Modulation of the CO₂ fixation in dinickel azacryptands†

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While bimetallic azacryptands are known to selectively coordinate CO₂, there is little knowledge on how different substitution patterns of the azacryptand cage structure influence CO₂ coordination. Stopped-flow UV-vis spectroscopy, electrochemical analysis and DFT calculations were performed on a series of dinickel azacryptands and showed different rates of CO₂ coordination to the complexes. We herein present data showing that the different flexibility of the azacryptands is directly responsible for the difference in the CO₂ uptake capability of dinickel azacryptand complexes.

Introduction

The fixation and utilization of CO₂ as a C1-building block is an important research field towards the recycling of the potent greenhouse gas CO₂. While enzymes like CO-dehydrogenases and ureases allow selective CO₂ fixation under mild and aqueous conditions, they are not cost effective for industrial use. Therefore, it is vital to develop materials that are as selective and efficient as enzymes but at a much lower cost. Indeed a number of synthetic approaches for the fixation and transportation of CO₂ have been reported, such as metal organic frameworks (MOFs), covalent organic frameworks (COFs) or even inorganic carbonates. Although they show promising properties, most of them have low selectivity towards CO₂ in the presence of other atmospheric gases and also low stability in the presence of moisture. Cryptands, such as bis-Tren azacryptands (Tren = tris[2-aminoethyl]amine), have been shown to allow selective fixation and transportation of small molecules (e.g. bicarbonates, azides or thiocyanates).

By using cryptands, nowadays frequently used for anion recognition as well as in metal chelation, an attempt for a comparable strategy for CO₂ fixation was made. The stability and selectivity of the resulting compounds for the fixation of small molecules depend on the cage size as well as on the effective size of the small molecules. As a result, the uptake and binding properties of small molecules (e.g. halogenides and pseudohalogenides) can be selectively tuned by increasing the size of the cryptand and/or altering the binding motifs. The size of the binding cavity of cryptands for a potential small molecule to enter can be rationally designed by using different linker molecules connecting both Tren-moieties (Scheme 1). Along this line, Nelson et al. recently showed crystallographic evidence for different CO₂ coordination in dicobalt-azacryptand complexes. While [Co₂LA₉Fur](ClO₄)₂ reveals a short Co–Co distance of 4.2924(3) Å and a M–OCO₂ bond length of 2.145(9) Å, the Co–Co distance

Scheme 1. Azacryptands LA₉ and imines LI₅ with different linker molecules Lₙ. The linkers are arranged according to their (i) different steric bulks on the central benzyl unit, (ii) capability to directly alter the electron density within the azacryptand cavity and (iii) different cage sizes.
in [Co,L₆H]ClO₄]₂ is significantly increased to 5.939(2) Å and the M—O—CO bond length is decreased to 1.920(6) Å. Mechanistic insight into the CO₂ fixation in [Cu₂L₆H]ClO₄]₃ and [Cu₂L₆H,par]ClO₄] was provided by Chen as well as Mooney et al., where they highlighted the necessity of an additional hydroxyl group on one metal site for successful CO₂ uptake.¹⁹,²¹ Likewise, DFT-calculations were reported for [Cu₂L₆H,par]ClO₄] with the lowest energy barrier for CO₂ binding reported for [Cu₂L₆H,par]ClO₄].²² Notably, alteration of the linker not only had an effect on the substrate binding but also had a strong influence on the metal binding strength as was shown for LA, L₆H, and L₆F.²² We recently showed that [NiL₆H]Cl(ClO₄)₃ is capable of performing rapid CO₂ uptake from air (k = 0.067 ± 0.005 M⁻¹ s⁻¹) and was able to reversibly bind CO₂ by substitution with azides.²³ Furthermore, we could show that the azide ligand could be replaced by atmospheric CO₂ in a quasi-reversible process upon irradiation with UV light. Surprisingly, [Ni₂L₆H,F]Cl(ClO₄)₃ did not reveal any observable CO₂ fixation. Inspired by our initial results on the different binding capabilities of [Ni₂L₆H,F] and [Ni₂L₆H,par] as well as the opposing theoretical reports on altered CO₂ binding by varied linker moieties, we set out to further experimentally and theoretically elucidate the effects of linker variations in azacryptand cages on the CO₂ uptake capability and kinetics.

