

亚磷酸锌结构单元调节的配位聚合物磷光寿命

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摘要 磷光凭借其独特的光学特性在生物成像、传感器、信息存储等众多领域展现出巨大应用潜力, 而对磷光寿命的精准调控是拓展其实际应用的关键。配位聚合物因结构可设计性强、组成灵活等优势, 成为构建可调变磷光材料的理想平台。本文选取可塑性优异的双齿柔性配体1,4,-二(咪唑-1-亚甲基)苯(BIMB), 通过巧妙调节合成原料的配比, 成功设计并合成了两例结构迥异的配位聚合物 $[\text{Zn}(\text{BIMB})_{0.5}(\text{HPO}_3) \cdot \text{H}_2\text{O}](\mathbf{1})$ 和 $[\text{Zn}(\text{BIMB})_{0.5}(\text{HPO}_3)](\mathbf{2})$, 其分别以链状和层状亚磷酸锌为无机构筑单元。借助稳态/瞬态荧光光谱仪对这两例化合物的光致发光性质进行了系统表征, 并结合精确解析的单晶结构深入分析了其构效关系。实验结果清晰表明, 从一维链到二维层, 刚性的亚磷酸锌结构单元可有效调变柔性配体BIMB的构型, 并限制其振动、转动, 抑制非辐射衰减, 从而将磷光寿命从几毫秒显著延长至百毫秒级, 实现1~2个数量级的调控幅度。该研究不仅揭示了无机构筑单元维度和拓扑结构对磷光寿命的关键调控作用, 也为通过晶体工程策略理性设计具有长寿命磷光的配位聚合物材料提供了新的思路与扎实的结构基础。

关键词 配位聚合物, 溶剂热合成, 柔性配体, 室温磷光

室温磷光(RTP)材料因其微秒到秒级发光寿命, 近十年在信息存储^[1-3]、化学传感^[4,5]、生物成像^[6,7]及防伪加密^[8,9]等领域展现出广阔应用前景。磷光源于三重激发态的辐射衰变, 通常需在低温(如77 K)或惰性气氛下观察, 这严重限制了其应用^[10-12]。早期的RTP研究主要集中在具有重原子效应的铱、铂等贵金属的配合物上。然而, 这类材料通常存在成本高、衰变时间短(仅几十微秒)及环境欠友好等局限^[13-15]。因此, 开发平价、长寿命、环保型RTP材料意义重大。由 d^{10} 构型过渡金属(如 Zn^{2+} 、 Cd^{2+} 、 Cu^+ 、 Ag^+ 等)构筑的金属有机配位聚合物凭借其结构可设计性强、构筑单元丰富、易于引入重原子效应以及刚性框架抑制非辐射跃迁等优势,

已成为构筑高效室温磷光材料的理想平台^[16-20]。其金属节点可发挥重原子效应促进三重态激子生成, 而刚性骨架及其间丰富的分子间相互作用则能有效稳定三重态激子^[21-24], 为构筑长寿命、高量子产率的室温磷光材料体系提供了坚实基础。

在晶体工程领域中, 水/溶剂热条件下, 亚磷酸与金属锌离子共组装可形成零维簇、一维链、二维层等多种结构单元, 可实现对有机配体多样的空间限域^[25-29]。常用配体多为芳香刚性分子, 近年来, 基于柔性配体构筑的配位聚合物逐渐引起人们的关注。一般将分子中至少含有一个 sp^3 杂化原子(通常是C、N或O), 且连接金属的基团可以绕着 sp^3 杂化的原子进行旋转的配体称

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为柔性配体^[30]。与刚性配体相比, 柔性配体在不同结构单元的限定下可形成更为丰富的构型/构象, 配体结构的多样性势必影响着聚合物中分子内/间的相互作用^[31,32]。这些作用力(如氢键、 π - π 堆积、卤键等)共同构筑了刚性微环境^[33~36]。一方面, 能有效限制分子振动和转动, 抑制非辐射能量耗散。另一方面, 特定的分子间作用模式可能创造新的磷光通道。对这类亚磷酸锌结构单元限定的柔性配体结构及对配位聚合物磷光性质调节的构效关系的研究, 不仅有助于深化对激发态过程的认识, 更能为具有长寿命、高磷光量子产率的磷光材料的设计合成提供重要的理论依据和实现路径, 推动其在先进光电技术中的应用。

