Molecular Thinking for Nanoplasmonic Design

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ABSTRACT The development of nanoplasmonics has been tremendous during the past two decades, driven in part by the improvements in colloidal synthesis of nanocrystals and manipulation of nanoparticle surface functionalities. This has granted access not only to exquisite control over the morphology of nanoparticles but also to novel multiparticle nanostructures with a variety of organizational motifs. Driven by such new possibilities, completely unforeseen plasmonic effects have been found, which let us think about applications in a variety of fields. In this Perspective, we discuss the evolution of plasmonic nanomaterials and their corresponding properties and correlations with molecular concepts that have been around for a long time. Additional thinking along these lines may lead to further expansion of nanoplasmonics and to multiple surprising discoveries in this field.

Through the first half of the 20th century, a great intellectual revolution in science boosted the development of powerful and sophisticated techniques that provided an accurate description of the structure of matter. The need to understand the relation between structure and function for both classical and novel materials in solid state physics has been an important driving force behind such progress. Meanwhile, supported by such technical advances, molecular biology quickly acquired a leading role in the burst of new scientific ideas (*e.g.*, DNA structure and structure–function correlation in proteins), which demanded the development of advanced molecular models reaching an unprecedented level of understanding in biological systems. In this context, chemistry has certainly profited from the marriage of all these intellectual approaches, providing a starting point for the design and fabrication of new synthetic systems by the combination of molecules with different chemical functionalities, which has undoubtedly revolutionized the nature and number of materials available to modern society.

Traditionally in materials chemistry, reasonable control over the preparation of inorganic solid state materials (*e.g.*, metals, ceramics, amorphous oxides) with macroscopic bulk properties (chemical, structural, thermodynamic, electronic, magnetic, optical, *etc.*) could be imparted by a judicious choice of reactants and synthetic experimental conditions.[1] However, the expected physical limitations that such conventional systems usually encounter in real applications, where advanced and enhanced capabilities and functionalities are demanded, led to the search for new functional composite materials based on the combination of individual components that either amplify or possess new properties unique to the ensemble.[2] Moreover, in many cases, where processability for the transformation of bulk systems into devices is a prerequisite, the modification of these conventional materials has been laborious and usually impractical.[3]

Synthetic chemistry, the covalent assembly of small components into larger molecules, has emerged as a powerful technique for devising novel materials, becoming a natural starting point for the bottom-up fabrication of devices.[4] This approach, used by living systems to build large complex structures from relatively small components (*e.g.*, proteins from amino acids), constitutes one of the most important approaches that currently drives nanotechnology. Therefore, chemists are ideally qualified to study systems not only at the molecular level but also at the nanoscale, where fine control over the structure, size, shape, and assembly of the nanosized building blocks is essential.[5] These molecular nanomaterials are excellent alternatives to conventional bulk materials for device fabrication due to their relatively easy preparation and processability, which

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hinges on the excellent solubility and sublimability of molecular components. For instance, molecules are essential in the preparation of organic–inorganic hybrid materials, where superior and novel properties are obtained, compared with their pure counterparts.[6]

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An area of nanotechnology where this organic–inorganic synergy can be fully exploited is nanoplasmonics, in which the excitation of localized surface plasmon resonances (LSPR) on nanostructures of (typically) coinage metals can be combined with molecular components to obtain molecular plasmonic devices with specific structural and photonic properties.[7] In particular, plasmonic metal nanoparticles offer the advantage of combining the three-dimensional (3D) control of particle size and shape with that of monolayer surface chemistry in metals, rendering them ideal building blocks for nanoarchitecture design.[8] The optical response in metal nanocrystals is strongly sensitive to their immediate environment, and the interaction between adjacent particles leads to a hybridization of the LSPR modes supported by the individual particles.[9] In fact, this hybridization model is based on molecular orbital theory, which has been used for decades to describe molecular structure and interactions, a similarity that explains a number of interesting distance-dependent optical phenomena, not only between nanoparticles but also between LSPRs and electronic transitions in molecules (*e.g.*, refractive index change, plasmonic–molecular resonance coupling, and surface-enhanced spectroscopies).[10]

A direct consequence of the inextricable linkage between the reactivity and optical properties in molecules and metal nanoparticles is the directional organization of nanocrystals as building blocks *via* molecular assembly (*e.g.*, dimers, polymers, and crystals), using the same approaches previously developed for molecules. Therefore, the spatial organization of nanoparticles has been extended to the replication of concepts observed at the molecular scale that unravel as yet unidentified new properties in nanoplasmonics (*e.g.*, plasmonic antiferromagnetism or plasmonic optical activity; see Table 1). In this Perspective, we highlight several molecular mimetic approaches to proceed from plasmonic atoms and molecules to plasmonic polymers and supercrystals with tailored optical properties and directionality. We illustrate this strategy by describing the energy of single nanocrystals, the assembly of functional nano-objects into larger plasmonic structures, and, finally, how the nanoparticles can be integrated within long-range ordered structures (Figure 1). We show how nanocrystals can be designed and organized to achieve properties both in solution and in the liquid crystalline or solid states that are not present in the individual components, with a particular focus on recent developments that have drastically changed the classical view of plasmonic metal nanoparticles.

