Supporting Information

Excited state proton transfer in the triplet state of 8-hydroxy-5-nitroquinoline : A transient absorption and time-resolved resonance Raman spectroscopic study

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Content

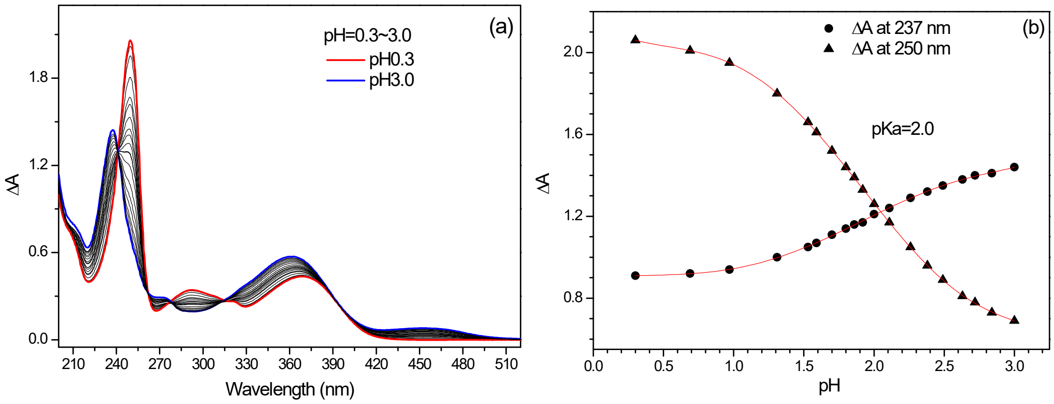


Fig.1S (a) UV-Vis spectra of 8-hydroxy-5-nitroquinoline in acetonitrile:water=1:1(v/v) in the presence of various concentrations of perchloric acid. (b) Measurements of pK_a for HO-QN-NO_2 in acetonitrile:water=1:1(v/v) solution.

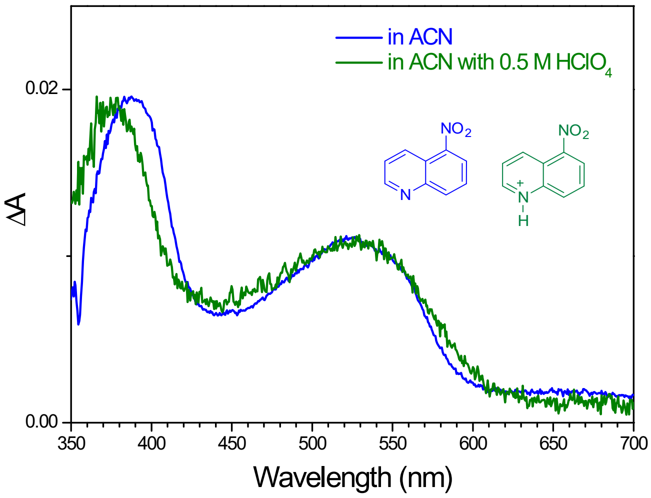


Fig.2S TA spectra recorded at 0 ns after 355 nm laser excitation of 5-nitroquinoline in acetonitrile under argon saturated conditions with 0.5 M $HClO_4$ and without acid present.

These spectra are assigned to the neutral and protonated triplets, respectively.

