Electron-Deficient Truxenone Derivatives and Their Use in Organic Photovoltaics

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Supporting Information

Experimental Section

All chemicals were purchased from commercial suppliers unless otherwise specified. 4,9,14-Tris(5-hexyl-2-thienyl)truxenone (**1**) was synthesised according to a literature procedure (*J. Mater. Chem. A*, 2013, **1**, 73). ^{1}H NMR spectra were recorded on a BRUKER 400 spectrometer in $CDCl_3$ solution at 298 K unless otherwise stated. The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA) using a TA Instruments Q50 under a continuous nitrogen purge of 60 mL/min. The samples were heated from room temperature to 600°C with a uniform heating rate of 10°C/min. Differential scanning calorimetry (DSC) was carried out with a TA Instruments DSC Q20. UV-Vis absorption spectra were recorded on a UV-1800 Shimadzu UV-Vis spectrophotometer. Cyclic voltammetry was performed with a standard three-electrode setup with a Pt-disk working electrode and an Ag/Ag^{+} reference electrode calibrated against Fc/Fc^{+} using an Autolab PGSTAT101 potentiostat. The measurements were carried out with 3×10^{-4} M solutions in anhydrous and deoxygenated dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. HOMO and LUMO energy values were obtained using the following equations: $E_{LUMO} = -(E_{red} - E_{Fc} + 4.8)$ eV and $E_{HOMO} = -(E_{ox} - E_{Fc} + 4.8)$ eV.

T1A, T2A and T3A. To a solution of **1** (203 mg, 0.230 mmol) and ethyl cyanoacetate (0.48 ml, 4.5 mmol) in anhydrous chlorobenzene (10 ml) cooled to 0°C was added titanium tetrachloride (0.21 ml, 1.9 mmol) and *N*-methylmorpholine (0.86 ml, 7.8 mmol). The dark reaction mixture was stirred and sonicated for 24 h at ambient temperature. A crude mixture of Knoevenagel adducts were subsequently obtained by filtering through a short pad of silica eluting with chloroform. At this stage, separation of adducts by column chromatography (silica, hexane/dichloromethane) can be performed for optimum yield of **T1A**. Alternatively, the Knoevenagel reaction can be repeated on the mixture using identical conditions as above for optimum yield of **T3A**.

T1A was obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.41 (d, J = 1.8 Hz, 1H), 9.08 (d, J = 1.7 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 1.6 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.52 – 7.27 (m, 7H), 6.83 – 6.69 (m, 3H), 3.93 (dd, J = 10.7, 7.1 Hz, 1H), 3.71 (dd, J = 10.7, 7.1 Hz, 1H), 2.85 (m, 6H), 1.74 (m, 6H), 1.41 (m, 18H), 1.06 – 0.86 (m, 12H).

T2A was obtained as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.66 (d, J = 1.8 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 1.7 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 1.4 Hz, 1H), 7.63 (m, 3H), 7.47 (d, J = 3.6 Hz, 1H), 7.39 (d, J = 3.7 Hz, 1H), 7.35 (d, J = 3.6 Hz, 1H), 6.88 – 6.79 (m, 3H), 4.02 – 3.66 (m, 4H), 2.87 (m, 6H), 1.75 (m, 6H), 1.51 – 1.29 (m, 18H), 1.01 (m, 6H), 0.92 (m, 9H).

T3A was obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (d, J = 8.4 Hz, 3H), 7.84 (d, J = 1.7 Hz, 3H), 7.61 (dd, J = 8.4, 1.7 Hz, 3H), 7.34 (d, J = 3.7 Hz, 3H), 6.85 (d, J = 3.7 Hz, 3H), 3.94 (m, 6H), 2.87 (t, J = 7.6 Hz, 6H), 1.73 (p, J = 7.6 Hz, 6H), 1.46 – 1.27 (m, 18H), 1.05 (t, J = 7.1 Hz, 9H), 0.91 (m, 9H).

We note that for all three truxenone adducts, small amounts (~10%) of isomers are present due to the E-Z isomerism associated with the tetrasubstituted double bonds. This has also been described by Zhang et al. in Org. Lett. 2006, 8, 2563-2566.

Device preparation

The substrates used in this study are glass substrates with 110 nm thick pre-patterned ITO (Kintec). Substrate cleaning consisted of sonication in detergent, deionized water and acetone, followed by submersion in hot isopropanol. Upon cleaning, ZnO is deposited from a Zn(acac) precursor solution in air and annealed at 300°C for 10 min. Truxenone and PCBM (Solenne bv.) layers are deposited from a chloroform solution under N_2 atmosphere. Materials were dissolved in a concentration of 10 mg/ml. The substrates with the acceptors were transferred in thermal evaporation chamber and left outgassing overnight at 10^{-7} Torr.
The donor materials, ZnPc (Sigma-Aldrich) and SubPc (Lumtec Corp.), were purified once using thermal gradient sublimation, and MoO_3 and Ag were used as received. Organic thin films were deposited by thermal evaporation in a high vacuum evaporator with a base pressure 10^{-7} Torr and growth rate of 1 Å/s, as monitored by a quartz crystal microbalance, and the substrate temperature was fixed to room temperature. The Ag cathode is evaporated through a shadow mask, defining an active area of 0.134 cm^2.

