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Journal of Photochemistry and Photobiology A: Chemistry 102 (1997) 231–235

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Platinum 2,2′:6′,2′-terpyridine complexes as probes for CMC determination of sodium dodecyl sulfate solutions

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Received 28 May 1996; accepted 23 July 1996

Abstract

The platinum complex $[Pt(terpy)(OH)]^+$ (terpy = 2,2′:6′,2′-terpyridine) is a molecular "light switch" for the determination of critical micelle concentration (CMC) in sodium dodecyl sulfate (SDS) micellar system in aqueous solution. No emission from $[Pt(terpy)(OH)]^+$ is observed when the complex is dissolved in water or in very dilute SDS solution but a strong luminescence with emission maximum at 605 nm and excited-state lifetime of 0.1 μs is observed once the SDS concentration reaches the CMC. The emission wavelength of the hydrophobic platinum complex $[Pt(mpterpy)(OH_2)]^{2+}$ (mpterpy = 4′-(*p*-methoxyphenyl)-2,2′:6′,2′-terpyridine) is also a sensitive parameter for CMC determination. Unlike $[Pt(terpy)(OH)]^+$, $[Pt(mpterpy)(OH_2)]^{2+}$ has an emission at 720 nm in SDS solution with concentration below CMC. When the concentration of SDS reaches the CMC, there is a sudden, large hypochromic shift of the emission maximum from 720 nm to 610 nm. The emission maximum of $[Pt(mpterpy)(OH_2)]^{2+}$ stays at 610 nm as the SDS concentration increases further beyond the critical micelle concentration.

Keywords: Platinum complexes; Critical micelle concentration; Micellar system

1. Introduction

The photochemistry and photophysics of sensitizers bound to micelles is an area of current interest [1–3]. This interest arises in part from the utilization of these systems in energy conversion schemes. Micelles are able to selectively sequester the sensitizer, quencher, and/or reaction products. Through judicious choice of micelle, it is possible to increase the quenching efficiency and inhibit the energy-degrading back-reactions. The study of photophysical properties, such as fluorescence excitation and emission spectra and their shifts, the relative intensity of vibronic bands, anisotropy, quantum yields, and excited-state lifetimes, of probes has provided significant information on the micellar structure at the molecular level. Micelle formation and determination of the critical micellar concentration (CMC) can be investigated by selecting an appropriate fluorescent probe. The fluorescence quenching in micelles is a valuable tool to measure micellar size as well as the dynamic properties of the aggregate and of the solubilized species in the host structure. Transition metal complexes are attractive candidates for inclusion in micelles because of the diversity of their photophysics and redox properties. Previous studies mainly focused on $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and its analogues [4–10]. This work presents our studies on micellar systems using $[Pt(terpy)(OH)]^+$ (terpy = 2,2′:6′,2′-terpyridine) and $[Pt(mpterpy)(OH_2)]^{2+}$ (mpterpy = 4′-(*p*-methoxyphenyl)-2,2′:6′,2′-terpyridine) as probes. The photophysics of the platinum complexes tend to be very sensitive to the local environment because of the availability of open coordination sites. A report of the DNA-binding properties of $[Pt(terpy)(OH)]^+$ has recently appeared [11].

2. Experimental

2.1. Materials

Potassium tetrachloroplatinate, 2,2′:6′,2′-terpyridine and deuterium oxide (99.8%) were purchased from Aldrich Chemical Co. Sodium dodecyl sulfate (ultrapure grade) was obtained from J.T. Baker Inc. Triton X-100 (BDH) was used as received. Deionized water was purified by double distillation over alkaline $KMnO_4$. $[Pt(terpy)(OH)]BF_4$ [12], 4′-(*p*-methoxyphenyl)-2,2′:6′,2′-terpyridine (mpterpy) [13] and $[Pt(mpterpy)(Cl)]BF_4$ [14] were prepared by literature methods.

