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Synthesis and Photophysical Properties of Yellow-Emitting Iridium Complexes. Effect of the Temperature on the Character of Triplet Emission

P. Ivanov · S. Stanimirov · S. Kaloyanova · I. Petkov

Abstract The parent study includes synthesis end photophysical characterization of four new phosphorescent cyclometalated iridium (III) complexes. The cyclometaled ligands used here are 2-(4-chlorophenyl)benzo[d]thiazole, 2(4isopropylphenyl)benzo[d] thiazole, 2-(4-methoxyphenyl)benzo[d] thiazole, 4-(benzo[d]thiazol-2-yl)-N,N-dimethylaniline. The auxiliary ligand is acetylacetone (Hacac). The photometric analyses show temperature dependence on phosphorescent spectra and the nature of the emitting state of the synthesized complexes. Using fluorescent and absorption spectroscopy we suggest an explanation of the observed effect points out the transition from ligand centered (LC) to MLCT main character of the emitting state. The quantitative photometric analysis states high phosphorescent quantum yields of the complexes in solution.

Keywords Ir complexes · Quantum yield · MLCT emitters · Phenylbenzothiazole

Introduction

Organometallic compounds possessing a heavy transition-metal element are one of the best and most intensively studied in a last decade emitters in phosphorescent organic light-emitting devices (OLEDs) [1–7]. These complexes contain a five-membered chelate ring with carbon and nitrogen atoms coordinated to the metal. Neutral homoleptic tris-ciclometalated $Ir(C^N)_3$ complexes [8–12] and heteroleptic bis-cyclometalated complexes $(C^N)_2IrL$ (L = ancillary ligand) based on 2-phenylpyridine (ppy) [13–16] and related ligands [17] are one of the most popular and thoroughly studied iridium complexes. The strong spin-orbit coupling effectively promotes intersystem crossing as well as enhances the subsequent emissive decay from the triplet excited state to the ground state. Usually obtained phosphorescence emission is due to relaxation of the triplet excitations which are with different nature. The electronic transitions responsible for phosphorescence in these complexes have been assigned to the mixture of metal-to-ligand charge transfer (^{1}MLCT, ^{3}MLCT) and ligand-centred (LC) $^3(\pi$-$\pi^*)$ lowest exited states [8, 10, 14, 17–19]. Iridium (III) with cyclometalating ligands prefer to form bis-cyclometalated complexes $(C^N)_2IrL$ (L-ancillary ligand) while the MLCT character of the lowest excited states is supposed to be highest with the maximum number of metal-carbon σ-bonds [8, 9, 15, 16].

Thompson et al. [17] reported a series of neutral iridium (III) complexes that exhibit different emissive colors. Recently, Grushin's group synthesized a series of iridium (III) complexes with fluorinated 2-arylpyridines and showed that the emissive colors of the materials can be finely tuned by systematic control of the nature and positions of the substituents on the ligands [20, 21]. These results prompted us to study systematically the substitutions into 2-phenylbenzothiazole and the effect on colors of the emission caused by substituents. In this paper, we report the synthesis and characterization of a series of iridium complexes having different substituted 2-phenylbenzothiazole ligands.

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Experimental

Instruments and Measurements

^{1}H NMR (600 MHz) spectra were recorded on a Bruker Avance-600 at room temperature. The ^{1}H-NMR spectra were referenced to internal TMS. The elemental analyses were made on Elementar Vario EL III. The UV and fluorescence spectra of the complexes in solutions and solid state were recorded on a Thermo Spectronic Unicam 500 spectrophotometer (spectral bandwidth 4 nm, data interval 1 nm) and a Varian Cary Eclipse fluorescence spectrophotometer (spectral bandwidth 2.5 nm, data interval 1 nm), respectively. The quartz plates (2×2 cm) were coated with polymer using the Laurell single wafer spin processor model WS-400A-6NPP. The thickness of the films was about 1 μm. Those films were obtained spinning 1 ml of solutions of the polymer with concentration 0.04 g/ml (the solvent was toluene) for 1 min with frequency 1000 rpm. The weight concentration of the complexes in the polymer matrix was 1 %.

