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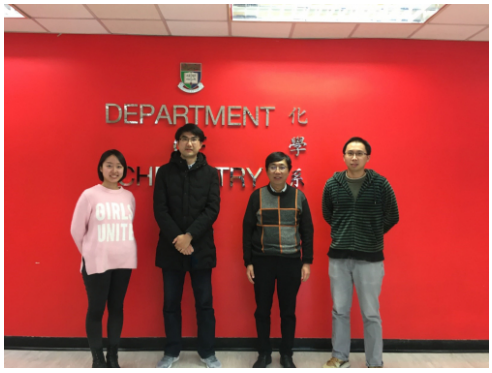
# Chemists resolve a long-standing challenging problem on Metal-Metal interaction




From the left: Dr Qingyun WAN, Dr Jun YANG, Professor Chi-Ming CHE and Dr Wai-Pong TO

A research team led by Professor Chi-Ming CHE and Dr Jun YANG, from the Research Division for Chemistry and Department of Chemistry at the Faculty of Science of the University of Hong Kong, has resolved a long-standing fundamental problem in the field of metal-metal closed-shell interaction. This work has been published in the journal Proceedings of the National Academy of Sciences (PNAS).

Metal-Metal closed-shell interaction, also known as metallophilicity, has a huge impact in diverse fields of chemistry, such as supramolecular chemistry and organometallic chemistry. Early reports on metallophilicity could be traced back to the 1970s. Many leading theoretical chemists around the world made contributions in the field, such as Roald Hoffmann (1981 Nobel Laureate in Chemistry), Pekka Pyykkö, etc.. Metallophilicity is important in the fabrication of self-assemblies by transition metal complexes, which has demonstrated profound applications in organic semiconductors, bio-sensing and functional optoelectronic materials.

Going beyond conventional wisdom

The term “metallophilicity” originated from Europe and has been extensively used by chemists as a guiding principle in molecular design studies and to rationalize the spectroscopic properties of transition metal complexes. Up to now, the general consensus of metallophilicity in the academic community is “attractive”, which has been conceived to come from orbital hybridization and/or relativistic effect of heavy metal atom, such as gold or platinum (3rd row metal in the elemental table). Together with Professor Che and Dr. Yang, Postdoctoral Fellow Dr. Qingyun WAN and co-workers questioned the conventional wisdom of coordination chemists, concluding that the metallophilicity is not an attractive interaction in organometallic complex, but is actually repulsive in nature due to strong M-M’ Pauli repulsion.

They performed a combined theoretical and experimental research on metallophilicity and observed strong M-M’ Pauli repulsion in organometallic complex having closed-shell electronic configurations, which will provide a new theoretical perspective on the possibility of making new

supramolecular materials with inexpensive earth-abundant transition metal complexes, such as that of palladium or silver or nickel (1st or 2nd row metals in the elemental table). It is also a crucial achievement in the fundamental understanding of weak intermolecular interactions.

Background and achievement

In the microworld of small molecules, there are many types of interactions. Metallophilicity describes the interaction between metal atoms as having closed-shell electronic configurations. In the early 1970s, chemists observed an interesting phenomenon that two closed-shell metal atoms could form a short metal-metal distance. A special “attraction” was proposed to exist between two metal atoms, pushing two metal atoms coming close. Many theoretical models were raised to account for such an attachment, such as the model of orbital hybridization or relativistic effect of the heavy metal. However, these theoretical models have conflictions with some experiment observations, like the relatively shorter Ag-Ag distance in Ag complexes compared to the Au-Au distance in the Au analogues. Thus, this problem has remained controversial for a long time and always plagued inorganic and theoretical chemists.

The researchers at HKU used high-level calculation methods and experimental techniques to investigate such a tough problem, and proved that the metallophilicity is repulsive in nature due to strong M-M’ Pauli repulsion. They concluded that orbital hybridization and relativistic effect would strengthen the metal-metal Pauli repulsion when forming a close metal-metal contact. Intermolecular dispersion and electrostatic interaction will counter-balance the metal-metal repulsion, leading to a short metal-metal distance. This theoretical model could well explain why Ag-Ag distance is shorter than the Au-Au distance, due to weaker Ag-Ag Pauli repulsion which is induced by less orbital hybridization in the Ag complex.

