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Supplementary Information

Rational Design of Organic Semiconductors with Low Internal

Reorganization Energies for Hole and Electron Transport:

Position Effect of Aza-Substitution in Phenalenyl Derivatives

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Figure S1. Molecular structures for PLY and its aza-derivatives.



Figure S2. Schematic illustrations of bond length and bond angle alterations between the anionic and neutral states for PLY and β -substituted aza-PLYs.



Figure S3. Schematic illustrations of bond length and bond angle alterations between the anionic and neutral states for PLY and α -substituted aza-PLYs.



Figure S4. Calculated λ 's of each totally symmetric vibrational mode for PLY, β 3N-PLY and α 6N-PLY.



Figure S5. Decomposition of λ^2 into the internal coordinates for PLY, β 3N-PLY and α 6N-PLY. The detailed data are listed in Table S5 to S7.



Figure S6. Totally symmetric vibrational normal modes for PLY, β 3N-PLY and α 6N-PLY. Aminations for these vibrational modes are attached in the Supplementary Information.



Figure S6 (continued). Totally symmetric vibrational normal modes for PLY, β 3N-PLY and α 6N-PLY.



Figure S7. Ionization potential (IP) for PLY and its aza-derivatives.



Figure S8. Electron affinity (EA) for PLY and its aza-derivatives.

Compound	Funcationals ^a	λ^+	λ^{-}
PLY	BLYP	15	32
	B3LYP	19	35
	ωB97	30	42
	OPT-LC- <i>ω</i> B97(<i>ω</i> = 0.246)	22	37
β 3N-PLY	BLYP	8	17
	B3LYP	9	18
	ωB97	13	20
	OPT-LC-ωB97(ω=0.258)	10	19
α 6N-PLY	BLYP	-	56
	B3LYP	58	68
	ωB97	66	93
	OPT-LC- <i>ω</i> B97(<i>ω</i> = 0.302)	63	81

Table S1. Internal reorganization energies for hole (λ^+ , in meV) and electron (λ^- , in meV) transfer of PLY, β 3N-PLY, and α 6N-PLY calculated with different functionals.

^aCalculated at the 6-31G(d,p) basis set

PLY		Bo	nd Lei	ngth		Bond Angle							
N-Freq	а	b	с	α-CH	β-CH		α	β	γ	δ	ø	α-CH	β-CH
627	0.0	0.1	1.1	0.0	0.0	(0.1	0.0	0.0	0.0	0.2	0.0	0.0
788	0.0	0.0	0.2	0.0	0.0	(0.2	1.6	0.0	0.0	0.0	0.5	0.5
1119	0.0	0.0	0.0	0.0	0.0	(0.0	0.0	0.0	0.0	0.0	0.1	0.0
1433	0.0	0.0	0.1	0.0	0.0	(0.0	0.0	0.0	0.0	0.1	0.4	0.0
1561	0.0	0.0	0.0	0.0	0.0	(0.0	0.1	0.0	0.0	0.0	0.3	0.0
3178	0.0	0.0	0.0	0.1	0.0	(0.0	0.0	0.0	0.0	0.0	0.0	0.0
3203	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sum	0.0	0.1	1.4	0.1	0.0		0.4	1.7	0.1	0.0	0.3	1.3	0.5
PLY		Bo	nd Lei	ngth		Bond Angle							
C-Freq	а	b	с	α -CH	β-CH		α	β	γ	δ	ø	α -CH	β-CH
630	0.0	0.1	1.0	0.0	0.0	(0.1	0.0	0.0	0.0	0.2	0.0	0.0
789	0.0	0.0	0.2	0.0	0.0	(0.2	1.7	0.0	0.0	0.0	0.5	0.5
1125	0.0	0.0	0.0	0.0	0.0	(0.0	0.0	0.0	0.0	0.0	0.0	0.0
1452	0.0	0.0	0.1	0.0	0.0	(0.1	0.0	0.0	0.0	0.1	0.5	0.0
1570	0.0	0.0	0.0	0.0	0.0	(0.0	0.1	0.0	0.0	0.0	0.3	0.0
3203	0.0	0.0	0.0	0.0	0.0	(0.0	0.0	0.0	0.0	0.0	0.0	0.0
3230	0.0	0.0	0.0	0.1	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sum	0.0	0.1	1.4	0.1	0.0	(0.4	1.7	0.1	0.0	0.3	1.4	0.5

Table S2. Internal reorganization energies (in meV) contributed from each bond length and bond angle in the normal mode (in cm⁻¹) of neutral and cationic states for PLY.

Table S3. Internal reorganization energies (in meV) contributed from each bond length and bond angle in the normal mode (in cm⁻¹) of neutral and cationic states for β 3N-PLY.

