Understanding room-temperature π-dimerisation of radical ions: Intramolecular π-[TTF]₂²⁺ in functionalised calix[4]arenes

Maria Fumanal,[a,b] Marçal Capdevila-Cortada[c,*] and Juan J. Novoa[a,*]

(a) Departament de Química Física and IQTCUB, Universitat de Barcelona, Av. Diagonal 645, 08028, Barcelona, Spain; (b) Current address: Laboratoire de chimie quantique, Institut de Chimie UMR7177 CNRS-Université de Strasbourg, 1 Rue Blaise Pascal BP 296/R8, F-67007 Strasbourg, France; (c) Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain.

E-mail: mcapdevila@iciq.es; juan.novoa@ub.edu
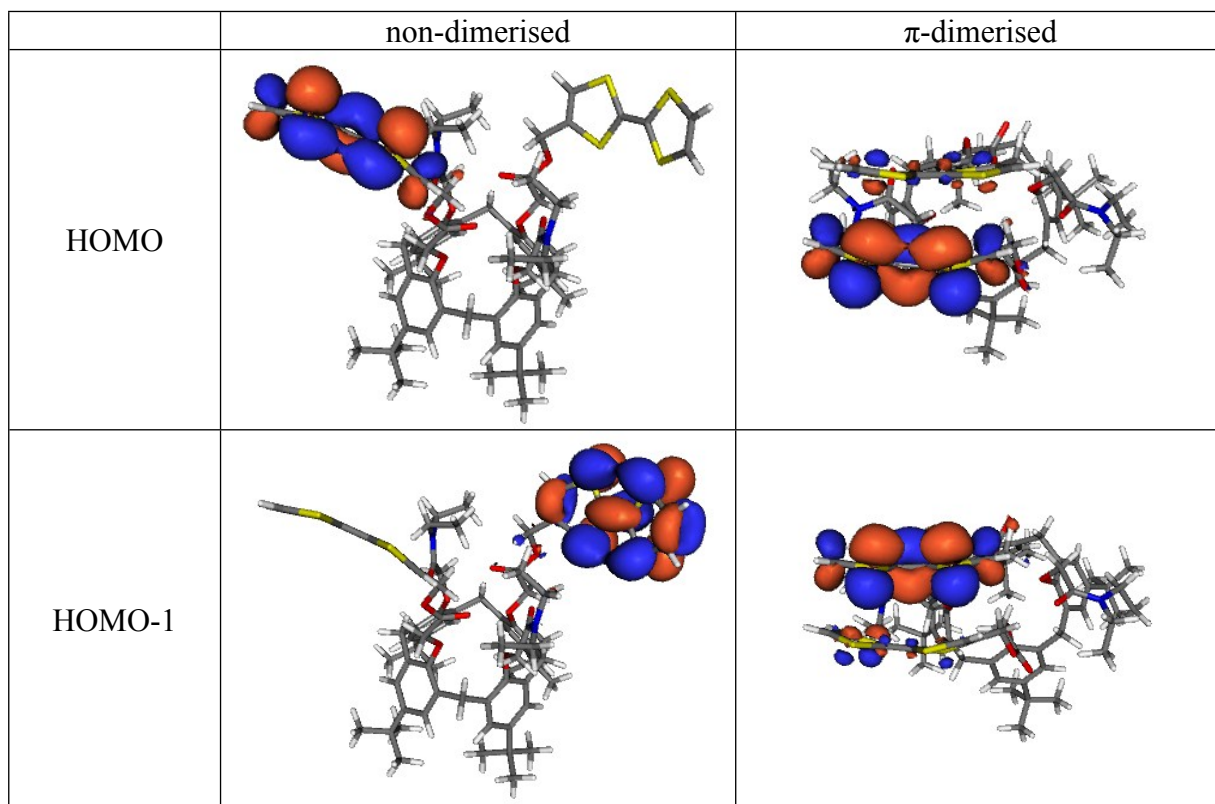
Electronic Supporting Information