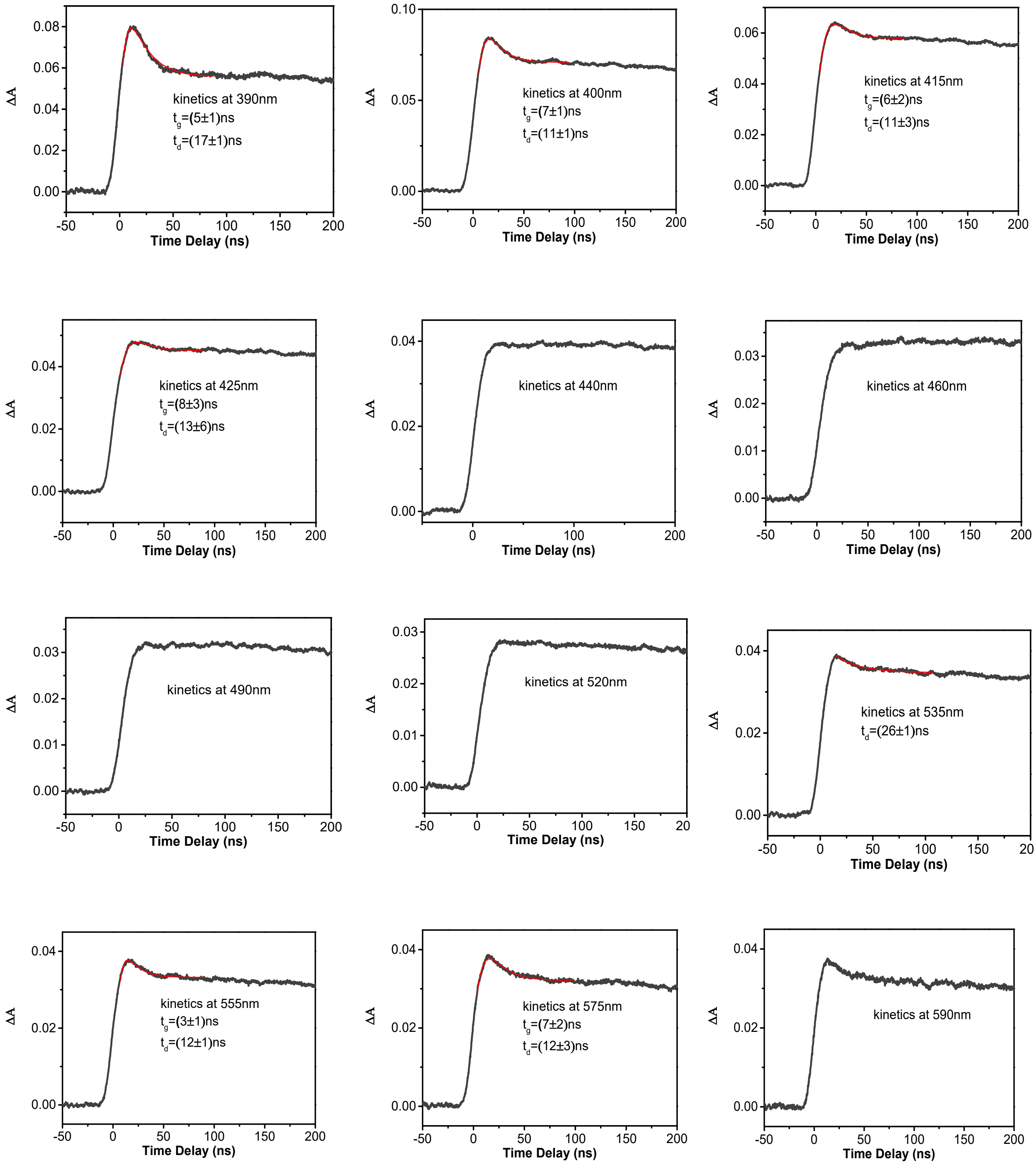


Fig.3S Plot of kinetics data at wavelengths 390–590 nm. The data were collected immediately after 355 nm laser excitation of 8-hydroxyquinoline in argon saturated acetonitrile.

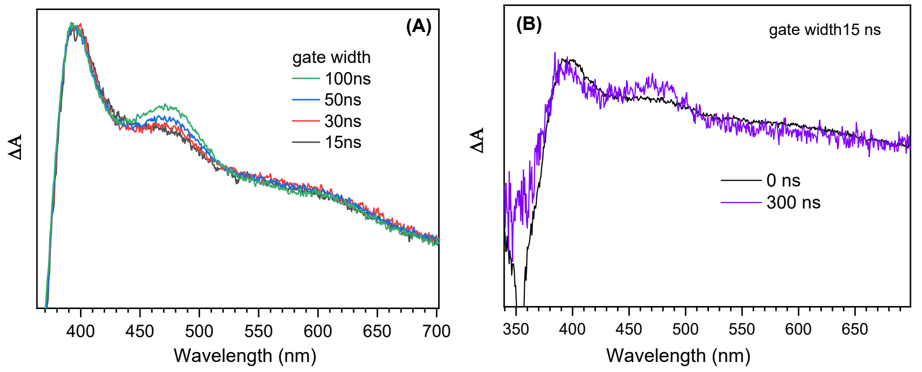


Fig.4S Normalized nanosecond TA spectra recorded in acetonitrile under air condition (A) immediately (0 ns) after the laser excitation with different gate width setups, and (B) with gate width of 15 ns.

