溶液加工型蒽类树枝状深蓝光材料的合成与表征

赵磊^{①②}, 王淑萌^{①②}, 丁军桥^{①*}, 王利祥^{①*}

① 中国科学院长春应用化学研究所, 高分子物理与化学国家重点实验室, 长春 130022;

② 中国科学院大学, 北京 100049

* 联系人, E-mail: junqiaod@ciac.ac.cn; lixiang@ciac.ac.cn

2015-06-11 收稿, 2015-07-15 修回, 2015-07-16 接受, 2015-09-09 网络版发表

国家重点基础研究发展计划(2015CB655001)和国家自然科学基金(21174144, 51322308)资助

摘要 采用9,10-二苯蒽(DPA)作为中心核, 一代至三代齐聚咔唑作为外围树枝, 设计合成了一系列溶液加工型树枝状深蓝光荧光材料Ent1, Ent2和Ent3. 不同于DPA容易在膜态下形成结晶, Ent1~Ent3均具有良好的热稳定性和形态稳定性, 玻璃化转变温度高达194~371℃. 同时, 咔唑树枝的引入, 有效地抑制了分子间的相互作用, 使得膜态下荧光量子效率从Ent1的46%提高至Ent2的52%和Ent3的67%. 通过旋涂工艺制备了深蓝光非掺杂器件, 发现第二代树枝状荧光材料Ent2表现出最优器件性能, 发光效率为2.63 cd/A, 色坐标CIE_(x,y)为(0.16, 0.10).

关键词 9,10-二苯蒽, 咔唑树枝, 溶液加工, 深蓝光荧光材料, 非掺杂器件

有机发光二极管(organic light-emitting diodes, OLEDs)具有主动发光、显示质量高、响应速度快、可视角度宽、低温特性好、超薄和能耗低等优点, 在平板显示和白光照明领域展现出广阔的应用前景^[1~11]. 为实现全彩色显示, 需要能够发射红光、绿光和蓝光的三基色发光材料. 相对于高效率 and 长寿命的红光和绿光材料而言, 蓝光材料, 尤其是深蓝光材料(色坐标CIE_y<0.10), 它的效率、寿命和色纯度都离实用化还有一段较大的差距^[12~18]. 因此, 开发高性能的深蓝光材料, 已经成为学术界和产业界的关注焦点.

蒽作为一类平面性结构单元, 被广泛用于深蓝光荧光材料的构建. 这是因为, 蒽类衍生物在溶液中具有宽的带隙和高的荧光量子效率^[19~27]. 但是, 该类材料在膜态下容易发生聚集或结晶, 导致荧光淬灭、光谱红移和稳定性变差^[21]. 针对这一问题, 许多课题组在蒽的2, 6, 9, 10位修饰上不同的取代基团, 报道了大量适合于真空蒸镀工艺的蒽类深蓝光材

料^[23,24,26]. 例如, Kim等人^[26]在9,10-二苯蒽(DPA)的外围引入大位阻的3,5-二苯基苯, 设计合成了深蓝光材料TAT(9,10-双[4'-(3'',5''-二苯基)联苯基]蒽). 它具有良好的热稳定性, 玻璃化转变温度高达150℃, 相应的非掺杂器件实现了高效稳定的深蓝光发射, 发光效率为3.64 cd/A, 色坐标CIE_(x,y)为(0.16, 0.09).

虽然溶液加工具有真空蒸镀无法媲美的低成本优势, 但是目前适合于溶液加工工艺的蒽类深蓝光材料研究较少, 且器件效率偏低. 本文采用DPA作为中心核, 一代至三代齐聚咔唑作为外围树枝, 设计合成了一系列具有良好溶液加工性能的树枝状深蓝光材料Ent1, Ent2和Ent3. 研究发现, 咔唑树枝的引入, 有效地改善了材料的形态稳定性和空穴注入能力, 同时减弱了分子之间的相互作用, 使得膜态荧光量子效率由Ent1的46%增加到Ent2的52%和Ent3的67%. 其中, 第二代树枝状荧光材料Ent2表现出最优的非掺杂深蓝光器件效率2.63 cd/A, 色坐标CIE_(x,y)为(0.16, 0.10). 该器件性能已经十分接近真空蒸镀型深

引用格式: 赵磊, 王淑萌, 丁军桥, 等. 溶液加工型蒽类树枝状深蓝光材料的合成与表征. 科学通报, 2016, 61: 325–332

Zhao L, Wang S M, Ding J Q, et al. Synthesis and characterization of solution-processible anthracene based deep-blue fluorescent dendrimers (in Chinese). Chin Sci Bull, 2016, 61: 325–332, doi: 10.1360/N972015-00647

蓝光蒽类小分子的水平.

