炔铜(I)纳米团簇的合成、结构规律与光电性质

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摘要 金属纳米团簇是由几个到上千个金属原子通过化学键或弱相互作用力组成的相对稳定的聚集体, 其尺寸一般小于3 nm. 这种超小的尺寸使它们具有量子尺寸效应, 进而展现出不同于块体金属材料的电子/几何结构和物理/化学性质. 相比其他过渡金属(如金和银), 铜具有储量大等明显优势, 并且炔基配体相比硫配体和膦配体等其他保护配体具有更丰富的配位模式. 近年来, 科学家一直探索着炔铜(I)纳米团簇的合成策略及规律. 结合本课题组的研究工作, 本文对原子精确的炔铜(I)纳米团簇的合成方法、晶体结构规律、光致发光等性质和应用进行了综述, 有助于理解其结构-性质间的构效关系; 并对炔铜(I)纳米团簇的研究和挑战进行了总结和展望.

关键词 金属纳米团簇, 炔铜团簇, 晶体结构, 光致发光

金属纳米团簇(metal nanoclusters, MNCs)是由几个到上千个金属原子通过化学键或弱相互作用力组成的相对稳定的聚集体, 其尺寸一般小于3 nm, 介于原子和金属纳米颗粒之间^[1]. 如图1所示, 这种超小的尺寸导致它们具有量子尺寸效应, 从而使它们呈现分立的电子能级结构, 展现出异于相块材的光学、磁学、手性以及催化等性质^[2~5]. 随着单晶X射线衍射技术(single crystal X-ray diffraction, SCXRD)、电喷雾电离质谱(electrospray ionization mass spectrometry, ESI-MS)的发展^[6], 越来越多的金属纳米团簇的晶体结构被准确地确定出来^[7], 其独特的电子/几何结构和物理/化学性质也被深入研究.

1859年, Boettger^[8]发现了第一个有机铜(I)化合物——乙炔铜(I)($\text{CuC}\equiv\text{CCu}$), 标志着炔铜(I)化合物的诞生. 1966年, Corfield和Shearer^[9]用 $\text{HC}\equiv\text{CPh}$ 合成了四核折线型 Cu_4 , 这是最早报道的原子精确的炔铜(I)纳米团簇. 后来, Naldini课题组^[10]、Gimeno课题组^[11]、Weiss课题组^[12]、Yam课题组^[13~19]、Bourassa课题组^[20]和

Mak课题组^[21]等报道了大量的三角形构型的 Cu_3 与四面体构型的 Cu_4 , 观察到Cu可与P、N、 $\text{C}\equiv\text{C}$ 配位, 并且炔基和Cu存在多种配位方式. 1993年, Weiss课题组^[12]得到了24核全炔基保护的铜(I)团簇 $[(\text{BuC}\equiv\text{CCu})_{24}]$, 标志着高核炔铜(I)纳米团簇的诞生. 过渡金属铜因具有较强的嗜金属作用, 易于构筑金属纳米团簇^[22], 并且铜具有明显优势, 例如铜的储量大而价格较低. 另外, 铜是生物必需元素, 具有良好的生物相容性. 但是从 Cu^0/Cu^+ (0.52 V)的半电池电位^[23]可以发现, Cu^+ 具有较高的活性, 稳定性较差, 易被氧化成 Cu^{2+} , 这使得铜(I)纳米团簇的合成、表征和性质研究较为困难. 由于稳定性差, 早期合成的铜团簇的金属核数大多较少, 金属与配体的配位模式也比较单一, 且晶体结构通常呈现特定的构型.

针对稳定性差的难题, 近年来人们发展了多种合成策略. 利用路易斯酸碱理论调控原子和分子的自组装, 以及采用不同的炔配体、硫配体和膦配体等在一定程度上提高了铜(I)纳米团簇的稳定性, 同时可以构

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图 1 单原子、簇和纳米粒子的几何尺寸和电子结构^[2,3]

Figure 1 Geometric and electronic structures of single atom, clusters, and nanoparticles^[2,3]

筑出多样的结构^[24~26], 如 $\text{Cu}_4\text{I}_6(\text{pr-ted})_2(\text{pr-ted}$: 1-丙基-1,4-二氮双环[2.2.2]辛烷)、 $[\text{Cu}_{25}\text{H}_{10}(\text{SPhCl}_2)_{18}]^{3-}$ 、 $[\text{Cu}_{54}\text{S}_{13}\text{O}_6(\text{tBuS})_{20}(\text{tBuSO}_3)_{12}]$ 等^[27~29]。目前, 已有许多铜(I)纳米团簇用于催化有机反应^[30]、储氢释氢^[31]、光致发光^[32]、生物传感^[33]、细胞成像^[34,35]等领域。炔配体比硫配体和膦配体具有更丰富的配位模式, 可以构筑更独特的晶体结构, 但炔配体和 Cu^+ 的反应极易生成难溶的聚合物。因此, 如何有效阻止或打断这种聚合, 是构筑成炔铜(I)团簇的研究重点。本文首先总结了炔铜(I)团簇的常用合成方法, 为后续研究提供参考。其次, 讨论了原子精确的炔铜(I)团簇的晶体结构, 总结了成键规律和配位模式。通过调控辅助配体的方式, 实现了多配体共同保护的炔铜(I)团簇的分离和晶体结构的精确确定。然后, 介绍了炔铜(I)团簇的性质和应用示例, 如光致发光性质、化学催化性质和电学性质。最后, 对炔铜(I)团簇的研究和挑战进行了总结与展望。该文有助于建立关于炔铜(I)团簇的数据库, 有助于对炔铜(I)团簇的配位模式、晶体结构规律与性质的关系有更全面的了解, 从而为后续构筑新型纳米铜(I)团簇材料提供思路。

1 炔铜(I)团簇的合成方法

与金和银团簇一样, 在铜(I)团簇的合成过程中, 引入的保护配体的空间效应可以防止团簇聚集, 降低团簇表面能, 进而防止团簇在液相合成过程中快速沉淀。在配体存在时控制反应动力学过程, 如配体浓度、前

驱体浓度、反应体系的酸碱度、温度和反应时间等, 可以影响前驱体的反应性, 对于获得单分散的铜(I)团簇同样至关重要。与金和银团簇的合成相比, 炔铜(I)团簇的合成条件更加严格, 需要严格控制 Cu^+ 不被氧化。通过调控不同的实验条件成功合成炔铜(I)团簇后, 再反向推测其中可能存在的自组装路径, 进而实现对炔铜(I)团簇材料更加系统的研究。下面介绍几种有效合成炔铜(I)团簇的方法。

1.1 溶剂热法

在高温高压的溶剂热条件下, Cu^+ 前驱体与炔配体反应产物的溶解性得到提高, 同时有效避免 Cu^+ 被空气中的氧气氧化, 再通过保温或降温结晶, 最终实现炔铜(I)团簇的有效合成。例如, 可以利用Cu粉和 Cu^{2+} 的归中反应生成的 Cu^+ 前驱体, 或者直接利用 Cu^+ 前驱体, 在合适的有机溶剂与炔配体充分分散后, 把反应溶液转移到密闭的高压反应釜中, 通过调控反应温度、保温时间、冷却速度等反应条件可以实现炔铜(I)团簇的制备。本课题组^[36]在80°C、保温24 h的溶剂热条件下成功合成了多种高产率炔铜(I)团簇。值得注意的是, 如果归中反应不充分或者配体具有氧化性, 结构中可能会有 Cu^{2+} 存在。Mak课题组^[37]使用溶剂热法合成炔铜团簇, Cu被原位氧化成 Cu^{2+} , 导致晶体结构中存在 Cu^{2+} 。

1.2 还原法

还原法是制备含有0价金属纳米团簇的常用方法。

还原法可分为直接还原法($\text{Cu}^+ \rightarrow \text{Cu}^0$)和阶梯还原法($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$)。直接还原法是将还原剂直接加入铜前驱体和炔配体的反应液中进行还原反应。反应过程中需注意还原剂的量,原则上需要保证形成的铜纳米颗粒沉淀较少,而溶液中依旧存在大量的铜前驱体,进而保证铜团簇的自组装过程得以进行。Hayton课题组^[38]报道了用还原剂二苯基硅烷还原 $\text{Cu}(\text{CH}_3\text{COO})_2$,合成了一个20核的混合价炔铜(0)/铜(I)团簇。阶梯还原法是先利用 Cu^{2+} 和铜粉的归中反应得到含有 Cu^+ 前驱体的溶液体系,再加入还原剂最终得到含有0价Cu的团簇。还原过程的快慢和还原剂的强弱对反应成功与否至关重要。还原剂的加入还能减少铜(I)团簇的氧化,提高其稳定性。Zheng课题组^[39]使用阶梯还原的策略,成功合成了一个53核的混合价炔铜(0)/铜(I)团簇。常用的强还原剂有硼氢化钠,弱还原剂包括二甲苯基硅烷、二苯基硅烷、*N,N*-二甲基甲酰胺等。

