Tuning the Photophysical Properties of Cyclometalated Ir(III) Complexes by a Trifluoroacetyl Group

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Four cationic Ir(III) complexes, [Ir(dpq)$_2$(bpy)]PF$_6$ (**1**), [Ir(dpq)$_2$(phen)]PF$_6$ (**2**), [Ir(tfapq)$_2$(bpy)]PF$_6$ (**3**), and [Ir(tfapq)$_2$(phen)]PF$_6$ (**4**) (dpqH = 2,4-diphenylquinoline, tfapqH = 2-(4′-trifluoroacetylphenyl)-4-phenylquinoline, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been synthesized and fully characterized. The structure of **4** was also confirmed by single-crystal X-ray diffraction. The electron-acceptor character of the trifluoroacetyl unit leads to a reduced HOMO-LUMO gap and consequently a red-shift of the UV/Vis absorption and luminescence spectra. The solvophobic character of the trifluoroacetyl unit gives rise to a molecule assembly in solution.

Key words: Iridium(III) Complex, Crystal Structure, Photoluminescence

Introduction

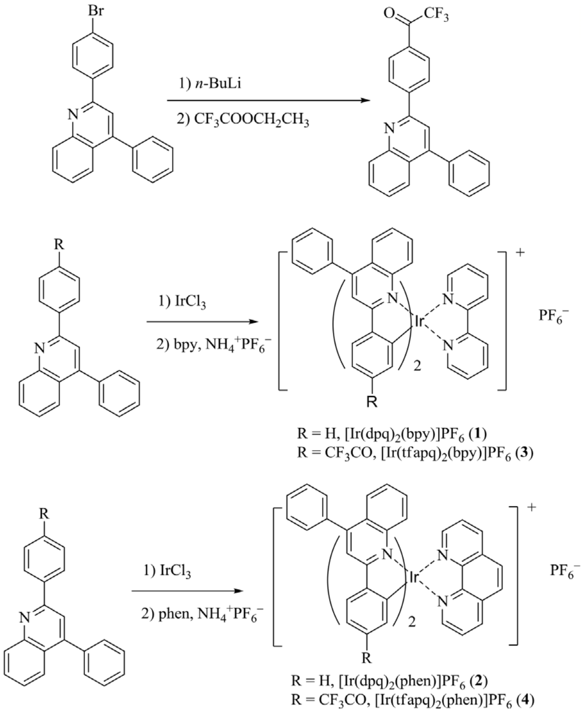
Due to their relatively short excited state lifetime, high photoluminescence efficiency and excellent color tuning, luminescent cyclometalated iridium(III) complexes have been widely used in organic light-emitting diodes (OLEDs), luminescence sensitizers, and biological imaging [1]. By changing the structure of the ligand one can modulate the HOMO and LUMO energies of Ir(III) complexes in order to tune the emission color and luminous efficiency [2 – 5]. For example, the emission wavelength of the iridium(III) complexes can cover the whole visible region by modification or variation of the cyclometalated 2-arylpyridine primary and the ancillary ligands [6]. The incorporation of fluorine into molecules results in profound changes in the physical and chemical properties of these compounds [7]. There are several effects of the fluorine in Ir-cyclometalated complexes. The first one is the strong electron-withdrawing effect on the ligand π system, and the second is the increase of the optical and thermal stability. The most important observation is that the fluorine can reduce the luminescence quenching. However, so far trifluoroacetyl iridium complexes have rarely been studied [8].

In the present paper, trifluoroacetyl groups were introduced into diphenylquinoline ligands of iridium(III) complexes in order to tune their photophysical properties. The synthesis and photophysical properties of the complexes were investigated to study the influence of the trifluoroacetyl group.

Experimental Section

General

The solvents were purified by routine procedures and distilled under an atmosphere of dry nitrogen before use. All reagents, unless otherwise specified, were purchased from Aldrich and were used as received. 2,4-diphenylquinoline (dpqH) and 2-(4′-bromophenyl)-4-phenylquinoline (bppqH) were obtained *via* Friedländer reactions [9, 10]. UV/Vis absorption spectra were obtained on a Shimadzu UV-2501 PC spectrophotometer. Positive-ion ESI mass spectra were obtained on a Perkin Elmer Sciex API 365 mass spectrometer. NMR spectra were recorded on a Bruker AV400 spectrometer using CDCl$_3$ as solvent. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Luminescence lifetimes were determined on an Edinburgh FL920 time-correlated pulsed single-photon-counting instrument.



