Supplementary Information

# Impact of Nitrogen Configuration on the Electronic Properties of Tailored Triphenilamine Derivatives as Hole Transport Materials for Perovskite Solar Cells: A Computational Chemistry Study

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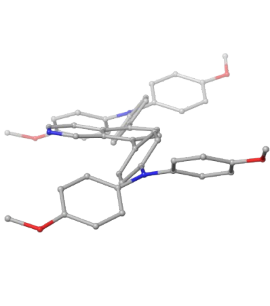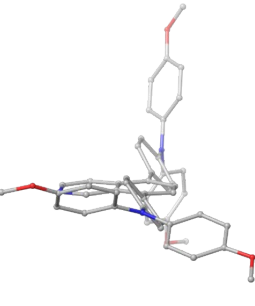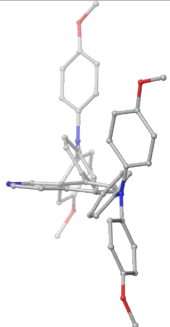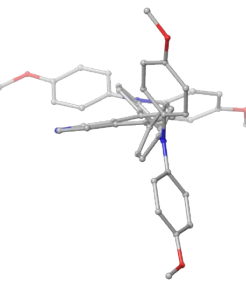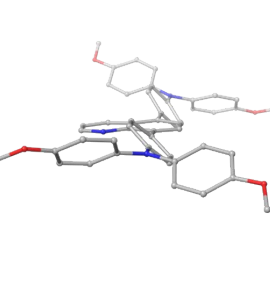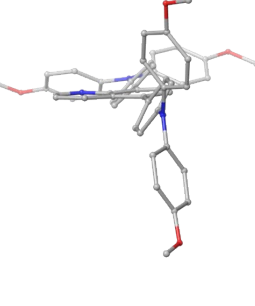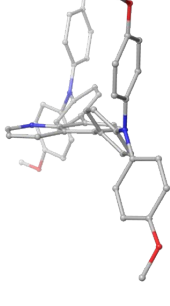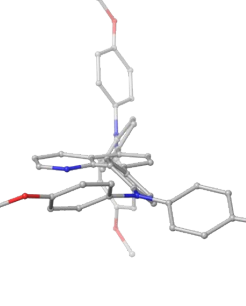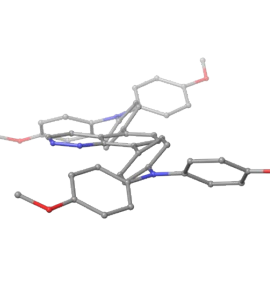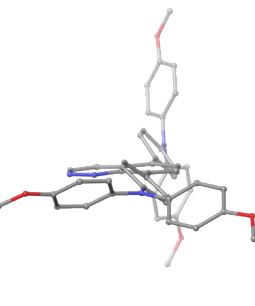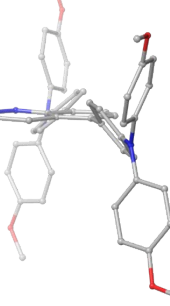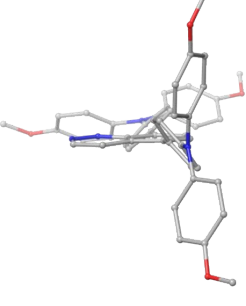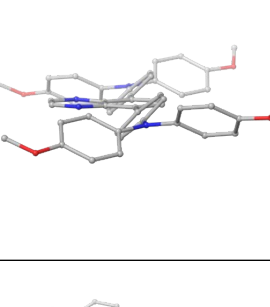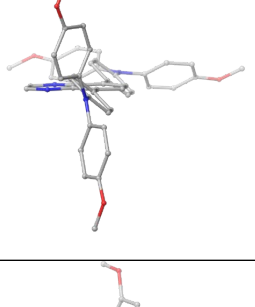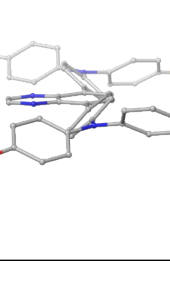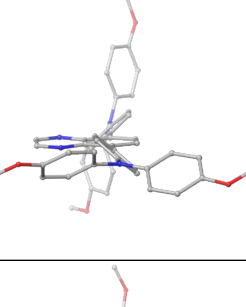
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**Table SI 1.** Electronic couplings of n-TPAM dimers calculated with ω-opt-B97X-3c/6-311G(d,p) and ω-opt-B97X-3c/vDZP at ω-opt-B97X-3c-MBD geometries using the DLPNO method.

