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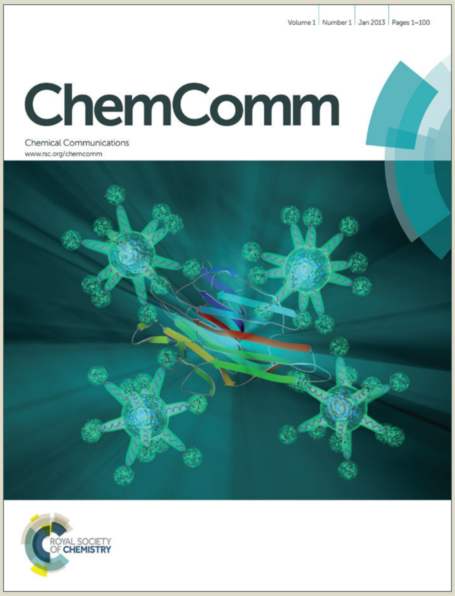

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ARTICLE TYPE

# New Frontiers in Hybrid Materials: Noble Metal Nanoparticles - Supramolecular Gel Systems

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The last decade has witnessed an increasing interest for the development of hybrid materials with novel properties. Noble metal NPs-gel materials represent a new class of hybrid composites envisaged by many to have a great potential for technological applications, as a consequence of beneficial integration of the NPs' properties with those deriving from the gelling compounds. This review article provides an up-to-date account of the most interesting and inspiring works published in the field, especially focusing on the preparation and characterization. Some examples of practical uses of such intriguing materials are also described.

## 1. Introduction

A major challenge in modern chemistry is represented by the search for novel materials for advanced applications.[1] In this respect, metal nanoparticles (NPs) have surely inspired material chemists and physicists during the last decades due to their surprising optical, electronic, magnetic and catalytic properties[2] with vast potential in many applicative areas.[3] As their physico-chemical attributes derive mainly from particle size and shape and inter-particle distance, NPs' properties result different either from those of bulk materials and from those of molecular compounds. Nowadays, NPs' synthesis and characterization are well established techniques but, perhaps surprisingly, NPs are not a discovery of modern science, as they have been identified in artifacts and works of art of Roman times, especially mosaics, and they were already employed in glass manufacturing by proto-historic communities during the Bronze-Age.[4]

Over the last decade, a very original research line has focused on the attempt to integrate NPs into unconventional environments, aiming at the production of hybrid materials. The coupling of material systems belonging to different dimensional scales into integrated novel composites is an exciting area of research. In particular, the integration of nano-objects within micro environments would eventually generate materials of macro dimensions whose properties might open new perspectives from the applicative and technological points of view.

If precise control of the process of transcription of chemical information from the molecular to the macroscopic level is feasible, complex functional materials can be assembled from simple building blocks.[5] When both organic and inorganic units are employed, the resultant composites may have advantages offered by the combination of complementary strengths and by the synergy among the properties of components derived from different chemical domains. This approach is significant not only for the design of nanodevices, but also for the fundamental understanding of the collective properties which may arise from inter-component interactions within the final composite assembly. The organization of NPs into well-defined and easily reproducible 2- and 3-D architectures is a particularly promising route for the construction of optoelectronic and biomedical devices.

Towards this end, a variety of strategies have been explored. A particularly promising one focuses on gel systems which have attracted considerable interest precisely in this respect. Indeed, the past decade has witnessed a blooming interest for the development of gel systems as structural partners for noble metal NPs, giving rise to unique novel materials: NPs-gel systems.

Gels are soft-materials generated by the entrapment of large quantities of solvent within a reticulated superstructure made of intertwined fibrils of varying dimensions which constitutes only a tiny fraction of the overall mass of the system (< 1%).[6a] Gels can be of chemical or physical nature, polymeric or generated by low molecular weight gelator (LMWG) molecules. The latter category has drawn significant attention due to the ever-growing possibilities that a fully supramolecular approach can indeed open up.[6,7] A non-covalent approach enables the construction of materials with a fine design and precise organization just above the molecular level. Moreover, non-covalent bonds are reversible and more susceptible to the environment, thus their use paves the way to adaptable and stimuli responsive materials. Despite the superior intrinsic robustness of polymeric gels and ease in mechanical manipulation,[8] cross-linking reactions do not allow a fine control of the material internal structure.

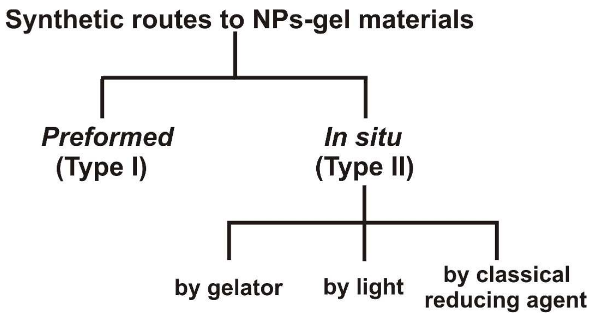
As this review intends to demonstrate, LMWG gel systems can indeed be advantageous for achieving the assembly of objects belonging to different dimensional domains into functional materials. Indeed, integrated NPs-gel systems are constituted by a combination of nanoscale objects, *i.e.,* the incorporated NPs, and micrometer-scale gel-fibers, all of them assembled into a macroscopic material. Most interestingly, the NPs distribution within the composite material might be far from homogeneous.

This strongly depends on gel morphology and, thus, the final properties of the nanoscale objects within the macroscopic materials might be modulated by the microscopic features of the gel internal structure.

This review article presents an account of the works related to the emerging field of supramolecular NPs-gel materials. Extensive discussions and numerous reviewing works on each separate structural element constituting these novel hybrid materials, *viz.*, LMWG gel systems and NPs, there already exist in the literature.[9] Therefore, we will here focus on the general aspects pertaining to the design of supramolecular NPs-gel systems and to the different ways of their preparation. To this end, we have selected prime examples which describe how these novel materials can be produced. The variables involved in the preparation of NPs-gel materials demand attention in order to key out common procedural features. Despite the quite large chemical variety of the species considered in this review, it was quite feasible to identify two main categories of works according to the synthetic pathway used in the material preparation. We had also cared to describe the structural and optical features of these novel materials which are usually investigated by physico-chemical tools (TEM, SEM, AFM, Surface Plasmon Resonance (SPR), X-Ray Powder Diffraction, etc.). In general, most of the research studies reported in this review are intended to look into the consequences that the entrapment into the gel environment of pre-formed NPs has on their properties, or into the effect that gelator molecules and their assembly exert on the formation and on the final stability of the NPs. More so, they are actually carried out aiming at specific improvement of one of the two components (*viz.*, the gel or the NPs) by the effect exerted by the presence of the other one in the composite. At variance with this *narrow* view, we and others strongly believe that the resulting materials can be thought as integrated systems which could lead to novel materials with unprecedented properties. Hence, the second part of this work is dedicated to put on display some of the most interesting practical uses that can be attained by NPs-gel systems.

## 2. Preparation & Characterization of NPs-gel composites

There exist a number of ways to produce NPs-gel composites. For simplicity's sake, we grouped the most interesting works into two main categories (Scheme 1) based on whether the NPs are formed prior to the assembly of the hybrid material (*type I*) or by an *in situ* process (*type II*).



**Scheme 1.** Different categories of NPs-gel material based on the preparation procedure used.

While *type I* group exemplifies procedures where the NPs are prepared by classical methods[10] and integrated into the gel matrix only afterwards, in *type II* group's examples the NPs are generated by *in situ* reduction, by chemical or physical stimuli, within the gel material or during its formation. The latter group includes reduction processes obtained by light absorption, or by chemical reduction attained by the gelator molecules themselves of by classical reducing agents ($NaBH_4$, etc.). As the reader might easily imagine, these two methods return different outcomes. Indeed, while the *type I* process embeds into the gel matrix NPs whose intrinsic properties are largely pre-determined, *type II* procedure partially empowers the gel formation process itself to determine the final NPs' characteristics. Another key aspect is constituted by the type of chemical protecting coverings (termed capping agents) employed in NPs synthesis. While necessary to ensure a prolonged stability of the NPs and avoid their aggregation,[11] capping agents provide additional variability and interest to these systems. Not only that, they mediate the interactions between the NPs and their surroundings, thus representing a functional interface.

