

Exploring the Nanomechanical Properties of a Coordination-bond Based Supramolecular Polymer

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Electronic Supplementary Information

Abstract Due to their dynamic nature and strength tunability, metallo-supramolecular polymers have been introduced into various materials. The mechanical strength of the metallo-supramolecular polymers in the system directly influences the mechanical properties (e.g., the toughness) of the materials. Therefore, it is necessary to explore the mechanical behavior of the metallo-supramolecular polymers. Herein, we present a single-molecule method to systematically explore the chain structure and mechanical properties of metallo-supramolecular polymer by using a loop protected architecture. Notably, we found that the mechanical stability of the individual chain, which is determined by the strength of terpyridine-Fe²⁺-terpyridine (tpy-Fe²⁺-tpy) bonds, was about 0.6–1.0 nN, depending on the pulling speed. This value is around three times higher than those measured using old methods. In addition, the unique loop protected structure further reduces the interference of non-specific polymer-AFM tip (or polymer-substrate) interactions on the quantification of the actual strength and kinetic parameter of noncovalent interactions in supramolecular polymers. Furthermore, the single chain flexibility of the metallo-supramolecular polymer was investigated and found to be comparable to the corresponding covalent analogues. Our findings provide a new way to explore the force response of supramolecular polymers composed of metal-ligand interactions and will be useful for the design of metallo-supramolecular polymer-based functional materials with tailored mechanical properties.

Keywords Supramolecular polymer; Single-molecule force spectroscopy; Coordination chemistry; Polymer mechanochemistry

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INTRODUCTION

Supramolecular polymers are assembled through noncovalent interactions, such as metal-ligand interactions,^[1,2] π - π interactions,^[3] host-guest interactions,^[4,5] hydrogen bond^[6,7] and so on.^[8] It has many advantages and is widely applicable in the construction of functional materials. First, the strength of the supramolecular polymer can be easily adjusted by combining different noncovalent components, thus changing the mechanical properties of the material.^[9] Second, the formation of the noncovalent interactions is often a thermodynamically spontaneous process, which is conducive to the preparation of self-healing materials.^[10] In addition, supramolecular polymers can also exhibit physical or chemical stimuli-responsiveness owing to noncovalent components,^[11] which are beneficial for obtaining smart multi-functional materials. These unique and

novel properties make supramolecular polymers have broad prospects in degradable materials, optoelectronic materials, biomedical materials and other related fields.^[12]

Metallo-supramolecular polymers that are polymerized using metal-ligand interaction as driving force have attracted immense attention due to their combination of traditional polymers and the electronic, magnetic and catalytic properties of metals.^[13–17] Among the numerous building blocks, terpyridine and its derivatives have been widely used in the construction of metallo-supramolecular polymers because of their rich coordination capabilities with different transition metals to form a wide variety of complexes.^[18–25] The mechanical properties, one of the key factors that determines the application of the materials, are influenced by the strength and dynamics of the polymer chains.^[26] Therefore, research on the mechanical response of the metallo-supramolecular polymer plays a crucial role in the design of high-performance metal-containing polymers materials. However, traditional ensemble characterization methods cannot provide quantitative information on the mechanical stability of an individual metallo-supramolecular polymer chain. Atomic force microscopy (AFM)-based single-molecule force spectroscopy (SMFS) is a powerful tool for investigating the mechanical be-

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havior and higher-order structure of the polymer chain at the single-molecule level.^[27–31] In recent decades, AFM-based SMFS has been widely applied to directly measure intra- and inter-molecular interactions^[32–49] of strong (covalent) bonds^[37–42] as well as weak interactions.^[43–49] This advanced technique has also been used to explore supramolecular polymers and can give direct information of structure and mechanical properties.^[50,51] However, in those old experiments, as long as the interactions between adjacent monomers get ruptured the SMFS experiment is terminated and it is normally quite difficult to reestablish the molecular link *in situ*. As a result, the detection efficiency was low. In addition, it is quite difficult to tell where the supramolecular polymer ruptures (*i.e.*, the monomer-monomer interaction or the polymer-AFM tip/substrate interaction) during stretching due to the lacking of force fingerprint. Therefore, it is impossible to explore the kinetic information on the chain breakage.

In this work, we designed a polymer that contained multiple tpy-M-tpy ($M = \text{Fe}^{2+}$ or Zn^{2+}) coordination bonds in the backbone with a protecting loop connecting the adjacent terpyridine groups (Fig. 1).^[52] This design allows more systematically study on the structure, stability, and dynamics of metallo-supramolecular polymer chain, while largely excluding or minimizing the contribution of non-specific interactions to the measurement and offers fingerprint force signals that can be used to identify and screen specific single-molecule rupture events.^[53] Sawtooth-pattern force curves were obtained during the AFM-SMFS experiments, which corresponded to the successive rupture of coordination

bonds in the metallo-supramolecular polymer. Kinetic parameters on the unbinding process of the tpy- Fe^{2+} -tpy coordination bond were achieved *via* dynamic force spectroscopy. The effect of cation on the mechanical properties of polymer chain was also explored, which is not achievable using normal supramolecular polymer without the protecting loop. In addition, the flexibility of the metallo-supramolecular polymer was obtained unambiguously with the help of force fingerprint. As a comparison, old sample preparation and measurements were performed on the same coordination bond, which produced unbinding forces that were about three times as small due to the large contribution of non-specific interactions. These experiments demonstrate a new method to detect the mechanical behavior of metallo-supramolecular polymers at the single-molecule level and provide quantitative information for the design of stress-responsive materials.

