Enhancing Charge Mobilities in Organic Semiconductors by Selective Fluorination: A Design Approach Based on a Quantum Mechanical Perspective
– Electronic Supporting Information (ESI) –

Buddhadev Maiti,[†,¶] Alexander Schubert,[†,‡,¶] Sunandan Sarkar,[†] Srijana Bhandari,[†] Kunlun Wang,[†] Zhe Li,[†] Eitan Geva,[‡] Robert J. Twieg,[†] and Barry D. Dunietz[*,†]

Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44242, USA, and Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA

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[†]Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44242, USA

[‡]Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA

[¶]These authors contributed equally to this work.

Electronic coupling analysis in terms of molecular orbitals

The electronic coupling coefficients for hole (Γ_h) and electron (Γ_e) transport can be interpreted within a simplified orbital picture. In all cases considered here, the H-1 and the L+1 *monomer* orbitals are energetically well-separated from H and L orbital energies, respectively, see ESI Figs. 2–8 (left hand side). Thus, in almost all cases (exceptions marked), the *dimer* orbitals H-1, H, L, and L+1, (ESI Figs. 2–8, right hand side) correspond to combinations of the *monomer* orbitals H and L. Assuming a) a small monomer-monomer orbital overlap and b) a symmetric arrangement, the energy splitting between *dimer* orbital energies of H-1 and H (L and L+1) directly reflects the hole (electron) coupling between the two *monomer* H (L) orbitals as illustrated in ESI Fig. 1.

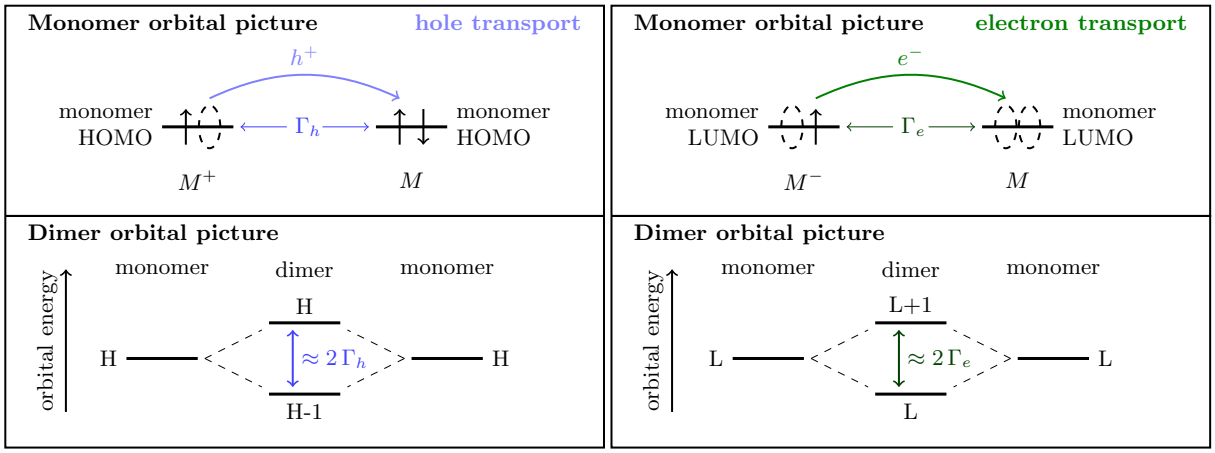
A comparison with the more quantitative CDFT-CI method in SI Tab. 1, shows a good qualitative agreement for symmetrically arranged molecules of Class II and Class III molecules, while coupling energies for Class I molecules are overestimated. The crystal structure of these molecules, Naph and Naph-F8, is a herringbone geometry. In such cases, each molecule in a dimer experiences a substantially different interaction. This leads to a symmetry-breaking, lifting the degeneracy between monomer electronic energy levels. The unequal contribution of the two monomer orbitals to the dimer orbitals results in an additional contribution to the energy splitting. Thus, a seemingly increased coupling is obtained, which is therefore omitted in SI Tab. 1. The Class I symmetry-breaking is well reflected in the dimer MOs, where the H-1, H, L, and L+1 are localized on a single monomer (see ESI Figs. 2 and 3), whereas Class II and III molecules typically show fully delocalized dimer orbitals.

Class II and III systems show significant electronic coupling for hole transport (Γ_h) and negligible coupling for electron transport (Γ_e). The larger conjugated system Pele-F6-T, however, shows significant coupling for both charge transport channels. In the simplified orbital picture, the negligible Γ_e coupling of naphthalene derivatives is reproduced by the near degeneracy of the L and L+1 dimer orbitals. The corresponding orbitals are illustrated with their energies in ESI Figs. 4 to 7 (r.h.s.). The dimer model of Class II systems reveals a π stacking arrangement with a lateral shift preferentially along the long molecular axis of the monomers with respect to each other. Since the dimer L lobes are oriented along the short molecular axis, this shift results in a reduced overlap of π^* lobes between the two monomers. The situation is sligthly different for the lobes of the π bonding H orbitals, which lie along the long molecular axis, thus maintaining a larger overlap for lateral shifts along this axis. The resulting interaction leads to the substantial splitting in the H-1 and H energies. We find a similar situation for the Class III molecules, Naph-F4-T1 and Naph-F4-T2. Here, the two monomer units are rotated with respect to each other in the dimer arrangement. Here, the high symmetry yields an effective cancellation between the L-lobe overlaps. The H lobes, on the other hand, are of different symmetry and perpendicular to the radial direction. Thus, they retain significant overlap during in-plane rotations.

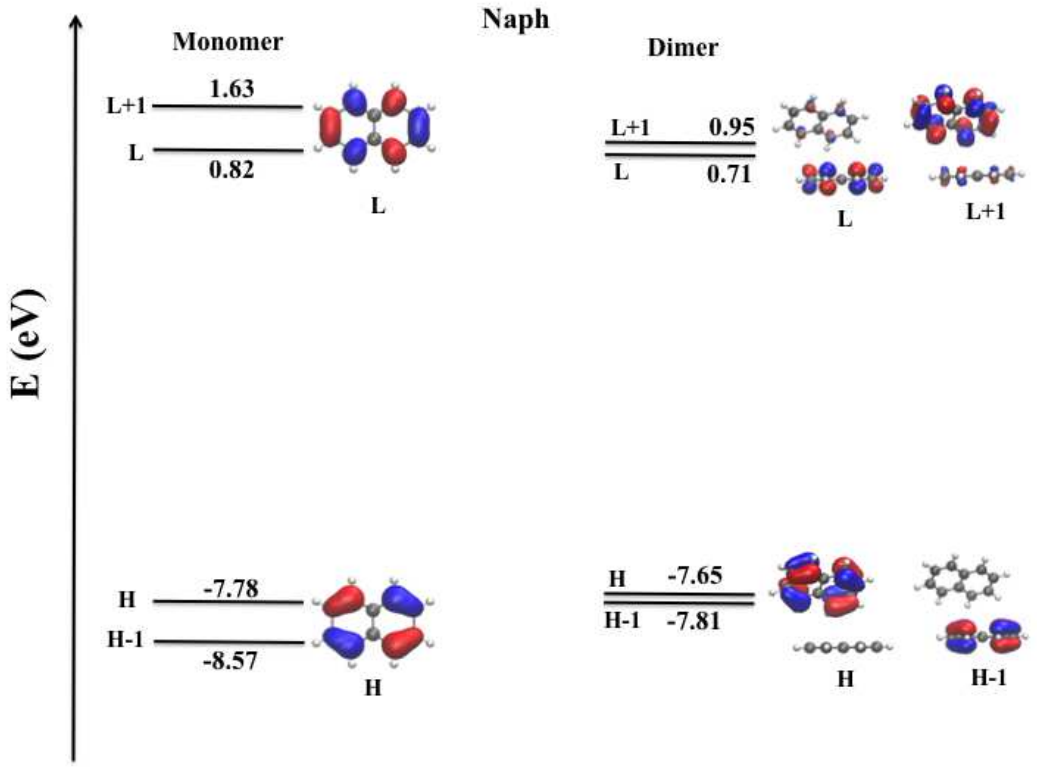
ESI Table 1. The electronic coupling coefficients for hole (Γ_h) and electron (Γ_e) transport. CDFT-CI values are compared to orbital energies based values provided in parenthesis.

