

基于TBRb/C₆₀异质结的亚带隙发光二极管的新奇磁场效应

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摘要 为了研究亚带隙发光二极管的微观过程, 本文选用红荧烯(Rb)衍生物2,8-Di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb)为空穴传输兼发光层, 富勒烯(C₆₀)为电子传输层, 制备了具有亚带隙开启电致发光特性的TBRb/C₆₀器件, 并测量了器件在不同温度和电流下的电致发光磁效应(magneto-electroluminescence, MEL)和磁电导效应(magneto-conductance, MC). 实验发现, 传统Rb/C₆₀器件MEL曲线仅表现为系间窜越(intersystem crossing, ISC)和三重态-三重态湮灭(triplet-triplet annihilation, TTA)过程决定的线形. 然而, TBRb/C₆₀器件MEL曲线表现出三段式变化的新奇磁场效应: 随着外加磁场的增加, MEL先快速增大(0 mT < |B| ≤ 27 mT), 再减小(27 mT < |B| ≤ 100 mT), 再缓慢增大(100 mT < |B| ≤ 300 mT). 结合MC曲线进行机理分析可知, 这种新奇现象主要归因于ISC、TTA和三重态激基复合物-电荷湮灭过程(triplet exciplex-charge annihilation, TECA)的综合效应. 其中, TECA过程是由于TBRb比Rb材料的空穴迁移率更小, 导致TBRb/C₆₀异质结界面多余的电子与三重态激基复合物(triplet exciplex, EX₃)发生猝灭. 大电流下, TECA过程增强, 而TTA过程基本不变; 低温下, TECA和TTA过程展现出相同的非单调变化, 即先减弱再增强. 本研究有助于深入理解亚带隙发光二极管中激发态间的微观演化过程, 为高性能亚带隙发光器件的设计提供思路.

关键词 亚带隙发光二极管, 电致发光磁效应, 磁电导效应, 三重态激基复合物-电荷湮灭过程, 三重态-三重态湮灭过程

近年来, 有机发光二极管(organic light-emitting diodes, OLEDs)因具有自发光、视角广、可弯曲等优点, 在照明、显示和信息产业领域展现出广阔的应用前景^[1-6]. OLEDs发光的关键机制是外加电压下电极注入的电子和空穴进行辐射复合. 由能量守恒原则可知, 器件电致发光过程产生光子的最小驱动电压(或开启电压 V_T)等于发光材料的带隙能量(E_g)除以基本电荷(e), 即 $V_T \geq E_g/e$ ^[7]. 然而, 人们在一些特殊器件中观察到 V_T

小于 E_g/e 的情况^[7-16], 并称之为亚带隙开启电致发光过程. 例如, Lian等人^[7]基于1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, 带隙为2.35 eV)制备的热激活延迟荧光器件最小电压为1.72 V. Vasilopoulou等人^[9]在基于bis(diphenylphosphine oxide)dibenzofuran (DBFPO)/diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide (TSPO1)界面激基复合物的高效率蓝光OLEDs中得到低于带隙(3.8 eV)的开启电压为2.5 V. Izawa等

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人^[10]基于2,5,8,11-tetratert-butylperylene (TBPe, 带隙为2.68 eV)制备的蓝光OLEDs开启电压低至1.47 V. 值得注意的是,早在2007年, Pandey等人^[11]在红荧烯(Rb)/富勒烯(C₆₀)异质结器件中获得的电致发光开启电压为0.9 V, 该值约为发光材料红荧烯带隙能量(2.2 eV)^[11]的一半. 目前, 尽管科研界已从不同角度对亚带隙电致发光的物理机制进行了深入研究, 并提出了多种解释, 主要包括俄歇电子机制^[11,12]、三重态-三重态湮灭机制^[13~15]、带间复合机制^[16]等, 但对激发态的微观演化过程仍需深入研究.

本工作中, 我们选用具有优异光物理特性的红荧烯衍生物材料TBRb^[17~19]作为空穴传输兼发光层, C₆₀作为电子传输层, 制备了TBRb/C₆₀器件. 利用有机磁场效应(包括电致发光磁场效应(magneto-electroluminescence, MEL)和磁电导效应(magneto-conductance, MC))这一灵敏且无接触的探测技术^[14,15,20,21], 深入研究了亚带隙发光二极管在不同偏置电流和温度下的激发态动力学. 实验发现, 传统Rb/C₆₀器件MEL曲线展现出两段式变化, 即MEL随着外加磁场的增大先快速增加再逐渐减弱, 表现出系间窜越(intersystem crossing, ISC)和三重态-三重态湮灭(triplet-triplet annihilation, TTA)机制决定的线形. 虽然TBRb/C₆₀器件与Rb/C₆₀器件具有相同的能级排布和电致发光光谱, 但它们的MEL线形却不同. TBRb/C₆₀器件MEL曲线展现出新奇的线形: 在0 mT<|B|≤27 mT的低磁场范围内, MEL随外加磁场的增加快速增大; 在27 mT<|B|≤100 mT的中等磁场范围内, MEL逐渐减小; 在100 mT<|B|≤300 mT的高磁场范围内, MEL逐渐增大且未出现饱和现象. 分析随电流和温度变化的MC曲线可知, 这种新奇的MEL线形主要由ISC、TTA和三重态激基复合物-电荷湮灭(triplet exciplex-charge annihilation, TECA)三种机制决定. 其中, 由于TBRb比Rb具有更小的空穴迁移率^[22], TBRb/C₆₀异质结界面多余的电子与三重态激基复合物(triplet exciplex, EX₃)发生TECA过程. 此外, 还探究了这两种过程的电流和温度依赖性. 具体来讲, 大电流下, 注入载流子增多导致EX₃数量增加, 从而引起TECA过程增强, TTA过程基本不随电流变化. 当温度从300 K降至100 K时, 载流子迁移率降低导致TECA过程减弱^[15,23], TTA过程的吸热特性^[18,24]使得该过程也会减弱; 当温度进一步降至20 K时, 由于热声子的扰动减弱, 使得三重态激子(EX₃和T₁)寿命延长^[23,25], TECA和TTA过程增强. 本研究揭示了亚带隙开启OLEDs的激发态动力学,

