

Dual nature of exciplexes: exciplex-forming properties of carbazole and fluorene hybrid trimers

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Supporting Information

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- I- Experiments section.
- II- Figures.

I- Experiments section.

For photophysical measurements, thin film samples were spin-coated on glass substrates using integrated into “MBRAUN MB EcoVap4G” glovebox spin-coater “Spin 150” at $v=1000$ rpm, $a=375$ rpm/s, $t=30$ s. 1 mg/ml CHCl₃ solutions of the studied materials were prepared for the spin-coating procedures. Exciplex-forming solid-state mixtures with molar concentration ratio 1:1 of donor and acceptor were performed for investigations of their exciplex-forming properties. Annealing of the studied samples was performed at 100 °C in inert atmosphere. The Edinburgh Instruments FLS980 spectrometer was exploited for photophysical measurements. For temperature dependent measurements, the cryostat “Oxford Instrument Optistat DN2) was used. PL decays were recorded using the PicoQuant LDH– D-C-375 laser as an excitation source ($\lambda_{ex}=374$ nm).

Prepatterned and precleaned ITO-coated glass substrates with a sheet resistance of 15 Ω /sq were used for devices fabrications. Organic and metal layers were deposited using integrated into glove box Kurt J. Lesker vacuum equipment. Before depositing of electron transporting/injecting layers and of top electrode, structures of devices consisting interface or volume exciplex-based light-emitting layer were annealed at 100 °C using hotplate inserted into the glovebox. LiF/aluminium as the cathode was thermally evaporated using a shadow mask forming active area of the devices 6 mm². Density-voltage and luminance-voltage characteristics were recorded utilizing Keithley 6517B electrometer, calibrated silicon photodiode PH100-Si-HA-D0 together with the Keithley

2400C source meter. Electroluminescence (EL) spectra were taken using an Avantes AvaSpec-2048XL spectrometer. Device efficiencies were estimated from the luminance, current density, and EL spectrum. CIE 1931 diagrams were obtained using EL spectra and the FLS980 software.

Surface morphology was investigated using atomic force microscopy (AFM). AFM experiments were carried out in air at room temperature using a NanoWizard III atomic force microscope (JPK Instruments AG), while data was analyzed using SurfaceXplorer and JPK SPM Data Processing software. The AFM images were collected using a V-shaped silicon cantilever (spring constant of 3 N/m, tip curvature radius of 10.0 nm and the cone angle of 20°) operating in a AC mode.

X-ray diffraction measurements at grazing incidence (XRDGI) were performed using a D8 Discover diffractometer (Bruker) with Cu K α (λ = 1.54 Å) X-ray source. Parallel beam geometry with 60 mm Göbel mirror (X-ray mirror on a high precision parabolic surface) was used. This configuration enables transforming the divergent incident X-ray beam from a line focus of the X-ray tube into a parallel beam that is free of K β radiation. Primary side also had a Soller slit with an axial divergence of 2.5° and a slit of 1.0 mm. The secondary side had a LYNXEYE (1D mode) detector with an opening angle of 2.16° and slit opening of 6.0 mm. Sample stage was a Centric Eulerian cradle mounted to horizontal D8 Discover with a vacuum chuck (sample holder) fixed on the top of the stage. X-ray generator voltage and current was 40.0kV and 40mA, respectively. The XRDGI scans were performed in the range of 3.0-90.0° with a step size of 0.067°, time per step of 19.2 s and auto-repeat function enabled. The XRDGI scans were performed at incidence angle of 1.5°. Processing of the resultant diffractograms was performed with DIFFRAC.EVA software.

II- Figures.

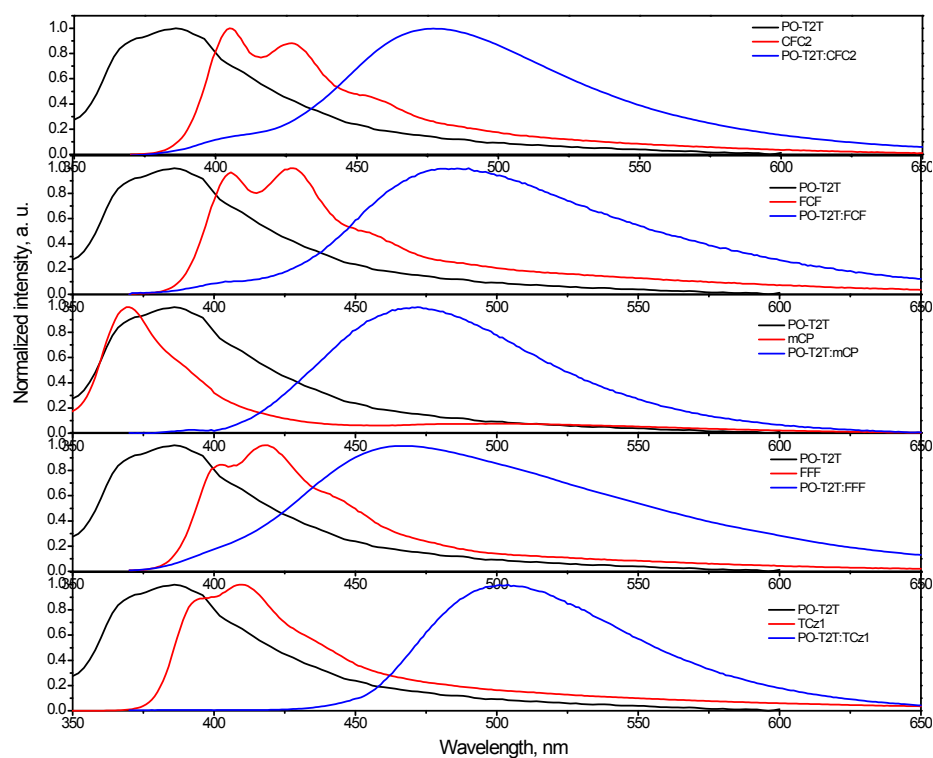


Figure S1. PL spectra of pure donors and acceptor TCz1, FCF, CFC2, FFF, mCP, and PO-T2T and their solid-state mixtures TCz1:PO-T2T, FCF:PO-T2T, CFC2:PO-T2T, FFF:PO-T2T and mCP:PO-T2T. In comparison to PL spectra of pure compounds, the red-shifts of PL spectra of the studied mixtures indicate the exciplex formations.