EXPERIMENTAL

Preparation of Functionalized Silicon Slices and AFM Tips

Silicon wafer was cut into 1.4 cm × 1.4 cm slices and immersed into a freshly prepared piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2=7/3$, V/V) for 20 min, followed by rinsing with deionized water, and drying in an oven at 115 °C for 40 min to remove remaining water. The vapor-phase deposition method was used to silanize the hydroxylated slices by putting them into a sealed desiccator filled with 3-aminopropyldimethylmethoxysilane (APDMMS) vapor for 3 h at room temperature. Subsequently, the slices

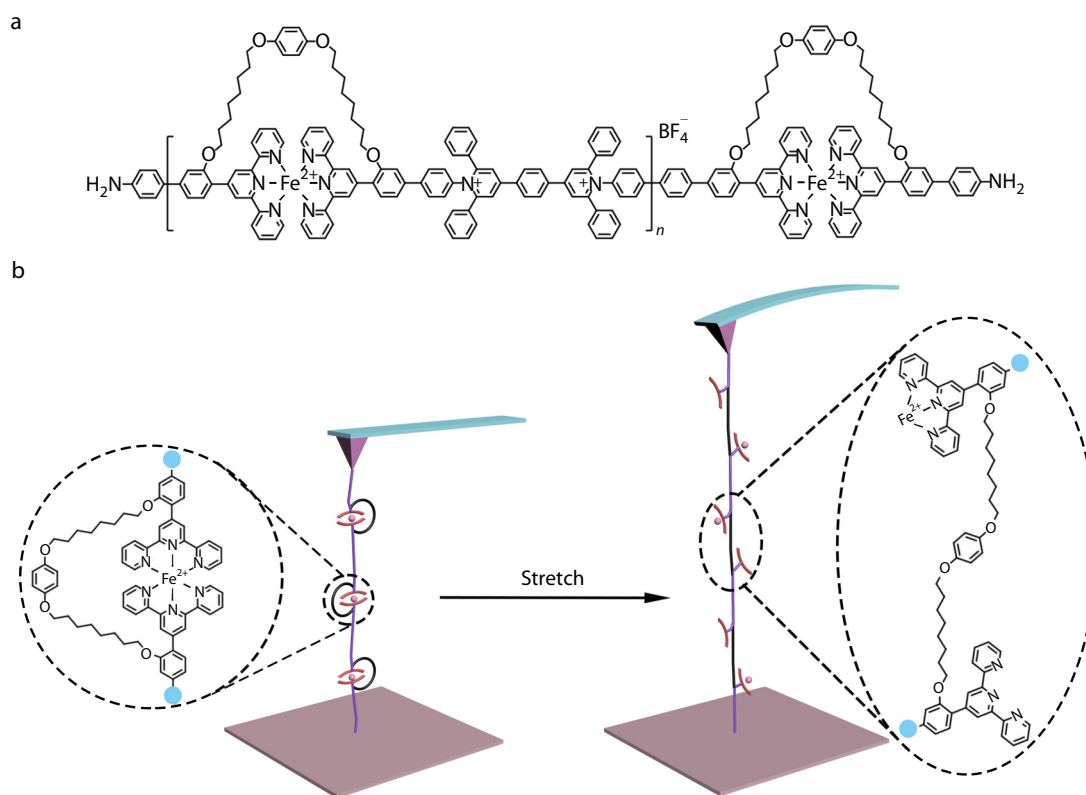


Fig. 1 Chemical structure and single-molecule force spectroscopy study of Polymer-Fe: (a) Chemical structure of Polymer-Fe; (b) Schematic illustration of the force-induced rupture of multiple coordination bonds in a single polymer chain.

were rinsed by methanol and heated in a 110 °C oven for 10 min. The AFM tip (MLCT, Bruker Nano, Santa Barbara, CA) was treated in the similar method to obtain the amino-group modified tip.

Preparation of Polymer-decorated Substrates and NHS-functionalized AFM Tips

Amino-group modified tip and substrate were soaked in a DMF solution containing 1-(3-(dimethylamino)-propyl)-3-ethylcarbodi-imide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS) and oxalic acid for 30 min and washed with DMF. After the activation step, the NHS-functionalized substrate was immersed into a DMF solution containing 2.5 mg/mL Polymer-Fe (or Polymer-Zn, Polymer-Blank) and then rinsed with DMF after 2 h to remove unfixed polymer chains.

Preparation of Terpyridine-decorated Substrates and AFM Tips

NH₂-functionalized tip and substrate were immersed into a DMF solution containing EDC, NHS and HOOC-PEG-COOH (MW=2000 Da) for 20 min, followed by rinsing with DMF. Subsequently, the activated substrate and tip were exposed to a solution of 2 mg/mL tpy-diphenyl-NH₂ prepared in DMF. Finally, the modified substrate and AFM-tip were washed thoroughly with DMF.

Preparation of Fe²⁺-terpyridine Complexes-decorated Substrates

A saturated solution of ferrous sulfate was prepared in DMF, and the supernatant was diluted 20 times and dropped 30 µL on the tpy-diphenyl-NH₂ modified substrate for 10 min at room temperature. After this procedure, the substrate was washed with DMF to remove uncoordinated Fe²⁺.

SMFS Experiments

All AFM-based SMFS experiments were performed on Force Robot or biological AFM NanoWizard II (JPK instrument AG, Berlin, Germany) in contact mode at room temperature. The AFM tips (MLCT, Bruker Nano, Santa Barbara, CA) were used and the spring constants of the cantilevers were measured by thermal noise method. The measured values were approximately 0.15–0.17 N/m. For polymer systems, a NHS-coated cantilever was put into contact with polymer-decorated substrate to pick up the NH₂-terminated polymers on the substrate (at contact force of 0.3–3 nN and contact time of 2–3 s). Similarly, when using old detection methods, a tpy-PEG cantilever was brought into contact with Fe²⁺-terpyridine (or terpyridine) complexes-decorated substrates (at ~0.2 nN for 2 s). Corresponding signals were obtained during the separation of the AFM tip and the substrate. The experimental buffer is DMF and the stretching speed was 1 µm/s in all experiments unless noted otherwise. All force curves were analyzed by using custom software written in Igor Pro (Wavemetrics) and the most probable values were obtained by fitting the histograms with Gaussian function.

