

Letter

Solution-processed anthracene-based molecular glasses as stable blue-light-emission laser gain media



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ARTICLE INFO

Article history:

Received 21 October 2014

Received in revised form 28 December 2014

Accepted 9 January 2015

Available online 19 January 2015

Keywords:

Optical gain properties

Solution-processed organic semiconductor lasers

9,10-disubstituted anthracenes

Fluorine atom substitution

Thermal stability

ABSTRACT

Two asymmetric 9,10-disubstituted anthracene-based, solution-processable, molecular glasses were studied in detail as thin-film laser gain media and were found to demonstrate very low amplified spontaneous emission (ASE) thresholds (0.75–1.1 $\mu\text{J}/\text{pulse}$). Distributed feedback (DFB) lasers fabricated with these materials by spin coating on top of pre-etched silica one-dimensional (1-D) gratings exhibited a minimum laser threshold of 5.7 nJ per pulse (17.7 $\mu\text{J cm}^{-2}$) and maximum slope efficiency of 3.6%. The thermal stability of the gain was also investigated, with ASE observed for thermal annealing at temperatures up to 300 °C without any significant increase in threshold. The high thermal stability and low laser threshold make these materials very promising gain media. Comparison of the two glasses demonstrated that whilst fluorine-substitution significantly lowers the HOMO and LUMO levels it does not dramatically affect the gain. Our results suggest a potential approach for materials synthesis to address the challenge of electrically pumping an organic laser.

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1. Introduction

Organic semiconductor optical gain materials have attracted considerable attention due to a combination of good optical and solution-processing characteristics [1–4]. In contrast to the more generally studied laser dyes, they are also charge transporting and therefore have the, as yet unrealised, potential of electrical pumping. Organic light-emitting devices (OLEDs) with anthracene-based blue emitters have been intensively studied [5–10] demonstrating promising device efficiencies and stabilities. Such

materials have also been used as laser gain media, exhibiting excellent optical properties for both molecular glass [11–13] and spiro-polymer [14] samples. The molecular glass films are generally deposited via thermal evaporation whereas solution-processed, anthracene-based glasses combining synthetic accessibility and robust intrinsic morphological stability have not been widely explored.

One specific report of asymmetric 9,10-disubstituted anthracene-based, solution-processable, glass-forming molecules, whose chemical structures are shown in Scheme 1, has, nevertheless, been previously published [15]. We have undertaken density functional theory (DFT) calculations of **1a** and **1b** using Gaussian 03 (B3LYP nonlocal density functional with a 6-31G(d) basis set) and report the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital, electronic wavefunction densities for

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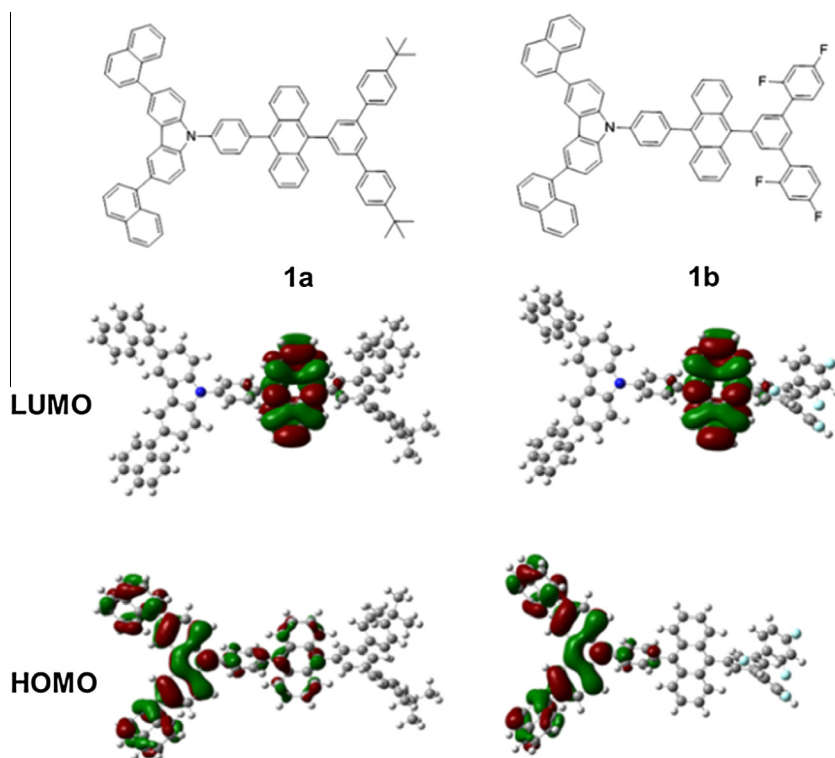
geometry-optimized structures in Scheme 1. There is a greater spatial separation of HOMO and LUMO wavefunction densities for **1b** than **1a** with the HOMO wavefunction largely removed from the anthracenyl moiety in the former case. It is also evident that the molecules have a significantly non-planar optimized geometry, a feature that may help to reduce concentration quenching relative to more planar anthracenyl derivatives and thereby yield higher photoluminescence quantum efficiencies [PLQEs] [8,15]. The calculated HOMO and LUMO energy levels are -5.20 eV and -1.73 eV for **1a**, and -5.50 eV and -2.11 eV for **1b**, respectively. The characterization of OLEDs based on these materials shows that they combine efficient and stable blue light emission with high spectral purity [15]. In addition, the relative lowering of the HOMO and LUMO energy levels in **1b** c.f. **1a**, leads to a lower working voltage. This latter behaviour is in agreement with previous results for electron-withdrawing fluorine substitution in organic optoelectronic materials [9,15–19]. Lowering the LUMO should also assist electron transport by reducing the probability of trapping [19]. The laser-gain-related properties of such solution-processed, anthracene-based, molecular glasses remain, however, unreported and whether the fluorine substitution has any adverse effects on optical gain via increased charge photogeneration or other non-radiative processes is unexplored. Here we study the optical gain properties of **1a** and **1b** and demonstrate that these materials possess encouragingly low laser thresholds and high thermal stability. The effect of fluorine atom substitution is also assessed. Our results suggest that solution-processed

anthracene-based blue emission glasses such as **1a** and **1b** represent a promising class of organic optoelectronic materials, deserving of further development.

2. Results and discussion

2.1. Optical properties

Samples of **1a** and **1b** were used, as provided, following synthesis in South China University of Technology under conventional Suzuki coupling conditions [15]. Molecule **1a** has a solubilizing 3,5-bis(4-*t*-butylphenyl)phenyl dendron attached at the anthracene 9-position and a 4-(3,6-di(naphthalen-1-yl)carbazol-9-yl)phenyl group attached at the opposite 10-position. The latter is expected to promote hole-injection and transport and help support glass formation and is consequently retained for that purpose in **1b** [15]. Different from **1a**, the 9-dendron in **1b**, namely 3,5-bis(2,4-difluorophenyl)phenyl, has fluorine atom substituents, in lieu of *t*-butyls, to facilitate electron injection and transport. These materials show good solubility in common organic solvents and have good film-forming properties. Fig. 1(a) and (b) shows, respectively, Atomic Force Microscopy (AFM) images of films (average thickness ≈ 115 nm) of **1a** and **1b** spin-coated from toluene. The measured root mean square roughness was <2 nm for films of **1a** and up to 3 nm for films of **1b**, evidencing a strong tendency to form homogeneous films via solution processing.



Scheme 1. Chemical structures of **1a** and **1b** and calculated LUMO and HOMO electronic wavefunction distributions for geometry optimized **1a** and **1b** structures.

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