Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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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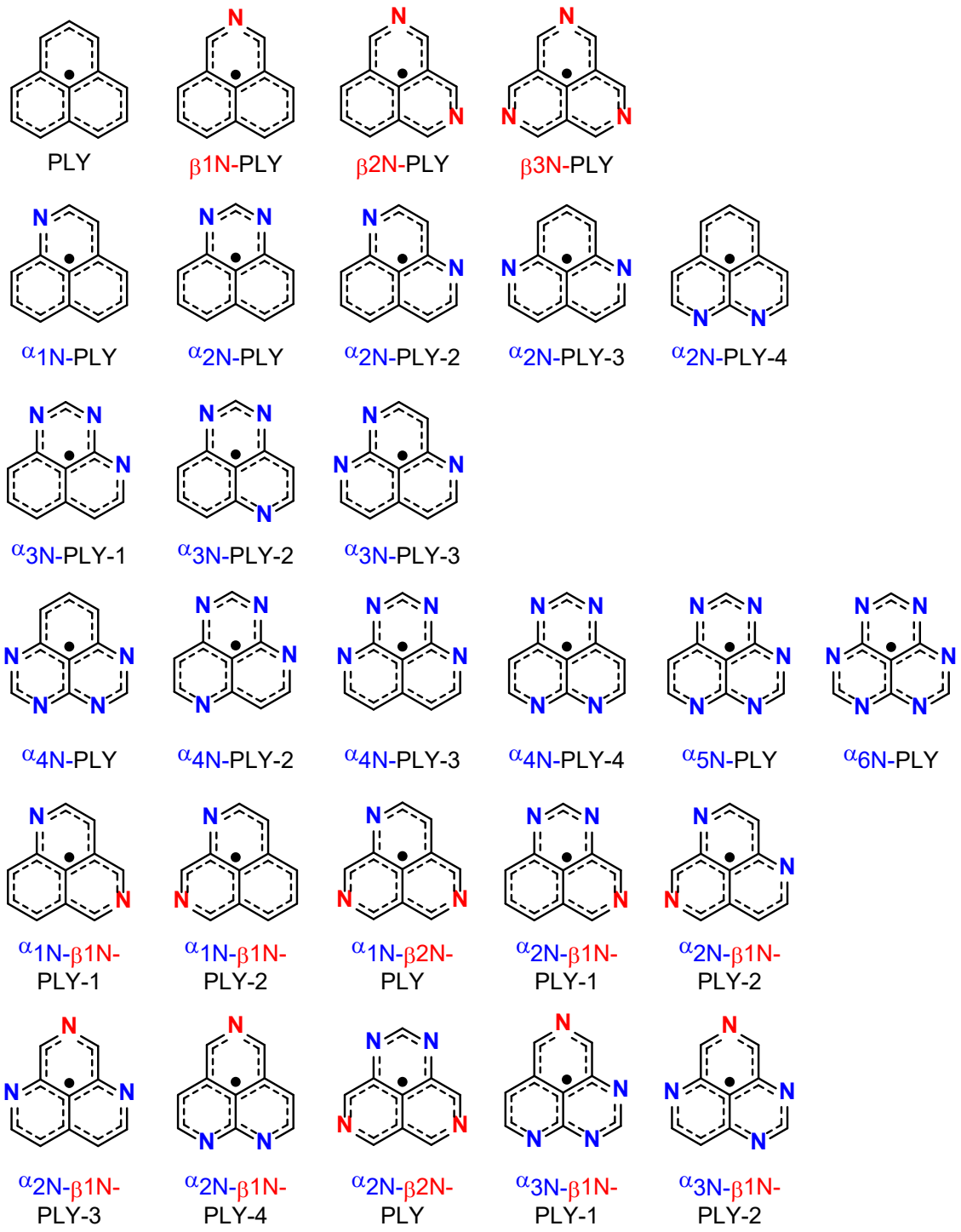

Figure S1. Molecular structures for PLY and its aza-derivatives.

