Journal of Organometallic Chemistry 880 (2019) 363–367

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, characterization and optical properties of novel Ir(III) complexes bearing *N*-heterocycle substituents

Meng Tang, Senqiang Zhu, Rui Liu*, Jia Wang, Zheng Zhang, Hongjun Zhu**

Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China

ARTICLE INFO

Article history:
Received 18 September 2018
Received in revised form
9 November 2018
Accepted 24 November 2018
Available online 26 November 2018

Keywords:
Ir(III) complex
N-heterocycle
Synthesis
Photophysics property
Nonlinear absorption

ABSTRACT

A series of cationic heteroleptic Ir(III) complexes with different *N*-heterocycle groups (*N*-phenothiazinyl, *N*-indolyl, *N*-carbazolyl, 3,6-di-*tert*-butyl-*N*-carbazolyl) were synthesized and characterized. The photophysical properties of these complexes were systematically investigated. All complexes exhibit strong $^{1}\pi$-π^{*} absorption bands in the UV region and broad ^{1}MLCT absorption bands in the visible region. In addition, these complexes exhibit weak absorption after 500 nm, which could be attributed to $^{3}\pi,\pi^{*}/^{3}$CT transition. All complexes exhibit broad and structureless emission bands from 568 nm to 627 nm at room temperature, which are originated from ^{3}MLCT/^{3}LLCT excited states. The electron donating substituents attached on the 2-phenylpyridine ligands cause a pronounced red-shift of the emission band. Except **1d**, all complexes show strong triplet transient absorptions from UV to visible region, which were assigned to the ^{3}MLCT/$^{3}\pi,\pi^{*}$ excited state. In addition, complexes 1a-1c all exhibit reverse saturable absorption (RSA) at 532 nm, which follows the trend of 1a>1b > 1c. The photophysical properties of these Ir(III) complexes can be influenced drastically by the substituents on 2-phenylpyridine ligands, which would be useful for rational design of optical functional materials.

Cyclometalated Ir(III) complexes have attracted extensive interest in the past decade, due to the strong spin–orbit coupling induced by the Ir(III) ion, which gives rise to efficient intersystem crossing and high phosphorescence quantum efficiencies. This unique feature makes the Ir(III) complexes promising candidates for applications in organic light-emitting devices (OLEDs) [1–4], organic light-emitting electrochemical transistor [5], low-power upconversion [6,7], photocatalysts [8–10] and nonlinear optics [11,12]. These applications are intrinsically based on their rich photochemical and photophysical properties. In addition, their photophysical properties can be modulated by structural modification of the ligands to meet the requirements for different applications.

Among these Ir(III) complexes, cationic heteroleptic Ir(III) complexes are more appealing because the ground-state and excited-state properties of these complexes can be readily tuned by modification of either the diimine (N^N) ligand or the cyclometalating 2-arylpyridine (C^N) ligands [13–17]. For example, the research conducted by Sun group demonstrated that π-conjugations on the N^N ligands could significantly change the excited-state absorption characteristics of the Ir(III) complexes, and thus strongly impact their photophysical properties [11]. In addition, 1,10-phenanthroline has been amply confirmed that its rigid and conjugated structure makes the density of the electron cloud of the nitrogen atom on the aromatic ring stronger, which is favorable for the efficient transfer of electron energy between atoms and the coordination with metal center. Furthermore, Thompson group reported Ir(III) complexes bearing electron donors and acceptors on monoanionic cyclometalating ligands [18], which indicate that cyclometalated ligands are a key factor in the physical properties of Ir(III) complexes due to the effect of functional substituents on the ligands. Therefore, a strategy for achieving superior nonlinear optical properties could be proposed by the introduction of different substituents.

Furthermore, the investigation on the nonlinear optical properties of Ir(III) complexes by modifying cyclometalating C^N ligands is still limited. We envision that by incorporating *N*-aryl chromophores (*N*-arylamines) with different electron-donating abilities on 2-arylpyridine ligands, ground state absorption and excited state absorption of these complexes will be significantly tuned, hence, their excited state absorption region could be extended accordingly.

