

A trisbipyridine tripodal ligand as toluene gelator. Phase transition-triggered binding of iron(ii)

Jean-Ernest Sohna Sohna and Frédéric Fages*

Photophysique et Photochimie Moléculaire (URA 348 CNRS), Université de Bordeaux I, 351 Cours de La Libération, 33405 Talence Cedex, France

The formation of a physical gel with toluene is reported for a trisbipyridine ligand which exhibits iron(ii) binding properties triggered by the gel-to-liquid phase transition.

During the course of investigations on the synthesis of new molecular receptors for transition-metal ions,¹ we discovered that the trisbipyridine ligand L¹ exhibited unanticipated solvent gelation properties.†

At room temperature, a solution of ligand L¹ in toluene is entirely transformed into a highly viscous thermoreversible gel. In a typical gelation experiment, a 1 mg sample of L¹ ($M_w = 838$) was added to 1 cm³ of toluene in a test tube, and the mixture was either heated or sonicated at room temperature until total dissolution. The resulting solution was allowed to stand undisturbed for *ca.* 2 h at room temperature. The obtained transparent gel mass could be inverted without any flow, and remained stable for several months in a stoppered tube. Using 2 mg of L¹, the gelation of the same volume of toluene was effected in only a few minutes. One molecule of the gel-forming tripodal molecule can therefore bind up to 8000 molecules of toluene. We determined T_{gel} of L¹ by the spectroscopic turbidity method. We measured the absorbance at 600 nm of a gel $\{[L^1] = 1.15 \text{ mg g}^{-1}\}$ prepared in a 10 mm optical cell. A value of 72 ± 1 °C was obtained by raising the temperature of the sample at a rate of 1 °C min⁻¹.

It was also found that 1 : 4 (molar ratio) CH₂Cl₂-diethyl ether and 2 : 3 CH₂Cl₂-*tert*-butyl methyl ether solvent mixtures could be gelled quite effectively $\{[L^1] = 1.2 \text{ mg g}^{-1}\}$. L¹ did not form gels with cyclohexane, pentane, methanol, Me₂SO, dichloromethane, chloroform, nitrobenzene, or *o*-xylene. The structurally related compounds L²-L⁴ did not gelate toluene.‡

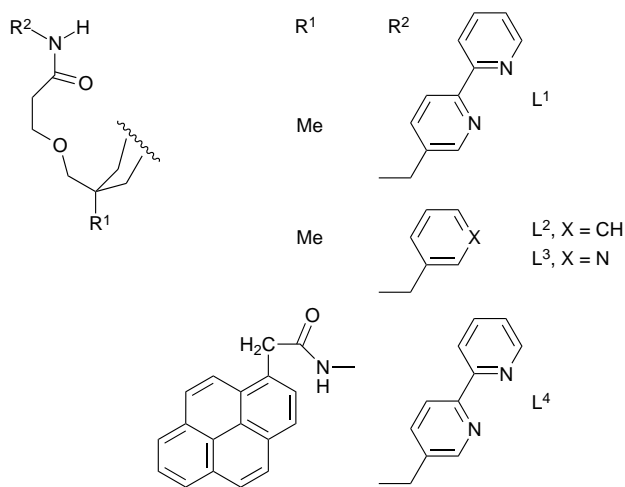
Over the last few years, the ability of several classes of low molecular-mass organic molecules to promote physical gelation of organic solvents has been reported.² This phenomenon has been explained on the basis of gelator molecules self-aggregation, which produces a three-dimensional network

encaging solvent molecules.^{2,3} van der Waals interactions and/or hydrogen bonding were invoked to account for supramolecular network formation. The FTIR spectrum (KBr) of a xerogel, obtained by the slow evaporation of toluene from a gel sample, was compared to that of L¹ crystallized from methanol. Bands at 3281 (NH), 1636 (amide I), and 1548 cm⁻¹ (amide II) cm⁻¹ were observed in the spectrum of the xerogel, whereas the corresponding bands in the spectrum of L¹ obtained from methanol were found at 3424, 3284, 1649 and 1556 cm⁻¹. This data are indicative of an enhanced manifestation of hydrogen-bonding interactions in the former sample relative to the latter. While intramolecular hydrogen bonds were shown to prevail in solution for a series of related tripod-like molecules incorporating amido linkages in each of the tripod chains,⁴ it is very likely that gelation of the apolar toluene solvent by L¹ could rather result from molecular self-aggregation through extensive intermolecular hydrogen bonding. The bipyridine subunits might play a specific role in the assembling process leading to gelation, although, as yet, this remains undemonstrated.§

A great variety of complexing agents containing three 2,2'-bipyridine chelating units have been synthesized previously and were shown to exhibit a strong affinity towards first-row transition-metal cations (M²⁺).⁵ Especially, some receptors bearing pendent 2,2'-bipyridyl-5-ylmethyl arms were found to form extremely stable $[M(\text{bipy})_3]^{2+}$ complexes in solution.⁶ Consistently, $[\text{FeL}^1]^{2+}$, prepared by reaction of L¹ with 1 mol equiv. of FeCl₂·4H₂O, was observed to be quite stable in aqueous media, and could be isolated by addition of an excess of potassium hexafluorophosphate. Its VIS spectrum in acetone ($\lambda_{max} = 520 \text{ nm}$, $\epsilon_{max} = 7220 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) was very close to that of $[\text{Fe}(\text{bipy})_3]^{2+}$ and of iron(ii) complexes⁶ of related ligands. The formation of the 1 : 1 complex in methanol ($[L^1] < 10^{-5} \text{ mol dm}^{-3}$) was confirmed spectrophotometrically by the method of continuous variations (Job plot).

