ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

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Cite this: *Chem. Commun.*, 2021, 57, 1254

Received 19th November 2020,
Accepted 22nd December 2020

DOI: 10.1039/d0cc07595g

rsc.li/chemcomm

Efficient NIR electrochemiluminescent dyes based on ruthenium(II) complexes containing an N-heterocyclic carbene ligand†

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Three new ruthenium(II) complexes containing an N-heterocyclic carbene (NHC) ligand (RuNHC) have been successfully synthesized and proved to be efficient near-infrared (NIR) ECL (electrogenerated chemiluminescence) luminophores. In addition to the advantages of the lower-charge main motif (+1), the much lower oxidation potentials, and the longer metal to ligand charge transfer (MLCT) absorption bands, most importantly, these RuNHC complexes show higher, or at least comparable, ECL efficiency compared with $Ru(bpy)_3^{2+}$ under the same experimental conditions; this demonstrates their great potential for applications in the NIR ECL imaging field in the future.

Electrogenerated chemiluminescence (ECL, also named electrochemiluminescence) is the phenomenon of light-emitting on the electrode through a series of chemical and electrochemical reactions. Since the first detailed studies of tri-2,2′-bipyridylruthenium(II) (also abbreviated as $Ru(bpy)_3^{2+}$) by Bard and co-workers in the 1970s,[1] and owing to the advantages of an ultra-high sensitivity and being free from the interferences from excitation light, the ECL phenomenon has been successfully developed into the most wide-spread commercially clinical diagnostic technique to date. In ECL-related studies, both in fundamental research and bioanalytical applications, exploring novel excellent luminophores with various colors and a high efficiency is always a hot topic and has received significantly more attention during the past few decades.[2,3] It is well known that compared with luminophores with an emission in the visible regions, near-infrared (NIR) luminophores have outstanding advantages in bioimaging fields owing to their excellent tissue penetration and negligible autofluorescence.[4] However, although both the kinds and numbers of ECL dyes have achieved significant advances in the past few decades, most of them are still limited to the visible regions and reports of NIR luminophores are relatively rare to date.[5] Most importantly, along with emerging cutting-edge research areas, such as single-particle/single-cell imaging combined with a novel ECL imaging platform,[6,7] developing novel high-efficiency NIR ECL luminophores has become more significant than ever.

Among the various kinds of ECL luminophores explored in recent years, novel metal complexes, a type of small molecular luminophore, have received significant attention owing to their tunable colors, high quantum efficiency, excellent photostability and bioconjugation abilities. One typical representative is the ruthenium(II) complex with an octahedron motif comprising six Ru–N bonds (containing three N^N bidentate ligands), such as $Ru(bpy)_3^{2+}$ and its derivatives. In order to meet the needs of downstream applications, incorporating substituents or changing the degree of π conjugation of these N^N bidentate ligands are both extensively employed to tune the photophysical properties of ruthenium(II) complexes, including the emission colors and quantum efficiencies.[8] However, owing to the limitations of the inherent natures of N^N ligands and Ru–N coordination bonds, the ruthenium(II)-based NIR luminophores haven't made a significant breakthrough so far.

As we know, the chemistry of N-heterocyclic carbene (NHC) is always an active research area and has a great impact on catalysis, materials sciences and medicine.[9] Owing to its strong donor ability and chemical stability, NHC is always one of the most important ligands in the architectures of organometallic complexes. Although metal–NHC complexes, as catalysts and as candidates for potential medicines, have been extensively studied, exploring the ECL luminophores from metal–NHC complexes is still very rare. In the past few years, inspired by

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† Electronic supplementary information (ESI) available: Experimental details, photophysical data, theoretical calculations, *etc.* See DOI: 10.1039/d0cc07595g

the emerging studies about iridium(III)–NHC complexes for deep-blue organic light emitting diode (OLED) dopant applications, both Hogan's[10] and our group[11] have independently pioneered ECL studies of iridium(III) complexes comprising NHC ligands. Unfortunately, incorporating NHC ligands into iridium(III) complexes increases the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and induces the emission wavelength of Ir–NHC complexes, giving a hypsochromic shift rather than a bathochromic shift.[12] Herein, no successful attempt to develop NIR ECL luminophores based on metal–NHC complexes have been reported to date.

