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Luminescent Tetrahedral Molecular Cages Containing Ruthenium(II) Chromophores

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Supporting Information



ABSTRACT: We have designed linear metalloligands which contain a central photoactive $[Ru(N^{\Lambda}N)_3]^{2+}$ unit bordered by peripheral metal binding sites. The combination of these metalloligands with Zn(II) and Fe(II) ions leads to heterometallic tetrahedral cages, which were studied by NMR spectroscopy, mass spectrometry, and photophysical methods. Like the parent metalloligands, the cages remain emissive in solution. This approach allows direct incorporation of the favorable properties of ruthenium(II) polypyridyl complexes into larger self-assembled structures.

1. INTRODUCTION

Self-assembled discrete supramolecular structures have demonstrated valuable applications in sensing,^{1–4} separations or selective encapsulation,^{5–7} drug delivery,^{8–10} and for control-ling substrate reactivity and catalysis.^{11–17} Metallosupramolecular cages¹⁸⁻²⁷ often assemble predictable three-dimensional architectures programmed by the coordination preferences of metal ions and geometries of organic linker units. Early examples of catalytic metallosupramolecular cages exploited the size restriction of the cavities to facilitate the reaction occurring inside.²⁸⁻³⁰ Recent focus has turned to transition-metal-catalyzed reactions, with the active species encapsulated within,³¹⁻³⁷ or appended to,^{38,39} the central cavity. While co-encapsulation has proven to be an effective approach for catalysis within cages, preorganizing the active units into the components of the cage structure itself is potentially a more robust method to ensure the catalyst cannot dissociate from the cage structure. Examples of luminescent cages⁴⁰⁻⁴⁸ have been reported, and recent work has demonstrated photoinduced energy transfer between cages and bound guests.⁴⁹⁻⁵¹ The ruthenium(II) complex [Ru- $(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) is perhaps the best known photosensitizer,⁵² and in recent years has continued to show its versatility in catalyzing a variety of photoredox reactions.^{53–59} These types of chromophores have been incorporated into

MOFs⁶⁰⁻⁶³ and molecular cages,^{41,64-68} and photocatalysis has been recently reported within a molecular cage formed with ruthenium(II) polypyridyl chromophores bridged by palladium(II) ions.⁶⁹ We reported $[Ru(tpy)_2]^{2+}$ units (tpy = 2,2':6',2"-terpyridine) functionalized with pendant pyridyl groups which could be assembled into discrete cages with palladium(II) ions,⁷⁰ although these cages are not emissive at room temperature, as expected for this class of bistridentate complexes.⁷¹ Herein, we report three new metallosupramolecular cages based on metalloligands bearing a photoactive $[Ru(N^N)_3]^{2+}$ motif where the useful photophysical properties are maintained in the cage structures.

Complex $[Ru(phen)_2(1)](PF_6)_2$ (Scheme 1) can be functionalized with additional binding sites for metal ions,⁷² with the installation of 4-pyridyl groups allowing the assembly of hetereodimetallic one-dimensional coordination polymers.⁷² In this work, a bidentate chelating site was chosen to direct the assembly of a discrete tetrahedral structure in conjunction with an octahedral metal ion, inspired by the work of Lindoy,^{73–75} Nitschke,^{51,76–82} Raymond,^{83–86} and Lusby.^{87–89}



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Scheme 1. Synthetic Route to Racemic Complexes $[Ru(phen)_2(3)](PF_6)_2$ and $[Ru(phen)_2(4)](PF_6)_2$ and the Numbering Scheme Adopted



Figure 1. Partial ¹H NMR spectra (500 MHz, CD₃CN) of (a) $[Ru(phen)_2(4)](PF_6)_2$; (b) $[Ru(phen)_2(3)](PF_6)_2$; (c) $[Ru(phen)_2(6)](PF_6)_2$; (d) $[Ru(phen)_2(7)](PF_6)_2$.