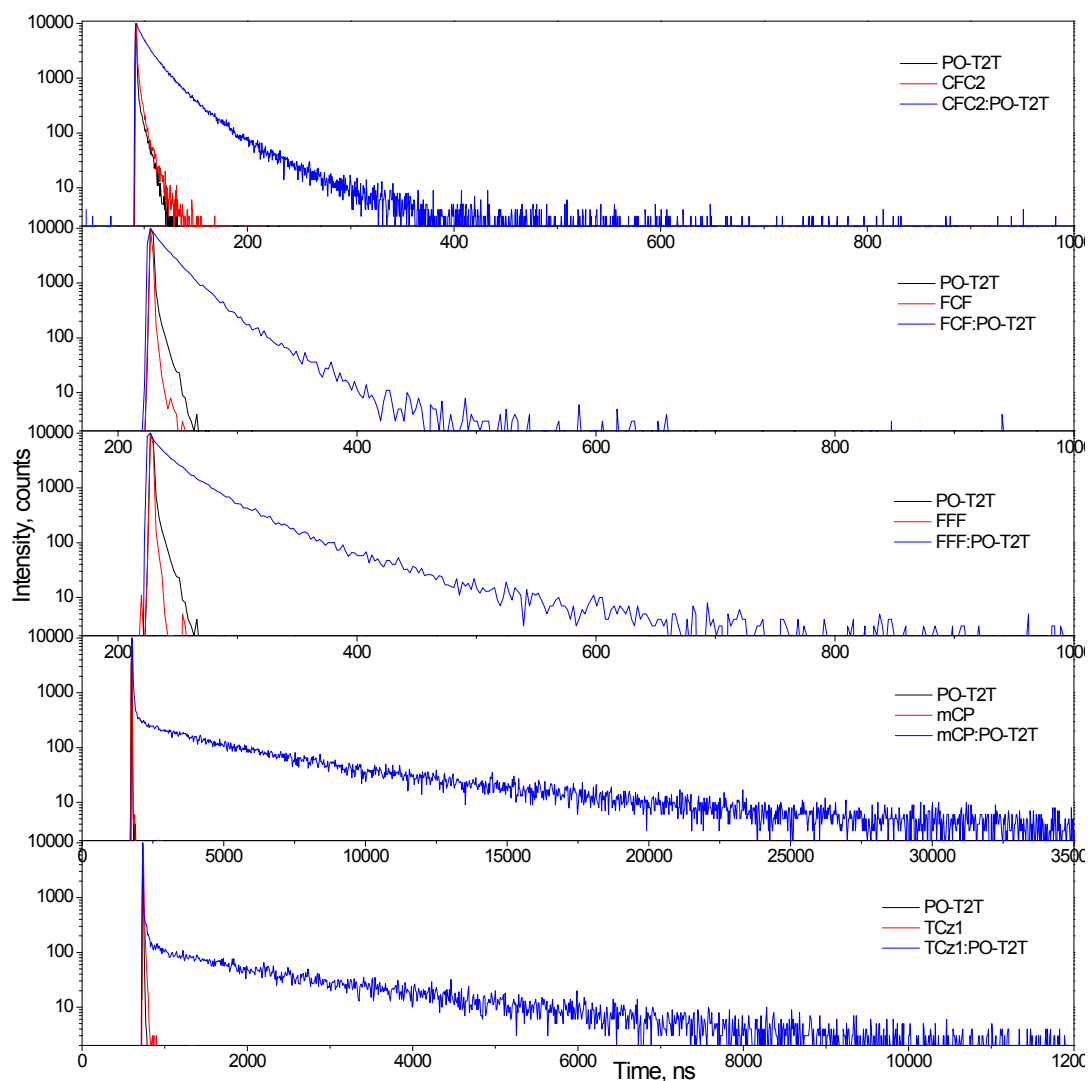
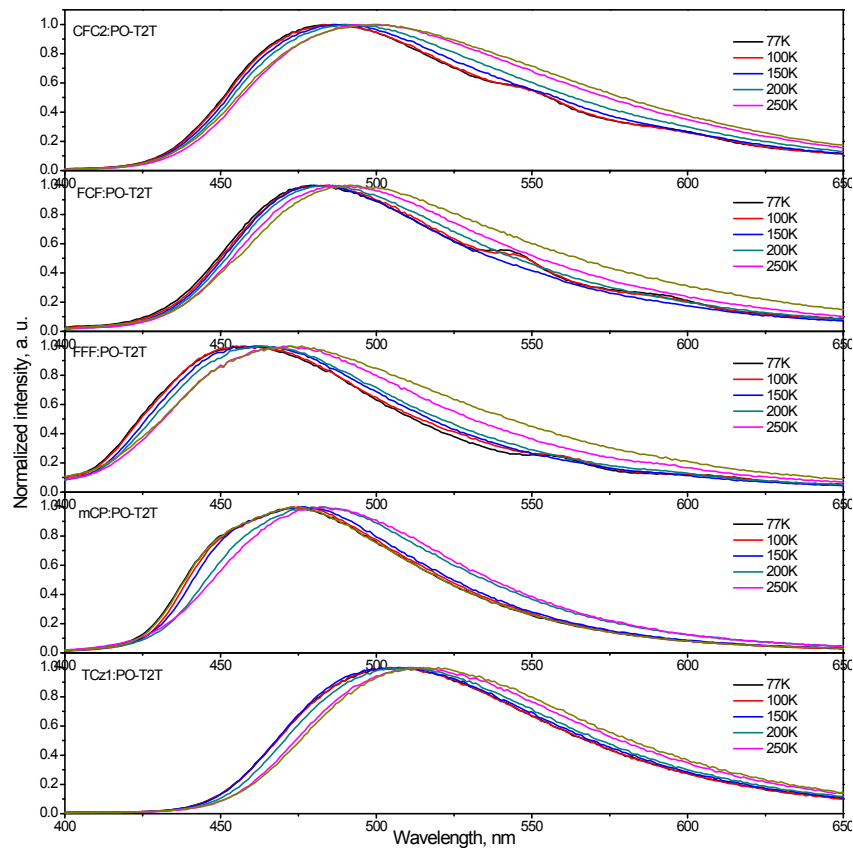
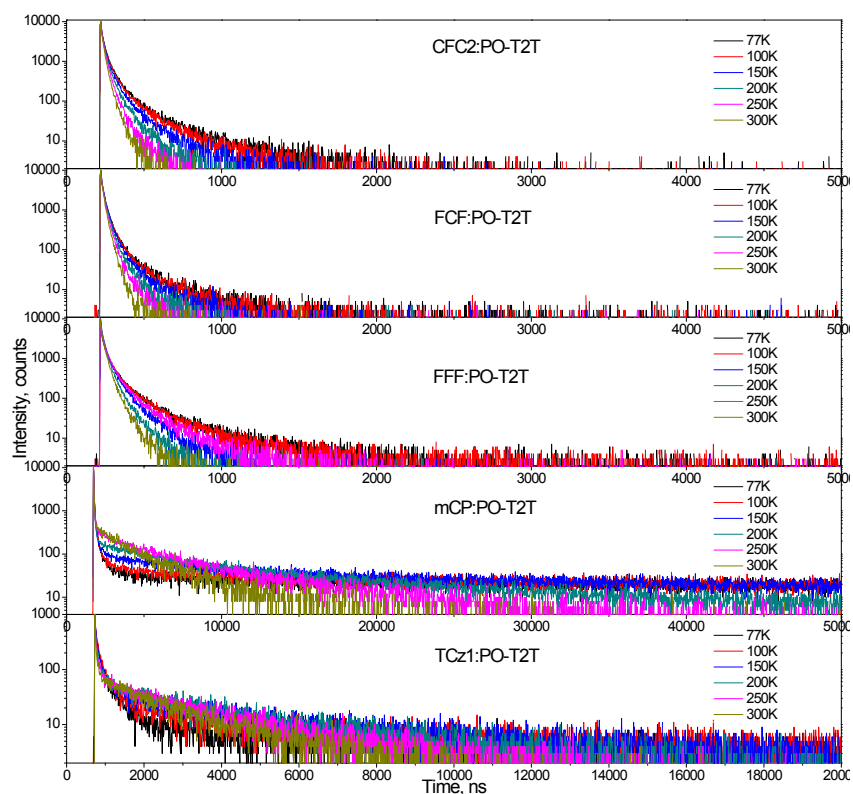


Figure S2. PL decays of pure donors and acceptor TCz1, FCF, CFC2, FFF, mCP, and PO-T2T and their solid-state mixtures TCz1:PO-T2T, FCF:PO-T2T, CFC2:PO-T2T, FFF:PO-T2T and mCP:PO-T2T. In comparison to PL decays of pure compounds, the long-lived component of PL decays of the studied mixtures indicate the exciplex formations.



a)



b)

Figure S3. PL spectra (a) and PL decays (b) of the studied solid-state mixtures TCz1:PO-T2T, FCF:PO-T2T, CFC2:PO-T2T, FFF:PO-T2T and mCP:PO-T2T at different temperatures.

