

多酸-查耳酮杂化分子的制备及其光交联性能

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摘要 光敏型多酸杂化分子及其光响应特性是目前多酸功能材料的研究重点. 本文采用共价修饰的方法将光敏型查耳酮基团嫁接至Anderson型多酸骨架上, 制备了一类新型的光敏杂化分子. 利用核磁共振、傅里叶变换红外、高分辨质谱、单晶X射线衍射等技术确认了多酸-查耳酮分子的结构; 并利用紫外光谱、核磁共振和凝胶渗透色谱技术详细研究了多酸-查耳酮分子的光交联特性. 该工作为新型光敏多酸杂化分子的制备及功能应用提供了良好借鉴.

关键词 多金属氧酸盐, 查耳酮, 光交联, 共价修饰, 杂化分子

多酸, 即多金属氧酸盐(polyoxometalates, POMs), 是一类由前过渡金属在其最高氧化价态通过氧原子桥连而成的金属氧簇化合物^[1,2]. 多酸分子基本构筑单元为{MO₆}八面体, 其中M代表V, Mo, W, Nb等过渡金属. 这些金属-氧八面体基本单元通过点、边、面的方式相互桥连, 形成了尺寸可调、结构各异的多酸大阴离子^[3]. 同时, 多酸结构中, 由于杂原子的掺杂、空位缺位基元、桥连元素、抗衡阳离子等不同, 形成了从几纳米到上百纳米, 甚至匹敌蛋白质分子大小的金属-氧簇合物^[4]. 多酸因其丰富的结构特征和物理化学特性, 近年来在能源^[5]、材料^[6,7]、生物^[8,9]、催化^[10,11]等领域受到了科学家的广泛关注. 通过共价修饰的方式“量身定制”多酸基有机-无机杂化分子, 不仅极大地丰富了多酸分子结构和研究领域, 而且有利于调节多酸自身物理化学性质、便于“自下而上”地设计与构筑多酸基先进功能材料^[12~14]. 例如, 通过将芳香稠环茚共价修饰到Anderson多酸上, 不仅

能够有效实现多酸杂化分子对细胞选择性吸附^[15], 而且通过 π - π 相互作用将多酸杂化分子与碳纳米管复合, 能够用于制备稳定、高效的锂离子电池负极材料^[16]. 这种有机-无机杂化分子的设计和应用, 不仅整合了无机多酸和有机功能基团的优势, 而且两者之间的协同作用也为新型多功能材料的制备提供了途径. 例如, 通过将有机 π 电子共轭体系二萘嵌苯^[17]、卟啉^[18]、螺吡喃^[19]、偶氮苯^[20]等基团共价修饰至多酸骨架上, 能够制备出新型的有机-无机电致变色、光致变色以及热致液晶材料.

光敏型多酸杂化分子作为一类性质独特的新型功能分子, 因其对不同波长光的响应性以及多酸分子内不同元素间的选择性氧化还原, 受到了多酸化学家和材料学家的高度关注. 例如, 通过光敏型香豆素基团的引入, 能够实现Anderson型多酸杂化分子在不同紫外光照射下的可逆聚合; 并且由于多酸存在的影响, 该过程具有明显的颜色变化且循环稳定

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性良好,显示出多酸杂化分子作为智能变色材料的潜能^[21].进一步研究结果表明,香豆素基团的可逆聚合过程伴随有多酸分子内元素的选择性氧化还原.例如,Wells-Dawson型多酸-香豆素杂化分子能够实现在聚合过程中多酸分子内 V^{5+} 到 V^{4+} 的部分还原,而高价态的 W^{6+} 则完全不受影响^[22].

查耳酮及其衍生物,作为黄酮类化合物的一种,通常是由芳香醛酮发生羟醛缩合而成,在有机染料、生物医药等领域具有广泛的应用^[23,24].同时,由于查耳酮结构中含有紫外光敏感的 α,β -不饱和羰基,能够在紫外光照下快速地发生 $[2\pi+2\pi]$ 环加成反应,因此,查耳酮及其衍生物也常被用作紫外光敏材料^[25].本文通过将查耳酮基团共价修饰至Anderson型多酸上,制备了一类新型的紫外光敏型多酸杂化分子,并利用单晶X射线衍射(单晶XRD)、高分辨电喷雾电离质谱(ESI-MS)等技术对该化合物进行了详细的结构表征.随后,借助紫外可见光谱(UV-Vis)、核磁共振氢谱(1H NMR)以及凝胶渗透色谱(GPC),对多酸-查耳酮杂化分子的光交联性质进行了系统研究.

