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Quantitative Sensitization Efficiencies in NIR-Emissive Homoleptic Ln(III) Complexes Using 2-(5-Methylpyridin-2-yl)-8hydroxyquinoline

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Supporting Information

ABSTRACT: A series of isostructural lanthanide complexes $[Ln(MPQ)_3]$ (Ln = Nd, Gd, Er, Yb, Lu) using a monoanionic tridentate methylpyridyl-substituted 8-hydroxyquinoline ligand (MPHQ = 2-(5-methylpyridin-2-yl)-8-hydroxyquinoline) have been prepared and characterized using elemental analysis (CHN), single-crystal X-ray diffraction (XRD), and ¹H NMR spectroscopy. This ligand forms homoleptic charge-neutral lanthanide complexes with three coordinated ligands arranged in an "up-up-down" fashion around the metal center. The photophysical properties of the Nd, Er, and Yb complexes were investigated using absorption and emission spectroscopy, with the latter species displaying efficient sensitization in the Near Infra-Red (NIR) region and a photoluminescence quantum yield (PLQY) as high as 1.0% in CH₂Cl₂ solution. The intersystem



crossing and energy-transfer processes involved in the antenna effect were further investigated using transient absorption techniques, which revealed essentially quantitative sensitization efficiencies for the NIR-emitting cations.

■ INTRODUCTION

Continuing research into the development of sensitized luminescence from trivalent lanthanide (Ln^{III}) ions has become increasingly prevalent due to their sharp optical bands, resistance towards photobleaching, and long-lived luminescence lifetimes.¹ In particular, the luminescence from materials based on Ln^{III} ions with Near Infra-Red (NIR) emission, such as Nd^{III} (890, 1060, and 1350 nm), Er^{III} (1520 nm), and Yb^{III} (980 nm) have emerging applications in electroluminescent devices and optical telecommunication.² Recently, brightly emissive Yb^{III} complexes with photoluminescence quantum yields (PLQY) as high as 25% in CH₂Cl₂ solution have been reported,⁵ and their use as biological probes for living cell imaging has been successfully demonstrated.⁶ In comparison to visible-emitting dyes, Ln^{III} complexes with NIR emission such as these can offer improvements for luminescence imaging, since these wavelengths suffer less interference from biological samples and hence can facilitate earlier and more accurate diagnosis and treatment of diseases in vivo.⁷ As a consequence of the Laporte selection rule, however, direct excitation of Ln^{III} metal cations is not efficient, and their absorbance is very weak.⁸ Hence, complexes containing strongly absorbing organic chromophores are required, acting as antennas to harvest incident light and transferring this energy to the metal, ultimately reaching the emissive $4f^*$ excited states.⁸

While considerable research efforts have focused on the use of 8-hydroxyquinoline (8-HQ) as a chelator to form stable complexes with Ln^{III} ions, a lack of control in metal complexation with this bidentate ligand has resulted in the isolation of species with different ligand to metal ratios.⁹⁻¹¹ Moreover, since 8-HQ is unable to fully saturate the Ln^{III} coordination sphere in the formation of charge-neutral tris complexes, there is a strong tendency for the deprotonated hydroxyl group to act as a bridge, resulting in the formation of polynuclear complexes.⁹⁻¹¹ This continues to be a difficulty in attempts to quantitatively correlate structural properties with photoluminescence.

In order to facilitate the synthesis of complexes with more predictable and controllable coordination properties, Shavaleev et al.,^{12,13} Wei et al.,¹⁴ and Bozoklu et al.¹⁵ have each shown that this limitation can be overcome by introducing another heteroaromatic moiety in the 2-position of the ring system, forming mono- or dianionic tridentate N,N,O-ligands (Figure 1). Similar N,N,O-type chelates have also been reported over the past decade, mostly from the Bünzli group, $^{16-20}$ but also from several other authors. $^{21-24}$ These types of chelating ligands are able to fully saturate the coordination sphere of the Ln^{III} cations and form stable charge-neutral complexes both in the solid state and in solution. Despite their interesting structural features and photophysical properties, to the best of our knowledge, further attempts to characterize the kinetic

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Figure 1. Chemical structures of various reported¹¹⁻¹⁴ Ln^{III} complexes utilizing tridentate N,N,O-type ligands.

profile of the electronically excited states and energy transfer processes involved in these complexes have not been reported.

Herein, we report on the synthesis, structure, and photophysical properties for a family of homoleptic charge-neutral Ln^{III} complexes, [Ln(MPQ)₃], derived from a simple monoanionic tridentate N,N,O-type ligand, 2-(5-methylpyridin-2-yl)-8-hydroxyquinoline (MPHQ). Sensitized NIR emission was observed for the Nd^{III}, Er^{III}, and Yb^{III} complexes in CH_2Cl_2 solution, with the latter demonstrating a PLQY of $\Phi =$ 1.0%. Although modest in comparison to some porphyrinbased sensitizers,^{5,6} this value nonetheless represents an improvement in comparison to similar ligands resulting in a similar Ln^{III} coordination environment.^{12,14,15} The energy transfer processes in the isolated $[Ln(MPQ)_3]$ complexes have also been investigated using transient absorption (TA) experiments in order to monitor the kinetic profiles of the lowest energy ligand centered singlet (S_1) and triplet (T_1) excited states. This approach is advantageous, as it has allowed the intersystem crossing and electronic energy transfer efficiencies to be quantified, providing an insight into the dynamics of the antenna effect for this type of chromophore as an energy donor.

RESULTS AND DISCUSSION

Synthesis. The tridentate MPHQ ligand was efficiently prepared in high purity following a previously reported synthesis for pyridyl-substituted 8-hydroxyquinolines,²⁵ using

an adaptation of a simple Friedländer condensation method. As summarized in Figure 2, the required prerequisite 2-amino-3-methoxybenzaldehyde (1) was readily prepared by reduction of the corresponding commercially available 2-nitro-3-methoxybenzaldehyde using elemental Fe(0) powder in aqueous ethanol. In parallel, 1-(5-methylpyridin-2-yl)ethanone (2) was prepared by the acetylation of commercially available 2-bromo-5-methylpyridine using previously reported procedures.²⁶ The product 3 obtained from condensation of 1 and 2 was then deprotected in 48% HBr at 150 °C overnight, to yield the target tridentate MPHQ ligand 4. In general, the synthesis of this ligand is scalable, high yielding, and results in high-purity products.

