物理学报 Acta Physica Sinica
Chinese Physical Society
Institute of Physics, CAS

基于衬底图形化与链取向技术实现平面光波导

方月婷 易建鹏 陈锦山 汪洪杰 池浪 夏瑞东

Design of planar waveguide based on patterning substrate and oriented polymer film

Fang Yue-Ting Yi Jian-Peng Chen Jin-Shan Wang Hong-Jie Chi Lang Xia Rui-Dong

引用信息 Citation: Acta Physica Sinica, 65, 056101 (2016) DOI: 10.7498/aps.65.056101
在线阅读 View online: http://dx.doi.org/10.7498/aps.65.056101
当期内容 View table of contents: http://wulixb.iphy.ac.cn/CN/Y2016/V65/I5

物理学报 Acta Phys. Sin. Vol. 65, No. 5 (2016) 056101

基于衬底图形化与链取向技术实现平面光波导*

方月婷 易建鹏 陈锦山 汪洪杰 池浪 夏瑞东†

(南京邮电大学信息材料与纳米技术研究院, 有机电子与信息显示国家重点实验室培育基地, 江苏省有机光电材料
协同创新中心, 南京 210023)

(2015 年 10 月 11 日收到; 2015 年 11 月 28 日收到修改稿)

采用喷墨打印的方法对衬底进行图形化, 结合链取向技术, 实现聚合物混合体 poly(9, 9-dioctylfluorene-co-benzothiadiazole)(F8BT, 主体) 和 red F(客体) 在指定区域链取向. 利用链取向区域内外的折射率差异, 设计出了各种宽度的薄膜光波导, 使光信号在链取向区域传播. 同时, 这一共混体系中主体的荧光光谱与客体的吸收光谱区域重叠, 可以使有效的能量传递发生, 利用主体向客体的能量传递机理, 使链取向处理后的聚合物混合体实现了红光发射.

关键词: 链取向, 衬底图形化, 薄膜光波导, 发光聚合物

PACS: 61.30.Gd, 45.70.Qj, 42.79.Gn, 72.80.Le **DOI:** 10.7498/aps.65.056101

1 引 言

有机半导体激光增益介质有许多独特的优点, 比如荧光量子效率高、增益光谱范围宽和受激发射截面大[1−5]. 这些特点使其在固态激光及光通信等领域有很多潜在应用, 因此近年来受到了科学界的极大关注. 然而, 常规的有机半导体因其载流子迁移率较低、热稳定性不足、抽运阈值较高等缺陷成为制约其作为增益介质广泛应用于激光器件、光放大及光波导的主要障碍[6−8]. 针对这些不足, 已有文献报道对某些蓝光和黄绿光聚合物光增益材料利用链取向技术, 可以使材料的定向光增益系数和载流子迁移率均得到了显著地改善[9,10]. 另一方面, 将两种激光增益聚合物共混, 利用主体向客体的能量传递, 提高客体荧光量子效率和降低激光阈值的研究也有报道[11]. 为此本文系统探索了链取向技术在两种聚合物混合体系及红光领域应用的可能性.

在有机光通信领域中急需解决的一个难题是如何将光信号耦合进入光波导. 光栅耦合是目前文献报道中相对有效的低损耗耦合手段[12−14], 但是光栅通常是通过电子束曝光、化学刻蚀等工艺制备而成, 由于工艺过程复杂导致光栅的制作成本很高, 并且光栅耦合条件苛刻, 不适合商业化应用, 因此, 开发工艺简单, 成本低的光波导器件制作技术, 实现信号光向光纤的耦合, 也是目前实现低成本、高容量聚合物光通信的关键. 已有文献报道, 链取向技术可以使材料的光折射率在沿链取向方向和垂直于链取向方向产生明显差异, 并均与未发生分子链取向时的折射率不同[10], 因此, 利用分子链取向区域内外的折射率差异, 可望实现光波导对光的限制作用和光耦合作用.

