Electronic Supplementary Information

Frontier orbitals stability of nitroxyl organic radicals probed by means of inner shell resonantly enhanced photoelectron spectroscopy

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Resonant Photoelectron Spectroscopy (ResPES)

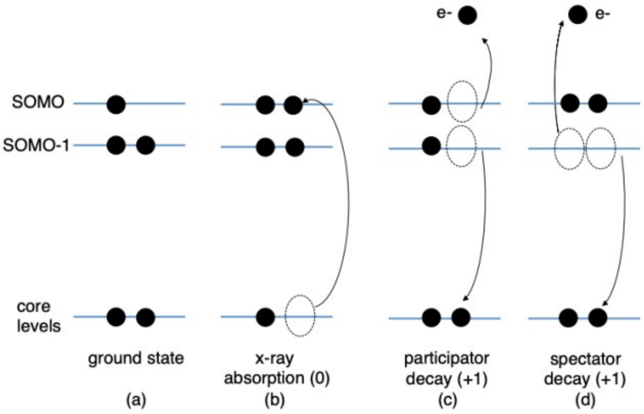

Figure S1. X-ray absorption-induced transition from the ground state core level to (a) an unoccupied or, in the case of radicals, (b) singly occupied molecular orbital (SOMO) level. From this excited state, two possible core-hole decay paths are shown: (c) participator decay and (d) spectator decay, leaving the system in an ionized +1 charged state.

In a Resonant Photoelectron Spectroscopy (ResPES) experiment (Fig.S1), the incident photon energy is varied across the resonances of the absorption edges under investigation, promoting a core electron into a resonant bound state (unoccupied orbitals, single occupied molecular orbitals - SOMO or Rydberg states). Then, the electrons emitted upon the non-radiative de-excitation processes are monitored.[1-4] When a non-radiative de-excitation occurs, the core hole is filled again and a valence electron can be emitted following two different decay paths. In the "participator decay" (Fig. S1c), the photoexcited electron itself is removed leaving the system in a valence single-hole state. In the "spectator decay" (Fig. S1d), a different electron fills the core-hole and a second electron is ejected, leaving the system in a valence two-hole/one-particle state. The former final state is equivalent to those accessible by direct PES and the corresponding decay channel is known as Resonant Photoemission, the latter to an Auger transition and is called Resonant Auger.

In ResPES, however, there are some additional advantages with respect to normal PES. First, the transition matrix elements describing the process are Coulomb-type rather than dipole-type, therefore ResPES could give access to cationic states normally forbidden via conventional PES, because of unfavourable dipole selection rules or of a small cross section. Second, for polyatomic molecules with several chemically non-equivalent atoms of the same species, ResPES is a powerful tool for the study of site-selected processes. Indeed, the core electron is selected from a specific atomic site, by tuning the photon energy on the chosen absorption threshold, below the core-electron ionization threshold. Therefore the subsequent non-radiative decay allows for the disentanglement of the electron emission spectra from core holes of different atoms of the same kind and to address questions on site- and state-selectivity in inner-shell excitation and decay. This is an important difference with respect to KVV Auger spectra, resulting from the unresolved superposition of decays of the same atomic species located in different molecular sites.

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3. P. Bolognesi P. O'Keeffe, Y. Ovcharenko, L. Avaldi and V. Carravetta, *J. Chem. Phys.*, 2012, **136**, 154308.
4. P. A. Brühwiler, O. Karis, and N. Mårtensson, *Rev. Mod. Phys.*,2002, **74**, 3, 703.

Table S1. The used Cartesian geometries (in Å) of the four NRs optimized at the B3LYP-D3/aug-cc-pVTZ level

