

Photodecomposition of Ferrocenedicarboxylic Acid in Methanol to Form an Electroactive Infinite Coordination Polymer and Its Application in Bioelectrochemistry

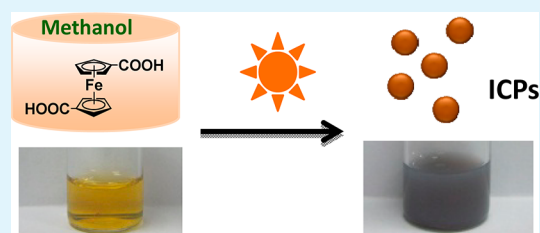
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S Supporting Information

ABSTRACT: Accurately characterizing the product of photodecomposition of ferrocene derivatives remains a longstanding challenge due to its structural complexity and strong dependence on the solvent and the substituent. Herein, photodecomposition of ferrocenedicarboxylic acid (FcDC) in methanol is found for the first time to form an electroactive infinite coordinate polymer (ICP) with uniform size, good water stability and photostability, and excellent electrochemical activity. The possible mechanism for the ICP formation is proposed based on the fission of the Fe-ring bond and deprotonation of FcDC under light irradiation. The dissociated Fe^{2+} is first oxidized to Fe^{3+} that consequently coordinates with the deprotonated ferrocene dicarboxylate to produce ICP nanoparticles. This work not only provides a new insight into the product formation of the photodecomposition of ferrocene derivatives but also offers a mild and simple route to the synthesis of electroactive ICPs.

KEYWORDS: ferrocenedicarboxylic acid, photodecomposition, infinite coordination polymer, bioelectrochemistry, laccase



INTRODUCTION

The unintentional discovery of the organometallic compound ferrocene and its analogues has largely promoted a rapid growth of organometallic chemistry and coordination chemistry. As one type of organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom, ferrocene has been used in various research fields. In these cases, ferrocene is relatively stable in most solvents under photoirradiation.^{1–3} However, some ferrocene derivatives are susceptible to light and thus have been widely used as luminescence quenchers,^{4,5} photoinitiators,^{6,7} and photosensitizers.⁸ The photosensitivity of ferrocene derivatives is strongly dependent on their structures. Earlier work on the photochemistry of ferrocenes has suggested that ferrocene itself or alkyl-substituted ferrocenes are quite inert in most solvents with the exception of halocarbons, while acylferrocenes are readily decomposed by light.² To date, some decomposition mechanisms have been proposed including oxidation of the iron atom,^{9,10} fission of the ligand–Fe bond,¹¹ fission of bonds between the cyclopentadienyl ligand, and attached groups to yield σ -ferrocenyl radicals.¹² However, the photodecomposition product, especially the formed aggregates, has scarcely been characterized and clarified presumably due to their structural complexity which is strongly dependent on the solvent and the substituent of the derivatives.

In this study, we investigate the photodecomposition of ferrocene dicarboxylic acid (FcDC) in methanol under natural light at room temperature and interestingly find that the photodecomposition of FcDC essentially forms a kind of

infinite coordination polymer (ICP) with a uniform size. As a family of new micro-/nanoscaled materials, ICPs are constructed from the metal ions and polydentate ligands by coordination polymerization and have been of great concern in these few years because of their unique properties such as self-adaptivity and structural tailorability^{13–16} and, as such, promising applications in many research fields.^{17–21} Very recently, our group has demonstrated that ICPs are useful for biosensor development through simultaneously encapsulating all the biosensing elements (i.e., enzyme, coenzyme, and electrocatalyst) into one single ICP particle, and this method greatly simplifies the procedure of biosensor preparation.^{22,23} In this study, we find that electrochemically active ICPs are readily formed by photodecomposition of FcDC in methanol. The formed ICP nanoparticles bear a uniform size, good water stability and photostability, and excellent electrochemical activity. This study not only provides a new insight into the product formation by photodecomposition of ferrocene derivatives but also offers a mild and simple route to synthesis of electrochemically active ICPs with excellent properties and promising applications.

