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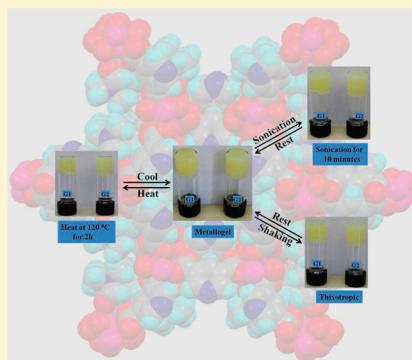
Solvent Dependent Formation of Metallogeles and Single-Crystal MOFs by La(III) and Ce(III) Connectors and 3,5-Pyridinedicarboxylate

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Supporting Information

ABSTRACT: Formation of new metallogeles containing La(III) (**G1**) and Ce(III) ions (**G2**) coordinating with conformationally rigid pyridine-3,5-dicarboxylate (3,5-PDC) in dimethylacetamide (DMA) solvent is reported. Single crystals of the corresponding metal–organic frameworks of La(III) and Ce(III), $[\text{Ln}(\text{III})(3,5\text{-PDC})_{1.5}(\text{DMF})]_n \cdot \text{DMF}$, ($\text{Ln} = \text{La}$ (**1**), Ce (**2**)) have been prepared as well by crystallizing the metallo-organic materials in dimethylformamide (DMF) solvent. The metallogeles formed have been characterized using environmental scanning electron microscopy (ESEM), scanning electron microscopy (SEM), tube inversion test, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), rheological studies, and FT-IR spectroscopy. The PXRD patterns indicate that the gel materials are amorphous in nature. The FT-IR spectra of the gels and single crystals reveal comparable fingerprints suggesting similar structural behavior in the two phases. The isomorphous crystal structures of the MOF materials reveal channeled architectures with molecules of the crystallization solvent trapped within them.



■ INTRODUCTION

Gels, the nonfluid colloidal network or polymeric network, are well-known materials that have a wide range of applications in our daily life starting from hair gel and contact lens to drug delivery for medicinal purpose.¹ Supramolecular-gels consist of a large amount of solvent molecules (nearly 99%) by weight in a very small amount of gelator material (1%). The highly complexed supramolecular network formed by the gelator traps solvent molecules through either covalent bond (chemical gel) or weak interactions (van der Waal, hydrogen bond, electrostatic interaction, etc.) (physical gel) and results in a gel material.² The traditional process of gel preparation is to heat the gelator molecule in a particular solvent or mixture of solvents to generate a clear solution (sol), followed by cooling the material to room temperature. Upon cooling, it yields a supramolecular assembly where the solvent molecules are immobilized and form a gel material. This thermoreversible process of heating and cooling that effects sol–gel interconversion is a stable process and can be repeated for a number of cycles without deterioration.³ The supramolecular gels can be divided into two categories, namely, (1) organogels and (2) hydrogels. Organogels are defined as the gelators that immobilize organic solvents to form a gel, whereas in hydrogels the solvent is water. A large number of low molecular weight gels (LMWG) are reported in the literature;⁴ however, the design and synthesis of supramolecular gels are not straightforward and most of them are generated by serendipity.⁵ Design of supramolecular gels with molecular components having flexible arms, including ureas,⁶ amides,⁷ nucleobases,⁸ fatty acids,⁹ amino acids,¹⁰ and porphyrin derivatives¹¹ based on crystal engineering approach, are well documented in the

literature. When metal atoms are incorporated into the gelation process, the resulting materials are referred to as metallogeles. A large number of metallogeles have been reported recently by Dastidar et al.,^{4a,6i,7a–e} Steed et al.,^{2a,6a–f} Weiss et al.,^{1a,4b,21} Maitra et al.,^{3,5c} and several other groups.¹² Metallogeles have numerous applications in catalysis,¹³ sensing,¹⁴ magnetic materials,¹⁵ and optics.¹⁶ Increase in the number of metallogeles during the past decades is a result of extensive study on coordination polymers¹⁷ and metal–organic frameworks¹⁸ (MOFs), aiming at materials with tailored properties.

