Electronic Supplementary Information

Fascinating Effect of Dehydrogenation on the transport properties of N-Heteropentacenes: Transformation from *p*- to *n*-type Semiconductor

Xiao-Dan Tang,[a, b] Yi Liao,*[a, b] Hua Geng,[c] Zhi-Gang Shuai*[c, d]

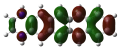
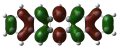
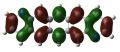
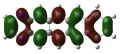
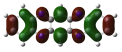
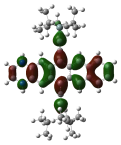
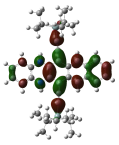
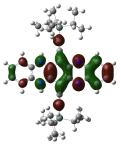
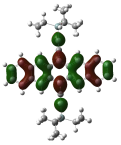
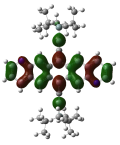
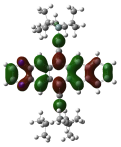
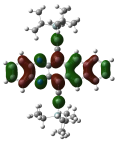
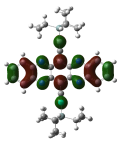
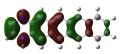
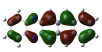
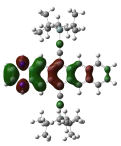
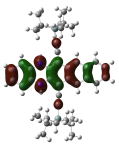
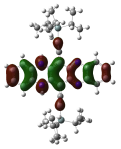
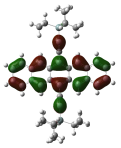
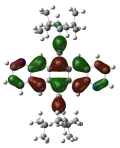
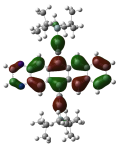
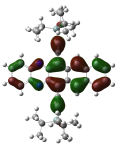
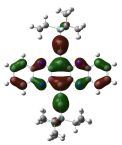
[a] *Department of Chemistry, Capital Normal University, Beijing 100048, People's Republic of China*
[b] *Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, People's Republic of China*
[c] *Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Science (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, P R China*
[d] *Key Laboratory of Organic OptoElectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, 100084 Beijing, P R China*

E-mail addresses: yliao@cnu.edu.cn, zgshuai@tsinghua.edu.cn

Table S1 The reorganization energies of **TIPS-DHDAP-2*p***, **TIPS-DHTAP-2*p***, **TIPS-DAP-2*p*** and **TIPS-TAP-2*p*** calculated with B3LYP/6-31G* and 6-31+G**

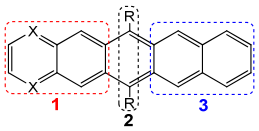
system	λ_h(meV)		λ_e(meV)	
	6-31G*	6-31+G**	6-31G*	6-31+G**
TIPS-DHDAP-2*p*	200.4	198.6	390.6	389.6
TIPS-DHTAP-2*p*	213.1	197.7	333.6	330.7
TIPS-DAP-2*p*	163.3	164.4	199.2	192.8
TIPS-TAP-2*p*	206.8	205.9	205.2	195.1

Table S2 Relative AIP, AEA, HOMO and LUMO energy level (unit: eV) of the systems calculated at B3LYP/6-31G* level

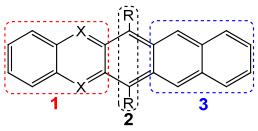
System	**DHDAP-1*p***	**DHDAP-2*p***	**DHTAP- 2*p***	**PEN**	**DAP- 1*t***	**DAP- 1*p***	**DAP-2p**	**TAP- 2*p***
N-PEN								
LUMO level	-1.524	-1.260	-1.895	-2.388	-2.685	-2.756	-2.899	-3.318
AEA	0.388	0.102	0.585	1.123	1.414	1.480	1.607	2.023
TIPS-N-PEN								
LUMO level	-2.017	-2.007	-2.467	-2.721	-2.938	-2.985	-3.422	-3.788
AEA	1.077	0.778	1.164	1.710	1.919	1.961	2.109	2.430
N-PEN								
HOMO level	-4.271	-4.545	-4.844	-4.597	-4.931	-4.903	-5.039	-5.651
AIP	5.602	5.872	6.165	5.888	6.246	6.219	6.357	6.980
TIPS-N-PEN								
HOMO level	-4.447	-4.967	-5.233	-4.620	-4.875	-4.854	-5.222	-5.576
AIP	5.531	5.766	6.026	5.660	5.911	5.895	5.990	6.309

AEA: adiabatic electron affinity; AIP: adiabatic ionization potential.