2. EXPERIMENTAL SECTION

2.1. General. Synthetic schemes and detailed spectroscopic assignments are given in the Supporting Information. ¹H and ¹³C{¹H} NMR assignments were made using 2D-NMR methods (COSY, HSQC, HMBC) and are unambiguous unless stated otherwise. 5-Bromo-2,2'-bipyridine,⁹⁰ 5,5'-dibromo-2,2'-bipyridine (1),⁹⁰ 5-bromo-2-(1,3-dioxolan-2-yl)pyridine,⁹¹ 2-(1,3-dioxolan-2-yl)-5-pyridineboronic acid pinacol ester,⁹² and [Ru(phen)₂(1)]-(PF₆)₂⁷² were prepared by reported procedures.

2.2. Single Crystal X-ray Diffraction. A summary of crystallographic data and refinement parameters is shown in Table S2. Data were deposited with the Cambridge Structural Database (CCDC entries: 1839130 and 1839131). Single crystals of { $[Ru(phen)_2(3)]$ -(PF₆)₂·0.5(MeCN)} were measured by Si<111> monochromated synchrotron X-ray radiation ($\lambda = 0.71073$ Å) (MX1 Beamline at the Australian Synchrotron). Single crystals of 2,2':5',3":6",2" -quaterpyridine {1.5(C₂₀H₁₅N₄)} were measured on a Bruker kappa-II CCD diffractometer using IµS Incoatec Microfocus Source with Mo K α radiation ($\lambda = 0.710723$ Å).

{[$Ru(phen)_2(3$]](PF_6)₂·0.5MeCN}. C₅₅H_{37.5}F₁₂N_{10.5}P₂Ru, M = 1236.46, red platelets, triclinic, space group P1, a = 12.290(3) Å, b = 14.930(3) Å, c = 15.050(3) Å, $\alpha = 109.38(3)^{\circ}$, $\beta = 100.72(3)^{\circ}$, $\gamma = 95.73(3)^{\circ}$, V = 2523.4(10) Å³, Z = 2, $\rho_{calc} = 1.627$ g cm⁻³, μ (Mo K α) = 0.471 mm⁻¹, T = 100(2) K, 84 390 reflections collected. Refinement of 726 parameters using 11 909 independent reflections against F^2 converged at final $R_1 = 0.0776$ (R_1 all data = 0.0886), $wR_2 = 0.2198$ (wR_2 all data = 0.2367), GooF = 1.065.

{1.5(2,2':5',3":6",2"''-Quaterpyridine)}. $C_{20}H_{14}N_4$, M = 310.35, colorless plate, monoclinic, space group $P2_1/c$, a = 26.627(4) Å, b =



Figure 2. Left: an ORTEP representation of the complex cation in the single crystal X-ray structure of { $[Ru(phen)_2(3)](PF_6)_2 \cdot 0.5MeCN$ }, with thermal ellipsoids shown at 30% probability. Ru: teal, C: gray, N: blue, H: white. Right: a CPK representation of the face-to-face and edge-to-face $\pi - \pi$ stacking interactions, with alternating complexes shown in red and blue. Anions and solvent molecules are omitted for clarity.





^aOnly three of the six ligands are shown for clarity.

7.2406(10) Å, c = 11.7009(15) Å, $\alpha = 90^{\circ}$, $\beta = 102.112(10)^{\circ}$, $\gamma = 90^{\circ}$, V = 2205.7(5) Å³, Z = 6, $\rho_{calc} = 1.402$ g cm⁻³, μ (Mo K α) = 0.086 mm⁻¹, T = 150(2) K, 19 035 reflections collected. Refinement of 325 parameters using 4816 independent reflections against F^2 converged at final $R_1 = 0.0524$ (R_1 all data = 0.0947), $wR_2 = 0.1494$ (wR_2 all data = 0.1932), GooF = 1.029.

