Supporting Information

Strategic functionalization of bromine and nitrogen at bay region of perylene triggers heavy atom effect and promotes intersystem crossing

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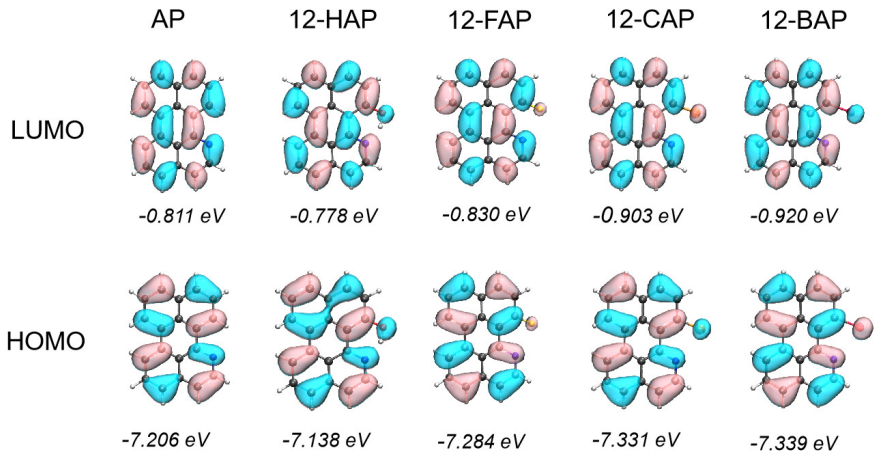

Fig. S1 Frontier molecular orbitals of AP and 12-XAP at S_0 geometry (ωB97X-D/6-31+G(d,p) level).

Table S1 Excitation energy of S_1 state and its molecular orbital contribution at S_0-geometry and S_1-geometry of AP and 12-XAP (ωB97X-D/6-31+G(d,p) level).

	S_0-geometry		S_1-geometry	
molecule	E_{ab}	MO contribution	E_{em}	MO contribution
AP	3.464	H → L (0.97)	3.063	H → L (0.97)
12-HAP	3.383	H → L (0.96)	3.059	H → L (0.97)
12-FAP	3.533	H → L (0.97)	3.126	H → L (0.97)
12-CAP	3.507	H → L (0.97)	3.100	H → L (0.97)
12-BAP	3.493	H → L (0.97)	3.087	H → L (0.97)

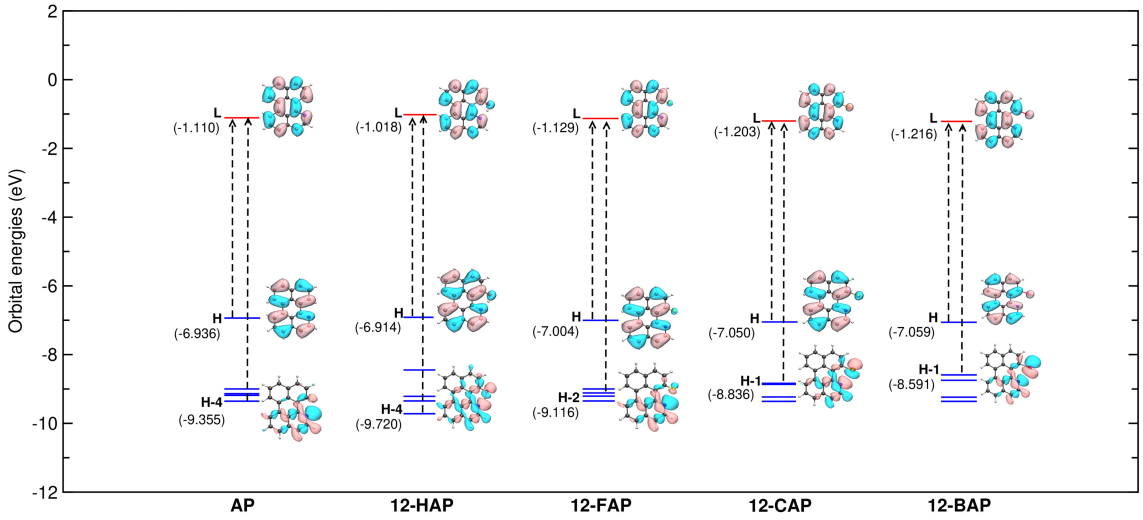

Fig. S2 Energy level diagram for frontier molecular orbitals of AP and 12-XAP at S_1 geometry. The H→L transition represents the $^1\pi\pi^*$ state across all systems. The H-4→L transition for AP and 12-HAP, H-2→L transition for 12-FAP, and H-1→L transition for 12-CAP and 12-BAP represents the $^3n\pi^*$ state (ωB97X-D/6-31+G(d,p) level).

Table S2 Calculated ΔST (in eV), V_{soc} (in cm^{-1}), and singlet-triplet mixing coefficient (λ) between S_1 and T_n states at S_1-geometry of AP and 12-XAP (ωB97X-D/aug-cc-pVTZ level). SOC matrix elements were evaluated using the effective one-electron SO operator with Chiodo-derived Z_{eff} values.