对深入理解多种微观机制的综合效应具有指导意义.

1 器件制备与测量

如图1(a)所示, TBRb/C₆₀器件的具体结构为ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 40 nm)/TBRb (35 nm)/Fullerence (C₆₀, 50 nm)/bathocuproine (BCP, 10 nm)/LiF/Al. 为了对比研究亚带隙开启有机发光器件的激发态动力学行为, 还制备了传统的Rb/C₆₀器件作为参考. 该器件除了发光层为Rb以外, 其他功能层参数与TBRb/C₆₀器件完全相同. 两器件的具体制备和性能测试方法如下: 先将PEDOT:PSS水溶液旋涂于ITO玻璃基底表面, 再将样品放于hotplate加热仪上烘烤, 使PEDOT:PSS均匀成膜. 而后, 将玻璃/ITO/PEDOT:PSS样品放入超高真空(<10⁻⁶ Pa)蒸镀系统, 将其他各功能层材料依次蒸镀到PEDOT:PSS薄膜表面. 材料的生长速率和厚度用INFICON公司生产的XTM/2型膜厚监测仪全程进行原位监测. 器件制备完成后, 从蒸镀系统取出. 为了降低空气中水氧对样品的影响, 应快速将样品安装于电磁铁两磁极间的真空闭循环冷却系统中. 电磁铁内部由铜线圈组成, 磁场的大小由通过线圈的电流大小来调节. 通过与高斯计相连的霍尔片可测量加在样品上的具体磁场值. 样品两端的电压由Keithley 2400万用表提供. 样品的发光信号由硅光电探头和亮度计测定, 有、无外加磁场的电致发光强度EL(B)和EL(0)由Keithley 2000输出, 有、无外加磁场时流过器件的电流强度I(B)和I(0)由Keithley 2400测量. SpectraPro-2300i光栅光谱仪用于测量器件的电致发光光谱. 整个测量系统由计算机的Labview软件控制. 最后, 将测量的数据导入编好程序的Origin软件进行计算, 就可以得到MEL和MC曲线. MEL和MC的定义式如下:

$$MEL = \frac{\Delta EL}{EL} = \frac{[EL(B) - EL(0)]}{EL(0)} \times 100\%, \quad (1)$$

$$MC = \frac{\Delta I}{I} = \frac{[I(B) - I(0)]}{I(0)} \times 100\%. \quad (2)$$

2 结果与讨论

2.1 器件的基本结构、能级排布及光电特性

图1(b)为TBRb/C₆₀器件和Rb/C₆₀器件的能级排布图. 据文献^[11,17]报道, TBRb与Rb分子具有相同的最高占有分子轨道(the highest occupied molecular orbital,

HOMO)和最低未占有分子轨道(the lowest unoccupied orbital, LUMO)能量值,使两器件具有相似的能量转移过程和激发态形成方式.具体来讲,如图1(b)所示,电激发条件下,ITO阳极注入的空穴经空穴注入层PEDOT:PSS的HOMO能级后跳跃至TBRb (或Rb)的HOMO能级.同时,Al阴极注入的电子经电子注入层LiF和电子传输层BCP后到达C₆₀的LUMO能级.由于TBRb (或Rb)与C₆₀的HOMO能级差和LUMO能级差($\Delta E_{\text{HOMO}} = 0.8 \text{ eV}$, $\Delta E_{\text{LUMO}} = 1.3 \text{ eV}$)较大^[13,17],使得电子和空穴在TBRb/C₆₀或Rb/C₆₀界面发生聚集并形成激基复合物.由于三重态激基复合物和TBRb (或Rb)三重态激子间能量差较小,激基复合物会通过Dexter能量转移过程形成TBRb (或Rb)中的三重态激子^[14],三重态激子发生湮灭形成的单重态激子可退激辐射产生荧光. TBRb/C₆₀器件和Rb/C₆₀器件室温的归一化EL谱如图1(c)所示.可以看出,两器件具有完全相似的EL谱,即TBRb/C₆₀器件的EL谱主峰位为569 nm,肩峰约为607 nm, Rb/C₆₀器件的EL谱主峰位为562 nm,肩峰约为602 nm.这说明两器件的发光只来源于TBRb和Rb,而不是界面激基复合物.同时,对于TBRb/C₆₀器件而言,温度降为20 K时,

