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Electronic Supplementary Information

Formation and infrared identification of protonated fluoranthene isomers 3-, 9-, and 10-$C_{16}H_{11}^+$ in solid *para*-H_2

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Table S1 Vibrational wavenumbers and IR intensities of $C_{16}H_{10}$ in *p*-H_2 and Ar matrixes and those predicted with the B3PW91/6-311++G(2d,2p) method.

Modes	Sym.[a]	Calculation		*p*-H_2		Ar
		cm^{-1} [b]	Intensity[c]	cm^{-1}	Intensity[d]	cm^{-1} [e]
ν_1	a_1	3088.9	19.8	3090.3		
ν_2	a_1	3084.2	16.7	3086.4		
ν_3	a_1	3071.9	14.9	3074.3		
ν_4	a_1	3068.3	2.9	3068.5		
ν_5	a_1	3061.4	1.1	3053.3		
ν_6	a_1	1616.0	3.0	1616.8	3.4	1616.5
ν_7	a_1	1613.3	1.2			
ν_8	a_1	1587.7	0.0			
ν_9	a_1	1460.7	60.4	1461.2	20	1461.8
ν_{10}	a_1	1430.9	14.6	1429.6	15.3	1429.2
ν_{11}	a_1	1418.0	1.0			
ν_{12}	a_1	1382.1	0.3			
ν_{13}	a_1	1322.6	0.2			
ν_{14}	a_1	1272.8	1.1	1263.2	2.3	
ν_{15}	a_1	1184.4	3.2	1184.0	2.1	1184.4
ν_{16}	a_1	1157.0	0.3			
ν_{17}	a_1	1105.2	2.7	1106.2	2.0	1106.3
ν_{18}	a_1	1045.1	4.5	1037.1	2.2	1036.7
ν_{19}	a_1	1027.3	4.2	1020.4	1.5	1033.3
ν_{20}	a_1	895.2	1.1			
ν_{21}	a_1	803.9	0.7			
ν_{22}	a_1	675.0	1.4	672.0	1.2	672.0
ν_{23}	a_1	564.6	2.6			
ν_{24}	a_1	489.6	2.0			
ν_{25}	a_1	356.0	0.2			
ν_{26}	a_2	974.2	0.0			
ν_{27}	a_2	967.6	0.0			
ν_{28}	a_2	903.8	0.0			
ν_{29}	a_2	868.7	0.0			
ν_{30}	a_2	783.7	0.0			
ν_{31}	a_2	738.8	0.0			
ν_{32}	a_2	645.1	0.0			
ν_{33}	a_2	570.1	0.0			
ν_{34}	a_2	432.5	0.0			
ν_{35}	a_2	255.9	0.0			
ν_{36}	a_2	127.1	0.0			
ν_{37}	b_1	975.0	1.2	969.0	0.7	
ν_{38}	b_1	939.0	1.7	937.3	1.4	936.3
ν_{39}	b_1	911.9	0.0			
ν_{40}	b_1	829.8	12.2	828.2	11.2	827.9
ν_{41}	b_1	776.6	113.8	777.6	100	775.0, 776.7
ν_{42}	b_1	624.1	16.7	618.7	14.1	619.3

ν_{43}	b_1	460.6	0.0			
ν_{44}	b_1	430.9	1.2			
ν_{45}	b_1	297.1	0.4			
ν_{46}	b_1	169.0	3.0			
ν_{47}	b_1	108.7	2.8			
ν_{48}	b_2	3083.5	32.2			
ν_{49}	b_2	3077.7	16.7			
ν_{50}	b_2	3071.1	1.6			
ν_{51}	b_2	3061.8	0.4			
ν_{52}	b_2	3061.0	1.0			
ν_{53}	b_2	1631.2	0.1			
ν_{54}	b_2	1619.0	0.6			
ν_{55}	b_2	1497.6	7.4	1492.1	1.6	1490.6, 1492.7
ν_{56}	b_2	1479.3	0.6			
ν_{57}	b_2	1446.4	12.3	1444.6	10.3	1444.2
ν_{58}	b_2	1376.0	1.3	1369.3	0.8	
ν_{59}	b_2	1291.3	0.1			
ν_{60}	b_2	1230.7	1.5	1229.7	0.9	1230.6
ν_{61}	b_2	1216.8	1.2	1216.2	1.1	1217.0
ν_{62}	b_2	1161.4	1.7	1158.6	1.1	1159.0
ν_{63}	b_2	1139.0	8.2	1137.8	6.9	1137.3, 1139.4
ν_{64}	b_2	1086.8	0.0			
ν_{65}	b_2	1023.8	2.2	1009.2	0.3	1019.2
ν_{66}	b_2	970.9	0.2			
ν_{67}	b_2	764.2	1.6	763.1	1.2	762.9
ν_{68}	b_2	742.9	29.0	746.5	24.5	744.5
ν_{69}	b_2	615.4	0.0			
ν_{70}	b_2	562.4	0.2	561.9	1.7	561.1
ν_{71}	b_2	473.4	0.6			
ν_{72}	b_2	210.6	0.1			

[a]Approximate symmetry species in the C_{2v} point group; see text for details. [b] Harmonic wavenumbers (cm^{-1}) scaled with factors 0.958 and 0.978 for regions above and below 2500 cm^{-1}, respectively. [c]The predicted IR intensities in km mol^{-1}. [d]Percentage integrated intensities relative to the most intense line at 777.6 cm^{-1}. [e]$C_{16}H_{10}$ in an Ar matrix from D. M. Hudgins and S. A. Sandford, *J. Phys. Chem. A*, 1998, **102***,* 353.

Table S2 Optimized ground-state coordinates of five isomers of protonated fluoranthene ($C_{16}H_{11}^+$) employed for harmonic vibrational calculations.

10-$C_{16}H_{11}^+$

C	1.352543000	2.881275000	0.000000000
C	0.057739000	2.320815000	0.000000000
C	-1.186668000	3.002631000	0.000000000
C	2.485613000	2.070724000	0.000000000
C	0.000000000	0.925831000	0.000000000
C	1.143839000	0.083970000	0.000000000
C	2.406190000	0.674769000	0.000000000
C	0.654492000	-1.253140000	0.000000000
C	-0.771496000	-1.217060000	0.000000000
C	-1.190761000	0.186975000	0.000000000
C	-2.386934000	0.868750000	0.000000000
C	-2.362418000	2.284258000	0.000000000
H	-3.304727000	2.815694000	0.000000000
H	-3.341608000	0.357705000	0.000000000
H	3.460849000	2.538896000	0.000000000
H	3.315543000	0.087010000	0.000000000
C	0.509346000	-3.742920000	0.000000000
C	-0.840697000	-3.660834000	0.000000000
C	-1.487550000	-2.391467000	0.000000000
H	1.474007000	3.957943000	0.000000000
H	-1.212715000	4.084923000	0.000000000
H	-2.571291000	-2.363128000	0.000000000
C	1.368392000	-2.539274000	0.000000000
H	2.056424000	-2.593346000	0.857946000
H	2.056424000	-2.593346000	-0.857946000
H	1.002737000	-4.706762000	0.000000000
H	-1.445410000	-4.557404000	0.000000000

