nature portfolio

Peer Review File

Combining Electron Transfer, Spin Crossover, and Redox Properties in Metal-Organic-Frameworks

Corresponding Author: Professor Saioa Cobo

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors described a rational design of a variety of Hofmann-type clathrates including various ligands, which revealed varied functional features with active redox SCO and/or ET molecules. I thoroughly enjoyed reading this article, which provided new ideas, and I believe it can be considered for publication in Nat. Commun. After addressing the following comments:

1. There are many typos throughout the ms as well as ESI which should be addressed. For example, …...the redox activity of the ligands within the structure leads to the a fully
reversible electrochemical reduction reaction on a spin …...
2. English should be improved.
3. Please avoid repetition of the sentences in introduction. For example, …. an external stimulus (temperature, light irradiation
or pressure) ……...
4. Hofmann clathrates fall into one of two major families: the [M(L)nM“(CN)4] (n = 1 or 2, L denotes a bis- or monodentate pyridine-like ligand (such as NH3 or H2O), M denotes a transition metal ion, and M” denotes Ni, Pd, or Pt.) and [M(L)n{M“(CN)2}2], where M” stands for either Cu, Ag, or Au). This should be revised in the introduction.
5. The direct powder precipitation of the compounds is obtained when K2[M(CN)4]·xH2O is added to a EtOH/H2O (1:1)..........the authors should define M here.
6. ….. containing the ligand and Fe(BF4)2·6H2O. ......what is (BF4)2?
7. The single crystal XRD shown in Scheme 2 should be labeled for clarity.
8. Can the authors provide some photographs of the gradual color change during the magnetic susceptibility measurements. And for the optical reflectivity measurements, it should be clearer and more obvious.
9. I wonder why did the authors performed electrolysis at negative potential/ -1.2V? It would be a reduction process rather than electrolysis. There is a misunderstanding.
10. Does the color change upon cooling and heating is reversible or not? This point should be addressed.
11. The authors ignored some bands at around 1560 and 1800 nm in Fig4a, why?
12. Does the SCO occur here between the metal centers, while the ET between ligands and/or metal centers and ligand? This should be addressed throughout the ms to differentiate between the two phenomena.
13. It is strange for me, the authors presented Fig. 8 in the ms before Fig. 5 and, at the same time, cited Fig. S10 in the introduction before the previous Figs.S1-9, why?
14. How did the authors collect the temperature dependent UV spectra while monitoring concentrations, especially when they pointed out in the ms that the materials do not dissolve?
15. The word " non-innocent behavior" is very broad here, please be more specific and explain it in every position this expression used.
16. The authors have two Figures 8 in the ms, please revise carefully.
17. Why did the authors not study the porous nature of their materials by nitrogen gas adsorption - desorption isotherms, I think it will offer interesting new insights?
18. At -0.78 V vs. Ag+|AgCl is a reduction process not electrolysis one.
19. Performing oxidation at 0V is meaningless.
20. References have many mistakes and typos which should be addressed.

Reviewer #2

(Remarks to the Author)
This submission reports a new family of Hofmann framework materials supported by terminal viologen ligands. Hofmann

frameworks are well known for their thermal spin-crossover properties, which are heavily studied. However, this study has an additional interest through their viologen components, which are redox active. This study addresses the interplay between iron-based spin-crossover and internal charge-transfer to the viologen centers.

The concept is not quite new, but it is the most detailed study yet reported for a framework material with this combination of properties. Moreover their modular material design is very flexible, and leads to predictable and reproducible framework structures. They are the first such multifunctional materials that allow straightforward chemical tuning, to allow optimization of their thermochromism or conductivity (although that is not discussed here).

There is more that could be done with these material, but the authors have achieved what they set out to do: to define their temperature-dependent electronic structures. That’s enough for an initial publication on this system, which is warranted and appropriate for the journal.

The following comments count as minor corrections.

(i) It can be hard to follow which material is being measured in each experiment. I’d consider numbering the compounds, for example as 1a-1d for M = Ni and 2a-2d for M = Pt where R = Me (1a/2a), Br (1b/2b), CO2Me (1c/2c) and NO2 (1d/2d). Or, they could call them 1R and 2R where R = Me, Br, CO2Me, NO2.

(ii) The Ni and Pt frameworks are treated almost interchangeably in different measurements. That could be valid, but [Ni(CN)4]2- Hofmann networks can undergo spin-crossover at temperatures up to 50 K below their Pd and Pt analogues. At least, we need a full set of magnetic data for all the Pt frameworks to confirm they behave similarly to the Ni materials in Figure 1. As it is, only magnetic data for one Pt framework seems to be presented, in Figures 3 and 8.
I would add such a Figure showing all the Ni and Pt framework magnetic data side-by-side, to the SI.

(iii) The origin of the iron(III) in some of the Moessbauer spectra isn’t really addressed. Is it an impurity? If so, it’s a large one – ca 15 % in some cases. It could also explain the higher magnetic moment shown by the CO2Me framework in Figure 1. The iron(III) content is temperature-dependent in one sample, but not in others. This matters because iron(II) is another potential electron donor in the internal redox.

(iv) Only analytical data for the Ni-containing frameworks are given in the SI. Elemental analyses and powder patterns should be included for all the new compounds in the study, including the Pt frameworks, to prove they were characterized as pure materials. Ideally that should include CHN microanalyses, not just ICP metal analyses.