* Corresponding author.
** Corresponding author.
E-mail addresses: rui.liu@njtech.edu.cn (R. Liu), zhuhj@njtech.edu.cn (H. Zhu).

https://doi.org/10.1016/j.jorganchem.2018.11.031
0022-328X/

In this work, a series of cationic heteroleptic Ir(III) complexes with different arylamino-substituents on 2-phenylpyridine ligands, structurally, *N*-phenothiazinyl, *N*-indolyl, *N*-carbazolyl, 3,6-di-*tert*-butyl-*N*-carbazolyl groups were synthesized (Scheme 1). These complexes based on 1,10-phenanthroline ligand as main ligand (N^N ligand) and modified 2-phenylpyridine as ancillary ligand (C^N ligand). The structural characterization and photophysical properties of these complexes were systematically investigated with the aim of understanding the structure-property correlations and developing novel functional materials. The synthetic details are provided in Supplementary Information.

The UV–vis absorption characteristics of complexes **1a**–**1d** were studied in CH_2Cl_2 at different concentrations (5×10^{-6} to 1×10^{-4} mol L^{-1}). The absorption obeyed the Beer's law in the studied concentration range, suggesting the absence of ground-state aggregation in this concentration range. The UV–vis absorption spectra of complexes **1a-1d** in CH_2Cl_2 solution is presented in Fig. 1. The band maxima and molar extinction coefficients for each complex are summarized in Table 1. The spectra of the complexes **1a-1d** consist of intense absorption bands below 300 nm, medium absorption bands between 300 and 500 nm, and broad weak tails above 500 nm. In comparison to their respective ligands (**2a-2d**, Fig. S1), the strong absorption bands of the Ir(III) complexes above 300 nm can be assigned to ligand-based $^1\pi,\pi^*$ transitions (Fig. 1), which are also in line with the other transition organometallic compounds reported previously [19–21]. The less intense bands in the range of 300–500 nm for complexes have a mixed ^{1}MLCT and ^{1}LLCT character in view of their relatively large extinction coefficients. A close examination of the UV–vis absorption spectra of these complexes revealed a very weak tail beyond 500 nm for complexes **1a-1d**. As reported for other Ir(III) complexes [22], these bands are attributed to the S_0-Tn absorption *via* the spin-forbidden $^3\pi,\pi^*/^3$CT transition. It is worth noting that the *N*-heterocycle substituents complexes exhibit red-shifted absorption of the charge-transfer absorption bands compared to those of their analogues without the *N*-heterocycle substituents [23,24].

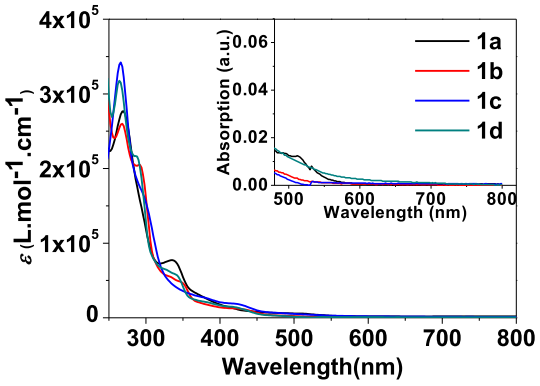
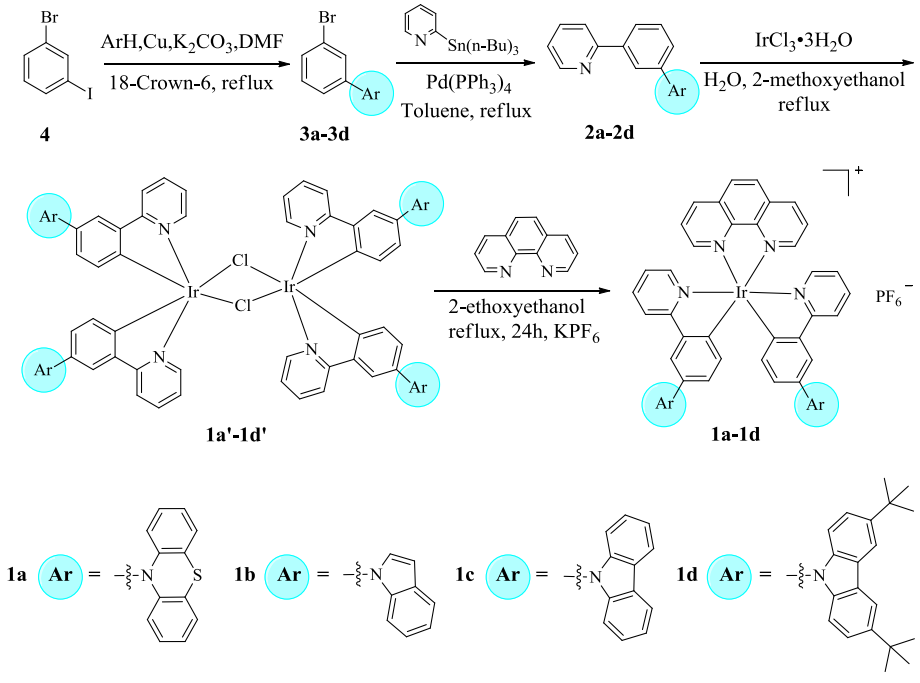