Synthesis of Iridium Complexes

Compounds (ligands) **3a**–**3d** (Scheme 1) were synthesized according to procedure reported else here [22] and were left us by proff. T. Deligeorgiev. The other initial reagents and solvents are trade compounds and they were used as supplied without other purification.

Synthesis of Compounds 3a–3d

Method A 2,2′-diaminodiphenyldisulfide **1** (2.5 mmol), the corresponding aldehyde **2a**–**2d** (5 mmol), PEG 200/400 (5 mL) and *p*-TsOH (0.1 mmol) were placed in a 25 mL Erlenmeyer flask. The reaction mixture was irradiated for 15 min (**3c**) or 10 min (**3d**) at 560 W in a microwave reactor. The mixture was allowed to cool down to room temperature and ethanol (10 mL) was added. The products (**3a**–**3d**) were precipitated by dilution with cold water (50 mL) and were isolated by filtration.

Method B *o*-Aminothiophenol **1a** (5 mmol), the corresponding aldehyde **2a**–**2d** (5 mmol), PEG 200/400 (5 mL) and *p*-TsOH

2a,3a:R=Cl, 2b,3b:R=OMe, 2c,3c:R=iPr, 2d,3d:R=N(Me)₂
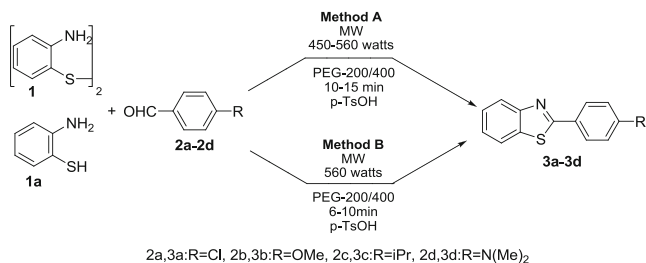
Scheme 1 Synthesis of 2-Arylbenzothiazole ligands
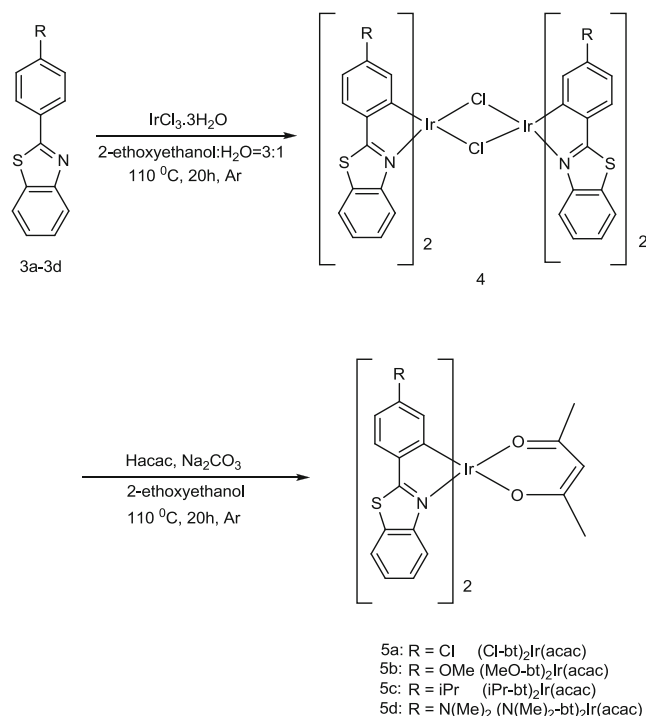
Scheme 2 Synthesis of μ-chloro-bridged iridium dimmer (4)

(0.1 mmol) were placed in a 25 mL Erlenmeyer flask. The reaction mixture was irradiated for 10 min (**3a**, **3b**, **3d**) or 5 min (**3c**) at 560 W in a microwave reactor. The mixture was allowed to cool down to room temperature and EtOH (10 mL) was added. The products (**3a**–**3d**) were precipitated by dilution with cold water (50 mL) and were isolated by filtration.

