Supporting Information

for

Femtosecond and Nanosecond LIBS Studies of Nitroimidazoles: Correlation between Molecular Structure and LIBS data

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Compound	Number of nitro groups	Number of C-C bonds	Number of C=C bonds	Number of C-N bonds	Number of C=N bonds	O/C stoichiometric ratio	O/H stoichiometric ratio	N/H stoichiometric ratio
Imidazole ($C_3H_4N_2$)	**0**	**0**	**1**	**3**	**1**	**0**	**0**	**0.5**
4-NIm ($C_3H_3N_3O_2$)	**1**	**0**	**1**	**4**	**1**	**0.67**	**0.67**	**1**
1,4-DNIm ($C_3H_2N_4O_4$)	**2**	**0**	**1**	**4**	**1**	**1.33**	**2**	**2**
2,4-DNIm ($C_3H_2N_4O_4$)	**2**	**0**	**1**	**5**	**1**	**1.33**	**2**	**2**
1M-4NIm ($C_4H_5N_3O_2$)	**1**	**0**	**1**	**5**	**1**	**0.5**	**0.4**	**0.6**
2M-4(5)-NIm ($C_4H_5N_3O_2$)	**1**	**0**	**1**	**4**	**1**	**0.5**	**0.4**	**0.6**
1M-2,4-DNIm ($C_4H_4N_4O4$)	**2**	**0**	**1**	**5**	**1**	**1**	**1**	**1**

Table 1 Molecular formula, number of nitro groups, number of C-C, C=C, C-N and C=N bonds and also the stoichiometric ratios of O/C, O/H and N/H of each molecule of nitroimidazoles.

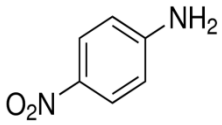
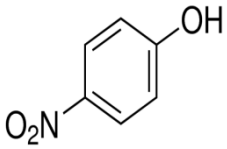
Compound	**Structure**	**C_2 Intensity (a.u.)**	**CN Intensity (a.u.)**	**CN/C_2**
4-Nitroaniline		1505	4928	3.3
4-Nitrophenol		886	3334	3.8

Table 2 The molecular bands CN, C_2 intensities and its CN/C_2 ratio of 4-Nitroaniline and 4-Nitrophenol with fs excitation in air atmosphere.

. Sample	Peak	Air (ns)	Argon (ns)
		ns LIBS	ns LIBS
4-NIm	**CN**	**3682±300**	**2806±80**
	C_2	**509±21**	**579±44**
	C	**779±26**	**787±21**
2,4-DNIm	**CN**	**673±126**	**1339±305**
	C_2	**538±36**	**789±138**
	C	**908±46**	**1044±125**

Table 3 Decay rates of CN, C_2 and C of 4-NIm and 2,4-DNIm in air and argon atmospheres with ns excitation. CN represents the strongest peak at 388.32 nm, whereas C_2 represents the strongest peak at 516.52 nm and C at 247.86 nm.

