# Time-controlled Solvothermal Synthesis of Melamine Cyanurate and Melamine Diborate: Experimental and Theoretical Insights

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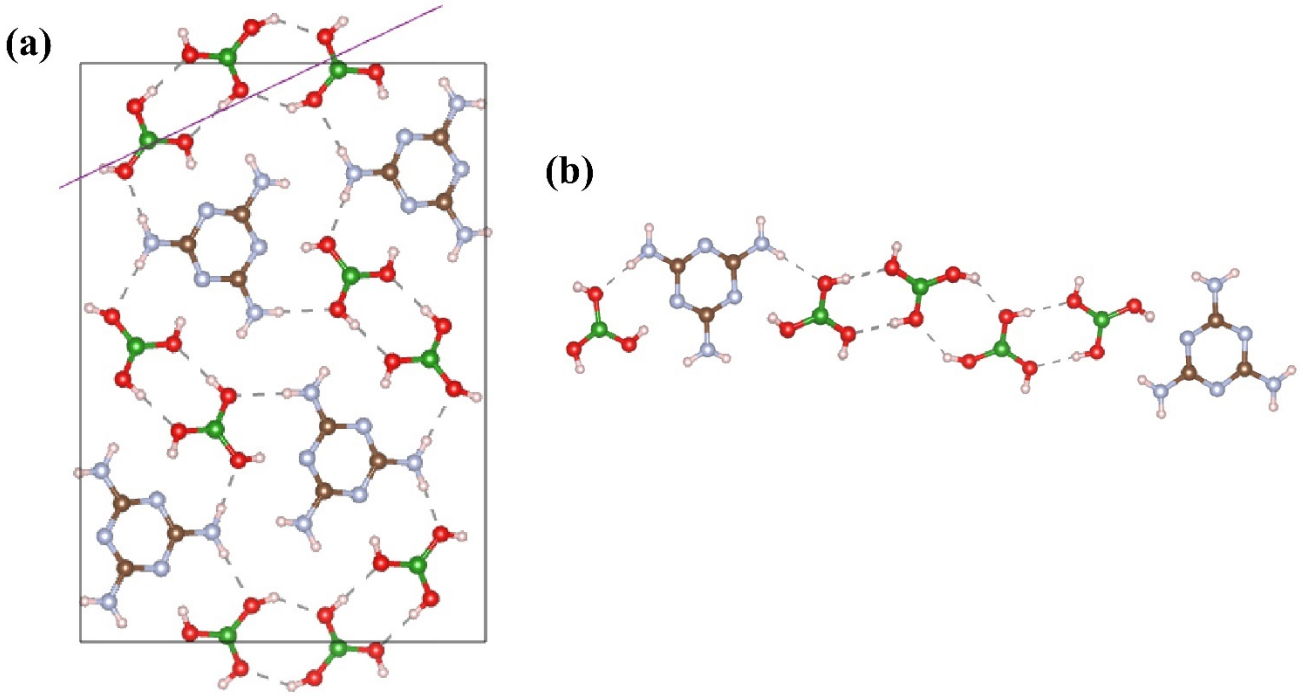



**Figure S1.** (a) Crystal structure of melamine diborate with (031) plane, and (b) arrangements of B, C, H, N, and O atoms along (031) plane, where green, brown, light pink, grey and red balls denote B, C, H, N, and O atoms.

