Electronic Supplementary Information

Effects of Terminal Biphenyl Ring Geometry on the Photophysical Properties of *closo-o*-Carboranyl–Anthracene Dyads

Ju Hyun Hong,‡[a] Sehee Im,‡[a] Yung Ju Seo[a], Na Young Kim[a], Chan Hee Ryu[a], Mingi Kim[a], and Kang Mun Lee*[a]

[a] Department of Chemistry, Institute for Molecular Science and Fusion Technology, Kangwon National University, Chuncheon 24341, Republic of Korea

‡ The first and second authors contributed equally to this work.

Contents

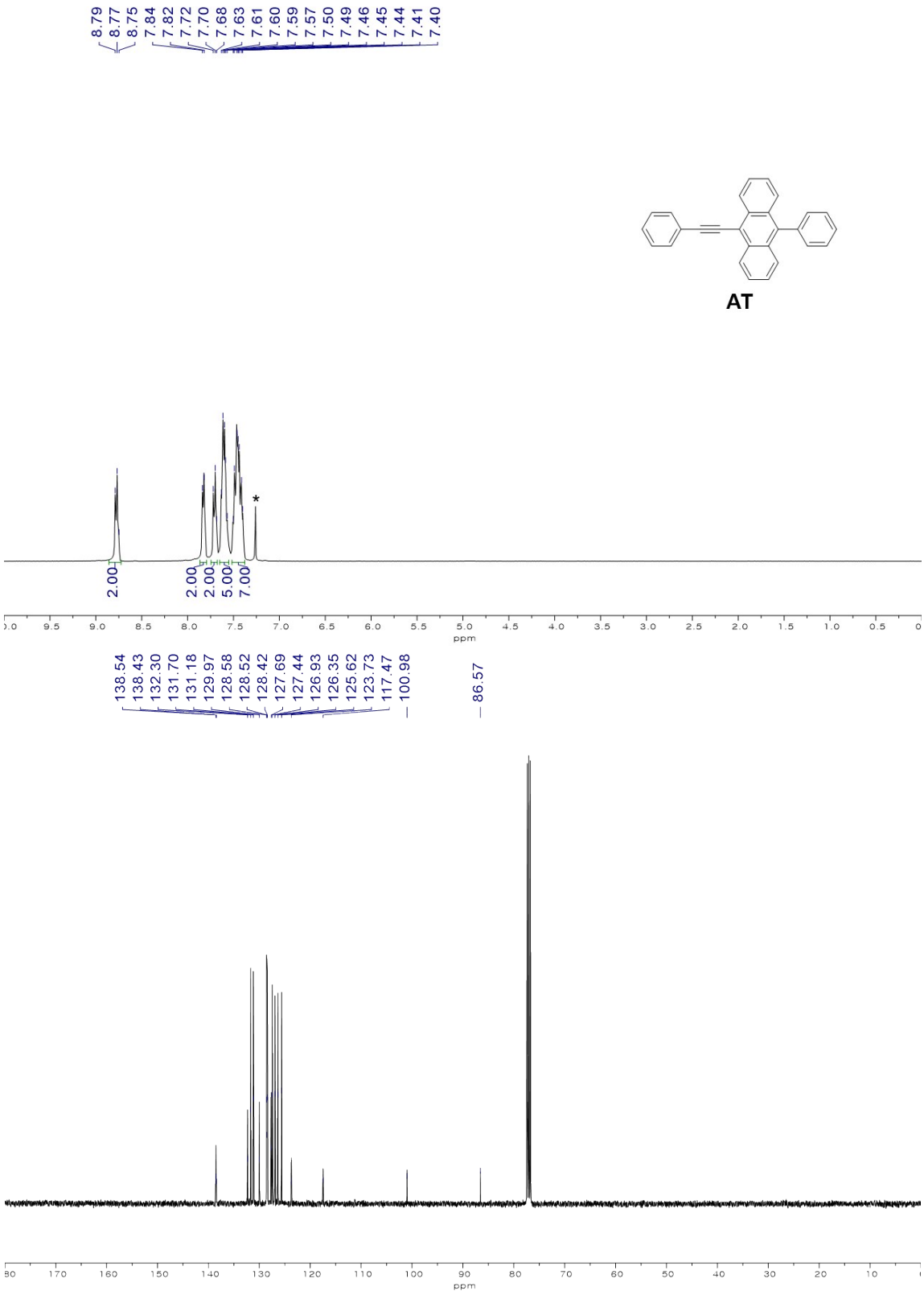

Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **AT** (∗ from residual CH_2Cl_2 in CD_2Cl_2).

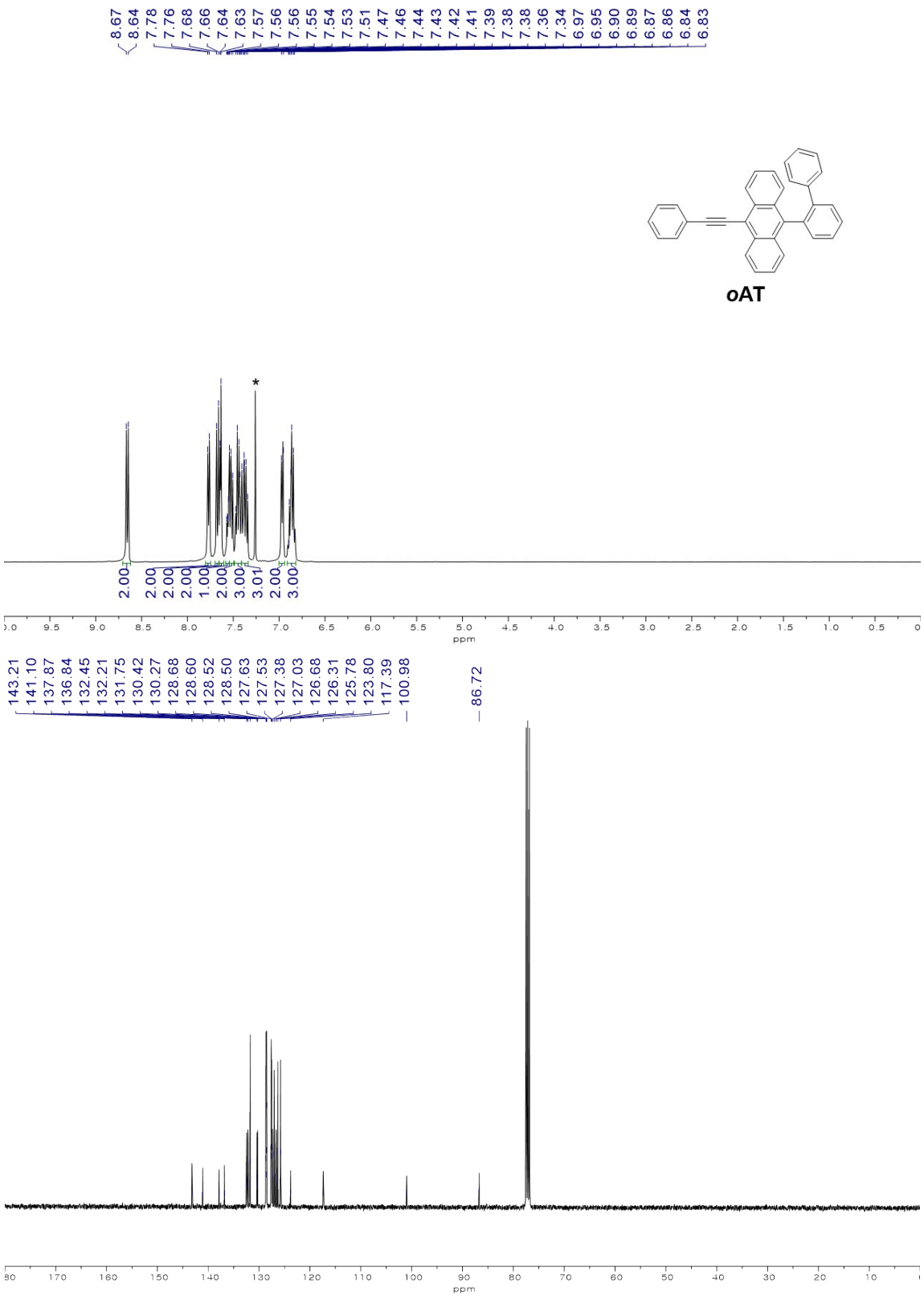

Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of ***o*AT** (∗ from residual $CHCl_3$ in $CDCl_3$).

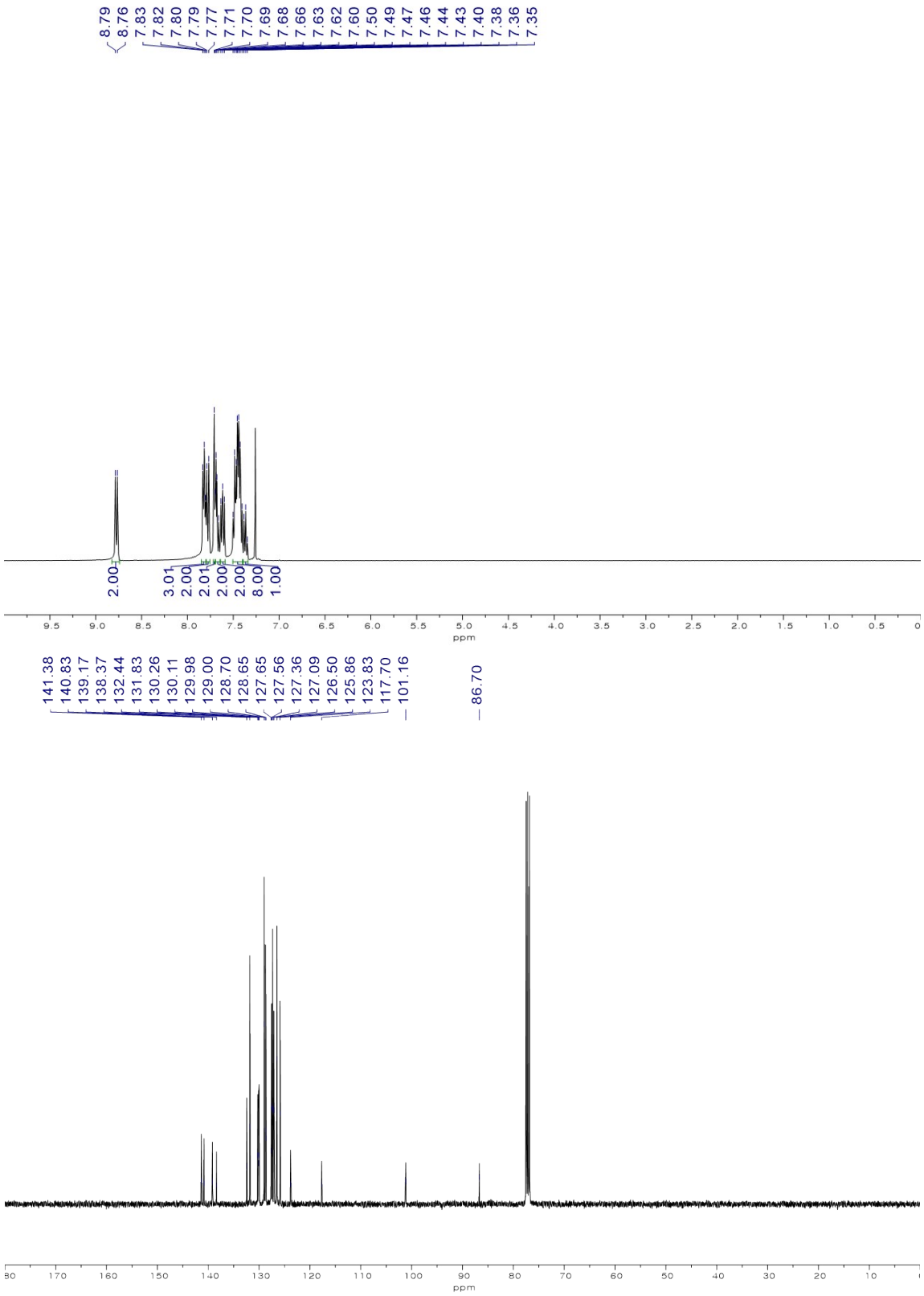

Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of ***m*AT** (∗ from residual $CHCl_3$ in $CDCl_3$).

