Supplementary Material for

# Deuterium Isotope Effect in Fluorescence of Gaseous Oxazine Dyes

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## 1. Supplementary Experimental Data and Methods

***Table S1:*** *Selected experimental parameters employed for relative brightness measurements*

| Species | *m/z* | Accumulation Times (ms) | Irradiation Power (mW) | Total Fluorescence Collection Time (s) |
|---|---|---|---|---|
| **cresyl violet** | 262 | 95,110,125 | 4.88 | 75 |
| **d-cresyl violet** | 266 | 100,125,150 | 4.88 | 75 |
| **darrow red** | 304 | 18,25,30 | 0.55 | 600 |
| **d-darrow red** | 307 | 18,42,58 | 0.55 | 600 |
| **oxazine 4** | 296 | 12,32,50 | 3.72 | 288 |
| **d-oxazine 4** | 298 | 12,32,50 | 3.72 | 288 |
| **oxazine 170** | 332 | 8,20,32.5 | 8.66 | 336 |
| **d-oxazine 170** | 334 | 15,20,28 | 8.66 | 336 |

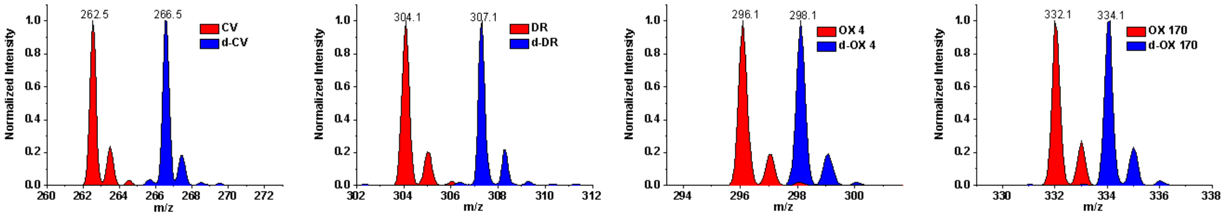


***Figure S1****: Overlay of mass spectrometry (MS) data from protonated (red) and deuterated (blue) forms of CV, DR, OX4 and OX170. The mass of each monoisotopic peak is noted on the spectra.*

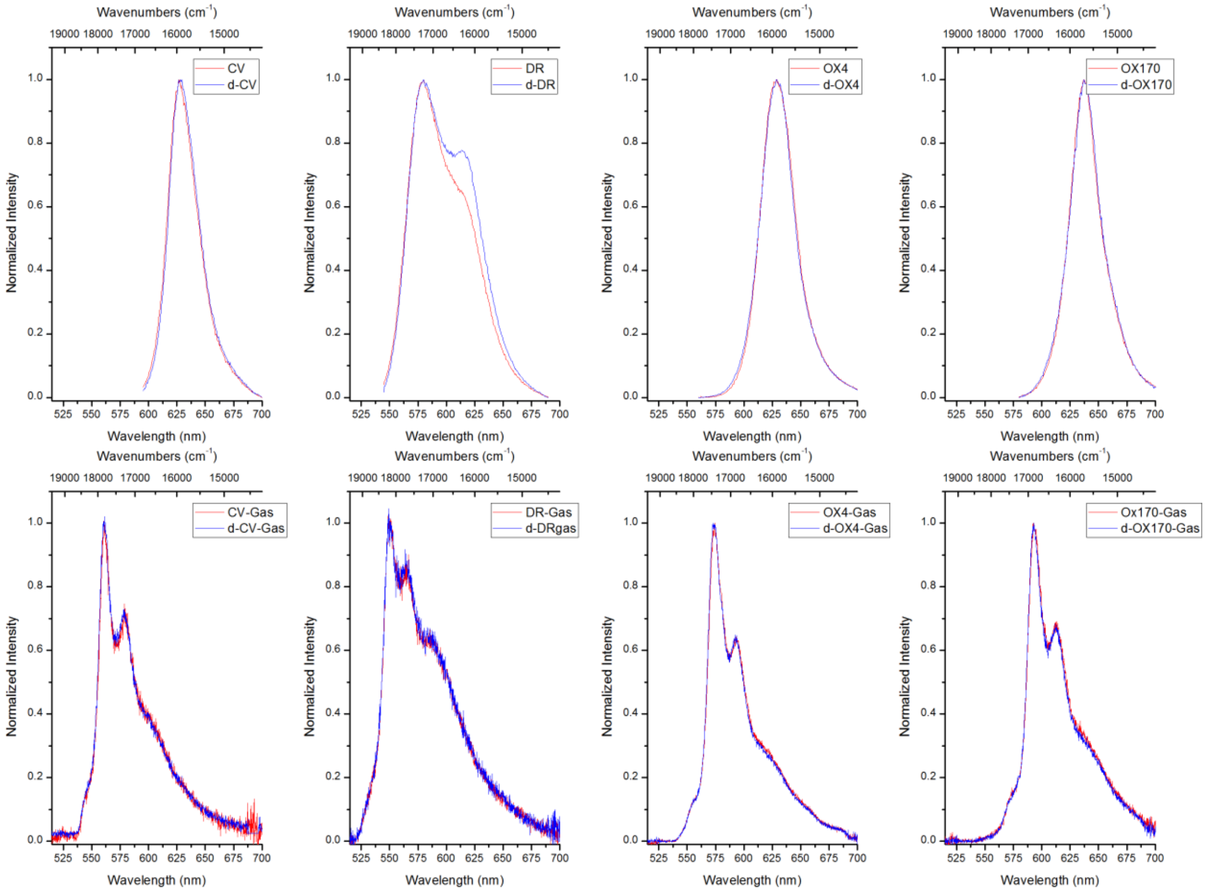


***Figure S2****: Emission spectra of four oxazine dyes in methanol (red) and in deuterated methanol (blue). Dye concentrations in each solution were ≤0.5 µM.*

## Solution Spectroscopy

All dyes were dissolved without any further purification in the condition they were obtained from the seller (Sigma Aldrich, MO, USA) in methanol (ACS grade, Sigma-Aldrich, MO, USA) or deuterated methanol ($CH_3OD$, Sigma-Aldrich, MO, USA) to make 0.5 µM solutions. Measurements were made using a LS-55 fluorescence spectrophotometer (PerkinElmer, MA, USA).

# 2. Supplementary Computational Information

## 1. Estimation of thermal energy available in $S_1$ during the emission and corresponding temperature

Here, we assume that the dye undergoes vertical absorption from $S_0$ minimum. Given that the experiments being carried out under low pressure of $<10^{-5}$ atm, we also assume that each molecule undergoes complete vibrational relaxation in the excited state before any collision such that the initial excitation energy is equally distributed amongst all the vibrations.

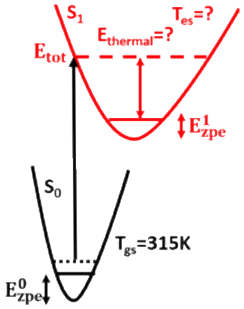


**Figure S3**: Schematic potential energy surfaces and relevant quantities

At 0K, before electronic excitation, the total energy of a molecule in $S_0$ is $E_0 = E^0_{elec} + E^0_{zpe}$ (Figure S2). At finite temperature T, there is thermal energy due to translational, rotational and additional vibrational motion, and the total energy in the ground state is $E_0 = E^0_{elec} + E^0_{zpe} + \Delta E_{vib}(T) + \Delta E_{rot}(T) + \Delta E_{trans}(T)$ , where

$$\Delta E_{trans}(T) = 1.5\ RT,$$

$$\Delta E_{rot}(T) = RT \text{ and}$$

$\Delta E_{vib}(T) = \sum_i \mathrm{R}\Theta_i/(\exp\left(\frac{\Theta_i}{T}\right) - 1)$, where $\Theta_i = h\nu_i/k_B$ is the vibrational temperature of $i^{th}$ normal mode with frequency $\nu_i$. The symbols R, h and $k_B$ stand for universal gas constant, Planck's constant and Boltzmann's constant. In the calculations an initial ion temperature of 315K is employed to reproduce estimated experimental conditions.

Upon vertical excitation, the total energy in $S_1$ is $E_0 + \Delta E_{elec} = E_{tot}$ at $S_0$ minimum geometry. In $S_1$, the difference between $E_{tot}$ and the sum $E^1_{elec} + E^1_{zpe}$ (at $S_1$ minimum geometry) is the thermal energy $E_{thermal}$ available in $S_1$, and we can calculate the temperature corresponding to this thermal energy by solving the equation $E_{thermal} - \left(\Delta E_{trans}(T_{es}) + \Delta E_{rot}(T_{es}) + \Delta E_{vib}(T_{es})\right) = 0$ , where $T_{es}$ is the unknown variable.

***Table S2**: Thermal energy and corresponding temperature in $S_1$ upon excitation from $S_0$ minimum assuming a starting temperature of 315 K.*

| Dye | $E_{thermal}$ (eV) | | $T_{es}$ (K) | |
|---|---|---|---|---|
| | H | D | H | D |
| Cresyl Violet | 0.69 | 0.71 | 378.0 | 376.5 |
| Oxazine 170 | 0.81 | 0.81 | 338.7 | 338.0 |
| Oxazine 4 | 0.76 | 0.76 | 338.8 | 337.9 |
| Darrow Red | 0.74 | 0.75 | 362.0 | 360.4 |

## 2. Cresyl Violet data

(a) $S_0$ optimized geometry obtained with TPSS/6-31G* ($\alpha_1$=0.0°, $\alpha_2$=0.01°)

| | | | |
|---|---|---|---|
| C | -2.887657 | 0.308418 | 0.010592 |
| C | -1.865235 | -0.690312 | 0.004255 |
| C | -0.462734 | -0.298586 | 0.004192 |
| C | -0.162523 | 1.104541 | 0.010642 |
| C | -1.137373 | 2.087714 | 0.016833 |
| C | -2.499929 | 1.716611 | 0.016938 |
| C | 2.143154 | 0.573382 | 0.004783 |
| C | 1.787415 | -0.814654 | -0.001515 |

| | | | |
|---|---|---|---|
| C | 2.852821 | -1.763202 | -0.007666 |
| H | 2.592442 | -2.818832 | -0.012470 |
| C | 4.163512 | -1.347331 | -0.007479 |
| C | 4.490271 | 0.051915 | -0.001085 |
| C | 3.451891 | 1.017728 | 0.005113 |
| H | -0.844313 | 3.135280 | 0.021548 |
| H | 4.971793 | -2.076404 | -0.012192 |
| H | 3.668389 | 2.083526 | 0.010029 |
| C | -4.241180 | -0.105650 | 0.010482 |
| C | -4.574924 | -1.455983 | 0.004341 |
| H | -5.621442 | -1.752957 | 0.004369 |
| C | -3.561494 | -2.434750 | -0.001888 |
| H | -3.826254 | -3.490141 | -0.006683 |
| C | -2.223380 | -2.055570 | -0.001925 |
| H | -5.050922 | 0.622292 | 0.015197 |
| H | -1.428409 | -2.796904 | -0.006680 |
| O | 1.140615 | 1.513515 | 0.010804 |
| N | 0.499548 | -1.227873 | -0.001720 |
| N | -3.437949 | 2.689012 | 0.023019 |
| H | -4.430260 | 2.487179 | 0.023420 |
| H | -3.172769 | 3.668309 | 0.027438 |
| N | 5.791209 | 0.435642 | -0.001037 |
| H | 6.541345 | -0.246532 | -0.005451 |
| H | 6.058305 | 1.413852 | 0.003363 |

(b) $S_1$ optimized geometry using TD-TPSS/6-31G* (planar minimum)

| | | | |
|---|---|---|---|
| C | -2.892220 | 0.319770 | -0.001650 |
| C | -1.881220 | -0.693560 | 0.012993 |
| C | -0.465194 | -0.341461 | 0.012130 |
| C | -0.164711 | 1.079547 | -0.006623 |
| C | -1.130514 | 2.070774 | -0.001937 |
| C | -2.496873 | 1.727410 | 0.012995 |
| C | 2.113279 | 0.519055 | -0.006623 |
| C | 1.791761 | -0.839658 | 0.013353 |
| C | 2.873257 | -1.755594 | 0.023534 |
| H | 2.628782 | -2.816039 | 0.039231 |
| C | 4.204686 | -1.347781 | 0.013552 |
| C | 4.518384 | 0.031921 | -0.007417 |
| C | 3.452979 | 0.986222 | -0.017301 |
| H | -0.821074 | 3.114246 | -0.001406 |
| H | 5.004024 | -2.085097 | 0.021500 |
| H | 3.643908 | 2.057217 | -0.033060 |
| C | -4.241053 | -0.091189 | -0.037044 |
| C | -4.588522 | -1.448884 | -0.036396 |
| H | -5.639281 | -1.730160 | -0.064624 |
| C | -3.591868 | -2.438390 | -0.004811 |
| H | -3.864373 | -3.491395 | -0.002866 |
| C | -2.251008 | -2.060874 | 0.015330 |
| H | -5.046089 | 0.640180 | -0.083772 |
| H | -1.454010 | -2.800258 | 0.029268 |

| | | | |
|---|---|---|---|
| O | 1.155963 | 1.487107 | -0.017938 |
| N | 0.454570 | -1.295706 | 0.022060 |
| N | -3.438125 | 2.713106 | 0.009512 |
| H | -4.410319 | 2.517715 | 0.215765 |
| H | -3.153769 | 3.682198 | 0.107665 |
| N | 5.804227 | 0.491206 | -0.017837 |
| H | 6.590184 | -0.151064 | -0.012416 |
| H | 6.018186 | 1.482669 | -0.035597 |

