Supporting Information for the manuscript

Multielectron Redox Chemistry of Lanthanide Ions Supported by Tetradentate Schiff Bases.

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**A) Ortep of the solid state structure of K₃[Tb(bis-salophen)]**

*Figure S.A.1.* Ortep view of the solid-state structure of \{[K₃Tb(bis-salophen)](py)₅\}_∞ 4. Hydrogen atoms and solvent molecules are omitted for clarity. The C-C bonds formed by reduction of the imine moieties of the salophen ligands are represented in yellow. Color code: terbium (green), potassium (purple), nitrogen (blue), oxygen (red) and carbon (grey).

*Figure S.A.2.* Detail of the solid-state molecular structure 4 representing the [Tb(bis-salophen)]³⁻ anion. The C-C bond formed by reduction of the imine moieties of the salophen ligands is represented in yellow. Color code: terbium (green), nitrogen (blue), oxygen (red) and carbon (grey).

*Figure S.A.3.* Representation of the two isomeric forms of [M(salophen)₂] complexes. a) meridional isomer. b) sandwich isomer.
B) $^1$H NMR spectra

Solution structure of $\text{K}[\text{Ln}^\text{R}(\text{salophen})_2]$: The $\text{K}[\text{Ln}^\text{R}(\text{salophen})_2]$ complexes are stable and soluble in common organic solvents such as THF, pyridine, acetonitrile, and the recorded mass spectra are in agreement with this formulation in solution.

The $^1$H NMR spectrum of the $\text{K}[\text{Nd}^{\text{Me}}(\text{salophen})_2]$ complex (Figure S.B.13) recorded in deuterated THF at room temperature shows two sets of seven signals in agreement with the presence in solution of the sandwich and meridional isomers in a ~ 1:2 ratio. The isomer ratio is solvent dependent (a ratio 1:1.4 is found in acetonitrile). The $^1$H NMR spectrum of the $\text{K}[\text{Nd}(\text{salophen})_2]$ and $\text{K}[\text{Nd}^{\text{IBu}}(\text{salophen})_2]$ complexes (Figures S.B.1 and S.B.15) recorded in deuterated THF at room temperature displays a series of broad peaks suggesting the presence of exchanging solution species. The spectrum of $\text{K}[\text{Nd}^{\text{IBu}}(\text{salophen})_2]$ remains broad at low temperature (243 K), while the $^1$H NMR spectrum of $\text{K}[\text{Nd}(\text{salophen})_2]$ recorded at 243 K in deuterated THF shows 14 resonances of equal intensity ranging from $\delta = 39.5$ to $\delta = -13.3$ ppm (Figure S.B.2) in agreement with the presence of two isomers in a 1:1 ratio.

The dynamic behaviour of the $\text{K}[\text{Ln}(\text{salophen})_2]$ complexes varies with the size of the Ln(III) ion with an increased rigidity observed for the smaller lanthanide ions (two sets of well resolved signals of equal intensity are observed for the Yb(III) complex at room temperature) (Figures S.B.8).

Figure S.B.1. $^1$H NMR spectrum (298 K, 400 MHz) in THF-$d_8$ of a ~5 mM solution of $\text{K}_2\text{salophen}$ and $\text{Nd}(\text{OTf})_3$ in a 2:1 ratio affording $\text{K}[\text{Nd}(\text{salophen})_2]$. 

○ THF
○ grease
Figure S.B.2. $^1$H NMR spectrum (243 K, 400 MHz) in THF-$d_8$ of a ~5 mM solution of K$_2$salophen and Nd(OTf)$_3$ in a 2:1 ratio affording K[Nd(salophen)$_2$].

![Diagram of NMR spectrum for K[Nd(salophen)$_2$]](image)

Figure S.B.3. $^1$H NMR spectrum (298 K, 200 MHz) in THF-$d_8$ of the complex K$_3$[Nd(bis-salophen)].

![Diagram of NMR spectrum for K$_3$[Nd(bis-salophen)]](image)
Figure S.B.4. $^1$H NMR spectrum (293K, 200 MHz) in THF-d$_8$ of the complex K$[\text{Eu(salophen)}_2]$. 

Figure S.B.5. $^1$H NMR spectrum (293K, 200 MHz) in THF-d$_8$ of the complex K$_3[\text{Eu(bis-salophen)}]$. 
Figure S.B.6. $^1$H NMR spectrum (273K, 400 MHz) in THF-d$_8$ of the complex $\text{K}[\text{Tb(salophen)}_2]$. 

