Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information: Using computational chemistry to design pump-probe schemes for measuring nitrobenzene radical cation dynamics

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Supplemental Figures

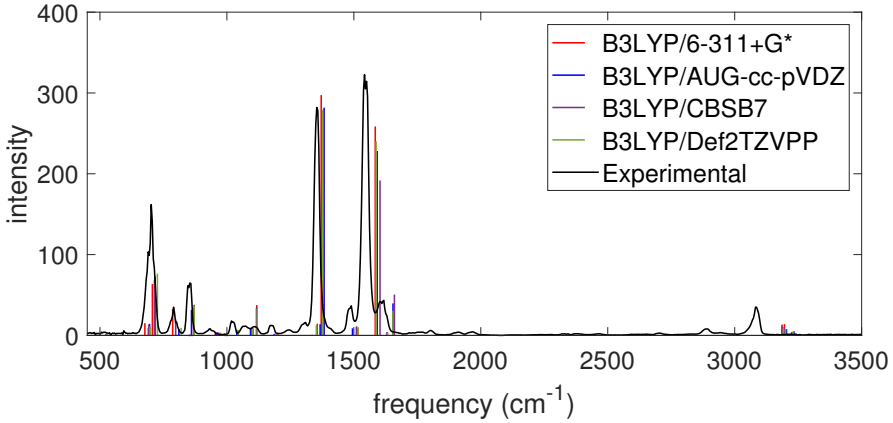

Figure S1: Experimental (black) and computed infrared spectra using the B3LYP functional with different basis sets for NB.

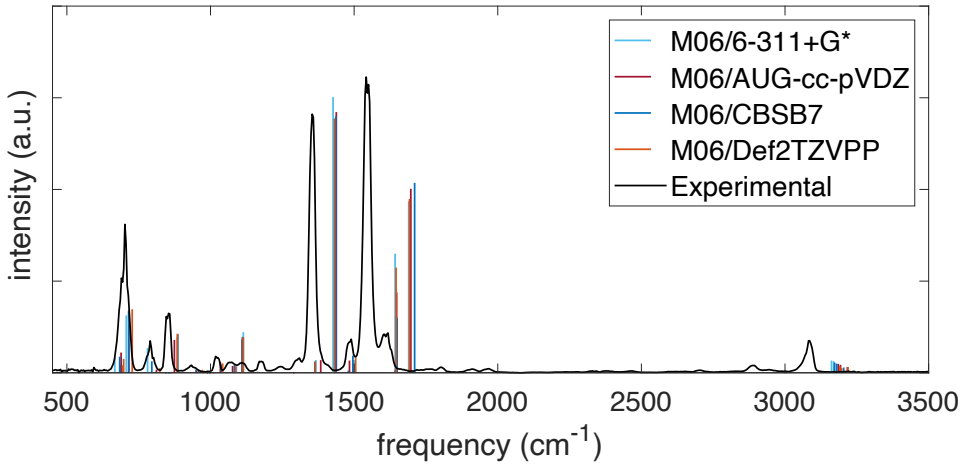

Figure S2: Experimental (black) and computed infrared spectra using the M06 functional with different basis sets for NB.

