Twisted intramolecular charge transfer state of a “push-pull” emitter

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1. Transient absorption measurements

Excited state dynamics of DCM in DMSO

The transient absorption spectra of DCM in the DMSO solution with 403 nm excitation were shown in Figure S1(a). In an early time delay (1 ps for example), the excited state absorption (ESA) band at 475 and 540 nm (shoulder), and the stimulated emission (SE) centered at 630 nm appeared. The ESA band at 475 nm showed a blue-shift to 465 nm, and the SE band a red-shift to 658 nm in 10 ps. These peak shifts in the ESA and SE bands of DCM represent the internal conversion to the intramolecular charge transfer (ICT) state and the subsequent vibrational relaxation as already reported in many previous studies. Once the population reaches the bottom of the potential surface of the ICT state, the transient absorption signal only shows a decrease in intensity without any major spectral change. The lifetime of the charge transfer state was obtained as 2.3 ns in our measurements. The global analysis with a sequential decay model gave the best fit to the experimental results, and three lifetimes of 0.9 ps, 3.6 ps, and 2.1 ns were resolved. The evolution-associated difference spectra (EADS) of the global analysis were shown in Figure 1(b), where the 0.9 ps component represents the locally-excited (LE) population in the S1 state. The 3.6 ps component is assigned as the vibrational relaxation of the charge-transferred (CT) state, and the longest (2.1 ns) component as the lifetime of the CT state.

Excited state dynamics of DCM in CHCl3

The transient absorption spectra of DCM in CHCl3 solution with 403 nm excitation shown in Figure S1(b) showed the ESA band in the range of 430-520 nm and the SE band in the range of 530-750 nm. The emission bands appearing as two bands at 572 and 635 nm in an early time delay of 0.5 ps were changed into a single emission band at 600 nm with a smaller bandwidth by the 2-10 ps delay and later. The ESA band also showed small spectral changes in 2-10 ps; the band became slightly broader with the appearance of a shoulder band at 525 nm. The ICT
formation was not observed in the CHCl₃ solution, and the vibrational relaxation of DCM in
the LE state was reported as ~7 ps.⁸ Similarly, the global analysis with a sequential decay model
resolved three kinetic components of 390 fs, 4.0 ps, and 620 ps as the corresponding EADS
were shown in Figure 1(c). The 4.0 ps and 620 ps components are considered as the vibrational
relaxation and the lifetime of the LE state, respectively. However, the identity of the fastest
(390 fs) component is not clear considering only the transient absorption results. As shown in
the femtosecond stimulated Raman spectroscopy (FSRS) results of DCM in the CHCl₃ solution
(shown in Figure 3), the 390 fs component is assigned as a small contribution from the CT
conformer of DCM in the S₁ state. Two SE bands appearing in the early time delays may
represent the co-excitation of the LE and CT states of DCM in the CHCl₃ solution. As clearly
shown later in the FSRS results, the CT population immediately converts to the LE state with
a time constant of 300 fs.
Figure S1. Transient absorption spectra of DCM in (a) DMSO and (b) CHCl$_3$ solution obtained with the 403 nm excitation.
2. Femtosecond Stimulated Raman measurements

Figure S2 shows the time-resolved stimulated Raman spectra of DCM in DMSO and CHCl₃ solution with 403 nm excitation. The ground state spectrum of DCM in each solution was subtracted from the transient Raman spectra at time delays between -1 and 100 ps. The background signal beneath all the Raman bands may represent the tail of the strong transient absorption signals in the probe wavelength of 850-950 nm. The increased Raman gains of the transient absorption signal represent the contribution from the SE. However, the SE background signals were perfectly removed in a low order polynomial fit. The difference stimulated Raman spectra of DCM after the polynomial fit were shown in Figure 2(a) and Figure 3(a). The amplitude, frequency, and bandwidth of each Raman band were obtained from the spectral fit with multiple Gaussian functions. The representative population changes and peak-shifts for the major vibrational bands of DCM in DMSO and CHCl₃ solution were summarized in Figure 2(b) and 3(b), respectively. Besides, the changes of bandwidth for the ν₉a (ph) at 1200 cm⁻¹ and the ν₈a,C=O,N at 2170 cm⁻¹ shown in Figure S3 also showed the time constant of 3-5 ps for the vibrational relaxation in the CT state of DCM in DMSO. All the population dynamics, frequency shifts, and bandwidth changes were fit with several exponential functions convoluted by a Gaussian representing the instrumental response function (IRF) of the experiment.

