掺杂浓度和温度对有机延迟荧光磁效应的影响

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摘要 在基于电荷转移(charge transfer, CT)态的发光器件中, CT态的演化及其相互作用对器件发光有重要影响. 将分子内CT态材料4-(Dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran(DCJTb)以不同浓度掺杂于磷光主体材料1,3-bis(9-carbazolyl)benzene (mCP)中, 通过测量器件电致发光的磁场效应(magneto-electroluminescence, MEL), 来研究器件中CT态及其相互作用. 在 ± 500 mT的磁场范围内, MEL曲线展示出奇特的变化: 当掺杂浓度从高浓度(20%)降至低浓度(5%)时, 低场部分从正转变为负; 而高场部分没有明显的浓度依赖关系, 均表现为缓慢下降. 另外, 在不同温度下MEL高低场部分的幅度都有很大变化. 这些变化表明, 器件中存在CT态的系间窜越、反向系间窜越过程, 以及CT态间的湮灭过程, 且这些过程受到掺杂浓度和温度的影响, 导致延迟发光的变化.

关键词 反向系间窜越, 三重态激子湮灭, 掺杂浓度, 温度, 延迟荧光, 有机发光磁效应

近年来, 电荷转移(charge transfer, CT)态发光器件因得到了较高的发光效率(外量子效率 $>10\%$)而成为了研究热点^[1-8]. 这是因为通过分子设计, 一些CT态材料的单重态(^1CT)和三重态(^3CT)之间的能级差可以变得非常小, ^3CT 通过吸热过程可转换为 ^1CT (即反向系间窜越reverse intersystem crossing, RISC), 从而产生延迟荧光, 最终实现高的外量子效率^[2,3,9,10]. 事实上, 在CT态器件中对发光有额外贡献的激发态演化过程不仅有RISC过程, 还有三重态激子湮灭(即triplet-triplet annihilation, TTA)过程, 即两个 ^3CT 通过相互作用产生一个额外的 ^1CT , 该 ^1CT 通过辐射退激产生延迟荧光, 从而也对总发光产生贡献^[11,12]. 大量的研究表明, RISC^[2,3,9,10]和TTA^[13-15]均是利用三重态实现高效率荧光OLED的重要途径, 且RISC和TTA共存可使荧光OLED中三重态的利用更充分^[16]. 然而, RISC和TTA过程很难共存于同一器件中^[17]. 所以,

人们对提高荧光OLED发光效率的探究主要集中在RISC^[2,3,18]或TTA^[11,15,18,19]单独存在的基础上, 二者共存的情况却少有研究, 特别是如何同时促进RISC和TTA过程还未见报道. 考虑到RISC和TTA都是三重态参与的自旋混合过程, 要想同时促进二者, 那么对三重态浓度和寿命的调控就显得尤为重要. 一般来说, 掺杂和工作温度往往可以较大程度地改变三重态浓度和寿命^[20-22]. 因此, 我们认为掺杂浓度和工作温度会对RISC和TTA共存体系产生重要影响, 并且非常有必要对其进行研究.

对于RISC和TTA共存的荧光OLED而言, 通过常规手段很难区分出延迟荧光来源于哪种演化过程. 而有机磁致发光(magneto-electroluminescence, MEL)作为一种新的探测方法, 能够有效识别器件内部不同的自旋混合过程^[23-25]. 研究发现, RISC主导的MEL表现为低场($B < 20$ mT)快速下降, 高场($B > 20$ mT)趋于

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饱和^[18]；而TTA起主要作用的MEL则表现为低场小幅度上升，高场大幅度下降^[18]。因此，本文通过对不同掺杂浓度及温度下的MEL的定性分析，发现掺杂浓度和温度可以明显改变RISC和TTA过程。这些发现丰富了多种微观机制下有机发光磁效应的理论内容，同时也为进一步提高器件的发光效率提供了思路。

本文以分子内CT态材料4-(Dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran(DCJTb)作为客体，制备了结构为ITO/Poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/N, N'-Di(naphthalen-1-yl)-N, N'-diphenylbenzidine(NPB)/1,3-bis(9-carbazolyl)benzene(mCP):DCJTb/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP)/LiF/Al的掺杂型器件。掺杂浓度分别为20%，14%，10%，7%，5%，并在20~300 K温度范围内测量了这些器件的MEL。这些MEL都由低场部分和高场部分组成。在室温下，MEL的低场部分在掺杂浓度较大时表现为快速上升($B < 5$ mT)，在掺杂浓度较小时则表现为快速下降，即随着掺杂浓度的减小，低场部分出现了正负转变；而高场部分($B > 20$ mT)均表现为单调地缓慢下降。另外，MEL还要受温度的影响：掺杂浓度为20%时，低场的上升幅度随着温度的降低而变小，但高场的下降幅度变大；掺杂浓度 $\leq 14\%$ 时，高低场的下降幅度都变大。这些MEL的变化表明，器件中存在ISC，RISC和TTA三个过程，而低的掺杂浓度和低温可以增大器件中 ^3CT 的寿命和浓度，从而可以更充分地利用 ^3CT 产生延迟荧光。

