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Graphical abstract

Photophysical Properties of Amphiphilic Ruthenium(II)-Complexes in Micelles

Eswaran Rajkumar*1,2, Paulpandian Muthu Mareeswaran1, Seenivasan Rajagopal1.

Photophysical properties of [Ru(dnbpy)3]2+ in the presence of different concentrations of Triton X-100.
Photophysical Properties of Amphiphilic Ruthenium(II)-Complexes in Micelles

Eswaran Rajkumar*1,2, Paulpandian Muthu Mareeswaran1, Seenivasan Rajagopal*1

Amphiphilic ruthenium(II)-complexes II-IV were synthesized and their photophysical properties investigated in the presence of anionic (SDS), cationic (CTAB) and neutral (Triton X-100) micelles. The absorption and emission spectral data in the presence of micelles show that these Ru(II)-complexes are incorporated in the micelles. There are two type of interactions between complexes I-IV and micelle: hydrophobic and electrostatic. In the presence of cationic micelle (CTAB), the hydrophobic interaction is predominant over electrostatic repulsion for binding of cationic complexes II-IV, with CTAB. In the presence of anionic micelles (SDS), electrostatic interactions seem to be important in the binding of II-IV to SDS. The hydrophobic interaction plays a dominant role in the binding of the neutral micelle, Triton X-100. Based on the steady state and luminescence experiments, the enhancement of luminescence intensity and longer lifetime in the presence of micelle, which is due to the protection of complexes against exposure to water in this environment.

Introduction

The wide range of functions performed by the biological membranes and membrane proteins has motivated researchers to look for simple model systems. A typical example of such membrane biomimetic model is a micelle, which is an organized assembly of surfactants in aqueous media. Micelles can mimic biosystems and also find extensive applications in solar energy conversion, storage and drug delivery. The structure of micelles (i.e., shape, size, aggregation number (N), hydration, etc.) depends on the architecture of the surfactant molecule, concentration, additives and the solution temperature. Molecules accommodated in molecular assemblies such as micelles, microemulsions, vesicles often achieve a greater degree of organization when compared to their geometries in homogeneous solution. The optical properties of luminescent probes are strongly affected by the change of polarity and rigidity of their environments. Below the critical micellar concentration (cmc), probes will exist mainly in an aqueous medium, whereas above the cmc they are incorporated into a micelle. The structure, dynamics and reactivity of a probe molecule in micelles are different from bulk media, since the polarity and viscosity at interface differ markedly from the bulk media.

The photophysics and photochemistry of ruthenium(II)-polypyridine complexes [Ru(NN)3]2+ (NN = 2,2’-bipyridine and its derivatives) are highly influenced by the change of solvent and the change in medium from homogeneous to heterogeneous. The [Ru(NN)3]2+ complexes have been extensively used as probes in micellar media and their photophysical properties like wavelength of emission maximum, emission intensity, excited state lifetime and emission quantum yield vary enormously with the nature of the surfactant and concentration. Many researchers reported the binding, partitioning and photosensitization of [Ru(NN)3]2+ complexes in both ionic and nonionic surfactant media. Demas and coworkers have studied the interaction of [Ru(NN)3]2+ complexes with ionic (CTAB and SDS) and neutral micelles (Triton X-100) and the emission spectra, lifetime and quantum yield change dramatically on micellization. They proposed a model to understand the binding site and local environment for the photosensitzers. The presence of hydrophobic groups like alkyl and aryl in the ligands of [Ru(NN)3]2+ leads to strong binding of [Ru(NN)3]2+ with micelles through hydrophobic interaction. The strength of binding depends on the combination of electrostatic attractions or repulsions and hydrophobic effects.

The use of [Ru(NN)3]2+ complexes carrying surfactants as ligands is of interest because of their potential applications in thin film devices, sensors and heterogeneous catalysis. Bowers et al. have extensively studied the surface and aggregation behavior of aqueous solutions containing Ru(II)-metallosurfactants. Castro et al. successfully designed a sensor for hydrocarbon, based on ruthenium(II)-complex, [Ru(NN)3]2+, where (NN = 4,4’-dinonyl-2,2’-bipyridine) which is able to detect reversibly and quantify both aromatic and aliphatic hydrocarbons in aqueous samples.

