

ARTICLE

Supplementary Information: Twisted-Internal Charge Transfer (TICT) state mechanisms may be less common than expected

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The supplementary electronic information provides additional information on the experimental absorption spectra of CBB and the calculated excited state energies and respective oscillator strengths. We also provide raw data for the Lippert-Mataga graph (Figure 4 of the main text). An additional figure illustrates that the dihedral angle θ_3 is the most meaningful coordinate when characterizing the TICT state. Another figure provides a different illustration of the electron redistribution between ground and excited state near the S_1 state minimum conformation and at the TICT state minimum. Finally, a detailed step-by-step instruction on the computational determination of excitation and emission wavelengths is given.

Table S1 Wavelengths, transition energies, and oscillator strengths obtained from Gaussian fits to the absorption spectra of CBB in cyclohexane and acetonitrile, and from ab initio calculations. Values were averaged for the two solvents.

Additional data tables and figures

We show additional data tables and figures in support of some statement made in the main text where indicated.

1. Absorption spectra and oscillator strengths

The absorption spectra of CBB were recorded in acetonitrile and in cyclohexane (Figure 2 in the main text) and were fitted to nine Gaussian functions.

Integration of the Gaussian fit curves allows us to estimate the oscillator strength, f , of the respective transitions (**Table S1**) using ¹

$$f = 4.31 \times 10^{-9} \frac{cm^2}{L mol} \int \epsilon(\theta) d\theta^*$$

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From **Table S1** it is apparent that all absorption bands in the 200 nm to 500 nm region are due to singlet-singlet transitions. The absorption maximum at 420 nm has been previously attributed to the $S_0 \rightarrow S_1$ transition as described in the main text. The maxima at 341 nm, 314 and 292 nm are tentatively assigned to a vibrational progression ($\nu_{0,1} \approx 2500 \text{ cm}^{-1}$) of the $S_0 \rightarrow S_2$ transition and the maximum at 284 nm could be attributable to either (or both) the $S_0 \rightarrow S_3$ or $S_0 \rightarrow S_4$ transition, which were calculated to be near 295 nm and 291 nm, respectively. Higher lying transitions could not be reliably assigned. Our TD-DFT calculation found over 30 singlet-singlet transitions below 200 nm, and many were nearly degenerate.

The absorption maxima in non-polar cyclohexane and polar acetonitrile are almost identical except for the $S_0 \rightarrow S_1$ transition

	absorption spectrum		ab initio	
	$\lambda_{\text{abs}} / \text{nm} ; E_{\text{abs}} / \text{cm}^{-1}$	f	$\lambda_{\text{abs}} / \text{nm} ; E_{\text{abs}} / \text{cm}^{-1}$	f
$S_0 \rightarrow S_1 (v'' \rightarrow v')$	426; 23400	0.02	426; 23400	0.64
$S_0 \rightarrow S_2 (0 \rightarrow 0)$	341; 29400	0.001	311; 32100	0.26
$S_0 \rightarrow S_2 (0 \rightarrow 1)$	314; 31900	0.064		
$S_0 \rightarrow S_2 (0 \rightarrow 2)$	292; 34200	0.002		
$S_0 \rightarrow S_3 / S_4$	284; 35200	0.016	295; 34000 / 291; 34300	0.17 / 0.28
$S_0 \rightarrow S_5$	255; 39300	0.049		
$S_0 \rightarrow S_6$	236; 42300	0.029		
$S_0 \rightarrow S_7$	230; 43500	0.060		
$S_0 \rightarrow S_8$	203; 49300	0.204		

in which we see a small difference depending on the solvent $\lambda_{\text{abs}}(\text{cyclohexane}) = 433 \text{ nm}$ and $\lambda_{\text{abs}}(\text{MeCN}) = 426 \text{ nm}$.

2. EEM Spectra and Analysis

Table SII shows peak maxima extracted by Gaussian fitting to the raw EEM data for the 21 mixtures of acetone and toluene. As a function of the volume fraction of acetone, we provide for the S_1 state and the S_2 state:

- the orientation polarization, Δf , calculated as described in the main text,
- the excitation and emission wavelengths, and
- the calculated Stokes shifts for the first excited state, V_{SS1} , and the second excited state, V_{SS2} .

Table SIII provides the same information for the five neat solvents that were added in this study. It supplements Table I in the main text. The data of Table SIII are displayed in Figure 4 of the main text.

