SUPPLEMENTAL INFORMATION

Vibrationally Assisted Direct Intersystem Crossing Between the Same Charge Transfer States for Thermally Activated Delayed Fluorescence: Analysis by Marcus-Hush Theory Including Reorganization Energy

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Determination of photophysical parameters

Intensity weighted mean lifetime values were used for polyexponential decays of prompt (PF) or delayed (DF) fluorescence. The ratio of DF and PF quantum yields ($\phi_{DF}/\phi_{PF}$) was determined as following:

$$\frac{\phi_{DF}}{\phi_{PF}} = \frac{A_{DF} \tau_{DF}}{A_{PF} \tau_{PF}}, \quad (S1)$$

where $A_{DF}$ and $A_{PF}$ are pre-exponential factors of prompt and delayed fluorescence lifetimes, respectively; $\tau_{PF}$ and $\tau_{DF}$ are lifetimes of prompt and delayed fluorescence, respectively. Rate constants of radiative ($k_r$) and nonradiative ($k_{nr}$) decay, and intersystem crossing ($k_{ISC}$) were given by equations:

$$k_r = \frac{\phi_{PF}}{\tau_{PF}}, \quad (S2)$$

$$k_{ISC} = \frac{\phi_{DF}}{\tau_{PF} \phi}, \quad (S3)$$

$$k_{nr} = \frac{1}{\tau_{PF}} - (k_r + k_{ISC}), \quad (S4)$$

where $\phi$ is PLQY ($\phi_{DF} + \phi_{PF}$).

Further, the quantum yields of ISC and rISC were calculated as

$$\phi_{ISC} = k_{ISC} \tau_{PF}, \quad (S5)$$

$$\phi_{rISC} = \frac{1 - \phi_{PF}}{\phi_{ISC}}. \quad (S6)$$

And finally, rate constant of rISC ($k_{rISC}$) was calculated as

$$k_{rISC} = \frac{\phi_{rISC}}{\tau_{DF}} (\phi / \phi_{PF}). \quad (S7)$$

Photophysical parameters are summarized below in Table S1.
Table S1. Photoluminescent and photophysical parameters in various media*

| Solvent                    | PL<sub>max</sub> [nm] | PLQY [%] | \(E_{1\text{CT}}\) (PL onset) [nm] | \(E_{3\text{CT}}\) [eV] | \(\Delta E_{1\text{CT}-3\text{LE}}\) [eV] | \(\Delta E_{1\text{CT}-3\text{CT}}\) [eV] | \(\phi_{\text{DF}}/\phi_{\text{PF}}\) | \(\tau_{\text{PF}}\) [ns] | \(\tau_{\text{DF}}\) [μs] | \(k_r\) | \(k_{nr}\) | \(k_{\text{ISC}}\) | \(k_{\text{ISC}}\) [10<sup>7</sup> s<sup>-1</sup>] |
|----------------------------|------------------------|----------|-----------------------------------|----------------|-----------------------------------|-----------------------------------|---------------------------------|----------------|----------------|--------|--------|--------|----------------|
| Hexane                     | 459                    | 71       | 426                               | 2.91           | 2.89                              | 0.094                             | 0.024<sup>a</sup>                | 1.1            | 15.4           | 32.0              | 2.2              | 0.9            | 3.4            | 0.007            |
| Benzene-hexane (1/2)       | 480                    | 60       | 436                               | 2.84           | 2.83                              | 0.026                             | 0.019<sup>a</sup>                | 0.5            | 21.3           | 8.4               | 1.9              | 1.3            | 1.5            | 0.017            |
| Benzene-hexane (1/1)       | 488                    | 68       | 443                               | 2.80           | 2.78                              | -0.022                            | 0.016<sup>a</sup>                | 0.8            | 23.1           | 5.8               | 1.7              | 0.8            | 1.9            | 0.030            |
| 5% Acetone in hexane       | 522                    | 100      | 451                               | 2.75           | 2.73                              | -0.069                            | 0.014<sup>a</sup>                | 1.2            | 31.9           | 6.1               | 1.4              | 0.0            | 1.7            | 0.036            |
| Benzene                    | 507                    | 100      | 455                               | 2.72           | 2.71                              | -0.095                            | 0.013<sup>a</sup>                | 1.5            | 25.1           | 4.5               | 1.6              | 0.0            | 2.4            | 0.055            |
| 10% Acetone in hexane      | 543                    | 73       | 465                               | 2.67           | 2.66                              | -0.15                             | 0.0115<sup>b</sup>              | 1.5            | 24.8           | 2.1               | 1.2              | 0.4            | 2.4            | 0.12             |
| 15% Acetone in hexane      | 561                    | 63       | 474                               | 2.62           | 2.61                              | -0.20                             | 0.0084<sup>b</sup>              | 1.3            | 22.7           | 1.4               | 1.2              | 0.7            | 2.5            | 0.16             |
| Chlorobenzene              | 550                    | 78       | 482                               | 2.57           | 2.56                              | -0.25                             | 0.0088<sup>b</sup>              | 1.6            | 28.3           | 1.7               | 1.0              | 0.3            | 2.2            | 0.16             |
| 25% Acetone in hexane      | 578                    | 52       | 495                               | 2.51           | 2.50                              | -0.31                             | 0.0066<sup>b</sup>              | 1.1            | 26.7           | 1.0               | 0.91             | 0.8            | 2.0            | 0.21             |
| o-Dichlorobenzene          | 573                    | 52       | 495                               | 2.51           | 2.50                              | -0.31                             | 0.0066<sup>c</sup>              | 1.1            | 26.7           | 1.0               | 0.91             | 0.8            | 2.0            | 0.21             |
| 75% Acetone in hexane      | 619                    | 9.8      | 517                               | 2.40           | 2.39                              | -0.42                             | 0.0045<sup>b</sup>              | 0.3            | 8.7            | 0.4               | 0.85             | 7.8            | 2.8            | 0.35             |
| Acetone                    | 638                    | 5.2      | 526                               | 2.36           | 2.35                              | -0.46                             | 0.0042<sup>b</sup>              | 0.2            | 5.8            | 0.3               | 0.74             | 13.4           | 3.1            | 0.38             |