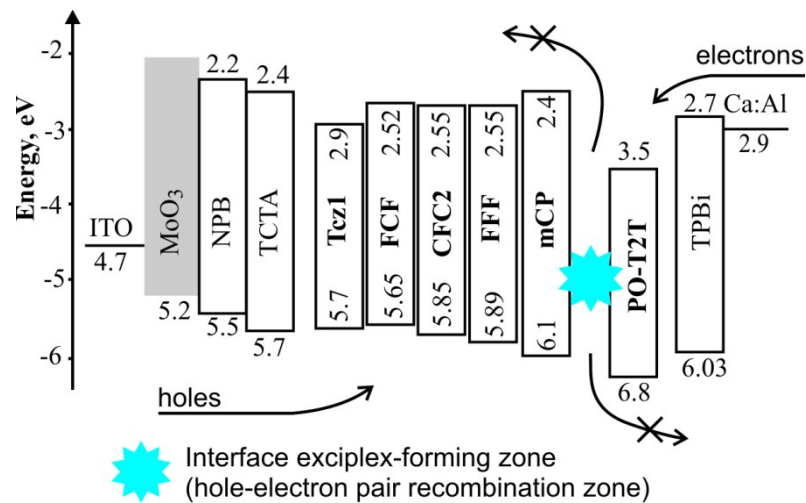
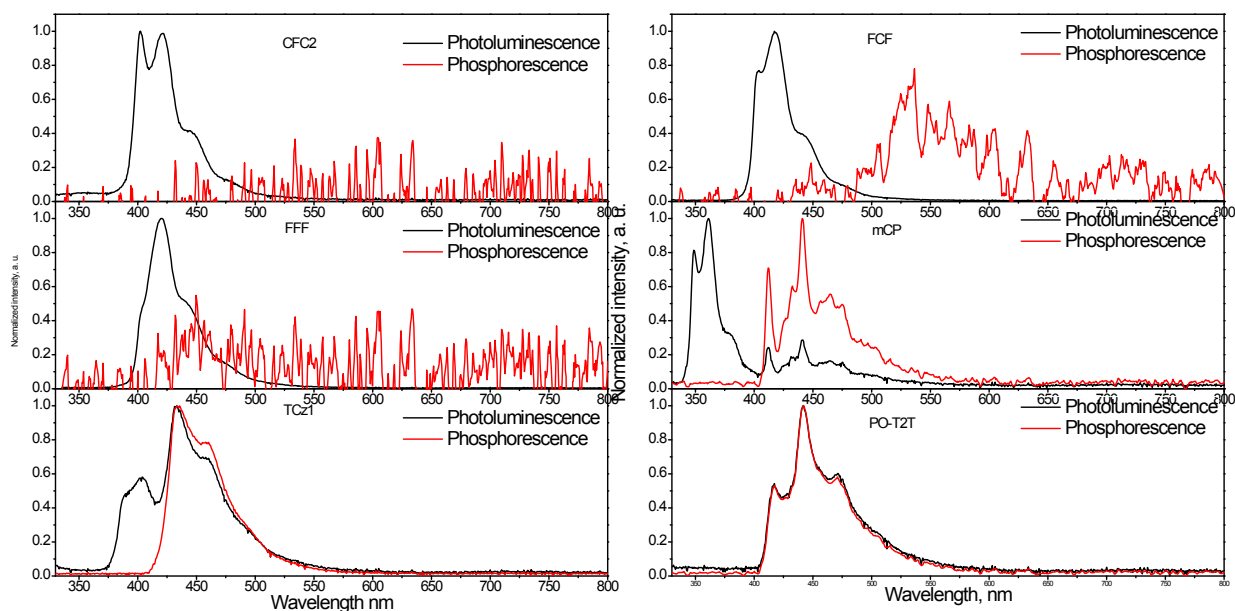
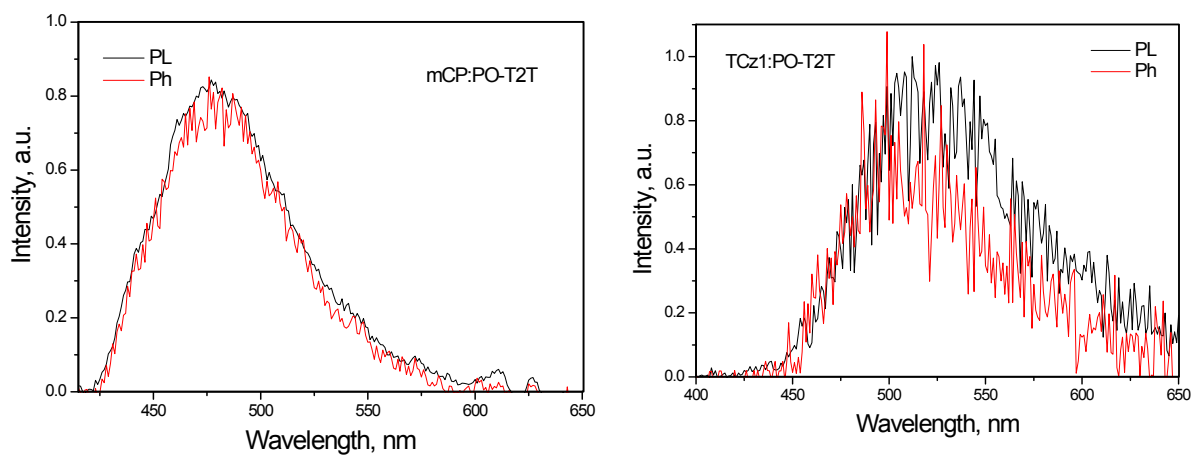


Figure S4. Equilibrium energy diagrams of the fabricated devices.



a)



b)

Figure S5. Photoluminescence and phosphorescence (recorded 50 ms after excitation) spectra of the THF solutions of TCz1, FCF, CFC2, FFF, mCP and PO-T2T recorded at 77K (a). Photoluminescence and phosphorescence (recorded 100 μ s after excitation) spectra of the studied solid-state mixtures mCP:PO-T2T and TCz1:PO-T2T at 77 K (b).

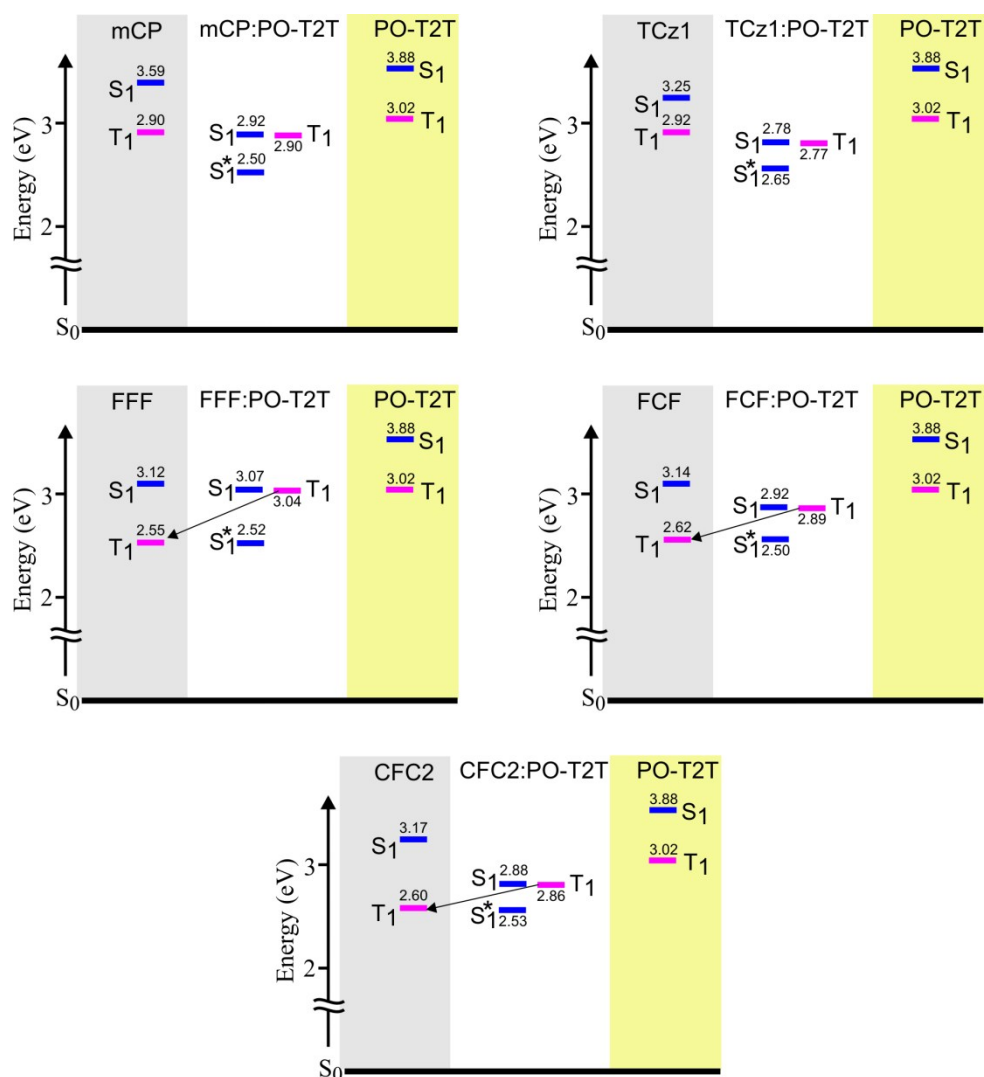
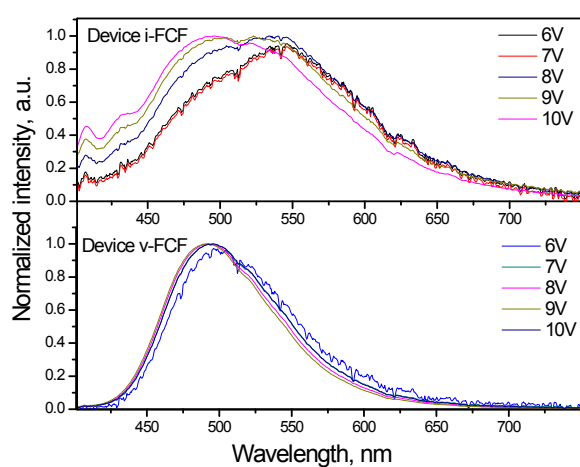
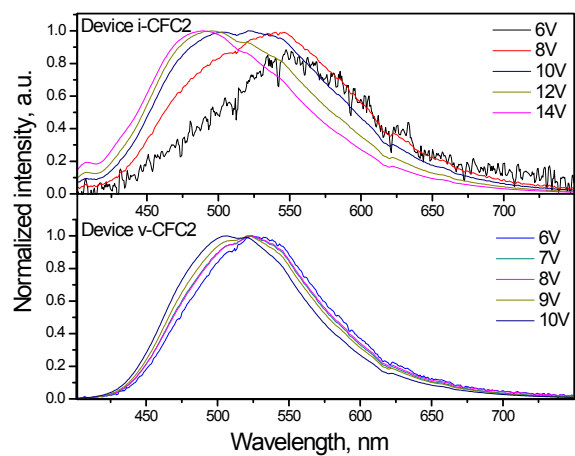


