Supporting Information

For the Article entitled

"The ratio and topology effects of benzodithiophene donor fragment to benzooxadiazole acceptor fragment on the optoelectronic properties of donor molecules toward solar cells materials".

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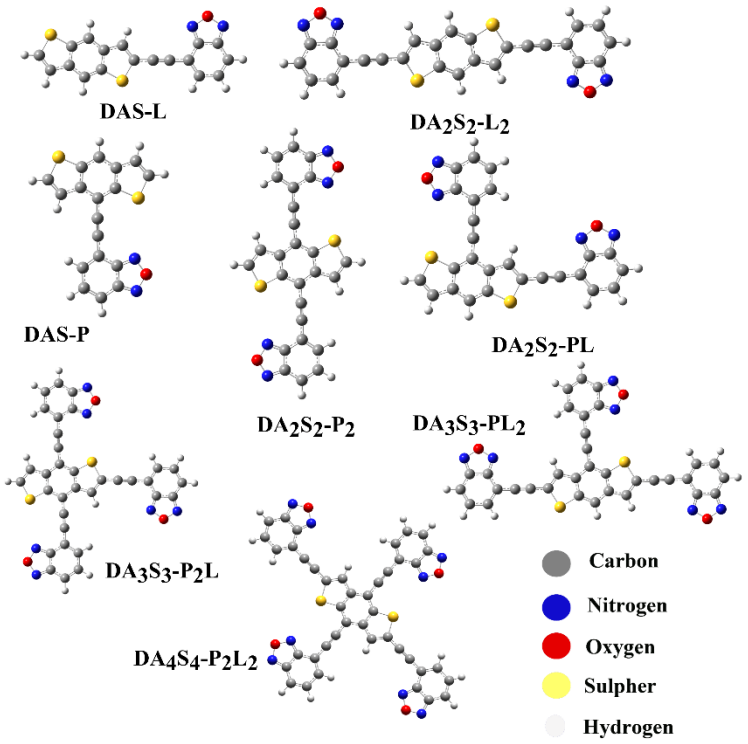


Fig. S1a Optimized geometry structures of the DA_n molecules.

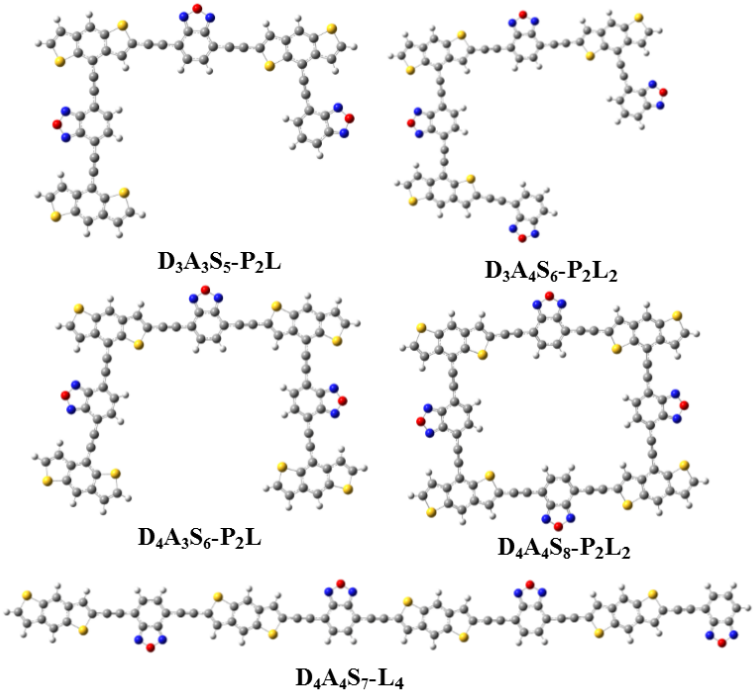


Fig. S1b Optimized geometry structures of the D_3A_n and D_4A_n molecules.

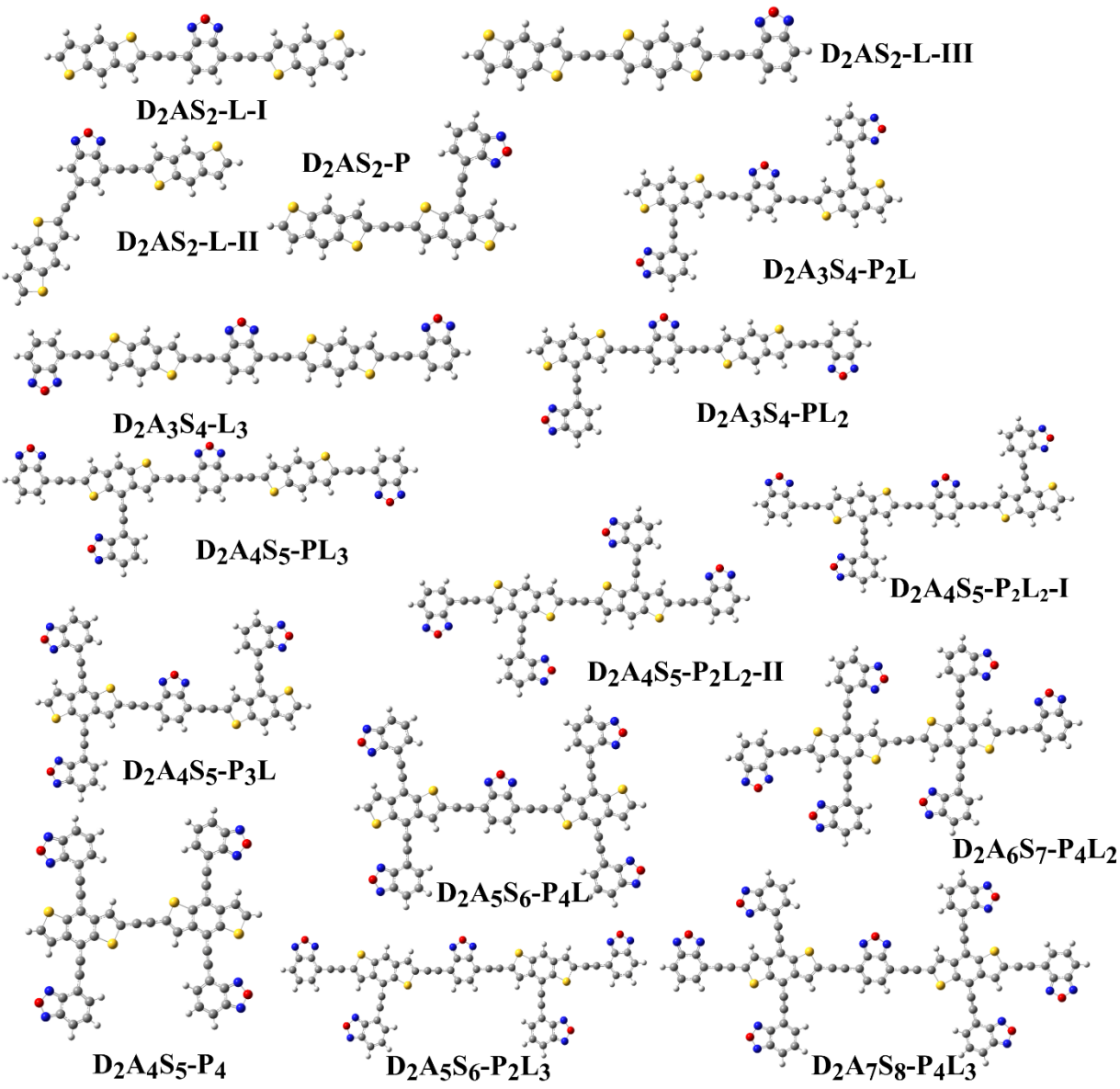


Fig. S1c Optimized geometry structures of the D_2A_n donor molecules.

SII: Frontier Molecular orbital (FMOs) of DA_n Designed Molecules

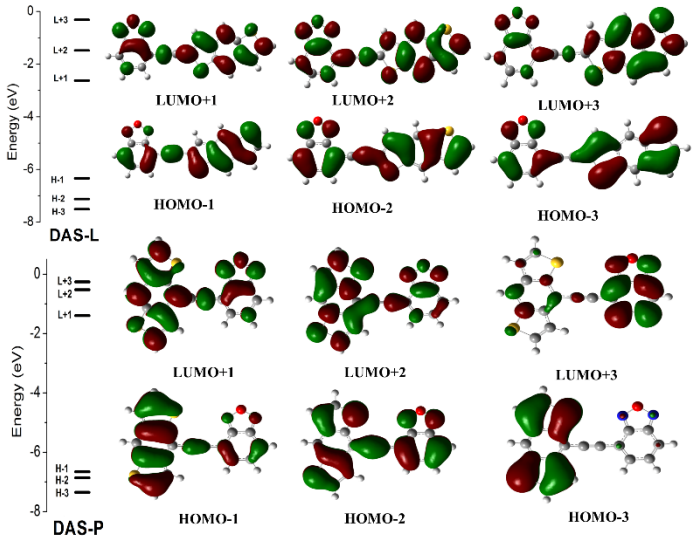


Fig. S2a FMOs energy level diagram for DA group molecules.

