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Metal nanoparticle fluids with magnetically induced electrical switching properties†

Younghoon Kim and Jinhan Cho*

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We report the successful preparation of solvent-free metal nanoparticle (NP) fluids with multiple-functionalities, such as rheological properties, magnetism, ionic conductivity, and electrical properties, allowing for facile synthesis and mass production. The gold nanoparticles (Au_{NPs}) used in this study were synthesized using tetraoctylammonium bromide (TOABr) in toluene and then directly phase-transferred to solvent-free low-molecular-weight (M_w) imidazolium-type ionic liquid media containing thiol groups (*i.e.*, IL-SH). Magnetic metal fluids (*i.e.*, MIL-SH–Au_{NPs}) were prepared by the addition of $FeCl_3$ powder to metal fluids (*i.e.*, IL-SH–Au_{NPs}). These fluids showed relatively high ionic and electrical conductivities compared with those of conventional metal NP fluids based on organic ILs with high M_w. Furthermore, it was demonstrated that these fluids could be used as electric switches operated using an external magnetic field in organic media.

Introduction

Metal nanoparticles with size-dependent electronic, optical, and catalytic properties have attracted considerable attention due to the number of potential applications, which range from catalysis to biology.[1–6] Although many different metal NPs with various sizes and shapes have been characterized,[7–10] the major challenges with developing such particles include the implementation of more than one property at the single-particle level and facile transformation of the physical form, which would allow us to explore novel technological applications. In particular, the preparation of metal NPs with magnetic properties may provide specific technological advantages for tuning the electrical, optical, and magnetic properties of their constituents, and the formed NPs can be used in emerging technologies such as dark-field imaging, magnetic resonance imaging (MRI), magnetically separable catalysts, and magneto-optical sensing.[11–14] Although numerous strategies for synthesizing magnetic metal NPs have been explored, including the development of core–shell,[15,16] dumbbell-like structures,[17–20] and self-assembly using colloidal templates,[13] in all of these instances, the functionalized metal NPs with magnetic properties appear and behave as physical forms like solids in the absence of solvents. Recently, an interesting class of inorganic NPs exhibiting liquid-like behavior at room temperature in the absence of solvents, conceived by Giannelis and co-workers,[21–25] was developed by grafting an organic modifier onto NPs by ligand exchange or hydrogen bonding. The organic modifier, an ionic liquid (IL),[26–30] allows for various inorganic NPs[21–25,30–34] to be handled, assembled, and used in ways not previously possible due to the unique properties of ILs, such as extremely low volatility, high thermal stability and ionic conductivity. In most cases, organic ILs with a high molecular weight ($M_w >\sim 10^3$) have been used as capping agents for the preparation of solvent-free NPs with fluidic behavior. For example, most metal NP assembly processes reported by other research groups exhibited relatively high sheet resistances $>10^6\ \Omega\ \square^{-1}$ at room temperature due to the particle–particle separation distances associated with the stabilizers, which exhibit bulky chain lengths. Furthermore, little work has been done to develop multifunctional fluids with metallic and magnetic properties, although a variety of inorganic NPs ranging from metal to magnetic NPs have been incorporated into IL systems.

Herein, we report on the development of multifunctional NP fluids with magnetic properties, ionic conductivity, and electrical properties that allow for facile synthesis and mass production. The main advantage of our approach is that the ligands of the metal NPs exhibit magnetic properties and fluidic behavior. In this study, we first synthesized imidazolium-type ILs with thiol groups (*i.e.*, IL-SH) showing a high affinity for metal NPs, and then gold NPs (Au_{NPs}) stabilized by tetra(octylammonium bromide) (TOABr) ligands in toluene were dispersed in IL-SH media *via* phase transfer between toluene and the IL-SH media. After preparing the metal NP-based ILs (*i.e.*, IL-SH–Au_{NPs}), metal fluids with magnetic properties (*i.e.*, MIL-SH–Au_{NPs}) were prepared by the addition of $FeCl_3$ powder to IL-SH–Au_{NPs}. It has been reported that ILs containing high-spin $FeCl_4^-$ (induced from $FeCl_3$ powder) can respond strongly to magnetic fields.[35,36] In this case, the ionic conductivity

