Optoelectronic Characteristics of Furan Substituted Thiophene/Phenylene Co-Oligomer Single Crystals for Organic Lasing

Supplementary Information File

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Contents

1. MPP and SDP

Using the least squares fitting method, the idea is to fit all the atoms in a molecule to a fitting plane. Once the atoms are fitted to a plane, MPP can be measured as the root mean square deviation of atoms to the fitting plane. SDP can be calculated as the difference in atomic distance to a fitting plane. So, MPP can measure an overall deviation of atoms, and SDP indicates the molecular span relative to the fitting plane.

The molecular planarity indices are also calculated for the gas phase molecules. The calculated values are 0.43 Å and 1.77 Å for BPTFT and 0.78 Å and 3.78 Å for BP3T.

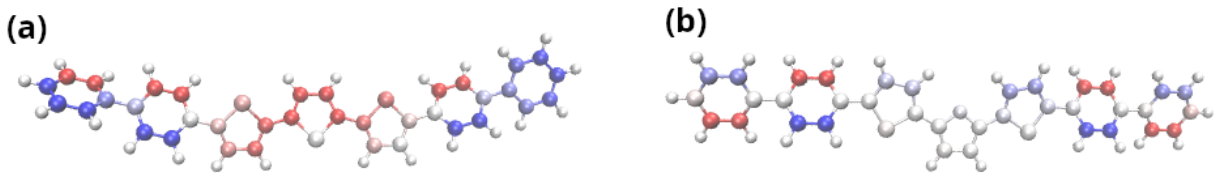

Figure S1: Planarity maps for (a) BP3T and (b) BPTFT calculated from the DFT optimized geometries.

2. Tauc plot

To calculate the frontier orbital gap (E_g), Tauc plots ($(\alpha h\nu)^2$ as a function of photon energy) are used. Here α is the absorption coefficient, obtained by dividing the absorbance with sample thickness, h is Planck's constant and ν is the photon frequency. Extrapolating the linear slope of $(\alpha h\nu)^2$ to zero absorption coefficient yield the E_{opt} value.

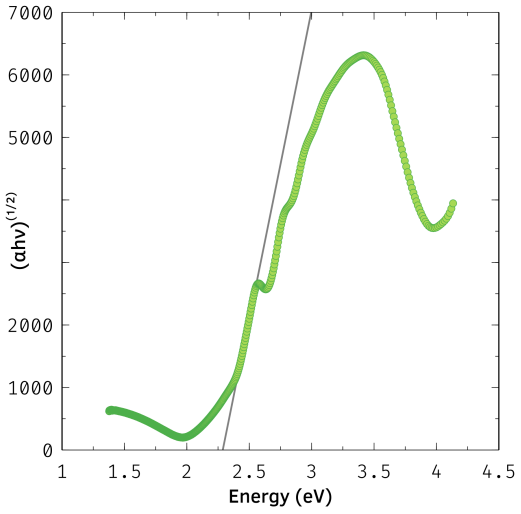

Figure S2: Tauc plot to calculate E_{opt} in BPTFT thin films.

3. Photophysical process

In a four-level system, the fluorescence quantum yield can be given as

$$\Phi_f = \frac{k_f}{k_f + k_{nr}} \tag{1}$$

where k_f is the fluorescence rate constant and k_{nr} is the non-radiative process. These two parameters can be further related by the fluorescence lifetime τ_f as $\tau_f = (k_f + k_{nr})^{-1}$. By combining the two relations, the k_f and k_{nr} can be described as $k_f = \Phi_f/\tau_f$ and $k_{nr} = (1 - \Phi_f)/\tau_f$.