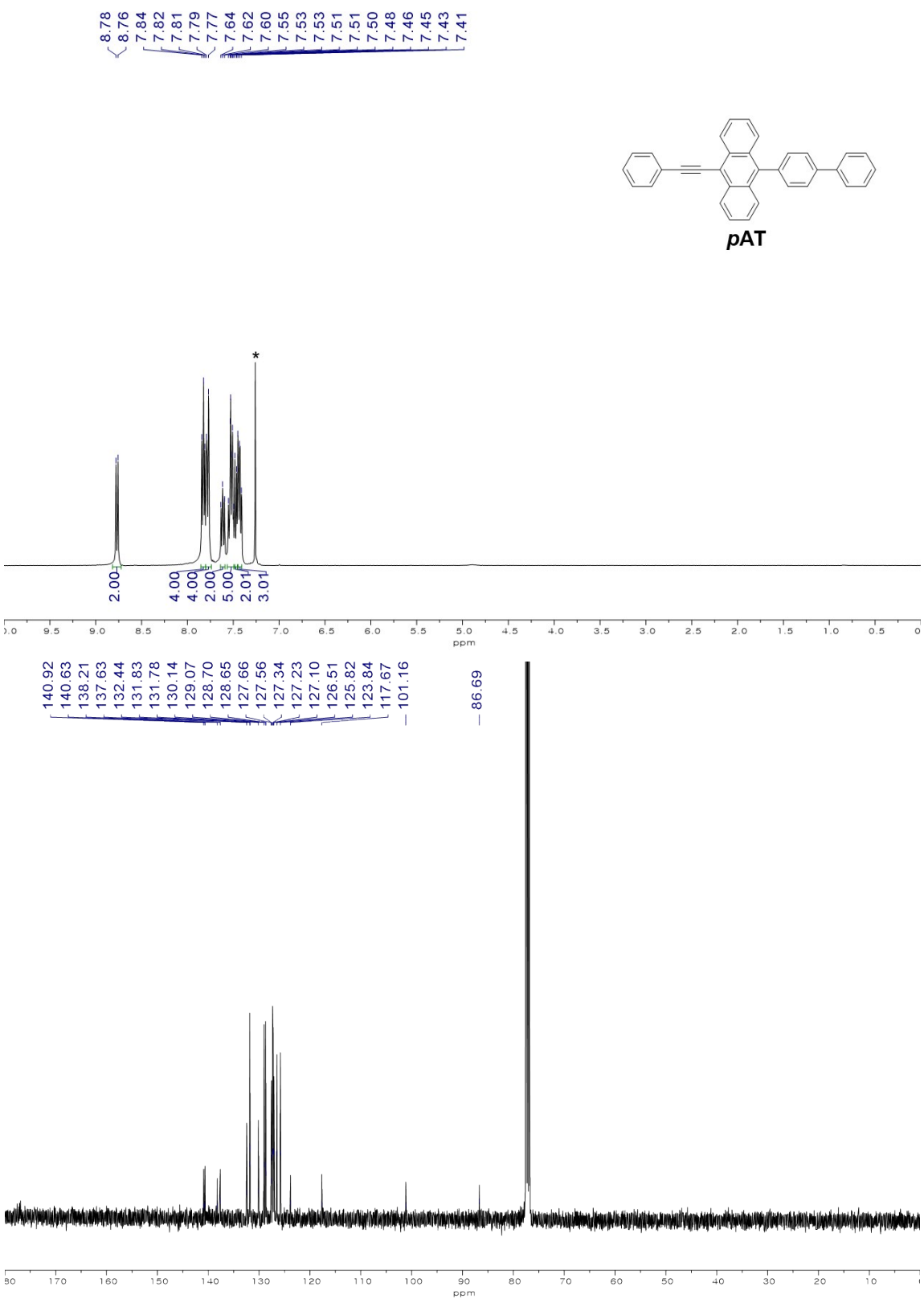

Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of ***p*AT** (∗ from residual $CHCl_3$ in $CDCl_3$).

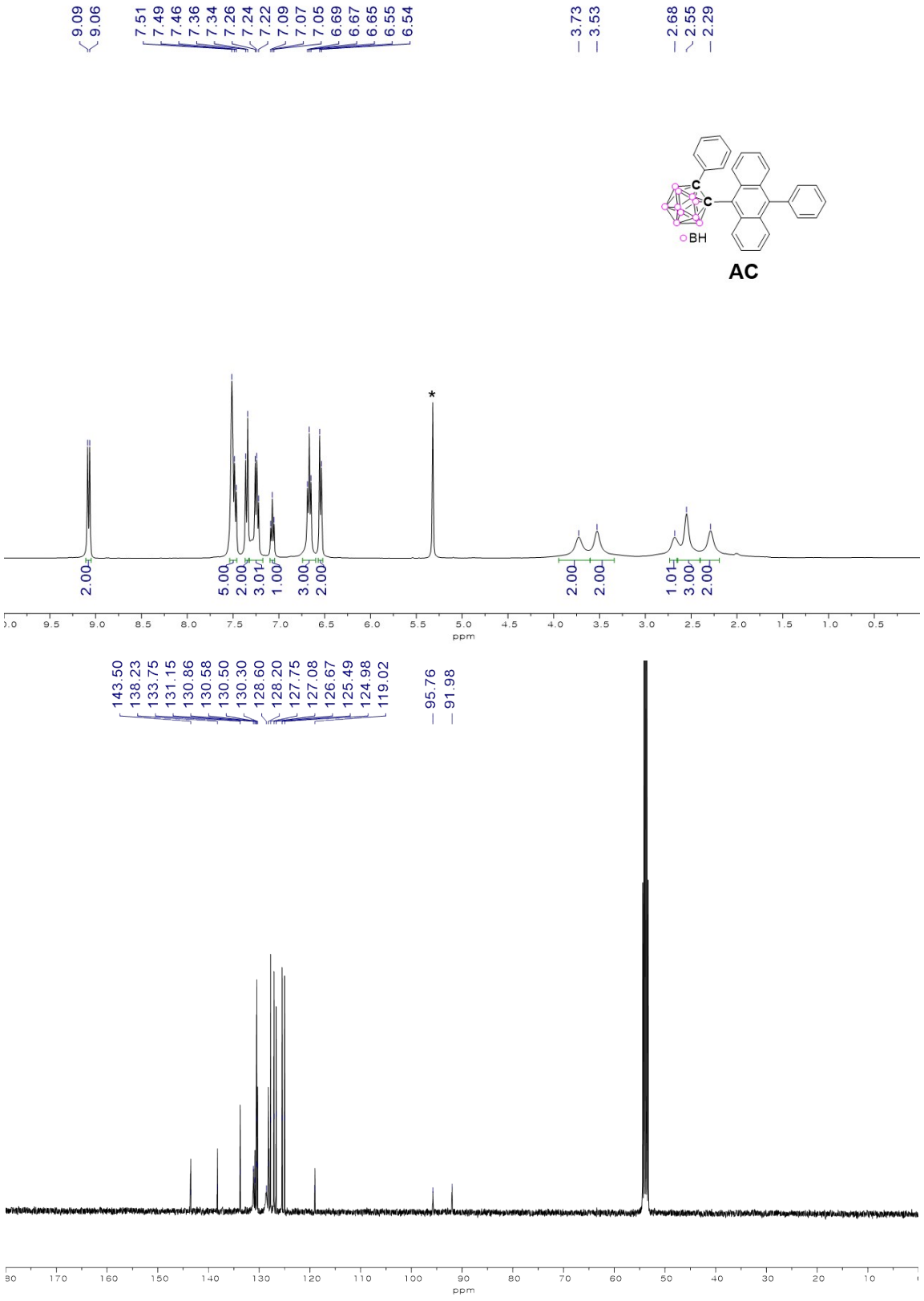

Fig. S5 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **AC** (∗ from residual CH_2Cl_2 in CD_2Cl_2).

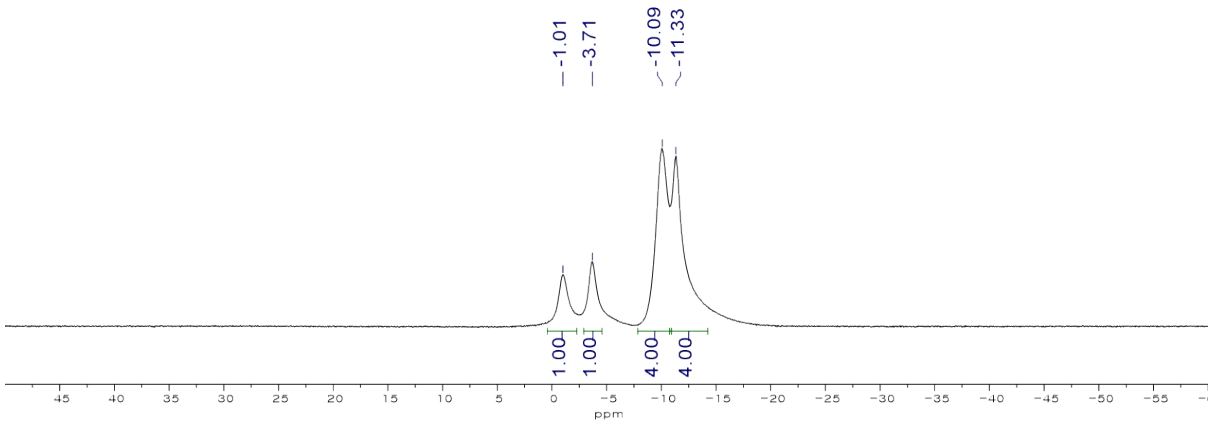

Fig. S6 $^{11}B\{^{1}H\}$ NMR spectra of **AC**.

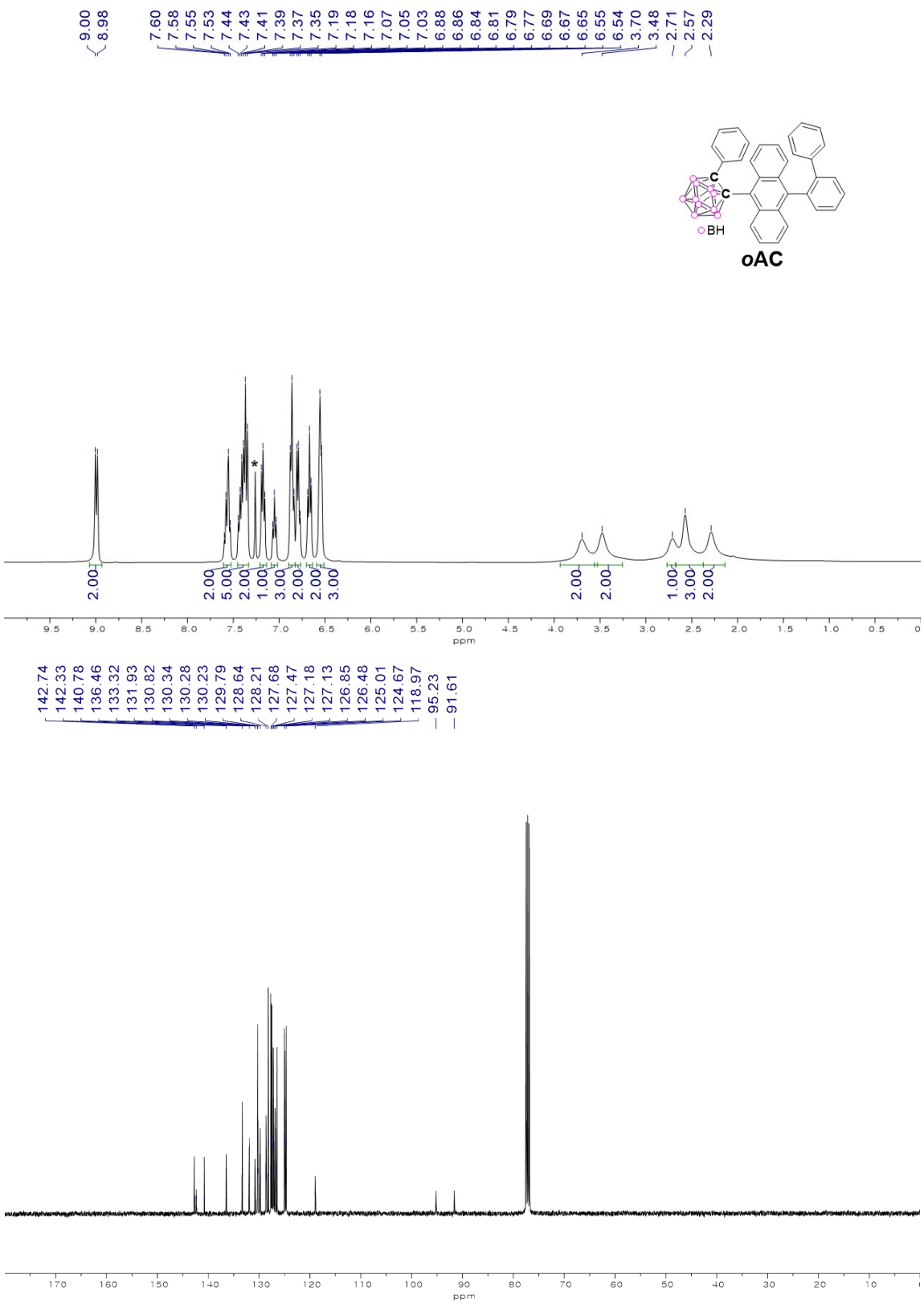

Fig. S7 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of ***o*AC** (∗ from residual $CHCl_3$ in $CDCl_3$).

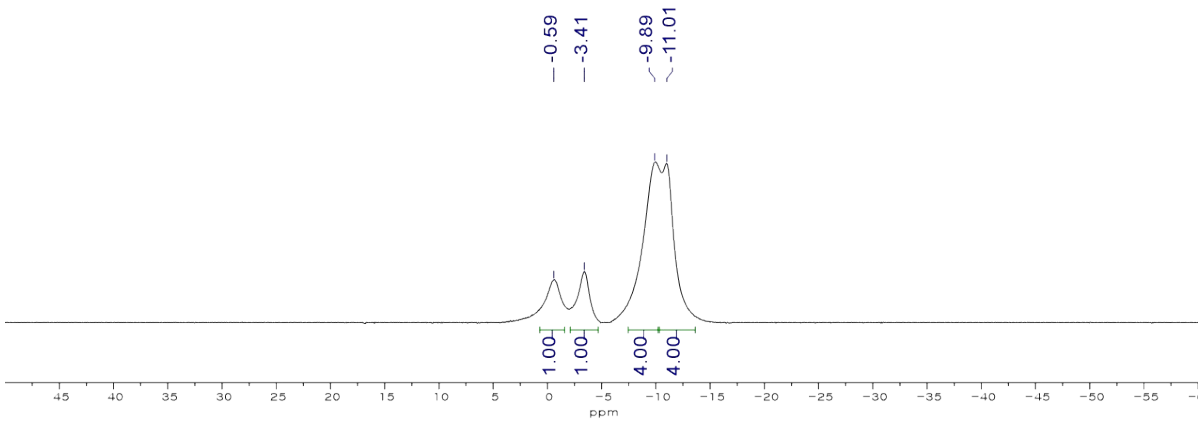

Fig. S8 $^{11}B\{^{1}H\}$ NMR spectra of ***o*AC**.