EL峰位略微发生了红移,与文献报道的Rb/C₆₀器件EL谱的温度依赖性一致^[14].此外,图1(d)及其插图展示了室温的亮度-电压和亮度-电流密度特性曲线.可以看出, TBRb/C₆₀和Rb/C₆₀器件在1 cd/m²亮度下对应的电致发光开启电压分别为1.0和1.2 V,这两个值约等于TBRb或Rb的带隙能量(2.2 eV)除以基本电荷的一半.两器件的亚带隙开启特性也与文献报道的实验结果一致^[14].据文献^[26]报道,外量子效率(external quantum efficiency, η_{EQE})主要与三个因素有关,包括EL光谱、亮度(luminance, L)和电流(I).当器件的EL光谱相同且通过器件的电流固定时, η_{EQE} 与 L 成正比,即可以表达为^[27]

$$\eta_{\text{EQE}} \propto kL, \quad (3)$$

其中, k 是与EL光谱和电流相关的系数.显然,从图1(c)和(d)的插图可以看出,室温下Rb/C₆₀与TBRb/C₆₀器件的EL谱基本重叠,并且在任一固定电流密度下, TBRb/C₆₀器件比Rb/C₆₀器件的亮度值更大.因此,根据式(3)可以判断TBRb/C₆₀器件的发光效率更高.下面,我们将通过分析MEL和MC响应曲线来探究TBRb/C₆₀器件的激发态微观演化机制.

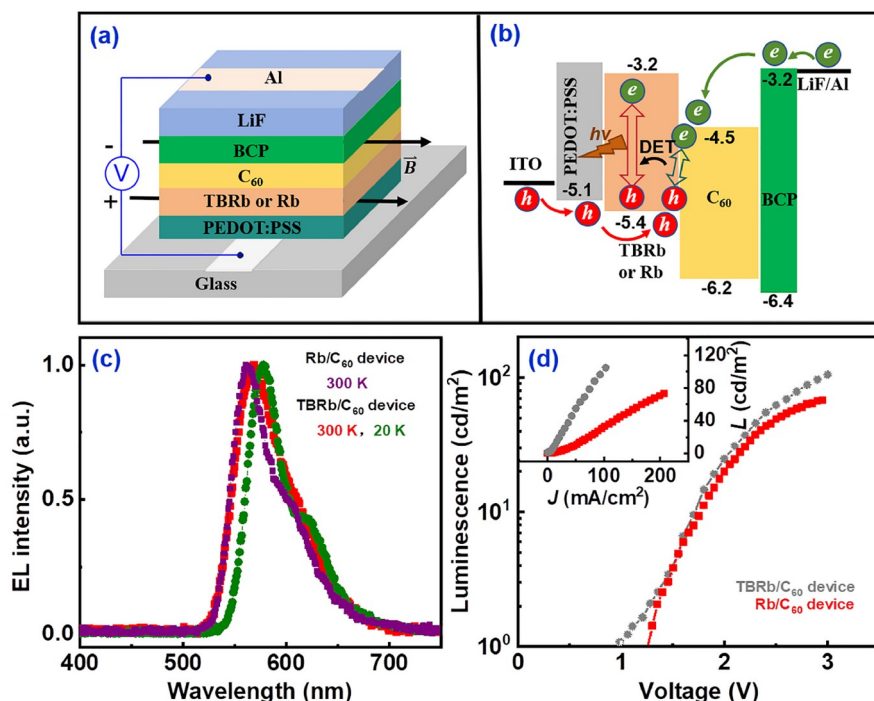


图1 TBRb/C₆₀器件和Rb/C₆₀器件的基本光电特性. (a) 基本结构; (b) 能级排布图、能量转移和发光过程; (c) 300和20 K温度下的归一化EL谱; (d) 亮度-电压和亮度-电流密度特性曲线

Figure 1 Basic optoelectronic characteristics of TBRb/C₆₀ and Rb/C₆₀-based devices. (a) Structure schematic of devices; (b) energy level alignments, energy transfer, and light emission processes; (c) normalized EL spectra at 300 and 20 K; (d) luminance-voltage and luminance-current density characteristic curves

2.2 室温下偏置电流对器件MEL曲线的影响

TBRb/C₆₀器件和Rb/C₆₀器件在室温(300 K)下MEL和MC响应曲线的电流依赖性如图2(a)~(d)所示. 可以看出, 尽管两器件具有相似的EL光谱和能级排布, 它们的MEL和MC曲线却展现出完全不同的线形. 具体来讲, 从图2(c)中可以看出, Rb/C₆₀器件的MEL曲线在 $|B| \leq 18$ mT的低磁场范围内, MEL值随 B 的增加而快速增大; 在 $18 \text{ mT} < |B| \leq 300$ mT高磁场范围内, MEL随 B 的增大逐渐减小. 该线形与文献报道的Rb/C₆₀器件中TTA过程决定的MEL线形一致^[14]. 图2(d)中Rb/C₆₀器件的MC曲线在低磁场范围内, MC值随 B 的增加快速减小; 在高磁场范围内, MC几乎不变, 展现出RISC过程决定的MC线形^[15]. 相比之下, TBRb/C₆₀器件的MEL值随外加磁场的增加先快速增大($0 \text{ mT} < |B| \leq 27$ mT), 再逐渐减小($27 \text{ mT} < |B| \leq 100$ mT), 再逐渐增大($100 \text{ mT} < |B| \leq 300$ mT), 如图2(a)所示; MC值先快速增大($|B| \leq 18$ mT), 再缓慢增大($18 \text{ mT} < |B| \leq 300$ mT), 如图2(b)所示. TBRb/C₆₀器件MEL曲线呈现出如此新奇的线形在文献中还未见报道过.