Complexation of MPHQ (4) with various $LnCl_3 \cdot 6H_2O$ salts (Ln = Nd, Gd, Er, Yb, Lu) was readily achieved using the appropriate 1:3 metal:ligand stoichiometry in MeOH as the solvent and with the addition of $NMe_4OH \cdot 5H_2O$ as a base to ensure deprotonation of the ligand. Notably, we obtained an optimal yield of the complex by first preparing the tetramethylammonium salt of the ligand, $(NMe_4)MPQ_1$ at room temperature, before addition of the LnCl₃ salt. After a short reflux period (ca. 2 h), the desired complexes were isolated by filtration as intensely colored air- and moisture-stable orange-red solids in good yield (50–70%), and elemental analyses confirmed the formulation of the complexes as $[Ln(MPQ)_3] \cdot nH_2O$, containing up to two co-crystallized water molecules.

Structural Studies. Single crystals of $[Ln(MPQ)_3]$ (Ln = Nd, Er, Yb) were obtained after slow cooling and evaporation of methanol solutions. All three complexes are isostructural, although the Yb^{III} and Er^{III} compounds were crystallized in the monoclinic $P2_1/c$ space group with two different complexes in the asymmetric unit, while the Nd^{III} complex crystallized in the $P2_1/n$ space group. Resulting crystallographic data for each complex are summarized in Table S1 in the Supporting Information, and a summary of bond lengths and angles is given in Table 1. The resulting X-ray structure for the Nd^{III} complex is shown as an example in Figure 3.

Considering only the donor atom positions, continuous shape measure (CShM) analysis of the structurally characterized $[Ln(MPQ)_3]$ complexes compared to the most common nine-coordinate (CN = 9) coordination geometries was undertaken using the SHAPE v2.1 software package^{27,28} (see Table S2 in the Supporting Information), yielding a close match to both the capped-square-antiprismatic ($C_{4\nu}$) and



Figure 2. Synthetic scheme for preparation of the MPHQ ligand. Reaction conditions: (a) Fe(0), $EtOH/H_2O$, 4 h, reflux; (b) (i) *n*-BuLi, (ii) DMA, Et_2O , -78 °C; (c) KOH, EtOH, under N₂, 20 h, reflux; (d) 48% HBr, under N₂, 150 °C, overnight; (e) $LnCl_3 \cdot nH_2O$, $NMe_4OH \cdot 5H_2O$, methanol, in air, reflux (Ln = Nd, Gd, Er, Yb, Lu).

Table	1. Selected	Bond Len	gths and Angl	es for [Ln((MPQ) ₃] Complexes ((Ln = Nd, Er, Yb)
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		bond length ^{a} (Å)			
complex ^b	Ln-O	Ln-N(q)	Ln-N(py)	torsion angle (deg) $py-q^c$	$Ln-Ln^d$ (Å)
[Nd(MPQ) ₃]	2.379(4)	2.596(4)	2.691(4)	3.60 ± 0.84	8.927(5)
	2.376(4)	2.634(4)	2.705(4)	8.15 ± 0.78	
	2.418(3)	2.686(4)	2.788(4)	10.65 ± 1.06	
	2.391 ± 0.023	2.640 ± 0.045	2.731 ± 0.052		
$[Er(MPQ)_3]$ (i)	2.318(5)	2.491(5)	2.585(5)	4.88 ± 1.21	8.666(4)
	2.293(4)	2.451(5)	2.583(5)	9.77 ± 2.42	
	2.328(5)	2.541(6)	2.719(6)	23.51 ± 1.49	
	2.313 ± 0.018	2.494 ± 0.045	2.629 ± 0.078		
$[Er(MPQ)_3]$ (ii)	2.308(5)	2.597(6)	2.751(7)	2.65 ± 0.35	
	2.270(5)	2.484(6)	2.571(6)	0.95 ± 0.63	
	2.293(5)	2.509(6)	2.605(6)	5.75 ± 1.06	
	2.290 ± 0.019	2.530 ± 0.059	2.642 ± 0.095		
$[Yb(MPQ)_3]$ (i)	2.271(3)	2.464(4)	2.572(4)	4.02 ± 0.95	8.583(4)
	2.261(3)	2.444(4)	2.576(4)	8.12 ± 1.39	
	2.297(3)	2.530(4)	2.757(4)	24.17 ± 2.18	
	2.276 ± 0.018	2.479 ± 0.045	2.635 ± 0.106		
$[Yb(MPQ)_3]$ (ii)	2.250(3)	2.464(4)	2.568(4)	1.98 ± 0.91	
	2.254(3)	2.599(4)	2.849(4)	0.42 ± 0.22	
	2.266(3)	2.479(4)	2.602(4)	6.05 ± 0.05	
	2.257 ± 0.008	2.514 ± 0.074	2.673 ± 0.153		

^{*a*}Values given in boldface type are averages and standard deviations of three coordinated ligands. N(q) and N(py) are nitrogen atoms of the quinoline and pyridine ring, respectively. ^{*b*}Two different molecules are found in the asymmetric unit cell of the Yb^{III} and Er^{III} complexes, while only one molecule is present in the asymmetric unit cell of the Nd^{III} complex. ^{*c*}The dihedral angle between the planes of pyridine and quinoline subunits. ^{*d*}The shortest distance between metal ions in the structure.



Figure 3. X-ray crystal structure of $[Nd(MPQ)_3]$ ·H₂O. Color scheme: C, gray; O, red; N, blue; Nd, yellow. Ellipsoids are shown at the 50% probability level, and cocrystallized solvent and H atoms are omitted for clarity.

tricapped-trigonal-prismatic (D_{3h}) geometries. Indeed, the calculated differences between these two geometries are only very slight, exemplified by the Er^{III} and Yb^{III} structures, for which the different complexes in the asymmetric unit have a different closest match. An insight into the differing coordination spheres present is provided by a closer examination of the coordination geometries (see Figure S5 in the Supporting Information), where the approximate D_{3h} and $C_{4\nu}$ geometries are highlighted. However, taking into consideration the connectivity of the organic ligand, the coordination polyhedron for the structurally characterized $[\text{Ln}(\text{MPQ})_3]$ complexes is best described as a distorted tricapped trigonal prism. In this case, the nitrogen atoms of the

quinoline rings which lie in-plane with the Ln^{III} ion occupy the capping positions, while the remaining donor atoms above and below this plane form the vertices of the trigonal prism. In all cases, the complexes display an "up–up–down" coordination mode for the deprotonated ligands, resulting in a meridional disposition of the phenolic oxygen donors, which reduces the overall symmetry of the complexes to C_1 .