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Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Korea. E-mail: jinhan71@korea.ac.kr; Fax: +82 2 926 6102; Tel: +82 2 3290 4852

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($\sim 1 \times 10^{-5}$ S cm^{-1} at room temperature) of MIL-SH–Au$_{NP}$ fluids is clearly superior to that of conventional solvent-free NP fluids ($\sim 10^{-6}$ S cm^{-1} at room temperature); additionally, the electrical sheet resistance of MIL-SH–Au$_{NP}$ fluids is easily controlled by the loading amount of Au$_{NP}$ dispersed in the fluids. In particular, we highlight the fact that the "ON/OFF" electrical switching of magnetic metal NP fluids can be accomplished by the magnetic attraction and retraction of the magnetic metal NP fluids to and from electrodes. These results suggest the possibility that magnetic metal fluids can be used as magnetically adjustable electric switches in organic media and furthermore can be developed into magnetic fluid actuators exhibiting electrical switching properties. To the best of our knowledge, our paper is the first to report the successful preparation of magnetic metal NPs exhibiting liquid behavior. Considering the fact that a variety of metal NPs can be stabilized using magnetic fluids, we believe that our approach can provide a basis for potential applications such as fluidic actuators with magnetic and electrical properties, ionic electrolytes for batteries, and magnetically separable catalysts for the petrochemical industry.

Experimental

Preparation of thiol-functionalized ionic liquid (MIL-SH)

Thiol-functionalized ionic liquid (IL-SH) was synthesized as follows: 1-methylimidazole (3.09 g, 37.67 mmol) and 3-chloro-1-propanethiol (5 g, 45.20 mmol) were refluxed for 72 h at 80 °C under argon-protected conditions. To synthesize the MIL-SH, anhydrous FeCl$_3$ was reacted with the prepared IL-SH in a one-to-one molar ratio (IL-SH : FeCl$_3$ = 1 : 1), and the mixtures were then magnetically stirred at 50 °C for 1 hour to allow for a complete reaction. The mixtures were mildly centrifuged (3000 rpm, 5 min) with excess isopropyl alcohol to remove the unreacted reagents. After drying by vacuum, a dark-brown product exhibiting liquid-like behavior (*i.e.*, MIL-SH) was obtained.

Preparation of MIL-SH–Au$_{NP}$

TOABr–Au$_{NPs}$ measuring ~7 nm in size dispersed in organic media[37] were phase-transferred to IL-SH media for various phase-transfer times. Then, anhydrous FeCl$_3$ was added to the IL-SH–Au$_{NPs}$ in a one-to-one molar ratio (IL-SH : FeCl$_3$ = 1 : 1), and the mixtures were magnetically stirred at 50 °C for 1 hour to allow for a complete reaction. The mixtures were mildly centrifuged (3000 rpm, 5 min) with excess isopropyl alcohol to remove the unreacted reagents. After drying by vacuum, a dark-wine-colored product exhibiting liquid-like behavior was obtained.

Measurements

The rheological properties of MIL-SH and MIL-SH–Au$_{NP}$ were measured using an MCR-301 (Anton Paar) rheometer. Their elastic and viscous moduli were obtained using the same rheometer in the temperature-sweep mode from 25 to 70 °C at a rate of 10 °C min^{-1} under a fixed angular frequency (1 s^{-1}) and strain amplitude (10%). The electrical properties were measured using a four point probe station (Mitsubishi Chemical Analytech Co., Ltd., MCP-T610). Ionic conductivities were measured as a function of temperature and frequency using broadband dielectric spectroscopy (Novocontrol-Concept 80). Magnetic properties, such as the field dependence of magnetization and reciprocal molar susceptibility, were investigated by a superconducting quantum interference device (SQUID, MPMS5) magnetometer. Raman spectra were measured using a LabRam ARAMIS Raman spectrometer (Horiba Jobin-Yvon) using the 633 nm line of a He–Ne laser. Thermogravimetric analysis (TGA) of all samples was performed using a TGA Q50 (TA Instruments). DSC was conducted from −100 to 50 °C using a DSC 131 Evo (SETARAM Instrumentation).