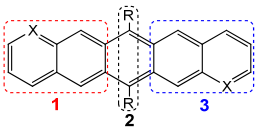
Table S3 The percentage composition of the LUMO and HOMO for all systems in terms of segments 1-3



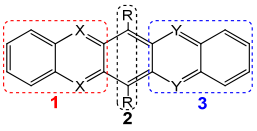
DHDAP-1*p*: X=NH; R=H
DAP-1*p*: X=N; R=H
TIPS-DHDAP-1*p*: X=NH; R=TIPS
TIPS-DAP-1*p*: X=N; R=TIPS



DHDAP-2*p*: X=NH; R=H
DAP-2*p*: X=N; R=H
TIPS-DHDAP-2*p*: X=NH; R=TIPS
TIPS-DAP-2*p*: X=N; R=TIPS



DAP-1*t*: X=N; R=H
TIPS-DAp-1*t*: X=N; R=TIPS



DHTAP-2*p*: X=NH; Y=N; R=H
TAP-2*p*: X=N; R=H
TIPS-DHTAP-2*p*: X=NH; Y=N; R=TIPS
TIPS-TAP-2*p*: X=Y=N; R=TIPS

System	1/%		2/%		3/%		all N atoms/%	
	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO
DHDAP-1*p*	29	*85*	20	*5*	51	*10*	6	*37*
DHDAP-2*p*	22	*72*	14	*10*	64	*18*	4	*33*
DHTAP-2*p*	21	*84*	14	*6*	65	*10*	28	*37*
PEN	38	*37*	24	*26*	38	*37*	0	*0*
DAP-1*t*	39	*36*	22	*28*	39	*36*	7	*5*
DAP-1*p*	51	*29*	21	*26*	28	*45*	15	*2*
DAP-2*p*	52	*21*	21	*26*	27	*53*	25	*8*
TAP-2*p*	40	*33*	20	*34*	40	*33*	36	*25*
TIPS-DHDAP-1*p*	31	*83*	40	*8*	29	*9*	7	*35*
TIPS-DHDAP-2*p*	33	*68*	40	*15*	27	*17*	8	*31*
TIPS-DHTAP-2*p*	32	*65*	21	*17*	47	*18*	32	*33.*
TIPS-PEN	30	*31*	40	*37*	30	*31*	0	*0*
TIPS-DAP-1*t*	31	*29*	38	*42*	31	*29*	5	*4*
TIPS-DAP-1*p*	37	*23*	37	*42*	26	*35*	9	*2*
TIPS-DAP-2*p*	43	*18*	33	*43*	24	*39*	20	*6*
TIPS-TAP-2*p*	34	*20*	32	*60*	34	*20*	31	*14*

Fig. S1 The evolution trends in λ_h and λ_e obtained with BLYP, B3LYP, PBE0 and BHHLYP methods and 6-31G* basis set.