### *2.1 Type I: Use of Pre-formed NPs*

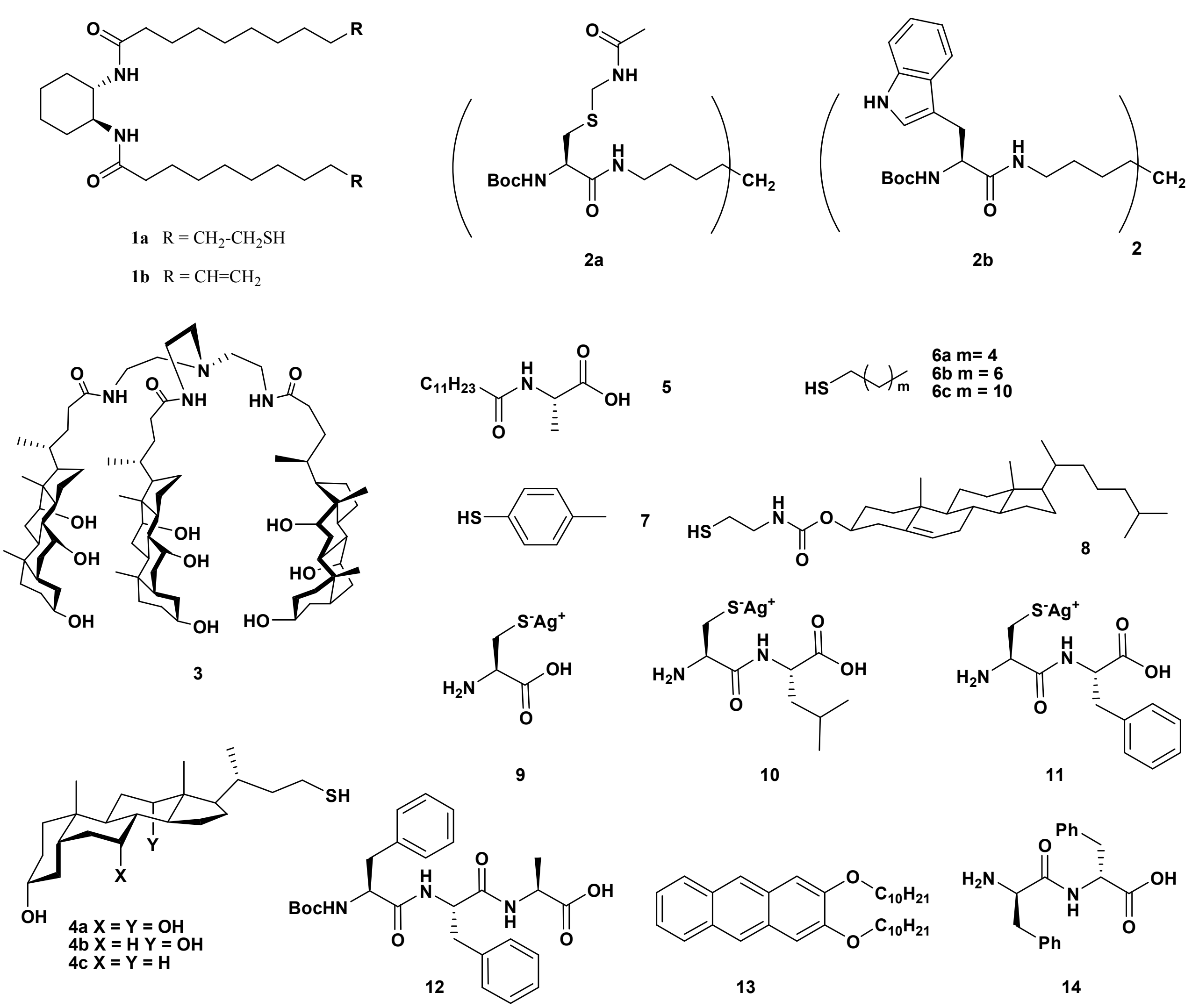
NPs tend to be fairly unstable in solution, and precautions must be taken into account in order to avoid aggregation phenomena. Organic monolayers are generally the capping agents which passivate the NPs surface and prevent precipitation. A viable integration of NPs into the gel material is contingent to a proper communication between the NPs chemical covering and the external environment based on chemical affinity.

The strong interaction that can be established between noble metals NPs and thiol groups can result essential in order to obtain NPs-gel materials. As described by Kimura, Shirai and co-workers,[12] gelator **1a** (Scheme 2), despite its reduced gelling ability compared to parent **1b** (Scheme 2), can still produce gel materials in several polar and apolar. Its two thiol units may be used as anchoring points for octanethiol-stabilized gold nanoparticles (1.7 ± 0.3 nm ∅, $SPR_{max}$ = 512 nm), synthesized independently by classical Brust method.[10]

A heated solution of **1a** in degassed toluene in the presence of octanethiol-stabilized AuNPs produced a gel upon cooling. TEM analysis revealed the presence of spatially organized AuNPs assembled onto the gel fibers (80-400 nm ∅). The better gelator, **1b**, was unable to generate the composite material. S*ite-exchange mechanism* is operating and a number of capping agents, originally onto the NPs, are replaced by the gelator thiol groups. The lack of -SH groups in **1b** precluded the essential direct gelator-NPs interaction.

The same concept is underlying the work by Smith *et. al.,* which reported on the stabilization and organization of AuNPs by cysteine-functionalised organogelator **2a** (Scheme 2).[13] In the presence of AuNPs, **2a** formed a gel material in toluene on whose fibers (75-200 nm ∅) the nanoparticles aligned, as shown by TEM images (Fig. 1a).

Most interestingly, NPs' coverage on the fibers was found to be dependent on the capping agent used, *viz.*, either octadecylsulfide (ODS) or hexadecylthiol (HTD). The replacement of capping thiols with the organogelator **2a**, via a *ligand exchange mechanism*, was occurring in both cases, but ODS showed a



**Scheme 2.** Molecular formulae for compounds **1-14.**

lesser degree of substitution, at least by looking at the more effective coating of the gel fibers by NPs, when HTD cappings were employed. A further confirmation of the actual active role of the sulfur atom in **2a** was proven by the outcome of a control experiment with a tryptophan functionalised gelator **2b** (Scheme 2). The latter species was ineffective in the organization of NPs. The authors, cleverly, also measured the average size of the AuNPs after the formation of the NPs-gel material and they found a slight shift in NPs' size distribution (from 2.8 ± 0.8 to 2.1 ± 1.0 nm ∅), which might indicate some reorganization occurring during the formation of the new material. In principle, the gel forming process could have an influence on pre-formed NPs as well, but this aspect is seldom investigated and the previous study, to the best of our knowledge, is one of the two only cases in which this additional check over was performed.

A different strategy, which focuses on the capping ligands as interaction mediators between NPs and the gelator is exemplified by the following interesting works. The tripodal bile-acid gelator **3** (Scheme 2) was known to form gel in a AcOH/$H_2O$ mixture (fibers of 50 nm ∅). Capping agents such as **4a-c** (Scheme 2) was envisaged to be able to interact with **3**,[14] in view of the well documented self-aggregation tendency of facially amphiphilic steroids. Indeed, while AuNPs capped with **4a-c** agents (1.5-3.5 nm ∅, $SPR_{max}$ = 520 nm) were found to be unstable in a AcOH/$H_2O$ mixture, they showed no sign of degradation within the gel materials made of **3**. TEM images show a regular arrangement of the NPs on the top of (and possibly inside) the gel fibers (Fig. 1b).

Bhattacharya and co-workers focused on a different gelator system, the *N*-lauroyl-L-alanine **5** (Scheme 2), which was already been subjected to extensive studies on its gelation properties of hydrocarbons (fibers of 50-100 nm ∅). The gel system provided a basis for systematic study[15] aimed at recognizing the effect on the gel's properties of the conspicuous NPs' presence well within the gel matrix, as seen by TEM for the example of NPs-gel system shown in Fig. 1c. Attention was given to identify the influence capping agents may exert on the morphological features and on the viscoelastic properties of AuNPs-gel nanocomposites. Different sets of capping agents were used, *e.g.:* 4-, 6-, and 10-carbon long alkyl- and aromatic thiols ,**6a-c** and **7**, and bile-acid derivative **8** (Scheme 2). SEM analyses showed that gel fibres made of **5** behaved in a considerably different manner depending

