Supporting Information

Exploring the evolution patterns of melem from thermal synthesis of melamine to graphitic carbon nitride

Yuhui Yi,[#a] Jie Wang,[#a] Yingli Niu,[a] Yu Yu,[a] Songmei Wu,*[a] Kejian Ding*[a]

[a] *School of Science, Beijing Jiaotong University, Beijing 100044, P.R. China.*

[#]*These authors contributed equally to this work.*

[*] *Corresponding Author, E-mail: dkjian@bjtu.edu.cn; smwu@bjtu.ed.cn.*

Outline

1. Possible formation of melem

2. Unimolecular reactions of melamine

3. Condensation of melamine or melem

4. Formation of melem

5. The FTIR results

6. References

1. Possible formation of melem
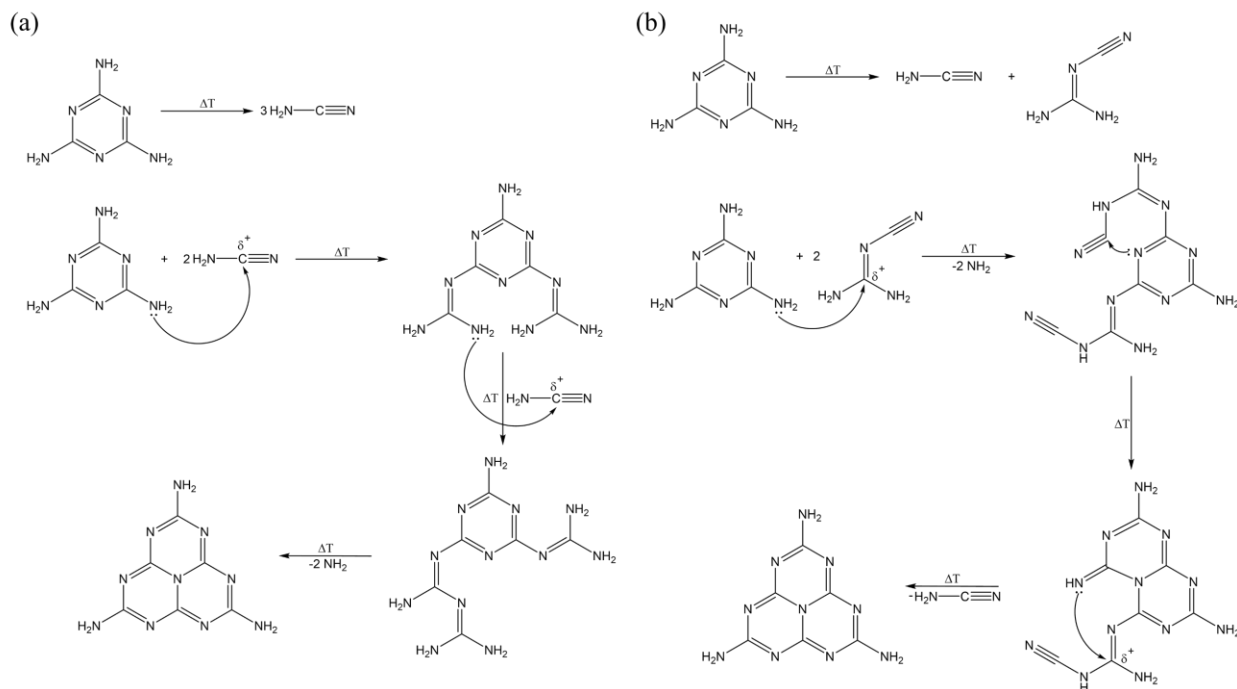
**Fig. S1** Two possible reaction paths to obtain melem with (a) cyanamide and (b) dicyanamide.

As shown in Fig. S1, Schnick et al. illustrated two possible reaction paths from melamine to melem, which involve the participation of cyanamide or dicyandiamide.[1] Specifically, the reaction of melamine with cyanamide was proposed by May,[2] while the reaction of melamine with dicyandiamide was suggested by Hosmane et al.[3] These two reaction paths occurred because of the existence of cyanamide or dicyandiamide during the synthesis. However, as mentioned by Algara-Siller et al., cyanamide might relate to the formation of TGCN, and dicyandiamide may be linked to the formation of HGCN.[4] Thus, it is necessary to verify these possibilities.

2. Unimolecular reactions of melamine
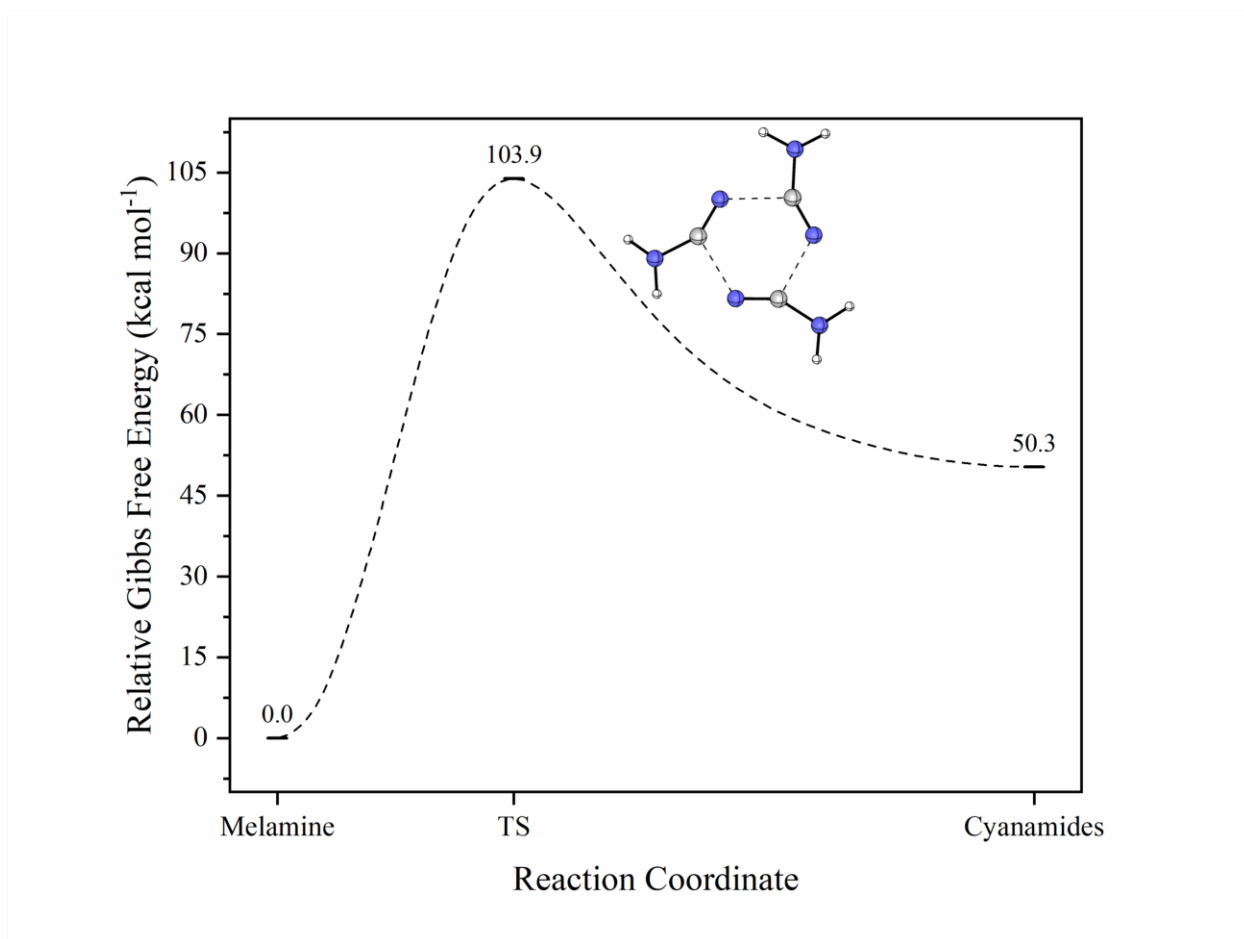
Fig. S2 The relative Gibbs free energies for the decomposition of melamine. TS: the transition state.

