Electronic Supplementary Information of

Comparison study of carbon clusters formation during thermal decomposition of 1,3,5-triamino-2,4,6-trinitrobenzene and benzotrifuroxan: a ReaxFF based sequential molecular dynamics simulation

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S1. Bond order cutoff table.

Table S1. Bond order cutoff for atom pairs employed in species analysis.

Atom type	Atom type	Bond order cutoff
C	N	0.3
C	C	0.55
C	O	0.65
C	H	0.4
O	O	0.65
N	O	0.4
O	H	0.4
H	H	0.55
H	N	0.55
N	N	0.55

S2. Relation of ln(C_t/C_0) and time during decomposition.

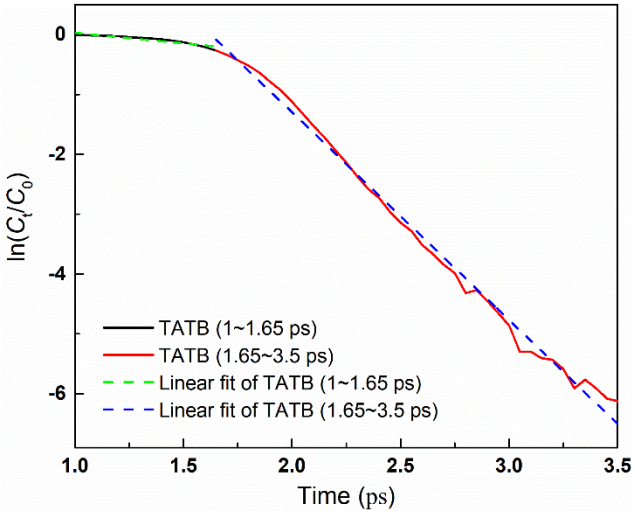

Figure S1. Relation of ln(C_t/C_0) and time of TATB.

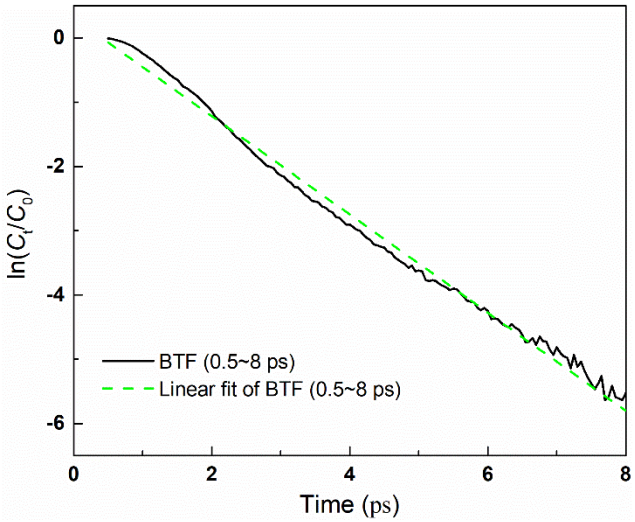

Figure S2. Relation of ln(C_t/C_0) and time of BTF.

S3. Chemical reactions statistics in the first 1 ps.

Table S2. Chemical reactions of TATB and BTF crystals in the first 1 ps.

	Time	Freq.	primary reactions
TATB	0~0.5 ps	2	$C_6H_6N_6O_6 \rightarrow C_6H_5N_6O_6 + H$
	0.5~1 ps	42	$C_6H_6N_6O_6 \rightarrow C_6H_5N_6O_6 + H$
		13	$C_6H_6N_6O_6 + C_6H_6N_6O_6 \rightarrow C_{12}H_{12}N_{12}O_{12}$
		12	$C_6H_6N_6O_6 + C_6H_6N_6O_6 \rightarrow C_6H_5N_6O_6 + C_6H_7N_6O_6$
		2	$C_6H_5N_6O_6 + H \rightarrow C_6H_6N_6O_6$
		2	$C_6H_6N_6O_6 \rightarrow C_6H_6N_5O_4 + NO_2$
BTF	0~0.5 ps	62	$C_6N_6O_6 + C_6N_6O_6 \rightarrow C_{12}N_{12}O_{12}$
		6	$C_6N_6O_6 + C_6N_6O_6 \rightarrow C_6N_6O_5 + C_6N_6O_7$
	0.5~1 ps	778	$C_6N_6O_6 + C_6N_6O_6 \rightarrow C_{12}N_{12}O_{12}$
		193	$C_6N_6O_6 + C_6N_6O_6 \rightarrow C_6N_6O_5 + C_6N_6O_7$
		90	$C_6N_6O_6 + C_6N_6O_6 + C_6N_6O_6 \rightarrow C_{18}N_{18}O_{18}$
		28	$C_6N_6O_6 + C_6N_6O_6 + C_6N_6O_6 \rightarrow C_{12}N_{12}O_{11} + C_6N_6O_7$

S4. Detailed discussions of carbon clusters formation process.

