CHAPTER 7

Trinuclear copper(II) complex with *myo*-inositol: A low molecular weight complex as hydrogelator.

7.1 Introduction

As mentioned in chapter **1**, trinuclear complexes can form supramolecular assemblies, which in tern can have enhanced magnetic and redox properties along with some entirely new characteristics. The formation of such supramolecular assemblies can be facilitated in presence of oxygen coordinating groups in the complexes. These lead to the formation of definite structures, not only in solids but also in solutions. Formation of ordered structures, in liquids or solutions is specially, interesting because they can have enormous applications with non-rigid or soft physical form. Recently, several reports have appeared on metallogels which belong to this form of soft materials.

Conventionally, one or a combination of four kinds of forces - ionic bonds, covalent bonds, hydrogen bonds and hydrophobic interactions - leads to the formation of gels. The gelators of organic solvents have recently attracted much attention. They do not only gelate organic solvents but also create novel fibrous superstructures which can be seen by SEM observation of the Xerogels.[1-12] Such type of fibrous structures (fibrils) are observed in case of hydrogels (Xerogels). A few studies have indicated that the gel network is reinforced by polymerization or three dimensional cross links.[13-14] Low molecular mass organic gelators (LMOGs) have gained considerable interest because of the advantages of organogel networks for various optical applications including enhanced charge transport, fluorescence and sensing abilities.[15-18] For these purposes, long alkyl chains or steroidal groups have been incorporated in to the gelator structure and have been necessary for the effective gelation process.[19-26] These organic gels are of particular interest in that being different polymer gels, fibrous aggregation of low molecular-weight compounds formed by non-covalent interactions are responsible for such gelation phenomena. To make organogels, many synthetic lipids have been derived from peptides,[27-36] and sugars.[37-39] Also, cholesterol based gels have been extensively studied for their use as templates for the designing of a variety of materials.[40-42]

In recent years, the discovery and design of specific hydrogels and hydrogelators is intended for varied applications from super-absorbent materials to biosensors. The environmentally sensitive hydrogels are considered as

promising materials for drug delivery and tissue engineering because of their ability to sense changes in pH, temperature or concentration of metabolite and to release their load as a result of this change.[43,44] Such hydrogels with additional functionalities offer highly specific bio-responsiveness.[45-52] However, finding biodegradable polymers for the biological applications becomes challenging.[53] Here hydrogelators[54] small molecules, capable of gelling aqueous solvents, can be more useful and are finding applications in tissue engineering[55] and controlled drug release[56,57]. Aggregation of these small molecule gelators or formation of supramolecular assemblies is through hydrogen bonds in organo gels and through hydrophobic interactions and / or π -staking in hydrogels.[58-60]

These kinds of interactions are important in biomolecules and several sugar based gelators.[61] *Myo*-inositol hexaphosphate hydrogel has recently found application for the prevention of a disease associated with the development of heterogeneous nucleants in soft tissues.[62] Hydrogel containing copolymers of opposite chirality have found medical applications within mammalian bodies.[63]

Very recently, metallogels are emerging as useful materials for varied applications.[64-66] These are coordination polymers, discrete organometallic molecules or metal complexes forming supramolecular assemblies or aggregates through noncovalent interactions,[54,67,68] including metal coordination itself. Such metallogels would find applications in environment, clinical treatment[69] catalysis[70] and ion separation techniques.[71]

A study of the influence of the metal ions in the organo-gels has been reported. It has been observed that the presence of metal ions may change the fiber structure; it does not induce an unfavorable destruction of the intermolecular aggregates but enhances the T_{gel}[72]. Metallogels are recently reported for 'uptake' of nonionic organic molecules from the aqueous phase.[73] Also molecular receptors for transition metal ions are being investigated in the form of gels.[74] A trisbipyridine ligand is reported as a molecular receptor for transition-metal ions endowed with solvent gelation properties.[4]

Presence of metal ions is also known to modify gel formation and help in chirality control and change of certain physical properties. An overview of the role

of metal coordination in molecular gelation has been presented by Fages.[75] Though a number of coordination polymer gels have been reported,[76] transition metal-ligand bonds, have been less explored in terms of the design and construction of gel materials.[77-80] The interest in low-molecular-weight gelators is for the high potential they have for a wide range of advanced functional nanoscale materials. Self assembly of such materials can be tuned by adding a second component.[81] A series of silver(I) and copper(II) complexes of bis-urea ligands form soft tunable metallogels[82] while silver(I) thiolates[83] and trimeric silver(I) pyrazolates[84] form supramolecular pH-responsive hydrogels and phosphorescent organogels, respectively.

It is evident that the presence of transition metal ions can attribute a range of interesting properties to the gels. Hence, it was thought of interest to see if a trinuclear complex can form a supramolecular assembly and lead to the formation of a gel. Hierarchical gelation by organooxotin nanoclusters has also been reported.[85] Iron(II) complexes formed by azobenzene substituted triazoles form photoresponsive gels.[86] Polypyridyl ligands appear to play an important role in the luminescent property of metallogels formed by rhenium(I) and platinum(II) complexes.[87,88]

A transition metal complex involving a polypyridyl ligand such as 2,2'-bipyridyl and *myo*-inositol, one of the most abundant natural isomers involved in inositol catabolism, appears to be an interesting candidate as molecular hydrogelator. Here, we report the pH triggered formation of hydrogel, the first of its kind, formed by trinuclear copper(II) complexes.

7.2 Experimental

Materials

AR grade *myo*-inositol was purchased from BDH. AR quality cupric acetate monohydrate, bipy and sodium hydroxide pellets for maintaining the pH of the solution, were purchased from Merck and used as received. Conductivity water used for the gel formation was lab made.

Synthesis of $[Cu_3ins(H_2O)_6]$ complex

An aqueous solution of 0.831g (4.163mmol) of cupric acetate monohydrate was mixed with a 30ml aqueous solution of 0.250g (1.387mmol) *myo*-inositol. The blue colour of copper(II) solution intensified on addition of inositol. The resulting solution was stirred for 10min. 0.2N NaOH solution was added drop wise to the clear blue solution. The colour slowly changed to green and intensified with increase in pH. Dark green coloured solid started precipitating at pH 9.8. The pH was held at 9.8. The reaction mixture was stirred magnetically for 1hr. The light green coloured microcrystalline solid was isolated by filtration and extensive washing with 60ml water and then ethanol. The product was dried in air.