Synthesis of Ir(III) μ-Chloro-Bridged Dimmers

Cyclometalated Ir(III) μ-chloro-bridged dimmers of general formula $(C^\wedge N)_2 Ir(\mu\text{-}Cl)_2 Ir(C^\wedge N)_2$ were synthesized by the method reported by Nonoyama. 2-Phenylbenzothiazole (**3a**–**3d**) (2.2 equiv), iridium trichloride hydrate (1 equiv), 2-ethoxyethanol: water = 3:1 were heated and stirred at 110 °C for 20–24 h under argon. After cooling to room temperature, the crude solution was filtrated to give an orange-yellow precipitate. Then the precipitate was washed with ethanol and hexane for several times. After dried of room temperature, a cyclometalated Ir(III) μ-chloro-bridged dimmer (4) was obtained.
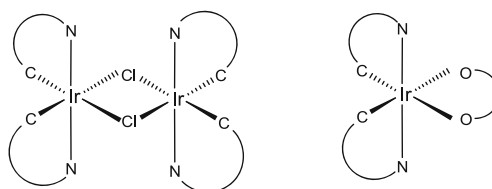

Fig. 1 The coordination geometries of $(C^\wedge N)_2 Ir(\mu\text{-}Cl)_2 Ir(C^\wedge N)_2$ and $(C^\wedge N)_2 Ir(acac)$ complexes

Table 1 Photophysical data for $(C^\wedge N)_2Ir(acac)$ complexes in Ar saturated CH_2Cl_2 solutions

Complex	Absorbtion λ (lgε)	Emission λ_{max}(nm)	Quantum yields
5a	272 (3.89), 320 (3.92), 331 (3.94), 400 (3.23), 442 (3.18)	552	0.40
5b	332 (4.2), 387 (3.77), 444 (3.50)	577	0.20
5c	275 (4.49), 303 (4.46), 318 (4.50), 331 (4.55), 403 (3.82), 442 (3.76)	555	0.37
5d	408 (4.41), 446 (4.08)	578	0.16

Synthesis of Iridium Acetylacetone Complex

Dimmer (4) , 2,4-pentanedione (2.5 equiv) and Na_2CO_3 (5 equiv) were heated and stirred at 110 °C in the presence of 2-ethoxyethanol under argon for 20 h. After cooling to room temperature, the crude product was filtrated to give an orange-yellow precipitate. Then the precipitate was washed with water, ethanol, and hexane for several times. Finally, the crude product was purified using liquid chromatography (silica, dichloromethane) and dried.

Iridium(III)bis[2-(4-chlorophenyl)benzothiazolato-N, $C^{2'}$]-acetylacetonate, (Cl-bt)$_2$Ir(acac): Yield: 80 %. ^{1}H NMR (600 MHz, CDCl$_3$) δ[ppm]: 1.79 (s, 6H), 5.16 (s, 1H), 6.33 (d, J=1.8 Hz, 2H), 6.92 (dd, J$_1$=1.8 Hz, J$_2$=8.4 Hz, 2H), 7.46–7.51 (m, 4H), 7.61 (d, J=7.8 Hz, 2H), 7.94–7.95 (m, 2H), 8.04–8.06 (m, 2H); C$_{31}$H$_{21}$Cl$_2$N$_2$S$_2$O$_2$Ir. Elemental analysis: Calc. C 47.69 %, H 2.71 %, N 3.59 %. Found: C 47.52 %, H 2.68 %, N 3.49 %.

Iridium(III)bis[2-(4-methoxyphenyl)benzothiazolato-N, $C^{2'}$]-acetylacetonate, (MeO-bt)$_2$(acac): Yield: 60 %. ^{1}H NMR (600 MHz, CDCl$_3$) δ[ppm]: 1.70 (s, 6H), 3.34 (s, 6H), 5.07 (s, 1H), 5.83 (d, J=2.4 Hz, 2H), 6.37 (dd, J$_1$=2.4 Hz, J$_2$=8.4 Hz, 2H), 7.29–7.34 (m, 4 H), 7.52 (d, J=8.4 Hz, 2H), 7.76–7.78 (m, 2H), 7.95–7.97 (m, 2H); C$_{33}$H$_{27}$N$_2$O$_4$S$_2$Ir. Elemental analysis: Calc. C 51.35 %, H 3.53 %, N 3.63 %. Found: C 51.25 %, H 3.50 %, N 3.58 %.

