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瞬态吸收和共振拉曼光谱研究硝基对联苯氮宾、氮宾离子反应活性的影响

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Investigation of the Influence of Nitro-Substitution on the Reaction of Biphenyl-Nitrene and Nitrenium Ion by Transient Absorption and Resonance Raman Spectroscopic Techniques

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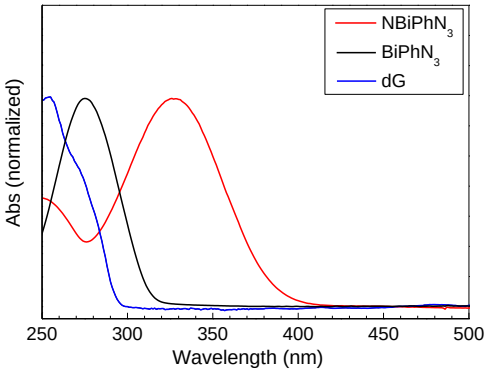


图 S1　$BiPhN_3$, 2'-脱氧鸟苷(dG), $NBiPhN_3$ 在乙腈中的紫外-可见吸收光谱

Fig.S1　UV-Vis absorption spectra of $BiPhN_3$, 2'-deoxyguanosine (dG) and $NBiPhN_3$ in acetonitrile

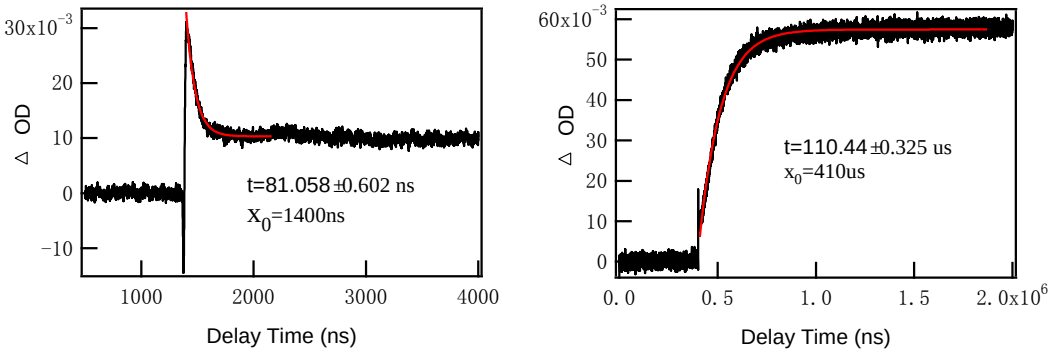
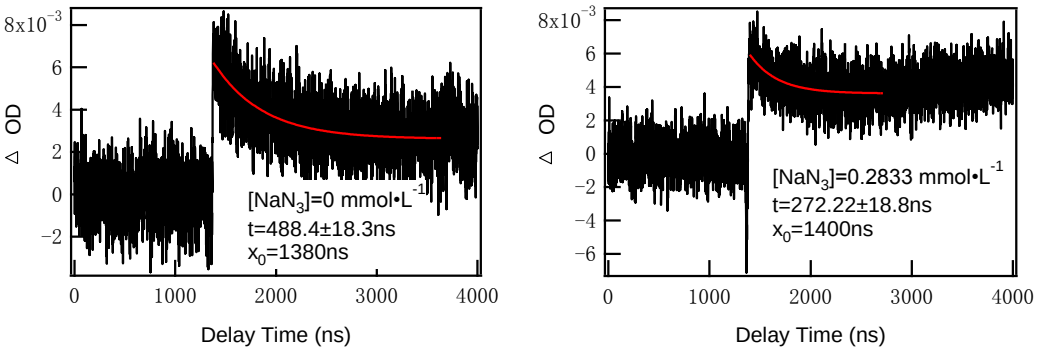


