

# The photophysics of a luminescent ruthenium polypyridyl complex with pendant $\beta$ -cyclodextrin; pH modulation of lifetime and photoinduced electron transfer

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**Abstract** At room temperature,  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})][\text{PF}_6]_2$ , (phen-CD is 6<sup>A</sup>-(5-amino-1, 10-phenanthroline)-6<sup>A</sup>-deoxy- $\beta$ -Cyclodextrin and bpy is 2,2'-bipyridine) exhibits an intense metal ligand charge transfer (MLCT) transition at 452 nm and a long lived luminescence, centred at 618 nm. We demonstrate, for the first time, that the luminescence quantum yield and lifetime of the Ru (II) polypyridyl centre depends markedly on the solution pH. The pH sensitive range extends from pH 3.9 to pH 13.2 and the luminescence quantum yield changes by more than 60% over this range. This pH sensitivity is attributed to protonation/deprotonation of the secondary amine group bridge between the phenanthroline unit and CD. The complex exhibits strong host-guest binding to anthraquinone and anthraquinone-2-carboxylic acid, with concomitant quenching of the  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  excited state. This quenching arises from efficient intramolecular electron transfer. The sensitivity of this photoinduced process to the protonation state of the bridge is discussed.

**Keywords** Cyclodextrin · Ruthenium polypyridyl · Luminescence · pH · Anthraquinone · Quenching · Electron transfer

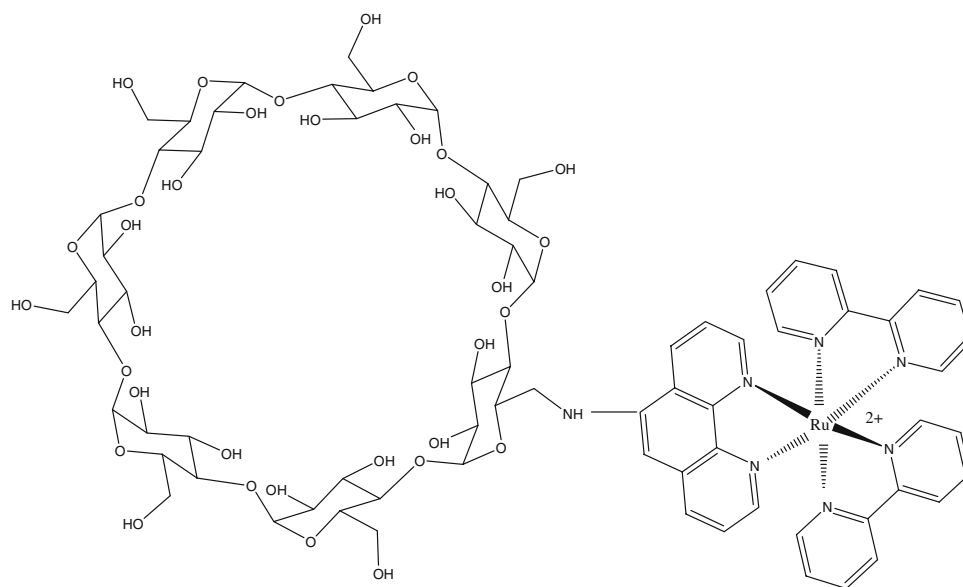
## Introduction

Cyclodextrin (CD), displays both a rich host-guest chemistry and versatile synthetic chemistry. An attractive proposition is to functionalise CD with luminophores in order to transduce molecular recognition events. Furthermore, such functionalised CDs are attractive as light addressable components in supramolecular assemblies, where the CD can be used to create an extended assembly through non-covalent host guest interactions. Luminescent transition metal complexes are particularly appealing components in the design of supramolecular and sensing systems. The incorporation of metal complexes confers useful photophysical properties including long-lived excited states and accessible redox properties allowing them to undergo photoinduced energy and electron transfer processes [1]. Evidence for the ability of CD to support electronic communication within a supramolecular structure is growing [2–4]. Our group previously reported on the synthesis of the photoactive complex  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ , shown in Scheme 1. In this system, 1,10-phenanthroline is linked via a secondary amine to the 6-position of the primary rim of  $\beta$ -cyclodextrin which was then coordinated to a ruthenium polypyridyl [5]. In the resulting structure, the secondary amine is anticipated to be basic.

In this contribution, we report on the pH sensitivity of the luminescence of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  and on the ability of supramolecular complex to support photoinduced electron transfer between an included guest and the ruthenium centre. We discuss the possibility of modulating this communication through protonation/deprotonation of the amine bridge, phen-CD is 6<sup>A</sup>-(5-amino-1, 10-phenanthro-

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**Scheme 1** Structure of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$

line)-6<sup>A</sup>-deoxy-  $\beta$ -Cyclodextrin and bpy is 2,2'-bipyridine.

