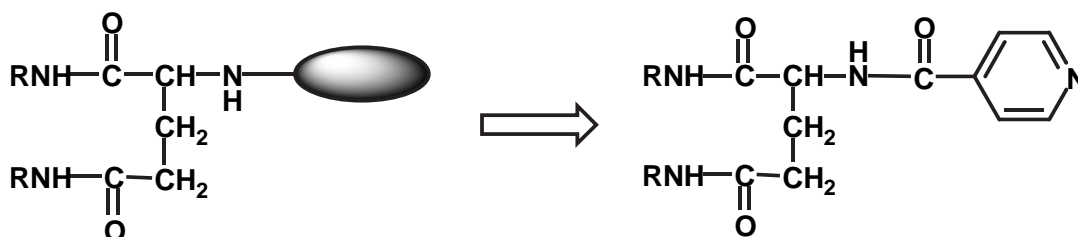


COORDINATION-INDUCED GELLATION: GLUTAMATE-DERIVED LIPIDS WITH LEWIS-BASIC SITES AND THEIR METAL COMPLEXES

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Over the last two decades, there has been a rapidly growing exploration of organogels, composite viscoelastic materials which spontaneously “self assemble” when small amounts (< 2 wt%) of an appropriate gelator are introduced into an organic liquid.¹ Interest in these materials is driven at a fundamental level by the desire to understand the complex self-assembly processes responsible for the formation of the three-dimensional entangled network of gelator strands, which immobilizes the solvent portion of the system. Additionally, organogels have numerous possible practical applications, such as optical components, sensors, low-dimensional conductors and membrane filters.² Applications such as acoustic dampening, thermal insulation and catalysis have been proposed for xero- and aerogels, the closely related materials which are produced by the removal of the solvent portion of gels.³ In addition to polymers, inorganic clays, and proteins, numerous classes of relatively low molecular mass species have been shown to act as gelators. Indeed, molecules as simple as n-alkanes have been shown to form gels with select solvents.⁴ While numerous small-molecule gelators have been identified, relatively few of these systems are based on organometallic or inorganic coordination complexes.⁵ To address this gap in the field, we have decided to undertake a comprehensive effort to design a new class of metallogelators based the glutamate lipid motif originally developed by Ihara and co-workers.⁶



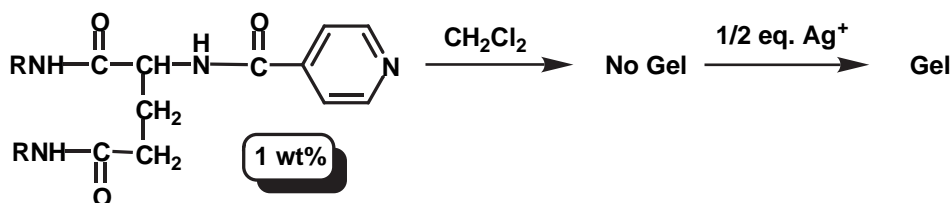
Our approach in this work has been to incorporate a Lewis-basic moiety, such as isonicotinic acid or 2,2'-bipyridine, as the head-group. In the former case, the free lipid shows behavior similar to those reported previously without Lewis-basic sites (Table 1).

Table 1. Gelation results 0.3wt% of lipid in a variety of solvents

Gel	Soluble	Precipitate
Benzene	Methanol	Ether
Toluene	Ethanol	Acetone
Xylene	THF	Acetonitrile
Tetrahydronaphthalene	Dichloromethane	Water
Cyclohexane	Chloroform	
Silicone oil		

Preliminary structural studies suggest that the packing in the gel strands is similar to that in the bulk.

We have explored the ability of this new ligand to form complexes with a variety of metal centers, including divalent ions such as Co^{2+} , Ni^{2+} and Cu^{2+} and monovalent ions such as Ag^+ and Au^+ , both before and after gelation. Notably, we have found that coordination of the ligand to a metal center can induce gelation. While the free ligand does not readily gel halogenated solvents such as CH_2Cl_2 , addition of Ag^+ to dilute solutions of the lipid results in rapid gelation.



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