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

Electronic Supplementary Information for

Theoretical Analysis of Electrochromism Under Redox of Bis(3-thienyl)/(2-thienyl)hexafluorocyclopentene: Effect of Charged and Substituted Systems

Zhi-Xiang Zhang, Pi-Xia Wang, Fu-Quan Bai*, Chui-Peng Kong, and Hong-Xing Zhang*

*State Key Laboratory of Theoretical and Computational Chemistry,
Institute of Theoretical Chemistry,
Jinlin University, Changchun 130023, People's-Republic of China.
E-mail: baifq@jlu.edu.cn, zhanghx@mail.jlu.edu.cn

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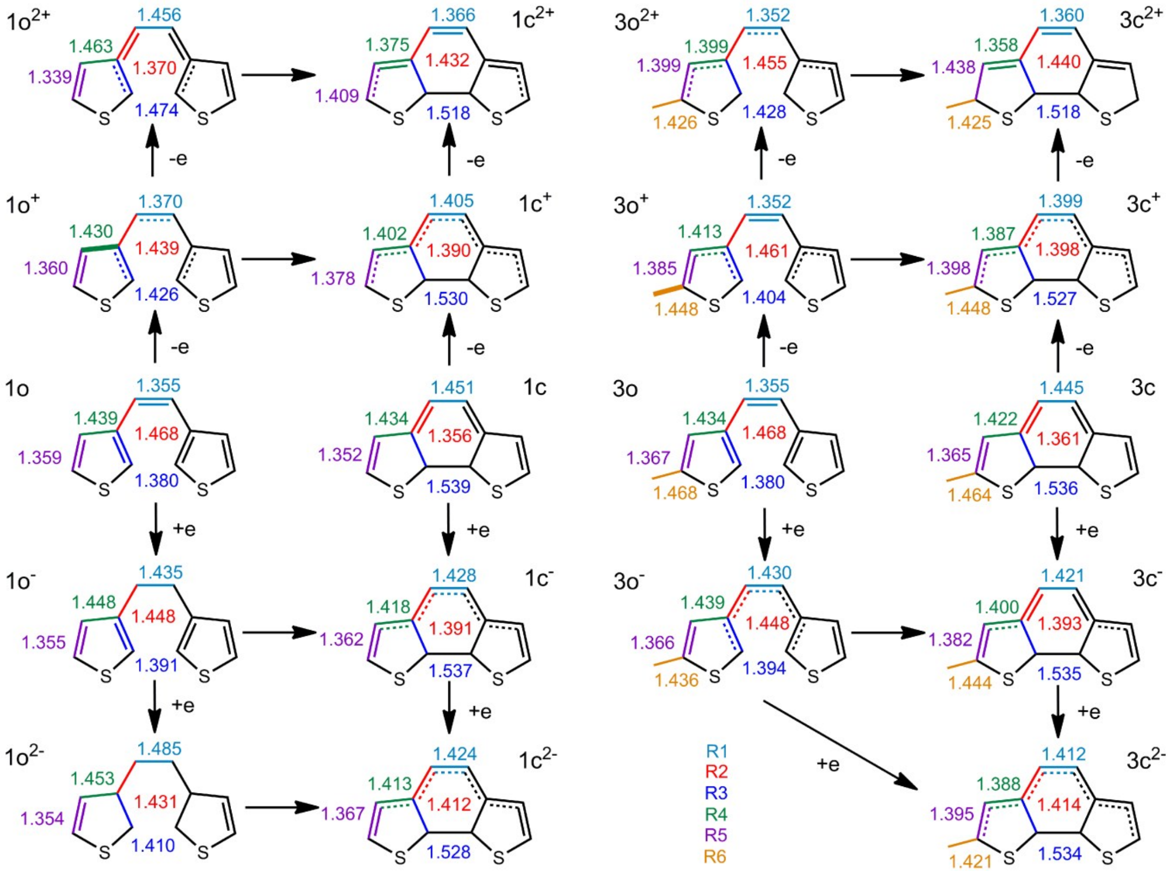

Fig. S1 The main bond lengths in different states and isomers of **1** and **3**.[1]

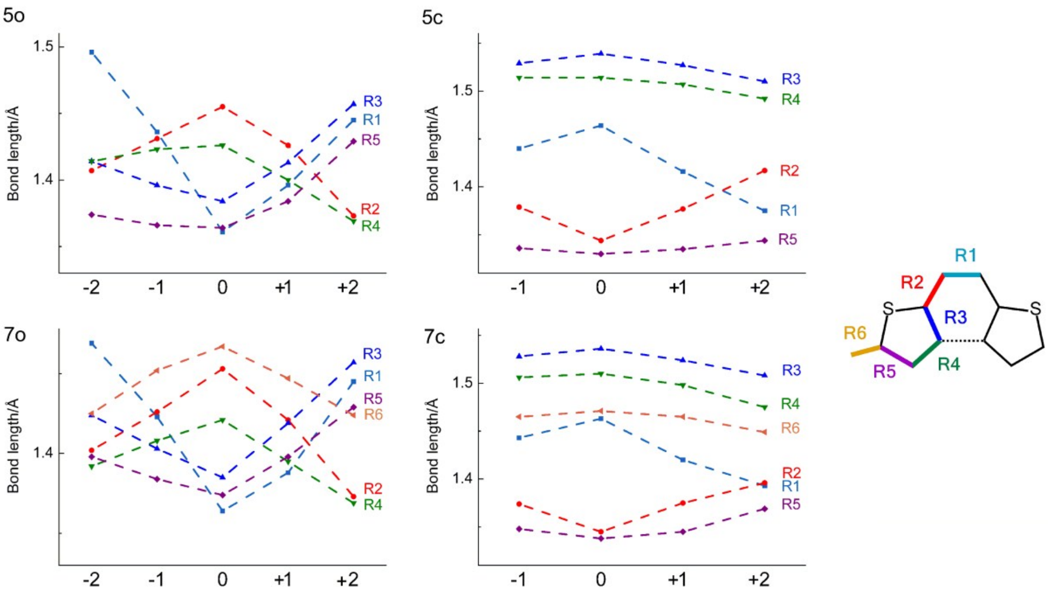

Fig. S2 The main bond lengths in different states and isomers of **5** and **7**. Every bond is represented by one color