RESULTS AND DISCUSSION

Investigation of Mechanical Stability of the Metallo-supramolecular Polymers

The polymer employed in this study was prepared using a transition metal complex and diphenylpyrylium derivatives (Polymer-Fe). In each repeated unit of the transition metal

complex, there is a tpy-Fe²⁺-tpy core with a bis-loop architecture (Fig. 1a). Detailed information about the synthesis and characterization of the polymer is shown in Schemes S1 and S2, Figs. S1–S10 (in the electronic supplementary information, ESI).

Both ends of the polymer chain have amino groups that can be chemically coupled to the AFM tip and the substrate surface *via* the amide bond. During the force spectroscopy measurements, a *N*-hydroxysuccinimide (NHS)-functionalized AFM tip was brought toward the silicon slide to pick up the polymer chain, which was covalently immobilized on the silicon substrate by one of the two amino groups on the polymer. When the AFM tip is in contact with the polymer, the NHS group on the AFM tip can react with the other amino group at the free end of the immobilized polymer chain, resulting in the formation of a polymer bridge between the AFM tip and the substrate. The polymer chain is stretched during the separation of the AFM tip and the substrate at a constant pulling speed (1000 nm·s⁻¹) (Fig. 1b). The AFM pulling experiments were performed in a liquid medium of dimethylformamide (DMF).

Fig. 2(a) shows a representative stretching curve obtained from Polymer-Fe. As can be seen from the force curve, a sawtooth pattern appears when the external force reaches about 770 pN. Such a sawtooth pattern can be attributed to the sequential unbinding of the individual tpy-Fe²⁺-tpy bonds (Fig. 2b).

In accordance with the study hypothesis, the distances between adjacent sawtooth peaks were very similar. Using the extended freely jointed chain (eFJC) model,^[54] the most probable value of ΔL was determined to be 1.7±0.2 nm (Fig. 2c), which agreed well with the theoretical length increments observed during the loop opening process (detailed information about the quantum chemical calculations on the length change is shown in Figs. S18 and S19 in ESI). In addition, the sawtooth pattern does not appear until the polymer chain is stretched to a certain length, which can exclude the contribution of nonspecific polymer-interface (polymer-substrate or polymer-AFM tip) interactions. In our current system, when a coordination bond ruptures, the protect linker will stretch, preventing the complete rupture of the supramolecular chain between the AFM tip and the substrate, followed by the release of hidden length. When this occurs, the stretching force decreases until the protect linker reaches its contour length, and the whole polymer chain is stretched again (Fig. 2b). This process can produce a small force peak in the stretching curve, and the sequential rupture of the coordination bonds and release of length produces the sawtooth pattern observed in the force curve. Another possible reason for observing the sawtooth pattern is the sequential desorption of the repeating unit in the polymer chain from the solid substrate.^[55] If this is the case, the sawtooth pattern would appear from the very beginning of the stretching process. However, in the actual force curves, the sawtooth peaks do not appear until a certain extension length (*e.g.*, ≥10 nm) is reached.

To determine the mechanical stability of the polymer chain, the peak forces in the sawtooth peaks were analyzed. The statistical results show that the most probable rupture force of the well-resolved small peaks is 769±78 pN (Fig. 2d), which corresponds to the mechanical strength of the tpy-Fe²⁺-tpy

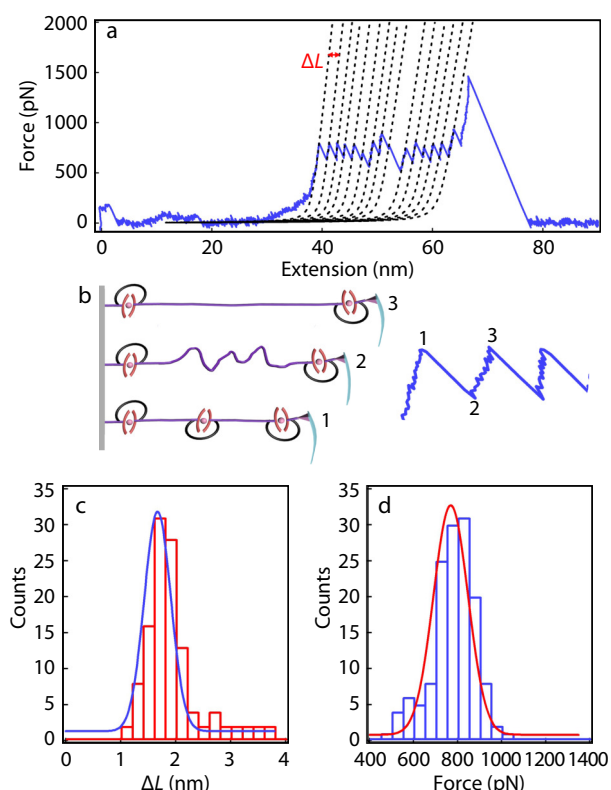


Fig. 2 Force-induced successive rupture of tpy-Fe²⁺-tpy coordination bond in metallo-supramolecular polymer. (a) Representative force-extension curve of Polymer-Fe obtained in DMF (blue curve). eFJC fit curves (black dashed lines) allow the contour length increments ΔL of each peak to be determined; (b) Schematic illustrations of the successive rupture of the coordination bonds; (c) Histogram of ΔL for all force-extension curves. Gaussian fitting (blue line) shows an average ΔL of 1.7 ± 0.2 nm; (d) Distribution of the rupture forces for the coordination bonds. Gaussian fitting (red trace) of the force histogram provides a calculated average force of 769 ± 78 pN.

coordination bond. This value is much higher than those of weak interactions such as hydrogen bonds, π - π , or hydrophobic interactions. This rupture force is also higher than most coordination bonds reported prior^[46–48] but is slightly lower than the stability of the recently reported palladium-carbine and ferrocene mechanophores, which requires about 1 nN to destroy.^[56,57] Therefore, the measured mechanical strength of tpy-Fe²⁺-tpy is reasonable.

