螺二芴和均三嗪构筑的主体材料的合成及应用

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摘要 设计并合成了4种基于螺二芴和均三嗪类的新型主体材料2-(2',7'-二叔丁基-9,9'-螺二芴-2-基)-4,6-二苯基-1,3,5-三嗪(DTSF-2-DP-TRZ)、2-(9,9'-螺二芴-2-基)-4,6-双(3,5-二-叔丁基苯基)-1,3,5-三嗪(SF-2-DTDP-TRZ)、2-(9,9'-螺二芴-4-基)-4,6-双(3,5-二-叔丁基苯基)-1,3,5-三嗪(SF-4-DTDP-TRZ)、2-(9,9'-螺二芴-4-基)-4,6-双(4-(叔丁基)苯基)-1,3,5-三嗪(SF-4-TDP-TRZ), 并对其结构和性能进行了表征. 利用热重分析、差热分析、紫外可见吸收、荧光、低温磷光、循环伏安法对其物理和化学性质进行了研究, 结果表明4种主体材料的热稳定性能优异, 紫外-可见光吸收峰位于280~355 nm之间; 光学带隙(E_g)分布在3.28~3.36 eV之间. 为了研究其在有机电致发光中的应用, 4个主体材料分别与绿光热激活延迟荧光材料共掺作为发光层, 通过旋涂法制备, 并研究其结构与性能之间的关联. 所制备的器件光电性能表现优异, 其中DTSF-2-DP-TRZ作为主体材料的器件最大亮度达到6600 cd/m², 最大电流效率为51.3 cd/A, 相应的最大外量子效率为16.6%.

关键词 主体材料, 螺二芴, 均三嗪, 热激活延迟荧光, 有机电致发光器件

有机电致发光器件(organic light-emitting diode, OLED)是目前最具发展潜力的新型显示技术之一. 因其具有自发光、驱动电压低、对比度高、视角广、适用温度范围广等性能优势, 受到基础研究和产业应用的广泛关注, 目前已逐步进入了手机显示屏市场, 正在积极向照明、医疗、光通讯等领域渗透^[1,2]. 但OLED仍然面临着寿命短、价格昂贵等缺点, 还需进一步解决这一实用化瓶颈. 发光层的设计和组合在OLED中起到关键作用, 它直接决定着器件的发光效率和寿命长短. 发展新型具有高发光效率、启动电压低、成膜性好、寿命持久、稳定性好的材料体系是这一领域研究的重要手段, 其中发光材料和主体材料的搭配更是关键^[3~8]. 螺二芴类化合物具有特殊的三维空间正交结

构、拥有较大的刚性共轭平面, 且存在螺共轭效应, 热稳定性较好^[9~11]; 1,3,5-三嗪类化合物(TRZ)因具有强的电子传输能力、空间对称和易被其他基团修饰的特点而备受关注^[12~16]. 在主体材料分子结构中引入三嗪结构单元作为共轭分子的核, 不仅能改善电子注入与传输性能, 而且也能提高其热稳定性. 因此, 本文将三嗪基团与螺二芴结合起来做结构骨架, 以期得到具有螺二芴和三嗪共同特点的多性能的主体材料, 并用叔丁基对其整体结构进行修饰, 增加溶解性, 利于采用湿法工艺制备器件. 本文设计并合成了基于上述特点的4种主体材料, 并对其物理、化学性质、电化学性质进行了系统的研究, 同时将它们作为主体材料制备成器件, 并对其发光性能作了系统的比较.

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1 实验

(i) 试剂和仪器. 碳酸钾、浓盐酸、二氯甲烷、四氢呋喃、甲苯、甲醇等均为国药集团化学试剂有限公司购买, 为分析纯; 四氢呋喃在氮气下用钠丝回流, 使用前蒸馏提纯. 三聚氯氰、溴苯、4-叔丁基溴苯、3,5-二叔丁基溴苯购买于安耐吉化学有限公司. 四(三苯基)磷钯($\text{Pd}(\text{PPh}_3)_4$)购买于西格玛奥德里奇(上海)贸易有限公司; 聚(3,4-二氧乙基噻吩)和聚苯乙烯磺酸混合水溶液(PEDOT-PSS)由百灵威科技有限公司购买; 2,4,5,6-四(9-呋喃基)-间苯二腈购于西安宝莱特光电科技有限公司, 8-羟基喹啉-锂, 1,3,5-三[(3-吡啶基)-3-苯基]苯购于吉林奥来德光电材料有限公司; 镁屑, 2,7-二叔丁基-9,9-螺二苈-2-硼酸, 9,9-螺二苈-2-硼酸, 9,9-螺二苈-4-硼酸等均从百灵威科技有限公司购买.

