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Surface-emitting Vertical Cavity with Vapor-grown Single Crystal of Cyano-substituted Thiophene/Phenylene Co-oligomer

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Abstract
Surface-emitting vertical half-cavities are fabricated with vapor-grown single crystals of 5,5'-bis(4'-cyano-biphenyl-4-yl)-2,2'-bithiophene (BP2T-CN) on a distributed Bragg reflector (DBR). Angle-resolved photoluminescence spectra indicate an exciton-photon coupling at room temperature. Under optical pumping, surface-emitting laser is obtained based on lying molecular orientation even in the half-cavity structure of air/BP2T-CN/DBR.

1. Introduction

Organic microcavities have been attracting attentions as a lasing medium based on exciton polariton [1]. Strong coupling between excitons and photons confined in the microcavity enhances the coherent radiation at lower excitation threshold compared to the conventional photon lasing [2]. The large oscillator strength and large binding energy in molecular excitons are capable of polariton formation and lasing at room-temperature. Recently, organic polariton lasers have been reported for molecular crystals [3], oligomer [4] and polymer thin films [5]. Those organic microcavities are typically fabricated by filling an organic layer between top/bottom distributed Bragg reflectors (DBRs). In such a vertical-cavity structure, the molecular orientation is responsible for an effective feedback amplification of surface emission since the transition diplole moment is highly anisotropic in π-conjugated oligomer or polymer species.

As one of superior organic lasing media, we have used thiophene/phenylene co-oligomers (TPCOs) and reported optically pumped lasing from their monolithic single-crystal cavities [6]. Most of TPCO molecules crystallize in a platelet form in which their linear oligomer axis is standing against the platelet surface. This molecular orientation is not favorable for the vertical-cavity surface-emitting laser (VCSEL) due to their in-plane emission behavior. On the other hand, we have recently found that the cyano-substituted TPCO, bis(4'-cyanobiphenyl-4-yl)thiophene (BP1T-CN), is crystalized in a platelet morphology in which the molecular axes obliquely orient against the crystal plane [7]. Due to this modified orientation, the single-crystal microcavity of BP1T-CN demonstrated VCSEL and polaritonic characteristics at room temperature [8,9].

In order to further clarify such intriguing behaviors of the cyano-substituted TPCO, here we fabricate single-crystal microcavities using vapor-grown 5,5'-bis(4'-cyano-biphenyl-4-yl)-2,2'-bithiophene (BP2T-CN, Fig. 1a**)** which has a longer π-electronic conjugation and a different molecular symmetry compared to BP1T-CN.

2. Sample Preparation and Characterization

Vapor-growth crystallization was carried out by heating a BP2T-CN powder in a N_2-flowed glass tube at 305 ºC for 24 hours. Along with the temperature gradient, platelet and rod-like crystals were precipitated at the downstream of the tube as shown in a fluorescence micrograph in Fig. 1b. Using a tungsten needle, a large single-crystal platelet was selected and transferred onto a DBR substrate (10 x 10 x 1 mm^3, $(SiO_2/Ta_2O_5)_{53}$, R > 99.5 % at λ = 440 - 600 nm) as schematically shown in Fig. 2a. From X-ray diffraction (XRD) analysis, the basal plane of the platelet crystal was indexed to (201) of a monoclinic form (a = 1.834, b = 0.724, c = 1.8446 nm, β = 100.5°) [10]. Since the molecular axis aligns parallel to this (201) plane, the platelet shows a bright green emission from the crystal surface. A typical crystal thickness was measured to be 2 μm using a profilometer.

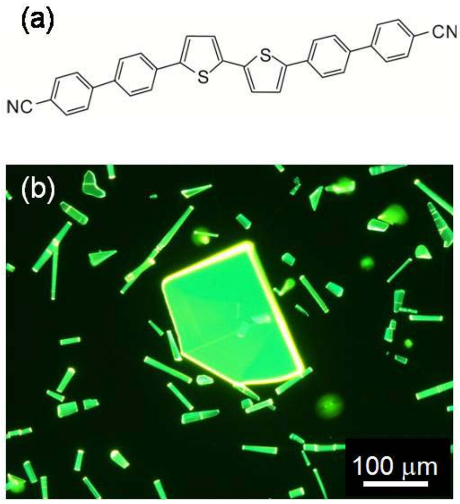

Fig. 1 Molecular structure of BP2T-CN (a) and fluorescence micrograph of vapor-grown crystals (b).

