**Abstract:** We report on the synthesis of highly homogenous, oval shaped and ultra-small organometallic Fe$_3$O$_4$-nanostructures (OM-Fe$_3$O$_4$-NS) using *H. perforatum* leaf extract. Analysis of extracts before and after the synthesis of OM-Fe$_3$O$_4$-NS by ultra-performance liquid chromatography-diode array detection coupled with mass spectrometry (UPLC-DAD-MS) has revealed the active participation of quinic acid, neo-chlorogenic acid, epicatechin, quercetin 3'-malonylglucoside, and hyperforin in the formation of metal organic framework (MOF). OM-Fe$_3$O$_4$-NS were thoroughly investigated for their physico-chemical properties using Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR), NanoDrop Ultraviolet and visible spectroscopy (UV) and Thermo-gravimetric analysis (TGA). Our results show that *H. perforatum* secondary metabolites have got a great potential in engineering the next-generation ultra-smart materials.

**Keywords:** Fe$_3$O$_4$-Nanostructures; green synthesis; *Hypericum perforatum*; Metal-organic framework

**1. Introduction**

Organometallic nanostructures (OMNS) hold promising applications in the multidisciplinary field of nanoscience and nanotechnology. The core idea behind the functionality of OMNS is the smart interaction of low molecular weight organic units with metals at nanoscale. These kind of interactions make OMNS more efficient in activity mainly because of tailored physicochemical properties [1–3]. For example, Ag OMNS of less than 40 nm size recently synthesized in our lab using *Hypericum perforatum* extract showed extraordinary performance against multidrug resistant bacteria in comparison to classical MNS and fourth generation antibiotics [1]. The interaction of flavonoids, namely quercetin and its derivatives as surface stabilizing agents have created the Ag nanospheres with high antimicrobial potential [1]. Development of carboxylate- linked metal nanostructures (MNS) for enhanced catalytic potential is another example of metal organic frame work (MOF) at 0D [4]. Carboxylate linkage with zirconium have also shown good results as water adsorbent material [5]. Similarly, 2D and 3D MOF have also shown significant advancement in the industrial and biotechnological applications [6,7].

Synthetic reagents have been used to fabricate different types of MNS from bulk metal salts [8]. Among these, iron (Fe) based MNS have gained prime importance mainly because of such characteristics of Fe like its high reactivity, superparamagnetic behavior, room temperature activation and a high surface area to charge ratio at the nanoscale [9,10]. Fe, one of the trace elements in human body has also gained more attention of nanotechnologists [11]. However, Fe-NS prepared through chemical methods were found to be not very biocompatible to healthy cells, mainly due to the use of synthetic reagents as reducing and capping agents during their production [12,13]. On the other hand, Fe-NS green synthesized using plant extracts were found to be better biocompatible and more effective because of the involvement of bio-reducing and bio-stabilizing agents [14].
It is well recognized fact that the biocompatibility, size, shape and reactivity of MNS or OMNS are dependent on the use of reducing and stabilizing agents applied during the process of synthesis (nucleation, NS growth, NS uniform size etc.) at nanoscale [15–18]. In case of physical and chemical methods for the engineering of MNS, properties and molecular behavior of synthetic reducing or capping agents like NaOH, NaBH₄, Na₃C₆H₅O₇, CH₃NaO₃S, C₂nH₄n+₂Oₙ+₁, C₁₉H₄₂BrN etc. are well known [15,17]. Probably, this is the reason that in literature we have sufficient knowledge on chemistry of the MNS synthesis by chemical methods under the influence of reducing or stabilizing agents. On the other hand, literature is deficient in providing sufficient knowledge on the influence of plant metabolites in the formation of MNS or OMNS [19]. This is because of the more complex nature of plant extracts having variety of bioactive compounds like flavonoids, isoflavonoids, alkaloids, terpenoids, quinones etc. Things become more complex to explain when it comes to the molecular similarity among majority of biomolecules in plants (e.g. quercetin glucoside and galactoside, different positional and/or steric isomers of chlorogenic acid, flavones, flavanones flavonols or flavanols etc.) [20,21]. In recent past, some of the studies have contributed in explaining the chelating potential of individual compounds like quercetin in the formation of MNS [22,23]. But the behavior of quercetin or other plant metabolites for the formation of MNS or OMNS have not been studied in complex mixtures of plant extracts. A significant growth of research in this regard is still demanded.

