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Change in Optoelectronic Properties of $ExBox^{+4}$ on Functionalization and Guest Encapsulation

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Supplementary Information

Table S1. The approximate diameter (R, in Å) of the $ExBox^{+4}$/functionalized $ExBox^{+4}$ moieties (along the horizontal and vertical directions respectively) in their respective free states as well after forming host-guest complexes.

Systems	R
$ExBox^{+4}$	14.86, 9.43
NH_2-$ExBox^{+4}$-F	14.76, 10.02
CN-$ExBox^{+4}$-NH_2	14.89, 10.23
NO_2-$ExBox^{+4}$-NH_2	14.52, 9.50
Cor@$ExBox^{+4}$	14.41, 7.31
NCor@$ExBox^{+4}$	14.83, 8.12
BCor@$ExBox^{+4}$	14.84, 7.60
BiPh@$ExBox^{+4}$	13.90, 8.60
TCNE@$ExBox^{+4}$	15.39, 7.69
TCNQ@$ExBox^{+4}$	15.05, 8.50
TTF@$ExBox^{+4}$	14.77, 8.69
Cor@NH_2-$ExBox^{+4}$-F	14.66, 8.02
NCor@NH_2-$ExBox^{+4}$-F	14.67, 7.99
BCor@NH_2-$ExBox^{+4}$-F	14.71, 8.03
BiPh@NH_2-$ExBox^{+4}$-F	14.57, 9.20

TCNE@NH_2-ExBox^{+4}-F	14.97, 10.11
TCNQ@NH_2-ExBox^{+4}-F	14.86, 8.49
TTF@NH_2-ExBox^{+4}-F	13.87, 9.33
Cor@CN-ExBox^{+4}-NH_2	14.33, 7.69
NCor@CN-ExBox^{+4}-NH_2	14.47, 7.48
BCor@CN-ExBox^{+4}-NH_2	14.63, 8.16
BiPh@CN-ExBox^{+4}-NH_2	14.80, 9.57
TCNE@CN-ExBox^{+4}-NH_2	15.12, 8.94
TCNQ@CN-ExBox^{+4}-NH_2	14.06, 8.54
TTF@CN-ExBox^{+4}-NH_2	14.33, 9.67
Cor@NO_2-ExBox^{+4}-NH_2	14.89, 8.05
NCor@NO_2-ExBox^{+4}-NH_2	14.88, 7.99
BCor@NO_2-ExBox^{+4}-NH_2	14.81, 7.48
BiPh@NO_2-ExBox^{+4}-NH_2	14.70, 8.63
TCNE@NO_2-ExBox^{+4}-NH_2	15.37, 8.18
TCNQ@NO_2- ExBox^{+4}-NH_2	13.86, 8.53
TTF@NO_2-ExBox^{+4}-NH_2	14.78, 8.77

Table S2. HOMO-LUMO gap (Gap) (in eV), Polarizability (α) (in a.u.^{3}) and Static first Hyperpolarizability (β) (in a.u.); dipole moment (μ) (in Debye) for all the studied guest/host systems in their respective free states.

Systems	**Gap**	α	β	μ
Cor	7.34	268.20	0.05	0.00
NCor	4.47	294.52	740.23	2.02
BCor	4.47	310.99	356.77	1.53
BiPh	9.19	125.15	0.00	0.00
TCNE	8.05	80.77	0.02	0.00
TCNQ	5.90	195.38	0.08	0.00
TTF	7.52	128.91	4.95	0.51
ExBox^{+4}	7.69	552.12	73.29	0.19
NH_2-ExBox^{+4}-F	6.50	561.32	417.32	2.35
CN-ExBox^{+4}-NH_2	6.42	575.05	698.13	4.62

NO_2-ExBox^{+4}-NH_2	6.47	576.79	472.07	10.83

Table S3. The components of dipole moment ($\mu_{x/y/z}$) and first hyperpolarizability ($\beta_{x/y/z}$) along x, y and z directions.

Systems	μ_x	μ_y	μ_z	β_x	β_y	β_z
ExBox^{+4}	0.00	0.00	0.08	0.00	0.00	122.14
NH_2-ExBox^{+4}-F	-0.35	0.75	-0.42	613.71	221.32	241.12
CN-ExBox^{+4}-NH_2	-0.24	1.33	-1.22	1120.16	184.84	254.79
NO_2-ExBox^{+4}-NH_2	-3.26	1.68	-2.16	755.79	68.72	207.59
Cor@ExBox^{+4}	0.00	0.00	0.00	1.60	-1.29	0.49
NCor@ExBox^{+4}	-0.57	0.00	0.32	8216.85	-35.73	-1494.00
BCor@ExBox^{+4}	-0.47	0.00	-0.80	-331.70	-0.12	837.06
BiPh@ExBox^{+4}	0.00	0.00	0.13	0.19	0.30	-46.78
TCNE@ExBox^{+4}	-0.57	0.00	0.08	213.51	2.42	-86.54
TCNQ@ExBox^{+4}	0.00	0.50	1.72	-5.51	-137.90	253.38
TTF@ExBox^{+4}	0.55	0.00	1.16	-59.80	0.03	80.80
Cor@NH_2-ExBox^{+4}-F	0.77	-0.60	-2.35	-590.29	-68.18	-105.62
NCor@NH_2-ExBox^{+4}-F	1.65	-0.41	-0.87	3232.56	-8092.73	-1745.90
BCor@NH_2-ExBox^{+4}-F	-1.18	0.54	-1.67	295.08	123.52	890.58
BiPh@NH_2-ExBox^{+4}-F	0.46	0.41	0.39	-920.58	111.64	-161.07
TCNE@NH_2-ExBox^{+4}-F	-1.43	0.01	-1.62	365.94	254.96	265.97
TCNQ@NH_2-ExBox^{+4}-F	-0.84	0.21	0.66	653.95	253.64	258.96
TTF@NH_2-ExBox^{+4}-F	1.33	0.47	-0.50	-211.55	239.61	-166.83
Cor@CN-ExBox^{+4}-NH_2	-0.36	1.14	-1.90	954.45	145.59	-0.70
NCor@CN-ExBox^{+4}-NH_2	-1.17	0.97	-1.65	19476.85	22742.71	1097.20
BCor@CN-ExBox^{+4}-NH_2	-1.31	1.16	-1.15	1262.96	-87.71	861.14
BiPh@CN-ExBox^{+4}-NH_2	0.12	-0.67	-0.94	-1313.42	-58.69	159.74
TCNE@CN-ExBox^{+4}-NH_2	0.13	1.30	-1.59	823.69	177.81	293.06
TCNQ@CN-ExBox^{+4}-NH_2	1.14	3.14	0.42	-1155.08	-468.83	226.98
TTF@CN-ExBox^{+4}-NH_2	-0.20	0.51	-0.67	1047.43	-71.31	76.16

Cor@NO_2-ExBox^{+4}-NH_2	-2.48	1.52	-3.30	821.82	84.26	-154.03
NCor@NO_2-ExBox^{+4}-NH_2	-3.49	-0.75	1.92	-2435.63	-19185.35	2200.60
BCor@NO_2-ExBox^{+4}-NH_2	-1.99	1.45	-2.82	846.12	455.10	-1214.00
BiPh@NO_2-ExBox^{+4}-NH_2	-2.60	1.66	-2.32	758.69	158.55	112.66
TCNE@NO_2-ExBox^{+4}-NH_2	-1.56	0.56	-1.99	708.58	39.38	223.12
TCNQ@NO_2-ExBox^{+4}-NH_2	2.90	0.94	0.65	-942.70	299.40	-237.77
TTF@NO_2-ExBox^{+4}-NH_2	-2.09	1.35	-0.89	733.19	212.88	176.94

Table S4. TDDFT results computed at the wb97xd/6-311+G(d,p) level for ExBox^{+4}/functionalized ExBox^{+4} and guest@ExBox^{+4}/functionalized ExBox^{+4} moieties where the various important excited states, oscillator strengths (*f*) associated with that particular electronic transition, vertical excitation energy associated (in eV) with that particular electronic transition, the percentage contribution of the dominant electronic transitions have been presented.

Systems	**Excited State Number**	***f***	**Vertical excitation energy**	**Dominant Transition**
ExBox^{+4}	1) 5	0.1535	4.99	HOMO-3 -> LUMO (35.47%) HOMO -> LUMO+2 (34.32%)
	2) 16	0.0891	5.33	HOMO-8 -> LUMO (14.14%) HOMO-3 -> LUMO+1 (13.94%)
Cor@ExBox^{+4}	1) 16	0.7883	4.66	HOMO-1 -> LUMO+4 (32.55%) HOMO -> LUMO+5 (29.99%)
NCor@ExBox^{+4}	1) 19	0.0463	3.69	HOMO-1 -> LUMO+4

				(44.90%) HOMO-1 -> LUMO+3 (15.39%)
BCor@ExBox^{+4}	1) 11	0.0499	3.50	HOMO -> LUMO+5 (77.30%)
BiPh@ExBox^{+4}	1) 13	0.4048	5.01	HOMO -> LUMO+8 (39.26%) HOMO -> LUMO+4 (9.48%)
TCNE@ExBox^{+4}	1) 11	1.1646	4.60	HOMO-12 -> LUMO (36.19%) HOMO-4 -> LUMO+1 10.22%)
TCNQ@ExBox^{+4}	1) 12	2.1618	4.40	HOMO-5 -> LUMO+2 (22.05%) HOMO-6 -> LUMO+1 (19.86%)
TTF@ExBox^{+4}	1) 12 2) 17	0.2482 0.1912	4.27 4.42	HOMO -> LUMO+6 (58.82%) HOMO -> LUMO+12 (7.83%) HOMO -> LUMO+11 (19.73%) HOMO-4 -> LUMO+1 (16.56%) HOMO-8 -> LUMO (15.45%)
NH_2-ExBox^{+4}-F	1) 8 2) 9	0.0696 0.0799	4.96 5.04	HOMO-2 -> LUMO (32.47%) HOMO-2 -> LUMO+1 (10.56%) HOMO-3 -> LUMO+2

				(24.93%) HOMO-4 -> LUMO (24.25%)
NCor@NH_2-$ExBox^{+4}$-F	1) 5	0.0360	1.85	HOMO -> LUMO+3 (32.47%) HOMO -> LUMO+10 (18.41%)
BCor@NH_2-$ExBox^{+4}$-F	1) 2 2) 12 3) 14	0.0115 0.0514 0.0308	1.39 3.50 3.61	HOMO-1 -> LUMO (97.57%) HOMO -> LUMO+5 (77.26%) HOMO-1 -> LUMO+5 (45.08%) HOMO-15 -> LUMO (28.99%)
BiPh@NH_2-$ExBox^{+4}$-F	1) 16	0.2065	5.04	HOMO-1 -> LUMO+8 (29.78%) HOMO-5 -> LUMO+1 (22.19%)
TCNQ@NH_2-$ExBox^{+4}$-F	1) 14	2.1478	4.40	HOMO-4 -> LUMO+2 (24.18%) HOMO-5 -> LUMO+1 (35.48%)
TTF@NH_2-$ExBox^{+4}$-F	1) 18	0.2109	4.52	HOMO -> LUMO+7 (49.92%) HOMO -> LUMO+13 (14.35%)
CN-$ExBox^{+4}$-NH_2	1) 4	1.9080	4.32	HOMO-1 -> LUMO+1 (48.37%) HOMO-3 -> LUMO (25.92%)
Cor@CN-$ExBox^{+4}$-NH_2	1) 19	0.6082	4.63	HOMO-1 -> LUMO+4

				(25.77%) HOMO -> LUMO+6 (23.31%)
NCor@CN-ExBox^{+4}-NH_2	1) 5 2) 19	0.0288 0.0547	1.71 3.62	HOMO -> LUMO+2 (73.90%) HOMO-1 -> LUMO+3 (48.86%) HOMO-1 -> LUMO+4 (19.91%)
BCor@CN-ExBox^{+4}-NH_2	1) 13 2) 14	0.0485 0.0436	3.48 3.51	HOMO-4 -> LUMO (48.26%) HOMO-2 -> LUMO (13.07%) HOMO -> LUMO+5 (47.52%) HOMO -> LUMO+4 (15.38%)
BiPh@CN-ExBox^{+4}-NH_2	1) 4 2)7	0.7245 0.2446	4.22 4.42	HOMO-3 -> LUMO (54.98%) HOMO-1 -> LUMO (11.46%) HOMO-4 -> LUMO+1 (32.20%) HOMO-7 -> LUMO+1 (18.68%)
TCNE@CN-ExBox^{+4}-NH_2	1) 11 2) 13	1.2801 0.1995	4.36 4.56	HOMO-3 -> LUMO+1 (54.13%) HOMO-2 -> LUMO+2 (13.33%) HOMO-13 -> LUMO (22.04%)

				HOMO-5 -> LUMO (20.70%)
TCNQ@CN-ExBox^{+4}-NH_2	1) 14	2.2069	4.38	HOMO-5 -> LUMO+1 (40.14%) HOMO-4 -> LUMO+2 (30.42%)
NO_2-ExBox^{+4}-NH_2	1) 5 2) 10	1.8641 0.1593	4.32 5.02	HOMO-1 -> LUMO+1 (51.97%) HOMO-3 -> LUMO (17.18%) HOMO-2 -> LUMO+2 (35.60%) HOMO-3 -> LUMO (12.47%)
Cor@NO_2-ExBox^{+4}-NH_2	1) 18 2) 19	0.4063 0.8516	4.58 4.61	HOMO-1 -> LUMO+6 (40.95%) HOMO -> LUMO+5 (35.25%) HOMO-1 -> LUMO+5 (27.46%) HOMO -> LUMO+6 (26.46%)
NCor@NO_2-ExBox^{+4}-NH_2	1) 5 2) 7	0.0476 0.0421	1.84 2.07	HOMO -> LUMO+12 (35.18%) HOMO -> LUMO+4 (23.46%) HOMO -> LUMO+4 (44.69%) HOMO -> LUMO+12 (24.75%)
BCor@NO_2-ExBox^{+4}-NH_2	1) 14	0.0292	3.50	HOMO-2 -> LUMO

				(30.48%) HOMO-16 -> LUMO (29.35%)
	2) 16	0.0414	3.54	HOMO-16 -> LUMO (38.65%) HOMO-6 -> LUMO (16.13%)
BiPh@NO_2-ExBox^{+4}-NH_2	1) 8	0.4975	4.41	HOMO-2 -> LUMO+1 (47.89%) HOMO-1 -> LUMO+1 (23.97%)
TCNQ@NO_2-ExBox^{+4}-NH_2	1) 15	2.1820	4.41	HOMO-3 -> LUMO+2 (40.25%) HOMO-4 -> LUMO+1 (27.05%)
TTF@NO_2-ExBox^{+4}-NH_2	1) 14	0.1729	4.27	HOMO -> LUMO+8 (22.85%) HOMO -> LUMO+14 (19.05%)

