CHEMISTRY OF MATERIALS

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Metal–Polymer Soft Framework Ion Gels: Linking Coordination Chemistry to Macroscopic Elasticity

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Cite This: *Chem. Mater.* 2026, 38, 5723–5731

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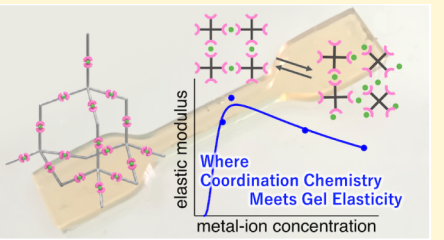
ABSTRACT: Linking molecular interactions to the macroscopic mechanical properties of soft materials remains a major challenge in soft-matter science. Here, we develop metal–polymer soft framework (MPF) ion gels, in which metal–ligand coordination complexes function as network-forming interchain bridges within a structurally homogeneous polymer network. Terpyridine-terminated TetraPEG prepolymers were cross-linked with divalent metal ions in an ionic liquid to form uniform coordination-bonded gel networks. The elastic modulus (G') increased in the order $Mg^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+}$, and this trend was quantitatively reproduced by modeling the equilibrium distribution of bis-terpyridine complexes, $M(tpy)_2^{2+}$, acting as network-forming interchain bridges in the polymer network. By integrating coordination thermodynamics with classical rubber elasticity, we established a quantitative framework that determines the stepwise equilibrium constants (K_1 and K_2) for mono- and bis-terpyridine complex formation and accurately predicts the nonmonotonic dependence of G' on metal-ion concentration. Furthermore, the stress relaxation time (τ) was found to increase with increasing coordination bond strength, indicating that the dynamic mechanical response is correlated with the strength of metal–ligand interactions. These results establish a quantitative framework linking coordination thermodynamics with macroscopic gel elasticity and further suggest that coordination interactions also play an important role in controlling the dynamic mechanical response, providing a basis for tuning the properties of coordination-bonded soft materials.



INTRODUCTION

Understanding how microscopic molecular interactions govern macroscopic mechanical properties remains a central challenge in soft-matter chemistry.[1−3] In polymer networks, elasticity and relaxation dynamics emerge from the collective response of countless transient and permanent cross-links.[1,4] Establishing a quantitative and predictive connection between the collective behavior of molecular bonds and the bulk mechanics of soft materials would transform the design of polymer networks from empirical optimization to molecular-level engineering.

Ion gels, polymer networks swollen with ionic liquids (ILs), provide a particularly attractive platform for exploring molecular design principles.[5−8] The IL component is not an inert solvent but a functional liquid that can impart ionic conductivity, (electro)chemical stability, and thermal stability to otherwise purely mechanical polymer networks.[9−13] When confined within the nanoscopic space of the network, the IL behaves as a "liquid guest" whose physicochemical functionality coexists with, yet is distinct from, the mechanical role of the polymer framework. In this sense, the ion gel represents a hybrid soft framework in which the polymer network dictates mechanical integrity, while the encapsulated IL contributes additional physicochemical functions.

Metal–ligand coordination chemistry offers an ideal molecular handle to bridge chemical bonding and macroscopic mechanics within such hybrid frameworks.[14−16] The reversible formation and dissociation of coordination bonds provide dynamic cross-linking points whose thermodynamic and kinetic parameters are well-defined. Hydrogels and ion gels incorporating coordination bonds, typically through catechol, bipyridine, or terpyridine ligands, have thus been explored as dynamic polymer networks exhibiting self-healing, stress relaxation, and tunable viscoelasticity.[15,17−24] Yet, most of these studies have been qualitative, correlating mechanical trends with the choice of metal ion, rather than quantitatively linking coordination chemistry to macroscopic elasticity and relaxation. A critical requirement for achieving such a quantitative relationship is a polymer network with molecular-level structural uniformity. Conventional polymer gels often suffer from inhomogeneous cross-linking and chain-length distributions, which blur the direct correspondence

Received: March 21, 2026
Revised: May 10, 2026
Accepted: May 12, 2026
Published: May 20, 2026

between molecular-scale events and bulk mechanical response.[25−27] In sharp contrast, tetra-arm poly(ethylene glycol) (TetraPEG) forms a nearly ideal, homogeneous network in which the density and spatial arrangement of cross-linking junctions are statistically uniform.[28−34] In addition, using a nonvolatile IL as the solvent ensures that both the polymer concentration and the coordination equilibria remain constant throughout the measurements. This compositional stability under fully closed conditions enables a consistent and quantitative linkage between molecular coordination chemistry and macroscopic mechanical response without compositional drift, something difficult to achieve in conventional solvent systems such as water or organic media. Owing to this structural uniformity, TetraPEG can form not only hydrogels but also organogels and ion gels swollen with organic electrolytes or ILs, while maintaining well-defined and reproducible network structures even in nonaqueous media.[35−38] This structural precision allows the mechanical properties to be interpreted solely in terms of the chemical nature and dynamics of the cross-links, without structural ambiguity.

