三重态激子浓度对激子-电荷反应中散射和解离过程的调控

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摘要 制备了4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran(DCM)掺杂4,4'-N,N'-dicarbazole-biphenyl(CBP)的有机发光二极管器件, 并利用有机磁电导(magneto-conductance, *MC*)作为一种灵敏的探测工具, 研究了器件的载流子传输特性. 发现器件的*MC*随注入电流、温度和掺杂浓度的变化呈现出正、负磁电导效应, 正磁电导和负磁电导分别由三重激发态与电荷反应(triplet-charge interaction, *TQI*)中的散射过程与解离过程所引起. 研究表明, 器件中*TQI*的散射和解离过程共存时, 注入电流、工作温度和掺杂浓度都是通过改变三重态(triplet, *T*)激子的浓度来调节磁电导使其发生正负转变, 即*T*激子浓度对*TQI*中的散射过程和解离过程有不同的作用: *T*激子浓度越大, *TQI*中载流子的散射通道越易占主导作用, 此时器件呈现出正磁电导效应; 反之, *T*激子浓度越小, *TQI*中三重态激子的解离通道越易占主导作用, 此时器件表现出负磁电导效应. 本工作为有机磁电导效应的有效调控提供了一条新途径, 也加深了对有机光电器件中电荷与激发态间相互作用的理解.

关键词 有机磁电导, 三重态激子, 散射通道, 解离通道

4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran(DCM)作为客体材料掺杂于tris(8-hydroxyquinoline)aluminum(*Alq*₃)或4,4'-N,N'-dicarbazole-biphenyl(CBP)主体材料中, 既可用于有机半导体发光器件中(organic light-emitting devices, OLEDs)以提高器件的发光效率^[1-3], 又可用于有机光泵浦激光器件中产生吸收和发射的分离^[4-7], 以减少在激光(lasing)波长处的光吸收, 有助于光致激光的产生. 其载流子的传输和导电性使电泵浦有机激光成为可能, 因此, 研究这类器件的电荷注入、自旋和传输等特性很有必要. 近年来, 大量的实验设计和理论探讨试图揭示这类器件中的内部微观机制^[8-10]. 最近研究表明, 载流子的输运对磁场表现出较强的依赖关系,

这使得有机磁电导(magneto-conductance, *MC*)作为一种非接触、对器件无损伤以及操作简便的探测方法, 被广泛应用于有机光电器件微观机制的研究中^[11-13]. *MC*是指有外加磁场和无外加磁场下器件传导电流发生的相对变化, 即 $MC=[I(B)-I(0)]/I(0)\times 100\%$. 器件在恒定偏压条件下, 外加磁场导致器件的传导电流增大(上升), 称为正磁电导效应; 反之, 外加磁场导致器件的传导电流减小(下降), 称为负磁电导效应.

近10年来, 许多研究组在不同的有机半导体材料中都发现了磁电导效应, 但对其背后的微观机理还没有形成统一的认识^[8-12,14]. 最近, 本课题组发现三重激发态与电荷反应(triplet-charge interaction, *TQI*)的散射过程和解离过程分别造成有机高分子材

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料中的正磁电导效应和负磁电导效应^[15,16], 高分子材料的特殊结构所形成的电荷转移态(charge transfer states, CTS)有利于发生TQI的解离过程, 而器件本身的激子态(exciton states, ES)则有利于发生TQI的散射过程, 两种状态间的竞争可产生负和正的磁电导效应. 然而, 小分子材料的正负磁电导微观机制与高分子材料的正负磁电导机理是否一致还有待进一步研究.