Figures

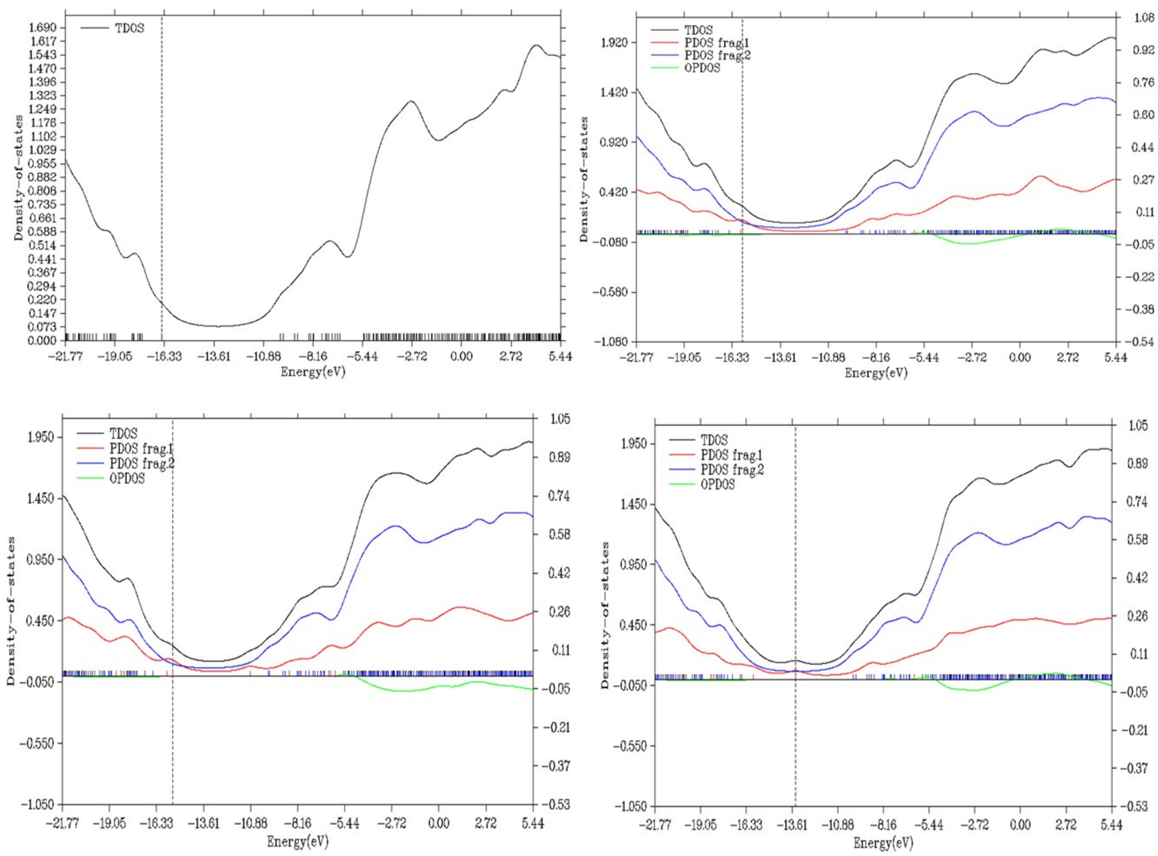

Figure S1. The TDOS plots of NH_2-ExBox^{+4}-F, Cor@NH_2-ExBox^{+4}-F, NCor@NH_2-ExBox^{+4}-F, BCor@NH_2-ExBox^{+4}-F respectively (in clockwise direction). Here frag1 denotes guest moieties whereas frag2 denotes the host. The vertical line designates the E_F whereas the vertical bars represent occupied and virtual orbitals.

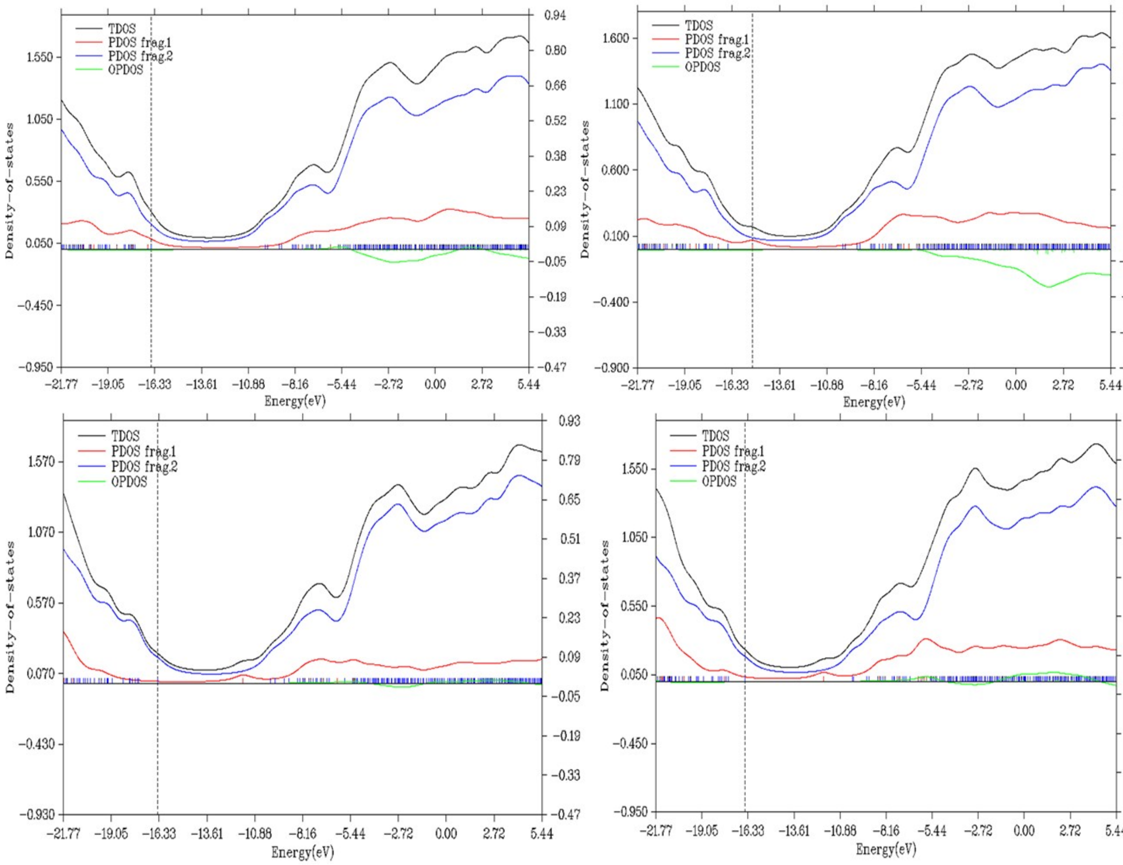

Figure S2. The TDOS plots of BiPh@NH_2-ExBox^{+4}-F, TTF@NH_2-ExBox^{+4}-F, TCNQ@NH_2-ExBox^{+4}-F, TCNE@NH_2-ExBox^{+4}-F respectively (in clockwise direction). Here frag1 denotes guest moieties whereas frag2 denotes the host. The vertical line designates the E_F whereas the vertical bars represent occupied and virtual orbitals.

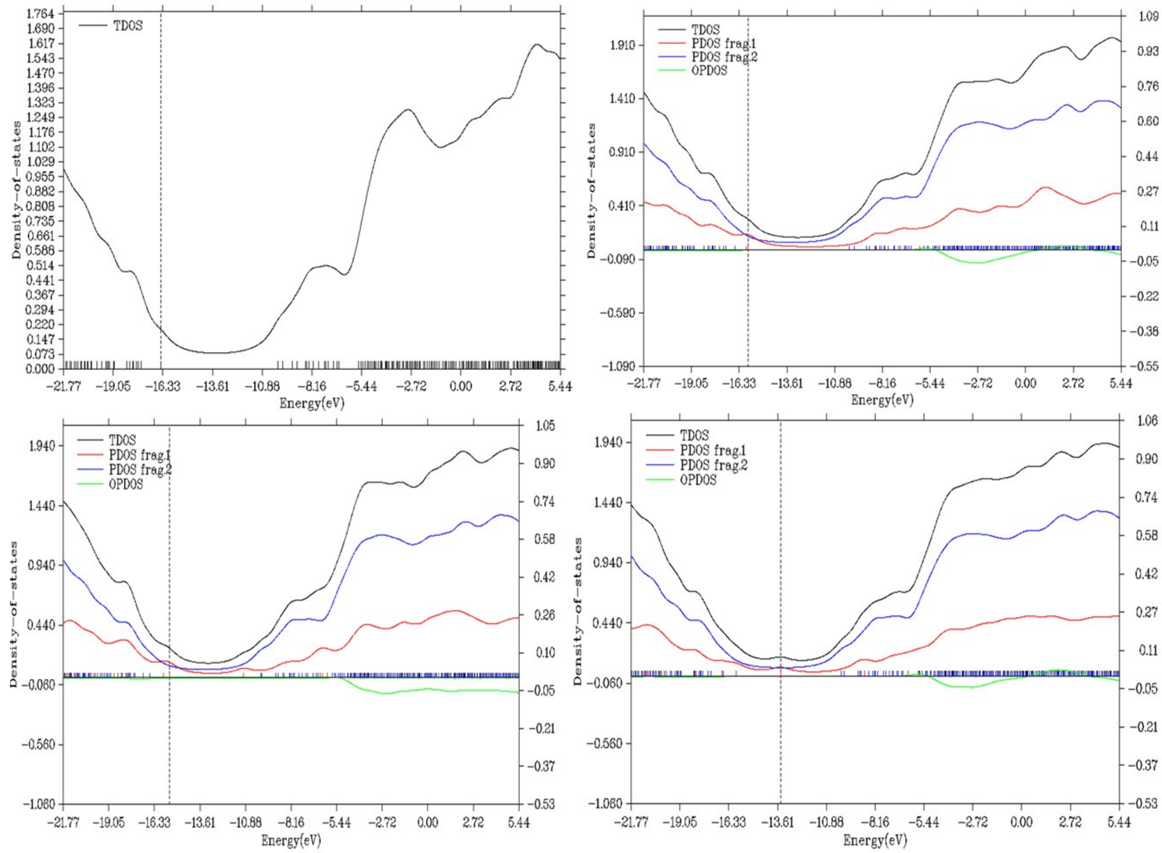

Figure S3. The TDOS plots of CN-ExBox^{+4}-NH_2, Cor@CN-ExBox^{+4}-NH_2, NCor@CN-ExBox^{+4}-NH_2, BCor@CN-ExBox^{+4}-NH_2 respectively (in clockwise direction). Here frag1 denotes guest moieties whereas frag2 denotes the host. The vertical line designates the E_F whereas the vertical bars represent occupied and virtual orbitals.

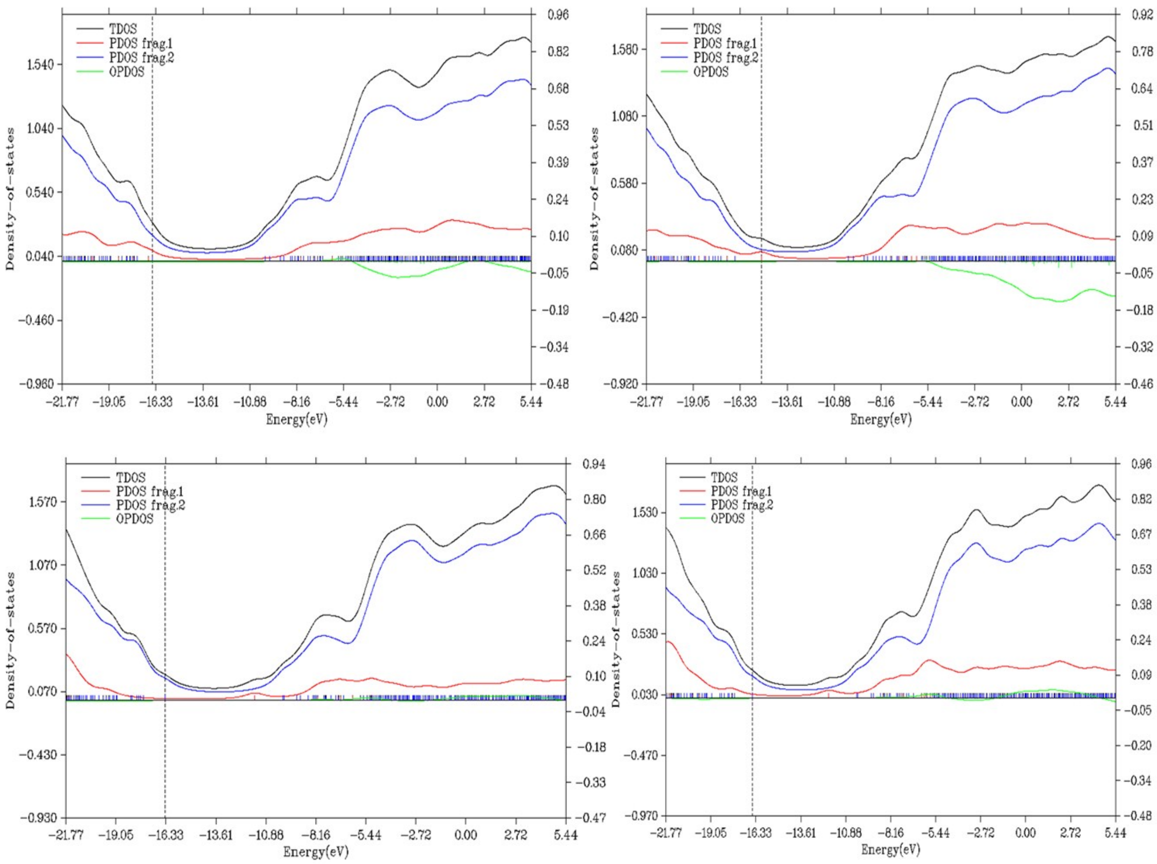

Figure S4. The TDOS plots of BiPh@CN-ExBox^{+4}-NH_2, TTF@CN-ExBox^{+4}-NH_2, TCNQ@CN-ExBox^{+4}-NH_2, TCNE@CN-ExBox^{+4}-NH_2 respectively (in clockwise direction). Here frag1 denotes guest moieties whereas frag2 denotes the host. The vertical line designates the E_F whereas the vertical bars represent occupied and virtual orbitals.

