Supplementary Information on

"Effect of triphenylsulfonium triflate addition in wide band-gap polymer light-emitting diodes: improved charge injection, transport and electroplex-induced emission tuning"

by

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Luminance turn-on voltage

The luminance – voltage characteristics of OLEDs based on CN-PPP, 15% wt. TPS-triflate and 30% wt. TPS-triflate in CN-PPP active layer for luminance values 0-12 cd/m^2 are depicted in Figure S1. From this plot the luminance turn-on voltage, which is defined here as the voltage where luminance equals 1 cd/m^2, can be easily discerned (see also relevant text in the main manuscript).
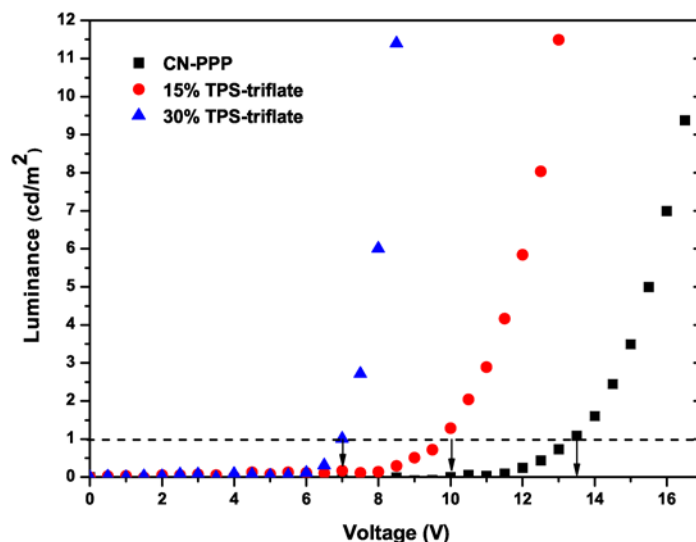

Fig. S1: *Enlarged region of Fig. 3b of the main manuscript depicting the luminance turn-on voltage of OLEDs based on CN-PPP (black squares), 15% wt. TPS-triflate (red circles) and 30% wt. TPS-triflate (blue triangles) in CN-PPP active layer.*

Photoluminescence quenching analysis

According to Stern-Volmer theory, dynamic (collisional) quenching is due to collisions between quenching agents and fluorophores, whereas in static quenching, the quenching agent forms a non-fluorescent complex with the quenching agent. Since from the photoluminescence data we do not have any indication for exciplex formation (see time-resolved photoluminescence study presented below), we restrict our analysis in terms of dynamic quenching, which is characterised by the Stern-Volmer equation:

$$I_0/I = 1 + K_D[Q],$$

where I_0 and I is the fluorescence intensity in the absence and presence of a quencher, respectively, K_D is the Stern-Volmer dynamic quenching constant and $[Q]$ is the concentration of the quenching agent. So, if we plot the (I_0/I)-1 = $f([TPS])$, where $[TPS]$ is the TPS % mol concentration, we get a linear plot, which is depicted in Fig. S2.
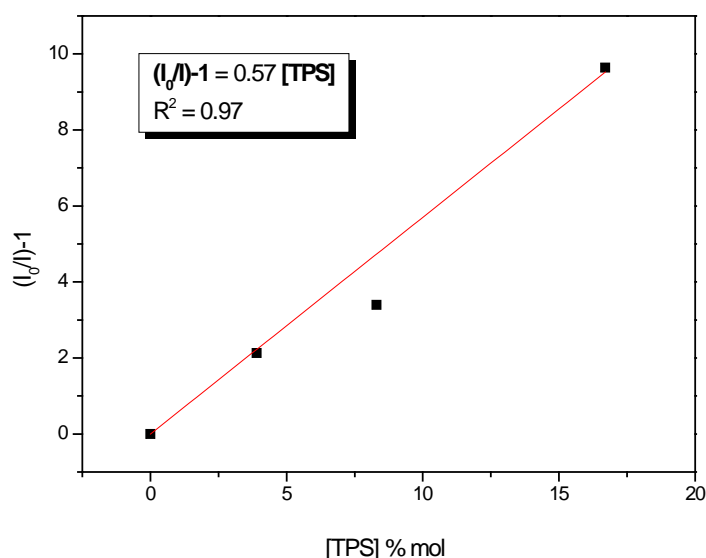
Fig. S2: *Stern-Volmer plot depicting data of CN-PPP PL Intensity $(I_0-I)-1$ as a function of TPS % mol concentration and the linear fit (straight line) to these data.*

