_4O_6$): C (61.88%), H (4.06%), N (12.55%). Found: C (61.44%), H (4.19%), and N (12.51%).

2.3 Synthesis of cobalt complexes

General procedure

Starting hydrazone (5×10^{-3} mol) was dissolved in DMF (20 mL), metal salt ($CoSO_4.7H_2O$) (2.5×10^{-3} mol) was dissolved in (30 mL) of distilled water then added to the hydrazone solution. The reaction mixture was maintained under alkali conditions, pH= 9-10 by slowly addition of sodium hydroxide solution 1M. The mixture was heated and vigorously stirred at 100°C, the reaction was followed by TLC until all ligand disappeared, then the mixture was cooled down to room temperature, poured into crushed ice (50 g) then filtrated off, washed by distilled water (50 mL) and dried. The crude product was purified by dissolving in 1,4-dioxan (20 mL) and then

re-precipitated by cyclohexane (30 mL). Preparative yields, melting points, NMR data, mass spectroscopy and elemental analysis are as follows.

Complex 3a

Preparative yield 89 %; mp >300°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm): 1.42 (6H, t, ^{3}J = 7.1 Hz, 2×CH_3); 4.38 (4H, q, ^{3}J = 7.1 Hz, 2×CH_2); 6.56 (2x1H, d, ^{3}J = 8.3 Hz); 6.60 (2x1H, m); 6.85 (2x1H, m); 7.29 (2x1H, t, ^{3}J = 7.2 Hz); 7.36 (2x2H, dd, ^{3}J = 8.0 Hz, ^{3}J = 7.2 Hz); 7.50 (2x2H, d, ^{3}J = 8.0 Hz); 8.17 (2x1H, d, ^{3}J = 7.8 Hz); 11.37 (2x1H, br. s, 2×–CONH–).

^{13}C-NMR (100 MHz, DMSO-d6, *δ*, ppm): 14.4 (2×CH_3), 59.5 (2×CH_2), 105.1, 122.9, 131, 131.5, 144.8, 146.8, 168 (2×all C), 113.7, 114.5, 117.3, 126.9, 127.6, 127.4, 127.9 (2× all CH), 164.5 (2×COO).

IR (KBr), ν_{max}/cm^{-1}: 3405, 3060, 2981, 1676, 1586, 1470, 1400, 1383, 1312, 1270, 1217, 1040, 848, 747, 697, 532.

MS analysis M_r= 758+Na. Negative-ion MS: m/z 757 $[M-H]^-$, 100%; m/z 711 $[M-H-C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{38}H_{30}N_6O_8CoNa$): C (58.47%), H (3.87%), N (10.77%). Found: C (58.90%), H (4.12%), N (10.80%).

Complex 3b

Preparative yield 79 %; mp >300°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm): 1.52 (6H, t, ^{3}J = 7.1, 2×CH_3); 4.40 (4H, q, ^{3}J = 7.1, 2×CH_2); 6.71 (2x1H, d, ^{3}J = 9.1 Hz); 7.35-7.44 (2x3H, m); 7.55 (2x2H, m); 7.88 (2x1H, dd, ^{3}J = 9.1 Hz and ^{4}J = 2.8 Hz); 9.06 (2x1H, d, ^{4}J = 2.8 Hz); 11.39 (2H, br. s, 2×–CONH–).

^{13}C-NMR (100 MHz, DMSO-d6, *δ*, ppm): 14.3 (2×CH_3), 59.9 (2×CH_2), 104.6, 123.2, 124.1, 130.4, 135.7, 136, 145.7, 146.5 (2×all C), 110, 116.5, 123.2, 128, 128.3, 128.5 (2× all CH), 163.8 (2×COO).

IR (KBr), ν_{max}/cm^{-1}: 3440, 3051, 2979, 1671, 1579, 1477, 1443, 1406, 1386, 1340, 1278, 1216, 1077, 828, 789, 752, 518.

MS analysis M_r= 848+Na. Negation-ion MS: m/z 847 $[M-H]^-$, 100%; m/z 801 $[M-H-C_2H_5OH]^-$ .Elemental analysis: calculated ($C_{38}H_{28}N_8O_{12}CoNa$): C (52.42%), H (3.24%), N (12.87%). Found: C (52.66%), H (3.59%), N (12.94%).

Complex 3c

Preparative yield 81 %; mp >300°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm): 1.34 (6H, t, ^{3}J = 7.1, 2×CH_3); 4.31 (4H, q, ^{3}J = 7.1, 2×CH_2);); 7.30 (2x1H, d,^{4}J = 2.0 Hz); 7.38-7.44 (2x3H, m); 7.55 (2x2H, dd, ^{3}J = 8.0 Hz); 7.64 (2x1H,dd, ^{3}J = 7.1 Hz, ^{4}J = 2.0 Hz); 8.30 (2x1H, d, ^{3}J = 7.1 Hz); 11.97 (2H, br. s, 2×–CONH–).

^{13}C-NMR (100 MHz, DMSO-d6, *δ*, ppm): 14.4 (2×CH_3), 59.9 (2×CH_2), 104.8, 126, 130.3, 136.2, 145.2, 146.6, 152.9, 166 (2×all C), 110.8, 110.9, 113.8, 128.1, 128.2, 128.7 (2× all CH), 163.8 (2×COO).

IR (KBr), ν_{max}/cm^{-1}: 3431, 3053, 2981, 2929, 1683, 1599, 1463, 1444, 1409, 1384, 1330, 1272, 1247, 1071, 818, 775, 742, 518.

MS analysis M_r= 848+Na. Negative-ion MS: m/z 847 $[M-H]^-$, 100 %; m/z 801 $[M-H-C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{38}H_{28}N_8O_{12}CoNa$): C (52.42%), H (3.24%), N (12.87%). Found: C (52.73%), H (3.61%), N (13.04%).

Complex 3d

Preparative yield 83 %; mp >300°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm): 1.43 (6H, t, ^{3}J = 7.1 Hz, 2×CH_3); 4.41 (4H, q, ^{3}J = 7.1 Hz, 2×CH_2);); 6.62 (2x1H, m); 6.88 (2x1H, m); 7.51-7.58 (2x2H, m); 7.65-7.74 (2x2H, m); 7.83-7.92 (2x3H, m); 7.99-8.05 (2x2H, m); 8.23 (2x1H, d, ^{3}J = 7.1 Hz); 11.57 (2H, br. s, 2×–CONH–).

^{13}C-NMR (100 MHz, DMSO-d6, *δ*, ppm): 14.3 (2×CH_3), 59.5 (2×CH_2), 105.4, 123, 128.5, 131.3, 132.1, 132.5, 145, 146.8, 168 (2×all C), 114.9, 117.3, 118.7, 125.8, 125.9, 126.1, 126.2, 126.9, 127, 127.3, 127.9 (2× all CH), 164.5 (2×COO), 820, 777, 746, 505.

IR (KBr), ν_{max}/cm^{-1}: 3419, 3055, 2979, 2930, 1662, 1587, 1471, 1400, 1384, 1312, 1268, 1235, 1194, 1102, 861, 777, 746, 505.

