Second coordination sphere effects in [FeFe]-Hydrogenase mimics

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Citation for published version (APA):
Fundamental studies of electron transfer processes across the rim of $M_{12}L_{24}$ nano-spheres
Introduction

Catalytic transformations are essential for the preparation of chemicals and materials in a sustainable manner.\textsuperscript{1-3} Although homogeneous catalysis is a well-developed field, there are challenges that remain.\textsuperscript{4} In general, the selectivity, stability and activity of the catalysts are issues to be solved.\textsuperscript{5} Controlling the selectivity and activity of homogeneous catalysts can be achieved by fine-tuning the electronic and steric properties of the ligands coordinated to the metal centers. In this respect, the developing field of cage catalysis has proven its potential to control those parameters.\textsuperscript{5} During the last several years, many reports have shown that homogeneous catalysts encapsulated into supramolecular assemblies display novel selectivity, affording products that cannot be prepared by conventional methods or can enhance the rates of reaction due to several reasons such as local environment effects and substrate preorganization.\textsuperscript{6-14} Cage catalysis is now rapidly developing and many examples spanning a wide variety of catalytic transformations can be found in literature.\textsuperscript{5} Among them, palladium catalyzed reactions, hydrolysis reactions, $S_N2$ reactions and rearrangement reactions.\textsuperscript{7,14,15} Interestingly, so far, there are no reports describing redox catalytic reactions taking place within cages. Furthermore, literature provides very little information about the feasibility of electron transfer from an electrode to a redox-active species encapsulated by a supramolecular cage. The few examples reported concern very small assemblies where the redox probe is readily accessible or in close proximity to the electrode surface so that a direct electron transfer is possible.\textsuperscript{16-18} Similarly, the reported redox-active cages are supramolecular assemblies where the outer-shell of the cage is functionalized with redox probes or the building blocks themselves are redox-active.\textsuperscript{16,19} For those reasons we decided to investigate electrochemical redox processes using redox-active centers encapsulated inside large supramolecular spheres.

To this end, we use the supramolecular $M_{12}L_{24}$ Fujita type cages because of their relatively large size and ease of functionalization of the standard ditopic bis(pyridine) building blocks, allowing for the independent study of different variables.\textsuperscript{20-22} In this chapter we describe the synthetic strategies undertaken to prepare different building blocks containing a redox-active moiety. Cages were synthesized and their electrochemical response and the resultant kinetics of the electrode were studied. This demonstrated the feasibility of electron transfer to redox-active moieties that are encapsulated either via covalent bonds or via supramolecular interactions.
Strategy

To study the thermodynamics and kinetics of the electrochemical electron transfer process to redox-active species encapsulated inside the cavity of cages, four different approaches were designed:

1. supramolecular encapsulation through hydrogen bonding interactions between a ferrocenyl sulfonate redox probe that binds to a cage decorated with a guanidinium interior, recently reported by our group (Figure 1).

2. a ferrocene moiety covalently attached to the ditopic bis(pyridine) building block through a flexible linker (Figure 2, A).

3. a tetrathiafulvalene moiety covalently attached to a planar and fully conjugated bis(pyridine) building block, resembling the structure of a molecular wire (Figure 2, B).

4. a tetrathiafulvalene containing bis(pyridine) building block featuring a biphenyl moiety with a built-in 90° twist between two adjacent aromatic rings to break the conjugation of the structure (Figure 2, C).

Figure 1. Schematic structure of guanidinium cage showing cooperative binding to sulfonate anions.

Figure 2. Molecular structure of building blocks A, B and C.
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Ferrocene was chosen as redox-active moiety, because of the anticipated synthetic ease and its well-defined electrochemistry. Tetrathiafulvalene (TTF), the redox-active moiety chosen for building blocks B and C, is another well-known compound that has received a lot of attention for its redox and magnetic properties. Some of the materials obtained from TTF-based compounds display organic superconducting properties or semiconducting behavior and are of particular interest for molecular electronics.23-25 Each five-membered ring of TTF contains 7π electrons; TTF undergoes two separate reversible oxidation events at very mild potentials, to afford two aromatic rings (6π electrons), with conversion of the central C=C double bond to a C-C single bond. The redox properties of TTF and its rigid planar configuration make it a suitable functional group for the current study.

Results and discussion

Synthesis and characterization of building blocks

The guanidinium building block was prepared according to a modified literature procedure.13 The yields and spectroscopic data are in line with the reported values. Ferrocenyl sulfonic acid was prepared by reaction of ferrocene with ClSO₃H in acetic anhydride. After recrystallization, it was converted to its tetrabutylammonium salt by reaction with an alcoholic solution of tetrabutylammonium hydroxide. The generated salt is very hygroscopic, always affording an oily substance upon removal of solvents. This issue was circumvented by dissolution of the mentioned oil into small amounts of water and subjecting the sample to a freeze-drying process. This method afforded an orange solid that was characterized by ¹H NMR spectroscopy and mass spectrometry.

The ferrocene containing building block A (FcBB) is easily prepared in four steps according to Scheme 1. The synthesis starts with a Williamson reaction between 2,6-dibromophenol and BOC protected 2-chloroethylamine to afford 1 in good yield. A palladium catalyzed Sonogashira reaction introduces the ethynylpyridine moieties. The BOC protecting group is then removed by reaction with trifluoroacetic acid. The resulting intermediate 3 is a useful synthon to introduce a wide variety of functionalities at the endo position of the building block through amide coupling reactions; furthermore it is relatively bench-stable and can be stored for extensive periods under ambient conditions in the dark. The last step is HATU assisted coupling of ferrocene carboxylic acid to the primary amine generated in situ after deprotonation of 3 with DIPEA. The desired FcBB A is obtained in 72% yield and 60% overall yield over four steps.
The first two steps of the synthesis of TTFBB, B (Scheme 2) are the preparation of tributylstannyl functionalized TTF, 5, and intermediate 4, according to modified literature procedures. A palladium catalyzed Stille coupling reaction between 4 and 5 affords 6 in excellent yield. The TMS protecting group is then hydrolyzed in situ by one equivalent of tetrabutylammonium fluoride. Subsequent addition of palladium catalyst and 1,3-dibromo-5-(tert-buty1)-2-iodobenzene, prepared from the corresponding aniline via a Sandmeyer reaction, affords intermediate 8. Lastly, a Sonogashira reaction introduces the ethynylpyridines to afford TTFBB B in good yield. Overall, the yield for this preparation is 30% over six steps. It is noted that some tetrathiafulvalene, from the first step, is carried through the entire synthesis. This impurity is easily removed during the last purification column; its removal at earlier stages, although possible, proved to be more challenging.
zene to afford the corresponding hydrazine. The following step is an acid catalyzed [5,5]-sigmatropic rearrangement to yield the tetramethyl-substituted benzidine. A Sandmeyer reaction affords the corresponding substituted diiodo-biphenyl derivative in quantitative yield. A palladium catalyzed Sonogashira reaction is carried out to install one acetylene-TMS group. Palladium catalyzed Stille coupling introduces the TTF moiety affording intermediate 13. After in situ deprotection of the TMS protecting group by one equivalent of tetrabutylammonium fluoride, the last two steps are Sonogashira reactions to introduce the central dibromobenzene ring and finally the ethynylpyridine groups. The overall yield is about 2.5% over 7 steps. Although the yield is low, the individual reactions were not optimized and the yields based on a single iteration of each reaction.

The last building block prepared is a standard ditopic bis(pyridine) backbone featuring a hydrogen atom at the *endo* position, BBH, D. This building block will be used to vary the concentration of redox probes inside the cages. BBH is readily prepared according to Scheme 4, in two steps in good yield from 2,6-dibromo-4-(tert-butyl)aniline through a Sandmeyer reaction carried out at high temperature. Intermediate 15 is then converted into building block D.
via a Sonogashira coupling under the same reaction conditions as described above.

Scheme 4. Synthetic route for the preparation of the non-functionalized building block, BBH, D.

The building blocks prepared have been characterized by $^1$H, $^{13}$C and DOSY NMR spectroscopy and high resolution mass spectrometry. NMR data are in agreement with the expected signals and values of the diffusion coefficients, and high resolution mass spectra are, in all cases, within 5 ppm error range.

Single crystals suitable for X-ray diffraction were grown either by layering a DCM solution of the building blocks with hexanes or by slow evaporation of solvents. The solid state structures of building blocks A, B and C are shown in Figure 3. The crystal structure for FcBB A, confirms the presence of the flexible linker that covalently connects the ferrocene unit to the rest of the bis(pyrine) backbone. The TTF building blocks B and C have a very rigid nature along the entire molecular structure. For TTFBB B, the angle between the central phenyl ring of the backbone and the TTF moiety is about 172 degrees and TTF adopts the usual boat conformation with the angle between the two hetero-rings of about 1.5 degrees, consistent with literature data. The twisted TTFBB C shows similar angles but the most important feature is the angle between the two phenyl rings along the linker structure of about 89.5 degrees.
Preparation and characterization of $M_{12}L_{24}$ cages

The supramolecular $M_{12}L_{24}$ assemblies were prepared according to general literature procedures, by mixing a divalent metal precursor (typically Pd$^{2+}$ or Pt$^{2+}$) with two equivalents of building block. After addition of a solvent (in general MeCN-$d_3$ or mixture of MeCN-$d_3$ and DCM-$d_2$ for solubility reasons) the solution were stirred overnight in a closed Schlenk flask at 60 °C. The characterization methods available to confirm the formation of the assemblies are showcased for the palladium assembly containing 24 FcBs, $(Pd_{12}A_{24})^{24+}$.