*Hypericum perforatum* is an important medicinal plant that belongs to *Hypericaceae* family and is cultivated worldwide for the extensive use as a therapeutic agent. *H. perforatum* owns variety of valuable compounds, which have the tremendous antioxidant potential as shown in figure 1 [24,25]. Secondary metabolites like quercetin glycosides such as quercitrin, and rutin; other flavonoids; hypericin and hyperforin from this plant are well-known in the treatment of human nervous system disorders as well as skin and infectious diseases. Importantly, hypericin and hyperforin capture the global market worth millions of dollars as an efficient and non-toxic antidepressant herbal medicine [26,27]. In our previous investigation, we have observed that some of the quercetin derivatives from *H. perforatum* extract were involved in the formation of organometallic Ag-NS [1]. This motivated us to further investigate the potential of *H. perforatum* extract in the formation of OM- Fe₃O₄-NS. Moreover, the secondary metabolites participating in the green synthesis of Fe₃O₄-nanostructures have not been identified so far. The work presented here provides significant knowledge for the development of zero dimensional (0D) ultra-smart MOF at nanoscale using redox energy of plant secondary metabolites.
Figure 1. Structural formulae of some secondary metabolites from *H. perforatum* extract presenting accessible active regions for redox action during OMNS synthesis.

2. Experimental Procedures

**Preparation of *H. perforatum* extract**

Briefly, 20 g of *H. perforatum* leaves were collected, washed in ultra-pure water and homogenized using mortar and pestle to make fine powder. Powdered leaves were transferred into Erlenmeyer flask containing 200 mL of 85% methanol (LC-MS grade, Merck™). The flask was transferred to an orbishaker (KS3000 IKA™) and agitated at 300 rpm under room temperature for 2 hours. After this, the mixture was subjected to sonication in an ultrasonic bath (Sonorex, Bandelin™) for 15 minutes. Then, the mixture was filtered through Whatman™ filter paper (2W, 90 mm). The filtrate was dried using standard drying procedure under vacuum at 40 °C using rotavapor (Buchi™). The residue obtained after drying was dissolved in 200 mL of ultrapure water (Mili-Q, Merck™).

**Synthesis of OM-Fe₂O₃-NS**

To synthesize OM-Fe₂O₃-NS, 0.1 M FeSO₄ 7H₂O (Sigma-Aldrich™) was added to Erlenmeyer flask containing 300 mL of the ultrapure water (Mili-Q, Merck™) and mixed using a hot plate magnetic stirrer (IKA™) at 85 °C. After 15 minutes, 30 mL of *H. perforatum* extract was added to the above mixture and the temperature of the reaction mixture was reduced to 65 °C. The reaction was continued for 3 hours until the color of the reaction mixture changed from pale green to brown. Once the color change was noticed, the reaction mixture was centrifuged at 10,000 rpm in Eppendorf™ - 5804-R centrifuge to pellet the OM-Fe₂O₃-NS. OM-Fe₂O₃-NS pellet was washed three times with ultrapure water (Mili-Q, Merck™) and subjected to low temperature drying at 45 °C for 24 hours in an oven (ED-056, Sigma-Aldrich™). The dried OM-Fe₂O₃-NS were stored in air tight jar for further characterization.

**Examination of *H. perforatum* extract before and after the fabrication of OM-Fe₂O₃-NS using Ultra-Performance Liquid Chromatography–Diode Array Detector (UPLC-DAD) coupled with Liquid Chromatography Mass Spectrometry (LC-MS)**
To understand the biomolecules participating in the synthesis, the composition of *H. perforatum* extract before and after synthesis of OM-FeO₃-NS was analyzed by UPLC in Acquity UPLC Platform (Waters™) equipped with a BEH C₁₈ column (150 x 2.1 mm, particle size 1.7 µm, Waters™) and photodiode array detector. For analysis, vials containing 1.5 mL of sample were loaded in an automated sample manager in UPLC. The temperature of the column was set at 40°C. The mobile phases used for the chromatographic separation were water with 0.1% formic acid (Buffer A) and acetonitrile (Buffer B). The following gradients was applied: 5% B to 1 min, 15% B to 2 min, 20% B to 9 min, 99% B to 15 min, isocratic 99% B through 1 min, 5% B to 17 min and re-equilibration for 3 min. The flow rate was adjusted to 350 µL/min. Temperature of the sample manager was 8°C and volume of injection was 2 µL. Ultraviolet and Visible (UV) absorbance was calibrated in the range of 220-600 nm wavelength. Afterward, chromatograms were composed at 270 nm wavelength and were comparatively investigated.