Very recently, the synthetic method used to obtain a ruthenium(II) complex with the general formula of [Ru(bpy)$_2$(C^C*)]$^+$ (bpy = 2,2′-bipyridne, C* represents carbene from imidazolium) has been revealed by the Strassner group.[13,14] This novel coordination model and the comparatively lower charged main motif of the complex attracted our attention and we became very curious about their performance in the ECL fields, especially for exploring NIR ECL luminophores for cutting-edge research. Herein, taking into account the conjugation effect and the electronic effect comprehensively, three novel ruthenium(II) complexes with different substituents, the coordination model of which is [Ru(DIP)$_2$(C^C*)]$^+$ (DIP = 4,7-diphenyl-1,10-phenoline, C* is carbene from benzoimidazolium), have been deliberately designed and successfully synthesized in this work (shown in Fig. 1). It is important to mention that the ECL performance of these novel kinds of ruthenium(II) complexes have been revealed for the first time in this work, and provides a novel avenue that can be used to explore metal complex-based NIR luminophores.

It is well known that the degree of conjugation of a ligand is one of the most significant factors that tunes the emission wavelength of the corresponding metal complexes. Herein, in order to make the wavelength of RuNHC complexes bathochromic shift intensely, 4,7-diphenyl-1,10-phenoline (DIP), with a large degree of conjugation, was deliberately chosen as an N^N coordination ligand, while *N*-methyl-*N*′-phenyl-benzo[*d*]imidazolium and its derivative were selected as the C^C* coordination ligands in this work. Meanwhile, the groups of –OMe and –CF$_3$ have also been employed to investigate the electronic effect of the substituent on the ECL properties. Eventually, three bis(4,7-diphenyl-1,10-phenoline) ruthenium(II) complexes comprising NHC ligands (abbreviated as RuNHC in this work) with different substituents (shown in Fig. 1) were rationally designed and successfully synthesized in this work. The detailed synthetic routes and the chemical structure characterization data have also been listed in the experimental section in the ESI† (Fig. S1–S12).

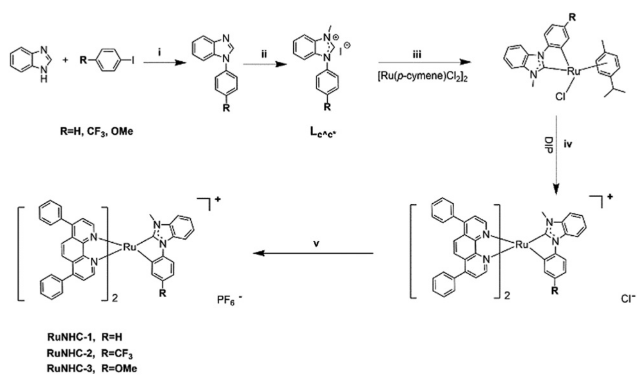

Fig. 1 The synthetic routes and chemical structures of the RuNHC complexes in this work: (i) CuI, L-proline, K$_2$CO$_3$, DMF; (ii) CH$_3$I, THF; (iii) [Ru(*p*-cymene)Cl$_2$]$_2$, Ag$_2$O, CH$_2$Cl$_2$, N$_2$; (iv) 4,7-diphenyl-1,10-phenoline(DIP), ethanol, reflux; and (v) ethanol, NH$_4$PF$_6$.

