by organic molecular beam deposition out of a resistively heated glass crucible at 450 K with a deposition rate of around 0.0001 ML s^{-1}. The substrate was kept at RT. The amount of dosed HtBDC molecules on the surface was controlled by keeping the crucible temperature constant and varying the exposure time (5 – 600 s). The STM images at low temperatures were obtained by cooling the sample down to the desired temperature after the deposition of the molecules at RT.

Received: February 13, 2001
Revised: April 20, 2001 [Z 16608]

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Organophosphorus Dendrimers as New Gelators for Hydrogels

Christelle Marmillon, Fabienne Gauffre, Tadek Gulik-Krzywicki, Christophe Loup, Anne-Marie Caminade,* Jean-Pierre Majoral,* Jean-Pierre Vors, and Elmar Rump

Owing to their numerous applications in different fields (cosmetics, health care, textile, paper, packaging, oil field, photographic industry, etc) gels continue to attract considerable attention.[1] They can be considered as composite materials made of a three-dimensional (3D) supramolecular network imprisoning a large quantity of liquid. The driving force for the formation of gels can be van der Waals, hydrophobic, fluorophobic, $\pi-\pi$ stacking, dipole – dipole, weak coordination interactions, or hydrogen bonds. A number of small molecules are able to form gels such as steroids, fatty acids, copper chelates, fluorinated alkanes, peptides, cyclic dipsipeptides, anthracene derivatives, amino pyridines, calixarenes. More sophisticated macromolecules such as bisarborols (bidirectional molecules with a lipophilic central chain substituted on the end with polyalcohol groups) were found to act also as gelators in water[2] or in hot solvent mixtures such as ethanol/water or dimethylformamide/water.[3] Very recently Aida et al.[4] described the formation of physical gels in acetonitrile with peptide core dendrimers.

Herein we report the first examples of the use of hydrosoluble dendrimers as new gelators in water that allow the confinement of a variety of organic and organometallic substances under very mild conditions.

Polycationic dendrimers **3-[G$_0$]** – **3-[G$_4$]** (P(S) core, generation 0 to 4, pyridinium chloride as terminal groups), **4-[G$_0$]** – **4-[G$_4$]** (P(S) core, ammonium chloride as terminal groups), **6-[G$_2$]** (P_3N_3 core, pyridinium chloride as terminal groups) are prepared in quantitative yield by reacting the corresponding dendrimers **1-[G$_0$]** – **1-[G$_4$]** or **2-[G$_2$]**[5] (terminal aldehyde groups) with either Girard-P reagent or Girard-T reagent in methanol (Scheme 1). The polycationic dendrimer **5-[G$_1$]** (P(S) core, pyridinium acetate as terminal groups) is obtained by anion exchange from **3-[G$_1$]** and sodium acetate. All dendrimers are characterized as a mixture of isomers around the terminal CH=N–NH–C(O)–CH$_2$ linkage as shown by ^{13}C NMR spectroscopy. Indeed two signals are detected at $\delta = 61.8 - 63.0$ for the terminal CH$_2$ groups and at $\delta = 162.3 - 168.1$ for the carbonyl groups. ^{1}H NMR spectra confirm the