9-$C_{16}H_{11}^+$

C	-1.199057000	2.997144000	0.000000000
C	0.048257000	2.323517000	0.000000000
C	1.339904000	2.891403000	0.000000000
C	-2.370555000	2.270762000	0.000000000
C	0.000000000	0.926235000	0.000000000
C	-1.186339000	0.181209000	0.000000000
C	-2.386646000	0.856293000	0.000000000
C	-0.768530000	-1.225498000	0.000000000
C	0.687778000	-1.248943000	0.000000000
C	1.151961000	0.097581000	0.000000000
C	2.411204000	0.695264000	0.000000000
C	2.480207000	2.090882000	0.000000000
H	3.451256000	2.567656000	0.000000000
H	3.322302000	0.110858000	0.000000000
H	-3.315936000	2.796870000	0.000000000

H	-3.337457000	0.338380000	0.000000000
C	-0.756423000	-3.679011000	0.000000000
C	0.716477000	-3.633847000	0.000000000
C	1.405757000	-2.466966000	0.000000000
H	-1.232045000	4.079240000	0.000000000
H	1.453116000	3.969107000	0.000000000
H	2.487654000	-2.463685000	0.000000000
C	-1.461668000	-2.384681000	0.000000000
H	-2.545235000	-2.397170000	0.000000000
H	-1.100579000	-4.284544000	0.854568000
H	1.243533000	-4.580224000	0.000000000
H	-1.100579000	-4.284544000	-0.854568000

1-$C_{16}H_{11}^{+}$

C	1.404965000	2.868243000	0.000000000
C	0.089565000	2.284156000	0.000000000
C	-1.133596000	2.982380000	0.000000000
C	2.501011000	2.081907000	0.000000000
C	0.000000000	0.884532000	0.000000000
C	1.095155000	0.022241000	0.000000000
C	0.597479000	-1.332912000	0.000000000
C	-0.825644000	-1.274253000	0.000000000
C	-1.213970000	0.154618000	0.000000000
C	-2.387397000	0.852932000	0.000000000
C	-2.320533000	2.275956000	0.000000000
H	-3.252231000	2.828107000	0.000000000
H	-3.354779000	0.368521000	0.000000000
H	3.487306000	2.528636000	0.000000000
C	0.505033000	-3.723222000	0.000000000
C	-0.880265000	-3.661497000	0.000000000
C	-1.563214000	-2.431073000	0.000000000
H	1.504877000	3.946040000	0.000000000
H	-1.146738000	4.064217000	0.000000000
H	-2.645185000	-2.415282000	0.000000000
C	1.262983000	-2.551972000	0.000000000
H	2.344458000	-2.604080000	0.000000000
C	2.448327000	0.591863000	0.000000000
H	3.017586000	0.202645000	0.858156000
H	3.017586000	0.202645000	-0.858156000
H	1.000272000	-4.684591000	0.000000000
H	-1.452537000	-4.580255000	0.000000000

2-$C_{16}H_{11}^{+}$

C	1.222496000	2.900403000	0.000000000
C	-0.008042000	2.289674000	0.000000000
C	-1.282698000	2.945617000	0.000000000
C	0.000000000	0.874017000	0.000000000

C	1.164558000	0.041555000	0.000000000
C	0.672547000	-1.343610000	0.000000000
C	-0.742212000	-1.309348000	0.000000000
C	-1.165646000	0.098263000	0.000000000
C	-2.377047000	0.763467000	0.000000000
C	-2.419427000	2.185893000	0.000000000
H	-3.386535000	2.670720000	0.000000000
H	-3.313479000	0.218646000	0.000000000
C	0.605522000	-3.728577000	0.000000000
C	-0.786156000	-3.694984000	0.000000000
C	-1.474424000	-2.484819000	0.000000000
H	1.307756000	3.982079000	0.000000000
H	-1.333831000	4.026530000	0.000000000
H	-2.556738000	-2.474933000	0.000000000
C	1.349082000	-2.551766000	0.000000000
H	2.430772000	-2.592355000	0.000000000
C	2.378159000	0.639928000	0.000000000
H	3.307272000	0.083758000	0.000000000
C	2.464779000	2.118688000	0.000000000
H	3.080551000	2.462801000	0.849899000
H	3.080551000	2.462801000	-0.849899000
H	1.115863000	-4.682588000	0.000000000
H	-1.341134000	-4.623864000	0.000000000

3-$C_{16}H_{11}^{+}$

C	0.083955000	2.261908000	0.000000000
C	-1.128738000	2.967873000	0.000000000
C	0.000000000	0.882053000	0.000000000
C	1.119034000	0.000163000	0.000000000
C	0.606379000	-1.343567000	0.000000000
C	-0.817422000	-1.275130000	0.000000000
C	-1.202765000	0.153753000	0.000000000
C	-2.383459000	0.851730000	0.000000000
C	-2.322400000	2.266599000	0.000000000
H	-3.251995000	2.821406000	0.000000000
H	-3.347488000	0.360531000	0.000000000
C	0.508365000	-3.731853000	0.000000000
C	-0.880150000	-3.660697000	0.000000000
C	-1.559265000	-2.431393000	0.000000000
H	-1.139941000	4.050271000	0.000000000
H	-2.641022000	-2.412461000	0.000000000
C	1.269425000	-2.567908000	0.000000000
H	2.350554000	-2.621482000	0.000000000
C	2.428140000	0.529222000	0.000000000
H	3.296964000	-0.114910000	0.000000000
C	2.571007000	1.884135000	0.000000000
H	3.568822000	2.308756000	0.000000000

C	1.450450000	2.851164000	0.000000000
H	1.584008000	3.527047000	0.858644000
H	1.584008000	3.527047000	-0.858644000
H	0.996396000	-4.696797000	0.000000000
H	-1.455638000	-4.577718000	0.000000000

Table S3 Comparison of vibrational wavenumbers (cm^{-1}) and IR intensities of 3-$C_{16}H_{11}^+$ and 9-$C_{16}H_{11}^+$ in a *p*-H_2 matrix and those predicted with the B3PW91/6-311++G(2d,2p) method.

