Electronic Supplementary Information: Anionic CO_2 activation in the anionic and di-anionic state of aza-naphthalene

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Figure S1 – S3

Optimized isomers and energetics of TAN-$(CO_2)_n$ (n = 2 -3) complexes.

Figure S4 –S7

In order to investigate the chemical reactivity with CO_2 molecules as a function of the number of nitrogen atoms in naphthalene, we performed theoretical calculations of the structure and energetics of nitrogen-containing naphthalene molecules in the anionic and dianionic states. As expected, the dianionic states of mono- and di-aza-naphthalene were found to be energetically unstable compared to reference neutral and anionic states. Depending on the position of the nitrogen atoms, the naphthalene molecules react differently to the CO_2 molecules. When nitrogen atoms are not too close to each other, they then react with CO_2 molecules in the anionic and di-anionic states. As for tri-aza-naphthalene, all nitrogen atoms interact with CO_2 molecules in the dianionic state but not in the anionic state.

Table S1 - S2

Table S1 shows the energetics of tetra-aza-naphthalene and CO_2 complexes in the neutral, anionic, and dianionic states.

Table S2 shows the energetics calculated using the various DFT functionals (B3LYP, BP86, and BPBE)
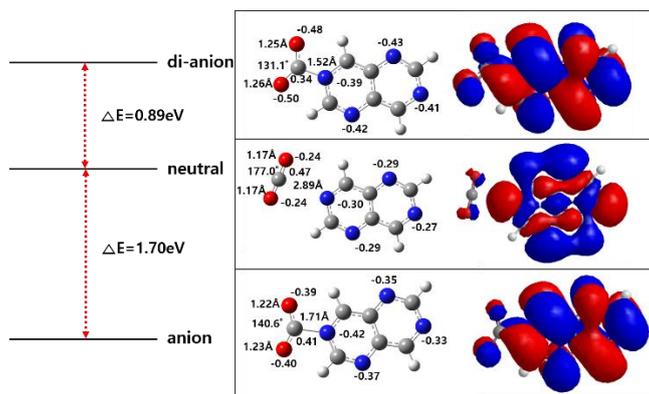
Figure S1. Neutral, anionic, and di-anionic geometries and calculated energies of the 2 & 4 isomer of $TAN_1(CO_2)_1$ optimized at the BP86/6-311g** level
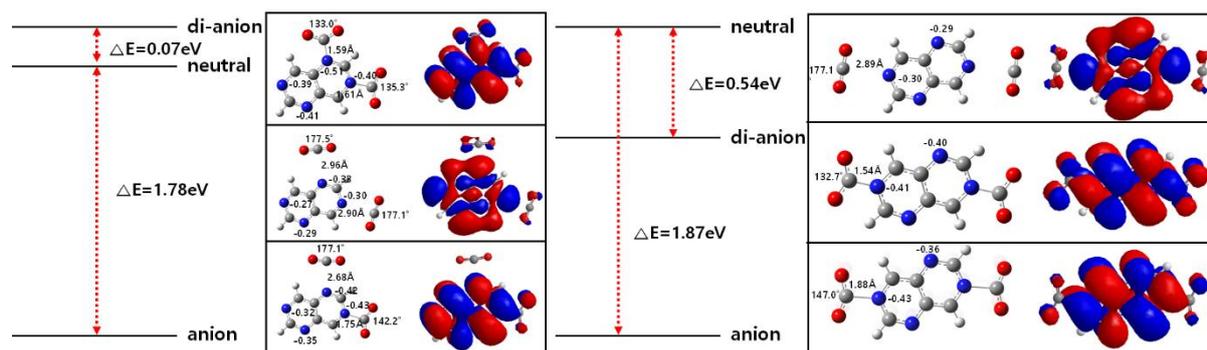
(a) CO_2 Position : 2, 4