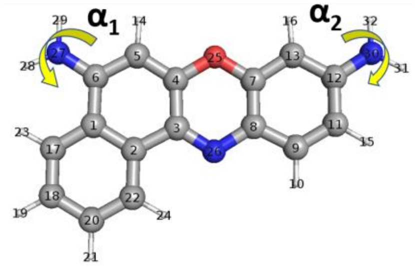
(c) $S_1$ optimized geometry using TD-TPSS/6-31G* after twisting $NH_2$ groups (twisted minimum)

| | | | |
|---|---|---|---|
| C | 0.019595 | -0.018820 | -0.004147 |
| C | 0.045739 | -0.009014 | 1.435669 |
| C | 1.303349 | -0.011903 | 2.146479 |
| C | 2.478215 | -0.024262 | 1.411967 |
| C | 2.496412 | -0.034276 | -0.014574 |
| C | 1.289758 | -0.031184 | -0.650552 |
| C | 3.742445 | -0.018159 | 3.394089 |
| C | 2.497037 | -0.005523 | 4.123813 |
| C | 2.602010 | 0.003748 | 5.551276 |
| H | 1.674791 | 0.013304 | 6.118754 |
| C | 3.826323 | 0.000725 | 6.182336 |
| C | 5.041940 | -0.011869 | 5.425297 |
| C | 4.979526 | -0.021366 | 4.008481 |
| H | 3.450689 | -0.043788 | -0.534611 |
| H | 3.881726 | 0.007973 | 7.269780 |
| H | 5.884394 | -0.031049 | 3.404619 |
| C | -1.236825 | -0.015650 | -0.677579 |
| C | -2.413502 | -0.003306 | 0.044214 |
| H | -3.367097 | -0.000986 | -0.479884 |
| C | -2.387858 | 0.006375 | 1.463475 |
| H | -3.325130 | 0.016074 | 2.016084 |
| C | -1.184555 | 0.003570 | 2.142839 |
| H | -1.293842 | -0.022841 | -1.765488 |
| H | -1.141269 | 0.010830 | 3.228390 |
| O | 3.718850 | -0.027744 | 2.013738 |
| N | 1.285404 | -0.002197 | 3.537602 |
| N | 1.298624 | -0.041491 | -2.127770 |
| H | 1.264299 | 0.822779 | -2.675084 |
| H | 1.253490 | -0.912800 | -2.663007 |
| N | 6.241849 | -0.014401 | 6.068579 |
| H | 7.117901 | -0.024321 | 5.559552 |
| H | 6.295177 | -0.008776 | 7.080475 |

(d) Parameters used in spectra calculation. Refer to Gaussian website for description of these keywords.

Keyword section: Freq=(FC,ReadFC,ReadFCHT)
ReadFCHT section: Prescreening=(MaxInt=5000,MaxC1=200,MaxC2=200),
MaxStatesI=1766,HWHM=50.0, Temperature=(value=T), where T=$T_{es}$ is chosen from Table S1.

(e) Oscillator strength plots for $\alpha_1$ and $\alpha_2$ .



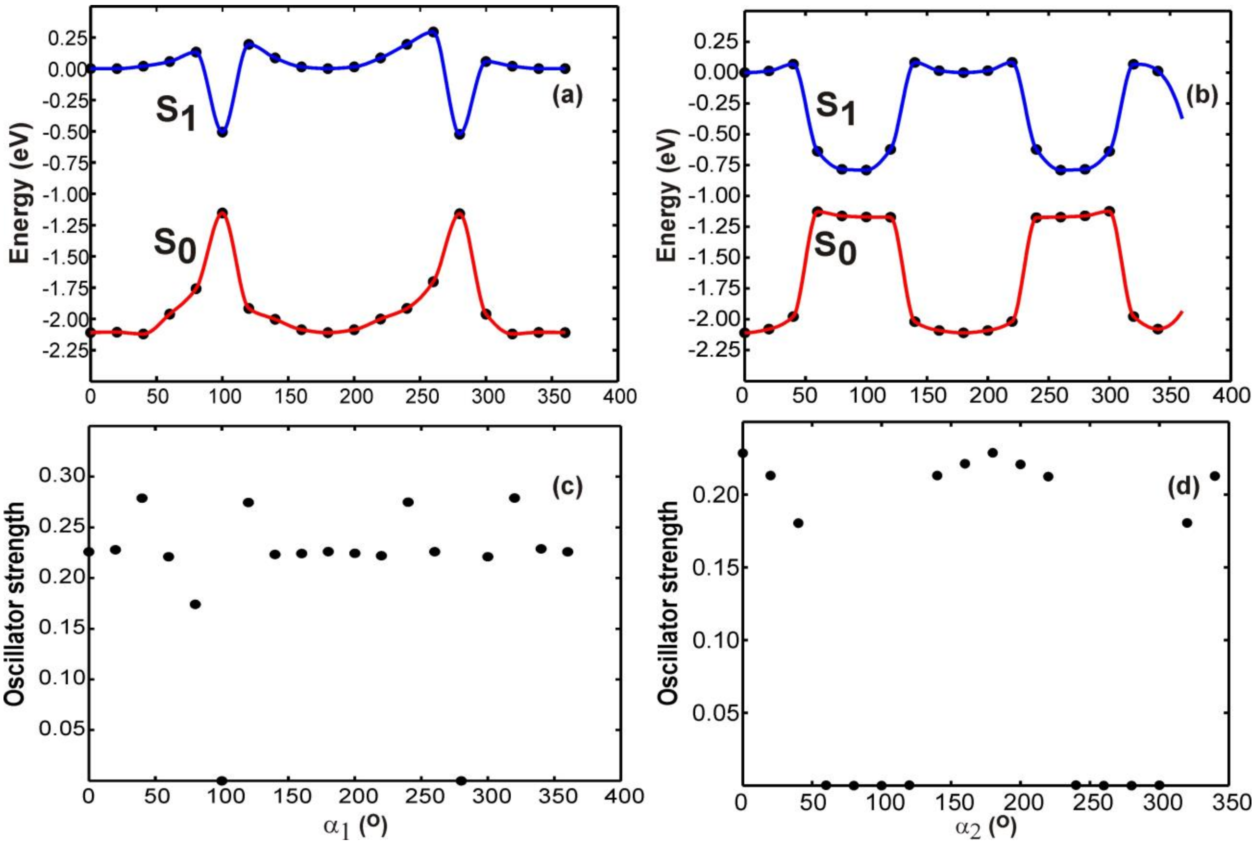
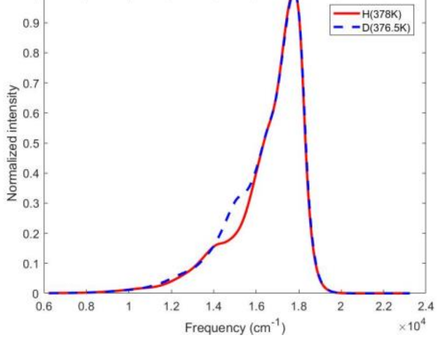


*Figure S4. (a-b) Electronic energies (shifted by the energy of the planar $S_1$ minimum) and (c-d) oscillator strength along the scan of dihedral torsional angles of the $NH_2$ groups in CV. $\alpha_1$ and $\alpha_2$ correspond to D(1,6,27,28) and D(11,12,30,31), respectively.*

(f) ***Figure S5*** Comparison of deuterated and non-deuterated forms of CV showing differences only in a small region of the spectrum.



(g) $T_1$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | -2.894181 | 0.324260 | 0.006515 |
| C | -1.860077 | -0.671411 | 0.003973 |
| C | -0.467220 | -0.296306 | 0.013486 |
| C | -0.166003 | 1.097205 | 0.025055 |
| C | -1.142340 | 2.083188 | 0.027741 |
| C | -2.510658 | 1.728188 | 0.018828 |
| C | 2.131002 | 0.564188 | 0.032017 |
| C | 1.776065 | -0.827284 | 0.020265 |
| C | 2.849982 | -1.766489 | 0.018681 |
| H | 2.589740 | -2.821959 | 0.009863 |
| C | 4.168078 | -1.355515 | 0.027866 |
| C | 4.486670 | 0.038382 | 0.039357 |
| C | 3.440100 | 1.002753 | 0.041383 |
| H | -0.839970 | 3.128594 | 0.036821 |
| H | 4.973934 | -2.087399 | 0.026413 |
| H | 3.655331 | 2.069203 | 0.050168 |
| C | -4.237755 | -0.107870 | -0.003040 |
| C | -4.560565 | -1.468203 | -0.014823 |
| H | -5.606103 | -1.769093 | -0.022049 |
| C | -3.544296 | -2.441048 | -0.017315 |
| H | -3.801107 | -3.498053 | -0.026507 |
| C | -2.209994 | -2.046348 | -0.007962 |
| H | -5.056644 | 0.610185 | -0.001547 |
| H | -1.402231 | -2.773418 | -0.009563 |
| O | 1.144645 | 1.530343 | 0.034429 |
| N | 0.487679 | -1.276517 | 0.010885 |
| N | -3.444283 | 2.716271 | 0.021583 |
| H | -4.438945 | 2.525528 | 0.016450 |
| H | -3.168060 | 3.692481 | 0.031216 |
| N | 5.787781 | 0.440934 | 0.048414 |
| H | 6.547712 | -0.232097 | 0.047409 |
| H | 6.041883 | 1.423633 | 0.056558 |

(h) $T_2$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | -2.895154 | 0.321297 | -0.003241 |
| C | -1.873777 | -0.699638 | 0.007620 |
| C | -0.463432 | -0.355251 | 0.015301 |
| C | -0.167504 | 1.021523 | 0.011965 |
| C | -1.136985 | 2.046281 | 0.011131 |
| C | -2.509746 | 1.714054 | 0.010576 |
| C | 2.119779 | 0.503663 | 0.017155 |
| C | 1.780273 | -0.871781 | 0.020904 |
| C | 2.881131 | -1.763708 | 0.024880 |
| H | 2.664084 | -2.829660 | 0.030823 |
| C | 4.209031 | -1.321629 | 0.024841 |
| C | 4.525506 | 0.058184 | 0.020251 |
| C | 3.448213 | 0.987097 | 0.015517 |
| H | -0.807709 | 3.083598 | 0.012392 |
| H | 5.014288 | -2.053986 | 0.027279 |
| H | 3.618956 | 2.061902 | 0.005147 |
| C | -4.258571 | -0.084477 | -0.028129 |
| C | -4.604359 | -1.424800 | -0.030844 |
| H | -5.652882 | -1.713990 | -0.052461 |
| C | -3.594670 | -2.422429 | -0.009874 |
| H | -3.875660 | -3.473690 | -0.011356 |
| C | -2.255907 | -2.061896 | 0.006580 |
| H | -5.056012 | 0.656036 | -0.058313 |
| H | -1.467349 | -2.809816 | 0.016593 |
| O | 1.144264 | 1.463355 | 0.015015 |

| | | | |
|---|---|---|---|
| N | 0.484933 | -1.326245 | 0.022071 |
| N | -3.428278 | 2.724010 | 0.000258 |
| H | -4.416239 | 2.546388 | 0.134182 |
| H | -3.131225 | 3.689301 | 0.091964 |
| N | 5.816840 | 0.512326 | -0.012164 |
| H | 6.589942 | -0.134111 | 0.102571 |
| H | 6.028388 | 1.494420 | 0.123936 |

(i) $T_3$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | -2.872008 | 0.336415 | -0.005821 |
| C | -1.862322 | -0.653892 | 0.025682 |
| C | -0.459407 | -0.287212 | 0.029873 |
| C | -0.168514 | 1.087810 | 0.001369 |
| C | -1.155040 | 2.087796 | 0.007089 |
| C | -2.504128 | 1.745466 | 0.016104 |
| C | 2.131004 | 0.551770 | 0.017254 |
| C | 1.790705 | -0.831512 | 0.046082 |
| C | 2.848341 | -1.764683 | 0.063925 |
| H | 2.597466 | -2.822365 | 0.085598 |
| C | 4.179508 | -1.345261 | 0.054401 |
| C | 4.489939 | 0.043519 | 0.025715 |
| C | 3.447015 | 0.998974 | 0.006916 |
| H | -0.842192 | 3.129993 | 0.016614 |
| H | 4.984606 | -2.077560 | 0.069331 |
| H | 3.654040 | 2.066606 | -0.017085 |
| C | -4.229920 | -0.108625 | -0.099174 |
| C | -4.573523 | -1.478478 | -0.098433 |
| H | -5.621033 | -1.761894 | -0.169620 |
| C | -3.571001 | -2.454584 | -0.018978 |
| H | -3.825696 | -3.511459 | -0.011290 |
| C | -2.236116 | -2.055456 | 0.036770 |
| H | -5.028857 | 0.621484 | -0.210009 |
| H | -1.426438 | -2.779067 | 0.088874 |
| O | 1.143475 | 1.517541 | -0.004005 |
| N | 0.473563 | -1.279414 | 0.056479 |
| N | -3.499192 | 2.707809 | -0.035789 |
| H | -4.362287 | 2.525379 | 0.469552 |
| H | -3.190880 | 3.671117 | 0.073177 |
| N | 5.802637 | 0.448954 | 0.015454 |
| H | 6.561406 | -0.224190 | 0.030785 |
| H | 6.055016 | 1.431348 | -0.004269 |