*PL<sub>max</sub> and PLQY – photoluminescence maximum and quantum yield, respectively; 
\(E_{1\text{CT}}\) – energy of the \(^1\text{CT}\) state obtained as onset of photoluminescence spectra; 
\(E_{3\text{CT}}\) – energy of the \(^3\text{CT}\) state calculated using \(E_{1\text{CT}}\) and \(\Delta E_{1\text{CT}-3\text{CT}}\); 
\(\Delta E_{1\text{CT}-3\text{LE}}\) – energy gap between \(^1\text{CT}\) and \(^3\text{LE}\) states obtained from the onsets of respective emissions; negative values indicate that \(E_{1\text{CT}} < E_{3\text{LE}}\). 
\(\Delta E_{1\text{CT}-3\text{CT}}\) – energy gap between \(^1\text{CT}\) and \(^3\text{CT}\) states obtained from Marcus-Hush equation and experimental \(k_{\text{ISC}}\) values corresponding to the dihedral angle of 90° (see text). 
\(\phi_{\text{DF}}/\phi_{\text{PF}}\) – ratio of quantum yields of delayed (DF) and prompt (PF) fluorescence; 
\(\tau_{\text{PF}}, \tau_{\text{DF}}\) – lifetimes of PF and DF, respectively; 
\(k_{\text{ISC}}, k_{\text{ISC}}, k_r, k_{nr}\) – rates of intersystem crossing, reverse intersystem crossing, radiative and nonradiative deactivation, respectively. 
<sup>a</sup> Values obtained by extrapolation of the \(\Delta E_{1\text{CT}-3\text{CT}} = E_{1\text{CT}}\) dependence. 
<sup>b</sup> Values obtained using Marcus-Hush equation and experimental \(k_{\text{ISC}}\) values. 
<sup>c</sup> Value predicted by TD-DFT calculations.
Analysis of molecular orbitals and nature of electronically excited states

The nature of states was assigned based on the orbitals involved in respective transitions available from single-point calculations using optimal geometry in corresponding state. Thus, based on the optimized geometry of T₁-state, calculated highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) involved in the T₁-S₀ transition are localized on separate fragments: 9,9-dimethyl-9,10-dihydroacridine (DMAC) and phenyl-s-triazine, respectively (Scheme S1). The T₁ state was thus assigned as a ³CT state. The same conclusion was made for the S₁ state (¹CT).

Molecular orbitals, both HOMO and LUMO, involved in the T₂-S₀ transition calculated using the optimized geometry of T₂-state, are localized on the phenyl-s-triazine fragment (Scheme S1). Therefore, the T₂ state was assigned as a ³LE state. Molecular orbitals involved in the T₃-S₀ transition calculated using the optimized geometry of T₃-state, are localized on the N-phenyl-DMAC fragment. The T₃ state was thus assigned as a second ³LE state.

| Opt. geometry | Assigned | Orbitals involved |
|---------------|----------|-------------------|
| S₁ and T₁*    | CT       | ![HOMO](image1) ![LUMO](image2) |
| T₂            | ³LE      | ![HOMO](image3) ![LUMO](image4) |
| T₃            | ³LE      | ![HOMO](image5) ![LUMO](image6) |

*geometries of the ¹CT and ³CT states are almost identical so only the ¹CT one is shown.

**Scheme S1.** Molecular orbitals involved in the electronic transitions of DMAC-TRZ

Experimentally, the CT nature of S₁ state was confirmed by the strong positive solvatofluorochromism (Figure 1, the main text). As was reported previously,¹ at 78 K, the phosphorescence spectra of DMAC-TRZ and its derivatives are independent of solvent polarity in the range of low polarities. Such phosphorescence thus originates from the triplet state of LE nature. In DMAC-TRZ, its maximum near 484 nm correlates well with the TDDFT calculated T₂-S₀ transition energy involving orbitals localized on the phenyl-s-
etriazine fragment. Such $^{3}$LE-state energy determined experimentally as onset of phosphorescence spectrum in methylcyclohexane equals 2.82 eV (440 nm). The $\Delta E_{1CT-3LE}$ values in various solvents were thus estimated using the $E_{1CT}$ values form the solvatofluorochromic measurements and the $E_{3LE}$ value mentioned above. The emission from $^{3}$CT-state was not registered experimentally in these investigations.
Table S2. Computational data for various rotational isomers is the $^3$CT-state geometry and rates of the $^3$CT→$^1$CT transition*