(b) CO_2 Position : 2, 6
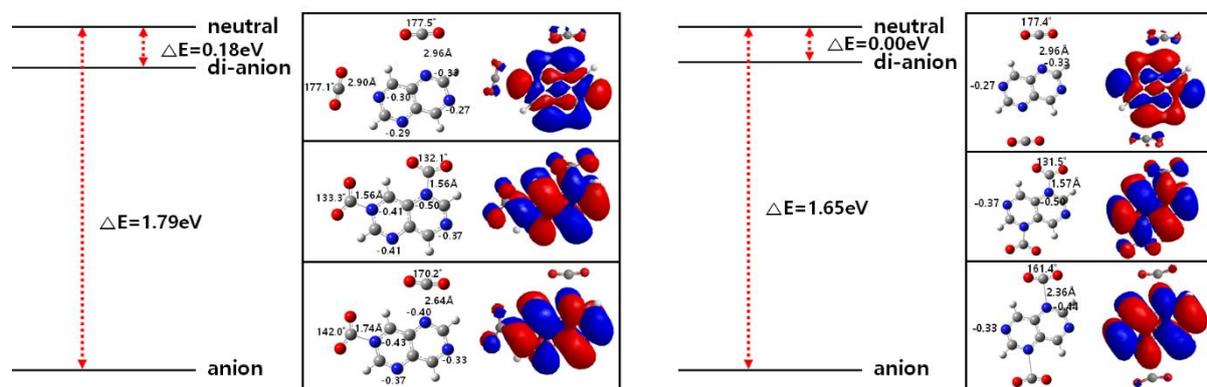
(c) CO_2 Position : 4, 6

(d) CO_2 Position : 4, 8

Figure S2. Neutral, anionic, and di-anionic geometries and calculated energies of $TAN_1(CO_2)_2$ optimized at the BP86/6-311g** level

