Supramolecular Control of Chloride Photorelease

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Supporting Information Placeholder

ABSTRACT: Supramolecular assembly is shown to provide control over excited-state (ES) chloride release. Two chromophores were designed with a ligand that recognizes halide ion and a luminescent ES whose dipole was directed toward or away from an associated chloride ion. The dipole orientation had little influence on the ground-state equilibrium constant, but induced a profound change in the ES equilibrium. Light excitation of $[\mathbf{1}^{2+}, \mathbf{Cl}^-]^+$ resulted in time dependent shifts in the photoluminescence spectra with the appearance of bi-exponential kinetics consistent with the photorelease of Cl^-. The ES equilibrium constant was lowered by a factor of 20, and resulted in nearly 45% dissociation of chloride. In contrast, light excitation of $[\mathbf{2}^{2+}, \mathbf{Cl}^-]^+$ revealed a 45 fold increase in the ES equilibrium constant. The data show that rational design and supramolecular assembly enables the detection and photorelease of chloride ions with the potential for future applications in biology and chemistry.

The important role halide ions play in chemistry and biology has inspired research into halide sensing.[1–10] The contactless nature of luminescent sensors is particularly attractive for fundamental study and has led to the rational design of chromophores that specifically recognize halides. Amides and functional groups capable of H-bonding have, in particular, been shown to recognize halide ions present in solution.[11–13] Herein two chromophores with a common ligand for halide coordination and a net charge of 2^+ for electrostatic attraction have been exploited for supramolecular association with chloride. The chromophores shown in **Figure 1** include another important design element: the orientation of the excited-state dipole. In chromophore $\mathbf{1}^{2+}$ the metal-to-ligand charge transfer (MLCT) excited state dipole is directed toward the halide binding site, while for $\mathbf{2}^{2+}$ it is directed away. This orientation had no significant influence on ground-state halide association, but did have a profound influence on the photoluminescence of both excited states. In the case of $\mathbf{1}^{2+}$, the excited-state equilibrium constant for chloride association was 20 times smaller than that of the ground state, and light excitation of the adduct $[\mathbf{1}^{2+}, Cl^-]^+$ resulted in photorelease of the chloride ion. In the case of $\mathbf{2}^{2+}$, no evidence for chloride release was observed but rather a 45-fold increase in the equilibrium constant was determined through the Förster cycle. Hence, supramolecular assembly can be utilized to recognize and photorelease chloride, behavior that may one day enable additional applications such as quantifying halide transport across artificial and natural membranes relevant to sea water desalination and cystic fibrosis related diseases.[14–16]

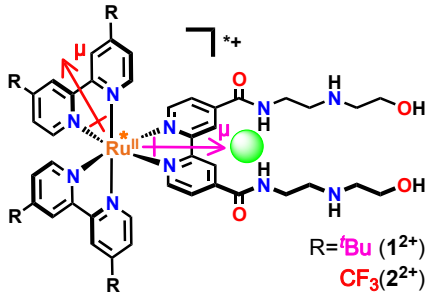

Figure 1. Proposed supramolecular assembly structure of $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$ and chloride (green sphere). The dipole orientation is indicated for the excited-state of $\mathbf{1}^{2+}$ (pink) and for $\mathbf{2}^{2+}$ (red).

The diamide ligand for halide recognition shown in **Figure 1** is abbreviated **daea** and was synthesized by refluxing 4,4'-dimethylester-2,2'-bipyridine in the presence of a large excess of 2-[(2-aminoethyl)amino]ethanol in methanol for 4h. Microwave irradiation of this ligand with $Ru(dtb)_2Cl_2$ (dtb = 4,4'-di-tert-butyl-2,2'-bipyridine) in H_2O gave complex $\mathbf{1}^{2+}$ that was further isolated as the PF_6 salt. Complex $\mathbf{2}^{2+}$ was obtained by refluxing the **daea** ligand with $Ru(btfmb)_2Cl_2$ (btfmb = 4,4'-bis(trifluoromethyl)-2,2'-bipyridine) and silver nitrate in H_2O:MeOH (1:1) for 5h. Ion metathesis was finally performed to obtain $\mathbf{2}^{2+}$ as a $B(ArF)_4$ salt. (See S.I. and Figure **S1**-**S6**) All subsequent experiments were performed in CH_2Cl_2. Square wave voltammetry was used to determine the $Ru^{III/II}$ and ligand based reduction potentials. Due to the electron withdrawing **btfmb** ligand, the $Ru^{III/II}$ potential of $\mathbf{2}^{2+}$ was found to be 410 mV more positive than that of $\mathbf{1}^{2+}$, and the first ligand based reduction potentials were -880 mV and -470 mV vs NHE for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively (**Figure S7**).

