Supporting information for: Conformational Analysis of the Supramolecular Complexation of Diaryl-Substituted Tetrathiafulvalene Vinylogues with Fullerenes

Ahmad I. Alrawashdeh[1],* Yuming Zhao[2],* and Jolanta B. Lagowski[1]*

[1]*Department of Physics and Physical Oceanography,* [2]*Department of Chemistry*

Memorial University of Newfoundland, St. John's, NL, Canada A1B 3X7

E-mail: aia638@mun.ca; yuming@mun.ca; jolantal@mun.ca

Table S1. Distortion energies (in eV) for the interacting of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level.*

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
Right	0.05	0.32	0.15	0.33	0.06	0.04
Middle	0.48	0.42	0.40	0.42	0.82	0.83
Left	0.21	0.10	0.16	0.21	0.30	0.24
Up	0.03	0.05	0.06	0.02	0.13	0.06
Down	0.03	0.04	0.07	0.11	0.00	0.01
Middle 2		0.45		0.47		0.82

*The amount of energy required to convert the shape of a molecule from its most stable configuration to a less stable one.

Table S2. Binding energies (E_b in eV) for the supramolecular complexes of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes (without and with BSSE corrections)[a] obtained at the B3LYP-D3/6-31G(d) level without and with chlorobenzene as a solvent.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
(a) Without solvent						
Right	1.22 (0.85)	1.45 (0.92)	1.35 (0.92)	1.59 (1.04)	1.43 (1.02)	1.44 (1.04)
Middle	1.08 (0.60)	1.35 (0.80)	1.36 (0.83)	1.54 (0.96)	1.08 (0.52)	1.26 (0.66)
Left	1.18 (0.81)	1.34 (0.92)	1.35 (0.92)	1.54 (1.05)	1.08 (0.70)	1.18 (0.79)
Up	0.84 (0.61)	0.80 (0.57)	0.80 (0.56)	0.80 (0.57)	0.74 (0.50)	0.77 (0.55)
Down	0.66 (0.46)	0.70 (0.50)	0.83 (0.58)	0.91 (0.65)	0.45 (0.32)	0.50 (0.36)
Middle 2		1.23 (0.71)		1.42 (0.86)		1.20 (0.61)
(b) With solvent						
Right	1.14	1.35	1.31	1.49	1.41	1.39
Middle	1.10	1.32	1.30	1.48	1.12	1.29
Left	1.14	1.28	1.30	1.47	1.03	1.14
Up	0.79	0.77	0.74	0.78	0.71	0.75
Down	0.64	0.68	0.79	0.87	0.44	0.49
Middle 2		1.21		1.36		1.22

[a] Values in brackets are with BSSE corrections.

Table S3. Relative conformational energies (in eV) for the supramolecular pairs of the three diaryl-TTFVs with C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without and with chlorobenzene as a solvent.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
(a) Without solvent						
Right	0.00	0.00	0.01	0.00	0.00	0.00
Middle	0.14	0.10	0.00	0.05	0.35	0.17
Left	0.04	0.12	0.00	0.06	0.36	0.25
Up	0.39	0.65	0.56	0.79	0.69	0.66
Down	0.56	0.75	0.52	0.68	0.99	0.93
Middle 2	-	0.22	-	0.18	-	0.24
(b) With solvent						
Right	0.00	0.00	0.00	0.00	0.00	0.00
Middle	0.04	0.04	0.01	0.01	0.28	0.10
Left	0.00	0.08	0.01	0.01	0.37	0.25
Up	0.35	0.58	0.57	0.71	0.70	0.64
Down	0.50	0.67	0.51	0.61	0.96	0.90
Middle 2	-	0.15	-	0.13	-	0.16

Table S4. Binding energies (E_b in eV) for the most stable supramolecular complexes of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes obtained at the B3LYP-D3 level with the Def2TZVP basis set.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
Right	0.91	1.10	1.07	1.24	1.13	1.15
Middle	0.91	1.14	1.15	1.30	0.94	1.10
Left	0.94	1.03	1.07	1.21	0.83	0.92