Two distinct Raman spectra of the LE and CT conformers of DCM in the S₁ excited state were obtained from the FSRS measurements in DMSO (polar) and CHCl₃ (less polar) solution. In the DMSO solution, the Raman spectra at early time delays (0.3 ps, for example, for LE state) and the later time delays (30 ps, for example, for CT state) are distinct from each other as shown in Figure 2(a). In the CHCl₃ solution, the Raman spectra at early time delays are somewhat complicated but they become very similar to the LE spectrum (observed at 0.3 ps in DMSO solution) at later time delays (30 ps, for example). Then the early delay (0.3 ps, for
example) Raman spectra of DCM in CHCl₃ solution can be understood as the sum of the spectral components for the LE and CT states.

The excited state spectrum of DCM in the LE and CT conformer state can be separately observed in the DMSO and CHCl₃ solutions. The early delay Raman spectrum of DCM in DMSO and the later delay spectrum in CHCl₃ are considered as the LE conformer spectrum. The later delay spectrum in DMSO is considered as the CT conformer spectrum. In Figure S4, the Raman spectrum of DCM in CHCl₃ at 0.3 ps was compared with the 2:1 scaled sum between the 0.3 ps (LE) and 30 ps (CT) spectrum in DMSO, and another 2:1 scaled sum between the 30 ps (LE) spectrum in CHCl₃ and the 30 ps (CT) spectrum in DMSO. The major peak positions in the Raman spectrum of DCM in CHCl₃ at 0.3 ps were very similar to two spectra composed of the LE and CT conformer spectra obtained from the DMSO and CHCl₃ solution. The Raman bands of DCM at 1057, 1312, 1425, and 1495 cm⁻¹ in Figure S4(a) show a single exponential decay of 300 fs time constant. From this, we confirm that two distinct Raman spectra of DCM were measured in the CHCl₃ solution and that the CT conformer which is excited simultaneously with the LE conformer converts rapidly to the LE conformer.
Figure S2. Difference stimulated Raman spectra of DCM in (a) DMSO and (b) CHCl₃ solution following the 403 nm photoexcitation. The solvent vibrational bands in the ground state spectra were marked by an asterisk (*).
Figure S3. The structural dynamics of DCM in DMSO; (a) $\nu_{9a}$ (ph) at 1200 cm$^{-1}$ and (b) $\nu_{\text{as, C=\text{N}}}$ at 2170 cm$^{-1}$.
Figure S4. Comparison of transient stimulated Raman spectra; (a) LE spectrum in DMSO (0.3 ps) + CT spectrum in DMSO (30 ps), (b) LE spectrum in CHCl$_3$ (30 ps) + CT spectrum in DMSO (30 ps), and (c) DCM spectrum in CHCl$_3$ (0.3 ps). These results show that the DCM spectrum in CHCl$_3$ at early time delays originate from both the LE and CT conformers in the S$_1$ excited state.
Global analysis of FSRS results

The global analysis with the sequential model was applied to the FSRS results of DCM in DMSO and CHCl₃ solution. Three kinetic components of 0.9 ps, 4.3 ps, and 1.1 ns were obtained for the FSRS results of DCM in the DMSO solution, and the corresponding EADS were shown in Figure S5(a). The EADS of 0.9 ps component shows clear differences in many vibrational bands from the spectrum of 4.3 ps component. The 0.9 ps component which is directly populated by the actinic pump, represents the LE conformer of DCM. The EADS of 4.3 ps and much longer 1.1 ns components shares many major vibrational bands with slight peak shifts. Thus the 4.3 ps component is assigned as the vibrational relaxation in the potential surface of the CT conformer and the 1.1 ns component represents the CT conformer of DCM. All three components of DCM obtained from the FSRS in DMSO are similar to those obtained from the transient absorption measurements.

Three kinetic components of 270 fs, 5.6 ps, and 1.0 ns were obtained from the FSRS of DCM in the CHCl₃ solution. The EADS of the three components are shown in Figure S5(b). The EADS of 270 fs component which represents the CT conformer of DCM, is very similar to the EADS of 1.1 ns component in DMSO solution, but small differences in several vibration bands still exist. The CT conformer was populated together with the LE conformer, and rapidly converts to the LE conformer, as clearly shown in Figure 3(b) and Figure 4. A more thorough global analysis with a branching and recombining dynamics between the CT and LE conformer of DCM would be needed. The 5.6 ps and 1.0 ns components in the dynamics of DCM in CHCl₃ are very similar to each other as the two components of the CT conformers showed the 4.3 ps and 1.1 ns components in the DMSO solution. Therefore, the 5.6 ps component is considered as the vibrational relaxation of the LE state, and the 1.0 ns is attributed to the lifetime of the LE state.