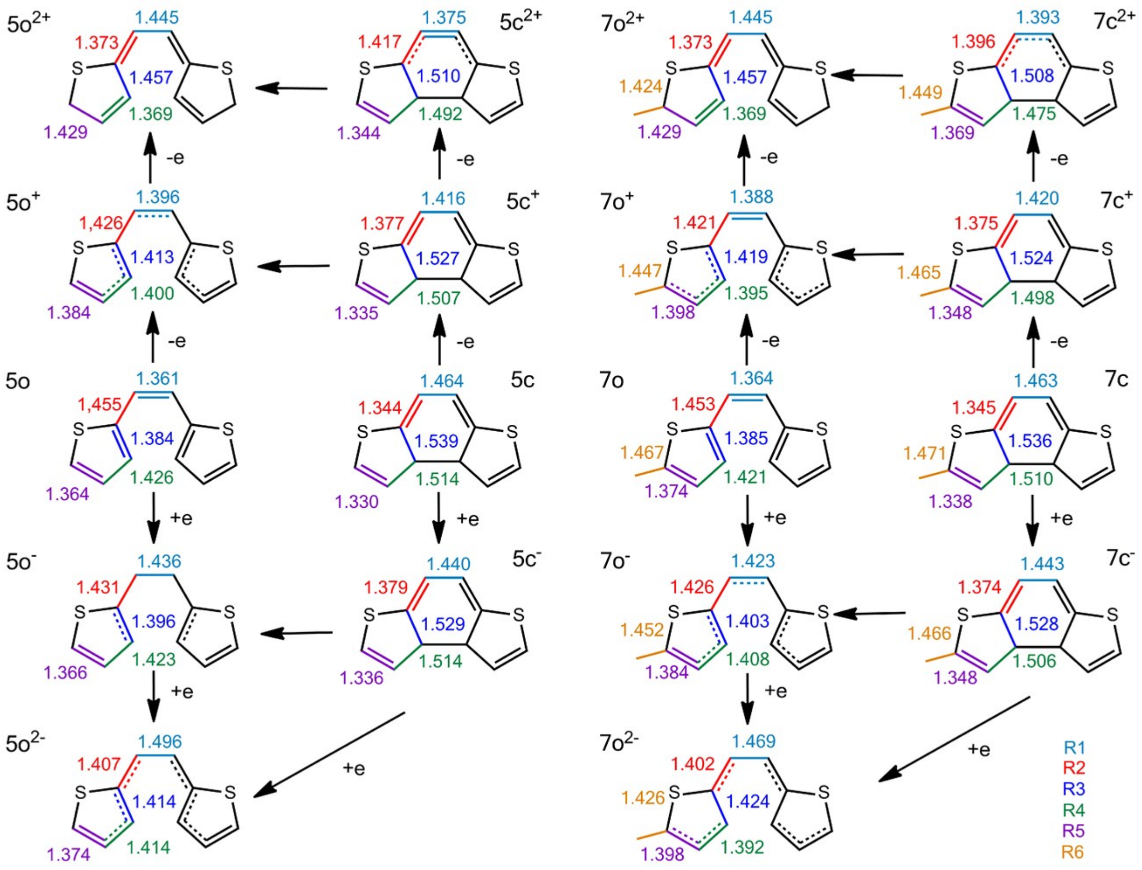

Fig. S3 The main bond lengths in different states and isomers of **5** and **7**.

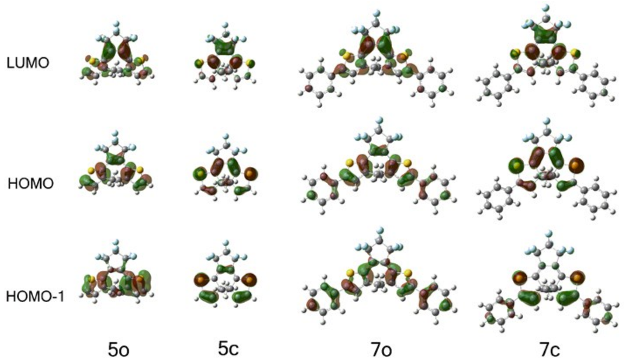

Fig. S4 Frontier orbitals of two isomers in **5** and **7**

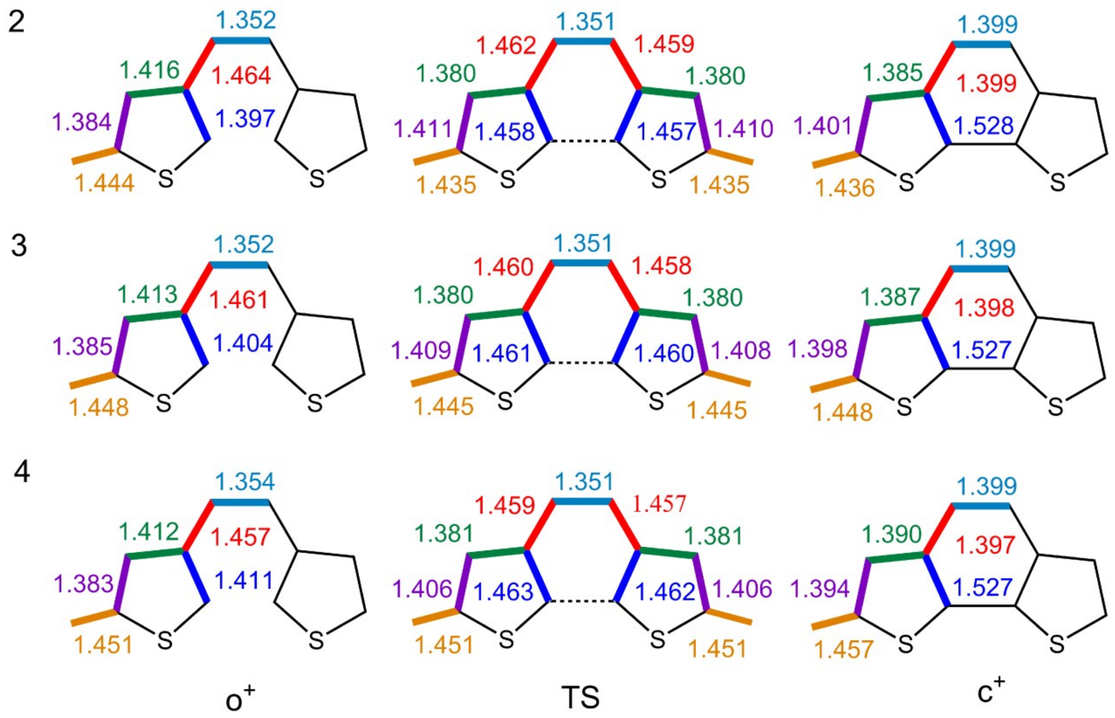

Fig. S5 The bond lengths of two isomers and transition state in monocation of **2-4**.