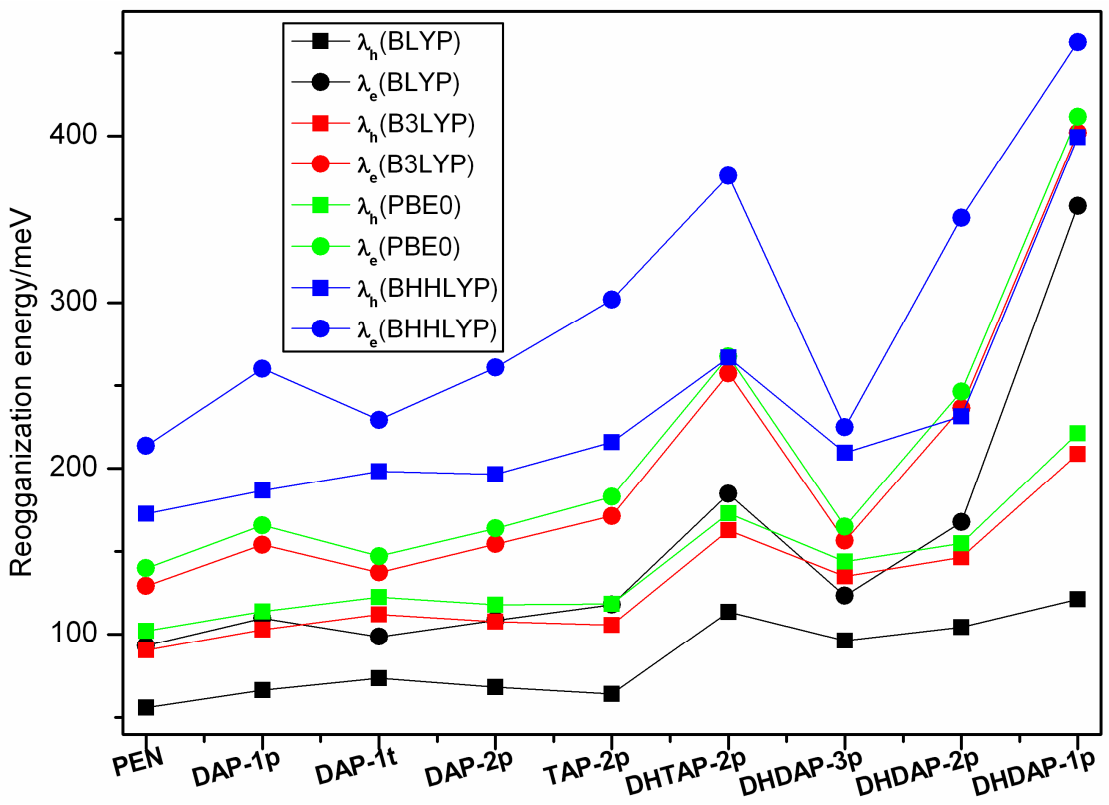


Fig. S2 The molecular packings and dimer type pathways (D1 and D2) of systems **TIPS-DAP-1*p*** (a) and **TIPS-DAP-1*t*** (b). The black, red and blue data represent π···π distance, V_e, and V_h of Dn, respectively.