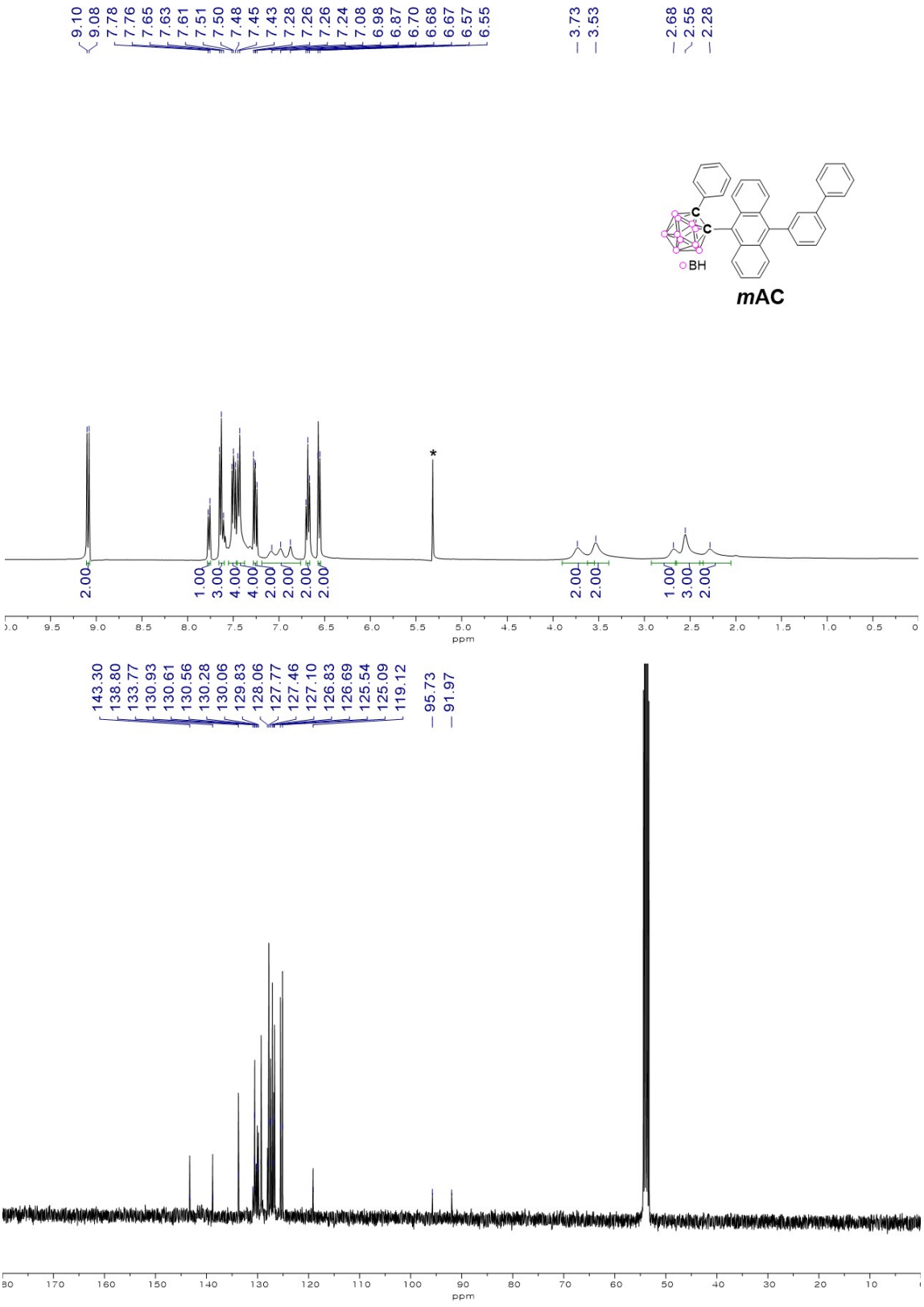

Fig. S9 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of ***m*AC** (∗ from residual CH_2Cl_2 in CD_2Cl_2).

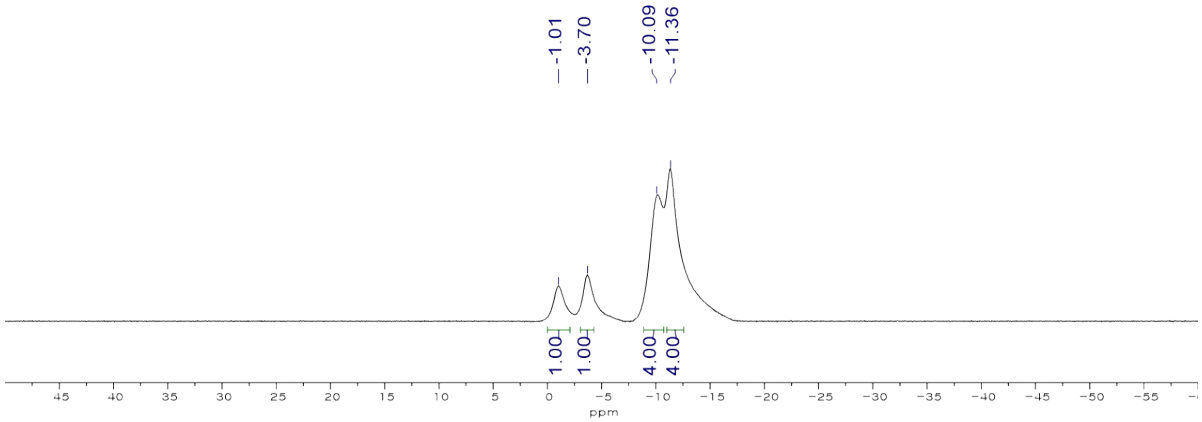

Fig. S10 $^{11}B\{^{1}H\}$ NMR spectra of ***m*AC**.

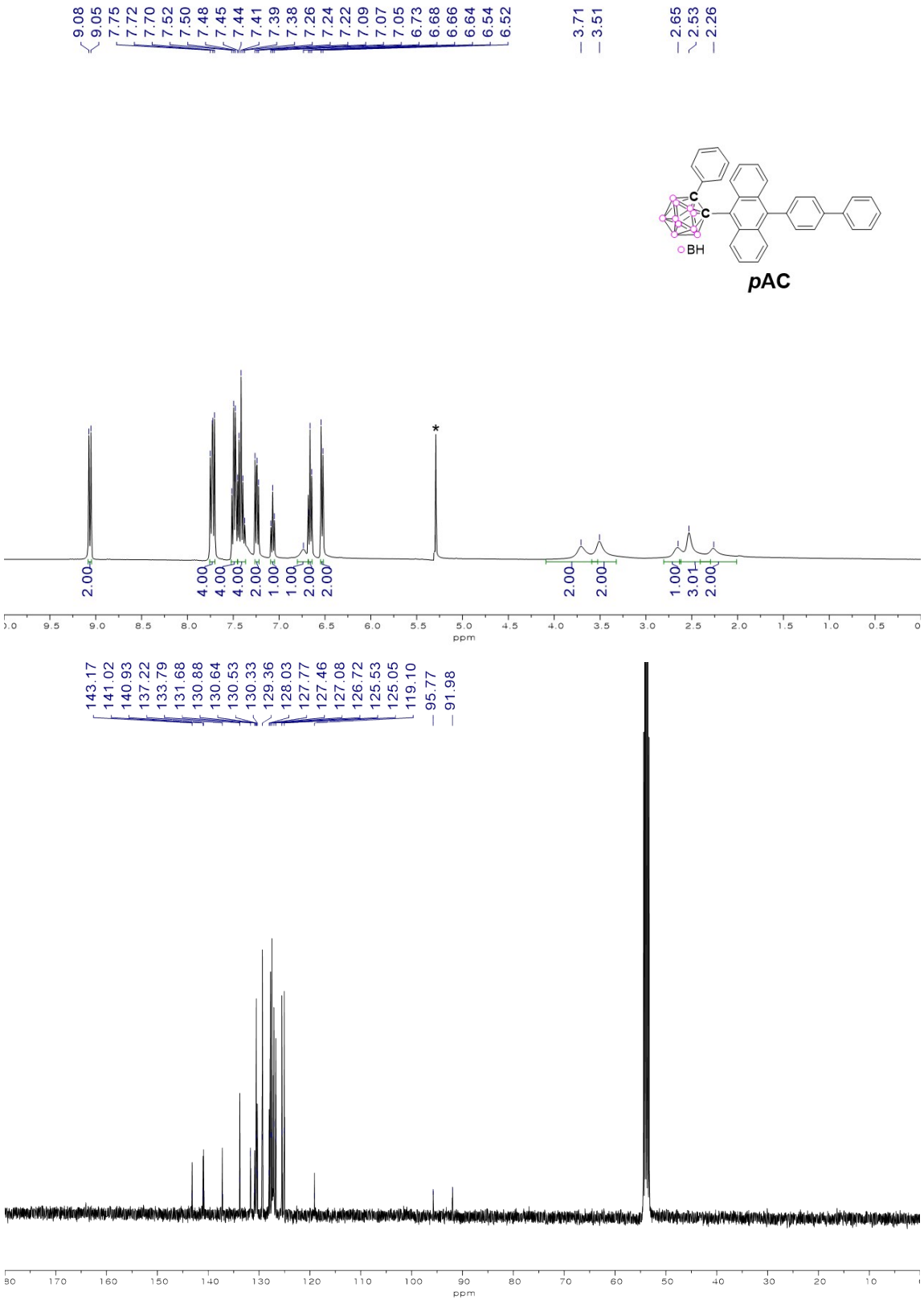

Fig. S11 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of ***p*AC** (∗ from residual CH_2Cl_2 in CD_2Cl_2).

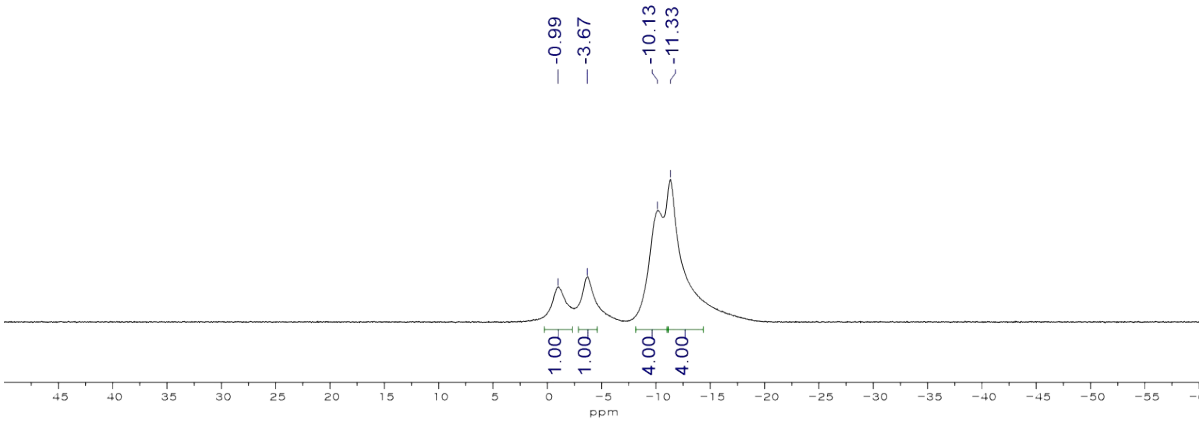

Fig. S12 $^{11}B\{^{1}H\}$ NMR spectra of ***p*AC**.

Table S1 Crystallographic data and parameters for **AC**, ***o*AC**, ***m*AC**, and ***p*AC**.

Compound	**AC**	***o*AC**	***m*AC**	***p*AC**
Formula	$C_{28}H_{28}B_{10}$	$C_{34}H_{32}B_{10}$	$C_{34}H_{32}B_{10}$	$C_{34}H_{32}B_{10}$
Formula weight	472.60	548.69	548.69	548.69
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	C2/c	P_{-1}	C2/c
a (Å)	10.494(2)	26.9408(13)	8.6757(3)	20.593(4)
b (Å)	20.153(4)	10.2620(5)	11.6721(4)	18.751(4)
c (Å)	13.056(3)	25.1467(13)	15.5210(7)	18.322(4)
α (°)	90	90	73.4476(9)	90
β (°)	108.95(3)	119.4985(15)	84.0392(16)	120.95(3)
γ (°)	90	90	86.0663(11)	90
V (Å^3)	2611.5(10)	6051.0(5)	1497.18(10)	6068(3)
Z	4	8	2	8
ρ_{calc}(g cm^{-3})	1.202	1.205	1.217	1.201
μ (mm^{-1})	0.062	0.063	0.064	0.063
F(000)	984	2288	572	2288
T (K)	293(2)	173(2)	173(2)	293(2)
Scan mode	*φ and ω scans*	*φ and ω scans*	*φ and ω scans*	*φ and ω scans*
hkl range	−13 < h < 13, −26 < k < 26, −16 < l < 16	−34 < h < 34, −13 < k < 13, −32 < l < 32	−11 < h < 11, −15 < k < 15, −20 < l < 20	−26 < h < 26, −24 < k < 24, −22 < l < 22
Measd reflns	25889	61641	37993	30155
Unique reflns [R_{int}]	5986 [0.0928]	6926 [0.0835]	7352 [0.0375]	6990 [0.0434]
Reflns used for refinement	5986	6926	7352	6990
Refined parameters	343	397	428	397
R_1[a] (I > 2σ(I))	0.0671	0.0727	0.0509	0.0508
wR_2[b] all data	0.1490	0.1697	0.1336	0.1844
GOF on F^2	1.008	1.048	1.047	1.002
ρ_{fin} (max/min) (e Å^{-3})	0.186, −0.188	0.266, −0.272	0.306, −0.212	0.215, −0.199

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR_2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **AC**, ***o*AC**, ***m*AC**, and ***p*AC**

	AC	***o*AC**	***m*AC**	***p*AC**
bond lengths (Å)				
C10–C27	1.513(3)	1.513(2)	1.5162(15)	1.5241(18)
C27–C28	1.834(3)	1.820(3)	1.8182(18)	1.814(2)
C28–C29	1.510(3)	1.501(3)	1.5025(19)	1.5026(19)
angles (°)				
C13–C9–C15	120.61(19)	118.39(17)	119.50(10)	120.40(13)
C9–C15–C16	121.2(2)	125.6(2)	118.48(10)	121.15(13)
C10–C27–C28	115.23(14)	114.17(14)	113.78(9)	114.97(10)
C27–C28–C29	116.72(16)	117.99(15)	117.36(9)	117.18(11)

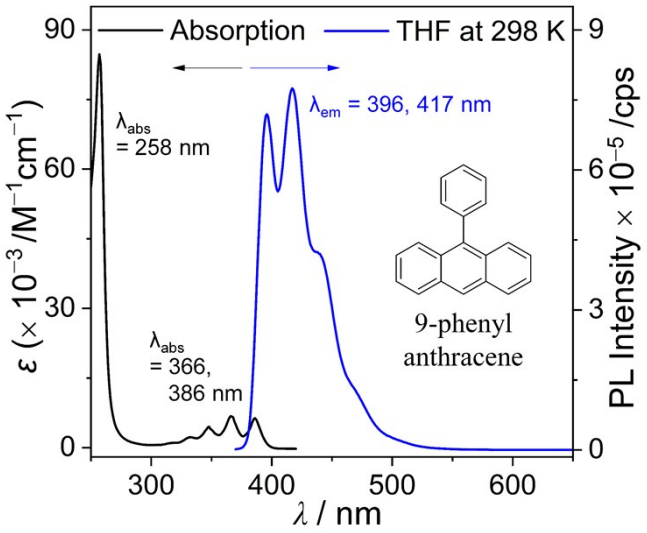

Fig. S13 UV-vis absorption (left side) and PL spectra (right side) for 9-phenylanthracene (λ_{ex} = 348 nm). Black line: absorption spectra in THF (1.0×10^{-5} M), blue line: PL spectra in THF (1.0×10^{-5} M) at 298 K.