To further prove that the sawtooth pattern in the force curves came from the sequential rupture of the coordination bond in the polymer and explore the reversibility of metallo-supramolecular polymer formation, cyclic single-molecule stretching-relaxation experiments were carried out on the same polymer chain. In these cyclic SMFS experiments, the polymer chain was stretched to a certain length to make part of the coordination bonds rupture, but this stretching was stopped before the polymer chain detached from either the substrate or the AFM tip. Afterward, the stretched polymer chain was completely relaxed at zero force for 2 s before a subsequent stretching cycle. In doing this, a single polymer chain could be manipulated repeatedly (Fig. 3a). Fig. 3(b) shows the successive force-extension curves obtained during

the repeat stretching-relaxation cycles. It can be found that during the first stretching cycle, the sequential rupture events of the coordination bonds are visible (shown as sawtooth peaks in the black trace); however, there was no sawtooth profile on the relaxation trace. A pronounced hysteresis between the stretching and relaxation traces could be observed, indicating that the ruptured coordination bond would not re-form immediately during relaxation and that the stretching-relaxation cycle was an energy-dissipating process. Interestingly, in the subsequent stretching curve, the sawtooth feature was again observed, indicative of the re-formation of tpy-Fe²⁺-tpy bonds after the polymer chain was relaxed. Such a relatively quick re-formation of the tpy-Fe²⁺-tpy bond indicates that the Fe²⁺ ion did not diffuse away from the ligand (terpyridine), and it is very likely that metal ions randomly bond to one side of the two terpyridine pairs to form a metastable structure (-Fe²⁺-tpy, see Fig. 1b). When the external force is removed, the metastable structure can find the other ligand to form the full tpy-Fe²⁺-tpy complex.^[58] This reversible binding behavior provides a foundation for further study in the self-healing properties of coordination bond-based responsive materials.

Dynamic Force Spectroscopy Analysis

To deepen our understanding of the bond-breaking process between terpyridine and Fe²⁺, the unbinding experiments were performed at six different pulling velocities, ranging from 100 nm·s⁻¹ to 5000 nm·s⁻¹. The molecular design in our current system made highly efficient and unambiguous data collection on rupture forces at different pulling speed possible. At each pulling speed, a characteristic sawtooth profile, which corresponded to the sequential rupture of coordination bonds, was obtained (Fig. S20 in ESI). The rupture forces of the tpy-Fe²⁺-tpy bond were plotted against the force-loading rate (LR), as shown in Fig. 4.

The Bell-Evans model was then used to fit the data and derive the main kinetic parameters.^[59,60] It was found that the rupture force increased linearly with the natural logarithm of the force loading rate, which indicates that the rupture of the tpy-Fe²⁺-tpy bond is a non-equilibrium process in the time scale of the single-molecule pulling experiment.^[43] And the kinetic parameters could be calculated according to Eq. (1):

$$F_{\text{rupture}} = \left(\frac{k_B T}{x_\beta} \right) \ln r + \left(\frac{k_B T}{x_\beta} \right) \ln \left(\frac{x_\beta}{k_B T k_{\text{off}}} \right) \quad (1)$$

where F_{rupture} is the rupture force, k_B is the Boltzmann constant, x_β is the distance from the binding to the transition state, T is the temperature in Kelvin, and r is the loading rate. The rate of spontaneous rupture at zero force (k_{off}) was calculated as $8.09 \times 10^{-3} \text{ s}^{-1}$, while the distance between the binding state and the rupture transition state (x_β) was equal to 0.066 nm, which is nearly half that of the Fe(III)-thiolate bond in rubredoxin.^[61] These parameters deepened our understanding of the molecular mechanism underlying the rupture of the tpy-Fe²⁺-tpy coordination bond and dynamic stability of the metallo-supramolecular polymer.

Effect of Cation Species

To further demonstrate the universality of the polymer-based experimental design, this method was also used to measure the mechanical stability of supramolecular polymers composed of terpyridine and zinc ions. Tpy-Zn²⁺-tpy complexes (Polymer-Zn)

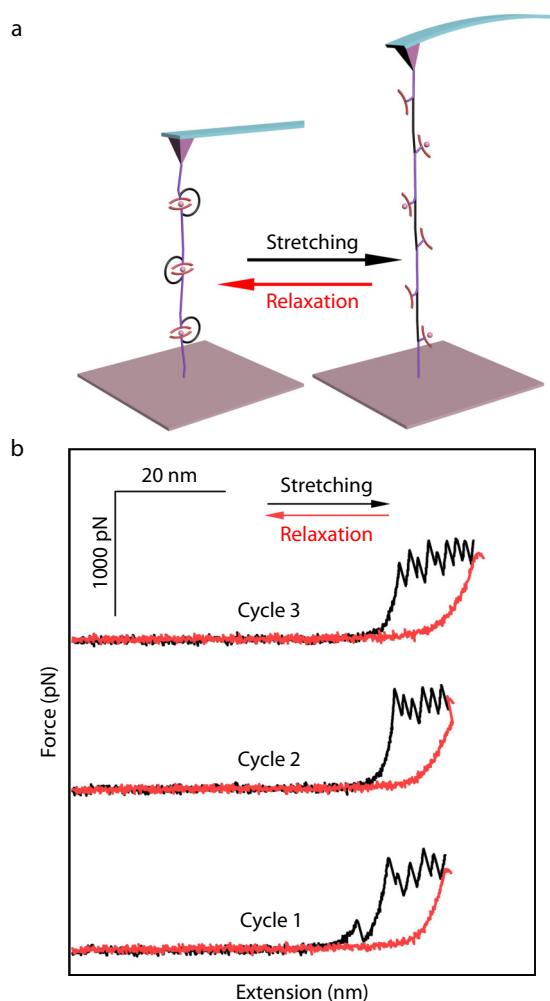


Fig. 3 SMFS study on the reversibility of metallo-supramolecular polymer. (a) Schematic representation of cyclic SMFS experiments; (b) Typical cyclic stretching-relaxation curves obtained on Polymer-Fe at a speed of $1000 \text{ nm}\cdot\text{s}^{-1}$. Black and red curves represent stretching and relaxation curves, respectively.