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Table SII Raw EEM data for 21 mixtures of acetone and toluene: Volume fraction of acetone, orientation polarization, Δf , calculated as described in the main text, excitation and emission wavelengths and calculated Stokes shifts, V_{SS} , (in cm^{-1}) for S_1 state and S_2 state. Wavelength data are accurate to within 0.5 nm.

Volume fraction of acetone	Δf	$\lambda_{Ex.}$ (nm)	$\lambda_{Em.}$ (nm)	V_{SS1}	$\lambda_{Ex.}$ (nm)	$\lambda_{Em.}$ (nm)	V_{SS2}
0.00	0.01 2	323.7	568.0	13290	439.0	567.9	517 0
0.05	0.03 1	336.5	574.8	12319	439.1	574.8	537 6
0.10	0.05	337.8	579.1	12332	439.2	579.2	550 1
0.15	0.06 7	338.8	584.3	12405	439.2	584.4	565 9
0.20	0.08 4	339.2	587.5	12458	438.8	587.6	577 1
0.25	0.10 0	339.5	590.0	12502	438.8	590.0	584 2
0.30	0.11 6	339.7	593.2	12576	438.6	593.1	594 1
0.35	0.13 1	340.1	594.8	12592	438.5	594.5	598 8
0.40	0.14 5	340.0	596.5	12648	438.2	596.6	605 9
0.45	0.15 9	341.0	603.6	12758	437.4	603.6	629 6
0.50	0.17 2	340.6	603.1	12778	437.2	603.3	629 5
0.55	0.18 -	340.8	605.5	12831	436.3	605.0	638 -

Table SIII Raw EEM data for 5 neat solvents: Orientation polarization, Δf , calculated as described in the main text, excitation and emission wavelengths and calculated Stokes shifts, V_{SS} , (in cm^{-1}) for S_1 state and S_2 state. Wavelength data are accurate to within 0.5 nm.

	Δf	$\lambda_{Ex.}$ (nm)	$\lambda_{Em.}$ (nm)	V_{SS1}	$\lambda_{Ex.}$ (nm)	$\lambda_{Em.}$ (nm)	V_{SS2}
Acetonitrile	0.30 5	312.40	619.1	15859	432.4	619.1	697 4
Cyclohexane	0.00 0	317.292	533.8	12784	441.8	533.8	389 9
Chloroform	0.14 8	314.218	592.3	14941	445.6	592.3	555 6

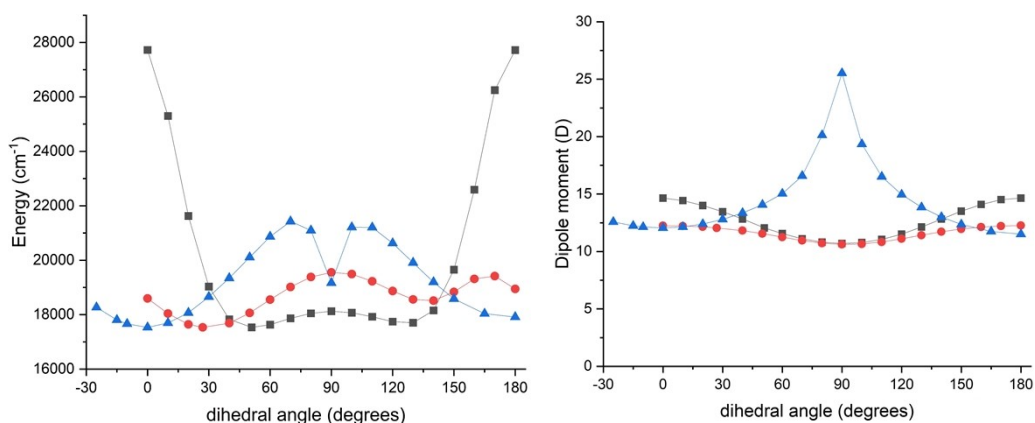


Figure S1: S_1 -state energy (left) and dipole moment (right) of CBB in acetone calculated as functions of dihedral angles θ_1 (black squares), θ_2 (red circles), and θ_3 (blue triangles). The respective other coordinates were held at their S_1 state minimum values, i.e. $\theta_1 = 52^\circ$, $\theta_2 = 28^\circ$, and $\theta_3 = 0$ degrees. Only variation of θ_3 leads to a large increase in dipole moment and a narrow energy minimum when the angle is close to 90 degrees.

