

1 **Efficient radical-based light-emitting diodes with doublet emission**

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15 Organic light-emitting diodes (OLEDs),¹⁻⁵ quantum-dot-based LEDs (QLEDs),⁶⁻¹⁰
16 perovskites-based LEDs¹¹⁻¹³ and micro-LEDs^{14,15} are in competition to provide the
17 basis for next-generation displays and active lighting, all offering attractive prospects
18 for lightweight and flexible units. Here we demonstrate efficient operation of
19 radical-based OLEDs,¹⁶ in which the emission comes from a spin doublet rather than a
20 singlet or triplet exciton. Whilst the emission process is still spin-allowed in these
21 systems, usefully, the classical triplet-limiting efficiency for OLEDs is circumvented
22 for doublets. Using a luminescent radical emitter, we demonstrate an OLED with
23 maximum external quantum efficiency (EQE) of 27% at a wavelength of 710 nm –
24 this being the highest reported value for deep-red/infrared LEDs. For a standard
25 closed-shell organic semiconductor, hole and electron states involve occupancy of
26 highest-occupied- and lowest-unoccupied molecular orbital, HOMO and LUMO, and
27 recombine to form singlet or triplet exciton states. Radical emitters have a
28 singly-occupied molecular orbital (SOMO) in the ground state, giving an overall
29 spin-1/2 doublet. If as expected on energetic grounds, both electron and hole occupy
30 this SOMO level, recombination returns the system to the ground state, giving no
31 light emission. However, in our very efficient LEDs, we achieve selective hole
32 injection into the HOMO and electron injection to the SOMO.

33 For the most part, stable, organic luminescent radicals have posed as curiosities of
34 chemistry with limited applications.¹⁷⁻²³ Photoexcitation of doublet ground state (D_0)
35 molecules generate doublet excited states. Spin-allowed emission, i.e. fluorescence, in
36 these molecules originates from the lowest-lying doublet excited state, D_1 (Fig. 1a).

37 By incorporating 3-substituted-9-(naphthalen-2-yl)-9H-carbazole (3NCz) and
38 3-substituted-9-phenyl-9H-carbazole (3PCz) to the core
39 tris(2,4,6-trichlorophenyl)methyl (TTM) radical, we obtained two new luminescent
40 radicals, TTM-3NCz and TTM-3PCz (Fig. 1b). The photoluminescence quantum
41 efficiency (PLQE) values in solid 4,4-bis(carbazol-9-yl)biphenyl CBP matrix film
42 (3.0% wt) are $85.6 \pm 5.4\%$ and $60.4 \pm 0.9\%$ for deep-red emission in TTM-3NCz

43 (707 nm) and TTM-3PCz (695 nm), respectively, and can be translated to excellent
44 device performance. See dashed lines in Fig. 1c for the photoluminescence spectra
45 (photoexcitation at 375 nm).

46 A series of OLEDs were made using TTM-3NCz and TTM-3PCz as emitters by
47 vacuum deposition processing (pressure $< 6 \times 10^{-7}$ Torr). The evaporation temperatures
48 of TTM-3NCz and TTM-3PCz under vacuum are below 473 K, which are much
49 lower than their respective thermal decomposition temperatures of 635 K and 640 K
50 (Extended Data, Fig. 1a), meaning that their thermal stabilities are sufficient to
51 withstand the thermal-evaporation process. The energy levels of the two compounds
52 were obtained from cyclic voltammetry (CV) measurements (Extended Data, Fig. 2a,
53 2c). Furthermore, in order to assess the electrochemical stabilities of TTM-3NCz and
54 TTM-3PCz, we scanned 20 cycles of CV curves (Extended Data, Fig. 2b, 2d). There
55 are no significant changes between curves, which indicates good redox stability for
56 TTM-3NCz and TTM-3PCz (in addition to good photo-stability, Extended Data, Fig.
57 3).