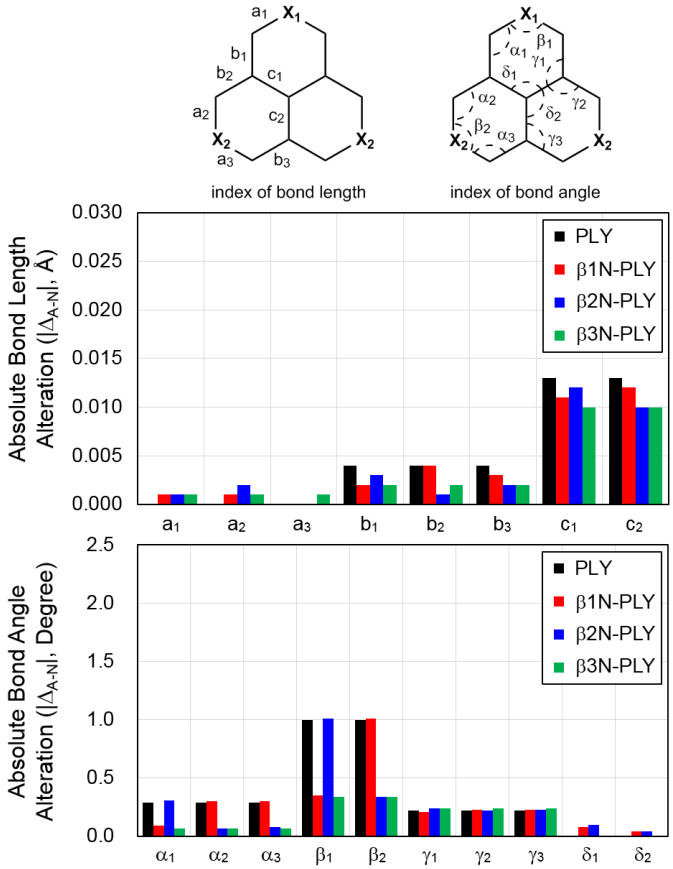

Figure S2. Schematic illustrations of bond length and bond angle alterations between the anionic and neutral states for PLY and β-substituted aza-PLYs.

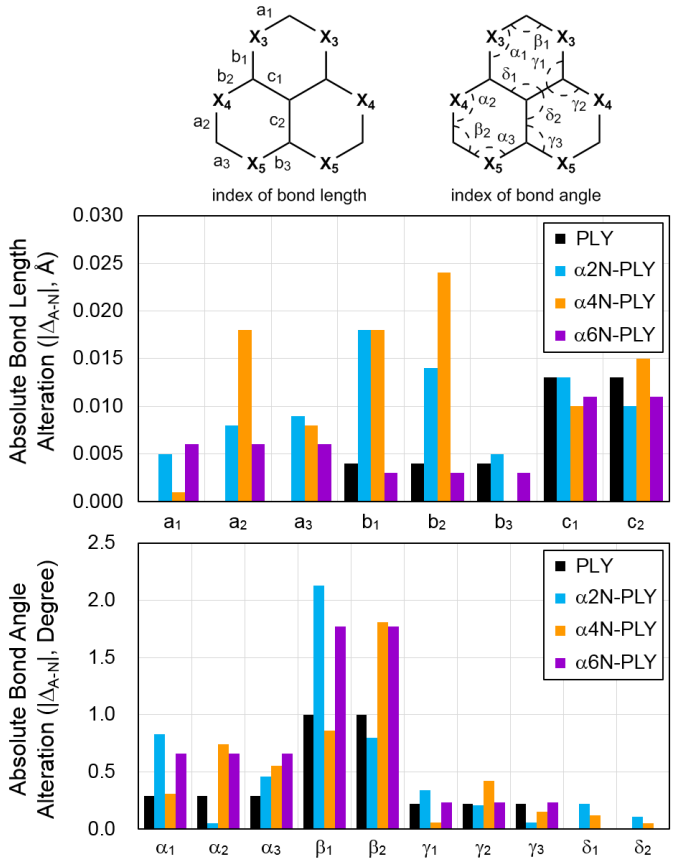

Figure S3. Schematic illustrations of bond length and bond angle alterations between the anionic and neutral states for PLY and α-substituted aza-PLYs.