本文利用喷墨打印技术实现了对衬底取向材料聚酰亚胺 (polyimide, 简称 PI) 的图形化, 结合链取向技术, 使共混发光聚合物薄膜在特定区域及特定方向的链取向, 利用区域内外的折射率差异, 提高光的限制能力, 实现光信号在高折射率的波导区域传播. 同时, 通过将两种激光增益聚合物共混, 利用主体向客体的能量传递机理, 实现了波长在 600—670 nm 的红光发射.

---

* 国家自然科学基金 (批准: 61376023, 61136003)、国家重点基础研究发展计划 (批准号: 2015CB932203)、南京邮电大学引进人才启动基金 (批准号: NY212013, NY212034) 和江苏高校优势学科建设工程 (PAPD) 资助的课题.

† 通信作者. E-mail: iamrdxia@njupt.edu.cn

2 实　验

2.1 样品制备

样品制备过程如图1所示. 首先在清洗干燥后的石英衬底上采用喷墨打印方法制备取向层PI图案. 所用喷墨打印机为Dimatix DMP-3000, 打印分辨率为846 dpi, 墨水为PI溶液. 取向层PI打印后在60 °C下退火15 min, 然后提高温度至300 °C退火1 h, 使取向层PI固化. 用摩擦的方法沿某一方向摩擦数次, 通过摩擦对PI层施加某一方向的应力, 使取向层分子链定向排列[9,10,15,16], 经上述处理后膜厚约为60 nm.

实验所采用的发光材料是poly(9, 9-dioctylfluorene-co-benzothiadiazole) (F8BT)和red F[5,17,18]. 将F8BT 和red F分别溶于甲苯, 制备出浓度均为20 mg/mL的溶液, 然后将两种溶液按F8BT : red F=9 : 1的比例混合. 主、客体材料F8BT和red F都是性能优良的聚合物激光增益材料. 两种材料的吸收及发射谱如图2所示, F8BT的发射谱和red F的吸收谱有很大的重叠, 两种材料共混后能够发生从F8BT向red F的有效的能量传递[5,19]. 将二元掺杂溶液通过旋涂的方法均匀涂布在取向层PI 上, 通过调控转速控制聚合物层膜厚为150—200 nm. 然后根据增益材料的熔点和晶化温度对它们进行热处理, 进而达到取向效果. 即在氮气保护下265 °C加热2 min, 然后逐渐降温至235 °C, 最后急速冷却至室温.

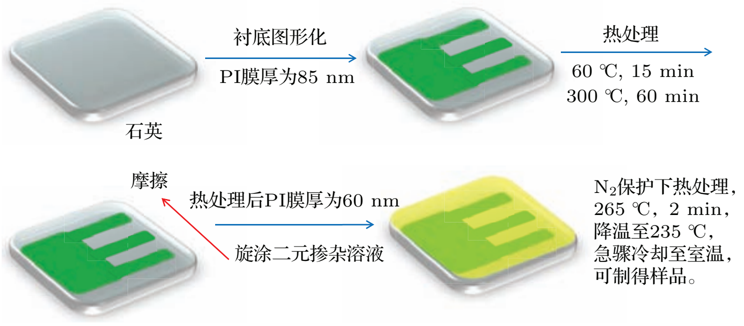

图1　(网刊彩色) 样品制备示意图

Fig. 1. (color online) The schematic of the chain alignment sample preparing.

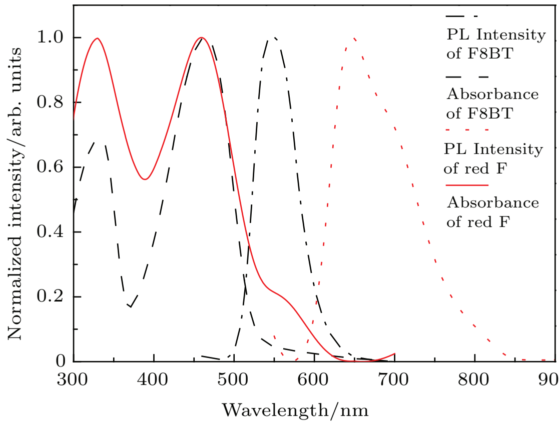

图2　(网刊彩色) F8BT和red F的吸收谱和发射谱

Fig. 2. (color online) The absorption spectra and the emission spectra of F8BT and Red F film.

