

功能超分子配合物化学与材料中Salamo/Salen类体系的构筑与性能研究进展

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摘 要

Salamo/Salen类配体因具有可设计的多齿配位空腔、较好的结构可调性以及优异的光学响应性能, 已成为功能超分子配合物化学与材料研究中的重要构筑单元。相较于传统salen体系, Salamo/half-salamo/bis(Salamo)及其杂化衍生物通过引入氧肟键显著提升了配体稳定性, 并进一步拓展了不对称配体、柔性链桥和多腔体结构的构筑空间。近年来, 相关研究已从单纯的配位结构报道发展到多核与异核组装、超分子弱相互作用调控、荧光/比色识别、理论计算辅助解析及环境与生物应用等多个层面。本文结合已提供文献, 对Salamo/Salen类体系的结构演化、同核和异核多核配合物的构筑规律、阴离子/溶剂/辅助配体的结构导向作用、荧光识别与多通道响应机制、DFT/TD-DFT与Hirshfeld表面分析在机理研究中的作用以及试纸、水样、植物和斑马鱼等实际应用进行了系统综述。总体来看, 该类体系在结构可设计性、功能集成性和应用可拓展性方面显示出明显优势, 但在普适构效关系建立、纯水体系稳定性、生物相容性和器件化等方面仍存在进一步提升空间。本文最后对该领域未来向多功能集成、原位可视化检测、智能响应材料和更高层级超分子体系发展的趋势进行了展望。

关键词

Salamo类配体, Salen类配体, 超分子配合物, 荧光识别, 多核配合物

Progress in the Construction and Properties of Salamo/Salen-Based Systems in Functional Supramolecular Coordination Chemistry and Materials

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Abstract

Salamo/Salen-type ligands, with their designable multidentate coordination cavities, excellent structural tunability, and superior optical response properties, have emerged as crucial building blocks in the chemistry and materials research of functional supramolecular complexes. Compared to traditional salen systems, Salamo/half-salamo/bis(Salamo) and their hybrid derivatives significantly enhance the stability of the ligands by introducing hydroxamate bonds, further expanding the construction space for asymmetric ligands, flexible chain bridges, and multi-cavity structures. In recent years, related research has evolved from the mere reporting of coordination structures to multiple levels, including polynuclear and heteronuclear assembly, regulation of supramolecular weak interactions, fluorescence/colorimetric recognition, theoretical calculation-assisted analysis, as well as environmental and biological applications. Based on the published literatures, this paper systematically reviews the structural evolution of Salamo/Salen-based systems, the construction rules of homonuclear and heteronuclear polynuclear complexes, the structure-directing effects of anions/solvents/auxiliary ligands, the mechanisms of fluorescence recognition and multi-channel response, the roles of DFT/TD-DFT and Hirshfeld surface analysis in mechanistic studies, as well as their practical applications in test papers, water samples, plants, and zebrafish. Overall, these systems exhibit obvious advantages in structural designability, functional integration, and application expandability. However, there remains room for further improvement in the establishment of universal structure-activity relationships, the stability in pure water systems, biocompatibility, and device fabrication. Finally, the paper prospects the future development trends of this field towards multi-functional integration, *in-situ* visualization detection, intelligent responsive materials, and higher-level supramolecular systems.

Keywords

Salamo-Type Ligands, Salen-Type Ligands, Supramolecular Complexes, Fluorescent Recognition, Polynuclear Complexes

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1. 引言

Schiff 碱配体尤其是 salen 类配体由于具有稳定的 N_2O_2 配位腔体、较为简便的合成路径以及良好的金属络合能力, 长期以来在配位化学、催化、发光和磁性材料等领域占据重要位置。然而, 传统 salen 体系中的 $C=N$ 键具有一定可逆性, 在潮湿条件下易发生交换与水解, 从而限制了不对称配体、长链柔性配体以及高稳定性功能体系的进一步发展[1]-[3]。