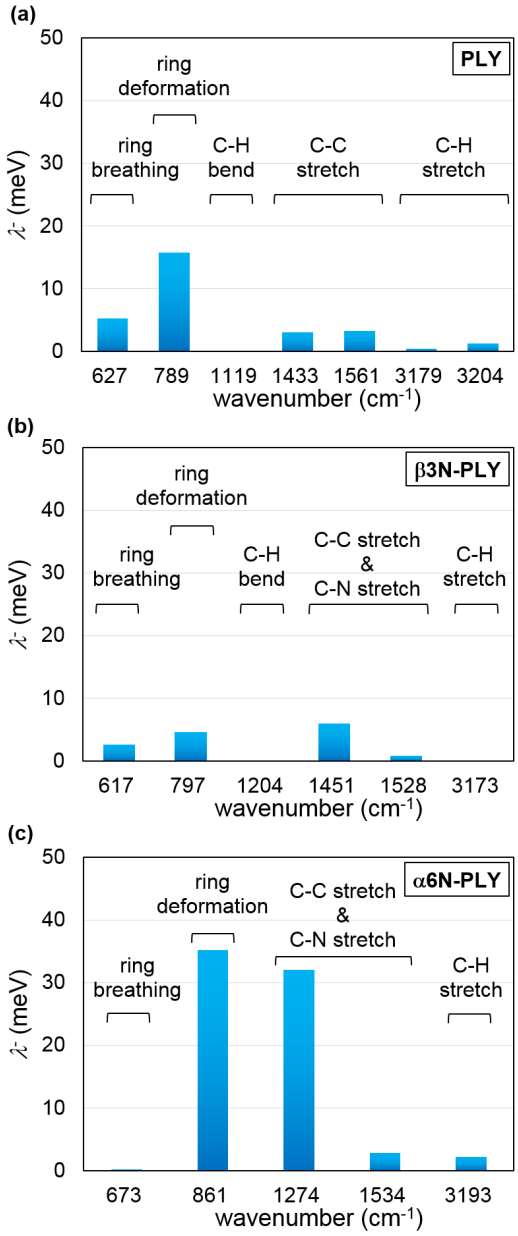

Figure S4. Calculated λ^-s of each totally symmetric vibrational mode for PLY, β3N-PLY and α6N-PLY.

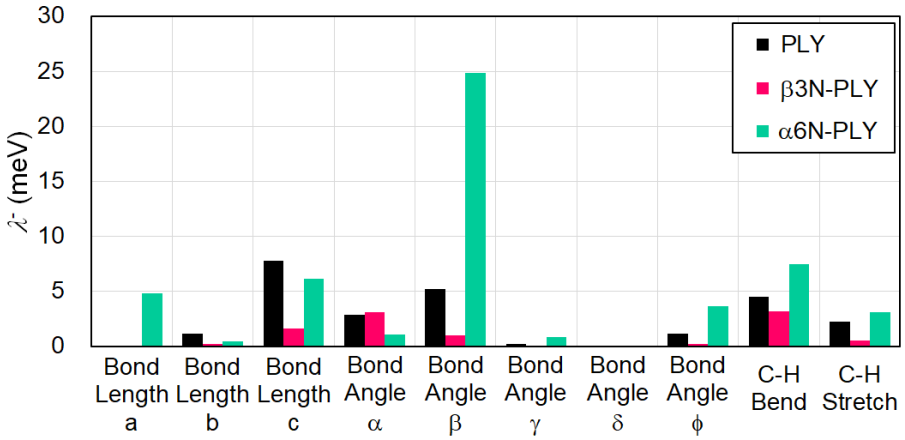

Figure S5. Decomposition of λ^- into the internal coordinates for PLY, β3N-PLY and α6N-PLY. The detailed data are listed in Table S5 to S7.