1 实验

(i) 试剂与仪器. 所用药品除碳酸钾、氢氧化钠和碘化钾购于北京化工厂外,其余均购于天津Alfa Aesar试剂公司;乙腈在使用前已经过氢化钙干燥处理. $[(n-C_4H_9)_4N]_4[\alpha-Mo_8O_{26}](Mo_8)$ 采用文献[26]报道方法制备, $Mn(OAc)_3 \cdot 2H_2O$ 的合成采用文献[27]已报道的方法. 1H NMR和 ^{13}C NMR采用Bruker AV400核磁共振仪测定;傅里叶转换红外光谱(FT-IR)通过溴化钾压片法在Bruker Vector 22红外光谱仪上测定;UV-Vis紫外光谱采用北京普析通用公司TU-1901紫外可见分光光度计测试;ESI-MS高分辨电喷雾质谱使用美国Waters公司Xevo G2 QT质谱仪测试;单晶XRD数据通过Xcalibur Eos Gemini单晶衍射仪($\lambda(Cu K\alpha)=1.54178 \text{ \AA}$)在150 K下测得,单晶解析与结构精修使用SHELXS-2014和SHELXL-2014软件程序;GPC使用安捷伦GPC 2600系列设备测试.

(ii) 化合物1的合成. 在500 mL单口烧瓶中加入苯乙酮(12.0 g, 0.1 mol), 氢氧化钠(10.0 g, 0.25 mmol), 无水乙醇125 mL以及去离子水30 mL, 搅拌30 min并冷却至室温. 采用恒压滴液漏斗向上述溶液中缓慢滴加4-羟基苯甲醛(12.2 g, 0.1 mol)的乙醇溶液50 mL, 控制反应温度在30℃, 搅拌反应24 h. 旋

蒸除去乙醇,将剩余黏稠液体倾入300 mL去离子水中,并用1 mol/L的盐酸溶液中和至pH 6,静置过夜. 抽滤分离得到粗产品,并用去离子水洗涤,最后在95%乙醇溶液中重结晶得到橙黄色固体粉末,产率32.8%. 1H NMR(氘代二甲亚砜, $DMSO-d_6$), δ 6.86 (d, 2H), 7.57(t, 2H), 7.66(t, 1H), 7.72(d, 2H), 7.74(s, 1H), 7.78(s, 1H), 8.13(d, 2H), 10.11(s, 1H). ^{13}C NMR($DMSO-d_6$), δ 115.80, 118.48, 188.98, 125.75, 128.30, 128.69, 131.00, 132.78, 137.95, 144.50, 160.14. FT-IR(KBr, cm^{-1}): ν 3235, 1649, 1598, 1560, 1511, 834.

(iii) 化合物2的合成. 取化合物1(2.24 g, 10 mmol)溶于80 mL丙酮溶液中,依次加入碳酸钾(4.51 g, 33 mmol)和催化量碘化钾,加热搅拌,缓慢滴加溴代乙酸乙酯(2.0 g, 12 mmol),回流反应24 h,薄层色谱法(TLC)监测反应进程. 反应完毕,旋蒸除去丙酮,加入适量去离子水洗涤,过滤并在空气中干燥得粗产品. 将粗产品在适量乙醇中重结晶得淡黄色针状晶体,产率75.4%. 1H NMR($DMSO-d_6$), δ 1.23(t, 3H), 4.19(m, 2H), 4.89(s, 2H), 7.03(d, 2H), 7.58(t, 2H), 7.67(t, 1H), 7.72(d, 1H), 7.81(s, 1H), 7.86(d, 2H), 8.15(d, 2H). ^{13}C NMR($DMSO-d_6$), δ 14.02, 60.71, 64.67, 114.95, 119.94, 127.94, 128.40, 128.73, 130.71, 132.95, 137.76, 143.77, 159.62, 168.44, 189.03. FT-IR(KBr, cm^{-1}): ν 3071, 2982, 2914, 1755, 1655, 1595, 1571, 1511, 1384, 1264, 1219.