Recently, we have reported the synthesis, structure, topology, and magnetic properties of some new coordination polymers based on the pyridine-3,5-dicarboxylic acid (3,5-H₂PDC) and 5-bromonicotinic acid linker with various transition and lanthanoid metals.¹⁹ During our studies, we have observed the formation of metallogeles (**G1** and **G2**) in the case of La(III) and Ce(III) complexes while attempting crystallization from DMA solvent. In this manuscript, we focus on the synthesis and characterization of these new gel materials and their responses under various stimuli and propose a possible reason for the formation of these gels by inspection of the corresponding MOF-type crystal structures obtained alternatively from DMF (instead of DMA) solvent.

■ RESULTS AND DISCUSSION

3,5-H₂PDC is a tridentate ligand with one pyridyl-N and two carboxylic acid coordinating arms that can bind with various

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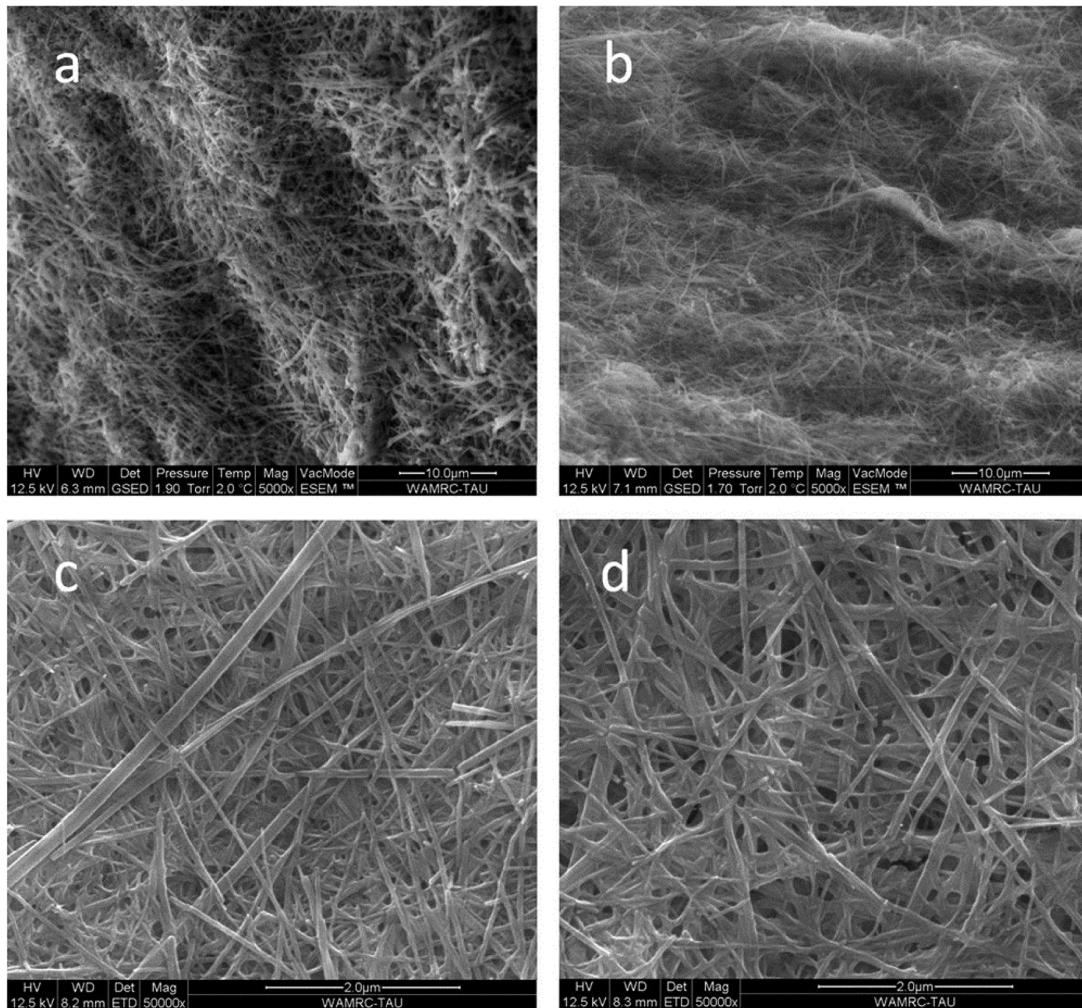


Figure 1. (a) ESEM micrograph of G1 (after drying in situ). (b) ESEM micrograph of G2 (after drying in situ). (c) SEM micrograph of the xerogel of G1. (d) SEM micrograph of the xerogel of G2.