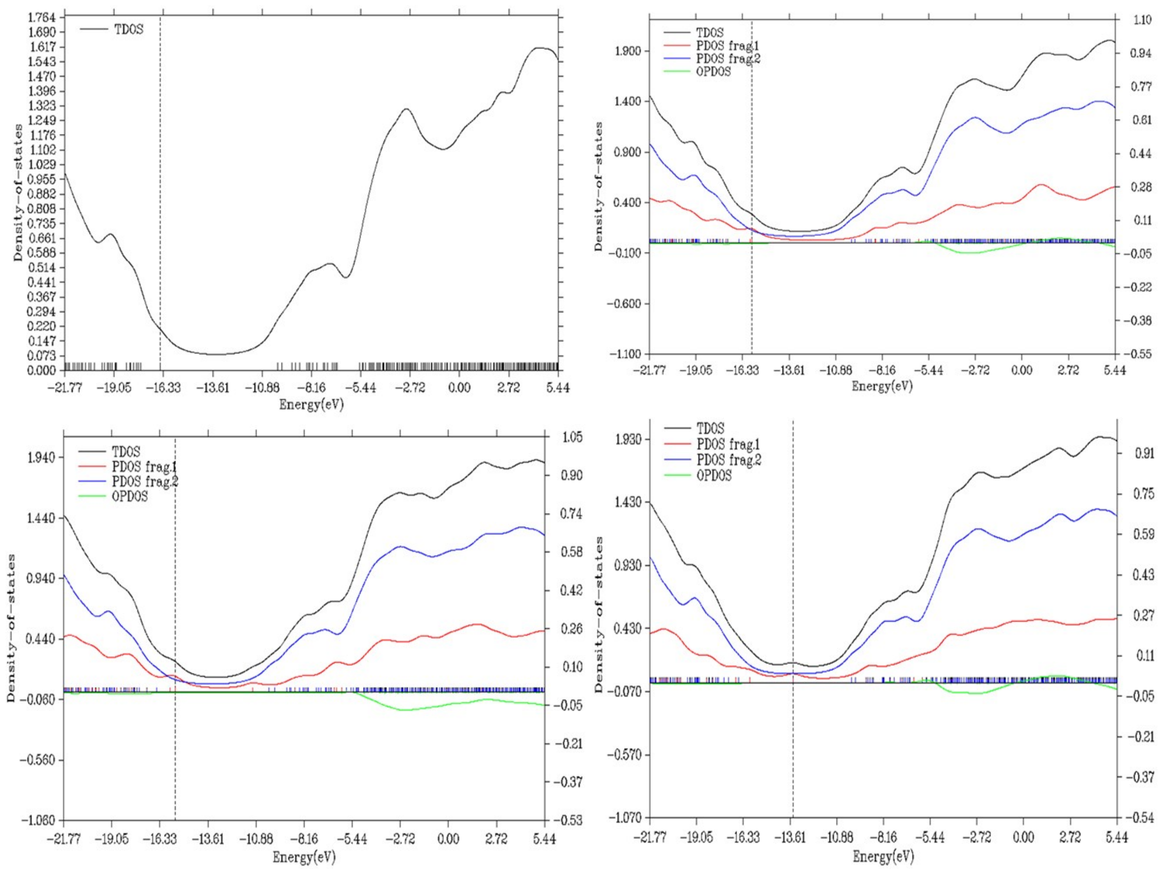

Figure S5. The TDOS plots of NO_2-ExBox^{+4}-NH_2, Cor@NO_2-ExBox^{+4}-NH_2, NCor@NO_2-ExBox^{+4}-NH_2, BCor@NO_2-ExBox^{+4}-NH_2 respectively (in clockwise direction). Here frag1 denotes guest moieties whereas frag2 denotes the host. The vertical line designates the E_F whereas the vertical bars represent occupied and virtual orbitals.

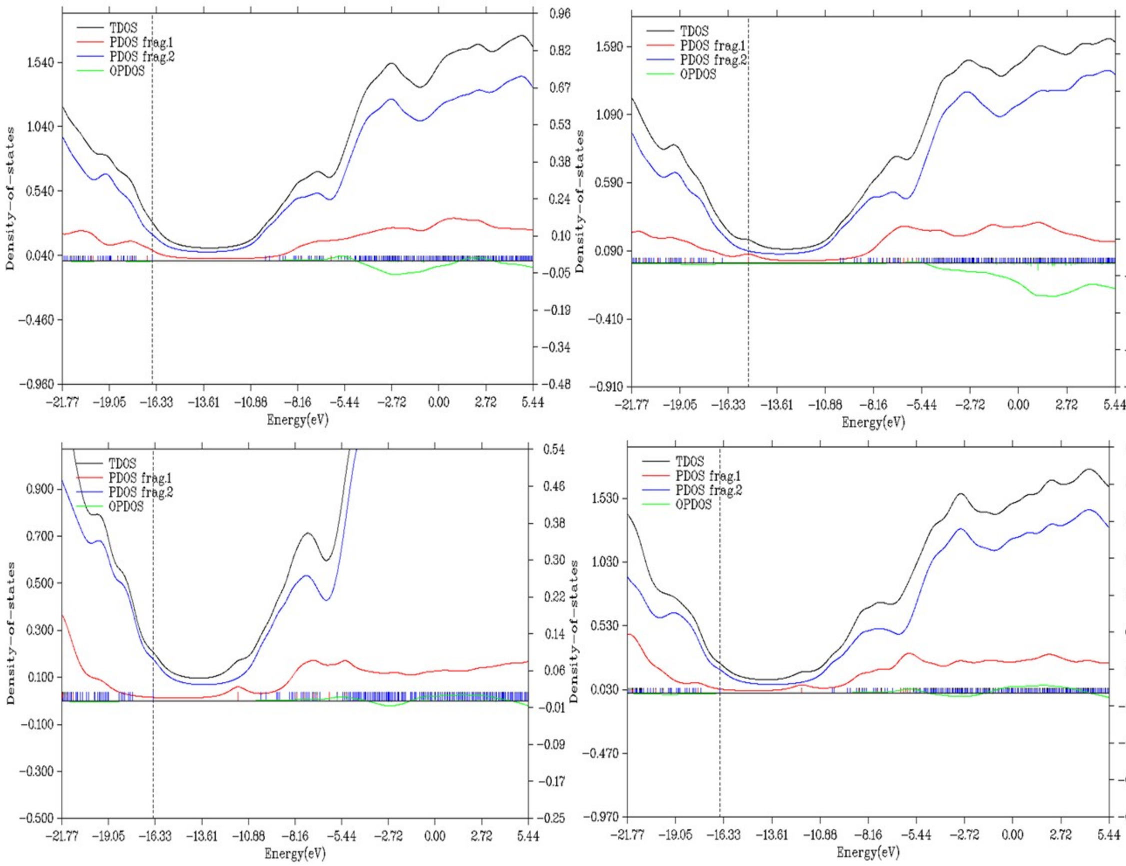

Figure S6. The TDOS plots of BiPh@NO_2-ExBox^{+4}-NH_2, TTF@NO_2-ExBox^{+4}-NH_2, TCNQ@NO_2-ExBox^{+4}-NH_2, TCNE@NO_2-ExBox^{+4}-NH_2 respectively (in clockwise direction). Here frag1 denotes guest moieties whereas frag2 denotes the host. The vertical line designates the E_F whereas the vertical bars represent occupied and virtual orbitals.

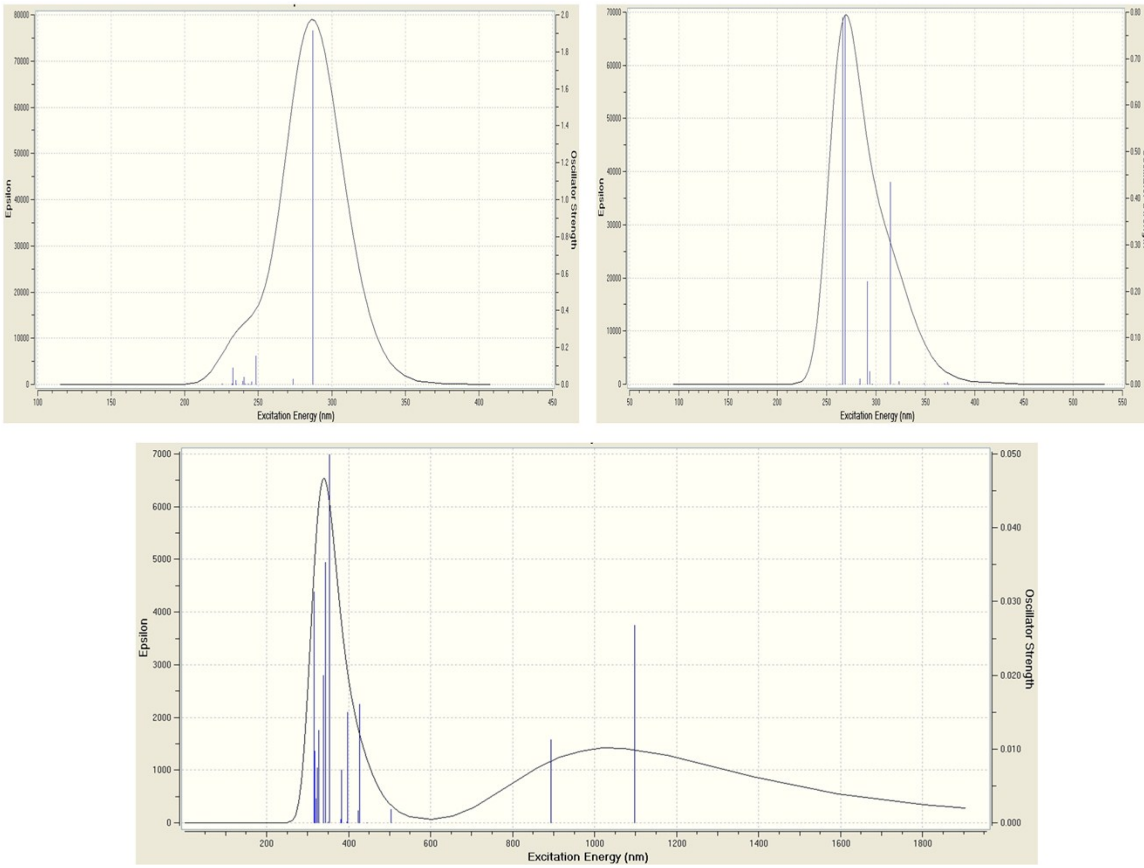

Figure S7. Absorption spectra of $ExBox^{+4}$, $Cor@ExBox^{+4}$ and $BCor@ExBox^{+4}$ respectively (in clockwise direction).

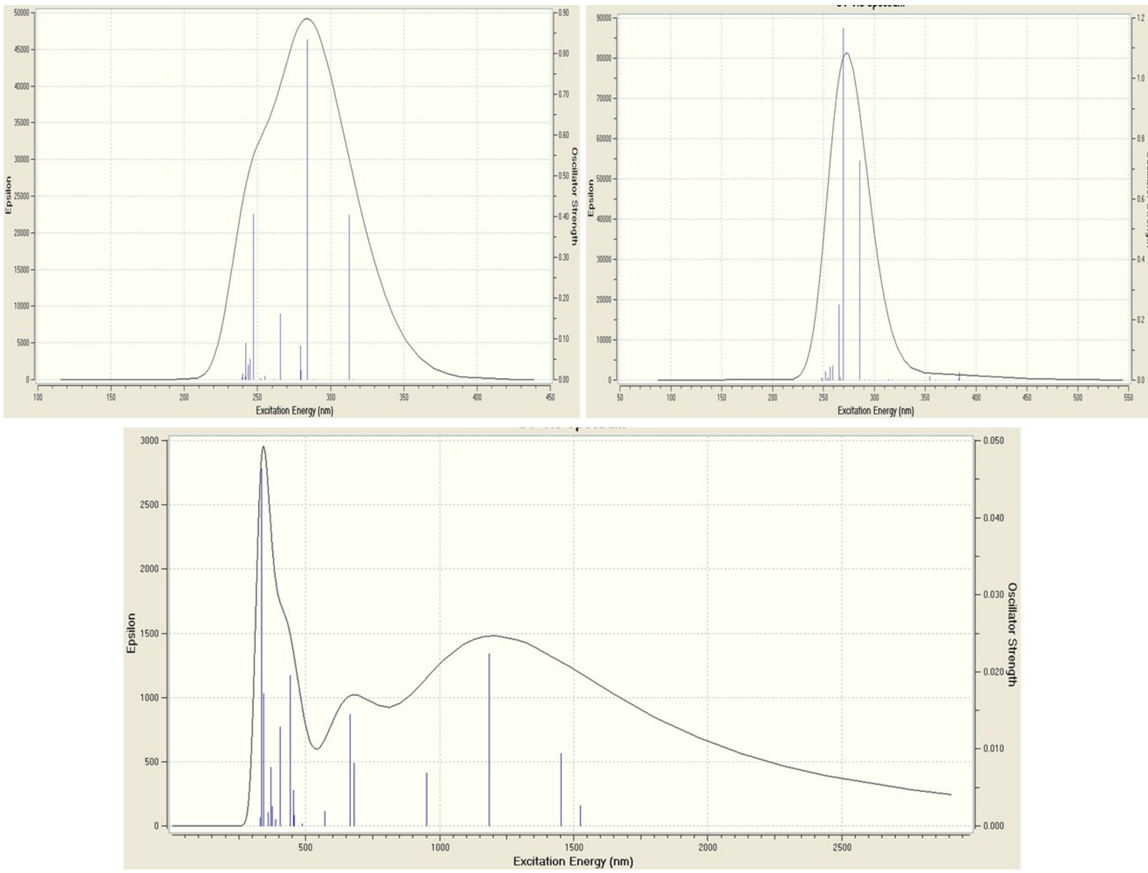

Figure S8. Absorption spectra of BiPh@ExBox^{+4}, TCNE@ExBox^{+4} and NCor@ExBox^{+4} respectively (in clockwise direction).

