

Supporting information

Influence of push-pull configuration on the electro-optical and charge transport properties of novel naphtho-difuran derivatives: A DFT Study

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2. Computational method

Density functional theory (DFT) has been used to optimize the initial molecular structures at the ground states (S_0) by applying the hybrid exchange correlation functional B3LYP¹⁻³ with 6-31G** basis sets⁴⁻¹¹. For excited states (S_1) time-dependent density functional theory (TD-DFT)¹¹⁻¹⁴ through the hybrid functional TD-B3LYP¹⁵⁻¹⁸ with the same basis set was used to optimized the geometries of the analogues.

Electronic, photophysical properties including absorption (λ_a), and emission (λ_e) wavelengths have been calculated at the same level of theory. The reorganization energy (λ) represents the geometric relaxation energy of a molecule from the charged (cation / anion) to the neutral state, and from the neutral to the charged (cation / anion) state. The reorganization energy for hole (λ_h) / electron (λ_e) was evaluated as:

$$\lambda_{h/e} = \lambda_{+/-} + \lambda_{1/2}. \quad (1)$$

where the energy of geometry relaxation from neutral to charged (cation/anion) state is $\lambda_{+/-}$, and the relaxation energy of a molecule from charged (cation/anion) state to neutral is $\lambda_{1/2}$ ^{19,20}. These two terms are calculated directly from the adiabatic potential energy surfaces for $\lambda_{h/e}$ ²¹⁻²³. The reorganization energy for hole (λ_h) is calculated as:

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$$\lambda_h = \lambda_+ + \lambda_1 = [E^1(R)^+ - E^0(R)^+] + [E^{+1}(R) - E^0(R)] \quad (2)$$

$$= IP_v - HEP \quad (3)$$

$E^0(R)$, $E^0(R)^+$ are the energies of neutral and charged (cations) species optimized at ground state, $E^{+1}(R)$ is the energy of neutral at the optimized charged (cations) species, and $E^1(R)^+$ is energy of the charge (cations) at the geometry of the optimized neutral species. IP_v and HEP are vertical ionization potential and hole extraction potential, respectively. The reorganization energy for electron (λ_e) will be evaluated as:

$$\lambda_e = \lambda_- + \lambda_2 = [E^1(R)^- - E^0(R)^-] + [E^{-1}(R) - E^0(R)] \quad (4)$$

$$= EEP - EA_v \quad (5)$$

$E^0(R)$ and $E^0(R)^-$ are the energies of neutral and charged (anion) species optimized at ground state, $E^{-1}(R)$ is the energy of neutral molecule at the geometry of the optimized charged (anion) species, and $E^1(R)^-$ is energy of the charged (anion) species at the geometry of the optimized neutral species. EA_v and EEP are vertical electron affinity and electron extraction potential, respectively. These reorganization energies for hole/electron, HEP (hole extraction potential) and EEP (electron extraction potential) were calculated using DFT at the B3LYP/6-31G** level for all the analogues. The ionization potential IP and electron affinity EA can be either for adiabatic excitations (a), optimized structure for both the neutral and charge molecule or vertical excitation (v), at the geometry of the neutral molecule. The adiabatic/vertical ionization potential (IP_a)/(IP_v) and electron affinity (EA_a)/(EA_v) have been calculated at the B3LYP/6-31G** level of theory as follows:

$$IP_a = E^0(R)^+ - E^0(R) \quad \text{and} \quad IP_v = E^1(R)^+ - E^0(R) \quad (6)$$

$$EA_a = E^0(R) - E^0(R)^- \quad \text{and} \quad EA_v = E^0(R) - E^1(R)^- \quad (7)$$

$E^0(R)$ is energy of the neutral at the ground state, the energies of charged (cation)/(anion) states represented by $E^0(R)^+$ and $E^0(R)^-$, whereas $E^1(R)^+$ and $E^1(R)^-$ correspond to the energies of charged (cation)/ (anion) states at the optimized geometry of the neutral molecule, respectively.

