

Redox-responsive carbometalated ruthenium and osmium complexes

Zhong-Liang Gong^{1*}, Chang-Jiang Yao¹, Jiang-Yang Shao¹, Hai-Jing Nie¹,
Jian-Hong Tang^{1,2} & Yu-Wu Zhong^{1,2*}

¹Beijing National Laboratory for Molecular Sciences; CAS Key Laboratory of Photochemistry, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100190, China

²University of Chinese Academy of Sciences, Beijing 100049, China

Received August 17, 2016; accepted August 28, 2016; published online November 2, 2016

Organometallic conjugated complexes have become an important type of stimuli-responsive materials because of their appealing electrochemical properties and rich photonic, electronic, and magnetic properties. They are potentially useful in a wide range of applications such as molecular wires, molecular switches, molecular machines, molecular memory, and optoelectronic detections. This review outlines the recent progress on the molecular design of carbometalated ruthenium and osmium complexes and their applications as redox-responsive materials with visible and near-infrared (NIR) absorptions and electron paramagnetic resonance as readout signals. Three molecule systems are introduced, including the symmetric diruthenium complexes, metal-amine conjugated bi-center system, and multi-center redox-active organometallic compounds. Because of the presence of a metal-carbon bond on each metal component and strong electronic coupling between redox sites, these compounds display multiple reversible redox processes at low potentials and each redox state possesses significantly different physical and chemical properties. Using electrochemical potentials as input signals, these materials show reversible NIR absorption spectral changes, making them potentially useful in NIR electrochromism and information storage.

stimuli-responsive materials, electro-active compounds, organometallic materials, triaryl amines, near-infrared, electrochromism

Citation: Gong ZL, Yao CJ, Shao JY, Nie HJ, Tang JH, Zhong YW. Redox-responsive carbometalated ruthenium and osmium complexes. *Sci China Chem*, 2017, 60: 583–590, doi: 10.1007/s11426-016-0341-5

1 Introduction

Stimuli-responsive compounds are important functional materials that can show reversible conformation or configuration changes on the molecular or supramolecular scale, in response to external stimuli such as light, electricity, magnetism, temperature, or chemicals. The structural changes in turn give rise to the distinct variations of the physical and chemical properties of the material, which can

be used as the output signals to distinguish the material in different states. These unique features have made responsive materials useful in a wide range of applications including chemical sensing, molecular machines, optoelectronic devices, energy conversion and storage, drug delivery, and medical diagnosis and treatment [1–5]. For instance, poly(*N*-isopropylacrylamide) is a typical thermal responsive functional material, which displays distinct conformation changes in response to temperature variations and has important applications in drug delivery [6]. Azobenzene and diarylethene derivatives are important photochromic molecules, which display reversible *cis/trans* or ring closing/

*Corresponding authors (email: gongzhongliang@iccas.ac.cn; zhongyuwu@iccas.ac.cn)

opening structural changes in response to light and have been widely used in photosensing, molecular switches, and photochromic devices [4,7–10]. Crown ether, cyclodextrin, and cucurbituril are typical chemical responsive functional materials that act as host molecules for various guest molecules with high selectivity and sensitivity such as secondary ammonium salts, viologen derivatives, and metal ions [11–15]. In addition, functional molecules that are responsive to external electric or magnetic fields are well known and have received much attention [16–18].

Redox-responsive compounds are a special type of responsive materials, which display reversible changes among different redox states in response to electrochemical potential or chemical oxidants or reductants. They are characterized by easy operation, high sensitivity, and good reversibility, etc. One of the key requirements in these materials is that they must contain a redox-active structural component, which is used to control the redox states and physical and chemical properties of the material [19–24]. For instance, the tetrathiafulvalene-containing rotaxane and catenane compounds reported by Stoddart and co-workers [25,26] are typical redox-responsive materials, which are potentially useful in molecular machines and molecular electronics. In addition, polyaniline is another classical redox-responsive material, which exhibit three different redox states in response to electrochemical potential changes: leucoemeraldine (the totally reduced form), emeraldine (the half oxidized form), and pernigraniline (the totally oxidized form) [27].

In addition to the purely organic molecules, redox-active organometallic complexes are important redox-responsive materials [28–30]. Ferrocene derivatives are a typical example of such functional materials. Because of the good reversibility and low potential of the redox processes, ferrocene-containing redox-responsive compounds have received intense interest in electrochemical sensing, molecular electronics, and molecular memory [23,28,31,32]. Polypyridine transition-metal complexes are important functional materials that have been widely used in various optoelectronic applications. However, normal polypyridine complexes have rather high oxidation potentials, which make them disadvantageous as redox-responsive materials. One method to significantly decrease the oxidation potential of polypyridine complexes is to introduce a metal-carbon bond to the molecule to give a carbometalated complex [33,34]. In addition to the relatively low oxidation potential, carbometalated complexes often display strong electronic coupling among different redox sites and tend to show significantly different absorption spectra in different redox states. Taking advantage of these appealing features, we and others have made much progress in the redox-responsive organometallic materials based on carbometalated complexes [35–37]. This review summarizes the recent progress on the redox-responsive carbometalated ruthenium and osmium complexes, including symmetric diruthenium complexes, metal-amine conjugated bi-center system, and multi-

center redox-active organometallic compounds.

2 Symmetric diruthenium complexes

Symmetric diruthenium complexes are important optoelectronic materials. They are model compounds for the studies of mixed-valence electronic coupling [38–40] and have important applications in molecular electronics [41,42]. When the ruthenium ion is connected to the bridging ligand with a ruthenium-carbon bond, the Ru(III/II) potential is distinctly decreased and the degree of metal-metal electronic communication is significantly enhanced. As a result, these carbometalated diruthenium complexes display strong intervalence charge-transfer (IVCT) transitions in the near-infrared (NIR) region in the mixed-valent state. However, these NIR absorptions are not present when the complex is in the homo-valent states. This forms the basis for the applications of carbometalated diruthenium complexes in NIR electrochromism and redox-responsive molecular switching.