Even though, few reports are available for the use of amphiphilic ruthenium(II)-complexes, the interaction between amphiphilic ruthenium(II)-complexes and micelles (anionic, cationic and neutral) are limited. Therefore, herein we study the photophysical properties of amphiphilic ruthenium(II)-complexes in the presence of micelles (anionic (SDS), cationic (CTAB) and neutral (Triton X 100)).

Experimental

Materials

The ligands 2,2’-bipyridine, 4,4’-dinonyl-2,2’-bipyridine and RuCl3·3H2O were purchased from Aldrich. All of the surfactants, namely SDS, CTAB and Triton X-100 were procured from Aldrich/Fluka and used as received. Triply distilled water was used throughout the experiment. The micellar solutions were freshly prepared to avoid aging. The three complexes, [Ru(bpy)3(phen)]2+ (I), [Ru(bpy)(phen)2]2+ (II), and [Ru(bpy)(phen)]2+ (IV) were prepared by reacting RuCl3·3H2O with the equivalent amount...
of ligands by known procedures\textsuperscript{33,34,50-51}. (The details were given in the supporting information)

**Absorption and emission spectral measurements**

Sample solutions of the metal complexes and the micelles have been freshly prepared for each measurement. The absorption spectral measurements were carried out using SPECORD S100 diode-array spectrophotometer. Steady state emission measurements were recorded with JASCO FP-6300 spectrofluorometer. All the sample solutions used for emission measurements were deaerated for about 20 min by dry nitrogen gas purging and keeping the solutions in cold water to ensure that there is no change in volume of the solution. Excitation wavelength used for the luminescence titration and quantum yield with micelles for complexes II, III and IV at 456, 460 and 466 nm respectively.

**Lifetime measurements**

Time resolved luminescence measurements were carried out using a diode laser-based time correlated single photon counting (TCSPC) spectrometer from IBH, U.K. In the present, 452 nm diode laser (40kHz) was used as the excitation source and Hamamatsu photomultiplier tube was used for the luminescence detection. The instrument response function for this system is \( \approx 1.2 \) ns and the luminescence decay was analyzed by using the software provided by IBH (DAS-6) and PTI global analysis software.

**Estimation of binding constant (K)**

A quantitative estimation of the binding of complexes II-IV with the micelles was obtained from the luminescence intensity data. Because the luminescence intensity of the probe molecule in aqueous and micellar environment differ significantly. Almgren et al\textsuperscript{25,33} used the following equation for the estimation of binding constant (K). According to this

\[
(I_\infty - I_0) / (I_t - I_0) = 1 + (K[M])^{-1}
\]

where \( I_\infty, I_0 \) and \( I_t \) are the relative intensities under complete micellization, in the absence of surfactant and in the presence of intermediate amounts of surfactants respectively. \( [M] \) represents the concentration of micelle which is given by the following equation 2.

\[
[M] = ([Surf] - cmc) / N
\]

[Surf] represents the surfactant concentration and \( N \) is the aggregation number of the micelle. The \( N \) values used in the calculation of \([M]\) are 62 for SDS, 60 for CTAB and 143 for Triton X-100.

**Results**

The structures of the \([Ru(NN)_3]^{2+}\) complexes used in the present study are shown in Chart 1.

**Chart 1:** The structures of the \([Ru(NN)_3]^{2+}\) complexes used in the present study.

**Photophysical properties in homogenous media**

Complexes I and II are freely soluble in water but complexes III and IV are water-insoluble, a feature attributed to the strong hydrophobic character of these complexes imposed by the long alkyl chains of the modified 2,2′-bipyridine ligands. Figures 1 and 2 show the normalized absorption and emission spectra of amphiphilic ruthenium(II)-complexes, II-IV. The photophysical properties of complexes I-IV are collected in aqueous and micellar media and given in Table 1. The absorption spectra of II-IV, exhibit the characteristic bands found in the parent ruthenium(II)-complex, \([Ru(bpy)_3]^{2+}\) and its derivatives\textsuperscript{24,56}. The intense absorption band in the 285-300 nm region is assigned to ligand centered transitions (\(\pi-\pi^*\)) and the band in the visible region (453 - 466 nm) to the metal-to-ligand charge transfer transition (d\(\pi\)(Ru) \(\rightarrow\) \(\pi^*(\text{ligand})\)). All the complexes are highly luminescent and show emission maxima in the range of 618 - 632 nm due to \(^{3}\text{MLCT}\) (d\(\pi\)(Ru) \(\rightarrow\) \(\pi^*(\text{ligand})\)) excited state. These absorption and emission spectral data show that though a red shift to the tune of 13 nm (453 nm to 466 nm) is observed in the absorption spectrum the emission maximum is red shifted to the tune of 36 nm (596 to 632 nm). The energy difference between ground state level of metal and ligand orbitals is lowered, when a long alkyl chain is introduced in the 4,4′-position of 2,2′-bipyridine in aqueous methanol. Complexes III and IV are weakly luminescent compared to complex II.

