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

Supporting Information: Reverse intersystem crossing mechanisms in doped triangulenes

Asier E. Izu,[†,‡] Jon M. Matxain,[†,‡] and David Casanova[*,†,¶]

†*Donostia International Physics Center (DIPC), 20018 Donostia, Euskadi, Spain.*

‡*Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia Saila, Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), PK 1072, 20080 Donostia, Euskadi, Spain.*

¶*IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Euskadi, Spain.*

E-mail: david.casanova@dipc.org

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1 Molecular symmetry

Table S1: Symmetry point group for the ground state geometry of the studied molecules.

molecule	symmetry
1B	C_{3h}
1N	D_{3h}
1BN3a	C_{3h}
1NB3a	C_{3h}
1BN3b	D_{3h}
1NB3b	D_{3h}
2B	D_{3h}
2N	D_{3h}
2BN3a	D_{3h}
2NB3a	C_{3h}
2BN3b	C_{3h}
2NB3b	C_{3h}
2BN3c	D_{3h}
2NB3c	D_{3h}
2B4N3	C_{3h}
2N4B3	C_{3h}

2 Method assessment

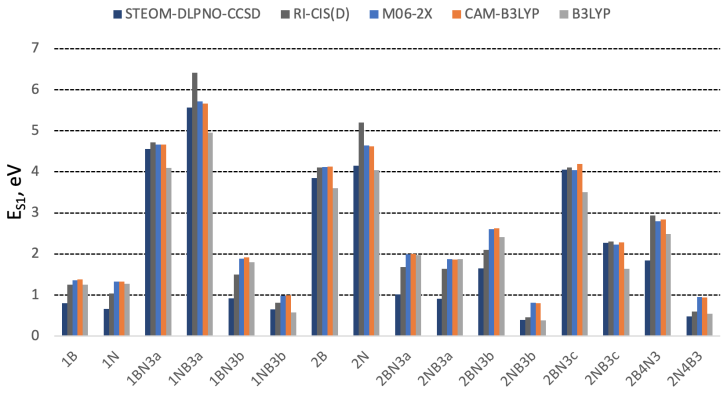

Figure S1: S_1 excitation energies (in eV) computed with different methods and the def2-TZVP basis set.

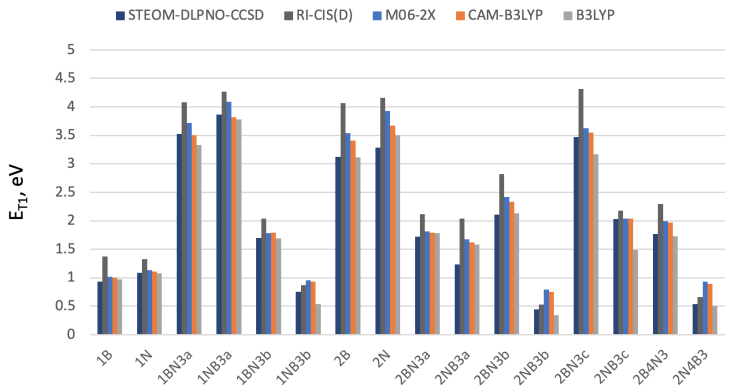

Figure S2: T_1 excitation energies (in eV) computed with different methods and the def2-TZVP basis set.

Table S2: SF-TDDFT/6-31(d) excitation energies (eV) and energy difference (in eV), and $\langle \hat{S}^2 \rangle$ of the two lowest excited states (R_1: root 1 and R_2: root 2).

molecule	$E(R_1)$	$\hat{S}^2(R_1)$	$E(R_2)$	$\hat{S}^2(R_2)$	$\Delta E_{R_2-R_1}$
1B	0.97	0.90	1.36	1.25	0.39
1N	1.11	0.89	1.56	1.29	0.39
1BN3a	4.23	2.01	5.52	0.47	1.25
1NB3a	4.37	2.01	5.78	1.02	1.41
1BN3b	1.22	1.13	2.46	1.15	1.24
1NB3b	1.08	1.06	1.31	1.29	0.23
2B	3.80	1.09	3.92	1.88	0.12
2N	4.25	1.06	4.31	1.90	0.06
2BN3a	2.19	2.00	2.49	1.04	0.30
2NB3a	1.02	1.35	1.74	2.68	0.72
2BN3b	1.96	1.09	2.44	2.35	0.49
2NB3b	0.95	1.08	1.10	1.39	0.15
2BN3c	3.93	2.06	4.12	1.04	0.19
2NB3c	2.11	1.39	2.29	0.79	0.18
2B4N3	2.10	1.98	2.33	1.11	0.23
2N4B3	1.11	1.06	1.25	1.36	0.14

Table S3: Thermally equilibrium triplet states through the Boltzmann distribution.

molecule	triplets in equilibrium
1B	1
1N	1
1BN3a	1-2
1NB3a	1-3
1BN3b	1
1NB3b	1
2B	1-2
2N	1-3
2BN3a	1-4
2NB3a	1
2BN3b	1-2
2NB3b	1
2BN3c	1-2
2NB3c	1-3
2B4N3	1-2
2N4B3	1

Table S4: Energies of molecules 2B4N3 and 1NB3a, for CIS and CIS(D) methods.