For the Nd^{III} complex, which has only one molecule in the asymmetric unit, all of the MPQ⁻ ligands are essentially planar, with a maximum deviation of only 0.18 Å due to a slight rotation between the quinoline and pyridyl groups, resulting in bond torsions which range from 3.6 to 10.7°. Similarly, for the Yb^{III} and Er^{III} complexes, which both have two independent molecules in the asymmetric unit, the MPQ⁻ ligands are again mostly planar, with a maximum deviations of 0.37 Å and torsion angles in the range of 0.4-9.8°. However, for one of the MPQ⁻ ligands, the torsional angles linking the pyridyl and quinoline ring systems are considerably more twisted, at ca. 24.2 and 23.5° for the Yb^{III} and Er^{III} complexes, respectively. Although this may be due in part to the smaller ionic radius of the Yb^{III} and Er^{III} cations, leading to more steric congestion at the metal center, we believe it is also likely due to differences in the crystal packing (vide infra). As summarized in Table 1, the observed Ln-O bond lengths are the shortest, ranging from 2.26 to 2.39 Å, while the Ln-N(q) bond lengths involving the quinoline are longer, ranging from 2.48 to 2.64 Å. The latter are slightly shorter on average than the Ln-N(py) bond lengths involving the pyridyl group, which range from 2.63 to 2.73 Å. On the whole, the metrics evaluated for each complex conform to the expected and well-known Ln^{III} contraction and confirm that the anionic oxygen donor atoms coordinate more effectively with the Ln^{III} ion than do the nitrogen atoms. The smallest intermolecular separations between adjacent metal

ions were ca. 8.67 and 8.58 Å for Er^{III} and Yb^{III} , and the separation was slightly longer for Nd^{III} at ca. 8.93 Å.

For each of the structurally characterized $[Ln(MPQ)_3]$ complexes, the number and identity of the co-crystallized solvent molecules differ, which, together with observed differences in their crystal packing (see Figures S2 and S3 in the Supporting Information), is likely determinant, resulting in their crystallization in differing space groups. For the $[Nd(MPQ)_3]$ ·H₂O complex, with a single molecule in the asymmetric unit, a pair of adjacent molecules related by the crystallographic inversion center form an efficient "head-totail" intermolecular $\pi - \pi$ stacking arrangement between coordinated MPQ⁻ ligands, with a separation of ca. 3.37 Å (see Figure S4 in the Supporting Information), which is also comparable to previously reported values for a structurally similar Nd^{III} complex.¹⁴ This interaction is propagated by the glide plane and 2-fold screw axis along b, forming repeating pairs of π -stacked dimers. By contrast, the [Yb(MPQ)₃]. (CH₃OH)₂ and [Er(MPQ)₃]·3H₂O complexes maintain this interaction for only one of the crystallographically unique complexes in the asymmetric unit, while the other is involved in a less efficient offset "head-to-head" π -stacking interaction.

As was mentioned, the coordinated ligands are arranged in an "up–up–down" fashion, yielding a meridional disposition of O donor atoms and resulting in an overall low-symmetry C_1 complex. This appears to be a very common coordination pattern and has been observed for the majority of tris monoanionic N,N,O Ln^{III} complexes which have been structurally characterized, ^{12–14,16–19,21,22} with the exception of only three rare examples which show C_3 symmetry.^{15,20,23} The relative scarcity of the "up–up–up" facial isomer can be rationalized by a consideration of relative energy in comparison to the meridional isomer, which we have undertaken using density functional theory (DFT) calculations for a model [Y(MPQ)₃] complex (vide infra).

¹H NMR Spectroscopy. We have investigated the formation of the desired ML_3 complexes in solution using ¹H NMR spectroscopy. Interestingly, a review of the literature revealed that the spectra for diamagnetic La^{III} and Lu^{III} complexes of monoanionic tridentate N,N,O type ligands are generally broad, especially for complexes with low C_1 symmetry, and can often be poorly informative.^{13,16,19,20} This can be attributed to the kinetic lability of the Ln^{III} cations, and we observe similarly broad ¹H NMR signals for the isolated [Lu(MPQ)₃] complex (see Figure S12 in the Supporting Information).

In contrast, ¹H NMR spectra we obtained for a comparable $[Y(MPQ)_3]$ complex in d_4 -MeOD are quite well resolved. The diamagnetic Y^{III} complex is also more soluble in comparison to the corresponding Lu^{III} complex, allowing for higher quality spectra to be collected, as shown in Figure 4. The proton resonances clearly display three sets of signals, which we attribute to three different ligands, and are consistent with the meridional geometry we observed for corresponding Ln^{III} complexes by X-ray crystallography. Most importantly, as expected for a low-symmetry C_1 complex, the spectrum displays three sharp singlets of equal intensity at 1.63, 1.69, and 1.73 ppm, which we assign to the three non-equivalent methyl groups.

Several of the aromatic signals could also be resolved into their respective spin systems using ${}^{1}H{-}^{1}H$ COSY experiments, which were undertaken for both the MPHQ ligand and the corresponding Y^{III} complex (see Figures S10 and S11, and S13



Figure 4. ¹H NMR spectrum of $[Y(MPQ)_3]$ (1 mM) in d_4 -MeOD. The signal of the residual solvent is denoted with an asterisk.

in the Supporting Information). In general, these signals were grouped into two regions, based on their chemical shifts between ca. 6.5-7.3 and ca. 7.5-8.4 ppm. In the former region, two sets of three doublets centered at 6.47, 6.58, 6.61 ppm and again at 6.89, 6.96, and 6.99 ppm are evident, which we assign to either the H1/H1'/H1" or H3/H3'/H3" protons based on their coupling to the triplet signal at 7.2-7.3 ppm. These appear in a repeating "1 + 2" pattern of one clearly resolved signal and two overlapping signals due to the similar environment of each ligand. Similarly, the complex multiplet from ca. 7.2 to 7.3 ppm could be resolved into three overlapping 1H triplet signals with the same 1 + 2 pattern, which we assigned to the H2/H2'/H2" protons based on the multiplicity. For the aromatic signals between ca. 7.5 and 8.4 ppm, a definitive assignment of individual signals was less conclusive, due to the overlapping of several peaks and unresolved coupling patterns. Nonetheless, it is clear from the ¹H NMR that the predominant form in solution is exclusively the meridional geometric isomer. Lastly, to verify that these signals originate from the same molecule, a ¹H diffusionordered NMR (2D-DOSY) experiment was carried out (see Figure S14 in the Supporting Information), confirming that all of the observed signals arise from a single $[Y(MPQ)_3]$ complex, with an estimated diffusion coefficient of ca. $3.17 \times$ $10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Density Functional Theory. To provide an insight into the observed selectivity for the meridional versus facial geometric isomers and to further characterize the ligandcentered excited states of the $[Ln(MPQ_3)]$ complexes, static and time dependent (TD) density functional theory (DFT) calculations using Gaussian 09 were performed. However, in order to avoid computationally expensive calculations involving open-shell 4*f* metal ions, a simplified model with a diamagnetic Y^{III} cation was used instead of the central Ln^{III} cation. The Y^{III} cation has an identical charge and similar ionic radius in comparison to the middle Ln^{III} cations,²⁹ and we have found this approach to be useful to gain an understanding of ligand-centered electronic structures.