1 实验

(i) 仪器和试剂. 样品中C, H, N元素的含量由Vario EL型元素分析仪(德国Various公司)测得; 核磁(^1H NMR和 ^{13}C NMR)由Bruker AV 300型核磁共振仪(德国Bruker公司)测得; 质谱由Autoflex III TOF激光解吸飞行时间质谱仪(MALDI-TOF, 德国Bruker公司)测得; 热失重分析(TGA)和差式扫描量热(DSC)由Perkins-Elmer 7型热分析仪(美国PE公司)测得; 紫外-可见吸收光谱由Perkin-Elmer UV-35型紫外可见光谱仪(美国PE公司)测得; 荧光光谱由Perkin-Elmer LS 50B型荧光光谱仪(美国PE公司)测得; 膜态发光量子效率由HAMAMATSU C9920-02型多通道光学分析仪统计积分球内的光子数计算得到; 循环伏安曲线由EG&G 283电化学工作站(美国华辰公司)测得; 原子力图像由SPA300HV型原子力显微镜(AFM, 日本Seiko公司)测得. 器件的电流-电压-亮度曲线以及电致发光光谱的测量均由计算机控制的Keithley 2400 Sourcemeter和PR650 SpectraScan Photometer完成. $\text{Pd}_2(\text{dba})_3$, $\text{P}(t\text{-Bu})_3$, $t\text{-BuONa}$ (Alfa试剂公司)和溶剂(天津精细化学有限公司)均为分析纯试剂; 中间体9,10-二(4-溴苯基)蒽^[28]和一代至三代咔唑树枝(D1~D3)^[29,30]根据文献方法合成.

枝(D1~D3)^[29,30]根据文献方法合成.

(ii) 蒽类树枝状深蓝光材料Ent1, Ent2和Ent3的合成. 蒽类树枝状深蓝光材料Ent1, Ent2和Ent3的合成路线如图1所示. 详细过程为: 在100 mL的三口圆底烧瓶中, 加入1 g(2 mmol)9,10-二(4-溴苯基)蒽、相应的一代至三代咔唑树枝(D1~D3)(5 mmol), 36 mg(0.04 mmol) $\text{Pd}_2(\text{dba})_3$ 和0.58 g(6 mmol) $t\text{-BuONa}$. 抽换气3次后, 再加入20 mL干燥好的甲苯和1.2 mL(0.16 mmol) $\text{P}(t\text{-Bu})_3$ 的10%正己烷溶液. 在氩气保护下, 110℃反应12 h. 反应结束后, 将反应混合物倒入水中, 用二氯甲烷萃取, 水洗3次, 有机相用无水 Na_2SO_4 干燥后, 减压除掉溶剂. 粗产物最后经过硅胶柱分离(淋洗剂为石油醚:二氯甲烷 = 9:1), 得到白色固体粉末.

Ent1: 产量1.3 g, 产率72%. ^1H NMR(300 MHz, CDCl_3) δ 8.21(d, J = 1.7 Hz, 4H), 7.93~7.86(m, 4H), 7.84(d, J = 8.3 Hz, 4H), 7.76~7.69(m, 4H), 7.63(d, J = 8.6 Hz, 4H), 7.57(dd, J = 8.7, 1.9 Hz, 4H), 7.52~7.44(m, 4H), 1.51(d, J = 7.0 Hz, 36H). ^{13}C NMR(101 MHz, CDCl_3) δ 143.09, 139.26, 137.69, 137.56, 136.58, 132.70, 130.08, 126.94, 126.51, 125.44, 123.72, 123.59, 116.34, 109.41, 34.79, 32.06. MS(MALDI-TOF) m/z : 884.5 [M^+]. Anal. Calcd for $\text{C}_{66}\text{H}_{64}\text{N}_2$:

图1 蒽类树枝状深蓝光材料Ent1~Ent3的合成路线

Figure 1 Synthesis of the anthracene-based deep-blue fluorescent dendrimers Ent1, Ent2 and Ent3

C, 89.55; H, 7.29; N, 3.16. Found: C, 89.60; H, 7.21; N, 3.16.