## Experimental

$\beta$ -Cyclodextrin (Aldrich), 5-nitro-1,10-phenanthroline (Aldrich), 2,2'-bipyridine (Aldrich),  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (Aldrich), Dimethylformamide (DMF) (Aldrich) and N-methyl-2-pyrrolidinone (NMP) HPLC grade (Aldrich), Britton-Robinson buffer tablets (BDH Chemicals Ltd.), anthraquinone and anthraquinone-2-carboxylic acid (BDH Chemicals Ltd) were used as received.

6<sup>A</sup>-deoxy-6<sup>A</sup>-P-toluenesulphonyl-  $\beta$ -Cyclodextrin [6], cis- $\text{Ru}(\text{bpy})_2\text{Cl}_2$  [7], and 6-(5-amino-1, 10-phenanthroline)-6<sup>A</sup>-deoxy-  $\beta$ -cyclodextrin, ( $\beta$ -CDphen) [5], were synthesized and purified according to published procedures.

Ruthenium (II) (Bisbipyridine)(6<sup>A</sup>-(5-amino-1, 10-phenanthroline)-6<sup>A</sup>-deoxy-  $\beta$ -Cyclodextrin

$[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  was synthesized as described previously, and purified using size-exclusion chromatography on Sephadex G-75, with water as eluent.  $\{M/z = 878.8, [\text{M}-2\text{PF}_6]^{2+}, 1637, [\text{M}-\text{PF}_6]^{+1}\}$ , structure was confirmed from 2D <sup>1</sup>H-NMR which conformed to previously reported values [5].

<sup>1</sup>H NMR spectra were recorded on a Bruker Advance series 400 MHz NMR spectrometer. Mass spectra were acquired using a positive ion mode on a Bruker LC/MS Esquire. Electronic absorption spectra

were measured on a Shimadzu 3500 UV-VIS/NIR spectrophotometer. Cyclic voltammetry was carried out using a CH Instruments CH602 electrochemical workstation. A conventional three-electrode cell was used, employing glassy carbon as working, Ag/AgCl as reference, and Pt wire as counter electrodes. Electrochemistry was conducted in DMF with 0.1 M tetrabutylammoniumtetrafluoroborate ( $\text{TBABF}_4$ ) as supporting electrolyte under an  $\text{N}_2$  atmosphere. pH titrations were performed in the pH range 7–13.2 using Britton-Robinson buffer. The pH was adjusted by adding conc. NaOH or conc.  $\text{H}_2\text{SO}_4$ . Steady-state emission spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer, and luminescence lifetimes were obtained using a Picoquant Fluotime 100 TCSPC system exciting at 470 nm and detecting at 600 nm. Quantum yields were measured using a comparative method [8]. In quenching studies, the luminophore/quencher concentrations were corrected for dilution.

## Results and discussion

### Electronic and photophysical properties

The UV/Vis spectrum for  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  shows a maximum around 455 nm assigned as a  $[\text{Ru}(t_{2g})^6 \rightarrow \text{Ru}^+(t_{2g})^5\pi^*(\text{bpy})]$  MLCT [5]. The complex exhibits an intense luminescence centred at 618 nm, with a lifetime, from TCSPC of 850 ns in

deaerated DMF, which is reduced to 168 ns in aerated media.

#### pH dependence of the photophysics of $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$

As the secondary amine bridge linking the metal centre to the CD is basic, it is of interest to see if deprotonation/protonation of this site impacts on the photophysics of the metalocyclodextrin. Ultimately, our objective was to determine if protonation/deprotonation of the amine linker could be used as a means to modulate the communication between an included species and the luminophore. Figure 1 shows the effect of pH on the emission spectra of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ . Increasing the pH of the medium results in a significant reduction in the emission intensity of the complex without changing the emission maximum. This latter point is consistent with the electronic spectroscopy, which similarly showed little change to absorbance maxima with pH. Figure 1(b) shows plots of the emission intensity as a function of pH. A single inflection point was observed over this pH range and a  $\text{pH}_i$  of approximately 11.5 was determined from the derivative of the plot. The  $\text{pK}_a$  for this process was estimated, from pH dependent UV absorbance data monitoring at 210 nm, to be 11.4. Comparison with  $\text{pK}_a$  of other secondary amines suggests that the amine is the most likely site of deprotonation at this pH [9]. Deprotonation of the CD hydroxyls are anticipated to occur at higher pH and would not be anticipated to leverage such a strong impact on the photophysics of the remote Ru centre [9]. The inset of Fig. 1a illustrates the effect of increasing the pH on the luminescence lifetime of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ . Consistent with decreased emission intensity at high pH, the luminescent lifetime decreases with increasing pH, e.g., in aerated solution, the lifetime of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  decreased from approximately 168 ns at pH 7

to 56 ns at pH 12 in aerated aqueous buffer. The  $\text{pH}_i$  was employed to estimate an excited state  $\text{pK}_a$  ( $\text{pK}_a^*$ ) for this complex, using the Ireland and Wyatt treatment, [10] of 14.5.