Calculations of molar susceptibility (χ_{mol}) and effective magnetic moment (μ_{eff})

The molecular weight (M_w) of MIL-SH was 354.91 g mol^{-1}. The sample mass of MIL-SH used for the measurement of magnetic properties was 37 mg. χ_{mol} is defined as follows:[38]

$$\chi_{mol} = \frac{M \cdot M_w}{H \cdot m}$$

(magnetization: M, external magnetic field: H, sample mass: m).

The μ_{eff} of MIL-SH was calculated at 300 K using the relations between χ_{mol} and μ_{eff} as follows:[38]

$$\mu_{eff} = \sqrt{\frac{3kT\chi_{mol}}{N_{Av}}} \times \frac{\mu_B}{\mu_B}$$

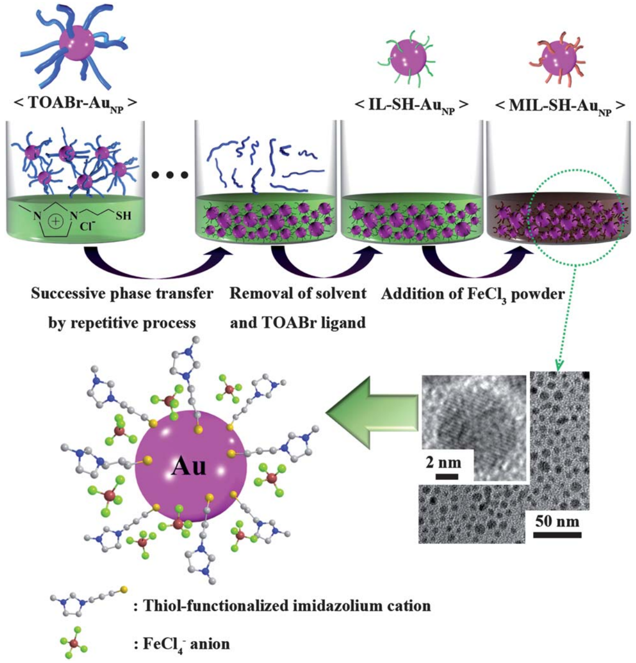
(Boltzmann's constant: k, absolute temperature: T, Avogadro's number: N_{Av}, Bohr magneton: μ_B).

For the 72 wt% MIL-SH–Au$_{NP}$, the measured sample mass used to investigate the magnetic properties was 19 mg.

Results and discussion

First, Au$_{NPs}$ with a diameter of approximately 7 nm were prepared using tetraoctylammonium bromide (TOABr) stabilizers in toluene. Thiol-functionalized imidazolium-type IL (IL-SH) ligands with liquid-like behavior at room temperature were synthesized using 1-methylimidazole and 3-chloro-1-propanethiol. In this case, the IL-SH ligands can be used as ligand-exchanging organics for the phase transfer of various hydrophobic metal NPs stabilized by oleic acid, palmitic acid, or TOABr from organic to IL-SH media due to the high affinity between the thiol moieties of IL-SH and the surfaces of metal NPs, as shown in Scheme 1. The successive phase transfer of metal NPs to IL-SH could easily increase the loading amount of metal NPs dispersed in IL-SH media. After synthesizing IL-SH–Au$_{NP}$ fluids with a loading amount of 72 wt% Au$_{NP}$ (see ESI, Fig. S1†), the addition of anhydrous FeCl$_3$ powder successfully produced magnetic metal ILs with high-spin FeCl$_4^-$ as an anion.

To confirm the presence of FeCl$_4^-$, which may have possibly induced the magnetic behavior of the particles in the IL media, the Raman spectra of IL-SH, MIL-SH, and MIL-SH–Au$_{NP}$ were obtained, as shown in Fig. 1a. As indicated, all of the ILs showed



Scheme 1 Schematics illustrating the preparation of solvent-free MIL-SH and MIL-SH–Au$_{NP}$.