仪器: 有机材料真空提纯装置购于沈阳慧宇真空有限公司; BIFLEX III质谱仪; Bruker-400超导核磁共振仪; Hitachi UV-3010型紫外-可见光谱仪; Hitachi F-4500荧光光谱仪; 电化学工作站CS300为武汉科斯特仪器有限公司; SHIMADZU DSC-60; KW-4A旋涂仪.

(ii) 合成路线. 合成路线如图1所示.

(iii) 主体材料的合成与表征. 化合物2-氯-4,6-二苯基-1,3,5-均三嗪的合成: 氮气保护下, 将镁屑(9.89 g, 406.72 mmol)和5 mL四氢呋喃, 一粒碘单质加入到干燥洁净三口玻璃瓶中, 滴加溴苯(25.54 g, 162.69 mmol)和50 mL四氢呋喃的混合溶液, 反应引发放热后, 保持微沸状态下继续滴加溴苯的四氢呋喃溶液, 滴完后升温回流2 h, 再降温至室温待用. 将三聚氯氰(10 g, 54.23 mmol)和50 mL四氢呋喃加入氮气保护下的三口烧瓶中, 滴加上述制好的格式试剂, 0~10℃慢速滴加, 滴完后, 升温回流1 h, 降至室温. 将反应完体系淬灭于稀盐酸水溶液中, 分出有机相, 用乙酸乙酯萃取水相两遍, 所有有机相合并, 用硫酸镁干燥后过滤, 真空旋干有机相得到固体, 用四氢呋喃/甲醇(体积比为1:3)进行重结晶两次得到灰色固体(9.43 g, 收率65%)^[17]. ^1H NMR(400 MHz, CDCl_3) δ 8.62(d, $J=7.3$ Hz, 4H), 7.63(t, $J=6.6$ Hz, 2H), 7.55(t, $J=7.2$ Hz, 4H); ^{13}C NMR(101 MHz, CDCl_3) δ 173.44, 172.83, 134.54, 133.62, 129.53, 128.92; MS(ESI) $m/z=268.0635(\text{M}+\text{H}^+)$ (calcd.268.0642)(图S1).

化合物2-(2',7'-二叔丁基-9,9'-螺二苈-2-基)-4,6-二苯基-1,3,5-三嗪(DTSF-2-DP-TRZ)的合成: 氮气保护下,

将2-氯-4,6-二苯基-1,3,5-均三嗪(8 g, 29.88 mmol), 2',7'-二叔丁基-9,9'-螺二苈-2-硼酸(14.12 g, 29.88 mmol), 四(三苯基)磷钯(345.32 mg, 0.299 mmol), 碳酸钾(8.26 g, 59.76 mmol)加入到50 mL甲苯、10 mL乙醇、10 mL水的混合溶液中搅拌, 加热回流3 h, 降温, 分出水相, 再用10 mL水洗涤一次, 然后用硫酸镁干燥过滤, 真空旋蒸除去溶剂后, 用二氯甲烷/正己烷(体积比为1:10)的淋洗剂进行柱层析得到白色固体(13.80 g, 收率70%)^[18]. 将白色固体在280℃, 真空度为 2.4×10^{-4} Pa下升华3 h得到白色升华品10.35 g. ^1H NMR(400 MHz, CDCl_3) δ 8.89(d, $J=6.5$ Hz, 1H), 8.65(s, 4H), 8.13~8.02(m, 2H), 7.96(s, 1H), 7.80(d, $J=7.0$ Hz, 2H), 7.53(d, $J=7.2$ Hz, 6H), 7.43(s, 3H), 7.16(s, 1H), 6.74(s, 3H), 1.16(s, 18H). ^{13}C NMR(101 MHz, CDCl_3) δ 171.46, 151.33, 150.88, 149.82, 148.44, 146.53, 140.65, 139.55, 136.33, 135.95, 132.47, 129.33, 129.06, 128.32, 127.65, 124.63, 124.39, 120.74, 120.11, 119.40, 66.82, 35.20, 31.81; MS(ESI) $m/z=660.3367(\text{M}+\text{H}^+)$ (calcd.660.3379)(图S2).