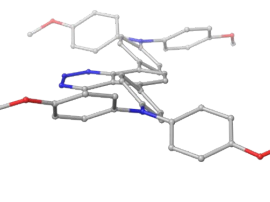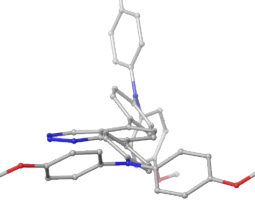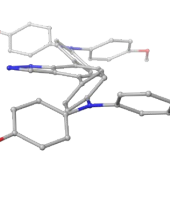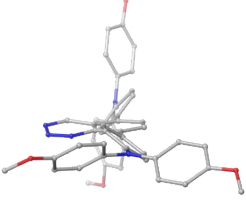| π-linker | conformer | $J_{eff}(h)$ meV | | se | ss |
|---|---|---|---|---|---|
| | ss | ωB97X-3c | | | |
| | | vDZP | 6-311G(d,p) | | |
| A | 1 | 144.13 | 142.95 | | |
| | 2 | 124.47 | 123.42 | | |
| | 3 | 109.25 | 108.12 | | |
| | 4 | 38.21 | 37.69 | | |
| | 5 | 22.74 | 22.79 | | |
| B | 1 | 157.24 | 155.57 | | |
| | 2 | 150.38 | 148.64 | | |
| | 3 | 109.68 | 108.96 | | |
| | 4 | 107.73 | 107.43 | | |
| | 5 | 39.55 | 34.06 | | |
| C | 2 | 147.39 | 146.33 | | |
| | 1 | 145.17 | 144.26 | | |
| | 3 | 123.95 | 123.02 | | |
| | 4 | 4.53 | 4.82 | | |
| D | 1 | 161.38 | 159.98 | | |
| | 2 | 161.35 | 158.88 | | |
| | 3 | 45.04 | 45.98 | | |
| | 4 | 16.04 | 16.98 | | |
| E | 2 | 155.12 | 153.98 | | |
| | 1 | 148.99 | 147.88 | | |
| | 3 | 112.71 | 110.80 | | |
| | 4 | 43.34 | 43.59 | | |
| F | 2 | 161.55 | 160.41 | | |
| | 1 | 159.30 | 158.27 | | |
| | 3 | 39.58 | 39.90 | | |

**Table SI 2.** Reorganisation energies of n-TPAM, YZ22, and YZ18 calculated with ω-opt-B97X-3c/vDZP, ω-opt-B97X-3c/6-311G(d,p) and M06/6-311G(d,p)

| | ω-opt-B97X-3c | | M06 |
|---|---|---|---|
| | vDZP | 6-311G(d,p) | 6-311G(d,p) |
| A-TPAM | 346.31 | 320.60 | 189.92 |
| B-TPAM | 268.76 | 271.03 | 191.70 |
| C-TPAM | 283.34 | 279.53 | 183.05 |
| D-TPAM | 321.84 | 311.21 | 185.83 |
| E-TPAM | 304.07 | 302.56 | 174.66 |
| F-TPAM | 291.25 | 302.54 | 161.32 |
| YZ22 | 149.78 | 148.91 | 128.20 |
| YZ18 | 187.81 | 179.51 | 133.80 |

| | | | | |
|---|---|---|---|---|
| A-TPAM | | | | |
| B-TPAM | | | | |
| C-TPAM | | | | |
| D-TPAM | | | | |
| E-TPAM | | | | |