Iridium(III)bis[2-(4-isopropylphenyl)benzothiazolato-N, $C^{2'}$]-acetylacetonate, (iPr-bt)$_2$(acac): Yield: 50 %. ^{1}H NMR (600 MHz, CDCl$_3$) δ[ppm]: 0.87 (d, J=3.0 Hz, 6H), 0.89 (d, J=3.0 Hz, 6H), 1.72 (s, 6H), 2.43–2.48 (m, 2H), 5.22 (s, 1H), 6.30 (d, J=1.8 Hz, 2H), 6.78 (dd, J$_1$=1.8 Hz, J$_2$= 7.8 Hz, 2H), 7.53–7.58 (m, 4 H), 7.67 (d, J=7.8 Hz, 2H), 8.12–8.14 (m, 2H), 8.18–8.20 (m, 2H); C$_{37}$H$_{35}$N$_2$O$_2$S$_2$Ir. Elemental analysis: Calc. C 55.83 %, H 4.43 %, N 3.52 %. Found: C 55.61 %, H 4.39 %, N 3,47 %.

Iridium(III)bis[4-(benzothiazolato-N,C$^{2'}$-2-yl)-N,N-dimethylaniline]-acetylacetonate, (N(Me)$_2$-bt)$_2$(acac): Yield: 70 %. ^{1}H NMR (600 MHz, CDCl$_3$) δ[ppm]: 1.71 (s, 6H), 2.51 (s, 12H), 5.08 (s, 1H), 5.58 (d, J=2.4 Hz, 2H), 6.15 (dd, J$_1$= 2.4 Hz, J$_2$=8.4 Hz, 2H), 7.20–7.22 (m, 2H), 7.26–7.28 (m, 2H), 7.39 (d, J=9 Hz, 2H), 7.69 (dd, J$_1$=0.6 Hz, J$_2$=7.8 Hz, 2H), 7.96 (dd, J$_1$=0.6 Hz, J$_2$=8.4 Hz, 2H); C$_{35}$H$_{33}$N$_4$O$_2$S$_2$Ir. Elemental analysis: Calc. C 52.68 %, H 4.17 %, N 7.02 %. Found: C 52.51 %, H 4.10 %, N 6.92 %.

Results and Discussion

Synthesis and Characterization of $(C^\wedge N)_2Ir(acac)$ Complexes

Iridium chloride reacts with cyclometaled ligands (R-bt) in refluxing 2-ethoxyethanol to give a cyclometalated complex [23]. The product of this reaction is a chloride-bridged dimmer (R-bt)$_2$Ir(μ-Cl)$_2$(R-bt)$_2$, R=Cl, OMe, iPr, N
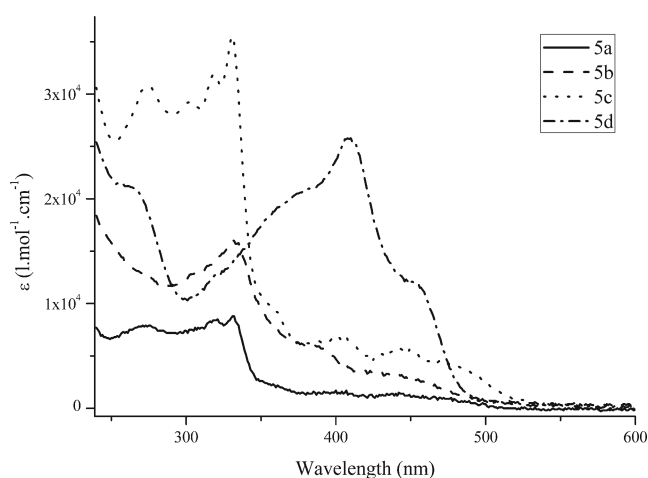

