中国激光

基于联苯衍生物的有机光电功能材料及器件的研究进展

尹璠，德健博，廖清*，付红兵

首都师范大学化学系光功能材料与器件北京市重点实验室，北京 100048

摘要 兼具高效发光和电荷传输特性的有机半导体是实现有机电泵浦激光的理想候选材料，但其分子设计与合成面临着巨大挑战。高载流子传输和高效固态发光效率之间存在着天然的矛盾，这是因为高载流子传输要求分子紧密堆积并具有强的分子间相互作用，但这种相互作用会显著降低固态发光效率。本文综述了近年来报道的兼具电荷传输特性和高发光效率的联苯衍生物的研究进展，重点介绍了约20余种基于联苯衍生物的有机半导体材料，包括分子的设计策略、相关的光电性能及其在光电器件方面的应用，为兼具高电荷传输特性和高发光效率的有机半导体材料的研究提供了指导和借鉴，同时为发展与实现有机电泵浦激光奠定了材料基础。本文还对该领域未来发展的挑战、方向及机遇进行了简单评述。

关键词 材料；联苯衍生物；光电集成；电荷传输；发光效率；有机电泵浦激光

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1 引 言

20世纪70年代导电高分子材料问世[1]，开启了有机光电子学这一新的研究领域[2-4]。有机半导体材料不仅具有优异的光电性能[5]，还具有种类丰富、易于功能化修饰[6]、可溶液加工[7]和柔韧性好[8]等独特优势，在大面积、柔性光电器件的制造领域具有重要的应用前景[9-10]。随着新材料研究的深入以及器件制备工艺的发展，有机光电子学在近几十年间取得了令人瞩目的进步[11]，有机半导体材料也逐渐从实验室走向了千家万户。例如，有机发光二极管(OLED)器件的外量子效率已从1%提高到30%以上[12]，已被应用于实际显示领域。作为有机半导体电致发光器件的另一个重要应用方向，有机电泵浦激光一直是基础研究和产业界关注的焦点。近年来，有机光泵浦激光的相关研究取得了巨大进展，有机光泵浦激光在激光显示[13]、光通信[14-15]、传感[16]、高亮度激光照明等领域展现出了巨大的应用潜力[17-18]。然而，它们绝大多数是依靠短脉冲激光进行泵浦的[19]，有机电泵浦激光仍是一个尚未被攻克的科学问题。其主要原因之一是缺乏能应用于电泵浦激光的有机半导体材料，它需要材料同时具有高载流子迁移率、高固态发光量子产率、高增益以及高稳定性。然而，高载流子传输和高效固态发光效率之间存在着天然的矛盾。这是因为高载流子传输要求分子紧密堆积并具有较强的分子间相互作用，但这种相互作用会显著降低固态发光效率。因此，发展兼具高传输特性、高固态发光效率、高增益特性的有机半导体是解决有机电泵浦激光瓶颈问题的重要途径之一。

目前，已报道的兼具高电荷传输特性、发光特性和增益特性的有机光电分子体系有联苯类、噻吩/苯共寡聚物、寡链聚苯乙烯类等[4]。1989年，联苯类分子以其较高的迁移率和良好的光电稳定性被作为空穴传输层和发光层首次应用于构筑有机发光二极管(OLED)器件[20]。随后，Adachi课题组[20]报道了一系列低阈值、强发光的联苯类衍生物，显示了其作为激光增益材料的潜力。如图1所示，联苯分子由两个单键连接的苯环构成，自由旋转的单键既保证了分子的整体共轭性，又赋予了联苯类分子聚集诱导发光的特性。更重要的是，联苯分子的对位可以通过Horner-Emmons等反应进行扩展，通过取代基的修饰赋予分子更好的电荷传输性质、发光性质和其他功能。

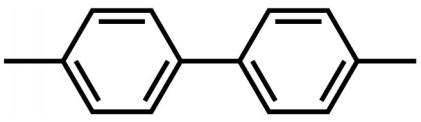

图1 联苯骨架的化学结构

Fig. 1 Chemical structure of biphenyl skeleton

本文总结了近年来以联苯为骨架或取代基的有机半导体分子材料，从分子结构、分子堆积及光电性质出发，总结了该类分子在有机光电器件中的应用，着重关

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通信作者：*liaoqing@cnu.edu.cn

注其在激光领域的应用以及实现有机电泵浦激光的潜力，以期为新型有机电泵浦激光材料的发展提供借鉴。

2 基于联苯衍生物的有机电致发光器件

有机电致发光是一个将电能直接转化为光能的过程，是指有机材料在电场或者电流作用下发光的现象。有机电致发光器件主要分为两大类：OLED和有机发光晶体管（OLET）。1963年，Pope等[21]利用蒽单晶制备了第一个OLED器件，但是该器件只有在驱动电压高达400 V时才能在10～20 μm厚度的蒽单晶中观察到电致发光现象，未能引起人们的研究兴趣。1987年，邓青云等[22]利用8-羟基喹啉铝作为有机电致发光层制得了OLED器件，其在低于10 V的驱动电压下可以达到高于1000 cd/m²的亮度，开辟了有机电致发光器件的新纪元，吸引了国际上越来越多的研究人员投身于有机电致发光材料及器件的研究[22]。在化学、物理、微电子等领域研究人员的共同努力下，多功能光电器件的研究得到了长足发展。

高性能器件的构筑需要具有高迁移率的发光材料。在众多的文献报道中，本课题组发现联苯衍生物作为经典的电荷传输层不仅具有较好的电荷传输特性，还具有优异的发光特性，是一类极具潜力的高性能光电材料，有可能为有机电泵浦激光提供材料基础。鉴于此，本课题组总结了目前基于联苯衍生物的OLED和OLET器件的相关研究进展。

2.1 联苯衍生物在OLED中的应用

OLED是一种基于有机发光材料制备而成的二极管器件，其结构类似于三明治结构，由阳极、阴极以及两者之间的有机活性层构成。有机活性层主要包括有机发光层以及可以提高发光性能的空穴传输层和电子传输层。早期的联苯衍生物主要作为OLED器件的空穴传输层材料。1989年，Adachi等[20]将联苯衍生物*N*,*N*′-二苯基-双(3-甲基苯基)-1,1′-联苯-4,4′-二胺(*N*,*N*′-diphenyl-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine，TAD)薄膜作为空穴传输层和发光层制备了OLED器件，但该器件的亮度仅达到了100 cd/m²，电流密度为100 mA/cm²。此外，*N*,*N*′-二苯基-*N*,*N*′-双(3-甲基苯基)-1,1′-联苯-4,4′-二胺(*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine，TPD)、α-萘基苯基联苯二胺(4,4′-Bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl，NPB)、4,4′-二(N-咔唑基)二联苯(4,4′-bis(carbazol-9-yl)biphenyl，CBP)等基于联苯骨架单键连接的有机分子，也是OLED器件中常用的空穴传输层材料[23-26]，它们都具有较高的电荷传输能力[27]，迁移率均在10^{-3}～10^{-4} cm²/(V·s)之间。图2给出了上述基于单键连接的联苯衍生物的分子结构式。比较特殊的是，Ichikawa等[28]早在2005年就报道了基于联苯噻吩共聚物α,ω-双(联苯基)三噻吩(α,ω-bis-biphenyl-terthiophene，BP3T)单晶的自波导放大自发辐射(ASE)，ASE阈值为8 μJ/cm²。Ichikawa等将金电极作为阳极，将金属Li、Al、Au分别作为阴极，将单晶置于阴极和阳极中间组成三明治器件结构，实现了双极性注入的单晶电致发光，并且该单晶表现出了对高电流密度良好的耐受性[28]。

