Supporting Information for:

# Proton-Driven Coordination-Induced Spin State Switch (PD-CISSS) of Iron(II) Complexes

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#### 1. Synthesis of the samples:

All syntheses were carried out under inert conditions using argon as inert gas. The sodium form of zeolite Y was purchased from *Sigma-Aldrich*, washed several times with deionized water to remove impurities and was dried at air. Before all preparations the raw zeolite was degassed several times and heated under vacuum to ensure that all channels are unclogged and accessible. The iron(II) chloride was prepared as described in literature.<sup>[1]</sup> 2,2'-bipyridine was of 99+% reagent grade (*Acros*) and was dried at 50 °C *in vacuo* prior to use. 2,6-bis(1H-pyrazol-3-yl) was synthesized according to the literature.<sup>[2]</sup> All solvents were purified as described in literature.<sup>[3]</sup>

**Fe(bipy)**<sub>3</sub>**Cl**<sub>2</sub> (1): The complex was synthesized using standard procedures. The product was found to be associated with two water molecules. MS [DEI(+), 70 eV ]: m/z = 156.07 [bipy]<sup>+</sup>. Fe(bipy)<sub>3</sub>Cl<sub>2</sub> · 2 H<sub>2</sub>O (631.34): C<sub>30</sub>H<sub>28</sub>Cl<sub>2</sub>FeO<sub>2</sub>N<sub>6</sub> Calcd. C 56.89, H 4.77, N 13.27; found C 56.05, H 4.74, N 12.95;

**Fe(bpp)**<sub>2</sub>**Cl**<sub>2</sub> (2): The preparation of salts of this complex except the chloride salt is described in the literature.<sup>[4]</sup> Since Fe(bpp)<sub>2</sub>Cl<sub>2</sub> does not precipitate easily the synthesis has been adjusted. All steps in this synthesis were carried out using Schlenk tube techniques and argon as inert gas. 1.5 g of FeCl<sub>2</sub> · 4 H<sub>2</sub>O (M = 198.81 g/mol, n = 7.55 mmol) and 2.1 equivalents of 2,6-di(1*H*-pyrazol-3-yl)pyridine (M = 211.23 g/mol, m = 3.35 g, n = 15.86 mmol) were dissolved in 20 mL of MeOH and heated to reflux for 1 h. After cooling to room temperature the MeOH was evaporated. The obtained brown-orange powder was washed with 5 × 20 mL of toluene to remove the ligand excess. The remaining precipitate was dried *in vacuo*. The resulting brown orange product was found to be associated with two water molecules. MS [DEI(+), 70 eV]: m/z = 211.09 [bpp]<sup>+</sup>. Fe(bpp)<sub>3</sub>Cl<sub>2</sub> · 2 H<sub>2</sub>O (585.23): C<sub>22</sub>H<sub>22</sub>Cl<sub>2</sub>FeO<sub>2</sub>N<sub>10</sub> Calcd. C 56.89, H 4.77, N 13.27; found C 56.05, H 4.74, N 12.95;

**Preparation of aqueous solutions with different pH-values:** The pH of the solutions was determined with a *Mettler Toledo MP 220* pH meter. All measurements have been conducted three times. The pH Meter was calibrated with a buffer solution pH 7.00 from *Fluka*. Acidic solutions between pH 6 and pH 1 have been prepared by adjusting the pH with 0.1 M HCl solution (pH 1, distilled water: pH 5.9) which was purchased from *Grüssing*. Acidic solutions below pH 1 have been adjusted with distilled water and conc. HCl which was purchased from *Bernd Kraft*. Solutions more basic than the used water have been adjusted with 0.1 M NaOH from *Grüssing*.

1@NaY: 1.0 g of excessively washed NaY is dried on air and subsequently heated under argon and vacuum several times with a heat gun to remove water. Another flask is prepared with 0.051 g (0.26 mmol) of iron(II)chloride tetrahydrate, 0.44 g (2.8 mmol) of 2,2'-bipyridine and 50 mL distilled MeOH. The red solution is transferred into the flask with the zeolite and the suspension was stirred for 2 h. Subsequent filtering (pore IV) and washing with 100 mL of toluene yields 0.9 g of a pink powder which is dried *in vacuo*; 0.13 % Fe, 0.26 % N, 12.31 % C, 3.05 % H.