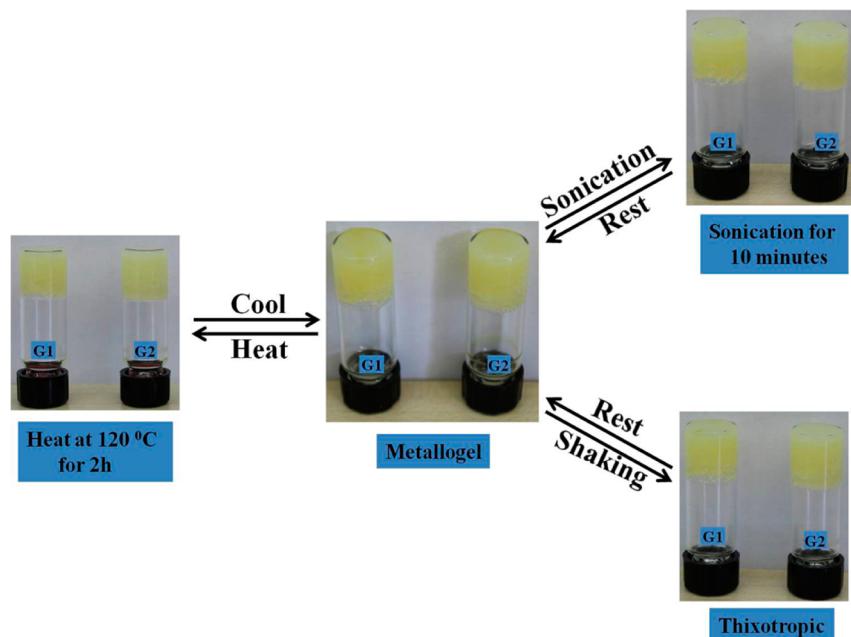


Figure 2. Metallogeles G1 and G2 (3.6 wt % in DMA) under thermal and mechanical stimuli.

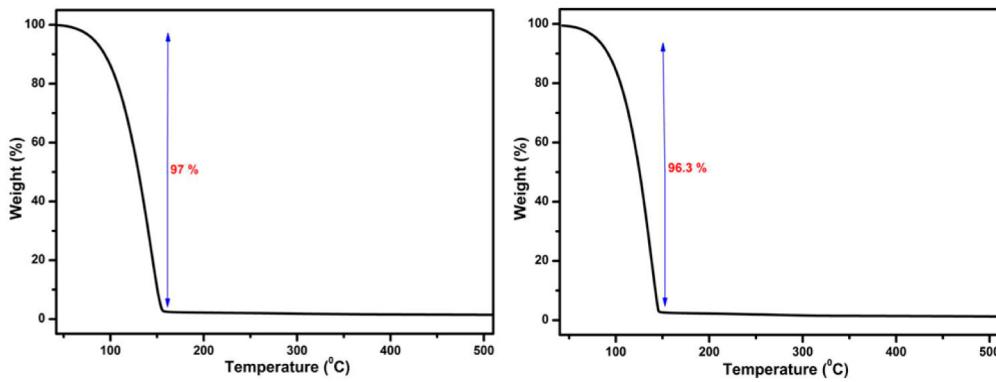


Figure 3. TGA plots of G1 (left) and G2 (right).

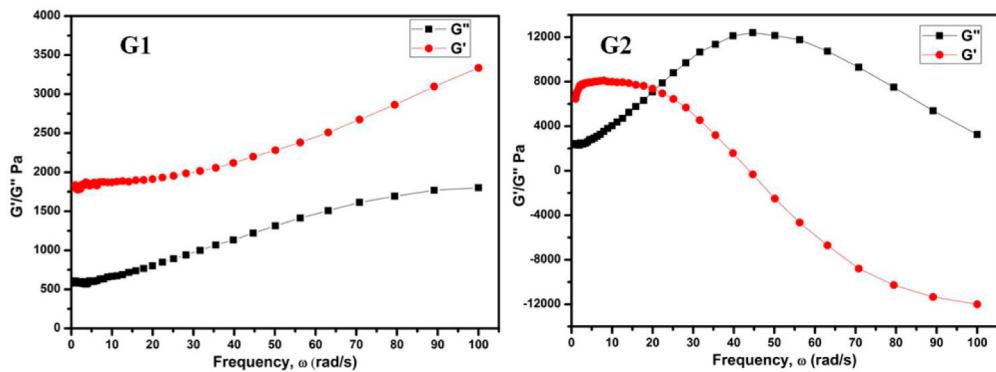


Figure 4. Dynamic frequency sweep experiments in rheological measurements of G1 and G2 with a constant applied strain of 0.125%.