(v) The formatting of the crystallographic Tables S9-S12 is untidy. They include different fonts; the information they contain is not consistent; and the page orientation for Table S12 is wrong. Please tidy them up.
Also, have the crystal structures been deposited with the Cambridge Database? If not please do so, and provide CCDC deposition numbers.

(vi) As well as refs 56-58, another coordination polymer showing an interplay between spin-crossover and ligand redox is in 10.1002/anie.201611824. They could also acknowledge molecular salts of metallate and radical anions, which can also show interplay between cation spin-crossover and anion redox. These were recently reviewed in 10.1016/j.ccr.2021.213819

(vii) The English is generally good and is always understandable. However the spelling of “synthetized” should be corrected to “synthesized”.

Reviewer #3

(Remarks to the Author)
This study into the use of viologen derivative ligands as thermochromic units in nickel complexes is interesting in that it presents a new system with some relatively interesting multifunctional properties (SCO and ET). The compounds prepared are characterized using a combination of X-ray structural analysis, advanced spectroscopic techniques, SQUID magnetometry and DFT calculations. Most conclusions drawn appear reasonable, but there are some gaps that I would like to authors to consider in a revised manuscript.
1. As far as I know, the thermochromism of viologen-based compounds occurs at temperatures higher than room temperature, but the thermochromism of the compounds reported in this paper occurs at room temperature. So what's the driving force for the electron transfer?
2. Raman and IR spectra are highly interfered by SCO. Since {Fe(R-pbpy)2[μ2-Ni(CN)4]2·2H2O} (R = COOCH3 and NO2) compounds do not show SCO, it is suggested to provide XPS spectra of them to fully demonstrate the existence and path of electron transfer.
3. The characteristic absorption peak of viologen radical (at about 600 nm) appeared in the absorption spectrum of the compound at room temperature. During the cooling process, the intensity of this peak was enhanced, which meant that electron transfer occurred at cooling, and the concentration of free radicals increased with the decrease of temperature. Do the EPR spectra of these compounds show signal characteristics for a radical at low temperatures?
4. Since the coloration is reversible, I think the author should provide reversible photographs of the coloration as well as the absorption spectra of the compounds.
5. Elemental analysis data for CNH should be provided. At the same time, the error of elemental analysis data for Fe(NO2-pbpy)2[μ2-Ni(CN)4]2·2H2O is too large, so it is suggested that the author further purify the compound.
6. checkCIF reports should be provided.

7. There are many grammatical errors in the text, please correct.

Reviewer #4

(Remarks to the Author)
This manuscript reports four isostructural 2D Hofmann-type coordination polymers (CPs) incorporating redox-active viologen ligands (R-pbpy+, R = CH3, Br, COOCH3, or NO2), where tetracyanoplatinate ions act as uncommon μ-bidentate bridges. The compounds with CH3 and Br represent the initial redox-active spin-crossover (SCO) CPs, exhibiting temperature-dependent color changes, manifesting thermochromism in all cases. Notably, the CH3 and Br compounds undergo color changes due to spin-state transitions, whereas the COOCH3 and NO2 compounds exhibit no SCO activity. Consequently, the observed thermochromic behavior in all compounds must involve additional factors beyond SCO, specifically the transformation between R-pbpy+ and R-pbpy radical, as confirmed in this study. To elucidate the electron transfer (ET) mechanism, various characterizations, including crystallographic, spectroscopic, and theoretical analyses, were conducted. The authors infer that the generation of R-pbpy radicals likely arises from ET, predominantly originating from the uncoordinated CN- moieties towards the redox-active R-pbpy+ entities. This research introduces a novel avenue for incorporating new functionalities within the Hofmann-type framework, with the reversible redox behavior showcasing the potential of electrochemistry in developing reversible multifunctional materials. The intriguing findings presented in this study suggest that, following substantial revisions, the manuscript may be suitable for publication in a prestigious journal such as Nature Communications.
1. The conclusion that "......the uncoordinated CN- moieties indicate the latter as the most likely origin of ET" is a major concern. However, the main text presents various pieces of evidence that suggest different outcomes. For instance, on page 7, the absorption band at 535 nm is linked to the generation of the CH3-pbpy radical. Furthermore, upon comparison with isostructural Zn derivatives, the results point towards the involvement of the FeII ion in the creation of this band. This analysis raises a critical question regarding the role of FeII. It remains ambiguous whether the author suggests that FeII contributes significantly to electron transfer (ET) in the formation of radicals or if it serves another function in the metal-to-ligand charge transfer (MLCT) transition. Conversely, given that no radicals are observed in the Zn derivatives, does this absence imply that ET occurs between FeII and R-pbpy instead? Clarifying these aspects is crucial for a more comprehensive understanding of the system under investigation.
2. On page 9, theoretical calculations propose that the experimental band seen at 580 nm originates from Fe-CH3-pbpy+ MLCT, implying it is SCO-dependent. Despite this, on page 8, the absorption intensity at 580 nm does not align with the SCO. Why?
3. Mössbauer spectroscopy confirms the presence of temperature-dependent Fe(III) populations in CH3- and Br-compounds, indicating that a small proportion of iron ions are involved in electron transfer (ET) towards the ligand. This suggests that both iron ions and uncoordinated CN- groups (Raman evidence) contribute to the ET process. Additionally, the confirmation of temperature-dependent Fe(III) populations in non-SCO NO2- and COOCH3-compounds through Mössbauer spectroscopy would provide further substantiation of the origin of ET.
4. Minor concerns include inconsistent spelling of the word “Hofmann” as “Hoffman” on pages 15-16, whereas it is correct for most of the main text. In page 4, single-crystal structures of compounds with R = CH3, Br, COOCH3 have been determined. The structure for R = NO2 is yet to be determined.