1.3 模板法

币族金属纳米团簇的合成过程常利用酸根阴离子^[40,41]、多金属氧酸盐^[42~44]、稀土离子^[45]等模板剂来构筑高核团簇。在铜(I)团簇的合成过程中,引入模板剂不仅能平衡团簇的电荷分布,有效阻止或打断炔配体和 Cu^+ 反应生成难溶的聚合物,还能与 Cu^+ 有多种配位方式,有助于得到尺寸更大、性质独特的铜(I)团簇,从而丰富了铜(I)团簇的结构和性质。本课题组^[36]通过引入 VO_4^{3-} 和 PO_4^{3-} 模板构筑了25核炔铜(I)团簇,观察到良好的光致发光和光电响应性质。

1.4 配体交换法

近年来,配体交换诱导的尺寸-结构转化过程成为合成金属纳米团簇的一种重要方法^[1,6]。配体交换对金属纳米团簇的金属核、几何形状、成键方式和电子跃迁有显著影响。一方面,新配体的加入可阻止铜(I)化合物的聚集进而促进炔铜(I)团簇的结晶。另一方面,新配体和铜之间可以形成多个配位点,在适当实验的条件下会生成一维、二维、甚至三维炔铜(I)团簇基聚合物。本课题组^[46]在溶剂热合成过程中使 CH_3CN 断裂成 $\text{C}\equiv\text{N}$,桥连14核炔铜(I)团簇,构筑了三维簇基聚合物。新配体的选取与合成条件的调控都会对炔铜(I)化合物的结构和性质产生重要影响。

目前,炔铜(I)团簇晶体的合成主要是将以上几种方法结合起来。在特定实验条件下,金属与配体生成团

簇的反应往往存在着一个介稳平衡态。此时反应体系一般会生成多种团簇,这些团簇之间存在尺寸、表面能、形状和溶解度的差异,可通过色谱进行分离。稳定性好的同种团簇在浓度升高到一定程度后即可结晶^[47]。

2 炔铜(I)团簇的晶体结构

炔铜(I)团簇晶体的稳定性受到许多因素的影响,包括化学成分、原子结构和表面配体;并且,炔铜(I)纳米团簇必须要稳定性好才能通过单晶X射线衍射技术和电喷雾电离质谱表征分析,精确确定其结构。因此,控制团簇金属核的尺寸和表面配体的几何结构对于提高稳定性至关重要。而团簇结构是决定性能的关键因素,只有通过团簇晶体结构的研究,才能揭示新结构和新性质之间的构效关系。下文从炔配体保护的铜(I)团簇、炔配体保护的混合价铜(0)/铜(I)团簇和模板构筑的炔铜(I)团簇3个方面总结了炔铜(I)团簇的成键规律与配位模式。

2.1 炔配体保护的铜(I)团簇

在Weiss课题组^[12]合成了24核全炔基保护的铜(I)团簇之后,2005年,Che课题组^[48]报道了一个20核全炔基保护的铜(I)团簇 $[\text{tBuC}\equiv\text{CCu}]_{20}$ 。该炔铜(I)团簇中有一个 Cu_8 单元环分别与另外两个 Cu_6 单元环配位。作者还用 $\text{PrC}\equiv\text{CH}$ 和 $\text{PhC}\equiv\text{CH}$ 两种炔得到了两种炔铜(I)聚合物 $[\text{PhC}\equiv\text{CCu}]_n$ 和成“Z字形”的片状结构 $[\text{PrC}\equiv\text{CCu}]_n$ 。此项工作为后续炔铜(I)化合物结构和性质研究提供了很好的参考。随后,Che课题组在全炔基保护的铜团簇研究方面做了十分系统的工作。不同炔基配体的性质会有很大不同,需要大量的摸索才能找到合适的实验条件。如图2所示,2016年,他们在不同溶剂中使用多种炔基配体成功合成了一系列结构不同的全炔基保护的铜(I)团簇 $[\text{Cu}(\text{C}\equiv\text{CTrip})]_8$ (记为 Cu_8)、 $[\text{Cu}(\text{C}\equiv\text{CPh}^t\text{Bu})]_{12}$ (记为 Cu_{12})、 $[(\text{Cu}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CTrip}))_{16}(\text{THF})_4]$ (记为 Cu_{16})、 $[(\text{Cu}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CTrip}))_{20}(\text{MeCN})_4]$ (记为 Cu_{20})、 $[(\text{Cu}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh}))_{10}(\text{NH}_3)_6]$ (记为 Cu_{10})和 $[(\text{Cu}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh}))_2(\text{NH}_3)]_\infty$ (记为 Cu_∞)^[49]。为了半定量表示炔基配体在金属核表面形成的空间位阻大小,他们引入了配体的空间结构与金属核心形成的“锥角 θ ”这一概念,并且证明锥角与形成配合物的核数有很好的相关性。随着配合物中炔基锥角的增大,配合物的结构由聚合态的 Cu_∞ 到相对较大的团簇 Cu_{20} ,再到相对较小的团簇

图2 全炔基配体保护的炔铜(I)团簇^[49]. (a) 4种炔基配体的化学结构式; Cu₈(b), Cu₁₆(c), Cu₂₀(d), Cu₁₀(e)和Cu_∞(f)的晶体结构. Cu, 橙色; N, 蓝色; C, 灰色

Figure 2 All-alkynyl ligand-protected alkynyl copper(I) clusters^[49]. (a) Chemical structures of the four alkynyl ligands; structures of Cu₈ (b), Cu₁₆ (c), Cu₂₀ (d), Cu₁₀ (e) and Cu_∞ (f). Cu, orange; N, blue; C, gray

Cu₈. 这些结果说明, 炔基配体上有较大的取代基有利于形成团簇, 而较小的取代基容易形成聚合物结构.

上文提到的全炔基配体保护的炔铜(I)团簇, 容易形成炔铜(I)聚合物, 合成难度较大. 引入桥连配体来共同保护团簇能降低团簇的表面能, 提高团簇分子在溶液中的稳定性, 是构筑团簇的常用策略. 从2002年起, Tasker课题组^[50]对炔配体和六氟乙酰丙酮(Hhfac)共同保护的铜(I)团簇进行了多年的研究. 通过Cu₂O和Hhfac的缩合反应, 尝试了多种炔配体, 成功合成了16和20核炔铜(I)团簇. 如图3(a)所示, 炔铜(I)团簇[Cu₁₆(C≡C^tBu)₈(hfac)₈]中有8个Cu原子通过与炔配体桥联形成一个笼状内壳, 另外8个Cu原子与hfac⁻配体配位连接形成外壳. 同年, 他们将HC≡C^tBu换为HC≡C-*n*-C₃H₇^[51], 得到了18核炔铜(I)团簇和晶体结构呈不对称圆盘状的[Cu₂₆(hfac)₁₁(C≡C-*n*-C₃H₇)₁₅], 如图3(c)所示. Tasker课题组^[52]使用不同的炔配体又合成了一系列核数为10~12的炔铜(I)团簇[Cu_{x+y}(hfac)_x(C≡CR)_y](x+y=10或12), 它们都有一个相同的Cu₄C₄核心. 如图3(d)所示, [Cu₁₂(hfac)₈(C≡CⁿPr)₄]的结构整体呈蝴蝶状, 有近似平面排列的Cu₁₂结构, 其中心Cu原子形成了稍不规则的正方形. 如图3(e)所示, 他们^[53]又用具有线性碳链的炔基配体RC≡C⁻(R: *n*-C₄H₉, *n*-C₅H₁₁, *n*-C₆H₁₃)合成了3个结构相似的26核炔铜(I)团簇[Cu₂₆(hfac)₁₂(C≡CR)₁₄], 从内到外

形成Cu₂-Cu₁₂-Cu₁₂三环双层结构. 如图3(b), (f)所示, 本课题组^[54]用HC≡C^tPr也得到了20核炔铜(I)团簇, 与Tasker课题组^[50]得到的20核炔铜(I)团簇结构相似, 其中8个hfac⁻配体正好两两位于簇核的上、下、左、右4个部位. Hfac⁻配体参与配位的铜团簇在溶液中稳定性很好, 对合成高核数的炔铜(I)团簇起到十分重要的作用.