本文制备了基于小分子材料CBP:*x*%DCM的掺杂发光器件, 发现在不同注入电流条件下呈现出正、负磁电导效应, 结合两个非洛仑兹经验公式对实验数据进行拟合, 验证了小分子材料器件的MC也是由TQI的散射过程和解离过程引起. 但是, 相对于高分子的长链结构容易形成CTS态, 由于小分子材料的分子空间结构范围小, 发现在器件CBP:*x*%DCM中难以形成CTS态, 因此小分子材料中TQI的散射过程和解离过程都是在ES态中发生的. 为了研究在ES态中TQI的散射过程和解离过程相互转变的原因, 本文通过改变器件的注入电流、温度和掺杂浓度, 结合目前研究较成熟的有机电致发光磁效应(magneto-electroluminescence, MEL)指纹式特性, 以及器件电流随电压的变化关系曲线, 分析发现三重态(triplet, T)激子浓度对正、负磁电导具有重要的调控作用. 即TQI的散射通道和解离通道对T激子浓度有不同的依赖关系: 散射通道在T激子浓度越高时越占主导, 而解离通道则在T激子浓度越低时越占主导. 显然, T激子浓度越高, 散射过程越强, 即载流子传输速率越慢, 这不利于激发态的形成和器件的发光; 然而, 在已知掺杂体系中, T激子浓度越高, 三重态激子湮灭(triplet fusion)越强, 则有利于发光. 这就为设计OLEDs器件时需要兼顾发光与电荷注入, 寻求两者最匹配的结构提供了较好参考, 同时, 也加深了对有机光电器件中电荷与激发态间相互作用微观机制的理解.

1 器件制备与测量

本文选用poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)修饰阳极ITO, 以增加电荷注入, 降低驱动电压; 4,4',4''-tris(*N*-3-methylphenyl-*N*-phenylamino)triphenylamine(*m*-MTDATA)作为空穴传输层, 发光层由DCM掺杂CBP构成, 4,7-diphenyl-1,10-phenanthroline(Bphen)为电子传输层; Al为阴极, LiF修饰Al电极以提高电子注入性能. 器

件结构为ITO/PEDOT:PSS/*m*-MTDATA(40 nm)/CBP:*x*%DCM(40 nm)/Bphen(40 nm)/LiF(1 nm)/Al(120 nm). 其中*x*为掺杂浓度, 分别制备了*x*为1%, 3%, 5%, 8%, 10%以及15%的器件. 首先将PEDOT:PSS溶液均匀旋涂于清洗干净的ITO玻璃基片上, 再在高真空状态下, 利用热阻蒸发在基片上沉积剩余各功能层. 最后将器件安装在处于电磁铁两磁极之间的闭循环冷却系统(Janis: CCS-350S)的冷头上, 器件电压由Keithley 2400提供, 它同时测量器件电流. 采用硅光电二极管探头和Keithley 2000测量器件的电致发光强度, 光谱由SpectraPro-2300i测得.

2 结果与讨论

图1(a)为器件的能级结构示意图. 当注入电流时, 空穴和电子分别从阳极ITO和阴极Al注入, 空穴经过*m*-MTDATA的最高占据分子轨道(HOMO), 电子经过Bphen的最低未占据轨道(LUMO)分别到达CBP的HOMO和LUMO上形成激发态, 激发态包括电荷转移态CTS和激子态ES两种状态^[15,16]. 图中客体材料DCM的LUMO比主体材料CBP的LUMO低0.2 eV, 而它的HOMO比CBP的高0.6 eV, 这使DCM能级陷于CBP能级之中, 产生能级陷阱. 因此, CBP中的激发态可通过能级陷阱捕获和Förster能量转移两种方式^[17,18], 将能量传递给DCM形成客体分子的激发态. 图1(b)中室温下器件CBP:1%DCM的归一化电致发光光谱, 它的峰位处于571 nm, 发光都来自客体DCM分子的ES态退激辐射. 由此可知, 在电注入条件下, 器件中的能量转移和载流子陷阱捕获机制的效率非常高, 使CBP激子能量全部转移到DCM中, 导致器件中只有DCM发光. 图1(b)中器件在掺杂浓度为8%和15%的归一化电致发光光谱, 发光也都来自DCM分子的ES态退激辐射, 不存在DCM分子的CTS态发光也无CBP发光. 并且, 随掺杂浓度的增大, 峰位有微小红移, 这是由DCM分子的聚集引起的^[11]. 由此可知, 与高分子材料中CTS态和ES态共存不同, 小分子材料CBP:*x*%DCM器件中, 只存在ES态, 因此器件中的三重激发态-电荷反应只存在于三重态激子与电荷之间, 并无三重电荷转移态-电荷反应的发生.