Reviewer #5

(Remarks to the Author)
The manuscript submitted by Cobo et al. describes a novel family of Hofmann-type bimetallic networks that combine spin crossover properties, electron transfer, and redox activity. This unique set of properties has been achieved by incorporating a pyridinium-based organic ligand into the metal-organic framework. This ligand is easily reducible and imparts both electron transfer (ET) and redox properties, along with spin crossover (SCO) based on the presence of octahedral [FeIIN6] sites.
The characterization of these multifunctional compounds has been achieved through a comprehensive physical study, incorporating SQUID measurements, Mössbauer spectroscopy, cyclic voltamperometry, X-ray diffraction, and optical reflectivity, among other techniques. The multifunctional approach proposed in this paper represents a highly promising advancement in the discovery of new stimuli-responsive materials for potential applications and therefore it merits consideration for publication in Nature Communications.
However, there are concerns regarding the presentation of the results throughout the manuscript, particularly those related to the synthesis and treatment of the samples. In my opinion, these concerns should be addressed by the authors before the manuscript can be considered for acceptance .
- The authors need to provide clarity, from the beginning of the paper, regarding which compounds have been studied. It appears that all structures have been examined using Pt derivatives (Fe(R-pbpy)2[η2-Pt(CN)4]2); however, the remaining physical characterizations have been conducted on the Ni derivatives (Fe(R-pbpy)2[η2-Ni(CN)4]2). The rationale for this discrepancy is not explained in the main text. The absence of magnetic or reflectivity studies on the Pt derivatives also requires clarification. In my opinion, it would be beneficial to dedicate an equivalent figure as Figure 1 to the Pt derivatives, to enhance the overall clarity and completeness of the manuscript.
- In the caption of Figure 3, it mentions "Temperature dependent UV-vis-NIR absorption spectra of Fe(CH3-pbpy)2[η2-Pt(CN)4]2)," while in the text when referring to Figure 3, it states, "Fig 3(b) shows the variation of the band intensities with respect to the magnetic properties of (Fe(CH3-pbpy)2[η2-Ni(CN)4]2·H2O)." This inconsistency raises confusion and needs to be addressed for clarity. It's essential to ensure that the caption and the corresponding text align correctly to accurately represent the content of Figure 3.

-There is a significant issue in Figure 8, where a comparison is made between magnetic behavior and structural parameters. However, the magnetic behavior is related to the Ni derivative (L=CH3-pbpy) (or, at least, it seems so), while the structural parameters are associated with Pt derivatives (L=CH3-pbpy). This comparison lacks coherence and does not make sense since, as widely known, the SCO properties of the Ni and Pt derivatives can vary significantly.

- In my opinion, the description of the structures appears somewhat vague and too brief. For example, based on the CIFs, some of the compounds crystallize with 2 molecules of water within the structure. This is very important, as the presence of guest molecules could impact the SCO, TE, and redox properties. Therefore, this should be explicitly mentioned and discussed in the text.
- In relation to the presence of guest water and concerning Figure 1, curiously, the two compounds that do not exhibit SCO are those lacking water in their structure. From the authors' perspective, are these two facts related? Please discuss this in the main text.
- Regarding the cyclic voltamperometry: In the caption of Figure 9, it is indicated that the measurements have been carried out versus NHE, whereas in the main text, it is stated that a Ag+ AgCl electrode has been used. Please clarify this discrepancy.
- Continuing with the CV: In the description of the CV curve, the authors claim that a 'reversible redox wave' is observed in Figure 9. However, it is evident that this statement is not accurate, as the cathodic and anodic peaks exhibit significantly different current intensities. It is essential to address what occurs after several cycles of voltage scan, and this issue should be thoroughly discussed in the main text.

Author Rebuttal letter:

RESPONSE TO REVIEWERS' COMMENTS:

We would like to thank the reviewers for the detailed suggestions for improvements regarding the manuscript. We have renewed the naming system of our compounds and corrected all found typos, grammatical errors and other inconsistencies throughout the manuscript. We have added new UV-Vis-NIR measurements to show the reversibility of the absorption changes. The figures for magnetic and optical measurements have been adjusted to better illustrate the differences between the measurements and we have added new data regarding Pt derivatives.

It is important to underline that this new family of compounds exhibits intricate electronic phenomena, including spin crossover and electron transfer(s), associated with electro-, thermo-, photo-, piezo- and solvatochromic properties, all of which are finely modulated by the substituted aryl group. Within this paper we have provided a first description of the crystal structure and thermochromism observed for selected members of this family, as well as the link between them. Humbly, we have to admit that we have not yet grasped the full complexity of these systems, but tried to outline the main features. Indeed, as noted by reviewer #2: âThere is more that could be done with these materials, but the authors have achieved what they set out to do: to define their temperature-dependent electronic structures.â

Please find below detailed responses to all questions.

Reviewer #1 (Remarks to the Author):

The authors described a rational design of a variety of Hofmann-type clathrates including various ligands, which revealed varied functional features with active redox SCO and/or ET molecules. I thoroughly enjoyed reading this article, which provided new ideas, and I believe it can be considered for publication in Nat. Commun. After addressing the following comments:

1. There are many typos throughout the ms as well as ESI which should be addressed. For example, â¦...the redox activity of the ligands within the structure leads to the a fully reversible electrochemical reduction reaction on a spin â¦...