EXPERIMENTAL SECTION

Reagents and Materials. 1,1'-Ferrocenedicarboxylic acid was purchased from TCI (Japan) and used as supplied. Methanol (HPLC

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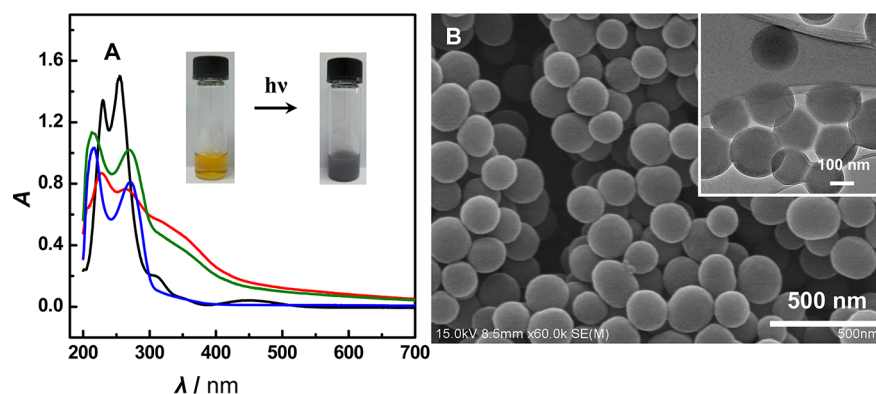


Figure 1. (A) UV-vis spectra of 5 mM FcDC methanol solution before (black curve) and after (green curve) exposure to natural light for 2 h and UV-vis spectra of the supernatant (blue curve) and the precipitate (red curve) after exposure to natural light for 2 h. Inset: photographs of 5 mM FcDC methanol solution before (left) and after (right) the solution was exposed to natural light for 2 h. (B) SEM image of formed ICP nanoparticles. Inset: TEM image of formed ICP nanoparticles.

grade) was obtained from Concord. Tech. Co. (Tianjin, China). Laccase (E.C. 1.10.3.2, from *Trametes versicolor*) was purchased from Sigma-Aldrich and purified with a method described in our earlier work.²⁴ Bovine serum albumin (BSA) was obtained from Proliant (USA). Aqueous solutions were all prepared with Milli-Q water (18.2 M Ω -cm).

Photodecomposition of Ferrocenedicarboxylic Acid. For the photodecomposition experiments, 1,1'-ferrocenedicarboxylic acid (FcDC) was first dissolved in methanol to give an orange solution. The solution was then exposed to natural light or a simulated sunlight xenon light source (Xenon lamp CEL S500, 15 mA, Aulight, Beijing, China) for a certain amount of time. Typically, when 5 mM FcDC methanol solution was exposed to natural light or a xenon light source for up to 2 h, the solution color turned to taupe, and taupe precipitates were formed at the same time. Then, the precipitates were centrifuged and washed with methanol at least three times, collected, and redispersed in the same amount of methanol for characterization. For the photodecomposition experiments in other solvents, the same procedures were conducted. Since FcDC bears a poor solubility in water, we first prepared ferrocenedicarboxylic disodium by a neutralization reaction and then dissolved equimolar of ferrocenedicarboxylic disodium into water for the photodecomposition experiments. All the photodecomposition experiments were carried out at room temperature.

UV-vis spectra were recorded by a TU-1900 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., China). Scanning electron microscopy (SEM) images of ICPs were taken in S4300 and S4800 field emission scanning electron microscopy (Hitachi, Japan). Transmission electron microscopy (TEM) measurements were carried out using a JEOL-1011 transmission electron microscope (Japan). Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Rigaku X-ray Diffractometer (D/max-2500) with an X-ray source of Cu K α ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 200 mA. Fourier transform infrared (FT-IR) spectra (KBr pellet) were collected on a Tensor-27 FT-IR spectrometer (Bruker, Germany). Electrospray ionization mass spectrometry (ESI-MS) experiments were performed with an LTQ XL mass spectrometer equipped with a nanospray source (Thermo Scientific, USA). The mass spectra were collected in negative ion mode, and a voltage of 1500 V was applied to the needle to produce the spray. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon.

