Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information - Understanding the interplay between solvent and nuclear rearrangements in the negative solvatochromism of a push-pull flexible quinolinium cation

Oliviero Cannelli,[†] Tommaso Giovannini,[†] Alberto Baiardi,[†] Benedetta Carlotti,[¶] Fausto Elisei,[¶] and Chiara Cappelli[*,†]

[†]*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*

[‡]*Laboratoire de Spectroscopie Ultrarapide, ISIC-FSB, École Polytechnique Fédérale de Lausanne, CH 1015 Lausanne, Switzerland*

[¶]*Department of Chemistry, Biology and Biotechnology and Centro di Eccellenza sui Materiali Innovativi Nanostrutturati (CEMIN), University of Perugia, via Elce di Sotto, 8, 06123 Perugia, Italy*

E-mail: chiara.cappelli@sns.it

In Fig. S1 labels of the π-chain atoms included in the calculation of BLA and DI are reported.

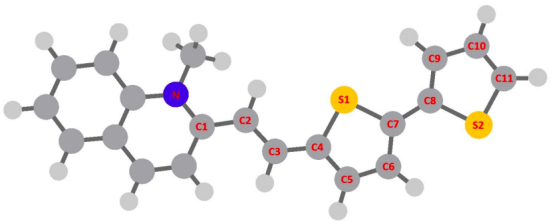


Figure S1: Atoms labeling of the molecular backbone chain

Table S1: Conformers' bond length and BLA (Å) in vacuum, evaluated with the B3LYP functional

	conf 1	conf 2	conf 3	conf 4
single bond length				
C_1-C_2	1.434	1.434	1.434	1.434
C_3-C_4	1.418	1.415	1.419	1.415
C_5-C_6	1.395	1.398	1.396	1.398
C_7-C_8	1.439	1.439	1.438	1.437
C_9-C_{10}	1.416	1.416	1.416	1.416
double bond length				
$N=C_1$	1.374	1.373	1.374	1.373
$C_2=C_3$	1.378	1.377	1.378	1.377
$C_4=C_5$	1.400	1.399	1.399	1.399
$C_6=C_7$	1.403	1.399	1.402	1.398
$C_8=C_9$	1.389	1.389	1.388	1.388
$C_{10}=C_{11}$	1.375	1.375	1.376	1.376
BLA	0.034	0.035	0.034	0.035

Table S2: Conformers' bond length and BLA (Å) in acetonitrile, evaluated with the B3LYP functional

B3LYP				
single bond length				
C_1-C_2	1.444	1.444	1.444	1.444
C_3-C_4	1.431	1.426	1.431	1.427
C_5-C_6	1.404	1.406	1.405	1.407
C_7-C_8	1.447	1.447	1.445	1.444
C_9-C_{10}	1.422	1.421	1.422	z 1.421
double bond length				
$N=C_1$	1.358	1.358	1.357	1.367
$C_2=C_3$	1.368	1.368	1.368	1.368
$C_4=C_5$	1.393	1.393	1.393	1.392
$C_6=C_7$	1.394	1.391	1.394	1.391
$C_8=C_9$	1.385	1.385	1.384	1.385
$C_{10}=C_{11}$	1.373	1.373	1.373	1.373
BLA	0.051	0.051	0.051	0.049
Relative BLA (%)	50	46	50	40

Table S3: Conformer 4 bond length and BLA (Å) in vacuum, evaluated with the CAM-B3LYP functional

CAM-B3LYP				
single bond length				
C_1-C_2	1.439	1.439	1.439	1.439
C_3-C_4	1.425	1.421	1.424	1.421
C_5-C_6	1.399	1.402	1.399	1.402
C_7-C_8	1.448	1.447	1.446	1.445
C_9-C_{10}	1.418	1.418	1.418	1.417
double bond length				
$N=C_1$	1.367	1.367	1.367	1.357
$C_2=C_3$	1.363	1.363	1.363	1.363
$C_4=C_5$	1.387	1.386	1.387	1.386
$C_6=C_7$	1.388	1.384	1.388	1.384
$C_8=C_9$	1.375	1.376	1.376	1.376
$C_{10}=C_{11}$	1.366	1.366	1.366	1.366
BLA	0.052	0.052	0.051	0.053

Table S4: Conformer 4 bond length and BLA (Å) in acetonitrile, evaluated with the CAM-B3LYP functional