Thin film and device characterization

Current-voltage characteristics of photovoltaic cells were measured in dark and under simulated solar light, using a Keithley 2602 in combination with an Abet solar simulator, calibrated to produce 100 mW cm^{-2} AM1.5G illumination. In the spectral response and reflection setup, light from Xe and quartz halogen lamps were coupled into a monochromator and their intensities calibrated with a Si photodiode. The light incident on the device was chopped and the modulated current signal detected with current-voltage and lock-in amplifiers. Reflection measurements were conducted with an integrating sphere. AFM images were collected using a Picoscan PicoSPM LE scanning probe operated in the tapping mode. Layer thicknesses of solution processed layers were measured with a Dektak profilometer.

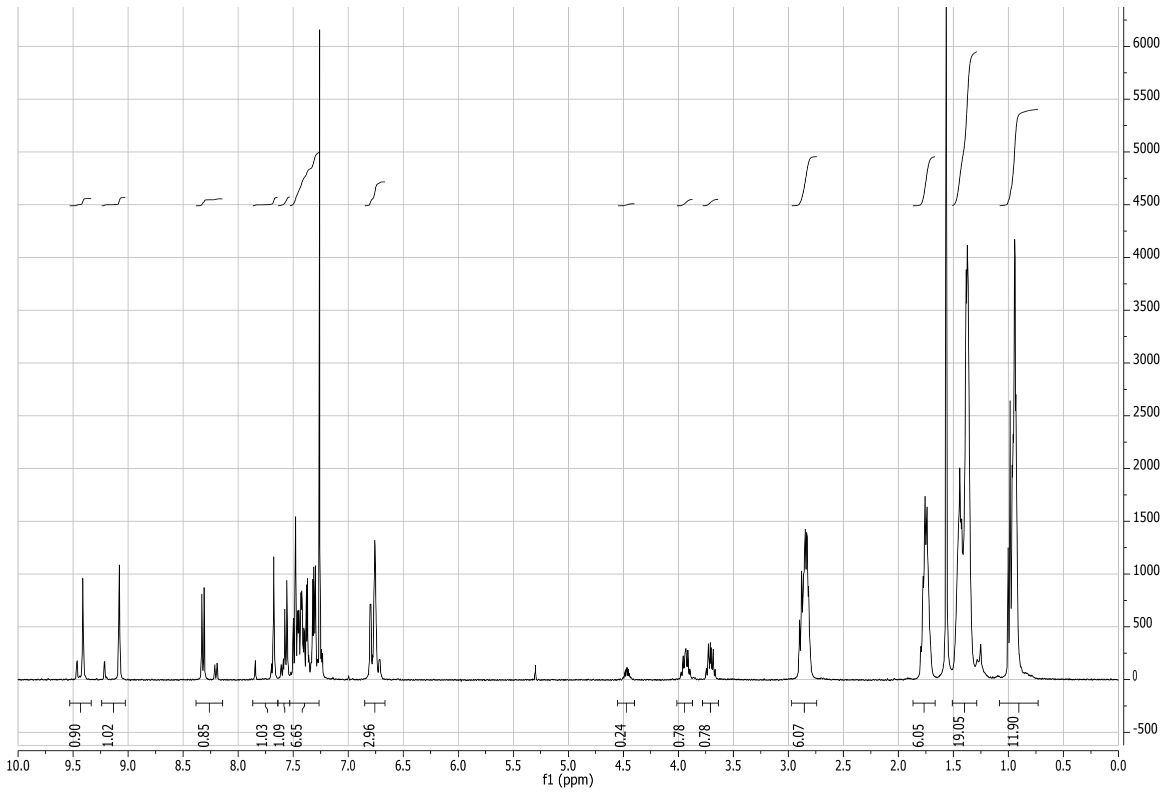

Figure S1 ^{1}H-NMR spectrum of **T1A**.