MS analysis M_r= 858+Na. Negative-ion MS: m/z 857 $[M-H]^-$, 100%; m/z 811 $[M-H-C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{46}H_{34}N_6O_8CoNa$): C (62.73%), H (3.89%), N (9.54%). Found: C (63.10%), H (4.20%), N (10.01%).

Complex 3e

Preparative yield 80 %; mp >300°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm): 1.47 (6H, t, ^{3}J = 7.1 Hz, 2×CH_3); 4.42 (4H, q, ^{3}J = 7.1 Hz, 2×CH_2); 6.75 (2x1H, d, ^{3}J = 7.2 Hz); 7.54-7.58 (2x3H, m); 7.70 (2x1H, d, ^{3}J = 8 Hz); 7.89-7.96 (2x4H, m); 8.10 (2x1H, m); 9.09 (2x1H, d, ^{4}J = 2.2 Hz); 12.01 (2H, br. s, 2×–CONH–).

^{13}C-NMR (100 MHz, DMSO-d6, *δ*, ppm): 14.3 (2×CH_3), 59.9 (2×CH_2), 104.9, 123.3, 127.9, 132.4, 132.6, 135.7, 136, 145.8, 146.5, 173.8 (2×all C), 110, 116.5, 124.2, 126.3, 126.5, 126.7, 127.2, 127.4, 127.5, 128.2 (2× all CH), 163.8 (2×COO).

IR (KBr), ν_{max}/cm^{-1}: 3431, 3055, 2979, 2928, 1672, 1580, 1477, 1407, 1385, 1340, 1282, 1215, 1191, 1078, 821, 787, 751, 517.

MS analysis M_r= 948+Na. Negative-ion MS: m/z 947 $[M-H]^-$, 100 %; m/z 901 $[M-H-C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{46}H_{38}N_6O_{12}CoNa$): C (56.90%), H (3.32%), N (11.54%). Found: C (57.07%), H (3.55%), N (11.98%).

Complex 3f

Preparative yield 84%; mp >300°C.

^{1}H-NMR (400 MHz, DMSO-d6, δ, ppm): 1.41 (6H, t, ^{3}J = 7.1 Hz, 2×CH_3); 4.42 (4H, q, ^{3}J = 7.1 Hz, 2×CH_2); 7.41 (2x1H, d, ^{4}J = 1.9 Hz); 7.55-7.59 (2x2H, m); 7.66-7.71 (2x2H, m); 7.91 (2x1H, m); 7.95 (2x2H, m); 8.10 (2x1H, m); 8.35 (2x1H, d, ^{3}J = 7.1 Hz); 11.96 (2H, br. s, 2×–CONH–).

^{13}C-NMR (100 MHz, DMSO-d6, *δ*, ppm): 14.4 (2×CH_3), 59.9 (2×CH_2), 105, 126.1, 127.9, 132.2, 132.5, 132.7, 145.3, 146.8, 153, 166 (2×all C), 110, 110.9, 113.6, 126.2, 126.7, 126.9, 127.4, 127.6, 127.9, 128.3 (2× all CH), 163.8 (2×COO).

IR (KBr), ν_{max}/cm^{-1}: 3441, 3061, 2981, 2926, 1680, 1600, 1462, 1437, 1410, 1384, 1326, 1278, 1224, 1193, 1071, 819, 780, 744, 515.

MS analysis M_r= 948+Na. Negative-ion MS: m/z 947 $[M-H]^-$, 100 %; m/z 901 $[M-H-C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{46}H_{38}N_6O_{12}CoNa$): C (56.90%), H (3.32%), N (11.54%). Found: C (57.17%), H (3.63%), N (11.83%).

2.4 Quantum chemical calculations

The theoretical calculation of hydrazones **2a – 2c** based on density functional theory (DFT) were carried out. The ground state geometry was optimized using B3LYP functional in combination with 6-311G(d,p) basis set. TD DFT calculations of excitation energies were carried

out with the same xc functional and the broader basis set 6-311+G(2d,p). Solvent effect was taken into account through non-equilibrium polarized continuum model (PCM). Modelling of the complexes on this theoretical level was out of the computational abilities. All calculation codes came from Gaussian09W program suite [16].

3. Results and discussion

3.1 Synthesis and NMR assignment

Two sets of hydrazones based on phenyl and 2-naphthyl pyrrolinone esters were prepared with at least 60% yield. The procedure of the preparation and purification was similar to the synthesis of only *para* substituted derivatives [11] (Scheme 1). Six cobalt (III) complexes were prepared from these hydrazone ligands with the reaction yields over 70 % (Scheme 2). The reaction mixture had to be vigorously stirred to facilitate an oxidation of Co(II) to Co(III). No base catalysed hydrolysis and consequent formation of *o,o´*-carboxyhydroxyazo complexes was observed.

NMR analysis of **2a-2f,** using also (**2b**) N^{15} analogue, prepared by the same procedure but with $Na^{15}NO_2$ (99% ^{15}N) for the diazotization of aniline derivative [10], confirmed, that all hydrazones exist as a mixture of two isomers and the *Z* isomer is more abundant than *E* isomer. ^1H chemical shifts of methyl and methylene protons of carboxy ester group indicate the *s-trans* conformation in the former and *s-cis* in the latter isomer [10].

Multinuclear magnetic resonance spectroscopy is undoubtedly a very useful tool for studies of metal complex azo dyes (see Refs. [17-20] and references cited therein). It is possible to characterize equivalence or non-equivalence of two ligands in 2:1 complexes, to determine which of two nitrogen atoms is involved in coordination, as well as to describe the coordination sphere of the metal atom, i.e. its coordination number. The compounds studied in this work differ from previously analysed samples in the structure of passive component while the active components (starting substituted hydroxyanilines) are the same as those previously used. Such a situation allows assignment of ^1H and ^{13}C chemical shifts of the most important parts of these complexes as shown in Tables 1 and 2 and Figure 1. Having accomplished this it can be concluded that both ligands in 2:1 complexes are equivalent (at least on the NMR time scale) since only one set of data were observed both in ^1H and ^{13}C NMR spectra. The ^1H and ^{13}C

chemical shifts of protons and carbons of active components are practically the same within an experimental error. It means that, in contrast to the starting ligands existing completely in hydrazone form, cobalt (III) complexes exist in (*E*)-azo configuration and cobalt atom is six-coordinated being bound to oxygens, which originate in hydroxyl and CONH groups, and nitrogens from substituted anilines as starting material for all ligands.

Figure 1

Table 1

Table 2

3.2 DFT structure of hydrazones

NMR analysis confirms the presence of both *E* and *Z* isomer in a reaction product and establishes the conformation of the ester group. Both isomers are probably stabilized by hydrogen bonding from N–H to C=O coming either from pyrrolinone (*Z* isomer) or ester group (*E* isomer) as shown in Figure 2. Such intramolecular H-bonding was found for phenylazo-pyrazolones in the former case [21] and for phenylazo *ß*–ketoesters in the latter case [21] by X-ray diffractometry. On the other hand, there is no experimental evidence, whether the hydrogen from phenol group can mediate the H-bond to more distant nitrogen. Consequently, the DFT optimization of the structures of both possible conformers with respect to hydroxyl orientation (Figure 2 for compound **2a**) was carried out for each isomer of compounds **2a**-**2c**. Relative energies are summarized in Table 3.