| Dihedral Angle [°] | $V_{3CT-1CT}$ [cm$^{-1}$] | $\Delta E_{1CT-3CT}$ [eV] | $\lambda_{1CT-3CT}$ [eV] | $k_{3CT\rightarrow1CT}$ [10$^7$ s$^{-1}$] | $\mu$ [%] | $\mu \cdot k_{3CT\rightarrow1CT}$ [10$^7$ s$^{-1}$] |
|--------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------------------|---------|-----------------------------------------------|
| 90                 | 0.00                        | 0.0066                      | 0.0066                      | 0.0000                                | 5.20    | 0.0000                                        |
| 89 and 91          | 0.01                        | 0.0068                      | 0.0068                      | 0.0224                                | 10.39   | 0.0023                                        |
| 88 and 92          | 0.02                        | 0.0076                      | 0.0076                      | 0.0824                                | 10.25   | 0.0084                                        |
| 87 and 93          | 0.03                        | 0.0089                      | 0.0089                      | 0.1631                                | 10.07   | 0.0164                                        |
| 86 and 94          | 0.04                        | 0.0107                      | 0.0107                      | 0.2459                                | 9.80    | 0.0241                                        |
| 85 and 95          | 0.05                        | 0.0130                      | 0.0130                      | 0.3186                                | 9.46    | 0.0302                                        |
| 84 and 96          | 0.06                        | 0.0159                      | 0.0159                      | 0.3723                                | 9.05    | 0.0337                                        |
| 83 and 97          | 0.07                        | 0.0192                      | 0.0192                      | 0.4042                                | 8.56    | 0.0346                                        |
| 82 and 98          | 0.07                        | 0.0230                      | 0.0230                      | 0.3187                                | 8.02    | 0.0256                                        |
| 81 and 99          | 0.08                        | 0.0273                      | 0.0273                      | 0.3231                                | 7.42    | 0.0240                                        |
| 80 and 100         | 0.09                        | 0.0320                      | 0.0320                      | 0.3143                                | 6.79    | 0.0213                                        |
| 75 and 105         | 0.13                        | 0.0621                      | 0.0621                      | 0.1458                                | 3.55    | 0.0052                                        |
| 70 and 110         | 0.16                        | 0.1012                      | 0.1012                      | 0.0378                                | 1.22    | 0.0005                                        |
| 65 and 115         | 0.19                        | 0.1467                      | 0.1467                      | 0.0075                                | 0.21    | 0.0000                                        |

**$V_{3CT-1CT}$** – SOCME value for the $^3$CT→$^1$CT transition; $\mu$ – statistical weight of a rotational isomer at room temperature calculated using relative energies of isomers in the $^3$CT state listed in Table S5.
Table S3. Rates of ISC and rISC as statistical sums for rotamers for all investigated media*

| Solvent                  | $Z_{3CT}$ [%] | $Z_{3LE}$ [%] | ISC [10$^{-7}$ s$^{-1}$] | rISC [10$^{-7}$ s$^{-1}$] |
|--------------------------|---------------|---------------|---------------------------|---------------------------|
|                          |               |               | $k_{1CT\rightarrow3CT}$ | $k_{3CT\rightarrow1CT}$  | $k_{1CT\rightarrow3LE}$ | $k_{3LE\rightarrow1CT}$ | $Z_{3CT}k_{3CT\rightarrow1CT}$ | $Z_{3LE}k_{3LE\rightarrow1CT}$ |
| Hexane                   | 5.6           | 94.4          | 0.26                      | 0.023                     | 1.3$\cdot$10$^{-3}$  | 0.032                     | 0.033                         |
| Benzene-hexane (1/2)     | 42.8          | 57.2          | 0.28                      | 0.039                     | 0.15                | 0.017                     | 0.085                         | 0.102                        |
| Benzene-hexane (1/1)     | 81.4          | 18.6          | 0.29                      | 0.053                     | 0.38                | 0.043                     | 0.070                         | 0.114                        |
| Acetone-hexane (5%)      | 96.3          | 3.7           | 0.31                      | 0.071                     | 0.87                | 0.068                     | 0.032                         | 0.100                        |
| Benzene                  | 98.6          | 1.4           | 0.32                      | 0.082                     | 1.32                | 0.081                     | 0.053                         | 0.134                        |
| Acetone-hexane (10%)     | 99.8          | 0.18          | 0.35                      | 0.111                     | 2.95                | 0.111                     | 0.014                         | 0.124                        |
| Acetone-hexane (15%)     | 100           | 2.8$\cdot$10$^{-2}$ | 0.38                     | 0.142                     | 5.55                | 0.142                     | 3.7$\cdot$10$^{-3}$            | 0.146                        |
| Chlorobenzene            | 100           | 5.1$\cdot$10$^{-3}$ | 0.40                     | 0.172                     | 9.49                | 0.172                     | 1.1$\cdot$10$^{-3}$            | 0.173                        |
| Acetone-hexane (25%)     | 100           | 1.3$\cdot$10$^{-3}$ | 0.43                     | 0.202                     | 12.5                | 0.202                     | 3.3$\cdot$10$^{-4}$            | 0.202                        |
| o-Dichlorobenzene        | 100           | 3.9$\cdot$10$^{-4}$ | 0.46                     | 0.229                     | 15.9                | 0.229                     | 1.2$\cdot$10$^{-4}$            | 0.229                        |
| Acetone-hexane (75%)     | 100           | 6.7$\cdot$10$^{-6}$ | 0.56                     | 0.338                     | 28.8                | 0.338                     | 2.5$\cdot$10$^{-6}$            | 0.338                        |
| Acetone                  | 100           | 1.4$\cdot$10$^{-6}$ | 0.58                     | 0.387                     | 31.8                | 0.387                     | 4.8$\cdot$10$^{-7}$            | 0.387                        |

*$Z_{3CT}$ and $Z_{3LE}$ – molar fractions of molecules coexisting in $^3$CT and $^3$LE states at 298.15 K, calculated using Boltzmann distribution law and energies of the respective triplet states listed in Table S1.