The absorption and photoluminescent (PL) spectra of the RuNHC complexes in acetonitrile solution are presented in Fig. 2 and the corresponding photographs of the RuNHC complexes in acetonitrile solution (40 μM) are shown in Fig. S13 (ESI†). As shown in Fig. 2A, these novel RuNHC complexes have an intense intra-ligand absorption band in the UV regions below 350 nm (ε is up to 10^5 M^{-1} cm^{-1}) and a moderate, broad and featureless MLCT (metal to ligand charge transfer) transition in the visible light region from 380 to 650 nm (ε is *ca.* 2.5 × 10^4 M^{-1} cm^{-1}). Compared with similar features observed in the absorption bands of these three NHC complexes, the corresponding absorption intensities have slight variations along with the changing substituents that have different electronic effects. It was found that the methoxy group, as an electron-donating substituent, would increase the absorption intensity of the RuNHC complexes, while the trifluoromethyl group as the electron-withdrawing substituent has a converse effect on the absorption intensity. Notably, compared with the traditional Ru(N^N)$_3^{2+}$ complexes reported in the literature,[15] the incorporation of the C^C* ligand in this work would not only induce the MLCT band of the RuNHC complexes to undergo a significant bathochromic shift, but it

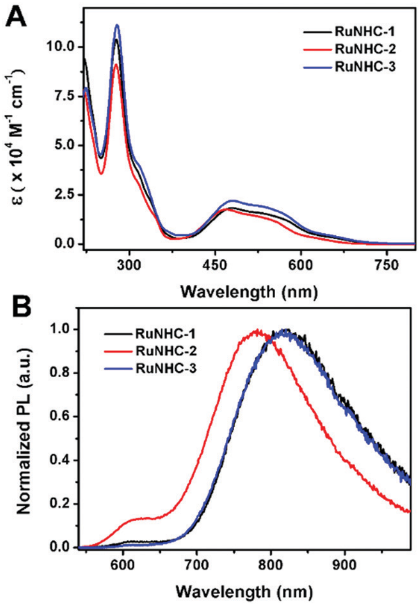

Fig. 2 Absorption (A) and normalized PL (B) spectra of the bis(4,7-diphenyl-1,10-phenoline)ruthenium(II) complexes with a C^C* cyclometalated carbene ligand (40 μM) in acetonitrile solution. λ_{ex} = 515 nm, under an argon-saturated atmosphere.

also obviously increases the absorption intensity, which is profoundly important to bioimaging technologies that require luminophores that possess long wavelength excitation.[16] The summarized photophysical data have also been listed in Table S1 in the ESI.†

Fig. 2B shows the PL spectra of the RuNHC complexes in acetonitrile solution at room temperature. All of these three RuNHC complexes display an NIR emission centered at *ca.* 780 or 820 nm under the excitation of 515 nm light. The PL spectra of RuNHC-2 with a substituent of $-CF_3$ has a distinct hypsochromic shift compared with that of RuNHC-1 and RuNHC-3. Moreover, a shoulder peak at 616 nm has also been observed in RuNHC-2, which may be related to the complicated compositions of the excited states for these novel complexes. Furthermore, using $Ru(bpy)_3^{2+}$ as the ref. 17, the PL quantum efficiencies of these RuNHC complexes have also been calculated and are listed in Table S1 in the ESI.† Accordingly, although these RuNHC complexes still have very low PL quantum efficiencies like most of the reported metal complex-based NIR luminescence,[18] RuNHC-2 with a $-CF_3$ substituent has a comparatively higher PL quantum efficiency compared with RuNHC-1 and RuNHC-3, which may provide a novel avenue to further design NIR luminophores with a high quantum efficiency through molecular structure modification with fluorine atoms.

Owing to the crucial roles of redox properties in the ECL studies, cyclic voltammetry (CV) was initially employed to investigate the electrochemical parameters of RuNHC complexes in this work. CV curves and the corresponding summarized electrochemical data of the RuNHC complexes have been presented in Fig. S14 (ESI†) and Table 1, respectively. All CV characterization in this work was carried out in an argon-saturated anhydrous acetonitrile solution with 0.1 M $TBAPF_6$ as the supporting electrolyte. Compared with that of $Ru(bpy)_3^{2+}$ and its derivatives,[10,19] these novel RuNHC complexes in this work displayed a much lower reversible oxidation wave with peak potentials at 0.72, 0.83 and 0.73 V *versus* a normal hydrogen electrode (NHE), respectively. Meanwhile, two reductive peaks of these RuNHC complexes have also been recorded in the range between −1.2 and −1.6 V *versus* NHE. Most of these reductive curves are reversible except the second reduction peak of RuNHC-1. Incorporating the electron-donating group of –OMe into the coordination NHC ligand would obviously improve the reversibility of the second reduction wave of RuNHC-3, while there are almost no changes in the position of the reduction potential peaks between RuNHC-1 and RuNHC-3. However, RuNHC-2 with the $-CF_3$ group substituent has a much higher oxidation potential and lower first reduction potential compared with RuNHC-1, in other words, RuNHC-2 has much larger energy gaps between the HOMO and LUMO derived from the above redox potential results, which are very consistent with the results of the PL experiment and theoretical calculations (listed in the ESI,† Fig. S15 and Table S2) in the sequence.