2.2 各向异性光谱测试方法

采用PerkinElmer LS55荧光分光光度计和Lambda35紫外/可见光分光光度计在室温下对样品的吸收谱和发射谱进行测试. 如图3所示, 对链取向后的样品, 分别测试了振动方向平行(Case 1)和垂直(Case 2)聚合物分子链两个方向的吸收谱和发射谱. 利用SPL-30C偏光显微镜观察样品在偏振光照射下的形貌及各向异性.

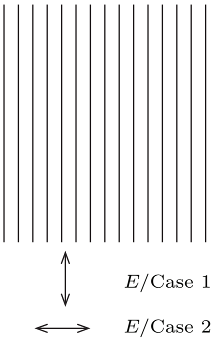

图3　样品各向异性光谱测试示意图　黑实线代表链取向的方向, E 代表光的偏振方向

Fig. 3. The diagram of the sample spectrum measurements. Black solid line represents the direction of the chain orientation, E represents the incident direction of light.

3 结果与讨论

图4为样品的原子力显微照片(atomic force microscope, AFM), 扫描面积为3 μm × 3 μm. 图4(a)为取向层聚酰亚胺的AFM照片, 它的粗糙度为RMS = 0.25 nm. 图4(b)为取向后的F8BT和red F的二元掺杂薄膜, 它的粗糙度为RMS = 1.23 nm. 由于在样品的制备过程中PI层经历了高温固化和摩擦, 活性层增益材料经历了热处理等过程, 薄膜的粗糙度略有增加, 但仍属于高平整度薄膜.

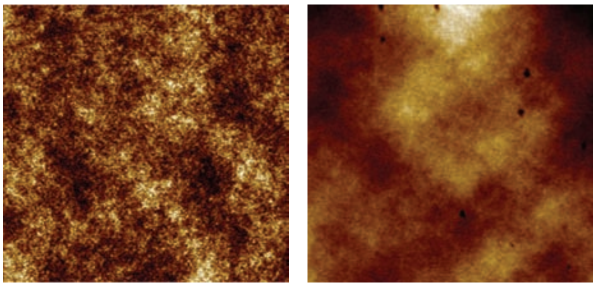
(a) (b)

图4 (网刊彩色) 原子力显微镜照片 (a) 摩擦后的聚酰亚胺取向层(RMS = 0.25 nm); (b) 取向后的二元掺杂薄膜(RMS = 1.23 nm)

Fig. 4. (color online) The atomic force microscope (AFM) images: (a) Robbed polyimide layer (RMS = 0.25 nm); (b) aligned binary blend films (RMS = 1.23 nm).

图5为共混聚合物在进行链取向处理后的偏振吸收光谱和偏振荧光光谱. 图5(a)显示, F8BT和red F共混薄膜的吸收光谱已具有明显的各向异性, 通过测量薄膜对不同偏振方向的光谱的吸收强度来观察链取向程度, 可以发现当入射光偏振方向与共混聚合物的链取向方向平行时(Case 1), 光吸收强度较入射光偏振方向与链取向方向垂直时(Case 2)的吸收强度明显增大, 且大于同样厚度未经链取向样品的光吸收强度. 在波长477 nm处, Case 1的吸收强度约为Case 2的5.9倍, 未取向薄膜的1.3倍. 就荧光发射谱而言, 与图2的F8BT荧光谱相比, 图5(b) 中已经看不到主体F8BT的发光, 说明F8BT将能量有效地传递给了客体red F, 实现了光在红光范围内输出. 由图5(b)还可以看出荧光谱也具有明显的各向异性, 在波长631 nm处, Case 1的发射强度为Case 2的5.5倍, 同样厚度未取向薄膜荧光强度的1.85 倍. 即在同一薄膜厚度下未取向的二元共混薄膜其吸收和发射强度均介于Case 1和Case 2之间.