Our final composition ($C_{54}H_3O_{15}N_4$) of TATB crystal is consist with that ($C_{57}H_8O_{28}N_6$) of Zhang et al.[1] in a much smaller system with 32 TATB molecules formed after cooled at the rate of 100 K/ps. The mass of the largest cluster during our simulation reaches 23019 amu, much larger than that (around 8000 amu) of Zhang et al.[1] Thus, larger system can form bigger clusters during heating process, while the final composition of the largest cluster after the cooling process is independent on the system size due to the dissociation of large clusters. Snapshots of several large clusters at the end of each process are shown in Fig. S3. Their detailed compositions are listed in Table S3. Stable geometries of carbon rich clusters formed in the end, which containing few hydrogen and nitrogen atoms and several oxygen atoms. Graphitic character are exhibits in most clusters (see Fig. S3), which is similar with bowl geometry of C_{20}[2]. Besides, carbon ring[2] and carbon chain[3, 4] are common in our stable clusters.

The carbon cluster formation at other temperatures in TATB (heated at 2500 K) and BTF (heated at 2500 and 5000 K) was tested. The evolutions of cluster mass ratio, as well as the mass and atomic ratios of the largest cluster are shown in Figs. S4~S7. The evolution trends of cluster mass ratio in TATB or BTF are similar when heated at different temperatures (see Figs. S7, 6, and 9). Clusters in BTF are less than those in TATB shortly after the decomposition beginning when heated at the same temperature. More clusters occur in TATB and BTF when heated at 2500 K compared to those when heated at 3500 K, which indicate that low temperature facilitates the formation of clusters. When BTF crystal is heated at 5000 K, less clusters are formed during the heating process compared to those when heated at 3500 K or 2500K, furthermore, all clusters dissociate at the end of expansion. Similarly, the mass of the largest cluster in TATB or BTF is higher when heated at lower temperature (see Figs. S4~S6, 7, and 10). The final compositions of the largest cluster in TATB and BTF when heated at 2500 K is $C_{77}H_6O_{33}N_{10}$ and $C_{56}O_{28}N_{12}$, respectively, which is larger than that when heated at 3500 K. Hydrogen, nitrogen, and oxygen atoms of the largest cluster in TATB and BTF escape slower when heated at lower temperature. More oxygen atoms are trapped in the largest cluster at the end of cooling process when heated at lower temperature, with the

atomic ratio of 0.239 and 0.429 in TATB and 0.258 and 0.500 in BTF when heated at 3500 and 2500 K, respectively.