Molecule	Γ_h [eV]	Γ_e [eV]
	6-31G(d)	
Naph	0.0005 (—)	0.060 (—)
Naph-F8	0.005 (—)	0.006 (—)
Naph-F4-C1	0.086 (0.109)	0.009 (0.014)
Naph-F4-C2	0.110 (0.190)	0.012 (0.027)
Naph-F4-T1	0.380 (0.367)	0.000 (0.000)
Naph-F4-T2	0.378 (0.395*)	0.000 (0.000)
Pele-F6-T	0.206 (0.231)	0.113 (0.136)
	cc-pVTZ	
Naph-F4-T2	0.363 (0.380*)	0.000 (0.000)

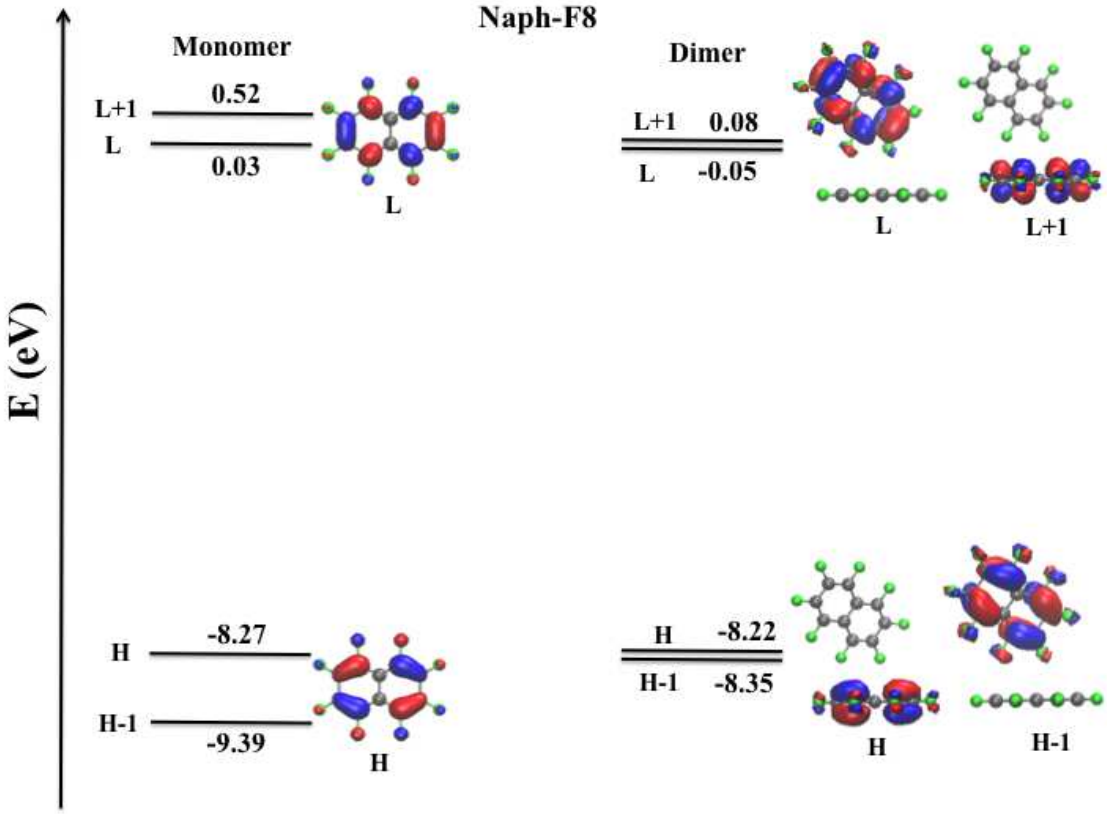
*The monomer HOMO superposition gives rise to the dimer orbitals H and H-3. Therefore, the H/H-3 splitting is considered in this case.



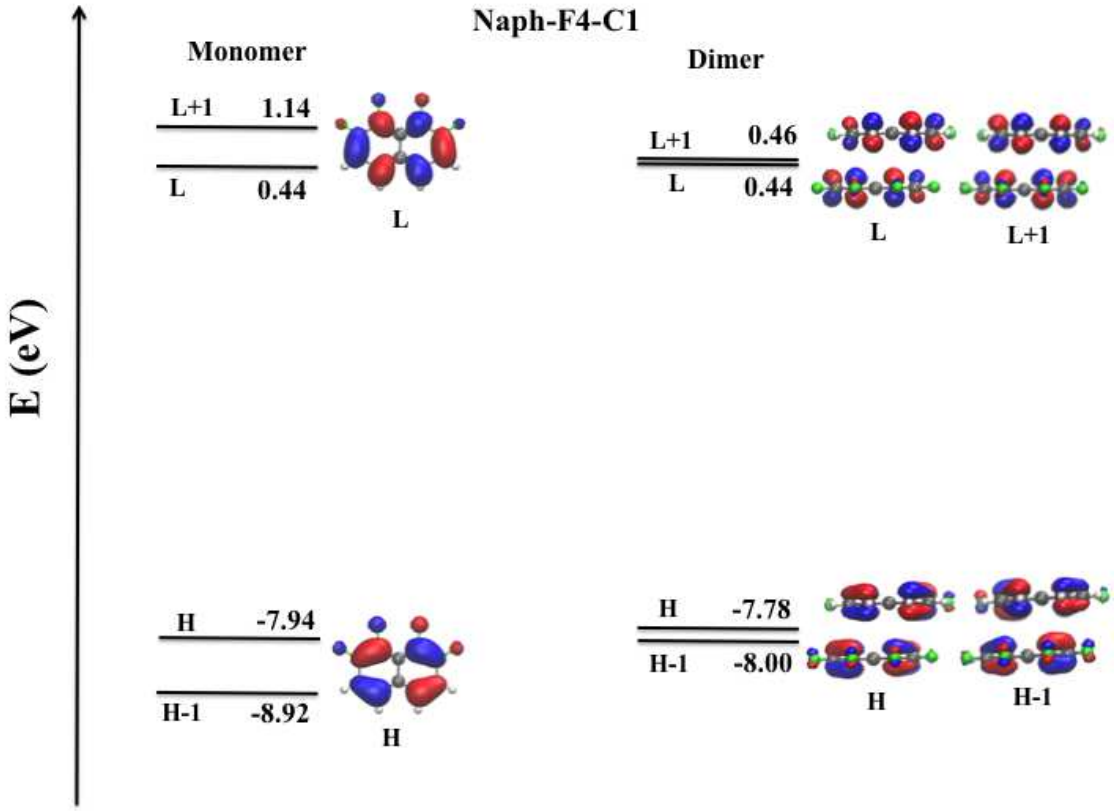
ESI Figure 1. Upper panels: Charge transport can be described in terms of the molecular orbital (MO) picture, when the *monomer* frontier orbitals, HOMO (H) and LUMO (L), are energetically well-separated from HOMO-1 and LUMO+1, respectively. Then, the hole (electron) transport, left (right) panel, takes place from the HOMO (LUMO) of the charged monomer M^+ (M^-) to an adjacent neutral monomer M. Lower panels: Assuming a small monomer-monomer orbital overlap, the *monomer*-to-*monomer* coupling for hole (Γ_h) and electron (Γ_e) transport is directly reflected in the energy splitting of the *dimer* orbital energies.



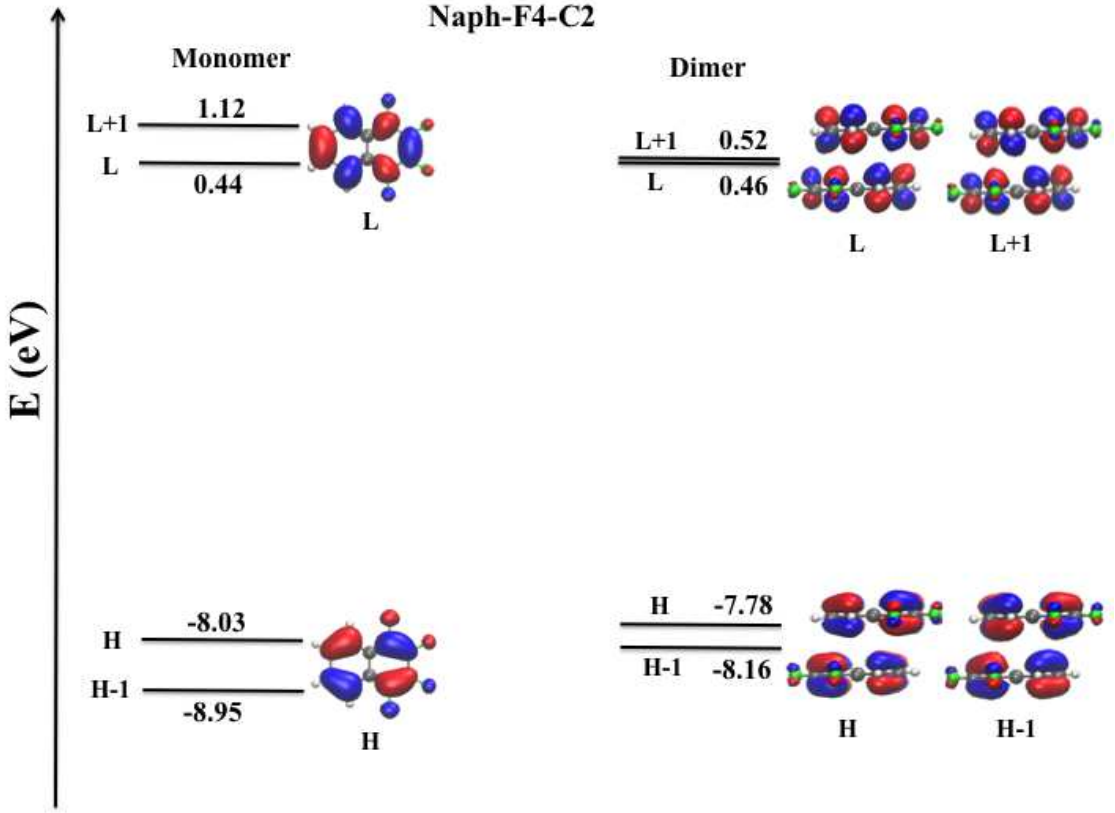
ESI Figure 2. The isosurface plots of monomer (left) and dimer (right) molecular orbitals (MOs) for Naph molecule (Class I). The dimer orbitals, H-1, H, L, and L+1, are in all considered cases combinations of the monomer orbitals H and L. Thus, the H-1/H (L/L+1) splitting indicates the hole (electron) transport coupling.