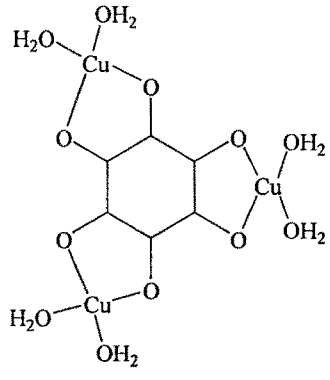


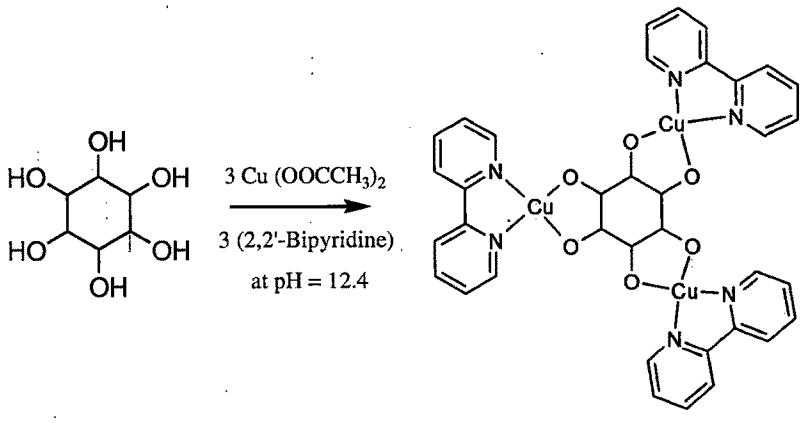
Fig. 7.1 Complex (1), $[Cu_3ins(H_2O)_6]$.

Preparation of the Cu-ins-bipy hydrogel

0.250g (1.388mmol) of *myo*-inositol was dissolved in 10ml of distilled water. 0.831g (4.163mmol) of cupric acetate monohydrate and 0.650g (4.162mmol) bipy were dissolved in 25ml of distilled water to get a blue colored $[Cubipy]^{2+}$ complex in solution. The later solution was then added in the solution of *myo*-inositol. A clear homogeneous blue coloured solution was obtained. No gelation was observed at this condition (pH = 5.3). The pH of this solution was slowly raised to 12.4 using 0.2N NaOH. From pH 9.8 the blue coloured solution, started converting to green. At pH 12.4 the solution became completely green in colour. The green solution was warmed on water bath and allowed to cool at RT when a green coloured transparent gel had formed. The reaction is schematized in

Scheme 7.1. The gelation was confirmed by the inverted test tube method. (**Fig. 7.2**).

Scheme: Formation of the trinuclear complex (2) hydrogelator.



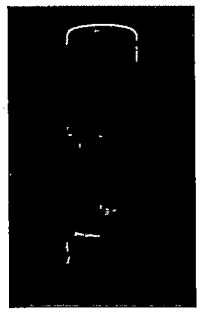


Fig. 7.2 Gel in inverted bottle of complexes [insCu_3(bipy)$_3$].

Preparation of Xerogel

1.600g of gel was dried in air oven at 120°C for three hrs. This resulted in the formation of dry green coloured powder (xerogel). 100mg of xerogel dissolved in 1.5ml water formed gel on warming to 60-70°C and subsequent cooling to RT.

Preparation of trinuclear complex [Cu_3(bipy)$_3$ins(H_2O)$_9$]

The Xerogel was extensively washed with ethanol and the resulting product was dried. The elemental analysis and mass spectral studies have indicated the formation of the title complex.

Physical Measurements

All the physical measurements, UV-vis, IR and ESI spectral analysis, FAB-Mass analysis were carried out using the instruments as mentioned earlier in

chapter two. (page no.79) The Scanning Electron Micrographs (SEM) were recorded using Jeol JSM-5610LV Scanning Electron Microscope. T_{gel} was determined by Ball Drop Method as described below.

Inverted Test Tube Method

100mg of Xerogel was dissolved in 1.6ml of distilled water and the test tube was warmed for the gel formation. The test tube was inverted and the gel was observed to be remaining undisturbed in the test tube.

Determination of T_{gel} (Ball Drop Method)

100mg of Xerogel was dissolved in 1.6ml of distilled water and the test tube was warmed for the gel formation. Thus the formation of gel was confirmed by the inverted test tube method. A 108mg weight glass ball was kept on the gel surface, and the whole test tube was kept in a beaker containing paraffin oil and heated. The temperature was noted when the glass ball touches the bottom of the test tube as T_{gel} temperature.

7.3 Results and Discussion

Inositol being a hexahydroxy compound some of its isomers are expected to have chelating ability. *Myo*-inositol when allowed to react with three equivalents of cupric acetate results in the formation of a trinuclear complex, $[Cu_3ins(H_2O)_6]$, at pH 9.8. Elemental analysis confirms the suggested formula. The complex has features of *myo*-inositol in its FTIR spectrum along with the stretching and bending vibrations in coordinated water. The FAB-Mass spectrum of the complex 1, (**Fig.7.3**) has a peak corresponding to the species $[insCu_3]^+$ at 363 (cald. 363) which confirms the trinucleating ability of inositol. Other peaks corresponding to $[insCu_2(H_2O)]^+$ at 276 (277), $[insCu_2(H_2O)_2]^+$ at 339 (338), $[insCu_3(H_2O)_2]^+$ at 399 (400) also support the formation of a trinuclear complex. The following fragments also have been observed with lower abundance. Fragment $[insCu_3(H_2O]_6]^+$ was observed at m/Z 470 (Calcd. 471), $[insCu_3(H_2O)_5]^+$ was observed at m/Z 453 (453), $[insCu_3(H_2O)_4]^+$ was observed at m/Z 435 (435), $[insCu_3(H_2O]_3]^+$ was observed at m/Z 418 (417), $[insCu_3H_2O]^+$ was observed at m/Z 381 (381), $[ins]^+$ was observed at m/Z 180 (180), $[ins+Cu]^+$ was observed at m/Z 242 (243), $[ins+2Cu]^+$ was observed at m/Z 306 (306), $[ins+3Cu]^+$ was

observed at m/Z 369 (369). All these fragments confirm the formation of copper hexa-aquo complex with inositol which can be formulated as $[Cu_3ins(H_2O)_6]$.

The molecule, being small and sufficiently polar, can get easily aquated rather than forming a gel at all pH values. It also does not form copper hydroxide at higher pH. However, this molecule provides the basic framework for the formation of discrete trinuclear complex with aromatic ligand replacing the water molecules in the above complex. These can be expected to have π-stacking or hydrophobic interactions leading to supramolecular assemblies and provide cavities for entrapping water molecules. Attempts were made to examine the possibility of metallogel formation by substituting water molecules by bipy at various pH.