were explored under the same conditions, where the core of the coordination complex is replaced by Zn^{2+} ions (Figs. S1–S6, S11–S15 in ESI). Characteristic sawtooth patterns were also obtained (Fig. S21a in ESI). The average rupture force and length increments between successive peaks are shown in Figs. S21(b) and S21(c) (in ESI). Fig. 5 shows a direct comparison between the spacing and peak force of the sawtooth pattern obtained in $\text{tpy-Zn}^{2+}\text{-tpy}$ and $\text{tpy-Fe}^{2+}\text{-tpy}$. It can be observed that the sawtooth spacings for both systems were similar (Fig. 5a), while the peak force decreases from 769 pN to 556 pN when the central metal ion is switched from Fe^{2+} to Zn^{2+} (Fig. 5b). According to the literature,^[62] the stability of $\text{Zn}^{2+}\text{-tpy}$ is weaker than that of $\text{Fe}^{2+}\text{-tpy}$, so the force needed to destroy the coordination bond was lower, which is in good agreement with our findings and suggests that the sawtooth pattern comes from the unbinding of the tpy-metal-tpy coordination bond.

Investigation of Single-chain Elasticity of Metallo-supramolecular Polymer

Apart from the mechanical stability, the elasticity/flexibility of

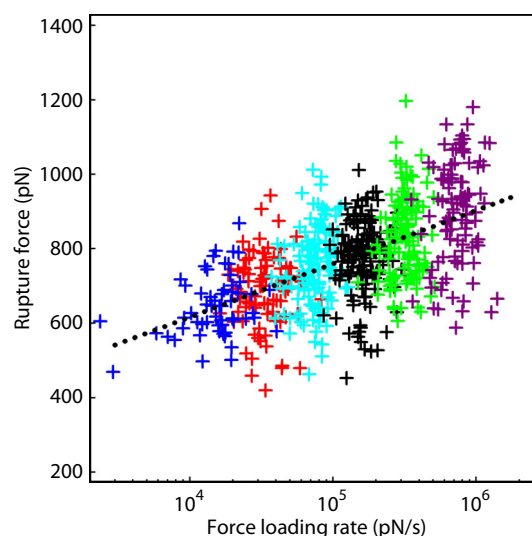


Fig. 4 Loading rate dependence of the rupture forces. The dotted line is the fit of the Bell-Evans model with fitting parameters of $x_{\beta}=0.066 \text{ nm}$ and $k_{\text{off}}=8.09\times 10^{-3} \text{ s}^{-1}$. Cantilever retraction velocities were varied: $100 \text{ nm}\cdot\text{s}^{-1}$ (blue), $200 \text{ nm}\cdot\text{s}^{-1}$ (red), $500 \text{ nm}\cdot\text{s}^{-1}$ (cyan), $1000 \text{ nm}\cdot\text{s}^{-1}$ (black), $2000 \text{ nm}\cdot\text{s}^{-1}$ (green), $5000 \text{ nm}\cdot\text{s}^{-1}$ (purple).

the supramolecular polymer is also an important parameter that affects the overall mechanical properties of the corresponding materials. Different from traditional covalent polymers, the repeat units in our current metallo-supramolecular polymer are connected by coordination bond, which exhibit smaller mechanical stability as compared with most of the covalent bonds. How much will such supramolecular interaction affect the flexibility of the polymer chain? To answer this question, worm-like chain (WLC) model was used to describe the flexibility of individual supramolecular polymer chain.^[63] The WLC fitting results showed that the persistence length for Polymer-Fe (or Polymer-Zn) is $1.37\pm 0.45 \text{ nm}$ (Fig. 6a). This result shows that the metallo-supramolecular polymer chain is relatively rigid, which is comparable to the rigidity of oxidized polyaniline (PANI).^[64] From the backbone structure (Fig. 1a), we can find that the repeating units between adjacent $\text{tpy-Fe}^{2+}\text{-tpy}$ complexes is composed of conjugated benzene rings, which is similar to

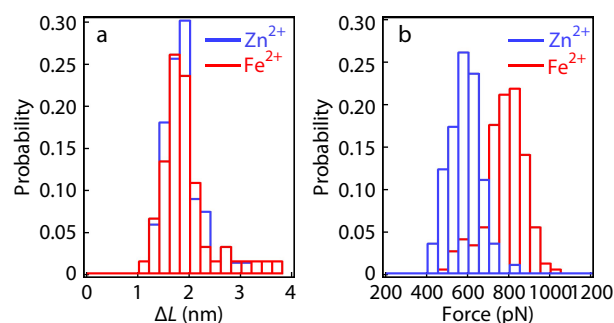


Fig. 5 Effect of cation species on the mechanical stability of polymers based on tpy-metal-tpy coordination bonds. (a) Distribution of length increments (ΔL) between adjacent peaks in the force-extension curves of Polymer-Fe ($\text{Fe}^{2+}\text{-tpy}$) (red bar) and Polymer-Zn ($\text{Zn}^{2+}\text{-tpy}$) (blue bar); (b) Distribution of the rupture forces for the coordination bonds of Polymer-Fe ($\text{Fe}^{2+}\text{-tpy}$) (red bar) and Polymer-Zn ($\text{Zn}^{2+}\text{-tpy}$) (blue bar).