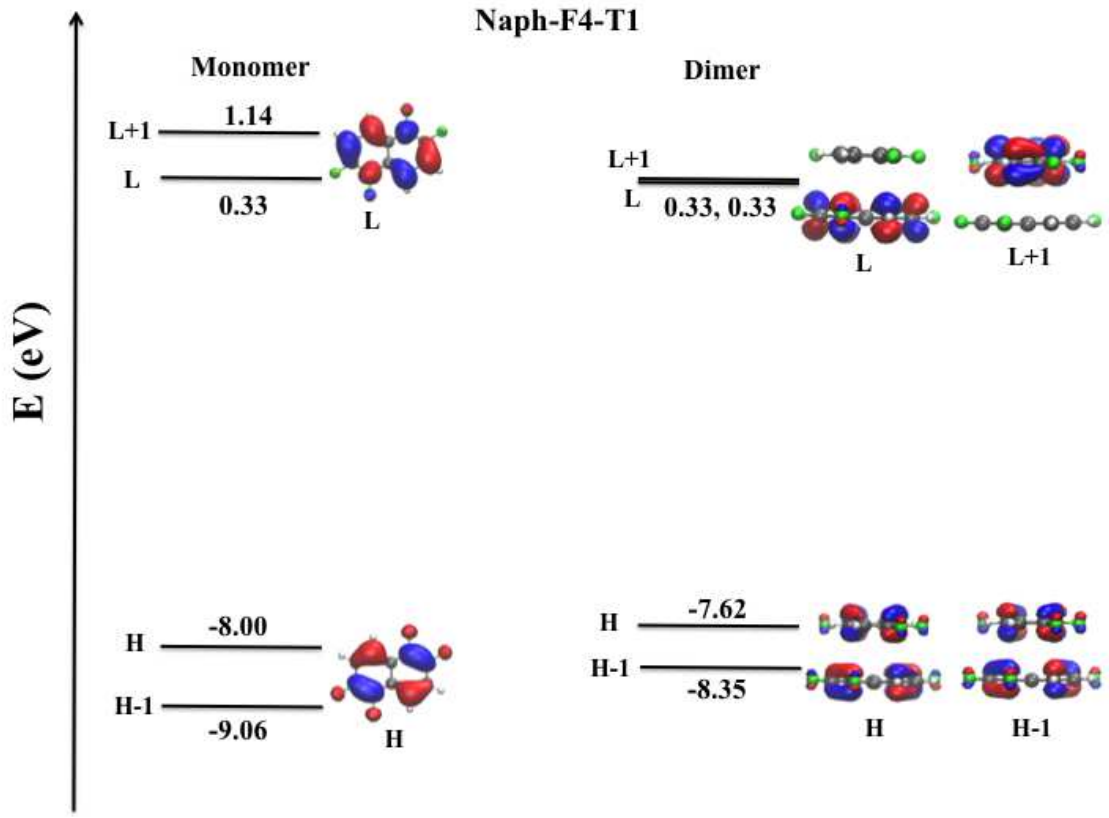
ESI Figure 3. The isosurface plots of molecular orbitals (MOs) for Naph-F8 molecule (Class I).



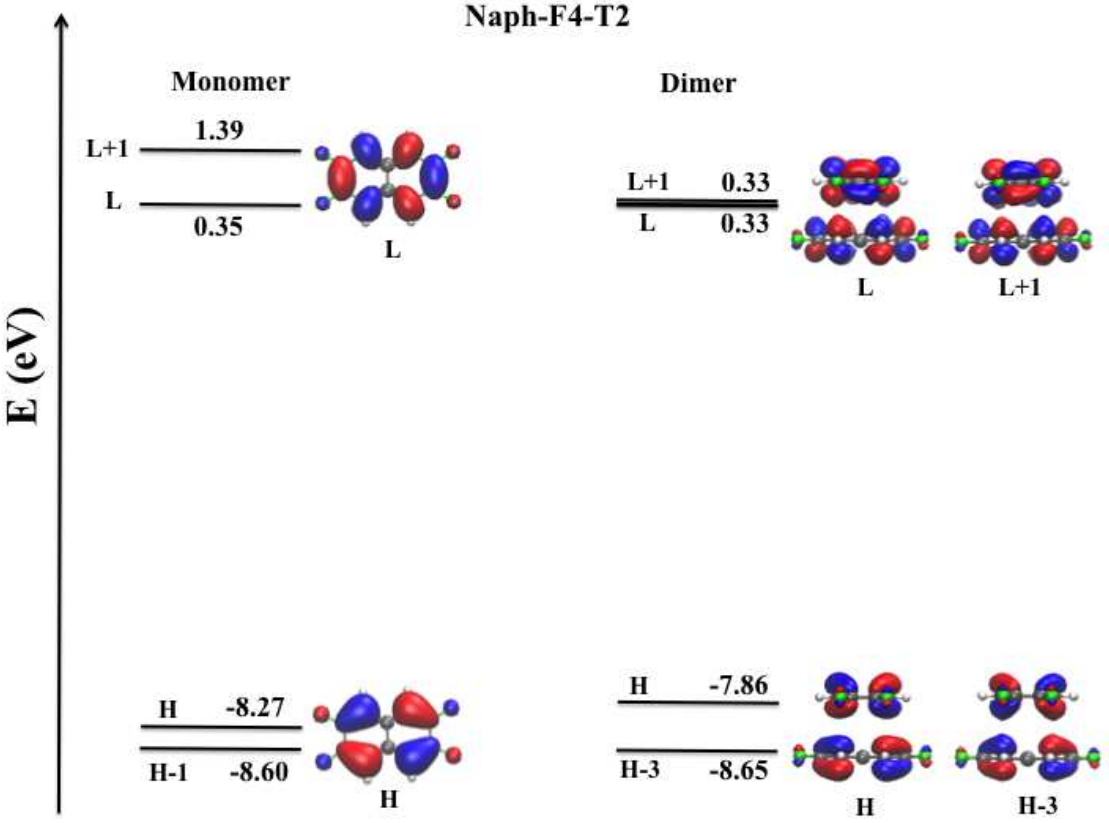
ESI Figure 4. The isosurface plots of molecular orbitals (MOs) for Naph-F4-C1 molecule (Class II).