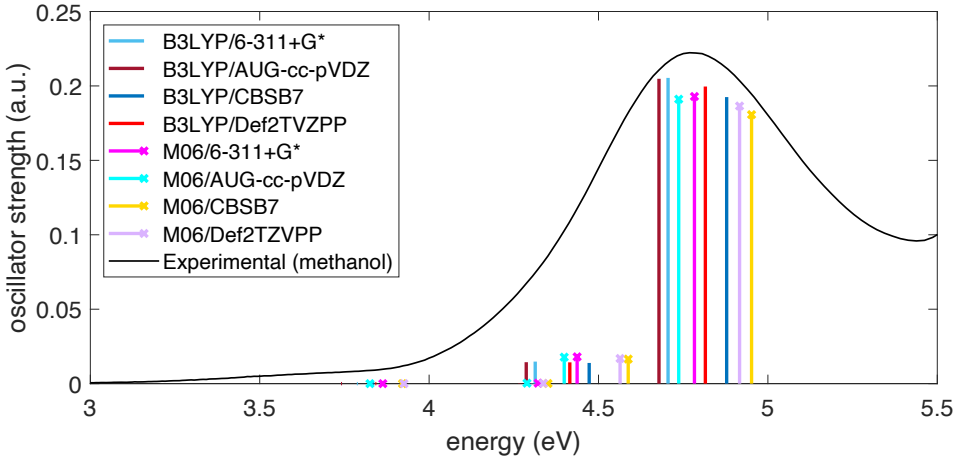

Figure S3: Experimental (black) and computed UV-Vis spectra using the B3LYP and M06 functionals with different basis sets for NB.

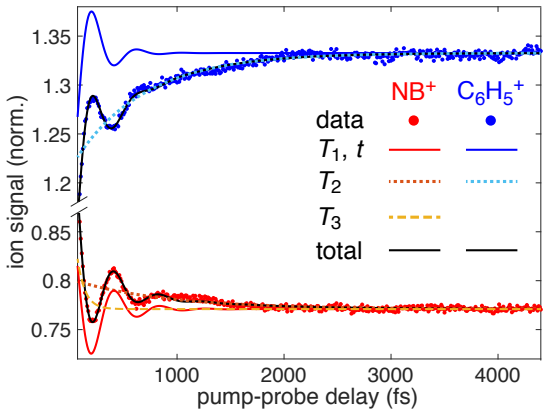

Figure S4: Ion signals (dots) of NB^+ (red) and $C_6H_5^+$ (blue) obtained with 650 nm probe pulses at 10^{12} W cm^{-2}, with fits to eq 1 in the main work (black lines) and components T_1, T_2, and T_3 (solid, dotted, and dashed lines). $C_6H_5^+$ did not require a T_3 component.

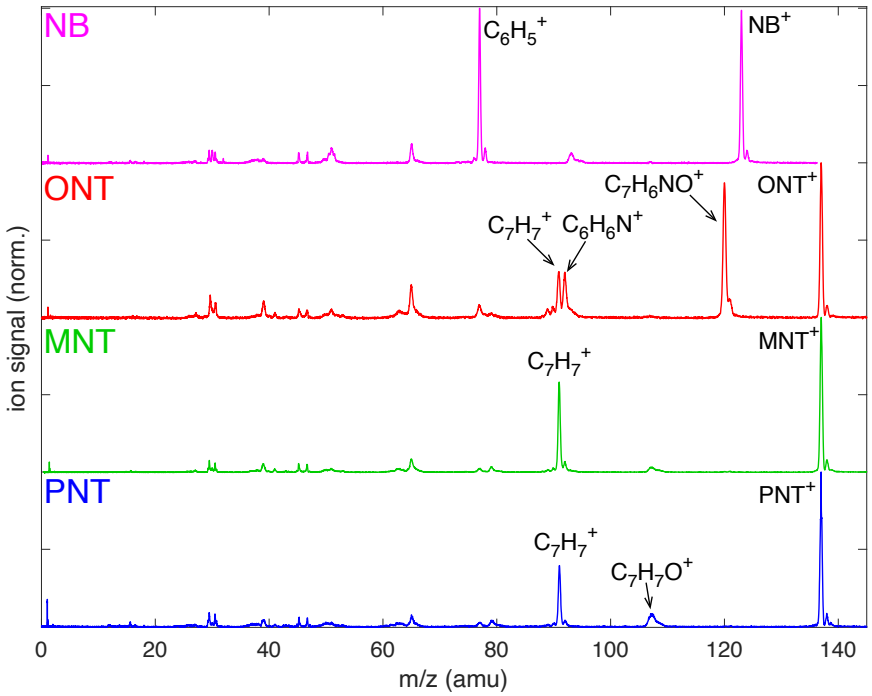

Figure S5: Mass spectra of NB (magenta), ONT (red), MNT (green), and PNT (blue) taken with 1300 nm pump only.