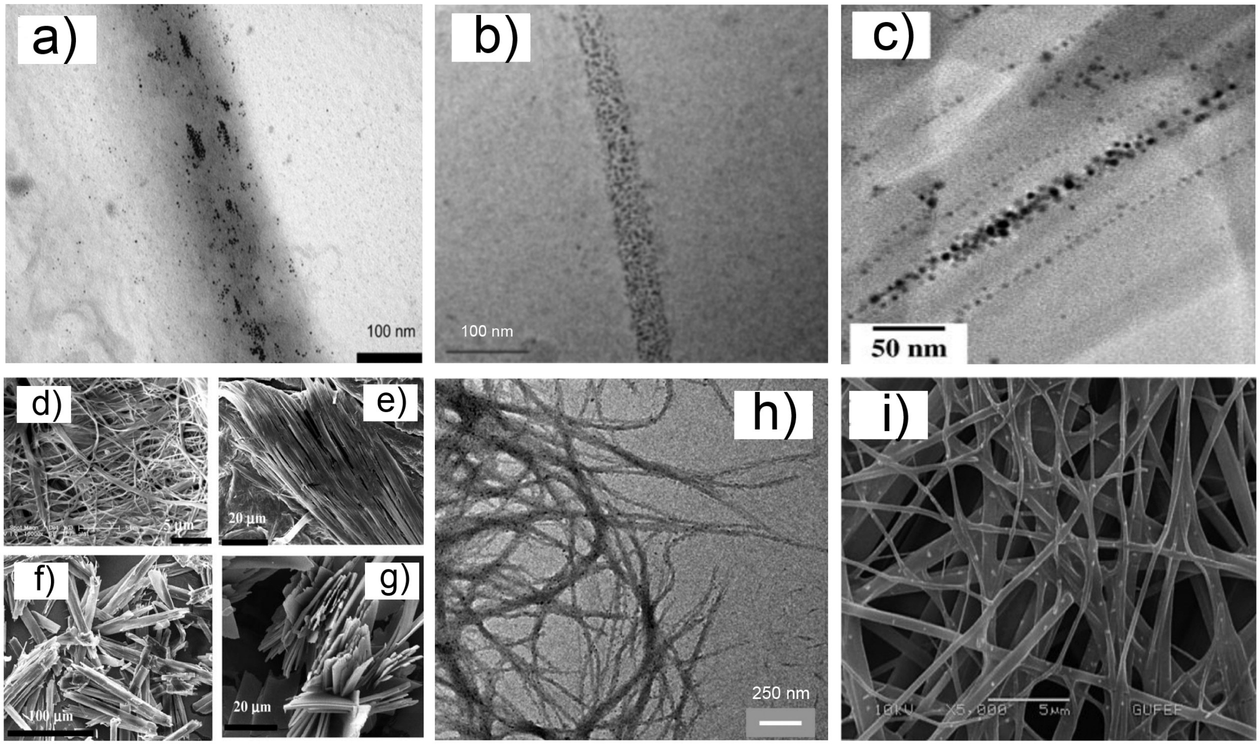


**Fig.** 1 SEM and TEM image of NPs-gel systems: a) TEM image of AuNPs stabilized by ODS and interacting with the fibers of **2a**, from ref. 13; b) TEM image of AuNPs stabilized by **4a** and interacting with the fibers **3**, from ref. 14; c) TEM image of AuNPs stabilized by **7** and interacting with gel fibers made of **5**, from ref. 15b reproduced with permission; Copyright © 2009, WILEY-VCH Verlag GmbH & Co; d) SEM images of xerogels of **5** (d) and of the hybrids **6c**-capped NPs-gel (e), **7**-capped NPs (f) and **8**-capped NPs (g), from ref. 15a, reproduced with permission Copyright © 2006, WILEY-VCH Verlag GmbH & Co; h) TEM image of AuNPs stabilized by **11** and interacting with gel fibers made of **12**, ref. 16, reproduced with permission Copyright © (2012) American Chemical Society; and i) SEM image of AuNPs stabilized by fluorous thiols HSR (R =$C_2H_4$-$C_8F_{17}$) and interacting with gel fibers made of Phe-Phe **14**, from ref. 18 reproduced with permission, Copyright © (2013) American Chemical Society.

on the capping agents covering the NPs (3.0 ± 0.8 to 6 ± 1 nm ∅, SPR$_{max}$ = 500-525 nm range). Upon addition AuNPs stabilized by aliphatic thiols **6a-c**, the gel reshaped as a thick network of collated fibers, while "rolled-tubular" type of aggregates formed upon addition of the NPs capped with the cholesterol-derivative **8**. Such morphologies, which also display thicker fibers, indicate increased fiber-fiber interactions induced by the presence of the NPs. Finally, **7**-capped AuNPs generated less dense, platelet-like structures (see Fig. 1d-g). Rheological study performed on the composites showed that the incorporation of alkanethiol- and cholesterolthiol-capped AuNPs (**6a-c** and **8**) improved the rigidity of the gel (higher yield stress values observed). On the contrary, **7**-capped AuNPs slightly decreased it. This data-set demonstrates well the importance of the gelator - capping agent relationship.

Banerjee and co-workers,[16] recently reported on the modulation of the mechanical properties of hybrid hydrogel materials incorporating AgNPs capped by cysteine (Cys, **9**) and cysteine-based dipeptides Cys-Leu (**10**) and Cys-Phe (**11**) (Scheme 2). The *N*-terminally protected tri-peptide **12** (Scheme 2) produces a stable supramolecular hydrogel (fibers of 80-150 nm ∅ by SEM). Cysteine-based capping ligands provide a dual function: *i.e.,* the cysteine fragment stabilizes the AgNPs (2.4-4.5 nm ∅), whereas the adjacent residue interacts with the hydrogelator molecules through hydrophobic interactions. Morphological studies of the hybrid hydrogel by TEM (Fig. 1h) confirmed the presence of AgNPs mainly along the hydrogel nanofibers. The mechanical strength of the gel can be modulated by varying the nature of the capping ligands, similarly to what seen in the previous examples, but also by varying the size and the amount of NPs employed. Increasing the total surface area of the NPs (by adding more NPs or by increasing their size) invariably leads to diminished gelator-gelator interactions which, in turn, lower the gel strength in all cases.

A similar behavior was also observed by Del Guerzo and co-workers who noticed a gradual decrease of stiffness of an organogel material made of the anthracene derivative **13** in *n*-butanol upon addition of increasing loads of AuNPs.[17] While the presence of the AuNPs (ca. 3 nm ∅, SPR$_{max}$ = 500 nm), capped with different linear alkyl- and perfluoroalkyl-thiols ($C_6H_{13}$, $C_{12}H_{25}$ and $C_2H_4$-$C_8F_{17}$), does not alter the morphology of the gel fibers (100-200 nm ∅), the hosted NPs do have a dramatic effect on the fluorescence of the gelator molecule, in a way that shows some degree of proportionality with the NPs' concentration. Indeed, the observed optical response, which is linear for NPs' loads < $10^{-5}$ molar ratios, suggests a regular decrease of inter-particle distance simply obtained by diluting the NPs content.

A last example reveals interesting relationship between NPs dimension and gel morphology. When a chloroform solution of AuNPs - pre-formed by classical reduction methods in the presence of sodium citrate - are added to a solution of diphenylalanine (Phe-Phe) dipeptide **14** in hexafluoropropanol, a gel is formed, as reported by Demirel *et. al.*[18] A SEM image of the obtained NPs-gel material is shown in Fig. 1i. Interestingly, significant differences in the gel morphology were observed depending on the average size of the NPs employed (10-60 nm ∅, $SPR_{max}$ = 495-533 nm), as evidenced by the SEM study. While 10 nm sized NPs did not practically change the original gel structure, increasing the dimensions of the nano-objects (up to 60 nm ∅) affected the gelator self-assembly process. The authors related this phenomenon to other works on protein adhesion to NPs' surface, where it was found that flatter NP surfaces can better adsorb proteins. The system can also undergo a laser-triggered gel disruption process. Indeed, illumination of the NPs-gel system by a green-laser, whose emission matches the absorption profile of the NPs, led to a transition to solution.

### *2.2 Type II: Synthesis of NPs-Gel Composites under In Situ Conditions*

The redox reaction which converts the metal salt of choice into metallic NPs may not be necessarily preformed prior to the gel formation. Rather, it could be achieved *in situ* within the gel materials. There exist certain variability in the procedures which follow this route and they essentially differ for the identity of the active reducing species. Interestingly, several examples demonstrate that structural features of the gelator molecule itself can act as efficient reducing sites.

John *et al.*[19] described two ways of making hybrid materials where *in situ* $HAuCl_4$ to AuNPs conversion was attained in the presence of a molecular species capable itself to act in dual roles: as a gelator and as a reducing agent. In the first case, the authors focused on the mono-substituted urea derivatives **15a-c** (Scheme 3), excellent ambidextrous gelators.[19a] In a typical procedure, a mixture of $HAuCl_4$ and gelator was heated to 50 °C, then allowed to cool down. The initial change of the solution from yellow to colourless progressed to a pink-coloured gel material at room temperature, identified as a AuNPs gel ($SPR_{max}$ = 553 nm). SEM and TEM analyses showed unchanged gel morphology, regardless of the presence of the AuNPs which were found to be spherically shaped (11-15 nm ∅) and dispersed mainly on the edges of the gel platelets (Fig. 2a).

Due to the terminal ureidic $NH_2$ group, compounds **15a-c** were suggested to be responsible of the reduction of Au(III) to Au(0). In order to test the above hypothesis, the acetanilide derivative **16** was synthesized (Scheme 3). Under the same conditions, it did form a gel material, but no nanoparticles were detected within. This fact, however, might not be a definitive proof and an electrochemical investigation on the redox potentials of the system could be helpful in this case.

