Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

The external electric field effect on the charge transport performance of organic semiconductors: a theoretical investigation

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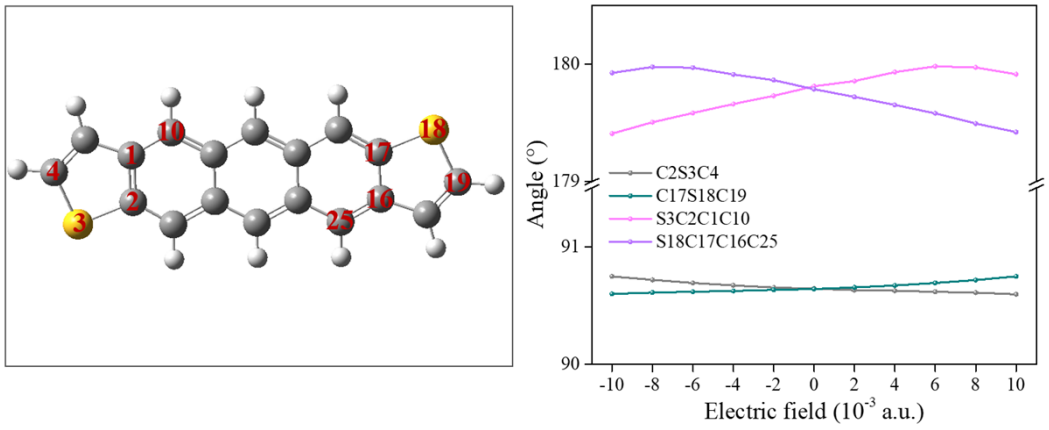

Fig. S1 Bond angle and dihedral angle of ADT at different electric field.

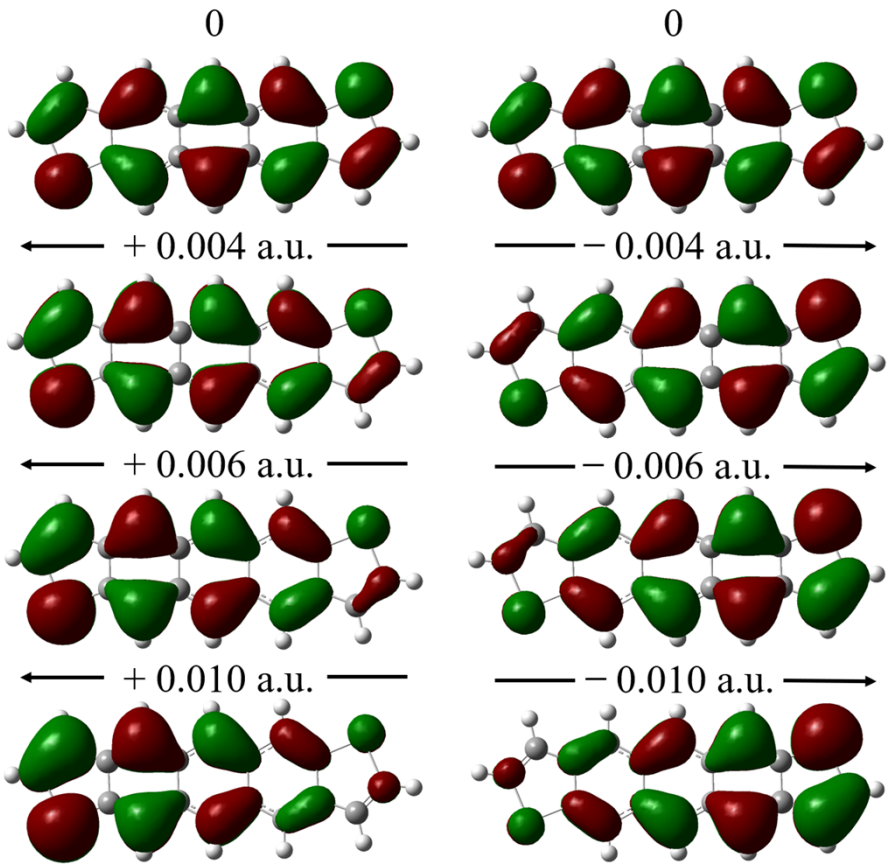

Fig. S2 HOMO distribution of ADT at different electric field.