The reaction of *myo*-inositol with three equivalents of copper and varying amounts of bipy was carried out. No gel formation was observed with 1 or 2 equivalents of bipy at all pH conditions and by varying the concentration.

Only the reaction of 10ml 2.5% aqueous solution (1.388mmol) of *myo*-inositol with 25ml aqueous solution containing three equivalents of $[Cu(bipy)]^{2+}$ complex, resulted in the formation of transparent green coloured gel at pH 12.4 on heating to 60-70°C and subsequent cooling to RT. Following a similar procedure with higher concentrations resulted in the formation of thick gel while lower concentration resulted in the formation of loose gel suspended in solution.

Drying the gel at 120^0C for 3hrs. resulted in the formation of xerogel. 100mg of xerogel dissolved in 1.5ml of water on heating at 60-70^0C and subsequent cooling to RT resulted in the formation of gel again. The T_{gel} determined by ball drop method is found to be 46^0C.

The Xerogel was thoroughly washed with ethanol to remove any unreacted reagents and dried in air. The ethanol washings of the xerogel when examined spectroscopically, were found to be free of bipy or $[Cubipy]^{2+}$ species **(Fig.7.4)**. This reconfirms the presence of all three equivalents of bipy in the gel. The ethanol washed residue is expected to be the trinuclear complex $[insCu_3(bipy)_3]$.

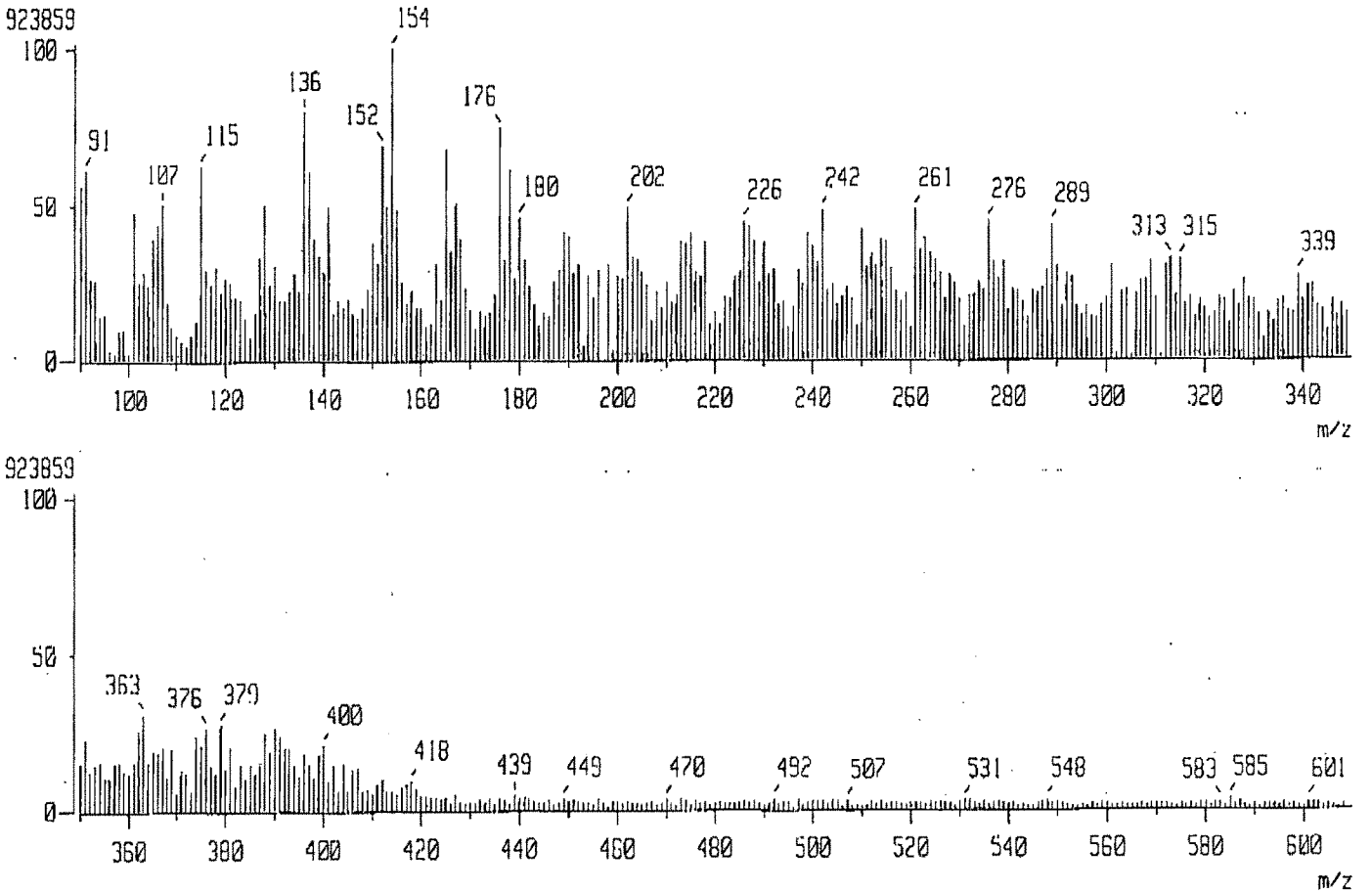


Fig.7.3 FAB-Mass spectrum of [ins$Cu_3(H_2O)_6$]

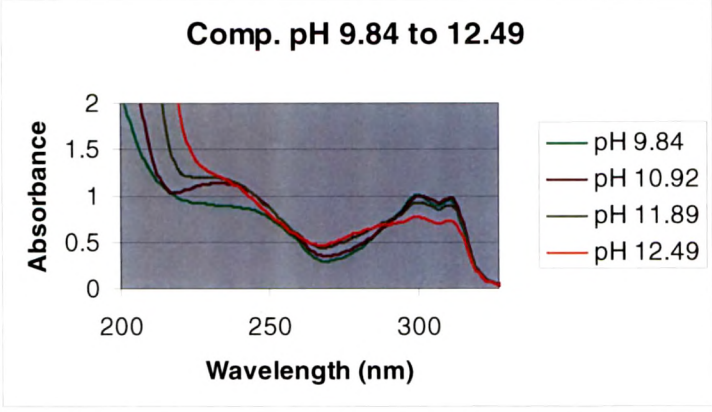


Fig. 7.4 Spectrum of the complex [ins$Cu_3(bipy)_3$] solutions at pH 9.8 to 12.4.