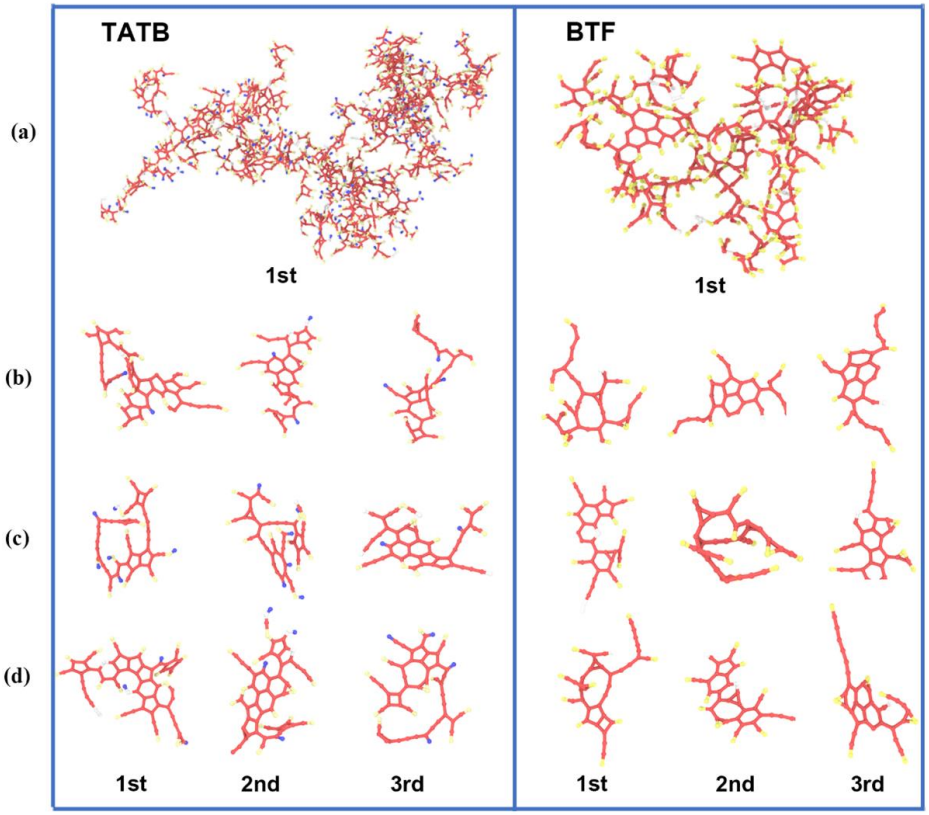

Figure S3. Snapshots of (a) the largest one at the end of the heating process, the largest three ones at the end of (b) the expansion process, (c) the cooling process cooled at 10 K/ps, and (d) the cooling process cooled at 100 K/ps. C, H, O, and N atoms are displays in red, blue, yellow, and white, respectively.

Table S3. Compositions of largest clusters at the end of (a) thermal decomposition for the largest one, (b) expansion, (c) cooling at 10 K/ps, and (d) cooling at 100 K/ps for the largest three ones.

		TATB	BTF
(a)	1st	$C_{793}H_{157}N_{79}O_{425}$	$C_{281}N_{23}O_{170}$
(b)	1st	$C_{57}H_3NO_{16}$	$C_{38}NO_{11}$
	2nd	$C_{47}H_3N_2O_{12}$	$C_{32}N_2O_{10}$
	3rd	$C_{47}H_3N_3O_{11}$	$C_{32}NO_7$
(c)	1st	$C_{46}H_6NO_{11}$	$C_{31}N_4O_8$

	2nd	$C_{43}H_6NO_{12}$	$C_{32}O_{10}$
	3rd	$C_{44}H_2N_4O_9$	$C_{33}N_2O_7$
(d)	1st	$C_{54}H_3N_4O_{15}$	$C_{36}NO_9$
	2nd	$C_{48}H_4N_3O_{12}$	$C_{32}N_2O_{10}$
	3rd	$C_{47}H_4O_{11}$	$C_{32}NO_7$

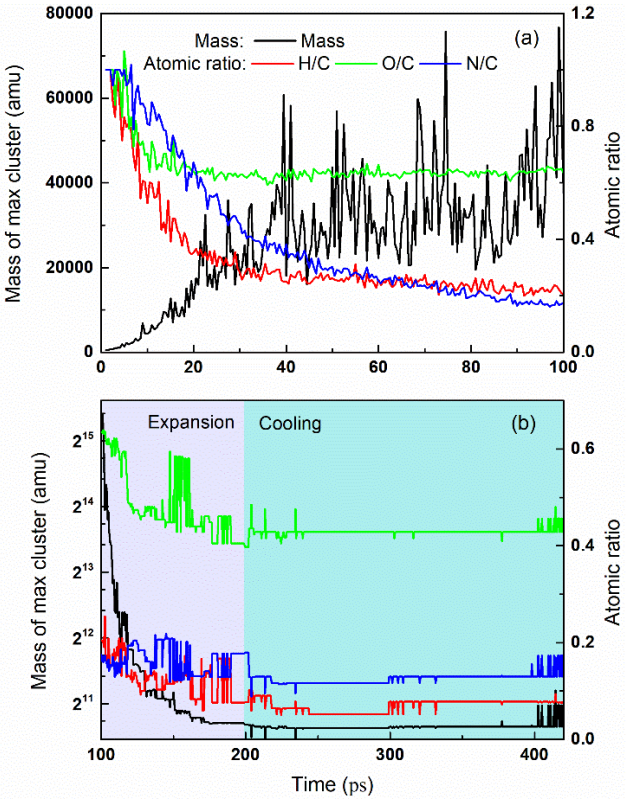

Figure S4. Evolutions of molecular mass and atomic ratios of the largest carbon cluster in TATB when heated at 2500 K: (a) heating process and (b) expansion and cooling processes.