	3-$C_{16}H_{11}^+$				**9-$C_{16}H_{11}^+$**			
	Calculation		*p*-H_2		Calculation		*p*-H_2	
Mode[a]	Wavenumber[b]	Intensity[c]	Wavenumber	Intensity[d]	Wavenumber[a]	Intensity[c]	Wavenumber	Intensity[e]
ν_1	3105.2	0.5			3101.0	0.2		
ν_2	3099.1	0			3099.6	0.7		
ν_3	3098.5	0			3097.4	0		
ν_4	3095.6	0			3087.9	0		
ν_5	3090.4	0.5			3086.4	0.2		
ν_6	3086.9	0			3081.8	2.3		
ν_7	3081.6	0			3080.8	0		
ν_8	3080.4	0			3079.8	0.5		
ν_9	3074.1	0.5			3078.0	0		
ν_{10}	2891.1	34.8			2882.0	40.6		
ν_{11}	1627.8	109.7			1641.8	91.7		
ν_{12}	1609.9	14.1			1620.7	6.2		
ν_{13}	1601.9	302.5			1605.1	109.9		
ν_{14}	1584.8	73.4	1585.6	21.4	1586.2	175.8	1586.5	50
ν_{15}	1536.3	6.6			1546.2	64.3	1540.2	15.9
ν_{16}	1520.9	470.7	1521.4	64.3	1499.3	21.4	1500.3	62.5
ν_{17}	1473.5	23.5			1494.9	230.4	1497.6	62.5
ν_{18}	1468.1	21.2			1454.6	61.3		
ν_{19}	1442.0	22.6			1441.1	4.1		
ν_{20}	1426.0	2.8			1421.0	135.0	1422.7	46.8
ν_{21}	1392.4	6.6	1390.1		1388.9	10.4		
ν_{22}	1362.8	26.4			1378.6	111.1	1366.6?	42
ν_{23}	1346.3	18.8			1354.1	24.4		
ν_{24}	1323.3	188.2	1318.0	100	1342.9	12.9		
ν_{25}	1309.5	59.7			1321.5	118.0	1319.9?	18.4
ν_{26}	1298.8	10.8			1309.5	154.1	1305.5	100
ν_{27}	1272.8	19.3			1276.4	5.1		
ν_{28}	1232.9	12.7	1226.3	3.6	1237.7	0.9		
ν_{29}	1197.4	14.1	1196.0	1.8	1229.5	25.8		
ν_{30}	1178.9	10.4			1193.1	9.7		
ν_{31}	1168.5	26.8	1170.8		1164.7	51.6	1164.8	10.5
ν_{32}	1156.1	13.6			1155.4	7.8		
ν_{33}	1134.0	18.8	1135.2		1114.4	15.4		
ν_{34}	1085.5	36.7	1088.2	42.9	1088.1	62.2	1089.9	100
ν_{35}	1079.2	35.7	1081.5	28.6	1057.1	8.5		
ν_{36}	1029.9	8.9	1025.6	7.1	1033.1	18.9		
ν_{37}	1021.2	4.2			1013.9	5.1		
ν_{38}	964.9	6.1	971.1	7.1	959.2	0.5		
ν_{39}	935.9	14.5			921.4	36.0	920.3	10.5
ν_{40}	873.1	1.8			864.2	13.1	860.7	7.9

ν_{41}	790.7	1.8	799.0	0.9		
ν_{42}	750.7	3.2	751.3	2.3		
ν_{43}	661.4	3.2	650.4	2.1		
ν_{44}	600.7	15.1	606.2	1.6		
ν_{45}	556.4	3.3	559.3	10.8		
ν_{46}	546.6	0.9	556.6	3.5		
ν_{47}	476.8	0.5	483.9	5.8		
ν_{48}	457.1	6.1	467.6	6.7		
ν_{49}	348.0	3.2	353.6	0.5		
ν_{50}	210.3	0.9	210.2	0.7		
ν_{51}	2902.3	5.6	2887.3	6.7		
ν_{52}	1151.3	0.9	1143.4	0		
ν_{53}	1003.1	0.5	1001.4	0		
ν_{54}	1001.8	1.4	1000.2	0.5		
ν_{55}	995.8	0.5	989.6	0		
ν_{56}	964.0	0.5	947.9	1.8		
ν_{57}	925.6	0.5	931.8	5.5		
ν_{58}	894.4	1.9	925.0	9.4		
ν_{59}	878.4	0	841.2	12.9		
ν_{60}	832.5	1.4	823.7	22.6	821.6	7.9
ν_{61}	792.1	53.2	802.4	18.0		
ν_{62}	757.4	7.5	769.7	50.0		
ν_{63}	756.4	71.1	759.3	0.2		
ν_{64}	698.8	0	674.6	8.1		
ν_{65}	644.6	0	617.2	1.2		
ν_{66}	555.7	5.2	582.0	13.1		
ν_{67}	461.3	1.4	458.1	1.2		
ν_{68}	440.1	0	436.3	0.7		
ν_{69}	416.8	1.9	408.4	0		
ν_{70}	320.3	2.8	321.2	3.9		
ν_{71}	270.1	0.9	262.1	0		
ν_{72}	208.8	4.7	222.6	0.7		
ν_{73}	148.4	1.4	172.8	4.1		
ν_{74}	118.2	0	115.4	0.2		
ν_{75}	101.6	4.7	100.2	6.2		

[a]The symmetry of the modes ν_1–ν_{50} is *a*' and ν_{51}–ν_{75} is *a*". [b]Harmonic wavenumbers scaled with factors 0.958 and 0.978 for regions above and below 2500 cm^{-1}, respectively. [c]The predicted IR intensities are in km mol^{-1}. [d]Integrated IR intensity as percentage of the most intense line at 1318.0 cm^{-1}. [e]Integrated IR intensity as percentage of the most intense line at 1089.9 and 1305.5 cm^{-1}.

Table S4 Comparison of vibrational wavenumbers (cm^{-1}) and IR intensities of 10-$C_{16}H_{11}^+$ in a *p*-H_2 matrix and those predicted with the B3PW91/6-311++G(2d,2p) method.

	10-$C_{16}H_{11}^+$			
	Calculation		*p*-H_2	
Modes[a]	Wavenumber[b]	Intensity[c]	Wavenumber	Intensity[d]
ν_1	3103.5	0.3		
ν_2	3099.9	0.8		
ν_3	3099.8	1.3		
ν_4	3087.2	1.3		
ν_5	3086.2	0		
ν_6	3083.9	0		
ν_7	3079.6	0		
ν_8	3078.3	0		
ν_9	3076.1	1.5		
ν_{10}	2891.5	25.4		
ν_{11}	1628.5	33.9		
ν_{12}	1620.1	1.5		
ν_{13}	1604.0	65.0		
ν_{14}	1587.3	14.1		
ν_{15}	1522.6	155.2	1520.0?	31
ν_{16}	1500.2	18.2	1504.0	6.7
ν_{17}	1469.2	86.1	1471.3?	23
ν_{18}	1441.6	30.6		
ν_{19}	1437.3	8.5		
ν_{20}	1418.7	197.9	1419.2	8
ν_{21}	1409.9	35.0		
ν_{22}	1385.2	144.7	1385.7	13.3
ν_{23}	1369.6	38.0	1341.3	10
ν_{24}	1338.4	257.0	1336.6	100
ν_{25}	1305.4	55.0		
ν_{26}	1287.2	192.8	1285.8	20
ν_{27}	1271.9	11.8		
ν_{28}	1231.5	9.3		
ν_{29}	1216.0	57.8		
ν_{30}	1196.0	3.9		
ν_{31}	1170.1	8.5		
ν_{32}	1158.8	22.9	1154.3	13.3
ν_{33}	1123.0	11.6	1126.6	3.3
ν_{34}	1091.4	94.6	1091.2	73.3
ν_{35}	1057.3	2.3		
ν_{36}	1047.5	26.2	1042.2	3.3
ν_{37}	1019.5	1.8		
ν_{38}	959.2	0.3		
ν_{39}	950.3	31.9	949.7	13.3
ν_{40}	863.0	1.8		
ν_{41}	799.3	3.1		