In the UV spectrum of the solution containing 1inositol:3Copper:3bipy, the absorption at ~250nm is found to shift gradually to higher energy (~240nm) with increase in pH. The intensity of absorption decreases at 300 and 310nm. The absorption at 300nm shifts to 297nm as the pH approaches to 12.4. (**Fig.7.4**). The small shifts in the energy of transitions within coordinated bipy can be due to the change in ligand field brought about by axial coordination of hydroxyl ion resulting in the change in energy of metal orbital.

In the ligand field region of the electronic spectra, an absorption maximum in [Cubipy] is observed at 675nm while the same is observed to shift to 657nm at natural pH corresponding to the increase in ligand field. At pH 12.4 the absorption maximum is observed at 665nm. Thus the coordination of inositol is evident.

It can be seen from the IR spectra that, the xerogel and the complex $[Cu_3(bipy)_3ins(H_2O)_9]$ both have important features of inositol and bipy. (**Fig.7.5**). They also show the presence of H-bonded water molecules.

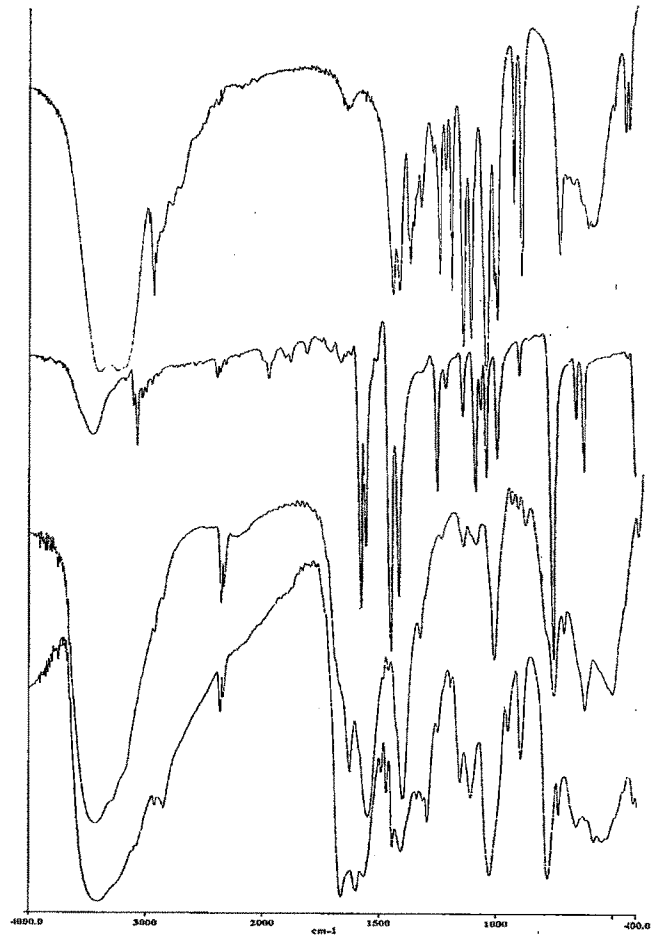


Fig.7.5 FTIR spectra of inositol, bipy, xerogel and complex [$insCu_3(bipy)_3$].

It was possible to record ESI mass spectrum of complex 2, as it is freely soluble in water. The ESI-MS analysis of the trinuclear complex [$insCu_3(bipy)_3$], shows the presence of species, $[H_3insCu_3(bipy)_3]^{3+}/3$ at m/Z at 278, $[H_3insCu_3(bipy)_3(H_2O)_9]^{3+}/3$ at m/Z 332, $[Cubipy]^+$ at m/Z 219, $[Cu(bipy)_2]^+$ at m/Z 375, [Cuinsbipy] at m/Z 393 and $[Cuins(bipy)_2]^+$ at m/Z 549 confirm the formation of trinuclear complex [$Cu_3ins(bipy)_3$].

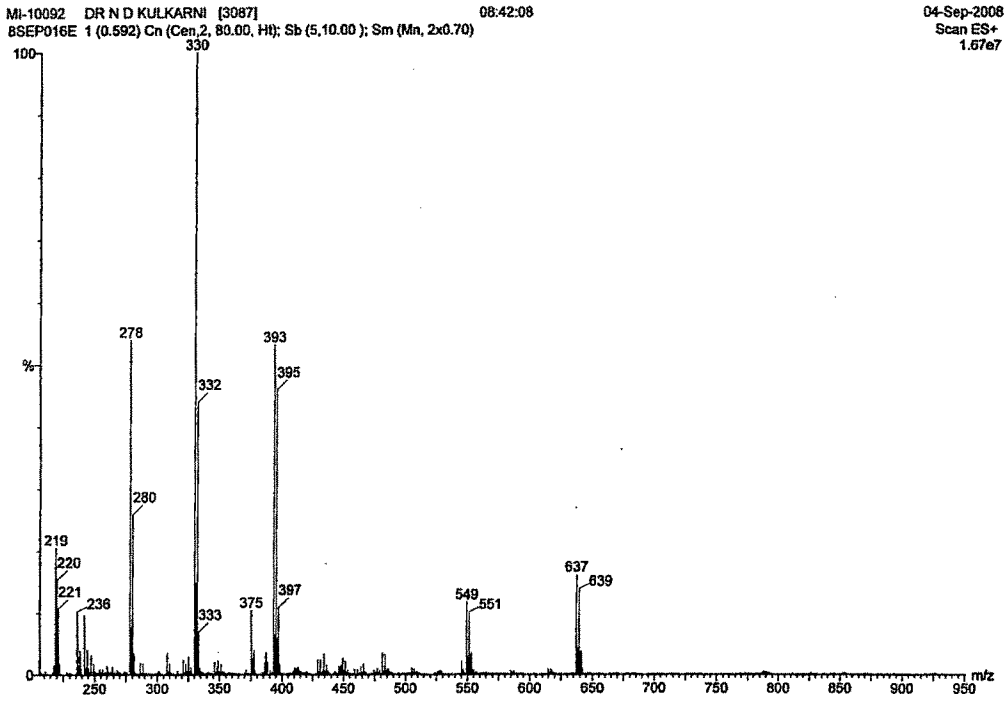


Fig. 7.6 ESI-MS spectrum of complex $[insCu_3(bipy)_3]$.