> In this Perspective, we highlight several molecular mimetic approaches to proceed from plasmonic atoms and molecules to plasmonic polymers and supercrystals with tailored optical properties and directionality.

Plasmonic Atoms and Molecules. A single gold atom comprises six energy levels occupied with electrons that can be excited to higher levels upon absorption of selected electromagnetic radiation with specific energy. These so-called interband transitions originate with absorption of light in the ultraviolet (UV) spectral range (>2.5 eV). In addition, a gold atom can also release energy by emission of light, as well as by light scattering. Light–matter interactions provide specific fingerprints of atoms, which find application mostly in elemental analyses. However, when gold atoms start to agglomerate into clusters consisting of at least 200 units, a new, free-electron system emerges, in which conduction electrons collectively oscillate in the presence of electromagnetic radiation giving rise to LSPRs (intraband-like transitions). This new entity—the plasmonic particle—can interact with electromagnetic radiations in a similar way to atoms (Figure 1), but optical phenomena (absorption, emission, or scattering) emerge in the visible spectral range (<2.6 eV) rather than the UV. While the interaction of light with metallic nanoparticles is determined by the plasmonic response, a compelling analogy exists between LSPRs in metal nanoparticles and wave functions in simple atoms and molecules.[11] Therefore, fundamental similarities between ordinary and "plasmonic" atoms explain why complex plasmonic phenomena are often explained in terms of atomic and molecular physics.

Historically, the LSPR-related bright colors of metal nanoparticles have driven rather aesthetically oriented applications. However,

TABLE 1. Important Related Concepts about the Interaction of Light with Molecules and Plasmonic Nanoparticles and Their Plasmonic Applications

molecular concept	plasmonic concept	plasmonic application	ref
solvatochromism	refractive index change	refractive index sensing	8, 10
electron transfer	hot electron transfer	conductivity, catalysis	12, 13
energy transfer	plasmon resonance energy transfer	SEF, SERS	14, 15, 23, 25, 56
luminescence	multiphoton photoluminescence	light-emitting systems	16
molecular resonance	magnetic plasmon propagation	plasmonic antiferromagnetism	21
chiral exciton coupling	chiral dipole–dipole coupling	plasmonic optical activity	38, 39, 40, 48

current knowledge of plasmonics theory and the effect of nearby molecules on light–particle interactions, optical events on the particles—especially absorption—find wide application in fields such as biosensing and energy conversion. Absorption of light by the particle may produce multiple collisions between the conduction electrons and the crystal lattice (phonons), leading to the formation of highly energetic species, so-called hot electrons/hot holes. It has recently been shown that hot electrons can be freely transferred to the conduction band of a closely located n-type semiconductor, producing electron flow (current)[12] or initiating catalytic reactions.[13] In this context, the plasmonic particles behave like organic dyes that absorb and transfer energy nonresonantly to the environment. On the contrary, plasmon resonance energy transfer (PRET), as an analogous phenomenon to Förster resonance energy transfer (FRET) between donor and acceptor molecules, permits the transfer of energy resonantly from a plasmonic nanostructure to a chemical species. Technically, the plasmon resonance band of the metallic nanoparticle should overlap with the electronic peak position of the absorber. The PRET effect has been used to explain metal-enhanced fluorescence (SEF)[14] and surface-enhanced Raman scattering (SERS).[15] These techniques open up new applications in visible absorption spectroscopy, especially toward *in vivo* cellular and molecular imaging down to the single-molecule detection limit. As flourophores, metal particles can also emit light in the process known as two-photon excitation emission, which arises due to the local electric field associated with the surface plasmon resonance.[16] Such emission has been predicted to improve biomolecular sensing.

To apply nanoplasmonics effectively in biological environments, particles should have sizes below 100 nm, providing maximum light-harvesting properties, and minimal structural hindrance. However, particles larger than 100 nm still provide enormous possibilities in energy conversion. By exploiting light scattering, one can control the flow of electromagnetic energy, which is crucial in photovoltaics or water-splitting devices.[17,18] Conceptually, light is preferentially trapped in the semiconductor film by multiple scattering, causing an increase in the optical path length within the cell, thereby reducing the physical thickness of the solar absorber and increasing its efficiency by 80%.[19] In summary, plasmon-related technological development requires a deep understanding and control over plasmon manipulation, especially on the architecture of single particles.