	non-dimerised	π-dimerised
HOMO		
HOMO-1		

Figure S1. HOMO and HOMO-1 molecular orbitals of π-dimerised and non-dimerised [calix]^0 obtained with M06-L/6-31G(d,p) using PCM for simulating the acetonitrile solvent.
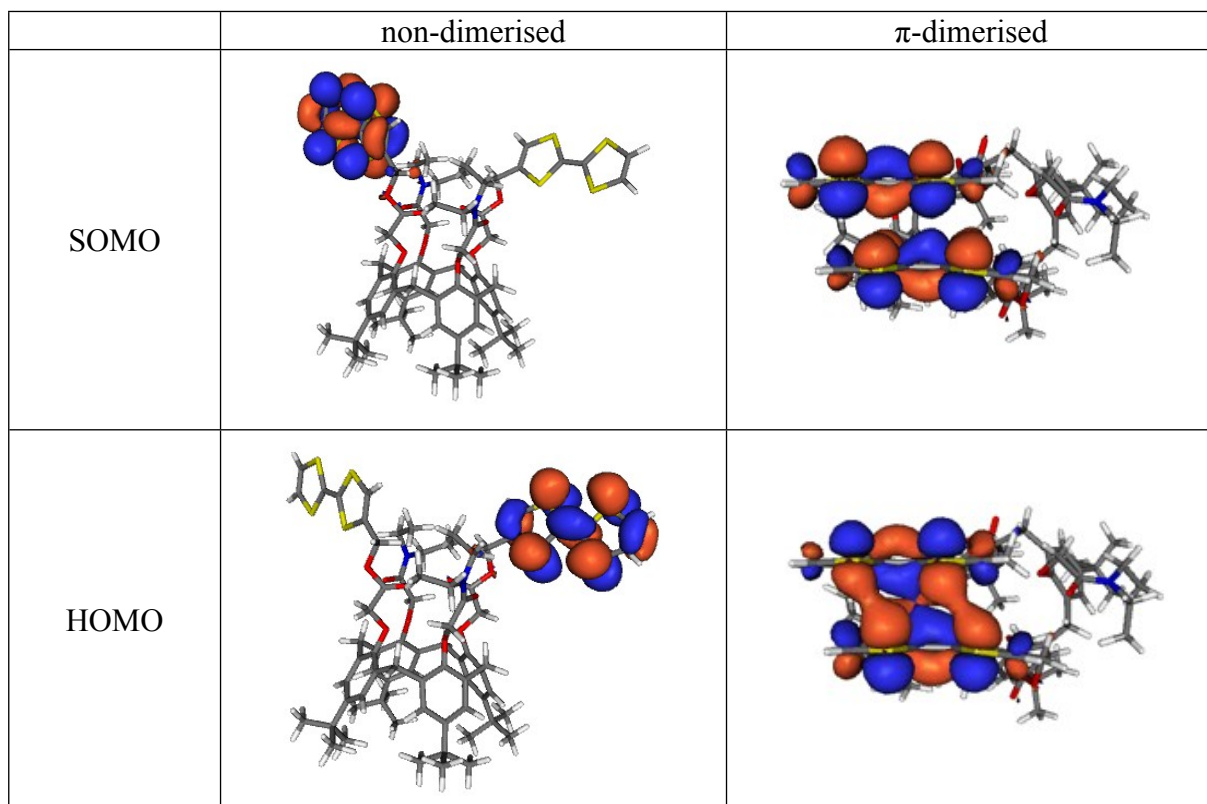
	non-dimerised	π-dimerised
SOMO		
HOMO		

Figure S2. SOMO and HOMO molecular orbitals of π-dimerised and non-dimerised [calix]•+ obtained with M06-L/6-31G(d,p) using PCM for simulating the acetonitrile solvent.