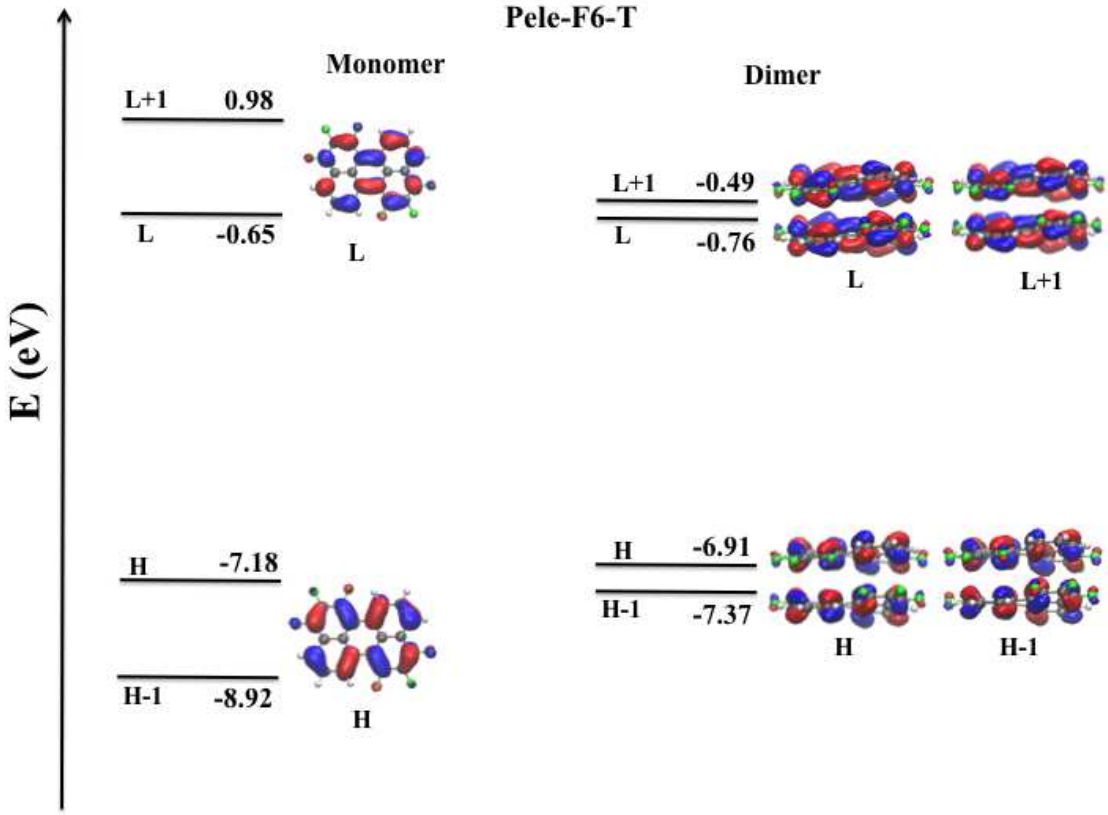
ESI Figure 5. The isosurface plots of molecular orbitals (MOs) for Naph-F4-C2 molecule (Class II).



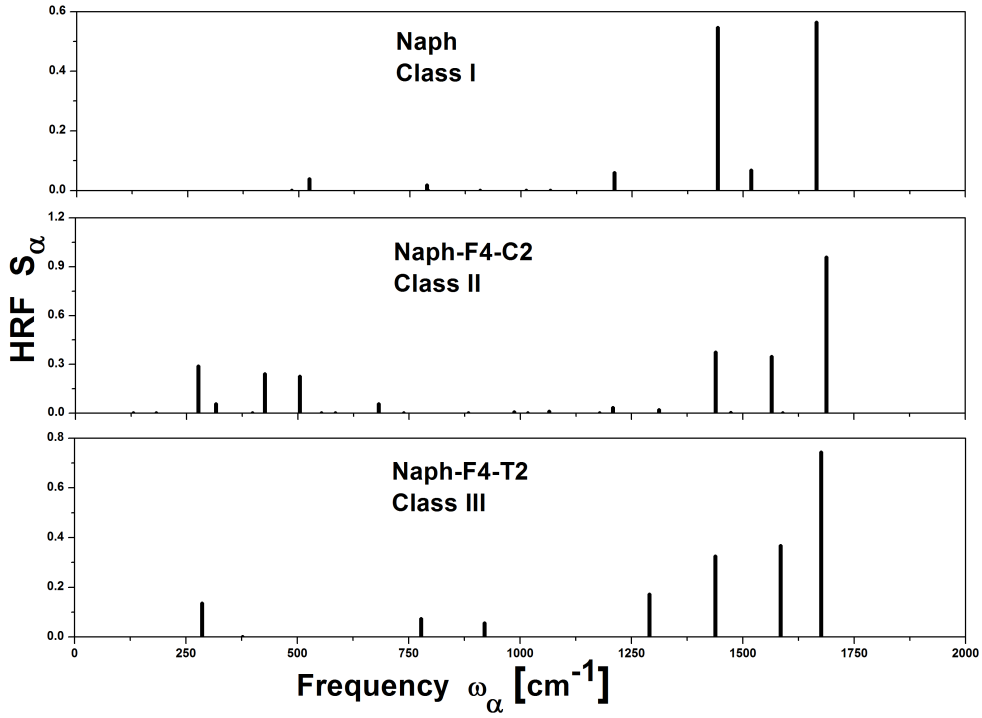
ESI Figure 6. The isosurface plots of molecular orbitals (MOs) for Naph-F4-T1 molecule (Class III).



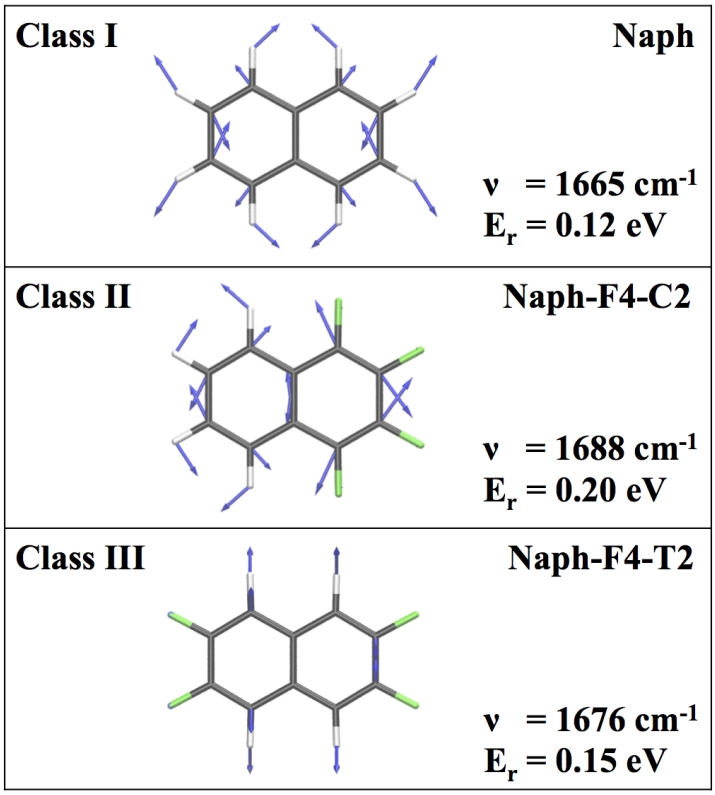
ESI Figure 7. The isosurface plots of molecular orbitals (MOs) for Naph-F4-T2 molecule (Class III).



ESI Figure 8. The isosurface plots of molecular orbitals (MOs) for Pele-F6-T molecule (Class III).



ESI Figure 9. Huang-Rhys factors S_α (HRFs) for Class I, Class II, and Class III molecules for each normal mode frequency ω_α.



ESI Figure 10. The dominant normal modes of hole transport for Class I, Class II, and Class III molecules. The arrows indicate the direction of the normal mode motions. The significant contribution of these modes can be understood within the simplified orbital picture: removing an electron from the dimer HOMO results in a weakening of bonds aligned with the π-lobes causing elongated bond lengths, whereas bonds of low orbital density are strengthened and contract.

Reorganization energies

ESI Table 2. Inner sphere reorganization energy (E_r^{in}) calculated with DFT using the ωB97XD functional with a 6-31G(d) and a cc-pVTZ basis set for the monomer model. The reorganization energy is obtained from the direct energy calculation and, in parenthesis, from HRFs calculation as outlined in the manuscript.

Molecule	E_r [eV]
6-31G(d)	
Naph	0.236 (0.241)
Naph-F8	0.458 (0.464)
Naph-F4-C1	0.362 (0.366)
Naph-F4-C2	0.380 (0.388)
Naph-F4-T1	0.394 (0.400)
Naph-F4-T2	0.330 (0.329)
Pele-F6-T	0.299 (0.300)
cc-pVTZ	
Naph-F4-T2	0.311 (0.308)

ESI Table 3. Comparison of FGR rate constants obtained from different Gaussian time windows with time constant $\tau_{\mathrm{sol}} = \hbar/\sqrt{k_B T\, E_r^{\mathrm{ex}}}$ representing different outer sphere solvation energies E_r^{ex}, see Eq. (1) in the manuscript.