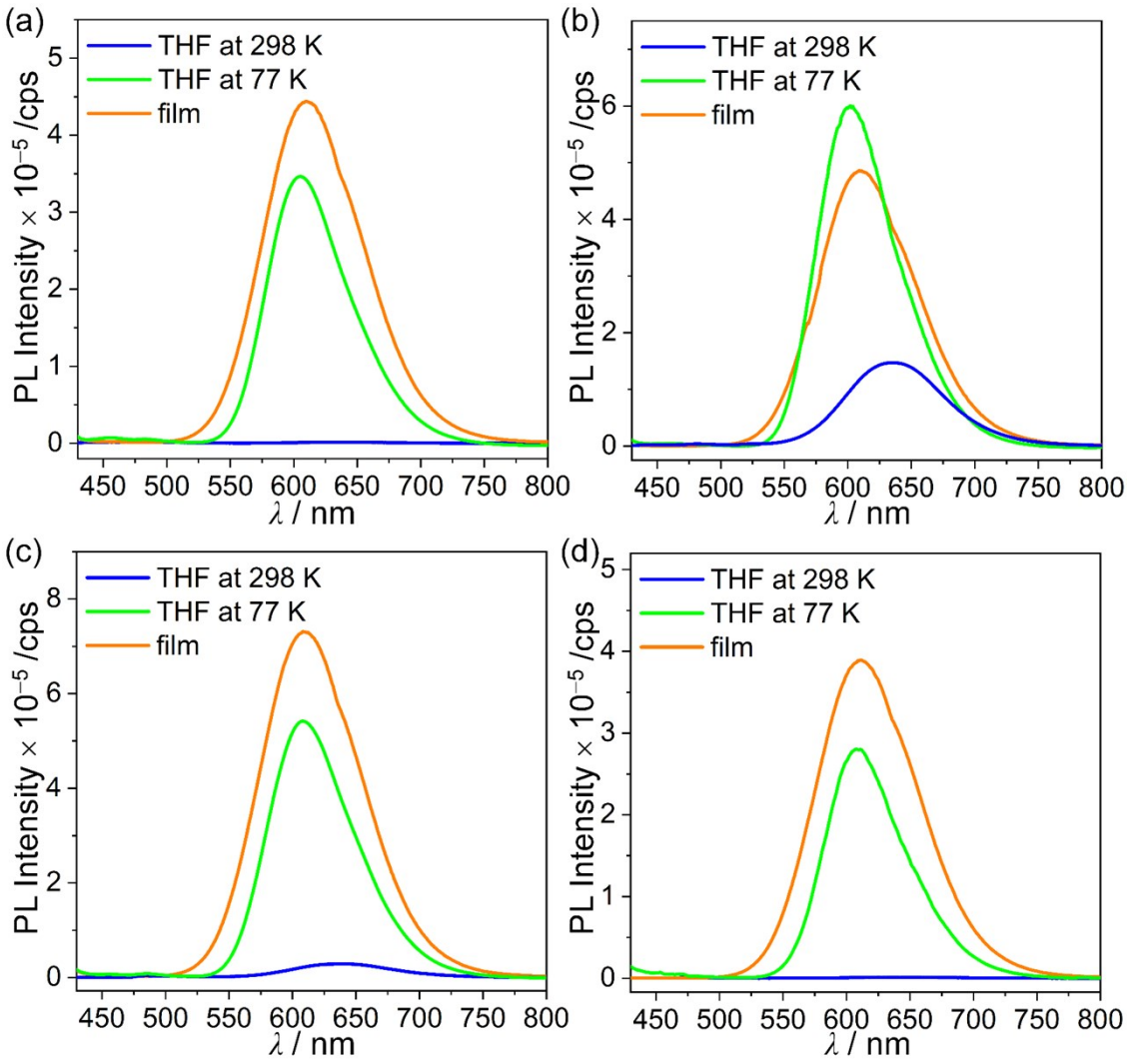

Fig. S14 Full range (430–800 nm) PL spectra of (a) **AC** (λ_{ex} = 421 nm), (b) ***o*AC** (λ_{ex} = 422 nm), (c) ***m*AC** (λ_{ex} = 423 nm), and (d) ***p*AC** (λ_{ex} = 423 nm) in various conditions.

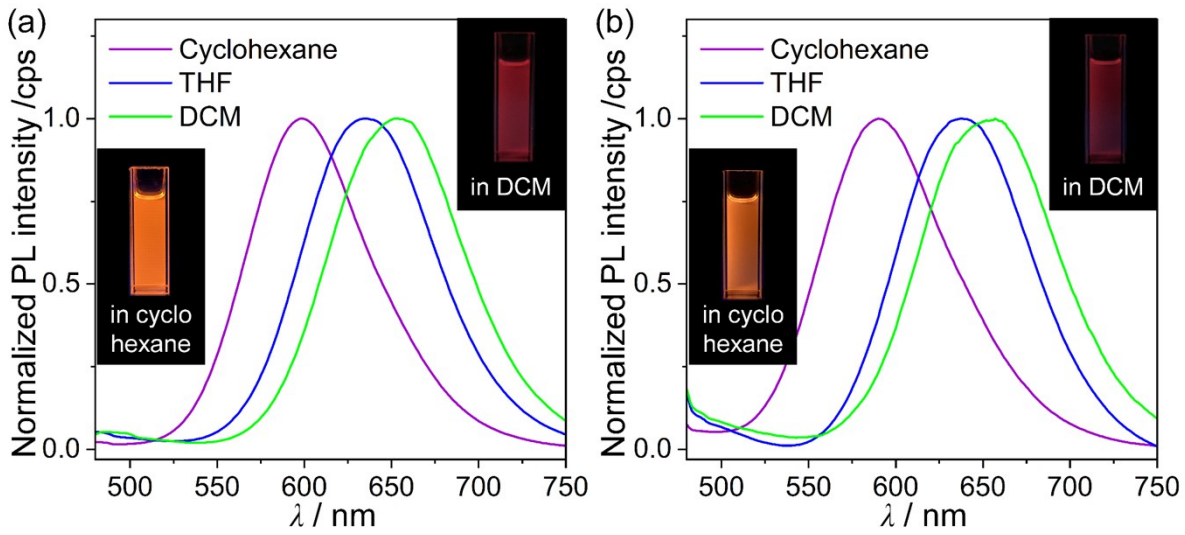

Fig. S15 PL spectra of (a) ***o*AC** and (b) ***m*AC** in various organic solvents (1.0×10^{-5} M).

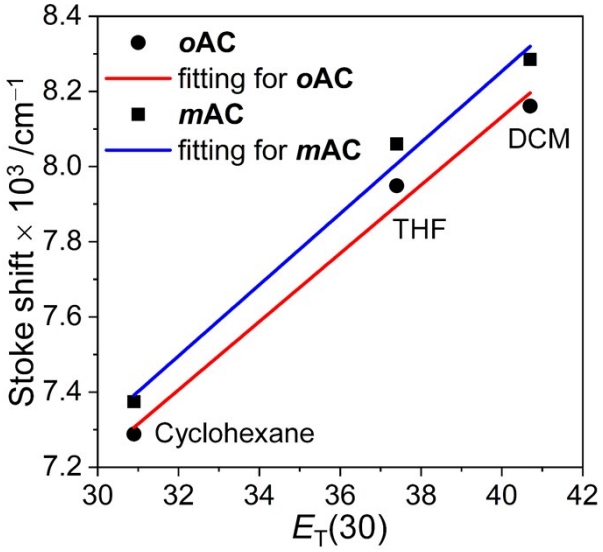

Fig. S16 Stokes shift as a function of the empirical solvent-polarity parameter [$E_T(30)$] for ***o*AC** and ***m*AC** and their Mataga-Lippert plots (R^2 = 0.98957 for ***o*AC** and 0.99044 for ***m*AC**).

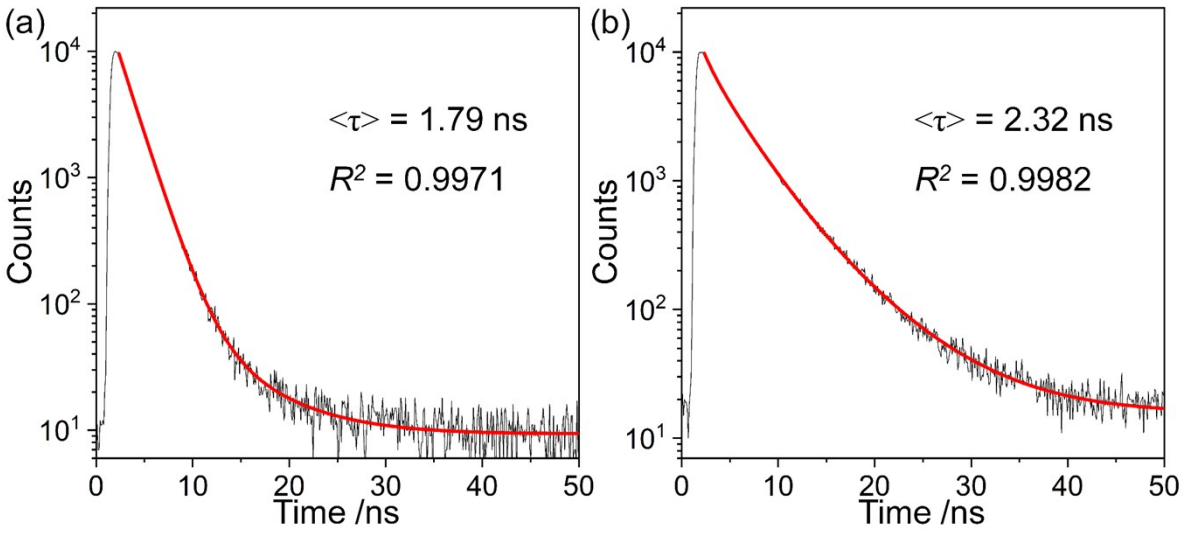

Fig. S17 Emission decay curves for (a) ***o*AC**, and (b) ***m*AC** in THF (1.0×10^{-5} M) at 298 K detected at each ICT based emission maxima at 298 K. Each red-line is its single exponential fitting curve for the decay curves.

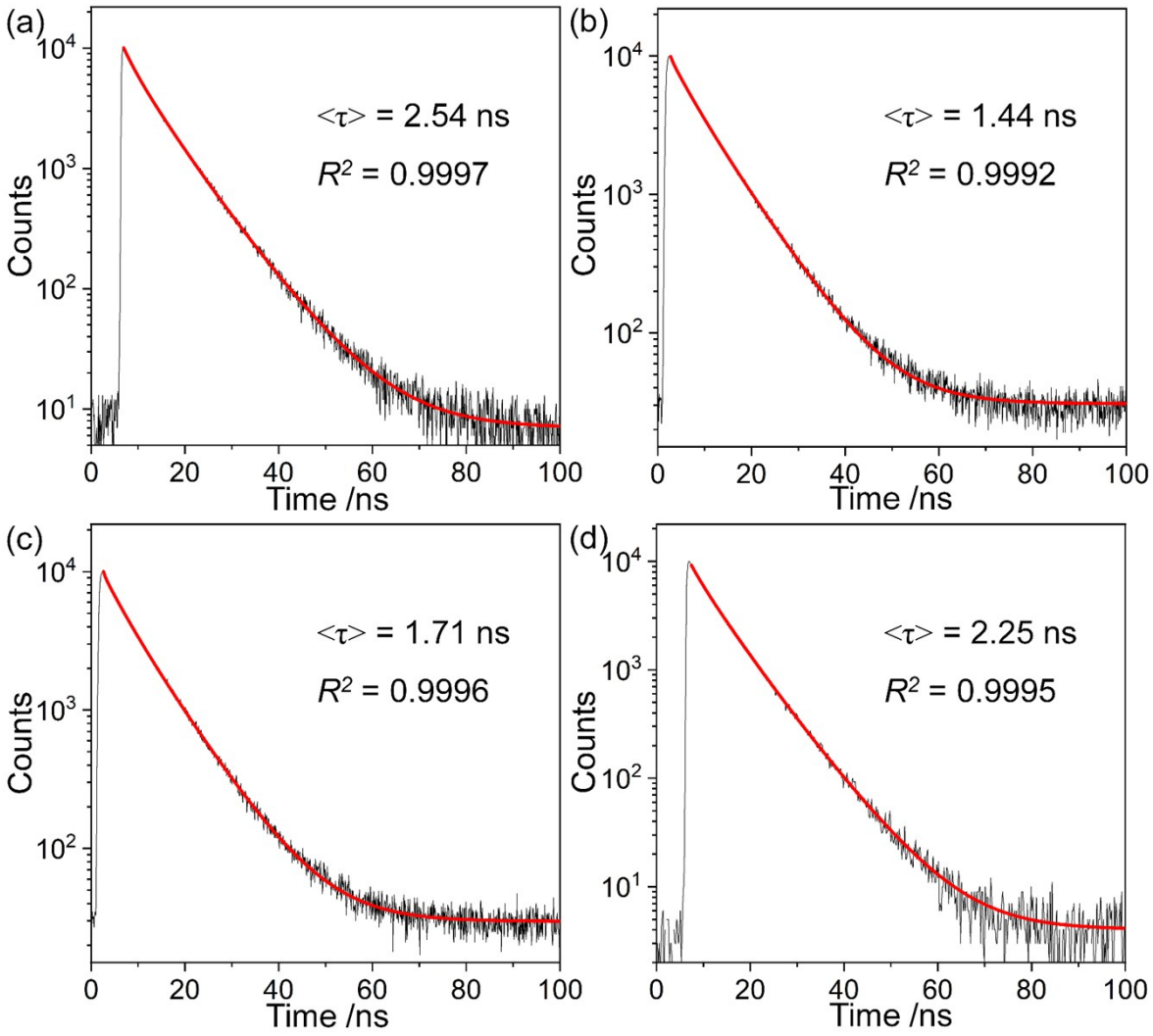

Fig. S18 Emission decay curves for (a) **AC**, (b) ***o*AC**, (c) ***m*AC**, and (d) ***p*AC** in the film state (5 wt% doped in PMMA) detected at each CT based emission maxima at 298 K. Each red-line is its single exponential fitting curve for the decay curves.