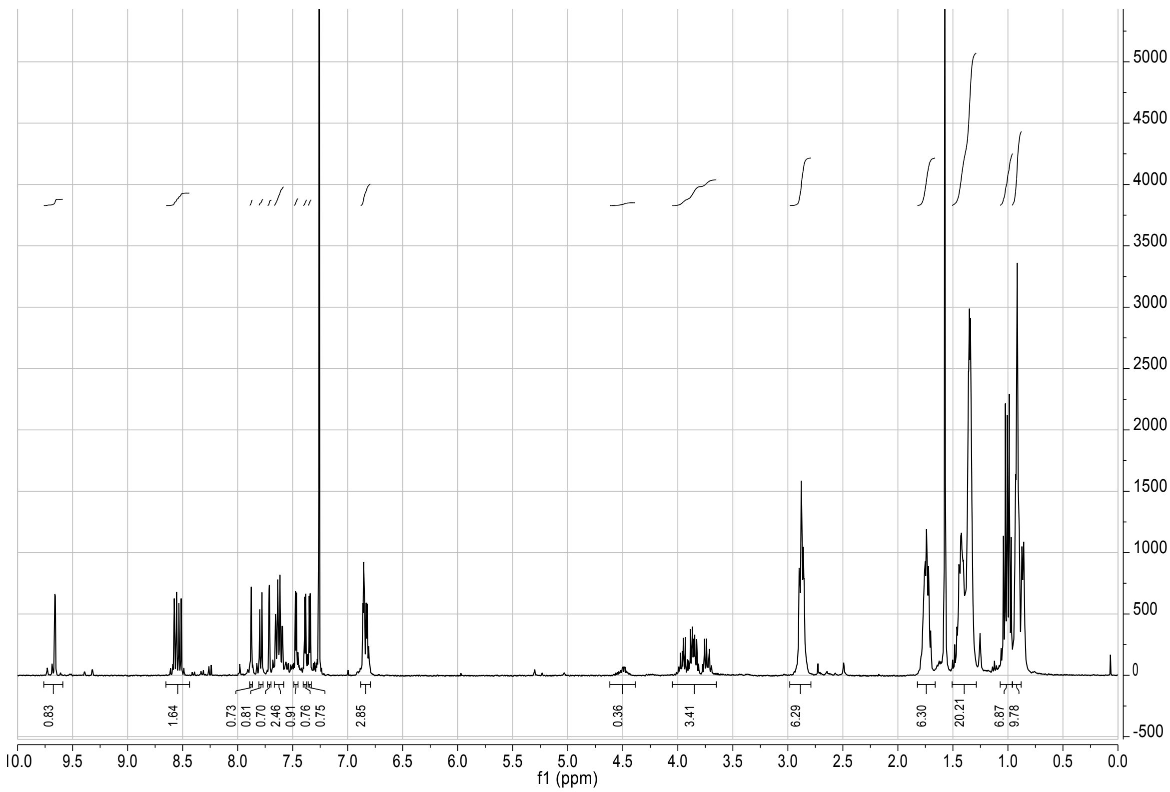

Figure S2 ^{1}H-NMR spectrum of **T2A**.

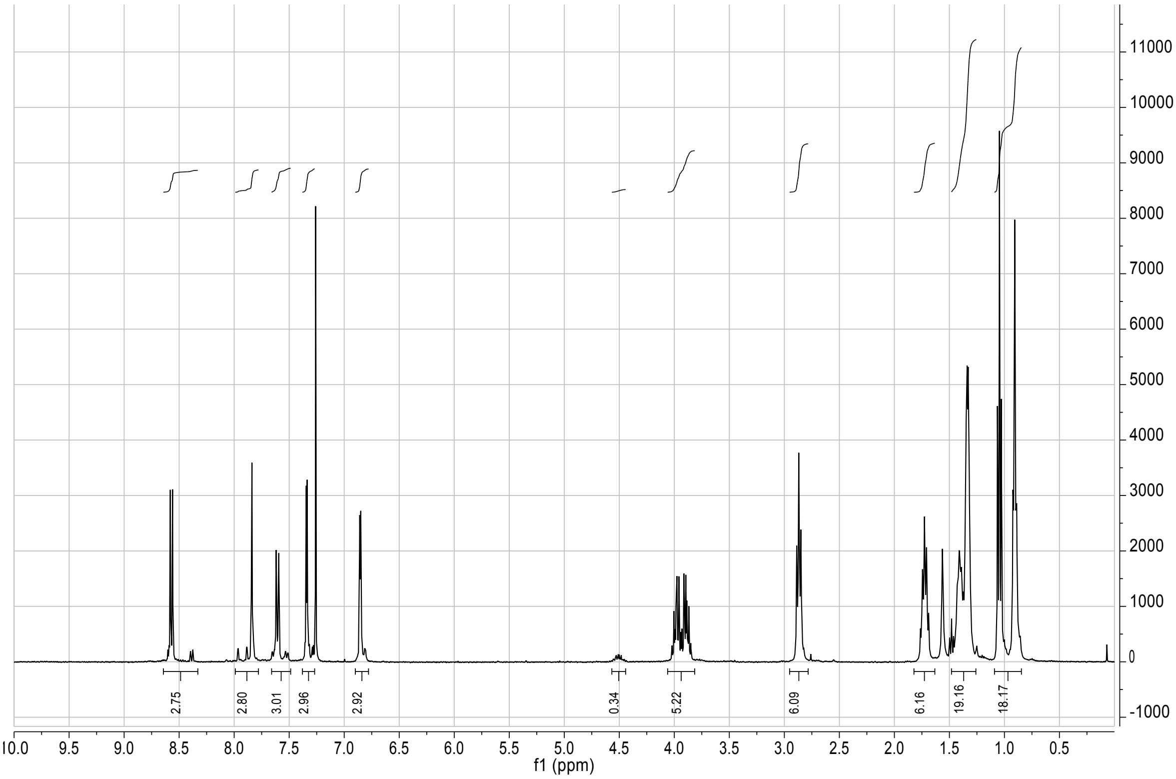

Figure S3 ^{1}H-NMR spectrum of **T3A**.