| | | | | |
|---|---|---|---|---|
| F-TPAM | | | | |
| YZ22 | | | | |
| YZ18 | | | | |
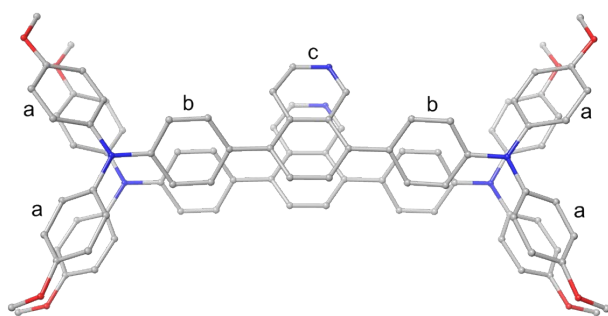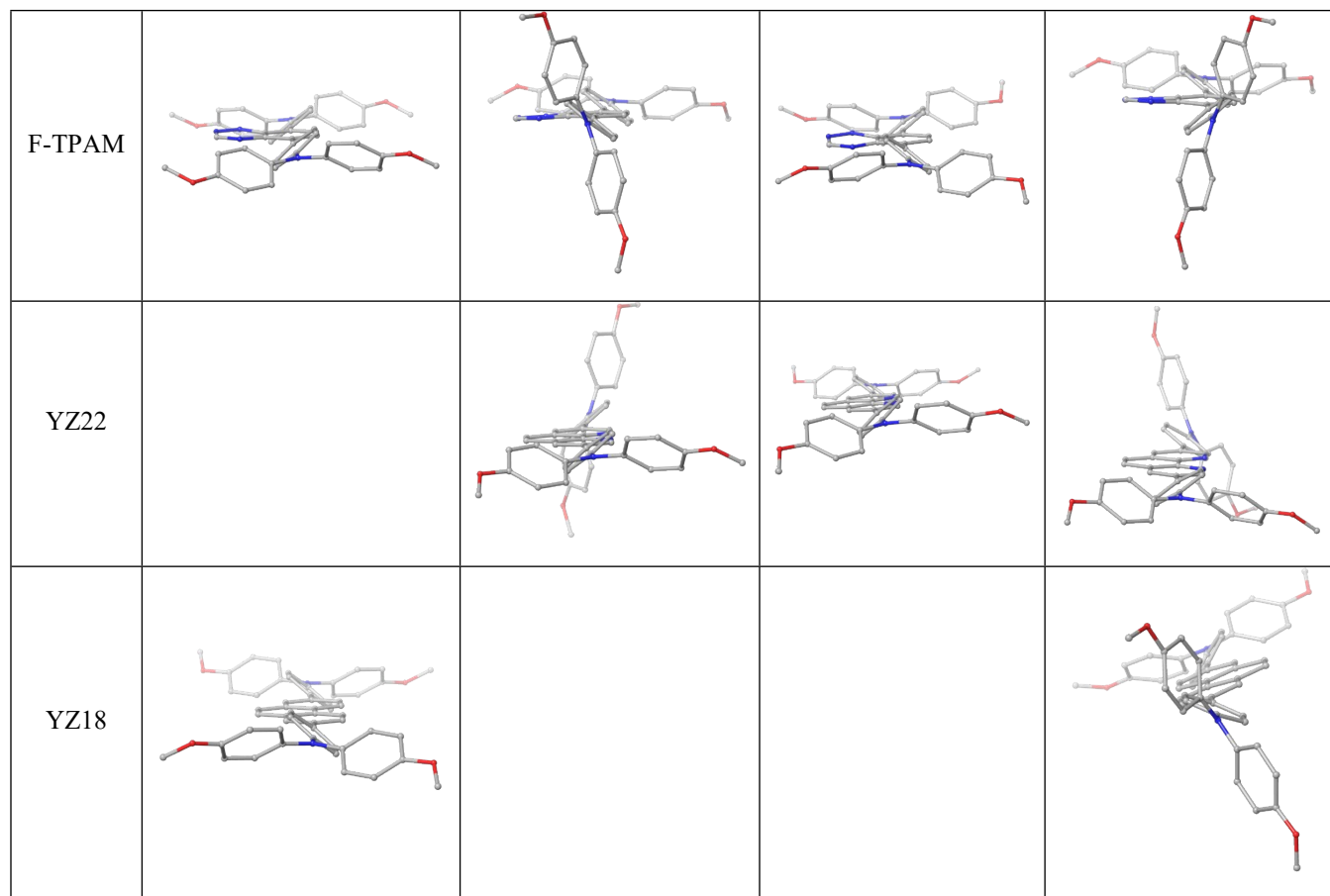
**Figure SI 1.** Labelling of π-π stacked rings of n-TPAM, YZ18, and YZ22 dimers.