(j) ISC rates for $S_1$->$T_2$ and $S_1$-$T_3$ channels (Table S3)

Table S3: ISC rates in CV for triplet channels

| State | ISC rate ($s^{-1}$) | |
|---|---|---|
| | H | D |
| $T_2$ | $4.9 \times 10^6$ | $4.4 \times 10^6$ |
| $T_3$ | $3.1 \times 10^4$ | $2.6 \times 10^4$ |

## 3. Oxazine 170 data

(a) $S_0$ optimized geometry using TPSS/6-31G* ($\alpha_1$=180.0°, $\alpha_2$=180.0°)

| | | | |
|---|---|---|---|
| C | 3.381505 | -0.574373 | -0.000006 |
| C | 2.247365 | -1.443308 | -0.000008 |
| C | 0.900788 | -0.888893 | -0.000001 |
| C | 0.771757 | 0.537381 | 0.000007 |
| C | 1.855131 | 1.401788 | 0.000007 |
| C | 3.167879 | 0.876981 | 0.000000 |
| C | -1.581001 | 0.282914 | 0.000009 |
| C | -1.394278 | -1.135175 | 0.000001 |

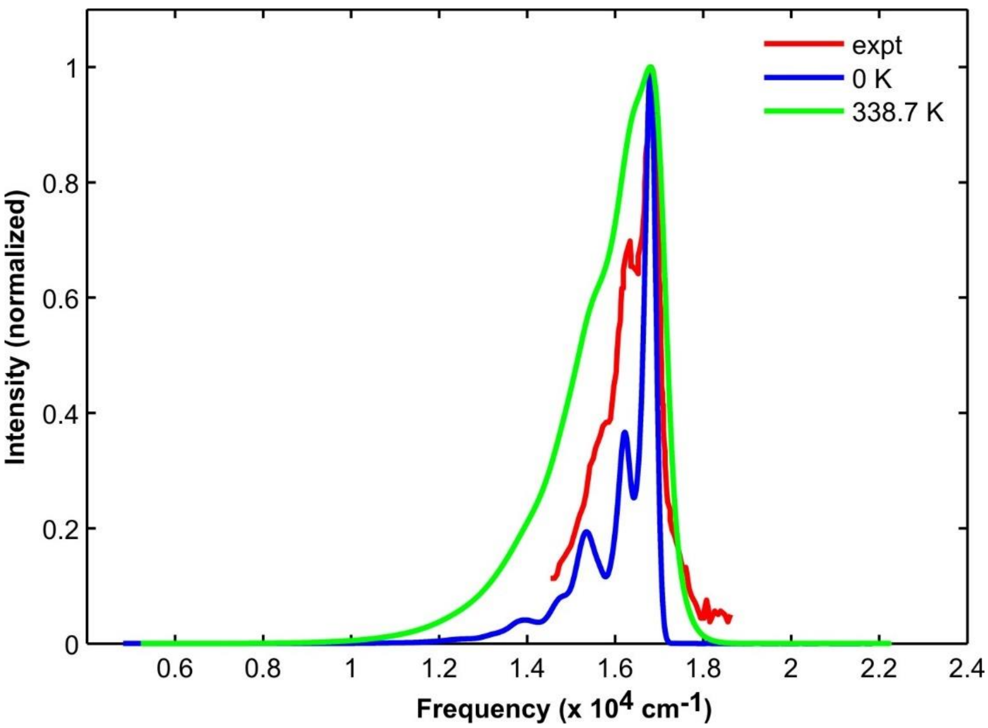
|  |  |  |  |
|---|---|---|---|
| C | -2.565950 | -1.948312 | -0.000002 |
| H | -2.421546 | -3.027024 | -0.000008 |
| C | -3.834140 | -1.407753 | 0.000002 |
| C | -3.978021 | 0.037661 | 0.000010 |
| C | -2.830186 | 0.873482 | 0.000014 |
| H | 1.674813 | 2.472279 | 0.000013 |
| H | -2.914830 | 1.956033 | 0.000020 |
| C | 4.672822 | -1.154532 | -0.000012 |
| C | 4.840266 | -2.535591 | -0.000019 |
| H | 5.843565 | -2.956427 | -0.000023 |
| C | 3.716283 | -3.384393 | -0.000022 |
| H | 3.850104 | -4.464293 | -0.000029 |
| C | 2.436124 | -2.842800 | -0.000017 |
| H | 5.569162 | -0.535500 | -0.000009 |
| H | 1.554890 | -3.479297 | -0.000018 |
| O | -0.474801 | 1.099201 | 0.000012 |
| N | -0.165407 | -1.699434 | -0.000004 |
| N | 4.225374 | 1.717596 | -0.000002 |
| H | 5.156847 | 1.314257 | -0.000013 |
| N | -5.223953 | 0.574471 | 0.000015 |
| H | -6.012012 | -0.066605 | 0.000012 |
| C | 4.160050 | 3.189013 | -0.000001 |
| H | 3.603527 | 3.519155 | 0.889429 |
| H | 3.603514 | 3.519157 | -0.889421 |
| C | 5.571851 | 3.779011 | -0.000011 |
| H | 6.129997 | 3.471241 | -0.894018 |
| H | 5.512548 | 4.873111 | -0.000009 |
| H | 6.130011 | 3.471239 | 0.893988 |
| C | -5.062932 | -2.287812 | 0.000000 |
| H | -5.687938 | -2.113356 | 0.889968 |
| H | -5.687940 | -2.113348 | -0.889966 |
| H | -4.778938 | -3.345155 | -0.000005 |
| C | -5.543009 | 2.009704 | 0.000022 |
| H | -5.091600 | 2.475419 | 0.889001 |
| H | -5.091603 | 2.475427 | -0.888953 |
| C | -7.059427 | 2.215216 | 0.000025 |
| H | -7.518680 | 1.772368 | 0.893631 |
| H | -7.286221 | 3.287220 | 0.000031 |
| H | -7.518683 | 1.772376 | -0.893583 |

(b) $S_1$ optimized geometry using TD-TPSS/6-31G* (planar minimum). There were convergence issues in the solution of Kohn-Sham equations when trying to find the optimized geometry with the twisted configuration of the amino groups, so we are unable to report that data. The lack of convergence indicates the presence of multi-configuration character in the ground electronic state, the exploration of which is beyond the scope of the current analysis.

|  |  |  |  |
|---|---|---|---|
| C | 3.391666 | -0.574245 | -0.000010 |
| C | 2.265287 | -1.455931 | 0.000006 |
| C | 0.900788 | -0.935660 | 0.000049 |
| C | 0.770873 | 0.511330 | 0.000095 |
| C | 1.850111 | 1.379256 | 0.000099 |
| C | 3.169815 | 0.877237 | 0.000039 |
| C | -1.559190 | 0.225578 | 0.000081 |

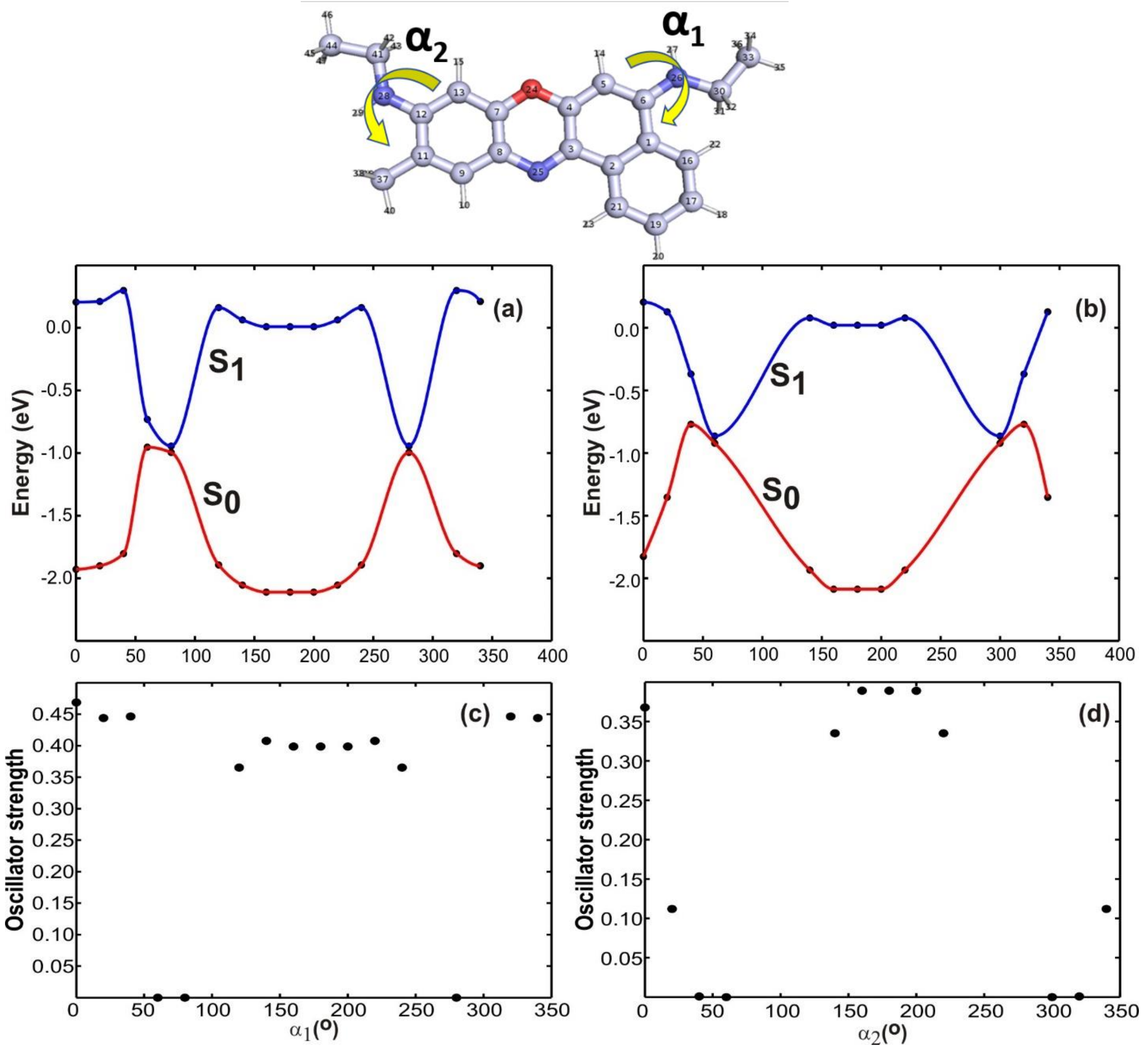
| | | | |
|---|---|---|---|
| C | -1.397990 | -1.163342 | 0.000059 |
| C | -2.573988 | -1.953450 | 0.000034 |
| H | -2.442461 | -3.034572 | 0.000023 |
| C | -3.856843 | -1.413333 | 0.000023 |
| C | -3.987989 | 0.014530 | 0.000027 |
| C | -2.829550 | 0.838785 | 0.000065 |
| H | 1.657408 | 2.448234 | 0.000127 |
| H | -2.892611 | 1.923209 | 0.000078 |
| C | 4.679087 | -1.151857 | -0.000056 |
| C | 4.857551 | -2.540998 | -0.000080 |
| H | 5.866452 | -2.948750 | -0.000111 |
| C | 3.746851 | -3.399250 | -0.000059 |
| H | 3.886149 | -4.478108 | -0.000073 |
| C | 2.462980 | -2.856985 | -0.000022 |
| H | 5.574083 | -0.531079 | -0.000064 |
| H | 1.579687 | -3.491047 | -0.000004 |
| O | -0.485724 | 1.076842 | 0.000113 |
| N | -0.125529 | -1.775000 | 0.000044 |
| N | 4.226553 | 1.730792 | 0.000008 |
| H | 5.162148 | 1.338565 | -0.000051 |
| N | -5.233150 | 0.593907 | 0.000000 |
| H | -6.031540 | -0.036676 | -0.000026 |
| C | 4.141682 | 3.197701 | 0.000019 |
| H | 3.579852 | 3.522978 | 0.889031 |
| H | 3.579752 | 3.522987 | -0.888926 |
| C | 5.544474 | 3.809202 | -0.000054 |
| H | 6.107034 | 3.509134 | -0.893990 |
| H | 5.469858 | 4.902428 | -0.000044 |
| H | 6.107132 | 3.509125 | 0.893817 |
| C | -5.087912 | -2.291047 | -0.000004 |
| H | -5.715007 | -2.120046 | 0.890112 |
| H | -5.714977 | -2.120030 | -0.890137 |
| H | -4.805441 | -3.349108 | -0.000009 |
| C | -5.530693 | 2.028252 | -0.000003 |
| H | -5.070369 | 2.491351 | 0.887821 |
| H | -5.070325 | 2.491356 | -0.887801 |
| C | -7.043395 | 2.260278 | -0.000040 |
| H | -7.509655 | 1.825735 | 0.893780 |
| H | -7.250248 | 3.336305 | -0.000046 |
| H | -7.509608 | 1.825735 | -0.893885 |