The TPS % mol concentration was calculated as the percentage of TPS-triflate mol versus monomer mol (see Table S1 below). To be more accurate, we should take into account that the excited state is not formed in a single monomer unit but in the so-called conjugated length, which involves usually 3-5 monomer units, and then we would get the TPS % mol concentrations that are mentioned in Table S1. This approximation does not change the linearity of the plot and since we do not perform any quantitative analysis here, we chose to present the TPS % mol concentration versus the monomer unit for simplicity reasons.

Table S1: *Correlation between TPS % wt and % mol concentration in the solid polymer film. The % mol concentration was calculated towards both single monomer unit and conjugated length of the polymer, which was approximated to 4 monomer units.*

TPS %wt	gr TPS-triflate	gr pol	mol TPS	mol monomer	mol conj. length (4 units)	TPS % mol	[TPS] % mol (4 units)
0%	0	100	0	0.437	1.747	0	0
7%	7	100	0.017	0.437	1.747	3.9	1
15%	15	100	0.036	0.437	1.747	8.3	2.1
30%	30	100	0.073	0.437	1.747	16.7	4.2

CN-PPP PL spectra versus polymer solution concentration

As the solution becomes more concentrated, a shoulder appears at 440 nm owing probably to increased aggregate formation in the solution. Note that the shape of the

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spectrum does not depend on the spin-coating speed and consequently on the film thickness but rather on the initial concentration of the solution.
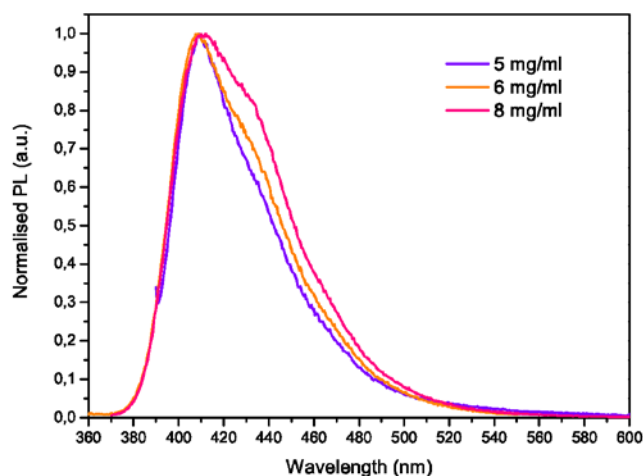

Fig. S3: *Normalised PL spectra of CN-PPP films spin-cast on quartz substrates from chloroform solutions with different concentrations. The solutions were not filtered and the spin-coating speed was adjusted so that all films had a thickness of about 80 nm.*

Time-resolved PL study

In order to clarify the origin of the above spectral feature and check if it is related to an excimer formation, we performed time-resolved photoluminescence measurements in CN-PPP films and films containing 15% wt of TPS-triflate in CN-PPP. The fluorescence decay curves have been analyzed at the maximum emission wavelength (410 nm) as well as at the blue (390 nm) and at the red edge of the spectrum (440 nm). The photoluminescence decay of the pristine CN-PPP film at 410 nm was fitted by a bi-exponential curve ($\chi^2 = 0.93$) with a short ~300 ps (70%) and a longer ~750 ps (30%) lifetime components. The short lifetime component became dominant when the fluorescence decay was recorded at the blue edge of the spectrum (λ_{em} = 390 nm), whereas the longer lifetime prevailed at the red edge of the spectrum (λ_{em} = 440 nm). These observations upon monitoring the excited state decay at increasing emission wavelengths indicate an enhanced contribution in the emission from lower energy sites with reduced decay rate. Upon addition of 15% TPS-triflate, the lifetime was reduced down to *ca.* 180 ps, approaching the instrumental pulse profile. According to the experimental data presented here the formation of an excimer species between excited and ground state polymeric chain segments is not unambiguously confirmed, since both lifetimes are extremely short, whereas excimer emission is generally characterized by slower decay rates.