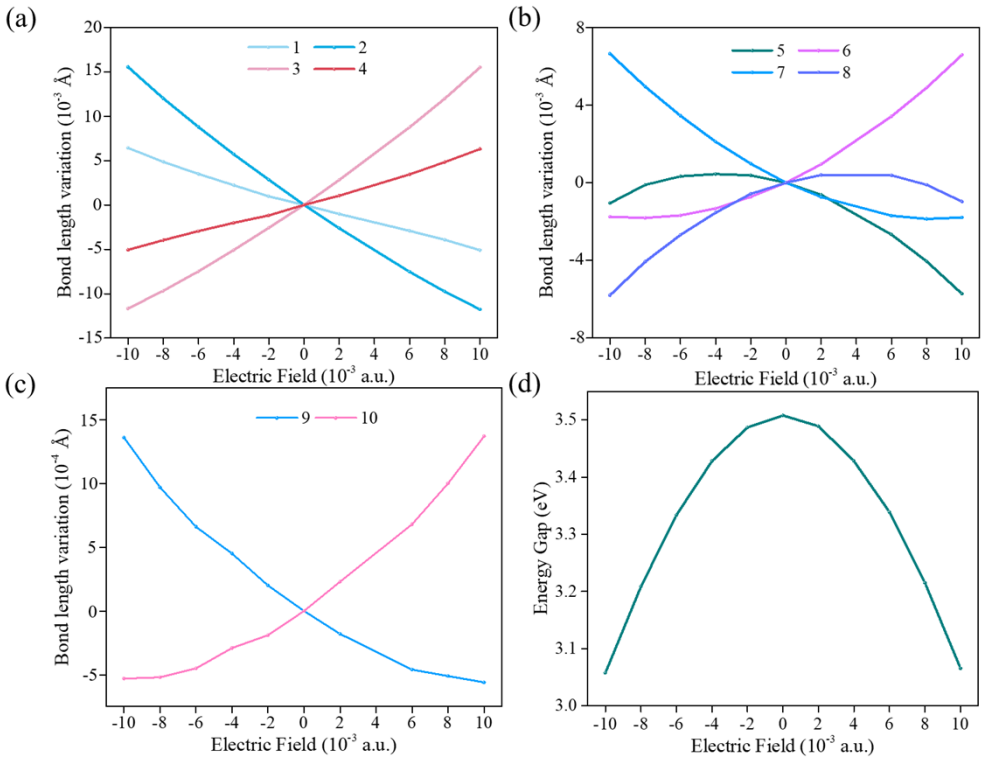

Fig. S3 Bond length variation at different electric field of (a) C-S bond (b) C-C bond and (c) C-H bond in NDT molecule. (d) The energy gap of HOMO and LUMO at different electric field.

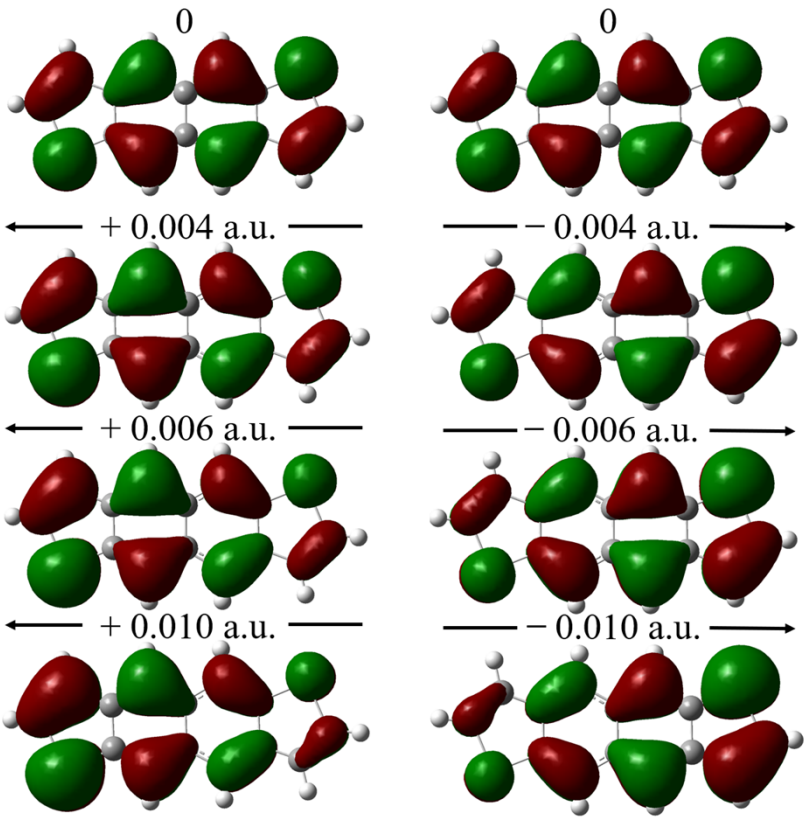

Fig. S4 HOMO distribution of NDT at different electric field.