Here, we present metal−polymer soft framework (MPF) ion gels that integrate a structurally well-defined polymer network with coordination-bonded interchain bridges and a functional IL environment. Terpyridine-terminated TetraPEG (TetraPEG-tpy) prepolymers were cross-linked via complexation with metal ions (Ni^{2+}, Co^{2+}, Zn^{2+}, and Mg^{2+}) in an IL medium. The tpy ligand was selected because its tridentate coordination enables the formation of highly stable octahedral $M(tpy)_2$ complexes (1:2 metal-to-ligand ratio) with divalent metal ions, particularly first-row transition metal ions. This geometry allows the tetrafunctional TetraPEG chains to form ideal tetrahedral (diamond-lattice-like) network junctions, providing a structurally well-defined polymer network. Owing to the high homogeneity of the TetraPEG network and the well-characterized equilibrium of metal-terpyridine complexation, this system provides a quantitative platform to correlate coordination chemistry with macroscopic mechanics. The elastic modulus is governed by the equilibrium concentration of bis-terpyridine complexes, $M(tpy)_2^{2+}$, which function as network-forming interchain bridges in the polymer network. In the context of rubber elasticity, these bridges correspond to elastically active junctions that contribute to the macroscopic elastic modulus, while the stress-relaxation time reflects the effective lifetime associated with network rearrangement mediated by dynamic metal−ligand coordination.

By unifying thermodynamic and kinetic descriptions of coordination interactions within a homogeneous polymer scaffold, we establish a molecular-level framework that quantitatively links coordination chemistry to the mechanical behavior of soft materials. This approach demonstrates how the elasticity and relaxation of ion gels can be chemically predicted from the equilibrium and dynamics of their interchain-bridge motifs while simultaneously retaining the unique functionalities of an IL-based medium.

EXPERIMENTAL SECTION

Materials

1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C_2mIm][TFSA]; Kanto Chemical) was used as received without further purification. The water content of the IL was confirmed to be below 100 ppm by Karl Fischer titration. Hydroxyl-terminated tetra-arm poly(ethylene glycol) (TetraPEG−OH, M_w = 20,000 g mol^{-1}; SINOPEG) and 4′-chloro-2,2′:6′,2″-terpyridine (Tokyo Chemical Industry), which served as the chelating ligand for end-group modification, were also used without further purification. Zinc(II) and Magnesium(II) bis(trifluoromethanesulfonyl)amide ($Zn(TFSA)_2$ and $Mg(TFSA)_2$; Tokyo Chemical Industry) were used as purchased, whereas Nickel(II) and Cobalt(II) bis(trifluoromethanesulfonyl)-amides ($Ni(TFSA)_2$ and $Co(TFSA)_2$) were synthesized according to the following procedure. Basic metal carbonates (MCO_3·2M-$(OH)_2$·$4H_2O$, M = Ni or Co, 25 mmol; Kanto Chemical or FUJIFILM Wako Pure Chemical) were dissolved in an aqueous solution of bis(trifluoromethanesulfonyl)amide acid (HTFSA, 180 mmol, 30 mL; Tokyo Chemical Industry). The mixture was stirred for 5 h, followed by three repetitions of recrystallization and vacuum filtration. The obtained solids were dried under vacuum for 2 days to afford the corresponding $M(TFSA)_2$ salts.

Preparation of TetraPEG-Based MPF Ion Gels

In this system, the coordination between metal ions and terpyridine-functionalized TetraPEG connects multiple polymer arms to form a percolated polymer network, in which the resulting metal−ligand complexes function as network-forming interchain bridges, analogous to well-defined network formation in tetra-functional polymer systems.[28,32,34] The coordination-bonded TetraPEG ion gels were synthesized through a two-step process:[39] terminal functionalization of TetraPEG−OH with terpyridine (tpy) ligands, followed by gelation via coordination complex formation between metal ions (M^{2+}) and the tpy ligands in an ionic liquid (IL), as illustrated in Figure 1. The

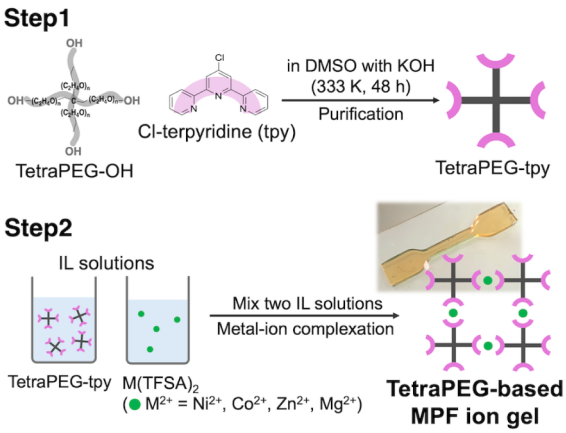


Figure 1. Schematic illustration of the synthesis procedure for TetraPEG-based MPF ion gels.

detailed procedure is as follows: (Step 1) TetraPEG−OH (M_w = 20,000 g mol^{-1}, 0.05 mmol) was dissolved in dimethyl sulfoxide (DMSO, 8 mL) in the presence of KOH (0.16 g, 3 mmol). Under an Ar atmosphere, 4′-chloro-2,2′:6′,2″-terpyridine (0.16 g, 0.6 mmol) was added to the solution, and the mixture was stirred at 333 K for 48 h to obtain the TetraPEG−tpy prepolymer. The resulting solution was poured into cold water to precipitate unreacted terpyridine, which was removed by vacuum filtration. The obtained DMSO solution containing TetraPEG−tpy was transferred into a cellulose dialysis membrane and dialyzed against deionized water for 7 days to remove residual DMSO and KOH. The resulting aqueous TetraPEG−tpy solution was concentrated and dried under reduced pressure, and the solid product was further purified by precipitation using tetrahydrofuran (THF) as a good solvent and diethyl ether (DEE) as a poor solvent. The yield of the synthesized TetraPEG−tpy was 65.2%. The terminal modification ratio, determined by ^{1}H NMR, was 97.6%, confirming that the hydroxyl groups of TetraPEG−OH were almost completely functionalized with terpyridine ligands (details are provided in the Supporting Information, Figure S1). (Step 2) IL ([C_2mIm][TFSA]) was used as the solvent herein to prepare two IL-based solutions: a TetraPEG−tpy/IL solution and a metal ion/IL solution containing $M(TFSA)_2$ (M = Ni, Co, Zn or Mg). To control