Results and discussion

Synthesis and characterization

The azacryptands L₄R were synthesized via a two-step synthesis according to literature procedures (Scheme 1).⁵,¹⁹,²⁰,²³–²⁶ In a first step, [2 + 3]-Schiff-base condensation of the respective dialdehydes and Tren afforded the imines L₄R in good yields (57–77%). The reaction of L₄R with KBF₄ yielded the azacryptands L₄R in good to excellent yields (66–99%). The molecular structures of the hexa-imines L₄H, L₄OMe, and L₄Me, and the hexa-amines L₄F and L₄O, are presented in Fig. S1 and S2. A simple way to investigate the influence of the linker molecule on the metal cryptand properties during CO₂ uptake is the application of the imine species L₄R since they are structurally more rigid than their amine counterparts. We therefore attempted complex formation of the hexa-imines with Ni(ClO₄)₂·6H₂O. The reaction solely afforded [[Tren]Ni(CH₃CN)₂]ClO₄] in 33% yield by a Ni-catalyzed imine hydrolysis in the presence of water of crystallization (Scheme 2).²⁷ The molecular structure was unequivocally confirmed by X-ray crystallography (Fig. S3†). Similar decomposition results were also observed for other hexa-imine azacryptands by ESI-MS. The only exception was L₄O, which afforded a mononuclear complex when reacted with MnCl₂; similar results are reported in the literature.²⁸

Due to the instability of the imine complexes in the presence of moisture, we did not further investigate the imines towards the possibility of CO₂ coordination and instead focused on the hexa-amines L₄R as ligands. The coordination reactions of L₄R with Ni(ClO₄)₂·6H₂O were performed under a nitrogen atmosphere to avoid any bicarbonate formation (Scheme 3). While the UV-vis spectra of [Ni₂L₄R]Cl(ClO₄)₃ (L₄R = L₄H, L₄F, L₄OMe, and L₄Me) showed absorption bands at ~390, 480, 560, and 620 nm, the spectra of [Ni₂L₄H]Cl(ClO₄)₃ (L₄H = L₄H,F, L₄O, and L₄Me) solely revealed a broad band at ~580 nm containing a shoulder at lower wavelengths (Fig. 1, S4 and S5†). While a detailed band assignment has not been possible, recent crystallographic studies on [Ni₂L₄H]Cl(ClO₄)₃ and [Ni₂L₄F]Cl(ClO₄)₃ suggest an overall unchanged
shared structural motif of the above-mentioned complexes. Likewise, ESI-MS experiments support a similar composition of the compounds by showing comparable mass patterns (Fig. S6†). Structural analysis revealed that one of the two Ni(II)-centers is coordinated by a water molecule and an acetonitrile, while the other is coordinated to a chloride. Notably, different molecular assemblies were observed upon the reaction of Ni(CIO4)2·6H2O with either LThio or LAcO,Me. The molecular structure of [Ni2LAcO,Me(Cl)(CIO4)]2 (Fig. 1) reveals two octahedrally coordinated Ni-centers. Each Ni-center is surrounded by four nitrogen-donor atoms of the Tren-ligand with an average Ni-N distance of 2.14 Å. Additionally, one phenolate linker is coordinated in a μ2-fashion, bridging both Ni-atoms with bonding distances of 2.164(2) [Ni(1)−O(1)] and 2.177(2) [Ni(2)−O(1)] Å. The coordination sphere of each Ni-center is completed by a non-bridging phenolate linker with Ni(1)−O(3) and Ni(2)−O(2) distances of 2.033(3) and 2.021(3) Å, respectively. While this compound appears to be a mixed valent Ni(u)/Ni(u)-species, its low synthetic yield (13%) stopped us from elucidating the exact electronic nature. It is possible that protonation of the ligand framework takes place to afford an all Ni(u)-species. Surprisingly, LThio revealed a different coordination behavior in the solid state where both Ni-atoms are coordinated on the outside of the cryptand cavity, as was reported for the structurally related complexes [CuLThio]2[O2S(O)CF3] and [AgLThio][CIO4]. Each Ni(u)-center is octahedrally coordinated to only three N-donor atoms of the Tren-moity as well as two additional acetonitriles and one water ligand. We assume that the different structure of [Ni2LThio](CIO4)2 compared to e.g. [Ni2LAcO,Me(Cl)(CIO4)]2 can be explained by a different metal binding affinity and therefore an altered complex stabilization, as was reported by Nelson and co-workers. We next investigated the CO2 fixation behavior of all [Ni2LAcO,Me(Cl)(CIO4)]2 complexes by UV-vis spectroscopy and ESI-MS. A clear change in the UV-vis spectra upon purging the [Ni2LAcO,Me(Cl)(CIO4)]2 (R = H, F, OMe, Me and Fur) solutions with CO2 is observed, showing a decrease in absorption intensity of the bands between 430–580 nm with the formation of an intense absorption band at about 610 nm (Fig. 2 and S4†). The amplitude of the absorption band as well as the disappearance of the original bands between 430–580 nm depends on the substitution pattern at the linker unit.