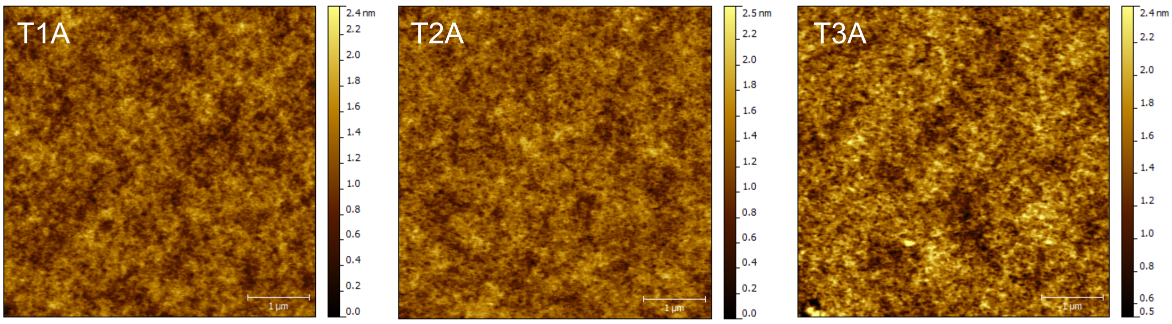

Figure S4 Topography scans by AFM of the solution processed truxenone layers using **T1A** (left), **T2A** (middle), and **T3A** (right). Roughnesses are in all three cases around 0.27 to 0.29 nm and scale bar is 1 µm.

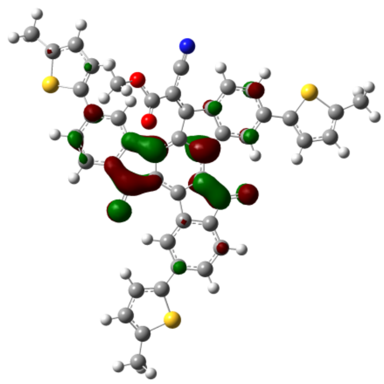

Figure S5 LUMO+1 orbital distribution for **T1A** calculated with Gaussian at the B3LYP/6-31G* level.

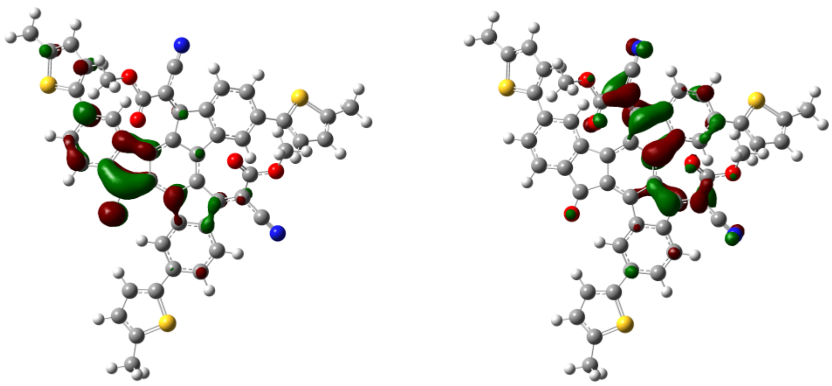

Figure S6 LUMO+2 (left) and LUMO+1 (right) orbital distributions for **T2A** calculated with Gaussian at the B3LYP/6-31G* level.

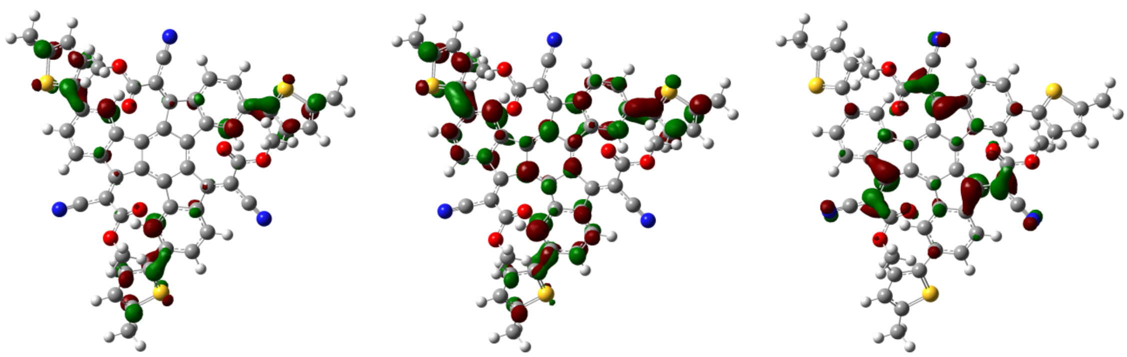

Figure S7 LUMO+3 (left), LUMO+2 (middle) and LUMO+1 (right) orbital distributions for **T3A** calculated with Gaussian at the B3LYP/6-31G* level.