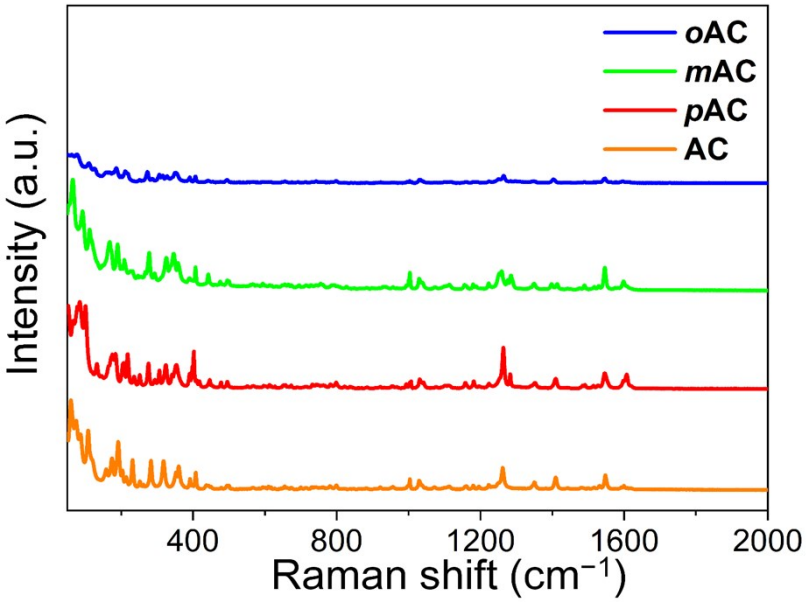

Fig. S19 Raman spectra of **AC**, ***o*AC**, ***m*AC**, and ***p*AC** (Laser: 785 nm (He-Ne laser), exposure time: 10 s, object: ×50 vis, power: 90 mW).

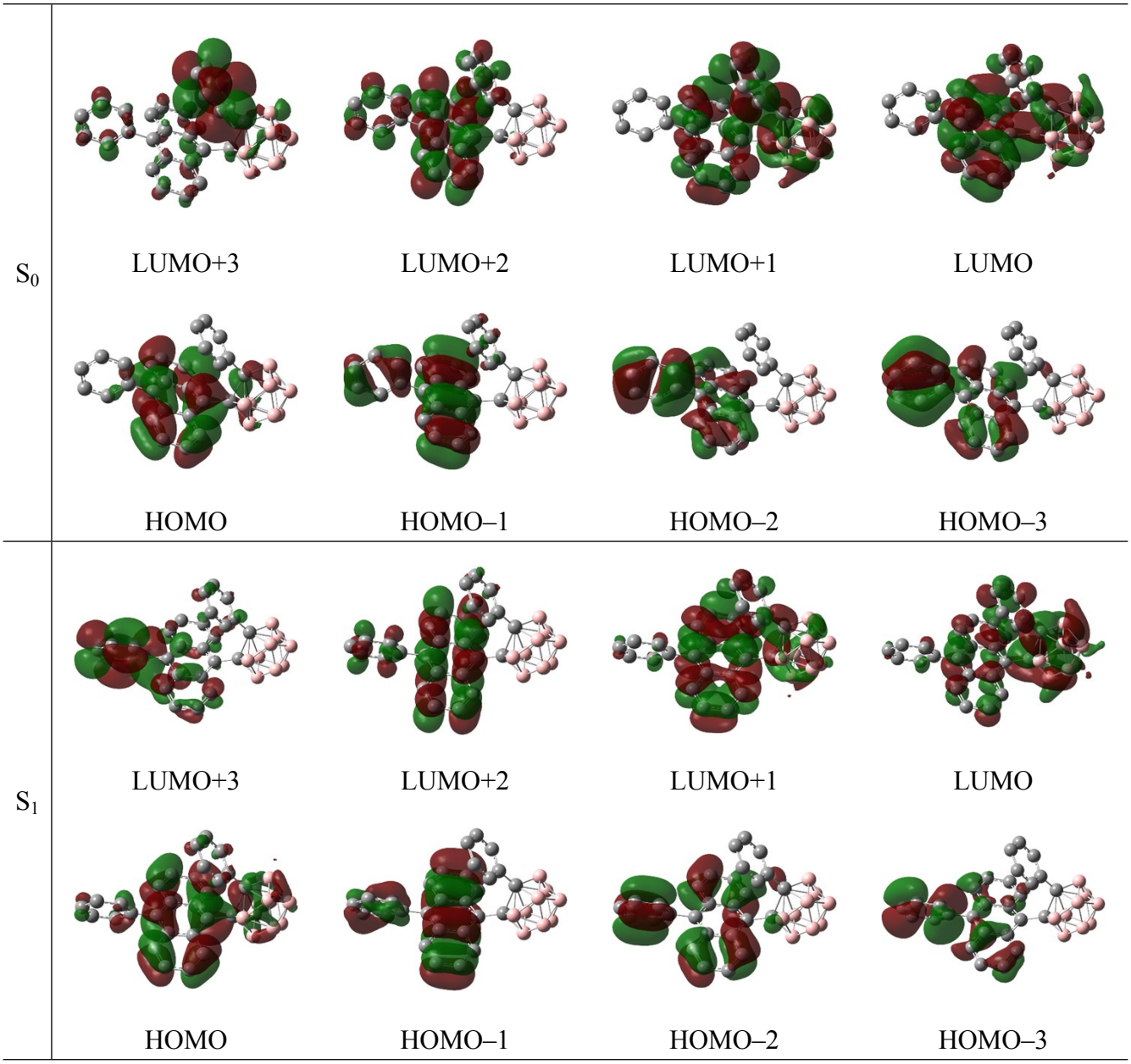

Fig. S20 The selected frontier orbitals of **AC** from TD-PBE0 calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S3 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **AC** from TD-PBE0 calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	442.22	0.2553	HOMO → LUMO (98.5%)
2	362.82	0.0175	HOMO → LUMO+1 (97.7%)
3	355.49	0.0539	HOMO−1 → LUMO (80.9%)
			HOMO → LUMO+2 (14.6%)
4	341.66	0.0001	HOMO−2 → LUMO (93.2%)
5	338.87	0.0064	HOMO−3 → LUMO (89.9%)
			S_1
1	628.91	0.3496	HOMO → LUMO (99.9%)
2	419.61	0.0146	HOMO−2 → LUMO (29.3%)
			HOMO−1 → LUMO (66.2%)
3	408.17	0.0113	HOMO−4 → LUMO (10.3%)
			HOMO → LUMO+1 (87.5%)
4	406.68	0.0395	HOMO−2 → LUMO (62.3%)
			HOMO−1 → LUMO (30.2%)
5	394.69	0.0252	HOMO−3 → LUMO (96.2%)

Table S4 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **AC** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

	E (eV)	carborane -phenyl	carborane	anthracene	anthracene 10-phenyl
			S_0		
LUMO+3	−0.43	80.5	7.8	6.6	5.2
LUMO+2	−0.79	8.1	4.3	78.0	9.6
LUMO+1	−1.66	24.5	35.8	39.5	0.2
LUMO	−2.67	5.1	31.4	62.3	1.2
HOMO	−5.61	0.6	7.0	91.2	1.1
HOMO−1	−6.79	2.1	0.2	85.1	12.6
HOMO−2	−6.95	0.7	0.7	25.1	73.5
HOMO−3	−6.96	0.1	1.6	33.7	64.7
			S_1		
LUMO+3	−0.50	2.8	0.7	15.6	80.9
LUMO+2	−0.74	2.0	2.9	87.2	7.8
LUMO+1	−2.06	6.1	16.5	75.5	1.8
LUMO	−3.37	10.0	57.4	30.8	1.8
HOMO	−5.54	2.5	11.3	82.6	3.6
HOMO−1	−6.91	0.2	0.4	88.9	10.6
HOMO−2	−6.98	0.5	3.0	58.2	38.3
HOMO−3	−7.02	0.1	0.2	15.8	83.9

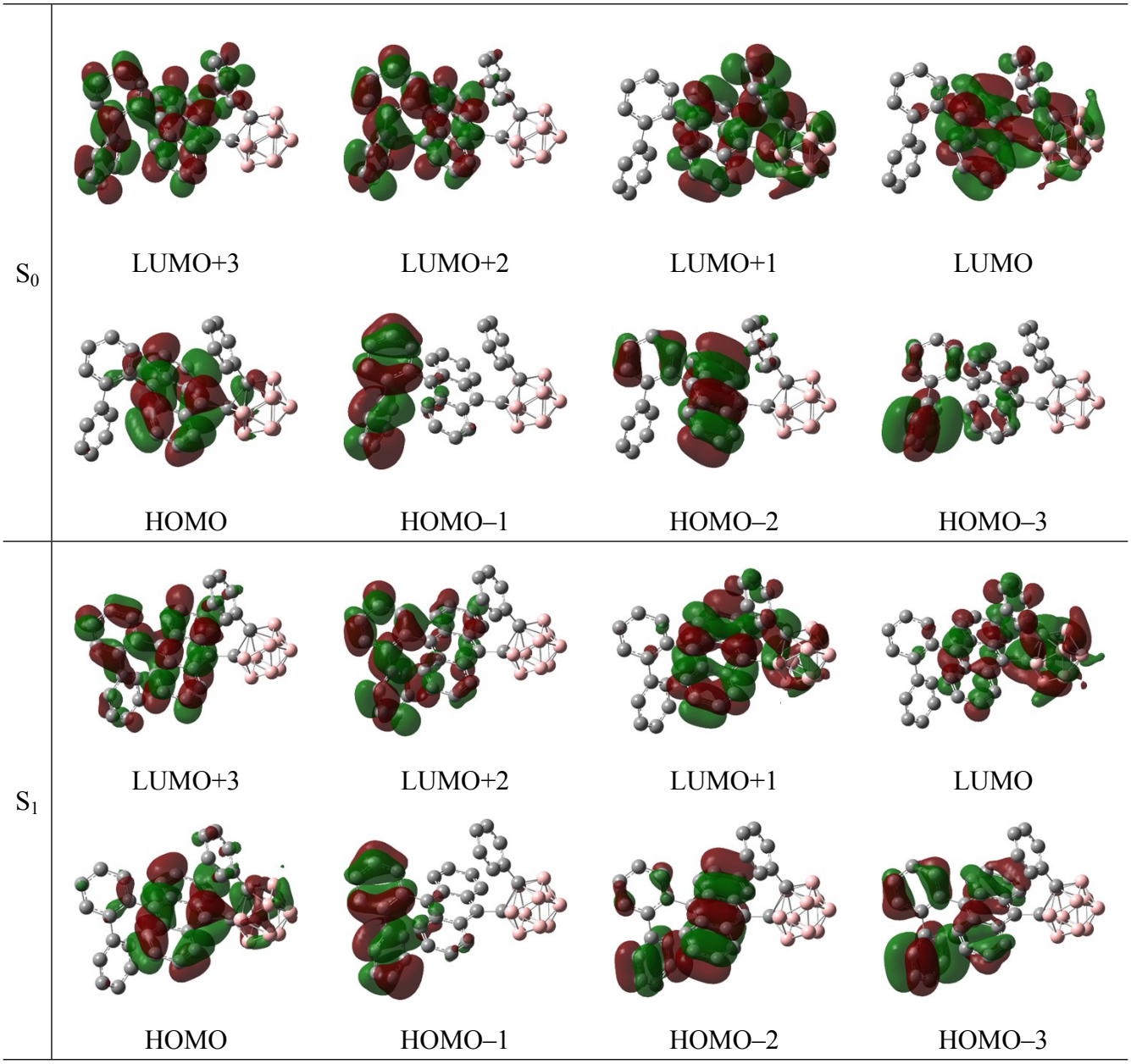

Fig. S21 The selected frontier orbitals of ***o*AC** from TD-PBE0 calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S5 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for ***o*AC** from TD-PBE0 calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	437.69	0.2828	HOMO → LUMO (98.5%)
2	393.88	0.0040	HOMO−1 → LUMO (98.2%)
3	365.22	0.0138	HOMO → LUMO+1 (97.6%)
4	357.23	0.0517	HOMO−2 → LUMO (80.4%)
			HOMO → LUMO+2 (9.0%)
			HOMO → LUMO+3 (6.0%)
5	343.48	0.0036	HOMO−4 → LUMO (49.9%)
			HOMO−3 → LUMO (41.1%)
			S_1
1	620.18	0.3616	HOMO → LUMO (100.3%)
2	484.49	0.0071	HOMO−1 → LUMO (98.8%)
3	421.66	0.0161	HOMO−4 → LUMO (20.6%)
			HOMO−2 → LUMO (72.6%)
4	410.07	0.0313	HOMO−4 → LUMO (33.1%)
			HOMO−3 → LUMO (56.8%)
5	408.51	0.0150	HOMO−5 → LUMO (10.3%)
			HOMO → LUMO+1 (88.2%)

