Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Calculating transition dipole moments of phosphorescent emitters for efficient organic light-emitting diodes

Mohammad Babazadeh,[a] Paul L. Burn,*[a] and David M. Huang*[b]

[a] Centre for Organic Photonics & Electronics, School of Chemistry and Molecular Biosciences
The University of Queensland, Queensland, 4072 Australia.
Fax: +61(07)33469273; Tel: +61 (0)733467614; E-mail: p.burn2@uq.edu.au

[b] Department of Chemistry, School of Physical Sciences
The University of Adelaide, Adelaide 5005, Australia.
E-mail: david.huang@adelaide.edu.au

Input files for the calculations discussed in the main paper are given below. The molecular geometries in the input files for geometry optimizations are the optimized geometries resulting from the calculations.

1. Gas-phase calculations

1.1 Geometry Optimization

Input file: BP86 ground-state geometry optimization in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 BP86 ground-state S0 geometry optimization (gas phase)

Atoms
Ir      0.00000000      0.00000000      0.00000000
N      -0.20165000     -1.84017100      1.09621300
N       1.69023500      0.74695200      1.10026100
N      -1.49257800      1.09283900      1.09790000
C       0.54518100     -2.88115700      0.60708000
C       2.21656700      1.91664800      0.61492600
C      -2.76748200      0.96785300      0.60839500
C       0.47367000     -4.14069200      1.22597600
C       3.33531100      2.48995200      1.24281100
C      -3.82267700      1.65710000      1.22983200
C      -0.34880500     -4.33779900      2.32561500
C       3.91184700      1.87883600      2.34677900
C      -3.58239100      2.46360300      2.33282700
C      -1.10733000     -3.26653600      2.80668900
C       3.36647700      0.68275200      2.82250700
C      -2.27535300      2.58351000      2.81420500
C      -1.00409800     -2.04300200      2.16009600
C       2.26268200      0.15523200      2.16754000
C      -1.26715000      1.88529900      2.16471800
H       1.06458500     -4.96410400      0.83081400
H       3.75077600      3.41621000      0.85188300
H      -4.83123000      1.55823100      0.83443000
H      -0.40484900     -5.31620300      2.80184200
H       4.78067400      2.32430500      2.83044200
H      -4.40185100      2.99902000      2.81136900
H      -1.77290000     -3.37378000      3.66090300
H       3.78858400      0.16138900      3.67937000
H      -2.03556800      3.21012400      3.67101000
H      -1.58020000     -1.17955800      2.48865800
H       1.80524900     -0.77800300      2.49186400
H      -0.23133800      1.95161100      2.49349100
C      -1.66912000     -0.46823700     -1.04520600
C       1.24109600     -1.21074900     -1.04479700
C       0.42986900      1.67982900     -1.04465700
C       1.35838600     -2.54877000     -0.55717500
C       1.52765800      2.45174200     -0.55400400
```

```
C     -2.88617700      0.09973100     -0.55764500
C     -4.11889800     -0.16350700     -1.18453900
C      2.20359600     -3.48426500     -1.18365100
C      1.91859700      3.64940600     -1.18234200
C     -4.17893200     -0.98878400     -2.29953800
C      2.94761800     -3.12357100     -2.29914400
C      1.23908700      4.11050600     -2.30200800
C     -2.99667100     -1.55544600     -2.79399100
C      2.84590900     -1.81661400     -2.79426000
C      0.15968300      3.36826200     -2.79938700
C     -1.77253000     -1.29947400     -2.17824800
C      2.01191400     -0.88469700     -2.17840500
C     -0.23348000      2.18188700     -2.18192800
H      2.28268700     -4.50204400     -0.79960600
H      2.75965100      4.22718000     -0.79702600
H     -5.03966100      0.27768800     -0.80089700
H     -5.13427200     -1.19131800     -2.78265800
H      3.60107400     -3.84944300     -2.78203300
H      1.54366200      5.03751100     -2.78675100
H     -3.03359700     -2.20453800     -3.67051500
H      3.42556500     -1.52409700     -3.67142700
H     -0.37968300      3.72183100     -3.67974200
H     -0.87052300     -1.75244500     -2.58869300
H      1.95236500      0.12272300     -2.58919300
H     -1.07460700      1.62569900     -2.59467700
End

Basis
type TZ2P
Core None
End

XC
GGA BP86
END

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

BECKEGRID
Quality verygood
End

RELATIVISTIC Scalar ZORA
```

End Input
eor

Input file: B3LYP ground state geometry optimization in gas phase

$ADFBIN/adf <<eor
Title Ir(ppy)3 B3LYP ground state S0 geometry optimization (gas phase)

Atoms
Ir 0.00000000 0.00000000 0.00000000
N -0.19567500 -1.86770600 1.09395000
N 1.71473500 0.76459800 1.09237100
N -1.51727300 1.10307400 1.09595700
C 0.54395700 -2.88707000 0.58573800
C 2.22772600 1.91517300 0.58444800
C -2.77031100 0.97667000 0.58752700
C 0.47525100 -4.15300600 1.17846800
C 3.35721000 2.48887100 1.17942700
C -3.83013900 1.67026900 1.18283900
C -0.34450300 -4.36453100 2.26963700
C 3.94795300 1.88557100 2.27254100
C -3.60110200 2.48149700 2.27697800
C -1.10267300 -3.30883500 2.76674200
C 3.41219100 0.70120400 2.76929700
C -2.30735300 2.60509300 2.77437100
C -0.99868700 -2.08081300 2.14273300
C 2.29836100 0.17661000 2.14292100
C -1.29793700 1.90081300 2.14735200
H 1.05789800 -4.96725900 0.77596000
H 3.77148400 3.40075600 0.77785000
H -4.82699600 1.57680100 0.78048000
H -0.40015900 -5.34394200 2.72583000
H 4.82295400 2.32759000 2.73032000
H -4.42009400 3.01958500 2.73555200
H -1.76569300 -3.43378600 3.61060600
H 3.84979000 0.19068300 3.61498500
H -2.08239800 3.23780800 3.62076300
H -1.57414600 -1.22998300 2.47843600
H 1.84910800 -0.74739800 2.47773800
H -0.27314400 1.96996100 2.48301900
C -1.67180300 -0.47731800 -1.04840700
C 1.25185700 -1.20662500 -1.04873000
C 0.41980600 1.68545700 -1.05051500
C 1.35904500 -2.54047400 -0.57671900
C 1.52143200 2.44594000 -0.57991600
C -2.87923000 0.10030700 -0.57717100
C -4.10155900 -0.15093100 -1.21498200
C 2.19391900 -3.47030400 -1.21103200
C 1.91133000 3.63103200 -1.21858600

```
C     -4.15433600     -0.97524100     -2.32389500
C      2.93735200     -3.10134100     -2.31692500
C      1.22254600      4.08532500     -2.32817000
C     -2.97857800     -1.55592300     -2.79873800
C      2.84921100     -1.79321200     -2.79235800
C      0.13466200      3.35313400     -2.80284100
C     -1.76521200     -1.31220300     -2.17067800
C      2.02483400     -0.86764600     -2.16811200
C     -0.25749500      2.17994700     -2.17380300
H      2.26828200     -4.48618600     -0.84700500
H      2.75390500      4.20433400     -0.85575100
H     -5.01766600      0.29515900     -0.85181900
H     -5.09849600     -1.16603300     -2.81599100
H      3.58003700     -3.82094600     -2.80595300
H      1.52625800      4.99913100     -2.82088400
H     -3.01238000     -2.20307500     -3.66693100
H      3.42884700     -1.49686000     -3.65827200
H     -0.40878700      3.70301500     -3.67221500
H     -0.87006200     -1.77316700     -2.56480200
H      1.97525100      0.13783700     -2.56244400
H     -1.10258400      1.63254900     -2.56777300
End