化合物2,4-二(4-叔丁基苯基)-6-氯-1,3,5-三嗪的合成: 氮气保护下, 将镁屑(4.61 g, 189.8 mmol)和3 mL四氢呋喃, 一粒碘单质加入到干燥洁净三口玻璃瓶中, 滴加4-叔丁基溴苯(20.22 g, 94.90 mmol)和32 mL四氢呋喃的混合溶液, 保持微沸状态下继续滴加4-叔丁基溴苯的四氢呋喃溶液, 滴完后升温回流2 h, 再降温至室温待用. 将三聚氯氰(7.0 g, 37.96 mmol)和35 mL四氢呋喃加入氮气保护下的三口烧瓶中, 滴加上述制好的格式试剂, 0~10℃慢速滴加, 滴完后, 升温回流1.5 h, 降至室温, 将反应完体系淬灭于稀盐酸水溶液中, 分出有机相. 用乙酸乙酯萃取水相两遍, 有机相合并, 用无水硫酸镁干燥后过滤, 50℃真空减压浓缩有机相得到固体, 用四氢呋喃/甲醇(体积比为1:3)进行重结晶两次得到灰色固体(7.78 g, 收率54%). ^1H NMR(400 MHz, CDCl_3) δ 8.53(d, $J=7.7$ Hz, 4H), 7.56(d, $J=7.8$ Hz, 4H), 1.39(s, 18H); ^{13}C NMR(101 MHz, CDCl_3) δ 173.23, 157.39, 131.87, 129.39, 125.95, 35.58, 31.53; MS(ESI) $m/z=380.1899(\text{M}+\text{H}^+)$ (calcd.380.1894)(图S3).

化合物2-(9,9'-螺二苈-4-基)-4,6-双(4-(叔丁基)苯基)-1,3,5-三嗪(SF-4-TDP-TRZ)的合成: 氮气保护下, 2,4-二(4-叔丁基苯基)-6-氯-1,3,5-三嗪(5 g, 13.16 mmol), 9,9'-螺二苈-4-硼酸(4.74 g, 13.16 mmol), 四(三苯基)磷钯(152.08 mg, 131.6 μmol), 碳酸钾(3.64 g, 26.32 mmol)加入50 mL甲苯、10 mL乙醇、10 mL水的混合溶液中搅

图 1 4个主体材料的合成路线
Figure 1 Synthetic routes of the hosts

拌, 加热回流2 h, 降温至室温, 分出水相, 再用15 mL水洗一次, 然后用无水硫酸镁干燥过滤, 55℃真空减压浓缩除去溶剂后, 用二氯甲烷/石油醚(体积比为1:10)淋洗剂进行柱层析分离得到白色固体(5.90 g, 收率68%). 将白色固体在280℃, 真空度为 3.5×10^{-4} Pa下升华2 h得到白色晶体升华品4.42 g. ^1H NMR (400 MHz, CDCl_3) δ 8.74 (d, $J=7.5$ Hz, 4H), 8.10 (d, $J=7.4$ Hz, 1H), 8.00 (d, $J=7.3$ Hz, 1H), 7.88 (d, $J=7.0$ Hz, 2H), 7.62 (d, $J=7.5$ Hz, 4H), 7.40 (s, 2H), 7.26 (s, 1H), 7.16 (s, 3H), 7.10 (s, 1H),

6.87 (d, $J=7.1$ Hz, 3H), 6.76 (d, $J=6.7$ Hz, 1H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.63, 171.67, 156.44, 150.51, 149.43, 148.95, 141.98, 141.20, 134.08, 133.51, 131.41, 129.19, 128.29, 127.75, 126.50, 125.87, 125.20, 124.40, 123.89, 120.15, 66.62, 35.51, 31.60; MS (ESI) $m/z=660.2726(\text{M}+\text{H}^+)$ (calcd.660.3379) (图S4).

