Supporting Information

X-Shaped Donor Molecules Based on Benzo[2,1-b:3,4-b´]dithiophene for Organic Solar Cells Devices with PDIs as Acceptors.

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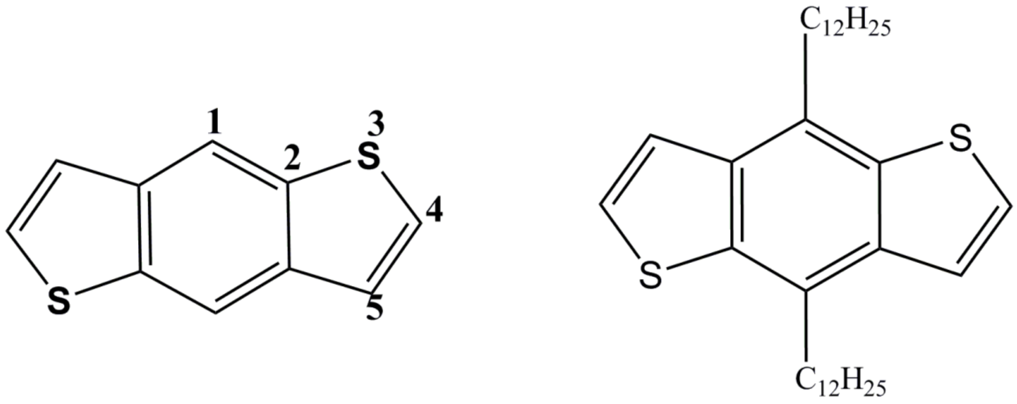
SI: Method Selection

For a proper method selection we did ground state and absorption calculation as following:



(A) (B)

Scheme S1: Molecular structure of (A) 4,8-didodecylbenzo[1,2-b:4,5-b]-dithiophene, of (B). Benzo[1,2-b′:4,5-b]-dithiophene (BDT).

Table S1: Selected optimized geometrical parameters of BDT by using five methods i.e.

PBE0/6-31G(d), B3LYP/6-31G(d), B3P86/6-31G(d), WB986/6-31G(d) and CAM-B3LYP/6-31G(d) .

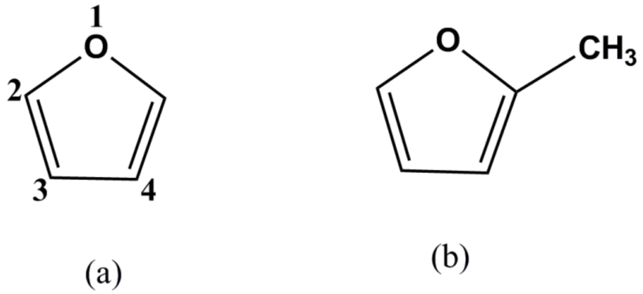
	PBE0	**B3LYP**	**B3P86**	**WB97XD**	**CAM-B3LYP**	**Exp.**[a]
C1-C2/Å	1.387	1.390	1.387	1.387	1.385	1.394
C2-S3/ Å	1.747	1.751	1.750	1.751	1.752	1.716
S3-C4/ Å	1.738	1.744	1.741	1.744	1.744	1.730
C1-C2-S3/°	126.8	126.8	126.8	126.8	126.8	127.8
C2-S3-C4/°	91.1	91.8	91.1	91.1	91.9	90.5

a reference [1]

Table S2: Calculated wavelength (λ_{abs}), and oscillator strength (*f*) of 4,8-didodecylbenzo[1,2-b′:4,5-b]-dithiophene calculated by Various methods .

Method	**λ_{abs} (nm)**	***f***
TD-PBE0/6-31G(d)	333	(0.22)
TD-B3LYP/6-31G(d)	345	(0.18)
TD-B3P86/6-31G(d)	319	(0.20)
TD-WB97XD/6-31G(d)	290	(0.25)
TD-CAM-B3LYP/6-31G(d)	290	(0.25)
EXP[b]	347	

b reference [2]



Scheme S2: Molecular structure of (a) Furan, of (b) methyl-furan.

Table S3: Selected optimized geometrical parameters of furan by using five methods i.e. PBE0/6-31G (d), B3LYP/6-31G (d), B3P86/6-31G(d), WB986/6-31G(d), and CAM-B3LYP/6-31G(d) .

	PBE0	**B3LYP**	**B3P86**	**WB97XD**	**CAM-B3LYP**	**EXP.[c]**
O1-C2/ Å	1.355	1.365	1.358	1.356	1.358	1.362
C2-C3/ Å	1.359	1.361	1.360	1.357	1.355	1.361
C3-C4/ Å	1.424	1.429	1.425	1.429	1.428	1.431
C2-O1-C5/ °	107.0	106.8	106.9	106.9	106.9	106.7
O1-C2-C3/ °	110.6	110.6	110.6	110.6	110.5	110.7

c reference [3]

Table S4: Calculated wavelength (λ_{abs}), and oscillator strength (*f*) Methyl-furan calculated by various methods.

Method	**λ_{abs} (nm)**	***f***
TD-PBE0/6-31G(d)	210	0.15
TD-B3LYP/6-31G(d)	230	0.15
TD-B3P86/6-31G(d)	200	0.14
TD-WB97XD/6-31G(d)	187	0.15
TD-CAM-B3LYP/6-31G(d)	187	0.15
EXP[d]	225	

d is Reference [4]

On the basis of geometrical parameters and absorption wavelength (λ_{max}) for BDT and furan (pi-spacer unit) with experimental one, we found that B3LYP functional is the best one for the calculations of our designed molecule. The difference in bond length for BDT and furan is less than 1Å (not more than 0.045 Å for BDT and 0.003Å for furan).

SII: FMOs of the building blocks

Table S5: Calculated energy data of the frontier molecular orbitals of DF, $B1_2$-DF -$B2_2$, and the 7As (A1-A7) (Eg is the difference of energy between HOMO and LUMO energy levels).

No.	**Name**	**HOMO (eV)**	**LUMO (eV)**	**Eg (eV)**
1	DF	-5.47	-1.08	4.39
2	$B1_2$-DF-$B2_2$	-4.55	-2.28	2.27
3	A7	-6.83	-1.42	5.41
4	A6	-6.7	-1.93	4.77
5	A5	-6.86	-2.44	4.62
6	A4	-6.99	-2.73	4.26
7	A3	-7.4	-2.97	4.43
8	A2	-7.5	-3.0	4.50
9	A1	-8.13	-3.94	4.19

SIII: Optimized structure and FMOs of $B1_2$ –DF–$B2_2$ fragment

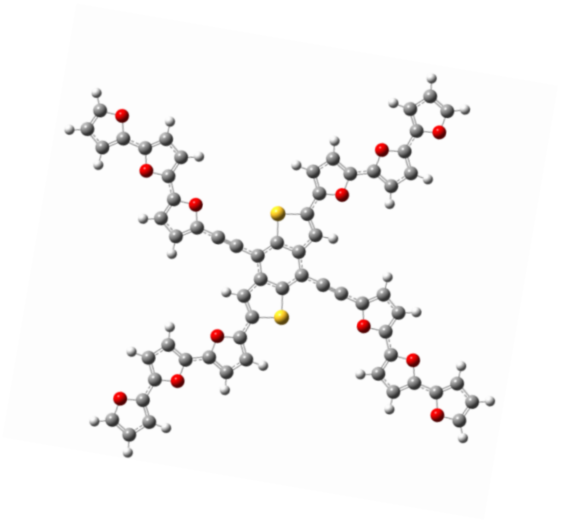


Fig. S1a The optimized structure of donor $B1_2$–DF–$B2_2$ fragment

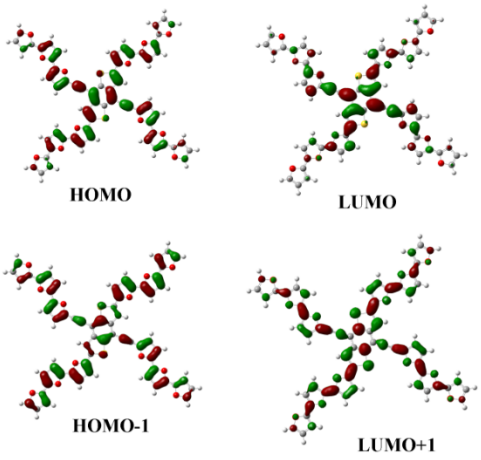


Figure S1b. FMOs diagram of $B1_2$-DF-$B2_2$

SIV: Energy levels and absorption spectra of five donors and $B1_2$–DF–$B2_2$ fragment