Figure 2

Table 3

There is generally a clear trend in DFT results: irrespective to the presence and position of the nitro substituent, *E* and *Z* isomers with the same conformation on the phenol unit are of similar energy, explaining thus the presence of both isomers in reaction product. The absolute values of energy prefer the *Z*-isomer in vacuum and the slightly more polar *E* isomer in a polar environment. A second H-bond supporting *s-cis* conformation of phenol ring is strongly preferred in all cases. An application of the last result as a definitive description of a final conformation is somewhat speculative as the computations do not take into account the specific interactions of phenol (H-bonding) with solvent or with another molecule in the solid-state. The results on *o*-hydroxy-phenylazo *ß*-ketoesters show the preference of a *s-trans* conformer [22] by X-ray diffractometry, although the model DFT calculation predicted the opposite situation. Consequently the excitation energies were calculated on both conformations of both isomers. Azo - enol tautomers were not studied so detailed, as they were not detected in DMSO solution by NMR. Several orientational calculations has shown, that irrespective to substituent their energies are about 17-19 kcal/mol higher as compared to the most stable hydrazone tautomer, explaining thus their absence in studied solutions.

3.3 Absorption and fluorescence of hydrazones

Originally, the absorption spectra of **2a**-**2f** were measured in NMP, in order to be directly comparable with previously reported derivatives with no *o*-hydroxy substituent on the phenyl ring [11]. While the spectra of compounds **2a** and **2d** without nitro substituent have one structureless band in visible region, only 3-4 nm hypsochromically shifted as compared to previously reported isomeric *p*-hydroxy derivatives [11], all four nitro derivatives has shown also the second, considerably bathochromically shifted, absorption band (Figure 3, Table 4). This new band was more intense and less shifted for the 5-nitro derivatives **2b** and **2e**, while less intense but remarkably more shifted for the 4-nitro-derivatives **2c** and **2f**. We consider the new long-wavelength band as an absorption band on O^--anion isomer, rising due to the presence of water in hygroscopic solvent (NMP) even if it is in very low concentration. This idea was supported both experimentally by the effect of added water on the spectra of **2b** in acetone (Figure 4), and

by PCM TD DFT computations of the anions, which qualitatively match the experiment (545 nm for **2b** and 684 nm for **2c**, compared to experimental values 545 nm and 624 nm, respectively). Higher concentration of an anion in 5-nitro derivatives as compared to 4-nitro derivatives and its absence in **2a** and **2d** was tentatively ascribed to an acidity of phenol protons, which probably behave in analogy with nitro-phenols only (pK_a = 9.89, 8.28 and 7.15 for phenol, *m*-NO_2-phenol and *p*-NO_2-phenol, respectively [23]).

Absorption spectra of compounds **2a-2f** were thus also measured at room temperature in THF, in which no long-wavelength absorption band was detected (Figure 5) and molar absorptivities could be estimated (Table 4). All hydrazones have broad absorption band with only one maximum as expected comparing with *para* substituted derivatives [11] with slight bathochromic shift about 8 nm when going from phenyl to 2-naphthyl derivative. A small bathochromic shift of non-dissociated forms is observed when going from THF to more polar NMP. Effect of nitro substitution is also quite small: 5-nitro substitution causes hypsochromic (and hypochromic) shift, while 4-nitro a bathochromic (and hyperchromic) shift, both about 10 nm.

Figure 3

Table 4

Figure 4

Figure 5

PCM (THF) TD DFT computed excitation energies of various isomers / conformers of compounds **2a-2c** qualitatively confirm the observed effect of a nitro group on the absorption spectra (Table 5). Nevertheless, quantitatively the effect of nitro substitution is slightly overestimated. The theoretical prediction is quite clear for **2a** and **2c**, i.e. irrespective to isomer / rotamer arrangement, there is only one strong band in visible area, corresponding to allowed S_0-S_1 (HOMO – LUMO) transition, while $S_0 – S_2$ transition is weak, with wavelength under 400 nm and of HOMO-1 – LUMO (**2a**) or HOMO – LUMO+1 (**2c**). The situation for **2b** is rather complicated, as original LUMO+1 orbital is considerably stabilized by 5-nitro substituent, so both HOMO – LUMO and HOMO – LUMO+1 transitions fall into the visible range and the

character of the lowest excited state depends on conformation of the phenol ring. Anyway, only one of these transitions is always strong and thus driving the absorption spectrum.

Table 5

All compounds under study show strong fluorescence in MTHF solvent glass, as shown in Figure 6 as an example. On the other hand only 4-nitro derivatives **2c** (Figure 7) and **2f** show weak fluorescence in solution (φF = 0.005 for **2c**) and in solid-state. There is a considerable effect of nitro substitution on the shape of low temperature fluorescence excitation and emission spectra. On the other hand, all of the compounds show fluorescence in MTHF solvent glass, as shown in Figure 6 as an example. There is a considerable effect of nitro substitution on the shape of fluorescence excitation and emission spectra. While 0-0 vibronic transition forms an absolute maximum in emission for all nitro derivatives, the excitation maxima correspond to 0-0 transition only in the case of 4-nitro derivatives **2c** and **2f**, which thus show the lowest change in geometry when going from the ground to the fluorescent excited state. The excitation and emission spectra show relatively low Stokes shift between both 0-0 vibronic transition, i.e. there were observed no specific spectral features, like abnormal Stokes shift, relating to excited state proton transfer [24]. The Stokes shift is considerably lower for nitro derivatives (e.g. 1730 cm^{-1} for **2a** vs. 860 cm^{-1} for **2c**), that further supports the above mentioned lowest reorganization in S_1 state for 4-nitro derivatives. There are no significant differences in the spectra of 5-nitro derivatives with respect to either unsubstituted or 4-nitro derivatives, so the fluorescence comes very probably from the same type of S_1 state, i.e. the lowest relaxed excited state of **2b** and **2e** is of the same HOMO – LUMO type as in other compounds, which means that the close in energy S_2 state of HOMO – LUMO+1 type does not affect the fluorescence ability.

As compared with the previously reported derivatives [11], the spectral maxima of *o*-hydroxy derivative **2a** in NMP are almost the same as for *p*-hydroxy derivative. 2-Hydroxy substitution brings a considerable bathochromic and bathofluoric shift (about 25 nm) for compound **2c** with respect to the 4-nitro derivative [11], i.e. the electron-donating effect of *o*-hydroxyl dominates the electron-accepting effect of the nitro group. The same reason (in S_1

state) leads to a considerable decrease of a room temperature fluorescence quantum yield of **2c** with respect to the 4-nitro derivative (φ_F = 0.1 in NMP [11]).