While single plasmonic particles exhibit similarities to atoms, an analogy also exists between multinanoparticle assemblies (dimers, polymers, crystals) and molecules. On the basis of molecular orbital theory, a plasmon hybridization model has been proposed that predicts how plasmon resonances vary upon clustering of plasmonic particles (Figure 1).[9] The plasmon hybridization model has been a fundamental concept in designing plasmon rulers,[20] in which interparticle distances and plasmon shifts are correlated through a simple mathematical expression. In practical terms, a plasmon ruler allows monitoring single-molecule biophysics (*e.g.*, transformation of macromolecules) even in three dimensions (3D), which may have significant impact on the future understanding of mechanisms behind biological processes. Moreover, the molecular origin of the plasmon hybridization model has facilitated the recent development of magnetic plasmons at optical frequencies (Figure 1).[21] The "plasmonic heptamer" has been used as a benzene analogue building block for the construction of cyclic aromatic structures, in which antiphase coupling gives rise to "plasmonic antiferromagnetic behavior". From an applications standpoint, plasmonic nanostructures with aromatic-like architectures can enhance plasmon propagation and may provide new opportunities for integrated optical devices or waveguides.

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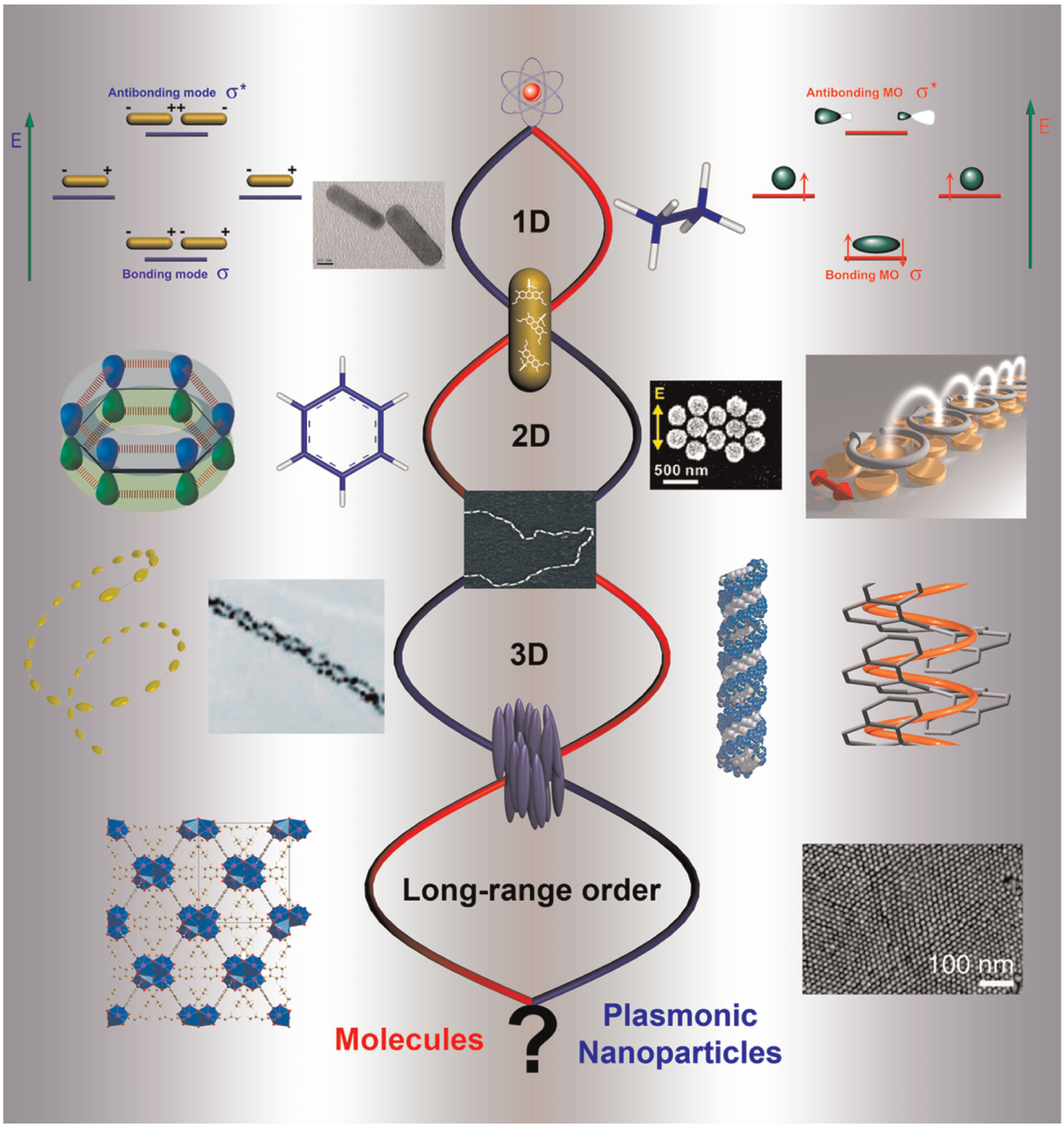