metal atoms to generate framework structures. Despite its commercial availability, relatively few polymeric and 3D framework coordination metal complexes are reported in the literature.²⁰ In order to carry out an extensive study on the coordination polymers of 3,5-H₂PDC, we prepared several crystallization batches with various transition metals and lanthanoid salts using different solvents.¹⁹

The reaction of 3,5-H₂PDC with La(NO₃)₂·6H₂O and Ce(NO₃)₂·6H₂O salts in DMA solvent yielded thick supramolecular gels (G1 and G2, respectively) upon cooling the clear solution. Similar crystallization using DMF afforded needle-shaped single crystals of the corresponding lanthanoid complexes of 3,5-PDC with solvent inclusion. The metallogels G1 and G2 formed have been characterized using ESEM, SEM, tube inversion test, rheological studies, TGA, FT-IR, and PXRD analyses.

Characterization of G1 and G2. Both the ESEM and SEM micrographs of the metallogels of G1 and G2 show highly fibrous networks. The fibers are polydispersed in nature with a diameter range of 24–180 nm and 25–170 nm for G1 and G2, respectively (Figure 1).

The metallogels G1 and G2 are quite stable when kept for more than a month under ambient conditions (room temperature and pressure) without deterioration. They are also nonresponsive to the multiple thermal and mechanical stimuli experiments and do not fall under gravity when the vials that contain the gels are kept upside down, indicating that the gels G1 and G2 are rather strong (Figure 2).

In order to get more insight on the gels G1 and G2, TGA and rheological analyses were carried out. The TGA analysis of G1 showed ~97% weight loss in the temperature range of 70–158 °C. Similar (~96.3%) weight loss has also been observed

for G2 in the temperature range of 70–148 °C. The observed weight losses are in good agreement with the composition of the gels (3.6 wt % in DMA). However, it is difficult to predict the nature of the solvents (trapped or included) as the solvent loss occurs in both cases in a wide temperature range. Yet, the higher temperature (158 °C in G1 vs 148 °C in G2) needed to remove all the solvents in the G1 sample may indicate that the solvents are more tightly held in G1 than in G2 (Figure 3).

Figure 4 depicts the results of frequency sweep experiments in dynamic rheology, wherein the elastic modulus (G') and loss modulus (G'') are plotted against angular frequency ω with a constant applied strain of 0.125%. The plots for G1 are characteristic of a strong viscoelastic material. The values of G' and G'' are nearly invariant up to the frequency of ~40 rad/s, while those of G' are larger than of G'' over the entire frequency range (0–100 rad/s). For G2, both G' and G'' were found to be highly fluctuating, suggesting lesser viscoelasticity.

Single Crystal MOFs of 1 and 2. On crystallizing the starting materials from DMF solvent, nice needle-shaped single crystals of 1 and 2 were obtained, and solved in orthorhombic *Pnma* space group. The two complexes are isomorphous (see Figure S1 and Table S1 in SI) to each other and are also isomorphous with the [Eu(3,5-PDC)_{1.5}(DMF)] reported earlier.^{20f} The asymmetric unit of complexes 1 and 2 consists of one symmetry independent La(III) or Ce(III) ion, one and a half molecules of 3,5-PDC, and one metal-coordinating and additional noncoordinated DMF species. The coordination environment of La(III) ion is shown in Figure 5 with nine coordinated atoms in a distorted monocapped square antiprism geometry. The metal ion is surrounded by eight O atoms from six carboxylate groups of 3,5-PDC and one coordinated DMF molecule (O21). Four out of six carboxylate groups bind to the