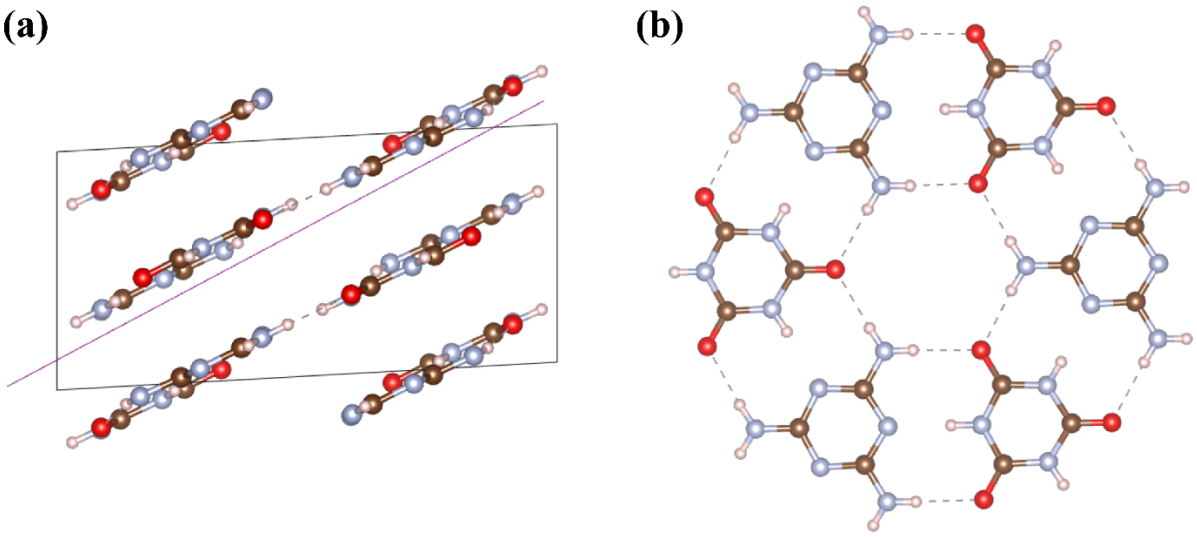
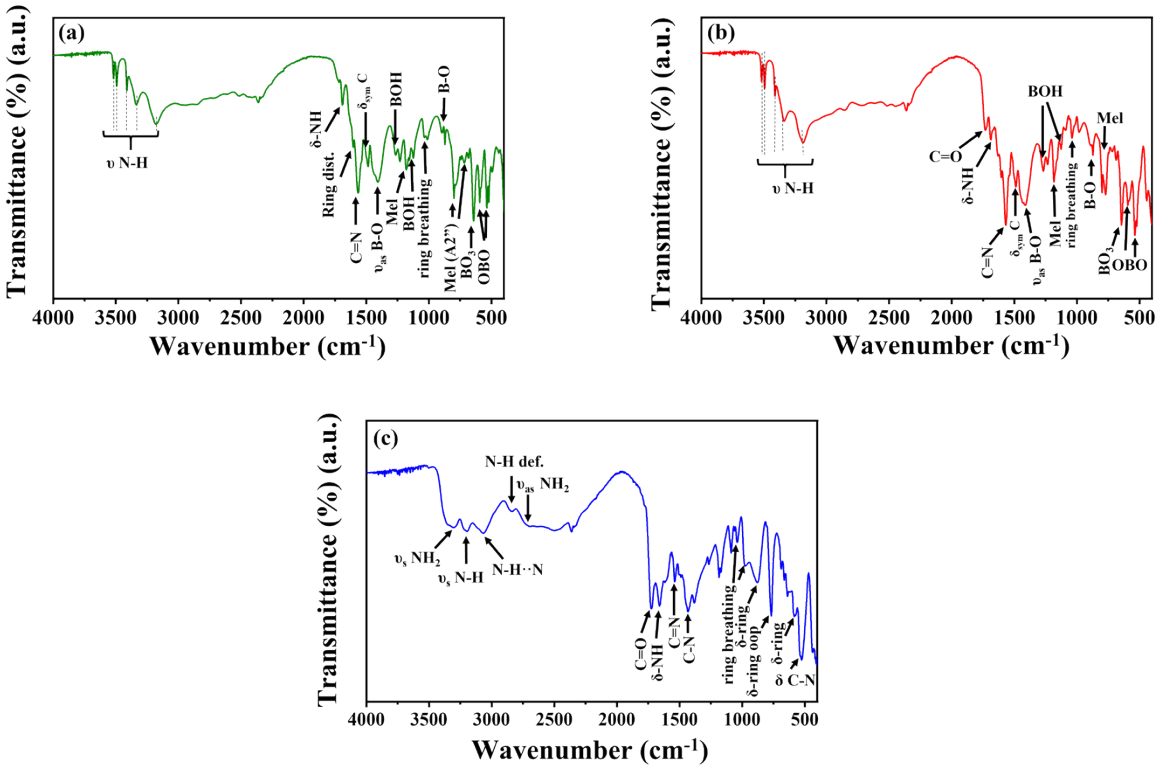



**Figure S2.** (a) Crystal structure of melamine cyanuric acid with (202) plane, and (b) arrangements of C, H, N, and O atoms along (202) plane, where brown, light pink, grey and red balls denote C, H, N, and O atoms.