Figure 1. Plasmonic nanostructures based on molecular concepts: red and blue lines respectively show the correlated evolution of molecules and plasmonic nanostructures, from atomic systems with disorder over both short and long distances, into crystals with both long-range and short-range order (following a bottom-up approach). Dimensionality increases as the manifold of specific combinations between molecules and nanocrystals increases, ranging from 1D plasmonic atoms and molecules, through plasmonic polymers with different dimensionalities (1D, 2D, and 3D), and finally 3D plasmonic supercrystals. The cooperative buildup of plasmonic architectures is achieved by the incorporation of molecules into the nanocrystal structures, which is represented by molecular–nanoparticle crossroads: single molecule–nanocrystal units, nanoparticle–nanoparticle polymers, and molecular–plasmonic liquid crystals. On the basis of molecular orbital theory (MO), the plasmon hybridization model is used to predict the plasmon resonance response in "unimolecular" nanoparticles and their covalently and/or self-assembled binuclear and multinuclear derivatives. Using this model, an interesting molecular concept such as aromaticity has been translated into the "plasmonic language" through magnetic plasmon propagation in benzene-like systems. In a further step of organization, mimicking biomacromolecules has led to the design of plasmonic polymers with controlled 3D chiral morphologies and outstanding optical activities. Finally, and perhaps still an open question, metal nanoparticles can be organized in plasmonic liquid and solid crystals to design new functional metamaterials that could eventually be integrated into complex molecular architectures to fabricate macroscopic plasmonic devices.

Plasmonic Polymers. Nanoplasmonics is expanding, along with rapid scientific developments in carbon-based polymer chemistry, due to the exciting possibilities for the preparation of novel materials *via* one- and two-dimensional (1D and 2D) directed assembly of nanocrystals, which mimics the structure of organic macromolecules.[22] The straightforward and specific assembly of the metal nanoparticles serves as a platform for different LSPR and FRET strategies for sensing molecular linkers.[23] Additionally, on the basis of the light confinement between neighboring plasmonic nanoparticles (nanoscale hot spots),[24] these polymer-based plasmonic materials have been used to build SERS sensors[25] and optoelectronic devices.[26]

In this context, plasmonic polymers can be considered as large nanostructures, built up by repetition of smaller nanosized units—metal nanoparticles—mimicking the structures of 1D and 2D molecular polymers and even block copolymers (see Figure 1). The bonding between the building blocks is of significant importance since covalent bonds lead to essentially irreversible linkage of the metal nanocrystals,[27] whereas noncovalent interactions may allow potentially reversible dynamic binding.[28] Typically, the synthesis of nanocrystals involves an initial chemical modification with thiolated molecules at certain regions of their crystallographic facets, followed by additional reactions to promote the binding of the different components. Despite the topological point defects present in metal nanoparticles,[29] spherical nanocrystals lack a geometrical preference toward site-specific functionalization, thus limiting their potential applications to form plasmonic polymers. In contrast, one of the most appealing advantages of metal nanorod scaffolds, as compared with their spherical counterparts, is their versatility toward chemical functionalization. Gold nanorods can be readily functionalized at the tips with, for example, dithiolated molecules of different lengths and flexibilities, building up plasmonic polymers through tip-to-tip irreversible bonds.[30] On the contrary, the molecular self-assembly strategy applied to plasmonic polymers is based on the edge functionalization of gold nanorods by thiolated organic polymers, whose chemical functionalities cooperate under certain experimental conditions (*e.g.*, solvent, temperature), forming reversible bonds at the nanorod–nanorod interface.[31]

Aiming at mimicking biomolecular polymers with increased dimensionality, recent efforts have led to the design of nanomaterials with controlled 3D chiral structures and morphologies.[32] Indeed, chiral plasmonic elements have been explored as promising metamaterial candidates for exotic optical functions such as nonlinear optics[33] or negative refractive index.[34] To achieve this, the concept of plasmonic polymerization has been extended to 3D complex structures with collective chiral organizations, where metal nanoparticles with different compositions, sizes, and shapes can be linked through covalent bonding or chemically/physically adsorbed onto molecular chiral templates (Figure 1). Recent reports have illustrated the promising potential of these chiral metallic nanostructures, which exploit the characteristic LSPR of metal colloids to produce intense optical activities due to significant differences in extinction between left and right circularly polarized light.[35] The origin of plasmonic collective chirality is based on interactions between nanoparticles assembled with 3D chiral order, which has been explained by means of a coupled dipole model, in which each particle is described as an interacting electric dipole, in a direct analogy with chirality in molecular systems.[36]

A remarkable example of a linker molecule that has been used for building chiral nanocrystal assemblies with high degree of control over the design and synthesis is DNA.[37] However, the chemical yields obtained in the production of optically active chiral ensembles *via* biopolymer linkage are still very low due to the formation of nonchiral byproducts, therefore requiring the use of separation and purification processes. As an alternative approach toward plasmonic polymers with amplified optical activity, macromolecular chiral fibers with specific chemical functionalities have been used as templates to adsorb metal nanoparticles.[38] Although spherical nanoparticles can be used, gold nanorods with 3D chiral organization appear to be significantly more efficient plasmonic nanoantennas, achieving intense and tunable optical activity at the visible–near-IR spectral region.[39] The origin of the high optical efficiency in anisotropic particles has been investigated theoretically through an LSPR hybridization model that mimics exciton coupling theory, commonly used in chemistry to explain the circular dichroism response of organic molecules. It turns out that, at high nanoparticle aspect ratios, the scattering contribution to the optical activity dominates over the absorption cross section.[40] In contrast to these near-field phenomena, it has been postulated that the optical rotary dispersion of the chiral surrounding medium may affect the LSPR modes in metal nanoparticles by far-field electromagnetic coupling, which might represent an important contribution to the optical activity of plasmonic polymers to be considered in the future.[41]

