Electronic Supplementary Information

Theoretical Study of Bridging Effect on the Charge Carrier Transport Properties of Cyclooctatetrathiophene and Its Derivatives

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Table S1 Selected bond lengths (unit: Å) of systems **1-4** at optimized ground state

System	Bond length	Expt.	B3P86		PBE0		B3LYP	
			6-31G(d,p)	6-31+G(d,p)	6-31G(d,p)	6-31+G(d,p)	6-31G(d,p)	6-31+G(d,p)
1	R(1,2)	1.462	1.454	1.455	1.455	1.456	1.459	1.460
	R(2,3)	1.731	1.742	1.741	1.738	1.737	1.756	1.755
	R(2,6)	1.377	1.381	1.382	1.380	1.381	1.383	1.384
	R(3,4)	1.712	1.719	1.719	1.716	1.716	1.731	1.731
	R(4,5)	1.358	1.363	1.366	1.363	1.365	1.365	1.367
	R(5,6)	1.450	1.429	1.429	1.428	1.429	1.434	1.435
	R(6,7)	1.467	1.469	1.469	1.469	1.470	1.475	1.476
2	R(1,2)	1.457	1.456	1.457	1.458	1.460	1.462	1.462
	R(2,3)	1.742	1.754	1.753	1.750	1.749	1.769	1.768
	R(2,6)	1.378	1.381	1.383	1.381	1.382	1.383	1.385
	R(3,4)	1.711	1.718	1.719	1.715	1.716	1.729	1.730
	R(4,5)	1.356	1.363	1.365	1.363	1.365	1.364	1.366
	R(5,6)	1.444	1.446	1.446	1.446	1.446	1.453	1.453
	R(5,8)	1.872	1.875	1.876	1.876	1.877	1.881	1.882
	R(6,7)	1.472	1.472	1.472	1.472	1.472	1.478	1.478
3	R(1,2)	1.463	1.450	1.451	1.451	1.452	1.456	1.456
	R(2,3)	1.738	1.748	1.747	1.743	1.743	1.762	1.762
	R(2,6)	1.384	1.385	1.386	1.384	1.385	1.387	1.388
	R(3,4)	1.713	1.716	1.716	1.713	1.713	1.727	1.728
	R(4,5)	1.351	1.362	1.363	1.361	1.363	1.362	1.364
	R(5,6)	1.430	1.438	1.439	1.437	1.438	1.444	1.444
	R(5,8)	1.771	1.758	1.757	1.755	1.754	1.769	1.769
	R(6,7)	1.459	1.458	1.458	1.458	1.458	1.465	1.464
4	R(1,2)	1.417	1.418	1.418	1.418	1.418	1.425	1.425
	R(2,3)	1.383	1.378	1.379	1.377	1.378	1.381	1.382
	R(2,6)	1.417	1.418	1.418	1.418	1.418	1.425	1.425
	R(3,4)	1.765	1.755	1.755	1.752	1.753	1.766	1.766
	R(4,5)	1.765	1.755	1.755	1.752	1.753	1.766	1.766
	R(5,6)	1.383	1.378	1.379	1.377	1.378	1.381	1.382
	R(5,8)	1.765	1.755	1.755	1.752	1.753	1.766	1.766
	R(6,7)	1.417	1.418	1.418	1.418	1.418	1.425	1.425

R: Bond Length (Å).

Table S2 Energies (unit: a.u.), ionization potential, electron affinity, hole and electron reorganization energy (unit: eV) of systems **1**-**4** at optimized ground and ionic states

