

Electronic Supplementary Material

**Solvent Effects on the Intramolecular Charge Transfer  
Excited State of 3CzClIPN: A Broadband Transient  
Absorption Study**

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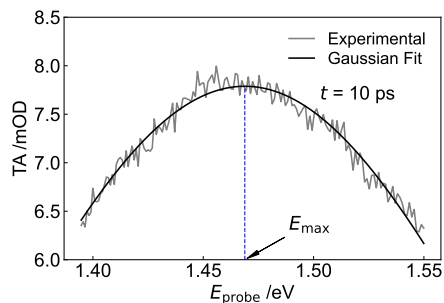
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# 1 Analysis of ultrafast spectral shifts

To analyse the temporal dependence of the spectral shifts, we first extracted the peak of the TA spectrum as a function of the time delay,  $t$ , as illustrated in Fig. S1. The probe photon energy corresponding to the TA maximum,  $E_{max}$ , was obtained by fitting TA data (grey trace) with a Gaussian Function (yellow trace) at each  $t$ .



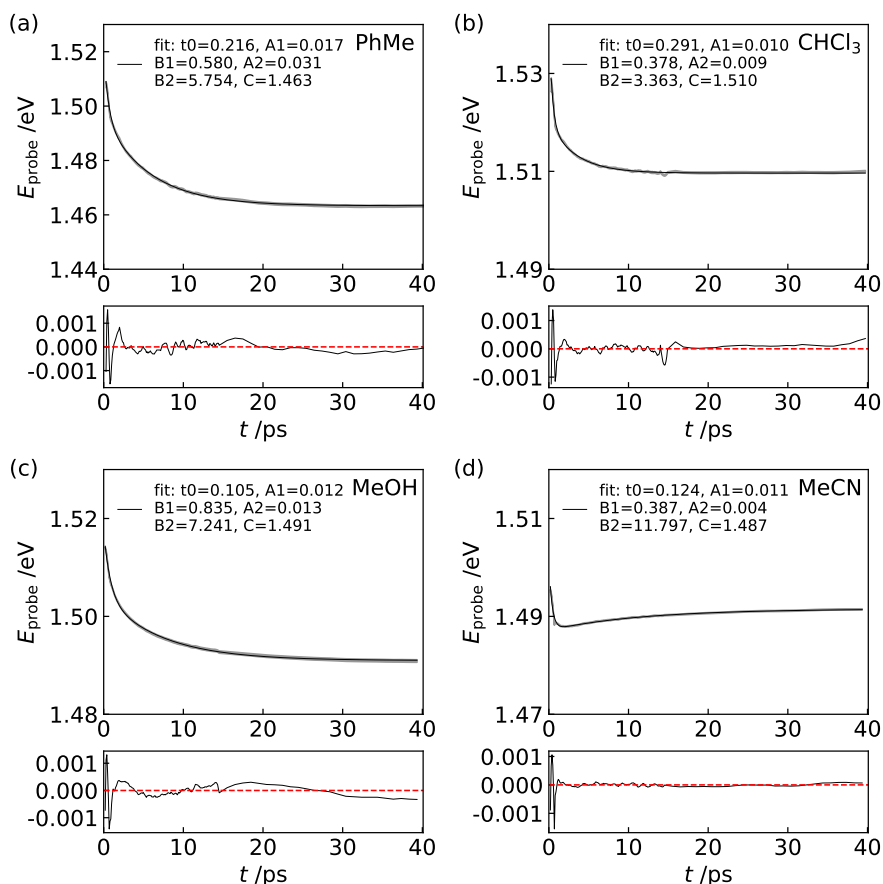
**Fig. S1** An example of Gaussian fitting analysis of the TA spectrum of 3CzClIPN in PhMe at  $t = 10$  ps. Raw TA data near the maximum (grey trace) and Gaussian fit (black trace) are shown. The position of the maximum is marked as  $E_{max}$ .

After this fitting procedure, the position of maximum was plotted as a function of  $t$  and fitted with the following exponential functions  $f(t)$  and  $g(t)$ ,

$$f(t) = A_1 \cdot \exp\left[\frac{-(t-t_0)}{B_1}\right] + A_2 \cdot \exp\left[\frac{-(t-t_0)}{B_2}\right] + A_3 \quad (1)$$

$$g(t) = A_1 \cdot \exp\left[\frac{-(t-t_0)}{B_1}\right] + A_2 \cdot \left\{1 - \exp\left[\frac{-(t-t_0)}{B_2}\right]\right\} + A_3 \quad (2)$$

$B_1$  and  $B_2$  are time constants,  $A_1$  and  $A_2$  are amplitudes, and  $A_3$  is an offset.  $f(t)$  was used to describe the time dependence in toluene (PhMe), chloroform ( $\text{CHCl}_3$ ) and methanol (MeOH), and  $g(t)$  was implemented for acetonitrile (MeCN).