The transition state for the decomposition from melamine to cyanamides was calculated by B3LYP/6-31g(d), which was used to obtain a reaction path by integrating the intrinsic reaction coordinate (IRC) and determine the structures of reactants and products. Then, the corresponding total electronic energies of melamine, cyanamides and the transition state were obtained by revDSD-PBEP86-D3(BJ)/cc-pVTZ, followed by the calculation of thermodynamic data by Shermo. The relative Gibbs free energies are shown in Fig. S2 with reference to the melamine's.
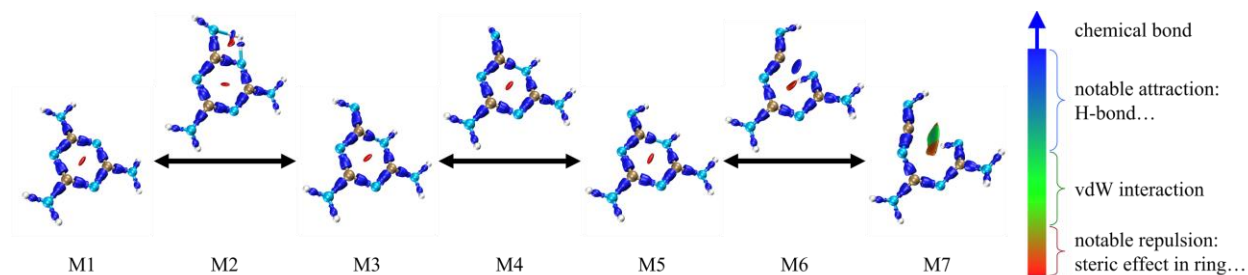
Fig. S3 The interaction region indicator (IRI) analysis for melamine's isomerization process.

As shown in Fig. S4, interaction region indicator (IRI) was used to analyze chemical bonds and weak interactions during melamine's isomerization process.[5] Combined with Fig. 2, the migration and vibration of hydrogens are shown from M1 to M5, which involves the weakening of C6-N10 bond. After that, C6-N10 bond can break as illustrated from M5 to M7. It is worth mentioning that the interaction between C6 and N10 in M6 is not H-bond but a notable interaction showing the process of change.
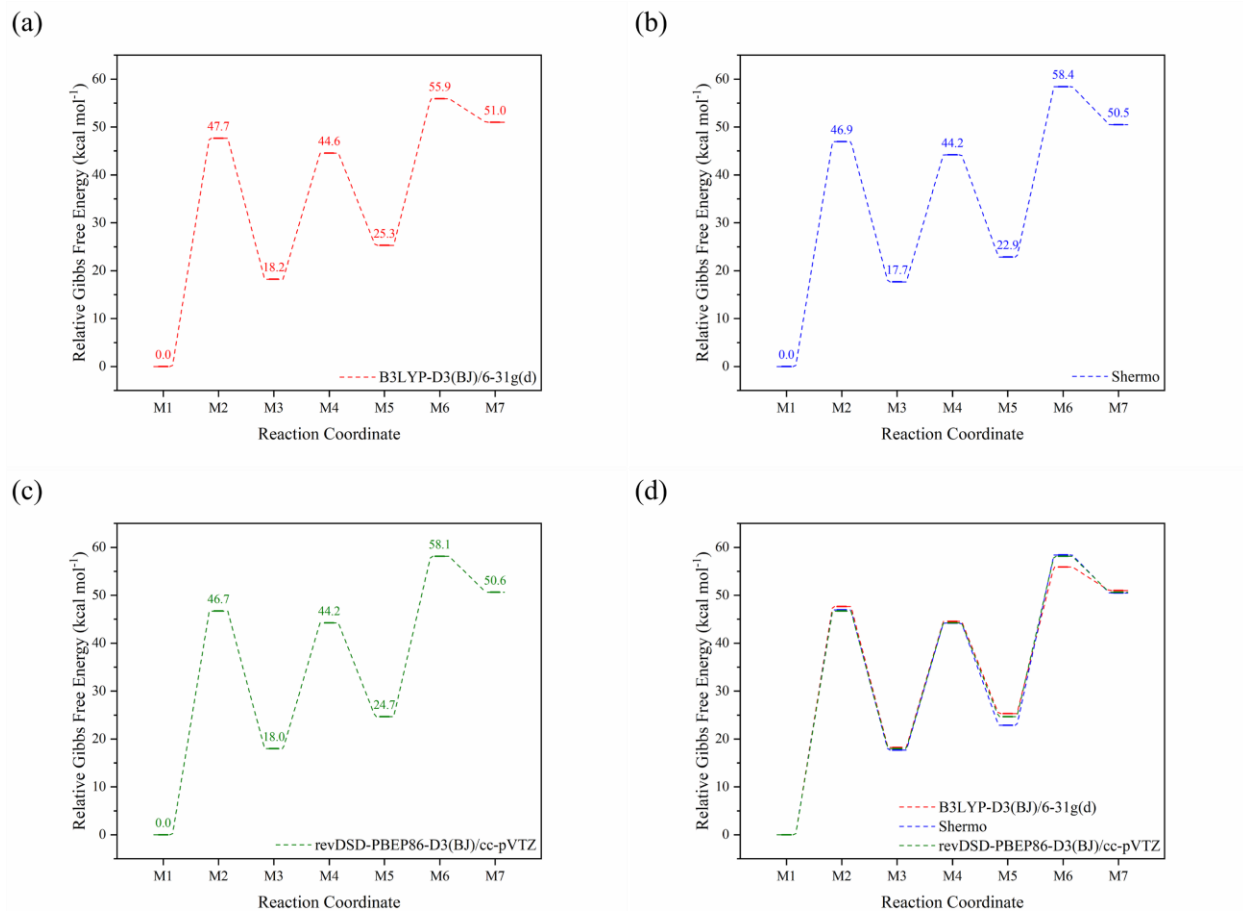
Fig. S4 The relative Gibbs free energies for the isomerization of melamine obtained by (a) B3LYP/6-31g(d), (b) Shermo and (c) revDSD-PBEP86-D3(BJ)/cc-pVTZ, and (d) the comparison of these data.