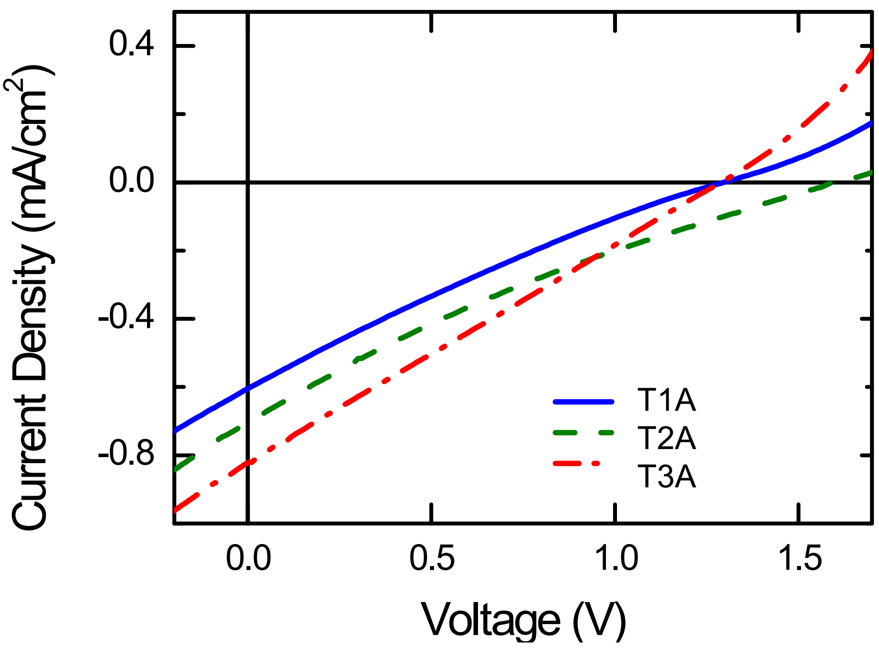

Figure S8 Current density-voltage (*J-V*) characteristics of the three SubPc devices measured under 100 mW/cm^2 intensity AM1.5G spectrum solar radiation.

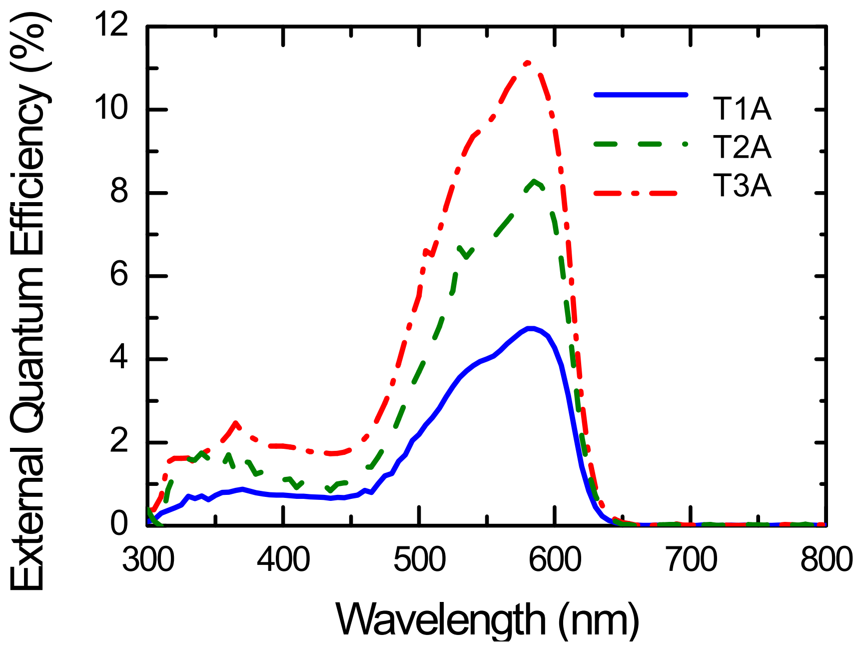

Figure S9 EQE plots for the three SubPc devices.