Metabolites from *H. perforatum* extract were traced using LC-MS QExactive (Thermo) system coupled with UPLC-DAD as described before [1]. Metabolites were diagnosed on the basis of fragmentation pattern of their [M+H]+ and [M-H]: ions and comparison to standards purchased from Sigma-Aldrich, Extrasynthese and with library of compounds already identified in our laboratory (NMR analysis).

**Morphological, elemental and thermal characterization of OM-FeO₃-NS**

Morphological examination of the OM-FeO₃-NS were performed using Transmission electron microscope (TEM) (HT7700, Hitachi™) operating at the accelerated voltage of 40kV and attached to Energy Dispersive X-ray (EDX) spectroscopy for elemental analysis. Images were taken at the resolution of 50 nm. For elemental analysis of the OM-FeO₃-NS, EDX measurements were performed at 200 nm during the TEM examination. For the analysis of surface stabilizing agents, morphological examination of OM-FeO₃-NS were further subjected to AFM testing (AFM, NT-MDT™, NTEGRA-prima).

In order to examine the MOF in OM-FeO₃-NS, OM-FeO₃-NS were subjected to thermal examination by Thermo-gravimetric analysis (TGA) (TGA-8000, PerkinElmer™). The progressive increase in temperature was adjusted between 10 °C – 800 °C with the increase rate of 10 °C/minute.

**Optical, crystallographic and chemical study of OM-FeO₃-NS**

Optical properties of green synthesized OM-FeO₃-NS were investigated using NanoDrop™ UV-Vis Spectrophotometer (One/One Microvolume, ThermoFisher™) under room temperature. The UV scans were performed between 200 nm to 800 nm with automated path length correction. Briefly, 1 mg/10 mL of dry samples of OM-FeO₃-NS prepared as above were subjected to UV scanning. After complete scan, data was processed and examined using OriginPro™ 8.5. Moreover, bandgap energy of the OM-FeO₃-NS were calculated using Tauc relation [28].

Phase purity, crystallite parameters and MOF of the OM-FeO₃-NS were tested using X-ray diffraction (XRD) technique (X’Pert³ Powder –PANalytical™). The diffraction angle was set between 15° to 80°. The source of the radiation was Cu Ka having wavelength of 1.5406 Å with operating voltage of 40kV (30 mA current flow) under ambient environment. Moreover, crystallite parameters were calibrated using Debye Scherer’s formula,

\[
D = 0.9λ/β \cosθ
\]

Where D is demonstrating average crystalline domain size perpendicular to the reflecting planes, λ is the wavelength of X-ray (1.5406 Å), β is the angular full width at half maximum (FWHM) in radians, and θ is the diffraction angle also called Bragg’s angle.

3. Results and Discussion

*Analysis of H. perforatum extract before and after OM-FeO₃-NS synthesis*
Chromatographic assessment of bioactive compounds from *H. perforatum* extract participating in the fabrication of OM-FeO$_3$-NS is depicted in Figure 2. Figure 2a shows the presence of quinic acid (RT=0.60), neo-chlorogenic acid (RT=2.63), 3-*p*-coumaroyl-quinic acid (RT=3.05), procyanidin B1 (RT=3.27), epicatechin (RT=3.46), rutin (RT=3.97), quercetin-3-glucoside (RT=4.05), quercetin (RT=4.43), quercetin 3'-malonylglucoside (RT=4.73), hypericin (RT=9.32) and hyperforin (RT=13.59).