Basis
type TZ2P
Core None
End

XC
hybrid B3LYP
END

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

BECKEGRID
Quality verygood
End

RELATIVISTIC Scalar ZORA

End Input
eor
```

Input file: BP86 TDDFT excited triplet-state geometry optimization in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 BP86 TDDFT excited triplet-state geometry optimization (gas phase)

Atoms
Ir      0.003252   -0.048694   -0.103035
N      -0.189849   -1.900377    0.997672
N       1.522436    0.759935    1.195369
N      -1.441397    1.159563    1.023909
C       0.619134   -2.906527    0.541933
C       2.126399    1.927958    0.664115
C      -2.728021    1.082233    0.564633
C       0.610327   -4.158288    1.178873
C       3.257829    2.450645    1.296550
C      -3.735419    1.856122    1.164028
C      -0.234662   -4.384743    2.256364
C       3.817183    1.850943    2.420310
C      -3.425537    2.709799    2.213471
C      -1.071653   -3.352838    2.693211
C       3.213544    0.646150    2.911668
C      -2.103603    2.785196    2.660285
C      -1.015567   -2.130787    2.036768
C       2.105908    0.153106    2.268988
C      -1.145001    1.996504    2.037704
H       1.267537   -4.949153    0.822207
H       3.711932    3.352786    0.886065
H      -4.757354    1.787016    0.796474
H      -0.245281   -5.355073    2.752494
H       4.699725    2.271765    2.897874
H      -4.204044    3.316712    2.676111
H      -1.756042   -3.488052    3.529032
H       3.611566    0.119041    3.777015
H      -1.811274    3.447655    3.473204
H      -1.641861   -1.292233    2.339277
H       1.623156   -0.760871    2.615397
H      -0.098292    2.015569    2.335414
C      -1.749427   -0.513190   -1.014506
C       1.278645   -1.193574   -1.093702
C       0.426537    1.688096   -1.102596
C       1.427263   -2.544406   -0.618098
C       1.488000    2.456860   -0.529996
C      -2.917166    0.157694   -0.550854
C      -4.170931   -0.088425   -1.137994
C       2.303619   -3.436223   -1.250925
C       1.857064    3.674545   -1.142302
C      -4.294039   -1.002679   -2.178222
C       3.044183   -3.025338   -2.357284
C       1.207942    4.126764   -2.289681
C      -3.158715   -1.686455   -2.631212
```

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C       2.918245   -1.711123   -2.835876
C       0.169247    3.378483   -2.847767
C      -1.911843   -1.455391   -2.051025
C       2.064028   -0.811194   -2.210775
C      -0.216011    2.169127   -2.243820
H       2.417294   -4.457844   -0.886061
H       2.658234    4.278762   -0.713682
H      -5.059156    0.435221   -0.782330
H      -5.267384   -1.187778   -2.632386
H       3.723858   -3.723913   -2.845376
H       1.512001    5.070267   -2.745542
H      -3.247329   -2.405761   -3.447266
H       3.502553   -1.392996   -3.700486
H      -0.344103    3.727678   -3.744672
H      -1.042949   -1.993624   -2.428762
H       1.980234    0.206890   -2.587413
H      -1.028549    1.592900   -2.688761
End

Basis
Type TZ2P
Core None
End

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

RELATIVISTIC Scalar ZORA

XC
GGA BP86
END

EXCITATION
Onlytrip
Lowest 1
END

EXCITEDGO
State A 1
Triplet
END

HFAtomsPerPass 1
```

```
EPRINT
SFO OrbPop GrossPop FragPop
FragPop Gross
Orbpop 90 40 tol=1e-4
Subend
End

End Input
eor
```

Input file: B3LYP TDDFT excited triplet-state geometry optimization in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 B3LYP TDDFT excited triplet-state geometry optimization (gas phase)

Atoms
Ir     0.04870100    -0.04006800    -0.06874300
N     -0.16222100    -1.92608500     1.03476600
N      1.47993400     0.80493000     1.19600500
N     -1.47840900     1.16942500     1.05867200
C      0.58453300    -2.93183000     0.51847000
C      2.10565600     1.96275500     0.65887300
C     -2.73989200     1.07746100     0.57537100
C      0.54189200    -4.20400100     1.09767500
C      3.24455600     2.46644800     1.26968400
C     -3.76244200     1.85144800     1.13732200
C     -0.27387100    -4.43674400     2.19024100
C      3.79400200     1.87950400     2.40336500
C     -3.48172700     2.70997100     2.18385100
C     -1.04393700    -3.39498900     2.69732400
C      3.15468800     0.71119400     2.92411200
C     -2.17890100     2.79219500     2.66441100
C     -0.95530600    -2.15673000     2.08547200
C      2.04356000     0.22572100     2.30871300
C     -1.20895900     2.00707600     2.06759400
H      1.14075900    -5.00420700     0.68889900
H      3.71724200     3.33933900     0.83918300
H     -4.76613500     1.78490400     0.74541200
H     -0.31266000    -5.42023800     2.64045000
H      4.68245700     2.28265200     2.86558200
H     -4.26831800     3.31502700     2.61688100
H     -1.69951300    -3.53401600     3.54541600
H      3.53968000     0.20409300     3.79837100
H     -1.91212400     3.45489600     3.47548100
H     -1.53139300    -1.31201300     2.43902800
H      1.54467600    -0.65708600     2.68285200
H     -0.17728000     2.03740100     2.38654200
C     -1.73231300    -0.48732200    -1.01487900
C      1.25933000    -1.21048000    -1.11294200
```

```
C      0.44178200     1.67879100    -1.11004100
C      1.38171600    -2.56070200    -0.65457800
C      1.47711700     2.47300900    -0.54420000
C     -2.90434400     0.14397800    -0.54137100
C     -4.15124800    -0.12018500    -1.12447300
C      2.22337100    -3.45911900    -1.30897700
C      1.83949500     3.67976700    -1.16901700
C     -4.26099100    -1.00922900    -2.17943000
C      2.95126800    -3.05650500    -2.42177700
C      1.20808900     4.09612700    -2.33007600
C     -3.11553800    -1.64359100    -2.65578500
C      2.84299500    -1.74546800    -2.88909700
C      0.19430700     3.31982100    -2.88855000
C     -1.87655400    -1.39017500    -2.07980900
C      2.01578100    -0.84030300    -2.24612500
C     -0.18164700     2.12503100    -2.27211800
H      2.32374200    -4.47857400    -0.95991500
H      2.61753600     4.29991200    -0.74124400
H     -5.04374200     0.36825500    -0.75532800
H     -5.22626300    -1.20732300    -2.62739800
H      3.60180200    -3.76199800    -2.92280800
H      1.50185600     5.02817700    -2.79767800
H     -3.18720400    -2.33944900    -3.48355400
H      3.41195500    -1.43445600    -3.75661000
H     -0.30301300     3.64081800    -3.79568500
H     -1.00645500    -1.89272700    -2.47933200
H      1.94033200     0.17106200    -2.61773600
H     -0.96986200     1.53286300    -2.71977600
End

Basis
Type TZ2P
Core None
End

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

RELATIVISTIC Scalar ZORA

XC
HYBRID B3LYP
END
```

```
EXCITATION
Onlytrip
Lowest 1
END

EXCITEDGO
State A 1
Triplet
END

HFAtomsPerPass 1

EPRINT
SFO OrbPop GrossPop FragPop
FragPop Gross
Orbpop 90 40 tol=1e-4
Subend
End

End Input
eor
```

Input file: BP86 UDFT triplet-state geometry optimization in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 UDFT triplet-state geometry optimization (gas phase)