图 S2　乙腈溶液中光解 $BiPhN_3$ 获得的 350 nm 处的动力学

Fig.S2　Kinetics at 350 nm, by photolysis of $BiPhN_3$ in acetonitrile solvent



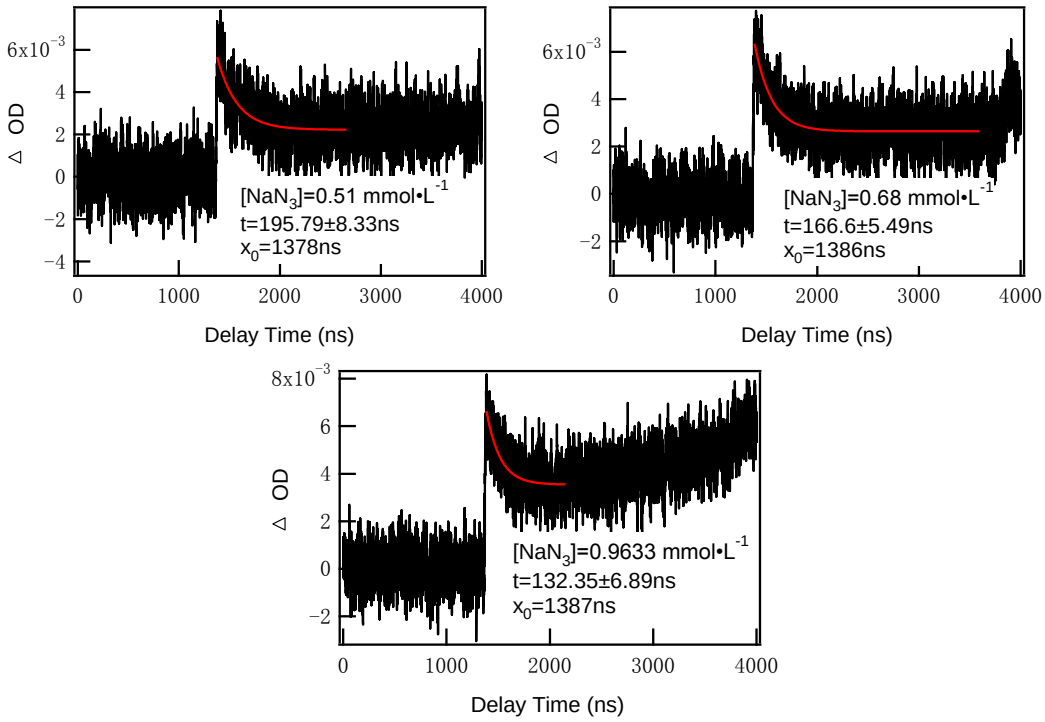
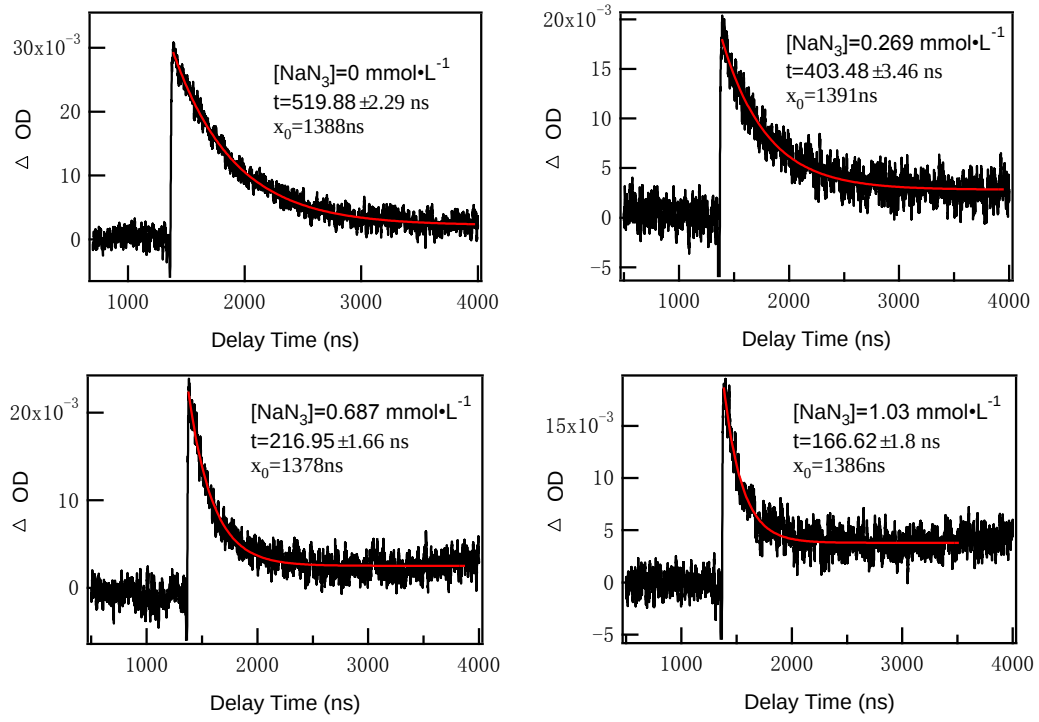