Scheme 1. Synthetic routes to iridium(III) complexes [Ir(dpq)$_2$(bpy)]PF$_6$ (**1**), [Ir(dpq)$_2$(phen)]PF$_6$ (**2**), [Ir(tfapq)$_2$(bpy)]PF$_6$ (**3**), and [Ir(tfapq)$_2$(phen)]PF$_6$ (**4**).

Synthesis of 2-(4′-trifluoroacetylphenyl)-4-phenylquinoline (tfapqH)

The synthetic routes to the ligands and the iridium(III) complexes are given in Scheme 1. To a stirred solution of diisopropylamine (1.2 g, 0.012 mol) in THF (10 mL) was added *n*-BuLi (2.66 M, 4 mL) dropwise at −40 °C, and the resulting mixture was stirred at −40 °C for 1 h and cooled to −78 °C. To the mixture was added bppqH (3.6 g, 0.010 mol) in THF (5 mL) while keeping the internal temperature below −70 °C, and the mixture was stirred at −78 °C for 1 h. After addition of ethyl trifluoroacetate (1.4 mL, 0.012 mol) in THF (2 mL) at −78 °C, the mixture was allowed to warm to 0 °C, quenched by addition of saturated aqueous NH$_4$Cl, and partitioned between EtOAc and water. The layers were separated, and the organic layer was washed with brine, dried over MgSO$_4$, and concentrated. The residue was purified by flash silica gel column chromatography (EtOAc-hexanes = 1 : 4) to give tfapqH (2.9 g, 77 %) as a colorless solid. – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.53 – 7.58 (m, 6H), 7.79 (t, J = 7.2 Hz, 1H), 7.88 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 8.4 Hz, 2H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.55, 149.85, 148.83, 146.05, 137.99, 130.70, 130.68, 130.66, 130.64, 130.34, 130.13, 130.4, 129.54, 128.74, 128.71, 128.10, 127.88, 127.29, 126.24, 125.79, 121.07, 119.22, 118.18, 115.28. – ^{19}F NMR (CDCl$_3$, 376 MHz): δ = −71.35 (s). – MS ((+)-ESI): m/z = 378 (calcd. 378 for C$_{23}$H$_{15}$NOF$_3$, [M+H]$^+$).

*Synthesis of the iridium complexes **1** – **4***

To a round-bottomed flask (25 mL), 2-ethoxyethanol (9 mL), 2,4-diphenylquinoline (0.56 g, 2.0 mmol), IrCl$_3$·3H$_2$O (0.20 g, 0.56 mmol) and water (3 mL) were added sequentially. The mixture was stirred under nitrogen at 120 °C for 24 h and cooled to r. t. The precipitate was collected and washed with ethanol and acetone, and then dried *in vacuo* to give the red dimer ([{Ir(μ-Cl)(dpq)$_2$}$_2$]) (0.32 g, 0.22 mmol).

In a round-bottomed flask, 0.08 g (0.05 mmol) of [{Ir(μ-Cl)(dpq)$_2$}$_2$] and 0.03 g (0.20 mmol) of 2,2′-bipyridine were mixed together in 10 mL of CH$_2$Cl$_2$. The solution was then stirred at r. t. for 6 h. To the solution was added a methanol solution with an excess of potassium hexafluorophosphate for the ion exchange. The product was filtered, washed with absolute ethanol, dried and purified by chromatography on a silica gel column using dichloromethane-ethyl acetate (v/v = 2 : 1) as eluent. An orange solid (88 mg, 83 %) of [Ir(dpq)$_2$(bpy)]PF$_6$ (**1**) was obtained. – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 6.67 (d, J = 7.9 Hz, 2H), 6.86 (t, J = 7.6 Hz, 2H), 6.97 (t, J = 8.8 Hz, 2H), 7.16 (t, J = 8.1 Hz, 2H), 7.28–7.33 (m, 4H), 7.38 (d, J = 8.8 Hz, 2H), 7.42 (t, J = 6.6 Hz, 2H), 7.56–7.64 (m, 6H), 7.76 (d, J = 8.7 Hz, 2H), 7.83 (t, J = 8.0 Hz, 2H), 8.03 (t, J = 6.3 Hz, 2H), 8.08 (s, 2H), 8.21 (d, J = 7.3 Hz, 2H), 8.36 (d, J = 8.4 Hz, 2H), 8.40 (d, J = 8.1 Hz, 2H), 8.69 (d, J = 7.8 Hz, 2H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 122.26, 125.52, 128.08, 129.07, 129.39, 129.41, 129.55, 129.59, 129.69, 129.86, 130.05, 130.22, 130.25, 130.27, 130.43, 130.46, 130.54, 131.63, 132.17, 133.28, 134.22, 135.77, 141.37, 148.79, 151.61, 162.00. – MS ((+)-ESI): m/z = 909 (calcd. 909 for C$_{52}$H$_{36}$N$_4$Ir, [M]$^+$).