3. RESULTS AND DISCUSSION

3.1. A Sexipyridine-Functionalized Metalloligand. We aimed to selectively install a ruthenium complex into a specific site of a linear ligand with three identical bidentate domains. This required a synthetic strategy where the desired ruthenium-containing chromophore is synthesized first, followed by elaboration directly upon the complex to introduce the additional binding sites. This approach is essential to ensure the ruthenium center, which can be generally considered to be substitution inert, is selectively placed in a single binding site of the ligand, with the remaining bidentate sites available for coordination with labile metal ions for selfassembly. We have previously shown heteroleptic ruthenium-(II) polypyridyl complexes functionalized with bromo substituents are suitable for palladium(0)-mediated crosscoupling reactions,⁷² and here the complex $[Ru(phen)_2(1)]$ - $(PF_6)_2$ (phen = 1,10-phenanthroline; 1 = 5,5'-dibromo-2,2'-





bipyridine, Scheme 1) was used. The required coupling partner, 5-(2,2'-bipyridine) boronic acid pinacol ester (2) was

Scheme 3. Synthesis of the Racemic Complex $[Ru(phen)_2(7)](PF_6)_2$ and the Numbering Scheme Adopted



Scheme 4. Synthesis of Cage [Zn-8]^{20+a}



^aOnly three of the six ligands are shown for clarity.

synthesized from 5-bromo-2,2'-bipyridine. This borylation was carried out by lithiation, quenching with tributylborate, followed by the addition of pinacol. The boronic ester has previously been synthesized using a Miyaura coupling method;⁹⁵ however, attempts to reproduce this reaction gave the homocoupled 2,2':5',3'':6'',2'''-quaterpyridine product as the major isolated species. See the Supporting Information for details.⁹³

The metalloligand $[Ru(phen)_2(3)](PF_6)_2$ (3 = 2,2':5',3": 6",2"":5"",3"":6"",2""'-sexipyridine) was synthesized by palladium(0)-catalyzed Suzuki coupling reaction between $[Ru-(phen)_2(1)](PF_6)_2$ and boronic ester 2. The reaction was carried out with Cs₂CO₃ and Pd(PPh₃)₄ in DMF at 120 °C for 45 min in a microwave reactor. The metalloligand complex $[Ru(phen)_2(3)](PF_6)_2$ was isolated in 84% yield as the PF₆⁻ salt from an aqueous workup with KPF₆. Attempts to prepare the free sexipyridine ligand (3) by reaction of 1 and 2 under identical conditions, or in other solvent mixtures (e.g., DMSO, dioxane/*i*-PrOH, DMF/DME/water), did not afford the desired compound. Instead, the major species identified in the reaction mixture were free 1 and 2,2':5',3'':6'',2'''quaterpyridine. The latter was isolated, and its single crystal X-ray structure determined (see section S7.2). This finding suggests that the bromo-functionalized ligand is relatively activated toward cross-coupling, with respect to dehalogenation, when coordinated to the ruthenium(II) center. The simpler model compound [Ru(phen)₂(4)](PF₆)₂ (4 = 3,3': 6',2'':5'',3'''-quaterpyridine) was prepared in 61% yield using an analogous procedure with 3-pyridineboronic acid neopentyl glycol ester.



Figure 4. A semi-empirical (PM3) model of cage $[Zn\text{-}8]^{20\text{+}}$. Hydrogen atoms are omitted for clarity. Zn(II) (purple) and Ru(II) (teal) are shown as balls; all bonds are shown as sticks. The Ru(II) ions are modeled as Δ isomers and the Zn(II) ions as Λ isomers. The top zinc(II) ion is shown coordinated to three separate residues colored red, green, and blue.