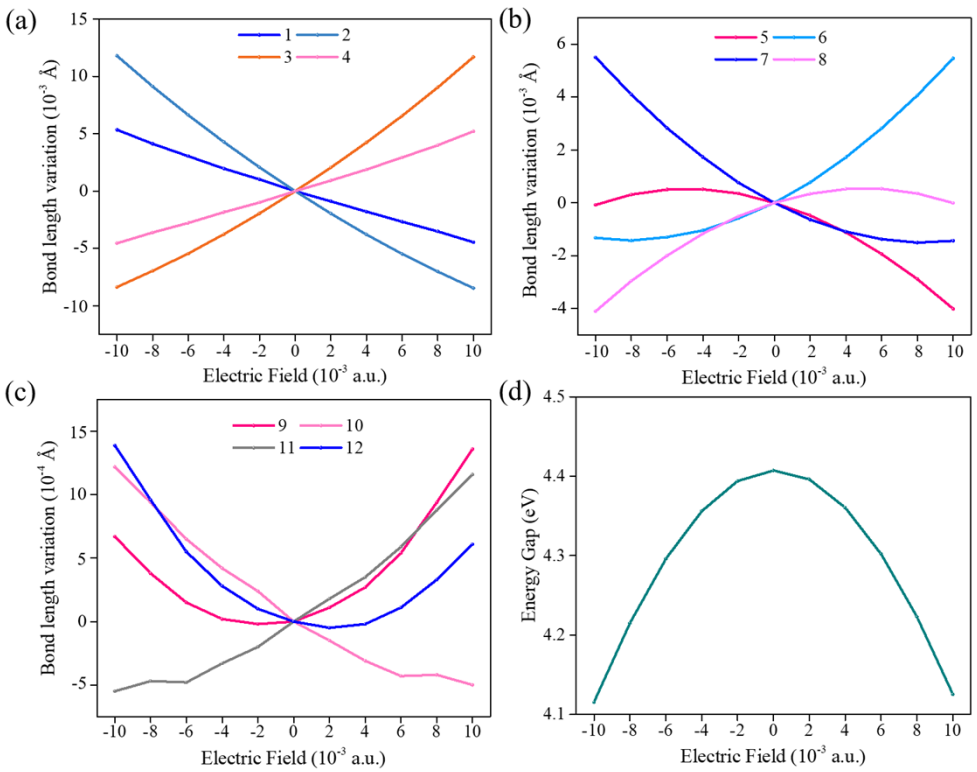

Fig. S5 Bond length variation at different electric field of (a) C-S bond (b) C-C bond and (c) C-H bond in BDT molecule. (d) The energy gap of HOMO and LUMO at different electric field.

