# **Electronic Supplementary Information (ESI)**

# Encapsulation Condition Dependent Photophysical Properties of Polypyridyl Ru(II) Complexes within Hydrogen-Bonded Capsules

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# Contents

- Materials and Instrumentations
- Preparation of complexes through heterogeneous conditions (Figures S1–7)
  - Host–guest complex [2⊃3](PF<sub>6</sub>)<sub>2</sub>

Photographic images of the reaction vessels for the encapsulation (Figure S1)

DOSY NMR spectra (Figure S2)

Enlarged <sup>1</sup>H NMR spectra (Figure S3)

<sup>19</sup>F NMR spectra (Figure S4)

Encapsulation experiments through a homogeneous process (Figures S5–S6)

Deformation of host-guest complexes in DMSO (Figure S7)

• Host–guest complex [2⊃4](PF<sub>6</sub>)<sub>2</sub>

<sup>1</sup>H NMR spectra (Figure S8)

- Dynamic light scattering (DLS) studies of the complexes (Figures S9–13)
- Photophysical data of the complexes (Figures S14–19, Table S1–3)
  - Host–guest complex  $[2\supset 3]^{2+}$  (Figures S14–16, Table S1)
  - Host–guest complex  $[2 \supset 4]^{2+}$  (Figures S17–19, Table S2)
- Modeling structure and VOIDOO calculation (Figures S20–21)
- References

#### **Materials and Instrumentations**

The <sup>1</sup>H, <sup>19</sup>F and DOSY NMR spectra were obtained at 500 MHz with Varian NMR System 500PS spectrometer. UV/Vis spectra were recorded on a Jasco V-560 spectrophotometer. The corrected emission spectra were obtained by using a Hamamatsu PMA-12 multichannel photodetector. Lifetime measurements were conducted by using a Hamamatsu C11200 streak camera as a detector and a nanosecond Q-switched Nd:YAG laser (Continuum Minilite<sup>TM</sup>). Emission quantum yields were determined by using a Hamamatsu Photonic Absolute PL Quantum Yield Measurement System C9920-02. Solvents and reagents were used as purchased. Resorcin[4]arene 1, <sup>1</sup>[Ru(bpy)<sub>3</sub>]X<sub>2</sub> (X = PF<sub>6</sub><sup>-</sup> ([**3**](PF<sub>6</sub>)<sub>2</sub>), OTf<sup>-</sup> ([**3**](OTf)<sub>2</sub>)), [Ru(phen)<sub>3</sub>]X<sub>2</sub> (X = PF<sub>6</sub><sup>-</sup> ([**4**](PF<sub>6</sub>)<sub>2</sub>), OTf<sup>-</sup> ([**4**](OTf)<sub>2</sub>)), were prepared according to an established method.<sup>1–3</sup>

#### Preparation of complexes through heterogeneous conditions





To a wet deuterated chloroform solution (0.7 ml (10 mM)) of resorcin[4]arene **1** (7.7 mg, 7.0  $\mu$ mol) was added [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> ([**3**](PF<sub>6</sub>)<sub>2</sub>, 2.0 mg, 2.3  $\mu$ mol). The suspension was heated at 50 °C for 3 h in the dark, resulted in the color change of the suspension from colorless to orange. After filtration through a membrane filter (pore size: 0.2  $\mu$ m) to remove undissolved Ru<sup>II</sup> complex, the formation of host–guest complex [**2**⊃**3**](PF<sub>6</sub>)<sub>2</sub> was confirmed by <sup>1</sup>H NMR spectroscopy and the stoichiometry of the host–guest complex was determined by the UV-vis absorption spectrum. Similar procedure was used for the preparation of stock solution (10 mM) for photophysical measurement using wet chloroform. The concentration of the host–guest complex [**2**⊃**3**](PF<sub>6</sub>)<sub>2</sub> for UV-Vis measurements was adjusted to 10 $\mu$ M by diluting the stock solution.



**Figure S1.** Photographic images of the reaction mixture for the encapsulation of  $[3](PF_6)_2$  within capsule 2 (left: in the presence of capsule 2, right: in the absence of capsule 2). The suspension turned orange in the presence of hexameric capsule 2, suggesting that  $[3](PF_6)_2$  was soluble in the cavity of 2 to form host–guest complex  $[2\supset3](PF_6)_2$ . Metastable host–guest complex  $[2\supset3](PF_6)_2$  in CHCl<sub>3</sub> gradually expel  $[3](PF_6)_2$  as a red precipitate.



