Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2022

Electronic Supplementary Information

Accumulating Bright Excitons on Hybridized Local and Charge Transfer Excited State for Organic Semiconductor Lasers

Rui Chen,[ab] Wu Zhou, [ab] Yanjun Gong, [ab] Zeyang Zhou, [ab] Hong Wang, [ab] Chenghu Dai, [a] Yong Sheng Zhao, [a] Yanke Che,[a] Chuang Zhang,*[a] and Jiannian Yao[a]

[a]*Key Laboratory of Photochemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*

[b]*University of Chinese Academy of Sciences, Beijing 100049, China.*

E-mail: zhangc@iccas.ac.cn

Experimental Details

Photophysical Characterization. The molecule 3F6 and 3F6-2BT were synthesized according to our previous reports [Anal. Chem., 2019, 91, 6408-6412; Adv. Sci., 2021, 8, 2002615.]. UV-vis absorption spectra were measured using a UV-vis spectrophotometer (Hitachi High-Tech Corporation, UH4150) at normal incidence, and the fluorescence spectra were measured using HITACHI® F-7000 Fluorescence Spectrometer. The RT (room temperature) transient photoluminescence decay characteristics were measured using a compact fluorescence lifetime spectrometer (Quantaurus-Tau C11367-35) at an excitation wavelength of 375nm and absolute PL quantum yield were determined using Hamamatsu Absolute PL Quantum Yield spectrometer C11347 coupled with an integrating sphere. Temperature-dependent PL spectra and transient PL decay were measured using the homemade measurement system consisting of a cryostat (Montana Instruments Cryostation s50), a spectrometer (Princeston Instruments HRS300), a charge-coupled device (CCD, Pixis 256), a time-to-digital converter (TDC, qutools quTAG) and photon counters (EXCELITAS SPCM-AQRH-14) with a time-correlated single photon counting (TCSPC) method, the excitation emission is 375 nm using a picosecond laser (YANGTZE SOTON LASER SC-Pro).

Lasing Characterization. The lasing actions of dye-PVK microspheres were measured with a homebuilt micro-PL system. A 375-nm pulse laser beam was employed as the excitation source to pump the micropillar resonators, which was generated from the optical parametric amplifier (Solstice, Spectra-Physics, 800 nm, 100 fs, 1000 Hz). The pump fluence was controlled with a neutral density filter and the pump beam was focused to a spot on the sample with an objective lens (Nikon, 20 ×, N.A. = 0.5). The emission was collected with the same microscope objective, then passed through a dichroic mirror and a 400 nm long-pass filter to eliminate the excitation beam. After being focused by a group of lenses onto a confocal iris, the collected PL signal was finally dispersed with a grating and recorded with a thermal-electrically cooled CCD (Princeton Instrument, ProEm 1600B).

OLED Fabrication and Characterization. The ITO substrates were cleaned carefully using toluene, acetone, tert-butanol for 20 min, respectively, by using an ultrasonic bath, and then dried under the temperature of 110 °C before treated by oxygen plasma. The blend solution of 3F6-and 3F6-2BT-PVK were prepared by dissolving laser dye molecules and PVK in chlorlbenzene (10 mg/mL) with different dopant concentration, respectively. In fabrication of OLEDs, a spin-cast layer of poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT:PSS) was used for hole transport; a layer spin-cast from 3F6-PVK and 3F6-2BT-PVK were used as the active layer, respectively; a deposit layer of 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)-benzene (TPBi) was used for electron transport; a thermally evaporated layer of LiF/Al cathode was capped on top. The hole-transport and active layers were fabricated by spin coating at 3000 RPM and annealed at 120°C for 30 min.1 The device structure is ITO/PEDOT: PSS (25 nm) /3F6-2BT(or 3F6)-PVK (1, 5, 10, 15, 20 wt%) (35 nm)/TPBi (40 nm)/LiF (1.5 nm)/Al (100nm) ,and the light-emitting area of OLEDs was 1 mm by 2 mm. The typical external quantum efficiency (EQE) of 3F6 doped OLEDs is ~0.5 %, and that of 3F6-2BT doped OLEDs is ~3.0 %.