(iv) 化合物3的合成. 将化合物2(0.68 g, 2.2 mmol)溶于10 mL $DMSO$ 溶液中,通入氮气30 min,依次加入碳酸钾(0.31 g, 2.2 mmol)和三羟甲基氨基甲烷(0.27 g, 2.2 mmol),室温条件下继续反应24 h. 反应结束,过滤除去碳酸钾,减压蒸干 $DMSO$ 溶剂,加入去离子水洗涤,空气中干燥后得粗产品. 将粗产品通过硅胶柱分离(洗脱剂为氯仿:甲醇=10:1, 体积比),得黄色固体粉末,产率23.6%. 1H NMR($DMSO-d_6$), δ 3.60 (d, 6H), 4.58(s, 2H), 4.76(t, 3H), 7.06(d, 2H), 7.23(s, 1H), 7.58(t, 2H), 7.69(t, 1H), 7.73(d, 1H), 7.84(d, 1H), 7.88(d, 2H), 8.15(d, 2H). ^{13}C NMR($DMSO-d_6$), δ 59.94, 61.91, 67.05, 115.18, 119.98, 128.41, 128.73, 130.76, 132.96, 137.53, 143.75, 159.48, 167.58, 189.02. FT-IR(KBr, cm^{-1}): ν 3431, 3378, 2919, 1665, 1593, 1568, 1511.

(v) 化合物4的合成. 称取 Mo_8 (0.50 g, 0.23 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (94 mg, 0.35 mmol)和化合物3(308 mg, 0.8 mmol)于24 mL圆底烧瓶中,加入乙腈10 mL溶解,加热回流16 h. 停止反应,过滤除去棕色不溶物,将滤液在乙醚中缓慢扩散得橙色块状晶体,产率65.8%. 1H NMR($DMSO-d_6$), δ 0.94(t, 36H),

1.32(m, 24H), 1.57(m, 24H), 3.16(t, 24H), 4.91(s, 4H), 7.02(d, 4H), 7.58(t, 4H), 7.67(t, 2H), 7.73(d, 2H), 7.83(d, 2H), 7.88(d, 4H), 8.17(d, 4H). ^{13}C NMR (DMSO- d_6), δ 13.53, 19.24, 23.05, 57.52, 63.78, 114.95, 119.74, 127.63, 128.44, 128.70, 130.78, 160.14, 162.29, 189.00. FT-IR(KBr, cm^{-1}): ν 3378, 2919, 1665, 1593, 1568, 1511, 940, 919, 668.

(vi) 化合物4晶体数据. $\text{C}_{376}\text{H}_{608}\text{Mn}_4\text{Mo}_{24}\text{N}_{28}\text{O}_{124}$, $M_r=10027.24$. 单斜晶系, 空间群 $C2/c$; $a=40.1554(10)$ Å, $b=13.8418(2)$ Å, $c=25.1309(4)$ Å; $\beta=114.929(2)$; $V=12666.9(5)$ Å 3 ; $Z=1$; $\rho=1.315$ g cm^{-3} ; $T=150(3)$ K; $R_1=0.0758$; $wR_2=0.2124$. 详细晶体学数据请参阅剑桥晶体结构数据库CCDC 1508809.

2 结果与讨论

2.1 合成与表征

本文采用“前修饰法”制备多酸-查耳酮杂化分子, 即先使用查耳酮分子对双功能连接子三羟甲基氨基甲烷(tris(hydroxymethyl)aminomethane, Tris)进行修饰, 得到Tris类衍生物 $^{[28]}$; 再通过传统一锅法 $^{[29]}$, 将Tris类衍生物共价嫁接至Anderson多酸(图1). 制得多酸-查耳酮杂化分子后, 首先进行了FT-IR测试, 并对谱图中的主要特征峰进行了归属. 例如, Anderson多

酸 $\text{Mo}=\text{O}$ 和 $\text{Mo}-\text{O}-\text{Mo}$ 的特征峰分别出现在940/919和668 cm^{-1} 处; 查耳酮上的 α , β -不饱和羰基以及苯环的骨架振动峰则分别出现在1665/1593和1568/1511 cm^{-1} 处. ^1H NMR和 ^{13}C NMR测试结果也清晰地显示出查耳酮分子和四丁基铵阳离子的信号峰, 并且峰面积积分与该化合物分子式相匹配. 以上实验数据表明, 查耳酮分子已经被成功嫁接至Anderson多酸上.