**S.2. FTIR studies of sample A, B and C**

The bonding characteristics of all the samples were analyzed using FTIR spectroscopy, as shown in Figure S3. The FTIR spectrum of sample A, shown in Figure S3a, and the peaks corresponding to each vibrations is represented in Table S2a. All these vibrations are characteristic of melamine diborate, confirming its successful formation through 12 hours reaction. The FTIR of sample B i.e., heated at for 24 hours, is shown in Figure S3b. The FTIR spectrum of sample B closely matches with the FTIR spectrum of sample A, with the additional appearance of the characteristic carbonyl (C=O) stretching vibration of cyanuric acid. The presence of C=O groups in sample B indicates the formation of mixed phase comprising melamine diborate and melamine cyanurate.

While on the other hand, the FTIR spectrum of sample C, shown in Figure S3c shows the formation of melamine cyanurate. The characteristics vibrations are represented in Table S2b. Therefore, the FTIR studies supports the formation of melamine diborate for sample A, mixed phase (melamine diborate + melamine cyanurate) for sample B and melamine cyanurate for sample




C. The FTIR findings are consistent with the XRD results.

**Figure S3.** The FTIR spectra of (a) sample A, (b) sample B and (c) sample C.

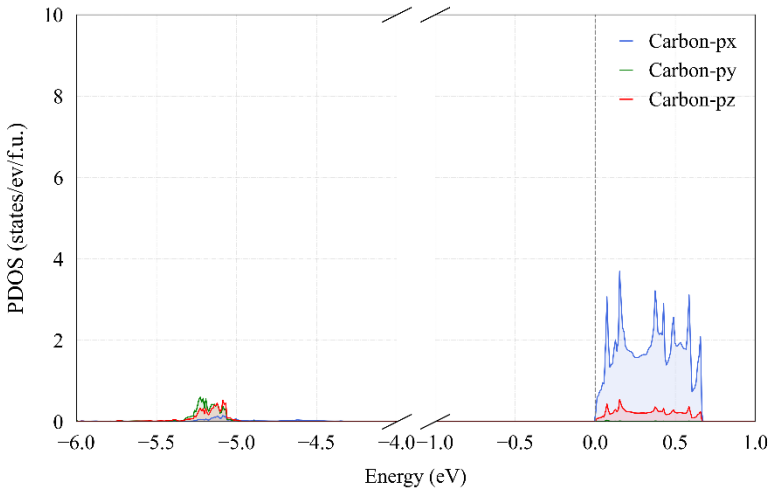



**Figure S4**. Projected density of states of carbon in melamine diborate.

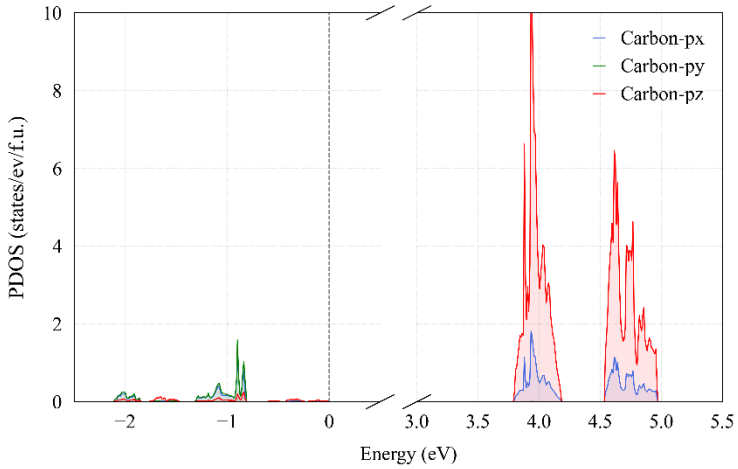



**Figure S5**. Projected density of states of carbon in melamine cyanurate

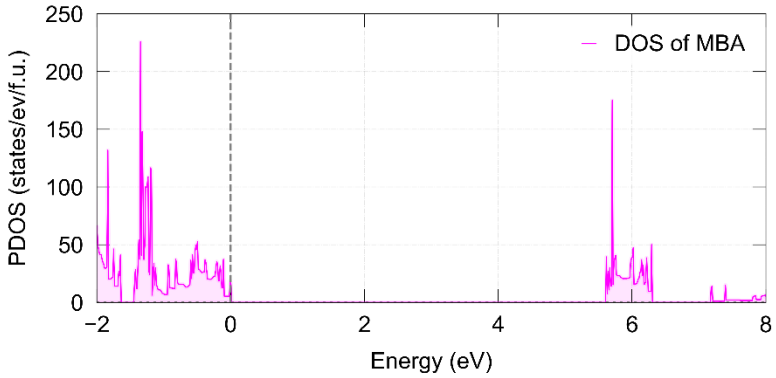



**Figure** S6. Density of states from HSE06 of MBA with a band gap about 5.6 eV.

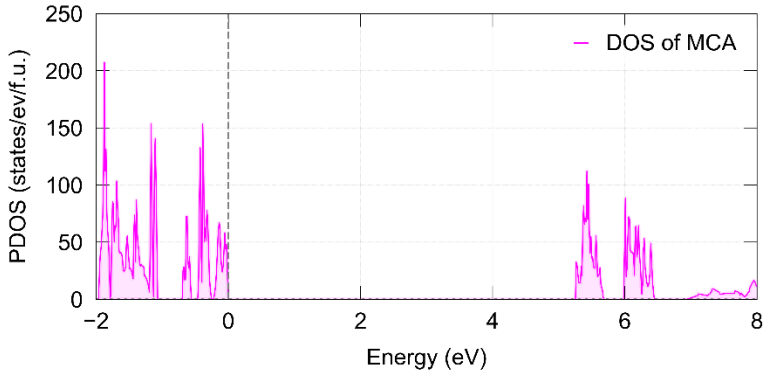



**Figure** S7. Density of states from HSE06 of MCA with a band gap about 5.3 eV.

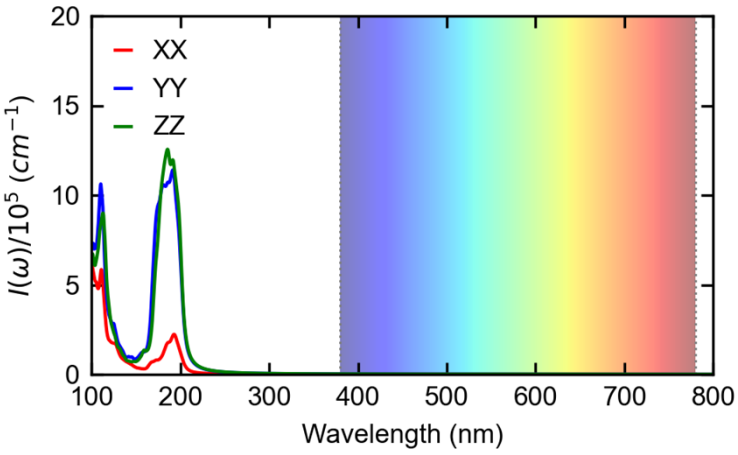



**Figure** S8. Optical absorption coefficients I(ω) of MBA, where the visible-light part is filled with the corresponding colors.

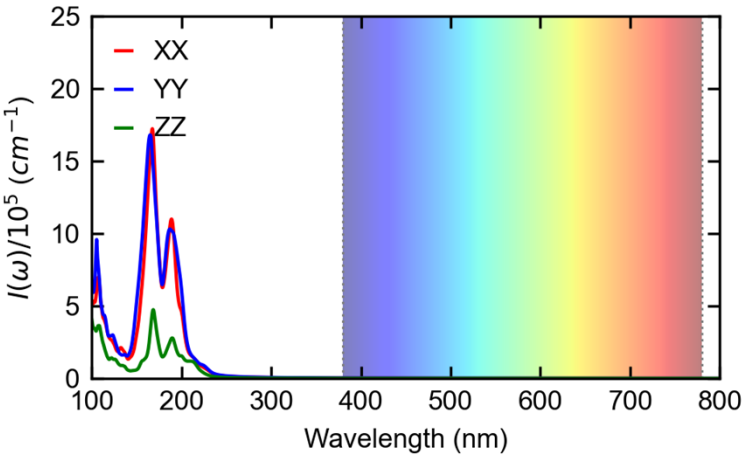



**Figure** S9. Optical absorption coefficients I(ω) of MCA, where the visible-light part is filled with the corresponding colors.