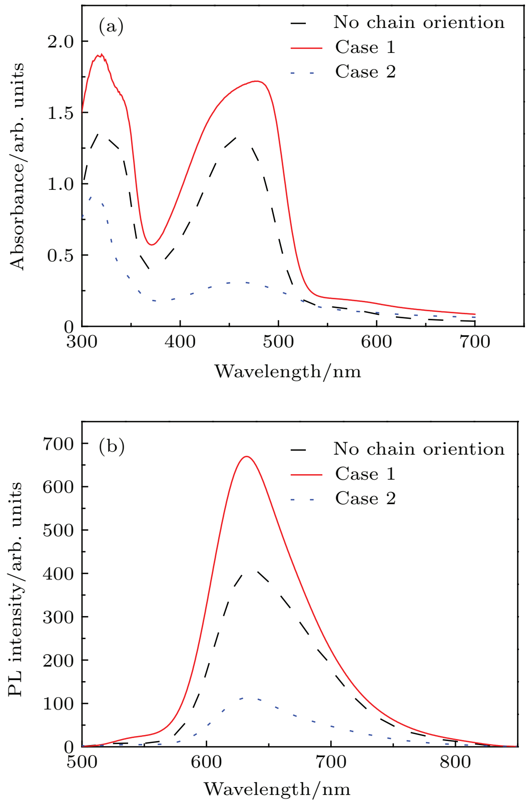

图5 (网刊彩色) (a) 二元掺杂薄膜的偏振吸收光谱; (b) 二元掺杂薄膜的偏振荧光强度. Case 1代表入射光偏振方向与链取向方向平行, Case 2代表荧光偏振方向与链取向方向垂直

Fig. 5. (color online) (a) Polarised absorption spectra for an aligned binary blend films; (b) polarised PL spectrum for the aligned binary blend film. Case 1 represents the polarized light parallel to the aligned chain direction, and Case 2 represents polarized light perpendicular to the aligned chain direction.

已有文献报道, 链取向不仅改变材料的迁移率[20], 还会使其折射率发生变化, 如F8BT, 沿着聚合物链长方向的折射率为2.1, 远大于未发生链取向材料的折射率(1.69), 而垂直于链长方向折射率为1.6, 小于未发生链取向材料的折射率[10]. 因此, 如果对薄膜上部分区域有选择的进行链取向, 就可以使薄膜上发生链取向的区域与其他区域产生折射率差异. 利用这一特点, 可以在聚合物厚度没有显著变化的前提下, 形成光波导. 为实现这一设想, 我们采用喷墨打印技术对PI层进行图形化, 具体操作是在石英衬底上设计打印出PI光波导图形, 在对PI图形预处理(见实验部分图1)后, 旋涂F8BT和red F共混溶液, 形成薄膜, 并对薄膜做链取向处理. 这样, 在有PI的区域, 聚合物会由于链取向而产生各向异性; 在没有PI的区域, 薄膜则不会发生链取向, 依然是各向同性的.

图6(a)为打印的PI图形，三个PI窄条纹的宽度为165.00 μm，间距约为210.00 μm，宽条纹的宽度为960.00 μm，这种设计可以使光信号从宽的一端耦合进入波导，再由窄的一端多道输出．在PI区域上的聚合物链取向后，对偏振方向沿着分子链方向的光的折射率大于PI图形外未发生链取向区域．如图6(b)所示，当振动方向平行分子链的偏振光(连续激光光源)照射时，光信号已被限制在链取向区域内，利用链取向后F8BT的折射率在平行分子链方向远大于未发生链取向区域折射率的特点[10]，可以大幅度减少光波导的泄露损耗，使光信号沿打印的光波导区域传播．同时，由于F8BT : red F混合薄膜，作为激光增益材料，其发射波长在600—670 nm，该光波导可用于传导数据通信常用波段650 nm的光信号，并且，在有抽运光源的作用下，可望实现对该波段信号的放大[16]．