Thank you for this comment, we have corrected all typos we found throughout the manuscript.

2. English should be improved.

The article was re-read multiple times and we have improved spelling and expressions.
3. Please avoid repetition of the sentences in introduction. For example, â¦. an external stimulus (temperature, light irradiation or pressure) â¦â¦...

We made an effort to avoid repetitions.

4. Hofmann clathrates fall into one of two major families: the [M(L)nMâ(CN)4] (n = 1 or 2, L denotes a bis- or monodentate pyridine-like ligand (such as NH3 or H2O), M denotes a transition metal ion, and Mâ denotes Ni, Pd, or Pt.) and [M(L)n{Mâ(CN)2}2], where Mâ stands for either Cu, Ag, or Au). This should be revised in the introduction.

We thank the referee for this comment and have included a more general description of Hofmann-type clathrates in the introduction, see page 2.

5. The direct powder precipitation of the compounds is obtained when K2[M(CN)4]Â·xH2O is added to a EtOH/H2O (1:1).........the authors should define M here.

This was corrected.

6. â¦.. containing the ligand and Fe(BF4)2Â·6H2O. ......what is (BF4)2?

We have added an index of all chemicals used in the SI (see section 1).

7. The single crystal XRD shown in Scheme 2 should be labeled for clarity.

We have added atom-labels to the scheme 2.

8. Can the authors provide some photographs of the gradual color change during the magnetic susceptibility measurements. And for the optical reflectivity measurements, it should be clearer and more obvious.

Unfortunately, we are not able to monitor the color change during magnetic measurements. However, we have added more optical images of the different compounds in order to better illustrate the color change upon cooling and heating and their reversibility.

9. I wonder why did the authors performed electrolysis at negative potential/ -1.2V? It would be a reduction process rather than electrolysis. There is a misunderstanding.

We have changed this in the manuscript.

10. Does the color change upon cooling and heating is reversible or not? This point should be addressed.

Please see answer to question 8.

11. The authors ignored some bands at around 1560 and 1800 nm in Fig4a, why?

This spectral region overlaps with signals from water/humidity, which is why we preferred to focus on the other areas of the spectra. We marked this in the legend of the figure.

12. Does the SCO occur here between the metal centers, while the ET between ligands and/or metal centers and ligand? This should be addressed throughout the ms to differentiate between the two phenomena.

The spin crossover process (in our case) is only involving the FeII atom, where a splitting of the d-orbitals allows for two possible spin states, either high spin (HS) or low spin (LS), with an interconversion between them. It is not an electron transfer coupled spin transition (ETCST), as often observed for Prussian blue analogue systems, neither valence tautomerism as observed for example in cobalt catecholates. In our case, all experimental evidence suggests that the electron transfer occurs between the CN (electron donating) and the bipyridinium (electron accepting) units, seemingly independent of the SCO. See also the answer to question 1 of referee #4.

13. It is strange for me, the authors presented Fig. 8 in the ms before Fig. 5 and, at the same time, cited Fig. S10 in the introduction before the previous Figs.S1-9, why?

The referee is right, we have corrected numeration errors in the manuscript as well as SI.

14. How did the authors collect the temperature dependent UV spectra while monitoring concentrations, especially when they pointed out in the ms that the materials do not dissolve?

We have measured the solid state UV-Vis spectra in diffuse scattering mode using an Integrating Sphere, thus, cannot monitor the concentrations. However, we can monitor relative changes of the band intensities by varying the temperature. This information can be found in the SI.

15. The word " non-innocent behavior" is very broad here, please be more specific and explain it in every position this expression used.

The referee is correct. With non-innocent behavior, we mean that the ligand is redox active. We have thus removed the instance where this expression was used to describe the role of the CN groups, instead of a redox property.

16. The authors have two Figures 8 in the ms, please revise carefully.

We are sorry. We have corrected numeration errors in the manuscript as well as SI.

17. Why did the authors not study the porous nature of their materials by nitrogen gas adsorption - desorption isotherms, I think it will offer interesting new insights?

We thank the author for the good remark; indeed BET, will offer new insights into this kind of compounds. We have already thought about this possibility, however, in our opinion this is out of the scope of this study.

18. At -0.78 V vs. Ag+|AgCl is a reduction process not electrolysis one.

We have changed this in the manuscript.

19. Performing oxidation at 0V is meaningless.

We have modified this sentence in the manuscript; what we intended to say was that the sample was re-oxidized.
20. References have many mistakes and typos which should be addressed.

Thank you for the careful reading. We have corrected all the mistakes we have found in the references.
Reviewer #2 (Remarks to the Author):

This submission reports a new family of Hofmann framework materials supported by terminal viologen ligands. Hofmann frameworks are well known for their thermal spin-crossover properties, which are heavily studied. However, this study has an additional interest through their viologen components, which are redox active. This study addresses the interplay between iron-based spin-crossover and internal charge-transfer to the viologen centers.

The concept is not quite new, but it is the most detailed study yet reported for a framework material with this combination of properties. Moreover their modular material design is very flexible, and leads to predictable and reproducible framework structures. They are the first such multifunctional materials that allow straightforward chemical tuning, to allow optimization of their thermochromism or conductivity (although that is not discussed here).

There is more that could be done with these material, but the authors have achieved what they set out to do: to define their temperature-dependent electronic structures. Thatâs enough for an initial publication on this system, which is warranted and appropriate for the journal.

The following comments count as minor corrections.