*(c) Figure S6: Oxazine 170 $S_1$ planar minimum → $S_0$ emission spectrum – comparison of theoretical spectra at 0K and 338.7K with experiment. Parameters used in the spectra calculation: Keyword section is same as CV, ReadFCHT section has TD=(time=1.d-9,2NStep=24, 2NstepWin=18). The theoretical spectra are aligned to experimental 0-0 band maximum.*


expt
0 K
338.7 K
Intensity (normalized)
0
0.2
0.4
0.6
0.8
1
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
Frequency (x $10^4$ $cm^{-1}$)

(d) Dihedral angle analyses:

***Figure S7****: Analysis of electronic energy and oscillator strength along the scan of dihedral angles involving torsional motion of NH-ethyl groups in oxazine 170. The barrier from a planar to a planar configuration to a twisted configuration (0.16 eV and 0.08 eV for $\alpha_1$ and $\alpha_2$ respectively) is more than the available thermal energy (0.029 eV corresponding to 338.7K) and hence, like CV, oxazine 170 cannot easily twist its amino groups. This accounts for the dominant fluorescence seen in experiments. The angle $\alpha_1$($\alpha_2$) corresponds to D(5,6,26,27) (D(13,12,28,29)).*



The twisting of the amino groups in oxazine 170 brings $S_1$ to a near-degeneracy with $S_0$. A natural transition orbital analysis revealed, similar to CV, a change in character from $\pi \rightarrow \pi^*$ to $n \rightarrow \pi^*$ (Figure S8).

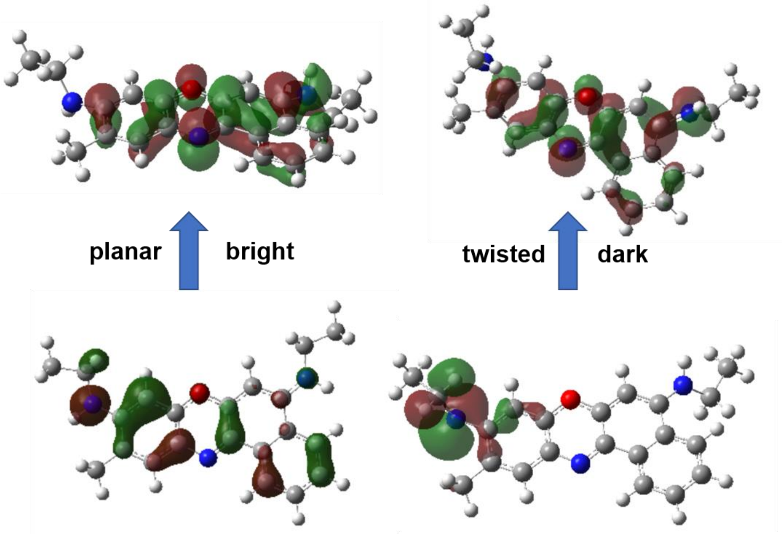


***Figure S8****: Natural transition orbital (NTO) analysis of oxazine 170 corresponding to $S_1$ planar minimum (left) and a low energy twisted configuration (right) from Figure S7. The bottom (top) orbital corresponds to a hole (particle) NTO.*

(e) $T_1$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | 3.389319 | -0.568532 | -0.000012 |
| C | 2.245213 | -1.434055 | -0.000011 |
| C | 0.901746 | -0.896063 | -0.000003 |
| C | 0.772811 | 0.522904 | 0.000002 |
| C | 1.859155 | 1.388031 | 0.000002 |
| C | 3.177108 | 0.876371 | -0.000005 |
| C | -1.571276 | 0.271404 | 0.000007 |
| C | -1.388339 | -1.148487 | 0.000004 |
| C | -2.562513 | -1.947951 | 0.000007 |
| H | -2.421656 | -3.026983 | 0.000006 |
| C | -3.841260 | -1.408004 | 0.000011 |
| C | -3.975968 | 0.029766 | 0.000011 |
| C | -2.821814 | 0.859214 | 0.000010 |
| H | 1.671165 | 2.457850 | 0.000006 |
| H | -2.901637 | 1.942578 | 0.000012 |
| C | 4.671669 | -1.161568 | -0.000020 |
| C | 4.828750 | -2.548145 | -0.000027 |
| H | 5.830618 | -2.972849 | -0.000033 |
| C | 3.702179 | -3.392359 | -0.000026 |
| H | 3.830241 | -4.472770 | -0.000031 |
| C | 2.426797 | -2.839626 | -0.000018 |
| H | 5.574142 | -0.550958 | -0.000021 |
| H | 1.536636 | -3.463224 | -0.000016 |
| O | -0.477134 | 1.113865 | 0.000007 |
| N | -0.158340 | -1.752628 | -0.000001 |
| N | 4.236067 | 1.731119 | -0.000005 |
| H | 5.169812 | 1.331871 | -0.000011 |
| N | -5.226119 | 0.581182 | 0.000014 |
| H | -6.016719 | -0.059134 | 0.000014 |
| C | 4.162528 | 3.200172 | 0.000001 |
| H | 3.602900 | 3.527003 | 0.889031 |
| H | 3.602897 | 3.527010 | -0.889025 |
| C | 5.570092 | 3.800416 | 0.000001 |

| | | | |
|---|---|---|---|
| H | 6.130395 | 3.496720 | -0.894025 |
| H | 5.502702 | 4.894042 | 0.000005 |
| H | 6.130398 | 3.496713 | 0.894023 |
| C | -5.063507 | -2.297015 | 0.000013 |
| H | -5.690386 | -2.130658 | 0.890243 |
| H | -5.690390 | -2.130658 | -0.890213 |
| H | -4.769291 | -3.351414 | 0.000013 |
| C | -5.543534 | 2.016015 | 0.000014 |
| H | -5.086660 | 2.477374 | 0.888355 |
| H | -5.086665 | 2.477374 | -0.888329 |
| C | -7.058938 | 2.227518 | 0.000019 |
| H | -7.520471 | 1.788032 | 0.893942 |
| H | -7.279170 | 3.300822 | 0.000018 |
| H | -7.520476 | 1.788030 | -0.893901 |

(f) $T_2$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | 3.398495 | -0.581385 | -0.000014 |
| C | 2.269833 | -1.473133 | -0.000011 |
| C | 0.907979 | -0.966180 | -0.000004 |
| C | 0.775794 | 0.437444 | -0.000002 |
| C | 1.850419 | 1.343855 | -0.000004 |
| C | 3.176014 | 0.855337 | -0.000007 |
| C | -1.554971 | 0.182219 | 0.000004 |
| C | -1.379897 | -1.215921 | 0.000004 |
| C | -2.579550 | -1.973101 | 0.000009 |
| H | -2.476987 | -3.057197 | 0.000010 |
| C | -3.862818 | -1.407668 | 0.000013 |
| C | -4.003146 | 0.015605 | 0.000011 |
| C | -2.831263 | 0.812015 | 0.000006 |
| H | 1.634679 | 2.408365 | -0.000002 |
| H | -2.871848 | 1.898022 | 0.000003 |
| C | 4.700953 | -1.148115 | -0.000024 |
| C | 4.887734 | -2.522358 | -0.000029 |
| H | 5.896616 | -2.929936 | -0.000037 |
| C | 3.772052 | -3.392201 | -0.000025 |
| H | 3.925118 | -4.469624 | -0.000030 |
| C | 2.486857 | -2.872266 | -0.000018 |
| H | 5.586454 | -0.513497 | -0.000030 |
| H | 1.613217 | -3.519076 | -0.000015 |
| O | -0.484235 | 1.027936 | 0.000000 |
| N | -0.145284 | -1.821392 | -0.000002 |
| N | 4.218401 | 1.736521 | -0.000006 |
| H | 5.159798 | 1.357187 | -0.000011 |
| N | -5.242483 | 0.606037 | 0.000012 |
| H | -6.050008 | -0.009917 | 0.000013 |
| C | 4.111057 | 3.201852 | 0.000001 |
| H | 3.546061 | 3.520421 | 0.889371 |
| H | 3.546068 | 3.520431 | -0.889369 |
| C | 5.505195 | 3.833330 | 0.000010 |
| H | 6.071606 | 3.540891 | -0.893871 |
| H | 5.414686 | 4.925291 | 0.000015 |
| H | 6.071599 | 3.540881 | 0.893891 |
| C | -5.093160 | -2.280883 | 0.000019 |
| H | -5.718740 | -2.095396 | 0.888591 |

|  |  |  |  |
|---|---|---|---|
| H | -5.718749 | -2.095396 | -0.888546 |
| H | -4.823263 | -3.341664 | 0.000018 |
| C | -5.512626 | 2.048933 | 0.000012 |
| H | -5.049906 | 2.504488 | 0.889399 |
| H | -5.049916 | 2.504486 | -0.889382 |
| C | -7.021959 | 2.303388 | 0.000020 |
| H | -7.494184 | 1.874821 | 0.893681 |
| H | -7.214420 | 3.382049 | 0.000019 |
| H | -7.494194 | 1.874818 | -0.893635 |

(g) $T_3$ optimized geometry using TD-TPSS/6-31G*

|  |  |  |  |
|---|---|---|---|
| C | 3.392419 | -0.560407 | -0.013061 |
| C | 2.248784 | -1.439514 | 0.012371 |
| C | 0.917653 | -0.901283 | 0.010226 |
| C | 0.777955 | 0.500898 | -0.012847 |
| C | 1.866052 | 1.382191 | -0.008462 |
| C | 3.176553 | 0.883316 | 0.006743 |
| C | -1.570538 | 0.241512 | -0.005793 |
| C | -1.396985 | -1.166366 | 0.019250 |
| C | -2.555523 | -1.963900 | 0.034365 |
| H | -2.427747 | -3.044566 | 0.053133 |
| C | -3.860321 | -1.406009 | 0.026165 |
| C | -3.978639 | 0.016952 | 0.000346 |
| C | -2.827899 | 0.835568 | -0.015613 |
| H | 1.665706 | 2.449241 | 0.004989 |
| H | -2.898994 | 1.919140 | -0.036214 |
| C | 4.669853 | -1.153523 | -0.077034 |
| C | 4.834240 | -2.547501 | -0.074190 |
| H | 5.838166 | -2.964286 | -0.122380 |
| C | 3.711830 | -3.405070 | -0.016723 |
| H | 3.850941 | -4.483770 | -0.011113 |
| C | 2.441264 | -2.862323 | 0.020069 |
| H | 5.565394 | -0.539320 | -0.157166 |
| H | 1.552296 | -3.486316 | 0.048969 |
| O | -0.474662 | 1.082518 | -0.022348 |
| N | -0.148576 | -1.780964 | 0.027278 |
| N | 4.250462 | 1.735108 | 0.021570 |
| H | 5.158074 | 1.346737 | 0.257432 |
| N | -5.247513 | 0.583301 | -0.007927 |
| H | -6.043151 | -0.048818 | -0.006913 |
| C | 4.154556 | 3.198384 | 0.064650 |
| H | 3.625620 | 3.510350 | 0.980866 |
| H | 3.553456 | 3.529350 | -0.794361 |
| C | 5.550219 | 3.823877 | 0.010968 |
| H | 6.072827 | 3.542428 | -0.911977 |
| H | 5.466770 | 4.916198 | 0.037554 |
| H | 6.157509 | 3.514115 | 0.872657 |
| C | -5.073689 | -2.303529 | 0.045261 |
| H | -5.702973 | -2.122228 | 0.931224 |
| H | -5.704089 | -2.158715 | -0.846746 |
| H | -4.775401 | -3.356766 | 0.066341 |
| C | -5.533144 | 2.013923 | -0.035320 |
| H | -5.056021 | 2.488220 | 0.838714 |
| H | -5.065929 | 2.453773 | -0.932725 |

| | | | |
|---|---|---|---|
| C | -7.041559 | 2.268678 | -0.031867 |
| H | -7.509503 | 1.859100 | 0.872833 |
| H | -7.232825 | 3.347286 | -0.052664 |
| H | -7.519842 | 1.823327 | -0.914075 |

(h) ISC rates for $S_1$->$T_2$ and $S_1$-$T_3$ channels (Table S4)

