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Communications

Luminescent Metallogels of Alkynylrhenium(I) Tricarbonyl Diimine Complexes

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Summary: A series of alkynylrhenium(I) tricarbonyl diimine complexes has been synthesized and shown to display rich thermotropic gelation behavior.

With the growing interest in the search for new advanced materials that show smart responsive behavior, a variety of investigations into organogels have emerged.[1,2] These kinds of materials have been found to show potential applications in materials science,[2a−c] drug delivery,[2d,e] and the construction of supramolecular nanostructures.[2f,g] The formation of gels in organic solvents by small organic molecules poses interesting challenges in the field of molecular recognition and self-assembly, requiring a stabilizing intermolecular interaction, and represents a balance between the tendency of the molecules to dissolve or to aggregate in organic solvents. The intermolecular interactions that cause the gelator molecules to self-assemble are usually noncovalent bonds, commonly van der Waals forces, hydrogen bonding, electrostatic attractions, and $\pi-\pi$ stacking interactions.[3] A key to the molecular design of a low-molecular-mass organic gelator (LMOG) is the control of the above noncovalent molecular forces. While there has been a growing interest in the study of organogels, corresponding studies in metallogels based on metal complexes are still relatively rare and are rather unexplored, despite numerous works on metal complexes with rich spectroscopic properties being known.[4] A particular class of transition-metal complexes that has aroused immense interest is the luminescent rhenium(I) tricarbonyl diimine complexes with their rich and promising photophysical

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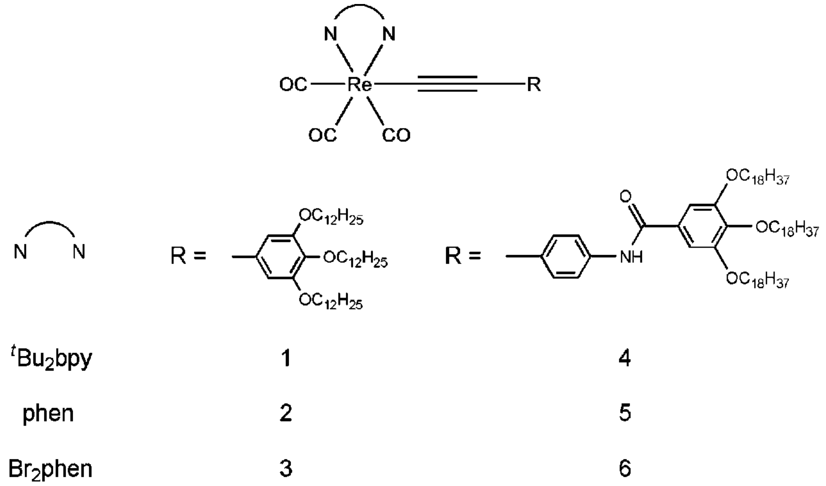
Chart 1



properties.[5,6] The metal-to-ligand charge-transfer (MLCT) excited states of these luminescent organometallic systems are well documented to show large responsive changes to changes in the environment.[5,6] The rich photophysical properties of the MLCT excited states of these metal complex systems are believed to serve as versatile spectroscopic reporters and probes for changes in the environment. Moreover, the fine balance and the interplay of the noncovalent interactions in these gelators can be readily modified by the judicious choice and rational design of the coordinating ligands in the organometallic system, which may hopefully give rise to a fine tuning of the gelation properties of the LMOG. Herein, we report the incorporation of these rhenium(I) tricarbonyl diimine chromophores into organogel systems to form luminescent metallogels.

Complex **1** was synthesized by refluxing a mixture of [Re(^{t}Bu$_2$bpy)(CO)$_3$Br], AgOTf, and 3,4,5-tris(dodecyloxy)-phenylacetylene (**L1**)[4a,7] in THF in the presence of Et$_3$N. Complexes **2** and **3** were similarly prepared by reaction with the corresponding rhenium(I) tricarbonyl diimine complex precursors. Complexes **4**−**6** were also similarly prepared using *N*-(4-ethynylphenyl)-3,4,5-tris(octadecyloxy)benzamide (**L2**)[4a] in place of **L1** (Chart 1).