Ent2: 产量1.9 g, 产率56%. ^1H NMR(300 MHz, CDCl_3) δ 8.35(s, 4H), 8.22(s, 8H), 8.08(d, $J = 8.3$ Hz, 4H), 8.01(d, $J = 3.3$ Hz, 2H), 7.98(d, $J = 2.8$ Hz, 4H), 7.94(d, $J = 4.9$ Hz, 4H), 7.91(s, 2H), 7.76(dd, $J = 8.7$, 2.0 Hz, 4H), 7.59(dd, $J = 6.9$, 3.2 Hz, 4H), 7.55~7.49(m, 8H), 7.43(d, $J = 8.1$ Hz, 8H), 1.52(s, 72H). ^{13}C NMR(101 MHz, CDCl_3) δ 142.64, 140.31, 140.16, 139.82, 138.88, 136.82, 136.41, 133.20, 131.15, 130.09, 127.12, 126.91, 126.11, 125.70, 124.23, 123.61, 123.19, 119.46, 116.27, 111.34, 109.13, 34.76, 32.07. MS(MALDI-TOF) m/z : 1770.0 $[(\text{M}+\text{H})^+]$. Anal. Calcd for $\text{C}_{130}\text{H}_{124}\text{N}_6$: C, 88.19; H, 7.06; N, 4.75. Found: C, 88.23; H, 7.11; N, 4.57.

Ent3: 产量2.4 g, 产率35%. ^1H NMR(300 MHz, CDCl_3) δ 8.63(d, $J = 1.8$ Hz, 4H), 8.30(d, $J = 1.7$ Hz, 8H), 8.17(d, $J = 1.7$ Hz, 16H), 8.12(dd, $J = 11.9$, 8.5 Hz, 8H), 8.04~7.94(m, 12H), 7.71(d, $J = 8.7$ Hz, 8H), 7.64(dd, $J = 8.7$, 1.8 Hz, 8H), 7.60(dd, $J = 6.8$, 3.2 Hz, 4H), 7.47(dd, $J = 8.7$, 1.8 Hz, 16H), 7.36(d, $J = 8.6$ Hz, 16H), 1.45(s, 144H). ^{13}C NMR(101 MHz, CDCl_3) δ 142.57, 141.40, 141.17, 140.23, 139.34, 136.56, 136.36, 133.41, 130.84, 130.30, 130.12, 127.29, 126.92, 126.57, 126.08, 126.82, 124.41, 123.57, 123.14, 120.15, 119.47, 116.23, 111.97, 111.09, 109.12, 34.74, 32.05. MS (MALDI-TOF) m/z : 3538.0 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{258}\text{H}_{244}\text{N}_{14}$: C, 87.52; H, 6.95; N, 5.54. Found: C, 87.59; H, 7.01; N, 5.49.

(iii) 器件制备. 将ITO导电玻璃依次用表面活性剂和清水重复冲洗3次, 最后用去离子水冲洗1次, 干燥, UVO处理30 min. 然后在处理后的ITO表面旋涂PEDOT:PSS(聚3,4-乙撑二氧噻吩: 聚苯乙烯磺酸盐), 转速为5000 r/min, 时间为60 s, 得到约40 nm厚的薄膜, 放入烘箱中于120℃加热40 min. 冷却后, 在PEDOT:PSS上旋涂发光层, 旋涂溶液是由树枝状深蓝光材料Ent1~Ent3配成的10 mg/mL氯苯溶液, 转速为1500 r/min, 时间为60 s. 发光层在 N_2 氛围下100℃热退火30 min后, 转移到真空镀膜机腔内抽真空. 当气压降至 4×10^{-4} Pa时, 继续在发光层上依次蒸镀55 nm厚的TPBI(1,3,5-三(1-苯基-1H-苯并咪唑-2-基)苯)作为电子传输层, 蒸镀1 nm厚的LiF和100 nm厚的Al作为阴极. 所蒸镀材料的厚度和沉积速度通过石英晶体振荡器来进行监控和检测. 电极蒸镀完后冷却30 min, 即可取出器件进行测试.