Tabulated theoretical results

	Neutral			Cation		
C	0.241731	0.000000	0.000037	0.239436	-0.005728	0.015543
C	-0.429303	-1.215050	0.000072	-0.423645	-1.231631	0.232515
C	-1.817324	-1.207038	0.000044	-1.792522	-1.216632	0.223226
C	-0.429303	1.215050	-0.000037	-0.427462	1.224794	-0.226463
C	-1.817323	1.207038	-0.000062	-1.796491	1.218089	-0.229544
C	-2.509993	0.000000	-0.000022	-2.485236	0.004167	-0.009561
N	1.718763	0.000000	0.000096	1.691325	0.001143	0.022143
O	2.286043	1.081198	0.000085	2.271968	-0.390600	1.004127
O	2.286045	-1.081198	-0.000190	2.192149	0.402257	-1.015975
H	0.133992	-2.135132	0.000127	0.145562	-2.133022	0.411568
H	-2.357594	-2.143644	0.000073	-2.354042	-2.124272	0.394744
H	-3.591754	0.000000	-0.000046	-3.567685	-0.000543	-0.020030
H	-2.357593	2.143644	-0.000112	-2.351615	2.129048	-0.402238
H	0.133993	2.135132	-0.000069	0.148641	2.122930	-0.400057

Table S1: Geometric coordinates for neutral and cationic NB optimized at the B3LYP/ Def2TZVPP level.

Atom	RMSD	MRMSD
C1	0.01385	0.01385
C2	0.11181	0.11181
C3	0.10986	0.10986
C4	0.10562	0.10562
C5	0.10675	0.10675
C6	0.02507	0.02507
N7	0.03129	0.03129
O8	1.83292	1.83292
O9	1.86775	1.86775
H10	0.19432	0.19432
H11	0.18418	0.18418
H12	0.02649	0.02649
H13	0.18032	0.18032
H14	0.18726	0.18726
All H atoms	0.16731	0.37412
All C atoms	0.08939	0.21896
All N atoms	0.03129	0.03129
All O atoms	1.85042	2.61689
All atoms	0.70897	2.65272

Table S2: Root-mean-square distances (RMSD) and modified root-mean-square distances (MRMSD, see definition in the main work) between neutral and cationic NB geometries optimized at the B3LYP/ Def2TZVPP level. Values are given in Å.

6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
49.44	0.00	52.63	0.00	55.51	0.00	51.42	0.00
168.56	0.86	169.83	0.83	170.36	0.93	169.46	0.93
255.75	0.98	257.25	1.11	253.88	0.82	256.82	0.88
394.76	0.85	395.76	1.07	394.44	1.12	395.89	1.04
416.89	0.00	417.99	0.00	418.36	0.00	420.13	0.00
439.68	1.03	444.99	0.51	447.72	0.69	450.06	0.54
526.65	1.15	527.30	1.20	523.20	1.32	526.38	1.26
627.63	0.05	627.16	0.03	621.10	0.05	628.61	0.04
676.89	15.08	692.17	13.43	691.00	9.15	697.20	11.04
696.86	8.33	697.23	8.92	695.43	14.28	698.22	8.82
706.48	63.58	714.63	68.73	716.81	73.18	726.31	76.34
786.44	32.61	798.37	19.71	810.90	7.79	819.72	9.54
853.33	0.00	859.61	0.00	849.94	0.00	862.79	0.00
868.79	34.18	871.06	37.85	860.57	31.69	871.10	35.96
954.12	4.39	964.63	4.01	957.47	3.06	973.11	3.60
990.30	0.00	999.15	0.00	995.34	0.00	1006.92	0.00
1010.57	0.16	1018.75	0.21	1012.90	0.23	1024.48	0.25
1020.07	0.31	1018.86	0.23	1016.79	0.04	1024.93	0.14
1043.67	6.03	1042.37	5.56	1038.91	6.91	1045.18	6.45
1102.75	8.85	1098.36	10.03	1093.02	8.62	1101.35	8.38
1117.63	37.52	1117.06	33.63	1117.07	34.21	1119.54	33.52
1188.41	0.70	1184.07	0.40	1174.37	0.53	1186.51	0.60
1199.93	3.45	1194.74	1.69	1186.23	1.95	1197.64	2.81
1344.03	0.06	1335.44	0.78	1319.05	0.04	1342.77	0.28
1355.90	14.48	1353.16	11.92	1367.20	13.82	1353.23	12.89
1371.42	297.31	1381.04	280.44	1383.20	281.80	1377.21	278.89
1491.98	0.25	1488.84	0.55	1473.43	0.07	1493.28	0.07
1515.56	8.90	1510.04	11.18	1494.63	8.75	1516.48	10.56
1584.35	258.52	1603.07	191.73	1591.84	228.16	1587.68	240.15
1632.54	3.80	1631.18	3.19	1629.41	3.61	1631.14	3.10
1654.50	30.41	1659.87	50.54	1654.22	39.58	1653.79	30.48
3173.63	0.92	3173.35	0.75	3182.97	0.63	3178.95	0.68
3186.59	13.39	3186.11	11.16	3195.16	8.85	3191.85	9.02
3195.87	13.90	3195.11	10.49	3204.07	7.75	3200.42	8.14
3226.52	0.02	3224.43	0.42	3233.07	0.57	3229.56	0.47
3226.75	3.72	3224.71	4.17	3233.44	5.11	3229.69	4.76

