Supplementary Information

Ultra-fast Triplet-triplet-annihilation-mediated High-lying Reverse Intersystem Crossing Triggered by Participation of nπ*-featured Excited States

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Supplementary Note 1. Synthetic procedures and characterization data

Supplementary Figure 1. Synthetic route. The detailed synthetic route to intermediates 1, 2
and 3 as well as target compound TPANI.

The intermediates 1 and 2 as well as reference compound CzNI were synthesized according to
reported procedure. 1, 2
The general synthetic procedures of 3 and TPANI were as follows:

Synthesis of (4-(diphenylamino)phenyl)boronic acid (3)

A solution of n-C₄H₉Li [in hexane, 15 mL, 41.6 mmol] was added dropwise to a solution of 3
(6.0 g, 20.8 mmol) in dry THF (130 mL) at −78 °C. After the addition was completed, the
reaction mixture was stirred 1 h at −78 °C and then allowed to warm to room temperature. The
mixture was stirred for 24 h, and then quenched by aqueous HCl solution (27 ml, 2 mol/L). The
organic layer was separated, and the aqueous layer was extracted with EA (3 × 50 mL). The
combined organic layers were washed with brine (3 × 40 mL) and dried over anhydrous MgSO₄,
then filtered and concentrated in vacuum. Then recrystallization with n-hexane/CH₂Cl₂ to
afford the product. Yield: 67%. Because of the instability of 3, the crude product was not further
purified.

Synthesis of 2-(4-(tert-butyl)phenyl)-6-(4-(diphenylamino)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (TPANI)

A flask was charged with 1 (1.5 g, 3.67 mmol), 3 (1.1 g, 0.52 mmol), Pd(PPh₃)₄ (0.13 g,
0.016 mmol), aqueous NaCO₃ (100 mL, 2 mol L⁻¹) solution, ethanol (40 mL) and toluene (60
mL), and the reaction mixture was stirred at 110 °C for 7 h under argon. After the completion
of the reaction, the reaction mixture was cooled down, then poured into 60 mL water and extracted with CH₂Cl₂ (30 mL × 3). The resultant organic phase was washed with brine, and dried over anhydrous Na₂SO₄. After the solvent was removed, the residue was purified using column chromatography on silica gel employing petroleum ether/CH₂Cl₂ (1/4). Then recrystallization with n-hexane CH₂Cl₂/methanol to afford the greenish-yellow solid product. Yield: 57%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.72–8.63 (m, 2H), 8.47 (dd, J₁ = 8.4 Hz, J₂ = 0.8 Hz, 1H), 7.80–7.71 (m, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 8.0 Hz, 4H), 7.27–7.21 (m, 8H), 7.11 (t, J = 7.2 Hz, 2H), 1.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 164.5, 164.7, 160.1, 151.4, 148.4, 147.4, 147.1, 133.1, 132.6, 131.8, 131.6, 131.3, 130.8, 130.1, 129.5, 129.2, 128.0, 128.0, 127.0, 126.5, 125.1, 123.7, 123.0, 122.5, 121.5, 34.7, 31.3. HRMS (ESI) m/z for C₄₀H₃₄N₂O₂H⁺ [M + H⁺] calcd.: 573.2542, found: 573.2538; C₄₀H₃₂N₂O₂Na⁺ [M + Na⁺] calcd.: 595.2361, found: 595.2356.

**Supplementary Note 2. Photophysical characterization and theoretical calculation results**

![Supplementary Figure 2. Absorption spectra.](image)

Normalized absorption spectra (10⁻⁵ M) of a) CzNI and b) TPANI in solvents with different polarity. Hex: hexane; Tol: toluene; BE: butyl ether; EA: ethyl acetate; DCM: dichloromethane; DMF: N,N-Dimethylformamide.





















ν_a-ν_f is the Stokes shift, f(ε, n) is the orientational polarizability of solvents³ given by

\[ f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \]

Where ε is the solvent dielectric constant and n is the solvent refractive index.
Supplementary Table 1. Photophysical data of CzNI and TPANI in dilute solution at room temperature.

| Solvent | $\varepsilon$ | $n$ | $f(\varepsilon, n)$ | $\lambda_{\text{abs}}$ a) (nm) | $\lambda_{\text{em}}$ b) (nm) | $\nu_{\text{a}-\text{f}}$ (cm$^{-1}$) | $\lambda_{\text{abs}}$ a) (nm) | $\lambda_{\text{em}}$ b) (nm) | $\nu_{\text{a}-\text{f}}$ (cm$^{-1}$) |
|---------|--------------|-----|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Hex     | 1.9          | 1.375 | 0.0012            | 383                           | 437                           | 3226                          | 410                           | 470                           | 3114                          |
| BE      | 3.08         | 1.399 | 0.096             | 391                           | 481                           | 4785                          | 417                           | 534                           | 5254                          |
| EA      | 6.02         | 1.372 | 0.1998            | 389                           | 524                           | 6623                          | 415                           | 602                           | 7485                          |
| CHCl$_3$| 4.81         | 1.446 | 0.1482            | 405                           | 534                           | 5965                          | 435                           | 602                           | 6377                          |
| DCM     | 8.93         | 1.424 | 0.2172            | 404                           | 558                           | 6831                          | 430                           | 645                           | 7752                          |
| DMF     | 37           | 1.427 | 0.2757            | 397                           | 602                           | 8578                          | 424                           | 706                           | 9421                          |

a) $\lambda_{\text{abs}}$ is the absorption peak at the long-wavelength side; b) $\lambda_{\text{em}}$ is the emission peak.