In the second example, *in situ* synthesis of AuNPs in a gel matrix was accomplished by employing the ascorbic acid derivative **17** (Scheme 2) which can form highly inter-digitated bilayer-like gels in water at low concentrations.[19b] The gelator design originates from the ability of ascorbic acid to reduce auric salts to metallic gold and the need of an amphiphilic character (introduced by the alkyl chain) to induce gelation. The addition of **17** to a $HAuCl_4$ solution, followed by heating, resulted in change of the solution colour, from yellow to colorless, which then progresses to the formation of a pink gel. The presence of the NPs into the materials was confirmed by the presence of telltale SPR band in the UV-vis spectrum ($SPR_{max}$ = 555 nm). SEM analysis showed that the sheet-like morphology of the gel did not change due to the presence of the AuNPs. Moreover, TEM images revealed that the AuNPs (11-18 nm ∅) were not assembled along fibers and were rather uniformly distributed within the gel matrix. Having in mind the different behavior described for the systems presented before, the lack of specific NP–gelator interactions might be responsible for that.

Banerjee and co-workers[20] studied the tripeptide organogelator **18** containing two Tyr residues (Scheme 3). Chloroauric acid was added to a gel made of **18** in basic MeOH:water 1:1 mixture and heated at 50°C. Once equilibrated at r.t., the characteristic yellow nuance of the $AuCl_4^-$ species was lost and the gel acquired a bluish-violet color ($SPR_{max}$ = 551 nm). AuNPs (15-40 nm ∅) were formed within the gel matrix. The hypothesis of Tyr residues acting as reducing agent was confirmed by the use of model tripeptide Boc-Ala-Phe-Ala-OMe (**19,** Scheme 3) which was found completely ineffective, under the investigated circumstances.

Similarly, *in situ* syntheses of gold nanoparticles in hydrogels made of the tryptophan-based dipeptide amphiphiles **20a-d** were reported (Scheme 3).[21] It was found that the different gel morphology observed for the four gelators constitutes a key factor in the formation of differently sized and shaped AuNPs. Both SPR data and TEM images corroborate the presence of nano-sheets, nano-wires, nano-octahedra and nano-decahedra NPs (10-200 nm ∅, $SPR_{max}$ = 515-688 nm) within the gel matrixes.

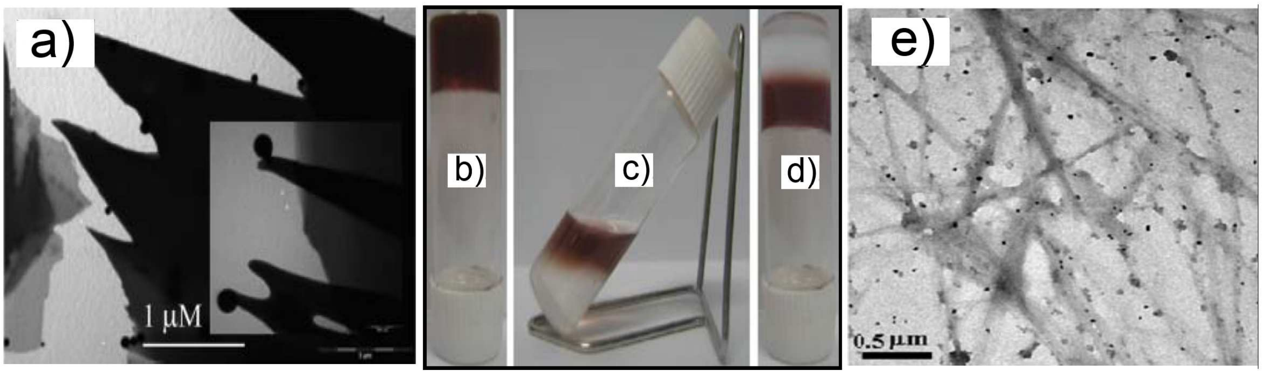
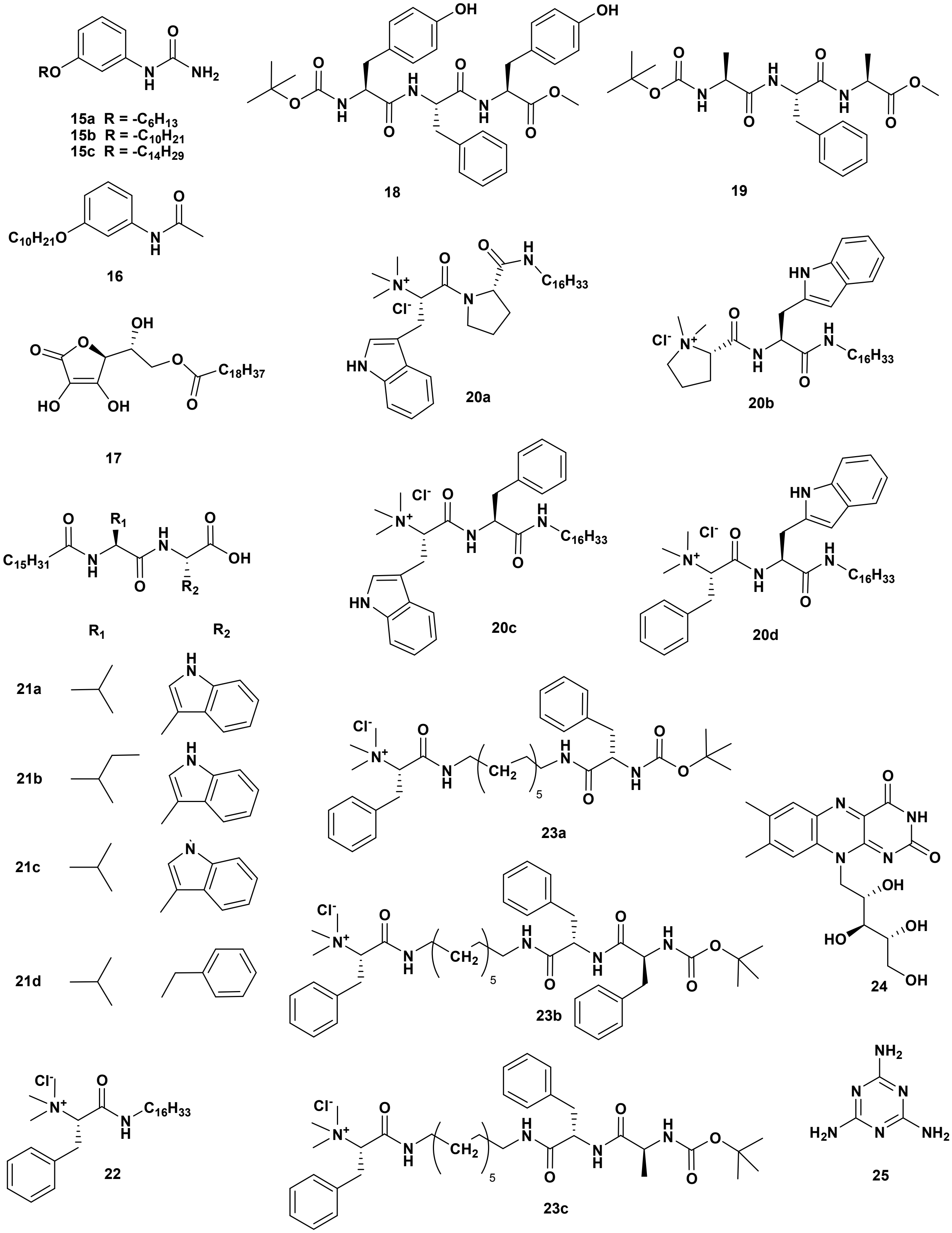


**Fig. 2** a) TEM image and magnification of AuNPs within the gel system made of **15a**, adapted with permission from ref. 19a; b-d) pictures of the process of NPs' transfer from hydro to organic gel system of **21a**, and e) TEM image of the AuNPs embedded in the gel; reproduced with permission from ref. 22.