As shown in Figure 1, the carbometalated diruthenium complex $\mathbf{1}^{2+}$ bridged by 1,2,4,5-tetra(pyrid-2-yl)benzene (tpb) shows two Ru(III/II) redox processes at +0.12 and +0.55 V vs. Ag/AgCl and strong electronic coupling is observed between two ruthenium components [43]. In response to the stepwisely applied electrochemical potentials from -0.1 V to $+0.8$ V, three redox states ($\mathbf{1}^{2+}$, $\mathbf{1}^{3+}$, and $\mathbf{1}^{4+}$) are accessible. A reversible reduction process from $\mathbf{1}^{4+}$ to $\mathbf{1}^{2+}$ could be realized by stepwisely decreasing the potential. The mixed-valent state $\mathbf{1}^{3+}$ was characterized by the intense IVCT absorptions at 1147 nm with ϵ_{\max} of $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and the Ru(III)-based rhombic electron paramagnetic resonance (EPR) signal with an average g factor ($\langle g \rangle$) of 2.144. Both IVCT absorptions and EPR signal were not observed for the homo-valent states $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$. The stepwise oxidation of $\mathbf{1}^{2+}$ to $\mathbf{1}^{3+}$ and $\mathbf{1}^{4+}$ could also be realized by adding proper amount of chemical oxidants such as cerium ammonium nitrate (CAN). In this sense, complex $\mathbf{1}^{2+}$ is a typical redox-responsive organometallic material with NIR absorption and EPR spectroscopy as the readout signals. It is useful as the active materials for NIR electrochromic films and devices [44].

Figure 2 shows another example of redox-responsive carbometalated diruthenium complex $\mathbf{2}^{2+}$, which is bridged by the biscyclometalating ligand 1,3,6,8-tetra(pyrid-2-yl)pyrene (tppyr). Complex $\mathbf{2}^{2+}$ shows two Ru(III/II) waves at +0.56 and +0.76 vs. Ag/AgCl in *N,N*-dimethylformamide (DMF) [45,46]. When $\mathbf{2}^{2+}$ was stepwisely oxidized by either electrochemical electrolysis or a chemical oxidant, it was transformed into $\mathbf{2}^{3+}$ and $\mathbf{2}^{4+}$. The mixed-valent state $\mathbf{2}^{3+}$ is characterized by the IVCT absorptions at 2080 nm with ϵ_{\max} of $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and a rhombic EPR signal with $\langle g \rangle$ of 2.199. In addition, the high homo-valent state $\mathbf{2}^{4+}$ was characterized by strong ligand-to-metal charge-transfer (LMCT) absorptions at 735 nm. These spectroscopic features could

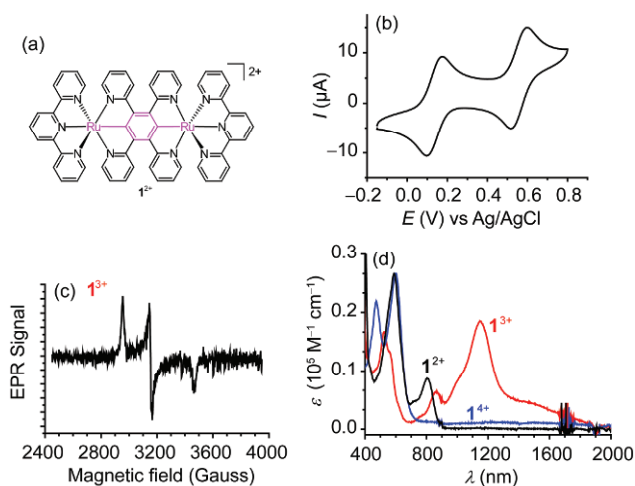


Figure 1 The tpb-bridged diruthenium complex 1^{2+} . (a) Molecular structure; (b) cyclic voltammogram (CV) in 0.1 M $n\text{-Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at 100 mV/s; (c) EPR spectrum of 1^{3+} at 77 K; (d) Vis/NIR absorption spectra at different redox state. Adapted from Ref. [43]. Copyright 2011 American Chemical Society (color online).

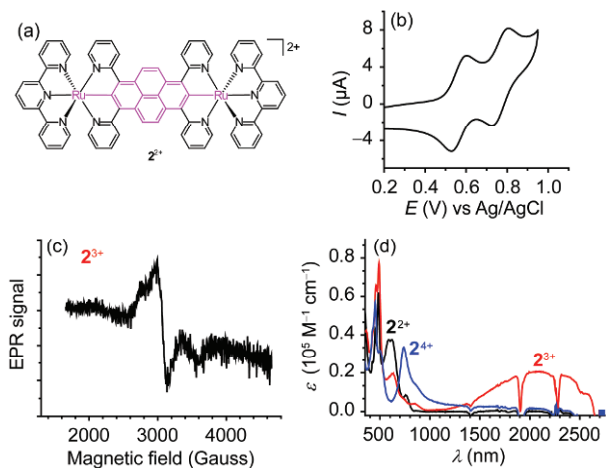


Figure 2 The tppyr-bridged diruthenium complex 2^{2+} . (a) Molecular structure; (b) CV in 0.1 M $n\text{-Bu}_4\text{NClO}_4/\text{DMF}$ at 100 mV/s; (c) EPR spectrum of 2^{3+} at 77 K; (d) Vis/NIR absorption spectra at different redox state. Adapted from Ref. [45]. Copyright 2015 American Chemical Society (color online).

be used as the readout signals for distinguishing the different redox states of **2**.

In addition to the above discussed 1^{n+} and 2^{n+} , cyclometalated diruthenium complexes 3^{n+} – 5^{n+} (Figure 3) bridged by 3,3',5,5'-tetra(pyrid-2-yl)-1,1'-biphenyl [47], 1,3,6,8-tetra(pyrid-2-yl)carbazole [48], and 3,3',5,5'-tetra(*N*-methylbenzimidazole)-1,1'-biphenyl [49], respectively, show similar redox-responsive properties. However, because of the different electronic nature of the bridging ligands and terminal ligands, these complexes show IVCT bands of different wavelength and intensity.