(i) It can be hard to follow which material is being measured in each experiment. Iâd consider numbering the compounds, for example as 1a-1d for M = Ni and 2a-2d for M = Pt where R = Me (1a/2a), Br (1b/2b), CO2Me (1c/2c) and NO2 (1d/2d). Or, they could call them 1R and 2R where R = Me, Br, CO2Me, NO2.

Thank you for your suggestion, we have renamed the compounds in order to make the manuscript more comprehensible.

(ii) The Ni and Pt frameworks are treated almost interchangeably in different measurements. That could be valid, but [Ni(CN)4]2- Hofmann networks can undergo spin-crossover at temperatures up to 50 K below their Pd and Pt analogues. At least, we need a full set of magnetic data for all the Pt frameworks to confirm they behave similarly to the Ni materials in Figure 1. As it is, only magnetic data for one Pt framework seems to be presented, in Figures 3 and 8. I would add such a Figure showing all the Ni and Pt framework magnetic data side-by-side, to the SI.

The referee is right. The magnetic measurements for all Pt compounds have been added.

(iii) The origin of the iron(III) in some of the Moessbauer spectra isnât really addressed. Is it an impurity? If so, itâs a large one â ca 15 % in some cases. It could also explain the higher magnetic moment shown by the CO2Me framework in Figure 1. The iron(III) content is temperature-dependent in one sample, but not in others. This matters because iron(II) is another potential electron donor in the internal redox.

We donât believe that the iron (III) is an impurity, as it shows a clear temperature dependence for some samples. Obviously, it also contributes to the magnetic signal. We made the effort to enrich some samples with 57Fe, but unfortunately, we still cannot unambiguously deconvolute the weak iron(III) signal for all samples, which makes a comparison difficult.

(iv) Only analytical data for the Ni-containing frameworks are given in the SI. Elemental analyses and powder patterns should be included for all the new compounds in the study, including the Pt frameworks, to prove they were characterized as pure materials. Ideally that should include CHN microanalyses, not just ICP metal analyses.

The ICP and PXRD data have been added for all Pt compounds and can be found in the SI. In addition, we have conducted a CHN analysis for all Ni and Pt compounds. (For your convenience we attached (with the SI for reviewers) the .cif file of the Pd derivative of the NO2 compound, whose structure we used to refine the powder pattern of the Ni and Pt derivatives.)

(v) The formatting of the crystallographic Tables S9-S12 is untidy. They include different fonts; the information they contain is not consistent; and the page orientation for Table S12 is wrong. Please tidy them up. Also, have the crystal structures been deposited with the Cambridge Database? If not please do so, and provide CCDC deposition numbers.

We have modified the formatting of the crystallographic tables to be consistent. The structures have been deposited with the Cambridge Database, the deposition numbers can be found in the SI (section 1 and 5: 2321396-2321412, 2327738, 2327739 and 2355273).

(vi) As well as refs 56-58, another coordination polymer showing an interplay between spin-crossover and ligand redox is in 10.1002/anie.201611824. They could also acknowledge molecular salts of metallate and radical anions, which can also show interplay between cation spin-crossover and anion redox. These were recently reviewed in 10.1016/j.ccr.2021.213819

Thank you for this comment, we have checked and included these references to offer a more detailed description of the subject.

(vii) The English is generally good and is always understandable. However the spelling of âsynthetizedâ should be corrected to âsynthesizedâ.

We have corrected this typo throughout the manuscript.
Reviewer #3 (Remarks to the Author):

This study into the use of viologen derivative ligands as thermochromic units in nickel complexes is interesting in that it presents a new system with some relatively interesting multifunctional properties (SCO and ET). The compounds prepared are characterized using a combination of X-ray structural analysis, advanced spectroscopic techniques, SQUID magnetometry and DFT calculations. Most conclusions drawn appear reasonable, but there are some gaps that I would like to authors to consider in a revised manuscript.

1. As far as I know, the thermochromism of viologen-based compounds occurs at temperatures higher than room temperature, but the thermochromism of the compounds reported in this paper occurs at room temperature. So what's the driving force for the electron transfer?

Thank you for this remark. The referee is correct, and the thermochromism of viologen based compounds generally spans from 50 Â°C to 180 Â°C. However, this concerns mostly molecular compounds, whereas we have included our derivative into a MOF structure. The structural and EPR data points to the stabilization of the dimeric form by ï°ïï° stacking, therefore likely lowering the temperature observed for the thermochromism. We have added this to the manuscript.

2. Raman and IR spectra are highly interfered by SCO. Since {Fe(R-pbpy)2[Âµ2-Ni(CN)4]2Â·2H2O} (R = COOCH3 and NO2) compounds do not show SCO, it is suggested to provide XPS spectra of them to fully demonstrate the existence and path of electron transfer.

Following the suggestion of the referee, we have conducted XPS analysis at room temperature for one of the compounds. However, in our experimental conditions it is very difficult to deconvolute the signal for FeII and FeIII in the spectra (see spectrum below), therefore we have not continued this study.

[Image redacted]

3. The characteristic absorption peak of viologen radical (at about 600 nm) appeared in the absorption spectrum of the compound at room temperature. During the cooling process, the intensity of this peak was enhanced, which meant that electron transfer occurred at cooling, and the concentration of free radicals increased with the decrease of temperature. Do the EPR spectra of these compounds show signal characteristics for a radical at low temperatures?

As mentioned on page 11, we were not able to detect a signal for a free radical in EPR at any temperature and any sample. This is explained by the ï°ïï° stacking found in the structure, indicating that dimerization can occur, where the radical electrons are combined in molecular orbitals. We do not have a better explanation for the absence of an EPR signal, but similar problems have been met in other solid state viologen derivatives displaying no or very faint EPR signals (see references 12 and 15 in the manuscript).