In Fig. S3(a)-(c), the relative Gibbs free energies for the isomerization of melamine were illustrated with reference to M1's respectively. Although Fig S3(d) compared these data in the same coordinate system, it should be mentioned that the Gibbs free energies are -446.430893, -445.7892067, -445.803863 Hartree for M1 gotten by these three methods respectively. Considering the Gibbs free energy of M1 calculated by revDSD-PBEP86-D3(BJ)/cc-pVTZ as the reference, Shermo performed reasonably as shown in Fig. 3.

3. Condensation of melamine

Transition state theory (TST) is an important method for calculation of rate constants in chemical reactions, and conventional formula is shown as

$$k_{TST}(T) = \sigma \frac{k_B}{h} \frac{Q_{TS}(T)}{\Phi_R(T)} \exp[-V^{\ddagger}/k_B T] \tag{1}$$

where T is the temperature; σ is the reaction-path symmetry number; k_B and h are Boltzmann's constant and Planck's constant respectively; $Q_{TS}(T)$ is the quantum mechanical transition state quasi-partition function without rotational symmetry numbers; $\Phi_R(T)$ is the reactant partition function with the zeroes of energy at the zero-point-exclusive energies of the saddle point and equilibrium reactants; $V^{\ddagger}$ is the energy barrier height.[6, 7] Excel calculator for calculating rate constants for unimolecular and bimolecular reactions based on TST is provided by Lu,[8] which is convenient to obtain rate constants corresponding to energy barriers.

The reaction process for both decomposition and condensation of melamine can be written as

$$X_0 \leftarrow X_1 \rightleftarrows X_2 \overset{X_1}{\rightarrow} X_3 \tag{2}$$

$$X_0 \overset{k_1^-}{\leftarrow} X_1 \tag{3}$$

$$X_1 \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} X_2 \tag{4}$$

$$X_1 + X_2 \overset{k_2^+}{\rightarrow} X_3 \tag{5}$$

where X_0 is cyanamides; X_1 is melamine; X_2 is melamine's tautomeric form; X_3 is melam; and k_i^+ and k_i^- are forward and backward rate constants respectively for i-th and (i+1)-th molecules. Then the reaction equations are shown as

$$\frac{d[X_3]}{dt} = k_2^+[X_2][X_1] \tag{6}$$

$$\frac{d[X_2]}{dt} = -k_2^+[X_2][X_1] + k_1^+[X_1] - k_1^-[X_2] \tag{7}$$

$$\frac{d[X_1]}{dt} = -k_2^+[X_2][X_1] - (k_0^- + k_1^+)[X_1] + k_1^-[X_2] \tag{8}$$

$$\frac{d[X_0]}{dt} = k_0^-[X_1] \tag{9}$$

The reaction rates for each step are shown in Table. S1, and Fig. S5 shows the concentration changes of melamine, melam, and cyanamide at 550 ℃, and concentrations of melam and cyanamide after 30 minutes of reaction at different reaction temperatures.

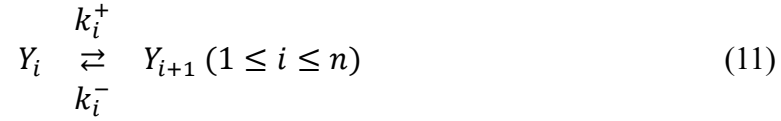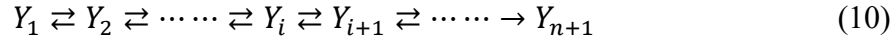Table. S1 The reaction rates for decomposition, isomerization, and condensation of melamine.