Magnetic Field Effect Measurements. Magneto-PL (MPL) measurements were performed using the homemade measurement system consisting of a computer-controlled electromagnet (Beijing Chaoruirenda Technology CR1), the excitation emission is 375 nm using a continuous wave laser (MDL-III-375), the PL signal of the samples were extracted using a calibrated silicon photodiode, and transformed into electrical signal using a photomultiplier (Thorlab PDA200C) and finally collected using a digital multimeter (Keithley DMM6500). For MEL measurement, the OLEDs were transferred to a vacuum chamber of cryostat (Oxford OptistatDry BLV) that was placed in a magnetic field B provided by an electromagnet (EastChanging EM4) with magnetic field up to 150mT. Electrical wires made of metallic alloys were used to keep the parasitic magneto-resistance below 0.001%. The OLEDs were operated at forward bias above turn-on voltages powered by a Keithley 2450 SourceMeter, and the EL emission was monitored with a silicon detector (Thorlabs PDA200C). The MEL is measured at a constant applied bias and defined as: MEL(B)=[EL(B)-EL(0)]/EL(0)×100%. The external magnetic field was swept at a rate of 10 mT s-1 in one direction and back for several cycles to improve the S/N ratio of MEL(B). The sensitivity of our MEL measurement was typically 0.05%, and the statistics on multiple OLEDs was given as error bars in the main text.

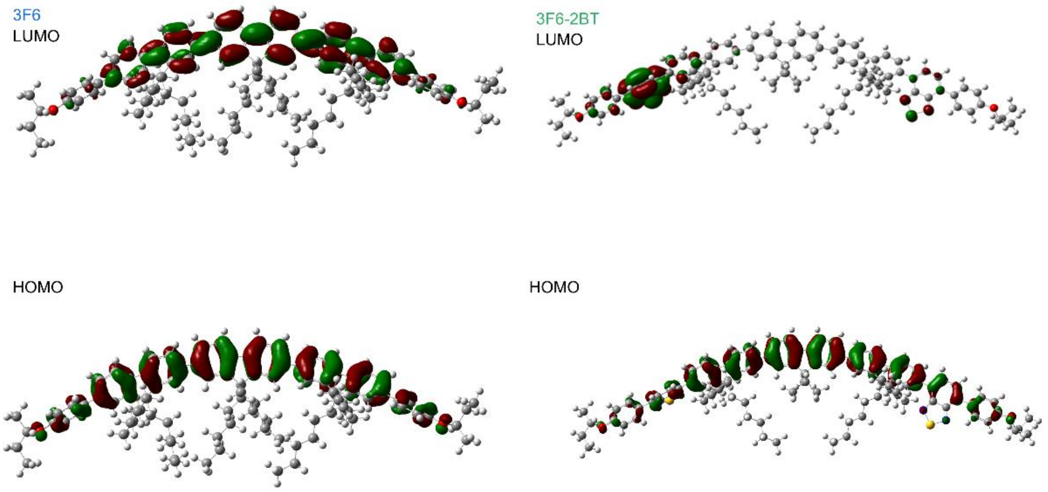

Fig. S1 DFT-calculated frontier molecular orbitals of 3F6 and 3F6-2BT molecules.

The hybridization of LE/CT states (HLCT characteristics) is related to the twisted angle between D and A moieties in the molecular structure. The co-planar alignment of D-A moieties is beneficial to the overlapping of wavefunctions and the formation of CT state. In comparison, the twisted structure of 3F6-2BT molecules allows for the separation of the molecular orbitals, and consequently leads to the partially overlapped wavefunctions, i.e., a hybridization of LE (D moieties) and CT (D-A moieties) states. DFT calculations reveal the partially separated LUMO and HOMO in 3F6-2BT. The twisted molecular structure of 3F6-2BT allows for the formation of an intercrossed LE and CT state that can provide a pathway for high emission efficiency and maintain long exciton lifetime.