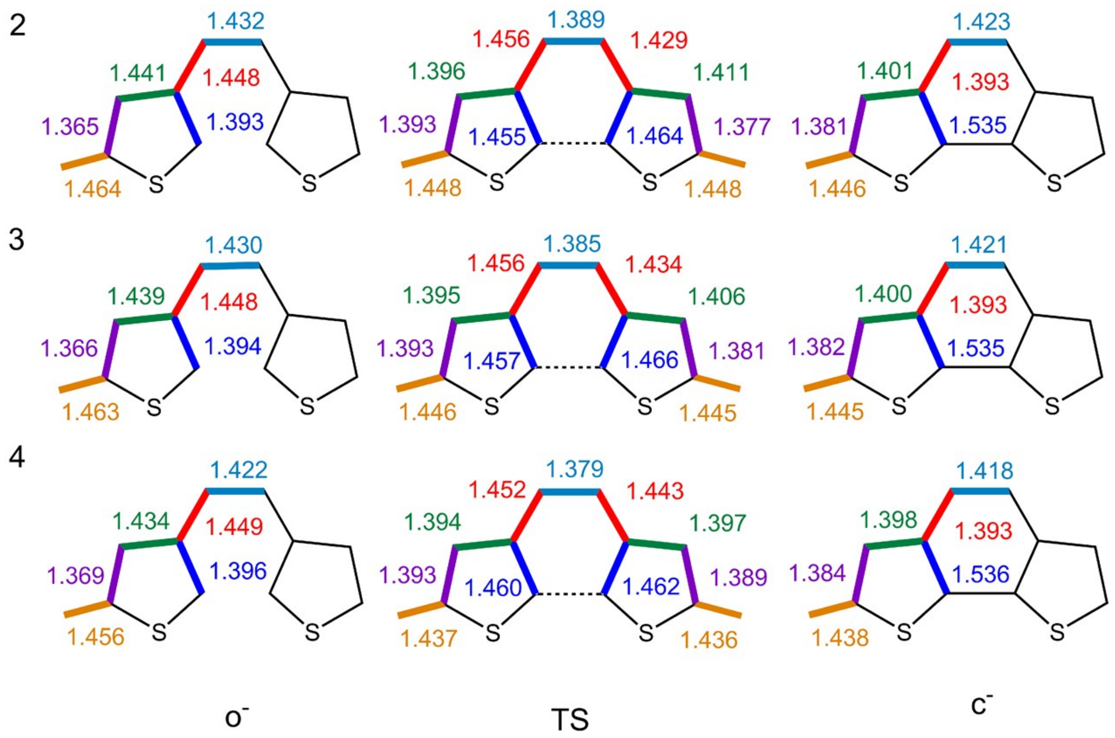

Fig. S6 The bond lengths of two isomers and transition state in monoanion of **2-4**.

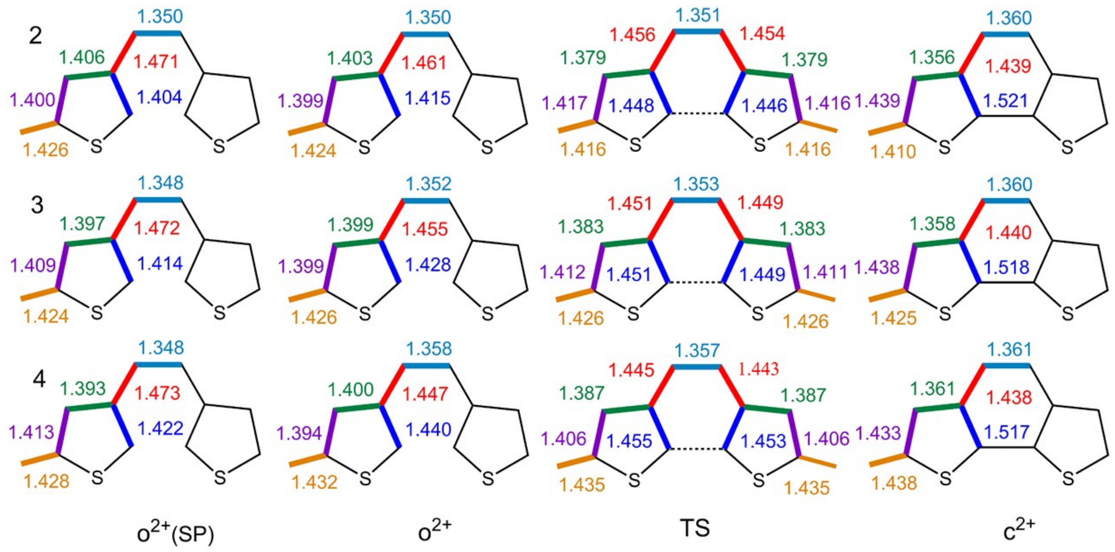

Fig. S7The bond lengths of two isomers and transition state in dication of **2-4.**

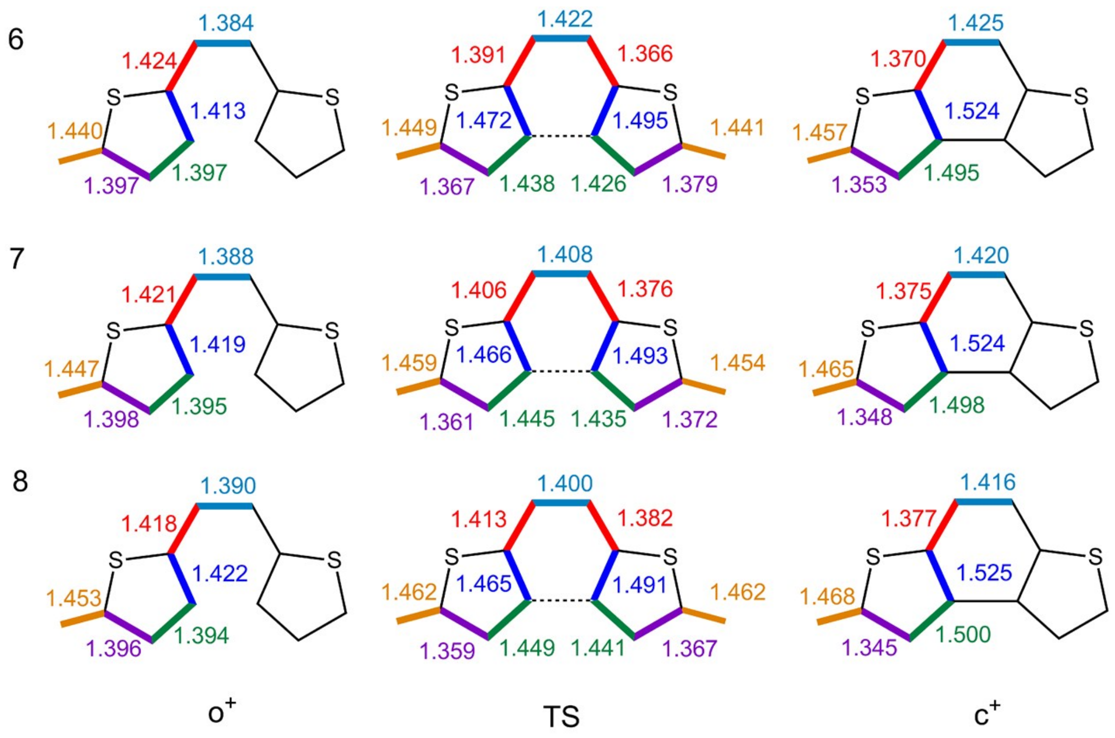

Fig. S8 The bond lengths of two isomers and transition state in monocation of **6-8.**

