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ARTICLE

Chemical Reaction within a Compact Non-Porous Crystal Containing Molecular Clusters without Lost of Crystallinity

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The very rare occurrence of a gas-solid chemical reaction is found to take place on a molecule within a compact non-porous crystal without destroying its long-range structural order and retaining similar crystal structures when the yellow crystals of $\text{Fe}^{\text{II}}(\text{mbm})_4\text{Cl}_4(\text{MeOH})_4$ were exposed to air to give black $[\text{Fe}^{\text{III}}(\text{mbm})_4\text{Cl}_4(\text{OH})_4] \cdot 2\text{H}_2\text{O}$. The latter cannot be synthesised directly. The original cluster has undergone exchange of methanol to hydroxide, oxidation of Fe(II) to Fe(III), change of stereochemistry and hydration while the packing and space-group remained unaltered.

Introduction

One of the requirements for a chemical reaction to take place is that the reactants should be within close proximity for electronic interactions to promote bond breaking and bond formation.¹ Thus, the high probability of reactants to get close is in the liquid or gas state. Reactions in the solid-state require repetitive grinding and mixing before heat treatment, while the crystalline state can then be obtained at high temperatures.² With the exception of oligomerization by irradiation or heat treatment there are rarely reactions that take place in the solid with retention of the crystallinity.³ Gas solid reactions take place at the surface and invariably destruct the crystalline state of the solid if the structure is non-porous. However, when it is porous the gaseous reactants can

penetrate the structure and modify it without destruction.⁴ Therefore, gas-solid reaction remains exotic and the advances made in the past twenty years in the field of porous metal-organic frameworks (MOF) are slowly changing our perceptions and have introduced several new conceptual synthetic approaches leading to good quality crystals.⁵⁻¹⁰ One prominent advance is post-synthetic modification (PSM) of a crystalline solid without destroying its crystalline state that has given rise to a new field of single-crystal-to-single-crystal (SC-SC) transformation.¹¹⁻¹⁸ Some notable events are *in-situ* (a) desolvation, (b) solvent exchange, (c) coordination at naked metal sites, and (d) reaction of the organic moiety. The most remarkable event is the replacement of the metal centres of a MOF without dissolving the crystals that has major importance for the development of smart and intelligent materials as it evidences the process of auto-repairing.¹⁶⁻¹⁸ All these advances are possible due to the strong connectivity through a combination of covalent and dative bonds within the frameworks and most importantly, their porous character that provides the space for the reactants to get to the reaction sites. But when the crystals are non-porous the compactness of the building units limits the reaction to the surface and consequently, the crystallinity is destroyed by any form of modification of the crystals through chemical reaction.¹⁹⁻²¹ This is even more likely if the crystals contain molecular units held by weak supramolecular interactions.²² Two interesting examples have been reported where discrete clusters transform to one-dimensional chain²³ and layer²⁴ and maintain the crystallinity. Notably, Atwood *et al* reported some non-porous organic solids absorbing various gases without chemical reaction in an SC-SC manner.²⁵⁻²⁹ Two features have been involved during SC-SC transformation from non-porous crystals containing discrete molecules. One is guest transport through the crystal lattice, such as coordinated ligand exchange^{20, 30-31} and addition of H_2 to coordinated ligand.³²⁻³³ The other is charge reorganisation between metal ion and ligand, such

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as metal complexes involving tautomerism³⁴⁻³⁸ and hydrogen-atom transfer.³⁹ Note that a dimolybdenum molecular pair having a $[\text{Mo}_2](\mu\text{-OH})_2[\text{Mo}_2]$ core undergoes a deprotonation process⁴⁰ and a dicobalt core is known to serve as active sites for oxygen chemisorption/desorption in a reversible SC-SC transformation.⁴¹ Therefore, it is considered that chemical reaction to a molecule within a compact crystalline solid involving not only guest transport but also change of the metal ion charge without destroying the crystal or perturbing the crystalline long-range order is really very rare. Here, we present a unique gas-solid reaction, which can be considered as a different form of rusting not of iron metal but of a tetranuclear Fe(II) molecular complex without destroying its crystalline state and the gaseous reactants are H_2O and O_2 from the atmosphere.