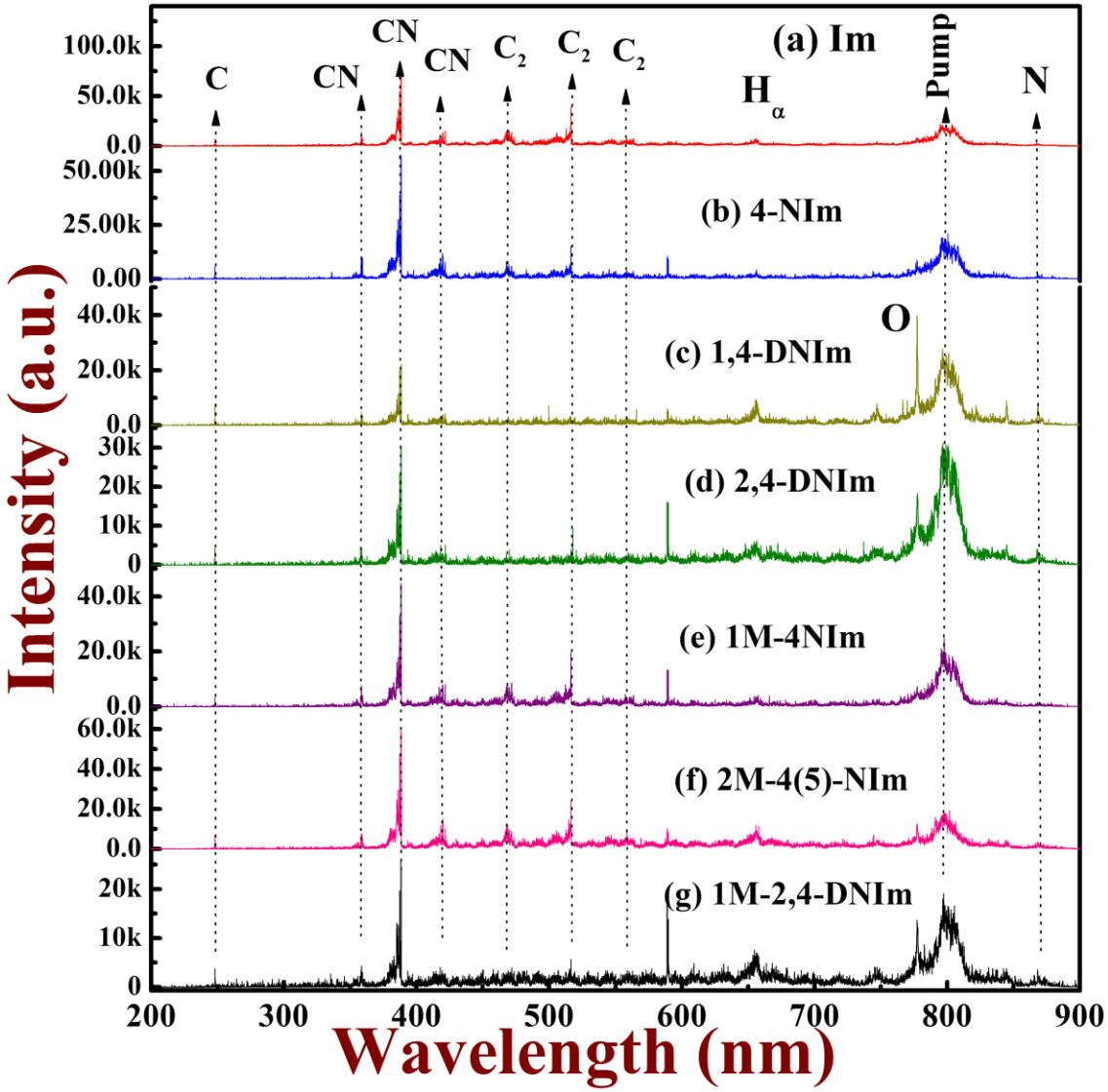


Figure 1 fs LIB spectra of all the seven molecules (a) Im (b) 4-NIm (c) 1,4-DNIm (d) 2,4-DNIm (e) 1M-4NIm (f) 2M-4(5)-NIm and (g) 1M-2,4-DNIm at gate delay 100 ns and gate width 800 ns at 1 mJ energy in air atmosphere.

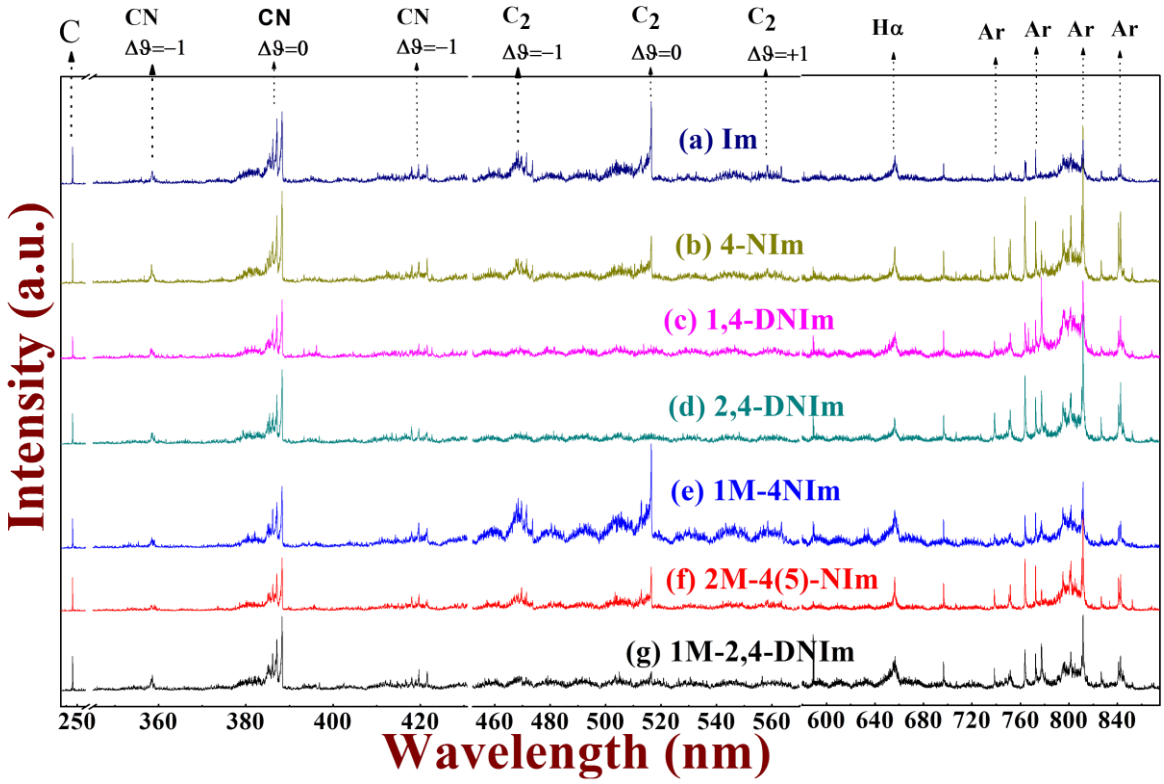


Figure 2 fs-LIB spectra of seven molecules (a) Im (b) 4-NIm (c) 1,4- DNIm (d) 2,4-DNIm (e) 1M-4NIm (f) 2M-4(5)-NIm and (g) 1M-2,4-DNIm recorded at gate delay 100 ns gate width 800 ns at 1 mJ energy in argon atmosphere (some spectra are offset for clarity).