The Ir(III) complexes [Ir(dpq)$_2$(phen)]PF$_6$ (**2**), [Ir(tfapq)$_2$(bpy)]PF$_6$ (**3**) and [Ir(tfapq)$_2$(phen)]PF$_6$ (**4**) (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) were prepared from the corresponding ligands by similar procedures.

*[Ir(dpq)$_2$(phen)]PF$_6$ (**2**)*

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 9.20 (d, J = 6.5 Hz, 3H), 8.59 (d, J = 5.5 Hz, 2H), 8.55 (d, J = 8.6 Hz, 1H), 8.27 (d, J = 8.4 Hz, 3H), 8.13 (s, 2H), 8.09 (d, J = 8.6 Hz, 1H), 7.90 (t, J = 5.8 Hz, 3H), 7.81 (s, 3H), 7.64 (dd, J = 4.5, 8.4 Hz, 4H), 7.58 (d, J = 7.4 Hz, 3H), 7.53 (d, J = 10 Hz, 3H), 7.32 (d, J = 8.8 Hz, 1H), 7.21 (t, J = 8.2 Hz, 1H), 7.12 (t, J = 8.0 Hz, 2H), 6.90 (t, J = 8.2 Hz, 1H), 6.73 – 6.79 (m, 3H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 169.19, 152.00, 150.52, 150.28, 148.07, 148.00, 146.76, 146.32, 145.87, 138.89, 136.47, 135.96, 135.15, 130.90, 130.52, 129.53, 129.42, 128.91, 128.67, 128.20, 127.25, 126.99, 126.72, 126.53, 126.32, 126.06, 124.54, 123.22, 123.03, 117.81. – MS ((+)-ESI): m/z = 933 (calcd. 933 for $C_{54}H_{36}N_4Ir$, $[M]^+$).

*[Ir(tfapq)$_2$(bpy)]PF$_6$ (**3**)*

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.11 (t, J = 7.0 Hz, 2H), 7.34 – 7.40 (m, 2H), 7.41 – 7.53 (m, 2H), 7.61 – 7.72 (m, 8H), 7.86 (t, J = 7.0 Hz, 2H), 7.91 (d, J = 9.7 Hz, 2H), 7.96 – 8.06 (m, 2H), 8.09 – 8.20 (m, 4H), 8.21 (s, 2H), 8.30 (d, J = 9.0 Hz, 1H), 8.42 (d, J = 6.8 Hz, 1H), 8.54 (d, J = 9.7 Hz, 2H), 8.58 (d, J = 7.1 Hz, 2H), 8.78 (s, 2H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.47, 169.33, 165.94, 165.67, 163.01, 157.93, 157.07, 151.49, 151.30, 148.59, 148.25, 146.89, 146.57, 145.06, 144.99, 139.82, 139.42, 136.05, 135.01, 132.65, 132.09, 131.93, 131.39, 130.91, 130.44, 130.05, 129.73, 128.62, 128.47, 128.30, 127.15, 127.07, 126.55, 126.10, 125.30, 125.27, 124.16, 123.88, 123.85, 123.73, 121.92, 121.38, 119.31, 118.45. – MS ((+)-ESI): m/z = 1101 (calcd. 1101 for $C_{56}H_{34}N_4O_2F_6Ir$, $[M]^+$).