molecule	T_n	ΔST	V_{soc}	λ
AP	T_1	-1.45	0.05	4.69×10^{-6}
	T_2	0.09	0.20	2.82×10^{-4}
	T_3	0.19	0.01	6.54×10^{-6}
	T_4	0.55	0.22	5.03×10^{-5}
	T_5	0.64	0.05	8.82×10^{-6}
	T_6	0.73	5.39	9.12×10^{-3}
12-HAP	T_1	-1.29	0.14	1.38×10^{-5}
	T_2	-0.05	0.46	1.10×10^{-3}
	T_3	0.30	0.24	1.00×10^{-4}
	T_4	0.37	0.07	2.20×10^{-5}
	T_5	0.45	0.23	6.31×10^{-5}
	T_6	0.98	0.42	5.27×10^{-5}
12-FAP	T_1	-1.46	0.08	6.74×10^{-6}
	T_2	0.04	0.20	5.82×10^{-4}
	T_3	0.17	0.01	1.08×10^{-5}
	T_4	0.47	7.09	1.87×10^{-3}
	T_5	0.51	0.25	6.00×10^{-5}
	T_6	0.56	0.02	3.96×10^{-6}
12-CAP	T_1	-1.44	0.06	5.22×10^{-6}
	T_2	0.04	0.18	5.29×10^{-4}
	T_3	0.20	0.03	1.74×10^{-5}
	T_4	0.24	18.95	9.72×10^{-3}
	T_5	0.50	0.19	4.73×10^{-5}
	T_6	0.57	0.11	2.45×10^{-5}
12-BAP	T_1	-1.43	0.03	2.55×10^{-6}
	T_2	0.05	0.24	6.14×10^{-4}
	T_3	0.15	88.94	7.27×10^{-2}
	T_4	0.21	0.03	1.80×10^{-5}
	T_5	0.49	0.24	6.12×10^{-5}
	T_6	0.57	0.24	5.24×10^{-5}

Table S3 The scaling factors (Z_{eff}) (derived from Chiodo approach) used in the effective one-electron spin–orbit operator.

element	Z_{eff}
C	3.01
N	3.95
O	5.02
F	6.21
Cl	13.98
Br	31.72

Table S4 Comparison of ΔST (in eV) and SOC (in cm^{-1}) between $^1\pi\pi^*$ and $^3n\pi^*$ states of 12-BAP across density functionals with aug-cc-pVTZ basis set. SOC were computed using the effective one-electron SO operator with Chiodo-derived Z_{eff} values.

	PBE0	B3LYP	ωB97X-D	CAM-B3LYP
ΔST	-0.09	-0.12	0.15	0.17
SOC	110.63	119.52	88.92	91.88

Table S5 Calculated ISC rate constants (k_{isc} in sec^{-1}) for AP and 12-XAP with the spin-orbit coupling (V_{soc} in cm^{-1}), electronic energy difference (ΔG in meV), reorganization energy (E_{r} in meV), and activation energy (E_{a} in meV). SOC matrix elements were evaluated using the effective one-electron SO operator with Chiodo-derived Z_{eff} values (ωB97X-D/aug-cc-pVTZ level).

molecule	$S_1 \longrightarrow T_n$	$\lvert V_{\text{soc}}\rvert$	ΔG	E_{r}	E_{a}	k_{isc}
AP	$S_1 \longrightarrow T_2$	0.20	-42.5	114.3	11.3	1.96×10^{7}
	$S_1 \longrightarrow T_6$	5.39	190.5	528.0	244.4	8.06×10^{6}
12-HAP	$S_1 \longrightarrow T_2$	0.46	-584.1	512.4	2.5	6.91×10^{7}
	$S_1 \longrightarrow T_3$	0.24	-258.3	566.1	41.9	3.91×10^{6}
12-FAP	$S_1 \longrightarrow T_2$	0.20	-86.9	116.6	1.89	1.12×10^{8}
	$S_1 \longrightarrow T_4$	7.09	-101.8	531.1	86.8	6.19×10^{8}
12-CAP	$S_1 \longrightarrow T_2$	0.18	-91.5	116.1	1.3	2.32×10^{7}
	$S_1 \longrightarrow T_4$	18.95	-323.7	525.3	19.3	6.04×10^{10}
12-BAP	$S_1 \longrightarrow T_2$	0.24	-83.3	113.7	2.0	4.07×10^{7}
	$S_1 \longrightarrow T_3$	88.92	-436.5	546.4	5.5	2.22×10^{12}

Table S6 Calculated absorption (E_{ab} in eV) and emission energies (E_{em} in eV) of the S_1 state, oscillator strength (f), and the fluorescent rate constants (k_{fl} in sec^{-1}) for bromo-substituted AP (*n*-BAP) (ωB97X-D/6-31+G(d,p) level).

molecule	E_{ab}	f_{ab}	E_{em}	f_{em}	k_{fl}
2-BAP	3.408	0.629	3.018	0.674	2.38×10^8
3-BAP	3.395	0.717	2.995	0.763	2.64×10^8
4-BAP	3.391	0.728	2.995	0.771	2.67×10^8
5-BAP	3.467	0.650	3.065	0.694	2.52×10^8
6-BAP	3.493	0.624	3.097	0.668	2.49×10^8
7-BAP	3.507	0.614	3.098	0.660	2.45×10^8
8-BAP	3.464	0.629	3.059	0.680	2.46×10^8
9-BAP	3.407	0.721	3.005	0.767	2.67×10^8
10-BAP	3.404	0.722	3.003	0.769	2.68×10^8
11-BAP	3.463	0.630	3.057	0.681	2.46×10^8
12-BAP	3.493	0.611	3.087	0.657	2.42×10^8