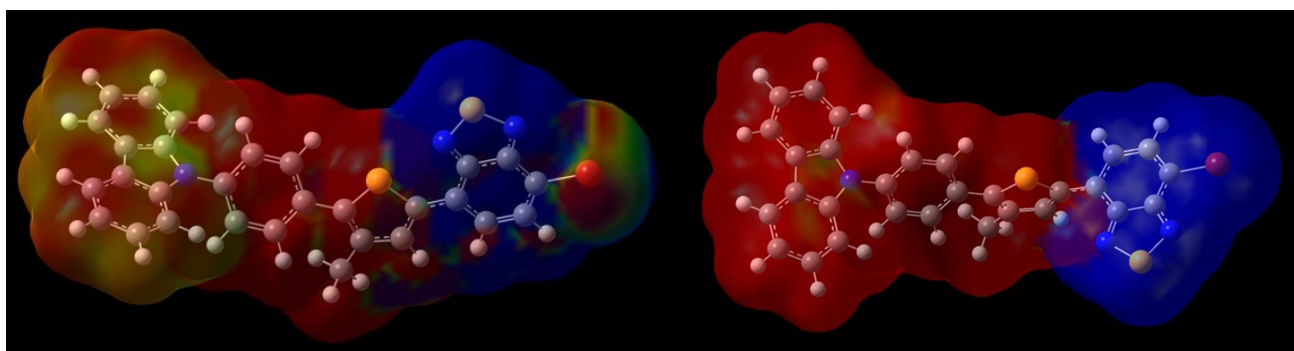


Figure S2: Electron density difference between excited state and ground state projected onto the SCF electron density surface for CBB in acetone when dihedral angle θ_3 is at (left) 0° and (right) 90° .

3. Determination of S_1 -state energies and dipole moments as a functions of dihedral angles

Figure S1 shows the energy and dipole moments of CBB in its excited S_1 -state in acetone. The values are calculated as described in the main text. All coordinates, i.e. bond lengths and angles, were held at the S_1 state minimum values, i.e. $\theta_1 = 52^\circ$, $\theta_2 = 28^\circ$, and $\theta_3 = 0$ degrees, while only the dihedral angles θ_1 , θ_2 , and θ_3 were scanned in turn. The computational experiment showed that only a change of dihedral angle θ_3 resulted in a large increase in dipole moment and a narrow energy minimum, i.e. this angle is the most meaningful reaction coordinate when trying to characterize the TICT state at which $\theta_3 = 90$ degrees.

4. Charge distribution of CBB in its excited state

Figure S2 provides another illustration of the dramatic difference in charge distribution in the CBB excited state when dihedral angle θ_3 is at either zero degrees or at right angles. The difference in charge distribution between the S_0 state and S_1 state is shown as a blue-red colour map on top of the electron density iso-surface. If θ_3 is close to zero degrees, the electron density shifts from the phenylthiophene (PT) bridge and from the bromine atom to the benzothiadiazole (BTD) acceptor group. In the TICT state ($\theta_3 = 90^\circ$) we observe the expected electron redistribution from the donor and linker groups to the

benzothiadiazole (BTD) acceptor group. The two conformations correspond to the two lower panels in Figure 7 of the main text.

5. Step-by-Step ab initio calculation of the energies and dipoles

The ab initio calculations were performed using Gaussian 16 to identify the molecular properties that are responsible for the observed solvatochromic shift.² We followed the procedure described in the Gaussian application notes by Guido and Caprasecca.³⁻⁷ The energy calculations were performed in four steps as shown in **Figure S3**. We determine the following molecular properties:

- (1) The S_0 -state conformation and energy of CBB in the Franck-Condon region. The molecular structure was optimized in the gas phase and in acetone and toluene solvent environments using density functional theory with the B3LYP/6-31+G(d,p) functional and basis set⁸ and the integral equation formalism variant of the Polarizable Continuum Model, IEFPCM.⁹

```
#p opt b3lyp/6-31+g(d,p) scrf=(iefpcm,
solvent=acetone) polar
```

The optimized ground state configuration was then used to calculate the ground state dipole moments using DFT with CAM-B3LYP/6-31+G(d,p).