CAM-B3LYP				
single bond length				
C_1-C_2	1.453	1.453	1.453	1.453
C_3-C_4	1.442	1.437	1.442	1.437
C_5-C_6	1.410	1.412	1.411	1.412
C_7-C_8	1.455	1.454	1.453	1.452
C_9-C_{10}	1.424	1.423	1.423	1.423
double bond length				
$N=C_1$	1.350	1.350	1.350	1.350
$C_2=C_3$	1.351	1.351	1.351	1.351
$C_4=C_5$	1.379	1.378	1.378	1.377
$C_6=C_7$	1.378	1.376	1.379	1.376
$C_8=C_9$	1.372	1.373	1.372	1.373
$C_{10}=C_{11}$	1.364	1.364	1.364	1.364
BLA	0.071	0.071	0.071	0.070
Relative BLA (%)	37	37	39	32

Even if the length of the $N-C_1$ bond suggests to classify it as a double bond, the characteristic DI seems to be compatible to that of a single bond. However, coherently to the calculation performed for the BLA, also in DIA the $N-C_1$ bond has been included in the double bond length section. The lower value of the $N-C_1$ bond is compatible with the charge transfer nature of the GS resonance form, which has a localized negative charge on the nitrogen atom (lowering the DI value, i.e. the shared electrons, and increasing the Localization Index).

Table S5: Conformer 4 DI and DIA in vacuum, evaluated with the B3LYP functional

	B3LYP
single bond strength	
C_1-C_2	1.19
C_3-C_4	1.27
C_5-C_6	1.36
C_7-C_8	1.18
C_9-C_{10}	1.29
double bond strength	
$N=C_1$	1.09
$C_2=C_3$	1.49
$C_4=C_5$	1.35
$C_6=C_7$	1.37
$C_8=C_9$	1.42
$C_{10}=C_{11}$	1.51
DIA	0.11

Table S6: Conformer 4 DI and DIA in acetonitrile, evaluated with the B3LYP functional

	B3LYP
single bond strength	
C_1-C_2	1.15
C_3-C_4	1.22
C_5-C_6	1.32
C_7-C_8	1.16
C_9-C_{10}	1.27
double bond strength	
$N=C_1$	1.11
$C_2=C_3$	1.54
$C_4=C_5$	1.39
$C_6=C_7$	1.41
$C_8=C_9$	1.45
$C_{10}=C_{11}$	1.54
DIA	0.18
Relative DIA (%)	64

Table S7: Conformer 4 DI and DIA in vacuum, evaluated with the CAM-B3LYP functional

	CAM-B3LYP
single bond strength	
C_1-C_2	1.15
C_3-C_4	1.22
C_5-C_6	1.32
C_7-C_8	1.14
C_9-C_{10}	1.27
double bond strength	
$N=C_1$	1.11
$C_2=C_3$	1.54
$C_4=C_5$	1.40
$C_6=C_7$	1.42
$C_8=C_9$	1.46
$C_{10}=C_{11}$	1.55
DIA	0.19

Table S8: Conformer 4 DI and DIA in acetonitrile, evaluated with the CAM-B3LYP functional

	CAM-B3LYP
single bond strength	
C_1-C_2	1.11
C_3-C_4	1.19
C_5-C_6	1.30
C_7-C_8	1.12
C_9-C_{10}	1.26
double bond strength	
$N=C_1$	1.12
$C_2=C_3$	1.58
$C_4=C_5$	1.42
$C_6=C_7$	1.45
$C_8=C_9$	1.48
$C_{10}=C_{11}$	1.56
DIA	0.24
Relative DIA (%)	26

The computed D_{CT} and μ_{CT} for the two functional B3LYP and CAM-B3LYP, both in vacuo and acetonitrile, are reported the following Tables for the different conformers.

Table S9: B3LYP and CAM-B3LYP D_{CT} (Å) and μ_{CT} (Debye) values for conformer 1 in vacuo and MeCN

	B3LYP		CAM-B3LYP	
Conformer 1	D_{CT}	μ_{CT}	D_{CT}	μ_{CT}
Vacuum	2.934	6.02	3.239	8.624
MeCN	4.593	12.651	3.986	12.855
Relative Variation	57%	110%	23%	49%

Table S10: B3LYP and CAM-B3LYP D_{CT} (Å) and μ_{CT} (Debye) values for conformer 2 in vacuo and MeCN

	B3LYP		CAM-B3LYP	
Conformer 2	D_{CT}	μ_{CT}	D_{CT}	μ_{CT}
Vacuum	2.851	5.901	3.068	8.174
MeCN	4.298	11.659	3.803	12.065
Relative Variation	51%	98%	24%	48%

Table S11: B3LYP and CAM-B3LYP D_{CT} (Å) and μ_{CT} (Debye) values for conformer 3 in vacuo and MeCN