Temperature (℃)	k_0^-	k_1^+	k_1^-	k_2^+
450	6.00E-19	0.101	111800	18.49
440	2.15E-19	0.101	111800	11.56
430	7.46E-20	0.03881	63840	7.13
420	2.52E-20	0.02357	47670	4.341
410	8.22E-21	0.01411	35300	2.605
400	2.60E-21	0.008325	25920	1.541
390	7.93E-22	0.004833	18850	0.8974
380	4.34E-22	0.002761	13580	0.5143
370	6.63E-23	0.00155	9692	0.2898
360	1.81E-23	0.000855	6843	0.1605
350	4.73E-24	0.000463	4779	0.08723
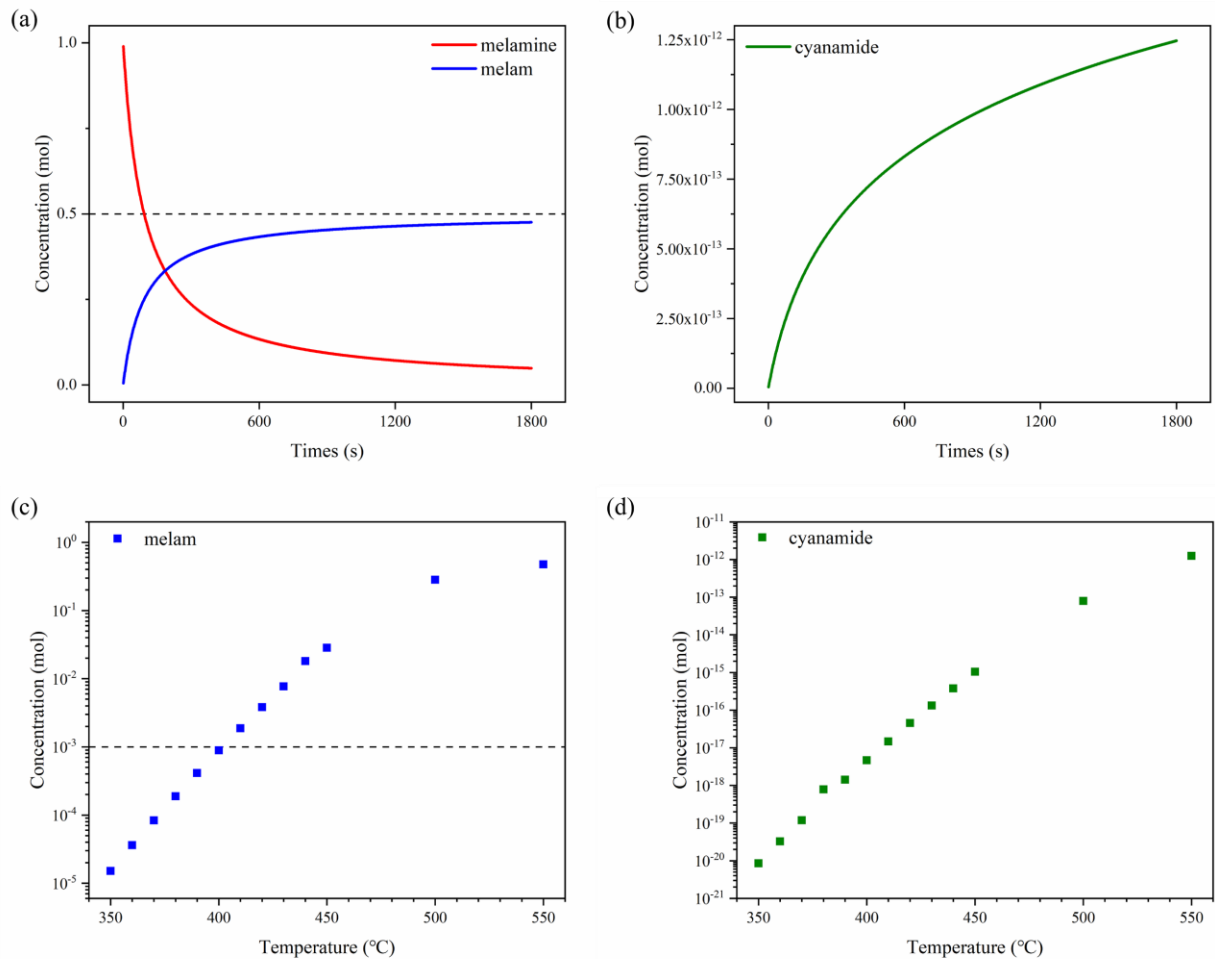
Fig. S5 The concentration changes of (a) melamine and melam compared with those of (b) cyanamide at 550 ℃, and the concentrations of (c) melam and (d) cyanamide after 30 minutes of reaction at different reaction temperatures.

The reaction process for n-step isomerization can be written as

$$Y_1 \rightleftarrows Y_2 \rightleftarrows \cdots\cdots \rightleftarrows Y_i \rightleftarrows Y_{i+1} \rightleftarrows \cdots\cdots \rightarrow Y_{n+1} \tag{10}$$

$$Y_i \underset{k_i^-}{\overset{k_i^+}{\rightleftarrows}} Y_{i+1} \ (1 \le i \le n) \tag{11}$$

If the concentration of isomerization intermediates is constant, there will be

$$\frac{d[Y_1]}{dt} = k_1^-[Y_{i+1}] - k_1^+[Y_i] \tag{12}$$

$$\frac{d[Y_i]}{dt} = k_i^-[Y_{i+1}] - (k_{i-1}^- + k_i^+)[Y_i] + k_{i-1}^+[Y_{i-1}] = 0 \ (2 \le i \le n) \tag{13}$$

$$\frac{d[Y_{n+1}]}{dt} = k_n^+[Y_n] \tag{14}$$

Then,

$$\frac{d[Y_{n+1}]}{dt} = \lambda_1[Y_n], \lambda_1 = k_n^+ \tag{15}$$

$$[Y_n] = \lambda_2[Y_{n-1}], \lambda_2 = \frac{k_{n-1}^+}{k_{n-1}^- + \lambda_1} \tag{16}$$

$$[Y_{n-1}] = \lambda_3[Y_{n-2}], \lambda_3 = \frac{k_{n-2}^+}{k_{n-2}^- + k_{n-1}^+ - k_{n-1}^- \lambda_2} \tag{17}$$