Two distinct excited state Raman spectra of DCM which represent the LE and CT conformer states are well represented by the EADS of DCM in DMSO and CHCl₃ solution. Figure 4(a) compares the EADS for the 270 fs component of CHCl₃ results and the 1.1 ns component of DMSO results for the CT conformer of DCM in the S₁ state. Figure 4(b) compares the EADS for the 1.0 ns component of CHCl₃ results and the 0.9 ps component of DMSO results for the LE conformer of DCM in the S₁ state.
Figure S5. EADS for the FSRS of DCM in (a) DMSO and (b) CHCl₃ solution.
3. DFT simulation for the excited state geometry and Raman spectra

Computational Details

The optimized structure and the Raman spectrum of DCM were simulated by a density functional theory (DFT) method, and the Gaussian 09 software was used. The structure of DCM and key notations for the dihedral rotations and normal mode vibrations are visualized in Figure S6. The ph and py refer to the phenyl and pyran ring, respectively, the \( C_a, C_b, C_c, \) and \( C_d \) notations were used to represent the skeletal vibrational modes of DCM.

The molecular geometry of DCM in the ground state was optimized by using the B3LYP exchange-correlation functional and 6-311G(d,p) basis set with the polarizable continuum model (PCM) for solvent effects. The potential energy surfaces of DCM in the gas phase, and in the CHCl\(_3\) and DMSO solution along the dihedral degree of freedoms for dimethylamino (DMA; \( \mu \)) and dimethylaminophenyl (DMAP; \( \delta \)) group rotation were estimated in the ground and excited singlet states. First, the molecular structures of DCM in the ground state with a fixed dihedral angle at a specific value. The potential energy curves in the ground state shown

![Molecular geometry of DCM](image)

**Figure S6.** Molecular geometry of DCM. The ph and py refer to the phenyl and pyran ring, respectively, the \( C_a, C_b, C_c, \) and \( C_d \) notations were used to represent the skeletal vibrational modes of DCM.
in Figure S7 were obtained by comparing the relative energy for the optimized structure at each
dihedral angle. The planar molecular geometry was preferred for both dihedral angle rotations
in all conditions, and the energy difference of the twisted molecular structures (δ or \(\mu = 90^\circ\))
relative to the ground planar geometry was estimated as 0.4-0.6 eV (40-60 kJ/mol). Then, the
vertical transition energies were calculated in a single point time-dependent (TD) DFT
simulation at the B3LYP/6-311G(d,p) level with the PCM level by using each optimized
structure with a specific dihedral angle \(\mu\) and \(\delta\). The potential energy curves of DCM in two
lowest excited states, \(S_1\) and \(S_2\) based on the single point TDDFT simulations in the gas phase,
and in the CHCl\(_3\) and DMSO solution were added in Figure S7. A local minimum for the
twisted (\(\mu = 90^\circ\)) DMA group was found in the \(S_1\) excited state regardless of the conditions;
the twisted geometry was located at about the same level as the \(S_1\) planar geometry in the gas
phase, but 0.2-0.3 eV above than the planar geometry in the solution conditions. However, for
the DMAP group rotation, the local minimum was located for the twisted (\(\delta = 90^\circ\)) geometry
only in the gas phase. The twisted geometry in the gas phase was located at about the same
level as the \(S_1\) planar geometry, and 0.2 eV higher than the planar geometry in the solution
conditions. The geometry optimization of DCM in the \(S_1\) excited state with no fixed degree of
freedom was further performed by using the twisted (\(\mu\) or \(\delta = 90^\circ\)) molecular geometry from
the potential energy calculations as the starting point. The optimized molecular structures of
DCM with the “twisted” DMA (\(\mu = 90.0^\circ\) for B3LYP/6-311G(d,p) and \(\mu = 90.0^\circ\) for
mPW1PBE/6-31G(d)) or DMAP group (\(\delta = 89.7^\circ\) for B3LYP/6-311G(d,p) and \(\delta = 96.4^\circ\) for
mPW1PBE/6-31G(d)) were obtained for the \(S_1\) CT state, which is considered compatible to the
previous reports by TDDFT methods.\(^{10-11}\) The optimized structures of DCM in the \(S_1\) excited
state by using the B3LYP and mPW1PBE correlation functionals are summarized in Figure S8
and Table S1.
**Figure S7.** Potential energy curve of DCM in the gas phase and in DMSO and CHCl$_3$ solution based on the ground state optimized geometry and the single point TDDFT simulations at the TD-B3LYP/6-311G(d,p) level; the dihedral rotations along (a) the dimethylamino (DMA) and (b) dimethylaminophenyl (DMAP) group were drawn separately.
Figure S8. The optimized structures of DCM in the S\textsubscript{1} excited state with (a) planar, (b) twisted dimethylamino (DMA) group, and (c) twisted dimethylaminophenyl (DMAP) group. The TDDFT simulations at the B3LYP/6-311G(d,p) and mPW1PBE/6-31G(d) levels were compared with the energy different from the S\textsubscript{1} minima.
Table S1. The optimized structure of DCM in the $S_1$ excited state with the “twisted” dimethylamino (DMA) and dimethylaminophenyl (DMAP) groups