化合物2,4-二(3,5-二叔丁基苯基)-6-氯-1,3,5-三嗪的合成: 氮气保护下, 将镁屑(3.30 g, 135.57 mmol)和5 mL四氢呋喃, 一粒碘单质加入到干燥洁净三口玻璃瓶中,

滴加3,5-二叔丁基溴苯(16.60 g, 59.65 mmol)和100 mL四氢呋喃的混合溶液, 保持微沸状态下滴加, 滴完后升温回流2 h, 再降温至室温待用. 将三聚氯氰(5 g, 27.33 mmol)和50 mL四氢呋喃加入氮气保护下的三口烧瓶中, 滴加制好的格式试剂, 5~10℃慢速滴加, 滴完后, 升温回流2 h, 降温至室温. 将反应完体系淬灭与水, 分出有机相, 用乙酸乙酯萃取水相两遍, 有机相合在一起, 用硫酸镁干燥后过滤, 50℃真空减压浓缩有机相得到固体, 用四氢呋喃和甲醇(体积比为1:2)进行重结晶两次得到灰色固体(7.07 g, 收率53%). ^1H NMR (400 MHz, CDCl_3) δ 8.51 (s, 4H), 7.72 (s, 2H), 1.44 (s, 36H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.79, 151.55, 134.04, 127.98, 123.73, 35.43, 31.76; MS(ESI) m/z =492.3151($\text{M}+\text{H}^+$) (calcd. 492.3146), 514.1911($\text{M}+\text{Na}^+$)(calcd.514.2965)(图S5).

化合物2-(9,9'-螺二苌-2-基)-4,6-双(3,5-二-叔丁基苯基)-1,3,5-三嗪(SF-2-DTDP-TRZ)的合成: 氮气保护下, 2,4-二(3,5-二叔丁基苯基)-6-氯-1,3,5-三嗪(5 g, 10.16 mmol), 9,9'-螺二苌-2-硼酸(3.66 g, 10.16 mmol), 四(三苯基)磷钼(117.40 mg, 101.6 μmol), 碳酸钾(2.81 g, 20.32 mmol)加入到50 mL甲苯、10 mL乙醇、10 mL水的混合溶液中搅拌, 加热回流2 h, 降温至室温, 分出水相, 再用15 mL水洗涤一次, 然后用无水硫酸镁干燥过滤. 55℃真空减压浓缩除去溶剂后, 用二氯甲烷和正己烷(体积比为1:8)淋洗剂进行柱层析分离得到白色固体(5.17 g, 收率66%). 将白色固体在290℃, 真空度为 2.1×10^{-4} Pa下升华3 h得到白色升华品4.03 g. ^1H NMR (400 MHz, CDCl_3) δ 8.74 (d, J =7.4 Hz, 1H), 8.48 (s, 4H), 8.08 (s, 1H), 8.05 (d, J =8.0 Hz, 1H), 7.97 (d, J =6.9 Hz, 1H), 7.88 (d, J =7.1 Hz, 2H), 7.64 (s, 2H), 7.46 (t, J =6.7 Hz, 1H), 7.38 (t, J =6.5 Hz, 2H), 7.22 (d, J =7.4 Hz, 1H), 7.12 (t, J =6.5 Hz, 2H), 6.91 (d, J =6.8 Hz, 1H), 6.80 (d, J =6.8 Hz, 2H), 1.40 (s, 36H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.95, 171.10, 151.13, 149.91, 149.61, 148.38, 145.56, 142.02, 141.56, 136.32, 135.60, 128.85, 128.64, 128.04, 126.84, 124.89, 124.65, 124.18, 123.18, 120.91, 120.12, 66.33, 35.36, 31.77; MS(ESI) m/z =772.4041 ($\text{M}+\text{H}^+$) (calcd.772.4631) (图S6).

化合物2-(9,9'-螺二苌-4-基)-4,6-双(3,5-二-叔丁基苯基)-1,3,5-三嗪(SF-4-DTDP-TRZ)的合成: 氮气保护下, 2,4-二(3,5-二叔丁基苯基)-6-氯-1,3,5-三嗪(3 g, 6.10 mmol), 9,9'-螺二苌-4-硼酸(2.20 g, 6.10 mmol), 四(三苯基)磷钼(70.44 mg, 0.061 mmol), 碳酸钾(1.68 g,

