Cyclometalated Ru\textsuperscript{II} Complexes with Improved Octahedral Geometry: Synthesis and Photophysical Properties

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Cyclometalated bis-tridentate ruthenium(II) complexes incorporating 2,6-diquinolin-8-ylpyridine ligands and exhibiting broad visible absorptions are described. A [Ru(N\textsubscript{4}N\textsubscript{4}N\textsubscript{4})(N\textsubscript{4}C\textsubscript{6}N\textsubscript{6})\textsuperscript{2+}] complex based only on ligands with expanded bite angles has a metal-to-ligand charge-transfer excited-state lifetime of 16 ns, which is attributed to a strong ligand field and therefore reduced deactivation via metal-centered states.

Ruthenium(II) poly(pyridyl) complexes continue to be of high interest owing to their remarkable photophysical properties, which are readily tuned by ligand modifications.\textsuperscript{1} Much of this work has involved tris-bidentate Ru\textsuperscript{II} complexes, which usually display a lowest excited state of metal-to-ligand charge-transfer (MLCT) character with lifetimes of around 1 μs. Structurally, however, these complexes are less attractive because they are chiral (A and A isomers) and geometrical isomers may form when they are incorporated in larger multinitrogen assemblies.\textsuperscript{2} The related achiral bis-tridentate complex [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} (tpy = 2,2\textsuperscript{′},6\textsuperscript{′}-terpyridine), in contrast, allows by virtue of its C\textsubscript{2} axis the facile preparation of linear multicomponent assemblies.\textsuperscript{3} However, the complex exhibits a short MLCT excited-state lifetime (0.25 ns),\textsuperscript{4} which has restricted its use. This is due to the efficient thermal population of metal-centered (MC) states, leading to rapid nonradiative decay, which has been attributed to the unfavorable bite angles of the tridentate ligands and therefore a weak ligand field.\textsuperscript{5}

Several strategies to increase the excited-state lifetimes have been reported,\textsuperscript{6} where a few approaches specifically aim at destabilizing the MC states. These include the use of 2,6-diquinolin-8-ylpyridine (dqp) ligands, which give improved octahedral geometries (Figure 1),\textsuperscript{7} or the use of strong-field cyclometalating ligands.\textsuperscript{8} The former approach has resulted in bis-tridentate Ru\textsuperscript{II} complexes that exhibit microsecond \textsuperscript{3}MLCT excited-state lifetimes,\textsuperscript{7} while the latter strategy has led to the recent development of a new class of sensitizers that show broad absorptions over much of the visible region for dye-sensitized solar cells.\textsuperscript{9} The anionic carbon significantly changes the electronic properties of the ligand, leading to both red-shifted absorptions and an increase of the excited-state lifetime by 1 order of magnitude compared to [Ru(tpy)]\textsuperscript{2+}. The excited-state decay in these N\textsubscript{4}N\textsubscript{6}C complexes has been attributed to a balance between activated decay via \textsuperscript{3}MC states and nonradiative decay governed by the energy gap law.\textsuperscript{10} Given the established effect on the \textsuperscript{3}MC states of the dqp ligands due to more octahedral coordination,\textsuperscript{7} we were interested in the effect of an N\textsubscript{4}C\textsubscript{6}N\textsubscript{4} donor set on the photophysical properties using these ligands (Figure 1), the first results of which are presented herein.


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The heteroleptic complexes 1 and 2 (Scheme 1) consist of one dqp ligand and a cyclometalating ligand, 1,3-dipyrind-2-yl-4,6-dimethylbenzene (dpyxH) and 1,3-diquinolin-8-ylbenzene (dqbH), respectively. The ligand dpyxH was prepared as reported previously, while dqbH was conveniently synthesized via Suzuki–Miyaura coupling of quinolin-8-ylboronic acid and 1,3-dibromobenzene using the previously reported protocol.

The synthesis of the cyclometalated RuII complexes was based on the initial coordination of dqp to RuCl3·H2O and the subsequent isolation of well-characterized mer-[Ru(dqp)-(MeCN)3]2+ (3). Reacting 3 with dpyxH in refluxing n-BuOH for 3.5 h gave complex 1 in 56% isolated yield as a dark-green solid (Scheme 1). In contrast, complex 2 required much longer reaction times under the same conditions. Following the reaction over time (liquid chromatography—mass spectrometry) showed the slow formation of 2, and even after 2 days of reflux, only low yields (19%) were obtained. Instead, complex 2 was conveniently prepared in ethylene glycol at 196 °C using microwave heating (1.5 h) to give the desired complex as a dark-purple solid in 57% isolated yield. The difference in the relative rates of formation of 1 and 2 in refluxing n-BuOH, the same conditions as those successfully used for the related N6 bis-dqp complexes, can be attributed to the lack of a central pyridyl unit in dqbH. In contrast to the lack of any downfield shifts characteristic for a dional complex. This is further supported by the X-ray structure of 2.