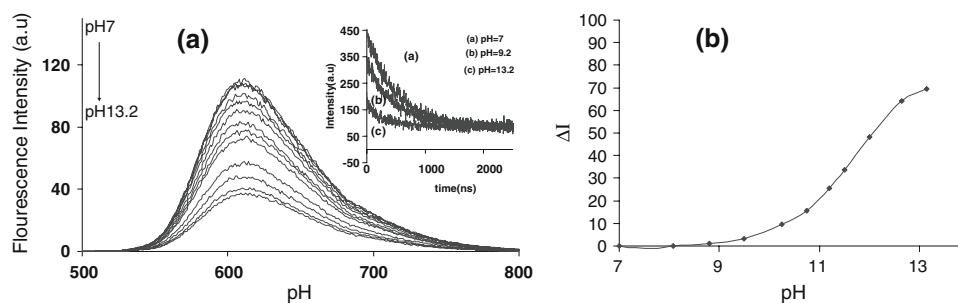
#### Luminescence quenching by anthraquinone guests

The ability of cyclodextrins to form inclusion complexes with polyaromatic guests is well known [11]. We investigated the inclusion of anthraquinone (AQ) and anthraquinone-2-carboxylic acid (AQC) with  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  as both are known to include in  $\beta$ -CD. Also, the ground state reduction potential is such that electron transfer from an excited Ru(II) polypyridyl centre is thermodynamically favourable [12, 13]. As  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  exhibits a relatively long-lived excited state, we anticipated particularly efficient quenching in these systems.

Figures 2a and b show the effect of addition of anthraquinone on the emission intensity of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  at pH 7 and 13.2, respectively. In both instances, efficient quenching of the ruthenium excited state was reflected in substantial decreases in the luminescence intensity with increasing quencher concentration. Similar spectral responses were observed for quenching by AQC. This behaviour may be interpreted in terms of the Stern Volmer equation:

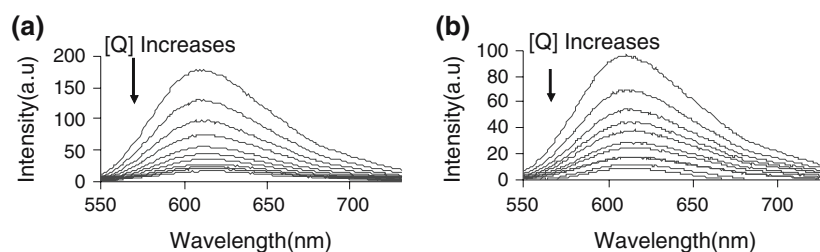
$$\frac{I_0}{I} \text{ or } \frac{\tau_0}{\tau} \text{ or } \frac{\phi_0}{\phi} = 1 + K_{sv}[Q] \quad (1)$$

where  $I_0$  and  $I$  are the luminescence intensities of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  in the absence and presence of quencher, respectively,  $\tau_0$ ,  $\tau$  and  $\phi_0$  and  $\phi$  are the respective excited state lifetimes and luminescence quantum yields in the absence and presence of quencher,  $[Q]$  is the concentration of the quenching species and  $K_{sv}$  is the Stern Volmer constant which is the product of  $k_q$  the quenching rate constant



**Fig. 1** (a) pH-dependent fluorescence titration of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ ,  $2.4 \times 10^{-5} \text{ mol dm}^{-3}$ , excited at 455 in Britton Robinson buffer, pH range from 7–13.2, inset, luminescent decay

of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ ,  $2.4 \times 10^{-5} \text{ mol dm}^{-3}$  at neutral, pH 9 and pH 12 (b) plot of the percentage change in fluorescence intensity ( $\Delta I$ ) at 618 nm as a function of pH