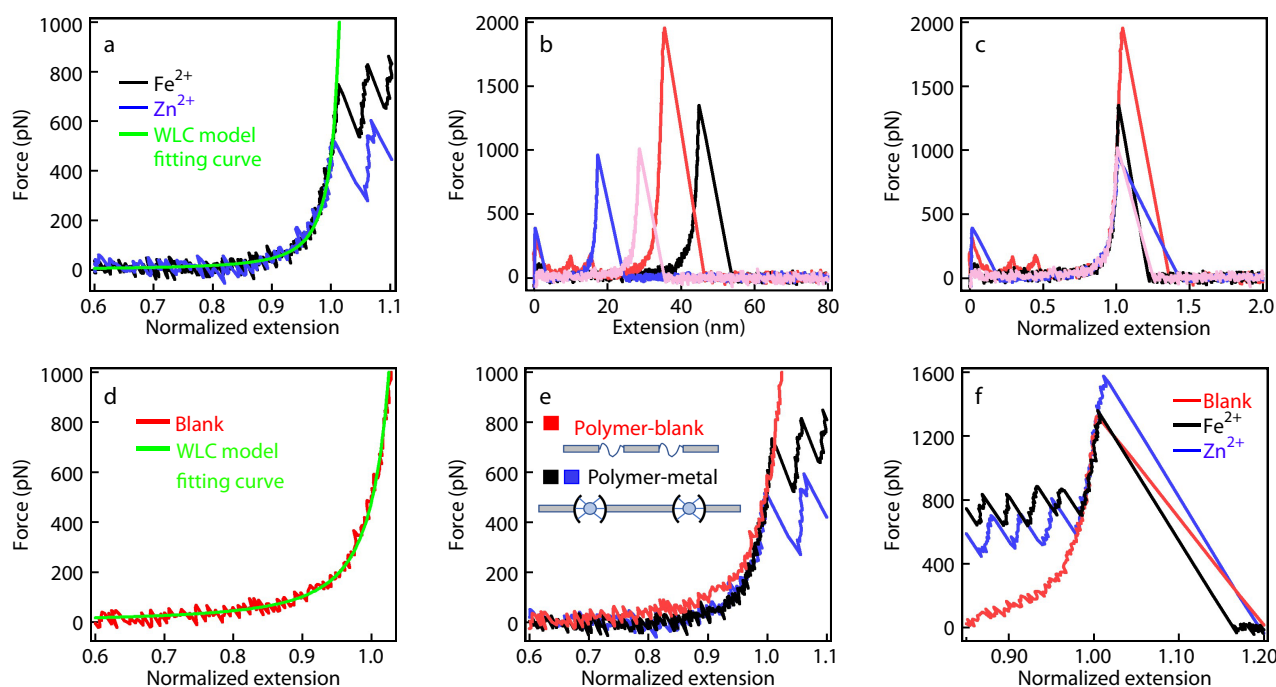


Fig. 6 Comparison on the flexibility of Polymer-Fe (Polymer-Zn) and Polymer-blank. (a) Typical normalized *F-E* curves of Polymer-Fe (black curve) and Polymer-Zn (blue curve) obtained in DMF. The green trace is a WLC fit to the force curve with a persistence length of $P=1.20$ nm. (b) Representative force-extension curves of Polymer-blank with different contour lengths in DMF at a pulling speed of $1000\text{ nm}\cdot\text{s}^{-1}$. (c) Normalized *F-E* curves of those shown in (b). (d) WLC fit (green trace) on a normalized *F-E* curves of Polymer-blank (red curve) obtained in DMF. The WLC fit produced a persistence length of $P=0.38$ nm. (e, f) Comparison of normalized *F-E* curves of Polymer-Fe (black trace), Polymer-Zn (blue curve) and Polymer-blank (red trace) before and after the sawtooth peaks.

that of oxidized PANI and quite rigid. The rigidity of the metallo-supramolecular polymer indicates that the “joint” (*i.e.*, the $\text{tpy-Fe}^{2+}\text{-tpy}$) in between the rigid repeating unit is not flexible. However, when the metal ion is removed the nano-mechanical properties of polymer chain (Polymer-blank) (Figs. S16 and S17 in ESI) become quite different. It is interesting to find that there is no sawtooth pattern in the stretching curve of Polymer-blank, and only a monotonic increase of force with extension can be observed, as shown in Fig. 6(b). The force curves can be normalized at their contour length and are well superimposed, which indicates that they originated from the stretching of the same kind of polymer chain (Fig. 6c). WLC fitting produces the persistence length of 0.38 ± 0.04 nm (Fig. 6d), indicating that polymer chain (Polymer-blank) becomes very flexible which is comparable to those of a common flexible polymer chain with ethylene backbones.^[65] This is reasonable since in the absence of metal ions and coordination bonds the polymer chain (polymer-blank) behaves like a three-section cudgel, whose flexibility is determined by the flexible joints/linkers (Fig. 6e). In our current system, the flexible linker is the protecting ethylene oxide loop (Fig. 1a). When the force-extension curves obtained in the absence and presence of metal ions were normalized at high force regions (*e.g.*, higher than the sawtooth peak), the normalized curves can be superimposed well (Fig. 6f), which further proves that the occurrence of small sawtooth peaks in the metallo-supramolecular polymer was caused by the sequential unbinding of coordination bonds in the backbone. Because after the rupture of all tpy-M-tpy ($M=\text{Fe}^{2+}$ or Zn^{2+}) coordination

bonds in the polymer chain (*i.e.*, when the sawtooth pattern stops), the single-chain elasticity of polymer with metal ions mainly comes from the contribution of bond angle and length change in the backbone (Fig. 1b), which is the same as that of Polymer-blank without metal ions.