Table S5. HOMO energies (in eV) for the interacting of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without a solvent and with chlorobenzene.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
(a) Without solvent						
Right	-4.80	-4.98	-4.82	-4.90	-4.81	-4.81
Middle	-4.79	-4.81	-4.79	-4.80	-4.81	-4.82
Left	-4.78	-4.87	-4.82	-4.82	-4.88	-4.83
Up	-4.73	-4.82	-4.72	-4.72	-4.88	-4.88
Down	-4.74	-4.76	-4.82	-4.81	-4.79	-4.79
(b) With solvent						
Right	-5.01	-5.19	-5.03	-5.11	-5.02	-5.01
Middle	-5.03	-5.06	-5.05	-5.06	-5.04	-5.05
Left	-5.04	-5.14	-5.09	-5.09	-5.07	-5.03
Up	-4.95	-5.05	-4.97	-4.98	-5.08	-5.07
Down	-4.98	-5.00	-5.06	-5.06	-4.99	-4.99

Table S6. LUMO energies (in eV) for the interacting of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without a solvent and with chlorobenzene.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
(a) Without solvent						
Right	-1.30	-1.48	-2.18	-2.21	-1.69	-1.69
Middle	-1.45	-1.40	-2.01	-2.01	-1.67	-1.66
Left	-1.58	-1.61	-2.29	-2.31	-1.81	-1.77
Up	-1.40	-1.45	-2.31	-2.31	-1.73	-1.73
Down	-1.47	-1.47	-2.20	-2.29	-1.72	-1.72
(b) With solvent						
Right	-1.30	-1.38	-2.08	-2.08	-1.66	-1.63
Middle	-1.39	-1.37	-2.00	-2.00	-1.70	-1.68
Left	-1.43	-1.46	-2.16	-2.17	-1.78	-1.71
Up	-1.31	-1.36	-2.15	-2.16	-1.64	-1.63
Down	-1.37	-1.37	-2.11	-2.15	-1.65	-1.65

Table S7. HOMO energies (in eV) for the supramolecular complexes of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without a solvent and with chlorobenzene.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
(a) Without solvent						
Right	-4.79	-5.01	-4.82	-4.91	-4.78	-4.79
Middle	-4.87	-4.90	-4.87	-4.89	-4.85	-4.86
Left	-4.87	-4.90	-4.89	-4.90	-4.91	-4.86
Up	-4.78	-4.84	-4.74	-4.74	-4.86	-4.89
Down	-4.74	-4.76	-4.84	-4.83	-4.77	-4.77
(b) With solvent						
Right	-4.98	-5.17	-4.99	-5.07	-4.99	-4.98
Middle	-5.04	-5.07	-5.06	-5.07	-5.05	-5.04
Left	-5.04	-5.12	-5.09	-5.08	-5.06	-5.02
Up	-4.93	-5.01	-4.97	-4.97	-5.01	-5.03
Down	-4.98	-4.99	-5.01	-5.02	-4.98	-4.98

Table S8. LUMO energies (in eV) for the supramolecular complexes of the three diaryl-TTFVs with each C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without a solvent and with chlorobenzene.

	Dinaphthyl-TTFV		Dianthryl-TTFV		Dipyrenyl-TTFV	
Conformer	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
(a) Without solvent						
Right	-3.35	-3.25	-3.34	-3.23	-3.30	-3.30
Middle	-2.99	-3.00	-2.96	-3.00	-2.83	-2.95
Left	-3.12	-3.12	-3.04	-3.16	-3.09	-3.14
Up	-3.11	-3.20	-3.31	-3.34	-3.23	-3.22
Down	-3.35	-3.38	-3.19	-3.19	-3.46	-3.44
(b) With solvent						
Right	-3.26	-3.19	-3.25	-3.18	-3.21	-3.23
Middle	-3.02	-3.06	-3.04	-3.06	-2.96	-3.03
Left	-3.17	-3.16	-3.13	-3.18	-3.17	-3.19
Up	-3.15	-3.18	-3.20	-3.22	-3.19	-3.19
Down	-3.21	-3.23	-3.18	-3.18	-3.26	-3.27