Complexes III and IV exhibited weakly luminescent and lower luminescence quantum yield when compared to complex II in aqueous methanol solution. This may be due to increased nonradiative decay processes. To have a better understanding of the excited state properties of these complexes, we have carried out nanosecond time resolved luminescence analysis in different media. Table 2 summarizes the luminescence lifetimes of II-IV, in the absence and presence of micelles. Complex, II, shows a single exponential decay in 1% methanol-99% water(v/v) (\(\tau = 324\) ns, Table 2). This observation is due to the freely soluble nature of II in water. Since the complexes III and IV are sparingly soluble in water, they show a biexponential decay profile in 1% methanol-99% water. The major species of the complexes III and IV, exhibit longer lifetime 210 ns (94.50%) and 118 ns (91.85%), while the minor species has a shorter lifetime of 21 (5.50%) and 17ns (8.15%) respectively. We assume the biexponential decay nature of the complexes III and IV are due to two spectroscopically different species in the excited state in 1% methanol-99% water.
Photophysical properties in microheterogeneous media

The study of stability and photophysical properties of a sensitizer under physiological conditions is important to evaluate its potential for various biological applications.

Table 1: Absorption ($\lambda_{max}$,nm) and emission maxima ($\lambda_{max}$,nm) quantum yield ($\Phi_{em}$) of [Ru(NN)$_3^{2+}$ and complexes II-IV, 1%methanol-99%water and in the presence of micelles.

<table>
<thead>
<tr>
<th>Additive</th>
<th>[Ru(bpy)$_3^{2+}$</th>
<th>[Ru(bpy)$_2$(dnbpy)$_2^{3+}$</th>
<th>[Ru(bpy)(dnbpy)$_3^{2+}$</th>
<th>[Ru(dnbpy)$_3^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% MeOH-H$_2$O</td>
<td>453</td>
<td>596</td>
<td>456</td>
<td>618</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>460</td>
<td>630</td>
<td>0.006</td>
</tr>
<tr>
<td>SDS</td>
<td>454</td>
<td>628</td>
<td>452</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td>0.042</td>
<td>461</td>
<td>632</td>
<td>0.018</td>
</tr>
<tr>
<td>CTAB</td>
<td>455</td>
<td>611</td>
<td>457</td>
<td>626</td>
</tr>
<tr>
<td></td>
<td>0.034</td>
<td>458</td>
<td>634</td>
<td>0.017</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>454</td>
<td>610</td>
<td>458</td>
<td>630</td>
</tr>
<tr>
<td></td>
<td>0.049</td>
<td>462</td>
<td>636</td>
<td>0.020</td>
</tr>
</tbody>
</table>

a from ref. 39,40 For parent and complex II, the concentration of micelles are 100mM, 50mM, 50mM for SDS, CTAB and Triton X-100 respectively. For complex III and IV concentration of micelles are 50mM, 10mM, 10mM for SDS, CTAB and Triton X-100 respectively.

The effect of adding surfactants on the photophysical properties of amphiphilic ruthenium(II)-complexes II-IV, in different micelles were investigated. For the sake of comparison we have included the data available for the parent complex, [Ru(bpy)$_3^{2+}$].