**Scheme 3.** Molecular Formulae for compounds **15-25**.

The same group has also reported a very intriguing process where *in situ* synthesized AuNPs–hydrogel nanocomposites could be converted into an AuNPs–organogel hybrid simply by alteration of pH.[22] The systems is based on the amphiphilic dipeptides **21a-c** (Scheme 3)**,** containing tryptophan residues, but surprisingly also with the derivative **21d**. In general, these derivatives have an interesting feature: their carboxylate form behaves as hydrogelator, while, the carboxylic acid form as organogelator. The whole process starts with formation of a AuNPs-hydrogel made by addition of aqueous HAuCl$_4$ to a preformed **21a-d** hydrogels (under stirring, pH = 9-10) up to reach a final gelator:Au(III) ratio of 10:1. The analysis of such material confirmed the presence of AuNPs based on colour change (Fig. 2b) and the appearance of the SPR band (SPR$_{max}$ 523-525 nm). After that, toluene was added to form a biphasic system and HCl$_{(aq.)}$ was used to convert the carboxylate into acid. This input led to a transfer of the gelators into the organic phase carrying the AuNPs along (Fig. 2c). The mixture eventually gelated with the simultaneous NPs entrapment (Fig. 2d). The novel materials were also duly analyzed by SEM and TEM imaging, X-ray diffraction, fluorescence and rheology. In particular, TEM images revealed the importance of the supramolecular networks in the stabilization of the nanoparticles in both hydro and organogel, as the AuNPs (12-14 nm and 15-17 nm for **21a-b** and **21c-d,** respectively) were found to be aligned on the surface of the amphiphilic nanofibers (Fig. 2e). Also, the mechanical strength of the nanocomposite improved, probably due to the formation of more compact and denser fibers. Questions remain on the rationale at the basis of the behavior of **21d**, which does not possess the reducing tryptophan moiety. Additional comparison with the behavior of simpler systems, and even with a simple linear aliphatic fatty acid (C$_{16}$) - which surprisingly succeeds in the formation of the material, although showing a limited NPs formation - indicates that the compelling presence of specific reducing moieties might not be quite so.

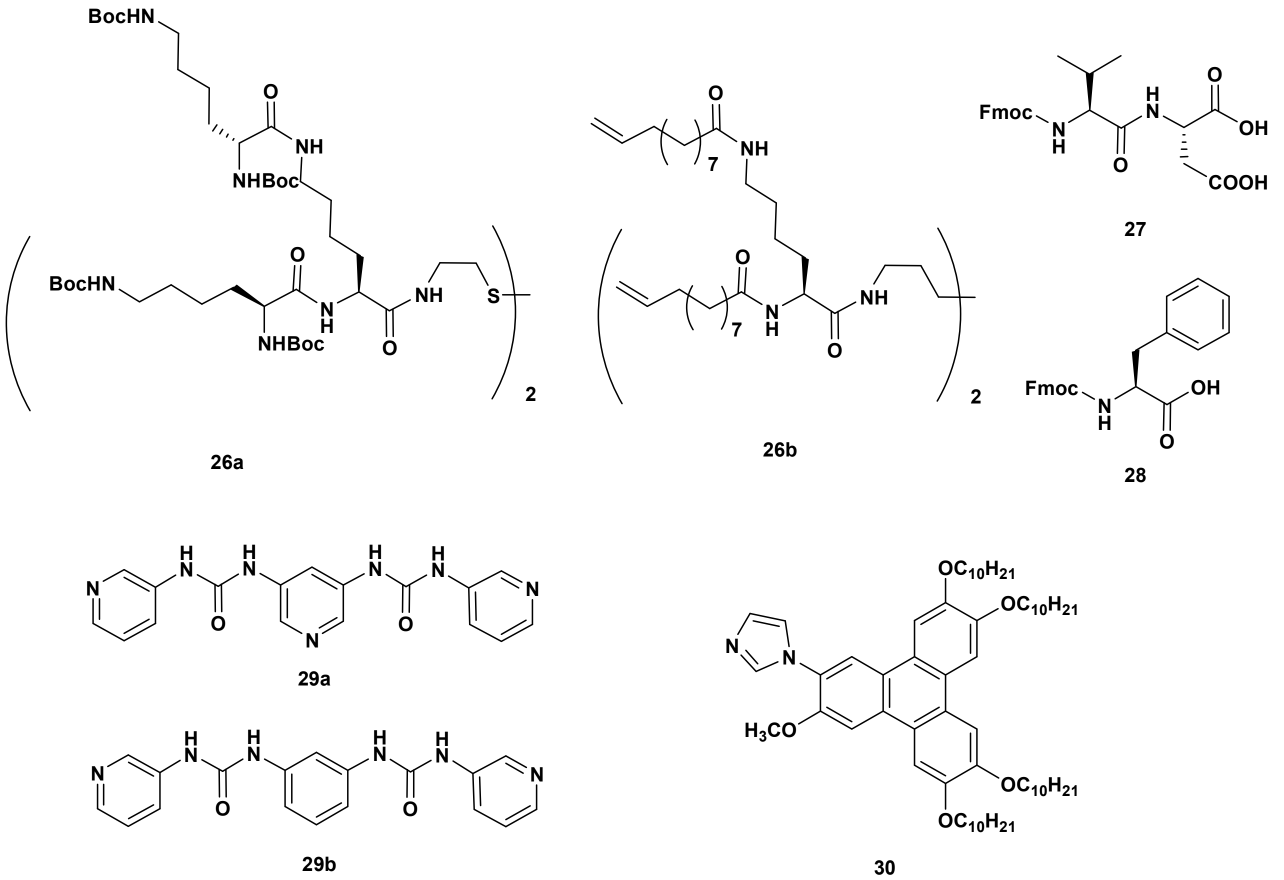
Indeed, the latter observation is supported by a recent work mainly related to gelator structural modifications aimed to provide enhanced gelling ability.[23] Here, it has been shown that the L-phenylalanine-based poor hydrogelator **22** (Scheme 3), and the more efficient tail-modified amphiphiles **23a-c** (Scheme 3) were capable of *in situ* synthesis of AuNPs within the gel material without the help of any external reducing agents. Interestingly, the identity of the gelator and its concentration relative to the Au(III) salt dictated on the shape and size of the resulting embedded AuNPs (spherical, triangular, polyhedral shapes, 15-45 nm ∅).

A very interesting example of bio-inspired system is given by the work of Nandi and co-worker,[24] which investigated the riboflavine (**24**) / melamine (**25**) two-component system with the purpose of NPs production (Scheme 3). Mixing different quantities of AgNO$_3$ powder with a 1:1 mixture of **24** and **25** in water, after homogenization at 90 °C, produces AgNPs-hydrogel composite (the riboflavin moiety acts as reducing agent). Spectroscopic and electron microscopy techniques reveal a well-defined morphologic transformation of the gel materials: the hollow tubes of the hydrogel are converted either into helical fibers, rod-like structures, or spheroidal aggregates simply depending on the concentration of metal salt used. Also, the size of the NPs drastically increases with the amount of AgNO$_3$ employed in the material production (12±4 – 52±8 nm ∅, SPR$_{max}$ = 535 nm; 1000 ± 200 nm ∅, SPR absent).

Under certain conditions, UV-light is capable to reduce metal salts to metallic NPs.[25] One of the first examples of UV-light induced formation of gel-NPs materials was presented by Chechik, Smith *et al.*.[26] The authors employed a gel material made of the dendritic gelator **26a** in toluene (Scheme 4). Chloroauric acid was transferred into a toluene phase by the use of a phase transfer agent (tetraoctylammonium bromide) and let to diffuse into the gel material. Once irradiated with a Hg-lamp, the gel initially changed its colour from yellow to colourless and finally to deep purple in the matter of few hours (indicating a two steps Au(III)$\rightarrow$Au(I)$\rightarrow$Au(0) transformation). In this case, the quaternary ammonium salt also acts as a sacrificial reductant species.[27] TEM images of the obtained NPs-gel system confirmed the presence of NPs within the gel matrix (13 nm ∅, SPR$_{max}$ = 550 nm). The gelator was found to be essential for nanoparticle formation, since the irradiation of a toluene solution of HAuCl$_4$ alone resulted in the deposition of bulk elemental gold. Indeed, the gelator acts as a stabilizer for the NPs, as shown by the fact that whenever the gel is disrupted (by heating or by adding MeOH) the NPs collapse into black aggregates. Interestingly, the hypothesis of specific sulfur-gold gelator–NPs interaction can be ruled out since a structurally related gelator **26b** (Scheme 4), devoid of the S-S bridge, practically behaves as **26a**.

Peptide- and amino acid-based hydrogels have been used for the *in situ* generation of fluorescent silver nanoclusters at room temperature under sunlight irradiation, conditions more suited to "green chemistry" protocols. The dipeptides Fmoc-Val-Asp-OH[28] (**27**) and Fmoc-protected L-phenylalanine[29] (**28**) were studied by Banerjee *et al.* in separate occasions (Scheme 4). The two compounds form a transparent, stable hydrogel (0.1-0.2% w/v). The preparation of the gel-NPs composites consists in the addition of a freshly prepared aqueous AgNO$_3$ to a solution of the gelator (DMSO in the case of **27**, and water for **28**). An Ag(I)-containing transparent hydrogels were immediately formed. Exposure to sunlight generated a light violet colour in few minutes, indicating the reduction of silver ions to silver nanoclusters (broad SPR$_{max}$ = 530 nm and 510 nm, for systems made of **27** and **28**, respectively). While such transformation does not lead to significant morphology changes for the gel made of **27**, the formation of Ag nanoclusters within the hydrogel of **28** produces a transition from helical nanofibers to nanovesicles (as observed by HR-TEM and X-ray diffraction, FE-SEM and AFM). Interestingly, the two systems are able to produce stable AgNPs of small size (1-3 nm ∅) and of narrow size distribution.