The formation of the assembly is firstly suggested by $^1$H NMR spectroscopy. Deshielding of the pyridine protons, caused by metal coordination, results in a low field shift of approximately 0.4 ppm of those protons, Figure 4. The symmetry and broadening of the $^1$H NMR spectrum for the cage solution is also indication for the formation of the large assemblies.
Secondly, DOSY NMR of the cage in MeCN-\(d_3\) shows a single diffusing species in solution with a logD value of -9.6 m\(^2\)s\(^{-1}\), Figure 5, in agreement with previously reported data.\(^{13,20,26}\) In contrast, the free building block, being considerably smaller than the full assembly, shows a logD value of -8.9 m\(^2\)s\(^{-1}\) under the same experimental conditions.

Figure 4. \(^1\)H NMR spectra of ferrocene building block \(A\) (bottom) and its palladium ferrocene cage, \((\text{Pd}_{12}A_{24})^{24+}\) (top). The shift of the pyridine peaks upon metal coordination is indicated by the black lines.

Figure 5. \(^1\)H DOSY NMR overlay for FcBB \(A\), showing a single diffusing species with a logD of -8.9 m\(^2\)s\(^{-1}\) and a palladium cage \((\text{Pd}_{12}A_{24})^{24+}\), showing a single diffusing species with a logD of -9.6 m\(^2\)s\(^{-1}\), in a mixture of MeCN-\(d_3\) and DCM-\(d_2\) at 25 °C.
Cold Spray Ionization (CSI-MS) mass spectrometry confirms the formation of the \([\text{Pd}_{12}\text{A}_{24}]^{24+}\) assembly. The experimental spectra show several signals belonging to the desired species, and in particular species from 9+ to 14+ with different numbers of counter anions can be identified, as shown in Figure 6. The measured signals and their isotopic patterns are in agreement with the simulated spectra.

**Figure 6.** CSI-MS spectra of measured and calculated species. \([\text{Pd}_{12}\text{A}_{24}(\text{BF}_4)_4]^{10+}\); found 1572.6057 m/z, calculated 1572.6041 m/z (top left); \([\text{Pd}_{12}\text{A}_{24}(\text{BF}_4)_4]^{11+}\); found 1421.7320 m/z, calculated 1421.7306 m/z (top right); \([\text{Pd}_{12}\text{A}_{24}(\text{BF}_4)_4]^{13+}\); found 1189.6188 m/z, calculated 1189.6945 m/z (bottom right); \([\text{Pd}_{12}\text{A}_{24}(\text{BF}_4)_4]^{14+}\); found 1098.4318 m/z, calculated 1098.5017 m/z (bottom left).

Regarding the TTF containing assemblies, the distance from the central phenyl ring of the backbone, to the end of the TTF moiety is about 1.5 nm for TTFBB B and about 2.0 nm for twistedTTFBB C. Given their rigid nature, it is unlikely that 24 of those building blocks can self-assemble into \(M_{12}L_{24}\) spheres due to steric hindrance. Spartan modeling at molecular mechanics level confirms this. To make nano-spheres based on the TTF containing building block, these can be mixed with the unfunctionalized building block D to generate cage assemblies of the type \(M_{12}DL_{24}\) (L = TTFBB B or twistedTTFBB C). A Spartan model of such a hybrid assembly is shown in Figure 7.
The \( M_{12} D_x L_{24-x} \) assemblies are prepared in a similar fashion as described before, by mixing the two different types of building blocks in the desired ratio, e.g. 23:1 up to 16:8 of compounds \( D(BBH):B(TTFBB) \) or \( C \), with 12 equivalents of a Pt\( ^{2+} \) source. This leads to a statistical distribution of assemblies containing different numbers of TTF units in their interior, with the major species resembling the ratio chosen. Only platinum(II) precursors can be used for this procedure, as the palladium(II) ions are susceptible to reduction by the TTF moiety, affording Pd black. NMR experiments confirm formation of the assemblies with the expected hydrodynamic radius, as deduced from the measured diffusion coefficient value by DOSY NMR.
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Exceeding the ratio of 16:8 of D(BBH):B(TTFBB) or C, during the assembly formation results in complicated ¹H NMR spectra, including the observation of species with lower diffusion coefficients than expected, indicating that the formation of the large assemblies is not quantitative.

The formation and characterization of the guanidinium cage was carried out as described in the literature method reported by our group. Encapsulation studies were done by titrating different equivalents of ferrocenyl sulfonate into a guanidinium cage solution; ¹H NMR was measured after each addition. The shift of all the relevant peaks is monitored and consistent with the ferrocene being encapsulated. About 24 equivalents of ferrocenyl sulfonate can be added to the cage solution, and the addition of an excess leads to formation of a precipitate. This precipitate is assumed to be guanidinium cage with 24 ferrocenyl sulfonate moieties encapsulated and ferrocenyl counterions at the outside. If more solvent is added to the NMR tube the precipitate stays undissolved, whereas if more guanidinium cage is added the precipitate dissolves and its ¹H NMR spectrum is identical to the one of a guanidinium cage with encapsulated ferrocenyl sulfonate.
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The encapsulation of the ferroceny derivative is also confirmed by DOSY NMR, as shown in Figure 10. A single diffusing species is present containing all the signals belonging to the cage itself and all the signals of the ferrocenyl species. No significant broadening of the ferrocenyl peaks is observed, suggesting that the exchange rate of ferrocene, if present, is slow on the timescale of the measurement. A second diffusing species with lower diffusion coefficient is present and identified as the tetrabutylammonium counterions that are released after binding the ferrocenyl sulfonate to the guanidinium.

Figure 9. $^1$H NMR spectra of a palladium guanidinium cage solution (bottom), tetrabutylammonium ferrocenyl sulfonate (top) and their mixture in 1:8 ratio (middle).

Figure 10. $^1$H DOSY NMR of a palladium guanidinium cage containing 8 equivalents of tetrabutylammonium ferrocenyl sulfonate. The ferrocenyl peaks have the same diffusion coefficient value as the cage peaks, indicating full encapsulation. The set of signals around logD = -8.75 belong to the tetrabutylammonium counterions that are not encapsulated.
Electrochemistry

Supramolecular approach

A titration of ferrocenyl sulfonate into a solution of guanidinium cage was carried out, monitoring the voltammetric response after every addition of the redox probe. The guanidinium cage itself does not show any electrochemical anodic response within the electrochemical potential window of interest. When ferrocenyl sulfonate is added to this solution, a new reversible wave appears ($E_{1/2} = 0.55 \text{ V vs. Ag/AgCl}$, $\Delta E_p = 70 \text{ mV}$). Increasing amounts of ferrocenyl sulfonate result in higher peak currents but no significant potential shift is observed as shown in Figure 11.

![Cyclic voltammogram](image)

**Figure 11.** Cyclic voltammogram of free tetrabutylammonium ferrocenyl sulfonate (red) and titration of different equivalents of this compound into a guanidinium cage solution.

After about 22 equivalents of ferrocenyl sulfonate, formation of a precipitate was observed. From this point, the peak current measured decreases with increasing amounts of ferrocenyl sulfonate, indicating that the ferrocenyl sulfonate is precipitating the cage from solution, acting as counterion for the guanidinium-functionalized cage. After about 50 equivalents of ferrocenyl sulfonate, a new reversible wave appears, with a cathodic shift of about 150 mV ($E_{1/2} = 0.40 \text{ V vs. Ag/AgCl}$). This last wave is identical to an authentic sample of free ferrocenyl sulfonate.

At first glance, the electron transfer process seems to be more energetically demanding, as suggested by the large potential shift of approximately 150 mV (~3.5 kcal mol$^{-1}$) measured between free and encapsulated ferrocenyl sulfonate. However, this shift in potential is ascribed to the interaction between the sulfonate and guanidinium functional groups. The hy-
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droge bonding between the two complementary groups is expected to effectively reduce the electron density at the ferrocene moiety, therefore rendering its oxidation more difficult. To support this, a titration was carried out, monitoring the shift of the peak potentials of ferrocenyl sulfonate upon addition of $n$-butylguanidinium. Indeed, a progressive anodic shift is observed with an increasing concentration of guanidinium, Figure 12.

Interestingly, about 25-30 equivalents of guanidinium salt are necessary to reproduce a similar potential shift as observed when the ferrocenyl sulfonate is encapsulated by the guanidinium cage. This is in line with the strong binding of the sulfonate inside the cage due to cooperative binding, as proposed previously.

The data and behavior observed are consistent with the ferrocene derivative being encapsulated throughout the electrochemical experiment. The first indication comes from the ferrocene peak potential, which remains constant during the entire titration experiment; therefore, the association constant must be extremely high, likely due to cooperative binding, as previously reported. A second indication comes from the symmetric shape of the voltammograms, which indicates that the ferrocene undergoes both electrochemical events (oxidation and back-reduction) at the inside of the cage. In fact, if the ferrocenyl sulfonate would leave the cage after the oxidation event and become back-reduced outside the cage, the shape of the voltammogram would be asymmetric with a peak potential separation $\Delta E_p$ of approximately 250 mV instead of the 70 mV measured.

