Supporting information

Less is More; Dilution Enhances Optical and Electrical Performance of a TADF Exciplex

Marco Colella^{*a*}, Andrew Danos^{*a**}, Andrew P. Monkman^{*a**}

^a Department of Physics, Durham University, South Road, DH1 3LE, UK

*Email: andrew.danos@durham.ac.uk *Email: a.p.monkman@durham.ac.uk

METHODS

Device fabrication OLEDs were fabricated on patterned ITO coated glass (VisionTek Systems) with a sheet resistance of 15 Ω /sq. Oxygen-plasma cleaned substrates were loaded into a Kurt J. Lesker Super Spectros deposition chamber, and both the small molecule and cathode layers thermally evaporated at pressure below 10⁻⁷ mbar. The materials used for the production of the devices were: N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) as hole injection layer (HIL), 4,4'-(Diphenylsilanediyl)bis(N,N-diphenylaniline) (TSBPA) as hole transporting layer (HTL) and exciplex donor, 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) as exciplex acceptor and electron transporting layer (ETL), lithium fluoride (LiF) as electron injection layer, and aluminium

(Al) cathode. 1,3-Bis(triphenylsilyl)benzene (UGH-3) or Bis[2(diphenylphosphino)phenyl]ether oxide (DPEPO) were used as host materials. NPB, UGH-3
and DPEPO were purchased from Sigma Aldrich and sublimed before use. TSBPA and POT2T were purchased from Lumtec and used as received.

Device characterization Freshly evaporated devices were encapsulated under inert atmosphere using UV-curable epoxy (DELO Katiobond) along the outer edges of the active area with a glass coverslip. Devices were then transferred into a calibrated 10-inch integrating sphere (Labsphere) and their electrical properties measured using an Agilent Source Measure Unit (6632B). Emission spectra were simultaneously measured using a calibrated fibre coupled spectrometer (Ocean optics USB4000).

Optical film characterization All photophysical measurement were performed on 100 nm thick vacuum deposited films on sapphire substrates to avoid any formation of aggregates. Steady-state absorption and emission spectra were acquired using a UV-3600 Shimadzu spectrophotometer and a Jobin Yvon Horiba Fluoromax-3 fluorimeter, respectively. Photoluminescence quantum yields were measured using a calibrated integrating sphere (Labsphere) with a 340 nm fibre coupled LED (Thorlabs M340L4) as excitation source and a fiber coupled USB UV-Vis spectrometer (Ocean Optics HR2000) for detection. The sphere was flushed with a stream of dry nitrogen gas for at least 30 minutes before measurement to prevent oxygen quenching of triplets.

Time-resolved emission spectra Spectra for decay series were obtained by exciting the sample under vacuum with a sub-nanosecond pulsewidth Nd:YAG laser (EKSPLA), using $\sim 100 \ \mu$ J of 355 nm output. A 337 nm nitrogen laser and ND filter wheel were used for power

dependence series. Sample emission was detected with a spectrograph and sub-nanosecond gated iCCD camera (Stanford Computer Optics).

SUPPORTING FIGURES



Figure S1 Normalised absorption spectra of evaporated neat TSBPA, neat PO-T2T and TSBPA:PO-T2T films.



Figure S2 Absorption spectra of evaporated TSBPA:PO-T2T exciplex films with increasing vol% of UGH-3.



Figure S3 Absorption spectra of evaporated TSBPA:PO-T2T exciplex films with increasing vol% of DPEPO.



Figure S4 (A) Room temperature photoluminescence decays of evaporated TSBPA:PO-T2T exciplex film. (B) Photoluminescence spectra of TSBPA:PO-T2T 1:1 ratio evaporated film at different delay times. (C) Linear fit of the log of the integrated intensity vs log of the laser power of TSBPA:PO-T2T 1:1 ratio evaporated film.



Figure S5 (A) Room temperature photoluminescence decays of evaporated TSBPA:PO-T2T exciplex films with increasing vol% of DPEPO. (B-F) Photoluminescence spectra of TSBPA:PO-T2T 1:1 ratio diluted in 10-90 vol% DPEPO evaporated film at different delay times.



Figure S6 (A) Room temperature photoluminescence decays of evaporated TSBPA:PO-T2T exciplex films with increasing vol% of UGH-3. (B-E) Photoluminescence spectra of TSBPA:PO-T2T 1:1 ratio diluted in 10-90 vol% UGH-3 evaporated film at different delay times.



Figure S7 (A-E) Linear fit of the log of the integrated intensity vs log of the laser power of TSBPA:PO-T2T 1:1 ratio evaporated film diluted in 10-90 vol% DPEPO.



Figure S8 (A-E) Linear fit of the log of the integrated intensity vs log of the laser power of TSBPA:PO-T2T 1:1 ratio evaporated film diluted in 10-90 vol% UGH-3.



Figure S9 (A) Room temperature photoluminescence decays of evaporated TSBPA:DPEPO and TSBPA:UGH-3 exciplex films. Photoluminescence spectra of (B) TSBPA:DPEPO and (C) TSBPA:UGH-3 1:1 ratio evaporated films at different delay times. (D) Distance dependence of residual donor emission (from main text Figure 2, UGH-3 series) corrected for differing exciplex PLQYs.