Plasmonic Supercrystals. Advances in materials research inarguably rely on thorough understanding of condensed-phase structure and its relationship to condensed-phase properties. In the case of molecular crystals, many studies have reinforced the notion that properties both in the liquid and solid states can be manipulated through careful design and selection of molecular components and have demonstrated that these properties strongly depend on the molecular organization in 3D space. These materials are based on infinite frameworks of molecular building blocks that are held together by weak van der Waals interactions and stronger hydrogen bonds and coordinative interactions. Furthermore, they can be classified into liquid crystals, where a short-range order between molecules is present but some distinct order over larger distances can be observed, and solid crystals, which have both long- and short-range order. Again following these molecular concepts (Figure 1), metal nanoparticles coated with rationally selected organic molecules have been arranged with a certain lattice periodicity to build up liquid crystals[42] and solid crystalline structures,[43] showing interesting collective plasmonic responses.

The use of liquid crystals in nanotechnology relies mainly on the physicochemical synergy between organic molecules and nanoparticles. Various general approaches toward the preparation of plasmonic liquid crystals have been considered so far. In the more usual methodology, presynthesized metal nanoparticles are coated with liquid crystalline compounds as ligands.[44] Alternatively, the nanoparticles can be dispersed in the mesophases by selecting capping agents that are chemically compatible with the surrounding medium.[45] Both approaches lead to high degrees of control over the sizes and shapes of the nanocrystals, and thus over the plasmonic responses of the materials, though significant distortions of the liquid crystalline phases can be induced.[46] In contrast, metal nanoparticles with reasonable monodispersity have been synthesized *in situ* within liquid crystals that preserve their original properties.[47]

Although liquid crystals have found multiple optical applications across different fields of chemistry and physics, few examples exist of the incorporation of metal nanoparticles into mesophases with relevant plasmonic properties. The reason might be related to both the anisotropic structure of liquid crystals at the molecular level, in which molecules with large aspect ratios are employed, and the extensive use of isotropic nanocrystals in the preparation of plasmonic liquid crystals. The stronger plasmonic response of anisotropic nanoparticles in these mesophases has been demonstrated by combination of gold nanorods with cholesteric liquid crystals, in which a chiral organization of the nanoantennas shows intense optical activity,[48] as well as in the preparation of metamaterials based on plasmonic mesophases with switchable polarization-sensitive plasmon resonances.[49] Even though, at this stage, these are just interesting conceptual examples and no devices have been realized with plasmonic liquid crystals, the next step will be the incorporation of such anisotropic metal nanoparticles into liquid crystal displays to manipulate light by particular orientations of the plasmonic material under mechanical, magnetic, or electric forces.

The idea that molecules self-assemble in different fashions as they change from the disordered isotropic liquid state to the rigorously 3D-ordered crystalline phase, passing through intermediate liquid crystalline phases has been explored in the field of plasmonic crystals as well. It has been shown that anisotropic nanocrystal superstructures can result from the formation of nematic and smectic liquid crystalline phases upon solvent evaporation, in which plasmonic nanoparticles are oriented in layers with close-packed hexagonal arrangement due to the self-assembly of amphiphilic capping molecules.[50] At this superior level of organization, the concept of self-assembly applied in crystal engineering and crystal structure prediction with organic molecules has been exploited in the preparation of 3D plasmonic superlattices (Figure 1).[51] In this context, self-assembly refers to the spontaneous organization of metal nanoparticles as discrete components through direct interactions between molecules located at the nanoparticle interfaces.[52] As a representative and enlightening example, DNA has gained popularity as a surface template in the formation of self-assembled colloidal supercrystals, providing fine control over interparticle spacing that can be used to tune the plasmonic properties of the crystal over micrometer length scales.[53] Indeed, the types of crystal structure obtained in these assemblies (*e.g.*, body-centered cubic, face-centered cubic) has been controlled by varying the length and flexibility of the DNA strands.[54]

Such facile and specific assembly of nanocrystals has served as a platform for building macroscopic systems with applications in plasmonic sensing, through colloidal synthesis of metal nanoparticles with tailored morphology and surface chemistry, followed by self-assembly into electrical and optical sensors.[55] For example, the fabrication of plasmonic crystals with high optical activity has recently exploited enhanced electric field concentration and nanoantenna effects to maximize the SERS signal at ultralow concentrations of biorelevant analytes.[56]

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OUTLOOK

The discussion so far has evidenced the recent evolution of nanoplasmonics hand-in-hand with concepts that have traditionally been used by chemists for the design and construction of novel materials. Although outstanding advances have been achieved extremely quickly, open questions remain regarding properties that are still to be discovered, mainly related to cooperative effects when metal nanoparticles are organized into perfectly defined 3D crystalline structures. Interestingly, the number of studies with real applications in nanoplasmonics decreases when the complexity and dimensionality of the plasmonic system increases from plasmonic atoms and molecules to supercrystals. For example, fundamental studies are required to determine the conditions required for the construction of supercrystals with a controlled number of monolayers or with tailored interparticle distances. In a way, this is again related to chemical concepts, such as phase diagrams, which have long been used in colloid science, even in a retroactive manner, since atomic and molecular theory has been strongly supported by studies of colloidal systems.[57] Additionally, recent demonstrations of the ability to build exotic crystalline lattices in binary supercrystals[58] suggests that we shall soon see a new burst of novel nanoplasmonic effects based on molecular concepts.