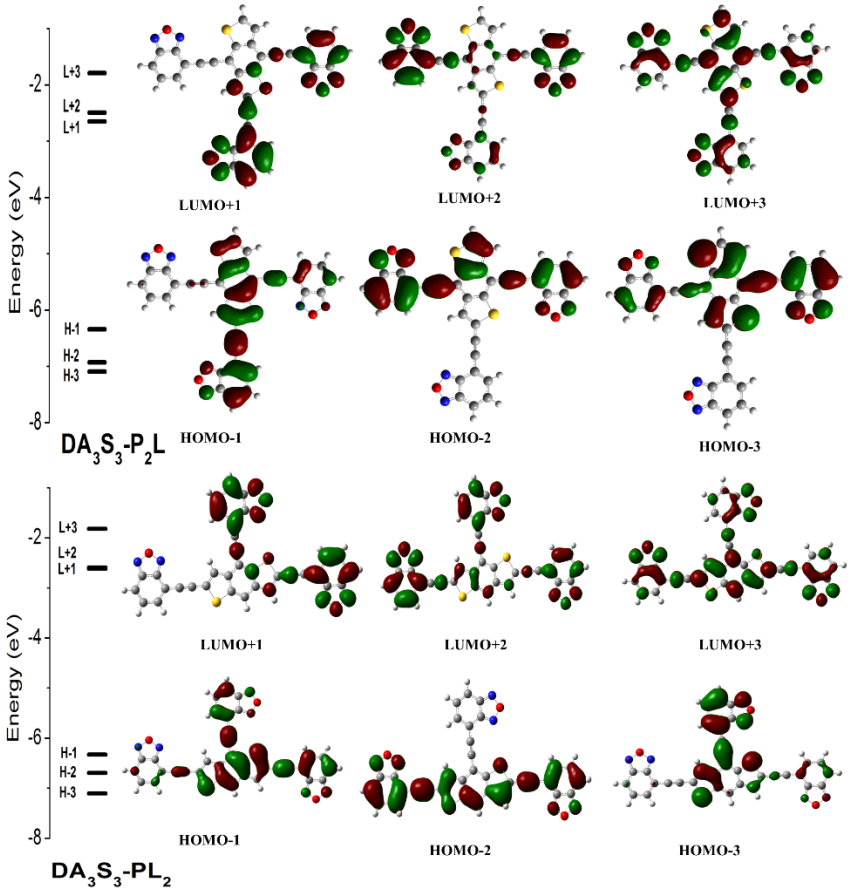


Fig. S2b FMOs energy level diagram for DA_3 group molecules.

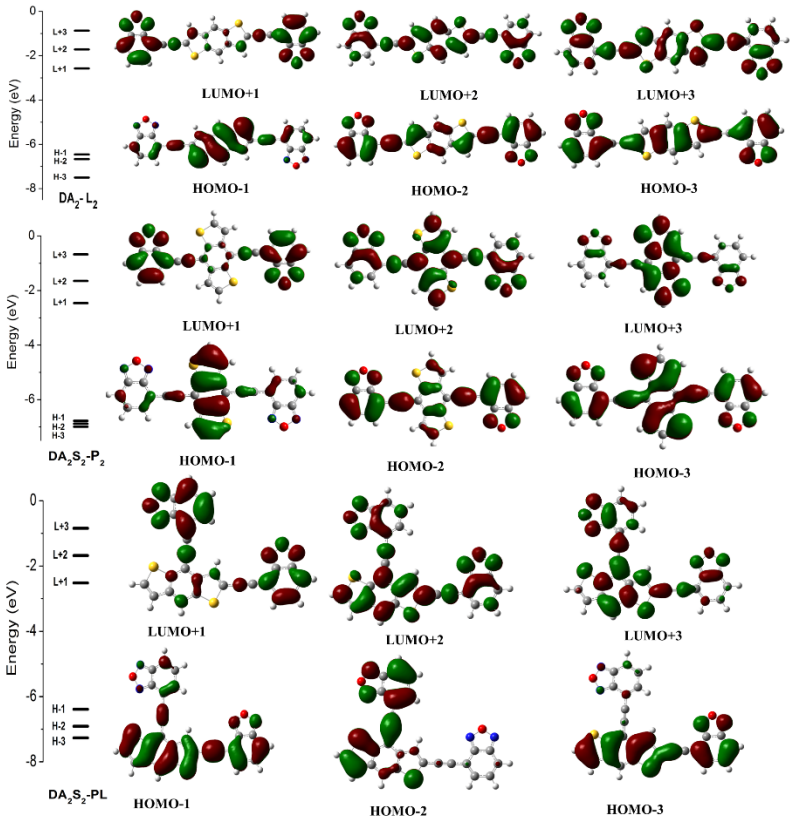


Fig. S2c FMOs energy level diagram for DA_2 group molecules.

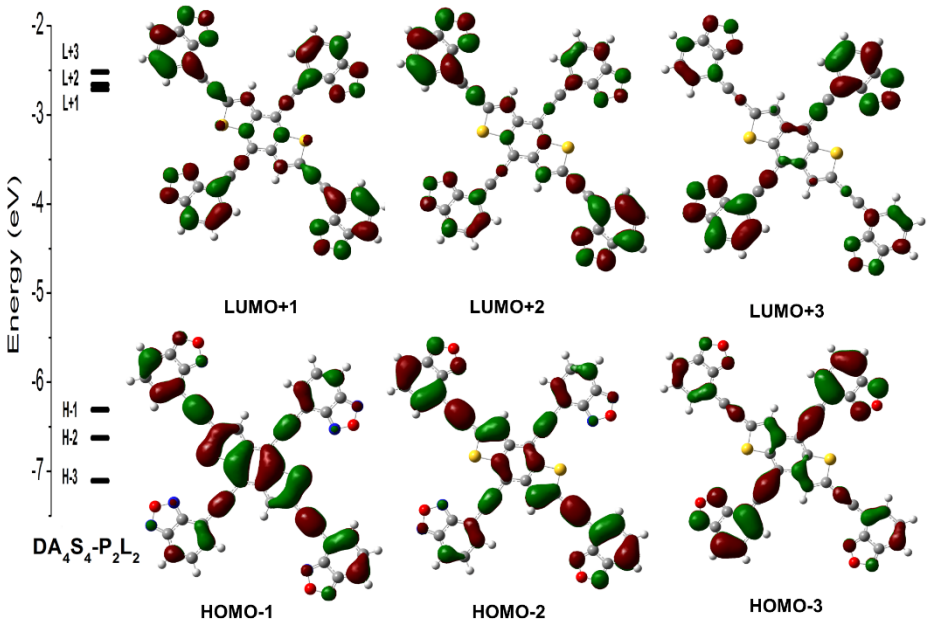


Fig. S2d FMOs energy level diagram for DA_4 group molecules

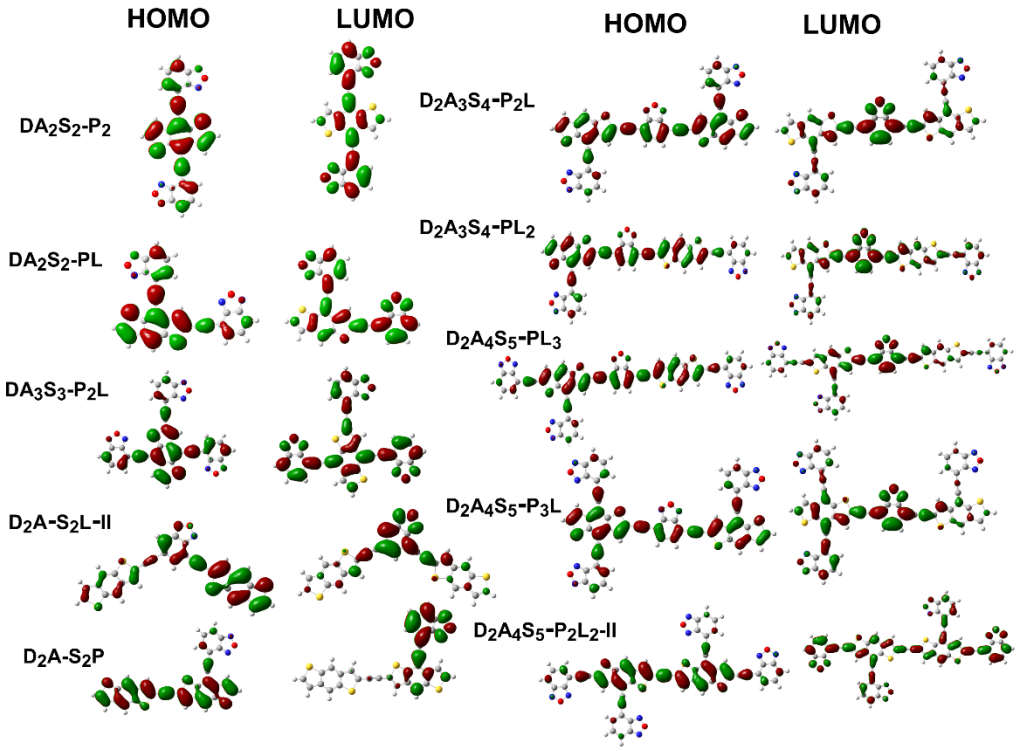


Fig. S2e HOMO and LUMO orbitals of DA_n and D_2A_n molecules.