除了上文提及的hfac⁻配体中的两个O可以在团簇表面配位Cu, 其他含氧配体(如CF₃OO⁻等)也可以与炔基配体共同保护铜团簇. Sun课题组^[55,56]采用归中反应溶剂热后得到3个^tBuC≡C⁻和CF₃COO⁻共同保护的14、15和16核簇炔铜(I)团簇, 它们具有良好的稳定性. 如图4(a), (b)所示, Cu₁₅的金属骨架形如一个五角形的双金字塔, 2个Cu₄采用折叠线的配位模式在它的4个相邻边缘配位. Cu₁₆核结构由14个表面Cu原子和2个内部Cu原子组成. 边缘融合的六边形组成骨架结构, 另外2个Cu键合在六边形的上、下两面. 根据路易斯酸碱理论, 不同于弱酸根CF₃COO⁻, 强酸根NO₃⁻与Cu⁺的配位能力要弱很多, NO₃⁻是否能和炔基共同保护铜团簇值得研究. 2019年, 本课题组^[46]用归中反应对反应条件进行了细微控制, 合成了两种由^tBuC≡C⁻和NO₃⁻共同保护的14和15核炔Cu(I)团簇(图4(c), (d)). 同年, Mak课题组^[37]也合成了2个15和28核炔Cu(I)团簇. 如图4(e), (f)所示, Cu₂₈中的2个MeO⁻桥连了2个Cu₁₄团簇, 而SO₄²⁻分别保

图 3 Hfac和炔配体共保护的铜(I)纳米团簇的晶体结构示意图. (a) $[\text{Cu}_{16}(\text{C}\equiv\text{C}'\text{Bu})_8(\text{hfac})_8]$ ^[50]; (b) $[\text{Cu}_{20}(\text{C}\equiv\text{CCH}_2\text{Ph})_{12}(\text{hfac})_8]$ ^[50]; (c) $[\text{Cu}_{26}(\text{hfac})_{11}-(\text{C}\equiv\text{C}-n-\text{C}_3\text{H}_7)_{15}]$ ^[51]; (d) $[\text{Cu}_{12}(\text{hfac})_8(\text{C}\equiv\text{C}^n\text{Pr})_4]$ ^[52]; (e) $[\text{Cu}_{26}(\text{hfac})_{12}(\text{C}\equiv\text{C}-n-\text{C}_6\text{H}_{13})_{14}]$ ^[53]; (f) $[\text{Cu}_{20}(\text{C}\equiv\text{C}'\text{Pr})_{12}(\text{hfac})_8]$ ^[54]. Cu, 橙色; O, 红色; F, 绿色; C, 灰色

Figure 3 Structures of copper(I) nanoclusters co-protected by hfac and alkynyl ligands. (a) $[\text{Cu}_{16}(\text{C}\equiv\text{C}'\text{Bu})_8(\text{hfac})_8]$ ^[50], (b) $[\text{Cu}_{20}(\text{C}\equiv\text{CCH}_2\text{Ph})_{12}(\text{hfac})_8]$ ^[50], (c) $[\text{Cu}_{26}(\text{hfac})_{11}(\text{C}\equiv\text{C}-n-\text{C}_3\text{H}_7)_{15}]$ ^[51], (d) $[\text{Cu}_{12}(\text{hfac})_8(\text{C}\equiv\text{C}^n\text{Pr})_4]$ ^[52], (e) $[\text{Cu}_{26}(\text{hfac})_{12}(\text{C}\equiv\text{C}-n-\text{C}_6\text{H}_{13})_{14}]$ ^[53], (f) $[\text{Cu}_{20}(\text{C}\equiv\text{C}'\text{Pr})_{12}(\text{hfac})_8]$ ^[54]. Cu, orange; O, red; F, green; C, gray

图 4 含O、S配体和炔配体共保护的铜(I)团簇的晶体结构示意图. (a) $[\text{Cu}_{15}(\text{'BuC}\equiv\text{C})_{10}(\text{CF}_3\text{COO})_5]$ ^[55]; (b) $[\text{Cu}_{16}(\text{'BuC}\equiv\text{C})_{12}(\text{CF}_3\text{COO})_4(\text{CH}_3\text{OH})_2]$ ^[55]; (c) $[\text{Cu}_{14}(\text{'BuC}\equiv\text{C})_{10}(\text{NO}_3)_4]$ ^[46]; (d) $[\text{Cu}_{15}(\text{'BuC}\equiv\text{C})_{14}(\text{NO}_3)_4]$ ^[46]; (e) $[\text{Cu}(\text{I})_{15}(\text{'BuC}\equiv\text{C})_{14}\text{NO}_3]$ ^[37]; (f) $[\text{Cu}(\text{I})_{28}(\text{'BuC}\equiv\text{C})_{22}(\text{SO}_4)_2(\text{OMe})_2]$ ^[37]; (g) $[\text{Cu}_{11}\text{H}_2\{\text{S}_2\text{P}(\text{O}'\text{Pr})_2\}_6(\text{C}\equiv\text{CPh})_3]$ ^[58]; (h) $[\text{PdCu}_{14}\text{H}_2(\text{S}_2\text{CN}'\text{Bu})_6(\text{C}\equiv\text{CPh})_6]$ ^[59]. Cu, 橙色; S, 黄色; P, 紫色; F, 绿色; O, 红色; N, 蓝色; C, 灰色; H, 青色

Figure 4 Structures of copper(I) nanoclusters co-protected by alkynyl and other O- or S-containing ligands. (a) $[\text{Cu}_{15}(\text{'BuC}\equiv\text{C})_{10}(\text{CF}_3\text{COO})_5]$ ^[55], (b) $[\text{Cu}_{16}(\text{'BuC}\equiv\text{C})_{12}(\text{CF}_3\text{COO})_4(\text{CH}_3\text{OH})_2]$ ^[55], (c) $[\text{Cu}_{14}(\text{'BuC}\equiv\text{C})_{10}(\text{NO}_3)_4]$ ^[46], (d) $[\text{Cu}_{15}(\text{'BuC}\equiv\text{C})_{14}(\text{NO}_3)_4]$ ^[46], (e) $[\text{Cu}(\text{I})_{15}(\text{'BuC}\equiv\text{C})_{14}\text{NO}_3]$ ^[37], (f) $[\text{Cu}(\text{I})_{28}(\text{'BuC}\equiv\text{C})_{22}(\text{SO}_4)_2(\text{OMe})_2]$ ^[37], (g) $[\text{Cu}_{11}\text{H}_2\{\text{S}_2\text{P}(\text{O}'\text{Pr})_2\}_6(\text{C}\equiv\text{CPh})_3]$ ^[58], (h) $[\text{PdCu}_{14}\text{H}_2(\text{S}_2\text{CN}'\text{Bu})_6(\text{C}\equiv\text{CPh})_6]$ ^[59]. Cu, orange; S, yellow; P, purple; F, green; O, red; N, blue; C, gray; H, cyan

护了簇的两头部分。

Liu课题组^[57]在铜团簇方面做了多年的系统研究,特别是用二硫代磷酸酯配体和炔配体共同构筑铜氢簇,与 hfac^- 、 CH_3COO^- 和 NO_3^- 等含O酸根离子与炔配体共同保护铜(I)团簇的策略类似。他们^[58]以 $[\text{Cu}_{20}\text{H}_{11}\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_9]$ 为铜源,使用3种不同的炔得到了 $[\text{Cu}_{11}\text{H}_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_6(\text{C}\equiv\text{CR})_3](\text{R}: \text{Ph}, \text{C}_6\text{H}_4\text{F}, \text{C}_6\text{H}_4\text{OMe})$ 。这类簇有着相似的晶体结构,如图4(g)所示。 Cu_{11}H_2 核具有五顶三角棱柱几何形状,其中两个H采用三角锥体配位模式。他们又将 $[\text{Cu}_{28}\text{H}_{15}(\text{S}_2\text{CN}^n\text{Bu}_2)_{12}]\text{PF}_6$ 和 $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ 反应,得到了含有0价Pd掺杂的铜氢簇 $[\text{PdCu}_{14}\text{H}_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_6(\text{C}\equiv\text{CPh})_6]^{[59]}$ 。如图4(h)所示,金属核 $\text{PdCu}_{14}\text{H}_2$ 的结构像双头二十面体,其中心被Pd占据。 PdH_2 以线性方式封装在 Cu_{14} 核中。二硫代磷酸酯配体中12个S与头顶和脚底的12个Cu配位,而6个 $\text{PhC}\equiv\text{C}^-$ 在簇的腰部配位。后来,他们用交换保护配体的方法又得到了 $[\text{Cu}_{15}\text{H}_2(\text{S}_2\text{CNR}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)(\text{R}: ^n\text{Bu}, ^i\text{Pr}, ^t\text{Bu})^{[60]}$,发现它们是双电子超原子 $[\text{Cu}_{13}(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_4]^+$ 的中间体。

2.2 炔配体保护的混合价铜(0)/铜(I)团簇

合成含有0价金属的团簇一直是本领域的难点。由于0价Cu的稳定性相比0价Au和Ag较差,所以合成稳定的含0价Cu团簇更加困难。迄今,仅有极少数量的含0价Cu配合物被报道。例如, Fischer课题组^[61-63]和Frenking课题组^[64]用 $\text{Cp}(\text{C}_5\text{H}_5)$ 、 $\text{Cp}^*(\text{C}_5\text{Me}_5)$ 和 $\text{cAAC}(\text{cyclic}(\text{alkyl})(\text{amino})\text{carbenes})$ 、环烷基-氨基卡宾得到了含0价Cu的配合物以及Cu-Zn、Cu-Au合金配合物、“Mackay”型团簇 $[\text{Cu}_{43}\text{Al}_{12}](\text{Cp}^*)_{12}$ 和 $[\text{Cu}(\text{cAAC})_2]$ 。Zheng课题