Figure S2. DOSY NMR spectra (500 MHz, CDCl<sub>3</sub>, r.t.) of (a) free  $[3](OTf)_2$  and (b)  $[2\supset 3](PF_6)_2$ .



**Figure S3.** Enlarged <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, r.t.) of (a)  $[3](OTf)_2$ , (b)  $[2\supset 3](PF_6)_2$ , (c)  $[2\supset 3](OTf)_2$  and (d) free hexameric capsule **2** in the aromatic region.



**Figure S4.** <sup>19</sup>F NMR spectra (470 MHz, CDCl<sub>3</sub>, r.t.) of (a)  $[2\supset 3](PF_6)_2$  and (b)  $[^nBu_4N]PF_6$ .  $C_6F_6$  in CDCl<sub>3</sub> was used as an external standard ( $\delta = -164.9$  ppm). The doublet signal ( $^1J_{P-F} = 705$  Hz) was only slightly shifted after formation of host–guest complex  $[2\supset 3](PF_6)_2$ , suggesting that the PF<sub>6</sub> anion is not involved in the encapsulation and self-assembly process of  $[2\supset 3]^{2^+}$ .

#### Encapsulation experiments through a homogeneous process

When the 6:1 mixture of resorcinarene 1 and  $[3](PF_6)_2$  were dissolved in acetone-d<sub>6</sub>, no broadening of the signals of 1 and no up-field shifts of those of  $[3](PF_6)_2$  were observed in the <sup>1</sup>H NMR spectra (Figure S5), indicating that  $[3](PF_6)_2$  was not encapsulated within 2 probably because resorcinarene 1 cannot form the hexameric capsule in polar solvents. After dying the solution, the residue was re-dissolved in CDCl<sub>3</sub> to afford a suspension which gradually gave red precipitate of  $[3](PF_6)_2$  after 30 min (Figure S6). <sup>1</sup>H NMR spectrum of the suspension only shows the signals of hexameric capsule 2, not  $[2\supset3](PF_6)_2$ .



**Figure S5.** a) Schematic representation of the experimental procedure for NMR study, and the <sup>1</sup>H NMR spectra of b) the 6:1 mixture of 1 and  $[3](PF_6)_2$  in acetone- $d_6$  and c) the suspension formed by re-dissolution of the residue in CDCl<sub>3</sub>.



**Figure S6.** Photographic images of (a) the 6:1 mixture of 1 and  $[3](PF_6)_2$  in acetone- $d_6$  and the changes of the re-dissolved solution ((b) just after re-dissolution, (c) 15 min. and (d) 60 min. after re-dissolution). Non-encapsulated  $[3](PF_6)_2$  gradually precipitated after re-dissolving in CDCl<sub>3</sub> owing to incomplete formation of  $[2\supset3](PF_6)_2$  in acetone- $d_6$ . The color of the filtrate (e) of the re-dissolved solution (60 min. after re-dissolution) was paled out compared with that of acetone solution (a), indicating that this procedure is not effective for the encapsulation of  $[3](PF_6)_2$ .

#### Deformation of host-guest complexes in DMSO

After CDCl<sub>3</sub> solutions of host-guest complexes  $[2\supset 3](PF_6)_2$  and  $[2\supset 3](OTf)_2$  were dried by evaporation, the residues were dissolved in DMSO-*d*<sub>6</sub>. The <sup>1</sup>H NMR spectra clearly showed the mixture containing resorcinarene monomer **1** and free Ru complex  $[3]^{2^+}$ . These results can prove no decomposition of **1** and  $[3]^{2^+}$  during the encapsulation process.



**Figure S7**. <sup>1</sup>H NMR spectra (500 MHz, r.t.) of (a)  $[2\supset 3](PF_6)_2$  (in CDCl<sub>3</sub>), (b) the residue of  $[2\supset 3](PF_6)_2$  after evaporation (in DMSO- $d_6$ ), (c)  $[2\supset 3](OTf)_2$  (in CDCl<sub>3</sub>), and (d) the residue of  $[2\supset 3](OTf)_2$  after evaporation (in DMSO- $d_6$ ).