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PII S1010-6030(96)04470-X

2.2. Physical measurements

UV–visible absorption spectra were recorded on a Milton Roy Spectronic 3000 photodiode array spectrophotometer. Steady state emission spectra were recorded on a Spex Fluorolog-2 spectrofluorometer equipped with a 450 W Xenon lamp and a rhodamine-B reference quantum counter. Emission lifetime was measured with a conventional laser system. The excitation source was the third harmonic (355 nm) of a Quanta-Ray Q-switched DCR-3 pulsed Nd–YAG laser (10 Hz, G-resonator). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope. The digitized signal was interfaced to an IBM personal computer and analyzed with a commercial software (Guru II).

Sample solutions for photophysical measurements were prepared by mixing an aqueous platinum complex with micellar solutions of different surfactant concentration and/or double distilled deionized water. The sample solution was then transferred to the 4 ml Pyrex bulb of a two-compartment photolysis cell which is also equipped with a 1 cm pathlength quartz cuvette [15]. The sample solution in the bulb was degassed by no less than three freeze–pump–thaw cycles before photophysical measurements. Unless otherwise specified, the concentration of platinum complexes was approximately 0.05 mM in all experiments.

3. Results and discussion

The emission of $[Pt(terpy)(OH)]^+$ at 621 nm in acetonitrile was assigned to be metal-to-ligand charge transfer transition involving d orbital of Pt and π^* orbital of the terpy ligand [12]. The excited state lifetime and emission maxima of $[Pt(terpy)(OH)]^+$ was found to depend strongly on the polarity of the solvent. In H_2O or D_2O no emission could be observed. Addition of sodium dodecyl sulfate (SDS) to an aqueous solution of $[Pt(terpy)(OH)]^+$ leads to an emission with λ_{max} at 592 nm (Fig. 1(A)). The emission decay curves of $[Pt(terpy)(OH)]^+$ in aqueous SDS solutions are monophasic with excited-state lifetime in 0.1 M SDS being 0.1 μs. Fig. 1(B) shows the excited-state lifetimes of $[Pt(terpy)(OH)]^+$ as a function of SDS concentration. No emission can be detected when the concentration of SDS is less than 6 mM. The lifetime of $[Pt(terpy)(OH)]^+$ increases gradually as the SDS concentration increases from 7 to 30 mM and levels off when the SDS concentration increases further. The initial increase in lifetime can be attributed to the formation of micelles when the concentration of surfactant reaches the CMC (the CMC for SDS is 8 mM [16]). As no emission is observed when the complex is dissolved in H_2O, the excited state of the complex should be strongly quenched by water molecule. When the surfactant concentration reaches the critical micelle concentration, the micelles create a protecting environment for the platinum complex so that quenching of the complex by water is prohibited.

The emission lifetime of the platinum complex in 0.1 M SDS/D_2O is 0.17 μs. The small isotope effect $\tau(D_2O)/\tau(H_2O)$ of 1.7 suggests that the quenching mechanism of the complex is different from that of dioxorhenium(V) complexes [17] which involves protonation of oxo groups. The most probable deactivation pathway of the platinum complex is via interaction with H_2O molecule at the open coordination site of $Pt(terpy)(OH)^+$. Another deactivation pathway may involve the interaction of water molecules with the terpyridine ligand in the excited state. Similar deactivating mechanism has been reported for $Ru(bpy)_3^{2+}$ which has an isotope effect $\tau(D_2O)/\tau(H_2O)$ of 1.2 [4].

The effect of ionic salts such as sodium sulfate and lithium trifluoromethanesulfonate on the emission lifetime of $Pt(terpy)(OH)^+$ in 0.1 M SDS has also been investigated. The increase in ionic strength upon addition of electrolyte will increase the average micellar size and raises the water concentration at the micellar interface. If the platinum complex is located at the micelle–solution interface, the emission lifetime of the complex will decrease as a result of increased exposure to water. Our results show that the emission lifetime of the complex decreases by about 10% upon addition of 0.1–0.5 M Na_2SO_4 or $LiCF_3SO_3$. This suggests that $[Pt(terpy)(OH)]^+$ resides at the Stern layer of the SDS micelle.

No emission is detected when Triton X-100 is added to the complex solution. For the neutral surfactant Triton X-100, binding of luminescent probe is possible only if the probe is sufficiently hydrophobic. The fact that no emission is observed for $[Pt(terpy)(OH)]^+$ suggest that its hydrophobic character is too modest to interact with Triton X-100.

