The Beauty of Chemical Complexity – From Simple Discrete Metal-Ligand Motifs to the Harnessing of Hierarchical Supramolecular Assembly, Nanostructures, Morphologies and Beyond

Vivian Wing-Wah Yam

Department of Chemistry, The University of Hong Kong,
Pokfulam Road, Hong Kong, PR China

Chemical complexity has played a pivotal role in our daily lives, all the way from biology to our materials world. In particular, supramolecular chemistry – chemistry beyond the molecule – has revolutionized our understanding of how molecules would fold, organize, pack, and align themselves and interact with each other through intra- and intermolecular non-covalent interactions to achieve the desired biological functions and materials properties. So far, the supramolecular assembly of molecules for the construction of well-defined morphologies and architectures mostly involves non-covalent interactions like electrostatic, hydrophobic, hydrogen bonding, halogen bonding, π-π stacking, etc. By incorporating metal centers, especially those of d^8 electronic configuration, such as Pt(II), Pd(II), Ni(II) and Rh(I), adopting a low-dimensional square-planar geometry, and closed-shell d^{10} electronic configuration, such as Au(I), Ag(I), Cu(I), Pt(0) and Pd(0), adopting a linear or trigonal planar geometry, non-covalent metal-metal interactions can become possible. Interestingly, these non-covalent metal-metal interactions are directional, and have the potential to lead to anisotropic optical and electronic properties. The most well-known examples include Pt(II) and Au(I); the latter is also referred to as aurophilicity. Most of them are prevalent in the solid state, and are not so readily observable in solution, except for binuclear and trinuclear complexes that are designed to deliberately pre-organize the metal centers, holding them close in proximity through bridging ligands. More recently, strategies to enhance the solubility of square-planar d^8 metal complexes in solution and to manipulate solvation properties have led to observation of non-covalent metal-metal interactions in solution [1]. In particular, square-planar Pt(II), Pd(II) and Rh(I) favor self-association by directional non-covalent metal-metal interactions to form highly organized supramolecular self-assembled nanostructures. Through judicious ligand design and maintaining a delicate balance among different non-covalent interactions, metal complexes with tunable and controllable morphological properties can be realized. To date, several classes of square-planar transition metal complexes have been reported to show a wide range of self-assembled nanostructures, ranging from spherical nanostructures to one-dimensional (1D) nanofibers, nanorods, nanotubes, to two-dimensional (2D) nano-rings and honeycomb-like networks to three-dimensional

(3D) hexagonal columnar assemblies, and even supramolecular tessellations by taking advantage of phase separation strategies [2]. Sophisticated complex supramolecular architectures like hexagonal bipyramids have also been constructed from self-assembly of a judiciously designed geometrically simple dinuclear platinum(II) terpyridine complex (Pt_2) via a bottom-up approach, with the complex molecules undergoing sequential self-assembly via $Pt\cdots Pt$, π-π stacking and hydrophobic interactions of trimeric Pt_2 units, that involves formation of primary crystalline nanorod-like particles, followed by oriented attachment to form pseudo-hexagonal intermediates and eventually self-repair to give highly symmetric hexagonal bipyramids, representing a novel example of nonclassical crystallization growth mechanism in supramolecular self-assembly [3]. Beyond nanostructure and morphology control, non-covalent metal-metal interactions can also lead to intriguing spectroscopic and luminescence properties that can be used to inform assembly-disassembly processes, host-guest binding, as well as conformation, structure and morphology changes associated with microenvironment changes, which can be correlated with structure-photophysical property relationships. An interesting example involves the controlled interconversion of an amphiphilic platinum(II) complex from spherical nanostructures that appear as magenta-colored solution in water to nanorods that appear as blue-colored solution in high acetone-water content, with their morphologies and colors well-correlated with the nature of the non-covalent interactions involved in the driving of the assembly and the corresponding tightness of the metal-metal interactions (Fig. 1) [4,5].

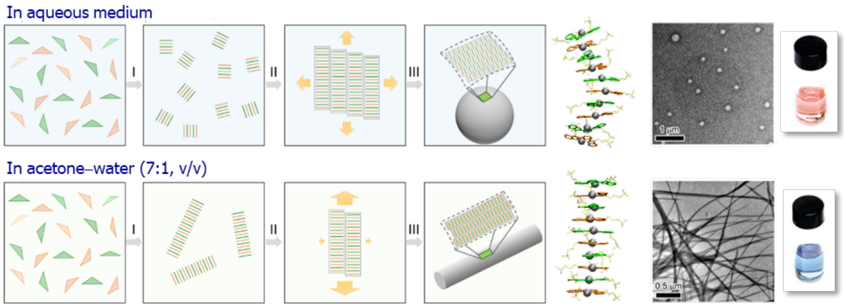

Fig. 1. Schematic diagram for the self-assembly of the platinum(II) complex at different solvent conditions.