组^[65]在2014年得到了 $[\text{Au}_{12+n}\text{Cu}_{32}(\text{SR})_{30+n}]^{4-}(n=0, 2, 4, 6)$,含有部分0价Au和Cu。Hayton课题组^[66]在2015年合成得到了 $[\text{Cu}_{25}\text{H}_{22}(\text{PPh}_3)_{12}]\text{Cl}$,其中含有二十面体 Cu_{13} 核心,并且有两个0价Cu,紧接着在2016年^[67]用配体交换生长法得到了也有两个0价Cu的29核铜氢簇 $[\text{Cu}_{29}\text{Cl}_4\text{H}_{22}(\text{Ph}_2\text{phen})_{12}]^+$ 。而关于炔基配体保护的混合价铜(0)/铜(I)团簇的报道更少。

2016年, Liu课题组^[68]以 $[\text{Cu}_{28}\text{H}_{15}(\text{S}_2\text{CN}^n\text{Bu}_2)_{12}]\text{PF}_6$ 为铜源,合成了两个炔铜团簇 $[\text{Cu}_{13}(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CR})_4]\text{PF}_6(\text{R}: \text{CO}_2\text{Me}, 3\text{-FC}_6\text{H}_4)$,这是首次得到有炔基保护的混合价铜(0)/铜(I)团簇,其为双电子超原子团簇,核结构为 $[\text{Cu}_{13}]^{11+}$ 。如图5(a)所示,该类铜团簇的 $[\text{Cu}_{13}]^{11+}$ 核心具有立方八面体排列,且具有面心立方结构(FCC), T_d 对称性,不同于Hayton课题组^[66]在2015年报道的 $[\text{Cu}_{25}\text{H}_{22}(\text{PPh}_3)_{12}]\text{Cl}$,其核心为二十面体 Cu_{13} 。立方八面体 $[\text{Cu}_{13}]^{11+}$ 共有8个三角面,其中有4个以 μ_3 的形式被炔配体配位,6个矩形面的每个面都以 μ_2 的形式被 $\text{S}_2\text{CN}^n\text{Bu}_2^-$ 配体桥接。Jin课题组^[69-71]分离并结晶了非FCC结构的纳米团簇 $\text{Au}_{28}(\text{SPh-}t\text{-Bu})_{20}$ 和 $\text{Au}_{36}(\text{SPh-}t\text{-Bu})_{24}$,发现非FCC结构比FCC结构的立方体更稳定。Liu课题组^[72,73]以此 $[\text{Cu}_{13}]^{11+}$ 核结构为基础做了一些更系统的拓展研究。掺入Ag、Au元素合成了结构类似的双电子超原子 $\text{M}@\text{Cu}_{12}(\text{M}=\text{Ag}, \text{Au})$ 团簇^[72,73],它们具有以0价Ag或Au为中心的 Cu_{12} 立方八面体核,表现出不同的稳定性和光致发光性质。2018年, Hayton课题组^[38]报道了混合价的炔铜(I)团簇 $[\text{Cu}_{20}(\text{C}\equiv\text{CPh})_{12}(\text{CH}_3\text{COO})_6]$,具有罕见的 $[\text{Cu}_4]^{2+}$ 核结构。如图5(b)所示,它含有一个四面体的 $[\text{Cu}_4]^{2+}$ 核,被 $[\text{Cu}_{16}(\text{C}\equiv\text{CPh})_{12}(\text{CH}_3\text{COO})_6]^{2-}$ 壳包裹,壳上的12个炔配体排列成4个 $[\text{cyclo-Cu}(\text{C}\equiv\text{CPh})]_3$

图5 混合价炔铜(0)/铜(I)团簇晶体结构示意图。(a) $[\text{Cu}_{13}(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{C-C}(\text{O})\text{OMe})_4]^+$ 的结构^[68]; (b) $[\text{Cu}_{20}(\text{C}\equiv\text{CPh})_{12}(\text{CH}_3\text{COO})_6]$ ^[38]; (c) $[\text{Cu}_{23}(\text{BuC}\equiv\text{C})_{13}(\text{CF}_3\text{COO})_6]$ ^[74]。Cu, 橙色; S, 黄色; F, 绿色; O, 红色; N, 蓝色; C, 灰色

Figure 5 Structure of mixed-valence copper(0)/copper(I) alkynyl nanoclusters. (a) Structure of $[\text{Cu}_{13}(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{C-C}(\text{O})\text{OMe})_4]^+$; (b) $[\text{Cu}_{20}(\text{C}\equiv\text{CPh})_{12}(\text{CH}_3\text{COO})_6]$ ^[38]; (c) $[\text{Cu}_{23}(\text{BuC}\equiv\text{C})_{13}(\text{CF}_3\text{COO})_6]$ ^[74]. Cu, orange; S, yellow; F, green; O, red; N, blue; C, gray

单元, 位于四面体的顶点. Sun课题组^[74]2020年使用阶梯还原的策略成功合成了 $[\text{Cu}_{23}(\text{tBuC}\equiv\text{C})_{13}(\text{CF}_3\text{COO})_6]$ (记为SD/Cu23a). 如图5(c)所示, Cu_{23} 纳米团簇由 CF_3COO^- 和 $\text{tBuC}\equiv\text{C}^-$ 配体共同保护, 有一种罕见的 $[\text{Cu}_4]^0$ 四电子超原子内核. CF_3COO^- 配体在该团簇的头部和脚部配位, 而团簇的腰部全为 $\text{tBuC}\equiv\text{C}^-$ 配体配位. 在 CH_2Cl_2 中结晶得到的晶体为 $R3c$ 空间群, 而在 CHCl_3 中结晶得到 R 空间群, 前者由范德华力和 $\text{C-H}\cdots\text{F}$ 相互作用结晶, 而后者由分子间 $\text{C-H}\cdots\text{Cl}$ 相互作用结晶. 不同的溶剂可以改变该炔铜(I)纳米团簇的结晶模式, 使之呈现不同的空间群. 这种采用溶剂诱导结晶模式的策略为合成多种空间群的炔铜(I)纳米团簇提供了思路.

2018年, Zheng课题组^[39]采用阶梯还原的策略, 成功合成了一个高核的混合价铜(0)/铜(I)团簇 $[\text{Cu}_{53}(\text{CF}_3-$

$\text{COO})_{10}(\text{C}\equiv\text{C}^t\text{Bu})_{20}\text{Cl}_2\text{H}_{18}]^+$. 如图6(a), (b)所示, 该团簇的晶体结构可分为 $\text{Cu}_3@\text{Cu}_{10}\text{Cl}_2@\text{Cu}_{20}@\text{Cu}_{20}$ 的4层同心壳层结构, 簇核直径为11 Å. 该团簇具有同心的 M_{12} 二十面体和 M_{20} 十二面体壳层 $\text{Cu}_{10}\text{Cl}_2@\text{Cu}_{20}$, 这种结构对于Au/Ag纳米团簇相当常见. Cu_{53} 上的20个 $\text{tBuC}\equiv\text{C}^-$ 配体只显示两种不同的配位模式, 其中10个与壳层1、2上的铜以 $\mu_3-\eta^1$ 、 η^1 、 η^2 配位方式配位, 另外10个以 $\mu_4-\eta^1$ 、 η^1 、 η^1 、 η^2 的配位方式分别与壳层1和壳层3上的铜配位. 随后, Zhang课题组^[75]得到了3种含有 Cu^0 的炔铜团簇 $[\text{Cu}_{53}(\text{C}\equiv\text{CR})_9(\text{dppp})_6\text{Cl}_3(\text{NO}_3)_9]$ (R: PhPh, Ph, 4-FPh) (记为 Cu_{53} 、 $\text{Cu}_{53}\text{-H}$ 、 $\text{Cu}_{53}\text{-F}$), 这是首次观察到含有0价Cu的团簇的非FCC结构, 具有32个自由电子. 如图6(c), (d)所示, 53个Cu原子分为两类. 其中41个直接参与ABABC层的构建, 每个层分别包含6、7、12、10

图6 两种53核混合价炔铜(0)/铜(I)团簇晶体结构示意图. (a) $[\text{Cu}_{53}(\text{RCOO})_{10}(\text{tBuC}\equiv\text{C})_{20}\text{Cl}_2\text{H}_{18}]^+$ 的整体结构示意图^[39]; (b) $\text{Cu}_3@\text{Cu}_{10}\text{Cl}_2@\text{Cu}_{20}@\text{Cu}_{20}$ 框架的逐个壳层的结构示意图^[39]; (c) $[\text{Cu}_{53}(\text{C}\equiv\text{CR})_9(\text{dppp})_6\text{Cl}_3(\text{NO}_3)_9]$ 的整体结构及 Cu_{53} 中41个Cu原子的分层结构示意图^[75]; (d) 其中的三角形金字塔金属核 Cu_5 ^[75]. Cu, 橙色; F, 浅绿色; Cl, 深绿色; P, 紫色; O, 红色; N, 蓝色; C, 灰色