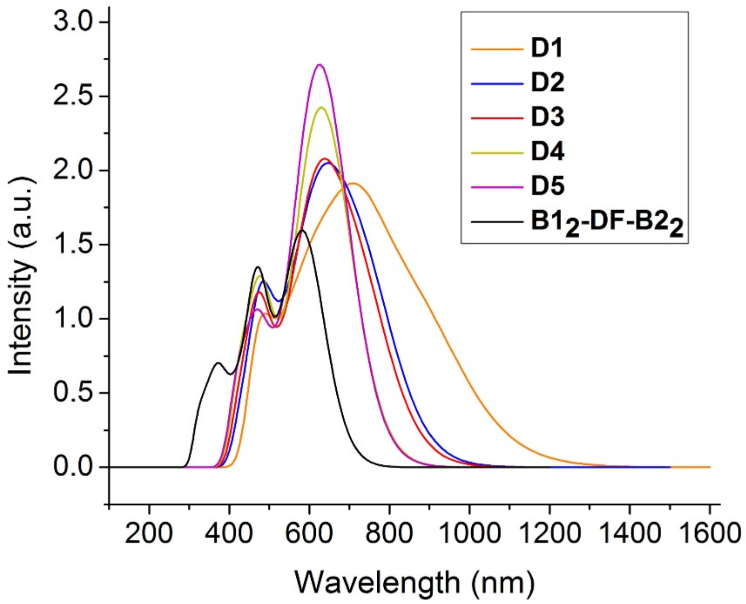


Fig. S2a Simulated absorption spectra of donors D1, D2, D3, D4, D5 and $B1_2$–DF–$B2_2$ fragment.

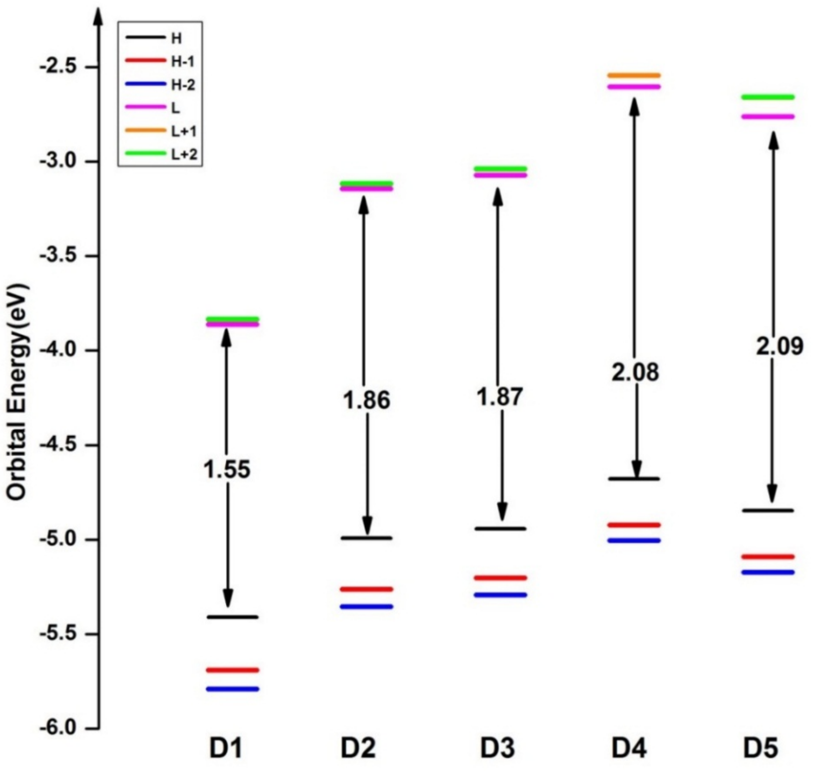


Figure S2b. Energy level diagram of the five Donors (D1-D5).

SV: Absorption properties table for donors and acceptors

Table S6: Calculated excitation energies (Ev), wavelength (λ_{abs}), oscillator strength (f), and composition in terms of molecular orbitals with related character (H = HOMO, L = LUMO) for D1, D2, D3, D4, D5, PDI1, PDI2, PDI3, PDI4 and PDI8.

D2	**Transition state**	**Ex (eV)**	**λ_{abs} (nm)**	**ƒ (a.u.)**	**Assignment**
	S0→S1	1.65	752	0.927	H→L (0.69) (ICT)
	S0→S2	1.69	732	0.6127	H→L+2 (0.70) (ICT)
	S0→S5	1.90	653	1.095	H-1→L (0.66) (ICT)
	S0→S7	1.94	637	0.703	H-1→L+2 (0.61) (ICT)
	S0→S10	2.06	600	0.390	H-2→L+1 (0.49) (ICT)
	S0→S12	2.08	594	0.213	H-2→L+3 (0.56) (ICT)
	S0→S13	2.12	585	0.369	H→L+4 (0.52) (π-π*) H-2→L+1 (0.31) (ICT)
	S0→S16	2.23	555	0.318	H-3→L+1 (0.62) (ICT)
	S0→S18	2.30	540	0.504	H-1→L+4 (0.66) (π-π*)
	S0→S20	2.57	482	0.838	H→L+5 (0.53) (π-π*)
	S0→S21	2.58	480	0.558	H-4→L (0.59) (ICT) H→L+5 (0.35) (π-π*)
	S0→S29	2.86	434	0.504	H-1→L+5 (0.45) (π-π*)
D3					
	S0→S1	1.67	740	0.934	H→L (0.69) (ICT)
	S0→S2	1.72	720	0.522	H→L+1 (0.70) (ICT)
	S0→S5	1.92	646	1.134	H-1→L (0.67) (ICT)
	S0→S6	1.97	629	0.714	H-1→L+1 (0.62) (ICT) H→L+4 (0.20) (π-π*)
	S0→S10	2.08	596	0.454	H-2→L+2 (0.48) (ICT)
	S0→S12	2.10	589	0.144	H-1→L+3 (0.68) (ICT)
	S0→S13	2.13	582	0.296	H→L+4 (0.50) (π-π*) H-2→L+2 (0.47) (ICT)
	S0→S16	2.25	551	0.361	H-3→L+2 (0.65) (ICT)
	S0→S18	2.30	538	0.356	H-1→L+4 (0.64) (π-π*) H-3→L+2 (0.23) (ICT)
	S0→S22	2.60	476	0.979	H→L+5 (0.51) (π-π*)
	S0→S25	2.64	470	0.345	H-4→L+1 (0.58) (π-π*)
	S0→S28	2.89	428	0.514	H-1→L+5 (0.46) (π-π*)
D4					
	S0→S1	1.84	674	1.48	H→L (0.68) (π-π*) H-1→L+1 (0.11) (ICT)
	S0→S2	1.93	643	0.815	H→L +1(0.67) (ICT)
	S0→S5	2.06	602	1.107	H-1→L (0.63) (ICT)
	S0→S6	2.12	585	0.814	H→L+4 (0.66) (π-π*), H-1→L+1 (0.13) (ICT)
	S0→S14	2.33	531	0.279	H-1→L+4 (0.59) (π-π*) H-2→L+3 (0.31) (ICT)