However, there are still major challenges in the precise construction of self-assembled heterostructures and nanostructures with segmented architectures. Although strategies like living supramolecular polymerization can achieve assemblies with well-defined dimensions and diverse architectures, the formation of segmented architectures that contain heterojunctions with a large lattice mismatch between the structurally different supramolecular monomers remains challenging. Furthermore, molecular p-n heterojunction structures that contain electron donor-acceptor contacts, represents another important challenge for development of organic electronic devices. Thus there is a strong need for developing new and simple strategies for the fabrication of nanostructures and heterostructures by self-assembly and co-assembly.

Considering a two-component system consisting of platinum(II) complexes and the block copolymer poly(ethylene glycol)-*b*-poly(acrylic acid) (PEG-*b*-PAA), their supramolecular co-assembly facilitated by metal-metal, π-π stacking, and electrostatic interactions can lead to the formation of supramolecular polymers (SPs) with 1D crystalline nanostructures. The anionic PAA block interacts with the cationic platinum(II) complexes to neutralize the charge, and trigger the stacking of platinum(II) complexes to form 1D crystalline core-shell nanofibers by metal-metal and π-π interactions, while the PEG block aids the solvation of the entire system in aqueous media and modulates the transverse growth of the 1D platinum(II) assemblies. Preparation of 1D nanostructures with precise dimensions and compositions can be achieved by variation of the molecular structures, structural parameters of the block copolymers and complex/polymer feed ratios. Sonication of the co-assemblies leads to mechanical defects, as well as removal of part of the PEG-*b*-PAA chains that are non-covalently connected to precursor nanofibers to form short patchy nanofibers with both side and end patches, followed by transverse and longitudinal self-assembly to form core-shell nanobelts [6]. Longitudinal growth of the platinum(II) complex-PEG-*b*-PAA co-assemblies can also be controlled by one-pot living supramolecular polymerization. Addition of a structurally dissimilar platinum(II) complex unimer to the SPs comprising another platinum(II) unimer and PEG-*b*-PAA leads to formation of unique nanorod-*block*-nanobelt nanostructured heterojunctions. The PAA block serves as adapters for the lattice mismatch between the nanorods and nanobelts from different complex unimers, while metal-metal and π-π stacking interactions are responsible for the living growth of the nanobelt along the longitudinal direction, leading to heterojunctions with a lattice mismatch as large as 21% [7]. To provide an in-depth insight into the factors that determine the formation of different morphologies, it is essential to establish an energy landscape to improve the fundamental understanding of both the thermodynamic and kinetic aspects in the co-assembly process. The rational selection of kinetic pathways by modulation of the kinetic barriers has shown interesting temporal properties in the morphological transformations of metastable assemblies, allowing the construction of highly complex SPs with well-defined dimensions, narrow size distributions and diverse architectures that cannot be achieved in conventional methods that only consider the thermodynamic aspect. In the case of co-assembly of block copolymers and platinum(II) complexes, it has been found that the core-shell nanobelts are the thermodynamic products, while core-shell nanofibers are kinetically trapped nanostructures with various kinds of treatments including thermal annealing, rapid quenching or sonication to fabricate distinct nanostructures [8].

More recently, a novel two-step approach for fabrication of segmented nanostructures with unique topologies, packing density and composition has been developed. Crystalline SPs of the positively charged organometallic complex are first prepared in aqueous media, followed by electrostatic interaction with the negatively charged PEG-*b*-PAA to initiate dynamic structure reconfiguration *in situ* to result in high-order nanostructures with distinct components. Different from the direct co-assembly of the complexes in monomeric form with PEG-*b*-PAA where flexible 1D nanofibers or nanoribbons are formed, this two-step co-assembly strategy enables the fabrication of multi-dimensional topological nanostructures. By changing the molecular structure of complexes and block copolymers, feed ratios and kinetics, different kinds of loop-shaped morphologies are obtained, driven by noncovalent metal-metal, π-π stacking and hydrophobic interactions. Modulation of kinetics in the structural reconfiguration process results in rational fabrication of heterostructures consisting of both rigid and flexible segments with unprecedented topologies and architectures, such as rod-loop, tri-, penta-, hepta- and multi-segmented block heterostructures with spatially distinct features (Fig. 2) [9]. These supramolecular co-assembled heterostructures can be further enriched by regulating the position and activity of the defect sites and the dimensions of the SPs through sonication and/or thermal annealing treatments. Furthermore, SPs formed from palladium(II) complexes are more susceptible to electrostatic co-assembly with PEG-*b*-PAA at their defect sites than the platinum(II) counterparts, attributed to the less tight Pd···Pd interactions than Pt···Pt interactions, as well as the higher lability of Pd^{II} than Pt^{II}. Such a co-assembly strategy provides a foundation for realizing the interplay of various intermolecular interactions and enabling heterojunction-related photonic and chemical applications by multi-component assemblies with spatially distinct features [10].