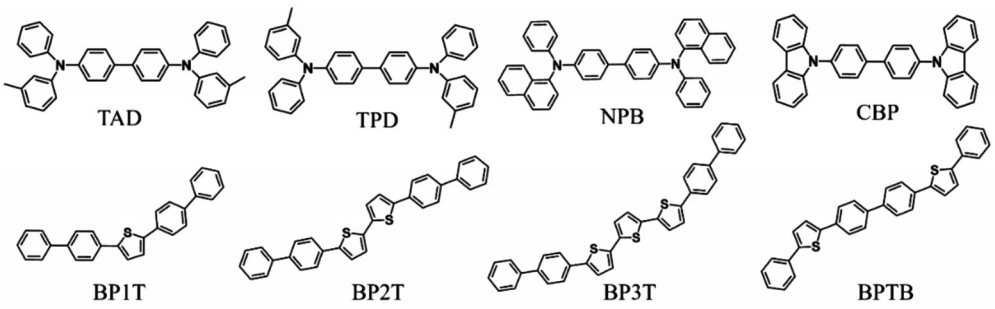

图2 通过碳碳单键连接的联苯衍生物的分子结构式

Fig. 2 Molecular structure of biphenyl derivatives linked by carbon-carbon single bonds

除了碳碳单键以外，碳碳双键连接的联苯衍生物(简称为“DSA衍生物”)也逐渐被应用于高迁移率发光器件的研究中。引入碳碳双键既保证了骨架的平面性，又延长了共轭链的长度，如图3所示。较长的共轭链为分子构象的调整提供了更大空间，并减少了紧密分子堆积带来的荧光猝灭。因此，这类材料能兼具高电荷传输特性和高发光特性。1995年，Hosokawa等[29]首次将DSA衍生物4,4′-双[(*E*)-4-(二苯胺基)苯乙烯基]-1,1′-联苯(4,4′-Bis[(*E*)-4-(diphenylamino)styryl]-1,1′-biphenyl，BDAVBi)和4,4′-双[2-{3-(乙基咔唑)}乙烯基]联苯(2,2′-([1,1′-Biphenyl]-4,4′-diyldi-2, 1-ethenediyl) bis [9-ethyl-9H-carbazole](ACI)，BCzVBi)作为OLED器件中的空穴传输发射层，实现了高效率和高亮度的蓝绿色发光器件，其外量子效率(EQE)达到了1.5%，最高亮度为4000 cd/m²；同年，Hosokawa等[24,29]又将4,4′-双(2,2-二苯基乙烯基)联苯(*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine，DPVBi)作为发光层，将BCzVBi作为掺杂，研制出了当时效率最高的蓝光OLED，其EQE实现了2.4%的突破。2004年，Liu等[30]利用混合主体分

子NPB与9,10-双(2'-萘基)蒽(9,10-bis(2′-naphthyl) anthracene,BNA)混合,再与客体BDAVBi进行掺杂,实现了高亮度长寿命的蓝光OLED器件;在初始亮度为10000 cd/m²的测试条件下,该器件的半衰期可达110 h。这一实验结果表明,将客体材料与主体材料掺杂的器件结构有助于消除异质结界面带来的荧光猝灭,延长器件寿命。2006年,Shih等[31]将蓝色荧光材料BDAVBi和橙色磷光材料掺杂到主体聚合物中,实现了高效的白光OLED,其EQE为6.12%,最大亮度可达到11306 cd/m²。Adachi课题组[32-34]设计了一种高效的非掺杂型OLED器件,如图4(a)所示。该器件以4,4′-双[(*N*-咔唑)乙烯基]二联苯(4,4′-bis

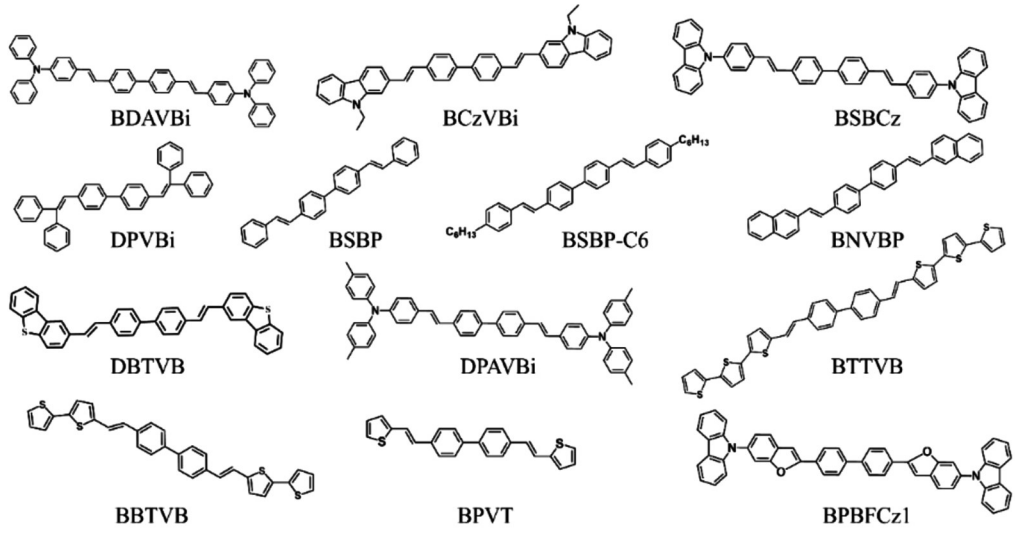

图3　通过碳碳双键连接的联苯衍生物的分子结构式

Fig. 3　Molecular structure of biphenyl derivatives linked by carbon-carbon double bonds