Finally, while the derivatives without an o-hydroxy substituent have shown solid-state fluorescence in the range 554-672 nm easily visually detectable, irrespective of the character of the p-substituent or of type of 5-aryl [11], the *o*-hydroxy substituent in the compounds under study either completely quenches the fluorescence, or considerably decreases its intensity (2c). The nature of this specific process is not very clear and will not be discussed, as there is a lack of information on the molecular packing and consequent interactions in the solid-state.

Figure 6

Figure 7

3.4 Absorption spectra of complexes

There was found no fluorescence of the complexes under study in solution, solvent glass and solid-state. The changes in absorption spectra induced by irradiation of diluted solutions are under study and will be published later. The absorption spectra of all synthesized complexes **3a-3f** were measured in NMP and THF immediately after preparation at room temperature. On the contrary to hydrazone series, no qualitative difference in spectral behaviour in both solvents was observed. The spectra are shown on Figures 8 and 9 and the spectral data are summarized in Table 6. The spectral curves do not show well-resolved vibronic structure but from the data it appears that in the case of **3a**, **3b**, **3d** and **3e** the absolute maximum is 0-1 band and a long wavelength shoulder band relates to 0-0 band, while the opposite is observed for **3c** and **3f**, i.e. 0-0 band is an absolute maximum and 0-1 band corresponds to a short wavelength shoulder. There is a moderate bathochromic (4-8 nm) shift when going from the phenyl to 2-naphthyl derivatives, but the rise of molar absorptivity accompanying conjugation extension is considerable. Azo complexes of *o,o´*-dihydroxy class show usually broad absorption bands with molar absorptivities under 50 000 $L.mol^{-1}.cm^{-1}$, so the absorption spectrum of e.g. compound **3f** with one relatively narrow band near 600 nm, resolved vibronic structure and ε over 80 000 $L.mol^{-}$

^{1}.cm^{-1} in NMP makes this type of complexes interesting for further structure / properties research, as e.g. DVD-R media require the values of ε over 100 000 L.mol^{-1}.cm^{-1} [7].

The absorption spectra of complexes are generally bathochromically shifted with respect to starting hydrazone ligands. The effect of the presence and position of the nitro group is considerably different. While a 5-nitro substituent causes small hypsochromic shift (about –10 nm of **2b** vs. **2a**), 4-nitro substituted compounds are a bit bathochromically shifted (about +10 nm of **2c** vs. **2a**) in the hydrazone series (Table 4). On the other hand, the effect of nitro substitution is much more specific in complex series (Table 6): 5-nitro substituent causes very small bathochromic shift (about +5 nm of **3b** vs. **3a**), while 4-nitro substitution shifts the corresponding vibronic bands more than 50 nm bathochromically (**3c** vs. **3a**). The computed excitation energies of strong allowed bands falling into the visible region of hypothetical (not detected) azo tautomers of ligands **2a**, **2b** and **2c** (452 nm, 454 nm and 531 nm in THF, respectively) show the same trend as the spectra of complexes, indirectly confirming the azo character of ligands in complexes, as derived also from NMR.

Table 6

Figure 8

Figure 9

4. Conclusion

All new keto-hydrazone dyes were present as a mixture of *E* and *Z* isomers, so the original expectations on improving the selectivity of a reaction towards only one isomer by its stabilization by additional H-bonding were not fulfilled. All compounds fluoresce strongly only in solvent glass at 77 K, while fluoresce in solution or in solid state is either very weak or totally absent. Thus the rigidity of the molecules in excited state by intramolecular H-bonding was not increased. In summary, there was not found any experimental evidence of the secondary H-bonding both in the ground and excited state. The effect of *o*-hydroxy substituent was thus only electron-donating.

Using these hydrazones as tridentate O–N–O´ ligands, six new symmetrical 2:1 octahedral Co(III) complexes were prepared. Multinuclear NMR proved that the starting mixture of hydrazone isomers was converted solely to *E*-azo configuration in the complexes. The considerably different effect of 4- and 5-nitrophenol substituents on the absorption spectra of the ligands and complexes was ascribed to azo character of an electronic structure of the ligands in complexes. 4-Nitrophenyl substituted complexes show relatively narrow absorption bands near 600 nm and high molar absorptivities, giving thus some perspective to this type of compounds in optical data recording. Further research of the structural modifications to improve these properties is now in progress.

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Table 1: ^{1}H, ^{13}C NMR data for compounds **3a, 3b** and **3c**

H/C No.	3a		3b		3c	
	δ(^{1}H)	**δ(^{13}C)**	**δ(^{1}H)**	**δ(^{13}C)**	**δ(^{1}H)**	**δ(^{13}C)**
1 (NH)	11.37	-	11.39	-	11.97	-
2	-	131.5	-	135.7	-	136.2
3	-	105.1	-	104.6	-	104.8
4	-	122.9	-	124.1	-	126
5	-	144.8	-	145.7	-	146.6
COO	-	164.5	-	163.8	-	163.8
CH2	4.38	59.5	4.40	59.9	4.31	59.9
CH3	1.42	14.4	1.52	14.3	1.34	14.4
1″	-	131	-	130.4	-	130.3
2″	7.50	127.6	7.56	128.3	7.55	128.2
3″	7.36	127.9	7.40	128	7.42	128.1
4″	7.29	127.4	7.40	128.5	7.38	128.7
1′	-	146.8	-	146.5	-	152.9
2′	-	168	-	173.8	-	166
3′	6.56	117.3	6.71	116.5	7.37	110.8
4′	6.84	126.9	7.87	123.2	-	145.2
5′	6.60	113.7	-	136	7.65	110.9
6′	8.17	114.5	9.06	110	8.30	113.8

Table 2: ^{1}H, ^{13}C NMR data for compounds **3d, 3e** and **3f**

H/C No.	3d		3e		3f	
	δ(^{1}H)	**δ(^{13}C)**	**δ(^{1}H)**	**δ(^{13}C)**	**δ(^{1}H)**	**δ(^{13}C)**
1(NH)	11.57	-	12.01	-	11.96	-
2	-	131.3	-	135.7	-	136.2
3	-	105.4	-	104.9	-	105
4	-	123	-	123.3	-	126.1
5	-	145	-	145.8	-	146.8
COO	-	164.5	-	163.8		163.8
CH_2	4.41	59.5	4.42	59.9	4.42	59.9
CH_3	1.43	14.3	1.47	14.3	1.41	14.4
1′	-	146.8	-	146.5	-	153
2′	-	168	-	173.8	-	166
3′	6.62	117.3	6.75	116.5	7.41	110.8
4′	6.88	125.9	7.70	126.3	-	145.3
5′	6.63	118.7	-	136	7.67	110.9
6′	8.23	114.9	9.09	110	8.35	113.6

3d 2-naphthyl δ(^{1}H): 7.51-8.03 (overlapped multiplets)

3d δ(^{13}C): 128.5, 132.1, 132.5 (all C), 125.8, 126.1, 126.2, 126.9, 127.0, 127.3, 127.9 (all CH)

3e 2-naphthyl δ(^{1}H): 7.54-8.10 (overlapped multiplets)

3e δ(^{13}C): 127.9, 132.4, 132.6 (all C), 124.2, 126.5, 126.7, 127.2, 127.4, 127.5, 128.2 (all CH)

3f 2-naphthyl δ(^{1}H): 7.57-8.10 (overlapped multiplets)

3f δ(^{13}C): 127.9, 132.5, 132.7 (all C), 126.2, 126.7, 126.9, 127.4, 127.6, 127.9, 128.3 (all CH)

Table 3: Relative energies of various conformers of **2a**-**2c** in vacuum and in THF (according to Figure 2).