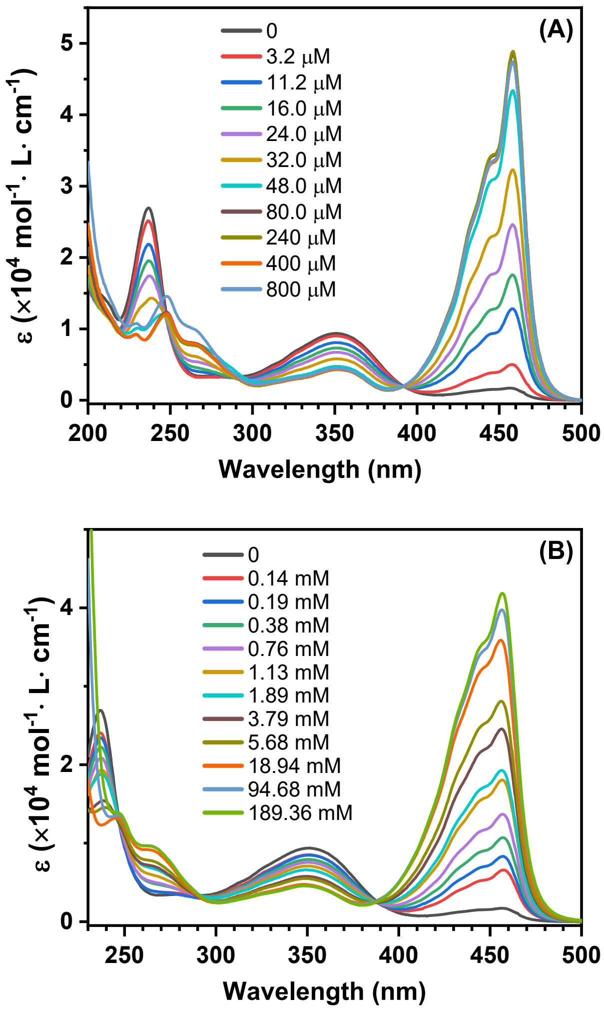
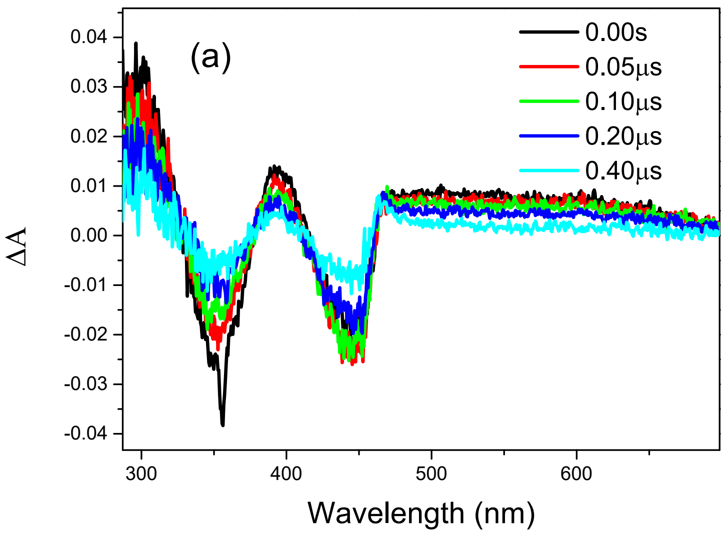


Fig.5S UV-Vis absorption spectra of 8-hydroxy-5-nitroquinoline in acetonitrile in the presence of various concentrations of (A) tetra-butylammonium hydroxide and (B) *t*-butylamine.