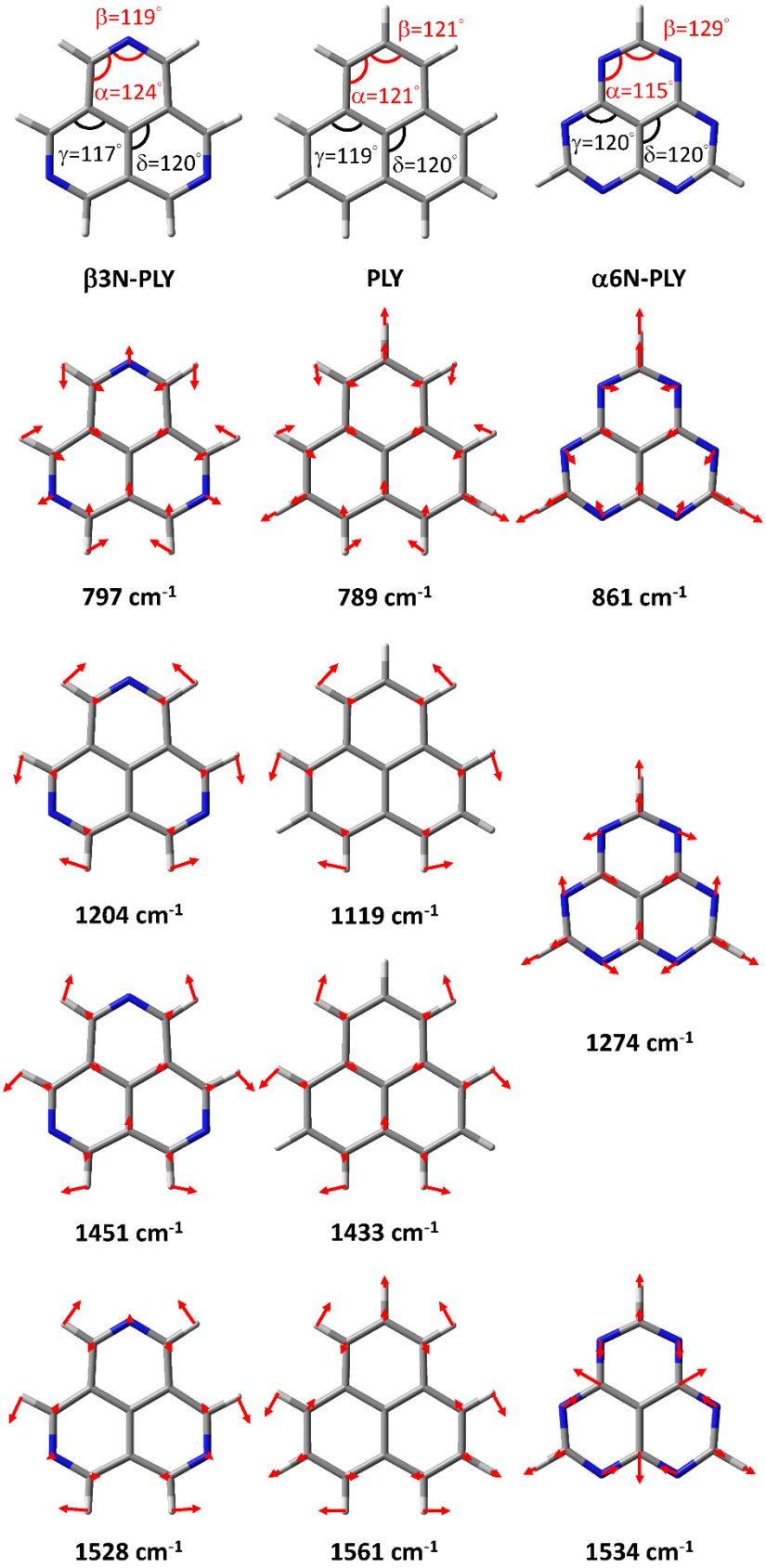

Figure S6. Totally symmetric vibrational normal modes for PLY, β3N-PLY and α6N-PLY. Aminations for these vibrational modes are attached in the Supplementary Information.