Fig. 1. UV–vis absorption spectra of **1a-1d** in CH_2Cl_2 (1×10^{-5} mol/L). The inset shows the expanded spectra in the spectral region 400–800 nm.

The normalized room-temperature emission spectra of complexes **1a-1d** in CH_2Cl_2 are shown in Fig. 2 and the emission data of **1a**–**1d** are summarized in Table 1. Upon excitation at the corresponding ^{1}MLCT band, a broad and structureless emission band appears from 568 nm to 627 nm for **1a-1d**. Considering the significant stokes shifts and sensitivity to oxygen quenching (Fig. S2), the emitting state of these complexes should be attributed to a triplet excited state (T_1 excited state). In comparison to their respective ligands (**2a**-**2d**, Fig. S3), these complexes show broad and unstructured emission bands and point to a higher ^{3}MLCT character and intraligand (IL) character in the excited state. Furthermore, the observed difference in emission should be attributed to the different natures of the substituents attached on the terminal *N*-heterocyclic unit, the *N*-heterocycle substituents complexes exhibit red-shifted of the charge-transfer emission bands compared to those of their analogues without the *N*-heterocycle substituents [23,24], especially the electron-donating ability of the substituents. Compared to **1c**, complex **1d** bearing stronger electron-donating 3,6-di-*tert*-butyl-*N*-carbazolyl groups shows pronounced red-shift



Scheme 1. Synthetic routes for complexes **1a**–**1d**.

Table 1
Photophysical parameters of complexes **1a-1d**.

Complex	λ_{abs}[a]/nm ($\varepsilon/10^5$ L mol^{-1} cm^{-1})	λ_{em}[b]/nm ($\tau_{em}/\mu s$, Φ_{em})	$\lambda_{T1\text{-}Tn}$/nm ($\tau_{TA}/\mu s$)[d]
1a	270 (2.85), 322 (0.77), 422 (0.117)	570 (3.00, 0.36)	540 (3.02)
1b	266 (2.62), 348 (0.49), 436 (0.098)	616 (0.12, 0.24)	525 (0.11)
1c	266 (3.49), 426 (0.179)	604 (0.06, 0.47)	520 (0.05)
1d	264 (3.27), 342 (0.58), 436(0.105)	627 ([c], 0.22)	[c]

[a] Electronic absorption band maxima in CH_2Cl_2 at R.T.
[b] Recorded in 1×10^{-5} mol/L CH_2Cl_2 solution at R.T.
[c] Too weak to be measured.
[d] Nanosecond TA band maxima, triplet extinction coefficients and triplet excited-state lifetimes in toluene at room temperature.

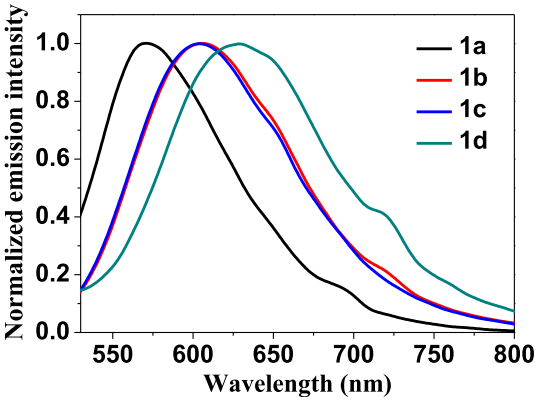


Fig. 2. Normalized emission spectra of **1a-1d** in CH_2Cl_2 (1×10^{-5} mol/L).

emission with structured feature. However, the emission quantum yield of **1d** decreases significantly by introducing *tert*-butyl groups on carbazole units, we ascribe the drastically reduced emission of **1d** to the enhanced intramolecular charge-transfer state, particularly the ^{3}LLCT state caused by the electron-donating *tert*-butyl-*N*-carbazolyl group in the Ir(III) complex.