The use of ^{1}H NMR spectroscopy provided insights into the coordination environment of the chloride ions. Anions are known to affect the local magnetic environment of neighboring nuclei, such that the chemical shift can report on the specific location of a halide ion.[17–20] Tetrabutylammonium chloride titrations into solutions of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ showed that the 3,3' protons on the **daea** ligand, as well as the amide protons, displayed significant downfield shifts, while the other resonances remained unchanged (**Figure S8 and S9**). These downfield shifts saturated after one equivalent of chloride was added, pointing towards a one-to-one stoichiometry. The ^{1}H NMR

data indicates that a single chloride ion binds to the two amide groups and the acidic H atoms of the bipyridine ligand, behavior that has been observed for halide self-assembly to related chromophores.[19]

The UV-Visible absorption spectra of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ in CH_2Cl_2 were typical of ruthenium polypyridyl complexes (**Figure 2**). The broad absorption from 400 to 500 nm was ascribed to metal-to-ligand charge-transfer (MLCT) transitions, while the features at or below 300 nm were assigned to ligand centered π to π* transitions. Upon absorption of visible light, both complexes displayed room temperature photoluminescence (PL) with maxima at 665 and 600 nm for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively.

Table 1. Photophysical Properties of Complexes $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and their chloride-ion-paired analogues in CH_2Cl_2.

	λ_{max} (nm)		τ (μs)	ϕ_{PL}	k_r	k_{nr}
	Abs	PL			(×10⁴ s⁻¹)	(×10⁵ s⁻¹)
$\mathbf{1}^{2+}$	474	665	1.18	0.061	5.2	8.0
$[\mathbf{1}^{2+},Cl^-]$	471	640	1.33	0.12	6.8	4.80
$\mathbf{2}^{2+}$	459	600	1.36	0.095	7.0	6.7
$[\mathbf{2}^{2+},Cl^-]$	469	630	1.78[a]	-b	-b	-b

[a]Estimated from the time-resolved PL of $\mathbf{2}^{2+}$ at one equivalent of chloride. [b]Unable to be determined due to precipitation of the complex at high chloride concentrations.

Chloride titration into solutions of $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$ induced significant spectral shifts in the MLCT absorption band that saturated after about one equivalent, consistent with strong ion-pairing of chloride, **Figure 2**. A Benesi-Hildebrand analysis revealed a large equilibrium constant of 5.1×10^5 M^{-1} for $\mathbf{1}^{2+}$ (**Figure S10**).[18,21] An accurate K_{eq} determination for $\mathbf{2}^{2+}$ was hindered by precipitation of the chromophore at high chloride concentrations, however the absorption changes over the chloride concentration allowed were in good agreement with that of $\mathbf{1}^{2+}$ from which a value of 5×10^5 M^{-1} was estimated (**Figure S11**).

The steady state PL spectra also shifted in energy as chloride was titrated into the solution. In the case of $\mathbf{1}^{2+}$*, the PL maximum blue-shifted and increased in intensity with increased Cl^- concentrations to about one equivalent. Previous reports have attributed related excited state interactions to halide-induced planarization of the two pyridyl rings.[22,23] For $\mathbf{2}^{2+}$*, the excited-state was localized on the **btfmb** ancillary ligand (as discussed below), and a red-shift in the PL was observed upon chloride titration. The red-shift was accompanied by a change in the PL intensity, but precipitation at higher chloride concentrations precluded a more detailed analysis.