Table S1. Calculated Singlet Excitation Energies and Oscillator Strengths for **T1A**

```
 Excited State 1: 2.1736 eV  570.41 nm  f=0.2318  <S**2>=0.000
     192 ->196         0.13818
     193 ->196        -0.21055
     194 ->196        -0.15614
     195 ->196         0.63097

 Excited State 2: 2.2024 eV  562.96 nm  f=0.0624  <S**2>=0.000
     193 ->196        -0.37765
     194 ->196         0.58475

 Excited State 3: 2.2597 eV  548.67 nm  f=0.1056  <S**2>=0.000
     193 ->196         0.55194
     194 ->196         0.34482
     195 ->196         0.25983

 Excited State 4: 2.4866 eV  498.61 nm  f=0.0463  <S**2>=0.000
     192 ->196        -0.10268
     194 ->197         0.10402
     195 ->197         0.67683

 Excited State 5: 2.5039 eV  495.17 nm  f=0.1349  <S**2>=0.000
     194 ->197         0.67585
     195 ->197        -0.10472

 Excited State 6: 2.6167 eV  473.83 nm  f=0.1605  <S**2>=0.000
     193 ->197         0.68111

 Excited State 7: 2.7276 eV  454.55 nm  f=0.0248  <S**2>=0.000
     191 ->196        -0.26434
     192 ->196         0.45460
     194 ->198        -0.23177
     195 ->196        -0.12221
     195 ->198        -0.34109

 Excited State 8: 2.7702 eV  447.56 nm  f=0.1928  <S**2>=0.000
     191 ->196        -0.44098
     194 ->198         0.51674

 Excited State 9: 2.8011 eV  442.63 nm  f=0.2701  <S**2>=0.000
     191 ->196         0.40345
     192 ->196         0.32663
     192 ->197        -0.22461
     194 ->198         0.37665

 Excited State 10: 2.8396 eV  436.62 nm  f=0.2706  <S**2>=0.000
     192 ->196         0.34207
     192 ->197         0.11392
     194 ->197         0.10121
     195 ->198         0.58329

 Excited State 11: 2.9233 eV  424.12 nm  f=0.1243  <S**2>=0.000
     191 ->196        -0.11180
     191 ->197        -0.14536
```

```
     192 ->197        -0.21551
     193 ->198         0.61260

 Excited State  12:  3.0511 eV  406.36 nm  f=0.4377  <S**2>=0.000
     191 ->196         0.15381
     191 ->198        -0.14978
     192 ->197         0.56065
     193 ->198         0.25202

 Excited State  13:  3.1040 eV  399.43 nm  f=0.0167  <S**2>=0.000
     185 ->196        -0.10857
     185 ->197        -0.11031
     185 ->198        -0.26122
     187 ->196         0.27504
     187 ->197         0.45264
     187 ->198         0.22305
     188 ->197         0.11426
     191 ->197         0.12215

 Excited State  14:  3.1610 eV  392.23 nm  f=0.0152  <S**2>=0.000
     185 ->197         0.39242
     185 ->198        -0.19300
     187 ->196        -0.24514
     187 ->197         0.26574
     187 ->198        -0.31575
     188 ->197         0.10391

 Excited State  15:  3.2208 eV  384.95 nm  f=0.4026  <S**2>=0.000
     191 ->197        -0.36764
     192 ->198         0.53180

 Excited State  16:  3.3017 eV  375.52 nm  f=0.0126  <S**2>=0.000
     185 ->196         0.10810
     185 ->197         0.28903
     187 ->196         0.45469
     187 ->197        -0.13917
     187 ->198        -0.16967
     188 ->196         0.27324
     189 ->196         0.19464

 Excited State  17:  3.3320 eV  372.11 nm  f=0.0143  <S**2>=0.000
     186 ->196         0.22062
     187 ->196        -0.18383
     189 ->196         0.33417
     190 ->196         0.46353
     191 ->197         0.22430

 Excited State  18:  3.3575 eV  369.28 nm  f=0.0819  <S**2>=0.000
     188 ->196         0.19897
     189 ->196        -0.20561
     190 ->196        -0.18298
     191 ->197         0.42483
     192 ->198         0.36691
     193 ->198         0.13067

 Excited State  19:  3.3833 eV  366.46 nm  f=0.0303  <S**2>=0.000
```

```
     187 ->196         -0.25390
     188 ->196          0.59706
     191 ->197         -0.16115
     192 ->198         -0.14853

 Excited State  20:    3.4140 eV  363.16 nm  f=0.0363  <S**2>=0.000
     186 ->196         -0.31294
     187 ->196         -0.16695
     189 ->196          0.51689
     190 ->196         -0.28499
```