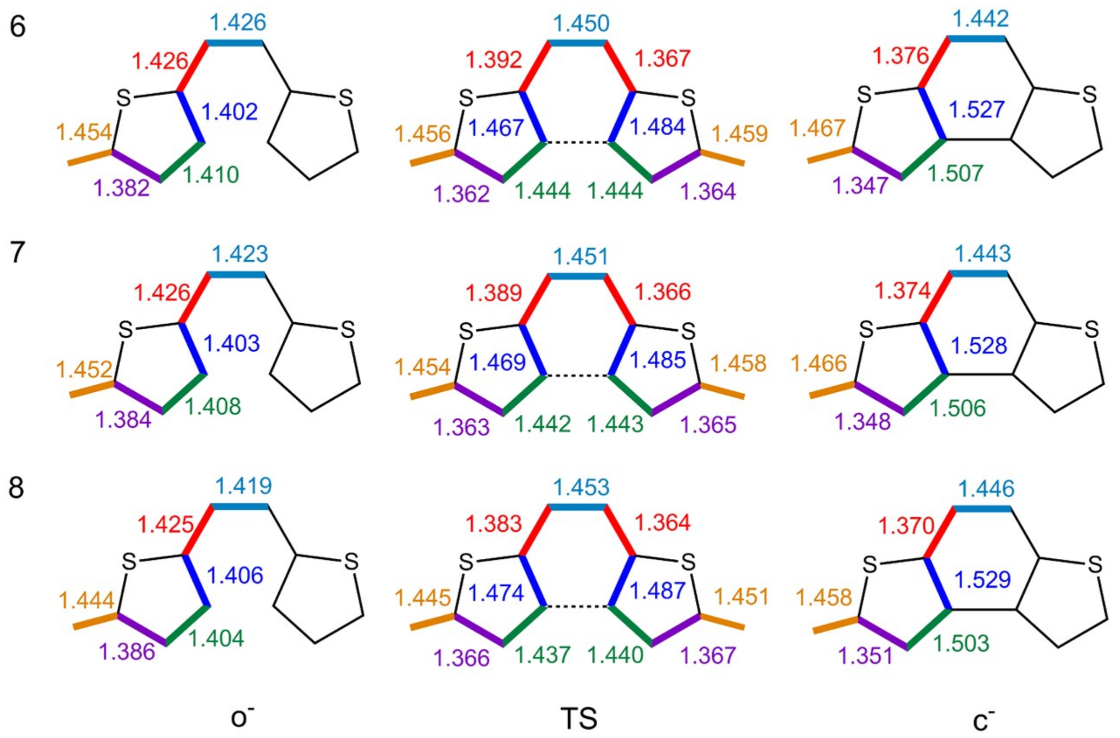

Fig. S9 The bond lengths of two isomers and transition state in monoanion of **6-8.**

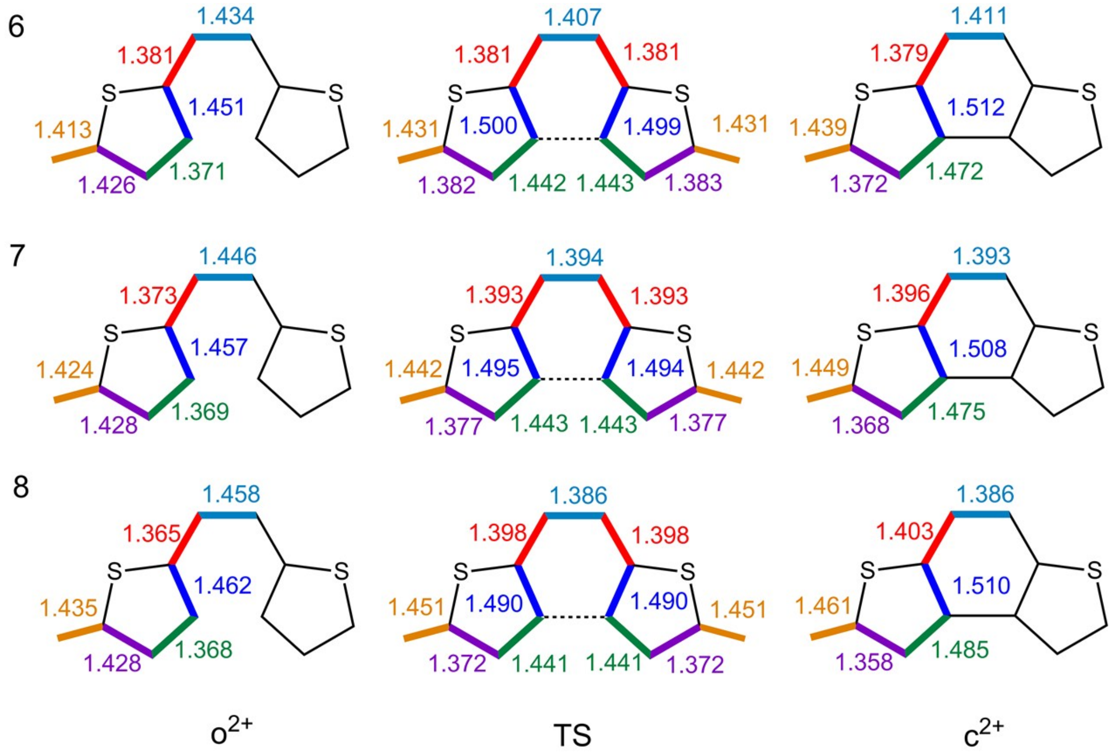

Fig. S10 The bond lengths of two isomers and transition state in dication of **6-8**.