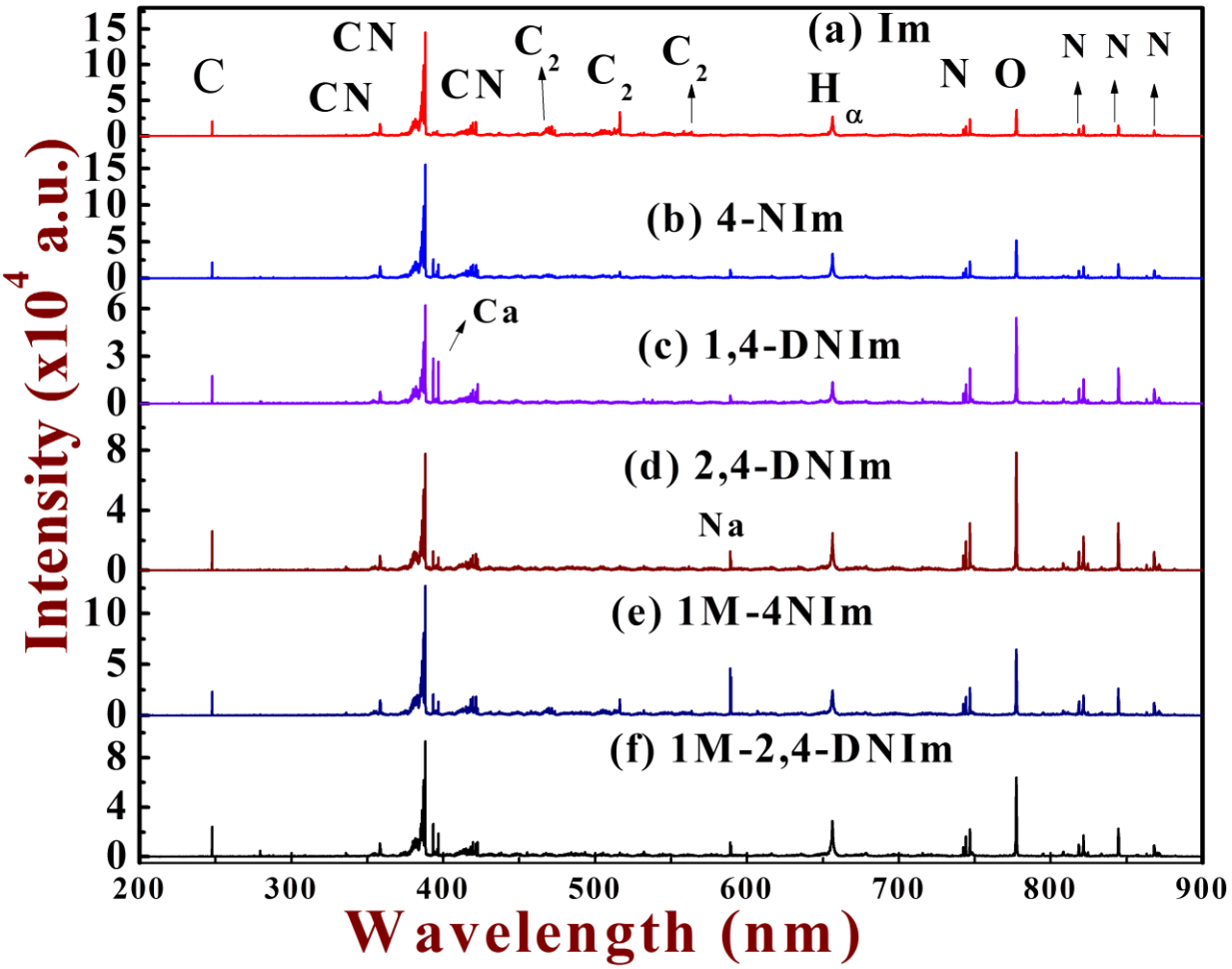


Figure 3 ns LIB spectra of six molecules of (a) Im (b) 4-NIm (c) 1,4-DNIm (d) 2,4-DNIm (e) 1M-4NIm and (f) 1M-2,4-DNIm at gate delay 1100 ns and gate width 10 us used typical energy ~25 mJ in air atmosphere.

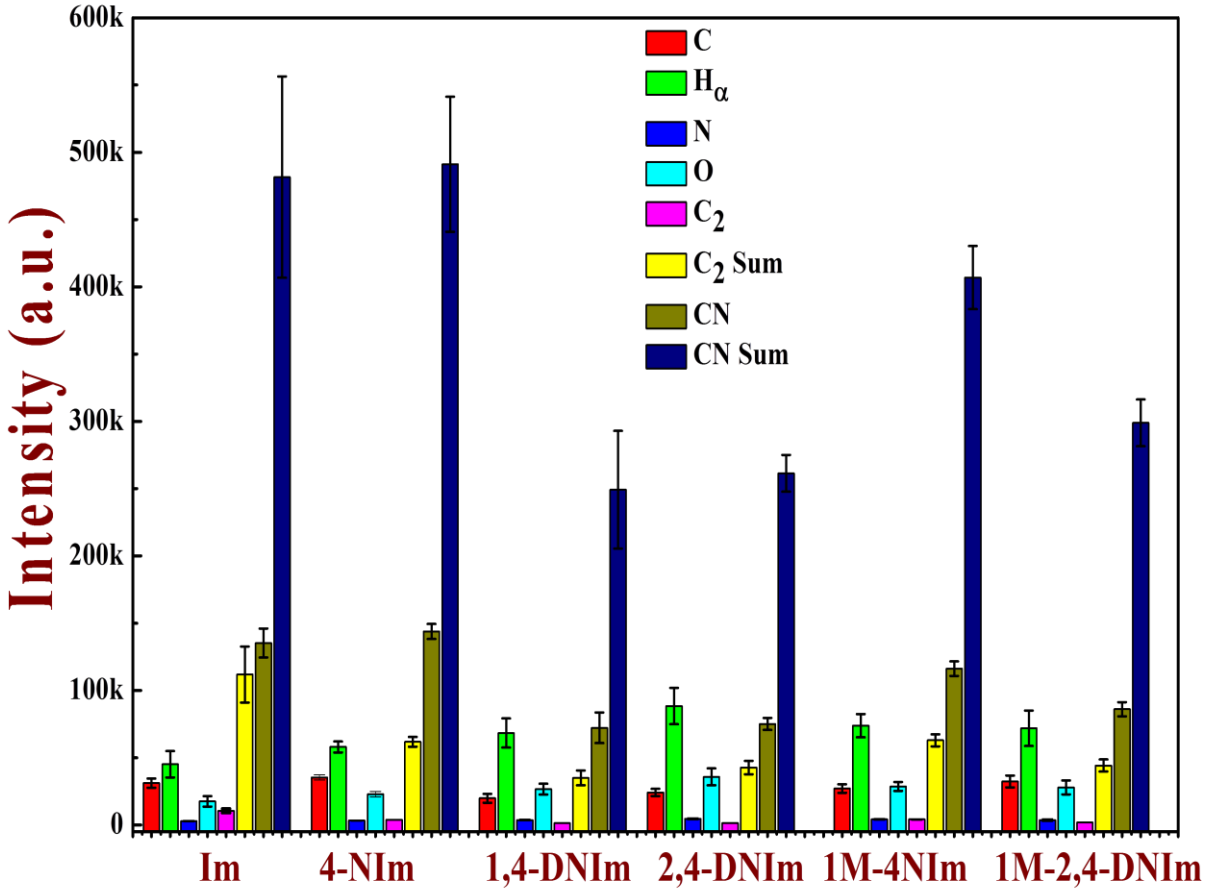


Figure 4 Bar plot of molecular (CN, CN^{Sum}, C_2 and C_2^{Sum}) and atomic emissions (C, H_α, O and N) intensities of six nitroimidazoles in ns LIP recorded in air. Each bar chart corresponds to an average intensity of 30 spectral events and the error bar represents standard deviation.