Results and Discussions

The yellow crystals of $\text{Fe}^{\text{II}}_4(\text{mbm})_4\text{Cl}_4(\text{MeOH})_4$ (**1**), obtained from solvothermal reaction of either $\text{Fe}^{\text{II}}\text{Cl}_2\cdot 4\text{H}_2\text{O}$ or $\text{Fe}^{\text{III}}\text{Cl}_3\cdot 6\text{H}_2\text{O}$ and (1-

methyl-1H-benzo[d]imidazol-2-yl)methanol (*Hmbm*) in methanol, neutralized by triethylamine, slowly convert to the black crystals of $[\text{Fe}^{\text{III}}_4(\text{mbm})_4\text{Cl}_4(\text{OH})_4]\cdot 2\text{H}_2\text{O}$ (**1-2d**) in air while retaining the crystal morphology (size and shape), and space-group $P-42_1c$, with discrete $\{\text{Fe}_4\text{O}_4\}$ units. **1-2d** undergoes an annealing process in the first 8 days to form **1-8d**, which then loses its crystallinity slowly to **1-180d** due to hydration (Figures 1, S1). The results obtained are quite unique and reveal a balance of stability as a function of time. Following the determination of the structures from several crystals under non-controllable conditions we selected three similar size virgin yellow crystals of **1** from one batch for a systematic study at ambient condition (27 °C and 56% RH). The first crystal was used for diffraction data collection within four hours which reproduced the structure found for several other crystals studied independently and giving consistent geometrical parameters. The second and third crystals were exposed to air under ambient condition for 2 days (**1-2d**) and 8 days (**1-8d**), respectively, before collecting data (Table S1).

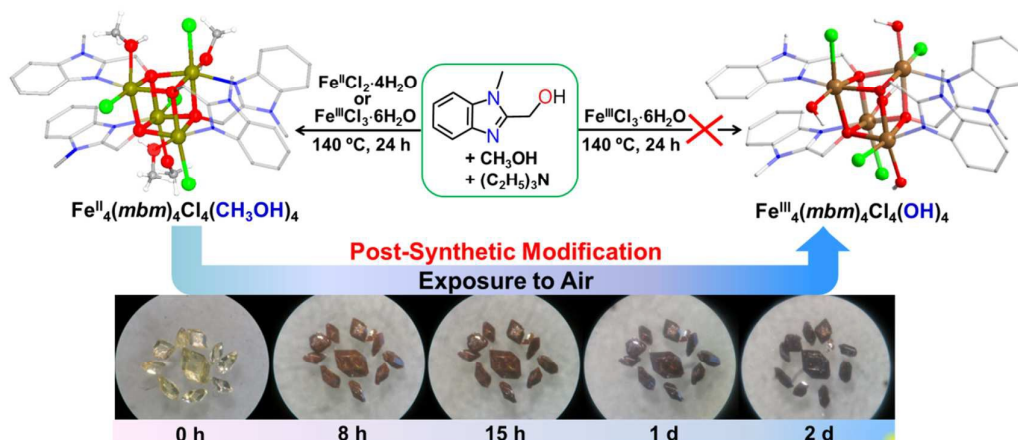


Fig. 1 Reaction leading to $\text{Fe}^{\text{II}}_4(\text{mbm})_4\text{Cl}_4(\text{MeOH})_4$ and its transformation to $[\text{Fe}^{\text{III}}_4(\text{mbm})_4\text{Cl}_4(\text{OH})_4]\cdot 2\text{H}_2\text{O}$. Top: Syntheses adopted. Bottom: Time-dependent microscope photographs of the crystals post-synthetically transformed during exposure to air (27 °C, 56% RH).