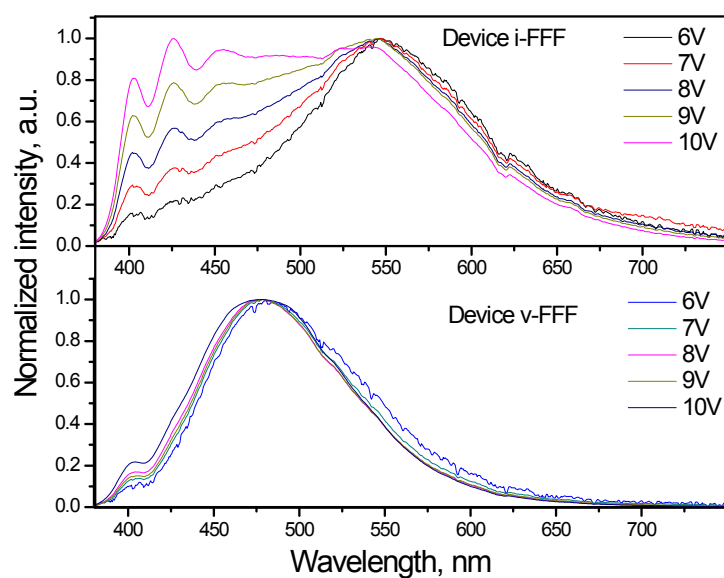
Figure S6. Jablonski diagrams for the tested exciplex-forming systems. S₀, S₁, and T₁ are ground, the first excited singlet and the first excited triplet energy levels. S*₁ is the first excited singlet which is taken from EL spectra of the annealed devices. The possible energy-losses through the triplet levels of selected donors are marked by the arrows.



a)



b)



c)

Figure S7. EL spectra at different voltages for devices i-FCF, i-CFC2, i-FFF and v-FCF, v-CFC2, v-FFF with the emitting layers based on the interface (i) and volume (v) exciplexes, respectively (a-c). High-energy bands are related to emission of donors in the devices i-FCF, i-CFC2, i-FFF.

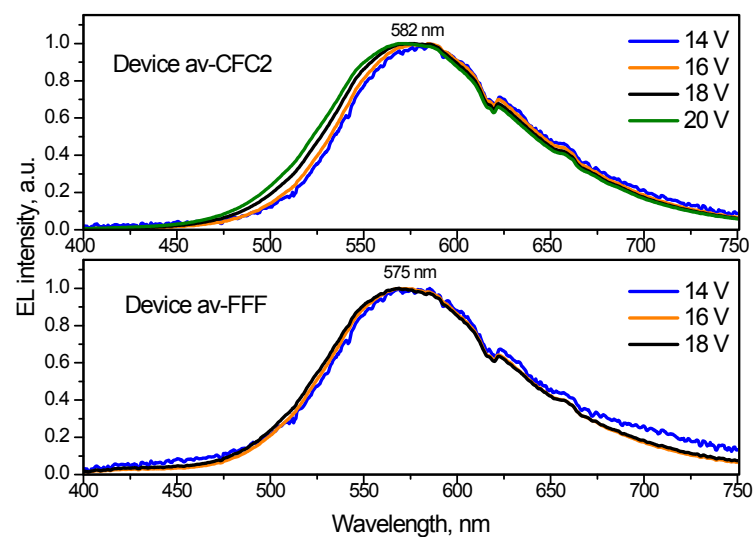
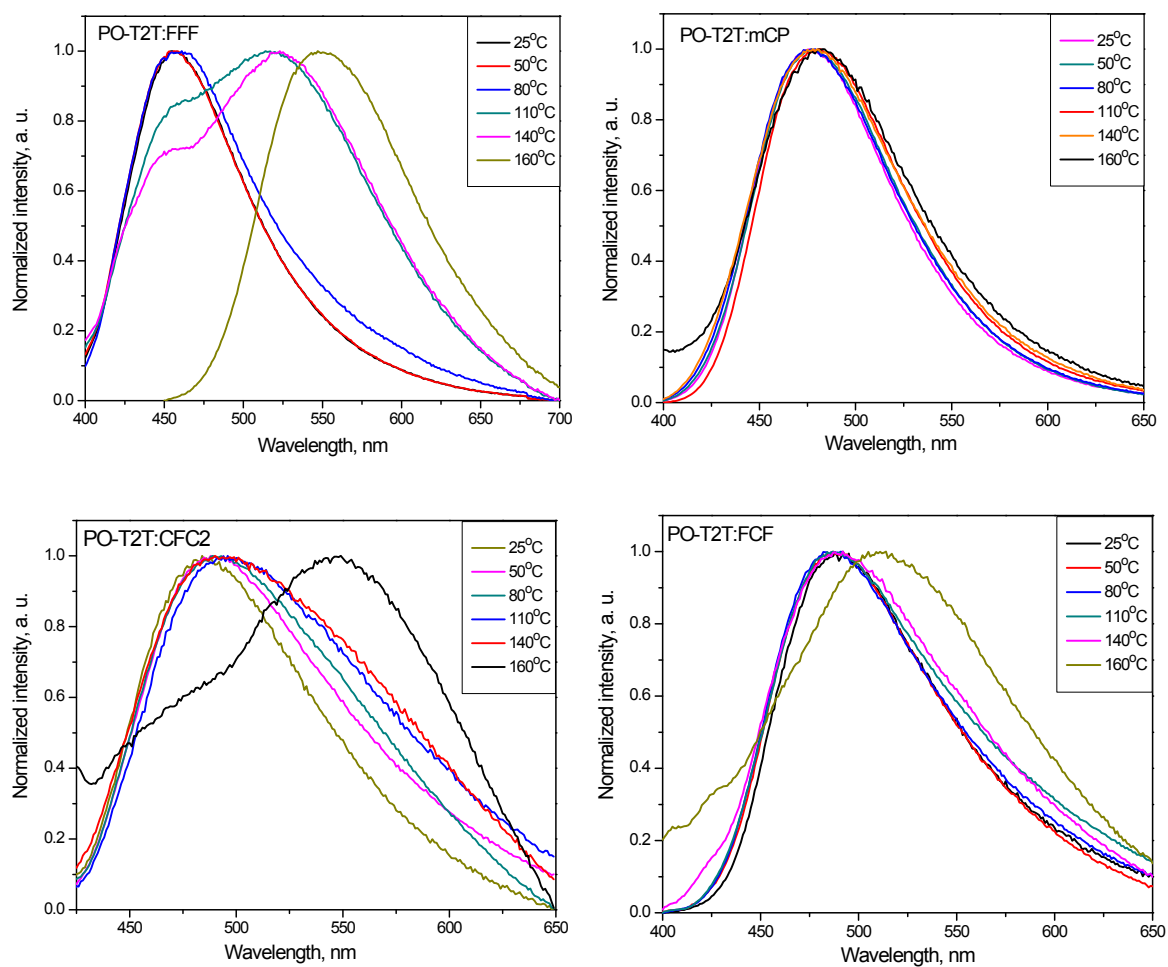


Figure S8. EL spectra of devices av-CFC2 and av-FFF.



