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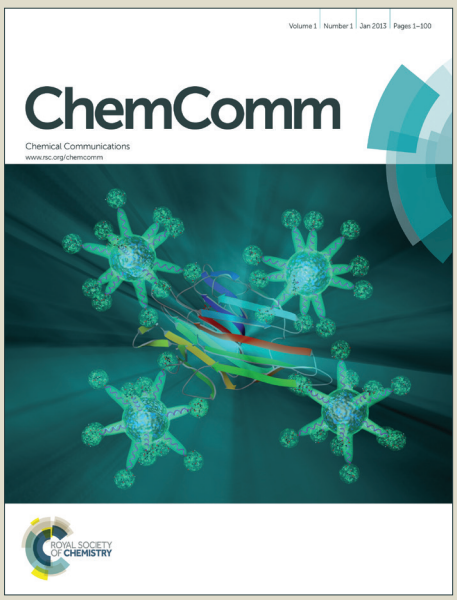

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Metal induced Gelation from Pyridine Cored Poly(Aryl Ether) Dendron with In-situ Synthesis and Stabilization of Hybrid Hydrogel Composite

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Metal induced gel formation from pyridine cored poly(aryl ether) dendron has been achieved. The gel is successfully utilized as a template for the *in-situ* synthesis of silver nanoparticles (AgNPs) in hydrogel networks without using any external reducing or capping agents for the development of exceptionally well-ordered AgNPs-hybrid hydrogel soft composite.

Supramolecular gels have numerous applications in fields such as optoelectronic devices, tissue engineering, and sensors. Over and above, they have also been utilized as structure-directing agents for synthesis of nanoporous materials, templates for assembling nanoparticles, and media for the growth of organic, inorganic crystals of high optical quality.[1] In the past decade, there has been a growing interest in the investigation of metal complexes as supramolecular metallogelators, which particularly involve low molecular weight gelators (LMWG). One of the reasons why the metal complexes of LMWG are preferred is the readiness with which they form metal-ligand coordination that could induce self-assembly and gel formation, leading to diverse applications in areas such as catalysis and magnetism.[2] An additional exciting property of such materials is their ability to act as templates for metallic nanoparticles. Recently, one-dimensional arrangements of metal nanoparticles were realized using gel composites and fibers.[3] Among various nanoparticles, silver nanoparticle have attracted more and more attention due to their antibacterial activity and extensive use in textile industry.[4] Nonetheless, reports on the *in-situ* synthesis of silver nanoparticles stabilized by supramolecular metallogels has been sporadic in nature.[5] Dendrimers and dendrons have attracted much attention due to their nanoscopic hyperbranched macromolecular structure with well-predictable three-dimensional shapes, which make them potential building blocks for the construction of organized functional materials.[6,7] To date, a number of organometallic dendrimers have been reported.[8] Surprisingly, limited number of examples of hierarchical self-assembly of metallo dendrimers and dendrons are reported.[9] In the present work, metal-induced self-assembly and gel formation, using pyridine capped poly(aryl ether) dendrons is described. More importantly, the gel medium is utilized as a template for the *in-situ* synthesis of silver nanoparticle. While poly(aryl ether) dendron derivatives have been utilized for various applications,[10] metal induced hydrogel formation and *in-situ* synthesis as well as stabilization of silver nanoparticle within the gel network has not been attempted. The nanoparticles formed exhibit exceptional stability and a uniquely ordered arrangement on the gel fibres as evident from the electron microscopic images.

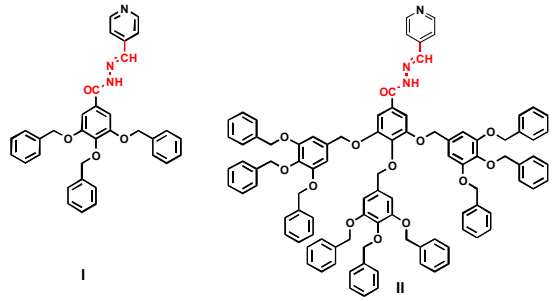

Fig. 1 Structure of the dendrons used

Pyridine-cored poly(aryl ether) dendrons were synthesized according to our previous method and detailed synthesis procedures are given in supporting information.[10e] The dendrons shown in Fig. 1 were completely soluble in common organic solvents such as tetrahydrofuran (THF) dichloromethane (DCM), as well as chloroform and no gel formation was observed even at higher concentration. Surprisingly instant gel formation was occurred when 0.50 equimolar amount of $AgNO_3$ in water has been added to a 0.25 wt% (1 equiv.) solution of compound **I** in THF. The colorless solution was suddenly turned to an opaque