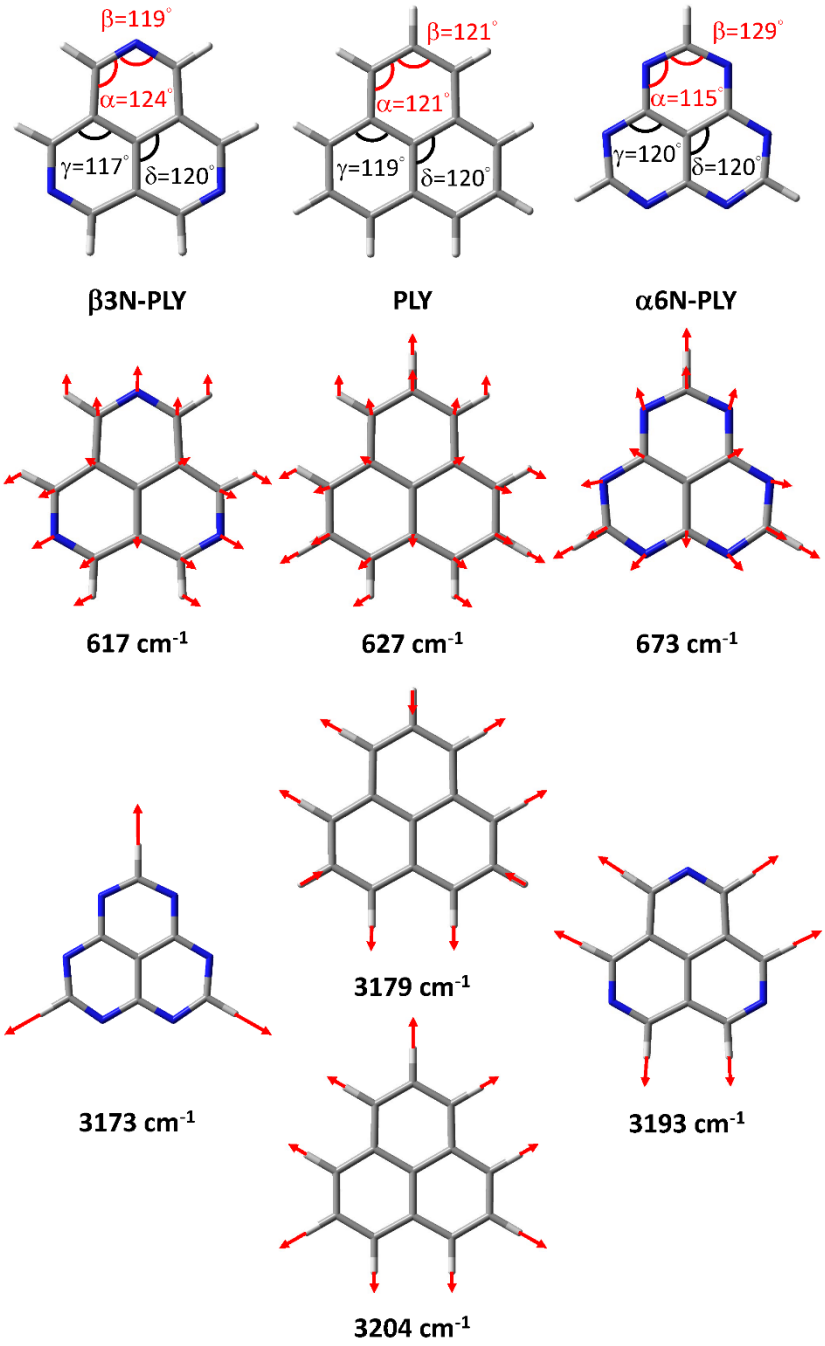

Figure S6 (continued). Totally symmetric vibrational normal modes for PLY, β3N-PLY and α6N-PLY.