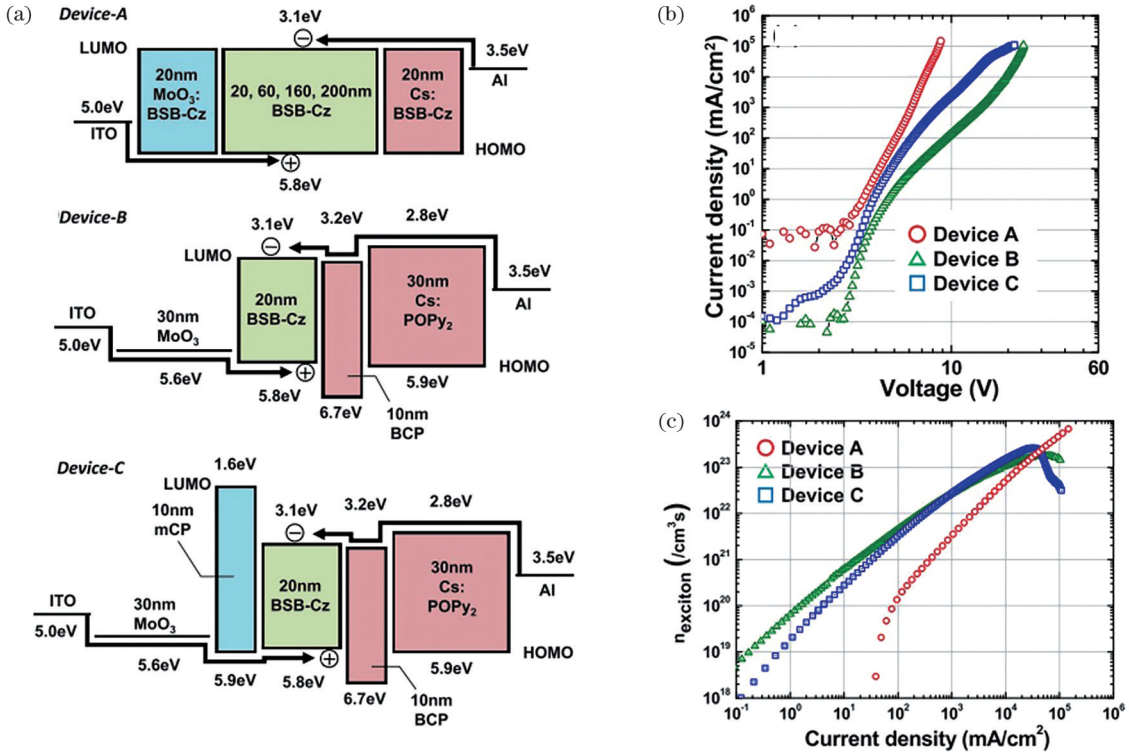

图4　基于BSBCz的新型非异质结构OLED器件[32-34]。(a)自上而下分别是带有单发射层BSBCz的OLED的能级图、带有空穴阻挡层的OLED的能级图以及带有电子阻挡层和空穴阻挡层的OLED的能级图;(b)器件A、B、C的电流密度-电压特性曲线;(c)器件A、B、C的激子密度-电流密度特性曲线

Fig. 4　Novel nonheterostructure OLED based on BSBCz[32-34]. (a) Energy level diagrams for OLEDs with a single emitter layer of BSBCz, OLEDs with a hole-blocking BCP layer, and OLEDs with electron-blocking mCP and hole-blocking BCP layers from top to bottom; (b) current density-voltage characteristic curves of devices A, B, and C; (c) exciton density ($\eta_{exciton}$)-current density characteristic curves of devices A, B, and C

[(*N*-carbazole)styryl]biphenyl,BSBCz)作为发射层[其最高占据分子轨道(HOMO)和最低未占分子轨道(LUMO)能级分别为3.1 eV和5.8 eV],发射层的两端分别利用MoO_3掺杂和金属铯掺杂的BSBCz薄膜作为空穴传输层和电子传输缓冲层。缓冲层的加入有效降低了载流子的注入势垒,从而抑制了高电流密度下的电致发光效率滚降,如图4(b)~(c)所示。该器件实现了高电流密度(超过100 A/cm^2)下平衡的双极型注入和传输,抑制了器件效率的滚降。早在2005年,Adachi课题组[35]就报道了基于BSBCz的薄膜的优异特性,6%-BSBCz:CBP薄膜有近乎100%的荧光量子产率和超低阈值的放大自发辐射。2019年,Adachi课题组[36]报道了基于BSBCz材料的电注入激光发射,他们将布拉格光栅与OLED器件结合,在电注入下观察到了明显的光谱窄化和清晰的阈值。

2.2 联苯衍生物在OLET中的应用

OLET是一种兼具有机场效应晶体管开关功能和有机发光二极管发光功能的集成器件,其结构与有机场效应晶体管类似。这样简单的结构大大简化了器件的加工工艺流程,有助于降低生产成本,减小器件的体积和功耗。相比于OLED器件的垂直结构,OLET是一种水平器件,主要由栅极、绝缘层、半导体活性层、源极、漏极组成。在这种结构中,发生各种物理、化学过程的有机半导体活性层暴露在外,这为研究各种器件的物理现象,如载流子注入、载流子传输、激子形成和激子复合过程,提供了一个优异平台。此外,在理论上,OLET器件可以达到极高的电流密度。因此,它是一种实现有机电泵浦激光器的理想器件。

在开发高性能OLET器件过程中,发展新型高性能有机半导体材料始终是材料学家关注的重点。OLET的半导体活性层需要同时兼顾强发光和高载流子迁移率。然而这两者是一对矛盾体:强发光的分子一般具有较弱的分子间相互作用,而较弱的分子间π—π相互作用会减弱其电荷传输性能;高载流子迁移率的材料一般具有非常紧密的分子排列堆积和极大的能级劈裂,这会导致严重的荧光猝灭。因此,如何调和发光与载流子传输之间的矛盾,是摆在研究者面前的重要科学问题,也是实现高性能OLET的最大障碍。目前,兼具强发光和高载流子传输特性的分子主要有并苯类[37-38]、噻吩乙烯共寡聚物等体系,而联苯类衍生物由于常作为经典的空穴传输层而被忽略。实际上,通过调研相关研究报道发现,联苯衍生物作为高性能有机光电材料在构筑高性能OLET方面具有巨大潜力。在这一小节中,本文主要聚焦基于联苯衍生物的有机发光场效应晶体管器件的相关研究进展,这些联苯衍生物主要包括单键连接的几个明星分子——2,5-双(4-联苯基)噻吩(2,5-bis(4-biphenylyl)-thiophene,BP1T)、2,5-双(4-联苯基)二噻吩(2,5-bis(4-biphenylyl)bithiophene,BP2T)、α,ω-双(联苯基)三噻吩(α,ω-Bis(biphenyl-4-yl)terthiophene,BP3T),以及双键连接的DSA衍生物。

2003年,Hepp等[39]报道了第一个单极性传输的有机发光场效应晶体管。Hepp等以并四苯薄膜作为有源层构建了传统的底部接触结构的OFET器件,并在Au电极附近观察到了电致发光。电致发光的强度可以通过改变栅极电压、源极电压、漏极电压进行调控,这为后续的OLET研究提供了重要参考。2009年,Bisri等[40]以BP3T单晶作为有源层构筑了有机发光晶体管,观察到了栅压调制下发光线的移动现象。同时他们发现,随着电流变化,电致发光光谱的半峰全宽明显减小。这为电驱动有机激光的研究奠定了基础。随后,也有不少关于BP3T-OLET器件的研究,研究人员从不同角度对器件进行优化,使器件性能大幅提高。Sawabe等[41]研究了旋涂聚甲基丙烯酸甲酯(PMMA)时使用的溶剂对器件电子传输性质的影响,结果发现将甲苯作为溶剂并对PMMA进行退火处理可以将器件的电流密度提高两个数量级;之后他们引入了电子注入缓冲层CsF,实现了更好的能级匹配;接着通过激光刻蚀技术引入电流限制结构来改善器件的性能,极大地提高了器件的电流密度(电流密度高达33 kA/cm^2)[42]。2015年,Maruyama等[43]通过纳米压印光刻法在BP3T晶体上刻蚀分布式反馈光栅结构,大幅提高了器件的品质因子。2019年,Kanagasekaran等[44]将分布式反馈光栅结构与OLET器件的介电层聚苯乙烯相结合,观测到了有机电泵浦激光的迹象。此外,还有BP1T、BP2T以及其相关拓展材料体系的报道,如4,4′-双(5-苯基噻吩-2-基)-1,1′-联苯(4,4′-bis(5-phenylthiophen-2-yl)-1,1′-biphenyl,BPTB)等,但该材料体系的相关器件的性能都不及BP3T器件[45-48]。