12.19 mmol)加入到45 mL甲苯、9 mL乙醇、9 mL水的混合溶液中搅拌, 加热回流2 h, 降温至室温, 分出水相, 再用10 mL水洗涤一次, 然后用无水硫酸镁干燥过滤. 55℃真空减压浓缩除去溶剂后, 用二氯甲烷/石油醚(体积比为1:12)淋洗剂进行柱层析分离得到白色固体(3.63 g, 收率77%). 将固体在290℃, 真空度为 5.5×10^{-4} Pa下升华2 h得到白色升华品2.54 g. ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 4H), 8.21 (d, J =7.1 Hz, 1H), 8.08 (d, J =6.5 Hz, 1H), 7.88 (d, J =6.8 Hz, 2H), 7.73 (s, 2H), 7.40 (s, 2H), 7.28 (s, 1H), 7.15 (d, J =6.9 Hz, 3H), 7.10 (d, J =7.6 Hz, 1H), 6.94~6.82 (m, 3H), 6.76 (s, 1H), 1.44 (s, 36H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.51, 151.42, 150.56, 149.34, 148.99, 141.97, 140.77, 135.43, 131.75, 128.51, 127.79, 127.64, 127.39, 126.60, 125.32, 124.35, 123.80, 123.53, 120.18, 65.98, 35.46, 31.83; MS (ESI) m/z =772.4046($\text{M}+\text{H}^+$) (calcd.772.4631) (图S7).

2 结果与讨论

2.1 热力学性质

借助示差热量扫描仪(DSC)和热重分析仪(TGA)两种热分析仪器对主体材料的热力学性质进行了测定. OLED主体材料热力学稳定性的好坏对其器件寿命及稳定性有着重要的意义, 尤其是用旋涂法制备的器件, 热力学稳定性好的主体材料可以延长器件的寿命, 提升器件的发光效率. 从DSC曲线(图2(a)), 可以观察到4个主体材料DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ的熔点(T_m)分别为259, 278, 170, 260℃. 在第二个循环加热过程观测到其玻璃化转变温度(T_g)分别为147, 151, 150, 165℃(图2(b)), 高的玻璃化转变温度说明其具备非晶态结构, 可以形成均匀的非晶薄膜, 分子结构中的叔丁基增加了其在溶剂中的溶解性, 有利于采用旋涂法制备出性能极好的薄膜特性. 另外, 我们根据热失重分析(图2(c))结果, 测定其失重5%的温度(T_d)分别为382, 346, 383, 371℃. 高的 T_d 表明4个主体材料具有良好的热稳定性能. 以上目标分子良好的热力学特性与其本身分子结构带有叔丁基的取代位置、数目多少都有密切联系, 也与螺二苌基团三维空间正交结构、螺共轭效应有重要的关系, 使其在制备过程中保证发光层稳定的形态特征, 有利于提高器件稳定性, 也体现了螺二苌和三嗪基团这类结构优越性.

图 2 (网络版彩色)4个主体材料DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ的DSC曲线熔点(a)、玻璃化转变温度 T_g (b)和热失重(TGA)分析图(c). 三者均在氮气保护下以10℃/min的速率升温测试得到
Figure 2 (Color online) DSC (a), glass transition temperature (T_g) (b), and TGA (c) curves of DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ, respectively. The data were measured at a heating rate of 10℃/min under N_2 atmosphere

2.2 电化学性质

循环伏安法测定材料的电化学性质是最简单可靠的方法. 准确测定有机电致发光材料的能级对OLED器件的研究至关重要. 图3为循环伏安(CV)曲线. 循环伏安法的测定以四丁基六氟磷酸铵为支持电解质, 二茂铁为外标物, 溶剂为二氯甲烷, Ag/AgCl(饱和氯化钾)为参比电极. 从循环伏安曲线中可以得到4个材料DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ的起始氧化电位分别为1.43, 1.65, 1.69, 1.40 eV. 最高占有分子轨道(HOMO)能级根据以下公式得出: $E_{HOMO} = -[E_{onset}^{ox} - E(Fc/Fc^+) + 4.8]$, 其中 E_{HOMO} 为待测材料的HOMO能级, E_{onset}^{ox} 为氧化电位起峰位置, $E(Fc/Fc^+)$ 为标准参考电位对应的能量. 通过计算得到HOMO分别为-5.88, -6.10, -6.14, -5.85 eV. HOMO能级与4CzIPN的能级相匹配, 具有较好的空穴传输性能. 最低未占有分子轨道(LUMO)由公式 $E_{LUMO} = E_{HOMO} + E_g$ 计算得到, LUMO值分别为-2.59, -2.82, -2.86, -2.49 eV, LUMO能级也与4CzIPN相匹配, 增加了电子的注入和传输, 因此4个化合物具有作为有机电致发光主体材料的巨大潜力.

