二辛基酞菁氧钒的合成、表征和半导体性质

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2015-06-18 收稿, 2015-07-18 修回, 2015-07-20 接受, 2015-08-13 网络版发表

国家自然科学基金(51333006)、国家重点基础研究发展计划(2014CB643504)和中国科学院先导专项(XDB12010300)资助

摘要 设计与合成了2,3-二辛基酞菁氧钒(2,3-C8OVPC), 2,16(17)-二辛基酞菁氧钒(*dp*-C8OVPC), 1,15-二辛基酞菁氧钒(1,15-C8OVPC)和1,18-二辛基酞菁氧钒(1,18-C8OVPC)4种可溶性酞菁氧钒衍生物, 研究了辛基位置对该类化合物的物理化学性质、固态薄膜形貌和有机薄膜晶体管(OTFT)器件性能的影响. 在溶液状态下, 辛基的位置对共轭分子的吸收光谱和前线轨道能级影响很小, 它们的最大吸收峰均在700 nm左右, 最高被占分子轨道(HOMO)和最低未占分子轨道(LUMO)能级分别约为-5.20和-3.80 eV. 在薄膜状态下, 吸收光谱显著红移, 且红移幅度与辛基的位置有关. 4个化合物在薄膜中均以edge-on的方式排列, 由它们制备的底栅-顶接触型OTFT器件的迁移率均大于0.1 cm²/(V s), 其中2,3-C8OVPC的迁移率最高, 达到0.19 cm²/(V s).

关键词 有机半导体, 酞菁, 溶液加工, 有机薄膜晶体管, 迁移率

溶液加工型有机薄膜晶体管(OTFTs)具有低成本、易实现大面积和柔性器件制备等优点^[1-3]. 近年来随着分子设计概念的发展和人们对器件工程认识的逐步深入, OTFT器件的性能取得了大幅提高, 小分子化合物和聚合物的迁移率均已超过10 cm²/(V s)^[4-13], 高于非晶硅器件的性能. 由于盘状共轭分子具有二维共轭结构, 在成膜过程中能够自组织形成柱状纳米结构, 分子间具有较大的 π 轨道重叠, 有利于载流子的传输^[14], 因此被认为是一类有发展潜力的溶液加工型高迁移率有机半导体材料. 目前, 已有多种盘状有机半导体用于溶液加工型OTFTs的研究^[15-25], 但仅有少数化合物的迁移率超过0.1 cm²/(V s)^[23-25].

酞菁衍生物具有18 π 电子二维共轭结构, 重组能比并五苯还小^[26], 是一类非常重要的高迁移率有机半导体材料. 特别是轴向取代的酞菁, 例如酞菁氧钒(OVPC), 其分子能够形成二维 π 堆积结构, 分子间的电子云重叠较大, 蒸镀型OTFTs器件的迁移率可达

4~10 cm²/(V s)^[26-28]. 在蒸镀型高迁移率材料的外围引入致溶基团是设计和合成溶液加工型高迁移率有机半导体材料的重要方法之一, 但对酞菁衍生物而言, 烷基链的取代位置对载流子传输性质影响巨大. 本课题组^[21,24,25]曾系统地研究了四烷基酞菁氧钒中烷基链位置对分子在薄膜中的堆积结构和OTFT性质的影响, 发现4个烷基链位于其中2个苯环上的ABAB型酞菁衍生物在层内遵循二维滑移 π 堆积模式, 且烷基链在晶体中位于半导体层上下2侧, 形成层状结构, 显著降低了烷基链对载流子传输性能的负面影响. 因此, 与外围四烷基取代酞菁氧钒和非外围四烷基取代酞菁氧钒相比, ABAB型四烷基酞菁氧钒的迁移率显著提高, 达到0.40 cm²/(V s)^[21,24]. 本文在上述工作的基础上, 进一步将烷基链的数目减少为2个, 设计并合成了2,3-二辛基酞菁氧钒(2,3-C8OVPC), 2,16(17)-二辛基酞菁氧钒(*dp*-C8OVPC), 1,15-二辛基酞菁氧钒(1,15-C8OVPC)和1,18-二辛基酞菁氧钒(1,18-C8OVPC)

引用格式: 董少强, 田洪坤, 耿延候, 等. 二辛基酞菁氧钒的合成、表征和半导体性质. 科学通报, 2016, 61: 315-324

Dong S Q, Tian H K, Geng Y H, et al. Synthesis, characterization and semiconducting properties of dioctyl substituted vanadyl phthalocyanines (in Chinese). Chin Sci Bull, 2016, 61: 315-324, doi: 10.1360/N972015-00665

(图1), 详细研究了这4个分子的基本物理化学性质、固态薄膜形貌和OTFT器件性能.

