

Electronic Supplementary Information for

**Photomolecular rotor dynamics of the oxindole-based
photoprotective bacterial pigment violacein**

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Steady state spectroscopy

Table S1 Absorption (abs) and fluorescence emission (em) maxima, in nm, recorded for violacein at the laboratory temperature ($T = 294$ K). Stokes shift ($\Delta\tilde{\nu}$ for band maxima) is given in cm^{-1} with $\pm 20 \text{ cm}^{-1}$ uncertainty.

	λ_{abs}	λ_{em}	$\Delta\tilde{\nu}$
acetonitrile	548	673	3389
ethylene glycol	575	700	3106

TA instrument response function

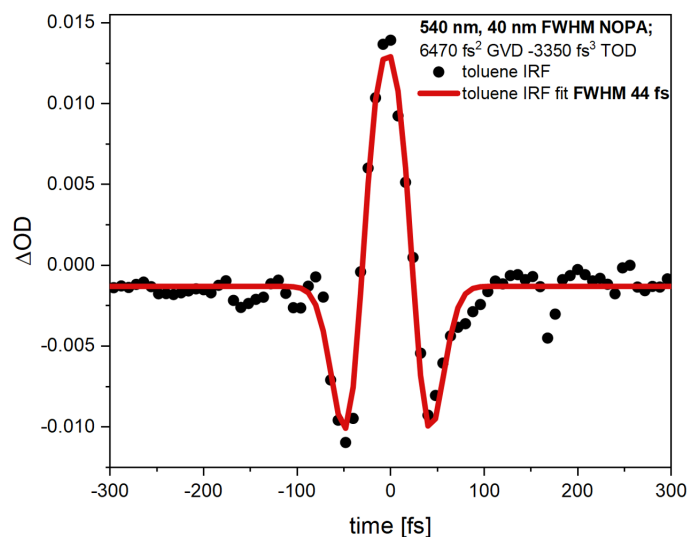


Fig. S1 Instrument response function (IRF) of the ultrafast TA instrument as described in the methods section. The IRF was determined through a fit of the non-resonant Kerr response of toluene solvent. Deconvolution yielded a <30 fs pump-pulse duration.

Critical point geometries

Cartesian coordinates (in Ångströms) of the main critical points on the gas-phase violacein potential energy surface are given below.

S_0

C -1.428178496 0.004127693 -1.078490824
C -0.258471336 0.715052862 -0.922773194
C -2.631738282 0.489989072 -0.553297946
C -0.314738656 1.915969132 -0.23451183
C -2.684174628 1.685880024 0.131333059
C -1.51210123 2.425869106 0.303261419
H -1.418930777 -0.935208867 -1.609648251
H 0.668959216 0.342640747 -1.326473598
H -3.643214858 1.995199257 0.506204274
H 1.6501916 2.710581273 -0.197352864
C 0.175811677 3.850355347 0.753491689
H 0.801200907 4.658797107 1.078723532
C -1.17393006 3.680288372 0.940051578
O -3.796657735 -0.193620257 -0.695066059
H -3.642757698 -1.002184103 -1.182898822
N 0.689892531 2.810473665 0.059651598
C -3.939117307 8.317015907 4.134374819
C -3.381017018 9.491386615 4.678497618
C -4.130952199 10.42312239 5.359484378
C -5.491374645 10.1767983 5.505662815
C -6.067742223 9.029195374 4.980768605
C -5.303783991 8.095259266 4.295369559
C -2.859018236 7.585980074 3.496521104
C -1.62537756 8.409844452 3.702724013
H -3.678833728 11.31323525 5.765689417
H -6.102344743 10.89032738 6.034731578
H -7.124072194 8.857234395 5.105129732
H -5.750772666 7.208567925 3.889848036
H -1.380629249 10.23343356 4.677707859
C -3.926672338 5.466122708 2.524483211
C -1.99859725 4.624873119 1.645857134
C -1.636417432 5.798924997 2.232667488
C -2.787330998 6.402477706 2.814184426
H -3.904566566 3.658789112 1.499607896
H -0.653456171 6.217525725 2.262709414
O -0.489012816 8.19596104 3.344962976
O -5.097697046 5.535009859 2.808667224
N -3.361983282 4.430702082 1.821806549
N -2.023443991 9.516306529 4.408623611