By a conservative estimation, there were more than 5,000 papers published in the literature related to “attractive metallophilicity”. The statement of “repulsive metallophilicity” is first proposed by the research team in their recent PNAS publication. This work was also recognized by Professor Harry GRAY in Caltech, who was awarded the Wolf Prize in Chemistry in 2004, one of the most honorable awards in the field.

About the research team

The research was conducted by a joint team under Professor Chi-Ming Che and Dr. Jun Yang from the Research Division for Chemistry and Department of Chemistry. Postdoctoral fellow Dr. Qingyun Wan from Professor Che’s group is the first author, while Dr. Wan, Dr. Yang and Professor Che are co-corresponding authors. Dr. Wai-Pong To, Research Assistant Professor from Professor Che’s group, is another chemist contributing to the research.

The research has secured continuous support from the Research Grants Council of Hong Kong, State Key Laboratory of Synthetic Chemistry at HKU and also the Information Technology Services of the University. The research team would also like to show their gratitude to the Basic Research Program-Shenzhen Fund, and the Major Program of Guangdong Basic and Applied Research.

About Professor Chi-Ming Che

Professor Chi-Ming Che received his BSc (1978) and PhD (1982) degrees from HKU. Following his research studies at the California Institute of Technology from 1980 to 1983, he joined HKU Chemistry in 1983 and was promoted to Chair Professor in 1992. From 1999-2016, he was appointed as Dr. Hui Wai-Haan Chair of Chemistry. He is currently the Zhou Guangzhao Professor in Natural Sciences and the Director of State Key Laboratory of Synthetic Chemistry at HKU.

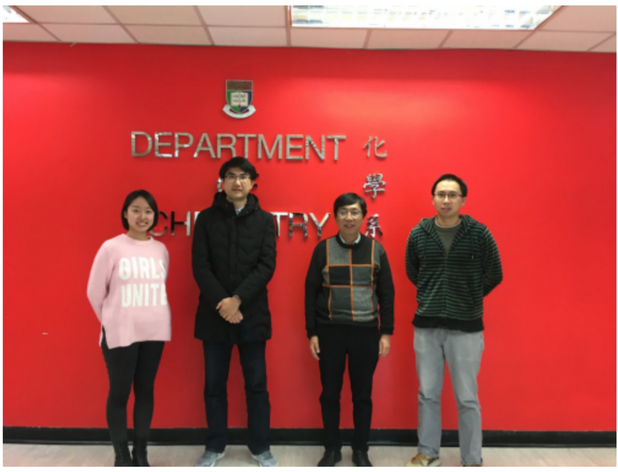


Tags: authors, california, California Institute of Technology, Caltech, community, director, Europe, Guangdong, Hong Kong, platinum, Professor, research, synthetic chemistry, technology, university, University of Hong Kong

# Chemists resolve a long-standing challenging problem on Metal-Metal interaction

17/01/2021 in Metals






A analysis staff led by Professor Chi-Ming CHE and Dr Jun YANG, from the Analysis Division for Chemistry and Division of Chemistry on the School of Science of the College of Hong Kong, has resolved a long-standing basic downside within the subject of metal-metal closed-shell interplay. This work has been revealed within the journal Proceedings of the Nationwide Academy of Sciences (PNAS).

Steel-Steel closed-shell interplay, also referred to as metallophilicity, has a big impact in various fields of chemistry, comparable to supramolecular chemistry and organometallic chemistry. Early experiences on metallophilicity could possibly be traced again to the 1970s. Many main theoretical chemists around the globe made contributions within the subject, comparable to Roald Hoffmann (1981 Nobel Laureate in Chemistry), Pekka Pyykkö, and so forth.. Metallophilicity is necessary within the fabrication of self-assemblies by transition metallic complexes, which has demonstrated profound purposes in natural semiconductors, bio-sensing and practical optoelectronic supplies.

Going past typical knowledge

The time period “metallophilicity” originated from Europe and has been extensively utilized by chemists as a guideline in molecular design research and to rationalize the spectroscopic properties of transition metallic complexes. To this point, the overall consensus of metallophilicity within the tutorial group is “engaging”, which has been conceived to come back from orbital hybridization and/or relativistic impact of heavy metallic atom, comparable to gold or platinum (third row metallic within the elemental desk). Along with Professor Che and Dr. Yang, Postdoctoral Fellow Dr. Qingyun WAN and associates questioned the traditional knowledge of coordination chemists, concluding that the metallophilicity shouldn’t be a beautiful interplay in organometallic advanced, however is definitely repulsive in nature as a consequence of sturdy M-M’ Pauli repulsion.