1 合成与方法

(i) 化合物的合成. 2,3-C8OVPc: 氩气氛下, 将邻苯二腈(**1**, 700 mg, 5.40 mmol)、4,5-二辛基邻苯二腈(**2**, 640 mg, 1.80 mmol)和三氯化钒(570 mg, 3.60 mmol)溶于10 mL *N,N*-二甲基乙醇胺(DMAE)中, 加热回流20 h, 降至110℃, 加入5 mL水, 继续反应5 h. 反应液冷至室温后倒入100 mL水中, 过滤后得到的固体用甲醇洗涤3次, 然后溶于10 mL氯仿, 沉降至200 mL甲醇中. 过滤得到的粗产物分别用甲醇和氯仿抽提至无色, 收集氯仿可溶部分, 以氯仿为淋洗剂进行硅胶柱色谱提纯, 最后用氯仿/环己烷混合溶剂重结晶, 得到产物170 mg, 产率12%. 质谱分析: (MALDI-TOF) $m/z=803.3$ (理论分子量: 803.34); 元素分析($C_{48}H_{48}N_8O$): 计算值(%)C, 71.72, H, 6.02, N, 13.94, 测量值C, 71.91, H, 5.93, N, 13.92.

5-辛基-1,3-二亚氨基异吲哚啉(**4**): 将甲醇钠(170 mg, 3.10 mmol)和4-辛基邻苯二腈(7.50 g, 31.2 mmol)溶于90 mL甲醇, 通入干燥氨气, 回流4 h. 反应液浓缩至50 mL进行重结晶, 得产物7.00 g, 产率87.5%. MALDI-TOF: $m/z=258.2$ [$M+H$] $^+$, (理论分子量: 257.19); 1H NMR(300 MHz, $CDCl_3$): δ 8.18(br,

3H), 7.60(br, 1H), 7.54(br, 1H), 7.41(d, $J=8.0$ Hz, 1H), 2.74(t, $J=8.0$ Hz, 2H), 1.66(m, 2H), 1.27(m, 10H), 0.88(m, 3H).

dp-C8H₂Pc: 将**4**(5.15 g, 20.0 mmol)和三乙胺(8.6 mL, 62.0 mmol)溶于150 mL 四氢呋喃(THF)中, 然后在0℃下10 min内滴加1,3,3-三氯异二氢氮杂茛(**3**, 4.41 g, 20.0 mmol)的THF(50 mL)溶液. 所得混合物在0℃搅拌1 h, 缓慢升至室温, 继续反应8 h. 过滤反应液, 将滤液转移至盛有对二苯酚(2.20 g, 20.0 mmol)和甲醇钠(3.24 g, 60.0 mmol)的反应瓶中, 加热回流6 h. 溶液浓缩至50 mL后沉降于500 mL甲醇, 所得沉淀以氯仿为淋洗剂, 用硅胶柱色谱提纯后, 再用甲苯/环己烷混合溶剂重结晶, 得产物1.60 g, 产率23%. MALDI-TOF: $m/z=738.4$ (理论分子量: 738.42); 1H NMR(400 MHz, $CDCl_3$): δ 8.56(br, 4H), 8.41(b, 4H), 7.66 (br, 4H), 7.58(d, $J=7.6$ Hz, 2H), 3.06(t, $J=7.8$ Hz, 4H), 1.66(m, 4H), 1.58(m, 4H), 1.55–1.43(br, 16H), 0.99(t, $J=6.3$ Hz, 6H), –3.40(br, 2H).

dp-C8OVPc: 氩气氛下, 将*dp*-C8H₂Pc(517 mg, 0.70 mmol)、硫酸氧钒(570 mg, 3.50 mmol)和尿素(4.20 g, 70.0 mmol)溶于*N*-甲基吡咯烷酮(NMP, 30 mL)和邻二氯苯(10 mL)中, 所得反应液加热至220℃, 搅拌8 h. 冷至室温后, 将反应液缓慢加入甲醇(500 mL)中, 过滤收集所得沉淀, 以氯仿为淋洗剂, 用硅胶柱色谱提纯, 再用氯仿/环己烷混合溶剂重结晶, 得产物360 mg, 产率65%. MALDI-TOF: $m/z=803.3$, (理论分子量: 803.34); 元素分析($C_{48}H_{48}N_8O$): 计算值(%)C, 71.72, H, 6.02, N, 13.94, 测量值C, 72.09, H, 5.93, N, 13.93.