*[Ir(tfapq)$_2$(phen)]PF$_6$ (**4**)*

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.78 – 6.98 (m, 2H), 7.12 (d, J = 9.7 Hz, 2H), 7.22 (d, J = 9.1 Hz, 2H), 7.25 – 7.34 (m, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.58 – 7.71 (m, 4H), 7.75 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 9.6 Hz, 1H), 8.04 – 8.12 (m, 2H), 8.16 – 8.21 (m, 2H), 8.41 (d, J = 6.5 Hz, 1H), 8.45 (d, J = 6.1 Hz, 1H), 8.50 – 8.55 (m, 2H), 8.58 (d, J = 5.8 Hz, 2H), 8.61 (s, 1H), 8.65 (s, 1H), 8.75 (d, J = 6.0 Hz, 2H), 8.80 (d, J = 8.6 Hz, 2H), 8.86 (t, J = 8.8 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.358, 167.877, 167.742, 154.412, 154.018, 152.986, 152.327, 147.852, 147.822, 147.792, 147.111, 146.520, 146.192, 145.987, 140.851, 136.329, 136.067, 136.058, 136.036, 131.089, 131.028, 130.854, 130.383, 130.372, 130.346, 130.338, 130.327, 130.302, 130.274, 130.247, 130.199, 130.187, 130.178, 130.172, 130.164, 130.158, 130.075, 129.979, 129.973, 129.735, 129.488, 129.482, 129.477, 129.455, 129.420, 129.375, 129.330, 129.307, 128.715, 128.677, 128.668, 128.654, 128.409, 128.405, 127.593, 126.652, 126.330, 126.049. – ^{19}F NMR ($CDCl_3$, 376 MHz): δ = −69.17, −70.60, −70.64, −71.06. – MS ((+)-ESI): m/z = 1125 (calcd. 1125 for $C_{58}H_{34}N_4O_2F_6Ir$, $[M]^+$).

Crystal structure determination

A suitable single crystals of **4** was obtained by recrystallization from a mixture of CH_2Cl_2, ethyl acetate and hexane at r. t. and mounted on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation at T = 296 K using an ω scan mode. Table 1 summarizes the cyrstal data and numbers pertinent to data collection and structure refinement.

Table 1. Crystal data, data collection parameters and details of the structure refinement for compound **4**.

Formula	$C_{60}H_{42}F_{12}IrN_4O_4P$
M_r	1334.15
Crystal size, mm^3	0.17 × 0.17 × 0.08
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	13.4991(17)
b, Å	13.9630(18)
c, Å	17.011(2)
α, deg	76.367(2)
β, deg	72.050(2)
γ, deg	63.592(2)
V, Å^3	2713.7(6)
Z	2
D_{calcd}, g cm^{-3}	1.60
$F(000)$, e	1324
θ range, deg	2.53 – 26.00
hkl range	±16, −16 → 17, −15 → 20
Refl. measured / unique / R_{int}	15142 / 10407 / 0.0348
Param. refined	693
$R(F)$ / $wR(F^2)$^{a} (all refs.)	0.0811 / 0.1521
GoF (F^2)^{b}	0.943
Largest diff. peak / hole, e Å^{-3}	1.70 / −1.22

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; [b] $GoF = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

CCDC 821882 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

*Synthesis and characterization of compounds **1** – **4***

The cyclometalating ligands dpqH and bppqH were prepared by Friedländer reactions. The trifluoroacetyl unit was introduced into bppqH at low temperatures using n-BuLi as metalating agent. The iridium complexes were synthesized in two steps using standard methods. The cyclometalated chloride-bridged dimers were prepared according to the reported procedures and were readily dissociated by N^N type ligands in high yield (Scheme 1). In general, the final cationic iridium complexes have lower solubilities in commonly used solvents than the corresponding complexes without a trifluoroacetyl group. There are two sets of NMR signals for the CF_3 units, thus the complexes deviate from ideal C_2 symmetry in solution as expected. This phenomenon is commonly encountered in cyclometalated iridium(III) complexes by our experience.

In order to confirm the 3-dimensional structure of these complexes, the crystal structure of **4** was determined. Red crystals of **4** were obtained from recrystal-