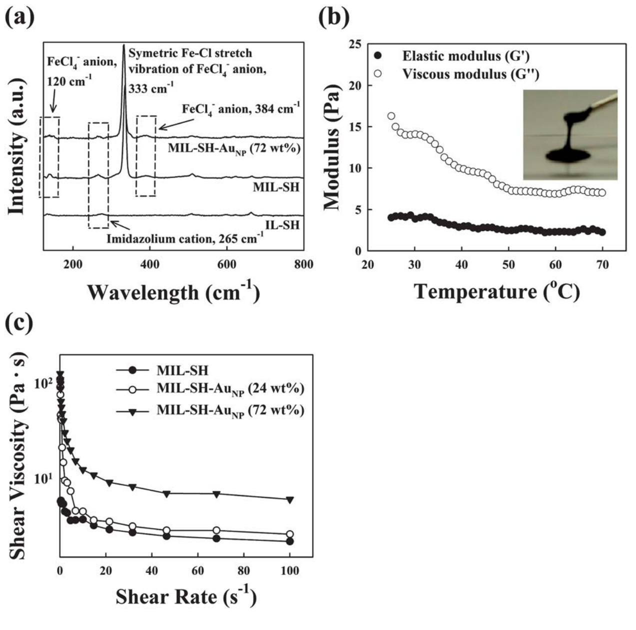


Fig. 1 (a) Raman spectra of IL-SH, MIL-SH and MIL-SH–Au$_{NP}$ obtained to confirm the presence of FeCl$_4^-$ anions. (b) Elastic and viscous moduli as a function of temperature for 72 wt% MIL-SH–Au$_{NPs}$ (*i.e.*, Au$_{NP}$ concentration of 72 wt%). The inset demonstrates the fluidic behavior of MIL-SH–Au$_{NPs}$ (72 wt%). (c) Shear viscosity of MIL-SH and MIL-SH–Au$_{NP}$ as a function of shear rate.

a weak Raman peak originating from the imidazolium cation at 265 cm^{-1}; however, MIL-SH and MIL-SH–Au$_{NPs}$ exhibited a strong Raman peak attributed to the symmetric Fe–Cl stretching vibration of FeCl$_4^-$ at 333 cm^{-1} and the Raman peak of the imidazolium cation mentioned above.[35,36] Furthermore, considering that the relative ratio of imidazolium Raman peaks to FeCl$_4^-$ peaks measured from MIL-SH was identical to that of MIL-SH–Au$_{NPs}$, the presence of Au$_{NPs}$ in the IL media did not affect the formation of FeCl$_4^-$ or the resulting magnetic properties (a detailed explanation will be provided in a later section).

The solvent-free MIL-SH–Au$_{NPs}$ displayed typical liquid-like behavior at room temperature, despite a loading amount of approximately 72 wt% Au$_{NPs}$, which was also confirmed by rheological results. That is, the viscous modulus (G'') was much higher than the elastic modulus (G') at temperatures ranging from 25 to 70 °C (Fig. 1b). These phenomena clearly indicate that the fluidic behavior of MIL-SH–Au$_{NPs}$ originated from the physical properties of the MIL-SH used as a ligand for the Au$_{NPs}$, although the measured modulus values (G' and G'') of the MIL-SH–Au$_{NPs}$ were higher than those of pure MIL-SH due to the presence of solid Au$_{NPs}$ (see ESI, Fig. S2†). Additionally, the rheological behavior of MIL-SH–Au$_{NPs}$ displayed non-Newtonian fluid behavior, showing an increasing shear viscosity with the increasing loading amount of Au$_{NP}$, which could be well explained by a shear thinning behavior model (Fig. 1c).[39]

Based on these results, the magnetic properties of the MIL-SH–Au$_{NPs}$ were examined by superconducting quantum interference device (SQUID) magnetometry. First, 19 mg of MIL-SH–Au$_{NP}$ was contained in a capsule, and the magnetic moment of the capsule was measured in the magnetic field range of −50 000 to +50 000 Oe. As shown in Fig. 2a, the magnetic curve of MIL-SH–Au$_{NP}$ measured at 300 K exhibited a linear response to the magnetic field without any coercivity, remanence, hysteresis, or saturation in the observed magnetic field range, suggesting paramagnetic properties. The linear paramagnetic curve clearly suggests that there was no interaction between the magnetic moments of the fluids at 300 K. From the slope of the magnetic field dependence, the magnetic mass susceptibility (χ_g) of MIL-SH–Au$_{NP}$ was determined to be approximately 3.45×10^{-5} emu g^{-1} (or magnetic molar susceptibility, $\chi_{mol} \sim 1.22 \times 10^{-2}$ emu mol^{-1}), and the resultant effective magnetic moment (μ_{eff}) calculated from χ_{mol} and μ_{eff} relations was measured to be approximately 5.42 Bohr magneton (μ_B).[40] In addition, the temperature dependence of the reciprocal paramagnetic molar susceptibility at a magnetic field of 10 000 Oe followed a typical Curie–Weiss law with a Weiss temperature of −13.3 K and a Curie constant $C = 3.73$ emu K mol^{-1} Oe^{-1} (Fig. 2b). These values are consistent with the previous results reported for