SIII: Frontier Molecular orbitals (FMOs) of the D_2A_n, D_3A_n and D_4A_n Designed Molecules

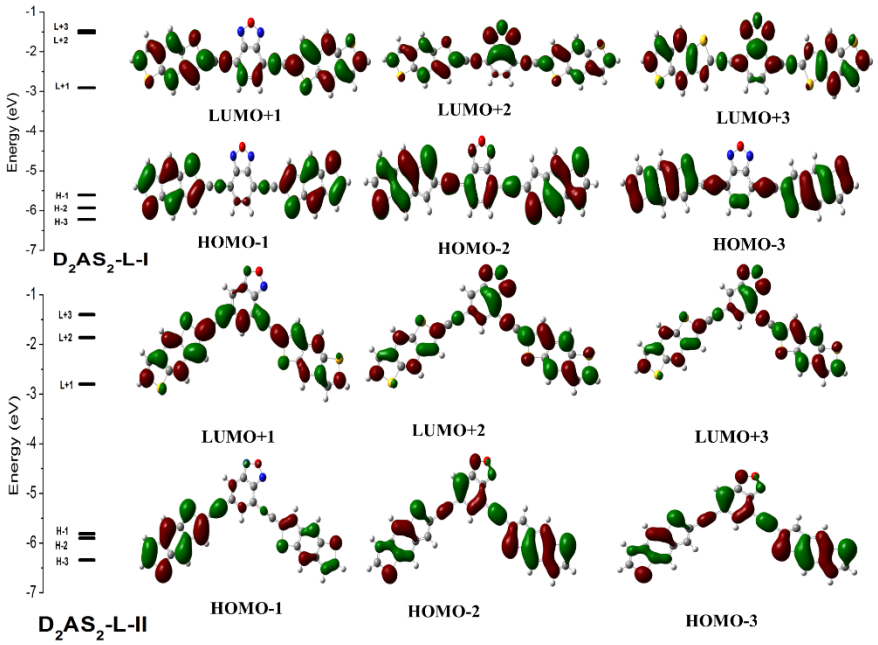


Fig. S3a FMOs energy level diagram for D_2A group molecules.

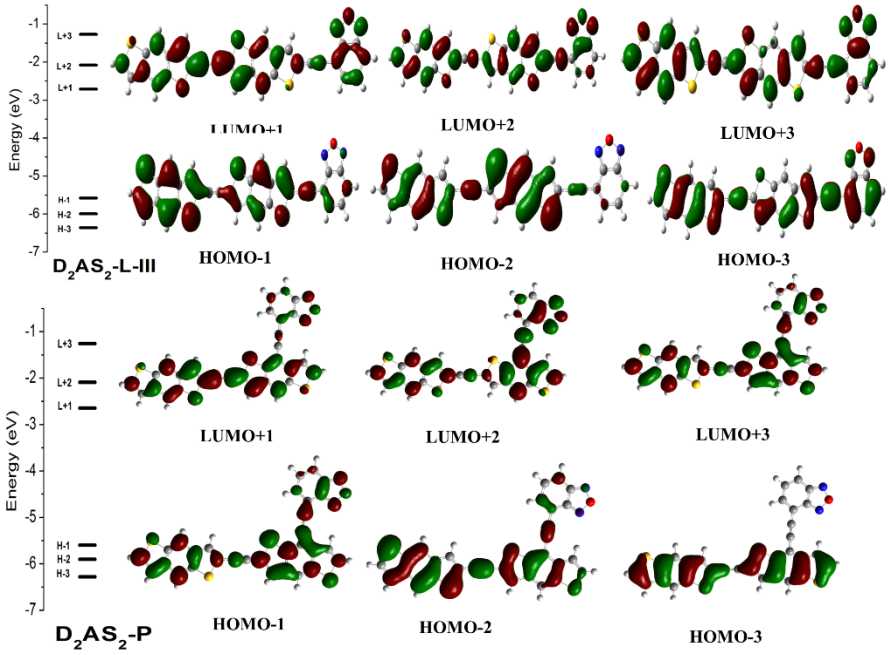


Fig. S3b FMOs energy level diagram for D_2A group molecules.

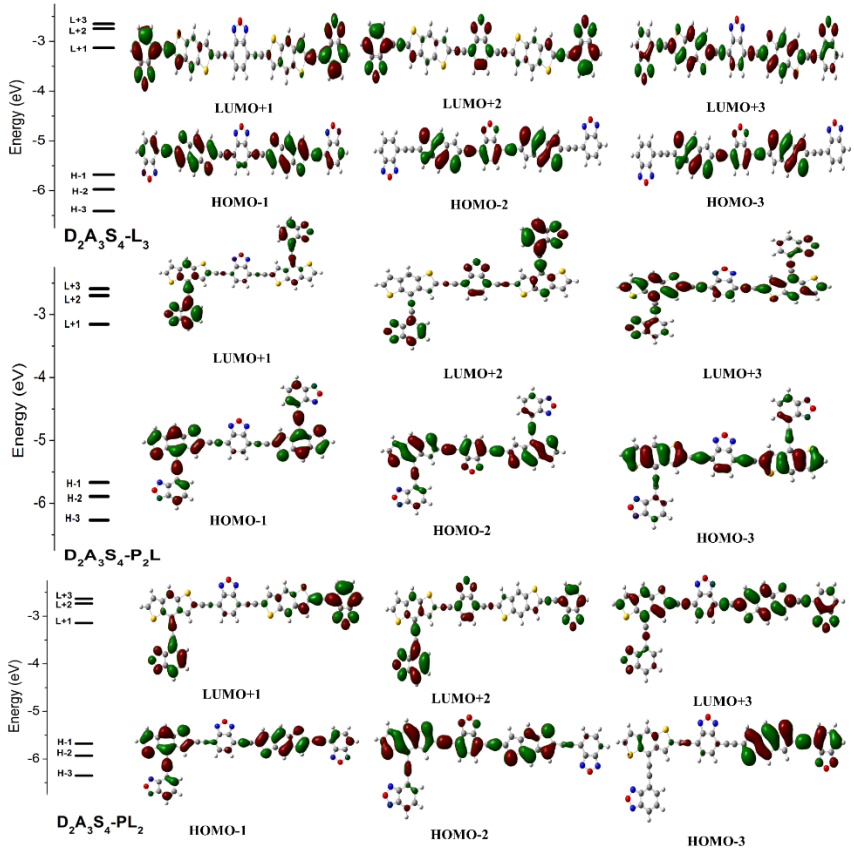


Fig. S3c FMOs energy level diagram for D_2A_3 group molecules.