The diruthenium complex **6** reported by Liu and co-workers [50] shown in Figure 4 is somewhat different in structure with respect to complexes **1**–**5**. The ruthenium

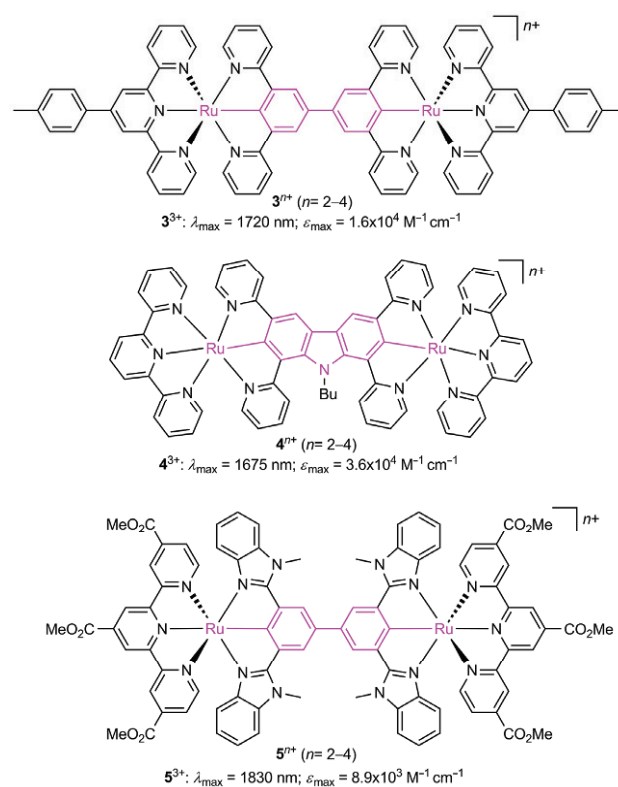


Figure 3 Symmetric diruthenium complexes 3^{n+} – 5^{n+} and the IVCT parameters in the mixed-valent state (color online).

components of complexes **1**–**5** have a bis-tridentate configuration and they are typical cyclometalated complexes. In contrast, the ruthenium components of **6** consist of a pentamethylcyclopentadiene and a diphosphine ligand and the ruthenium ions are connected to the terminal alkynes of the bridging ligand with a ruthenium-carbon bond. Complex **6** shows two redox processes at -0.39 and -0.064 V vs. ferrocene(+0). It shows interesting redox-responsive switching with multiple readout signals. Upon stepwise oxidation with a chemical oxidation (ferrocenium hexafluorophosphate), **6** was transformed into 6^+ and 6^{2+} . Complex 6^+ was characterized by intense absorptions at 600 nm ($\epsilon_{\text{max}} = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 1390 nm ($\epsilon_{\text{max}} = 2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Complex 6^{2+} shows intense absorptions at 754 nm with ϵ_{max} of $1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Another appealing feature of **6** is that its different redox states could also be distinguished by IR spectra. The $\nu(\text{C}\equiv\text{C})$ bands of **6**, 6^+ , and 6^{2+} appeared at 2056, 1961, and 1914 cm^{-1} , respectively. In addition, a single-line EPR signal was observed for 6^+ , while other two redox states are EPR inactive.

In addition to complex **6**, Liu and co-workers [38,39,51, 52] have recently prepared a series of diruthenium complexes bridged by different polyaromatic alkynyl or vinyl ligands. Figure 5 shows two representative examples, where the two ruthenium ions were bridged by a 2,7-dialkynyl pyrene or 2,6-divinylanthracene bridge, respectively [39, 51]. These complexes display similar three-state redox switch-

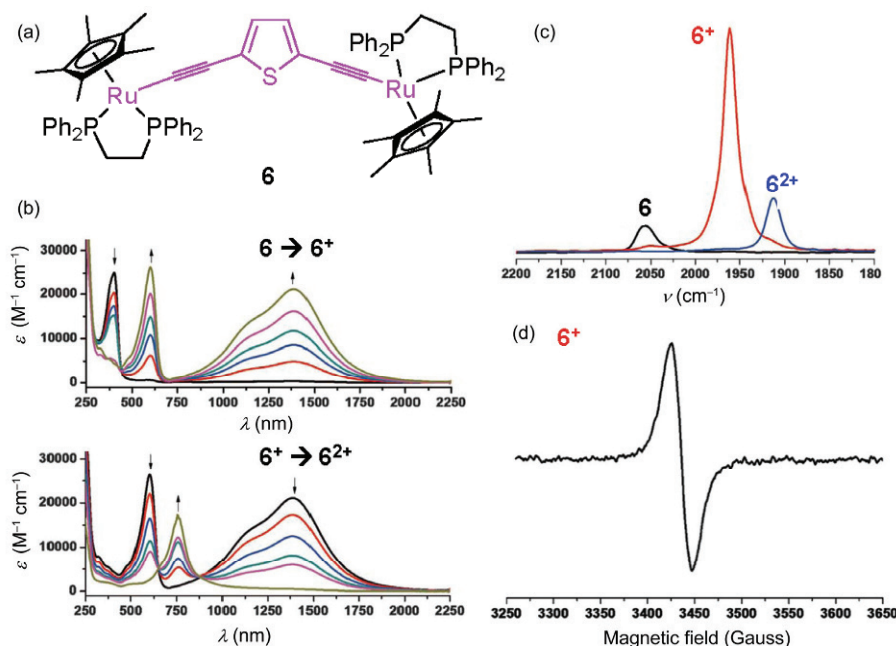


Figure 4 The thiophene-bridged alkyne diruthenium complex **6**. (a) Molecular structure; (b) absorption spectral changes in CH_2Cl_2 upon stepwise oxidation with ferrocenium hexafluorophosphate; (c) IR spectra of 6^{n+} at different redox states; (d) EPR spectrum of 6^+ at 298 K. Adapted from Ref. [50]. Copyright 2013 John Wiley & Sons, Inc. (color online).

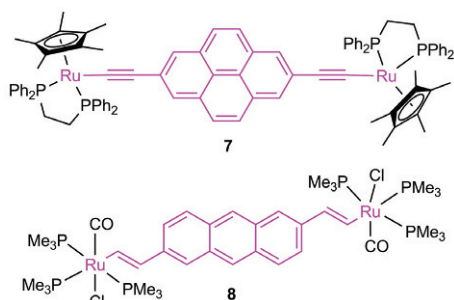


Figure 5 Diruthenium complexes **7** and **8** (color online).

ching with multiple readout signals (NIR absorption, EPR, and IR spectra), as have been discussed for complex **6**.