Table S6 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of ***o*AC** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

	E (eV)	carborane -phenyl	carborane	anthracene	anthracene 10-phenyl	terminal -phenyl
			S_0			
LUMO+3	−0.69	10.4	3.3	45.7	24.6	15.9
LUMO+2	−0.92	2.0	1.5	35.1	35.4	26.1
LUMO+1	−1.67	24.3	36.2	38.9	0.3	0.3
LUMO	−2.69	5.0	31.0	61.9	1.6	0.4
HOMO	−5.60	0.6	7.0	89.3	2.1	0.9
HOMO−1	−6.39	0.0	0.0	2.8	41.8	55.3
HOMO−2	−6.79	2.0	0.2	84.4	12.6	0.8
HOMO−3	−6.88	0.1	0.4	11.2	5.0	83.2
			S_1			
LUMO+3	−0.69	2.1	2.2	67.5	21.8	6.5
LUMO+2	−0.93	0.2	0.5	20.4	44.7	34.1
LUMO+1	−2.06	6.0	16.2	76.0	1.4	0.5
LUMO	−3.38	10.1	57.9	30.3	1.4	0.3
HOMO	−5.55	2.5	11.1	82.8	2.7	1.0
HOMO−1	−6.40	0.0	0.0	3.6	40.2	56.2
HOMO−2	−6.89	0.2	0.5	70.9	4.4	24.0
HOMO−3	−6.90	0.2	0.2	23.7	13.6	62.3

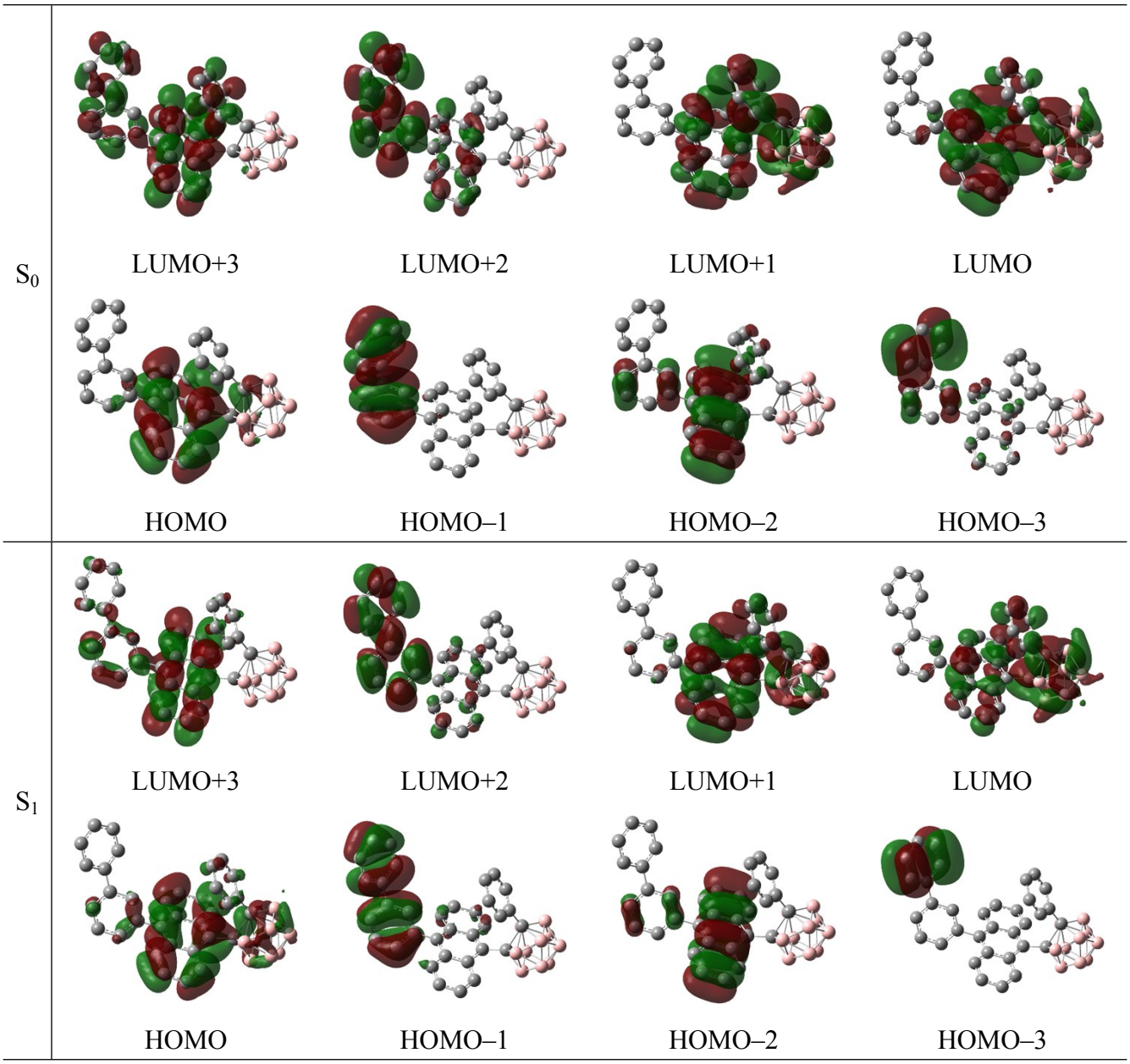

Fig. S22 The selected frontier orbitals of ***m*AC** from TD-PBE0 calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S7 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for ***m*AC** from TD-PBE0 calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	439.04	0.2475	HOMO → LUMO (98.4%)
2	392.77	0.0010	HOMO−1 → LUMO (98.8%)
3	362.07	0.0213	HOMO → LUMO+1 (97.8%)
4	354.62	0.0507	HOMO−2 → LUMO (80.3%)
			HOMO → LUMO+3 (10.3%)
5	338.52	0.0020	HOMO−4 → LUMO (81.7%)
			HOMO−3 → LUMO (12.7%)
			S_1
1	619.90	0.3520	HOMO → LUMO (99.9%)
2	487.76	0.0031	HOMO−1 → LUMO (99.1%)
3	419.32	0.0166	HOMO−4 → LUMO (14.0%)
			HOMO−2 → LUMO (80.5%)
4	408.25	0.0125	HOMO−5 → LUMO (11.5%)
			HOMO → LUMO+1 (87.5%)
5	402.22	0.0434	HOMO−4 → LUMO (73.0%)
			HOMO−2 → LUMO (16.1%)

Table S8 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of ***m*AC** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

	E (eV)	carborane -phenyl	carborane	anthracene	anthracene 10-phenyl	terminal -phenyl
			S_0			
LUMO+3	−0.72	12.2	4.6	64.6	9.2	9.3
LUMO+2	−1.03	0.9	0.6	15.2	46.9	36.3
LUMO+1	−1.64	26.2	36.7	36.9	0.2	0.1
LUMO	−2.65	4.7	29.6	64.4	1.2	0.1
HOMO	−5.61	0.6	6.9	91.4	1.1	0.1
HOMO−1	−6.29	0.0	0.0	1.6	46.0	52.3
HOMO−2	−6.80	2.6	0.3	87.4	9.4	0.2
HOMO−3	−6.95	1.0	0.3	4.7	7.3	86.7
			S_1			
LUMO+3	−0.71	2.0	2.7	83.0	9.2	3.1
LUMO+2	−1.03	0.0	0.2	7.9	51.8	40.1
LUMO+1	−2.06	6.1	16.6	75.5	1.8	0.0
LUMO	−3.38	10.0	57.4	30.9	1.8	0.0
HOMO	−5.54	2.5	11.2	82.4	3.6	0.3
HOMO−1	−6.32	0.0	0.1	3.0	43.6	53.4
HOMO−2	−6.92	0.1	0.6	93.3	5.7	0.3
HOMO−3	−6.96	0.0	0.0	0.7	1.0	98.3

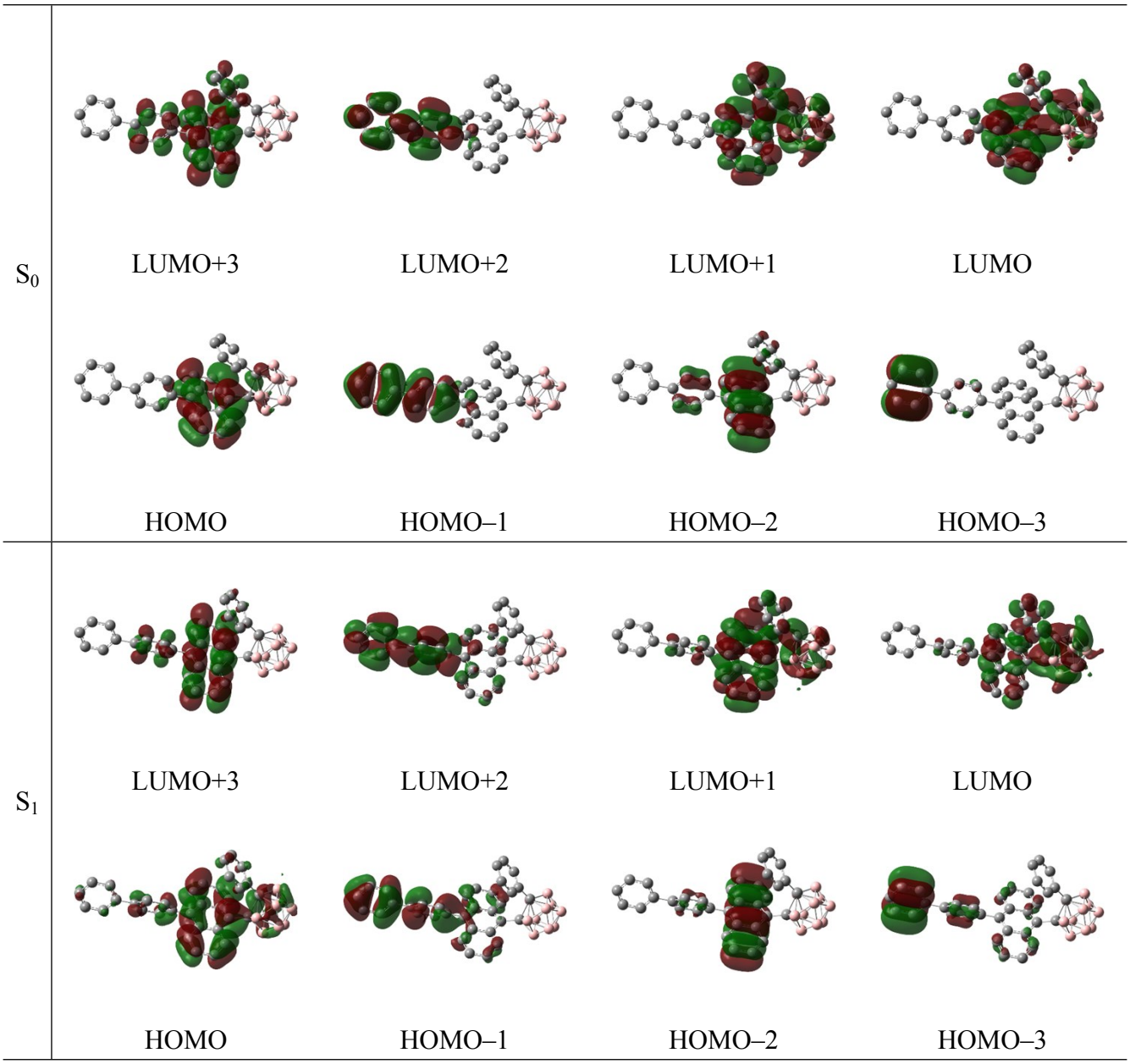

Fig. S23 The selected frontier orbitals of ***p*AC** from TD-PBE0 calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S9 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for ***p*AC** from TD-PBE0 calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	441.17	0.2863	HOMO → LUMO (98.4%)
2	399.37	0.0015	HOMO−1 → LUMO (97.7%)
3	362.45	0.0213	HOMO → LUMO+1 (97.7%)
4	353.88	0.0523	HOMO−2 → LUMO (79.0%)
			HOMO → LUMO+3 (16.0%)
5	337.69	0.0076	HOMO−4 → LUMO (87.7%)
			S_1
1	625.44	0.4292	HOMO → LUMO (99.9%)
2	481.08	0.0509	HOMO−1 → LUMO (98.7%)
3	418.36	0.0127	HOMO−4 → LUMO (18.3%)
			HOMO−2 → LUMO (74.5%)
4	412.34	0.0284	HOMO → LUMO+1 (91.2%)
5	403.18	0.0461	HOMO−4 → LUMO (65.6%)
			HOMO−2 → LUMO (21.9%)

Table S10 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of ***p*AC** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

	E (eV)	carborane -phenyl	carborane	anthracene	anthracene 10-phenyl	terminal -phenyl
			S_0			
LUMO+3	−0.80	7.9	4.1	75.9	11.6	0.4
LUMO+2	−0.99	0.0	0.1	2.5	53.5	43.9
LUMO+1	−1.65	25.1	36.3	38.4	0.2	0.0
LUMO	−2.67	5.0	30.7	63.2	1.2	0.0
HOMO	−5.61	0.6	6.9	91.2	1.2	0.1
HOMO−1	−6.26	0.0	0.0	2.8	46.3	50.9
HOMO−2	−6.81	2.5	0.3	91.9	4.9	0.4
HOMO−3	−6.94	0.0	0.1	1.5	2.0	96.4
			S_1			
LUMO+3	−0.74	1.9	2.9	86.7	8.2	0.3
LUMO+2	−1.10	0.0	0.1	9.2	52.0	38.7
LUMO+1	−2.06	6.4	17.7	72.1	2.9	0.8
LUMO	−3.37	9.6	57.8	29.9	2.3	0.3
HOMO	−5.51	2.5	8.4	83.1	4.0	1.9
HOMO−1	−6.33	0.1	0.2	10.0	39.2	50.5
HOMO−2	−6.92	0.1	0.7	96.5	2.2	0.5
HOMO−3	−6.97	0.0	0.3	5.8	4.6	89.3

Table S11 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **AC**, ***o*AC**, ***m*AC**, and ***p*AC** in S_1 state upon the changes (0–180°) of Ψ_2 value