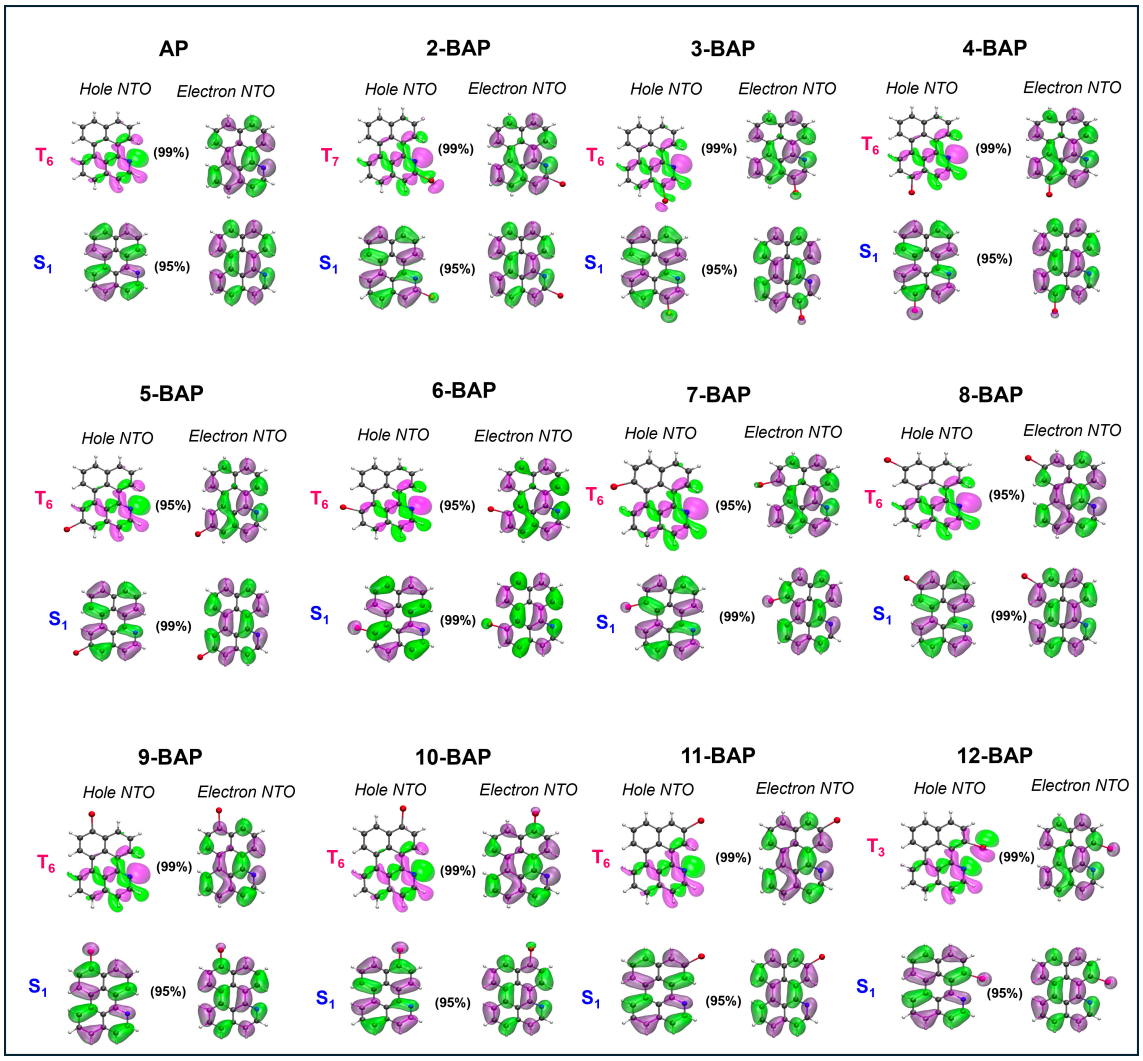

Fig. S3 Natural transition orbitals for $^1\pi\pi^*$ and $^3n\pi^*$ states of *n*-BAP at S_1-geometry (ωB97X-D/6-31+G(d,p) level).

Table S7 Calculated ΔST (in eV), V_{soc} (in cm^{-1}), and singlet-triplet mixing coefficient (λ) between S_1 and T_n states at S_1-geometry of *n*-BAP (ωB97X-D/aug-cc-pVTZ level). SOC matrix elements were evaluated using the effective one-electron SO operator with Chiodo-derived Z_{eff} values.

molecule	T_n	ΔST	V_{soc}	λ
2-BAP	T_1	-1.43	0.02	1.88×10^{-6}
	T_2	0.11	0.13	1.44×10^{-4}
	T_3	0.19	0.09	6.17×10^{-5}
	T_4	0.55	0.10	2.22×10^{-5}
	T_5	0.63	0.16	3.14×10^{-5}
	T_6	0.94	0.06	7.89×10^{-6}
	T_7	1.02	35.86	4.35×10^{-3}
3-BAP	T_1	-1.41	0.04	3.88×10^{-6}
	T_2	0.11	0.23	2.63×10^{-4}
	T_3	0.22	0.09	5.41×10^{-5}
	T_4	0.54	0.02	4.30×10^{-6}
	T_5	0.66	0.14	2.74×10^{-5}
	T_6	0.86	29.52	4.26×10^{-3}
	T_7	1.04	0.18	2.18×10^{-5}
4-BAP	T_1	-1.41	0.01	9.35×10^{-7}
	T_2	0.10	0.16	1.91×10^{-4}
	T_3	0.22	0.10	5.92×10^{-5}
	T_4	0.54	0.02	5.62×10^{-6}
	T_5	0.66	0.16	3.04×10^{-5}
	T_6	0.80	8.36	2.61×10^{-3}
	T_7	1.04	0.22	7.08×10^{-5}
5-BAP	T_1	-1.44	0.04	3.71×10^{-6}
	T_2	0.08	0.08	1.23×10^{-4}
	T_3	0.17	0.02	1.77×10^{-5}
	T_4	0.52	0.08	1.90×10^{-5}
	T_5	0.60	0.20	4.19×10^{-5}
	T_6	0.74	4.17	7.02×10^{-4}
	T_7	0.84	0.01	1.38×10^{-6}
6-BAP	T_1	-1.43	0.01	8.09×10^{-7}
	T_2	0.06	0.10	1.95×10^{-4}
	T_3	0.19	0.02	1.14×10^{-5}
	T_4	0.51	0.02	3.86×10^{-6}
	T_5	0.55	0.27	6.08×10^{-5}
	T_6	0.73	7.25	1.23×10^{-3}
	T_7	0.85	0.17	2.55×10^{-5}
7-BAP	T_1	-1.44	0.08	7.30×10^{-6}
	T_2	0.06	0.21	4.14×10^{-4}
	T_3	0.19	0.02	1.64×10^{-5}
	T_4	0.53	0.32	7.44×10^{-5}
	T_5	0.60	0.24	5.05×10^{-5}
	T_6	0.68	8.46	1.54×10^{-3}
	T_7	0.85	0.24	3.47×10^{-5}
8-BAP	T_1	-1.45	0.04	3.11×10^{-6}
	T_2	0.10	0.16	2.06×10^{-4}
	T_3	0.16	0.01	8.15×10^{-6}
	T_4	0.50	0.12	2.95×10^{-5}
	T_5	0.61	0.26	5.40×10^{-5}
	T_6	0.71	5.21	9.10×10^{-4}
	T_7	0.93	0.03	4.59×10^{-6}
9-BAP	T_1	-1.42	0.06	5.35×10^{-6}
	T_2	0.11	0.04	4.52×10^{-5}
	T_3	0.21	0.05	3.15×10^{-5}
	T_4	0.59	0.28	5.83×10^{-5}
	T_5	0.73	0.11	1.86×10^{-5}
	T_6	0.76	5.32	8.69×10^{-4}
	T_7	0.96	0.12	1.50×10^{-5}
10-BAP	T_1	-1.42	0.03	2.33×10^{-6}
	T_2	0.09	0.08	1.14×10^{-4}
	T_3	0.22	0.00	2.79×10^{-6}