	S0→S21	2.59	478	1.418	H→L+5 (0.68) (π-π*)
	S0→S27	2.88	430	0.732	H-1→L+5 (0.62) (π-π*)
D5					
	S0→S1	1.85	670	1.705	H→L (0.69) (π-π*)
	S0→S2	1.98	625	1.105	H→L +1(0.68) (ICT)
	S0→S5	2.06	600	1.274	H-1→L (0.65) (π-π*)
	S0→S7	2.18	567	0.658	H→L+4 (0.61) (π-π*) H-2→L+2 (0.12) (ICT)
	S0→S8	2.25	551	0.117	H-1→L +1(0.60) (ICT) H→L+4 (0.31) (π-π*)
	S0→S13	2.35	526	0.130	H-2→L+3 (0.68) (ICT) H-1→L+1 (0.18) (π-π*)
	S0→S17	2.49	497	0.246	H-3→L+2 (0.68) (π-π*)
	S0→S20	2.65	467	0.968	H→L+5 (0.66) (π-π*)
	S0→S27	2.93	422	0.607	H-1→L+5 (0.63) (π-π*)
	S0→S28	2.99	413	0.136	H-5→L (0.61) (π-π*)
PDI1					
	S0→S1	2.45	507	0.668	H→L(0.70) (π-π*)
PDI2					
	S0→S1	2.37	522	0.545	H→L(0.71) (π-π*)
	S0→S15	4.30	288	0.264	H→L+4 (0.61) (π-π*)
PDI3					
	S0→S1	2.26	548	0.612	H→L(0.71) (π-π*)
	S0→S26	5.03	246	0.133	H-5→L+1 (0.51) (π-π*)
PDI4					
	S0→S1	2.30	540	0.553	H→L(0.71) (π-π*)
PDI8					
	S0→S1	2.126	583	0.470	H→L(0.70) (π-π*)
	S0→S2	2.71	458	0.164	H-1→L(0.68) (π-π*)
	S0→S7	3.38	373	0.134	H→L+2(0.61) (π-π*)
	S0→S20	4.34	285	0.191	H→L+4 (0.61) (π-π*)
	S0→S21	4.48	276	0.253	H-1→L+3 (0.64) (π-π*)

SVI: Percentage composition of building fragments

Table S7: Molecular orbital compositions (in percentage) of D1, D2, D3, D4and D5 (D F = electron-rich fragment. B1=π-bridge1, B2=π-bridge2, and A = electron-deficient fragments)

D1	**Energy Level**	**DF**	**B1**	**B2**	**A1**
	L+5	19	9	35	37
	L+4	38	6	20	36
	L+3	1	81	3	16
	L+2	1	81	15	4

	L+1	1	80	8	11
	L	2	79	11	8
	H	28	6	26	40
	H-1	14	10	42	34
	H-2	6	12	42	40
	H-3	5	15	36	44
	H-4	29	15	14	42
D2	**Energy Level**	**DF**	**B1**	**B2**	**A2**
	L+5	14	29	29	28
	L+4	36	19	34	11
	L+3	1	1	12	86
	L+2	1	5	9	85
	L+1	1	12	1	86
	L	3	10	8	79
	H	27	28	41	4
	H-1	13	43	36	8
	H-2	6	44	40	10
	H-3	5	37	46	12
	H-4	29	15	43	13
D3	**Energy Level**	**DF**	**B1**	**B2**	**A3**
	L+5	20	32	38	10
	L+4	36	18	34	12
	L+3	1	8	5	86
	L+2	1	5	9	85
	L+1	1	8	6	85
	L	4	8	11	77
	H	27	27	42	4
	H-1	12	40	39	9
	H-2	6	43	41	10
	H-3	4	34	48	14
	H-4	29	14	42	15
D4	**Energy Level**	**DF**	**B1**	**B2**	**A4**
	L+5	20	34	35	11
	L+4	29	15	26	30
	L+3	1	5	6	88
	L+2	1	7	5	87
	L+1	1	6	6	87
	L	11	11	17	61
	H	25	30	41	4
	H-1	11	43	38	8
	H-2	6	46	39	9
	H-3	5	36	47	12
	H-4	28	16	42	14

D5	Energy Level	DF	B1	DF2	A5
	L+5	23	32	34	11
	L+4	25	13	23	39
	L+3	1	15	3	81
	L+2	1	3	16	80
	L+1	1	11	10	78
	L	16	14	24	46
	H	25	30	40	5
	H-1	11	42	37	10
	H-2	5	46	37	12
	H-3	4	33	47	16
	H-4	27	16	39	18

SVII: HOMO and LUMO energy levels of the donors and acceptors

Table S8: Calculated energy levels of the Ds donors (D1-D5) and PDIs acceptors (PDI1-PDI8), Eg is the energy difference between HOMO and LUMO energy level.

Name	**HOMO (eV)**	**LUMO (eV)**	**Eg (eV)**
D1	-5.41	-3.86	1.55
D2	-5.00	-3.14	1.86
D3	-4.94	-3.07	1.87
D4	-4.68	-2.60	2.08
D5	-4.85	-2.76	2.09
PDI1[b]	-6.00	-3.46	2.54
PDI2[a]	-6.60	-4.09	2.51
PDI3	-5.70	-3.13	2.57
PDI4	-6.03	-3.52	2.51
PDI5	-6.29	-3.81	2.48
PDI6[b]	-5.73	-3.34	2.39
PDI7	-6.04	-3.73	2.31
PDI8[b]	-5.57	-3.29	2.28

a reference [5]

b reference [6]

SVII: The effect of substituents on D1

The absorption properties comparison of D1 is made with previously studied sulpher and thiophene analogue X1[e], two furan rings containing molecule instead of three rings (D1b).