In order to see further fragmentation of the complex FAB-Mass spectrum (**Fig. 7.7**) was recorded. Though poor quality FAB-Mass was obtained due to poor solubility of complex 2 in suitable solvents, it does confirm the presence of coordinated water and bipy in the complex. In the FAB-Mass the molecular ion peak $[Cu_3(bipy)_3ins(H_2O)_9]+3H^+$ has been observed at 330 and 333. Other significant fragments include, $[insCu_3(bipy)_2(H_2O)_6]^+$ at m/Z 783 (cald,783), $[insCu_3(bipy)_2(H_2O)_5]^+$ at m/Z 765 (765), $[insCu_3(bipy)_2]^+$ at m/Z 675 (675), $[insCu_2(bipy)_2]^+$ at m/Z 612 (612), $[insCu_3(bipy)]^+$ at m/Z 519 (519), $[insCu_2bipy(H_2O)]^+$ at m/Z 474 (474), $[insCubipy(H_2O)]^+$ at m/Z 409 (411), $[Cu(bipy)_2]^+$ at m/Z 375 (375), $[insCu_3(bipy)_2(H_2O)_5]^+/3$ at m/Z 254 (255), $[Cubipy]^+$ at m/Z 219 (219), and $[ins-H]^+$ at 179 (180), $[bipy]^+$ at m/Z 157 (156) which confirm the trinuclear copper(II) complex formation.

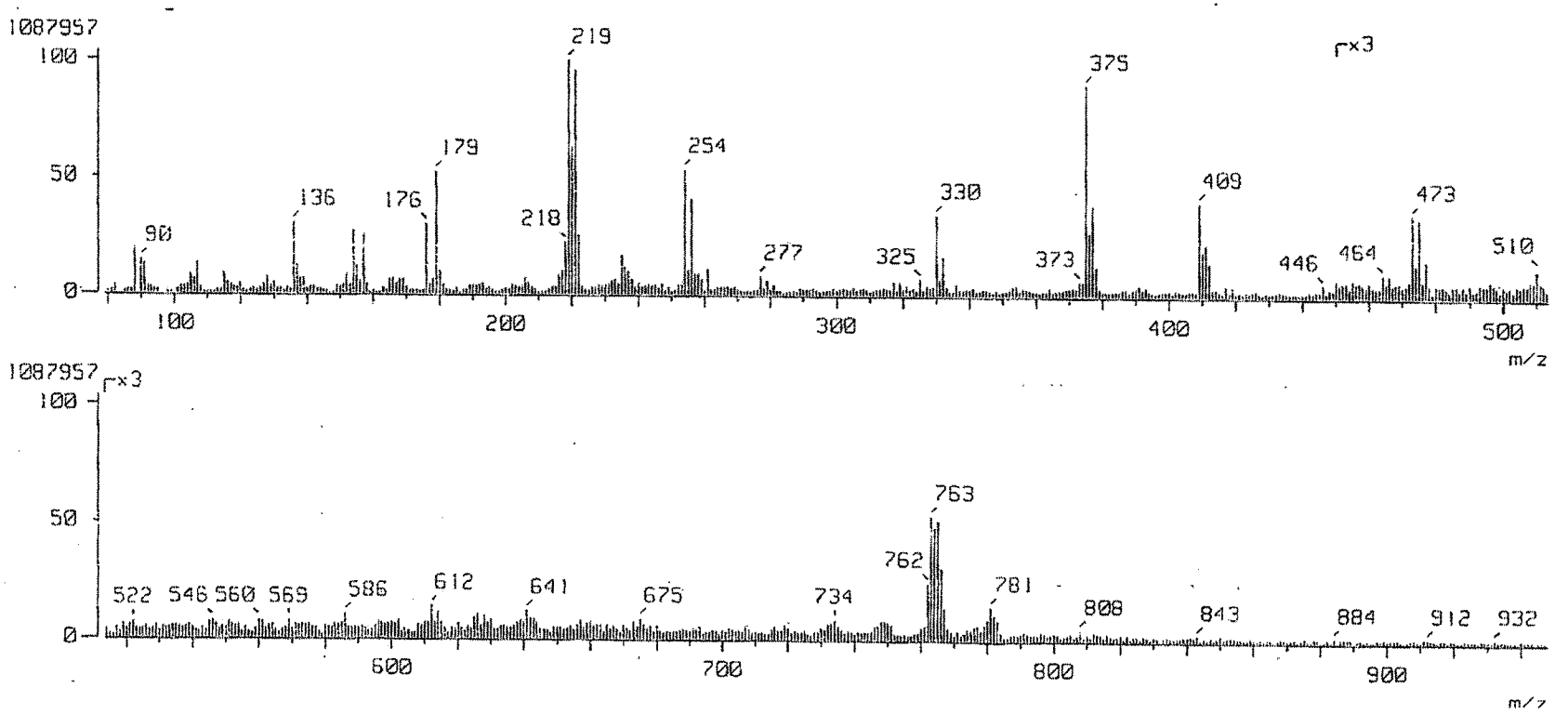


Fig.7.7 FAB-Mass spectrum of xerogel of complex $[ins(Cu)_3(bipy)_3]$

The formation of gel can be explained on the basis of self-aggregation of complex molecules, which produces a three-dimensional network encaging solvent molecules.[89] Thus the complex $[Cu_3(bipy)_3ins(H_2O)_9]$ acts as a gelator. The ethanol washed xerogel, however, does not form a gel on adding water, instead the gel is formed on addition of 1.5ml water of pH 12.4. Thus, both bipy as well as the hydroxyl ion seem to have important role in the gel formation.

In order to obtain visual insights into the aggregation mode in the gel phase, dry samples of hydrogel fibers have been prepared and the scanning electron micrographs (SEM) were recorded. These are presented in **Fig.7.8**. The micrographs show compact fibrous structure made up of fibrils each having 2-4μm diameter and >50μm length.