ν_{42}	751.9	10.5		
ν_{43}	646.9	10.3		
ν_{44}	602.5	1.8		
ν_{45}	558.5	6.2		
ν_{46}	553.3	3.6		
ν_{47}	481.3	18.8		
ν_{48}	465.2	13.6		
ν_{49}	351.1	3.1		
ν_{50}	205.6	1.3		
ν_{51}	2902.4	8.2		
ν_{52}	1137.5	0.5		
ν_{53}	1001.1	0		
ν_{54}	999.8	0.5		
ν_{55}	989.3	0		
ν_{56}	973.5	1.3		
ν_{57}	945.6	0.3		
ν_{58}	930.7	0		
ν_{59}	869.3	6.9		
ν_{60}	833.9	24.9	832.5	6.7
ν_{61}	771.4	48.3		
ν_{62}	768.2	22.6		
ν_{63}	718.1	23.1		
ν_{64}	656.2	2.1		
ν_{65}	614.7	2.1		
ν_{66}	574.3	7.7		
ν_{67}	455.2	1.0		
ν_{68}	442.2	0		
ν_{69}	402.6	0		
ν_{70}	327.2	0.3		
ν_{71}	247.4	1.3		
ν_{72}	199.7	9.0		
ν_{73}	172.3	3.6		
ν_{74}	113.8	4.1		
ν_{75}	93.6	0.5		

[a]The symmetry of the modes ν_1–ν_{50} is *a*' and ν_{51}–ν_{75} is *a*". [b]Harmonic wavenumbers scaled with factors 0.958 and 0.978 for regions above and below 2500 cm^{-1}, respectively. [c]The predicted IR intensities are in km mol^{-1}. [d]Integrated IR intensity as percentage of the most intense line at 1336.6 cm^{-1}.

Table S5 Scaled harmonic vibrational wavenumbers (cm^{-1}) and IR intensities (km mol^{-1}) of 1-$C_{16}H_{11}^+$ and 2-$C_{16}H_{11}^+$ predicted with the B3PW91/6-311++G(2d,2p) method.

	1-$C_{16}H_{11}^+$		2-$C_{16}H_{11}^+$	
Mode[a]	Wavenumber[b]	Intensity	Wavenumber[b]	Intensity
ν_1	3104.7	0.3	3103.2	0.3
ν_2	3100.1	0	3101.4	1.7
ν_3	3096.2	0	3091.5	1.5
ν_4	3095.1	0.3	3090.7	1.2
ν_5	3094.2	0	3088.9	1.7
ν_6	3085.2	0	3082.5	0.1
ν_7	3081.7	0.9	3080.7	1.2
ν_8	3081.1	0	3077.8	0.9
ν_9	3080.8	0.3	3073.5	1.7
ν_{10}	2893.7	38.9	2869.5	45.3
ν_{11}	1624.0	26.3	1631.8	89.9
ν_{12}	1615.5	115.9	1616.1	41.8
ν_{13}	1607.5	45.9	1610.3	59.8
ν_{14}	1593.8	27.5	1592.5	1.1
ν_{15}	1558.1	316.6	1564.4	0.7
ν_{16}	1507.3	120.3	1527.5	24.9
ν_{17}	1476.8	60.8	1483.5	1.1
ν_{18}	1463.2	10.4	1460.5	45.4
ν_{19}	1430.7	7.9	1442.6	13.3
ν_{20}	1419.5	31.3	1417.8	44.4
ν_{21}	1404.2	22.5	1406.7	112.0
ν_{22}	1380.2	13.0	1369.2	15.7
ν_{23}	1365.2	177.0	1343.1	9.3
ν_{24}	1307.8	71.6	1328.5	5.5
ν_{25}	1301.3	36.1	1298.2	3.9
ν_{26}	1288.9	5.4	1286.5	97.1
ν_{27}	1258.5	21.2	1269.1	62.3
ν_{28}	1226.7	12.7	1231.9	5.8
ν_{29}	1219.6	93.1	1217.9	9.2
ν_{30}	1182.2	13.3	1187.2	7.1
ν_{31}	1171.0	3.8	1168.6	1.7
ν_{32}	1156.2	9.8	1157.7	24.8
ν_{33}	1115.5	72.2	1128.2	2.4
ν_{34}	1090.6	5.1	1091.7	14.8
ν_{35}	1064.2	15.5	1038.0	2.7
ν_{36}	1024.4	3.5	1035.4	8.8
ν_{37}	1021.4	15.8	1026.4	3.2
ν_{38}	963.2	1.9	963.2	4.9
ν_{39}	932.5	28.8	933.3	19.3
ν_{40}	884.0	3.2	875.7	10.5
ν_{41}	780.0	0.9	783.3	3.2
ν_{42}	754.3	1.9	753.7	0.6
ν_{43}	663.4	0.6	669.7	2.4
ν_{44}	605.2	7.0	607.4	1.2
ν_{45}	554.5	4.4	556.6	0.3
ν_{46}	541.9	5.4	551.4	4.0

ν_{47}	484.6	0.3	483.6	0.6
ν_{48}	456.5	8.9	465.8	7.5
ν_{49}	348.4	7.0	352.1	1.1
ν_{50}	208.2	0.9	210.6	0.3
ν_{51}	2905.4	8.5	2870.9	11.8
ν_{52}	1138.8	0.3	1134.1	0.1
ν_{53}	1005.9	1.3	1001.4	0.3
ν_{54}	1002.0	0	997.6	0
ν_{55}	991.7	0.3	968.8	10.0
ν_{56}	964.0	1.9	958.2	0.8
ν_{57}	927.4	0	645.2	6.9
ν_{58}	896.2	0	883.7	0
ν_{59}	877.4	6.6	863.1	0
ν_{60}	838.8	40.5	824.7	4.1
ν_{61}	778.3	1.9	775.2	62.6
ν_{62}	761.4	14.2	758.7	0
ν_{63}	755.3	44.6	756.4	40.2
ν_{64}	688.6	0.9	676.7	5.3
ν_{65}	624.7	20.9	610.2	11.3
ν_{66}	553.9	0.9	582.0	0.8
ν_{67}	470.3	2.2	453.5	0.7
ν_{68}	419.5	2.5	429.1	1.4
ν_{69}	406.6	0.3	412.0	0.1
ν_{70}	333.8	2.2	293.1	0.3
ν_{71}	271.4	0	262.3	2.0
ν_{72}	192.9	0.3	231.2	1.5
ν_{73}	148.7	10.4	154.7	6.8
ν_{74}	117.7	0.3	115.5	0.9
ν_{75}	100.8	0.6	109.3	4.9

[a]The symmetry of the modes ν_1–ν_{50} is *a*' and ν_{51}–ν_{75} is *a*". [b]Harmonic wavenumbers scaled with factors 0.958 and 0.978 for regions above and below 2500 cm^{-1}, respectively.