Supplementary Table 2. Photophysical data of CzNI and TPANI in dilute solution at room temperature.

| Solvent | $\lambda_{\text{em}}$ a) (nm) | PLQY a) (%) | $\lambda_{\text{em}}$ b) (nm) | PLQY a) (%) |
|---------|-------------------------------|-------------|-------------------------------|-------------|
| Hex     | 437                           | 83.6        | 470                           | 84.1        |
| BE      | 481                           | 60.5        | 534                           | 61.9        |
| CHCl$_3$| 534                           | 58.9        | 602                           | 59.7        |
| EA      | 524                           | 66.3        | 602                           | 44.7        |
| THF     | 521                           | 65.8        | 607                           | 40.9        |
| DCM     | 558                           | 62.8        | 645                           | 32.4        |
| DMF     | 602                           | 0.31        | 706                           | <0.1        |

a) PLQY: relative PL quantum yield, determined using quinoline sulfate as the reference (PLQY: 44%).
In nonpolar $n$-hexane, the double emission bands of CzNI ($\lambda_{em} = 437$ nm and 458 nm) are identified to be vibrational structures of its local singlet excited state ($1^{1}\text{LE}$) rather than two different excited state species. This deduction has been verified by the excitation spectra and transient PL measurements. As shown in Supplementary Figure 3a, the two emission bands of the $n$-hexane solution of CzNI show identical excitation spectra, indicating that the two emission bands originate from the same excited state species rather than impurities. Furthermore, both the two emission bands show similar transient PL decay curves (Supplementary Figure 3b), indicating that the two bands originate from similar excited state species.

**Supplementary Figure 4. PL spectra.** Normalized Photoluminescence spectra of a) CzNI and b) TPANI in toluene ($10^{-5}$ M).
**Supplementary Figure 5. Transient PL decay profiles.** Transient PL decay curves of a) CzNI and b) TPANI in toluene solution under a N₂ atmosphere at RT (10⁻⁵ M, λ_ex = 370 nm).

**Supplementary Table 3.** Lifetime data of CzNI and TPANI in toluene solution under a N₂ atmosphere at RT (λ_ex = 370 nm).

| Compound | λ_em (nm) | Lifetime (ns) | Weight | χ² | PLQY (%) | k_f (10⁻⁸ s⁻¹) |
|----------|-----------|---------------|--------|----|---------|----------------|
| CzNI     | 473       | 3.69          | 100%   | 1.08 | 43%     | 1.1×10⁸        |
| TPANI    | 520       | 4.89          | 100%   | 1.18 | 50%     | 1.0×10⁸        |

**Supplementary Figure 6. PL spectra.** Normalized Photoluminescence spectra of a) CzNI neat film (λ_ex = 390 nm) and b) TPANI neat film (λ_ex = 420 nm).
Supplementary Figure 7. Transient PL decay profiles. Transient PL decay curves of TPANI neat film at time-range windows of a) 400 ns and b) 340 µs respectively under a N₂ atmosphere at RT (λ_{ex} = 370 nm).

Supplementary Table 4. Lifetime data of TPANI neat film under a N₂ atmosphere at RT.

| Measurement window | Lifetime       | Weight | χ²  |
|--------------------|----------------|--------|-----|
| 400 ns             | τ₁ = 7.26 ns   | 87%    | 1.28|
|                    | τ₂ = 22.38 ns  | 13%    |     |
| 340 µs             | τ₁ = 22.52 ns  | 99.9%  | 1.04|
|                    | τ₂ = 22.43 µs  | 0.1%   |     |

As illustrated in Supplementary Figure 7 and Supplementary Table 4, not only prompt fluorescence (PF), but also delayed fluorescence (DF) component (lifetime: ~µs) can be clearly identified. Nevertheless, the relative weight of the DF component is very low, which may arise from the rather low triplet density under photo-excitation at room temperature.

Supplementary Figure 8. Delayed emission spectra of solution samples. Delayed emission spectra with a delay time of 30 ms for a) CzNI and b) TPANI in iodoethane solutions (5×10⁻⁵ M, gate time: 41 ms) at 77 K.
After a relatively long delay time of 30 ms, the two emission bands ($\lambda_{em} \approx 590$ nm for CzNI, $\lambda_{em} \approx 600$ nm for TPANI) are still discernable, which differ from the corresponding steady PL in both shape and position, confirming their phosphorescence character.

**Supplementary Figure 9.** Delayed emission spectra of film sample. Delayed emission spectra with different delay time (gate time: 41 ms) of TPANI neat film at 77 K ($\lambda_{ex} = 420$ nm).

**Supplementary Figure 10.** Potential energy scan calculation of TPANI. Potential energy scan of TPANI conformations in the ground state calculated in the toluene solution at the CAM-B3LYP/6-31g(d) level. Scanned dihedral angle highlighted in orange.

A relaxed potential energy surface scan modelling for TPANI conformations in the ground state was conducted by progressively modulating the dihedral angle between the D and A units using toluene as the solvent. As shown in Supplementary Figure 10, for the lowest-energy conformation of TPANI, its dihedral angle is calculated to be ca. 50°, which is quite close to that observed in the single crystal sample (45°). Hence, the D-A dihedral angles for TPANI in toluene may be analogous to that in crystal.
Supplementary Figure 11. Transition nature of CzNI and TPANI in T₁ states. The natural transition orbitals (NTO) of a) CzNI and b) TPANI in T₁ excited states revealed by TDDFT calculations by employing the LC-ωPBE functional with the 6-31+G(d) basis set.