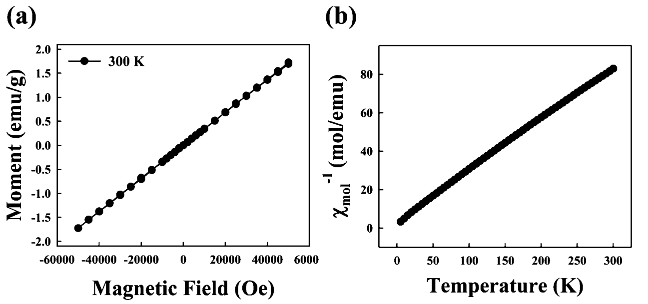


Fig. 2 (a) Magnetization of 72 wt% MIL-SH–Au$_{NPs}$ as a function of the external magnetic field measured at 300 K. (b) The reciprocal molar susceptibility curve of 72 wt% MIL-SH–Au$_{NPs}$ obtained to confirm the paramagnetic properties of the fluid.

high-spin d^5 Fe(III) ions and $FeCl_4^-$ ion-based magnetic fluids.[35,41] Furthermore, considering that the magnetic properties of MIL-SH without Au_{NPs} were similar to those of the MIL-SH–Au_{NPs} (see ESI, Fig. S3†), it is reasonable to conclude that the paramagnetic properties of the MIL-SH–Au_{NPs} originate from the $FeCl_4^-$ ions within MIL-SH ILs. Although it has been reported that 4.4 nm Au_{NPs} stabilized by the dodecanethiol ligand could exhibit very weak ferromagnetic behavior at room temperature, we did not detect any ferromagnetic properties for Au_{NPs} with a diameter of approximately 7 nm.[42]

We also investigated the temperature-dependent ionic conductivity (σ) of the MIL-SH–Au_{NP} fluids, as shown in Fig. 3a. The ionic conductivity of the MIL-SH–Au_{NP} fluids rapidly increased from 8×10^{-12} S cm^{-1} to 1.74×10^{-5} with an increase in temperature from 210 to 300 K, which follows the Vogel–Tammann–Fulcher (VTF) model.[43–45] The ionic conductivity displayed a plateau at temperatures below 210 K. This plateau implies that the fluidity of the MIL-SH–Au_{NPs} in the solid phase (*i.e.*, crystalline phase) makes no contribution to the conductivity. In contrast, the ionic conductivity of the MIL-SH ILs containing no Au_{NPs} increased sharply above 225 K because the pure MIL-SH ligands possess relatively strong interionic interactions compared with those of the MIL-SH ILs bound to the Au_{NP} surface (*i.e.*, MIL-SH–Au_{NPs}), which exhibit a disordered hybrid structure;[46,47] thus, MIL-SH begins to behave as a fluid above 225 K (see ESI, Fig. S4†). It was reported by Li *et al.* that a decrease in interionic interactions in IL media causes an extreme increase in ionic conductivity.[46] This phenomenon was confirmed by an analysis of the differential scanning calorimetry (DSC) traces of the ILs during heating. In particular, the glass transition temperatures (T_g) of MIL-SH and MIL-SH–Au_{NP} were measured to be approximately 225 K and 210 K, respectively (Fig. 3b). It was reported by Yoshida and Saito that T_g behavior is observed instead of melting temperature (T_m) behavior when the alkyl groups in alkyl-methylimidasolium ILs are changed from ethyl to butyl groups.[48]