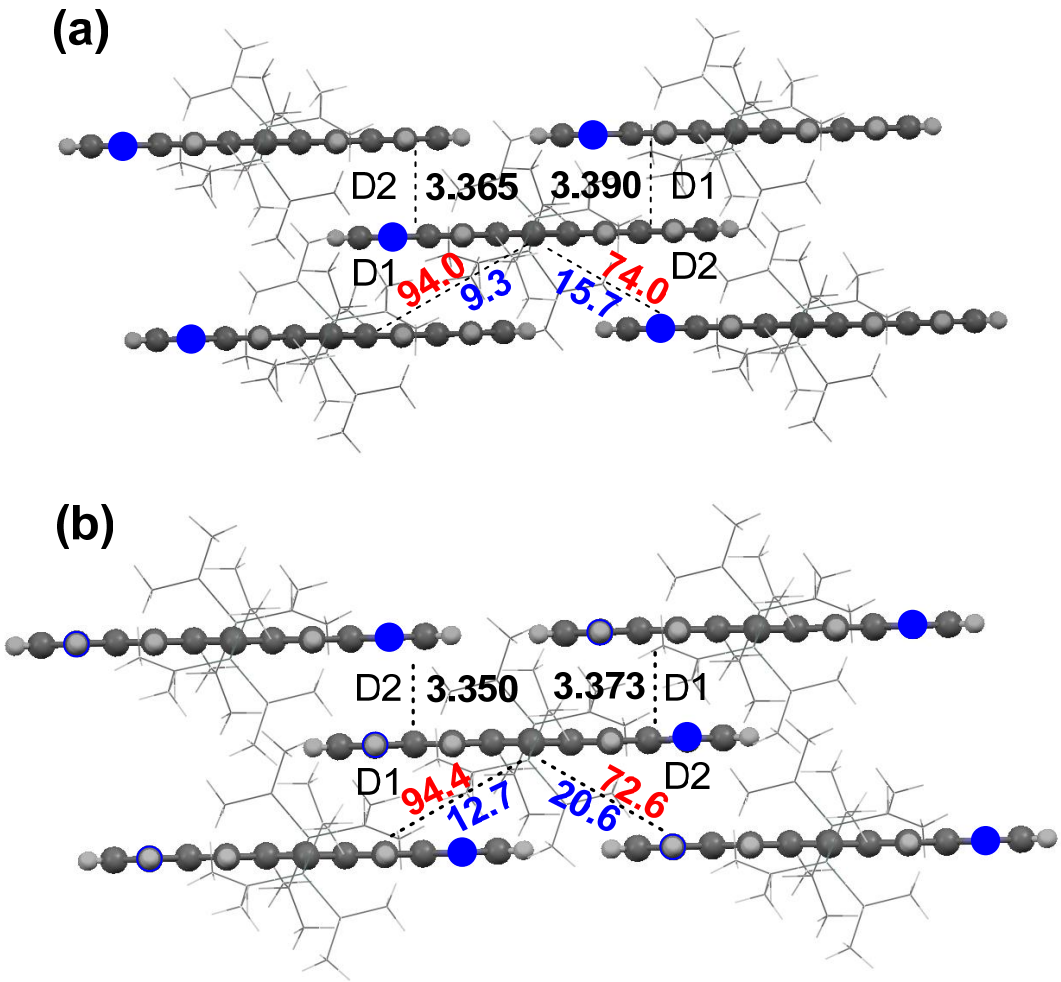


Fig. S3 The relative energy curves of **DHTAP-2*p*** (blue) and **TIPS-DHTAP-2*p*** (black) from 1D-parallel to 2D-brick arrangement with ωB97XD (solid line), B97D (dash line) and B3LYP-D (dot line) functionals at 3-21G* level.

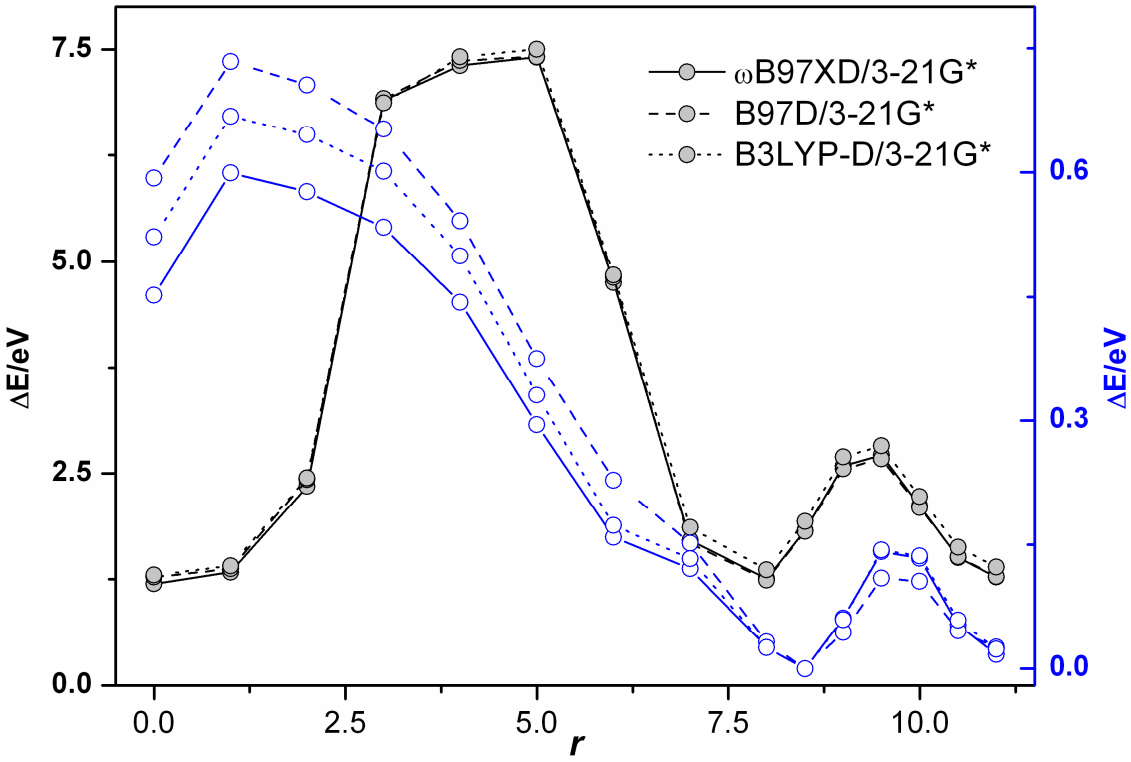


Fig. S4 NBO analysis of C-H···π interactions in **TIPS-DHTAP-2*p*** with 1D-parallel arrangement.