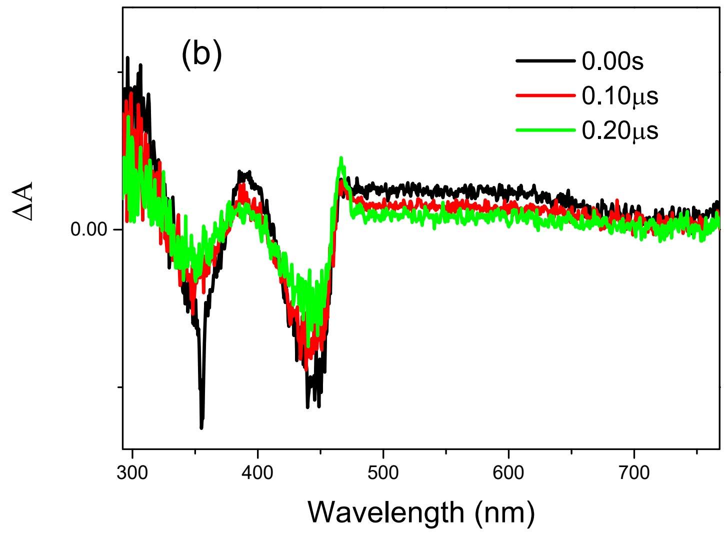


Fig.6S Nanosecond TA spectra after excitation of 8-hydroxy-5-nitroquinoline under argon condition in acetonitrile solution containing (a) 3.79 mM TBA and (b) 5.68 mM TBA.

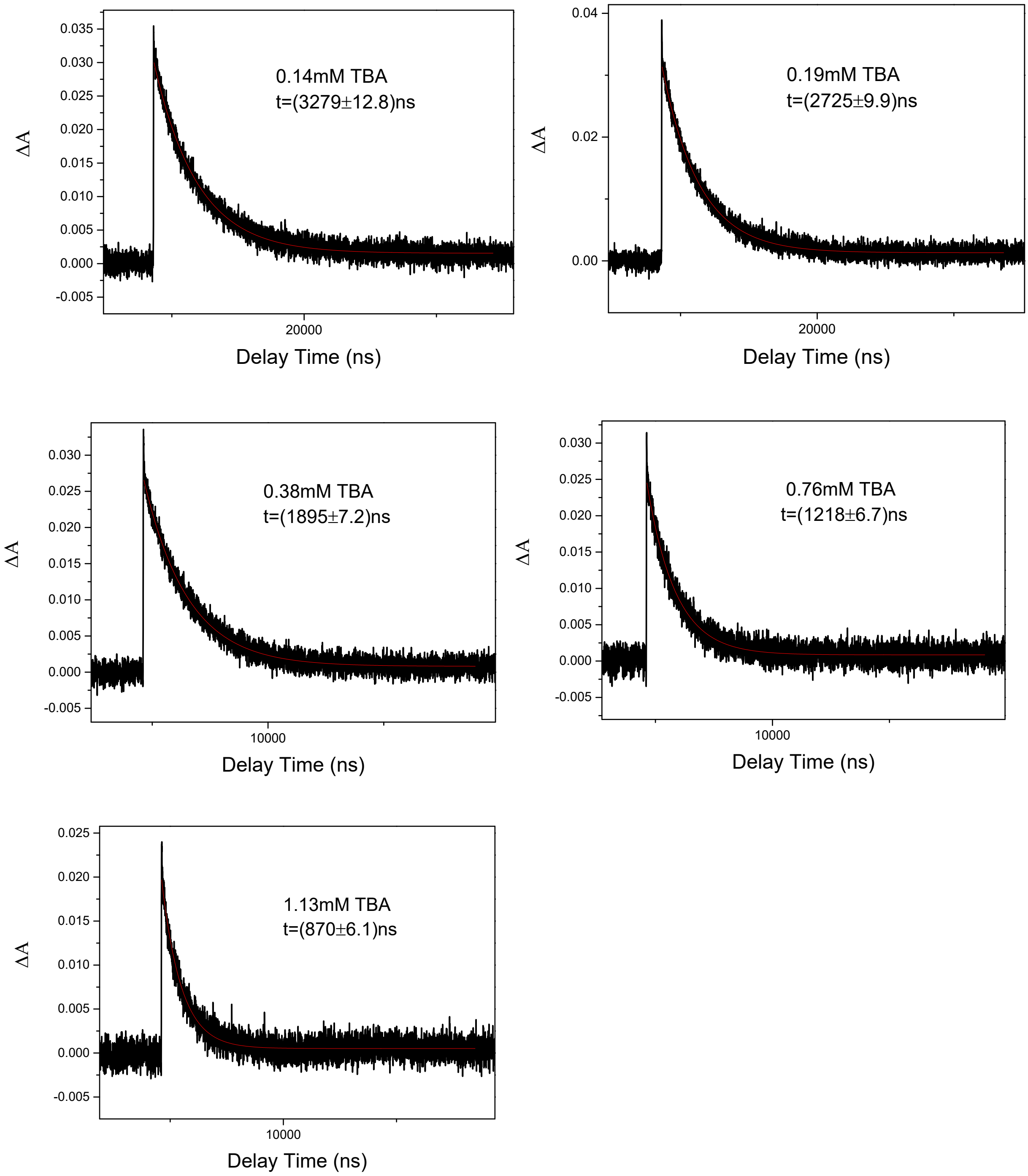


Fig.7S Fitting mono-exponential functions to the kinetics of 8-hydroxy-5-nitroquinoline under argon condition at 400 nm obtained in acetonitrile containing various concentrations of TBA.