	B3LYP		CAM-B3LYP	
Conformer 3	D_{CT}	μ_{CT}	D_{CT}	μ_{CT}
Vacuum	2.933	6.018	3.226	8.456
MeCN	4.639	12.763	4.012	12.863
Relative Variation	58%	112%	24%	52%

Table S12: B3LYP and CAM-B3LYP D_{CT} (Å) and μ_{CT} (Debye) values for conformer 4 in vacuo and MeCN

	B3LYP		CAM-B3LYP	
Conformer 4	D_{CT}	μ_{CT}	D_{CT}	μ_{CT}
Vacuum	2.895	6.028	3.042	7.928
MeCN	4.377	11.882	3.829	11.966
Relative Variation	51%	97%	26%	51%

VTs for the four most stable conformers in vacuo and acetonitrile are reported in the following table using the CAM-B3LYP functional (6-31+G* basis set). The results are are very similar in all the cases.

Table S13: CAM-B3LYP VTs (nm) for the 4 conformers in vacuo and MeCN

	VT	
	vacuum	MeCN
Conformer 1	471	449
Conformer 2	465	446
Conformer 3	476	455
Conformer 4	470	455

In figure S2 are compared the TD—AH spectra of the four conformers obtained at 0 K in vacuo, each one shifted for its 0-0 energy. All of them are very similar, with a small difference for conformer 1 which, however, contributes less than 2% in vacuo.

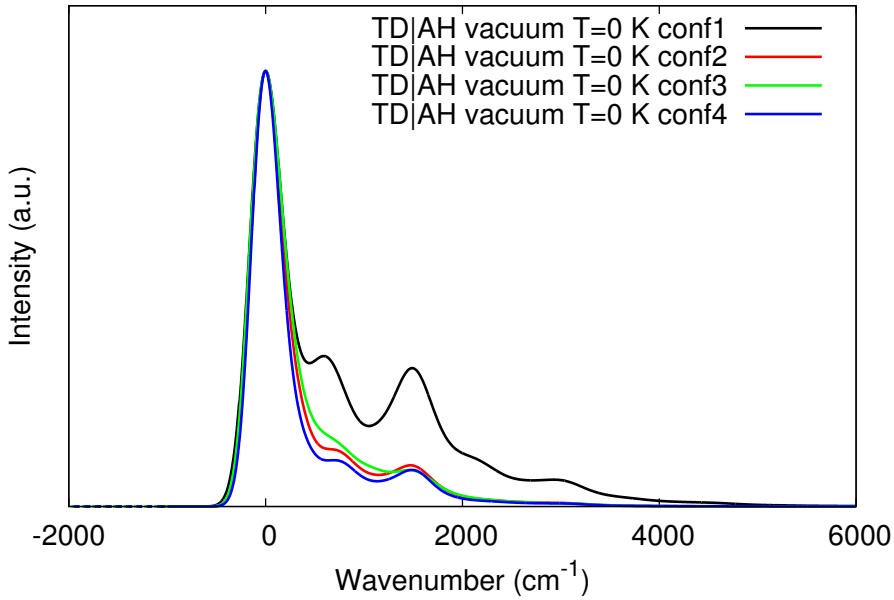


Figure S2: Comparison of TD AH spectra of the four conformers at 0 K in vacuo. Calculations were performed in internal coordinates by using B3LYP (GS frequencies) and CAM-B3LYP (0-0 energy and ES frequencies). Spectra are shifted with respect to the their 0-0 transition

The comparison between the computation of Time-Independent (TI) and Time-Dependent (TD) vibronic spectra is reported in Fig. S3 for conformer 4, where both spectra have been shifted for its 0-0 transition energy. The two spectra give the same prediction, although the TI approach provides further information about the most intense transitions that contribute to the band. The TD spectrum has been reported using a Gaussian broadening with Half Width at Half Maximum (HWHM) of 135 cm^{-1}, while, in the TI case, the stick spectrum is shown.