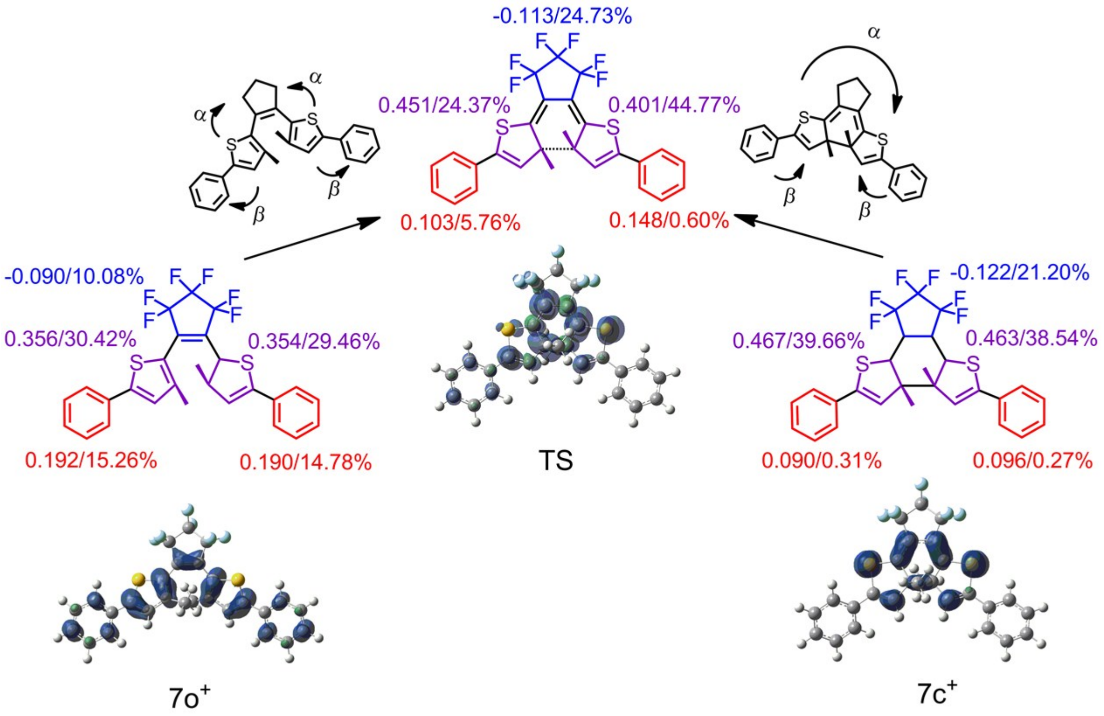

Fig. S11 The charge distribution/spin population(percentagewise) on different groups of isomers and transition state in **7**$^+$.[2]

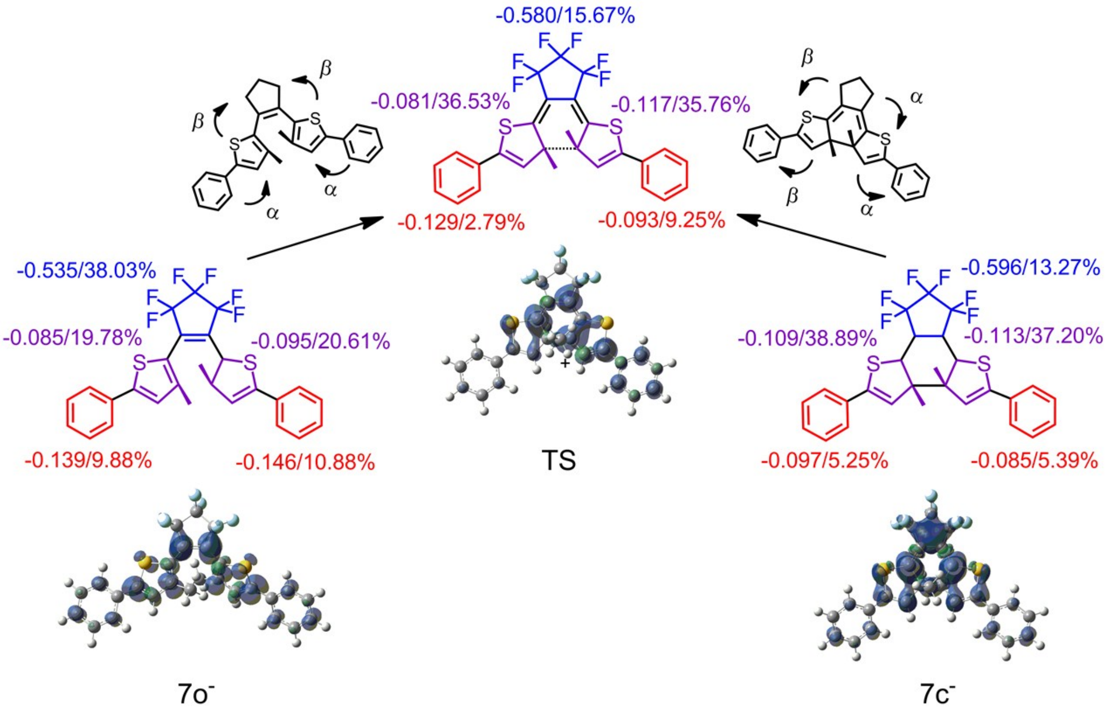

Fig. 12 The charge distribution/spin population(percentagewise) on different groups of isomers and transition state in $\mathbf{7}^-$.

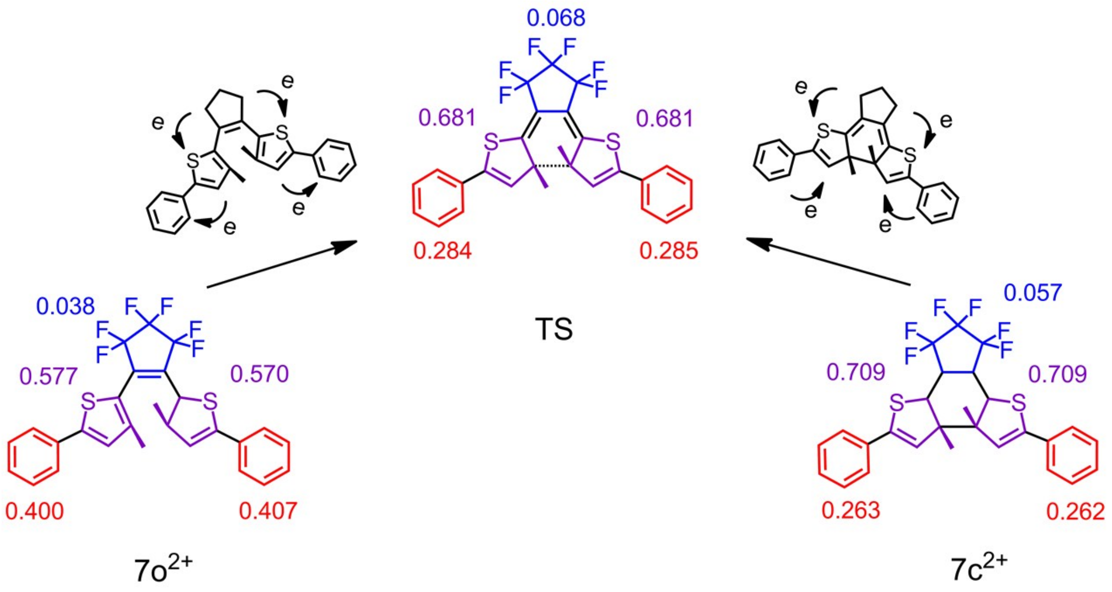

Fig. 13 The charge distribution on different groups of isomers and transition state in **7^{2+}**.