S_{1,p}

C -1.395170733 -0.003399623 -1.089307283
C -0.235101289 0.726211595 -0.921776806
C -2.608872837 0.462230223 -0.573497339
C -0.315342065 1.922585185 -0.23149848
C -2.682432281 1.658756089 0.115365027
C -1.523958255 2.408344353 0.295294728
H -1.365687008 -0.94147793 -1.623230084
H 0.698674532 0.364806207 -1.320552285
H -3.648844737 1.953026422 0.482895738
H 1.639472209 2.748243574 -0.174463498
C 0.151346876 3.865099311 0.766205463
H 0.7660472 4.678864952 1.096477687
C -1.214119354 3.67016525 0.942513841
O -3.766385713 -0.226664349 -0.719420524
H -3.61519528 -1.036843662 -1.20556596
N 0.675218246 2.836905738 0.076561048
C -3.910307747 8.328101446 4.134627945
C -3.351845818 9.527195128 4.691714213
C -4.113339134 10.45581261 5.372648567
C -5.468803283 10.20337356 5.514574894
C -6.044271418 9.042523987 4.982942275
C -5.289828164 8.112394542 4.302857526
C -2.857587969 7.616945416 3.513577469
C -1.645120962 8.390162038 3.693510915
H -3.669691048 11.34981737 5.781952071
H -6.087192461 10.90939817 6.040291455
H -7.102531322 8.872785666 5.108835836
H -5.733424677 7.224373007 3.896777329
H -1.348078101 10.22663498 4.664996373
C -3.943931989 5.468301039 2.530324176
C -2.053422161 4.568296496 1.625981673
C -1.698600976 5.806105444 2.250899494
C -2.825024896 6.383073131 2.811712452
H -3.937489854 3.639729239 1.496932791
H -0.720088388 6.241590634 2.292100896
O -0.493509476 8.180609161 3.333038944
O -5.126799232 5.495773946 2.794112684
N -3.37336932 4.40231569 1.809299268
N -2.016415847 9.527058244 4.411356089

S_{1,T}

C -1.575397363 -0.492962067 -0.253727748
C -0.61692659 -0.182770059 0.687784688
C -2.611298416 0.402608629 -0.54233586
C -0.72148487 1.037359555 1.328958799
C -2.708135942 1.621522945 0.106553109
C -1.750480678 1.950170338 1.058779554
H -1.528183487 -1.436508481 -0.774080506
H 0.179550126 -0.873193267 0.910098057
H -3.529259205 2.261800746 -0.161962825
H 0.912629392 1.166919476 2.689623337
C -0.366593619 2.792834841 2.65821989
H 0.130998172 3.384916717 3.400516677
C -1.515464733 3.090508119 1.927844435
O -3.561869705 0.12512313 -1.458678188
H -3.408127352 -0.731710522 -1.857280993
N 0.093282365 1.597480401 2.306942274
C -3.448217 8.017149609 4.741052044
C -3.161302959 9.39990227 4.950382159
C -3.638043754 10.08654592 6.042868362
C -4.425229827 9.405132584 6.970915842
C -4.715463905 8.057926002 6.788141724
C -4.236942688 7.359708034 5.689401053
C -2.799057081 7.646977232 3.542790728
C -2.118628052 8.770205141 3.003943172
H -3.406287588 11.13180882 6.179028431
H -4.808731935 9.928669195 7.831396832
H -5.326102525 7.543329258 7.514142302
H -4.476875061 6.314515661 5.571002147
H -2.025542086 10.73481536 3.751389081
C -3.75432039 5.931460232 1.825645628
C -2.217917055 4.291354497 2.090150087
C -1.89111901 5.358396863 3.009461803
C -2.770114986 6.370680201 2.885462735
H -3.760056158 4.111317158 0.690969843
H -1.050238999 5.349018229 3.673525724
O -1.428630551 8.900028428 1.99127579
O -4.716263582 6.453611049 1.368973156
N -3.307617997 4.634987534 1.413392141
N -2.371706495 9.811349662 3.907597776

MECP

C 6.314310335 -0.147408736 -0.31962282
C 5.727018528 -1.364907062 -0.04338849
C 5.53922752 1.008807705 -0.458365516
C 4.354147832 -1.386999115 0.095701386
C 4.16065289 0.97204066 -0.309763892
C 3.561081238 -0.242965913 -0.02348116
H 7.384239413 -0.085343416 -0.433609175
H 6.324522766 -2.255347421 0.054196577
H 3.621790417 1.894551679 -0.42931334
H 3.797588154 -3.414846079 0.501566184
C 2.252427041 -2.068737806 0.419849321
H 1.450986991 -2.753604059 0.612990487
C 2.193506925 -0.686202194 0.188224798
O 6.077796128 2.205098731 -0.744486724
H 7.033783261 2.157956954 -0.775338228
N 3.498869145 -2.466843324 0.361655756
C -3.751100948 -0.148323527 -0.486325
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C -5.070642893 -0.623217215 -2.452968434
C -3.833038277 -0.378628798 -1.856629273
C -2.730282044 0.111106941 0.467507317
C -3.258589503 0.264111095 1.743185966
H -7.085013873 -0.453246661 0.261266028
H -7.182981791 -0.867761942 -2.188987373
H -5.110257028 -0.78449955 -3.520645515
H -2.946627738 -0.374949434 -2.474017789
H -5.274679291 0.135591661 2.336576802
C -0.608350488 1.5922062 0.032630392
C 0.986040514 -0.005521654 0.176783362
C -0.342656731 -0.641925626 0.357568292
C -1.319697753 0.250263577 0.289071919
H 1.563190127 1.951629682 -0.132850564
H -0.480376193 -1.685747897 0.547486624
O -2.737394194 0.50306967 2.85281506
O -0.974051138 2.688568318 -0.135347557
N 0.8411834 1.2691057 0.003526659
N -4.643042486 0.079536293 1.566281257