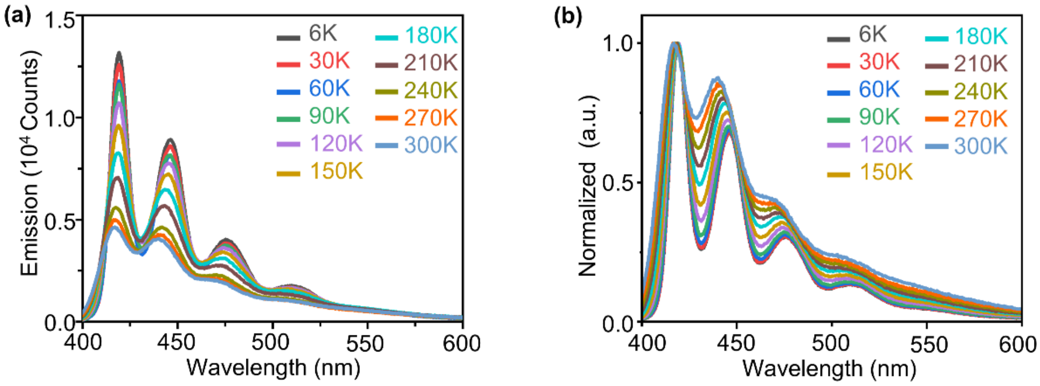

Fig. S2 (a) Temperature-dependent PL spectra of 3F6 film, and (b) corresponding normalized PL spectra.

With the temperature decreases to 6 K, the PL intensity of 3F6 gradually increases, and the vibronic sub-bands also become more obvious, indicating the locally excited state (LE) characteristics of 3F6.

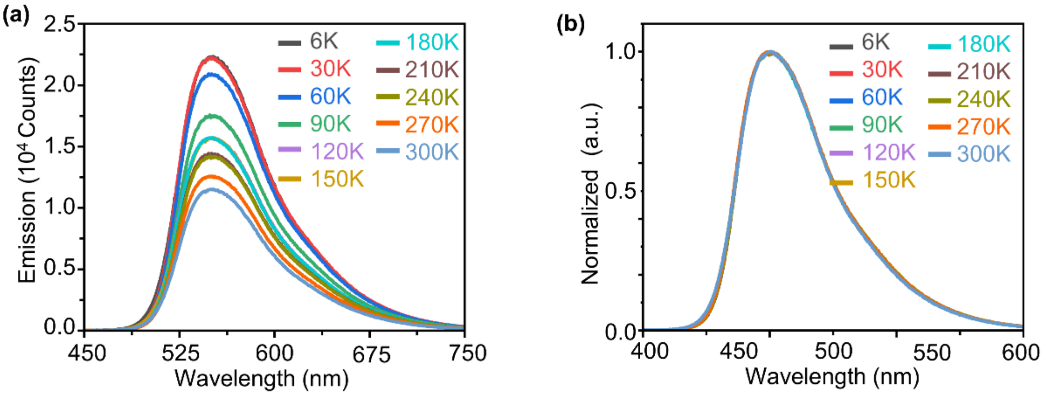

Fig. S3 (a) Temperature-dependent PL spectra of 3F6-2BT film, and (b) corresponding normalized PL spectra.

Among the temperature from 6 K to 300 K, the shape of PL spectra of 3F6-2BT shows negligible changes, and PL intensity shows a different temperature-dependence below and above 150 K, indicating the HLCT state is the emissive species in the full temperature range, but the LE and CT component dominants at above 150 K and below 150 K, respectively.

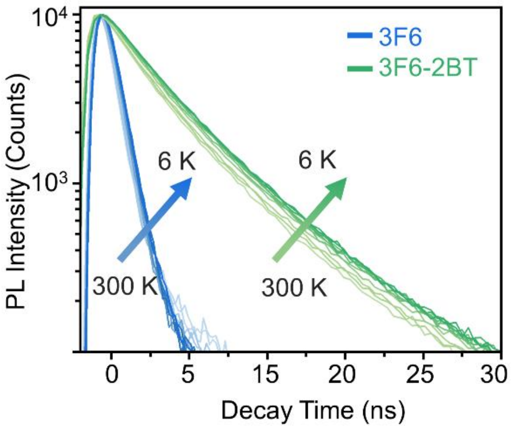

Fig. S4 Temperature-dependent transient PL decays of 3F6 and 3F6-2BT, respectively.