$k_{1CT\rightarrow3LE}$ and $k_{3LE\rightarrow1CT}$ calculated using $\lambda_{solv} = 0.3$ eV (Table S9 and S10)
Prediction of the rate of radiative deactivation ($k_r$). The rate of radiative deactivation was obtained as a statistical sum of respective values for each rotational isomer calculated using Strickler-Berg law:

$$k_r = \sum_\theta \frac{0.668 \cdot f(\theta) \cdot n^2}{\lambda_{S1-S0}(\theta) \cdot 10^7}$$  \hspace{1cm} (S8),

where $\lambda_{S1-S0}(\theta)$ and $f(\theta)$ are wavelength in nanometer and oscillator strength of $S_1$-$S_0$ transition for each rotational isomer, respectively; $n$ is refractive index of o-dichlorobenzene ($n = 1.551$).

**Table S4.** TD-DFT predicted energy ($\lambda_{S1-S0}$) and oscillator strengths ($f$) of $S_1$-$S_0$ transition, and calculated radiative deactivation constants ($k_r$) for various dihedral angles*

| Dihedral Angle $\theta$ [°] | $\lambda_{S1-S0}$ [nm] | $f$ | $k_r$ [10$^7$ s$^{-1}$] | $\mu$ [%] | $\mu \cdot k_r$ [10$^7$ s$^{-1}$] |
|-----------------------------|------------------------|-----|----------------------|----------|-------------------------------|
| 90 | 611.49 | 0.0000 | 0.000 | 7.37 | 0.0000 |
| 89 and 91 | 611.22 | 0.0002 | 0.009 | 14.2 | 0.0012 |
| 88 and 92 | 610.98 | 0.0008 | 0.034 | 13.6 | 0.0047 |
| 87 and 93 | 610.61 | 0.0018 | 0.078 | 12.7 | 0.0099 |
| 86 and 94 | 610.13 | 0.0031 | 0.134 | 11.5 | 0.0154 |
| 85 and 95 | 609.49 | 0.0049 | 0.212 | 10.2 | 0.0215 |
| 84 and 96 | 608.72 | 0.0070 | 0.304 | 8.70 | 0.0264 |
| 83 and 97 | 607.77 | 0.0096 | 0.418 | 7.23 | 0.0302 |
| 82 and 98 | 606.76 | 0.0125 | 0.546 | 5.84 | 0.0319 |
| 81 and 99 | 605.58 | 0.0158 | 0.692 | 4.57 | 0.0316 |
| 80 and 100 | 604.29 | 0.0194 | 0.854 | 3.48 | 0.0297 |
| 75 and 105 | 596.13 | 0.0428 | 1.935 | 0.56 | 0.0109 |
| 70 and 110 | 585.64 | 0.0740 | 3.467 | 0.04 | 0.0015 |
| 65 and 115 | 573.47 | 0.1124 | 5.492 | 0.001 | 0.0001 |
| Sum |  |  |  |  |  | 0.215 |

* $\mu$ – statistical weight of a rotational isomer in $^1$CT-state at room temperature calculated using relative energies of isomers listed in Table S5.

**Figure S1.** Dependence of the TD-DFT predicted energy gaps between singlet and triplet states on the dihedral angle between donor and acceptor fragments
Theoretical model including rotational isomers and vibrationally-enhanced SOC

Corrections for various polarity. Alignment of the potential curves of $^1\text{CT}$, $^3\text{CT}$, and $^3\text{LE}$ states predicted on the TD-TDF/B3LYP level of theory is in excellent correlation with the experimental data in the media of relatively high polarity (like $\text{o}$-dichlorobenzene and 75% mixture of acetone in hexane). To mimic less and more polar medium, the energies of $^1\text{CT}$ and $^3\text{CT}$ states were corrected for each media according to the procedure below.

Unconstrained geometry optimizations of DMAC-TRZ were conducted for various excited states. The nature of each excited state was established by the analysis of molecular orbitals involved in respective transitions. The $\Delta E_{^1\text{CT}-^3\text{CT}}$ and $\Delta E_{^1\text{CT}-^3\text{LE}}$ values were calculated using electronic energies ($E_{\text{(TD-DFT)}}$) of respective states in their energetic minima (Table S5), verified by the absence of imaginary (negative) vibrational frequencies. Next, starting with the optimized geometry in each excited state, the value of dihedral angle between DMAC and phenyl ring of acceptor fragment was scanned with a 1 degree step from 89° to 60°. Energies of respective states were calculated by single-point calculations. The $\Delta E_{^1\text{CT}-^3\text{CT}}$ and $\Delta E_{^1\text{CT}-^3\text{LE}}$ values for each rotational isomer were calculated using thus obtained energies.