为了进一步确证, 我们使用乙腈为溶剂, 在负离子模式下进行了高分辨电喷雾质谱测试. 如图2所示, 质荷比 $m/z=2167.81$ 处的单电荷碎片峰归属为 $\{[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[(\text{MnMo}_6\text{O}_{24})\{(\text{CH}_2)_3\text{CNHCOCH}_2\text{OC}_6\text{H}_4\text{C}_2\text{H}_2\text{COC}_6\text{H}_5\}_2]\}^-$, $m/z=962.96$ 处的双电荷碎片峰归属为 $\{[(n\text{-C}_4\text{H}_9)_4\text{N}][(\text{MnMo}_6\text{O}_{24})\{(\text{CH}_2)_3\text{CNHCOCH}_2\text{OC}_6\text{H}_4\text{C}_2\text{H}_2\text{COC}_6\text{H}_5\}_2]\}^{2-}$, $m/z=1364.59$ 处的三电荷碎片峰则归属为 $\{[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[(\text{MnMo}_6\text{O}_{24})\{(\text{CH}_2)_3\text{CNHCOCH}_2\text{OC}_6\text{H}_4\text{C}_2\text{H}_2\text{COC}_6\text{H}_5\}_2]\}^{3-}$. 通过乙醚扩散法, 培养出多酸-查耳酮分子的单晶, 并使用单晶XRD进一步确证了该分子的结构. 如图3所示, 多酸-查耳酮分子的晶体结构属于单斜晶系, 具有 $C2/c$ 点群; 从结构中可以看出Anderson多酸骨架是由6个 $\{\text{MoO}_6\}$ 八面体和1个中心 $\{\text{MnO}_6\}$ 六面体以共点、共边、共面的形式构成, 而查耳酮分子则通过Tris以反

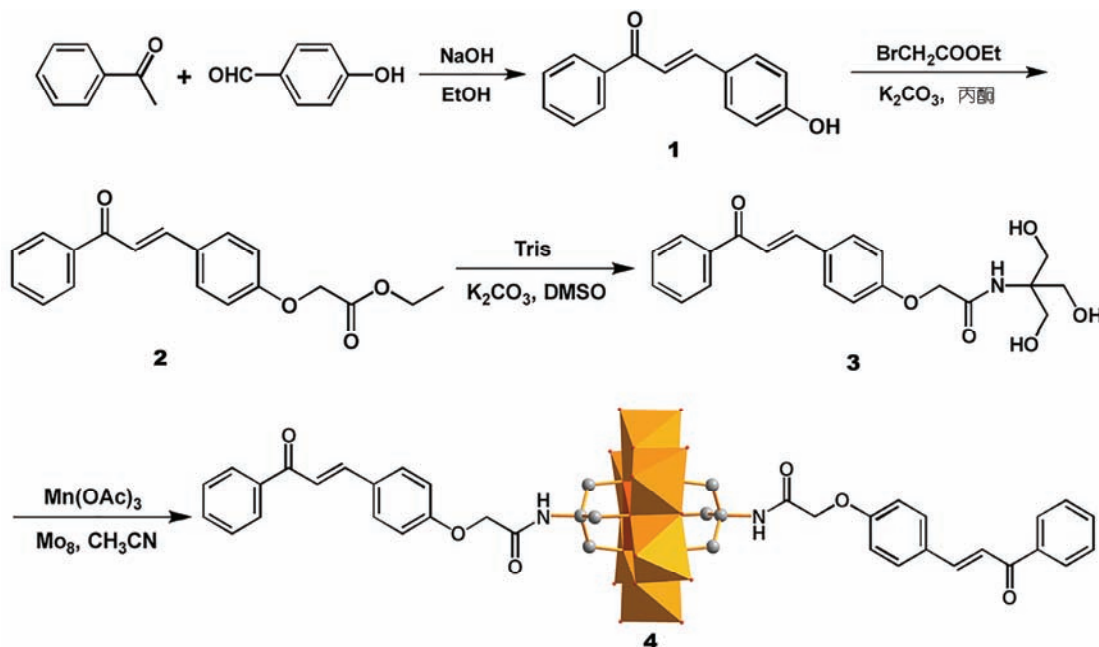


图1 (网络版彩色)多酸-查耳酮杂化分子合成示意图. 为清晰表示, 四丁基溴化铵阳离子已省略

Figure 1 (Color online) Schematic representation of the synthetic procedure of POM-chalcone hybrid. Tetrabutylammonium counter cation has been omitted for clarity

