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# Journal of Organometallic Chemistry

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## CV of Toshikazu Hirao



Toshikazu Hirao was born in Osaka, Japan in 1949, and graduated from Kyoto University in 1973, where he obtained his doctorate in 1978. He became Assistant Professor at Osaka University in 1978 and was a postdoctoral fellow at the University of Wisconsin under Professor Barry M. Trost (1981–1982). His research was related to the development of synthetic methodology using organometallic and phosphorus compounds, receiving the Chemical Society of Japan Award for Young Chemists in 1984. He was promoted to Associate Professor in 1992 and Professor in 1994. He is now the library director of Osaka University and was a visiting professor at Kyushu University (2007).

He was the director of the Chemical Society of Japan (2003–2005) and head of numerous projects including (i) “Construction of dynamic redox systems based on nano-space control” (Grant-in-aid for scientific research on priority areas supported by the Ministry of education, science, sports and culture, Japan, 2001–2003), (ii) research project of Frontier research center, Osaka University (2003–2005), and (iii) joint-research project between Japan and Germany (2003–2005). He has organized major scientific international meetings, as exemplified by the 3rd international symposium on chemistry and biological chemistry of vanadium (2001), the 1st and 2nd international symposium on nano-structure and redox systems (2002, 2004), and the 8th international

symposium on organic reactions (2006). Additionally, his outstanding scientific persona is represented by a member of international advisory committees or organizing committees, for example, the international symposium on organic reactions, the international symposium on advances in electrochemical science and technology, the international symposium on organic reactions, the international symposium on chemistry and biological chemistry of vanadium, the international symposium in bioorganometallic chemistry, and the IUPAC international symposium on macromolecular complexes.

His current research interests include construction of efficient systems for electron transfer, allowing the development of new methods in organic synthesis, and novel redox-active systems consisting of transition metal complexes and/or  $\pi$ -conjugated compounds. The research is extended to the development of the chemistry of nonplanar  $\pi$ -conjugated compounds. Artificial bioconjugates in bioorganometallic chemistry provide key compounds in his research to construct the dimensionally-controlled systems. His high impact research has opened up an entirely new aspect of synthetic methodology, coordination chemistry, materials chemistry, and bioconjugate chemistry. With over 240 highly creative publications and 50 books and review articles, he has left his pioneering mark. Based on his superb achievements, he is

frequently invited as a key speaker at a lot of international universities and meetings. He received the “Vanadis Award” for the outstanding contributions to the progress, application, and exploration of vanadium in science in 2008. The main achievements are as follows.

(1) *Biorganometallic conjugates*: A combination of the ferrocene as a central reverse-turn scaffold with dipeptide pendant groups has been demonstrated to induce antiparallel  $\beta$ -sheet-like, type II  $\beta$ -turn-like, and  $\gamma$ -turn-like structures depending on the chirality and sequence. This architectural control of the dimensional structures utilizing minimum-sized peptide chains with chiral centers and hydrogen bonding sites provides a versatile approach to artificial highly-ordered systems. Crystal engineering in bioorganometallic chemistry is developed.

The redox-active ferrocene bearing a long alkylene chain is aggregated along the backbone of double helical DNA to afford the redox-active (outer) and hydrophobic (inner) spheres.

(2) *Synthetic reactions via electron transfer*: One-electron oxidation capability of oxovanadium(V) compounds has been demonstrated to induce synthetically useful oxidative transformations. Selective carbon–carbon bond formation occurs via ligand coupling through intermetallic interaction between vanadium species and main-group organometallics. Bio-inspired (bromoperoxidase) and environmentally harmonic vanadium-catalyzed bromination is attained.

Low-valent vanadiums are employed in reductive transformations. Catalytic reactions for one-electron reduction have been achieved by using multi-component catalytic systems. Especially, the diastereoselective catalytic pinacol coupling provides a synthetically useful method.

(3) *Hybrid  $\pi$ -conjugated systems*: The hybrid d, $\pi$ -conjugated systems composed of redox-active  $\pi$ -conjugated molecules or polymers like polyanilines and transition metals are constructed to permit the potential field reflected by both redox properties. Chirality induction of the  $\pi$ -conjugated chain is attained by chiral complexation. These complexes are applied to efficient catalysts and electronic materials. The thus-organized conjugated palladium(II) complex is reduced to small and well-dispersed nanoparticles. Use of a porphyrin and the corresponding zinc complex as a molecular scaffold provides a dimensionally orientated  $\pi$ -conjugated system bearing  $\pi$ -conjugated pendant groups for photoreflactive electron transfer.

Bowl-shaped  $\pi$ -conjugated “sumanene”, which possesses a key partial  $C_{3v}$  symmetric structure of fullerene, is synthesized for the first time.  $\pi$ -Extended  $\pi$ -bowls are synthesized through molecular transformations of sumanene. A concave-bound iron complex is synthesized by ligand exchange of a cyclopentadienyl ring of ferrocene with sumanene. The concave  $\pi$ -bent surface is demonstrated to serve as a ligand to give the corresponding d, $\pi$ -conjugated bowl complex.

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