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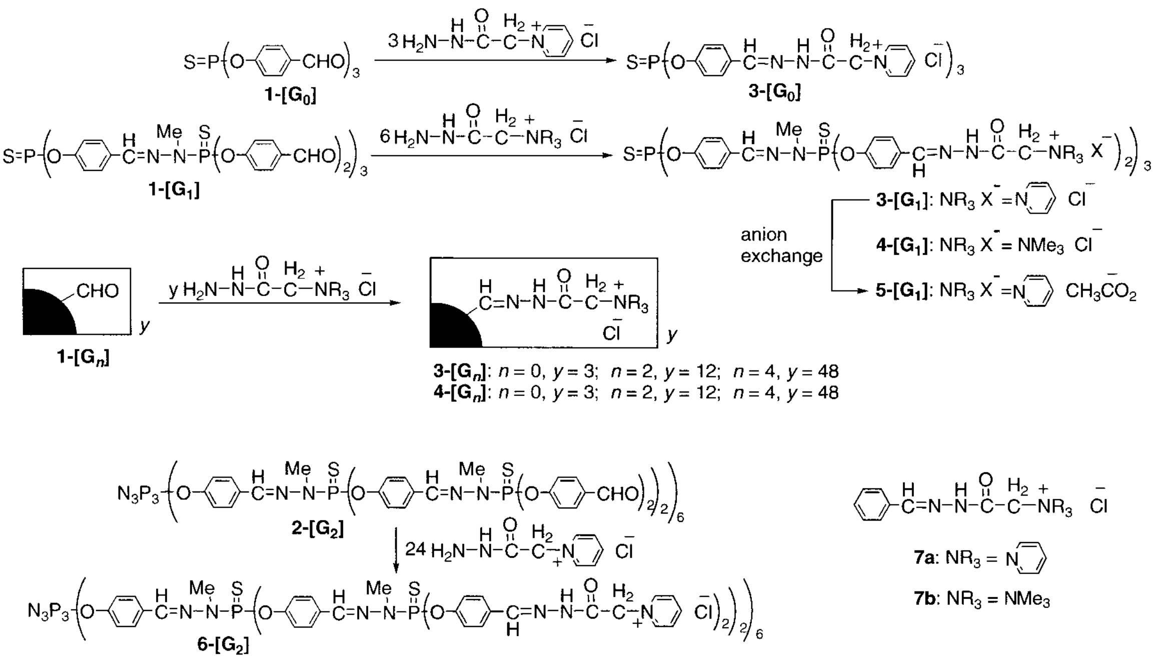

Scheme 1. Preparation of dendrimers **3-[G$_0$]**–**3-[G$_4$]**, **4-[G$_0$]**–**4-[G$_4$]**, **5-[G$_1$]**, and **6-[G$_2$]**.

presence of such inseparable isomers as already noted for other Girard derivatives.[6] Dendrimers of generation 1 to 4 form reversible rigid gels when dissolved in water. In general, gelation is observed at concentrations of 1.5–1.8% in weight. At lower concentrations, a gel phase separates and leaves a layer of free water. Around 7500 water molecules are estimated to be gelled by a molecule of dendrimer of generation 1 (**3-[G$_1$]**, **4-[G$_1$]**, **5-[G$_1$]**) and around 70000 by a molecule of dendrimer of generation 4 (**3-[G$_4$]**, **4-[G$_4$]**), that is gelation of about 1200–1400 molecules of water per terminal ammonium or pyridinium unit, regardless of the generation considered. The gelation time is strongly dependent on the experimental conditions and on the nature of terminal groups. The best results are obtained when an aqueous solution of dendrimer is heated at 60–65 °C for 11–13 days. Dendrimers **3-[G$_n$]** ($n = 1-4$) form gels more quickly than dendrimers **4-[G$_n$]** ($n = 1-4$) and only slight changes were observed when moving from the lowest generation ($n = 1$) to the highest dendrimer ($n = 4$) or when moving from a trifunctionalized core (**3-[G$_1$]**–**3-[G$_4$]** or **4-[G$_1$]**–**4-[G$_4$]**) to a hexafunctionalized one (**6-[G$_2$]**) (Table 1). Introduction of defects at the surface of dendrimers through incomplete Schiff reactions between starting dendrimers **1-[G$_n$]** and Girard-P or Girard-T reagents does not hinder the formation of gels. $Cl^-/CH_3CO_2^-$ ion exchange leads to an acceleration of the gelation process: gelation with **5-[G$_1$]** (acetate as counteranion), for example, is achieved in four days at 60–65 °C, whereas gelation with **3-[G$_1$]** (chlorine as counteranion) requires twenty days. Interestingly, no gelation is detected with the monomers **7a**, **b** resulting from the condensation reaction between benzaldehyde and Girard-P or -T reagents.

Remarkably gelation time is also dramatically shortened in the presence of hydrosoluble components (by 10 to 30%) such as buffer (TRIS (tris(hydroxymethyl)aminomethane), etc), metal salts (Ni, Y, Er acetates), acids (citric, ascorbic, lactic, L-tartric, etc), dithioerythritol (DTE), sodium salt of ethylenediaminetetraacetate (EDTA) (Table 2, Figure 1). In-

Table 1. Gelation of polycationic dendrimers (1.8%) in aqueous solutions at 60–65 °C (Cl^- as counterion).

