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Preface

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This is a special *Coord. Chem. Rev.* issue entitled "Functional Hybrid Nanomaterials: Design, Synthesis, Structure, Properties, and Applications". The choice of this particular topic is obvious: functional nanomaterials are the bricks and mortars of nanotechnology! In fact, for the first time in human history, man can now change the fundamental properties of matter, tailor make materials with desirable attributes, and fabricate functional devices of any dimension.

A functional material may be defined as a material that performs a particular function/response upon stimulation/excitation. No doubt we are at the dawn of an unprecedented scientific and technological revolution. The design and synthesis of functional nanomaterials, and systematic studies of their structures and properties, are prerequisites to the fabrication and manufacturing of nanodevices of great importance in nanotechnology and in many practical applications. The hybrid nanomaterials, in particular, take advantage of the superior, often complementary and synergistic, qualities of different types of materials (organic, inorganic, organometallic, polymeric, etc.). It is currently an important area of materials research and technology. That is why we think it would be useful and beneficial to publish a special issue on this particular topic.

It is hoped that this particular special issue will provide an overview of the current state-of-the-art development of the subject. As stated many times over by the authors of the articles included in this issue, "the name of the game" in this field is to provide composition and structural control of the resulting hybrid nanomaterials or composites, thereby allowing tuning and optimization of their electronic, chemical, physical, or biological properties for a particular application.

This thematic issue has 15 invited reviews, each authored by leaders in the respective fields. They cover a wide variety of topics dealing with the syntheses and fabrication of hybrid nanomaterials, their unique and interesting properties, and possible applications in nanotechnology. The materials discussed include two-dimensional (2D) surface assembly, three-dimensional (3D) crystals such as metal-organic frameworks (MOFs), polyoxometalates (POMs), nanomaterials such as nanodots, nanowires and nanotubes, nanocomposites, and many others. Their structures may range from discrete clusters to extended frameworks and may contain 1, 2, or 3D frameworks, core–shell or layer-by-layer architectures. The bonding may involve metal coordination, ionic, covalent, dative bond formation, weak hydrogen-bond or π–π interactions. These functional hybrid or composite nanomaterials exhibit a broad range of interesting properties such as catalytic, electronic, optical, electrical, magnetic, spintronic, ferroelectric, thermal, and mechanical. The potential applications discussed are hydrogen and methane storage, selective gas adsorption, catalysis, sensors, membranes, drug storage and delivery, batteries, energy storage and conversion, to name just a few. The articles are highlighted below:

In "Two-dimensional Molecular Porous Networks Constructed by Surface Assembling," Wu and co-workers present an up-to-date account of various two-dimensional molecular porous networks that possess periodically arranged voids of different symmetries. As the void size, as well as the separation between the pores, may be stepwise tuned, the voids could host guest molecules or serve as cavities for chemical reactions. Various strategies utilized to tune weak non-covalent inter-molecular interactions such as van der Waals force, dipole–dipole interaction, hydrogen-bond and metal-ligand coordination are described. The controllability, tunability, stability, and potential applications of these molecular porous networks are discussed.

In "Potential Applications of Metal-Organic Frameworks", Zhou and co-workers first give a general review of structure and synthesis of metal-organic frameworks (MOFs), followed by a discussion of various possible applications of MOFs such as hydrogen and methane storage, selective gas adsorption, catalysis, magnetic properties, luminescence, sensors, as well as drug storage and delivery.

In "Molecular Engineering for Synthesizing Novel Structures of Metal-organic Frameworks and their Potential Applications," Qiu and Zhu review MOFs that are constructed from metal ions or metal ion clusters and bridging organic linkers and their potential applications. Specifically, chiral MOFs, MOFs with zeolite topology, Mesoporous MOFs, MOF membranes, and MOFs constructed from clusters and rare earths are described. Three strategies for synthesizing high-porosity MOFs are discussed. Potential applications include hydrogen and methane storage, molecular separation, catalysis, and sensor.

In "Ferroelectric Metal-Organic Coordination Compounds (MOCCs)," Zhang, Ye, and Xiong present a review of recent works on the synthesis and design of noncentrosymmetric or homochiral metal-organic coordination compounds or polymer (MOCCs or MOCPs) which belongs to one of ten polar point groups with potential ferroelectric properties. By using homochiral organic ligands as building blocks, a series of ferroelectric MOCCs (or MOCPs) has been synthesized via crystal engineering strategy. Their structure, function, and potential applications are discussed.

In "Structures and Properties of Hybrid Heavy Main-group Iodometalates (M = Bi or Pb)," Wu, Wu and Chen review the struc-

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tural features of iodoplumbates and iodobismuthates in terms of the aggregation and connections of the primary MI_6 octahedral unit. The cation effect, ligand effect and hetero metal-iodine bonding effect are summarized. Interesting optical, thermal and ferroelectric properties are discussed.

