



Encapsulation condition dependent photophysical properties of polypyridyl Ru(II) complexes within a hydrogen-bonded capsule

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Controlling the encapsulation equilibrium is a key strategy to affect host–guest associations. Ruthenium(II) polypyridyl complex salts suspended in a chloroform solution of resorcin[4]arene afforded a host–guest complex which showed structured emission spectra even in the solution state. In contrast, a host–guest complex obtained through homogeneous encapsulation conditions by using soluble ruthenium(II) polypyridyl complex salts showed broadened emission spectra which strongly depended on the amount of the host owing to the encapsulation equilibrium. These results demonstrate that a simple modulation of the encapsulation technique is indeed promising and a facile approach to control the photophysical properties of supramolecular complexes.

Molecular recognition via noncovalent interactions typically proceeds under thermodynamic control, involving encapsulation equilibrium that strongly depends on size, shape, charge, chirality of guest and host molecules, and competitive solvents as well.¹ When a guest molecule is strongly trapped within a self-assembled host, the supramolecular compound often shows unusual selectivity and physical properties owing to effective separation of the guest molecule from the solvents and confinement of guest conformation in the cavity of the host.² Thus, one of the key strategies to create remarkable phenomena based on host–guest associations is *how to control encapsulation equilibrium*. The examples for controlling the encapsulation equilibrium of hydrogen-bonded hosts were reported by Purse and co-workers using a neat condition of guest molecules or liquid paraffin wax as a solvent.^{3a,b} Furthermore, they recently reported molecular recognition of hydrogen-bonded hexameric capsule through ball milling methods in the solid state.^{3c} These techniques allow the formation of host–guest complexes that were unobtainable via homogeneous process.

We have recently studied emissive supramolecular complexes constructed via self-assembly and encapsulation under homogeneous conditions, whose photophysical properties can be tuned by noncovalent interactions.⁴ The finding of a new technique to obtain the host–guest complexes through *heterogeneous* encapsulation conditions encouraged us to investigate their photophysical properties. Herein we report the encapsulation study of ruthenium(II) polypyridyl complexes within hydrogen-bonded capsules through heterogeneous encapsulation conditions and compare the luminescent properties with those obtained under homogeneous encapsulation conditions (Fig. 1).

Dicationic Ru^{II} polypyridyl complexes typically show environment-sensitive ³MLCT emission, leading to their extensive photophysical studies under various conditions.⁵ The solubility of the guest complex salts is easily adjusted by variation of the counter anions. These features are indeed suitable to unveil the relationship between the encapsulated states of the guests, and to study the photophysical properties of the supramolecular complexes through two different encapsulation processes by using an identical self-assembled host, a guest cation, and solvents. As a result, we found that Ru^{II} complexes trapped within the hydrogen-bonded capsule through heterogeneous conditions showed considerably unique photophysical properties, which are far different from those of not only free Ru^{II} complex cation but also of trapped complexes formed through a homogeneous process.

As shown in our previous work,^{4a} self-assembly of resorcin[4]arene **1** with eight water molecules forms hexameric self-assembled capsule **2** with a large cavity, which is stabilized by a reversible hydrogen-bond network in wet apolar solvents⁶ and can accommodate cationic organic compounds and organometallic catalyst performing enzymatic transformations in the capsule (Fig. 1).^{7,8} When [Ru(bpy)₃](PF₆)₂ (bpy = 2,2'-bipyridine), **[3](PF₆)₂**, was suspended in a wet chloroform solution of resorcin[4]arene **1** and stirring at 50 °C for 3 h, the Ru^{II} complex was trapped within a hydrogen bonded capsule **2** to afford the host–guest complex **[2⊃3](PF₆)₂**, as judging from the solution color change

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from colorless to orange (Fig. S1†).⁹ After residual Ru^{II} complex was removed by filtration, the quantitative formation of host–