Dendrimers	Gelation time[a] [days]	Dendrimers	Gelation time[a] [days]
3-[G$_0$]	partial gelation	**4-[G$_0$]**	no gelation
3-[G$_1$]	20	**4-[G$_1$]**	75
3-[G$_2$]	20	**4-[G$_2$]**	75
3-[G$_4$]	13	**4-[G$_4$]**	60
5-[G$_1$][b]	4	**6-[G$_2$]**	11

[a] Gelation was regarded as finished when all the solution is geled. [b] Acetate as counteranion.

Table 2. Gelation of dendrimers **3-[G$_4$]** and **4-[G$_4$]** (1.8%) in water at 60–65 °C with confinement of various components.

Components	pH	Gelation time [h][a]
	3-[G$_4$]	
$Ni(Ac)_2 \cdot 4H_2O$ 10%	6.6	12
$Ni(Ac)_2 \cdot 4H_2O$ 30%	6.0	7
$Y(Ac)_3 \cdot 4H_2O$ 20%	6.0	12
$Er(Ac)_3 \cdot 4H_2O$ 10%	5.8	4
TRIS buffer	9.3	3
D,L-lactic acid		8
ascorbic acid 10%	2.0	12
L-tartric acid 10%		12
citric acid 10%	1.4	5[b]
DTE 2.3%		96
EDTA, 4Na 10%		3
$Er(Ac)_3 \cdot 4H_2O$ 10%	5.8	240[c]
	4-[G$_4$]	
$Ni(Ac)_2 \cdot 4H_2O$ 10%	6.6	48
TRIS buffer	9.3	48
EDTA, 4Na 10%		20

[a] Gelation was regarded as finished when all the solution is geled. [b] Bad cohesion of the gel. [c] Room temperature.

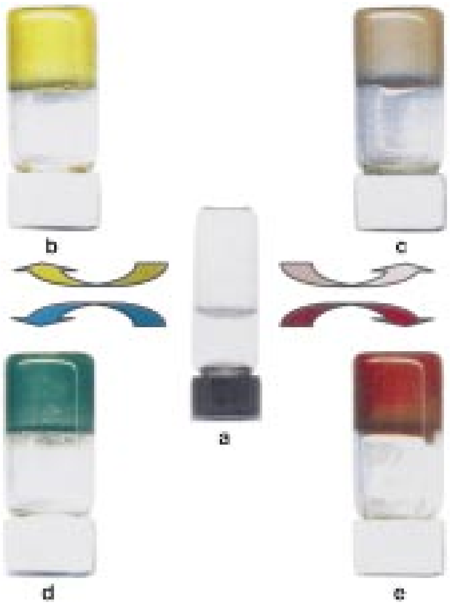

Figure 1. Rigid gels shown in upturned flasks. a) Hydrogel formed with **3-[G$_4$]** (1.8 % in water). b) Hydrogel formed with **3-[G$_4$]** (1.8 % in water) and TRIS buffer (10 %). c) Hydrogel formed with **3-[G$_4$]** (1.8 % in water) and Er(OAc)$_3$ · 4 H$_2$O, 10 %. d) Hydrogel formed with **3-[G$_4$]** (1.8 % in water) and Ni(OAc)$_3$ · 4 H$_2$O (10 %). e) Hydrogel formed with **3-[G$_4$]** (1.8 % in water) and ascorbic acid (10 %).

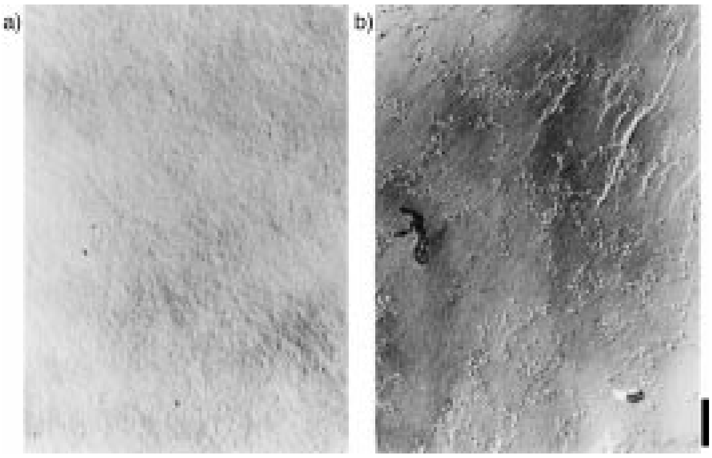

Figure 2. Freeze-fracture electron micrographs of a sample of dendrimer **3-[G$_4$]** (2 %) in water/glycerol (70/30); bar: 500 nm for both figures. a) Solution prior to gelation. b) Gel. Aggregates appear as black dots (the white streaks are shadows due to the freeze-fracture technique).

deed gelation and confinement take place at room temperature in a few hours for dendrimers of generations 1 – 4. Remarkably too, a rigid gel is formed with dendrimer **3-[G$_0$]** in the presence of erbium acetate after heating at 60 – 65 °C for 12 h.