58 1-Bis[4-[N,N-di(4-tolyl)amino]phenyl]cyclohexane (TAPC)¹ and
59 2,4,6-tris[m-(diphenylphosphinoyl)phenyl]-1,3,5-triazine (POT2T)²⁴ were used as 35
60 nm hole- and 70 nm electron-transporting layers, respectively. The radicals were
61 doped into a CBP host to form the light-emitting layer (thickness 25–40 nm). Due to
62 the larger energy band gap of CBP when compared to the dopant molecules, see Fig.
63 1d inset, sequential charge trapping is expected to be the main route for the creation of
64 doublet excitons. A thin layer (10 nm) of
65 4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PYMPM)²⁵ was inserted
66 between light-emitting and PO-T2T layers to remove unwanted green emission (likely
67 CBP:PO-T2T exciplex). Best LED performance was found to be ITO/MoO₃ (3
68 nm)/TAPC (35 nm)/CBP:TTM-3NCz (3.0 wt %) (40 nm) or CBP:TTM-3PCz (3.0
69 wt %) (25 nm)/B3PYMPM (10 nm)/PO-T2T (70 nm)/LiF (0.8 nm)/Al (100 nm).

70 Plots of EQE against current density for the OLEDs are given in Fig. 1d
71 (TTM-3NCz = red, TTM-3PCz = black). The corresponding electroluminescence (EL)
72 spectra peak at 710 nm (TTM-3NCz) and 703 nm (TTM-3PCz); the devices have true
73 deep-red/near-infrared emission (Fig. 1c). Maximum EQE values of $27 \pm 5\%$ for
74 TTM-3NCz and $17 \pm 3\%$ for TTM-3PCz OLEDs suggest near 100% internal quantum
75 efficiency (IQE) for electroluminescence when considered with the film PLQE values
76 and a 30% light-out-coupling coefficient.⁵ To the best of our knowledge, the
77 maximum EQE of TTM-3NCz-based device is the highest value for all
78 deep-red/infrared LEDs²⁶⁻²⁸ (see Table S2), and respectable $> 10\%$ EQE values are
79 obtained at 1 mA/cm^2 . The near-identical EL and PL spectra (Fig.1 c) for TTM-3NCz
80 and TTM-3PCz show that EL and PL emission originate from the same electronic
81 transition ($D_1 \rightarrow D_0$).

82 Current density-voltage-EL characteristics for the TTM-3NCz and
83 TTM-3PCz-based devices are given in Fig. 1e and 1f. The plot positions associated
84 with the maximum EQE values are denoted by arrows and occur in the device turn-on
85 regions, above the experimental noise levels. Besides the performance of the
86 champion devices shown in Fig. 1, the performance of another five TTM-3NCz
87 ($\text{EQE}_{\text{max}} = 27\text{--}16\%$) devices are shown in Extended Data, Fig. 4. The EL spectra are
88 unchanged for a wide range of operating current densities: $6 \mu\text{A/cm}^2\text{--}1.6 \text{ mA/cm}^2$
89 (Extended Data, Fig. 5).

90 We note that TTM-3NCz and TTM-3PCz contain ‘donor’-3NCz/-3PCz and
91 ‘acceptor’-TTM radical groups which resemble the classical TADF motif. In Fig. 2a
92 absorption and photoluminescence spectra for the molecules are plotted with
93 reference to TTM. Introduction of the ‘donor’ group to the TTM moiety leads to the
94 appearance of a new absorption band at $\sim 620 \text{ nm}$ and an accompanying $\sim 0.38 \text{ eV}$ red
95 shift in PL. High ‘charge transfer’-CT character is expected for the first excited state
96 of TTM-3NCz and TTM-3PCz, i.e. significant spatial separation with little overlap for
97 the -3NCz/-3PCz-centred-highest occupied molecular orbital (HOMO) and
98 TTM-centred-singly occupied molecular orbital (SOMO). These frontier molecular

99 orbitals (MOs) can be used to describe electronic transitions for ground state (D_0)
100 absorption to the lowest excited state (D_1) and in photo- and electro-luminescence
101 ($D_1 \rightarrow D_0$). The same (δ^-)TTM–donor(δ^+) dipole moment orientation is expected for D_1
102 versus D_0 , but with greater magnitude in the excited state. This is supported by the
103 observation of strong, positive solvatochromic effects (see Fig. 2a, 2b:
104 photoexcitation at 375 nm). Increasing the solvent polarizability index leads to
105 increasing Stokes' shifts. The slope for the Lippert-Mataga plot of the TTM-3NCz
106 molecules in Fig. 2c reflects the change in dipole moment ($\Delta\delta$) upon photoexcitation,
107 and shows a fitting contrast with the solvent-independent behaviour (i.e. $\Delta\delta \sim 0$) for
108 TTM. In TTM the D_1 excited state is more local excited-‘LE’ in nature (i.e.
109 significant HOMO/SOMO overlap).