为了对比TBRb/C₆₀和Rb/C₆₀器件MEL曲线在不同

磁场范围内的电流依赖性, TBRb/C₆₀器件MEL的低场效应值(low-field effect value of MEL, MEL_{LFE})、中场效应值(mediate-field effect value of MEL, MEL_{MFE})和高场效应值(high-field effect value of MEL, MEL_{HFE})的绝对值可以分别定义为: $|MEL_{LFE}| = |MEL(27 \text{ mT}) - MEL(0 \text{ mT})|$ 、 $|MEL_{MFE}| = |MEL(100 \text{ mT}) - MEL(27 \text{ mT})|$ 和 $|MEL_{HFE}| = |MEL(300 \text{ mT}) - MEL(100 \text{ mT})|$. Rb/C₆₀器件MEL的低场效应值和高场效应值被定义为: $|MEL_{LFE}| = |MEL(18 \text{ mT}) - MEL(0 \text{ mT})|$ 和 $|MEL_{HFE}| = |MEL(300 \text{ mT}) - MEL(18 \text{ mT})|$. 为了进一步解释两器件MEL曲线存在较大差异的原因, MC曲线的低场效应值(low-field effect value of MC, MC_{LFE})和高场效应值(high-field effect value of MEL, MC_{HFE})的绝对值分别定义为: $|MC_{LFE}| = |MC(18 \text{ mT}) - MC(0 \text{ mT})|$ 和 $|MC_{HFE}| = |MC(300 \text{ mT}) - MC(18 \text{ mT})|$. 因此, 图2(a)~(d)中MEL和MC值在不同磁场范围下随电流的变化被总结在图2(e)和(f)中. 从图2(e)中可以看出, Rb/C₆₀器件的 $|MEL_{LFE}|$ 值随电流变化较小, $|MEL_{HFE}|$ 值随电流增大而增加, 表明TTA过程会随注入载流子的增多而增强; 从图2(f)中可以看出, 随着电流增大, $|MC_{LFE}|$ 值明显增大, $|MC_{HFE}|$ 变化较

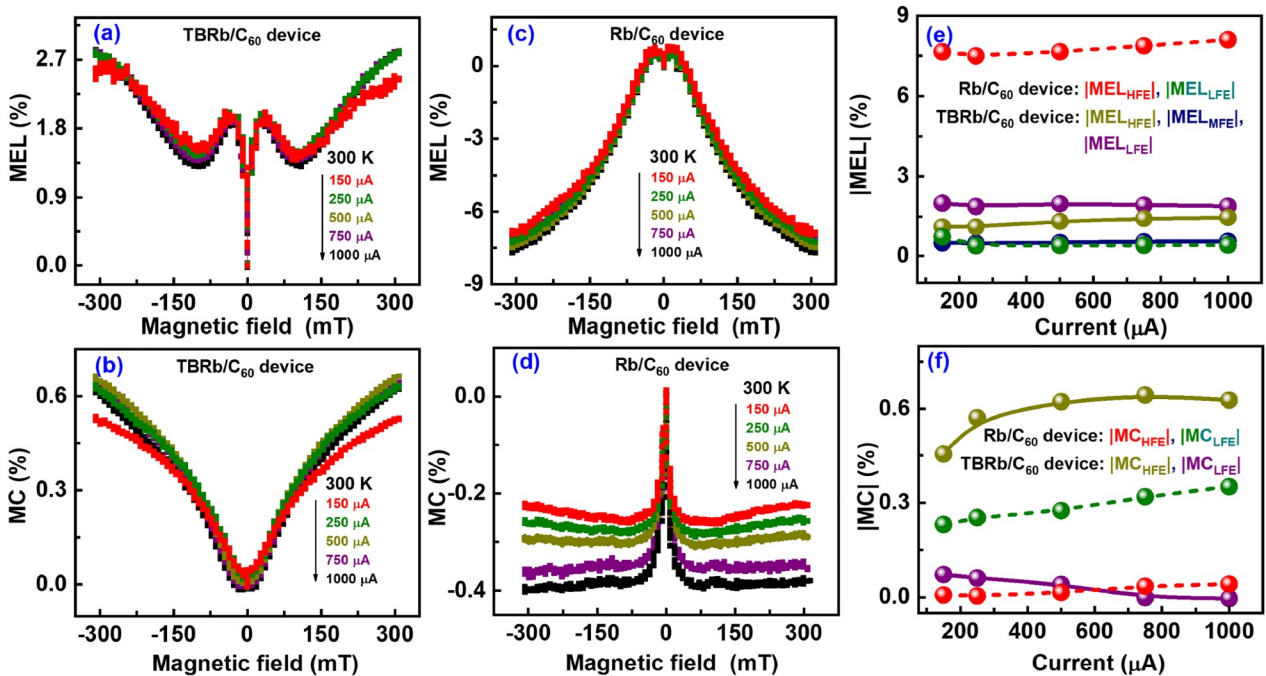


图2 TBRb/C₆₀和Rb/C₆₀器件在室温不同偏置电流下的MEL和MC响应曲线. TBRb/C₆₀器件MEL (a)和MC (b)曲线的电流依赖性; Rb/C₆₀器件MEL (c)和MC (d)曲线的电流依赖性; 不同磁场范围下MEL (e)和MC (f)值随电流的变化