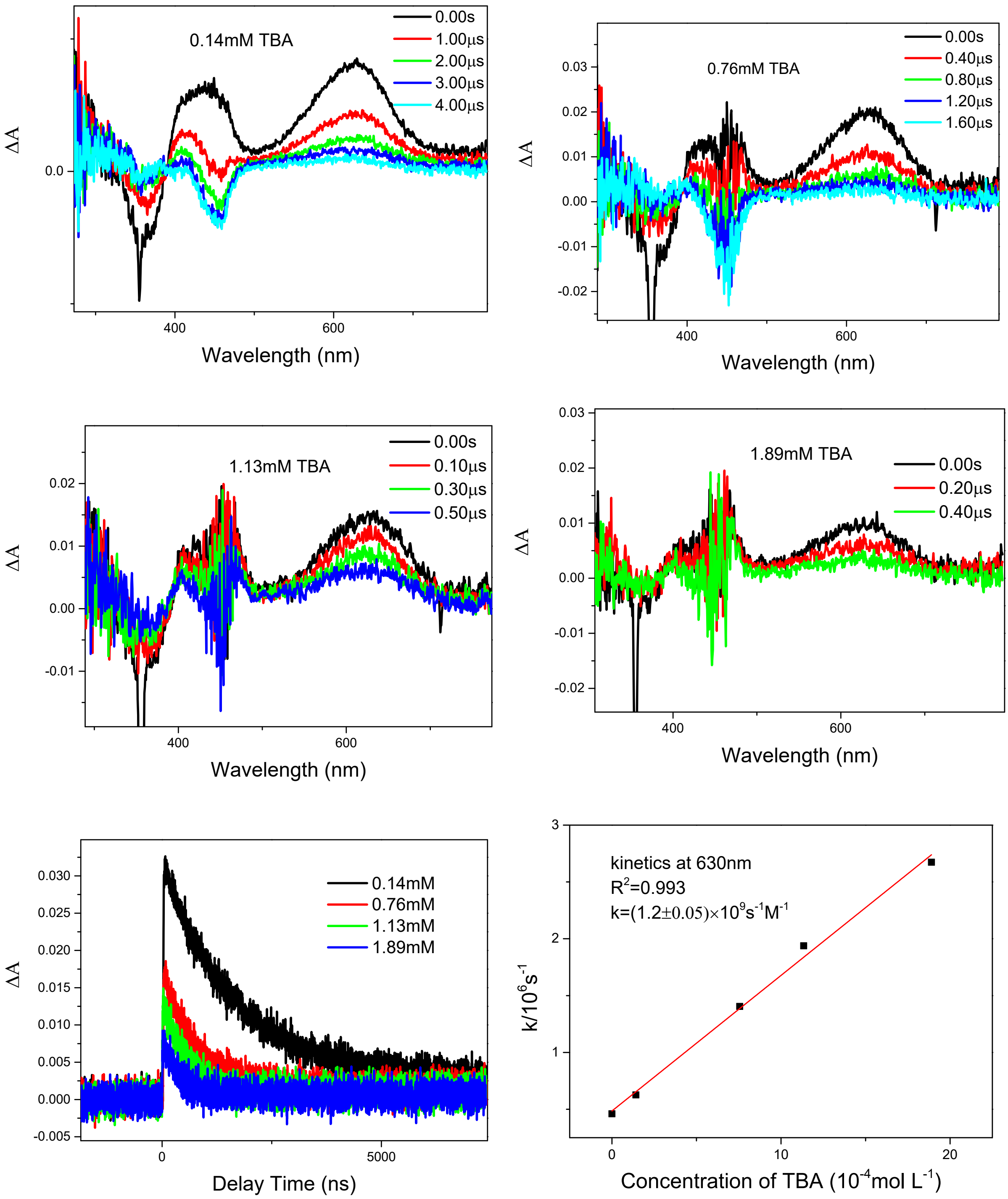


Fig.8S Nanosecond TA spectra and kinetic data at 630 nm obtained after excitation of 4-nitro-1-naphthol under argon condition in acetonitrile solution containing various concentrations of TBA.