2 结果与讨论

2.1 蒽类树枝状深蓝光材料的合成

如图1所示, 蒽类树枝状深蓝光材料的合成采用Buchwald反应. 以9,10-二(4-溴苯基)蒽和一代至三代咔唑树枝为起始原料, 以 $\text{Pd}_2(\text{dba})_3/\text{P}(t\text{-Bu})_3$ 为催化剂, 在 $t\text{-BuONa}$ 的作用下, 于110℃反应12 h即可得到蒽类树枝状深蓝光材料Ent1, Ent2和Ent3. 所有最终产物都经过硅胶柱层析法分离提纯, 产率在35%~72%之间. 我们注意到, 随着树枝代数的增加, 产率由Ent1的72%逐渐降低到Ent2的56%和Ent3的35%, 这可能是空间位阻效应所导致的. Ent1, Ent2和Ent3的化学结构以及纯度均得到了核磁共振氢谱、碳谱、质谱和元素分析的表征证实, 同时它们能够很好地溶解在二氯甲烷、四氢呋喃、甲苯、氯苯等常用有机溶剂中, 表现出优异的可溶液加工性能.

2.2 蒽类树枝状深蓝光材料的热学性质与形态稳定性

TGA曲线显示, Ent1, Ent2和Ent3具有良好的热稳定性, 它们的热分解温度均在490℃以上(图2(a)). 同时, DSC测试结果表明, 材料的玻璃化转变温度对树枝代数有较大的依赖性. 随着代数的增加, 玻璃化转变温度从Ent1的194℃逐渐升高至Ent2的285℃和Ent3的371℃(图2(b)和表1). 此外, 不同于中心核单元DPA在165℃呈现出较强的结晶峰^[25], Ent1~Ent3在30~400℃的扫描范围内没有观察到结晶峰和熔融峰的出现. 这些结果说明, 大位阻咔唑树枝的引入, 能够有效地限制分子的热运动并阻止结晶过程的发生, 促使材料形成稳定的无定形薄膜, 从而有利于制备长寿命的有机电致发光器件.

为了进一步揭示所形成无定形薄膜的热稳定性, 采用AFM表征了它们热退火前后的薄膜形态. 具体的操作步骤是, 将Ent1~Ent3分别配成10 mg/mL的氯苯溶液, 旋涂在PEDOT:PSS修饰的ITO玻璃基底上制备成膜. AFM结果显示, Ent1, Ent2和Ent3的薄膜没有针孔缺陷, 表面平整, 表面粗糙度分别为0.39, 0.38和0.33 nm(图3(a)~(c)). 随后, 将这些原始薄膜在空气中于120℃加热2 h后, 发现表面粗糙度略微增加到0.43, 0.47和0.39 nm, 但薄膜形态在热退火前后没有明显变化(图3(d)~(f)). 这说明, Ent1~Ent3均能通过溶液旋涂的方式制备得到高质量的无定形薄膜.

图2 Ent1~Ent3的TGA曲线(a)和DSC曲线(b)

Figure 2 TGA(a) and DSC(b) curves of Ent1, Ent2 和 Ent3

且它们具有良好的热稳定性.

2.3 蒽类树枝状深蓝光材料的光物理和电化学性质

蒽类树枝状深蓝光材料Ent1~Ent3在甲苯溶液中的紫外-可见吸收光谱和荧光光谱以及膜态下的荧光光谱见图4, 相应数据列在表1中. 在溶液中, Ent1~Ent3的吸收光谱主要表现来自于中心核DPA的弱 $\pi-\pi^*$ 吸收峰(397/377/356 nm)和来自于外围咔唑树枝的强特征吸收峰(298 nm). 随着树枝代数的增加, 位于298 nm处的吸收峰强度逐渐增加. 同时, Ent1, Ent2和Ent3的最大发射峰分别位于434, 430和427 nm, 荧光量子效率分别为98%, 88%和85%. 在荧光光谱中没有观察到齐聚咔唑的发射, 表明发生了从外围树枝到中心核的完全能量转移.

在膜态下, Ent1~Ent3的荧光光谱位于448~451 nm, 和溶液中的光谱相比大约红移了20 nm左右, 且荧光量子效率明显降低(46%~67%). 这说明, 该系列材料在膜态下均存在着一定程度的聚集现象. 但是, 随着树枝代数的增加, 分子间的相互作用得到了有效的抑制, 膜态光谱从Ent1的451 nm蓝移到Ent3的448 nm, 相应的荧光量子效率从46%增加到67%.