Table S5. Energies of the excited states and gaps between them.

| Dihedral Angle [°] | $E_{^1\text{CT}}$ [au] | $E_{^3\text{CT}}$ [au] | $E_{^3\text{LE}}$ [au] | $\Delta E_{^1\text{CT}-^3\text{CT}}$ [eV] | $\Delta E_{^1\text{CT}-^3\text{LE}}$ [eV] | $\Delta E_{^1\text{CT}-^3\text{CT}}$ [eV] | $\Delta E_{^1\text{CT}-^3\text{LE}}$ [eV] |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 90                | -1607.76452079  | -1607.76476132  | -1607.74397545  | 0.0065          | -0.559          | 0.024           | 0.094           |
| 85                | -1607.76417036  | -1607.76467305  | -1607.74347908  | 0.0137          | -0.563          | 0.049           | 0.090           |
| 80                | -1607.76315795  | -1607.76435939  | -1607.74202884  | 0.0327          | -0.575          | 0.118           | 0.078           |
| 75                | -1607.76143695  | -1607.76374597  | -1607.73979476  | 0.0628          | -0.589          | 0.227           | 0.064           |
| 70                | -1607.75899058  | -1607.76273759  | -1607.73691709  | 0.1020          | -0.601          | 0.368           | 0.052           |
| 65                | -1607.75567303  | -1607.76121844  | -1607.73334284  | 0.1509          | -0.608          | 0.545           | 0.045           |

Table S6. Vertical transition energies of DMAC-TRZ calculated using PCM

| Medium           | Vertical transition energy [nm] |
|-----------------|-------------------------------|
|                 | $S_0-S_1$ | $S_1-S_0$ |
| Vacuum          | 516       | 612       |
| Chloroform      | 500       | 597       |
| Formamide       | 496       | 593       |
DFT fails to predict medium polarity influence on the spectral properties of D-A emitters. Polarized continuum model, most extensively used for this purpose predicts incorrectly the solvent effect. (Table S6). To mimic medium of different polarity, minimum $^1\text{CT}$ energy, energies of rotational isomers in $^1\text{CT}$ state as well as all vertical transitions involving $^1\text{CT}$ state were corrected by a correction factor $C$, obtained using experimental $\Delta E_{^1\text{CT}-3\text{LE}}$ value (Table S1) for each medium:

$$C = E_{3\text{LE}} - E_{^1\text{CT}} + \Delta E_{^1\text{CT}-3\text{LE}}$$

(S9),

where $E_{3\text{LE}}$ and $E_{^1\text{CT}}$ are the energies of respective states in their optimized geometries from Table S5 (dihedral angle 90°). Obtained $C$ values are listed below (Table S7):

**Table S7. Correction factors for various media**

| Solvent                  | $\Delta E_{^1\text{CT}-3\text{LE}}$ [eV] | $C$  |
|--------------------------|-----------------------------------------|------|
| Hexane                   | 0.094                                   | 0.65 |
| Benzene-hexane (1/2)     | 0.026                                   | 0.58 |
| Benzene-hexane (1/1)     | -0.022                                  | 0.54 |
| Acetone-hexane (5%)      | -0.069                                  | 0.49 |
| Benzene                  | -0.095                                  | 0.46 |
| Acetone-hexane (10%)     | -0.15                                   | 0.41 |
| Acetone-hexane (15%)     | -0.20                                   | 0.36 |
| Chlorobenzene            | -0.25                                   | 0.31 |
| Acetone-hexane (25%)     | -0.28                                   | 0.28 |
| o-Dichlorobenzene        | -0.31                                   | 0.25 |
| Acetone-hexane (75%)     | -0.42                                   | 0.14 |
| Acetone                  | -0.46                                   | 0.10 |

For each medium, the $\Delta E_{^1\text{CT}-3\text{LE}}$ values at various dihedral angles ($\theta$) were calculated as follows:

$$\text{“}\Delta E_{^1\text{CT}-3\text{LE}}(\theta)\text{”} = (E_{^1\text{CT}}(\theta) + C) - E_{3\text{LE}}(\theta)$$

(S10),

The example of such calculations for hexane is listed in Table S5.

As the $\Delta E_{^1\text{CT}-3\text{CT}}$ value changes also with the change of dihedral angle, for each medium, its value for each rotational isomer “$\Delta E_{^1\text{CT}-3\text{CT}}^{\text{Solvent}(\theta)}$” was calculated proportional to that at 90°. In the example with hexane:

$$\text{“}\Delta E_{^1\text{CT}-3\text{CT}}^{\text{Hexane}(\theta)}\text{”} = \text{“}\Delta E_{^1\text{CT}-3\text{CT}}(\theta)\text{”} \cdot \frac{\text{“}\Delta E_{^1\text{CT}-3\text{CT}}^{\text{Hexane}(\theta)}\text{”}}{\text{“}\Delta E_{^1\text{CT}-3\text{CT}}\text{”}}$$

(S11),

where
“ΔE_{1CT-3CT}(θ)” – computational value for respective dihedral angle from Table S5;
“ΔE_{1CT-3CT}” – computational value for 90° dihedral angle from Table S5;
“ΔE_{1CT-3CT}^{Hexane}” – experimental value listed for each medium in Table S1.

The example of such calculations for hexane is listed in Table S5.