τ_{sol}	80 fs	60 fs	40 fs	20 fs	10 fs
E_r^{ex}	2.63 meV	4.68 meV	10.5 meV	42.1 meV	169 meV
Molecule	k_{FGR} [s^{-1}]	k_{FGR} [s^{-1}]	k_{FGR} [s^{-1}]	k_{FGR} [s^{-1}]	k_{FGR} [s^{-1}]
6-31G(d)					
Naph	8.89×10^{10}	6.68×10^{10}	4.46×10^{10}	2.27×10^{10}	1.13×10^{10}
Naph-F8	2.94×10^{11}	2.34×10^{11}	1.86×10^{11}	1.43×10^{11}	1.17×10^{11}
Naph-F4-C1	2.36×10^{14}	1.80×10^{14}	1.27×10^{14}	7.73×10^{13}	5.51×10^{13}
Naph-F4-C2	2.28×10^{14}	1.81×10^{14}	1.43×10^{14}	1.05×10^{14}	8.10×10^{13}
Naph-F4-T1	2.11×10^{15}	1.69×10^{15}	1.39×10^{15}	1.11×10^{15}	8.96×10^{14}
Naph-F4-T2	6.63×10^{15}	5.05×10^{15}	3.35×10^{15}	1.97×10^{15}	1.27×10^{15}
Pele-F6-T	8.15×10^{14}	7.48×10^{14}	6.71×10^{14}	5.36×10^{14}	4.13×10^{14}
cc-pVTZ					
Naph-F4-T2	7.15×10^{15}	5.42×10^{15}	3.73×10^{15}	2.02×10^{15}	1.29×10^{15}

ESI Table 4. Marcus rate constants for different values of E_r^{ex} (see ESI Tab. 3).

E_r^{ex}	0 meV	35 meV	50 meV
Molecule	k_M [s^{-1}]	k_M [s^{-1}]	k_M [s^{-1}]
6-31G(d)			
Naph	8.29×10^{8}	5.52×10^{8}	4.65×10^{8}
Naph-F8	8.07×10^{9}	4.75×10^{9}	4.05×10^{9}
Naph-F4-C1	5.94×10^{12}	4.05×10^{12}	3.44×10^{12}
Naph-F4-C2	7.63×10^{12}	5.21×10^{12}	4.43×10^{12}
Naph-F4-T1	7.99×10^{13}	5.46×10^{13}	4.64×10^{13}
Naph-F4-T2	1.73×10^{14}	1.17×10^{14}	9.95×10^{13}
Pele-F6-T	7.13×10^{13}	4.81×10^{13}	4.07×10^{13}
cc-pVTZ			
Naph-F4-T2	2.02×10^{14}	1.37×10^{14}	1.16×10^{14}

ESI Table 5. The energy E with respect to the equilibrium geometry and hole coupling Γ_h of Naph-F4-C2 (Class II) and Naph-F4-T2 (Class III) molecule with respect to the lateral shift and the torsional angle, respectively.

Molecule											
	Shift [Å]	0.0	0.4	0.8	1.2	1.6	2.0	2.4	2.8	3.2	3.6
Naph-F4-C2	E [eV]	0.000	0.007	0.040	0.078	0.094	0.096	0.109	0.154	0.211	0.259
	Γ_h [eV]	0.110	0.071	0.010	0.043	0.064	0.040	0.015	0.083	0.142	0.163
	Angle [°]	0	10	20	30	40	50	60	70	80	90
Naph-F4-T2	E [eV]	0.078	0.066	0.042	0.022	0.014	0.023	0.013	0.009	0.004	0.000
	Γ_h [eV]	0.314	0.298	0.286	0.294	0.248	0.104	0.191	0.304	0.357	0.378

Optimized structures

ESI Table 6. The atomic coordinates of the optimized Naph monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	-0.0000004226179781	-0.7119036451840839	0.0002608755938919
C	-1.2430906960043391	-1.3990751785321334	0.0003635791585515
C	-2.4275258078130877	-0.7080332424051891	0.0002712486701538
C	-2.4275249800591063	0.7081176044353606	0.0000788771597916
C	-1.2430891245815616	1.3991582476740720	-0.0000234041560188
C	0.0000003784126378	0.7119853329584729	0.0000678333786860
C	1.2430907248686061	1.3991568401128394	-0.0000360764840203
C	2.4275257915328554	0.7081148957744768	0.0000543447430132
C	2.4275249938491461	-0.7080359776694700	0.0002471880021348
C	1.2430891383028679	-1.3990765660417999	0.0003514437253088
H	-1.2392834804207871	-2.4862192730045631	0.0005025193408425
H	-3.3738248854709583	-1.2405409246542392	0.0003481481135154
H	-3.3738234520478159	1.2406264081223957	0.0000093109860302
H	-1.2392808064780538	2.4863023378966531	-0.0001621071793666
H	1.2392835506798467	2.4863009525492936	-0.0001744493488605
H	3.3738248566772473	1.2406226343965714	-0.0000248156604199
H	3.3738234568528895	-1.2405447902633961	0.0003158625239135
H	1.2392807470406393	-2.4862206681713048	0.0004908744173926

ESI Table 7. The atomic coordinates of the optimized Naph-F8 monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	-0.0000004162822361	-0.7147872215006967	0.0002564995131682
C	-1.2437839921362104	-1.3939137311850616	0.0003596328475669
C	-2.4249929534576542	-0.7038907441795940	0.0002679369894612
C	-2.4249921404776993	0.7039751162084847	0.0000838331393824
C	-1.2437823901770459	1.3939967517250840	-0.0000214194229014
C	0.0000004173000382	0.7148688522318017	0.0000690454978752
C	1.2437839637710073	1.3939953995016909	-0.0000334210791111
C	2.4249929399878489	0.7039724170423114	0.0000594354872221
C	2.4249921439805382	-0.7038934377516588	0.0002433548250051
C	1.2437824178571171	-1.3939151246432595	0.0003475104862666
F	-1.2884740304290971	-2.7244742795801230	0.0005379125826518
F	-3.5878270248575883	-1.3442854796835133	0.0003610615685539
F	-3.5878254503067257	1.3443712475861371	0.0000037655623558
F	-1.2884709699146204	2.7245573154791956	-0.0002010913329524
F	1.2884739273313275	2.7245559362312806	-0.0002116560330653
F	3.5878270096405918	1.3443671683370200	-0.0000324347645160
F	3.5878254901834943	-1.3442895079493524	0.0003245449350852
F	1.2884710407099744	-2.7244756898757871	0.0005267421824914

ESI Table 8. The atomic coordinates of the optimized structure of Naph-F4-C1 monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	-1.2497813491018794	0.6841131289166540	0.0000000000000000
C	0.0000006099461023	0.0185331804596102	0.0000000000000000
C	0.0000004704867990	-1.4101310941236238	0.0000000000000000
C	-1.2376285878032525	-2.1055833746235746	0.0000000000000000
C	-2.4297967266788292	-1.4314260931750480	0.0000000000000000
C	-2.4200935255465379	-0.0264844367195963	0.0000000000000000
C	1.2497826959660012	0.6841128933086148	0.0000000000000000
C	2.4200947671162170	-0.0264849062684262	0.0000000000000000
C	2.4297977141558618	-1.4314265866885614	0.0000000000000000
C	1.2376294107305428	-2.1055836379302040	0.0000000000000000
F	-1.3107044167731219	2.0218660334959919	0.0000000000000000
F	1.3107060025929855	2.0218657943550902	0.0000000000000000
F	3.5816634388740916	0.6399594128781294	0.0000000000000000
F	-3.5816620449287058	0.6399600878449172	0.0000000000000000
H	-1.2258078241500829	-3.1908607143594310	0.0000000000000000
H	-3.3853993347408391	-1.9437840394455046	0.0000000000000000
H	3.3854002534943772	-1.9437846593606156	0.0000000000000000
H	1.2258084463602694	-3.1908609885644252	0.0000000000000000

ESI Table 9. The atomic coordinates of the optimized structure of Naph-F4-C2 monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	-0.0313623163098950	-0.7114718261235673	0.0002587078974422
C	-1.2676585607979842	-1.4058297260246728	0.0003600861810461
C	-2.4477384377642570	-0.7076718531289575	0.0002687440956883
C	-2.4477376435643401	0.7077562744624164	0.0000828096297170
C	-1.2676569799393267	1.4059128070435443	-0.0000204013806700
C	-0.0313615243164432	0.7115535134298315	0.0000683770054225
C	1.2115380728752616	1.3878391954553844	-0.0000361709855137
C	2.3959132026726917	0.7056318235817836	0.0000553260685353
C	2.3959124075979665	-0.7055528630844614	0.0002469846856652
C	1.2115365160490017	-1.3877588820765174	0.0003507348822838
H	-1.2643818012479895	-2.4901275903710811	0.0004938612355356
H	-3.3937719889549451	-1.2393549153509362	0.0003429772738547
H	-3.3937705865511885	1.2394404313792484	0.0000178781376211
H	-1.2643790078131063	2.4902106694123116	-0.0001542936036508
F	1.2324478622413837	2.7260103952622448	-0.0002227547786508
F	3.5650137597815759	1.3456833970458126	-0.0000412844887792
F	3.5650122423686974	-1.3456057557373349	0.0003316004746955
F	1.2324447663959677	-2.7259301071810893	0.0005380706542972