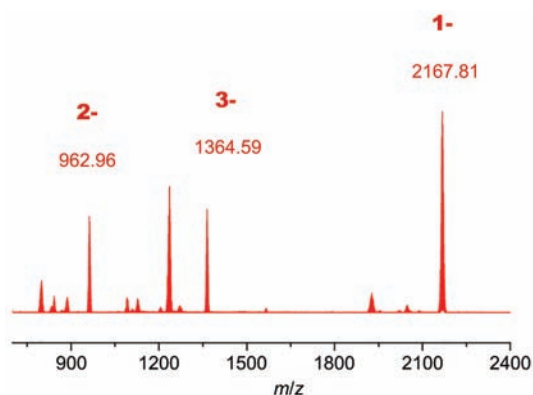


图2 (网络版彩色)多酸-查耳酮杂化分子的高分辨质谱图
Figure 2 (Color online) The ESI-MS spectrum of POM-chalcone hybrid

式结构共价嫁接在Anderson多酸两边。

2.2 光交联反应

查耳酮与香豆素、肉桂酸类衍生物相似,其分子结构中含有光敏的 α , β -不饱和羰基,在不同波长紫外光照射下能够发生可逆的 $[2\pi+2\pi]$ 光二聚交联反应。因此,我们首先采用紫外光谱系统地研究了多酸-查耳酮分子在DMSO溶液中的光交联特性。如图4(a)所

示,多酸-查耳酮分子的特征吸收峰出现在332 nm附近,随着365 nm紫外光的照射,该吸收峰不断降低。与此同时,一个新的吸收峰在245 nm附近出现,并且随着紫外光照时间的延长而不断增强。这是由于在365 nm紫外光照射下,查耳酮基团中不饱和双键因光交联反应而不断消耗,因此其在332 nm处的特征吸收峰不断降低;同时,不饱和双键 $[2\pi+2\pi]$ 光交联反应生成的环丁烷结构不断增加,其在245 nm处的特征吸收峰随之增强。多酸-查耳酮分子的吸收强度在长波处的减少及短波处的增加,导致光谱在278 nm附近出现了一个等吸收点。图4(b)所示为紫外照射过程中多酸-查耳酮分子在不同时间点的光交联率。光交联率由公式 $C(\%)=(A_0-A_T)/A_0$ 计算得到,其中, A_0 和 A_T 分别为查耳酮基团中不饱和双键在紫外光照前($t=0$)和紫外照射一段时间($t=T$)的特征吸收峰强度。由图可知,多酸-查耳酮分子的最终光交联率稳定在37.45%。

随后,我们对多酸-查耳酮分子 $[2\pi+2\pi]$ 光交联产物进行了恢复实验。如图4(c)所示,在254 nm紫外光照下,该化合物在332 nm附近的吸收峰强度不断增加,而在245 nm附近的吸收峰强度则不断降低。该实验结果表明, $[2\pi+2\pi]$ 光交联反应生成的环丁烷结构