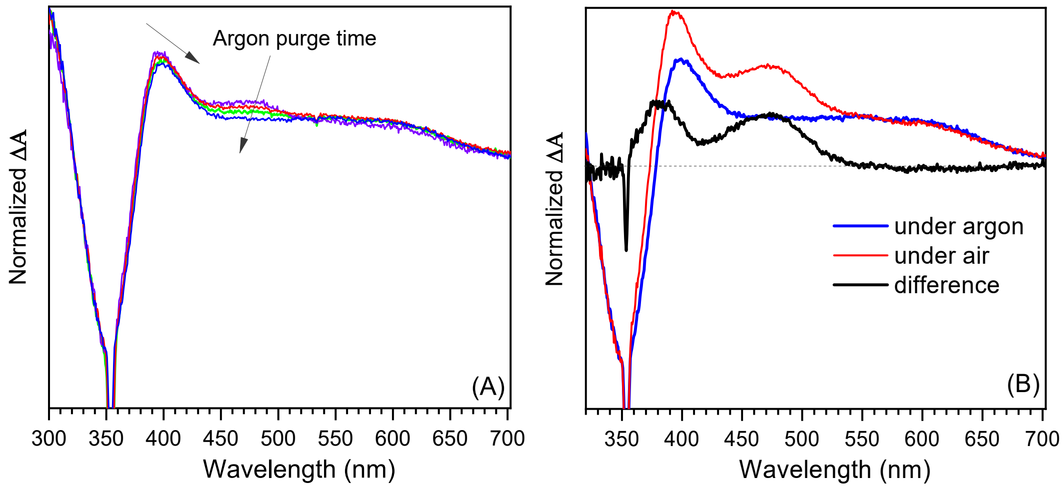


Fig.9S (A) Nanosecond TA spectra recorded at 0 ns in acetonitrile with varying argon purged time and (B) Nanosecond TA spectra recorded at 0 ns in acetonitrile under argon and air conditions. The spectra were normalized using the ground state bleaching. The difference spectrum is obtained by subtracting spectrum under argon from the one under air by removing the ground state bleaching.

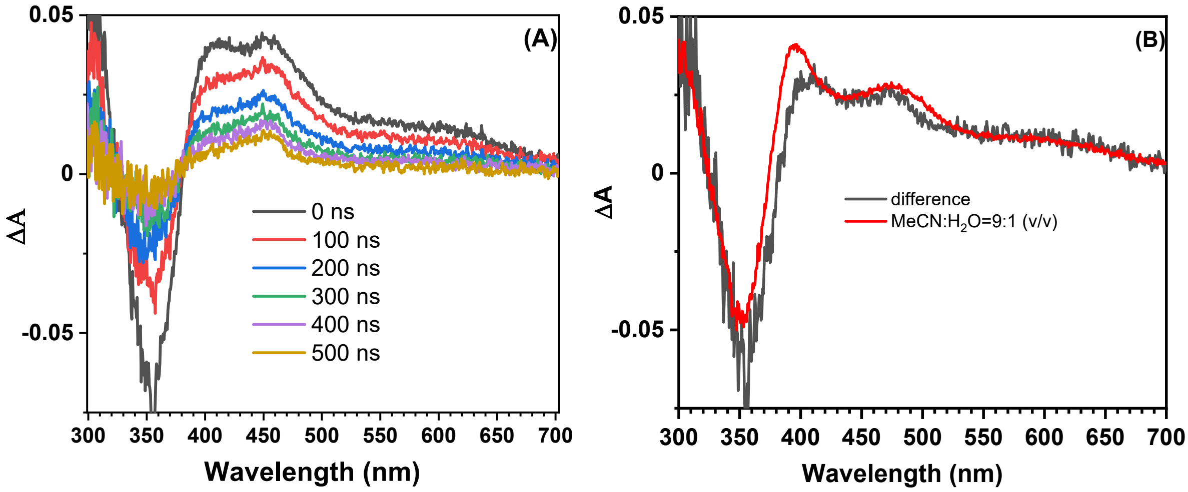


Fig.10S (A) Nanosecond TA spectra recorded after excitation of 8-hydroxy-5-nitroquinoline under air condition in MeCN:H_2O=9:1 (v/v). (B) A comparison of the TA spectrum recorded at 0 ns under air condition in MeCN:H_2O=9:1 (v/v) to the difference spectrum by subtracting the scaled 500 ns spectrum from the 0 ns spectrum in graph A.

