SUPPORTING INFORMATION

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Stable photoinduced charge separation in heptacene

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Experimental and Computational Details

The α-diketone **2** was synthesized as described previously.[1] Matrix experiments were carried out according to standard techniques[2] with APD CSW-20 displex closed-cycle helium cryostats. The photopresursor **2** was sublimed out of a quartz tube, which was resistively heated to 220–227 °C by Ta wire coiled around it, onto cold CsI (IR experiments) or sapphire windows with a large excess of argon, nitrogen (both Messer Griesheim, 99.9999%), or xenon (Air Liquide, 4.0), which were dosed to 2.0 sccm by a mass flow controller (MKS Mass Flo Type 247 four-channel read out). The windows were kept at 30 K, 28 K, or 55 K during deposition of argon, nitrogen, or xenon, respectively by resistive heating using an Oxford ITC 503 temperature controller. IR spectra were measured on Bruker IFS 66 and IFS 66/S spectrometers using a resolution of 0.5 cm^{-1}, while electronic spectra were measured using a Cary 5000 spectrometer.

The computational investigations used the B3LYP[3, 4] hybrid functional as implemented in Gaussian[5] for the optimization of the geometry and computation of harmonic vibrational frequencies of heptacene and its singly charged radical ions in conjunction with the 6-31G* basis set. All B3LYP computations were performed with Gaussian 03.[5] Electronic excitations of heptacene were computed using the RICC2[6, 7] method in conjunction with the TZVP[8] basis set employing the Turbomole[9] program. For the radical ions, time-dependent B3LYP was used in conjunction with the 6-31G* basis set for obtaining excitation energies, as the D_1 values of CC2 theory were unacceptably large (>0.08).

IR Spectral Data of Heptacene

Table S1. Mid-IR spectroscopic data of heptacene measured in an argon matrix at 15 K. For comparison theoretical data obtained at the RB3LYP/6-31G* level of theory is given. Due to the large number of IR active modes only those having a computed relative intensity larger than 5% are given.

Symmetry	Mode Number	ν_{exp}/cm^{-1}	rel. Intensity/%	ω_{theor}/cm^{-1}	rel. Intensity/%
B$_{2u}$	137	3085, 3054, 3039 [a]	combined: 116.3 [a]	3209.6	113.5
B$_{1u}$	136			3197.3	59.3
B$_{2u}$	133			3183.6	12.8
B$_{1u}$	131			3180.5	65.8
B$_{2u}$	130			3179.8	6.8
B$_{1u}$	119			1689.8	8.2
B$_{2u}$	95	1319	5.1	1362.5	8.9
B$_{1u}$	93	1309	13.1	1333.4	46.7
B$_{1u}$	77	1129	3.1	1160.4	5.6
B$_{3u}$	70	953	6.4	963.5	5.6
B$_{3u}$	65	901	100.0	922.1	100.0 [b]
B$_{3u}$	59	863	6.7	880.6	12.5
B$_{3u}$	51	799	4.3	812.4	6.1
B$_{3u}$	43	741, 733	78.3	751.5	44.5
B$_{2u}$	40			749.0	6.7
B$_{2u}$	33	602	4.7	615.7	9.5
B$_{3u}$	25	468	2.6	475.6	9.7
B$_{3u}$	23	461	2.7	472.7	10.3

[a] The bands due to the ν(CH) stretching vibrations are broad and not resolved. The three maxima are given and the entire feature was integrated. [b] Absolute intensity: 127.1 km mol^{-1}.

UV/vis Data of Heptacene

Table S2. Tentative assignment of experimental and comparison with computed (RICC2/TZVP//B3LYP/6-31G*) electronic transition energies and oscillator strengths f (in a.u.) for heptacene.

State	Experiment, Ar 10 K			RICC2/TZVP		
	λ/nm	ω/eV	$\Delta\nu$/cm^{-1}	λ/nm	ω/eV	f
	211	5.88	0	---	---	---
4^1B_{2u}	243	5.09	0	232	5.35	0.003
3^1B_{2u}	not obs.	not obs.	not obs.	265	4.67	0.001
4^1B_{1u}	268	4.63	0	289	4.29	0.064
	320	3.88	1705.1			
	326 [a]	3.80	1130.0			
	329	3.77	850.2			
2^1B_{2u}	338	3.66	0	310	3.99	5.407
3^1B_{1u}	355	3.49	0	338	3.67	0.030
2^1B_{1u}	not obs.	not obs.	not obs.	362	3.42	0.002
	414	2.99	1405.4			
1^1B_{2u}	440 [a]	2.82	0	416	2.98	0.010
	601	2.06	3632.6			
	610	2.03	3403.5			
	657	1.89	2222.9			
	670	1.85	1919.6			
	690	1.80	1485.9			
	704	1.76	1202.0			
	728 [a]	1.70	735.5			
1^1B_{1u}	769	1.61	0	736	1.68	0.049
[a] Most intensive feature within a system.						

Spectral Data of Radical Ions and Tentative Assignments

Table S3. Experimental and computed (TD-UB3LYP/6-31G*//UB3LYP/6-31G*) transition wavelengths (λ in nm) and oscillator strengths (in a.u.) for heptacene radical ions.

Heptacene Radical Cation, $^2B_{2g}$				Heptacene Radical Anion, $^2B_{3u}$			
State	Ar, 10 K	Theory	f	State	Ar, 10 K	Theory	f
	407						
	449						
	466						
3^2B_{3u}	not obs.	491.4	0.002	2^2B_{1g}	472	466.0	0.151
2^2A_u	480	495.9	0.217	3^2B_{2g}	not obs.	474.2	0.001
2^2B_{3u}	not obs.	628.9	0.000	2^2B_{2g}	not obs.	604.6	0.000
	971				991		
	1060						
	1087						
	1117						
	1146						
1^2A_u	1248 [a]	1023.9	0.391	1^2B_{1g}	1152	942.2	0.445
1^2B_{3u}	2134	1908.3	0.009	1^2B_{2g}	not obs.	2101.4	0.009
[a] Most intense band within a system.							

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