2007年,Sakanoue等[49]报道了首个基于DSA衍生物4,-4′-双(苯乙烯基)联苯(4,4′-bis(styryl)biphenyl,BSBP)的薄膜双极性OLET器件。Sakanoue等通过真空蒸镀制备了平整的BSBP薄膜以及对称的Al源、漏电极。器件的迁移率为0.01 cm^2/(V·s),荧光量子产率为20%。器件在沟道内出现了明显的电致发光,转移曲线也表明了电子和空穴的共存和复合,但由于Al电极与BSBP的HOMO(5.6 eV)、LUMO(2.7 eV)能级具有较大势垒,器件的性能还有较大提升空间。2008年,Sakanoue等[50]在之前工作的基础上发展了一种新型的非对称电极制备方法,利用光刻胶作为掩模进行角度沉积,实现了沟道长度为1 μm的OLET器件。他们将4,4′-双[(*E*)-2-(4-己基苯基)乙烯基]联苯(4,4′-bis[(*E*)-2-(4-hexylphenyl)vinyl]biphenyl,BSBP-C6)作为有源层,将Au/Al作为非对称源、漏电极。这种器件的电流比传统器件增大了50倍,空穴迁移率达到了0.035 cm^2/(V·s)。然而,由于缺乏晶体结构信息,关于DSA衍生物的结构与性能之间关系的研究远远落后于其在光电器件中的应用研究。Tao课题

组[51-52]首次报道了基于4,4′-双(2-噻吩基-乙烯基)联苯(4,4′-bis(2-thienylvinyl)bipheny,BPVT)、4,4′-双(2-噻吩[3,2-b]噻吩乙烯基)联苯(4,4′-bis(2-thieno[3,2-b]thienylvinyl)biphenyl,BPVDT)分子的单晶结构,分析后发现它们都呈典型的鱼骨状堆积,但BPVDT的C—H—π相互作用比BPVT更强。这对DSA材料光电性能的研究有很大启发。2012年,Tao课题组[53]设计合成了4,4′-双((*E*)-2-(萘基-2-基)乙烯基)-1,1′-联苯(4,4′-bis((*E*)-2-(naphthalen2-yl)vinyl)-1,1′-biphenyl,BNVBP),然后利用物理气相沉积法可控制备了两种生长取向的微纳晶体,探究了其电荷传输的各向异性。研究结果显示,该晶体的电子迁移率高达2.49 $cm^2/(V\cdot s)$。Yin等[54]发现BPVT等单晶都具有非常好的低阈值激光行为,并在此基础上进行了拓展性研究,具体内容将在3.1节展开描述。近期,Yin等[55]进一步拓展设计合成了4,4′-双(2-二苯并噻吩基-乙烯基)联苯分子(4,4′-bis(2-dibenzothiophenylvinyl)-biphenyl,DBTVB),并将其应用于低阈值微纳激光和高性能OLET中。二苯并噻吩基团的引入延长了共轭链,在保证分子平面性的同时为分子构象的旋转提供了空间。DBTVB单晶的荧光量子产率高达85%,并表现出了优异的低阈值激光特性。Yin等利用Au/MoO_3-Ca/CsF作为不对称电极,制备了有机发光场效应晶体管器件,该器件具有较高的电致发光特性和优异的双极性电荷传输能力,空穴和电子迁移率分别可达3.55、2.37 $cm^2/(V\cdot s)$,如图5所示。在栅压的调控下可以清晰地观察到P型和N型发光线在沟道中移动,直至移动到电极边缘。该器件的电致发光EQE高达4.03%,是目前报道的性能最好的单晶OLET器件[55]。这项工作为强发光高电荷传输特性的有机半导体的设计合成提供了新思路,为实现有机电泵浦激光奠定了材料基础。

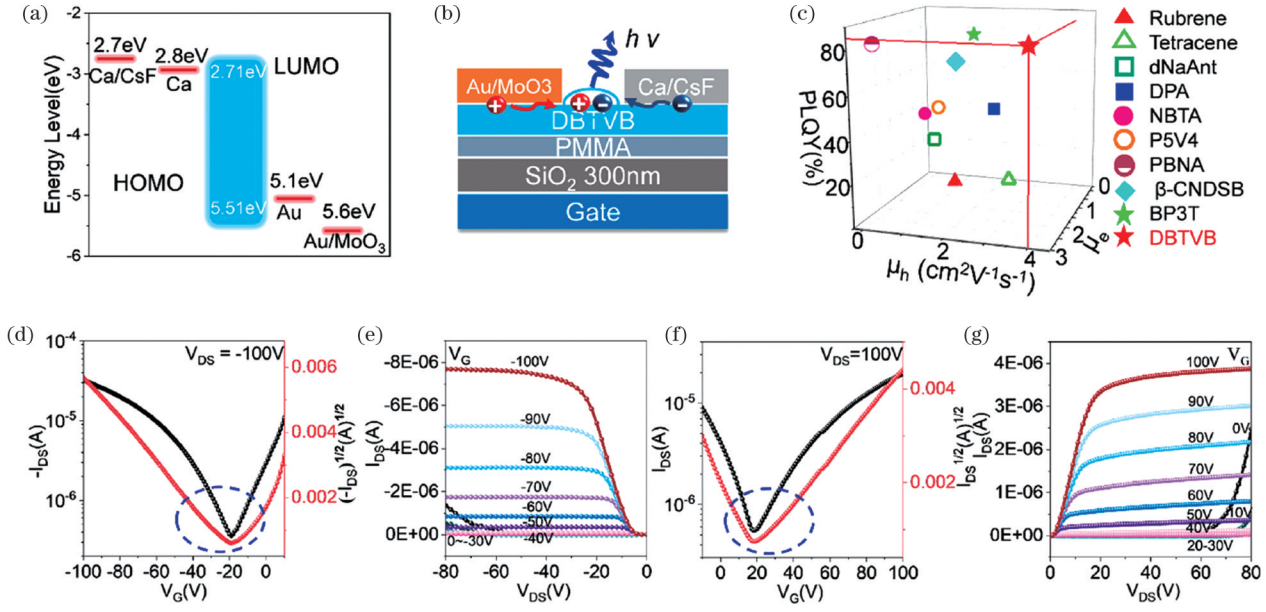

图5 基于DBTVB的OLET器件的性能[55]。(a)OLET器件的能级图;(b)OLET器件示意图;(c)至今为止报道的单组分高性能OLET器件的总结;(d)~(e)P型操作模式下的转移和输出曲线;(f)~(g)N型操作模式下的转移和输出曲线

Fig. 5 Characteristics of OLET devices based on DBTVB[55]. (a) Energy-level alignment of OLET device; (b) schematic diagram of OLET device; (c) summary map of single-component high-performance OLET devices reported so far; (d)–(e) transfer and output curves under P-type operation mode; (f)–(g) transfer and output curves under N-type operation mode

3 基于联苯衍生物的有机固态激光器

目前已报道的联苯类分子多为杆状分子。杆状分子结构使得分子在自组装过程中倾向于形成鱼骨状排列,这样的排列方式可以有效减小由分子间π—π相互作用而引起的荧光猝灭,并且可以保证载流子的高效传输[56-57]。联苯类衍生物通常具有较大的斯托克斯位移、跃迁偶极矩及激发态振子强度,这些特性保证了其具有良好的发光性质。因此,联苯类衍生物是良好的激光增益材料。本节主要讨论基于联苯类衍生物的固态激光器的性质,总结已有的分子体系及激光增益行为。