The DFT optimized structures for meridional and facial isomers of the $[Y(MPQ)_3]$ complex using the CAM-B3LYP functional and mixed LANL2DZ/6-31G* basis sets were computed in the gas phase, and their respective electrostatic potential distributions, computed on the molecular surface defined by a 0.002 electron bohr⁻³ contour of the electron density, are depicted in Figure 5. Interestingly, and in



Figure 5. Results from DFT calculations showing electrostatic potential (ESP) mapped onto total electron density for the facial (left) and meridional (right) isomers of $[Y(MPQ)_3]$ viewed along the pseudo-3-fold rotational axis, respectively.

agreement with our results, the meridional isomer is predicted to be considerably more stable than the corresponding facial isomer, by ca. 27 kJ/mol. As a rationale, we note that the close proximity of the three coordinated oxygen atoms for the facial isomer results in considerable negative charge (within ca. 3.1 Å), and it may be the increase in electrostatic repulsion which leads to preferential formation of the meridional species. This also agrees with the "up–up–down" meridional coordination pattern being more commonly observed in the literature.^{12–14,16–19,21,22,24}

To improve our understanding of the ligand-centered electronic structures, additional TD-DFT calculations were undertaken for both the deprotonated MPQ⁻ ligand and the meridional $[Y(MPQ)_3]$ complex using the same basis set as above, and the results are detailed in Tables S3 and S4 and Figures S15 and S16 in the Supporting Information. To summarize, for the MPQ⁻ ligand, the lowest energy S₁ and T₁ excited states are predicted to be located at ca. 454 nm (22030 cm^{-1}) and 722 nm (13850 cm^{-1}) respectively, and a consideration of the HOMOs and LUMOs involved reveals this to be an intraligand charge transfer (ILCT) transition, with considerable $n-\pi^*$ character. Similarly, for the Y^{III} complex, the lowest energy S_1 and T_1 excited states are predicted to be located at ca. 427 nm (23400 cm^{-1}) and 637 nm (15700 cm⁻¹), which also have principally $n-\pi^*$ character together with a small contribution of $\pi - \pi^*$ character.

Photophysical Studies. The UV-vis absorption spectra for the MPHQ ligand and the corresponding $[Ln(MPQ)_3]$ complexes (Ln = Nd, Gd, Er, Yb, Lu) in CH₂Cl₂ at room temperature are shown in Figure 6. As expected, the ligand displays several bands in the UV region, corresponding to $\pi \rightarrow \pi^*$ transitions within the pyridine and the quinoline chromophores. Upon deprotonation of the MPHQ ligand using Me₄NOH and with MeOH as the solvent, a relatively broad absorption band at ca. 405 nm is observed (see Figure S17 in the Supporting Information). This matches well to the estimated lowest energy S₁ excited state obtained from TD-DFT calculations for the deprotonated ligand, and based on the HOMOs/LUMOs involved (see Table S4 and Figure S15 in the Supporting Information), we assign this peak to a primarily $n \rightarrow \pi^*$ transition.



Figure 6. UV–vis absorption spectra of MPHQ ligand and $[Ln(MPQ)_3]$ complexes in CH_2Cl_2 at room temperature.

For the corresponding $[Ln(MPQ)_3]$ complexes, a broad absorption band with a peak maximum at ca. 465 nm and ε value of ca. 11000 M^{-1} cm⁻¹ is apparent in the visible region. In contrast to a previous report¹⁴ for Ln^{III} complexes of a structurally similar ligand, we also assign this visible absorption band to an $n \rightarrow \pi^*$ transition, which agrees well with the corresponding TD-DFT calculation undertaken for the [Y- $(MPQ)_3$ complex and is experimentally supported by an observed blue shift of the absorption maximum by ca. 30 nm when MeOH was used as the solvent (see Figure S18 in the Supporting Information). The position of this $n \rightarrow \pi^*$ band is also within the same region for other similar HQ derivatives reported by Shavaleev et al.,^{12,13} using the same solvent system. This band accounts for the orange color of the complexes in both the solid state and solution. On the other hand, the narrow absorption band with a maximum at ca. 320 nm and ε value of 150000 M⁻¹ cm⁻¹ remains essentially unchanged using either MeOH or CH2Cl2 as solvent and thus is correspondingly assigned as a $\pi \to \pi^*$ transition.

Since the Lu^{III} cation does not contain any $4f^*$ excited states, and the 4f* metal-centered accepting levels of Gd^{III} are located at high energy (e.g., ${}^6P_{7/2}$ at 32220 cm⁻¹), organic complexes of these metal ions typically display only ligandcentered photophysical processes. Moreover, the low-temperature emission spectra of the latter are often used to estimate the position of an organic ligand's lowest energy triplet state. A comparison of the room-temperature emission spectra for the Lu^{III} and Gd^{III} complexes and the corresponding 77 K emission spectra for the $[Gd(MPQ)_3]$ complex in a 4:1 (v/v) EtOH:MeOH glassing solvent is shown in Figure S19 in the Supporting Information. At room temperature, a very broad and weak emission band at ca. 620 nm (16130 cm⁻¹) is observed for the Gd^{III} complex, while a similar band is observed for the Lu^{III} complex which is qualitatively more intense. Interestingly, the emission spectrum for the Gd^{III} complex at 77 K shows only an increase in intensity for the observed broad emission band, which is also slightly blue shifted to ca. 600 nm (16000 cm⁻¹). Based on the observed blue shift in frozen solution, and the lack of any new emission peaks, we attribute this emission to enhanced fluorescence from the ligand-centered singlet excited state. This is also corroborated by TCSPC measurements for the [Lu(MPQ)₃] complex in the same solvent system, which yielded a decay lifetime on the nanosecond time scale (see Figure S20 in the Supporting Information). Hence, any emission from the lowest

energy T_1 state if present must be very weak or alternately may be masked by the increase in S_1 emission intensity.