(a) CO₂ Position : 2, 4, 6   (b) CO₂ Position : 4, 6, 8
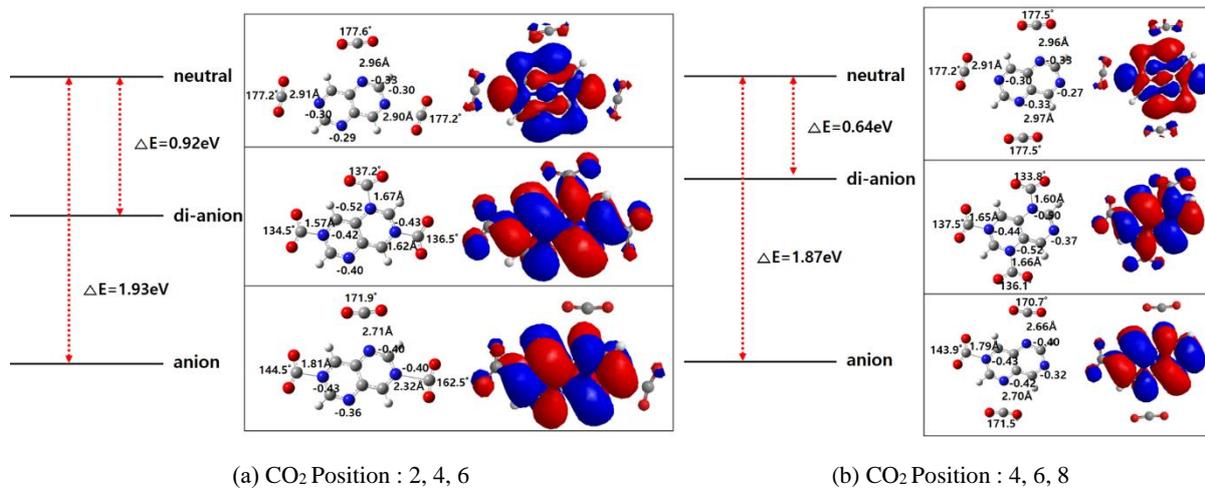
Figure S3. Neutral, anionic, and di-anionic geometries and calculated energies of $TAN_1(CO_2)_3$ optimized at the BP86/6-311g** level
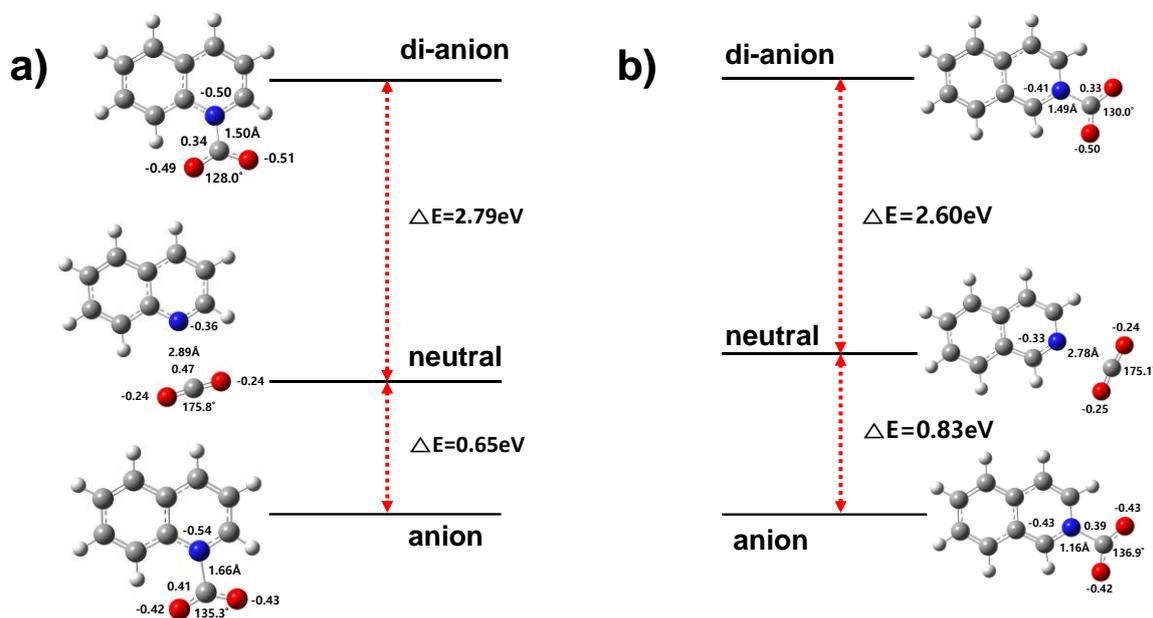
**Figure S4.** Optimized geometries and their energetics of quinoline (a) and iso-quinoline (b) in the neutral, anionic, and di-anionic states.
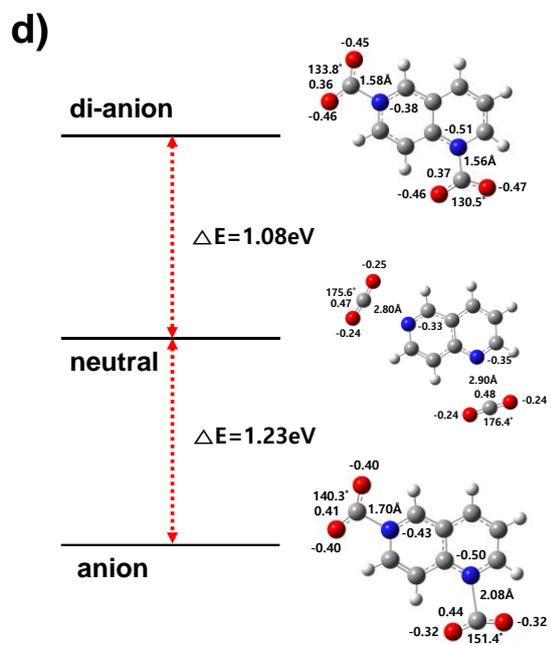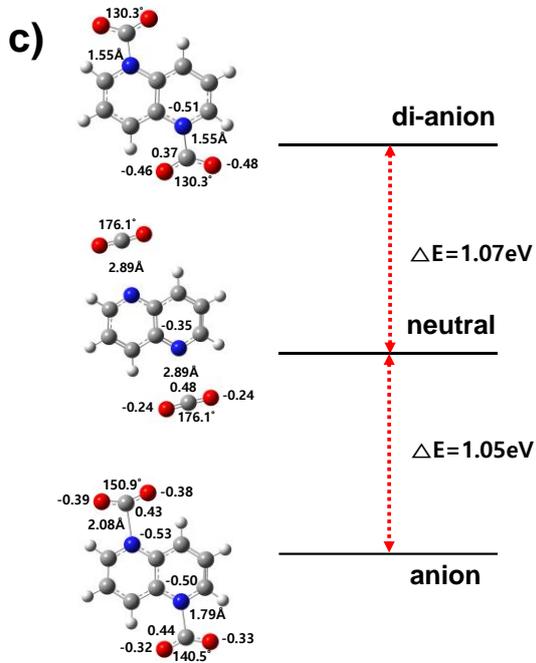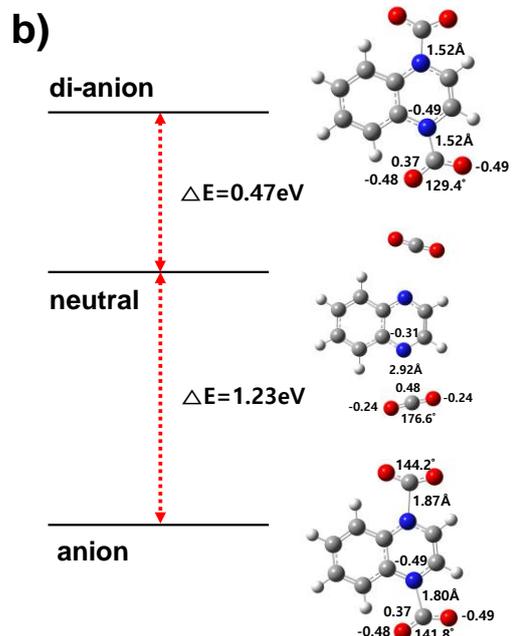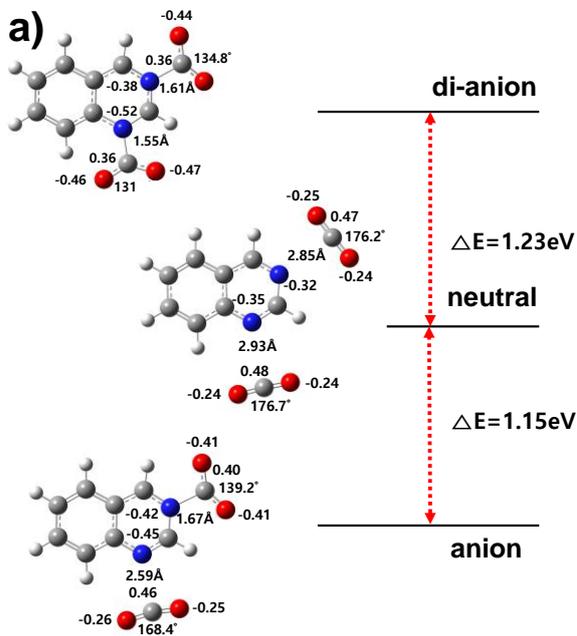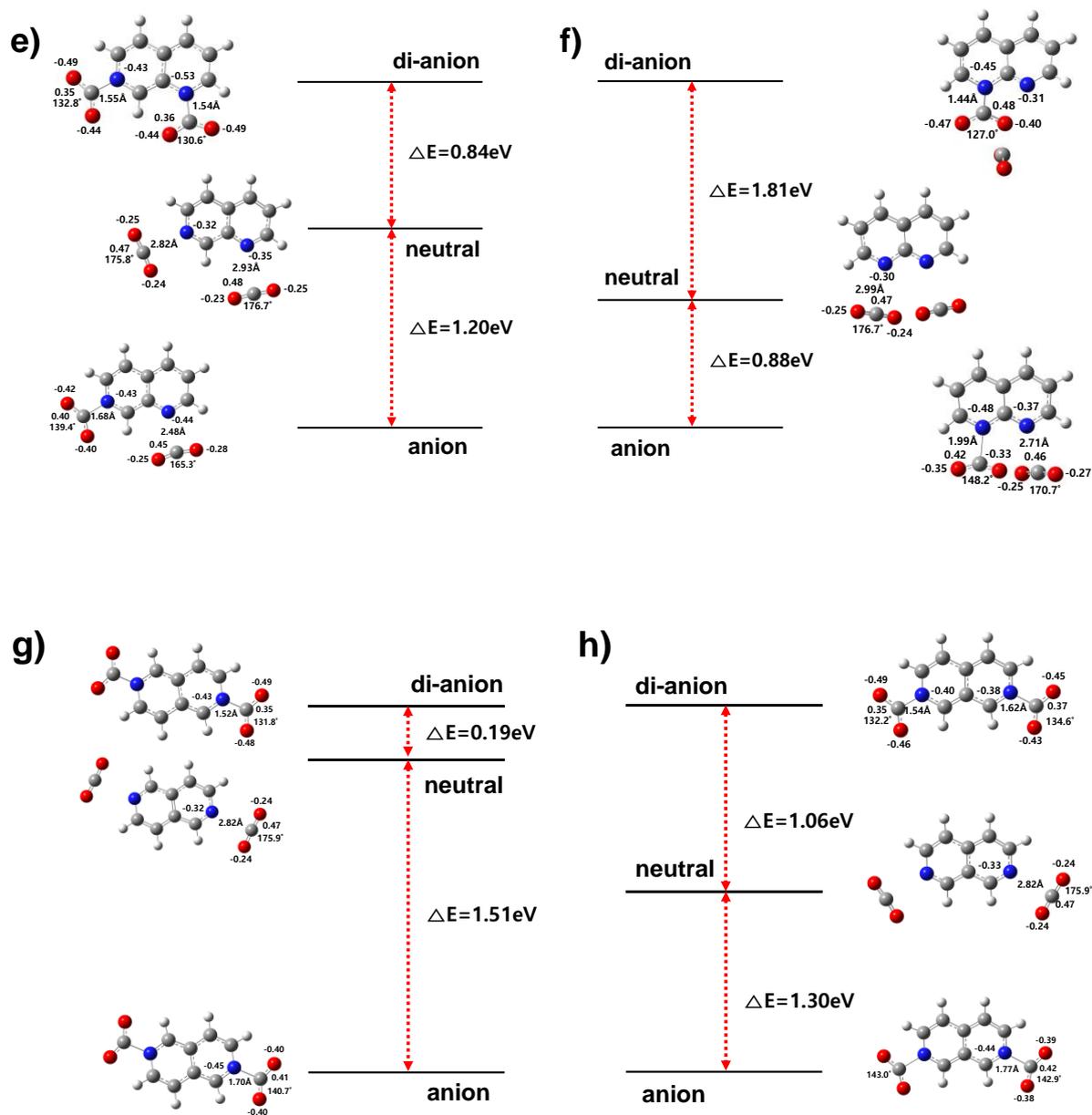
Figure S5. Optimized geometries and their energetics of di-azanaphthalene, (a) quinazoline, (b) quinoxaline, (c) 