110 It is critical that the dopant emitters possess high PLQE for good LED
111 performance. PLQE values of 49% and 46% are obtained for toluene solutions of
112 TTM-3NCz and TTM-3PCz, respectively. The Energy Gap Law generally precludes
113 efficient deep-red/infrared light emission but does not appear to be strictly followed
114 for dopants with appreciable CT-character in emission.²⁷ In favour of OLEDs, the
115 non-radiative decay pathways were found to be further reduced when 3% wt doped in
116 CBP films, giving rise to the PLQE values of 90% (TTM-3NCz) and 61%
117 (TTM-3PCz) which were reported above.

118 To explore the nature of the doublet excited states, we performed nanosecond
119 transient absorption (TA) and PL (trPL) studies on toluene solutions containing
120 TTM-3NCz and TTM-3PCz. Excitation wavelengths of 532 nm and 600 nm were
121 used for TA and trPL, respectively, and chosen so to excite the broad absorption band
122 associated with the $D_0 \rightarrow D_1$ transition. In the ns-trPL measurements, we observe an
123 emission spectrum that closely resembles the steady-state PL for TTM-3NCz and
124 TTM-3PCz. There is no temporal evolution in the spectra. Furthermore, from the
125 overlaid TA and trPL profiles (Fig. 2d), it is apparent that there are no excited state
126 species living beyond the emission lifetime. Whilst dark, triplet states usually occur at
127 lower energy than emissive singlet states for closed-shell systems, we consider that

128 there are no equivalent triplet states to hinder emission for the open-shell TTM-3NCz
129 and TTM-3PCz molecules. Further discussion of the transient absorption
130 measurements can be found in SI 2.

131 The PL kinetics can be fitted with a mono-exponential function to yield lifetimes
132 of 17.2 ns (TTM-3NCz) and 21.2 ns (TTM-3PCz). In combination with the PLQE
133 values, the radiative decay rates are: TTM-3NCz = $2.9 \times 10^7 \text{ s}^{-1}$, TTM-3PCz = $2.1 \times$
134 10^7 s^{-1} . These values are an order of magnitude larger than those associated with
135 delayed emission from typical TADF molecules (ca.
136 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile, 4CzIPN). This is particularly
137 important for LEDs as higher radiative rates mean reduced exciton-charge
138 annihilation issues in efficiency roll-off.

139 Finally, the molecular properties and photophysics for TTM-3NCz/TTM-3Cz
140 molecules can be reconciled with density functional theory calculations. Using
141 UKS-DFT and UKS-TDDFT with B3LYP functional and 6-31G** basis set, the
142 nature of the electronic states is revealed. We interpret the computational results
143 within the MO diagram shown in Figure 3a. The scheme begins with TTM and
144 considers interactions between benzene HOMO/LUMO moieties and the central
145 carbon $2p_z$ orbital. A relatively strong, 374–378 nm absorption peak found for TTM
146 and TTM-donor-type molecules is attributed to a SOMO \rightarrow LUMO transition. The
147 SOMO has electron density on every other atom of the TTM group, and can be
148 determined from first principles, along with the overall HOMO, as outlined in SI 3
149 using group- and Hückel theory. The derived SOMO has the same form as obtained
150 by DFT (Fig. 3b). In TTM, TTM-3NCz and TTM-3PCz, the overall LUMO mirrors
151 the LUMO of the -TTM benzene groups (Fig. 3a).