4-辛基-1,3-二亚氨基异吲哚啉(**5**): 将甲醇钠(120 mg, 2.2 mmol)和3-辛基邻苯二腈(6.00 g, 22.0 mmol)溶于甲醇(40 mL), 通入干燥氨气, 回流12 h. 反应液浓缩至20 mL冷至–20℃进行重结晶, 得产物4.80 g, 产率85%. MALDI-TOF: $m/z=258.2$ [$M+H$] $^+$ (理论分子量: 257.19); 1H NMR(300 MHz, $CDCl_3$): δ 8.44 (br, 3H), 7.48–7.26(br, 3H), 3.21(b, 1H), 3.00(b, 1H), 1.72(m, 2H), 1.27(m, 10H), 0.88(m, 3H).

1,15(18)-二辛基酞菁(*dnp*-C8H₂Pc): 氩气氛下, 将**5**(4.63 g, 18.0 mmol)和三乙胺(7.8 mL, 55.8 mmol)溶于THF(150 mL), 在0℃下10 min内滴加**3**(3.97 g, 18.0 mmol)的THF(50 mL)溶液. 所得混合物在0℃下搅拌1 h, 缓慢升至45℃, 继续反应12 h. 过滤反应液, 将滤液转移至盛有对二苯酚(1.98 g, 18.0 mmol)和甲醇钠(2.92 g, 54.0 mmol)的反应瓶中回流12 h. 溶

图1 二辛基酞菁钒的分子结构

Figure 1 Chemical structures of dioctyl substituted vanadyl phthalocyanines

液浓缩至50 mL后沉降于500 mL甲醇, 所得沉淀分别用氯仿、氯苯抽提, 浓缩氯苯抽提产物, 得到1.30 g, 产率20%。MALDI-TOF: $m/z=738.4$ (理论分子量: 738.42); ^1H NMR(400 MHz, $\text{C}_2\text{D}_4\text{Cl}_4$): δ 9.16–9.06(m, 6H), 8.11–8.00(m, 8H), 4.35(br, 4H), 2.43(m, 4H), 1.97(m, 4H), 1.68(m, 4H), 1.40(b, 12H), 1.02(t, $J=6.0$ Hz, 6H), -1.56 (br, 2H)。

1,15-C8OVPC和1,18-C8OVPC在氩气氛下, 将 *dnp*-C8H₂Pc(887 mg, 1.20 mmol)、硫酸氧钒(978 mg, 6.0 mmol)和尿素(7.21 g, 120.0 mmol)溶于NMP(20 mL)和邻二氯苯(20 mL)中, 所得反应液回流搅拌8 h。冷至室温后, 将反应液缓慢加入甲醇(500 mL)中, 过滤所得沉淀溶于氯仿(30 mL), 再次用甲醇(400 mL)沉淀。所得沉淀以氯仿为淋洗剂, 用硅胶柱色谱分离, 得到1,15-C8OVPC(250 mg, 产率26%)和1,18-C8OVPC(160 mg, 产率17%)。1,15-C8OVPC: MALDI-TOF: $m/z=803.3$ (理论分子量: 803.34), 元素分析($\text{C}_{48}\text{H}_{48}\text{N}_8\text{OV}$): 计算值(%)C, 71.72, H, 6.02, N, 13.94。测量值C, 71.94, H, 5.92, N, 13.99; 1,18-C8OVPC: MALDI-TOF: $m/z=803.3$ (理论分子量: 803.34), 元素分析($\text{C}_{48}\text{H}_{48}\text{N}_8\text{OV}$): 计算值(%)C, 71.72, H, 6.02, N, 13.94。测量值C, 71.90, H, 5.93, N, 13.95。