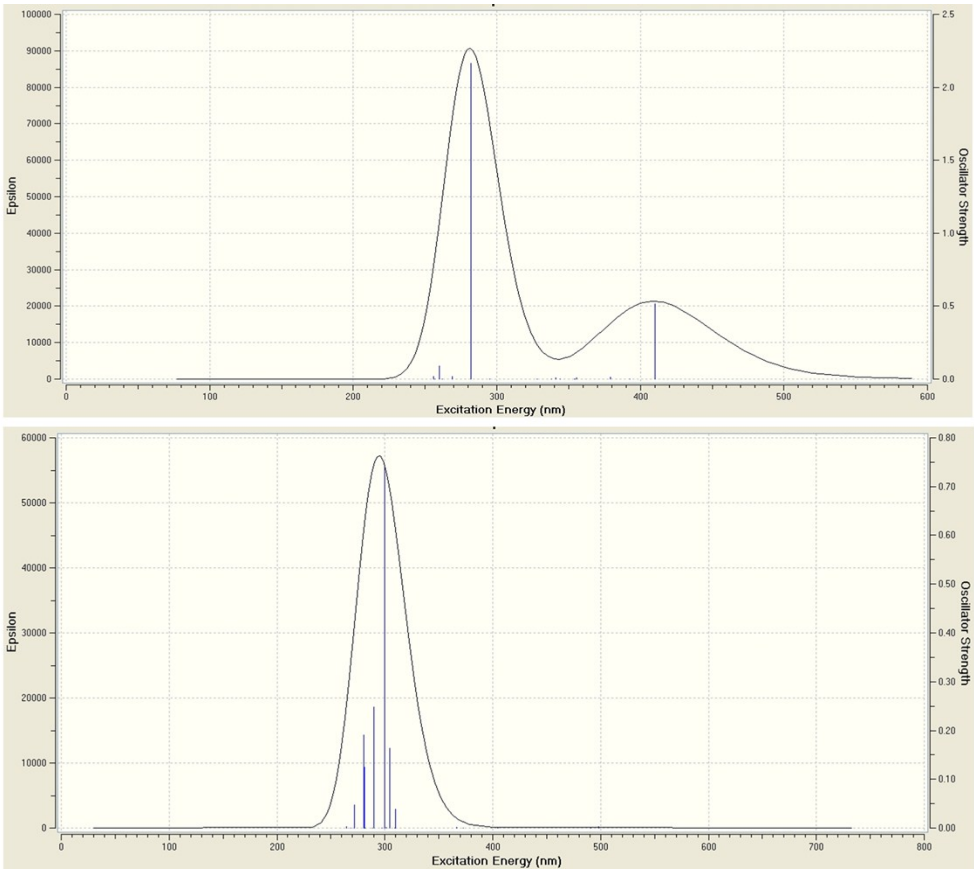

Figure S9. Absorption spectra of TCNQ@ExBox^{+4} (top) and TTF@ExBox^{+4} respectively.

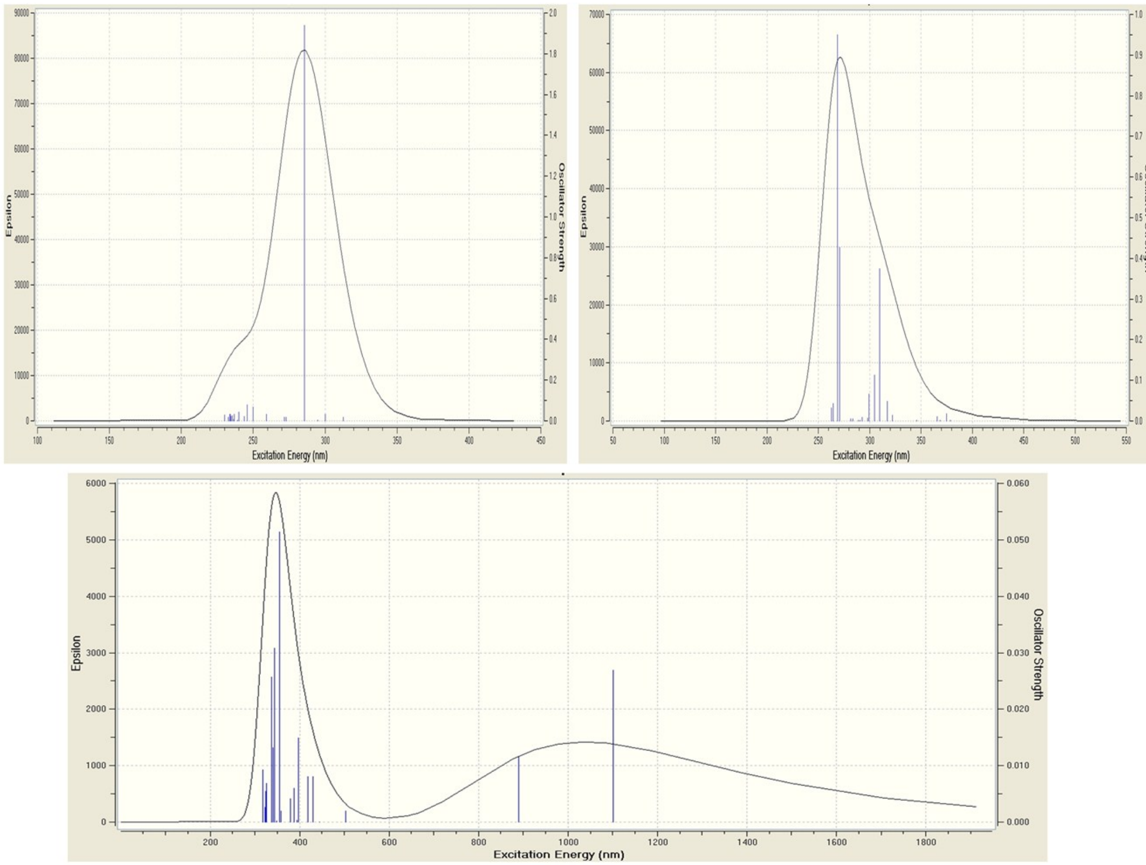

Figure S10. Absorption spectra of NH_2-ExBox^{+4}-F, Cor@NH_2-ExBox^{+4}-F and BCor@NH_2-ExBox^{+4}-F respectively (in clockwise direction).

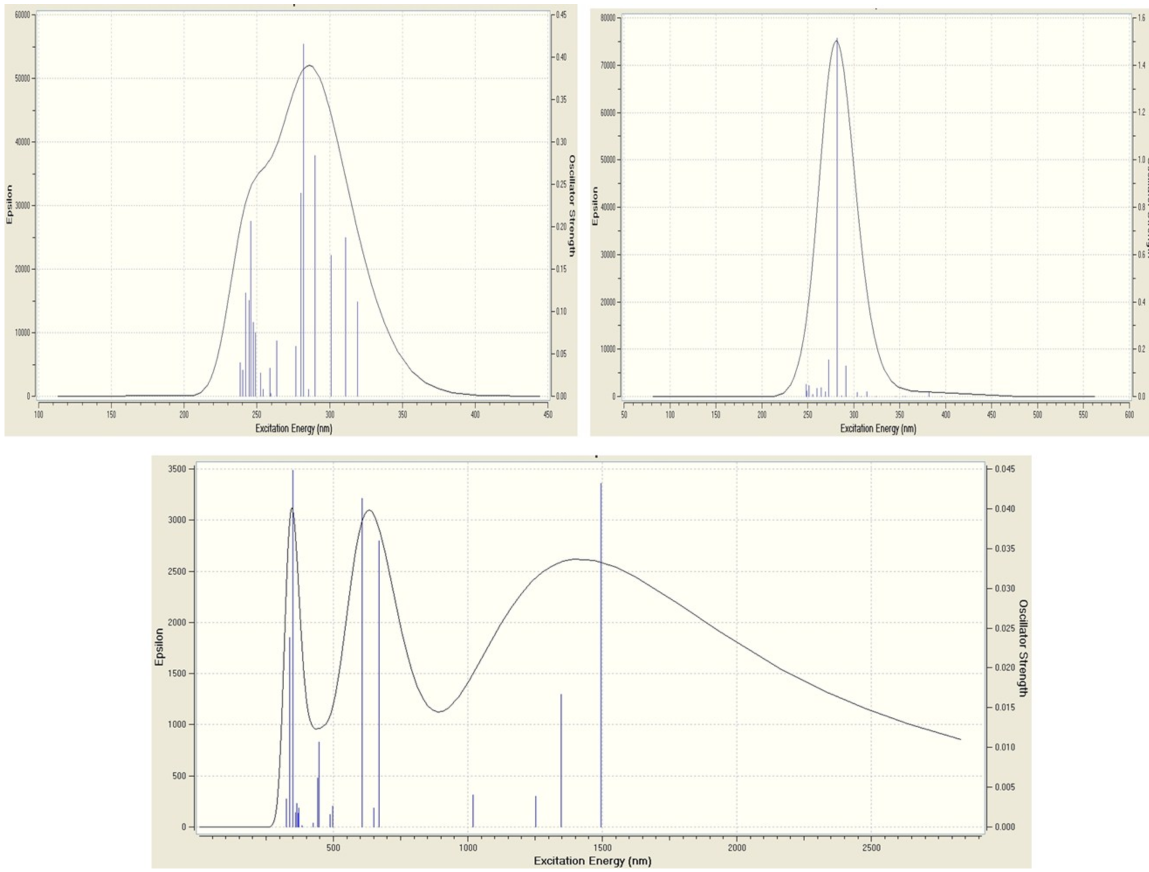

Figure S11. Absorption spectra of BiPh@NH_2-ExBox^{+4}-F, TCNE@NH_2-ExBox^{+4}-F and NCor@NH_2-ExBox^{+4}-F respectively (in clockwise direction).

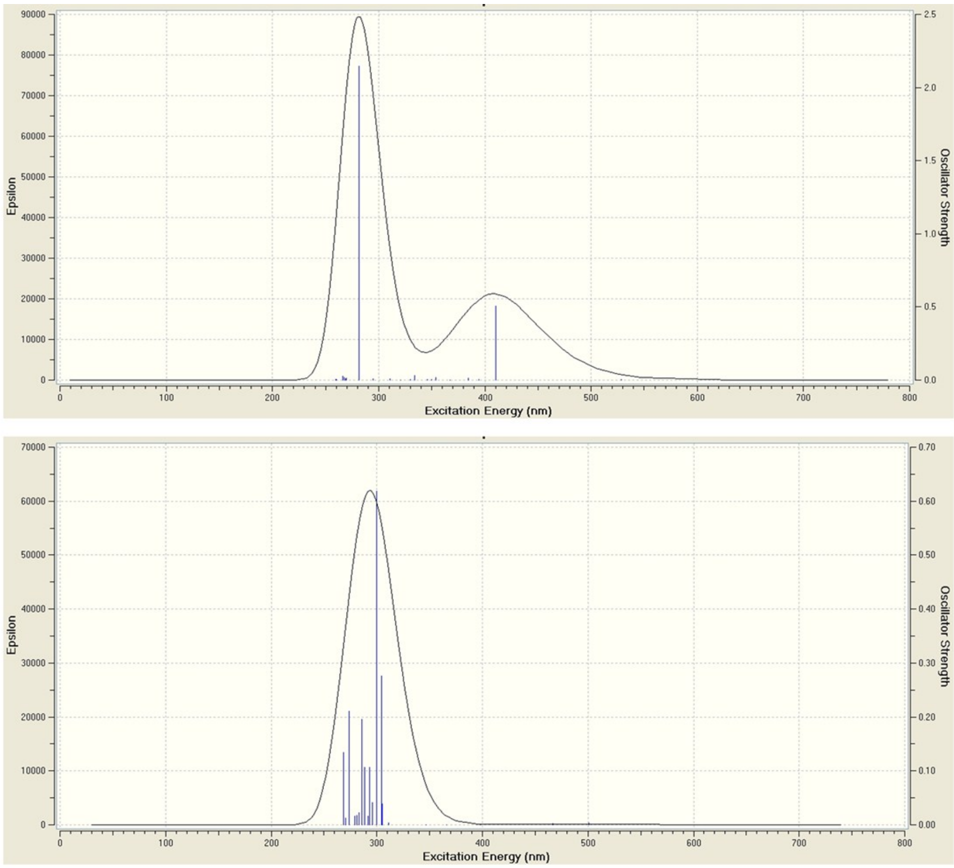

Figure S12. Absorption spectra of TCNQ@NH_2-ExBox^{+4}-F (top) and TTF@NH_2-ExBox^{+4}-F respectively.

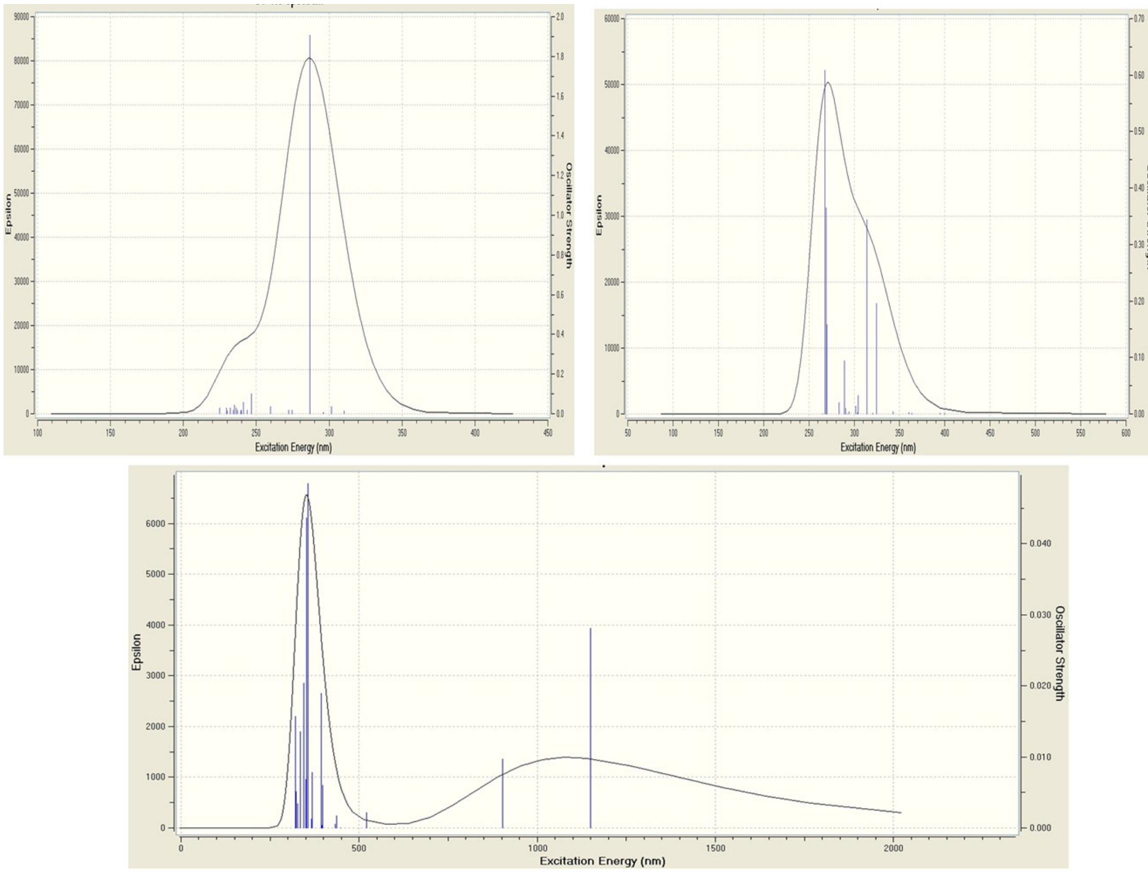

Figure S13. Absorption spectra of CN-ExBox^{+4}-NH_2, Cor@CN-ExBox^{+4}-NH_2 and BCor@CN-ExBox^{+4}-NH_2 respectively (in clockwise direction).