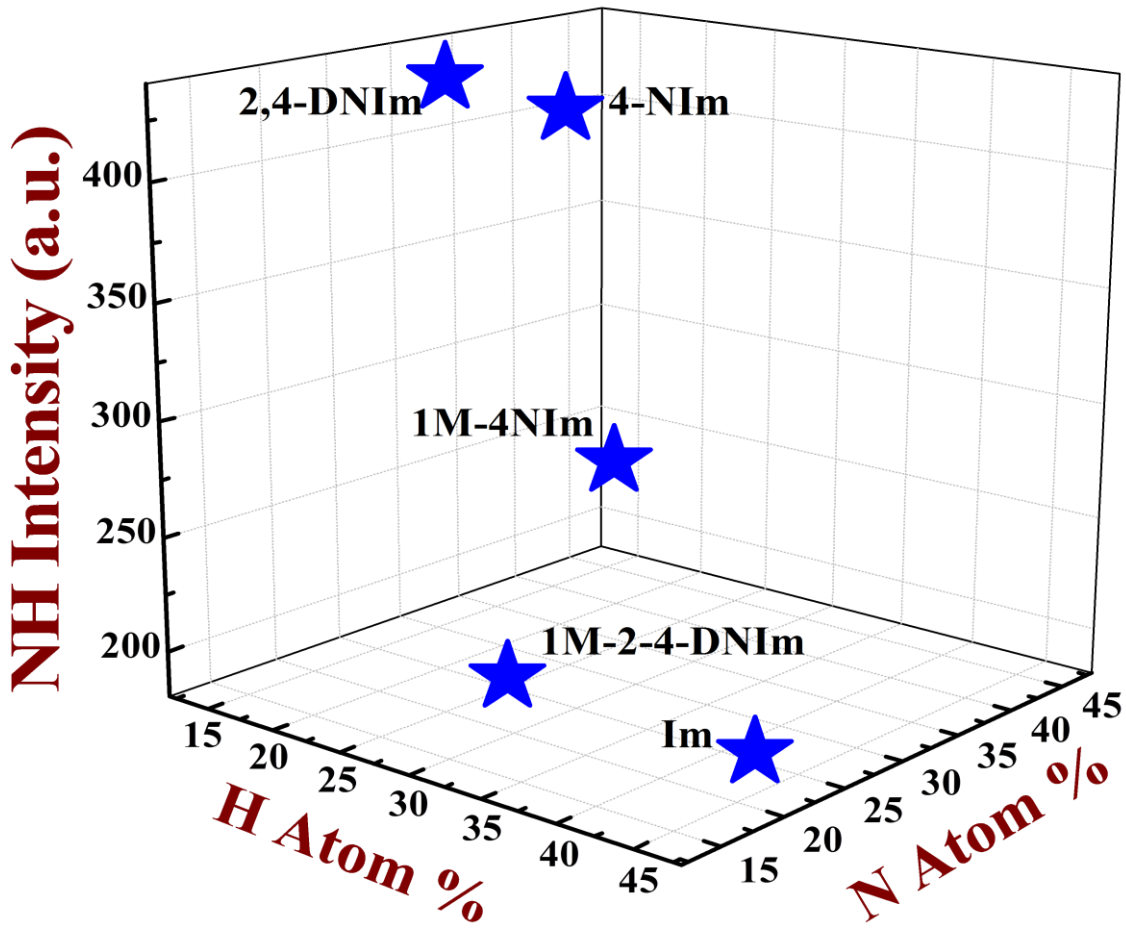


Figure 5 3D plot showing absence of any correlation between NH molecular emission intensity versus the H atom % and N atom %. A gate delay at 67 ns and a gate width of 800 ns in air and ~1 mJ energy with fs excitation were used for recording the spectra in air.