Effect of anionic micelles, SDS

In order to understand the ground state interaction between amphiphilic ruthenium(II)-complexes II-IV, and SDS we have recorded the absorption spectrum in the absence and in the presence of different concentrations of SDS and the spectra are shown in supporting information (Figures S1–S2). The increase in the concentration of anionic micelle (SDS) resulted in a slight change in the absorption intensity of III with a slight blue shift of about 3 nm. Similar observations were made with I and II in the presence of SDS. Complex III shows a shift in emission maximum 632 nm to 636 nm along with an increase in intensity (Figure 3). Such a bathochromic shift in the emission maximum of [Ru(bpy)$_3^{2+}$] with the change of the medium from aqueous to SDS micelle is a well-documented phenomenon. The complex II shows an emission maximum at 618 nm in aqueous medium. The initial addition of SDS causes a red shift in the emission maximum from 618 nm to 628 nm with decrease in emission intensity. A similar decrease in the luminescence intensity is quite common at the lower concentrations of various surfactants which is ascribed to the formation of premicellar aggregates. A further increase in the concentration of SDS brings back the emission maximum close to the value in aqueous medium (630 to 620 nm) along with enhancement in its luminescence intensity. Complexes I and II exhibit a single exponential decay in SDS micelle, whereas complex III and IV shows a biexponential decay. Major component exhibit longer lifetime in the SDS micelle and minor component have negligible contribution to the decay. In the presence of SDS micelles, II-IV show all three complexes relatively longer lifetime (Table 2). For example the lifetime of IV in the presence of anionic micelle is almost three times of that in the aqueous medium.

In order to mimic the biological membranes, we have employed anionic, cationic and neutral surfactants that can form micellar structures at and above critical micellar concentration(CMC).
Experimental observations substantiate the importance of hydrophobic interactions. These interesting experimental observations substantiate the importance of hydrophobic interactions. Complexes II-IV show a longer excited state lifetime (~1.5 to 3 fold increase in \( \tau \) value) in the presence of CTAB as observed in the presence of SDS. The inference from this observation is that the coulombic repulsion between the like charges of the Ru(II) complexes and micellar surface is offset by the strong hydrophobic interaction between the alkyl chain and micelle.

**Effect of neutral micelle, (Triton X-100)**

In addition to the anionic and cationic micelles, we have investigated the effect of adding nonionic micelle Triton X-100 on the photophysical properties of II-IV. Absorption spectrum of amphiphilic ruthenium(II) complexes were slightly altered in the presence of different concentrations of neutral micelle. For example, the addition of neutral surfactant to complex IV, resulted in a small increase in the \( \varepsilon \) value with a blue shift of about 5 nm at the absorption maximum (*vide infra*). Figure 5 shows the effect of adding of Triton X-100 on the emission spectra of the complex IV. All the amphiphile ruthenium(II) complexes II-IV, showed red shift in the range of 6–14 nm in the emission maximum along with enhancement in luminescence intensity with increase in [TX-100] (supporting information Figures S5 and S6).

Discussion

In the presence of micelles, all the three ruthenium(II) complexes, II-IV, showed luminescence enhancement when compared to that in aqueous medium. This is attributed to the microencapsulation of the ruthenium(II)-complexes into the micellar medium, resulting in the change in the microenvironment experienced by the ruthenium(II) complexes. These microenvironmental changes include higher viscosity, lower dielectric constant and polarity. Micelles are characterized by three distinct regions: a nonpolar core region formed by the hydrocarbon chains of the surfactant, a compact Stern layer having the head groups and relatively wider Gouy-Chapman layer containing the counter ions. Depending upon the nature of the probe and micelle, a probe molecule can bind either to head group region or to the nonpolar core region of the micelle.

The two microenvironments (the Stern layer and the core region) of the micelles have quite different properties. The core
region is usually characterized by a highly viscous hydrocarbon like environment with a very low degree of water penetration. The Stern layer mainly consists of polar head groups, bound counter ions and largely structured water molecules. Since, the nature of micelles depends on nature of head group and core region, the probe is located in different region in accordance with their nature. The excited state lifetime of [Ru(bpy)]^{2+} in SDS micellar solution (τ = 712 ns) is longer than those in aqueous solution (τ = 600 ns). Since the cationic complex must bind to the surface of the anionic micelle, the excited state complex will be shielded to some extent from attack by the solvent water molecules. The parent complex [Ru(bpy)]^{2+} does not undergo primary electrostatic interaction with cationic or non-ionic micelles. Miesel et al. reported a red shift in emission maximum for this complex in SDS micellar solutions and ascribed this shift to a static interaction of [Ru(bpy)]^{2+} with hydrocarbon chain rather than with the polar head group.