以 Akine 等提出的 salamo 体系为代表, 研究者通过在 salen 骨架中引入 O-alkyl oxime 单元, 有效降低了 $C=N$ 键的交换活性, 使配体对亚胺复分解的抵抗能力显著增强, 从而为稳定构筑不对称配体和多腔体配体奠定了基础[1], 随后, salamo-like、half-salamo、bis(salamo)、single-armed salamo 以及 salamo-salen-salamo、salamo-salophen 等杂化骨架不断涌现, 配体从单一四齿体系逐渐发展为双腔体、三腔体乃至开放冠醚样多配位点体系[4][5]。从已提供文献可以看出, 这一类体系的研究重点已经由“能否形成配合物”逐步转向“如何通过结构设计获得特定核数、特定金属组合、特定光学响应与特定应用场景”。一方面, 同核二核、三核、四核和六核配合物不断被报道; 另一方面, 3d-3d、3d-s 和 3d-4f 异核体系借助不同金

属离子的尺寸匹配和硬软酸碱差异, 构筑出具有独特几何构型和功能特征的超分子配合物。此外, 阴离子、溶剂和辅助配体对组装路径的导向作用、Hirshfeld 表面与 DFT 计算对弱相互作用和电子结构的解释, 也使这一方向呈现出鲜明的结构-性能耦合特征[6]-[12]。

基于上述背景, 本文拟围绕 Salamo/Salen 类体系的结构演化、配位组装规律、荧光识别与功能材料表现、理论分析方法和应用前景展开综述, 以期为后续在功能超分子配合物化学与材料领域中的设计与应用提供参考[13]-[47]。

2. Salamo/Salen 类体系的结构演化与配体设计

从分子骨架上看, Salamo/Salen 类体系的发展实质上体现为配体稳定性、腔体多样性和功能耦合能力的同步提高。经典 salen 配体以 N,N'-disalicylideneethylenediamine 及其衍生物为代表, 其优势在于 N₂O₂ 配位腔体构型清晰、反应路径成熟。但当研究者试图进一步引入不同取代基以构建不对称配体, 或希望通过柔性桥链构筑更高层级的多核体系时, 传统 C=N 键的可逆性就会导致配体重排和组分混杂。

Salamo 配体的提出有效解决了这一矛盾。O-alkyl oxime 结构的引入显著提高了配体对亚胺交换的抵抗能力, 使其在水/有机混合体系中仍然保持较高稳定性。相关基础研究显示, salamo 配体及其中间体 monooxime 对 C=N 交换表现出远高于对应 salen 体系的稳定性, 为不对称配体和多位点配体的可控合成提供了可能。这一点也是后续 half-salamo、bis(salamo)和杂化 salamo-salen-salamo 体系得以迅速发展的根本原因[1] [4]。

在具体配体设计方面, 当前文献主要呈现以下几类趋势。第一, 对称与非对称设计并行发展。对称 bis(salamo)配体有利于构筑中心对称的二核或四核体系, 而非对称 salamo-like 配体则更容易产生不同金属位点、不同配位模式以及差异化的荧光响应。第二, 链长与柔性可调。通过将桥链由乙撑延长至丙撑, 或引入萘环、喹啉、吡啶、茚等芳香片段, 可明显改变配体刚柔程度和分子共轭程度, 从而影响金属进入特定空腔的倾向以及最终组装体的光物理性质。第三, 功能基团耦合增强。带有甲氧基、卤素、二乙氨基、苄基和喹啉等取代基的配体, 不仅改变了供体原子的电子性质, 也同时提供了潜在的荧光发色团、电子给受体单元或弱相互作用位点[2] [3] [5]。

随着配体结构不断复杂化, 研究者逐步实现了从单腔体到多腔体、从封闭 N₂O₂ 位点到 N₃O、O₆ 乃至冠醚样开放位点的转变。这样的结构演化使不同半径、不同硬度的金属离子能够在同一配体骨架中被选择性容纳, 为多核和异核功能配合物的定向组装提供了前提[6]-[10]。

3. 多核与异核功能配合物的构筑规律

对于 Salamo/Salen 类体系而言, 金属离子、配体骨架和反应条件之间的协同匹配, 是决定最终核数与几何构型的关键因素。从已报道成果来看, 同核二核和四核体系是最常见的结构类型。例如 Ni、Co、Cu 和 Zn 等过渡金属常进入 N₂O₂ 腔体形成二核或四核配合物; 当桥联乙酸根、甲氧基、卤离子或辅助配体参与时, 可进一步形成更高核数的簇合物或配位聚合物[4] [11] [12] [14]-[16] [20]-[23] [27] [28] [33] [36]-[39] [45] [48]。