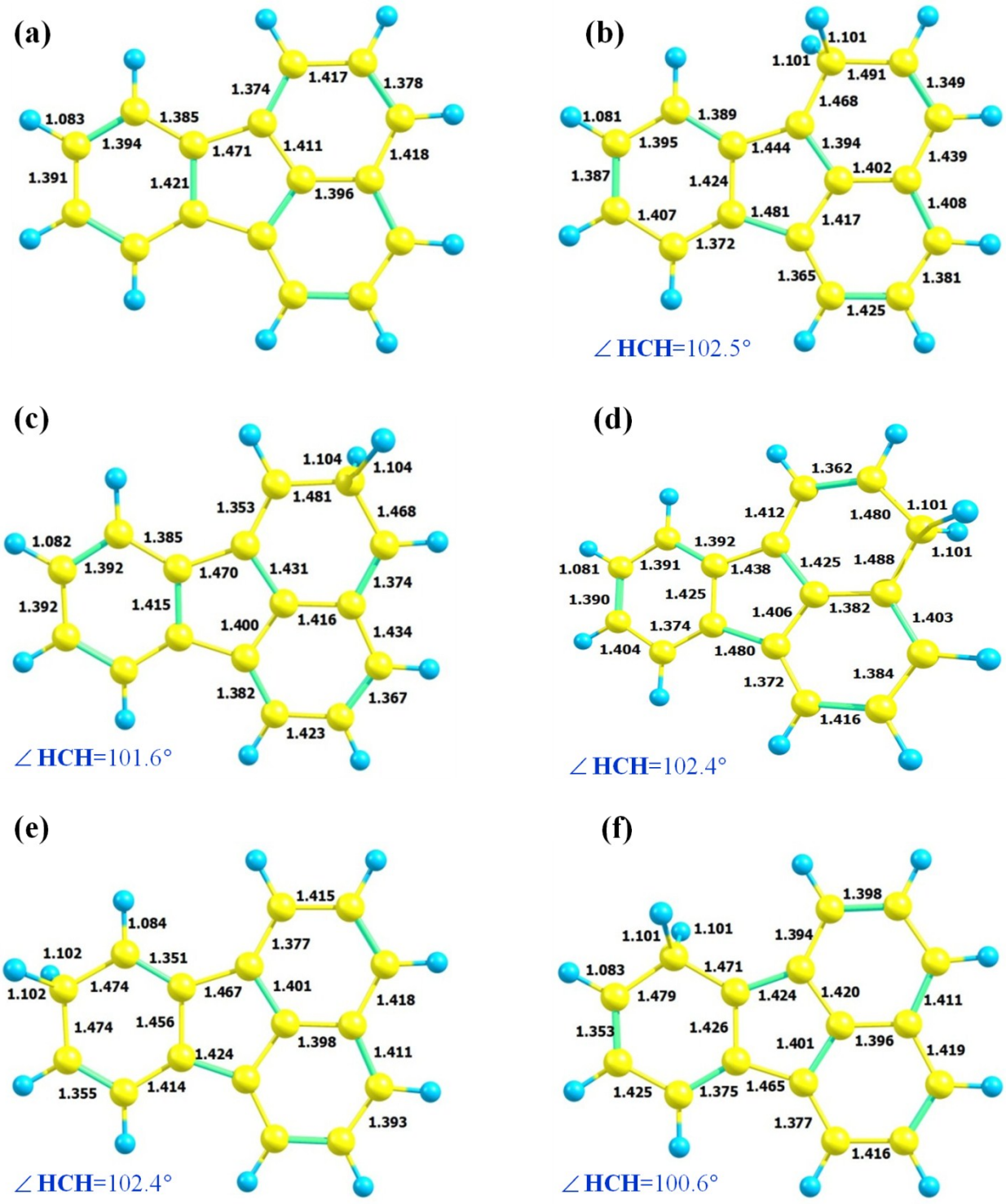

Fig. S1 Ground-state structures of (a) fluoranthene $C_{16}H_{10}$, (b) 1-$C_{16}H_{11}^{+}$, (c) 2-$C_{16}H_{11}^{+}$, (d) 3-$C_{16}H_{11}^{+}$, (e) 9-$C_{16}H_{11}^{+}$, and (f) 10-$C_{16}H_{11}^{+}$ optimized with the B3PW91/6-311++G(2d,2p) method. Bond lengths are in Angstrom (Å).

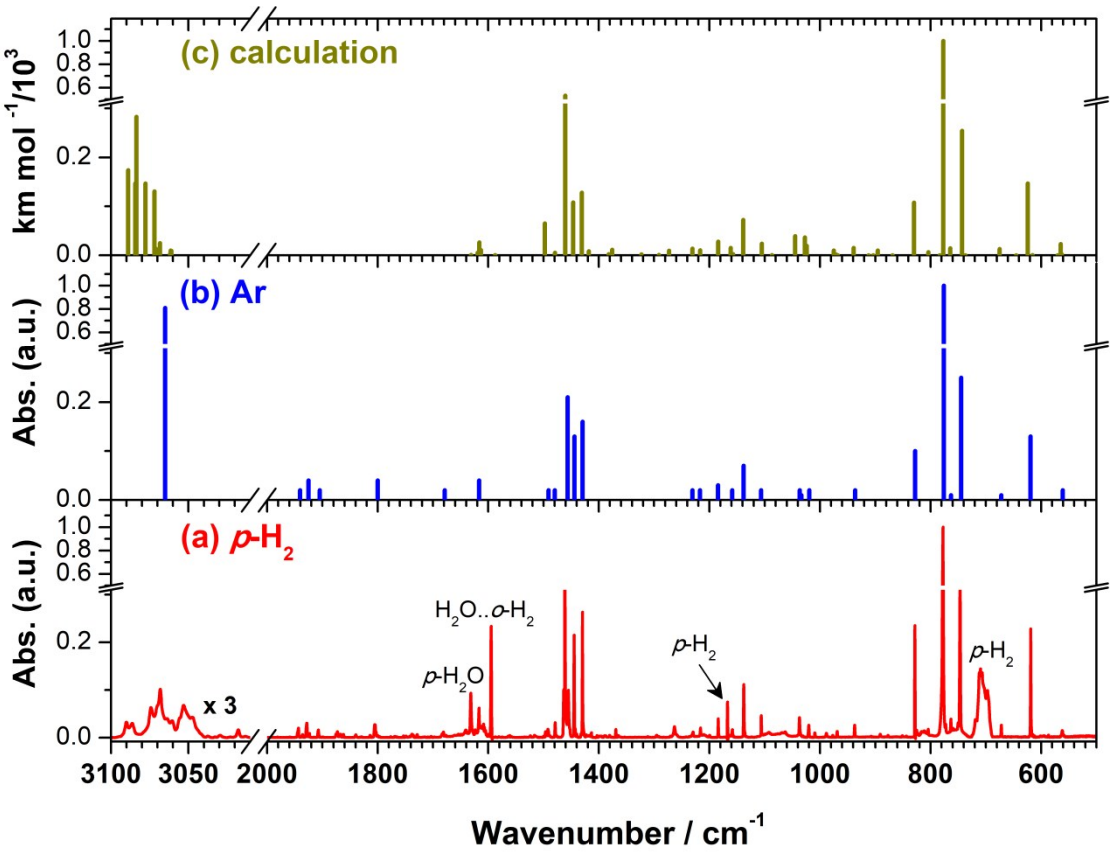

Fig. S2 Comparison of IR spectrum of $C_{16}H_{10}$ in (a) *p*-H_2 matrix, (b) Ar matrix, and (c) predicted with the B3PW91/6-311++G(2d,2p) method using scaled harmonic vibrational wavenumbers.