4. Since the coloration is reversible, I think the author should provide reversible photographs of the coloration as well as the absorption spectra of the compounds.

As suggested by the referee, we have added images as well as UV-Vis-NIR absorption spectra taken before and after cycling to demonstrate that the process is fully reversible (see SI Fig S22).

5. Elemental analysis data for CNH should be provided. At the same time, the error of elemental analysis data for Fe(NO2-pbpy)2[Âµ2-Ni(CN)4]2Â·2H2O is too large, so it is suggested that the author further purify the compound.

We have added the CNH analysis data to the SI, and resynthesized the {Fe(NO2-pbpy+)2[Âµ2-Ni(CN)4]2Â·2H2O} in order to ensure its purity, however, error is still large (14.5% Ni instead of 12.1% as expected). One should note that this compound has a lower degree of crystallinity in comparison with the others (see figure S15) and thus certainly a larger amount of defects, which can explain the deviation from the ideal stoichiometry. Nevertheless, we would like to mention that we succeeded to obtain a single crystal structure of the Pd derivative of this compound: i) The structural unit of this Pd derivative is the same as the rest of the family and ii) the unit cell of the Ni and Pt derivatives could be determined by Rietveld refinement of the respective powder X-ray diffractograms using the Pd single crystal. For your convenience we attached (with the SI for reviewers) the .cif file of the Pd derivative of the NO2 compound, whose structure we used to refine the powder pattern of the Ni and Pt derivatives.

6. checkCIF reports should be provided.

All checkCIF reports were added to the SI.

7. There are many grammatical errors in the text, please correct.

We apologize for the typos and grammatical errors in the text, and we have revised the manuscript to correct them.
Reviewer #4 (Remarks to the Author):

This manuscript reports four isostructural 2D Hofmann-type coordination polymers (CPs) incorporating redox-active viologen ligands (R-pbpy+, R = CH3, Br, COOCH3, or NO2), where tetracyanoplatinate ions act as uncommon Î¼-bidentate bridges. The compounds with CH3 and Br represent the initial redox-active spin-crossover (SCO) CPs, exhibiting temperature-dependent color changes, manifesting thermochromism in all cases. Notably, the CH3 and Br compounds undergo color changes due to spin-state transitions, whereas the COOCH3 and NO2 compounds exhibit no SCO activity. Consequently, the observed thermochromic behavior in all compounds must involve additional factors beyond SCO, specifically the transformation between R-pbpy+ and R-pbpy radical, as confirmed in this study. To elucidate the electron transfer (ET) mechanism, various characterizations, including crystallographic, spectroscopic, and theoretical analyses, were conducted. The authors infer that the generation of R-pbpy radicals likely arises from ET, predominantly originating from the uncoordinated CN- moieties towards the redox-active R-pbpy+ entities. This research introduces a novel avenue for incorporating new functionalities within the Hofmann-type framework, with the reversible redox behavior showcasing the potential of electrochemistry in developing reversible multifunctional materials. The intriguing findings presented in this study suggest that, following substantial revisions, the manuscript may be suitable for publication in a prestigious journal such as Nature Communications.

1. The conclusion that "......the uncoordinated CN- moieties indicate the latter as the most likely origin of ET" is a major concern. However, the main text presents various pieces of evidence that suggest different outcomes. For instance, on page 7, the absorption band at 535 nm is linked to the generation of the CH3-pbpy radical. Furthermore, upon comparison with isostructural Zn derivatives, the results point towards the involvement of the FeII ion in the creation of this band. This analysis raises a critical question regarding the role of FeII. It remains ambiguous whether the author suggests that FeII contributes significantly to electron transfer (ET) in the formation of radicals or if it serves another function in the metal-to-ligand charge transfer (MLCT) transition. Conversely, given that no radicals are observed in the Zn derivatives, does this absence imply that ET occurs between FeII and R-pbpy instead? Clarifying these aspects is crucial for a more comprehensive understanding of the system under investigation.

In addition to the SCO, at least one electronic phenomenon can be observed. For example, the nitro derivative shows clear thermochromic behavior (with hysteresis) without an SCO event. As discussed in relation with the MÃ¶ssbauer (see answer 3 to reviewer #2) and UV visible spectra, an involvement of the iron centers in some of the observed electronic phenomena is likely. Nevertheless, what is omnipresent is the modification of the IR frequencies of the CN groups.
We are currently conducting experiments to show a clear correlation between the redox potential (electron donating-withdrawing ability) of the ligands versus the distance between the uncoordinated CN and the nearest aromatic ring (see figure below). Ligands with electron withdrawing groups show reduced distances in order to stabilize the electron deficient pyridinium units, thus increasing the possibility to have an ET from the donating CN groups.
It is also important to remark that contrary to the SCO, the ET events are certainly largely incomplete. This can be seen for example in the MÃ¶ssbauer spectra of the nitro derivative through the progressive apparition of several HS FeII doublets upon cooling.
We have made modifications to the conclusion to better clarify these points.
[Image redacted]

The redox potential E1/2 of the ligand and clathrates as a function of the distance ÎNCNâring.

2. On page 9, theoretical calculations propose that the experimental band seen at 580 nm originates from Fe-CH3-pbpy+ MLCT, implying it is SCO-dependent. Despite this, on page 8, the absorption intensity at 580 nm does not align with the SCO. Why?