Figure 6 Structures of two 53-nuclear mixed-valence copper(0)/copper(I) alkynyl nanoclusters. (a) Total structure^[39] of $[\text{Cu}_{53}(\text{RCOO})_{10}(\text{tBuC}\equiv\text{C})_{20}\text{Cl}_2\text{H}_{18}]^+$; (b) shell-by-shell diagrams of the framework, $\text{Cu}_3@\text{Cu}_{10}\text{Cl}_2@\text{Cu}_{20}@\text{Cu}_{20}$ ^[39]; (c) total structure of $[\text{Cu}_{53}(\text{C}\equiv\text{CR})_9(\text{dppp})_6\text{Cl}_3(\text{NO}_3)_9]$ and layered structure of 41 Cu atoms in Cu_{53} ^[75]; (d) the triangular pyramid metal core Cu_5 ^[75]. Cu, orange; F, light green; Cl, dark green; P, purple; O, red; N, blue; C, gray

和6个Cu原子,最底部三角形层的堆叠方向与HCP结构相反.剩余的12个Cu原子与6个双齿dppp配体配位. Cu_{53} 的金属核心有5个Cu原子,形成三角形双金字塔构形.由 Cu^{2+} 到 Cu^+ 、 Cu^+ 和 Cu^0 混合物的价态变化的分析结果可以推断, NaBH_4 将部分 Cu^+ 还原为 Cu^0 ,而不是直接将 Cu^{2+} 还原为 Cu^0 .

2.3 模板构筑的炔铜(I)团簇

炔配体和 Cu^+ 反应极易生成难溶的聚合物,使得单种簇的合成和分离具有很大的挑战性.如前文所述, hfac^- 、 CF_3OO^- 、 NO_3^- 、 SO_4^- 和硫配体等桥连配体可以防止炔铜(I)团簇的聚集,有利于稳定团簇表面,合成较大的炔铜(I)团簇.而阴离子模板同样有利于构筑高核炔铜(I)团簇.Mak课题组^[21,37,76,77]在利用模板构筑的炔铜(I)团簇方面进行了系统的研究.他们利用具有丰富的末端氧原子和高电荷密度的缺位多氧阴离子作为模板^[76],模板离子有助于聚集更多的 Cu^+ ,通过 Cu^+-O 配位键诱导 Cu^+ 壳层的形成.类似于用模板法合成银

团簇^[78],研究得到了两个核数更高的炔铜(I)团簇: $[(\text{Mo}_4\text{O}_{16})@\text{Cu}_{33}(\text{BuC}\equiv\text{C})_{24}]\cdot\text{BF}_4$ 、 $[(\text{Mo}_4\text{O}_{16})@\text{Cu}_{33}]$ 和 $[(\text{Mo}_5\text{O}_{19})_2@\text{Cu}_{62}(\text{BuC}\equiv\text{C})_{34}(\text{MoO}_4)_2(\text{OTf})_2(\text{OH})_4]\cdot(\text{OTf})_2$ 、 $[(\text{Mo}_5\text{O}_{19})_2@\text{Cu}_{62}]$,其结构如图7(a),(b)所示.反应过程中, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ 在 H_2O 存在下分解成了 $\text{Mo}_4\text{O}_{16}^{8-}$ 和 $\text{Mo}_5\text{O}_{19}^{8-}$,其作为团簇核心也能有效地分散 Cu^+ 壳层上的正电荷分布.2019年,他们用归中反应加入 $\text{RC}\equiv\text{CH}$ (R: tBu , Pr)^[37],得到了2个15与28核炔铜(I)簇 $\text{Cu}_{15}^{\text{I}}$ 和 $\text{Cu}_{28}^{\text{I}}$,又尝试用 Na_3VO_4 和 tBuPO_3H_2 引入多氧钒酸盐模板,得到了2个高核混合价Cu(I)/Cu(II)纳米团簇 $\{[\text{Cu}^{\text{II}}\text{O}_6]@\text{Cu}_{47}^{\text{I}}(\text{PrC}\equiv\text{C})_{33}\}^{4+}$ 、 $[\text{Cu}^{\text{II}}\text{O}_6]@\text{Cu}_{47}^{\text{I}}$ 和 $[\text{Cu}^{\text{II}}\text{O}_4]\cdot[\text{VO}_4]_2@\text{Cu}_{46}^{\text{I}}(\text{BuC}\equiv\text{C})_{27}(\text{tBuPO}_3)_2(\text{H}_2\text{O})\}^{3+}$ 、 $[\text{Cu}^{\text{II}}\text{O}_4]\cdot[\text{VO}_4]_2@\text{Cu}_{46}^{\text{I}}$,如图7(c),(d)所示. Na_3VO_4 和 tBuPO_3H_2 反应生成了离子化合物 $[\text{V}_{10}\text{O}_{28}]_2\cdot[\text{H}_3\text{O}]_{12}$ 后,它将 Cu^0 原位氧化生成 Cu^{II} .中心 Cu^{II} 阳离子通过形成 $\text{Cu}^{\text{I}}-\text{O}-\text{Cu}^{\text{II}}$ 配位模式充当模板剂的作用. $[\text{Cu}^{\text{II}}\text{O}_4]\cdot[\text{VO}_4]_2@\text{Cu}_{46}^{\text{I}}$ 除了核中心有 Cu^{II} 阳离子,还有2个 $[\text{VO}_4]^{3-}$ 阴离子模板,金属核被27个 $\text{tBuC}\equiv\text{C}^-$ 配体和2个 tBuPO_3^{2-} 配体保护.

图7 基于多氧阴离子模板构筑的炔铜(I)纳米团簇的晶体结构示意图. (a) $(\text{Mo}_4\text{O}_{16})@\text{Cu}_{33}$ ^[76]; (b) $(\text{Mo}_5\text{O}_{19})_2@\text{Cu}_{62}$ ^[76]; (c) $[\text{Cu}^{\text{II}}\text{O}_6]@\text{Cu}_{47}^{\text{I}}$ ^[37]; (d) $[\text{Cu}^{\text{II}}\text{O}_4]\cdot[\text{VO}_4]_2@\text{Cu}_{46}^{\text{I}}$. Cu(I), 橙色; Cu(II), 浅蓝色; Mo, 深蓝色; V, 绿色; P, 紫色; S, 黄色; O, 红色; N, 深蓝色; C, 灰色

Figure 7 Structures of copper(I) alkynyl nanoclusters based on polyoxoanion templates. (a) $(\text{Mo}_4\text{O}_{16})@\text{Cu}_{33}$ ^[76]; (b) $(\text{Mo}_5\text{O}_{19})_2@\text{Cu}_{62}$ ^[76]; (c) $[\text{Cu}^{\text{II}}\text{O}_6]@\text{Cu}_{47}^{\text{I}}$ ^[37]; (d) $[\text{Cu}^{\text{II}}\text{O}_4]\cdot[\text{VO}_4]_2@\text{Cu}_{46}^{\text{I}}$ ^[37]. Cu(I), orange; Cu(II), light blue; Mo, dark blue; V, green; P, purple; S, yellow; O, red; N, dark blue; C, gray

Mak课题组^[21]在2001年发现, $\text{Me}_3\text{SiC}\equiv\text{CH}$ 可以断裂成乙炔离子($-\text{C}\equiv\text{C}-$), 其在 Cu_4 金属笼中起到模板剂的作用. 2017年, 他们又尝试使用异丙基乙炔($\text{Pr}-\text{C}\equiv\text{CH}$)作为炔配体前驱体^[77]. Cu^+ 的存在使 $\text{Pr}-\text{C}\equiv\text{CH}$ 在 80°C 时产生催化裂解, 从而得到 $-\text{C}\equiv\text{C}-$ 模板, 进一步聚集得到核数更大的炔铜(I)团簇. 如图8(a)~(d)所示, 他们通过此种方法得到了4种炔铜(I)团簇: 蝴蝶状的 $[(\text{C}\equiv\text{C})@(\text{Cu}_{24}(\text{PrC}\equiv\text{C})_{14}(\text{HCOO})_8)]((\text{C}\equiv\text{C})@(\text{Cu}_{24a}))$ 、马蹄形的 $[(\text{C}\equiv\text{C})@(\text{Cu}_{24}(\text{PrC}\equiv\text{C})_{13}(\text{CH}_3\text{COO})_9)]((\text{C}\equiv\text{C})@(\text{Cu}_{24b}))$ 、环状双层结构的 $[(\text{C}\equiv\text{C})_6@(\text{Cu}_{48}(\text{PrC}\equiv\text{C})_{24}(\text{CF}_3\text{COO})_{12})]$ 、 $[(\text{C}\equiv\text{C})_6@(\text{Cu}_{48})]$ 和目前核数最高的炔铜(I)团簇 $[(\text{C}\equiv\text{C})_{18}@(\text{Cu}_{92}(\text{PrC}\equiv\text{C})_{50}(\text{H}_2\text{O})_2(\text{NO}_3)_4)]\cdot(\text{NO}_3)_3((\text{C}\equiv\text{C})_{18}\text{Cu}_{92})$. 如图8(d), (f)~(h)所示, Cu_{92} 呈现复杂的多层结构, 其有一个晶体反转中心, 可以被视为由3个子结构组成. 子结构I为最上面的 Cu_5 单元. 子结构II是一个飞盘状的 Cu_{15} 单元, 由3个 $\text{C}_2@(\text{Cu}_7)$ 基序以边缘共享的方式融合而成. 子结构III是大三角形 Cu_{28} 单元, 由 Cu_{22} 同心圆环和环绕它的 Cu_6 组成. Cu_{22} 由3个 $\text{C}_2@(\text{Cu}_6)$ 和3个 $\text{C}_2@(\text{Cu}_7)$ 单元围绕伪 C_3 轴排列而成. 在上述4种晶体中观察到了多种 $-\text{C}\equiv\text{C}-$ 的配位方式, 显著丰富了 $-\text{C}\equiv\text{C}-$ 可同时作为保护配体和模板剂的晶体结构.