In analogy to our recent finding for [Ni2LAcO,Me(H)(Cl)(CIO4)], such changes can be attributed to the coordination of CO2 within the cavity of the cryptand to afford a bicarbonate dinickel complex. ESI-MS analysis further supports the fixation of either 12CO2 or 13CO2 for the reported complexes by the appearance of the [Ni2LAcO,Me(H)(HCO3)] mass-peak (Fig. S7 and S8†). Notably, while the color changes of the complexes upon reaction with CO2 are usually unclear from dark to light blue, [Ni2LAcO,Me(Cl)(CIO4)]2 reveals a distinct color change upon CO2 fixation from blue to red (Fig. S9 and S10†). In contrast, no apparent changes could be observed for the complexes comprising the LThio, LAcO,Me, LAcPy, or LAcOH,Me moiety. Likewise, ESI-MS analysis solely revealed the mass peaks of the starting complexes. It can thus be assumed that these complexes do not possess the capability to fixate CO2 under the described reaction conditions, although a small shift of the main band from 564 nm to 571 nm was observed in the UV-vis spectrum upon CO2 addition to [Ni2LAcO,Me(H)(Cl)(CIO4)]. ESI-MS showed a new mass-peak at m/z = 756, which clearly indicates a reaction of [Ni2LAcO,Me(H)(Cl)(CIO4)]2 to afford a new complex. This behavior can most likely be attributed to the formation of [Ni2LAcO,Me(CN)(Cl)(CIO4)] comprising a bridging CN−-ligand but no coordinated bicarbonate. Further evidence for the presence of a CN− ligand was provided by IR spectroscopy showing a signal at 2022 cm−1 that can be assigned to a bridging CN−-moiety. A similar observation was recently reported for [Cu2LAcO,Me(CN)(Cl)(CIO4)], which was obtained via C–C bond cleavage of a coordinated acetonitrile.

**Kinetic analysis**

To further evaluate the differences of the azacryptand platform we performed UV-vis stopped-flow investigations. We expected a significant alteration of the CO2 uptake kinetics with different substitution patterns. The time-dependent absorption changes were measured at different temperatures (15–45 °C) and CO2 concentrations. The obtained absorption changes were then fitted using a pseudo-first order equation of the type \( A = A_0 \exp(-k_{obs}t) \) (A = absorbance, \( A_0 = \) initial absorbance, \( t = \) time in s) (Tables 1, S1–S3 and Fig. 3, S1†). The obtained data clearly demonstrate that the CO2 uptake rate is dependent upon the substitution pattern of the dinickel aza-

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** UV-vis spectra (MeCN/MeOH 4:1, RT) of the reaction of [Ni2LAcO,Me(Cl)(CIO4)]2 with CO2: (a) [Ni2LAcO,Me], (b) [Ni2LAcO,Me] + CO2, (c) [Ni2LAcO,Me]+[CN] + CO2, and (d) [Ni2LAcO,Me]+[CO2].
Table 1  $k_2$ values obtained from the slope of the plot of $k_{obs}$ vs. the CO$_2$ concentration at 298.15 K