3.1 有机微纳米晶体激光器

随着有机材料自组装方法的成熟,有机微纳米晶体材料在光子学领域取得了长足发展。通过气相或液相自组装而成的微纳晶体具有平整且光滑的表面以及较大的折射率,能对光产生很好的限域作用[58-59]。然而,大多数联苯类衍生物的溶解性较差[60],只能通过物理气相传输法或熔融法制备晶体[28],从而在一定程度上限制了对其单晶结构及自组装晶体激光性质的研究。近期,Yin等[54]设计合成了三种联苯类噻吩寡聚物[4,4′-双(2-噻吩基-乙烯基)联苯,BPVT;4,4′-双(2-二噻吩基-乙烯基)联苯,BBTVB;4,4′-双(2-三

噻吩基-乙烯基)联苯,BTTVB],并通过物理气相法制备了三种分子的大尺寸单晶和形貌规整的六边形微纳晶体,如图 6(a)~(c)所示。通过对共轭链的长度进行控制,Yin 等实现了蓝、绿、黄三色激光发射,并通过瞬态吸收光谱证明了三线态吸收与增益的重叠可以提高激光阈值。Dong 等[61]报道了基于 BP2T 分子微晶的双波段可调控激光发射,如图 6(d)、(e)所示。他们通过控制温度实现了对 0→1 和 0→2 能级激光发射的调控。随后,他们又通过物理气相传输法将 BP1T 和 BP3T 共沉积[如图 6(f)所示][59],向 BP1T 微晶中可控比例地掺杂 BP3T 分子,通过 BP3T 的吸收对微晶中 BP1T 的光谱进行调控,实现了在所有振动能级(0→1、0→2、0→3 和 0→4)上的激光输出。

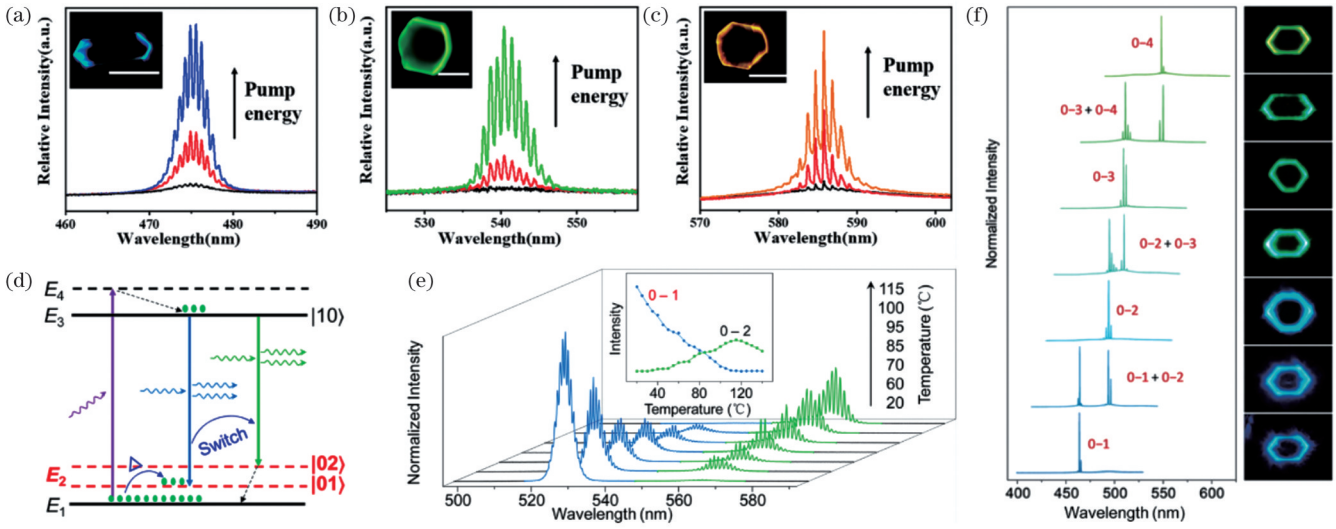

图 6　基于联苯衍生物的有机微纳米晶体激光器。(a)BPVT 在 475 nm 下的高分辨发光光谱和激光发射图片;(b)BBTVB 在 541 nm 下的高分辨发光光谱和激光发射图片;(c)BTTVB 在 588 nm 下的高分辨发光光谱和激光发射图片;(d)~(e)双波长可切换的振动激光的示意图和激光光谱;(f)BP1T 微晶与 BP3T 掺杂的归一化激光光谱和发射图片

Fig. 6　Organic micro/nao-crystal lasers based on biphenyl derivatives. (a) High-resolution PL spectrum and image of laser emissions at 475 nm of BPVT; (b) high-resolution PL spectrum and image of laser emissions at 541 nm of BBTVB; (c) high-resolution PL spectrum and image of laser emissions at 588 nm of BTTVB; (d)-(e) schematic illustration and lasing spectra of dual-wavelength switchable vibronic laser; (f) normalized lasing spectra and PL images of BP3T doped BP1T microcrystals

3.2　(准)连续光(CW)泵浦激光器

目前所报道的有机半导体固态激光器多使用脉冲宽度在 100 fs~10 ns 之间的脉冲光作为泵浦源,它们的重复频率通常在 10 Hz~10 kHz 之间。由于激发光的脉冲宽度远小于脉冲间隔,激子可以在脉冲间隔内通过辐射/非辐射跃迁、系间窜越等过程回到基态,因此使用脉冲光进行泵浦可以有效减少热积累、浓度猝灭、三线态猝灭等过程造成的有机材料热降解及激子非辐射损耗[62-63]。

在使用连续光/准连续光(泵浦光重复频率大于 1 MHz 或脉冲宽度大于 10 μs)泵浦的情况下,有机增益介质的热降解问题是实现激光增益的主要障碍之一。研究人员提出了多种改善有机介质热降解问题的方法,如开发新型高热稳定性增益材料[64]、使用高导热率(如蓝宝石)基底以及使用新型封装技术[65],这些方法可以有效提高有机增益材料的稳定性。除此以外,三重态激子在光泵浦过程中通过系间窜越产生,并且其寿命较长(通常大于 1 μs),在连续光泵浦时不断积累,这会造成激光增益波长范围内较强的三重态吸收(TA,即 $T_1 \rightarrow T_n$ 过程),而且高浓度的三重态激子也会导致单重态-三重态激子猝灭(STA)[66]。TA 会显著提高激光阈值。已有研究表明,引入三(4-咔唑-9-苯基)胺(tris(4-carbazoyl-9-ylphenyl)amine,TCTA)和氧气三重态猝灭剂可以有效减少三重态激子的积累,进而降低激光阈值并提升长时间泵浦下激光增益的稳定性[66-67]。除此以外,通过合理的分子设计减小 TA 与激光增益区的重叠,也是减小三重态激子影响的有效途径。Sandanayaka 等[65]设计合成了 BSBCz 分子,该分子的系间窜越效率很低,在有氧气的情况下三线态激子会被完全猝灭,并且在激光增益波长范围内的 TA 几乎可以忽略不计。因此,BSBCz 分子是实现连续光泵浦的重要候选者。Sandanayaka 等将一、二阶混合光栅作为谐振腔(这种特殊的光栅结构可以有效降低激光阈值并同时实现面发射激光,如图 7 所示),在光栅表面蒸镀了以 CBP 作为主体、BSBCz 作为客体、掺杂比为 6% 的混合膜,该薄膜的荧光量子产率高达(96±2)%。他们分别使用脉宽为 0.8 ns、重复频率高达 80 MHz 的泵浦光以及脉宽长达 30 ms 的长脉冲光进行泵浦。高频脉冲泵浦下的激光阈值为 0.25 μJ/cm^2,长脉冲泵浦下的激光阈值约为 100 W/cm^2。然而,在