**2@NaY:** 1.0 g of excessively washed NaY is dried on air and subsequently heated under argon and vacuum several times with a heat gun to remove water. Another flask is prepared with 0.051 g (0.26 mmol) of iron(II)chloride tetrahydrate, 0.36 g (1.7 mmol) of 2,6-bis(1*H*-pyrazol-3-yl)pyridine and 50 mL distilled MeOH. The orange-brownish solution is transferred into the flask with the zeolite. The suspension was stirred for 4 h. Subsequent filtering (pore IV) and washing with 100 mL of toluene yields 0.9 g of a yellow powder which is dried *in vacuo*; 0.36 % Fe, 0.97 % N, 9.11 % C, 2.61 % H.

The samples **1** and **2** were fully characterized in the solid state by elemental analysis (C, H, N), AAS (Fe), TGA, solid-state NMR, UV-Visible and Evanescent-Wave-IR spectroscopy. Mössbauer spectroscopy was used to distinguish between the different possible iron sites in the zeolite cavity. The results confirm the formation of the complexes solely in the supercages, the absence of complexes on the surface (IR, UV-Vis, Mössbauer) and were used to determine the sample composition (CHN, AAS, Mössbauer).

#### 2. Methods

<sup>1</sup>H-NMR spectra were recorded on a *Varian Unity Inova 300* spectrometer from *Agilent Technologies* at 300 MHz in D<sub>2</sub>O/H<sub>2</sub>O mixtures; pH-values have been adjusted with 0.1 M HCl and concentrated HCl. Data had been calibrated by D<sub>2</sub>O (4.79 ppm) and fitted with *Spinworks*. <sup>57</sup>Fe Mössbauer spectra were recorded in transmission geometry in a constant-acceleration mode using a conventional Mössbauer spectrometer equipped with a 50mCi <sup>57</sup>Co(Rh) source. The samples were prepared under ambient conditions. The spectra were fitted using Recoil 1.05 Mössbauer Analysis Software. The isomer shift values were reported with respect to  $\alpha$ -Fe as a reference at room temperature. Magnetic susceptibility data were collected using a MPMSXL-5 SQUID magnetometer under an applied field of 20 000 Oe over the temperature range 150 K – 400 K (solid state) and 260 K – 350 K (solution). The solid samples were prepared in gelatin capsules. The liquid samples were held within a plastic

straw that was sealed to give a suitable reservoir. The data were corrected for the diamagnetic contributions of the ligands (tabulated Pascal's constants), the sample holder and the solvent in case of the solutions. The high spin molar fraction was calculated as  $\gamma_{\text{HS}} = (\chi_{\text{M}}T)/(\chi_{\text{M}}T)_{(S=2)}$ where  $(\chi_M T)_{(S=2)}$  is the theoretical value for a complex with the total spin S of 2. The longitudinal relaxation time  $T_1$  was monitored with a STELAR FFC 2000 relaxometer. The measurements were conducted in an extended glass straw and at 300 K ± 1 K. The Larmorfrequency was varied between 10 kHz and 10 MHz with  $v = \gamma B/2\pi$  where  $\gamma$  is the gyromagnetic ratio and B is the external magnetic field. The molar relaxivity  $\Delta r_1$  was calculated as:  $\Delta r_1 = \frac{R_1 - R_1^{LM}}{c}$ ;  $R_1$  = observed longitudinal relaxation,  $R_1^{LM}$  = observed longitudinal relaxation of the solvent. Elemental analysis (C, H, N) was done on a Vario EL III that was produced by Elementar Analysensysteme GmbH. Acetanilide was used as standard reference. For the weighed portion a precision balance was used ( $\Delta m = 0.0001 \text{ mg}$ ). Mass spectra were recorded on a Finnigan MAT 8500 with a data system MASPEC II. UV-Vis spectra were recorded on a Cary 300 UV-Vis from Agilent Technologies with a special sample holder for solids in the reflective mode. For calibration a reference sample with 100 % transmission was used. Thermogravimetric analysis was carried out with a TGA 2050 (TA instruments). IR-spectra were recorded with a Perkin Elmer Spectrum 100 FT-IR spectrometer. <sup>1</sup>H spectra were recorded on a Bruker Avance III HD 400 spectrometer operating at a B<sub>0</sub> field of 9.4 T using a double-resonance 4 mm Bruker MAS probe and at a rotation frequency of 5 kHz. Chemical shifts of <sup>1</sup>H were referenced indirectly to TMS using adamantane. The  $^1H$  one-pulse experiments were acquired using a 90° pulse lengths of 3.0  $\mu s$ with a recycle delay of 0.5 s. T<sub>1</sub> measurements were done without spinning using the inversion-recovery scheme with inter-pulse delays varying from 50 µs up to 2.0 s. The resulting curve were then fitted using the equation displayed in Figure S8.