Table 1 Electrochemical data from the RuNHC complexes presented in this work

Complex	E_P^{ox}	E_P^{red}	λ_{max} of ECL	Φ_{ECL}[a]	Φ_{ECL}[b]
RuNHC-1	0.72^c	-1.32^c; -1.53^d	808	132%	42%
RuNHC-2	0.83^c	-1.34^c; -1.53^c	784	314%	100%
RuNHC-3	0.73^c	-1.30^c; -1.50^c	802	126%	40%

[a] Potential scan experiment, refers to $Ru(bpy)_3^{2+}$ (Φ_{ECL} is defined as 100%), TPA as the co-reactant. [b] Potential stepping experiment, refers to $Ru(bpy)_3^{2+}$ (Φ_{ECL} is defined as 100%), TPA as the co-reactant. [c] Reversible. [d] Quasi-reversible.

Based on the above mentioned redox properties derived from CV techniques (including the electrochemical data of co-reactants listed in Fig. S16 in the ESI†), ECL studies were finally performed. In order to obtain the best experimental conditions for ECL generation, both the concentration and kinds of co-reactant have been optimized for these novel RuNHC complexes. These experimental data have also been shown in Fig. S17 and S18 (ESI†). Accordingly, it was easily observed that *n*-tripropylamine (TPA) is much better than 2-(dibutylamino)ethanol (DBAE) and triethylamine (TEA) for all of these three RuNHC complexes in the positive scanning ECL model and the best ratio of [TPA]/[RuNHC] is 400. Herein, the plots of CV and ECL *versus* potential have been presented in Fig. 3A–C. Owing to the large ratio of [TPA]/[RuNHC], the oxidation wave of RuNHC was intensely covered up and the oxidation wave recorded in Fig. 3 can be ascribed to TPA.[20] As shown in Fig. 3, along with the oxidation of TPA, these RuNHC complexes exhibited increasing ECL signals and the ECL intensity reached a peak value at *ca.*1.4 V *versus* NHE.

Furthermore, the ECL studies with a potential stepping mode have also been carried out in this work. The ECL intensity at various concentrations of TPA in the potential stepping model have also been recorded and demonstrated in Fig. S19 (ESI†). Along with the increase of the concentration of TPA, the ECL intensity was also enhanced accordingly and reached the peak value when the ratio of [TPA]/[RuNHC] was 400 for all of

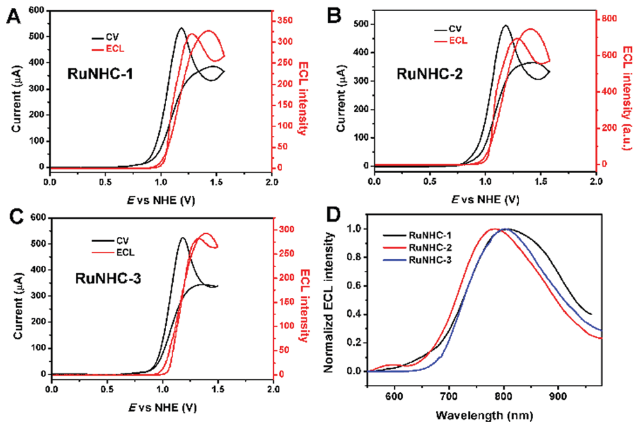

Fig. 3 The ECL performance of RuNHC complexes in this work. (A–C) CV and ECL intensity *vs.* potential plots of 0.1 mM RuNHC complexes in acetonitrile solutions containing 0.1 M $TBAPF_6$ and 40 mM TPA. The scan rate is 50 mV s^{-1}. (D) Normalized ECL spectra of 0.1 mM RuNHC complexes in acetonitrile solution containing 40 mM TPA and 0.1 M $TBAPF_6$ under potential stepping conditions. The potential was set at 1.6 V *versus* NHE.