Table 1. Summary of Calculated Diffusion Coefficients and Hydrodynamic Radii Measured by NMR in CD_3CN^a

compound	$\frac{diffusion\ coefficient/}{10^{-10}\ m^2\ s^{-1}}$	hydrodynamic radius/Å
$[\operatorname{Ru}(\operatorname{phen})_2(3)](\operatorname{PF}_6)_2$	10.4 ± 0.5	6.2 ± 0.3
$[Ru(phen)_2(7)](PF_6)_2$	11.7 ± 0.3	5.4 ± 0.2
$[Fe-5](PF_6)_{20}$	5.51 ± 0.05	11.6 ± 0.1
$[Zn-5](PF_6)_{20}$	5.60 ± 0.05	11.4 ± 0.1
$[Zn-8](PF_6)_{20}$	4.35 ± 0.08	14.7 ± 0.3
^a Hydrodynamic radii calculated using the Stokes–Einstein equation		

Complexes $[Ru(phen)_2(3)](PF_6)_2$ and $[Ru(phen)_2(4)]$ - $(PF_6)_2$ were characterized in detail by ¹H and ¹³C NMR, electrospray ionization mass spectrometry (ESI-MS), absorption and emission properties, and for $[Ru(phen)_2(3)](PF_6)_2$ also by single crystal X-ray diffraction. The ¹H NMR spectra are shown in Figure 1, and all signals were assigned using the methods previously described.⁹⁴ Upon exchange of bromo groups for pyridyl functional groups, the ¹H NMR signals of the phenanthroline ligands are largely unaffected by the changes in the bpy ligand. The signals corresponding to the central bpy unit are in similar environments in [Ru(phen)₂-(3)](PF₆)₂ and [Ru(phen)₂(4)](PF₆)₂, with the protons shifted further upfield in the model complex. Similarly, comparison of the signals for the B rings (see Scheme 1 for atom labeling) in the complexes shows that the protons are shifted further downfield in $[Ru(phen)_2(3)](PF_6)_2$, with the most pronounced change shown for H^{B3} upon substituting a pyridyl ring in the 2-position, causing a shift of 1.05 ppm.

Single crystals of $[Ru(phen)_2(3)](PF_6)_2$ suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into an acetonitrile solution of the complex. The structure is shown in Figure 2 and contains a single complex in the asymmetric unit. The spy ligand (3) in the structure is slightly bent due to coordination of the ruthenium(II) center to the central bipyridyl unit (angle between atom C26, the center of

the C37-C40 bond, and atom C53 is 170°). One of the terminal bpy units is involved in weak face-to-face $\pi - \pi$ stacking with the central bpy unit of an adjacent complex (centroid-to-plane distance of 3.485 Å), whereas the other terminal bpy unit is engaged in closer edge-to-face interactions (centroid of ring containing N10 to C3i = 3.33(1) Å, centroid···H-C = 2.58 Å, i = 1 = x, y, z). The terminal bpy ligand not involved in face-to-face stacking is the more planar, with the two pyridyl rings almost perfectly coplanar (angle between the least-squares planes of the two rings = 2.96° ; the angle between the least-squares planes of the two rings of the other terminal bpy unit is 11.14°). Coplanarity is expected for free 2,2'-bipyridine units due to favorable intramolecular N... HC interactions. The complexes are assembled via weak phenyl-phenyl embraces⁹⁶⁻⁹⁸ between the equivalent phenanthroline ligands of adjacent complexes (plane-to-plane separation 3.464 Å).

The $[Ru(phen)_2(3)](PF_6)_2$ complex was self-assembled into molecular cages by reaction with labile metal(II) ions. The selfassembly was attempted with a variety of first row transition metals—iron(II), cobalt(II), cobalt(III), nickel(II), and zinc-(II)—to probe a number of possible structures from different preferred coordination geometries. However, using iron(II) and zinc(II) gave the most success in the self-assembly, while the other metal ions produced species that were difficult to identify or isolate.