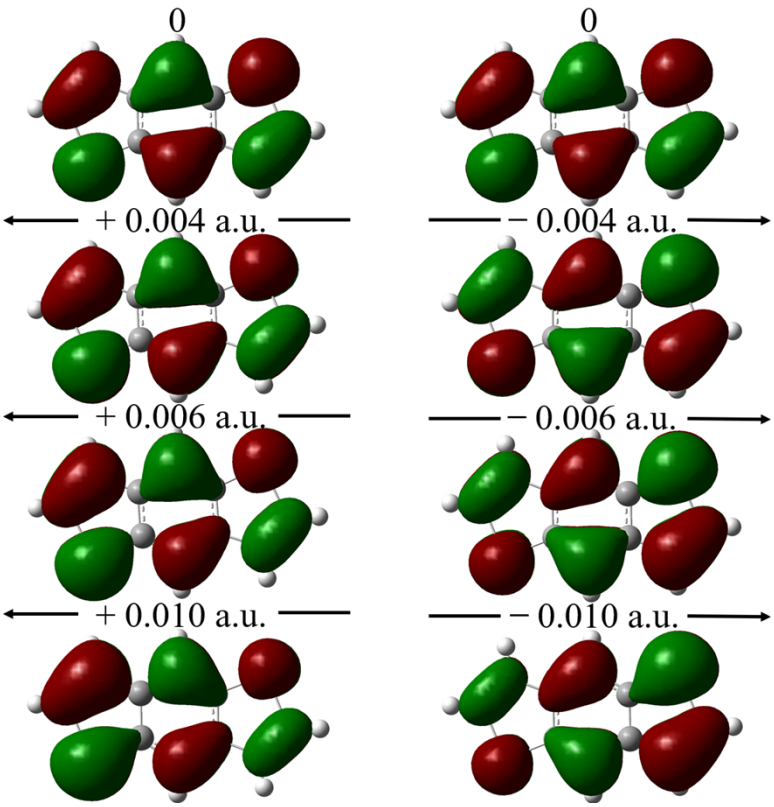

Fig. S6 HOMO distribution of BDT at different electric field.

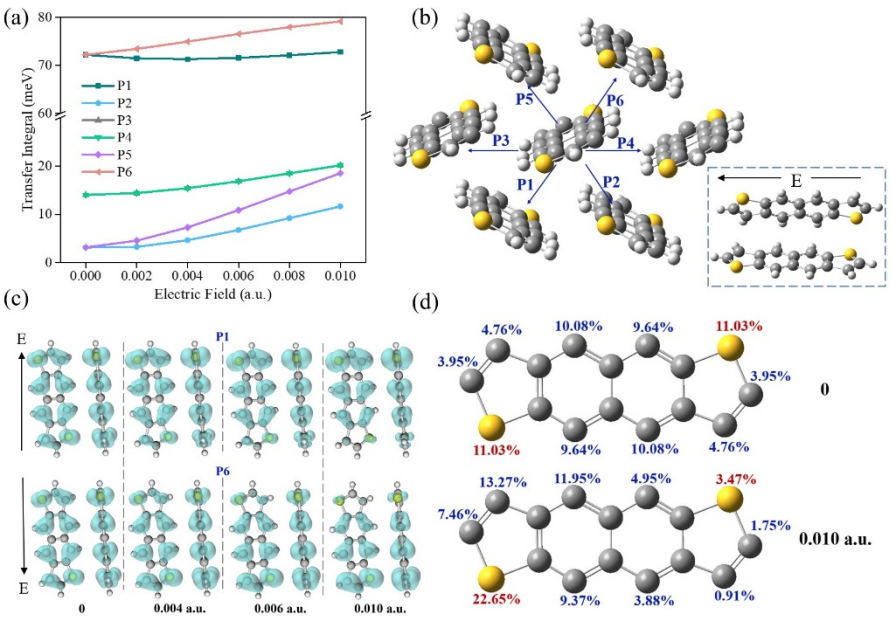

Fig. S7 (a) Transfer Integral of NDT single crystals at different electric field. (b) The stacking modes of NDT in the xy-plane. The insert figure is the enlarged view of dimer molecules in P1 directions. And the direction of electric field is along z-axis. (c) The electron density of HOMO and HOMO-1 orbitals of dimers in P1 and P6 directions at different electric field. (d) The full atom contributions of HOMO orbital of NDT single molecule at 0 and 0.010 a.u. electric field. For clarity, the H atoms are omitted due to the low contributions.