1,5–naphthyridine, (d) 1,6–naphthyridine, (e) 1,7–naphthyridine, (f) 1,8–naphthyridine, (g) 2,6–naphthyridine, (h) 2,7–naphthyridine, in the neutral, anionic, and di-anionic states.
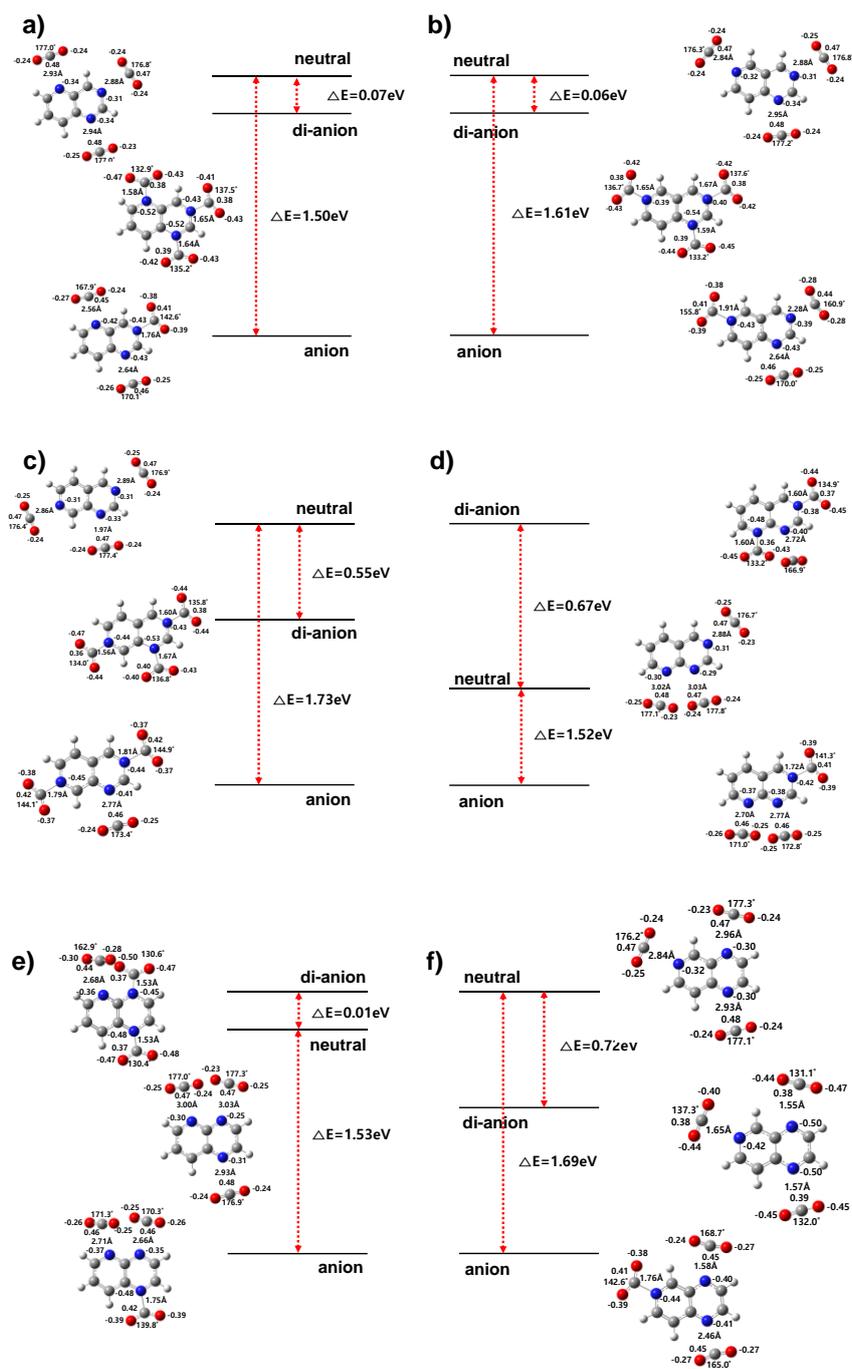
Figure S6. Optimized geometries and their energetics of tri-azanaphthalene, (a) pyrido[3,2-d]pyrimidine, (b) pyrido[4,3-d]pyrimidine