Table S4: ISC rates in OXA170 for triplet channels

| State | ISC rate ($s^{-1}$) | |
|---|---|---|
| | H | D |
| $T_2$ | 6.4 x $10^6$ | 6.4 x $10^6$ |
| $T_3$ | 1.6 x $10^5$ | 1.5 x $10^5$ |

## 4. Oxazine 4 data

(a) $S_0$ optimized geometry using TPSS/6-31G* ($\alpha_1$=180.0°, $\alpha_2$=180.0°)

| | | | |
|---|---|---|---|
| C | -1.152772 | -1.349631 | -0.000004 |
| C | -1.183191 | 0.086104 | 0.000001 |
| C | -2.363438 | 0.803535 | 0.000004 |
| C | -3.594677 | 0.095209 | 0.000001 |
| C | 1.179716 | 0.086074 | 0.000001 |
| C | 1.149266 | -1.349729 | -0.000004 |
| C | 2.405383 | -2.031907 | -0.000005 |
| H | 2.374697 | -3.119740 | -0.000009 |
| C | 3.606542 | -1.360012 | -0.000003 |
| C | 3.591280 | 0.094817 | 0.000001 |
| C | 2.360143 | 0.803254 | 0.000004 |
| H | -2.333041 | 1.888978 | 0.000009 |
| H | 2.329875 | 1.888711 | 0.000010 |
| O | -0.001641 | 0.782543 | 0.000004 |
| N | -0.001751 | -2.050247 | -0.000006 |
| N | -4.773412 | 0.762268 | 0.000004 |
| H | -5.625865 | 0.208942 | 0.000004 |
| N | 4.770092 | 0.761694 | 0.000004 |
| H | 5.622525 | 0.208342 | 0.000008 |
| C | -3.610090 | -1.359573 | -0.000004 |
| C | -2.408997 | -2.031620 | -0.000006 |
| C | -4.939173 | 2.224441 | 0.000009 |
| H | -4.440386 | 2.638124 | -0.889066 |
| H | -4.440392 | 2.638118 | 0.889090 |
| C | -6.425333 | 2.588759 | 0.000005 |
| H | -6.928895 | 2.197486 | 0.893753 |
| H | -6.536844 | 3.678767 | 0.000009 |
| H | -6.928889 | 2.197493 | -0.893750 |
| C | 4.936084 | 2.223916 | 0.000008 |
| H | 4.437331 | 2.637616 | -0.889066 |
| H | 4.437352 | 2.637611 | 0.889097 |
| C | 6.422308 | 2.587896 | -0.000010 |
| H | 6.925762 | 2.196522 | -0.893775 |
| H | 6.534108 | 3.677878 | -0.000006 |
| H | 6.925785 | 2.196514 | 0.893739 |
| C | -4.927482 | -2.100373 | -0.000006 |
| H | -5.529488 | -1.859413 | -0.890231 |
| H | -4.759549 | -3.182146 | -0.000011 |

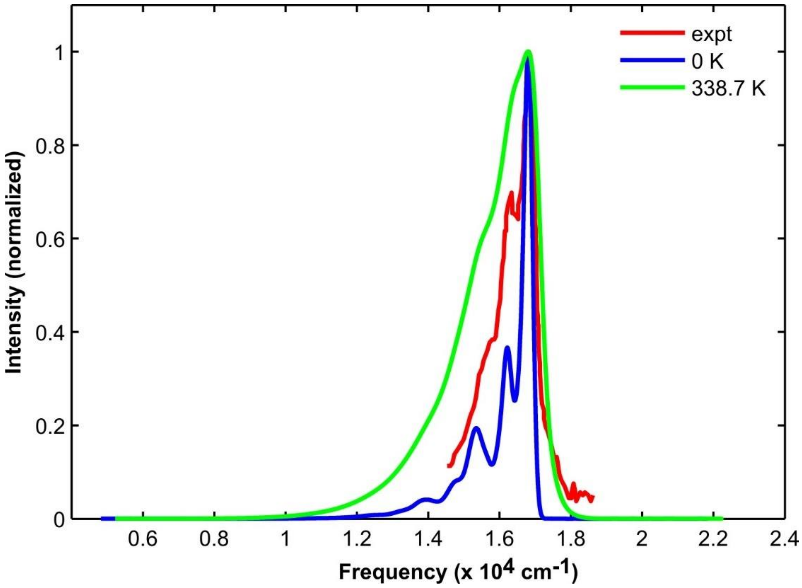
| | | | |
|---|---|---|---|
| H | -5.529487 | -1.859420 | 0.890220 |
| C | 4.923875 | -2.100909 | -0.000004 |
| H | 5.525880 | -1.859972 | -0.890232 |
| H | 5.525880 | -1.859977 | 0.890225 |
| H | 4.755877 | -3.182672 | -0.000007 |
| H | -2.378472 | -3.119467 | -0.000010 |

(b) $S_1$ optimized geometry using TD-TPSS/6-31G* (planar minimum). There were convergence issues in the solution of Kohn-Sham equations when trying to find the optimized geometry with the twisted configuration of the amino groups, so we are unable to report that data. The lack of convergence again, indicates the presence of multi-configuration character in the ground electronic state, the exploration of which is beyond the scope of the current analysis.

| | | | |
|---|---|---|---|
| C | -1.151965 | -1.420062 | 0.000079 |
| C | -1.155758 | -0.027601 | 0.000153 |
| C | -2.367592 | 0.739078 | 0.000161 |
| C | -3.624690 | 0.061116 | 0.000064 |
| C | 1.184859 | 0.009917 | 0.000170 |
| C | 1.157769 | -1.437630 | 0.000174 |
| C | 2.441259 | -2.072916 | 0.000091 |
| H | 2.446278 | -3.161067 | 0.000045 |
| C | 3.631665 | -1.366787 | 0.000077 |
| C | 3.598024 | 0.085308 | 0.000112 |
| C | 2.348188 | 0.756299 | 0.000148 |
| H | -2.294570 | 1.823012 | 0.000205 |
| H | 2.286881 | 1.840976 | 0.000144 |
| O | -0.016701 | 0.703426 | 0.000192 |
| N | 0.040930 | -2.173826 | 0.000088 |
| N | -4.783231 | 0.790594 | 0.000014 |
| H | -5.653516 | 0.264529 | -0.000085 |
| N | 4.768861 | 0.780348 | 0.000019 |
| H | 5.633523 | 0.247645 | -0.000040 |
| C | -3.643949 | -1.362987 | -0.000044 |
| C | -2.422376 | -2.048841 | -0.000031 |
| C | -4.902130 | 2.254143 | 0.000064 |
| H | -4.393885 | 2.659450 | -0.889072 |
| H | -4.394049 | 2.659379 | 0.889327 |
| C | -6.376810 | 2.663996 | -0.000056 |
| H | -6.891058 | 2.287472 | 0.893734 |
| H | -6.454689 | 3.756910 | -0.000019 |
| H | -6.890893 | 2.287544 | -0.893971 |
| C | 4.895145 | 2.243127 | -0.000026 |
| H | 4.385222 | 2.646208 | -0.888761 |
| H | 4.385406 | 2.646250 | 0.888797 |
| C | 6.370494 | 2.649516 | -0.000192 |
| H | 6.884465 | 2.271694 | -0.893841 |
| H | 6.452495 | 3.742177 | -0.000225 |
| H | 6.884654 | 2.271735 | 0.893367 |
| C | -4.963065 | -2.098543 | -0.000159 |
| H | -5.566420 | -1.852940 | -0.889639 |
| H | -4.805427 | -3.182024 | -0.000237 |
| H | -5.566498 | -1.853083 | 0.889308 |
| C | 4.957023 | -2.088797 | 0.000004 |
| H | 5.555525 | -1.834187 | -0.889223 |

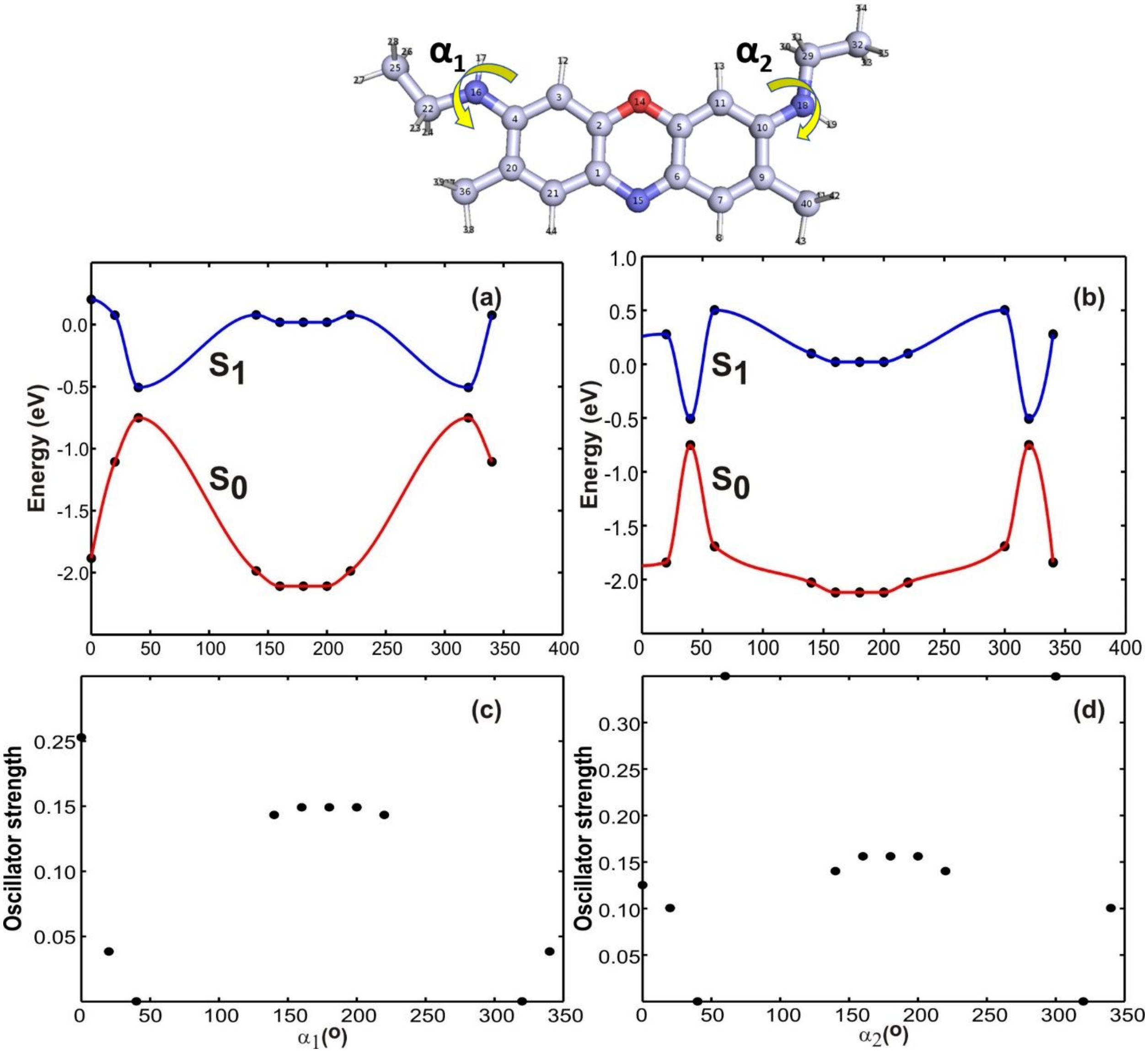
| | | | |
|---|---|---|---|
| H | 5.555595 | -1.834248 | 0.889203 |
| H | 4.808289 | -3.173162 | -0.000026 |
| H | -2.426780 | -3.138341 | -0.000097 |

(c) ***Figure S9***: *Oxazine 4 $S_1$ planar minimum → $S_0$ emission spectrum – comparison of theoretical spectra at 0K and 338.8K with experiment. Parameters used in the spectra calculation: Keyword section is same as CV, ReadFCHT section has TD=(time=1.d-9,2NStep=24, 2NstepWin=18). The theoretical spectra are aligned to experimental 0-0 band maximum.*



(d) Dihedral angle analyses:

***Figure S10****: Analysis of electronic energy and oscillator strength along the scan of dihedral angles involving torsional motion of NH-ethyl groups in oxazine 4. The barrier from a planar to a twisted configuration (0.08eV and 0.50 eV for $\alpha_1$ and $\alpha_2$ respectively) is more than the available thermal energy (0.029 eV corresponding to 338.7K) and hence, like CV and oxazine 170, oxazine 4 cannot easily twist upon electronic excitation. The angle $\alpha_1$( $\alpha_2$) corresponds to D (3,4,16,17) (D(11,10,18,19)).*



The twisting of the amino groups in oxazine 4 brings $S_1$ to a near-degeneracy with $S_0$ like oxazine 170. A natural transition orbital analysis revealed, similar to CV and oxazine 170, a change in character from π→π* to n→ π* (Figure S11).

