Local Coordination and Reactivity of a Pt Single-Atom Catalyst as Probed by Spectroelectrochemical and Computational Approaches

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The interaction between isolated transition-metal atoms and neighboring dopants in single-atom catalysts (SACs) plays a key role in adsorption strength tuning and catalytic performance engineering. Clarifying the local coordination structures of SACs is therefore of great importance and yet very challenging at the atomic level. Here, we employ a SAC with isolated Pt species anchored on nitrogen-doped carbon as a prototype and investigate the local coordination environment around Pt sites with the CO probe molecule by combined electrochemical infrared (IR) spectroscopy and density functional theory calculations. Two types of Pt coordination structures are clearly revealed, involving a Pt–C moiety with weak CO binding and a pyrrolic Pt–N–C moiety with strong CO binding, highlighting the Pt local coordination structure-dependent CO binding strength. This inventory then allows a comparative COad electrooxidation mechanism study on an identified pyrrolic Pt–N–C moiety of the Pt SAC and a bulk Pt surface toward the feedback loop between theory and experiment. A much higher coupling barrier for COad and OHad is noted on the simulated Pt–N–C site than that on Pt(111), making the Langmuir–Hinshelwood pathway kinetically unfavorable on the Pt SAC. In contrast, a lower theoretical limiting potential is predicted for CO oxidation on pyrrolic Pt–N–C with free H2O in favor of the Eley–Rideal pathway and qualitatively agrees with the experimental kinetics. The present methodology may promote the understanding of the SAC structure–activity relationship and the discovery of novel SACs.

Keywords: platinum single-atom catalyst, coordination environment, spectroelectrochemistry, carbon monoxide, density functional theory
Introduction

Transition-metal single-atom catalysts (TM-SACs) are well-known for their maximum atom efficiency, superb specific activity, and distinctive catalytic performance, as well as their low-coordinated nature for surface chemistry studies.1,3 Actually, the past 10 years have seen a rapid expansion in the number of publications regarding the synthesis, characterization, and application of TM-SACs in the vast realm ranging from thermal catalysis to electrocatalysis. Due to the high surface free energy of these isolated TM atoms, strong metal-support interactions are needed for anchoring or dispersing these TM atoms individually onto a support to prevent aggregation.4–7

Metal oxide supports like FeOx,8 and CeO29 are usually employed in thermal catalysis, and heteroatom-doped carbon supports are widely used in electrocatalysis because of their large surface area, high electron conductivity, and chemically inert nature.10,11 Moreover, due to the abundant defects in a carbon support11,13 that is used to host these isolated metal species, a variety of tuning structures exist, for both metal atom centers and adjacent coordinative dopants, toward desired catalytic pathway manipulation. For example, Fe–N–C moieties have been intensively investigated as an alternative to Pt for oxygen reduction reaction (ORR), in which pyridinic (Pyd) and quaternary Fe–N–C groups are identified as the surface active sites for the 4e– pathway in acid and alkaline media.14,15 In contrast, the recent report demonstrates that by switching the neighboring dopant N to O, the 2e– pathway is dominant for ORR on the Fe–O–C moiety with the H2O2 selectivity >95% in both neutral and alkaline media owing to the change of active sites from Fe in the Fe–N–C moiety to C in the Fe–O–C moiety.16

Resolving the specific atomic configuration and exploring the delicate coordination environment of SACs is quite valuable yet very challenging. So far, aberration-corrected scanning transmission electron microscopy (AC-STEM) and X-ray absorption fine structure ( XAFS) spectroscopy are the two most widely used techniques to probe the structural information of SACs.1,7,18 The former directly captures images at atomic resolution within a selected area, typically at a scale of a few nanometers, to demonstrate the transition-metal dispersion. The latter provides averaged information of the electronic structure from near-edge and the coordination structure from extended-edge over a bulk TM-SAC sample. Although XAFS could be operated at operando electrochemical conditions to track structural evolution during reactions, it is hard to distinguish the fine metal-metalloid coordination like M–C/N/O, due to their similarity in scattering paths and scattering intensities.16,19 As an alternative, vibrational spectroscopy with selected probe molecules16,20 could be a convenient and sensitive tool to differentiate active motifs under operando conditions as well as to probe the dynamic interfacial chemistry during (electro-)catalysis on SACs.