1 器件的制备与测量

本实验制备了结构为ITO/PEDOT:PSS(40 nm)/NPB(60 nm)/mCP:DCJTb(30 nm)/BCP(50 nm)/LiF/Al的器件，其中PEDOT:PSS为空穴注入层，NPB作为空穴传输层，mCP作为发光主体材料，DCJTb作为荧光染料掺杂剂(发光客体材料)和BCP作为电子传输层兼空穴阻挡层。所制备器件的掺杂浓度分别为20%，14%，10%，7%，5%。实验前，将带有ITO阳极的玻璃衬底依次使用清洗液(Decon 90，浓度4%，水浴温度为60℃)、去离子水对玻璃基片反复超声清洗，之后再用无水乙醇、丙酮脱水。PEDOT:PSS层采用旋涂法制备，并用DEKTAK 6m台阶仪测得的膜厚分别在40 nm左右。传入超高真空腔体内($\sim 10^{-5}$ Pa)用有机分子束沉积方法依次生长有机层和LiF。其中掺杂层采用共蒸

发方法获得，掺杂浓度是通过调节二者的速率比例来控制的。Al阴极采用热阻蒸发方法制备。蒸发速率及薄膜厚度采用INFICON公司的膜厚检测仪(XTM/2)进行原位监测。器件的有效发光面积为2 mm×2 mm。

测量时，将器件快速从腔体取出并固定在高真空闭循环冷却系统(Janise:CCS-340S)的冷头上，冷头内的温度在300~20 K连续可调。外部磁场是由位于样品托两侧的电磁铁提供，磁场方向平行于器件的膜面，磁场大小由计算机控制电磁铁(Lakeshore:EM647)获得，并由置于样品附近的高斯计(Lakeshore 421)实时监控。Keithley 2400为器件加载偏置电压，并同时测量通过器件的电流。在恒压偏置下，器件的电致发光强度由硅光电探测器测得并通过Keithley 2000输出。测量温度通过温控单元(Lakeshore 331)读取。

2 实验结果

2.1 CT态的演化过程及ISC，RISC和TTA的MEL特征曲线

图1(a)为在外磁场作用下CT态器件中ISC，RISC以及TTA的演化过程示意图。对于分子内CT态材料而言，其电子给体-受体基团相互分离^[18]，可以实现单三态能级差很小。此时，不仅单重态可以转换成三重态($^1\text{CT} \rightarrow ^3\text{CT}$ ，系间窜越，ISC)，三重态也可以在环境热辅助作用下转换成单重态($^3\text{CT} \rightarrow ^1\text{CT}$ ，RISC)^[2,3]。ISC过程和RISC过程互为逆过程，此时 $^1\text{CT} \leftrightarrow ^3\text{CT}$ 的相互转换处于动态平衡状态。未加外磁场时，三重态三个能级($^3\text{CT}_{+1}$ ， $^3\text{CT}_0$ ， $^3\text{CT}_{-1}$)是简并的，都可以与单重态相互转换；而外加磁场大于超精细场时，三重态之间的简并解除，仅剩三重态 $^3\text{CT}_0$ 可与单重态相互转换^[18,26-28]。因此，外加磁场会抑制 $^1\text{CT} \leftrightarrow ^3\text{CT}$ 的相互转换。当外加磁场抑制 $^1\text{CT} \rightarrow ^3\text{CT}$ 的ISC过程时，单重态增加，瞬时发光增强，MEL的表现如图1(b)中正方形图标所在直线所示；当外加磁场抑制 $^3\text{CT} \rightarrow ^1\text{CT}$ 的RISC过程时，单重态减少，导致延迟荧光减弱，MEL的表现如图1(b)中圆形图标所在直线所示。TTA过程是指两个 ^3CT 相互碰撞，产生一个中间态的($^3\text{CT} \cdots ^3\text{CT}$)，进而演化生成一个 ^1CT 和一个基态。在外加磁场为0时，九组($^3\text{CT} \cdots ^3\text{CT}$)中只有具有单重态特征的那一组可转换成单重态激子；而随着外加磁场逐渐增大，具有单重态特征的 $^3\text{CT} \cdots ^3\text{CT}$ 在所有的中间态中的比率将先增大再减小，从而影响单重态的数目^[29]，

图1 (网络版彩色)(a) CT态的演化过程示意图; (b) ISC, RISC以及TTA的MEL曲线示意图

Figure 1 (Color online) (a) Schematic evolution in CT state device; (b) schematic MEL curves for ISC, RISC and TTA

表现出的MEL如图1(b)中三角形图标所在直线所示.