Figure 2 Room-temperature MEL and MC response curves of TBRb/C₆₀ and Rb/C₆₀-based devices at different bias currents. Current-dependent MEL (a) and MC (b) curves for TBRb/C₆₀-based devices; current-dependent MEL (c) and MC (d) curves for Rb/C₆₀-based devices; current-dependent MEL (e) and MC (f) values at different ranges of magnetic fields

小,表明RISC过程会随注入载流子的增多而增强,这些变化规律与文献[15]保持一致.对于TBRb/C₆₀器件,从图2(e)和(f)中可以看出,|MEL_{LFE}|和|MEL_{MFE}|值基本不随偏置电流变化,而|MC_{LFE}|值随电流增大而减小,|MC_{HFE}|和|MEL_{HFE}|值随电流增大而明显增大.这些变化看似复杂,实际上也不难理解.据文献[28,29]报道,有机半导体器件的EL与电流和外量子效率间的关系为: $EL \propto I \times \eta$. 由于外加磁场的变化会引起EL、 I 和 η 的变化,因此, $\Delta EL/EL = \Delta I/I + \Delta \eta/\eta$. 类比式(1)和(2),可以定义效率磁效应(或称磁效率, magneto-efficiency, $M\eta$)为 $M\eta = \Delta \eta/\eta$ 且 $\Delta \eta = \eta(B) - \eta$, 其中 $\eta(B)$ 和 η 分别表示有、无外加磁场 B 时的外量子效率.也就是说, MEL实际上等于MC和 $M\eta$ 之和[28~31]. 换句话说, MC的产生机制也常被用来辅助解释MEL的变化. 根据指纹式MC曲线可知[15,32], ISC过程决定的MC曲线表现为半高全宽为几mT的倒置洛伦兹线形, TECA过程决定的MC曲线表现为半高半宽为50~100 mT的倒置非洛伦兹线形. 因此, 图2(b)中MC曲线的低场由ISC决定, 高场由TECA过程决定, 说明图2(a)中MEL曲线除了包含ISC和TTA过程的作用以外, 还包含了TECA过程的作用. 下面具体分析TBRb/C₆₀器件具有复杂MEL线形的原因.

2.3 机理分析

电激发条件下, TBRb/C₆₀器件中载流子的复合和激发态间的相互转化过程如图3所示. 具体来讲, 电极

注入的电子和空穴载流子到达TBRb/C₆₀界面后, 形成能量简并的单重态极化子对(singlet polaron pair, PP₁)和三重态极化子对(triplet polaron pair, PP₃). 这些极化子对能够参加3个演化通道: (1) 以 d_S 和 d_T 的速率常数直接解离形成二次载流子; (2) 以 k_S 和 k_T 的速率常数分别形成单重态激基复合物(singlet exciplex, EX₁)和三重态激基复合物(triplet exciplex, EX₃); (3) 在超精细作用下发生自旋混合, 即相互转化($PP_1 \leftrightarrow PP_3$), $k_T > k_S$ 导致PP-ISC过程($PP_1 \rightarrow PP_3$)通常占主导[33]. 此外, 激基复合物在超精细作用下也可发生相互转化($EX_1 \leftrightarrow EX_3$). 由于EX₁态的寿命较短, 使EX-RISC过程($EX_3 \rightarrow EX_1$)通常占主导[34]. 对于EX₃态而言, 除了进行EX-RISC过程外, 还参与了两个过程: (1) 由于TBRb的空穴迁移率($2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)[22]低于C₆₀的电子迁移率($1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)[35], 激基复合物界面会聚集一些多余的电子载流子并与EX₃态发生湮灭(即TECA过程); (2) EX₃态与T₁态间较小的能量差使EX₃态还可以通过Dexter能量转移过程形成TBRb中的T₁态. 两个T₁态发生聚合(TTA, $T_1 + T_1 \rightarrow (TT)_1 \rightarrow S_1 + S_0$)可以形成S₁态. 最后, S₁态退激回到基态并向外发射光子产生荧光. 由于TBRb/C₆₀器件中几乎没有电子注入势垒且空穴注入势垒约为0.3 eV, TBRb的HOMO和C₆₀的LUMO间能量差约为0.9 eV, 导致TBRb/C₆₀器件的驱动电压应为1.2 eV左右, 该值约为TBRb带隙的一半. 因此, TBRb中TTA过程也是产生亚带隙电致发光的原因.