图 S3　光解 $NBiPhN_3$ 在乙腈:水 3:7 (*V*:*V*))溶液中含有不同浓度 NaN_3 的 440 nm 处的动力学

Fig.S3　Kinetics at 440 nm, by photolysis of $NBiPhN_3$ under different concentration of NaN_3, in acetonitrile: water(3:7 (*V* : *V*)) solvent



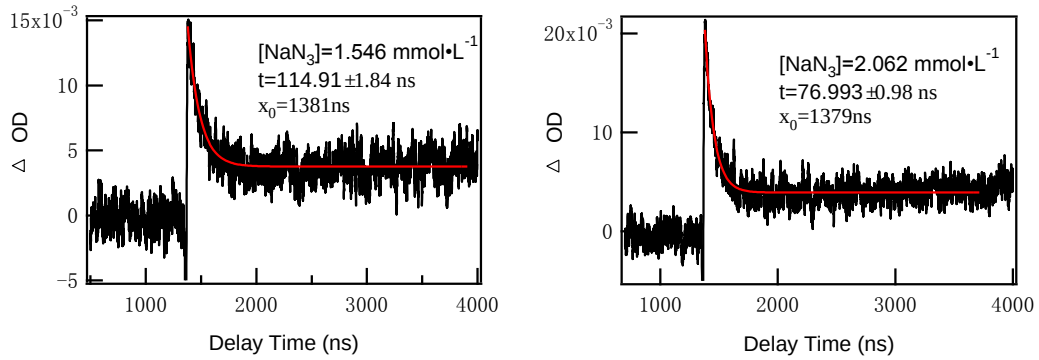


图 S4　光解 $NBiPhN_3$ 在乙腈:水(3:7 (*V*:*V*))溶液中含有不同浓度 NaN_3 的 520 nm 处的动力学

Fig.S4　Kinetics at 520 nm, by photolysis of $NBiPhN_3$ under different concentration of NaN_3, in acetonitrile:water (3:7 (*V*:*V*)) solvent