(ii) 分析和测试仪器。核磁共振谱图由Bruker 300或400 MHz波谱仪测得, 测试温度为室温, 内标为四甲基硅烷, 溶剂为 CDCl_3 。元素分析用Flash-EA1112元素分析仪测定。基质辅助激光解吸电离飞行时间(MALDI-TOF)质谱采用LDI-1700型激光飞行质谱仪(American Linear Scientific Inc.)采集, 基质为葱三酚。热失重(TGA)在Perkin-Elmer TGA-7上进行测试, 升温速率为 $10^\circ\text{C}/\text{min}$, 氮气流速为20 mL/min。差热扫描量热(DSC)在Perkin-Elmer DSC-7上进行测试, 加热(冷却)速率为 $10(-10)^\circ\text{C}/\text{min}$ 。紫外-可见-近红外吸收光谱在Perkin-Elmer Lambda35型紫外-可见分光光度计上测量, 相应的能隙为 $E_g^{\text{opt}} = 1240/\lambda_{\text{abs}}^{\text{onset}}$ 。电化学性质采用上海晨华CHI 660a型电化学工作站和三电极体系表征, 对电极、参比电极和工作电极分别为铂丝、饱和甘汞电极(SCE)和直径为2 mm的铂电极。样品为 1×10^{-3} mol/L的二氯甲烷溶液, 支持电解质为0.1 mol/L的 Bu_4NPF_6 , 扫描速度为50 mV/s, 电位用二茂铁标定, 能级采用公式 $\text{HOMO} = -(4.80 + E_{\text{onset}}^{\text{ox}})$ eV和 $\text{LUMO} = -(4.80 + E_{\text{onset}}^{\text{re}})$ eV计算。薄膜X射线衍射(XRD)用Bruker D8 Discover X射线衍射仪测试。选区电子衍射(SAED)用JEM-1011型号电子显微镜测

试。薄膜形貌用原子力显微镜(AFM, SPI3800N, Seiko Instruments Inc.)以敲击模式表征。

(iii) 有机薄膜晶体管的制备和测试。OTFT器件采用底栅-顶接触构型。以表面覆盖有300 nm的 SiO_2 的n型重掺杂硅片为基底和栅电极, 电容为10 nF/cm²。 SiO_2 层按照文献[29]方法用辛基三氯硅烷(OTS)修饰后, 通过溶液旋涂沉积半导体薄膜, 溶剂为氯仿, 浓度为7 mg/mL, 旋膜速度1000 r/min。最后真空蒸镀金源、漏电极, 电极厚度约为40 nm, 器件的沟道宽(W)和长(L)分别为3 mm和100 μm 。器件的电学性质由两套Keithley 236仪器在室温和空气条件下进行测试。

2 结果与讨论

2.1 2,3-C8OVPC, *dp*-C8OVPC, 1,15-C8OVPC和1,18-C8OVPC的合成

2,3-C8OVPC, *dp*-C8OVPC, 1,15-C8OVPC和1,18-C8OVPC的合成如图2所示。2,3-C8OVPC由摩尔比为3:1:4的邻苯二腈(1)、4,5-二辛基邻苯二腈(2)和三氯化钒反应制备^[30], 产率为12%。化合物4和5通过相应的邻苯二腈衍生物在甲醇中与氨气反应制备。4和5分别与1,3,3-三氯异二氢氮杂茛(3)反应, 获得ABAB型酞菁衍生物*dp*-C8H₂Pc和*dnp*-C8H₂Pc, 产率分别为23%和20%。*dp*-C8H₂Pc与硫酸氧钒反应, 转化为*dp*-C8OVPC, 产率为67%。*dnp*-C8OVPC和硫酸氧钒反应所得的2个异构体1,15-C8OVPC和1,18-C8OVPC, 可通过硅胶柱色谱分离, 产率分别为26%和17%。由于酞菁钒衍生物具有顺磁性, 无法通过核磁共振波谱分析产物结构, 所得产物的结构经元素分析和MALDI-TOF质谱确认。图3给出了*dp*-C8OVPC的MALDI-TOF质谱图, 测量结果与计算结果十分吻合。而在通常情况下, 酞菁分子极易发生超分子自组装而形成多聚体, 使得结构表征较为困难^[31–33]。

2.2 2,3-C8OVPC, *dp*-C8OVPC, 1,15-C8OVPC和1,18-C8OVPC的热性能

2,3-C8OVPC, *dp*-C8OVPC, 1,15-C8OVPC和1,18-C8OVPC的分解温度分别为432 $^\circ\text{C}$, 446 $^\circ\text{C}$, 442 $^\circ\text{C}$ 和418 $^\circ\text{C}$ 。2,3-C8OVPC, 1,15-C8OVPC和1,18-C8OVPC在加热过程中仅有1个相转变, 分别位于322 $^\circ\text{C}$, 349 $^\circ\text{C}$ 和261 $^\circ\text{C}$, 对应结晶熔融过程。*dp*-C8OVPC有2个相转