Conflict of Interest: The authors declare no competing financial interest.

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REFERENCES AND NOTES

1. Stein, A.; Keller, S. W.; Mallouk, T. E. Turning Down the Heat: Design and Mechanism in Solid-State Synthesis. *Science* **1993**, *259*, 1558–1564.
2. Ronald, F. G. A Review of Recent Research on Mechanics of Multifunctional Composite Materials and Structures. *Compos. Struct.* **2010**, *92*, 2793–2810.
3. Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Willson, C. G.; Whitesides, G. M. New Approaches to Nanofabrication: Molding, Printing, and Other Techniques. *Chem. Rev.* **2005**, *105*, 1171–1196.
4. Balzani, V.; Credi, A.; Venturi, M. The Bottom-Up Approach to Molecular-Level Devices and Machines. *Chem.—Eur. J.* **2002**, *8*, 5524–5532.
5. Whitesides, G. M. Nanoscience, Nanotechnology, and Chemistry. *Small* **2005**, *1*, 172–179.
6. Sanchez, C.; Julián, B.; Belleville, P.; Popall, M. Applications of Hybrid Organic−Inorganic Nanocomposites. *J. Mater. Chem.* **2005**, *15*, 3559–3592.
7. Van Duyne, P. R. Molecular Plasmonics. *Science* **2004**, *306*, 985–986.
8. Liz-Marzán, L. M. Nanometals: Formation and Color. *Mater. Today* **2004**, *7*, 26–31.
9. Prodan, E.; Radloff, C.; Halas, N. J.; Nordlander, P. A. Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science* **2003**, *302*, 419–422.
10. Chen, H.; Ming, T.; Zhao, L.; Wang, F.; Sun, L.-D.; Wang, J.; Yan, C.-H. Plasmon−Molecule Interactions. *Nano Today* **2010**, *5*, 494–505.
11. Klimov, V. V.; Guzatov, D. V. Plasmonic Atoms and Plasmonic Molecules. *Appl. Phys. A: Mater. Sci. Process.* **2007**, *89*, 305–314.
12. Knight, M. W.; Sobhani, H.; Nordlander, P.; Halas, N. J. Photodetection with Active Optical Antennas. *Science* **2011**, *332*, 702–704.
13. Christopher, P.; Xin, H.; Linic, S. Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nat. Chem.* **2011**, *3*, 467–472.
14. Lakowicz, J. R.; Ray, K.; Chowdhury, M.; Szmacinski, H.; Fu, Y.; Zhang, J.; Nowaczyk, K. Plasmon-Controlled Fluorescence: A New Paradigm in Fluorescence Spectroscopy. *Analyst* **2008**, *133*, 1308–1346.
15. Nie, S.; Emory, S. R. Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering. *Science* **1997**, *275*, 1102–1106.
16. Huang, J.-S.; Kern, J.; Geisler, P.; Weinmann, P.; Kamp, M.; Forchel, A.; Biagioni, P.; Hecht, B. Mode Imaging and Selection in Strongly Coupled Nanoantennas. *Nano Lett.* **2010**, *10*, 2105–2110.
17. Atwater, H. A.; Polman, A. Plasmonics for Improved Photovoltaic Devices. *Nat. Mater.* **2010**, *9*, 205–213.
18. Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat. Mater.* **2011**, *10*, 911–921.
19. Warren, S. C.; Thimsen, E. Plasmonic Solar Water Splitting. *Energy Environ. Sci.* **2012**, *5*, 5133–5146.
20. Reinhard, B. M.; Siu, M.; Agarwal, H.; Alivisatos, A. P.; Liphardt, J. Calibration of Dynamic Molecular Rulers Based on Plasmon Coupling between Gold Nanoparticles. *Nano Lett.* **2005**, *5*, 2246–2252.
21. Liu, N.; Mukherjee, S.; Bao, K.; Brown, L. V.; Dorfmüller, J.; Nordlander, P.; Halas, N. J. Magnetic Plasmon Formation and Propagation in Artificial Aromatic Molecules. *Nano Lett.* **2011**, *12*, 364–369.
22. Nie, Z.; Petukhova, A.; Kumacheva, E. Properties and Emerging Applications of Self-Assembled Structures Made from Inorganic Nanoparticles. *Nat. Nanotechnol.* **2010**, *5*, 15–25.