图2(a)中方块为器件CBP:1%DCM在室温下注入电流为150 μ A时的磁电导曲线, 其特征线型为: 低场($0 < |B| < 27$ mT)迅速上升, 高场(27 mT $|B| < 300$ mT)稍缓上升至300 mT也未达到饱和, 分析发现他们分

图1 (网络版彩色)器件CBP:x%DCM的结构及光谱图. (a) 能级结构示意图; (b) 室温下归一化电致发光谱(掺杂浓度 x 分别为1%, 8%和15%), 插图为DCM和CBP的分子结构

Figure 1 (Color online) The diagram and spectrum of device CBP: $x\%$ DCM. (a) The energy diagram of the device; (b) the normalized electroluminescence spectrum of the device at room temperature (the doping concentration x are 1%, 8% and 15%). The inset shows the chemical structures of CBP and DCM molecules

图2 (网络版彩色)器件CBP:1%DCM在不同温度和注入电流下的MC实验(方块)曲线及拟合(实线)曲线. (a) 室温下, 150 μ A时的实验(方块)和拟合(实线)曲线, 插图为散射过程原理图; (b) 100 K时, 25 μ A下的实验(方块)和拟合(实线)曲线; (c) 20 K时 10 μ A下的实验(方块)和拟合(实线)曲线, 插图为解离过程原理图

Figure 2 (Color online) The MC curves (square) and their fitted lines (solid lines) of device CBP: 1%DCM. (a) Under an injection current of 150 μ A at RT, inset shows the schematic of scattering process; (b) under an injection current of 25 μ A at 100 K; (c) under an injection current of 10 μ A at 20 K, inset shows the schematic of dissociation process

别是主要由系间窜越((inter-system crossing, ISC)和TQI中散射过程所引起^[15,16,18,19]. 其中ISC过程比TQI中散射过程弱很多, 故在本文中不做重点讨论. 为了证明器件中的激子反应就是TQI的散射过程, 采用两个非洛伦兹公式对实验数据进行拟合, 即 $MC = \alpha B^2 / (|B| + B_L)^2 + \beta B^2 / (|B| + B_H)^2$, 其中 B 表示外加磁场, α 和 β 分别表示拟合系数, B_L 和 B_H 分别表示低场和高场的特征磁场, 其中低场处于 $0 \rightarrow 27$ mT范围内, 高场处于 $27 \rightarrow 300$ mT范围内^[8,16,19]. 图2(a)中实线为两个非洛伦兹公式的拟合曲线, 拟合得出 B_L 和 B_H 分别为2.7和100 mT, 他们都分别都处于低、高磁场的有效范围

内, 且拟合曲线与实验曲线高度相符, 这说明器件中的激子反应确实是TQI的散射过程. 图2(a)插图为散射通道原理图: 自由电荷在传输过程中与T激子发生散射, 从而降低电荷的传输速率. 而外加磁场抑制这个散射过程, 使电荷的运动速率增加, 导致电流增大, 产生正MC. 因此可把该磁场范围内的缓慢上升线型归为TQI中散射通道的MC特征指纹.