Reorganization energies of the \(^3\)LE→\(^1\)CT and \(^1\)CT→\(^3\)LE transitions (Figure 3) were calculated as follows

\[
\lambda_{3LE-1CT}(θ) = E_{1CT}^{3LE}(θ) - E_{1CT}^{1CT}(θ) \quad (S12),
\]
\[
\lambda_{1CT-3LE}(θ) = E_{3LE}^{1CT}(θ) - E_{3LE}^{3LE}(θ) \quad (S13),
\]

where

\(E_{1CT}^{3LE}(θ)\) – TD-DFT energy of the \(^1\)CT state at the \(^3\)LE geometry at given dihedral angle value \(θ\); \(E_{3LE}^{1CT}(θ)\) – TD-DFT energy of the \(^3\)LE state at the \(^1\)CT geometry at given dihedral angle value \(θ\). These values are listed in Table S8.

**Table S8.** Energies of states in non-optimal geometries and reorganization energies

| Dihedral Angle [°] | \(E_{1CT}^{3LE} [\text{au}]\) | \(E_{3LE}^{1CT} [\text{au}]\) | \(\lambda_{1CT-3LE} [\text{eV}]\) | \(\lambda_{3LE-1CT} [\text{eV}]\) |
|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 90                | -1607.756846                  | -1607.737375                 | 0.1796                        | 0.2088                        |
| 85                | -1607.756471                  | -1607.736974                 | 0.1770                        | 0.2095                        |
| 80                | -1607.755313                  | -1607.735792                 | 0.1697                        | 0.2135                        |
| 75                | -1607.753388                  | -1607.733989                 | 0.1580                        | 0.2190                        |
| 70                | -1607.750780                  | -1607.731688                 | 0.1423                        | 0.2234                        |
| 65                | -1607.747374                  | -1607.728820                 | 0.1231                        | 0.2258                        |

**Prediction of rISC rates. \(^3\)CT→\(^1\)CT transition.**

Parameters for calculations of \(^3\)CT→\(^1\)CT transition rate for various rotational isomers using Marcus-Hush equation and the B3LYP predicted ΔE_{1CT-3CT} values are presented in Table S2.

For media with \(E_{1CT} \leq 2.67\) eV, experimental \(k_{\text{isc}}\) was used for calculation of ΔE_{1CT-3CT} using Marcus-Hush equation and assuming ΔE_{1CT-3CT} = \(\lambda_{1CT-3CT}\). For less polar media, ΔE_{1CT-3CT} were obtained by extrapolation (Figure 2H in the main text). Reconstructed \(k_{\text{isc}}\) values for all media are shown in Table S3.
**Prediction of rISC rates.** \(^{3}\text{LE} \rightarrow \text{1CT} \text{ transition.} \) Examples of calculations of \(^{3}\text{LE} \rightarrow \text{1CT} \text{ transition rates} \) for various rotational isomers using Marcus-Hush equation are presented in Table S9.

**Table S9.** Calculation of the \(^{3}\text{LE} \rightarrow \text{1CT} \) transition parameters*

Hexane, \(\Delta E_{\text{1CT}-3\text{LE}} = 0.094 \text{ eV.} \)

| Dihedral Angle [°] | \(\Delta E_{\text{1CT}-3\text{LE}}\) [eV] | \(\lambda_{3\text{LE}-1\text{CT}}\) [eV] | \(\mu\) [%] | \(k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(\mu k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(\mu k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) |
|-------------------|---------------------------------|---------------------|--------|------------------|------------------|-------------|------------------|
| 90               | 0.094                           | 0.2088              | 40.6   | 0.092            | 0.037            | 0.032       | 0.013            |
| 85 and 95        | 0.090                           | 0.2095              | 48.0   | 0.098            | 0.047            | 0.035       | 0.017            |
| 80 and 100       | 0.078                           | 0.2135              | 10.3   | 0.115            | 0.012            | 0.040       | 0.004            |
| 75 and 105       | 0.064                           | 0.2190              | 1.0    | 0.131            | 0.001            | 0.045       | 0.000            |
| 70 and 110       | 0.052                           | 0.2234              | 0.0    | 0.134            | 0.000            | 0.046       | 0.000            |
| 65 and 115       | 0.045                           | 0.2258              | 0.0    | 0.120            | 0.000            | 0.041       | 0.000            |
| **Sum**          |                                 |                     |        | **0.098**        | **0.034**        |             |                  |

Benzene-hexane (1:2), \(\Delta E_{\text{1CT}-3\text{LE}} = 0.026 \text{ eV.} \)

| Dihedral Angle [°] | \(\Delta E_{\text{1CT}-3\text{LE}}\) [eV] | \(\lambda_{3\text{LE}-1\text{CT}}\) [eV] | \(\mu\) [%] | \(k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(\mu k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(\mu k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) |
|-------------------|---------------------------------|---------------------|--------|------------------|------------------|-------------|------------------|
| 90               | 0.026                           | 0.2088              | 40.6   | 0.419            | 0.170            | 0.142       | 0.058            |
| 85 and 95        | 0.022                           | 0.2095              | 48.0   | 0.443            | 0.213            | 0.150       | 0.072            |
| 80 and 100       | 0.010                           | 0.2135              | 10.3   | 0.497            | 0.051            | 0.169       | 0.017            |
| 75 and 105       | -0.004                          | 0.2190              | 1.0    | 0.540            | 0.005            | 0.183       | 0.002            |
| 70 and 110       | -0.016                          | 0.2234              | 0.0    | 0.533            | 0.000            | 0.181       | 0.000            |
| 65 and 115       | -0.023                          | 0.2258              | 0.0    | 0.467            | 0.000            | 0.159       | 0.000            |
| **Sum**          |                                 |                     |        | **0.440**        | **0.149**        |             |                  |