It should be mentioned here that Lahiri and co-workers [53,54] have recently developed a series of diruthenium complexes bridged by a redox-noninnocent ligand with an anionic oxygen and/or nitrogen coordination site. These complexes also display multistate redox switching in response to low electrochemical potentials. However, these complexes do not contain a ruthenium-carbon bond in structure and do not belong to carbometalated complexes. Their redox-responsive behavior is thus not further discussed.

3 Metal-amine conjugated bi-centre system

The compounds discussed in the above section are redox symmetric. The presence of strong electronic coupling leads

to the redox potential splitting of the complex and the appearance of intense IVCT NIR absorptions in the mixed-valent state. The shortcomings of these complexes include the low yield of synthesis and low solubility of the product. These two issues can however be alleviated by using a monoruthenium complex with a redox-active amine unit that is connected to the metal component with a short conjugated bridge. Triaryl amines are well-known organic hole-transporting materials that possess well-defined redox behaviour [55,56]. In addition, triaryl amines and carbometalated ruthenium complexes have comparable oxidation potentials, which is beneficial for maintaining a high degree of electronic coupling between two components.

As shown in Figure 6, the cyclometalated ruthenium-amine conjugated asymmetric complex 9^+ displays two redox couples at +0.27 and +0.68 V vs. Ag/AgCl [57], which were caused by the stepwise oxidations of the triarylamine and ruthenium component, respectively. Because of the low oxidation potential, complex 9^+ is very sensitive to chemical oxidant or electrochemical potential and it can be readily oxidized to 9^{2+} and 9^{3+} . Complex 9^{2+} is characterized by a strong absorption band at 1050 nm with ϵ_{max} of $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and a single line EPR signal at room temperature. Complex 9^{3+} can be distinguished by an intense absorption band at 710 nm caused by the N^{2+} -localized transitions. In addition, the three redox states of 9^{n+} show completely different solution colors (violet, red, and blue for 9^+ , 9^{2+} and 9^{3+} , respectively), which can be used as an additional readout signal for the redox-stimulated switching process. The spectroscopic and color changes of 9^{n+} in solution can

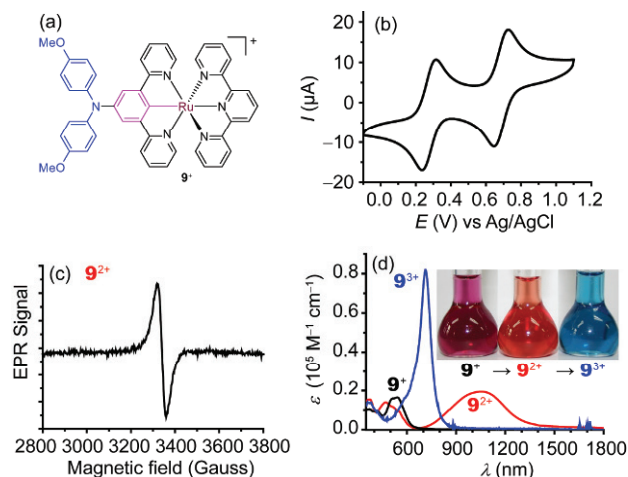


Figure 6 The ruthenium-amine conjugated complex 9^+ . (a) Molecular structure; (b) CV in 0.1 M $n\text{-Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at 100 mV/s; (c) EPR spectrum of 9^{2+} at room temperature; (d) Vis/NIR absorption spectra and pictures of the solution at different redox states. Adapted from Ref. [57]. Copyright 2012 The Royal Society of Chemistry (color online).

be transformed into thin film state when the molecule was functionalized with suitable polymerizable groups [58], which forms the basis for building two-wavelength electrochromic devices with a flip-flap molecular logic function.

Figure 7 shows the redox-responsive behavior of the triarylamine-derived styryl ruthenium complex 10 developed by Winter and co-workers [59]. Complex 10 shows two redox couples at -0.12 and $+0.27$ V vs. ferrocene(+0). In response to a positive electrochemical potential, 10 was transformed into 10^+ and 10^{2+} stepwisely. The three redox states of 10 show a similar set of absorption spectra with respect to those of the above-discussed complex 9 . In addition, complex 10^+ shows a multi-line EPR signal at room temperature. Another interesting feature of complex 10 is that its three redox states display significantly different IR spectra. Specifically, the Ru(CO) band experiences a blue shift from 1910 to 1944 cm^{-1} during the first and then to 1985 cm^{-1} during the second oxidation.

In addition to ruthenium-amine conjugated system, cyclometalated osmium-amine conjugated complex has been reported. Figure 8 shows the redox-responsive behavior of complex 11^+ [60], which is the osmium analogous of the ruthenium complex 9^+ . Due to the electron-rich nature of the osmium ion, the redox potentials of 11^+ ($+0.18$ and $+0.59$ V vs. Ag/AgCl) are further negatively shifted with respect to those of 9^+ . The three redox states of 11 have very rich visible and NIR absorptions. Complex 11^+ shows rich singlet and triplet metal-to-ligand charge-transfer ($^1\text{MLCT}$ and $^3\text{MLCT}$) transitions between 400 and 1200 nm. Complex 11^{2+} is characterized by the amine-to-osmium(III) charge-transfer at 970 nm and the Os(III)-localized d-d transitions at 1950 nm. Meanwhile, the N^{3+} -localized transitions at 700 nm were observed for the doubly-oxidized state 11^{3+} . The three redox states of 11 are purple, wine, and dark

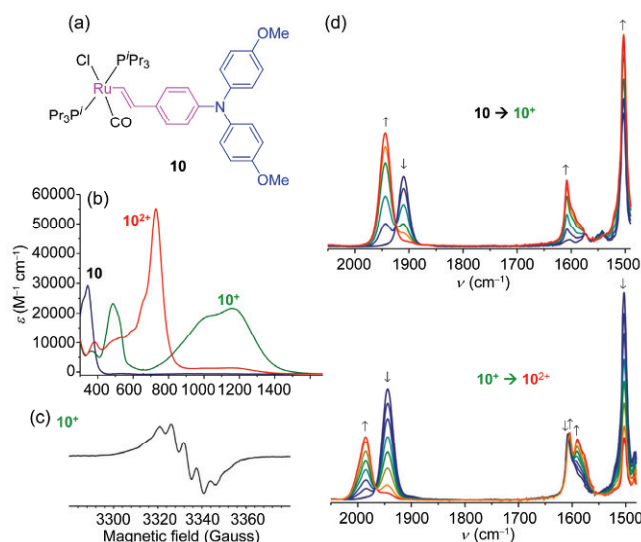


Figure 7 The ruthenium-amine conjugated complex 10 . (a) Molecular structure; (b) Vis/NIR absorption spectra at different redox states; (c) EPR spectrum of 10^+ at room temperature; (d) IR spectral changes upon stepwise oxidations by electrolysis. Adapted from Ref. [59]. Copyright 2012 Walter de Gruyter GmbH (color online).