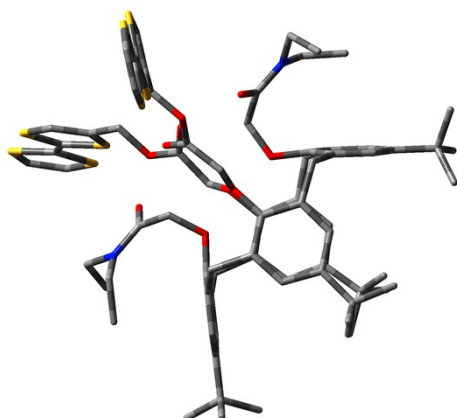**Figure S3.** Optimum geometry of [calix]$^{2+}$ molecule in its conformation **C** non-dimerised form, obtained at the M06-L/6-31G(d,p) level, in PCM-acetonitrile. The hydrogen atoms are hidden for clarity.
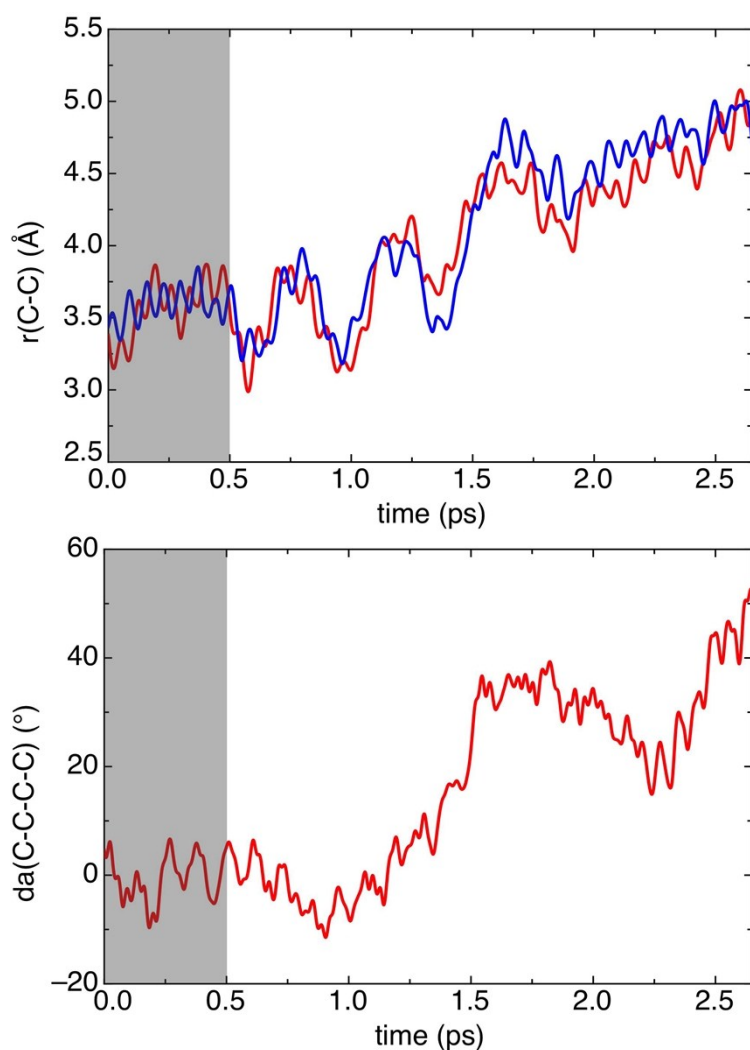
Figure S4. Time evolution of the two r(C-C) distances between the central carbon atoms of the TTF units of the [calix]$^{2+}$ (*top*) and the dihedral angle C-C-C-C defined by these central C atoms (*bottom*) along the AIMD simulations performed in implicit acetonitrile solution. The grey region denotes equilibration. The initial configuration prior equilibration was the π-dimerised [calix]$^{2+}$ form.
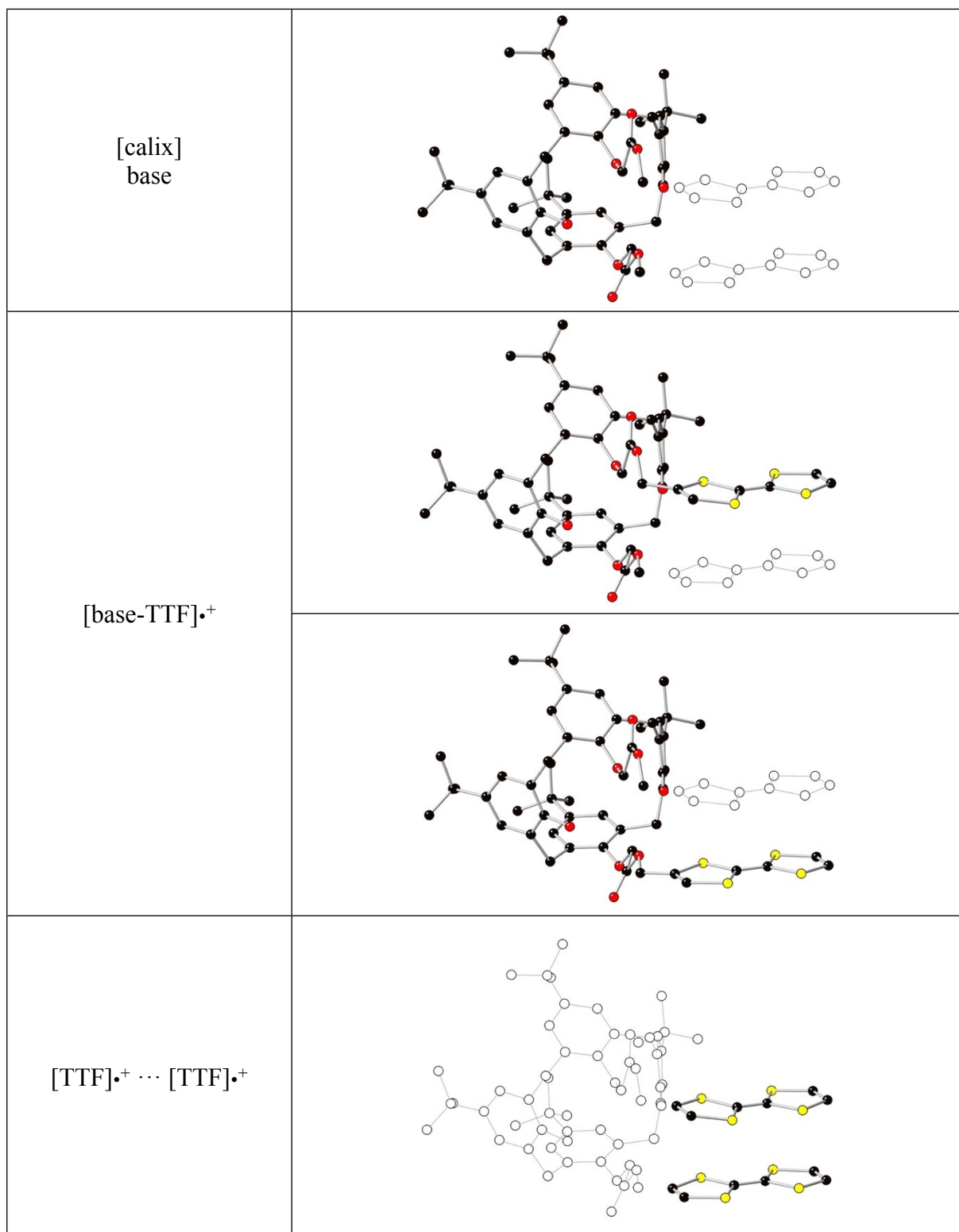
[calix] base	
[base-TTF]•+	
[TTF]•+ ··· [TTF]•+	