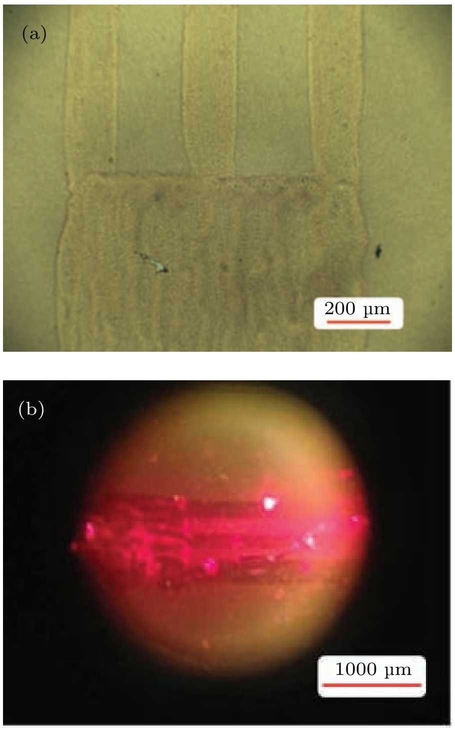

图6 (网刊彩色) (a) 打印的PI图形; (b) 光在链取向形成的光波导中传播

Fig. 6. (color online)(a) Printed PI pattern; (b) light propagation along plane optical waveguide fabricated via patterning chain alignment area.

为进一步确认样品链取向区域内外的光各向异性差异，我们在偏光显微镜下观察了薄膜表面．图7显示在偏振光照射下，F8BT : red F共混薄膜上看到的波导图案．当入射光偏振方向与薄膜分子链取向一致时，取向部分要比未取向的部分亮，如图7(a)所示．当入射光偏振方向与分子链取向方向垂直时，取向部分要比未取向部分暗，如图7(b)所示．可见，偏光显微镜观察结果也清楚地显示样品上有PI的区域，经链取向处理后，已具有光的各向异性，并与PI之外的区域有明显不同．

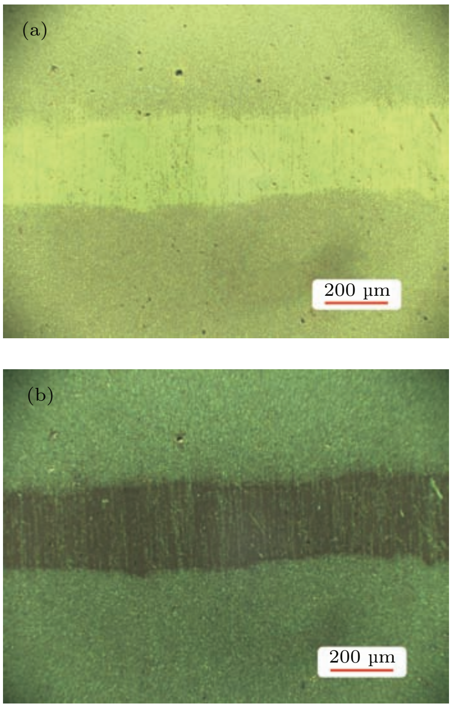

图7 (网刊彩色) 平面光波导薄膜的偏光显微镜照片 (a) 入射光偏振方向与链取向方向平行; (b) 入射光偏振方向与链取向方向垂直

Fig. 7. (color online) Polarized microscopy image of plane waveguide films: (a) The polarization of the incident light parallel to the direction of chain orientation; (b) the polarization of the incident light perpendicular to the direction of chain orientation.