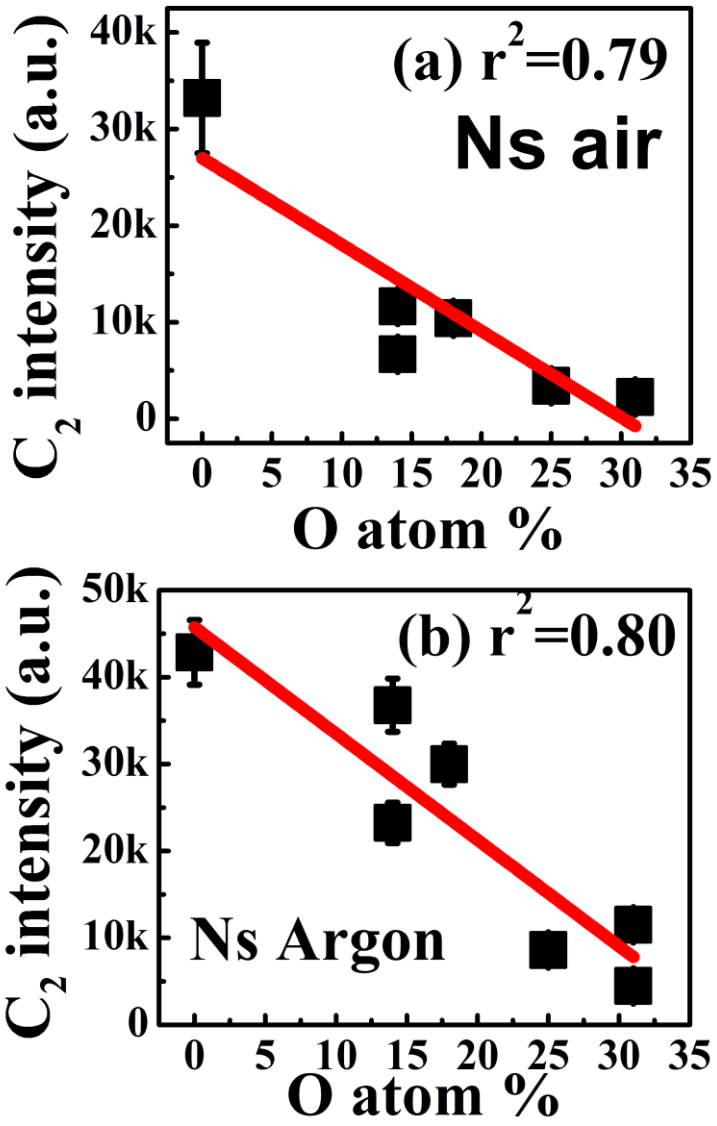


Figure 6 The correlation between the C_2 intensities versus O atom % with ns excitations in **(a)** air and **(b)** argon atmospheres.

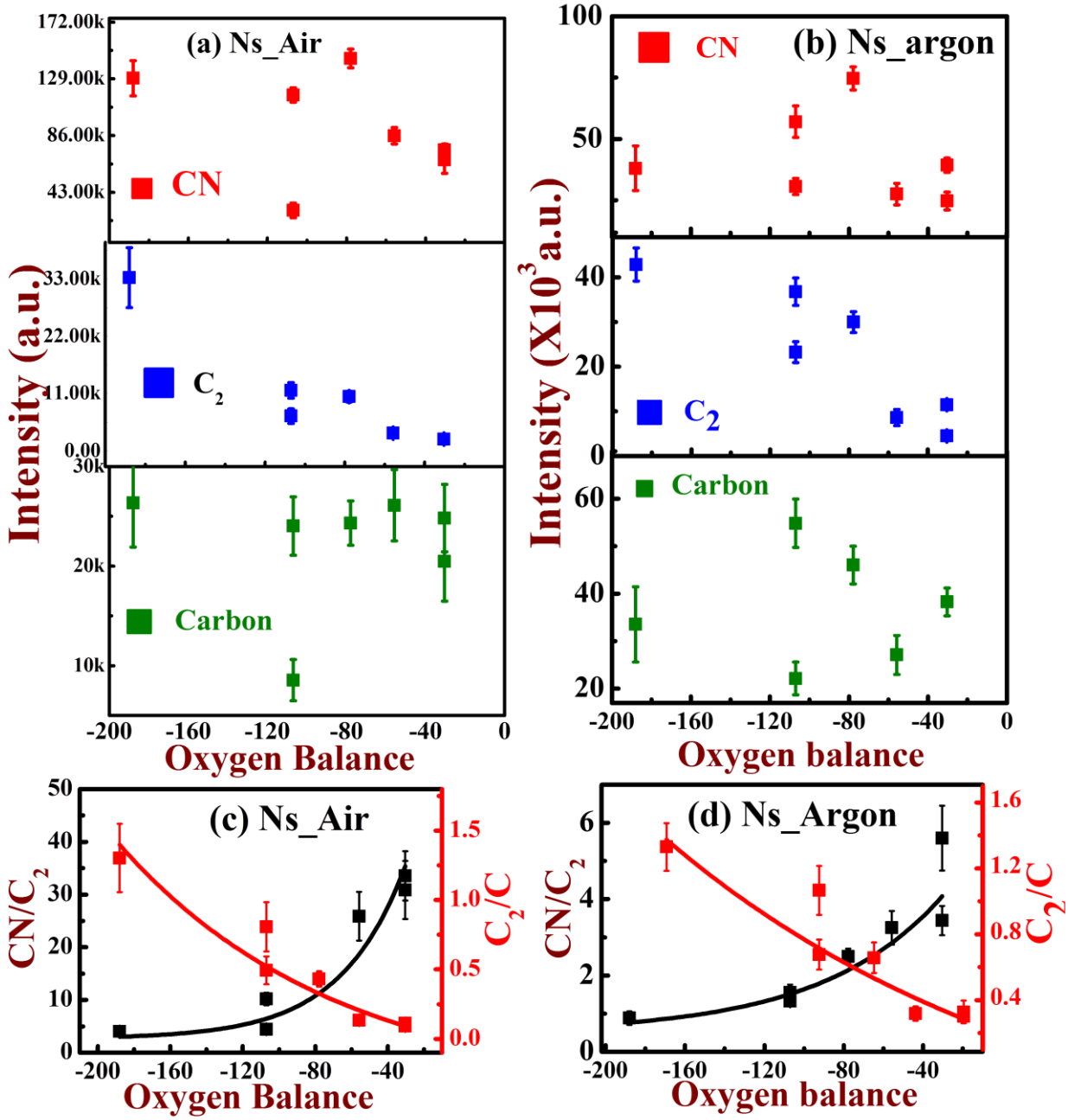


Figure 7 LIB signal intensity of molecular bands CN (388.32 nm), C_2 (516.52 nm) and C (247.86 nm) of **(a)** ns excitation in air **(b)** argon correlating with OB. Molecular emission intensity to atomic emission line intensity ratios of CN/C_2 versus C_2/C to with ns excitation in **(c)** air **(d)** argon atmospheres of seven molecules of nitroimidazoles correlating with their OB.