Table S3: Calculated harmonic frequencies (cm^{-1}) and intensities for NB using the B3LYP functional with different basis sets.

6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
50.72	0.00	53.21	0.00	58.70	0.00	55.11	0.00
167.49	0.91	168.40	0.87	168.98	0.93	169.02	0.99
257.90	0.88	258.41	1.02	255.89	0.77	256.14	0.83
397.78	0.96	397.95	1.14	396.18	1.24	396.57	1.19
411.71	0.00	412.22	0.00	412.35	0.00	417.06	0.00
430.11	0.95	437.21	0.52	441.38	0.70	446.39	0.42
529.65	0.79	530.24	0.86	525.60	0.97	528.68	0.86
617.95	0.07	617.26	0.03	609.87	0.05	619.14	0.05
666.86	16.50	683.78	17.57	687.02	8.37	694.28	8.04
693.74	7.39	693.90	7.65	688.85	22.07	697.63	15.20
706.85	62.62	714.98	67.52	715.83	67.97	727.42	69.28
780.89	26.93	795.68	12.47	811.88	3.42	823.58	4.99
849.43	0.00	853.54	0.00	842.65	0.00	860.39	0.00
884.06	38.83	886.20	42.27	874.29	35.89	884.54	42.60
948.79	4.01	957.95	3.71	950.40	2.68	971.21	3.28
987.72	0.00	994.72	0.00	987.56	0.00	1008.69	0.00
1008.33	0.09	1011.02	0.14	1002.52	0.15	1018.89	0.31
1012.53	0.19	1012.61	0.13	1011.10	0.02	1028.45	0.08
1040.45	8.63	1038.00	9.24	1034.35	11.89	1042.33	10.27
1090.14	6.61	1083.13	8.36	1076.86	7.44	1087.94	7.26
1114.28	44.29	1111.12	39.20	1110.01	36.45	1114.24	38.98
1163.48	1.18	1158.78	0.83	1147.82	1.03	1164.55	1.05
1180.24	0.20	1175.24	0.03	1167.64	0.08	1180.12	0.08
1312.09	0.03	1304.66	0.32	1288.28	0.00	1314.35	0.08
1366.71	13.91	1363.38	12.27	1383.75	13.80	1364.89	12.30
1426.68	300.74	1436.38	279.62	1437.92	284.35	1431.54	277.47
1482.28	0.99	1479.88	2.37	1468.81	0.75	1487.30	1.04
1499.92	13.83	1495.72	18.75	1483.78	13.37	1505.29	16.33
1642.64	129.90	1643.76	2.62	1643.96	3.21	1645.70	2.27
1644.91	3.13	1649.48	60.11	1648.03	87.73	1646.02	114.83
1690.06	187.10	1710.63	207.20	1697.32	200.75	1692.71	189.55
3147.31	1.81	3158.56	1.57	3173.23	1.02	3175.52	1.35
3161.88	13.33	3172.51	11.11	3185.44	9.72	3190.55	7.22
3169.30	12.73	3179.82	10.03	3193.23	8.69	3196.86	5.24
3194.88	0.01	3204.25	0.32	3217.20	6.28	3219.36	6.34
3194.91	5.34	3204.34	5.76	3217.43	0.30	3219.41	0.65

Table S4: Calculated harmonic frequencies (cm^{-1}) and intensities for NB using the M06 functional with different basis sets.