4. Fluorescence lifetime

Strickler - Berg relation is one of the widely used empirical relations to estimate the fluorescence rate constant [1,2]. It relates the absorption coefficient and fluorescence of an emissive system as,

$$k_f = 1.511 \times 10^3 \frac{\int I(E)dE}{\int E^{-3} I(E)dE} n^2 \frac{g_1}{g_u} \int \epsilon_m(E) dln E \tag{2}$$

Here, I(E) denotes the fluorescence spectrum, n is the refractive index, ϵ_m is the molar extinction coefficient, $g_{1,u}$ are degeneracies of the lower and upper states, and for fluorescence $g_1/g_u = 1$. The equation can be further simplified by introducing the oscillator strength f and by removing the spectral shapes and solvent effects as [2],

$$k_f = 4.34 \times 10^7 \frac{E_f^3}{E_A} n^2 f \tag{3}$$

Where E_f and E_A are the vertical energies from PL and absorption spectrum, and the oscillator strength f can be obtained from the relation $f = 3.843 \times 10^{-5} \int \epsilon_m(E)dE$. The molar extinction coefficient ϵ_m can be calculated from the absorption spectrum as $\epsilon_m = \frac{\alpha\lambda}{4\Pi}$.

It is worth noting that the accuracy of the relation is not limited to the simplifications; rather, it arises due to the inconsistencies in experimental measurements. In particular, errors related to fluorescence and PLQY measurements significantly affect the accuracy [3,4].

5. Hole-electron analysis

The hole and electron analysis was also performed for the S_4, S_6 and S_7 states. However, their overall contribution is very less compared to the S_1 state. For example the oscillator strength f_{osc} of S_1 is about 2.93 (arb) and the corresponding values for the states S_4, S_6 and S_7 are 0.12, 0.17 and 0.11, respectively.

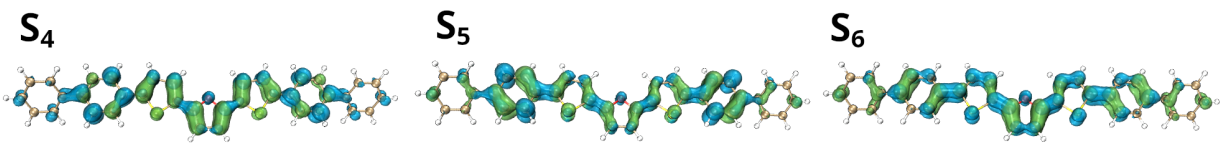

Figure S3: Hole-electron distribution in S_4, S_6 and S_7 states of BPTFT.

6. Optical pumping and VSL setups

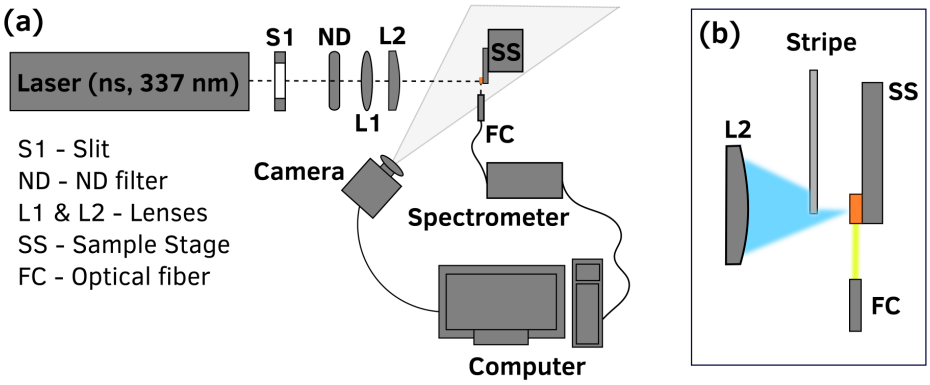

Figure S4: (a) Optical pumping and (b) VSL setups

7. Stimulated emission cross-section

By using the fluorescence spectrum and the lifetime values, the stimulated emission cross-section can be calculated as [5],

$$\sigma(\lambda) = \frac{\lambda^4 \Phi_f}{8\pi n^2(\lambda) c \tau_f} \tag{4}$$