Host–guest complex [2⊃4](PF<sub>6</sub>)<sub>2</sub>



To a wet chloroform solution of resorcin[4]arene 1 (7.7 mg, 7.0  $\mu$ mol) was added [Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> ([4](PF<sub>6</sub>)<sub>2</sub>, 2.1 mg, 2.3  $\mu$ mol). The suspension was heated at 50 °C for 3 h in the dark, resulted in a color change of the suspension to orange. After filtration through a membrane filter (pore size: 0.2  $\mu$ m) to remove undissolved Ru<sup>II</sup> complex, the formation of host–guest complex [2⊃4](PF<sub>6</sub>)<sub>2</sub> was confirmed by <sup>1</sup>H NMR spectroscopy and the stoichiometry of the host–guest complex was determined by the UV-vis absorption spectrum.



**Figure S8.** <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, r.t.) of (a) [4](OTf)<sub>2</sub>, (b)  $[2\supset 4](PF_6)_2$ , and (c) free hexameric capsule 2. Broadening signals of 2 after encapsulation of  $[4]^{2+}$  suggest formation of host–guest complex  $[2\supset 4](PF_6)_2$ .

#### Dynamic light scattering (DLS) studies of the complexes

DLS data of the stock solutions of the samples (100  $\mu$ M, CHCl<sub>3</sub>) were recorded by using a Malvern HPPS (High Performance Particle Sizer). The correlation curves were fitted with biexponential decay function presumably due to trace amounts of some oligomeric impurities over 20 nm in the solutions. The volume distribution analysis suggested that the small components assigned to the target compounds were predominant in the solutions.



Figure S9. DLS data of free capsule 2 in CHCl<sub>3</sub>.



**Figure S10.** DLS data of (a)  $[2\supset 3](PF_6)_2$  which were obtained through the heterogeneous encapsulation process and (b)  $[2\supset 3](PF_6)_2$  after an addition of free capsule 2 (12 eq.).



Figure S11. DLS data of  $[2\supset 3](OTf)_2$  which were obtained through the homogeneous encapsulation process. (a, b)  $[3](OTf)_2$  in the presence of 1 (a) 6 eq. and (b) 18 eq.



Figure S12. DLS data of (a)  $[2\supset 4](PF_6)_2$  which were obtained through the heterogeneous encapsulation process and (b)  $[2\supset 4](PF_6)_2$  after an addition of free capsule 2 (12 eq.).



Figure S13. DLS data of  $[2\supset 4](OTf)_2$  which were obtained through the homogeneous encapsulation process. (a, b)  $[4](OTf)_2$ , in the presence of 1 (a) 6 eq. and (b) 18 eq.

#### Photophysical data of the complexes

All measurements were performed at room temperature under degassed conditions. Emission decay curve was analysed by the equation  $(I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2))$  using the nonlinear least-squares method. The averaged emission lifetime  $(\tau_{ave})$  was estimated by the equation  $(\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2))$ .

## Host–guest complex $[2\supset 3]^{2+}$



**Figure S14.** Emission decay curves of [**3**](OTf)<sub>2</sub>,  $[2\supset 3]$ (OTf)<sub>2</sub>, and  $[2\supset 3]$ (PF<sub>6</sub>)<sub>2</sub> in CHCl<sub>3</sub> at room temperature (10  $\mu$ M; excitation wavelength:  $\lambda_{ex} = 355$  nm).



**Figure S15.** (a) Normalized emission spectra of  $[2\supset 3](PF_6)_2$ , in the presence of free 1 ( $[2\supset 3](PF_6)_2$ : 10 µM, free 1: 0, 60, 120, 180 µM, excitation wavelength:  $\lambda_{ex} = 355$  nm), and (b) emission decay curves of the complexes (10 µM, excitation wavelength:  $\lambda_{ex} = 355$  nm) in CHCl<sub>3</sub> at room temperature. The normalized emission spectra of  $[2\supset 3](PF_6)_2$ , in the presence of various amounts of free 1 coincided with that in the absence of 1. This result suggests that the exchange reaction of 1 in  $[2\supset 3](PF_6)_2$  with free 1 is remarkably slow.