, (c) pyrido[3,4-d]pyrimidine, (d) pyrido[2,3-d]pyrimidine, (e) pyrido[3,2-b]pyrazine, (f) pyrido[3,4-b]pyrazine, in the neutral, anionic, and di-anionic states.
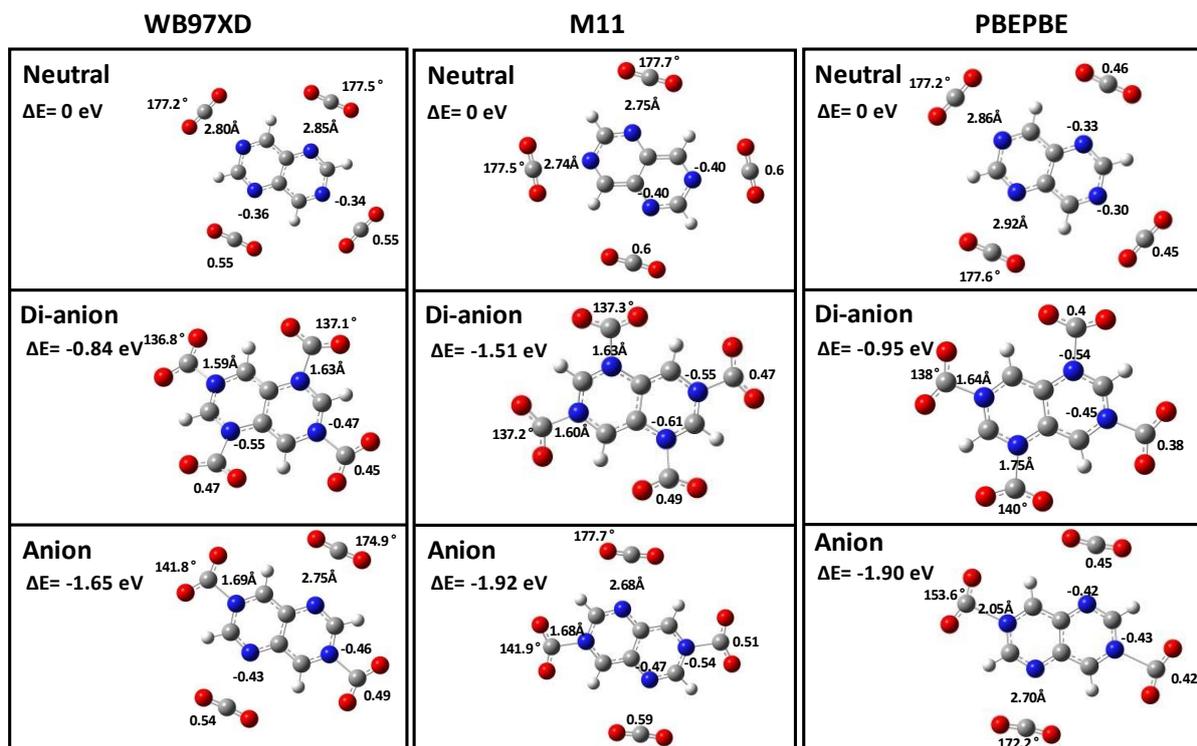
Figure S7. Optimized geometries and their energetics of $TAN_1(CO_2)_4$ optimized using various DFT functionals: WB97XD, M11, PBEPBE with 6-311G** basis set.