6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
37.48	0.05	67.63	0.06	31.82	0.05	53.87	0.03
63.13	0.32	96.41	4.46	51.54	0.26	74.35	5.78
159	0.61	189.65	7.2	157.41	0.75	169.1	6.16
247.06	6.61	273.52	16.91	240.18	6.54	248.4	11.43
363.34	1.25	363.84	3.04	361.37	0.39	362.93	1.97
365.06	1.19	368.22	0.33	362.46	1.76	366.48	0.67
394.98	0.65	408.62	6.52	395.2	0.76	401.63	4.02
496.05	0.77	513.14	6.01	496.56	0.59	504.76	2.22
622.38	35.02	622.78	35.06	620.3	32.14	628.64	33.46
669.75	0.02	666.41	0.12	660.45	0	668.15	0.34
724.81	17.12	719.52	26.2	719.29	12.96	729.37	15.28
792.2	53.13	786.07	47.06	786.53	44.11	793.56	42.42
802.73	39.28	800.39	50.69	796.98	3.82	808.64	30.08
804.94	3.14	815.32	2.85	800.42	33.78	816.63	11.3
965.23	5.2	967.31	5.81	959.35	4.93	976.14	7.03
980.51	58.9	982.32	62.17	980.75	55.58	983.67	58.1
1003.5	0.01	1001.54	0.05	995.37	0.03	1007.61	0.02
1008.27	0.16	1012.9	0.1	999.61	0.46	1023.49	0.06
1020.1	0.73	1017.8	1.04	1012.91	0.65	1034.91	0.64
1068.92	3.23	1079.5	5.09	1070.26	3.92	1077.45	4.2
1142.2	7.62	1136.09	0.75	1142.44	5.1	1142.34	2.03
1162.93	3.9	1156.73	5.16	1152.22	2.63	1162.3	3.54
1219.69	10.09	1211.72	7.24	1206.51	9.29	1216.86	9.67
1297.21	14.78	1303.47	10.68	1290.38	8.62	1301.35	11.61
1385.46	20.14	1335.19	186.52	1368.12	7.64	1370.44	107.73
1392.31	19.14	1388.05	21.68	1397.29	19.97	1392.74	22.04
1404	15.47	1400.97	10.48	1417.67	13.33	1404.14	7.65
1444.64	79.87	1462.56	116.99	1442.53	122.95	1468.36	128.06
1466	114.59	1485.11	167.63	1460.07	79.33	1471.78	111.72
1521.39	37.17	1514.05	31.52	1506.64	44.49	1522.2	34.53
1645.31	106.9	1626.34	99.84	1642.33	100.3	1638.84	98.4
3201.78	0.01	3195.9	0.39	3201.93	0.56	3197.64	0.52
3211.06	1.1	3206.67	3.25	3212.13	1.01	3209.04	2.59
3213.08	6.75	3209.74	8.74	3213.98	12.13	3211.01	9.57
3221.08	25.62	3216.81	29.74	3222.62	36.94	3218.85	32.12
3223.3	0.09	3219.75	6.92	3224.78	0.61	3221.33	3.79

Table S5: Calculated harmonic frequencies (cm^{-1}) and intensities for NB cation using the B3LYP functional with different basis sets.