The presence of $\{\text{Fe}_4\text{O}_4\}$ cubic core is the key feature of the three structures in which Fe and O atoms occupy alternate corners of a slightly distorted cube (Fig. 2, Table S2).⁴²⁻⁴⁵ They all adopt the non-centrosymmetric space group $P-42_1c$. The asymmetric unit of **1** contains one Fe, one *mbm*, one Cl and one MeOH. The Fe exhibits six-coordination with one terminal Cl in *cis*-position to one O atom from terminal MeOH within the same plane of the cube, and two O atoms from two *mbm*, one N atom and one O atom from a chelating *mbm* in an orthogonal plane (Fig. 2a, b). In contrast the asymmetric unit of **1-2d** contains the same atoms except that a OH has replaced the MeOH (Fig. 2c, d). The Fe centre of **1-2d** has the same coordination sphere but the Cl is now in the place of methanol and the hydroxide is the position of the Cl. The replacement of the neutral methanol by the charged hydroxide increases the oxidation state of Fe from two to three. The Fe(II)–O distances of **1** lie in the narrow range 2.107–2.181 Å. The Fe(III)–O distances of **1-2d** were found to lie in a wide range 2.019–2.230 Å. The Fe–O–Fe bridging angles for **1** fall in a narrow range 96.32–99.66° but again a wide range of 97.64–103.32° for **1-2d**. The

distances and angles are comparable to those reported for other $\{\text{Fe}_4\text{O}_4\}^{\text{II+}}$ in the literature.⁴²⁻⁴⁵ **1-2d** and **1-8d** have the same Fe coordination sphere but with slightly different structural parameters, Fe–O distances of 2.054–2.251 Å and Fe–O–Fe bridging angles of 97.94–103.90°. The Fe–OH distances are 2.019 Å (**1-2d**) and 2.055 Å (**1-8d**). Given the ease of deprotonation of terminal hydroxide leading to the formation of iron oxides,^{46,47} the stability of **1-2d** and **1-8d** is quite remarkable.⁴⁸

To our best knowledge, it also has the highest number (4) of terminal hydroxide in a discrete coordination complex. Surprisingly, there is no discrete cluster containing the fully oxidised $\text{Fe}^{\text{III}}_4\text{O}_4$ cubane reported, but it exists for a series of octanuclear $\{\text{Fe}_8\}$ complexes with central $\text{Fe}^{\text{III}}_4\text{O}_4$.^{49,50} The 24 known discrete $\{\text{Fe}_4\text{O}_4\}$ cubanes are either divalent Fe(II) or mixed-valent Fe(II)/(III) (Table S3). Therefore, we attempted to synthesize **1-2d** directly by using $\text{Fe}^{\text{III}}\text{Cl}_3\cdot 6\text{H}_2\text{O}$ as the starting material, but all attempts have so far resulted in only the yellow crystals of **1**. This can be due to poor stability under ambient condition or ferric ion tends to connect by



oxo ligand to form $\{Fe^{III}_4O_6\}$ layer in solution.⁴³ Consequently, **1-2d** and **1-8d** represent the first discrete ferric cubes with terminal hydroxide ligand. The stability of the terminal hydroxide ligand is possibly stabilized by a combination of steric hindrance provided by the bulky ligand and the H-bond between clusters (Figures S2-S3). It is an interesting feature to note that the coordinated Cl atom changes its position during the transformation from **1** to **1-2d** and **1-8d**, while other O and N atoms from *mbm* ligand remain in their original positions.⁵¹ This suggests the *mbm* ligand is strongly bonded compared to the methanol. It also implies an intermediate five-coordinated Fe is formed by the initial departure of the methanol. It is logical to assume that the transformation proceeds gradually from nucleation sites at the surface to the entire crystal without losing its crystallinity. However, all endeavours to remove MeOH from the crystals of **1** under vacuum while retaining its crystallinity has been unsuccessful.