同核体系的一个重要特征是: 金属中心的几何构型往往并非单纯由金属种类决定, 而是与配体柔性、阴离子类型以及溶剂分子是否参与配位密切相关。以 Ni(II)和 Cu(II)体系为例, 文献中同时出现了扭曲八面体、四方锥、三角双锥以及双螺旋中心对称结构等多种构型。这说明在 Salamo 类多腔体配体中, 局部供体环境和桥联方式的微小差异足以改变整体核数和空间堆积方式[4] [11] [12] [14] [16] [36] [38] [45]。

异核体系是该类研究更具特色的部分。通过将 Cu(II)、Zn(II)等 3d 金属置于 N₂O₂ 腔体, 而将 Ca(II)、Sr(II)、La(III)、Ce(III)、Pr(III)等较大半径离子引入 O₆ 或冠醚样位点, 可以获得 3d-s 或 3d-4f 异核三核体

系。典型例子包括 $[\text{Cu}_2\text{Ln}]$ 、 $[\text{Zn}_2\text{Ln}]$ 和 $[\text{Cu}_2\text{Ca/Sr}]$ 等配合物。这些体系中,不同金属离子的选择性定位不仅来源于离子半径差异,也与氧亲和性、阴离子桥联模式和空腔柔性密切相关。相比同核体系,异核配合物更容易表现出丰富的光学和超分子行为,因此在功能材料方向具有更高潜力[6]-[10] [35]。另一个值得重视的规律是反应条件对组装路径的深刻影响。许多文献显示,同一配体在不同金属盐、不同阴离子或不同溶剂环境中,可能分别形成二核、三核、四核乃至一维链状配位聚合物。也就是说,Salamo/Salen 类体系的组装并非静态结果,而是对“配体-金属-阴离子-溶剂-辅助配体”多变量耦合的动态响应。正因如此,该类体系非常适合作为研究可控自组装和结构调控策略的模型平台[4] [6] [7] [14] [16] [19]-[23] [27] [35] [37] [38]。

4. 阴离子、溶剂与辅助配体的结构导向作用

在 Salamo/Salen 类功能配合物中,阴离子并不只是电荷补偿单元,往往直接参与配位组装并主导核数与拓扑结构的形成。乙酸根是最常见的桥联阴离子之一,它既可以以单齿或双齿方式与金属配位,也可以桥联相邻金属中心,从而促进二核、三核或四核结构的生成。硝酸根、 NCS^- 、 Cl^- 等阴离子则常通过改变配位数、端位/桥联模式和立体位阻,显著影响金属中心的几何构型与组装产物[14] [16] [28] [30] [37] [38] [40]。

相关研究中,“counteranion-driven self-assembly”与“counteranion-solvent-dependent construction”已成为高频主题。同一配体与 Zn(II) 或 Ni(II) 反应时,若使用 OAc^- 、 NO_3^- 、 NCS^- 或 Cl^- 等不同阴离子,往往会得到完全不同的构筑结果。某些体系中,阴离子甚至能够诱导金属由扭曲三角双锥转变为扭曲四方锥,或者由离散多核体系延伸为一维聚合链。这种现象说明阴离子既影响局部配位平衡,也参与决定最终超分子堆积[14] [16] [19] [27] [28] [37] [39] [40]。

溶剂效应同样不可忽视。甲醇、乙醇、DMF、DMSO 或氯仿等溶剂不仅会影响配体溶解性和反应动力学,而且经常直接作为端位配体占据金属轴向位点,从而改变金属中心配位数和空腔刚柔程度。某些四核 Ni(II) 或 Cu(II) 体系中,溶剂分子与 acac^- 、 OAc^- 共同参与配位,显著提升了结构复杂性并诱导形成三维氢键网络[4] [14] [22] [37]。