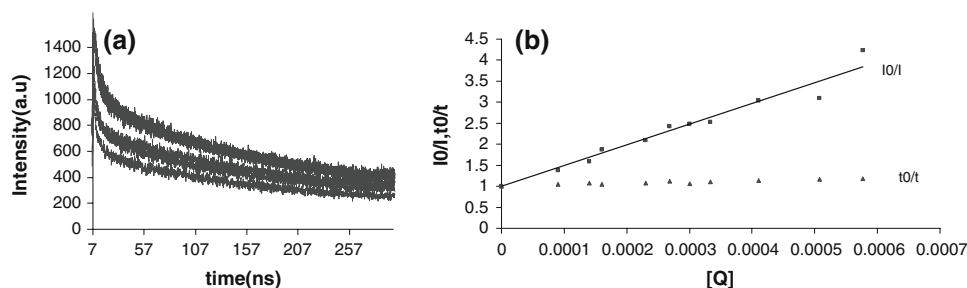


**Fig. 2** Emission spectra of CD-Ru  $2.4 \times 10^{-5} \text{ mol dm}^{-3}$ , on addition of increasing aliquots of  $1 \times 10^{-3} \text{ mol dm}^{-3}$  AQ. (0.90–577  $\mu\text{mol dm}^{-3}$  of AQ) (a) at pH 7 and (b) at pH 13.2

and  $\tau_0$ . For dynamic luminescence quenching, the slopes of  $I_0/I$ ,  $\phi_0/\phi$  and  $\tau_0/\tau$  plots versus quencher concentration  $[Q]$  are expected to be indistinguishable and equal to  $k_q\tau_0$ . Therefore, to confirm that associative quenching was occurring; the impact of increasing AQ concentration on the luminescent lifetime of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  was probed. Addition of quencher, either AQ or AQC, results in a biexponential decay of the luminescence, the first component,  $\tau_1$ , is essentially unchanged from that of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ . The second component is short lived with a lifetime of 5 ns for AQ and 4 ns for AQC. The former we attribute to unassociated complex and the short lifetime component to the complex containing included AQ or anthraquinone carboxylic acid. As shown in Fig. 3b, after the first addition of quencher these lifetimes do not change, on increasing concentration of AQ or AQC to within experimental error. However, the relative contribution of each component to the overall decay is sensitive to the quencher concentration, the % contribution from the shorter component increases with increasing quencher concentration. This behaviour is consistent with static quenching, whereby a ground state association complex forms between donor and acceptor. Under these circumstances, the

slope of Eq. 1 becomes  $K$  corresponding to the association constant between host and guest. Figure 3b shows plots of  $I_0/I$  vs  $[Q]$  for the anthraquinones at neutral pH. The photophysical and quenching data at both neutral and high pH are contained in Table 1. The stability constant for the inclusion complexes formed between  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  and the anthraquinone were evaluated from the slopes as  $14,657 \pm 2,200 \text{ M}^{-1}$  for AQC and  $4,920 \pm 560 \text{ M}^{-1}$  for AQ (Table 1). The association constant was nearly three times higher for the carboxyl containing AQ which we attribute to cooperative H-bonding of the carboxyl group with the CD hydroxyl in addition to inclusion. The Stern-Volmer plots of the luminescence intensity show pronounced positive deviations from linearity without reaching a plateau at higher AQ concentrations. This is attributed to the fact that the resulting anthraquinone-CD complex is itself, luminescent, albeit weakly, whereas application of Eq. (1) assumes that the product species is non-luminescent. The association constants were obtained from the linear portion of the plots at lower quencher concentrations.

The appearance of a short lived component of the luminescence decay and the decreased intensity of the inclusion complexes is attributed to photoinduced



**Fig. 3** (a) Emission decay of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ ,  $2.4 \times 10^{-5} \text{ mol dm}^{-3}$ , in the absence of quencher and in the presence of 577  $\mu\text{mol dm}^{-3}$  AQ. (b) Plots of  $I_0/I$  and  $\tau_0/\tau$  vs  $[Q]$  for the  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  and anthraquinone pH 7

**Table 1** Fluorescence lifetimes and electron-transfer rate constants of self-assembling systems consisting of CD-Ru and quinones

Quinones	$\tau_1$ (neutral) ns	$\tau_2$ (neutral) ns	$\tau_1$ (basic) ns pH = 12.2	$\tau_2$ (basic) ns	$K_{\text{ass}}$ ( $M^{-1}$ )	$k_{\text{et}}$ ( $s^{-1}$ ) pH 7	$k_{\text{et}}$ ( $s^{-1}$ ) pH 13
Without	168 ± 9		56 ± 4				
AQC	161 ± 10	5.0 ± 0.5	52 ± 5	3.62 ± 0.5	14,657 ± 2,200	$1.93 \times 10^8$	$2.5 \times 10^8$
AQ	158 ± 7	4.0 ± 0.4	54 ± 5	4.20 ± 0.4	4,920 ± 560	$2.4 \times 10^8$	$2.2 \times 10^8$