The photoluminescence of **1a-1d** in different solvents was investigated to further understand the nature of the emission, the solvent-dependency emission spectra of **1a-1d** are manifested in Fig. 3, and the emission quantum yields of these four complexes in different solvents are summarized in Table 2. A negative solvatochromic effect is observed for **1a** and **1b**. However, a slight positive solvatochromic effect is observed for **1d,** while minor solvatochromic effect is observed for **1c**. These indicating that the emitting states for these complexes are configurationally mixed excited states or the emitting state changes in different solvents.

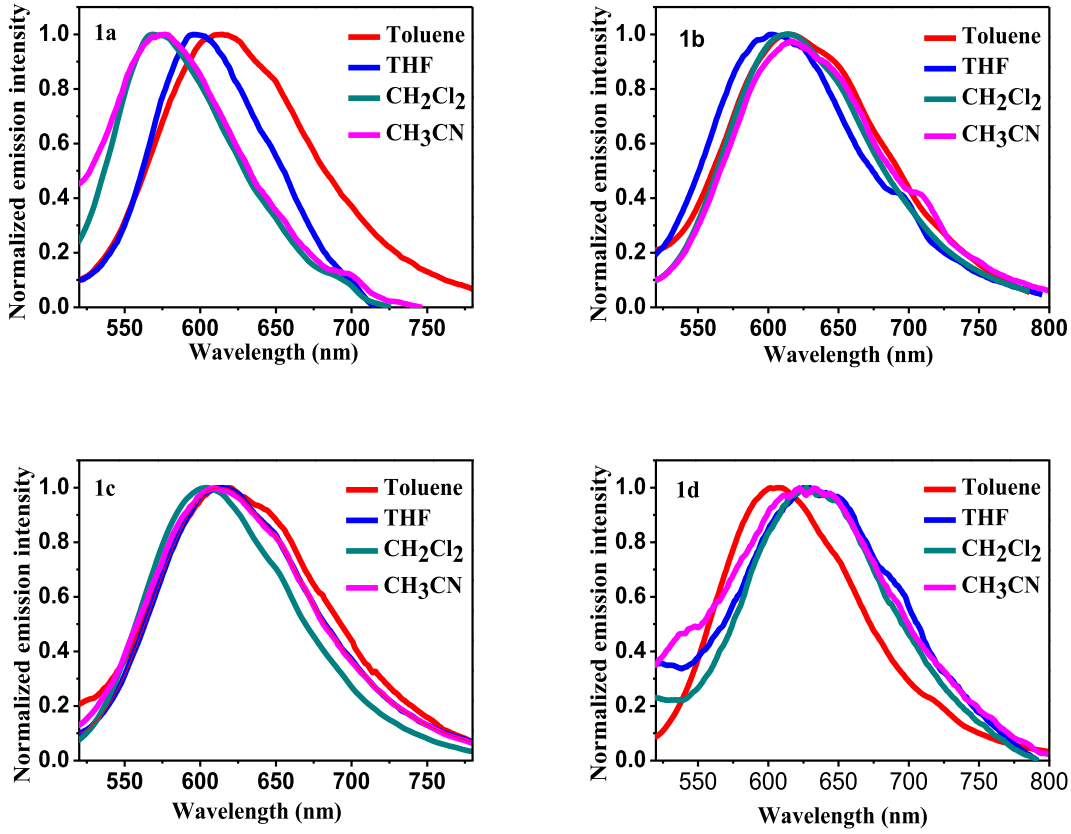


Fig. 3. Emission spectra of **1a-1d** (1×10^{-5} mol/L) in different solutions.

Table 2
Emission energy and quantum yields of **1a**–**1d** in different solvents.

