

**Supplementary Information:**

**High-Performance Solution-Processed Red Hyperfluorescent OLEDs Based on Cibalackrot**

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**Table of Contents**

Table S1 Photophysical properties in solution.....	2
Table S2 Photophysical properties in neat films.....	2
Table S3 Photophysical properties of Cibalackrot B blend films .....	6
Figure S1 UV-Vis absorption, fluorescence, and phosphorescence of compounds in solution and neat film.....	3
Figure S2 Normalised absorption, and PL spectra of thin films containing varying mol% of Cibalackrot with TADF material 4CzIPN or 4CzIPN- <sup>t</sup> Bu.....	4
Figure S3 Solid state TCSPC prompt and delayed fluorescence decay of thin films .....	5
Figure S4 EQEs (%) (>100 cd m <sup>-2</sup> ) of hyperfluorescent OLEDs <i>versus</i> electroluminescent peak wavelength ( $\lambda_{EL}$ ) (nm). .....	6
References. ....	7

**Table S1** Photophysical properties in solution

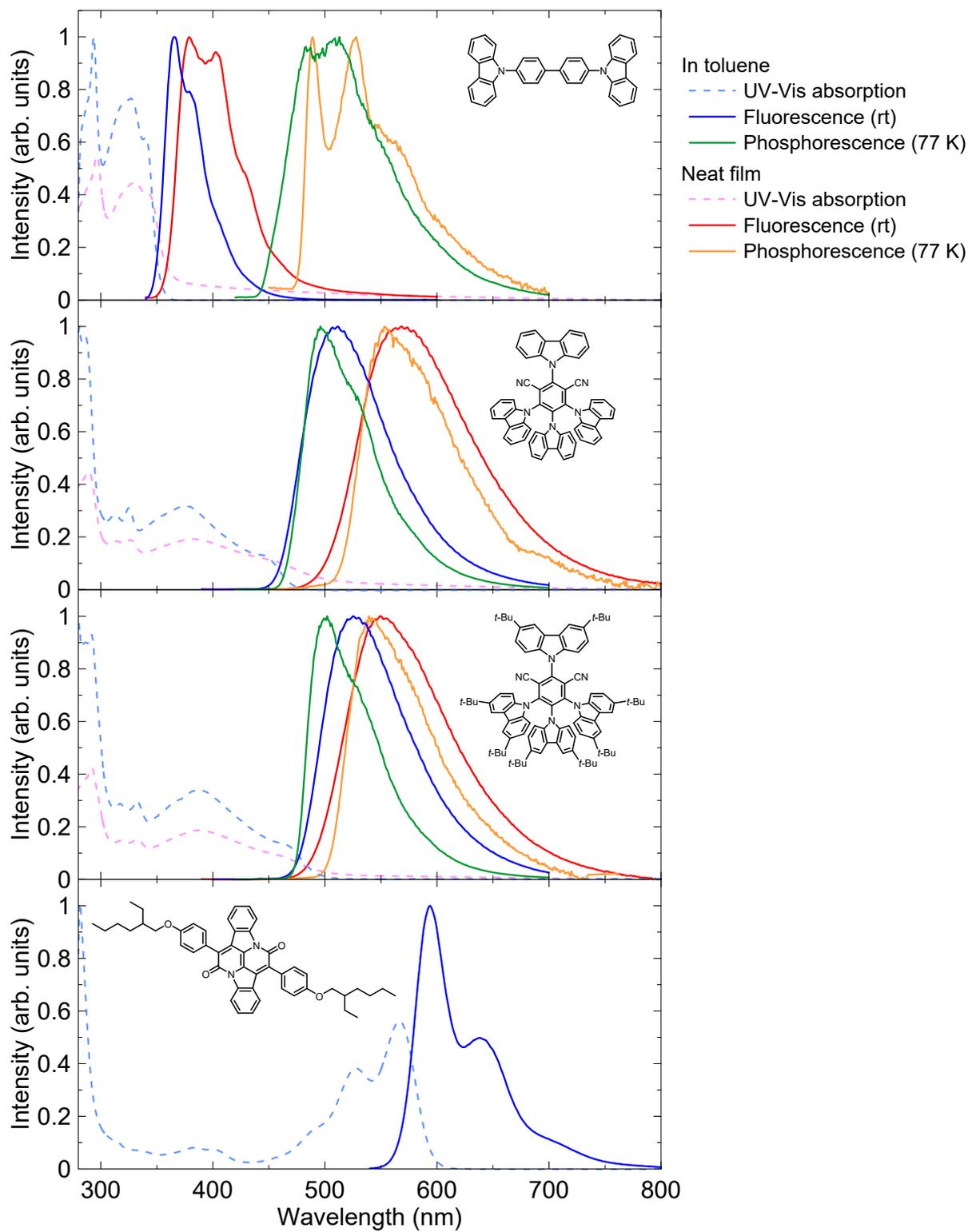
Compound <sup>a</sup>	$\lambda_{\text{abs}}$ (nm) <sup>b</sup>	$E_{\text{g}}^{\text{opt}}$ (eV) <sup>c</sup>	$\lambda_{\text{fluo}}$ (nm) <sup>b</sup>	$S_1$ (eV) <sup>c</sup>	$\lambda_{\text{phos}}$ (nm) <sup>d</sup>	$T_1$ (eV) <sup>c</sup>	$\Delta E_{\text{ST}}$ (eV)
CBP	294, 327, 340	3.52	366	3.56	487, 512	2.77	0.79
4CzIPN- <sup>t</sup> Bu	280, 387, 467	2.53	525	2.61 (2.61) <sup>e</sup>	502	2.61	<0.01
4CzIPN	281, 374, 449	2.65	512	2.70 (2.69) <sup>e</sup>	496	2.65	0.05
Cibalackrot	281, 527, 567	2.09	594	2.18	– <sup>f</sup>	– <sup>f</sup>	– <sup>f</sup>