The fact that the supramolecular assembly of chloride ions caused a PL blue-shift for $\mathbf{1}^{2+}$* and a PL red-shift for $\mathbf{1}^{2+}$* can be understood based on the location of the associated halide ion relative to the excited-state dipole. For this class of chromophores, Blakley and De Armond have shown that the charge transfer dipole is directed toward the ligand that is most easily reduced.[24] The first reduction potential of $\mathbf{1}^{2+}$ is -880 mV vs. NHE, which compares favorably to that of the related $[Ru(bpy\text{-}CONHEt)_3]^{2+}$ (-880 mV vs NHE),[25] but not that of $[Ru(dtb)_3]^{2+}$ (-1000 mV).[26] Therefore, in $\mathbf{1}^{2+}$ the excited-state dipole is directed toward the **daea** ligand, and the luminescent excited-state was well formulated as $[Ru^{III}(daea^-)(dtb)_2]^{2+}$*, with the dipole directed toward the halide binding site. Hence halide self-assembly in the excited state is formally described with an anionic ligand that destabilizes the excited-state resulting in a blue-shift.

In contrast, the electron withdrawing groups in $\mathbf{2}^{2+}$ lower the reduction potential to -470 mV, that compares reasonably with the -530 mV first reduction of $[Ru(btfmb)_3]^{2+}$.[27] The excited-state of $\mathbf{2}^{2+}$ is hence well formulated as $[Ru^{III}(daea)(btfmb^-)(btfmb)]^{2+}$* Halide supramolecular assembly is to a ligand that is not directly aligned with the charge transfer dipole that stabilizes the excited-state resulting in a red-shifted PL spectrum.

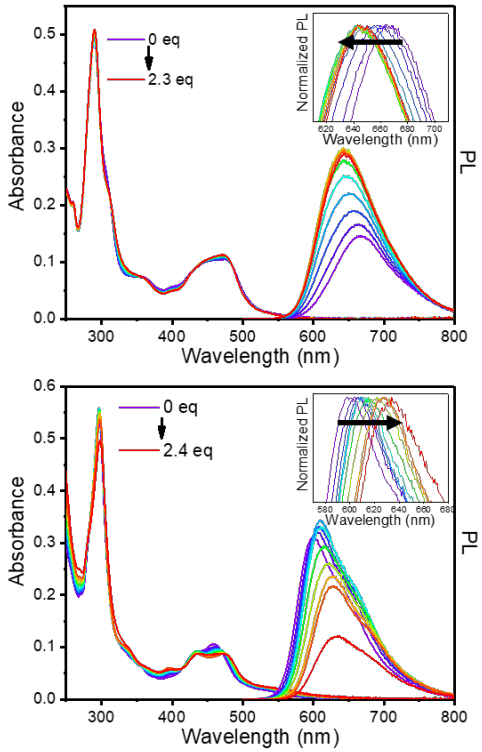

Figure 2. Absorption and PL changes of $\mathbf{1}^{2+}$ (top) and $\mathbf{2}^{2+}$ (bottom) upon titration of chloride from 0 to 2.3/2.4 equivalents in CH_2Cl_2. Inset shows the normalized PL shifts upon titration of chloride.

Pulsed light excitation provided photoluminescence decays that were well described by a first-order kinetic model and yielded lifetimes of τ = 1.18 μs and 1.37 μs for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively. Chloride titration studies with $\mathbf{1}^{2+}$, led to the appearance of bi-exponential kinetics (**Figure S12 and S13**). At large chloride concentrations, a single exponential decay was again recovered with a τ = 1.33 μs. Quantum yield measurements performed in the absence and presence of excess chloride allowed the radiative and non-radiative rate constants for excited state decay to be determined, **Table 1**. This analysis revealed that the increased lifetime and PL intensity associated with Cl- assembly to $\mathbf{1}^{2+}$, resulted from an ~ two-fold change in the non-radiative rate constant. The analogous titration study with $\mathbf{2}^{2+}$ was frustrated by precipitation, however no evidence for bi-exponential excited state relaxation was observed.