Thank you for this input. Indeed, we have re-measured the UV-Vis-NIR curves to be sure that there is no error. The band at 580 nm has contributions from both the ET and the SCO phenomena, which explains why it doesnât follow the magnetic curve. On the other hand, the band at 780 nm aligns with the SCO, because it has no contribution from the ET.

3. MÃ¶ssbauer spectroscopy confirms the presence of temperature-dependent Fe(III) populations in CH3- and Br- compounds, indicating that a small proportion of iron ions are involved in electron transfer (ET) towards the ligand. This suggests that both iron ions and uncoordinated CN- groups (Raman evidence) contribute to the ET process. Additionally, the confirmation of temperature-dependent Fe(III) populations in non-SCO NO2- and COOCH3-compounds through MÃ¶ssbauer spectroscopy would provide further substantiation of the origin of ET.

Following the suggestion of the referee we have recorded further Mossbauer spectra for the NO2 derivative (enriched in 57Fe). The presence of iron(III) is not obvious, but some interesting information can be extracted, such as the successive emergence of novel Fe(II) HS species while decreasing the temperature, which must be related to the ET processes. On the other hand, the quality of the spectra for the ester derivative is poor, therefore we cannot extract any meaningful information.

4. Minor concerns include inconsistent spelling of the word âHofmannâ as âHoffmanâ on pages 15-16, whereas it is correct for most of the main text.

We have corrected the spelling of the word âHofmannâ throughout the manuscript, as well as removed any other typos and grammatical errors that we found.

In page 4, single-crystal structures of compounds with R = CH3, Br, COOCH3 have been determined. The structure for R = NO2 is yet to be determined.

Please see answer 5 to reviewer 3.
Reviewer #5 (Remarks to the Author):

The manuscript submitted by Cobo et al. describes a novel family of Hofmann-type bimetallic networks that combine spin crossover properties, electron transfer, and redox activity. This unique set of properties has been achieved by incorporating a pyridinium-based organic ligand into the metal-organic framework. This ligand is easily reducible and imparts both electron transfer (ET) and redox properties, along with spin crossover (SCO) based on the presence of octahedral [FeIIN6] sites.
The characterization of these multifunctional compounds has been achieved through a comprehensive physical study, incorporating SQUID measurements, MÃ¶ssbauer spectroscopy, cyclic voltamperometry, X-ray diffraction, and optical reflectivity, among other techniques. The multifunctional approach proposed in this paper represents a highly promising advancement in the discovery of new stimuli-responsive materials for potential applications and therefore it merits consideration for publication in Nature Communications.
However, there are concerns regarding the presentation of the results throughout the manuscript, particularly those related to the synthesis and treatment of the samples. In my opinion, these

concerns should be addressed by the authors before the manuscript can be considered for acceptance .

- The authors need to provide clarity, from the beginning of the paper, regarding which compounds have been studied. It appears that all structures have been examined using Pt derivatives (Fe(R-pbpy)2[Î·2-Pt(CN)4]2); however, the remaining physical characterizations have been conducted on the Ni derivatives (Fe(R-pbpy)2[Î·2-Ni(CN)4]2). The rationale for this discrepancy is not explained in the main text. The absence of magnetic or reflectivity studies on the Pt derivatives also requires clarification. In my opinion, it would be beneficial to dedicate an equivalent figure as Figure 1 to the Pt derivatives, to enhance the overall clarity and completeness of the manuscript.

We thank the reviewer for this remark. Please see answer 2 to the reviewer 2.

- In the caption of Figure 3, it mentions "Temperature dependent UV-vis-NIR absorption spectra of Fe(CH3-pbpy)2[Î·2-Pt(CN)4]2)," while in the text when referring to Figure 3, it states, "Fig 3(b) shows the variation of the band intensities with respect to the magnetic properties of (Fe(CH3-pbpy)2[Î·2-Ni(CN)4]2Â·H2O)." This inconsistency raises confusion and needs to be addressed for clarity. It's essential to ensure that the caption and the corresponding text align correctly to accurately represent the content of Figure 3.

We have corrected this mistake in the manuscript, indeed, all measurements for the Me compounds have been done for the Pt derivative.

-There is a significant issue in Figure 8, where a comparison is made between magnetic behavior and structural parameters. However, the magnetic behavior is related to the Ni derivative (L=CH3-pbpy) (or, at least, it seems so), while the structural parameters are associated with Pt derivatives (L=CH3-pbpy). This comparison lacks coherence and does not make sense since, as widely known, the SCO properties of the Ni and Pt derivatives can vary significantly.

The referee is right, now the figure 8 refers exclusively to the platinum derivative.

- In my opinion, the description of the structures appears somewhat vague and too brief. For example, based on the CIFs, some of the compounds crystallize with 2 molecules of water within the structure. This is very important, as the presence of guest molecules could impact the SCO, TE, and redox properties. Therefore, this should be explicitly mentioned and discussed in the text.
- In relation to the presence of guest water and concerning Figure 1, curiously, the two compounds that do not exhibit SCO are those lacking water in their structure. From the authors' perspective, are these two facts related? Please discuss this in the main text.