Electronegativity defined by Pauling “the power of an atom in molecule to attract electron to itself”²⁴ influences the electron transfer parameters and electron transfer rate. The absolute electronegativities (χ) were calculated by the following relation as mentioned in refs.,^{23, 25, 26}:

$$\chi = \frac{IP\nu + EA\nu}{2} \quad (8)$$

In the next step, the calculations related to term transfer integrals is performed. To calculate the transfer integrals, inter-molecular nearest-neighboring hopping pathways have been generated using the single-crystal structures. There are two widely employed approaches to obtain transfer integrals; one is Koopmans’ theorem based method²⁷ and other one is direct evaluation method for the frontier molecular orbitals (FMOs)^{28, 29}. By Koopmans’ theorem the transfer integrals are computed as half of HOMO or LUMO levels splitting for electrons/holes. Bredas et al³⁰ have extensively investigated the transport parameters by frontier orbital splitting on many conjugated systems and found it suitable. Similarly Valeev et al.³¹ also cautioned recently that due to the crystal environment the site-energy correction should be taken into account when the dimer is not co-facially stacked. We also have used the direct approach^{28, 29} to investigate the charge transport properties in this study. The hole/electron transfer integrals in this approach can be expressed as:

$$t_{h/e} = \langle \phi_{LUMO/HOMO}^{0,site1} | F^0 | \phi_{LUMO/HOMO}^{0,site2} \rangle = \langle \phi_{LUMO/HOMO}^{0,site1} | h_{core} | \phi_{LUMO/HOMO}^{0,site2} \rangle + \sum_{l(occ)} (\langle \phi_{LUMO/HOMO}^{0,site1} \phi_l^0 | \phi_{LUMO/HOMO}^{0,site2} \phi_l^0 \rangle - \langle \phi_{LUMO/HOMO}^{0,site1} \phi_{LUMO/HOMO}^{0,site2} | \phi_l^0 \phi_l^0 \rangle) \quad (9)$$

here $t_{h/e}$ is the hole/electron transfer integrals, whereas $\phi_{LUMO/HOMO}^{0,site1}$ and $\phi_{LUMO/HOMO}^{0,site2}$ correspond to the HOMOs and LUMOs of the two consecutive molecules when there is no contact between the adjacent molecules, whereas F^0 is the Fock operator with unperturbed molecular orbitals for the dimer of a fixed pathway. It has been already reported that “in excitons formation the spin dependence of the charge recombination rates” can be contributed by the exchange term³². The procedure of standard self-consistent field (SCF) can be used to calculate separately the molecular orbitals which are not interacting with each

other for two individual molecules. In equation (4) the orbitals which have no interaction would be used to construct the two-electron integrals and the dimer Fock matrix. The non-interacting molecular orbitals and density matrix associated to these orbitals have been used to evaluate the Fock matrix of the dimer structure. To construct the density matrix of F^0 , the molecular non-interacting orbitals have been used. Fock matrix can be expressed as:

$$F = SC\varepsilon C^{-1} \quad (10)$$

In this equation ‘S’ corresponds to the dimer overlap matrix from the crystal structure. The eigenvalue and Kohn–Sham orbital (ε and C) were obtained from the Fock matrix of zeroth-order by “diagonalizing the Fock matrix without any self-consistent field iteration”³². To obtain the intermolecular transfer integrals the Fock matrix of the dimers with molecular orbitals of unperturbed monomer have been directly evaluated at the pw91pw91/6-31G** level of theory. This functional has been reported for giving the best description of intermolecular transfer integral term by Huang and Kertesz³³. This direct method for the transfer integral has been reported equivalent to “the site-energy corrected frontier orbital splitting method” by Yang et al³⁴ and the computation of the transfer integrals has been made remarkably simple by this direct method. Intermediate neglect of differential overlap (INDO) based calculations often overestimate transfer integrals which use the “energy-splitting-in-dimer” method³¹ and orthogonalisation of the basis set has also ignored in this approach, hence the direct method was used as it has been verified to give good, precise and exact results in the literature^{28, 34-37}.