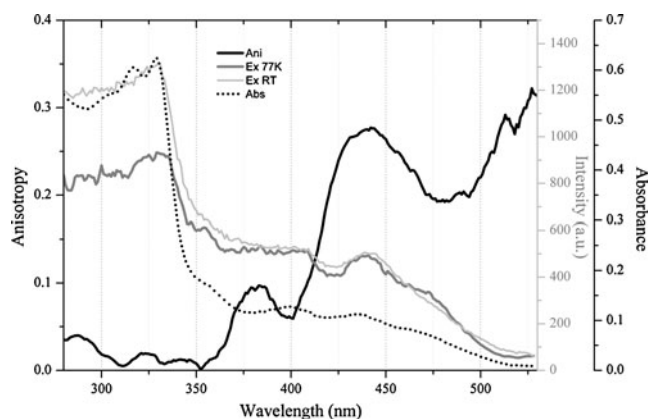**Fig. 2** Absorption spectra of solutions of the complexes in CH_2Cl_2

Fig. 3 Gray lines—normalized corrected excitation spectra of 5a solutions in CH_2Cl_2 monitored at 557 nm, recorded at RT and 77 K; Dotted line—absorption spectra of the same solution at RT; Black line—Anisotropy of the polystyrene film doped with 5a (1 % wt.) at RT
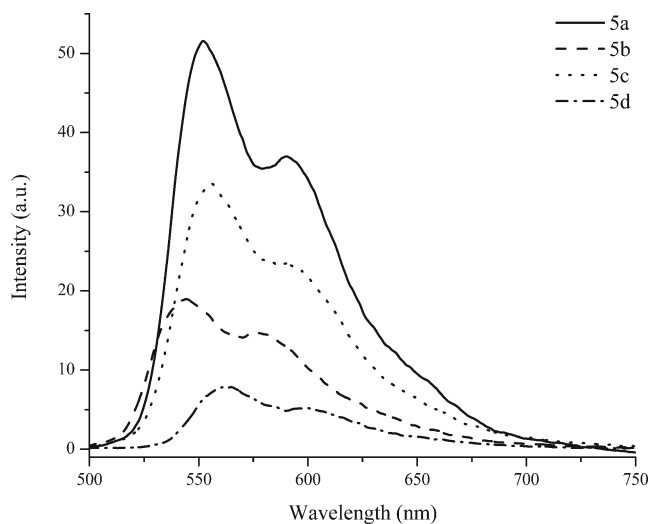
Fig. 4 Emission spectra of 10^{-5} M Ar saturated solutions of the complexes in CH$_2$Cl$_2$ excited at 400 nm and RT

(Me)$_2$. We have found that cyclometalation reaction is a general one, giving good yields of the corresponding (C^N)$_2$Ir(μ-Cl)$_2$Ir(C^N)$_2$ dimmers (C^N = cyclometalated ligand). The dimmers formation reactions proceed under mild conditions, giving good yields of the organometallic

complexes. Those yields are typically greater than 70 % (Scheme 2). All of the ligands used here have heterocyclic nitrogen and a sp^2-hybridized carbon in such position so the cyclometalation reaction leads to a five-membered ring. The NMR spectra of these complexes are consistent with the heterocyclic rings of the C, N ligands being in a trans disposition, as shown in Fig. 1 [15]. The chloride-bridged complexes form a racemic mixture of ΔΔ/ΛΛ dimmers that are characterized by pronounced downfield shifts in the ^{1}H NMR resonance of heterocyclic protons nearest to the bridging chlorides [24].

The emissive monomer complexes can be obtained by treating of the chloride-bridged dimmers with a bidentate, anionic ancillary ligand (Hacac) (Scheme 2). These reaction give (C^N)$_2$Ir(acac) in high yield, typically greater than 60 %. The (C^N)$_2$Ir(acac) complexes prepared are orange-yellow precipitate. Their solutions are emissive at room temperature, with λ$_{max}$ values between 550 and 580 nm, Table 1.