准连续光泵浦条件下，如何保持增益材料的低阈值依旧是尚未解决的难题。在上述工作的基础上，Oyama等[68]对BSBCz分子内不稳定的双键进行桥联，合成了4，4′-双（2-苯并呋喃-3-咔唑）联苯（4，4′-bis（2-benzofuran-3-carbazole）biphenyl，BPBFCz1）分子。通过引入氧原子桥联双键可以有效抑制顺反异构的发生，大幅提高分子的光稳定性并进一步减小TA与增益区的重叠。近期也有新的研究表明，实现三重态激子的高效利用对于实现连续光泵浦激光器具有重大意义[69]。

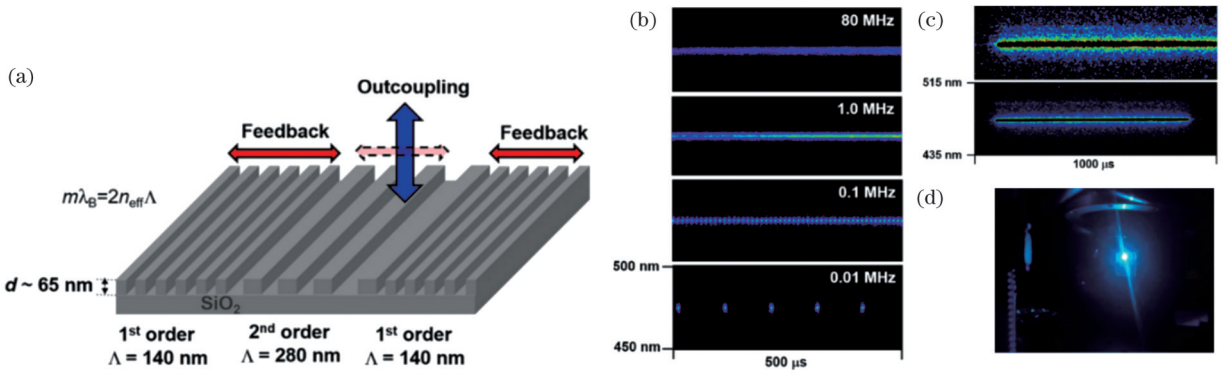

图7　连续光泵浦激光器[65]。(a)混合阶DFB光栅结构示意图；(b)条纹相机图像显示了来自代表性BSBCz:CBP封装的混合阶DFB器件的激光振荡，重复频率为0.01～80 MHz；(c)条纹相机图像显示了利用BSBCz:CBP（BSBC和CBP的质量分数分别为20%和80%）薄膜作为增益介质，并分别通过30 ms、2.0 kW/cm²脉冲（上图）和800 ms、200 W/cm²脉冲（下图）泵浦的激光发射；(d)在长脉冲状态下工作的DFB器件的照片（激发，30 ms）

Fig. 7　CW pumped lasers[65]. (a) Schematic representation of mixed-order DFB grating structure; (b) streak camera images showing laser oscillations from a representative BSBCz:CBP encapsulated mixed-order DFB device at repetition frequency from 0.01 to 80 MHz; (c) streak camera images showing laser emission integrated over 100 pulses from an encapsulated mixed-order DFB device using a BSBCz:CBP (20% : 80%) film as gain medium and optically pumped by pulses of 30 ms and 2.0 kW/cm² (top) or 800 ms and 200 W/cm² (bottom); (d) photograph of DFB device operating in long-pulse regime (excitation, 30 ms)

3.3　有机激子极化激元激光器

激子极化激元（EPs）是由微腔内的光子与活性层中的激子发生强耦合后形成的一种半光半物质的玻色子准粒子。光子和激子组分使得激子极化激元具有极轻的有效质量（约为电子质量的$1/10^4$～$1/10^5$）和强非线性，因而激子极化激元成为实现玻色-爱因斯凝聚（BEC）的重要候选者[70]。由于继承了微腔内光子的耗散特性，激子极化激元具有很短的本征寿命，从而导致激子极化激元向基态的凝聚是一个动态过程。当泵浦能量大于阈值（激子极化激元的耗散）时，激子极化激元会在宏观上凝聚到极化激元的基态并发出相干光，即产生极化激元激光。因此，不同于传统的光子激光，极化激元激光不需要发生粒子数反转，其激光阈值也比传统的光子激光低1～2个数量级[71-72]。故而，有机激子极化激元激光器被认为是实现电泵浦激光的有潜力的候选者。

与传统的无机半导体不同，有机半导体材料具有独特的高度局域的Frenkel激子，其具有高的激子结合能和振子强度，因此有机半导体材料可在室温下实现拉比劈裂能大于150 meV的激子-光子强耦合，并且能够实现极化激元凝聚[73-74]。Ren等[75]报道了基于4，4′-双[4-(二对甲苯基氨基)苯乙烯基]联苯(4，4′-bis[4-(di-p-tolylamino)styryl]biphenyl，DPAVBi)分子单晶微米带微腔的激子极化激元激光器。他们使用了一种不常见的厚腔结构，将晶体夹在上下两层银膜中间，实现了一个正失谐能微腔，产生了类激子性质的较重的激子极化激元，如图8(a)～(c)所示。这种重激子极化激元可以在室温下形成稳定的宏观凝聚，并产生具有良好空间相干性的激光。近期，Adachi课题组[76]报道了基于BSBCz衍生物BSBCz-EH（2-乙基己基基团）的极化激元激光器，验证了更大的极化激元散射速率有助于实现低阈值有机激子极化激元激光，如图8(d)所示。

要实现有机电泵浦极化激元激光还需要研究人员将重点集中在以下两个方面：一，开发低凝聚阈值的新型有机半导体材料，这些材料应具备大跃迁偶极矩、高激子结合能和窄吸收线宽等特征，这些特征有利于实现室温下的强激子-光子偶合[77]；二，制备高品质因子微腔，以有效延长极化激元的寿命，降低凝聚阈值[78]。

实现有机电泵浦激光是无数有机半导体器件领域研究人员的目标[79]。目前已报道的最有可能实现有机电泵浦激光的是BSBCz分子和BP3T分子，这两个分子的共同特征是具有很大的净增益值且具有良好的导电性[56]。Sandanayaka等[36]于2019年报道了首例基于BSBCz分子的电注入有机激光二极管，如图9(a)～(c)所示。研究人员使用一、二阶混合光栅作为谐振腔，在脉冲电流泵浦下观察到了光谱强度的非线性增长以及光谱窄化，阈值为650 A/cm²。在另一项研究中，Kanagasekaran等[44]制备了基于BP3T的单晶发光场效应晶体管，如图9(d)～(f)所示，通过在修饰层聚苯乙烯(PS)上刻蚀一阶光栅结构来增强晶体的

