

A 3.0 μs Room Temperature Excited State Lifetime of a Bistridentate Ru^{II}–Polypyridine Complex for Rod-like Molecular Arrays

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Light-induced electron and energy transfer in molecular arrays is being extensively studied in view of artificial photosynthesis¹ and molecular electronics.² The ideal photosensitizer for this purpose should have an excited state with high energy and sufficiently long lifetime to promote the desired electron and/or energy transfer processes. In this context, [Ru(bpy)₃]²⁺ derivatives (bpy = 2,2'-bipyridine) have been widely used due to the favorable properties of their lowest excited triplet metal-to-ligand charge transfer (³MLCT) state, including room temperature ³MLCT lifetimes up to 1 μs , high emission quantum yields, and strong oxidizing and reducing capability.³ In tris(diimine)-based donor–chromophore–acceptor assemblies, however, different isomers are formed in most cases, which precludes the desired vectorial electron transfer and complicates kinetic analyses.⁴ In contrast, the achiral [Ru(tpy)₂]²⁺ complex (tpy = 2,2':6',2''-terpyridine) gives rod-like donor–photosensitizer–acceptor assemblies when substituted at the 4'-position of the tpy ligands, but the complex is practically nonluminescent at room temperature and its short excited state lifetime ($\tau = 0.25$ ns)⁵ limits its use as a photosensitizer. The short lifetime is due to deactivation via short-lived metal-centered (³MC) states that are thermally populated from the ³MLCT state.^{3,5} Recent strategies to prolong the excited state lifetime of bistridentate Ru^{II} complexes include modified tpy ligands to increase the energy gap between the ³MLCT and ³MC states.⁵ However, this approach often results in a substantial decrease in ³MLCT energy that makes these chromophores less useful in photosensitizer applications. An alternative strategy is to increase the ligand field, and thus the energy of the ³MC states, by making the complex more octahedral. With the insertion of a methylene group between two pyridines in a tpy ligand, six-membered chelates may be formed. Following this strategy, we recently reported a Ru^{II}–bistridentate complex with a much longer excited state lifetime ($\tau = 15$ ns in CH₃CN) than that in [Ru(tpy)₂]²⁺ without any substantial decrease in excited state energy.⁶

Herein, we report a new, near octahedral bistridentate Ru^{II} complex involving *only* six-membered chelates, based on the 2,6-bis(8'-quinoliny)pyridine ligand, **bqp**. The structure is particularly attractive as it leaves the 4-positions of the central pyridines available for future preparation of linear donor–chromophore–acceptor assemblies for vectorial electron migration. Because of the strong ligand field, its ³MLCT state lifetime at room temperature is dramatically increased and is even longer than the 1 μs observed for the pivotal [Ru(bpy)₃]²⁺.

Complex **1** (Figure 1) was designed to fulfill the criteria of octahedral coordination and to have a near C₂-axis for substitution

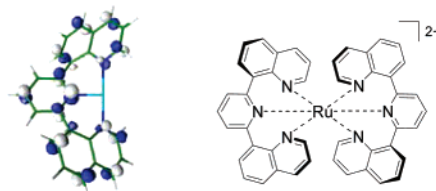


Figure 1. Left: Distribution of LUMO over one of the ligands (the rest of the complex was omitted for clarity). Right: The structure of **1**.

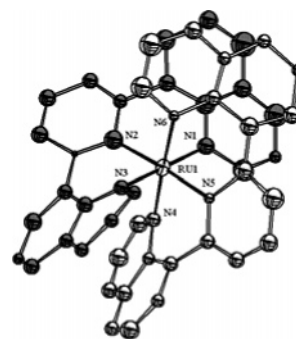


Figure 2. Thermal ellipsoid view of **1** (50% probability, 100 K).

of donor and acceptor units. First, DFT calculations with the Gaussian03 program package,⁷ employing the B3LYP⁸ exchange correlation functional together with the LANL2DZ⁹ effective core potential and accompanying basis set (B3LYP/LANL2DZ), were used to optimize the singlet geometry of the complex. Selected bond lengths and angles are given in Table S1. The optimized geometry indeed suggests a more octahedral coordination than in [Ru(tpy)₂]²⁺, with N1–Ru–N3 bite angles of 179.6° as compared to the experimental value of 158.4° in [Ru(tpy)₂]²⁺.¹⁰

Following the calculations, the 2,6-bis(8'-quinoliny)pyridine ligand **bqp** was synthesized in 80% yield via the Suzuki–Miyaura coupling reaction of quinoline-8-boronic acid and 2,6-dibromopyridine following the procedures developed by Buchwald and co-workers.¹¹ The coupling reaction works well also for various 4-substituted 2,6-dihalopyridines, which is essential in the preparation of linear assemblies and will be reported in due course. Using microwave heating, complex **1** was subsequently prepared in 87% yield from Ru(DMSO)₄Cl₂ and 2 equiv of **bqp** in ethylene glycol at 196 °C.

The complex was characterized by ¹H NMR, ESI mass spectrometry, and elemental analysis, which were in accordance with the assigned structure (see Supporting Information). The X-ray crystal structure of complex **1** is shown in Figure 2, and selected bond lengths and bond angles are given in Table S1. A twisted arrangement is evident, with dihedral angles of approximately 35

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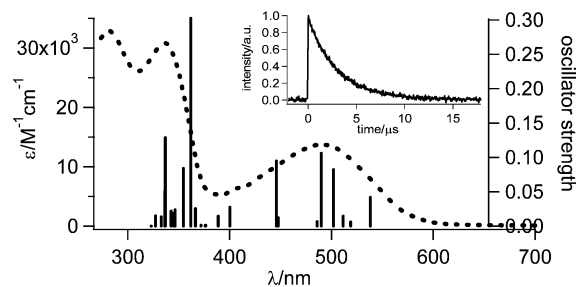


Figure 3. Calculated (bars; EtOH) and experimental (dotted; acetonitrile) UV-vis electronic spectrum of **1**. Inset: Emission decay trace at room temperature in oxygen-free MeOH:EtOH.