The electronic absorption spectra of complexes **1**−**6** show intense high-energy absorption bands at ca. 270−360 nm, ascribed to an admixture of intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the diimine and alkynyl ligands. In addition, low-energy absorptions at ca. 400−450 nm with extinction coefficients on the order of 10^3 dm^3 mol^{-1} cm^{-1} were observed, assigned to the [dπ(Re) → π^*(diimine)] metal-to-ligand charge transfer (MLCT) transition, probably mixed with some [π(C≡CR) → π^*(diimine)] alkynyl-to-diimine ligand-to-ligand charge transfer (LLCT) character.[6c,e,g,h]

Upon excitation at $\lambda \geq 350$ nm, the complexes displayed a moderately intense emission band in THF solution at 580−650 nm. The long-lived emission with lifetimes in the submicrosecond range, typical of rhenium(I) tricarbonyl diimine complexes, was suggestive of a triplet parentage. With reference to previous spectroscopic studies on other related rhenium(I) alkynyl complexes,[6c,e,g,h] the luminescence was assigned as derived from excited states of a ^{3}MLCT [dπ(Re) → π^*(diimine)] origin, with some mixing of ^{3}LLCT [π(C≡CR) → π^*(diimine)] character.

The complexes were tested for their gelation properties in various organic solvents by the "stable to inversion of a test tube" method. All the complexes formed an opaque but stable

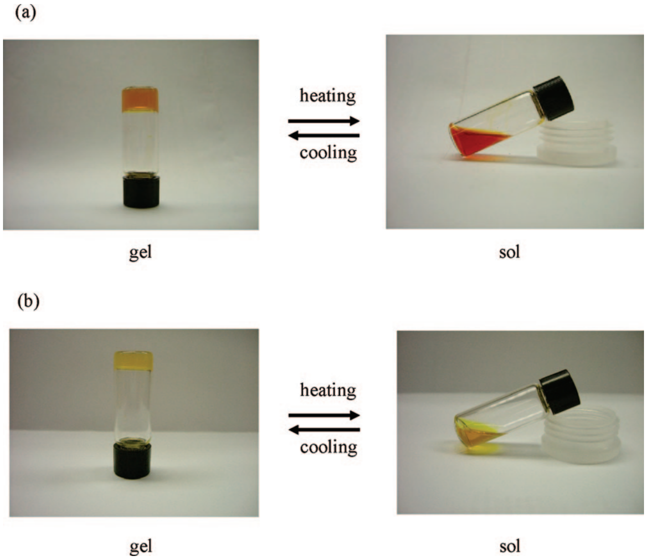


Figure 1. Representative images of (a) the gel formed from **1** in hexane (10 wt %) and (b) the gel formed from **4** in DMSO (9 wt %). The sol−gel transition is found to be thermally reversible, and the gel is stable toward inversion of a test tube for more than 1 week.

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Table 1. Summary of Gelation Properties in Various Solvents[a]

solvent	1	2	3	4	5	6
DMSO	G (7)	G (8)	G (10)	G (9)	G (10)	G (12)
hexane	G (10)	P	P	I	I	I
acetone	S	P	P	G (12)	P	I

[a] Legend: G = opaque gel; I = insoluble; P = precipitation; S = soluble. The values given in parentheses are the minimum concentrations (mg mL^{-1}) needed to achieve gelation (critical gelation concentration) at 25 °C.

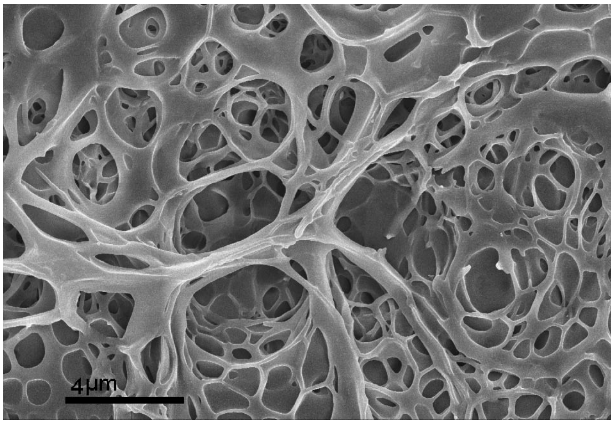

Figure 2. Representative SEM image of xerogel formed from **1** in DMSO (7 wt %).

yellow to orange metallogel with a low critical gelation concentration (cgc) (7 mg mL^{-1}) in DMSO, as shown in Figure 1. In addition, complexes **1** and **4** with ^{t}Bu$_2$bpy moieties were found to be more soluble than the other complexes with other diimine ligands, and they showed gelation properties in *n*-hexane and acetone, respectively, while the other complexes gave only precipitation or insoluble suspensions in these solvents (Table 1). This demonstrates the importance of the design of the coordinating ligands in governing the interplay and the fine balance of noncovalent interactions in the formation of gels.