Figure S.B.7. $^1$H NMR spectrum (298K, 400 MHz) in THF-d$_8$ of the complex $\text{K}_3[\text{Tb(bis-salophen)}]$. 
Figure S.B.8. $^1$H NMR spectrum (298K, 400 MHz) in THF-$d_8$ of the complex K[Yb(salophen)$_2$].

Figure S.B.9. $^1$H NMR spectrum (243K, 400 MHz) in THF-$d_8$ of the complex K$_3$[Yb(bis-salophen)].
Figure S.B.10. $^1$H NMR spectrum (298K, 400 MHz) in THF-d$_8$ of the reaction mixture of NdI$_2$ with 2 equivalents of K$_2$salophen a) before addition of K b) after addition of K. Yellow : K[Nd(salophen)$_2$] ; purple K$_3$[Nd(bis-salophen)].

a) [NMR spectrum diagram a)]

b) [NMR spectrum diagram b)]
Figure S.B.11. $^1$H NMR spectrum (298K, 400 MHz) in THF-$d_8$ of the reaction mixture of EuI$_2$ with 2 equivalents of K$_2$salophen: Yellow: K[Eu(salophen)$_2$]; purple K$_3$[Eu(bis-salophen)].

Figure S.B.12. $^1$H NMR spectrum (243K, 400 MHz) in THF-$d_8$ of the reaction mixture of EuI$_2$ with 2 equivalents of salophenK$_2$: Yellow: K[Eu(salophen)$_2$]; purple K$_3$[Eu(bis-salophen)].
Figure S.B.13. $^1$H NMR spectrum (298K, 200 MHz) in THF-$d_8$ of the complex $\text{K}[\text{Nd}^{\text{Me} \text{salophen}}]_2$.

Figure S.B.14. $^1$H NMR spectrum (298K, 200 MHz) in THF-$d_8$ of the complex $\text{K}_3[\text{Nd}(\text{bis-Me} \text{salophen})]$. 
Figure S.B.15. $^1$H NMR spectrum (298 K, 400 MHz) in THF-$d_8$ of the complex K[Nd(\text{salophen})$_2$].

Figure S.B.16. $^1$H NMR spectrum (298 K, 200 MHz) in THF-$d_8$ of the complex K$_3$[Nd(bis-tBu salophen)].
Figure S.B.17. $^1$H NMR spectrum (243K, 400 MHz) in THF-d$_8$ of K$_3$[Nd(bis-salophen)] after reaction with two equivalents of AgOTf affording K[Nd(salophen)$_2$].

Figure S.B.18. $^1$H NMR spectrum (298K, 400 MHz) in THF-d$_8$ of K$_3$[Tb(bis-salophen)] after reaction with two equivalents of AgOTf affording K[Tb(salophen)$_2$].
Figure S.B.19. $^1$H NMR spectrum (243K, 400 MHz) in THF-$d_8$ of K$_3$[Nd(bis-salophen)] after reaction with one equivalent of 9,10-phenanthrenequinone affording K[Nd(salophen)$_2$].

Figure S.B.20. $^1$H NMR spectrum (243K, 400 MHz) in THF-$d_8$ of K$_3$[Nd(bis-salophen)] after reaction with one equivalents of I$_2$ affording K[Nd(salophen)$_2$].
Figure S.B.21. $^1$H NMR spectrum (243K, 400 MHz) in THF-d$_8$ of K$_3$[Nd(bis-salophen)] after reaction with dry oxygen affording K[Nd(salophen)$_2$] and K$_2$salophen.

Figure S.B.22. $^1$H NMR spectrum (298K, 200 MHz) in pyridine-d$_5$ of the complex K[Nd(bis-H$_2$salophen)].
**Figure S.B.23.** $^1$H NMR spectrum (298K, 200 MHz) in pyridine-d$_5$ of the crude reaction of 1 equivalent of K$_2$salophen with NdI$_3$(THF)$_4$. The same spectrum is obtained when the reaction is performed with Nd(OTf)$_3$.

![NMR spectrum](image1)

**Figure S.B.24.** $^1$H NMR spectrum (298K, 200 MHz) in pyridine-d$_5$ of the crude mixture of the reaction of complex [Nd$_2$(cyclo-salophen)] with AgOTf.

![NMR spectrum](image2)
C) ES-MS spectra

Figure S.C.1. ESI mass spectrum (positive ionisation mode) of the complex K[Nd(salophen)₂].

Figure S.C.2. ESI mass spectrum (positive ionisation mode) of the complex K₃[Nd(bis-salophen)].
Figure S.C.3. ESI mass spectrum (positive ionisation mode) of the complex $\text{K}[\text{Eu(salophen)}_2]$.