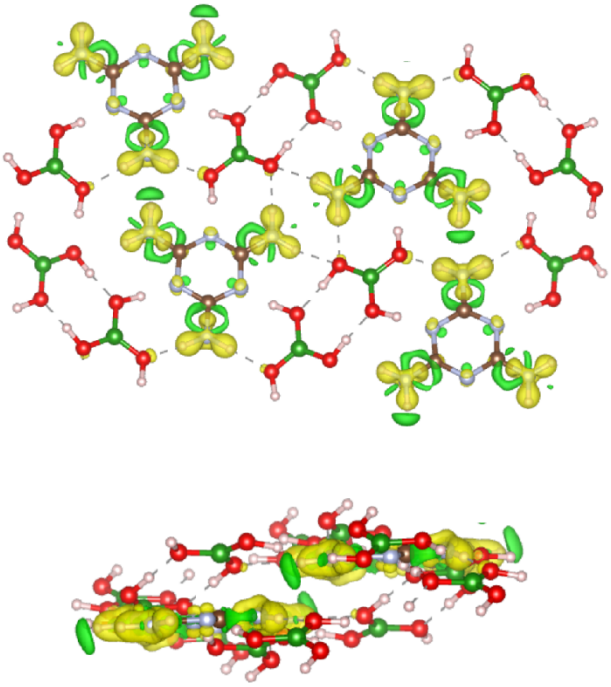


**Figure** S10. Differential charge maps $n_{diff}$ of MBA. The yellow and green colors denote positive and negative charge, respectively.

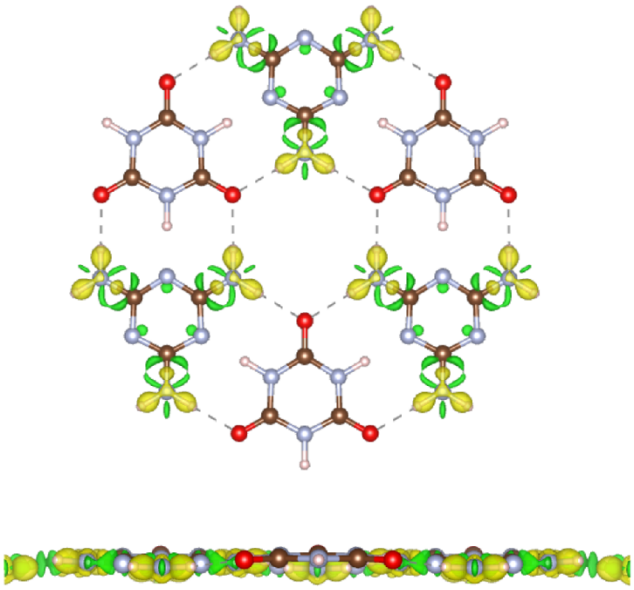


**Figure** S11. Differential charge maps $n_{diff}$ of MCA. The yellow and green colors denote positive and negative charge, respectively.

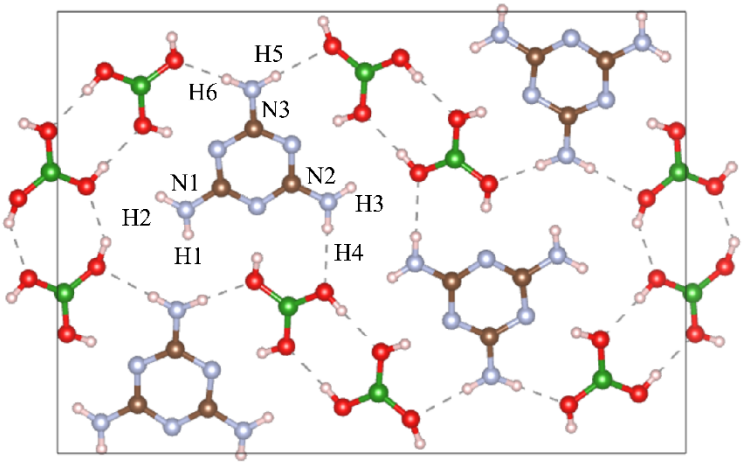



**Figure** S12. N—H bonds with label of amino in melamine diborate.

**Table S1a.** XRD data for sample A and simulated melamine diborate in the crystal structure with space group 14 ($P2_1/c$ symmetry)[1]