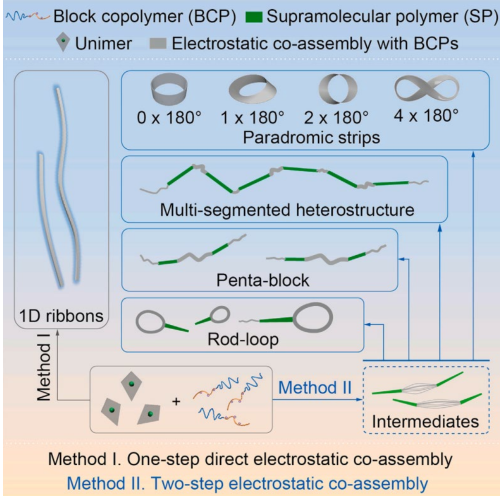

Fig. 2. Programmable fabrication of a library of uncommon multi-dimensional topological nanostructures.

Research on the supramolecular assembly of single-component and multi-component systems have emerged as an important field in supramolecular chemistry and materials science. Directional metal-metal interactions can play a major role in dictating the complex supramolecular nanostructures and morphologies; the nature and tightness of which can be inferred by the resultant photophysical properties. Thus an in-depth understanding of the interplay of various non-covalent interactions, especially the tunable strength of the metal-metal interactions aided by ligand-ligand dispersion forces and the wide range of metal centers and ligands that can be involved, with a fine control of their competitive and cooperative forces, will play crucial roles in governing their assembly processes and hierarchical nanostructures as well as their photophysical properties; the latter of which can lead to tunable excited state properties for photoluminescence, photoresponse and photoreactivities relevant for optoelectronics, sensing and photocatalytic activities. The assembly mechanisms of the supramolecular system should be elucidated to further advance the field, which requires considerations on both the thermodynamics and kinetics of the assembly processes and extension into out-of-equilibrium systems. It is envisaged that breakthroughs in development of processing methods and strategies for preparation of supramolecular nanostructures and heterostructures with high selectivity and specificity will provide important insights and bring substantial impact to the fabrication of organic heterojunction semiconductors. This will also foster the development of optical, catalytic, sensing, electrical, & optoelectronic devices based on multi-block co-assemblies with spatially distinct features.

Acknowledgments

V.W.-W.Y. acknowledges support from the General Research Fund (HKU 17311224) and Collaborative Research Fund (C7075-21GF) of the Research Grants Council of Hong Kong SAR, PR China, and the ITC to the State Key Laboratory of Synthetic Chemistry.

References

1. M. H.-Y. Chan, V. W.-W. Yam, *J. Am. Chem. Soc.* **144**, 22805 (2022).
2. J. K.-L. Poon, S. Y.-L. Leung, M.-Y. Leung, V. W.-W. Yam, *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2022829118 (2021).
3. H.-Z. Wang, M. H.-Y. Chan, Z. Chen, Z.-Y. Chen, M.-Y. Leung, *et al.*, *Chem* **9**, 3573 (2023).
4. C. Po, A. Y.-Y. Tam, K. M.-C. Wong, V. W.-W. Yam, *J. Am. Chem. Soc.* **133**, 12136 (2011).
5. X. Zheng, M. H.-Y. Chan, A. K.-W. Chan, S. Cao, M. Ng, *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **119**, e2116543119 (2022).
6. K. Zhang, M. C.-L Yeung, S. Y.-L. Leung, V. W.-W. Yam, *Chem* **2**, 825 (2017).
7. K. Zhang, M. C.-L Yeung, S. Y.-L. Leung, V. W.-W. Yam, *Proc. Natl. Acad. Sci. U.S.A.* **114**, 11844 (2017).
8. K. Zhang, M. C.-L Yeung, S. Y.-L. Leung, V. W.-W. Yam, *J. Am. Chem. Soc.* **140**, 9594 (2018).
9. Z. Geng, P. L.-Y. Chiu, M. H.-Y. Chan, V. W.-W. Yam, *Chem* **10**, 1225 (2024).
10. Z. Geng, K. Ip, P. L.-Y. Chiu, E. K.-H. Wong, V. W.-W. Yam, *Angew. Chem. Int. Ed.* **64**, e202500166 (2025).