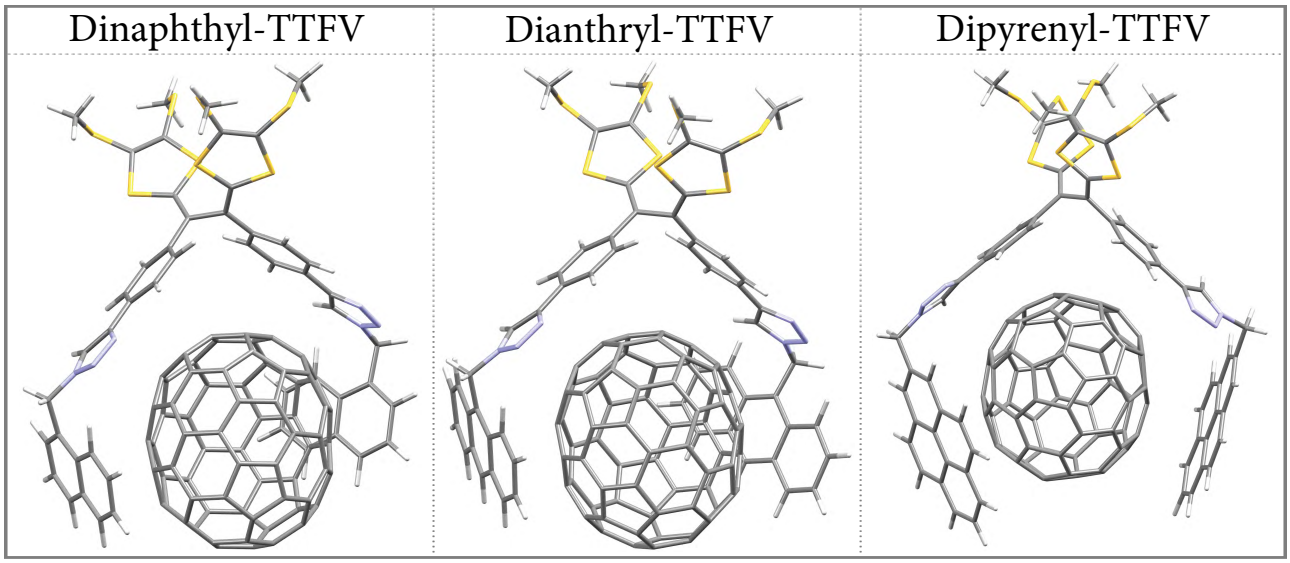

Figure S1. Optimized geometries for the middle-2 supramolecular complexes of the three diaryl-TTFVs and C_{70} fullerene obtained at the B3LYP-D3/6-31G(d) level (similar results are obtained at the PCM/B3LYP-D3/6-31G(d) level in chlorobenzene).