System	Functional	Basis set	E_{Cation}	$E_{Neutral}$	E_{Anion}	IP(v)	IP(a)	EA(v)	EA(a)	λ_h	λ_e
1	B3P86	6-31G(d,p)	-2210.0881075	-2210.3571340	-2210.3931649	7.568	7.321	0.666	0.980	0.461	0.596
		6-31+G(d,p)	-2210.1002825	-2210.3752495	-2210.4200940	7.739	7.482	0.915	1.220	0.475	0.586
	PBE0	6-31G(d,p)	-2205.7034100	-2205.9528436	-2205.9660378	7.047	6.787	0.028	0.359	0.482	0.612
		6-31+G(d,p)	-2205.7161051	-2205.9717796	-2205.9942733	7.226	6.957	0.293	0.612	0.496	0.612
	B3LYP	6-31G(d,p)	-2207.0115655	-2207.2565503	-2207.2692495	6.915	6.666	0.039	0.346	0.466	0.584
		6-31+G(d,p)	-2207.0273261	-2207.2804251	-2207.3046243	7.144	6.887	0.361	0.659	0.479	0.573
2	B3P86	6-31G(d,p)	-2947.534437	-2947.7803584	-2947.8349442	6.859	6.692	1.315	1.485	0.333	0.343
		6-31+G(d,p)	-2947.5491366	-2947.8004877	-2947.8642194	7.004	6.840	1.570	1.734	0.325	0.333
	PBE0	6-31G(d,p)	-2941.5835889	-2941.8095766	-2941.8420537	6.323	6.149	0.706	0.884	0.345	0.358
		6-31+G(d,p)	-2941.5991006	-2941.8307903	-2941.8728734	6.474	6.305	0.974	1.145	0.336	0.345
	B3LYP	6-31G(d,p)	-2943.3513985	-2943.5731034	-2943.6043313	6.205	6.033	0.678	0.850	0.343	0.346
		6-31+G(d,p)	-2943.3708127	-2943.6000931	-2943.6429880	6.405	6.239	1.004	1.167	0.333	0.333
3	B3P86	6-31G(d,p)	-3004.591308	-3004.8525017	-3004.9246206	7.245	7.107	1.855	1.962	0.277	0.214
		6-31+G(d,p)	-3004.6025190	-3004.8682377	-3004.9484503	7.364	7.231	2.078	2.183	0.271	0.209
	PBE0	6-31G(d,p)	-2999.3894623	-2999.6309558	-2999.6815311	6.714	6.571	1.265	1.376	0.287	0.223
		6-31+G(d,p)	-2999.4009830	-2999.6471642	-2999.7062402	6.838	6.699	1.498	1.608	0.280	0.217
	B3LYP	6-31G(d,p)	-3000.9746242	-3001.2111741	-3001.2601625	6.580	6.437	1.218	1.333	0.288	0.228
		6-31+G(d,p)	-3001.9889451	-3001.2319739	-3001.2915943	6.752	6.613	1.510	1.622	0.281	0.221
4	B3P86	6-31G(d,p)	-3799.0648494	-3799.3467742	-3799.3700778	7.735	7.672	0.385	0.634	0.125	0.424
		6-31+G(d,p)	-3799.0773569	-3799.3622767	-3799.3987307	7.814	7.753	0.794	0.992	0.121	0.352
	PBE0	6-31G(d,p)	-3793.0456946	-3793.3092257	-3793.3086928	7.236	7.171	-0.256	-0.015	0.129	0.419
		6-31+G(d,p)	-3739.0584052	-3739.3250604	-3739.3389243	7.317	7.256	0.170	0.377	0.123	0.361
	B3LYP	6-31G(d,p)	-3794.9088466	-3795.1662324	-3795.1659147	7.066	7.004	-0.224	-0.009	0.125	0.393
		6-31+G(d,p)	-3794.9243865	-3795.1864453	-3795.2033125	7.193	7.131	0.292	0.459	0.123	0.317

All the data are calculated with high precision (OPT=Tight, Integral(Grid=UltraFineGrid), and SCF=Tight). IP(v): vertical ionization potential. IP(a): adiabatic ionization potential. EA(v): vertical electron affinity. EA(a): adiabatic electron affinity. λ_h: hole reorganization energy. λ_e: electron reorganization energy.