TEMPO

H	1.237999	1.414879	-1.583387
H	2.153042	1.898711	-0.168563
H	-0.000000	3.149004	-0.349911
H	-0.000000	2.178839	1.103008
H	-2.153041	1.898713	-0.168566
H	-1.237998	1.414877	-1.583387
H	1.676121	-1.208983	1.775275
H	2.769664	0.168318	1.567046
H	1.109511	0.432873	2.096640
H	2.027629	-0.831081	-1.936330
H	3.310649	-0.319016	-0.828854
H	2.454974	-1.848513	-0.559342
H	-1.109512	0.432875	2.096640
H	-2.769665	0.168312	1.567048
H	-1.676114	-1.208983	1.775275
H	-2.454981	-1.848510	-0.559336
H	-3.310648	-0.319010	-0.828860
H	-2.027625	-0.831088	-1.936328
N	0.000000	-0.749806	-0.210150
C	1.325784	-0.070906	-0.029025
C	1.241091	1.392326	-0.490075
C	0.000000	2.119652	0.012829
C	-1.241091	1.392326	-0.490076
C	-1.325786	-0.070904	-0.029025
C	1.740419	-0.172427	1.449003
C	2.344318	-0.820390	-0.893397
C	-1.740418	-0.172427	1.449003
C	-2.344319	-0.820389	-0.893396
O	-0.000001	-2.019342	-0.065258

DTBN

N	-0.003163	0.532286	-0.196316
O	0.031616	1.809575	-0.120116
C	1.353390	-0.113363	-0.012671
C	1.828866	0.175407	1.420961
C	2.295176	0.565422	-1.018853
C	1.375432	-1.619602	-0.277499
C	-1.497467	-0.678326	1.408719
C	-2.413535	0.984914	-0.211459
C	-1.360779	-0.112552	-0.013546

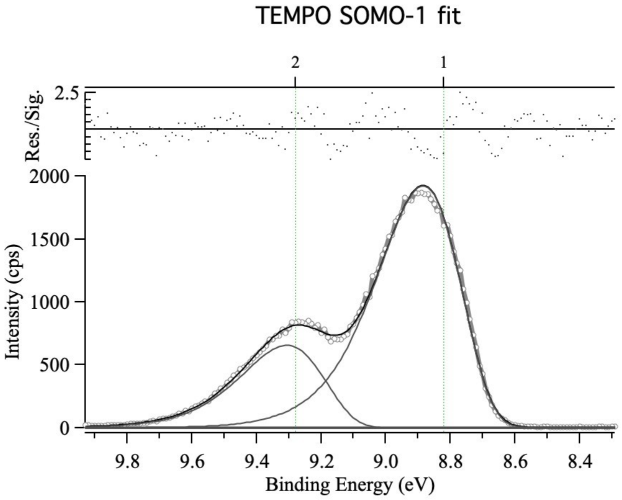
C	-1.607425	-1.202144	-1.070048
H	2.337118	1.636805	-0.846636
H	1.951972	0.393117	-2.039474
H	3.297620	0.148916	-0.916803
H	2.395970	-1.970324	-0.123185
H	1.098527	-1.853929	-1.303321
H	0.737294	-2.181550	0.399421
H	2.862579	-0.150875	1.541265
H	1.220984	-0.348763	2.156971
H	1.774163	1.243857	1.619419
H	-1.320051	0.103449	2.146454
H	-2.315539	1.772259	0.529880
H	-2.509405	-1.059886	1.552070
H	-0.806790	-1.496626	1.598845
H	-3.401969	0.533728	-0.121796
H	-2.323540	1.440181	-1.195923
H	-2.665815	-1.463733	-1.066032
H	-1.050309	-2.114290	-0.885436
H	-1.355537	-0.833470	-2.064211

nit8

H	-0.734706	-0.299117	-1.571307
H	0.155090	-2.330453	-0.567009
H	-0.002049	-1.660691	1.060578
H	2.095228	-1.022496	2.010405
H	3.460471	-0.606819	0.973066
H	2.779283	-2.242646	0.921907
H	2.547859	-1.971929	-1.589133
H	3.104841	-0.290373	-1.537987
H	1.541451	-0.679446	-2.259503
H	0.030657	3.060272	-0.477858
H	-1.550516	2.365111	-0.916340
H	-0.105004	1.973718	-1.862541
H	-0.572455	0.446762	2.150806
H	-1.734563	1.608570	1.490434
H	-0.083569	2.122393	1.887706
H	-3.624640	-1.867581	0.545405
H	-1.997305	-2.450313	0.597160
N	-2.644335	-1.716760	0.378945
N	1.230358	0.682414	0.095174
C	0.200398	-1.411653	0.017134
C	1.582692	-0.748235	-0.078636
C	2.539357	-1.184093	1.028094
C	2.231936	-0.936488	-1.456023
C	-0.223529	0.992606	0.063821
C	-0.787453	-0.345030	-0.480964
C	-0.688477	1.308192	1.491816
C	-0.480573	2.178133	-0.859384
C	-2.269181	-0.535014	-0.181852
O	-3.082654	0.330625	-0.454035
O	2.108846	1.573495	0.298247