The pyridyl bis(urea) gelator, **29a** developed by Steed *et al.* (Scheme 4) is also interesting.[30] Addition of AgBF$_4$ to a 7:3 THF:water solution of **29a**, followed by sonication, yielded a homogeneous gel materials. Exposition to ambient light transformed the material into a AgNPs composite in 1-2 weeks time. A detailed systematic study, performed by varying the AgBF$_4$:gelator and the THF:water ratios and the ambient light exposition time, led to the following conclusions: i) the size and size's distribution of the AgNPs strongly depended on the AgBF$_4$:gelator ratio. While a 1:1 ratio produces small particles (2-6 nm ∅, SPR$_{max}$ = 430 nm), and clearly attached to the gel fibers (Fig. 3a), increasing the initial AgBF$_4$ load leads to larger particles (5-50 nm ∅ up to 100 nm ∅), with evident signs of particles aggregation; ii) a 1.5 AgBF$_4$:gelator ratio seems to be optimal for the structural stability of the gel materials. Compound



**Scheme 4.** Molecular Formulae of compounds **26-30**.

**29b** (Scheme 4), devoid of the donor N atom on the central ring, does not form any gel material under the same experimental conditions. This strongly hints at the active role of all the three pyridyl rings on **29a** to form the AgNPs materials.

Heterocyclic-metal coordination is applied also in another described by Kimura *et al.*[31] Here, the self-assembly of the imidazole-containing polycyclic aromatic **30** leads to gel materials in 2-methoxyethanol (Scheme 4). The addition of a solution of AgNO$_3$ to the gel material, in the dark, produced a novel gel species, where coordination of the Ag(I) ions to the imidazole units took place (as evidenced by $^1$H-NMR, MALDI-TOF and the fluorescence quenching of the initially emitting gel). UV light irradiation transformed the material. TEM imaging (Fig. 3b) reveals the presence of gel fibers nicely decorated with abundant AgNPs (8 nm ∅, SPR$_{max}$ = 400-700 nm).

Finally, the following examples show cases where an external reducing agent is employed for the reduction of silver and gold cations to elemental species. Taubert and co-workers[32] successfully synthesized an AgNPs-gel system by using mixtures of **31a** and **31b** (Scheme 5). Two-component LMWG systems[33] represent a less frequent approach for gel preparation which hinges on the use of two pro-gelator molecules capable of forming a gel only in the presence of each other. This is the case for the two tri-peptides **31a** and **31b**. By varying the molar ratio of the two components a modulation of the properties of the material can be achieved. The two tri-peptides are constituted by a Val-Val-Val and a Val-Val-Cys sequence, respectively, and the results show that the NPs assembly was controlled by the fraction of cysteine-containing gelator present within the gel system. The reduction of AgNO$_3$ was accomplished in a hot *n*-butanol solution of the oligopeptides by addition of DMF. The latter species is known to reduce silver ion to metallic silver even at room temperature.[34] Cooling afforded a gel material embedded with AgNPs. Interestingly, the shape and the size of the AgNPs could be tuned by varying the **31a**:**31b** ratio. While small spherical particles were obtained at higher doses of **36b** (9 nm ∅), larger particles of complex shapes (plate-like and raspberry-like) were obtained at lower contents of **31b** (>100 nm ∅). XPS and SERS studies indicated a strong interaction between the S atom of the cysteine residue of **31b** with silver, a feature absent in the case of tri-peptide **31a**.

Maitra and co-workers studies the Ca(II)-induced gel formation by sodium cholate, **32** (Scheme 5) for the preparation of AgNPs- and AuNPs-gel materials.[35] The AuNPs in the hydrogel were generated *in situ* by doping the calcium cholate hydrogel with AuCl$_3$ salt, and slowly diffusing sodium cyanoborohydride through the hydrogel. The reduction of Au(III) to AuNPs produced magenta-coloured material (SPR$_{max}$ = 490 nm). Notably, the molar ratio between Ca(II) and Au(III) ions was found to play an important role in control of agglomeration and rheological properties of AuNPs-gel hybrid and this could be probably attributed to the competition between the two metals for the coordinating carboxylate groups in **32**. Similarly, when a Ag(I)-doped calcium cholate hydrogel was prepared and treated with sodium cyanoborohydride solution a yellowish brown hydrogel material containing AgNPs was obtained (SPR$_{max}$ = 415 nm). TEM images revealed the presence of Ag- and Au-NPs (1.5–2 nm ∅) mainly distributed on the junction zones between gel fibres.

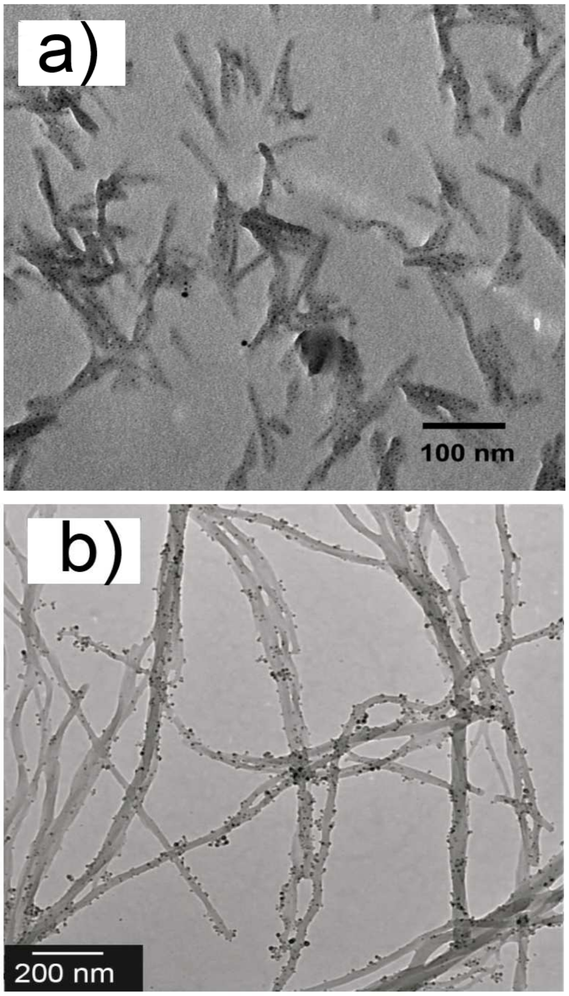


**Fig. 3** TEM images of NPs-gel systems: a) AgNPs within the gel made of a 1:1 $AgBF_4$:**29a** mixture, after exposition to light, from ref. 30; b) AgNPs deposited over the fibers of **30**, from ref. 31 kindly provided by Prof. M. Kimura.

Kang, Gao and co-workers[36] developed a cyclic β-aminoalcohol gelator **33** (Scheme 5) derived from 1,2,3,4-tetrahydroisoquinoline and capable of gel formation in various aprotic solvents. The toluene gel of **33** exhibits an enhanced stability towards metal ions and quaternary ammonium salts such as tetraoctylammonium chloroaurate $(TOA)AuCl_4$ with respect to its non-fluorinated analogue. This feauture becomes relevant in the preparation of AuNPs-gel materials. Indeed, addition of the gelator **33** to a $(TOA)AuCl_4$ solution in toluene, followed by heating, yielded, upon cooling, a gel and a colour change, from red to colourless, due to reduction of Au(III) to Au(I). Further reduction of Au(I) to Au(0) was attained putting the material to react with aqueous $NaBH_4$. This example represents an "intermediate" case where reduction is achieved only partially by the gelator and an external reducing agent is needed. TEM images of the AuNPs-containing xerogel show the presence of spherical NPs (5-9 nm ∅) arranged along the gel fibers. Strong interactions between Ag(I) cations and fluorine atoms are suggested as responsible for the fast disruption of the upon addition of silver ions.