| degree of freedom | B3LYP/6-311G(d,p) | mPW1PBE/6-31G(d) |
|------------------|------------------|-----------------|
|                  | DMSO             | DMSO            | EtOH$^a$ |

1. dimethylamino (DMA)

| bond angle (°)   |                  |                  |                  |
|------------------|------------------|------------------|------------------|
| C19-N18-C20      | 121.9            | 121.7            | 121.7            |
| C14-C15-C16      | 120.8            | 120.9            | 120.9            |
| C19-N18-C15      | 119.1            | 119.2            | 119.2            |
| N18-C15-C14      | 119.6            | 119.5            | 119.5            |

| dihedral angle $\mu$ (°) |                  |                  |                  |
|--------------------------|------------------|------------------|------------------|
| C19-N18-C15-C16          | 89.7             | 87.8             | 87.8             |
| C19-N18-C15-C14          | 90.3             | 92.2             | 92.2             |
| C20-N18-C15-C16          | 90.3             | 91.8             | 91.8             |
| C20-N18-C15-C14          | 89.7             | 88.2             | 88.2             |

2. dimethylaminophenyl (DMAP)

| bond angle (°)   |                  |                  |                  |
|------------------|------------------|------------------|------------------|
| C13-C12-C17      | 117.7            | 117.6            | 117.6            |
| C12-C11-C10      | 122.8            | 122.4            | 122.3            |
| C17-C12-C11      | 121.2            | 121.0            | 121.0            |

| dihedral angle $\delta$ (°) |                  |                  |                  |
|-----------------------------|------------------|------------------|------------------|
| C17-C12-C11-C10             | 89.7             | 96.4             | 95.4             |

$^a$ from Ref. 11

$^b$ The rotation angle ($\mu$) of the DMA group is evaluated as the average of two dihedral angles, $\angle(C19$-N18-C15-C16) and $\angle(C19$-N18-C15-C14), or $\angle(C20$-N18-C15-C16) and $\angle(C20$-N18-C15-C14).
**Vibrational assignments of DCM in the ground state**

The vibrational assignments for DCM in the ground state were based on the optimized geometry by the DFT simulation at the B3LYP/6-311G(d,p) level with PCM (DMSO) shown in Figure S8(a). The Raman frequencies and intensities for the vibrational normal modes of DCM obtained from the DFT simulation at the B3LYP/6-311G(d,p) level were compared with the experimental Raman spectrum in Figure S9. The simulated vibrational frequencies of DCM with the scaling factor of 0.967 for the B3LYP/6-311G(d,p) level appears quite different from the experimental results as compared in Figure S9(a) and (b). However, we found that the simulated vibrational frequencies of DCM from the DFT method become very similar to the experimental results except the $\nu_{\text{C=N}}$ modes at 2190 (sh) and 2207 cm$^{-1}$ when a slightly larger scaling factor of 0.984 was applied as shown in Figure S9(c). The vibrational assignments for the major vibrational normal modes of DCM were summarized in Table S2 and also displayed in Figure S10.