最近, 本课题组^[36]用1-磷酸萘基酯($1\text{-NaphOPO}_3\text{-H}_2$)和磷酸苯二钠($\text{PhOPO}_3\text{Na}_2$)成功合成了一维线性化合物 $[\text{Cu}_{16}(\text{BuC}\equiv\text{C})_{12}(\text{PhOPO}_3)_2]_n$ 和 $[\text{Cu}_{16}(\text{BuC}\equiv\text{C})_{12}(1\text{-NaphOPO}_3)_2]_n$. 磷酸酯配体起到桥连 Cu_{16} 簇基结构的作用. 通过引入模板前驱体 NH_4VO_3 得到了 $[\text{VO}_4@(\text{Cu}_{25}(\text{BuC}\equiv\text{C})_{19}(1\text{-NaphOPO}_3))](\text{VO}_4@(\text{Cu}_{25}))$, 以及在碱性条件下 $1\text{-NaphOPO}_3\text{H}_2$ 发生水解得到了 $[\text{PO}_4@(\text{Cu}_{25}(\text{BuC}\equiv\text{C})_{19}(1\text{-NaphOPO}_3))](\text{PO}_4@(\text{Cu}_{25}))$. 这两种炔铜(I)团簇具有相似的灯笼状结构, 如图8(e)所示. Cu_{25} 金属核上部 Cu_{12} 和下部 $\text{Cu}@(\text{Cu}_{12})$ 构成六方反棱镜, VO_4^{3-} 模板中的O采用 μ_7 配位模式将上、下两部分连接起来. 1-NaphOPO_3^{2-} 基团位于 Cu_{25} 金属核头顶部, 并且19个 $\text{BuC}\equiv\text{C}-$ 保护配体在 Cu_{25} 金属核的头部、腰部和底部配位.

$\text{Au}(\text{I})$ 、 $\text{Ag}(\text{I})$ 和 $\text{Cu}(\text{I})$ 都有相似的 d^{10} 价电子层排布, 意味着 $\text{Cu}(\text{I})$ 可以与 $\text{Au}(\text{I})$ 和 $\text{Ag}(\text{I})$ 共同构筑高核纳米团簇. Chen课题组^[79]和Williams课题组^[80]先后合成了十二面体笼状结构的 $[\text{Cl}@(\text{Ag}_8\text{Cu}_6(\text{C}\equiv\text{C}-\text{Fc})_{12})]\text{OH}$ 和 $[\text{Cl}@(\text{Ag}_8\text{Cu}_6(\text{C}\equiv\text{C}-\text{Bu})_{12})]\text{BF}_4$. 2016年, Mak课题组^[81]合成了9个炔基配体 $\text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ ($\text{R}: \text{Pr}, \text{Bu}, \text{chx}$)保护的铜银双金属纳米团簇, 呈笼型结构, 都具有三角平面的 CuAg_3 核心. Wang课题组^[82]合成了 $[\text{Au}_{19}\text{Cu}_{30}(\text{C}\equiv\text{CR})_{22}(\text{Ph}_3\text{P})_6\text{Cl}_2](\text{NO}_3)_3$ ($\text{R}: 3\text{-SC}_4\text{H}_9$ 或 Ph), 这是一个具有22个自由电子的超原子团簇. 炔基配体配位到该纳米团簇表面 Ph_3P 剩余的空位上. 它有多层“俄罗斯套娃”结构 $\text{Au}@(\text{Au}_{12}@(\text{Cu}_{30}@(\text{Au}_6)))$, 包括中心二十面体 $\text{Au}@(\text{Au}_{12})$ 、二十面体 Cu_{30} 和椅子状六边形 Au_6 外壳, 与Zhu课题

组^[83]合成的 $[\text{Ag}_{19}\text{Cu}_{30}(\text{C}\equiv\text{CR})_{22}(\text{Ph}_3\text{P})_6\text{Cl}_2](\text{NO}_3)_3$ 类似. 该团簇具有22个自由电子, 符合 $2N+1$ 规则 ($N=11$), 是一个具有22个自由电子的超原子团簇. 炔基配体配位到该纳米团簇表面 Ph_3P 剩余的空位上. 它有多层“俄罗斯套娃”结构 $\text{Au}@(\text{Au}_{12}@(\text{Cu}_{30}@(\text{Au}_6)))$, 包括中心二十面体 $\text{Au}@(\text{Au}_{12})$ 、二十面体 Cu_{30} 和椅子状六边形 Au_6 外壳, 与Zhu课题

图8 基于 $-\text{C}\equiv\text{C}-$ 模板构筑的炔铜(I)纳米团簇的晶体结构示意图^[77]. (a) $(\text{C}\equiv\text{C})@(\text{Cu}_{24a})$; (b) $(\text{C}\equiv\text{C})@(\text{Cu}_{24b})$; (c) $(\text{C}\equiv\text{C})_6@(\text{Cu}_{48})$; (d) $(\text{C}\equiv\text{C})_{18}@(\text{Cu}_{92})$; (e) $\text{VO}_4@(\text{Cu}_{25})$; (f) $(\text{C}\equiv\text{C})_{18}@(\text{Cu}_{92})$ 的金属核结构(f)、子结构II(g)和III(h). Cu, 橙色; V, 绿色; P, 紫色; O, 红色; N, 深蓝色; C, 灰色. Figure 8 Structures of copper(I) alkynyl nanoclusters based on $-\text{C}\equiv\text{C}-$ template^[77]. (a) $(\text{C}\equiv\text{C})@(\text{Cu}_{24a})$; (b) $(\text{C}\equiv\text{C})@(\text{Cu}_{24b})$; (c) $(\text{C}\equiv\text{C})_6@(\text{Cu}_{48})$; (d) $(\text{C}\equiv\text{C})_{18}@(\text{Cu}_{92})$; (e) $\text{VO}_4@(\text{Cu}_{25})$; (f) $(\text{C}\equiv\text{C})_{18}@(\text{Cu}_{92})$ the core structure (f), substructure II (g) and III (h) of $(\text{C}\equiv\text{C})_{18}@(\text{Cu}_{92})$. Cu, orange; V, green; P, purple; O, red; N, dark blue; C, gray

组^[83]合成的 $[\text{Ag}_{61}\text{Cu}_{30}(\text{SAdm})_{38}\text{S}_3](\text{BPh}_4)$ 结构类似. 2019年, Sun课题组^[84]合成了 $[\text{Ag}_{74-x}\text{Cu}_x\text{O}_{12}(\text{PhC}\equiv\text{C})_{50}]$ (平均 $x=37.9$). 金属核内封装了12个间隙 $\mu_4\text{-O}^{2-}$, 作用与阴离子模板类似, 均匀地填充在2个扭曲的 Cu_4 四面体中, 诱导了 Cu^{I} 和 Ag^{I} 的聚集.

3 炔铜(I)团簇的性质及应用

金属纳米团簇提供了与更小的原子、分子和更大的金属纳米颗粒之间的联系^[85]. 对于单核金属配合物, 它们的电子结构与配体和溶剂密切相关^[86]. 然而, 对于金属纳米团簇和金属纳米粒子, 由于金属原子之间的电子轨道重叠, 情况变得更加复杂. 当金属纳米团簇的原子数增加到 >40 时, HOMO和LUMO之间的带隙变得比单核金属配合物的带隙小. 对于较大的金属纳米颗粒, 将形成连续的能级^[87]. 因此, 它们的性质也会随着粒径的变化而变化. 经过多年的研究, 铜纳米团簇凭借这种特殊的能级分布, 展现出丰富的光学、催化和电学性质. 此外, 由于铜金属储量丰富, 铜团簇在光致发光材料、催化剂、生物传感器、生物成像剂和电子器件方面有着广泛的应用^[88-90]. 而原子精确的炔铜(I)团簇有助于理解结构和性质之间的关系, 有利于探讨性质的机理和制定改进的策略. 下文分别讨论了炔铜(I)团簇的光致发光、化学催化和电学性质.