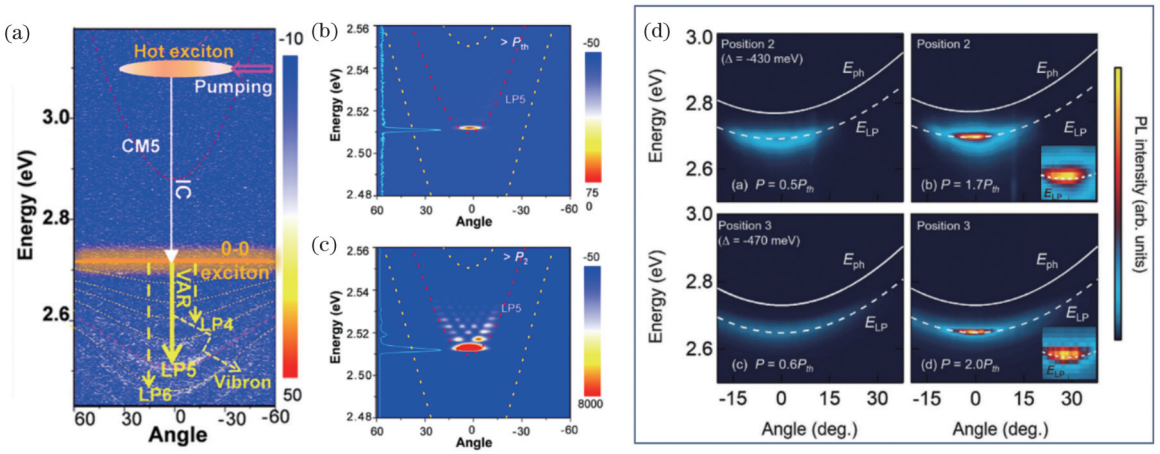

图 8　基于 DSA 衍生物的激子极化激元激光[75-76]。(a)DPAVBi 微腔在激光能量小于阈值时的极化激元发射[75];(b)DPAVBi 微腔在激光能量大于阈值时的极化激元发射[75];(c)极化激元开始在大角度占据高能量离散能级[75];(d)BSBCz-EH 微腔在激光能量小于阈值和大于阈值时的极化激元发射[76]

Fig. 8　Polariton lasers based on DSA derivatives[75-76]. (a) Polariton emission of DPAVBi microcavity when laser energy is less than threshold[75]; (b) polariton emission of DPAVBi microcavity when laser energy is more than thrshold[75]; (c) polaritons start to occupy high-energy discrete levels at large angles[75]; (d) polariton emission BSBCz-EH microcavities when laser energy is less than threshold and more than threshold[76]

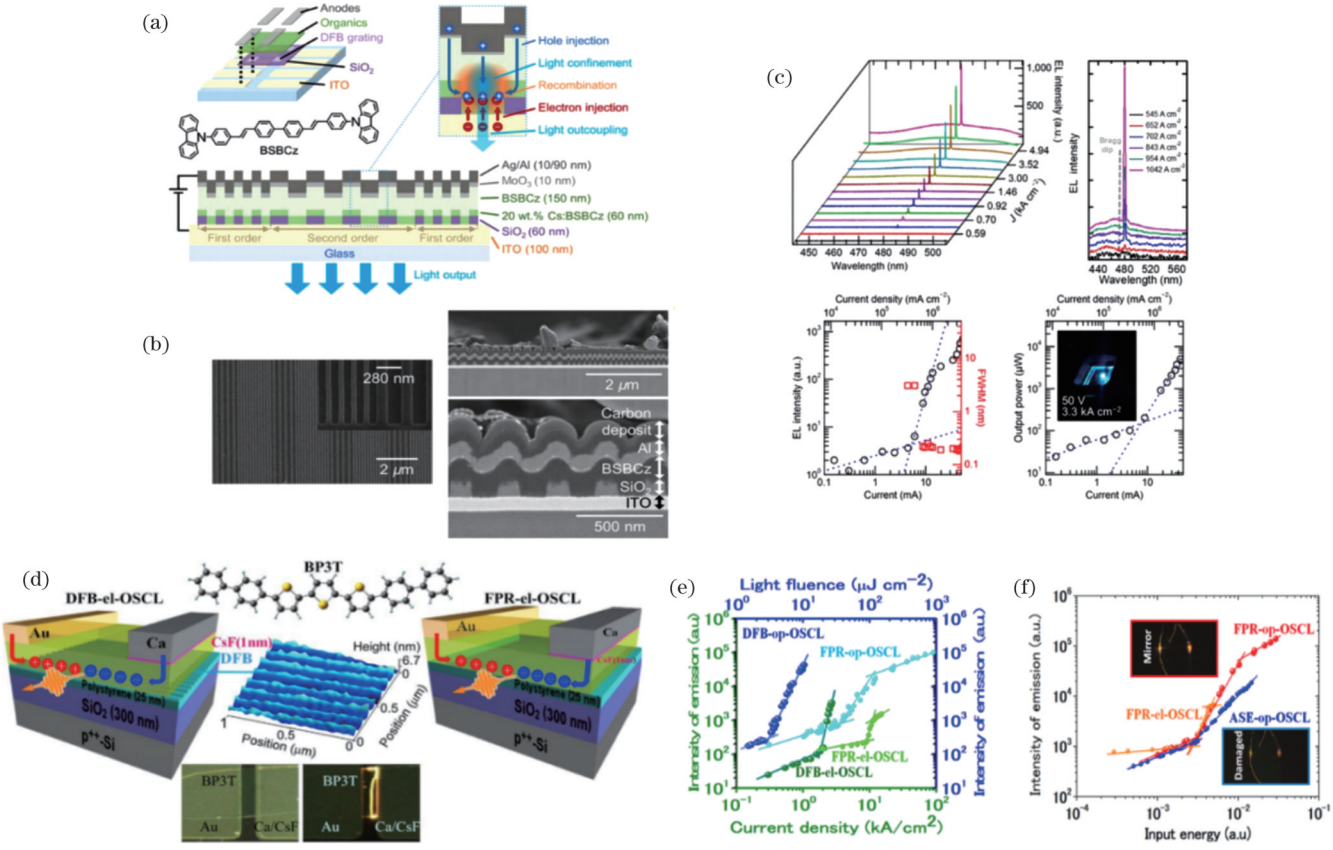

图 9　电注入激光的迹象[36,44]。(a)有机半导体激光二极管(OSLD)示意图[36];(b)DFB 光栅的 SEM 图像和 OSLD 横截面的 SEM 图像[36];(c)BSBCz 激光器件的发射光谱和阈值[36];(d)基于 BP3T 微晶的电驱动模式操作和激光发射的 DFB 及 FRP-el-OSCL 器件[44];(e)发射强度与电流密度或光通量的函数[44];(f)光驱动下 ASE 与激光的发射强度-光通量关系对比[44]

Fig. 9　Indication of current-injection lasing[36,44]. (a) Schematic representation of organic semiconductor laser diodes (OSLD)[36]; (b) SEM images of DFB grating and cross-section SEM image of OSLD[36]; (c) emission spectra and threshold of BSBCz OSLDs[36]; (d) DFB- and FRP-el-OSCL devices in electrically driven mode operation and laser emission based on BP3T microcrystals[44]; (e) intensity of emission as a function of current density or light fluence[44]; (f) comparison of relationship of intensity of emission versus light fluence between ASE and laser in optically driven mode[44]