**Figure 2.** UPLC-DAD results, (a) *H. perforatum* extract, showing peaks related to identified compounds (b) *H. perforatum* extract after OM-FeO$_3$-NS fabrication (residue) showing difference in the intensity of peaks which reflects utilization of metabolites during OM-FeO$_3$-NS synthesis. The difference is obvious in peak intensities (from *H. perforatum* extract) related to quinic acid (RT=0.60), neo-chlorogenic acid (RT=2.63), epicatechin (RT=3.46), quercetin 3'-malonylglucoside (RT=4.73), and hyperforin (RT=13.59). (c) [M-H] of secondary metabolites identified in *H. perforatum* extract and involved in the green synthesis of OM-FeO$_3$-NS.
Figure 2(b) reveal that quinic acid, neo-chlorogenic acid, epicatechin, quercetin 3'-glucoside-7-acetate, and hyperforin from *H. perforatum* extract have contributed to the synthesis of OM-FeO3-NS. These phytochemicals were involved as reducing and stabilizing agents throughout the physicochemical changes in modification of bulk FeSO4.7H2O to highly homogenous and extremely small OM-FeO3-NS. Though rutin was traced in higher concentration, and its redox properties are well known [29], but, interestingly, it was not involved in the process of OM-FeO3-NS formation. It should be mentioned that several studies have hypothesized the involvement of rutin as the principal molecule from the plant extract involved in the synthesis of MNS [30–33]. It can be explained that this was probably due to the higher molecular weight of this biomolecule with comparatively lower ionizing power in complex mixture of *H. perforatum* extract. On the other hand, structural and biochemical analysis of neo-chlorogenic acid reveals that it characterized with a greater solubility (3.44 g/L) and a lower molecular weight compared to rutin [34,35]. Perhaps, the lower molecular weight of neo-chlorogenic acid promotes its activation at a low temperature of 65 °C in a complex environment. This molecule also has significant polar surface area (164.75 Å²) and polarizability power (33.42 Å³) [35]. Hence, it can be concluded that because of these leading characteristics, neo-chlorogenic acid and its natural breakdown product – quinic acid, present in the *H. perforatum* extract have contributed in the initial redox action for the saturation of Fe3+ to Fe-metabolite complex and the subsequent reduction to form crystallite planes. Moreover, epicatechin and quercetin 3'-malonylglucoside also possess high solubility rate and polarizability power in aqueous media [36,37], so the ionized Fe3+ have also been aided by these two candidates to attain Fe-metabolite complexation phase. The –OH from benzyl functional groups of these two molecules are mainly responsible for this redox process. In this manner, the reaction will last until the supersaturation of all of the Fe3+ with Fe-metabolite complex. Indeed, both of the metabolites have competitively participated along with quinic acid and neo-chlorogenic acid in the final step of the reaction. This typical behaviour of quercetin and their derivatives to participate at nanoscale was also found similar to our previous investigations [1]. As soon as the FeO3 atomic planes start to raise to orient unit cell foundation, it will lead to the formation of different energy crystallite planes. Metabolites were attracted towards the higher energy crystallite planes and act as surface stabilizing agents to inhibit the growth [1]. This also explains that the free reaction energy of the system in a heterogeneous mixture only reinforced the activation of specific molecules at a lower temperature. The reaction will progress till the attachment of all the activated stabilizing agents to form a stable OM-FeO3-NS.

Furthermore, the catalytic properties of hyperforin are well known as this compound from *H. perforatum* is mainly responsible for the therapeutic properties like serotonin reuptake inhibitor for the treatment of various type of psychological disorders [38,39]. Interestingly, we found that in the green synthesis of OM-FeO3-NS the participation of hyperforin also plays a significant role in the development of organic complex with metal core to stabilize the overall structural dynamics of the OM-FeO3-NS. Moreover, the examination of the relative concentration of hyperforin in plant extract after the synthesis of OM-FeO3-NS revealed the complete utilization of this highly active metabolite. The potential role of hyperforin as the surface stabilizing agent for the synthesis of MNS or OMNS has not been investigated so far. Moreover, we can say that the reactivity of hyperforin is metal specific as we previously observed that in the case of Ag OMNS synthesis with the same plant extract, its role was not significant compared to quercetin and its derivatives [1]. Understanding the reaction chemistry of hyperforin and its derivatives is of prime importance in order to achieve synergistic effect in the form of MOF to develop the next generation nano-therapeutics.