基于前述设计理念, 本研究选用柔性的1,4-二(咪唑-1-亚甲基)苯(BIMB)作为有机发光配体。该配体具有良好的构象可塑性。通过将BIMB引入至不同投料比的亚磷酸锌溶剂热合成体系, 利用金属配位驱动的空间限域效应, 成功实现了柔性配体的构型调控, 制备出两种新型亚磷酸锌基配位聚合物 $[\text{Zn}(\text{BIMB})_{0.5}(\text{HPO}_3)_2 \cdot \text{H}_2\text{O}]$ (1)和 $[\text{Zn}(\text{BIMB})_{0.5}(\text{HPO}_3)]$ (2), 并详细研究了它们的微观结构与发光性质间的关联。

1 实验

1.1 材料和试剂

合成中使用的试剂和溶剂均为市售产品, 未经进一步纯化即直接使用。

1.2 数据采集及测试仪器

在Mo-K α 射线($\lambda = 0.71073 \text{ \AA}$)下, 用XtaLAB-mini衍射仪在293(2) K下采集了两种配位聚合物的晶体学数据。采用SHELX-2016软件对结构进行解析。采用Cu-

K α 1射线($\lambda = 1.54076 \text{ \AA}$), 在飞利浦X'Pert-MPD衍射仪上采集粉末X射线衍射(PXRD)数据。荧光、磷光光谱由日立F-4700光谱仪测量。在配备氙弧灯(Xe900)、微秒闪光灯(uF2)和皮秒脉冲二极管激光器(EPL-280)的爱丁堡FLS920光谱仪上测量了时间分辨衰减光谱。紫外-可见吸收光谱在普析TU-1901分光光度计上测定。

2 结果与讨论

2.1 配合物1和2的结构表征

配合物1的单晶XRD分析确认其在 $P2(1)/n$ 空间群中结晶。结构解析显示, 其基本结构单元包含一个 Zn^{2+} 离子、一个 $[\text{HPO}_3^{2-}]$ 基团、半个BIMB配体分子以及一个晶格水分子(图1(a))。中心 Zn^{2+} 离子呈现 $[\text{ZnNO}_3]$ 四面体配位模式, 由一个来自BIMB分子的氮原子和三个来自不同 $[\text{HPO}_3^{2-}]$ 基团的氧原子配位。结构中, $\text{Zn}-\text{N}$ 键长为 $2.001(6) \text{ \AA}$, $\text{Zn}-\text{O}$ 键长范围为 $1.905(5) \sim 1.951(5) \text{ \AA}$, $\text{P}-\text{O}$ 键长为 $1.509(5) \sim 1.526(5) \text{ \AA}$ 。BIMB配体的构型分析表明, 其咪唑环与中心苯环的平面夹角 79.96° , 苯环所在平面近乎垂直平分连接其对位的两个咪唑环(图S1(a))。 HPO_3^{2-} 四面体通过O原子与 $[\text{ZnNO}_3]$ 四面体交替连接形成 $[\text{Zn}_2(\text{HPO}_3)_2]$ 四元环, 该四元环进一步连接, 形成一维的 $[\text{Zn}(\text{HPO}_3)]_n$ 链状结构(图1(b))。链与链通过 Zn^{2+} 离子与BIMB配体两端的咪唑N原子配位连接, 形成如图1(c)所示的二维层状结构。

单晶结构解析确定配合物2归属为 $P2(1)/c$ 空间群。其基本结构单元由一个 Zn^{2+} 离子、一个 $[\text{HPO}_3^{2-}]$ 基团以及半个BIMB配体分子构成(图2(a))。中心 Zn^{2+} 离子同样呈现 $[\text{ZnNO}_3]$ 四面体几何构型。该配位环境由一个来自BIMB配体的N原子和三个来自 $[\text{HPO}_3^{2-}]$ 基团的O原子提供。相关键长数据如下: $\text{Zn}-\text{N}$ 键长为 $2.002(2) \text{ \AA}$;