图5给出了Ent1~Ent3的循环伏安曲线. 在正向扫描过程中, Ent1~Ent3均存在多个可逆的氧化峰. 根据第一个氧化峰的起始值($E_{\text{onset}}^{\text{ox}}$), 采用式 $E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{ox}} + 4.8 \text{ V})$ 计算得到Ent1, Ent2和Ent3的最高占据分子轨道(HOMO)能级分别为-5.51, -5.37和-5.34 eV. 在负向扫描过程中, 没有检测到Ent1~Ent3的还原行为. 因此, 我们结合HOMO能级和光学带隙计算得到Ent1, Ent2和Ent3的最低未占据分

图3 Ent1~Ent3 薄膜热退火前后的AFM图像比较

Figure 3 Comparison of 3D AFM topographic images of Ent1, Ent2 and Ent3 between the pristine film and annealed film

图4 Ent1~Ent3在甲苯溶液中的紫外-可见吸收光谱和发射光谱(a)以及膜态发射光谱(b)

Figure 4 UV-Vis and PL spectra(a)in toluene and PL spectra(b)as spin-coated films of Ent1, Ent2 and Ent3

表1 Ent1~Ent3的物理性质

Table 1 Summary of the physical data of Ent1, Ent2 and Ent3

化合物	$T_d(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$	$\lambda_{\text{abs}}^{\text{a})}(\text{nm})$	$\lambda_{\text{em}}^{\text{a})}(\text{nm})$	$\Phi_{\text{PL}}^{\text{b})}(\%)$	$\lambda_{\text{em}}^{\text{c})}(\text{nm})$	$\Phi_{\text{PL}}^{\text{d})}(\%)$	HOMO (eV)	LUMO (eV)
Ent1	498	194	397, 377, 356, 298	434	98	451	46	5.51	2.53
Ent2	523	285	397, 376, 352, 298	430	88	451	52	5.37	2.37
Ent3	519	371	397, 375, 350, 298	427	85	448	67	5.34	2.33

a) 浓度为 $10^{-6} \text{ mol L}^{-1}$ 甲苯溶液中测得数据; b) 以 9,10-二苯蒽为标样甲苯溶液中测得数据; c) 膜态下测得数据; d) 用积分球测得膜态数据

图5 Ent1~Ent3的循环伏安曲线

Figure 5 CV characteristics of Ent1~Ent3

子轨道(LUMO)能级分别为-2.53, -2.37和-2.33 eV. 值得注意的是,随着树枝代数的增加, HOMO能级逐渐升高,和PEDOT:PSS修饰的ITO阳极(-5.20 eV)之间的注入势垒逐渐减小,说明咪唑树枝的引入可以在一定程度上提高空穴的注入能力.

2.4 蒽类树枝状深蓝光材料的电致发光性能

采用Ent1, Ent2和Ent3作为发光层,我们通过溶

液旋涂的方式制备了非掺杂器件,器件结构为ITO\ PEDOT:PSS(40 nm)\Ent1~Ent3(40 nm)\TPBI(55 nm)\ LiF(1 nm)\Al(100 nm)(图6(a)). 其中, TPBI被用来作为电子传输层. 如图6(b)所示, Ent1, Ent2和Ent3均表现出深蓝光发射,最大发射峰分别为444, 444和440 nm, 对应的色坐标 $\text{CIE}_{(x,y)}$ 分别为(0.16, 0.11), (0.16, 0.10)和(0.16, 0.09),已经十分接近美国国家电视系统委员会制定的蓝光标准(0.14, 0.08).

图6(c)和(d)分别给出了Ent1~Ent3的电流密度-电压-亮度曲线以及发光效率随电流密度的变化曲线,相关器件数据列于表2. 随着树枝代数的增加, HOMO能级的增加有利于空穴的注入,使得器件的启亮电压由Ent1的4.2 V降低到Ent2的3.8 V. 但是,对于Ent3而言,启亮电压反而升高至4.8 V. 这是因为,在空穴注入变得更为容易的同时,电子注入由于LUMO能级过高变得相对困难. 两者共同作用的结果,导致在Ent3的器件中空穴和电子之间的失衡. 因此,我们可以合理的推测,含有二代咪唑树枝的Ent2表现出最为平衡的载流子注入和传输能力,电流密度和亮度均大于Ent1和Ent3. 与之对应, Ent2的器件性能最优,最大亮度为 4650 cd/m^2 ,最大发光效率为 2.63 cd/A ,最大外量子效率为2.48%.