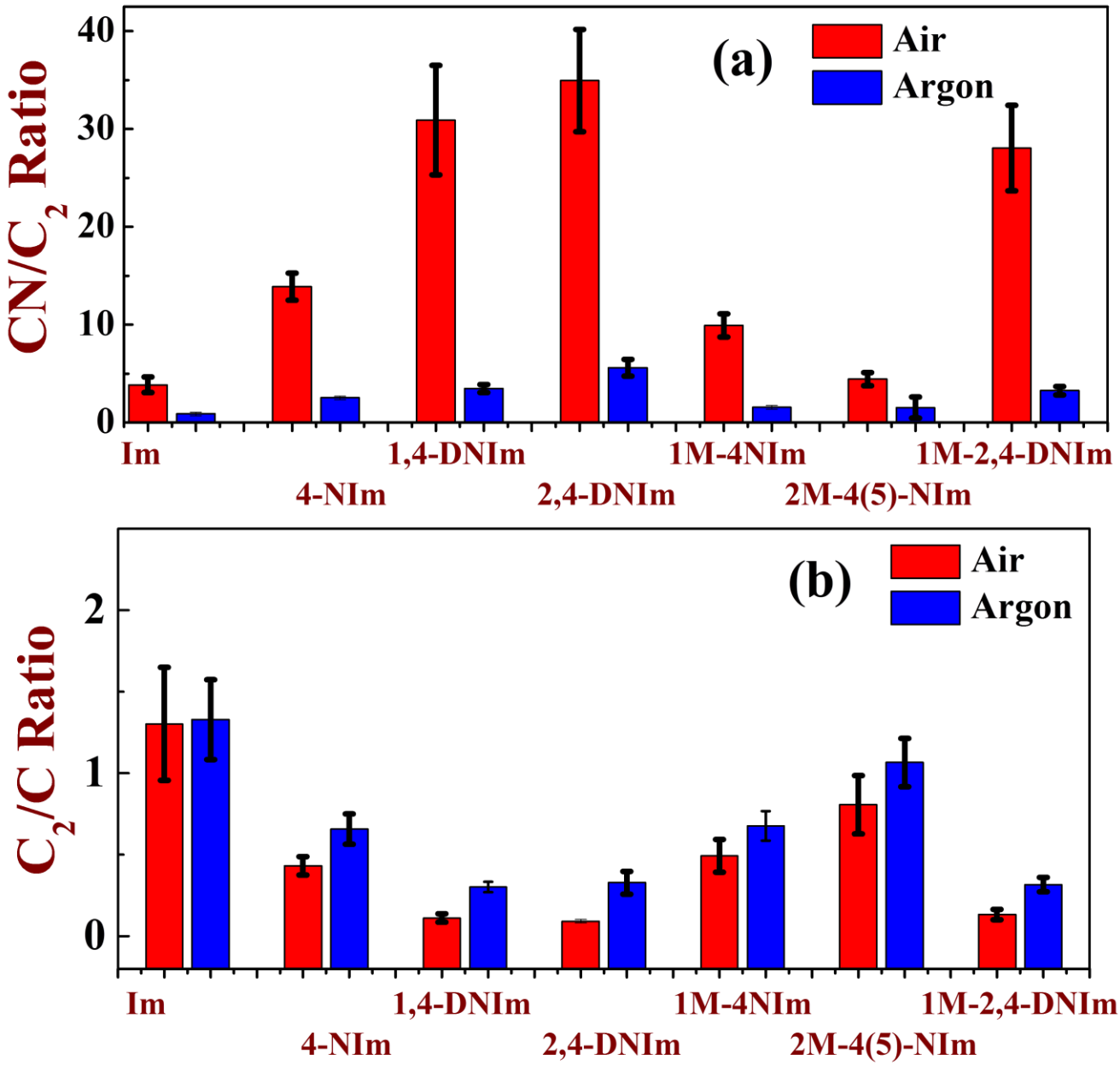


Figure 8 (a) The molecular intensity ratio CN/C_2 and **(b)** C_2/C ratio in air and argon atmospheres of nitroimidazoles with ns excitation. 30-40 individual spectra in air and 20 spectra in argon were considered and the average value of intensity was calculated in each case and error bars represents the standard deviation of each one.