3. Optical Measurements

Angle-resolved photoluminescence (PL) spectra of the air/BP2T-CN/DBR half-cavity were taken under CW-excitation with a diode laser (λ = 405 nm). The excitation beam was incident from the DBR substrate and the emission was detected with a CCD spectrometer as a function of angle with respect to the surface normal of the BP2T-CN crystal. As shown in a color map spectra in Fig. 2b, two series of dispersions with small and large curvatures due birefringence in the crystal are observed in E = 2.0 - 2.5 eV and θ = -30 - 60°. Note that multiple splits are observed when these two dispersions are anticrossing. This characteristic angle dependence was simulated using a phenomenological 6x6 Hamiltonian describing interactions between one exciton and five photonic modes. As a result, the coupling constant of polaritonic interaction between excitons and cavity photons were estimated to be 90 meV.

Optically pumped PL measurements of the air/BP2T-CN/DBR half-cavity were carried out using an excitation source of a Q-switched solid state laser (λ = 355 nm, 1.4 ns duration, 1 kHz). The excitation power was varied with two rotatable gradient ND filters. PL spectra taken from the surface normal of the BP2T-CN crystal were recorded as a function of excitation density. As shown in Fig. 3, a gain-narrowed emission peak emerges at λ = 532 nm (E =2.33 eV) when the excitation densities exceeds a threshold of ~400 μJ/cm^2. This emission position coincides with that of the third cavity photon mode at θ = 0° calculated without exciton-photon coupling. Therefore, we consider that this amplified emission is ascribed to photon lasing in the air/BP2T-CN/DBR half-cavity. In order to further achieve polariton lasing from the condensate state, we need to decrease the crystal thickness and fabricate a full-cavity structure (DBR/BP2T-CN/DBR).

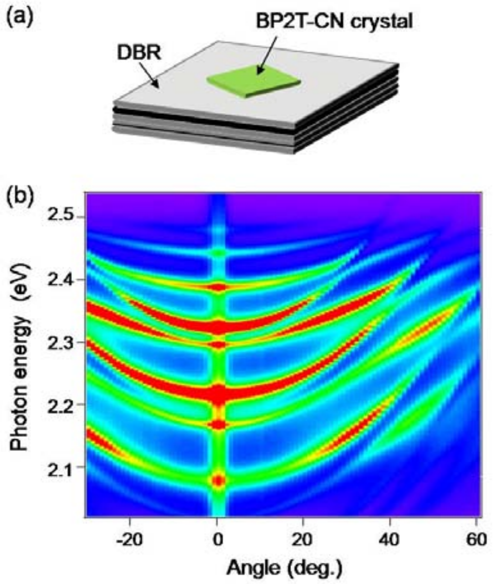

Fig. 2 Schematic diagram of air/BP2T-CN/DBR half-cavity structure (a) and its angle-resolved PL spectra (b).

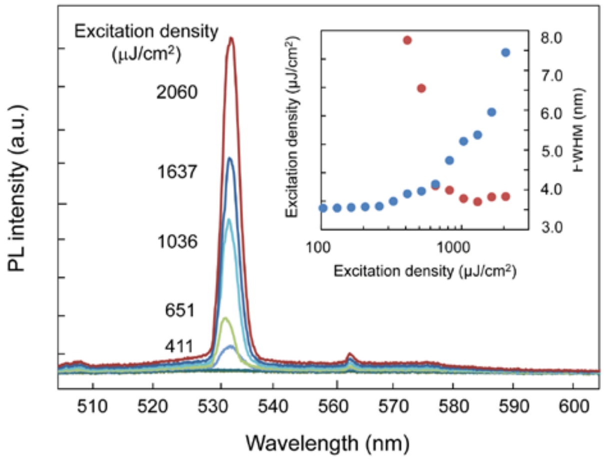

Fig. 3 Excitation density dependence of PL spectra taken from air/BP2T-CN/DBR half-cavity. The inset shows integrated PL peak intensity and linewidth as a function of excitation density.

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