Confinement and gelation are not pH-dependent: both dendrimers form gels in the pH range of 2 – 9 in aqueous solutions containing the above-mentioned components. The resulting translucent gels are stable for several months, they do not flow, and can even be crushed into pieces. The internal structure of the gels was examined by freeze-fracture electron microscopy. The samples were prepared with a water/glycerol (70/30) mixture as solvent in order to prevent the formation of ice crystals during the freezing stage. Electron micrographs of a **3-[G$_4$]** sample prior to and after gelation are displayed in Figures 2 a and b, respectively. The size of the dendrimer (the diameter is approximately 7 – 8 nm for a dendrimer of generation 4) is of the order of the limit of resolution by this technique. Prior to gelation (Figure 2 a) the texture is homogeneous and the isolated dendrimers can only be seen as small dots on very careful examination of the micrograph, while after gelation the images (Figure 2 b) reveal a network of aggregated dendrimers that contrasts clearly with the smooth areas of solvents. The geometry of the network resembles that found in gels from other types of particles (milk proteins, clay), which is not surprising since dendrimers can be considered as nanoscale particles. In addition, observation of Figure 2 b and other freeze-fracture electron micrographs suggests that the dendrimers are not covalently bonded in the gel state. Indeed, the dendrimer network does not seem continuous, which means that some molecules of dendrimers are left on the other side of the fracture when they are pulled apart. This is usually not the case when elements are linked by covalent bonds. The assumption of noncovalent bonds between dendrimers in the gel (i.e. the gel is a so-called "physical" gel) is supported by several observations of reversibility. For instance, addition of acetonitrile to the surface of gels allows the progressive dissolution of gels,[7] which can be formed again through slow removal of acetonitrile at room temperature. Gel formation is, however, not thermoreversible.

Most types of weak interactions known to favor the formation of gels can occur for dendrimers **3** – **6**: intermolecular hydrogen bonding, face-to-face π – π aromatic stacking, and hydrophobic effects due to the internal backbone of dendrimers. Figure 3 illustrates these supramolecular interactions for dendrimers **3-[G$_n$]**. Moreover acceleration of the rate of gelation of dendrimers in the presence of acetates could be explained by the bridging of anions which probably participate to the formation of the networks.

The relative ease with which hydrogels with polycationic phosphorus-containing dendrimers are obtained is in marked contrast with what is reported for the formation of hydrogels from water-soluble linear phosphorus polymers, that is polyphosphazenes. For instance, ^{60}Co gamma irradiation of a poly[bis(methoxyethoxyethoxy)]phosphazene is necessary to promote cross-linking, through formation of intermolecular carbon – carbon bonds, which converts this water-soluble polymer to a material that imbibes water to form a pH-sensitive hydrogel.[8] Moreover, the possibility to incorporate ligands or metals within the cascade structure of dendrimers or at the core various functional groups[9] renders the hydrogels made from dendrimers much more attractive for new applications in different fields such as drug delivery, enzyme or antigen immobilization, and catalysis.

Remarkably, freeze-drying of gels **3-[G$_2$]** – **3-[G$_4$]** at low temperature gave rise to opaque aerogels which retained the size and form of the hydrogels. Aerogels were characterized by scanning electron microscopy, which showed some ramified fiberlike constructions (Figure 4).