图2(b)为100 K时25 μ A下器件CBP:1%DCM的MC实验(方块)曲线和拟合(实线)曲线, 其特征线型为: 低场迅速下降, 高场先下降后上升, 同时通过两个非洛伦兹公式拟合得出 B_L 和 B_H 分别为4.7和129

mT; 图2(c)为20 K时10 μA 下的MC实验(方块)曲线和拟合(实线)曲线, 其特征线型为: 低场迅速下降, 高场稍缓下降至150 mT逐渐趋于饱和, 拟合得出 B_L 和 B_H 分别为3.4和90 mT. 这些拟合所得的低、高特征磁场数值也都分别处于低、高磁场的有效范围内, 且两个非洛伦兹公式的拟合曲线与实验曲线高度相符. 由此可知图2(c)中下降MC为外加磁场对TQI中解离过程的作用^[15,16,20,21], 插图了解离通道原理图: T激子与器件中自由电荷发生反应而解离成自由电荷, 从而使器件中的电流增加, 而外加磁场抑制这个反应, 导致电流的减小, 产生负的MC. 因此可把该磁场范围内的下降线型归为TQI中解离通道的MC特征指纹. 图2(b)为TQI中散射和解离过程共存时, 外加磁场对两者共同作用, 导致正、负磁电导共存. 因此, 在小分子材料CBP:x%DCM的掺杂器件中, ES态中TQI的散射和解离过程分别导致正、负磁电导效应. 接下来讨论正负磁电导相互转变的原因.

2.1 注入电流对TQI过程的影响

图3(a)~(d)为器件CBP:1%DCM在温度为RT, 200, 100和20 K下不同注入电流时的磁电导. 由上述

分析可知磁场范围内的上升线型为TQI中散射通道的MC特征指纹, 下降线型为TQI中解离通道的MC特征指纹. 其中TQI中散射过程应满足: 随注入电流的增大, T激子浓度越高导致散射过程越强, 磁场的抑制作用越明显, 使MC上升幅度增大. 图3(a)和(b)中正磁电导的上升幅度随注入电流的增加(10 μA →150 μA)逐渐增大, 满足散射过程的这一规律. TQI中解离过程应满足: 随注入电流的增大, T激子浓度越高导致解离过程越强, 磁场抑制越多的解离反应, 使负MC下降幅度增大. 而图3(d)中负磁电导的下降幅度随注入电流的增加(10 μA →150 μA)逐渐减小, 不符合解离过程的这一规律.

从图3(c)中同时出现正负磁电导效应, 分析发现: 器件中同时存在TQI的散射和解离两个过程, 大注入电流下散射过程更容易发生, 小注入电流下解离过程更容易发生, 从而得到大注入电流时的MC幅度比小注入电流时的MC幅度高. 因此, 图3(c)和(d)中MC随注入电流的增加(10 μA →150 μA), 下降幅度逐渐减弱而上升幅度逐渐增强, 这是器件中TQI反应由解离通道逐渐向散射通道转变的结果. 因为解离和散射过程都是T激子直接参与的反应, 而随注入电

图3 (网络版彩色)器件CBP:1%DCM在不同温度条件下注入电流为10, 25, 50, 100和150 μA 的MC曲线. (a) RT; (b) 200 K; (c) 100 K; (d) 20 K
Figure 3 (Color online) The MC curves of device CBP:1%DCM at various temperature when the injection currents are 10, 25, 50, 100 and 150 μA , respectively. (a) RT; (b) 200 K; (c) 100 K; (d) 20 K

流的增大T激子浓度增加,所以可推测出当TQI的解离通道和散射通道共存时,T激子浓度对两个通道具有调控作用:T激子浓度越高越易发生TQI的散射过程,T激子浓度越低越易发生TQI的解离过程.