Supplementary Table 5. Structure data of CzNI and TPANI single crystal.

|                  | CzNI                | TPANI               |
|------------------|---------------------|---------------------|
| Empirical formula| Ca₄H₆N₂O₂           | Ca₄H₆N₂O₂           |
| Formula weight   | 626.76              | 572.67              |
| Temperature/K    | 302.0               | 103.0               |
| Crystal system   | monoclinic          | monoclinic          |
| Space group      | P2₁/n               | C2/c                |
| a/Å              | 15.1168(5)          | 30.275(2)           |
| b/Å              | 8.4894(2)           | 15.7440(11)         |
| c/Å              | 28.0109(10)         | 13.6204(8)          |
| α/°              | 90                  | 90                  |
| β/°              | 98.6780(10)         | 104.046(2)          |
| γ/°              | 90                  | 90                  |
| Volume/Å³        | 3553.56(19)         | 6298.0(7)           |
| Z                 | 4                   | 8                   |
| ρcalc/g/cm³      | 1.172               | 1.208               |
| μ/mm¹            | 0.071               | 0.074               |
| F(000)           | 1328.0              | 2416.0              |
| Crystal size/mm³ | 0.43 × 0.32 × 0.09  | 0.25 × 0.05 × 0.05  |
| Radiation        | MoKα (λ = 0.71073)  | MoKα (λ = 0.71073)  |
| 2Θ range for data collection/° | 4.824 to 55.04 | 4.9 to 55.186 |
| Index ranges     | -19 ≤ h ≤ 19, -11 ≤ k ≤ 10, -36 ≤ l ≤ 36 | -39 ≤ h ≤ 39, -19 ≤ k ≤ 20, -17 ≤ l ≤ 17 |
| Reflections collected | 48695            | 55392               |
| Independent reflections | 8165 [Rint = 0.0980, Rsigma = 0.0727] | 7215 [Rint = 0.1639, Rsigma = 0.0837] |
| Data/restraints/parameters | 8165/21/439 | 7215/0/400 |
| Goodness-of-fit on F² | 1.025              | 0.988               |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0709, wR₂ = 0.1914 | R₁ = 0.0494, wR₂ = 0.0977 |
| Final R indexes [all data] | R₁ = 0.1154, wR₂ = 0.2235 | R₁ = 0.1126, wR₂ = 0.1175 |
| Largest diff. peak/hole /e Å⁻³ | 0.56/-0.39 | 0.15/-0.20 |
**Supplementary Table 6.** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for CzNI. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom | $x$  | $y$  | $z$   | $U_{eq}$ |
|------|------|------|-------|----------|
| O1   | 6671.5(17) | 10919(3) | 5595.2(8) | 85.5(7)  |
| O2   | 7501.5(15) | 9516(2)  | 7158.3(7) | 74.9(6)  |
| N1   | 7108.6(13) | 10192(2) | 6374.5(7) | 49.6(5)  |
| N2   | 2939.7(14) | 38(2)    | 6362.6(8) | 53.8(5)  |
| C3   | 5951.2(14) | 7564(3)  | 6233.3(8) | 41.2(5)  |
| C1   | 10344(2)   | 15345(5) | 6527.7(18)| 108.0(14)|
| C2   | 9475(2)    | 15538(3) | 6743.8(13)| 76.0(9)  |
| C44  | 8857.0(18) | 14122(3) | 6413.9(13)| 72.5(9)  |
| C4   | 9109(2)    | 12755(3) | 6374.5(8) | 49.6(5)  |
| C5   | 5842(2)    | 11474(3) | 6291.1(12)| 69.8(8)  |
| C6   | 7696.6(17) | 11544(3) | 6449.9(9) | 50.7(6)  |
| C7   | 7053.5(17) | 9221(3)  | 6775.2(9) | 51.2(6)  |
| C8   | 6426.7(15) | 7875(3)  | 6695.4(8) | 44.5(5)  |
| C9   | 6323.2(17) | 6907(3)  | 7075.3(9) | 52.3(6)  |
| C10  | 5756.5(17) | 5592(3)  | 7001.6(9) | 51.3(6)  |
| C11  | 5294.3(15) | 5226(3)  | 6556.8(9) | 45.2(5)  |
| C12  | 4715.1(15) | 3798(3)  | 6498.2(9) | 46.4(5)  |
| C13  | 4862.6(17) | 2577(3)  | 6182.9(10)| 53.5(6)  |
| C14  | 4325.4(17) | 1249(3)  | 6120.6(10)| 54.2(6)  |
| C15  | 3607.0(16) | 1175(3)  | 6377.5(9) | 46.8(6)  |
| C16  | 2804.3(16) | -1308(3) | 6054.2(10)| 50.7(6)  |
| C17  | 2738.7(19) | -1149(3) | 5564.4(10)| 58.8(7)  |
| C18  | 2536.3(19) | -2432(3) | 5267.1(10)| 61.4(7)  |
| C19  | 2399.3(17) | -3914(3) | 5105.4(13)| 74.0(8)  |
| C20  | 2128(2)    | -5287(3) | 5339(2)   | 173(2)   |
| C21  | 2318(5)    | -6818(5) | 5339(2)   | 173(2)   |
| C22  | 1178(2)    | -5064(5) | 4886.1(17)| 111.8(15)|
| C23  | 4014.9(15) | 3663(3)  | 6763.3(9) | 45.4(5)  |
| C24  | 3455.0(15) | 2364(3)  | 6702.5(8) | 43.9(5)  |
| C25  | 2650.8(16) | 1933(3)  | 6896.2(8) | 46.3(5)  |
| C26  | 2168.1(18) | 2634(3)  | 7224.1(10)| 57.9(7)  |
| C27  | 1386.4(19) | 1930(4)  | 7309.9(11)| 66.3(7)  |
| C28  | 1069.6(19) | 574(4)   | 7063.7(11)| 68.1(8)  |
| C29  | 1538.7(18) | -153(3)  | 6744.9(10)| 60.5(7)  |
| C30  | 2340.8(16) | 525(3)   | 6668.0(9) | 49.2(6)  |
| C31  | 5372.2(15) | 6231(3)  | 6158.0(8) | 43.7(5)  |
| C32  | 4873.1(16) | 6032(3)  | 5692.0(9) | 51.6(6)  |
| C33  | 4957.8(18) | 7046(3)  | 5321.6(10)| 58.1(7)  |
| C34  | 5552.2(17) | 8304(3)  | 5393.0(9) | 52.4(6)  |
| C35  | 6039.5(16) | 8572(3)  | 5842.0(9) | 45.3(5)  |
| C36  | 6620.2(18) | 9971(3)  | 5916.2(9) | 54.2(6)  |
| Atom | $x$     | $y$     | $z$     | $U$(eq)  |
|------|---------|---------|---------|----------|
| C37  | 9016(3) | 17034(4)| 6531.6(17)| 104.2(13) |
| C38  | 9705(4) | 15660(5)| 7294.7(16)| 126.7(17) |
| C39  | 7994.7(19)| 14150(3)| 6741.0(11)| 62.4(7)   |
| C40  | 7422.5(18)| 12878(3)| 6656.2(10)| 58.5(7)   |
| C41  | 2698(2)  | -2772(3)| 6248.9(10)| 62.5(7)   |
| C42  | 2492(2)  | -4058(3)| 5945.9(11)| 66.0(8)   |
| C43  | 2676(3)  | -5235(6)| 4678.3(18)| 126.8(15) |