On the one hand, the vibrational frequency and intensity of a surface probe molecule like CO are closely related to the coordination nature of surface metal sites, which is associated with their dispersion and electronic structures.21 On the other hand, the kinetics study of such an adsorbate oxidation removal could in turn deepen the understanding of the local coordination environment in a SAC. Actually, the reactivity of the surface probe on the isolated metal atoms is largely dependent on the surrounding coordination environment, thus serving as a more relevant indicator of catalytic behavior.20 In recent thermocatalysis reports, the CO adsorption and oxidation have been applied to investigate the Pt–O–Cu24 and Pt–O–Ce25 SAC moieties at the solid and gas interface. Unfortunately, no such attempt has been fulfilled yet under electrochemical conditions at the SAC and electrolyte interface, given the complex coordination environment of heteroatom-doped carbon support as well as the limited surface sensitivity of the conventional reflection absorption infrared (IR) technique.

In this work, we employ isolated Pt atoms anchored on nitrogen-doped carbon nanotubes (Pt-CNT) as a model SAC and demonstrate clearly the presence of Pt–C and Pt–N–C coordination moieties in the SAC by combined spectroelectrochemical and computational approaches involving the surface CO probe. During COad electrooxidation, the dynamic interfacial chemistry is probed by in situ attenuated total reflection IR (ATR-IR) at the molecular level and the reaction energetics is interpreted from density functional theory (DFT) calculations. In contrast to the predominant Langmuir–Hinshelwood (L–H) mechanism for COad oxidation on bulk Pt surface, the Eley–Rideal (E–R) mechanism is more favorable on the pinpointed pyrrolic (Pyr) Pt–N–C moiety.

Experimental and Computational Methods

Material synthesis

The Pt-CNT catalyst was prepared by the impregnation and reduction method.16 Briefly, a 7.2 mM Pt(II) stock solution was first prepared by dissolving K2PtCl4 salt (AR; Sinopharm, Shanghai, China) into Millipore water (18.2 MΩ-cm). A carbon suspension was prepared by mixing 40 mg multiwalled carbon nanotubes (Carbon Nanotubes Plus GCM389, used as received) with 30 mL of Millipore water, and tip sonicated (JY92-IIN; Scientz, Ningbo, Zhejiang Province, China) for 30 min till a homogeneous dispersion was accomplished. Then 400 μL of Pt2+ solution, given a raw atomic ratio of Pt:C to be ~0.08 atom %, was dropwise added into CNT solution under vigorous stirring, followed by quick freezing in

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liquid nitrogen. The as-prepared K$_2$PtCl$_4$/CNT powder was mixed with urea at a mass ratio of 1:10, then heated in a tube furnace to 800 °C under a gas flow of 100 sccm Ar (99.999%; Wetry-SH, Shanghai, China) for 60 min, and kept at the same temperature for another 60 min before cooling to room temperature. N-CNT was prepared by the same thermo annealing method without the K$_2$PtCl$_4$ preadsorption and freeze-drying steps.

**Material characterization**

The morphology of Pt-CNT catalyst was characterized by bright-field transmission electron microscopy (TEM) using a JEM-2010 microscope (JEOL, Akishima Shi, Japan). Dark-field STEM characterization was carried out using a JEM ARM200F aberration-corrected transmission electron microscope (JEOL) under 200 kV. Drift correction was applied during acquisition. X-ray photoelectron spectroscopy (XPS) was obtained with a AXIS Ultra DLD spectrometer (Kratos Analytical, Trafford Park, Manchester, UK), using monochromatic Al K$_\alpha$ radiation (1486.6 eV) and a low energy flood gun as neutralizer. The binding energies were calibrated by referencing the C 1s peak at 284.8 eV. The Casa XPS program was employed for surface componential content analysis. The XAFS data at Pt L$_3$-edge (11,564 eV) of the Pt-CNT sample and PtO$_2$ and Pt foil references were collected at room temperature at the beamline BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF; XAFS station) using a Si(311) double-crystal monochromator. The synchrotron radiation was operated at an energy of 3.5 GeV and a current between 150 and 210 mA. The obtained data were processed and fitted using the IFEFFIT-based Athena and Artemis programs with the theoretical standards calculated using FEFF8. The photon energy was calibrated using the first inflection point of the Pt L$_3$-edge in Pt metal foil. The K range was 3.1–13.8 Å$^{-1}$ for Pt foil and PtO$_2$, and 3.1–10.6 Å$^{-1}$ for Pt-CNT sample. The fitting analysis of Pt-CNT extended XAFS (EXAFS) was carried out with either Pt–C, Pt–N, or Pt–C and Pt–N paths using an iterative least-squares technique. Appropriate X-ray absorption near-edge structure (XANES) references (Pt foil and PtO$_2$) were used for linear combination fitting (LCF) of the Pt-CNT sample.

