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

Simulation of Charge-Transfer, UV-VIS and Resonance Raman Spectra of Push-Pull Systems: a TDDFT and CASPT2 Comparison

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Supporting Information

1. Dimensionless normal coordinates

***Table S1**. Main dimensionless normal coordinate displacements of pNA and $[pNA]^-$ calculated from the multiconfiguration approach, and from the cartesian gradient of the TDDFT calculations.*

pNA				**$[pNA]^-$**			
		TDDFT	XMS-CASPT2			TDDFT	XMS-CASPT2
Normal Mode	ω (cm^{-1})	Δ_i	Δ_i	Normal Mode	ω (cm^{-1})	Δ_i	Δ_i
17	822	0.333336	0.555542	15	802	0.098587	-0.875610
19	867	0.620528	-1.008829	18	830	-0.000073	0.011196
24	1127	0.416465	-0.319512	23	1132	-0.268702	1.086047
26	1197	-0.471066	0.314336				
27	1296	0.781484	1.539596	27	1307	0.223491	-0.781489
36	1639	-0.282270	0.338579	34	1639	-0.168425	0.853782

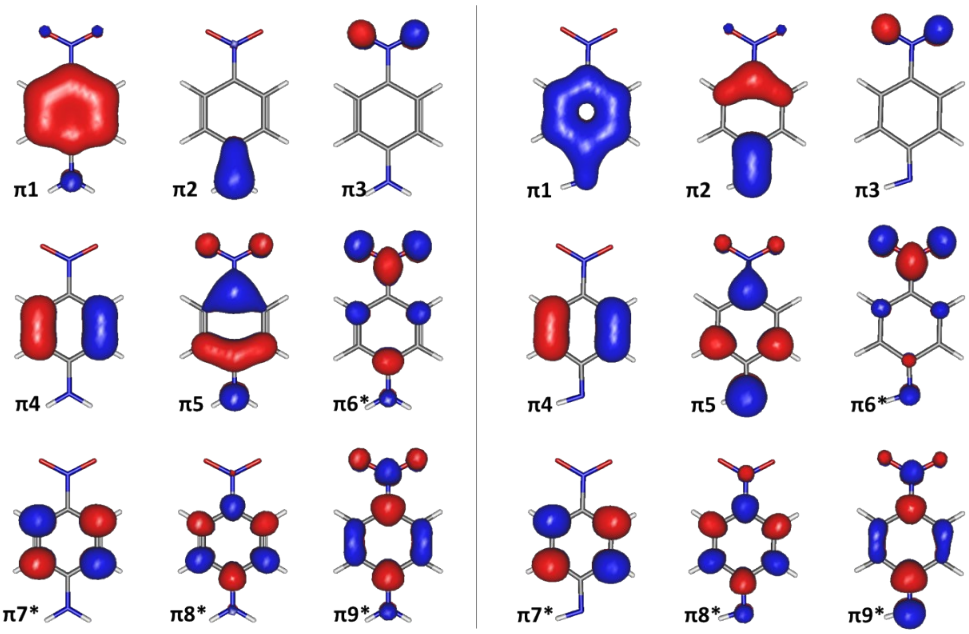

***Figure S1**. pNA (left) and [pNA]⁻ (right) active spaces in terms of averaged valence natural orbitals, containing 10 electrons distributed between 9 π/π* obtained at the SA(5)-CASSCF(10,9)/aug-cc-pVDZ level of theory, at the optimized ground states geometries.*

3. XYZ coordinates of optimized geometries of pNA and [pNA]⁻

B3LYP-D3/aug-cc-pVDZ

pNA

C	0.828746	1.652721	-0.094350
C	1.599108	0.457989	-0.065503
C	0.979832	-0.775790	-0.019073
C	-0.425666	-0.851642	0.001680
C	-1.206603	0.319475	-0.024025
C	-0.589300	1.554211	-0.070633
N	-1.065731	-2.130224	0.048307
O	-0.363151	-3.156764	0.068006
O	-2.308629	-2.182773	0.067992
N	1.433739	2.863678	-0.140176
H	2.686739	0.525578	-0.082780
H	1.570584	-1.688157	0.001655
H	-2.291080	0.245891	-0.007233
H	-1.186729	2.465514	-0.091564
H	2.439771	2.944320	-0.173307
H	0.891816	3.714612	-0.178923