3.1 光致发光性质

炔铜(I)团簇的光致发光来源主要是因为电荷的转移, 包括金属到配体的电荷转移(metal-to-ligand charge transfer, MLCT)和配体到金属中心的电荷转移(ligand-to-metal charge transfer, LMCT)两种过程. $\text{Cu}(\text{I})$ 的 d^{10} 外电子层构型避免了 $d-d$ 跃迁, 因此, 以配体为中心的LUMO可以参与金属到配体的电荷转移过程. 虽然纳米团簇光致发光的量子产率比较低, 但是其性质可以通过多种方法进行调整, 例如聚集诱导发射^[91,92]、合金化金属核^[93,94]和更换保护配体^[95,96]. 因此, 研究铜纳米团簇的光致发光性质与应用是很有价值和意义的. Yam课题组^[13-19]在1996年对炔基配体保护的 Cu_3 和 Cu_4 团簇的光致发光性质做了比较系统的研究. 近几年, 具有光致发光性质、原子精确的高核炔铜(I)团簇陆续被报道. Sun课题组^[55,56]合成了 $^t\text{BuC}\equiv\text{C}^-$ 和 CF_3COO^- 保护的14、15和16核炔铜(I)团簇, 虽然3种团簇核数相近, 但保护配体和核结构的不同可以调控荧光的发射峰. 14核炔铜(I)团簇在室温下的固体荧光发射以580 nm为

中心, 而15和16核炔铜(I)团簇在近红外区域显示出独特的热致变色发光. 将温度从298 K冷却至93 K后, 前者的发射峰在710~793 nm之间单调红移, 荧光增强17倍, 而后者分别在273~123和123~93 K范围内显示异常的红移和蓝移发射. 这些14、15和16核炔铜(I)团簇的近红外荧光发射谱带可暂定为自旋禁止的 $^3\text{LMCT}$ ($^t\text{BuC}\equiv\text{C}^- \rightarrow \text{Cu}_x$)激发态, 其中混合了受亲铜相互作用扰动的团簇中心(^3CC)特征. 另外, 通过杂金属的掺杂可以提高铜(I)团簇的量子产率. Liu课题组^[72,73]将Au掺杂到 $[\text{Cu}_{13}(\text{S}_2\text{CN}^n\text{Bu})_6(\text{C}\equiv\text{CPh})_4]^+$ 的核心, 在MeTHF溶液中77 K时有高达59%的量子产率.

模板剂的引入也能调控团簇的荧光发射. 2016年, Mak课题组^[76]通过归中反应得到了4个炔铜(I)团簇. 当激发波长 $\lambda>330$ nm时, 观察到簇合物 Cu_{17} 和 Cu_{18} 的最大发射集中在约700 nm处. POM模板与 $\text{Cu}(\text{I})$ 的配位可能影响了来自 $^3\text{LMCT}$ ($^t\text{BuC}\equiv\text{C}^- \rightarrow \text{Cu}_n$)的激发态, $(\text{Mo}_4\text{O}_{16})\text{-@Cu}_{33}$ 和 $(\text{Mo}_5\text{O}_{19})_2\text{@Cu}_{62}$ 分别在680和670 nm处出现发射蓝移. Mak课题组^[77]又得到4个高核炔铜(I)团簇, 2个24和48核炔铜(I)团簇具有独特的热致变色发光性质. 2019年, Mak课题组^[37]合成了炔铜(I)团簇 $\text{Cu}_{15}^{\text{I}}$ 和 $\text{Cu}_{28}^{\text{I}}$, 都表现出热致变色发光性质. $\text{Cu}_{15}^{\text{I}}$ 随温度升高而显著蓝移, 而 $\text{Cu}_{28}^{\text{I}}$ 仅表现出10 nm的蓝移.

具有手性光学活性的贵金属簇在处于激发电子态下可能会产生圆偏振发光(circularly polarized luminescence, CPL), 这在加密信息传输和存储、手性材料及生物编码方面具有潜在应用. Zang课题组^[97]利用含有炔基和苯基官能团的手性配体来获得了原子精确、在室温下具有CPL性能的 $\text{Cu}(\text{I})$ 炔基纳米团簇 R/S-Cu_{14} . 如图9所示, 含有 R/S-Cu_{14} 的纯 CH_2Cl_2 溶液不具有光致发光性质. 随着正己烷浓度的增加, R/S-Cu_{14} 表现出明显的聚集诱导增强效应(aggregation-induced emission, AIE). 结晶态的 R/S-Cu_{14} 簇显示出强烈的红色发射, 以及来自其手性激发电子态的CPL性能. R/S-Cu_{14} 簇的AIE和结晶诱导增强效应(crystallization-induced emission, CIE)触发了其CPL信号. 他们又将这些纳米团簇的AIE效应进一步应用于HeLa和NG108-15细胞的成像, 表现出良好的生物相容性. 这些发现揭示了铜团簇发光和手性的起源, 并为CPL活性金属簇开辟了一条新途径.

本课题组^[36]在2021年用1-磷酸萘基酯(1-NaphO- PO_3H_2)和磷酸苯二钠($\text{PhOPO}_3\text{Na}_2$)合成了一维线性化合物 $[\text{Cu}_{16}(^t\text{BuC}\equiv\text{C})_{12}(\text{PhOPO}_3)_2]_n$ 与 $[\text{Cu}_{16}(^t\text{BuC}\equiv\text{C})_{12}(1-$

图9 R/S- Cu_{14} 团簇的晶体结构示意图和光学性质^[97]. (a) R/S- Cu_{14} 团簇的合成过程与在结晶状态和溶液中的手性光学性能的示意图; (b) 镜面对称的R/S- Cu_{14} 金属框架; (c) R- Cu_{14} 在不同浓度的正己烷溶液中的荧光照片($f = \text{vol}_{\text{正己烷}} / \text{vol}_{\text{正己烷} + \text{二氯甲烷}}$); (d) R- Cu_{14} 的发射光谱

Figure 9 Structures and optical properties of R/S- Cu_{14} nanoclusters^[97]. (a) Synthesis of the desired R/S- Cu_{14} nanoclusters and illustration of the chiroptical properties of R- Cu_{14} nanoclusters in the crystalline state and in solution; (b) the metal frameworks in R/S- Cu_{14} with mirror symmetry; (c) fluorescence photographs of R- Cu_{14} in solutions with different fractions of n-hexane ($f = \text{vol}_{\text{n-hexane}} / \text{vol}_{\text{n-hexane} + \text{DCM}}$); (d) emission spectra of R- Cu_{14}

$\text{NaphOPO}_3)_2]_n$. 通过引入模板又得到了 $\text{VO}_4@ \text{Cu}_{25}$ 和 $\text{PO}_4@ \text{Cu}_{25}$. 通过比较溶液态、非晶态和晶态的发光强度,发现这4种化合物存在结晶诱导增强效应,可归因于分子之间的萘基或苯环基团的 $\text{C}-\text{H} \cdots \pi$ 和 $\pi \cdots \pi$ 相互作用.

3.2 化学催化性质

铜基纳米材料已被证明能够催化多种化学反应,包括N-和O-芳基化、叠氮炔环加成反应(“Click”反应)、硝基酚还原、CO和乙醇氧化等^[98-100]. 1981年, Sneed课题组^[101]首次报道了原子精确的铜(I)团簇 $[\text{HCuPPh}_3]_6$ 用于催化还原 CO_2 . 近年来,铜纳米团簇的快速发展已经产生了一批新型预催化剂^[102,103]. Che课题组^[48]、Zhu课题组^[104]、Yam课题组^[105]、Wang课题组^[106]、Zhang课题组^[107]和Liu课题组^[24]等都发现了铜纳米团簇可用于多种催化反应,并且具有良好的催化性能和稳定性.

最近,炔基配体稳定的Cu(I)纳米团簇被发现可用于叠氮炔环加成(Cu^{I} -catalyzed azide-alkyne cycloaddition, CuAAC, 即“Click”反应)等反应的催化. 2015年, Straub课题组^[108]合成了具有辅助N-杂环卡宾(NHC)配体和丙炔酸乙酯($\text{C} \equiv \text{C}-\text{CO}_2\text{Et}$)的保护的炔铜(I)团簇

Cu_8 . 在 -5°C 的 CD_2Cl_2 中,用0.4%(mol)和1.2%(mol)的 Cu_8 催化丙炔酯与叠氮苄酯的CuAAC反应,10 min之内即可完成反应,具有很高的活性. NHC作为辅助配体配位Cu对反应性双核乙炔中间体的电子和空间稳定性至关重要. 阻碍热力学聚集促进了有机叠氮化物底物的配位和转化. 炔配体保护的混合价铜(0)/铜(I)团簇也表现出优异的催化性能. 2018年, Hayton课题组^[38]合成了含有0价铜的20核炔铜团簇,发现将该团簇固定在二氧化硅上可以高效催化CuAAC反应,转化率超过90%. 与未固定的簇相比,经二氧化硅固定的簇在催化前和催化后都没有大的结构变化. 这项研究首次证明了原子精确的有机配体保护的金属纳米团簇在催化过程中可以保持其结构的完整性. Zhang课题组^[75]合成的3种含有 Cu^0 的炔铜团簇 Cu_{53} 、 $\text{Cu}_{53}-\text{H}$ 和 $\text{Cu}_{53}-\text{F}$ 有非常好的稳定性. 催化CuAAC反应的结果表明, $\text{Cu}_{53}-\text{F}$ 相对于 Cu_{53} 和 $\text{Cu}_{53}-\text{H}$ 表现出更高的转化率,10 h内转化率和选择性均高达99%以上. 其原因可能与晶体结构中赤道位置上的 NO_3^- 和 CH_3COO^- 被位阻更小的 Cl^- 取代有关,使团簇表面暴露出更多的活性位点,进而使催化性能提升. 更好地了解炔铜(I)团簇的晶体结构为开发更有效的CuAAC催化剂奠定了基础.