辅助配体则为配位聚合物和功能性组装提供了新的设计手段。通过引入 4,4'-联吡啶、1,4-di(pyridin-4-yl)benzene 等桥联配体,可以将原本离散的 salamo-like 金属配合物扩展为一维链状或锯齿状配位聚合物,并由此赋予体系对硝基酚、重铬酸根、硫离子等客体的高效荧光识别能力。从构筑学角度看,阴离子、溶剂和辅助配体三者共同构成了 Salamo/Salen 类体系实现结构精细调控的重要抓手[21] [23]。

5. 超分子组装特征与弱相互作用

除了一级配位键之外,Salamo/Salen 类体系中的超分子弱相互作用也是稳定结构和调控性能的重要因素。从大量结构报道可知,氢键、 $\pi\cdots\pi$ 堆积、 $\text{C-H}\cdots\pi$ 相互作用、卤素相关作用乃至 lone pair- π 作用,常共同决定晶体堆积方式和超分子维度。许多离散二核或三核配合物在晶体中通过 $\text{C-H}\cdots\text{O}$ 、 $\text{O-H}\cdots\text{O}$ 、 $\text{C-H}\cdots\text{N}$ 等相互作用进一步拓展为一维链、二维层或三维网络[4] [6] [7] [11]-[13] [15] [21] [22] [27] [28] [35] [36] [38] [45]。

对于含芳香片段的配体,如萘环、喹啉、茈基或双芳环桥链, $\pi\cdots\pi$ 堆积往往格外显著。这些相互作用不仅增加了晶体稳定性,也可能影响激发态能量转移和荧光强度。某些单臂或半 salamo 体系中,卤素取代基和芳环的存在进一步增强了分子间堆积,使配体或配合物在聚集态中表现出与溶液态不同的光谱响应。例如部分 AIE 或聚集增强型体系,就是通过抑制分子内运动与促进分子间有序堆积来获得更强发光表现[15] [28] [31] [41] [44]。

值得注意的是,许多文献已不再满足于定性描述“存在氢键或 π 堆积”,而是采用 Hirshfeld 表面、二维指纹图谱、IRI 和 ESP 等方法对弱相互作用进行定量或可视化分析。借助这些理论和图谱手段,研究者能够明确指出 $\text{H}\cdots\text{H}$ 、 $\text{H}\cdots\text{O}$ 、 $\text{H}\cdots\text{C}$ 等接触在晶体堆积中的贡献比例,并识别潜在亲电/亲核位点,从而使“结构-堆积-性能”的联系更加清晰[4] [6] [7] [13]-[15] [20]-[22] [27] [28] [36]-[38] [40] [45]。

因此,从功能超分子材料的角度来看,Salamo/Salen 类配体及其配合物的价值不仅体现在一阶配位结构的多样性,更体现在其通过弱相互作用进一步演化为更高层级有序结构的能力。这种能力为发光材料、识别材料和响应材料的设计提供了广阔空间[4] [6] [7] [11]-[15] [20]-[23] [27] [28] [35]-[38] [45]。

6. 光学性质与荧光识别性能

荧光和比色响应是目前 Salamo/Salen 类体系最活跃的研究方向之一。与许多传统识别分子相比,这类体系具有两个突出优点:其一,配体骨架易于引入电子给体、电子受体和芳香发色团;其二,金属离子进入配位腔后能够显著改变分子的电荷分布、构象自由度和能级结构,因此易产生灵敏而直观的光谱变化[2] [3] [5] [17]-[19] [24]-[26] [29]-[34] [41]-[50]。

从识别对象看, Cu^{2+} 和 Fe^{3+} 是最常见的阳离子靶标。这与两者在环境与生命体系中的重要性以及它们对荧光的强猝灭效应有关。大量文献报道了对 Cu^{2+} 、 Fe^{3+} 、 Zn^{2+} 、 Ni^{2+} 、 Al^{3+} 、 Hg^{2+} 等离子的识别,其中 Cu^{2+} 体系往往表现为明显的荧光猝灭和/或可见颜色变化,而 Zn^{2+} 、 Al^{3+} 等则更容易产生荧光增强或蓝移、红移响应。除金属离子外, H_2PO_4^- 、 PO_4^{3-} 、 HPO_4^{2-} 、 S^{2-} 、 ClO^- 、 SCN^- 、 HSO_4^- 、 $\text{B}_4\text{O}_7^{2-}$ 和 $\text{Cr}_2\text{O}_7^{2-}$ 等阴离子,以及谷氨酸、精氨酸、甲醛等小分子和氨基酸,也在近年来成为重要识别目标[2] [3] [5] [17]-[20] [24]-[26] [29]-[34] [41]-[50]。就识别模式而言,Salamo/Salen 类体系已从单信号识别拓展到双通道识别、继电式识别和比率型识别。一类典型策略是“on-off-on”顺序识别:配体先与某金属离子结合导致荧光猝灭,再通过目标阴离子或硫醇对金属的竞争作用或置换作用实现荧光恢复,从而完成二次识别。另一类策略是比率型识别,即通过发射峰位或双峰强度比的变化,提高抗干扰能力和结果可靠性。对于需要现场可视检测的应用场景,这些策略尤其重要[2] [5] [18] [24] [26] [30] [31] [42] [43] [47]。