In OSMs order of magnitude could affect the carrier mobility among the different dimers. The thin film phases contain grain boundaries. Actual materials could not be described by the diffusion constant due to the insufficiency caused by the inhomogeneities in OMs^{11, 38}. The random walk method was performed to simulate the diffusion process of the charge carrier when inhomogeneities are present in the materials. In random walk approach, initially we chose a molecule (arbitrary site) as the preparatory position for the

charge within the bulk ^{11, 39, 40}. We have evaluated the diffusion constant; assuming the charge motion as homogeneous random walk ^{11,41} by the following equation:

$$D = \lim_{t \rightarrow \infty} \frac{1}{2n} \frac{\langle x(t)^2 \rangle}{t} \approx \frac{1}{2n} \sum_i d_i^2 k_i p_i = \frac{1}{2n} \frac{\sum_i d_i^2 k_i^2}{\sum_i k_i} \quad (11)$$

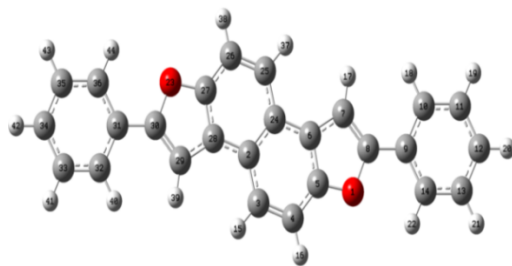
where d is the mass center between the two molecules of the dimers and the spatial dimensionality is n , which is equal to 3. The $1/k$ is the inverse rate constant of the hopping time among two consecutive

molecules. The specific hopping route probability is $p_i = \frac{k_i}{\sum_i k_i}$, this is 3-d averaged diffusion process.

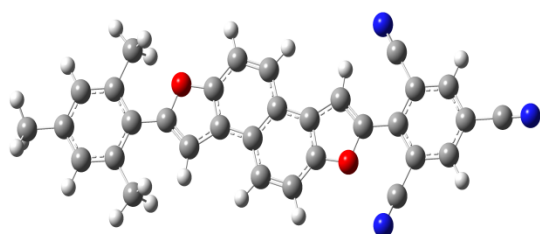
The carrier mobility μ can be evaluated with the help of Einstein relation as:

$$\mu = eD/K_B T \quad (12)$$

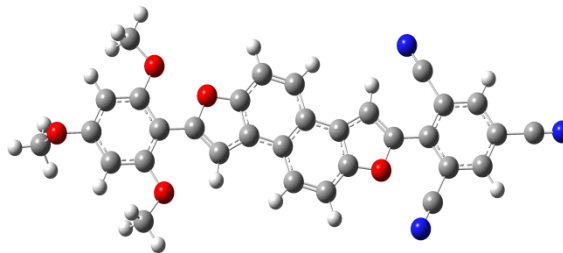
here μ corresponds to the carrier mobility, D represents charge diffusion constant, e is for electronic charge, T is temperature and K_B donates the Boltzmann constant. It can be seen that the electron transfer rate and the mobility are linearly proportional to each other. Applying the above mentioned mechanism, it was presumed that the hopping of localized electron possible only between contiguous molecules, which is opposite to the band-like picture, in that case the delocalization of electron, took place in various molecules. All these first-principles calculations were carried out using Gaussian 09 package ⁴².



DPNDF with atom numbers



Compound 1 = CH3- π -CN



Compound 2 = OCH3- π -CN

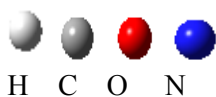


Figure S1. DPNDF with labeling, position of attached groups and new molecules.

Table S1:

B3LYP/6-31G** level Optimized bond lengths and bond/dihedral angles values for neutral, cation and anion structures of both the compounds