<table>
<thead>
<tr>
<th>[Ni$_2$L$_A$]$^R$</th>
<th>$k_2$ [M$^{-1}$ s$^{-1}$]</th>
<th>[Ni$_2$L$_A$]$^R$</th>
<th>$k_2$ [M$^{-1}$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L$_A^H$</td>
<td>6.7 x $10^{-2}$</td>
<td>L$_A$</td>
<td>1.6 x $10^{-2}$</td>
</tr>
<tr>
<td>L$_A^F$</td>
<td>2.0 x $10^{-2}$</td>
<td>L$_A^{Me}$</td>
<td>9.8 x $10^{-4}$</td>
</tr>
<tr>
<td>L$_A^{OMe}$</td>
<td>1.9 x $10^{-2}$</td>
<td>L$_A^{Bu}$</td>
<td>4.8 x $10^{-4}$</td>
</tr>
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Fig. 3 Plot of $k_{obs}$ vs. the CO$_2$ concentration of L$_A^R$ in MeCN at 298.15 K for the reaction of [Ni$_2$L$_A$]$^R$ with CO$_2$.

Fig. 4 Molecular structure of [Ni$_2$L$_A$(N$_3$)](ClO$_4$)$_3$. Hydrogen atoms, solvent molecules and counter anions were omitted for clarity.

cryptand complex. Notably, the CO$_2$ fixation is slower in [Ni$_2$L$_A$]$^R$][Cl](ClO$_4$)$_3$ complexes with sterically more bulky groups according to L$_A^H > L_A^F > L_A^{OMe} > L_A^{Bu}$. In addition, the application of the furan linker molecules results in a significant decrease of the rate of CO$_2$ uptake. This kinetic trend is valid for all temperatures measured (Tables S2 and S3†). The small $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values obtained from the Eyring-plots indicate that the coordination of CO$_2$ in all substrates proceeds in more than one step. Therefore these small values reflect a more complex association of CO$_2$ and thus pre-equilibrium and activation enthalpies compose the apparent $\Delta G^\ddagger$ value. Comparable changes of the reaction rates upon alteration of the reactive site environment were previously reported by Holm and co-workers on [Ni$^{III}$[pyN$_2$]$^{R2}$][OH]$.^{3,3}$ In contrast, we present an example that exhibits no obvious alteration of the steric bulk on the metal center.

Azide fixation

A likely explanation for the alteration of the CO$_2$ uptake kinetics is a decisive change of the Ni-Ni distance and cavity size due to the influence of the linker. A similar hypothesis was reported by Nelson and co-workers. Likewise, the particular shape of the formed HCO$_3^-$ anion can play a significant part in the destabilization within the dinickel complex as one C-O bond is directed towards the opening of the cavity and can interfere with the ligand periphery. As such, the uptake of linear molecules, e.g. azides, should not be dramatically influenced by the alteration of the substitution pattern. Along this line we and others have shown structural evidence for the successful azide coordination into the cavity of L$_A^R$. Even when no CO$_2$ binding was observed, such complexes, e.g. [Ni$_2$L$_A^{Bu}$]([Cl](ClO$_4$)$_3$, allowed for rapid coordination of N$_3^-$ between both nickel atoms. Correspondingly, we tested the capability of [Ni$_2$L$_A^R$][Cl](ClO$_4$)$_3$ to allow azide coordination. All investigated azacryptands, except [Ni$_2$L$_A^{OH,Me}$](ClO$_4$)$_2$, show fixation of N$_3^-$, which is obvious from the changes in their UV-vis spectra by the formation of a new common absorption band at about 350 nm (Fig. S12†). Additionally, ESI-MS analysis further confirms the formation of an azide complex and reveals the respective [Ni$_2$L$_A^R$(N$_3$)] mass peaks. Crystals suitable for X-ray crystallography were obtained for [Ni$_2$L$_A^F$(N$_3$)](ClO$_4$)$_3$ (Fig. 4) and the results confirm the incorporation of N$_3^-$ between the two Ni-centers. It is notable that the Ni-Ni distance (6.275 Å) is significantly larger than in [Ni$_2$L$_A^{Bu}$(N$_3$)](ClO$_4$)$_3$ (6.129 Å) and [Ni$_2$L$_A^{Bu}$(N$_3$)](ClO$_4$)$_3$ (6.119 Å).$^{23,33}$