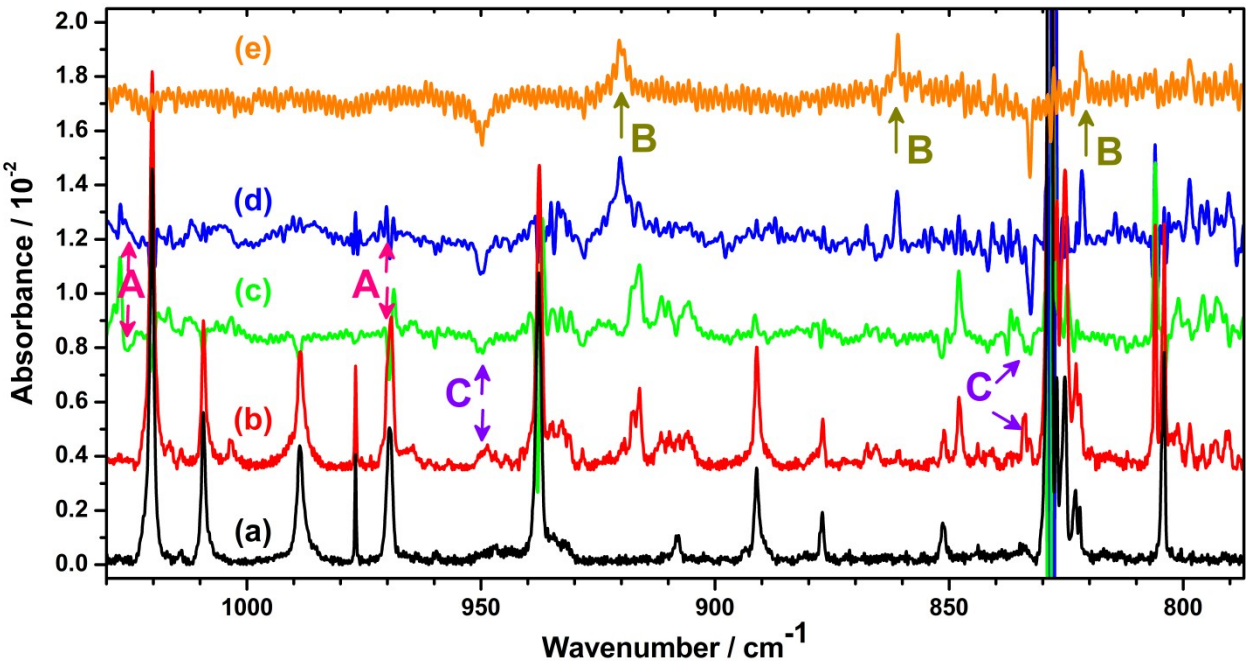

Fig. S3 Spectra recorded at varied stages of experiment in region 788−1030 cm^{-1}. (a) Absorption spectrum of parent $C_{16}H_{10}$/*p*-H_2 deposited at 3.2 K for 8 h; (b) Spectra measured after electron bombardment during deposition of $C_{16}H_{10}$/*p*-H_2 for 8 h; (c) Difference spectra after keeping the matrix in darkness for 18 h; (d) difference spectra after secondary photolysis at 520 nm for 50 min; (e) Difference spectra obtained on irradiating the matrix with light at 520 nm for 10 min in a separate experiment. The lines are groups according to the intensity correlation in each experimental step to groups A, B and C, as designated.

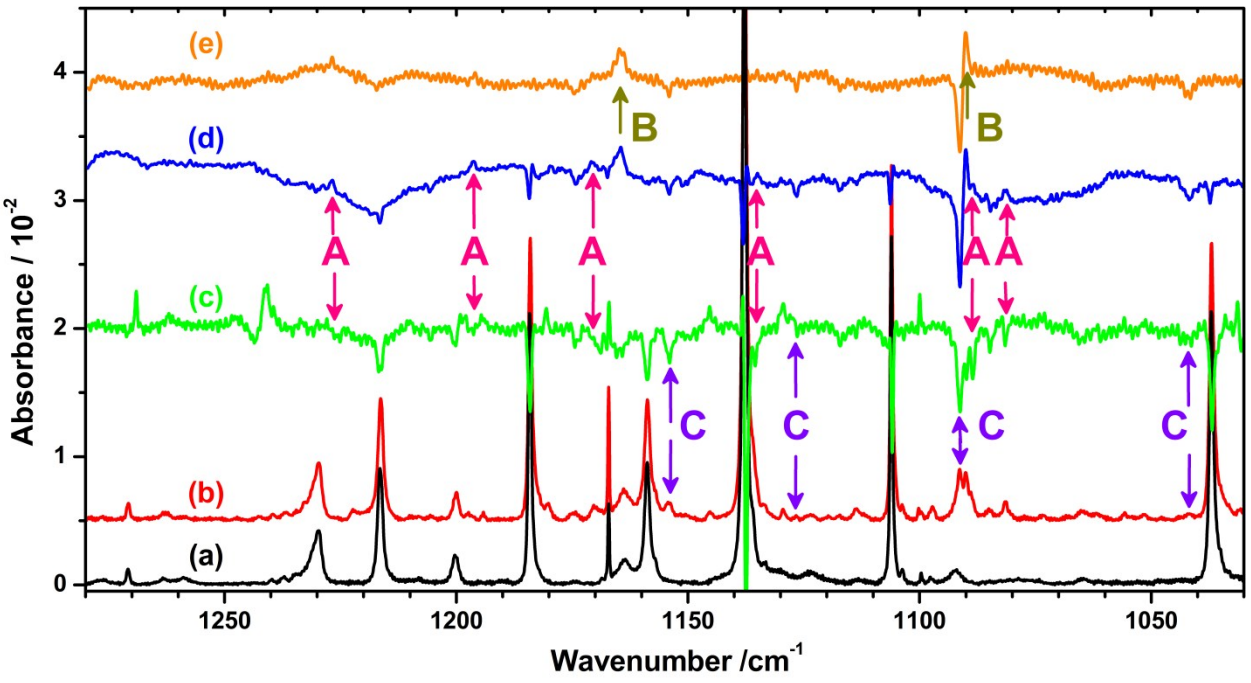

Fig. S4 Spectra recorded at varied stages of experiment in region 1030−1280 cm^{-1}. (a) Absorption spectrum of parent $C_{16}H_{10}$/*p*-H_2 deposited at 3.2 K for 8 h; (b) Spectra measured after electron bombardment during deposition of $C_{16}H_{10}$/*p*-H_2 for 8 h; (c) Difference spectra after keeping the matrix in darkness for 18 h; (d) difference spectra after secondary photolysis at 520 nm for 50 min; (e) Difference spectra obtained on irradiating the matrix with light at 520 nm for 10 min in a separate experiment. The lines are groups according to the intensity correlation in each experimental step to groups A, B and C, as designated.