They carried out a mixed theoretical and experimental analysis on metallophilicity and noticed sturdy M-M’ Pauli repulsion in organometallic advanced having closed-shell digital configurations, which is able to present a brand new theoretical perspective on the potential for making new supramolecular supplies with cheap earth-abundant transition metallic complexes, comparable to that of palladium or silver or nickel (1st or 2nd row metals within the elemental desk). It’s also a vital achievement within the basic understanding of weak intermolecular interactions.

Background and achievement

Within the microworld of small molecules, there are a lot of forms of interactions. Metallophilicity describes the interplay between metallic atoms as having closed-shell digital configurations. Within the early 1970s, chemists noticed an fascinating phenomenon that two closed-shell metallic atoms may kind a brief metal-metal distance. A particular “attraction” was proposed to exist between two metallic atoms, pushing two metallic atoms coming shut. Many theoretical fashions had been raised to account for such an attachment, such because the mannequin of orbital hybridization or relativistic impact of the heavy metallic. Nonetheless, these theoretical fashions have conflictions with some experiment observations, just like the comparatively shorter Ag-Ag distance in Ag complexes in comparison with the Au-Au distance within the Au analogues. Thus, this downside has remained controversial for a very long time and at all times plagued inorganic and theoretical chemists.

The researchers at HKU used high-level calculation strategies and experimental methods to research such a troublesome downside, and proved that the metallophilicity is repulsive in nature as a consequence of sturdy M-M’ Pauli repulsion. They concluded that orbital hybridization and relativistic impact would strengthen the metal-metal Pauli repulsion when forming an in depth metal-metal contact. Intermolecular dispersion and electrostatic interplay will counter-balance the metal-metal repulsion, resulting in a brief metal-metal distance. This theoretical mannequin may properly clarify why Ag-Ag distance is shorter than the Au-Au distance, as a consequence of weaker Ag-Ag Pauli repulsion which is induced by much less orbital hybridization within the Ag advanced.

By a conservative estimation, there have been greater than 5,000 papers revealed within the literature associated to “engaging metallophilicity”. The assertion of “repulsive metallophilicity” is first proposed by the analysis staff of their current PNAS publication. This work was additionally acknowledged by Professor Harry GRAY in Caltech, who was awarded the Wolf Prize in Chemistry in 2004, probably the most honorable awards within the subject.

Concerning the analysis staff

The analysis was performed by a joint staff underneath Professor Chi-Ming Che and Dr. Jun Yang from the Analysis Division for Chemistry and Division of Chemistry. Postdoctoral fellow Dr. Qingyun Wan from Professor Che’s group is the primary creator, whereas Dr. Wan, Dr. Yang and Professor Che are co-corresponding authors. Dr. Wai-Pong To, Analysis Assistant Professor from Professor Che’s group, is one other chemist contributing to the analysis.

The analysis has secured steady assist from the Analysis Grants Council of Hong Kong, State Key Laboratory of Artificial Chemistry at HKU and likewise the Info Know-how Companies of the College. The analysis staff would additionally like to point out their gratitude to the Fundamental Analysis Program-Shenzhen Fund, and the Main Program of Guangdong Fundamental and Utilized Analysis.

About Professor Chi-Ming Che

Professor Chi-Ming Che obtained his BSc (1978) and PhD (1982) levels from HKU. Following his analysis research on the California Institute of Know-how from 1980 to 1983, he joined HKU Chemistry in 1983 and was promoted to Chair Professor in 1992. From 1999-2016, he was appointed as Dr. Hui Wai-Haan Chair of Chemistry. He’s at present the Zhou Guangzhao Professor in Pure Sciences and the Director of State Key Laboratory of Artificial Chemistry at HKU.