综上所述, 我们可以看到, 不同的单、三重态相互转换过程对应着不同的MEL特征曲线. 因此, 通过测量并分析不同条件下的MEL曲线, 我们就可以对这些转换过程有一个清晰的认识.

2.2 掺杂浓度对MEL的影响

在300 K下, 注入电流均为100 μ A时, 器件MEL随掺杂浓度的变化如图2(a)所示. 为了更好地显示低场部分变化情况, 图2(b)给出了(-80~80 mT)区间的MEL. MEL定义为: $MEL = \Delta EL / EL = [EL(B) - EL(0)] / EL(0) \times 100\%$, 其中 $EL(0)$ 和 $EL(B)$ 分别是无、有磁场时器件的电致发光强度. 从图1(a)可以看出, 掺杂浓度较高时的MEL表现为先快速上升再缓慢下降, 而掺杂浓度较低时的MEL则先小幅度地快速下降再大幅度地缓慢下降. 也就是说随掺杂浓度的减小, MEL在低磁场($B \leq 20$ mT)范围内的线型发生了正负转变, 而在高磁场部分($20 \text{ mT} \leq B$)则线型均表现为下降且幅度

单调递增. 图2(b)可观察到-80~80 mT磁场范围内各浓度MEL的变化趋势明显不同: 当掺杂浓度为20%时, MEL随磁场增加而上升; 而掺杂浓度介于10%~14%范围内时, MEL表现为先有一个幅度非常小的下降再上升; 当掺杂浓度降低至 $\leq 7\%$ 时, MEL随磁场的增大先快速下降再缓慢下降. 本文在3个阶段分别选取了一个浓度的器件进行了降温处理, 用来探究温度对MEL的影响.

2.3 温度对MEL的影响

图3分别给出了掺杂浓度为20%, 10%以及5%的器件在不同温度下的MEL曲线, 其注入电流均为100 μ A. 其中(a), (c), (f)对应的磁场为(-500~500 mT), 可以看出, 随着温度的降低, 各浓度器件的MEL高场下降幅度明显增加. 为了更清晰地展示低场变化情况, 图3(b), (d), (e)把磁场变化范围限定在(-80~80 mT). 我们发现, 低场部分在掺杂浓度为20%时, 上升幅度随着温度的降低而减小; 低于10%时, 转变为

图2 (网络版彩色)室温下不同DCJT-B掺杂浓度的器件分别在 ± 500 mT(a)和 ± 80 mT(b)磁场范围内的电致发光磁效应, 注入电流密度为100 μ A
Figure 2 (Color online) The MEL curves of DCJT-B doped devices with different doping concentrations at room temperature, the injection currents are 100 μ A. (a) B ranges within ± 500 mT; (b) B ranges within ± 80 mT

图3 (网络版彩色)DCJTB掺杂浓度为20%、10%和5%的器件在同一电流密度(100 μ A),不同温度下的电致发光磁效应,其中(a), (c), (f) 对应的磁场为(-500~500 mT), (b), (d), (e)对应的磁场为(-80~80 mT)

Figure 3 (Color online) The MEL curves of DCJTB-doped devices changing with the different temperatures. From top to bottom, the doping concentrations are 20%, 10% and 5%, respectively. The left hand ((a), (c), (f)) is for MELs within ± 500 mT and the right hand ((b), (d), (e)) is for MELs within ± 80 mT, the injection currents are 100 μ A

下降且随着温度的降低而增大。

3 分析与讨论

本文选用的掺杂客体DCJTB是一种典型的分子内CT态材料^[18]。在DCJTB掺杂型器件中,空穴、电子分别从阳极、阴极注入,在电场的作用下,彼此相互靠近并在客体DCJTB中复合成CT态。基于自旋统计原理,这些CT态分为1/4的单重态¹CT和3/4的三重态³CT。与激子型分子相比,DCJTB分子中电子和空穴之间的距离较大,使得它的单三重态能级差非常小(仅为0.352 eV)^[18],最终导致DCJTB器件中不仅能发生¹CT $\rightarrow$ ³CT过程,还能在环境的热激发下发生³CT $\rightarrow$ ¹CT过程,如图1(a)所示。所以,¹CT $\leftrightarrow$ ³CT之间的相互

