## **Supplementary Information for**

# A Hydrophilic Monodisperse Conjugated Starburst Macromolecule with Multidimensional Topology as Electron Transport/Injection Layer for Organic Electronics

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1.1 Optical properties of TrOH in various solvents.

| <b>Table S1.</b> Optical properties of TrOH in various solve |
|--|
|--|

| Compound - | $\lambda_{(abs)}^{a}$ (nm) |      |     |      |      |      | $\lambda_{(em)}^{b}$ (nm) |      |      |      |      |      |
|------------|----------------------------|------|-----|------|------|------|---------------------------|------|------|------|------|------|
|            | THF                        | DMSO | DMF | EtOH | MeOH | Film | THF                       | DMSO | DMF  | EtOH | MeOH | Film |
| TrOH       | 364                        | 368  | 365 | 360  | 359  | 368  | 404,                      | 409, | 407, | 402, | 402, | 414, |
|            |                            |      |     |      |      |      | 427                       | 431  | 429  | 424  | 424  | 434  |

<sup>*a*</sup> Absorption peak. <sup>*b*</sup> Emission peak.

#### 1.2 Device performance with TrOH/Al as cathode



Fig. S1 a) Current efficiency vs. brightness; b) EL spectra of the devices with TrOH/Al at vaying

driving voltages.

#### 1.3 Device performance with TrOH/Ag as cathode



Fig. S2 Device performance of ITO/PEDOT:PSS/F3Py/TrOH/Ag: a) Current density and brightness

vs. voltage; b) luminous efficiency vs. current density.

Table S2 Device performance of ITO/PEDOT:PSS/F3Py/TrOH/Ag

| Cathode | V <sub>on</sub> <sup>a</sup><br>(V) | Luminance<br>(max)<br>(cd m <sup>-2</sup> ) | $LE_{max}$ (cd A <sup>-1</sup> ) |  |
|---------|-------------------------------------|---|----------------------------------|--|
| TrOH/Ag | 7.7                                 | 771   | 0.31                             |  |

<sup>a</sup>Turn-on voltage at a brightness of 1 cd m<sup>-2</sup>

1.4 Device performance of TrOH as ETL in comparison with those of its polymer counterpart

### PFN-OH with varying batches and small-molecule counterpart DIFN-OH



Fig. S3 Device performance with configuration of ITO/PEDOT:PSS/F3Py/ PFN-OH (from different batch), or DIFN-OH, or TrOH/Al

Table S3. Device performance with configuration of ITO/PEDOT:PSS/F3Py/ PFN-OH (from different batch), or DIFN-OH, or TrOH/Al

|         | ,       |         |      |          |                   |                  |
|---------|---------|---------|------|----------|-------------------|------------------|
|         | Mn      | Mw      | PDI  | $V_{on}$ | LE <sub>max</sub> | L <sub>max</sub> |
|         | (g/mol) | (g/mol) |      | (V)      | (cd/A)            | $(cd/m^2)$       |
| PFN-OH  | 17000   | 62200   | 3.54 | 2.1      | 0.68              | 2636             |
| Batch 1 | 17900   | 03300   |      | 5.1      | (at 5.2 V)        | (at 8.3 V)       |
| PFN-OH  | 12000   | 22200   | 1.80 | 2.1      | 1.96              | 2208             |
| Batch 2 | 18000   | 32300   |      | 5.1      | (at 5.2 V)        | (at 7.2 V)       |
| PFN-OH  | 14400   | 44800   | 3.11 | 2.2      | 1.10              | 1399             |
| Batch 3 | 14400   |         |      | 5.2      | (at 5.2 V)        | (at 7.2 V)       |
| DIFN-OH | 1078.8  | 1079.5  | 1.00 | 2.0      | 0.33              | 2210             |
|         |         |         |      | 3.8      | (at 7.7V)         | (at 8.3 V)       |
| TrOU    | 3908.8  | 3911.6  | 1.00 | 26       | 3.01              | 8360             |
| IrOH    |         |         |      | 3.0      | (at 6.2 V)        | (at 7.2 V)       |
|         |         |         |      |          |                   |                  |



Fig. S4 Structure of DIFN-OH

#### 1.5 Film morphology



**Fig. S5** 3D atomic force microscopy (AFM) image of (a)PFN-OH atop F3Py/PEDOT:PSS/ITO (b)TrOH atop F3Py/PEDOT:PSS/ITO. The size of the image is 5 μm ×5 μm.



Fig. S6 Atomic force microscopy (AFM) image image TrOH atop ITO. The size of the image is 2  $\mu$ m ×2  $\mu$ m.



**Fig. S7** Dynamic light scattering (DLS) of PFN-OH (0.2 mg/mL) and TrOH (3 mg/mL) in ethanol **1.5 NMR and Mass spectra** 



Fig. S8 <sup>1</sup>H NMR spectra of 6.



**Fig. S9**  $^{13}$ C NMR spectra of **6**.



Fig. S10<sup>1</sup>H NMR spectra of PreTF2.



Fig. S11 <sup>13</sup>C NMR spectra of **PreTF2**.