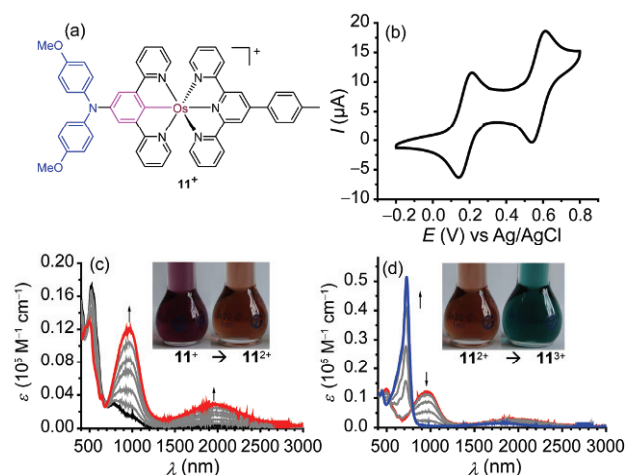


Figure 8 The osmium-amine conjugated complex 11^+ . (a) Molecular structure; (b) CV in 0.1 M $n\text{-Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at 100 mV/s; (c,d) Vis/NIR absorption spectral changes and pictures of the solution upon stepwise oxidations. Adapted from Ref. [60]. Copyright 2014 The Royal Society of Chemistry (color online).

cyan for 11^+ , 11^{2+} and 11^{3+} , respectively. Because of the strong spin-coupling effect to the osmium ion, no EPR signal was detected for 11 at different redox states.

The above discussed complexes all show reversible absorption spectral changes in the visible to NIR region, which makes them useful in electrochromic devices. Recently, a ruthenium-amine conjugated complex 12^+ was reported (Figure 9), which is redox-responsive and useful for ion sensing [61]. The cyclometalated ruthenium complex 12^+ contains a dipyridylamine recognition site which is connected to the metal component by an amide bond. This complex is able to selectively recognize Cu^{2+} in $\text{CH}_3\text{CN}/$

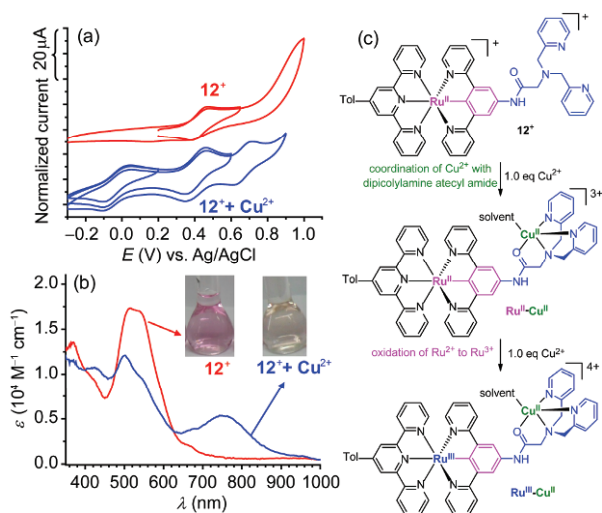


Figure 9 Cyclometalated complex 12^+ for Cu^{2+} sensing. (a) CV spectral changes in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1) upon addition of 1 equiv. Cu^{2+} ; (b) absorption spectral and solution color change upon addition of 2 equiv. Cu^{2+} ; (c) ion recognition mechanism. Tol is *p*-tolyl group. Adapted from Ref. [61]. Copyright 2013 American Chemical Society (color online).

H_2O (4:1) mixed solvent by multi-channel readouts. In the presence of one equivalent of Cu^{2+} , two new redox couples at -0.03 and $+0.66$ V vs. Ag/AgCl appeared, in addition to the original wave at around $+0.40$ V of 12^+ . When more than one equivalent of Cu^{2+} was added, big changes were observed to the absorption spectrum, as evidenced by the decrease of the MLCT band at 516 nm and the appearance of a new LMCT band at 750 nm. At the same time, the color of the solution turned pale yellow from violet. These electrochemical and spectroscopic responses were rationalized by a coordination-followed-by-oxidation mechanism [61]. When complex 12^+ was deposited on electrode surfaces, practically useful thin films for Cu^{2+} sensing could be developed [62].

4 Multi-centre organometallic systems

Molecular materials with multiple redox processes are useful for molecular electronics, molecular memory, and other optoelectronic fields [63–65]. By using these materials, redox-responsive processes with multi-step spectral changes are possible.

Figure 10 shows the redox responsive properties of a triarylamine-bridged cyclometalated diruthenium complex 13^{2+} [66,67]. This complex is an appealing three-centre system with a large degree of charge delocalization among the ruthenium-amine-ruthenium framework. It shows three consecutive redox couples at $+0.21$, $+0.44$, and $+1.03$ V vs. Ag/AgCl, which points to the presence of four readily accessible redox states by either chemical oxidation or electrochemical electrolysis. Three-step NIR absorption spectral changes were observed when 13^{2+} was stepwisely oxidized.