6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
71.29	0.90	58.64	0.48	62.64	0.89	47.60	0.32
82.05	0.61	75.02	1.13	73.87	0.39	69.90	0.85
173.26	1.36	164.96	0.62	168.93	1.05	158.38	0.46
259.10	5.37	259.69	5.96	256.29	5.48	252.15	6.22
355.27	2.17	355.53	2.75	350.75	1.63	359.30	2.55
366.40	4.47	368.41	3.51	365.10	5.00	366.69	3.57
377.68	0.48	374.39	0.56	375.27	0.44	379.46	0.55
474.65	1.11	481.88	0.83	465.38	1.14	486.73	0.70
612.54	31.67	609.46	29.52	608.73	28.25	620.05	27.10
672.81	4.00	673.05	2.42	664.71	4.26	671.99	3.63
730.15	25.19	725.70	30.72	721.98	20.02	734.51	20.80
795.27	1.03	795.73	25.63	784.65	0.69	805.03	2.84
799.95	28.89	796.71	3.15	799.38	23.96	813.13	23.53
820.11	13.17	813.99	19.49	812.24	7.98	816.14	13.01
951.82	6.61	951.75	6.97	946.76	6.18	966.49	7.25
980.05	63.07	980.19	60.90	977.16	54.50	983.83	62.11
995.93	0.05	992.09	0.68	985.64	2.61	1001.62	0.45
1001.53	0.09	993.51	0.59	989.62	1.48	1019.64	0.05
1005.20	0.57	1002.67	0.27	996.17	0.53	1024.51	0.41
1052.56	1.88	1054.71	3.18	1046.55	2.21	1061.38	2.88
1142.41	7.74	1139.32	5.14	1131.58	3.40	1144.20	6.58
1145.76	3.33	1140.70	3.31	1139.23	4.55	1147.20	2.99
1202.19	9.28	1197.89	9.60	1190.57	10.18	1203.16	10.08
1286.87	11.71	1284.72	8.88	1272.97	8.09	1291.15	9.63
1363.61	6.43	1358.77	5.71	1343.82	4.93	1370.14	6.00
1417.55	27.34	1413.44	26.18	1420.98	21.75	1413.69	25.46
1439.35	127.28	1434.20	130.26	1421.74	147.79	1441.33	66.65
1447.31	21.88	1444.46	13.81	1455.01	0.04	1449.45	76.62
1515.78	53.48	1510.73	53.67	1508.73	58.52	1519.75	50.43
1582.22	160.42	1568.31	120.02	1602.43	148.24	1564.21	142.38
1664.33	68.61	1660.02	80.47	1662.97	60.80	1664.35	74.73
3158.00	0.65	3165.05	1.46	3177.65	1.57	3178.63	2.64
3175.78	4.88	3184.61	5.54	3195.73	4.74	3199.96	8.41
3176.08	7.81	3184.66	11.28	3196.09	9.74	3200.03	9.57
3186.10	25.65	3194.70	33.70	3206.28	30.19	3210.04	40.28
3187.84	0.23	3196.32	0.57	3207.65	0.44	3211.69	1.33

Table S6: Calculated harmonic frequencies (cm^{-1}) and intensities for NB cation using the M06 functional with different basis sets.

	6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
State	EE	f	EE	f	EE	f	EE	f
S1	3.7867	0	3.835	0	3.74	0	3.8413	0
S2	4.3037	0.0003	4.3277	0.0001	4.2676	0.0003	4.3423	0.0002
S3	4.3132	0.0148	4.4725	0.0139	4.2867	0.0144	4.4153	0.0143
S4	4.7053	0.2054	4.8783	0.1925	4.6785	0.2048	4.8154	0.1996
S5	5.9144	0.001	6.0127	0.0001	5.8483	0.0026	5.9682	0
S6	6.0367	0.0621	6.1241	0.055	5.9704	0.0594	6.0931	0.0604
S7	6.3457	0	6.2888	0	6.237	0.0001	6.305	0
S8	6.4389	0.177	6.5457	0.1777	6.3824	0.1899	6.4839	0.1916
S9	6.5271	0	6.6172	0	6.4134	0	6.5238	0
S10	6.7257	0	6.6559	0	6.6026	0	6.6699	0

Table S7: Calculated excitation energies (eV) and oscillator strengths (a.u.) for NB using the B3LYP functional with different basis sets under the TDDFT formalism.