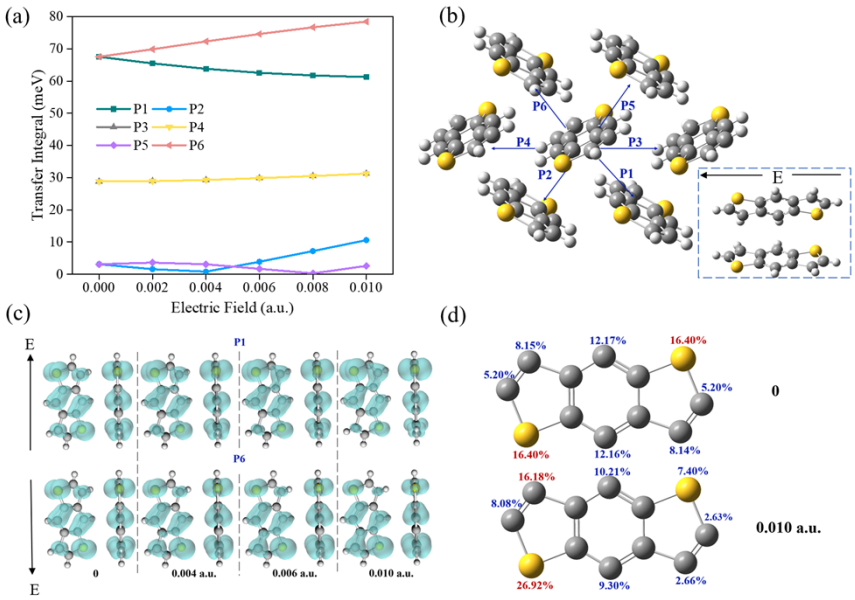

Fig. S8 (a) Transfer Integral of BDT single crystals at different electric field. (b) The stacking modes of BDT in the xy-plane. The insert figure is the enlarged view of dimer molecules in P1 directions. And the direction of electric field is along z-axis. (c) The electron density of HOMO and HOMO-1 orbitals of dimers in P1 and P6 directions at different electric field. (d) The full atom contributions of HOMO orbital of BDT single molecule at 0 and 0.010 a.u. electric field. For clarity, the H atoms are omitted due to the low contributions.

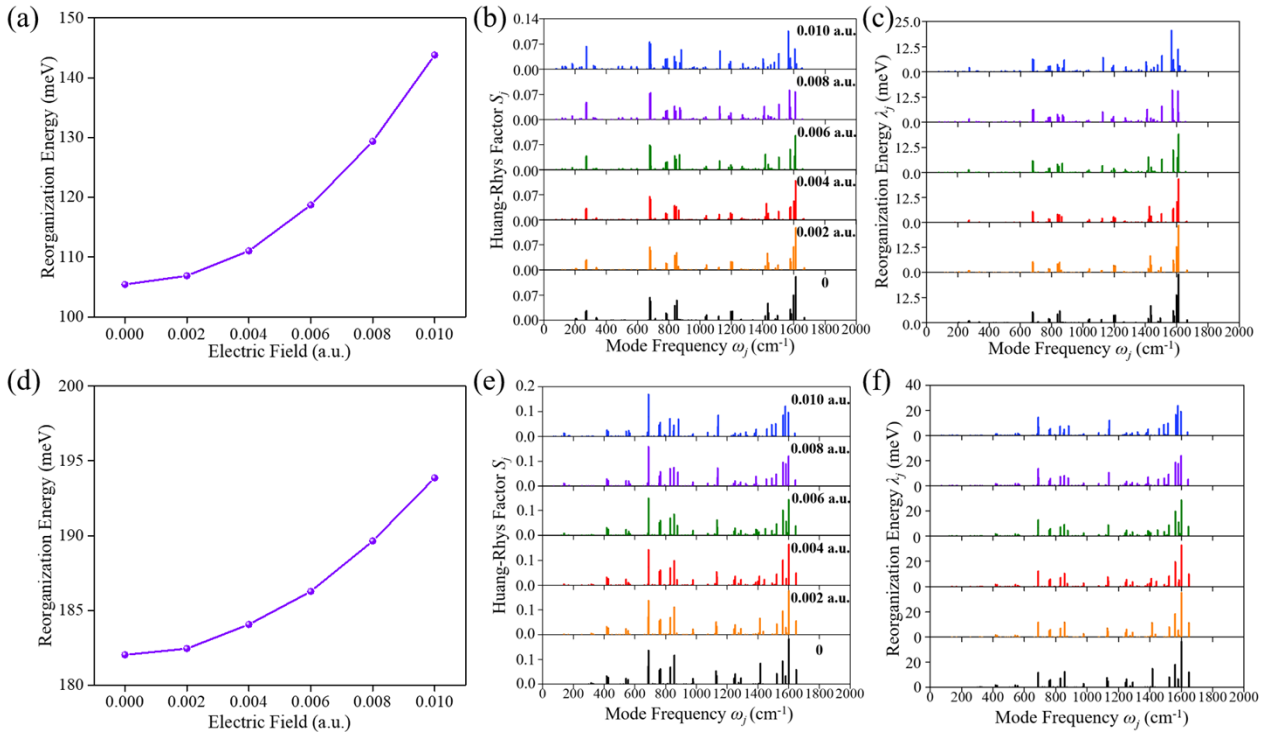

Fig. S9 Reorganization energy λ of NDT (a) and BDT (d) at different electric field. Huang-Rhys factor S_j (b) and reorganization energy λ_j (c) versus mode frequency ω_j between neutral and positively charged NDT at different electric field. Huang-Rhys factor S_j (e) and reorganization energy λ_j (f) versus mode frequency ω_j between neutral and positively charged BDT at different electric field.