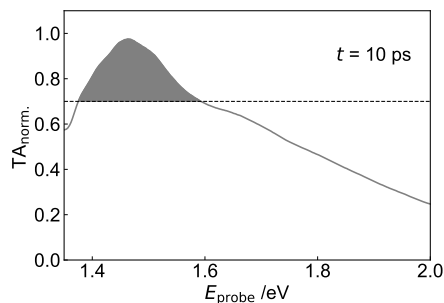


**Fig. S2** Analysis of temporal dependence of the TA maximum of 3CzCIIPN in PhMe (a), CHCl<sub>3</sub> (b), MeOH (c), and MeCN (d). The top graphs present exponential fits (black traces) of the temporal profiles (grey traces). The widths of the grey traces refer to the standard deviations of the mean values in Gaussian fit, and the panels at the bottom correspond to the obtained residuals in exponential fit.

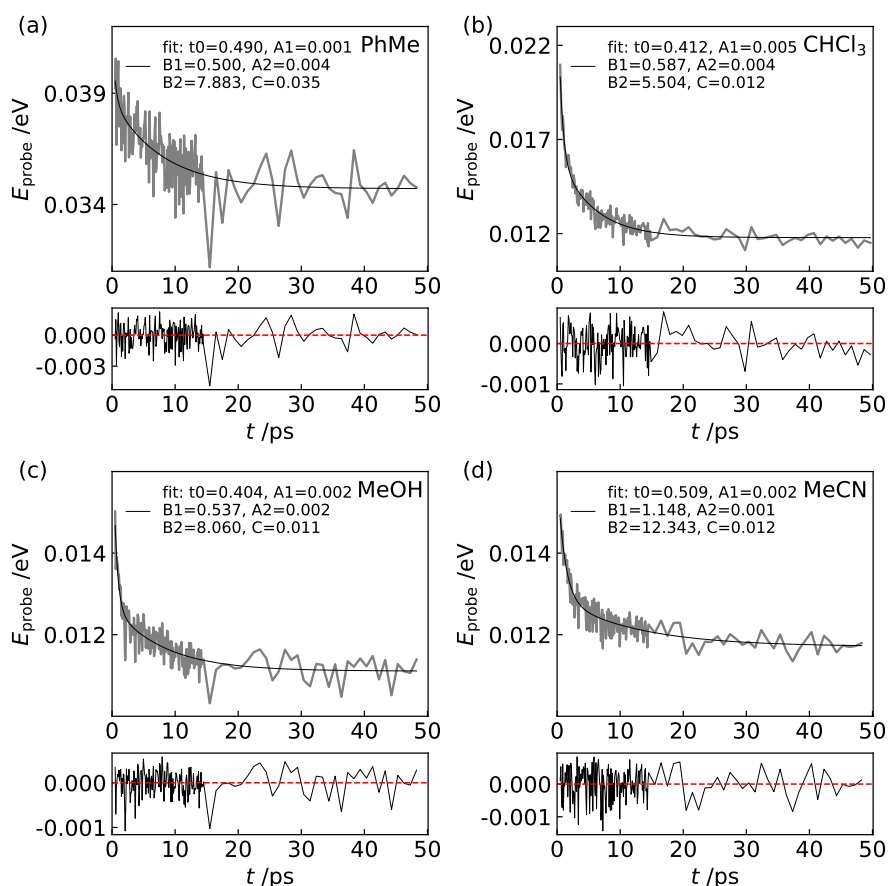
## 2 Analysis of ultrafast spectral narrowing

To examine the phenomenon of spectral narrowing, we integrated the area under the curve of normalized spectra over 0.7 to focus on the main peak using the trapezoidal method of integration. Subsequently, the acquired area data were plotted as a function of  $t$  and fitted with an exponential function  $h(t)$ .

$$h(t) = A_1 \cdot \exp\left[-\frac{(t-t_0)}{B_1}\right] + A_2 \cdot \exp\left[-\frac{(t-t_0)}{B_2}\right] + A_3 \quad (3)$$



**Fig. S3** An example of the area calculation for a TA spectrum of 3CzCIIPN in PhMe at  $t = 10$  ps. The area selected beneath the raw data (grey trace) is depicted in grey. The calculated value is 0.0358 eV.