As an example, 3 equiv of $[Ru(phen)_2(3)](PF_6)_2$ and 2 equiv of $Fe(BF_4)_2 \cdot 6H_2O$ were reacted in acetonitrile at 80 °C for 24 h, followed by anion metathesis with aqueous KPF_6 . The resulting red solid was collected on Celite and washed with water, then dissolved in acetonitrile. The self-assembled structures are consistent with the $[Fe_4L_6](PF_6)_{20}$ stoichiometry expected for the tetrahedral cage $[Fe-5](PF_6)_{20}$ (Scheme 2). High resolution electrospray ionization (ESI) mass spectrometry revealed highly charged 4+, 5+, and 6+ species for iron(II)-containing cages corresponding to the loss of counterions, in each case matching calculated isotope patterns (see Figures S3 and S4). The ¹H NMR spectrum of the reaction of $[Ru(phen)_2(3)](PF_6)_2$ with $Fe(BF_4)_2 \cdot 6H_2O$ (Figure S17) shows a mixture of species in solution, so we monitored the assembly process over time to investigate whether this was due to prematurely terminating the reaction before thermodynamic equilibrium had been reached.

The reaction of $[Ru(phen)_2(3)](PF_6)_2$ with $Fe(BF_4)_2 \cdot 6H_2O$ in CD₃CN was monitored by ¹H NMR at 80 °C for several days (Figure S19). Upon initial mixing of the reagents, a broad featureless ¹H NMR spectrum is observed, consistent with a kinetic mixture of different oligomeric products. After heating, the spectrum becomes simpler with sharper signals suggesting the presence of several similar products. After 24 h, no further changes in the ¹H NMR spectrum were observed, and the reaction appears to be complete and that the end product mixture is a thermodynamic minimum. The reaction was treated with aqueous KPF₆, and the resulting precipitate was collected on Celite, washed with water, and redissolved in CD₃CN. It is clear one of the species present in the reaction is removed (decomposed) by this procedure; for example, the signal at 9.0 ppm disappears after workup. The number of separate signals in the spectrum after workup indicated the major product formed has low symmetry (i.e., not T symmetry). The concentration dependence of the mixture was also studied in CD₃CN (Figure S23), and although signals became sharper at lower concentrations, no evidence for a



Figure 5. All samples were measured in acetonitrile at 298 K with $[Ru^{II}] \approx 0.06$ mM. (a, b) Absorption spectra of the metalloligands and the respective cages formed with Zn(II) and Fe(II) metal centers. Extinction coefficients are normalized to the concentration of ruthenium(II) centers present for comparison. The Zn(II) cages display the same absorption profiles as the mononuclear complexes, showing that self-assembly with Zn(II) has no effect on absorption energies. (c, d) Normalized emission ($\lambda_{ex} = 450$ nm) of the metalloligands and their respective cages formed with Zn(II) and Fe(II) metal centers. The cages retain the emissive properties of the ligands, with some quenching which is more prevalent in cage [Zn-8](PF_6)_{20}.

change in the product distribution was observed over the concentration range studied (~0.2 to 1 mM). The related reaction of $[Ru(phen)_2(3)](PF_6)_2$ and $Zn(NTf_2)_2$ in acetonitrile gave a self-assembled product with highly charged HR-ESI-MS signals corresponding to sequential loss of PF_6^- anions from the tetrahedral cage $[Zn-5](PF_6)_{20}$ (Figure 3), and the ¹H NMR spectrum was also consistent with the product distribution similar to that described with iron(II) (Figure S17).

It is known that related, but smaller, tetrahedral cages formed with short, rigid ligands can exist as mixtures of stereoisomers which differ only in the stereochemistry of the vertices (Λ or Δ).^{78,79} However, in the case of cage $[M-5]^{20+}$, the ruthenium(II) center on the metalloligands can also be Λ or Δ configuration. This combination will give rise to the possibility of many diastereomers with a large number of slightly different proton environments to result in the observed complicated spectrum. Free rotation about the carbon-carbon bonds between the bpy units of the metalloligand would allow the $[Ru(phen)_2(bpy)]$ units to rotate to avoid any unfavorable steric clashes between neighboring units. This may result in ruthenium(II) centers on adjacent metalloligands being sufficiently close to cause noticeable differences in their ¹H NMR environments, but not so restricted that the stereochemistry of one center can dictate the stereochemistry of the next. Similarly, the stereochemistry of the ruthenium(II) centers can be expected to have little influence on the

stereochemistry of the vertices simply due to the geometrical arrangement of the groups.