Benzene-hexane (1:1) mixture, \(\Delta E_{\text{1CT}-3\text{LE}} = -0.022 \text{ eV.} \)

| Dihedral Angle [°] | \(\Delta E_{\text{1CT}-3\text{LE}}\) [eV] | \(\lambda_{3\text{LE}-1\text{CT}}\) [eV] | \(\mu\) [%] | \(k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(\mu k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) | \(\mu k_{3\text{LE} \rightarrow 1\text{CT}} \left[10^{7} \text{ s}^{-1}\right]\) |
|-------------------|---------------------------------|---------------------|--------|------------------|------------------|-------------|------------------|
| 90               | -0.022                          | 0.2088              | 40.6   | 1.073            | 0.436            | 0.364       | 0.148            |
| 85 and 95        | -0.026                          | 0.2095              | 48.0   | 1.123            | 0.539            | 0.381       | 0.183            |
| 80 and 100       | -0.038                          | 0.2135              | 10.3   | 1.226            | 0.127            | 0.418       | 0.043            |
| 75 and 105       | -0.052                          | 0.2190              | 1.0    | 1.292            | 0.013            | 0.444       | 0.004            |
| 70 and 110       | -0.064                          | 0.2234              | 0.0    | 1.243            | 0.001            | 0.430       | 0.000            |
| 65 and 115       | -0.071                          | 0.2258              | 0.0    | 1.074            | 0.000            | 0.373       | 0.000            |
| **Sum**          |                                 |                     |        | **1.115**        | **0.379**        |             |                  |
Table S9 continued.

Benzene, $\Delta E_{1\text{CT}-3\text{LE}} = -0.095$ eV.

| Dihedral Angle [°] | $\Delta E_{1\text{CT}-3\text{LE}}$ [eV] | $\lambda_{3\text{LE}-1\text{CT}}$ [eV] | $\mu$ [%] | $k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] | $\mu k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] | $k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] | $\mu k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] |
|---------------------|----------------------------------------|-----------------------------------|----------|---------------------|---------------------------------|---------------------|---------------------------------|
| 90                  | -0.095                                 | 0.2088                            | 40.6     | 3.627               | 1.474                           | 1.281               | 0.520                           |
| 85 and 95           | -0.099                                 | 0.2095                            | 48.0     | 3.745               | 1.798                           | 1.327               | 0.637                           |
| 80 and 100          | -0.111                                 | 0.2135                            | 10.3     | 3.934               | 0.407                           | 1.411               | 0.146                           |
| 75 and 105          | -0.125                                 | 0.2190                            | 1.0      | 3.966               | 0.038                           | 1.443               | 0.014                           |
| 70 and 110          | -0.137                                 | 0.2234                            | 0.0      | 3.681               | 0.002                           | 1.357               | 0.001                           |
| 65 and 115          | -0.144                                 | 0.2258                            | 0.0      | 3.112               | 0.000                           | 1.157               | 0.000                           |
| **Sum**             |                                        |                                   |          | 3.719               | 1.318                           |                     |                                 |

Acetone, $\Delta E_{1\text{CT}-3\text{LE}} = -0.46$ eV.

| Dihedral Angle [°] | $\Delta E_{1\text{CT}-3\text{LE}}$ [eV] | $\lambda_{3\text{LE}-1\text{CT}}$ [eV] | $\mu$ [%] | $k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] | $\mu k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] | $k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] | $\mu k_{3\text{LE}-1\text{CT}}$ [10$^7$ s$^{-1}$] |
|---------------------|----------------------------------------|-----------------------------------|----------|---------------------|---------------------------------|---------------------|---------------------------------|
| 90                  | -0.460                                 | 0.2088                            | 40.6     | 35.56               | 14.44                           | 32.42               | 13.17                           |
| 85 and 95           | -0.464                                 | 0.2095                            | 48.0     | 34.54               | 16.59                           | 31.94               | 15.34                           |
| 80 and 100          | -0.476                                 | 0.2135                            | 10.3     | 30.99               | 3.20                            | 29.68               | 3.07                            |
| 75 and 105          | -0.490                                 | 0.2190                            | 1.0      | 26.35               | 0.26                            | 26.19               | 0.25                            |
| 70 and 110          | -0.502                                 | 0.2234                            | 0.0      | 21.20               | 0.01                            | 21.75               | 0.01                            |
| 65 and 115          | -0.509                                 | 0.2258                            | 0.0      | 16.44               | 0.00                            | 17.21               | 0.00                            |
| **Sum**             |                                        |                                   |          | 34.50               | 31.84                           |                     |                                 |

* $\mu$ – statistical weight of a rotational isomer in $3\text{LE}$-state at room temperature calculated using relative energies of isomers listed in Table S5.
Prediction of ISC rates. $^1$CT→$^3$CT transition. Rates of the $^1$CT→$^3$CT transition in various media were calculated as statistical sums for various rotational isomers using Marcus-Hush equation. The used $\Delta E_{1CT-3CT}$ values were calculated using equation S11 and are listed in Table S1. SOCME values are listed in Table S2. The $\lambda_{1CT-3CT}$ values were assumed equal to the $\Delta E_{1CT-3CT}$ ones. Thus obtained $k_{1CT→3CT}$ values for all media are listed in Table S3.

Prediction of ISC rates. $^1$CT→$^3$LE transition.