2.2 温度对TQI过程的影响

为了验证T激子浓度对TQI的解离和散射通道具有较好调控作用,下面通过改变温度来影响激子寿命从而来调节T激子的浓度,以此来观察MC的改变.采用目前研究较成熟的MEL曲线来观察激子浓度的变化,与MC类似,MEL定义为有、无外加磁场下器件电致发光强度的相对变化率,即 $MEL = [EL(B) - EL(0)] / EL(0) \times 100\%$ ^[17,22,23].电致发光为单重态激子(singlet, S)退激辐射产生,T激子虽不直接参与发光,但通过激子湮灭反应($T_1 + T_1 \rightarrow S_1 + S_0 \rightarrow hv + S_0$,即TTA过程),可以间接影响器件发光^[3,17,23],且TTA有自己特征的MEL线型,因此可通过MEL曲线来观察T激子浓度的变化.图4(a)和(c)为器件CBP:1%DCM在不同温度条件下,注入电流为50 μA 的MEL和MC曲线;图4(d)和

(f)为器件CBP:10%DCM在不同温度条件下,注入电流为50 μA 的MEL和MC曲线.

图4(a)中,器件CBP:1%DCM在室温下MEL线型为:低场微小上升,高场大幅度下降.已知低场快速上升为外加磁场对极化子对(polaron pair)系间窜越ISC的作用所引起的,高场下降为外加磁场对TTA作用的结果^[3,17,23],并且MEL下降幅度随T激子浓度的增加而增大.图4(a)中随温度的降低,低场上升幅度增加,高场下降幅度减小,可知T激子浓度随温度的降低而减少.而图4(d)中,器件CBP:10%DCM的MEL随温度的降低,低场上升幅度减少,高场下降幅度增加,可知T激子浓度随温度的降低而增加.一般情况下,因为T激子的寿命随温度降低而增长,所以降低温度T激子浓度是增加的^[17,24,25],如图4(d)所示.把图4(a)中T激子浓度随温度的降低而减少称为反常温度效应.

结合本组之前对这种反常温度效应现象的研究,分析表明^[23]:在CBP:1%DCM器件中,虽然由于CBP能量的快速转移以及主客体间能级陷阱的共同作用,

图4 (网络版彩色)器件CBP:x%DCM在注入电流为50 μA , 温度分别为RT, 200, 100和20 K条件下的特征曲线. (a) 掺杂浓度x为1%的MEL曲线; (b) x为1%的归一化电致发光谱; (c) x为1%的MC曲线; (d) x为10%的MEL曲线; (e) x为10%的归一化电致发光谱; (f) x为10%的MC曲线

Figure 4 (Color online) The characteristic curves of device CBP:x%DCM under an injection current of 50 μA at RT, 200, 100 and 20 K, respectively. (a) The MEL curves of device CBP:1%DCM; (b) the normalized electroluminescence spectrum of device CBP:1%DCM; (c) the MC curves of device CBP:1%DCM; (d) the MEL curves of device CBP:10%DCM; (e) the normalized electroluminescence spectrum of device CBP:10%DCM; (f) the MC curves of device CBP:10%DCM

导致大量激发态激子聚集于DCM中,但是随温度的降低,*m*-MTDATA/CBP异质结上形成的激基复合物浓度增加,激子浓度相对减少,从而导致T激子浓度随温度的降低而相对减少,出现反常温度效应.这也可从图4(b)中CBP:1%DCM(掺杂浓度为1%)器件分别在室温和20 K时的归一化电致发光谱图得到验证.温度为20 K时,主峰位(571 nm)左侧存在两个微小肩峰,这在室温下并不存在,其中肩峰(405 nm)来自于CBP分子的电致发光,肩峰(480 nm)则来自于激基复合物发光^[1,23].因此随温度的降低,激基复合物的增加会使T激子的相对浓度减小,从而导致反常的温度效应.而CBP:10%DCM(掺杂浓度为10%)器件的电致发光谱如图4(e)所示,他们在室温和低温下都无激基复合物发光,因此高掺杂浓度器件无这种反常的温度效应.