Attempts to synthesize $[Pt(mpterpy)(OH)]^+$ using the literature method for $[Pt(terpy)(OH)]^+$ were unsuccessful due to the low solubility of $[Pt(mpterpy)(Cl)]^+$ in water. However, owing to lability of the Cl group, the complex should exist either as $[Pt(mpterpy)(OH_2)]^{2+}$ or $[Pt(mpterpy)(OH)]^+$ in dilute aqueous solution. Indeed, addition of $AgNO_3$ to an aqueous solution of $[Pt(mpterpy)(Cl)](CF_3SO_3)$ would make the solution turbid, indicating the formation of AgCl. The molar conductivity (Λ_m) of $[Pt(mpterpy)(Cl)](CF_3SO_3)$ in water is 270 μS, which is consistent with the molar conductivity of an 1:2 electrolyte [18]. This suggests that the chloride ligand has dissociated from the platinum center and the complex exists in the form of $[Pt(mpterpy)(OH_2)]^{2+}$ in aqueous solution.

In contrast to $[Pt(terpy)(OH)]^+$, $[Pt(mpterpy)(OH_2)]^{2+}$ displays emission in SDS solutions with concentration well below CMC. At [SDS] below 4 mM, the $[Pt(mpterpy)(OH_2)]^{2+}$ solution becomes turbid and some orange precipitates can be observed. The precipitates show rather intense luminescence at 720 nm. The UV–visible absorption spectrum of $[Pt(mpterpy)(OH_2)]^{2+}$ in water shows intense absorption peaks at 258, 336 and 409 nm. In 0.5 mM SDS solution, the absorption bands at 336 nm disappears and the UV–visible spectrum shows absorption bands at 271 and 430 nm (Fig. 2). The difference in UV–visible absorption spectrum of the complex in this surfactant con-