ESI Table 10. The atomic coordinates of the optimized structure of Naph-F4-T1 monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	-1.2536144174488908	1.4020731915745264	0.0000000000000000
C	-0.0150015727756884	0.7115849631869213	0.0000000000000000
C	0.0150026703888963	-0.7115849764417942	0.0000000000000000
C	-1.2258446887419985	-1.3896242828596759	0.0000000000000000
C	-2.4101032596019487	-0.7042377284711555	0.0000000000000000
C	-2.4317814605342742	0.7023795623984220	0.0000000000000000
C	1.2258457835959653	1.3896242959579326	0.0000000000000000
C	2.4101043918457714	0.7042377420116708	0.0000000000000000
C	2.4317825693837287	-0.7023795805259223	0.0000000000000000
C	1.2536155229397696	-1.4020732329449208	0.0000000000000000
F	3.5649140187219590	1.3793894772988398	0.0000000000000000
F	-3.5649128500048026	-1.3793894618631166	0.0000000000000000
F	1.2328494613958032	2.7280353324510247	0.0000000000000000
F	-1.2328484067731029	-2.7280353079586841	0.0000000000000000
H	-1.2595780132712280	2.4855038954894373	0.0000000000000000
H	-3.3949302700357471	1.2003619005550783	0.0000000000000000
H	3.3949314140624027	-1.2003618509214391	0.0000000000000000
H	1.2595791068533773	-2.4855039389371325	0.0000000000000000

ESI Table 11. The atomic coordinates of the optimized structure of Naph-F4-T2 monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	1.2025822372058772	2.2023858204085269	-1.6987852987242729
C	-0.1193758911469557	1.8699726409666368	-1.6988545821504122
C	-0.5034343129234335	0.5034341067338469	-1.6988949970160605
C	0.5034187596337567	-0.5034030919868958	-1.6989057996281787
C	2.2023415305488934	1.2026416435855067	-1.6987957358191157
C	1.8699509542913206	-0.1193221059802011	-1.6988759787745582
C	-1.8699659895468090	0.1193531460941816	-1.6988594545809221
C	-2.2023571983279879	-1.2026108889283937	-1.6987947543712114
C	-1.2025981761116640	-2.2023546862533183	-1.6988051563858984
C	0.1193603179686172	-1.8699410841698216	-1.6988808328475886
H	-0.8696818332617569	2.6537845093458112	-1.6987359815677987
H	-2.6537903973402979	0.8696459707851012	-1.6987409488416505
F	-3.4794667769000891	-1.5967553092979214	-1.6987334339905538
F	-1.5967219254110918	-3.4794701383653046	-1.6987530946575460
H	0.8696657659847871	-2.6537534161215532	-1.6987801873637303
H	2.6537749375586213	-0.8696152715696307	-1.6987751030294871
F	3.4794508996605611	1.5967872053837084	-1.6987391695907623
F	1.5967070981176457	3.4795009493697067	-1.6987194906602450

ESI Table 12. The atomic coordinates of the optimized structure of Pele-F6-T monomer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	1.2722731452603540	0.6720752900904734	0.0161868404378164
C	1.2223651746313553	-0.7608058014290741	-0.0365682083251675
C	2.4236061579238899	-1.4185426154106671	-0.2125569820167169
F	2.5145242901150460	-2.7488590789019671	-0.3372449384861888
C	3.6623995410735688	-0.7543809954883730	-0.2775758986934904
F	4.7704176234141569	-1.4737399909217854	-0.4478269182694219
C	3.7068665604439590	0.6010217316623252	-0.1577049949339348
F	4.8868049701202985	1.2254476858117846	-0.1935874635796236
C	2.5220908480250785	1.3538840542826276	0.0021705183933010
C	2.5881760157926372	2.7597189313627539	0.1345146851053324
C	1.4299251155055179	3.4721051950983566	0.2869633359364097
C	0.1827187280299231	2.8243821274399998	0.2540958632581492
C	0.0752894639513899	1.4520691495433860	0.0896582421690267
C	-1.2227516486975323	0.7604921681255766	-0.0359137548852668
C	-2.4241917426360806	1.4182236268522834	-0.2109281870440169
F	-2.5154449048791432	2.7486319377688608	-0.3344449455789385
C	-3.6628974481435361	0.7539647557593194	-0.2758955198991381
F	-4.7710764653631736	1.4732839869137313	-0.4453316403838647
C	-3.7072171316687834	-0.6015366343283263	-0.1569459252516140
F	-4.8871172584533280	-1.2260013410829562	-0.1928290918302166
C	-2.5223644331648596	-1.3543280518703356	0.0023713722189524
C	-1.2726132699762678	-0.6723898526887110	0.0162235055120421
C	-0.0755852956897506	-1.4523941706586454	0.0893339148808536
C	-0.1828433721332157	-2.8246373484412062	0.2541138675600061
C	-1.4300002049741347	-3.4724890520537173	0.2871424962041667
C	-2.5882889298753127	-2.7602124739435023	0.1345890194532624
H	3.5561707933046427	3.2462552317009634	0.1246146129968359
H	1.4605578606172016	4.5502448761744283	0.4064611112674517
H	-0.7034212123974719	3.4303049893989614	0.3599853776854098
H	0.7034243750863477	-3.4303749186919830	0.3602348113254107
H	-1.4605415818644316	-4.5505991316403991	0.4069388981340661
H	-3.5562557633783576	-3.2468142804341573	0.1247559966390965

ESI Table 13. The atomic coordinates of the optimized structure of Naph dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	2.3283490879053250	6.1272077291925582	9.3905893570596373
C	3.1234196607439082	6.9345106957972265	8.6167253816522997
C	3.5324156267421616	6.5234762728049551	7.3199182500543722
C	4.3460949027215108	7.3383594393645497	6.4881364416190817
C	1.9072766597169899	4.8631823871606672	8.9103896163626857
H	2.0143829893286398	6.4582185362658322	10.3764848186740029
H	3.4536639714062702	7.9017576401986567	8.9877202104629070
H	4.6746415090883335	8.3050995531611118	6.8619747055263014
H	1.2731444567682244	4.2326936519607390	9.5267782584016150
C	3.1079412923403931	5.2541567469877313	6.8384421947974356
C	4.7174812364454741	6.9136263603387071	5.2375796794214908
C	2.2972229395089103	4.4359181032521615	7.6670813213276494
C	3.5051307761740307	4.8432407875961889	5.5381027867193495
C	4.2889123674270442	5.6522742212373878	4.7560040246272495
H	5.3403400350080794	7.5440334641108322	4.6104046840291701
H	1.9813113238944604	3.4672698192411180	7.2915725534888889
H	3.1669452060772159	3.8770395024445161	5.1723289586006702
H	4.5903064570463368	5.3261799635668714	3.7645675561007028
C	0.2327812996882109	3.2224468459876010	4.8410781204767943
C	-0.5456194792823699	4.0126701762756811	5.6475650700010132
C	-0.9364763277826152	3.5708191322104939	6.9391330269526268
C	-1.7276639610519495	4.3739251444308564	7.8017672504756606
C	0.6580098295240357	1.9469009390306655	5.2858678461394142
H	0.5364009800742707	3.5782182097318342	3.8608753338520310
H	-0.8710354788424856	4.9930126155641847	5.3088615707283289
H	-2.0555965217064767	5.3497720916758889	7.4530809594110536
H	1.2750663568376777	1.3304887329178241	4.6394643294170823
C	-0.5054525319119265	2.2912182823909282	7.3884847855744775
C	-2.0742623261811834	3.9289706705671343	9.0519915164360025
C	0.2943847497315970	1.4921355456127590	6.5287934207810041
C	-0.8769873002801094	1.8589491584472830	8.6896562288274932
C	-1.6417577692669205	2.6574104123059810	9.5016381918503079
H	-2.6825792835388764	4.5499875555430984	9.7021096671448834
H	0.6237963163228277	0.5163800934453981	6.8769132104428756
H	-0.5407252098442089	0.8838646184697475	9.0337466313675439
H	-1.9256038408327967	2.3125849007109025	10.4918600411959861