2.3 光物理性能研究

4个主体材料在280 nm的吸收峰是由芳香基团产生 $\pi \rightarrow \pi^*$ 跃迁所决定的, 而在310 nm左右(314, 308, 309, 309 nm)的吸收峰主要是由螺茛环 $\pi \rightarrow \pi^*$ 跃迁引起的. 另外, 350 nm左右(355, 348, 346, 352 nm)的吸收峰应是由螺二茛和三嗪结构组成的共轭分子骨架发生 $\pi \rightarrow \pi^*$ 跃迁而产生的(表1).

根据紫外-可见光吸收图谱(图4(a)), 我们还可以计

图 3 (网络版彩色)循环伏安(CV)曲线
Figure 3 (Color online) Cyclic voltammetry (CV) curves of the hosts

算出4个材料的HOMO能级和LUMO能级的差(E_g), 其中 $E_g = 1240/\lambda$, λ 为材料的吸收带边, 据此计算出DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ的能隙 E_g 分别3.29, 3.28, 3.28, 3.36 eV, 可见4个主体材料的能隙相对接近.

图4(b)给出了4个主体材料DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ在薄膜状态下的荧光光谱图, 其相应的发射峰分别是395, 405, 408, 388 nm^[19]. 在低温77 K下(图5), 我们测定了4个材料的磷光光谱, 其磷光发射峰分别为505, 519, 522, 525 nm, 因此可判断该类材料适合做绿光材料的主体. 另外, 我们看到DTSF-2-DP-TRZ和SF-4-TDP-TRZ在450 nm有较明显发射峰, 据此估算出4个主体材料的三线态能级分别是2.45, 2.38, 2.37, 2.36 eV, 也较为接近.

表1 4个材料的紫外-可见光吸收特性比较

Table 1 UV-vis absorption properties of the hosts

材料名称	吸收峰值波长(nm)	吸收带边(nm)	光学带隙(eV)
DTSF-2-DP-TRZ	280, 314, 326, 355	376	3.29
SF-2-DTDP-TRZ	281, 308, 348	377	3.28
SF-4-DTDP-TRZ	282, 309, 346	377	3.28
SF-4-TDP-TRZ	280, 309, 334, 352	368	3.36

图4 (网络版彩色)4个主体材料在薄膜状态下的紫外-可见光吸收光谱图(a)和荧光发射光谱图(b)

Figure 4 (Color online) UV-vis absorption spectra (a) and fluorescence spectra (b) of the hosts in films, respectively

图5 (网络版彩色)低温77 K薄膜状态测定磷光发射光谱图

Figure 5 (Color online) Phosphorescence spectra of the hosts at 77 K in film states

2.4 器件性能

为了研究上述4个主体材料在OLED发光层中的应用,制备了如图6(a)所示的器件^[20-23]。其中ITO作为阳极, PEDOT:PSS为聚3,4-乙烯二氧噻吩/聚苯乙烯磺酸盐,用作空穴注入和传输层; 4CzIPN为2,4,5,6-四(9-咔唑基)-间苯二腈,属于热激活延迟荧光机制的纯有机发光材料,可以利用反向系间窜越实现激子的完全利用; DPEPO是二[2-((氧代)二苯基膦基)苯基]醚,用作空穴阻挡层; TmPyPB为1,3,5-三[(3-吡啶基)-3-苯基]苯,用

作电子传输材料; Liq为8-羟基喹啉-锂,用于提高电子注入; 最后是蒸镀的Al阴极^[24]。4个主体材料DTSF-2-DP-TRZ, SF-4-TDP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ分别以90:10质量比与4CzIPN掺杂作为发光层,相应的器件分别命名为器件A, B, C, D,我们对相应器件的发光性能进行了测试和表征。通过计算得到4个材料的HOMO分别为-5.88, -6.10, -6.14, -5.85 eV。HOMO能级与4CzIPN的能级相匹配,具有较小的空穴注入势垒。最低未占有分子轨道(LOMO)通过计算得到LOMO值分别为-2.59, -2.82, -2.86, -2.49 eV, LUMO能级基本也与4CzIPN相匹配,有利于电子的注入和传输,具体如图6(b)能级分布图所示。

从图7我们可以看出, 4个器件的电致发光光谱非常相似, 与4CzIPN的光致发光光谱的谱型基本一致。但是器件C和D的光谱有所蓝移, 可能是主体非完全能量转移造成的光谱叠加有关。4个器件A, B, C, D的电致发光波长峰值分别为516, 516, 502, 506 nm, 位于蓝绿偏绿光区。