gel. Gel formation was confirmed by vial inversion technique. In addition, compound **I** (1 equiv.) also showed robust green metallogel formation in the presence of 0.5 equiv. copper acetate. Silver complex gel was not thermo-reversible and gradually lost solvent upon heating. Whereas copper complex gel was thermo reversible and T_{gel} was found to be 60 °C. Compound **II** showed partial gel formation, presumably due to steric hindrance, which prevents effective coordination with the metal ions and intramolecular hydrogen bonding. This suggests that the self-assembly in the present system is due to the synergistic effect of hydrogen bonding between dendron monomers and pyridine-metal ion coordination. The presence of H-bonding has been evidenced from FT-IR spectrum of the gel where intense peaks at 3228 cm^{-1} and 1649 cm^{-1} were observed. These peaks correspond to the stretching frequency of H-bonded –NH and CONH, respectively, in the gel system (Fig. S1, ESI). While hydrogen bonding in the self-assembly was a necessary condition, it was not sufficient for gelation. The decisive driving force for gelation was metal ion coordination.

The morphological properties of the dendron based metallogels were obtained through scanning electron microscopy (SEM). Fig. 2a and 2b depict selected SEM images of the xerogel of compound **I** with $AgNO_3$. These xerogel consist of 3D entangled fiber aggregate with diameter range 50-100 nm and length in several micrometer scale. Most likely, the fibers observed in the electron micrographs consist of bundles of gelator aggregates. Similar structures have been observed for compound I-Cu complex gel systems (Fig. 2b).

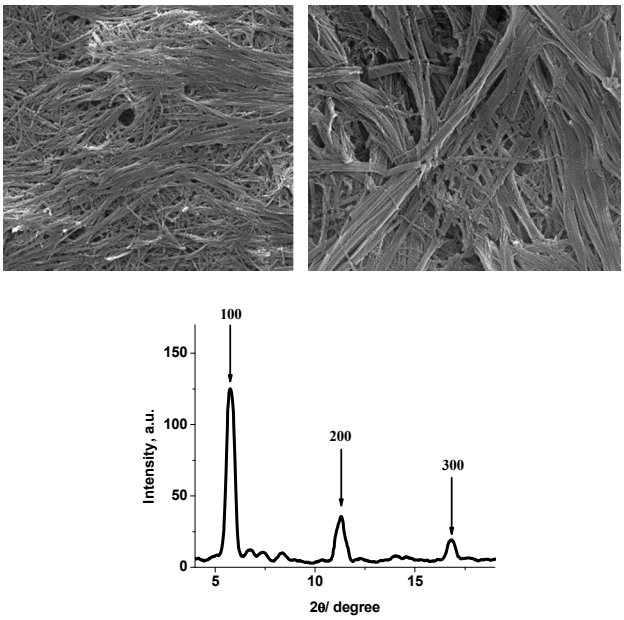

Fig. 2: SEM image of metallogel a) **I**-Ag gel, b) **I**-Cu gel and c) Powder-XRD pattern of silver complex gel of **I**

To gain additional insight into the structures that comprise the gel formed from the compounds, powder X-ray diffraction (XRD) was employed. XRD of the xerogel gave a reflection ratio 1:2:3, suggesting that molecules have been arranged in the lamellar pattern (Fig. 2c).[11] The end-to-end distance in the dendron wedges of **I**/Ag+, calculated by CPK molecular modeling method, is approximately 15.31 Å. Powder-XRD results also suggest that d = 15.30 Å, which is in good agreement with the results from the model study. Based on this, a schematic representation of the lamellar formation is given in the supporting information (Fig.S2, ESI). Similar XRD pattern was observed for compound **I**-Cu gel (Fig. S3).

Rheological studies are essential to understand valuable information regarding the structural correlation with viscoelasticity properties of the materials. In principle, the storage (or elastic) modulus G' represents the solid like character and energy stored while the loss (or viscous) modulus G" reflects the liquid like behavior and energy lost. Fig. 3 displays the frequency sweep response of the organogel of compound **I** in the presence of silver (I) and copper (II) ions. It can be seen that G' is an order of magnitude higher than G", confirming that the gel have predominantly elastic nature rather than viscous character, and this is a re-confirmation of the proposed network structure of the coordination polymeric gel. Fig. 3 also suggests that **I**-Ag gel shows larger value for the modulus, compared to that of **I**-Cu gel. Consequently silver (I) gel is stronger than copper (II) gel. Furthermore, the organogel exhibits minimal frequency dependence during the frequency range of 0.1 to 100 rad s^{-1}.