<sup>a</sup> In toluene. <sup>b</sup> Measured in ambient conditions. <sup>c</sup> Calculated from  $\lambda_{\text{onset}}$ . <sup>d</sup> Measured at 77 K with a delay. <sup>e</sup> Values in parenthesis indicate  $S_1$  at 77 K. <sup>f</sup> Could not be detected.

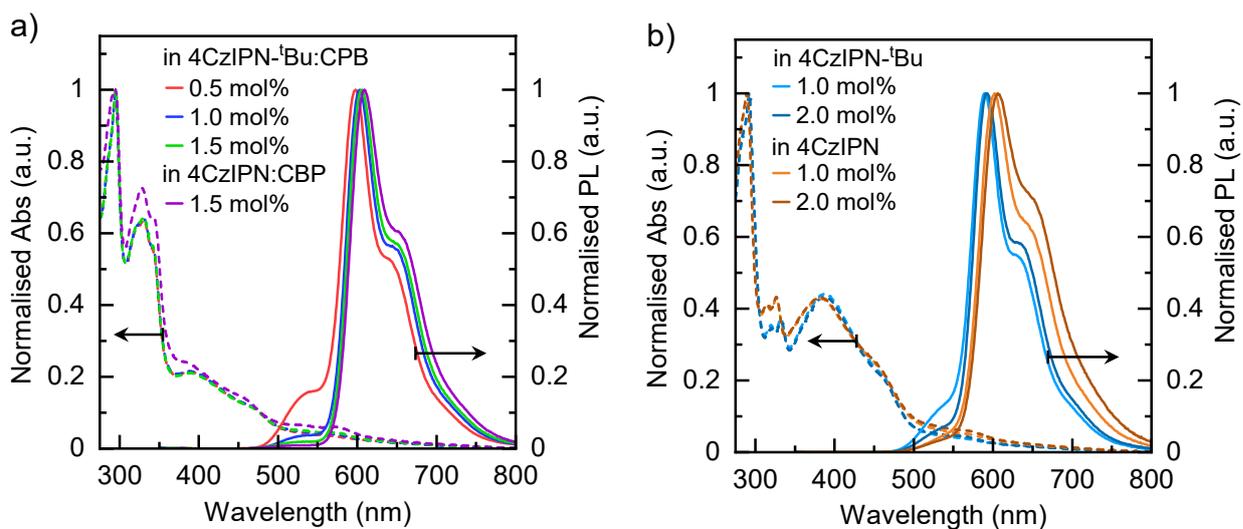
**Table S2** Photophysical properties in neat films

Compound <sup>a</sup>	$\lambda_{\text{abs}}$ (nm) <sup>b</sup>	$E_{\text{g}}^{\text{opt}}$ (eV) <sup>c</sup>	$\lambda_{\text{fluo}}$ (nm) <sup>b</sup>	$S_1$ (eV) <sup>c</sup>	$\lambda_{\text{phos}}$ (nm) <sup>d</sup>	$T_1$ (eV) <sup>c</sup>	$\Delta E_{\text{ST}}$ (eV)
CBP	296, 330, 343	3.43	379, 403	3.46	489, 528	2.60	0.86
4CzIPN- <sup>t</sup> Bu	292, 387, 457	2.41	550	2.52 (2.48) <sup>e</sup>	539	2.46	0.06
4CzIPN	289, 381, 452	2.46	568	2.47 (2.43) <sup>e</sup>	553	2.41	0.06