在机制层面,LMCT、ICT、PET、CHEF、FRET、ESIPT 和 AIE 等概念几乎贯穿全部研究。对过渡金属而言,配位常导致配体到金属电荷转移增强,或者因顺磁性引起荧光猝灭;对 Al^{3+} 、 Zn^{2+} 等非顺磁离子,则往往通过抑制分子内转动或促进刚性化而增强发光。对于引入两个发色团的体系,FRET 可通过能量供受体距离与谱带重叠实现颜色和峰位变化;对于具有聚集态响应特征的单臂或半 salamo 体系,AIE 则为温度、pH 和离子多刺激响应提供了新的实现途径[2] [3] [5] [18] [24] [26] [29]-[31] [41]-[43] [47]-[50]。

总体而言,Salamo/Salen 类体系已逐步形成“结构设计-配位作用-能级调节-信号输出”的较为清晰的工作链条,这也是其能够在功能识别材料方向快速发展的根本原因[2] [3] [5] [17]-[20] [24]-[26] [29]-[34] [41]-[50]。

7. 理论计算在结构与性能研究中的作用

随着体系复杂度提升,单靠实验表征已经难以完整解释结构形成原因与荧光响应机制。因而,DFT、TD-DFT、Hirshfeld 表面分析、ESP 和 IRI 等理论方法在 Salamo/Salen 类研究中被广泛引入,并逐渐成为论文中的“标准配置”[4] [6] [7] [13] [14] [20] [22] [27] [29]-[31] [36]-[38] [41]-[45]。

其中,DFT 最常用于比较配体与配合物的 HOMO/LUMO 能级分布、能隙大小和电荷分布特征。通过前线轨道分析,研究者可以判断配位后电子云主要集中于发色团、供体位点还是金属中心,并据此解释荧光增强、猝灭或峰位移动的来源。TD-DFT 则进一步帮助理解电子跃迁类型、吸收峰归属和激发态变化,对于说明 FRET、ICT 和 CHEF 等机制尤其重要[4] [6] [7] [13] [14] [20] [22] [27] [29]-[31] [36]-[38] [41]-[45]。

[41]-[45]。

ESP 和 MEP 分析主要用于寻找识别反应的潜在活性位点。对于阴离子识别体系,通过静电势分布可以较好地预测哪个酚羟基、氧肟氮或芳香取代基更容易参与结合;对于多金属自组装体系,静电势分析也有助于理解不同金属在不同空腔中的选择性进入行为。IRI 分析则在揭示弱相互作用方面优势突出,能够可视化显示氢键、范德华接触、 π 堆积等相互作用区域,并与晶体结构分析形成互补。需要指出的是,这些理论方法的真正价值不在于“增加计算部分”,而在于搭建实验现象和分子层面机制之间的桥梁。当理论结果与晶体学、光谱学和滴定实验形成一致证据链时,Salamo/Salen 类体系的结构构筑和识别机理便能得到更可靠的解释。今后随着计算资源和模型精度提升,理论方法将在该方向发挥更加核心的指导作用[4] [6] [7] [13] [14] [20] [22] [24]-[26] [29]-[31] [36]-[38] [41]-[43]。