Figure 12. Left: voltammetric titration of free tetrabutylammonium ferrocenyl sulfonate (red) and subsequent addition of different equivalents of $n$-butylguanidinium hexafluorophosphate (blue). Right: plot of peak potentials vs. number of equivalents of $n$-butylguanidinium hexafluorophosphate added. The insert shows the same dataset on a natural logarithmic scale.
Covalent encapsulation approach

Regarding the electrochemical behavior of the supramolecular assemblies containing redox-active moieties covalently bound to the building block backbone, three different cage samples will be discussed: \((\text{Pd}_{12}\text{A}_{24})^{24+}\) containing 24 ferrocene units, \((\text{Pt}_{12}\text{D}_{23}\text{B})^{24+}\) containing one TTFBB and \((\text{Pt}_{12}\text{D}_{23}\text{C})^{24+}\) containing one twisted TTFBB.

The cyclic voltammograms of all systems clearly show a single reversible wave, corresponding to the oxidation of the redox probe. In the case of the TTF containing samples, a second single reversible wave is present at more anodic potentials, corresponding to the double oxidation of the TTF moiety, Figure 13 (right), but all further analysis will be limited to the first oxidation of the TTF moiety.

![Figure 13](image)

**Figure 13.** Left: cyclic voltammograms, at different scan speeds, of the first reversible oxidation of the TTF cage \((\text{Pt}_{12}\text{D}_{16}\text{B})^{24+}\) containing on average 8 equivalents of TTFBB B. Right: oxidation behavior of the same sample including the second oxidation of the TTF moiety by cyclic voltammetry (blak) and by differential pulse voltammetry (red).

Comparison of the dataset obtained for the cage samples with the dataset obtained for their respective free building blocks reveals a shift of the half-wave potential towards more anodic values when the redox-active probes are encapsulated at the interior of the spheres. Table 1 summarizes the values of the half-wave potentials measured and their relative shift.
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Table 1. Values for the half-wave potential for the cage samples and their respective building blocks. The potentials are referenced to the couple Ag/AgCl.

<table>
<thead>
<tr>
<th></th>
<th>FcBB A</th>
<th>TTFBB B</th>
<th>twistedTTFBB C</th>
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<tbody>
<tr>
<td>Free building block (L)</td>
<td>0.612 V</td>
<td>0.400 V</td>
<td>0.320 V</td>
</tr>
<tr>
<td>Cage ($M_{12}DL_{24-x}$)$_{24+}$</td>
<td>0.665 V</td>
<td>0.415 V</td>
<td>0.330 V</td>
</tr>
<tr>
<td>x=0</td>
<td>0.415 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=23</td>
<td>0.330 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potential difference $\Delta E_{1/2}$</td>
<td>53 mV</td>
<td>15 mV</td>
<td>10 mV</td>
</tr>
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</table>

The respective half-wave potentials shift toward more positive values, implies that oxidation of the redox probes is more difficult when encapsulated into the supramolecular cage. A plausible explanation for this behavior is the different local environment in the cavity of the cage. In fact, the redox probes are effectively confined within the space defined by the cavity of the sphere, where the local environment might be different than the bulk solution.

Interestingly, voltammograms of cages containing more than one redox-active fragment feature a single oxidation wave. This can be seen in Figure 13 for the cage sample ($Pt_{12}D_{16}B_{8}$)$_{24+}$ but also in Figure 14 showing voltammograms for a cage sample containing 24 ferrocene building blocks, ($Pd_{12}A_{24}$)$_{24+}$.

Figure 14. Cyclic voltammograms recorded at different scan speeds for a sample of the ferrocene cage, ($Pd_{12}A_{24}$)$_{24+}$, showing a single oxidation wave for the 24 ferrocene units present at the interior of the cage.

The redox-active moieties are encapsulated within the volume defined by the 5 nm diameter cage, hence they are in close proximity to one another. This may lead to dependency of the
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Oxidation potential of the different units due to electronic and electrostatic communication. Instead, as suggested by the single oxidation wave observed, the probes are all electrochemically identical, independent and isolated from each other. This behavior is often seen in literature for ferrocenyl or TTF dendrimers and polymers, both in solution or immobilized on electrode surfaces. \(^{27-29}\) Important for this behavior is the fast molecular tumbling rate of the cage in solution. The tumbling rate can be roughly estimated through Newtonian motion laws of spherical objects. It depends on the viscosity of the solvent and it is proportional to the volume of the object itself. \(^{30}\) For a spherical object of about 5 nm in diameter, in acetonitrile at room temperature, the tumbling rate is roughly \(2 \times 10^8\) s\(^{-1}\). As the tumbling rate of the cage in solution is considerably faster than the timescale of the voltammetric experiment, all redox-active probes within the molecular cage are similar, even at very fast scan speeds, and on average equally distant from the electrode surface. \(^{31}\) This phenomenon alone is not sufficient to explain the single-wave behavior upon a given electrochemical event. Electrostatic repulsion of the newly generated charges inside the cavity of the cage does not seem to influence the redox potential of other nearby units. Considering that the solution for the electrochemical experiment always contains large amounts of supporting electrolyte, which is a salt such as TBAPF\(_6\), it is likely that upon a particular electrochemical event, where charges are generated inside the cavity of the sphere, electrolyte anions or cations, depending on the direction of the electrochemical event, diffuse out of the cage, effectively keeping its net charge constant. Without accumulation of charges within the cavity of the sphere, the electrostatic repulsion is minimized. Further insights on this topic will be presented in the next chapter.

Analysis of the peak current against the square root of the scan speed plots provides further details on the electrochemical process. The first observation is that, both for the cages and building blocks, the plots show a linear trend over a broad scan speed range in all cases, Figure 15. This indicates a Nernstian behavior of the species under investigation; the Nernstian equilibrium at the electrode surface is satisfied at all the scan rates measured. The linear trend is also an indication that the analytes under investigation are in solution and do not adsorb to the electrode surface during the electrochemical measurement.
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In general, for the cage samples, the slopes of the straight lines obtained are smaller than those of their respective building blocks, which is in line with their difference in size. The Randles–Sevcik equation shows that a lower diffusion coefficient for the cages as compared to the free building blocks translates into a smaller slope. The diffusion coefficients calculated from cyclic voltammetry are, within experimental error, in agreement with those obtained from DOSY NMR.

$$i_p = 0.4463 \, nFAC \left( \frac{nFvD}{RT} \right)^{1/2}$$

**Equation 1.** Randles–Sevcik equation where $i_p$ is the peak potential, $n$ the number of electrons, $F$ the Faraday constant, $A$ the surface area of the electrode, $C$ the analyte concentration, $v$ the scan speed, $D$ the diffusion coefficient, $R$ the gas constant and $T$ the temperature.

**Figure 15.** Plots of peak current vs. square root of the scan speed for the cage solutions (black and red circles) and their respective building blocks (blue and green squares). Top left: $(\text{Pd}_{12}A_{24})^{2+}$ and FcBB A. Top right: $(\text{Pt}_{12}D_{23}B)^{2+}$ and TTFBB B. Bottom: $(\text{Pt}_{12}D_{23}C)^{2+}$ and twistedTTFBB C.
In order to evidence differences in the electron transfer process between encapsulated redox-active species and free building blocks and between the different type of linkers used, the datasets were further interrogated to obtain the heterogeneous electron transfer rate constants, $k^0$. The method chosen was originally proposed by Nicholson in 1965 and revised by Paul and Leddy in 1995.32,33 This method is based on peak potential separation; it relates $k^0$ to a parameter $\psi$ which can be calculated from the parametric equation proposed by Paul and Leddy. The two parameters $M$ and $B$ are slightly dependent on the transfer coefficient $\alpha$, which can be obtained by various methods, under very well-defined conditions.34 Nevertheless, when the Nicholson’s method is used, exact determination of $\alpha$ is not strictly necessary, as small deviations from 0.5 have a negligible effect on the calculated heterogeneous electron transfer constant, especially when the diffusion coefficient of the reduced and oxidized analytes are similar.32,33 Therefore, its value is often assumed to be 0.5 meaning that the electron transfer is equally fast in both redox directions. Because this method relies on the peak potential separation, for it to be reliable, it is of primary importance that any residual solution resistance is properly compensated.

For the ferrocene building block $A$ and its cage, $\alpha$ is assumed to be 0.5, in line with the very symmetrical shape of the plots of the peak potential $E_p$ vs. the natural logarithm of the scan speed $\ln(\nu)$, Figure 16. A different situation is observed for the TTF containing cages and for the twisted-TTFBB $C$, for which the plots of $E_p$ vs. $\ln(\nu)$ (Figure 17 and Figure 18), are not symmetric. Typically, increasing the scan speed results in increasing peak potential separation; the oxidation peak shifts to more positive values, while the reduction peak shifts to more negative potentials. The datasets measured show that the forward peak behaves accordingly but the peak potential of the back reductive scan is somewhat constant or tends to shift to more positive potentials. This deviation is associated with the variation of the transfer coefficient $\alpha$, specifically $\alpha<0.5$. In both cases the trend of the variation of the peak potential of the back reductive scan (red circles) is indicative of electron transfer where the transfer coefficient $\alpha<0.5$. With all the mentioned information, the values of $k^0$ can be calculated (Table 2).

\[
\psi = \frac{\left( \frac{D_A}{D_B} \right)^\alpha k^0}{\sqrt{\left( \frac{nF}{RT} \right) n\nu D_A}} \quad \Delta E_p \left( \frac{nF}{RT} \right) = \frac{M}{\psi} + B
\]

Equation 2. Left: Nicholson method for determining the heterogeneous rate of electron transfer $k^0$. Right: Paul and Leddy method for determining $\psi$. Values for the parameters $M$ and $B$ are listed in their publication.
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**Figure 16.** Left: plot of peak potential vs. natural logarithm of the scan speed for the free ferrocene building block A. Right: similar plot for the cage sample $(Pd_{12}A_{24})^{24+}$.