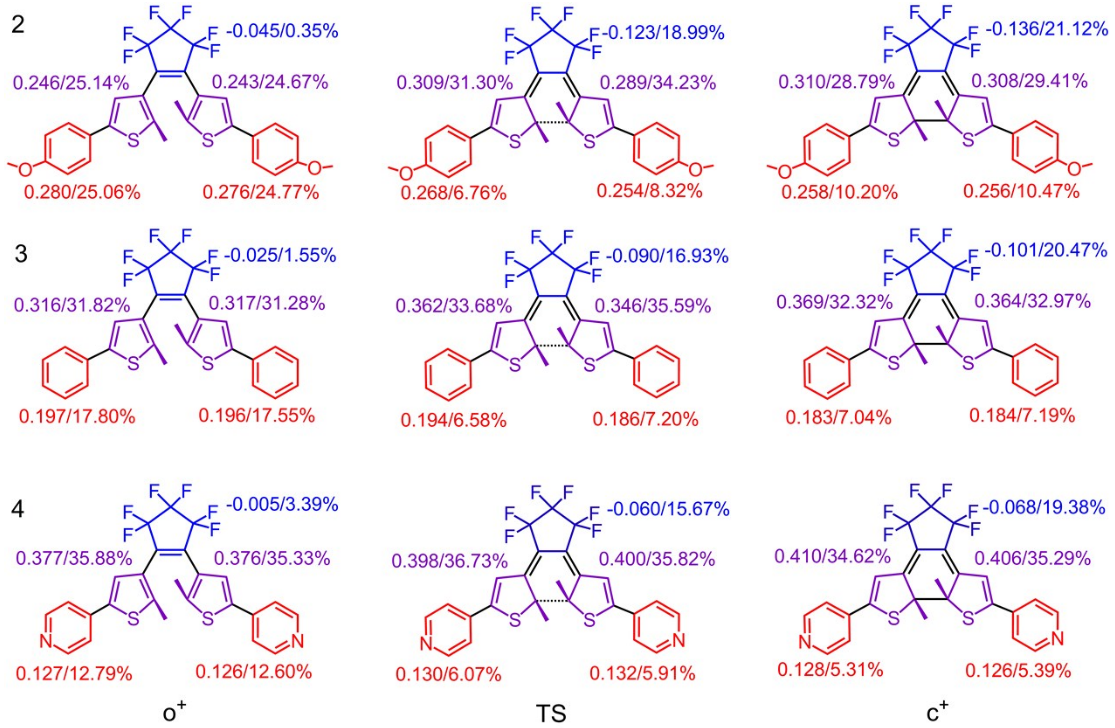

Fig. S14 The charge distribution/spin population(percentagewise) on different groups of isomers and transition state in **2^+-4^+.**

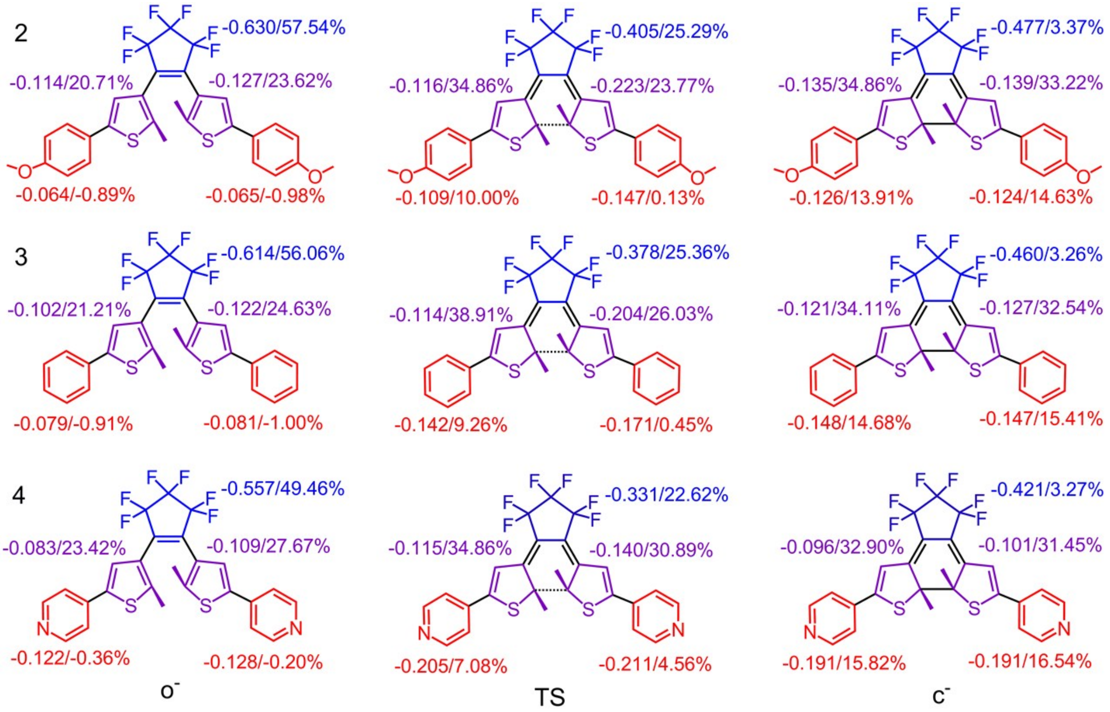

Fig. S15 The charge distribution/spin population(percentagewise) on different groups of isomers and transition state in **2^{-}-4^{-}.**

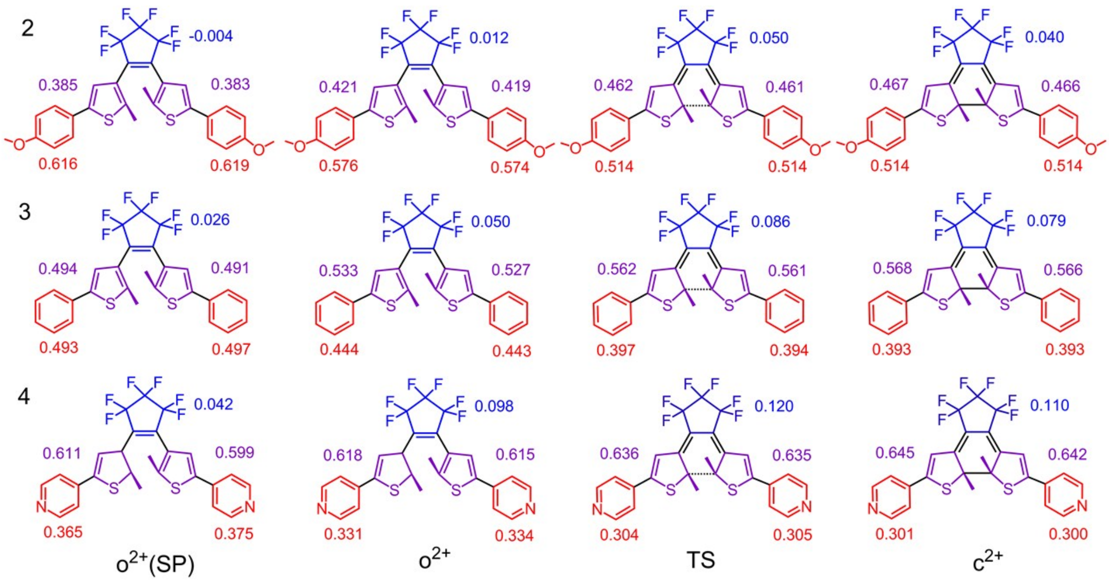

Fig. S16 The charge distribution/spin population on different groups of isomers and transition state in **2^{2+}-4^{2+}.**