Where Φ_f is the PLQY, c is the velocity of light, n is the effective refractive index calculated using [6],

$$n = \frac{\lambda^2}{2\Delta\lambda L} \tag{5}$$

8. Crystal dimensions

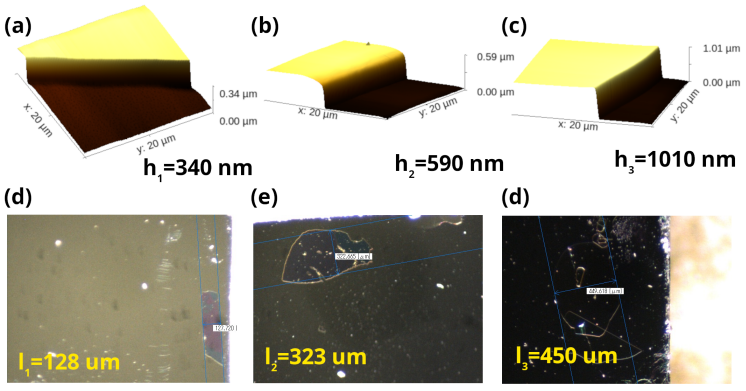

Figure S5: (a-c) Thickness profiles of some crystals using AFM. (d-f) Crystal widths measured using microscope

9. Gain narrowing profiles

The emission profiles are thickness dependent. Only for thickness more than 500 nm the system emits in dual wavelength. However the gain narrowing for both the peaks is more observable only around 700 nm of thickness. In cases, where thickness exceeds 1 micron the 0-2 band predominates over 0-1 band.

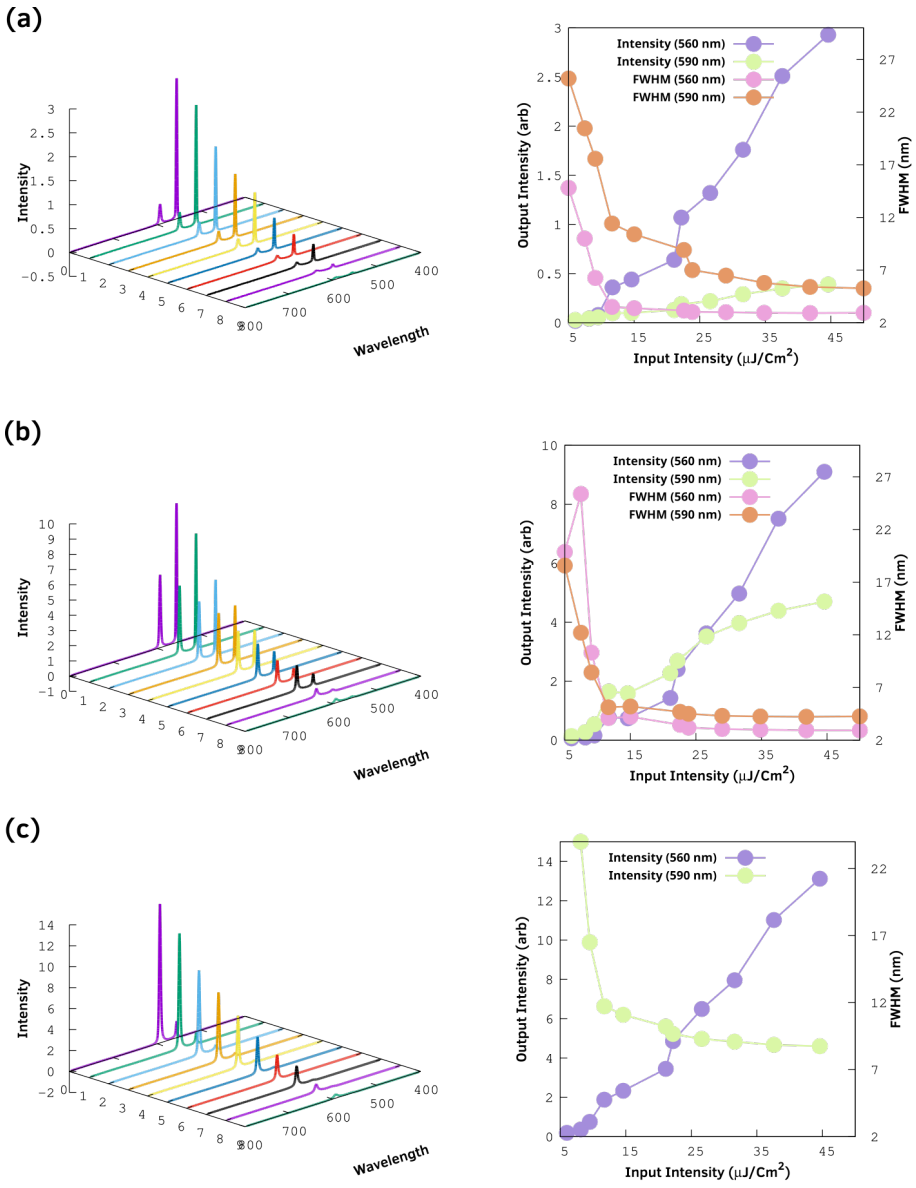

Figure S6: Gain narrowing profiles of BPTFT with thickness (a) $\sim$ 400 nm (b) $\sim$ 650 nm and (c) $\sim$ 1 micron