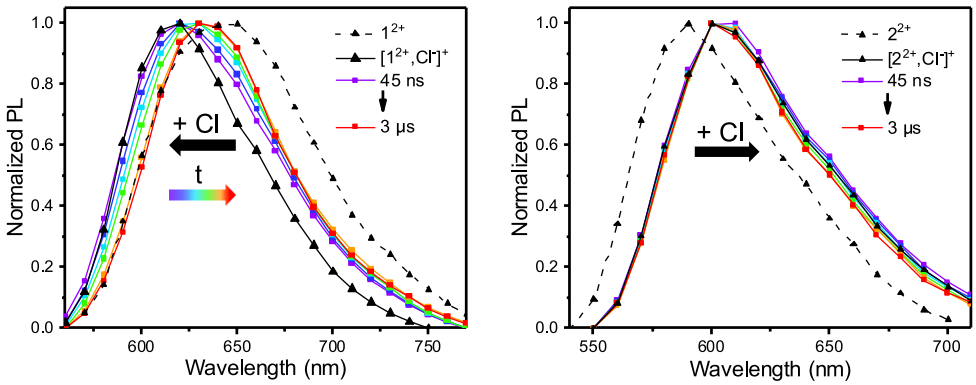

Figure 3. Transient photoluminescence spectra obtained 45 ns (purple square) and at longer (purple to red) time delays after pulsed 500 nm laser excitation of $[Ru(dtb)_2(daea)]^{2+}$, $\mathbf{1}^{2+}$ (left) and $[Ru(btfmb)_2(daea)]^{2+}$, $\mathbf{2}^{2+}$ (right) in the presence of one equivalent of chloride. The photoluminescence spectra of the non-ion-paired complexes is also given for reference (Black triangle, dashed lined). The bold black arrow indicated the spectral shift expected for chloride self-assembly. The colored arrow indicates the time dependent spectral shift.

The PL spectrum recorded at fixed delay times after pulsed light excitation were measured and found to be very informative. Representative data are shown in **Figure 3** for $\mathbf{1}^{2+}$ with one equivalent of chloride, abbreviated $[\mathbf{1}^{2+},Cl^-]^+$.

The PL spectrum measured 3 µs after excitation was considerably red shifted from that measured at a 45 ns delay time. Spectra recorded at intermediate times showed a continuous spectral shift to lower energy. This transient data is consistent with light excitation resulting in Cl^- release followed by re-equilibration. For $\mathbf{2}^{2+}$, the addition of chloride did not affect the time-resolved PL, which was well described by a first order kinetic model throughout the titration. Transient PL experiments of $\mathbf{2}^{2+}$ with an equivalent of chloride did not show any time-dependent color change. It should be noted that the PL spectra measured in these transient experiments were different from the steady state spectral data in **Table 1** and **Figure 2** that were corrected for the fluorimeter spectral response.

A square scheme with ground and excited state equilibrium is proposed like those commonly used to understand photoacid/base chemistry, **Figure 4**.[23,28–31] The ground state equilibrium is associated with the excited state equilibrium through light absorption to yield the thermally equilibrated photoluminescent excited-state. The differential rate equations for the two excited-state species A* and B*, where A is either $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$ and B is either $[\mathbf{1}^{2+},Cl^-]^+$ or $[\mathbf{2}^{2+},Cl^-]^+$, are given in equations 1 and 2. The analytical solutions for these equations have been derived elsewhere[28–30] and were used to fit the experimental data. An interesting point is that the rate constants extracted from a bi-exponential fit do not correspond to relaxation of the two excited states present (i.e. k_1 and k_2), but rather report on the entire equilibrium system and hence provide the excited state equilibrium constant, K^*_{eq}.

