Supporting Information for

Probing charge behaviour in multilayer organic light-emitting diodes via electronic sum-frequency generation spectroscopy

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Figure S1. The energy diagrams with respect to the vacuum level of the organic materials used in each OLED device. HOMO/LUMO energies of each material and the work functions of IZO and Mg:Ag in **Fig. S1** are cited from below references.

References

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Figure S2. Spectral bandwidth of the output light when 1064 and 532 nm lights are irradiated to OLED1 at 62° and 70°, respectively.



Figure S3. ESFG spectrum of the 100 nm thick HAT-CN film on CaF₂. Polarization combination is ppp.



Figure S4. Transient ESFG (rise and fall) intensities of three different OLED devices at four visible wavelengths upon the application of the square wave pulse bias.



Figure S5. Transient EL emission of three OLED devices when square wave pulse voltage is applied.