Table S2. Calculated Singlet Excitation Energies and Oscillator Strengths for **T2A**

```
 Excited State   1:    2.1165 eV  585.81 nm  f=0.1713  <S**2>=0.000
     213 ->217          0.15474
     215 ->217          0.10564
     215 ->218         -0.10871
     216 ->217          0.66419

 Excited State   2:    2.1662 eV  572.35 nm  f=0.0262  <S**2>=0.000
     214 ->218         -0.19481
     215 ->217          0.64559

 Excited State   3:    2.2196 eV  558.59 nm  f=0.0255  <S**2>=0.000
     214 ->217          0.47475
     215 ->218         -0.44366
     216 ->218          0.25074

 Excited State   4:    2.2424 eV  552.91 nm  f=0.2253  <S**2>=0.000
     214 ->217         -0.39596
     214 ->218         -0.14416
     216 ->218          0.53367

 Excited State   5:    2.2938 eV  540.52 nm  f=0.1673  <S**2>=0.000
     212 ->218         -0.11267
     214 ->217          0.25692
     214 ->218          0.27177
     215 ->218          0.42984
     216 ->217          0.13574
     216 ->218          0.34976

 Excited State   6:    2.3369 eV  530.55 nm  f=0.0380  <S**2>=0.000
     214 ->217         -0.16229
     214 ->218          0.59032
     215 ->217          0.22383
     215 ->218         -0.24982

 Excited State   7:    2.5869 eV  479.28 nm  f=0.0273  <S**2>=0.000
     212 ->217         -0.21144
     213 ->217         -0.39546
     213 ->218          0.26048
     216 ->217          0.12887
     216 ->219          0.43483
```

```
Excited State 8: 2.6062 eV  475.73 nm  f=0.0327  <S**2>=0.000
    212 ->217         0.41503
    213 ->217        -0.12460
    213 ->218        -0.36883
    214 ->219        -0.10844
    216 ->219         0.35494

Excited State 9: 2.6637 eV  465.47 nm  f=0.1464  <S**2>=0.000
    212 ->217        -0.18624
    212 ->218        -0.13417
    212 ->219        -0.13035
    213 ->217         0.33825
    213 ->218         0.10309
    215 ->219         0.43125
    216 ->219         0.29956

Excited State 10: 2.7059 eV  458.19 nm  f=0.4151  <S**2>=0.000
    212 ->217        -0.17532
    213 ->217        -0.36299
    213 ->218        -0.16316
    214 ->219        -0.27015
    215 ->219         0.36986
    216 ->219        -0.25699

Excited State 11: 2.7827 eV  445.55 nm  f=0.0315  <S**2>=0.000
    212 ->217        -0.10969
    212 ->218         0.51448
    213 ->217         0.13604
    214 ->219        -0.38283
    215 ->218         0.11524
    215 ->219        -0.13989

Excited State 12: 2.8343 eV  437.45 nm  f=0.4226  <S**2>=0.000
    212 ->217        -0.32262
    212 ->218         0.27117
    213 ->218        -0.36584
    214 ->219         0.39567

Excited State 13: 2.8658 eV  432.64 nm  f=0.5151  <S**2>=0.000
    212 ->217         0.27221
    212 ->218         0.30346
    213 ->218         0.30275
    214 ->219         0.27102
    215 ->218         0.10791
    215 ->219         0.33686

Excited State 14: 3.0558 eV  405.74 nm  f=0.2221  <S**2>=0.000
    213 ->219         0.67013

Excited State 15: 3.1448 eV  394.25 nm  f=0.0079  <S**2>=0.000
    207 ->217         0.10789
    207 ->218        -0.12544
    207 ->219         0.26903
    208 ->217         0.22945
    208 ->218        -0.24668
    208 ->219         0.47384
```

```
 Excited State 16: 3.2927 eV  376.54 nm  f=0.0500  <S**2>=0.000
     208 ->217         0.35956
     210 ->217         0.13169
     211 ->217         0.53017
     212 ->219        -0.14011

 Excited State 17: 3.3100 eV  374.57 nm  f=0.0022  <S**2>=0.000
     207 ->217         0.32831
     208 ->217         0.35249
     208 ->218         0.14926
     208 ->219        -0.14030
     209 ->217        -0.15082
     210 ->217         0.26630
     211 ->217        -0.28387
     211 ->218         0.12103
     212 ->219         0.13932

 Excited State 18: 3.3507 eV  370.02 nm  f=0.0199  <S**2>=0.000
     207 ->217        -0.12967
     209 ->217         0.56751
     210 ->217         0.30280
     211 ->217        -0.17542
     211 ->218         0.10229
     212 ->219        -0.12686

 Excited State 19: 3.3741 eV  367.46 nm  f=0.0349  <S**2>=0.000
     207 ->217         0.31111
     208 ->217         0.10035
     209 ->217         0.36627
     210 ->217        -0.34376
     210 ->218        -0.11581
     211 ->218        -0.17534
     212 ->219         0.24508

 Excited State 20: 3.3854 eV  366.23 nm  f=0.0182  <S**2>=0.000
     207 ->218        -0.10733
     208 ->217        -0.30153
     210 ->217         0.25183
     210 ->218         0.21931
     211 ->217         0.24802
     211 ->218         0.16014
     212 ->219         0.40497
```