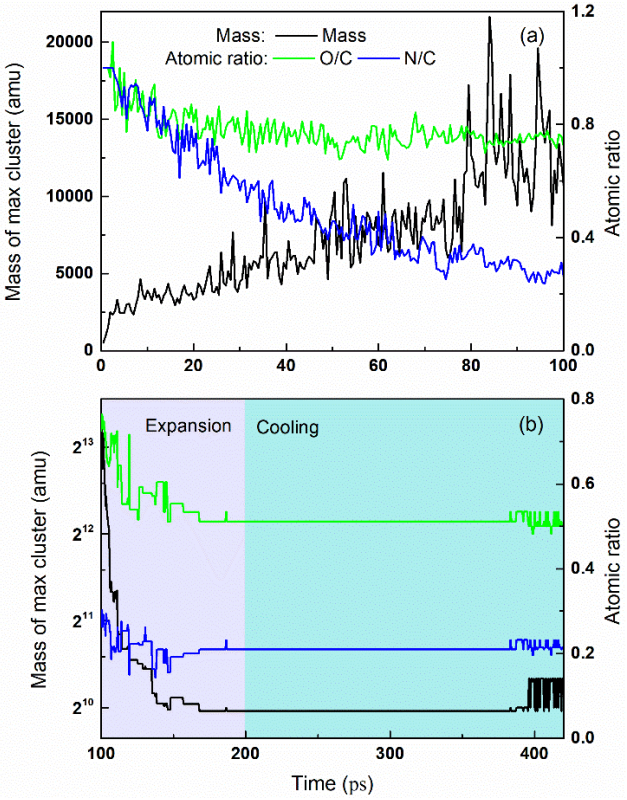

Figure S5. Evolutions of molecular mass and atomic ratios of the largest carbon cluster in BTF when heated at 2500 K: (a) heating process and (b) expansion and cooling processes.

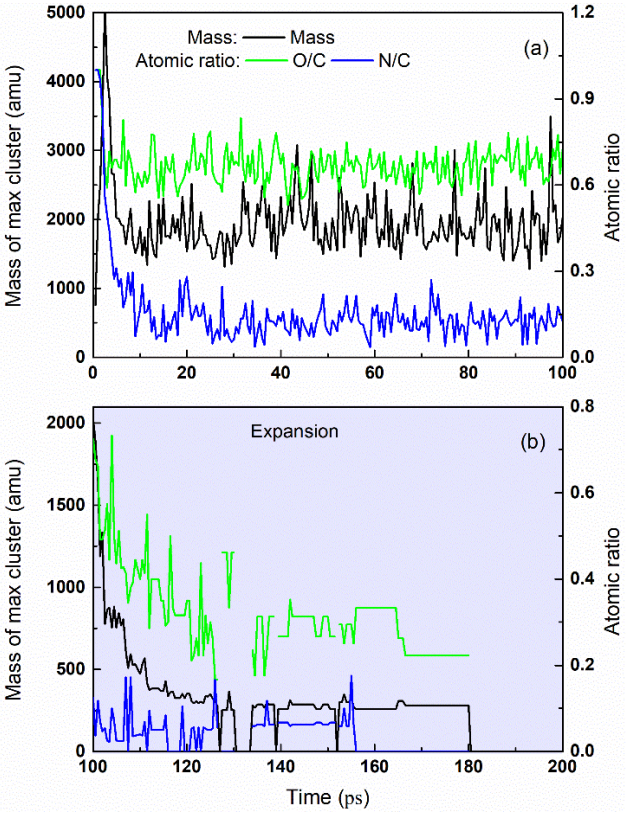

Figure S6. Evolutions of molecular mass and atomic ratios of the largest carbon cluster in BTF when heated at 5000 K: (a) heating process and (b) expansion process.

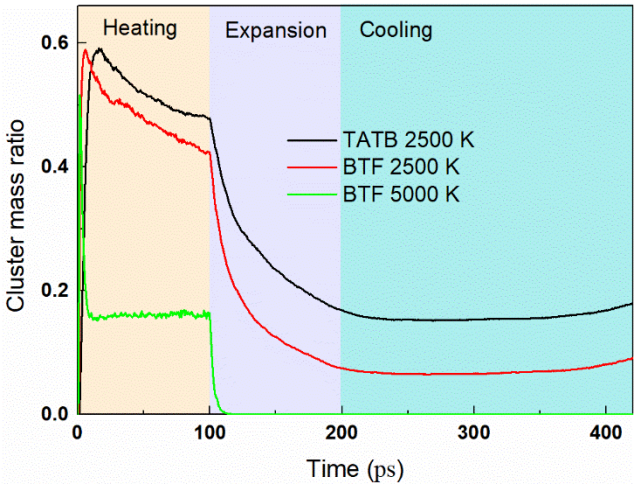

Figure S7. Evolutions of the cluster mass ratio in TATB and BTF crystals.

S5. References

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