Following the suggestion of the referee we extended the discussion of the crystal structures. Hydrogen bonds between the water molecules and the uncoordinated CN units of the structure are certainly important. We are currently exploring other guest molecules and notably we observed strong differences in the SCO properties comparing the dehydrated to the hydrated compounds. As for the lack of SCO properties, we believe that the main reason is electron-withdrawing nature of the COOCH3 and NO2 groups (see figure in the answer 1 to the referee 4), even if the solvent molecules can have an impact as well. We have put an increased effort to locate water molecules in the structures not exhibiting SCO and were indeed able to place them, at least in partial occupation. We believe that within these structures the water molecules show a high disorder, which is why they are difficult to observe in XRD, however, they are not absent as we first thought. As the SCO properties are strongly influenced by the hydrogen bonds formed by guests, it is possible that this disorder impacts the materials SCO behavior.

- Regarding the cyclic voltamperometry: In the caption of Figure 9, it is indicated that the measurements have been carried out versus NHE, whereas in the main text, it is stated that a Ag+ AgCl electrode has been used. Please clarify this discrepancy.

Thank you for this remark, this error has been corrected in the manuscript. The measurements were indeed carried out vs. an Ag+|AgCl reference electrode.

- Continuing with the CV: In the description of the CV curve, the authors claim that a 'reversible redox wave' is observed in Figure 9. However, it is evident that this statement is not accurate, as the cathodic and anodic peaks exhibit significantly different current intensities. It is essential to address what occurs after several cycles of voltage scan, and this issue should be thoroughly discussed in the main text.

It should be noted that carrying out electrochemical measurements with solid state compounds is difficult, and we have, therefore, tested many different options. On reason for the higher current intensity upon reoxidation could stem from the measurement set-up, more exactly the PVA-Borax gel that is used in order to fix the powder to the electrode. If we measure the CV in a smaller interval (switching to oxidation right after the reduction wave), the re-oxidation peak is much smaller. Nevertheless, the referee is correct and we have therefore labeled the redox behavior as quasi-reversible in the manuscript.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I have no more comments on the revised manuscript.

Reviewer #2

(Remarks to the Author)
The authors response to the reviews is considered, and useful. They have done extra measurements which address some gaps in the data, and help to clarify some ambiguities. They have also followed recommendations that make the manuscript easier to read.

It is as clear as can be that there is an internal redox equilibrium in these materials, which may influence spin-crossover in 1a/1b and 2a/2b but does not depend on it. There is evidence that dangling CN ligands and/or the Fe centers may act as electron donors for this process, in different materials.

The authors are still investigating this system, which may help clarify these remaining questions. For now, I don't think anything more is required for an initial communication describing these novel materials. This can be published without further revision.

Reviewer #3

(Remarks to the Author)
The authors have revised the MS according to the comments, and the current version meets the standard for publication in nature communication.

Reviewer #4

(Remarks to the Author)
The article has effectively addressed the issues I raised. The author has supplemented numerous experiments and made substantial revisions to enhance the quality of the article. To my knowledge, the article is now ready for publication with only minor revisions needed.
1. In line 51, when x = 2 or 4, the charge of the cyanometallate anion should be either 1- or 2-.
2. In line 79 and line 87, there is inconsistency and inaccuracy in the abbreviated and full terms of pbpy⁺. As indicated in the final part of line 87, it is more appropriate to write it as R-pbpy⁺, i.e., in both line 79 and line 87 as R-pbpy⁺ = 1-(4-R-phenyl)-4,4′-bipyridinium.
3. In line 95, the molecular formula is missing a right brace, and the subscript in the space group notation should be 1 instead of 2.

Reviewer #5

(Remarks to the Author)
The authors have rigorously and concisely implemented all the reviewers' suggestions while convincingly addressing all their questions. The document has significantly improved in both substance and form, substantially enhancing its quality. In my opinion, the article deserves to be published in Nature Communications in its current state.

Author Rebuttal letter:

RESPONSE TO REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

I have no more comments on the revised manuscript.

Reviewer #2 (Remarks to the Author):

The authors response to the reviews is considered, and useful. They have done extra measurements which address some gaps in the data, and help to clarify some ambiguities. They have also followed recommendations that make the manuscript easier to read.
It is as clear as can be that there is an internal redox equilibrium in these materials, which may influence spin-crossover in 1a/1b and 2a/2b but does not depend on it. There is evidence that dangling CN ligands and/or the Fe centers may act as electron donors for this process, in different materials.
The authors are still investigating this system, which may help clarify these remaining questions. For now, I don't think anything more is required for an initial communication describing these novel materials. This can be published without further revision.

Reviewer #3 (Remarks to the Author):

The authors have revised the MS according to the comments, and the current version meets the standard for publication in nature communication.

Reviewer #4 (Remarks to the Author):

The article has effectively addressed the issues I raised. The author has supplemented numerous experiments and made substantial revisions to enhance the quality of the article. To my knowledge, the article is now ready for publication with only minor revisions needed.
1. In line 51, when x = 2 or 4, the charge of the cyanometallate anion should be either 1- or 2-.
2. In line 79 and line 87, there is inconsistency and inaccuracy in the abbreviated and full terms of pbpy+. As indicated in the final part of line 87, it is more appropriate to write it as R-pbpy+, i.e., in both line 79 and line 87 as R-pbpy+ = 1-(4-R-phenyl)-4,4â²-bipyridinium.
3. In line 95, the molecular formula is missing a right brace, and the subscript in the space group notation should be 1 instead of 2.
Thank you for these remarks, we have modified the manuscript accordingly.

Reviewer #5 (Remarks to the Author):

The authors have rigorously and concisely implemented all the reviewers' suggestions while convincingly addressing all their questions. The document has significantly improved in both substance and form, substantially enhancing its quality. In my opinion, the article deserves to be published in Nature Communications in its current state.