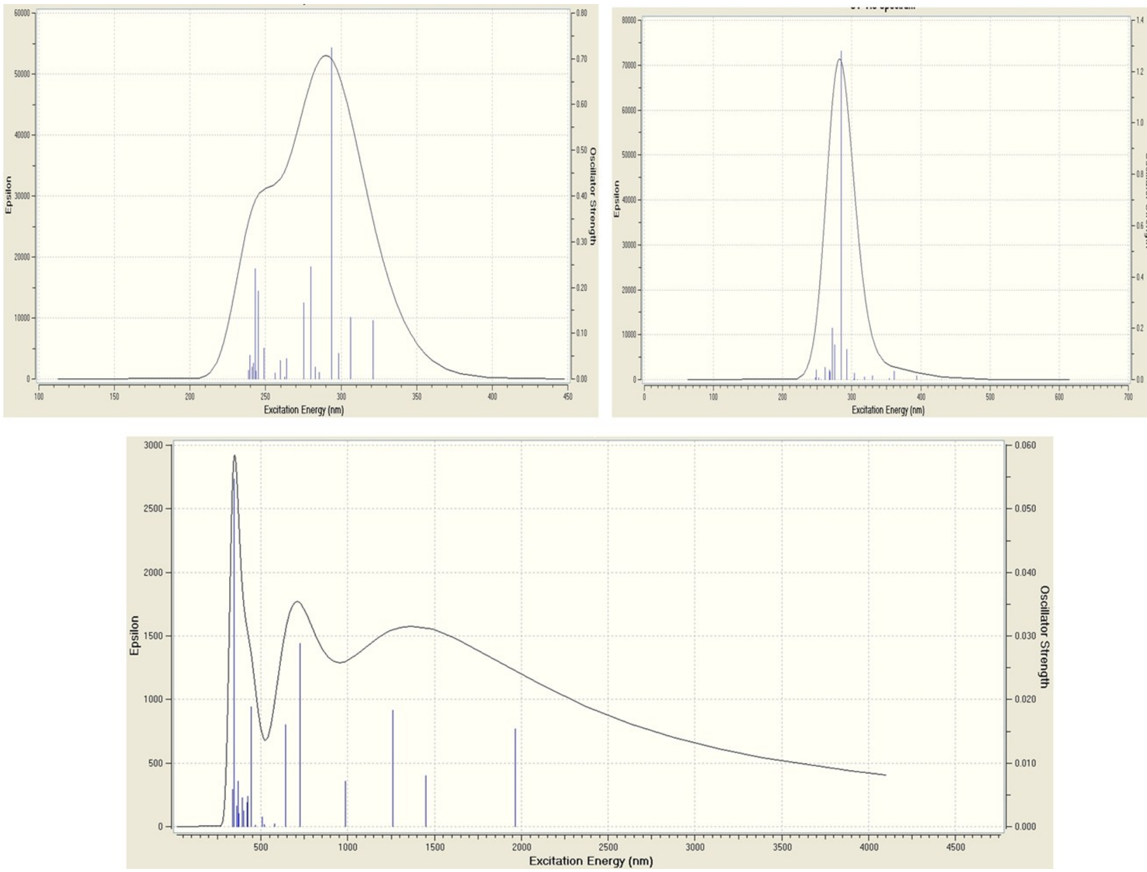

Figure S14. Absorption spectra of BiPh@CN-ExBox^{+4}-NH_2, TCNE@CN-ExBox^{+4}-NH_2 and NCor@CN-ExBox^{+4}-NH_2 respectively (in clockwise direction).

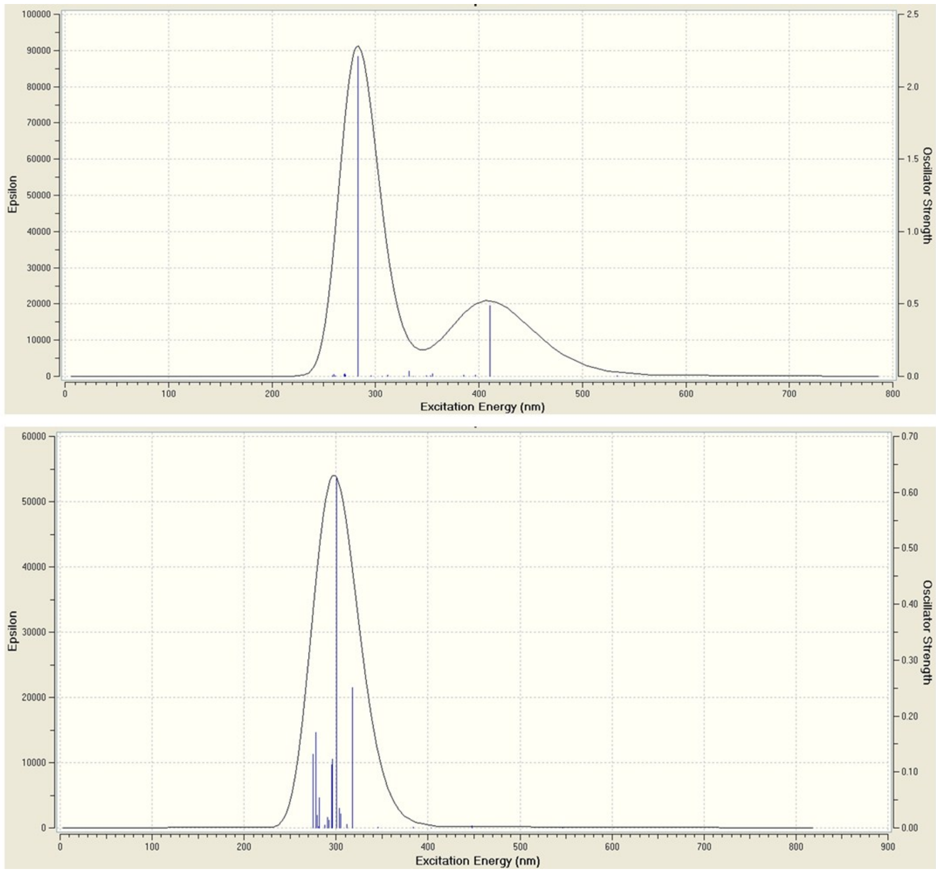

Figure S15. Absorption spectra of TCNQ@CN-ExBox^{+4}-NH_2 (top) and TTF@CN-ExBox^{+4}-NH_2 respectively (in clockwise direction).

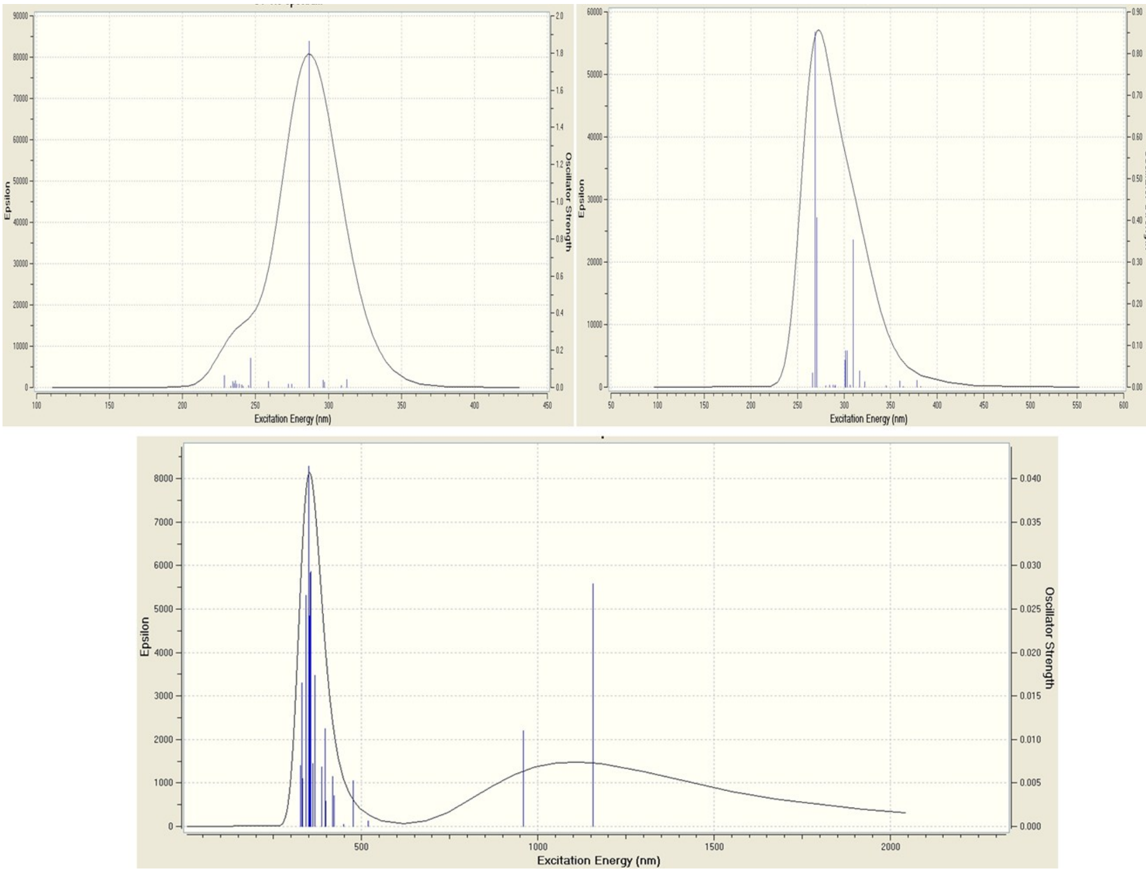

Figure S16. Absorption spectra of NO_2-ExBox^{+4}-NH_2, Cor@NO_2-ExBox^{+4}-NH_2 and BCor@NO_2-ExBox^{+4}-NH_2 respectively (in clockwise direction).

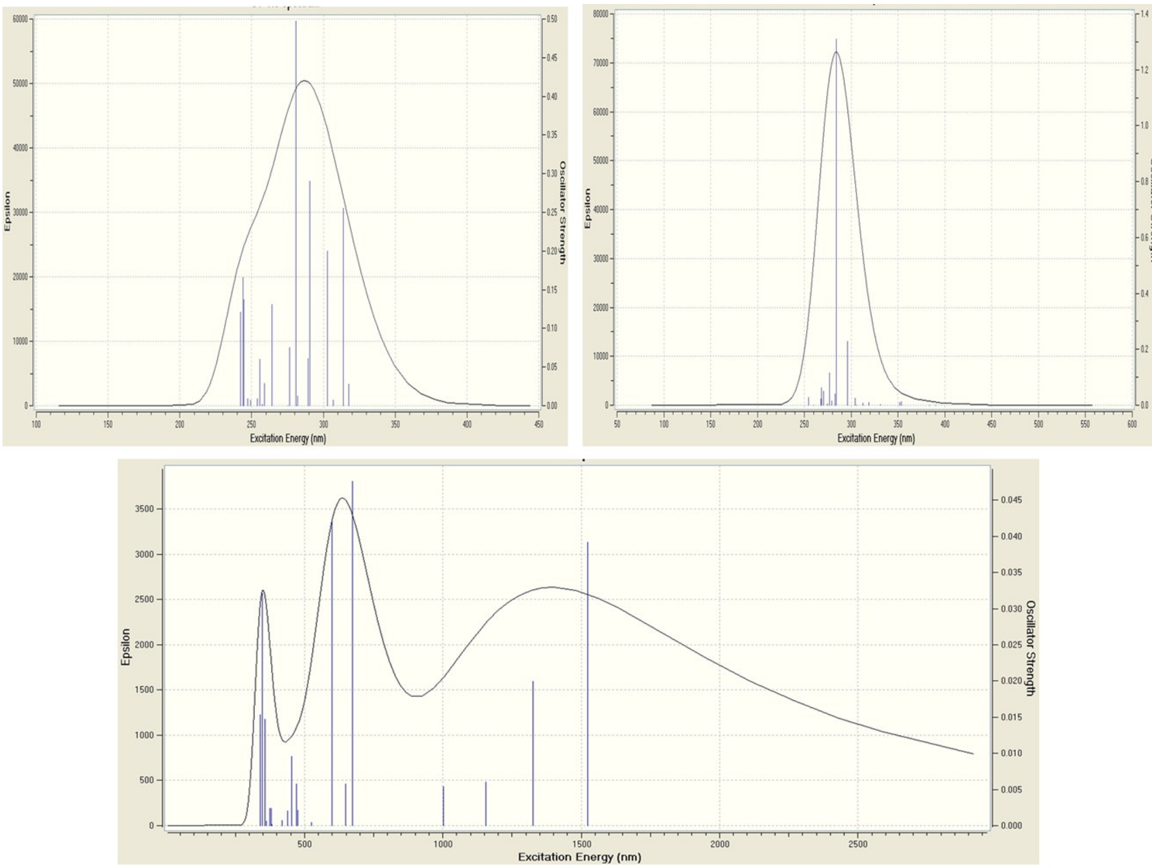

Figure S17. Absorption spectra of BiPh@NO_2-ExBox^{+4}-NH_2, TCNE@NO_2-ExBox^{+4}-NH_2 and NCor@NO_2-ExBox^{+4}-NH_2 respectively (in clockwise direction).