The vibrational modes appearing at 1170, 1190, and 1214 cm$^{-1}$ in the ground spectrum of DCM in DMSO are matched to the $\nu_{9a} + \delta_{\text{CH3}}$ (ph), $\nu_{9a} + \delta_{\text{CH3}}$ (ph) + $\nu_{\text{C-CH3}}$ (py), and $\nu_{9a}$ (ph) + $\delta_{\text{CH}}$ (py) modes, respectively. The vibrational bands in the region of 1250-1450 cm$^{-1}$ are also well matched to the simulated results, and most of these modes are related to the $\delta_{\text{CH3}}$ and $\delta_{\text{CH}}$ modes. The strong bands at 1497, 1527 (sh), 1548, 1600, 1620, 1650 cm$^{-1}$ in the ground spectrum of DCM in DMSO are assigned as the $\delta_{\text{CH3}}$ (ph), $\nu_{19b}$ (py) + $\delta_{\text{CH3}}$ (ph), $\nu_{19a} + \delta_{\text{CH3}}$ (ph), $\nu(C_a=C_b) + \nu_{8a}$ (ph) (symmetric), $\nu(C_a=C_b) + \nu_{8a}$ (ph) (asymmetric), and $\nu_{8a}$ (py), respectively. The separate bands appearing at 2190 (sh) and 2207 cm$^{-1}$ in the ground spectrum of DCM are unambiguously assigned as the $\nu_{\text{as,C=N}}$ and $\nu_{\text{s,C=N}}$, respectively.

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$^1$ shoulder band
Figure S9. Ground state Raman spectra of DCM; (a) stimulated Raman spectrum in DMSO solution, (b) simulated spectrum by the DFT method at B3LYP/6-311G(d,p) level (with a scaling factor of 0.967) with PCM (DMSO). The experimental spectrum appears very similar to (c) the simulated spectrum rescaled with a slightly larger scaling factor of 0.984.
Figure S10. Vibrational normal modes of DCM in the ground state obtained from the DFT simulation at the B3LYP/6-311G(d,p) level with PCM (DMSO). The DFT results and vibrational assignments were summarized in Table S2.
**Table S2. Vibrational assignments of DCM in the ground state**

|      | Experimental | Calculated\(^1\) | Vibrational assignments\(^2,3\) |
|------|--------------|------------------|--------------------------------|
|      | in CHCl\(_3\) | in DMSO | B3LYP/6-311G(d,p) PCM (DMSO) |                |
| -    | 1061         | 1044            | \(\delta_{\text{CH}_{3}\text{CH}}\) (py) |
| 1170 | 1170         | 1144            | \(\nu_9 + \delta_{\text{CH}}\) (ph) |
| 1186 | 1190         | 1164            | \(\nu_9 + \delta_{\text{CH}}\) (ph) + \(\nu_{\text{C}-\text{CH}}\) (py) |
| 1212 | 1214         | 1192            | \(\nu_9\) (ph) + \(\delta_{\text{CH}}\) (py) |
| -    | 1275         | 1256            | \(\delta_{\text{CH}}\) (py) |
| 1302 | 1308         | 1282            | \(\delta_{\text{CH}}\) (Cs=C\(_b\)) |
| 1335 | 1339         | 1316            | \(\nu_3\) (ph) + \(\delta_{\text{CH}}\) (Cs=C\(_b\)) |
| 1366 | 1363         | 1347            | \(\nu_{\text{C} = \text{N}} + \delta_{\text{CH}_{3}\text{CH}}\) (ph) |
| 1387 | 1389         | 1370            | \(\delta_{\text{CH}_{3}}\) (py) |
| 1417 | 1417         | 1392            | \(\delta_{\text{CH}_{3}} + \nu_{16}\) (py) |
| -    | 1444         | 1417            | \(\delta_{\text{CH}_{3}}\) (py) |
| 1478 | 1476         | 1450            | \(\nu(C_{c}\equiv C_{d}) + \delta_{\text{CH}_{3}\text{CH}}\) (py) |
| 1501 | 1497         | 1470            | \(\delta_{\text{CH}_{3}}\) (ph) |
| 1527 | 1527         | 1501            | \(\nu_{19a}\) (py) + \(\delta_{\text{CH}}\) (ph) |
| 1552 | 1548         | 1512            | \(\nu_{19a} + \delta_{\text{CH}}\) (ph) |
| 1599 | 1600         | 1572            | \(\nu(C_{c}=C_{b}) + \nu_{18a}\) (ph) (symmetric) |
| 1620 | 1620         | 1605            | \(\nu(C_{a}=C_{b}) + \nu_{18a}\) (ph) (asymmetric) |
| 1652 | 1650         | 1623            | \(\nu_{18a}\) (py) |
| -    | 2190         | 2200            | \(\nu_{\text{as},\text{C} \equiv \text{N}}\) |
| 2210 | 2207         | 2224            | \(\nu_{\text{as},\text{C} \equiv \text{N}}\) |

\(^1\) Calculated vibrational frequencies were rescaled with a factor of 0.967.\(^{12}\)

\(^2\) The \(\nu\) and \(\delta\) denote stretching and bending vibrations, respectively.