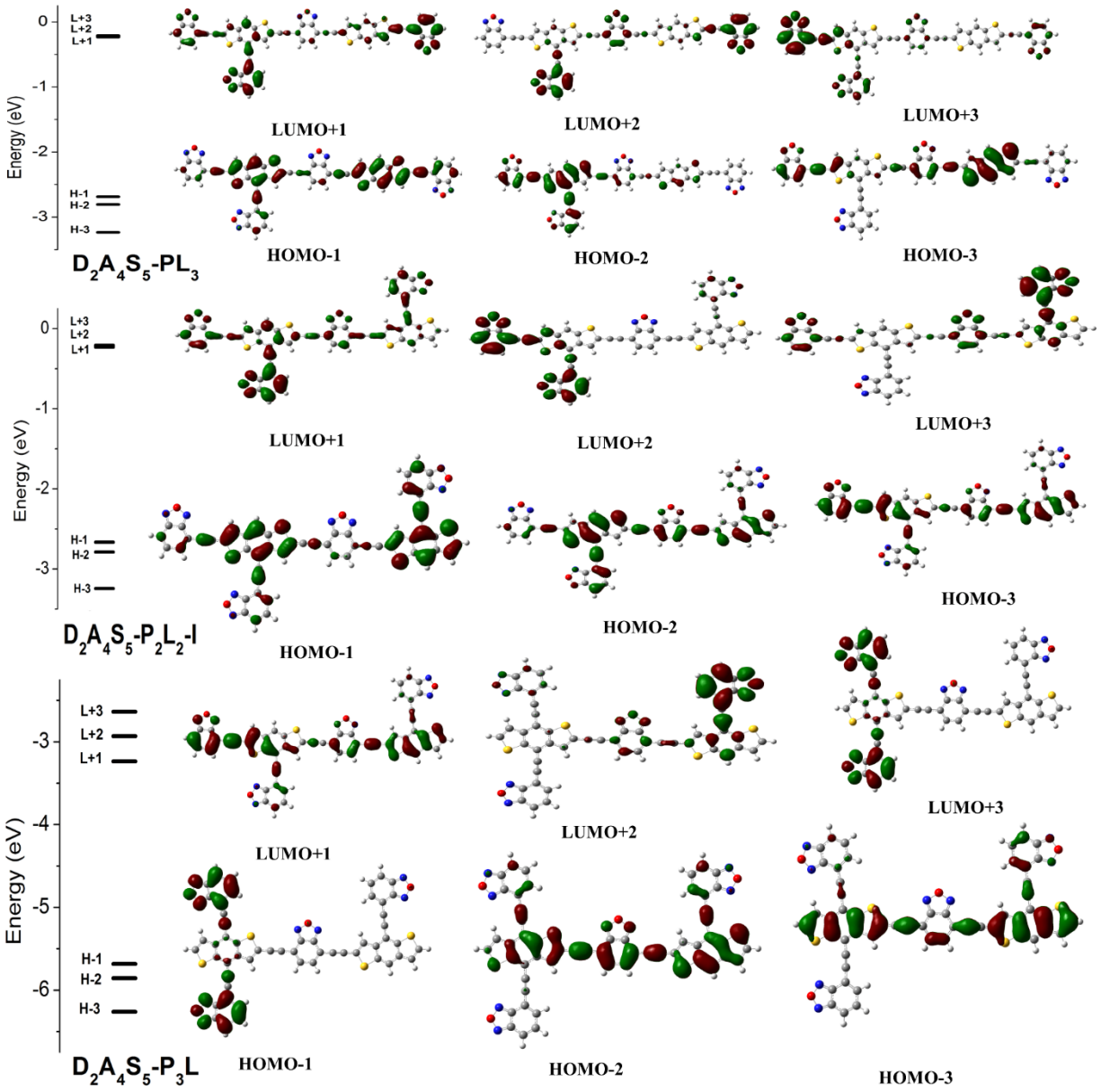


Fig. S3d FMOs energy level diagram for D_2A_4 group molecules.

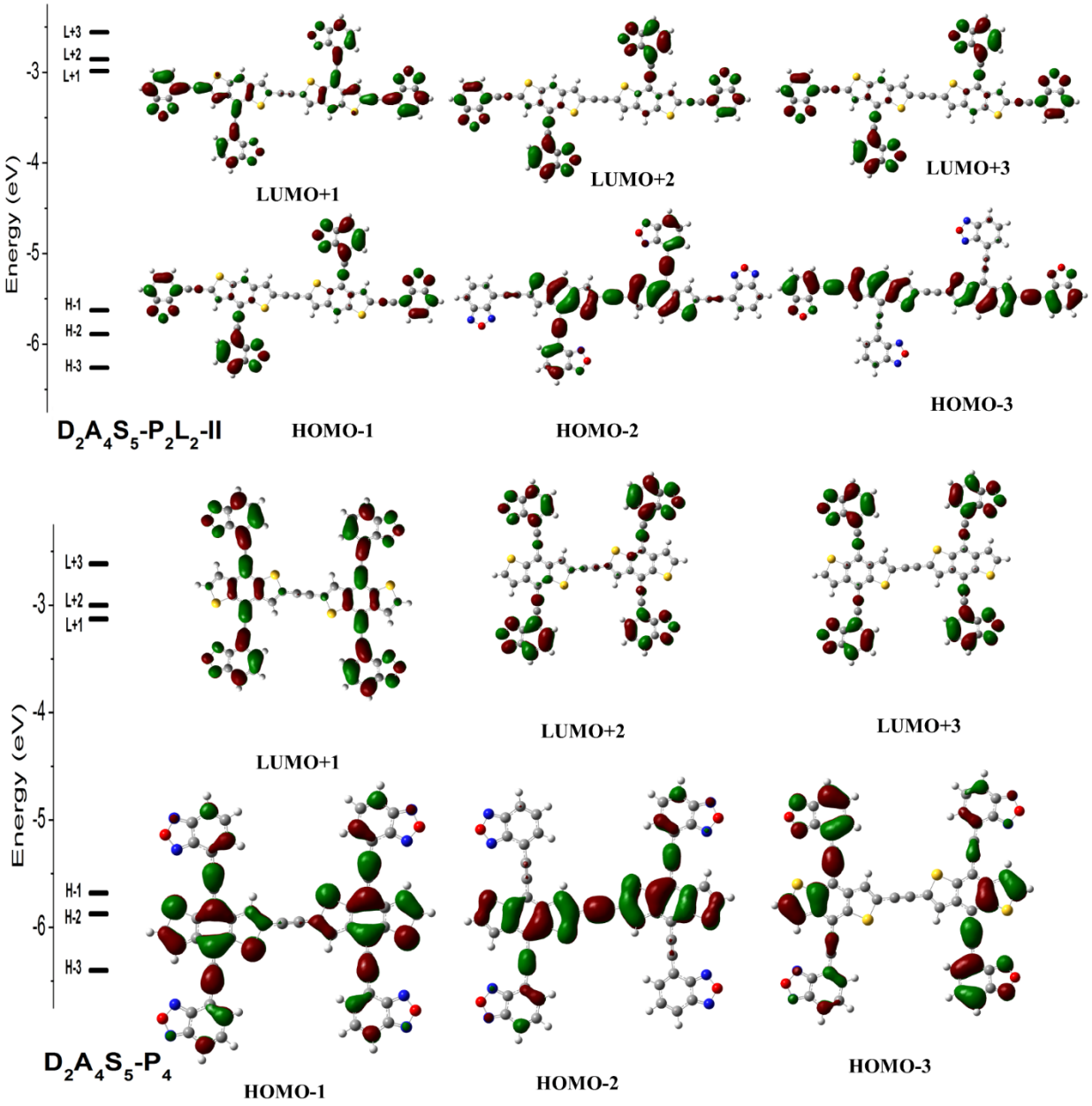


Fig. S3e FMOs energy level diagram for D_2A_4 group molecules.

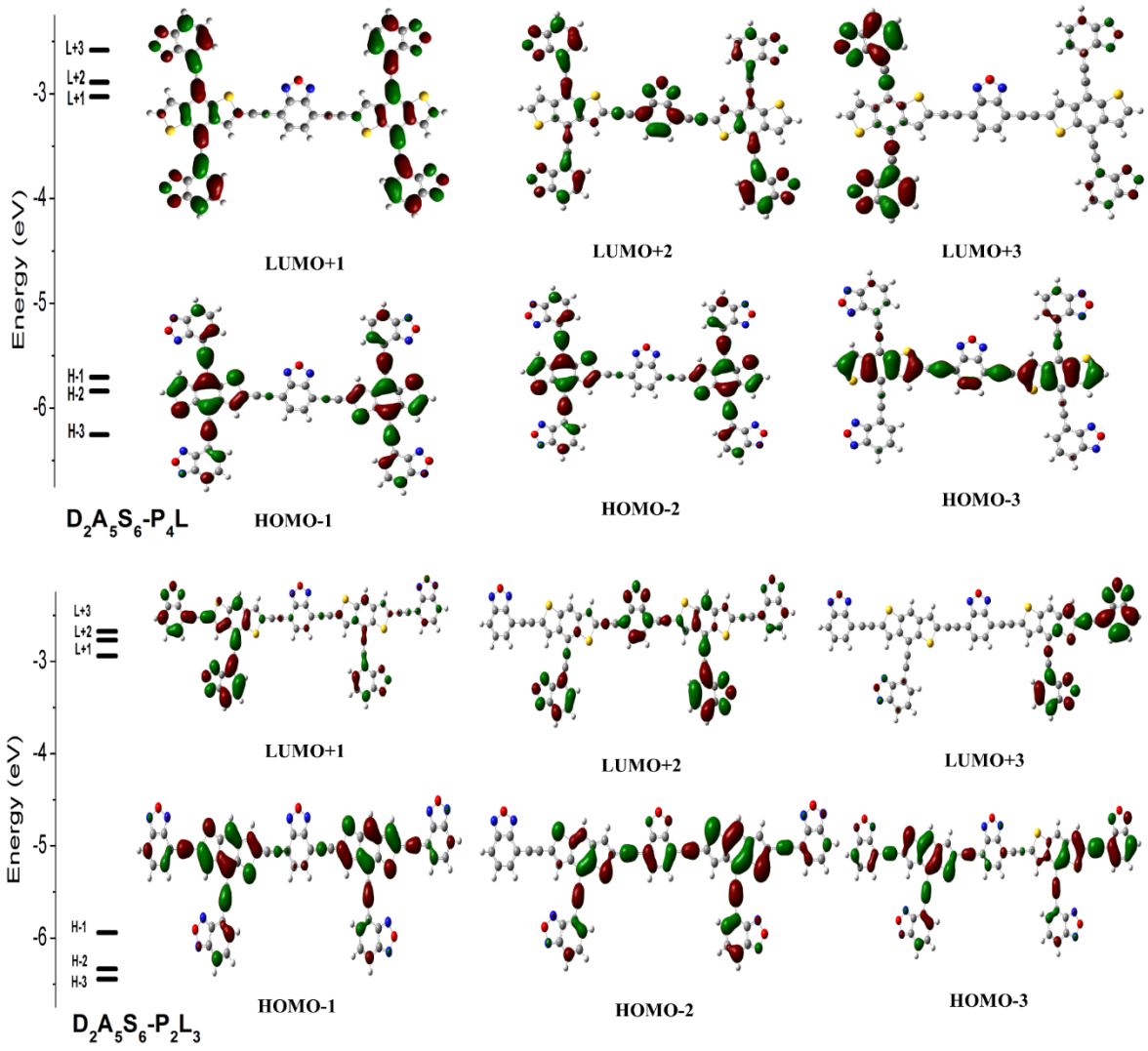


Fig. S3f FMOs energy level diagram for D_2A_5 group molecules.