S₁[‡]

C -1.257319958 -0.097282321 -0.848578656
C -0.137611824 0.46984189 -0.278635021
C -2.502391002 0.533166044 -0.758001868
C -0.296866368 1.672670821 0.384136348
C -2.654510395 1.731957501 -0.084331115
C -1.538289433 2.313173024 0.505908045
H -1.173744984 -1.039683722 -1.366216301
H 0.822063828 -0.016432176 -0.343577304
H -3.639731359 2.160952834 -0.048398535
H 1.624525878 2.247940932 1.075468667
C 0.062403936 3.523505498 1.579754678
H 0.633317374 4.253931098 2.119300721
C -1.302490374 3.509979256 1.295950368
O -3.609951639 -4.80281E-05 -1.317837631
H -3.401738474 -0.833536433 -1.740011118
N 0.644771039 2.448823638 1.041936356
C -3.743442125 8.243022361 4.276223743
C -3.358571342 9.589557115 4.57479739
C -3.980539367 10.32310852 5.560439637
C -5.003234018 9.724235239 6.288959009
C -5.397403132 8.412321969 6.014741173
C -4.781393173 7.66780259 5.027993983
C -2.954870872 7.822078857 3.196143619
C -2.055386698 8.865630854 2.835308787
H -3.682413123 11.33898768 5.76344545
H -5.503377952 10.28433058 7.061727531
H -6.212212073 7.97561102 6.571972241
H -5.113382156 6.664135629 4.813891159
H -1.890942148 10.8063075 3.647501242
C -3.996730217 5.859406489 1.833812823
C -2.178339042 4.510259171 1.729943537
C -1.846637831 5.661087959 2.550269975
C -2.885478039 6.51408016 2.582212114
H -3.974450706 4.006252417 0.785407778
H -0.886733675 5.834716375 2.996645378
O -1.155101302 8.909171727 1.997902697
O -5.129268269 6.193465339 1.65129969
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N -2.348896309 9.920303718 3.713788154

MECP-PYR

C -1.501105564 1.517640376 -1.827326675
C -0.519938323 2.28196163 -1.231186538
C -2.165510922 0.51111791 -1.113600999
C -0.200594022 2.010381017 0.090559437
C -1.843566992 0.238076243 0.198557645
C -0.836196915 0.984870936 0.809195358
H -1.770173288 1.700905196 -2.856365944
H -0.025993317 3.065018861 -1.782944439
H -2.398953033 -0.519795553 0.722974577
H 1.307417251 3.371439112 0.705184265
C 0.641533381 2.017183539 2.160093691
H 1.281556576 2.33588895 2.960981622
C -0.272055505 0.998477905 2.134971882
O -3.150048496 -0.232799103 -1.679559033
H -3.317243281 0.068845426 -2.571768618
N 0.696797002 2.617622207 0.944673129
C -0.888192528 -1.158047635 8.050301128
C -0.341795333 -0.55676486 9.208819352
C -0.419457368 -1.143755275 10.45175446
C -1.064346392 -2.371672197 10.55231674
C -1.622335435 -2.978689194 9.433759248
C -1.54904058 -2.381101827 8.187615124
C -0.574484082 -0.3027596 6.941358242
C 0.178591294 0.844494626 7.483814265
H 0.010968057 -0.671767773 11.3198005
H -1.13411801 -2.855762077 11.5127671
H -2.125039497 -3.926481717 9.534371271
H -2.005540736 -2.857038064 7.341521979
H 0.734071525 1.265021471 9.453164522
C -1.24588412 -1.820776548 5.057754481
C -0.563272756 0.052984227 3.202158281
C -0.458152466 0.441795668 4.604407088
C -0.753759685 -0.486019861 5.569098265
H -1.004504511 -1.452196015 2.05334676
H -0.213609041 1.448060295 4.890194601
O 0.655357797 1.806365432 6.912460586
O -2.295318856 -2.333247498 5.190155087
N -0.949888192 -1.149393482 3.013440339
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