Shinkai's group reported previously the case of a cholesterol-based gelator bearing a crown ether moiety. The gelation ability of this system was shown to respond to alkali-metal cations.⁷ To our knowledge, L¹ is the first example of a molecular receptor for transition-metal ions endowed with solvent gelation properties. A gelled toluene solution of ligand L¹ showed drastically reduced complexation ability towards iron(ii) salts.

When 0.5 cm³ of water was carefully deposited at the top of a toluene gel sample prepared in a 10 mm diameter test-tube from 0.5 cm³ of toluene $\{[L^1] = 1.2 \text{ mg g}^{-1}\}$, we observed that (i) the aqueous phase, despite being denser, occupied the upper layer and (ii) the biphasic system remained stable indefinitely. When the same experiment was carried out with water containing an excess of Fe(SO₄)·7H₂O, the gel mass was similarly unaltered after 24 h. As compared to the blank experiment, only a slight modification of the shape of the interface layer between gelled toluene and isotropic water was noticed. Furthermore, the latter phase slowly turned pink, probably due to the extraction of some ligand molecules from the gel into the isotropic water phase driven by complexation equilibria. When the system was heated above T_{gel} , the gel collapsed, which led to mixing and the inversion of toluene and water, with, simultaneously, a deep red colouring of the aqueous



solution. VIS absorption spectroscopy indicated that the total amount of ligand L¹ initially dissolved in toluene was then transferred to water as the iron(ii) chelate. In the blank experiment, L¹ was not extracted into water.

Polymer gels that can take up or release molecules upon phase transition are of considerable interest for a wide range of applications.⁸ The properties of the new gelator L¹ could lead to the development of supramolecular devices for applications.

We are grateful to the CNRS, the Université de Bordeaux I and La Région Aquitaine for financial support.

Footnotes

† Compound L¹ was prepared by a simple two-step procedure. 1,1,1-Tris-(carboxyethoxymethyl)ethane was activated *via* DCC-mediated condensation with *N*-hydroxysuccinimide to give the corresponding active triester. The latter was reacted in dmf with 3.3 mol equiv. of 5-aminomethyl-2,2'-bipyridine to afford L¹ (white solid) in 80% yield. Mp 91 °C, ¹H NMR (CD₃OD): δ 0.80 (s, 3 H), 2.45 (t, 6 H), 3.25 (s, 6 H), 3.65 (t, 6 H), 4.45 (s, 6 H), 7.4 (m, 3 H), 7.8 (m, 6 H), 8.25 (m, 6 H), 8.60 (m, 6 H). Satisfactory elemental analyses and mass spectrometry data were obtained.

‡ L²–L⁴ were characterized by proton NMR spectroscopy and mass spectrometry. The synthesis of L⁴, together with its metal cation binding and photophysical studies, will be published elsewhere.

§ L² and L³ do not gelate. Furthermore, we also noticed the conspicuous propensity of a series of related molecular systems symmetrically

substituted with two or three 5-amidomethyl-2,2'-bipyridine moieties to aggregate strongly even in polar solvents.

References

- 1 F. Fages, B. Bodenant and T. Weil, *J. Org. Chem.*, 1996, **61**, 3956.
- 2 T. Brotin, R. Utermöhlen, F. Fages, H. Bouas-Laurent and J.-P. Desvergne, *J. Chem. Soc., Chem. Commun.*, 1991, 416; H. T. Stock, N. J. Turner and M. McCague, *J. Chem. Soc., Chem. Commun.*, 1995, 2063 and references therein.
- 3 P. Terech, I. Furman, R. G. Weiss, H. Bouas-Laurent, J.-P. Desvergne and R. Ramasseul, *Faraday Discuss.*, 1995, **102**, 345.
- 4 I. Dayan, J. Libman, A. Shanzer, C. E. Felder and S. Lifson, *J. Am. Chem. Soc.*, 1991, **113**, 3431.
- 5 R. Ziessel and J.-M. Lehn, *Helv. Chim. Acta*, 1990, **73**, 1149 and references therein; P. Belser, A. von Zelewsky, M. Franck, C. Seel, F. Vögtle, L. De Cola, F. Barigelletti and V. Balzani, *J. Am. Chem. Soc.*, 1993, **115**, 4076.
- 6 P. Sheldon, W. Errington, P. Moore, S. C. Rawle and S. M. Smith, *J. Chem. Soc., Chem. Commun.*, 1994, 2489; R. F. Beeston, S. L. Larson and M. C. Fitzgerald, *Inorg. Chem.*, 1989, **28**, 4187.
- 7 K. Murata, M. Aoki, T. Nishi, A. Ikeda and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1991, 1715.
- 8 T. Tanaka, C. Wang, V. Pande, A. Y. Grosberg, A. English, S. Masamune, H. Gold, R. Levy and K. King, *Faraday Discuss.*, 1995, **102**, 201.

Received, 28th October 1996; Com. 6/07346H