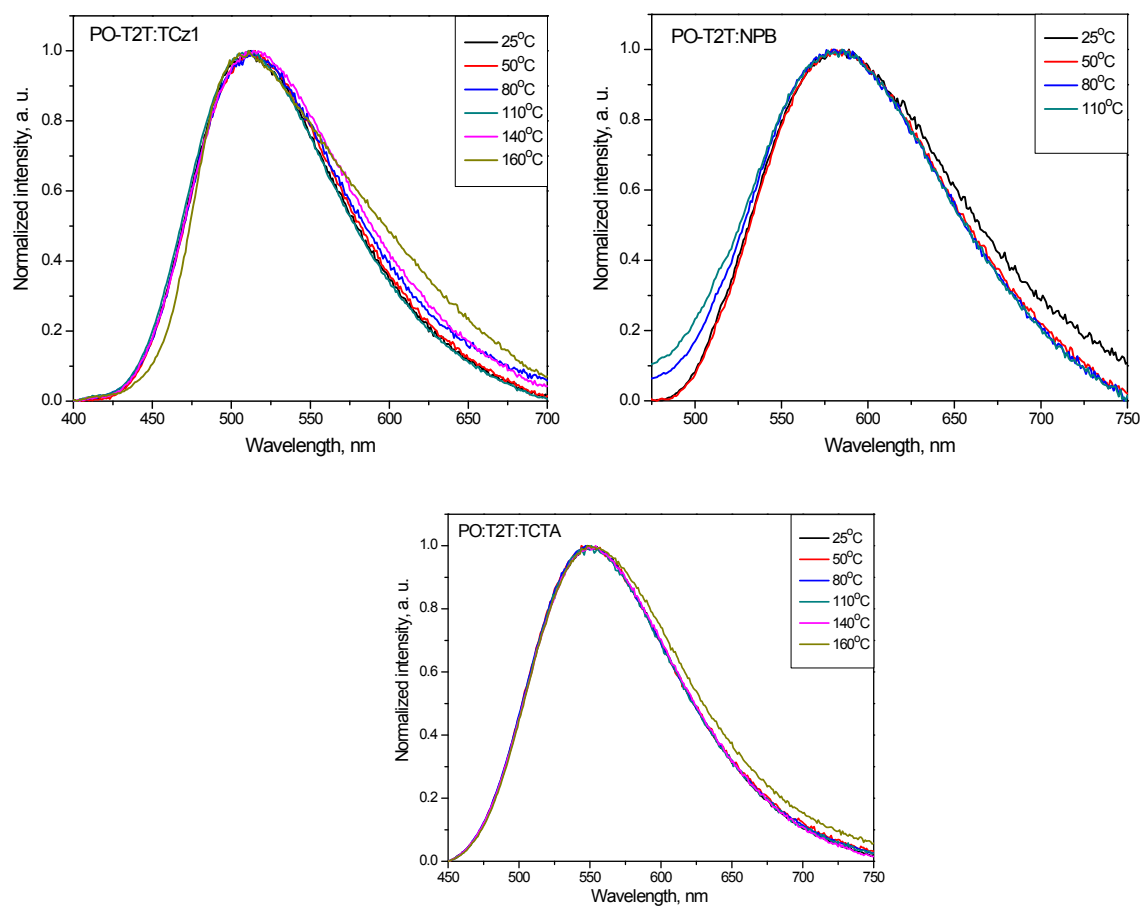


Figure S9. PL spectra of annealed and non-annealed studied films at different temperatures.

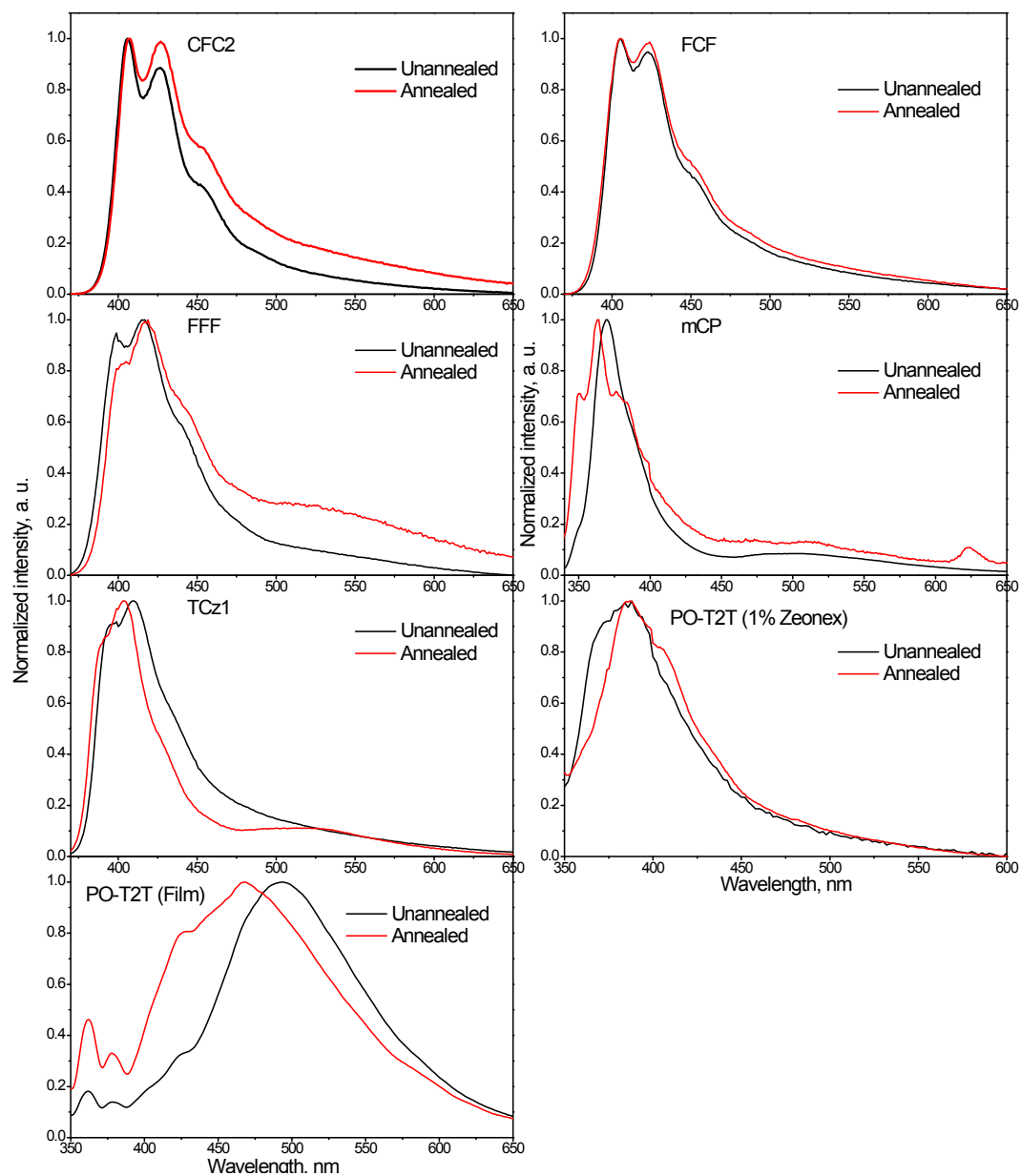


Figure S10. PL spectra of non-doped films for TCz1, FCF, CFC2, FFF, mCP and PO-T2T before and after annealing.