ESI Table 14. The atomic coordinates of the optimized structure of Naph-F8 dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	5.5452130330028435	0.5405987052168461	11.8182574254535968
C	5.9543614104158618	1.5242984682860812	12.7539146978460973
C	7.2303146509064549	1.5394880768327430	13.2462500066950373
C	8.1660256196077903	0.5720376136375872	12.8305514013495721
C	4.2340921212524956	0.4922678512552465	11.2843747929485989
F	5.1003183047602176	2.4564721397030809	13.1715531814541169
F	7.6106368697292179	2.4621386402564269	14.1225039593778714
F	9.3977379133677132	0.6177710898008225	13.3242691003799418
F	3.3213013220340524	1.3910565685846066	11.6476125407339097
C	6.4925542840603798	-0.4443537208438788	11.4022053138900183
C	7.8059460227155810	-0.3930311724619587	11.9311529527811988
C	3.8756054129881008	-0.4735006201055880	10.3837215861247678
C	6.0851359785199879	-1.4263323660245726	10.4663083738038249
F	8.7192921538193033	-1.2869399171903060	11.5616995474934399
C	4.8087178553207623	-1.4450460588091933	9.9762436333186049
F	2.6473013178259701	-0.5126137996660304	9.8814453153645019
F	6.9424233581292629	-2.3492529768059618	10.0388402817941778
F	4.4358326708266356	-2.3603076808913768	9.0893146981828608
C	7.5022575495243640	2.9703459488472617	6.0245229116405952
C	7.1313382576294311	3.8439583368666357	4.9717441768013151
C	5.9321623676659794	3.7007306028972269	4.3280961300980918
C	5.0358043822254972	2.6833186086445147	4.7085102463466884
C	8.7355512852847319	3.0831778214200751	6.7142213186312549
F	7.9474357429599465	4.8197878823301794	4.5811266906856387
F	5.5894371218918453	4.5181141764360193	3.3402447218046194
F	3.8814037205844811	2.5701249670199307	4.0643029023753678
F	9.6079945974782515	4.0331989017097980	6.3889080339452518
C	6.5918162296047971	1.9397452079817126	6.4102019650704811
C	5.3574599631870763	1.8252063731987060	5.7244064632715590
C	9.0615090406886338	2.2179679107274599	7.7231268282742001
C	6.9670029726534501	1.0614203821121488	7.4561956612264053
F	4.4822008151154806	0.8798925120308033	6.0578556405100494
C	8.1682247227811455	1.1949205288297322	8.0950363287279838
F	10.2165281293431782	2.3273404275849443	8.3672186115015030
F	6.1477257400174752	0.0847174812365960	7.8424108835467186
F	8.5188000620813931	0.3592810893516999	9.0672826765498051

ESI Table 15. The atomic coordinates of the optimized structure of Naph-F4-C1 dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	5.4510725881335143	5.8375247849368908	6.2613030696831498
C	5.9495519185601751	5.9334497433406241	4.9901500125451390
C	6.2188250304305841	4.7927043127741333	4.2156732240867614
C	5.9760370443497006	3.5529897533530472	4.7445688176797907
C	5.4563862800510741	3.4070725948021403	6.0571847223728721
C	5.1789976355151044	2.1249922153189837	6.5990911175267621
C	4.6585431223798484	1.9893902526499980	7.8586229126995493
C	4.3945326924298831	3.1412864298240102	8.6185075908847129
C	4.6414416916534194	4.3962063937588614	8.1316029257936027
C	5.1863141547426395	4.5720776974453816	6.8370220785130105
F	5.1964959236961041	6.9608232048124679	6.9422312208579875
F	6.1676058433662462	7.1495509189069821	4.4719620232357586
H	6.6083352620176470	4.9200691307291873	3.2118240036357291
H	6.1707021864330587	2.6616796465403270	4.1569675430809250
H	5.3784700415624114	1.2484663998898298	5.9912673668216669
H	4.4290607459622215	1.0187009541419585	8.2843687039807659
F	3.8712762955708659	3.0142485882466330	9.8450695723320027
F	4.3455968708186550	5.4545172997568452	8.8959531643237657
C	1.5964336821778708	2.2472730671253900	6.5623473848175502
C	1.0979536376759391	2.1513469632954947	7.8335000473869014
C	0.8286804618050904	3.2920915605555496	8.6079782500637343
C	1.0714690891820322	4.5318069684698976	8.0790840814123381
C	1.5911201444325875	4.6777249418239624	6.7664682377428189
C	1.8685085174269866	5.9598059613597254	6.2245630946402359
C	2.3889635863687895	6.0954092728066156	4.9650316936288847
C	2.6529746379340398	4.9435138051231933	4.2051461738900766
C	2.4060648909188664	3.6885933135239672	4.6920491437498892
C	1.8611920384431679	3.5127206770081854	5.9866296263339009
F	1.8510110299530687	1.1239752890476349	5.8814183559105535
F	0.8798991464546939	0.9352453040802281	8.3516867068864808
H	0.4391621202681065	3.1647237469229905	9.6118470699432468
H	0.8767987304756600	5.4231425247264013	8.6667033204678692
H	1.6690352065882488	6.8363311807101290	6.8323874755314993
H	2.6184451281604151	7.0660990247521536	4.5392864665100126
F	3.1762333915970249	5.0705527876605538	2.9785852582369166
F	2.7019092324638572	2.6302832897795225	3.9276975427933474

ESI Table 16. The atomic coordinates of the optimized structure of Naph-F4-C2 dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	5.4745197579857239	5.8637149969977518	6.3101779616533458
C	5.9754814566061079	5.9870668632948174	5.0454215589964457
C	6.2339167774147839	4.8342757079178567	4.2738928517905785
C	5.9811863015158302	3.5948453068981920	4.7897320116737925
C	5.4610578644229051	3.4335655892505477	6.0951223038928903
C	5.1663527492518311	2.1555169374526568	6.6326971807817552
C	4.6450305571958177	2.0483514678099595	7.8964558176970066
C	4.3959453862492026	3.2037951680037935	8.6745096944533149
C	4.6674577898050833	4.4526052006239398	8.1777689450705981
C	5.2051271467556139	4.5950549510084846	6.8744652659438872
F	5.2152083227734671	6.9677768553843213	7.0196754518259876
F	6.2089926710903933	7.1843111884863555	4.5061902227680530
F	6.7094657088322673	4.9864679911289693	3.0373302196971670
F	6.2147710985353015	2.5137646238348657	4.0361581047457937
H	5.3513447866232005	1.2732904883009284	6.0302255942963816
H	4.4076629887011034	1.0693164549400727	8.3008704323426716
H	3.9752927941859109	3.1020329445906967	9.6696693151002062
H	4.4657176688553717	5.3393172661031789	8.7688449125989454
C	1.5729860945871810	2.2210850734769392	6.5134770020114141
C	1.0720243938260792	2.0977336253130385	7.7782334411166767
C	0.8135892901740719	3.2505250209890484	8.5497618511234261
C	1.0663197438475145	4.4899552494851642	8.0339222674423656
C	1.5864481178420342	4.6512345435277975	6.7285318877232339
C	1.8811532930074277	5.9292830149292612	6.1909566329008401
C	2.4024753605770681	6.0364480340804514	4.9271979026556991
C	2.6515603183458407	4.8810040889335946	4.1491443259684111
C	2.3800479022435725	3.6321942130235225	4.6458854747348513
C	1.8423786355776142	3.4897449324405625	5.9491892424365860
F	1.8322974703458395	1.1170229370212048	5.8039799196186870
F	0.8385133073826555	0.9004894622011816	8.3174651978413792
F	0.3380405512317756	3.0983331722042258	9.7863246121739760
F	0.8327348678104188	5.5710361636718551	8.7874958137234458
H	1.6961617097592787	6.8115096609675305	6.7934280649263012
H	2.6398431372580506	7.0154828766929835	4.5227830056872671
H	3.0722129145254025	4.9827659880727824	3.1539846700515679
H	2.5817880648582587	2.7454819409414775	4.0548098425351045

ESI Table 17. The atomic coordinates of the optimized structure of Naph-F4-T1 dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	-1.4020297396543888	-1.2530226711633419	3.4150592472377235
C	-0.7111411091777434	-0.0152048064311024	3.4305835322283458
C	0.7111413391194755	0.0152057732089329	3.4305836511585901
C	1.3881322416501092	-1.2246677181796248	3.4007980158010529
C	0.7028364180976894	-2.4076168155577462	3.3672301392900068
C	-0.7032359731988524	-2.4311284755621707	3.3801765683262008
C	-1.3881319880278959	1.2246686900904047	3.4007977144965236
C	-0.7028361060408722	2.4076177687153146	3.3672299238631478
C	0.7032362949335500	2.4311294366019496	3.3801763842992578
C	1.4020300002812411	1.2530236044670613	3.4150592999579210
F	-1.3797086599878994	3.5601871535989593	3.2988443729471637
F	1.3797089772467519	-3.5601861994052095	3.2988447800335989
F	-2.7261585435918616	1.2313158207191939	3.3626536344255658
F	2.7261588057828683	-1.2313147975373773	3.3626541484891601
H	-2.4853999903168380	-1.2586466403180137	3.4091777802888572
H	-1.2018533897192030	-3.3930504320905177	3.3487730928481048
H	1.2018536691986192	3.3930514147389932	3.3487730297564302
H	2.4854002501663799	1.2586474933022853	3.4091778192255271
C	-1.2530227063266737	1.4020299133046581	0.0849405659917850
C	-0.0152048662927857	0.7111412445107621	0.0694163545722430
C	0.0152057093830480	-0.7111412000442920	0.0694164177803493
C	-1.2246678017950301	-1.3881320882734218	0.0992020987391237
C	-2.4076168615640188	-0.7028361982508315	0.1327698538330594
C	-2.4311285255972139	0.7032361930620313	0.1198233286839044
C	1.2246685781809470	1.3881321979117769	0.0992021708924008
C	2.4076177019731468	0.7028363952214833	0.1327701757530476
C	2.4311293793869613	-0.7032360026457948	0.1198237045245387
C	1.2530235867784618	-1.4020297850390726	0.0849408262694365
F	3.5601870523185561	1.3797089975064263	0.2011558106114314
F	-3.5601862713130807	-1.3797087019466419	0.2011552682975656
F	1.2313156023345413	2.7261587600288921	0.1373461085583395
F	-1.2313149072413969	-2.7261586440603329	0.1373461472012733
H	-1.2586465657248171	2.4854001614493217	0.0908220170250864
H	-3.3930504933694254	1.2018535872923604	0.1512266594932875
H	3.3930513574952483	-1.2018533917787715	0.1512271082791689
H	1.2586475346123733	-2.4854000374464920	0.0908222488206990