分析器件CBP:1%DCM的MEL曲线可知,随温度的降低T激子浓度逐渐减少.同时如图4(c)所示,器件MC随温度的降低,正磁电导逐渐减弱而负磁电导逐渐增加,即激子反应从散射过程占主导逐渐转变到解离过程占主导.而分析器件CBP:10%DCM的MEL曲线可知,随温度的降低T激子浓度逐渐增加.同时如图4(f)所示,器件MC随温度的降低,负磁电导逐渐减小而正磁电导逐渐增加,即激子反应的解离过程逐渐减弱同时散射过程逐渐增强,直至散射过程完全占主导.综上所述可知,改变温度不能直接调控TQI的散射和解离过程,而是温度改变导致T激子浓度的变化,调节了TQI的两通道:T激子浓度越高越易发生TQI的散射过程,T激子浓度越低越易发生TQI的解离过程.

2.3 掺杂浓度对TQI过程的影响

为了进一步验证T激子浓度对TQI中散射与解离过程的调控,制作不同掺杂浓度的器件来调节T激子的浓度,从而观察MC的改变.图5(a)和(b)为室温下注入电流为100 μ A时器件CBP:*x*%DCM(掺杂浓度*x*分别为1%, 3%, 5%, 8%, 10%和15%)的MEL和MC曲线.图5(a)中器件MEL随掺杂浓度的增加,低场上升幅度从0.18%增加到4.9%;而高场下降幅度从1.18%减小到0.12%,从中可知T激子浓度随掺杂浓度的增加而减少,这是由于高掺杂浓度时激子的淬灭作用所引起^[1,26,27].同时,从图5(d)插图中电致发光-电流变化关系曲线可知,器件发光随掺杂浓度的增加而

减弱,这也进一步证明了高掺杂浓度时,激子存在自我淬灭作用使激子浓度减少,导致发光减弱.

图5(b)中不同掺杂浓度下,器件高场MC都为正磁电导,但其上升幅度随掺杂浓度的增加而逐渐减小(0.55% $\rightarrow$ 0.06%).低场MC随掺杂浓度的增加,由0.06%的正磁电导逐渐转变为-0.1%的负导磁电导.其中掺杂1%, 8%和15%器件在小场($|B| < 20$ mT)范围内的MC如图5(c)所示,图中掺杂1%的器件在小场范围内为正磁电导,而掺杂8%的器件在小场范围内为先负后正的磁电导,掺杂15%的器件在小场范围内为负磁电导.综上所述由图5(a)和(b)可知,器件掺杂浓度逐渐增大,T激子浓度会逐渐减少,导致散射过程逐渐减弱,解离过程逐渐增强.总之,通过分析不同掺杂浓度下器件MC,再次验证了:散射通道在T激子浓度越高时越占优势;反之,T激子浓度越低时解离通道越占优势.

图5(d)为各掺杂浓度器件的电压与电流变化关系曲线,器件开启电压随掺杂浓度的增加(1% $\rightarrow$ 15%),从5.7 V减小到3.0 V,即掺杂浓度越低开启电压越高.可用上述观点解释:掺杂浓度越低,T激子浓度越高,散射过程越易发生,从而使自由电荷迁移率下降,导致工作电压增大.这为我们在器件制作过程中提供较好参考,即需要同时兼顾发光效率和电荷注入.综上所述,通过改变掺杂浓度调节T激子浓度,可对TQI的散射和解离过程进行调控:T激子浓度高时越易发生TQI的散射过程,T激子浓度越低时越易发生TQI的解离过程.

3 结论

本文通过分析CBP:*x*%DCM器件的磁电导随注入电流、掺杂浓度和温度的变化,利用非洛仑兹经验公式对实验数据进行拟合,发现上升的正MC是由TQI的散射通道引起,下降的负MC为TQI的解离通道引起的.由于两个通道都有T激子的参与,引入MEL直接观察T激子浓度的变化,分析与之对应的MC发现并证实了器件内的TQI的散射和解离通道受T激子浓度的调控:TQI的散射过程在T激子浓度越高时越易发生,解离过程在T激子浓度越低时越易发生.尽管这与高分子材料器件的正负磁电导有类似之处,即TQI的散射和解离通道是产生正、负磁电导的原因,但与高分子材料器件中电荷转移态和激子态分别调控解离和散射通道所不同的是:器件CBP:*x*%DCM