10. PL spectrum

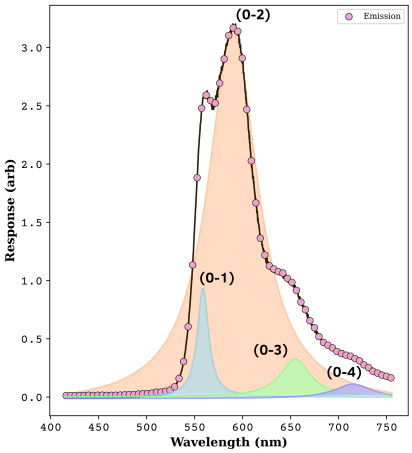

Figure S7: PL spectrum recorded with 405 nm diode laser with a high resolution spectrometer

11. Mass spectrum

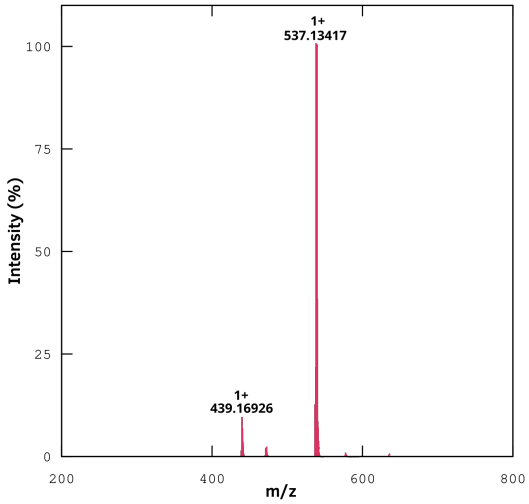

Figure S8: Mass mass spectrometry result of BPTFT using atmospheric pressure chemical ionisation (APCI) method. The chemical formula for BPTFT is $C_{36}H_{24}S_2O$. Considering the mass of each atom as C: 12.01 Da, H: 1.01 Da, S: 32.07 Da, O: 16.00 Da, the observed peak at 537.13 Da confirms the BPTFT's atomic composition. The data is recorded for the as-synthesised compound. The role of impurities in optoelectronics characteristics would be minimal since the crystals are grown using a three-zone furnace with a two-time sublimed material.

12. Thermogravimetric analysis

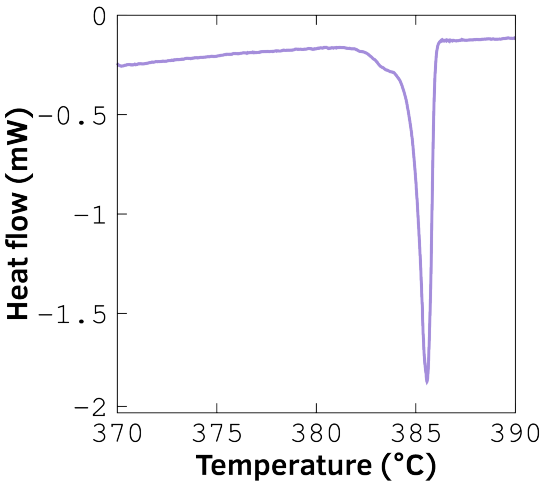

Figure S9: DSC curve for as-synthesized BPTFT. The spectrum was recorded in Ar atmosphere at a rate of 20 °C/min. Sample weight is 2.9 mg and an endothermic peak was observed near 380 °C. There is no weight loss due to decomposition occurs below the sublimation temperature because the molecular structure does not change after crystal grown by PVT. Therefore, it can be said that BPTFT does not decompose below the sublimation temperature.

12. References

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