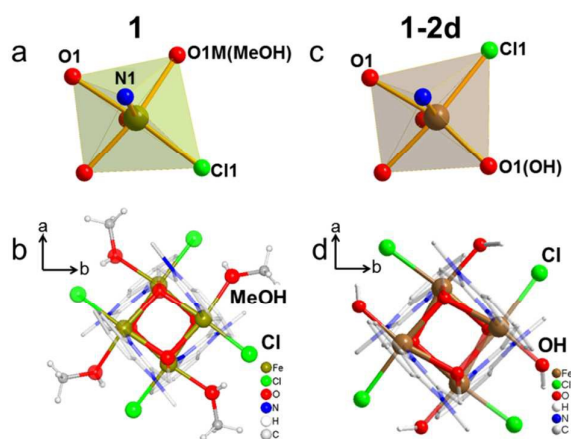


Fig. 2 Details of the crystal structures of **1** (left, a and b) and **1-2d** (right, c and d). Top: coordination modes of Fe; Bottom: discrete clusters viewed along the *c*-axis showing the different orientations of the Cl atoms.

The slow post-synthetic SC-SC modification provides an opportunity to track this progressive gas-solid reaction closely. Given the change of colour our first conclusion is the compound is being oxidized, which was subsequently, confirmed by crystallography. We then performed an experiment to show water is also required. When **1** is kept in anhydrous methanol no change of colour was observed after 2 days but when exposed to air it darkens (Fig. S4). It suggests the departed methanol is first replaced by water followed by oxidation leading to Fe^{III} and hydroxide.⁵² Powder X-ray diffraction (PXRD) data suggest the reaction can be stopped by keeping the samples under nitrogen. Time-dependent PXRD with exposure times in air up to 240 days (Fig. S5) reveal the samples diffract well for the first 8 days, but very poorly by 20 days. The result suggests the crystallinity and long-range order of the cluster in the structure of **1** are maintained up to at least 8 days. Although the diffracting power progressively weakens leading to an almost amorphous solid as a function of time; the presence of the peak at $2\theta = 9.0^\circ$ for **1-180d** indicates the existence of short-range order in the structure up to 180 days.

In addition, time dependent crystallography was studied on one single crystal. A yellow crystal of **1** was used to collect oscillation frames for one orientation as a function of exposure time in air up to 50 h (Figures 3, S6), while on the diffractometer in the enclosure of the Bruker machine under controlled atmosphere (27 °C; 56% humidity). A zoom on a selected area of the frames shows a pair of Bragg reflections, one weak and the other strong, and the intensity ratio changes slowly to 24 h but by 48 h only one is present (Fig. 3b). This suggests the progressive transformation of the phases and the existence of two diffracting lattices from one crystal at the intermediate times without loss of the crystalline state.^{53,54} We should also note that the presence of the weak peak in the first frame indicates the crystal has already been partially oxidised during the mounting of the crystal. There are different effects involving SC-SC transformations that have been reported. These are loss of solvents, exchange of solvents, reaction of the organic ligands, and exchange of the metal. In this context, the SC-SC transformation of **1** to **1-2d** possesses the most chemical changes (Table S4). Crystallography found both **1** and **1-2d** adopt the same space-group and possess $\{Fe_4O_4\}$ cores with four chemical changes.

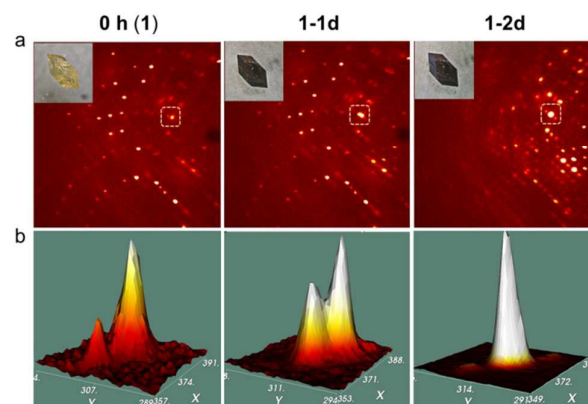


Fig. 3 Single crystal X-ray diffraction as a function of exposure time. (a) Diffraction frames and (b) 3D shapes of selected Bragg reflections for **1** after exposure to air for 0 h (left), 24 h (middle) and 48 h (right).