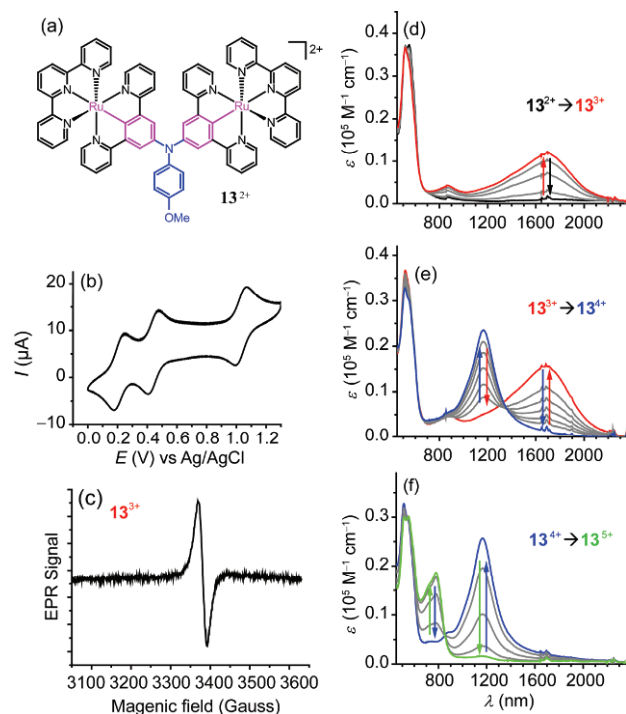


Figure 10 The amine-bridged diruthenium complex 13^{2+} . (a) Molecular structure; (b) CV in $0.1 \text{ M } n\text{-Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ at 100 mV/s ; (c) EPR spectrum of 13^{3+} at room temperature; (d) Vis/NIR absorption spectral changes upon stepwise oxidations. Adapted from Ref. [66]. Copyright 2015 John Wiley & Sons, Inc. (color online).

Complexes 13^{3+} , 13^{4+} , and 13^{5+} were characterized by a unique absorption band at 1680, 1170, and 750 nm, respectively. In addition, complex 13^{3+} can be read out by a single-line EPR signal at room temperature. This complex is useful for mimicking a flip-flap-flop ternary molecular gate [66].

When a cyclometalated diruthenium complex was used as an organometallic bridge to connect two distal triarylamine segments, an amine-ruthenium-ruthenium-amine type of tetra-centre complex 14^{2+} was obtained (Figure 11) [68]. It shows four redox couples at $+0.38$, $+0.48$, $+0.83$, and $+0.91$ V vs. Ag/AgCl. The former two couples are associated with the amine oxidations and the latter two are ascribed to the oxidations of the ruthenium components. The two distal amines can be stepwisely oxidized, which means that efficient electronic communication is present between them. When 14^{2+} was oxidized into 14^{3+} and 14^{4+} , a NIR absorption band at 1186 nm appeared. This band decreased when 14^{4+} was further oxidized into 14^{5+} and 14^{6+} , accompanied by the appearance of the N^+ -localized transitions at around 800 nm. The one-electron-oxidized form 14^{3+} was characterized by a single-line EPR readout signal. When the ruthenium ions of 14^{2+} were replaced by the electron-rich osmium ions, an amine-osmium-osmium-amine analogous was obtained [69]. It shows very similar four-step redox-responsive behaviour as was observed for 14^{2+} .

In addition to cyclometalated ruthenium or osmium metal

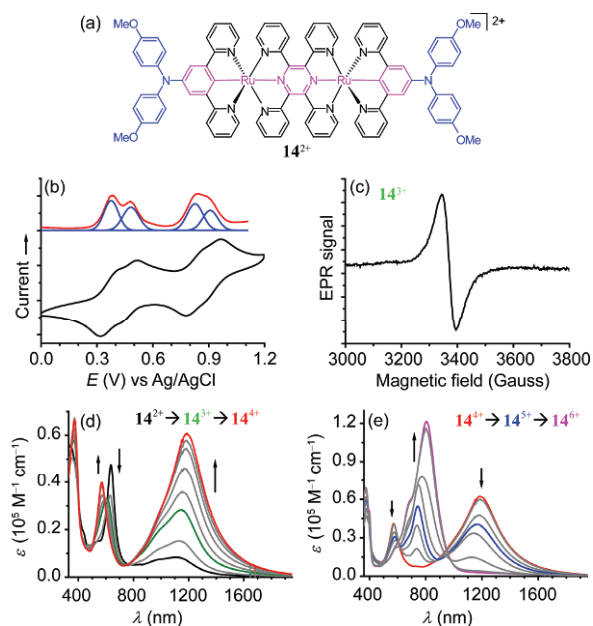


Figure 11 The ruthenium-amine conjugated four-center compound 14^{2+} . (a) Molecular structure; (b) CV and differential pulse voltammogram (DPV) in 0.1 M $n\text{-Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ at 100 mV/s; (c) EPR spectrum of 14^{3+} at room temperature; (d, e) Vis/NIR absorption spectral changes upon stepwise oxidations. Adapted from Ref. [68]. Copyright 2013 American Chemical Society (color online).

components, alkynyl or vinyl carbometalated ruthenium complexes have been used to generate multi-centre systems. For instance, Humphrey and co-workers [70] reported the ferrocene-alkynyl ruthenium-triarylamine conjugated tri-centre compound **15** and the triruthenium complex **16** with a triphenylamine core (Figure 12). Complex **15** displays three consecutive redox couples at +0.19, +0.56, and +0.93 V and complex **16** displays five redox waves at +0.20, +0.45, +0.69, +0.90, and +1.08 V vs. Ag/AgCl, respectively. Accordingly, four and six redox states have been distinguished for **15** and **16**, respectively, by absorption and IR spectra. A similar vinyl carbometalated triruthenium complex with a triphenylamine core was reported by Winter and co-workers [59]. In addition, Liu and co-workers [52] recently reported that the alkynyl carbometalated triruthenium complex **17** with a terthiophene bridged showed three consecutive redox couples at -0.24 , -0.16 , and $+0.11$ V vs. ferrocene(+0). The four-step redox-responsive behaviour of **17** can be monitored by absorption and IR spectral changes.