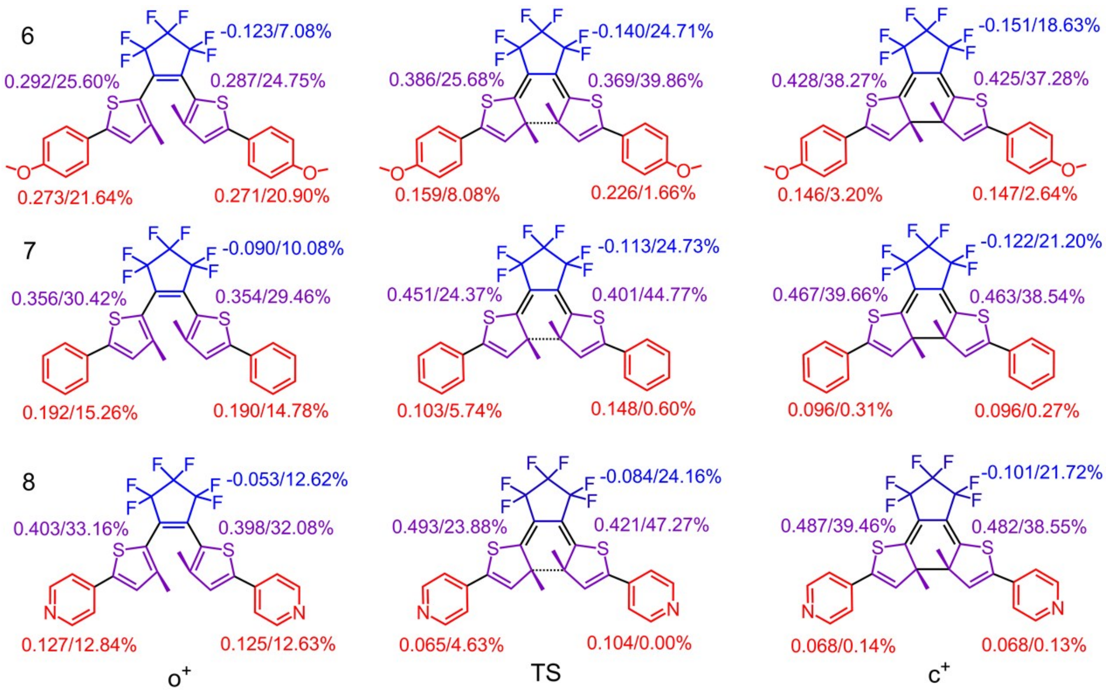

Fig. S17 The charge distribution/spin population on different groups of isomers and transition state in **6⁺-8⁺**.

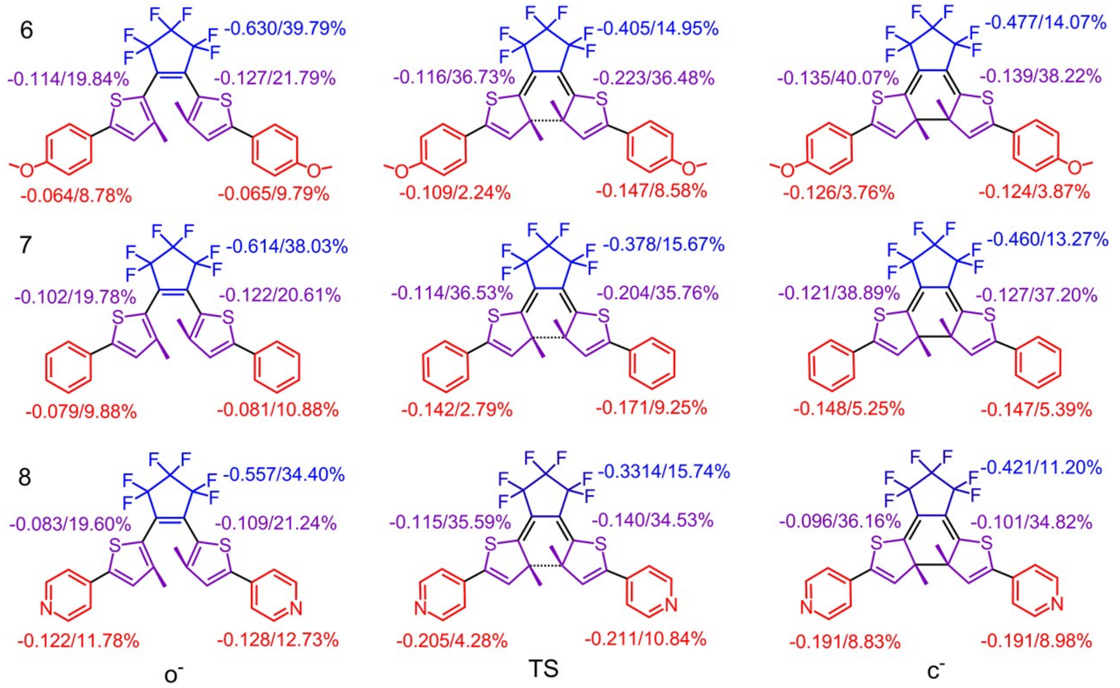

Fig. S18 The charge distribution/spin population on different groups of isomers and transition state in **6^--8^-.**