Atoms
Ir      0.00160200     -0.00120900     -0.08602900
N      -0.21047200     -1.81278000      1.05839600
N       1.66963200      0.72345800      1.06127800
N      -1.45869300      1.08602100      1.06279100
C       0.55325400     -2.86656200      0.58118700
C       2.19805000      1.91488100      0.58590300
C      -2.75325800      0.95749300      0.58416400
C       0.53339600     -4.09865800      1.26472600
C       3.26528100      2.52118500      1.27874300
C      -3.80896500      1.58943600      1.27127200
C      -0.26977400     -4.27606500      2.37605900
C       3.81419600      1.91946600      2.39565700
C      -3.55955300      2.36514700      2.38830900
C      -1.07026400     -3.20315400      2.81918300
C       3.28953900      0.68587800      2.83538500
C      -2.23009600      2.51444700      2.83404600
C      -1.00150800     -2.00226500      2.13351800
C       2.22443500      0.13766400      2.14153500
C      -1.22583200      1.85691000      2.14414800
H       1.15926500     -4.91407400      0.90735800
H       3.65468500      3.47370700      0.92453000
```

H -4.82822400 1.46001800 0.91259100
H -0.28382700 -5.23146300 2.89881200
H 4.64022600 2.39145400 2.92594900
H -4.37893900 2.85374000 2.91391500
H -1.73187400 -3.29897500 3.67729300
H 3.69974500 0.16394900 3.69711900
H -1.98121000 3.12812200 3.69705000
H -1.59310600 -1.14150700 2.44198400
H 1.77812900 -0.80766300 2.44692900
H -0.18448800 1.93370500 2.45363500
C -1.68007000 -0.47469000 -1.09252500
C 1.25285100 -1.21688400 -1.09373100
C 0.42778800 1.68856300 -1.09635300
C 1.32405500 -2.56870600 -0.60656000
C 1.56146200 2.42816000 -0.60671900
C -2.88313400 0.14522100 -0.60631200
C -4.11171600 -0.08247400 -1.26100300
C 2.14230000 -3.51426500 -1.25921000
C 1.97463700 3.60648300 -1.26354800
C -4.17619400 -0.92545300 -2.36207600
C 2.90294200 -3.14516900 -2.36045200
C 1.27899000 4.07579600 -2.36939500
C -3.01492200 -1.56511900 -2.82536900
C 2.86782500 -1.82054200 -2.82639900
C 0.14998900 3.38234600 -2.83644000
C -1.79248500 -1.34733200 -2.19087200
C 2.06266700 -0.87473000 -2.19312800
C -0.26960700 2.21503700 -2.19970600
H 2.18422700 -4.54449400 -0.90532200
H 2.84560300 4.15834900 -0.90973100
H -5.02209800 0.40275700 -0.90874100
H -5.12952500 -1.09168100 -2.86353100
H 3.52868400 -3.88451800 -2.86015100
H 1.60927500 4.98440400 -2.87268500
H -3.06731600 -2.22826600 -3.68939000
H 3.46639700 -1.53226800 -3.69103200
H -0.39532500 3.75337600 -3.70471000
H -0.89820800 -1.83782700 -2.57337600
H 2.03390400 0.14433100 -2.57681300
H -1.13677700 1.67954900 -2.58416700
End

RELATIVISTIC Scalar ZORA

Unrestricted
Charge 0 2

Basis
type TZ2P
Core None

```
End

XC
GGA BP86
END

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

BECKEGRID
Quality verygood
End

End Input
eor
```

1.2 TDDFT excited-state energy calculations

Input file: B3LYP TDDFT (ground-state geometry) spin-orbit perturbation calculation (pSOC-TDDFT) in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 (BP86/TZ2P S0 optimised) B3LYP TDDFT relativistic spin-orbit perturbation (gas phase)

Atoms
Ir      0.00000000      0.00000000      0.00000000
N      -0.20165000     -1.84017100      1.09621300
N       1.69023500      0.74695200      1.10026100
N      -1.49257800      1.09283900      1.09790000
C       0.54518100     -2.88115700      0.60708000
C       2.21656700      1.91664800      0.61492600
C      -2.76748200      0.96785300      0.60839500
C       0.47367000     -4.14069200      1.22597600
C       3.33531100      2.48995200      1.24281100
C      -3.82267700      1.65710000      1.22983200
C      -0.34880500     -4.33779900      2.32561500
C       3.91184700      1.87883600      2.34677900
C      -3.58239100      2.46360300      2.33282700
C      -1.10733000     -3.26653600      2.80668900
C       3.36647700      0.68275200      2.82250700
C      -2.27535300      2.58351000      2.81420500
C      -1.00409800     -2.04300200      2.16009600
```

C 2.26268200 0.15523200 2.16754000
C -1.26715000 1.88529900 2.16471800
H 1.06458500 -4.96410400 0.83081400
H 3.75077600 3.41621000 0.85188300
H -4.83123000 1.55823100 0.83443000
H -0.40484900 -5.31620300 2.80184200
H 4.78067400 2.32430500 2.83044200
H -4.40185100 2.99902000 2.81136900
H -1.77290000 -3.37378000 3.66090300
H 3.78858400 0.16138900 3.67937000
H -2.03556800 3.21012400 3.67101000
H -1.58020000 -1.17955800 2.48865800
H 1.80524900 -0.77800300 2.49186400
H -0.23133800 1.95161100 2.49349100
C -1.66912000 -0.46823700 -1.04520600
C 1.24109600 -1.21074900 -1.04479700
C 0.42986900 1.67982900 -1.04465700
C 1.35838600 -2.54877000 -0.55717500
C 1.52765800 2.45174200 -0.55400400
C -2.88617700 0.09973100 -0.55764500
C -4.11889800 -0.16350700 -1.18453900
C 2.20359600 -3.48426500 -1.18365100
C 1.91859700 3.64940600 -1.18234200
C -4.17893200 -0.98878400 -2.29953800
C 2.94761800 -3.12357100 -2.29914400
C 1.23908700 4.11050600 -2.30200800
C -2.99667100 -1.55544600 -2.79399100
C 2.84590900 -1.81661400 -2.79426000
C 0.15968300 3.36826200 -2.79938700
C -1.77253000 -1.29947400 -2.17824800
C 2.01191400 -0.88469700 -2.17840500
C -0.23348000 2.18188700 -2.18192800
H 2.28268700 -4.50204400 -0.79960600
H 2.75965100 4.22718000 -0.79702600
H -5.03966100 0.27768800 -0.80089700
H -5.13427200 -1.19131800 -2.78265800
H 3.60107400 -3.84944300 -2.78203300
H 1.54366200 5.03751100 -2.78675100
H -3.03359700 -2.20453800 -3.67051500
H 3.42556500 -1.52409700 -3.67142700
H -0.37968300 3.72183100 -3.67974200
H -0.87052300 -1.75244500 -2.58869300
H 1.95236500 0.12272300 -2.58919300
H -1.07460700 1.62569900 -2.59467700
End

SOPERT
Relativistic scalar ZORA

Basis

```
Type TZP
Core None
End

AddDiffuseFit

SCF
Iterations 300
End

XC
HYBRID B3LYP
End

EXACTDENSITY

Excitations
Lowest 20
End

LOCORB
end

EPRINT
 SFO OrbPop GrossPop FragPop
 FragPop Gross
 Orbpop 90 30 tol=1e-4
 Subend
End

End Input
eor
```

Input file: B3LYP TDDFT (ground-state geometry) spin-orbit SCF calculation (SOC-TDDFT) in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 (BP86/TZ2P S0 optimised) B3LYP TDDFT relativistic spin-orbit SCF (gas phase)

Atoms
Ir      0.00000000      0.00000000      0.00000000
N      -0.20165000     -1.84017100      1.09621300
N       1.69023500      0.74695200      1.10026100
N      -1.49257800      1.09283900      1.09790000
C       0.54518100     -2.88115700      0.60708000
C       2.21656700      1.91664800      0.61492600
C      -2.76748200      0.96785300      0.60839500
C       0.47367000     -4.14069200      1.22597600
C       3.33531100      2.48995200      1.24281100
```

C	-3.82267700	1.65710000	1.22983200
C	-0.34880500	-4.33779900	2.32561500
C	3.91184700	1.87883600	2.34677900
C	-3.58239100	2.46360300	2.33282700
C	-1.10733000	-3.26653600	2.80668900
C	3.36647700	0.68275200	2.82250700
C	-2.27535300	2.58351000	2.81420500
C	-1.00409800	-2.04300200	2.16009600
C	2.26268200	0.15523200	2.16754000
C	-1.26715000	1.88529900	2.16471800
H	1.06458500	-4.96410400	0.83081400
H	3.75077600	3.41621000	0.85188300
H	-4.83123000	1.55823100	0.83443000
H	-0.40484900	-5.31620300	2.80184200
H	4.78067400	2.32430500	2.83044200
H	-4.40185100	2.99902000	2.81136900
H	-1.77290000	-3.37378000	3.66090300
H	3.78858400	0.16138900	3.67937000
H	-2.03556800	3.21012400	3.67101000
H	-1.58020000	-1.17955800	2.48865800
H	1.80524900	-0.77800300	2.49186400
H	-0.23133800	1.95161100	2.49349100
C	-1.66912000	-0.46823700	-1.04520600
C	1.24109600	-1.21074900	-1.04479700
C	0.42986900	1.67982900	-1.04465700
C	1.35838600	-2.54877000	-0.55717500
C	1.52765800	2.45174200	-0.55400400
C	-2.88617700	0.09973100	-0.55764500
C	-4.11889800	-0.16350700	-1.18453900
C	2.20359600	-3.48426500	-1.18365100
C	1.91859700	3.64940600	-1.18234200
C	-4.17893200	-0.98878400	-2.29953800
C	2.94761800	-3.12357100	-2.29914400
C	1.23908700	4.11050600	-2.30200800
C	-2.99667100	-1.55544600	-2.79399100
C	2.84590900	-1.81661400	-2.79426000
C	0.15968300	3.36826200	-2.79938700
C	-1.77253000	-1.29947400	-2.17824800
C	2.01191400	-0.88469700	-2.17840500
C	-0.23348000	2.18188700	-2.18192800
H	2.28268700	-4.50204400	-0.79960600
H	2.75965100	4.22718000	-0.79702600
H	-5.03966100	0.27768800	-0.80089700
H	-5.13427200	-1.19131800	-2.78265800
H	3.60107400	-3.84944300	-2.78203300
H	1.54366200	5.03751100	-2.78675100
H	-3.03359700	-2.20453800	-3.67051500
H	3.42556500	-1.52409700	-3.67142700
H	-0.37968300	3.72183100	-3.67974200
H	-0.87052300	-1.75244500	-2.58869300