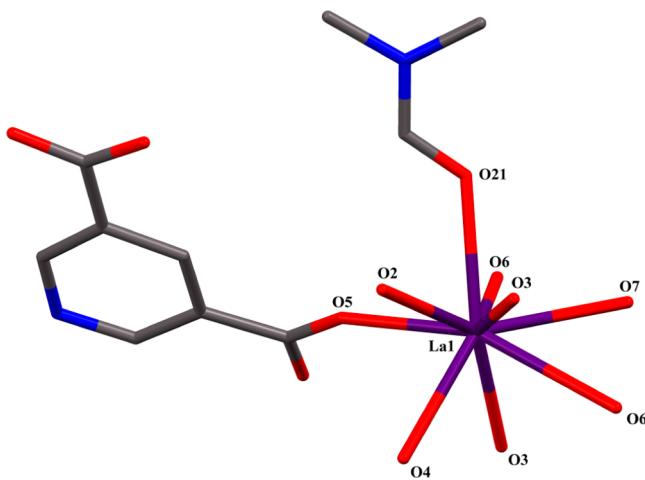


Figure 5. Coordination environment of La(III) ion (hydrogen atoms are omitted for clarity). All the metal-coordinated O-sites (except for O21) are of the six surrounding 3,5-PDC linkers.

central metal ion in a $\mu^2\text{-}\eta^2\text{-}\eta^1$ mode, and the other two in a $\mu^2\text{-}\eta^1\text{-}\eta^1$ modes. The lanthanoid ion connectors form parallel polymeric chains along the a -axis of the crystal (as construction pillars) and the carboxylate groups of 3,5-PDC interconnect between these chains in perpendicular directions. The resulting structure represents a 3D $\{6^6 \times 8 \times 10^3\}_2\{6\}_3$ polymeric framework with wide hexagonal channels propagating along the a -axis (Figure 6). The channel walls are lined with the metal-

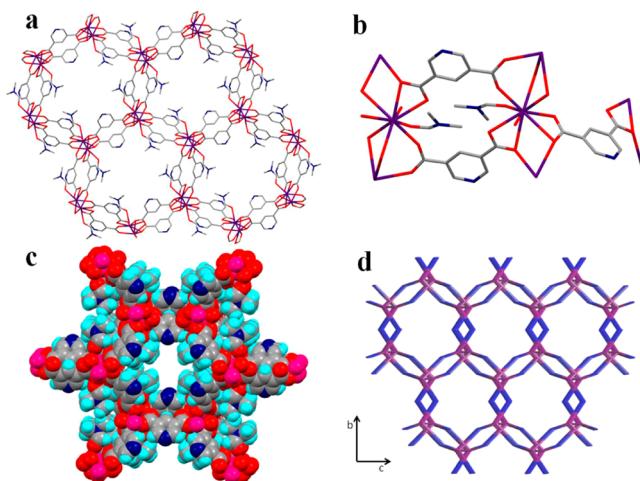


Figure 6. (a) Crystal packing of **1** showing the hexagonal channel (down the a -axis). (b) Bridging between the two metal centers with their coordination environments. (c) Space-filling view of the hexagonal intralattice channel formed in **1**. Its interior is lined by the metal-coordinated DMF ligand and the pyridyl-N sites. (d) Simplified (node and linker) framework structure of metal complex **1** (purple = metal cluster, blue = ligand). In the crystal structures of **1** and **2** these channels are accommodated by noncoordinated DMF molecules.

coordinated DMF ligand as well as the pyridyl ring of 3,5-PDC. The pyridyl-N of the latter is not involved in metal-coordination, due to the strongly oxophilic nature of the lanthanoids, and remains exposed to possible interaction with the channel-accommodated solvent. The interstitial channels centered at 0, 1/4, 3/4 and 0, 3/4, 1/4 are occupied by disordered molecules of the DMF crystallization solvent (which could not be modeled reliably from the diffraction data). An

earlier study of the isomorphous Eu-derivative showed that the solvated compound and its guest-free phase (after releasing the channel-trapped solvent and the metal-coordinated DMF) retain their basic 3D framework,^{20f} confirming genuine porosity of this material. They latter exhibited type I N_2 sorption at 77 K with a Langmuir surface area of $537 \text{ m}^2 \text{ g}^{-1}$.

PXRD and FT-IR Analysis. It is very important to know the structure of the particular gel material in order to understand the mechanism of its formation. As the gel materials are microcrystalline or amorphous in nature, in order to understand their molecular structure, generally powder-XRD and FT-IR spectra of the gels are compared with those of the single crystals obtained from different solvent conditions.²¹ Powder XRD patterns of as synthesized **G1** and **G2** and also xerogel²² of **G1** and **G2** show nearly amorphous nature. The comparative diffraction patterns of **G1** and **1** are shown in Figure 7 (for **G2** and **2**, see Figure S3 in SI).