## 3. Details for the Characterization of the samples



3.1.pH and T-dependent UV-Vis Spectroscopy of 1

**Figure S1.** A) pH-dependent UV-Vis spectra of  $[Fe(bipy)_3]^{2+}$  (c = 0.010 mmol/L) showing the disappearance of the MLCT band when the pH of the solution is lowered. B) Excerpt of the *T*-dependent UV-Vis spectra of  $[Fe(bipy)_3]^{2+}$  (c = 0.084 mmol/L) at pH 2 showing the disappearance of the MLCT band with increasing temperature. C) picture of  $[Fe(bipy)_3]^{2+}$  solutions (for all c = 0.020 mmol/L) at different pH showing a pronounced influence on the color of the complex due to the mechanism discussed in the manuscript.

### 3.2.Brønsted acid sites of NaY and 1@NaY



**Figure S2.** <sup>1</sup>H solid state MAS NMR spectra of NaY and **1@NaY**. The Brønsted acid sites in the zeolite are typically observed between 3.5 and 4.5 ppm depending on the zeolite source.<sup>[5]</sup> In the NaY starting material they were observed at 3.7 ppm and their presence in **1@NaY** is confirmed by a peak at 3.8 ppm. The environment is acidic due to a shift of 0.2 ppm from 3.6 ppm as shown by *Yan et al.*<sup>[5]</sup> Incorporated water is found at 3.0 ppm (NaY) and 3.4 ppm (**1@NaY**). The impregnated sample was washed with toluene which signals appear at 2.6 ppm and 7.4 ppm; 0.2 ppm deep-field-shifted compared to solution.<sup>[6]</sup> Due to the low complex loading the resonances of the ligand are hidden by the toluene signals.

If we assume 260 molecules of water in the unit cell and 0.5 bronstead acid sites, the "concentration" of protons gives a theoretical pH of 1. As part of the protons are bound to the zeolite cavity the actual pH is higher, but it can be lowered further if water is removed by heating. Thus pH = 1 is easily attainable.

## 3.3. Optical Characterization of 1@NaY and 2@NaY

The optical spectra as received after synthesis (Manuscript, Figure 2) revealed only small differences between the materials and the bulk complex. The maximum of the MLCT-envelope of the  $[Fe(bipy)_3]^{2+}$  sample **1@NaY** is shifted towards 530 nm with 520 nm of the bulk what is characteristic for the small confinement. The *d*-*d* transition at 350 nm is *Laporte*-forbidden and therefore very weak.<sup>[7]</sup> The optical spectrum of **2@NaY** is mostly identical to the one reported by Halcrow *et al.*<sup>[4]</sup> The MLCT envelope is slightly red-shifted from 450 to 460 nm as it is observed for the bulk material in DMF. In our case it is also attributed to the interaction with the supercage. The shoulder at 550 nm is not assigned in the literature but belongs probably also to the MLCT-envelope. The  $\pi$ - $\pi$ \* transition appears at 310 nm. A *d*-*d* transition is not observed what highlights the high symmetry of the complex.

Upon heating for both samples a color change is observed that is displayed in **Fig. S3**. The reason for this behavior is discussed in the manuscript in detail.



Figure S3. Photographs of 1 (sample 4A on the left hand side) and 2 (sample 4B on the right hand side) put on a filter paper (upper row) and their corresponding color change when positioned on a heating plate (lower row). The reversibility of the color change is demonstrated in the movie M1.