β3N-PLY		Bond Length						Bond Angle							
N-Freq	a	b	с	α-CH	β-CH		α	β	γ	δ	φ	α -CH	β-CH		
617	0.0	0.0	0.2	0.0	_		0.2	0.0	0.0	0.0	0.0	0.0			
797	0.0	0.0	0.0	0.0			0.1	0.1	0.0	0.0	0.0	0.1			
1204	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	0.0	0.2			
1451	0.0	0.0	0.1	0.0	—		0.2	0.0	0.0	0.0	0.0	0.6			
1528	0.0	0.0	0.0	0.0	_		0.0	0.0	0.0	0.0	0.0	0.2			
3172	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	0.0	0.0			
Sum	0.0	0.0	0.3	0.0			0.5	0.1	0.0	0.0	0.0	1.0			
β3N-PLY		Bo	nd Ler	ngth			Bond Angle								
C-Freq	a	b	с	α-CH	β-CH		α	β	γ	δ	φ	α-CH	β-CH		
616	0.0	0.0	0.2	0.0	_		0.2	0.0	0.0	0.0	0.0	0.0	_		
795	0.0	0.0	0.0	0.0	—		0.1	0.1	0.0	0.0	0.0	0.1	—		
1208	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	0.0	0.1	—		
1464	0.0	0.0	0.2	0.0			0.2	0.0	0.0	0.0	0.0	0.7			
1529	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	0.0	0.2	_		
3186	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	0.0	0.0	_		
Sum	0.0	0.0	0.3	0.0			0.5	0.1	0.0	0.0	0.0	1.0			

α6N-PLY		Bo	nd Ler	ngth		Bond Angle							
N-Freq	а	b	с	α-CH	β-CH	α	β	γ	δ	ø	α-CH	β-CH	
673	0.0	0.0	0.0	—	0.0	0.0	0.0	0.0	0.0	0.0		0.0	
861	0.2	0.0	0.7	—	0.0	3.5	7.0	0.1	0.0	0.2	—	2.1	
1275	3.0	0.0	1.2	—	0.0	0.5	0.8	0.4	0.0	2.0	—	0.2	
1534	0.0	0.0	0.1	—	0.0	0.1	0.1	0.0	0.0	0.0	—	0.0	
3192	0.0	0.0	0.0	—	0.2	0.0	0.0	0.0	0.0	0.0	—	0.0	
Sum	3.2	0.0	2.1		0.2	4.1	7.9	0.5	0.0	2.2		2.4	
GAN DI V						Bond Angle							
aon-PL I		Bo	nd Ler	ngth				Bo	ond An	gle			
C-Freq	a	Bo b	nd Ler c	ngth α-CH	β-CH	α	β	<u>Β</u> α	ond An δ	gle ø	α-CH	β-CH	
C-Freq 674	a 0.0	Bo b 0.0	nd Ler c 0.0	ngth α-CH —	β-CH 0.0	α 0.0	β 0.0	<u>γ</u> 0.0	$\frac{\delta}{0.0}$	gle	α-CH	β-CH 0.0	
<u>C-Freq</u> 674 848	a 0.0 0.2	Bo b 0.0 0.0	nd Ler <u>c</u> 0.0 0.7	ngth α-CH —	β-CH 0.0 0.0	α 0.0 3.3	β 0.0 6.6	γ 0.0 0.0	$\frac{\delta}{0.0}$	gle	α-CH	β-CH 0.0 2.0	
<u>C-Freq</u> 674 848 1270	a 0.0 0.2 3.3	Bo b 0.0 0.0 0.0	nd Ler c 0.0 0.7 1.4	ngth α-CH — —	β-CH 0.0 0.0 0.0	α 0.0 3.3 0.5	β 0.0 6.6 0.9	$\begin{array}{r} & & \\ \hline \gamma \\ \hline 0.0 \\ 0.0 \\ 0.5 \end{array}$	<u>δ</u> 0.0 0.0 0.0	gle φ 0.0 0.2 2.2	α-CH	β-CH 0.0 2.0 0.3	
<u>C-Freq</u> 674 848 1270 1546	a 0.0 0.2 3.3 0.0	Bo 0.0 0.0 0.0 0.0 0.0	nd Ler c 0.0 0.7 1.4 0.1	ngth α-CH — — —	β-CH 0.0 0.0 0.0 0.0	α 0.0 3.3 0.5 0.1	β 0.0 6.6 0.9 0.1	γ 0.0 0.0 0.5 0.0	δ 0.0 0.0 0.0 0.0 0.0 0.0	gle φ 0.0 0.2 2.2 0.0	α-CH 	β-CH 0.0 2.0 0.3 0.0	
<u>C-Freq</u> 674 848 1270 1546 3230	a 0.0 0.2 3.3 0.0 0.0	Bo 0.0 0.0 0.0 0.0 0.0 0.0	nd Ler c 0.0 0.7 1.4 0.1 0.0	ngth α-CH — — — —	β-CH 0.0 0.0 0.0 0.0 0.2		β 0.0 6.6 0.9 0.1 0.0	γ 0.0 0.0 0.5 0.0 0.0	δ 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	gle φ 0.0 0.2 2.2 0.0 0.0 0.0	α-CH	β-CH 0.0 2.0 0.3 0.0 0.0	