Figure S5. Fragments considered to evaluate their contribution to the total potential energy curve of the [calix]$^{2+}$: the [calix]-base, the [base-TTF]•+ and the [TTF]•+···[TTF]•+. The hydrogen atoms are hidden for clarity.

Table S1. Mulliken atomic charges of the two TTF fragments at the ground state of the different oxidation states of the π-dimerised and non-dimerised [calix]$^{n+}$ (n = 0-2) obtained with M06-L/6-31G(d,p) using PCM for simulating the acetonitrile solvent.

| | non-dimerised | | π-dimerised | |
	TTF1	TTF2	TTF1	TTF2
[calix]^0	0.00	0.01	-0.07	0.01
[calix]$^{\bullet+}$	0.00	0.89	0.45	0.30
[calix]$^{2+}$	0.89	0.89	0.87	0.82

Table S2. Electron density (in atomic units) at the bond critical points depicted in Figure 5 of the main text. The C_1 and C_4 are averaged values of the outer carbon atoms.

	π-[TTF]$_2^{2+}$	π-dimerised [calix]$^{2+}$
Density @ C_1-C_1 bcp	$4.2 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}$
Density @ S_1-S_1 bcp	$1.1 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$
Density @ S_2-S_2 bcp	$1.1 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$
Density @ C_2-C_2 bcp	$6.2 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$
Density @ C_3-C_3 bcp	$6.2 \cdot 10^{-3}$	$6.1 \cdot 10^{-3}$
Density @ S_3-S_3 bcp	$1.1 \cdot 10^{-2}$	$9.4 \cdot 10^{-3}$
Density @ S_4-S_4 bcp	$1.1 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$
Density @ C_4-C_4 bcp	$4.2 \cdot 10^{-3}$	$3.8 \cdot 10^{-3}$