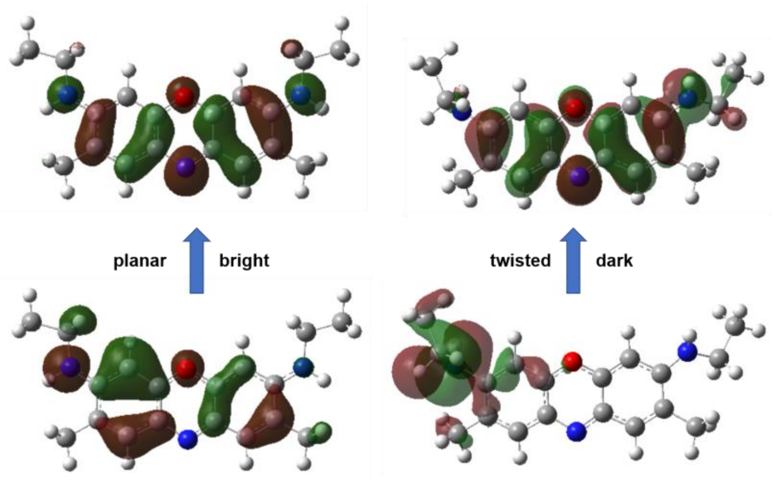


***Figure S11****: Natural transition orbital (NTO) analysis of oxazine 4 corresponding to $S_1$ planar minimum (left) and a low energy twisted configuration (right) from Figure S10. The bottom (top) orbital corresponds to a hole (particle) NTO.*

(e) $T_1$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | -1.153171 | -1.366972 | -0.000023 |
| C | -1.179919 | 0.066988 | -0.000051 |
| C | -2.359274 | 0.787684 | -0.000049 |
| C | -3.596362 | 0.089057 | -0.000015 |
| C | 1.176380 | 0.066693 | -0.000058 |
| C | 1.149600 | -1.366950 | -0.000034 |
| C | 2.405916 | -2.032988 | -0.000022 |
| H | 2.382087 | -3.120839 | -0.000013 |
| C | 3.617242 | -1.356501 | -0.000013 |
| C | 3.592882 | 0.088649 | -0.000023 |
| C | 2.355851 | 0.787356 | -0.000053 |
| H | -2.320741 | 1.873342 | -0.000070 |
| H | 2.316942 | 1.872991 | -0.000065 |
| O | -0.001682 | 0.786724 | -0.000078 |
| N | -0.001777 | -2.106505 | -0.000025 |
| N | -4.779291 | 0.773254 | -0.000004 |
| H | -5.634686 | 0.222061 | 0.000020 |
| N | 4.775872 | 0.772659 | -0.000004 |
| H | 5.631247 | 0.221381 | 0.000017 |
| C | -3.620913 | -1.356024 | 0.000009 |
| C | -2.409495 | -2.032687 | 0.000003 |
| C | -4.939534 | 2.234126 | -0.000006 |
| H | -4.434562 | 2.642263 | -0.888344 |
| H | -4.434512 | 2.642269 | 0.888300 |
| C | -6.422946 | 2.609073 | 0.000035 |
| H | -6.929589 | 2.222702 | 0.894031 |
| H | -6.524704 | 3.699977 | 0.000036 |
| H | -6.929640 | 2.222699 | -0.893931 |
| C | 4.936533 | 2.233560 | 0.000011 |
| H | 4.431699 | 2.641864 | -0.888313 |
| H | 4.431661 | 2.641848 | 0.888321 |
| C | 6.420059 | 2.608005 | 0.000047 |
| H | 6.926558 | 2.221445 | -0.893941 |
| H | 6.522210 | 3.698876 | 0.000062 |

| | | | |
|---|---|---|---|
| H | 6.926519 | 2.221424 | 0.894049 |
| C | -4.932985 | -2.105956 | 0.000034 |
| H | -5.537810 | -1.872308 | -0.890306 |
| H | -4.755307 | -3.186046 | 0.000040 |
| H | -5.537784 | -1.872295 | 0.890389 |
| C | 4.929491 | -2.106259 | 0.000001 |
| H | 5.534180 | -1.872449 | -0.890365 |
| H | 5.534159 | -1.872453 | 0.890384 |
| H | 4.752000 | -3.186386 | -0.000003 |
| H | -2.385906 | -3.120549 | 0.000018 |

(f) $T_2$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | -1.150584 | -1.446756 | 0.000044 |
| C | -1.172915 | -0.030336 | 0.000091 |
| C | -2.357216 | 0.732624 | 0.000097 |
| C | -3.613522 | 0.068577 | 0.000044 |
| C | 1.169736 | -0.030522 | 0.000084 |
| C | 1.147262 | -1.446831 | 0.000042 |
| C | 2.425256 | -2.068972 | 0.000000 |
| H | 2.439600 | -3.157634 | -0.000034 |
| C | 3.633257 | -1.364403 | -0.000009 |
| C | 3.610197 | 0.068310 | 0.000033 |
| C | 2.354122 | 0.732376 | 0.000087 |
| H | -2.281786 | 1.816742 | 0.000134 |
| H | 2.278582 | 1.816496 | 0.000124 |
| O | -0.001595 | 0.691596 | 0.000121 |
| N | -0.001821 | -2.188272 | 0.000027 |
| N | -4.776896 | 0.789796 | 0.000029 |
| H | -5.647557 | 0.266461 | 0.000001 |
| N | 4.773847 | 0.789197 | 0.000016 |
| H | 5.644403 | 0.265756 | -0.000017 |
| C | -3.636768 | -1.364037 | 0.000011 |
| C | -2.428891 | -2.068559 | 0.000015 |
| C | -4.888227 | 2.254490 | 0.000012 |
| H | -4.378136 | 2.655528 | -0.889422 |
| H | -4.378255 | 2.655544 | 0.889507 |
| C | -6.360764 | 2.671904 | -0.000092 |
| H | -6.877112 | 2.297625 | 0.893550 |
| H | -6.434292 | 3.765132 | -0.000105 |
| H | -6.876990 | 2.297610 | -0.893798 |
| C | 4.885056 | 2.253848 | 0.000020 |
| H | 4.374944 | 2.654911 | -0.889404 |
| H | 4.375046 | 2.654902 | 0.889507 |
| C | 6.357545 | 2.671492 | -0.000064 |
| H | 6.873839 | 2.297265 | -0.893765 |
| H | 6.430936 | 3.764724 | -0.000064 |
| H | 6.873945 | 2.297258 | 0.893573 |
| C | -4.959033 | -2.091996 | -0.000023 |
| H | -5.559074 | -1.838123 | -0.888988 |
| H | -4.809489 | -3.176311 | -0.000040 |
| H | -5.559100 | -1.838155 | 0.888934 |
| C | 4.955329 | -2.092623 | -0.000057 |
| H | 5.555480 | -1.838808 | -0.888989 |
| H | 5.555517 | -1.838853 | 0.888863 |

| | | | |
|---|---|---|---|
| H | 4.805662 | -3.176908 | -0.000081 |
| H | -2.443041 | -3.157256 | -0.000014 |

(g) $T_3$ optimized geometry using TD-TPSS/6-31G*

| | | | |
|---|---|---|---|
| C | -1.166369 | -1.387108 | 0.000077 |
| C | -1.182309 | 0.034689 | 0.000113 |
| C | -2.365829 | 0.764164 | 0.000113 |
| C | -3.600317 | 0.077726 | 0.000068 |
| C | 1.179013 | 0.034692 | 0.000109 |
| C | 1.162856 | -1.387333 | 0.000063 |
| C | 2.404937 | -2.051213 | -0.000002 |
| H | 2.395696 | -3.139431 | -0.000057 |
| C | 3.637894 | -1.352814 | -0.000003 |
| C | 3.597053 | 0.077299 | 0.000059 |
| C | 2.362563 | 0.763851 | 0.000114 |
| H | -2.317056 | 1.849145 | 0.000120 |
| H | 2.313931 | 1.848845 | 0.000140 |
| O | -0.001620 | 0.749505 | 0.000126 |
| N | -0.001758 | -2.141876 | 0.000043 |
| N | -4.796783 | 0.778739 | 0.000009 |
| H | -5.657023 | 0.237296 | -0.000034 |
| N | 4.793629 | 0.778241 | 0.000011 |
| H | 5.653834 | 0.236773 | -0.000045 |
| C | -3.641277 | -1.352579 | 0.000042 |
| C | -2.408650 | -2.050782 | 0.000046 |
| C | -4.925982 | 2.233325 | -0.000012 |
| H | -4.406961 | 2.635322 | -0.886122 |
| H | -4.407059 | 2.635342 | 0.886146 |
| C | -6.398112 | 2.649192 | -0.000102 |
| H | -6.914791 | 2.275597 | 0.893597 |
| H | -6.471298 | 3.742364 | -0.000121 |
| H | -6.914690 | 2.275573 | -0.893849 |
| C | 4.922790 | 2.232751 | 0.000032 |
| H | 4.403801 | 2.634877 | -0.886053 |
| H | 4.403926 | 2.634843 | 0.886205 |
| C | 6.394945 | 2.648633 | -0.000066 |
| H | 6.911507 | 2.275008 | -0.893827 |
| H | 6.468198 | 3.741797 | -0.000050 |
| H | 6.911634 | 2.274974 | 0.893609 |
| C | -4.947274 | -2.108804 | -0.000019 |
| H | -5.554638 | -1.876264 | -0.889341 |
| H | -4.768130 | -3.188816 | -0.000056 |
| H | -5.554678 | -1.876334 | 0.889294 |
| C | 4.943559 | -2.109524 | -0.000083 |
| H | 5.551120 | -1.877146 | -0.889339 |
| H | 5.551180 | -1.877231 | 0.889155 |
| H | 4.764059 | -3.189461 | -0.000127 |
| H | -2.399024 | -3.139041 | 0.000009 |

(h) ISC rates for $S_1$->$T_2$ and $S_1$-$T_3$ channels (Table S5)

Table S5: ISC rates in OXA170 for triplet channels

| State | ISC rate ($s^{-1}$) | |
|---|---|---|
| | H | D |
| $T_2$ | 1.7 x $10^5$ | 1.9 x $10^5$ |
| $T_3$ | 2.5 x $10^6$ | 2.5 x $10^6$ |

## 5. Darrow red data

(a) $S_0$ optimized geometry using B3LYP/6-31G* ($\alpha_1$=180.0°, $\alpha_2$=180.0°)

| | | | |
|---|---|---|---|
| C | 3.785894 | 0.516530 | -0.000649 |
| C | 2.912874 | -0.606546 | -0.002183 |
| C | 1.469387 | -0.408049 | 0.001219 |
| C | 0.981960 | 0.944802 | 0.006059 |
| C | 1.815291 | 2.041294 | 0.007617 |
| C | 3.212172 | 1.858939 | 0.004378 |
| C | -1.218321 | 0.109501 | 0.007903 |
| C | -0.688232 | -1.208285 | 0.003125 |
| C | -1.618787 | -2.279739 | 0.001888 |
| H | -1.232823 | -3.293494 | -0.001732 |
| C | -2.965139 | -2.027137 | 0.005194 |
| C | -3.479395 | -0.689674 | 0.009950 |
| C | -2.573216 | 0.387484 | 0.011298 |
| H | 1.385993 | 3.037709 | 0.011334 |
| H | -3.668563 | -2.854693 | 0.004188 |
| H | -2.887494 | 1.419722 | 0.014888 |
| C | 5.178112 | 0.292145 | -0.004064 |
| C | 5.690988 | -0.995157 | -0.008810 |
| H | 6.765629 | -1.146666 | -0.011383 |
| C | 4.823437 | -2.097792 | -0.010279 |
| H | 5.227587 | -3.105301 | -0.013996 |
| C | 3.450812 | -1.904766 | -0.007004 |
| H | 5.880185 | 1.120135 | -0.003075 |
| H | 2.769083 | -2.747431 | -0.008101 |
| O | -0.351129 | 1.163735 | 0.009265 |
| N | 0.643168 | -1.440034 | -0.000125 |
| N | 4.003356 | 2.943021 | 0.005980 |
| H | 5.009782 | 2.881183 | 0.003875 |
| H | 3.607257 | 3.872844 | 0.009443 |
| N | -4.850148 | -0.571569 | 0.012890 |
| H | -5.360674 | -1.450364 | 0.011679 |
| C | -5.787605 | 0.494219 | 0.017229 |
| O | -6.958656 | 0.180326 | 0.018792 |
| C | -5.315497 | 1.927066 | 0.019625 |
| H | -4.717439 | 2.150502 | 0.909828 |
| H | -4.720068 | 2.154378 | -0.871354 |
| H | -6.203345 | 2.559968 | 0.022347 |