In "Magnetic Lanthanide Transition Metal Organic–Inorganic Hybrid Materials: from Discrete Clusters to Extended Frameworks," Huang, Jiang, and Hong review the structures and magnetic properties of lanthanide–transition–metal hybrid materials. These compounds are categorized based on the structure features and organic ligands used.

In "Construction of Host–Guest Hybrid Composites Based on Polyoxometalate Supramolecular Assembly," Lu and co-workers provide a review on polyoxometalates (POMs), a large family of metal-oxygen clusters of the early transition metals in high oxidation states. POMs are capable of directing supramolecular assembly via cation-anion interaction or hydrogen-bonding interactions. POMs can be used as anionic templates to build 1, 2, and 3D metal organic framework or core–shell type nanoclusters. A series of host–guest composites based on the supramolecular interaction between POMs and cationic organometallic fragments, as well as their properties and applications, are discussed.

In "Synthesis of Multifunctional Multiferroic Materials from Organometallics," Takoudis, Singh, and Yang review recent developments in the synthesis of multiferroic materials from organometallics via metalorganic chemical vapor deposition (MOCVD) and chemical solution deposition (CSD). Recent efforts on fabrication of single-phase multiferroics and improvements in properties of single-phase materials through doping/substitution using MOCVD and CSD are reviewed. Single-phase multiferroics have weak coupling between ferroic properties. Heterostructures are more promising for device applications since the coupling in such structures is much stronger. They also offer tailorabilities in composition, microstructure and orientation for optimized the coupling.

In "Optical Property and Functionality of Hybrid Semiconducting Nanomaterials," Li and Zhang provide an overview of the optical and electronic properties of hybrid semiconductor nanomaterials (including doped, composite, and complex structures) and their potential applications in different fields.

In "Theoretical Calculations of Structures and Properties of One-dimensional Silicon-based Nanomaterials: Particularities and Peculiarities of Silicon and Silicon-containing Nanowires and Nanotubes," Teo, Huang, Zhang, and Li review the recent theoretical calculations of the structures and properties (including mechanical, optical, electrical, and magnetic) of silicon-based nanowires and nanotubes, with special emphasis on the particularities and peculiarities of silicon and silicon carbide nanowires and nanotubes. These calculations allow not only rationalization of the observed experimental results, but also predictions of yet-unknown nanostructures and their properties.

In "Amorphous Silica Nanoparticle based Hybrid for Trace Analysis," Zhao and co-workers provide a review on silica-based hybrid nanomaterials composed of amorphous silica nanoparticles and a functional component. The functional component can be a molecule or another type of nanomaterial. In this review, the authors describe several types of silica nanohybrids. The functional components include regular fluorophores, chemiluminescent molecules, drug molecules, quantum dots, gold nanomaterials, magnetic nanoparticles and nanocatalysts. The synthetic strategies, properties and potential applications are discussed.

In "Design and Modeling of Transition Metal-doped Carbon Nanostructures," Stoyanov, Titov, and Kral describe theoretical calculations of carbon nanostructures substitutionally doped with transition metal atoms, providing tunable chemical reactivity and electronic properties with potential applications in molecular electronics, catalysis, light-harvesting and nanomechanics, etc.

In "Atomic Detail Observation of Adsorbed Molecules and Metal Clusters on Carbon Nanotube Electron Emitters," Saito provides a review on the molecular images and dynamics of adsorbates on carbon nanotube (CNT) electron emitters revealed by field emission microscopy (FEM). Molecular shapes of species such as simple gaseous molecules (e.g. hydrogen, nitrogen, carbon dioxide, and methane) and complex molecules (e.g. aluminum clusters) adsorbed on CNTs can be observed.

In "Functional Materials for Energy Storage & Conversion with High Efficiency," Chen and Peng discuss the role of functional materials in energy storage and conversion systems such as batteries, fuel cells, and solar cells. In particular, the design, structure and properties of the functional materials in the applications of aqueous $H_2(H)/H^+$, non-aqueous Li/Li^+, non-aqueous Mg/Mg^{2+}, and photon to electron systems are reviewed.

In "Polymer/Clay and Polymer/Carbon Nanotube Hybrid Organic–Inorganic Composites Made by Sequential Layering of Nanometer Scale Films," Podsiadlo, Shim, and Kotov review the Layer-by-layer assembly (LBL) technique for the design and manufacturing of a wide variety of composite materials based on sequential adsorption of nanometer scale layers of polymers and inorganic colloids. The LBL method provides composition and structural control to the resulting hybrid composites, thereby allowing tuning and optimization of their properties.

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