Compound	Configuration on C=N bond (Isomer)	Conformation on C–N bond (Rotamer)	Relative ground state energy in vacuum [1] (kcal/mol)	Relative ground state energy in THF [2] (kcal/mol)
2a	***E***	***s-cis***	**1.340**	**0.000**
		s-trans	**7.362**	**3.758**
	Z	***s-cis***	**0.000**	**0.860**
		s-trans	**6.064**	**3.932**
2b	***E***	***s-cis***	**0.276**	**0.000**
		s-trans	**7.910**	**4.358**
	Z	***s-cis***	**0.000**	**1.362**
		s-trans	**5.897**	**4.805**
2c	***E***	***s-cis***	**0.635**	**0.000**
		s-trans	**5.615**	**3.170**
	Z	***s-cis***	**0.000**	**1.405**
		s-trans	**4.950**	**3.874**

[1] B3LYP/6-311G(d,p), the most stable conformation of **2b** is 0.737 kcal/mol more stable than **2c**

[2] PCM (THF) B3LYP/6-311+G(2d,p), the most stable conformation of **2b** is 0.378 kcal/mol more stable than **2c**

Table 4: Absorption and fluorescence maxima of compounds **2a-2f** at room (NMP and THF) and low (MTHF) temperature (all compounds are the mixtures of *E* and *Z* isomers).

Compound	**Absorption maxima in NMP [nm]**	**Absorption maxima in THF [nm]**	**Absorption coefficient in THF [L.mol^{-1}.cm^{-1}]**	**Excitation (77 K)**		**Emission (77 K)**	
				0-1	0-0	0-0	0-1
2a	460	454	33550	469	493	539	567
2b	468, 546	445	27800	463	484	509	539
2c	477, 624	465	41350	471	505	528	555
2d	466	463	39200	477	499	541	570
2e	470, 555	453	37350	464	493	514	547
2f	484, 639	473	45000	484	512	535	573

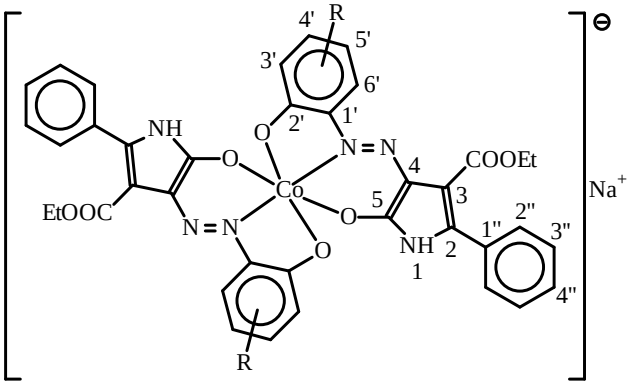
Table 5: PCM (THF) TD DFT excitation energies (λ_{00}) and oscillator strengths (f_{osc}) of **2a-2c** for various isomers and conformers as shown on Figure 2 for **2a**.

Compound	Configuration on C=N bond (Isomer)	Conformation on C–N bond (Rotamer)	HOMO→LUMO		HOMO → LUMO+1 resp. HOMO-1 → LUMO	
			λ_{00}	f_{osc}	λ_{00}	f_{osc}
2a	*E*	*s-cis*	460	0.759	364	0.066
		s-trans	449	0.786	349	0.010
	Z	*s-cis*	471	0.819	378	0.012
		s-trans	459	0.849	363	0.028
2b	*E*	*s-cis*	440	0.849	470	0.051
		s-trans	482	0.060	433	0.775
	Z	*s-cis*	456	0.731	465	0.160
		s-trans	484	0.084	447	0.762
2c	*E*	*s-cis*	490	0.964	395	0.034
		s-trans	485	1.004	388	0.059
	Z	*s-cis*	502	0.970	396	0.025
		s-trans	498	0.995	390	0.056

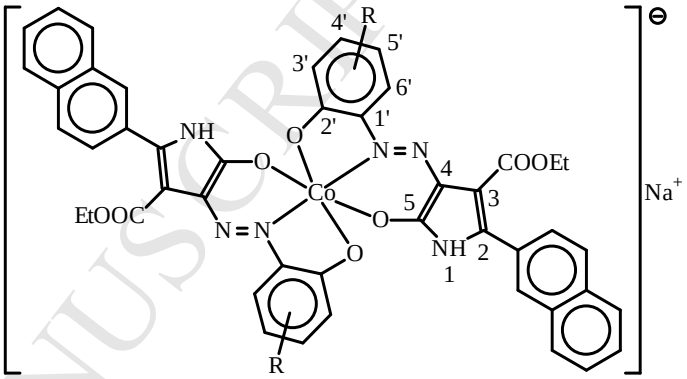
Table 6: Absorption maxima and molar absorption coefficient of complexes **3a-3f** in THF

Dye	**Absorption maxima in NMP [nm]**	**Absorption coefficient in NMP [L.mol^{-1}.cm^{-1}]**	**Absorption maxima in THF [nm]**	**Absorption coefficient in THF [L.mol^{-1}.cm^{-1}]**
3a	519	41600	514	34000
3b	525	60000	519, 546 (s)	38700
3c	600	63200	566 (s), 591	50300
3d	529	53000	518	39000
3e	532	77000	526, 553 (s)	52400
3f	604	84000	574 (s), 597	62500

Underlined values represent the absolute absorption maxima



	R
3a	—H
3b	5'—NO_2
3c	4'—NO_2



	R
3d	—H
3e	5'—NO_2
3f	4'—NO_2

Figure 1: C, H numbering used in NMR assignment of synthesized cobalt complexes.