Electrochemistry. Electrochemical measurements were carried out with a computer-controlled electrochemical analyzer (CHI 660B, Shanghai, China) in a two-compartment and three-electrode cell. Glassy carbon electrodes (GC, 3 mm diameter) were used as substrate electrodes to investigate the electrochemical property and bioelec-

trochemical application of the as-formed ICPs. GC electrodes were first polished with emery paper and 0.3 and 0.05 μm alumina slurry on a polishing cloth, then sonicated in acetone and Milli-Q water (each for 3–5 min), and finally rinsed with Milli-Q water thoroughly. For the electrochemical studies, ICPs were confined onto GC electrodes by dip-coating 4 μL of ICP dispersion (10 mg/mL) in methanol onto GC electrodes, and the electrodes were then air-dried. The ICP-based enzyme electrodes were prepared by dip-coating 4 μL of mixed enzyme solution consisting of laccase (2 μL , purified), BSA (1 μL , 1%), and glutaraldehyde (2 μL , 1%) onto the ICP-modified electrodes, and the electrodes (laccase/ICP-modified GC electrodes) were then air-dried prior to the electrochemical measurements. For all electrochemical measurements, the ICP-modified electrodes were used as working electrode, a platinum spiral wire as counter electrode, and a Ag/AgCl electrode (KCl-saturated) as reference electrode. A 0.1 M acetic acid–sodium acetate (HAc–NaAc pH 6.0) buffer was used as electrolyte. Electrochemical measurements were conducted at room temperature.

RESULTS AND DISCUSSION

As shown in Figure 1A (inset), when a methanol solution of FcDC was exposed to natural light at room temperature for 2 h, we surprisingly found that the solution color changed from initial orange to taupe with the formation of taupe precipitate. To shed light on this change, UV-vis spectroscopy was conducted, as displayed in Figure 1A. FcDC itself (before light exposure) shows absorption bands at 230, 255, 310, and 451 nm (black curve), which were ascribed to the aromatic ring (230 and 255 nm) and the metal-ring charge transfer (310 and 451 nm) of FcDC, respectively.² After exposure to natural light for 2 h, the resulting mixture exhibits three obvious absorption peaks at 213, 270, and 345 nm (green curve). To assign these peaks, the mixture was centrifuged, and then both the supernatant and the precipitate were subjected to UV-vis spectroscopic measurements. We found that only two absorption peaks at 213 and 270 nm were observed for the supernatant (blue curve), corresponding to the absorption of aromatic ring, demonstrating the photodecomposition of FcDC because of the disappearance of metal-ring charge transfer absorption peak (Figure 1A, blue curve). Differently, the precipitate exhibits three absorption peaks for both the aromatic ring (228 and 264 nm) and metal-ring charge transfer (345 nm), suggesting that the as-formed precipitate contains a ferrocene unit. SEM and TEM images reveal that the precipitate consists of nanometer-scaled solid spherical particles with a uniform size of around 100 nm (Figure 1B). XRD results

show that these particles are amorphous (Figure S1, Supporting Information).

To systematically study the photodecomposition phenomena of FcDC in methanol, we used a xenon light source, instead of natural light, to induce the photodecomposition in a more controllable manner. A comparison of the photodecomposition under visible light and full spectrum light irradiation suggests that the decomposition under visible light irradiation occurs with no obvious difference from that under full spectrum light irradiation (data not shown). This result essentially shows that the dissociation of FcDC was initiated from the metal-ring charge transfer since it exhibits the adsorption peak in the visible region (i.e., 451 nm, Figure 1A). As reported previously, in the compounds with their ferrocenyl units substituted by electron-withdrawing groups, visible light promotes one-electron transition from the Fe^{2+} ion to the cyclopentadienyl unit, and this leads to the expel of the Fe^{2+} ion into the solvent.²⁵ The time-dependence feature of FcDC photodecomposition was also studied with the xenon light source, as displayed in Figure 2.