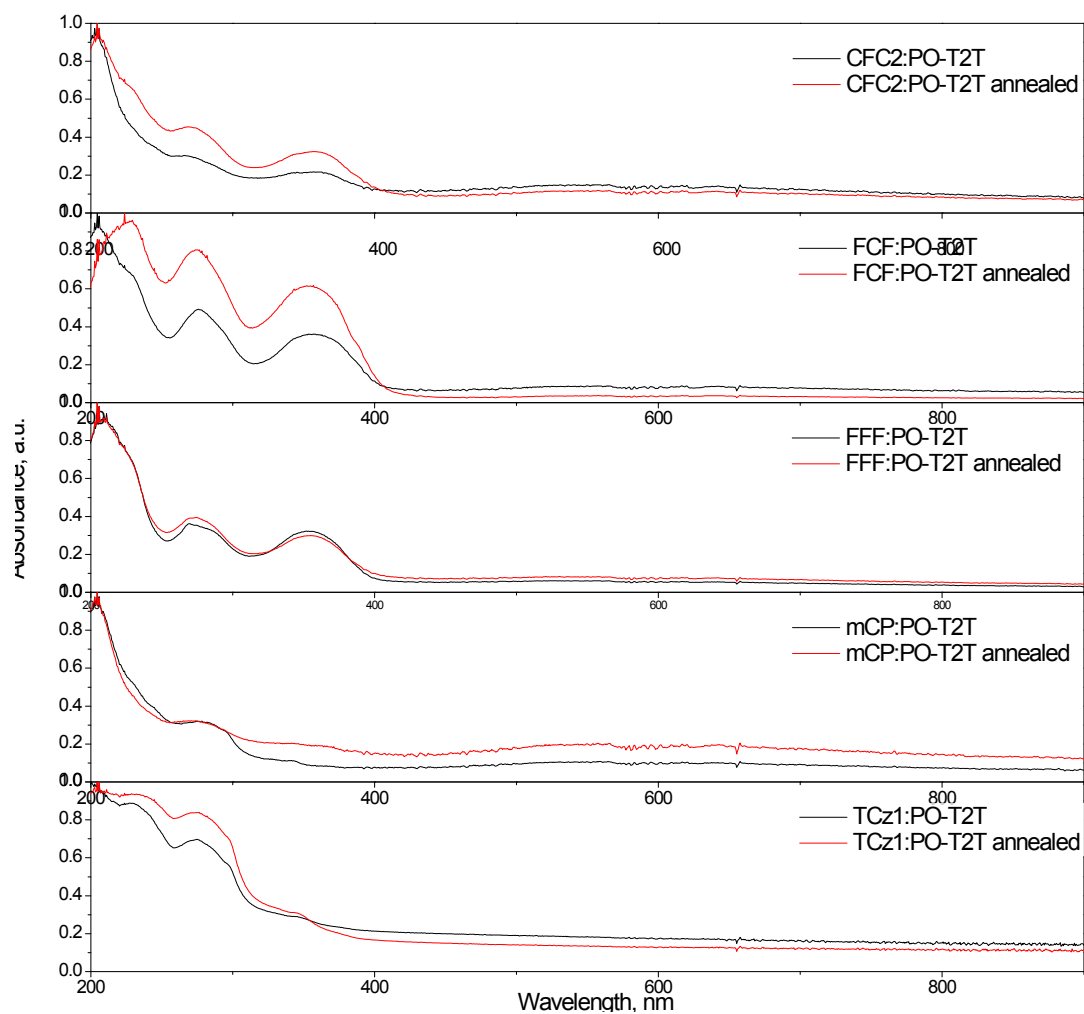


Figure S11. UV absorbance spectra of the studied samples before and after annealing.

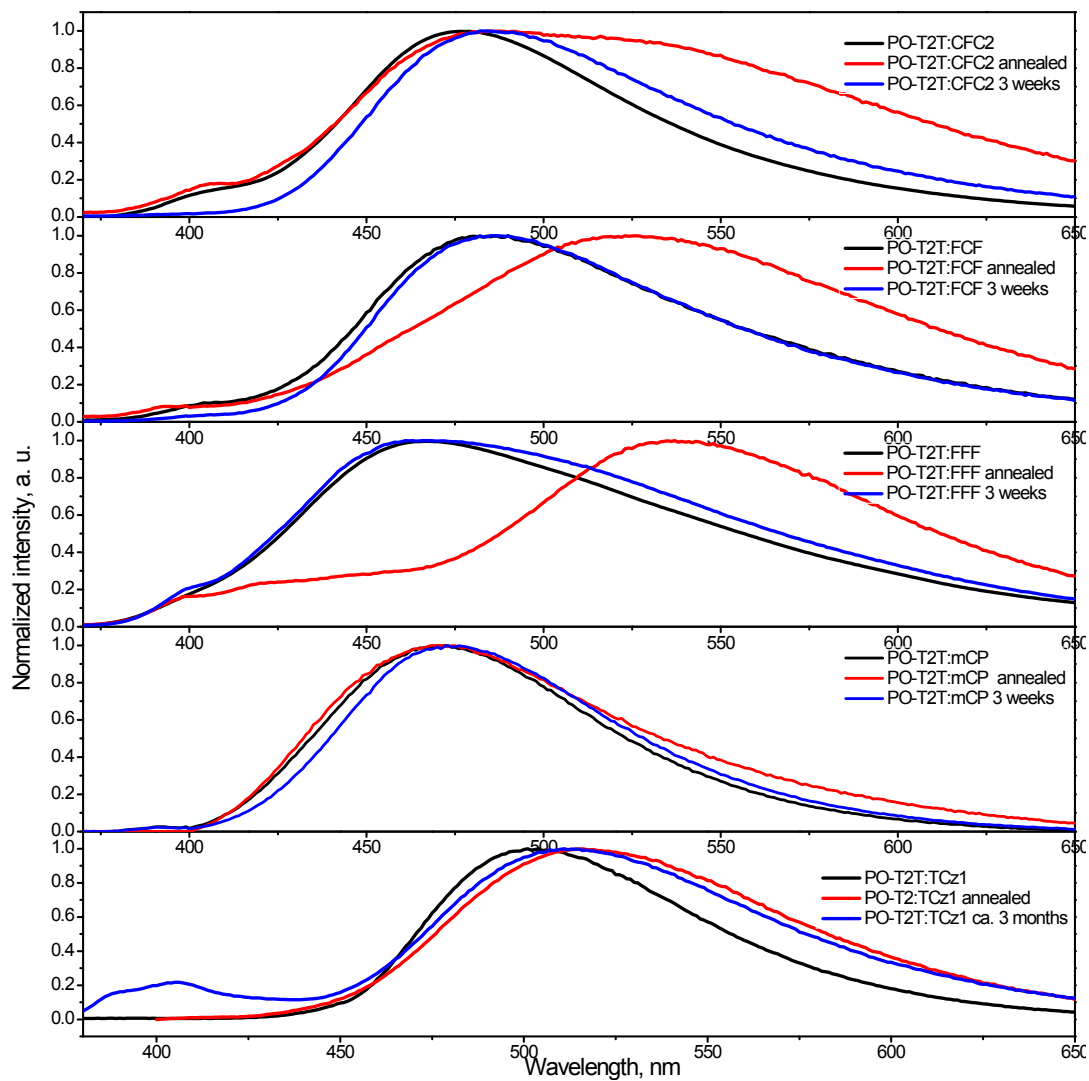


Figure S12. PL spectra high-energy and low-energy emission of the exciplexes recorded after preparation samples and after they were kept during three weeks in laboratory conditions.