**Spectroelectrochemical measurements**

A CH Instruments 440 A workstation (Shanghai, China) was employed to record the electrochemical response. Certain amounts of HClO$_4$ (ACS Grade, 70%; Sigma-Aldrich, Darmstadt, Germany) were dissolved in Millipore water to prepare the 0.1 M electrolyte. All electrolytes were deaerated with Ar prior to and throughout the measurements.

In situ electrochemical ATR-IR measurements were run on a Pt-CNT catalyst layer- or Pt overlayer-covered Au film on a hemicylindrical Si prism using a Nicolet iS50 spectrometer (Thermo Fisher Scientific, Carlsbad, California, USA) equipped with an MCT detector at a spectral resolution of 4 cm$^{-1}$ with an $\rho$-polarized IR radiation at an incidence angle of ca. 70°. A graphite rod (99.995%; Sigma-Aldrich) was used as the counter electrode and a CH Instruments saturated calomel electrode (SCE) as the reference electrode. All potentials measured against SCE were converted to the RHE scale using the relationship $E$ (vs RHE) = $E$ (vs SCE) + 0.241 V + 0.0591 x pH, where the pH value of 0.1 M HClO$_4$ was determined to be ∼1.0. All the spectra are shown in the absorbance unit as $-\log(I/I_0)$, where $I$ and $I_0$ represent the intensities of the reflected radiation of the sample and reference spectra, respectively. To prepare the Pt-CNT cast working electrode, 2 mg of as-prepared Pt-CNT catalyst was mixed with 1 mL of ethanol and 10 μL of Nafion 117 solution (5%; Sigma-Aldrich), and sonicated for 30 min to get a homogeneous catalyst ink. Approximately 50 μL of catalyst ink was further diluted into 1 mL of ethanol and air-brushed onto Au/Si within an area of ∼0.64 cm$^2$. Electrochemical deposition was used to prepare the Pt film working electrode on Au/Si, by cycling the potential from 0.45 to −0.2 V versus SCE for 15 cycles in 0.1 M HClO$_4$ + 10 mM H$_2$PtCl$_6$. Other ATR-IR experimental details regarding the electrosless deposition of the Au film and the spectral cell setup can be found elsewhere.

**Computational details**

We performed DFT calculations using the Vienna Ab initio Simulation Package (VASP)$^{29,30}$ with BEEF-vdW exchange-correlation functional$^{31}$ and projector augmented wave (PAW) method.$^{32}$ To calculate energetics and vibrational frequencies, we performed tight geometry optimizations with energy and force criteria for self-consistent iteration and ionic relaxation set to $10^{-6}$ eV and 0.01 eV/Å, respectively. All plane waves with a kinetic energy smaller than 500 eV are included. Using these computational settings, we first optimized bulk structures of graphene and Pt, which resulted in C–C distance of 1.423 Å and Pt lattice parameter of 3.993 Å. We then constructed an (8 × 8) supercell of grapheme consisting of 72 carbon atoms and modeled various single Pt atom-incorporated systems, as shown in the Supporting Information. For these systems, we used Gamma point (single k-point) sampling. For the bulk Pt system, we modeled a (3 × 3) Pt (111) surface with four layers, where the bottom two layers were fixed during all geometry optimizations with (3 × 3 × 1) k-points. In all cases, we added a sufficient vacuum (~15 Å) to avoid imaginary interactions between repeating atomic structures in the z-direction.