$$[Y_{n+2-t}] = \lambda_t[Y_{n+1-t}], \lambda_t = \frac{k_{n+1-t}^+}{k_{n+1-t}^- + k_{n+2-t}^+ - k_{n+2-t}^- \lambda_t}, 3 \le t \le n \tag{18}$$
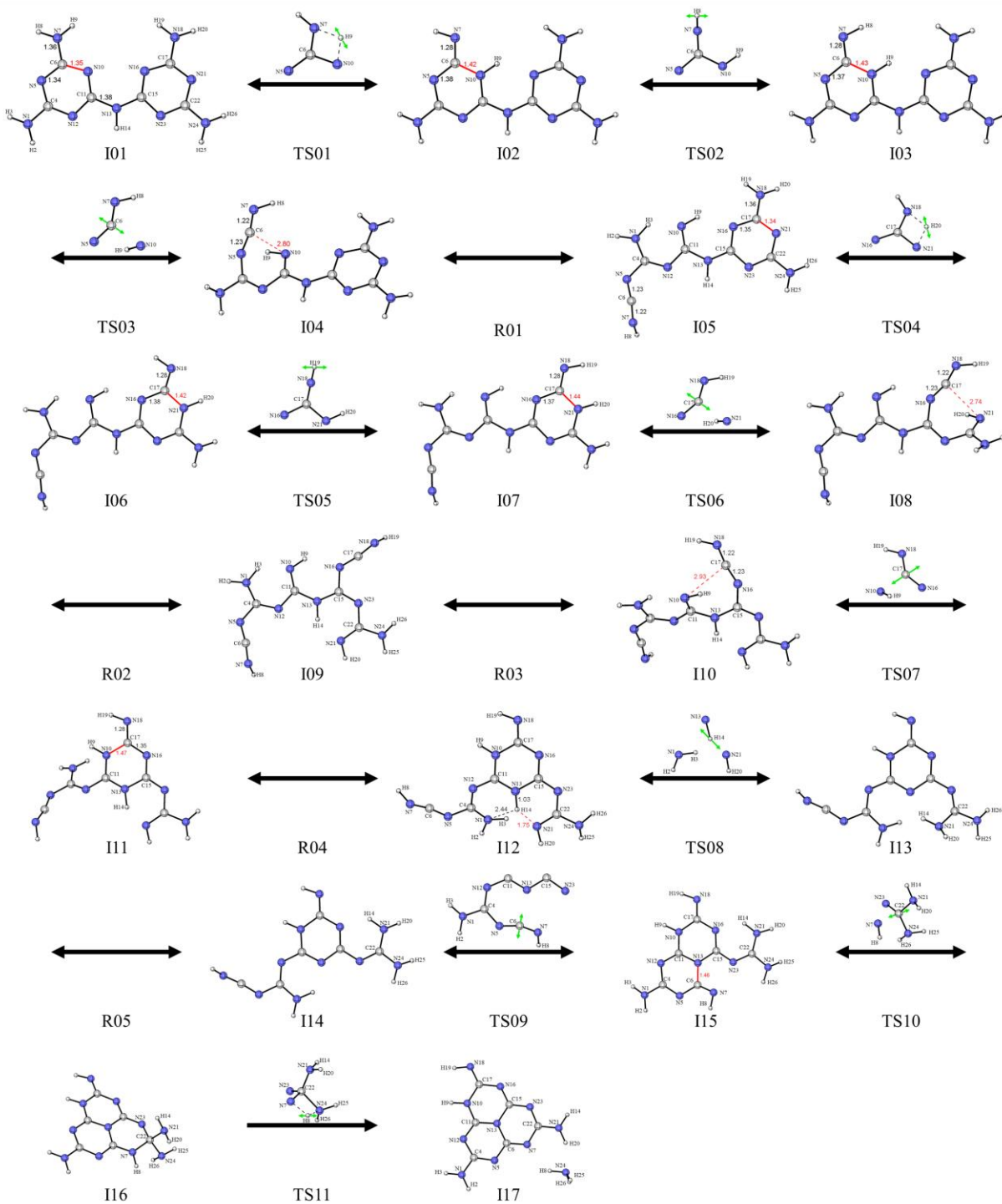
Thus,

$$Y_1 \xrightarrow{k_{iso}} Y_{n+1} \tag{19}$$

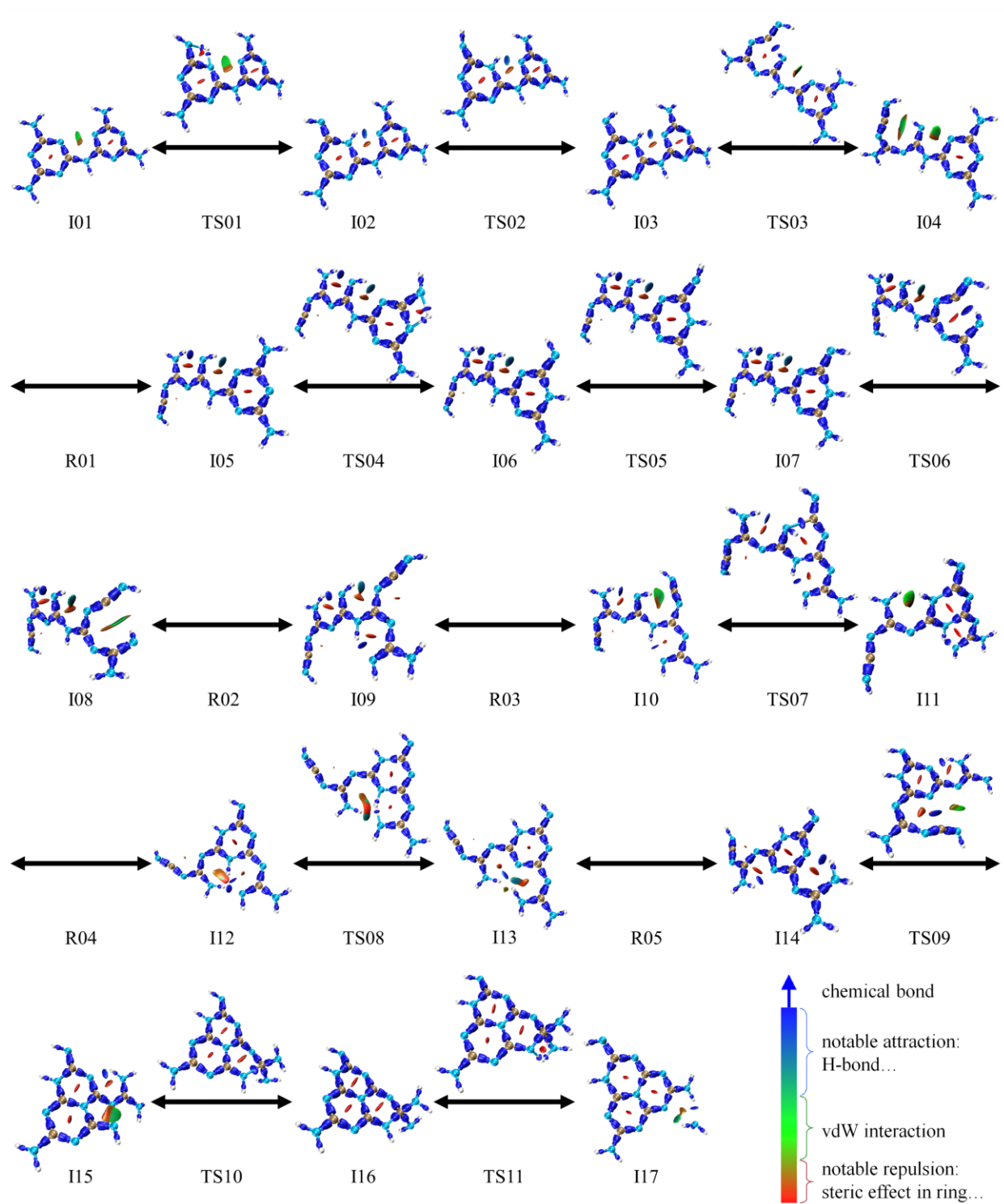$$\frac{d[Y_{n+1}]}{dt} = k_{iso}[Y_1] \tag{20}$$