4 结 论

本文展示了利用喷墨打印和链取向技术，基于聚合物激光增益介质F8BT和red F共混(F8BT : red F = 9 : 1)薄膜制备平面光波导的方法．这种方法具有制作工艺简单、成本低廉等优点．首先利用喷墨打印机打印出预先设计的各种PI取向层图案．然后，通过PI对沉积在其上的聚合物进行链取向处理．由于聚合物层中链取向区域沿分子链方向的折射率高于未发生链取向区域，从而将振动方向平行于分子链方向的光限制在取向区．由于所选择的聚合物材料在取向前后折射率差值较大，因此可以明显降低波导的光泄露损耗．同时，由于所选择的共混体系有效的主客体能量传

递, F8BT : red F 混合薄膜的发射波长在600—670 nm, 使该光波导可用于传导数据通信用650 nm波段的光信号. 我们所用聚合物为激光增益介质, 进一步优化, 可望在光抽运作用下对波导中传播的光信号实现放大.

参考文献

[1] McGehee M D, Heeger A J 2000 *Adv. Mater.* **12** 1655

[2] Bisri S Z, Takenobu T, Iwasa Y 2014 *J. Mater. Chem. C* **2** 2827

[3] Forrest S R, Thompson M E 2007 *Chem. Rev.* **107** 923

[4] Zhang Q, Zeng W J, Xia R D 2015 *Acta Phys. Sin.* **64** 094202 (in Chinese) [张琪, 曾文进, 夏瑞东 2015 物理学报 **64** 094202]

[5] Xia R D, Heliotis G, Hou Y, Bradley D D C 2003 *Org. Electron.* **4** 165

[6] Tessler N, Pinner D J, Cleave V, Ho P K H, Friend R H, Yahioglu G, Barny P L, Gray J, de Souz M, Rumbles G 2000 *Synthetic Met.* **115** 57

[7] Baldo M A, Holmes R J, Forrest S R 2002 *Phys. Rev. B* **66** 035321

[8] Giebink N C, Forrest S R 2009 *Phys. Rev. B* **79** 073302

[9] Heliotis G, Xia R D, Whitehead K S, Turnbull G A, Samuel I D W, Bradley D D C 2003 *Synthetic Met.* **139** 727

[10] Xia R D, Campoy-Quiles M, Heliotis G, Stavrinou P, Whitehead K S, Bradley D D C 2005 *Synthetic Met.* **155** 274

[11] Xia R D, Stavrinou P N, Bradley D D C, Kim Y 2012 *J. Appl. Phys.* **111** 123107

[12] Tsiminis G, Wang Y, Kanibolotsky A L, Inigo A R, Skabara P J, Samuel I D W, Turnbull G A 2013 *Adv. Mater.* **25** 2826

[13] Xia R D, Cheung C, Ruseckas A, Amarasinghe D, Samuel I D W, Bradley D D C 2007 *Adv. Mater.* **19** 4054

[14] Yang B, Li Z Y, Xiao X, Nemkova Anastasia, Yu J Z, Yu Y D 2013 *Acta Phys. Sin.* **18** 184214 (in Chinese) [杨彪, 李智勇, 肖希, Nemkova Anastasia, 余金中, 俞育德 2013 物理学报 **18** 184214]

[15] Li W, Gao Z Q, Mi B X, Wei H 2009 *Journal of Nanjing University of Posts and Telecommunications (Natural Science)* **29** 90 (in Chinese) [李巍, 高志强, 密保秀, 黄维 2009 南京邮电大学学报 (自然科学版) **29** 90]

[16] Li W C, Liu Y G, Xuan L 2011 *Acta Phys. Sin.* **60** 046101 (in Chinese) [李文萃, 刘永刚, 宣丽 2011 物理学报 **60** 046101]

[17] Xia R D, Heliotis G, Stavrinou P N, Bradley D D C 2005 *Appl. Phys. Lett.* **87** 031104

[18] Heliotis G, Xia R D, Bradley D D C, Turnbull G A, Samuel I D W, Andrew P, Barnes W L 2004 *J. Appl. Phys.* **96** 6959

[19] Amarasinghe D, Ruseckas A, Vasdekis A E, Turnbull G A, Samuel I D W 2009 *Adv. Mater.* **21** 107