The vibrational frequencies were calculated by a finite difference of the Hessian matrix as implemented in atomic simulation environment (ASE),$^{33}$ where the adsorbed
CO molecule was displaced by 0.005 Å in x-, y-, and z-directions. The energies of gas-phase CO$_2$, HCOOH, H$_2$, and adsorbed COOH$^*$ were corrected by +0.41, +0.20, +0.09, and +0.20 eV, respectively, to account for inaccurate descriptions of the C=O double bond and H-H bond in BEEF-vdW functional. The energies of COOH$^*$, CO$_n^*$, and OH$_n^*$ were further corrected by adding solvation corrections. To construct free-energy diagrams of CO electrooxidation, we converted electronic energies into free energies by adding free-energy corrections for adsorbates (COOH$^*$, CO$_n^*$, and OH$_n^*$) and gaseous molecules (CO, H$_2$, CO$_2$, and H$_2$O). The free-energy correction values are summarized in Supporting Information Table S1. The free energies of the potential-dependent reaction steps involving a proton-electron pair ($\text{H}^+ + e^-)$ were treated using the computational hydrogen electrode (CHE) method. The effect of the electrode potential was applied by shifting the electron free energy by $-\Delta G_{\text{elec}}$, where $e$ and $U_{\text{elec}}$ are the elementary charge of electron and the electrode potential, respectively. For example, for the COOH$^*$ $\rightarrow$ + CO$_2$ + ($\text{H}^+ + e^-$) reaction, the free energy at the potential $U_{\text{elec}}$ was calculated as $\Delta G (U = U_{\text{elec}}) = \Delta G (U = 0) - eU_{\text{elec}}$. Thus, for CO electro-oxidation, the largest $U_{\text{elec}}$ that makes all electrochemical reaction steps energetically downhill is defined as the “theoretical onset potential” or “limiting potential ($U_l$),” which corresponds to the experimental onset potential to achieve the arbitrarily set current density.

Results and Discussion

To prepare atomically dispersed Pt SAC, diluted K$_2$PtCl$_4$ stock solution was first dispersed with commercial surface-functionalized CNTs in Millipore water. Due to the large surface area and the carboxylic functional groups, the CNTs possess a high adsorption capacity to Pt cations in aqueous solution. The mixture was freeze-dried overnight and the obtained powder was thermo annealed with urea as the N source under Ar-saturated 0.1 M HClO$_4$ were recorded prior to the spectroelectrochemical measurements. Typical hydrogen evolution was seen on Pt-CNT below 0.05 V versus RHE without conventional Pt voltammetric features (Supporting Information Figure S5), consistent with the dominant presence of highly isolated Pt atoms. Thereafter, CO was bubbled through the electrolyte at a fixed potential of 0.4 V to attain CO saturation. The time-evolved ATR-IR spectra are shown in Figure 2a, consisting of three CO$_{ad}$ peaks at 2130, 2026, and 1970 cm$^{-1}$, respectively. Augmentation of these signals arises from the increasing CO coverage, which is most notable for the latter two peaks during the 1 h course. Figure 2b compares the spectra of CO$_{ad}$ on Pt-CNT, Pt, and Au films, where detailed ATR-IR spectra on control samples can be found in Supporting Information Figures S6–S8. The 2130–cm$^{-1}$ peak in Figure 2a can thus be safely ascribed to CO$_{ad}$ on partly exposed Au substrate. Neither CO$_L$ (~2082 cm$^{-1}$) nor bridge-bonded CO$_B$ (~1868 cm$^{-1}$) on Pt terrace sites or large Pt assemblies were observed, consistent with the highly isolated nature of Pt atoms in the Pt-CNT. Moreover, the frequencies of the $\nu$(CO$_2$) band on the Pt-CNT are nearly independent of CO coverage, indicating the absence of dipole-dipole interactions from neighboring CO$_{ad}$ molecules, thereby reinforcing the atomic dispersion of isolated Pt sites.