```
H      1.95236500      0.12272300     -2.58919300
H     -1.07460700      1.62569900     -2.59467700
End

relativistic spinorbit zora

Basis
Type TZP
Core None
End

AddDiffuseFit

SCF
Iterations 300
End

XC
HYBRID B3LYP
End

EXACTDENSITY

Excitations
Lowest 3
End


EPRINT
 SFO OrbPop GrossPop FragPop
 FragPop Gross
 Orbpop 90 30 tol=1e-4
 Subend
End

End Input
eor
```

Input file: B3LYP TDDFT (excited triplet geometry) spin-orbit perturbation calculation (pSOC-TDDFT) in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 (BP86/TZ2P T1 TDDFT optimised) T1 B3LYP TDDFT relativistic spin-orbit perturbation (gas phase)

Atoms
Ir       0.003252   -0.048694   -0.103035
N       -0.189849   -1.900377    0.997672
N        1.522436    0.759935    1.195369
N       -1.441397    1.159563    1.023909
C        0.619134   -2.906527    0.541933
```

C	2.126399	1.927958	0.664115
C	-2.728021	1.082233	0.564633
C	0.610327	-4.158288	1.178873
C	3.257829	2.450645	1.296550
C	-3.735419	1.856122	1.164028
C	-0.234662	-4.384743	2.256364
C	3.817183	1.850943	2.420310
C	-3.425537	2.709799	2.213471
C	-1.071653	-3.352838	2.693211
C	3.213544	0.646150	2.911668
C	-2.103603	2.785196	2.660285
C	-1.015567	-2.130787	2.036768
C	2.105908	0.153106	2.268988
C	-1.145001	1.996504	2.037704
H	1.267537	-4.949153	0.822207
H	3.711932	3.352786	0.886065
H	-4.757354	1.787016	0.796474
H	-0.245281	-5.355073	2.752494
H	4.699725	2.271765	2.897874
H	-4.204044	3.316712	2.676111
H	-1.756042	-3.488052	3.529032
H	3.611566	0.119041	3.777015
H	-1.811274	3.447655	3.473204
H	-1.641861	-1.292233	2.339277
H	1.623156	-0.760871	2.615397
H	-0.098292	2.015569	2.335414
C	-1.749427	-0.513190	-1.014506
C	1.278645	-1.193574	-1.093702
C	0.426537	1.688096	-1.102596
C	1.427263	-2.544406	-0.618098
C	1.488000	2.456860	-0.529996
C	-2.917166	0.157694	-0.550854
C	-4.170931	-0.088425	-1.137994
C	2.303619	-3.436223	-1.250925
C	1.857064	3.674545	-1.142302
C	-4.294039	-1.002679	-2.178222
C	3.044183	-3.025338	-2.357284
C	1.207942	4.126764	-2.289681
C	-3.158715	-1.686455	-2.631212
C	2.918245	-1.711123	-2.835876
C	0.169247	3.378483	-2.847767
C	-1.911843	-1.455391	-2.051025
C	2.064028	-0.811194	-2.210775
C	-0.216011	2.169127	-2.243820
H	2.417294	-4.457844	-0.886061
H	2.658234	4.278762	-0.713682
H	-5.059156	0.435221	-0.782330
H	-5.267384	-1.187778	-2.632386
H	3.723858	-3.723913	-2.845376
H	1.512001	5.070267	-2.745542

```
H       -3.247329   -2.405761   -3.447266
H        3.502553   -1.392996   -3.700486
H       -0.344103    3.727678   -3.744672
H       -1.042949   -1.993624   -2.428762
H        1.980234    0.206890   -2.587413
H       -1.028549    1.592900   -2.688761
End

SOPERT
Relativistic scalar ZORA

Basis
Type TZP
Core None
End

AddDiffuseFit

SCF
Iterations 300
End

XC
HYBRID B3LYP
End

EXACTDENSITY

Excitations
Lowest 20
End

LOCORB
end

EPRINT
 SFO OrbPop GrossPop FragPop
 FragPop Gross
 Orbpop 90 30 tol=1e-4
 Subend
End

End Input
eor
```

Input file: TDDFT (excited triplet geometry) state spin-orbit SCF calculation (SOC-TDDFT) in gas phase

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 (BP86/TZ2P T1 TDDFT optimised) T1 B3LYP TDDFT relativistic spin-orbit SCF calculation
```

Atoms

Ir	0.003252	-0.048694	-0.103035
N	-0.189849	-1.900377	0.997672
N	1.522436	0.759935	1.195369
N	-1.441397	1.159563	1.023909
C	0.619134	-2.906527	0.541933
C	2.126399	1.927958	0.664115
C	-2.728021	1.082233	0.564633
C	0.610327	-4.158288	1.178873
C	3.257829	2.450645	1.296550
C	-3.735419	1.856122	1.164028
C	-0.234662	-4.384743	2.256364
C	3.817183	1.850943	2.420310
C	-3.425537	2.709799	2.213471
C	-1.071653	-3.352838	2.693211
C	3.213544	0.646150	2.911668
C	-2.103603	2.785196	2.660285
C	-1.015567	-2.130787	2.036768
C	2.105908	0.153106	2.268988
C	-1.145001	1.996504	2.037704
H	1.267537	-4.949153	0.822207
H	3.711932	3.352786	0.886065
H	-4.757354	1.787016	0.796474
H	-0.245281	-5.355073	2.752494
H	4.699725	2.271765	2.897874
H	-4.204044	3.316712	2.676111
H	-1.756042	-3.488052	3.529032
H	3.611566	0.119041	3.777015
H	-1.811274	3.447655	3.473204
H	-1.641861	-1.292233	2.339277
H	1.623156	-0.760871	2.615397
H	-0.098292	2.015569	2.335414
C	-1.749427	-0.513190	-1.014506
C	1.278645	-1.193574	-1.093702
C	0.426537	1.688096	-1.102596
C	1.427263	-2.544406	-0.618098
C	1.488000	2.456860	-0.529996
C	-2.917166	0.157694	-0.550854
C	-4.170931	-0.088425	-1.137994
C	2.303619	-3.436223	-1.250925
C	1.857064	3.674545	-1.142302
C	-4.294039	-1.002679	-2.178222
C	3.044183	-3.025338	-2.357284
C	1.207942	4.126764	-2.289681
C	-3.158715	-1.686455	-2.631212
C	2.918245	-1.711123	-2.835876
C	0.169247	3.378483	-2.847767
C	-1.911843	-1.455391	-2.051025
C	2.064028	-0.811194	-2.210775

```
C       -0.216011    2.169127   -2.243820
H        2.417294   -4.457844   -0.886061
H        2.658234    4.278762   -0.713682
H       -5.059156    0.435221   -0.782330
H       -5.267384   -1.187778   -2.632386
H        3.723858   -3.723913   -2.845376
H        1.512001    5.070267   -2.745542
H       -3.247329   -2.405761   -3.447266
H        3.502553   -1.392996   -3.700486
H       -0.344103    3.727678   -3.744672
H       -1.042949   -1.993624   -2.428762
H        1.980234    0.206890   -2.587413
H       -1.028549    1.592900   -2.688761
End

relativistic spinorbit zora

Basis
Type TZP
Core None
End

AddDiffuseFit

SCF
Iterations 300
End

XC
HYBRID B3LYP
End

EXACTDENSITY

Excitations
Lowest 3
End

EPRINT
 SFO OrbPop GrossPop FragPop
 FragPop Gross
 Orbpop 90 30 tol=1e-4
 Subend
End