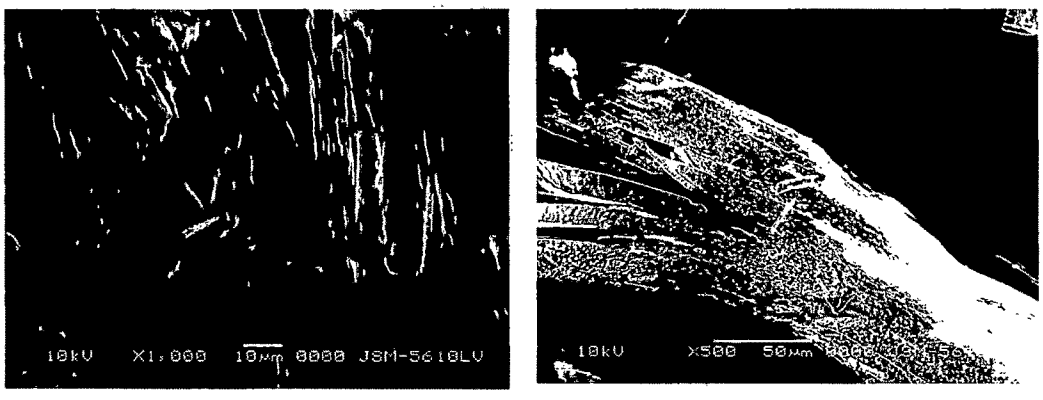
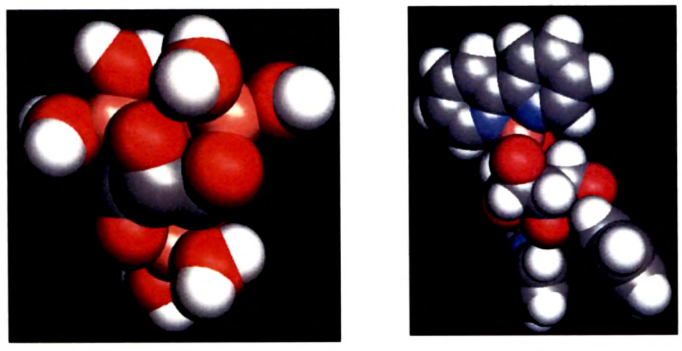


Fig. 7.8 SEM pictures of Xerogel of Complex $[insCu_3(bipy)_3]$.

Geometry optimization of the complexes $[insCu_3(bipy)_3]$ using Universal Force Field (UFF) indicates the presence of intramolecular π-stacking (**Fig.7.9**). The optimization up to 1st layer of solvation with water (**Fig.7.10**) indicates the presence of both intra and intermolecular π-stacking between coordinated bipy and formation of large voids.



(a) (b)

Fig. 7.9 Energy minimized structures of [ins$Cu_3(H_2O)_6$] and [insCu_3(bipy) $_3$] using Universal force Field. (Space filling model)

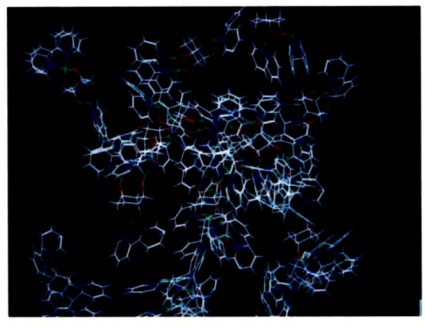


Fig.7.10 Complex [insCu_3(bipy)$_3$], after 1st level salvation.

As the hydroxyl ions are essential for gel formation, they must be forming inter-molecular –OH bridges between the trinuclear complex molecules through axial coordination and also probably through H-bonding with *myo*-inositol. A close examination of the sugar-based hydrogelators reported earlier[45] reveals that the sugars with one axial OH can have more H-bonds and close-packing with π-stacking between the phenyl substituents making them better gelators. *Myo*-inositol has striking similarity, with one axial –OH, thus there can be similar H-bonding and orientational effects. It appears that the fibrous super-structure is formed due to the presence of axial coordination and H-bonding by –OH, and the π-stacked bipy are helping in the formation of hydrophobic cavities that can hold water molecules to form a gel. Thus, the complex [Cu_3(ins)(bipy)$_3$] is the first discrete trinuclear complex of its type with gel forming ability. This opens a new area of research in gel forming trinuclear metal complexes and functional supramolecular assemblies.

References

(1) De Vries E. J. and Kellogg, R. M. *J. Chem. Soc., Chem. Commun.,* 1993, 238.

(2) Takafuji, M.; Ihara, H.; Hirayama, C.; Hachisako, H. and Yamada, K. *Liquid Cryst.,* 1995, **18**, 97.

(3) Sohna J. -E. S. and Fages, F. *J. Chem. Soc., Chem. Commun.,* 1997, 327.

(4) Otsumi, E.; Kamasas, P. and Weiss, R. G. *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 1234 and references cited therein.

(5) Terech, P.; Furman, I. and Weiss, R. G. *J. Phys. Chem.,* 1995, **99**, 9558 and references cited therein.

(6) Murata, K.; Aoki, M.; Suzuki, T.; Hanada, T.; Kawabata, H.; Komori, T.; Ohseto, F. Udea, K. and Shinkai, S. *J. Am. Chem. Soc.,* 1994, **116**, 6664 and references cited therein.

(7) James, T. D.; Murata, K.; Harada, T.; Ueda, K. and Shinkai, S. *Chem. Lett.,* 1994, 273.

(8) (a) Jeong, S. W.; Murata, K. and Shinkai, S. *Supramol. Sci.,* 1996, **3**, 83; (b) Jeong, S. W. and Shinkai, S. *Nanotechnology,* 1997, **8**, 179.

(9) Brotin, T.; Utermohlen, R.; Fages, F.; Bouas-Laurent, H. and Desvergne, J.-P. *J. Chem. Soc., Chem. Commun.,* 1991, 416.

(10) van Esch, J.; De Feyter, S. R.; Kellogg, M.; De Schryver, F. and Feringa, B. L. *Chem. Eur. J.,* 1997, **3**, 1238.

(11) Shinkai S. and Murata, K. *J. Mater. Chem.,* 1998, **8,** 485.

(12) de Loos, M.; van Esch, J.; Stokroos, I. R.; Kellog, H. and Feringa, B. H. *J. Am. Chem. Soc.,* 1997, **119**, 12675.

(13) (a) Inoue, K.; Ono, Y.; Kanekiyo, Y.; Kiyonaka, S.; Hamachi I. and Shinkai, S. *Chem. Lett.,* 1999, 225; (b) Inoue, K.; Ono, Y.; Kanekio,Y.; Hanabusa, K. and Shinkai, S. *Chem. Lett.,* 1999, 429.

(14) Amanokura, Natsuki.; Kanekiyo, Yasumasa.; Shinkai Seiji and Reinhoudt, David N, *J. Chem. Soc., Perkin Trans.* 2, 1999, 1995.

(15) Seo, Y. J.; Bhuniya, S.; Kim, B. H. *Chem. Commun.* 2007, 1804.