Furthermore, at temperatures below 210 K, the ionic conductivity of the MIL-SH–Au_{NPs} was strongly influenced by changes in frequency rather than changes in temperature. In this case, the dependence of the ionic conductivity on frequency followed a power law: $\sigma(\omega) \propto \omega^1$ (Fig. 3c). Additionally, at temperatures above 210 K, the ionic conductivity of the MIL-SH–Au_{NPs} remained constant at low frequency (*i.e.*, 0.1–10^2 Hz) but gradually increased with increasing frequency from 10^2 to 10^6 Hz (Fig. 3d). Despite the reduced mobility of the MIL-SH–Au_{NP} fluids, it is interesting to note that the ionic conductivity of the MIL-SH–Au_{NP} fluids measured at room temperature is 10–100 times higher than the conductivities of inorganic NP ILs reported by other research groups.[22,25] This phenomenon is mainly due to the high ionic conductivity of MIL-SH with a relatively small M_w compared with that of ILs based on bulky organic or polymer ligands.

Furthermore, the electrical properties of the MIL-SH–Au_{NPs} were measured as a function of the loading amount of Au_{NPs}. For the MIL-SH fluids composed of imidazolium cations and $FeCl_4^-$ anions without Au_{NPs}, the electrical sheet resistance was measured to be 6.06×10^6 Ω $\square^{-1}$. However, the sheet resistance of the MIL-SH–Au_{NPs} notably decreased with the increasing loading amount of Au_{NPs} from 0 to 65 wt% and then reached a plateau at $\sim 3.71 \times 10^4$ Ω $\square^{-1}$ above a loading amount of 65 wt% Au_{NPs} (Fig. 4a). The saturated sheet resistance indicates that the minimum inter-particle distance between MIL-SH–Au_{NPs} stabilized by low-molecular-weight

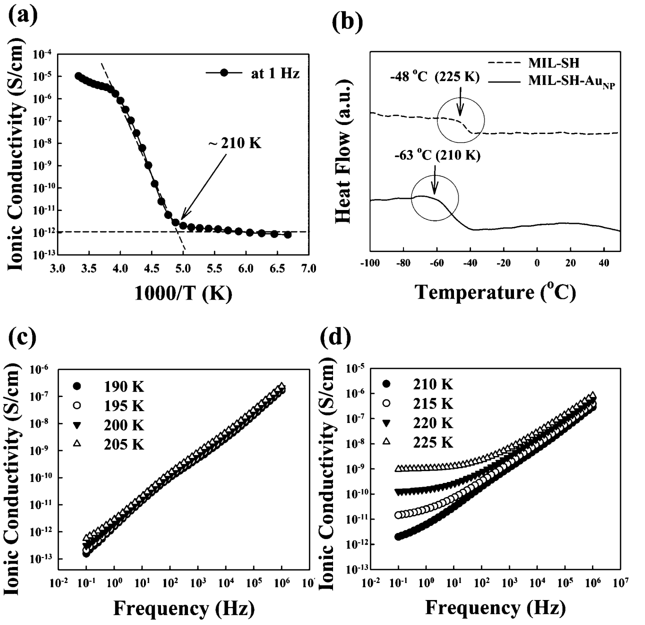


Fig. 3 (a) Temperature-dependent ionic conductivity of 72 wt% MIL-SH–Au_{NPs} measured at a fixed frequency of 1 Hz. (b) DSC analysis of pure MIL-SH and 72 wt% MIL-SH–Au_{NPs}. Frequency-dependent ionic conductivity of 72 wt% MIL-SH–Au_{NPs} at temperatures (c) below and (d) above the glass transition temperature (T_g).