molecule	T_n	ΔST	V_{soc}	λ
	T_4	0.59	0.28	5.92×10^{-5}
	T_5	0.73	0.12	2.08×10^{-5}
	T_6	0.76	4.83	7.83×10^{-4}
	T_7	0.97	0.12	1.57×10^{-5}
11-BAP	T_1	-1.45	0.06	5.23×10^{-6}
	T_2	0.10	0.18	2.25×10^{-4}
	T_3	0.15	0.01	1.25×10^{-5}
	T_4	0.49	0.11	2.74×10^{-5}
	T_5	0.60	0.27	5.55×10^{-5}
	T_6	0.70	8.66	1.53×10^{-3}
	T_7	0.93	0.02	3.03×10^{-6}
12-BAP	T_1	-1.43	0.03	2.55×10^{-6}
	T_2	0.05	0.24	6.14×10^{-4}
	T_3	0.15	88.92	7.27×10^{-2}
	T_4	0.21	0.03	1.80×10^{-5}
	T_5	0.49	0.24	6.12×10^{-5}
	T_6	0.57	0.23	4.99×10^{-5}
	T_7	0.91	0.02	3.32×10^{-6}

Table S8 Calculated ISC rate constants (k_{isc} in sec^{-1}) for *n*-BAP with the spin-orbit coupling (V_{soc} in cm^{-1}), electronic energy difference (ΔG in meV), reorganization energy (E_r in meV), and activation energy (E_a in meV). SOC matrix elements were evaluated using the effective one-electron SO operator with Chiodo-derived Z_{eff} values (ωB97X-D/aug-cc-pVTZ level).

molecule	$S_1 \longrightarrow T_n$	$\lvert V_{soc} \rvert$	ΔG	E_r	E_a	k_{isc}
2-BAP	$S_1 \longrightarrow T_2$	0.13	-10.3	109.0	22.3	5.55×10^6
	$S_1 \longrightarrow T_7$	35.86	478.4	534.4	479.9	3.93×10^3
3-BAP	$S_1 \longrightarrow T_2$	0.23	-16.3	109.5	19.8	1.91×10^7
	$S_1 \longrightarrow T_6$	29.52	338.4	509.9	352.8	3.71×10^5
4-BAP	$S_1 \longrightarrow T_2$	0.16	-28.8	115.9	16.4	1.30×10^7
	$S_1 \longrightarrow T_6$	8.36	244.8	535.2	284.2	4.13×10^5
5-BAP	$S_1 \longrightarrow T_2$	0.08	-45.2	114.1	10.4	3.26×10^6
	$S_1 \longrightarrow T_6$	4.17	187.9	533.2	243.8	4.92×10^5
6-BAP	$S_1 \longrightarrow T_2$	0.10	-194.3	240.7	2.2	4.81×10^6
	$S_1 \longrightarrow T_6$	7.25	194.4	522.7	245.9	1.38×10^6
7-BAP	$S_1 \longrightarrow T_2$	0.21	-193.5	240.8	2.3	2.11×10^7
	$S_1 \longrightarrow T_6$	8.46	147.6	521.2	214.5	6.35×10^6
8-BAP	$S_1 \longrightarrow T_2$	0.16	-36.2	116.7	13.9	1.13×10^7
	$S_1 \longrightarrow T_6$	5.21	165.2	528.4	227.6	1.44×10^6
9-BAP	$S_1 \longrightarrow T_2$	0.04	-15.4	109.1	20.1	5.73×10^5
	$S_1 \longrightarrow T_6$	5.32	218.4	524.6	263.1	3.83×10^5
10-BAP	$S_1 \longrightarrow T_2$	0.08	-45.4	116.4	10.8	3.18×10^6
	$S_1 \longrightarrow T_6$	4.83	223.3	526.0	266.8	2.73×10^5
11-BAP	$S_1 \longrightarrow T_2$	0.18	-32.5	116.2	15.1	1.37×10^7
	$S_1 \longrightarrow T_6$	8.66	153.6	531.0	220.7	5.20×10^6
12-BAP	$S_1 \longrightarrow T_2$	0.24	-83.3	113.7	2.0	4.07×10^7
	$S_1 \longrightarrow T_3$	88.92	-436.5	546.4	5.5	2.22×10^{12}