**Table SI 4.** Average distance between ring centres ($^{R}c$) of π-π stacked rings obtained from geometry optimisation at the dftb3-3ob-MBD level of theory; a, b, and c correspond to the Figure SI 1 labelling.

| conformer | a | b | c |
|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| | 1 | 4.25 | 4.00 | 3.93 |
| | 2 | 4.26 | 4.07 | 4.11 |
| A-TPAM | 3 | 4.18 | 4.49 | 4.71 |
| | 4 | 4.19 | 4.15 | 4.38 |
| | 5 | 3.94 | | 3.60 |
| | 1 | 4.22 | 3.96 | 3.74 |
| | 2 | 4.22 | 4.00 | 4.04 |
| B-TPAM | 3 | 4.27 | 4.16 | 3.86 |
| | 4 | 4.23 | 3.96 | 3.70 |

|  |  |  |  |  |
|---|---|---|---|---|
|  | 5 | 4.18 | 4.22 | 3.87 |
|  | 1 | 4.27 | 3.93 | 3.72 |
|  | 2 | 4.28 | 3.95 | 3.96 |
| C-TPAM | 3 | 4.41 | 4.04 | 3.64 |
|  | 4 |  |  | 3.51 |
|  | 1 | 4.22 | 3.92 | 3.61 |
|  | 2 | 4.26 | 3.88 | 3.91 |
| D-TPAM | 3 |  |  |  |

| | | | | |
|---|---|---|---|---|
| | 4 | | | |

| | | | | |
|---|---|---|---|---|
| | 1 | 4.24 | 3.97 | 3.72 |
| | 2 | 4.26 | 3.90 | 3.59 |
| E-TPAM | 3 | 4.20 | 4.02 | 3.83 |
| | 4 | 4.15 | 4.11 | 4.03 |
| | 1 | 4.21 | 3.94 | 3.58 |
| F-TPAM | 2 | 4.21 | 4.30 | 3.90 |
| | 3 | | | |

| | | | | | |
|---|---|---|---|---|---|
| Average | | 4.22 | 4.05 | 3.86 | |

**Table SI 5.** Geometrical characteristics of YZ18, YZ22, and n-TPAM dimers calculated with r2scan-3c/def2-mTZVPP geometry optimisations.

| cnf | | $R_c$ | | $\overline{\theta}_a$ | |
|---|---|---|---|---|---|
| | | r2scan-3c | Dftb3-MBD | r2scan-3c | Dftb3-MBD |
| A | s | 4.40 | 4.18 | 21.0 | 4.6 |
| | e | 4.30 | 4.10 | 28.9 | 3.8 |
| B | s | 4.32 | 4.12 | 25.6 | 3.8 |
| | e | 4.23 | 4.04 | 24.7 | 4.4 |
| C | s | 4.43 | 4.12 | 25.6 | 4.1 |
| | e | 4.39 | 4.05 | 26.3 | 3.3 |
| D | s | 4.26 | 4.08 | 21.7 | 3.2 |
| | e | 4.21 | 3.99 | 18.1 | 3.9 |
| E | s | 4.38 | 4.21 | 26.5 | 4.8 |
| | e | 4.23 | 4.04 | 26.2 | 4.0 |
| F | s | 4.33 | 4.16 | 27.2 | 4.1 |
| | e | 4.19 | 3.99 | 23.0 | 4.3 |
| YZ22 | s | 4.22 | 4.01 | 24.1 | 3.8 |
| | e | 4.31 | 3.97 | 19.8 | 3.3 |
| YZ18 | e | 4.26 | 3.98 | 22.5 | 3.8 |
| | s | 4.24 | 4.00 | 22.5 | 4.4 |