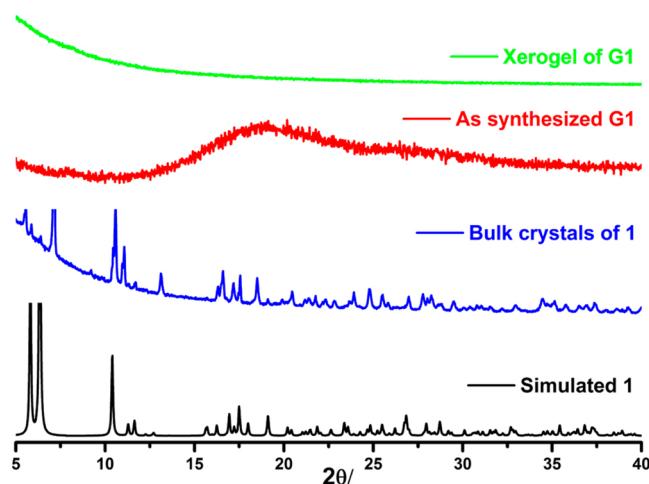


Figure 7. PXRD of as synthesized **G1** and xerogel of **G1** along with the simulated and experimental powder pattern of **1**.

In order to compare the structural features of the gels (**G1** and **G2**) with single crystals of **1** and **2**, we recorded FT-IR of the xerogel of **G1** and **G2** and also bulk crystals of **1** and **2**. Here, remarkable similarities in the peak positions of **2** and xerogel of **G2** are observed (Figure 8). The FT-IR spectrum of the xerogel of **G1** shows some broad peaks in the region of $1200\text{--}1800 \text{ cm}^{-1}$. However, the peaks at lower wavenumber

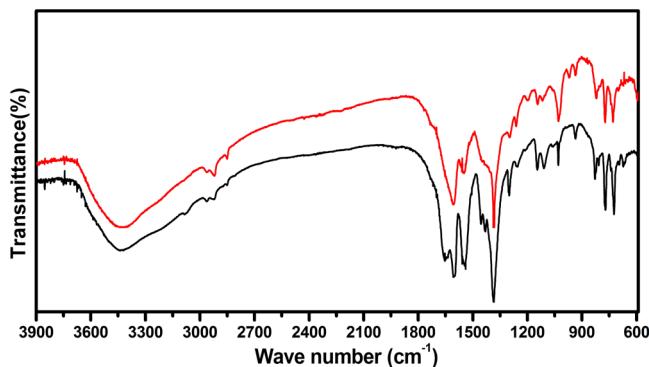


Figure 8. Comparison of FT-IR spectra of xerogel of **G2** (red) and bulk crystals of **2** (black). Note the fingerprint similarity for **2** and xerogel of **G2**.

show excellent matching with the spectrum of bulk crystals of **1** (see Figure S4 in SI).²² The presence of functional group peaks at equivalent regions of the spectra clearly depicts structural similarity of local environments in corresponding materials.

CONCLUSIONS

In the present study, we have observed the formation of attractive metallogels on crystallizing 3,5-H₂PDC with La(III) and Ce(III) salts in DMA solvent. The gels **G1** and **G2** are characterized using ESEM, SEM, tube inversion test, TGA, rheological studies, FT-IR, and PXRD analysis and are stable toward various external stimuli (thermal and mechanical). Both ESEM and SEM micrographs of **G1** and **G2** show highly fibrous polymeric networks. The TGA, rheology, and also the physical characteristics of the gels suggests that **G1** is much stronger compare to **G2**.²² Single crystals of the two complexes **1** and **2** were obtained while crystallizing from DMF (rather than DMA) solvent and show isomorphous behavior with large hexagonal channels filled with solvent molecules. Comparison of the FT-IR of xerogel of **G1** and **G2** with single crystals of **1** and **2** shows structural similarity between the materials. Based on these findings we tentatively conclude that in both the solvents (DMF and DMA) similar coordination polymeric networks are formed having the hexagonal channels with solvent-accessible pyridyl sites. Because of the larger size of the DMA, the solvents are immobilized in the channels leading to the formation of metallogels **G1** and **G2**. Efforts to afford metallogels with other lanthanoid derivatives and appropriately sized solvent function are underway. Our preliminary findings of the gels **G1** and **G2** may provide some additional insight into the gel chemistry of metallo-organic materials, highlighting the importance of MOF architectures in gel synthesis.