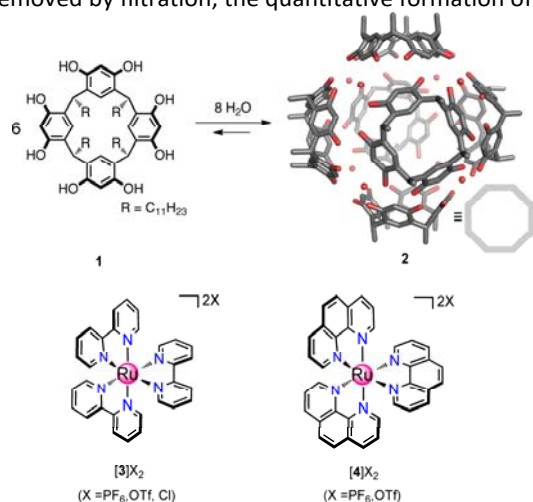


Fig. 1 Hydrogen bonded capsule **2** and emissive Ru^{II} complexes.

guest complex $[2\supset 3](PF_6)_2$ was confirmed by NMR spectroscopy (Fig. 2). The ¹H NMR spectrum of $[2\supset 3](PF_6)_2$ showed significant broadening of host signals similar to those obtained from a homogeneous solution containing **1** and Ru^{II} complex salt $[3](OTf)_2$ soluble in CHCl₃ (Fig. 2b–d).^{8b} In contrast, the guest signals were clearly observed which were considerably up-field shifted owing to the shielding effect from the capsule, suggesting that $[3]^{2+}$ was strongly bound within **2** via multiple cation-π interactions and the guest release process was effectively hampered due to the insolubility of free $[3](PF_6)_2$ in CHCl₃ (Fig. 2c). The diffusion-ordered NMR spectroscopy (DOSY) also supported the formation of the host–guest complex with the observation of a single band of diffusion coefficient ($D = 3.5 \pm 0.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) close to that of the host capsule **2**. Significant reduction of the diffusion coefficient was observed, as compared with that of free $[3](OTf)_2$ in CDCl₃ ($\Delta D \approx -4.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) (Fig. S2†).^{10,11} The ¹⁹F NMR signals assigned to the counter anion (PF₆[−]) did not shift significantly ($\Delta\delta \approx -0.3 \text{ ppm}$), implying that the counter anion does not participate in the encapsulation and self-assembly process of $[2\supset 3]^{2+}$ (Fig. S4†).

Electronic absorption spectra revealed the stoichiometry of the host–guest complex through heterogeneous conditions (Fig. 3a). The absorption intensities around 450 nm for $[2\supset 3](PF_6)_2$ (10 μM solution based on **2**) are similar to that of free $[3](OTf)_2$ (10 μM). Given that the absorption coefficient of $[3]^{2+}$ is not affected significantly by enclathration within the capsule, these results suggest 1:1 stoichiometry between hexameric capsule **2** and the guest. Notably, the absorption maximum derived from ¹MLCT transition of $[3]^{2+}$ around 450 nm was largely blue-shifted ($\Delta\lambda = -14 \text{ nm}$) in $[2\supset 3](PF_6)_2$, strongly suggesting that the host–guest complex $[2\supset 3]^{2+}$ obtained through heterogeneous conditions is still maintained in the diluted solution (micromolar concentration) presumably due to the effective template effect of $[3]^{2+}$ for the formation of $[2\supset 3]^{2+}$ and solvophobic effect between $[3]^{2+}$ and CHCl₃.^{12,13} In contrast, host–guest complex $[2\supset 3](OTf)_2$ showed no

shifting ($\Delta\lambda \approx 0 \text{ nm}$) of the absorption maximum. This indicates the escape of $[3]^{2+}$ from the cavity of **2** in the host–guest complex constructed via the homogeneous process at micromolar concentration, due to better solubility of the complex salt $[3](OTf)_2$ in CHCl₃.