**Figure 17.** Left: plot of peak potential vs. natural logarithm of the scan speed for the free TTFBB B. Right: similar plot for the cage sample $(Pt_{12}D_{23}B)^{24+}$.
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Table 2. Calculated values for the heterogeneous rate of electron transfer \( k_0 \) for the cages and their respective free building blocks. The values reported are in cm\( \cdot \)s\(^{-1}\).

<table>
<thead>
<tr>
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<th>FcBB ( A )</th>
<th>TTFBB ( B )</th>
<th>twistedTTFBB ( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free building block ( (L) )</td>
<td>0.0319</td>
<td>0.0260</td>
<td>0.0126</td>
</tr>
<tr>
<td>Cage ( (M_{12}D_xL_{24-x})^{24+} )</td>
<td>0.0050 ( x=0 )</td>
<td>0.0117 ( x=23 )</td>
<td>0.0028 ( x=23 )</td>
</tr>
<tr>
<td>Factor difference</td>
<td>6.4</td>
<td>2.2</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The large decrease in \( k_0 \), observed for the ferrocene based cage compared to its free building block, is expected as the linker, connecting the ferrocene moiety with the rest of the building block, is not conjugated. The feasibility of electron transfer is attributed to the flexibility of the linker itself, allowing the redox probes to bend toward the large cage windows. Direct electron transfer from the electrode surface could thus happen.

For TTF containing cages, where the redox-active probes are located in the interior of the sphere, electron transfer cannot happen directly by bending the unit towards the cage windows due to the rigidity of the linker. For the cage containing TTFBB \( B \), the kinetics of electron transfer between free building block and its cage differ by only a factor of 2. This suggests that the cage framework has little influence on the electron transfer kinetics. The reason for the fast kinetics of electron transfer is attributed to the fully conjugated linker resembling the structure of a molecular wire, facilitating the electron transfer step.
In the cage containing building block C the TTF moiety is not only deeply buried into the cavity of the cage, but also has a 90° twist along the rigid linker connecting it to the rest of the backbone. For this system the rate of electron transfer is slowed down by about 4.5 times compared to its free building block. The 90° twist introduced in the linker structure effectively breaks the conjugation between the electrochemical TTF probe and the section of the building block that is connected to the outside. This prevents any frontier orbital overlap, hampering fast electronic communication between the TTF moiety and the rest of the structure, thus leading to slower electron transfer kinetics.

In order to corroborate the observations described above, DFT geometry optimizations and orbital computations were performed to gain information regarding frontier orbitals of building blocks B and C. For both structures, the HOMO is mainly located at the TTF moiety and the LUMO is predominately located at the backbone of the building block. A closer inspection at the orbitals of TTFBB B reveals a delocalization of the HOMO that extends from the TTF moiety to the adjacent phenyl ring and even to the carbon-carbon triple bond, Figure 19 (left). The LUMO shows a similar delocalization extending from the bis(pyridine) backbone all the way to the TTF moiety, Figure 19 (right). This broad overlap of the frontier orbitals nicely showcases the molecular wire structure of TTFBB B. In contrast, the computed orbitals of building block C show no delocalization of the orbitals across the knot point introduced by the 90° twist as shown in Figure 20.

**Figure 19.** Computed orbitals for TTFBB B. Left: HOMO. Right: LUMO. The HOMO-LUMO energy difference is 2.30 eV.

**Figure 20.** Computed orbitals for twisted TTFBB C. Left: HOMO. Right: LUMO. The HOMO-LUMO energy difference is 2.34 eV.
Second coordination sphere effects in [FeFe]-Hydrogenase mimics

This set of experiments shows that it is possible to vary the kinetics of electron transfer from the electrode surface to a redox moiety encapsulated within the interior of a supramolecular cage. The nature of the linker connecting the redox probe to the backbone of the building block plays a crucial role for the feasibility of the electron transfer and it determines its kinetics. The three building blocks discussed show fast electrode kinetics when studied as free species in solution. The electrode kinetics of cages containing building block A or C is slowed to the limit of reversibility, approaching semi-reversible rates. This is not a general effect of the cage, as shown by the supramolecular assembly containing building block B, where the electron transfer kinetic stays within the reversible regime.

Structural integrity of the supramolecular structure upon the electrochemical event

So far, the data suggest that the supramolecular structure of the cage retains its integrity upon the electrochemical event. To prove the stability of the oxidized assembly at longer timescales, the oxidation events were monitored by EPR spectroscopy. A cage solution of the type \( \text{Pt}_{12}\text{D}_{16}\text{B}_{8}^{24+} \) containing on average 8 equivalents of TTFBB B was subjected to electrolysis at constant potential at 0.7 V vs. Ag/AgCl. The plot of the current measured in time is shown in Figure 21 (left) together with its integration plot, which is informative about the average number of electrons transferred per cage. The calculated number of electrons transferred during the electrolysis confirms that all the TTF present in the sample is oxidized by one electron.

Assuming that the cage would be intact after the electrochemical oxidation, the supramolecular assembly would now contain several \((\text{TTF})_{2}^{+}\) radicals within the volume of the cage, possibly leading to changes in its EPR spectrum. Room temperature EPR of the radical cation of the free building block shows the expected quartet pattern of a mono-substituted TTF, with the radical coupling with the three remaining hydrogen atoms, Figure 21 (right, black line). Hyperfine coupling with the sulfur atoms is also visible although the intensity is rather low. In contrast, the EPR spectrum of the oxidized cage shows a very broad signal, Figure 21 (right, red line).
Broadening of the EPR signal is commonly observed and reported in literature. The reason behind this behavior in the current system is ascribed to zero-field splitting, generated from interaction of radicals within the hollow cavity of the cage. The radicals are forced in close proximity to one another. To support this statement, cage solutions containing decreasing amounts of TTFBB have been prepared and subjected to electrolysis and room temperature EPR. Going from cages containing on average 8 equivalents of TTFBB, to cages containing 1, 0.5, and 0.25, the broadening of the EPR signal decreases. These low equivalents of TTFBB were required to minimize the broadening. This is likely due to a-p interaction of the TTF containing building blocks in solution, leading to preorganization of a few units, prior to cage formation. This would result in deviation from the expected statistical distribution of cages with preferential formation of cages containing more redox-active moieties than expected based on the different building blocks ratio.

The EPR measurements suggest that TTF radicals are interacting with each other when confined into a $\text{M}_{12}\text{L}_{24}$ cage. To gain insights into the nature of such interactions, the mono-oxidation process was followed by spectroelectrochemistry coupled to UV-visible spectroscopy. Spectroelectrochemistry was measured for three samples, in particular, free TTFBB and for the cage containing on average 1 and 8 equivalents of TTFBB. Figure 22 shows the normalized difference spectra obtained after mono-oxidation of the mentioned samples.
Second coordination sphere effects in [FeFe]-Hydrogenase mimics

From literature, it is known that one-electron oxidation of TTF generates very stable and deeply colored radical cations. It is also known that the generated radicals can interact with each other to generate dimers such as \((\text{TTF}^+)\). In more controlled systems, where two TTF units are forced in close proximity, it is possible to generate mixed valence dimers, \((\text{TTF}_2)^+\).\(^{37-41}\) Such TTF mixed valence species, \((\text{TTF}_2)^+\), absorb in the UV-vis-NIR spectrum around 900 nm together with a broad absorption with a maximum at about 2000 nm, whereas the radical dimer, \((\text{TTF}^+)\), shows maximum absorptions around 600 nm and 800 nm.\(^{37-41}\) Accordingly, for the free TTF building block only a band at 650 nm was observed, indicating the absence of radical dimerization and formation of mixed valence species. For the cage solution containing on average 8 equivalents of TTFBB, a new absorption is present around 850 nm together with an increased absorption at 600 nm. This is consistent with radical dimer absorption. Typically, the extinction coefficient for the charge transfer band around 800 nm is higher than the one for the absorption around 600 nm. Assuming that this is true also for the system under investigation, it implies that the extent of radical dimerization or radical interaction is a minor effect; most radicals within the cage are probably isolated as \((\text{TTF}^+)\). The data for the cage solution containing one equivalent of TTFBB show a similar behavior as the free building block.

Overall, the experiments presented support the retention of the full supramolecular structure of the cage upon electrochemical event. Furthermore, the combination of EPR and spectroelectrochemistry measurements reveals interaction of the radicals confined into the cavity of the supramolecular cage assigned as radical dimer of the type \((\text{TTF}^+)\).