Both transient PL decay of 3F6 and 3F6-2BT increase with the temperature decreases, but compared to the little change of 3F6 (<0.20 ns in the range from 6 K to 300 K), 3F6-2BT shows an obvious change (~ 0.58 ns) from 300 K to 150 K and then the decay of 3F6-2BT becomes slower (~0.13 ns), which is consistent with the temperature-dependent PL intensity.

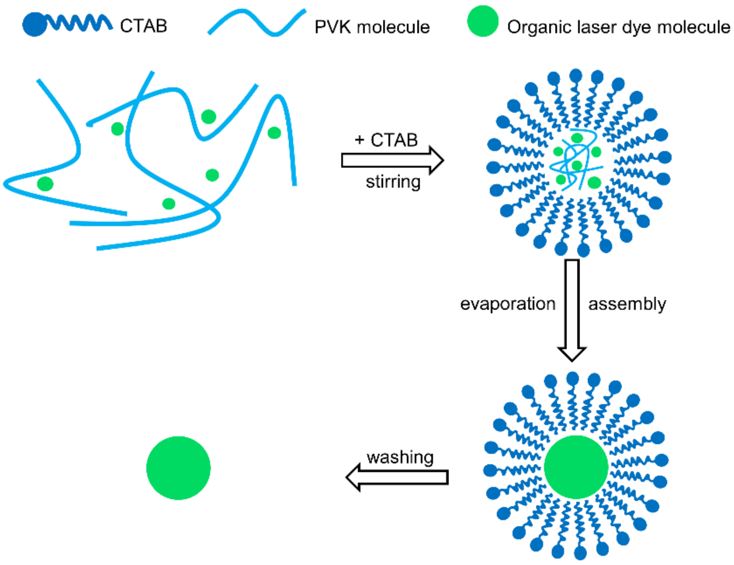

Fig. S5 Fabrication process of organic laser dye molecule-PVK microspheres

The dye-doped microspheres were prepared through an emulsion-solvent-evaporation method. In a typical preparation, a mixture of PVK (10 mg/mL) and organic laser dye molecule. The (concentration was ~20 wt % relative to the PVK) in dichloromethane solution (100 µL) was added into an aqueous solution (1 mL) of CTAB (2 mM), which was subsequently treated with vigorous stirring for 30 minutes. The dichloromethane was totally evaporated after aging for 2 hours, and the colloid dispersion of organic laser dye molecule-PVK microspheres were thus obtained. The precipitate was filtered and washed for several times to remove CTAB. The microspheres were re-dispersed in the aqueous solution and drop-casted on substrates for further characterizations.

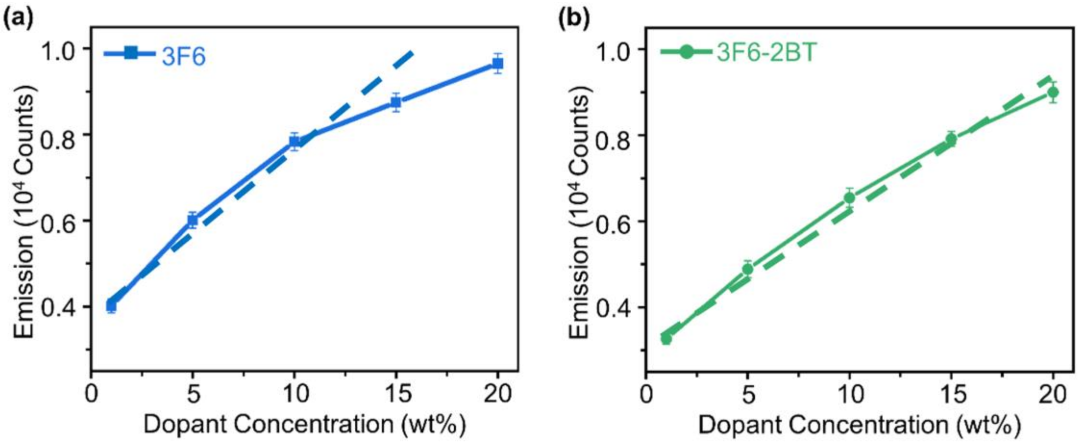

Fig. S6 PL intensity as a function of doping concentration for (a) 3F6-PVK and (b) 3F6-2BT-PVK blends.