Table 1. Emission Properties of **1** in Ar-Purged MeOH:EtOH

	1		[Ru(tpy) ₂] ²⁺ ^a	
	298 K	77 K	298 K	77 K
$\tau_{em}/\mu s$	3.0	8.5	2.5×10^{-4}	11
Φ_{em}	0.02	0.06		0.48
λ_{em}^{max}	700	673		598

^a See ref 6b.

and 39° between the quinolines and central pyridine ring systems of each tridentate ligand. The determined bite angles are 177.6(7)° for both ligands, which is close to the calculated value. Most importantly, in contrast to the parent [Ru(tpy)₂]²⁺, the geometry around the ruthenium ion in **1** is very close to octahedral as a result of the larger bite angles of the **bqp** ligand.

Electrochemical measurements show a reversible Ru^{III/II} redox couple at $E_{1/2} = 0.71$ V vs Fc⁺⁰, which is lower than that in [Ru(tpy)₂]²⁺ ($E_{1/2} = 0.92$ V).^{6b} The first ligand-based reduction is reversible and occurs at -1.70 V, which is also lower than that in [Ru(tpy)₂]²⁺ ($E_{1/2} = -1.62$ V).^{6b}

The calculations confirm that HOMO is metal-centered, while LUMO and LUMO+1 are both ligand-centered orbitals, leading to a lowest excited state with MLCT character. The B3LYP/LANL2DZ time-dependent DFT¹² calculation of excitations in ethanol, simulated using the PCM model,¹³ reveals a close similarity to the experimentally observed absorption spectrum (Figure 3). The broad absorption feature between 400 and 600 nm is attributed to the lowest ¹MLCT transitions ($\lambda_{abs}^{max} = 490$ nm; $\epsilon = 1.4 \times 10^4$ M⁻¹cm⁻¹). The higher energy bands are mostly due to ligand-centered transitions.

The emission properties of complex **1** are summarized in Table 1. The observed excited state lifetime at room temperature in oxygen-free EtOH:MeOH solution is 3.0 μ s, as shown by both time-resolved emission (Figure 3, inset) and transient absorption experiments. This is, to the best of our knowledge, the longest MLCT state lifetime reported for a Ru^{II}-polypyridyl complex at room temperature.^{14–16} The long excited state lifetime can be rationalized by the more octahedral coordination around the ruthenium core as shown by the X-ray crystal structure and calculations, which raises the energy of the short-lived ³MC states. The small difference in lifetime between 298 and 77 K is in sharp contrast to typical bistridentate Ru^{II} complexes and confirms that activated decay via ³MC states is not a very prominent decay pathway. Preliminary temperature-dependent lifetime measurements up to 363 K allows us to put a lower limit on the activation energy for population of

the ³MC states as high as $E_a = 4800$ cm⁻¹.¹⁷ This is a dramatic increase compared to $E_a = 1500$ cm⁻¹ for [Ru(tpy)₂]²⁺,¹⁸ and allows for the long lifetime of **1**.

The complex has a strong absorption in the visible region, an excited ³MLCT state energy of 1.84 eV, good redox properties, and it allows for symmetric substitution on the central pyridines. Thus, with a 3.0 μ s excited state lifetime at room temperature, our new bistridentate Ru^{II} complex **1** is a promising candidate for the construction of rod-like, photoactive molecular assemblies.

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Supporting Information Available: Synthetic, experimental, and computational details, complete ref 7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) The free **bqp** ligand and the in situ prepared [Zn(**bqp**)₂]²⁺ complex exhibited emission at much shorter wavelengths (Supporting Information), showing that the emission in **1** is not due to a ligand-centered state.
- (15) (a) A room temperature emission lifetime in acetonitrile of 0.82 μ s was recently reported for a bistridentate Ru^{II}-carbene complex which was attributed to a MLCT state (ref 15b). The authors, however, also reported that the emission lifetime was longer in water (3.1 μ s), which is in contrast to both theoretical expectations and experimental results for Ru^{II} complexes. A peculiar emission rise-time of a few hundred nanoseconds was present in their water data but not explained, which suggests that this particular result should be taken with caution. (b) Son, S. U.; Park, K. H.; Lee, Y.-S.; Kim, B. Y.; Choi, C. H.; Lah, M. S.; Jang, Y. H.; Jang, D.-J.; Chung, Y. K. *Inorg. Chem.* **2004**, *43*, 6896–6898.
- (16) (a) This is in contrast to bichromophoric systems with a low energy organic π - π^* triplet state serving as reservoir (see e.g. ref 16b). Although the observed Ru MLCT emission decays more slowly due to repopulation from the π - π^* state, the emission and chemical reaction yields of the MLCT state are not increased. (b) Wang, X.; Del Guerzo, A.; Schmehl, R. H. *J. Photochem Photobiol. C* **2004**, *5*, 55–77.
- (17) With an observed lifetime of 1.2 μ s at 363 K, and a frequency factor for crossing to the ³MC states of at least 5×10^{12} s⁻¹, E_a must be >4800 cm⁻¹.
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