图6 Ent1~Ent3的器件性能。(a) 器件结构和主要有机材料的分子式;(b) EL光谱;(c) 电流密度-电压-亮度曲线;(d) 发光效率-电流密度曲线
Figure 6 (a) Schematic diagram of the EL device configuration and molecular structure of the material used in the devices; (b) EL spectra at 100 cd/m^2 ; (c) current density-voltage-brightness characteristics; (d) the current density dependence of the luminous efficiency

表2 Ent1~Ent3的器件性能

Table 2 Device performance for Ent1~Ent3

器件	$V_{\text{on}}^{\text{a)}}$ (V)	$L_{\text{max}}^{\text{b)}}$ (cd m^{-2})	$\eta_{\text{c,max}}^{\text{c)}}$ (cd A^{-1})	$\eta_{\text{p,max}}^{\text{d)}}$ (lm W^{-1})	$\eta_{\text{ext,max}}^{\text{e)}}$ (%)	$\text{CIE}_{(\text{x}, \text{y})}^{\text{f)}$
Ent1	4.2	2418	1.96	1.46	1.76	(0.16, 0.11)
Ent2	3.8	4648	2.63	2.07	2.48	(0.16, 0.10)
Ent3	4.8	3011	2.36	1.78	2.36	(0.16, 0.09)

a) 启亮电压; b) 最大亮度; c) 最大流明效率; d) 最大功率效率; e) 最大外量子效率; f) 色坐标

3 结论

采用DPA作为中心核, 通过引入具有空穴传输能力的一至三代咔唑树枝, 设计合成了溶液加工型蒽类树枝状深蓝光材料Ent1, Ent2 和Ent3. 咔唑树枝的引入, 提高了材料的热稳定性和形态稳定性, 解决了DPA发光核容易结晶的问题; 同时分子间的相互作用

得到了有效地抑制, 膜态荧光量子效率由Ent1的46%增加到Ent2的52%和Ent3的67%. 此外, 随着代数的增加, 该类材料的空穴注入能力提高, 电子注入能力下降, 最终导致含二代咔唑树枝的Ent2表现出最佳的电子/空穴注入平衡性. 以Ent2为发光层, 利用旋涂工艺制备的非掺杂深蓝光器件的最大发光效率达到2.63 cd/A , 外量子效率达到2.48%, 色坐标 $\text{CIE}_{(\text{x}, \text{y})}$ 为(0.16, 0.10).

参考文献

- Tang C W, Vanslyke S A. Organic electroluminescent diodes. Appl Phys Lett, 1987, 51: 913–915
- Baldo M A, Thompson M E, Forrest S R. High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer. Nature, 2000, 403: 750–753
- D'Andrade B W, Forrest S R. White organic light-emitting devices for solid-state lighting. Adv Mater, 2004, 16: 1585–1595
- Wu C C, Lin Y T, Wong K T, et al. Efficient organic blue-light-emitting devices with double confinement on terfluorenes with ambipolar carrier transport properties. Adv Mater, 2004, 16: 61–70
- Su S J, Gommori E, Sasabe H, et al. Highly efficient organic blue- and white-light-emitting devices having a carrier- and exciton-confining structure for reduced efficiency roll-off. Adv Mater, 2008, 20: 4189–4194