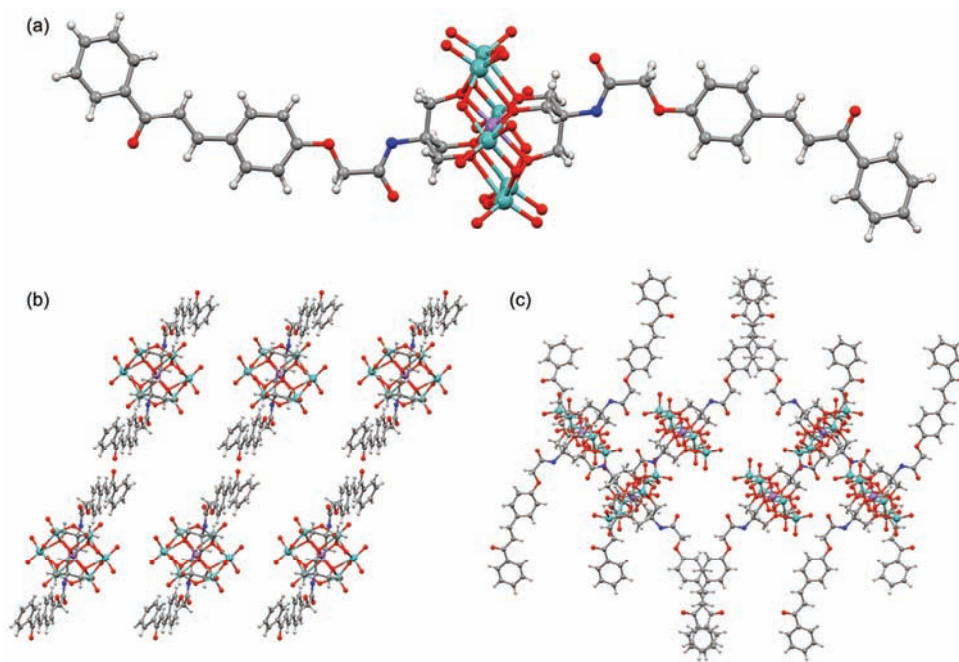


图3 (网络版彩色)(a) 多酸-查耳酮杂化分子晶体结构; (b) 多酸-查耳酮杂化分子沿b轴方向的晶体堆积图; (c) 多酸-查耳酮杂化分子沿c轴方向的晶体堆积图。为清晰表示,四丁基溴化铵阳离子已省略

Figure 3 (Color online) (a) The crystal structure of POM-chalcone hybrid. (b) X-ray crystal packing structure of POM-chalcone viewed from b axis. (c) X-ray crystal packing structure of POM-chalcone viewed from c axis. Tetrabutylammonium counter cations have been omitted for clarity

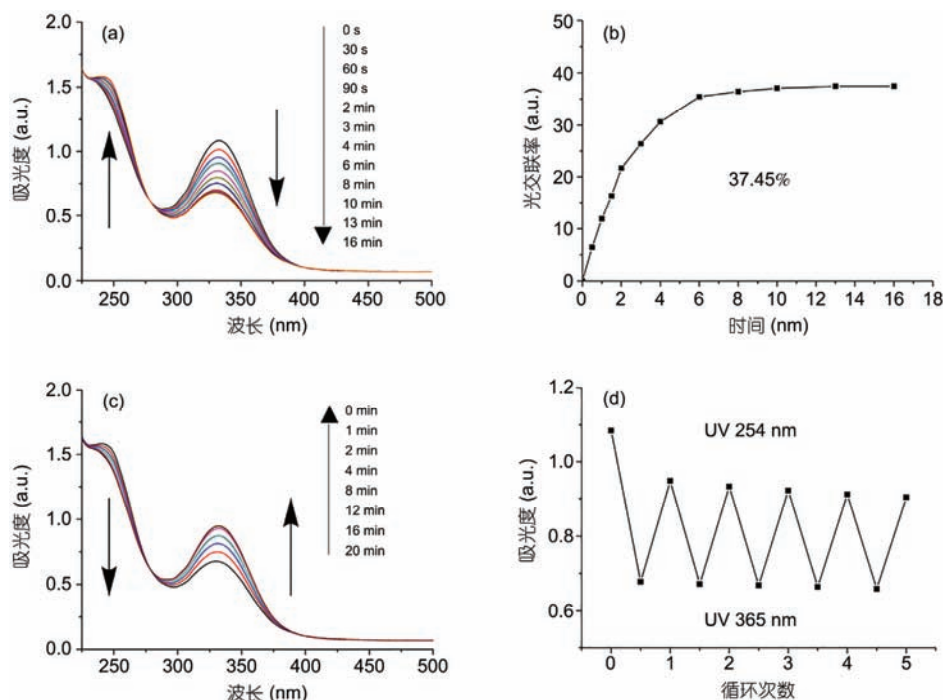


图4 (网络版彩色)(a) 多酸-查耳酮杂化分子在 365 nm紫外光照射下的UV-Vis谱图; (b) 多酸-查耳酮杂化分子的光交联率; (c) 多酸-查耳酮杂化分子在 254 nm紫外光照射下的UV-Vis恢复谱图; (d) 多酸-查耳酮杂化分子UV-Vis循环实验