Table S9 Cartesian coordinates for the optimized ground state geometry of AP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.412312	-2.425607	-0.000026
C	0.717752	-1.233170	-0.000010
C	-0.757202	-1.224227	0.000004
N	-1.384327	-2.386614	0.000015
C	-2.736363	-2.393897	0.000022
C	-3.503724	-1.259041	0.000011
C	-2.862444	0.004579	-0.000003
C	-3.578023	1.226727	-0.000020
C	-2.891464	2.414341	-0.000038
C	-1.482578	2.436920	-0.000034
C	-0.738851	1.270592	-0.000008
C	0.740910	1.259204	0.000009
C	1.488951	2.421989	0.000037
C	2.897079	2.397531	0.000040
C	3.567808	1.201704	0.000016
C	2.849478	-0.020281	-0.000004
C	3.525251	-1.267718	-0.000022
C	2.820062	-2.444720	-0.000034
C	1.426301	0.004233	-0.000003
C	-1.443416	0.027670	-0.000000
H	0.848765	-3.351700	-0.000030
H	-3.198950	-3.377093	0.000033
H	-4.587347	-1.321146	0.000012
H	-4.663683	1.207795	-0.000020
H	-3.432463	3.355371	-0.000055
H	-0.991026	3.402577	-0.000052
H	0.998531	3.388582	0.000058
H	3.444616	3.334359	0.000059
H	4.653804	1.174402	0.000015
H	4.611753	-1.273213	-0.000024
H	3.341958	-3.396117	-0.000048

Table S10 Cartesian coordinates for the optimized S_1 state geometry of AP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.438198	-2.440784	-0.000003
C	0.715069	-1.224712	-0.000002
C	-0.725073	-1.235776	-0.000001
N	-1.344631	-2.445283	-0.000001
C	-2.673890	-2.449530	-0.000001
C	-3.468375	-1.304617	-0.000001
C	-2.853840	-0.035870	-0.000002
C	-3.575361	1.178422	-0.000002
C	-2.898027	2.392717	-0.000003
C	-1.508527	2.433895	-0.000003
C	-0.738102	1.242436	-0.000001
C	0.705683	1.253786	0.000001
C	1.451822	2.459813	0.000003
C	2.840313	2.441905	0.000003
C	3.533846	1.237333	0.000001
C	2.840078	0.007207	-0.000001
C	3.524091	-1.229642	-0.000002
C	2.826188	-2.433160	-0.000004
C	1.409274	0.014627	-0.000001
C	-1.426481	-0.002569	-0.000001
H	0.874385	-3.366365	-0.000003
H	-3.145710	-3.429780	-0.000000
H	-4.550509	-1.391136	-0.000001
H	-4.661036	1.151960	-0.000002
H	-3.457610	3.322616	-0.000005
H	-1.018342	3.399837	-0.000004
H	0.943835	3.416394	0.000006
H	3.387658	3.379014	0.000005
H	4.620214	1.231738	0.000001
H	4.610657	-1.227731	-0.000003
H	3.370604	-3.371988	-0.000005

Table S11 Cartesian coordinates for the optimized T_2 state geometry of AP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.448013	-2.448569	-0.000001
C	0.708702	-1.232797	-0.000000
C	-0.721856	-1.247518	-0.000000
N	-1.345799	-2.443791	0.000000
C	-2.687656	-2.454660	0.000001
C	-3.469809	-1.320041	0.000001
C	-2.838504	-0.042727	0.000000
C	-3.585174	1.184036	-0.000000
C	-2.915504	2.391290	-0.000001
C	-1.519665	2.443916	-0.000001
C	-0.734421	1.259988	-0.000001
C	0.700399	1.271355	0.000000
C	1.452142	2.466283	0.000001
C	2.854253	2.448198	0.000001
C	3.536360	1.254773	0.000001
C	2.819783	0.017675	0.000000
C	3.530438	-1.237793	-0.000000
C	2.841399	-2.435103	-0.000001
C	1.420593	0.023494	-0.000000
C	-1.440710	-0.003538	-0.000000
H	0.893592	-3.378879	-0.000001
H	-3.150421	-3.438334	0.000001
H	-4.552458	-1.395241	0.000001
H	-4.669821	1.145802	0.000000
H	-3.477319	3.320115	-0.000002
H	-1.040710	3.414897	-0.000002
H	0.950166	3.425802	0.000002
H	3.397517	3.387585	0.000002
H	4.622009	1.235270	0.000000
H	4.616040	-1.221572	-0.000000
H	3.385828	-3.373914	-0.000001

Table S12 Cartesian coordinates for the optimized ground state geometry of 12-HAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.450539	0.036309	0.000059
C	0.742693	1.273940	-0.000026
C	-0.733055	1.255663	0.000034
C	-1.416171	0.002814	0.000217
C	-0.698856	-1.233282	0.000354
C	0.757000	-1.213911	0.000227
C	-2.837327	-0.010932	0.000272
C	-3.553704	1.203330	0.000142
C	-2.884726	2.405853	-0.000027
C	-1.482767	2.423590	-0.000077
C	-1.407318	-2.442169	0.000576
C	-2.828710	-2.441357	0.000611
C	-3.514896	-1.265157	0.000460
C	2.869902	0.011052	-0.000033
C	3.581924	1.229918	-0.000189
C	2.891844	2.419790	-0.000259
C	1.487705	2.444434	-0.000184
N	1.403890	-2.377181	0.000256
C	2.759889	-2.390458	0.000170
C	3.517341	-1.255606	0.000035
O	-0.812253	-3.630409	0.000806
H	0.176517	-3.457902	0.001046
H	-3.333591	-3.400815	0.000782
H	-4.601475	-1.269271	0.000502
H	-4.639886	1.174273	0.000182
H	-3.432952	3.341874	-0.000117
H	-0.986945	3.387425	-0.000207
H	0.995452	3.409444	-0.000252
H	4.667488	1.213870	-0.000255
H	3.434265	3.360088	-0.000375
H	3.217594	-3.374625	0.000204
H	4.600696	-1.313449	-0.000035