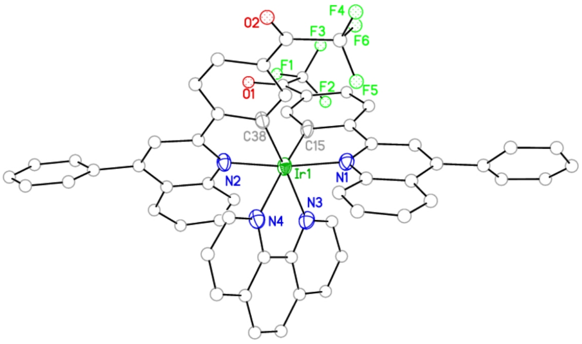


Fig. 1 (color online). Perspective view of the $[Ir(tfapq)_2(phen)]^+$ cation in **4** with selected displacement ellipsoids drawn at the 30 % probability level. H atoms omitted. Selected distances (Å) and angles (deg): C(15)–Ir(1) 1.987(8), C(38)–Ir(1) 1.985(8), Ir(1)–N(3) 2.166(6), Ir(1)–N(4) 2.181(7), Ir(1)–N(1) 2.086(6), Ir(1)–N(2) 2.092(6); C(38)–Ir(1)–C(15) 94.7(3), C(15)–Ir(1)–N(1) 79.8(3), C(15)–Ir(1)–N(2) 95.4(3), C(38)–Ir(1)–N(3) 171.5(3), N(1)–Ir(1)–N(3) 83.9(2), C(38)–Ir(1)–N(4) 96.1(3), N(1)–Ir(1)–N(4) 105.0(2), N(3)–Ir(1)–N(4) 76.1(3), C(38)–Ir(1)–N(1) 95.0(3), C(38)–Ir(1)–N(2) 79.1(3), N(1)–Ir(1)–N(2) 172.2(2), C(15)–Ir(1)–N(3) 93.4(3), N(2)–Ir(1)–N(3) 102.6(2), C(15)–Ir(1)–N(4) 167.7(3), N(2)–Ir(1)–N(4) 80.9(2).

lization using a mixture of CH_2Cl_2, ethyl acetate and hexane at r. t. The molecular structure of complex **4** is depicted in Fig. 1, including selected bond lengths and angles. Complex **4** consists of a cationic distorted octahedrally coordinated iridium(III) center ligated by two tfapq ligands and a phen ligand with $[PF_6]^-$ as counter anion. The two tfapq ligands chelate the iridium center with N-N in the *trans* and C-C in the *cis* configuration. The *cis* C-C chelate arrangement implies that there is a stronger *trans* influence of the phenyl group over that of the pyridyl group [11]. The Ir–C bond lengths ranging from 1.985(8) to 1.987(8) Å are within the range reported for closely related complexes [12 – 14]. The Ir–N bond lengths of the tfapq ligands spanning from 2.086(6) to 2.092(6) Å are within the range reported for other mononuclear complexes containing analoguous Ir[C^N] moieties [15]. For the same reason of *trans* influence, the Ir–C bonds are shorter than the Ir–N bonds. Moreover, the Ir–N bond lengths between the Ir center and the phen ancillary ligand (from 2.166(6) to 2.181(7) Å) are longer than those between the Ir center and the tfapq ligands because of stronger donating and back-bonding interactions between the aryl groups of tfapq and the iridium atom. The phen chelation results in an N(3)–Ir(1)–N(4) bond angle of 76.1(3)°, appreciably smaller than the ideal value of 90°. Furthermore, the C–C and C–N bond lengths and angles are within normal ranges and are in agreement with corresponding parameters described for similarly constituted complexes [16].

*Photophysical properties of compounds **1** – **4***

Fig. 2 compares the UV/Vis absorption spectra of the new Ir(III) complexes in CH_2Cl_2 solution at r. t. Complexes **1** and **2** have similar spectra. The strong absorption bands between 250 nm and 320 nm in the ultraviolet region are assigned to the spin-allowed π-π^* transition of the ligands. The moderately intense

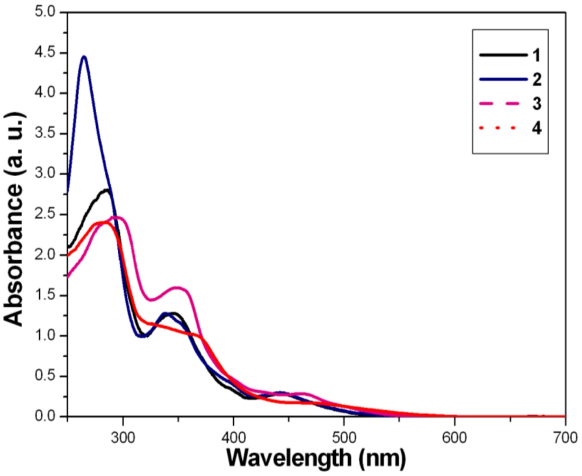


Fig. 2 (color online). UV/Vis absorption spectra of the new iridium(III) complexes **1** – **4** in CH_2Cl_2.