Compound 1					
Parameters	Neutral	Cation	$\Delta 1$	Anion	$\Delta 2$
C ₁₉ -C ₂₀	1.397	1.418	0.021	1.394	-0.003
C ₂₀ -C ₂₁	1.435	1.403	-0.032	1.435	0.000
C ₂₁ -C ₂₂	1.368	1.405	0.037	1.369	0.001
C ₂₂ -C ₂₃	1.471	1.438	-0.033	1.47	-0.001
C ₂₃ -C ₂₄	1.412	1.438	0.026	1.416	0.004
C ₂₃ -C ₂₈	1.418	1.441	0.023	1.42	0.002
C ₁₀ -C ₉ -C ₁₄	116.30	117.32	1.02	114.44	-1.86
O ₁₈ -C ₂₂ -C ₂₁	110.09	109.01	-1.08	109.85	-0.24
O ₁₈ -C ₂₂ -C ₂₃	116.94	118.08	1.14	116.90	-0.04
C ₂₀ -C ₂₁ -C ₂₂ -C ₂₃	179.62	178.49	-1.13	178.93	-0.69
O ₁₈ -C ₂₂ -C ₂₃ -C ₂₄	130.02	153.25	23.23	134.27	4.25
O ₁₈ -C ₂₂ -C ₂₃ -C ₂₈	50.55	27.02	-23.53	46.21	-4.34
C ₂₁ -C ₂₂ -C ₂₃ -C ₂₄	50.40	28.31	-22.09	46.76	-3.64
C ₂₁ -C ₂₂ -C ₂₃ -C ₂₈	129.02	151.42	22.40	132.76	3.74
Compound 2					
C ₉ -C ₁₀	1.428	1.421	-0.007	1.462	0.034
C ₉ -C ₁₄	1.428	1.421	-0.007	1.459	0.031
C ₁₁ -C ₁₂	1.399	1.399	0.000	1.412	0.013
O ₁ -C ₈ -C ₇	109.97	110.64	0.67	108.78	-1.19
C ₈ -C ₉ -C ₁₄	122.01	121.61	-0.34	123.09	1.08
C ₁₀ -C ₉ -C ₁₄	116.21	117.23	1.02	114.38	-1.83

C ₁₀ -C ₁₁ -C ₁₂	120.67	120.30	-0.37	121.99	1.32
C ₁₁ -C ₁₂ -C ₁₃	118.83	119.41	0.58	117.33	-1.50
C ₁₂ -C ₁₃ -C ₁₄	121.14	120.67	-0.47	122.23	1.09
C ₅ -C ₁ -C ₈ -C ₉	178.53	178.90	0.37	179.86	1.33
C ₆ -C ₇ -C ₈ -C ₉	178.20	178.86	0.66	179.85	1.65
C ₁ -C ₈ -C ₉ -C ₁₀	162.18	152.06	-10.12	179.19	17.01
C ₁ -C ₈ -C ₉ -C ₁₄	17.60	27.72	10.12	0.85	-16.75
C ₇ -C ₈ -C ₉ -C ₁₀	19.63	29.02	9.39	0.94	-18.69
C ₇ -C ₈ -C ₉ -C ₁₄	160.59	151.19	-9.40	179.02	18.43

$\Delta 1$ =Cation-Neutral; the positive value means lengthening/increasing of bond length/angles.

$\Delta 2$ =Anion-Neutral; the negative value means shortening/decreasing of bond length/angles.

Table S2:

The energies (in Hartrees)[†] of optimized structures at B3LYP/6-31G** level of theory

	Neutral E ⁰ (R)	Cation E ⁰ (R) ⁺	Cat_OPT_ Neut_SP ^a E ⁺¹ (R)	Neut_O PT_Cat _SP ^b E ¹ (R) ⁺	Anion E ⁰ (R) ⁻	An_OPT_ Neut_SP ^c E ⁻¹ (R)	Neut_OPT _An_SP ^d E ¹ (R) ⁻
Compound 1	-1545.5611	-1545.3155	-1545.5555	-1545.3092	-1545.6256	-1545.5571	-1545.6208
Compound 2	-1771.1752	-1770.949	-1771.1678	-1770.9411	-1771.2345	-1771.1109	-1771.2299

^a: The energy of neutral molecule at the geometry of the optimized charged cation species.

^b: The energy of the charged cation species at the geometry of the optimized neutral species.

^c: The energy of neutral molecule at the geometry of the optimized charged anion species.

^d: The energy of the charged anion species at the geometry of the optimized neutral species.

[†] The λ_h , λ_e , IPa/v and EAa/v have been calculated by equations 2, 4, 6 and 7, respectively, and all values were converted to eV (1 Hartrees = 27.2116 eV)

Table S3:

The neutral optimized coordinates of the structures at B3LYP/6-31G** level of theory