- 6 Jiang Z Q, Liu Z Y, Yang C L, et al. Multifunctional fluorene-based oligomers with novel spiro-annulated triarylamine: Efficient, stable deep-blue electroluminescence, good hole injection, and transporting materials with very high T_g . *Adv Funct Mater*, 2009, 19: 3987–3995
- 7 Kamtekar K T, Monkman A P, Bryce M R. Recent advances in white organic light-emitting materials and devices(WOLEDs). *Adv Mater*, 2010, 22: 572–582
- 8 Zhu M R, Wang Q A, Gu Y, et al. Efficient deep-blue emitters comprised of an anthracene core and terminal bifunctional groups for nondoped electroluminescence. *J Mater Chem*, 2011, 21: 6409–6415
- 9 Jiang G X, Bian C L, Ding J Q, et al. Synthesis and characterization of blue light-emitting poly(aryl ether)s containing pyrimidine-incorporated oligofluorene pendants with bipolar feature. *Chin J Polym Sci*, 2013, 31: 787–797
- 10 Xia D B, Wang B, Chen B, et al. Self-host blue-emitting iridium dendrimer with carbazole dendrons: Nondoped phosphorescent organic light-emitting diodes. *Angew Chem Int Edit*, 2014, 53: 1048–1052
- 11 Wang X C, Zhao L, Shao S Y, et al. Poly(spirobifluorene)s containing nonconjugated diphenylsulfone moiety: Toward blue emission through a weak charge transfer effect. *Macromolecules*, 2014, 47: 2907–2914
- 12 Wang X C, Zhao L, Shao S Y, et al. Tunable charge transfer effect in poly-(spirobifluorene)s with different electron-rich side chains. *Polym Chem*, 2014, 5: 6444–6451
- 13 Hung W Y, Chi L C, Chen W J, et al. A carbazole-phenylbenzimidazole hybrid bipolar universal host for high efficiency RGB and white PhOLEDs with high chromatic stability. *J Mater Chem*, 2011, 21: 19249–19256
- 14 Ho C L, Chi L C, Hung W Y, et al. Carbazole-based coplanar molecule(CmInF) as a universal host for multi-color electrophosphorescent devices. *J Mater Chem*, 2012, 22: 215–224
- 15 Lin M S, Chi L C, Chang H W, et al. A diarylborane-substituted carbazole as a universal bipolar host material for highly efficient electrophosphorescence devices. *J Mater Chem*, 2012, 22: 870–876
- 16 Chen B, Ding J Q, Wang L X, et al. A solution-processable phosphonate functionalized deep-blue fluorescent emitter for efficient single-layer small molecule organic light-emitting diodes. *Chem Commun*, 2012, 48: 8970–8972
- 17 Yu M Q, Wang S M, Shao S Y, et al. Starburst 4,4',4'''-tris(carbazol-9-yl)-triphenylamine-based deep-blue fluorescent emitters with tunable oligophenyl length for solution-processed undoped organic light-emitting diodes. *J Mater Chem C*, 2015, 3: 861–869
- 18 Peng T, Ye K Q, Liu Y, et al. Novel beryllium complex as the non-doped emitter for highly efficient deep-blue organic light-emitting diode. *Org Electron*, 2011, 12: 1914–1919
- 19 Chien C H, Chen C K, Hsu F M, et al. Multifunctional deep-blue emitter comprising an anthracene core and terminal triphenylphosphine oxide groups. *Adv Funct Mater*, 2009, 19: 560–566
- 20 Huang J H, Su J H, Li X, et al. Bipolar anthracene derivatives containing hole- and electron-transporting moieties for highly efficient blue electroluminescence devices. *J Mater Chem*, 2011, 21: 2957–2964
- 21 Zhu M R, Ye T L, Li C G, et al. Efficient solution-processed nondoped deep-blue organic light-emitting diodes based on fluorene-bridged anthracene derivatives appended with charge transport moieties. *J Phys Chem C*, 2011, 115: 17965–17972
- 22 Chen Y H, Lin S L, Chang Y C, et al. Efficient non-doped blue light emitting diodes based on novel carbazole-substituted anthracene derivatives. *Org Electron*, 2012, 13: 43–52
- 23 Zheng C J, Zhao W M, Wang Z Q, et al. Highly efficient non-doped deep-blue organic light-emitting diodes based on anthracene derivatives. *J Mater Chem*, 2010, 20: 1560–1566
- 24 Ye S H, Chen J M, Di C A, et al. Phenyl-substituted fluorene-dimer cored anthracene derivatives: Highly fluorescent and stable materials for high performance organic blue- and white-light-emitting diodes. *J Mater Chem*, 2010, 20: 3186–3194
- 25 Wu C L, Chang C H, Chang Y T, et al. High efficiency non-dopant blue organic light-emitting diodes based on anthracene-based fluorophores with molecular design of charge transport and red-shifted emission proof. *J Mater Chem C*, 2014, 2: 7188–7200
- 26 Kim S K, Yang B, Ma Y, et al. Exceedingly efficient deep-blue electroluminescence from new anthracenes obtained using rational molecular design. *J Mater Chem*, 2008, 18: 3376–3384
- 27 Lee K H, You J N, Kang S, et al. Synthesis and electroluminescent properties of blue-emitting t-butylated bis(diarylaminoaryl) anthracenes for OLEDs. *Thin Solid Films*, 2010, 518: 6253–6258
- 28 Shin H, Kang H, Kim B, et al. Effect of the length of side group substitution on optical and electroluminescence properties. *Bull Korean Chem Soc*, 2014, 35: 3041–3046
- 29 Ding J Q, Lu J H, Cheng Y X, et al. Solution-processible red iridium dendrimers based on oligocarbazole host dendrons: Synthesis, properties, and their applications in organic light-emitting diodes. *Adv Funct Mater*, 2008, 18: 2754–2762
- 30 Wang X D, Wang S M, Ma Z H, et al. Solution-processible 2,2-dimethyl-biphenyl cored carbazole dendrimers as universal hosts for efficient blue, green, and red phosphorescent OLEDs. *Adv Funct Mater*, 2014, 24: 3413–3421