To alleviate some of the complexity caused by this isomerism, $[Ru(phen)_2(3)](PF_6)_2$ was prepared as the enantiopure Λ isomer. This was achieved by resolving $[Ru(phen)_2(py)_2]^{2+}$ (py = pyridine) into its enantiomers,⁹⁹ followed by chelation of 1 to form Λ -[Ru(phen)₂(1)](PF₆)₂.⁷² The Suzuki coupling with 2 was also carried out in the microwave as for the racemic complex, giving Λ -[Ru(phen)₂-(3)](PF₆)₂ in 47% yield. The formation of cage [Fe-5]²⁰⁺ with the enantiopure metalloligand Λ -[Ru(phen)₂(3)](PF₆)₂ resulted in some simplification of the ¹H NMR spectrum compared to that of the cage assembled with the racemate (Figure S20). There was a significant increase in the proportion of the product with the signal at 9.0 ppm, which was removed during workup, as occurred for the racemic case. The final isolated sample has a relatively simple spectrum and suggests a single major tetrahedral cage species. Circular dichroism spectra of Λ -[Ru(phen)₂(3)](PF₆)₂ and its selfassembled $[Fe-5](PF_6)_{20}$ cage are essentially identical (Figure \$31), indicating that the only chirality in the cage arises from the ruthenium(II) centers; i.e., the orientation of the metal ions at the vertices is not influenced by the chirality of the metalloligand.

3.2. A Cage with Capped Vertices. To use the assembled cages for photoredox applications, two key requirements are (i) the photophysical properties of the ruthenium(II)

chromophores must be preserved in the assembled species and (ii) the cages must not disassemble, even at very low (catalytic) concentrations. Transition metal centers such as iron(II) can be highly effective for quenching ruthenium(II) excited states by acting as effective electron acceptors/ donors.^{100–102} A safer option is to opt for d^{10} metal ions as the vertices of the cage, such as zinc(II), which are generally resistant to redox processes. However, the d^{10} configuration leads to two consequences: the Zn-N bonds are typically labile, and there are no strong coordination geometry preferences around the zinc(II) center. These issues create difficulties with using zinc(II) ions for self-assembly. We were inspired by Würthner and co-workers,³ who prepared an impressive tetrahedral cage with zinc(II) vertices and the pyridylimine chemistry used extensively by Nitschke.^{77,80,103-106} In that example, a perylene bisimide featuring 2-pyridylcarboxaldehyde substituents was condensed with a tridentate capping unit, tren (tren = tris(2-aminoethyl)amine), and a source of zinc(II) ions to form tris-(pyridylimine) binding units as the vertices of the cage. A 1:0.9:0.7 ratio of diastereomeric cages was reported at 50 °C in CD₃CN, consistent with the poor transfer of chiral information between the vertices expected for long ligands.³ We would expect a similar situation for our ruthenium(II)-containing cages prepared using the same approach, although these cages would be significantly smaller. Suzuki coupling of [Ru(phen)2-(1)](PF₆)₂ and a pyridyl unit with a protected aldehyde group and a boronic ester gave $[Ru(phen)_2(6)](PF_6)_2$ which was deprotected to generate the desired dialdehyde complex $[Ru(phen)_2(7)](PF_6)_2$ in 85% yield over these two steps (Scheme 3). The complexes were also fully characterized by ¹H and ¹³C NMR, electrospray ionization mass spectrometry (ESI-MS), and absorption and emission properties. The ¹H NMR spectra are shown in Figure 1, and display similar trends as $[\operatorname{Ru}(\operatorname{phen})_2(3)](\operatorname{PF}_6)_2$ and $[\operatorname{Ru}(\operatorname{phen})_2(4)](\operatorname{PF}_6)_2$ upon substituting pyridyl groups for the bromo functionalities, with the signal of H^{B3} being shifted downfield by 0.38 ppm on substitution.