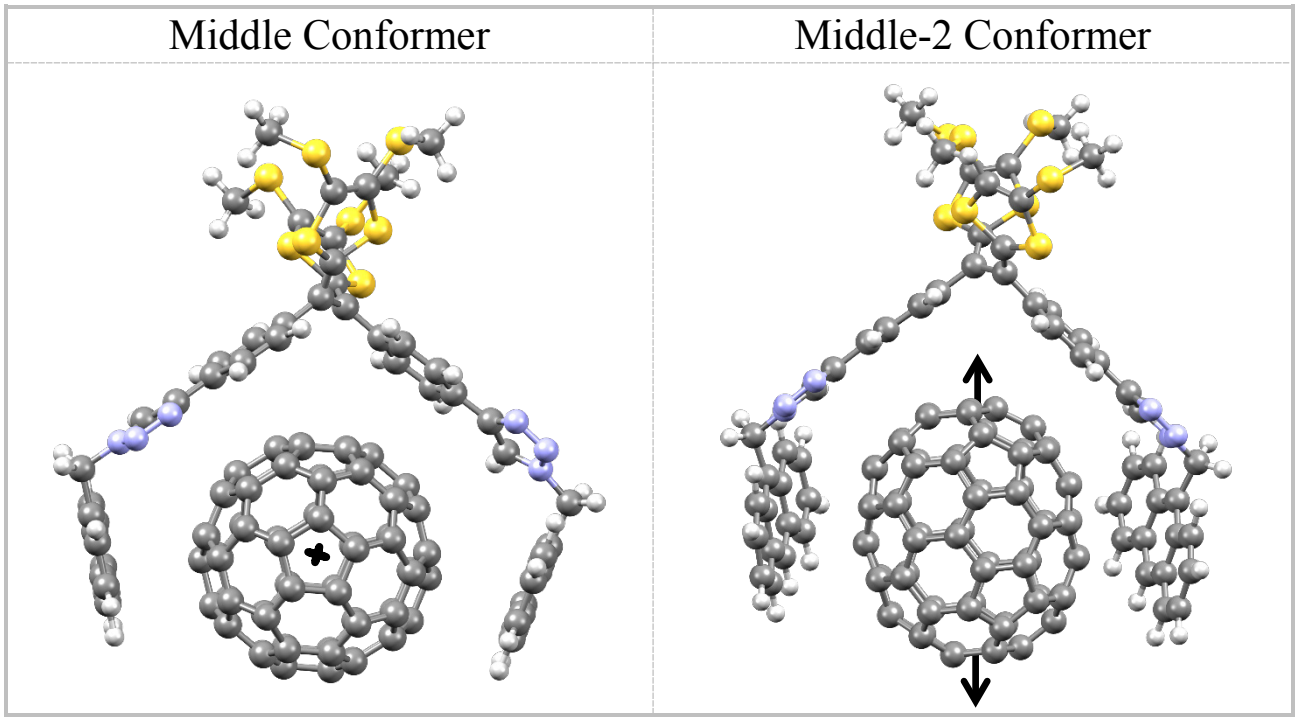

Figure S2. Examples of the "middle" and "middle-2" supramolecular complexes of diaryl-TTFVs and C_{70} (the arrows show the direction of the long-axis of C_{70}).

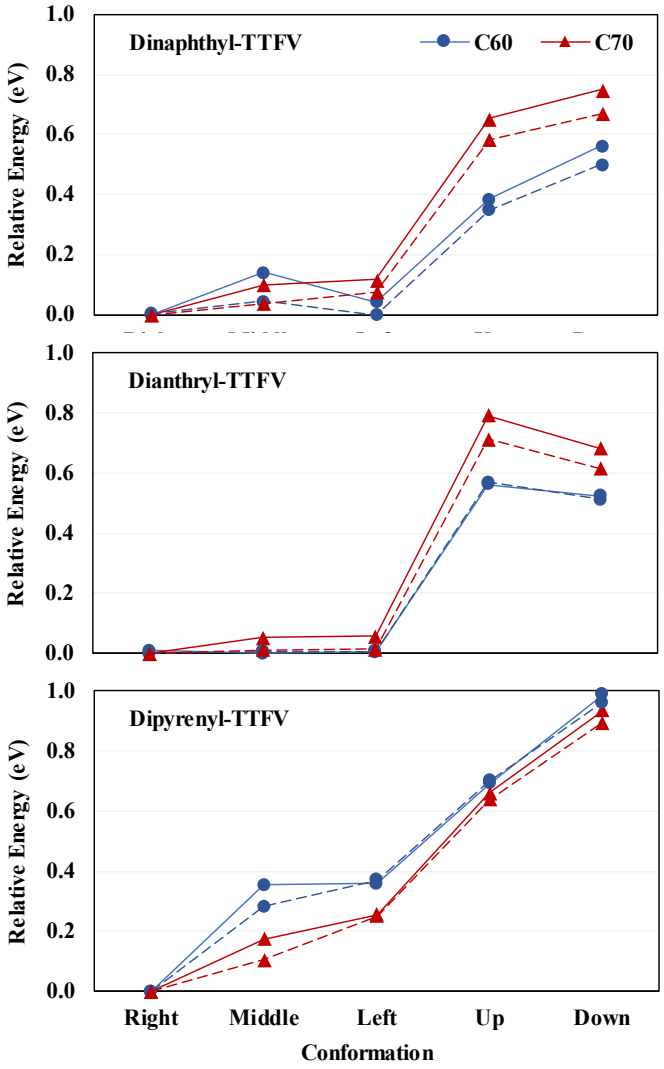

Figure S3. Relative conformational energies (in eV) for the supramolecular pairs of diaryl-TTFVs (**2a-c**) with C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without a solvent (solid line) and with chlorobenzene (dashed line).