	6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
State	EE	f	EE	f	EE	f	EE	f
S1	3.8634	0.0000	3.9214	0.0000	3.8254	0.0000	3.9259	0.0000
S2	4.3217	0.0003	4.3510	0.0001	4.2889	0.0003	4.3373	0.0002
S3	4.4369	0.0180	4.5877	0.0165	4.3988	0.0178	4.5637	0.0169
S4	4.7832	0.1929	4.9518	0.1807	4.7368	0.1911	4.9164	0.1865
S5	5.9566	0.0092	6.0762	0.0172	5.9064	0.0098	6.0378	0.0133
S6	6.1733	0.0000	6.4048	0.0499	5.9839	0.0000	6.3253	0.0642
S7	6.2717	0.0613	6.4430	0.1995	6.1272	0.0065	6.3828	0.2188
S8	6.3098	0.1967	6.5820	0.0000	6.1928	0.0615	6.5503	0.0000
S9	6.3259	0.0055	6.6217	0.0000	6.2307	0.2100	6.5568	0.0000
S10	6.5348	0.0000	6.8241	0.0000	6.3944	0.0000	6.7779	0.0000

Table S8: Calculated excitation energies (eV) and oscillator strengths (a.u.) for NB using the M06 functional with different basis sets under the TDDFT formalism.

	6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
State	EE	f	EE	f	EE	f	EE	f
D1	0.6386	0	0.6424	0	0.6448	0	0.6657	0
D2	1.1537	0.001	1.149	0.003	1.1669	0.001	1.1853	0.0025
D3	1.4923	0	1.4226	0.0034	1.5243	0	1.5346	0.0012
D4	1.7183	0.0799	1.6651	0.0694	1.7276	0.0779	1.7529	0.0777
D5	3.0281	0.0007	3.0017	0.0006	2.9696	0.0007	2.9779	0.0007
D6	3.0411	0	3.0679	0	3.059	0	3.153	0
D7	3.4059	0.0022	3.3944	0.0019	3.3869	0.002	3.4435	0.0017
D8	3.6041	0.0003	3.5643	0.0006	3.5396	0.0003	3.5556	0.0004
D9	3.7937	0.0074	3.6724	0.0088	3.7663	0.0039	3.7625	0.0077
D10	3.7989	0.0171	3.9523	0.0141	3.7838	0.0201	3.9489	0.0167

Table S9: Calculated excitation energies (eV) and oscillator strengths (a.u.) for NB cation using the B3LYP functional with different basis sets under the TDDFT formalism.

	6-311+G*		CBSB7		AUGCCPVDZ		DEF2TZVPP	
State	EE	f	EE	f	EE	f	EE	f
D1	0.6416	0.0000	0.6354	0.0000	0.6319	0.0000	0.6669	0.0000
D2	1.2956	0.0008	1.2138	0.0007	1.3078	0.0007	1.2172	0.0007
D3	1.6794	0.0001	1.5694	0.0001	1.7022	0.0001	1.6340	0.0001
D4	1.7905	0.0706	1.7225	0.0669	1.7842	0.0650	1.7620	0.0681
D5	3.0271	0.0007	2.9810	0.0007	2.9583	0.0007	2.9656	0.0007
D6	3.3725	0.0040	3.3697	0.0047	3.3405	0.0044	3.3778	0.0043
D7	3.4568	0.0001	3.4360	0.0002	3.4066	0.0001	3.4573	0.0002
D8	3.6111	0.0002	3.5802	0.0001	3.5515	0.0002	3.6056	0.0001
D9	3.9137	0.0283	3.9402	0.0290	3.8823	0.0299	3.9888	0.0303
D10	4.0236	0.0012	4.0303	0.0013	3.9935	0.0014	4.0484	0.0011

Table S10: Calculated excitation energies (eV) and oscillator strengths (a.u.) for NB cation using the M06 functional with different basis sets under the TDDFT formalism.

	neutral geometry		cation geometry	
transition	EE (eV)	f (a.u.)	EE (eV)	f (a.u.)
$D_0 \rightarrow D_1$	0.0929	0.000004	0.1385	0.000007
$D_0 \rightarrow D_2$	1.1993	0.000000	1.3287	0.000000
$D_0 \rightarrow D_3$	1.3146	0.000634	1.5099	0.000877
$D_0 \rightarrow D_4$	1.3755	0.000001	1.6319	0.000003
$D_0 \rightarrow D_5$	3.1485	0.040960	3.1052	0.040215

Table S11: Excitation energies (EE) and oscillator strengths (f) for NB cation at the optimized neutral and cation geometries at the EOM-EE-CCSD/6-311+G* level of theory.