(b) $S_1$ optimized geometry using TD-B3LYP/6-31G* (planar minimum)

| | | | |
|---|---|---|---|
| C | 3.778451 | 0.536243 | -0.000853 |
| C | 2.902631 | -0.587978 | 0.001994 |
| C | 1.467309 | -0.414148 | -0.002636 |
| C | 0.981808 | 0.937447 | -0.010299 |
| C | 1.816207 | 2.039725 | -0.013080 |
| C | 3.211713 | 1.880077 | -0.008822 |
| C | -1.202144 | 0.091414 | -0.009968 |
| C | -0.681203 | -1.221210 | -0.003525 |
| C | -1.620230 | -2.284894 | -0.002129 |

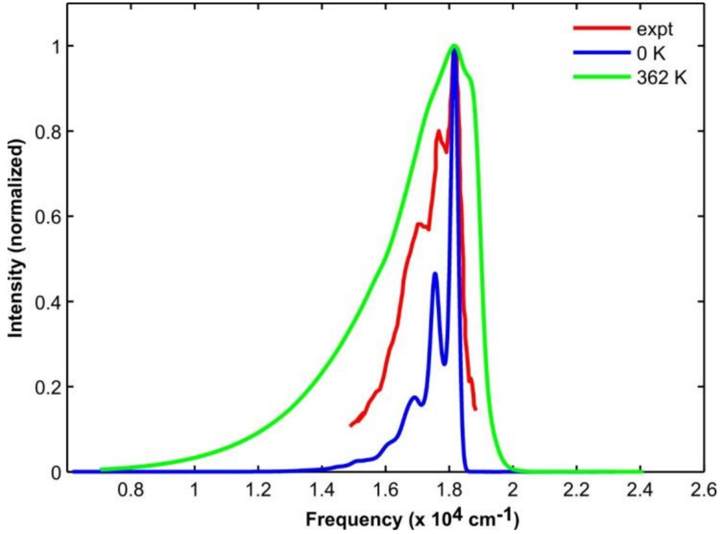
| | | | |
|---|---|---|---|
| H | -1.232615 | -3.298426 | 0.002583 |
| C | -2.975327 | -2.044423 | -0.005662 |
| C | -3.481407 | -0.713624 | -0.010182 |
| C | -2.564181 | 0.365440 | -0.014317 |
| H | 1.374440 | 3.031318 | -0.018919 |
| H | -3.673649 | -2.876136 | -0.002971 |
| H | -2.876148 | 1.398610 | -0.025074 |
| C | 5.164564 | 0.293189 | 0.004298 |
| C | 5.678200 | -1.007147 | 0.011867 |
| H | 6.753601 | -1.154477 | 0.015658 |
| C | 4.814970 | -2.106364 | 0.014526 |
| H | 5.212957 | -3.115960 | 0.020360 |
| C | 3.440705 | -1.898508 | 0.009604 |
| H | 5.874480 | 1.114503 | 0.002650 |
| H | 2.746000 | -2.730600 | 0.011391 |
| O | -0.364153 | 1.174111 | -0.014622 |
| N | 0.669124 | -1.487255 | 0.000499 |
| N | 4.005814 | 2.974839 | -0.012177 |
| H | 5.011691 | 2.921059 | -0.010586 |
| H | 3.603588 | 3.901198 | -0.018082 |
| N | -4.853380 | -0.569935 | -0.016222 |
| H | -5.376626 | -1.442708 | -0.039063 |
| C | -5.776447 | 0.507192 | 0.013882 |
| O | -6.951510 | 0.199095 | -0.005906 |
| C | -5.293866 | 1.934036 | 0.070886 |
| H | -4.674494 | 2.114805 | 0.956036 |
| H | -4.717413 | 2.196506 | -0.823175 |
| H | -6.177023 | 2.571793 | 0.119275 |

(c) $S_1$ optimized geometry using TD-B3LYP/6-31G* (twisted minimum)

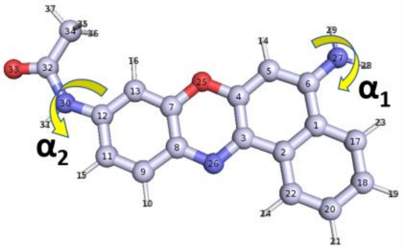
| | | | |
|---|---|---|---|
| C | 3.619860 | -0.384158 | -1.646705 |
| C | 2.836995 | -1.052362 | -0.660605 |
| C | 1.385755 | -0.924874 | -0.647356 |
| C | 0.805752 | -0.107145 | -1.672832 |
| C | 1.550894 | 0.539879 | -2.635816 |
| C | 2.950516 | 0.414751 | -2.657366 |
| C | -1.311209 | -0.561992 | -0.763050 |
| C | -0.703574 | -1.349326 | 0.230050 |
| C | -1.535353 | -1.949549 | 1.189006 |
| H | -1.068461 | -2.556067 | 1.957381 |
| C | -2.917177 | -1.767336 | 1.159446 |
| C | -3.466916 | -0.933400 | 0.190304 |
| C | -2.689818 | -0.348247 | -0.802310 |
| H | 1.038987 | 1.134187 | -3.386023 |
| H | -3.551647 | -2.261294 | 1.888036 |
| H | -3.116941 | 0.270831 | -1.583826 |
| C | 5.024202 | -0.524355 | -1.600702 |
| C | 5.633100 | -1.302160 | -0.630417 |
| H | 6.714655 | -1.393870 | -0.614847 |
| C | 4.855155 | -1.966430 | 0.331838 |
| H | 5.335196 | -2.576839 | 1.090425 |
| C | 3.476570 | -1.838630 | 0.316153 |
| H | 5.657614 | -0.012614 | -2.318868 |

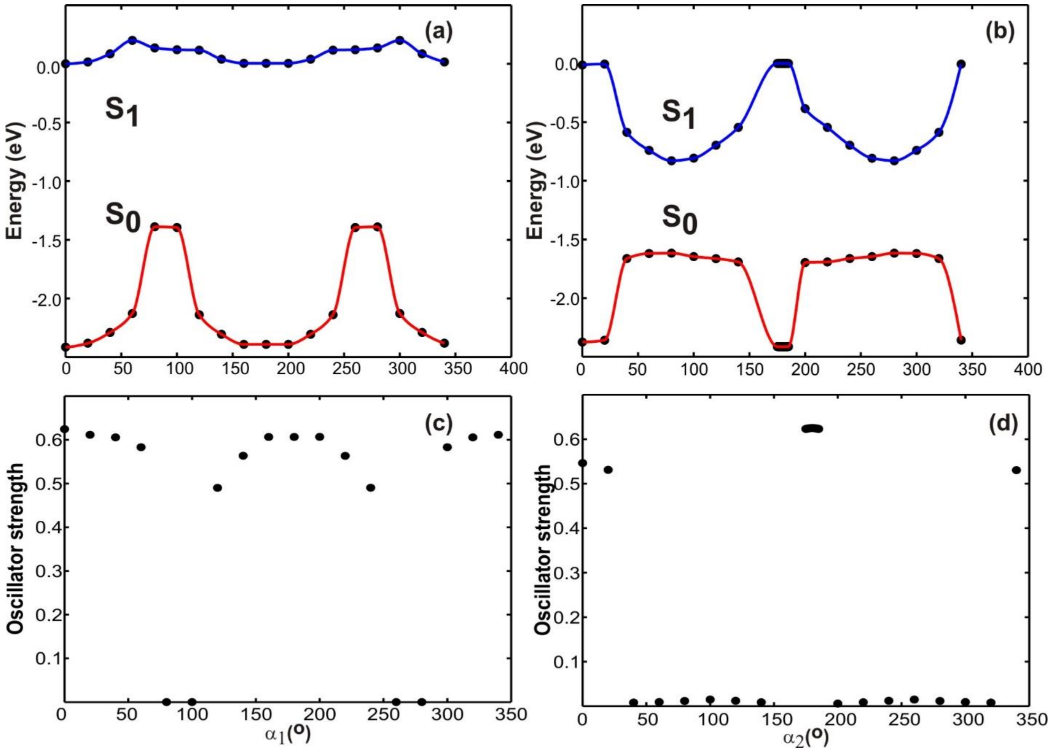
| | | | |
|---|---|---|---|
| H | 2.858889 | -2.337929 | 1.053649 |
| O | -0.554613 | 0.048782 | -1.728229 |
| N | 0.669677 | -1.537933 | 0.286268 |
| N | 3.656323 | 1.057817 | -3.619455 |
| H | 3.175527 | 1.551125 | -4.357140 |
| H | 4.639107 | 0.888461 | -3.761345 |
| N | -4.923661 | -0.802089 | 0.097198 |
| H | -5.429083 | -1.487745 | -0.469027 |
| C | -5.658803 | 0.062818 | 0.725065 |
| O | -6.930403 | 0.024559 | 0.614552 |
| C | -5.137426 | 1.166521 | 1.625140 |
| H | -4.755214 | 0.723339 | 2.546894 |
| H | -4.335140 | 1.704692 | 1.122029 |
| H | -5.953771 | 1.848614 | 1.864087 |

*(d)* ***Figure S12****: Darrow red $S_1$ planar minimum → $S_0$ emission spectrum – comparison of theoretical spectra at 0K and 362.0 K with experiment. Parameters used in the spectra calculation: Keyword section is same as CV, ReadFCHT section has TD=(time=1.d-9,2NStep=24, 2NstepWin=18). The theoretical spectra are aligned to experimental 0-0 band maximum.*



(e) ***Figure S13****: Analysis of electronic energy and oscillator strength along the scan of dihedral angles involving torsional motion of NH-ethyl and $NH_2$ groups in darrow red. The results are similar to CV and oxazine 170, in the sense that the molecule cannot easily twist from a planar to a twisted configuration along α due to a larger barrier (0.20eV) due to insufficient energy (0.03eV). The twisting along $\alpha_2$ is possible however, since there is no barrier. Despite this, the radiative pathway dominates, indicating that simultaneous twisting of the groups is required to compete with fluorescence. The angle α1 (α2) corresponds to D(5,6,27,28) ( D(13,12,30,31)).*





Additionally, a natural transition orbital analysis (Figure S14) shows a change in character (and oscillator strength) from being radiative to non-radiative. Because of this, non-radiative pathways are likely important for the $S_1$ decay in Darrow red, similar to CV and oxazine 170.

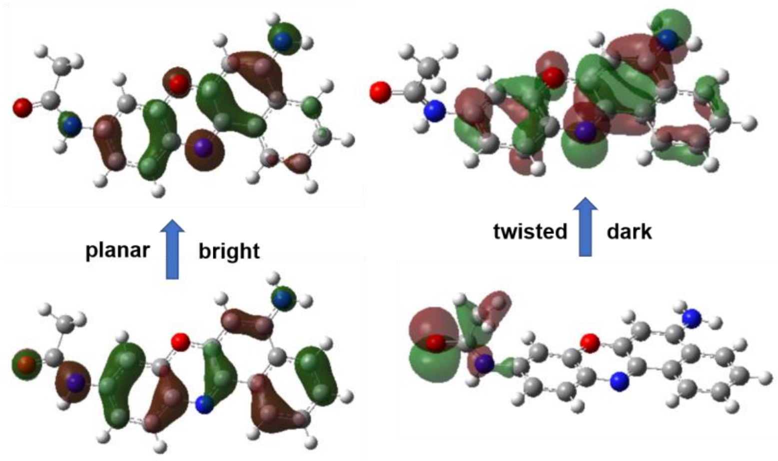


***Figure S14***: *Natural transition orbitals for two $S_1$ minima of darrow red: (left) planar bright, $\pi \rightarrow \pi^*$ excitation; (right) twisted dark, $n \rightarrow \pi^*$ excitation. The bottom (top) orbital corresponds to a hole (particle) NTO.*

(f) T1 optimized geometry using TD-B3LYP/6-31G*

| | | | |
|---|---|---|---|
| C | 3.719969 | -0.582504 | -1.804547 |
| C | 2.901527 | -0.908913 | -0.676851 |
| C | 1.488795 | -0.657160 | -0.693253 |
| C | 0.934281 | -0.074553 | -1.864250 |

| | | | |
|---|---|---|---|
| C | 1.697569 | 0.251179 | -2.967183 |
| C | 3.089266 | 0.011207 | -2.970670 |
| C | -1.183701 | -0.127727 | -0.853495 |
| C | -0.579408 | -0.715239 | 0.308691 |
| C | -1.456510 | -1.013997 | 1.392796 |
| H | -1.013757 | -1.458607 | 2.277493 |
| C | -2.805537 | -0.756377 | 1.334813 |
| C | -3.378672 | -0.172358 | 0.168724 |
| C | -2.525329 | 0.136039 | -0.929312 |
| H | 1.211511 | 0.694188 | -3.830912 |
| H | -3.420347 | -1.004538 | 2.186507 |
| H | -2.927246 | 0.581806 | -1.834169 |
| C | 5.096799 | -0.851677 | -1.731514 |
| C | 5.659156 | -1.422659 | -0.591569 |
| H | 6.726349 | -1.619023 | -0.564502 |
| C | 4.856377 | -1.741481 | 0.511451 |
| H | 5.299966 | -2.185992 | 1.396555 |
| C | 3.493747 | -1.487835 | 0.469805 |
| H | 5.757292 | -0.621289 | -2.562181 |
| H | 2.850366 | -1.724616 | 1.308673 |
| O | -0.405836 | 0.189850 | -1.941498 |
| N | 0.735221 | -0.984085 | 0.407939 |
| N | 3.801401 | 0.343312 | -4.067972 |
| H | 3.349810 | 0.756021 | -4.872801 |
| H | 4.797609 | 0.198163 | -4.134225 |
| N | -4.711647 | 0.126736 | 0.003597 |
| H | -4.956554 | 0.539098 | -0.893349 |
| C | -5.897945 | 0.014261 | 0.779024 |
| O | -6.915135 | 0.409191 | 0.247730 |
| C | -5.856837 | -0.563792 | 2.169987 |
| H | -5.500016 | -1.599291 | 2.163009 |
| H | -5.211692 | 0.025687 | 2.830180 |
| H | -6.875276 | -0.542998 | 2.558882 |