https://doi.org/10.1021/acs.chemmater.6c00832
Chem. Mater. 2026, 38, 5723−5731

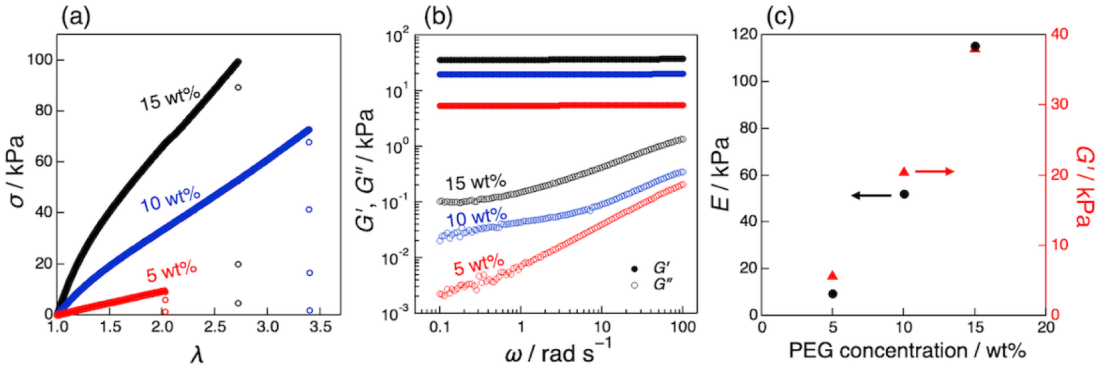


Figure 2. (a) Stress–elongation (σ–λ) curves of TetraPEG-based MPF ion gels cross-linked by Ni^{2+}–tpy complexation, measured at polymer concentrations of 5, 10, and 15 wt %. The molar ratio of metal ions to total terminal tpy units was fixed at c_M/c_{tpy} = 0.5. (b) Storage (G', filled circles) and loss (G'', open circles) moduli as a function of frequency for the same ion gels. (c) Dependence of Young's modulus (E, black circles) and shear modulus (G', red triangles) on polymer concentration.

the gelation time, a small amount of HTFSA was added to the TetraPEG–tpy/IL solution. The molar ratios of HTFSA to terminal tpy units were adjusted to approximately 2:1 (0.03 M). In contrast, no HTFSA was added to the Mg^{2+} system because gelation did not proceed in the presence of HTFSA. Both IL solutions were mixed at room temperature, during which spontaneous complexation between M^{2+} ions and terminal tpy ligands occurred, leading to the formation of transparent TetraPEG-based MPF ion gels. The polymer concentrations of the prepared ion gels were 5, 10, and 15 wt %, and the M^{2+} ion concentrations ranged from 7.6 to 46 mM.

Experimental Methods

Mechanical stretching measurements were performed using dumbbell-shaped samples (rectangular portion: 2.0 × 12.0 × 2.0 mm^3) of the TetraPEG-based MPF ion gels at a constant stretching velocity of 30 mm min^{-1} using a mechanical testing apparatus (STB-1225S; A&D Company). Rheological measurements of the ion gels were performed using a stress-controlled rheometer (MCR-302; Anton Paar) equipped with a parallel-plate geometry (PP-25; 25 mm diameter), as follows. First, the IL solution containing metal salts and dissolved TetraPEG–tpy prepolymer was placed between the plates, and the time dependence of the storage (G') and loss (G'') moduli during the gelation process was recorded at 298 K. The frequency and strain were set to 1 Hz and 1%, respectively. After confirming the gelation completion time, defined as the point at which G' reached a constant plateau value (see Figure S2), the frequency dependence and stress relaxation of the fully gelled ion gel were subsequently measured under the same configuration. In the frequency-dependence measurements, the angular frequency was varied from 0.1 to 100 rad s^{-1} at a strain amplitude of 1%. Stress relaxation measurements were performed under the same parallel-plate configuration. A constant strain of 1% was applied, and the decay of the stress was monitored until the relaxation process reached completion. The measurements were conducted at different temperatures: 293, 323, and 353 K for the Ni^{2+} system, and 293 K for the Co^{2+}, Zn^{2+}, and Mg^{2+} systems. Small-angle X-ray scattering (SAXS) measurements were performed at the BL40B2 beamline of SPring-8 (Hyogo, Japan). The X-ray wavelength and camera length were set to 0.10 nm and 4288.2 mm, respectively. The measurements were conducted at room temperature (ca. 298 K) using a PILATUS3 S 2 M (Dectris Ltd., Baden, Switzerland) detector with an exposure time of 30 s. Repeated measurements confirmed the absence of radiation damage. The sample solutions were gelled in situ within quartz capillaries (Hilgenberg GmbH, Malsfeld, Germany) with a diameter of 1 mm and used for the measurements. The obtained scattering data were normalized by the exposure time, transmittance, and sample thickness. Background scattering from the capillary and the IL (solvent) was subtracted, taking into account the volume fraction of the IL. Density functional theory (DFT) calculations were performed using the Gaussian 09 software package.[40] Geometry optimizations for the M–tpy complexes, as well as for the isolated M^{2+} ions and tpy ligands, were carried out at the M06/def2-TZVP level of theory, followed by normal frequency analyses to confirm that all optimized structures corresponded to true energy minima without any imaginary frequencies. The binding energies (ΔE_{bind}) were evaluated as the electronic energy difference between the optimized complex and the sum of its constituent components (M^{2+} and tpy), without applying any basis-set superposition error (BSSE) correction, according to the following equation, defined as E_{SCF} (complex) − E_{SCF} (M^{2+}) − 2E_{SCF} (tpy). High-spin states were used for Ni^{2+} (triplet, d^8) and Co^{2+} (quartet, d^7), and a singlet for Zn^{2+} (d^{10}) and Mg^{2+}.