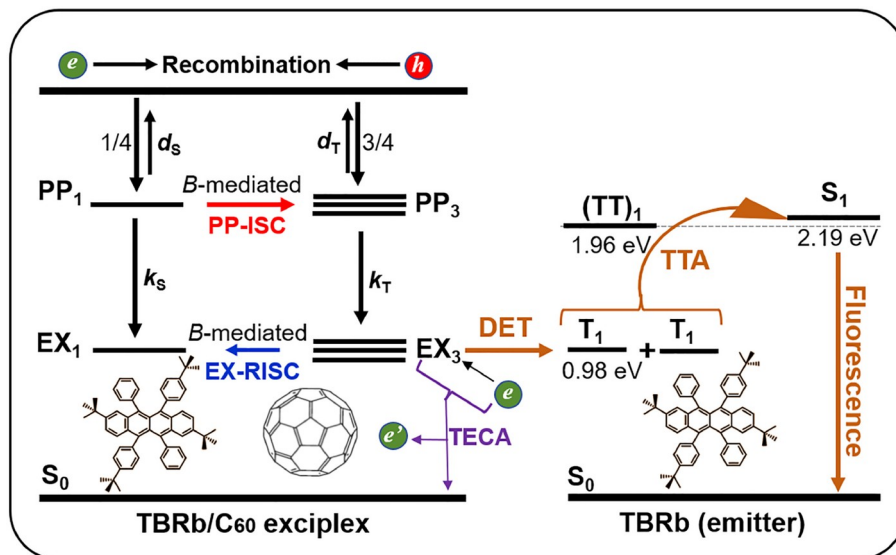


图3 TBRb/C₆₀器件在电激发条件下异质结界面激发态的形成、能量转移过程和TECA过程示意图

Figure 3 The formation methods of excited states, energy transfer process, and TECA process of the heterojunction interface in the TBRb/C₆₀-based device under electrical excitation

从以上分析可知, TBRb/C₆₀器件包含了4种激发态转化机制: PP-ISC、EX-RISC、TECA和TTA. 其中, 由于PP-ISC和EX-RISC由超精细作用决定, 其指纹式MEL曲线的特征磁场仅为几毫特斯拉, 理论上讲, 它们的共同作用决定了低场MEL线形. 然而, 这两个过程具有近似相反的指纹式MEL曲线^[15,32], 且图2(a)的低场表现为倒置洛伦兹线形. 因此, 可以判断PP-ISC对低场MEL线形起决定作用. 同时, 结合TECA和TTA过程决定的特征MEL曲线的演化规律^[15,32]可知, 图2(a)中MEL曲线中场由TTA过程决定, 高场由TECA过程决定. 室温下, 随着偏置电流的增大, 形成的PP态和EX态数量增加, ISC和RISC同步增加, 导致总体表现出来的ISC过程基本不随电流变化. 虽然载流子迁移率不会随电流变化, 但大电流下注入载流子增多导致EX₃态数量增多, 因此TECA过程增强, TTA过程基本不变.

2.4 温度对器件MEL响应曲线的影响

为了进一步分析环境温度对TBRb/C₆₀器件中新奇MEL线形的影响, 我们还测量了器件在200和100 K温度下MEL和MC曲线随偏置电流的变化, 如图4所示. 可以清晰地看出, TBRb/C₆₀器件在200和100 K温度的

不同偏置电流下, MEL和MC曲线具有与室温(图2(a)和(b))完全相似的线形, 即MEL值随外加磁场的增加先快速增大(0 mT<|B|≤27 mT), 再逐渐减小(27 mT<|B|≤100 mT), 再逐渐增大(100 mT<|B|≤300 mT). 也就是说, 低温下MEL仍主要由ISC、TTA和TECA机制决定, 而MC由ISC和TECA过程决定, 只是各机制的强度随温度发生了变化. 为了更加清晰地分析温度对各微观机制的影响, TBRb/C₆₀器件MEL和MC曲线的温度依赖性如图5(a)和(b)所示. 同时, 与之对应的不同磁场范围的MEL和MC值随温度的变化被总结在图5(c)和(d)中. 此外, Rb/C₆₀器件MEL曲线的温度依赖性和不同磁场范围MEL值随温度的变化被呈现在图5(e)和(f)中. 从图5(e)中可以看出, 随着温度降低, Rb/C₆₀器件的MEL线形基本不变. 从图5(f)中可以看出, Rb/C₆₀器件的|MEL_{LFE}|随温度基本不变, |MEL_{HFE}|随温度的降低而明显增大, 说明TTA过程在低温下增强了, 与文献报道的Rb/C₆₀器件中TTA的温度依赖性一致^[14]. 相比之下, 从图5(d)中可以看出, |MC_{LFE}|随温度基本不变, |MC_{HFE}|随温度降低先减小再增大, 说明TECA过程在低温下先减弱再增强. 从图5(c)中可以看出, |MEL_{LFE}|随温度基本不变, |MEL_{MFE}|和|MEL_{HFE}|值均随温度的降低而先减弱再增