$$k_{iso} = \prod_{t=1}^{n} \lambda_t \tag{21}$$

and k_{iso} is the equivalent reaction rate for the total n-step isomerization reaction which will be

used to estimate the reaction time of melam's isomerization.

4. Formation of melem

Fig. S6 The isomerization of melam to form melem; I: intermediates; TS: transition states; R: rotations.

Fig. S7 The IRI analysis for the isomerization of melam; I: intermediates; TS: transition states; R: rotations.

Conformation search:

(1) Molecular Dynamics (MD) simulation under GFN0-xTB with xtb

md.inp
$md
    temp= 1000 //Temperature (K)
    time= 100.0 //Total simulation time (ps)
    dump= 50.0 // Frequency of writing (fs)
    step= 1.0 // Step length (fs)
    hmass=1 //Hydrogen's mass in simulation compared with the actual mass
    shake=1 // SHAKE algorithm used to constrain all chemical bond related to hydrogen
$end

The content of the file *md.inp*, which contains the MD task settings of xtb, is as shown as above. After obtained the structure of I04 (I08, I11 or I13) with *.xyz* format, the xtb program can proceed with the command *xtb T01.xyz --input md.inp --omd --gfn 0*. The final file *xtb.trj* was renamed to *traj.xyz* for the next calculation step.

(2) Batch optimization of frames in *traj.xyz* via Molclus combined with xtb

Put *traj.xyz* in the *Molclus* directory, and related parameters in *settings.ini* are as follows.

settings.ini
    iprog= 4
   itask= 0
    xtb_arg= "--gfn 0 --chrg 0 --uhf 0"

After the optimization task with command *./molclus*, the optimized structures and energies of each frame are stored in *isomers.xyz* in the current directory, which is followed by the structural deduplication and energy sorting with command ./isostat. The energy deduplication threshold is 0.5 kcal/mol, and the structural deduplication threshold is 0.5 Angstroms. The non-repetitive structures are generated in cluster.xyz in the current directory, which can be generated to the Gaussian task with command *./xyz2QC* for the further optimization.