图2 二辛基酞菁氧钒的合成路线

Figure 2 Synthesis of dioctyl-substituted vanadyl phthalocyanines

图3 $dp\text{-C8OVPC}$ 的MALDI-TOF质谱图(插图为局部放大图)Figure 3 MALDI-TOF MS spectra of $dp\text{-C8OVPC}$. Insets show the enlarged MS spectra

变, 分别位于215℃和235℃, 分别对应结晶-液晶转变和液晶-各相同性转变. 1,15-C8OVPC的熔点比1,18-C8OVPC的熔点高88℃, 可归因于前者具有高的对称性. $dp\text{-C8OVPC}$ 表现出较复杂的相转变行为, 可能与其是两种异构体的混合物有关.

2.3 光物理和电化学性质

从表1和图4可见, 4种酞菁氧钒衍生物的溶液UV-vis-NIR吸收光谱差别不大, 其中2,3-C8OVPC和 $dp\text{-C8OVPC}$ 的最大吸收均为697 nm, 1,15-C8OVPC和1,18-C8OVPC的最大吸收均为701 nm, 较前两者红移4 nm. 与溶液态光谱相比, 薄膜态吸收光谱的Q带吸收峰明显红移, 在近红外区出现, 这表明4种化合物在固态能够形成二维 π 堆积结构^[34-36]. 热退火对Q带吸收峰的影响与分子结构有关, 如图4(a)所示, 2,3-C8OVPC的薄膜退火前的最大吸收在805 nm, 随退火温度的升高Q带吸收峰逐渐红移且吸收强度增大, 150℃退火后, 吸收峰出现在822 nm, 强度达到最大. 这种现象与ABAB型的四烷基酞菁氧钒OVPC-C12类似^[25]. $dp\text{-C8OVPC}$ 的初始膜的最大吸收出现在822 nm, 退火后光谱变化不明显, 只是吸收强度略有增大. 1,15-C8OVPC和1,18-C8OVPC的吸收光谱明显不同, 1,15-C8OVPC初始膜的最大吸收出现在843 nm, 说明分子间相互作用较强; 1,18-C8OVPC初始膜的最大吸收为785 nm, 退火后光谱发生蓝移, 150℃退火后蓝移到773 nm, 与非外围四烷基酞菁氧钒的光谱相似^[24].

表 1 二辛基酞菁钒的热性能、能级和吸收光谱数据

Table 1 Thermal, energy levels and optical properties of dioctyl substituted vanadyl phthalocyanines

化合物	T_d^a (°C)	T_{DSC}^b (°C) (ΔH (J/g))	HOMO ^c (eV)	LUMO ^c (eV)	E_{CV}^d (eV)	λ_{max}^{Sol} (nm)	$\lambda_{max}^{Film d)}$ (nm)
2,3-C8OVPC	432	322(48.6)	-5.14	-3.77	1.37	697	805(822)
<i>dp</i> -C8OVPC	446	215(7.6), 235 (23.5)	-5.16	-3.78	1.38	697	822(822)
1,15-C8OVPC	442	349(41.2)	-5.18	-3.75	1.43	701	843(843)
1,18-C8OVPC	418	261(61.5)	-5.19	-3.76	1.43	701	785(773)

a) 5%热失重温度; b) 从二次加热DSC曲线所得的相转变温度; c) 根据公式 $HOMO = -(4.80 + E_{onset}^{ox})$ eV和 $LUMO = -(4.80 + E_{onset}^{re})$ eV计算, E_{onset}^{ox} 和 E_{onset}^{re} 分别为由循环伏安法测定的氧化和还原起始电位; d) 初始薄膜的最大吸收峰位, 括号中为退火后的最大吸收峰位

图 4 2,3-C8OVPC (a), *dp*-C8OVPC (b), 1,15-C8OVPC (c) 和 1,18-C8OVPC (d) 的溶液(10^{-5} mol/L 的氯仿溶液)和薄膜紫外-可见-近红外吸收光谱. 薄膜由 5 mg/mL 的氯仿溶液在石英片上旋涂制备, 薄膜热退火时间为 15 min