By comparison, ligand-centered visible emission is not observed for the Yb^{III}, Er^{III}, and Nd^{III} complexes. Instead, each of these show characteristic emission bands in the NIR region, as shown in Figure 7, which are characteristic for each metal ion.



Figure 7. NIR emission spectra of $[Ln(MPQ)_3]$ complexes in CH_2Cl_2 solution at room temperature (λ_{ex} 465 nm).

The spectrum for the Nd^{III} complex displays three emission bands at ca. 890 nm, 1060 and 1350 nm, corresponding to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}, {}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$, and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ transitions, respectively, which are further split by crystal field effects.^{30,31} The Er^{III} complex shows the characteristic, albeit very weak, emission band at ca. 1520 nm, which is assigned to the ${}^{4}I_{13/2} \rightarrow$ ${}^{4}I_{15/2}$ transition. In contrast, the emission spectrum for the Yb^{III} complex is very intense, revealing a highly resolved ${}^2F_{5/2} \rightarrow$ ${}^{2}F_{7/2}$ transition at ca. 980 nm, with several minor peaks due to the presence of hot bands³¹ and crystal field splitting of the single electronic transition.³⁰ Notably, the observed splitting pattern for this transition is very similar to that for the Yb^{III} ML₃ complex reported by Wei et al.,¹⁴ which can be understood given the identical nature of the first coordination sphere and which further confirms the formation of a lowsymmetry C_1 complex in the present case.

Photoluminescence Efficiency. To quantify the overall efficiency of the NIR emission, photoluminescence quantum yield (PLQY) measurements were undertaken for the Yb^{III}

complex using $[Yb(TTA)_3(H_2O)_2]$ (where TTA = 2thenoyltrifluoroacetonate)³² as a suitable reference (Φ_{PL} = 0.12% in toluene). The result we obtain of Φ_{PL} = 1.0% in CH_2Cl_2 (see Figure S21 in the Supporting Information) remains modest in comparison to reports using similar 8hydroxyquinoline derivatives with comparable coordination environments.^{12,14,15} In order to obtain a better comparison with the quantum yield of $\Phi_{PL} = 0.90\%$ recently reported by Wei et al.¹⁴ for a structurally very similar $[Yb(PND)_3]$ complex (where PND = 6-(pyridin-2-yl)-1,5-naphthyridin-4-ol), we also undertook additional PLQY measurements using the same 10:1 (v/v) CH₃CN:MeOH mixed solvent system. In this case, we obtained a value of $\Phi_{\rm PL}$ = 0.70% (see Figure S22 in the Supporting Information), which is lower than the corresponding measurement in CH₂Cl₂ most likely due to competitive nonradiative quenching of the emissive $4f^*$ excited state by coupling to OH vibrational overtones of the solvent. Importantly, we note the value of 0.35% used by Wei et al. as the PLQY for the reference standard $[Yb(TTA)_3(H_2O)_2]$ in toluene is higher than a more recent value of $\Phi_{\rm ref}$ = 0.12% reported by the original authors.^{32,33} We opted to use the lower value for Φ_{ref} since this appears to be more consistent with time-resolved luminescence lifetime measurements.³² Correcting for the difference in $\Phi_{\rm std}$ we obtain a value of Φ_{PL} = 0.31% for [Yb(PND)₃] and hence note that the PLQY obtained for $[Yb(MPQ)_3]$ represents an approximate 2-fold improvement in the overall photoluminescence efficiency when compared under identical conditions. We suggest that the reason for this improvement is likely related to the differing electronic structures of the substituted 8-hydroxyquinoline (MPQ⁻) vs 4-hydroxy-1,5-naphthyridine (PND⁻) chromophores. In particular, the latter has a lowest energy T_1 state at ca. 18940 cm⁻¹. In the present case, unfortunately the lowest energy triplet state could not be located using low-temperature measurements but nonetheless cannot be any higher than the lowest energy singlet state, located at 16130 cm⁻¹.

Transient Absorption Spectroscopy. Finally, in an effort to rationalize the NIR photoluminescence efficiency, and to gain an insight into the intersystem crossing and energy transfer processes occurring in these complexes, we have undertaken a series of transient absorption (TA) experiments. Using a combination of nanosecond and femtosecond time scales, the kinetic profiles for formation and subsequent decay of the lowest energy ligand-centered S₁ and T₁ excited states



Figure 8. (a) Observed femtosecond transient absorption (fs-TA) spectra at selected time delays for $[Gd(MPQ)_3]$ in CH₂Cl₂ (λ_{ex} 470 nm). (b) Corresponding decay kinetics and global fits at selected wavelengths from 350 to 650 nm. (c) Resulting decay associated difference spectra (DADS) and lifetime summary from global fitting analysis (see text for details).

Table 2. Summary of the Excited-State Lifetimes for the $[Ln(MPQ)_3]$ Complexes (Ln = Lu, Gd, Yb, Er, Nd) in	CH ₂ Cl ₂ Solution
(λ_{ex} 470 nm) Obtained by a Combination of fs-TA and ns-TA Experiments	

complex	S ₁ (ps)	$k_{\rm obs} \ (10^{10} \ {\rm s}^{-1})$	$\Delta\Phi_{\rm ISC}$ (%)	T_1 (ns)	$k_{\rm obs} \ (10^{10} \ {\rm s}^{-1})$	$k_{\rm EET} \ (10^{10} \ { m s}^{-1})$	Φ_{EET} (%)	η_{sens} (%)
[Lu(MPQ) ₃]	440.1 ± 2.3	0.23	N/A	298.8 ± 4.1	0.00033	N/A	N/A	N/A
$[Gd(MPQ)_3]$	49.1 ± 0.4	2.04	88.9	266.1 ± 1.2	0.00038	N/A	N/A	N/A
$[Yb(MPQ)_3]$	10.9 ± 0.2	9.17	97.5	0.0415 ± 0.0006	2.41	2.41	>99.9	97.4
$[Er(MPQ)_3]$	18.2 ± 0.3	5.56	95.9	0.0986 ± 0.0010	1.01	1.01	>99.9	95.8
$[Nd(MPQ)_3]$	3.3 ± 0.1	33.3	99.3	0.0263 ± 0.0002	3.80	3.80	>99.9	99.2

have been evaluated for each of the $[Ln(MPQ)_3]$ complexes (Ln = Lu, Gd, Yb, Er, Nd). The resulting fs-TA spectra for the Gd^{III} complex as a representative example are shown in Figure 8, while data for the remaining complexes are shown in Figures S23–S28 in the Supporting Information.