(3) Optimization of muti-step task via Gaussian 16 by DFT

The results of optimization will contain failed tasks and recycled structures, but only tasks successfully optimized without recycled structures are considered. Thus, the structures with minimum energies for each conformation search are as shown as I05, I09, I12 and I14.
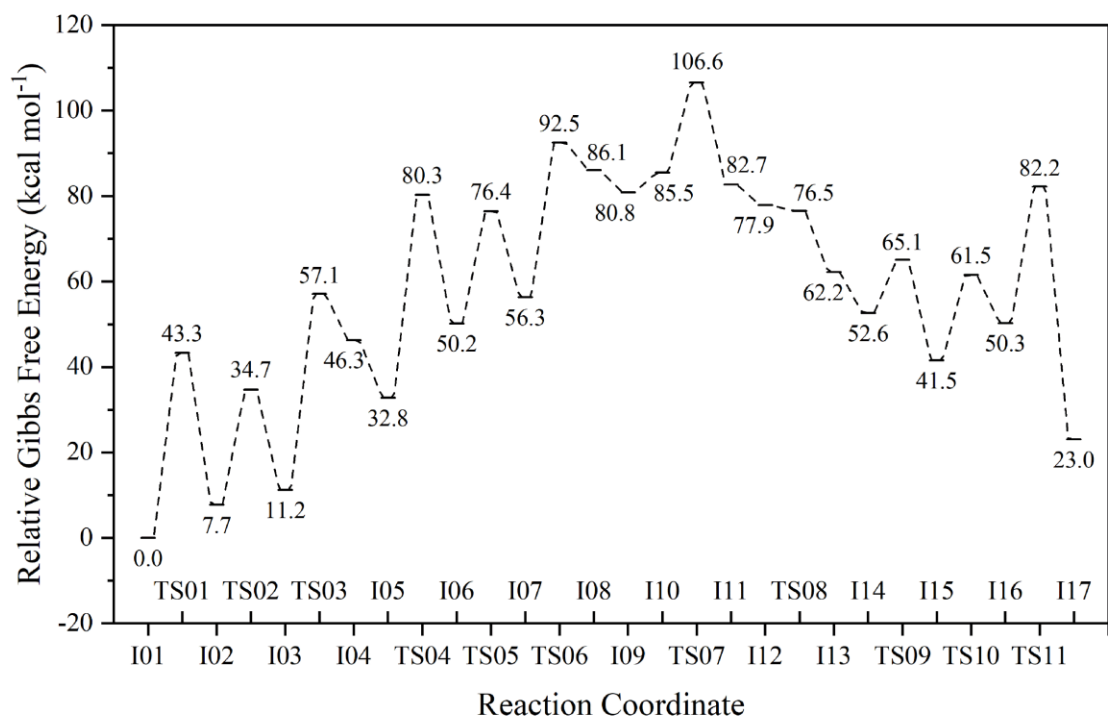
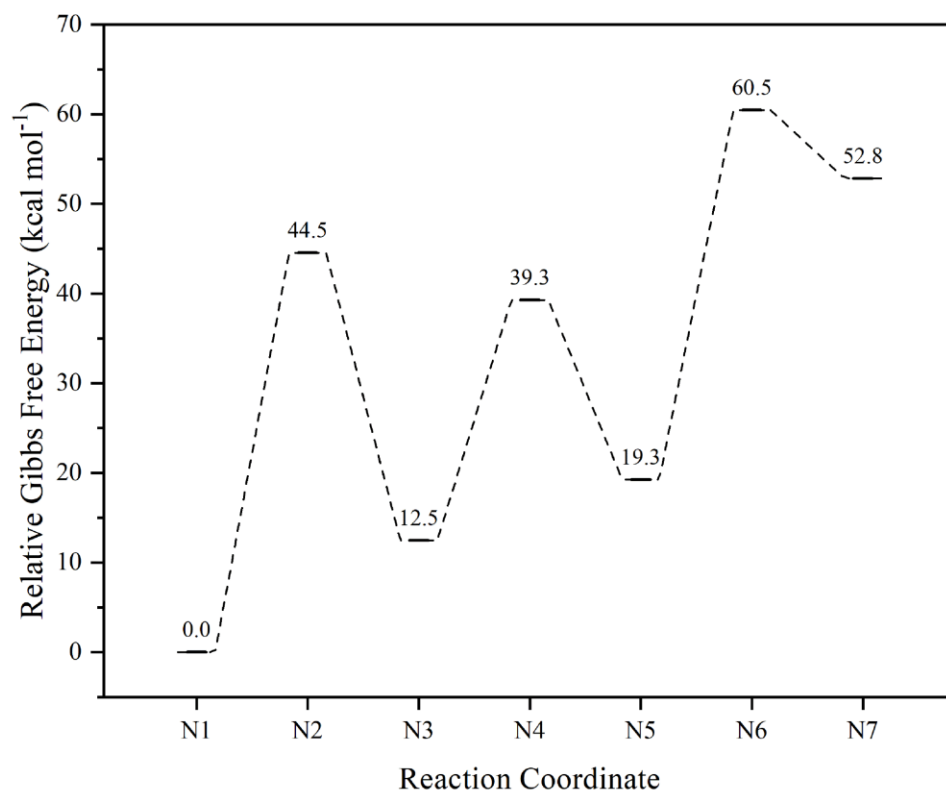**Fig. S8** The relative Gibbs free energy for the isomerization of melam; I: intermediates; TS: transition states; R: rotation.
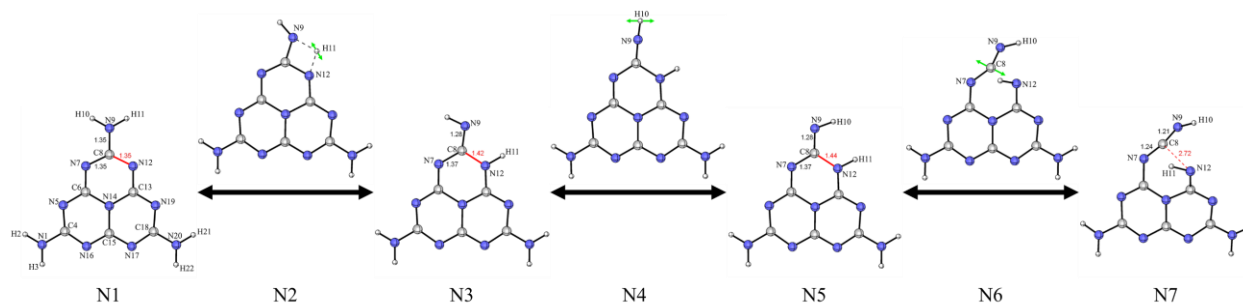
Fig. S9 The isomerization process of melem. N1: melem; N3, N5, N7: intermediates; N2, N4, N6: transition

states.
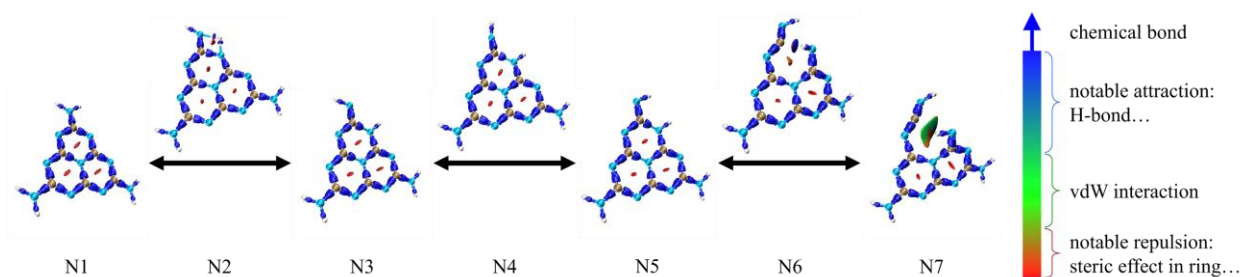
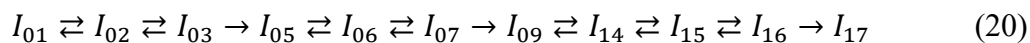**Fig. S10** The interaction region indicator (IRI) analysis for melem's isomerization process.

Fig. S11 The relative Gibbs free energies for melem's isomerization.

Estimation of reaction rate and reaction time

Taking every continues energy change as one step and regarding the formation of carbodiimines as irreversible reactions, the reaction can be abbreviated as the following.

$$I_{01} \rightleftarrows I_{02} \rightleftarrows I_{03} \rightarrow I_{05} \rightleftarrows I_{06} \rightleftarrows I_{07} \rightarrow I_{09} \rightleftarrows I_{14} \rightleftarrows I_{15} \rightleftarrows I_{16} \rightarrow I_{17} \qquad (20)$$

Thus, the energy barriers (ΔG^+ and ΔG^-) and corresponding reaction rates (k^+ and k^-) are shown in Table. S2, and equivalent reaction rates (k_{iso}) and reaction time for the isomerization of melam at different temperatures.

Table. S2 The energy barriers (ΔG^+ and ΔG^-) and corresponding reaction rates (k^+ and k^-) for the isomerization reaction.