Table S13 Cartesian coordinates for the optimized S_1 state geometry of 12-HAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.483499	0.098788	0.000005
C	0.885344	1.386747	-0.000007
C	-0.554678	1.502616	-0.000002
C	-1.349924	0.317793	0.000006
C	-0.742254	-0.967470	0.000003
C	0.689849	-1.075323	0.000010
C	-2.778542	0.424010	0.000011
C	-3.374668	1.697204	0.000011
C	-2.591358	2.848184	0.000004
C	-1.206379	2.762023	-0.000003
C	-1.581941	-2.141436	-0.000007
C	-2.978053	-2.011161	0.000005
C	-3.558277	-0.760795	0.000016
C	2.905650	-0.040989	0.000017
C	3.712144	1.116413	0.000007
C	3.122802	2.375778	-0.000009
C	1.739818	2.517694	-0.000013
N	1.241218	-2.324789	0.000048
C	2.568118	-2.438177	0.000066
C	3.432240	-1.353136	0.000044
O	-1.068593	-3.358295	-0.000045
H	-0.056761	-3.253738	-0.000124
H	-3.572700	-2.917486	-0.000001
H	-4.641016	-0.669522	0.000019
H	-4.458290	1.774283	0.000015
H	-3.068823	3.822776	0.000003
H	-0.629037	3.677771	-0.000009
H	1.321760	3.516584	-0.000019
H	4.792892	1.011315	0.000015
H	3.746845	3.263811	-0.000014
H	2.959200	-3.451933	0.000093
H	4.505355	-1.513139	0.000055

Table S14 Cartesian coordinates for the optimized T_2 state geometry of 12-HAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.461908	0.071419	0.000431
C	0.867873	1.367742	0.000707
C	-0.563174	1.483958	0.000740
C	-1.360080	0.321795	0.000126
C	-0.769985	-0.982162	-0.000092
C	0.632428	-1.085374	0.000326
C	-2.798595	0.451828	-0.000542
C	-3.393360	1.775009	0.000079
C	-2.601269	2.898799	0.001003
C	-1.211130	2.775441	0.001335
C	-1.603835	-2.174921	-0.000778
C	-3.019346	-1.977595	-0.002130
C	-3.593114	-0.685307	-0.001810
C	2.877918	-0.084568	0.000203
C	3.689459	1.056173	0.000290
C	3.110292	2.326757	0.000598
C	1.737984	2.489835	0.000810
N	1.231229	-2.317082	0.000345
C	2.580187	-2.481756	-0.000045
C	3.418636	-1.415934	-0.000127
O	-1.124286	-3.348846	-0.000517
H	0.552272	-3.096273	0.000242
H	-3.638943	-2.867844	-0.003140
H	-4.674220	-0.581619	-0.002560
H	-4.476110	1.853276	-0.000185
H	-3.052202	3.885531	0.001501
H	-0.613279	3.677291	0.002138
H	1.336274	3.494778	0.001034
H	4.769105	0.943282	0.000017
H	3.748268	3.205170	0.000664
H	2.927450	-3.507683	-0.000172
H	4.491527	-1.566265	-0.000507

Table S15 Cartesian coordinates for the optimized ground state geometry of 12-FAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.508462	-0.078561	0.000000
C	0.723085	1.119011	0.000005
C	-0.749304	1.002811	-0.000004
C	-1.355225	-0.298934	-0.000001
C	-0.559077	-1.487207	0.000002
C	0.914014	-1.374789	-0.000007
C	-2.773874	-0.426074	0.000001
C	-3.579356	0.741653	-0.000006
C	-3.004605	1.979480	-0.000014
C	-1.602022	2.093618	-0.000013
C	2.922126	0.056747	0.000001
C	3.466071	1.364329	0.000013
C	2.613083	2.433989	0.000022
N	1.266031	2.322196	0.000017
C	1.750220	-2.477982	-0.000021
C	3.150981	-2.342578	-0.000022
C	3.735455	-1.101706	-0.000009
C	-3.373228	-1.707641	0.000010
C	-2.594282	-2.835726	0.000018
C	-1.194337	-2.717173	0.000014
F	-1.145419	3.349567	-0.000022
H	2.994974	3.451189	0.000033
H	4.542017	1.507784	0.000015
H	4.815714	-0.991689	-0.000008
H	3.766421	-3.236708	-0.000031
H	1.339880	-3.480500	-0.000031
H	-0.612081	-3.630770	0.000021
H	-3.049520	-3.820440	0.000027
H	-4.457061	-1.780111	0.000012
H	-4.660309	0.637663	-0.000005
H	-3.591794	2.890596	-0.000021