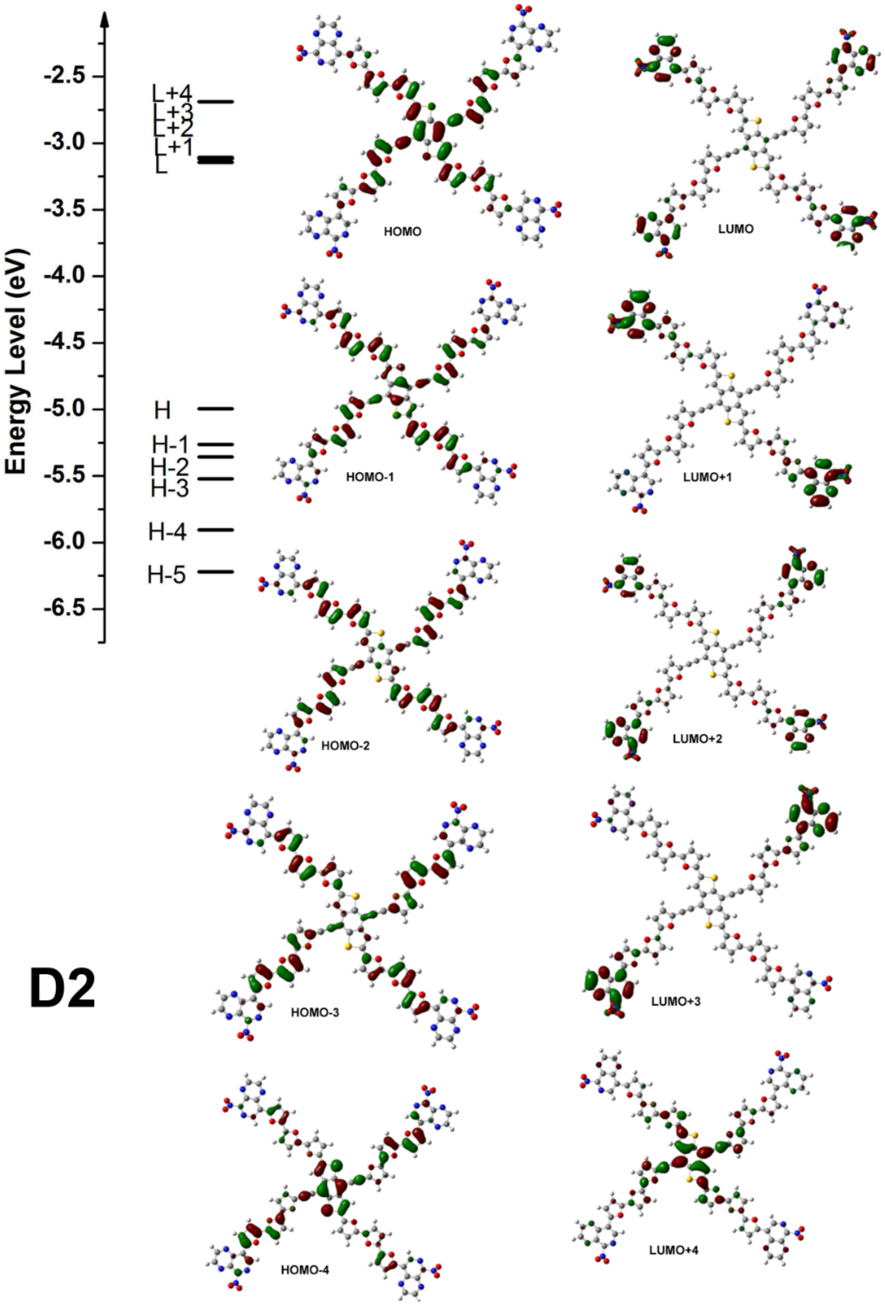
Table S9: Calculated energy gap (Eg), wavelength (λ_{ab}) and first excitation energy (Ex) at the TD-DFT (B3LYP/6-31G (d) level of theory.

Name	**Eg (eV)**	**λ_{ab} (nm)**	**Ex (eV)**
X1	1.71	817	1.52
D1a	1.72	816	1.52
D1b	1.68	829	1.49
D1	1.55	898	1.38

The furan (pi-spacer) containing analogue of X1 (D1a) is built and compared with X1 (here X1 is also calculated at the B3LYP/6-31G (d) level of theory for comparison purpose).

e is reference [7]

SVIII: FMOs of the D2, D3, D4 and D5.



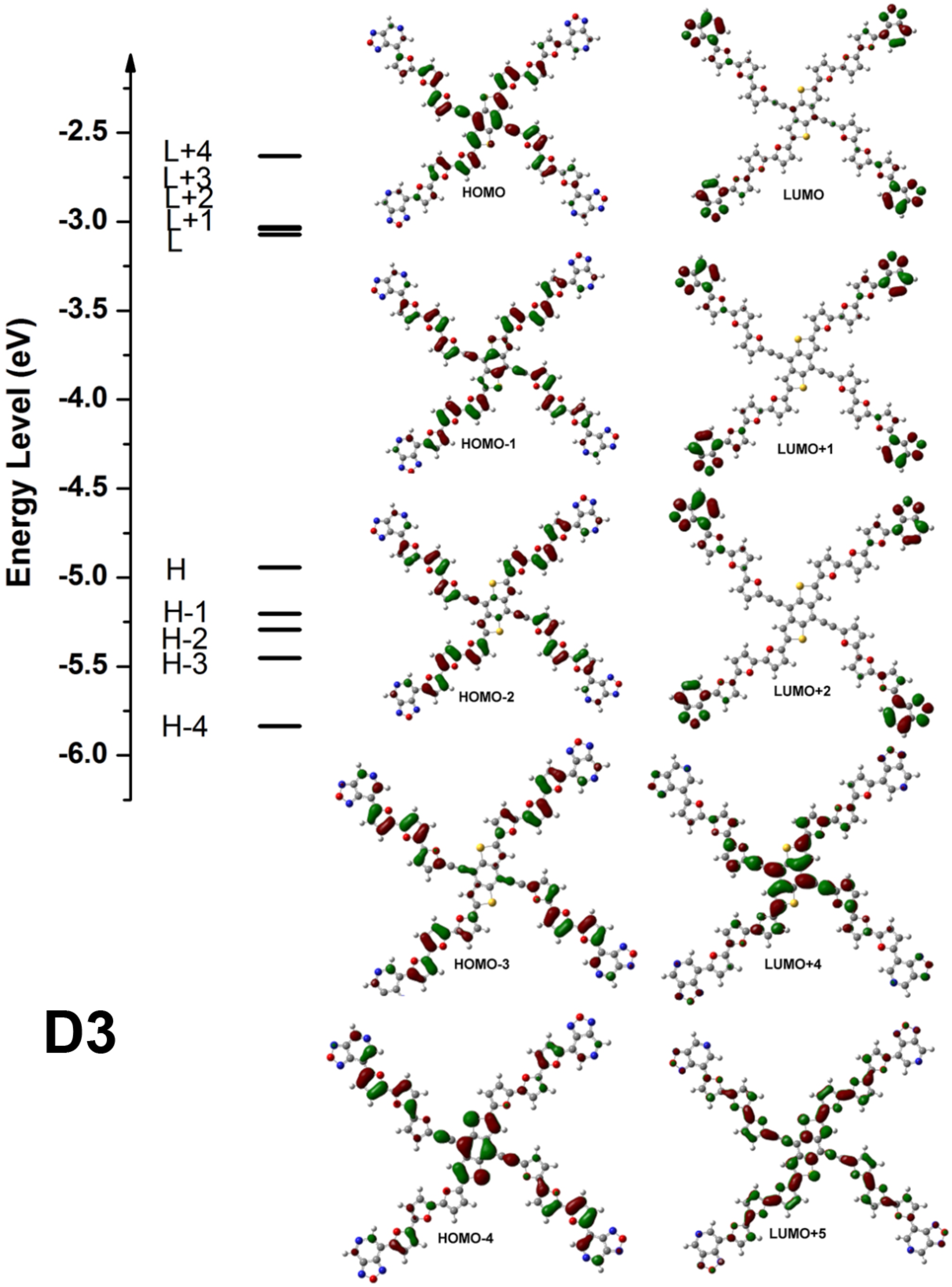
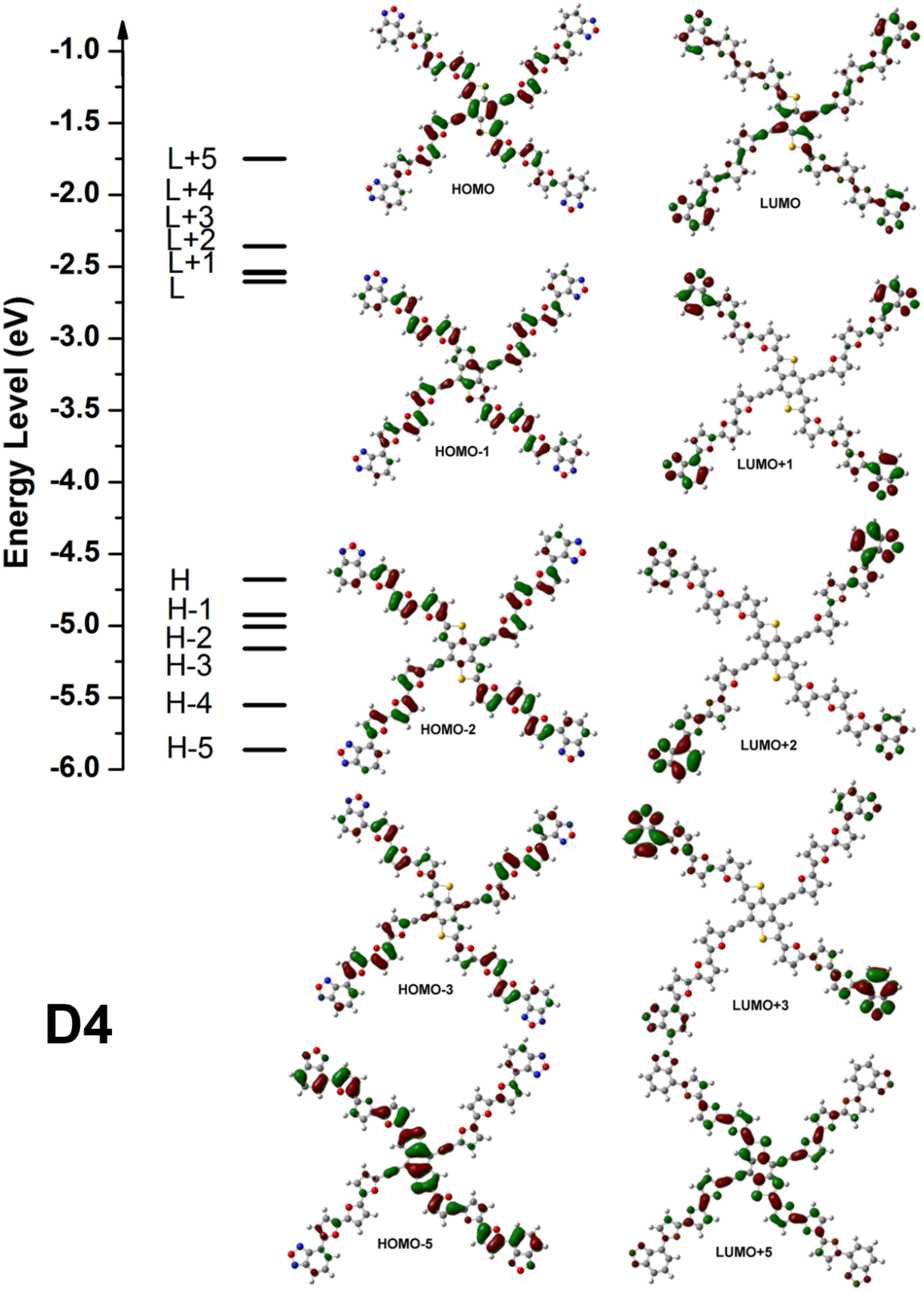