**Supplementary Table 7.** Hydrogen atom coordinates ($\text{Å} \times 10^{4}$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for CzNI.

| Atom | $x$     | $y$     | $z$     | $U$(eq)  |
|------|---------|---------|---------|----------|
| H1A  | 10204   | 15252   | 6183    | 162      |
| H1B  | 10652   | 14415   | 6657    | 162      |
| H1C  | 10719   | 16249   | 6608    | 162      |
| H4   | 9678    | 12693   | 6327    | 87       |
| H5   | 8734    | 10565   | 6190    | 84       |
| H9   | 6629    | 7122    | 7382    | 63       |
| H10  | 5693    | 4950    | 7263    | 62       |
| H13  | 5338    | 2661    | 6009    | 64       |
| H14  | 4440    | 438     | 5915    | 65       |
| H17  | 2831    | -170    | 5431    | 71       |
| H18  | 2490    | -2299   | 4935    | 74       |
| H21A | 1882    | -7032   | 5547    | 259      |
| H21B | 2904    | -6801   | 5526    | 259      |
| H21C | 2290    | -7624   | 5097    | 259      |
| H22A | 1004    | -5890   | 4657    | 168      |
| H22B | 1112    | -4063   | 4725    | 168      |
| H22C | 805     | -5094   | 5135    | 168      |
| H23  | 3921    | 4447    | 6982    | 54       |
| H26  | 2369    | 3559    | 7382    | 69       |
| H27  | 1066    | 2369    | 7536    | 80       |
| H28  | 526     | 150     | 7117    | 82       |
| H29  | 1327    | -1070   | 6585    | 73       |
| H32  | 4477    | 5191    | 5636    | 62       |
| H33  | 4616    | 6892    | 5020    | 70       |
| H34  | 5621    | 8966    | 5137    | 63       |
| H37A | 8866    | 16921   | 6188    | 156      |
| H37B | 9414    | 17913   | 6603    | 156      |
| H37C | 8481    | 17209   | 6670    | 156      |
| H38A | 10143   | 16473   | 7377    | 190      |
| H38B | 9941    | 14672   | 7423    | 190      |
| H38C | 9174    | 15911   | 7429    | 190      |
| H39  | 7797    | 15053   | 6881    | 75       |
| Atom   | x      | y      | z      | U(eq) |
|--------|--------|--------|--------|-------|
| H40    | 6851   | 12931  | 6740   | 70    |
| H41    | 2763   | -2899  | 6582   | 75    |
| H42    | 2414   | -5040  | 6081   | 79    |
| H43A   | 2531   | -6137  | 4475   | 190   |
| H43B   | 3304   | -5246  | 4802   | 190   |
| H43C   | 2533   | -4291  | 4494   | 190   |

**Supplementary Table 8.** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for TPANI. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.
Supplementary Table 9. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for TPANI.

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H21  | 2779  | 5190  | 4140  | 34    |
| H28  | 2712  | 1160  | 3167  | 35    |
| H26  | 3314  | 1955  | 5989  | 34    |
| H27  | 3091  | 870   | 4848  | 37    |
| H20  | 3218  | 4935  | 5777  | 36    |
| H15  | 3975  | 2701  | 6529  | 39    |
| H35  | 1980  | 3927  | -1308 | 40    |
| H14  | 4408  | 2650  | 8181  | 42    |
| H36  | 2472  | 3564  | 223   | 38    |
| H17  | 3132  | 4400  | 7348  | 37    |
| H1   | 3517  | 2914  | 9991  | 39    |
| H18  | 3566  | 4367  | 8990  | 41    |
| H2   | 3199  | 3051  | 11376 | 43    |
| H33  | 949   | 4120  | 67    | 45    |
| H32  | 1438  | 3738  | 1599  | 43    |
| H12  | 4870  | 4375  | 9049  | 51    |
| H5   | 4615  | 4246  | 11486 | 50    |
| H3   | 3577  | 3804  | 12802 | 52    |
| H40A | 1558  | 4462  | -2658 | 68    |
| H40B | 1053  | 4291  | -3329 | 68    |
| H40C | 1344  | 3528  | -2714 | 68    |
| H4   | 4287  | 4385  | 12859 | 60    |
| H11  | 5654  | 4214  | 9296  | 63    |
| H8   | 4845  | 2393  | 10893 | 64    |
| H10  | 6032  | 3157  | 10351 | 68    |
| H39A | 689   | 3249  | -1900 | 83    |
| H39B | 435   | 4003  | -2603 | 83    |
| H39C | 481   | 4029  | -1408 | 83    |
| H38A | 881   | 5439  | -1186 | 95    |
| H38B | 804   | 5484  | -2389 | 95    |
| H38C | 1305  | 5590  | -1675 | 95    |
| H9   | 5629  | 2263  | 11154 | 82    |
Supplementary Figure 12. ORTEP drawing. ORTEP drawing of a) compound CzNI and b) compound TPANI (ellipsoids at 50% probability).