Figure 4 (Color online) (a) The UV-Vis spectra of POM-chalcone hybrid under 365 nm UV irradiation. (b) The photopolymerization conversion of POM-chalcone hybrid. (c) The UV-Vis spectra of POM-chalcone hybrid under 254 nm UV irradiation. (d) Reversible absorbance changes at 332 nm over five consecutive cycles of 365 and 254 nm irradiation

发生了解离, 导致溶液中多酸-查耳酮单体的数量不断增加. 照射20 min后, 化合物紫外光谱不再发生变化, 表明光解离反应完毕. 此时, 多酸-查耳酮分子单体数量约为原来的87%. 循环实验结果表明, 多酸-查耳酮分子的光交联反应具有良好的可逆性, 在连续5个循环之后, 化合物单体的数量仍能保持在起始数量的85%左右(图4(d)).

图5为多酸-查耳酮分子在365 nm紫外光照前后的核磁氢谱. 从图中可以看出, 紫外光照后芳香区查耳酮基团所出的信号峰发生了明显变化. 其中, 不饱和双键上H₃和H₄的化学位移最为显著, 分别从7.83和7.73移动至4.80, 表明化合物发生[2 π +2 π]光交联反应生成了新的环丁烷结构. 由于光交联反应的发生, 查耳酮基团中苯环氢的化学位移也因化学环境的变化发生了明显改变. 例如, H₅的化学位移由光照前8.17移动至光照后7.97, 向高场移动了0.2; 苯环上H₂的化学位移则从7.88移动至7.52, 向高场移动了0.36; 苯环上H₁的化学位移也由7.02向高场移动了0.16至6.86. 以上实验结果均表明, 多酸-查耳酮分子在365 nm紫外光照下发生了光交联反应. 紫外光照

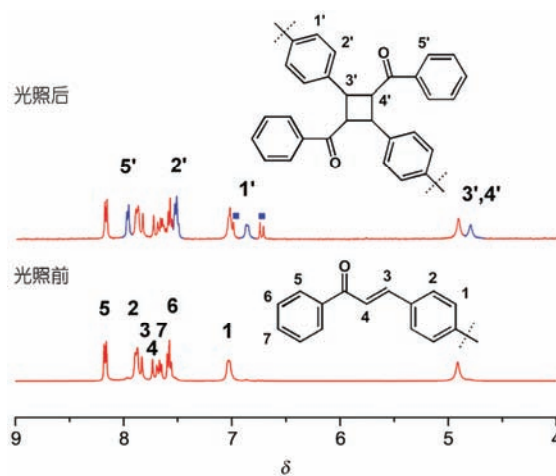


图5 (网络版彩色)多酸-查耳酮杂化分子紫外光照前后的核磁氢谱对比图

Figure 5 (Color online) The ¹H NMR spectra of POM-chalcone hybrid before and after UV 365 nm irradiation

后, 化合物在6.99和6.73处所出的两重峰(图5中方块标注)则是由于查耳酮从反式结构变为顺式结构时不饱和双键氢的化学位移.

为进一步确证多酸-查耳酮杂化分子在365 nm紫

外光照下的光交联产物,使用GPC对交联反应的原溶液进行了监测,溶液浓度为1.0 mg/mL,溶剂为DMF,进样量为20 μ L,进样速率为1.0 mL/min.从图6可知,多酸-查耳酮分子发生 $[2\pi+2\pi]$ 光交联反应生成的一维链状聚合物的重均分子量约为 9.78×10^5 g/mol,溶液多分散系数为1.45.

3 结论

本文采用共价修饰的方法,设计构筑了一类新型的多酸-查耳酮光敏杂化分子.利用高分辨电喷雾质谱以及单晶XRD等技术详细表征了该化合物的结构组成,并利用紫外光谱和核磁技术系统研究了多酸-查耳酮分子在溶液中的光交联特性.研究表明,多酸-查耳酮分子在365 nm紫外光照射下能够发生 $[2\pi+2\pi]$ 光交联反应,生成一维链状聚合物,GPC测试结果显示该聚合物重均分子量可达 9.78×10^5 g/mol;在254 nm光照下,该多酸聚合物能够发生解离并恢复至单体状态,