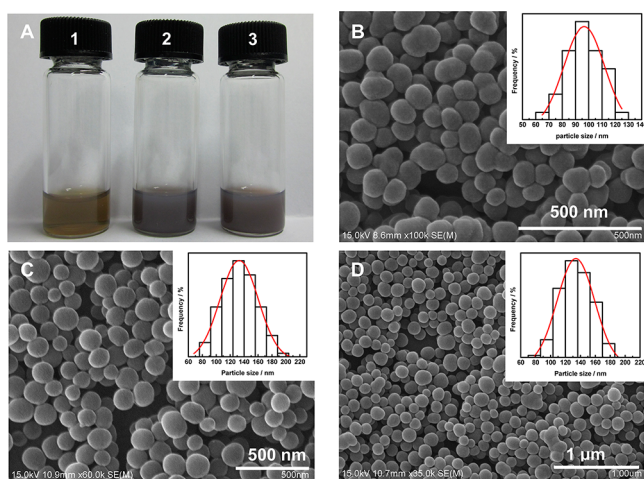


Figure 2. (A) Photographs of 5 mM FcDC methanol solution photodecomposed by ultraviolet visible light at different time points of 2 min (vial 1), 2 h (vial 2), and 5 h (vial 3) after light exposure. (B–D) SEM images of the formed particles after the FcDC was photodecomposed at different time points of 2 min (B), 2 h (C), and 5 h (D) after light exposure. Inset: the histograms of particle size distribution at the corresponding time.

The color of FcDC solution changed as early as 2 min after exposure to ultraviolet visible light (Figure 2A vial 1), indicating that the photodecomposition was a fast dissociation process. The histogram of the particle size distribution analysis reveals that the average diameter of the particles formed by 2 min photodecomposition of FcDC was around 96 ± 13 nm (Figure 2B). After being exposed to light for up to 2 h, the morphology of the particles did not obviously change, but the size of the particles increased to 133 ± 24 nm (Figure 2C). When the exposure time was increased to 5 h, there was almost no change in either morphology or particle size (133 ± 20 nm for 5 h, Figure 2D). These results demonstrate that 2 h was enough to complete the photodecomposition, which could also be supported by the UV–vis spectra, in which there was no absorption peak of FcDC in the supernatant (Figure 1A, blue curve). Moreover, these results also demonstrate that the formed particles were quite stable under light irradiation, and no obvious change was observed from 2 to 5 h after light exposure.

We have also investigated the photodecomposition of FcDC in other polar solvents, i.e., alcohol and water (Figure S2, Supporting Information). In these two solvents, FcDCs were photodecomposed under both natural light and the xenon light source at room temperature. However, the precipitates show no regular morphology, suggesting that the particle formation by photodecomposition was strongly solvent-dependent.

To clarify the components of the formed precipitate, X-ray photoelectron spectroscopy (XPS) was conducted, as depicted in Figure 3A. There are two peaks at 711.9 and 708.2 eV in the energy region of $\text{Fe } 2p_{3/2}$, which are consistent with the energy region of Fe^{3+} that coordinates with carboxyl and Fe^{2+} in FcDC,^{26,27} respectively. Combining with UV–vis results of the precipitate (Figure 1A, red curve), the strong absorption peak of metal-ring charge transfer (345 nm) demonstrates the existence of Fe^{2+} originated from the ferrocene in the particles, while the existence of Fe^{3+} in the precipitate could be possibly elucidated from the instability of the free ferrous ions produced in the FcDC decomposition process, which is quickly oxidized into ferric ions.² Electrospray ionization mass spectrometry (ESI-MS) of the supernatant further confirmed the photodecomposition of FcDC since it shows a strong peak at m/z 219.33, which was presumably ascribed to the dimer of carboxylic acid substituted cyclopentadiene (Figure S3, Supporting Information).²⁸ These results lead us to hypothesize that the formed ferric ions could coordinate with FcDC to