# 3.4. Determination of the complex position of 1@NaY and 2@NaY

Evanescent-wave-IR measurements show that no adhesion of complexes on the surface is taking place for both composite samples. This proves the incorporation of the complex in the zeolite. The corresponding spectra are given in the **Fig. S4**. Vibrations between 600 and 1200 cm<sup>-1</sup> belong to the zeolite lattice while the small vibrations around 1600 cm<sup>-1</sup> belong to water which is incorporated in the aluminosilica framework.<sup>[8]</sup>



Figure S4. Evanescent-wave-IR measurements of the discussed samples. Relative transmission is plotted against the wave number. The spectra were recorded between 600 and  $1800 \text{ cm}^{-1}$ . Denoted from top to bottom: 1@NaY, 2@NaY.

#### 3.5. Mössbauer Spectroscopy of the composite materials

Mössbauer spectroscopy is a powerful method to distinguish the different iron species in the zeolite (small cavities or supercage, coordinating ligands). Consequently, Mössbauer spectra were recorded at room temperature for both samples. The obtained Mössbauer parameters are summarized in **Table S1**. In **Figure S5** the Mössbauer spectrum of **1@NaY** and **2@NaY** is given. Only one LS doublet is detected in both cases. For **1@NaY**, the observed doublet can be clearly assigned to  $[Fe(bipy)_3]^{2+}$  and no indications of other species (e.g. mono- and bis-bipyridine coordinated species<sup>[9,10]</sup>) are observed, in agreement with results of Lunsford et al.<sup>[11–13]</sup> The Mössbauer spectrum of **2@NaY** is also in agreement with the formation of the homoleptic complex  $[Fe(bpp)_2]^{2+}$  inside of the zeolite. Surprisingly no indication for the presence of a HS species at room temperature is observed indicating a strong influence of the zeolite matrix on the spin state of the iron complex. In agreement with this, no indication for a color change upon cooling is observed. This indicates that the magnetic properties are significantly influenced by the zeolite environment as reported before for cobalt and iron complexes encapsulated in a zeolite matrix.<sup>[14]</sup>



Figure S5. Mössbauer spectra of the composite materials 1@NaY and 2@NaY at room temperature.

Table S1. Compilation of the Mössbauer parameters of the samples discussed.

	Spin-state	$\delta$ [mm s <sup>-1</sup> ]	$E_{\rm Q}  [{\rm mm \ s}^{-1}]$	<i>Γ</i> /2 [mm s <sup>-1</sup> ]	Population [%]
1@NaY	LS	0.230(29)	0.341(59)	0.241(53)	100
2@NaY	LS	0.288(22)	0.720(37)	0.251(30)	100

# 3.6. Thermogravimetric Analysis of the composite materials

Thermogravimetric analysis was used to follow the removal of the water from the zeolite cavities upon heating. For both samples a mass loss upon heating above room temperature is observed due to the release of water that is in very good agreement with the change of the magnetic moment in the SQUID magnetometer. Slight differences between the temperatures are due to the different measurement setups (TG: atmospheric pressure, SQUID: vacuum).



Figure S6. Thermogravimetric analysis of the samples 1@NaY and 2@NaY.

# 3.7. <sup>1</sup>H-NMR-spectroscopy of 1

Complex 2 is paramagnetic in aqueous solution at room temperature and was thus not investigated. Different concentrations of 1 were used and found to be of no influence on the obtained spectra.



**Figure S7.** Comparison of the <sup>1</sup>H-NMR spectra for the free ligand 2,2'-bipyridine and the complex  $[Fe(bipy)_3]^{2+}$  at representative pH-values (5.9, 1.0 and 0.2) For the free ligand at pH 5.9 the unprotonated ligand and at pH 1.0 and pH 0.2 (not given as identical to 1.0) the protonated ligand is observed in D<sub>2</sub>O/H<sub>2</sub>O mixtures. This is in agreement with only one pK<sub>A</sub> value reported in literature (4.43). For the complex, at pH 1.0 the protonated species is observed that is discussed in detail in the manuscript. In contrast to the free ligand, at pH 0.2 a new species is observed that is most likely a doubly protonated species. Details of the different peak positions are given in Table S2 and S3. Please note that for the protons 3 and 4 the signal of the protonated complex and the protonated free bipy ligand is different at pH 1.0 due to differences in the symmetry.