Figure S.C.4. ESI mass spectrum (positive ionisation mode) of the complex $\text{K}_3[\text{Eu(bis-salophen)}]$. 
Figure S.C.5. ESI mass spectrum (positive ionisation mode) of the complex $\text{K}[\text{Tb(salophen)}_2]$.

Figure S.C.6. ESI mass spectrum (positive ionisation mode) of the complex $\text{K}_3[\text{Tb(bis-salophen)}]$. 
Figure S.C.7. ESI mass spectrum (positive ionisation mode) of the complex K[Yb(salophen)$_2$].

Figure S.C.8. ESI mass spectrum (positive ionisation mode) of the complex K$_3$[Yb(bis-salophen)].
Figure S.C.9. ESI mass spectrum (positive ionisation mode) of the complex K[Nd(Me-salophen)₂].

Figure S.C.10. ESI mass spectrum (negative ionisation mode) of the complex K₃[Nd(bis-Me-salophen)].
Figure S.C.11. ESI mass spectrum (negative ionisation mode) of the complex K[Nd(\text{Bu}_{2}salophen)_{2}].

Figure S.C.12. ESI mass spectrum (negative ionisation mode) of the complex K_{3}[Nd(\text{bis-Bu}_{2}salophen)].
**Figure S.C.13.** ESI mass spectrum (positive ionisation mode) of the complex $\text{K}[\text{Nd(bis-salophenH}_2)]$.

**Figure S.C.14.** ESI mass spectrum (positive ionisation mode) of the complex $\text{K}[\text{Nd(salophen)}_2]$ formed from the reaction of 9,10-phenanthrenequinone with $\text{K}_3[\text{Nd(bis-salophen)}]$. 

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D) UV-vis spectra

Figure S.D.1. UV/visible spectra (298 K) of 0.5 mM THF solutions of complexes.

Figure S.D.2. UV/visible spectra (298 K) of 0.5 mM THF solutions of complexes.
**Figure S.D.3** UV/visible spectra (298 K) of 0.5 mM solutions of K$_3$[Nd(bis-salophen)] in various solvents showing an hypsochromic shift of the absorption band when the polarity of the solvent increase. Red : 1,4-Dioxane ($\lambda_{\text{max}}$ = 574 nm ; dielectric constant $\varepsilon$ = 2.22 ; $E_T$ = 36,0); Blue: Tetrahydrofuran ($\lambda_{\text{max}}$ = 567 nm ; dielectric constant $\varepsilon$ = 7.52 ; $E_T$ = 37,4); Green:Pyridine ($\lambda_{\text{max}}$ = 559 nm ; dielectric constant $\varepsilon$ = 13.26 ; $E_T$ = 40,2).

**Figure S.D.4.** UV/visible cells containing 0.5 mM THF solutions of K$_3$[Nd(bis-salophen)] (left) and K[Nd(salophen)$_2$] (right).
Figure S.D.5 UV/visible spectrum (298 K) of a 0.5 mM THF solution of complex K₂[Nd₂(cyclo-salophen)(THF)₂].
E) Electrochemistry

S.E.1) Determination of the number of electrons associated to the redox events

The number of electrons exchanged during the oxidation of complex \( K_3[\text{Nd(bis-salophen)}] \) was determined by the combination of a chronoamperometry experiment and a study of the stationary regime obtained at a platinum microelectrode. A solution of \( K_3[\text{Nd(bis-salophen)}] \) and a solution of ferrocene (20 mM in complex with 0.1 M [Bu₄N][PF₆] supporting electrolyte in pyridine) were prepared. A chronoamperometry study was carried out on both solutions using exactly the same experimental conditions (platinum disk \((d = 5 \, \text{mm})\) working electrode, platinum wire counter electrode and Ag/AgCl reference electrode). The plot of the current \( i \) versus \( t^{1/2} \) (Figures S.E.1.1) obey the Cottrell equation\{ A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley, New York, 2001 \}:

\[
i = k t^{1/2} \quad \text{with} \quad k = n F A C D^{1/2} (\pi)^{1/2}
\]

where \( i \) is the current, \( n \) the number of electrons, \( F \) the Faraday constant, \( A \) the electroactive area of the electrode, \( D \) the diffusion coefficient of the species and \( t \) the time.