Fig. S3a FMOs of the donors D2 and D3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-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
L+5
L+4
L+3
L+2
L+1
L
H
H-1
H-2
H-3
H-4
H-5
HOMO
LUMO
HOMO-1
LUMO+1
HOMO-2
LUMO+2
HOMO-3
LUMO+3
HOMO-5
LUMO+5

D4

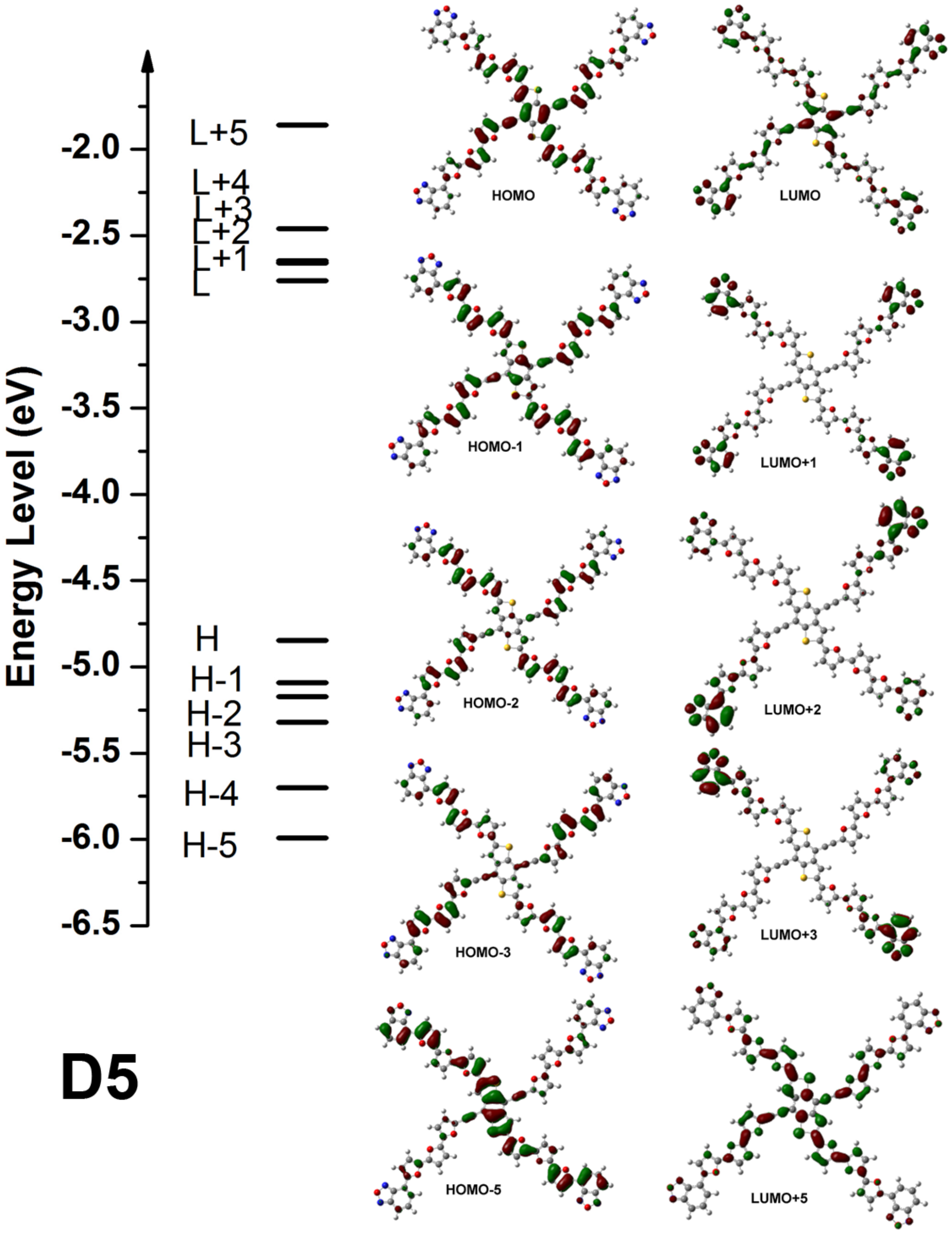


Fig. S3a FMOs of the donors D4 and D5

SIX: Non-linear fit relation equation

Then we also tried to develop a mathematical relation between FMOs of donor molecules and their building. The non-linear curve fit relation expression is as following:

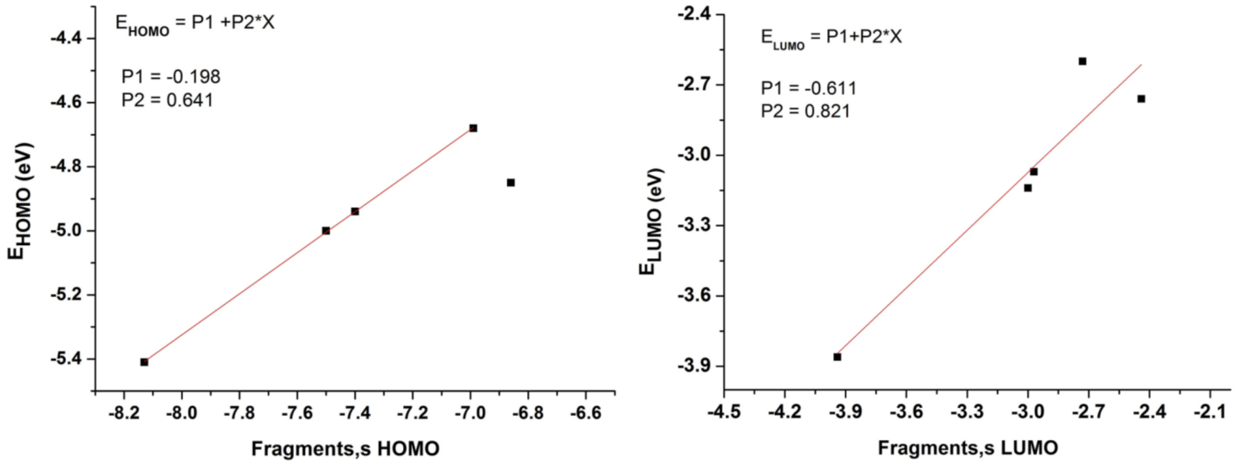
$$E_{\mathrm{HOMO\,(D)}} = P1 + P2\ E_{\mathrm{HOMO\ (Accp)}} \quad \text{(I)}$$

$$E_{\mathrm{LUMO\,(D)}} = P'1 + P'2\ E_{\mathrm{LUMO\ (Accp)}} \quad \text{(II)}$$

Where $E_{\mathrm{HOMO\,(D)}}$ and $E_{\mathrm{LUMO\,(D)}}$ is representing the HOMO and LUMO energy levels of donor molecules while P1 (P′1) and P2 (P′2) are correlation coefficients of the donor and acceptor fragments respectively which relate the FMOs of the donor and acceptor fragments with FMOs of the cross ponding donor compounds. $E_{\mathrm{HOMO\,(Accp)}}/E_{\mathrm{LUMO\,(Accp)}}$ is HOMO/LUMO energy level of acceptor fragments (Fig. S4).

We solved the equation I and II for example for D1, which provided extent of dependence of FMO energy levels of donor compounds with respect to its building blocks (supporting information). Fig. S4 is showing that P2 has larger values than P1 both for HOMOs and LUMOs which means acceptor fragments predominantly effecting the positions of HOMO/LUMO of donor molecules while donor fragment has small contribution in this respect. As here we have one common donor fragment while five acceptor fragments which are effecting due to their more electron withdrawing ability the positions of HOMO/LUMO and Eg of donor compounds. But it is also clear from Fig. S4 that there is no more reliable non-linear fit equation relationship between FMOs of all donor molecules and their building units in our case as all points are not within the range of this relation and.

But this kind of detailed analysis between FMOs of the donor-acceptor fragments relative to donor compound may be very assistive for sorting out the new facts about FMOs and Eg of the resulting donor molecules.



I **II**

Fig. S4 Non-linear fit relation between FMOs of donor molecules and their fragments.

For HOMO of D1

$E_{\text{HOMO (D)}} = \text{P1} + \text{P2}\ E_{\text{HOMO (Accp)}}$ (I)

= -0.198 + 0.641 (-8.13)

= -0.198 - 5.21

$\mathbf{E_{\text{HOMO (D)}} = -\ 5.41\ eV}$

As

$\text{P1} = \text{a1}^{*}\ E_{\text{HOMO (Dcore)}}$

So having the value of P1 and $E_{\text{HOMO (Dcore)}}$ we can find the value of a1 as following:

$\text{P1}/\ E_{\text{HOMO (Dcore)}} = \text{a1}$

-0.198/-4.55 = a1

0.044 = a1

Again the value of P1 can be confirmed here as:

$\text{P1} = \text{a1}^{*}\ E_{\text{HOMO (Dcore)}}$

P1= 0.044* -4.55

P1= -0.198

For LUMO of D1

$E_{LUMO\ (D)} = P'1 + P'2\ E_{LUMO\ (Accp)}$ (II)

$= -0.611 + 0.821\ (-3.94)$

$= -0.611 - 3.23$

$\mathbf{E_{LUMO\ (D)} = -3.85\ eV}$

As

$P'1 = a'1 * E_{LUMO\ (Dcore)}$

So having the value of P′1 and $E_{LUMO\ (Dcore)}$) we can find the value of a′1 as following:

$P'1 / E_{LUMO\ (Dcore)} = a'1$

-0.611/-2.28 = a′1

0.268 = a′1

Again the value of P′1 can be confirmed here as:

$P'1 = a1 * E_{LUMO\ (Dcore)}$

P′1= 0.2.68 * -2.28

P′1= -0.611

Hence, it proved that equation I and II are similar to Equation I′ and II′ i.e;

$$E_{HOMO\ (D)} = P1 + P2\ E_{HOMO\ (Accp)} \quad (I)$$

$$E_{LUMO\ (D)} = P'1 + P'2\ E_{LUMO\ (Accp)} \quad (II)$$

Or

$$E_{HOMO\ (D)} = a1 * E_{HOMO\ (Dcore)} + b1\ E_{HOMO\ (Accp)} \quad (I')$$

$$E_{LUMO\ (D)} = a'1 * E_{LUMO\ (Dcore)} + b'2\ E_{LUMO\ (Accp)} \quad (II')$$

SX: Natural Transition Orbital (NTO) Analysis

Table S10a: Calculated state of excitation, type of excitation, excitation energy (E) and eigenvalue (λ_i) at the TD-DFT (B3LYP/6-31G (d) level of theory for D1 molecule.

Exc.State	E (eV)	Type	λ_i
S1	1.38	ICT (B1$_2$-DF-B2$_2$ → A1)	0.99
S3	1.41	ICT (B1$_2$-DF-B2$_2$ → A1)	0.99
S5	1.66	ICT (B1$_2$-DF-B2$_2$ → A1)	0.98
S17	1.70	π-π* and ICT (B1$_2$-DF-B2$_2$ → A1)	0.68 and 0.28
S18	1.80	π-π* and ICT (B1$_2$-DF-B2$_2$ → A1)	0.56 and 0.38