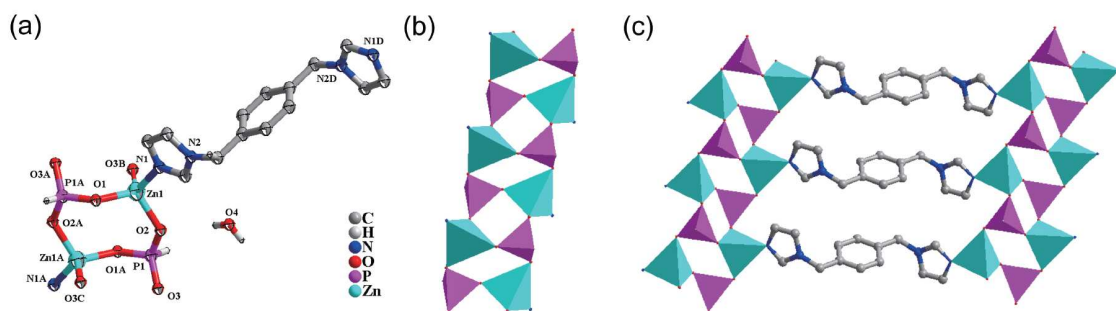


图1 (网络版彩色)配合物1的结构。(a) 不对称单元; (b) 一维亚磷酸锌链; (c) 二维层状结构

Figure 1 (Color online) Structure of complex 1. (a) Asymmetric unit; (b) 1D zinc phosphite chain; (c) 2D layer structure

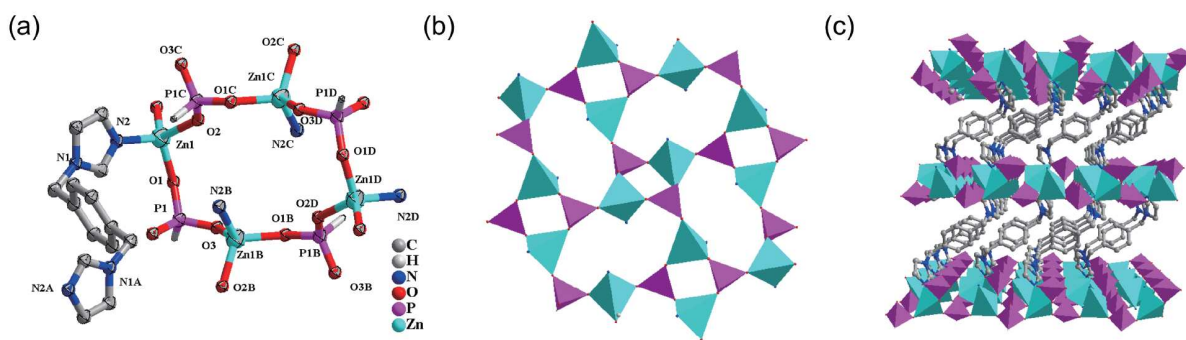


图2 (网络版彩色)配合物2的结构. (a) 不对称单元; (b) 二维亚磷酸锌层; (c) 三维柱-层结构

Figure 2 (Color online) Structure of complex 2. (a) Asymmetric unit; (b) 2D zinc phosphite layer; (c) 3D pillar-layer structure

Zn—O键介于1.915(2)~1.944(2) Å之间; P—O键在1.501(2)~1.516(2) Å范围内. 在结构上(图2(b)), 4个[ZnNO₃]四面体单元与4个以P原子为中心四面体单元交替连接, 共同构筑成一个八元环结构. 相邻的八元环之间通过共享顶点O原子相互连接, 最终形成一种由四元环和八元环交替排列的二维无机层状网络. BIMB配体通过其咪唑基团的N原子与上述亚磷酸锌层中的Zn²⁺离子配位, 从而起到“柱撑”作用, 将相邻的二维层连接起来, 最终组装成三维的“柱-层”(pillar-layer)框架结构(图2(c)).