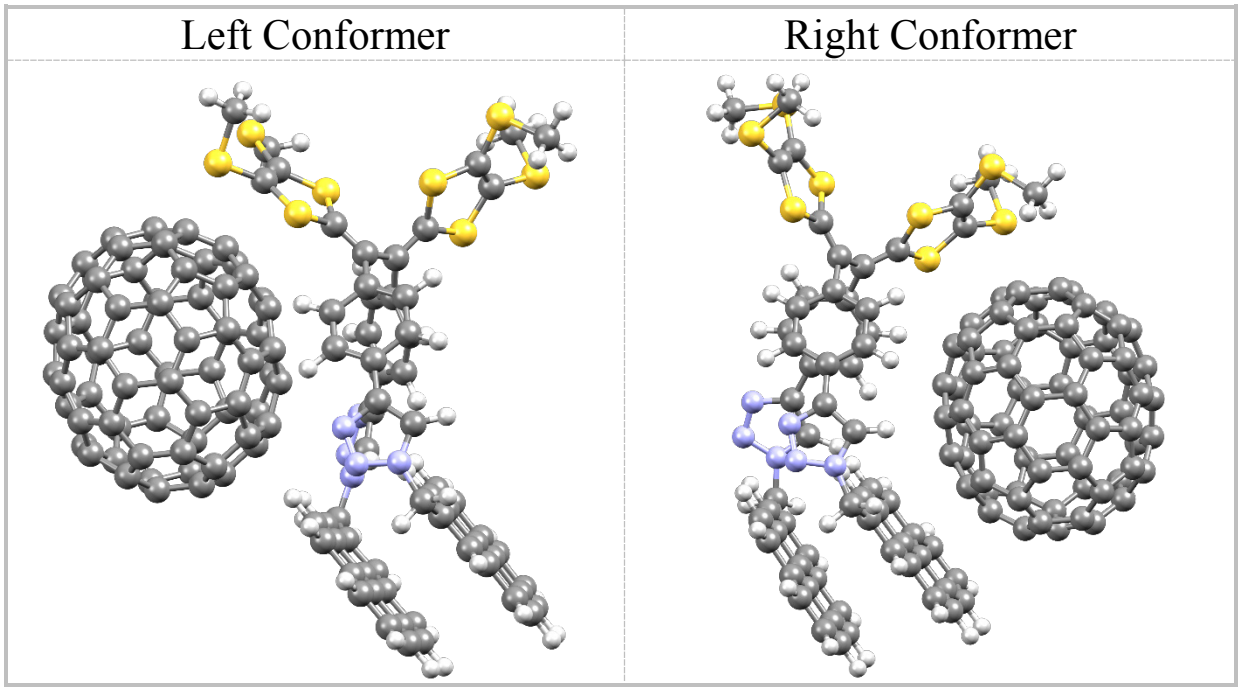

Figure S4. Examples of optimized geometries for the "left" and "right" supramolecular complexes of diaryl-TTFVs and C_{70} obtained at the B3LYP-D3/6-31G(d) level.

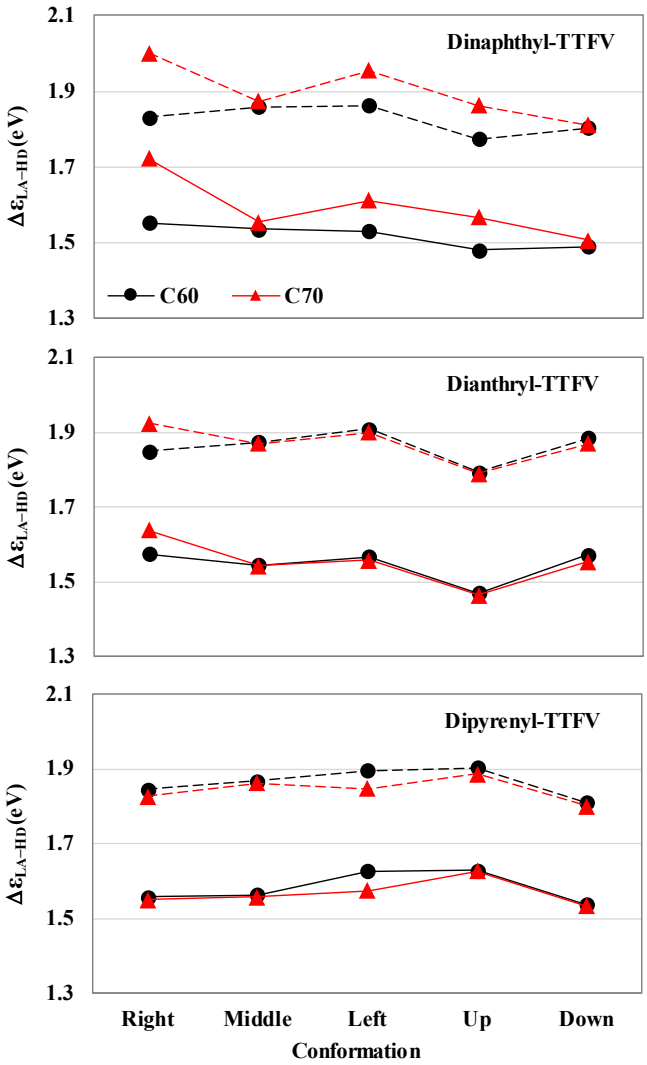

Figure S5. $\Delta\epsilon_{L_A-H_D}$ values (in eV) for the three diaryl-TTFVs in supramolecular pairs with each of C_{60} and C_{70} fullerenes obtained at the B3LYP-D3/6-31G(d) level without a solvent (solid line) and with chlorobenzene (dashed line).