从图8(a)可以看出, 以DTSF-2-DP-TRZ为主体的器件具有较好的电学性能; 从器件的电压和亮度关系曲线可以看出(图8(b)), 4个器件的启亮电压(亮度为10 cd/m²)分别约为8.2, 9.6, 11.5, 9.3 V, 器件C的启亮电压最高, 远超过其他3个器件的启亮电压, 主要是其主

图 6 (网络版彩色)器件结构(a)和能级分布(b)示意图
Figure 6 (Color online) Schematic diagram of the devices (a) and energy level alignments (b)

图 7 (网络版彩色)4个器件的归一化电致发光光谱比较
Figure 7 (Color online) Normalized EL spectra of the devices

体材料的载流子传输较差导致的。当电压为10 V时, 器件A的亮度为1475 cd/m^2 , 随着电压的增加, 亮度急剧增大, 最大亮度达到6600 cd/m^2 ; 器件B在10 V下的亮度为22.5 cd/m^2 , 随着电压的增加, 最大亮度在18 V达到3719 cd/m^2 ; 器件C在10 V时还没点亮, 但亮度在20 V可达到4941 cd/m^2 ; 器件D的最大亮度达到6280 cd/m^2 。

从图9(a)的电流效率曲线图可以得出4个器件A, B, C, D的最大电流效率分别为51.4, 29.4, 21.0, 31.1 cd/A 。DTSF-2-DP-TRZ作为主体材料制备的器件A的电流效率最大。从功率效率曲线图来看4个器的最大功率效率分别为18.0, 8.4, 5.1, 9.8 lm/W (图9(b))。DTSF-2-DP-TRZ作为主体材料制成的器件A的功率效率最大, 器件C(SF-2-DTDP-TRZ)的功率效率较低主要是其驱动电压比较高造成的。外量子效率(EQE)是检测OLED将电子转化为光子的重要指标。从图9(c)中可以得出4个器件A, B, C, D的最大外量子效率分别为16.6%, 9.6%, 7.5%, 10.7%。综上所述, 器件A基于DTSF-2-DP-TRZ作为主体材料具有较为优越的电学和光学性能。

以上分析表明, DTSF-2-DP-TRZ作为主体材料的

图 8 (网络版彩色)4个器件的电压-电流密度曲线(a)和电压-亮度关系曲线(b)
Figure 8 (Color online) Current density (a) and luminance (b) vs. voltage curves of the devices

图 9 (网络版彩色)4个器件的电流(a)、功率(b)、外量子效率(c)和电流密度曲线比较
Figure 9 (Color online) Current efficiency (a), power efficiency (b), and external quantum efficiency curves (c) of the devices

性能比较好, 跟它的分子结构是紧密相关的。在该分子中, 叔丁基是给电子基团, 螺二苄也是给电子基团, 两者结合在一起增加了给电子能力, 显著提高了三线态能级, 与三嗪基团的电子传输性能很好地结合在同一

个分子中,且两者可以很好地调控分子内的电荷转移,减少激子能量的损失.

3 结论

本文基于螺二芴和均三嗪主基团骨架设计合成了4种新型主体材料DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, SF-4-TDP-TRZ,这4个材料都具有非常优异的热稳定性能.采用旋涂法制备基于绿光热激

活延迟荧光材料4CzIPN的器件,结果表明,DTSF-2-DP-TRZ作为主体材料因其较高的三线态能级和较好的载流子传输性能,使得器件最大亮度达到6600 cd/m²,最大外量子效率可达16.6%.本文系统地比较了基于螺二芴和三嗪单元构筑的4个主体材料的物理、化学特性,并比较其在湿法制备的OLED中的性能差异,很好地体现了主体材料的结构与性能之间的关系,为开发高性能主体材料提供了参考.