$$\frac{d[A*]}{dt} = -(k_{12} + k_1)[A^*] + (k_{21})[B^*] \quad (1)$$

$$\frac{d[B*]}{dt} = -(k_{21} + k_2)[B^*] + (k_{12})[A^*] \quad (2)$$

Application of this kinetic analysis to $\mathbf{1}^{2+*}$ gave the forward ($k_{12} = 5.60\times10^{10}$ M^{-1} s^{-1}) and reverse ($k^{21} = 2.46\times10^{6}$ s^{-1}) rate constants that corresponds to $K^*_{eq} = 2.3\times10^4$ M^{-1} which differs from that of the ground state by a factor of 20 ($K_{eq} = 5.1\times10^5$ M^{-1}).

It should be emphasized that this analysis is for the thermally equilibrated excited state, and the rate constant for chloride dissociation in the initially formed Franck-Condon excited-state may be much larger as relaxation back to the luminescent excited state occurs with the transfer of considerable electron density from the **daea** ligand back to the metal. The kinetic data is nevertheless important for understanding the behavior of the luminescent excited state. For example, 500 ns after photoexcitation of $[\mathbf{1}^{2+},Cl^-]^+$ about 45% of the excited states have dissociated chloride (**Figure S14**).

Complex $[\mathbf{2}^{2+},Cl^-]^+$ displayed remarkably different excited state behavior than $[\mathbf{1}^{2+},Cl^-]^+$. In the time-resolved PL, the decay kinetics remained first-order even after the addition of chloride. Also, photoexcitation of the ion-paired complex did not result in time dependent shifts in the PL spectra. Nonetheless, in regards to the red-shift of the photoluminescence between $\mathbf{2}^{2+}$ and $[\mathbf{2}^{2+},Cl^-]^+$, an increased binding constant is expected. This was confirmed through Förster cycle analysis that showed a 45-fold increase in the excited-state equilibrium constant (**Table 2**).

Table 2: Equilibrium constants for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ with chloride in the ground and excited-state.

	K_{eq} (M^{-1})	K_{eq}* (M^{-1})	k_{12} (10^{10} M^{-1} s^{-1})	k_{21} (10^6 s^{-1})
$[\mathbf{1}^{2+},Cl^-]^+$	5.1×10^5	2.3×10^4	5.60	2.46
$[\mathbf{2}^{2+},Cl^-]^+$	5×10^5	2×10^7 [a]	[b]	[b]

[a]Estimated using a Förster cycle. [b]There was no spectroscopic evidence for differing ground and excited state equilibrium, precluding kinetic analysis.

The supramolecular assembly of chloride ions resulted in excited states that either retained, $[\mathbf{2}^{2+},Cl^-]^{+*}$, or released, $[\mathbf{1}^{2+},Cl^-]^{+*}$, chloride ions. The former are useful for chloride sensing,[1,2,12,13] while the latter may be exploited for delivery.[32–37] The current state-of-the-art for light induced release of halide ions are non-luminescent Pt^{IV} complexes.[38] For example, ultraviolet or d-d excitation of $PtBr_6^{2-}$ in water results in Br^- release in good yield.[39–42] Illumination of $PtCl_6^{2-}$ also gave the aquation product and free Cl^-, but the mechanism was complicated by additional redox chemistry.[43,44]