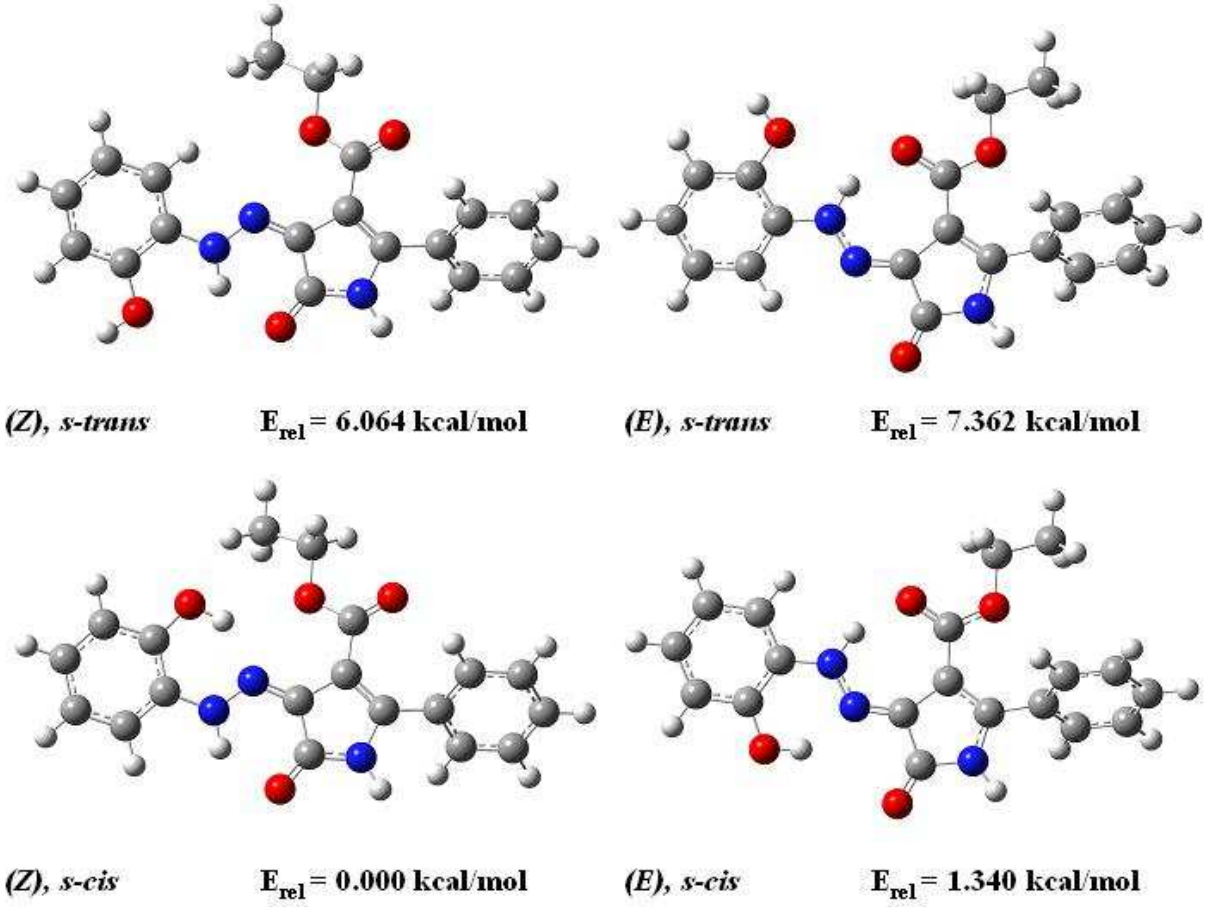


Figure 2: DFT structures of **2a** *Z/E* isomers / (on phenol) conformers under study with relative energies in vacuum.

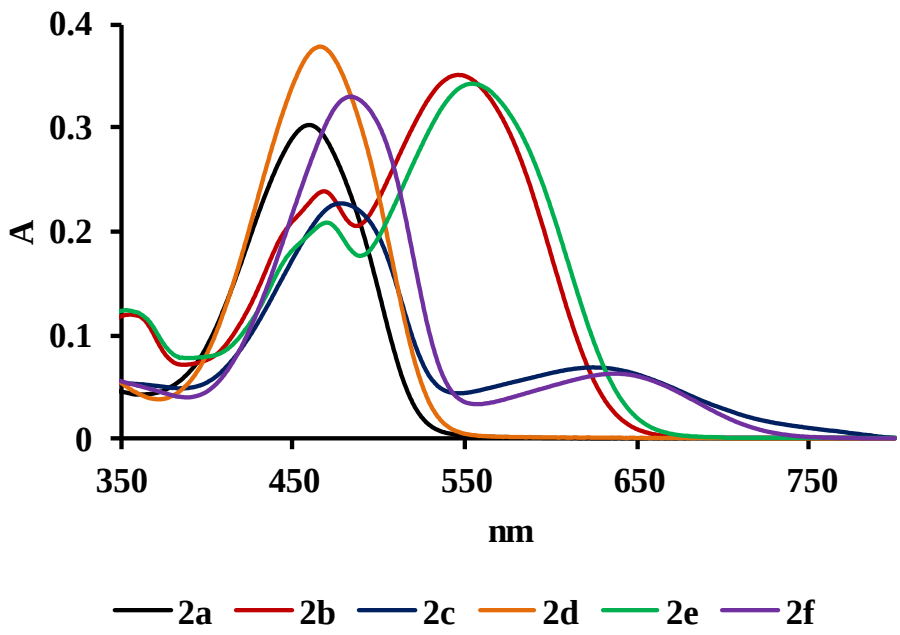


Figure 3: Absorption spectra of **2a-2f** in NMP.

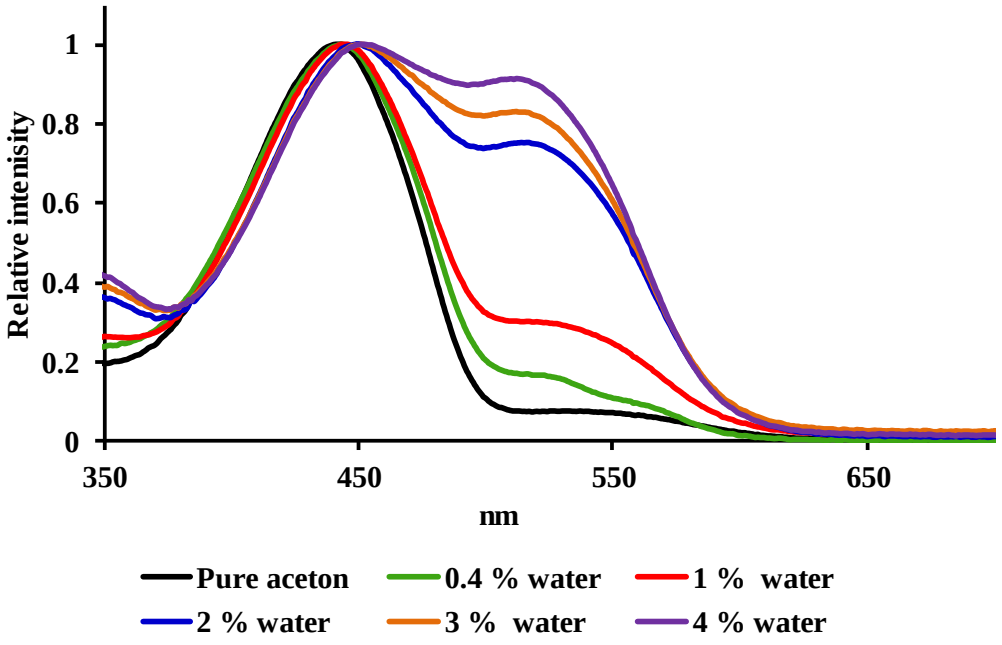


Figure 4: Absorption spectra of **2b** in acetone in presence of different concentration of water.