# 港大破解化學界難題 優化半導體製造

時間：2021-01-18 04:23:40 來源：大公報


圖：港大團隊首次發現嗜金屬相互作用具排斥性。\受訪者供圖

【大公報訊】香港大學表示，該校化學系主任支志明與化學系助理教授楊軍率領的研究團隊，已破解「閉殼層金屬─金屬之間相互作用」（又稱嗜金屬相互作用）這一困擾無機化學界多年的難題，該理論在過渡金屬配合物的自組裝過程中十分重要，並能廣泛應用於有機半導體、生物傳感和功能性光電材料中。研究成果現已在期刊《美國國家科學院院刊》（PNAS）發表。

港大指，到目前為止，學術界對嗜金屬作用的普遍共識是「相互吸引的」，其作用原理被認為是由軌道雜化或重金屬原子的相對論效應所導致。支志明和楊軍率領的研究團隊，運用精密的計算方法和實驗技術，印證了金屬─金屬之間強烈的泡利排斥作用導致嗜金屬具排斥性，而非傳統認為的互相吸引。

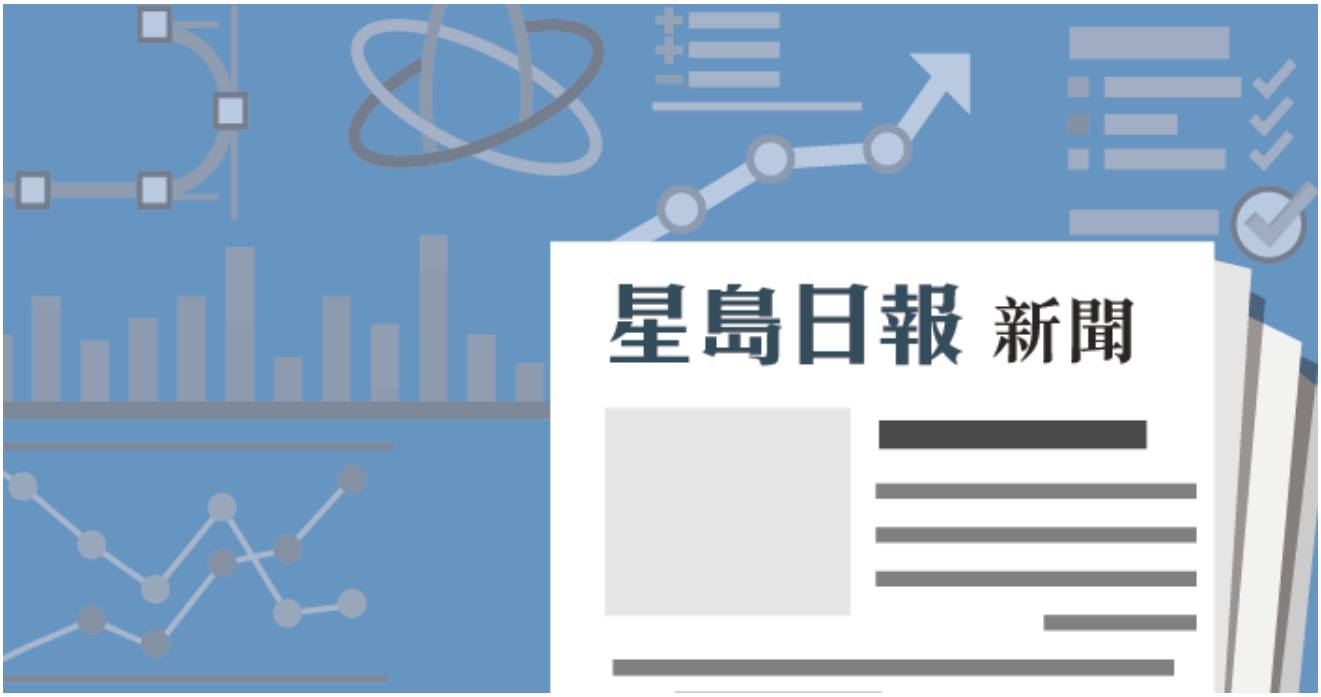
研究團隊在PNAS期刊中首次提出，「嗜金屬相互作用」其實是具有相互排斥性，而軌道雜化和相對論效應會增強金屬─金屬之間的泡利排斥作用，而分子間的色散力和靜電相互作用將抵銷金屬與金屬之間的排斥力，從而導致金屬與金屬之間相互接近。港大表示，這項發現對於閉殼層金屬配合物相關的研究具有長遠的影響，並為製造可替代貴重金屬的新型超分子材料（例如鈀、銀或鎳的過渡金屬配合物）提供理論支持，有助化學研究人員更了解分子間弱相互作用。