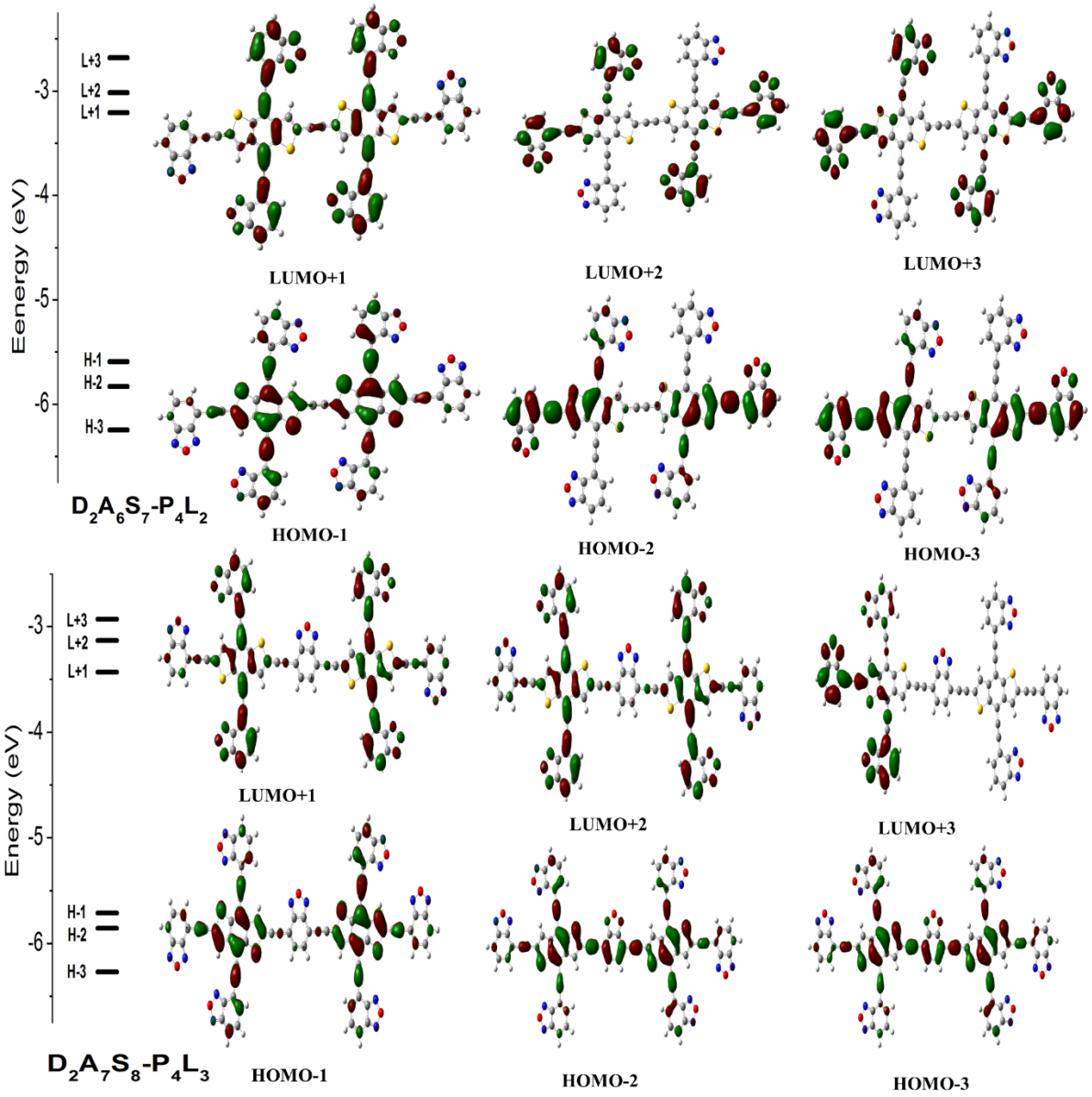


Fig. S3g FMOs energy level diagram for D_2A_6 and D_2A_7 group molecules.

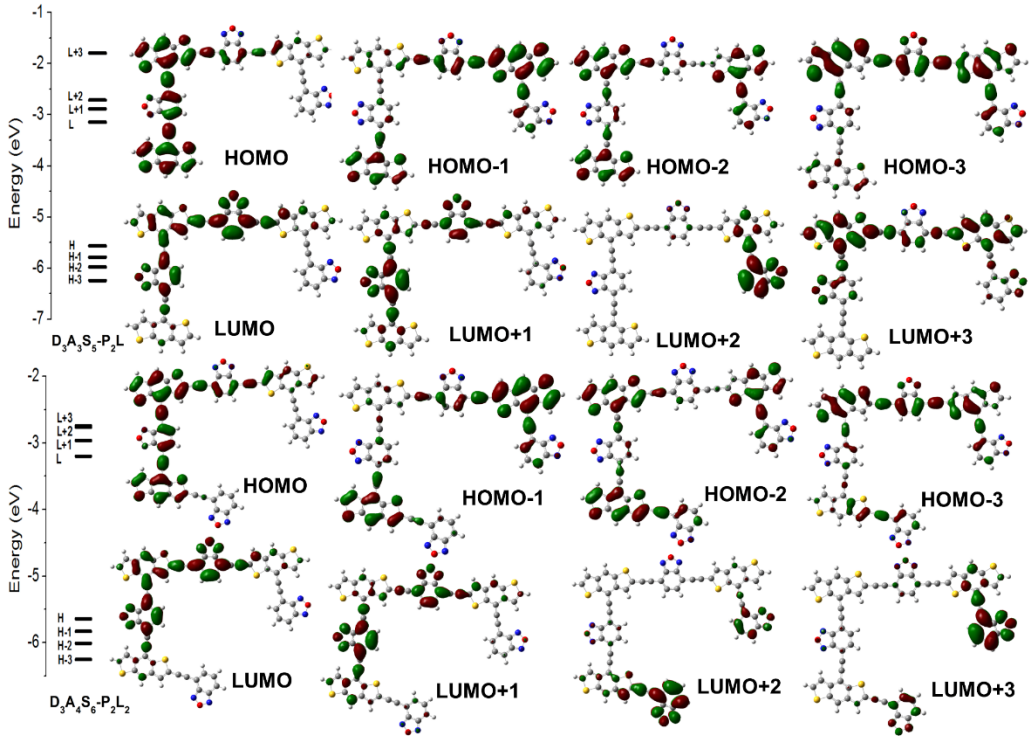


Fig. S3h FMOs energy level diagram for D_3A_n molecules.

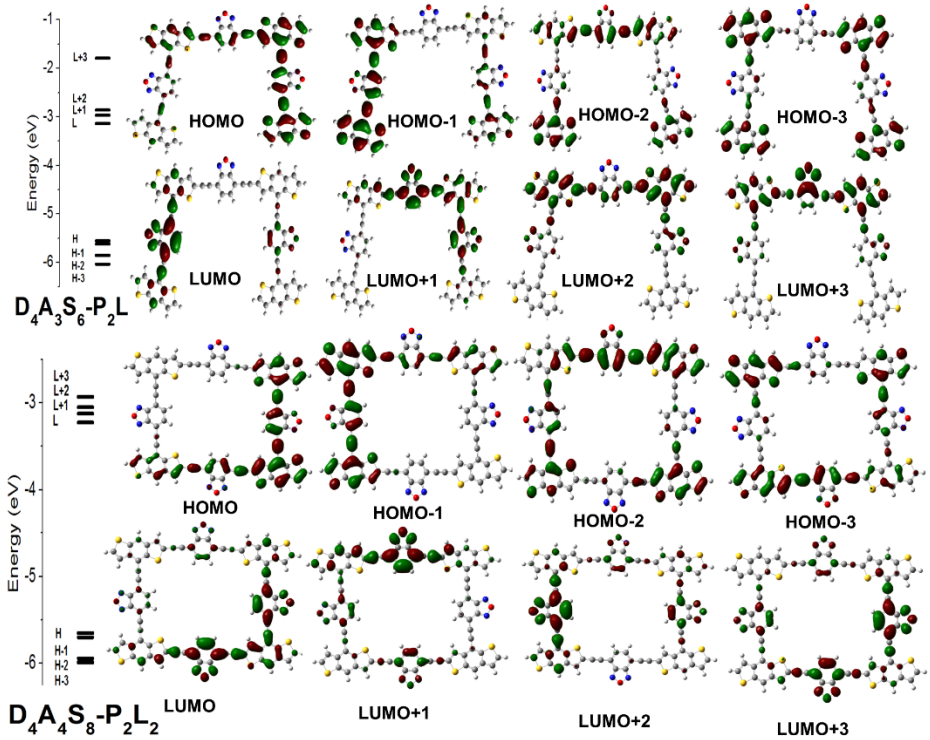


Fig. S3i FMOs energy level diagram for D_4A_n molecules.