As expected, the TA spectra for each complex display essentially identical spectral features, since the ultrafast processes being investigated are all ligand based. However, the relevant time scales were found to be highly dependent on the identity of the chelated metal ion. Upon excitation at λ_{ex} 470 nm, a relatively sharp excited state absorption (ESA) is immediately apparent, centered at ca. 550 nm, together with a second ESA peak which is visible as a shoulder at ca. 350 nm. These features simultaneously decay on a relatively short time scale, yielding spectra at longer time delays which feature much broader and less well resolved ESA features, which are longer lived and have a notable absorption band at ca. 650 nm. For the $[Lu(MPQ)_3]$ complex, both the short- and long-lived ESA signals were resolved using ns-TA measurements (see Figure S23 in the Supporting Information). We assign the short-lived component (ca. 0.7 ns) to S_1 excited state decay, which we note agrees with TCSPC measurements for ligand-based fluorescence lifetime from the $[Lu(MPQ)_3]$ complex. Instead, we assign the long-lived component (ca. 299 ns) to the ligandcentered T1 excited state, which could be confirmed by an increase in the apparent lifetime obtain in degassed measurements.

For the Gd^{III} complex, only the long-lived decay component was observed (ca. 266 ns), and the ns-TA data could be well reproduced using a simple monoexponential decay function (see Figure S24 in the Supporting Information), which suggests that the S₁ excited state lifetime is shorter than the instrument response function (IRF) of our ns-TA setup (ca. 100 ps) and also is in accord with the less intense ligand-based fluorescence observed in the steady state. Moreover, for the other paramagnetic Ln^{III} complexes (Ln = Nd, Er, Yb), no TA signals were observed on the nanosecond time scale, implying that the decays of the both the S₁ and T₁ excited states for these complexes are ultrafast.

As a result, to elucidate the dynamics involved for these complexes, we turned to femtosecond TA (fs-TA), which was also used to more accurately characterize the decay of the S_1 excited state for the $[Lu(MPQ)_3]$ complex. In all cases, our fit of the fs-TA data included the presence of two components, and the dynamics for the ΔA signals for each complex were fit globally at all wavelengths in the range of the measured spectra using the biexponential equation

$$\Delta A_t = A_1 e^{-1/\tau_1(t)} + A_2 e^{-1/\tau_2(t)}$$

where ΔA_t is the intensity of the ΔA signal at time (*t*), A_1 and A_2 are pre-exponential scaling factors, and τ_1 and τ_2 are the evaluated lifetimes. For the Lu^{III} and Gd^{III} complexes, the long-lived values were fixed to our results from ns-TA measure-

ments. A summary of the S_1 and T_1 excited state lifetimes obtained from this global analysis procedure for each of the $[Ln(MPQ)_3]$ complexes is given in Table 2.

As anticipated, the lifetime of the S1 excited state for $[Gd(MPQ)_3]$ is much smaller than that of $[Lu(MPQ)_3]$, and lifetimes for the Yb^{III}, Er^{III}, and Nd^{III} complexes are also comparatively short. Since we do not expect the radiative $(k_{\rm R})$ decay pathways to differ significantly within this family of isostructural complexes, the large decrease in the S1 excited state lifetime must be necessarily attributed to an increase in nonradiative deactivation (k_{NR}) and, in particular, is evidence that intersystem crossing (ISC) is much more efficient for complexes of the paramagnetic Ln^{III} cations. This is supported by a large increase in the relative intensity of the $T_1 \rightarrow T_n$ ESA features observed by fs-TA for these complexes (see Figures S25–S28 in the Supporting Information). Numerically, we can estimate the increase in ISC efficiency (Δ ISC) from the inverse of the excited state lifetimes in comparison to the Lu^{III} complex, with results also summarized in Table 2, which reveal that the increase in the ISC process is very efficient, ranging from 90 to 100% depending on the Ln^{III} cation. For the Nd^{III} , Yb^{III}, and Er^{III} complexes, we note that the decrease in S₁ excited state lifetimes could also be due to the potential for a singlet-mediated energy transfer pathway, but if present, this can only represent a small component since the $T_1 \rightarrow T_n$ signal intensity would otherwise also decrease, which is not observed experimentally.

Interestingly, the T_1 excited state lifetimes for the Yb^{III}, Er^{III}, and Nd^{III} complexes are also very short and were well resolved on the picosecond time scale, whereas the Lu^{III} and Gd^{III} complexes were instead much longer lived. In this case, the much shorter lifetimes can be rationalized due to the presence of competing energy transfer pathways for the former, which are not possible in the case of the Gd^{III} or Lu^{III} complexes. Using the equations

$$k_{\text{EET}} = 1/\tau_{\text{q}} - 1/\tau_{\text{u}}$$
$$\Phi_{\text{EET}} = 1 - \tau_{\text{q}}/\tau_{\text{u}}$$

where τ_q and τ_u are the observed lifetimes of the T_1 excited state in the presence or absence of the $4f^*$ acceptor as a quencher, we are able to calculate the corresponding rates and quantum yields of the triplet mediated energy transfer process for each Ln^{III} cation.

As summarized in Table 2, the resulting rate constants (k_{EET}) and quantum yields (Φ_{EET}) reveal that energy transfer from the lowest energy T₁ excited state to the NIR-emitting Ln^{III} cations is extremely efficient (>99.9% in all cases). Interestingly, the fastest energy transfer rate constant is obtained for the Nd^{III} complex, which can be rationalized by the presence of several potential 4*f** accepting levels, resulting in an improved spectral overlap. Moreover, using Φ_{EET} in conjunction with the highly efficient ISC processes, the overall sensitization efficiency $(\eta_{\rm sens})$ can be estimated using the equation

$$\eta_{\rm sens} = \Phi_{\rm ISC} \Phi_{\rm EET}$$

The results in this case for $Ln^{III} = Yb$, Er, Nd are all higher than 95%, revealing that sensitization of the emitting $4f^*$ metal cations can be considered to be an essentially quantitative process for these $[Ln(MPQ)_3]$ complexes.