值得关注的是, 与配合物1相比, 配合物2中的BIMB配体构象发生显著变化. 两个咪唑环分布于中心苯环所在平面上下两侧, 且咪唑环平面与苯环平面间的夹角减小至75.22°(图S1(b)). 虽然1和2分子组成上只相差一分子水, 但其结构有较大差异, 配合物1为二维层状结构, 而配合物2为三维柱层结构. 根据文献报道, 水/溶剂热合成配位聚合物过程中, 结晶水可通过配位竞争直接调控次级结构单元的结构, 并通过晶格填充及氢键作用间接调控晶体的拓扑与堆积^[37,38], 晶体结构的变化势必影响柔性配体BIMB的构型, 进而影响分子内及分子间的相互作用, 最终可能对其发光性能产生影响. 配合物1和2的详细晶体学参数汇总于表S1, 完整的键长键角数据请参见表S2和S3. 两者的PXRD图如图S2所示, 实验谱图与基于各自单晶结构模拟得到的谱图高度吻合, 表明了两种配合物为纯相.

2.2 配合物1和2的光致发光性质探究

配合物1和2在室温环境中的即时光谱和延迟光谱表明, 二者均展现出独特的兼具激发依赖与不依赖的发射特征. 其中, 配合物1(图3(a))在300 nm处存在与激

发波长无关的恒定荧光峰, 同时可见位于400 nm处一个小肩峰; 另一发射区域则具有显著的激发依赖性, 当激发波长从320 nm增至420 nm时, 其发射峰值由400 nm红移至480 nm(图3(c)). 类似地, 2在300 nm处也表现为不依赖激发波长的恒定发射峰和位于400 nm处的小肩峰, 但其激发依赖发射区的红移范围较1稍宽: 在相同的激发波长变化下, 发射峰从390 nm移动至480 nm(图S3(a), (c)). 二者的延迟发射光谱与即时光谱表现相似, 均同时包含波长恒定的发射峰和随激发红移而同步红移的发射区域(图3(b)和S3(b)). 激发波长小于300 nm时, 磷光发射峰恒定于480 nm左右, 当激发光从320 nm逐渐增至400/420 nm时, 1的磷光峰由520 nm红移至570 nm, 伴随余辉颜色从青绿色渐变至黄色; 2的磷光发射则从525 nm的绿色偏移至580 nm的橙色(图3(d)和图S3(d), S4). 配合物2的激发和发射范围较1有所红移.

为探究配合物1和2的发光来源, 测试了配体BIMB溶于DMF的稀溶液的发射光谱, 如图S5所示, BIMB在260 nm紫外光激发下呈现出分别位于300 nm和400 nm的双发射峰, 与配位聚合物1和2的发光很接近, 表明两例配合物位于300 nm(伴有400 nm肩峰)的恒定发射源于有机配体BIMB. 当激发波长为310 nm时, BIMB的发射峰出现在340 nm, 随着激发波长红移至370 nm, BIMB呈现出分别位于407、430、458 nm的一组发射峰, 与两例配合物的发光很不同, 表明1和2的激发依赖的发光并不只来源于BIMB, 推测其可能源于亚磷酸中含有孤对电子的氧原子与BIMB发生的电荷转移. 紫外-可见吸收光谱如图S6所示, 在约240~300 nm(配合物2稍红移至320 nm)处表现出强吸收带, 可归因于配体内[$\pi \rightarrow \pi^*$]跃迁; 在约300~400 nm(配合物2为