Table S16 Cartesian coordinates for the optimized S_1 state geometry of 12-FAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.495006	-0.057938	0.000000
C	0.692422	1.120853	0.000004
C	-0.744967	0.983314	-0.000001
C	-1.331537	-0.323240	0.000001
C	-0.516071	-1.491648	0.000001
C	0.919781	-1.354319	-0.000004
C	-2.756931	-0.474848	0.000003
C	-3.577797	0.670916	0.000001
C	-3.020989	1.939886	-0.000005
C	-1.643897	2.085741	-0.000007
C	2.916130	0.089584	0.000000
C	3.437034	1.395151	0.000008
C	2.554425	2.474273	0.000016
N	1.232917	2.365957	0.000014
C	1.783434	-2.481670	-0.000011
C	3.164957	-2.328287	-0.000012
C	3.736246	-1.063981	-0.000006
C	-3.321757	-1.769798	0.000007
C	-2.515138	-2.898454	0.000009
C	-1.133634	-2.769534	0.000006
F	-1.193894	3.340723	-0.000017
H	2.945179	3.489721	0.000024
H	4.509755	1.561124	0.000009
H	4.815708	-0.944823	-0.000006
H	3.798388	-3.209573	-0.000018
H	1.374519	-3.483922	-0.000016
H	-0.530373	-3.668111	0.000008
H	-2.965536	-3.885674	0.000013
H	-4.403496	-1.869584	0.000009
H	-4.657038	0.551201	0.000002
H	-3.634208	2.833616	-0.000009

Table S17 Cartesian coordinates for the optimized T_4 state geometry of 12-FAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.507455	-0.075988	0.000001
C	0.630523	1.073413	0.000003
C	-0.782810	0.944771	0.000002
C	-1.357105	-0.370675	0.000001
C	-0.525718	-1.531221	0.000001
C	0.940267	-1.372164	-0.000001
C	-2.776151	-0.506594	0.000001
C	-3.595417	0.657874	0.000001
C	-3.034589	1.911651	0.000001
C	-1.645135	2.035154	0.000002
C	2.918311	0.116084	0.000001
C	3.449611	1.466488	0.000002
C	2.583643	2.521158	0.000004
N	1.282287	2.246128	0.000005
C	1.823316	-2.460523	-0.000004
C	3.200227	-2.282890	-0.000005
C	3.749491	-1.004095	-0.000002
C	-3.340434	-1.802280	0.000001
C	-2.530779	-2.914281	0.000002
C	-1.135415	-2.780979	0.000002
F	-1.112103	3.284195	0.000002
H	2.878834	3.563849	0.000005
H	4.517124	1.648688	0.000002
H	4.826891	-0.868653	-0.000002
H	3.850466	-3.151489	-0.000007
H	1.433975	-3.471538	-0.000007
H	-0.537656	-3.684430	0.000003
H	-2.970591	-3.906581	0.000003
H	-4.421735	-1.905297	0.000001
H	-4.674426	0.541897	0.000001
H	-3.640542	2.810864	0.000001

Table S18 Cartesian coordinates for the optimized ground state geometry of 12-CAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.600857	0.038454	0.000000
C	0.567297	1.031347	-0.000002
C	-0.856690	0.608343	-0.000005
C	-1.141598	-0.806401	-0.000003
C	-0.097427	-1.786993	0.000003
C	1.313535	-1.355911	-0.000000
C	-2.489198	-1.267213	-0.000005
C	-3.545379	-0.325157	-0.000012
C	-3.277625	1.010146	-0.000013
C	-1.943035	1.480710	-0.000008
C	2.951147	0.482643	0.000000
C	3.197822	1.876779	0.000001
C	2.129857	2.730764	-0.000001
N	0.844653	2.319153	-0.000003
C	2.373194	-2.246954	-0.000005
C	3.708820	-1.805605	-0.000005
C	4.001395	-0.465724	-0.000002
C	-2.779712	-2.651708	0.000001
C	-1.764588	-3.571488	0.000011
C	-0.432049	-3.130601	0.000012
Cl	-1.847398	3.221710	-0.000007
H	2.273414	3.808115	-0.000001
H	4.215786	2.253250	0.000001
H	5.029482	-0.116438	-0.000002
H	4.508724	-2.539166	-0.000009
H	2.196523	-3.315625	-0.000010
H	0.347272	-3.882699	0.000022
H	-1.978832	-4.635097	0.000017
H	-3.818932	-2.967615	-0.000001
H	-4.572093	-0.678785	-0.000015
H	-4.080651	1.737739	-0.000018

Table S19 Cartesian coordinates for the optimized S_1 state geometry of 12-CAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.583385	0.061512	0.000001
C	0.541423	1.037672	0.000002
C	-0.843612	0.609358	-0.000001
C	-1.116837	-0.803023	0.000000
C	-0.063678	-1.766613	0.000003
C	1.308156	-1.327834	-0.000001
C	-2.466217	-1.284561	-0.000001
C	-3.529708	-0.361528	-0.000005
C	-3.278331	0.995755	-0.000007
C	-1.975976	1.490184	-0.000004
C	2.940166	0.512008	-0.000000
C	3.174261	1.898647	0.000003
C	2.080450	2.759522	0.000006
N	0.816045	2.363364	0.000006
C	2.395463	-2.241762	-0.000006
C	3.710245	-1.793971	-0.000007
C	3.990751	-0.435300	-0.000004
C	-2.728401	-2.670516	0.000002
C	-1.691869	-3.592206	0.000007
C	-0.379245	-3.151064	0.000007
Cl	-1.895686	3.227309	-0.000008
H	2.237306	3.836544	0.000009
H	4.186732	2.289591	0.000003
H	5.017795	-0.082416	-0.000004
H	4.521478	-2.514711	-0.000012
H	2.215955	-3.309085	-0.000010
H	0.413333	-3.887453	0.000012
H	-1.906435	-4.655881	0.000011
H	-3.761392	-3.006413	0.000001
H	-4.552574	-0.725557	-0.000006
H	-4.100721	1.701543	-0.000010