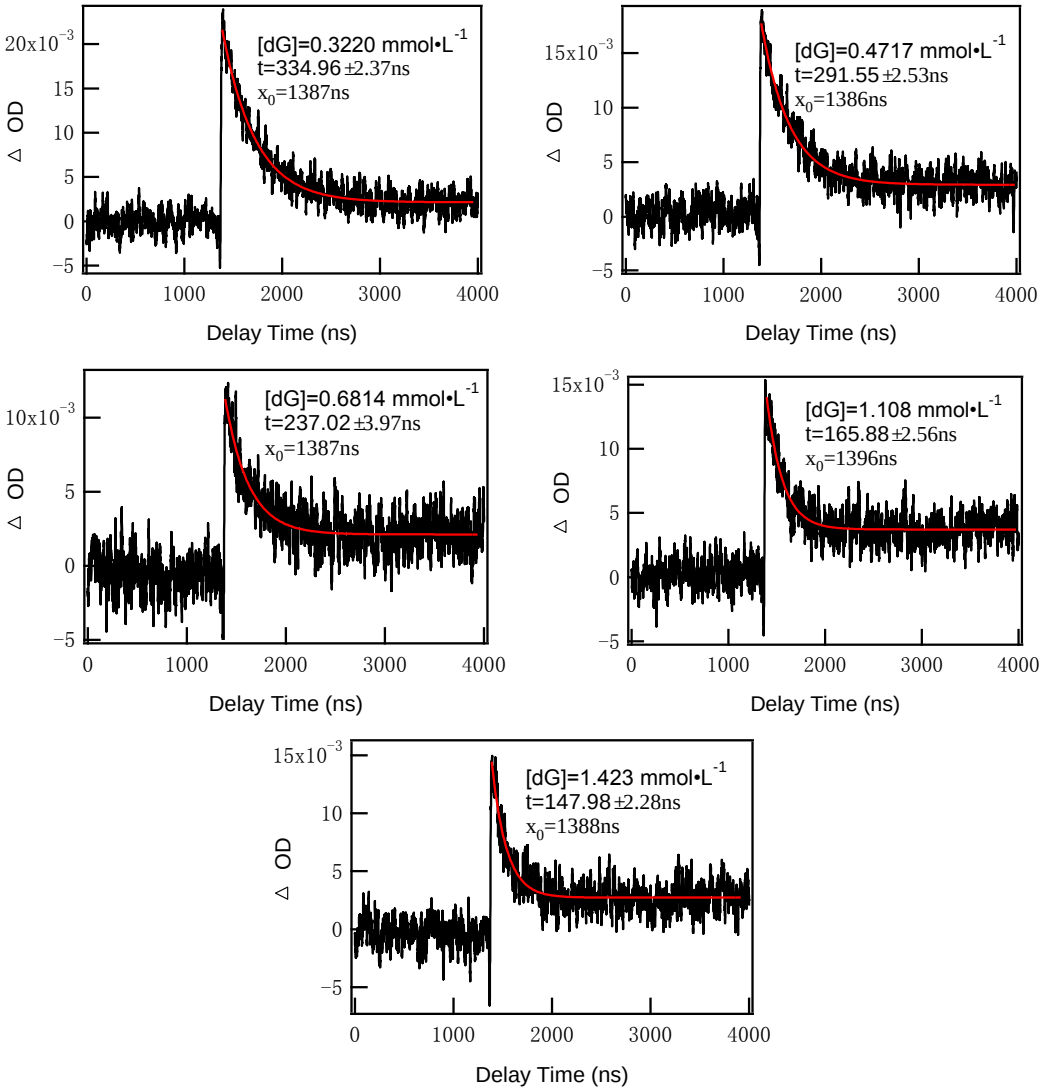
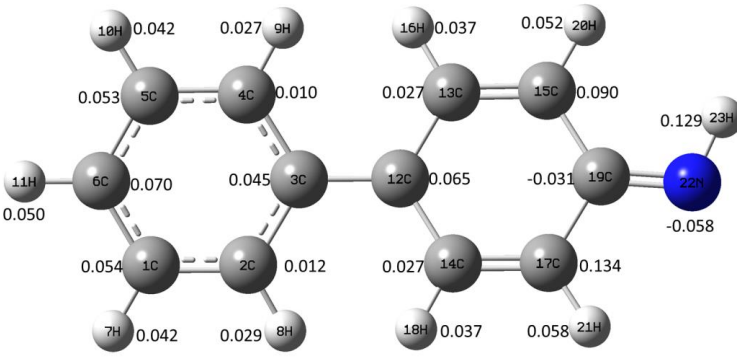


图 S5　光解 $NBiPhN_3$ 在乙腈:水(3:7 (*V*:*V*))溶液中含有不同浓度 2'-脱氧鸟苷(dG)

的 520 nm 处的动力学

Fig.S5　Kinetics at 520 nm, by photolysis of $NBiPhN_3$ under different concentration of 2'-deoxyguanosine (dG), in acetonitrile:water (3:7 (*V*:*V*)) solvent



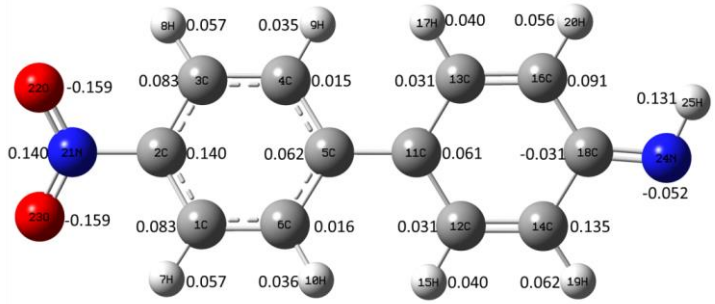


图 S6　自然键轨道(NBO)计算的两种氮宾离子的电荷分布

Fig.S6　Natural Bond Orbital (NBO) analysis of the charge distribution for the two nitrenium ions

表 S1　在 B3LYP/6-31G(*d*)水平下计算三重态氮宾 $NBiPh^3N$ 的振子强度、波长

Table S1　B3LYP/6-31G(*d*) calculated oscillator strength and wavelength for triplet nitrene $NBiPh^3N$