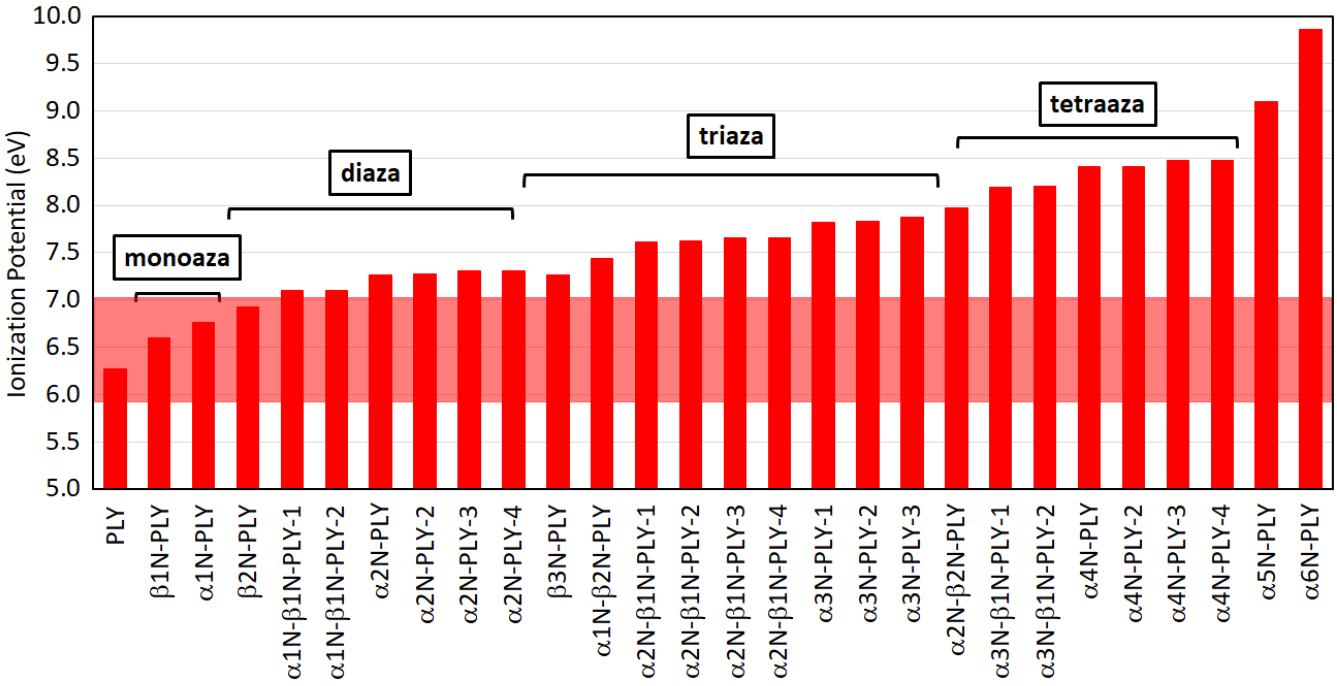

Figure S7. Ionization potential (IP) for PLY and its aza-derivatives.