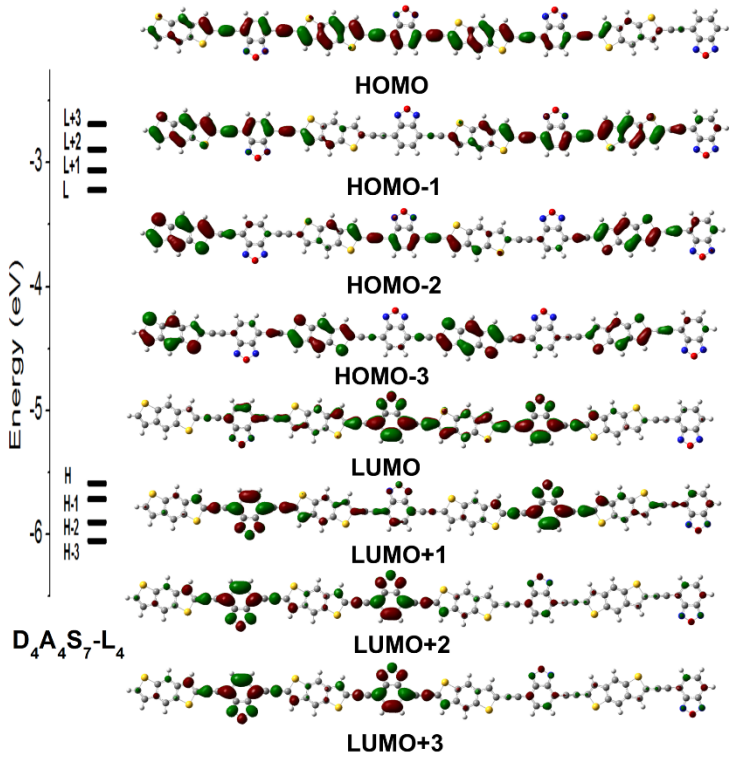


Fig. S3j FMOs energy level diagram for $D_4A_4S_7$-L_4 molecule.

SIV: Absolute Values of The Bond Length

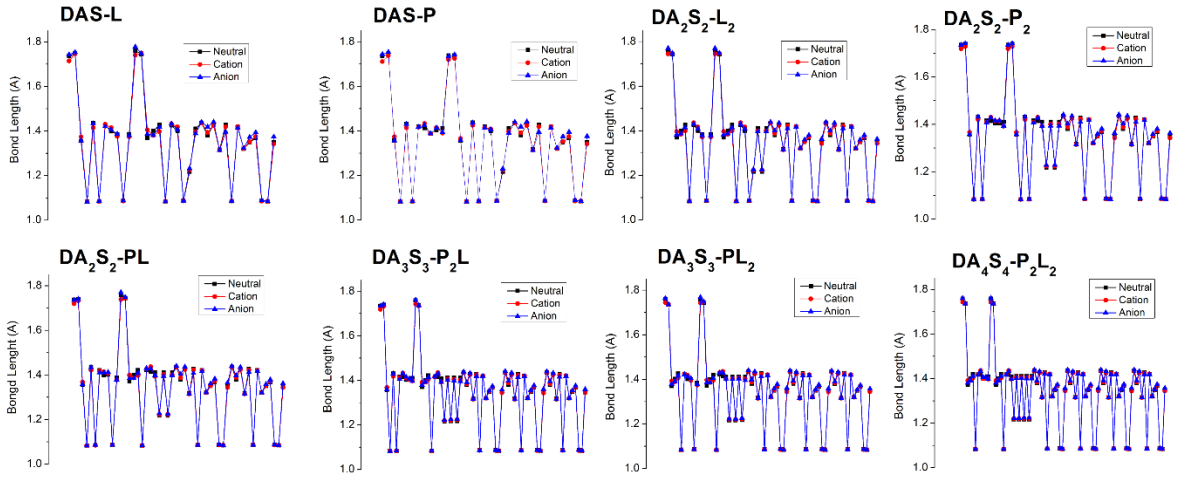


Fig. S4a Absolute values of the bond length differences between the neutral and ionic states for DA_n designe molecules.

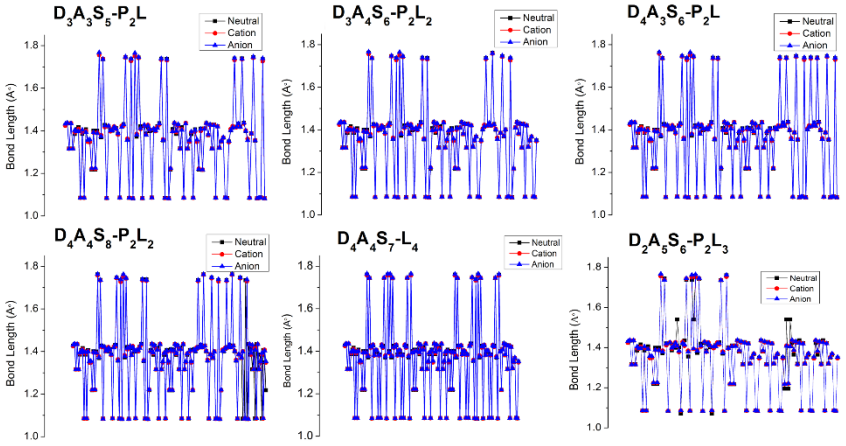


Fig. S4b Absolute values of the bond length differences between the neutral and ionic states for $D_2A_5S_6$-P_2L_3, D_3A_n and D_4A_n designed molecules.

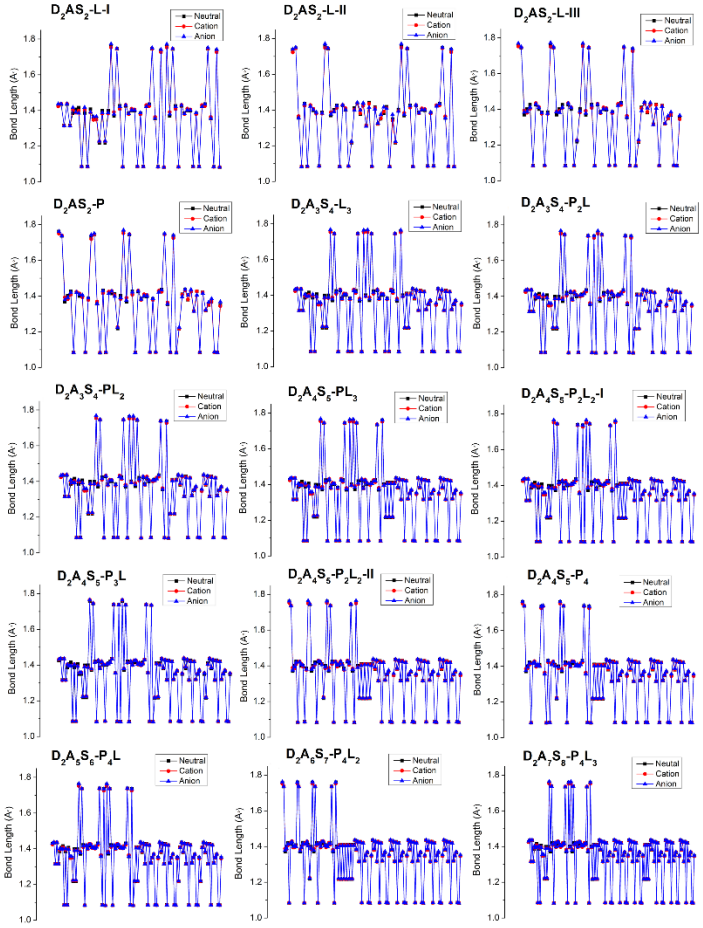


Fig. S4c Absolute values of the bond length differences between the neutral and ionic states for D_2A_n designe molecules.

SV: FMOs Energy Data

Table S1 Calculated energy data (in eV) of the FMOs of the DA_n designed donor molecules. (E_{HOMO} = HOMO energy levels; E_{LUMO} = LUMO energy levels; and Eg = E_{LUMO} - E_{HOMO}).