nit9

H	0.081578	-2.381507	0.254082
H	-1.768365	-1.255764	-2.052824
H	-3.264658	-0.846740	-1.202898
H	-2.521081	-2.438248	-0.966335
H	-2.484682	-2.062817	1.547568
H	-3.234108	-0.470975	1.322754
H	-1.715267	-0.615153	2.218710
H	-0.219551	2.763630	1.103171
H	1.451294	2.157707	1.247725
H	0.127720	1.327556	2.077294
H	0.448355	1.149451	-2.225119
H	1.648098	2.044696	-1.272231
H	-0.009228	2.664166	-1.435239
H	3.758790	-1.891449	-0.252226
H	2.193482	-2.468107	-0.679233
N	2.759323	-1.786857	-0.207501
N	-1.254784	0.633510	-0.164755
C	-0.115071	-1.326418	0.122679
C	-1.521573	-0.807995	0.059885
C	-2.317420	-1.378081	-1.119889
C	-2.286046	-1.004415	1.376818
C	0.183001	1.010912	-0.073412
C	0.805392	-0.366205	0.035149
C	0.598415	1.765679	-1.338498
C	0.404904	1.874080	1.176111
C	2.283619	-0.536323	0.075268
O	3.029926	0.385387	0.364295
O	-2.184360	1.490810	-0.234803



Peak	Area	Mis	B.E. (eV)	fwhm (eV)
1	650		8.9	0.31
2	221		9.3	0.31

Area Peak1/Area Peak2 = 2.9

Figure S2. TEMPO SOMO-1 photoelectron spectrum, with its fitting analysis. Skewed Gaussians were employed, considering the unresolved intramolecular vibration modes progression, usually giving rise to an asymmetric tail on the high binding energy side of photoemission peaks.[5-7]

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6. I. Minkov, F. Gel'mukhanov, H. Ågren, R. Friedlein, C. Suess and W. R. Salanek, *J. Phys. Chem. A* 2005, **109**, 7, 1330.
7. O. Kwon, V. Coropceanu, N. E. Gruhn, J. C. Durivage, J. G. Laquindanum, H. E. Katz, J. Cornil and J. L. Brédas, *J. Chem. Phys.*, 2004, **120**, 17, 8186.

Table S2. The vertical ionization thresholds (in eV at the (TD)-B3LYP//mixed level) for the valence ionizations of the four NRs, and the norms of the Dyson spin orbitals (multiplied by 10^5) between the N1s/O1s → π* CV states and the valence ionized states.

TEMPO			
state	**(TD)-B3LYP**	**O**	**N**
$1^1A'$	7.28	1.35	10.32
$1^3A''$	8.51	1.37	9.86
$1^1A''$	9.37	0.96	6.27
$2^1A'$	10.01	1.00	7.27
$3^1A'$	10.45	1.00	7.71
$2^1A''$	10.46	1.00	7.27
$3^1A''$	10.80	0.87	7.07
$4^1A''$	11.08	0.96	8.24
$4^1A'$	11.37	0.98	7.14
$5^1A''$	11.40	0.95	7.43
$6^1A''$	11.67	0.90	7.40
$5^1A'$	11.91	1.01	7.57

DTBN			
state	**(TD)-B3LYP**	**O**	**N**
1^1A_1	7.21	1.14	9.40
1^3A_1	8.50	1.20	9.03
2^1A_1	9.42	0.79	6.83
3^1A_1	10.44	0.96	6.82
4^1A_1	10.78	1.61	7.91
5^1A_1	10.82	1.24	5.35
6^1A_1	11.29	1.18	6.10
7^1A_1	11.44	0.89	6.36
8^1A_1	11.50	0.84	7.16
9^1A_1	11.57	0.80	6.25
10^1A_1	11.96	0.99	4.00
11^1A_1	12.09	1.55	7.65