152 HOMO \rightarrow SOMO transitions give rise to the lowest energy absorption bands in
153 both TTM-3NCz (616 nm) and TTM (541 nm) in toluene, with significant CT- and
154 LE-character for the former and latter types. This arises as the
155 TTM-3NCz/TTM-3PCz HOMOs are primarily hybrids of the most anti-bonding

156 combinations of -TTM and carbazole-group HOMOs (Fig. 3b). On going from TTM
157 to TTM-3NCz, the TTM MO diagram is perturbed as depicted in Fig. 3a.
158 Unexpectedly good agreement is found between the absorption spectra and
159 UKS-TDDFT peak positions²⁹ in TTM-3NCz: HOMO → SOMO, experimental = 616
160 nm, calculated = 622 nm. More detailed discussions of the MO diagram and
161 electronic structure calculations can be found in SI 3 and 4.

162 The SOMO → HOMO transitions as depicted in Fig. 3b are associated with
163 luminescence. However, whilst the route to efficient doublet emission for the
164 open-shell molecules must involve these orbitals, thermodynamics would dictate that
165 electrons and holes are both stabilized by occupancy of the SOMO level following
166 electrical injection (see Fig. 4a). It would not be possible to realize doublet excited
167 states for light emission by this scheme.

168 As shown in Fig. 1d (inset), the electrodes are biased for selective hole and
169 electron injection into the -3NCz/-3PCz HOMO and -TTM SOMO levels,
170 respectively (ca. Energy Gap Law). If injection of the hole into the HOMO occurs
171 before the electron into the SOMO, positively charged, singlet and triplet
172 intermediates are expected (see Fig. 4b). It is possible that the positively charged
173 singlet intermediate for the former case could ‘relax’ before the electron falls upon the
174 SOMO, but this loss pathway to D₁-formation is spin forbidden for the triplet
175 intermediates. On the other hand, if injection of the electron into the SOMO occurs
176 first, this gives the negatively charged singlet intermediate also shown in Fig. 4b. In
177 this second scenario, holes that travel via CBP HOMO levels, could encounter
178 negatively-charged TTM-3NCz sites to form D₁ by tunnelling of the hole between the
179 carbazoles of CBP and TTM-3NCz. The hole could also hop between TTM-3NCz
180 sites, when avoiding the aforementioned singlet ‘relaxation’. To date, it is noteworthy
181 that TTM-donor-type molecules have been found to make much better OLEDs than
182 TTM,³⁰ and thereby provides some indirect evidence for the mechanism in Fig. 4b.

183 The discussion in Fig. 4b considers hole injection sequentially to the CBP host and
184 then onto the TTM-3NCz HOMO level. We can also consider models for operation
185 without participation of the CBP in which charge annihilation of TTM-3NCz anions
186 and cations generates the same D_1 excited state. This would require that energy
187 levels are substantially lowered and raised following oxidation and reduction,
188 respectively, so that the TTM-3NCz cation ‘SOMO’ and anion ‘HOMO’ would
189 become more favourably aligned for electron transfer to yield $D_0 + D_1$, as illustrated
190 schematically in Fig. 4c. Though energy shifts on charging are expected, indications
191 from cyclic voltammetry (Extended Data, Fig. 2) suggest these shifts are too small to
192 achieve the level alignment indicated in Fig. 4c.

193 At this stage, the precise route from electrical injection to luminescence is
194 unclear but appears to be, undoubtedly, efficient.

195 In this work, we have demonstrated highly efficient radical-based OLEDs with
196 EQE values which far exceed those for other LEDs with deep-red/near-IR emission.
197 Our scheme is based on using open-shell, doublet dopants which undergo emission
198 following donor-radical charge-transfer. The SOMO in these molecules facilitates
199 exceptional LED performance and its novel spin properties offer many possibilities
200 for exploitation in other fields of optoelectronics.

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293 **Author Statements**

294 X.A., S.D. and H.G. designed and synthesized the luminescent radicals, and
295 performed the steady-state spectroscopy. E.W.E. performed the transient
296 photoluminescence (trPL) measurements and the quantum chemical calculations.
297 T.J.H.H. devised the group theory treatment. A.J.G. conducted the transient absorption
298 (TA) spectroscopy measurements. X.A., Y.C. and F.L. optimized the devices.