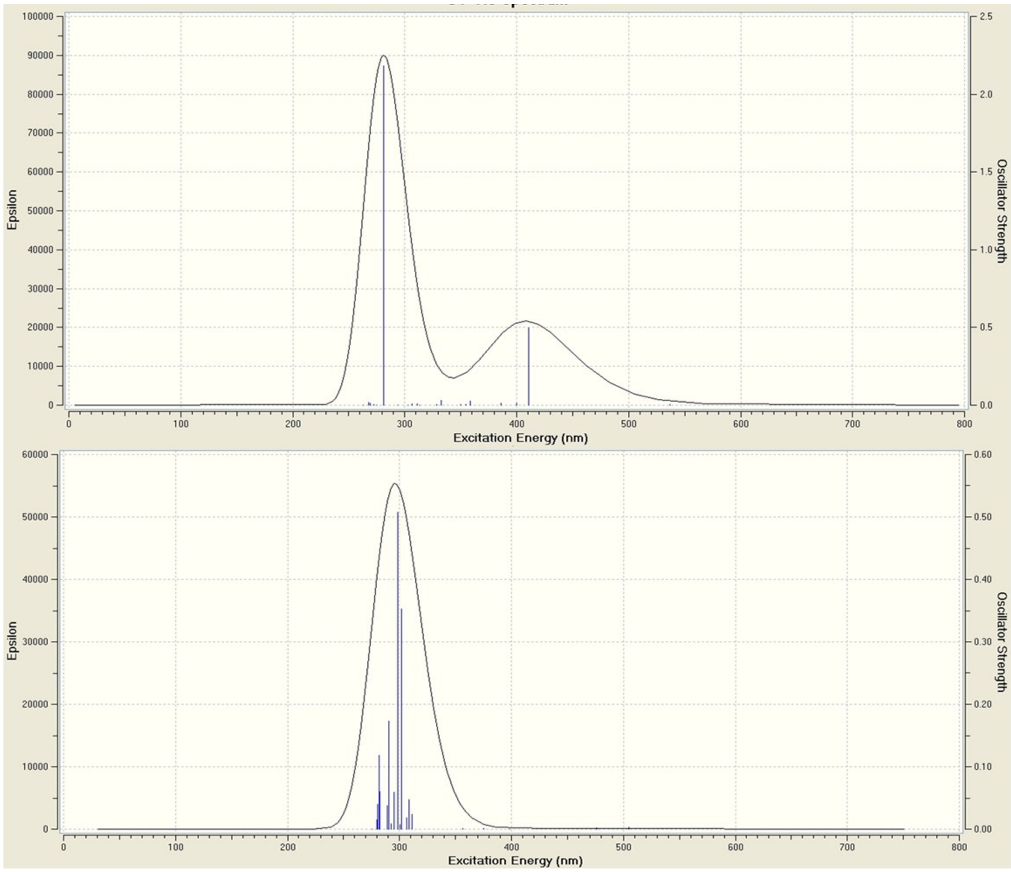

Figure S18. Absorption spectra of TCNQ@NO_2-ExBox^{+4}-NH_2 (top) and TTF@NO_2-ExBox^{+4}-NH_2 respectively.

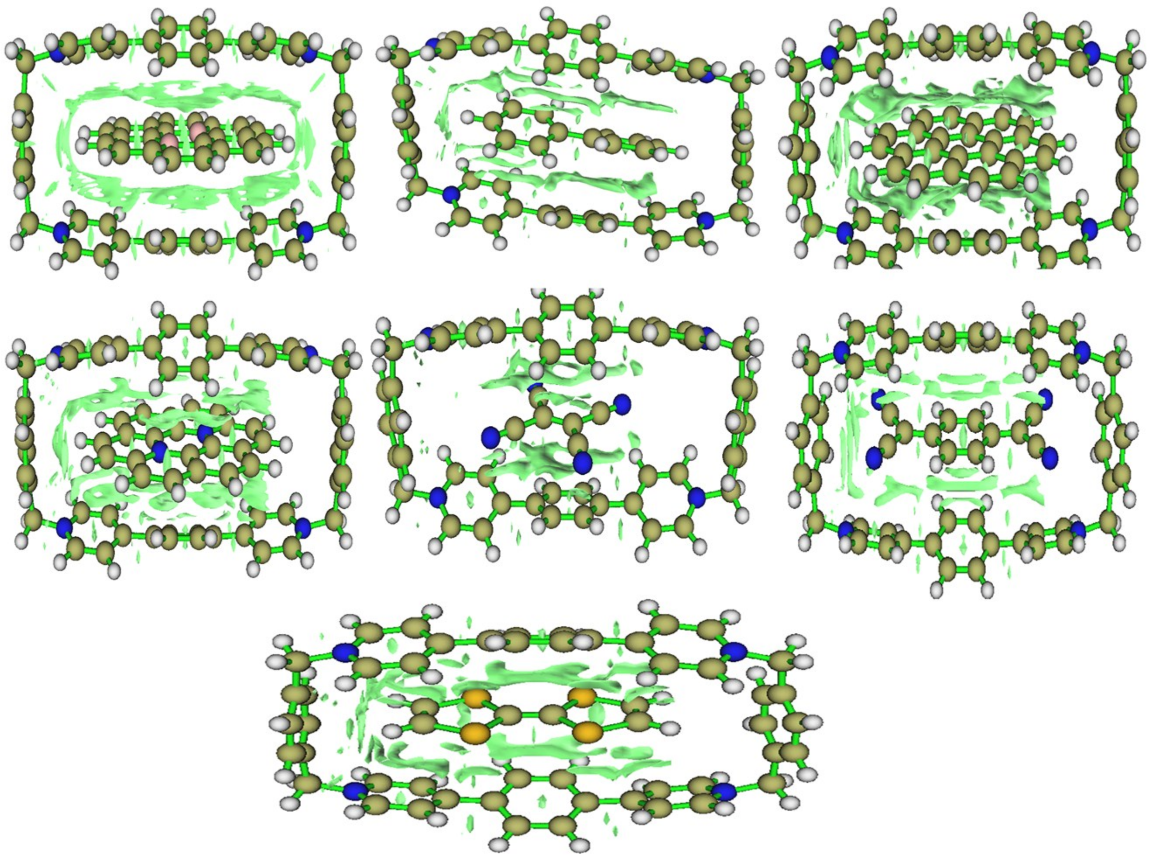

Figure S19: NCI isosurface of BCor@ExBox^{+4}, BiPh@ExBox^{+4}, Cor@ExBox^{+4}, TCNQ@ExBox^{+4}, TTF@ExBox^{+4}, NCor@ExBox^{+4}, TCNE@ExBox^{+4} (in clockwise direction).

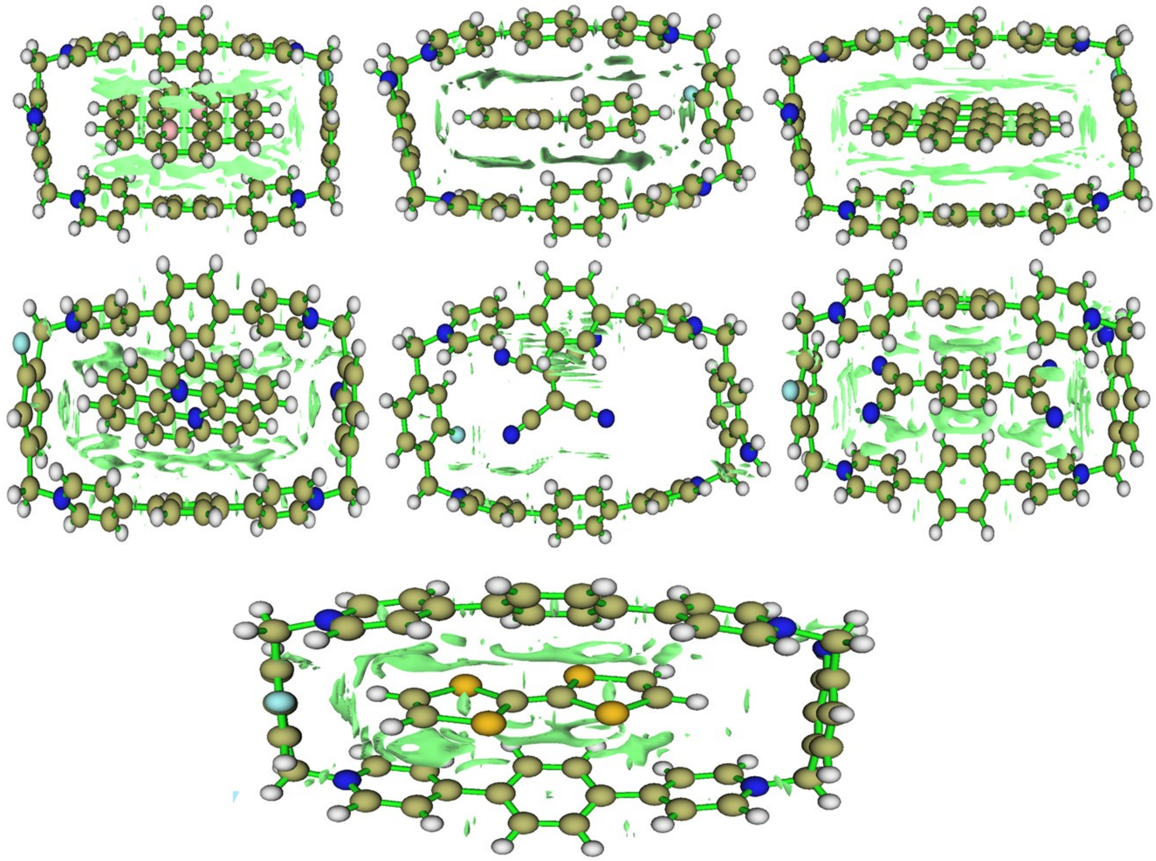

Figure S20: NCI isosurface of BCor@NH_2-ExBox^{+4}-F, BiPh@NH_2-ExBox^{+4}-F, Cor@NH_2-ExBox^{+4}-F, TCNQ@NH_2-ExBox^{+4}-F, TTF@NH_2-ExBox^{+4}-F, NCor@NH_2-ExBox^{+4}-F, TCNE@NH_2-ExBox^{+4}-F (in clockwise direction).

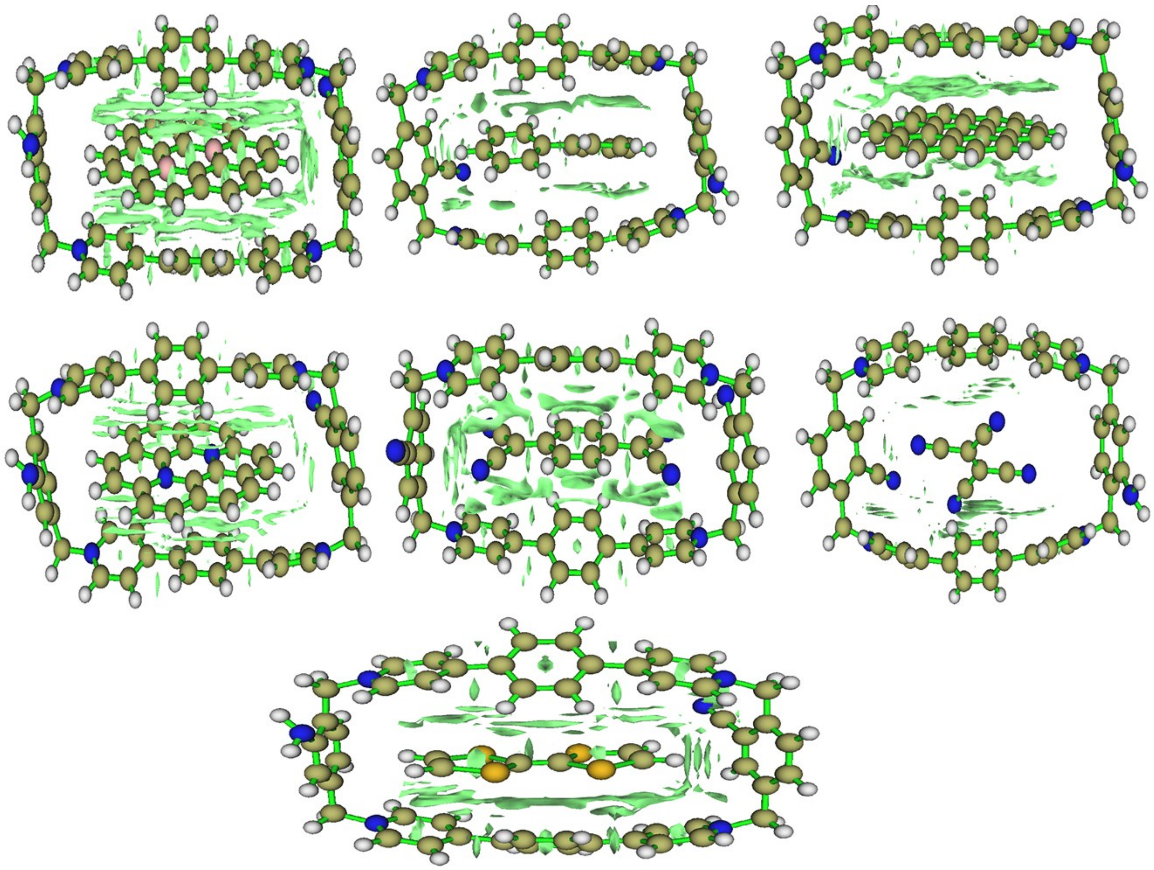

Figure S21: NCI isosurface of BCor@NH_2-ExBox^{+4}-CN, BiPh@NH_2-ExBox^{+4}-CN, Cor@NH_2-ExBox^{+4}-CN, TCNE@NH_2-ExBox^{+4}-CN, TTF@NH_2-ExBox^{+4}-F, NCor@NH_2-ExBox^{+4}-F, TCNQ@NH_2-ExBox^{+4}-F (in clockwise direction).

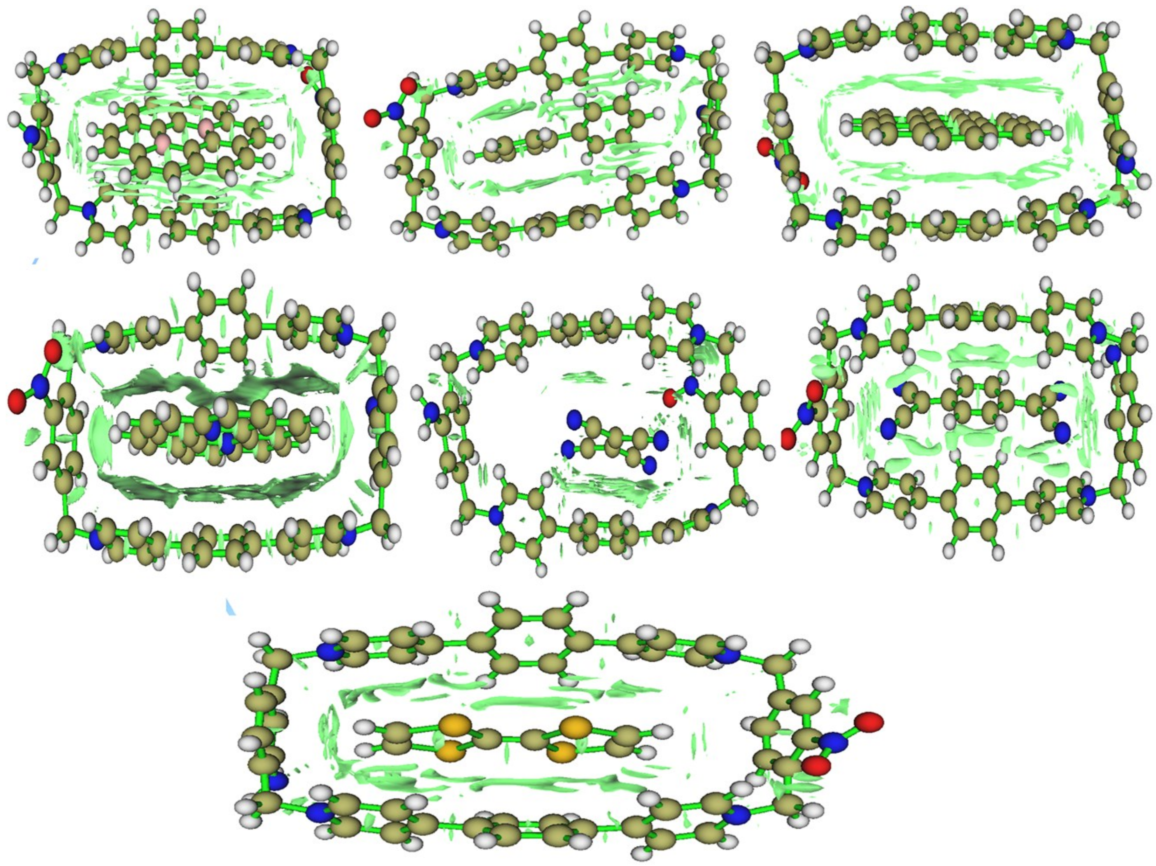

Figure S22: NCI isosurface of BCor@NO_2-ExBox^{+4}-NH_2, BiPh@NO_2-ExBox^{+4}-NH_2, Cor@NO_2-ExBox^{+4}-NH_2, TCNQ@NO_2-ExBox^{+4}-NH_2, TTF@NO_2-ExBox^{+4}-NH_2, NCor@NO_2-ExBox^{+4}-NH_2, TCNE@NO_2-ExBox^{+4}-NH_2 (in clockwise direction).