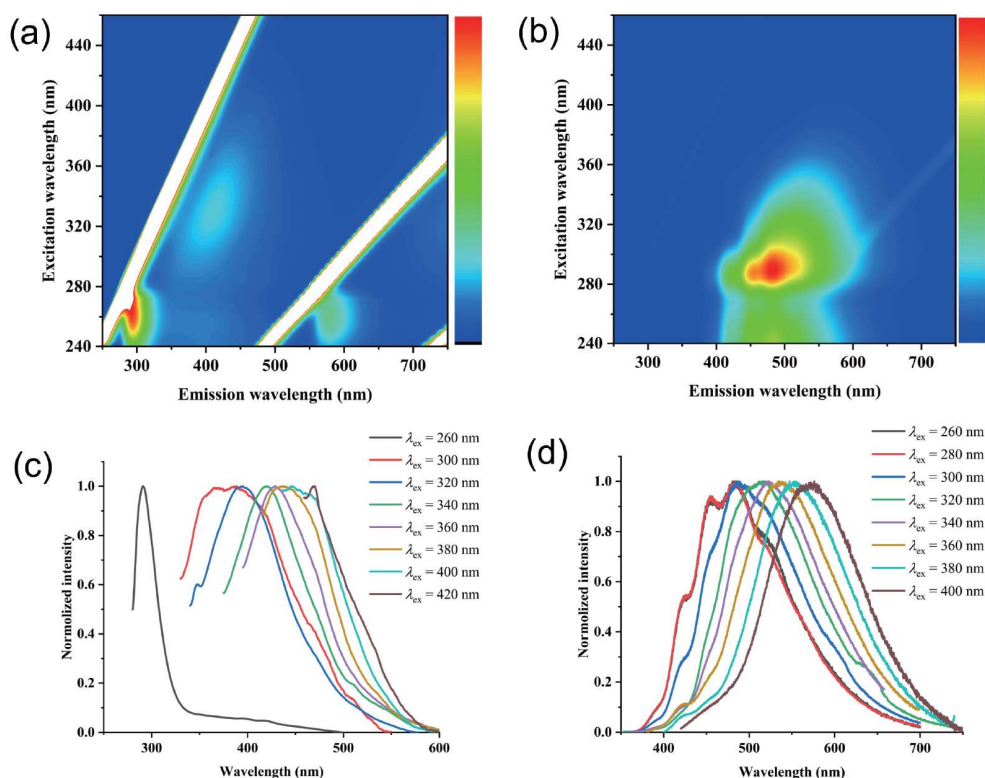


图3 (网络版彩色)配合物1的光谱表征。(a) 三维即时光谱及(c) 相应激发波长下的荧光发射光谱; (b) 三维延迟光谱及(d) 相应激发波长下的磷光发射光谱。三维光谱中发光强度由蓝到红依次增强

Figure 3 (Color online) Spectroscopic characterization of complex **1**. (a) 3D prompt spectra and (c) corresponding fluorescence emission spectra under the marked excitation wavelengths. (b) 3D delayed spectra and (d) corresponding phosphorescence emission spectra under the marked excitation wavelengths. The luminous intensity increases successively from blue to red

320~450 nm)处表现出中等强度的肩峰, 可归因于亚磷酸的氧到配体电荷转移跃迁, 与前述激发依赖的发光归属相符。

为了进一步探究无机结构单元对配位聚合物发光性质的影响, 采用时间分辨技术记录了两例配合物发光的动态衰减曲线。有趣的是, 虽然**1**和**2**的荧光、磷光发射波长很相似, 它们的荧光寿命也相近, 但在不同发射波长处的磷光寿命却有着明显的区别。图S7和S8为两例聚合物的荧光衰减曲线, 表S4列出了相应拟合的寿命数值。**1**和**2**的荧光衰减曲线在300和400 nm处均符合双指数函数拟合, 二者的各寿命组分的寿命值 τ 和相应的相对振幅 B 均相近, 由此计算出的平均寿命也相仿, 300 nm处分别为1.12和1.17 ns; 400 nm处分别为2.10和2.56 ns, 配合物**2**的荧光寿命略长于**1**。**1**和**2**在450、520和550 nm处的磷光衰减曲线和拟合结果如图4和表1所示, 均符合双指数函数拟合。以二者在450 nm处的磷光寿命为例, 拟合都得到一短一长两个寿命组