Scanning electron microscopy (SEM) images were recorded to study the morphology of the DMSO xerogel (air-dried gel) formed by the complexes. Gel samples of **1** in DMSO (7 wt %) were slowly evaporated to dryness, and the resultant xerogels were examined. A representative SEM image is shown in Figure 2. A dense network of continuous fibrous structures, which is characteristic of LMOGs, was observed for all samples. The approximate diameter of the fibers was 200 nm.

A temperature-dependent UV−vis absorption study was performed in the temperature range 25−75 °C. The UV−vis absorption spectra of the gel and sol forms of **1** are shown in Figure 3a and b. Upon an increase in the temperature, the MLCT absorption band at ca. 400−450 nm gradually dropped in absorbance, as the opaque gel became a clear sol in hexane and DMSO. Concomitant with this drop in intensity, a red shift of the MLCT band was observed on going from the gel to the sol form of **1** in hexane. In contrast, a blue shift of the MLCT band was observed on going from the gel to the sol form in DMSO for all the complexes.

The shift of the MLCT absorption band of **1** to higher energy in the gel state relative to that in the sol form in hexane can be ascribed to rigidochromism resulting from the transition of dynamic nanostructures of the fluid sol form to its solidified gel form. Such a rigidochromic effect is commonly observed in the MLCT excited state of related ruthenium(II) and rhenium(I) polypyridyl systems.[8] Conversely, in DMSO, which is a more polar solvent than hexane and presumably a poorer solvent for the neutral alkynylrhenium(I) complexes, a shift of the MLCT energy to the red has been observed upon gelation. It is likely that aggregation occurs in DMSO gel via $\pi-\pi$ stacking interactions between the aromatic moieties that give rise to the observed MLCT changes. A similar phenomenon has also been observed in other organogel systems in DMSO,[9] attributed to J-aggregate formation.[10]

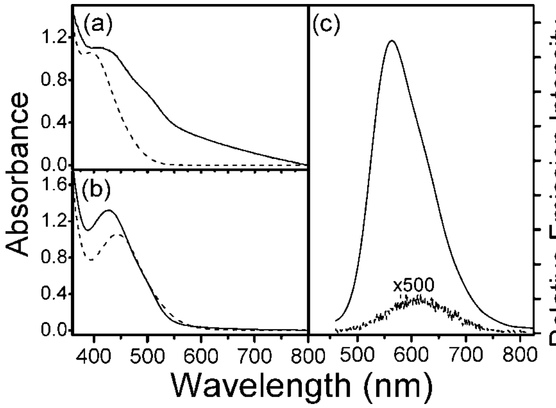

Figure 3. (a) UV−vis absorption spectra of the DMSO gel of **1** at 25 °C (—) and the DMSO sol at 75 °C (- - -). (b) UV−vis absorption spectra of the hexane gel of **1** at 25 °C (—) and the hexane sol at 55 °C (- - -). (c) Corrected emission spectra of the DMSO gel of **1** at 25 °C (—) and the DMSO sol at 75 °C (- - -).

Upon excitation at the absorption maxima or at the wavelength with the same absorbance of the gel and sol forms, the DMSO metallogels emit strongly at 580−650 nm; upon an increase in the temperature, their emission intensity dropped and was almost "turned off" in the sol form (Figure 3c). Such luminescence enhancement in the gel state is in line with the increased rigidity of the media in the gel state, which reduces molecular vibrations and motions and hence slows down the nonradiative deactivation pathways. Similar phenomena have also been reported in other luminescent organogels and metallogels.[4,9,11]

In conclusion, an alkynylrhenium(I) tricarbonyl diimine system was found to form metallogels, which showed a detectable color and emission changes during the sol−gel transition. This property can serve as a probe for microenvironmental changes. The fine balance and the interplay of the

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noncovalent interactions in these gelators can be readily modified by the judicious choice and rational design of the coordinating ligands in the organometallic system.

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Supporting Information Available: Text, tables, and figures giving details of the syntheses, characterization data, photophysical data for the newly synthesized complexes, and UV−vis absorption and emission spectra of the gel and sol forms of complexes **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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