nit8					
state	**(TD)-B3LYP**	O_{amd}	N_{amd}	O_{nit}	N_{nit}
1^1A_1	7.16	0.22	22.17	0.14	1.08
1^3A_1	8.50	0.48	24.28	0.15	1.96
2^1A_1	8.15	0.16	15.79	0.10	2.04
3^1A_1	8.58	0.16	16.13	0.12	0.76
4^1A_1	9.67	0.16	13.35	0.15	0.84
5^1A_1	10.61	0.22	14.60	0.35	0.91
6^1A_1	10.74	0.13	18.91	0.20	1.17
7^1A_1	11.04	0.34	16.22	0.80	1.06
8^1A_1	11.34	0.31	12.77	0.12	1.68
9^1A_1	11.56	0.24	18.17	0.24	0.72
10^1A_1	11.80	0.18	14.02	0.31	0.82
11^1A_1	11.87	0.20	15.80	0.29	1.13

nit9					
state	**(TD)-B3LYP**	**O_{amd}**	**N_{amd}**	**O_{nit}**	**N_{nit}**
1^1A_1	7.29	1.05	11.27	0.64	4.31
1^3A_1	8.61	1.21	14.46	0.66	4.44
2^1A_1	8.29	0.75	8.07	0.45	3.35
3^1A_1	8.69	0.74	8.24	0.45	3.15
4^1A_1	9.13	0.77	8.14	0.46	2.82
5^1A_1	9.79	0.74	7.95	0.55	2.91
6^1A_1	10.96	0.76	7.97	0.57	3.12
7^1A_1	11.22	0.81	7.67	0.43	2.88
8^1A_1	11.40	0.86	8.33	1.20	3.20
9^1A_1	11.53	0.36	2.83	0.00	0.30
10^1A_1	11.63	0.76	7.21	0.50	2.87
11^1A_1	11.88	0.74	8.26	0.52	3.10

Table S3. The lowest core-to-valence (CV) excitation energies and core-electron binding energies (CEBE, for DTBN only; the CEBE values for the remaining NRs can be found in Refs. 25 and 27) calculated using the ΔDFT//mixed method (eV). No relativistic corrections for the 1s core contraction were applied.

	TEMPO		**DTBN**		**nit8**				**nit9**			
method	**N**	**O**	**N**	**O**	**N_{nit}**	**O_{nit}**	**N_{amd}**	**O_{amd}**	**N_{nit}**	**O_{nit}**	**N_{amd}**	**O_{amd}**
ΔB3LYP CV	399.3	529.0	399.4	529.0	399.4	529.3	401.7	531.3	399.4	529.3	400.8	530.5
ΔB3LYP CEBE			405.8	535.9								
ΔCAM-B3LYP CV	399.3	529.0	399.3	529.1	399.4	529.3	401.7	531.3	399.4	529.3	400.8	530.6
ΔCAM-B3LYP CEBE			405.9	536.1								
expt. CV	399.4	529.3	399.4	529.3	399.4	529.8	401.8	531.9	399.5	529.7	401.8	531.3
expt. CEBE			406.4	537.0								

Table S4. Comparison of the performances of several methods used to calculate the vertical ionization energies (eV) in TEMPO. The triplet coupled states (formally, the ionizations from the β spin-orbitals) are given in parentheses. The average absolute deviations (AAD) are calculated with respect to the IP-UADC(3) singlet states.

state	**(TD)-B3LYP**	**(TD)-CAM-B3LYP**	**EPT-P3+**	**IP-UADC(3)**^{a}
$1^1A'$	7.28	7.53	7.42	7.5636
$1^3A''$	8.51	8.73	9.06	9.3336
$1^1A''$	9.37	9.70	9.63	9.5483
$2^1A'$	10.01	10.95	(10.33) 10.99	(10.1730) 10.6061
$3^1A'$	10.45	11.41	(10.96) 11.34	(11.1088) 11.1279
$2^1A''$	10.46	11.62	(11.30) 11.43	(11.1699) 11.5106
$3^1A''$	10.80	11.69	(11.60) 11.57	(11.5387) 11.7879
$4^1A''$	11.08	12.21	(11.84) 12.26	(11.8347) 12.0296
$4^1A'$	11.37	12.39	(12.26) 12.46	(12.0836) 12.4244
$5^1A''$	11.40	12.56	(12.75) 12.76	(12.4321) 12.4968
$6^1A''$	11.67	12.69	(12.78) 12.90	(12.8374) 12.8804
$5^1A'$	11.91	13.06	(12.80) 13.18	(12.9658)
AAD	**0.83**	**0.18**	**0.18**	

^{a}IP-UADC(3)/aug(nH)-cc-pVTZ level results taken from Ref. 69

Table S5. The equilibrium geometries of the lowest CV states (N 1s and O 1s) of DTBN (in Å) calculated at the B3LYP-D3//mixed level.