RESULTS AND DISCUSSION

Mechanical Properties

To understand how the static mechanical properties of the MPF gels arise from the equilibrium state of coordination interchain bridges, we first examined their macroscopic elasticity. Because the network topology of TetraPEG is nearly ideal, variations in elasticity can be attributed primarily to changes in the population of metal–ligand complexes rather than to structural heterogeneity. Figure 2a shows the stress–elongation (σ–λ) curves of the TetraPEG-based MPF ion gels cross-linked with Ni^{2+} ions. The measurement was performed on fully gelled samples, after confirming gelation completion, defined as the point where G' reached a constant plateau value (see Figure S2). The polymer concentrations were 5, 10, and 15 wt %, and the molar ratio of metal ions to terminal tpy ligands was fixed at c_M/c_{tpy} = 0.5. The stress σ gradually increased with increasing elongation ratio λ, and the breaking stress (σ_{max}) reached 9.4 kPa for the 5 wt % ion gel (maximum elongation, λ_{max} = 2.0), 72.8 kPa for the 10 wt % gel (λ_{max} = 3.4), and 99.4 kPa for the 15 wt % gel (λ_{max} = 2.8), respectively. The Young's modulus (E) was determined from the initial slope of the σ–λ curves and found to be 9.3, 52.1, and 115.3 kPa for the ion gels with polymer concentrations of 5, 10, and 15 wt %, respectively. Figure 2b shows the storage (G') and loss modulus (G'') as a function of frequency (ω) obtained for the TetraPEG-based MPF ion gels. At all polymer concentrations examined, the G' values remained nearly constant over the measured ω range and were consistently higher than the corresponding G'' values. This behavior corresponds to a typical rubbery plateau, indicating that the formed M^{2+}–tpy complexes acting as network-forming interchain bridges are stable within the experimental time scale, confirming the elastic network structure of the gels. The

https://doi.org/10.1021/acs.chemmater.6c00832
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dependence of the Young's modulus (E) and storage modulus (G') on polymer concentration is summarized in Figure 2c. Both values exhibited a linear relationship with polymer concentration, indicating that the elastic modulus of the ion gels is directly controlled by the polymer concentration, that is, by the density of elastically active junctions. Furthermore, the ratio of E to G' ($E \approx 3G'$) was close to the theoretical value expected for isotropic elastic networks, implying that the coordination-bonded polymer network is nearly homogeneous. In addition, previous studies on TetraPEG in [C_2mIm][TFSA] have shown that the overlap concentration (c^*) is approximately 4−5 wt % for $M_w \approx 20\,000$ g mol^{-1} and scales as $c^* \propto M_w^{-4/5}$.[41] Because the polymer concentrations employed in this study are at or above this range, the polymer chains are expected to be in the overlap regime, where intermolecular interactions and network formation are possible. This is consistent with the observed development of elasticity with increasing polymer concentration. In this concentration regime, a percolated network is formed, which enables the emergence of macroscopic elasticity. This interpretation is further supported by small-angle X-ray scattering (SAXS) measurements (see the Supporting Information: Figure S3 and Table S1), which confirm the network homogeneity of the present MPF ion gels, in good agreement with previous reports on chemically interchain-bridged TetraPEG ion gels (Figure S3a).[35,41] No scattering peak arising from network inhomogeneity was observed; instead, all MPF ion gels examined herein exhibited a monotonic q^{-2}-dependence (q: scattering vector), well described by the Ornstein−Zernike function, which is characteristic of homogeneous TetraPEG networks.[29,35,41,42] This scattering profile was retained irrespective of the metal-ion species or polymer concentration (Figures S3b and S3c, respectively).

Figure 3 shows the variation in the G' values of 5 wt % TetraPEG-based MPF ion gels as a function of metal ion concentration (c_M) for M^{2+} = Ni^{2+}, Co^{2+}, Zn^{2+}, and Mg^{2+}. The frequency-dependent data used to determine these G' values are provided in Figure S4. For the transition metal ions, the G' values increased in the order Zn^{2+} < Co^{2+} < Ni^{2+}. This trend is consistent with the order of the thermodynamic stability of the M−tpy complexes, as reflected in their equilibrium formation constants, which qualitatively parallels the ligand field stabilization energy (LFSE) sequence. For example, for the aqua complexes $[M(H_2O)_6]^{2+}$, the degree of stabilization increases in the order Zn^{2+} (0 kJ mol^{-1}) < Co^{2+} (−89 kJ mol^{-1}) < Ni^{2+} (−122 kJ mol^{-1}) calculated based on the ligand-field splitting energy (10 Dq);[43] see the Supporting Information for details. These differences in stability are directly reflected in variations in the equilibrium distribution of the M−tpy complexes that function as network-forming interchain bridges, as discussed later.