图5 (网络版彩色)室温下, 器件CBP: $x\%$ DCM (掺杂浓度 x 分别为 1%, 3%, 5%, 8%, 10%和 15%) 在注入电流为 100 μA 时的特征曲线. (a) MEL 曲线; (b) MC 曲线; (c) x 分别为 1%, 8% 和 15% 器件在小场范围内的 MC 曲线; (d) 电流-电压关系变化曲线, 插图为电致发光-电流变化曲线

Figure 5 (Color online) The characteristic curves of device CBP: $x\%$ DCM under an injection current of 100 μA at room temperature (the doping concentrations are 1%, 3%, 5%, 8%, 10% and 15%). (a) MEL; (b) MC; (c) the MC curves of devices under small magnetic field when the doping concentrations are 1%, 8% and 15%; (d) the current-voltage curves and inset shows the electroluminescence-current curves

中难以形成电荷转移态, 即解离和散射过程都由激子态所引起, 两个过程都受T激子浓度的调控. 这不仅

加深了对小分子材料OLEDs中激子反应和电荷传输性质的理解, 也进一步丰富了有机磁效应的表现形式.

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Summary for “三重态激子浓度对激子-电荷反应中散射和解离过程的调控”

Triplet induced competition between scattering and dissociation process in exciton-charge reaction

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Magneto-conductance (*MC*) refers to the relative change rate of conduction current with and without external magnetic field *B* and is used as the sensitive detection tools to study the carrier transport characteristics in organic semiconductor devices. This provides a non-contact approach to tune conduction current properties because the carrier transport shows strong dependence on magnetic field. In general, the magnetic phenomenon where the values of conduction current of device are growing at constant bias upon the application of external magnetic field is named positive *MC* effect. Inversely, when the *B*-induced current value is decreased it is named negative *MC* effect. Recently, researchers had found that the scattering and dissociation processes of triplet-charge interaction (TQI) respectively caused the positive and negative *MC* in organic polymer materials, the charge transfer states (CTS) led to dissociation process of TQI, and the exciton states (ES) led to scattering processes, and the rivalry between the two states could tune the *MC* between positive and negative. However, it remains further study whether the micro mechanism of positive and negative *MC* in small molecule materials is similar to that in polymer materials. In this work, organic light-emitting diodes (OLEDs) that based on small molecule materials had been fabricated through doping the 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) into 4,40-N,N0-dicarbazole-biphenyl (CBP) as an active layer. Here, we demonstrate that the *MC* of the device could be changed between positive and negative which were caused by the scattering and dissociation processes of TQI by fitting the *MC* curves with the combination of two non-Lorentzian empirical equations. The electroluminescence spectrum of CBP:*x*%DCM shows that small molecule materials were difficult to form CTS, although it had similar theory with polymer materials. As a result, both the scattering process and dissociation process in TQI had been caused by ES in CBP:*x*%DCM, and it was necessary to study the transformation mechanism between these two processes in ES. Therefore, it had been found that changing the injection currents, the temperature and the doped concentration could alter the concentration of triplet excitons, consequently leading to the positive and negative *MC*. This means that the scattering process and dissociation process in TQI have opposite dependences on the concentration of triplet excitons in CBP:*x*%DCM. The scattering process plays a major role when the concentrations of triplet excitons are large enough, yielding positive *MC*. On the other hand, the dissociation process plays an important role when the concentrations of triplet excitons are low enough, producing negative *MC*. This finding provides a new pathway to efficiently tune the organic magneto-conductance, and further to understand the microscopic mechanism of the interaction between charges and excite states in organic optoelectronic devices.

organic magneto-conductance, triplet excitons, scattering process, dissociation process

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