End Input
Eor
```

2. Dielectric medium calculations

2.1 Geometry optimization

Input file: BP86 ground-state geometry optimization in dielectric medium

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 ground-state S0 geometry optimization (dielectric medium)

Atoms
Ir    -0.00006000     0.00004200    -0.04113600   R=1.967
N     -0.19597300    -1.83826600     1.05964800   R=1.608
N      1.68997600     0.74860000     1.05959700   R=1.608
N     -1.49410200     1.08970300     1.05877200   R=1.608
C      0.55439300    -2.88044000     0.57267300   R=1.700
C      2.21651100     1.92040900     0.57390400   R=1.700
C     -2.77170900     0.96080200     0.57149600   R=1.700
C      0.49431700    -4.13753500     1.20069000   R=1.700
C      3.33566100     2.49622900     1.20172500   R=1.700
C     -3.83041300     1.64216300     1.19859800   R=1.700
C     -0.32076200    -4.33231400     2.30799000   R=1.700
C      3.91386600     1.88579700     2.30690300   R=1.700
C     -3.59173200     2.44686900     2.30492000   R=1.700
C     -1.08405000    -3.26146100     2.78674900   R=1.700
C      3.36958200     0.68793400     2.78372200   R=1.700
C     -2.28275000     2.57310900     2.78367600   R=1.700
C     -0.99229700    -2.04033600     2.13093600   R=1.700
C      2.26516300     0.15796600     2.12875800   R=1.700
C     -1.27102900     1.88198600     2.12893900   R=1.700
H      1.08873500    -4.96070100     0.80749900   R=1.350
H      3.75047700     3.42344800     0.80965400   R=1.350
H     -4.84045800     1.53848600     0.80544900   R=1.350
H     -0.36742200    -5.30849300     2.79208800   R=1.350
H      4.78330000     2.33286200     2.79044000   R=1.350
H     -4.41392700     2.97609800     2.78808000   R=1.350
H     -1.74450500    -3.36701100     3.64656100   R=1.350
H      3.79322500     0.16662800     3.64129100   R=1.350
H     -2.04409400     3.19923800     3.64252700   R=1.350
H     -1.57208200    -1.17743900     2.45753800   R=1.350
H      1.80875600    -0.77657800     2.45394000   R=1.350
H     -0.23377100     1.95336700     2.45527100   R=1.350
C     -1.66881600    -0.46760200    -1.08868300   R=1.700
C      1.23889300    -1.21188000    -1.08876400   R=1.700
C      0.42970300     1.67949400    -1.08807700   R=1.700
C      1.36024600    -2.54999900    -0.59906500   R=1.700
C      1.52698800     2.45409500    -0.59704300   R=1.700
C     -2.88828300     0.09677100    -0.59954200   R=1.700
C     -4.12122600    -0.16281800    -1.23079100   R=1.700
C      2.20116100    -3.48815100    -1.23059300   R=1.700
```

```
C      1.91863000      3.65226900     -1.22713400    R=1.700
C     -4.17867700     -0.98142700     -2.35265500    R=1.700
C      2.93709000     -3.12934400     -2.35389500    R=1.700
C      1.24043600      4.11052900     -2.35057100    R=1.700
C     -2.99385400     -1.54506300     -2.84892700    R=1.700
C      2.83167600     -1.82189500     -2.85124800    R=1.700
C      0.16190100      3.36503000     -2.84940800    R=1.700
C     -1.76983600     -1.29255400     -2.22825300    R=1.700
C      2.00196400     -0.88769000     -2.22981500    R=1.700
C     -0.23211700      2.17868000     -2.22919600    R=1.700
H      2.28277100     -4.50646800     -0.84557600    R=1.350
H      2.75894900      4.23238400     -0.84092500    R=1.350
H     -5.04374000      0.27645800     -0.84628400    R=1.350
H     -5.13382100     -1.18083300     -2.83989400    R=1.350
H      3.58689900     -3.85705300     -2.84133100    R=1.350
H      1.54540400      5.03765000     -2.83730400    R=1.350
H     -3.02866500     -2.18863700     -3.73089400    R=1.350
H      3.40482900     -1.53103200     -3.73451600    R=1.350
H     -0.37610600      3.71625000     -3.73281400    R=1.350
H     -0.86585600     -1.74263100     -2.64018700    R=1.350
H      1.93905000      0.11998000     -2.64218200    R=1.350
H     -1.07265100      1.62002600     -2.64254300    R=1.350
End

Fragments
 C  t21.C
 H  t21.H
 Ir t21.Ir
 N  t21.N
End

SOLVATION
  Surf Delley
  Solv Eps=3.5 Rad=5.4 Cav0=0.0 Cav1=0.0067639 Emp=0.5
  Charged method=CONJ
  C-Mat Exact
  SCF VAR ALL
  LPRT
END

Basis
type TZ2P
Core None
End

XC
GGA BP86
END

SCF
```

```
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

BECKEGRID
Quality verygood
End

RELATIVISTIC Scalar ZORA

End Input
eor
```

Input file: BP86 TDDFT relativistic excited triplet state geometry optimization in dielectric medium

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 TDDFT excited triplet-state geometry optimization (dielectric medium)

Atoms
Ir      -0.000984   -0.035476   -0.105798    R=1.967
N       -0.195980   -1.885639    1.005988    R=1.608
N        1.576982    0.729164    1.139289    R=1.608
N       -1.441173    1.148961    1.033911    R=1.608
C        0.608567   -2.894837    0.551657    R=1.700
C        2.136561    1.929311    0.633603    R=1.700
C       -2.727514    1.067801    0.576515    R=1.700
C        0.595772   -4.144705    1.191615    R=1.700
C        3.234554    2.495387    1.311589    R=1.700
C       -3.742371    1.809885    1.202151    R=1.700
C       -0.245910   -4.363257    2.272134    R=1.700
C        3.783614    1.901570    2.431604    R=1.700
C       -3.438288    2.638366    2.272224    R=1.700
C       -1.076381   -3.326414    2.709716    R=1.700
C        3.217448    0.669054    2.901941    R=1.700
C       -2.115243    2.719864    2.715731    R=1.700
C       -1.018511   -2.108012    2.048825    R=1.700
C        2.142314    0.143822    2.221543    R=1.700
C       -1.150412    1.960328    2.068731    R=1.700
H        1.246799   -4.939583    0.835268    R=1.350
H        3.656979    3.426275    0.933264    R=1.350
H       -4.765605    1.733520    0.842010    R=1.350
H       -0.259774   -5.331552    2.769977    R=1.350
H        4.632521    2.355129    2.940867    R=1.350
H       -4.222461    3.218712    2.756399    R=1.350
H       -1.756928   -3.455775    3.548338    R=1.350
H        3.615009    0.148184    3.770494    R=1.350
```

```
H       -1.830608    3.362118    3.546217    R=1.350
H       -1.640850   -1.267741    2.351611    R=1.350
H        1.684177   -0.790689    2.546066    R=1.350
H       -0.104429    1.984194    2.366846    R=1.350
C       -1.745002   -0.501594   -1.028583    R=1.700
C        1.279252   -1.198803   -1.093885    R=1.700
C        0.421180    1.692329   -1.110563    R=1.700
C        1.417120   -2.543238   -0.610602    R=1.700
C        1.510398    2.446934   -0.556988    R=1.700
C       -2.912299    0.168562   -0.559649    R=1.700
C       -4.163860   -0.062128   -1.156731    R=1.700
C        2.291646   -3.444303   -1.236612    R=1.700
C        1.901258    3.648637   -1.198071    R=1.700
C       -4.284681   -0.960995   -2.210873    R=1.700
C        3.036761   -3.043691   -2.341823    R=1.700
C        1.240673    4.100195   -2.338007    R=1.700
C       -3.151393   -1.645568   -2.667923    R=1.700
C        2.921372   -1.731246   -2.825152    R=1.700
C        0.169507    3.374163   -2.868467    R=1.700
C       -1.906936   -1.429257   -2.076702    R=1.700
C        2.068683   -0.823953   -2.205098    R=1.700
C       -0.232301    2.179636   -2.241187    R=1.700
H        2.396757   -4.463892   -0.866590    R=1.350
H        2.730150    4.235800   -0.800690    R=1.350
H       -5.051225    0.459873   -0.799149    R=1.350
H       -5.256099   -1.134079   -2.672641    R=1.350
H        3.711449   -3.748801   -2.825996    R=1.350
H        1.562801    5.027399   -2.814456    R=1.350
H       -3.240449   -2.352810   -3.493605    R=1.350
H        3.508601   -1.420591   -3.689759    R=1.350
H       -0.351032    3.725685   -3.759848    R=1.350
H       -1.038994   -1.967701   -2.455466    R=1.350
H        1.990902    0.192418   -2.587353    R=1.350
H       -1.065696    1.617486   -2.663851    R=1.350
End