Table S1. Calculated Energies of Tetraazanaphthalene-$(CO_2)_n$ Complexes[b]

	CO_2 position		Anoin (ΔE)	Di-anion (ΔE)
TAN$_1$	-	BP86	1.32	-2.73
		BPBE	1.20	-2.98
		B3LYP	1.13	-3.12
TAN$_1$(CO$_2$)$_1$	4	BP86	1.54	-1.06
		BPBE	1.37	-1.37
		B3LYP	1.27	-1.46
	6	BP86	1.70	-0.89
		BPBE	1.53	-1.18
		B3LYP	1.43	-1.26
TAN$_1$(CO$_2$)$_2$	2, 4	BP86	1.78	-0.07
		BPBE	1.60	-0.43
		B3LYP	1.45	-0.56
	2, 6	BP86	1.87	0.54
		BPBE	1.66	0.20
		B3LYP	1.45	0.15
	4, 6	BP86	1.79	0.18
		BPBE	1.61	-0.17
		B3LYP	1.45	-0.25
	4, 8	BP86	1.65	0.00
		BPBE	1.46	-0.36
		B3LYP	1.40	-0.45
TAN$_1$(CO$_2$)$_3$	2, 4, 6	BP86	1.93	0.92
		BPBE	1.72	0.52
		B3LYP	1.60	0.31
	4, 6, 8	BP86	1.87	0.64
		BPBE	1.67	0.23
		B3LYP	1.56	0.08
TAN$_1$(CO$_2$)$_4$	2, 4, 6, 8	BP86	2.00	1.13
		BPBE	1.77	0.69
		B3LYP	1.71	0.46

[b]All energies in eV. Calculated energies were obtained at the BP86, BPBE, B3LYP/6-311g** level.

Table S2. Calculated Energies of Tetraazanaphthalene-$(CO_2)_n$ Complexes[a]

	TAN$_1$	TAN$_1$(CO$_2$)$_1$		TAN$_1$(CO$_2$)$_2$				TAN$_1$(CO$_2$)$_3$		TAN$_1$(CO$_2$)$_4$
CO_2 position	-	4	6	2, 4	2, 6	4, 6	4, 8	2, 4, 6	4, 6, 8	2, 4, 6, 8
Anoin (ΔE)	1.32	1.54	1.70	1.78	1.87	1.79	1.65	1.93	1.87	2.00
Di-anion (ΔE)	-2.73	-1.06	-0.89	-0.07	0.54	0.18	0.00	0.92	0.64	1.13

[a]All energies in eV. Calculated energies were obtained at the BP86/6-311g** level.