Table S4. Internal reorganization energies (in meV) contributed from each bond length and bond angle in the normal mode (in cm⁻¹) of neutral and cationic states for α 6N-PLY.

Table S5. Internal reorganization energies (in meV) contributed from each bond length and bond angle in the normal mode (in cm⁻¹) of neutral and anionic states for PLY.

PLY		Bond Length						Bond Angle								
N-Freq	a	b	с	α-CH	β-CH		α	β	γ	δ	ø	α-CH	β-CH			
627	0.0	0.5	3.3	0.0	0.0		0.6	0.0	0.1	0.0	0.5	0.0	0.0			
788	0.0	0.0	0.4	0.0	0.0		0.6	2.5	0.0	0.0	0.0	0.6	0.8			
1119	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0			
1433	0.0	0.0	0.2	0.0	0.0		0.1	0.0	0.0	0.0	0.1	0.5	0.0			
1561	0.0	0.0	0.0	0.0	0.0		0.0	0.1	0.0	0.0	0.0	0.4	0.0			
3178	0.0	0.0	0.0	0.1	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0			
3203	0.0	0.0	0.0	0.9	0.1		0.0	0.0	0.0	0.0	0.0	0.0	0.0			
Sum	0.0	0.6	3.9	1.0	0.1		1.4	2.7	0.1	0.0	0.6	1.5	0.8			
PLY		Bo	nd Lei	ngth		Bond Angle										
A-Freq	a	b	с	α-CH	β-CH		α	β	γ	δ	ø	α -CH	β-CH			
622	0.0	0.5	3.5	0.0	0.0		0.7	0.0	0.1	0.0	0.5	0.0	0.0			
784	0.0	0.0	0.3	0.0	0.0		0.6	2.4	0.0	0.0	0.0	0.6	0.7			
1113	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0			
1406	0.0	0.0	0.1	0.0	0.0		0.1	0.0	0.0	0.0	0.1	0.4	0.0			
1552	0.0	0.0	0.0	0.0	0.0		0.0	0.1	0.0	0.0	0.0	0.4	0.0			
3115	0.0	0.0	0.0	0.4	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0			
3161	0.0	0.0	0.0	0.6	0.1		0.0	0.0	0.0	0.0	0.0	0.0	0.0			
Sum	0.0	0.6	3.9	1.0	0.1		1.4	2.5	0.1	0.0	0.6	1.4	0.8			