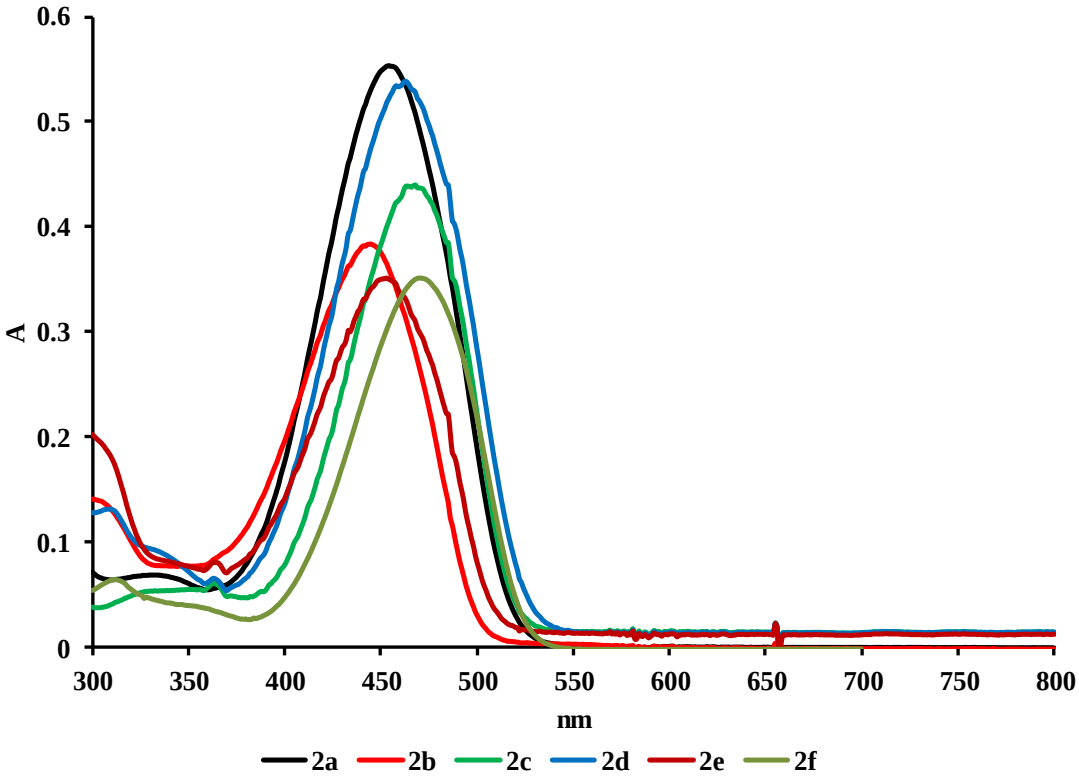


Figure 5: Absorption spectra of hydrazones **2a-2f** in THF.

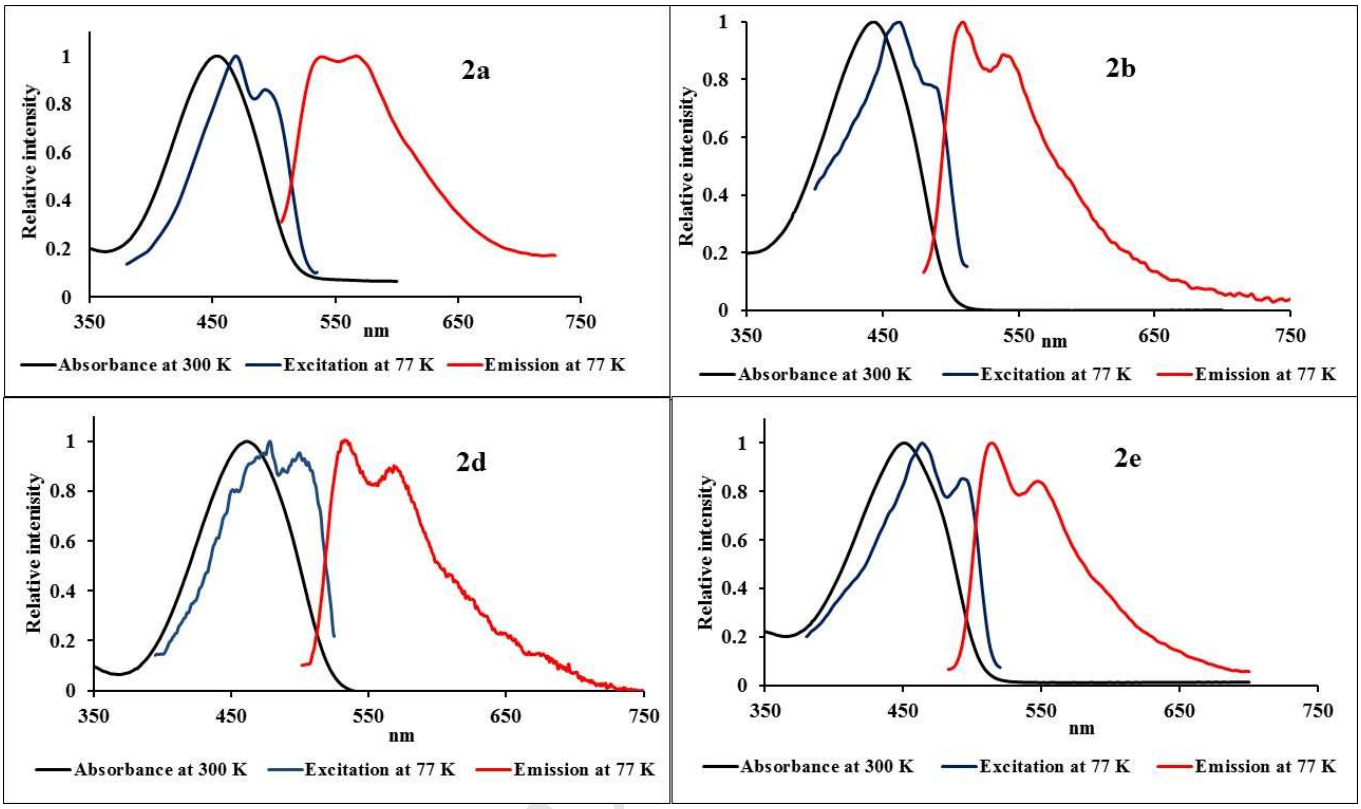


Figure 6: Absorption (room temperature) and fluorescence excitation and emission spectra in MTHF at 77 K for **2a**, **2b**, **2d**, **2e**