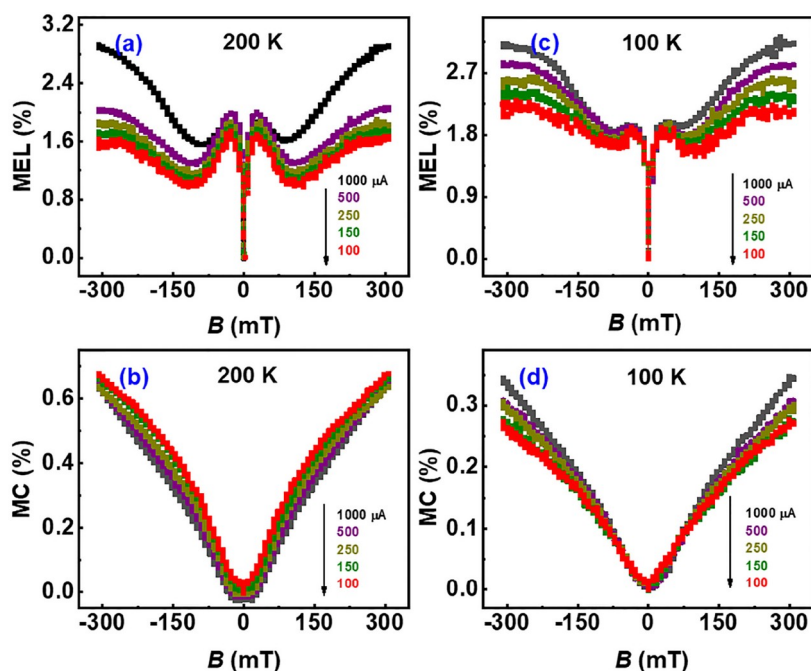


图4 TBRb/C₆₀器件在不同温度下的MEL和MC曲线. 200 K温度下MEL (a)和MC (b)曲线的电流依赖性; 100 K温度下MEL (c)和MC (d)曲线的电流依赖性

Figure 4 The MEL and MC response curves of the TBRb/C₆₀-based device at different temperatures. Current-dependent MEL (a) and MC (b) curves at 200 K; current-dependent MEL (c) and MC (d) curves at 100 K

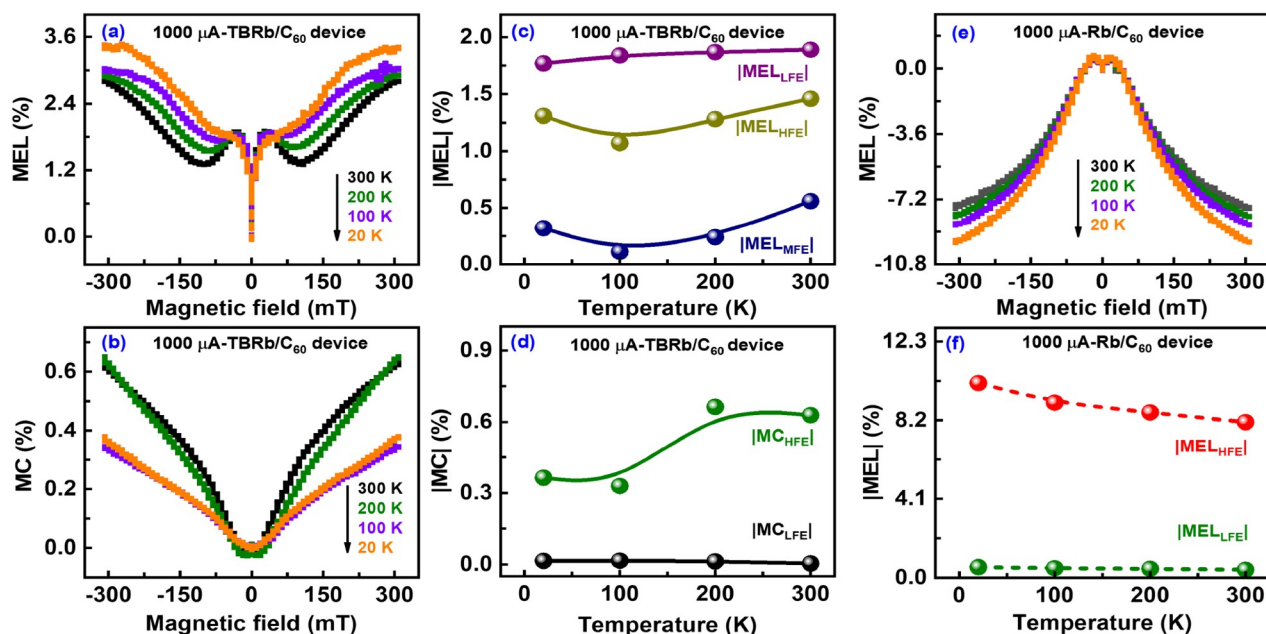


图 5 TBRb/C₆₀器件在1000 mA电流下MEL (a)和MC (b)曲线的温度依赖性; MEL (c)和MC (d)在不同磁场范围下的幅值随温度的变化; Rb/C₆₀器件在1000 mA电流下MEL曲线的温度依赖性(e)和MEL曲线在不同磁场范围下的幅值随温度的变化(f)

Figure 5 The temperature-dependent MEL (a) and MC (b) curves of the TBRb/C₆₀-based device at 1000 mA; the amplitudes of MEL (c) and MC (d) as a function of temperature for the TBRb/C₆₀-based device; the temperature-dependent MEL curves (e) and MEL amplitudes (f) of the Rb/C₆₀-based device at 1000 mA

大, 说明TECA和TTA过程先减弱再增强. 本文认为TECA过程的非单调变化是由两种作用的竞争作用所致: (1) 低温下载流子的迁移率降低使得TECA过程减弱^[15,23]; (2) 低温下热声子的扰动作用减弱导致EX₃态寿命延长^[23,25], 该作用将促进TECA过程. 同理, TTA过程的非单调变化也取决于两个因素: (1) 对于TBRb分子而言, 其S₁和T₁态能量分别为2.19和0.98 eV^[18,24]. 显然, $2E(T_1) < E(S_1)$, 说明TBRb中TTA过程是个吸热过程, 该特性使得TTA在一定温度范围(300~100 K)随着温度的降低而减弱, 这一特性与Rb中TTA过程的温度依赖性相反^[14]. (2) 在更低温度(100~20 K)下, T₁激子寿命的延长将导致TTA过程的增强^[15,25].