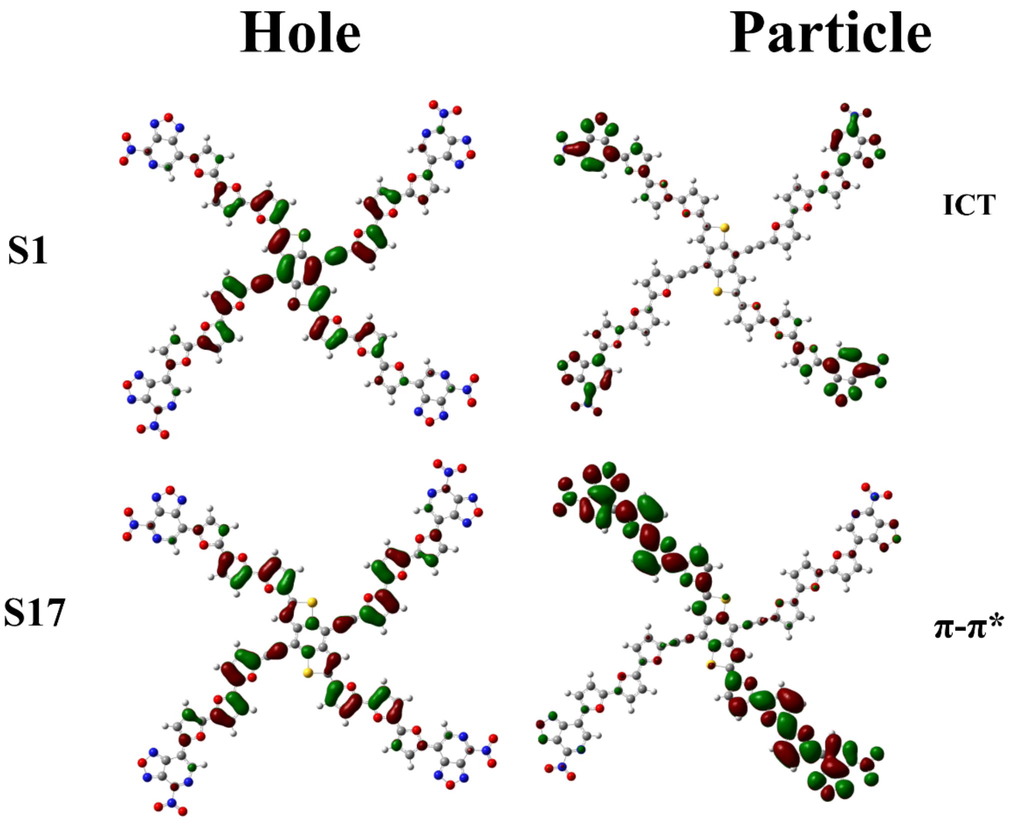


Fig. S5a Natural Transition Orbitals of the Hole and electron (particle) pair for D1.

Table S10b: Calculated state of excitation, type of excitation, excitation energy (E) and eigenvalue (λ_i) at the TD-DFT (B3LYP/6-31G (d) level of theory for D2 molecule

Exc.State	E (eV)	Type	Assignment	λ_i
S1	1.65	ICT ($B1_2$-DF-$B2_2$ → A2)	$\psi_{HOMO} \rightarrow \psi'_{LUMO}$	0.95
S5	1.90	ICT ($B1_2$-DF-$B2_2$ → A2)	$\psi_{HOMO\text{-}1} \rightarrow \psi'_{LUMO}$	0.86
S18	2.30	π-π* and ICT ($B1_2$-DF-$B2_2$ → A2)	$\psi_{HOMO-1} \rightarrow \psi'_{LUMO+4}$ and $\psi_{HOMO-3} \rightarrow \psi'_{LUMO+1}$	0.86
S20	2.57	π-π* and ICT ($B1_2$-DF-$B2_2$ → A2)	$\psi_{HOMO} \rightarrow \psi'_{LUMO+5}$ and $\psi_{HOMO-2} \rightarrow \psi'_{LUMO+5}$	0.66 and 0.40
S29	2.86	π-π*	$\psi_{HOMO-1} \rightarrow \psi'_{LUMO+5}$	0.45 and 0.41

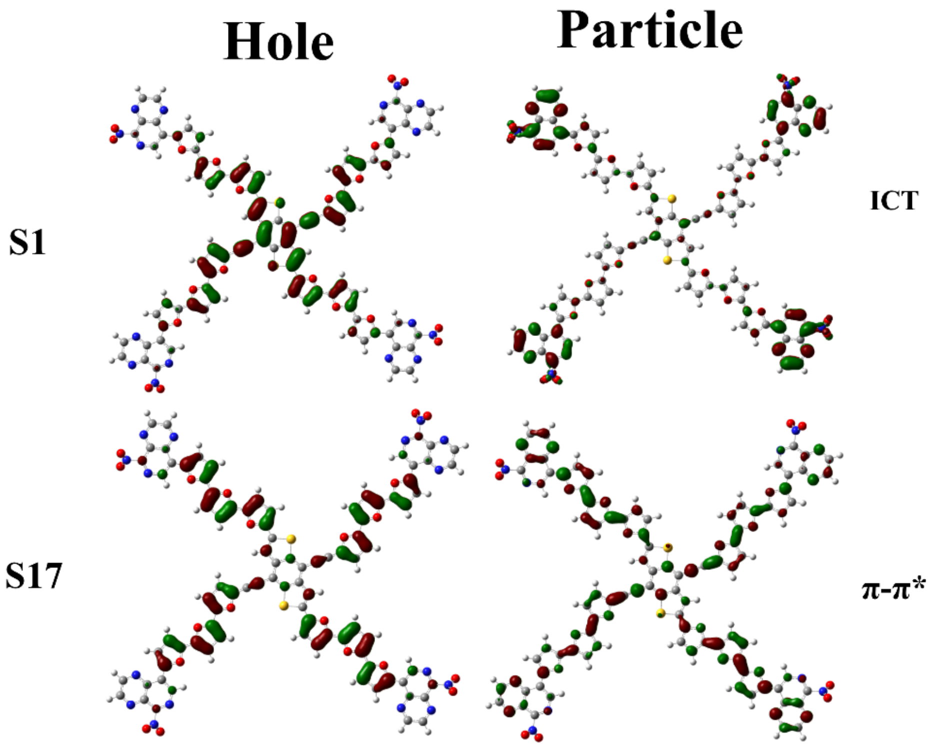


Fig. S5b Natural Transition Orbitals of the Hole and electron (particle) pair for D2.

Table S10c: Calculated state of excitation, type of excitation, excitation energy (E) and eigenvalue (λ_i) at the TD-DFT (B3LYP/6-31G (d) level of theory for D3 molecule.

Exc.State	E (eV)	Type	Assignment	λ_i
S1	1.67	ICT ($B1_2$-DF-$B2_2$ → A3)	$\psi_{HOMO} \rightarrow \psi'_{LUMO}$	0.96
S5	1.92	ICT ($B1_2$-DF-$B2_2$ → A3)	$\psi_{HOMO\text{-}1} \rightarrow \psi'_{LUMO}$	0.66
S18	2.31	π-π*	$\psi_{HOMO\text{-}1} \rightarrow \psi'_{LUMO+4}$	0.65
S22	2.60	ICT ($B1_2$-DF-$B2_2$ → A3) and π-π*	$\psi_{HOMO\text{-}4} \rightarrow \psi'_{LUMO+1}$ and $\psi_{HOMO} \rightarrow \psi'_{LUMO+5}$	0.28 and 0.5
S28	2.89	π-π* and ICT ($B1_2$-DF-$B2_2$ → A3)	$\psi_{HOMO\text{-}1} \rightarrow \psi'_{LUMO+5}$ and $\psi_{HOMO\text{-}5} \rightarrow \psi'_{LUMO}$	0.46 and 0.31

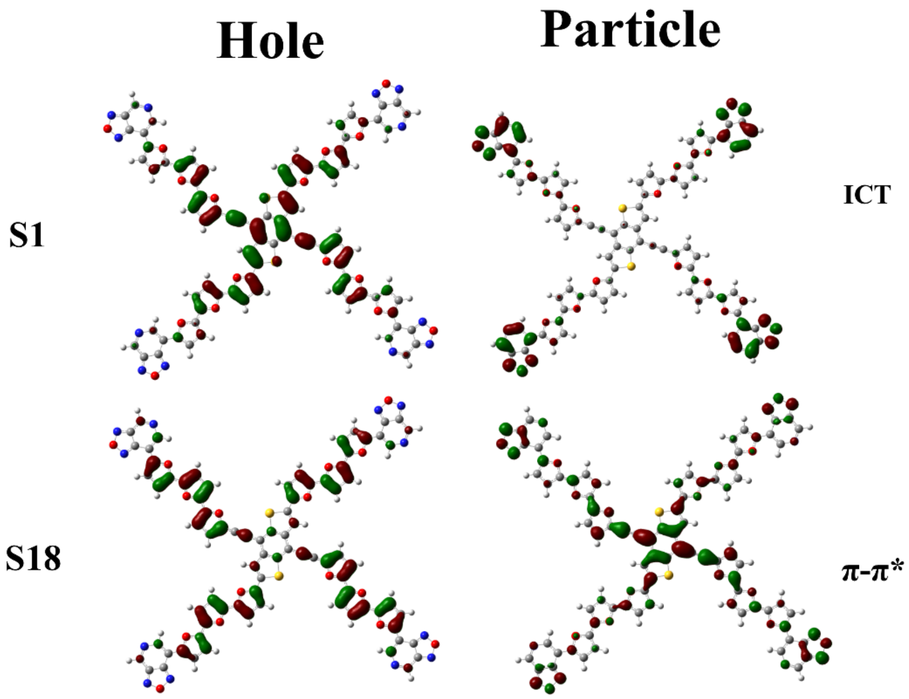


Fig. S5c Natural Transition Orbitals of the Hole and electron (particle) pair for D3.