Neutral					
Compound 1			Compound 2		
X	Y	Z	X	Y	Z

-3.193390	1.335857	0.573845	0.573845	0.573845	0.573845
0.838829	0.509776	0.221677	0.221677	0.221677	0.221677
0.416025	1.872824	0.765683	0.765683	0.765683	0.765683
-0.913585	2.234922	0.919888	0.919888	0.919888	0.919888
-1.842241	1.185524	0.507031	0.507031	0.507031	0.507031
-1.500557	-0.169256	-0.031442	-0.031442	-0.031442	-0.031442
-2.738033	-0.876361	-0.304534	-0.304534	-0.304534	-0.304534
-3.740094	0.070403	0.074651	0.074651	0.074651	0.074651
-5.185869	-0.000953	0.022864	0.022864	0.022864	0.022864
-5.884999	-1.194699	-0.107404	-0.107404	-0.107404	-0.107404
-7.280241	-1.265582	-0.157963	-0.157963	-0.157963	-0.157963
-8.044309	-0.150416	-0.069566	-0.069566	-0.069566	-0.069566
-7.387526	1.035518	0.061622	0.061622	0.061622	0.061622
-5.990839	1.117604	0.103609	0.103609	0.103609	0.103609
1.175771	2.647613	1.064792	1.064792	1.064792	1.064792
-1.236382	3.268896	1.327792	1.327792	1.327792	1.327792
-2.874393	-1.944439	-0.737969	-0.737969	-0.737969	-0.737969
-7.768389	-2.192608	-0.254088	-0.254088	-0.254088	-0.254088
-7.962583	1.906268	0.121149	0.121149	0.121149	0.121149
3.916542	-1.359805	-0.542725	-0.542725	-0.542725	-0.542725
-0.121998	-0.555150	-0.194193	-0.194193	-0.194193	-0.194193
0.295544	-1.913160	-0.733234	-0.733234	-0.733234	-0.733234
1.632731	-2.260314	-0.878391	-0.878391	-0.878391	-0.878391
2.560835	-1.213331	-0.473339	-0.473339	-0.473339	-0.473339
2.215497	0.139181	0.065032	0.065032	0.065032	0.065032
3.462085	0.849382	0.340092	0.340092	0.340092	0.340092
4.459767	-0.086080	-0.036758	-0.036758	-0.036758	-0.036758
5.927307	0.013238	-0.018011	-0.018011	-0.018011	-0.018011
6.592946	0.811872	-0.308189	-0.308189	-0.308189	-0.308189
7.989206	0.890059	-0.322538	-0.322538	-0.322538	-0.322538
8.747185	0.207914	-0.036309	-0.036309	-0.036309	-0.036309
8.067921	-0.568953	0.274872	0.274872	0.274872	0.274872
6.677676	-0.683707	0.290947	0.290947	0.290947	0.290947
-0.458033	-2.693715	-1.034215	-1.034215	-1.034215	-1.034215
1.956884	-3.294505	-1.287517	-1.287517	-1.287517	-1.287517
3.612531	1.918286	0.754858	0.754858	0.754858	0.754858
8.496983	1.499172	-0.550591	-0.550591	-0.550591	-0.550591
8.637734	-1.096098	0.513728	0.513728	0.513728	0.513728
5.857483	1.582409	-0.114140	-0.114140	-0.114140	-0.114140

5.002121	1.027157	-0.150787	-0.150787	-0.150787	-0.150787
5.472935	2.537858	0.183825	0.183825	0.183825	0.183825
6.530073	1.812796	0.229618	0.229618	0.229618	0.229618
6.015867	-1.520809	-0.167563	-0.167563	-0.167563	-0.167563
5.178702	-0.990877	-0.225394	-0.225394	-0.225394	-0.225394
5.613128	-2.453466	-0.576982	-0.576982	-0.576982	-0.576982
6.734587	-1.774063	0.627207	0.627207	0.627207	0.627207
10.254839	0.285124	-0.079002	-0.079002	-0.079002	-0.079002
10.695965	-0.598723	-0.959927	-0.959927	-0.959927	-0.959927
10.611734	1.163718	-0.156743	-0.156743	-0.156743	-0.156743
10.651598	0.332188	-1.865051	-1.865051	-1.865051	-1.865051
-9.474119	-0.222625	-1.163576	-1.163576	-1.163576	-1.163576
-10.635567	-0.282426	0.939420	0.939420	0.939420	0.939420
-5.454169	2.377718	0.093136	0.093136	0.093136	0.093136
-5.142075	3.429607	1.818577	1.818577	1.818577	1.818577
-5.204175	-2.383526	1.160929	1.160929	1.160929	1.160929
-4.700949	-3.375059	0.204905	0.204905	0.204905	0.204905
			11.243574	-0.116692	0.108489
			10.096172	-0.901631	1.225049
			10.109795	-1.347655	-0.507254