Fabry-Pérot 谐振作用。在高于 1 kA/cm^2 的电流泵浦下观察到了光谱强度的非线性增大以及光谱窄化。然而，由于相关研究中还缺少一些证明激光出现的关键证据，如激光阈值前后电致发光寿命衰减的变化以及空间相干性等数据[80]，且相关报道数量很少，因此实现有机电泵浦激光依旧是亟待攻破的难题。

4 结束语

对电泵浦激光的追求是一个长期目标，需要化学、材料科学、器件物理和工程等领域科学家的共同努力。从材料学角度看，开发同时具备高迁移率和高发光性能的材料对于实现有机电泵浦激光具有重要意义。本文着重总结了已报道的联苯衍生物材料在有机发光二极管、有机发光晶体管、有机微纳激光器、有机极化激元激光器等器件上的应用，这一类材料以其优异的光电特性成为实现电泵浦激光的重要候选材料。尽管目前对联苯衍生物的探究已经取得了一些重要进展，但仍面临许多挑战亟待解决：1）高迁移率强发光材料依然很少，而且高迁移率、强发光性能与分子结构之间的关系尚不清楚，仍需要进一步探索；2）三线态激子的积累是器件失效的主要原因，如何高效地将三线态激子用于受激发射过程，提升器件的稳定性和效率，仍需要进一步探索；3）器件的品质因子仍需要提高，以增强器件发光的限域、放大能力。

相信在这一领域取得越来越多的突破之后，有机材料电泵浦激光的黎明时刻就会到来。电泵浦激光有助于缩小当前微电子电路与纳米光子电路之间的差距，实现激光显示、精准医疗、可穿戴设备以及信息和通信技术的革命。

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Recent Developments of Organic Optoelectronic Functional Materials and Devices Based on Biphenyl Derivatives

Yin Fan, De Jianbo, Liao Qing*, Fu Hongbing

Beijing Key Laboratory for Optical Materials and Photonic Devices, Department of Chemistry, Capital Normal University, Beijing 100048, *China*

Abstract

Significance Organic semiconductors, which combine high-efficiency light-emission and charge-transport properties, are ideal candidates for realizing organic electrically pumped lasers. However, there are still many challenges in the design and synthesis of materials with such properties. This is because of the intrinsic contradiction between high carrier transport and efficient solid-state emission efficiency in organic solids. High carrier transport requires intense molecular packing and strong intermolecular interactions; however, such interactions can significantly reduce solid-state luminescence efficiency.

This review summarizes the recent research advances of biphenyl derivatives with charge transport properties and high luminescence efficiency. Approximately 20 biphenyl derivatives are introduced, including molecular design strategies and related optoelectronic properties and their application in optoelectronic devices. This review on organic conductive materials based on biphenyl derivatives with high luminous efficiency provides meaningful guidance and a material foundation for the development of organic electrically pumped lasers. This paper also briefly reviews challenges, development directions, and opportunities for the future development of the field.

Progress Organic electroluminescence is a process of directly converting electrical energy into light. It occurs in organic materials where they emit light under the action of an applied electric field or current. Organic electroluminescent devices are mainly divided into two categories: organic light-emitting diodes (OLEDs) and organic light-emitting transistors (OLETs). In 1963, Pope *et al.* reported the preparation of the first OLED using anthracene single crystals; however, electroluminescence was only observed in anthracene single crystals with a thicknesses of 10–20 μm when the driving voltage was as high as 400 V.

The construction of high-performance devices requires light-emitting materials with high mobility. In numerous literature reports, we have found that biphenyl derivatives serve as classical charge transport layers and have excellent light-emitting properties and large optical gain at the same time. In 2010, Adachi *et al.* reported a new type of non-heterostructure OLED device, in which BSBCz molecules are used as the emission layer (its HOMO and LUMO energy levels were 3.1 eV and 5.8 eV, respectively). They introduced two buffer layers at the ends of the emission layer with MoO_3 and the metal cesium-doped BSBCz film acts as hole and electron transport interlayers. The addition of the buffer layers effectively reduces the carrier injection barrier, thereby suppressing the roll-off of electroluminescence efficiency at high current density.

OLET is an integrated device that has both the switching function of an organic field effect transistor (OFET) and the light-emitting function of OLED, which can avoid complex OFET gate voltage switching to drive OLED. This can greatly simplify device fabrication and be easily integrated into display circuits. Recently, Yin *et al.* develop a novel 4, 4′-bis (2-dibenzothiophenylvinyl)-bipheny (DBTVB) molecule based on extending the biphenyl skeleton. The introduction of dibenzothiophene groups not only extends the conjugated chain but also provides the space for the rotation of the molecular conformation to ensure the planarity of the molecule. The single crystal of this molecule exhibits a fluorescence quantum yield of up to 85% and excellent bipolar transport properties with hole and electron mobilities of 3. 55 and 2. 37 $cm^2 \cdot V^{-1} \cdot s^{-1}$. Simultaneously, this single crystal also exhibits excellent laser properties. A DBTVB-based OLET was fabricated with Au/MoO_3-Ca/CsF as an asymmetric electrode. The external quantum efficiency of the device is as high as 4. 03%, which is the best OLET device reported so far.

Because of the rod-shaped molecular structure, the molecules tend to form a herringbone arrangement during the self-assembly process, which can effectively reduce the fluorescence quenching caused by the intermolecular π—π interaction and ensure the efficient transport of carriers. Biphenyl derivatives usually have a large Stokes shift, large transition dipole moment, and excited state oscillator strength, which ensure their good luminescence properties. Therefore, biphenyl derivatives have inherent advantages as laser gain materials. As a typical biphenyl derivative, the 4, 4′-bis [(N-carbazole) styryl] biphenyl (BSBCz) molecule has very low intersystem crossing efficiency. Therefore, in the presence of oxygen, the triplet excitons generated by optical pumping are completely quenched and the triplet excited state absorption (TA) in the laser gain wavelength range is almost negligible. These advantages make it a strong candidate for realizing a continuous-wave optically pumped laser. Ren *et al.* reported an exciton-polariton laser based on the optical microcavity consisting of a 4, 4′-bis [4-(di-p-tolylamino)styryl] biphenyl (DPAVBi) single-crystal sandwich in two layers of silver films. Such exciton polaritons can form stable macroscopic condensations at room temperature and generate lasing emission with good spatial coherence.

Conclusions and Prospects The pursuit of organic electrically pumped lasers is a long-term goal that requires the joint effort of scientists in the fields of chemistry, materials science, device physics, and engineering. From the perspective of materials science, developing materials with high mobility and high luminescence properties is important for realizing organic electric pumped lasers. In this review, we summarize the reported applications of biphenyl derivatives in photoelectric devices, including OLEDs, OLETs, organic micro/nano-lasers, organic polariton laser, and organic electrically pumped lasers. The excellent photoelectric properties of these materials make them potential candidates for electrically pumped lasers.

We believe that organic electrically pumped laser will be realized soon, following more and more breakthroughs in this field. The organic electrically pumped lasers can bridge the gap between current microelectronic and nanophotonic circuits to revolutionize laser displays, precision medicine, wearable devices, and information and communication technologies.

Key words materials; biphenyl derivative; photoelectricity integration; charge transfer; luminous efficiency; electrically pumped organic laser