5 Conclusions

Bi-centre or multi-centre carbometalated ruthenium or osmium complexes possess low redox potentials and a high degree of charge delocalization. They are excellent redox-responsive organometallic materials which show significantly different physical and spectroscopic properties at different redox states. The redox-responsive processes were

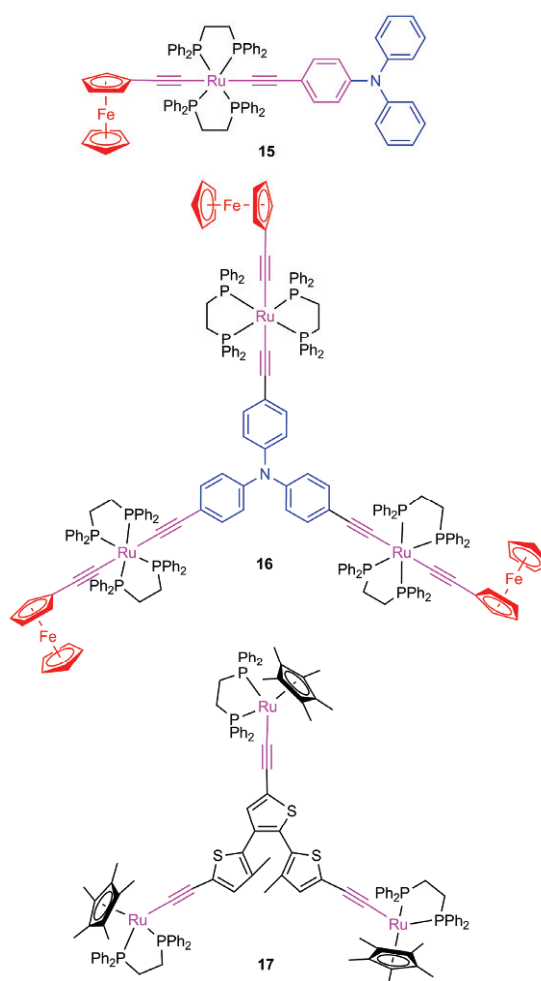


Figure 12 Multi-centre compounds **15**–**17** (color online).

performed with chemical oxidants or electrochemical potentials as input signals and NIR absorption, IR, and EPR spectral changes as readout signals. These materials are potentially useful in molecular electronics, NIR electrochromism, information storage, and ion sensing. It would be interesting in the future to develop smart responsive molecular materials that can be readily synthesized and triggered by multiple input signals. In addition, it would also be critical to transform the solution-based demonstrations to electrode-confined surfaces for practical applications [71].

Acknowledgments This work was supported by the National Natural Science Foundation of China (21271176, 21472196, 21521062, 21501183), the Ministry of Science and Technology of China (2012YQ120060), and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB 12010400).

Conflict of interest The authors declare that they have no conflict of interest.

- Li H, Qu DH. *Sci China Chem*, 2015, 58: 916–921
- Guragain S, Bastakoti BP, Malgras V, Nakashima K, Yamauchi Y. *Chem Eur J*, 2015, 21: 13164–13174
- Ngarkar SS, Desai AV, Ghosh K. *Chem Asian J*, 2014, 9: 2358–2376