Table S4:

The cation optimized coordinates of the structures at B3LYP/6-31G** level of theory

Cation					
Compound 1			Compound 2		
X	Y	Z	X	Y	Z
-3.204519	1.335886	-0.174360	-0.383778	-0.383778	-0.383778
0.825389	0.529220	-0.086322	-0.139280	-0.139280	-0.139280
0.409774	1.872683	-0.226164	-0.496964	-0.496964	-0.496964
-0.935615	2.228592	-0.264618	-0.602412	-0.602412	-0.602412
-1.855512	1.193171	-0.157005	-0.334325	-0.334325	-0.334325
-1.511914	-0.165616	-0.014069	0.027425	0.027425	0.027425
-2.746090	-0.868483	0.063956	0.209850	0.209850	0.209850
-3.743016	0.078412	-0.035623	-0.047693	-0.047693	-0.047693
-5.198612	0.000905	-0.002710	-0.013112	-0.013112	-0.013112
-5.881835	-1.169762	-0.430487	-0.265628	-0.265628	-0.265628
-7.277883	-1.245476	-0.412075	-0.243796	-0.243796	-0.243796
-8.037917	-0.155890	0.028719	0.024083	0.024083	0.024083

-7.389011	1.006274	0.461345	0.281568	0.281568	0.281568
-5.991650	1.089833	0.451833	0.268777	0.268777	0.268777
1.159444	2.652870	-0.303424	-0.694007	-0.694007	-0.694007
-1.256461	3.258785	-0.365584	-0.871851	-0.871851	-0.871851
-2.893588	-1.929354	0.185381	0.500147	0.500147	0.500147
-7.768310	-2.150177	-0.751687	-0.447180	-0.447180	-0.447180
-7.968004	1.849953	0.818337	0.504788	0.504788	0.504788
3.904156	-1.366353	0.125663	0.363078	0.363078	0.363078
-0.133273	-0.533155	0.023314	0.133137	0.133137	0.133137
0.287165	-1.882351	0.156839	0.486250	0.486250	0.486250
1.632584	-2.249956	0.197720	0.586501	0.586501	0.586501
2.551834	-1.220501	0.098582	0.323051	0.323051	0.323051
2.210283	0.147736	-0.051045	-0.028869	-0.028869	-0.028869
3.431269	0.833401	-0.129653	-0.197423	-0.197423	-0.197423
4.460875	-0.115791	-0.018160	0.048863	0.048863	0.048863
5.894597	-0.007189	-0.001353	0.014029	0.014029	0.014029
6.538846	1.079501	-0.688585	-0.072109	-0.072109	-0.072109
7.923962	1.162995	-0.656219	-0.099270	-0.099270	-0.099270
8.720058	0.237092	0.033914	-0.046254	-0.046254	-0.046254
8.077683	-0.812072	0.706110	0.032948	0.032948	0.032948
6.698204	-0.973576	0.702744	0.061301	0.061301	0.061301
-0.467126	-2.658834	0.230913	0.679013	0.679013	0.679013
1.941383	-3.282948	0.304248	0.851666	0.851666	0.851666
3.574804	1.897301	-0.211105	-0.476650	-0.476650	-0.476650
8.409033	1.971179	-1.195918	-0.153288	-0.153288	-0.153288
8.681254	-1.525743	1.258847	0.062744	0.062744	0.062744
5.802727	2.122889	-1.497344	0.038939	0.038939	0.038939
4.995090	1.697979	-2.098312	0.051030	0.051030	0.051030
5.373973	2.903878	-0.857589	0.608439	0.608439	0.608439
6.496376	2.621350	-2.176908	0.914476	0.914476	0.914476
6.132388	-2.131137	1.492608	-0.574259	-0.574259	-0.574259
5.322626	-1.822332	2.158853	-0.812559	-0.812559	-0.812559
5.730082	-2.908348	0.836936	-0.100599	-0.100599	-0.100599
6.918608	-2.579239	2.102738	0.108929	0.108929	0.108929
10.217615	0.350338	0.026303	-0.078932	-0.078932	-0.078932
10.631988	-0.179010	-0.841641	-0.132579	-0.132579	-0.132579
10.541950	1.391767	-0.044982	-1.042274	-1.042274	-1.042274
10.659760	-0.096051	0.920343	0.751526	0.751526	0.751526
-9.468539	-0.231949	0.040975	-0.128093	-0.128093	-0.128093
-10.629109	-0.294782	0.050668	0.131241	0.131241	0.131241
-5.424125	2.300988	0.973732	1.021426	1.021426	1.021426
-5.036662	3.297565	1.429198	-0.773187	-0.773187	-0.773187
-5.172957	-2.315887	-0.919953	0.164254	0.164254	0.164254
-4.614772	-3.260026	-1.306112	-0.024536	-0.024536	-0.024536
			-11.225197	0.003627	-0.062149
			-10.128748	-1.139505	-0.883770
			-10.145634	-1.033493	0.909318