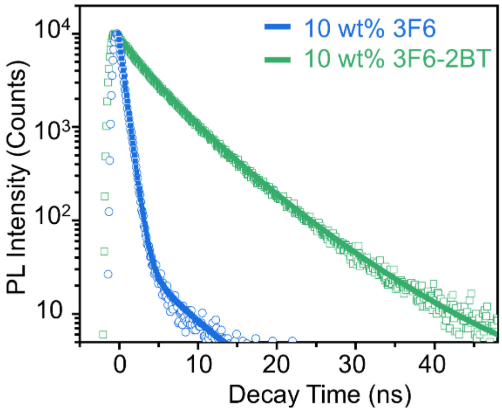

Fig. S7 Transient PL decay curves measured from 3F6-PVK and 3F6-2BT-PVK blends.

The photoluminescence lifetime measured from the 3F6-2BT-PVK blend (5.17 ns) is sufficiently longer than that for the 3F6-PVK blend (0.82 ns).

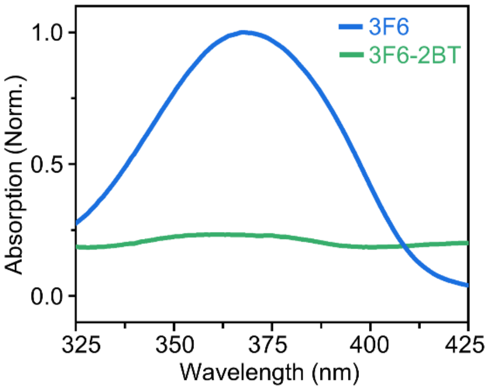

Fig. S8 Absorption spectra of 3F6- and 3F6-2BT-PVK microspheres.

In order to evaluate the lasing performance of 3F6-2BT, the absorption spectra of both microspheres were measured. The absorption of 3F6 at 375 nm is ~5 times than that of 3F6-2BT, so we normalized the pump fluence with respect to the absorption coefficient to evaluate the exciton utilization of 3F6-2BT.

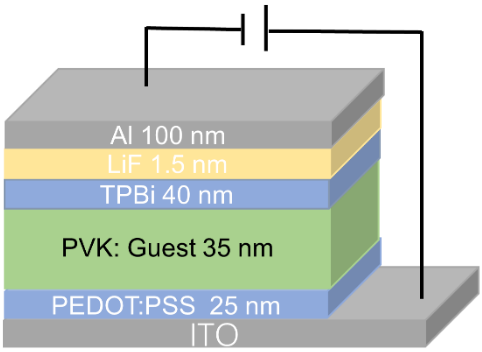

Fig. S9 Devices structure of organic laser dye molecule doped OLEDs.

The device architecture is ITO (WF 5.1 eV)/PEDOT:PSS (WF 5.3 eV)/PVK (HOMO 5.8 eV, LUMO 2.3 eV) doped with 3F6 (HOMO 5.0 eV, LUMO 1.4 eV) or 3F6-2BT (HOMO 5.1 eV, LUMO 2.3 eV)/TPBi (LUMO 6.2 eV, HOMO 2.7 eV)/LiF, Al (WF 3.2 eV). WF, HOMO, LUMO indicates work function, highest occupied molecular orbital, lowest unoccupied molecular orbital.

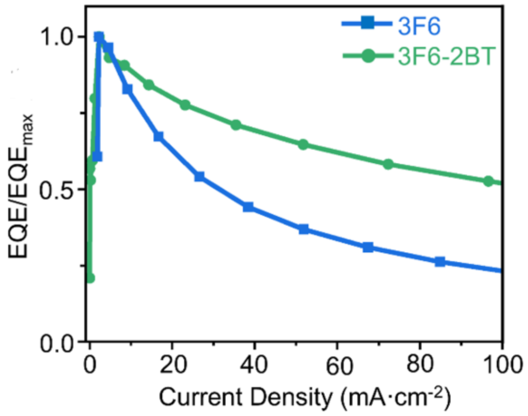

Fig. S10 EQE/EQE$_{max}$ as a function of current density in the 3F6 and 3F6-2BT OLEDs. The roll-off in EQE is less obvious in the 3F6-2BT OLED compared with the 3F6 device.