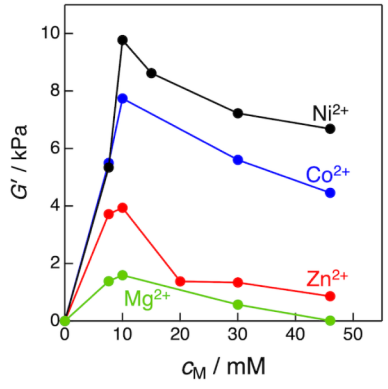

Figure 3. Storage modulus (G') of 5 wt % TetraPEG-based MPF ion gels as a function of metal ion concentration (c_M) for M^{2+} = Ni^{2+}, Co^{2+}, Zn^{2+}, and Mg^{2+}.

When Li^+ ions were used as the central metal ions in the TetraPEG−tpy/IL system, no gelation occurred (Figure S5) because the Li−tpy interaction is essentially electrostatic, lacking the orbital overlap required for coordination bonding; as a result, the Li−tpy complex is not stably formed. In contrast, Mg^{2+} ions induced gelation, and the resulting G' was lower than that of the Zn^{2+} system (Figure 3, green). Although Mg^{2+} lacks d orbitals for strong orbital overlap, its higher charge density compared to Li^+ leads to stronger electrostatic interactions with the tpy ligand, allowing the formation of coordination complexes sufficient to generate a percolated network.

When examining the dependence on the metal ion concentration (c_M), all M^{2+} systems exhibited a similar trend: the G' value increased sharply up to approximately 10 mM, followed by a gradual decrease beyond this concentration. To rationalize this behavior, a quantitative analysis was conducted by considering the complexation equilibrium governing the formation of the M−tpy complexes.

Quantitative Analysis of Gel Elasticity Based on Metal−Ligand Complexation Equilibrium

In the coordination-bonded MPF ion gels investigated in this study, the concentration of network-forming interchain bridges (M−tpy complexes), which directly determines the elastic modulus, can be described based on the complexation equilibrium between the metal ions and terpyridine ligands. Similar approaches have been reported for metal-coordinated hydrogel systems, where quantitative relationships between coordination equilibria and macroscopic elasticity have been established. In such systems, the concentration of elastically active junctions has been predicted using equilibrium constants for metal−ligand complexation determined in aqueous solutions together with the acid dissociation constant of the ligand (pK_a).[19,44] In contrast, in IL systems, experimental determination of metal−ligand complexation equilibria remains highly challenging, and experimental equilibrium constants are rarely available.

The complexation reaction between the metal ions (M^{2+}) and terpyridine (tpy) ligands proceeds in two successive steps:

$$M^{2+} + \text{tpy} \rightleftarrows M(\text{tpy})^{2+}$$

$$M(\text{tpy})^{2+} + \text{tpy} \rightleftarrows M(\text{tpy})_2^{2+}$$

The stepwise formation constants are defined as

$$K_1 = [M(\text{tpy})^{2+}]/([M^{2+}][\text{tpy}])$$

and

$$K_2 = [M(\text{tpy})_2^{2+}]/([M(\text{tpy})^{2+}][\text{tpy}])$$

Here, $M(tpy)^{2+}$ and $M(tpy)_2^{2+}$ are referred to as the mono- and bis-complexes, respectively, and the latter functions as an elastically active junction in the network. The total metal ion concentration is given by $c_M = [M^{2+}] + [M(tpy)^{2+}] + [M(tpy)_2^{2+}]$. By solving these mass-balance equations, the concentration distribution of each metal species (free M^{2+},

https://doi.org/10.1021/acs.chemmater.6c00832
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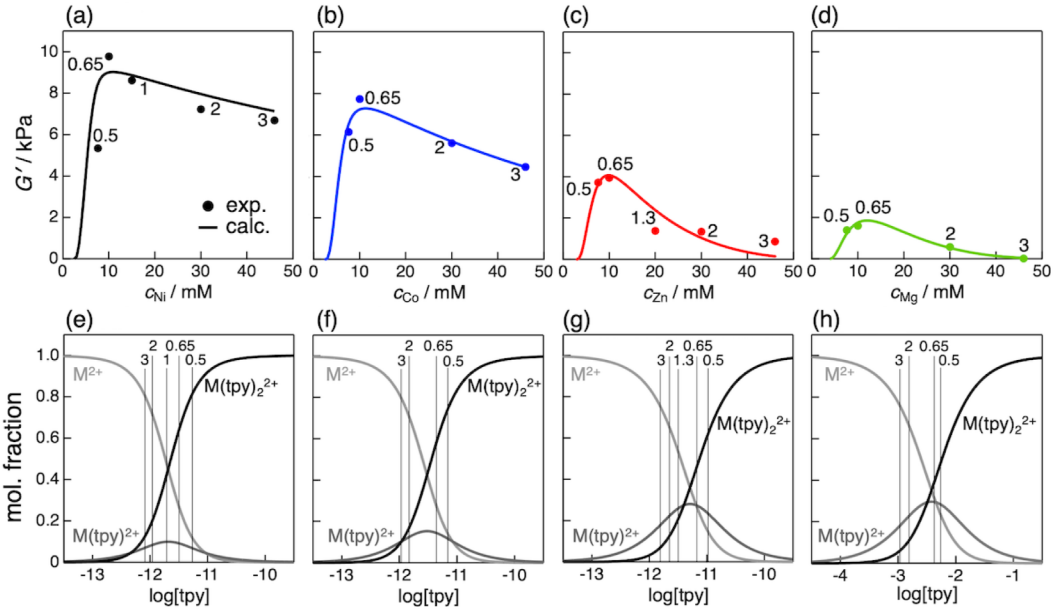