Table S5:

The anion optimized coordinates of the structures at B3LYP/6-31G** level of theory

Anion	
Compound 1	Compound 2

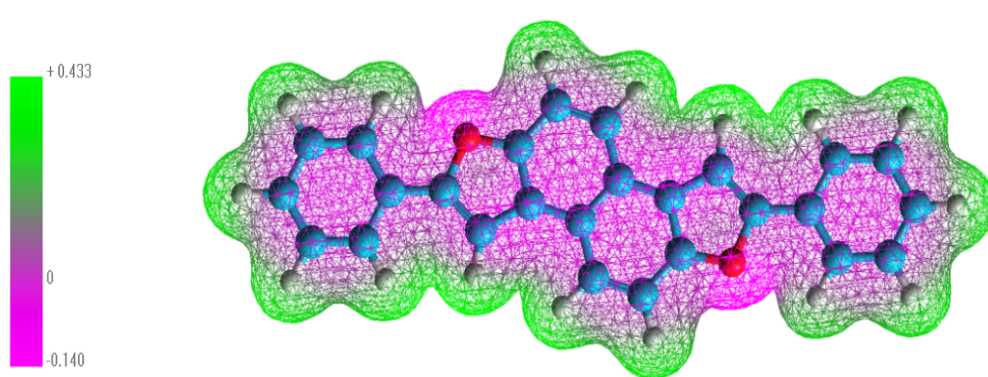
X	Y	Z	X	Y	Z
-3.192108	1.327126	0.206957	0.408578	0.408578	0.408578
0.852595	0.533612	0.060751	0.153301	0.153301	0.153301
0.435112	1.870236	0.277538	0.554966	0.554966	0.554966
-0.913829	2.209874	0.338121	0.662864	0.662864	0.662864
-1.837585	1.182982	0.176655	0.359813	0.359813	0.359813
-1.498098	-0.162595	-0.042581	-0.043688	-0.043688	-0.043688
-2.723563	-0.865801	-0.150227	-0.250007	-0.250007	-0.250007
-3.754687	0.068452	0.006416	0.033291	0.033291	0.033291
-5.169624	-0.002603	0.003753	0.014681	0.014681	0.014681
-5.892215	-1.255736	-0.199988	-0.342338	-0.342338	-0.342338
-7.278010	-1.317412	-0.199355	-0.359877	-0.359877	-0.359877
-8.076964	-0.170161	-0.001579	-0.032472	-0.032472	-0.032472
-7.408295	1.063277	0.198338	0.319682	0.319682	0.319682
-6.025385	1.161852	0.203806	0.347348	0.347348	0.347348
1.187391	2.643546	0.399349	0.782509	0.782509	0.782509
-1.244645	3.229372	0.504321	0.968770	0.968770	0.968770
-2.853575	-1.921098	-0.319661	-0.567385	-0.567385	-0.567385
-7.756409	-2.278308	-0.356398	-0.633123	-0.633123	-0.633123
-7.993116	1.963428	0.352788	0.576041	0.576041	0.576041
3.935988	-1.332801	-0.242097	-0.414936	-0.414936	-0.414936
-0.112564	-0.524274	-0.106958	-0.158098	-0.158098	-0.158098
0.311021	-1.864175	-0.326185	-0.560440	-0.560440	-0.560440
1.644952	-2.221079	-0.386376	-0.670171	-0.670171	-0.670171
2.574777	-1.184646	-0.218450	-0.364675	-0.364675	-0.364675
2.230723	0.149616	-0.005595	0.032472	0.032472	0.032472
3.479365	0.848291	0.104406	0.234547	0.234547	0.234547
4.480846	-0.074082	-0.041406	-0.040171	-0.040171	-0.040171
5.947526	0.017822	-0.006891	-0.024761	-0.024761	-0.024761
6.621467	1.035289	-0.725235	-0.488729	-0.488729	-0.488729
8.018520	1.097886	-0.672598	-0.506344	-0.506344	-0.506344
8.777792	0.188937	0.063635	-0.053768	-0.053768	-0.053768
8.095721	-0.803216	0.774625	0.428305	0.428305	0.428305
6.704458	-0.909202	0.757407	0.449820	0.449820	0.449820
-0.449805	-2.629229	-0.448156	-0.785966	-0.785966	-0.785966
1.963842	-3.244082	-0.552285	-0.975641	-0.975641	-0.975641
3.623283	1.901855	0.292911	0.538654	0.538654	0.538654
8.525389	1.879208	-1.235393	-0.865701	-0.865701	-0.865701
8.664448	-1.512885	1.372331	0.794607	0.794607	0.794607
5.890188	2.060639	-1.562339	-0.055277	-0.055277	-0.055277
5.032424	1.626443	-2.081811	-0.074245	-0.074245	-0.074245
5.503956	2.885213	-0.951015	0.723780	0.723780	0.723780
6.564595	2.498576	-2.304038	1.040019	1.040019	1.040019
6.046204	-1.988205	1.587734	-0.695370	-0.695370	-0.695370
5.216460	-1.587087	2.178122	-0.992696	-0.992696	-0.992696
5.626803	-2.781819	0.963188	-0.919182	-0.919182	-0.919182
6.770465	-2.436672	2.273828	0.952475	0.952475	0.952475
10.286616	0.255306	0.075971	-0.116984	-0.116984	-0.116984
10.724169	-0.457036	-0.635435	-1.467621	-1.467621	-1.467621
10.646126	1.251632	-0.198383	-0.729182	-0.729182	-0.729182
10.690362	0.010394	1.064058	-2.344772	-2.344772	-2.344772
-9.491810	-0.250293	-0.003550	-1.771201	-1.771201	-1.771201
-10.659924	-0.316912	-0.005139	1.439899	1.439899	1.439899
-5.541877	2.493795	0.422065	0.655371	0.655371	0.655371
-5.285297	3.616318	0.607191	2.284764	2.284764	2.284764
-5.240291	-2.506866	-0.415310	1.779930	1.779930	1.779930
-4.767882	-3.559576	-0.595880	0.334813	0.334813	0.334813
			11.267475	-0.152792	0.191806