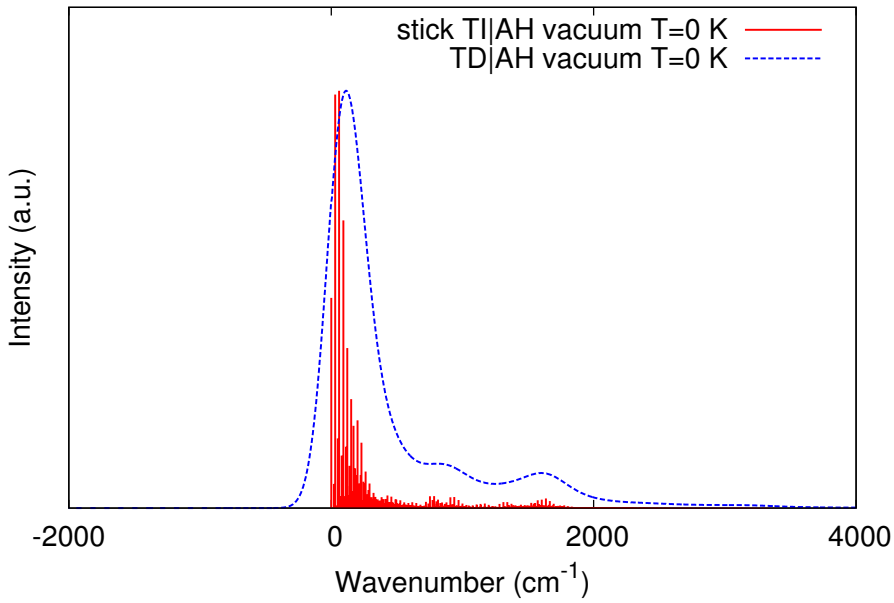
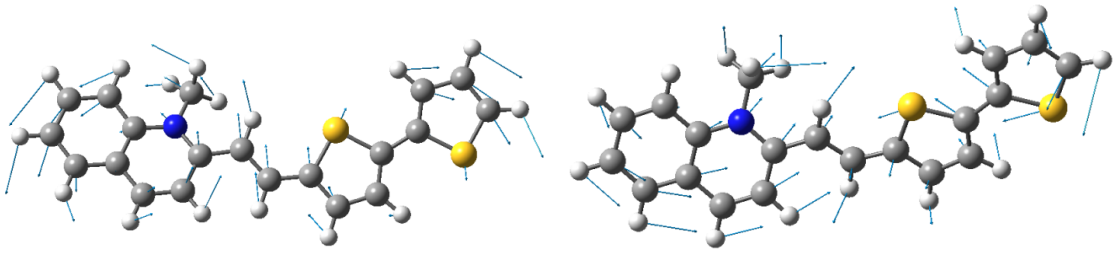


Figure S3: Comparison of TI and TD AH spectra at 0 K in vacuo. Calculations were performed in internal coordinates by using B3LYP (GS frequencies) and CAM-B3LYP (0-0 energy and ES frequencies). Both spectra are shifted with respect to the 0-0 transition. Data refer to conformer 4.

The main transitions are found to be excitation from the GS ground level to ES ground and excited vibrational levels, assigned to specific low frequency normal modes, particularly of 29.93 cm^{-1} and 141.74 cm^{-1}. These modes correspond to an overall distortion of the molecules. A graphical representation of these modes is given as ESI (Fig. S4).

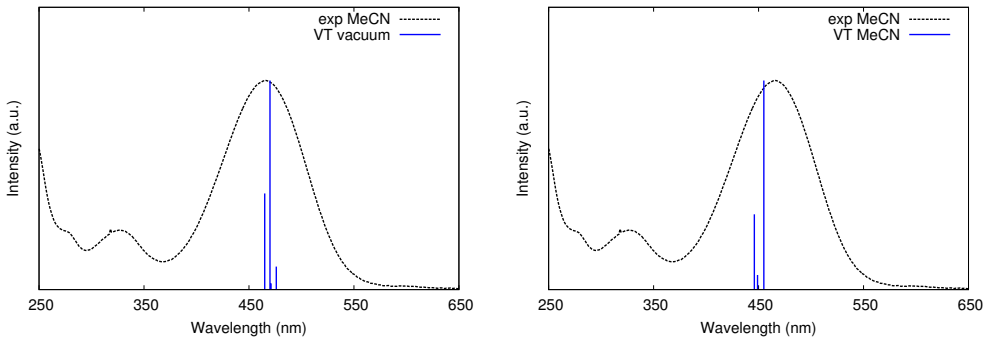


(a) 29.93 cm^{-1} (b) 141.74 cm^{-1}

Figure S4: Nuclear displacements along the 29.93 cm^{-1} (left) and 141.74 cm^{-1} (right) active normal modes involved in the absorption process. B3LYP/6-31+G* in vacuo for conformer 4

In Fig. S5 the comparisons between the normalized experimental spectrum and VTs

computed for the four conformers, weighted for their Boltzmann factor evaluated at 298 K, are reported, both in vacuo and MeCN. The very good agreement with the experimental absorption maximum is misleading, since the computation completely miss the fundamental contribution of the thermal effects.



(a) (b)

Figure S5: Comparison between experimental normalized spectrum in acetonitrile and theoretical predictions (CAM-B3LYP/6-31+G*) of VTs in vacuo (a) and MeCN (b) of the four stable conformers, weighted for their Boltzmann population.