the three RuNHC complexes. Meanwhile, TPA also outperformed DBAE and TEA in the following optimization studies for the kinds of co-reactant in the potential stepping mode, as shown in Fig. S20 in the ESI.† Based on the optimized kinds and concentrations of the co-reactant, the ECL spectra of these RuNHC complexes have also been recorded under the potential stepping mode. The spectra and wavelength data are shown in Fig. 3D and Table 1, respectively. Just as expected, these novel complexes exhibit NIR ECL emission centered at 808, 784 and 802 nm for RuNHC-1, RuNHC-2 and RuNHC-3, respectively. To the best of our knowledge, these novel complexes display the longest ECL wavelength among the reported ruthenium(II) complexes so far,[5] which is very important to the development of ruthenium(II)-based NIR luminophores. The further potential stepping ECL with BPO as a ''reductive-oxidation'' co-reactant and annihilation ECL were also performed and characterized and are shown in Fig. S21 and S22 (ESI†), respectively. However, their ECL intensities are much lower than that of the ''oxidation–reduction'' ECL. In addition, these RuNHC complexes showed a good water solubility and the ECL performances of RuNHC in aqueous ProCell solutions are shown in Fig. S23 (ESI†).

Finally, the ECL quantum efficiencies (Φ_{ECL}) of these novel RuNHC complexes with TPA as a co-reactant were also calculated using $Ru(bpy)_3^{2+}$ as a reference in acetonitrile solution. The data for Φ_{ECL} both in the positive potential scanning experiment and potential stepping experiment are listed in Table 1. Obviously, the ECL performance is closely related to the ECL generation pathway. Generally, the novel RuNHC complexes in this work demonstrated significantly better ECL properties in the positive potential scanning experiments than that in the potential stepping mode. Although these RuNHC complexes have various ECL efficiencies in different ECL pathways, RuNHC-2 with the $-CF_3$ substituent is more outstanding than (or at least equal to) $Ru(bpy)_3^{2+}$, both in terms of positive potential scanning ECL and potential stepping ECL. It should be noted that the similar positive effect of CF_3 on OLED devices has also been reported by Tong and co-workers recently.[21]

In conclusion, in order to exploit ruthenium(II)-based NIR luminophores, three novel ruthenium(II) complexes comprising one NHC ligand and two DIP ligands (abbreviated as RuNHC in this work) have been deliberately designed and successfully synthesized in this work. As expected, the incorporation of NHC ligands makes the emission of these novel complexes undergo a large bathochromic shift ($>$170 nm referenced to $Ru(bpy)_3^{2+}$) compared with traditional ruthenium(II) complexes comprising three N^N ligands, such as $Ru(bpy)_3^{2+}$ and its derivatives. It should be emphasized that enhancement effects of the trifluoromethyl group, both on the PL and ECL quantum efficiency, have been identified in this work. Based on the optimized experimental conditions (including the kinds and concentrations of co-reactants and the potential applied pathways), RuNHC-2 with a CF_3 substituent with TPA as a co-reactant in acetonitrile solution exhibited an ECL efficiency that was three times higher compared with $Ru(bpy)_3^{2+}$ in positive potential scanning mode under the same experimental conditions. In our opinion, these novel complexes, with excellent ECL quantum efficiency and exhibiting the longest emission wavelength of previously reported ruthenium(II) complexes, demonstrated in this work could pave the way for the further development of ECL cutting-edge research.

This work was supported by the National Natural Science Foundation of China (NSFC No. 22034003, 21505097), and the Excellent Youth Project of Suzhou University of Science and Technology, Qing Lan Project of Jiangsu province. The authors also thank the Supercomputing Center, CNIC, CAS, for calculation support.

Conflicts of interest

There are no conflicts to declare.

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