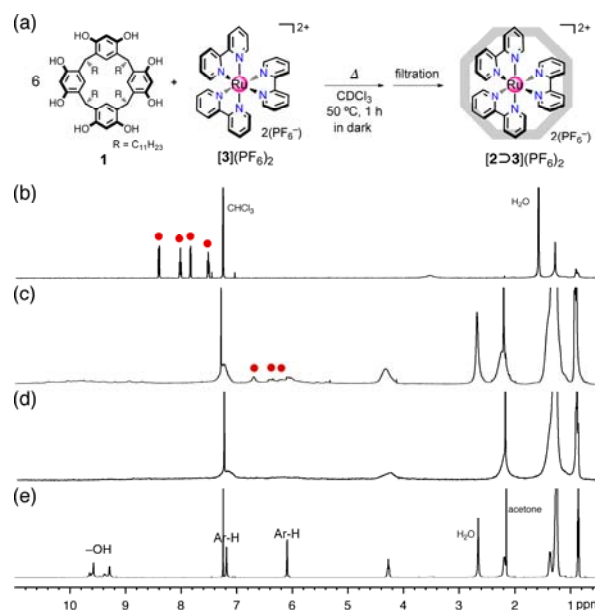


Fig. 2 (a) Schematic representation of the encapsulation of $[3](PF_6)_2$ within hexameric capsule **2** under the suspended conditions. ¹H NMR spectra (500 MHz, CDCl₃, r.t.) of (b) $[3](OTf)_2$ (1.6 mM), (c) host–guest complex $[2\supset 3](PF_6)_2$ obtained from the suspension (10 mM solution of **1**; signals of $[3]^{2+}$ are indicated by red circles), (d) host–guest complex $[2\supset 3](OTf)_2$ (solution containing **1** (10 mM) and $[3](OTf)_2$ (1.6 mM)), and (e) free hexameric capsule **2** (10 mM solution of **1**).

The emission properties of these two types of host–guest complexes, whose emissions were originated from ³MLCT excited states of $[3]^{2+}$, were also significantly different (Fig. 3b, Table 1). The host–guest complexes $[2\supset 3](OTf)_2$ and $[2\supset 3](PF_6)_2$ showed reddish yellow ($\lambda_{em} = 590 \text{ nm}$, $\Phi = 6\%$, $\tau_{ave} = 690 \text{ ns}$) and yellow phosphorescence ($\lambda_{em} = 581 \text{ nm}$, 620 nm (sh), $\Phi = 3\%$, $\tau_{ave} = 730 \text{ ns}$), respectively, upon excitation at 430 nm in deaerated solutions. These broad emission bands were both largely blue-shifted from that of free $[3](OTf)_2$ in CHCl₃ ($\lambda_{em} = 627 \text{ nm}$, $\Phi = 12\%$, $\tau = 850 \text{ ns}$), because the emissions from ³MLCT excited states were sensitive to the polarity of solvent and cavity as well as the rigidity around the complex.⁵ However, these results revealed that the encapsulated Ru^{II} complexes in the heterogeneous conditions are located in a more apolar and rigid environment, as compared with those in the homogeneous conditions. These features have also been observed in our previous results for an Ir^{III} complex.^{4a} Notably, the broad structured emission spectrum of $[2\supset 3](PF_6)_2$ almost coincides with that of $[3](PF_6)_2$ in the solid state, indicating that the guest complex cation is almost completely trapped within the capsule even in solution state due to a very low solubility of complex salt $[3](PF_6)_2$ in CHCl₃. Since the tight encapsulation effectively inhibits the thermal vibration of the guest molecules as well as the collision of excited nuclei with the solvent, the encapsulation-induced emission enhancement (EIEE) is expected.^{4a,14} However, the decrease of quantum yield

suggests that the destabilized ³MLCT excited states generated by encapsulation induced thermal activation to higher lying nonradiative ³dd excited state even at room temperature and/or aggregation-induced quenching took place by the tight encapsulation.⁵