To prepare the desired cage [Zn-8]²⁰⁺, 3 equiv of $[Ru(phen)_2(7)](PF_6)_2$, 2 equiv of tren, and 2 equiv of $Zn(NTf_2)_2$ were reacted in acetonitrile at 50 °C for 5 h, followed by anion exchange with aqueous KPF₆ as described previously (Scheme 4). High resolution ESI-MS (Figures S5 and S6) showed a series of highly charged (7+, 6+, 5+, 4+) signals with isotope patterns matching the calculated patterns for sequential loss of PF_6^- from $[Zn-8](PF_6)_{20}$. Additional higher mass signals of the same charge were observed for each of these signals, possibly corresponding to the encapsulation of neutral solvent molecules. The aromatic region of the ¹H NMR spectrum (Figure S18) is considerably simpler than those of the $[M-5]^{20+}$ cages, in part due to this cage having fewer proton environments. The signals are broad and consistent with a collection of equilibrated isomers. The concentration dependence of the mixture was also studied in CD₃CN (Figure S24), and although some hydrolysis was observed at low (~0.1 mM) concentrations, no significant change in the product distribution was observed. This is also consistent with the formation of discrete species of the same size, as opposed to mixtures of oligomers which might be expected to show more pronounced concentration dependence.

Using variable temperature NMR in DMSO- d_6 , we monitored the ¹H NMR spectrum over a range from 25 to

125 °C (Figure S22). At higher temperatures, the aromatic signals do significantly sharpen, yet are unable to reach a completely symmetrical fast exchange regime. Significantly, on cooling the sample back to room temperature, a spectrum identical to that prior to heating was obtained, verifying the observed changes are not due to irreversible decomposition of the cage and suggesting a highly robust structure.

The self-assembly of cage [Zn-8]²⁰⁺ was also monitored in CD₃CN with the reaction mixture maintained at 50 °C for 5 days (Figure S21). Immediately after mixing, the aldehyde is consumed, as expected, and significant shifts in the signals of the methylene linkers of the tren residue are observed. The aromatic region of the ¹H NMR spectrum did not display any further changes after 5 h of heating. However, the aliphatic region did continue to undergo significant changes. Initially, a series of relatively sharp signals between 4.0 and 2.5 ppm are observed, potentially due to partially condensed tren units (that would still be expected to be reasonable ligands for zinc(II)). Following extensive heating, the methylene groups are able to adopt a wide range of relative conformations which must be close in energy in part due to the flexible coordination geometry of the zinc(II) center. After workup, all of the sharp signals from the aliphatic region are removed, suggesting these may be structures that feature free amine groups that might result in higher solubility in water.

3.3. Molecular Modeling. In order to estimate the size of the tetrahedral cage $[Zn-8]^{20+}$, a simple PM3 model was calculated and is shown in Figure 4. The estimated length of one edge of the tetrahedron is approximately 26 Å, and the central cavity has a volume of approximately 340 Å³.

3.4. Diffusion NMR Studies. Diffusion NMR, often presented as DOSY plots, is a powerful tool for differentiating species on the basis of their rates of diffusion, and for estimating their relative sizes. It has become a standard tool of supramolecular chemists for characterizing molecular cages and capsules.¹⁰⁷⁻¹¹⁰ We measured the diffusion coefficients of the mononuclear $[Ru(phen)_2(3)](PF_6)_2$ and $[Ru(phen)_2(7)]$ - $(PF_6)_2$ complexes, in addition to the self-assembled cage structures formed from these components; the data are shown in Table 1. The measured diffusion coefficients of the mononuclear complexes correspond to hydrodynamic radii of 5.4 and 6.2 Å. From the X-ray crystal structure of $[Ru(phen)_2(3)](PF_6)_2$, the smallest box that encapsulates the cation is approximately $25.6 \times 9.6 \times 10.7$ Å which might suggest a hydrodynamic radius ~ 8 Å if this volume is approximated as a sphere. The observed hydrodynamic radius is a little shorter, perhaps not surprising given the complex is far from being approximately a sphere.