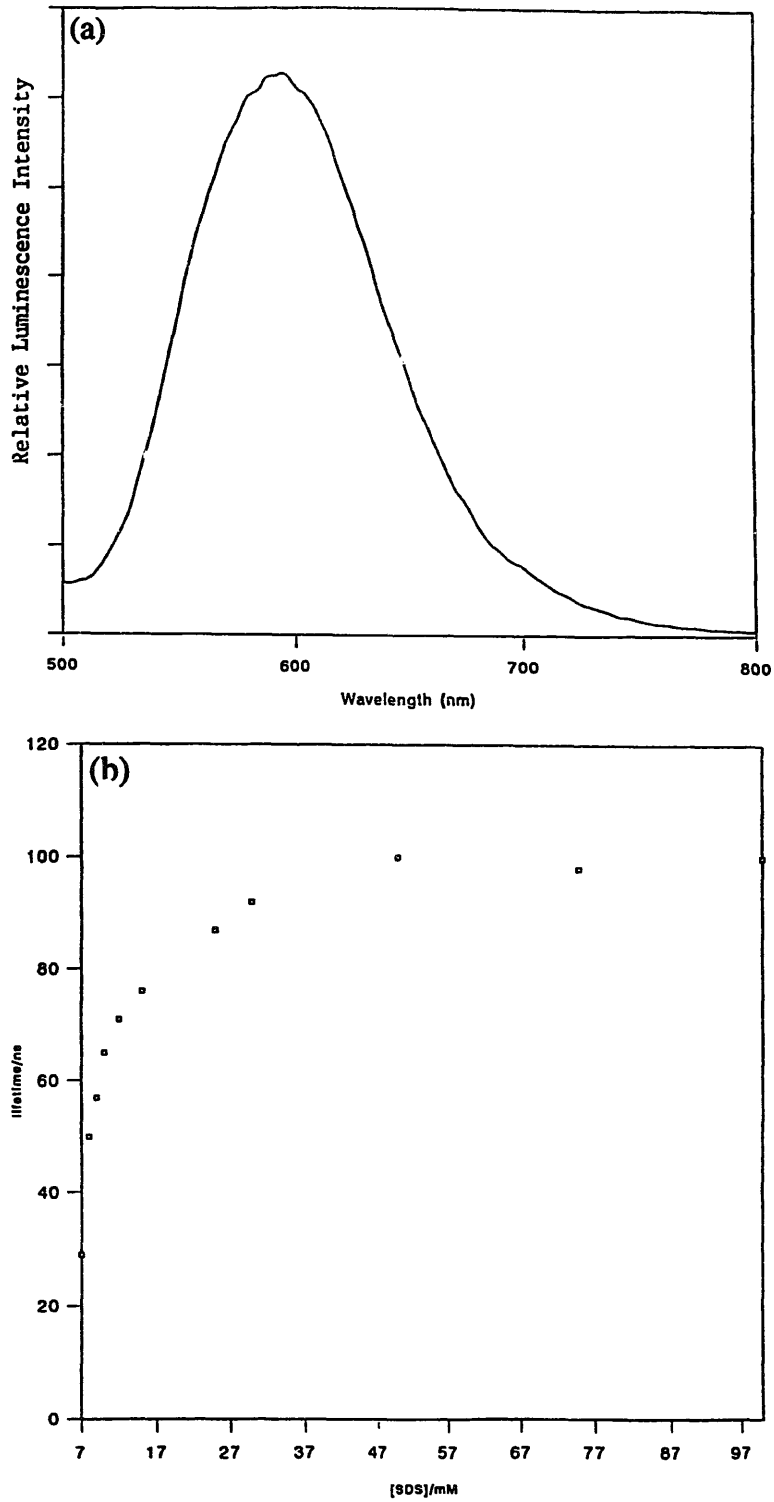

Fig. 1. (A) Steady-state emission spectrum of $[Pt(terpy)(OH)]^+$ in 0.1 M SDS. Excitation wavelength = 340 nm. (B) Excited-state lifetime titration curve for $[Pt(terpy)(OH)]^+$ with [SDS]. Excitation wavelength = 355 nm; emission monitored at 592 nm.

centration from that in water suggests that there is ground state association of $[Pt(mpterpy)(OH_2)]^{2+}$ with SDS. This can be attributed to premicellar effect associated with the formation of undefined aggregates between complex and surfactant molecules. The emission observed in this SDS concentration range is due to solid suspensions of $[Pt(mpterpy)(OH_2)]_x(DS)_y$ in which the complex ion is buried in the surfactant molecules such that it is well protected from the surrounding water.

When [SDS] is increased to above 4 mM, no precipitates were observed. The emission intensity at 720 nm decreases gradually with the increase in [SDS]. This can be attributed to less free surfactant molecules are available for premicellar aggregates formation when the SDS concentration

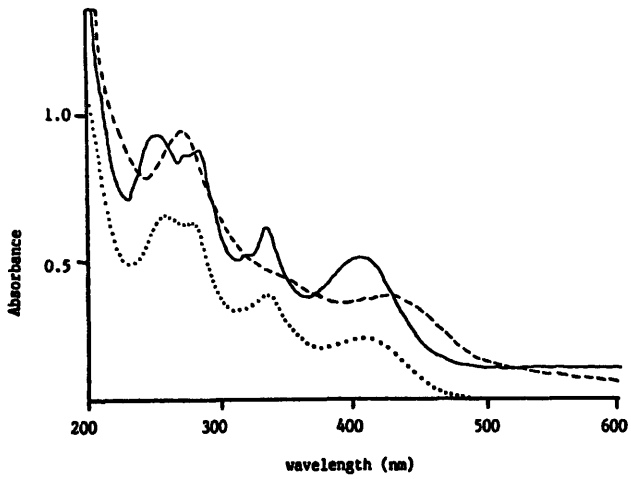

Fig. 2. UV–visible absorption spectra of $[Pt(mpterpy)(OH_2)]^{2+}$ in water (· · ·), 0.5 mM SDS (— — —) and 0.1 M SDS (———).