Ψ_2	0°		30°		60°		90°		120°		150°		180°	
	λ_{calc} (/nm)	f_{calc}	λ_{calc} (/nm)	f_{calc}	λ_{calc} (/nm)	f_{calc}	λ_{calc} (/nm)	f_{calc}	λ_{calc} (/nm)	f_{calc}	λ_{calc} (/nm)	f_{calc}	λ_{calc} (/nm)	f_{calc}
AC	650.89	0.4427	644.30	0.4239	630.66	0.3756	628.91	0.3366	632.75	0.3689	651.44	0.4234	661.00	0.4426
***o*AC**	667.83	0.4439	654.04	0.4061	649.58	0.3776	625.90	0.3239	649.65	0.3718	664.71	0.3950	669.82	0.4454
***m*AC**	661.66	0.4720	642.41	0.4560	638.28	0.3994	629.48	0.3253	641.54	0.4005	646.44	0.4635	672.01	0.4705
***p*AC**	664.51	0.5905	633.73	0.5428	633.18	0.4417	626.40	0.3681	661.08	0.4384	631.60	0.5491	664.73	0.5902

Table S12 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	0.242984	1.201730	3.603178
C	-0.232878	-0.005492	4.118408
C	1.180126	1.204651	2.572160
C	0.243980	-1.211274	3.600732
C	1.659298	-0.002597	2.035084
C	1.181115	-1.211327	2.569705
C	2.694625	-0.001121	0.955742
C	2.079352	0.001252	-0.958258
H	-0.112853	2.145408	4.004499
H	-0.962770	-0.006611	4.922165
H	4.278339	1.538948	2.006888
H	1.544852	2.150121	2.190440
H	-0.111076	-2.156054	4.000148
H	2.143316	2.296857	0.157384
H	5.039582	2.479297	-0.774178
H	1.546626	-2.155720	2.186067
H	4.278385	-1.543895	2.002889
H	6.463465	-0.000392	0.386545
H	2.930366	1.525979	-2.691808
H	2.143441	-2.297083	0.151641
H	5.566122	0.003400	-2.526355
H	5.039648	-2.477141	-0.780425
H	2.930391	-1.518900	-2.695777
B	4.112404	0.885715	1.033957
B	2.797439	1.354110	-0.083465
B	4.497417	1.437414	-0.603789
B	4.112346	-0.888158	1.031664
B	5.320033	0.000013	0.066812
B	3.264657	0.888274	-1.755195
B	2.797429	-1.353678	-0.087001
B	4.802189	0.002165	-1.617249
B	4.497465	-1.435688	-0.607486
B	3.264760	-0.883636	-1.757534
C	0.589495	0.001488	-1.166497
C	-0.157239	1.228679	-1.205183
C	-0.157212	-1.225618	-1.208313
C	0.398227	2.494286	-1.577283
C	-1.574978	1.218327	-0.906294
C	-1.574946	-1.216043	-0.909362
C	0.398253	-2.490254	-1.583666
C	-0.340509	3.650962	-1.578558
H	1.415971	2.546492	-1.925450
C	-2.296029	2.455767	-0.862067
C	-2.246489	0.000844	-0.675270
C	-2.295981	-2.453603	-0.868295
H	1.415982	-2.541561	-1.932009
C	-0.340462	-3.646939	-1.587870
C	-1.700779	3.644925	-1.182173
H	0.124396	4.577881	-1.900513
H	-3.346346	2.426423	-0.599703
C	-1.700719	-3.641935	-1.191440
H	-3.346299	-2.424944	-0.605866
H	0.124454	-4.573021	-1.912210
H	-2.269573	4.569070	-1.163701
H	-2.269499	-4.566132	-1.175313
C	-3.677880	0.000276	-0.234762
C	-4.722662	0.001479	-1.171152
C	-3.990663	-0.001454	1.132779
C	-6.052873	0.000937	-0.747493
H	-4.490264	0.002831	-2.232045
C	-5.321369	-0.001980	1.554188
H	-3.187555	-0.002362	1.863969
C	-6.355314	-0.000784	0.615651
H	-6.851366	0.001869	-1.483489
H	-5.549100	-0.003311	2.616016
H	-7.390162	-0.001198	0.944462

Table S13 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	1.257617	-3.926395	1.529128
C	0.916334	-4.639634	0.375874
C	1.916848	-2.704901	1.431591
C	1.248179	-4.118663	-0.878545
C	2.258097	-2.164722	0.173046
C	1.907251	-2.897469	-0.981178
C	2.983799	-0.889802	0.068326
C	1.853908	1.210264	-0.097868
H	1.009267	-4.324370	2.508574
H	0.399183	-5.591111	0.453915
H	4.703800	-1.267496	1.710004
H	2.178698	-2.163290	2.333550
H	0.992753	-4.666995	-1.780483
H	2.076864	0.113018	2.170348
H	4.796950	1.600157	2.350134
H	2.162120	-2.506170	-1.959616
H	4.697741	-1.526395	-1.498350
H	6.449392	0.578188	-0.057007
H	2.493856	3.098872	1.320341
H	2.068115	-0.237572	-2.162411
H	5.054938	3.223050	-0.267912
H	4.784805	1.202369	-2.590492
H	2.485897	2.846593	-1.803406
B	4.292244	-0.465900	0.937472
B	2.692782	0.396032	1.204163
B	4.299870	1.253684	1.326894
B	4.289212	-0.610715	-0.863217
B	5.262270	0.658117	-0.061063
B	2.914427	2.170687	0.716612
B	2.688183	0.196352	-1.256823
B	4.446809	2.203893	-0.184191
B	4.293097	1.023713	-1.522543
B	2.909966	2.027493	-1.060507
C	0.346865	1.250473	-0.098487
C	-0.404842	1.311287	1.129323
C	-0.412665	1.118392	-1.316862
C	0.154869	1.766152	2.355928
C	-1.791451	0.895471	1.161122
C	-1.809503	0.744149	-1.273588
C	0.139876	1.381642	-2.601048
C	-0.547993	1.752305	3.550873
H	1.152212	2.171001	2.363824
C	-2.447773	0.805753	2.420492
C	-2.477095	0.557585	-0.034102
C	-2.525554	0.614853	-2.496127
H	1.154934	1.729599	-2.680428
C	-0.594145	1.263651	-3.771631
C	-1.848874	1.231468	3.592997
H	-0.076373	2.129462	4.452126
H	-3.449806	0.398057	2.455061
C	-1.935014	0.859206	-3.723353
H	-3.571524	0.339099	-2.456833
H	-0.123331	1.495328	-4.721231
H	-2.388277	1.167251	4.532237
H	-2.515318	0.759454	-4.634683
C	-3.882525	0.070453	-0.003423
C	-4.931928	0.894310	0.443280
C	-4.188055	-1.233795	-0.434473
C	-6.245406	0.426349	0.459236
H	-4.715505	1.909649	0.760803
C	-5.500790	-1.702457	-0.406560
H	-3.387593	-1.882540	-0.776657
C	-6.533669	-0.873885	0.038370
H	-7.043947	1.079863	0.797126
H	-5.716063	-2.715873	-0.731521
H	-7.556253	-1.238204	0.054952

Table S14 Cartesian coordinates of the ground state (S_0) fully optimized geometry of ***o*AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	-2.096804	3.856766	0.349474
C	-1.724102	4.231820	-0.942692
C	-2.697835	2.620109	0.576345
C	-1.966036	3.363584	-2.008949
C	-2.936005	1.732830	-0.487131
C	-2.565802	2.126337	-1.784880
C	-3.616259	0.421482	-0.254216
C	-2.479211	-1.179918	0.185467
H	-1.923866	4.527923	1.184875
H	-1.256498	5.195761	-1.118376
H	-5.551263	1.253253	0.989574
H	-2.989024	2.349793	1.583619
H	-1.689330	3.648185	-3.019201
H	-3.045008	0.322745	2.172293
H	-5.555853	-1.366118	2.517967
H	-2.753479	1.468637	-2.624525
H	-5.305789	0.601132	-2.014176
H	-7.051060	-1.228842	-0.178708
H	-2.917572	-2.725841	2.048408
H	-2.676883	-0.644801	-2.303405
H	-5.360377	-3.674774	0.490960
H	-5.160511	-2.412771	-2.310374
H	-2.674336	-3.369880	-0.918609
B	-5.062558	0.259058	0.572822
B	-3.524032	-0.292966	1.297115
B	-5.004589	-1.265210	1.471819
B	-4.920421	-0.115897	-1.155024
B	-5.867800	-1.186870	-0.090442
B	-3.453892	-2.086837	1.211901
B	-3.307404	-0.865073	-1.339789
B	-4.891265	-2.601412	0.296427
B	-4.774871	-1.872110	-1.326763
B	-3.312443	-2.461560	-0.514302
C	-0.997164	-0.930371	0.253444
C	-0.371406	-0.485425	1.467871
C	-0.175572	-1.000247	-0.923030
C	-0.897412	-0.731912	2.776194
C	0.898512	0.208458	1.410713
C	1.088378	-0.292542	-0.964901
C	-0.502665	-1.775502	-2.081167
C	-0.282487	-0.278198	3.916105
H	-1.775959	-1.344341	2.888564
C	1.479810	0.711873	2.620209
C	1.577848	0.363113	0.183552
C	1.834171	-0.262149	-2.187759
H	-1.361295	-2.425230	-2.059473
C	0.277869	-1.778666	-3.209505
C	0.908731	0.484664	3.842706
H	-0.709401	-0.522668	4.883996
H	2.413208	1.257132	2.551020
C	1.443584	-0.977051	-3.286193
H	2.742524	0.325631	-2.219437
H	-0.001684	-2.408831	-4.048346
H	1.378060	0.856366	4.747925
H	2.034064	-0.955252	-4.196536
C	2.797140	1.234321	0.105219
C	4.119141	0.732740	0.028914
C	2.586407	2.622504	0.069119
C	5.175637	1.653350	-0.091703
H	3.648229	3.516895	-0.047812
C	1.568066	2.996764	0.119634
C	4.951755	3.027340	-0.130029
H	6.191870	1.273889	-0.136948
H	3.456684	4.585144	-0.076355
H	5.791580	3.710052	-0.216889
C	4.449413	-0.722698	0.051739
C	3.978187	-1.578857	1.060367
C	5.293183	-1.258948	-0.936466
C	4.333680	-2.927933	1.074455
H	3.348933	-1.185324	1.850795
C	5.646337	-2.608227	-0.923789
H	5.661514	-0.613584	-1.728662
C	5.166155	-3.448991	0.082045
H	3.963616	-3.570965	1.867671
H	6.293080	-3.002326	-1.702266
H	5.439899	-4.499772	0.093864

Table S15 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of ***o*AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	-3.259420	3.978722	0.194252
C	-2.995887	4.389436	-1.116085
C	-3.542659	2.644518	0.469893
C	-3.025024	3.449213	-2.150631
C	-3.575351	1.682970	-0.562815
C	-3.307739	2.113957	-1.879939
C	-3.907139	0.278584	-0.279228
C	-2.233975	-1.347754	0.255313
H	-3.244857	4.701671	1.004527
H	-2.772102	5.430369	-1.328755
H	-5.845187	0.593151	1.113878
H	-3.748747	2.339614	1.489711
H	-2.826953	3.758328	-3.172689
H	-3.014478	0.253124	2.052696
H	-5.225428	-1.852764	2.621004
H	-3.330359	1.395310	-2.691418
H	-5.530586	-0.111055	-2.013246
H	-6.799599	-2.119146	-0.030371
H	-2.497384	-2.836294	2.178580
H	-2.589842	-0.697601	-2.163122
H	-4.723154	-4.172802	0.641277
H	-4.742201	-2.936091	-2.191861
H	-2.191021	-3.521954	-0.864947
B	-5.142473	-0.240189	0.644286
B	-3.410656	-0.471028	1.209220
B	-4.725455	-1.690696	1.554240
B	-4.965933	-0.634933	-1.110146
B	-5.643778	-1.841694	0.023552
B	-3.080958	-2.294950	1.301512
B	-3.169524	-1.010950	-1.184031
B	-4.429547	-3.041999	0.416104
B	-4.446308	-2.315809	-1.221366
B	-2.906871	-2.684826	-0.429498
C	-0.780532	-0.946872	0.311952
C	-0.187978	-0.425667	1.519191
C	0.049757	-0.959916	-0.864718
C	-0.748219	-0.638876	2.809113
C	1.048109	0.324359	1.464639
C	1.270130	-0.182555	-0.909737
C	-0.269898	-1.712946	-2.029922
C	-0.181061	-0.128455	3.967174
H	-1.624895	-1.254207	2.911623
C	1.584379	0.859036	2.669706
C	1.747963	0.490654	0.241971
C	1.975100	-0.085175	-2.140820
H	-1.114189	-2.380209	-2.013842
C	0.490915	-1.660258	-3.187733
C	0.984306	0.647378	3.898047
H	-0.645187	-0.339070	4.924905
H	2.501295	1.432778	2.617297
C	1.602818	-0.809280	-3.259375
H	2.832686	0.573215	-2.194116
H	0.209029	-2.270064	-4.039534
H	1.426525	1.062075	4.797865
H	2.175722	-0.724786	-4.176868
C	2.953650	1.370691	0.175554
C	4.272252	0.879479	-0.002322
C	2.744890	2.759681	0.254316
C	5.320762	1.808039	-0.120121
C	3.799587	3.661182	0.136439
H	1.732321	3.128736	0.386148
C	5.095493	3.181120	-0.056114
H	6.333443	1.435642	-0.239947
H	3.608217	4.728362	0.190239
H	5.929493	3.870516	-0.144889
C	4.600273	-0.574224	-0.057491
C	4.152847	-1.469931	0.927833
C	5.412832	-1.070591	-1.090874
C	4.500939	-2.820026	0.875447
H	3.549824	-1.106293	1.752441
C	5.758097	-2.421148	-1.144749
H	5.762316	-0.394380	-1.865679
C	5.301828	-3.301711	-0.161818
H	4.150681	-3.494311	1.651376
H	6.379790	-2.785197	-1.957402
H	5.570072	-4.353094	-0.202352