N 1s

H	2.1805501835	1.7650443735	-0.5876432966
H	1.9167101185	0.6806736223	-1.9656504811
H	3.2777552008	0.3831325745	-0.8650189892
H	2.4588785655	-1.8880966793	-0.5591986075
H	1.0420737274	-1.6624348605	-1.5848540155
H	0.8691819588	-2.2735148537	0.0807130228
H	2.8476836988	-0.3455506047	1.4754270095
H	1.2321435531	-0.7978084319	2.0244807581
H	1.6317233269	0.9193046555	1.7921307002
H	-1.2425990241	0.4842716103	2.0717604065
H	-2.2380240291	1.8531354892	0.1259900853
H	-2.5915237553	-0.6221702825	1.7229182883
H	-0.9480684167	-1.2592513949	1.8359086768
H	-3.3594296626	0.5521063309	-0.3620698776
H	-2.1526539682	1.1783280813	-1.5051987121
H	-2.6507145212	-1.5948244633	-0.8254099040
H	-1.0764131507	-2.2592790660	-0.4351291470
H	-1.2710284991	-1.2047548053	-1.8540039036
N	-0.0061673767	0.4586011247	-0.1946810198
C	1.3673946451	-0.1519230987	-0.0492827046

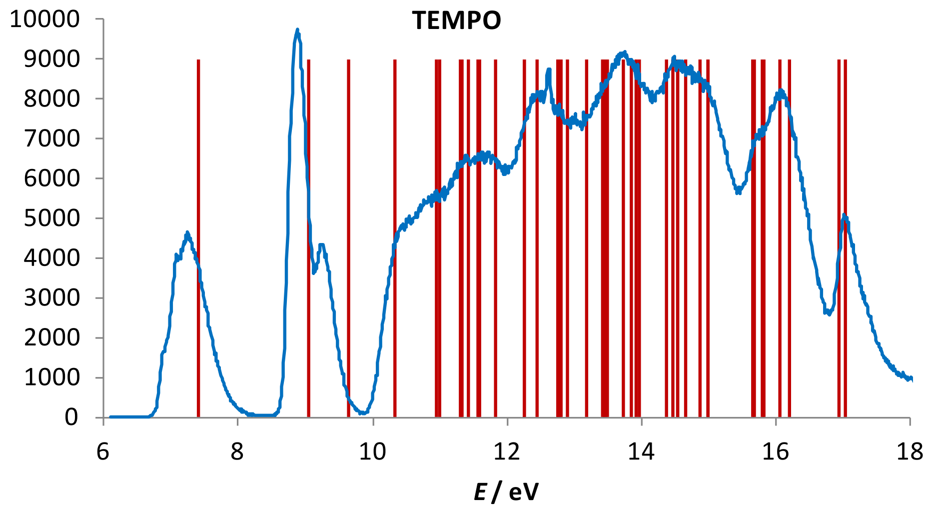
C	1.7879770590	-0.0870803481	1.4109258862
C	2.2445934704	0.7340482586	-0.9247480230
C	1.4107218168	-1.5808311287	-0.5623964452
C	-1.5422610084	-0.4020087569	1.5127264137
C	-2.3428264780	0.9434139498	-0.4556666484
C	-1.3736440887	-0.1306114472	0.0292544665
C	-1.5805864097	-1.3775757657	-0.8217713186
O	0.0379360639	1.8261389166	0.3611673799