An interesting question that follows the above observations is “How water and oxygen molecules go through a non-porous crystalline structure?” Indeed, a very rarely observed process. For the case of solvation of crystals containing calixarene, Atwood *et al.* suggested the guest can be transported through the non-porous solid *via* dynamic van der Waals cooperativity and expansion of the entire solid.^{27,29} This is not the case here. Therefore, we propose the following plausible process for our case. Because the intercluster interaction between clusters in the structure of **1** is weak the MeOH at the surface of the crystal can easily be dissociated leaving a vacant site at the metal centre for reaction with O_2 and H_2O . Since the new oxidised molecular unit is smaller than the original one the surface is hydrated and the water can move further to neighbouring molecules provoking further reaction, which then propagates through the whole crystal. The expected exothermic energy from the oxidation reaction drives the removal of further MeOH. In contrast, the strong intercluster interaction in the structure of **1-2d**,



help to maintain the long-range order of the single-crystal lattice. It is also different from the case of rusting of iron, for example, the iron crystals are chewed away by the presence of H₂O and O₂ (often catalysed by acidic gases) to form iron-oxide crystals at the surface.

The oxidation of Fe(II) to Fe(III) introduces a change of spin and orbital states of the magnetic ions. Therefore, we have followed the changes to the magnetic properties using a SQUID magnetometer, HF-EPR and Mössbauer spectroscopy (further details are given in the ESI). The high temperature susceptibility data reveal a change from dominant ferromagnetic ($\theta = +2.8(2)$ K for **1**, from Curie–Weiss law fitting) to strong antiferromagnetic exchange ($\theta = -53.0(2)$ K for **1-2d**) with time (Fig. 4a and Table S5). The fitting of the magnetic data (Fig. S7) correlates well with those observed for related compounds and calculated using DFT (Table S6).^{42-45,49,50} From the HF-EPR spectra at low temperature and different frequencies g -values of 1.49, 2.92, 3.61 and 5.50 and three energy gaps of 27, 46, and 190 GHz were extracted (Fig. S8), which confirm the ZFS of the Fe(II) in **1**. These gaps are in good agreement with the values of $D = 14.3(1)$ cm⁻¹ and $E = 2.1(1)$ cm⁻¹ obtained from the modelling the high temperature data.⁵⁵⁻⁵⁹ **1-2d**, **1-8d** and **1-180d** have only two resonances corresponding to g -values of 2.19 and 2.11 for **1-2d**, 2.08 and 2.04 for **1-8d**, 2.09 and 1.99 for **1-180d** but with small energy gaps of ~20 GHz consistent with singlet Fe(III) ions.⁴¹ Due to the increasing AF exchange energy with time, the isothermal magnetization is harder to saturate with field (Fig. 4b). Moreover, Mössbauer spectroscopy also confirmed that all Fe(II) ions in the molecular cluster completely oxidised to Fe(III) and gives more accurate proportion of the different valences (Figures 4c, S9-10; Tables S8-S10). Temperature dependence of the ac-susceptibility for **1** and **1-2d** indicates there is no single-molecule magnetic behaviour above 1.8 K (Fig. S11).

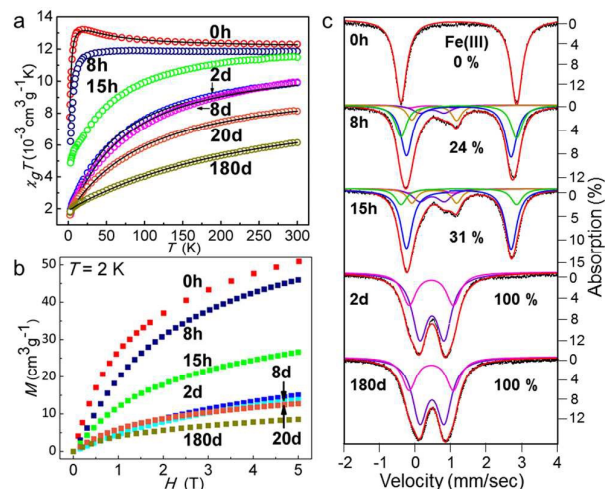


Fig. 4 (a) Temperature dependence of $\chi_g T$ in 1 kOe for samples exposed to air for different periods of time. Solid lines represent the theoretical fits using the parameters given in the ESI; (b) their isothermal magnetisation at 2 K. (c) Zero-field ⁵⁷Fe Mössbauer spectroscopy at 80 K for the fresh sample (**1**), and those exposed to air for **1-8h**, **1-15h**, **1-2d**, and **1-180d**. The simulations shown in red correspond to the sum of all components.