EXPERIMENTAL SECTION

Materials. 3,5-Pyridine-dicarboxylic acid was obtained from Merck, La(NO₃)₃·6H₂O was obtained from Sigma-Aldrich; Ce(NO₃)₃·6H₂O was obtained from Strem Chemicals. DMF and DMA were obtained from Bio-Lab ltd, Israel and Merck, respectively.

Physical Measurements. Electron microscopic studies were made using the Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM). Powder X-ray diffraction of all samples were recorded on Bruker D8 Advance diffractometer using Cu K α X-radiation ($\lambda = 1.54056 \text{ \AA}$) over a 2θ range of 5–40° at a scan rate of 1° min⁻¹. Infrared spectra were recorded on a NICOLET 6700, FT-IR spectrophotometer as pressed KBr disks. Rheology experiments were carried out in Rheometric Scientific from Ares. Thermogravimetric analyses (TGA) were carried out on a PerkinElmer Pyris 1 (5 °C/min, flowing N₂(g)). The X-ray measurements (Bruker-ApexDuo diffractometer, Mo K α λ microfocus X-ray source) were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil to minimize crystal deterioration, possible structural disorder, and related thermal motion effects, and to optimize the precision of the structural results. These structures were solved by direct methods and refined by full-matrix least-squares (SIR-97, SHELXTL-2013, and SHELXL-97).^{23,24} All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in idealized/calculated positions and were refined using a riding model. The disordered noncoordinating DMF solvent accommodated in the intralattice channels of **1** and **2** could not be reliably modeled by discrete atoms. Its contribution was thus subtracted by the Squeeze technique, using the PLATON software.²⁵

Syntheses. *Synthesis of G1 (~3.6% wt).* A mixture of 3,5-H₂PDC (10 mg, 0.06 mmol) and La(NO₃)₃·6H₂O (26 mg, 0.06 mmol) are taken in a screw-capped glass sample vial (4 mL) containing 1 mL DMA. The solution is sonicated well to get a clear solution and then

heated at 120 °C for 24 h in a bath-reactor. An opaque amorphous gel **G1** is obtained on cooling the material to room temperature.

FT-IR of xerogel (KBr disc cm⁻¹): 1612, 1382, 1308, 1269, 1255, 1198, 1146, 1029, 972, 930, 831, 774, 725, 601.

Synthesis of G2 (~3.6% wt). This was prepared by similar methodology as described for **G1** using Ce(NO₃)₃·6H₂O instead of La(NO₃)₃·6H₂O.

FT-IR of xerogel (KBr disc cm⁻¹): 1603, 1552, 1386, 1293, 1253, 1197, 1149, 1116, 1028, 972, 932, 820, 772, 731.

Synthesis of 1. A mixture of 3,5-H₂PDC (5 mg, 0.03 mmol) and La(NO₃)₃·6H₂O (13 mg, 0.03 mmol) are taken in a screw-capped glass sample vial (4 mL) containing 2.5 mL DMF. The solution is sonicated well to get a clear solution and then heated at 120 °C for 24 h in a bath-reactor. Needle-shaped white crystals of **1** were obtained on cooling to room temperature. Crystals were separated by filtration and washed with water and DMF and dried in air. Yield: 65%.

FT-IR (KBr disc cm⁻¹): 1650, 1598, 1546, 1390, 1295, 1250, 1207, 1145, 1107, 1029, 931, 828, 770, 726, 595.

Synthesis of 2. This was prepared by similar methodology as described for **1** using Ce(NO₃)₃·6H₂O instead of La(NO₃)₃·6H₂O. Yield: 64%.

FT-IR (KBr disc cm⁻¹): 1653, 1604, 1548, 1388, 1298, 1250, 1202, 1146, 1109, 1025, 937, 825, 777, 729.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information files, crystallographic parameter table, crystal packing diagram of **2**, TGA of **1** and **2**, PXRD of **G2** and **2**, FT-IR spectra of **1** and **G1**. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 979166–979167 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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