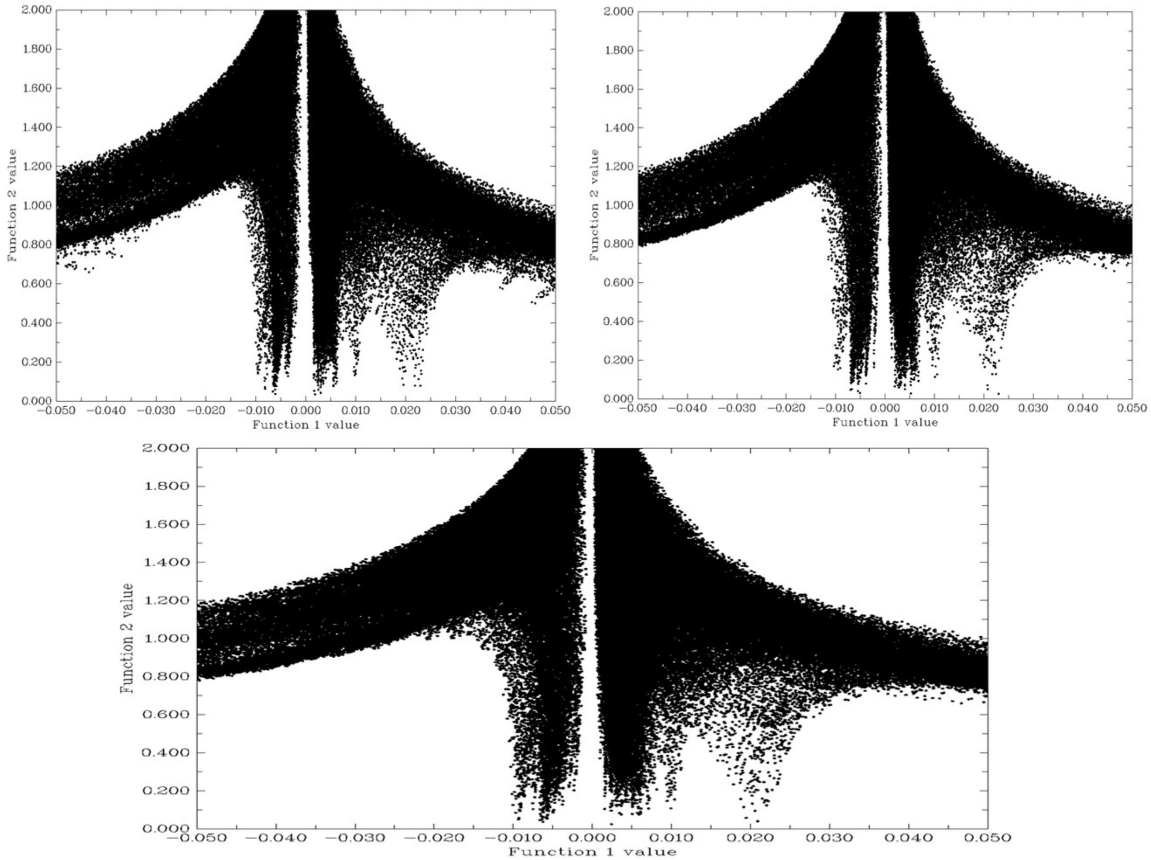

Figure S23: Scatter plot of sign(λ_2)ρ (function 1) versus *s* (function 2) for BCor@ExBox^{+4}, Cor@ExBox^{+4} and NCor@ExBox^{+4} (in clockwise direction). All throughout the manuscript, sign(λ_2)ρ has been designated as function 1 whereas *s* has been designated as function 2.

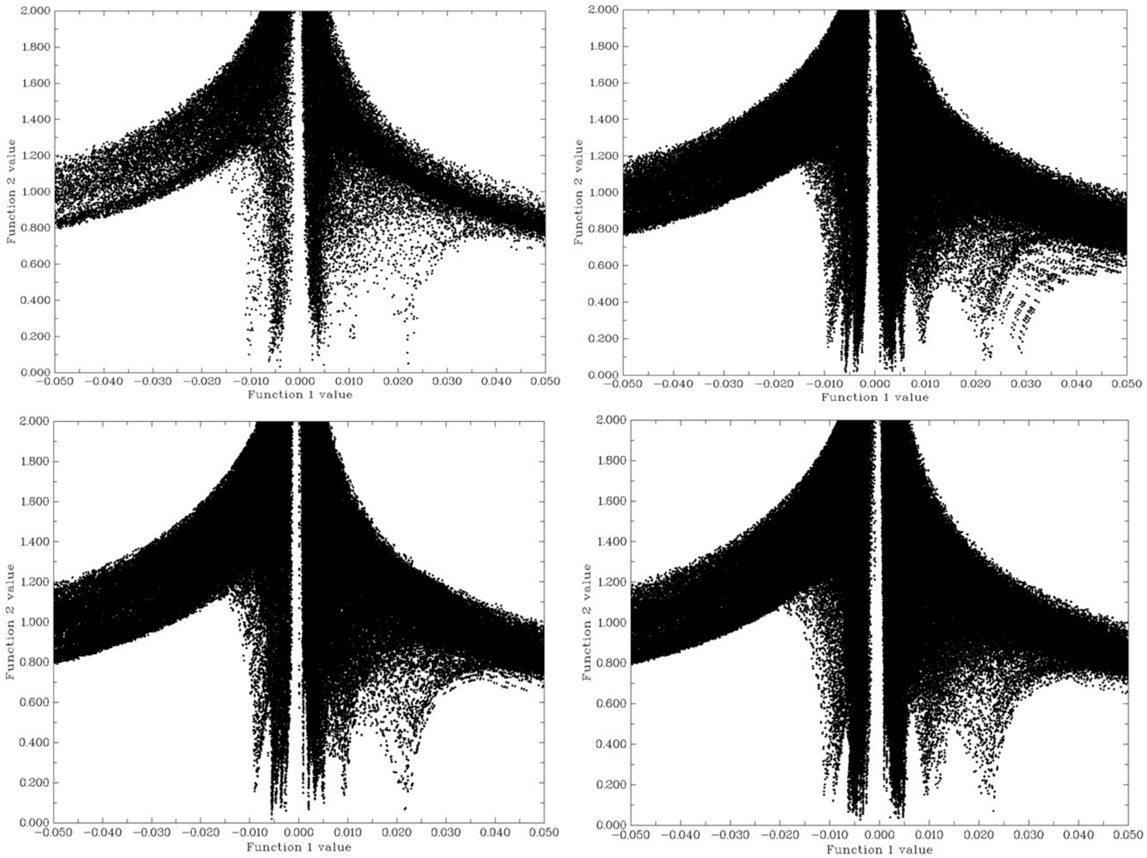

Figure S24: Scatter plot of sign(λ_2) ρ versus s for BiPh@ExBox^{+4}, TTF@ExBox^{+4}, TCNQ@ExBox^{+4}, TCNE@ExBox^{+4} (in clockwise direction).

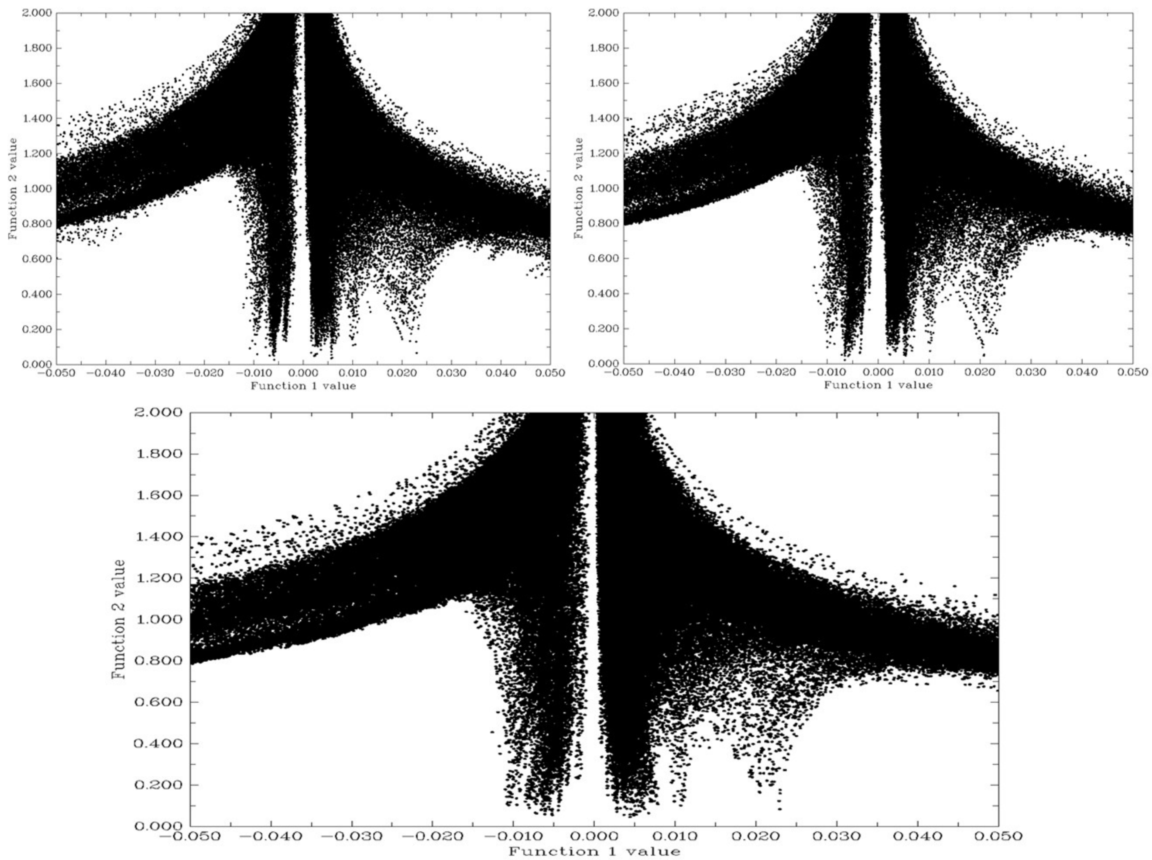

Figure S25: Scatter plot of sign(λ_2) ρ versus s for BCor@ NH_2-ExBox^{+4}-F, Cor@ NH_2-ExBox^{+4}-F and NCor@ NH_2-ExBox^{+4}-F (in clockwise direction).

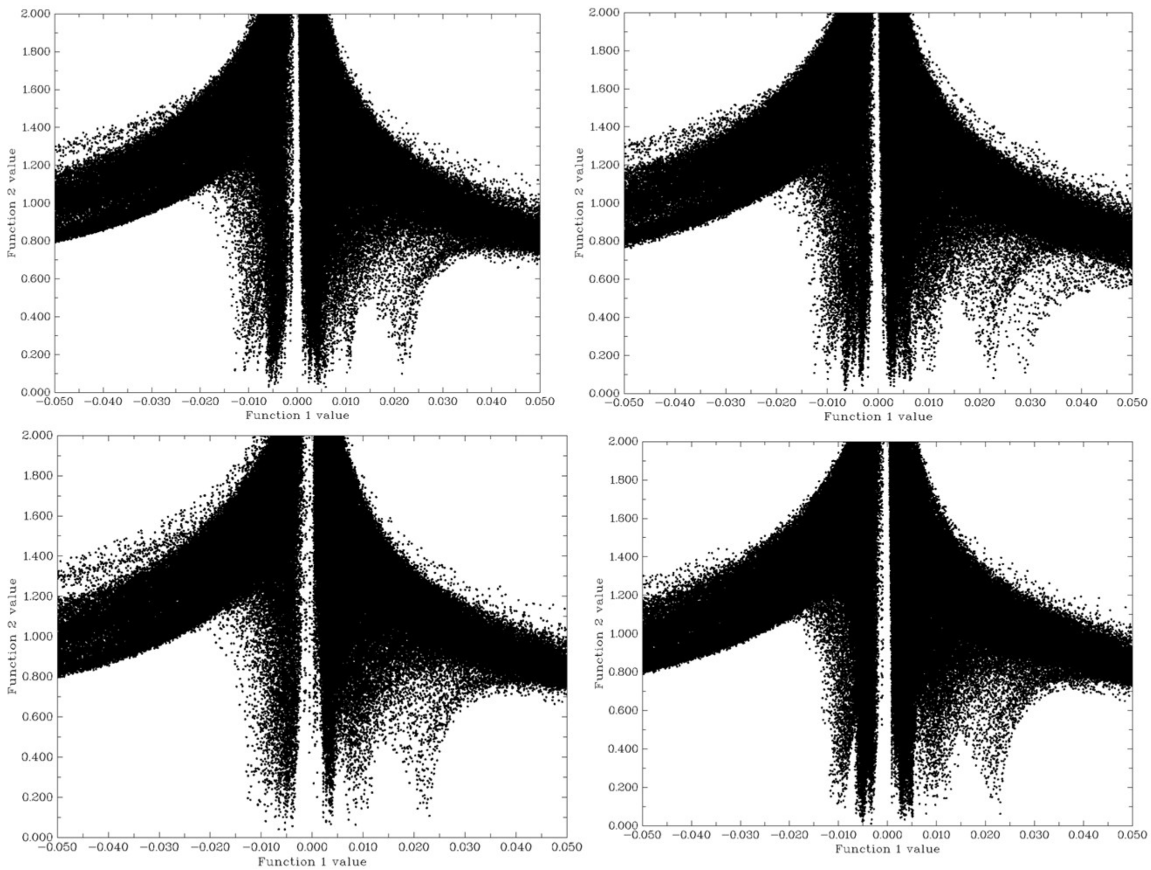

Figure S26: Scatter plot of sign(λ_2) ρ versus s for BiPh@NH_2-ExBox^{+4}-F, TTF@NH_2-ExBox^{+4}-F, TCNQ@NH_2-ExBox^{+4}-F, TCNE@NH_2-ExBox^{+4}-F (in clockwise direction).