Where AQ is Anthraquinone and AQC is Anthraquinonecarboxylic acid

electron transfer between the excited Ru centre and the included guest. The driving force for the electron transfer can be determined using Eq. (2).

$$\Delta G^0 = [E_{(D^+/D)} - E_{(A/A^-)}] - E_{0-0} \quad (2)$$

where  $E_{(D^+/D)}$ , and  $E_{(A/A^-)}$  are the oxidation and reduction potentials of donor and acceptor sites respectively.  $E_{0-0}$  is the zero-zero spectroscopic energy. The reduction potential of AQ is  $-0.58$  V and AQC is  $-0.74$  V. The oxidation potential of Ru (II/III) is  $1.10$  V vs Ag/AgCl. Providing exergonic driving forces of  $-0.42$  eV and  $-0.26$  eV respectively for excited state electron transfer. Energy transfer from ruthenium to the AQ is precluded, as it would be strongly endergonic, in addition there is little spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.

The rates of photoinduced process can be assessed from Eq. (3)

$$k_{\text{et}} = 1/\tau_2 - 1/\tau_1 \quad (3)$$

where  $\tau_2$  is the lifetime of the inclusion complex, taken to be the short component of the decay, and  $\tau_1$  is the lifetime of  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ . AQ inclusion at the CD is anticipated to induce negligible structural perturbation at the Ruthenium centre. On this basis it is reasonable to assume electron transfer alone is responsible for the reduced lifetimes and that the non-radiative decay pathways available the ruthenium centre remain unchanged for the inclusion complex.

From Eq. (3) then, the rate of electron transfer was estimated to be  $2.4 \times 10^8 \text{ s}^{-1}$  for the AQ inclusion complex and  $1.9 \times 10^8 \text{ s}^{-1}$  for AQC. As described,  $\Delta G$  for electron transfer was estimated to approximately 50% lower for AQC compared with AQ. The electron transfer rate is correspondingly, greater for the AQ complex, but the discrepancy between the two values is not as large as expected on thermodynamic grounds. However, as described,  $K_{\text{assoc}}$  for AQC and  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  is considerably larger than for AQ, which is likely to be due to cooperative hydrophobic-hydrophobic and H-bonding interactions for AQC. It is

tempting to speculate that the reason why the electron transfer rate observed for AQC, is larger than anticipated on thermodynamic grounds is due to the H-bonding interaction. Bridging of this kind is widely recognized to promote electron transfer [14].

The state of protonation of the amine bridge has surprisingly little effect on the rate of  $k_{\text{et}}$  for the  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ -AQ complex where the difference in rate for neutral and basic media is negligible. The electron transfer rate is measurably greater for the AQC complex in basic media, increasing from  $1.9 \times 10^8 \text{ s}^{-1}$  at pH 7 to  $2.5 \times 10^8 \text{ s}^{-1}$  at pH 13. However, this behaviour is attributed to deprotonation of the carboxyl on AQC, which reduces the thermodynamic driving force for electron transfer and may also enhance H-bridging between the carboxylate and the hydroxyls of the CD which should remain protonated at this pH.

## Conclusions

We have conducted detailed photophysical studies on the luminescent host  $[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$ . The complex exhibits a strong pH dependent luminescence, which is attributed to protonation/deprotonation of the secondary amine bridge linking the CD and ruthenium polypyridyl centre. From emission studies, the  $\text{p}K_{\text{a}}$  for the amine was determined to be 11.5.

$[\text{Ru}(\text{bpy})_2(\text{phen-CD})]^{2+}$  forms host guest complexes with AQ and Anthraquinone carboxylic acid, with association constants of  $4,920 \pm 560 \text{ M}^{-1}$  and  $14,657 \pm 2,200 \text{ M}^{-1}$ . The AQ guest appears to participate in efficient photoinduced electron transfer from the excited ruthenium polypyridyl centre. The possibility that protonation/deprotonation at the amine linker can be used to modulate electronic communication between the CD and luminophore was explored. However, the rate of photoinduced electron transfer appeared to be relatively insensitive to the state of protonation of the bridge.

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- Whereby  $PK_a^* = pH_i + \log(\tau_{HB}/\tau_{B^-})$ ,  $pH_i$  is inflection point from the pH dependent emission data and  $\tau_{HB}$  and  $\tau_{B^-}$  are the lifetimes of the protonated and deprotonated species respectively.
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