Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information:

Excited State Two Photon Absorption in the Near Infrared of Surprisingly stable Radical Cations of (Ferrocenyl)indenes

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Table S1. Calculated excitation energies (eV) for $\mathbf{1^+}$ and $\mathbf{1\text{-}6CH_3^+}$ in DCM, oscillator strengths (*f*) and contribution of monoelectronic transitions (above 10%).

	$\mathbf{1^+}$			$\mathbf{1\text{-}6CH_3^+}$		
	E (eV)	*f*		E (eV)	*F*	
1	1.0184	0.348e-1	77β→78β (87%)	0.96057	0.351e-1	101β→102β (76%) 99β→102β (20%)
2	1.0300	0.218e-3	75β→78β (97%)	1.0889	0.498e-3	98β→102β (90%)
3	1.2278	0.234e-1	76β→78β (87%)	1.1697	0.416e-01	101β→102β (19%) 99β→102β (69%)
4	1.5346	0.240e-3	74β→78β (97%)	1.9495	0.299e-01	97β→102β (71%) 96β→102β (25%)
5	2.0050	0.938e-3	73β→78β (100%)	1.9686	0.114e-01	97β→102β (23%) 96β→102β (75%)
6	2.1489	0.846e-2	72β→78β (94%)	2.3170	0.282e-02	95β→102β (96%)
7	2.4240	0.104	78α→79α (69%) 77β→79β (19%)	2.4709	0.682e-01	94β→102β (56%) 102α→103α (32%)
8	2.5090	0.137e-1	71β→78β (88%)	2.4745	0.933e-01	94β→102β (40%) 102α→103α (43%)
9	2.5315	0.272e-2	70β→78β (90%)	2.7909	0.233e-01	101β→103β (36%) 93α→102α (26%) 102α→104α (18%)
10	2.7409	0.892e-4	78α→80α (95%)	2.8143	0.715e-02	102α→104α (80%)

11	2.9252	0.120	77β→79β (47%) 76α→79α (15%) 78α→79α (11%) 76β→79β (11%)	2.9135	0.467e-01	101α→103α (44%) 93β→102β (28%)
12	3.0210	0.351e-1	76β→79β (44%) 76α→79α (23%) 78α→81α (12%)	2.9279	0.155e-01	100α→103α (37%) 100β→103β (36%)
13	3.0579	0.972e-4	75β→79β (55%) 75α→79α (39%)	2.9321	0.357e-01	101α→103α (43%) 93β→102β (17%) 100α→103α (11%) 100β→103β (11%)
14	3.1765	0.108e-2	77α→79α (92%)	2.9801	0.193e-01	92β→102β (80%)
15	3.2278	0.193e-1	69β→78β (85%)	3.0004	0.189e-01	99α→103α (30%) 99β→103β (38%)
16	3.2620	0.238e-3	68β→78β (99%)	3.1310	0.424e-02	91β→102β (99%)
17	3.2876	0.880e-4	77β→80β (69%) 76α→80α (20%)	3.2299	0.384e-02	99α→104α (17%) 101β→104β (69%)
18	3.3696	0.104	77β→81β (33%) 78α→81α (32%)	3.2624	0.358e-01	102α→105α (32%) 98α→103α (22%) 101β→105β (18%)
19	3.3941	0.599e-2	76α→79α (48%) 76β→79β (29%)	3.3185	0.431e-02	98β→103β (82%)
20	3.4599	0.270e-2	75α→80α (30%) 75β→80β (27%) 76β→80β (12%)	3.3270	0.189e-02	100α→104α (25%) 100β→103β (15%) 100β→104β (31%)
21	3.4679	0.456e-03	75β→80β (19%) 75α→80α (19%) 75α→79α (19%)	3.3348	0.263e-02	100α→104α (26%) 100α→104α (22%) 100β→103β (22%) 100β→104β (22%)
22	3.5104	0.256e-03	75α→79α (21%) 76β→80β (17%) 76α→80α (15%) 75β→79β (14%)	3.3560	0.207e-01	99α→103α (34%) 99β→103β (30%) 102α→105α (11%)
23	3.5843	0.115e-02	74α→79α (80%)	3.4129	0.659e-04	101α→104α (34%)
24	3.6015	0.387e-04	67β→78β (99%)	3.4523	0.714e-02	99β→104β (32%) 99α→104α (18%) 98α→104α (16%) 98α→103α (12%)
25	3.6232	0.193e-02	77α→80α (96%)	3.4660	0.419e-01	98α→103α (46%) 101β→105β (11%)
26	3.6286	0.149e-01	73α→79α (75%)	3.5258	0.841e-03	90β→102β (97%)
27	3.6713	0.210e-02	74β→79β (90%)	3.5718	0.182e-02	89β→102β (11%)
28	3.7757	0.639e-01	72α→79α (71%)	3.6867	0.892e-01	101β→105β (28%) 96α→103α (23%) 97α→103α (21%) 102α→105α (14%)

Fig. S1. Comparison of the linear optical spectra of the solutions of $\mathbf{1}^{+}$ and $\mathbf{1\text{-}6CH_3}^{+}$ before (red line) and after (black line) NLT measurements did not reveal photodegradation and this is evidence of the very high stability of these radical cations (complete spectra are shown on the left, spectra details in proximity of the wavelength of irradiation are shown on the right).