Figure 4 Solution (10^{-5} mol/L in chloroform) and film UV-vis-NIR absorption spectra of 2,3-C8OVPC (a), *dp*-C8OVPC (b), 1,15-C8OVPC (c) and 1,18-C8OVPC (d). The films were prepared by spin-casting 5 mg/mL $CHCl_3$ solution on quartz substrates. Thermal annealing of the films was conducted for 15 min

用循环伏安方法测量了4个化合物的能级, 发现烷基链的位置对它们的能级影响较小. 外围取代的2,3-C8OVPC和*dp*-C8OVPC的HOMO能级分别为-5.14和-5.16 eV, LUMO能级分别为-3.77和-3.78 eV; 非外围取代的1,15-C8OVPC和1,18-C8OVPC的HOMO能级分别为-5.18和-5.19 eV, LUMO能级分别为-3.75和-3.76 eV, HOMO能级略低于外围取代的2,3-C8OVPC和*dp*-C8OVPC, LUMO能级则略有升高. 由于烷基链的弱给体作用, 它们的HOMO能级和LUMO能

级与四烷基酞菁钒相比都有所降低^[21,24,25].

2.4 有机薄膜晶体管器件性能

制备了4个化合物的底栅-顶接触型OTFTs器件, 器件的制备和测试均在空气环境下进行, 基于初始薄膜和优化温度退火薄膜的器件性能列于表2. 4个化合物的OTFT器件都表现出p-型(空穴)传输特性, 典型转移和输出曲线见图5. 2,3-C8OVPC的初始膜的迁移率最低, 为 $(1.5 \pm 0.3) \times 10^{-2} \text{ cm}^2/(\text{V s})$, 150°C热退火

后迁移率提高到 $0.19\text{ cm}^2/(\text{V s})$, 阈值电压为 $-5\sim-1\text{ V}$, 电流开关比达到 10^5 . *dp*-C8OVPC的初始膜迁移率为 $0.10\pm0.01\text{ cm}^2/(\text{V s})$, 热退火对器件迁移率影响不大, 120°C 退火后的迁移率为 $0.11\pm0.01\text{ cm}^2/(\text{V s})$. 1,15-C8OVPC薄膜的迁移率退火前后差别也不大, 初始膜迁移率为 $0.11\pm0.02\text{ cm}^2/(\text{V s})$, 120°C 退火后的迁移率为 $0.14\pm0.02\text{ cm}^2/(\text{V s})$; 1,18-C8OVPC的初始膜迁移率为 $(5.9\pm0.4)\times10^{-2}\text{ cm}^2/(\text{V s})$, 100°C 退火后的迁移率升高到 $0.14\pm0.01\text{ cm}^2/(\text{V s})$, 阈值电压 $-15\sim-10\text{ V}$, 开关比 10^5 . 这4个化合物的迁移率与非外围四己基酞菁

氧钒的异构体I3的迁移率相当($0.13\text{ cm}^2/(\text{V s})$)^[24], 但低于ABAB型四辛基酞菁氧钒OVPC-C8的迁移率($0.4\text{ cm}^2/(\text{V s})$)^[25].

2.5 薄膜微结构和形貌

用薄膜XRD, SAED和AFM表征了4个化合物的薄膜形貌. 如图6(a)所示, 2,3-C8OVPC的初始膜没有衍射峰出现, 说明初始膜的有序度较低; 经 150°C 热退火后, XRD图中可观察到四级衍射峰, 初级衍射峰对应的层间距为 2.79 nm , 大于ABAB型四辛基酞菁

图5 2,3-C8OVPC(a, e, 150°C 退火)、*dp*-C8OVPC(b, f, 120°C 退火)、1,15-C8OVPC(c, g, 120°C 退火)和1,18-C8OVPC(d, h, 100°C 退火)的OTFT器件的转移曲线(a~d)和输出曲线(e~h)

Figure 5 Representative output (a~d) and transfer characteristics (e~h) of OTFT devices based on thermally annealed films of 2,3-C8OVPC (a, e), *dp*-C8OVPC (b, f), 1,15-C8OVPC (c, g) and 1,18-C8OVPC (d, h). The annealing was done in nitrogen for 15 minutes at 150°C for 2,3-C8OVPC, 120°C for *dp*-C8OVPC and 1,15-C8OVPC, 100°C for 1,18-C8OVPC