Table S3. Calculated Singlet Excitation Energies and Oscillator Strengths for **T3A**

```
 Excited State 1: 2.1389 eV  579.68 nm  f=0.0064  <S**2>=0.000
     235 -> 240        0.15830
     236 -> 238        0.46236
     236 -> 239        0.11327
     237 -> 238       -0.11592
     237 -> 239        0.45951

 Excited State 2: 2.1455 eV  577.89 nm  f=0.0363  <S**2>=0.000
```

```
    233 -> 239       -0.15440
    234 -> 238       -0.15621
    236 -> 238        0.11954
    236 -> 239       -0.44548
    237 -> 238        0.46164
    237 -> 239        0.12166

Excited State 3: 2.1828 eV  568.01 nm  f=0.1117  <S**2>=0.000
    235 -> 238        0.29250
    236 -> 238        0.39465
    236 -> 239       -0.20574
    237 -> 238       -0.20821
    237 -> 239       -0.38731

Excited State 4: 2.1832 eV  567.90 nm  f=0.1092  <S**2>=0.000
    235 -> 239       -0.31962
    236 -> 238        0.20273
    236 -> 239        0.38567
    237 -> 238        0.38226
    237 -> 239       -0.19327

Excited State 5: 2.2085 eV  561.39 nm  f=0.0949  <S**2>=0.000
    235 -> 238       -0.37730
    235 -> 239        0.45199
    236 -> 238        0.15423
    236 -> 240       -0.19041
    237 -> 239       -0.18084
    237 -> 240        0.12626

Excited State 6: 2.2086 eV  561.36 nm  f=0.0970  <S**2>=0.000
    235 -> 238        0.46328
    235 -> 239        0.37617
    236 -> 239        0.17892
    236 -> 240        0.12811
    237 -> 238        0.14493
    237 -> 240        0.18865

Excited State 7: 2.4052 eV  515.48 nm  f=0.1123  <S**2>=0.000
    233 -> 239        0.11141
    234 -> 238       -0.11595
    234 -> 240       -0.11325
    235 -> 239       -0.17197
    236 -> 239       -0.11947
    237 -> 238       -0.11339
    237 -> 240        0.60177

Excited State 8: 2.4055 eV  515.42 nm  f=0.1124  <S**2>=0.000
    233 -> 238       -0.11342
    233 -> 240        0.11364
    234 -> 239       -0.11380
    235 -> 238       -0.18655
    236 -> 238        0.10740
    236 -> 240        0.60191
    237 -> 239       -0.11446

Excited State 9: 2.4355 eV  509.08 nm  f=0.0188  <S**2>=0.000
```

```
    233 -> 239         0.21587
    234 -> 238         0.21468
    235 -> 240         0.61070
    236 -> 238        -0.11118
    237 -> 239        -0.10952

Excited State 10: 2.4892 eV  498.08 nm  f=0.0275  <S**2>=0.000
    233 -> 238        -0.22545
    233 -> 239         0.37632
    234 -> 238         0.37874
    234 -> 239         0.22526
    235 -> 240        -0.26044
    236 -> 239        -0.11324
    237 -> 238         0.11288

Excited State 11: 2.6407 eV  469.51 nm  f=0.1291  <S**2>=0.000
    233 -> 238        -0.42654
    233 -> 239        -0.17994
    234 -> 238        -0.18449
    234 -> 239         0.42778
    235 -> 240         0.15955
    236 -> 239         0.11775
    237 -> 238        -0.11790

Excited State 12: 2.6650 eV  465.24 nm  f=0.6211  <S**2>=0.000
    233 -> 238         0.39985
    233 -> 240         0.11980
    234 -> 239         0.39807
    234 -> 240        -0.31212
    236 -> 240         0.12210
    237 -> 240        -0.15869

Excited State 13: 2.6656 eV  465.12 nm  f=0.6219  <S**2>=0.000
    233 -> 239         0.40089
    233 -> 240         0.31265
    234 -> 238        -0.39646
    234 -> 240         0.12048
    236 -> 240        -0.15890
    237 -> 240        -0.12241

Excited State 14: 2.8261 eV  438.71 nm  f=0.2254  <S**2>=0.000
    233 -> 238         0.21409
    233 -> 240         0.11418
    234 -> 239         0.21402
    234 -> 240         0.57992
    236 -> 240         0.12014
    237 -> 240         0.12176

Excited State 15: 2.8265 eV  438.64 nm  f=0.2253  <S**2>=0.000
    233 -> 239        -0.21490
    233 -> 240         0.57976
    234 -> 238         0.21356
    234 -> 240        -0.11455
    236 -> 240        -0.12172
    237 -> 240         0.11970
```

```
Excited State 16: 3.3291 eV  372.42 nm  f=0.0972  <S**2>=0.000
    229 -> 238        0.30069
    232 -> 238        0.61211

Excited State 17: 3.3298 eV  372.35 nm  f=0.0969  <S**2>=0.000
    229 -> 239        0.30063
    232 -> 239        0.61561

Excited State 18: 3.3678 eV  368.15 nm  f=0.0009  <S**2>=0.000
    230 -> 238        0.49840
    231 -> 239        0.49022

Excited State 19: 3.3734 eV  367.53 nm  f=0.0009  <S**2>=0.000
    230 -> 238        0.39805
    230 -> 239       -0.24217
    230 -> 240        0.14522
    231 -> 238       -0.31364
    231 -> 239       -0.38572

Excited State 20: 3.3737 eV  367.50 nm  f=0.0006  <S**2>=0.000
    230 -> 238        0.26317
    230 -> 239        0.32133
    231 -> 238        0.44878
    231 -> 239       -0.29847
    231 -> 240       -0.14461
```