[20] Redecker M, Bradley D D C, Inbasekaran M, Woo E P 1999 *Appl. Phys. Lett.* **74** 1400

Design of planar waveguide based on patterning substrate and oriented polymer film*

Fang Yue-Ting Yi Jian-Peng Chen Jin-Shan Wang Hong-Jie Chi Lang Xia Rui-Dong†

(*Key Laboratory for Organic Electronics and Information Displays, Jiangsu National Synergetic Innovation Center for Advanced Materials, Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210023, China*)

(Received 11 October 2015; revised manuscript received 28 November 2015)

Abstract

Semiconducting conjugated polymersused for light emitting devices (LEDs), lasers and amplifiers have received considerable attention due to their low cost and easy fabrication through spin-coating and photochemical processing. A

---

* Project supported by the National Natural Science Foundation of China (Grant Nos. 61376023, 61136003), the National Basic Research Program of China (Grant No. 2015CB932203), the Startup Fund for Talent Introduction of Nanjing University of Posts and Telecommunications, China (Grant Nos. NY212013, NY212034), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), China.

† Corresponding author. E-mail: iamrdxia@njupt.edu.cn

promising material for LED and laser applications is poly(9, 9-dioctylfluorene-co-benzothiadiazole) (F8BT). F8BT has a low stimulated emission threshold and exhibits a large net optical gain at 570 nm. It also shows liquid crystallinity and can be readily aligned into a monodomain by using an alignment layer, polyimide (PI). Oriented film of F8BT exhibits that its charge carrier mobility is increased by more than one order of magnitude compared with isotropic film. The refractive index of the material is also greatly affected by the orientation of the polymer chain. Furthermore, it has been reported that low threshold laser can be achieved by blending P3HT or red-F solution into F8BT via energy transfer.

Here we report a planar waveguide structure obtained via patterning chain oriented area on F8BT : red-F (9 : 1) blend polymer film. The blend solution is obtained by mixing the F8BT solution with red-F solution (with the same concentration, 20 mg/mL in toluene) with a ratio of 9 : 1. The designed waveguide patterns are obtained by inkjet-printing the PI solution onto the pre-cleaned quartz substrates. Thin films (150–200 nm thick) of F8BT : red F are deposited onto PI by spin coating (2000 rpm). The chain alignment treatment is performed by the following procedure: the films are kept in N_2 at 265 °C for 2 min, then they are cooled down to 235 °C at a rate of 1 °C / min, finally they are cooled down to room temperature sharply. The PI contacted area on the film becomes anisotropic, while the area without PI keeps isotropic. The refractive index parallel (perpendicular) to the chain direction is significantly increased (reduced) in the PI contacted area compared with outside the PI area. Therefore, the waveguide confinement could be achieved without changing the thickness of the film. Experimental investigations, including AFM images, polarized microscopy images, polarized absorption, and PL spectra of the patterned samples, clearly show the difference between the aligned area and isotropic area.

The large percentage of overlap between the emission spectrum of F8BT and the absorption spectrum of red-F solution leads to an efficient energy transfer from F8BT (host) to red-F solution (guest), resulting in a red emission at a wavelength between 600–670 nm from the blend. The polarized absorption and PL spectra of the aligned F8BT : red-F film demonstrate that the absorption intensity of the polarized light parallel to the aligned chain is 5.9 times that perpendicular to the aligned chain at a wavelength of 477 nm, and their ratio is 5.5 at a wavelength of 631 nm.

Our demonstration suggests that patterning chain oriented area can be a promising approach to achieving planar waveguide devices by utilizing the refraction index contrast within and beyond the chain oriented region, and the substrate of polyimide (PI) could be patterned with various widths and shapes by the use of inkjet printing technology.

Keywords: chain orientation, patterned the substrate material, film waveguide, light emission polymer

PACS: 61.30.Gd, 45.70.Qj, 42.79.Gn, 72.80.Le **DOI:** 10.7498/aps.65.056101