Conclusions

In summary, the progressive post-synthetic transformation of the yellow ferrous cubane cluster, Fe^{II}₄(mbm)₄Cl₄(MeOH)₄, to its dark ferric congener, [Fe^{III}₄(mbm)₄(OH)₄Cl₄]·2H₂O, as a function of exposure to air has been observed and explored using crystallography, magnetometry, HF-EPR, and Mössbauer spectroscopy. This unique single-crystal-to-single-crystal transformation prevails up to 8 h as the Fe^{II} is oxidised to Fe^{III}, but the crystallinity degrades slowly afterwards due to disorder induced by water intake. Although SC-SC transformations involving non-porous molecular materials have been reported, to our best knowledge, none undergoes such abundant guest transport through the crystal lattice, dioxygen entering and methanol departing. Notably, four chemical changes were noted: (a) replacement of methanol by hydroxide (Fig. S12), (b) a coordination site swapping of the chlorine atom within the Fe octahedron (c) the oxidation of Fe and (d) hydration. The consequence of these changes is reflected in the SQUID magnetometry where a progressive change from ferromagnetic coupling with considerable single-ion anisotropy for the virgin yellow crystals to strongly antiferromagnetic coupling and weak anisotropy for the oxidised dark crystals. Mössbauer confirms the complete oxidation of Fe^{II} to Fe^{III} and gave more accurate proportions of the two valences at different times. This astonishing retention of the crystalline state through the three chemical changes on a molecule can be regarded as a gas-solid-state reaction.

Experimental

All the reagents were obtained from commercial sources and used without further purification. Elemental analyses for C, H, and N were performed on a Vario Micro Cube. Infrared spectra were recorded by transmission through KBr pellets containing ca. 0.5% of the compounds using a PE Spectrum FT-IR spectrometer (400-4000 cm⁻¹). The X-ray powder diffraction patterns were measured at 293 K on a Bruker APEX-II CCD diffractometer (Mo K α , $\lambda = 0.71073$ Å). Magnetization data for polycrystalline samples were measured in the temperature range of 2–300 K and field of ± 50 kOe using a Quantum Design MPMS XL-7 SQUID magnetometer. High frequency electron paramagnetic resonance (HF-EPR) spectra were measured on locally developed instruments at the Wuhan National High Magnetic Field Center, China and Institute of Materials Research, Sendai, Japan. The Nuclear Gamma Resonance (Mössbauer) spectra were recorded in zero-field at 80 K on a constant acceleration spectrometer. The source consisted of a ~8 mCi ⁵⁷Co dispersed in a rhodium foil. This instrument was fitted with a Janis cryostat that was cooled using liquid nitrogen. The powder samples were contained in custom-made plastic containers. Spectral simulations were performed using the WMOSS software (WEB research, Edina, MN). Isomer shifts are quoted relative to the centroid of the iron metal spectrum recorded at room-temperature.