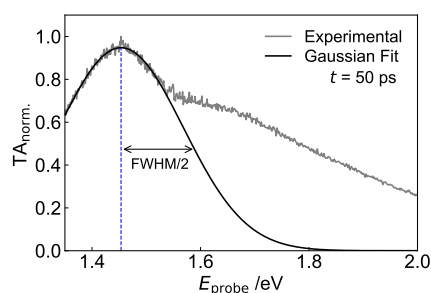


**Fig. S4** Analysis of temporal dependence of the area under the TA spectrum of 3CzClIPN in PhMe (a),  $\text{CHCl}_3$  (b), MeOH (c), and MeCN (d). The top graphs present exponential fits (black traces) of the temporal profiles (grey traces). The bottom panels correspond to the obtained residuals.

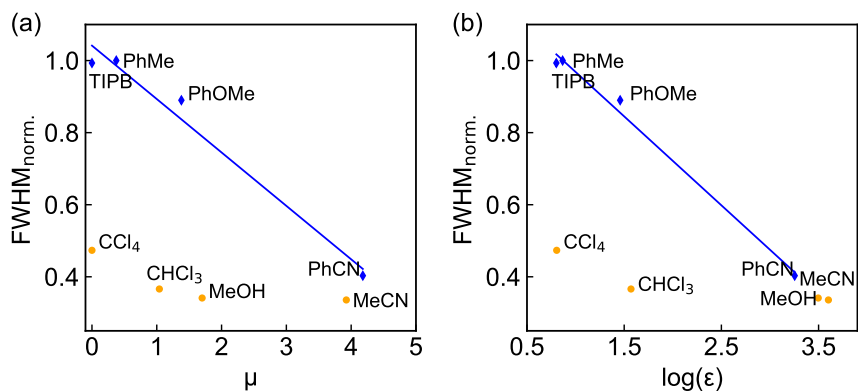
### 3 Analysis of spectral broadening via Gaussian fitting

The spectral width can be estimated either by calculating areas as discussed in the previous section or by determining the peak width through Gaussian fitting. Fig. S5 depicts typical results for a TA spectrum of 3CzClIPN in PhMe. We have normalized the obtained full width at half maximum (FWHM) values by the value obtained in PhMe. Fig. S6 shows the FWHM values as functions of the solvent's molecular dipole moment (a) and dielectric constant (b).

As can be observed, the results obtained using FWHM and the peak's area are, as expected, in excellent agreement.



**Fig. S5** An example of the full width at half maximum (FWHM) calculation for a TA spectrum of 3CzCIIPN in PhMe at  $t = 50$  ps. The raw data (grey trace) is fitted by the Gaussian function (black trace), obtaining  $\text{FWHM} = 0.271 \text{ eV} \pm 0.002 \text{ eV}$ .