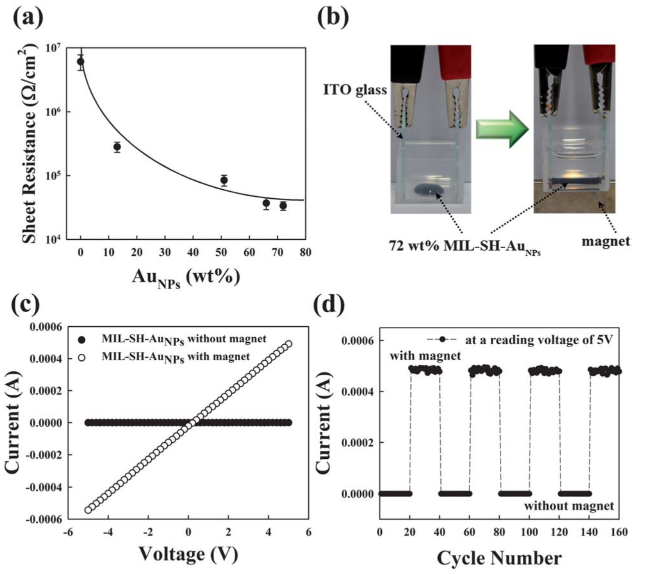


Fig. 4 (a) The measured sheet resistance of MIL-SH–Au_{NPs} as a function of the Au_{NP} concentration using the four-point probe method. (b) The digital images show the magnetic response of the 72 wt% MIL-SH–Au_{NP} fluids between two ITO electrodes to an external magnet. (c) *I–V* curves and (d) cycling tests of MIL-SH and 72 wt% MIL-SH–Au_{NP} fluids under the effects of an external magnet.

MIL-SH was attained at a loading amount of 65 wt% Au_{NPs}. These results can be explained by the electrical percolation theory, which states that both a tunneling effect (affected by the distance between stabilizers) and close contact between metal NPs enable facile electron flow in metal NP films.[49,50] In particular, considering that MIL-SH–Au_{NP} fluids simultaneously exhibit electrical properties and a paramagnetic response, these multifunctional fluids can be used as electric switches with magnetic control in organic media, as shown in Fig. 4b, and furthermore can be used to develop magnetic fluid actuators with electrical switching properties. To confirm the possibility of developing such devices, we investigated the electrical switching properties of the MIL-SH–Au_{NP} fluids using a semiconductor parametric analyzer. The MIL-SH–Au_{NP} ionic fluids immersed in a toluene bath with ITO electrodes on both sides exhibited a reversible ON/OFF switching of their electrical conductivity according to the degree of magnetic attraction and retraction of the fluids to and from the electrodes, respectively (Fig. 4b–d). These results indicate that MIL-SH–Au_{NP} ionic fluids can be effectively applied to develop magnetically controllable electric switches or actuators in organic media.

Furthermore, it is also highlighted that the MIL-SH–Au_{NP} can be effectively applied to catalytic films for nitric oxide (NO) oxidation.[51,52] For confirming this possibility, MIL-SH–Au_{NP} with cationic imidazolium groups was layer-by-layer-assembled with an anionic polyelectrolyte such as poly(sodium 4-styrenesulfonate) (PSS) onto the ITO electrode. In the case of a bare ITO electrode, there is almost no response for NO. However, the (cationic MIL-SH–Au_{NPs}/anionic PSS) film-coated ITO electrode exhibited a new oxidation peak at ~0.82 V, and the peak current increases with increasing concentration of $NaNO_2$, which suggests that Au_{NPs} are catalytic to the oxidation of NO (see ESI, Fig. S5†).

Conclusions

In conclusion, we successfully prepared multi-functional ILs with rheological, magnetic, and conductive properties (*i.e.*, ionic and electrical conductivity). MIL-SH–Au_{NP} fluids with highly concentrated Au_{NPs} (*i.e.*, 72 wt%) exhibited a relatively high ionic conductivity of $\sim 1.74 \times 10^{-5}$ S cm^{-1}. Additionally, the electrical sheet resistance of these fluids significantly decreased with the increasing loading amount of Au_{NPs} from 0 to 72 wt% and then reached a plateau at $3.71 \times 10^4\ \Omega\ \square^{-1}$, despite a further increase in the Au_{NP} concentration. Furthermore, it was demonstrated that the ON/OFF electrical switching of the MIL-SH–Au_{NP} fluids could be controlled by an external magnet, which could be effectively applied to develop magnetic fluid actuators controlled by electrical stimuli. We believe that our approach may provide a basis for designing the physicochemical properties of a variety of metal NPs and furthermore preparing multifunctional metal fluids.

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