分: 其中**1**的较短的寿命 $\tau_1 = 1.4$ ms($B_1 = 77\%$), 较长的寿命 $\tau_2 = 17.7$ ms($B_2 = 23\%$), 平均寿命 $\tau_{\text{avg}} = 5.1$ ms。**2**的较短的寿命 $\tau_1 = 24.1$ ms($B_1 = 42\%$), 较长的寿命 $\tau_2 = 360.8$ ms($B_2 = 58\%$), 平均寿命 $\tau_{\text{avg}} = 219.4$ ms。配合物**2**的磷光寿命较**1**提升了2个数量级。图S9所示为两例配合物在254 nm紫外光激发下的荧光及余辉照片。

为理解配合物**1**和**2**磷光寿命的差异, 对其结构进行了详细的分析(图1, 2和5)。亚磷酸锌结构单元的不同(**1**中为一维链, **2**中为二维层)及在空中的排列方式导致两例配位聚合物分别为二维层状结构和三维柱层结构, 其中配体BIMB采取完全不同的两种构型, 分别为“一”字形和“S”型(图S1)。同时**1**和**2**中存在全然不同的分子内/分子间相互作用。如**1**中C—H $\cdots\pi$ 为2.91 Å(124.31°)、3.51 Å(151.05°)、3.68 Å(129.35°); C—H $\cdots$ N的距离为3.70 Å(121.59°)、3.99 Å(132.72°); C—H $\cdots$ O为2.56 Å(149.39°)、2.92 Å(148.47°)和3.10 Å(108.05°)。**2**中C—H $\cdots\pi$ 为3.13 Å(128.88°);

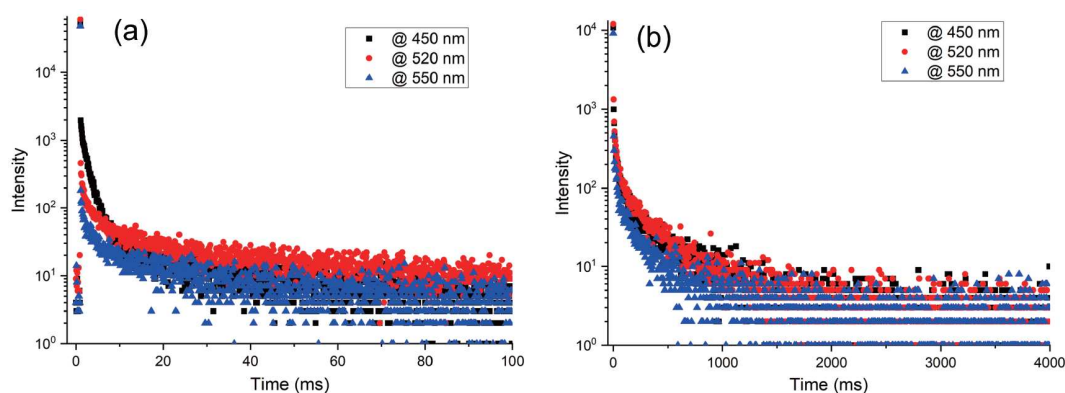


图 4 (网络版彩色)配合物1(a)和2(b)在标记的发射波长下的磷光衰减曲线

Figure 4 (Color online) Phosphorescence decay curves of complexes 1 (a) and 2 (b) at denoted excitation wavelengths

表 1 配合物1和2在不同发射波长下拟合的磷光寿命

Table 1 Fitting parameters of time-resolved phosphorescence decay traces of compounds 1 and 2

	τ_1 (ms)	B_1 (%)	τ_2 (ms)	B_2 (%)	τ_{avg} (ms)	CHISQ
1@450	1.4	77	17.7	23	5.1	1.5
2@450	24.1	42	360.8	58	219.4	1.4
1@520	1.4	27	21.6	73	16.1	1.4
2@520	19.0	35	317.4	65	213.0	1.4
1@550	1.4	23	18.5	77	14.6	1.3
2@550	18.2	35	239.7	65	162.2	1.1

C-H $\cdots$ N的距离为3.98 Å(126.91°); C-H $\cdots$ O为2.43 Å(145.48°)、2.78 Å(131.82°)和3.65 Å(128.16°). 综

合分子间作用的角度和距离, 2较1具有更强的分子内/分子间相互作用, 可以更好地抑制分子运动, 稳定三重态激子. 此外, 结晶水分子的O-H高频振动对配合物1的发光具有一定猝灭作用^[39,40]. 以上两点均导致2具有更长的磷光寿命. 综上, 结构变化引起的配体构型/构象差异导致了不同强度的分子内/分子间相互作用. 这些作用调节了分子的非辐射能量耗散, 进而调变其发光寿命.