Synthesis and characterization of solution-processible anthracene-based deep-blue fluorescent dendrimers

ZHAO Lei^{1,2}, WANG ShuMeng^{1,2}, DING JunQiao¹ & WANG LiXiang¹

¹ State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China;

² University of Chinese Academy of Sciences, Beijing 100049, China

Anthracene has been intensively studied as an attractive building block for deep-blue fluorescent emitters due to its wide band gap and high photoluminescence quantum yield (PLQY) in dilute solution. In solid state, however, these anthracene derivatives seem to aggregate or crystallize, leading to the quenched fluorescence, red-shifted emission and poor device lifetime. Therefore, there are few reports about anthracene-based deep-blue emitters suitable for solution-processed undoped devices. To this end, herein we have designed and synthesized a series of solution-processible deep-blue fluorescent dendrimers (Ent1, Ent2 and Ent3) by using 9,10-diphenylanthracene (DPA) as the central core and 1st to 3rd generation oligocarbazole as the peripheral dendron. Unlike DPA that tends to crystallize in the solid state, Ent1~Ent3 are thermally stable, showing very high glass transition temperatures up to 194–371°C without any related signals from the crystallization or melting processes. As determined by atomic force microscopy (AFM), in addition, both the pristine and annealed films of Ent1~Ent3 have a fairly smooth surface with a root-mean-square roughness of 0.33–0.47 nm, indicative of their morphology stability. Meanwhile, the introduction of dendrons can effectively suppress the intermolecular interactions and thus enhance the film PLQY from 46% of Ent1 to 52% of Ent2 and 67% of Ent3. Correspondingly, as a result of the much richer electron-cloud density from the higher generation dendron, the highest occupied molecular orbital (HOMO) energy level is increased from –5.51 eV of Ent1 to –5.37 eV of Ent2 and –5.34 eV of Ent3, which is beneficial for the hole injection. Solution-processed undoped organic light-emitting diodes (OLEDs) are subsequently fabricated with a configuration of ITO/PEDOT:PSS(40 nm)/Ent1~Ent3(40 nm)/TPBI(55 nm)/LiF(1 nm)/Al(100 nm). All the dendrimers display a bright deep-blue emission with Commission International De L'Eclairage (CIE) coordinates of (0.16, 0.11), (0.16, 0.10) and (0.16, 0.09) for Ent1, Ent2 and Ent3, respectively. Noticeably, the turn-on voltage is firstly down from 4.2 V of Ent1 to 3.8 V of Ent2, and then up to 4.8 V of Ent3. This observation means that, albeit the facilitated hole injection, the electron injection would become more difficult in Ent3 owing to its shallow lowest unoccupied molecular orbital (LUMO) level. Therefore, among Ent1~Ent3, more balanced charge injection/transporting and efficient recombination could be expected for the 2nd generation dendrimer Ent2. Consequently, Ent2 obtains the best device performance, revealing a maximum luminous efficiency of 2.63 cd/A, a maximum power efficiency of 2.07 lm/W and a maximum external quantum efficiency of 2.48%. Our results demonstrate a promising approach to the development of solution processible deep-blue fluorescent emitters for undoped OLEDs applications.

9,10-diphenylanthracene, carbazole dendron, solution-processible, deep-blue fluorescent emitters, undoped OLEDs

doi: 10.1360/N972015-00647