Tabulated curve fitting results

Tables S12 through S15 give the coefficients extracted from fitting transient ion signals obtained at conditions indicated to eq 1 in the main text.

eq (1)	NB^+	$C_6H_5^+$	$C_4H_3^+$
a	0.11 ± 0.02	0.13 ± 0.02	–
T_1 (fs)	242 ± 15	176 ± 15	–
t (fs)	426 ± 10	421 ± 14	–
ϕ (rad)	-0.04 ± 0.08	3.07 ± 0.09	–
b	0.031 ± 0.003	-0.116 ± 0.004	-0.024 ± 0.003
T_2 (fs)	870 ± 100	654 ± 28	230 ± 60
c	0.14 ± 0.06	–	0.016 ± 0.003
T_3 (fs)	72 ± 27	–	1660 ± 460
d	0.771 ± 0.001	1.333 ± 0.001	0.339 ± 0.001

Table S12: Coefficients extracted from transients at 650 nm, 10^{12} W cm^{-2} fitted to eq (1).

eq (1)	NB^+	$C_6H_5^+$	$C_4H_3^+$
a	0.14 ± 0.02	0.28 ± 0.04	0.045 ± 0.008
T_1 (fs)	239 ± 15	153 ± 13	365 ± 64
t (fs)	430 ± 9	516 ± 22	464 ± 20
ϕ (rad)	-0.08 ± 0.09	3.37 ± 0.08	3.42 ± 0.25
b	0.076 ± 0.005	-0.144 ± 0.002	-0.32 ± 0.01
T_2 (fs)	736 ± 44	1770 ± 90	193 ± 13
c	0.27 ± 0.06	–	0.094 ± 0.004
T_3 (fs)	79 ± 16	–	3100 ± 500
d	0.771 ± 0.001	1.608 ± 0.001	0.538 ± 0.001

Table S13: Coefficients extracted from transients at 650 nm, 10^{13} W cm^{-2} fitted to eq (1).

eq (1)	NB^+	$C_6H_5^+$	$C_4H_3^+$
a	0.05 ± 0.01	0.053 ± 0.014	–
T_1 (fs)	225 ± 41	139 ± 26	–
t (fs)	426 ± 10	362 ± 36	–
ϕ (rad)	-0.05 ± 0.21	2.47 ± 0.31	–
b	0.033 ± 0.002	-0.043 ± 0.002	-0.013 ± 0.006
T_2 (fs)	841 ± 75	808 ± 46	260 ± 160
c	0.12 ± 0.11	–	0.012 ± 0.006
T_3 (fs)	38 ± 37	–	960 ± 390
d	0.826 ± 0.001	1.212 ± 0.001	0.264 ± 0.001

Table S14: Coefficients extracted from transients at 800 nm, 10^{12} W cm^{-2} fitted to eq (1).

eq (1)	NB^+	$C_6H_5^+$	$C_4H_3^+$
a	0.08 ± 0.01	0.20 ± 0.02	–
T_1 (fs)	244 ± 24	147 ± 12	–
t (fs)	439 ± 15	417 ± 19	–
ϕ (rad)	-0.13 ± 0.19	2.64 ± 0.13	–
b	0.085 ± 0.003	-0.126 ± 0.002	-0.157 ± 0.005
T_2 (fs)	842 ± 31	1560 ± 70	191 ± 11
c	0.36 ± 0.09	–	0.088 ± 0.003
T_3 (fs)	51 ± 11	–	1680 ± 110
d	0.364 ± 0.001	1.409 ± 0.001	0.338 ± 0.001

Table S15: Coefficients extracted from transients at 800 nm, 10^{13} W cm^{-2} fitted to eq (1).