The checkCIF results of compound indicates there is one A-level alert in its structure regarding solvent accessible voids. The solvent accessible voids (261 Å\(^3\) per unit cells) can be attributed to the removal of solvent molecules before data collection because the boiling point of dichloromethane, the solvent used to cultivate single crystals, is low and easy to volatilize.
**Supplementary Table 10.** The NTO of TPANI in different excited states revealed by TDDFT calculations by employing the LC-ωPBE functional with the 6-31+G(d) basis set.

|   | Hole | Particle | Weight | Excited state transition nature | Excitation energy (eV) |
|---|------|----------|--------|-------------------------------|------------------------|
| S₁ | ![Hole Image](image1) | ![Particle Image](image2) | 0.928  | CT + ππ* (LEₐ)               | 2.765                  |
| S₂ | ![Hole Image](image3) | ![Particle Image](image4) | 0.909  | nπ* + ππ* (LEₐ)              | 3.454                  |
| S₃ | ![Hole Image](image5) | ![Particle Image](image6) | 0.739  | CT + ππ* (LEₐ)               | 3.825                  |
| T₁ | ![Hole Image](image7) | ![Particle Image](image8) | 0.946  | ππ* (LEₐ)                    | 1.727                  |
| T₂ | ![Hole Image](image9) | ![Particle Image](image10) | 0.687  | ππ* (LEₐ) + ππ* (LEₐ)        | 2.767                  |
| T₃ | ![Hole Image](image11) | ![Particle Image](image12) | 0.727  | CT + ππ* (LEₐ)               | 3.154                  |
| T₄ | ![Hole Image](image13) | ![Particle Image](image14) | 0.729  | ππ* (LEₐ)                    | 3.352                  |
| T₅ | ![Hole Image](image15) | ![Particle Image](image16) | 0.648  | ππ* (LEₐ) + CT               | 3.420                  |
| T₆ | ![Hole Image](image17) | ![Particle Image](image18) | 0.865  | ππ* (LEₐ)                    | 3.608                  |
| T₇ | ![Hole Image](image19) | ![Particle Image](image20) | 0.656  | ππ* (LEₐ) + ππ* (LEₐ)        | 3.682                  |
| T₈ | ![Hole Image](image21) | ![Particle Image](image22) | 0.757  | ππ* (LEₐ) + nπ*              | 3.759                  |

For S₂ excited state in TPANI, the “hole” is mainly located at carbonyl six-membered ring, while the “particle” is distributed on the naphthalene skeleton. Therefore, we can conclude that the S₀→S₂ transition is an nπ*-dominated transition nature. While for T₄ excited state in TPANI, both the “hole” and “particle” are mainly located at carbonyl six-membered ring and
naphthalene skeleton in TPANI. Therefore, we can conclude that the $S_0 \rightarrow T_4$ transition is a $\pi \pi^*$ transition nature.

![Diagram showing allowed and forbidden transitions](image)

**Supplementary Figure 13. El-Sayed’s rule.** Schematic diagram of El-Sayed’s rule.

According to El-Sayed rule, the rate of RISC is also determined by the molecular orbital type of singlet and triplet states, for instance, a $\pi \pi^*$ triplet state could transition to an $n \pi^*$ singlet state, but not to a $\pi \pi^*$ triplet state, and an $n \pi^*$ triplet state could transition to a $\pi \pi^*$ triplet state, but not to an $n \pi^*$ triplet state and vice versa. The NTO of $T_4 \rightarrow S_2$ in TPANI contains both the $\pi \pi^*$ and $n \pi^*$ transition character, which obeys El-sayed’s rule and promotes the $m$-hRISC process from $T_4$ state to $S_2$ state. Meanwhile, the small $\Delta E_{ST}$ between $T_4$ and $S_2$ in TPANI also prompts the $m$-hRISC process.

![Energy levels diagram](image)

**Supplementary Figure 14. Calculated excited state energy levels for TPANI.** Simulated singlet and triplet state energy levels revealed by TD-DFT calculations by employing the LC-ωPBE functional with the 6-31+G(d) basis set.
Since the $T_4 \rightarrow S_2$ process is calculated to show an ultra-large $m$-hRISC rate of $2.1 \times 10^9$ s$^{-1}$, most of the $T_4$ excitons produced by triplet-channel TTA are estimated to be quickly converted to $S_2$ excitons. In view of the different transition characters of the $T_4$ ($^3$LE$_A$-dominated) and $T_3$ ($^3$LE$_D$-dominated) states of TPANI (vide Supplementary Table 10), the $T_4 \rightarrow T_3$ internal conversion (IC) process may be not quite fast. Although the $T_2$ state also displays some $^3$LE$_A$-character, the relatively large $\Delta E_{(T_2,T_0)}$ ($\sim$0.6 eV) should be adverse to the $T_4 \rightarrow T_2$ IC process. Consequently, both the $T_4 \rightarrow T_3$ and the $T_4 \rightarrow T_2$ IC processes may be not quite effective. Nevertheless, considering that the $T_2 \rightarrow S_1$ direct hRISC ($d$-hRISC) process has a moderate rate of $4.9 \times 10^7$ s$^{-1}$ (vide Supplementary Table 11), once $T_2$ excitons are generated through direct electro-injection, the $T_2 \rightarrow S_1$ $d$-hRISC process could occur.

**Supplementary Table 11.** Calculated energy gap, spin–orbit coupling matrix element (SOCME) values between the singlet and triplet states, and the corresponding higher-lying reverse intersystem crossing rate constants ($k_{\text{hRISC}}$) of TPANI under Marcus reorganization energy of 0.20 eV at 300 K.

| hRISC process | $\Delta E_{S_mT_n}$ (eV) | SOCME (cm$^{-1}$) | $k_{\text{hRISC}}$ (s$^{-1}$) |
|---------------|--------------------------|-----------------|------------------|
| $T_2 \rightarrow S_1$ | $-0.002^a$ | 0.75 | $4.9 \times 10^7$ |
| $T_3 \rightarrow S_2$ | 0.30 | 4.07 | $5.0 \times 10^4$ |
| $T_4 \rightarrow S_2$ | 0.102 | 9.66 | $2.1 \times 10^9$ |
| $T_5 \rightarrow S_2$ | 0.034 | 1.99 | $1.6 \times 10^8$ |

$^a$ Negative values indicate that the singlet energy level is lower than the triplet energy level.