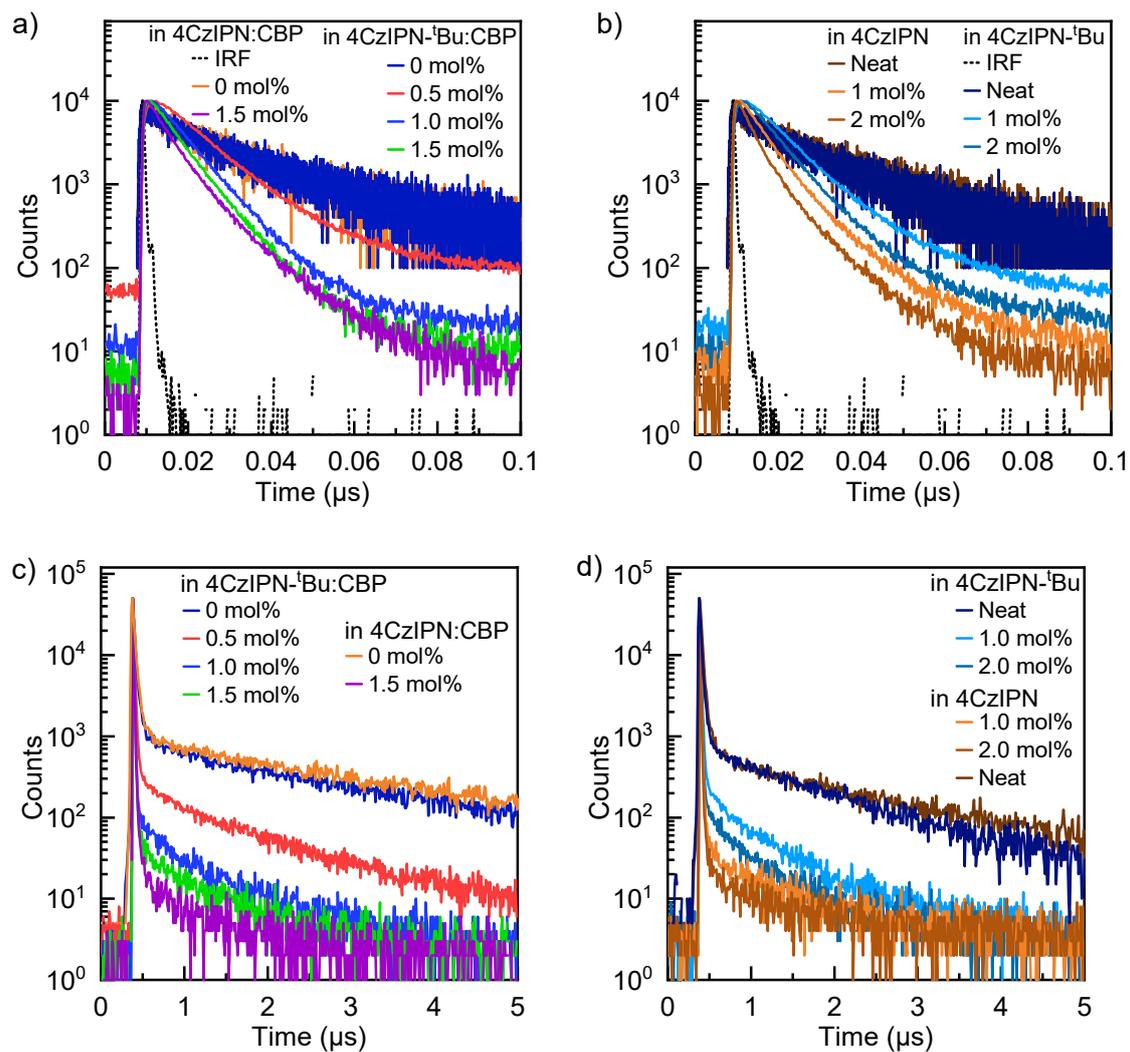
<sup>a</sup> Spin-coated onto a quartz substrate from chloroform. <sup>b</sup> Measured in ambient conditions. <sup>c</sup> Calculated from  $\lambda_{\text{onset}}$ . <sup>d</sup> Measured at 77 K with a delay. <sup>e</sup> Values in parenthesis indicate  $S_1$  at 77 K.