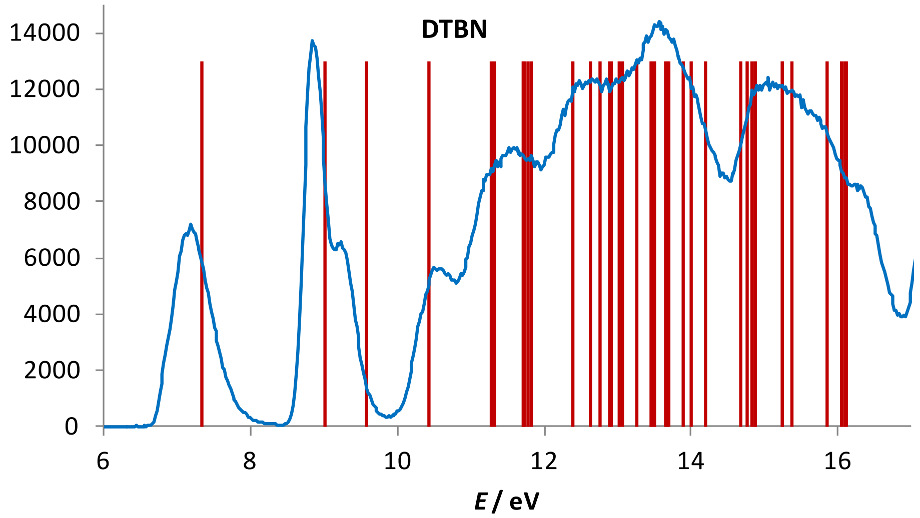
O 1s

H	2.3224512073	1.7571629192	-0.5401678756
H	2.0693060030	0.7040153838	-1.9393351944
H	3.3405130733	0.3241491128	-0.7568359533
H	2.4700327276	-1.8769463321	-0.5594255296
H	1.0709208166	-1.6536564728	-1.6157214276
H	0.8629882138	-2.2640626070	0.0403281379
H	2.7646771812	-0.3417328876	1.5106139141
H	1.1369128526	-0.7903075522	2.0062805517
H	1.5649668986	0.9184876445	1.8171386417
H	-1.1513331652	0.4698397946	2.0893139640
H	-2.2951210063	1.8505440189	0.1886670858
H	-2.5200270495	-0.5969528695	1.7453782477
H	-0.8897979812	-1.2634589657	1.8061078778
H	-3.3812880749	0.5349066565	-0.2798663225
H	-2.2404498531	1.2131371226	-1.4603946436
H	-2.6982138091	-1.5964532544	-0.7333987925
H	-1.0923233607	-2.2488468133	-0.4584160295
H	-1.3948496931	-1.2137745332	-1.8666763571
N	-0.0129811064	0.4365582252	-0.4329848500
C	1.3340617609	-0.1304243062	-0.0778285662
C	1.7076196327	-0.0812167158	1.4082271793
C	2.3293684981	0.7215523848	-0.8787724684
C	1.4221594750	-1.5692371392	-0.5860413127
C	-1.4731647218	-0.3925146545	1.5037451300
C	-2.3770520169	0.9455963137	-0.4103196818
C	-1.3417617626	-0.1103421022	0.0067250840
C	-1.6316950114	-1.3734504135	-0.8128520294
O	0.0334632715	1.7679110426	0.1771912203

Table S6. The norms of the Dyson spin orbitals between the N1s/O1s → π* CV states and the lowest singlet and triplet valence ionized states calculated at the N 1s and O 1s CV minimum geometries

		B3LYP// mixed						**CAM-B3LYP//mixed**		
state	**N**	**ratio N**	**O**	**ratio O**		**state**	**N**	**ratio N**	**O**	**ratio O**
1^1A_1	14.80		1.580			1^1A_1	14.61		1.513	
1^3A_1	15.43	0.96	1.600	0.99		1^3A_1	15.27	0.96	1.545	0.98


TEMPO
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
6
8
10
12
14
16
18
E / eV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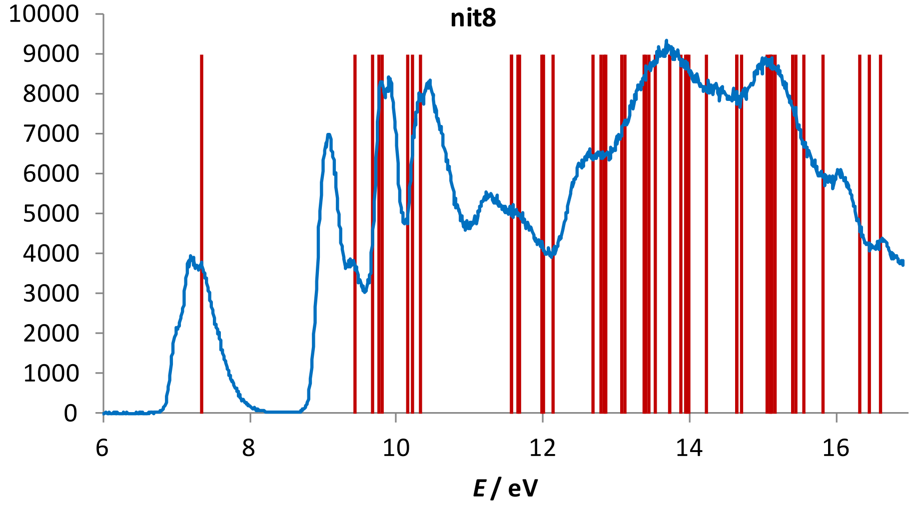
12000
10000
8000
6000
4000
2000
0
6
8
10
12
14
16
E / eV