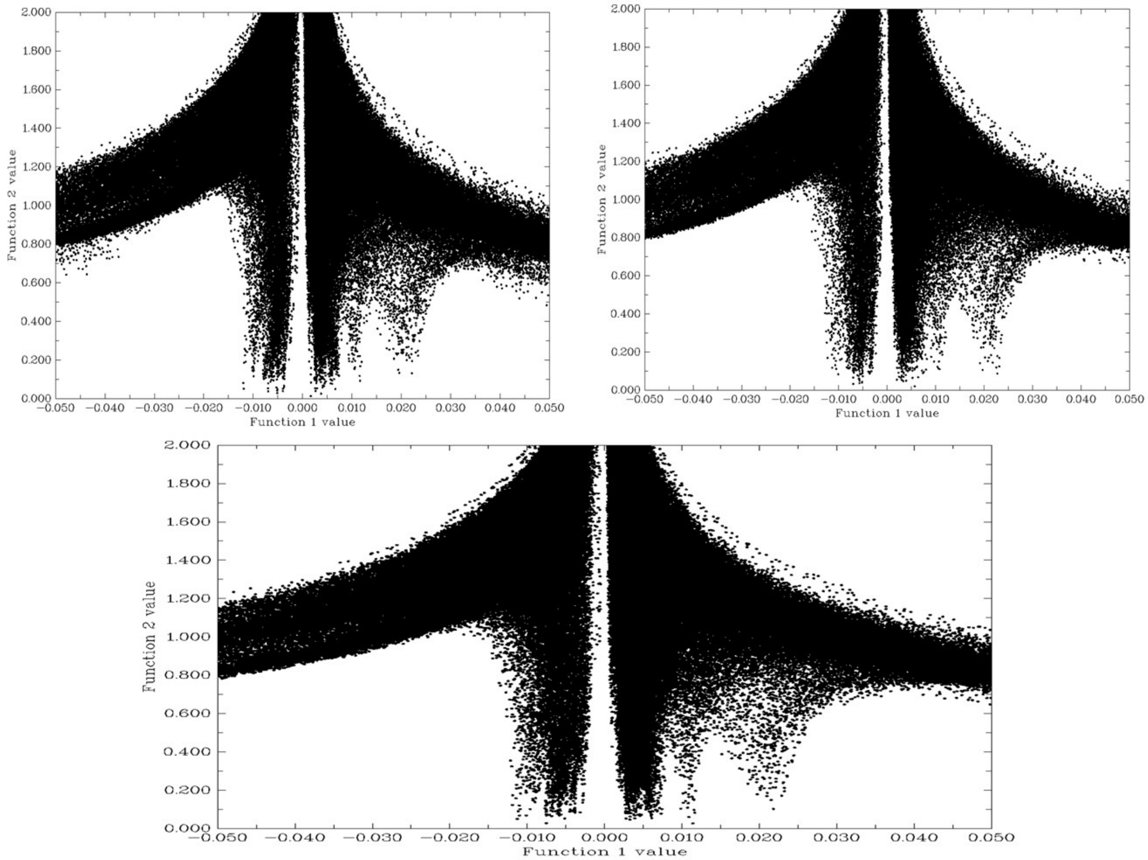

Figure S27: Scatter plot of sign(λ_2) ρ versus s for BCor@CN-ExBox^{+4}-NH_2, Cor@CN-ExBox^{+4}-NH_2 and NCor@CN-ExBox^{+4}-NH_2 (in clockwise direction).

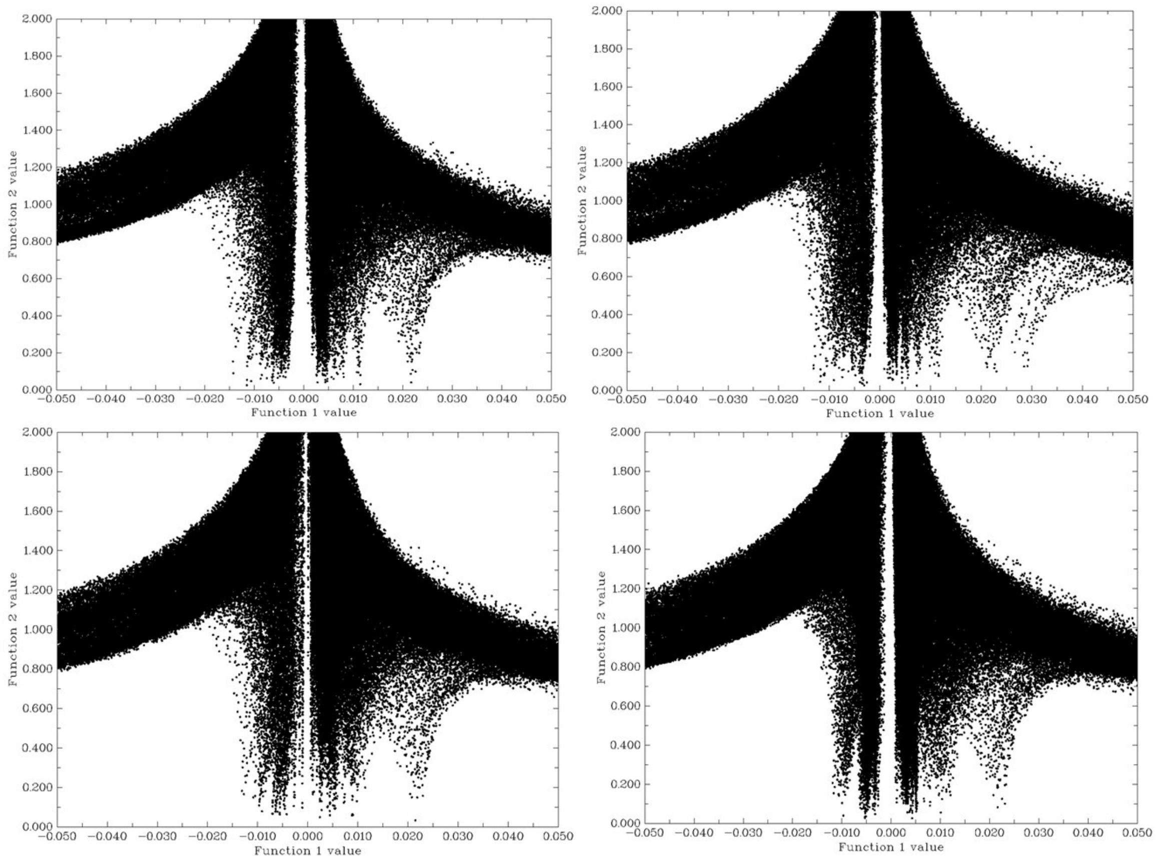

Figure S28: Scatter plot of sign(λ_2) ρ versus s for BiPh@CN-ExBox^{+4}-NH_2, TTF@CN-ExBox^{+4}-NH_2, TCNQ@CN-ExBox^{+4}-NH_2, TCNE@CN-ExBox^{+4}-NH_2 (in clockwise direction).

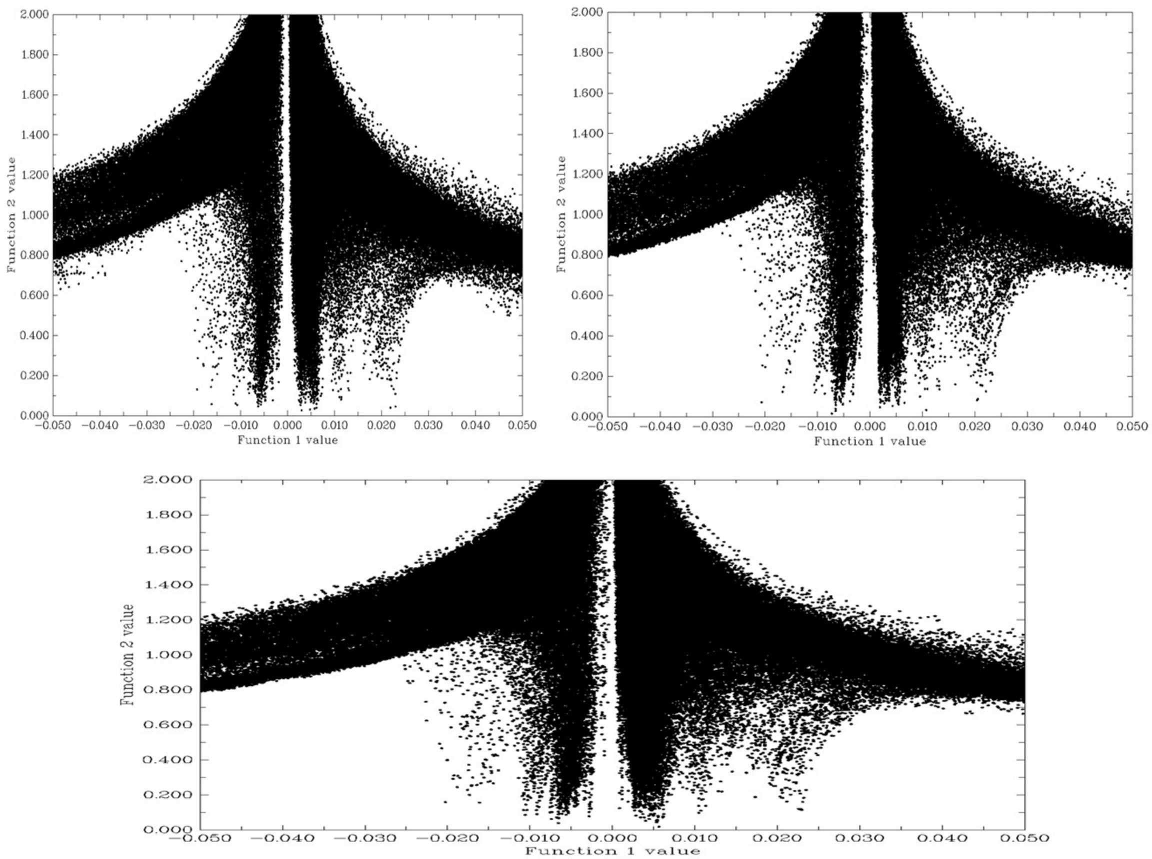

Figure S29: Scatter plot of sign(λ_2)ρ versus s for BCor@NO_2-ExBox^{+4}-NH_2, Cor@NO_2-ExBox^{+4}-NH_2 and NCor@NO_2-ExBox^{+4}-NH_2 (in clockwise direction).

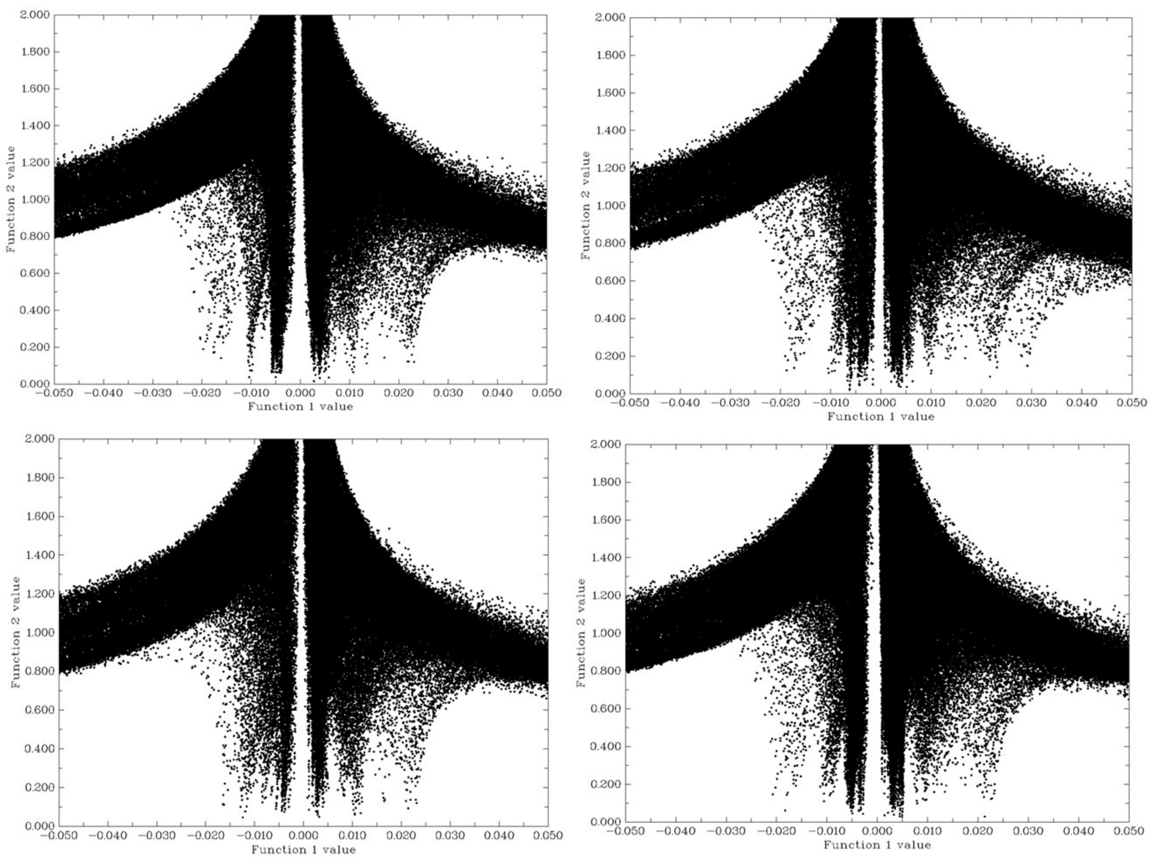

Figure S30: Scatter plot of $\mathrm{sign}(\lambda_2)\,\rho$ versus s for BiPh@NO_2-ExBox^{+4}-NH_2, TTF@NO_2-ExBox^{+4}-NH_2, TCNQ@NO_2-ExBox^{+4}-NH_2, TCNE@NO_2-ExBox^{+4}-NH_2 (in clockwise direction).