CONCLUSIONS

We have demonstrated that the 2-(5-methylpyridin-2-yl)-8quinolinolate (MPQ⁻) ligand is an efficient tridentate N,N,O ligand, forming charge-neutral nine-coordinate mononuclear [Ln(MPQ)₃] complexes with a variety of Ln^{III} cations, which have been well characterized in solution and the solid state. For the Ln = Yb, Er, Nd complexes, these display characteristic metal-centered luminescence in the NIR region upon visible excitation. In particular, the Yb^{III} complex displayed a relative PLQY of 1.0%, which is higher than those for previously reported complexes which use a similar ligand system and coordination environment. The photophysical properties for all of the Ln^{III} complexes herein were investigated by means of absorption, emission, and transient absorption spectroscopy. For the Yb^{III}, Er^{III}, and Nd^{III} complexes, extremely efficient intersystem crossing from the singlet to triplet state and subsequent ultrafast energy transfer from the ligand-centered triplet to metal-centered 4f* excited states was observed, and analysis of the kinetic profiles for these states reveals that the antenna effect can be considered to be essentially quantitative in these complexes.

EXPERIMENTAL SECTION

General Considerations. All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Jiaton) and were used without further purification unless otherwise noted. Selected solvents (THF, diethyl ether, CH₃CN) were obtained from a PureSolv solvent purification system. MeOH for metal complexation was dried over activated molecular sieves (3 Å) prior to use. Highpurity (99.9%) commercially obtained $LnCl_3 \cdot xH_2O$ metal salts (Ln = Nd, Gd, Er, Yb, Lu, x = 6) were used in all metal complexation reactions. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers, and all signals were referenced to the corresponding residual solvent peak. Gas chromatography mass spectrometry measurements (GCMS) were performed using a Shimadzu GCMS-QP2010 Ultra instrument with a Shimadzu EI source. Elemental analyses (C, H, N) were conducted by the University of Queensland School of Chemistry and Molecular Biosciences Microanalytical Service using a Thermo Scientific Flash 2000 Organic Elemental Analyzer.

Synthesis. The required 2-amino-3-methoxybenzaldehyde $(1)^{25}$ and 2-acetyl-5-methylpyridine $(2)^{26}$ were prepared according to published procedures.

8-Methoxy-2-(5-methylpyridin-2-yl)quinoline (3). A solution of KOH (4.62 g, 82.4 mmol) in ethanol (18 mL) was added to a solution of 1 (4.62 g, 30.6 mmol) and 2 (5.20 g, 38.5 mmol) in ethanol (284 mL). The reaction mixture was heated at reflux for 20 h under an N₂ atmosphere. The reaction mixture was then cooled to room temperature and concentrated in vacuo. The residue was dissolved in dichloromethane, washed with water and brine, and extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by chromatography on neutral alumina, with petroleum spirit/ethyl acetate (100/0, 90/10, 20/80) as eluent, affording 3 as a pale yellow crystalline powder (6.87 g, 90%). ¹H NMR (CDCl₃): δ 8.59 (m, 2H), 8.53 (s, 1H), 8.22 (d, 1H, J = 9 Hz), 7.64 (d, 1H, J = 9 Hz), 7.39 (m, 2H), 7.05 (dd, 1H, J = 9, 3 Hz), 4.11 (s, 3H), 2.40 (s,

3H). ¹³C NMR (CDCl₃): δ 155.5, 155.2, 153.8, 149.5, 139.7, 137.4, 136.7, 133.7, 129.2, 126.8, 121.6, 119.6, 119.4, 107.9, 56.2, 18.4. Anal. Calcd: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.22; H, 5.66; N, 11.12. GCMS (EI): m/z calcd for C₁₆H₁₄N₂O, 250.11; found, 249 [M – H]⁺ and 250 [M]⁺

2-(5-Methylpyridin-2-yl)-8-hydroxyquinoline (4). A solution of 3 (6.00 g, 24.1 mmol) in HBr (48%, 352 mL) was heated at 150 °C overnight under an N2 atmosphere. The reaction mixture was cooled to room temperature and poured into a flask containing 1 L of cold distilled water. The yellow precipitate was collected, extracted with dichloromethane. and washed with saturated aqueous NaHCO3 solution. Notably, caution should be taken to ensure the pH of the aqueous solution is within the 5-7 pH range, to avoid protonation/ deprotonation equilibria. The combined organic layer was dried over anhydrous MgSO4 and concentrated in vacuo to give 4 as a tan solid (5.25 g, 92%). ¹H NMR (CDCl₃): δ 8.56 (d, 2H, J = 9 Hz), 8.46 (d, 1H, J = 6 Hz), 8.33 (s, 1H, OH), 8.24 (d, 1H, J = 9 Hz), 7.65 (dd, 1H, J = 9, 3 Hz), 7.43 (t, 1H, J = 9 Hz), 7.34 (dd, 1H, J = 6, 3 Hz), 7.18 (dd, 1H, J = 6, 3 Hz), 2.43 (s, 3H). ¹³C NMR (CDCl₃): δ 154.0, 153.0, 152.2, 149.7, 137.6, 137.5, 136.9, 134.1, 128.3, 127.8, 121.0, 119.6, 117.8, 110.1, 18.4. Anal. Calcd: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.23; H, 5.15; N, 11.80. GCMS (EI): m/z calcd for C₁₅H₁₂N₂O, 236.09; found, 236 [M]⁺.

Complexation. Ligand 4 (3 equiv) was dissolved in MeOH (3 mL), and to the resulting pale yellow solution was added 3.6 equiv of $N(CH_3)_4OH$ in MeOH (2 mL). The resulting bright yellow solution was stirred at room temperature for 20 min. A solution of $LnCl_3$ · xH_2O (1 equiv) in MeOH (2 mL) was added dropwise. Upon addition, the reaction mixture turned a distinct orange-red. The reaction mixture was refluxed for ca. 2 h, during which time an orange-red precipitate formed. Strict control of the refluxing time was not required. The suspension was cooled to room temperature, and the precipitate was filtered, thoroughly washed with cold methanol/water (10/1) followed by diethyl ether, and then dried under high vacuum.

 $[Yb(MPQ)_3]$ ·H₂O. Yield: 30 mg (0.033 mmol, 60%). Orange-red solid. Anal. Calcd: C, 60.26; H, 3.93; N, 9.37. Found: C, 59.99; H, 3.80; N, 9.11.