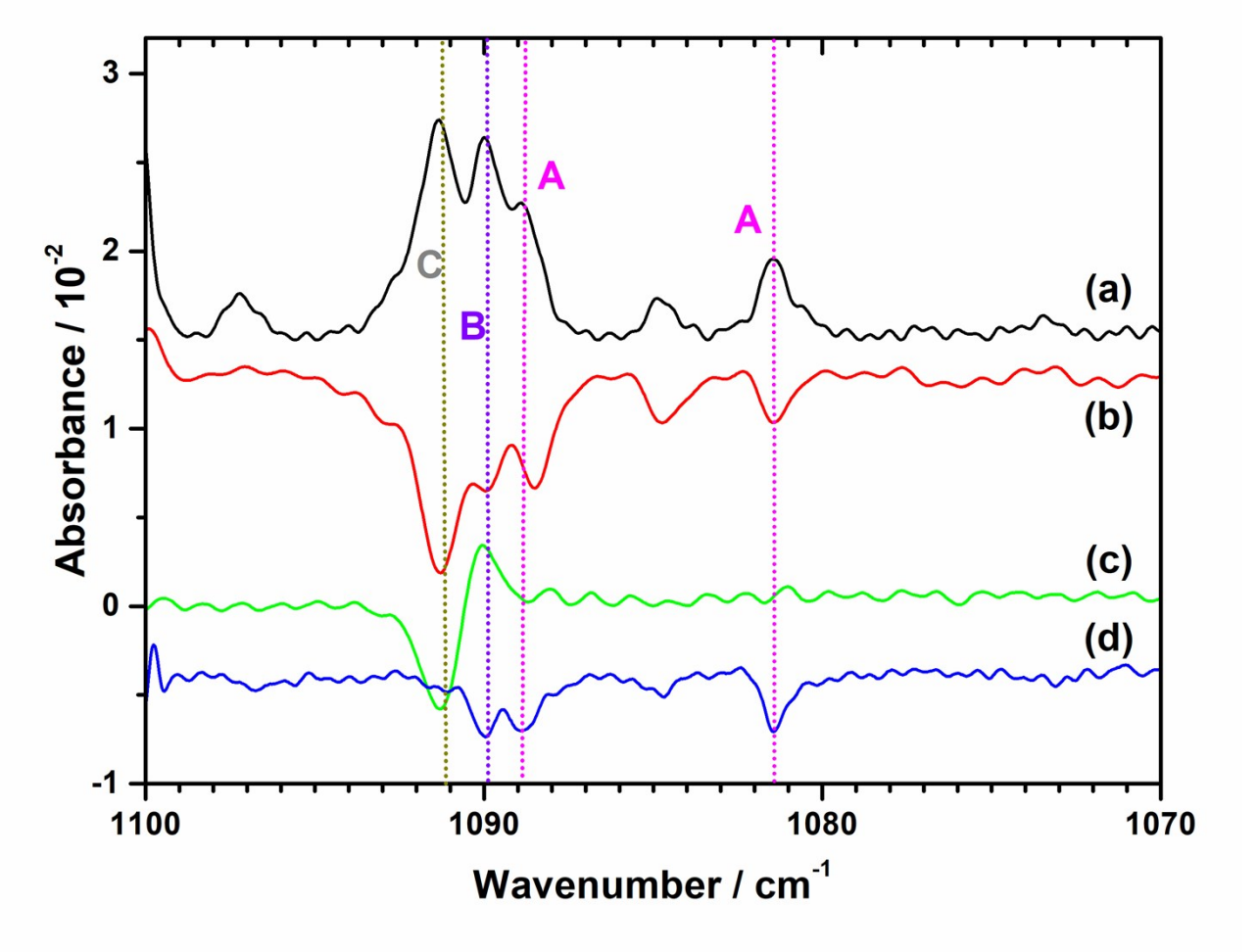

Fig. S5 Expanded spectra recorded at varied stages of experiment in region 1070−1100 cm^{-1}. (a) Spectra measured after electron bombardment during deposition of $C_{16}H_{10}$/*p*-H_2 for 8 h; (b) Difference spectra after keeping the matrix in darkness for 18 h; (c) Difference spectra obtained on irradiating the matrix with light at 520 nm for 10 min; (d) Difference spectra obtained on irradiating the matrix with light at 460 nm for 20 min. The lines are groups according to the intensity correlation in each experimental step to groups A, B and C, as designated.

