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Communication

Synthesis and electrochemical and spectroscopic studies of a *N*,*N*,*N*',*N*'-tetraphenylbenzidine-bridged bis(2,2'-bipyridine) ligand and diruthenium complex

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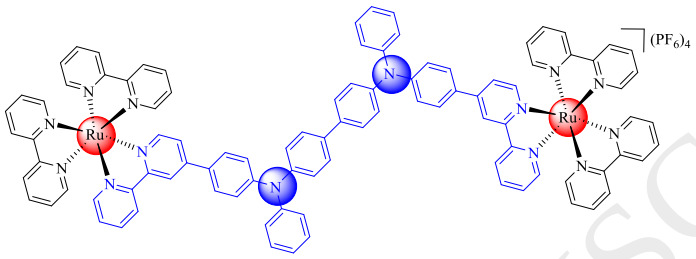
Graphical abstract



A *N*,*N*,*N*',*N*'-tetraphenylbenzidine-bridged bis(2,2'-bipyridine) ligand and corresponding diruthenium complexes were synthesized and characterized. They show rich multistep redox processes due to the stepwise oxidations of the amine units and ruthenium components. Their absorption and emission spectral changes in response to electrochemical stimulus were examined by spectroelectrochemical measurements.

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ABSTRACT

A *N*,*N*,*N*',*N*'-tetraphenylbenzidine-bridged bis(2,2'-bipyridine) ligand and corresponding diruthenium complexes were synthesized and characterized. They show rich multistep redox processes due to the stepwise oxidations of the amine units and ruthenium components. Their absorption and emission spectral changes in response to electrochemical stimulus were examined by spectroelectrochemical measurements. DFT and TDDFT calculations were performed to complement the experimental results.

Polypyridyl transition metal complexes possess appealing electrochemical and photophysical properties. They are widely used in a range of optoelectronic applications, including solar cells [1-3], light-emitting devices [4-6], molecular electronics [7,8], and ion sensing and bioimaging [9-11]. Among them, metal complexes functionalized with additional redox-active organic motifs show multistep redox processes and rich absorption and emission properties. They are particularly useful for electrochromism [12-14], information storage [15], and intelligent materials with multi-stimuli responsiveness [16].

Triarylamines are important molecular materials with good electron-donating and hole-transporting abilities [17-19]. The combination of triarylamine and transition metal complexes has been shown to afford molecular materials with rich redox and photophysical properties [20,21]. Considering the presence of electronic coupling among different structural motifs in these hybrid compounds, it would be interesting to examine the mutual influence of individual components on their optoelectronic properties. We have recently reported a series of metal-amine conjugated complexes which exhibit metal-mediated amine-amine electronic coupling [22,23], amine-mediated metal-metal communication [24], and amine-modified emission properties of ruthenium complexes [25]. In this contribution, a *N*,*N*,*N*',*N*'-tetraphenylbenzidine-bridged bis-bpy (bpy = 2,2'-bipyridine) ligand **3** and the corresponding diruthenium

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