The excited state properties of [Ru(bpy)]^{2+} are not much affected in the presence of the cationic micelle CTAB and it remains in the aqueous phase because of coulombic repulsion from the cationic micelle. Thus the addition of CTAB has little effect on the excited state properties of [Ru(bpy)]^{2+}. However the trend changes when we introduce long alkyl chain in the ligand of Ru(II) complexes. The binding constants of [Ru(NN)]^{2+} as well as complexes II-IV, with the micelles are determined from the luminescence intensity data and are given in Table 3. Binding constant of [Ru(bpy)]^{2+} in SDS is 440 M^{-1}, whereas it is 320 M^{-1} in CTAB. This is due to the effect of similar charges on the probe and surfactant interface. However the introduction of long alkyl group in the 4,4'-position of 2,2'-bipyridine ligand facilitates the binding to the cationic micelles and binding constants in the anionic and cationic are almost similar.

After observing a considerable shift in the absorption and emission spectra, we have measured the excited state lifetime of [Ru(NN)]^{2+}. As expected a large change is observed in the excited state lifetime in the presence of CTAB. In the case of [Ru(dnbpy)]^{2+}, though the lifetime is 118 ns in the micellar-free medium, it increases with the concentration of CTAB, it attains maximum 334 ns at high [CTAB]. As the complex carries long hydrocarbon chains in the 2,2'-bipyridine ligand, it binds with cationic micelle which results in the increase in lifetime. The increase in the lifetime in the presence of micelle can be explained in terms of a model proposed by Demas et al. (Figure 6).

The model shown in Figure 6 leads to eqn. 3 for the rate of decay of excited state [Ru(NN)]^{2+} which relates the observed emission lifetime to $k_r$, $k_{nr}$ and $k_{ddr}$:

$$\frac{1}{\tau} (T) = k + k_{ddr}$$

$$k = k_r + k_{nr}$$

Table 2: Lifetime data (τ, ns (relative amplitude)) of [Ru(NN)]^{2+} and complexes, II-IV, in homogenous and heterogeneous media.

<table>
<thead>
<tr>
<th>Additive</th>
<th>[Ru(bpy)]^{2+}</th>
<th>Complex, II</th>
<th>Complex, III</th>
<th>Complex, IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% MeOH-H_{2}O</td>
<td>600</td>
<td>324</td>
<td>210 (94.50%)</td>
<td>118 (91.85%)</td>
</tr>
<tr>
<td>SDS</td>
<td>712</td>
<td>534</td>
<td>428 (98.85%)</td>
<td>334 (97.66%)</td>
</tr>
<tr>
<td>CTAB</td>
<td>567</td>
<td>587</td>
<td>446 (98.79%)</td>
<td>328 (96.51%)</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>585</td>
<td>630</td>
<td>465 (98.55%)</td>
<td>415 (98.88%)</td>
</tr>
</tbody>
</table>

Table 3: Binding constant values for [Ru(bpy)]^{2+} and complexes II-IV with micelles.