299 E.W.E., R.H.F. and F.L. initiated, designed and supervised the work. E.W.E., R.H.F.
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303 **Figure Legends**

304 **Figure 1. LEDs with doublet emission.** a) Doublet emission following photo- and electrical-
305 excitation. b) Chemical structures for TTM, TTM-3NCz and TTM-3PCz. c)
306 Electroluminescence (solid lines) and photoluminescence (dotted lines, 375 nm excitation)
307 spectra for TTM-3NCz (red)- and TTM-3PCz (black). d) External quantum efficiency-current
308 density (EQE-J) curves for TTM-3NCz (red) and TTM-3PCz (black) LEDs. Inset:
309 TTM-3NCz device layout; SOMO = -3.7 V (cyclic voltammetry – Extended Data, Fig. 2) and
310 HOMO = -6.0 V (approximated by 9-phenylcarbazole). Black triangle and red circle markers
311 denote current density-voltage (J-V) and radiance-V profiles for e) TTM-3NCz and f)
312 TTM-3PCz. Radiance levels corresponding to EQE_{max} lie above the background noise level.

313

314 **Figure 2. Doublet photophysics.** Steady-state a) UV-Vis and b) PL profiles for $10 \mu\text{M}$
315 TTM-3NCz in solvents of varying orientation polarizability index, f . Reference measurements
316 for $10 \mu\text{M}$ TTM in toluene are denoted by black dotted lines. Photoexcitation wavelength =
317 375 nm. c) Lippert-Mataga plot of Stokes' shift versus f for TTM-3NCz (red circles) and
318 TTM (black triangles). d) Overlaid kinetic profiles for PL (all-integrated, red circles; 600 nm
319 excitation at $6.5 \mu\text{J}/\text{cm}^2$ fluence) and transient absorption (600–700 nm averaged, black
320 squares; 1550–1650 nm averaged, black triangles; 532 nm excitation at $35.7 \mu\text{J}/\text{cm}^2$ fluence).
321 Sample concentration = $10\text{--}100 \mu\text{M}$.

322

323 **Figure 3. Electronic structure for doublets: from HOMO to SOMO.** a) Molecular orbital
324 diagrams for TTM and TTM-3NCz. Structures are geometry optimized for the D_1 state by
325 UKS-TDDFT (B3LYP, 6-31G**), and the molecular orbitals involved in a monoelectronic
326 depiction for $D_1 \rightarrow D_0 + h\nu$ are shown in b).

327

328 **Figure 4. Doublet electroluminescence mechanism.** a) Scheme depicts how
329 thermodynamically-favoured SOMO electron and hole injection does not realize the emissive
330 doublet excited state. b) Electroluminescence by selective HOMO and SOMO hole and
331 electron injection. c) Electroluminescence by TTM-3NCz/TTM-3PCz charge annihilation
332 mechanism.

333

334 **Methods**

335 **Synthesis of Doublet Emitters.** The precursors of TTM-3NCz and TTM-3PCz were
336 prepared by Suzuki-coupling of tris(2,4,6-trichlorophenyl)methane (HTTM) and
337 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl-‘3NCz’/‘3PCz’. Radicals were generated
338 from the precursors by treatment with potassium *t*-butoxide in tetrahydrofuran,
339 followed by oxidation of the resulting carbanions with *p*-chloranil. Full synthesis and
340 characterization details are described in Supplementary Information (SI) 1.2.

341 **Device-physics.** Current density-voltage-electroluminescence (J-V-EL)
342 characteristics were measured using a Keithley 2400 sourcemeter, Keithley 2000
343 multimeter and a calibrated silicon photodiode.

344 **Photo-physics.** UV/Vis absorption spectra were measured on a Shimadzu UV-2550
345 spectrometer. Fluorescence spectra were recorded on a Shimadzu 5301PC
346 spectrometer. The absolute fluorescence quantum yields were obtained using an
347 Edinburgh Instruments FLS920 spectrometer with the integrating sphere method.
348 Photoluminescence lifetimes were measured either by an Edinburgh Instruments
349 FLS980 spectrometer (time resolution) or Andor iStar DH740 CCI-010 ICCD camera
350 with Andor SR303i spectrograph (time and spectral resolution). Experimental details
351 for the transient absorption measurements are given in the Supplementary
352 Information.