Fragments
 C  t21.C
 H  t21.H
 Ir t21.Ir
 N  t21.N
End

SOLVATION
  Surf Delley
  Solv Eps=3.5 Rad=5.4 Cav0=0.0 Cav1=0.0067639 Emp=0.5
  Charged method=CONJ
  C-Mat Exact
  SCF VAR ALL
END
```

```
RELATIVISTIC Scalar ZORA

Basis
type TZ2P
Core None
End

XC
GGA BP86
END

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

EXCITATIONS
Onlytrip
Lowest 1
END

EXCITEDGO
State A 1
Triplet
END

BECKEGRID
Quality verygood
End

End Input
eor
```

Input file: BP86 UDFT triplet-state geometry optimization in dielectric medium

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 UDFT triplet-state geometry optimization (dielectric medium)

Atoms
Ir      0.00172000     -0.00115700     -0.08262300    R=1.967
N      -0.20948700     -1.81457400      1.05945600    R=1.608
N       1.66865800      0.72542800      1.06252800    R=1.608
N      -1.46036000      1.08457500      1.06545100    R=1.608
C       0.55213100     -2.86778800      0.57957200     R=1.700
```

C	2.19974700	1.91399000	0.58228900	R=1.700
C	-2.75286100	0.96070500	0.58253600	R=1.700
C	0.52867400	-4.10382200	1.25700800	R=1.700
C	3.27206400	2.51949700	1.26969700	R=1.700
C	-3.80979400	1.59763800	1.26407800	R=1.700
C	-0.27683700	-4.28318800	2.36667600	R=1.700
C	3.82200900	1.91869600	2.38661800	R=1.700
C	-3.56081200	2.37252600	2.38220000	R=1.700
C	-1.07419500	-3.21009800	2.81410800	R=1.700
C	3.29377900	0.68846700	2.83243400	R=1.700
C	-2.23326500	2.51512700	2.83451300	R=1.700
C	-1.00136800	-2.00584700	2.13368200	R=1.700
C	2.22393400	0.14180200	2.14382400	R=1.700
C	-1.22845300	1.85284000	2.14898900	R=1.700
H	1.15234700	-4.92002700	0.89784600	R=1.350
H	3.66422900	3.46972300	0.91247800	R=1.350
H	-4.82848500	1.47350300	0.90220600	R=1.350
H	-0.29412600	-5.24051900	2.88552800	R=1.350
H	4.65100700	2.38924700	2.91327500	R=1.350
H	-4.38006900	2.86488100	2.90425500	R=1.350
H	-1.73453900	-3.30734800	3.67296400	R=1.350
H	3.70326300	0.16945300	3.69621300	R=1.350
H	-1.98631900	3.12544700	3.70038000	R=1.350
H	-1.58920300	-1.14447900	2.44727900	R=1.350
H	1.77414100	-0.79968300	2.45573700	R=1.350
H	-0.18863800	1.92318200	2.46471100	R=1.350
C	-1.67920000	-0.47602100	-1.09098100	R=1.700
C	1.25424600	-1.21435200	-1.09166800	R=1.700
C	0.42469500	1.68722700	-1.09569100	R=1.700
C	1.32517400	-2.56712600	-0.60651000	R=1.700
C	1.56146200	2.42614400	-0.60945700	R=1.700
C	-2.88191400	0.14658200	-0.60768900	R=1.700
C	-4.11105000	-0.08004400	-1.26331700	R=1.700
C	2.14543700	-3.51219900	-1.25917400	R=1.700
C	1.97481200	3.60422800	-1.26905600	R=1.700
C	-4.17592100	-0.92522500	-2.36359600	R=1.700
C	2.90788000	-3.14125500	-2.35936500	R=1.700
C	1.27614300	4.07349300	-2.37369400	R=1.700
C	-3.01477500	-1.56811800	-2.82460000	R=1.700
C	2.87293200	-1.81543800	-2.82423700	R=1.700
C	0.14370200	3.38130400	-2.83747900	R=1.700
C	-1.79230900	-1.35032200	-2.18784500	R=1.700
C	2.06553000	-0.87096000	-2.18968400	R=1.700
C	-0.27501700	2.21436700	-2.19728500	R=1.700
H	2.18808900	-4.54254200	-0.90581200	R=1.350
H	2.84705800	4.15575000	-0.91792700	R=1.350
H	-5.02113300	0.40672500	-0.91245300	R=1.350
H	-5.12911300	-1.09065200	-2.86575200	R=1.350
H	3.53484500	-3.87981100	-2.85888100	R=1.350
H	1.60637500	4.98126900	-2.87875200	R=1.350

```
H     -3.06752500     -2.23287600     -3.68757200     R=1.350
H      3.47274200     -1.52606000     -3.68781900     R=1.350
H     -0.40325200      3.75278800     -3.70468100     R=1.350
H     -0.89809600     -1.84371900     -2.56751800     R=1.350
H      2.03706600      0.14918500     -2.57123700     R=1.350
H     -1.14472300      1.67967900     -2.57782000     R=1.350
End

Fragments
 C  t21.C
 H  t21.H
 Ir t21.Ir
 N  t21.N
End

SOLVATION
   Surf Delley
   Solv Eps=3.5 Rad=5.4 Cav0=0.0 Cav1=0.0067639 Emp=0.5
   Charged method=CONJ
   C-Mat Exact
   SCF VAR ALL
END

RELATIVISTIC Scalar ZORA

Unrestricted
Charge 0 2

Basis
type TZ2P
Core None
End

XC
GGA BP86
END

SCF
Iterations 200
End

GEOMETRY
Optim
Converge grad=0.0001
End

BECKEGRID
Quality verygood
End
```

End Input
eor

2.2 Single-point DFT/UDFT calculations

Input file: BP86 DFT single-point energy calculation in dielectric medium

$ADFBIN/adf <<eor
Title Ir(ppy)3 (BP86/TZ2P TDDFT-gas phase optimized T1) B3LYP/TZP single-point energy calculation in dielectric medium