Table S20 Cartesian coordinates for the optimized T_4 state geometry of 12-CAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.596199	0.085170	0.000000
C	0.465398	0.979114	0.000001
C	-0.871817	0.515764	0.000000
C	-1.101111	-0.904584	-0.000000
C	-0.008008	-1.822515	0.000000
C	1.372673	-1.310981	-0.000001
C	-2.440015	-1.390094	-0.000000
C	-3.524532	-0.464053	-0.000001
C	-3.296079	0.886902	-0.000001
C	-1.978788	1.371387	0.000000
C	2.912763	0.626155	0.000000
C	3.083210	2.065390	0.000002
C	1.980961	2.867910	0.000003
N	0.780861	2.284151	0.000003
C	2.499679	-2.144306	-0.000003
C	3.787737	-1.624818	-0.000004
C	3.999113	-0.249491	-0.000002
C	-2.666449	-2.782344	0.000001
C	-1.605022	-3.660609	0.000002
C	-0.289092	-3.186539	0.000002
Cl	-1.735102	3.106911	0.000002
H	2.011517	3.950943	0.000004
H	4.071124	2.509278	0.000002
H	5.007721	0.152539	-0.000002
H	4.637170	-2.300045	-0.000006
H	2.378819	-3.221029	-0.000006
H	0.516509	-3.910757	0.000003
H	-1.784741	-4.731182	0.000004
H	-3.688199	-3.150440	0.000000
H	-4.540603	-0.844930	-0.000001
H	-4.123065	1.588601	-0.000001

Table S21 Cartesian coordinates for the optimized ground state geometry of 12-BAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	2.025373	0.392738	-0.000006
C	0.635918	0.290914	-0.000006
C	-0.119973	-0.988209	-0.000006
N	0.555282	-2.117902	-0.000014
C	-0.099707	-3.297716	-0.000014
C	-1.462735	-3.403167	-0.000008
C	-2.234625	-2.216118	-0.000002
C	-3.649299	-2.241039	0.000002
C	-4.350505	-1.062354	0.000005
C	-3.676709	0.172385	0.000004
C	-2.294162	0.245313	0.000002
C	-1.556195	1.522632	0.000002
C	-2.228281	2.733165	0.000009
C	-1.555487	3.964961	0.000006
C	-0.186057	3.985768	-0.000003
C	0.546346	2.775367	-0.000007
C	1.960867	2.807389	-0.000013
C	2.677840	1.648901	-0.000011
C	-0.123543	1.518662	-0.000005
C	-1.552453	-0.969081	-0.000001
Br	3.267536	-1.049646	0.000007
H	0.531346	-4.182465	-0.000020
H	-1.951300	-4.372263	-0.000008
H	-4.162632	-3.197637	0.000003
H	-5.435935	-1.072355	0.000007
H	-4.277067	1.073744	0.000005
H	-3.311291	2.751536	0.000017
H	-2.124403	4.888688	0.000010
H	0.358036	4.925599	-0.000005
H	2.470796	3.766008	-0.000016
H	3.760913	1.671792	-0.000013

Table S22 Cartesian coordinates for the optimized S_1 state geometry of 12-BAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	2.072285	0.255451	0.000036
C	0.636960	0.226224	0.000004
C	-0.168626	-0.979140	-0.000023
N	0.456449	-2.178372	-0.000074
C	-0.268808	-3.287318	-0.000073
C	-1.659897	-3.313577	-0.000032
C	-2.356933	-2.091516	-0.000003
C	-3.769405	-2.022932	0.000025
C	-4.411963	-0.793184	0.000049
C	-3.677575	0.385777	0.000042
C	-2.257610	0.366433	0.000014
C	-1.471332	1.573367	-0.000003
C	-2.101070	2.845658	-0.000015
C	-1.362855	4.016914	-0.000030
C	0.023493	3.957694	-0.000030
C	0.695497	2.718646	-0.000015
C	2.103688	2.674255	-0.000009
C	2.767358	1.464335	0.000022
C	-0.045426	1.492334	-0.000005
C	-1.592219	-0.883434	-0.000004
Br	3.225612	-1.248818	0.000133
H	0.293169	-4.219345	-0.000113
H	-2.197252	-4.256482	-0.000037
H	-4.341377	-2.945984	0.000029
H	-5.496331	-0.747717	0.000071
H	-4.214281	1.325432	0.000057
H	-3.180846	2.916371	-0.000015
H	-1.869351	4.976360	-0.000040
H	0.611172	4.871081	-0.000040
H	2.666620	3.602606	-0.000018
H	3.851101	1.444521	0.000042

Table S23 Cartesian coordinates for the optimized T_3 state geometry of 12-BAP with ωB97X-D/6-31+G(d,p) level

Atoms	X	Y	Z
C	1.977139	0.326891	-0.000128
C	0.578442	0.300838	-0.000029
C	-0.160225	-0.901953	0.000005
N	0.461315	-2.097280	0.000088
C	-0.126452	-3.303532	0.000057
C	-1.487032	-3.380358	0.000001
C	-2.273719	-2.164930	-0.000012
C	-3.669375	-2.172637	-0.000025
C	-4.373652	-0.972411	-0.000034
C	-3.704558	0.245556	-0.000021
C	-2.304795	0.310487	-0.000010
C	-1.555560	1.577785	0.000022
C	-2.191618	2.818539	0.000042
C	-1.461937	4.010524	0.000063
C	-0.082498	3.992442	0.000055
C	0.613000	2.767190	0.000023
C	2.040847	2.720816	-0.000016
C	2.709181	1.523805	-0.000099
C	-0.129715	1.551595	0.000015
C	-1.595629	-0.914370	-0.000005
Br	2.906886	-1.329667	-0.000423
H	0.521433	-4.172089	0.000159
H	-1.972234	-4.349188	0.000035
H	-4.199261	-3.120389	-0.000029
H	-5.458919	-0.984539	-0.000039
H	-4.291334	1.156456	-0.000008
H	-3.273387	2.879700	0.000044
H	-1.991884	4.957861	0.000079
H	0.481493	4.920505	0.000063
H	2.596361	3.652866	-0.000026
H	3.793627	1.499550	-0.000187