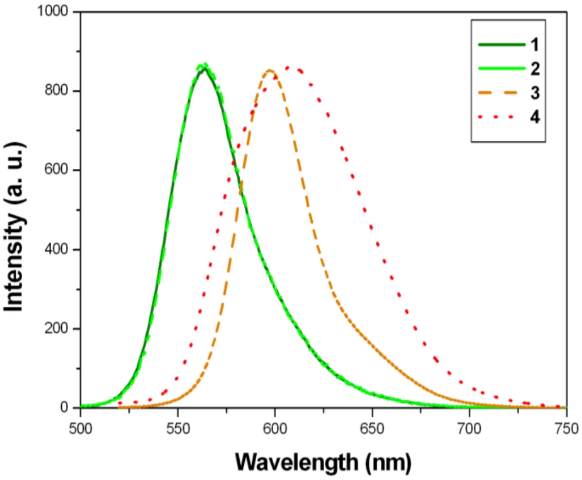


Fig. 3 (color online). The room temperature photoluminescence spectra of the new complexes **1** – **4** in CH_2Cl_2 solution (λ_{ex} = 420 nm).

Table 2. Photoluminnescence performances of the new complexes **1** – **4**.

Complex	λ_{em} (nm)	φ	$\langle\tau\rangle$ (ns)
1	564	0.95	705
2	564	0.79	693
3	597	0.28	$\tau_1 = 237$, $\tau_2 = 577$
4	609	0.53	$\tau_1 = 219$, $\tau_2 = 575$

bands at 345 nm probably correspond to a spin-allowed singlet metal-to-ligand charge-transfer (^{1}MLCT) [17]. The weak absorption bands at *ca.* 450 nm can be assigned to a spin-forbidden triplet metal-to-ligand charge-transfer (^{3}MLCT). Compared to **1** and **2**, the corresponding absorption bands of complexes **3** and **4** have an obvious red-shift after the introduce of the trifluoroacetyl unit. The results indicated that **3** and **4** have a reduced energy band gap (E_g) because the absorption edge reflects the magnitude of E_g.

The r. t. photoluminescence spectra of the new complexes in CH_2Cl_2 solution are shown in Fig. 3. Complexes **1** and **2** have almost the same spectra. They emit intense luminescence with an emission wavelength of 562 nm. The full width at half maximum (FWHM) of this transition is 45 nm. The emission wavelength of **3** is red-shifted to 597 nm compared with that of **1**, and the FWHM is 42 nm, which is consistent with the UV/Vis absorption result. The red-shift of the emission spectra is related to the influence of an electron-acceptor substituent [18]. The emission wavelength of **4** is 609 nm with a FWHM of 81 nm. It also has a red shift as compared to that of **2**.

Table 2 presents the luminescence lifetimes of the four iridium complexes in CH_2Cl_2 at r. t. Complexes **1** and **2** show a single exponential decay, and the lifetime is 705 and 693 ns, respectively. However, complexes **3** and **4** show a double-exponential decay which is related to strong intermolecular interactions and may be ascribed to the incorporation of the solvophobic trifluoroacetyl groups into the ligands. The short lifetime (τ_1) of **3** is 237 ns, and its contribution is 54 %, while the long short lifetime (τ_2) is 577 ns and its contribution 46 %. Complex **4** showed smaller values of τ_1 (219 ns, 69 %) and τ_2 (575 ns, 31 %) as compared to those of **3**. In general, the radiative lifetime of the cyclometalated iridium complexes falls in the microsecond and submicrosecond range [19], and the experimental decay times are also in this range. The phosphorescence quantum efficiency (φ) of **1** and **2** in degassed CH_2Cl_2 solution is *ca.* 0.95 and 0.79, respectively, with an aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\varphi = 0.042$) as the standard solution [20]. The efficiency of **3** and **4** is *ca.* 0.28 and 0.53, respectively. It is lower than that of **1** and **2**, which may also be related to the strong intermolecular interactions. Anyway, these complexes are remarkably bright compared to similar cationic iridium complexes found in the literature [21].

In summary, four new cationic iridium complexes have been prepared, and the photophysical influence of the trifluoroacetyl unit has been investigated. The electron-acceptor character of the trifluoroacetyl group led to a reduced HOMO-LUMO gap and consequently to a red-shift of the UV/Vis absorption and luminescence spectra. At the same time, the solvophobic character of the trifluoroacetyl unit led to a molecule assembly in solution. These new iridium complexes are also found to be efficient emitters. Introduction of a trifluoroacetyl unit into iridium complexes can thus serve for the design of efficient electroluminescent materials.

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