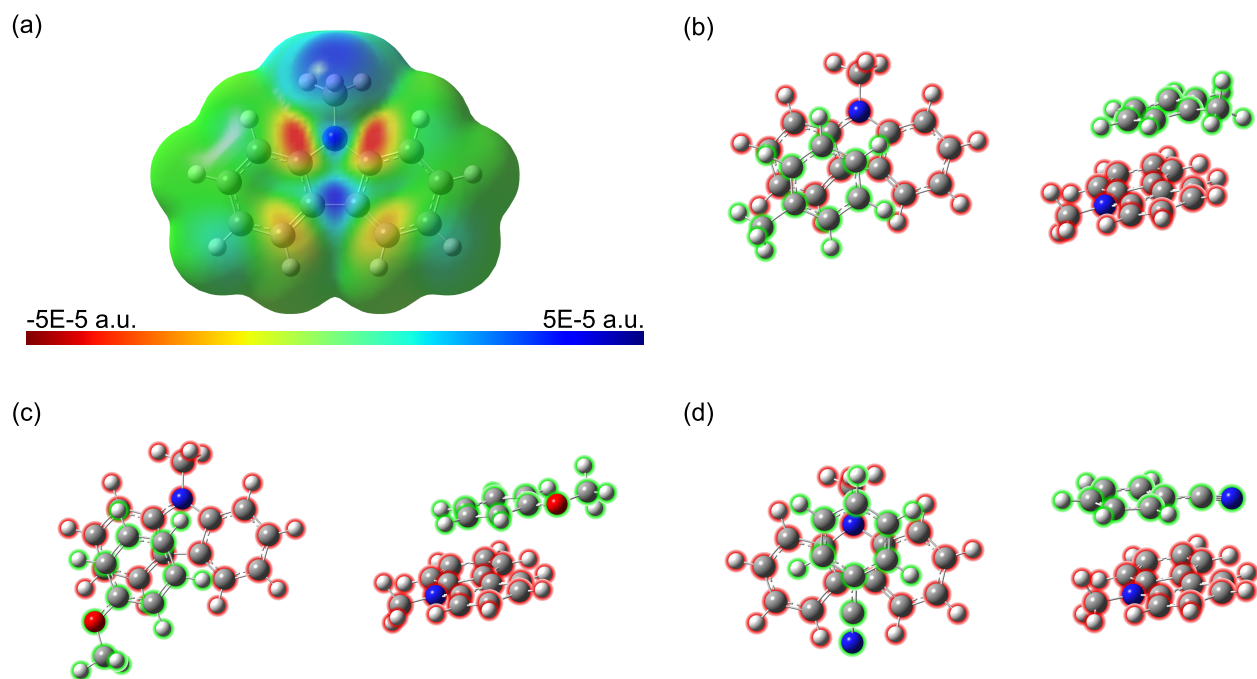


**Fig. S6** FWHM in Gaussian fit on the TA peak as a function of the solvent's molecular dipole moment (a) and dielectric constant (b).

## 4 Quantum chemistry calculations

Structural models of PhMe, PhOMe, PhCN, and CzMe were generated with GaussView and optimized at the B3LYP/6-311+G(d) level using the Gaussian 16 software package<sup>1-3</sup>. These models were built upon the initial optimization of CzMe-Benzene systems, where Counterpoise and Empirical Dispersion Corrections were applied. We optimized separately CzMe and benzene and then placed benzene parallel to the central five-membered ring structure of CzMe. We further optimized the structure of CzMe-PhMe/PhOMe/PhCN systems after introducing side groups (-Me, -OMe, and -BN) in the benzene fragment. These groups were added at the opposite site to the Me group in CzMe in order to minimize steric effects. Based on these structures, 'Charge = 1 Multiplicity = 2' was applied for Cz<sup>+</sup>Me act as a model system for the excited Cz<sup>+</sup> group(s) in the ICT state of 3CzCIIPN. We obtained the following corrected interaction energies: Cz<sup>+</sup>Me-PhMe = -12.03 kcal mol<sup>-1</sup>, Cz<sup>+</sup>Me-PhOMe = -15.30 kcal mol<sup>-1</sup>, and Cz<sup>+</sup>Me-PhCN = -11.26 kcal mol<sup>-1</sup>.

The optimization of the single Cz<sup>+</sup>Me molecule began with the pre-optimized CzMe structure, employing the same B3LYP/6-311+G(d) level of theory. The TD-DFT calculation was conducted, and a state with a transition energy of 1.6987 eV, similar to what was observed in the TA spectrum, was specifically chosen. This state was found to be the first excited state presenting a strong oscillator strength ( $f \approx 0.1$ ), and it was used to generate the electron density difference (EDD) map shown in Fig. S7(a).



**Fig. S7** (a) Electron density difference (EDD) map obtained from the difference in electron density of the selected electronic excited state and ground state of  $\text{Cz}^+\text{Me}$ . The red areas correspond to electron deficiency and the blue areas correspond to electron abundance. (b-d) Optimized molecular structures of  $\text{Cz}^+\text{Me-PhMe}$  (b),  $\text{Cz}^+\text{Me-PhOMe}$  (c),  $\text{Cz}^+\text{Me-PhCN}$  (d) systems illustrated from two views. For clarity, the  $\text{Cz}^+\text{Me}$  and solvent molecules were highlighted in red and green, respectively.

## Notes and references

- [1] M. Streiter, T. G. Fischer, C. Wiebeler, S. Reichert, J. Langenickel, K. Zeitler and C. Deibel, *J. Phys. Chem. C*, 2020, **124**, 15007–15014.
- [2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji *et al.*, *Gaussian 16 Revision C.01*, 2016, Gaussian Inc. Wallingford CT.
- [3] R. Dennington, T. A. Keith and J. M. Millam, *GaussView Version 6*, 2019, Semichem Inc. Shawnee Mission KS.