**Figure S16.** (a) Normalized emission spectra of  $[3](OTf)_2$ , in the presence of various amount of 1 ( $[3](OTf)_2$ : 10 µM, free 1: 0, 10, 30, 60, 90, 120 µM, Excitation wavelength:  $\lambda_{ex} = 355$  nm) and (b) emission decay curves of the complexes ( $[3](OTf)_2$ : 10 µM, excitation wavelength:  $\lambda_{ex} = 355$  nm) in CHCl<sub>3</sub> at room temperature. The emission spectra were gradually changed with increasing the amount of 1 owing to the self-assembly and encapsulation equilibrium. The emission spectrum of  $[3](OTf)_2$  in the presence of excess amount (12 equiv.) of 1 is similar to that of  $[2\supset3](PF_6)_2$ , suggesting that the encapsulation state of  $[2\supset3](PF_6)_2$  was far from the thermodynamic equilibrium state of 2 and  $[3](OTf)_2$  in 1:1 ratio.

Table S1. Photophysical data of [3](OTf)<sub>2</sub> in the presence of various amount of 1.

	$6 \xrightarrow[HO]{HO}{R} \xrightarrow{R} \xrightarrow{R} \xrightarrow{R} \xrightarrow{OH}{OH} + HO \xrightarrow{HO}{HO} \xrightarrow{HO}{HO} \xrightarrow{R} \xrightarrow{R} \xrightarrow{OH} \xrightarrow{OH} \xrightarrow{HO}{HO} \xrightarrow{HO}{HO} \xrightarrow{R} \xrightarrow{R} \xrightarrow{R} \xrightarrow{OH} \xrightarrow{OH} \xrightarrow{HO}{HO} \xrightarrow{HO} \xrightarrow{HO}{HO} \xrightarrow{HO} \xrightarrow{HO} \xrightarrow{HO}{HO} \xrightarrow{HO} \xrightarrow{HO}{$		[ <b>3</b> ](OTf) <sub>2</sub>		$(CHCl_3)$				
[ <b>1</b> ] [µM]	[ <b>3</b> ](OTf) <sub>2</sub> [µM]	λ <sub>emi</sub> [nm]	Φ[%]	A <sub>1</sub>	τ <sub>1</sub> [ns]	A <sub>2</sub>	τ <sub>2</sub> [ns]	χ2	$ au_{\sf ave} [{\sf ns}]$
0	10	627	12	0.17	850 <sup>a</sup>				
10	10	607	6	0.81	270	0.19	900	1.02	550
30	10	599	6	0.83	350	0.17	970	1.07	580
60	10	590	6	0.81	350	0.19	1140	1.04	690
90	10	589	5	0.79	350	0.21	1190	1.02	750
120	10	580	5	0.86	340	0.14	1370	1.07	750

<sup>a</sup> Analyzed by a single exponential decay.

Host–guest complex  $[2\supset 4]^{2+}$ 



**Figure S17.** (a) The UV-Vis absorption (10  $\mu$ M, CHCl<sub>3</sub>, r.t.) and enlarged spectra around 450 nm of host–guest complex [2⊃4](OTf)<sub>2</sub> (obtained from the 6:1 mixture of 1 and [4](OTf)<sub>2</sub>), host–guest complex [2⊃4](PF<sub>6</sub>)<sub>2</sub> (obtained through the heterogeneous encapsulation technique), free [4](OTf)<sub>2</sub>, and hexameric capsule 2. (b) Normalized emission spectra of the complexes.  $\lambda_{ex} = 355$  nm. (c) Emission decay curves of [3](OTf)<sub>2</sub>, [2⊃4](OTf)<sub>2</sub>, and [2⊃4](PF<sub>6</sub>)<sub>2</sub> in CHCl<sub>3</sub> at room temperature (10  $\mu$ M; excitation wavelength:  $\lambda_{ex} = 355$  nm).



**Figure S18.** (a) Normalized emission spectra of  $[2\supset 4](PF_6)_2$ , in the presence of free 1 ( $[2\supset 4](PF_6)_2$ : 10 µM, free 1: 0, 60, 120, 180 µM, excitation wavelength:  $\lambda_{ex} = 355$  nm) and (b) emission decay curves of the complexes (10 µM, excitation wavelength:  $\lambda_{ex} = 355$  nm) in CHCl<sub>3</sub> at room temperature. The normalized emission spectra of  $[2\supset 4](PF_6)_2$ , gradually shifted in the presence of various amounts of free 1. This result suggests that exchange of 1 between  $[2\supset 4](PF_6)_2$  and free 1 accelerated and encapsulated  $[4]^{2+}$  was affected by CHCl<sub>3</sub> solvents like that in  $[2\supset 4](OTf)_2$ .