The large SOC matrix element (SOCME) value of 9.66 cm$^{-1}$ between $T_4$ and $S_2$ states of TPANI could be attributed to the quite different transition nature of $T_4$ ($\pi\pi^*$) and $S_2$ ($n\pi^*$) states.
Supplementary Figure 15. TA spectra of TPANI. Transient absorption spectra a) under N\textsubscript{2} and b) under O\textsubscript{2} atmosphere. TA decay profiles at c) 800 nm and d) 870 nm of TPANI in iodomethane solutions (5 × 10\textsuperscript{-4} M) under N\textsubscript{2} and O\textsubscript{2} atmosphere at RT (λ\textsubscript{ex} = 355 nm).

As illustrated in Supplementary Figure 15, in the absence of oxygen, TPANI manifests obvious excited state absorption (ESA) bands, and the TA decay profiles demonstrate the presence of significant long-lived excited species with lifetime of microsecond scales. However, when the atmosphere was changed from N\textsubscript{2} to O\textsubscript{2}, the corresponding excited state absorption intensity is significantly decreased, indicating that both the two ESA bands can be attributed to the absorption of triplet states.
Supplementary Figure 16. CV spectra. Cyclic voltammogram of a) CzNI and b) TPANI in MeCN solution (5 × 10^{-4} M).

Supplementary Figure 17. Thermal stability of CzNI and TPANI. TGA thermogram of a) CzNI and c) TPANI; DSC thermograms of b) CzNI and d) TPANI.
Supplementary Note 3. Electroluminescence characterization

Supplementary Figure 18. EL characteristics of Device A and B. a) Device structure, b) EL spectra at current density of 641 and 1016 mA cm\(^{-2}\), respectively, c) \(J-V-L\) characteristics, d) EQE-\(J\) curves of the CzNI and TPANI-based OLEDs, and e) chemical structures of the materials employed in the devices. Device structure: ITO/NPB (30 nm) /CBP (3 nm) /EML (20 nm) /BPhen (50 nm) /LiF (1.2 nm) /Al (120 nm), in which CzNI and TPANI were used as EML for Device A and B, respectively.
Supplementary Figure 19. Transient EL spectra at different driving voltages for TPANI-based Device B (pulse width: 5 μs).

Supplementary Figure 20. EL characteristics of Device C and D. a) EL spectrum at current density of 110 mA cm⁻², b) EQE-J curves of the CzNI-based Device C (Inset: J-V-L characteristics). c) J-V-L characteristics of the TPANI-based Device D. d) Chemical structures of the materials employed in the Device C and D. Device structure: ITO/PEDOT:PSS (40 nm)/TAPC (20 nm)/mCP (10 nm)/EML (20 nm)/TmPyPB (50 nm)/LiF (1.2 nm)/Al (120 nm), in which CzNI and TPANI were used as EML for Device C and D, respectively.
**Supplementary Figure 21.** $n$–$\lambda$ spectra. Refractive indexes ($n$) at different wavelength of the materials used in the optical simulation.

**Supplementary Figure 22.** Optical simulation and transient EL profiles of CzNI-based Device C. a) Simulated photon distributions of all loss channels as a function of the electron transport layer (ETL) thickness for CzNI-based Device C. The loss channels include substrate-guided mode, absorbed mode, guided mode and evanescent mode. b) Transient EL spectra at different driving voltages, c) the fitting result of the single-logarithmic EL decay curve, and d) the fitting result of the double-logarithmic EL decay profile in a time range of 10–90 $\mu$s of CzNI-based Device C (pulse width: 500 $\mu$s, bias: 8 V, a reverse-pulse voltage of $-10$ V was applied just after forward-pulse bias during the measurements).
Supplementary Figure 23. Transient EL profiles of TPANI-based Device D. Transient EL spectra at different driving voltages for TPANI-based Device D (pulse width: 500 μs, a reverse-pulse voltage of −10 V was applied just after forward-pulse bias during the measurements).

In an OLED, EQE = γ_{e-h} × ϕ_{PL} × EUE × η_{out}, where γ_{e-h} is the electron-hole balance ratio; ϕ_{PL} is the PL quantum efficiency of the emitting layer; EUE is the exciton utilization efficiency (namely total radiative singlet ratio); and η_{out} is the light out-coupling efficiency. Here, the η_{out} values of CzNI-based Device C and TPANI-based Device D are 29.7% and 33.1%, respectively (as shown in Figure 6 and Supplementary Figure 20), and the PLQY values of CzNI and TPANI neat film under N₂ atmosphere are 61.9% and 50.6%, respectively. Therefore, assuming the utilization of the maximum γ_{e-h} value as 100%, the EUE_{max} of CzNI-based Device C and TPANI-based Device D are calculated to be 22.1% and 46.7%, respectively. Note that this EUE_{max} value of TPANI-based device is higher than the spin statistical limit of TTA-OLED whose singlet and triplet TTA channels are both opened (40.0%, vide Figure 1b), it can be deduced that additional TTA-m-hRISC process and/or direct hRISC (d-hRISC) process (from T₂ to S₁) should contribute to the triplet harvesting in this device.
Supplementary Figure 24. Transient EL profiles. Transient EL spectra of TPANI-based Device D at 6 V and 8 V.