转换过程是一个动态平衡过程,而转换方向与单三重态的相对浓度和各自寿命密切相关。当三重态的数量很多且寿命很长时,RISC过程产生的¹CT将大于ISC过程产生的³CT,转换方向为³CT $\rightarrow$ ¹CT;反之,则为¹CT $\rightarrow$ ³CT。为了延长三重态的寿命,我们选用了mCP作为主体材料,是因为mCP的三重态能级(~ 2.91 eV)比DCJTB的三重态能级(~ 1.974 eV)高很多,能够抑制DCJTB三重态激子将能量回传给主体材料。此外,掺杂的引起“能级陷阱”效应^[20,30],还可以使TTA过程在室温下发生。因此,在DCJTB掺杂型器件中,ISC, RISC以及TTA过程均可以发生。

DCJTB器件的MEL在这里表现出两种线型:一种是在低场范围内快速上升,而后缓慢下降;另一种是

先在低场范围内快速下降,再继续缓慢下降,如图2(a)所示.前一种线型较为常见,其低场由ISC主导,高场由TTA决定^[30].而后一种线型比较奇特,很少见到,我们认为应该是RISC与TTA共同作用的结果.为了证明我们的观点,我们选取了掺杂浓度为10%的器件在温度20 K时的MEL并对其进行分解,发现RISC主导的MEL可由一个洛伦兹经验公式拟合得很好^[31]: $MEL=A_1 \times B^2/(B^2+B_1^2)$;而TTA主导的MEL则可由一个洛伦兹经验公式和一个非洛伦兹经验公式叠加得到^[32]: $MEL=A_2 \times B^2/(B^2+B_2^2)+A_3 \times B^2/(B+B_3)^2$.其中, B 为外磁场的大小, B_1 , B_2 和 B_3 分别为标志着饱和场大小的拟合参数.从图4中可以看出,拟合曲线(实线)与实验曲线(空心图形)基本重合,且分解出的RISC和TTA过程所对应的MEL曲线分别与其特征曲线(如图1(b)所示)相一致.拟合过程中所使用的参数 B_1 约为4 mT,也与超精细场大小相吻合.因此,我们可以初步确定该线型的MEL低场由RISC主导,而高场由TTA主导.

为了进一步证明ISC和TTA复合模型以及RISC和TTA复合模型的合理性,我们详细分析了低场和高场的MEL随掺杂浓度的变化,如图2(a)和(b)所示.当掺杂浓度从20%降至14%时,低场MEL由上升变为下降;随着掺杂浓度进一步降低,低场下降幅度增大.这是因为降低掺杂浓度能够增加三重态寿命^[33].有机材料中电子的自旋弛豫时间约 10^{-9} s^[27],而自旋反转能够发生的一个前提条件是激子的寿命大于自旋弛豫时间^[31].随着掺杂浓度降低, mCP分子将更有效地隔离DCJTB分子,主客体之间的“能级陷阱”效应变强;同时,客体材料DCJTB的三重态能量能够被主体材料mCP很好地限制住,而不能把能量回传给mCP^[3].

这两方面都会延长三重态寿命并增加三重态的数量,使RISC过程产生的单重态数量增加.当掺杂浓度为20%时,由于三重态寿命较短,ISC过程产生的三重态数量大于RISC过程产生的单重态数量,所以ISC占主导;但掺杂浓度降低到14%以下时,由于三重态寿命变长, RISC过程产生的单重态数量大于ISC过程产生的三重态数量,使得RISC占主导.而且,掺杂浓度越低, RISC引起的MEL的绝对值减小.与低场MEL类似,高场MEL随着掺杂浓度降低,三重态寿命变长, TTA反应强度增强,其幅值也增大^[30],如图2(a)所示.上述低场和高场MEL随掺杂浓度的变化,说明DCJTB器件中确实存在RISC和TTA,且掺杂浓度低时这两个过程更强.