Figure 22. Difference normalized spectra for the mono-reduced TTFBB B (black), cage sample \((\text{Pt}_{12}\text{D}_{23}\text{B})^{24+}\) (red) and cage sample \((\text{Pt}_{12}\text{D}_{16}\text{B})^{24+}\).
Conclusions

In this work we have demonstrated the feasibility of the electron transfer of redox-active species encapsulated into $M_{12}L_{24}$ supramolecular assemblies. The linker connecting the redox probe to the cage building block is a useful handle to tune the rate of electron transfer. Envisioning that an (electroactive) catalyst can be encapsulated into the $M_{12}L_{24}$ supramolecular assembly, the nature of the linker employed could potentially be exploited to fine-tune and match the electron transfer rate to the rate at which the catalyst operates. This strategy could be advantageous in order to avoid accumulation of reducing/oxidizing equivalents which could potentially be harmful to the catalyst.

Acknowledgments

Maximilian Dürr (Univ. Erlangen-Nuernberg) is thanked for acquisition of the CSI-MS data on the cage samples. Jarl Ivar van der Vlugt and Wojciech Dzik are acknowledged for X-ray data collection and refinement of the crystal structures. Vivek Sinha is thanked for the help and support with DFT calculations. Simon Mathew is thanked for fruitful discussion and suggestions.
Experimental

Materials and methods

General procedures: all synthetic procedures were carried out under an argon atmosphere using standard Schlenk techniques. All commercially available chemicals were used as received without further purification. Solvents used for synthesis were dried via the most suitable method, distilled and degassed. Column chromatography was performed open to air using solvents as received.

Electrochemistry: Cyclic voltammetry was performed on 1 mM solution of analyte (unless otherwise stated) containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The voltammograms were recorded using a PG-STAT302 N potentiostat at glassy carbon disk electrode (2 mm diameter). A platinum coil was used as auxiliary electrode and a leak free silver electrode (inner compartment 3 M KCl/Ag).

Electrolysis experiment were carried in a two compartment cell using Duocel® reticulated vitreous carbon foam as working electrode (used as received from ERG Aerospace Corporation) and a leak free silver electrode (inner compartment 3 M KCl/Ag). Platinum auxiliary electrode was separated from the main solution by a P4 glass frit. Both compartment contained 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Spectroelectrochemistry was performed in an optically transparent thin layer Ottle cell with platinum working electrode, platinum auxiliary electrode and silver wire as reference electrode, containing 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

EPR spectroscopy: Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten), on an ELEXSYS 680 spectrometer and using an in-house developed setup based on the resonator ER4116X-MD-5-W1. All oxidation were carried out electrochemically, in acetonitrile solution containing 0.2 M tetrabutylammonium hexafluorophosphate. After electrolysis was completed, samples were transferred, under inert conditions, to a melting point glass capillary that was then placed inside a standard EPR tube.

Mass analysis: mass spectra for all compounds were collected on an AccuTOF GC v 4g, JMS-T100G-CV mass spectrometer (JEOL, Japan).

Mass spectrometry on cage samples: CSI-MS measurements were acquired on a UHR-ToF Bruker Daltonik (Bremen, Germany) maXis, and ESI-ToF MS with a resolution of at least
40.000 FWHM, coupled to a Bruker cryospray unit. Positive-ion detection mode with a source voltage between 5 kV and 6 kV were used. The flow rates were 280 uL/hour. Nitrogen drying gas was kept at -35 °C and the spray gas was kept at -40 °C. The machine was calibrated prior to every experiment via direct infusion of the Agilent ESI-ToF low concentration tuning mixture, which provided an m/z range of singly charged peaks up to 2700 Da in both ion modes.

**DFT calculations**: Gas phase geometry optimizations were computed with Orca program at RI-DFT/BP86 level with def2-SVP basis set. Frontier orbitals were computed with single point calculation at DFT/B3LYP with def2-TZVP basis set.

**X-ray crystal structure determination**: X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software. Absorption correction and scaling was performed with SADABS. The structures were solved using intrinsic phasing with the program SHELXT. Least-squares refinement was performed with SHELXL-2013 against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times Ueq of the attached C atoms.

**Synthesis of compounds**

**Synthesis of 4-(trimethylsilanylethynyl)pyridine hydrochloride**: this compound was prepared according to a modified literature procedure, affording comparable yield but can be performed on several grams scale, has significantly easier workup and no chromatography is needed. A 500 mL round bottom three neck flask equipped with mechanical stirrer was charged with 15 g of finely grinded p-bromo pyridine hydrochloride (1 equiv, 77.14 mmol). The flask was
purged with argon before 40 mL of degassed methanol were added. The suspension was stirred at room temperature for 10 minutes before 230 mL of degassed triethylamine were added. After the addition, 0.270 g of PdCl$_2$(PPh$_3$)$_2$ (0.5 mol%) and 0.105 g of Cul (0.7 mol%) were added as solids against a positive pressure of argon. After stirring the suspension for few minutes, 16.4 mL of degassed (trimethylsilyl)acetylene (1.5 equiv, 115.71 mmol) were added by syringe. The mixture immediately turned dark and was stirred at room temperature until completeness. The reaction can be checked by TLC (eluent ethylacetate:hexanes 2:1) and was considered finished after 1 hour. After this time, the suspension was filtered through a glass frit and the solids washed with diethyl ether. All the volatiles were removed at the rotary evaporator, being careful to fully remove triethylamine, to afford a dark oil. To this residue, 500 mL of diethyl ether were added and the resulting suspension filtered through Celite. Hydrochloric acid, generated by addition of concentrated H$_2$SO$_4$ to solid NaCl, was bubbled for 15 minutes into the dark, clear ether solution obtained after filtration, causing the formation of an off white precipitate. This suspension was filtered and the solids washed with diethyl ether before they were subjected to overnight drying under vacuum to afford 15.8 g of the title compound 97% yield. $^1$H NMR (CD$_3$OD, ppm) δ 8.86 (m, 4H), δ 8.09 (m, 4H), δ 0.34 (s, 9H).

**Synthesis of 4-ethynyl pyridine hydrochloride:** A 500 mL round bottom flask was charged with 5 g of 4-(trimethylsilanylethynyl)pyridine hydrochloride (1 equiv, 23.6 mmol) and 10 mL of methanol. The flask was purged with argon and cooled with an ice/salt bath before 17.5 mL DBU (5 equiv, 118 mmol) and 425µL of water (1 equiv, 23.6 mmol) were added to the flask. The solution was stirred for 10 minutes before 6.75 mL of acetic acid (5 equiv, 118 mmol) followed by 400 mL of diethyl ether were added to the flask. The resulting suspension was stirred at room temperature for 10 minutes then dried with magnesium sulfate and filtered through a plug of Celite. Hydrochloric acid, generated by addition of concentrated H$_2$SO$_4$ to solid NaCl, was bubbled for 15 minutes into the ether solution obtained after filtration, causing the formation of an off white precipitate. This suspension was filtered and the solids washed with diethyl ether and hexane then dried under vacuum overnight to afford 3.13 g of the title compound in 95% yield. $^1$H NMR (CD$_3$OD, ppm) δ 8.91 (m, 4H), δ 8.17 (m, 4H), δ 4.84 (s, 1H).
Synthesis of compound 1: A round bottom Schlenk flask was charged with 2.5 g of 2,6-dibromophenol (1 equiv, 9.92 mmol) and 6.86 g of K$_2$CO$_3$ (5 equiv, 49.6 mmol). 50 mL of dry and degassed DMF were added followed by slow addition of 1.78 g of N-(tert-butoxycarbonyl)-2-chloroethylamine (1 equiv, 9.92 mmol) prepared according to literature procedure. The mixture was stirred overnight at 90 °C then was cooled to room temperature and the volatiles removed under reduced pressure. To the residue, 100 mL of water were added and the suspension extracted with dichloromethane (4x50 mL) then dried over MgSO$_4$ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with diethyl ether:triethylamine 9:1 to afford a white solid 3.76 g, 96%. $^1$H NMR (CD$_2$Cl$_2$, ppm) δ 7.57 (d, $J = 8.0$ Hz, 2H), 6.94 (t, $J = 8.0$ Hz, 1H), 5.24 (br s, 1H), 4.12 (t, $J = 5.1$ Hz, 2H), 3.57 (q, $J = 5.1$ Hz, 2H), 1.48 (s, 9H).

Synthesis of compound 2: A round bottom Schlenk flask was charged with 1, 1.9 g (1 equiv, 4.82 mmol), 1.74 g of 4-ethynylpyridine hydrochloride (2.6 equiv, 12.5 mmol) and 36.6 mg of CuI (0.05 mmol). The flask was flushed with argon before a degassed mixture of 40 mL of THF and 20 mL of triethylamine was added. A separate Schlenk flask was charged with 110.67 mg of Pd(PhCN)$_2$Cl$_2$ (6 mol%) and 167.4 mg of P(tBu)$_3$·HBF$_4$ (12 mol%). To this mixture, 5 mL of triethylamine and 10 mL of THF were added. The mixture was stirred for five minutes before it was transferred to the first flask by syringe. The mixture was stirred at 45 °C overnight then cooled to room temperature, quenched with water and extracted with ethyl acetate (4x50 mL). The organics were washed with water (2x50 mL) and brine (2x50 mL) then dried over MgSO$_4$ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with dichloromethane:methanol 96:4 to afford a white solid 1.79 g, 85% yield. $^1$H NMR (CD$_2$Cl$_2$, ppm) δ 8.66 (m, 4H), 7.63 (d, $J = 7.7$ Hz, 2H), 7.46 (m, 4H), 7.21 (t, $J = 7.7$ Hz, 1H), 4.48 (t, $J = 5.1$ Hz, 2H), 3.60 (q, $J = 5.1$ Hz, 2H), 1.39 (s, 9H).