Name	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg (eV)
DAS-L	-5.80	-2.63	3.17
DAS-P	-5.70	-2.56	3.14
DA_2S_2-L_2	-5.82	-2.85	2.97
DA_2S_2-P_2	-5.66	-2.89	2.77
DA_2S_2-PL	-5.75	-2.83	2.92
DA_3S_3-P_2L	-5.72	-3.03	2.69
DA_3S_3-PL_2	-5.80	-3.00	2.80
DA_4S_4-P_2L_2	-5.75	-3.18	2.57

Name	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg (eV)
D_2AS_2-L-I	-5.61	-2.91	2.7
D_2AS_2-L-II	-5.81	-2.80	3.01
D_2AS_2-L-III	-5.58	-2.71	2.87
D_2AS_2-P	-5.60	-2.65	2.95
$D_2A_3S_4$-L_3	-5.68	-3.13	2.55
$D_2A_3S_4$-P_2L	-5.67	-3.15	2.52
$D_2A_3S_4$-PL_2	-5.68	-3.14	2.54
$D_2A_4S_5$-PL_3	-5.70	-3.23	2.47
$D_2A_4S_5$-P_2L_2-I	-5.69	-3.24	2.45
$D_2A_4S_5$-P_3L	-5.68	-3.24	2.44
$D_2A_4S_5$-P_2L_2-II	-5.63	-2.99	2.64
$D_2A_4S_5$-P_4	-5.68	-3.13	2.55
$D_2A_5S_6$-P_4L	-5.71	-3.30	2.41
$D_2A_5S_6$-P_2L_3	-5.72	-3.29	2.43
$D_2A_6S_7$-P_4L_2	-5.59	-3.21	2.38
$D_2A_7S_8$-P_4L_3	-5.71	-3.43	2.28

Table S2 Calculated energy data (in eV) of the FMOs of the D_2A_n designed donor molecules.

Table S3 Calculated energy data (in eV) of the FMOs of the D_3A_n and D_4A_n designed donor molecules.

Name	HOMO (eV)	LUMO (eV)	Eg (eV)
$D_3A_3S_5$-P_2L	-5.57	-3.14	2.43
$D_3A_4S_6$-P_2L_2	-5.64	-3.20	2.44
$D_4A_3S_6$-P_2L	-5.55	-3.14	2.41
$D_4A_4S_8$-P_2L_2	-5.65	-3.22	2.43
$D_4A_4S_7$-L_4	-5.59	-3.22	2.37

SVI: Total Molecular Energy of the Designed Molecules

Table S4 Total energies of the DA_n investigated molecules in KJ/mol.

Name	Total Energy	Name	Total Energy
DAS-L	-4385626.77	DA_2S_2-PL	-5672352.90
DAS-P	-4385625.80	DA_3S_3-P_2L	-6959079.03
DA_2S_2-L_2	-5672351.93	DA_3S_3-PL_2	-6959079.03
DA_2S_2-P_2	-5672352.90	DA_4S_4-P_2L_2	-8245693.24

Table S5 Total energies of the D_2A_n, D_3A_n and D_4A_n investigated molecules in KJ/mol.

Name	Total Energy	Name	Total Energy	Name	Total Energy
D_2AS_2-L-I	-7681166.38	$D_2A_4S_5$-PL_3	-11541421.00	$D_2A_6S_7$-P_4L_2	-14114940.80
D_2AS_2-L-II	-7681161.56	$D_2A_4S_5$-P_2L_2-I	-11541421.97	$D_2A_7S_8$-P_4L_3	-15401679.48
D_2AS_2-L-III	-7681170.24	$D_2A_4S_5$-P_3L	-11541427.76	$D_3A_3S_5$-P_2L	-13550193.00
D_2AS_2-P	-7681174.10	$D_2A_4S_5$-P_2L_2-II	-11541425.83	$D_3A_4S_6$-P_2L_2	-14836943.25
$D_2A_3S_4$-L_3	-10254669.78	$D_2A_4S_5$-P_4	-11541433.54	$D_4A_3S_6$-P_2L	-16845712.36
$D_2A_3S_4$-P_2L	-10254670.75	$D_2A_5S_6$-P_4L	-12828183.80	$D_4A_4S_8$-P_2L_2	-18329071.69
$D_2A_3S_4$-PL_2	-10254670.75	$D_2A_5S_6$-P_2L_3	-12828176.08	$D_4A_4S_7$-L_4	-16845697.89

SVII: Absorption Properties

Table S6 Calculated excitation energies (Ex), wavelength (λ_{abs}), oscillator strength (*f*), and composition in terms of molecular orbitals with related character (H = HOMO, L = LUMO) for DA_4S_4-P_2L_2, $D_2A_6S_7$-P_4L_2, $D_2A_7S_8$-P_4L_3, $D_3A_4S_6$-P_2L_2, $D_4A_4S_8$-P_2L_2 and $D_4A_4S_7$-L_4.

Donor Name	Transition state	Ex (eV)	λ_{abs} (nm)	*f* (a.u.)	Assignment
DA_4S_4-P_2L_2	S0→S1	2.24	554	0.20	H→L
	S0→S4	2.69	460	1.44	H-1→L
	S0→S7	3.15	394	0.33	H-1→L+1
	S0→S17	3.91	317	0.38	H-1→L+4, H→L+5.
$D_2A_6S_7$-P_4L_2	S0→S1	2.05	605	1.32	H→L
	S0→S5	2.50	495	0.33	H→L+2
	S0→S7	2.61	474	1.64	H-2→L, H→L+2.
$D_2A_7S_8$-P_4L_3	S0→S1	1.93	642	2.27	H→L
	S0→S5	2.43	510	1.88	H-2→L, H-1→L+1
	S0→S15	2.91	426	0.42	H-3→L+3, H-2→L+2.
$D_3A_4S_6$-P_2L_2	S0→S1	2.00	617	1.35	H→L
	S0→S3	2.34	530	0.79	H→L+1, H-1→L
	S0→S6	2.59	479	0.25	H-1→L+1, H→L+3
	S0→S8	2.66	465	0.85	H-3→L, H-2→L+1
	S0→S12	2.86	434	0.16	H-4→L, H-4→L+1
	S0→S21	3.34	371	0.23	H-6→L, H-4→L+2.
$D_4A_4S_8$-P_2L_2	S0→S1	1.97	629	0.37	H→L, H-1→L+1
	S0→S2	2.19	566	1.30	H-1→L+2, H→L
	S0→S4	2.25	549	0.97	H-1→L+1, H→L+1
	S0→S5	2.27	546	0.51	H-1→L+1, H-1→L+2
	S0→S6	2.32	534	0.32	H→L+2, H→L
	S0→S9	2.46	503	1.18	H-2→L+1, H-1→L+2
	S0→S10	2.48	498	0.28	H-3→L , H-2→L+1, H-1→L+2
	S0→S13	2.58	479	0.32	H-2→L+2 , H→L+3
	S0→S16	2.73	454	0.16	H-3→L+3, H-3→L+1
	S0→S18	2.80	443	0.32	H-5→L, H-5→L+1.
$D_4A_4S_7$-L_4	S0→S1	1.96	631	6.36	H→L

S0→S4	2.41	514	0.54	H-1→L+1, H→L+2
S0→S6	2.49	496	0.18	H-1→L+1, H→L
S0→S12	2.78	446	0.50	H-5→L, H-4→L

SVIII: Diploe Moments (μ)

Table S7 Dipole moments values for the all DA_n, D_2A_n, D_3A_n and D_4A_n investigated molecules.

Name	**μ (Debye)**	**Name**	**μ (Debye)**
DAS-L	3.94	$D_2A_4S_5$-PL_3	4.86
DAS-P	3.67	$D_2A_4S_5$-P_2L_2-I	7.48
DA_2S_2-L_2	0.41	$D_2A_4S_5$-P_3L	5.47
DA_2S_2-P_2	0.10	$D_2A_4S_5$-P_2L_2-II	0.53
DA_2S_2-PL	5.17	$D_2A_4S_5$-P_4	0.72
DA_3S_3-P_2L	3.72	$D_2A_5S_6$-P_4L	3.65
DA_3S_3-PL_2	3.64	$D_2A_5S_6$-P_2L_3	11.36
DA_4S_4-P_2L_2	0.20	$D_2A_6S_7$-P_4L_2	0.52
D_2AS_2-L-I	3.62	$D_2A_7S_8$-P_4L_3	3.83
D_2AS_2-L-II	4.97	$D_3A_3S_5$-P_2L	3.83
D_2AS_2-L-III	4.03	$D_3A_4S_6$-P_2L_2	3.90
D_2AS_2-P	4.10	$D_4A_3S_6$-P_2L	5.04
$D_2A_3S_4$-L_3	3.47	$D_4A_4S_8$-P_2L_2	5.81
$D_2A_3S_4$-P_2L	3.51	$D_4A_4S_7$-L_4	1.42
$D_2A_3S_4$-PL_2	3.09		

Dipole moments (μ) of all designed molecules are summarized in supporting information. We made a comparison of μ values with optical properties i.e., the largest intensity of absorption and λ_{max} wavelength for all designed molecules. Among the DA_n, D_2A_n, D_3A_n and D_4A_n molecules, almost all the molecules show inverse relation of μ values with respect to the largest intensity of absorptions, while few exception have also been observed in the case of $D_2A_5S_6$-P_4L, $D_2A_5S_6$-P_2L_3, $D_2A_6S_7$-P_4L_2, $D_2A_7S_8$-P_4L_3 molecules and DA_3 group as μ values are directly proportional to largest intensity of absorption because of different shapes. The order of intensity and μ trends for DA_n molecules are of DA_4S_4-P_2L_2> DA_2S_2-L_2> DA_3S_3-PL_2> DA_2S_2-P_2> DA_3S_3-P_2L > DA_2S_2-PL> DAS-P > DAS-L and DA_2S_2-PL>DA-L> DA_3S_3-P_2L> DAS-P > DA_3S_3-PL_2> DA_2S_2-L_2 > DA_4S_4-P_2L_2 > DA_2S_2-P_2 respectively. The comparative analysis of dipole moment with respect to λ_{max} has shown that like intensity, majority of our designed molecules display inverse relation.