353 **Electronic Structure Calculations.** For the ground state, unrestricted Kohn-Sham
354 (UKS)-DFT calculations were performed with the Orca package (version 4.0.1) using
355 the B3LYP functional and 6-31G** basis set. For the excited states,
356 UKS-time-dependent DFT (UKS-TDDFT) was employed with the Tamm-Dancoff
357 approximation. All calculations were treated in vacuo.

358

359 **Data Availability Statement**

360 The datasets underlying this work are available at DOI. [to be added in proofs].

361

362 **Extended Data Figure Legends**

363 **Figure 1. TTM-3NCz and TTM-3PCz: Thermal stability and EPR.**

364 a) TGA measurements show thermal decomposition temperatures of 362°C (TTM-3NCz) and
365 367°C (TTM-3PCz).

366 b) EPR spectra for solid samples at room temperature

367

368 **Figure 2. Electrochemical properties and stability.**

369 Cyclic voltammograms of a) TTM-3NCz and c) TTM-3PCz in CH₂Cl₂. For both TTM-3NCz
370 and TTM-3PCz, average of cathodic and anodic potentials give: reduction potential = -1.1 V;
371 first oxidation potential = +0.4 V; second oxidation potential = +0.9 V. Multi-cycle CV
372 measurements (20 cycles) of b) TTM-3NCz and d) TTM-3PCz in CH₂Cl₂.

373

374 **Figure 3. Photostability of TTM and TTM-3NCz.**

375 Luminescence intensity plots for TTM-3NCz and TTM solutions (10 μM, cyclohexane). A
376 pulsed laser at 355 nm with an energy density of 315 kW/cm² (pulse width: 8 ns; frequency:
377 10 Hz) was used under ambient conditions.

378

379 **Figure 4. Device reproducibility for TTM-3NCz.**

380 a) External quantum efficiency versus current density plots for five TTM-3NCz devices. Peak
381 EQE_{max} values: 1) 25 %, 2) 27 %, 3) 20 %, 4) 24 %, 5) 16 %. EQE at 1 mA/cm²: 1) 8 %, 2)
382 10 %, 3) 7 %, 4) 9 %, 5) 7 %.

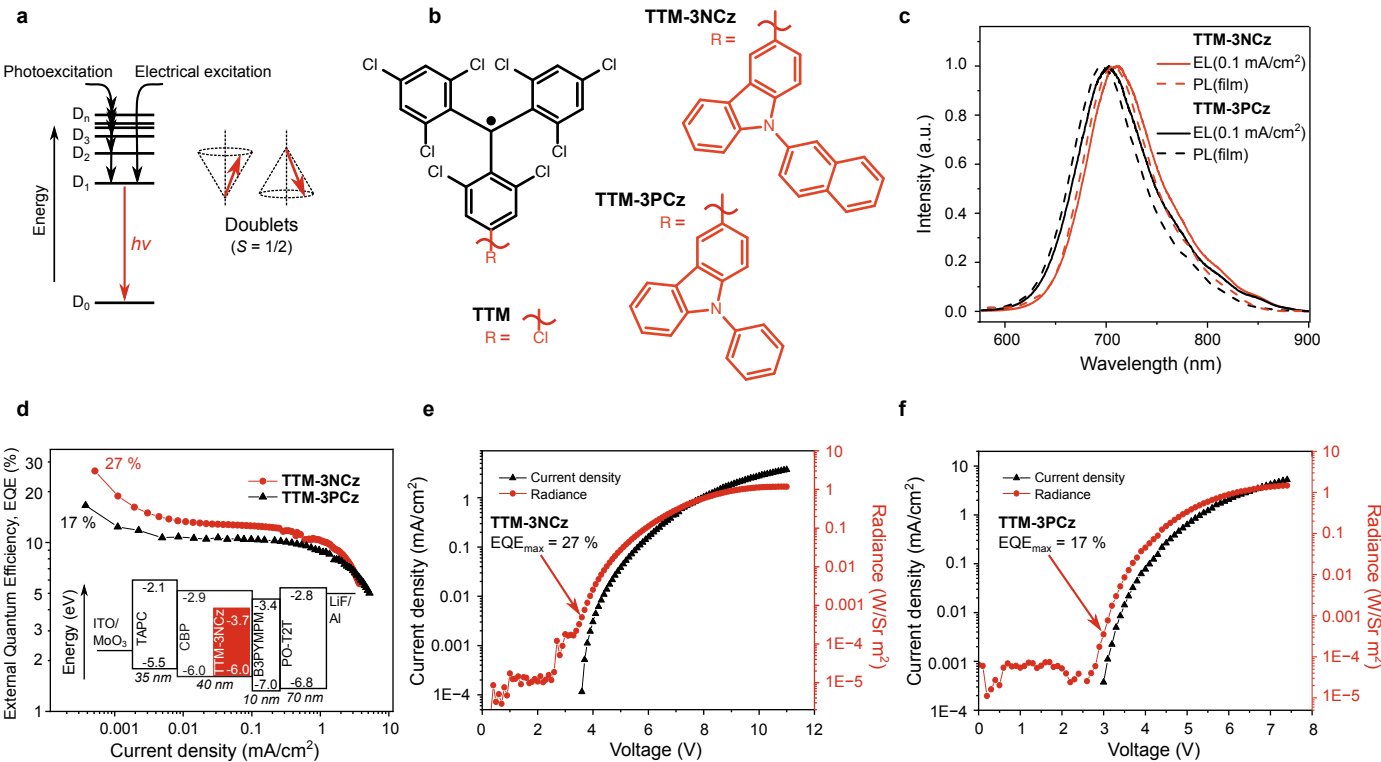
383 b) Radiance versus voltage plots for five TTM-3NCz devices. Radiance levels for EQE_{max} are
384 indicated, and can be distinguished from noise.