	λ_{em}/nm (Φ_{em})[a]			
	Toluene	THF	CH_2Cl_2	CH_3CN
1a	615 (0.30)	595 (0.34)	570 (0.36)	558 (0.33)
1b	612 (0.22)	603 (0.37)	616 (0.24)	617 (0.37)
1c	606 (0.37)	625 (0.41)	627 (0.47)	622 (0.44)
1d	612 (0.35)	615 (0.27)	604 (0.22)	609 (0.37)

[a] Degassed aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\Phi_{em} = 0.042$, excited at 436 nm) was used as the reference for the emission quantum yield measurement.

Considering the structureless feature of the emission spectra, the emitting states for **1a-1d** are predominantly ^{3}MLCT/^{3}LLCT in nature. In addition, in a non-coordinating solvent like CH_2Cl_2, higher quantum yields are observed for these complexes in comparison to coordinating solvent like CH_3CN. This provides evidence for the involvement of the ^{3}MLCT character in the emitting state of these complexes. The solvent induced quenching by coordinating solvents is a common feature for transition-metal complexes with a ^{3}MLCT emitting state.

In order to understand the triplet excited-state properties of **1a**–**1d**, the triplet transient absorption (TA) of these complexes in toluene and monitoring the decay characteristics. The time-resolved triplet TA spectra of **1a, 1b, 1c** recorded upon excitation at 355 nm at room temperature in deaerated toluene solutions are shown in Fig. 4. The TA absorption band maxima, the excited-state lifetimes deduced from the decay of the TA, which are listed in Table 1. It is obvious that the TA spectral features of Ir(III) complexes **1a, 1b, 1c** exhibit broad positive absorption bands from 300 nm to 550 nm. The TA spectrum of **1a** is drastically different from other complexes, it exhibits broad positive absorption bands from 300 nm to 800 nm, which was tentatively assigned to the ^{3}MLCT/$^3\pi,\pi^*$ excited state. Meanwhile, the TA spectra of **1b** and **1c** show bleaching bands from 600 nm to 700 nm. The triplet excited state giving rise to the observed TA for **1b** and **1c** could be assigned to the ^{3}MLCT/^{3}LLCT excited state. According to the literature [25–27], it is not surprised that the TA spectra of **1d** was unable to be measured, because the shorter excited state lifetime as indicated by the emission lifetime. These spectral information obtained from TA spectra of the complexes helps us to understand the excited state properties and to predict the spectral region where reverse saturable absorption occurs, which could be useful for nonlinear optics.

In order to study non-linear optical behaviors properties of the complexes, nonlinear transmission measurements were carried out in toluene solutions for all complexes at 532 nm using 4.1 ns laser pulses. For easy comparison, the linear transmission of all sample solutions was adjusted to 80% in a 2 mm cuvette at 532 nm to ensure that the same numbers of molecules are populated to the excited states. In such a case, the degree of reverse saturable absorption (RSA) will be determined by the excited-state absorption. The transmission *vs*. incident fluence curves for these complexes are presented in Fig. 5. Three complexes exhibit strong RSA properties at 532 nm for ns laser pulses, following the order of **1a** > **1b** > **1c**. In addition, compared with the $[Ir(ppy)_2(phen)]^+$ without *N*-heterocycle substituents [24], *N*-heterocycle substituents on ancillary ligands influence the non-linear optical properties of Ir(III) complexes significantly.

In summary, four Ir(III) complexes were synthesized and their photophysical properties were systematically investigated. All complexes exhibit strong absorption bands in the UV region, and broad structureless bands in visible region, which can be assigned as the ligand-based $^1\pi,\pi^*$ transitions and ^{1}MLCT transitions,