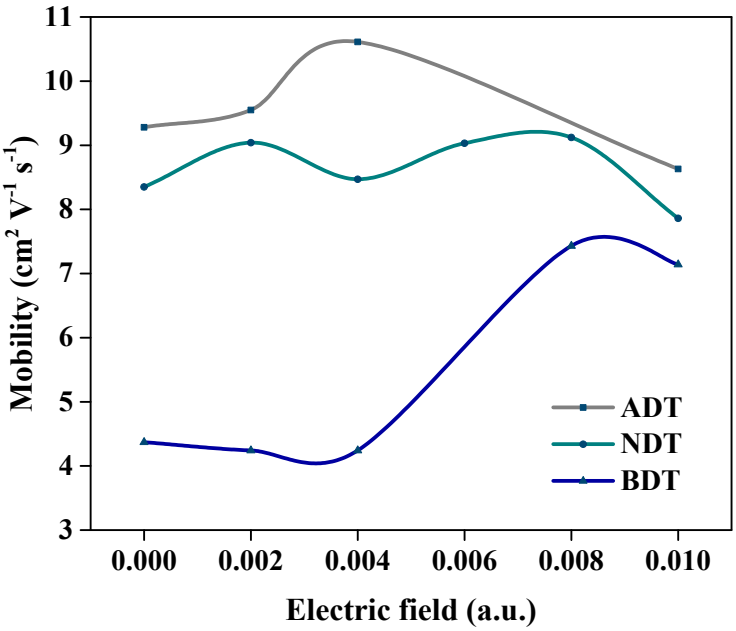

Fig. S10 The hole mobility of ADT, NDT and BDT along the crystallographic b-axis under different electric field.