[a]Average angle between the planes of the π-π stacked rings of end-cap TPAM

**Figure SI 2** Contour plots of electron spin densities and MBIS fragment charge populations of cation n-TPAM, YZ22, and YZ18. The numbers on the left and right of each contour plot indicate the TPAM fragment charge, and the number in the middle is the core charge. a)$\omega$B97X-3c/vDZP b)M06/6-311G(d,p) c) $\omega$-opt-B97X-3c/vDZP
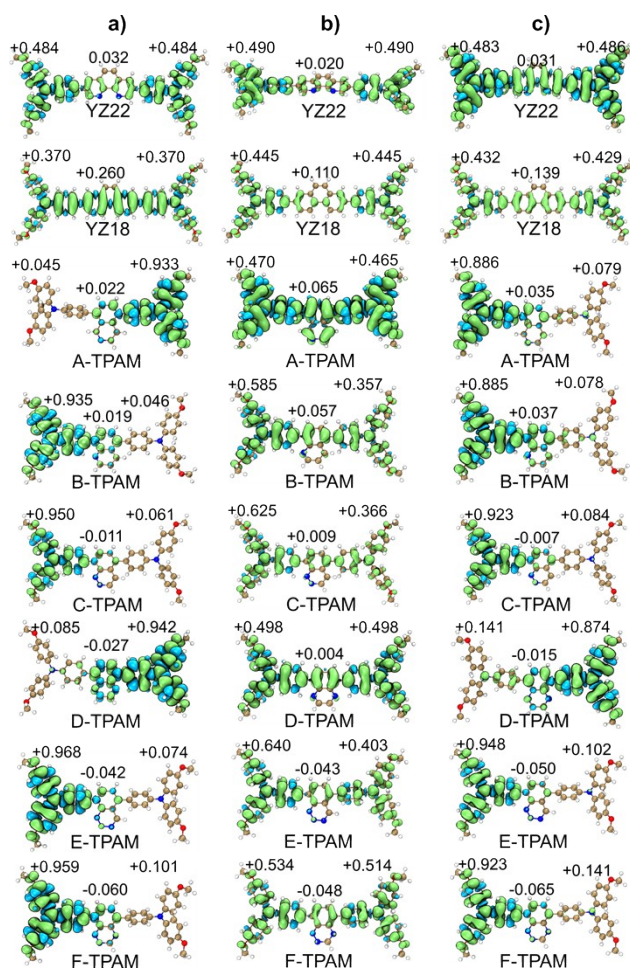
**Table SI 6.** Wavelength of the lowest energy excitation($\lambda_{max}$), oscillator strength, and the HOMO(H0)-LUMO(L0) transitions of n-TPAM, YZ22, and YZ18 calculated with $\omega$-opt-B97X-3c/vDZP

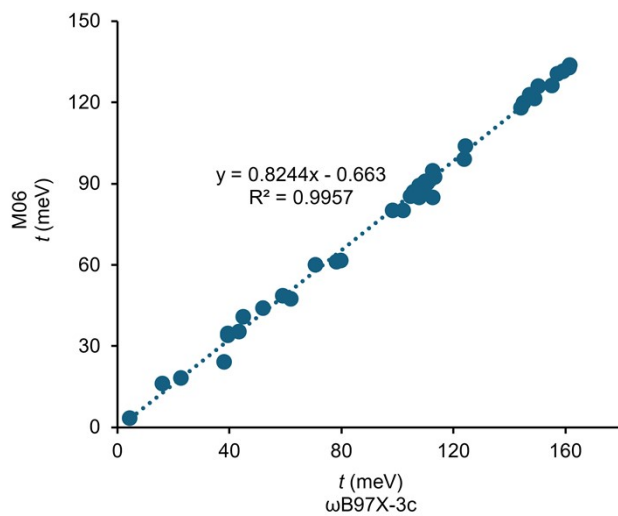|  | $\lambda_{max}$(nm) | Oscilator strength(f) | H0 → L0 electronic transitions (%) |
|---|---|---|---|
| A-TPAM | 331.4 | 1.2221 | 67.3 |
| B-TPAM | 349.9 | 0.9950 | 72.2 |
| C-TPAM | 412.1 | 0.1160 | 19.3 |
| D-TPAM | 385.7 | 0.6913 | 78.9 |
| E-TPAM | 394.3 | 0.7514 | 75.2 |
| F-TPAM | 470.6 | 0.0398 | 6.7 |
| YZ18 | 329.6 | 2.4885 | 62.1 |
| YZ22 | 336.2 | 2.3432 | 64.0 |

**Figure SI 3** Scatter plot of the correlation coefficient ($R^2 = 0.9957$) between the charge transfer integral (t) computed with ωB97X-3c/vDZP and M06/6-311G(d,p) functionals using the DIPRO method.
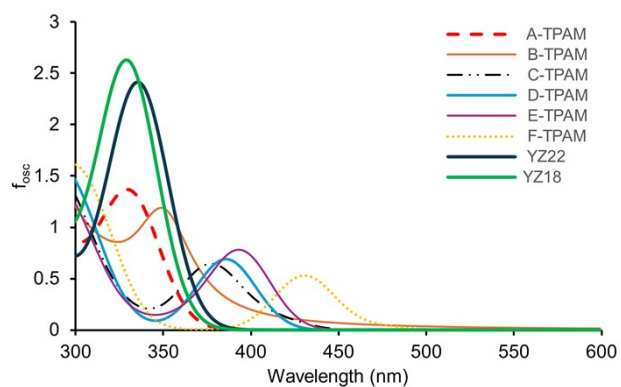


**Figure SI 4** UV-Vis absorption spectrum of n-TPAM, YZ22, and YZ18 molecules computed using 40 roots with TD-DFT ω-opt-B97X-3c/vDZP.