The general coordination of azides within the cavity and the alteration of the Ni-Ni distances within structurally comparable metal complexes underline the influence of the substitution pattern. It also shows that CO$_2$ is a key component in the different uptake kinetics. Furthermore, the successful incorporation of negatively charged azides additionally shows that the lone pairs of the furan, pyridine or thiophene linker cannot be a major reason for the weak or no CO$_2$ binding in [Ni$_2$L$_A^{Bu}$]([Cl](ClO$_4$)$_3$, or [Ni$_2$L$_A^{Fur}$](ClO$_4$)$_3$, respectively. In light of the acidic properties of CO$_2$ in an aqueous environment, changes of the substitution pattern might also alter the basicity of the coordinating N-donors and thus the nucleophilicity of the metal atoms. This hypothesis, however, has to be ruled out since the redox potentials of the complexes did not show a trend when electron withdrawing groups (e.g. F) or electron donating groups (e.g. tBu, Me) were installed. For all complexes, multiple irregular electron transfer steps can be observed at ~1.5 V vs. Fe/Fe$^+$, which we were not able to assign (Fig. S13†).

Theoretical analysis

In order to rationalize the experimentally observed differences in CO$_2$ binding of [Ni$_2$L$_A^R$][Cl](ClO$_4$)$_3$ complexes, DFT calcu-
lations were performed for complexes with R = H, F, Me and tBu (Fig. 5a). Both Ni²⁺ centers were found to be in the high-spin state (S = 1) consistent with the observed octahedral and trigonal-bipyramidal coordinations of the Ni²⁺ centers and this finding is in line with previous SQUID measurements.²³ The two triplet states were found to be exchange-uncoupled by broken-symmetry calculations. Though the substituents differ in their electron-donating and withdrawing capacities, no electronic effect was observed at the nickel ions as well as at all amines, as became apparent from unchanged Mulliken charges, bond distances and orbital compositions. The latter is in-line with the experimental observation that no clear correlation between the CO₂ uptake kinetics and electron donating capacity of the substituent could be found.

However, a noticeable steric effect was observed in the calculations in that rotation of the phenyl groups leads to a steric clash with the bulky tBu-substituent (Fig. 5b) while the smaller CH₃ groups allow larger rotational flexibility of the ligand. For R = H and F, the phenyl rotation is essentially unhindered (Fig. 5c).

The bulkiness and flexibility of the substituent correlates with the observed CO₂ uptake kinetics, suggesting that these two factors help in tuning the kinetics and that it is most likely the rate-determining step in the reaction mechanism. Moreover, since the electronic structure at the nickel centers and the amines are the same for all of the complexes, every complex shows that with increasing steric demand of the linker, the flexibility of the azacryptand core is decreased, providing a kinetic barrier to the initial coordination of CO₂. In contrast to this, functional groups pointing out of the cavity show an increasing CO₂ fixation rate with decreasing steric demand (L₄⁵₆₇ BF > L₄⁵₆₇ OMe > L₄⁵₆₇ Me > L₄⁵₆₇ F > L₄⁵₆₇ H). Both DFT calculations and cyclic voltammetry demonstrate that there are no electronic effects at the nickel centers as a result of the different substituents. Therefore, we attribute the observed changes in reactivity to structural changes. Furthermore, the DFT calculations performed herein show that with increasing steric demand of the linker, the flexibility of the azacryptand core is decreased, providing a kinetic barrier to the initial coordination of CO₂. In contrast to the binding of CO₂, all dinickel complexes show fixation of azides. The results clearly show that controlling the flexibility of the cryptand can regulate binding of different substrates. With this in hand, new applications might be accessible for azacryptands, e.g. within catalysis or gas separation utilizing cryptands as the ligand platform.

**Conclusion**

The coordination of CO₂ in dinickel azacryptands can be manipulated through the presence of different linker molecules comprising Tren cages. UV-vis spectroscopic analyses, as well as ESI-MS analyses clearly show an influence of different functional groups on the CO₂ uptake. Functional groups pointing into the cryptand cavity, as in L₄⁵₆₇ Par, L₄⁵₆₇ Py or L₄⁵₆₇ Thio, and L₄⁵₆₇ OMe significantly slow down or even prohibit a coordination of CO₂. In contrast to this, functional groups pointing out of the cavity show an increasing CO₂ fixation rate with decreasing steric demand (L₄⁵₆₇ BF > L₄⁵₆₇ OMe > L₄⁵₆₇ Me > L₄⁵₆₇ F > L₄⁵₆₇ H). Both DFT calculations and cyclic voltammetry demonstrate that there are no electronic effects at the nickel centers as a result of the different substituents. Therefore, we attribute the observed changes in reactivity to structural changes.