Synthesis of compound 3: A round bottom flask was charged with 2, 1.79 g (1 equiv, 4.07 mmol) dissolved in 20 mL of dichloromethane. 15 mL of trifluoroacetic acid were slowly added and the solution was stirred at room temperature for 1 h. The volatiles were removed
under vacuum to afford a light brown solid which was thoroughly washed with dichloromethane and isolated in quantitative yield. \(^1\)H NMR (CD\(_3\)CN, ppm) \(\delta\) 8.80 (m, 4H), 8.00 (m, 4H), 7.83 (d, \(J = 7.7\) Hz, 2H), 7.38 (t, \(J = 7.7\) Hz, 1H), 7.05 (br s, 3H), 4.62 (t, \(J = 5.2\) Hz, 2H), 3.52 (br m 2H).

**Synthesis of FcBB, A**: A round bottom Schlenk flask was charged with 260 mg of ferrocene carboxylic acid (1 equiv, 1.13 mmol) and 473 mg of HATU (1.1 equiv, 1.24 mmol). The flask was flushed with argon before a degassed mixture of 30 mL of dry THF and 0.64 mL of DIPEA (2.5 equiv, 2.83 mmol) was added. This mixture was stirred for 1 hour. A separate Schlenk flask was charged with 770 mg of compound 3, (1 equiv, 1.13 mmol). After dissolving the compound in 10 mL of dry THF, 2.5 mL of DIPEA (10 equiv, 11.30 mmol) were added and the mixture stirred for few minutes before it was transferred to the first flask. The reaction mixture was stirred for additional 2 hours at room temperature then quenched with water and extracted with ethyl acetate (4x50 mL). The organics were washed with water (2x50 mL) then saturated NaHCO\(_3\) solution (2x50 mL). 1 M HCl was added causing the product to go into the water phase. The aqueous phase was then washed with ethyl acetate (2x50 mL) before 5 M NaOH was added and the product extracted back into the organic phase which was washed with brine (2x50 mL) then dried over MgSO\(_4\) and the volatiles removed under vacuum. The residue was recrystallized from dichloromethane and hexane to afford a light yellow solid, 473 mg, 72% yield. \(^1\)H NMR (CD\(_3\)CN, ppm) \(\delta\) 8.61 (m, 4H), 7.62 (d, \(J = 7.8\) Hz, 2H), 7.48 (m, 4H), 7.21 (t, \(J = 7.7\) Hz, 1H), 6.72 (br s, 1H), 4.61 (q, \(J = 2.2\) Hz, 2H), 4.52 (t, \(J = 5.6\) Hz, 2H), 4.28 (q, \(J = 2.2\) Hz, 2H), 4.09 (s, 5H), 3.83 (q, \(J = 5.7\) Hz, 2H). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), ppm) \(\delta\) 169.8, 149.9, 134.9, 130.5, 125.3, 123.9, 116.4, 91.6, 89.1, 76.0, 74.2, 70.3, 69.6, 68.0, 40.0. HR FD-MS (m/z) found 551.1291 expected 551.1297, C\(_{33}\)H\(_{25}\)FeN\(_3\)O\(_2\)

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Fundamental studies of electron transfer processes across the rim of \( \text{M}_{12}\text{L}_{24} \) nano-spheres

**Synthesis of compound 5:** compound 5 was prepared according to a modified literature procedure.\(^\text{45}\) An argon flushed Schlenk round bottom flask was charged with 700 mg (3.42 mmol) of TTF and 20 mL of dry THF. The solution was cooled to -78 °C in a dry ice/acetone bath then 1.37 mL (1.05 equiv, 3.59 mmol) of nBuLi 2.5 M were added dropwise during the course of 15 minutes. The solution was left stirring under these conditions for 60 min then 975µL (1.05 equiv, 3.59 mmol) of nBu\(_3\)SnCl. The solution was stirred for extra 30 min before it was allowed to warm to room temperature over the course of 2 hours. The reaction was quenched with 100 mL of water and extracted with ethyl acetate (3x50 mL). The combined organic layers were dried over MgSO\(_4\) and the volatiles removed under vacuum to afford the crude product, 1.81 g which was used without further purification. \(^1\)H NMR (CD\(_2\)Cl\(_2\), ppm) \( \delta \) 6.31(s, 2H), \( \delta \) 6.14(s, 1H), \( \delta \) 1.53 (m, 6H), \( \delta \) 1.34 (m, 6H), \( \delta \) 1.09 (m, 6H), \( \delta \) 0.90 (t, \( J = 6.5 \) Hz, 9H).

**Synthesis of compound 6:** A round bottom Schlenk flask was charged with crude 5, 1.81 g (1 equiv, 3.65 mmol), 0.926 g of 1-Bromo-4-[2-(trimethylsilyl)ethynyl]benzene (1 equiv, 3.65 mmol) and 0.211 g of Pd(PPh\(_3\))\(_4\) (5 mol%). The flask was purged with argon before 100 mL of degassed toluene were added. The mixture was refluxed overnight then cooled to room temperature and the volatiles removed under reduced pressure. The residue was dissolved over MgSO\(_4\) and the volatiles removed under vacuum to afford a bright orange compound in 92% yield, 1.208 g. \(^1\)H NMR (CD\(_2\)Cl\(_2\), ppm) \( \delta \) 7.43 (m, 4H), \( \delta \) 6.66 (s, 1H), \( \delta \) 6.42 (s, 2H), \( \delta \) 0.22 (s, 9H).

**Synthesis of compound 7:** a round bottom flask was charged with H\(_2\)SO\(_4\) (20 mL) and cooled in ice bath for 15 minutes. 2.471 g of NaNO\(_2\) (1.01 equiv, 35.86 mmol) were carefully added

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to the flask maintaining the temperature below 5 °C. A solution of 10 g of 2,6-dibromo-4-tert-butyl aniline (1 equiv, 32.57 mmol) in 100 mL of acetic acid was added dropwise over the course of 3 hours being careful to maintain the temperature always below 5 °C. After the addition, the mixture was allowed to warm to room temperature and stirred for additional 4 hours. After this time, a solution of 39.32 g of KI (7.3 equiv, 236.86 mmol) and 8.26 g I₂ (1 equiv, 32.57 mmol) in 75 mL of water was added and the mixture stirred overnight at room temperature. The resulting mixture was quenched by pouring it in a 1.5 L, 15% solution of sodium hydroxide and then extracted with ethyl acetate (4x150 mL). The organic phase was washed with water (2x100 mL) and brine (2x100 mL) then dried over MgSO₄ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with petroleum ether to afford a white solid 12.90 g, 95% yield. ¹H NMR (CD₂Cl₂, ppm) δ 7.63 (s, 2H), δ 1.31 (s, 9H).

Synthesis of compound 8: A round bottom Schlenk flask was charged with 6, 1.208 g (1 equiv, 3.21 mmol) and 20 mL of degassed THF. To this solution 3.2 mL of tetrabutylammonium fluoride (1 M solution, 1 equiv, 3.21 mmol) was added and the solution was stirred at room temperature in the dark for 2 hours. The completeness of the reaction was check by TLC, after which the volatiles were removed under vacuum. To the same flask, 1.334 g of compound 7 (1 equiv, 3.21 mmol) and 0.350 mg of Pd(PPh₃)₄ (10 mol%) were added. The flask was purged with argon before 60 mL of degassed THF and 20 mL of degassed triethylamine were added. The mixture was refluxed overnight then cooled to room temperature, quenched by addition of water and extracted with ethyl acetate (3x100 mL). The organics were then dried over MgSO₄ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with dichloromethane:hexane 1:2 to afford a red crystalline solid 0.740 g, 39% yield. ¹H NMR (CD₂Cl₂, ppm) δ 7.66 (s, 2H), δ 7.64 (m, 2H), δ 7.47 (m, 2H), δ 6.71 (s, 1H), δ 6.42 (s, 2H), δ 1.34 (s, 9H).

Synthesis of TTFBB, B: A round bottom Schlenk flask was charged with 9, 0.740 g (1 equiv, 1.24 mmol), 0.452 g of 4-ethylpyridine hydrochloride (2.6 equiv, 3.29 mmol) and 9.5 mg of CuI (0.05 mmol). The flask was flushed with argon before a degassed mixture of 40 mL of THF and 20 mL of triethylamine was added. A separate Schlenk flask was charged with 28.6 mg of Pd(PhCN)₂Cl₂ (6 mol%) and 43.3 mg of P(tBu)₃·HCl (0.12 mol%). To this mixture, 5 mL of triethylamine and 10 mL of THF were added. The mixture was stirred for five minutes before it was transferred to the first flask by syringe. The mixture was refluxed overnight then cooled to room temperature, quenched with water and extracted with dichloromethane (4x50 mL). The organics were washed with water (2x50 mL) and brine (2x50 mL) then dried over MgSO₄ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with dichloromethane:methanol 94:6 to afford a red crystalline solid 0.715 g, 90% yield. ¹H NMR (CD₂Cl₂, ppm) δ 8.66 (m, 4H), δ 7.72 (s, 2H), δ 7.60 (m, 2H), δ 7.48
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(m, 4H), $\delta$ 7.46 (m, 2H), $\delta$ 6.72 (s, 1H), $\delta$ 6.43 (s, 2H), $\delta$ 1.41 (s, 9H). $^{13}$C NMR (CD$_2$Cl$_2$, ppm) $\delta$
151.8, 149.4, 134.9, 132.4, 131.7, 130.4, 130.0, 126.1, 124.7, 122.6, 119.0, 118.9, 115.2, 97.0, 91.9, 90.4, 88.0, 34.7, 30.5. HR ESI-MS (m/z) found 638.0976 expected 638.0979, C$_{38}$H$_{26}$N$_2$S$_4$.