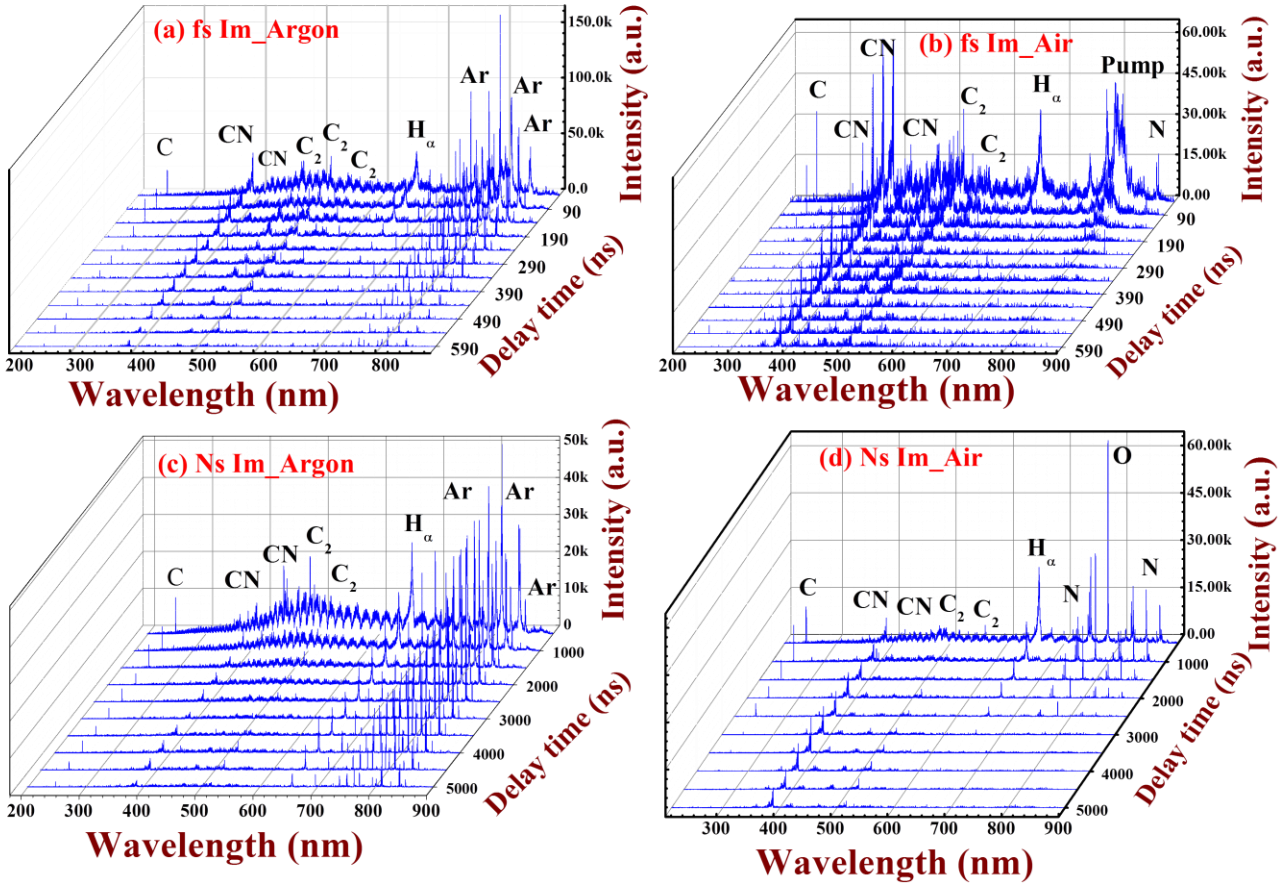


Figure 9 Time resolved spectra of Imidazole obtained with fs laser excitation in **(a)** argon and **(b)** air atmospheres at gate width of 50 ns and 90 ns initial gate delay with step 50 ns were utilized to record the spectra. Ns excitation the time resolved spectra of Imidazole in **(c)** argon **(d)** air atmospheres. A gate width of 500 ns and 500 ns gate delay with step 500 ns were utilized to record the spectra.

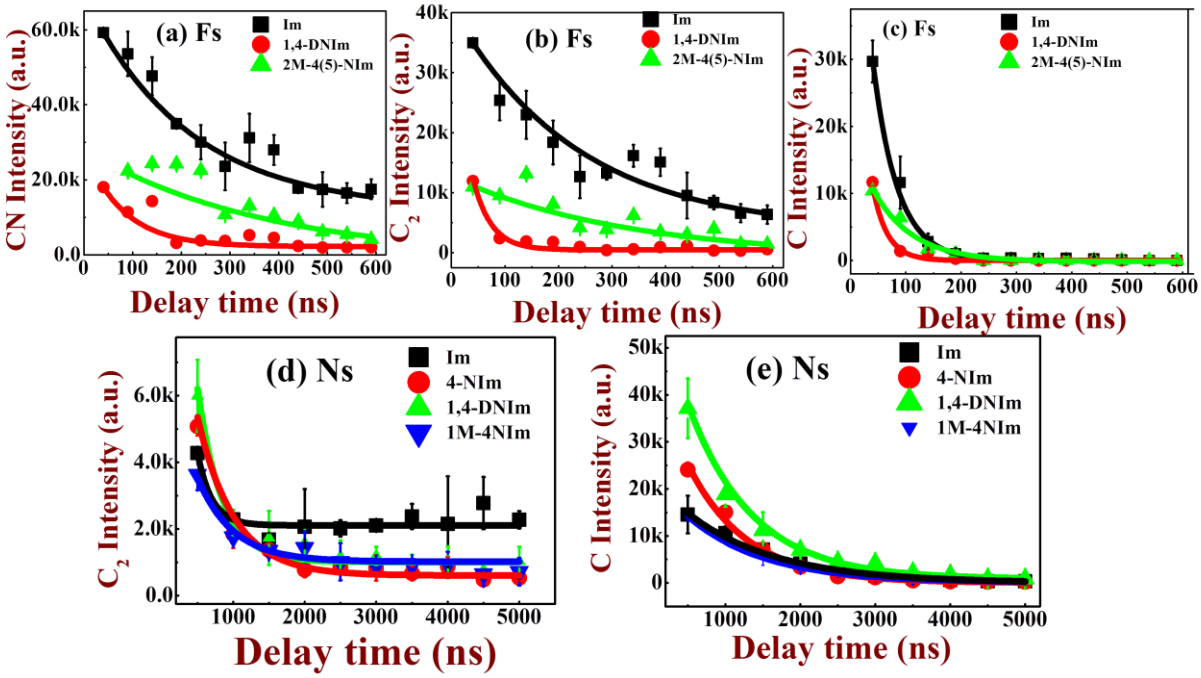


Figure 10 Time resolved emission decays of the molecular bands of the CN (388.32 nm), C_2 (516.52 nm) and C (247.86 nm) at gate delay of 90 ns, gate width 50 ns with (a-c) fs excitation and (d, f) ns excitation a gate delay 500 ns and gate width 500 ns were used for Im, 4-NIm, 1,4-DNIm and 2M-4(5)-NIm (or) 1M-4NIm in air atmosphere.