(g) T2 optimized geometry using TD-B3LYP/6-31G*

| | | | |
|---|---|---|---|
| C | 3.765533 | 0.547622 | -0.019900 |
| C | 2.890454 | -0.599147 | 0.037698 |
| C | 1.454367 | -0.449282 | -0.044701 |
| C | 0.979408 | 0.872829 | -0.181534 |
| C | 1.808881 | 2.006865 | -0.250092 |
| C | 3.204355 | 1.868736 | -0.178791 |
| C | -1.207983 | 0.051222 | -0.200303 |
| C | -0.692510 | -1.256330 | -0.071030 |
| C | -1.657348 | -2.284752 | -0.033838 |
| H | -1.305441 | -3.306538 | 0.063566 |
| C | -3.028166 | -2.015517 | -0.101705 |
| C | -3.522671 | -0.703231 | -0.215015 |
| C | -2.576757 | 0.348299 | -0.289703 |
| H | 1.347565 | 2.983124 | -0.362484 |
| H | -3.730281 | -2.843086 | -0.058704 |
| H | -2.868718 | 1.378271 | -0.444578 |
| C | 5.161414 | 0.333660 | 0.083657 |
| C | 5.677432 | -0.937440 | 0.225721 |
| H | 6.750657 | -1.078841 | 0.305097 |

| | | | |
|---|---|---|---|
| C | 4.812938 | -2.060718 | 0.271574 |
| H | 5.231395 | -3.056213 | 0.381895 |
| C | 3.448636 | -1.889760 | 0.181254 |
| H | 5.852597 | 1.169869 | 0.064120 |
| H | 2.770516 | -2.734053 | 0.219568 |
| O | -0.360879 | 1.117694 | -0.263460 |
| N | 0.643624 | -1.519111 | 0.009880 |
| N | 3.981564 | 2.980304 | -0.243336 |
| H | 4.985797 | 2.929496 | -0.307423 |
| H | 3.568311 | 3.885923 | -0.411545 |
| N | -4.891944 | -0.498980 | -0.328103 |
| H | -5.439584 | -1.313805 | -0.590345 |
| C | -5.752290 | 0.567284 | 0.007769 |
| O | -6.940291 | 0.405493 | -0.182660 |
| C | -5.178262 | 1.835588 | 0.597658 |
| H | -4.389524 | 1.642321 | 1.331376 |
| H | -4.776844 | 2.482512 | -0.191727 |
| H | -5.999517 | 2.368503 | 1.078684 |

(h) T3 optimized geometry using TD-B3LYP/6-31G*

| | | | |
|---|---|---|---|
| C | 3.716652 | -0.542344 | -1.776011 |
| C | 2.909739 | -0.956444 | -0.655719 |
| C | 1.476775 | -0.748866 | -0.646594 |
| C | 0.938212 | -0.123794 | -1.791158 |
| C | 1.699005 | 0.284682 | -2.900471 |
| C | 3.089763 | 0.082695 | -2.916892 |
| C | -1.184403 | -0.260582 | -0.830277 |
| C | -0.608912 | -0.886169 | 0.297622 |
| C | -1.517229 | -1.248944 | 1.311485 |
| H | -1.119148 | -1.750886 | 2.187368 |
| C | -2.894995 | -1.006594 | 1.214807 |
| C | -3.445432 | -0.361308 | 0.094591 |
| C | -2.556283 | 0.006631 | -0.948411 |
| H | 1.190933 | 0.754096 | -3.737161 |
| H | -3.531174 | -1.347490 | 2.019117 |
| H | -2.915132 | 0.503864 | -1.844805 |
| C | 5.114561 | -0.765513 | -1.717655 |
| C | 5.693336 | -1.368826 | -0.621164 |
| H | 6.766509 | -1.529342 | -0.596483 |
| C | 4.893554 | -1.778221 | 0.473977 |
| H | 5.359368 | -2.252968 | 1.331893 |
| C | 3.530099 | -1.572862 | 0.453059 |
| H | 5.758901 | -0.458762 | -2.535188 |
| H | 2.901907 | -1.876085 | 1.282319 |
| O | -0.404394 | 0.121062 | -1.876749 |
| N | 0.728751 | -1.135361 | 0.399587 |
| N | 3.799021 | 0.489091 | -3.999976 |
| H | 3.334627 | 0.895618 | -4.798786 |
| H | 4.786783 | 0.314815 | -4.094528 |
| N | -4.788278 | -0.070186 | -0.102704 |
| H | -5.058615 | 0.169642 | -1.052057 |
| C | -5.913941 | 0.043546 | 0.744553 |
| O | -6.973086 | 0.307579 | 0.212742 |
| C | -5.754660 | -0.133881 | 2.235220 |

| | | | |
|---|---|---|---|
| H | -5.672343 | -1.196208 | 2.493540 |
| H | -4.878194 | 0.390749 | 2.627573 |
| H | -6.656416 | 0.259695 | 2.705836 |

(i) ISC rates for $S_1$->$T_2$ and $S_1$->$T_3$ channels (Table S6)

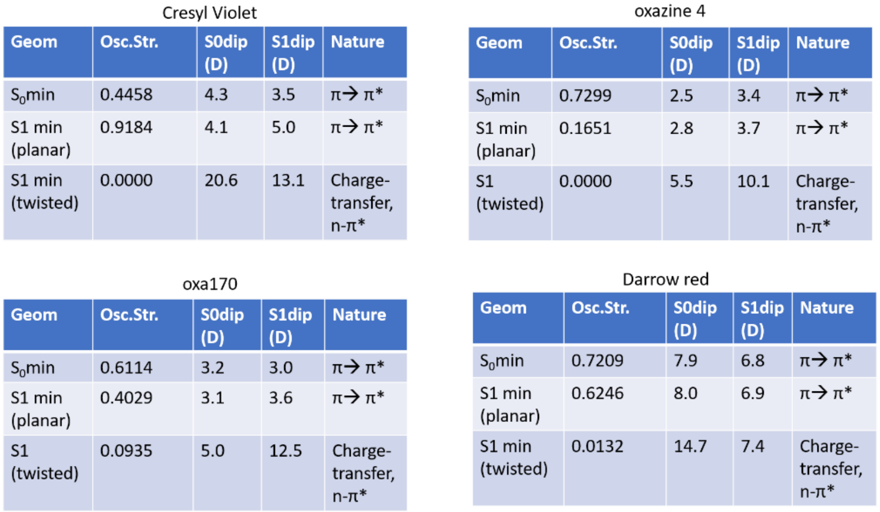
Table S6: ISC rates in DR for triplet channels

| State | ISC rate ($s^{-1}$) | |
|---|---|---|
| | H | D |
| $T_2$ | 5.1 x $10^5$ | 4.9 x $10^5$ |
| $T_3$ | 3.6 x $10^4$ | 3.6 x $10^4$ |

## 6. Analysis of permanent dipole moments of $S_0$ and $S_1$ states:

All dyes show change in character with large changes in permanent dipole moments (Table S7). The natural transition orbitals at twisted configurations were seen to be of n→π* type, and also denote intramolecular charge-transfer type of transition.

*Table S7: Comparison of permanent dipoles of ground and excited states*



Cresyl Violet

| Geom | Osc.Str. | S0dip (D) | S1dip (D) | Nature |
|---|---|---|---|---|
| $S_0$min | 0.4458 | 4.3 | 3.5 | π→ π* |
| S1 min (planar) | 0.9184 | 4.1 | 5.0 | π→ π* |
| S1 min (twisted) | 0.0000 | 20.6 | 13.1 | Charge-transfer, n-π* |

oxazine 4

| Geom | Osc.Str. | S0dip (D) | S1dip (D) | Nature |
|---|---|---|---|---|
| $S_0$min | 0.7299 | 2.5 | 3.4 | π→ π* |
| S1 min (planar) | 0.1651 | 2.8 | 3.7 | π→ π* |
| S1 (twisted) | 0.0000 | 5.5 | 10.1 | Charge-transfer, n-π* |

oxa170

| Geom | Osc.Str. | S0dip (D) | S1dip (D) | Nature |
|---|---|---|---|---|
| $S_0$min | 0.6114 | 3.2 | 3.0 | π→ π* |
| S1 min (planar) | 0.4029 | 3.1 | 3.6 | π→ π* |
| S1 (twisted) | 0.0935 | 5.0 | 12.5 | Charge-transfer, n-π* |

Darrow red

| Geom | Osc.Str. | S0dip (D) | S1dip (D) | Nature |
|---|---|---|---|---|
| $S_0$min | 0.7209 | 7.9 | 6.8 | π→ π* |
| S1 min (planar) | 0.6246 | 8.0 | 6.9 | π→ π* |
| S1 min (twisted) | 0.0132 | 14.7 | 7.4 | Charge-transfer, n-π* |

## 7. Calculations of non-radiative intersystem crossing and internal conversion rates

The non-radiative intersystem crossing (ISC) rates are calculated using pure spin Born-Oppenheimer (BO) states $S_1$ and $T_n$ from the Gaussian program. They can be treated as diabatic states because to within first order, they are only coupled through the spin-orbit coupling (SOC) potential operator[2]. We will also make the Condon approximation that the SOC is independent of nuclear motion and assume that the initial and final state vibrational populations are at equilibrium. Within this framework, the $S_1$ population decay can derived as[3,4]

$$P_1(t) = \exp[-2Re\{V_{SOC}^2 \int_0^t dt'(t-t')\chi(t-t')\}]$$

where the time correlation function $\chi(t-t')$ contains vibrational overlaps between the two electronic states and $V_{SOC}$ is the spin orbit coupling evaluated at the donor ($S_1$) minimum. The exponent is recast in the form of a product $g(t)=k_{ISC}\,t$, and a linear fit to the equation $P_1(t) \approx 1 - k_{ISC}t$ gives the slope as the estimate of the ISC rate constant.

For obtaining rates of internal conversion (IC) between $S_1$ and $S_0$, the same expression for the population dynamics as in the ISC case was employed with substitution of $|V_{SOC}|^2$ to the absolute square of the nonadiabatic vector $|V_{NAC}|^2$

$= \sum_i |\langle S_1|\nabla_i|S_0\rangle|^2/M_i^2$, where $|S_1\rangle, |S_0\rangle$ are BO states, $\nabla_i = \partial/\partial Q_i$ is the derivative with respect to normal mode coordinate $Q_i$ and $M_i$ is the effective mass of normal mode $Q_i$. This substitution introduces another approximation for the matrix elements of nuclear states

$$\langle \chi_n|\nabla_i|\chi'_m\rangle \approx \langle \chi_n|\chi'_m\rangle,$$

where $\chi_n, \chi'_m$ are vibrational wavefunctions of harmonic approximations of $S_1$ and $S_0$ surfaces respectively. The approximation involving the nuclear derivative of the vibrational functions can be justified by large density of states of $S_0$ vibrational states at the height of the $S_1$ minimum, which makes individual differences between nuclear integrals less significant.

***Table S8:*** *Properties for the $S_1$ bright minimum: 1) absolute magnitude of the nonadiabatic coupling with the $S_0$ state* (cm$^{-1}$)*, 2) adiabatic electronic gaps (eV) and spin orbit couplings* (cm$^{-1}$ *) for the $T_{1\text{-}3}$ states.*

| Dye | $\lvert V_{NAC}\rvert$ | | $T_1$ | | $T_2$ | | $T_3$ | |
|---|---|---|---|---|---|---|---|---|
| | H | D | Gap | $\lvert V_{SOC}\rvert$ | Gap | $\lvert V_{SOC}\rvert$ | Gap | $\lvert V_{SOC}\rvert$ |
| CV | 9.5751 | 8.6084 | 0.98 | 0.0431 | 0.25 | 0.1677 | -0.09 | 0.0592 |
| DR | 11.8004 | 11.2984 | 1.14 | 0.0538 | 0.29 | 0.2807 | 0.92 | 0.1580 |
| OX4 | 8.7114 | 8.2402 | 1.09 | 0.0713 | 0.45 | 0.0774 | 0.11 | 0.0971 |
| OX170 | 10.5530 | 10.0470 | 1.00 | 0.0134 | 0.23 | 0.1518 | -0.08 | 0.1412 |

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