23. Xu, L.; Kuang, H.; Wang, L.; Xu, C. Gold Nanorod Ensembles as Artificial Molecules for Applications in Sensors. *J. Mater. Chem.* **2011**, *21*, 16759–16782.
24. Alvarez-Puebla, R.; Liz-Marzán, L. M.; García de Abajo, F. J. Light Concentration at the Nanometer Scale. *J. Phys. Chem. Lett.* **2010**, *1*, 2428–2434.
25. Lee, A.; Andrade, G. F. S.; Ahmed, A.; Souza, M. L.; Coombs, N.; Tumarkin, E.; Liu, K.; Gordon, R.; Brolo, A. G.; Kumacheva, E. Probing Dynamic Generation of Hot-Spots in Self-Assembled Chains of Gold Nanorods by Surface-Enhanced Raman Scattering. *J. Am. Chem. Soc.* **2011**, *133*, 7563–7570.
26. Choulis, S. A.; Mathai, M. K.; Choong, V.-E. Influence of Metallic Nanoparticles on the Performance of Organic Electrophosphorescence Devices. *Appl. Phys. Lett.* **2006**, *88*, 213503(1−3).
27. Shibu Joseph, S. T.; Ipe, B. I.; Pramod, P.; Thomas, K. G. Gold Nanorods to Nanochains: Mechanistic Investigations on Their Longitudinal Assembly Using α,ω-Alkanedithiols and Interplasmon Coupling. *J. Phys. Chem. B* **2005**, *110*, 150–157.
28. Nie, Z.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. Self-Assembly of Metal-Polymer Analogues of Amphiphilic Triblock Copolymers. *Nat. Mater.* **2007**, *6*, 609–614.
29. DeVries, G. A.; Talley, F. R.; Carney, R. P.; Stellacci, F. Thermodynamic Study of the Reactivity of the Two Topological Point Defects Present in Mixed Self-Assembled Monolayers on Gold Nanoparticles. *Adv. Mater.* **2008**, *20*, 4243–4247.
30. Pramod, P.; Thomas, K. G. Plasmon Coupling in Dimers of Au Nanorods. *Adv. Mater.* **2008**, *20*, 4300–4305.
31. Fava, D.; Nie, Z.; Winnik, M. A. Kumacheva, E. Evolution of Self-Assembled Structures of Polymer-Terminated Gold Nanorods in Selective Solvents. *Adv. Mater.* **2008**, *20*, 4318–4322.
32. Gibaud, T.; Barry, E.; Zakhary, M. J.; Henglin, M.; Ward, A.; Yang, Y.; Berciu, C.; Oldenbourg, R.; Hagan, M. F.; Nicastro, D.; *et al.* Reconfigurable Self-Assembly through Chiral Control of Interfacial Tension. *Nature* **2012**, 10.1038/nature10769.
33. Gubler, U.; Bosshard, C. Optical Materials: A New Twist for Nonlinear Optics. *Nat. Mater.* **2002**, *1*, 209–210.
34. Pendry, J. B. A Chiral Route to Negative Refraction. *Science* **2004**, *306*, 1353–1355.
35. Guerrero-Martínez, A.; Alonso-Gómez, J. L.; Auguié, B.; Cid, M. M.; Liz-Marzán, L. M. From Individual to Collective Chirality in Metal Nanoparticles. *Nano Today* **2011**, *6*, 381–400.
36. Govorov, A. O.; Gun'ko, Y. K.; Slocik, J. M.; Gérard, V. A.; Fan, Z.; Naik, R. R. Chiral Nanoparticle Assemblies: Circular Dichroism, Plasmonic Interactions, and Exciton Effects. *J. Mater. Chem.* **2011**, *21*, 16806–16818.
37. Chen, W.; Bian, A.; Agarwal, A.; Liu, L.; Shen, H.; Wang, L.; Xu, C.; Kotov, N. A. Nanoparticle Superstructures Made by Polymerase Chain Reaction: Collective Interactions of Nanoparticles and a New Principle for Chiral Materials. *Nano Lett.* **2009**, *9*, 2153–2159.
38. Kuzyk, A.; Schreiber, R.; Fan, Z.; Pardatscher, G.; Rolle, E.-M.; Högele, A.; Simmel, F. C.; Govorov, A. O.; Liedl, T. DNA-Based Self-Assembly of Chiral Plasmonic Nanostructures with Tailored Optical Response. *Nature* **2012**, *483*, 311–314.
39. Guerrero-Martínez, A.; Augié, B.; Alonso-Gómez, J. L.; Džolić, Z.; Gómez-Graña, S.; Žinić, M.; Cid, M. M.; Liz-Marzán, L. M. Intense Optical

Activity from Three-Dimensional Chiral Ordering of Plasmonic Nanoantennas. *Angew. Chem., Int. Ed.* **2011**, *50*, 5499–5503.