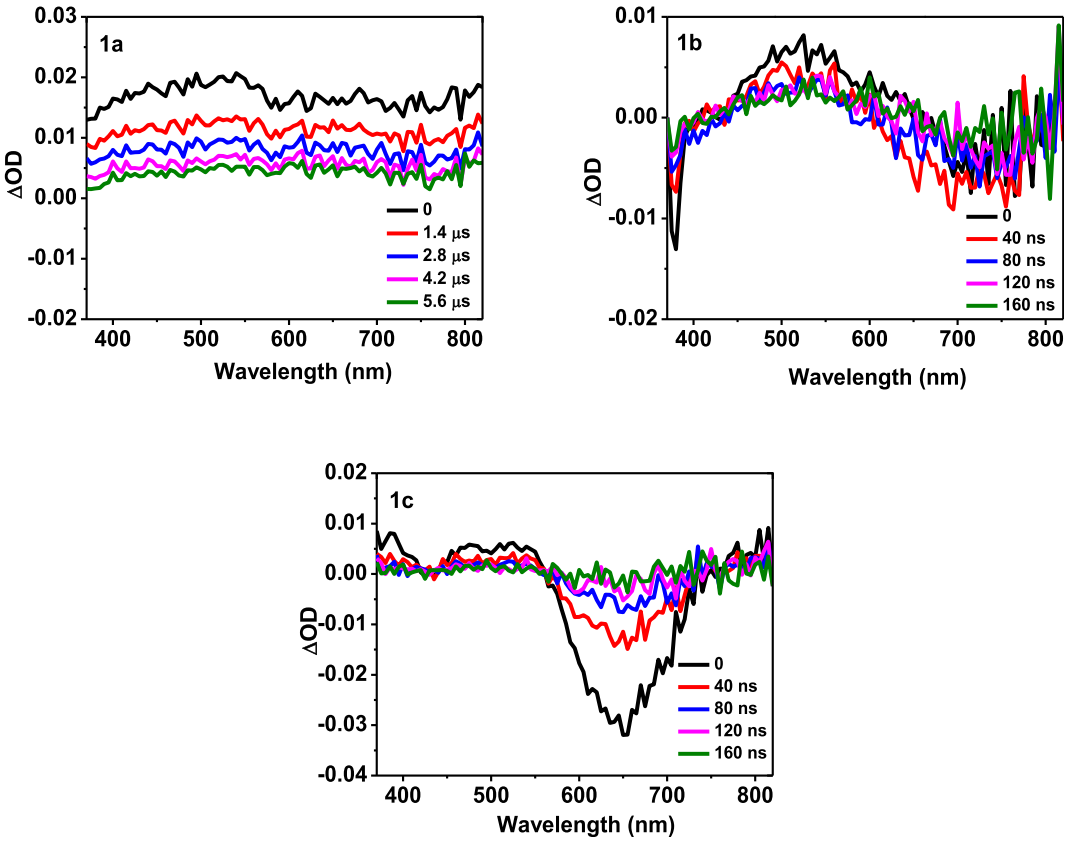


Fig. 4. The time-resolved triplet transient difference absorption spectra of **1a-1c** in toluene solution.

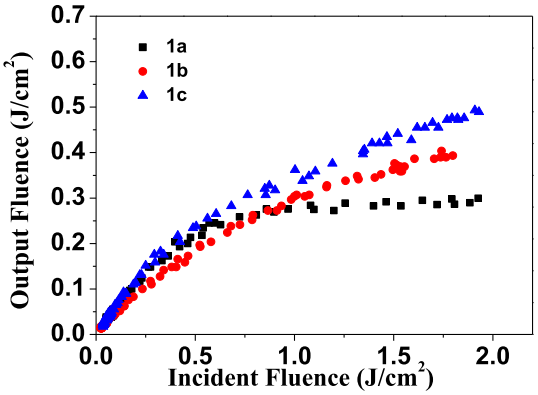


Fig. 5. Output energy density *vs* incident energy density of complexes 1a-1c in toluene for 4.1 ns laser pulses at 532 nm. The linear transmission for all samples was adjusted to 80% in a 2 mm cuvette at 532 nm.

respectively. In addition, all complexes exhibit weak absorption after 500 nm, which come from mixed $^3\pi$-π^*, ^{3}LLCT and ^{3}MLCT. Our studies reveal that electron-donating substituents on 2-phenylpyridine ligands cause a pronounced red-shift of emission bands. All the complexes exhibit broad absorption bands in their triplet transient difference absorption spectra, which are attributed to the ancillary ligand localized triplet excited states. The complexes **1a**, **1b**, **1c** exhibit broad absorption bands in their triplet transient difference absorption spectra, which are also influenced by these attached substituents. These complexes exhibit strong RSA properties at 532 nm for ns laser pulses, which was significantly influenced by the *N*-heterocycle substituents on ancillary ligands. These studies indicate that the photophysical properties of these Ir(III) complexs can be tuned drastically by the different aryl substituents, which not only builds a foundation in both experiment and theory of the further study on the synthesis and photophysical properties of cyclometalated iridium complexes, but also provides experiment and theory reference with the cyclometalated Ir(III) complexes for the applications in nonlinear optics.