Table S3 Ionization potential, electron affinity, hole and electron reorganization energy (unit: eV) of systems **4** at optimized ground and ionic states

Basis set	Methods	Hartree-Fock-like exchange	IP(v)	IP(a)	EA(v)	EA(a)	λ_h	λ_e
6-31G(d,p)	BLYP	0.00	6.516	6.465	0.010	0.178	0.102	0.324
	O3LYP	0.12	6.911	6.855	-0.196	0.060	0.112	0.426
	B3LYP	0.20	7.066	7.004	-0.224	-0.009	0.125	0.393
	B3P86	0.20	7.735	7.672	0.385	0.634	0.125	0.424
	PBE0	0.25	7.236	7.171	-0.256	-0.015	0.129	0.419
	MPW1K	0.37	7.933	7.553	-0.975	0.103	0.820	1.440
	BHHLYP	0.50	7.869	7.442	-1.158	-0.124	0.951	1.644
	MP2		8.175		-0.862			
6-31+G(d,p)	BLYP	0.00	6.678	6.629	0.598	0.691	0.099	0.205
	O3LYP	0.12	7.024	6.968	0.346	0.497	0.111	0.289
	B3LYP	0.20	7.193	7.131	0.292	0.459	0.123	0.317
	B3P86	0.20	7.814	7.753	0.794	0.992	0.121	0.352
	PBE0	0.25	7.317	7.256	0.170	0.377	0.123	0.361
	MPW1K	0.37	7.628	7.553	-0.073	0.103	0.151	0.337
	BHHLYP	0.50	7.525	7.442	-0.254	-0.124	0.166	0.286

IP(v): vertical ionization potential. IP(a): adiabatic ionization potential. EA(v): vertical electron affinity. EA(a): adiabatic electron affinity. λ_h: hole reorganization energy. λ_e: electron reorganization energy.

Table S4 Selected geometry parameters of systems **1-4** at optimized neutral and ionic states based on B3P86/6-31+G(d,p) level

	1			**2**			**3**			**4**		
	Neutral	Cation	Anion	Neutral	Cation	Anion	Neutral	Cation	Anion	Neutral	Cation	Anion
R(1,2)	1.455	1.430	1.429	1.457	1.430	1.432	1.451	1.421	1.425	1.418	1.409	1.430
R(2,3)	1.741	1.740	1.773	1.753	1.750	1.779	1.747	1.745	1.772	1.379	1.387	1.390
R(2,6)	1.382	1.412	1.406	1.383	1.412	1.404	1.386	1.416	1.404	1.418	1.409	1.430
R(3,4)	1.719	1.717	1.731	1.719	1.719	1.730	1.716	1.716	1.736	1.755	1.753	1.758
R(4,5)	1.366	1.365	1.363	1.365	1.363	1.362	1.363	1.364	1.360	1.755	1.753	1.758
R(5,6)	1.429	1.425	1.433	1.446	1.443	1.452	1.439	1.438	1.440	1.379	1.387	1.390
R(5,8)	-	-	-	1.876	1.885	1.859	1.757	1.750	1.763	1.755	1.753	1.758
R(6,7)	1.469	1.448	1.453	1.472	1.448	1.461	1.458	1.429	1.441	1.418	1.409	1.430
A(1,2,3)	120.0	118.3	117.4	116.6	116.4	115.7	117.9	118.3	117.9	112.5	112.5	112.2
A(1,2,6)	129.1	130.6	132.4	133.6	133.7	134.9	132.2	132.0	132.5	135.0	135.0	135.0
A(2,3,4)	92.10	92.02	92.35	92.70	92.43	92.76	93.66	93.46	93.30	112.7	112.7	112.9
A(2,6,5)	112.2	111.5	111.5	113.1	112.5	112.2	111.6	111.3	111.2	112.5	112.5	112.2
A(2,6,7)	125.1	127.5	128.4	133.2	133.7	134.0	137.8	138.0	137.5	135.0	135.0	135.0
A(3,4,5)	111.6	112.3	111.1	111.8	112.8	111.5	109.8	111.0	109.7	89.63	89.67	89.73
A(4,5,6)	113.3	113.5	115.1	112.5	112.4	114.2	115.0	114.6	116.2	112.7	112.7	112.9
A(5,6,7)	122.6	120.6	119.9	113.6	113.7	113.8	110.6	110.7	111.3	112.5	112.5	112.2
A(8,5,4)	-	-	-	135.7	135.1	134.7	130.2	130.5	129.9	134.6	134.7	133.4
A(8,5,6)	-	-	-	111.1	112.3	110.9	114.7	115.0	113.8	112.7	112.7	112.9
D(1,2,3,4)	-176.9	-173.8	-174.3	-172.0	-171.3	-174.3	-179.7	-179.8	-180.0	-180.0	-180.0	-172.0
D(1,2,6,5)	176.7	172.3	173.8	170.0	168.8	173.2	179.7	179.8	180.0	179.8	180.0	170.1
D(3,2,1,3′)	50.35	33.92	33.42	22.29	17.09	12.72	0.628	0.244	0.019	0.000	0.000	0.000