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补充材料

图S1 化合物2-氯-4,6-二苯基-1,3,5-均三嗪的氢谱、碳谱和质谱

图S2 化合物2-(2',7'-二叔丁基-9,9'-螺二芴-2-基)-4,6-二苯基-1,3,5-三嗪(DTSF-2-DP-TRZ)的氢谱、碳谱和质谱

图S3 化合物2,4-二(3,5-二叔丁基苯基)-6-氯-1,3,5-三嗪的氢谱、碳谱和质谱

图S4 化合物2-(9,9'-螺二芴-4-基)-4,6-双(4-(叔丁基)苯基)-1,3,5-三嗪(SF-4-TDP-TRZ)的氢谱、碳谱和质谱

图S5 化合物2,4-二(3,5-二叔丁基苯基)-6-氯-1,3,5-三嗪的氢谱、碳谱和质谱

图S6 化合物2-(9,9'-螺二芴-2-基)-4,6-双(3,5-二叔丁基苯基)-1,3,5-三嗪(SF-2-DTDP-TRZ)的氢谱、碳谱和质谱

图S7 化合物2-(9,9'-螺二芴-4-基)-4,6-双(3,5-二叔丁基苯基)-1,3,5-三嗪(SF-4-DTDP-TRZ)的氢谱、碳谱和质谱

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Summary for “螺二芴和均三嗪构筑的主体材料的合成及应用”

Design and synthesis of host materials based on spirofluorene and s-triazine moieties and the applications in organic light-emitting devices

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Organic light-emitting devices (OLEDs) attract intensive attentions from both fundamental and applied researchers due to their unique properties of flexibility, light-weight, color-tunability, high electroluminescent efficiency, and ease of device fabrication. The design of the emitting layer (EML) of OLEDs plays a dominant role in ruling the electroluminescent performances. Typically, the EML is composed of a host and an organic emitter. As the emerging emitters for OLEDs, thermally activated delayed fluorescence (TADF) materials are capable of utilizing 100% of the electrically generated excitons. However, the device performances are also limited by charge injection from the electrodes, charge balance in the EML, and the outcoupling schemes.

In this contribution, we designed four host materials for the TADF emitter, which were synthesized based on spirofluorene and s-triazine moieties. The physical and chemical properties were characterized via thermogravimetric analysis, differential scanning calorimetry, UV-vis absorption, fluorescence, phosphorescence, cyclic voltammetry measurements. It is found that the four host materials exhibited excellent thermal stability and the peaks of the UV-vis absorption located between 280 and 355 nm, which led to freedom of self-absorption. From the low temperature phosphorescent spectra (77 K), we can determine that the peak wavelengths are 505, 519, 522, 525 nm respectively for DTSF-2-DP-TRZ, SF-2-DTDP-TRZ, SF-4-DTDP-TRZ, and SF-4-TDP-TRZ, which make them ideal as a host for green TADF emitters.

To evaluate their performances in the electroluminescence, these host materials were blended with the green TADF emitter, i.e., 2,4,5,6-tetrakis(carbazole-9-yl)-1,3-dicyanobenzene (4CzIPN) with nearly 100% photoluminescence quantum yield, as the emitting layers processed by spin-coating. The used glass substrate was covered with pre-patterned indium tin oxide (ITO). After routine cleaning procedures, the ITO glass substrate was treated with UV-ozone for 20 min. And then the conducting polymer poly(styrene sulfonic acid)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) was spin-coated onto the substrate, following with thermal anneal in the glove box. Later, the EML was spin-coated onto PEDOT:PSS from chlorobenzene solution. To improve the charge balance and thus high radiative recombination, we deposited the additional hole blocking layer, electron transporting layer, and electron injection layer onto the EML via vacuum process.

By comparing the electroluminescent performances of the devices with the four hosts, we figure out the structure-property relationship. It is well known that the host materials played roles in ruling the exciton utilization. The electroluminescent spectra of the devices are similar with a slight deviation of the peak wavelengths, i.e., 516, 516, 502, and 506 nm respectively for the case using DTSF-2-DP-TRZ, SF-4-TDP-TRZ, SF-2-DTDP-TRZ, and SF-4-DTDP-TRZ as the hosts, which could be ascribed to the different polarity of the host-guest environment and the slightly incomplete of host-guest energy transfer. In our investigation, we found that the host DTSF-2-DP-TRZ exhibited high glass transition temperature, well-match energy levels, and bipolar charge injection. Therefore, the device with DTSF-2-DP-TRZ rendered a maximum brightness of 6600 cd/m², a maximum current efficiency of 51.3 cd/A, and a maximum external quantum efficiency of 16.6%, which are superior to those of the devices with the other hosts. This work provides a guidance for exploring host materials for efficient OLEDs with TADF as the emitter. Further works on material and device optimization would lead to better electroluminescent performances to meet the requirements of mass production.

host materials, spirofluorene, s-triazine, thermally activated delayed fluorescence, organic light-emitting devices

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