Acknowledgements

We greatly acknowledge the financial support in part by National Natural Science Foundation of China (21602106), Natural Science Foundation of Jiangsu Province-Outstanding Youth Foundation (BK20170104), "Six Talent Peaks Project in Jiangsu Province (XCL-037), Strategic Pioneer Program on Space Science, Chinese Academy of Sciences (XDA15013100, XDA15013101) and Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX18_1065).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.11.031.

References

[1] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, Homoleptic cyclometalated iridium complexes with highly efficient red phosphorescence and application to organic light-emitting diode, J. Am. Chem. Soc. 125 (2003) 12971–12979.
[2] S.T. Parker, J.D. Slinker, M.S. Lowry, M.P. Cox, S. Bernhard, G.G. Malliaras, Improved turn-on times of iridium electroluminescent devices by use of ionic liquids, Chem. Mater. 17 (2005) 3187–3190.
[3] B.S. Du, C.H. Lin, Y. Chi, J.Y. Hung, M.W. Chung, T.Y. Lin, G.H. Lee, K.T. Wong, P.T. Chou, W.Y. Hung, H.C. Chiu, Diphenyl(1-naphthyl)phosphine ancillary for assembling of red and orange-emitting Ir(III) based phosphors; strategic synthesis, photophysics, and organic light-emitting diode fabrication, Inorg. Chem. 49 (2010) 8713–8723.
[4] W.Y. Wong, G.J. Zhou, X.M. Yu, H.S. Kwok, Z.Y. Lin, Efficient organic light-emitting diodes based on sublimable charged iridium phosphorescent emitters, Adv. Funct. Mater. 17 (2007) 315–323.
[5] Y. Zhou, S.T. Han, G.J. Zhou, W.Y. Wong, V.A.L. Roy, Ambipolar organic light-emitting electrochemical transistor based on a heteroleptic charged iridium(III) complex, Appl. Phys. Lett. 102 (2013), 083301.
[6] W. Zhao, F.N. Castellano, Upconverted emission from pyrene and di-*tert*-butylpyrene using Ir(ppy)$_3$ as triplet sensitizer, J. Phys. Chem. 110 (2006) 11440–11445.
[7] A.A. Rachford, R. Ziessel, T. Bura, P. Retailleau, F.N. Castellano, Boron dipyrromethene (bodipy) phosphorescence revealed in [Ir(ppy)$_2$(bpy-C≡C-Bodipy)]$^+$, Inorg. Chem. 49 (2010) 3730–3736.
[8] K.A. Belmore, R.A. Vanderpool, J.C. Tsai, M.A. Khan, K.M. Nicholas, Transition-metal-mediated photochemical disproportionation of carbon dioxide, J. Am. Chem. Soc. 110 (1988) 2004–2005.
[9] B. Matt, J. Moussa, L.M. Chamoreau, C. Afonso, A. Proust, H. Amouri, G. Izzet, Elegant approach to the synthesis of a unique heteroleptic cyclometalated iridium(III)-polyoxometalate conjugate, Organometallics 31 (2012) 35–38.
[10] X. Zhou, J. Yang, C. Li, Theoretical study of structure, stability, and the hydrolysis reactions of small iridium oxide nanoclusters, J. Phys. Chem. 116 (2012) 9985–9995.
[11] L. Liu, N. Dandu, J. Chen, Y. Li, Z. Li, S. Liu, C. Wang, S. Kilina, B. Kohler, W.F. Sun, Influence of different diimine (N^N) ligands on the photophysics and reverse saturable absorption of heteroleptic cationic iridium(III) complexes bearing cyclometalating 2-{3-[7-(Benzothiazol-2-yl)fluoren-2-yl] phenyl}pyridine (C^N) ligands, J. Phys. Chem. C 118 (2014) 23233–23246.
[12] L. Liu, N. Dandu, C. McCleese, Y. Li, T. Lu, H. Li, D. Yost, C. Wang, S. Kilina, C. Burda, W.F. Sun, Influence of a naphthaldiimide substituent at the diimine ligand on the photophysics and reverse saturable absorption of PtII diimine complexes and cationic IrIII complexes, Eur. J. Inorg. Chem. 2015 (2015) 5241–5253.