As shown in Supplementary Figure 24, the ratio of delayed-to-steady state emission ($I_{\text{delay}}/I_{\text{steady}}$) for TPANI-based Device D at 6 V is obviously larger than that at 8 V because the triplet excitons at higher driving voltage may be quenched by charges or go through other quenching processes which would lead to the decrease of delayed component.\textsuperscript{5} Utilizing the $I_{\text{delay}}/I_{\text{steady}}$ value for Device D at 6 V, the proportion of singlet excitons via singlet-channeled TTA and triplet-channeled TTA-m-hRISC ($\eta_{DF}$ is the proportion of singlet excitons generated via TTA-involved processes, i.e., $\eta_{TTA} + \eta_{TTA-m-hRISC}$) could be calculated. If there is no direct hRISC ($d$-hRISC) process contributing to EL, according to the formula $I_{\text{delay}}/I_{\text{steady}} = \eta_{DF}(\eta_S + \eta_{DF})$,\textsuperscript{6,7} where $\eta_S$ is electrically generated singlet exciton (25.0%), the $\eta_{DF}$ in Device D was calculated to be ca. 10.2%. Based on the fact that the sum of $\eta_S$ and $\eta_{DF}$ (35.2%) is much lower than the EUE\textsubscript{max} (46.7%) of Device D, it can be deduced that the direct hRISC ($d$-hRISC) process should also contribute to the triplet utilization in this device. In this case, according to the updated formula $I_{\text{delay}}/I_{\text{steady}} = \eta_{DF}(\eta_S + \eta_{DF} + \eta_{d-hRISC})$, the $\eta_{DF}$ in Device D could be recalculated to be ca. 13.5% (29% × 46.7%), and thus the corresponding singlet exciton generation proportion from $d$-hRISC process ($\eta_{d-hRISC}$) was calculated to be 8.2%.
Supplementary Note 4. Equations

Supplementary equations for the TTA model

When TTA process occurs, after pulse off immediately, the T\(_1\) density can be expressed as follows\(^8\)

\[
\frac{d[T(t)]}{dt} = -k_T[T(t)] - \gamma_{TT}[T(t)]^2
\] (1)

where \(k_T\) is the monomolecular decay rate constant of the triplet excitons, \(T(t)\) is the T\(_1\) density at time of \(t\), \(\gamma_{TT}\) is the rate constant of bimolecular TTA process of T\(_1\) excitons. At high triplet densities, \(\gamma_{TT}[T(t)]^2 >> k_T[T(t)]\), thus Supplementary Equation 1 can be expressed as follows

\[
\frac{d[T(t)]}{dt} = -\gamma_{TT}[T(t)]^2
\] (2)

Supplementary Equation 2 can be further expressed as below:

\[
\int \frac{1}{[T(t)]^2} \cdot d[T(t)] = \int -\gamma_{TT} dt
\] (3)

the solution of Supplementary Equation 3 is given by Supplementary Equation 4

\[
\frac{1}{[T(t)]=\gamma_{TT} t + C
\] (4)

\(C\) is a constant which equals \(\frac{1}{[T(0)]}\), thus Supplementary Equation 4 can be expressed as below:

\[
\frac{1}{[T(t)]=\gamma_{TT} t + \frac{1}{[T(0)]}
\] (5)

The intensity of the delayed fluorescence (\(I_{DF}\)) induced by the TTA-involved processes can be expressed as Supplementary Equation 6:

\[
I_{DF} \propto [T(t)]^2 = \left(\gamma_{TT} t + \frac{1}{[T(0)]}\right)^{-2}
\] (6)
As shown in Figure 4i and 6f, the EL decay profile of TPANI-based devices in double-log form was well-fitted by the above TTA model, verifying that triplet excitons can be harvested through TTA-involved processes in this device. In the case of CzNI-based Device C, however, only a slope of −1.0 could be observed in the similar time region (vide Supplementary Figure 22d), excluding the significant TTA-involved triplet exciton utilization in this device.

Supplementary equations for triplet dynamics process

The states in Figure 7 can be expressed as follows:

\[
\frac{d[S_1]}{dt} = \frac{1}{4}G + 0.082G - (k_{r} + k_{nr})[S_1] + k_{IC}[S_m]\tag{7}
\]

\[
\frac{d[T_1]}{dt} = \frac{3}{4}G - 0.082G - \frac{1}{2}k_1[T_1]^2 - 2\frac{3}{4}k_1[T_1]^2 - k_{m}[T_1] + k_{IC}[T_n] + 2k_{-1}[^1(TT)] + 2k_{-1}[^3(TT)]\tag{8}
\]

\[
\frac{d[^1(TT)]}{dt} = \frac{1}{4}k_1[T_1]^2 - k_{-1}[^1(TT)] - k_{S}[^1(TT)]\tag{9}
\]

\[
\frac{d[^3(TT)]}{dt} = \frac{3}{4}k_1[T_1]^2 - k_{-1}[^3(TT)] - k_{T}[^3(TT)]\tag{10}
\]

\[
\frac{d[T_n]}{dt} = k_{1}[^1(TT)] - k_{m-hRISC}[T_n] - k_{IC}[T_n]\tag{11}
\]

\[
\frac{d[S_m]}{dt} = k_{S}[^1(TT)] + k_{m-hRISC}[T_n] - k_{IC}[S_m]\tag{12}
\]

where \([S_1], [T_1], [T_n], [S_m],[^1(TT)],[^3(TT)]\) are the densities of the S_1, T_1, T_n, S_m excitons, and singlet-featured and triplet-featured intermediate states in sequence; \(G\) is the term for exciton generation; \(k_1\) and \(k_{-1}\) are the rate constants of the generation of TT pair via the collision of two T_1 excitons and the dissociation of TT pair respectively; \(k_{S}\) and \(k_{T}\) are the rate constants of internal conversion (IC) process from \(^1(TT)\) and \(^3(TT)\) intermediate states to \(S_m\) and \(T_n\) respectively; \(k_{m-hRISC}\) is the rate constant of hRISC process from \(T_n\) to \(S_m\) state in the TTA-\(m\)-hRISC process; \(k_{IC}\) and \(k_{IC}^{T_n}\) are the rate constants of IC processes from \(S_m\) to \(S_1\) and from \(T_n\) to \(T_2\) state, respectively; \(k_{nr}\) and \(k_{nr}^{T_n}\) are the rate constants of non-radiative processes from \(S_1\) to \(S_0\) and from \(T_1\) to \(S_0\), respectively.
For the steady state condition,

\[
\frac{d[1](TT)}{dt} = \frac{d[3](TT)}{dt} = \frac{d[S_m]}{dt} = \frac{d[T_a]}{dt} = \frac{d[T_1]}{dt} = 0
\]  