(16) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* 2004, **43,** 1229.

(17) Ryu, S. Y.; Kim, S.; Seo, J.; Kim, Y. –W.; Kwon, O. –H.; Jang, D. –J.; Park, S. Y. *Chem. Commun.* 2004, 70.

(18) Egelkamp, H.; Middlebeek, S.; Nolte, R. J. M. *Science,* 1999, **284,** 785.

(19) Vemula, P. K.; Aslam, U.; Mallia, V. A.; John, G. *Chem. Mater.* 2007, **19,** 138.

(20) John, G.; Zhu, G.; Li, J.; Dordick, J. S. *Angew. Chem., Int. Ed.* 2006, **45,** 4772.

(21) Jung, J. H.; Do, Y.; Lee, Y. -A.; Shimizu, T. *Chem. Eur. J.* 2005, **11,** 5538.

(22) Lee, S. J.; Lee, S. S.; Kim, J. S.; Lee, J. Y.; Jung, J. H.; *Chem. Mater,* 2005, **17,** 6517.

(23) Terech, P.; Weiss, R. G. *Chem. Rev.* 1997, **97,** 3133.

(24) Jung, J. H.; John, G.; Masuda, M.; Yoshida, K.; Shinkai, S.; Shimizu, T. *Langmur,* 2001, **17,** 7229.

(25) Jung. J. H.; Shinkai, S.; Shimizu, T.; *Chem. Eur. J.* 2002, **8,** 2684.

(26) Kiyonaka, S.; Shinkai, S.; Hamachi, I. *Chem. Eur. J.* 2003, 976.

(27) Ihara, H.; Hachisako, H.; Hirayama, C.; Yamada, K. *J. Chem. Soc., Chem. Commun.* 1992, 1244.

(28) Takafuji, M.; Ihara, H.; Hirayama, C.; Hachisako, H.; Yamada, K. *Liq. Cryst.* 1995, **18,** 97.

(29) Ihara, H.; Shudo, K.; Hirayama, C.; Hachisako, H.; Yamada, K. *Liq. Cryst.* 1996, **20,** 807.

(30) Hachisako, H.; Ihara, H.; Kamiya, T.; Hirayama, C.; Yamada, K.; *Chem. Commun.* 1997, 19.

(31) Ihara, H.; Yoshitake, M.; Takafuji, M.; Yamada, T,; Sagawa, T.; Hirayama, C.; Hachisako, H.; *Liq. Cryst.,* 1999, **26,** 1021.

(32) Hachisako, H.; Nakashima, H.; Ihara, H. *Chem. Lett.* 1999, 1165.

(33) Hanabusa, K.; Tange, J.; Taguchi, Y.; Koyama, T.; Shirai, H. *J. Chem. Soc., Chem. Commun.* 1993, 390.

(34) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed. Engl.* 1996, **35,** 1949.

(35) Yamada, N.; Koyama, E.; Kaneko, M.; Seki, H.; Ohtsu, H.; Furuse, T. *Chem. Lett.* 1995, 387.

(36) Yamada, N.; Matsubara, k.; Narumi, K.; Sato, Y.; Koyoma, E.; Ariga, K. *Colloids Surf.,* A 2000, **169,** 271.

(37) Yamasaki, S.; Tsutsumi, H. *Bull. Chem. Soc., Jpn.* 1994, **67,** 2053.

(38) Fuhrhop, J.–H.; Schnieder, P.; Rosenberg, J.; Boekema, E. *J. Am. Chem. Soc.* 1987, **109,** 3387.

(39) Garner, C. M.; Terech, P.; Allegraud, J.-J.; Mistrot, B.; Nguyen, P.; Geyer, A.; Rivera, D. *J. Chem. Soc., Fraraday Trans.* 1998, **94,** 2173.

(40) Ono, Y.; Nakashima, K.; Sano, M.; Kanekiyo, Y.; Inoue, K.; Hojo, J.;

Shinkai, S.; *Chem. Commun.,* 1998, 1477.

(41) Jung, J. H.; Ono, Y.; Shinkai, S. *Angew. Chem. Int. Ed.* 2000, **39,** 1862.

(42) Jung, J. H.; Ono, Y.; Sakurai, K.; Sano, M.; Shinkai, S. *J. Am. Chem. Soc.,* 2000, **122,** 8648.

(43) Huanghao Yang, Haipeng Liu, Huaizhi Kang and Weihong Tan, *J. Am. Chem. Soc.,* 2008, **130,** 6320.

(44) Jongseong Kim, Neetu Singh and L. Andrew Lyon, *Chem. Mater,* 2007, **19,** 2527.

(45) Jongseong Kim, Neetu Singh and L. Andrew Lyon, *Biomolecules,* 2007, **8,** 1157.

(46) (a) Miyata, T.; Asami,N.; Uragami,T. *Nature* 1999, **399,**766.(b) Miyata, T.; Jige, M.; Nakaminami, T. *Proc. Natl. Acad. Sci. U.S.A.* 2006, **103,** 1190.

(47) (a) Lin, D. C.; Yurke, B.; Langrana, N. A. *J. Biomech. Eng.* 2004, **126,** 104 (b) Murakami,Y.;Maeda,M. *Macromolecules* 2005,**38,** 1535-1537. (c) Liedl, T.; Dietz, H.; Yurke, B.; Simmel, F. *Small* 2007, **3,** 1688. (d) Wei, B.; Cheng, I.; Luo, K. Q.; Mi, Y. *Angew. Chem., Int. Ed.* 2008, **47,** 331.

(48) (a) Li, C.; Madsen, J.; Armes, S. P.; Lewis, A. L. *Angew. Chem.; Int. Ed.* 2006, **45,** 3510. (b) Oh, J. K.; Siegwart, D. J.; Lee, H.; Sherwood, G.; Peteanu, L.; Lollinger, J. O.; Kataoka, K.; Matyjaszewski, K. *J. Am.Chem. Soc.* 2007, **129,** 5939.

(49) Thomton, P. D.; Mart, R. J.; Ulijn, R. V. *Adv. Mater.* 2007, **19,** 1252.

(50) (a) Ehrick, J. D.; Deo, S. K.; Browning, T. W.; Bachas, L. G.; Madou, M. J.; Daunert, S.; *Nat. Mater.* 2005, **4,** 298. (b) Murphy, W. L.; Dillmore, W. S.; Modica, J.; Mrksich, M. *Angew. Chem., Int. ed.* 2007, **46,** 3066.