Among DA_n, D_2A_n, D_3A_n and D_4A_n molecules, only some molecules like $D_2A_6S_7$-P_4L_2, $D_2A_7S_8$-P_4L_3 and all members of D_2A_4 group demonstrate direct relation with respect to λ_{max}.

SIX: Molecular Orbital Compositions (in percentage)

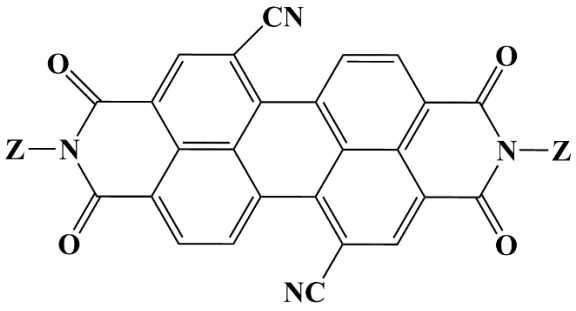
Table S8 Molecular orbital composition in percentage from π-spacer and donor-acceptor fragments DA_n, D_2A_n, D_3A_n and D_4A_n designed donor molecules.

Molecule	Energy Level	Acceptor Fragments	π-spacer	Donor Fragments
DAS-L	HOMO	11	9	**80**
	LUMO	**80**	8	12
DAS-P	HOMO	12	11	**77**
	LUMO	**80**	8	12
DA_2S_2-L_2	HOMO	19	17	64
	LUMO	**68**	11	**21**
DA_2S_2-P_2	HOMO	20	18	**62**
	LUMO	**69**	13	18
DA_2S_2-PL	HOMO	18	16	**66**
	LUMO	**69**	11	10
DA_3S_3-P_2L	HOMO	22	20	**58**
	LUMO	**63**	14	23
DA_3S_3-PL_2	HOMO	21	19	**60**
	LUMO	62	13	25
DA_4S_4-P_2L_2	HOMO	25	22	**53**
	LUMO	**57**	16	27

Molecule	Energy Level	Acceptor Fragments	Ethyne (π-spacer)	Donor Fragments
D_2AS_2-L-I	HOMO	17	18	**65**
	LUMO	**62**	15	23
D_2AS_2-L-II	HOMO	14	10	**76**
	LUMO	**71**	11	18
D_2AS_2-L-III	HOMO	5	15	**80**
	LUMO	**68**	10	22
D_2AS_2-P	HOMO	3	13	**84**
	LUMO	**77**	8	15
$D_2A_3S_4$-L_3	HOMO	21	22	**57**
	LUMO	**58**	16	26
$D_2A_3S_4$-P_2L	HOMO	19	20	**61**
	LUMO	**59**	16	25
$D_2A_3S_4$-PL_2	HOMO	20	21	**59**

	LUMO	**59**	16	25
$D_2A_4S_5$-PL_3	HOMO	22	22	**56**
	LUMO	**57**	17	26
$D_2A_4S_5$-P_2L_2-I	HOMO	22	22	**56**
	LUMO	**57**	17	26
$D_2A_4S_5$-P_3L	HOMO	22	22	**56**
	LUMO	**57**	17	26
$D_2A_4S_5$-P_2L_2-II	HOMO	16	15	**69**
	LUMO	**58**	10	32
$D_2A_4S_5$-P_4	HOMO	15	20	**65**
	LUMO	**56**	15	29
$D_2A_5S_6$-P_4L	HOMO	22	22	**56**
	LUMO	**56**	17	27
$D_2A_5S_6$-P_2L_3	HOMO	22	23	**55**
	LUMO	**55**	17	28
$D_2A_6S_7$-P_4L_2	HOMO	17	23	**60**
	LUMO	**50**	17	33
$D_2A_7S_8$-P_4L_3	HOMO	25	24	**51**
	LUMO	**53**	19	28
$D_3A_3S_5$-P_2L	HOMO	17	20	**63**
	LUMO	**59**	16	25
$D_3A_4S_6$-P_2L_2	HOMO	18	20	**62**
	LUMO	**58**	16	26
$D_4A_3S_6$-P_2L	HOMO	17	19	**64**
	LUMO	**57**	17	26
$D_4A_4S_8$-P_2L_2	HOMO	18	20	**62**
	LUMO	**56**	16	28
$D_4A_4S_7$-L_4	HOMO	20	23	**57**
	LUMO	**56**	17	27

SX: Chemical Structure of PDIs



PDI1 = -$(CH_2)_7$ CH_3

PDI9 = -$CH(n\text{-}C_8H_{17})_2$

Fig. S6 Chemical structures of the PDIs.

Table S9 The Calculated energy data (in eV) of the FMOs of the PDI1 and PDI9 acceptor molecules.

Name	HOMO (eV)	LUMO (eV)	Eg (eV)
PDI1	-6.75	-4.00	2.75
PDI9	-6.76	-3.97	2.79

SXI: Absorption spectrum

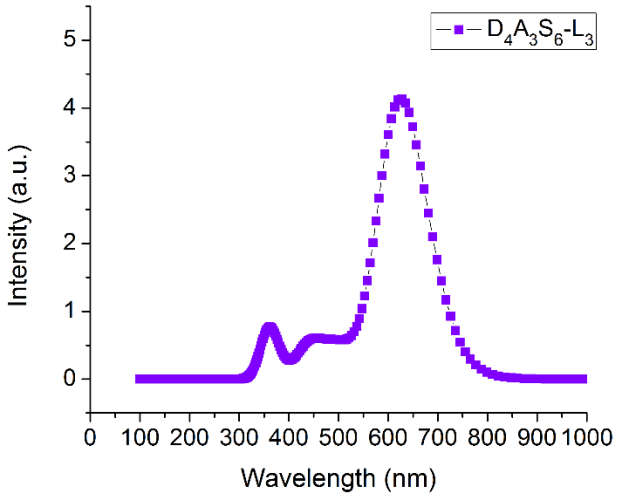


Fig. S6 Absorption spectrum of $D_4A_3S_6$-L molecule.

SXII: Reorganization Energy Values

Table S10 Electron (λ_e) and hole (λ_h) reorganization energy values for DA_n, D_2A_n, D_3A_n and D_4A_n designed molecules.

Name	λ_e (eV)	λ_h (eV)	Name	λ_e (eV)	λ_h (eV)
DAS-L	0.258	0.214	$D_2A_4S_5$-PL_3	0.142	0.142
DAS-P	0.258	0.137	$D_2A_4S_5$-P_2L_2-I	0.157	0.136
DA_2S_2-L_2	0.170	0.201	$D_2A_4S_5$-P_3L	0.135	0.113
DA_2S_2-P_2	0.203	0.128	$D_2A_4S_5$-P_2L_2-II	0.101	0.151
DA_2S_2-PL	0.169	0.160	$D_2A_4S_5$-P_4	0.103	0.133
DA_3S_3-P_2L	0.158	0.130	$D_2A_5S_6$-P_4L	0.111	0.100
DA_3S_3-PL_2	0.152	0.168	$D_2A_5S_6$-P_2L_3	0.131	0.134
DA_4S_4-P_2L_2	0.134	0.133	$D_2A_6S_7$-P_4L_2	0.102	0.149
D_2AS_2-L-I	0.213	0.191	$D_2A_4S_5$-PL_3	0.117	0.111
D_2AS_2-L-II	0.211	0.112	$D_3A_3S_5$-P_2L	0.125	0.111
D_2AS_2-L-III	0.194	0.193	$D_3A_4S_6$-P_2L_2	0.111	0.106
D_2AS_2-P	0.151	0.189	$D_4A_3S_6$-P_2L	0.108	0.104
$D_2A_3S_4$-L_3	0.134	0.151	$D_4A_4S_8$-P_2L_2	0.100	0.101
$D_2A_3S_4$-P_2L	0.161	0.140	$D_4A_4S_7$-L_4	0.114	0.115
$D_2A_3S_4$-PL_2	0.145	0.148			

SXIII: Long Range Functional Comparison

Table S11 Calculated excitation energies (Ex), wavelength (λ_{abs}) and oscillator strength (f) based on TDDFT at the different levels of theory.

Method	DA_4S_4-P_2L_2		$D_2A_5S_6$-P_4L		$D_2A_5S_6$-P_2L_3	
	λ_{max} (nm)	f (a.u.)	λ_{max} (nm)	f (a.u.)	λ_{max} (nm)	f (a.u.)
TD-PBE0/6-31G(d)	554	0.92	607	1.35	603	2.84
TD-WB97XD/6-31G(d)	428	1.31	444	2.17	443	3.68
TD-CAM-B3LYP/6-31G(d)	440	1.24	459	2.12	460	3.55

The End