(13)

Thus,

\[
[1](TT) = \frac{1}{4} \frac{k_1}{k_{-1} + k_S} [T_1]^2
\]  

(14)

\[
[3](TT) = \frac{3}{4} \frac{k_1}{k_{-1} + k_T} [T_1]^2
\]  

(15)

\[
[T_a] = \frac{k_T}{k_{IC} + k_{m-hRISC}} [1](TT)
\]  

(16)

\[
[S_m] = \frac{k_S}{k_{IC}} [1](TT) + \frac{k_{m-hRISC}}{k_{IC}} [T_a] = \frac{1}{4} \frac{k_1}{k_{IC}} \frac{k_S}{k_{-1} + k_S} [T_1]^2 + \frac{3}{4} \frac{k_{m-hRISC}}{k_{IC}} \frac{k_T}{k_{IC} + k_{m-hRISC}} \frac{k_1}{k_{-1} + k_T} [T_1]^2
\]  

(17)

Thus, the ratio of the \( \eta_{TTA-m-hRISC} \) (the proportion of singlet excitons via triplet-channel TTA process, namely TTA-m-hRISC) to \( \eta_{TTA} \) (the proportion of singlet excitons via singlet-channel TTA process) can be expressed as follows:

\[
\frac{\eta_{TTA-m-hRISC}}{\eta_{TTA}} = \frac{k_{m-hRISC} [T_a]}{k_S [1](TT)} = \frac{3}{4} \frac{k_{m-hRISC}}{k_{IC} + k_{m-hRISC}} \frac{k_T}{k_{IC} + k_{m-hRISC}} \frac{k_1}{k_{-1} + k_T} [T_1]^2
\]

\[
= \frac{3}{4} \frac{k_{m-hRISC}}{k_{IC} + k_{m-hRISC}} \frac{1}{k_{IC} + k_{-1} + k_T}
\]

(18)

The \( k_{-1} \) can be negligible in amorphous film due to the very low diffusion rate of triplet excitons.\(^8\) Thus, Supplementary Equation 18 can be further expressed as below:

\[
\frac{\eta_{TTA-m-hRISC}}{\eta_{TTA}} = \frac{3}{4} \frac{k_{m-hRISC}}{k_{IC} + k_{m-hRISC}}
\]  

(19)

Considering that the \( k_{m-hRISC} \) of TPANI is calculated to be as large as \( 2.1 \times 10^9 \) s\(^{-1}\), and meanwhile the relatively large calculated \( \Delta E_{(T_1T_3)} \) (~0.6 eV) may lead to a relatively slow \( T_4 \rightarrow T_2 \) IC process, it is assumed that \( k_{m-hRISC} \gg k_{IC} \) and thus the \( \eta_{TTA-m-hRISC}/\eta_{TTA} \) is 3. Consequently, the total \( \eta_{DF} \) of 13.5% in Device D can be divided into two parts: \( \eta_{TTA} \) of ca. 3.4% and \( \eta_{TTA-m-hRISC} \) of ca. 10.1%.
The $k_{m-hRISC}$ derived from second-order perturbation theory can be expressed as follows:

$$k_{m-hRISC} = \frac{2\pi}{\hbar} \left| \left\langle \Psi_{S_{m}+S_{0}} \left| \hat{H}_{SOC} \right| \Psi^{(TT)} \right\rangle \right| + \sum_{n} \frac{\langle \Psi_{T_{n}+S_{0}} | \hat{H}_{SOC} | \Psi_{T_{n}+S_{0}} \rangle \langle \Psi_{T_{n}+S_{0}} | \hat{H}_{el} | \Psi^{(TT)} \rangle}{E^{(TT)} - E_{T_{n}+S_{0}}} \right|^{2}$$

where $\Psi_{S_{m}+S_{0}}$, $\Psi^{(TT)}$, and $\Psi_{T_{n}+S_{0}}$ are the wave functions of each state. Similarly, $E_{S_{m}+S_{0}}$, $E^{(TT)}$ are the energy levels of each state. $\hat{H}_{SOC}$ and $\hat{H}_{el}$ are the Hamiltonians for spin-orbit and electron-electron interactions, respectively. According to Supplementary Equation 20, the interactions between $^{3}(TT)$ and $S_{m}$ can be mediated by $T_{n}$ state. For the large $k_{m-hRISC}$, the energy gap between $^{3}(TT)$ and $T_{n}$ states should have a small value, while the RISC process from $T_{n}$ to $S_{m}$ states should possess large spin–orbit coupling (SOC) interactions. For TPANI, TD-DFT calculations indicated that $2 \times T_{1}$ and $T_{4}$ states displayed a relatively small energy gap of 0.0102 eV, meanwhile $T_{4}$ and $S_{2}$ states showed large SOC matrix element (SOCME) value of 9.66 cm$^{-1}$. As a result, a large $k_{m-hRISC}$ of $2.1 \times 10^{9}$ s$^{-1}$ could be realized.
Supplementary Note 5. $^1$H, $^{13}$C NMR spectra and High resolution mass spectrometry

Supplementary Figure 25. The $^1$H NMR spectrum of TPANI in CDCl₃.
Supplementary Figure 26. The $^{13}$C NMR spectrum of TPANI in CDCl$_3$.

Supplementary Figure 27. The high resolution ESI mass spectrum of TPANI.
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