(51) Dong, L.; Agrawal, Abhishek K.; Beebe, David J. and Jiang, Hangrui *Nature,* 2006, **442,** 551.

(52) Webb, Sarab, *Anal. Chem.* 2006, 7378.

(53) Uhrich, K. E.; Cannizaro, S. M.; Langer, R. S.; Shakesheff, K. M.; *Chem.Rev.*1999, **99,** 3181.

(54) Estroff, Lara A. and Hamilton, Andrew D. *Chem. Rev.,* 2004, **104(3),** 1201.

(55) Lee, K. Y.; Mooney, D. J.; *Chem. Rev.* 2001, **101,** 1869.

(56) Xing, B.; Yu, C. W.; Chow, K. H.; Ho, P. L.; Fu, D.; Xu, B. *J. Am.Chem. Soc.* 2002, **124,** 14846.

(57) Tiller, J. C. *Angew. Chem., Int. Ed. Engl.* 2003, **42,** 3072.

(58) Fenniri, H.; Mathivanan, P.; Vidale, K. L.; Sherman, D. M.; Hallenga, K.;

Wood, K. V.; Stowell, J. G. *J. Am. Chem. Soc.* 2001, **123,** 3854.

(59) Israelachvili, J. N. Intermolecular and surface Forces, 2nd ed.; Academic Press: New York, 1991.

(60) Ajayaghosh, A. and George, Subi J. *J. Am. Chem. Soc.* 2001, **123,** 5148.

(61) Amanoikura, Natsuki,; Kanekiyo, Yasumasa,; Shinkai, Seiji and Reinhoudt, David N. *J. Chem. Soc. Perkin Trans.* 2, 1999, 1995.

(62) U.S. Patent 2005, 0255091.

(63) Ihara, Hirotaka.; Sakurai, Toshihiko.; Yamada, Taisuke.; Hashimoto, Toshitaka; Takafuji, Makoto.; Sagawa, Takashi and Hachisako, Hiroshi, *Langmuir,* 2002, **18,** 7120.

(64) (a) Holtz, J. H.; Holtz, J. S. W.; Munro, C. H. and Asher, S. A. *Anal. Chem.*1998, **70,** 780; (b) J. H. Holtz and S. A. Asher, *Nature,* 1997, **389,** 829.

(65) Gelman, F.; Blum, J. and Avnir, D. *J. Am. Chem. Soc.* 2000, **122,** 11999.

(66) Lai, E. and Birren, B. W. Electrophoresis of Large DNA Molecules:Theory and Applications, Cold Spring Harber, NY, 1990.

(67) Xing, B.; Choi, M. F.; Xu, B. *Chem. Commun.* 2002, 362.

(68) (a) Terech, P.; and Weiss, R. *Chem. Rev.* 1997, **97,** 3133. (b) Van Esch, J. H. and Feringa, B. L. *Angew. Chem. Int. Ed.* 2000, **39,** 2263.

(69) Gelman, F.; Blum, J. and Avnir, D. *J. Am. Chem. Soc.,* 2000, **122,** 11999.

(70) Lai, E. and Birren, B. W. Electrophoresis of large DNA molecules: Theory and Applications, Cold Spring Harbor, NY, 1990.

(71) U.S. Patent 2007, 0066574.

(72) Holtz, J. H.; Holtz, J. S. W.; Munro, C. H. and Asher, S. A. *Anal. Chem.,* 1998, **70,** 780; (b) Holtz, J. H. and Asher, S. A. *Nature,* 1997, **389,** 829.

(73) Fages, F.; Bodenant, B. and Weil, T. *J. Org. Chem* 1996, **613,** 956.

(74) (a) Hanabusa, K.; Okuri, K.; Karaki, K. and Shirai, H. *J. Chem. Soc., Chem. Commun.,* 1992, 1371 and references cited theirin; (b) Hanabusa, K.; Yamada, Y.; Kimura, M.; and Shirai, H. *Angew. Chem., Int. Ed. Engl.,* 1996, **35,** 1949; (c) Hanabusa, K.; Shimura, K.; Hirose, K.; Kimura, M. and Shirai, H. *Chem. Lett.,* 1997, 191.

(75) Fages, F. *Angew. Chem., Int. Ed.,* 2006, **45,** 1680.

(76) Xing, B.; Choi, M. F. and Xu, B. *Chem.–Eur. J.,* 2002, **8(21),** 5028. and references therein.

(77) Hirst, A. R. and Smith, D. K. *Chem.–Eur. J.,* 2005, **11,** 5496.

(78) Meide-Gundert, G. L.; Fischer, Klein, Vogtle, M. F. ; Heuze, K. J.; Pozza, Vallier, L. M. Fages, F. *Angew. Chem.* 2001, **113,** 3266.

(79) Sohana, J. S. ; Fages, F. *Chem. Commun.* 1997, 327.

(80) Xing, B.; Choi,M.-F.; Xu, B. *Chem. Commun.* 2002, 362.

(81) Xing, Benag,; Choi Min-Fai and Xu, Bing, *Chem. Comm.* 2002, 362.

(82) Applegarth, L.; Clark, N.; Richardson, A. C.; Parker, A. D.; Radosavljevic-Evans, M. I.; Goeta, A. E.; Howard, J. A. K. and Steed, J. W. *Chem. Commun.,* 2005, 5423.

(83) Odriozola, I.; Loinaz, I.; Pomposo, J. A. and Grande, H. J. *J. Mater. Chem.,* 2007, **17,** 4843.

(84) Kishimura, A.; Yamashita, T. and Aida, T. *J. Am. Chem. Soc.,* 2005, **127,** 179.

(85) Hahn, U.; Hirst, A. R.; Delgado, J. L.; Kaeser, A.; Delavaux- Nicot, B.; Nierengarten, J.-F. and Smith, D. K. *Chem. Commun.,* 2007, 4943.

(86) Kume, S.; Kuroiwa, K. and Kimizuka, N. *Chem. Commun.,* 2006, 2442.

(87) Lam, S.-T.; Wang, G. and Yam, V. W.-W. *Organometallics,* 2008, **27,** 4545.

(88) Tam, A. Y.-Y.; Wong, K. M.-C.; Wang, G. and Yam, V. W.-W. *Chem. Commun.,* 2007, 2028.

(89) Terech, P.; Furman, I.; .Weiss, R. G.; Bousas-Laurent, H.; Desvergne, J.-P. and Ramasseul, R. *Faraday Discuss.,* 1995, **102,** 345.