**Figure S19.** (a) Normalized emission spectra of [4](OTf)<sub>2</sub>, in the presence of various amount of 1 ([4](OTf)<sub>2</sub>: 10  $\mu$ M, free 1: 0, 10, 30, 60, 90, 120  $\mu$ M, Excitation wavelength:  $\lambda_{ex} = 355$  nm) and (b) emission decay curves of the complexes ([4](OTf)<sub>2</sub>: 10  $\mu$ M, excitation wavelength:  $\lambda_{ex} = 355$  nm) in CHCl<sub>3</sub> at room temperature. The emission spectra were gradually changed with increasing the amount of 1 owing to the self-assembly and encapsulation equilibrium.

			2(OTf <sup>-</sup> ) Tf) <sub>2</sub>	CHCl <sub>3</sub> [2⊃4](OTf) <sub>2</sub>					
[ <b>1</b> ] [µM]	[ <b>4</b> ](OTf) <sub>2</sub> [µM]	λ <sub>emi</sub> [nm]	Φ[%]	A <sub>1</sub>	τ <sub>1</sub> [ns]	A <sub>2</sub>	τ <sub>2</sub> [ns]	χ2	$ au_{\sf ave}$ [ns]
0	10	627	3	0.25	200 <sup>a</sup>				
10	10	598	5	0.78	620	0.22	1800	1.02	1150
30	10	577	5	0.79	630	0.21	1870	1.14	1180
60	10	576	5	0.76	600	0.24	1890	1.00	1240
90	10	576	5	0.84	700	0.16	2360	1.11	1350
120	10	572	5	0.76	770	0.24	2430	1.01	1600

Table S2. Photophysical data of [4](OTf)<sub>2</sub> in the presence of various amount of 1.

<sup>a</sup> Analyzed by a single exponential decay.

Complex	λ <sub>emi</sub> [nm]	Φ[%]	A <sub>1</sub>	τ <sub>1</sub> [ns]	A <sub>2</sub>	τ <sub>2</sub> [ns]	χ2	$ au_{\sf ave} [{\sf ns}]$
[ <b>3</b> ](OTf) <sub>2</sub>	627	12	0.26	850 <sup>a</sup>				
[ <b>2</b> ⊃ <b>3</b> ](OTf) <sub>2</sub>	590	6	0.81	350	0.19	1140	1.04	690
[ <b>2</b> ⊃ <b>3</b> ](PF <sub>6</sub> ) <sub>2</sub>	581	3	0.88	290	0.12	1390	1.06	730
[ <b>3</b> ](PF <sub>6</sub> ) <sub>2</sub>	621	11	0.18	820 <sup>a</sup>				
[ <b>4</b> ](OTf) <sub>2</sub>	599	3	0.95	200 <sup>a</sup>				
[ <b>2</b> ⊃ <b>4</b> ](OTf) <sub>2</sub>	576	5	0.76	600	0.24	1890	1.00	1240
[ <b>2</b> ⊃ <b>4</b> ](PF <sub>6</sub> ) <sub>2</sub>	562	5	0.82	670	0.18	2030	1.04	1210
[ <b>4</b> ](PF <sub>6</sub> ) <sub>2</sub>	603	5	0.85	390 <sup>a</sup>				

Table S3. Photophysical data of the complexes in CHCl<sub>3</sub> at r.t.

<sup>a</sup> Analyzed by a single exponential decay.

#### **Modeling structure and VOIDOO calculation**

In order to estimate the central void volumes of capsule **2** and molecular volumes of the complex cations, the VOIDOO calculations based on their crystal structures were performed. The following parameters were modified from the default for the calculations:

#### **Cavity calculations**

Primary grid spacing: 0.1 Nr of detection cycles: 30 Nr of Maximum number of detection cycles: 30 Maximum number of volume-refinement cycles: 30 Type of cavity volume: Probe-occupied: occupied by rolling probe Minimum size of secondary grid: 1 Grid for plot files: 0.15

## Volume calculations

Nr of volume-refinement cycles: 30



**Figure S20.** A molecular modeling of  $[2\supset 3]^{2^+}$ . Hexameric capsule 2 is shown with lines and Ru complex cation  $[3]^{2^+}$  is shown in a space filling depiction. Hydrogen atoms and water molecules of the capsule are omitted for clarity.



**Figure S21.** (a) The void (light greenish blue mesh) of hexameric capsule **2**. (b) The molecular volumes of the complex cations. The values were calculated by the VOIDOO program (probe radius = 1.40 Å). Packing coefficients (PC) were estimated by using these values.

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