Investigation of $\text{tpy-Fe}^{2+}\text{-tpy}$ Coordination Bond by the Old SMFS Method

As a control, the mechanical strength of a single $\text{tpy-Fe}^{2+}\text{-tpy}$ coordination bond was measured using old SMFS method. The experimental scheme is depicted in Fig. 7(a).

To measure this, the tip was linked with an exposed terpyridine moiety, using poly(ethylene glycol) (PEG) as the linker (MW, 2000 Da), and gradually brought toward the substrate to interact with the tpy-Fe^{2+} complex immobilized on the silicon substrate and construct the $\text{PEG-tpy-Fe}^{2+}\text{-tpy-PEG}$ system (detailed information about the synthesis and characterization of terpyridine unit is provided in Scheme S1 and Figs. S1–S3 in ESI).^[66] When the AFM tip was moved away from the substrate, the newly formed $\text{tpy-Fe}^{2+}\text{-tpy}$ coordination bond may rupture. Fig. 7(b) shows typical force curves that have a single-rupture peak, while Fig. 7(c) shows a histogram of the rupture force at a stretching speed of $1000\text{ nm}\cdot\text{s}^{-1}$. It is worth noting that the most probable rupture force of the complex was 291 ± 179 pN (shown as blue columns in Fig. 7c), which is significantly lower than that obtained in the polymer-based system (769 ± 78 pN, Fig. 8), although there is a small population of rupture forces between 600 and 1200 pN. This difference may be ascribed to the contribution of nonspecific interactions, *e.g.*, between PEG–terpy

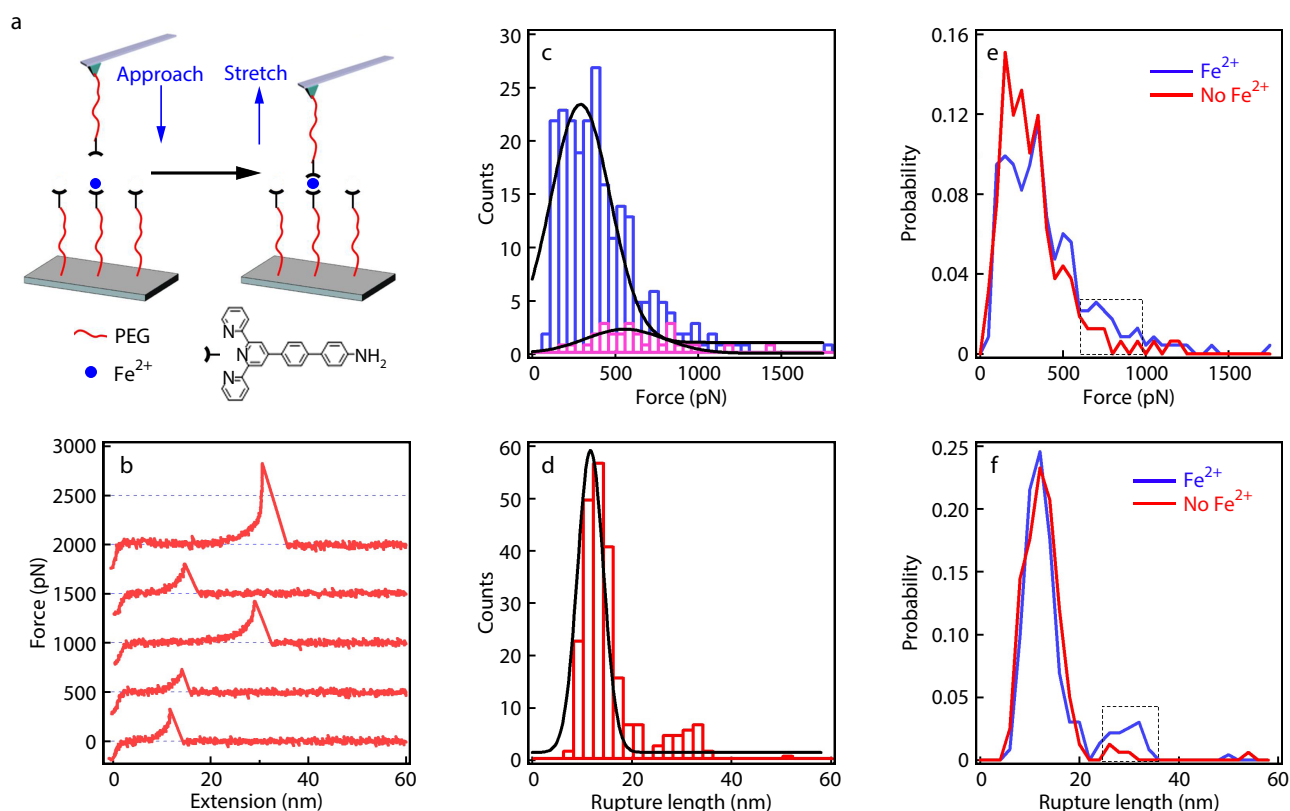


Fig. 7 Force-induced rupture of tpy-Fe²⁺-tpy coordination bond by old SMFS method. (a) Schematic illustration of the old SMFS experiments on coordination bond; (b) Typical force-extension curves for PEG-tpy-Fe²⁺-tpy-PEG complexes at a pulling speed of 1000 nm·s⁻¹ when measured using old methods; (c) Histograms of the rupture force of the PEG-tpy-Fe²⁺-tpy-PEG complexes. Gaussian fitting (black trace) shows average forces of 291 ± 179 pN (blue columns) and 559 ± 239 pN (pink columns); (d) Histogram and Gaussian fit of the rupture length of PEG-tpy-Fe²⁺-tpy-PEG complexes; the most probable length is 11.7 ± 2.6 nm; (e) Superposition of the force distribution of the single peak obtained under different conditions; (f) Superposition of the rupture length distribution of the single peak obtained under different conditions.

and the solid substrate (or the AFM tip). If this is the case, the rupture length should be half that of the PEG-tpy-Fe²⁺-tpy-PEG complex and close to the contour length of the PEG linker. The rupture length distributions were then analyzed, and the results show that the most probable rupture length was 11.7 ± 2.6 nm (see Fig. 7d). The observed length is much shorter than the theoretical length of the PEG-tpy-Fe²⁺-tpy-PEG system (≈32 nm, Fig. 6a) while is similar to the contour length of a single PEG spacer, although there is a small population of rupture lengths above 20 nm.