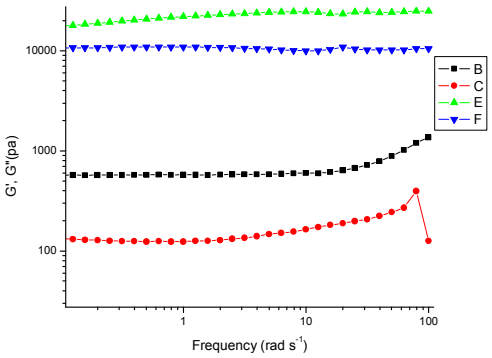

Fig. 3 Frequency dependence of the dynamic storage modulus (G′) and the loss modulus (G″) of cupper (II) (E, F) and silver (I) (B, C) metallogels

More interestingly, silver complex gel slowly undergoes the reduction of silver ion to form silver nanoparticles without any external reducing agent/UV-light irradiation. The formation of silver nanoparticles was visually observed through the formation of a yellow color after 24 h. The gel fibers were not destructed after the formation of silver nanoparticle. The UV-vis spectrum of the nanoparticles shows a broad absorption band with the maximum at 440 nm, which is the typical plasmon absorption of spherical silver nanoparticles (Fig. S4). Powder-XRD pattern of the gel fiber embedded with silver nanoparticles was recorded and is given in Fig. S5. The sharp peaks between 20 -60 clearly show the presence of nano silver on the gel fibers. The formation of silver nanoparticles was further confirmed by transmission electron microscopy (TEM) (Fig.S6) and EDAX (Fig.S7). The size of these particles ranges in a narrow region of 5 to 8 nm and

the nanoparticle size is increased to 10-20 nm upon keeping the system for three days (Fig. 4). Furthermore, increasing the ratio of Ag ion to the dendron leads to faster formation of nanoparticle, but with slightly increased size. As-synthesized nanoparticle is highly stable for several months. The FE-SEM and TEM images of the xerogel clearly showed the formation of spherical silver nanoparticles with 10-20 nm size, which are mostly arranged in an exceptionally well-defined manner, along the fibers (Fig. 4).

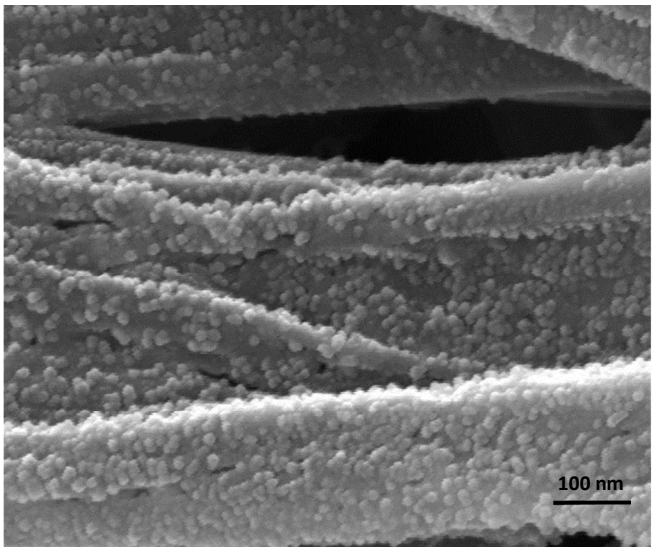

Fig. 4 HR-SEM image of nanoparticle embedded gel formed from compound **I** after 3 days.

This is due to the ability of the gel to form the metallogel in the initial phase and subsequent reduction of the metal ion by the gel *in*-situ. The oxidation state of Ag in the gel fibers was determined by X-ray photoelectron spectroscopy (XPS). The dendron-capped silver nanoparticles typically exhibit two peaks at 368.2 and 374.2 eV from $Ag3d_{5/2}$ and $Ag3d_{3/2}$ orbitals respectively (Fig. S8), which indicates the presence of Ag(0).[12]

In summary, we have developed low molecular weight metallogel systems based on poly(aryl ether) dendron derivatives containing pyridine unit attached through an acylhydrazone linkage, which can act as an efficient gelator to form novel metallogel systems. Dendron show excellent gel formation in the presence of silver and copper metal ions. Multiple noncovalent interactions such as metal ion–pyridine coordination and H-bonding synergistically promoted the formation of efficient metallogels. The metallogel containing silver ion undergoes *in-situ* reduction leading to the formation of silver nano-particles adhering to the gel fibres in a unique fashion. Results suggest that the gels act not only a reducing agent but as a good host system also for stabilizing silver nano-particles.

We thank Nano Mission, Department of Science and Technology, Govt. of India for financial support.

Notes and references

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Electronic Supplementary Information (ESI) available: Powder-XRD experiments, TEM image. See DOI: 10.1039/b000000x/

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