Atoms
Ir 0.003252 -0.048694 -0.103035 R=1.967
N -0.189849 -1.900377 0.997672 R=1.608
N 1.522436 0.759935 1.195369 R=1.608
N -1.441397 1.159563 1.023909 R=1.608
C 0.619134 -2.906527 0.541933 R=1.700
C 2.126399 1.927958 0.664115 R=1.700
C -2.728021 1.082233 0.564633 R=1.700
C 0.610327 -4.158288 1.178873 R=1.700
C 3.257829 2.450645 1.296550 R=1.700
C -3.735419 1.856122 1.164028 R=1.700
C -0.234662 -4.384743 2.256364 R=1.700
C 3.817183 1.850943 2.420310 R=1.700
C -3.425537 2.709799 2.213471 R=1.700
C -1.071653 -3.352838 2.693211 R=1.700
C 3.213544 0.646150 2.911668 R=1.700
C -2.103603 2.785196 2.660285 R=1.700
C -1.015567 -2.130787 2.036768 R=1.700
C 2.105908 0.153106 2.268988 R=1.700
C -1.145001 1.996504 2.037704 R=1.700
H 1.267537 -4.949153 0.822207 R=1.350
H 3.711932 3.352786 0.886065 R=1.350
H -4.757354 1.787016 0.796474 R=1.350
H -0.245281 -5.355073 2.752494 R=1.350
H 4.699725 2.271765 2.897874 R=1.350
H -4.204044 3.316712 2.676111 R=1.350
H -1.756042 -3.488052 3.529032 R=1.350
H 3.611566 0.119041 3.777015 R=1.350
H -1.811274 3.447655 3.473204 R=1.350
H -1.641861 -1.292233 2.339277 R=1.350
H 1.623156 -0.760871 2.615397 R=1.350
H -0.098292 2.015569 2.335414 R=1.350
C -1.749427 -0.513190 -1.014506 R=1.700
C 1.278645 -1.193574 -1.093702 R=1.700
C 0.426537 1.688096 -1.102596 R=1.700
C 1.427263 -2.544406 -0.618098 R=1.700
C 1.488000 2.456860 -0.529996 R=1.700

```
C       -2.917166    0.157694   -0.550854 R=1.700
C       -4.170931   -0.088425   -1.137994 R=1.700
C        2.303619   -3.436223   -1.250925 R=1.700
C        1.857064    3.674545   -1.142302 R=1.700
C       -4.294039   -1.002679   -2.178222 R=1.700
C        3.044183   -3.025338   -2.357284 R=1.700
C        1.207942    4.126764   -2.289681 R=1.700
C       -3.158715   -1.686455   -2.631212 R=1.700
C        2.918245   -1.711123   -2.835876 R=1.700
C        0.169247    3.378483   -2.847767 R=1.700
C       -1.911843   -1.455391   -2.051025 R=1.700
C        2.064028   -0.811194   -2.210775 R=1.700
C       -0.216011    2.169127   -2.243820 R=1.700
H        2.417294   -4.457844   -0.886061 R=1.350
H        2.658234    4.278762   -0.713682 R=1.350
H       -5.059156    0.435221   -0.782330 R=1.350
H       -5.267384   -1.187778   -2.632386 R=1.350
H        3.723858   -3.723913   -2.845376 R=1.350
H        1.512001    5.070267   -2.745542 R=1.350
H       -3.247329   -2.405761   -3.447266 R=1.350
H        3.502553   -1.392996   -3.700486 R=1.350
H       -0.344103    3.727678   -3.744672 R=1.350
H       -1.042949   -1.993624   -2.428762 R=1.350
H        1.980234    0.206890   -2.587413 R=1.350
H       -1.028549    1.592900   -2.688761 R=1.350
End

Fragments
 C  t21.C
 H  t21.H
 Ir t21.Ir
 N  t21.N
End

SOLVATION
   Surf Delley
   Solv eps=3.5 rad=5.4 cav0=0.0 cav1=0.0067639 Emp=0.5
   Charged method=CONJ
   C-Mat Exact
   SCF VAR ALL
END

Relativistic scalar ZORA

Basis
Type TZP
Core None
End

XC
```

```
  HYBRID B3LYP
END

End Input
eor
```

2.3 TDDFT excited state energy calculations

Input file: TDDFT relativistic spin-orbit perturbation calculation in dielectric medium

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 (T1 gas-phase optimized TDDFT BP86/TZ2P) B3LYP TDDFT relativistic spin-orbit perturbation in dielectric medium

Atoms
Ir       0.003252   -0.048694   -0.103035 R=1.967
N       -0.189849   -1.900377    0.997672 R=1.608
N        1.522436    0.759935    1.195369 R=1.608
N       -1.441397    1.159563    1.023909 R=1.608
C        0.619134   -2.906527    0.541933 R=1.700
C        2.126399    1.927958    0.664115 R=1.700
C       -2.728021    1.082233    0.564633 R=1.700
C        0.610327   -4.158288    1.178873 R=1.700
C        3.257829    2.450645    1.296550 R=1.700
C       -3.735419    1.856122    1.164028 R=1.700
C       -0.234662   -4.384743    2.256364 R=1.700
C        3.817183    1.850943    2.420310 R=1.700
C       -3.425537    2.709799    2.213471 R=1.700
C       -1.071653   -3.352838    2.693211 R=1.700
C        3.213544    0.646150    2.911668 R=1.700
C       -2.103603    2.785196    2.660285 R=1.700
C       -1.015567   -2.130787    2.036768 R=1.700
C        2.105908    0.153106    2.268988 R=1.700
C       -1.145001    1.996504    2.037704 R=1.700
H        1.267537   -4.949153    0.822207 R=1.350
H        3.711932    3.352786    0.886065 R=1.350
H       -4.757354    1.787016    0.796474 R=1.350
H       -0.245281   -5.355073    2.752494 R=1.350
H        4.699725    2.271765    2.897874 R=1.350
H       -4.204044    3.316712    2.676111 R=1.350
H       -1.756042   -3.488052    3.529032 R=1.350
H        3.611566    0.119041    3.777015 R=1.350
H       -1.811274    3.447655    3.473204 R=1.350
H       -1.641861   -1.292233    2.339277 R=1.350
H        1.623156   -0.760871    2.615397 R=1.350
H       -0.098292    2.015569    2.335414 R=1.350
C       -1.749427   -0.513190   -1.014506 R=1.700
C        1.278645   -1.193574   -1.093702 R=1.700
```

```
C       0.426537    1.688096   -1.102596 R=1.700
C       1.427263   -2.544406   -0.618098 R=1.700
C       1.488000    2.456860   -0.529996 R=1.700
C      -2.917166    0.157694   -0.550854 R=1.700
C      -4.170931   -0.088425   -1.137994 R=1.700
C       2.303619   -3.436223   -1.250925 R=1.700
C       1.857064    3.674545   -1.142302 R=1.700
C      -4.294039   -1.002679   -2.178222 R=1.700
C       3.044183   -3.025338   -2.357284 R=1.700
C       1.207942    4.126764   -2.289681 R=1.700
C      -3.158715   -1.686455   -2.631212 R=1.700
C       2.918245   -1.711123   -2.835876 R=1.700
C       0.169247    3.378483   -2.847767 R=1.700
C      -1.911843   -1.455391   -2.051025 R=1.700
C       2.064028   -0.811194   -2.210775 R=1.700
C      -0.216011    2.169127   -2.243820 R=1.700
H       2.417294   -4.457844   -0.886061 R=1.350
H       2.658234    4.278762   -0.713682 R=1.350
H      -5.059156    0.435221   -0.782330 R=1.350
H      -5.267384   -1.187778   -2.632386 R=1.350
H       3.723858   -3.723913   -2.845376 R=1.350
H       1.512001    5.070267   -2.745542 R=1.350
H      -3.247329   -2.405761   -3.447266 R=1.350
H       3.502553   -1.392996   -3.700486 R=1.350
H      -0.344103    3.727678   -3.744672 R=1.350
H      -1.042949   -1.993624   -2.428762 R=1.350
H       1.980234    0.206890   -2.587413 R=1.350
H      -1.028549    1.592900   -2.688761 R=1.350
End

Fragments
 C  t21.C
 H  t21.H
 Ir t21.Ir
 N  t21.N
End

SOLVATION
   Surf Delley
   Solv eps=3.5 rad=5.4 Neql=3.2 cav0=0.0 cav1=0.0067639 Emp=0.5
   Charged method=CONJ
   C-Mat Exact
   SCF VAR ALL
END

SOPERT NCALC=3
Relativistic scalar ZORA

Basis
Type TZP
```

```
Core None
End

AddDiffuseFit

SCF
Iterations 300
End

XC
HYBRID B3LYP
End

EXACTDENSITY

Excitations
Lowest 20
NTO
End

LOCORB
end

EPRINT
 SFO OrbPop GrossPop FragPop
 FragPop Gross
 Orbpop 90 30 tol=1e-4
 Subend
End

End Input
Eor
```

Input file: TDDFT excited triplet state spin-orbit SCF calculation (SOC-TDDFT) in dielectric medium

```
$ADFBIN/adf <<eor
Title Ir(ppy)3 (T1 gas-phase optimized TDDFT BP86/TZ2P)  B3LYP TDDFT relativistic spin-orbit SCF in dielectric medium