	ΔG^+ (kcal/mol)	ΔG^- (kcal/mol)
I_{01}	43.26	35.52
I_{02}	27.00	23.50
I_{03}	45.84	/
I_{05}	47.50	30.12
I_{06}	26.20	20.04
I_{07}	36.18	/
I_{09}	25.71	53.94
I_{14}	12.50	23.59
I_{15}	20.01	11.27
I_{16}	31.95	/

5. The FTIR results
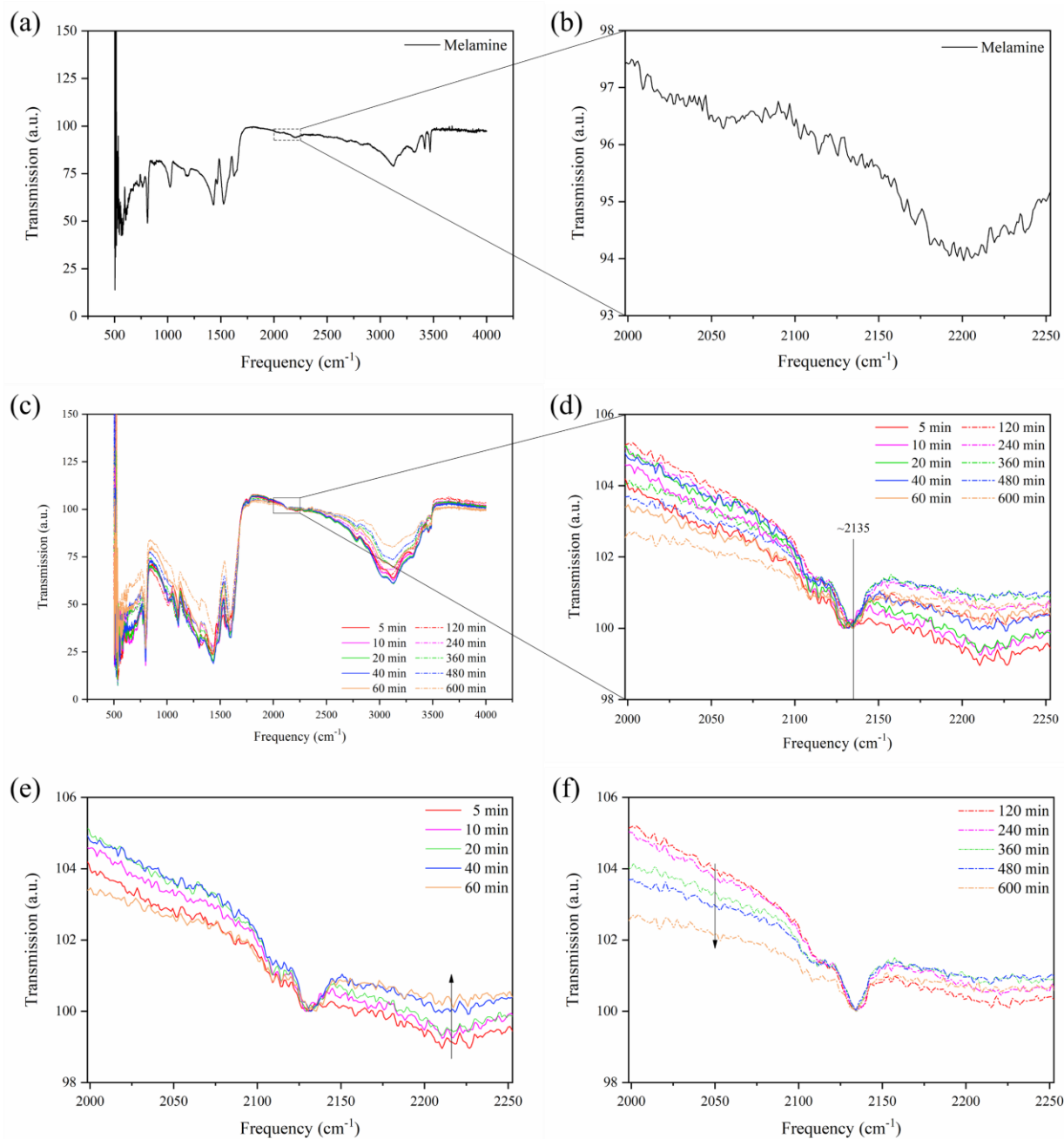
Fig. S12 The FTIR spectra of melamine with frequencies in the region (a) 500 - 4500 cm^{-1} and (b) 2000 - 2250 cm^{-1}; the FTIR spectra of mixed products with frequencies in the region (c) 500 - 4500 cm^{-1} and (d) 2000 - 2250 cm^{-1}; the FTIR spectra of mixed products with frequencies in the region 2000 - 22500 cm^{-1}, whose preserved time is (e) less than 120 minutes or (f) greater than or equal to 120 minutes.

For FTIR spectra, there are two thing deserving attention, which are the frequency and intensity of each peak. Furthermore, the frequency of a peak corresponds to a vibration mode, and the intensity of the peak relates to the number of detected molecules having the vibration mode. Thus, the peak's intensity is easily affected by the number of detected materials. For example, Fig. S12(a) and (b) shows the FTIR spectra of melamine with frequencies in the region 500 - 4500 cm^{-1} and 2000 - 2250 cm^{-1} respectively. The signal near 2200 cm^{-1} indicates the existence of nitrile $(-C \equiv N)$ left in the melamine industrial production process. As shown in Fig. 7(a), the signals near 2135 cm^{-1} have different intensities which makes it difficult to compare these data, and these data were adjusted to make the peaks at the same position as shown in Fig. S12(c) and (d). In this case, the variation of intensities may be caused by the reduction of nitrile $(-C \equiv N)$ and increasing of carbodi-imine $(-N = C = N -)$. Specifically, when the preserved time is less than 120 minutes, the number of nitrile $(-C \equiv N)$ reduced but still affected the detection of carbodi-imine $(-N = C = N -)$, while the impact decreases with the preserved time as shown in Fig. S12(e). Moreover, the signal of carbodi-imine $(-N = C = N -)$ gradually increase to a stable value as shown in Fig. S12(f). Therefore, the variation of signal near 2135 cm^{-1} can prove the existence of carbodi-imine $(-N = C = N -)$.

6. References

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