Figure 4. (a–d) Experimental storage moduli (G'; symbols) and calculated curves (solid lines) for 5 wt % TetraPEG-based MPF ion gels containing (a) Ni^{2+}, (b) Co^{2+}, (c) Zn^{2+}, and (d) Mg^{2+} ions. The calculated curves were obtained from the equation: $G_{calc} = \alpha\nu RT$, using the optimized equilibrium constants. The numerical values shown in each panel represent the molar ratio of total metal ions to total terminal tpy ligands (c_M/c_{tpy}: 0.5–3), corresponding to c_M = 7.6–46 mM. (e–h) Equilibrium species distributions of the free metal ions (M^{2+}, light gray), monotpy complexes ($M(tpy)^{2+}$, gray), and bis-tpy complexes ($M(tpy)_2^{2+}$, black) in the ionic liquid medium, obtained using the optimized equilibrium constants for (e) Ni^{2+}, (f) Co^{2+}, (g) Zn^{2+}, and (h) Mg^{2+} systems. The molar fractions of each species (x_M, $x_{M(tpy)}$, and $x_{M(tpy)2}$) were defined as follows: $x_M = 1/(1 + K_1[tpy] + K_1K_2[tpy]^2)$; $x_{M(tpy)} = K_1[tpy]/(1 + K_1[tpy] + K_1K_2[tpy]^2)$; $x_{M(tpy)2} = K_1K_2[tpy]^2/(1 + K_1[tpy] + K_1K_2[tpy]^2)$. The vertical lines indicate the equilibrium points at which the total tpy concentration, $c_{tpy} = [tpy] + [Htpy^+] + [M(tpy)^{2+}] + 2[M(tpy)_2^{2+}]$ = 15 mM, is satisfied for each c_M/c_{tpy} ratio.

$M(tpy)^{2+}$ complex, and $M(tpy)_2^{2+}$ complex) can be obtained. The concentration of the $M(tpy)_2^{2+}$ complex, which acts as the interchain bridge in the gel network, is expressed as

$$[M(tpy)_2^{2+}] = \frac{K_1K_2[tpy]^2}{1 + K_1[tpy] + K_1K_2[tpy]^2}c_M \quad (1)$$

In the present MPF ion gel system, however, the complexation equilibrium must be considered together with the acid–base equilibrium of the tpy ligand, because a strong acid (HTFSA) was added to control the gelation kinetics. Terpyridine can be protonated according to the equilibrium: $tpy + H^+ \rightleftarrows Htpy^+$, where the acid dissociation constant of the protonated terpyridine species ($Htpy^+$) is defined as $K_a = [H^+][tpy]/[Htpy^+]$. As a result, only the deprotonated tpy species is available for coordination with metal ions. Accordingly, the total concentration of tpy ligands was expressed as $c_{tpy} = [tpy] + [Htpy^+] + [M(tpy)^{2+}] + 2[M(tpy)_2^{2+}]$ = 15 mM, which corresponds to the concentration of terminal tpy groups in the 5 wt % MPF ion gels. The total proton concentration was expressed as $c_H = [H^+] + [Htpy^+]$, where c_H is the concentration of added HTFSA (0.03 M). By combining the acid–base equilibrium, the proton mass balance, and the metal–ligand complexation equilibria, the following equation for the free tpy concentration [tpy] was obtained:

$$c_{tpy} = [tpy] + \frac{c_H[tpy]}{K_a + [tpy]} + \left(\frac{K_1[tpy] + 2K_1K_2[tpy]^2}{1 + K_1[tpy] + K_1K_2[tpy]^2}\right)c_M \quad (2)$$

Because c_{tpy} and c_M are fixed experimental parameters, eq 2 represents a nonlinear equation with respect to the [tpy] and was therefore solved numerically for each c_M. The physically meaningful solution satisfying $0 \le [tpy] \le c_{tpy}$ was selected and the obtained [tpy] value was then substituted into eq 1 to calculate the concentration of the bis-terpyridine complex, $[M(tpy)_2^{2+}]$, which contributes to network connectivity and functions as an elastically active junction within the MPF ion gel network.

Using the resulting concentration of $M(tpy)_2^{2+}$, the elastic modulus of the MPF ion gels was quantitatively analyzed based on classical rubber elasticity theory. The elasticity of the gels is expressed by the classical rubber elasticity relation (affine network model), $G = \nu RT$, where ν (mol m^{-3}) is the effective molar density of network strands, T (K) is the absolute temperature, and R (J K^{-1} mol^{-1}) is the gas constant ($R = N_Ak$, with N_A and k being Avogadro's and Boltzmann's constants, respectively). For the present MPF ion gels, ν was calculated from the reaction efficiency (or conversion) p between the metal ions and tpy ligands, based on the tree-like network theory.[30] The p, defined as the concentration ratio of tpy ligands within bis-tpy complexes to total terminal tpy (i.e., $p = 2[M(tpy)_2^{2+}]/c_{tpy}$), was evaluated from the equilibrium distribution of the free M^{2+}, mono-, and bis-tpy complexes, calculated from K_1 and K_2. The ν was then determined from p according to the tree-like network model,[30] as described in detail in the Supporting Information. Here, it should be noted that the modulus of a polymer gel is influenced not only by the network connectivity but also by polymer–solvent interactions. Recent studies on ideal homogeneous TetraPEG hydrogels have revealed that water molecules contribute to the energy elasticity through hydration effects, leading to "negative energy elasticity" that reduces G'.[45−49] Therefore, in the present ion gel systems, the polymer–IL interactions must also

https://doi.org/10.1021/acs.chemmater.6c00832
Chem. Mater. 2026, 38, 5723−5731

be considered. To account for such effects, the calculated modulus was defined as