ESI Table 18. The atomic coordinates of the optimized structure of Naph-F4-T2 dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	1.2011142824646615	2.2004368604581455	-1.6953730461885721
C	-0.1203722378421339	1.8692310844742783	-1.7189122952606828
C	-0.5034617974726789	0.5034624245738092	-1.7302784914260598
C	0.5034482278598003	-0.5034314289691652	-1.7302886911177802
C	2.2003940810141267	1.2011729405876235	-1.6953834347768204
C	1.8692105812891382	-0.1203190072831889	-1.7189331357761206
C	-1.8692240792361066	0.1203500299947720	-1.7189182578510618
C	-2.2004074594939520	-1.2011422125850055	-1.6953846251423101
C	-1.2011277377850946	-2.2004061765409575	-1.6953945915399826
C	0.1203586877010814	-1.8692002278023334	-1.7189386384320626
H	-0.8706575092927902	2.6528410465024677	-1.7041420494553789
H	-2.6528461015364830	0.8706226863471939	-1.7041484671480704
F	-3.4779061203017414	-1.5953147495849831	-1.6609935507383877
F	-1.5952790293285191	-3.4779114419665125	-1.6610119368376750
H	0.8706441100987320	-2.6528103597622050	-1.7041859491855920
H	2.6528327500448583	-0.8705918305857694	-1.7041807804552618
F	3.4778929621562602	1.5953450925371031	-1.6609962219610850
F	1.5952656424304033	3.4779417381357796	-1.6609765673348089
C	2.2004276667659823	-1.2011375140067504	1.6953687300375115
C	1.8692219335462303	0.1203488204544018	1.7189205029445731
C	0.5034532446285536	0.5034384005452831	1.7302853217960672
C	-0.5034406201626788	-0.5034716230659165	1.7302815385564287
C	1.2011636788129916	-2.2004172621428242	1.6953654740495743
C	-0.1203283124386844	-1.8692339125120820	1.7189134486987654
C	0.1203407344105220	1.8692007564958546	1.7189377758349011
C	-1.2011514669630858	2.2003842820813984	1.6954025901205125
C	-2.2004153731746969	1.2011045263272053	1.6953988783533358
C	-1.8692093963403653	-0.1203820898189084	1.7189302700194524
H	2.6528320300968606	0.8706341830186303	1.7041622031346091
H	0.8706133614977799	2.6528230175724881	1.7041801057224779
F	-1.5953239850413068	3.4778832637973558	1.6610233551354712
F	-3.4779205448090496	1.5952560569063297	1.6610155100693766
H	-2.6528194110104790	-0.8706674086016502	1.7041657518557116
H	-0.8706011612450755	-2.6528558448847344	1.7041491095191159
F	1.5953358195709053	-3.4779158434421835	1.6609668180156960
F	3.4779326497421312	-1.5952886420037033	1.6609733466386627

ESI Table 19. The atomic coordinates of the optimized structure of Pele-F6-T dimer molecule using ωB97XD functional and 6-31G(d) basis set. The unit of atomic position is in Å.

C	1.3639572706259733	1.8820697495333374	-0.0291098769526770
C	0.6083947097919512	1.9660493960964611	1.1805231228237620
C	1.2644721605609641	2.2809372422593546	2.3590193819281722
H	0.7085357396576800	2.3820903562701856	3.2785861801690284
C	2.6591786802535067	2.4530237423829058	2.4045239830777505
H	3.1317136038513085	2.6878020972007510	3.3524535580363874
C	3.4175446085797820	2.2825219565721691	1.2779557306943647
H	4.4983258771644712	2.3533668897938194	1.3069539736776474
C	2.7792703819230606	1.9913766408268181	0.0511166126046251
C	3.5413816599509831	1.7617093626535281	-1.1160081652557337
C	2.9371375868087353	1.4514436660672589	-2.2966645491565010
C	1.5329757735629996	1.4122505181277398	-2.3715659475300024
C	0.7170381716737776	1.6669955143713966	-1.2892563636497236
C	-0.7533623138569870	1.7027759024579456	-1.3717343541729194
C	-1.4408955214057748	1.7681874746667072	-2.5722837555722622
H	-0.9038163235626279	1.8515173715548257	-3.5043680366031711
C	-2.8445103277079906	1.7053369334550410	-2.6235612815385725
H	-3.3380565388237331	1.7463795609412944	-3.5883683188603923
C	-3.5738767894236987	1.5406551483302657	-1.4778238091768527
H	-4.6524996872188353	1.4385661036893440	-1.5029961520598334
C	-2.9079098728570325	1.4957586111315417	-0.2321124429337622
C	-1.4952055894133838	1.6334168028716416	-0.1533248673899229
C	-0.8356473919131915	1.6755057623713663	1.1177597231098455
C	-1.6086737574379215	1.4112963860203003	2.2296718003124756
C	-2.9983622216115862	1.2018282410626580	2.1624106350823498
C	-3.6320307796247646	1.2694202391267282	0.9584192007103943
F	4.8739360096395439	1.8088484214461624	-1.0515040187975109
F	3.6453447665714651	1.1757076494886072	-3.3883574059453769
F	1.0540193388698940	1.0942870362567445	-3.5787752960952139
F	-1.0959885650170380	1.3230861766080468	3.4617055605142286
F	-3.6639932090629981	0.9331625248179644	3.2821852858695575
F	-4.9514247541207572	1.0757601720373040	0.8976916436933021
C	2.7368313926092176	-2.0256582141942117	-2.5426782551050002
C	-2.5556891312012811	-2.1396437026529465	2.7597927479969546
C	1.3361378407492206	-2.0712203184527502	-2.4278042312567951
C	-1.1632417540473061	-1.9866999323477412	2.6379896650914345
C	-3.3598031702472806	-2.0940909233089950	1.6535853505370115
C	3.5138856797091753	-1.7360856461757443	-1.4543733611959069
C	0.6983918302867247	-1.8625573100296762	-1.2159203506016869
C	-0.5562647822138783	-1.8168626653069428	1.4046786087643059
C	-2.7726384465720568	-1.9553794270505165	0.3755502181668622
C	2.8994443337577303	-1.5407807977601942	-0.1967257474706599
C	-1.3609532375327362	-1.8708462921304134	0.2257466997006434
C	1.4907206701279085	-1.6575717267682530	-0.0448991149572876
C	-0.7677421571016663	-1.8057253124463768	-1.0771917404146745
C	0.8845411613387837	-1.5485575144865653	1.2486697018277231
C	-3.5820840672231471	-1.8363096837333679	-0.7758957286693076
C	3.6747043268657289	-1.1907370935338191	0.9303898907566152
C	1.7047445147627704	-1.1646236172713735	2.2893161288899182
C	-1.6270980481950226	-1.6566819827622412	-2.1448107220391117
C	3.0917627728069741	-0.9801436764053914	2.1431073946301700
C	-3.0270073711322092	-1.6636214655814960	-2.0074991979193824
F	-4.9109453564148344	-1.8478814511189405	-0.6493959046561988
F	4.9921362078116482	-1.0238098402638276	0.7953002923413299
F	1.2440074950124098	-0.9259577045003493	3.5216195152413095
F	3.8037771248390482	-0.5949606283722565	3.1986352009010930
F	-1.1965991843506134	-1.4811374032083136	-3.3987841170280895
F	-3.7777062975657607	-1.4783430252807905	-3.0899994353782039
H	3.1937169612437306	-2.1854823210986214	-3.5134638366936755
H	-2.9897790619555256	-2.2447487795536976	3.7481780733783214
H	0.7578880522177323	-2.2599604452950182	-3.3193960819039958
H	-0.5713633873037531	-1.9807763487186185	3.5404722017258363
H	-4.4391392383826425	-2.1446561299189484	1.7343462538938110
H	4.5912259768575092	-1.6500462941873293	-1.5340526844534821