Atoms
Ir      0.003252   -0.048694   -0.103035 R=1.967
N      -0.189849   -1.900377    0.997672 R=1.608
N       1.522436    0.759935    1.195369 R=1.608
N      -1.441397    1.159563    1.023909 R=1.608
C       0.619134   -2.906527    0.541933 R=1.700
C       2.126399    1.927958    0.664115 R=1.700
C      -2.728021    1.082233    0.564633 R=1.700
C       0.610327   -4.158288    1.178873 R=1.700
C       3.257829    2.450645    1.296550 R=1.700
C      -3.735419    1.856122    1.164028 R=1.700
```

C -0.234662 -4.384743 2.256364 R=1.700
C 3.817183 1.850943 2.420310 R=1.700
C -3.425537 2.709799 2.213471 R=1.700
C -1.071653 -3.352838 2.693211 R=1.700
C 3.213544 0.646150 2.911668 R=1.700
C -2.103603 2.785196 2.660285 R=1.700
C -1.015567 -2.130787 2.036768 R=1.700
C 2.105908 0.153106 2.268988 R=1.700
C -1.145001 1.996504 2.037704 R=1.700
H 1.267537 -4.949153 0.822207 R=1.350
H 3.711932 3.352786 0.886065 R=1.350
H -4.757354 1.787016 0.796474 R=1.350
H -0.245281 -5.355073 2.752494 R=1.350
H 4.699725 2.271765 2.897874 R=1.350
H -4.204044 3.316712 2.676111 R=1.350
H -1.756042 -3.488052 3.529032 R=1.350
H 3.611566 0.119041 3.777015 R=1.350
H -1.811274 3.447655 3.473204 R=1.350
H -1.641861 -1.292233 2.339277 R=1.350
H 1.623156 -0.760871 2.615397 R=1.350
H -0.098292 2.015569 2.335414 R=1.350
C -1.749427 -0.513190 -1.014506 R=1.700
C 1.278645 -1.193574 -1.093702 R=1.700
C 0.426537 1.688096 -1.102596 R=1.700
C 1.427263 -2.544406 -0.618098 R=1.700
C 1.488000 2.456860 -0.529996 R=1.700
C -2.917166 0.157694 -0.550854 R=1.700
C -4.170931 -0.088425 -1.137994 R=1.700
C 2.303619 -3.436223 -1.250925 R=1.700
C 1.857064 3.674545 -1.142302 R=1.700
C -4.294039 -1.002679 -2.178222 R=1.700
C 3.044183 -3.025338 -2.357284 R=1.700
C 1.207942 4.126764 -2.289681 R=1.700
C -3.158715 -1.686455 -2.631212 R=1.700
C 2.918245 -1.711123 -2.835876 R=1.700
C 0.169247 3.378483 -2.847767 R=1.700
C -1.911843 -1.455391 -2.051025 R=1.700
C 2.064028 -0.811194 -2.210775 R=1.700
C -0.216011 2.169127 -2.243820 R=1.700
H 2.417294 -4.457844 -0.886061 R=1.350
H 2.658234 4.278762 -0.713682 R=1.350
H -5.059156 0.435221 -0.782330 R=1.350
H -5.267384 -1.187778 -2.632386 R=1.350
H 3.723858 -3.723913 -2.845376 R=1.350
H 1.512001 5.070267 -2.745542 R=1.350
H -3.247329 -2.405761 -3.447266 R=1.350
H 3.502553 -1.392996 -3.700486 R=1.350
H -0.344103 3.727678 -3.744672 R=1.350
H -1.042949 -1.993624 -2.428762 R=1.350
H 1.980234 0.206890 -2.587413 R=1.350

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H       -1.028549    1.592900   -2.688761 R=1.350
End

Fragments
 C  t21.C
 H  t21.H
 Ir t21.Ir
 N  t21.N
End

SOLVATION
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   Solv eps=3.5 rad=5.4 Neql=3.2 cav0=0.0 cav1=0.0067639 Emp=0.5
   Charged method=CONJ
   C-Mat Exact
   SCF VAR ALL
END

relativistic spinorbit zora

Basis
Type TZP
Core None
End

AddDiffuseFit

SCF
Iterations 300
End

XC
HYBRID B3LYP
End

EXACTDENSITY

Excitations
Lowest 3
NTO
End


EPRINT
 SFO OrbPop GrossPop FragPop
 FragPop Gross
 Orbpop 90 30 tol=1e-4
 Subend
End
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End Input
eor

Table S1: Selected bond lengths of Ir(ppy)3 (in Å) in the S0 and T1 optimized geometries at B3LYP/TZ2P level of theory

	S0	T1	(S0-T1)
Ir-N1	2.173	2.195	-0.022
Ir-N2	2.172	2.089	0.083
Ir-N3	2.173	2.251	-0.078
Ir-C1	2.030	1.981	0.049
Ir-C2	2.030	2.048	-0.019
Ir-C3	2.030	2.066	-0.036

Table S2: Comparison of the selected bond lengths of $Ir(ppy)_3$ (in Å) in the T_1 optimized in *vacuo* and in the dielectric medium (ϵ=3.5) at UDFT/BP86/TZ2P level of theory

	in *vacuo*	dielectric medium
Ir-N1	2.150	2.149
Ir-N2	2.153	2.153
Ir-N3	2.153	2.153
Ir-C1	2.014	2.014
Ir-C2	2.015	2.015
Ir-C3	2.016	2.017

Table S3: Emission energies and radiative lifetimes of $Ir(ppy)_3$ in gas phase for individual substates in S_0 and T_1 structures at BP86 and B3LYP

Geometry optimization			**TDDFT calculation**		**Emission (eV)**			**Radiative lifetimes (s)**		
Functional	Basis set	Spin state	Functional	Basis set	$T_{1,1}$	$T_{1,2}$	$T_{1,3}$	$T_{1,1}$	$T_{1,2}$	$T_{1,3}$
BP86	TZ2P	Singlet	B3LYP	TZP	2.500	2.506	2.507	0.432×10^{-3}	0.224×10^{-5}	0.214×10^{-5}
BP86	TZ2P	Singlet	BP86	TZP	1.990	2.004	2.004	0.862×10^{-2}	0.281×10^{-5}	0.275×10^{-5}
B3LYP	TZ2P	Singlet	B3LYP	TZP	2.546	2.551	2.551	0.205×10^{-3}	0.257×10^{-5}	0.311×10^{-5}
B3LYP	TZ2P	Singlet	BP86	TZP	2.005	2.018	2.018	0.133×10^{-1}	0.278×10^{-5}	0.274×10^{-5}
BP86	TZ2P	Triplet	B3LYP	TZP	2.000	2.001	2.015	0.160×10^{-2}	0.124×10^{-4}	0.330×10^{-5}
BP86	TZ2P	Triplet	BP86	TZP	1.524	1.528	1.534	0.736×10^{-2}	0.267×10^{-4}	0.843×10^{-5}
B3LYP	TZ2P	Triplet	BP86	TZP	1.504	1.508	1.513	0.805×10^{-2}	0.331×10^{-4}	0.903×10^{-5}
B3LYP	TZ2P	Triplet	B3LYP	TZP	1.885	1.889	1.898	0.173×10^{-2}	0.321×10^{-4}	0.505×10^{-5}

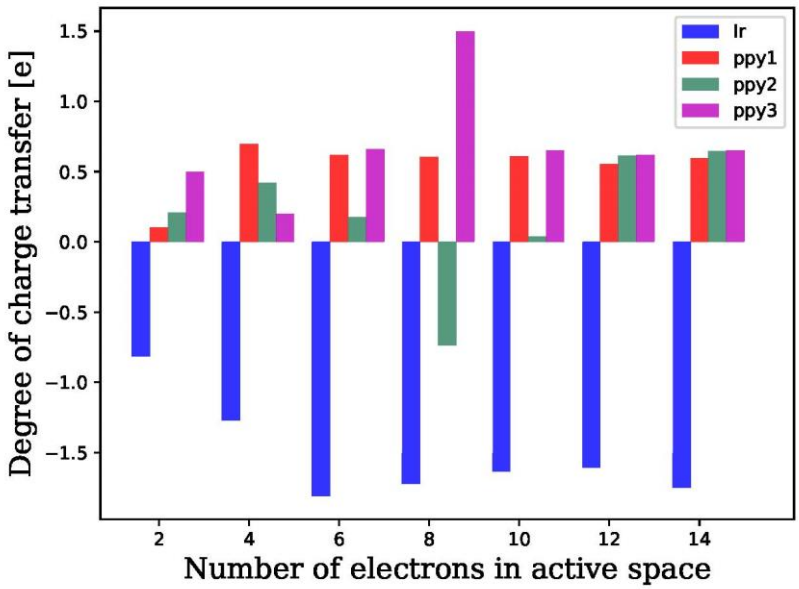

Figure S1: Degree of charge transfer for emission process (charge in ground state minus charge in excited triplet state) in $Ir(ppy)_3$ on the iridium atom and the three ligands as a function of number of electrons in the active space based on S_0 geometry