10.096270	-0.745228	1.398975
10.119702	-1.446274	-0.244275

Table S6:

The Transfer integrals (meV), Centre-to-Centre Distance (Å) and mobilities (cm²/V s) for hole and electron for DPNDF analogues for the four pathways at DFT/pw91pw91/6-31g** level of theory

Molecules	Pathways	Transfer Integrals ^c		Centre-to-Centre Distance	Mobility ^c	
		V _h ^a	V _e		Hole ^b	Electron
Compound 1	i	65.1	114.1	5.071	0.49	2.09
	ii	-20.6	118.4	5.078	4.89×10 ⁻³	2.43
	iii	-2.9	6.2	7.661	4.37×10 ⁻⁶	4.15×10 ⁻⁵
	iv	-15.9	5.7	19.106	2.46×10 ⁻²	1.85×10 ⁻⁴
Compound 2	i	12.9	67	5.078	5.89×10 ⁻³	2.66×10 ⁻⁸
	ii	-6.5	-92	7.661	8.64×10 ⁻⁴	2.15×10 ⁻⁷
	iii	2.65×10 ⁻³	6.64×10 ⁻³	11.969	5.84×10 ⁻¹⁷	1.43×10 ⁻²³
	iv	-0.15738	0.21216	19.108	1.85×10 ⁻⁹	3.79×10 ⁻¹⁷



DPNDF

Figure S2: Molecular electrostatic potential surfaces of two compounds.

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