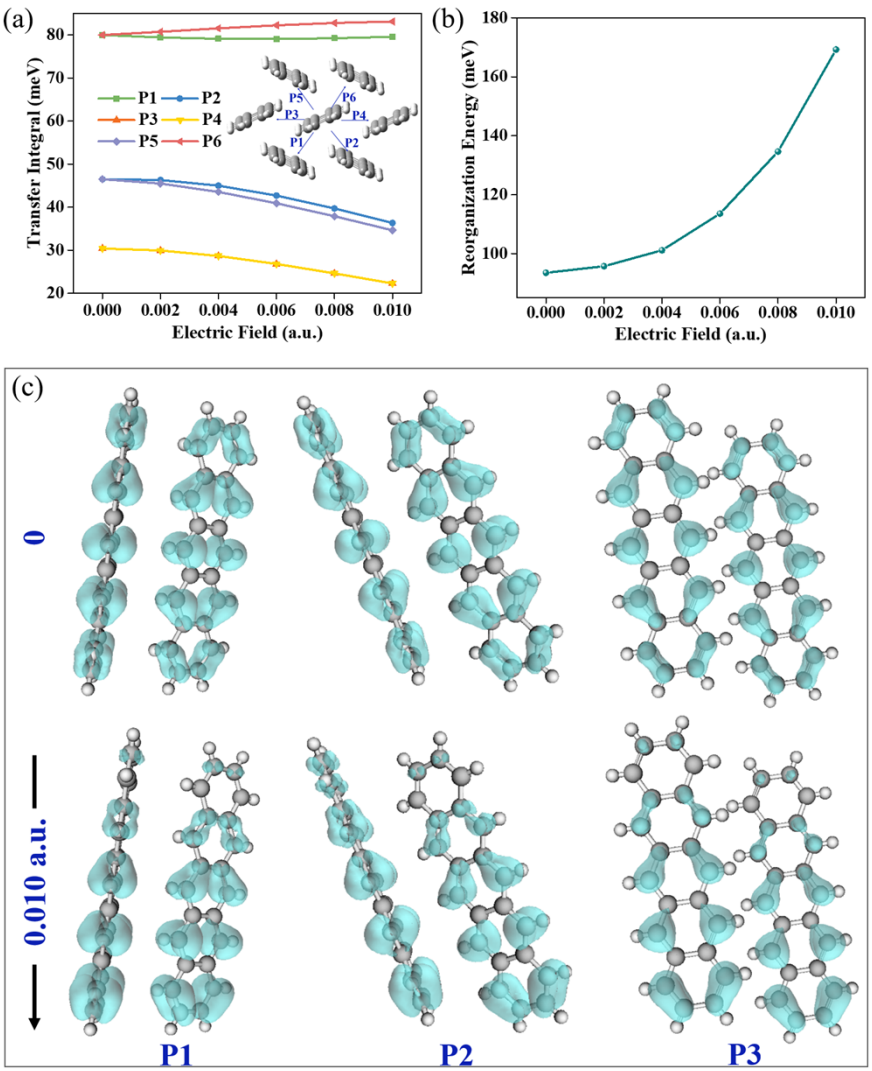

Fig. S11 (a) Transfer integral and (b) reorganization energy of pentacene single crystals at different electric field. The insert figure shows the packing modes of pentacene in the xy-plane. (c) The electron density of HOMO and HOMO-1 orbitals of pentacene dimers in P1, P2 and P3 directions at different electric field.

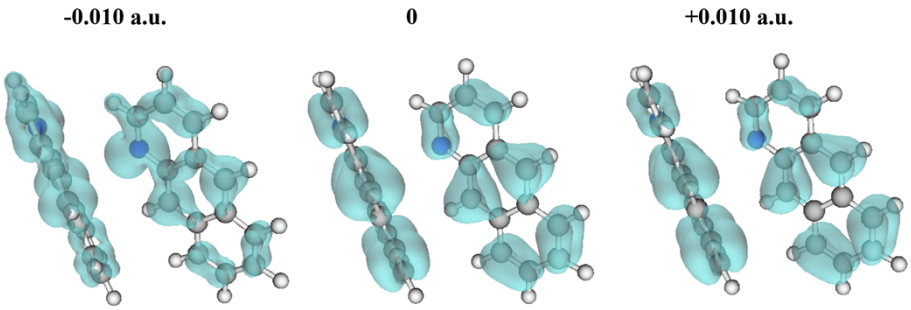

Fig. S12 Electron density of 1-azaanthracene dimer in P1 direction at different electric field. (Considering the difference in energy degeneracy, HOMO and HOMO-1 orbitals are chosen in 0 and +0.010 a.u. electric field, and the isosurface value is set to 0.003. HOMO-3 ~ HOMO orbitals are chosen in -0.010 a.u. electric field, and the isosurface value is set to 0.006 for clarity.)

Table S1. Hole transfer integrals (V), reorganization energies (λ) and charge transfer rate constant (k) of **NDT** and **BDT** at different external electric field.

NDT												
EEF (a.u.)	**Transfer Integral (meV)**						**λ (meV)**	**k ($\times10^{12}$ s^{-1})**				
	P1	**P2**	**P3**	**P4**	**P5**	**P6**		**P1**	**P2**	**P3(4)**	**P5**	**P6**
0	72.22	3.19	14.06	14.06	3.19	72.22	105.43	96.94	0.19	3.68	0.19	96.94
0.002	71.50	3.30	14.43	14.42	4.59	73.44	106.89	93.04	0.20	3.79	0.38	98.15
0.004	71.32	4.68	15.44	15.43	7.33	74.97	111.05	87.25	0.38	4.09	0.92	96.41
0.006	71.58	6.81	16.87	16.87	10.90	76.55	118.72	78.94	0.72	4.38	1.83	90.28
0.008	72.12	9.24	18.51	18.50	14.76	77.99	129.36	69.25	1.14	4.56	2.90	80.98
0.010	72.80	11.67	20.17	20.16	18.54	79.17	143.78	58.24	1.50	4.47	3.78	68.88
BDT												
EEF (a.u.)	**Transfer Integral (meV)**						**λ (meV)**	**k ($\times10^{12}$ s^{-1})**				
	P1	**P2**	**P3**	**P4**	**P5**	**P6**		**P1**	**P2**	**P3(4)**	**P5**	**P6**
0	67.54	3.14	28.81	28.81	3.14	67.54	182.03	30.79	0.07	5.59	0.07	30.79
0.002	65.48	1.60	28.94	28.94	3.64	69.86	182.45	28.79	0.02	5.62	0.09	32.77
0.004	63.80	0.84	29.30	29.30	3.11	72.27	184.06	26.78	0.46	5.64	0.06	34.37
0.006	62.56	3.88	29.85	29.85	1.72	74.59	186.27	25.05	0.10	5.70	0.02	35.62
0.008	61.72	7.23	30.52	30.52	0.28	76.67	189.64	23.41	0.32	5.72	0	36.12
0.010	61.23	10.62	31.26	31.25	2.64	78.43	193.86	21.87	0.65	5.70	0.04	35.89