Examples of calculations of the $^1$CT→$^3$LE transition rates for various rotational isomers using Marcus-Hush equation are presented in Table S10.

Table S10. Calculation of the $^1$CT→$^3$LE transition parameters*

| Dihedral Angle [°] | $\Delta E_{1CT-3LE}$ [eV] | $\lambda_{1CT-3LE}$ [eV] | $\mu$ [%] | $k_{1CT→3LE}$ [10$^7$ s$^{-1}$] | $\mu k_{1CT→3LE}$ [10$^7$ s$^{-1}$] | $k_{1CT→3LE}$ [10$^7$ s$^{-1}$] | $\mu k_{1CT→3LE}$ [10$^7$ s$^{-1}$] |
|------------------|------------------------|-------------------------|--------|-------------------------------|---------------------------------|-----------------------------|---------------------------------|
| 90               | -0.094                 | 0.1796                  | 34.1   | 3.67                          | 1.25                            | 1.29                        | 0.441                           |
| 85 and 95        | -0.090                 | 0.1731                  | 47.0   | 3.71                          | 1.74                            | 1.30                        | 0.612                           |
| 80 and 100       | -0.078                 | 0.1538                  | 16.1   | 3.30                          | 0.53                            | 1.14                        | 0.184                           |
| 75 and 105       | -0.064                 | 0.1281                  | 2.6    | 3.42                          | 0.089                           | 1.16                        | 0.030                           |
| 70 and 110       | -0.052                 | 0.1007                  | 0.2    | 3.37                          | 6.6·10$^{-3}$                    | 1.13                        | 2.2·10$^{-3}$                   |
| 65 and 115       | -0.045                 | 0.0746                  | 0.0    | 3.32                          | 1.9·10$^{-4}$                    | 1.09                        | 6.4·10$^{-5}$                   |

**Sum**                   |                        |                         |        | 3.62                          | 1.27                            |

Hexane, $\Delta E_{1CT-3LE} = 0.094$ eV.

Benzene, $\Delta E_{1CT-3LE} = -0.095$ eV.

| Dihedral Angle [°] | $\Delta E_{1CT-3LE}$ [eV] | $\lambda_{1CT-3LE}$ [eV] | $\mu$ [%] | $k_{1CT→3LE}$ [10$^7$ s$^{-1}$] | $\mu k_{1CT→3LE}$ [10$^7$ s$^{-1}$] | $k_{1CT→3LE}$ [10$^7$ s$^{-1}$] | $\mu k_{1CT→3LE}$ [10$^7$ s$^{-1}$] |
|------------------|------------------------|-------------------------|--------|-------------------------------|---------------------------------|-----------------------------|---------------------------------|
| 90               | 0.095                  | 0.1796                  | 34.1   | 0.092                         | 0.0314                          | 0.032                      | 0.0111                          |
| 85 and 95        | 0.099                  | 0.1731                  | 47.0   | 0.089                         | 0.0421                          | 0.032                      | 0.0149                          |
| 80 and 100       | 0.111                  | 0.1538                  | 16.1   | 0.070                         | 0.0113                          | 0.025                      | 4.1·10$^{-3}$                   |
| 75 and 105       | 0.125                  | 0.1281                  | 2.6    | 0.061                         | 1.6·10$^{-3}$                    | 0.023                      | 5.9·10$^{-4}$                   |
| 70 and 110       | 0.137                  | 0.1007                  | 0.2    | 0.051                         | 9.9·10$^{-5}$                    | 0.019                      | 3.8·10$^{-5}$                   |
| 65 and 115       | 0.144                  | 0.0746                  | 0.0    | 0.043                         | 2.5·10$^{-6}$                    | 0.017                      | 9.9·10$^{-7}$                   |

**Sum**                   |                        |                         |        | 0.086                         | 0.031                           |
Table S10 continued

Acetone, $\Delta E_{1CT-3LE} = -0.46$ eV.

| Dihedral Angle [°] | $\Delta E_{3LE-\text{ICT}}$ [eV] | $\lambda_{1CT-3LE}$ [eV] | $\mu$ [%] | $\lambda_{\text{solv}} = 0.2$ eV | $\lambda_{\text{solv}} = 0.3$ eV |
|-------------------|-------------------|-----------------|--------|-----------------|-----------------|
|                   | 0.460             | 0.1796          | 34.1   | 4.2·10^{-7}     | 4.4·10^{-7}     |
| 90 and 95         | 0.464             | 0.1731          | 47.0   | 3.4·10^{-7}     | 3.8·10^{-7}     |
| 80 and 100        | 0.476             | 0.1538          | 16.1   | 1.6·10^{-7}     | 2.1·10^{-7}     |
| 75 and 105        | 0.490             | 0.1281          | 2.6    | 6.5·10^{-8}     | 1.1·10^{-7}     |
| 70 and 110        | 0.502             | 0.1007          | 0.2    | 2.2·10^{-8}     | 5.5·10^{-8}     |
| 65 and 115        | 0.509             | 0.0746          | 0.0    | 7.7·10^{-9}     | 2.9·10^{-8}     |
| Sum               | 0.490             | 0.1281          | 2.6    | 6.5·10^{-8}     | 1.1·10^{-7}     |

* $\mu$ – statistical weight of a rotational isomer in $^1$CT-state at room temperature calculated using relative energies of isomers listed in Table S5.

Summary of the ISC and rISC rates as statistical sums for rotamers calculated according to the Marcus-Hush equation is presented in Table S3.

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