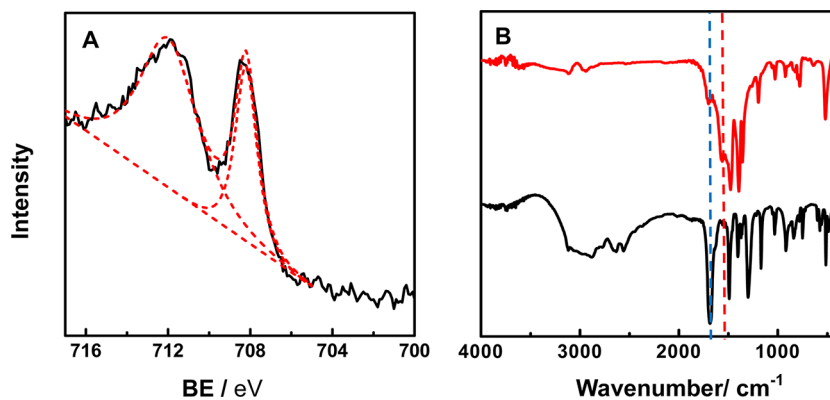


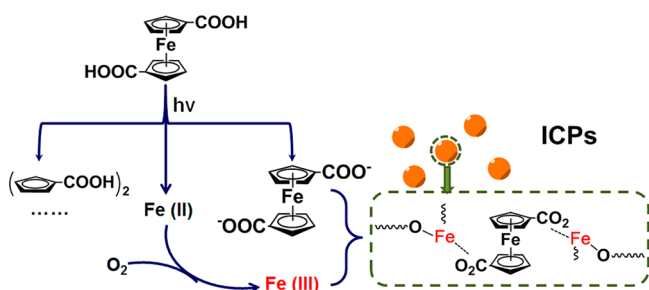
Figure 3. (A) XPS result of the as-formed precipitate for $\text{Fe}2p_{3/2}$. (B) FT-IR spectra of 1,1'-ferrocenedicarboxylic acid (black curve) and the as-formed particles (red curve).

form a new kind of ICPs, which are constructed from the metal ions and polydentate ligands by coordination polymerization, first reported by Mirkin et al. in 2005.²⁹ Our hypothesis was verified by fourier transform infrared (FT-IR) spectroscopy (Figure 3B). Pure FcDC exhibits a characteristic peak at 1687 cm^{-1} , which was ascribed to C=O stretching frequency, while for the as-formed precipitate this peak obviously red-shifts to 1560 cm^{-1} , demonstrating the coordination of Fe^{3+} with the carboxylate.³⁰

To further confirm our hypothesis, ferric ion solution (5 mM, FeCl_3) was added into FcDC (5 mM) solution in methanol. Unfortunately, there were no precipitate formed. We thus mixed ferric ion solution (5 mM) with the disodium salt of FcDC (5 mM) in methanol, and the precipitate was quickly produced. Although the precipitate formed under this condition does not exhibit a regular morphology and uniform size distribution (Figure S4, Supporting Information), it exhibits almost the same UV-vis absorption and FT-IR spectra (Figure S5, Supporting Information) as those of the photodecomposition product of FcDC (Figure 1A and Figure 3B), suggesting that the precipitate formed during the FcDC photodecomposition process is formed through the coordination of Fe^{3+} with the deprotonated form of FcDC in the process of photolysis.

On the basis of the results demonstrated above, we proposed that the nanoparticles formed during the FcDC photodecomposition process could be one kind of ICPs, and the mechanism underlying the ICP formation might proceed as follows (Scheme 1): when FcDC was exposed to light, it

Scheme 1. Proposed Mechanism for the Formation of ICPs



dissociates into Fe^{2+} , a dimer of carboxylic acid substituted cyclopentadiene, and other intermediate products (e.g., the other possible cyclopentadiene radicals). Meanwhile, the

deprotonation of FcDC occurs under light irradiation.³ The dissociated Fe^{II} species is further oxidized into Fe^{III} by O_2 and Fe^{III} coordinates with the deprotonated FcDC to form ICPs, as shown in Scheme 1.

In addition to its good photostability and water stability, the as-formed ICPs exhibit a good electrochemical property. As typically depicted in Figure 4A, the as-formed ICP shows one pair of well-defined redox peaks at ca. 0.48 V with a peak-to-peak potential separation of 77 mV at the scan rate of 100 mV s^{-1} , suggesting that the as-formed ICPs will keep the electrochemical property inherent in FcDC. Moreover, the redox peak currents obtained at the ICP-modified GC electrode show a good linear relationship with the square root of the potential scan rate within a range from 20 to 1000 mV s^{-1} (Figure S6, Supporting Information) and little dependence of the redox potential on the scan rate was observed. These results demonstrate a fast diffusion-controlled redox process of the surface-confined ICPs presumably with an electron-hopping mechanism in the ICP particles, as reported previously.³¹ The excellent electrochemical properties of the ICPs prepared by photodecomposition of FcDC solution in methanol substantially enable their applications in the development of advanced bioelectronics devices such as biosensors and biofuel cells, as demonstrated below.