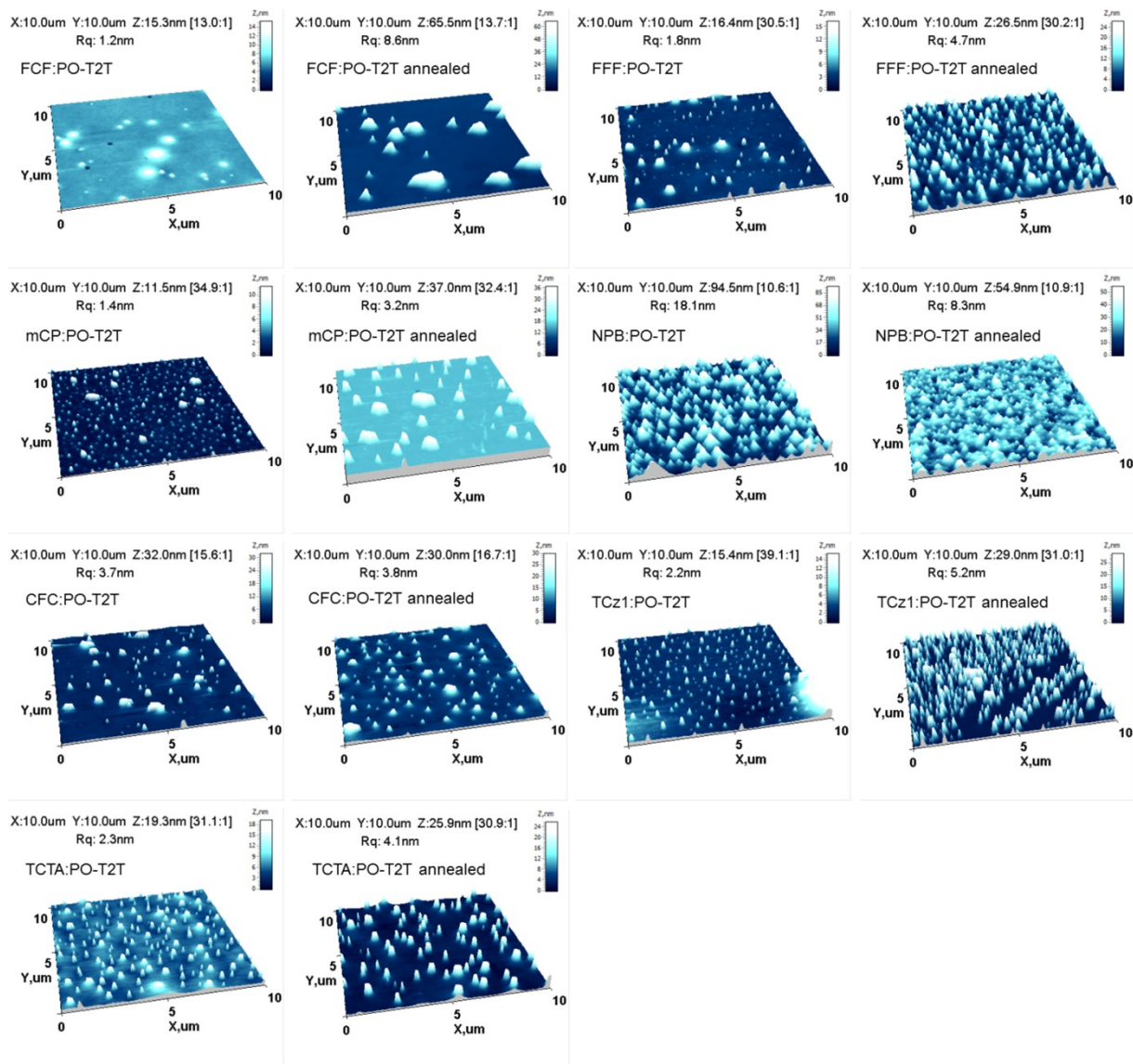


Figure S13. AFM topographical images with normalized Z axis in nm of spin coated solid-state mixtures FCF:PO-T2T, mCP:PO-T2T, CFC:PO-T2T, TCTA:PO-T2T, NPB:PO-T2T, FFF:PO-T2T and TCz1:PO-T2T on glass substrates before and after annealing with root mean square roughness (Rq) indicated, respectively.

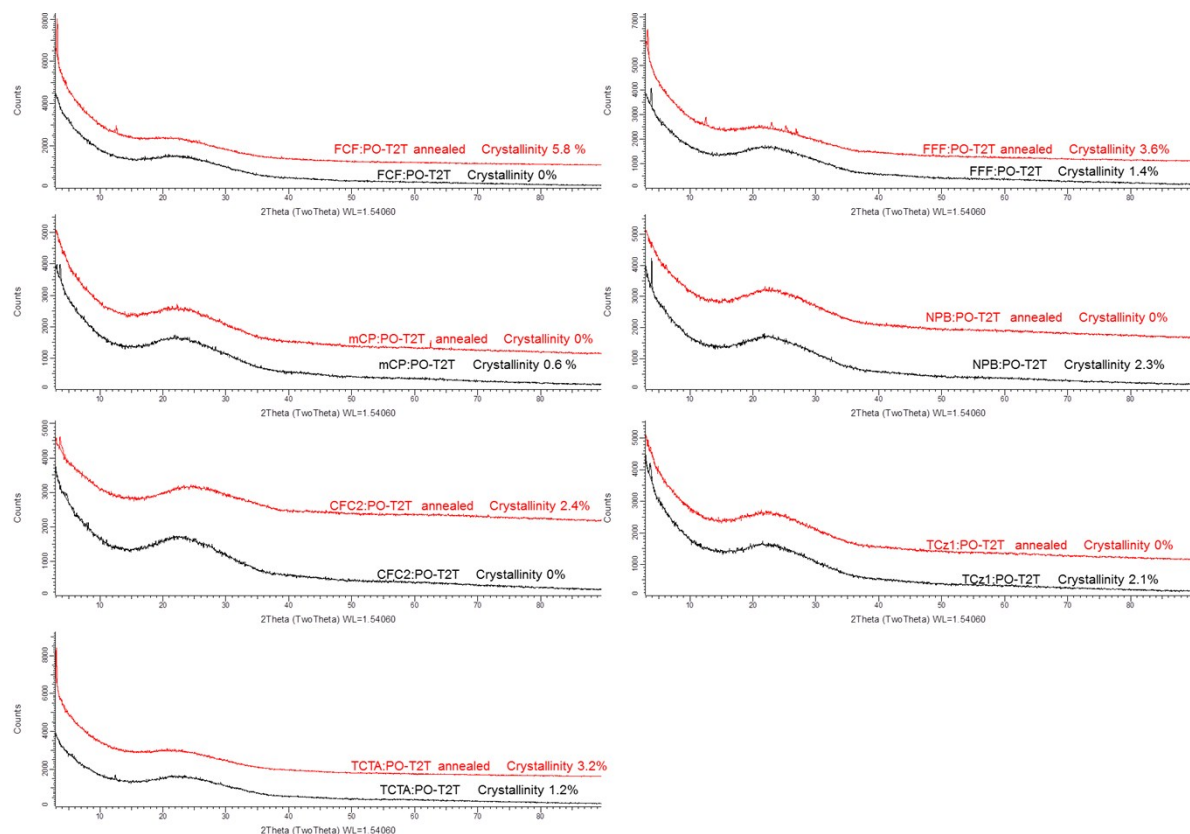


Figure S14. X-ray diffraction patterns of solid-state mixtures FCF:PO-T2T, mCP:PO-T2T, CFC2:PO-T2T, TCTA:PO-T2T, NPB:PO-T2T, FFF:PO-T2T and TCz1:PO-T2T on glass substrates before and after annealing with crystallinity values indicated.

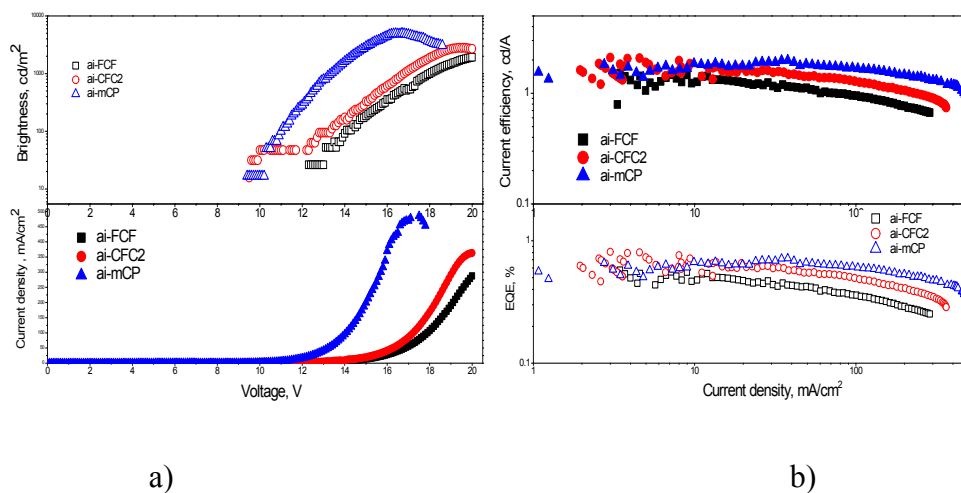


Figure S15. Current density/brightness versus applied voltages (a); and current/external quantum efficiencies versus applied current densities (b) for annealed interface exciplex-based devices ai-FCF, ai-CFC2, and ai-mCP with structures ITO/ MoO₃ (0.4nm)/ NPB (30nm)/ TCTA (15nm)/ FCF, CFC2, or mCP (10nm)/ PO-T2T (10nm)/ TPBi (60 nm)/ LiF (0.4 nm)/ Al (60nm), respectively.

To obtain the ratio of the low-energy state which contributed to device efficiencies, we fitted the PL spectra of annealed exciplex-forming systems by Gaussian fitting with two peaks (Figure S16). The fitting was done in OriginPro program. The ratio of the low-energy state was presented in Table 1 as relationship of area 2 to area 1 (area2/area1) where area 1 is related to high-energy spectra while area 2 is related to low-energy spectra. The obtained ratio area2/area1 approximately present the ratio of the low-energy state since high-energy spectra (peak 1) and low-energy spectra (peak 2) are characterized by different maxima and different shapes in comparison to those of EL spectra of non-annealed and annealed devices (Figure S18). However, even at such approximants, it is seen that high EQE values are related to low area2/area1 values thus low ratio of the low-energy state to whole exiplexes (Table 1). While, low EQE values related to high area2/area1 values thus high ratio of the low-energy state (Table 1).