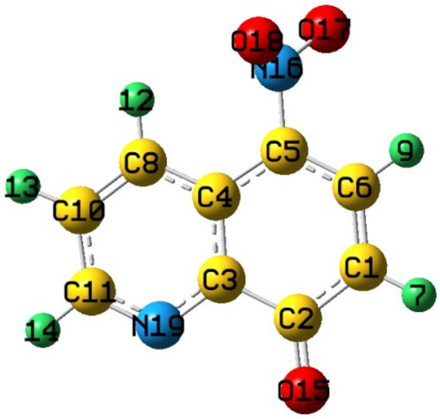
The two spectra in graph B appear to agree in the region of 430-500 nm, indicating that T_1 state NO_2-QN-O^- is generated in MeCN:H_2O=9:1 (v/v) mixed solution.

Table 1S Tentative vibrational assignments for T_1 state of NO_2-QN-O^- in ACN.

Mode	Calculation			Experimental frequency (cm-1)		Assignment (PED%)
	Frequency (cm-1)		Raman activity	435 nm probe	266 nm probe	
	Original	Calibrated				
υ_{46}	1618	1645	344	1627	1630	$\nu C_{10}C_8(23)+\nu N_{19}C_{11}(11)+\nu N_{19}C_3(15)+\nu C_4C_8(15)$
υ_{45}	1580	1604	357		1608	$\nu C_{11}C_{10}(26)+\nu C_4C_8(13)+\delta C_3N_{19}C_{11}(12)$
υ_{44}	1558	1581	3487	1592	1592	$\nu O_{15}C_2(68)$
υ_{43}	1532	1553	371	1555		$\nu C_1C_6(37)+\nu C_5C_4(10)$
υ_{42}	1492	1511	565	1505	1497	$\nu N_{19}C_3(12)+\nu C_6C_5(13)+\nu C_4C_8(10)+\delta H_{14}C_{11}N_{19}(16)$
υ_{41}	1454	1471	101	1477	1464	$\nu C_6C_5(12)+\delta H_9C_6C_1(11)+\delta H_7C_1C_6(19)+\delta H_{13}C_{10}C_{11}(14)$
υ_{40}	1416	1430	115		1431	$\delta H_9C_6C_1(11)+\delta H_{12}C_8$C10(18)+δH14C11N19(17)+ $\delta N_{19}C_{11}C_{10}(10)$
υ_{39}	1372	1384	199	1386	1387	$\nu C_5C_4(22)$
υ_{38}	1328	1337	725		1329	$\nu N_{19}C_{11}(39)$
υ_{37}	1304	1312	420			$\nu N_{19}C_3(10)+\nu O_{17}N_{16}(15)+\nu N_{16}C_5(25)$
υ_{36}	1292	1299	368	1290	1294	$\nu N_{19}C_3(33)+\delta H_{14}C_{11}N_{19}(10)$
υ_{35}	1230	1233	223		1230	$\nu C_2C_1(20)$
υ_{34}	1190	1191	234			$\nu C_6C_5(18)+\delta H_9C_6C_1(22)$
υ_{33}	1167	1167	1403	1153		$\nu O_{17}N_{16}(38)+\nu O_{18}N_{16}(28)+$δH7C1C6(13)
υ_{32}	1152	1151	155		1149	$\nu C_{10}C_8(16)+\delta H_{12}C_8C_{10}(21)+\delta H_{13}C_{10}C_{11}(22)$
υ_{31}	1138	1136	267		1138	$\nu O_{18}N_{16}(34)+\delta C_3N_{19}C_{11}(10)+\delta H_7C_1C_6(14)$
υ_{30}	1102	1098	25			$\nu C_1C_6(11)+\nu C_2C_1(12)+\delta C_3N_{19}C_{11}(14)+\delta H_9C_6C_1(14)$
υ_{29}	1065	1058	164		1055	$\nu C_{11}C_{10}(38)$
υ_{28}	1010	1000.6	0.3			$\rho tH_{12}C_8C_{10}C_{11}(25)+\rho tH_{13}C_{10}C_{11}N_{19}(45)+\rho tH_{14}C_{11}N_{19}C_3(16)+\rho tN_{19}C_{11}C_{10}C_8(10)$
υ_{27}	990	979	161	980		$\nu O_{17}N_{16}(10)+\nu N_{16}C_5(12)+\delta C_4C_8C_{10}(10)$

a: B3LYP/6-311+G(d,p) calculated frequency; b: Calibration equation: y=1.06x-70;