\(^3\) The ph and py in parenthesis refer to the phenyl and pyran ring, respectively. The \(\text{C}_{\text{a}}=\text{C}_{\text{b}}\) represents the central olefinic double bond, and the \(\text{C}_{\text{c}}=\text{C}_{\text{d}}\) represents the double bond between the dicyanomethylene group and the pyran ring as shown in Figure S6.
Vibrational assignments of DCM in the excited state

The vibrational assignments of DCM in the excited states are considered challenging since the molecule faces substantial changes in the molecular structure, dipole moment, etc. in the excited state. In general, the molecular structure calculations in the excited state, for example, by the TDDFT methods are considered incomplete and need be improved substantially.\textsuperscript{14-15} Nonetheless, we adopted the TDDFT simulations with the several hybrid functionals and basis sets for tentative vibrational assignments of the normal modes of DCM in the excited states. The molecular structures and Raman spectra of DCM in the LE and CT conformer states of the S\textsubscript{1} excited state were estimated by using the B3LYP/6-311G(d,p) and mPW1PBE/6-31G(d) simulations as described in the previous section. The molecular geometry of DCM in the LE (“planar” geometry) or the CT conformers (“twisted” along with the DMA or DMAP group) of the S\textsubscript{1} state obtained from these simulations do not show major differences between the exchange-correlation functionals or the basis sets used. As clearly shown in Figure S11, the differences in the simulated Raman spectra of DCM for the LE or CT conformers between the B3LYP/6-311G(d,p) and mPW1PBE/6-31G(d) simulation results are quite small except the $\nu_{\text{C=N}}$ modes. The frequencies of the $\nu_{\text{C=N}}$ modes of DCM obtained from the B3LYP/6-311G(d,p) simulations are strongly (~100 cm\textsuperscript{-1}) blue-shifted from those with the mPW1PBE/6-31G(d) simulations although the frequencies of other major vibrational modes are slightly red-shifted with the B3LYP functionals. In Figure S12, the simulated Raman spectra of DCM in the S\textsubscript{1} state were compared between the optimized geometries of the planar, twisted DMA and DMAP group obtained from the TDDFT simulations at the B3LYP/6-311G(d,p) and mPW1PBE/6-31G(d) levels. See Figure S8 and Table S1 for each optimized structures.

The $\nu_{\text{C=N}}$ modes observed at 2170 cm\textsuperscript{-1} (LE) and 2175 and 2212 cm\textsuperscript{-1} (CT) in the transient Raman measurements showed not much changes in the simulated Raman spectra by TDDFT except the largely blue-shifted modes obtained from the B3LYP/6-311G(d,p) simulation
results with the twisted DMAP group. Since the changes in the relative intensities and vibrational assignments between the symmetric and asymmetric modes of $v_{C=N}$ appeared not changed, the blue-shifts shown from the B3LYP/6-311G(d,p) simulation results with the twisted DMAP group would not be considered for the evidence of structure identification in the excited state. The red-shifts of $v_{C=N}$ upon the ICT or charge separation in the excited states have been reported by time-resolved infrared absorption measurements.\textsuperscript{16-18} It is interesting to note that another weak symmetric $v_{C=N}$ band appears at 2212 cm\textsuperscript{-1} in the ICT state as shown in Figure 5. The appearance of the $v_s$, $C=N$ mode which is invisible in the S\textsubscript{1}/LE state or S\textsubscript{0} ground state may represent the changes in the molecular structure or symmetry (from “planar” to “twisted”, e.g.) accompanying the ICT.