nit8
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9000
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4000
3000
2000
1000
0
6
8
10
12
14
16
E / eV

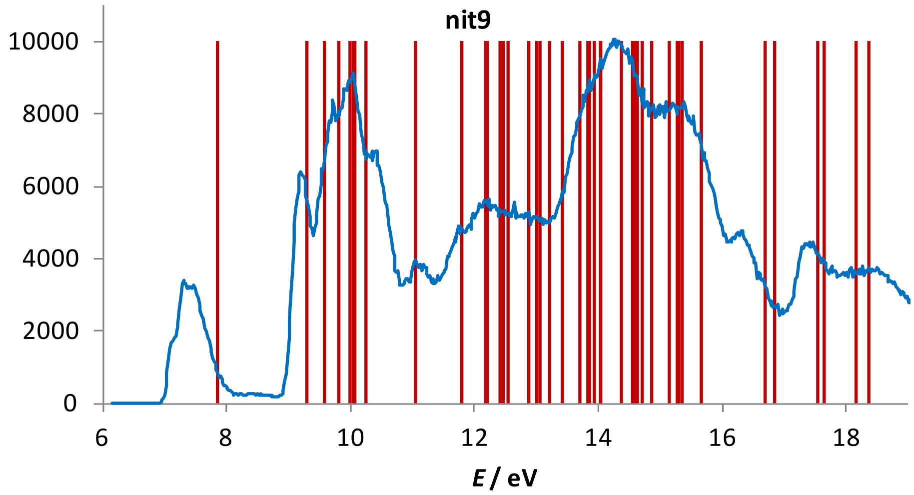

Figure S3. The experimental valence PES spectra of the four NRs with superimposed EPT-P3+/cc-pVTZ stick spectra

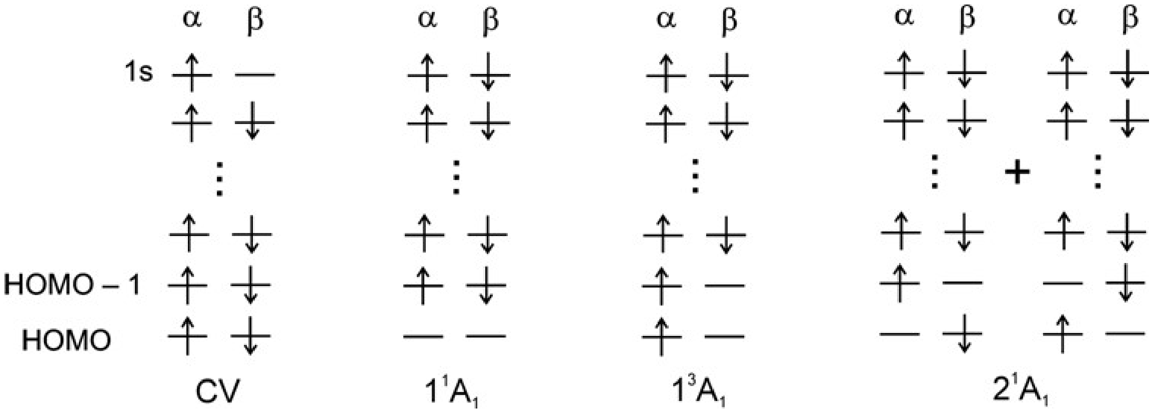

Figure S4. Schematic representations of the electronic configurations of the initial (CV) and three of the final states (1^1A_1, 1^3A_1, and 2^1A_1 (for simplicity, the levels of the α and β spin blocks are drawn as having equal orbital energy)