3.3 电学性质

目前,关于炔铜(I)纳米团簇电学性质的研究尚处于起步阶段.2018年,Zheng课题组^[39]成功合成了一个53核的混合价铜(0)/铜(I)团簇(ZNF/Cu_{53}),其高度溶于 Et_2O ,有助于在固体基材(例如钙钛矿)上快速组装形成高质量的纳米团簇膜,如图10(a)~(c)所示.通过在室温下将 Cu_{53} 薄膜碘化原位生成 CuI 薄膜,用其作为空穴传输层,得到的钙钛矿型太阳能电池具有14.3%的光电转换效率.2019年,Mak课题组^[37]合成了 $\text{Cu}^{\text{I}}_{15}$ (记为1)、 $\text{Cu}^{\text{I}}_{28}$ (记为2)、 $[\text{Cu}^{\text{II}}\text{O}_6]@\text{Cu}^{\text{I}}_{47}$ (记为3)和 $[\text{Cu}^{\text{II}}\text{O}_4]_2@ \text{Cu}^{\text{I}}_{46}$ (记为4),将它们的块状晶体样品制备成颗粒,并夹在Cu和Al电极之间,以制造用于测量的器件,如图10(d),(e)所示.1和2表现出介电常数约为5.0的频率无关的介电行为,其对应于低介电态,且为绝缘体.相反,3和4对100 Hz的频率有着高介电常数,且是热激活半导体,它们的电导率与具有中等电导率的半导体Cu(II)材料相当.微量的Cu(II)作为掺杂剂,可以改变Cu(I)纳米团簇的电学性质.引入的Cu(II)触发了从Cu(I)到Cu(II)的价间电荷转移(interval charge transfer, IVCT),使它们具有半导体的电学性质.

用一定频率的光照射到金属纳米团簇上,若光子的能量等于或大于该团簇的禁带宽度,则价带中的电子吸收光子后进入导带,产生电子-空穴对.由于团簇

具有不同的电特性以及光子能量的差异,会产生不同的光电效应.如果给具有这类性能的团簇施加一定电场,在超过一定频率的光照下会有与结构相关的电流产生^[109~111].2020年,Sun课题组^[112]用Hpzt(吡嗪-2-硫醇)合成了一系列铜(I)团簇基聚合物,具有良好的光致发光和光生电流性质.同时,他们报道的23核四电子超原子炔铜(I)团簇 SD/Cu_{23a} ^[74]在50 W、420 nm光照和0.6 V的偏置电场作用下,具有良好的光生电流性质,如图10(f)所示.2021年,本课题组^[36]合成的 $\text{VO}_4@\text{Cu}_{25}$ 和 $\text{PO}_4@\text{Cu}_{25}$,在0.5 V的偏置电场作用下,在不同波长的光照下,表现出不同的光生电流响应.

4 结语与展望

炔配体保护的金属铜(I)纳米团簇材料是连接原子尺度和纳米颗粒尺度的重要桥梁之一,也是团簇化学的重要研究领域.结合本课题组近期的工作,本文总结了原子精确的炔铜(I)团簇材料的几种常用合成方法:溶剂热法、还原法、模板法和配体交换法.根据路易斯酸碱理论选择合适的保护配体降低团簇的表面能,以及控制反应动力学过程,对于成功获得单分散的炔铜(I)团簇十分重要.现阶段已经报道的原子精确的炔铜(I)团簇可归纳为3个部分:(1)炔配体和含有O、S的配体可以共同保护炔铜(I)团簇,能有效降低团簇的表面能,提高团簇的稳定性;(2)还原剂的加入可以获得

图 10 炔(I)铜团簇具有的部分电学性质. ZNF/Cu_{53} (a)和 CuI (b)在钙钛矿薄膜上的器件结构与横截面的扫描电子显微镜(SEM)图像^[39]; (c) CuI 基钙钛矿太阳能电池的能级图^[39]; (d) 制造用于介电和电气测量的电子器件^[37]; (e) 在室温下记录的1~4的频率相关介电常数^[37]; (f) SD/Cu_{23a} 的光电流响应^[74]

Figure 10 Partial electrical properties of copper(I) alkynyl nanoclusters. Device structure and cross-sectional SEM image of ZNF/Cu_{53} (a) and CuI (b) on perovskite films^[39]; (c) energy-level diagram of CuI -based perovskite solar cell^[39]; (d) fabrication of an electronic device for dielectric and electrical measurements^[37]; (e) frequency-dependent dielectric constants of 1–4 recorded at room temperature^[37]; (f) photocurrent responses of SD/Cu_{23a} ^[74]

含有0价铜的超原子结构, 展现出独特的性质; (3) 阴离子模板剂不仅能平衡团簇的电荷分布还有多种配位方式, 能获得结构更新、体积更大的炔铜(I)团簇. 综述原子精确的炔铜(I)团簇能更好地理解结构-性质的关系, 深入理解光致发光、化学催化和电学等性质与晶体结构的关系便于探索它们的应用领域. 尽管在研究炔铜(I)团簇材料的合成和性质方面取得了显著进展, 但探索它们合适的应用领域仍有很大的发展空间. 比如, 充

分利用结晶诱导发光、聚集诱导发光和圆偏振发光机理来提升发光性能; 引入磁性元素来构筑单分子磁体; 引入小位阻配体提高团簇表面未占有率进而提升化学催化性能; 研究混合价铜(0)/铜(I)团簇的电化学性能. 在未来关于炔铜(I)团簇的研究应该发挥出金属铜储量、价格低、生物相容性好等优势. 最后, 我们相信, 基于对构筑原子精确的铜(I)团簇材料的研究会制备出更多的新型纳米材料, 必将展现广阔的发展前景.

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Summary for “炔铜(I)纳米团簇的合成、结构规律与光电性质”

Synthesis, crystal structures and photoelectric properties of copper(I) alkynyl nanoclusters

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Metal nanoclusters (NCs) are composed of several to thousands of metal atoms with a diameter of < 3 nm. Such metal NCs exhibit dramatically unique electronic/geometric structures and physical/chemical properties which differ from those of bulk metal materials. Among metal NCs, coinage metal (Au, Ag, and Cu) NCs have received extensive attention because of their chirality, optical and catalytic properties. Cu is more abundant than Au and Ag, yet copper(0)/copper(I) is more reactive and easier to oxidize than silver or gold, which makes it more difficult to prepare Cu NCs and investigate their properties. By taking guidelines from Au and Ag NC research, thiolate, phosphine, and alkynyl ligand-protected Cu NCs have recently received increasing attention. Alkynyl ligands have more abundant coordination modes compared to thiolate and phosphine ligands. Some copper(I) alkynyl NCs with unique crystal structures, good stability and rich properties have been recently reported. Herein, firstly, this paper introduces recent advances in developing efficient synthetic methods for copper(I) alkynyl NCs, highlighting the underlying physical and chemical properties that make the delicate control of their sizes and surfaces possible. The synthesis of copper(I) alkynyl NCs can be roughly classified into four categories: Solvothermal, reduction, template, and ligand exchange. Generally, the steric effect of the introduced protective ligand breaks their polymeric structures and improves solubility. Some copper(I) alkynyl NCs can also be produced by adjusting the auxiliary ligands and anionic templating agents. In addition, the concentration of ligands and precursors, pH and temperature of the reaction system can be used to adjust the reaction kinetics, and this leads to the formation of the monodisperse copper(I) alkynyl NCs. Secondly, we discuss recent advances in the structural determination of copper(I) alkynyl NCs, of which the size and shape can be controlled to a certain extent by the judicious choice of templating anions and auxiliary ligands. The atomically precise nature of their structures enables the investigation of the structure-property relationship, which may further optimize their performance. One of the most important properties of copper(I) alkynyl NCs is the luminescence, which offers potential applications as photoelectric detectors and in sensing and bio-imaging. We highlight some examples of copper(I) alkynyl NCs to demonstrate their photoelectric properties. Finally, the brief conclusion and outlook on the research and challenges of copper(I) alkynyl NCs are presented. We expect this review will serve as an introduction and reference for researchers who are interested in exploring metal NCs.

metal nanoclusters, copper alkynyl nanoclusters, crystal structure, photoluminescence

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