Based on the TDDFT simulations results, the excited state Raman bands of DCM in the S\textsubscript{1}/LE state at 1436 and 1471 cm\textsuperscript{-1} are assigned as $\delta_{CH_3}$ (ph) and $\delta_{CH_3}$ (ph) + $v_{19b}$ (py), respectively. The major Raman bands in the S\textsubscript{1}/LE state at 1563 (sh), 1580, and 1635 cm\textsuperscript{-1} are assigned as the symmetric and asymmetric $v(C_a=C_b)$ + $v_{8a}$ (ph), and $v_{8a}$ (py), respectively. The S\textsubscript{1}/LE bands at 1156 and 1200 cm\textsuperscript{-1} are assigned as $v_{9a} + \delta_{CH_3}$ (ph) and $v_{9a}$ (ph), respectively, by considering the vibrational mode comparison between the bands at 1139 and 1186 cm\textsuperscript{-1} in the simulated spectrum for the S\textsubscript{1} state (planar) at B3LYP/6-311G(d,p) level and those at 1144 and 1192 cm\textsuperscript{-1} for the ground state. The $v_{9a}$ (ph) mode showed blue-shifts upon the ICT (1200 $\rightarrow$ 1212 cm\textsuperscript{-1}), which was not clearly explained by the DFT simulation results for both twisted structures of DMA or DMAP. Overall, the vibrational frequencies of DCM in the S\textsubscript{1} state (planar) seem to be slightly red-shifted from those obtained from the ground state geometry of DCM in the frequency range of 1500-2300 cm\textsuperscript{-1}. Another medium band at 1495 cm\textsuperscript{-1} in the LE spectrum of DCM in CHCl\textsubscript{3} (see Figure 3(a)) and at $\sim$1500 cm\textsuperscript{-1} (sh) in the LE spectrum in DMSO (see Figure 2(a)) is assigned as the $v_{8b}$ (ph) mode. This band shows no major peak shifts
upon the rotation of the DMA or DMAP group in the excited state according to the TDDFT simulations.

The transient Raman bands of DCM in the S$_1$/CT state were also assigned based on the TDDFT simulation results. The vibrational bands appearing at 1057 and 1288 cm$^{-1}$ in the CT spectrum was assigned as $v_{14}$ (ph) and $v_{15}$ (ph) mode, respectively, which is estimated to appear at 1090 (1095) and 1263 (1267) cm$^{-1}$ for the twisted geometry of DMA group.$^{ii}$ The strong CT band at 1492 cm$^{-1}$ which appeared blue-shifted during the ICT was assigned as $v_{19b}$ (py) + $v_{19a}$ (ph) mode, where the vibrational mode analysis and peak shift were better supported by the twisted geometry of the DMA group in the S$_1$ state. Another medium-strong CT band at 1428 cm$^{-1}$ was assigned as $v_{19a}$ (ph) + $\delta_{CH}$ (py) mode. The skeletal vibrational modes at 1564 (sh), 1579, and 1635 cm$^{-1}$ assigned as the symmetric and asymmetric $\nu$(C$_a$=C$_b$) + $v_{8a}$ (ph), and $v_{8a}$ (py), respectively, for the LE structure, showed no major spectral changes with the DMA rotation. However, it is clear that the symmetrically and asymmetrically coupled vibrations of $\nu$(C$_a$=C$_b$) and $v_{8a}$ (ph) modes break up into the decouple vibrational modes of $\nu_{C=C}$ + $\delta_{CH}$ (C$_a$=C$_b$) and $v_{8a}$ (ph) at 1573 (1575) and 1616 (1621) cm$^{-1}$ as predicted by the TDDFT simulations for the DMAP rotated conformers. The vibrational assignments for the transient Raman bands of DCM obtained in the S$_1$/LE and S$_1$/CT states were summarized in Table S3 in addition to the major vibrational frequencies of DCM obtained from the TDDFT simulations on the planar and “twisted” geometries of DMA and DMAP groups.

$^{ii}$ Frequencies outside the parentheses represent the simulated values at B3LYP/6-311G(d,p) level and those within the parentheses at mPW1PBE/6-31G(d) level.
Figure S11. Simulated Raman spectra and optimized geometries of DCM in the $S_1$ excited state; the TDDFT simulations at the mPW1PBE/6-31G(d) level (solid lines)$^{10}$ and the B3LYP/6-311G(d,p) level (dotted lines) with PCM (DMSO).
Figure S12. Calculated vibrational spectra for the optimized structures of DCM in the $S_1$ excited state from the DFT simulations at (a) B3LYP/6-311G(d,p) and (b) mPW1PBE/6-31G(d) levels. The spectral changes expected for $\nu_{19a}$, $\nu_{19b}$, or $\delta_{CH3}$ modes were displayed with color-codes.
**Figure S13.** Vibrational normal modes of DCM with the twisted geometry of the dimethylamino (DMA) group ($\mu = 90.0^\circ$) obtained from the TD-B3LYP/6-311G(d,p) simulations with PCM (DMSO). The DFT results and vibrational assignments were summarized in Table S3.
Table S3. Comparison between the vibrational frequencies in the excited SRS of DCM and calculated vibrational frequencies from different structures of DCM