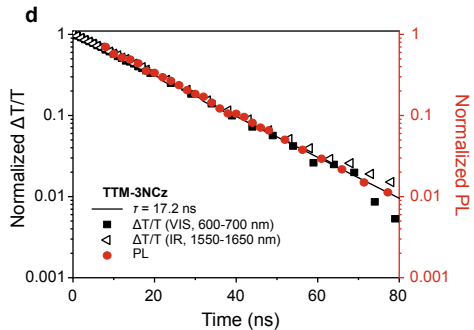
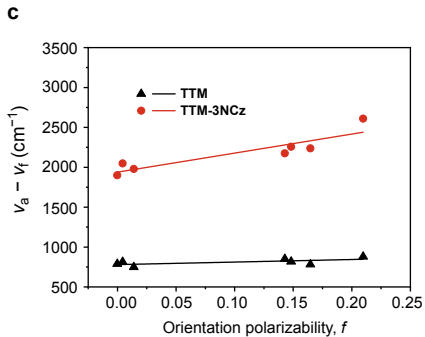
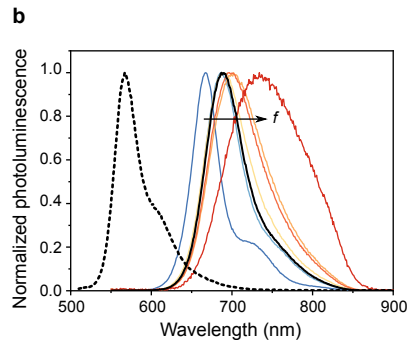
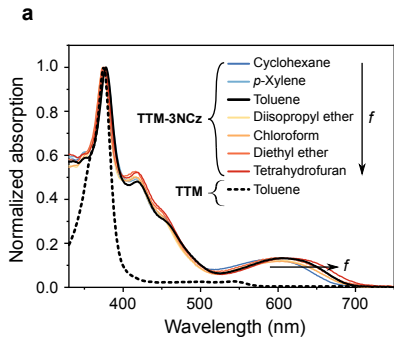
385 c) Current density versus voltage plots for five TTM-3NCz devices.