3 总结与展望

本文利用溶剂热合成技术, 在Zn²⁺离子、柔性配体BIMB及亚磷酸共存条件下, 成功制备出两种新型配位

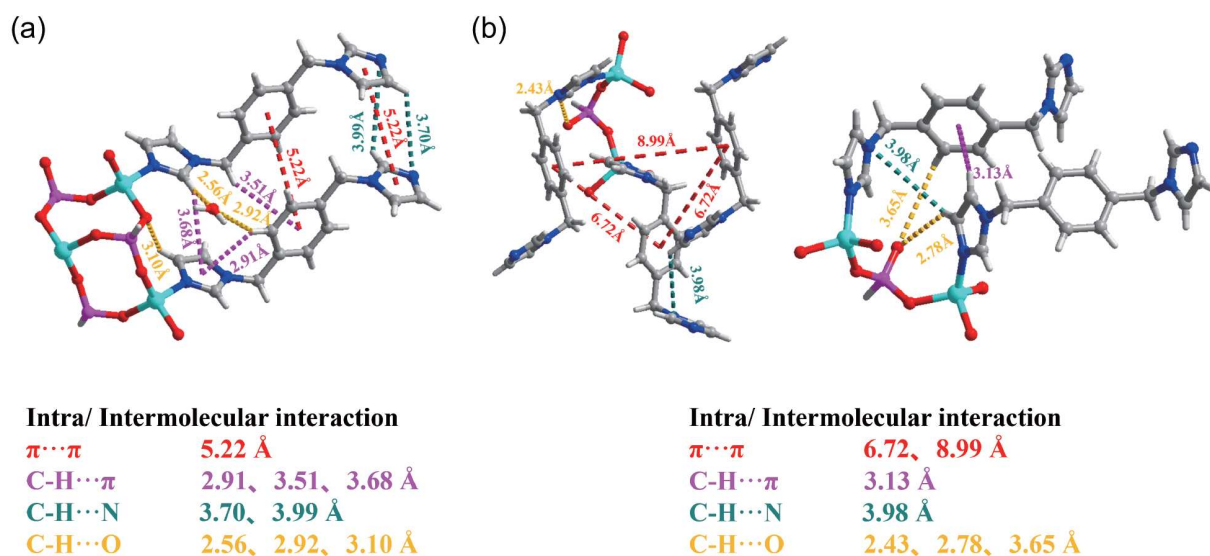


图 5 (网络版彩色)配合物1(a)和2(b)的分子内和分子间作用力

Figure 5 (Color online) Intramolecular and intermolecular forces of complexes 1 (a) and 2 (b)

聚合物**1**和**2**。结构解析显示, 配合物**1**中, BIMB两端的咪唑基团分别桥接两条亚磷酸锌链, 构筑出二维层状网络; 而配合物**2**中BIMB配体与亚磷酸锌层中的 Zn^{2+} 离子配位, 从而起到“柱撑”作用, 将相邻的二维层连接起来, 最终组装成三维柱层框架。在亚磷酸锌次级骨架的空间约束下, BIMB配体呈现特定构型、构象,

导致两例配合物中产生强度各异的分子间/内作用力, 且三维结构中的作用力强于二维结构, 进而显著影响其三重激发态寿命。配合物**1**的寿命在10 ms上下, 而配合物**2**的寿命长达200 ms以上。本工作不仅为理性设计具有长寿命磷光性质的配位聚合物材料提供了全新思路, 更为相关功能材料的设计奠定了重要结构基础。