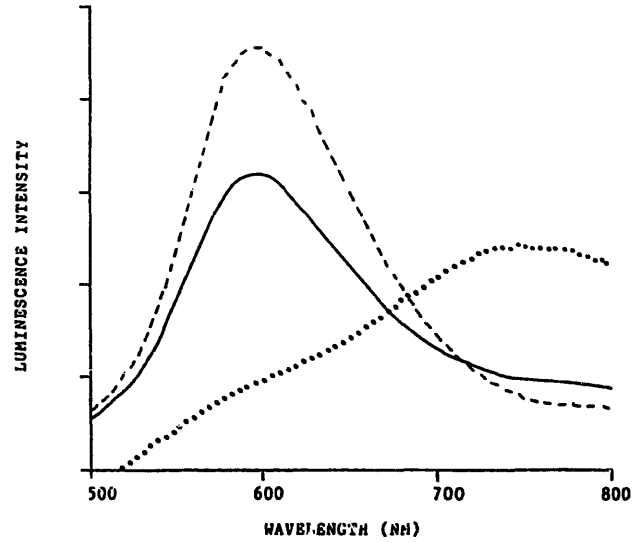

Fig. 3. Steady-state emission spectra of $[Pt(mpterpy)(OH_2)]^{2+}$ in 7 mM (· · ·), 8 mM (———) and 9 mM (— — —) SDS. Excitation wavelength = 340 nm.

approaches CMC. There is a sudden, large hypochromic shift in emission maximum, from 720 to 610 nm, when the concentration of SDS is increased from 7 to 8 mM (Fig. 3). Besides, changes also occur in the UV–visible absorption spectrum of the complex. The intense absorption band at 336 nm reappears as the SDS concentration increases to 8 mM. The absorption spectrum of the complex in 8 mM SDS is similar to that in pure water. The emission intensity at 610 nm increases rapidly when [SDS] > 8 mM until it reaches its maximum at [SDS] ≈ 10 mM.

Table 1 summarizes the lifetime data for the complex. The emission lifetimes of $[Pt(mpterpy)(OH_2)]^{2+}$ in 0.1 M SDS with H_2O and D_2O as solvent are 2.0 and 3.1 μs respectively. The decay curves are monophasic which suggest that only one emitting species is present. This further confirms that $[Pt(mpterpy)(OH_2)]^{2+}$ is the only species present in water. The isotope effect of 1.55 is only slightly smaller than that of $[Pt(terpy)(OH)]^+$. On the other hand, the emission lifetime of $[Pt(mpterpy)(OH_2)]^{2+}$ in 0.1 M SDS is not sensitive to the addition of electrolytes such as Na_2SO_4 and $Li(CF_3SO_3)$. This suggests that $[Pt(mpterpy)(OH_2)]^{2+}$, due to its hydrophobic character, might be buried deeper inside the SDS micelle compared with that of $[Pt(terpy)(OH)]^+$. However, water molecules can still reach the complex by penetration of the micelle surface via deep clefts or fjords [4], which can explain the isotope effect of 1.55.

In contrast to $[Pt(terpy)(OH)]^+$, $[Pt(mpterpy)(OH_2)]^{2+}$ does emit in Triton X-100 solution with emission λ_{max} at 548 nm. Binding with Triton X-100 is largely due to hydrophobic interactions between the complex and the micelle since electrostatic interactions are absent. The successful binding of $[Pt(mpterpy)(OH_2)]^{2+}$ to Triton X-100 can thus be attributed to the hydrophobic character of the platinum complex. The steady-state emission spectrum of $[Pt(mpterpy)(OH_2)]^{2+}$ in 0.1 M Triton X-100 is shown in Fig. 4(a). Fig. 4(b) shows a plot of the emission intensity of $[Pt(mpterpy)(OH_2)]^+$ versus the concentration of Triton X-100. The emission intensity increases monotonically with the concentration of Triton X-100 and approaches a maximum value at [Triton X-100] = 60 mM. The increase in emission intensity with [Triton X-100] reflects the binding

Table 1
Lifetime data for $[Pt(terpy)(OH)]^+$ and $[Pt(mpterpy)(OH_2)]^{2+}$

Surfactant	Solvent	Lifetime (ns)	
		$[Pt(terpy)(OH)]^+$	$[Pt(mpterpy)(OH_2)]^{2+}$
–	CH_3CN	170[a]	–
–	CH_2Cl_2	2000[a]	–
–	H_2O	< 10	< 10
–	D_2O	< 10	< 10
0.1 M SDS	H_2O	100	2000
0.1 M SDS	D_2O	165	3100
0.1 M SDS	H_2O, 0.1 M $LiCF_3SO_3$	90	1996
0.1 M SDS	H_2O, 0.1 M Na_2SO_4	92	2000
0.1 M Triton X-100	H_2O	–	3400
0.1 M Triton X-100	D_2O	–	5940

[a] From Ref. [12].