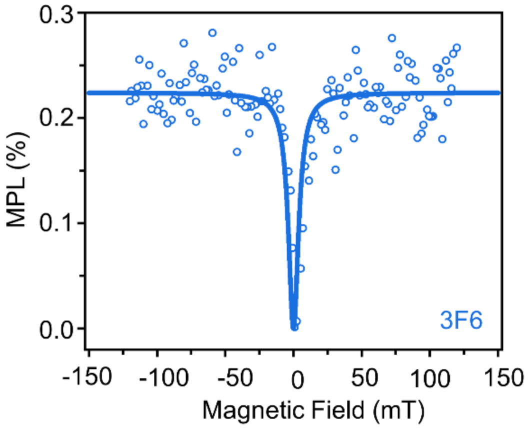

Fig. S11 MPL of 3F6 blend obtained at 300 μJ cm^{-2}. Excitation wavelength is 375 nm.

The MPL of 3F6 blend shows only narrow component with a width of ~4.85 mT, indicating the spin-mixing process in LE state governed by the hyperfine interaction.

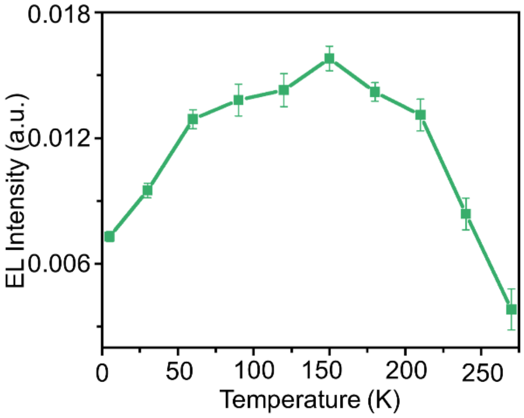

Fig. S12 Temperature-dependent EL intensity measured from the 3F6-2BT OLED (20 wt%) at 100 mA cm^{-2}.

The EL intensity of 3F6-2BT OLEDs at 100 mA cm^{-2} shows a maximum at ~150K, which is consistent with the photophysical properties of 3F6-2BT (Fig. 1e and 1f).

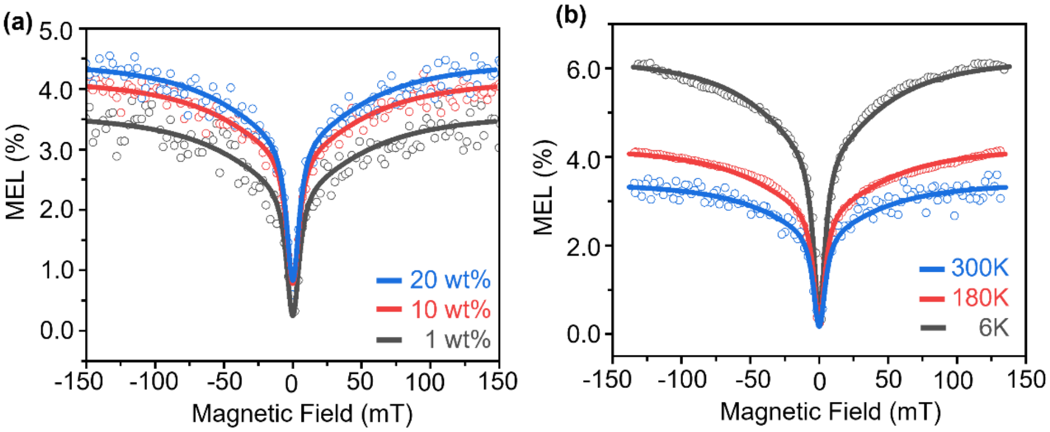

Fig. S13 (a) MEL(B) curves measured from 3F6 OLEDs with various doping concentrations at room temperature. Current density is 500 mA cm^{-2}. (b) MEL(B) curves measured from the 3F6 OLED (20 wt%) at various temperatures. Current density is 100 mA cm^{-2}. No broad MEL component (MEL$_{CT}$) could be observed at either high doping concentration or low temperature.