	CIS			CIS(D)		
molecule	$E(S_1)$	$E(T_1)$	ΔE_{ST}	$E(S_1)$	$E(T_1)$	ΔE_{ST}
2B4N3	3.79	2.57	1.22	2.32	2.29	0.03
1NB3a	7.02	3.37	3.65	5.87	4.26	1.61

Table S5: S_1 and T_n energies (eV) and SOCC values (cm^-1), SOC_n refers to the SOCC between S_1 and T_n.

	$E(S_1)$	T_1	T_2	T_3	T_4	T_5	T_6	SOC_1	SOC_2	SOC_3	SOC_4	SOC_5	SOC_6
1B	0.80	0.93	2.02	2.02	3.31	3.31	6.08	0.03	0.00	0.00	4.33	4.33	0.04
1N	0.67	1.09	2.05	2.05	4.83	5.37	5.54	0.00	0.02	0.03	0.01	0.00	3.50
1BN3a	4.55	3.53	3.59	3.90	5.53	5.54	6.27	0.03	0.01	0.00	0.32	0.32	0.95
1NB3a	5.57	3.86	3.87	3.90	5.37	5.54	7.05	1.19	0.86	0.49	0.11	0.86	0.03
1BN3b	0.92	1.70	2.12	2.12	2.22	2.23	3.27	0.03	10.46	10.52	0.02	0.00	0.09
1NB3b	0.65	0.75	1.89	1.90	2.45	3.10	3.10	0.00	0.00	0.01	0.00	0.01	0.01
2B	3.85	3.12	3.16	3.73	3.77	4.18	5.66	0.01	0.00	0.00	0.00	0.00	0.21
2N	4.15	3.28	3.28	3.29	3.52	3.98	5.31	0.02	0.01	0.01	0.00	0.00	0.00
2BN3a	1.02	1.72	1.72	1.74	1.82	2.79	2.79	0.00	0.00	0.00	0.13	0.01	0.01
2NB3a	0.91	1.23	1.47	1.47	1.78	3.06	3.07	0.04	0.00	0.00	0.03	0.00	0.00
2BN3b	1.65	2.11	2.11	2.25	2.61	2.61	3.33	0.03	0.02	0.00	10.57	10.57	0.15
2NB3b	0.39	0.45	1.81	1.81	1.91	1.91	2.04	0.01	0.00	0.00	0.62	0.61	0.00
2BN3c	4.05	3.47	3.48	3.67	3.67	3.70	4.00	0.00	0.00	0.03	0.00	0.89	0.00
2NB3c	2.27	2.03	2.08	2.09	2.70	2.71	3.81	0.00	0.14	0.01	0.79	0.38	0.02
2B4N3	1.84	1.77	1.77	2.38	2.49	2.49	2.63	0.04	0.01	0.02	0.68	0.66	0.68
2N4B3	0.48	0.54	1.89	1.90	1.90	1.90	2.14	0.00	0.00	0.00	1.07	1.07	0.00

Table S6: Transition energies (in eV) and SOCCs (in cm^{-1}) of excited singlets states (S_n) nearly degenerated to S_1. SOC_m refers to the SOCC between S_n and T_m.

	1NB3a(S_2)	1NB3a(S_3)	2B(S_2)	2N(S_2)
$E(S_n)$	5.589	5.596	3.873	4.152
$E(T_1)$	3.864	3.864	3.124	3.282
$E(T_2)$	3.874	3.874	3.156	3.282
$E(T_3)$	3.902	3.902	3.727	3.286
$E(T_4)$	5.367	5.367	3.767	3.523
$E(T_5)$	5.541	5.541	4.183	3.982
$E(T_6)$	7.053	7.053	5.664	5.313
SOC_1	0.06	0.05	0	0
SOC_2	0.07	0.05	0.01	0.02
SOC_3	0.04	0.02	0.02	0.01
SOC_4	2.97	2.94	0	0
SOC_5	3.5	3.8	0	0.03
SOC_6	0.69	0.77	0.24	0