**Morphological, elemental and thermal examination of OM-FeO3-NS**

**Hr-TEM findings of OM-FeO3-NS (Figure 3a)** depicts an oval shape orientation with the average size of 38 nm. As we can see, the prepared OM-FeO3-NS are highly homogenous and well dispersed. Geometry of OM-FeO3-NS reflects a high density from the core with greater aggregation of metal crystallite running smoothly and horizontally across the oval shape while the outer surface of the OM-FeO3-NS is hybridized with more precipitation of plant metabolites and less concentration of metal crystallite coordinating with each other to form metal organic framework. Interestingly, core...
density and surface smoothness are found consistent through all of the OM-Fe$_2$O$_3$-NS which reveals that activation and participation of metabolites from *H. perforatum* extract are highly specific.

Smart engineering performed by quinic acid, neo-chlorogenic acid, epicatechin, quercetin 3'-malonylglucoside, and hyperforin at nanoscale to tune the size and shape of OM-Fe$_2$O$_3$-NS homogeneously is further elaborated by AFM findings (Figure 3b). The light and dark band of color spectrum observed in the homogenized surface topography of OM-Fe$_2$O$_3$-NS in AFM validates the coordination of plant metabolites with metallic core density of OM-Fe$_2$O$_3$-NS. The homogeneity of the OM-Fe$_2$O$_3$-NS (oval shape) is also clearly visible. Moreover, the involvement of *H. perforatum* extract metabolites as surface stabilizing agents was further examined using TGA (Figure 3c).

Decomposition of OM-Fe$_2$O$_3$-NS subject to high temperature was observed in three phases. In the first phase from the increase in temperature between 30 °C to 100 °C, the slight weight loss was primarily due to the loss of surface adsorbed H$_2$O molecules at 100 °C and decomposition of hyperforin around 80 °C. Water loss at 100 °C is well evidenced in the existing literature [1]. The second phase shows a consistent weight loss between 300 °C to 500 °C which is associated with the combustion of plant metabolites entrapped on the surface of OM-Fe$_2$O$_3$-NS. High temperature oxygen loss was noticed at the third phase when the temperature of the sample increased above 600 °C. The loss of plant metabolites and oxygen at high temperature were also observed in our previous findings [1,40]. Overall, the TGA analysis summarized that the green synthesized OM-Fe$_2$O$_3$-NS are of hybrid nature with strongly coordinated MOF.

Elemental analysis of the prepared OM-Fe$_2$O$_3$-NS is shown in Figure 3d which demonstrates that the OM-Fe$_2$O$_3$-NS are chiefly composed of oxygen (O), iron (Fe) and carbon (C) atoms without any other contaminants. Carbon mass is mainly coming from the skeleton of plant metabolites coordinating as surface stabilizing agent in the formation of OM-Fe$_2$O$_3$-NS.

Figure 3. (a)- TEM micrograph showing highly homogenous, core dense and oval shape OM-Fe$_2$O$_3$-NS. Possible aggregation of secondary metabolites from *H. perforatum* as surface stabilizing agent forming network directed from surface to the core is also shown along with TEM micrograph. (b)- AFM images (2D and 3D) presenting homogenous surface of OM-Fe$_2$O$_3$-NS with MOF. (c)- TGA plot showing progressive weight loss of OM-Fe$_2$O$_3$-NS with increase in temperature from 30 °C to 900 °C. (d)- EDX graph presenting elemental composition of OM-Fe$_2$O$_3$-NS.
Figure 4a shows the UV absorption peak at 290 nm of the synthesized OM-FeO$_3$-NS procured from the reaction mixture and observed before the low temperature drying. The absorption maxima shifted from 290 nm to 325 nm after the standard drying at 60 °C. The typical exciton absorption at 325 nm strongly predicting that the FeO$_3$ participating in the formation of OM-FeO$_3$-NS is chemically of γ–phase which is quite much evident from the literature [41,42]. The difference between the absorption maxima from 290 nm to 325 nm is mainly because of two reasons. First is the facial interference of secondary metabolites distorting the surface Plasmon resonance of the FeO$_3$ atoms within OM-FeO$_3$-NS which results in the absorption at 290 nm. Secondly, the low temperature standard drying of OM-FeO$_3$-NS resulted in the phase transformation of α-FeO$_3$ into γ–FeO$_3$ based OM-FeO$_3$-NS reflecting superior physicochemical properties. Moreover, drying procedure also caused the red shift of absorption maxima from 290 nm to 325 nm.