Table S2. Hole transfer integrals (V), reorganization energies (λ) and charge transfer rate constant (k) of **pentacene** at different external electric field.

EEF (a.u.)	Transfer Integral (meV)						λ (meV)	k ($\times 10^{12}$ s^{-1})				
	P1	P2	P3	P4	P5	P6		P1	P2	P3(4)	P5	P6
0	79.97	46.48	30.40	30.40	46.48	79.97	93.50	141.63	47.85	20.47	47.85	141.63
0.002	79.40	46.31	29.95	29.95	45.50	80.72	95.72	135.07	45.95	19.22	44.36	139.60
0.004	79.09	44.99	28.68	28.68	43.55	81.52	101.12	123.74	40.04	16.27	37.52	131.47
0.006	79.04	42.70	26.82	26.82	40.91	82.23	113.57	103.42	30.18	11.91	27.71	111.94
0.008	79.22	39.70	24.63	24.63	37.90	82.78	134.62	77.84	19.55	7.52	17.82	85.00
0.010	79.55	36.32	22.29	22.29	34.65	83.11	169.25	50.11	10.45	3.93	9.51	54.69

Table S3. Hole transfer integrals (V), reorganization energies (λ) and charge transfer rate constants (k) of **1-Azaanthracene** at different external electric field.

EEF (a.u.)	Transfer Integral (meV)						λ (meV)	k ($\times 10^{12}$ s^{-1})				
	P1	P2	P3	P4	P5	P6		P1	P2	P3(4)	P5	P6
-0.010	26.19	28.17	38.97	38.97	27.62	14.23	162.26	5.93	6.87	13.14	6.60	1.75
-0.008	23.82	25.08	38.00	38.00	23.38	14.46	159.82	5.06	5.61	12.89	4.88	1.87
-0.006	21.18	23.79	37.56	37.56	22.65	14.84	158.64	4.06	5.13	12.78	4.65	2.00
-0.004	19.37	22.87	37.61	37.61	22.34	14.99	158.09	3.42	4.77	12.91	4.55	2.05
-0.002	18.08	21.19	37.85	37.85	22.01	14.94	157.97	2.99	4.10	13.10	4.43	2.04
0	17.08	20.99	38.17	38.17	21.55	14.73	158.78	2.64	3.98	13.18	4.20	1.96
0.002	16.25	19.98	38.53	38.53	20.96	14.39	160.04	2.35	3.55	13.21	3.91	1.84
0.004	15.49	18.89	38.90	38.90	20.23	13.93	161.82	2.09	3.10	13.17	3.56	1.69
0.006	14.75	17.74	39.26	39.26	19.38	13.38	164.52	1.83	2.65	12.96	3.16	1.50
0.008	14.02	16.53	39.60	39.60	18.43	12.76	168.28	1.58	2.19	12.57	2.72	1.30
0.010	13.26	15.27	39.91	39.91	17.40	12.07	173.00	1.33	1.76	12.03	2.29	1.10

Table S4. Hole mobility of 1-Azaanthracene at different external electric field along x- and y-axis.

EEF (a.u.)	Mobility ($cm^2/V/s$)	
	x-axis	**y-axis**
-0.010	1.94	5.76
-0.008	1.61	5.48
-0.006	1.42	5.30
-0.004	1.32	4.99
-0.002	1.21	5.09
0	1.09	5.03
0.002	1.01	4.75
0.004	0.93	4.72
0.006	0.78	4.63
0.008	0.71	4.49
0.010	0.61	4.64