Photophysical Properties

Figure 2 present absorption spectra of the complexes studied here. The spectra are not well resolved and show complicate structure due to overlapping of various bands. Such spectra
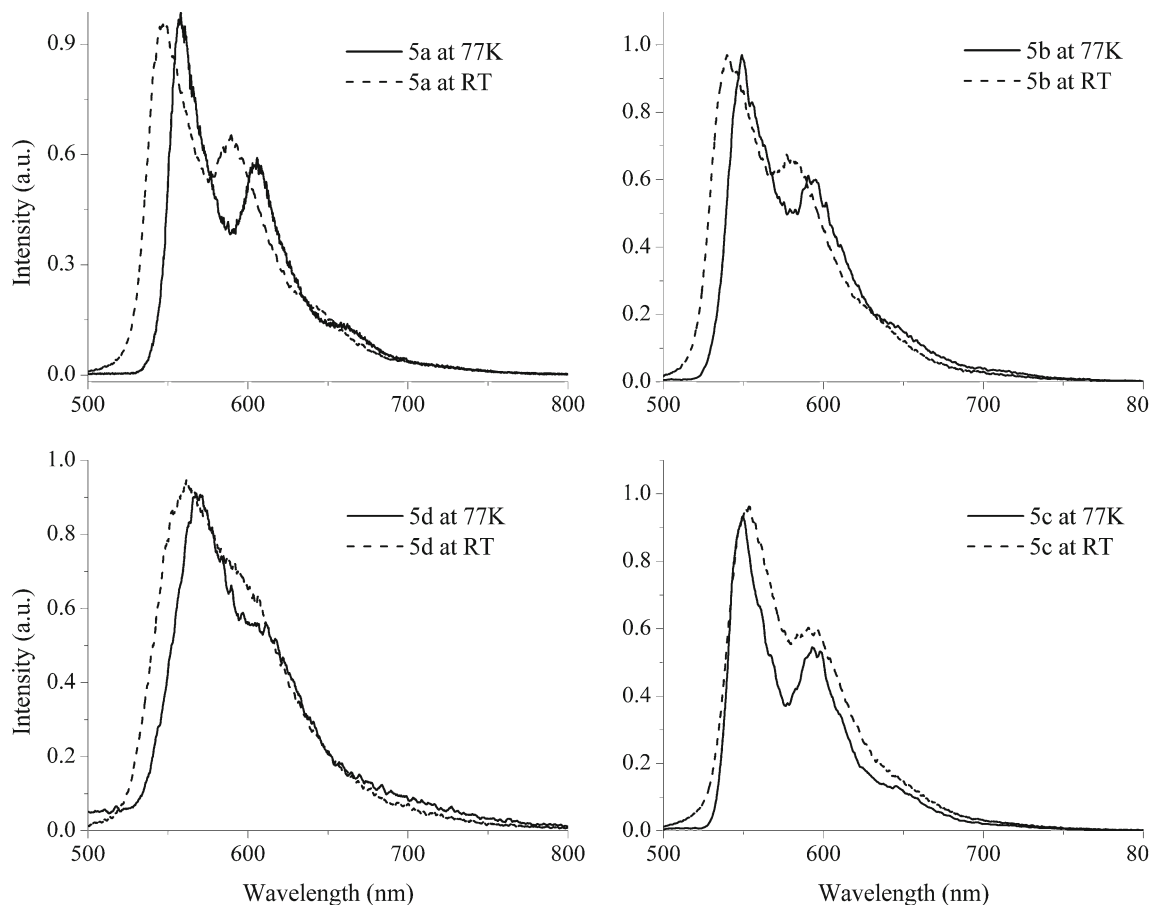

Fig. 5 Normalized emission spectra of the complexes in tetrachloromethane at room temperature and 77 K

are typical for that kind of complexes. The spectra for the first three compounds are similar and can be consider as two parts. The region below 360 nm contains bands for electronic transitions, which lead to excitations in ligands themselves. Most probably, the band around 330 nm is due to transition to lowest singlet ligand centered (^{1}LC) excited state. This is consistent with publications about similar complexes published before [17]. The shoulders above 360 nm are assigned to singlet and triplet metal-to-ligand charge transfer (^{1}MLCT, ^{3}MLCT) bands, respectively. Effective spin-orbit coupling (SOC) in these complexes relax the spin forbiddance and mix the singlet and triplet states making the band for resonant transition $^1S_0 \rightarrow {}^3$MLCT detectable in absorption spectrum (around 480 nm). The band for ^{1}MLCT transition is centered at 440 nm. Absorption spectrum of the 5 d (Fig. 2) looks different. Due to strong electron-donating properties of –N(CH$_3$)$_2$ group ^{1}LC band is shifted to low energies and overlap the bands for MLCT transitions.