 $[Er(MPQ)_3]$ -2H₂O. Yield: 28 mg (0.031 mmol, 54%). Orange-red solid. Anal. Calcd: C, 59.45; H, 4.10; N, 9.24. Found: C, 59.43; H, 3.73; N, 9.10.

[Nd(MPQ)₃]·2H₂O. Yield: 34 mg (0.038 mmol, 69%). Orange-red solid. Anal. Calcd: C, 61.00; H, 4.21; N, 9.48. Found: C, 61.06; H, 3.89; N, 9.43.

 $[Lu(MPQ)_3]$ ·H₂O. Yield: 30 mg (0.033 mmol, 59%). Orange-red solid. Anal. Calcd: C, 60.14; H, 3.93; N, 9.35. Found: C, 60.02; H, 3.97; N, 9.19.

 $[Gd(MPQ)_3]$ ·H₂O. Yield: 22 mg (0.024 mmol, 60%). Orange-red solid. Anal. Calcd: C, 61.35; H, 4.00; N, 9.54. Found: C, 61.01; H, 3.91; N, 9.31.

[Y(MPQ)₃]·2H₂O Yield: 26 mg (0.031 mmol, 55%). Orange-red solid. Anal. Calc'd. (%) C 65.06, H 4.49, N 10.12, Found C 65.30, H 4.19, N 10.07.

X-ray Crystallography. Single-crystal X-ray diffraction (SXRD) data were collected using either an Oxford Diffraction Gemini CCD diffractometer operating at 190 K and employing graphite-monochromated Cu/Mo K α radiation ($\lambda = 1.5418/0.71073$ Å) generated from a sealed tube at 190 K, or using beamline MX1 of the Australian Synchrotron facility with silicon double crystal mono-chromated radiation at 100 K.^{34,35} Data integration and reduction were performed using CrysAlis Pro³⁶ and XDS, respectively.³⁷ Empirical absorption corrections (ψ scans) were applied using CrysAlisPro³⁶ or SADABS at the Australian Synchrotron facility. Structures were solved by SHELXT,³⁸ and subsequent refinements were carried out using SHELX programs³⁹ via the Olex2 (Version 1.2) interface.⁴⁰ All non-H atoms were refined anisotropically. Molecular images were produced using Mercury (Version 3.7).⁴¹

Photophysical Characterization. All photophysical measurements were undertaken using matching quartz cuvettes (either 1 cm or 1 mm path length) and were referenced to the solvent used (CH₂Cl₂) as a blank. Stock solutions of the Ln(III) metal complexes used for absorption and emission measurements were prepared at ca. 2×10^{-5} M in CH₂Cl₂. UV-visible absorption spectra were recorded using an Agilent Cary 60 UV-vis spectrometer and the Cary WinUV Scan Application (Version 5.0.0.999). Emission and excitation spectra were measured using a Horiba JY FluoroLog-311 spectrofluorimeter and the FluorEssence (Version 3.1.5.11) software package. For measurements in the NIR region, a liquid N₂ cooled InGaAs detector (DSS-IGA020L) was used, with excitation provided by a standard 450 W Xe arc lamp. Low-temperature (77 K) phosphorescence measurements were undertaken using the same FluoroLog-311 spectrofluorimeter with the sample dissolved in a 4/1 EtOH/MeOH (v/v) glassing solvent, loaded into a quartz tube filled with liquid N2. All spectrophotometric data were processed using Igor (Wavemetrics, Version 6.1.1.2). Femtosecond transient absorption measurements were undertaken using an amplified laser system (Spitfire ACE, Spectra Physics) as the excitation source, delivering ca. 100 fs 800 nm laser pulses at a 1 kHz repetition rate. Approximately 0.1 mJ of this output was attenuated and focused onto a 3 mm CaF2 window to generate a white light continuum probe pulse in the visible region from ca. 350 to 650 nm. The remainder of the laser fundamental was coupled to an OPA system (Topas Prime, Light Conversion) delivering femtosecond tunable excitation pulses at 470 nm, and the pump pulse polarization was set to the magic angle with respect to the probe. The absorbance of samples was ca. 0.6 over the 2 mm path length cell used, and samples were continuously stirred mechanically. The instrument response function (IRF) had a full width at halfmaximum (fwhm) of ca. 200 fs, as measured experimentally by a Gaussian fit to the scattered laser excitation profile, and all femtosecond spectra were corrected for the chirp of the probe pulses. For sub-nanosecond transient absorption measurements, a white light continuum from ca. 380 to 900 nm was generated using a pulsed Nd:YAG based Leukos-STM super continuum light source, the timing of which was controlled electronically using the sync out of the amplified laser system. The instrument response function (IRF) for this setup dictated by the electronic timing resolution was ca. 100 ps. The resulting time traces were analyzed globally using commercially available software (Igor, Version 6.1.2.1, Wavemetrics). Quantum yields were determined by the optically dilute method with an optical density of less than 0.1. $[Yb(TTA)_3(H_2O)_2]$ (where TTA = thenoyltrifluoromethylacetylacetonate; $\Phi_{PL} = 0.12\%^{32}$) was used as the reference. Excitation wavelengths of 465 and 345 nm were used for the sample and reference, respectively.

DFT Calculations. Static and time dependent DFT calculations were performed using the Gaussian 09W package (Revision B.01).⁴² Molecular structures for the MPQ anion and the corresponding facial and meridional [Y(MPQ)₃] isomers were optimized in the gas phase, employing the CAM-B3LYP functional with the 6-31G* basis set for C, H, N, and O atoms and the LanL2DZ basis set for the Y atom. Subsequent frequency calculations of the optimized structures were performed to ensure that no imaginary vibrational frequencies were present. Molecular mechanics (MM) single-point energy calculations for the facial and meridional isomers were performed using the same Gaussian 09W package with standard UFF force field parameters for all atoms. Semiempirical PM7/Sparkle⁴³ single-point energy calculations for the facial and meridional isomers were undertaken using MOPAC2016.44 All single-point energy calculations were performed using the DFT optimized geometry. A summary of the most significant results is presented in Tables S3 and S4 and Figure S15 and \$16 in the Supporting Information.

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.8b01438.

Details of X-ray crystallography, additional NMR spectra, DFT calculations, and additional absorption, emission, and transient absorption spectra (PDF)

Accession Codes

CCDC 1844144–1844147 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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Notes

The authors declare no competing financial interest.

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