$$G_{calc} = \alpha \nu RT \quad (3)$$

where α is an empirical correction factor that compensates for deviations from ideal rubber elasticity arising from polymer−IL interactions and the highly ionic environment, and G_{calc} corresponds to the experimentally observed G'. The value of α was determined using a chemically cross-linked TetraPEG ion gel (polymer concentration: 5 wt %) prepared via a Michael addition reaction between thiol- and maleimide-terminated TetraPEG prepolymers[36,38,45] in [C_2mIm][TFSA] ionic liquid. From the experimentally measured modulus (G'_{chem}, Figure S6) and the effective molar strand density (ν_{chem}), α was calculated as $\alpha = G'_{chem}/(\nu_{chem}RT)$. The ν_{chem} was estimated based on the tree-like theory using polymer concentration and reaction efficiency p (determined from time-dependent UV−vis spectroscopy; Figure S7), as detailed in the Supporting Information. Using the obtained ν_{chem}, the α value in [C_2mIm][TFSA] was determined to be 0.58. With this α value, the equilibrium constants K_1, K_2, and K_a were optimized by least-squares fitting of the experimental storage moduli (G_{exp}, = G') to the calculated values (G_{calc}), by minimizing the residual sum of squares, $\Sigma[G_{exp} - G_{calc}]^2$. In the fitting, the initial value of K_a was set to $pK_a \approx 10$, based on the known shift of acid−base equilibria toward higher pK_a values in [C_2mIm][TFSA] relative to aqueous solutions, as reported in our previous potentiometric titration studies in the IL system.[50,51] The optimized pK_a values remained close to this initial estimate, indicating that the fitting was not overly sensitive to K_a. The resulting fitted curves and the experimental data are shown in Figure 4.

Figures 4a−4c present the experimentally measured G' (symbols) and calculated G curves (solid lines) for the 5 wt % TetraPEG-based MPF ion gels containing Ni^{2+}, Co^{2+}, and Zn^{2+}, respectively. The calculated results successfully reproduced the experimental data for all M^{2+} systems, yielding the optimized equilibrium constants: $\log K_1 = 11.0$, $\log K_2 = 12.3$, and $pK_a = 10.1$ for Ni^{2+}; $\log K_1 = 11.1$, $\log K_2 = 12.0$, and $pK_a = 10.2$ for Co^{2+}; $\log K_1 = 11.2$, $\log K_2 = 11.4$, and $pK_a = 10.1$ for Zn^{2+}. The Mg^{2+} system also showed good agreement between the experimental and calculated G' vs c_M profiles (Figure 4d), and the equilibrium constants were determined to be $\log K_1 = 2.3$ and $\log K_2 = 2.5$. These values are summarized in Table S2, together with literature values for aqueous systems for comparison. Compared with aqueous systems, the pK_a and complexation constants ($\log K_1$, $\log K_2$) in the IL are appreciably larger, indicating that both ligand deprotonation and metal−ligand coordination are substantially enhanced. These results reflect the specific solvation and coordination environment in ILs. Notably, this work provides a quantitative framework to determine these equilibrium constants in IL systems by combining equilibrium analysis with macroscopic elasticity, which has not been established previously.

The corresponding equilibrium distributions of the free M^{2+}, $M(tpy)^{2+}$, and $M(tpy)_2^{2+}$ species calculated using these optimized constants are shown in Figure 4e−h. For all the M^{2+} systems, the bis-complex $M(tpy)_2^{2+}$ predominates in the low metal ion concentration region ($c_M \sim 7.6$−10 mM, corresponding to c_M/c_{tpy} ratios of 0.5−0.65). As c_M increases, the equilibrium shifts toward dissociation, leading to the dominance of monocomplex and free M^{2+} species. Consequently, the number of interchain bridges decreases, resulting in a reduction of G'. Indeed, when the concentration of the bis-terpyridine complex, $[M(tpy)_2^{2+}]$, calculated from the optimized equilibrium constants, is plotted as a function of c_M (Figure S8), the resulting profiles directly correspond to the c_M-dependence of G' shown in Figure 4a−d for all metal ion systems. The overall trend in G' ($Mg^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+}$) is also consistent with the sequence of the attainable concentration of $M(tpy)_2^{2+}$ determined by the equilibrium constants.

Furthermore, because the formation of $M(tpy)_2^{2+}$ depends on the overall stoichiometric ratio of metal ions to tpy ligands (c_M/c_{tpy}), the static mechanical properties of the MPF ion gels can be systematically tuned by adjusting this ratio, which provides a quantitative molecular basis for elasticity control in coordination-bonded polymer networks. These observations demonstrate that the equilibrium distribution of mono- and bis-tpy complexes directly governs the macroscopic stiffness of the MPF ion gels. This quantitative correspondence highlights that static elasticity can be predicted from coordination thermodynamics alone, a level of control rarely achieved in conventional polymer networks.