表2 二辛基酞菁氧钒的OTFT器件性能

Table 2 Device performances of dioctyl-substituted vanadyl phthalocyanines

化合物	热退火温度($^\circ\text{C}$)	迁移率($\text{cm}^2/(\text{V s})$)	阈值电压(V)	电流开关比
2,3-C8OVPC	初始	0.015 ± 0.003	$-7\sim-5$	10^4
	150	0.17 ± 0.02	$-5\sim-2$	10^5
<i>dp</i> -C8OVPC	初始	0.10 ± 0.01	$-7\sim-4$	10^5
	120	0.11 ± 0.01	$-8\sim-2$	10^5
1,15-C8OVPC	初始	0.11 ± 0.02	$-5\sim-2$	10^5
	120	0.14 ± 0.02	$-3\sim-1$	10^5
1,18-C8OVPC	初始	0.059 ± 0.004	$-14\sim-7$	10^5
	100	0.14 ± 0.01	$-15\sim-10$	10^5

氧钒OVPc-C8的层间距(1.96 nm)^[25]。由理论计算所得的2,3-C8OVPc沿烷基链伸展方向的分子长度约为1.81 nm, 远小于XRD测定的层间距, 故推测2,3-C8OVPc分子在薄膜中以双层方式呈egde-on方式排列, 并且烷基链与共轭核分别排列。退火薄膜的SAED图中可以观察到2个清晰的衍射环, 分别对应于11.9和5.7 Å, 相近的衍射值(12.4和5.96 Å)在ABAB型四辛基酞菁氧钒OVPc-C8薄膜中也存在, 说明2,3-C8OVPc分子在面内具有较高的有序度, 并与ABAB型四辛基酞菁氧钒OVPc-C8的排列相类似。*dp*-C8OVPc和1,15-C8OVPc的薄膜在退火(120℃)前后均只观察到初级衍射峰(图6(b)和6(c)), 退火薄膜的SAED图中也只能观察到弱的衍射环, 二者XRD图中初级衍射峰所对应的层间距分别为1.85和2.25 nm, 表明分子同样以egde-on方式在基底上排列。1,18-C8OVPc的初始薄膜的XRD图中也只有初级衍射峰, 但退火后出现三级衍射峰, SAED图中可观察到一个对应层间距为12.3 Å的强衍射环, 其退火薄膜的XRD图中初级衍射峰所对应的层间距只有1.43 nm,

明显短于其他3个分子。考虑到在真空沉积的OVPc薄膜中, 分子以edge-on方式排列时对应的层间距为1.18 nm^[37]。因此, 我们推测1,18-C8OVPc在薄膜中同样以edge-on模式, 与其他3个分子不同的是, 烷基链沿平行于基底的方向排列。由上述结果可以发现, 热退火可以显著提高2,3-C8OVPc和1,18-C8OVPc薄膜的结晶度, 而对*dp*-C8OVPc和1,15-C8OVPc薄膜的结晶度影响较小, 因此, 热退火对基于2,3-C8OVPc和1,18-C8OVPc的器件的迁移率影响较大。

图7是4个分子的薄膜在热退火前后的AFM高度图。可以发现, 2,3-C8OVPc初始膜具有细小的纤维状结构, 表面粗糙度(RMS)较低(1.3 nm)。退火后晶粒尺度增大, 表现出粒状形貌, 同时RMS增大到2.5 nm。由薄膜XRD表征结果可知, 这种变化可能是由退火后薄膜的结晶性和有序度提高造成的, 同时带来电荷传输性能的提高。*dp*-C8OVPc的初始薄膜即具有较长的纤维结构, RMS为2.8 nm, 120℃退火后出现尺寸较大的晶粒。但未对器件的性能产生影响, 这可能与其是混合物有关。1,15-C8OVPc的初始薄膜

图6 2,3-C8OVPc (a), *dp*-C8OVPc (b), 1,15-C8OVPc (c)和1,18-C8OVPc (d)的初始和退火薄膜的XRD衍射图(插图为退火薄膜的SAED图)

Figure 6 Thin film XRD patterns of 2,3-C8OVPc (a), *dp*-C8OVPc (b), 1,15-C8OVPc (c) and 1,18-C8OVPc (d). Insets show the SAED patterns of annealed films

图7 2,3-C8OVPC (a, e), *dp*-C8OVPC (b, f), 1,15-C8OVPC (c, g)和 1,18-C8OVPC (d, h)的初始(a~d)和退火薄膜(e~h)的AFM高度图。热退火温度分别为150℃(e), 120℃(f, g)和100℃(h)(图中标尺长度为1 μm)