Table S10d: Calculated state of excitation, type of excitation, excitation energy (E) and eigenvalue (λ_i) at the TD-DFT (B3LYP/6-31G (d) level of theory for D4 molecule.

Exc.State	**E (eV)**	**Type**	**Assignment**	**λ_i**
S1	1.84	π-π* and ICT ($B1_2$-DF-$B2_2$ → A4)	$\psi_{HOMO} \rightarrow \psi'_{LUMO}$ and $\psi_{HOMO\text{-}\mathbf{1}} \rightarrow \psi'_{LUMO+1}$	0.92 And 0.20
S5	2.06	π-π*	$\psi_{HOMO\text{-}\mathbf{1}} \rightarrow \psi'_{LUMO}$	0.80
S14	2.33	π-π* and ICT ($B1_2$-DF-$B2_2$ → A4)	$\psi_{HOMO\text{-}1} \rightarrow \psi'_{LUMO+4}$ and $\psi_{HOMO\text{-}\mathbf{2}} \rightarrow \psi'_{LUMO+3}$	0.70 and 0.19
S21	2.59	π-π*	$\psi_{HOMO} \rightarrow \psi'_{LUMO+5}$	0.93
S27	2.88	π-π*	$\psi_{HOMO\text{-}1} \rightarrow \psi'_{LUMO+5}$ and $\psi_{HOMO\text{-}4} \rightarrow \psi'_{LUMO+4}$	0.77 and -0.13

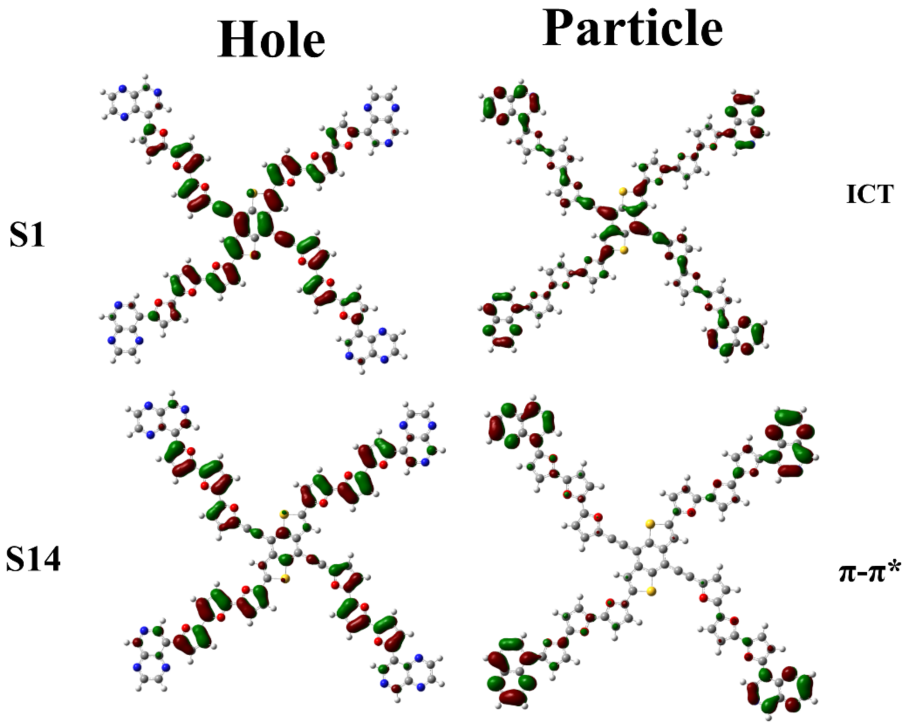


Fig. S5d Natural Transition Orbitals of the Hole and electron (particle) pair for D4.

Table S10e: Calculated state of excitation, type of excitation, excitation energy (E) and eigenvalue (λ_i) at the TD-DFT (B3LYP/6-31G (d) level of theory for D5 molecule.

Exc.State	E (eV)	Type	Assignment	λ_i
S1	1.85	π-π*	$\psi_{HOMO} \rightarrow \psi'_{LUMO}$	0.95
S2	1.93	ICT (B1$_2$-DF-B2$_2$ → A5)	$\psi_{HOMO} \rightarrow \psi'_{LUMO+1}$	0.92
S5	2.06	π-π*	$\psi_{HOMO\text{-}\mathbf{1}} \rightarrow \psi'_{LUMO}$	0.87
S17	2.49	π-π*	$\psi_{HOMO-3} \rightarrow \psi'_{LUMO+2}$	0.68
S28	2.98	π-π*	$\psi_{HOMO-5} \rightarrow \psi'_{LUMO}$	0.75

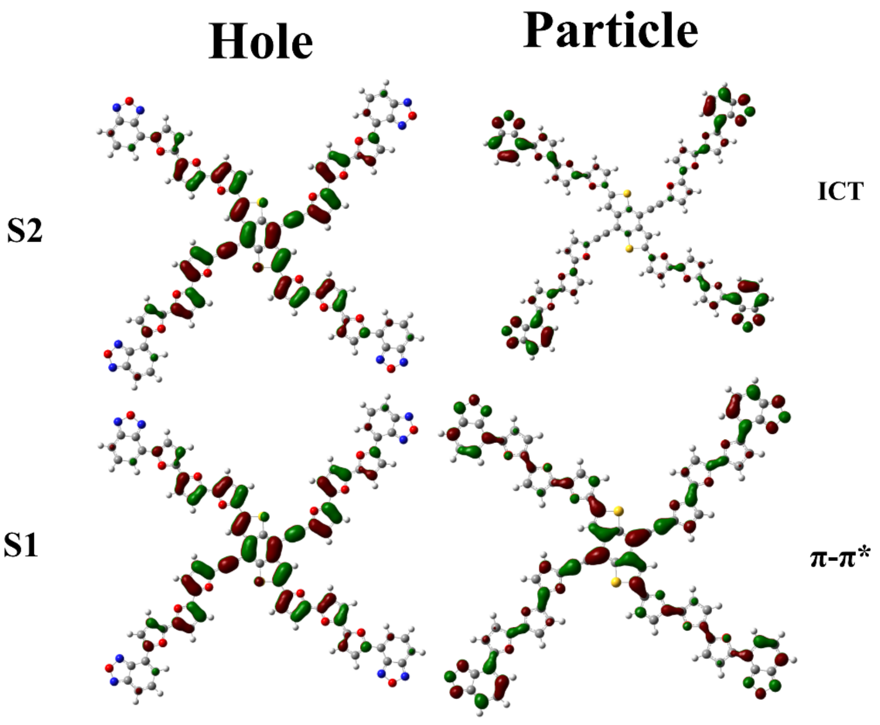


Fig. S5e Natural Transition Orbitals of the Hole and electron (particle) pair for D5.

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