Role of Coordination Bond on Stress Relaxation Behavior

While the equilibrium concentration of coordination complexes determines the static elasticity, the dynamic mechanical response of the MPF gels is closely related to the nature of coordination bonding.[52,53] To explore this connection, we analyzed the stress relaxation behavior of the MPF ion gels, which sensitively captures the time scale of bond dissociation and reformation. Figure 5a shows the stress relaxation curves

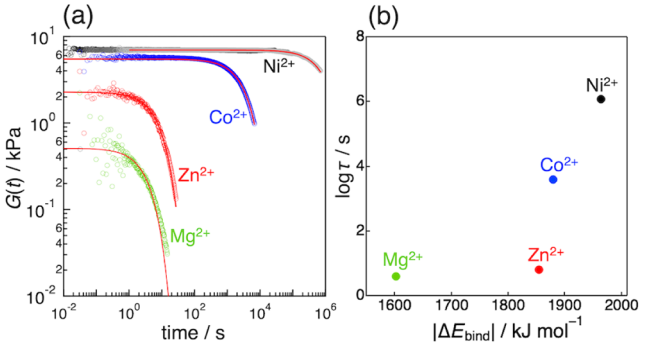

Figure 5. (a) Stress relaxation curves of 5 wt % TetraPEG ion gels (M^{2+} = Ni^{2+}, Co^{2+}, Zn^{2+}, and Mg^{2+}) at c_M = 7.6 mM (c_M/c_{tpy} = 0.5). The Ni^{2+} data represent a time−temperature superposition master curve constructed from measurements at 293, 323, and 353 K (referenced to 293 K), whereas the Co^{2+}, Zn^{2+}, and Mg^{2+} data were obtained at 293 K. Solid lines represent the fitting results using a single-exponential relaxation model, $G(t) = G_0 \exp(-t/\tau)$. (b) Correlation between the relaxation time (log τ) and the binding energy (ΔE_{bind}) of the $M(tpy)_2^{2+}$ complexes obtained from DFT calculations.

obtained for the 5 wt % TetraPEG-based MPF ion gels at c_M = 7.6 mM (c_M/c_{tpy} = 0.5). Under the experimental condition (strain amplitude, 1%), the MPF ion gels (Ni^{2+}, Co^{2+}, Zn^{2+}, and Mg^{2+} systems) were confirmed to exhibit linear viscoelastic behavior, via strain-dependent measurements (Figure S9). Structural relaxation was found to occur on longer time scales in the order $Mg^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+}$, corresponding to the increasing strength of the coordination bonds. The obtained relaxation curves were fitted with a conventional single-exponential function, $G(t) = G_0 \exp(-t/\tau)$, from which the

https://doi.org/10.1021/acs.chemmater.6c00832
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relaxation time (τ) was determined. The resulting τ values were 4.0 s for Mg^{2+}, 6.5 s for Zn^{2+}, 3.9×10^3 s for Co^{2+}, and 1.2×10^6 s for Ni^{2+}, respectively. Figure 5b shows the experimentally determined τ plotted against the binding energies (ΔE_{bind}, shown as absolute values) of the $M(tpy)_2^{2+}$ complexes obtained from DFT calculations. The optimized lowest-energy structures of the M−tpy complexes are provided in Figure S10. The plot shows a qualitative positive correlation, indicating that stronger M−tpy coordination interactions lead to longer relaxation times. This result suggests that the structural relaxation of the MPF ion gels is closely related to the strength of the interchain bridges formed by the $M(tpy)_2^{2+}$ complexes. Accordingly, the nature of the metal−ligand coordination not only governs the static elasticity but also influences the dynamic mechanical response. These findings suggest that the mechanical properties of MPF ion gels can be tuned through appropriate selection of the metal ions and ligand combinations.

CONCLUSIONS

In summary, this study provides a quantitative molecular-level framework linking coordination chemistry with polymer science, thereby enabling rational control of the macroscopic elasticity of coordination-bonded MPF ion gels. The equilibrium-based analysis revealed that the elastic modulus of the MPF ion gels is dominated by the concentration of bis-terpyridine complexes ($M(tpy)_2^{2+}$) acting as network-forming interchain bridges. In contrast, the dynamic viscoelasticity is correlated with the strength of the metal−ligand coordination interactions. These results clarify how molecular equilibrium determines the static elasticity and suggest that metal−ligand coordination interactions also play an important role in the dynamic mechanical response of soft materials, providing a link between molecular-level coordination interactions and macroscopic mechanical properties.

In particular, both the nonmonotonic dependence of G' on c_M and its variation across different metal ions ($Mg^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+}$) can be consistently explained by the attainable concentration of the bis-terpyridine complex. The equilibrium constants determined for these systems were higher than those reported in aqueous solutions, indicating a pronounced shift in coordination equilibria in the IL environment. Furthermore, the stress relaxation behavior shows a correlation with the binding energy of the coordination bonds, providing a consistent relationship between coordination strength and relaxation dynamics. These results provide a basis for understanding how coordination thermodynamics and interactions influence macroscopic mechanical properties in this class of materials. While further extension to a broader range of metal ions, ligand motifs, and polymer architectures will be necessary to establish general applicability, the present findings suggest that coordination chemistry offers a viable strategy for tuning the elasticity and dynamics of polymer networks within the scope examined in this study.

ASSOCIATED CONTENT

Data Availability Statement

A preliminary version of this work has been deposited as a preprint on ChemRxiv.[54]

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.6c00832.

Experimental and analysis; ^{1}H NMR spectrum (Figure S1); G' and G'' as a function of reaction time (Figure S2); SAXS profiles (Figure S3); G' and G'' as a function of frequency (Figure S4); photograph of TetraPEG-tpy gelation using Li^+ (Figure S5); G' of chemically cross-linked ion gel (Figure S6); time-dependent UV−vis spectra (Figure S7); concentrations of each metal species vs c_M (Figure S8); strain-dependent measurements (Figure S9); optimized geometries of M^{2+}−tpy complexes (Figure S10); fitting parameters obtained from SAXS (Table S1); equilibrium constants (Table S2) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by JSPS KAKENHI [Grant Numbers, JP23H02066 (K.F.), JP23K26759 (K.F.), JP22H00340 (K.F.), JP23H02030 (T.U.), and JP23K26723 (T.U.)].

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