As expected, the self-assembled structures have smaller diffusion coefficients than the mononuclear metalloligands. For cages $[Fe-5]^{20+}$ and $[Zn-5]^{20+}$, these correspond to hydrodynamic radii of 11.6 and 11.4 Å, respectively. For cage $[Zn-8]^{20+}$, the expected length (from a PM3 model) for one edge of the tetrahedron is approximately 26 Å. Such a tetrahedron which would fit inside a sphere of radius 16 Å and, as this is a more reasonable approximation for a sphere, we observe good agreement with the calculated hydrodynamic radius (14.7 Å). It must be emphasized that, in estimating sizes, no consideration has been given to the volume of the many anions present which must diffuse with the cationic cage, and it is remarkable that there is any agreement at all with predicted sizes. That said, there is no doubt the mononuclear complexes have been assembled into much larger structures, consistent with the proposed tetrahedral cages.

3.5. Photophysical Properties. Finally, we turn our attention to the photophysical properties of the cages. Figure 5a shows the absorption spectra of $[Ru(phen)_2(3)](PF_6)_2$ $[Fe-5](PF_6)_{20}$, and $[Zn-5](PF_6)_{20}$, normalized for the concentration of ruthenium(II) in all cases. The absorption spectra of $[Ru(phen)_2(3)](PF_6)_2$ and $[Zn-5](PF_6)_{20}$ are essentially identical as the coordination of zinc(II) to the terminal bpy groups will not generate a new chromophore. In both compounds, the MLCT band has a maximum absorption at 450 nm and the ligand-centered transitions appear at higher energies, with the extended conjugation of ligand 3 resulting in the absorbance band at 350 nm. In cage $[Fe-5](PF_6)_{20}$, coordination of the iron(II) ions shifts the energy of this ligand-centered transition. Figure 5b makes the same comparison between $[Ru(phen)_2(7)](PF_6)_2$ and [Zn-8]- $(PF_6)_{20}$. Here, some change in the absorption spectrum is observed as an aldehyde group is being replaced with an imine, which has some influence on the electronic properties of the ruthenium(II) center. Panels (c) and (d) in Figure 5 compare the emission data for the mononuclear complexes with the cage structures, normalized for absorption at 450 nm. In cages $[Zn-5](PF_6)_{20}$ and $[Fe-5](PF_6)_{20}$, minimal quenching is observed relative to the mononuclear parent complexes and both cages remain strongly emissive in solution. The emission energy of $[Fe-5](PF_6)_{20}$ is blue-shifted compared to both [Zn- $5](PF_6)_{20}$ and its parent complex. Cage $[Zn-8](PF_6)_{20}$ also remains emissive in solution, although it experiences a noticeably greater level of quenching compared to the [M-**5**](PF_6)₂₀ cages.

4. CONCLUSIONS

Using a metalloligand approach, we have installed inert luminescent $[Ru(bpy)_3]$ -like complexes on the linker units of tetrahedral molecular cages. These cages retain the photophysical properties of the parent complexes and are not susceptible to disassembly, even at low concentrations. The formation of a complicated mixture of stereoisomers, even where the stereochemistry of the ruthenium centers was controlled, prevents a detailed analysis of their host–guest chemistry, but we anticipate this approach will prove useful for preparing functional molecular photoreactors.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01157.

Synthetic procedures, NMR and ESI-MS data, and additional experimental details are reported (PDF)

Accession Codes

CCDC 1839130 and 1839131 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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