港大博士萬晴雲是期刊論文第一作者，她與楊軍、支志明皆為共同通訊作者。研究得到香港研資局、香港大學合成化學國家重點實驗室，以及港大資訊科技服務的支持。

最新要聞

BASTILLE POST 巴士的報

2021年 1月 18日 星期一




# 港大團隊破解無機化學難題

2021年01月18日03:00 最後更新: 04:31

閉殼層金屬—金屬之間的相互作用，一直是困擾無機化學界多年的難題，香港大學理學院化學研究部及化學系教授支志明的研究團隊，運用精密的計算方法和實驗技術，解開這個難題，印證了金屬之間強烈的泡利排斥作用，導致嗜金屬具排斥性。研究成果已在期刊《美國國家科學院院刊》（PNAS）發表。

金屬—金屬閉殼相互作用（又稱嗜金屬相互作用），在有機半導體、生物傳感和功能性光電材料中有廣泛應用，學術界對嗜金屬作用的普遍共識是「相互吸引的」，其作用原理被認為是由軌道雜化或重金屬原子的相對論效應所導致。然而，支志明與化學系助理教授楊軍率領的研究團隊發現，金屬—金屬之間具有強烈的泡利排斥作用，導致嗜金屬作用在本質上互相排斥，推翻了化學家的傳統觀點。

今次發現對於閉殼層金屬配合物相關研究具有長遠影響，為製造可替代貴重金屬的新型超分子材料，譬如鈀、銀或鎳的過渡金屬配合物提供理論支持，亦讓化學研究人員更了解分子間弱相互作用。

# 港大團隊破解無機化學難題

2021-01-18 00:00

(星島日報報道)閉殼層金屬—金屬之間的相互作用，一直是困擾無機化學界多年的難題，香港大學理學院化學研究部及化學系教授支志明的研究團隊，運用精密的計算方法和實驗技術，解開這個難題，印證了金屬之間強烈的泡利排斥作用，導致嗜金屬具排斥性。研究成果已在期刊《美國國家科學院院刊》（PNAS）發表。

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# 港大團隊破解無機化學難題 為製造新型超分子材料提供新觀點

2021-01-17 16:11

來源：香港商報

香港大學表示，該校化學系系主任支志明及化學系助理教授楊軍率領的研究團隊，已破解了閉殼層金屬—金屬之間的相互作用這一困擾無機化學界多年的難題。該團隊之研究成果現已在期刊《美國國家科學院院刊》發表。

「金屬—金屬閉殼相互作用」可稱為「嗜金屬相互作用」，它在超分子化學和有機金屬化學等多個化學領域均具有巨大影響，於1970年代初期便有化學家觀察到兩個閉殼金屬原子之間會形成較短的金屬-金屬距離。港大表示，雖然許多理論化學家提出理論模型去解釋上述現象，但理論卻與一些實驗結果相違背，例如在晶體結構中，金-金之間的距離比銀-銀之間的距離要長，由於問題無法用現有的理論模型解釋，因而一直是無機和理論化學界的難題。

支志明與楊軍率領的研究團隊，運用精密的計算方法和實驗技術來解開上述難題。研究團隊觀察到具有閉殼電子構型的有機金屬配合物中，有著很強的金屬-金屬泡利排斥作用；研究團隊在《美國國家科學院院刊》則首次提出「嗜金屬相互作用」其實具有相互排斥性，而軌道雜化和相對論效應會增強金屬-金屬之間的泡利排斥作用、分子間的色散力和靜電相互作用將抵消金屬與金屬之間的排斥力，從而導致金屬與金屬之間相互接近，亦正好解釋了為何銀-銀之間的距離比金-金之間的距離要短。

港大表示，支志明與楊軍的研究亦獲得2004年沃爾夫化學獎得獎人—加州理工大學教授Harry Gray的高度評價。這項研究由化學研究部及化學系支志明教授和楊軍博士所率領的團隊完成。萬晴雲博士是第一作者，她與楊博士和支教授皆為共同通訊作者。支志明團隊的研究助理教授杜偉邦博士亦有份

參與研究。研究得到香港研究資助局、香港大學合成化學國家重點實驗室，以及港大資訊科技服務的支持。團隊亦感謝深圳市基礎研究計劃和廣東省基礎研究與應用研究重大計劃的支持。

[責任編輯：劉深]