X-ray crystal analysis of 1 and 2 confirmed meridional coordination of the tridentate ligands (Figures 2 and 3). Complex 1 shows the expected nonideal bite angle of the cyclometalated dpyx ligand [159.0(3)°] with coplanar arrangement of the benzene and pyridyl units (Figure 2). The Ru1–N1 and Ru1–C19 bond lengths are within the expected range for such ligands. In contrast, the dqp ligand adopts a helical conformation with a close to ideal bite angle [179.6(2)°], similar to that observed for other RuII complexes containing the dqp ligand (N–Ru–N bite angles ∼ 178–180° and dihedral angles ∼ 35–40°). However, the Ru1–N1 bond length in 1 is considerably longer [2.150(6) Å] than what has previously been observed as a result of the trans influence of the anionic donor.

In complex 2, both tridentate ligands show almost ideal bite angles (Figure 3). As has been noted previously for [Ru(dap)(dpy)]2+, both ligands adopt the same helical arrangements (λ,δ or δ,δ), resulting in an almost coplanar arrangement of
quinoxaline pairs. The dihedral angles and the bond lengths for the tridentate ligands are similar to those found for the dqp ligand in complex 1, with an elongated Ru–N pyridyl distance [2.087(5) Å] due to the trans influence of the anionic carbon.

The redox properties were studied by cyclic voltammetry, which showed reversible metal-based oxidations (RuIII/II) at −0.05 and −0.08 V (vs Fc) for 1 and 2, respectively. These are cathodically shifted by approximately 0.8 V as a result of the paramagnetic RuII species. For the NMR green impurity in thin-layer chromatography and broad signals in NMR for the metal oxidation and first ligand reduction, agrees well with the finding that the difference in the potential which showed reversible metal-based oxidations (RuIII/II) at carbon.

The absorption spectra show intense ligand-centered (LC) transitions in the UV region and broad MLCT transitions in the visible region, even broader than those observed for related N2C complexes. Combined with the preferred geometries and nanosecond excited-state lifetimes, the favorable absorption chromophores for a multitude of applications.

The absorption spectra show intense ligand-centered (LC) transitions in the UV region and broad MLCT transitions in the visible region, the latter extending beyond ~750 nm, which is more bathochromically shifted than is usually observed for these types of RuII complexes (Figure 4). This agrees well with the finding that the difference in the potential for the metal oxidation and first ligand reduction, ΔE1/2, is somewhat smaller for dqp-based complexes than for normal ruthenium(II) polypyridyl complexes. Notably, complex 1 exhibits two distinct absorption maxima, tentatively attributed to MLCT transitions involving the cyclometalated (high-energy) and noncyclometalated ligands, while 2 features a single broad band that extends from 400 to ~750 nm.

Both complexes are practically nonluminescent at room temperature, and the excited-state lifetimes were therefore determined by transient absorption spectroscopy, which showed monoeponential ground-state recoveries with τ = 1.8 and 16 ns for 1 and 2, respectively (see the Supporting Information). Both complexes display structured emission at 77 K with spectral shapes typical for ruthenium(II) polypyridyl complexes (Figure 4). The luminescence maxima are similar, 830 and 824 nm for 1 and 2, respectively. The similar behavior for 1 and 2 can be attributed to the lowest excited states involved, both originating from a dqp-based 3MLCT state.

The 3MLCT lifetime of 1 is somewhat shorter than that for the analogous tpy-based [Ru(Me-tpy)(dpb)]2+ (dpb = 1,3-pyrid-2-ylbenzene) complex (4.0 ns), which is probably due to its lower 3MLCT energy and increased nonradiative decay according to the energy gap law. The more octahedral complex 2, however, has almost the same 3MLCT energy as 1 but shows a longer lifetime. Because the chromophoric ligand is the same (with the same degree of emission spectral distortion, electronic coupling, etc.), we tentatively attribute this to a stronger ligand field in 2.

In summary, RuII complexes 1 and 2 are the first reported examples where dqp ligands with a close to 180° bite angle have been combined with tridentate ligands with an N2C donor set. The strong donor set in these complexes leads to broad and intense absorptions over much of the visible region, even broader than those observed for related N2C complexes. Combined with the preferred geometries and nanosecond excited-state lifetimes, the favorable absorption properties render these types of complexes as promising new chromophores for a multitude of applications.

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Supporting Information Available: Synthetic details, X-ray crystal data, COSY spectra, cyclic voltammograms, transient absorption traces for 1 and 2, and references. This material is available free of charge via the Internet at http://pubs.acs.org.

(12) Complex 2 is slowly oxidized when exposed to air, as indicated by a green impurity in thin-layer chromatography and broad signals in NMR ascribed to the presence of the paramagnetic RuIII species. For the NMR experiment, this was conveniently suppressed by the addition of a small amount of NaBH4.

(13) Complex 2 shows a very weak emission above 800 nm that was not quantified.