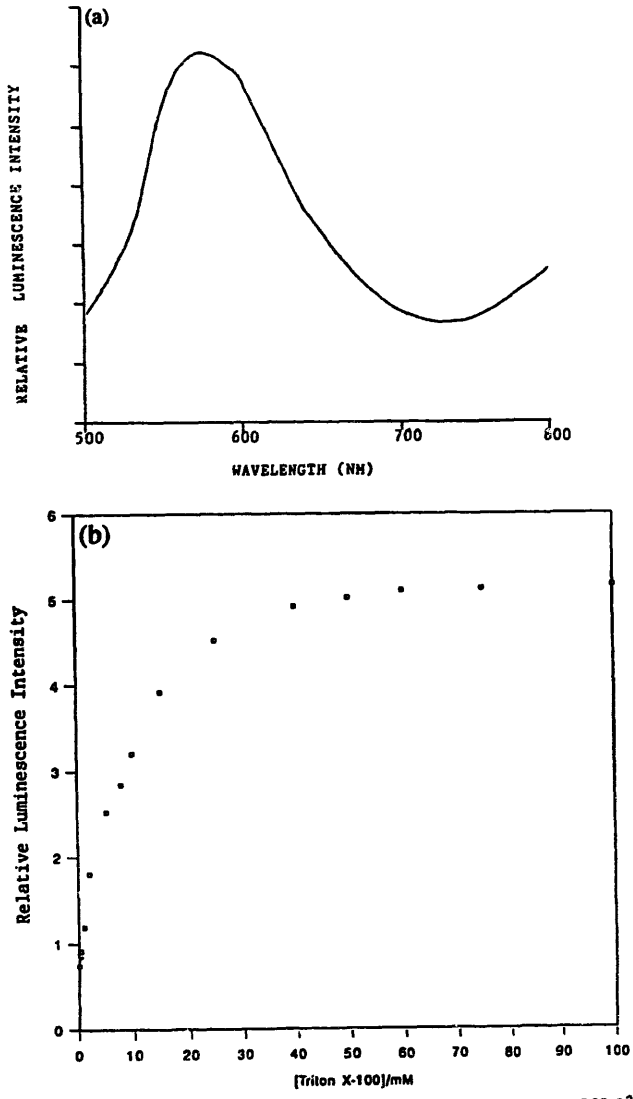

Fig. 4. (a) Steady-state emission spectrum of $[Pt(mpterpy(OH_2)]^{2+}$ in 0.1 M Triton-X 100. (b) Emission intensity titration curve for $[Pt(mpterpy(OH_2)]^{2+}$ with [Triton-X 100]. Excitation wavelength = 420 nm.

of the complex to the surfactant. The emission lifetimes of $[Pt(mpterpy)(OH_2)]^{2+}$ in 0.1 M Triton X-100 with H_2O and D_2O as solvents are 3.4 and 5.9 μs respectively. The relatively large isotope effect of 1.7 of the complex suggests that the complex may reside in the outer sheath of the Triton X-100 micelle [19]. The decay curves of the complex are monophasic.

4. Conclusion

This work has demonstrated that the emission properties of $[Pt(terpy)(OH)]^+$ and $[Pt(mpterpy)(OH_2)]^{2+}$ are sensitive to microenvironmental changes and can be used as probes for micellar structure determination. The emission of $[Pt(terpy)(OH)]^+$ is completely quenched in water but the complex emits rather strongly in 0.1 M SDS. Therefore, this complex is a true molecular switch (yes or no response), with the emission intensity enhancement factor greater than 10^3. It is also expected that the photochemical and photophysical properties of platinum(II) terpyridine complexes can be tuned by careful design of the auxiliary ligands and the substituents on the terpyridine ligands. In terms of applications, these findings suggest that platinum(II) terpyridine complexes are potential luminescence probes in the determination of micelle structure.

Acknowledgements

We acknowledge support from the Hong Kong Polytechnic University and the Croucher Foundation. Professor C.M. Che (The University of Hong Kong) is thanked for the use of his laser laboratory.

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