As a clue for the kind and exact position of the absorption bands, the anisotropy spectrum of 5a in polystyrene matrix at room temperature can be used (Fig. 3). The transition moments of the absorption bands have different orientation compared with transition moment of the emitting state. One can see the transition moment of the ^{1}MLCT transition is almost parallel to emitting state transition moment. In contrary, the angle between vectors of transition moments of the absorbing ^{1}LC and ^{3}MLCT, and emitting states is obviously bigger. Well known is that transitions from states with different symmetry and multiplicity may have parallel orientation of their transition dipole moments and contrary, the transitions from states with same symmetry and different multiplicity or different symmetry and same multiplicity have perpendicular orientation of their transition dipole moments. That means the nature of the emitting state should has ^{3}LC character concerning $^1S_0 \rightarrow {}^1$MLCT transition has almost parallel orientation of the transition dipole moment as this of transition from emitting state.

The yellow-greenish emission, which appears after irradiation of the solutions of the complexes, studied here with UV light, points the maximum of the phosphorescent spectrum around 555 nm (Fig. 4). The spectra on Fig. 4 have couple long wavelength shoulders due to vibrational substructure of the electronic transition. At 77 K that vibrational structure is more define and the shoulders appear as peaks. The maximum of the phosphorescent emission for complexes is at different wavelength. The bands for complexes containing π-electron-donating group such as –Cl, –OCH$_3$ and –N(CH$_3$)$_2$ are red shifted in comparison with bands of the other Ir complex studied here. This is typical for (π,π*) emitting states which energy is very sensitive to extend of the conjugated π-electron system. One can see (Fig. 4) the red shift of the emission increase with increase of the π-electron-donating properties of the substituents.
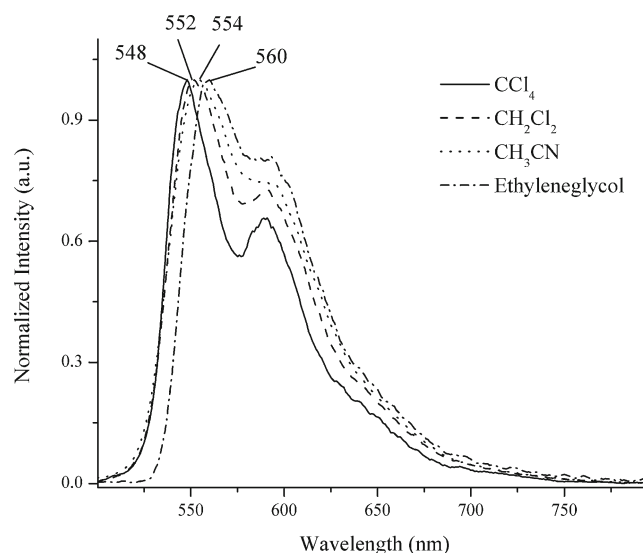

Fig. 6 Normalized emission spectra of 5a in various solvents at RT

Introducing flexible group in phenylbenzothiazole moiety of the complexes, such as –OCH$_3$ and –N(CH$_3$)$_2$ decrease phosphorescent quantum yield (Table 1). Those groups possess number of low energy vibrations, which enhance nonradiative deactivation pathways. That vibronic coupling is common quenching mechanism for phosphorescent emission.