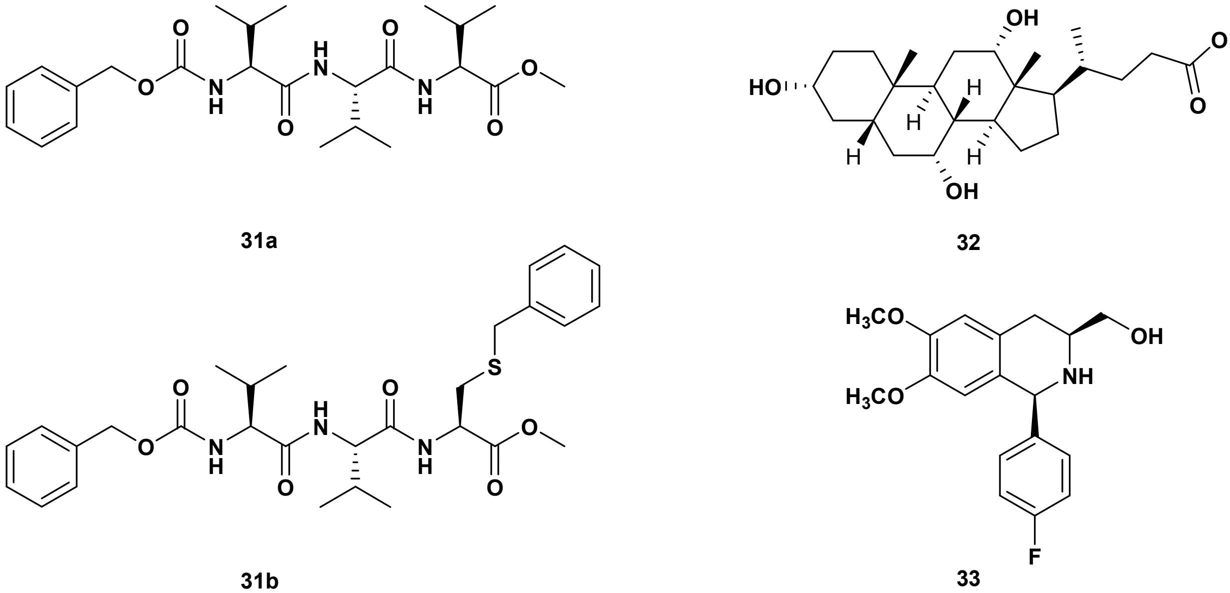
## 3. Applications

The rich diversity of systems which can be employed as structural basis for the incorporation of NPs and, thus, generate novel materials fully reverberates into quite ample opportunities for the development of practical applications. One of the most intriguing consequences of the integration of gels' constitutional features with the intrinsic properties of metal NPs is represented by the exchange of structural information between object of different scales. From this point of view, NPs-gel systems based on LMWG systems seem definitely superior since, as said, they permit to design the material internal structure to quite an extent. Frequently, LWMGs contain a chiral center and it is well known that this structural feature can be translated from the molecular level to the nano- and micro-scale object during the self-assembly process. Self-assembled fibrillar objects, such as rods, tapes, or tubes, can be helically twisted, coiled, or wound around one another to give multiple helices or even coiled coils. These structures might be intrinsically chiral and, consequently, possess a right- or left-handedness. The incorporation of metals into such superstructures, could translate the chiral feature of the gelator superstructure to the embedded nano-objects. Not only that, the spatial distribution of NPs can be directed by the gelator structural properties. This can be of crucial importance in optoelectronic materials. In particular, SPR effects are critically determined not only by the shape and size of NPs, but also by their arrangement and local dielectric environment.[37] Attempts towards this direction are starting to appear in the literature. For example, the Ag(I)-coordinated metallo-gelator, **34** (Scheme 6) was employed to prepare a composite materials made of chiral AgNPs entrapped into the organogel.[38] In this case, hydroquinone was used as reducing agent. The chirality of the resulting NPs embedded in the gel (10-20 nm ∅) was inferred by the observation of a strong bisignated circular dichroism (CD) spectrum (negative and positive maxima at 398 nm and 442 nm, respectively). The chirality of the nanoparticles originated and was transferred to NPs from the chiral gel fibers rather than from the individual gelator molecules. Indeed, the gel state is essential for imparting the chirality to the NPs which, when prepared from solution, do not show any sign of chirality. The use of intrinsically chiral NPs is one of ways to obtain optical activity at the nanoscale.

A different concept, simple and effective, was based on the use of pre-assembled fibrous materials obtained by a adding preformed NPs into a fluid dispersion of the chiral anthraquinone-based oxalamide gelators **35** (*R* and *S*, Scheme 6).[39] The self-assembled fibers served as chiral templates for 3D arrangement of gold nanorods (NRs) into the hybrid materials, thus transferring the chirality from the fibers to the NPs. Indeed, CD measurements revealed intense plasmon-induced Cotton effect (*R* and *S* derivatives) with strong anisotropy. Notably, spherical NPs show no such behavior indicating a crucial role of the NP's shape.

Achieving catalysis by means of NPs-gel systems is a quite appealing thought. Noble metals such as Ag and Au are used for catalysis in numerous important chemical transformations.[40] To achieve a high performance at low cost, precious catalysts are required to have a large surface/volume ratio. Hence, NPs are highly attractive species to serve as catalysts and their incorporation into gel networks might represent an winning strategy in catalyst design.

Two notable examples exist in the literature. The non-symmetric bis-tetrazole based ligand **36**, described by Lee, Jung and co-workers,[41] is able to form gel in water under basic pH conditions in the presence of AgNO$_3$ or AgClO$_4$ salts. Over time, a progressive change of the gel colour, from white to brown, and TEM images proved the reduction of the Ag(I) cation to metallic AgNPs within the gel material. The data also show that the size-distribution of the NPs can be modulated by changing the gelator:Ag salt ratio (1-3 nm ∅ for a 1:2 ratio, 2-5 nm ∅ for a 1:4 ratio). Catalytic activity of the new material was essayed by investigating the reduction of a simple model compound 4-nitrophenol (4NP) to 4-aminophenol (4AP). The test was performed by percolating a solution containing 4NP and NaBH$_4$ through a glass column filled with the AgNPs-gel material. It is well known that the 4NP to 4AP conversion in the presence of NaBH$_4$ is thermodynamically favoured but kinetically slow and this transformation is often chosen as a model reaction for testing the catalytic activity of various metallic species.[42] The NPs-gel system based on **36** affords the desired product with high yield and no alteration of the catalytic material was detected. An *electron-relay* mechanism in which the electron transfer from the hydride to the substrate occurs mediated by the AgNPs was suggested, in line with previous studies.[43]



**31a**

**32**

**31b**

**33**

**Scheme 5.** Molecular Formulae for compounds **31**-**33**.

In Banjerjee's laboratory, a three component hybrid material composed of a gel matrix containing both graphene oxide (GO) fragments and gold-NPs has been created and studied.[44] The key ingredient is the hydrogelator molecule, the pyrene-conjugated tryptophan based compound **37**. The intrinsic gelating properties of **37** in phosphate buffered solution are contingent to the presence of large surface aromatics and a Try group, both crucial features. As shown, the pyrene unit is capable to establish interaction with the flat GO fragments, while the Try group allows for *in situ* formation of gold NPs. The morphology of the tri-hybrid hydrogel studied by TEM and FE-SEM revealed the coexistence of three distinctly different nanostructures: nanofibers, nanosheets and nanoparticles deriving from the self-assembly of **37**, the GO and the AuNPs, respectively. The catalytic activity was tested on the reduction of aromatic nitro group of 4NP and 4-nitroaniline (4NA) in the presence of NaBH$_4$. The authors put at comparison this tri-hybrid material with an hybrid AuNPs composite obtained by an *in situ* process between **37** and Au(III) ions. The latter system would be *per se* rightfully part of the collection of example of this review, being itself a novel AuNPs gel system. However, its catalytic properties are indeed surpassed by those of the tri-hybrid system, thus proving the successful synergy between the GO and the AuNPs within the hydrogel matrix. A comparison between the novel catalytic systems just described with other systems reported in the literature is limited due to the lack of experimental details, especially on the kinetic model assumed which is needed to extract reliable quantitative information from the kinetic data.[43]