8. 实际应用与功能材料前景

从目前文献发展趋势看,Salamo/Salen 类体系已经明显超出“结构化学展示”的范畴,而逐步向可应用的功能材料方向推进。最直接的应用是试纸与便携检测。许多荧光探针可通过浸渍纸条或薄膜实现肉眼可见的颜色/荧光变化,从而用于 Cu^{2+} 、 Fe^{3+} 、 H_2PO_4^- 等离子快速现场检测。与大型仪器相比,这种方式成本低、操作简单,更适合环境监测与教学示范。进一步的发展是实际样品检测。已有研究将相关探针用于实际水样、饮料、肉类或鱼类提取液中 Cu^{2+} 、 $\text{B}_4\text{O}_7^{2-}$ 、 HCHO 和其他污染物的检测,并取得较好的回收率和抗干扰表现。这表明 Salamo/Salen 类识别材料并非只能在理想溶液体系中工作,而具备一定复杂基质适应能力[2] [5] [23]-[26] [44] [50]。

在生物和类生物应用方面,部分体系已被拓展到植物、斑马鱼和细胞成像。如针对 H_2PO_4^- 、 Al^{3+} 等目标的探针已用于豆芽、绿豆芽、斑马鱼乃至 HeLa 细胞中的荧光观察。这类研究虽然仍处于探索阶段,但已经显示出 Salamo/Salen 类体系在活体或半活体可视化监测方面的潜力。尤其是通过引入大共轭片段、提升水相稳定性和降低细胞毒性后,该类探针有望在环境毒物追踪和生物过程监测中发挥更大作用[41]-[43] [50]。

此外,配位聚合物和多核金属簇也使 Salamo/Salen 类体系在光学材料、催化前体和多响应材料领域具有进一步延展空间。未来若能在结构可控、自组装可放大和器件界面兼容等方面取得突破,其在功能超分子材料中的应用广度仍将持续增加[21]-[37]。

9. 存在问题与发展趋势

尽管 Salamo/Salen 类体系发展迅速,但从领域整体看仍存在若干共性问题。首先,多数研究仍停留在“新配体-新结构-新响应”的案例累积阶段,尚未形成足够清晰、可迁移的构效关系模型。例如,桥链长度、取代基电子效应、金属半径和阴离子类型分别如何定量影响核数、发射峰位和识别灵敏度,仍缺少系统归纳[35]-[45]。

其次,许多光谱识别工作仍依赖高比例有机溶剂体系,这在环境与生物应用中会限制实际可用性。尤其是面向活体成像和复杂水环境时,体系的纯水稳定性、背景荧光干扰、离子强度适应性和长期储存稳定性都需要进一步提高。第三,理论计算虽被普遍采用,但在部分研究中仍偏向“结果佐证”,尚未充分发挥前瞻性设计作用。若能将理论预测前移至配体设计阶段,将更有利于形成高效开发模式[29]-[50]。

面向未来,本文认为该方向可重点沿以下路径推进:一是构建更明确的结构-组装-性能数据库,推动由经验式设计走向规则化设计;二是发展更适合纯水或弱有机体系工作的探针和配合物,提高环境与生物适用性;三是加强多功能集成,通过将发光、识别、催化、磁性和自组装行为耦合,获得真正意义上的智能响应材料;四是推动器件化和场景化应用,如柔性试纸、薄膜传感层和可视检测平台;五是结

合原位表征和多尺度理论模拟, 进一步揭示该类体系在自组装与响应过程中的动态机制[29]-[43]。

10. 结论

Salamo/Salen 类体系以其优良的配体稳定性、灵活的多腔体结构设计能力以及显著的结构 - 性能耦合效应, 已经成为功能超分子配合物化学与材料研究中的重要分支。本文基于已提供文献梳理了该类体系从骨架演化、金属组装、超分子作用、荧光识别、理论分析到实际应用的发展脉络。可以看到, 该类体系的核心竞争力在于: 既能通过多位点、多金属和多阴离子的协同作用构筑丰富的配位结构, 又能借助电子结构调控实现可视化和多通道功能输出。

总体而言, Salamo/Salen 类体系正处于由“结构报道驱动”向“功能设计驱动”和“应用牵引驱动”过渡的阶段。随着更加稳定的水相体系、更明确的构效规律和更高效的应用平台不断建立, 该类体系在环境检测、生物成像、智能响应材料和高层级超分子功能材料等方向具有广阔前景[1]-[50]。

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