Studding photophysical properties of the complexes in different solvents, we observe temperature dependence of the position of the maximum of phosphorescence emission. We cannot explain this shift with rigidochromisum and other well-known effects. We observe that direction and amount of the spectral shift depends on solvent polarity and temperature (Figs. 5, 6 and 7). The lowest emitting state of such kind of complexes is usually quantum mechanical mixture of number of electronic transitions, which determine the
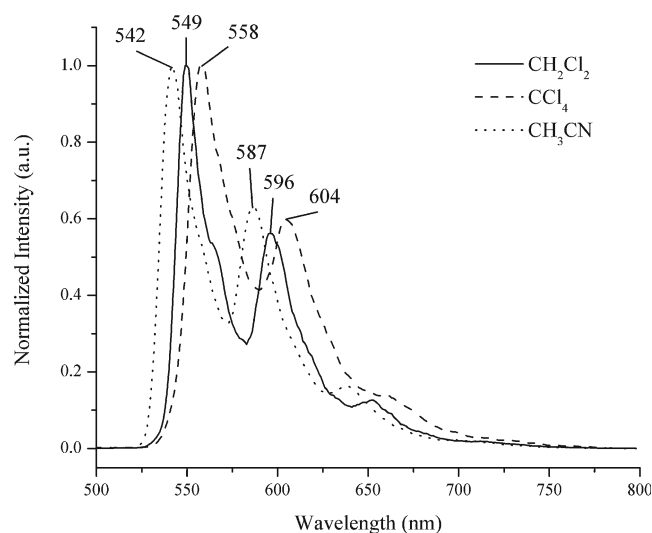

Fig. 7 Normalized emission spectra of 5a in various solvents at 77 K

character of the emission. The wave function of this state can be expressed by the equation below:

$$\Psi_{T_1} = \sqrt{1-\alpha^2}\left|^3LC\right\rangle + \alpha\left|^1MLCT\right\rangle$$

α is mixing coefficient and can be approximated with the formula:

$$\alpha = \frac{\left\langle ^3LC\left|H_{SO}\right|^1MLCT\right\rangle}{\Delta E}$$

where $\left\langle ^3LC\left|H_{SO}\right|^1MLCT\right\rangle$ is the spin-orbital coupling element, characterizing the strength of spin-orbit coupling between ^3LC and ^1MLCT transitions. Note that the value of α also includes contributions from spin-orbit coupling between the ^1MLCT and ^3MLCT states, and between the ^3MLCT and ^3LC states [25].

Usually, the lowest excited state inherits almost all photophysical properties (except oscillator strength) of the state with the biggest mixing coefficient. In this case we consider ^3MLCT as the lowest excited state, nevertheless, at room temperature the emission has $^3(\pi,\pi^*)$ character due to admixture of the ^3LC into wave-function of the emitting state. One can see the batochromic shift in emission spectra of the complexes with increase of the solvent polarity (Fig. 6). This is typical behavior for emitters with (π,π^*) character of the excited state. At low temperature, the shift is hypsochromic with increase of the solvent polarity. We explain this effect consider change in character of the emitting state. It is well known that one of the main mechanisms for quantum mechanical mixing of the states is trough vibrational coupling. At low temperature when the vibrations are hardly restricted the configuration interaction between ^3LC and ^3MLCT states is leak and character of the emitting state become mostly (d,π^*). In that case, energy of the transition from excited to ground state increase with increase of the solvent polarity (Fig. 7). The decrease in vibrational coupling between states at low temperatures is notable also concerning the excitation spectra of the complexes (Fig. 3). It is noteworthy that intensity of the emission excited into the range of the ^1LC band decrease about 1/3 with decrease of the temperature.

Conclusions

Studding this series of four heteroleptic Ir(III) complexes we define the effect of the substituent into cyclometalated benzothiazole moiety of the Ir complex. As these complexes are $^3(\pi,\pi^*)$ emitters they are sensitive to extend of the conjugated π-system. In this way π electron-donating substituents shift the emission band to low energies. Moreover, flexibility of these groups is crucial for phosphorescent quantum yield. We find that

dimethylamino and methoxy derivatives have lower quantum yield. The lowest triplet state of these complexes, where the emission comes from, is quantum mechanical mixture of MLCT and LC states. Contribution of each of these states in that mixture defines the nature of the phosphorescent emission. That contribution is determined by the mixing coefficient α and depends on extend of spin-orbital coupling, configuration interactions and energy difference between states. In this study we find that phosphorescent properties of the complexes depend on temperature. As a reason for this we point out change in nature of the emitting state. We suggest transition from ^3LC to ^3MLCT dominant character of the T_1 state going from room temperature to 77 K. We make this conclusion after study of the phosphorescent spectra of the complexes in solutions with different polarity.

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