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# Controlling the supramolecular polymerization of dinuclear isocyanide gold(I) arylethynylene complexes through tuning the central π-conjugated moiety†

Na Zhou,‡[a] Rebekah Hailes,‡[b] Youzhi Zhang,[c] Zuofeng Chen, [a] Ian Manners[d] and Xiaoming He *[c]

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Three dinuclear gold(I) *p*-arylene(diethynyl) complexes with the same peripheral isocyanide ligation and different central conjugated moieties have been prepared and their supramolecular polymerization was comprehensively studied. The central, core-forming π-conjugated arylene moieties present in the complexes have been shown to exhibit a pronounced influence on the resulting photophysical properties, self-assembly mechanisms, morphologies and gelation behavior of the supramolecular polymers. Complexes **1** and **2** bearing biphenylene and phenylene central chromophores exhibit a cooperative mechanism during the supramolecular polymerization, with the appearance of pronounced low-energy phosphorescence attributed to the aurophilic interactions. In contrast, compound **3** with a central benzothiadiazole moiety was found to undergo self-assembly *via* an isodesmic mechanism. Due to the presence of stronger π–π interactions, complexes **1** and **3** possess lower $\Delta G_0$ values for self-assembly and a stronger tendency to form metallogels. Given the balance between the non-covalent interaction enthalpy of the core-forming moieties and intercoronal chain repulsion, **1** and **3** tend to form one-dimensional fibers, while **2** with a short central chromophore is likely to form zero-dimensional spherical aggregates.

## Introduction

Supramolecular polymerization is now widely recognized as a strategy tool for the creation of polymeric materials.[1–4] In contrast to classical polymers, the presence of potentially reversible non-covalent interactions provides access to outstanding functionalities such as stimuli-responsive or self-healing characteristics. Through manipulating a range of non-covalent intermolecular interactions, such as hydrogen-bonding, π–π stacking, hydrophobic–hydrophobic and/or electrostatic interactions, it is possible to form linear supramolecular polymers rather than undefined aggregates to fulfill a multitude of tasks. In particular, π-conjugated molecules and polymers that form stacked structures have attracted much attention as building blocks due to their wide range of applications which include light-harvesting, sensing, and photocatalysis.[5,6] The optoelectronic properties of these aggregates strongly depend on the π-conjugated central core and their intermolecular orientations. A variety of π systems, such as polythiophene,[7,8] polyfluorene,[9,10] perylene diimide,[11] oligo(*p*-phenylenevinylene),[12] azobenzene,[13] porphyrin,[14,15] hexabenzocoronenes,[16] and Pt(II) metal complexes,[17–24] have been successfully utilized to fabricate supramolecular polymers for various applications. In many cases, strong π–π stacking of the chromophore leads to significant emission quenching, which is undesirable for utilizing their luminescence properties. In the last decade, mechanistic insights into supramolecular polymerization have been significantly enriched.[1–3,25] Two different types of mechanisms, namely isodesmic and cooperative processes, have been demonstrated to be involved in most of the self-assembly systems.[1–3] Recent advances have witnessed the seeded living self-assembly of π conjugated organic molecules to provide access to complex nanoscale 1D and 2D morphologies with unprecedented levels of control of dimensions *via* cooperative mechanisms.[7–21] Minor structural variations have been demonstrated to exhibit a significant effect on self-assembly mechanisms.

The chemistry of organogold(I) complexes has received much attention because of the presence of aurophilic Au(I)–Au(I)

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[a] *School of Chemical Science and Engineering, Tongji University, Shanghai 200092, P. R. China*
[b] *School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*
[c] *School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, P. R. China. E-mail: xmhe@snnu.edu.cn*
[d] *Department of Chemistry, University of Victoria, 3800 Finnerty Rd, Victoria, British Columbia, V8P 5C2, Canada. E-mail: imanners@uvic.ca*

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‡ These authors contributed equally to this work.

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**作者:** **Zhou, N (Zhou, Na);** Hailes, R (Hailes, Rebekah); Zhang, YZ (Zhang, Youzhi); Chen, ZF (Chen, Zuofeng); Manners, I (Manners, Ian); He, XM (He, Xiaoming)

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**地址:** [Zhou, Na; Chen, Zuofeng] Tongji Univ, Sch Chem Sci & Engn, Shanghai 200092, Peoples R China.

[Hailes, Rebekah] Univ Bristol, Sch Chem, Bristol BS8 1TS, Avon, England.

[Zhang, Youzhi; He, Xiaoming] Shaanxi Normal Univ, Sch Chem & Chem Engn, Xian 710119, Shaanxi, Peoples R China.

[Manners, Ian] Univ Victoria, Dept Chem, 3800 Finnerty Rd, Victoria, BC V8P 5C2, Canada.

**通讯作者地址:** He, XM (通讯作者)，Shaanxi Normal Univ, Sch Chem & Chem Engn, Xian 710119, Shaanxi, Peoples R China.

**电子邮件地址:** imanners@uvic.ca; xmhe@snnu.edu.cn

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