**Experimental**

**General techniques**

All reactions were performed under either a dry N₂ atmosphere using standard Schlenk techniques or in a glovebox. All
solvents were dried according to standard methods. H, C NMR spectra were recorded on a Bruker DPX-200 NMR, Bruker DPX-250 NMR or a DPX-400 NMR spectrometer at room temperature. Peaks were referenced to residual H signals from the deuterated solvent and are reported in parts per million (ppm). IR spectra were measured with a Bruker Tensor 27 FT-IR spectrometer as a KBr pellet and are reported in cm⁻¹. Mass spectra were measured with a Shimadzu QP-2010 instrument. The dialdehydes as well as the azacryptands L₄HFF were measured on an Oxford Xcalibur diffractometer performing φ and ω scans at 170(2) K. Diffraction intensities were measured using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). [Ni₂L₄(H)(ClO₄)]₃, [Ni₂L₄-Thi](ClO₄)₄ and L₄OH were measured on a SuperNova diffractometer performing φ and ω scans at 100(2) K. Diffraction intensities were measured using graphite-monochromatized Cu Kα radiation (λ = 1.54184 Å). [Ni₂L₄-OH,Me](ClO₄)₂, L₄Me and L₄OMe were measured on a STOE IPDS I diffractometer performing ω scans at 170(2) K. Diffraction intensities were measured using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Data collection, indexing, initial cell refinements, frame integration, final cell refinements, and absorption corrections were accomplished with the program Crysalis Pro (Agilent Technologies, Version 1.171.37.34, 2014) and X-AREA, respectively. Space groups were assigned by analysis of the metric symmetry and systematic absences (determined by XPREP) and were further checked by PLATON. Space groups were solved by direct methods and refined against all data in the reported 2θ ranges by full-matrix least-squares on F² with the SHELXL program suite, using the OLEX2 interface. The program PLATON SQUEEZE was used for the structures L₄PF and [Ni₂L₄-Thi](ClO₄)₄ to eliminate non-refinable solvent molecules. Crystallographic data as well as refinement parameters are presented in Tables S4–S7 in the ESL.

**Stopped-flow measurements**

Time-dependent spectrophotometry was measured with a UV-Vis spectrophotometer S600 from Analytik Jena and a SFA-20 Rapid Kinetics Accessory from Hi-Tech Scientific. Temperature control was obtained with an attached cryostat and a cuvette-holder with a temperature-unit. The used MeCN-solutions were prepared from a stock-solution of MeCN saturated with CO₂ ([CO₂]₂₉₈K = 0.28 mol L⁻¹) and degassed MeCN. The complex was synthesized in situ in degassed MeCN under an N₂ atmosphere.

**Electrochemical analysis**

The electrochemical studies were performed on a Gamry Reference 600 in 100 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte, 20 mM NiI(ClO₄)₂·6H₂O and 10 mM La₃⁺ in degassed MeCN. Glassy carbon, Pt wire and Ag/AgNO₃ (10 mM) in MeCN were used as working, counter and reference electrodes respectively. Cyclic voltammograms (CV) were recorded between −2.0 and +1.5 V at 100 mV s⁻¹ in degassed MeCN and after CO₂ purging. The working electrode was polished with alumina paste 0.3 µm (Buehler) before each measurement. The solutions were purged for 10, 20, 60 and 120 seconds with CO₂. The results are reported versus Fe/Fe⁺.

**DFT calculations**

All calculations have been performed with the ORCA program. The BP86 functional was used along with the Def2-svp basis set. The resolution of the identity (RI) approximation has been employed to speed up the calculation time. Scalar relativistic effects are included in zero order regular approach (ZORA). Solvent effects were taken into account by using the COSMO solvation model.

**General synthetic procedure for L₄**

In a typical experiment, the respective dialdehyde (3.6 mmol) was dissolved in MeCN (100 mL). A solution of Tren (2.5 mmol) in MeCN (20 mL) was added dropwise to the solution within 3 h. The solution was stirred at RT for 12 h and the formed solid was filtered off, washed with MeCN and dried in a vacuum to give the hexa-imine L₄⁺.