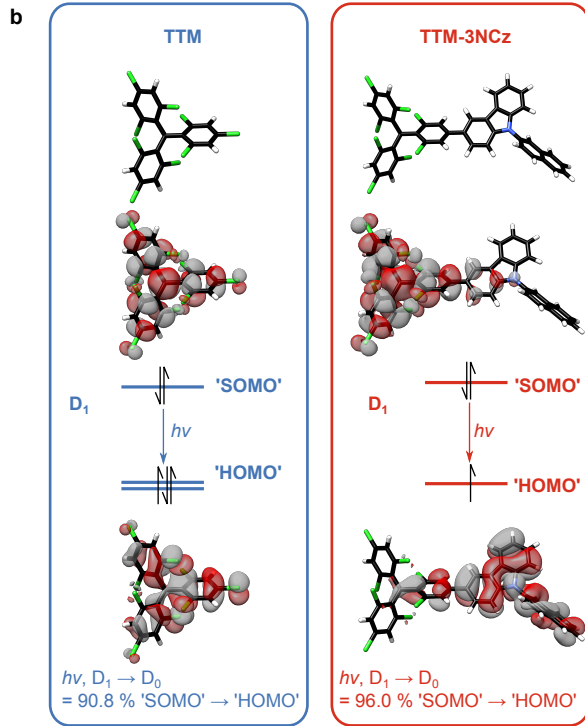
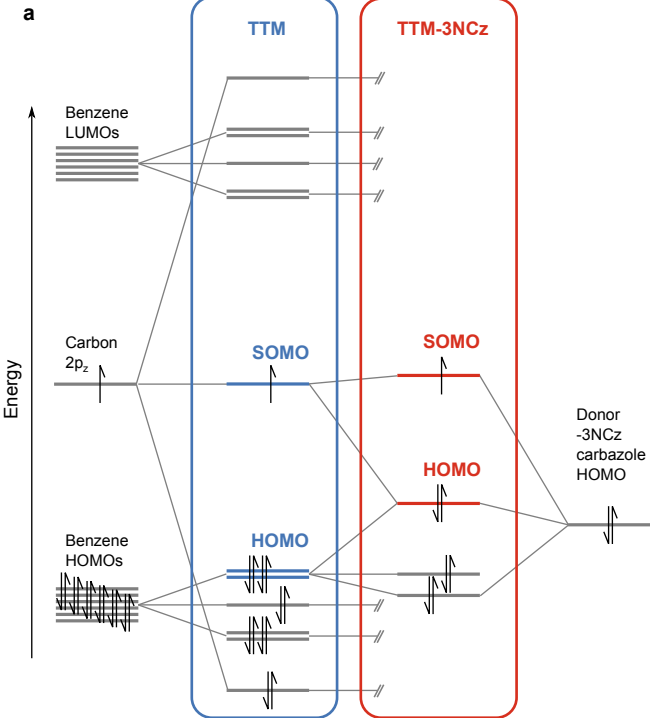
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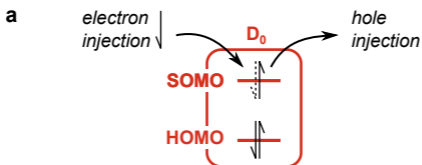
387 **Figure 5. Device stability for TTM-3NCz.**

388 EL spectra for TTM-3NCz devices operated at current densities between 0.006 and 1.6
389 mA/cm². There is no current dependence.

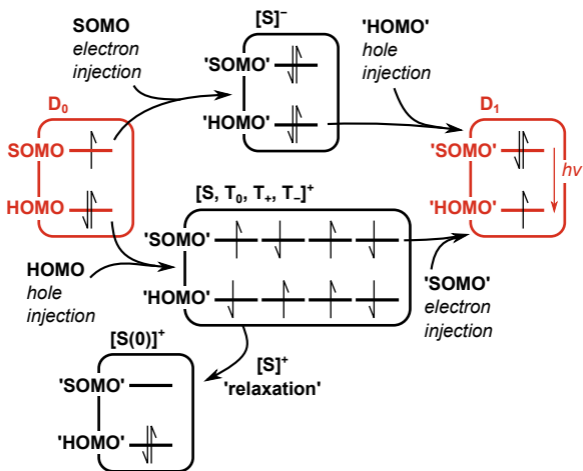








b CBP-TTM-donor charge injection



c TTM-donor charge annihilation