λ/nm	Oscillator strength
492.54	0.0270
431.83	0.0000
424.27	0.0068
392.81	0.4584
388.46	0.0212
371.51	0.0040
347.83	0.0008

331.52	0.0008
330.64	0.0004
327.63	0.0000
316.31	0.0052
311.53	0.0000
301.86	0.1427
299.00	0.0187
290.07	0.0893
288.81	0.0030
287.89	0.0020
287.74	0.0002

表 S2　详细的三重态氮宾 $NBiPh^3N$ 实验和计算振动频率指认

Table S2　Full comparision of Experimental Raman frequencies to the calculated ones for the triplet nitrene $NBiPh^3N$, and the vibration descriptions from computations

Mode	ν/cm^{-1}		Description
	Scaled[a] Calc.	Expt.	
ν_1	2992(352)		
ν_2	2991 (108)		
ν_3	2968(575)		
ν_4	2967(109)		
ν_5	2963(24)		
ν_6	2962(66)		
ν_7	2951(218)		
ν_8	2950(32)		
ν_9	1568(23)	1581	C-C str[b]. + N-O str.
ν_{10}	1567(5533)	1569	C-C str. + C-H bend
ν_{11}	1532(7251)	1550	C-C str. + C-H bend
ν_{12}	1514(7)		
ν_{13}	1473(272)	1454	C-H bend
ν_{14}	1460(0.9)		
ν_{15}	1427(83)	1418	C-H bend
ν_{16}	1396(93)	1400	C-C str. + C-H bend
ν_{17}	1390(8)		
ν_{18}	1331(7521)	1350	C-N-O str.
ν_{19}	1321(37)	1335	C-C str.
ν_0	1306(29)		

ν_{21}	1297(6)		
ν_{22}	1271(5420)	1272	C-C str. + C-N str + C-H bend
ν_{23}	1270(10)		
ν_{24}	1244(57)	1243	C-C str. + C-H bend
ν_{25}	1191(658)	1190	C-H bend
ν_{26}	1161(1241)	1143	C-H bend
ν_{27}	1125(2)		
ν_{28}	1119(4)		
ν_{29}	1113(2271)	1104	C-C str. + C-H bend
ν_{30}	1030(40)		
ν_{31}	1018(125)		
ν_{2}	992(8)		
ν_{33}	986(2)		
ν_{34}	985(12)		
ν_{35}	977(0.7)		
ν_{36}	975 (10)		
ν_{37}	891(0.7)		
ν_{38}	877(215)		N-O str. + ring deformation
ν_{39}	861(42)		
ν_{40}	852(306)		C-H bend (out)
ν_{41}	852(3)		
ν_{42}	834(134)		C-H bend (out)
ν_{43}	791(10)		
ν_{44}	769(8)		
ν_{45}	755(1)		
ν_{46}	734(0.8)		
ν_{47}	683(9)		
ν_{48}	667(24)		
ν_{49}	651(1)		
ν_{50}	597(6)		
ν_{51}	5591(5)		
ν_{52}	553(2)		
ν_{53}	511(6)		
ν_{54}	491(0.3)		
ν_{55}	483(166)	494	Ring torsion
ν_{56}	466 (94)	467	Ring torsion
ν_{57}	440(7)		
ν_{58}	409(9)		
ν_{59}	338(0.4)		

ν_{60}	322(11)
ν_{61}	300(2)
ν_{62}	236(0.4)
ν_{63}	184(6)
ν_{64}	180(79)
ν_{65}	156(19)
ν_{66}	154(4)

[a]Scaled=0.8838×calculated frequencies+112.787; [b]str.=stretching

表 S3　在 BPW91/cc-PVDZ 水平下计算单线态氮宾离子 $NBiPhNH^+$的振子强度、波长

Table S3　BPW91/cc-PVDZ calculated oscillator strength and wavelength for the singlet nitrenium ion (open-shell) $NBiPhNH^+$

λ/nm	Oscillator strength
1024.59	0.0699
943.09	0.0002
716.11	0.0000
673.33	0.0005
631.59	0.0018
472.35	0.0240
439.60	0.5259
377.76	0.0051
350.49	0.0380
337.83	0.0002
312.74	0.0019
309.57	0.0014
306.77	0.1520
295.93	0.0045
286.75	0.0113
285.67	0.0078
283.67	0.0147
280.32	0.0009