由于RISC和TTA过程都受三重态寿命和浓度的调控,而三重态的寿命和浓度又与电流密度和工作温度有关^[23],因此,我们还研究了电流密度和工作温度对MEL的影响.结果发现电流密度对MEL影响较小,所以这里只针对工作温度对MEL的影响进行讨论,如图3所示.掺杂浓度和注入电流密度不变时,器件MEL的低场和高场部分的线型均不随着温度改变,但幅度却有明显变化:掺杂浓度为20%时,低场上升幅度随温度降低而减少;掺杂浓度为10%和5%时,低场下降幅度随温度降低而增大.这是因为温度主要通过影响三重态的寿命来调控RISC过程及其MEL.在低温条件下,环境的热激发能减少,从而抑制RISC;另一方面,温度越低,三重态被声子等热噪声淬灭的几率越小,寿命就越长,从而促进RISC.与声子等的热辅助作用相比,三重态的寿命对RISC过程的影响更大.而TTA过程也受三重态寿命的影响^[23],导致低温时高场下降幅度增大.所以,温度低时RISC和

图4 (网络版彩色)DCJTB器件分别在 ± 500 mT(a)和 ± 80 mT(b)磁场范围内的实验测得MEL曲线及拟合曲线

Figure 4 (Color online) The experimental and fitting MEL curves for DCJTB-doped device. (a) ± 500 mT; (b) ± 80 mT

TTA过程也更强.

4 结论

本文以DCJTB为掺杂客体制备了RISC与TTA共存的CT态发光器件, 并对其发光磁效应进行了研究. 结果发现, 低场部分的MEL随着掺杂浓度降低由上升转换为下降, 且下降幅度越来越大; 高场部分的MEL

则一直下降, 且单调递增. 低场的下降趋势由RISC过程主导, 而高场的下降趋势则由TTA过程主导. 另外, 掺杂浓度和工作温度对RISC和TTA共同产生延迟荧光的磁效应也有重要影响, 我们发现低掺杂浓度和低温更有利于DCJTB的 ^3CT 发生RISC和TTA过程. 这些发现对理解CT态演化过程以及如何提高CT态器件的三重态利用率都具有一定参考价值.

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The influence of doping concentration and temperature on magnetic field effect of delayed fluorescence in organic light-emitting diode

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Up to date, both reverse intersystem crossing (RISC) and triplet-triplet annihilation (TTA) are effective approaches to improve the internal efficiency of fluorescent OLEDs, because they can make the best of triplet excitons to generate delayed fluorescence. The energy difference between singlet and triplet excited states (ΔE_{S-T}) of special intramolecular charge transfer (CT) species is quite small, which make it possible for the participation of the CT species in RISC and TTA. When the RISC and TTA coexist in fluorescent OLEDs, the utilization of triplet excitons should be much better. The goal of this work was to demonstrate the feasibility of the coexistence. However, determining whether the coexistence happens in fluorescent OLEDs is not an easy task, because the general methods can hardly distinct the delayed fluorescence is originated from which approaches. Fortunately, both RISC and TTA are highly spin-dependent processes that can generate sizable magneto-electroluminescence (MEL) responses in OLEDs. Typically, the MEL response of RISC is a low-field effect, i.e., the MEL decreases rapid within the low-field regime (<5 mT) and then tends to saturation. Differently, the MEL of TTA exhibits a slight increase within the range of 20 mT but a remarkable decrease in the high-field regime (>20 mT). Hence, the MEL can be used as a novel tool to discern RISC and TTA in fluorescent OLEDs. Following such strategy, in this work, we firstly fabricated the devices by doping different concentrations of intramolecular CT states specie 4-(Dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran (DCJTB) into phosphor host material 1,3-bis(9-carbazolyl)benzene (mCP) and then measured the MEL responses of these devices at room temperature. It exhibited that the sign of low-field (<5 mT) component turned from positive to negative as the doping concentration decreasing from 20% to 5%, this was same to the situation for the high-field ($B>20$ mT) but was more prominent. These results are quite similar to the theoretical MEL curves of RISC in low-field (<5 mT) and TTA in high-field ($B>20$ mT), respectively. Thus, we believe that the delayed fluorescence of DCJTB-doped devices is caused by RISC and TTA simultaneously. Moreover, the RISC and TTA rates increase as the doping concentration decreasing. Subsequently, more remarkable RISC-dominated low-field and TTA-dominated high-field decrease of MEL were observed with decreasing temperature from 300 to 20 K. It is attributed to the fact that low temperature can significantly enhance RISC and TTA. In summary, low doping concentration and low temperature are more favorable to the coexistence of RISC and TTA in the DCJTB-doped devices. This work has a certain reference value for the improvements of internal quantum efficiency of fluorescent OLEDs via enhancing the utilization efficiency of triplet.

reverse intersystem crossing, triplet-triplet annihilation, doping concentration, temperature, delayed fluorescence, magneto-electroluminescence

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