Synthesis of compound 9: This compound was prepared according to a modified literature procedure. A round bottom Schlenk flask equipped with a condenser and a dropping funnel was charged with 10 g of 3,5-dimethylnitrobenzene (1 equiv, 66.15 mmol) and 25 g of zinc powder (5.8 equiv, 384 mmol). The flask was flushed with argon before degassed ethanol 60 mL was added. The mixture was heated to reflux then a degassed solution of 15 g of NaOH (5.6 equiv, 375 mmol) in 50 mL of water was carefully added dropwise over the course of 1 hour. After the addition was completed the mixture was refluxed for additional 2 hours then more zinc powder was added 10 g and the reflux continued for other 2 hours. The mixture was allowed to cool to room temperature. Diethyl ether 200 mL was added and the mixture filtered through Celite. The solution obtained was washed with water (3x100 mL), the organics dried over magnesium sulfate and the volatiles removed under vacuum. The crude prod-
uct containing few impurities was used in the next step without further purification. $^1$H NMR (CD$_2$Cl$_2$, ppm) $\delta$ 7.57 (s 2H), $\delta$ 6.51 (s, 4H), $\delta$ 5.63 (br s, 2H) $\delta$ 2.27 (s, 12H).

Synthesis of compound 10: The crude 13 was dissolved in 100 mL of toluene. To this solution, 100 mL 6 M HCl were added and the mixture stirred vigorously at room temperature for 2 hours. The organic layer was discarded and the aqueous phase was washed with ethyl acetate (3x50 mL). The pH of the aqueous phase was adjusted to about 14 by addition of 5 M NaOH causing the formation of white precipitate which was extracted with ethyl acetate (3x100 mL). The organic layer was washed with slightly basic water (3x50 mL) dried over magnesium sulfate and the volatiles removed under vacuum to afford an off white solid 7.45 g, 47% yield over two steps, which was used in the next step without further purification. $^1$H NMR (CD$_2$Cl$_2$, ppm) $\delta$ 6.50 (s, 4H), $\delta$ 3.49 (br s, 4H) 1.84 (s, 12H).

Synthesis of compound 11: This compound was prepared according to a modified literature procedure. Crude compound 14, 2.9 g (1 equiv, 12.1 mmol) was dissolved in acetonitrile 100 mL then 2 M HCl, 100 mL was added. The solution was cooled to $-10$ °C in an ice-salt bath. 2.09 g of solid NaNO$_2$ (2.5 equiv, 30.25 mmol) were added portion wise over the course of 30 minutes maintaining the temperature around $-10$ °C. After the addition was complete, the mixture was stirred for 30 minutes at $-10$ °C before 20 g of KI (10 equiv, 120 mmol) was slowly added. The mixture was allowed to warm to room temperature over the course of 1 hour and stirred overnight at room temperature. Orange precipitate forms and it is collected by filtration, dissolved in ethyl acetate and washed with water (3x50 mL). The organic layer is dried over magnesium sulfate and the volatiles removed under vacuum to afford 5.45 g of product in 97% yield. This material was used in the next step without further purification. $^1$H NMR (CD$_2$Cl$_2$, ppm) $\delta$ 7.54 (s, 4H), $\delta$ 1.87 (s, 12H).

Synthesis of compound 12: A round bottom Schlenk flask was charged with 15, 2.50 g (1 equiv, 5.41 mmol), 5 mg of Cul (0.025 mmol) and Pd(PPh$_3$)$_2$Cl, 17.5 mg (0.025 mmol). The flask flushed with argon before a degassed mixture of 180 mL of THF and 20 mL of triethylamine was added. To this mixture, TMS-acetylene 0.5 mL (0.65 equiv, 3.5 mmol) were added and the mixture stirred at room temperature over night. The volatiles were removed under vacuum and the residue was purified by silica column chromatography with dichloromethane:hexane 1:2 to afford about 1.4 g of the unreacted excess of starting material 15, then the desired product as white crystalline solid 0.750 g, 49.6% yield. $^1$H NMR (CD$_2$Cl$_2$, ppm) $\delta$ 7.54 (s, 2H), $\delta$ 7.27 (s, 2H), $\delta$ 1.88 (s, 6H), $\delta$ 1.86 (s, 6H), $\delta$ 0.28 (s, 9H).

Synthesis of compound 13: A round bottom Schlenk flask was charged with 16, 0.750 g (1 equiv, 1.74 mmol), Pd(PPh$_3$)$_4$, 100 mg (5 mol%) and crude compound 5, 1 g (1.1 equiv, 2.0 mmol). The flask flushed with argon before degassed toluene, 50 mL was added. The mix-
tured overnight, allowed to cool to room temperature before the volatiles were removed under vacuum. The residue was purified by silica column chromatography with dichloromethane:hexane 1:1 to afford the desired product as yellow solid, 0.560 g, 63.4% yield. ¹H NMR (CD₂Cl₂ ppm) δ 7.29 (s, 2H), δ 7.24 (s, 2H), δ 6.62 (s, 1H), δ 6.42 (s, 2H), δ 1.92 (s, 6H), δ 1.90 (s, 6H), δ 0.29 (s, 9H).

**Synthesis of compound 14:** A round bottom Schlenk flask was charged with 17, 560 mg (1 equiv, 1.10 mmol) and 20 mL of degassed THF. To this solution 1.1 mL of tetrabutylammonium fluoride (1 M solution, 1 equiv, 1.1 mmol) were added and the solution was stirred at room temperature in the dark for 1 hour. The completeness of the reaction was check by TLC. To the same flask under continuous argon purging, 0.552 g of compound 7 (1.2 equiv, 1.32 mmol), 130 mg of Pd(PPh₃)₄ (10 mol%) and a degassed mixture of THF 40 mL and triethylamine 20 mL were added. The mixture was refluxed overnight then cooled to room temperature, quenched by addition of water and extracted with ethyl acetate (3x100 mL). The organics were then dried over MgSO₄ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with dichloromethane:hexane 1:2 to afford a yellow solid 0.405 g, 50% yield. ¹H NMR (CD₂Cl₂ ppm) δ 7.66 (s, 2H), δ 7.44 (s, 2H), δ 7.26 (s, 2H), δ 6.63 (s, 1H), δ 6.42 (s, 2H), δ 1.95 (s, 12H), 1.35 (s, 9H).

**Synthesis of twistedTTFBB, C:** A round bottom Schlenk flask was charged with 18, 0.400 g (1 equiv, 0.55 mmol), 0.200 g of 4-ethynylpyridine hydrochloride (2.6 equiv, 1.43 mmol) and 4.1 mg of CuI (0.05 mmol). The flask was flushed with argon before a degassed mixture of 40 mL of THF and 20 mL of triethylamine was added. A separate Schlenk flask was charged with 12.6 mg of Pd(PhCN)₂Cl₂ (6 mol%) and 19.2 mg of P(tBu)₃·HCl (0.12 mol%). To this mixture, 5 mL of triethylamine and 10 mL of THF were added. The mixture was stirred for five minutes before it was transferred to the first flask by syringe. The mixture was refluxed overnight then cooled to room temperature, quenched with water and extracted with dichloromethane (4x50 mL). The organics were washed with water (2x50 mL) and brine (2x50 mL) then dried over MgSO₄ and the volatiles removed under vacuum. The residue was purified by silica column chromatography with dichloromethane:methanol 94:6 to afford a yellow powder 0.150 g, 35.4% yield. ¹H NMR (CD₂Cl₂ ppm) δ 8.65 (m, 4H), δ 7.72 (s, 2H), δ 7.53 (m, 4H), δ 7.42 (s, 2H), δ 7.27 (s, 2H), δ 6.64 (s, 1H), δ 6.42 (s, 2H), δ 1.97 (s, 6H), δ 1.91 (s, 6H), δ 1.42 (s, 9H). ¹³C NMR (CD₂Cl₂ ppm) δ 151.4, 149.7, 140.5, 139.5, 136.0, 135.8, 131.1, 130.8, 130.6, 129.9, 125.9, 125.3, 124.6, 121.3, 119.0, 118.9, 112.8, 111.0, 108.8, 98.2, 92.2, 90.2, 86.1, 34.6, 30.5, 19.3, 19.2. HR FD-MS (m/z) found 770.1898 expected 770.1918, C₄₈H₃₈N₂S₄.
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**Synthesis of compound 15**: 5 g of 2,6-dibromo-4-tert-butyl-benzenamine (1 equiv, 16.3 mmol) were dissolved in 200 mL of ethanol and the solution heated to 50 °C. 25 mL of concentrated H$_2$SO$_4$ were added dropwise to this solution and the temperature was raised to 70 °C. 3.1 g of NaNO$_2$ (2.7 equiv, 44.6 mmol) were added portion wise over the course of 2 hours. After the addition was completed the temperature was raised to 80 °C and the mixture stirred at this temperature overnight. The mixture was then poured over ice and extracted with ethyl acetate (3x100 mL). The organics were washed with brine (2x50 mL) and dried over MgSO$_4$, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether 40-60 °C) to afford 4.32 g, 91%. **$^1$H NMR (CD$_2$Cl$_2$, ppm)** δ 7.53 (m, 1H), δ 7.52 (m, 2H), δ 1.33 (s, 9H).