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After 1 h nonstop CO bubbling, an Ar flow was sparged into the electrolyte to remove dissolved CO. During the 4000 s Ar purge, the 1970 cm\(^{-1}\) peak remained largely the same while the 2026 cm\(^{-1}\) peak almost disappeared over time (Figure 2c), implying the existence of two different CO binding sites on the Pt-CNT. To better interpret the above Pt–CO\(\text{L}_{3}\) IR signals, quantitative analysis of the CO binding strength, \(\Delta G_{\text{CO}}\), over various Pt coordination moieties ranging from single carbon vacancy (SV) to four carbon vacancy sites was carried out using DFT calculations (Supporting Information Figure S9 and Table S1). We considered the formation energy of Pt single-atom coordinated in defective carbon vacancy with or without neighboring N-moieties of Pyd and Pyr species, and the most stable moieties are depicted in Figure 2d for both Pt-C and Pt-N-C coordination structures.\(^{48-50}\) The Pt(111) model surface was employed as a reference, with a simulated \(\Delta G_{\text{CO}}\) of \(-0.9\) eV and a calculated CO\(_2\) wavenumber of 2047 cm\(^{-1}\) without a scaling correction,\(^{51}\) which approximates calculated literature values\(^{52,53}\) and the experimental value of 2082 cm\(^{-1}\). Though the M–N\(_4\) structure-like metal porphyrin or

Figure 1 | Physical characterizations of Pt-CNT catalyst. (a) High-resolution TEM image, (b) AC-STEM image, (c) Pt \(\text{L}_{3}\)-edge EXAFS spectra in the \(R\) space, and (d) corresponding XANES spectrum of Pt-CNT in comparison with Pt foil and PtO\(_2\) references. (e) Simulated charge density distribution of the Pt single-atom confined in graphene vacancies with or without neighboring N dopant. Blue and yellow represent electron depletion and accumulation, respectively.
phthalocyanine is a widely used model moiety in SAC studies with Co or Fe central atom, it was noted that the carbon double vacancy (DV) anchored Pt–N₄–CDV configuration was not energetically favorable for CO binding with COL desorbing spontaneously from the site, which largely excludes its contribution to the observed IR peaks. A much stronger CO adsorption strength was noticed on Pyr Pt–N–C₁Vac as compared with Pt–C counterparts, together with a redshift of simulated ν(COL) frequency on the former Pt–N–C coordination. In contrast, weaker CO adsorption with a blueshift was observed for Pt–C coordination (Pt–C₅V and Pt–C₄Vac moieties). From both the highly sensitive ATR-IR characterization of CO₀ ads and the theoretical modeling, the 2026 cm⁻¹ band reflects the weak CO adsorption at the Pt–C coordination sites and the 1970 cm⁻¹ band reflects the strong CO adsorption at the Pt–N–C coordination sites. In other words, the distinct coordination structures around Pt atoms of a SAC can be differentiated by electrochemical ATR-IR spectroscopy.

To further investigate the effect of coordination structure on catalytic activity, we compared CO₀ ads...
electrooxidation on the identified Pyr Pt–N–C moiety of the Pt-CNT versus the bulk Pt surface. Figures 3a and 3b show series of potential-resolved IR spectra taken during the positive-going potential sweep on the Pt-CNT and the Pt film, respectively. The frequency of ν(CO) band shifts linearly from 1970 to 1985 cm$^{-1}$ on Pt-CNT during the positive-going potential sweep from 0.4 to 1.2 V, whereas that of ν(CO) on bulk Pt increases from 2071 to 2078 cm$^{-1}$ at 0.4–0.6 V and then decreases to 2066 cm$^{-1}$ at more positive potentials. At double-layer potential region, the electrochemical Stark-tuning effect ($d\nu/DE$) is mainly responsible for the observed ν(CO) blueshift on both Pt-CNT and bulk Pt, which is proportional to the surface electric field and directly related to the applied potential. At CO$_{ad}$ oxidation potentials, the decreased ν(CO) frequency for bulk Pt is mainly associated with the largely weakened dipole–dipole interaction from decreased CO$_{ad}$ coverage that overrides the Stark effect. In contrast, since the lateral CO–CO interaction is negligible for isolated Pt sites, the ν(CO) frequency increases monotonically with increasing potential due to the sole Stark-tuning effect. On the bulk Pt surface, CO$_{ad}$ oxidation starts at ca. 0.6 V as derived from both the onset potential in Figure 3c and the fast decay of the integrated ν(CO) band intensity in Figure 3d. In contrast, the oxidation removal of CO$_{ad}$ on the Pt-CNT starts at ~0.8 V with a small oxidation current plateau due to the low Pt content. As noted in Figure 2d and Supporting Information Table S1, the stronger CO binding strength on the Pyr Pt–N–C moiety than on the bulk Pt surface at least partly accounts for this sluggish CO oxidation kinetics. To better interpret the different CO$_{ad}$ oxidation behaviors, DFT calculations were carried out to study the reaction energetics from the following two CO$_{ad}$ electrooxidation pathways.