Enzyme-based bioelectronic devices, such as biosensors and biofuel cells, have recently attracted much attention because of their potentiality in implantable energy and biomedical applications.^{32–35} In this case, the electron transfer between an enzyme and electrode is one of the key points influencing the performances of the devices. Most of the redox enzymes lack direct electrical communication with electrodes because of the steric hindrance of their peptide shells surrounding the redox active centers. To solve this problem, various mediators have been used to shuttle the electron transfer between enzymes and electrodes to trigger a bioelectrochemical response.^{36,37} To investigate the potentiality of the as-formed ICP particles as an electron transfer mediator for the enzymes, laccase was employed as a model for bioelectrochemical studies. As one of the most important multicopper enzymes (MCOs), laccase is an extracellular blue copper enzyme in plants and fungi, which catalyzes the oxidation of phenols and amines, concomitantly with the four-electron reduction of molecular oxygen into water, and can be widely used as the biocathodic catalyst for the O_2 reduction in biofuel cells.^{38,39} As shown in

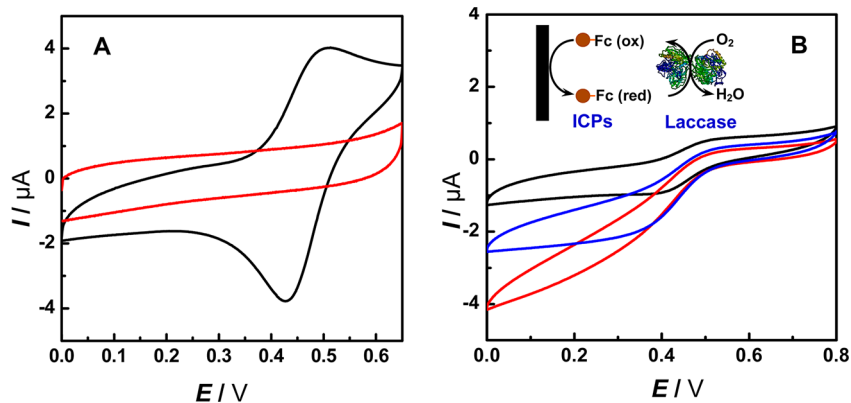


Figure 4. (A) CVs obtained at the ICP-modified (black curve) and bare (red curve) GC electrodes in 0.10 M HAC-NaAc buffer (pH 6.0). Scan rate, 100 mV s^{-1} . The initial potential was 0.0 V. (B) CVs obtained at the laccase/ICP-modified GC electrodes in 0.10 M HAC-NaAc buffer (pH 6.0) saturated with N_2 (black curve), ambient air (blue curve), or O_2 (red curve). Scan rate, 20 mV s^{-1} .

Figure 4B, the presence of O₂ in solution results in an obvious increase of the reduction peak current and a decrease of the reversed oxidation peak current of ICP, suggesting that the O₂ reduction occurs under the bioelectrocatalysis of laccase with ICP as the redox mediator to shuttle the electron transfer of laccase (Figure 4B, inset). All these results demonstrate the as-formed ICP serves well as a mediator to efficiently transduce the biorecognition events accomplished on enzymes into electronic readout and is thus very attractive for development of integrative bioelectronics devices such as biosensors and biofuel cells.

CONCLUSIONS

In summary, we have, for the first time, found that the photodecomposition of FcDC in methanol produces electroactive ICP. The mechanism for the ICP formation is proposed based on the fission of the Fe-ring bond, the oxidation of the ferrous to ferric, and deprotonation of FcDC under light irradiation. Ferric ion coordinates with the deprotonated ferrocene dicarboxylate to form ICP particles with a uniform size, good photostability and water stability, and excellent electrochemical activity. This study not only provides a new possible mechanism for the photodecomposition of ferrocene derivatives but also offers a mild and simple method to synthesize electroactive ICPs with excellent bioelectrochemical applications.

ASSOCIATED CONTENT

Supporting Information

Additional spectral data such as XRD data of the ICPs, the photodecomposition in different solvents, and ESI spectra of the supernate. Characterization of precipitates formed by mixing ferric and FcDNA. Additional CVs at different scan rates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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