(2) The S_1 excited state energies and S_1 dipole moments determined in the same Franck-Condon region and in a dielectric continuum but without the reaction field. In the example below, the calculation includes four singlet excited states; the energy is determined for the first excited state (root=1). This S_1 excited state is calculated using the CAM-B3LYP/6-31+G(d,p) model with the corrected Linear Response, cLR by Caricato et al.⁴ (PisaLR) where the solvent environment is “frozen” to reflect the near-instantaneous nature of the excitation process using IOP(10/74=10).

```
#p td=(singlets,nstates=4,root=1,noneq)
cam-b3lyp/6-31+g(d,p)/def2sv
scrfl=(solvent=acetone,pisalr)
iop(10/74=10)
```

This calculation also provided the excitation energy from which the TD-DFT ground state energy was obtained by subtracting the excitation energy from the S_1 energy (Table III of the main text). The S_0 ground state energy for CBB in the gas phase that was obtained in this way was used as a reference for all other energy values in the main text.

(3) The geometry of the molecule once it is relaxed to its global minimum on the S_1 excited state potential energy surface. We perform a full geometry optimization of the isolated molecule and of the molecule in the two solvent environments using TD-DFT² and the CAM-B3LYP/6-31+G(d,p) (IEF-PCM) model.^{8,10} Here, the geometry of the CBB molecule is optimized in the first excited state (root=1).

```
#p opt td=(singlets,nstates=1,root=1,eqsolv)
cam-b3lyp/6-31+g(d,p)/def2sv
scrfl=(iefpcm,solvent=acetone)
polar
```

In this step, the solvent is equilibrated with solute in the excited state (eqsolv).

(4) The ground and S_1 excited state energies of CBB in the geometry corresponding to the potential energy minimum of the S_1 state. Their difference was determined in gas phase and in the acetone and toluene solvent environments. The calculation was done in two steps. In Step 4A, the reaction field of the solute must converge with the optimized geometry for the solute in the first excited state. As in step (2) the state-specific equilibrium solvation of the excited state at its equilibrium geometry (IOP(10/74=20)) is determined. The solvation correction needs to be saved for use in the next step (nonequilibrium=save).

```
#p opt td=(singlets,nstates=4,root=1,eqsolv)
cam-b3lyp/6-31+g(d,p)/def2sv
scrfl=(pisalr,solvent=acetone,read,nonequilibrium=save)
iop(10/74=20)
```

In the output file of this job, the total energy of the molecule which is equilibrated with solvent in the excited state before emission based on the corrected linear response can be found in the section “PCM State-Specific 1st Order Perturbation Theory - Equilibrium solvation”.

In Step 4B, the energy of the ground state is determined using the first excited state optimized geometry

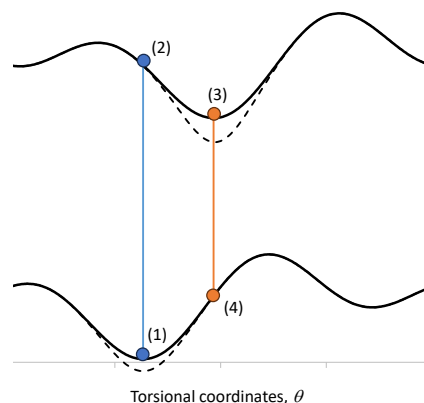


Figure S3 Energies were determined for the ground state, S_0 , and the excited state, S_1 , in, both the Franck-Condon Region (1) and (2) at the potential energy minimum of the S_1 state, (3) and (4), respectively. The calculations were performed with TD-DFT using CAM-B3LYP/6-31G+pd as described in the text.

(geom=checkpoint) via a non-equilibrium solvation calculation in solution. In addition, the solvent reaction field in equilibrium with the first excited state density (nonequilibrium=read, guess=read) is also calculated. The geometry of the molecule and its reaction field of the solvent are obtained from the corrected linear-response excited state calculation (oldchk=step4A.chk) above.

```
--link1--
%oldchk=step4A.chk
%chk=step4B.chk

#p cam-b3lyp/6-31+g(d,p)/def2sv
scrfl=(solvent=acetone,nonequilibrium=read)
guess=read NoSymm
geom=checkpoint polar
```

The ground state energy in the output file is described in the “SCF Done: E(RCAM-B3LYP)” section. The emission energy is obtained by subtracting the energy of step 4B from step 4A. The entire procedure is derived from an article published by Ciro Guido and Stefano Caprasecca.³⁻⁷

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