**Table S2:** <sup>1</sup>H-NMR peak positions in ppm for **1** ( $[Fe(bipy)_3]^{2+}$ ) in D<sub>2</sub>O/H<sub>2</sub>O at different pH-values. 3, 4, 5 and 6 are assigned with respect to the typical nomenclature. 3\*, 4\*, 5\* and 6\* represent the emerging signals for the protonated species. 3\* and 4\* cannot be separated.

	3 (d)	4 (t)	5 (t)	6 (d)	3*, 4* (m)	5* (m)	6* (d)
pН	8.558,	8.089,	7.360,	7.517,			
5.9	8.585	8.115, 8.140	7.381, 7.403	7.534	-	-	-
pН	8.541,	8.071,	7.341,	7.500,	8.414, 8.442,	7 807 7 017 7 037	8.868,
3.8	8.568	8.097, 8.112	7.363, 7.384	7.517	8.464, 8.487	7.097, 7.917, 7.937	8.852
pН	8.532,	8.062,	7.333,	7.490,	8.408, 8.435,	7.894, 7.887, 7.911,	8.844,
2.9	8.559	8.088, 8.114	7.354, 7.376	7.509	8.458, 8.481	7.927, 7.934	8.862
pН	8.534,	8.064,	7.335,	7.489,	8.410, 8.844,	7.890, 7.895, 7.912,	8.846,
1.9	8.560	8.090, 8.115	7.356, 7.378	7.507	8.459, 8.480	7.927, 7.934	8.863
pН	8.508,	8.038,	7.310,	7.458,	8.283, 8.412,	7 865 7 872 7 008	8.820,
1.0	8.535	8.065, 8.089	7.332, 7.355	7.478	8.432, 8.450	7.805, 7.872, 7.908	8.838

**Table S3:** <sup>1</sup>H-NMR peak positions in ppm for 2,2'-bipyridine in  $D_2O/H_2O$  at different pH-values.

	<b>3, 4 (m, d)</b>	5 (m)	6 (d)
рН 5.9	8.007, 8.010, 8.028, 8.046	7.509, 7.531, 7.535, 7.554	8.626, 8.642
pH 1.0	8.358, 8.371	7.816, 7.832, 7.847, 7.863	8.755, 8.772

We would like to point out that the existing data does essentially not support an acid decomposition under complete dissociation of the complex  $[Fe(bipy)_3]^{2+}$  into  $[Fe(bipy)_2S_2]^{2+}$  (S denotes to solvent molecules) and bipyH<sup>+</sup> in the presented pH-area. The SQUID-data at pH 1.0 and 300 K verifies that around 25 % of all iron complexes are in a paramagnetic HS state. When we assume the above mentioned dissociation process would take place we would find the overall composition as follows:



We cannot find this **10** % of protonated compound (1:9 ratio) in <sup>1</sup>H-NMR (area of the signals). Instead we are finding nearly **30** % of a protonated species which fully supports our depicted half-bonded three-step mechanism.

If we assume again a complete dissociation based on around 30 % of protonated species as found at pH 1.0 and 300 K via integration of the <sup>1</sup>H-NMR signals we would get following composition based on a 30:70 ratio of protonated and unprotonated bipyridine:

<b>3</b> $[Fe(bipy)_2S_2]^{2+}$	+	$3$ bipy $\mathbf{H}^+$	+	<b>7/3</b> $[Fe(bipy)_3]^{2+}$
$\downarrow$				$\downarrow$

56 % paramagnetic, HS

44 % diamagnetic, LS

Since 25 % of paramagnetic molecules and not 56 % are found via SQUID-measurements this also fully supports our depicted mechanism and shows that essentially no complete acid decomposition is taking place. The integrals of the different species are summarized in Table S4.

**Table S4:** Integrals in <sup>1</sup>H-NMR for **1** ( $[Fe(bipy)_3]^{2+}$ ) in D<sub>2</sub>O/H<sub>2</sub>O at different pH-values. The sum was normalized to give 24 protons. 3\* and 4\* are too close to be separated. The integrals of the <sup>1</sup>H-NMR spectra were used to calculate the percentage of protonated molecules  $\gamma$ H<sup>+</sup> by dividing the sum of the integrals belonging to the new signals (3\*, 4\*, 5\* and 6\*) through the total sum of the integrals belonging to both complexes.