L₄OMe: white solid, 85% yield. H NMR (400 MHz, CDCl₃): δ [ppm] = 7.73 (d, 6H), 7.60 (s, 6H), 5.17 (s, 3H), 3.90 (s, 9H), 3.77 (s, 6H), 3.32 (s, 6H), 2.80 (s, 12H). C NMR (100 MHz, CDCl₃): δ [ppm] = 160.8, 160.6, 138.4, 125.9, 112.8, 60.1, 56.2, 56.0. ESI-MS calc. for [C₃₉H₄₀F₃N₈]+: m/z = 677.38. Found: m/z = 677.08. IR (KBr, cm⁻¹): 2948, 2875, 2823, 1643, 1590, 1454, 1372, 1197, 1156, 1063, 1030, 863, 697, 657. Anal. calc. for [C₃₉H₄₀N₈]+: 14.26, 10.46, 6.84, 6.32, 8.29, 7.35. Found: N, 15.75; C, 65.73; H, 8.9.

L₄Me: white solid, 85% yield. H NMR (400 MHz, CDCl₃): δ [ppm] = 8.00 (s, 6H), 7.57 (s, 6H), 5.18 (s, 3H), 3.76 (s, 6H), 3.31 (s, 6H), 3.05-2.62 (m, 12H), 2.54 (s, 9H). C NMR (100 MHz, CDCl₃): δ [ppm] = 161.2, 139.1, 136.9, 130.2, 128.0, 60.1, 56.1, 21.4. ESI-MS calc. for [C₃₉H₄₀N₈]+: m/z = 629.41. Found: m/z = 629.24. IR (KBr, cm⁻¹): 2947, 2871, 2802, 1641, 1439, 1372, 1333, 1289, 1158, 1068, 1032, 921, 866, 739, 691. Anal. calc. for [C₃₉H₄₀N₈]+: 14.26, 10.46, 6.84, 6.32, 8.29, 7.35. Found: N, 15.77; C, 73.44; H, 7.74.

L₄: white solid, 62% yield. H NMR (400 MHz, CDCl₃): δ [ppm] = 7.88 (dd, 6H), 7.58 (dd, 6H), 5.30 (s, 3H), 3.73 (s, 6H), 3.32 (s, 6H), 2.80 (s, 12H). C NMR (100 MHz, CDCl₃): δ [ppm] = 165.0, 162.5, 159.3 (d, J = 2.7 Hz), 139.5 (d, J = 7.4 Hz), 127.8, 114.2, 113.9, 60.0, 55.8. ESI-MS calc. for [C₃₉H₄₀F₃N₈]+: m/z = 641.33. Found: m/z = 641.00. IR (KBr, cm⁻¹): 3070, 2945, 2905, 2885, 2838, 2734, 1644, 1611, 1432, 1383,
The hexa-imine \( \text{L}^R \) (1.0 mmol) was dissolved in dry MeOH (50 mL) and heated to reflux. KBH\(_4\) (11.7 mmol) was then added in small portions. The reaction mixture was heated under reflux overnight, cooled to RT and the solvent was removed under reduced pressure. The residue was suspended in 2 M \( \text{NH}_2\text{Cl} \) solution (40 mL), extracted with DCM (3 × 40 mL) and dried over MgSO\(_4\). The organic solvent was removed under reduced pressure and the remaining solid was dried in a vacuum to give \( \text{L}^R \) (1.0 mmol).

**General synthetic procedures for \( \text{L}^R \)**

The hexa-imine \( \text{L}^R \) was isolated by recrystallization from MeCN/Et\(_2\)O, or through slow evaporation of the solvent.

**General synthetic procedures for \([\text{Ni}_2\text{L}^R]^+(\text{Cl})_4(\text{ClO}_4)_4\) (\(x = 2−4; y = 0, 1\)−2)**

The respective compound \( \text{L}^R \) (0.038 mmol) was dissolved in 2 mL degassed MeCN/MeOH or MeCN/MeOH/MeOH 4:1. A solution of Ni(\(\text{ClO}_4\))\(_2\)-6\(\text{H}_2\text{O}\) (0.078 mmol) in MeCN/MeOH 4:1 was added and the mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the residue was obtained by recrystallization from MeCN/Et\(_2\)O, or through slow evaporation of the solvent.

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Notes and references

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