**Synthesis of BBH, D**: A round bottom Schlenk flask was charged with 11, 2.52 g (1 equiv, 8.63 mmol), 3.13 g of 4-ethynylpyridine hydrochloride (2.6 equiv, 22.44 mmol) and 66 mg of CuI (0.05 mmol). The flask was flushed with argon before a degassed mixture of 40 mL of toluene and 20 mL of triethylamine was added. A separate Schlenk flask was charged with 198 mg of Pd(PhCN)$_2$Cl$_2$ (6 mol%) and 300 mg of P(tBu)$_3$·HCl (0.12 mol%). To this mixture, 5 mL of triethylamine and 10 mL of toluene were added. The mixture was stirred for five minutes before it was transferred to the first flask by syringe. The mixture was heated overnight at 60 °C, then cooled to room temperature, quenched with water and extracted with dichloromethane (4x100 mL). The organics were washed with water (2x50 mL) and brine (2x50 mL) then dried over MgSO$_4$ and the volatiles removed under vacuum. The residue was purified by gradient silica column chromatography with dichloromethane:acetone 9:1. The desired product eluted with dichloromethane:acetone 2:1 to afford an off white crystalline solid 2.19 g, 75.5% yield. **$^1$H NMR (CD$_2$Cl$_2$, ppm)** δ 8.60 (br, 4H), δ 7.64 (s, 2H), δ 7.58 (s, 1H), δ 7.42 (m, 4H), δ 1.35 (s, 9H). **$^{13}$C NMR (CD$_2$Cl$_2$, ppm)** δ 154.1, 151.8, 151.8, 133.9, 132.7, 131.8, 131.8, 127.4, 127.3, 124.2, 94.8, 88.7, 36.6, 32.7. **HR FD-MS (m/z)** found 336.1620 expected 336.1626, C$_{24}$H$_{20}$N$_2$. 

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Synthesis of compound 16, ferrocenyl sulfonic acid: Ferrocene 2 g (1 equiv, 10.7 mmol) was suspended in acetic anhydride 60 mL and the mixture cooled with ice. 0.71 mL of $\text{ClSO}_3\text{H}$ (1.25 g, 1 equiv, 10.7 mmol) was added dropwise over the course of 1 hour. The mixture was allowed to warm to room temperature and stirred for additional 2 hours then poured over ice, stirred for 1 hour and extracted with diethyl ether. The volatiles were removed under vacuum and the residue recrystallized from toluene/pentane mixture to afford the desired compound, 2.5 g, 90% yield. $^1\text{H NMR (D}_2\text{O, ppm)} \delta 4.56 \text{ (br, 2H)}, \delta 4.37 \text{ (br, 7H)}$.

Synthesis of compound 17, ferrocenyl sulfonate tetrabutylammonium: Ferrocene sulfonic acid 20 300 mg (1 equiv, 1.13 mmol) was dissolved in methanol then 1.13 mL of a 1 M solution of tetrabutylammonium hydroxide (1 equiv, 1.13 mmol) was added. The mixture was stirred for few minutes before the volatiles were removed under vacuum. This compound was found to be very hygroscopic and always affording oil upon vacuum removal of solvents, therefore some water was added and the sample was freeze-dried affording an orange solid. $^1\text{H NMR (CD}_3\text{CN, ppm)} \delta 4.40 \text{ (t, } J = 1.9 \text{ Hz, 2H)}, 4.24 \text{ (s, 5H)}, 4.09 \text{ (t, } J = 1.9 \text{ Hz, 2H)}, 3.31 - 2.97 \text{ (m, 8H)}, 1.97 \text{ (m, 8H)}, 1.62 \text{ (m, 8H)}, 1.38 \text{ (m, 8H)}, 0.99 \text{ (t, } J = 7.3 \text{ Hz, 12H}).$ HR ESI(neg)-MS ($m/z$) found 264.9616 expected 264.9622, ($m$) $C_{10}H_9FeO_3S$. Found 772.2029 expected 772.2093, ($2m + TBA$) $C_{36}H_{54}FeNO_6S_2$.

Crystallographic details:

FcBB, A: $C_{33}H_{25}FeN_3O_2$. Fw = 551.41, yellow needle, $0.20 \times 0.11 \times 0.10$ mm, Tetragonal, $I4_1/a$ (No: 88), $a = 24.833 (3)$ Å, $c = 17.086 (3)$ Å, $V = 10537 (3)$ Å$^3$, $D_x = 1.390$ g/cm$^3$, $\mu = 0.61$ mm$^{-1}$. 41611 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.595$ Å$^{-1}$. 4633 reflections were unique ($R_{\text{int}} = 0.116$), of which 3205 were observed [$I>2\sigma(I)$]. 355 parameters were refined with 0 restraints. $R1/wR2 [I > 2\sigma(I)]: 0.0366/0.0865 R1/wR2 [all refl.]: 0.0731/0.0744$. S = 0.99. Residual electron density between $-0.36$ and 0.25 e/Å$^3$.

TTFBB, B: $C_{38}H_{26}N_2S_4$. Fw = 638.85, orange plate, $0.56 \times 0.35 \times 0.20$ mm, Triclinic, $P$ (No: 2), $a = 9.1542 (3)$, $b = 10.4410 (4)$, $c = 17.0912 (6)$ Å, $\alpha = 78.573 (2)$, $\beta = 86.194 (2)$, $\gamma = 82.405 (2)$, $V = 1585.77 (10)$ Å$^3$, $Z = 2$, $D_x = 1.338$ g/cm$^3$, $\mu = 0.33$ mm$^{-1}$. 36086 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.627$ Å$^{-1}$. 6546 reflections were unique ($R_{\text{int}} = 0.065$), of which 4874 were observed [$I>2\sigma(I)$]. 400 parameters were refined with 0 restraints. $R1/wR2 [I > 2\sigma(I)]: 0.0392/0.0910 R1/wR2 [all refl.]: 0.0652/0.1069$. S = 0.94. Residual electron density between $-0.35$ and 0.46 e/Å$^3$.

twistedTTFBB, C: $C_{48}H_{38}N_2S_4$. Fw = 771.04, yellow needle, $0.58 \times 0.30 \times 0.21$ mm, Orthorhombic, $Pbcn$ (No: 60), $a = 22.841 (1)$, $b = 9.4123 (4)$, $c = 42.3819 (18)$ Å, $V = 9111.5 (7)$ Å$^3$, $Z = 8$. 

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$D_s = 1.124 \text{ g/cm}^3, \mu = 0.24 \text{ mm}^{-1}$. 61958 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.597 \text{ Å}^{-1}$. 8072 reflections were unique ($R_{\text{int}} = 0.061$), of which 5799 were observed [I>2σ(I)]. 494 parameters were refined with 0 restraints. R1/wR2 [I > 2σ(I)]: 0.1061/0.3004 R1/wR2 [all refl.]: 0.1400/0.3116. S = 2.06. Residual electron density between -0.55 and 0.51 e/Å$^3$. 


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Appendix

Ferrocene building block A and ferrocene cage; electrochemistry.

Figure 23. Cyclic voltammograms recorded at different scan speeds for FcBB A.

Figure 24. Cyclic voltammograms recorded at different scan speeds for a sample of the ferrocene cage (Pd$_{12}$A$_{24}$)$^{24+}$. 

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TTF building block B and TTF cage; electrochemistry.

Figure 25. Cyclic voltammograms recorded at different scan speeds for TTFBB B.

Figure 26. Cyclic voltammograms recorded at different scan speeds for the cage solution (Pt_{12}D_{23}A)^{24+}.
Twisted TTF building block C and its cage; electrochemistry.

**Figure 27.** Cyclic voltammograms recorded at different scan speeds for twisted TTFBB C.

**Figure 28.** Cyclic voltammograms recorded at different scan speeds for a platinum cage (Pt\(_{12}D_{24}C\))\(^{24+}\).
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TTF building block B and its cage; spectroelectrochemistry.

Figure 29. Spectroelectrochemistry of TTFBB B, normal spectra (left), difference spectra (right).

Figure 30. Spectroelectrochemistry of a cage solution (Pt_{12}D_{20}B)_{24}^{2+}, normal spectra (left), difference spectra (right).

Figure 31. Spectroelectrochemistry of a cage solution (Pt_{12}D_{23}B)_{24}^{2+}, difference spectra.
Figure 32. Uv-vis spectrum in acetonitrile of TTF building block B (blue) and twisted TTFBB C (black) and comparison with bulk TTF (red) showing increasing HOMO-LUMO gap corresponding to increased π delocalization of the orbitals.

Figure 33. HOMO (-4.80 eV) and LUMO(-2.50 eV) of TTFBB B.

Figure 34. HOMO-1 (-5.89 eV) and LUMO+1 (-2.26 eV) of TTFBB B.
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Figure 35. HOMO (-4.68 eV) and LUMO (-2.34 eV) of twisted TTF building block C.

Figure 36. HOMO-1 (-5.91 eV) and LUMO+1 (-2.24 eV) of TTF building block C.

Figure 37. C: HOMO-2 (-6.08 eV) of TTF building block C.
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