pNA - anion

C	0.866666	1.735533	-0.000011
C	1.621548	0.489649	-0.000012
C	1.008122	-0.734440	-0.000005
C	-0.414257	-0.829895	-0.000003
C	-1.191110	0.366817	0.000000
C	-0.580801	1.591590	-0.000006
N	-1.034426	-2.071617	0.000008
O	-0.336235	-3.128609	0.000002
O	-2.298870	-2.147815	0.000010
N	1.406759	2.940048	-0.000016
H	2.711630	0.552102	-0.000020
H	1.597809	-1.648803	-0.000010
H	-2.276204	0.290264	-0.000001
H	-1.179489	2.503528	-0.000011
H	2.426961	2.851498	-0.000020

XMS-CASPT2/aug-cc-pVDZ.

pNA-S0

C	0.83878377	1.68292983	0.00000970
C	1.60914815	0.48971438	0.00004635
C	0.98733788	-0.76089899	0.00005349
C	-0.41570441	-0.83406308	0.00007729
C	-1.20198217	0.33025771	0.00004944
C	-0.57775914	1.57965851	0.00004774
N	-1.06851335	-2.14396577	-0.00006920
O	-0.33963441	-3.14973397	-0.00011337
O	-2.31039280	-2.16764229	-0.00009617
N	1.44968276	2.90870802	-0.00009366
H	2.70233526	0.55363985	0.00001538
H	1.57036010	-1.68354826	0.00008586
H	-2.28969874	0.24039284	0.00008246
H	-1.18494070	2.49095670	0.00000993
H	2.45675704	2.98518695	-0.00014188
H	0.90426074	3.75873759	-0.00012335

pNA-S1

C	0.83301173	1.67138711	0.00001552
C	1.62729810	0.47441356	-0.00000088
C	1.01196069	-0.77312896	0.00001756
C	-0.42128417	-0.84517649	0.00003225
C	-1.22665506	0.34258753	0.00001697
C	-0.60093582	1.58497378	0.00000226
N	-1.04707204	-2.10101331	-0.00002753
O	-0.27259076	-3.13856800	-0.00003537
O	-2.34176619	-2.10750935	-0.00003539

N	1.43905719	2.88744399	-0.00004594
H	2.71977435	0.56153394	-0.00003172
H	1.56300044	-1.71401134	0.00004753
H	-2.30966873	0.21605772	0.00004836
H	-1.18896062	2.50981690	-0.00003064
H	2.45206153	2.96724628	-0.00006941
H	0.89280935	3.74427665	-0.00006358

pNA anion-S0

C	0.88131769	1.76375249	-0.00001236
C	1.62694339	0.50284159	-0.00001277
C	1.00425707	-0.73580871	-0.00000757
C	-0.41109856	-0.82447466	0.00000669
C	-1.19077468	0.36567231	-0.00000264
C	-0.57297725	1.60389565	-0.00000794
N	-1.05640200	-2.12016095	-0.00000617
O	-0.34224633	-3.15017135	0.00001145
O	-2.30862471	-2.16783456	0.00001682
N	1.40471572	2.98212646	-0.00001657
H	2.72538079	0.55672265	-0.00001843
H	1.58116712	-1.66541160	-0.00001132
H	-2.28061208	0.27020549	-0.00000264
H	-1.16586551	2.52652034	-0.00001048
H	2.43292346	2.85197420	-0.00002006

pNA anion-S1

C	0.88628523	1.72810511	-0.00001086
C	1.64910998	0.51706692	-0.00001037
C	1.01034984	-0.76579681	-0.00000105
C	-0.40140669	-0.82090495	-0.00001212
C	-1.18246522	0.35133200	-0.00001073
C	-0.55035625	1.59858801	-0.00000542
N	-1.08314576	-2.11337521	-0.00002555
O	-0.32614913	-3.15077407	-0.00000247
O	-2.36559325	-2.13822805	0.00004950
N	1.37337635	3.00249439	-0.00001648
H	2.74601851	0.58235801	-0.00002260
H	1.56040155	-1.70834092	0.00001058
H	-2.26888425	0.23556855	-0.00001049
H	-1.12680034	2.53004139	-0.00000277
H	2.40736353	2.91171496	-0.00002317