- 4 Bléger D, Hecht S. *Angew Chem Int Ed*, 2015, 54: 11338–11349
- 5 Zarzar LD, Aizenberg J. *Acc Chem Res*, 2014, 47: 530–539
- 6 Jochumab FD, Theato P. *Chem Soc Rev*, 2013, 42: 7468–7483
- 7 Qu DH, Wang QC, Zhang QW, Ma X, Tian H. *Chem Rev*, 2015, 115: 7543–7588
- 8 Xu K, Zhao J, Cui X, Ma J. *J Phys Chem A*, 2015, 119: 468–481
- 9 Xu K, Zhao J, Cui X, Ma J. *Chem Commun*, 2015, 51: 1803–1806
- 10 Xiao C, Zhao WY, Zhou DY, Huang Y, Tao Y, Wu WH, Yang C. *Chin Chem Lett*, 2015, 26: 817–824
- 11 Zhang M, Yan X, Huang F, Niu Z, Gibson HW. *Acc Chem Res*, 2014, 47: 1995–2005
- 12 Ma X, Tian H. *Acc Chem Res*, 2014, 47: 1971–1981
- 13 Guo DS, Liu Y. *Acc Chem Res*, 2014, 47: 1925–1934
- 14 Zhang SJ, Wang Q, Cheng M, Qian XH, Yang Y, Jiang JL, Wang LY. *Chin Chem Lett*, 2015, 26: 885–888
- 15 Zhang M, Gao J, Chen J, Cai M, Jiang J, Tian Z, Wang H. *Sci China Chem*, 2016, 59: 848–852
- 16 Huang C, Rudnev AV, Hong W, Wandlowski T. *Chem Soc Rev*, 2015, 44: 889–901
- 17 Rikken RSM, Nolte RJM, Maan JC, van Hest JCM, Wilson DA, Christianen PCM. *Soft Matter*, 2014, 10: 1295–1308
- 18 van Rhee PG, Rikken RSM, Abdelmohsen LKEA, Maan JC, Nolte RJM, van Hest JCM, Christianen PCM, Wilson DA. *Nat Commun*, 2014, 5: 5010
- 19 Wang Q, Cheng M, Zhao Y, Yang Z, Jiang J, Wang L, Pan Y. *Chem Commun*, 2014, 50: 15585–15588
- 20 Hu XY, Chen Y, Liu Y. *Chin Chem Lett*, 2015, 26: 862–866
- 21 Lou Z, Li P, Han K. *Acc Chem Res*, 2015, 48: 1358–1368
- 22 Canevet D, Sallé M, Zhang G, Zhang D, Zhu D. *Chem Commun*, 2009: 2245–2269
- 23 Nakahata M, Takashima Y, Yamaguchi H, Harada A. *Nat Commun*, 2011, 2: 511
- 24 Klajn R, Stoddart JF, Grzybowski BA. *Chem Soc Rev*, 2010, 39: 2203–2237
- 25 Fahrenbach AC, Bruns CJ, Li H, Trabolsi A, Coskun A, Stoddart JF. *Acc Chem Res*, 2014, 47: 482–493
- 26 Fahrenbach AC, Bruns CJ, Cao D, Stoddart JF. *Acc Chem Res*, 2012, 45: 1581–1592
- 27 Moriuchi T, Hirao T. *Acc Chem Res*, 2012, 45: 347–360
- 28 Fabre B. *Acc Chem Res*, 2010, 43: 1509–1518
- 29 Whittell G, Hager MD, Schubert US, Manners I. *Nat Mater*, 2011, 10: 176–188
- 30 Sakamoto R, Wu KH, Matsuoka R, Maeda H, Nishihara H. *Chem Soc Rev*, 2015, 44: 7698–7714
- 31 Ni M, Zhang N, Xia W, Wu X, Yao C, Liu X, Hu XY, Lin C, Wang L. *J Am Chem Soc*, 2016, 138: 6643–6649
- 32 Gong ZL, Zhong YW. *Sci China Chem*, 2015, 58: 1444–1450
- 33 Gong ZL, Shao JY, Zhong YW. *J Electrochem*, 2016, 22: 244–259
- 34 Jiang X, Zhu N, Zhao D, Ma Y. *Sci China Chem*, 2016, 59: 40–52
- 35 Zhong YW, Gong ZL, Shao JY, Yao J. *Coord Chem Rev*, 2016, 312: 22–40
- 36 Tang JH, Yao CJ, Cui BB, Zhong YW. *Chem Rec*, 2016, 16: 754–767
- 37 Shen JJ, Zhong YW. *Sci Rep*, 2015, 5: 13835–13835
- 38 Kong DD, Xue LS, Jang R, Liu B, Meng XG, Jin S, Ou YP, Hao X, Liu SH. *Chem Eur J*, 2015, 21: 9895–9904
- 39 Zhang J, Zhang MX, Sun CF, Xu M, Hartl F, Yin J, Yu GA, Rao L, Liu SH. *Organometallics*, 2015, 34: 3967–3978
- 40 Zhang DB, Wang JY, Wen HM, Chen ZN. *Organometallics*, 2014, 33: 4738–4746
- 41 Wen HM, Yang Y, Zhou XS, Liu JY, Zhang DB, Chen ZB, Wang JY, Chen ZN, Tian ZQ. *Chem Sci*, 2013, 4: 2471–2477
- 42 Zhang LY, Zhang HX, Ye S, Wen HM, Chen ZN, Osawa M, Uosakic K, Sasaki Y. *Chem Commun*, 2011, 47: 923–925
- 43 Yao CJ, Zhong YW, Yao J. *J Am Chem Soc*, 2011, 133: 15697–15706
- 44 Yao CJ, Zhong YW, Nie HJ, Abruna HD, Yao J. *J Am Chem Soc*, 2011, 133: 20720–20723
- 45 Yao CJ, Nie HJ, Yang WW, Yao J, Zhong YW. *Inorg Chem*, 2015, 54: 4688–4698
- 46 Yao CJ, Yao J, Zhong YW. *Inorg Chem*, 2012, 51: 6259–6263
- 47 Yang WW, Shao JY, Zhong YW. *Eur J Inorg Chem*, 2015, 2015: 3195–3204
- 48 Wang L, Yang WW, Zhong YW, Yao J. *Dalton Trans*, 2013, 42: 5611–5614
- 49 Shao JY, Yang WW, Yao J, Zhong YW. *Inorg Chem*, 2012, 51: 4343–4351
- 50 Ou QP, Xia JL, Zhang J, Xu M, Yin J, Yu GA, Liu SH. *Chem Asian J*, 2013, 8: 2023–2032
- 51 Ou QP, Zhang J, Xu M, Xia JL, Hartl F, Yin J, Yu GA, Liu SH. *Chem Asian J*, 2014, 9: 1152–1160
- 52 Zhang J, Sun CF, Zhang MX, Hartl F, Yin J, Yu GA, Rao L, Liu SH. *Dalton Trans*, 2016, 45: 768–782
- 53 Mondal P, Chatterjee M, Paretzki A, Beyer K, Kaim W, Lahiri GK. *Inorg Chem*, 2016, 55: 3105–3116
- 54 Mondal P, Das A, Lahiri GK. *Inorg Chem*, 2016, 55: 1208–1218
- 55 Shi J, Chai Z, Tang R, Hua J, Li Q, Li Z. *Sci China Chem*, 2015, 58: 1144–1151
- 56 Xiao J, Shi J, Li D, Meng Q. *Sci China Chem*, 2015, 58: 221–238
- 57 Yao CJ, Zheng RH, Shi Q, Zhong YW, Yao J. *Chem Commun*, 2012, 48: 5680–5682
- 58 Cui BB, Yao CJ, Yao J, Zhong YW. *Chem Sci*, 2014, 5: 932–941
- 59 Polit W, Exner T, Wuttke E, Winter RF. *Biolnorg React Mech* 2012, 8: 85–105
- 60 Nie HJ, Shao JY, Yao CJ, Zhong YW. *Chem Commun*, 2014, 50: 10082–10085
- 61 Gong ZL, Zhong YW. *Organometallics*, 2013, 32: 7495–7502
- 62 Gong ZL, Cui BB, Yang WW, Yao J, Zhong YW. *Electrochim Acta*, 2014, 130: 748–753
- 63 Kurita T, Nishimori Y, Toshimitsu F, Muratsugu S, Kume S, Nishihara H. *J Am Chem Soc*, 2010, 132: 4524–4525
- 64 Simao C, Mas-Torrent M, Crivillers N, Lloberas V, Artes JM, Gorostiza P, Veciana J, Rovira C. *Nat Chem*, 2011, 3: 359–364
- 65 Flamigni L, Collin JP, Sauvage JP. *Acc Chem Res*, 2008, 41: 857–871
- 66 Cui BB, Tang JH, Yao J, Zhong YW. *Angew Chem Int Ed*, 2015, 54: 9192–9197
- 67 Tang JH, Shao JY, He YQ, Wu SH, Yao J, Zhong YW. *Chem Eur J*, 2016, 22: 10341–10345
- 68 Yao CJ, Zhong YW, Yao J. *Inorg Chem*, 2013, 52: 4040–4045
- 69 Sun MJ, Nie HJ, Yao JN, Zhong YW. *Chin Chem Lett*, 2015, 26: 649–652
- 70 Grelaud G, Cifuentes MP, Schwich T, Argouarch G, Petrie S, Stranger R, Paul F, Humphrey MG. *Eur J Inorg Chem*, 2012, 2012: 65–75
- 71 Shao JY, Yao CJ, Cui BB, Gong ZL, Zhong YW. *Chin Chem Lett*, 2016, 2016, 27: 1105–1114