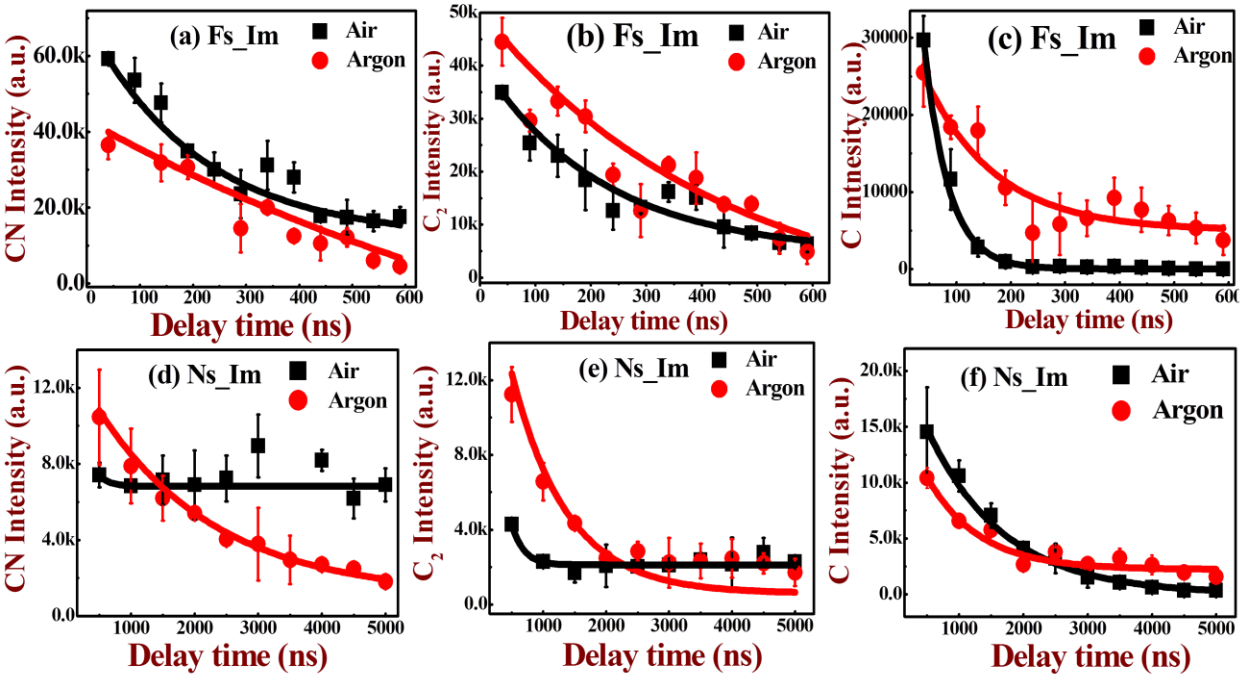


Figure 11 Temporal decay plots of molecular bands of CN at 388.32 nm, C_2 at 516.52 nm and atomic emission of C at 247.86 nm of Imidazole with (a-c) fs excitation and (d-f) ns excitation in air and argon atmospheres. Each data point represents the average of three individual measurements and error bars represents the standard deviation of each data point

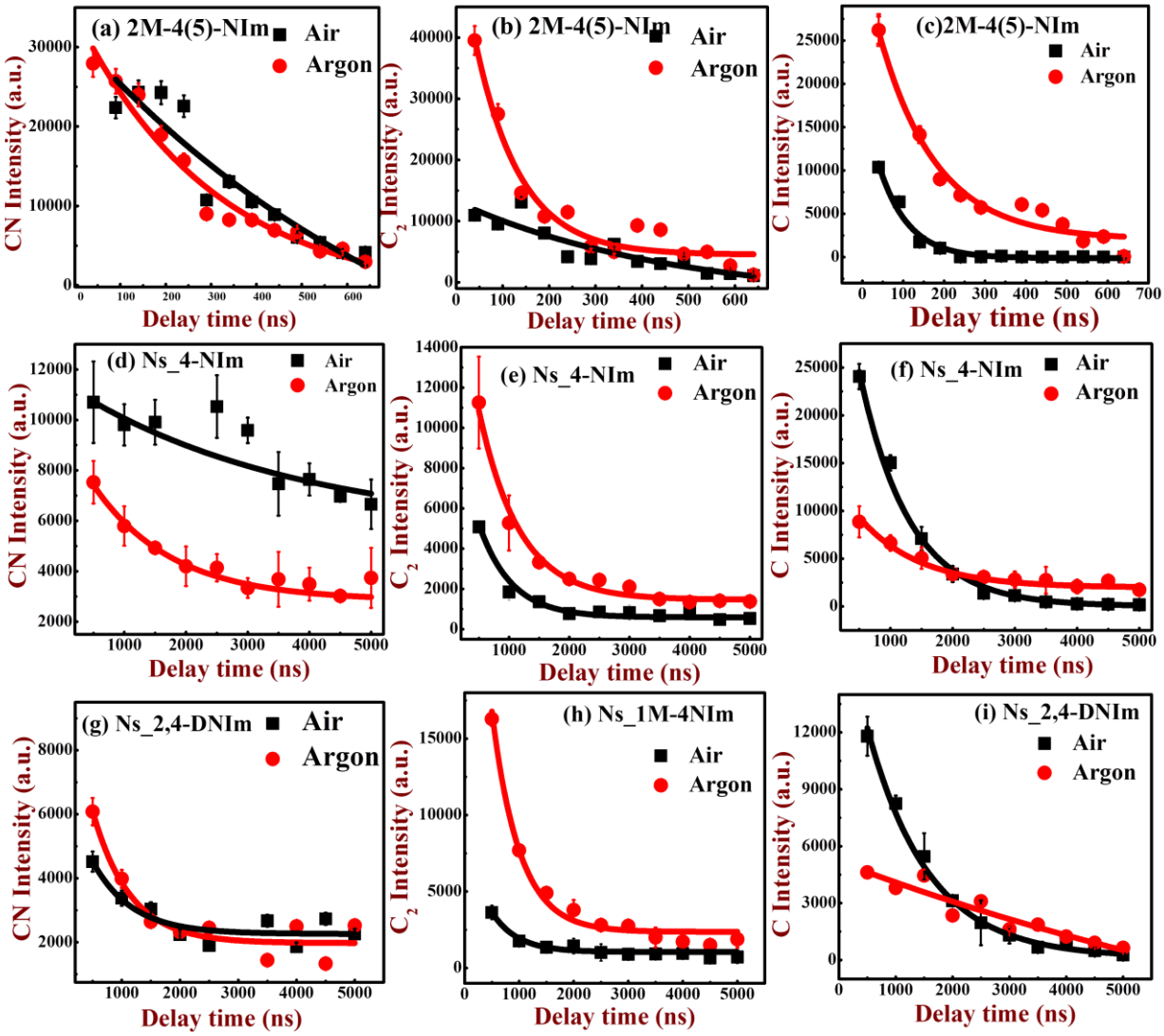


Figure 12 Time resolved emission decays of CN (388.32 nm), C_2 (516.52 nm) and C (247.86 nm) of (a-c) 2M-4(5)-NIm with fs excitation, (d-f) 4-NIm and (g, i) 2,4-DNIm with ns excitation and finally (h) 1M-4NIm with ns excitation in air, argon atmospheres.