As the concentration of the ferrocene solution is equal to the one of the \( K_3[\text{Nd(bis-salophen)}] \) solution, and as the number of electrons involved in the oxidation of ferrocene is 1, the ratio of the director coefficient \( k \) of the plot measured for the ferrocene and the \( K_3[\text{Nd(bis-salophen)}] \) solutions is :

\[
k_{\text{Nd}}/k_{\text{Fc}} = n (D/D')^{1/2}
\]

where \( D' \) is the diffusion coefficient for ferrocene, \( D \) is the diffusion coefficient for \( K_3[\text{Nd(bis-salophen)}] \) and \( n \) is the number of electrons involved in the oxidation of \( K_3[\text{Nd(bis-salophen)}] \).

**Figure S.E.1.1** \( i \) vs \( t^{1/2} \) plot of the chronoamperometry data obtained from a 20 mM ferrocene solution (blue diamonds) and a 20 mM \( K_3[\text{Nd(bis-salophen)}] \) (red diamonds) in a 0.1 M [Bu₄N][PF₆] pyridine solution.

In parallel, the intensity of the current at a microelectrode in stationary regime was measured for both solutions (Figure S.E.1.2). The value of the limiting current is given by the following relation:

\[
i_{\text{lim}} = 4 n F r C D
\]

where \( i \) is the current, \( n \) the number of electrons, \( F \) the Faraday constant, \( D \) the diffusion coefficient of the species, \( r \) the radius of the platinum microdisk and \( C \) the concentration of the complex in the bulk solution.
Similarly, the ratio of the limit intensities measured for the ferrocene and the $\text{K}_3\text{[Nd(bis-salophen)]}$ solutions is:

$$i_{\text{lim Nd}}/i_{\text{lim Fc}} = nD/D'$$

where $D'$ is the diffusion coefficient for ferrocene, $D$ is the diffusion coefficient for $\text{K}_3\text{[Nd(bis-salophen)]}$ and $n$ is the number of electrons involved in the oxidation of $\text{K}_3\text{[Nd(bis-salophen)]}$.

**Figure S.E.1.2** $i$ vs $E$ plot of a 20 mM ferrocene solution (blue curve) and a 20 mM $\text{K}_3\text{[Nd(bis-salophen)]}$ (red curve) in a 0.1 M $[\text{Bu}_4\text{N}]\text{[PF}_6\text{]}$ pyridine solution obtained in stationnary regime at a platinum microdisk (0.5 mV/s scan rate).

![Graph of $i$ vs $E$](image)

The number of electrons exchanged during the oxidation of complex $\text{K}_3\text{[Nd(bis-salophen)]}$ is then given by:

$$n = (k_{\text{Nd}}/k_{\text{Fc}})^2/(i_{\text{lim Nd}}/i_{\text{lim Fc}}).$$

From our data (Table S.E.1.1), we find $n = 1.90_{\pm}0.1$

Accordingly, the process observed by electrochemistry for the oxidation of the bis-salophen ligand involves a **transfer of 2 electrons**.

**Table S.E.1.1** Electrochemistry data.

<table>
<thead>
<tr>
<th>$k_{\text{Nd}}$ (mA$\cdot$s$^{1/2}$)</th>
<th>$k_{\text{Nd}}$ (mA$\cdot$s$^{1/2}$)</th>
<th>$i_{\text{lim Nd}}$ ($\mu$A)</th>
<th>$i_{\text{lim Fc}}$ ($\mu$A)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.092</td>
<td>0.099</td>
<td>0.65</td>
<td>1.44</td>
<td>1.9</td>
</tr>
</tbody>
</table>
S.E.2) Scan-rate studies:

Figure S.E.2.1 Scan-rate effect on the cyclovoltammogram of a 20mM solution of K$_3$[Nd(bis$^\text{Me}$salophen)] in pyridine performed with a microdisc platinum working electrode. Scan-rate range: 10mV/s (blue) to 1000 mV/s (yellow). Insert: Plot of the anodic peak current ($i_{\text{pA}}$) versus the square-root of the scan-rate ($v^{1/2}$) ($v =$ 10 to 10000 mV/s). The linear variation of the peak current with the square-root of the scan rate is in agreement with the Randles-Sevcik equation. (A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley, New York, 2001.)

Figure S.E.2.2 Fast-scan cyclovoltammogram of a 20mM solution of K$_3$[Nd(bis$^\text{Me}$salophen)] in pyridine performed with a microdisc platinum working electrode. Scan-rate range: 5000mV/s (dark green) to 50000 mV/s (light green).
No reversibility could be detected in the scan-rate range 10mV/s to 50000mV/s. For fast-scan studies, even when using a microelectrode, the signal is affected by the IR drop, but does not show any reversibility.