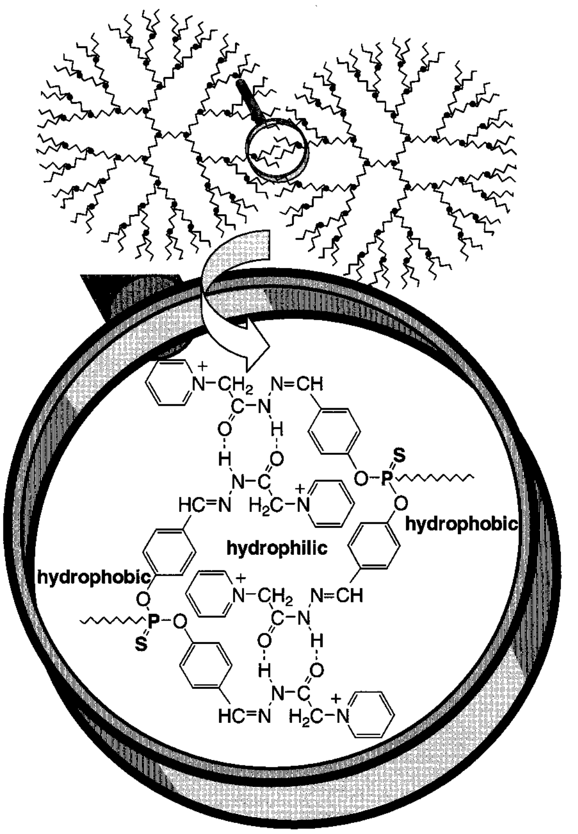

Figure 3. Supramolecular interactions (hydrogen bonds, π–π aromatic stacking, hydrophobic effects) as driving forces for the formation of gels.

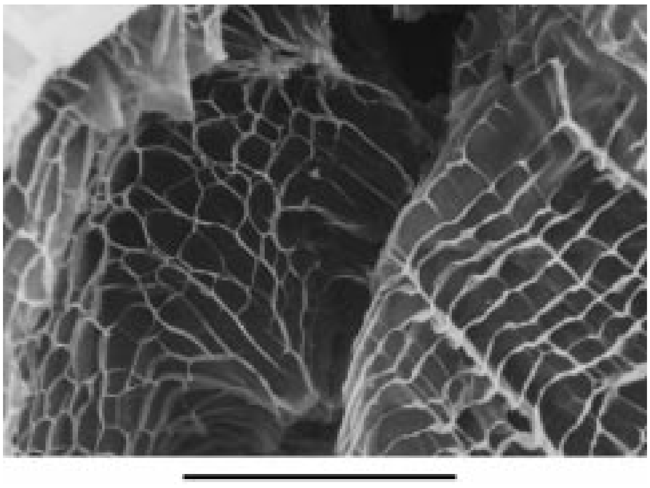

Figure 4. SEM image of a freeze-dried gel (**3-[G$_4$]**) (20 kV); bar: 200 μm.

In conclusion we have described a new type of gel based on phosphorus-containing dendrimers. These gels can be obtained under very mild conditions and allow the confinement of a number of active substances.

Received: December 14, 2000
Revised: April 17, 2001 [Z16273]

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trans-[Fe(CN)$_4$(CO)$_2$]$^{2-}$, a 21st Century [Fe(CN)(CO)] Compound**

Jianfeng Jiang and Stephen A. Koch*

[Fe^{II}(CN)$_5$(CO)]$^{3-}$ was reported in the 19th century,[1] and [Fe(CN)(CO)$_4$]$^{1-}$ was characterized in the 20th century.[2] Here we report the synthesis and characterization of the third monomeric iron complex with exclusively CO and CN$^-$ ligands.[3] The discovery of the [Fe(CN)(CO)] moieties at the catalytic centers of NiFe and Fe-only hydrogenases[4] dramatically increased interest in Fe compounds with CN$^-$ and CO ligands.[5] These enzymes provided the first examples of either CO or CN$^-$ as native ligands in a metalloprotein. Simple [Fe(CN)(CO)] complexes are possible intermediates in the biosynthesis of the [Fe(CN)$_y$(CO)$_x$] centers in hydrogenases and are possible complexes in prebiotic chemistry.[6]

trans-[Fe(CN)$_4$(CO)$_2$]$^{2-}$ (**1**) is generated in solution by the simple addition of 4 equiv of NaCN to an aqueous solution of FeCl$_2$·4H$_2$O under an atmosphere of CO. The anion was isolated as the colorless crystalline solid Na$_2$(dmf)$_4$-**1**, which is

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[**] This work was supported by a National Institutes of Health Grant (GM 58000). We thank Professors Michelle Millar and Albert Haim for discussion.