Synthesis



A mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol, 198 mg), *Hmbm* (3.0 mmol, 486 mg), triethylamine (0.1 mL) and methanol (8 mL) was sealed in a 15 mL Teflon-lined steel autoclave and heated at 140 °C for one day. After the autoclave has been cooled to room temperature at a rate of 10 °C min^{-1} , light yellow rhombic crystals of **1** were obtained. Yield, 220 mg, 20% (based on Fe). Anal. for **1**: Calcd. for $[\text{Fe}^{\text{II}}_4(\text{C}_9\text{H}_9\text{N}_2\text{O})_4\text{Cl}_4(\text{CH}_3\text{OH})_4]$: C 42.21, H 4.61, N 9.85; Found (%): C 41.54, H 4.63, N 9.80. Using the alternative starting material $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.33 mmol, 73 mg) and *Hmbm* (1.0 mmol, 162 mg), triethylamine (0.1 mL) and methanol (8 mL) under similar conditions resulted in light yellow rhombic crystals of **1** (75 mg, yield 30%). Fe(III) is reduced to Fe(II) under solvothermal condition in the presence of methanol. Compound **1-2d**, **1-8d** and **1-180d** were obtained by exposing crystals of **1** to air at ambient temperature for 2, 8 and 180 days, respectively (Fig. S1). The reaction time somehow varies upon the change of ambient temperature and humidity. The rate of this blackening appears to be faster for the smaller crystals. The final phase of the black crystals was then identified by X-ray diffraction, while the solvent was confirmed using TG-IR, and EA. Calcd. for $[\text{Fe}^{\text{III}}_4(\text{C}_9\text{H}_9\text{N}_2\text{O})_4\text{Cl}_4(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (**1-2d**): C 38.81, H 3.98, N 10.06; Found (%): C 38.86, H 3.95, N 10.05. Calcd. for $[\text{Fe}^{\text{III}}_4(\text{C}_9\text{H}_9\text{N}_2\text{O})_4\text{Cl}_4(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (**1-8d**): C 38.81, H 3.98, N 10.06; Found (%): C 38.89, H 3.99, N 10.03. Calcd. for $[\text{Fe}^{\text{III}}_4(\text{C}_9\text{H}_9\text{N}_2\text{O})_4\text{Cl}_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ (**1-180d**): C 37.60, H 4.21, N 9.24; Found (%): C 37.51, H 3.92, N 9.79. The supplementary crystallographic data can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The CCDC reference numbers are 1509668 (**1**), 1509669 (**1-2d**) and 1509670 (**1-8d**). Crystal data for (**1**): *P*-42₁*c*, *a* = 11.148(2) Å, *c* = 19.893(4) Å, *V* = 2472.3(10) Å³, *Mr* = 1138.09, *D_c* = 1.529 g·cm⁻³, *Z* = 2, *R*₁ = 0.0322 (*I* > 2σ(*I*)), *wR*₂ = 0.0819 (all data), *S* = 1.067, Flack parameter = -0.013(6). (**1-2d**): *P*-42₁*c*, *a* = 10.960(1) Å, *c* = 18.392(1) Å, *V* = 2209.3(10) Å³, *Mr* = 1109.96, *D_c* = 1.669 g·cm⁻³, *Z* = 2, *R*₁ = 0.0479 (*I* > 2σ(*I*)), *wR*₂ = 0.1243 (all data), *S* = 1.100, Flack parameter = 0.03(4). (**1-8d**): *P*-42₁*c*, *a* = 11.084(1) Å, *c* = 18.299(1) Å, *V* = 2248.2(7) Å³, *Mr* = 1109.96, *D_c* = 1.640 g·cm⁻³, *Z* = 2, *R*₁ = 0.0484 (*I* > 2σ(*I*)), *wR*₂ = 0.1505 (all data), *S* = 1.145, Flack parameter = 0.002(14).

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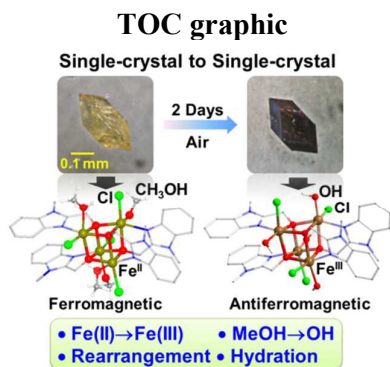


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The yellow crystal containing {Fe^{II}₄O₄} cube is progressively post-synthetically modified to black with {Fe^{III}₄O₄} cube via single-crystal-to-single-crystal transformation upon exposure to air, where water and oxygen enhance the gas-solid oxidation reaction.