<table>
<thead>
<tr>
<th>Additive</th>
<th>[Ru(bpy)]^{2+}</th>
<th>Complex, II</th>
<th>Complex, III</th>
<th>Complex, IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>440</td>
<td>820</td>
<td>760</td>
<td>980</td>
</tr>
<tr>
<td>CTAB</td>
<td>320</td>
<td>940</td>
<td>720</td>
<td>1250</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>-</td>
<td>1050</td>
<td>790</td>
<td>2130</td>
</tr>
</tbody>
</table>
where $k_d$ and $k_{nr}$ are the radiative and nonradiative rate constants for the deactivation of $^3$MLCT state and $k_{dd}$ represents the sum of radiative and nonradiative decay rate constants for the depopulation of the corresponding state. These parameters provide the information about the effect of micellization on the excited state energy degradation. Since the value of the excited state lifetime and quantum yield increases on micellization, $k_r$, $k_{nr}$ and/or $k_{dd}$ are likely to be affected. Within the experimental error, $k_r$ is invariant on micellization. Thus, the change in it arises from changes in the nonradiative decay. Table 1 shows the increase in quantum yield in the presence of micelles. The increase in quantum yield is due to decrease in the rate of nonradiative decay from the excited state. It has already been indicated that the relaxation to the ground state via the dd state is also markedly affected by micellization and the $k_{dd}$ are reduced by $\sim 50\%$. This could be attributed to the microencapsulation of the $[\text{Ru(NN)}_2]^{2+}$ into the micellar medium, resulting in the change in the microenvironment experienced by the ruthenium(II) complexes. In the presence of cationic micelle hydrophobic interaction is predominant over electrostatic repulsion leading to large binding constants relative to SDS. The substantial enhancement of emission intensity and longest excited state lifetime of complexes II-IV in the presence of neutral surfactant Triton X-100 indicate the strong binding of the probe with the neutral micelle. This can be explained by a dominant role of hydrophobic interactions due to presence of long hydrocarbon in the 4,4'-position of 2,2'-bipyridine with the alkyl chain of the surfactant. In Table 1, the emission quantum yield of II-IV increased in the presence of micelles, especially more pronounced in the case of neutral micelle. For example, complex IV has the quantum yield of 0.002 in homogeneous media, whereas in the presence of neutral micelle it increases to 0.021. This is due to the decrease in the rate of nonradiative decay.

Figure 6: Energy level diagram showing the pathways of energy degradation for $[\text{Ru(NN)}_2]^{2+}$. The proposal of slow non-radiative decay in the presence of micelle is supported by the red shift observed in the emission spectrum of $[\text{Ru(NN)}_2]^{2+}$ in the presence of CTAB. This red shift in emission indicates stabilization of $^3$MLCT state in micelles compared to aqueous medium. This leads to more energy gap between $^3$MLCT and dd states thereby suppressing the decay of the excited state via nonradiative dd state. Similar explanation has been provided in other rigid media which inhibited the MLCT-dd interconversion by destabilizing ligand field or dd states, thereby increasing the MLCT-dd energy gap.

Demas et al. reported that $[\text{Ru(bpy)}_3]^{2+}$ exhibit large solvent exposures and negligible spectral shifts due to weak interaction with either the Triton X-100 monomer or micelles. Also, the +2 charge of the complex favors salvation by water than Triton X-100. These two factors provide a reasonable explanation for the observed lack of interaction between $[\text{Ru(bpy)}_3]^{2+}$ and Triton X-100. Thus the lifetime of $[\text{Ru(bpy)}_3]^{2+}$ was unaffected by the addition of Triton X-100. Amphiphilic ruthenium(II)-complexes II-IV showed red shift in the range of 6–14 nm in the emission maximum along with enhancement in luminescence intensity with increase in [TX-100]. The substantial enhancement of emission intensity and longest excited state lifetime of complexes II-IV in the presence of neutral surfactant Triton X-100 indicate the strong binding of the probe with the neutral micelle. This can be explained by a dominant role of hydrophobic interactions due to presence of long hydrocarbon in the 4,4'-position of 2,2'-bipyridine with the alkyl chain of the surfactant.

Conclusion

In the presence of micelles, amphiphilic ruthenium(II)complexes showed moderate changes in the absorption spectrum, whereas enormous increase in their emission intensity and emission lifetimes indicating the binding of these complexes with micelles. The interactions of amphiphilic complexes were more pronounced in neutral micelles when compared to the charged micelles. The hydrophobic interaction plays a dominant role in the binding of II-IV to the neutral micelle Triton X-100. The binding of cationic complexes II-IV, with CTAB can be attributed to a dominant role of hydrophobic interactions over electrostatic repulsion. Electrostatic interactions seem to be important in the binding of II-IV to SDS. These results demonstrate that the introduction of amphiphilic moiety in the fluorescent probe leads to favorable photophysical properties which can lead to their potential applications as sensors for biological systems.

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Notes

4. G. Vaccaro, A. Bianchi, M. Mauri, S. Bonetti, F. Meinnardi, A. Sanguineti, R. Simonetti and L. Beverina, Direct monitoring of self-assembly of

References

4. G. Vaccaro, A. Bianchi, M. Mauri, S. Bonetti, F. Meinnardi, A. Sanguineti, R. Simonetti and L. Beverina, Direct monitoring of self-assembly of


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