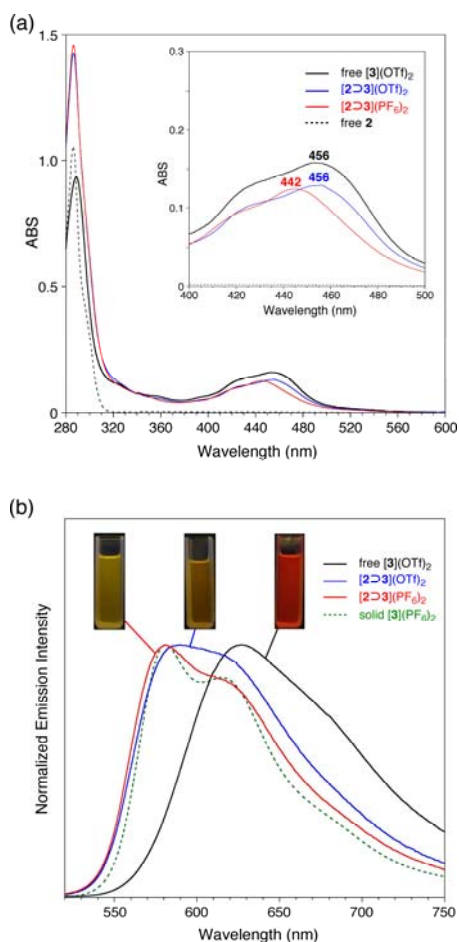


Fig. 3 (a) Electronic absorption spectra (10 μM , CHCl_3 , r.t.) with enlarged spectra around 450 nm and (b) normalized emission spectra ($\lambda_{\text{ex}} = 430 \text{ nm}$) of host-guest complex $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{OTf})_2$ (obtained from the 6:1 mixture of **1** and $[\mathbf{3}](\text{OTf})_2$) (—), host-guest complex $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$ (obtained through the heterogeneous encapsulation technique) (—), free $[\mathbf{3}](\text{OTf})_2$ (—), hexameric capsule **2** (- - -), and solid $[\mathbf{3}](\text{PF}_6)_2$ (····).

Next, we examined the self-assembly and encapsulation equilibrium of $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$ by addition of free resorcin[4]arene **1** to the diluted solution (CHCl_3 , 10 μM) of host-guest complex. Interestingly, the emission spectra, an indicator of the environmental change of the encapsulated complex cation, did not change after adding various amounts of free **1**, suggesting that the exchange reaction of **1** in $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$ with free **1** is extremely slow (Fig. S15[†]). In contrast, the emission spectra of host-guest complex $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{OTf})_2$ gradually changed with increasing amount of **1** similar to our previous result (Fig. S16[†]).^{4a} This feature was derived from the reversible self-assembly and encapsulation process of $[\mathbf{2}\rightleftharpoons\mathbf{3}]^{2+}$ which is due to the lower stability of the hydrogen-bonded capsules at micromolar concentration in the homogeneous conditions. It is noted that the

emission spectrum of $[\mathbf{3}](\text{OTf})_2$ in the presence of excess amount (12 equiv.) of **1** resembled that of $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$. This result strongly suggest that most of $[\mathbf{3}]^{2+}$ was trapped within the capsule at this point and the encapsulation state of host-guest complex $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$ is far from the thermodynamically equilibrium state of **1** and $[\mathbf{3}](\text{OTf})_2$ in a 6:1 solution mixture. Probably, the different behaviors of $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$ and $[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{OTf})_2$ toward the encapsulation equilibrium brought out the significant differences of photophysical properties.