Figure 7 AFM height images of pristine (a~d) and annealed films (e~h) of 2,3-C8OVPC (a, e), *dp*-C8OVPC (b, f), 1,15-C8OVPC (c, g) and 1,18-C8OVPC (d, h). The annealing temperature were 150℃ for 2,3-C8OVPC (e), 120℃ for *dp*-C8OVPC (f) and 1,15-C8OVPC (g) and 100℃ for 1,18-C8OVPC (h) (the bar is 1 μm long)

和退火后薄膜均呈现尺寸~1 μm的晶粒, RMS较大, 分别达到12.9和13.6 nm, 会对器件的性能产生不利影响, 因此热退火后, 器件的性能改变不大。而1,18-C8OVPC的初始膜呈现较为平整的粒状薄膜(RMS为0.9 nm), 退火后晶粒尺寸变大, 导致晶界的数目减少, 有利于提高材料的电荷传输能力。

3 结论

合成并表征了4种二辛基酞菁氧钒, 其中*dp*-C8OVPC为2种异构体的混合物。发现辛基的位置对

分子固态下的堆积行为影响较大。*dp*-C8OVPC, 1,15-C8OVPC和1,18-C8OVPC的初始薄膜就具有一定的有序性, 退火对*dp*-C8OVPC和1,15-C8OVPC的薄膜的有序度影响不大, 因此, 退火前后二者的OTFT迁移率差别不大; 而退火后1,18-C8OVPC的薄膜的结晶度有所提高, 器件迁移率也相应提高。2,3-C8OVPC的初始薄膜为无定形态, 而退火后结晶度明显提高, 因此, 退火前后其OTFT器件的迁移率差1个数量级。基于4种化合物退火薄膜的OTFT器件的迁移率均超过0.1 cm²/(V s), 其中2,3-C8OVPC的迁移率最高, 达到0.19 cm²/(V s)。

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Synthesis, characterization and semiconducting properties of dioctyl substituted vanadyl phthalocyanines

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Solution processible organic semiconductors have attracted great attention in recent years due to their applications in printable electronics, such as organic thin-film transistor (OTFT). This type of device requires semiconductors characterized by low reorganization energies and strong intermolecular electronic interaction. Phthalocyanines are 18 π -electron disc-like aromatic macrocycles with two-dimensional (2D) π -electron delocalization over the whole molecule, and are featured with low reorganization energies and close π - π stacking. Moreover, tight 2D cofacial π - π stacking, which is beneficial for charge transport in the channel of OTFTs, can be realized by incorporating axially substituted metals or large metals in the core of phthalocyanines. Introducing alkyl substituents can endow phthalocyanines good solubility in organic solvents. However, the number and positions of alkyl substituents have great influence on the packing structures thereby OTFT performance of phthalocyanines. In the current paper, four dioctyl substituted vanadyl phthalocyanines, i.e. 2,3-dioctyl vanadyl phthalocyanine (2,3-C8OVPC), 2,16(17)-dioctyl vanadyl phthalocyanine (*dp*-C8OVPC), 1,15-dioctyl vanadyl phthalocyanine (1,15-C8OVPC) and 1,18-dioctyl vanadyl phthalocyanine (*dp*-C8OVPC), were synthesized, and the effect of the positions of octyl groups on their photophysical properties, OTFT performance was studied in detail. All four compounds are soluble in organic solvents such as chloroform and exhibit excellent thermal stability with the decomposition temperature (T_d) beyond 400°C. In dilute solution, the positions of octyl groups have negligible influence on their absorption spectra and frontier molecular orbital energy levels. Their absorption maxima ($\lambda_{\max}$) are all at ca. 700 nm and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels are -5.2 and -3.8 eV, respectively. From solution to film, their absorption spectra exhibited a remarkable bathochromic shift. In film state, four compounds all can form ordered thin films, in which they arrange in an edge-on way. Bottom gate and top contact OTFTs based on thermally annealed films of these four compounds were fabricated via solution spin-casting. All compounds showed p-type transport behavior with field-effect mobility above 0.1 cm²/(V s) 2,3-C8OVPC displayed the best OTFT device performance. A mobility of 0.19 cm²/(V s) has been demonstrated when the films were annealed at 150°C.

organic semiconductors, phthalocyanine, solution processing, organic thin-film transistors, mobility

doi: 10.1360/N972015-00665