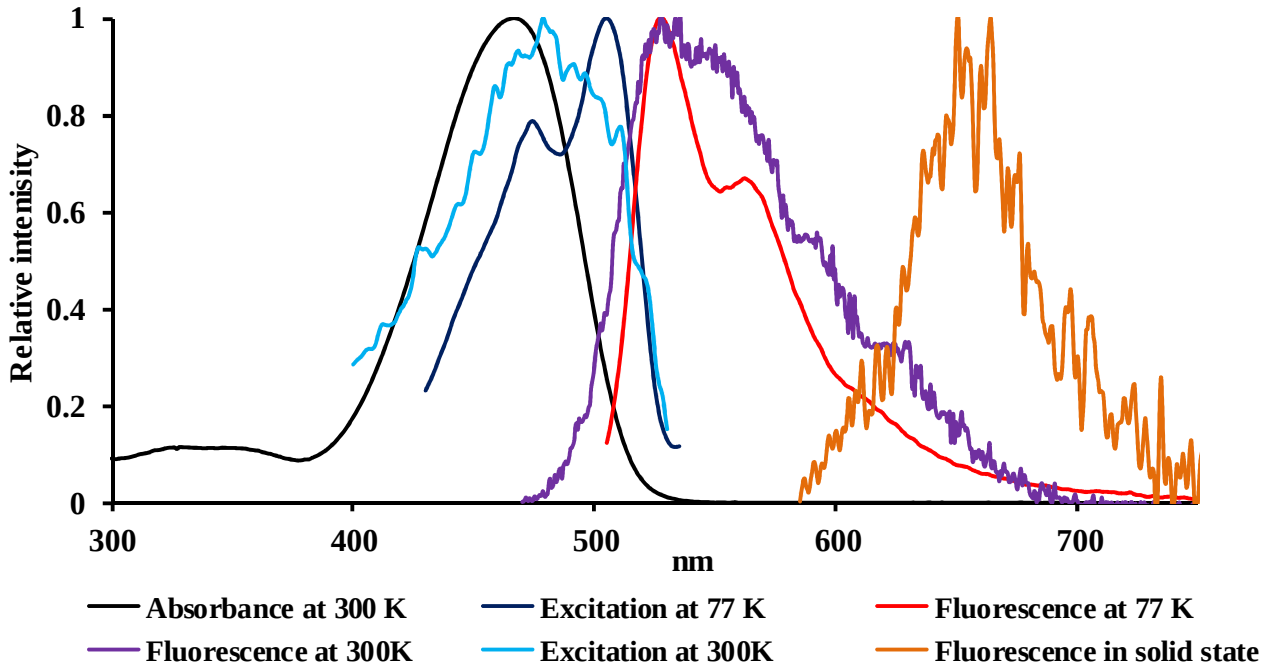


Figure 7: Absorption at room temperature (MTHF), excitation and emission spectra at low temperature (MTHF) of compound **2c** together with its solid-state emission at room temperature.

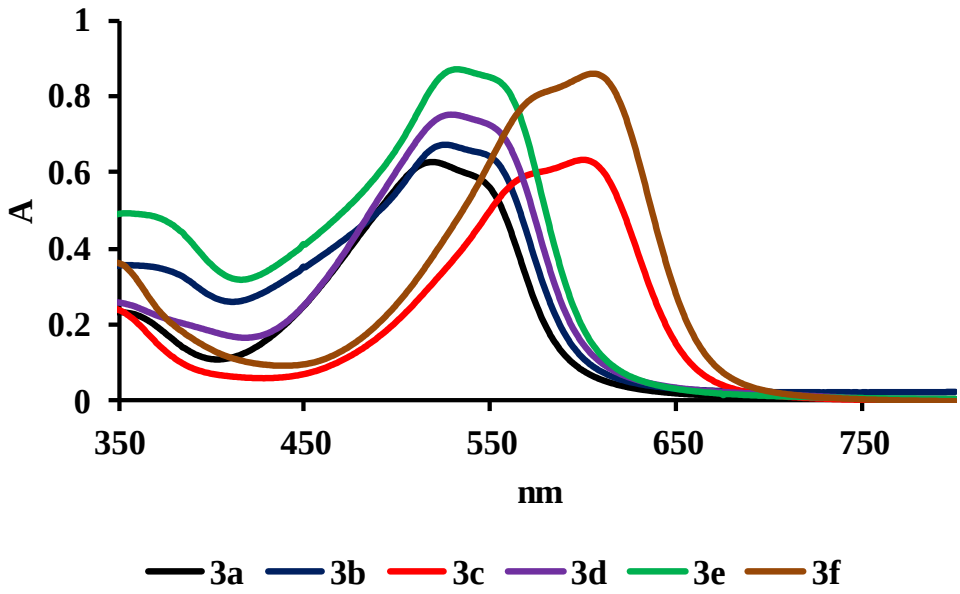


Figure 8: Absorption spectra of complexes **3a-3f** in NMP.

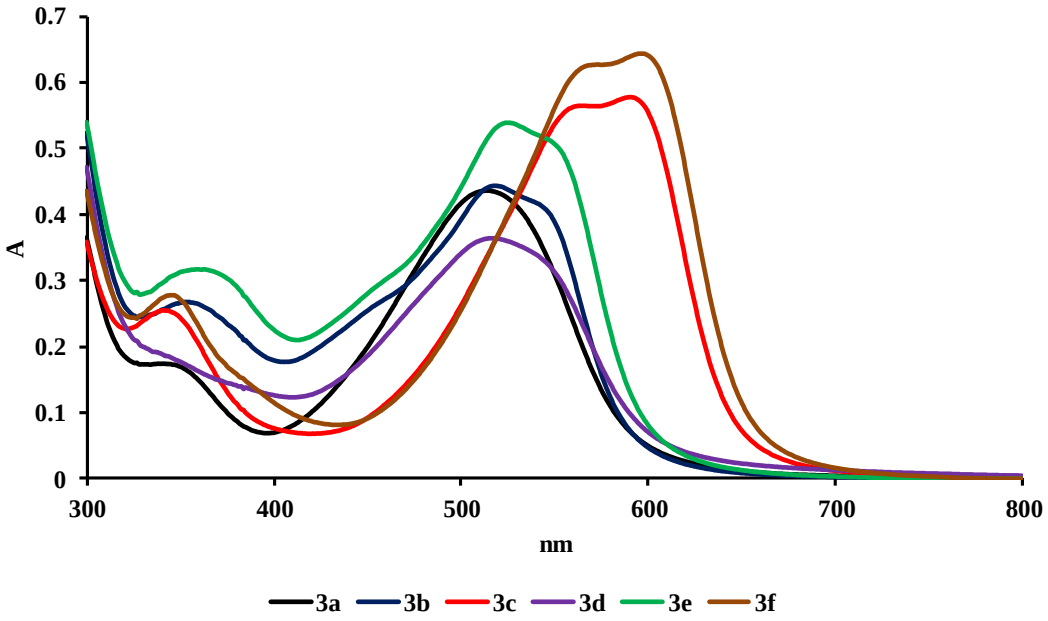


Figure 9: Absorption spectra of complexes **3a-3f** in THF.

- Six new *o*-hydroxy substituted hydrazones based on pyrrolinone esters were prepared as a mixture of *E* and *Z* isomers.
- Their absorption and fluorescence spectra were studied experimentally and theoretically by TD DFT.
- Six new 2:1 symmetrical Co(III) complexes were prepared using these hydrazones as tridentate ligands.
- The starting mixture of hydrazone isomers was converted solely to *E*-azo configuration in complexes by NMR spectroscopy.
- Different effect of nitro group position in ligands and complexes on the absorption spectra was discussed.