Table S16 Cartesian coordinates of the ground state (S_0) fully optimized geometry of ***m*AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	-0.100773	3.085286	-1.224585
C	-0.794846	3.322895	-0.036445
C	1.162473	2.498498	-1.194722
C	-0.208633	2.980764	1.183679
C	1.757409	2.137620	0.026628
C	1.055642	2.395652	1.216508
C	3.126804	1.535191	0.056846
C	3.280781	-0.456156	0.041543
H	-0.540848	3.357331	-2.178841
H	-1.781419	3.775443	-0.060099
H	4.226395	3.124216	-1.446206
H	1.689141	2.327390	-2.125425
H	-0.733896	3.170370	2.114404
H	2.968813	0.610672	-2.254692
H	6.005703	0.845949	-2.369423
H	1.497808	2.144576	2.172434
H	4.161708	3.098014	1.631117
H	6.830017	2.440070	0.139612
H	4.754743	-1.736056	-1.459776
H	2.878408	0.568329	2.345274
H	7.102644	-0.596508	0.119885
H	5.903800	0.801764	2.585677
H	4.691568	-1.761448	1.580928
B	4.427845	2.154900	-0.797748
B	3.647104	0.627259	-1.298551
B	5.417294	0.789814	-1.340318
B	4.391820	2.140311	0.974859
B	5.893006	1.711347	0.114400
B	4.699508	-0.746032	-0.817451
B	3.591100	0.604844	1.415343
B	6.051714	-0.044085	0.102712
B	5.358356	0.765130	1.532317
B	4.662101	-0.760924	0.953393
C	1.975471	-1.204671	0.008261
C	1.320001	-1.502796	-1.234634
C	1.269854	-1.525996	1.217498
C	2.000731	-1.645283	-2.485515
C	-0.111264	-1.726959	-1.257106
C	-0.160664	-1.752328	1.176271
C	1.898334	-1.691742	2.492545
C	1.337031	-1.902613	-3.658858
H	3.077007	-1.607707	-2.511450
C	-0.773063	-1.931096	-2.511429
C	-0.846439	-1.754260	-0.054943
C	-0.872795	-1.989668	2.396645
H	2.972359	-1.651380	2.564418
C	1.187320	-1.975812	3.631564
C	-0.075456	-2.013322	-3.685200
H	1.906404	-2.033827	-4.574021
H	-1.848795	-2.056595	-2.508121
C	-0.224274	-2.094767	3.596441
H	-1.946479	-2.122218	2.344989
H	1.718729	-2.123778	4.566793
H	-0.592719	-2.191565	-4.622535
H	-0.778878	-2.297941	4.506961
C	-2.342232	-1.821833	-0.085538
C	-3.016246	-3.049415	-0.152421
C	-3.084792	-0.635641	-0.037191
C	-4.411503	-3.076301	-0.171880
H	-2.449831	-3.974917	-0.188541
C	-4.489032	-0.647627	-0.059682
H	-2.558156	0.310577	0.041105
C	-5.141892	-1.890206	-0.127756
H	-4.931415	-4.027779	-0.231005
H	-6.225942	-1.925664	-0.170099
C	-5.259031	0.623034	-0.012864
C	-6.467903	0.708371	0.699278
C	-4.798219	1.771877	-0.679686
C	-7.190526	1.900308	0.743622
H	-6.832283	-0.158657	1.241918
C	-5.520734	2.963867	-0.634917
H	-3.879685	1.724149	-1.256699
C	-6.720176	3.033638	0.077084
H	-8.118249	1.945132	1.306564
H	-5.151147	3.836512	-1.165661
H	-7.282875	3.961663	0.111494

Table S17 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of ***m*AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	0.719707	4.081083	0.212044
C	0.338287	4.133650	1.556223
C	1.744509	3.232756	-0.195813
C	0.999516	3.330860	2.490767
C	2.421434	2.415484	0.734776
C	2.025051	2.481135	2.087762
C	3.526829	1.542509	0.311346
C	3.172759	-0.718003	-0.384190
H	0.216463	4.704381	-0.521197
H	-0.464091	4.793405	1.871999
H	4.773452	3.096715	-1.040707
H	2.032950	3.203806	-1.240535
H	0.714560	3.367501	3.538052
H	2.694491	1.160105	-2.011904
H	5.691266	0.918231	-2.789617
H	2.531861	1.866069	2.822791
H	5.152207	2.101078	1.997286
H	7.259635	1.468333	-0.179029
H	4.173008	-1.568571	-2.448358
H	3.207211	-0.184799	2.088191
H	6.840792	-1.367124	-1.055786
H	6.276000	-0.612514	1.888486
H	4.543236	-2.537289	0.509063
B	4.760749	1.972933	-0.659049
B	3.503682	0.770468	-1.246131
B	5.264606	0.652338	-1.711915
B	4.972861	1.414446	1.045925
B	6.175944	0.977712	-0.204400
B	4.355021	-0.854172	-1.521450
B	3.794455	0.006556	1.082528
B	5.930856	-0.679664	-0.716774
B	5.602095	-0.231195	0.985934
B	4.565749	-1.405310	0.161303
C	1.777873	-1.288745	-0.396422
C	0.914504	-1.152007	-1.543287
C	1.205320	-1.900792	0.775910
C	1.407636	-0.887574	-2.851234
C	-0.515842	-1.323840	-1.409623
C	-0.230835	-2.027238	0.909091
C	1.993393	-2.401265	1.849817
C	0.577508	-0.766859	-3.955322
H	2.468938	-0.819217	-3.014122
C	-1.337729	-1.174594	-2.561285
C	-1.093390	-1.687427	-0.164305
C	-0.764371	-2.475542	2.149803
H	3.065748	-2.414361	1.757535
C	1.437061	-2.920072	3.009101
C	-0.810511	-0.893791	-3.809204
H	1.013134	-0.582536	-4.931682
H	-2.406496	-1.309682	-2.455489
C	0.045589	-2.922569	3.178895
H	-1.838362	-2.471568	2.284181
H	2.087453	-3.304851	3.787461
H	-1.467620	-0.796618	-4.667110
H	-0.397761	-3.277277	4.103479
C	-2.571997	-1.765233	-0.014953
C	-3.217621	-2.995535	0.202036
C	-3.348007	-0.597382	-0.091906
C	-4.604248	-3.042728	0.335967
H	-2.633663	-3.909340	0.245508
C	-4.743642	-0.629813	0.051140
H	-2.847721	0.355945	-0.229145
C	-5.361534	-1.874701	0.264262
H	-5.098539	-3.997842	0.485009
H	-6.442121	-1.929685	0.349240
C	-5.544591	0.620060	-0.019720
C	-6.666609	0.803902	0.806986
C	-5.201475	1.648509	-0.914521
C	-7.419666	1.975542	0.740669
H	-6.936647	0.034009	1.523405
C	-5.954412	2.820231	-0.980278
H	-4.353583	1.519702	-1.580417
C	-7.066884	2.988934	-0.153089
H	-8.278177	2.099831	1.394096
H	-5.676129	3.598597	-1.684661
H	-7.653264	3.901346	-0.204550

Table S18 Cartesian coordinates of the ground state (S_0) fully optimized geometry of ***p*AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	1.167873	3.609701	0.954279
C	0.615032	3.311009	2.201097
C	2.215073	2.842607	0.448414
C	1.125439	2.244412	2.943408
C	2.730124	1.759458	1.181387
C	2.173248	1.475969	2.440235
C	3.880039	0.960704	0.654777
C	3.482723	-0.671184	-0.440140
H	0.786103	4.442711	0.372448
H	-0.200773	3.909639	2.594580
H	5.343107	2.829395	0.057733
H	2.637478	3.093489	-0.516676
H	0.710650	2.009035	3.918466
H	3.429973	1.529324	-1.731823
H	6.413408	1.122073	-2.209442
H	2.562592	0.658169	3.033642
H	5.332023	1.115974	2.618296
H	7.689568	0.834166	0.584617
H	4.525323	-1.184522	-2.610051
H	3.416084	-1.028821	2.086962
H	7.122283	-1.654076	-1.082149
H	6.396428	-1.635380	1.908934
H	4.514615	-2.876690	-0.080943
B	5.283886	1.647365	0.052803
B	4.104160	0.865580	-1.039344
B	5.851571	0.635032	-1.284460
B	5.278459	0.661087	1.526947
B	6.588832	0.466202	0.334357
B	4.752382	-0.733079	-1.542200
B	4.095419	-0.641675	1.213502
B	6.261886	-0.972228	-0.629671
B	5.841793	-0.963104	1.103399
B	4.745835	-1.718216	-0.069717
C	2.024371	-0.977065	-0.650367
C	1.290530	-0.393772	-1.739301
C	1.282636	-1.759661	0.299405
C	1.887460	0.048875	-2.962668
C	-0.151105	-0.275010	-1.654187
C	-0.159093	-1.632148	0.366920
C	1.871083	-2.724774	1.177535
C	1.157866	0.627596	-3.970752
H	2.936502	-0.123537	-3.134883
C	-0.867160	0.390212	-2.702017
C	-0.847572	-0.819498	-0.556417
C	-0.885397	-2.353655	1.369370
H	2.920620	-2.950647	1.092541
C	1.132697	-3.438679	2.087875
C	-0.236384	0.837454	-3.830277
H	1.657746	0.915887	-4.890510
H	-1.939136	0.503235	-2.597252
C	-0.263004	-3.230339	2.214920
H	-1.958303	-2.215684	1.422097
H	1.626654	-4.181402	2.706987
H	-0.799831	1.319594	-4.622727
H	-0.834020	-3.784131	2.953262
C	-2.316633	-0.579556	-0.398923
C	-3.261991	-1.412050	-1.015290
C	-2.777986	0.492399	0.378608
C	-4.626645	-1.178100	-0.858812
H	-2.926021	-2.243434	-1.627897
C	-4.142957	0.723333	0.534409
H	-2.061607	1.143680	0.870744
C	-5.095953	-0.106314	-0.080650
H	-5.336019	-1.823878	-1.366976
H	-4.472588	1.545737	1.161703
C	-6.551388	0.141112	0.086866
C	-7.059292	1.450692	0.145176
C	-7.458042	-0.928184	0.191604
C	-8.425201	1.682708	0.303258
H	-6.382049	2.293085	0.041692
C	-8.824066	-0.696189	0.348666
H	-7.087198	-1.948564	0.174140
C	-9.313960	0.610354	0.405452
H	-8.796111	2.702923	0.337991
H	-9.505182	-1.537741	0.435135
H	-10.377616	0.791056	0.528101

Table S19 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of ***p*AC** in THF from TD-PBE0 calculations (in Å)

Atom	X	Y	Z
C	1.999520	4.036788	-1.265172
C	1.565414	4.617133	-0.069495
C	2.829044	2.919752	-1.244491
C	1.976314	4.069631	1.149626
C	3.251803	2.354279	-0.022554
C	2.805662	2.952503	1.175244
C	4.155162	1.192866	0.001785
C	3.339180	-1.049933	0.024954
H	1.690695	4.457067	-2.217733
H	0.915780	5.486919	-0.087605
H	5.795454	1.927529	-1.602131
H	3.161250	2.481316	-2.178735
H	1.649702	4.515767	2.084348
H	3.395651	0.214228	-2.168459
H	6.298187	-0.851225	-2.429887
H	3.120006	2.539926	2.127268
H	5.768761	1.972979	1.611940
H	7.799137	0.238195	0.045876
H	4.239546	-2.727258	-1.510974
H	3.357897	0.276790	2.183875
H	6.797163	-2.587640	0.077400
H	6.254396	-0.783327	2.525946
H	4.210979	-2.682763	1.623404
B	5.508827	1.024872	-0.886785
B	4.049902	-0.038638	-1.219445
B	5.761829	-0.646347	-1.388478
B	5.494339	1.049973	0.918094
B	6.635679	-0.010803	0.039619
B	4.524191	-1.789291	-0.846184
B	4.029157	-0.002353	1.254219
B	6.049995	-1.661862	0.057737
B	5.736708	-0.606281	1.470089
B	4.508073	-1.764117	0.937510
C	1.856442	-1.298592	0.015644
C	1.114719	-1.379782	-1.218303
C	1.089910	-1.355055	1.236884
C	1.726712	-1.677308	-2.467764
C	-0.313089	-1.140941	-1.231211
C	-0.344644	-1.173880	1.211501
C	1.679399	-1.633584	2.500957
C	1.028845	-1.665594	-3.664901
H	2.766820	-1.953950	-2.493241
C	-0.970678	-1.031487	-2.488045
C	-1.035624	-0.981895	-0.017747
C	-1.067795	-1.252853	2.433720
H	2.733809	-1.839590	2.559971
C	0.941365	-1.710181	3.671850
C	-0.324130	-1.298127	-3.681849
H	1.542576	-1.919567	-4.586071
H	-2.011099	-0.734271	-2.506468
C	-0.444269	-1.503540	3.643165
H	-2.143796	-1.139404	2.408682
H	1.443891	-1.943443	4.604684
H	-0.865770	-1.227034	-4.619380
H	-1.031083	-1.563635	4.553866
C	-2.486281	-0.678389	-0.019949
C	-3.424826	-1.546454	-0.611067
C	-2.971084	0.496676	0.587666
C	-4.783077	-1.250669	-0.596103
H	-3.084431	-2.469139	-1.070157
C	-4.328026	0.796930	0.586617
H	-2.270619	1.183874	1.051774
C	-5.267081	-0.070142	-0.002662
H	-5.477181	-1.937537	-1.069655
H	-4.667060	1.707366	1.070394
C	-6.714982	0.247541	0.004829
C	-7.163241	1.576840	-0.103704
C	-7.678252	-0.771521	0.120676
C	-8.524562	1.875474	-0.097645
H	-6.441205	2.378889	-0.221395
C	-9.039291	-0.471740	0.128332
H	-7.358194	-1.802734	0.233101
C	-9.468900	0.852859	0.018776
H	-8.848309	2.907710	-0.192169
H	-9.765068	-1.273336	0.228182
H	-10.529334	1.085894	0.024096