ν:stretch; δ: in-plane bending; ρt:torsion; PED: potential energy distribution; only contributions larger than 10% were give.

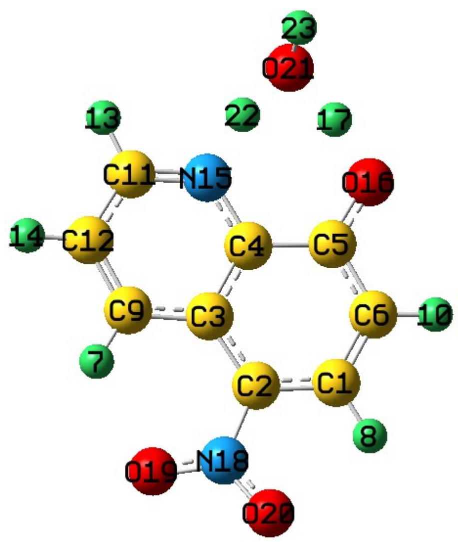


Ttransition state of transformation of NO_2-QN-OH to NO_2-QNH-O with the help of water in acetonitrile

SCF Done: E(RB3LYP) = -758.317300648

The imaginary frequency: -1349.06 cm^{-1}

C	-1.28717200	-1.79036400	0.01081500
C	-1.55521800	-0.42399800	0.00262000
C	-0.47751900	0.52164300	0.00137100
C	0.85645500	0.00523500	-0.01308100
C	1.12273900	-1.43285300	-0.03227000
C	0.00398000	-2.28208600	-0.01099900
H	-1.59739600	2.36904500	0.08568300
H	-2.12168500	-2.47736100	0.01639100
C	-0.61163800	1.93560200	0.05836100
H	0.18124900	-3.34989200	-0.02393000
C	1.76777000	2.17014500	0.03301900
C	0.49586100	2.75004400	0.07240200
H	2.67264900	2.76624400	0.03617800
H	0.39475600	3.82617900	0.11517200
N	1.92221000	0.85808900	-0.00256700
O	2.31153500	-1.94378400	-0.06758400
H	3.29994000	-1.21023200	-0.05021000
N	-2.94338100	-0.04146900	-0.01269100
O	-3.25740700	1.12267200	-0.29848000
O	-3.79582300	-0.90139800	0.24697800
O	4.08010800	-0.33184800	-0.07321700
H	3.11864600	0.37910000	-0.00596200
H	4.60118500	-0.30477100	0.73847400



Ttransition state of transformation of NO_2-QN-OH to NO_2-QNH-O in acetontirile.

SCF Done: E(UB3LYP) = -681.762045465
The imaginary frequency: -1604.11 cm^{-1}

C	0.10222900	-2.39336000	0.00000000
C	-1.14990700	-1.71718900	0.00000000
C	-1.14689200	-0.27877200	0.00000000
C	0.00000000	0.53833800	0.00000000
C	1.24703000	-0.20715000	0.00000000
C	1.25633600	-1.64951300	0.00000000
H	0.13943900	-3.47541100	0.00000000
C	-0.25244400	1.92115600	0.00000000
H	2.22125200	-2.13121100	0.00000000
C	-1.58152200	2.38212000	0.00000000
C	-2.64336800	1.49041200	0.00000000
H	0.56689100	2.62070500	0.00000000
H	-1.78235200	3.44489300	0.00000000
H	-3.67639400	1.81345000	0.00000000
N	-2.40876300	0.16645000	0.00000000
O	-2.35654000	-2.19631900	0.00000000
H	-2.89501100	-1.05598800	0.00000000
N	2.50011400	0.44694300	0.00000000
O	3.54310700	-0.26491400	0.00000000
O	2.53817700	1.70792700	0.00000000