In general, the L–H mechanism is widely accepted for CO* electrooxidation on continuous Pt sites with neighboring OH* species resulting from dissociative adsorption of H$_2$O:

$$\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* \rightarrow \cdot + \text{CO}_2 + \text{H}^+ + \text{e}^- (L–H \text{ mechanism})$$

While on isolated Pt sites, the E–R mechanism is also considered, in which H$_2$O molecule directly interacts with the adsorbed CO* to form COOH* on an isolated Pt atom:

$$\text{CO}^* + \text{H}_2\text{O} \rightarrow \text{COOH}^* + \text{H}^+ + \text{e}^- \rightarrow \cdot + \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- (E–R \text{ mechanism})$$
where * represents the active site (Figure 4a). Free-energy diagrams of these two pathways are comparatively plotted in Figures 4b and 4c for Pt(111) and the Pt–2NPyr–C1Vac moiety, respectively, together with free-energy corrections summarized in Supporting Information Tables S2 and S3. The thermodynamic limiting potentials are annotated as \( U_L \) and the activation barriers for CO–OH coupling are included as blue lines. We noted that 0.7 eV activation barrier predicts reasonable kinetics at room temperature.\(^5\) The L–H pathway was found to predominate on the Pt(111) surface with a low coupling barrier of 0.36 eV and a theoretical onset potential of \( \sim 300 \) mV earlier compared with the E–R pathway. This is in good agreement with earlier reports that neighboring OH* species arising from dissociated H2O could largely aid in removing COad on the Pt site.\(^5,6,0,62\)

With regard to the L–H pathway on the strong CO* binding site of representative Pt–N–Cpyr moiety as strong CO* binding site via either the L–H mechanism (left panels) or E–R mechanism (right panels) without the applied potential, i.e., \( U = 0 \) V\(_{\text{RHE}}\). Most stable configuration of (CO* + OH*) and relevant energy barrier of the coupling step to form COOH* (marked in blue) are shown as inserts. \( U_L \) represents the theoretical limiting potential that makes all electrochemical reaction steps energetically downhill (marked in black arrows).

**Figure 4** | (a) Schematic of COad electrooxidation steps and corresponding free-energy diagrams on (b) Pt (111) surface and (c) representative Pt–N–Cpyr moiety as strong CO* binding site via either the L–H mechanism (left panels) or E–R mechanism (right panels) without the applied potential, i.e., \( U = 0 \) V\(_{\text{RHE}}\). Most stable configuration of (CO* + OH*) and relevant energy barrier of the coupling step to form COOH* (marked in blue) are shown as inserts. \( U_L \) represents the theoretical limiting potential that makes all electrochemical reaction steps energetically downhill (marked in black arrows).

A synergistic investigation combining in situ spectroelectrochemistry and ab initio simulation has been applied to study the local coordination environment and the reactivity of Pt-CNT SAC. Using CO as a probe molecule, two different Pt coordination structures, that is, a Pyr Pt–N–C moiety with strong CO* binding and a Pt–C moiety with weak CO* binding, have been successfully titrated. Furthermore, a unique COad electrooxidation mechanism on the pinpointed pyrrolic Pt–N–C moiety of the Pt-CNT SAC is spectrally and energetically revealed
at the molecular level. This synergetic approach on the Pt-CNT prototype provides insights into the SAC structure-activity relationship, and we also expect more potential coordination structures discernable with appropriate surface probe molecules coupled with advanced first-principle calculations. Given a broad range of applications for SACs, the demonstrated methodology here may deepen the mechanistic understanding and promote the discovery of novel SACs with precise structural engineering.

Supporting Information

Supporting Information is available and includes additional TEM images, EXAFS fitting curves and LCF at near-edge XPS spectra, cyclic voltammograms, time-resolved ATR-IR spectra on control samples, coordinative moieties illustration, and a list of computational details.

Conflict of Interests

The authors declare no conflict of interest.

Acknowledgments

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