[13] F. Neve, M. La Deda, A. Crispini, A. Bellusci, F. Puntoriero, S. Campagna, Cationic Cyclometalated Iridium Luminophores: photophysical, Redox, and Structural Characterization, 23, 2004, pp. 5856–5863.
[14] Q. Zhao, S.J. Liu, M. Shi, C.M. Wang, M.G. Yu, L. Li, F.Y. Li, T. Yi, C.H. Huang, Series of new cationic iridium(III) complexes with tunable emission wavelength and excited state properties: structures, theoretical calculations, and photophysical and electrochemical properties, Inorg. Chem. 45 (2006) 6152–6160.
[15] S. Ladouceur, D. Fortin, E. Zysman-Colman, Role of substitution on the photophysical properties of 5,5′-Diaryl-2,2′-bipyridine (bpy*) in [Ir(ppy)$_2$(bpy*)] PF_6 complexes: a combined experimental and theoretical study, Inorg. Chem. 49 (2010) 5625–5641.
[16] R.D. Costa, F. Monti, G. Accorsi, A. Barbieri, H.J. Bolink, E. Ortí, N. Armaroli, Photophysical properties of charged cyclometalated Ir(III) complexes: a joint theoretical and experimental study, Inorg. Chem. 50 (2011) 7229–7238.
[17] S. Ladouceur, D. Fortin, E. Zysman-Colman, Enhanced luminescent iridium (III) complexes bearing aryltriazole cyclometallated ligands, Inorg. Chem. 50 (2011) 11514–11526.
[18] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, Synthesis and characterization of facial and meridional tris-cyclometalated iridium(III) complexes, J. Am. Chem. Soc. 125 (2003) 7377–7387.
[19] I.E. Pomestchenko, F.N. Castellano, Solvent switching between charge transfer and intraligand excited states in a multichromophoric platinum(II) complex, J. Phys. Chem. 108 (2004) 3485–3492.
[20] K. Haskins-Glusac, I. Ghiviriga, K.A. Abboud, K.S. Schanze, Photophysics and photochemistry of stilbene-containing platinum acetylides, J. Phys. Chem. B 108 (2004) 4969–4978.
[21] X.S. Li, Y. Liu, J. Luo, Z.Y. Zhang, D.Y. Shi, Q. Chen, Y.F. Wang, J. He, J.M. Li, G.T. Lei, W.G. Zhu, Synthesis and optoelectronic properties of a hetero-bimetallic Pt(II)–Ir(III) complex used as a single-component emitter in white PLEDs, Dalton Trans. 41 (2012) 2972–2978.
[22] C. Wang, L. Lystrom, H. Yin, M. Hetu, S. Kilina, S.A. McFarland, W.F. Sun, Increasing the triplet lifetime and extending the ground-state absorption of biscyclometalated Ir(III) complexes for reverse saturable absorption and photodynamic therapy applications, Dalton Trans. 45 (2016) 16366–16378.
[23] M.S. Lowry, W.R. Hudson, R.A. Pascal, Accelerated luminophore discovery through combinatorial synthesis, J. Am. Chem. Soc. 126 (2004) 14129–14135.
[24] Y.H. Li, R. Liu, Z.J. Li, S. Kilina, W.F. Sun, Effects of extended π-conjugation in phenanthroline (N^N) and phenylpyridine (C^N) ligands on the photophysics and reverse saturable absorption of cationic heteroleptic iridium(III) complexes, J. Phys. Chem. C 118 (2014) 6372–6384.
[25] F.Q. Guo, W.F. Sun, Y. Liu, K. Schanze, Synthesis, photophysics, and optical limiting of Pt(II) 4′-tolylterpyridyl arylacetylide complexes, Inorg. Chem. 44 (2005) 4055–4065.
[26] P. Shao, Y.J. Li, W.F. Sun, Cyclometalated Pt(II) complex with strong and broadband nonlinear optical response, J. Phys. Chem. 112 (2008) 1172–1179.
[27] J. Yi, B.G. Zhang, P. Shao, Y.J. Li, W.F. Sun, Synthesis and photophysics of Pt(II) 6-phenyl-4-(9,9-dihexylfluoren-2-yl)-2,2′-bipyridine complexes with phenothiazinyl acetylide ligand, J. Phys. Chem. 114 (2010) 7055–7062.