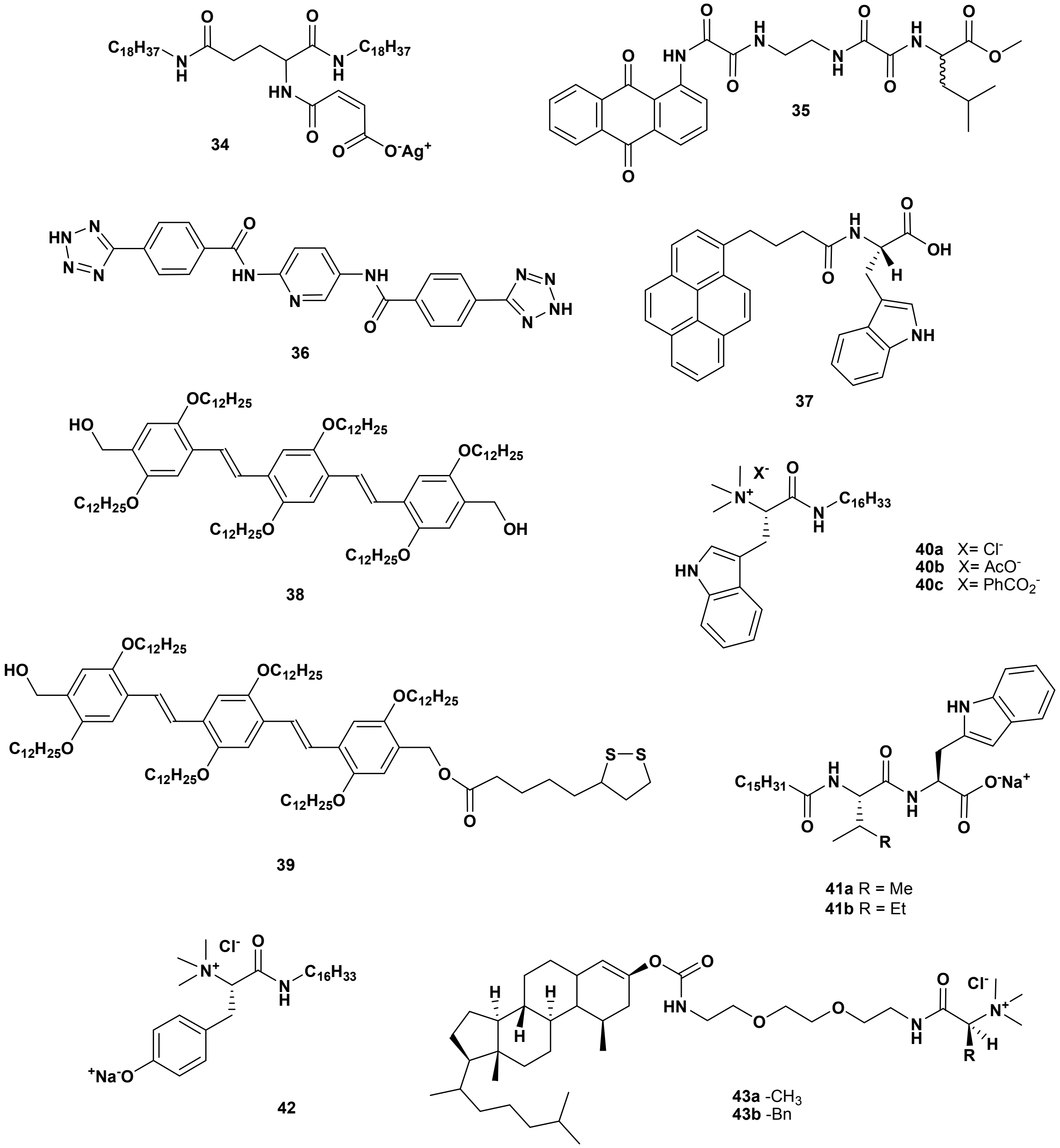
Novel optical properties emerge in the novel linear hybrid system in which AuNPs are bound to π-conjugated oligo(*p*-phenylenevinylene) supramolecular aggregates described by Meskers, Schenning and co-workers.[45] The authors employed the gelator molecule **38** (Scheme 6) in toluene as a scaffold for the spatial organization of AuNPs capped with the derivative **39** (obtained by the introduction of a disulfide moiety in **38**). The AuNPs capped with **39**, interact with the gel materials made of **38**, also by influencing its critical gelation concentration (cgc). More importantly, as visualized by the TEM images, the NPs are found to align on both sides of gel tapes – 40 nm wide and 7 nm high (minimum detected) - giving rise to a hybrid material. Such alignment was not induced by drying effect and cryo-TEM images confirmed the distribution of the NPs in the composite.

The spectroscopic data on the novel material confirm the electronic communication between the gel tapes made of **38** and the **39**–AuNPs since the fluorescence of OPV derivative **38** was considerably quenched in the hybrid material - the emission intensity was reduced by a factor of 33 in comparison with the emission intensity of **38** alone - with a concomitant decrease in its lifetime. Photoinduced absorption (PIA) studies confirm the presence of dynamic process that takes place on a nanosecond time scale and involves diffusion of the electronic excitations through the tape toward the AuNPs.

Another application of NPs-gel materials derives from the fact that silver and silver-NPs are known - since roman times - to possess antimicrobial activity and their use in the healthcare industry is nowadays well established.[46] In general, AgNPs are routinely found to be more effective against gram-negative bacteria than gram-positive ones and, for this reason, the work done by Das and co-workers[47] on the use of AgNPs-gel materials with high antimicrobial activity is particularly interesting.

Following various *in situ* procedures, compounds **40a-c**, **41a-b, 42** and **43a-b** (Scheme 6), can afford AgNPs-gel materials.

Table 1 summarizes the antimicrobial activity of the AgNPs gel composites made with **40-43**, as minimum inhibitory concentration (MIC) calculated referring to the gelator



**Scheme 6.** Molecular Formulae for compounds **34-43**.

concentration and to the metal concentration (in parenthesis). As clearly seen, the effectiveness of the activity observed spans over two orders of magnitude of concentration but, in general, the nanocomposites exhibited excellent antibacterial activity against both Gram-positive and Gram-negative bacteria. In some of the most effective cases, as **40a** and especially for **40b-c**, the increment in efficacy is remarkably high, between ca. 10- to 50-fold. These data can be compared, although only qualitatively, with those reported for various AgNP suspensions,[48] and it must be noted that compounds **40a-c** showed already antimicrobial activity *per se*.[47b]

**Table 1.** Minimum Inhibitory Concentration (μg/mL) expressed as gelator concentration and silver concentration (in parenthesis) for the AgNPs-gel systems based on **40-43** in against Gram-Positive (+) and Gram-Negative (–) Bacteria.[47]

| | + | | – | |
|---|---|---|---|---|
| | *B. Subtilis* | *S. Aureus* | *E. Coli* | *K. Aerogens* |
| **40a** | 20 (7.4) | 10 (3.7) | 60 (22.2) | 80 (29.6) |
| **40b** | 3 | 2 | 100 | 20 |
| **40c** | 5 | 2 | 50 | 25 |
| **41a** | 100 (56) | 150 (84) | 150 (84) | 75 (42) |
| **41b** | 200 (74) | 200 (74) | 200 (74) | 100 (37) |
| **42** | 20 (7.8) | 10 (2.8) | 75 (21) | 55 (15.4) |
| **43a** | 70 | 50 | 100 | 75 |
| **43b** | 30 | 20 | 60 | 50 |

## 4. Conclusions:

By paraphrasing the famed French scientist Berthelot, chemistry has the unparalleled privilege, uniquely among other sciences, to create its own subject. This prerogative translates into virtually infinite opportunities for the discovery of novel species and materials. This concept applies well in the case of the NPs-gel hybrid materials.

Despite extensive investigations on both the supramolecular chemistry of LMWGs and the preparation and physico-chemical properties of noble NPs, the integration of these components into a single entity represents a very recent and highly welcome novelty in the field of functional, smart materials.

This review intends to put on display the works at the *avant-garde* on the developments of noble metal NPs-gel systems. These materials originate from the combination of objects belonging to different scale domains. Micrometer-scaled fibers, created by the self-assembly of the gelator monomers, interact with nano-clusters of noble metals, in what eventually makes up a macroscopic object. Such inter-domains crossing is reckoned of great and increasing importance in supramolecular and material chemistry and, undoubtedly, will enable advances in both fields.

Noble metal NPs-gels hybrids can be obtained by several different procedures and their features can be characterized *inter alia* by a combination of Electronic Microscopy (SEM, TEM, etc.) and UV-vis Spectroscopy. Both preparation and characterization of NPs-gel materials are described in this review. In particular, we put strong emphasis in the description of the various synthetic pathways which are grouped into two different categories: *type I* and *type II*, depending on whether the NPs are formed prior to the material formation or by an *in situ* process. The many variables involved in the preparation of NPs-gel materials and the lack of a comprehensive and accepted view on the influence of the preparation on the final properties of the material demanded attention.

Although many of the works surveyed here focus on the study of the effect that one of the components may exert onto the other, in terms of both structural and/or optical features, we believe that these new materials can be indeed considered entities by their own rights. As said, the exploitation of their novel emerging properties could engender remarkable developments and some applications have been already reported. NPs-gel materials were indeed tested as novel catalysis, as antimicrobial supports and for the construction of chiral optical materials. Despite these applicative developments, the research on this topic, so far, has had many features in common with the exploration of a *terra incognita* and many aspects of the integration of NPs into gel materials are not completely comprehended. In particular, attention should be given to identify whether the presence of NPs can contribute to an additional stabilization of the gel matrix, or not and, eventually, to what extent. The mode of NPs-gel hybrid preparation (pre-formed NPs or *in situ* generated NPs) is obviously relevant to this issue.

Also, the influence of the presence of NPs towards the self–assembly process of the gelator is not yet completely understood. Let alone the role of NPs formation process in the resultant material properties. For example, although some authors believe that *in situ* NPs formation could allow for the retention of the original gelator self-assembly process, the data collectively reviewed here strongly indicate quite a variability of behaviors, depending on the identity of the gelator species and the experimental conditions employed.

Although at its early stage of development, and despite many fundamental questions that remain still unanswered, NPs-gel materials represent a promising field of research and we expect a thriving future ahead.

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