40. Auguié, B.; Alonso-Gómez, J. L.; Guerrero-Martínez, A.; Liz-Marzán, L. M. Fingers Crossed: Optical Activity of a Chiral Dimer of Plasmonic Nanorods. *J. Phys. Chem. Lett.* **2011**, *2*, 846–851.
41. Abdulrahman, N. A.; Fan, Z.; Tonooka, T.; Kelly, S. M.; Gadegaard, N.; Hendry, E.; Govorov, A. O.; Kadodwala, M. Induced Chirality through Electromagnetic Coupling between Chiral Molecular Layers and Plasmonic Nanostructures. *Nano Lett.* **2012**, *12*, 977–983.
42. Bisoyi, H. K.; Kumar, S. Liquid-Crystal Nanoscience: An Emerging Avenue of Soft Self-Assembly. *Chem. Soc. Rev.* **2010**, *40*, 306–319.
43. Nykypanchuk, D.; Maye, M. M.; Lelie, D.; van der; Gang, O. DNA-Guided Crystallization of Colloidal Nanoparticles. *Nature* **2008**, *451*, 549–552.
44. In, I.; Jun, Y.-W.; Kim, Y. J.; Kim, S. Y. Spontaneous One-Dimensional Arrangement of Spherical Au Nanoparticles with Liquid Crystal Ligands. *Chem. Commun.* **2005**, 800–801.
45. Gardner, D. F.; Evans, J. S.; Smalyukh, I. I. Towards Reconfigurable Optical Metamaterials: Colloidal Nanoparticle Self-Assembly and Self-Alignment in Liquid Crystals. *Mol. Cryst. Liq. Cryst.* **2011**, *545*, 3/[1227]–21/[1245].
46. Wojcik, M. M.; Gora, M.; Mieczkowski, J.; Romiszewski, J.; Gorecka, E. Pociecha, D. Temperature-Controlled Liquid Crystalline Polymorphism of Gold Nanoparticles. *Soft Matter* **2011**, *7*, 10561–10564.
47. Mallia, V. A.; Vemula, P. K.; John, G.; Kumar, A.; Ajayan, P. M. *In Situ* Synthesis and Assembly of Gold Nanoparticles Embedded in Glass-Forming Liquid Crystals. *Angew. Chem., Int. Ed.* **2007**, *46*, 3269–3274.
48. Wang, R.-Y.; Wang, H.; Wu, X.; Ji, Y.; Wang, P.; Qu, Y.; Chung, T.-S. Chiral Assembly of Gold Nanorods with Collective Plasmonic Circular Dichroism Response. *Soft Matter* **2011**, *7*, 8370–8375.
49. Liu, Q.; Cui, Y.; Gardner, D.; Li, X.; He, S.; Smalyukh, I. I. Self-Alignment of Plasmonic Gold Nanorods in Reconfigurable Anisotropic Fluids for Tunable Bulk Metamaterial Applications. *Nano Lett.* **2010**, *10*, 1347–1353.
50. Guerrero-Martínez, A.; Pérez-Juste, J.; Carbó-Argibay, E.; Tardajos, G.; Liz-Marzán, L. M. Gemini Surfactant-Directed Self-Assembly of Monodisperse Gold Nanorods into Standing Superlattices. *Angew. Chem., Int. Ed.* **2009**, *48*, 9484–9488.
51. Kowalczyk, B.; Walker, D. A.; Soh, S.; Grzybowski, B. A. Nanoparticle Supracrystals and Layered Supracrystals as Chemical Amplifiers. *Angew. Chem., Int. Ed.* **2010**, *49*, 5737–5741.
52. Grzelczak, M.; Vermant, J.; Furst, E. M.; Liz-Marzán, L. M. Directed Self-Assembly of Nanoparticles. *ACS Nano* **2010**, *4*, 3591–3605.
53. Cheng, W.; Campolongo, M. J.; Cha, J. J.; Tan, S. J.; Umbach, C. C.; Muller, D. A.; Luo, D. Free-Standing Nanoparticle Superlattice Sheets Controlled by DNA. *Nat. Mater.* **2009**, *8*, 519–525.
54. Jones, M. R.; Macfarlane, R. J.; Lee, B.; Zhang, J.; Young, K. L.; Senesi, A. J.; Mirkin, C. A. DNA-Nanoparticle Superlattices Formed from Anisotropic Building Blocks. *Nat. Mater.* **2010**, *9*, 913–917.
55. Liu, S.; Tang, Z. Nanoparticle Assemblies for Biological and Chemical Sensing. *J. Mater. Chem.* **2010**, *20*, 24–35.
56. Alvarez-Puebla, R. A.; Agarwal, A.; Manna, P.; Khanal, B. P.; Aldeanueva-Potel, P.; Carbó-Argibay, E.; Pazos-Pérez, N.; Vigderman, L.; Zubarev, E. R.; Kotov, N. A.; *et al.* Gold Nanorods 3D-Supercrystals as Surface Enhanced Raman Scattering Spectroscopy Substrates for the Rapid Detection of Scrambled Prions. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 8157–8161.
57. Antonietti, M.; Göltner, C. Superstructures of Functional Colloids: Chemistry on the Nanometer Scale. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 910–928.
58. Schevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. Structural Diversity in Binary Nanoparticle Superlattices. *Nature* **2006**, *439*, 55–59.