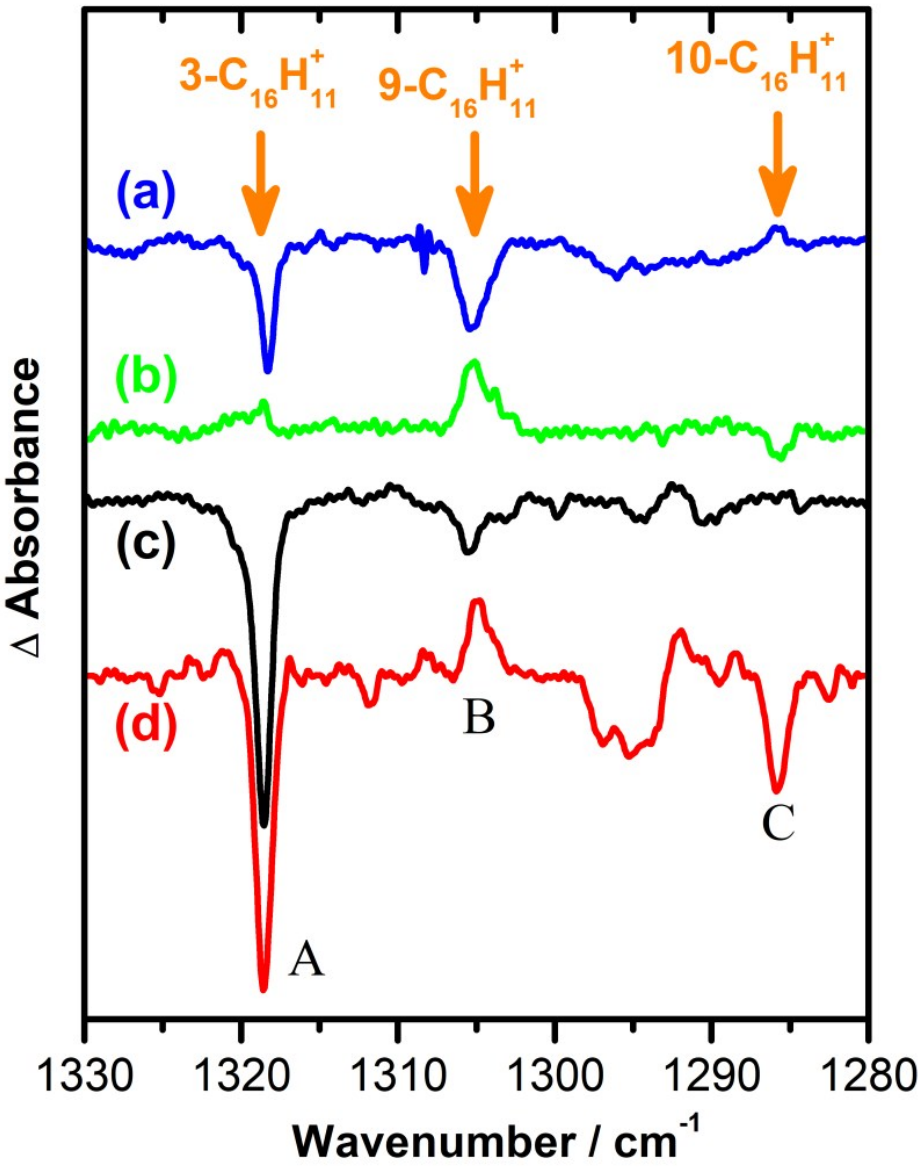

Fig. S6 Difference spectra in region 1280−1330 cm^{-1} obtained upon secondary photolysis at 375, 460 and 520 nm. (a) Upon irradiation of the electron bombarded $C_{16}H_{10}$/*p*-H_2 matrix at 375 nm for 20 min; (b) Upon irradiation at 520 nm for 20 min; (c) Upon Irradiation at 460 nm for 20 min on a matrix in which 10-$C_{16}H_{11}^+$ is nearly depleted after irradiation at 520 nm. (d) Upon irradiation of the freshly prepared electron-bombarded $C_{16}H_{10}$/*p*-H_2 matrix at 460 nm for 20 min. Bands corresponding to 3-, 9-, and 10-$C_{16}H_{11}^+$ are indicated.

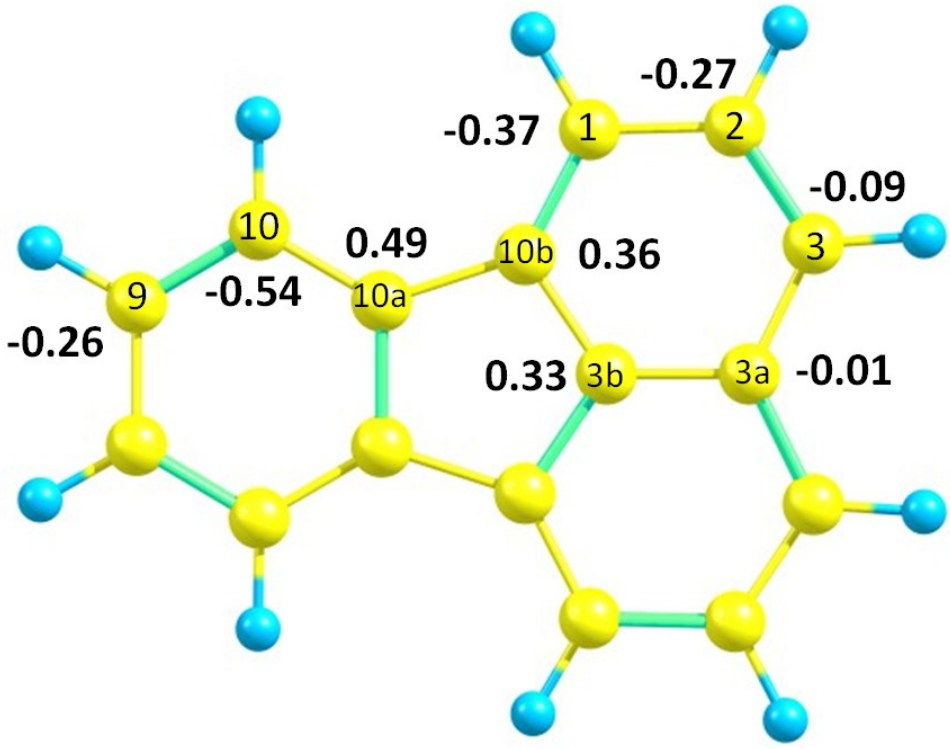

Fig. S7 Mullikan charge population of fluoranthene ($C_{16}H_{10}$).

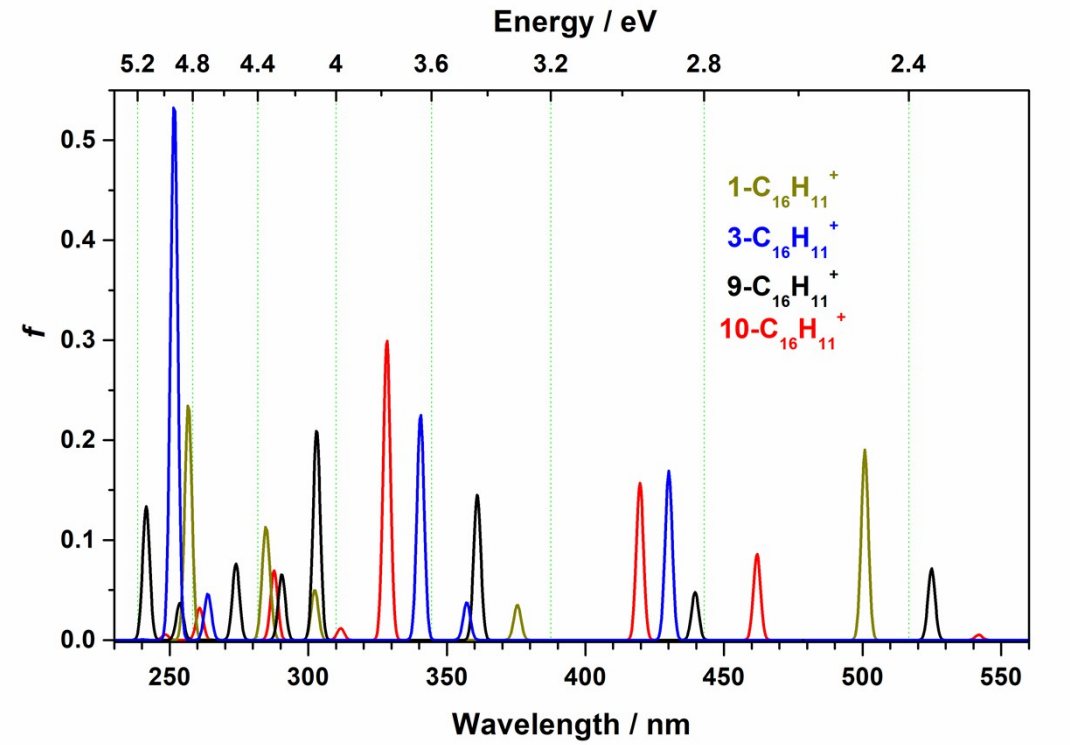

Fig. S8 Predicted UV-Vis spectra of 1-, 3-, 9-, and 10-$C_{16}H_{11}^{+}$ with the TD-DFT/6-311++G(2d,2p) method**.**