**Figure S1** UV-Vis absorption, fluorescence, and phosphorescence of compounds (inset) in solution and neat films.



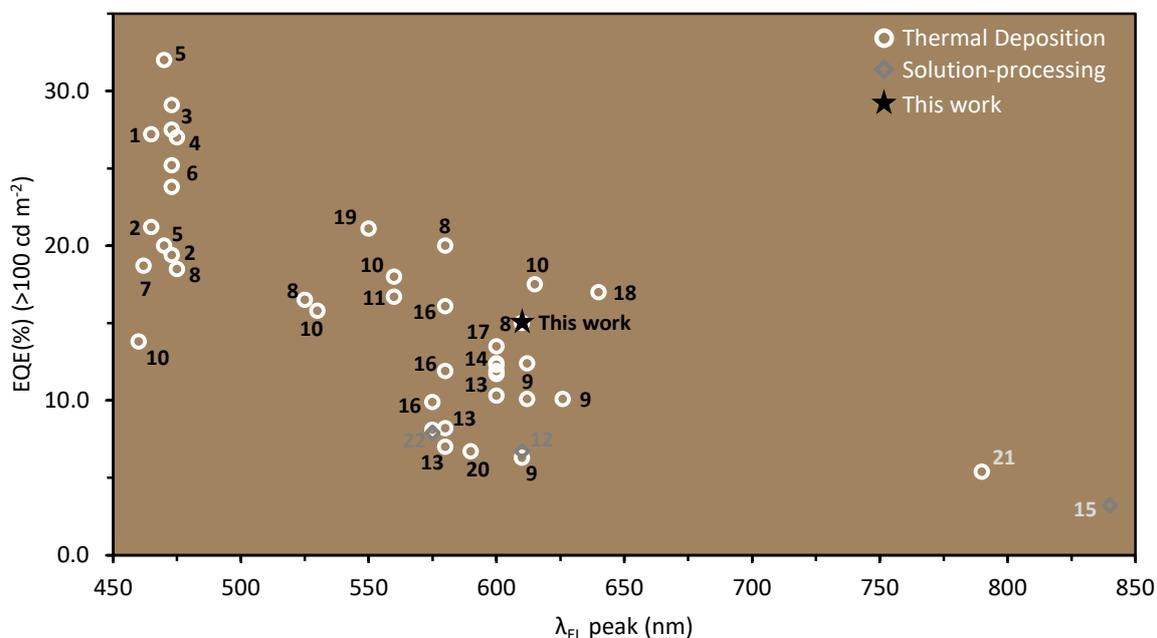
**Figure S2** Normalised absorption (dashed lines), and PL (solid lines) spectra of thin films containing varying mol% of Cibalackrot with TADF material 4CzIPN or 4CzIPN-<sup>t</sup>Bu. a) ternary blends containing TADF:CBP  $\approx$ 30:70 mol%, or b) a binary blend with TADF material. All films were spin-coated from 0.5 wt% chloroform solution.



**Figure S3** Solid state TCSPC prompt and delayed fluorescence decay of thin films containing varying mol% of Cibalackrot with a TADF material of 4CzIPN or 4CzIPN-<sup>t</sup>Bu. a) Prompt fluorescence decay of ternary blends containing TADF:CBP  $\approx$ 30:70 mol%, compared with binary blends of TADF:host, b) prompt fluorescence decay of binary blend with TADF material, c) delayed fluorescence decay of ternary blends, and d) delayed fluorescence decay of binary blends. All films were spin-coated from 0.5 wt% chloroform solution.

Blend Ratio (mol%)			Host	$\lambda_{Abs}$ (nm)	$\lambda_{PL}$ (nm)	PLQY (%)	$\tau_p$ (ns)	$\tau_d$ (ns)
Cibalackrot	TADF							
0.5	29.5	4CzIPN- <sup>t</sup> Bu	CBP	295, 330 (343 sh), 390 (462 sh)	540, 598 (639 sh)	79	18.5	836
1.0	29.0	4CzIPN- <sup>t</sup> Bu	CBP	295, 330 (343 sh), 390 (462 sh)	603 (642 sh)	77	9.7	564
1.5	28.5	4CzIPN- <sup>t</sup> Bu	CBP	295, 330 (343 sh), 390 (462 sh)	606 (647 sh)	74	7.2	603
1.5	28.5	4CzIPN	CBP	295, 327 (344 sh), 378 (454 sh)	609 (649 sh)	69	6.68	509
1.0	99.0	4CzIPN- <sup>t</sup> Bu	–	292, 320, 332, 386 (452 sh)	590 (631 sh)	70	12.8	562
2.0	98.0	4CzIPN- <sup>t</sup> Bu	–	292, 320, 332, 386 (452 sh)	592 (632 sh)	65	9.32	469
1.0	99.0	4CzIPN	–	289, 316, 327, 382, (450 sh)	604 (640 sh)	58	7.44	618
2.0	98.0	4CzIPN	–	289, 316, 327, 382, (450 sh)	606 (649 sh)	47	5.72	498

**Table S3** Photophysical properties of Cibalackrot B blend films



**Figure S4** EQEs (%) ( $>100 \text{ cd m}^{-2}$ ) of hyperfluorescent OLEDs *versus* electroluminescent peak wavelength ( $\lambda_{EL}$ ) (nm). White circles represent devices fabricated by using thermal deposition, grey diamonds represent devices fabricated by using solution processing, and the black star represents this work. Reference according to number label.<sup>1-22</sup>

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