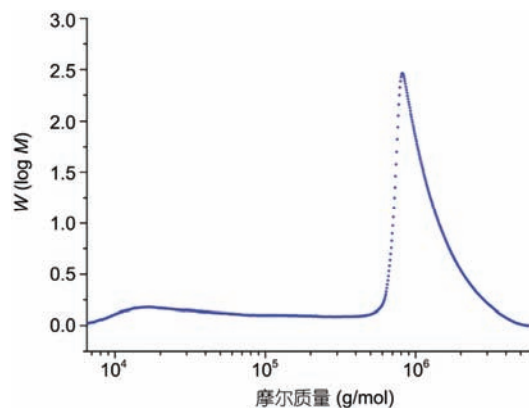


图6 (网络版彩色)多酸-查耳酮杂化分子在365 nm紫外照射后的GPC图

Figure 6 (Color online) The GPC spectrum of POM-chalcone hybrid after UV 365 nm irradiation

其5个循环的恢复率仍保持在85%左右.后续工作将着重研究多酸-查耳酮杂化分子及其光交联特性在智能响应器件、非线性光学以及液晶领域的应用.

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Summary for “多酸-查耳酮杂化分子的制备及其光交联性能”

Preparation of polyoxometalate-chalcone hybrid and its photo-polymerization property

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Photo-sensitive polyoxometalate-based hybrid materials have attracted much attention in recent years due to their unique photo-responsive properties. Here we represent a new type of photo-sensitive polyoxometalate-based hybrid by covalently tethering chalcone moieties onto Anderson cluster. Various techniques including nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), electrospray ionization-mass spectrometry (ESI-MS) and single-crystal X-ray diffraction have been utilized to characterize the structure and composition of the resultant hybrid. The ¹H and ¹³C NMR spectra show well resolved peaks that can be unambiguously assigned and are in good accordance with the molecular structure. Characteristic stretching vibrations of MO and Mo–O–Mo bonds can be found at 940 and 668 cm⁻¹ in the FT-IR spectrum respectively, whilst the chalcone moieties give stretching bands at 1665/1593 cm⁻¹ (C=O–C=C) and 1568/1511 cm⁻¹ (C=C). The ESI-MS spectrum of the hybrid provides us more convincing structural informations. For instance, the isotopic peaks observed at *m/z*=2167.81 can be clearly ascribed to the anionic fragment of $\{[(n-C_4H_9)_4N]_2[(MnMo_6O_{24})\{(CH_2)_3CNHCOCH_2OC_6H_4C_2H_2COC_6H_5\}_2]\}^-$, suggesting the successful modification of Anderson cluster with chalcone molecules. Single-crystal X-ray diffraction analysis reveals that the hybrid crystallizes in a mono-clinic system with a *C2/c* space group, where organic chalcone moieties are covalently bonded to the Anderson cluster via μ^3 -oxo bridging ligands. The photo-polymerization properties of the hybrid have been investigated in detail using UV-Vis spectroscopy, ¹H NMR, and gel permeation chromatography. For example, when irradiated at UV light of 365 nm the hybrid undergoes a $[2\pi+2\pi]$ cycloaddition reaction, leading to an absorbance decrease at wavelength of 332 nm in the UV-Vis spectrum. Meanwhile, a new absorbance peak attributed to the generated cyclobutane structure is observed at 245 nm. This process gives a total photo-polymerization conversion of 37.45%, and is found able to restore when exposed to UV light of 254 nm. After five cycles of alternative irradiation at 365 and 254 nm, the amount of the hybrid monomer can still maintain at 85% of the original ones. The ¹H NMR spectrum of the hybrid also shows significant changes when irradiated at UV light of 365 nm. Signals of the unsaturated carbonyl groups of the chalcone moieties at δ 7.83 and 7.73 shift to high field after irradiation, and give corresponding cyclobutane signal at δ 4.80. These results are in accordance with the results of UV-Vis spectroscopy. Weight-average molecular weight of the resulting hybrid polymer is 9.78×10^5 g/mol as demonstrated by the gel permeation chromatography analysis. This work may provide a new pathway for the fabrication and functional application of novel photo-sensitive polyoxometalate-based hybrids.

polyoxometalate, chalcone, photo-polymerization, covalent modification, hybrid molecular

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