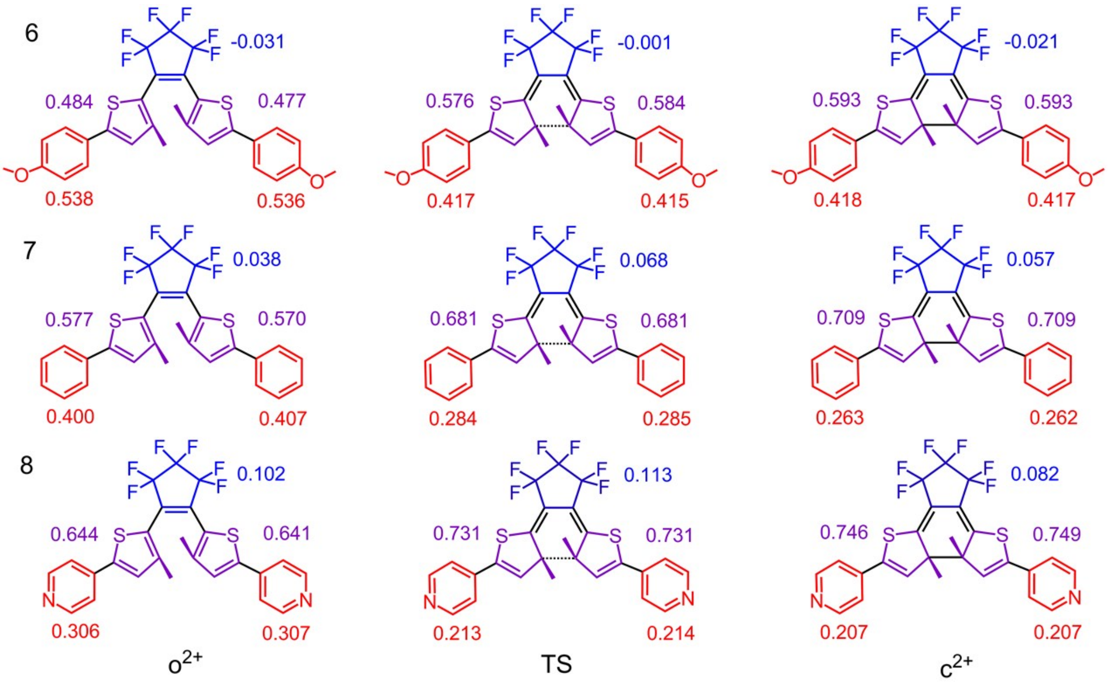

Fig. S19 The charge distribution/spin population on different groups of isomers and transition state in **6^{2+}-8^{2+}**.

Table S1 The energy barrier (eV) between isomer and TS in **1**-**8** under monocation. TS is chosen as standard zero point. For checking the accurancy of results, we list the data of computational methods B2PLYP, MP2, and B3LYP-D, respectively.

	B2PLYP				MP2				B3LYP-D			
	o^+	**TS**	**c^+**	**ΔE**	**o^+**	**TS**	**c^+**	**ΔE**	**o^+**	**TS**	**c^+**	**ΔE**
1	-1.32	0	-1.36	0.04	-0.64	0	-0.43	0.03	-0.81	0	-1.02	0.05
2	-1.33	0	-1.68	0.34	-0.76	0	-1.09	0.34	-0.93	0	-1.10	0.17
3	-1.24	0	-1.64	0.39	-0.68	0	-1.04	0.39	-0.86	0	-1.04	0.18
4	-1.07	0	-1.54	0.47	-0.65	0	-1.01	0.47	-0.82	0	-0.99	0.17
5	-1.97	0	-0.89	1.08	-1.33	0	-0.99	1.08	-1.51	0	-0.96	0.65
6	-2.12	0	-0.67	1.45	-1.78	0	-0.79	1.25	-1.91	0	-0.69	1.22
7	-2.06	0	-0.76	1.31	-1.60	0	-0.85	1.31	-1.79	0	-0.78	1.01
8	-2.04	0	-0.79	1.25	-1.50	0	-0.89	1.45	-1.71	0	-0.84	0.87

Table S2 The energy barrier (eV) between isomer and TS in **1**-**8** under monoanion. TS is chosen as standard zero point. For checking the accurancy of results, we list the data of computational methods B2PLYP, MP2, and B3LYP-D, respectively.

	B2PLYP				MP2				B3LYP-D			
	o^-	**TS**	**c^-**	**ΔE**	**o^-**	**TS**	**c^-**	**ΔE**	**o^-**	**TS**	**c^-**	**ΔE**
1	-0.84	0	-0.93	0.09	-1.07	0	-1.12	0.05	-1.14	0	-1.18	0.04
2	-0.88	0	-1.26	0.38	-0.72	0	-1.04	0.32	-0.91	0	-1.20	0.29
3	-0.82	0	-1.18	0.36	-0.63	0	-1.01	0.38	-0.84	0	-1.19	0.35
4	-0.79	0	-1.10	0.31	-0.47	0	-0.97	0.50	-0.73	0	-1.15	0.42
5	-1.51	0	-1.07	0.44	-1.70	0	-0.67	1.03	-1.84	0	-0.65	1.19
6	-1.73	0	-0.99	0.74	-1.72	0	-0.56	1.16	-1.91	0	-0.53	1.38
7	-1.82	0	-0.94	0.88	-1.74	0	-0.53	1.21	-1.94	0	-0.52	1.42
8	-1.92	0	-0.86	1.06	-1.81	0	-0.48	1.33	-2.00	0	-0.48	1.52

Table S3 The energy barrier (eV) between isomer and TS in **1**-**8** under dication. TS is chosen as standard zero point. For checking the accurancy of results, we list the data of computational methods B2PLYP, MP2, and B3LYP-D, respectively.

	B2PLYP				MP2				B3LYP-D			
	o^{2+}	**TS**	**c^{2+}**	**ΔE**	**o^{2+}**	**TS**	**c^{2+}**	**ΔE**	**o^{2+}**	**TS**	**c^{2+}**	**ΔE**
1	-0.37	0	-1.44	1.07	-0.12	0	-1.23	1.12	-0.23	0	-1.13	0.90
2	-0.10	0	-1.58	1.48	-0.30	0	-1.08	0.78	-0.23	0	-1.08	0.85
3	-0.08	0	-1.59	1.51	-0.11	0	-1.09	0.98	-0.12	0	-1.07	0.95
4	-0.07	0	-1.56	1.49	-0.05	0	-1.09	1.04	-0.06	0	-1.06	1.00
5	-1.14	0	-0.62	0.52	-0.65	0	-0.51	0.14	-0.90	0	-0.45	0.45
6	-2.15	0	-0.03	2.12	-1.52	0	-0.07	1.45	-1.83	0	-0.05	1.78
7	-1.82	0	-0.14	1.68	-1.25	0	-0.08	1.17	-1.56	0	-0.08	1.48
8	-1.55	0	-0.27	1.28	-1.03	0	-0.15	0.88	-1.33	0	-0.17	1.16

Table S4 The spin population (percentagewise) on the reactive C3 atoms of two isomers in **6**-**8** under monocation and monoanion.

	monocation		**monoanion**	
	left	right	left	right
6o	3.77	3.74	8.87	9.36
7o	5.44	5.36	8.24	8.65
8o	6.77	6.61	7.17	7.46
6c	1.95	1.95	1.84	1.98
7c	1.77	1.77	1.88	2.01
8c	1.65	1.65	1.96	2.07

Reference

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