	3	4	5	6	3*, 4*	5*	6*	γH <sup>+</sup>
рН 5.9	6.079	5.996	5.972	5.954	0.000	0.000	0.000	0.00
рН 3.8	5.815	5.518	5.512	5.644	0.733	0.303	0.474	0.06
рН 2.9	5.145	5.123	5.593	5.404	1.389	0.740	0.605	0.11
рН 1.9	5.249	4.937	5.111	5.136	1.779	0.823	0.966	0.15
рН 1.0	4.151	3.965	4.452	4.416	3.510	1.715	1.790	0.29

pKa values have been determined based on the experimental <sup>1</sup>H-NMR- and SQUID-data for the acid-base-reaction as follows:

$$Fe(bipy)_{3}H^{3+} + H_{2}O \leftrightarrow H_{3}O^{+} + Fe(bipy)_{3}^{2+}$$
$$K = \frac{c[H_{3}O^{+}] * c[Fe(bipy)_{3}^{2+}]}{c[H_{2}O] * c[Fe(bipy)_{3}H^{3+}]}; where c[H_{2}O] = const$$

$$K_{a} = K * c[H_{2}O] = \frac{c[H_{3}O^{+}] * c[Fe(bipy)_{3}^{2+}]}{c[Fe(bipy)_{3}H^{3+}]} ; pK_{a} = -\log(K_{a} * 1\frac{mol}{L})$$

$$pK_{a} = -\log\left\{\frac{c[H_{3}O^{+}] * c[Fe(bipy)_{3}^{2+}]}{c[Fe(bipy)_{3}H^{3+}]} * 1\frac{mol}{L}\right\}$$

$$pH 1.0, 300 K:$$

$$c[H_3O^+] = 0.1 \frac{mol}{L}, c[Fe(bipy)_3^{2^+}] = 3.08 \frac{mmol}{L}, c[Fe(bipy)_3H^{3^+}] = 3.92 \frac{mmol}{L}$$
  
 $pK_a = 1.1$   
 $pH 2.0, 300 K$ :

$$c[H_{3}O^{+}] = 0.01 \frac{mol}{L}, c[Fe(bipy)_{3}^{2+}] = 5.04 \frac{mmol}{L}, c[Fe(bipy)_{3}H^{3+}] = 1.96 \frac{mmol}{L}$$
$$pK_{a} = 1.5$$
$$\overline{pK_{a}} = 1.3$$

*Comparison*:  $pK_a(HCl) = -7$ ,  $pK_a(Fe(H_2O)_6^{3+}) = 2.5$ ,  $pK_a(bipy) = 4.43$ 

We find an average  $pK_a$  value of 1.3 for Fe(bipy)<sub>3</sub>H<sup>3+</sup> and an corresponding average  $pK_b$  value of 12.7 for Fe(bipy)<sub>3</sub><sup>2+</sup>.

Literature: Riedel, Anorganische Chemie, 6. Auflage (de Gruyter, 2004); C.V. Krishnan, C. Creutz, H.A. Schwarz, N. Sutin, *J. Am. Chem. Soc.* **1983**, 105, 5617-5623.; NIST Database, acid dissociation constants



# 3.8. Solid-State NMR Spectroscopy of the composite materials

**Figure S8.** <sup>1</sup>H inversion-recovery experiments via solid-state NMR to determine the relaxation time  $T_1$  of the water molecules bound inside the interzeolitic channels. Top: Sample **2@NaY** dried in vacuo at 400 K (left) and satured above water vapour for 1 d (right). Sample **1@NaY** treated with a droplet of 0.1 M HCl and saturated above water vapour for 1 d. Relaxation times  $T_1$  have been measured at 300 K (middle, left), 320 K (middle, right), 340 K (bottom, left) and 375 K (bottom, right).



**3.9.** Optical response of 1@NaY upon heating and upon changing the pH of suspensions in water

**Figure S9.** Proposed mechanisms leading to the formation of protonated and pentacoordinated species inside the supercage. Top: Interzeolitic proton defects undergo a competitive acid-base reaction with ligands in the near surrounding and change thereby the magnetism of the iron centers. Bottom: External protons move through the channels and attach to the nitrogen-donor. In both cases the six-coordinated diamagnetic LS complex switches to a penta-coordinated paramagnetic HS complex with a free coordination side. The pictures show the color change of the composite material upon heating (top) and as suspension in aqueous solution with different pH (bottom).

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