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补充材料

- 图S1 配合物1(a)和2(b)中配体的构型
- 图S2 配合物1(a)和2(b)的粉末XRD表征图
- 图S3 配合物2的三维即时光谱(a)及相应激发波长下的荧光发射光谱(c); 三维延迟光谱(b)及相应激发波长下的磷光发射光谱(d)
- 图S4 配合物1(a)和2(b)在CIE 1931色度图中标注激发波长下的磷光色坐标
- 图S5 配体BIMB的DMF稀溶液(浓度为10 $\mu\text{mol/L}$)在260 nm(a)和310&370 nm(b)激发下的发射光谱
- 图S6 配合物1(a)和2(b)的UV-Vis谱图
- 图S7 配合物1(a)和2(b)在300 nm的荧光衰减曲线
- 图S8 配合物1(a)和2(b)在400 nm的荧光衰减曲线
- 图S9 配合物1和2在254 nm紫外光激发下的荧光和磷光照片
- 表S1 配合物1和2的晶体结构信息
- 表S2 配合物1的部分键长键角
- 表S3 配合物2的部分键长键角
- 表S4 配合物1和2在不同发射波长下拟合的荧光寿命

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Summary for “亚磷酸锌结构单元调节的配位聚合物磷光寿命”

Phosphorescence lifetimes of coordination polymers modulated by zinc phosphite building block

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Over the past decade, room-temperature phosphorescent (RTP) materials have shown broad application prospects in information storage, chemical sensing, bioimaging, and anti-counterfeiting encryption, owing to their luminescent lifetimes ranging from microseconds to seconds. Phosphorescence arises from the radiative decay of triplet excited states and is usually observed only at low temperatures (e.g., 77 K) or under inert atmospheres, which severely restricts its practical applications. Early RTP research primarily focused on complexes of precious metals such as iridium and platinum, which exhibit heavy-atom effects. However, such materials generally suffer from limitations including high cost, short decay times (only tens of microseconds), and poor environmental compatibility. Therefore, developing low-cost, long-lifetime, and environmentally friendly RTP materials is of great significance. Metal-organic coordination polymers constructed from d^{10} configuration transition metals (e.g., Zn^{2+} , Cd^{2+} , Cu^+ , Ag^+ , etc.) have emerged as ideal platforms for creating high-performance RTP materials. This is attributed to their distinct advantages, including high structural tunability, diverse building units, facile introduction of heavy-atom effects, and suppression of nonradiative transitions through rigid frameworks. The metal nodes in these polymers exert a heavy-atom effect, promoting the generation of triplet excitons. Meanwhile, the rigid skeletons and abundant intermolecular interactions effectively stabilize these excitons, providing a solid foundation for constructing RTP systems with long lifetimes and high quantum yields. In this study, two novel coordination polymers (denoted as **1** and **2**) were successfully synthesized via a solvothermal method under the coexistence of Zn^{2+} ions, the flexible ligand BIMB, and phosphorous acid. Structural analysis demonstrated that in complex **1**, the imidazole groups at both ends of the BIMB ligand bridge two separate zinc phosphite chains, forming a two-dimensional (2D) layered network. In contrast, in complex **2**, the BIMB ligand coordinates with Zn^{2+} ions within the zinc phosphite layers and acts as a “pillar” connecting adjacent 2D layers to assemble into a three-dimensional (3D) pillar-layered framework. Under the spatial confinement of the zinc phosphite secondary framework, the BIMB ligand adopts specific configurations and conformations, leading to intermolecular and intramolecular interactions of different strengths in the two complexes; the interaction strength in the 3D structure is greater than that in the 2D structure. The photoluminescence properties of these two compounds were systematically characterized, and the structure–activity relationship was analyzed in combination with their single-crystal structures. The experimental results clearly show that from 1D chains to 2D layers, the rigid zinc phosphite structural units more effectively suppress nonradiative decay of BIMB, thereby significantly modulating the phosphorescence lifetime: the lifetime of complex **1** is approximately 10 ms, while that of complex **2** extends to over 200 ms. This study not only reveals the key regulatory role of the dimension and topological structure of inorganic building blocks on phosphorescence lifetime but also provides new insights and a solid structural basis for the rational design of coordination polymer materials with long-lived phosphorescence through crystal engineering strategies.

coordination polymers, solvothermal synthesis, flexible ligand, room temperature phosphorescence

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