B3N-PLY		Bo	nd Lei	ngth		Bond Angle								
N-Freq	a	b	с	α -CH	β-CH		α	β	γ	δ	φ	α -CH	β-CH	
617	0.0	0.1	0.6	0.0	_	_	0.8	0.2	0.0	0.0	0.0	0.1		
797	0.0	0.0	0.1	0.0			0.2	0.3	0.0	0.0	0.0	0.1	—	
1204	0.0	0.0	0.0	0.0			0.2	0.0	0.0	0.0	0.0	0.5		
1451	0.0	0.0	0.2	0.0			0.3	0.0	0.0	0.0	0.0	0.5	—	
1528	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	0.0	0.4	—	
3172	0.0	0.0	0.0	0.3			0.0	0.0	0.0	0.0	0.0	0.0	_	
Sum	0.0	0.1	0.8	0.3			1.5	0.5	0.0	0.0	0.1	1.6		
B3N DI V	Bond Length						Bond Angle							
p311-1 L 1		Bo	nd Lei	ngth		_			Bo	ond Ang	gle			
A-Freq	а	Bo b	nd Lei c	ngth α-CH	β-CH	-	α	β	<u>γ</u>	ond Ang δ	gle ø	α-CH	β-CH	
<u>A-Freq</u> 616	a 0.0	Bo b 0.1	nd Lei c 0.6	$\frac{\alpha - CH}{0.0}$	β-CH	-	α 0.8	β 0.2	γ 0.0	$\frac{\delta}{0.0}$	gle	α-CH 0.1	β-CH	
<u>A-Freq</u> 616 795	a 0.0 0.0	Bo 0.1 0.0	nd Lei c 0.6 0.1	ngth α-CH 0.0 0.0	β-CH	-	α 0.8 0.2	β 0.2 0.2	γ 0.0 0.0	$\frac{\delta}{0.0}$	φ 0.0 0.0	α-CH 0.1 0.1	β-CH	
A-Freq 616 795 1200	a 0.0 0.0 0.0	Bo 0.1 0.0 0.0	nd Lei c 0.6 0.1 0.0	ngth α-CH 0.0 0.0 0.0	β-CH	_	α 0.8 0.2 0.2	β 0.2 0.2 0.0	γ 0.0 0.0 0.0	δ 0.0 0.0 0.0 0.0	φ 0.0 0.0 0.0	α-CH 0.1 0.1 0.6	β-CH	
A-Freq 616 795 1200 1430	a 0.0 0.0 0.0 0.0	Bo 0.1 0.0 0.0 0.0	nd Lei <u>c</u> 0.6 0.1 0.0 0.1	ngth α-CH 0.0 0.0 0.0 0.0	β-CH — —	_	α 0.8 0.2 0.2 0.3	β 0.2 0.2 0.0 0.0	γ 0.0 0.0 0.0 0.0 0.0	$\frac{\delta}{0.0}$ 0.0 0.0 0.0 0.0	φ 0.0 0.0 0.0 0.0 0.0	α-CH 0.1 0.6 0.5	β-CH	
A-Freq 616 795 1200 1430 1524	a 0.0 0.0 0.0 0.0 0.0	Bo 0.1 0.0 0.0 0.0 0.0	nd Lei c 0.6 0.1 0.0 0.1 0.0	ngth α-CH 0.0 0.0 0.0 0.0 0.0 0.0	β-CH — — —	_	α 0.8 0.2 0.2 0.3 0.0	β 0.2 0.2 0.0 0.0 0.0	γ 0.0 0.0 0.0 0.0 0.0 0.0 0.0		φ 0.0 0.0 0.0 0.0 0.0 0.0	α-CH 0.1 0.6 0.5 0.4	β-CH — — —	
A-Freq 616 795 1200 1430 1524 3129	a 0.0 0.0 0.0 0.0 0.0 0.0	Bo 0.1 0.0 0.0 0.0 0.0 0.0	nd Lei c 0.6 0.1 0.0 0.1 0.0 0.0 0.0		β-CH — — — —	_	α 0.8 0.2 0.2 0.3 0.0 0.0	β 0.2 0.0 0.0 0.0 0.0 0.0	γ 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0		gle φ 0.0 0.0 0.0 0.0 0.0 0.0 0.0	α-CH 0.1 0.6 0.5 0.4 0.0	β-CH	

Table S6. Internal reorganization energies (in meV) contributed from each bond length and bond angle in the normal mode (in cm⁻¹) of neutral and anionic states for β 3N-PLY.

Table S7. Internal reorganization energies (in meV) contributed from each bond length and bond angle in the normal mode (in cm⁻¹) of neutral and anionic states for α 6N-PLY.

α6N-PLY		Bond Length						Bond Angle								
N-Freq	а	b	с	α-CH	β-CH		α	β	γ	δ	ø	α-CH	β-CH			
673	0.1	0.1	0.6	_	0.0	-	0.0	0.0	0.0	0.0	0.1	_	0.0			
861	0.1	0.0	0.7	—	0.0		0.4	10.5	0.0	0.0	0.2	—	3.2			
1275	2.2	0.0	1.4		0.0		0.1	1.3	0.4	0.0	1.6		0.4			
1534	0.1	0.1	0.3		0.0		0.0	0.4	0.0	0.0	0.1		0.1			
3192	0.0	0.0	0.0		1.7		0.0	0.0	0.0	0.0	0.0		0.0			
Sum	2.5	0.2	3.0		1.7		0.5	12.2	0.4	0.0	1.9		3.6			
α6N-PLY		Bo	nd Lei	ngth		Bond Angle										
A-Freq	а	b	с	α-CH	β-CH		α	β	γ	δ	ø	α-CH	β-CH			
671	0.1	0.1	0.7	_	0.0	-	0.0	0.0	0.0	0.0	0.1		0.0			
873	0.1	0.0	0.8		0.0		0.4	11.0	0.0	0.0	0.2	_	3.3			
1279	1.9	0.0	1.2	_	0.0		0.0	1.1	0.3	0.0	1.4		0.3			
1519	0.1	0.1	0.4		0.0		0.1	0.6	0.0	0.0	0.1		0.2			
3104	0.0	0.0	0.0		1.4		0.0	0.0	0.0	0.0	0.0		0.0			
Sum	2.3	0.3	3.1	_	1.4		0.5	12.7	0.4	0.0	1.7		3.8			