R: Bond Length (Å); A: Bond Angle (º); D: Dihedral Angle (º).

Fig. S1 The evolution trends in IP(a), EA(a), λ_h and λ_e from molecule **1** to **4** with B3P86, B3LYP and PBE0 methods. The black, blue and red values are calculated by B3P86, B3LYP and PBE0 methods, respectively. The dashed and solid lines represent 6-31G(d,p) and 6-31+G(d,p) basis sets, respectively. The green λ values are computed with BHHLYP/6-31+G(d,p).

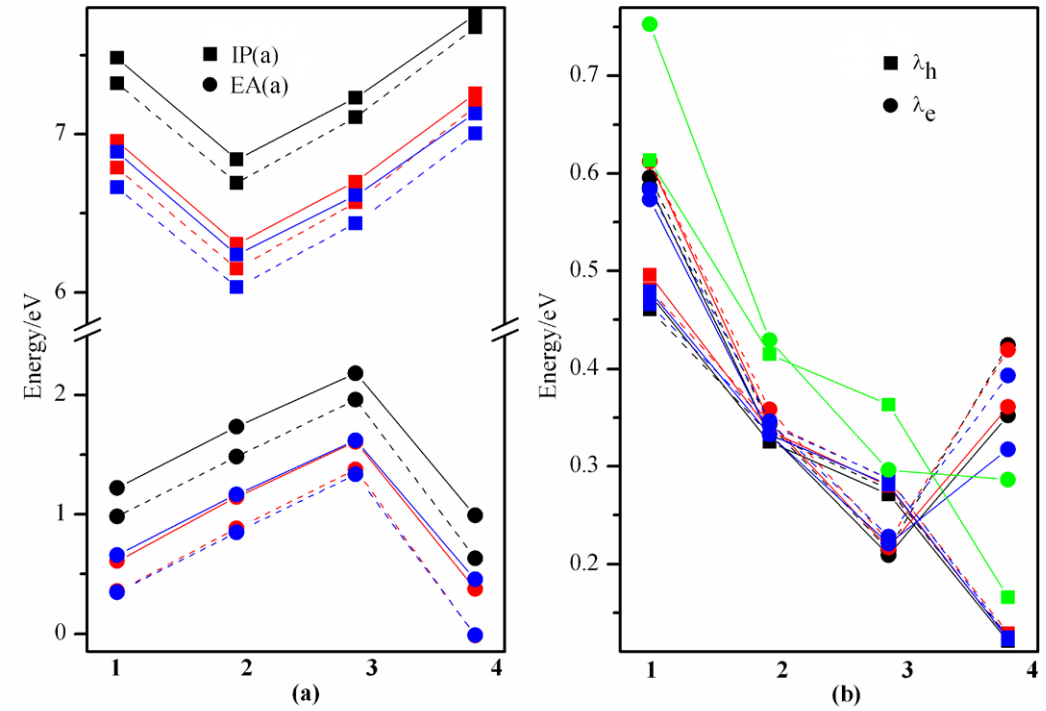

Fig. S2 Density of states (total DOS in black line and sulfur atoms partial DOS in red line) of system **4**