To exclude the contribution of nonspecific interactions, the rupture force data were screened with a length window, and rupture forces with rupture lengths longer than 24 nm were analyzed. The pink columns in Fig. 7(c) show the distribution of rupture forces with rupture lengths ≥24 nm. A broad distribution of the rupture force data was observed, with a peak value at around 560 pN; this maximum approached the value obtained by our polymer-based method (769 ± 78 pN). This result indicated that the length window aids in the exclusion of contribution from nonspecific interactions. However, the efficiency of data collection is greatly reduced during the screening process. To confirm that the observed major force peak came from nonspecific interactions, the pulling experiment was performed in the absence of Fe²⁺ (Fig. S22a in ESI). Statistical analysis of typical force curves showed that the rup-

ture force was 246 ± 135 pN and the rupture length was 12.1 ± 3.4 nm (Figs. S22b–S22d in ESI). No coordination bonds would form under these conditions due to the absence of Fe²⁺. Therefore, the rupture force must arise from nonspecific interactions between PEG-tpy and the solid substrate (or AFM tip). To compare these results, rupture force and length distribution in the presence and absence of Fe²⁺ were superimposed (Figs. 7e and 7f). These distribution histograms were shown to be very similar apart from the small population of rupture forces above 600 pN and rupture lengths above 24 nm (the dotted box in Figs. 7e and 7f). These results further support our hypothesis that nonspecific interactions contribute greatly to old measurements, and it is quite difficult to unambiguously identify the real rupture signal from the coordination bond, which caused much smaller measured force value of coordination bond (compare the black and red histograms in Fig. 8).

If an old method is used to measure the mechanical strength of the coordination bond, a large number of single-peak force curves must be collected and selected within the "length window". However, force curves with a shorter rupture length due to the rupture of coordination bond would also be discarded, resulting in a decrease in detection efficiency. The above results show that the polymer system can avoid the interference of molecule/substrate (or the AFM tip)

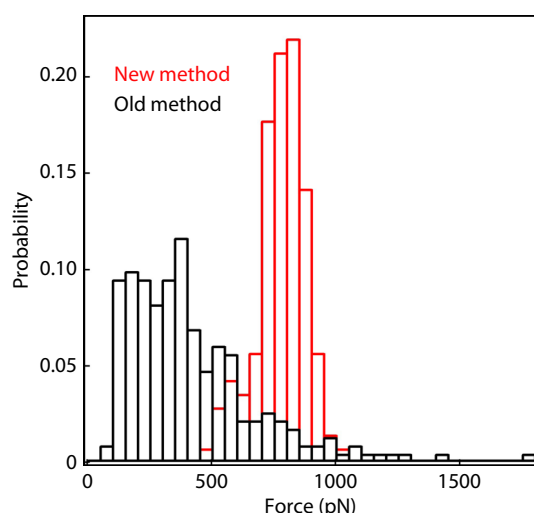


Fig. 8 A comparison on the rupture forces obtained by the new method and old method. Distribution of the rupture force for the coordination complex using old (black columns) and the new polymer-based (red column) SMFS methods.

interactions, and the sawtooth fingerprint in our polymer-based system is more recognizable, allowing for the bond strength to be measured more accurately and efficiently.

CONCLUSIONS

In summary, our results showed that the metallo-supramolecular polymer system with protecting loops is an ideal design to systematically investigate the mechanical properties of coordination bonds-based supramolecular polymer at the single-molecule level via AFM-based SMFS. Our results show that at a normal pulling speed (e.g., $1000 \text{ nm}\cdot\text{s}^{-1}$), the terpyridine-based metallo-supramolecular polymer ruptured at a force of about 770 pN depending on the pulling speed and metal ion species. This force value is nearly three times higher than that measured using PEG-based old method at a similar force loading rate. In the meantime, our current experimental strategy provides more accurate and efficient measurement approach of the metal-ligand interaction than the old single coordination bond detection method. Furthermore, our results also demonstrate that caution should be taken when the traditional PEG-based molecule coupling/immobilization method is adopted for unbinding measurements or biochip detection.

It is worth noting that in the field of polymer mechanochemistry, the quantification on the mechanical stability of the mechanophores is crucial for its further application. In addition, mechanophores exhibit different mechanical stabilities, ranging from a few piconewtons to several hundred or several thousand piconewtons,^[34,37,41,45] are needed for different level of force sensing. Currently, the research on the stability of mechanophores mainly focuses on the high- and low-force regions. The mechanical strength of this metal-terpyridine-based complex is moderate (several hundred pN), and may be used as a useful mechanophore in the design/preparation of more extensive and precise force response materials.

Moreover, adaptive chemistry is a promising direction in the development of supramolecular chemistry,^[67–69] and the

dynamic tunability and reversibility of coordination bonds, will play very important roles in this regard. The structure and properties of the metallo-supramolecular complex can be adapted by exchanging and recombining different ligands and metal ions in the complex under external physical or chemical stimuli. Our research lays a solid foundation for the study of coordination-bond based adaptive chemistry in complex supramolecular systems, which will be quite useful to disclose the molecular mechanism of the adaptive processes. The relevant research is underway.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2797-y>.

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