| Experimental (DMSO) | B3LYP/6-311G(d,p) | mPW1PBE/6-31G(d) | Vibrational assignments\(^1,2\) |
|---------------------|-------------------|------------------|--------------------------------|
| LE (0.3 ps)         | CT (30 ps)        | planar           | DMA rotated (\(\mu=90.0^\circ\)) | DMAP rotated (\(\delta=89.7^\circ\)) | planar | DMA rotated (\(\mu=90.0^\circ\)) | DMAP rotated (\(\delta=96.4^\circ\)) | |
| - 1057             | -                 | 1090             | 1089             | -                  | 1095 | 1092 | \(\nu_{13}\) (ph) | |
| 1156 1156           | 1139              | 1115             | -                 | 1147              | 1123 | - | \(\nu_{9a} + \delta_{CH_3}\) (ph) | |
| 1200 1212           | 1186              | 1160             | 1164             | 1191              | 1167 | 1156 | \(\nu_{8a}\) (ph) | |
| - 1288             | -                 | 1263             | -                 | -                 | 1267 | - | \(\nu_{14}\) (ph) | |
| 1436 -              | 1466              | 1467             | 1464             | 1469              | 1465 | 1462 | \(\delta_{CH_3}\) (ph) | |
| - 1428             | -                 | 1477             | -                 | -                 | 1485 | - | \(\nu_{19a}\) (ph) + \(\delta_{CH}\) (py) | |
| 1471 -              | 1488              | -                | -                 | 1492              | - | - | \(\delta_{CH_3}\) (ph) + \(\nu_{19b}\) (py) | |
| - 1492             | -                 | 1505             | -                 | -                 | 1511 | - | \(\nu_{19b}\) (py) + \(\nu_{18a}\) (ph) | |
| 1495\(^3\)         | -                 | 1495             | 1523             | -                 | 1501 | 1523 | \(\nu_{8b}\) (ph) | |
| - -                | 1506              | 1512/1515        | 1516             | -                 | 1519 | - | \(\nu_{19a} + \delta_{CH_3}\) (ph) | |
| 1563\(^{ab}\)      | 1564\(^{ah}\)    | 1542             | 1554             | -                 | 1548 | 1561 | \(\nu(C\equiv C) + \nu_{8a}\) (ph), symmetric | |
| - -                | -                 | 1573             | -                | -                 | 1575 | - | \(\nu_{C\equiv C} + \delta_{CH}(C\equiv C)\) | |
| 1580 1579           | 1598              | 1588             | -                 | 1605              | 1596 | - | \(\nu(C\equiv C) + \nu_{8a}\) (ph), asymmetric | |
| - -                | -                 | 1616             | -                | -                 | 1621 | \(\nu_{8a}\) (ph) | |
| 1635 1635           | 1620              | 1624             | 1627             | 1623              | 1626 | 1628 | \(\nu_{8a}\) (py) | |
| 2170 2175           | 2176              | 2178             | 2235             | 2138              | 2141 | 2134 | \(\nu_{8b,C=N}\) | |
| - 2212             | 2201              | 2203             | 2264             | 2164              | 2165 | 2158 | \(\nu_{8b,C=N}\) | |

\(^1\) Vibrational assignments are based on calculated vibrational frequencies in the excited state at the B3LYP/6-311G (d,p) and mPW1PBE/6-31G(d) levels, and frequencies were rescaled with a factor of 0.967.\(^{12}\)

\(^2\) \(\nu\) and \(\delta\) denotes stretching and bending, respectively. The ph and py in parenthesis refer to the benzene and pyran ring, respectively, and \(C_a=C_b\) represents the ethylenic double bond as shown in Figure S6.

\(^3\) observed from CHCl\(_3\) solution

\(^{ab}\) shoulder band
4. FSRS of 4-dimethylamino-4'-nitrostilbene

Figure S14. (a) FSRS of 4-dimethylamino-4'-nitrostilbene in CHCl₃ with 403 nm excitation, (b) simulated Raman spectra for the optimized structures in the ground and excited states by the (TD)DFT method at B3LYP/6-311G(d,p) level, and (c) the major vibrational modes of νC=C and ν8a of phenyls for the planar and twisted nitrophenyl conformers in the excited state (adapted from ref. 19-20).
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