3 结论

本工作利用MEL和MC响应曲线, 研究了基于TBRb/C₆₀异质结的亚带隙开启电致发光器件中激发态演化机制随温度和偏置电流的变化. 实验发现, 与传统的

Rb/C₆₀器件相比, TBRb/C₆₀器件在不同温度下的MEL曲线均展现出新奇的三段式变化: ISC过程决定的低场变化; TTA过程决定的中场变化; TECA机制决定的高场变化. ISC过程具有较弱的电流和温度依赖性; TTA过程随电流的增大而基本不变, 随温度的降低先减弱再增强; TECA过程随电流的增大而增强, 随温度的降低先减弱再增强. 分析载流子迁移率、激发态能量和寿命随温度和电流的变化可知, 注入电流增大时, 尽管载流子迁移率不受电流变化影响, 增加的注入载流子将形成更多的EX₃态使得TECA过程增强, 而TTA过程变化不大. 当温度从300 K降至100 K时, 载流子迁移率降低导致TECA过程减弱, 本身的吸热特性将导致TTA过程也减弱, 而随着温度进一步降低至20 K时, EX₃和T₁态的寿命延长使得TECA和TTA过程增强. 本研究工作深入分析了各微观机制随电流和温度的变化, 加强了对亚带隙发光器件中多种机制共同作用的理解.

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Summary for “基于TBRb/C₆₀异质结的亚带隙发光二极管的新奇磁场效应”

Novel magnetic field effects in TBRb/C₆₀-based OLEDs with sub-bandgap turn-on electroluminescence

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In order to study the microscopic processes in devices with sub-bandgap turn-on voltages, a rubrene (Rb) derivative named 2,8-di-tert-butyl 5,11-bis (4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb) was selected as the hole-transporting and emission layer, and fullerene (C₆₀) was used as the electron transport layer to fabricate the devices with the planar heterojunction of the TBRb/C₆₀ interface. The TBRb/C₆₀ device possesses the property of sub-bandgap turn-on electroluminescence. In order to clearly analyze the microscopic mechanisms in TBRb/C₆₀ devices, we also prepared traditional Rb/C₆₀ devices as reference devices. Simultaneously, we also measured the temperature and current dependences of magneto-electroluminescence (MEL) and magneto-conductance (MC) response curves for TBRb/C₆₀ and Rb/C₆₀ devices. The experimental results show that the MEL curves of traditional Rb/C₆₀ devices decide by the intersystem crossing (ISC, PP₁→PP₃) from singlet to triplet polaron pairs (PP₁ and PP₃) and triplet-triplet annihilation (TTA, T₁+T₁→S₁+S₀) processes. However, the MEL curves of the TBRb/C₆₀ device show a novel magnetic field effect with a three-stage variation: With the increase of the applied magnetic field, MEL firstly increases rapidly (0 mT<|B|≤27 mT), then decreases (27 mT<|B|≤100 mT), and then increases slowly (100 mT<|B|≤300 mT). According to the analysis of current-dependent MC curves, this novel phenomenon is mainly attributed to the combined effect of ISC, TTA and triplet exciplex charge annihilation (TECA). Notably, since the hole carrier mobility of TBRb is smaller than that of the Rb material, the existence of excess electron carriers at the TBRb/C₆₀ heterojunction interface can interact with triplet exciplex (EX₃) via TECA process (EX₃+e→e'+S₀). At large currents, although carrier mobility remains constant, the increased number of injected carriers can increase the amount of EX₃, leading to the enhancement of the TECA process. At the same time, since the essentially unchanged Dexter energy transfer process does not result in an increase in the number of T₁ as the injection current increases, the TTA process does not vary significantly with the injection current. When the temperature drops from 300 K to 100 K, the decreased carrier mobility can weaken the TECA process, while the endothermic characteristic of the TTA process causes it to decrease. This anomalous endothermic property is due to the singlet state energy (2.19 eV) of the TBRb material being higher than twice the triplet exciton energy (0.98 eV). When the temperature decreases from 100 K to 20 K, the prolonged lifetime of EX₃ and T₁ states can lead to the increase of TECA and TTA processes, respectively, with decreasing temperature. This study is helpful in understanding the microscopic evolution of excited states in OLEDs with sub-bandgap electroluminescence, and provides ideas for the design of high-performance devices.

light-emitting diodes with sub-bandgap turn-on voltage, magneto-electroluminescence, magneto-conductance, triplet-exciplex-charge annihilation process, triplet-triplet annihilation process

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