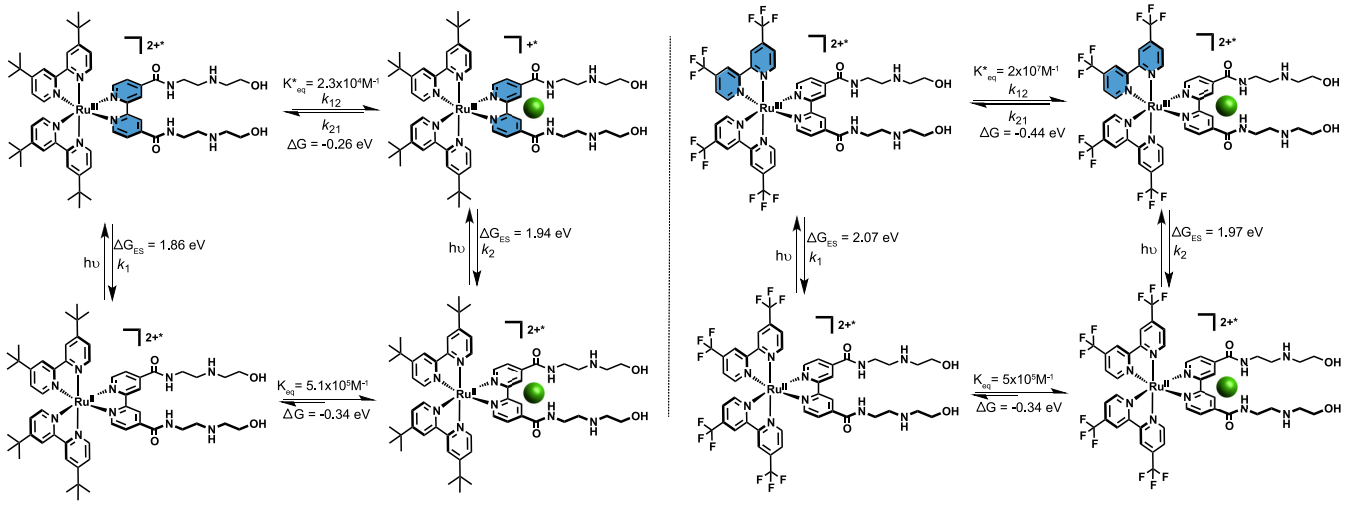

Figure 4. Square Scheme for ground and excited-state equilibria of $[Ru(dtb)_2(daea)]^{2+}$, $\mathbf{1}^{2+}$ (left) and $[Ru(btfmb)_2(daea)]^{2+}$, $\mathbf{2}^{2+}$ (right) in the presence of chloride. Förster cycle analysis was used to calculate K^*_{eq} for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. The calculated K^*_{eq} for $\mathbf{1}^{2+}$ is consistent with the kinetic analysis from the square scheme.

In both cases, a large excess of halide was necessary to restore the initial platinum complex. The photo-release described here has the advantage of rapid release of Cl- in about 150 ns. The self-assembly of the photo-released Cl- was advantageous for signal averaging with pulsed lasers, but is not ideal for many other applications. For biological and desalination applications,[14–16] halide self-assembly must occur in water where irreversible release may be desired. The supramolecular assembly described here takes advantage of the Coulombic attraction of the dication chromophore and the halide anion, as well as the H-bonding properties of the daea ligand. The low dielectric constant of the organic solvent utilized here enhances the Coulombic attraction, and for application in aqueous environments, the halide recognition ability of the ligand would require enhancement. The difference in ground and excited state equilibrium constants combined with advances in halide sensing in water,[1] suggests that fine tuning can be realized.

In conclusion, two ruthenium chromophores, $[Ru(dtb)_2(daea)]^{2+}$ ($\mathbf{1}^{2+}$) and $[Ru(btfmb)_2(daea)]_{2+}$ ($\mathbf{2}^{2+}$), exhibited very different excited state behaviors in the supramolecular assembly with chloride. When the excited state dipole was directed away from the daea halide receptor ligand, as was the case for $[\mathbf{2}^{2+},Cl^-]^+$, the equilibrium constant for chloride assembly in the excited state was greater than in the ground state. In dramatic contrast, when the excited state dipole was oriented toward the chloride anion, as was the case for $[\mathbf{1}^{2+},Cl^-]^+$, the excited state equilibrium constant was reduced by a factor of 20 from that of the ground state, which resulted in the rapid loss of the chloride ion upon light absorption. Overall, the data show that with appropriate synthetic design, luminescent excited states that rapidly release or completely retain a chloride ion can be realized.

ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization for newly reported compounds, ^{1}H NMR titration, time-resolved photoluminescence decay, electrochemistry and UV-Vis titration. The Supporting Information is available free of charge on the ACS Publications website.

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