Molecular modeling studies of $[\mathbf{2}\rightleftharpoons\mathbf{3}]^{2+}$ on the basis of their X-ray structures clearly support that one Ru^{II} complex cation perfectly fits within the hexameric capsule (Fig. S20[†]). According to Rebek's 55% rule of the molecular recognition within hydrogen-bonded capsules,¹⁵ the large internal cavity (1330 \AA^3) of the hexameric capsule should optimally encapsulate guest molecules with volumes of around 730 \AA^3 . However, the Ru^{II} complex cation $[\mathbf{3}]^{2+}$ (463 \AA^3) gave a packing coefficient (PC) of 35%, estimated by VOIDOO (Fig. S21[†]).^{16,17} This low value suggests that the cation- π interactions between **2** and $[\mathbf{3}]^{2+}$, as well as co-encapsulation of solvent molecules (CHCl_3 , 75 \AA^3) with $[\mathbf{3}]^{2+}$, effectively contributed to the formation of the host-guest association.

Table 1 Photophysical data in CHCl_3 at r.t.^a

Complex	λ_{abs} (nm) ^d	λ_{em} (nm)	Φ (%)	τ (ns)
$[\mathbf{3}](\text{OTf})_2$	456	627	12	850
$[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{OTf})_2^b$	456	590	6	690 ^e
$[\mathbf{2}\rightleftharpoons\mathbf{3}](\text{PF}_6)_2$	442	581	3	730 ^e
$[\mathbf{3}](\text{PF}_6)_2^c$	450	621	11	820
$[\mathbf{4}](\text{OTf})_2$	450	599	3	200
$[\mathbf{2}\rightleftharpoons\mathbf{4}](\text{OTf})_2^b$	449	576	5	1240 ^e
$[\mathbf{2}\rightleftharpoons\mathbf{4}](\text{PF}_6)_2$	447	562	5	1210 ^e
$[\mathbf{4}](\text{PF}_6)_2^c$	445	603	5	390

^aAll measurements were performed using 10 μM sample solutions under degassed conditions. ^b[**1**]: 60 μM , Ru^{II} complex: 10 μM , ^cin CH_3CN , ^dMaximum peak of ¹MLCT transition. ^eThe averaged emission lifetime was estimated by the equation ($\tau_{\text{ave}} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$).

When the guest complex cation $[\text{Ru}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline), $[\mathbf{4}]^{2+}$, with more sterically demanding ligands was employed, the supramolecular complex showed effective separation of solvent molecules from emitters by tight encapsulation within the capsule. Host-guest complex $[\mathbf{2}\rightleftharpoons\mathbf{4}](\text{PF}_6)_2$ obtained from a suspension of resorcin[4]arene **1** and $[\mathbf{4}](\text{PF}_6)_2$ clearly showed structured emission spectrum at room temperature even in the solution state (Fig. S17b[†]). In general, the emissions derived from ³MLCT excited states of polypyridyl Ru^{II} complexes show a broad spectrum at room temperature in solution and a structured spectrum in a glassy matrix at low temperature (77 K) due to the reorganization of solvent molecules around excited species.⁵ Larger molecular size of $[\mathbf{4}]^{2+}$ (516 \AA^3) effectively expels solvent molecules (CHCl_3) from the cavity of **2**, resulted in the inhibition of excited state stabilization by solvent reorganization. The packing coefficient (PC = 39%) of $[\mathbf{2}\rightleftharpoons\mathbf{4}]^{2+}$ calculated via VOIDOO

supported that, at most, three solvent molecules are co-encapsulated within the capsule (Fig. S21†).

Conclusions

In conclusion, we have demonstrated a new technique for the formation of host–guest complexes through heterogeneous encapsulation conditions, by using hydrogen-bonded capsules and emissive polypyridyl Ru^{II} complexes in organic solvents. The host–guest complex obtained through suspension conditions showed a significant higher-energy shift of the emission maximum and structured emission spectra even in the solution state at room temperature. This indicates that the Ru^{II} complexes are almost completely trapped to form a highly aggregated structure and solvent reorganization in the exited state is effectively hampered within the capsule. Thus, the present work provides us with a facile approach to obtain unusual host–guest complexes which are far from the thermodynamic equilibrium state and to develop new luminescent supramolecular complexes via guest recognition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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