Following the Tauc relation, the calibrated value of the bandgap energy of the OM-FeO$_3$-NS is 2.1 eV. Usually for the Fe based MNS, the calcination temperature of more than 300 °C is required to improve the crystalline phase to get major transformation in the bandgap energy [43]. This is one of the major drawbacks because as the high temperature may enhance one property but affect other physicochemical parameters like the morphology of the MNS. In the present work, the participation of the secondary metabolites has not only generated stable MOF at nanoscale but also provided enough energy to the growing crystallite to remain intact. So, the OM-FeO$_3$-NS possess transformed bandgap energy of 2.1 eV even at low temperature drying.

Crystallographic parameters of the green fabricated OM-FeO$_3$-NS show hybrid crystallinity as detailed in Figure 4b. The X-ray diffractions related to the organometallic phase are traced at 20.41°, 21.22°, 22.13°, 27.36°, 37.48°, 43.38°and 49.79°. However, apart from the hybrid chemistry of the prepared material, the Bragg peaks (210, 220, 221, 311, 400, 421, 422, 511, 440 and 533) related to γ–FeO$_3$ crystallite planes are found preserved in the crystallographic geometry of OM-FeO$_3$-NS. The crystallite size of the OM-FeO$_3$-NS is calculated using the Scherer’s equation and from the broadening of peaks. Due to the hybrid nature of average of the OM-FeO$_3$-NS, FWHM of prominent peaks (210, 221, 311 and 440) were considered and their mean average was taken for further calculation. It was found that the average crystallite size was 8 nm. So, each OM-FeO$_3$-NS was made up of multiple crystallite of 8 nm each within MOF.

The diffraction observed at 27.36° specifically corresponds to the quercetin family which was also detected in case of OM-Ag-NS [1]. Moreover, the prominent diffraction peaks traced at 20.41°, 21.22° and 22.13° are well indexed to the neo-chlorogenic acid precipitation within the MOF of OM-FeO$_3$-NS and this diffraction pattern is quite similar to the recently developed chlorogenic acid mediated nano-composites [44].
Figure 4. Optical and crystallographic studies of OM-Fe₂O₃-NS. (a) NanoDrop-UV analysis showing OM-Fe₂O₃-NS absorption peaks at 290 nm and 325 nm. (b) XRD diffractogram depicting diffraction peaks related to OM-Fe₂O₃-NS. The peaks marked with green dots correspond to the organometallic phase.

Chemical analysis of OM-Fe₂O₃-NS based on vibrational bond frequencies (FTIR spectrum) is shown in Figure 5. The vibrational bond frequencies coming between 2500 and 4000 cm⁻¹ relate to C-O-H, C-O, H-O-H, C-C and C-H bond vibration modes. Comparative analysis of H. perforatum extract and the residue collected after reaction indicates the utilization of secondary metabolites as evidenced with the decrease of the intensity of vibrational bond frequencies coming from the extract. Some of the peaks that appeared in figure 5 (c) represented more complexity which is obvious because of the organometallic surface interference during the bond vibrations. The utilization of secondary metabolites in the redox process changed the color of the whole reaction mixture at the end of the reaction which may be also deduced from the Figure 5. The overall FTIR analysis confirmed the findings from the UPLC analysis. Figure 5c reveals the complete picture of MOF in OM-Fe₂O₃-NS with diverse range of molecular bond vibrations mainly coming from terminal functional groups responding to IR radiations. The typical Fe-O bond frequencies are traced around 500 cm⁻¹. Similar vibrational bond frequencies around 500 cm⁻¹ were reported previously in the green synthesized Fe based NS [45,46].
Figure 5. FTIR spectra in the comparative mode showing (a) H. perforatum extract, (b) residue and (c) OM-Fe$_2$O$_3$-NS.

Conclusion

We have successfully demonstrated that H. perforatum extract could be efficiently used in the fabrication of ultra-small OM-Fe$_2$O$_3$-NS. Further dissection of the reaction revealed the involvement of many secondary metabolites including hyperforin in the synthesis. The involvement of hyperforin as the surface stabilizing agent also provides a strong hope for the development of nano-therapeutics with efficient pharmaceutical properties in the near future.

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