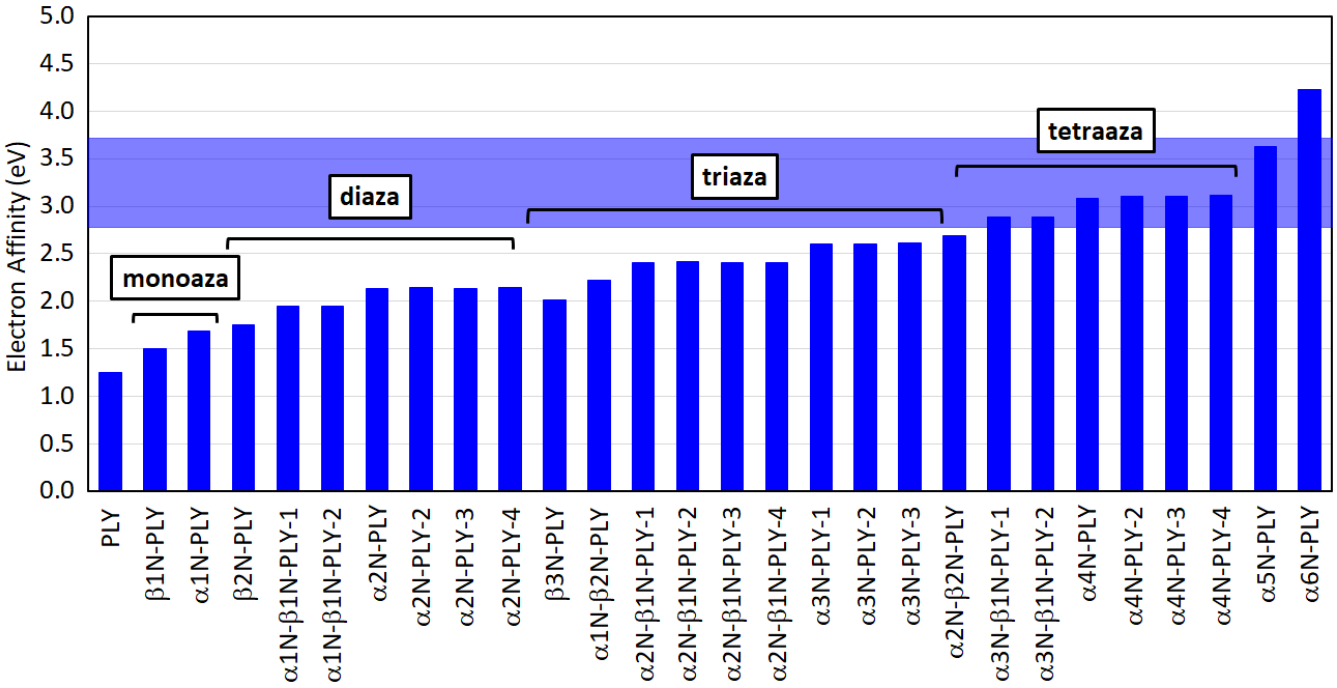

Figure S8. Electron affinity (EA) for PLY and its aza-derivatives.

Table S1. Internal reorganization energies for hole (λ^+, in meV) and electron (λ^-, in meV) transfer of PLY, β3N-PLY, and α6N-PLY calculated with different functionals.

Compound	Funcationals[a]	λ^+	λ^-
PLY	BLYP	15	32
	B3LYP	19	35
	ωB97	30	42
	OPT-LC-ωB97(ω = 0.246)	22	37
β3N-PLY	BLYP	8	17
	B3LYP	9	18
	ωB97	13	20
	OPT-LC-ωB97(ω = 0.258)	10	19
α6N-PLY	BLYP	-	56
	B3LYP	58	68
	ωB97	66	93
	OPT-LC-ωB97(ω = 0.302)	63	81

[a]Calculated at the 6-31G(d,p) basis set

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.

PLY	Bond Length					Bond Angle						
N-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	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	Bond Length					Bond Angle						
C-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	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 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 β3N-PLY.

β3N-PLY	Bond Length					Bond Angle						
N-Freq	a	b	c	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	Bond Length					Bond Angle						
C-Freq	a	b	c	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	—

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 α6N-PLY.

α6N-PLY	Bond Length					Bond Angle						
N-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	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

α6N-PLY	Bond Length					Bond Angle						
C-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	α-CH	β-CH
674	0.0	0.0	0.0	—	0.0	0.0	0.0	0.0	0.0	0.0	—	0.0
848	0.2	0.0	0.7	—	0.0	3.3	6.6	0.0	0.0	0.2	—	2.0
1270	3.3	0.0	1.4	—	0.0	0.5	0.9	0.5	0.0	2.2	—	0.3
1546	0.0	0.0	0.1	—	0.0	0.1	0.1	0.0	0.0	0.0	—	0.0
3230	0.0	0.0	0.0	—	0.2	0.0	0.0	0.0	0.0	0.0	—	0.0
Sum	3.5	0.0	2.1	—	0.2	3.9	7.6	0.6	0.0	2.4	—	2.3

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	c	α-CH	β-CH	α	β	γ	δ	ϕ	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	Bond Length					Bond Angle						
A-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	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

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 β3N-PLY.

β3N-PLY	Bond Length					Bond Angle						
N-Freq	a	b	c	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	—

β3N-PLY	Bond Length					Bond Angle						
A-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	α-CH	β-CH
616	0.0	0.1	0.6	0.0	—	0.8	0.2	0.0	0.0	0.0	0.1	—
795	0.0	0.0	0.1	0.0	—	0.2	0.2	0.0	0.0	0.0	0.1	—
1200	0.0	0.0	0.0	0.0	—	0.2	0.0	0.0	0.0	0.0	0.6	—
1430	0.0	0.0	0.1	0.0	—	0.3	0.0	0.0	0.0	0.0	0.5	—
1524	0.0	0.0	0.0	0.0	—	0.0	0.0	0.0	0.0	0.0	0.4	—
3129	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	—	1.6	0.5	0.0	0.0	0.1	1.7	—

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 α6N-PLY.

α6N-PLY	Bond Length					Bond Angle						
N-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	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	Bond Length					Bond Angle						
A-Freq	a	b	c	α-CH	β-CH	α	β	γ	δ	ϕ	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