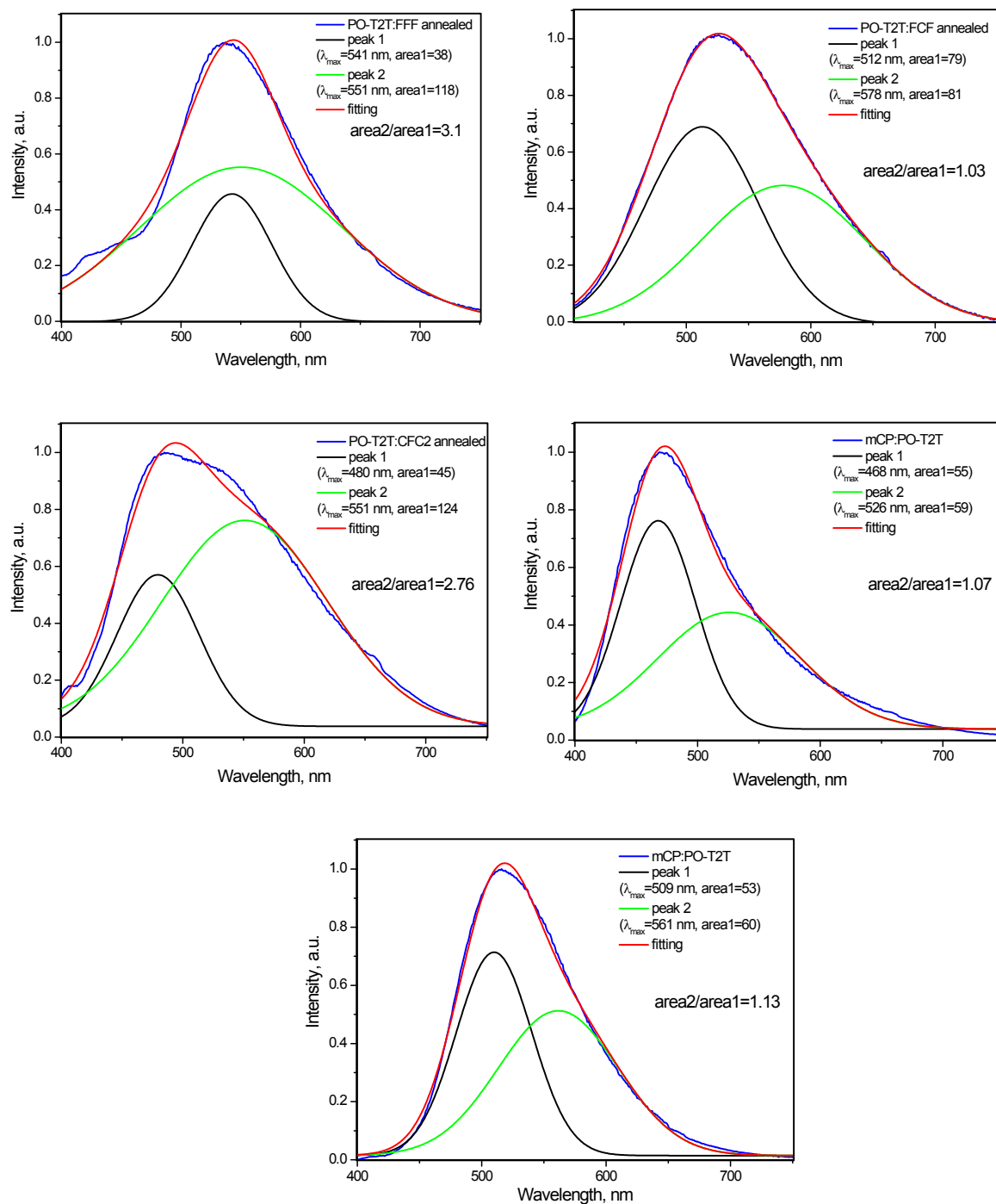


Figure S16. PL spectra and Gaussian fitting results for annealed exciplex-forming systems.

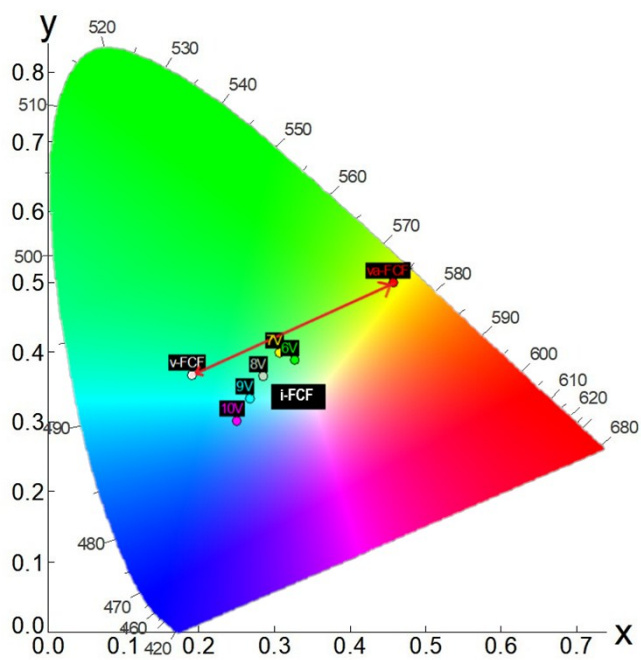


Figure S17. CIE coordinates at different voltages and photo of the device i-FCF at 8V.

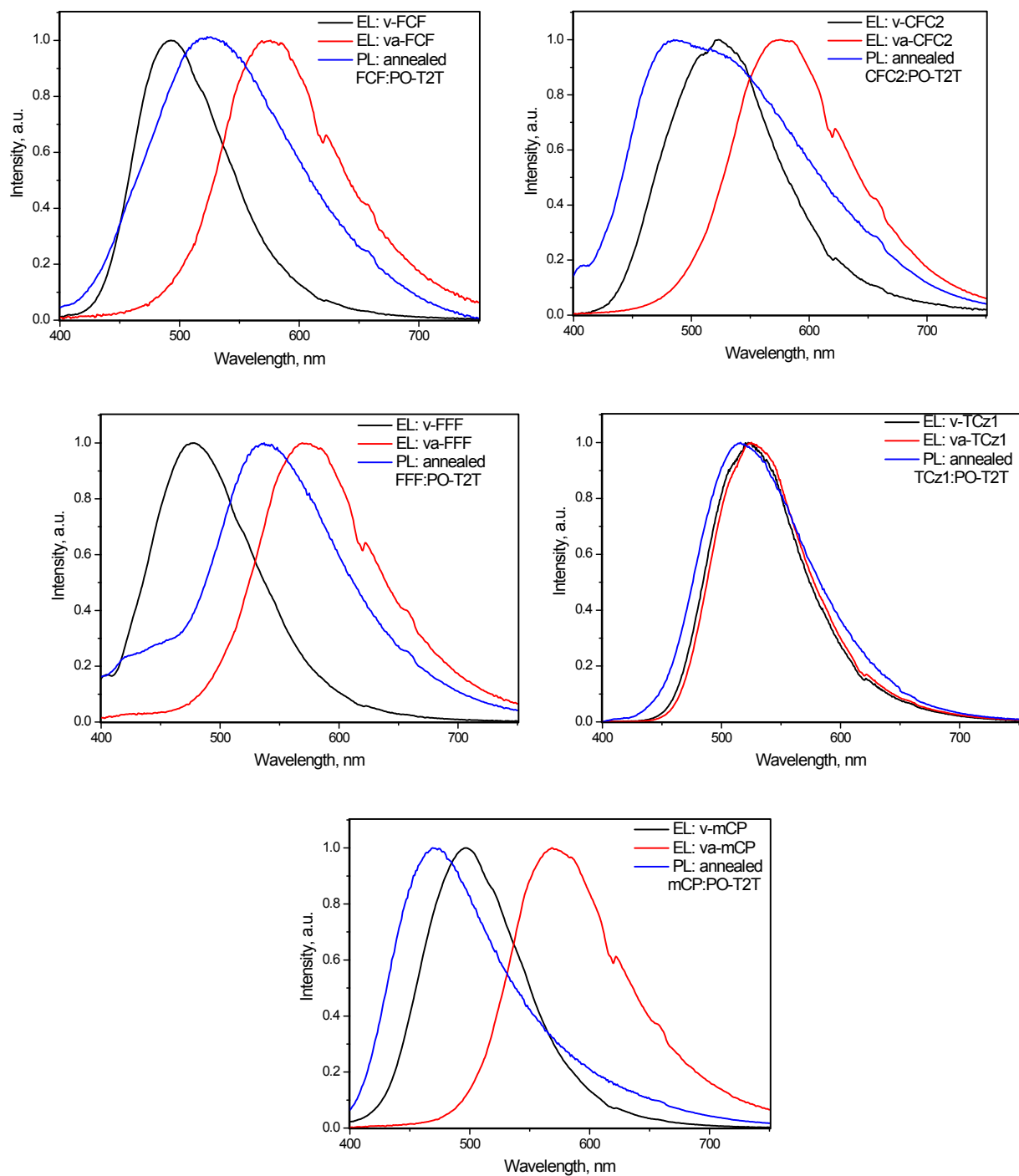


Figure S18. PL spectra of annealed exciplex-forming systems and EL spectra of non-annealed and annealed devices.