| Diffraction 2θ (This work) | Diffraction 2θ (Calculated) | Diffraction 2θ [7] | Planes (hkl) |
|---|---|---|---|
| 7.5 | 7.9 | 7.7 | 011 |
| 8.7 | 9.2 | 8.8 | 020 |
| 10.6 | 11.3 | 10.8 | 021 |
| 12.4 | 12.9 | 12.6 | 002 |
| 13.2 | 13.7 | 13.3 | 012 |
| 14.5 | 15.3 | 14.6 | 031 |
| 18.4 | 19.0 | 18.3 | 032 |
| 18.6 | 19.6 | 18.7 | 041 |
| 21.5 | 22.6 | 21.7 | 042 |
| 22.8 | 24.0 | 23.1 | 033 |
| 25.1 | 26.0 | 25.3 | 004 |
| 26.1 | 28.3 | 26.3 | 120 |
| 27.0 | 29.4 | 27.3 | 121 |
| 27.6 | 29.1 | 27.4 | $10\bar{2}$ |
| 28.3 | 30.4 | 28.3 | 102 |
| 28.8 | 30.8 | 28.6 | 112 |
| 29.3 | 31.2 | 29.1 | 131 |
| 30.8 | 33.0 | 31.0 | $14\bar{1}$ |
| 31.8 | 33.7 | 31.4 | 141 |
| 32.6 | 34.2 | 32.8 | 063 |
| 33.5 | 36.0 | 33.8 | $15\bar{1}$ |
| 34.7 | 36.5 | 34.9 | $10\bar{4}$ |
| 35.5 | 37.5 | 35.7 | 080 |
| 36.3 | 37.8 | 36.5 | 045 |
| 36.9 | 38.5 | 37.0 | 064 |
| 37.7 | 39.8 | 38.0 | 082 |
| 38.1 | 39.8 | 38.5 | 016 |
| 38.8 | 41.3 | 38.8 | 134 |
| 40.2 | 42.2 | 40.5 | 074 |
| 40.8 | 43.2 | 41.1 | $16\bar{3}$ |
| 41.7 | 44.3 | 41.9 | $17\bar{2}$ |
| 42.2 | 43.9 | 42.2 | $13\bar{5}$ |
| 43.7 | 46.6 | 43.9 | 180 |
| 44.0 | 46.2 | 44.2 | 084 |
| 45.1 | 48.0 | 45.3 | 145 |
| 48.0 | 50.8 | 47.9 | 190 |
| 50.5 | 53.3 | 50.8 | $18\bar{4}$ |

**Table S1b.** XRD data for sample C and simulated melamine cyanurate in the crystal structure with space group 12 (I2/m symmetry)[2]

| Diffraction (2θ) (This work) | Intensity (This work) | Diffraction (2θ) [8] | Intensity [8] | Planes (hkl) [8] |
|---|---|---|---|---|
| 10.9 | 70 | 10.9 | 75 | 110 |
| 18.4 | | 18.4 | | 020 |
| 21.4 | | 22.0 | 20 | 220 |
| 27.8 | 100 | 28.7 | 100 | 202 |
| 33.5 | | 33.3 | 12 | 330 |
| 37.3 | | 37.3 | | 040 |
| 40.0 | | 40.1 | | 141 |
| 50.3 | | 50.3 | | 532 |
| 57.3 | | 57.4 | | 060 |

**Table S2a.** FTIR spectral data of sample A and assigned vibrations

| | Wave number ($cm^{-1}$) | |
|---|---|---|
| **Vibrations** | **Melamine diborate[9]** | **Sample A** |
| ν $NH_2$ | 3524, 3498, 3417, 3356 | 3518, 3493, 3412, 3339 |
| $\nu_{sym}$ N-H | | 3184 |
| δ $NH_2$ | 1697 | 1692 |
| Ring distortion | 1611 | 1604 |
| C=N | | 1566 |
| Symmetric bending of the C atoms of triazine ring | 1492 | 1485 |
| Asymmetric stretching of B–O in $BO_3$ | 1456 | 1410 |
| BOH bend (E) | 1278, 1236 | 1265, 1231 |
| Melamine bands | 1186 | 1180 |
| BOH bend (A) | 1126 | 1124 |
| Symmetric $A_1'$ ring breathing mode involving N atoms | 1041, 1013 | 1036, 1013 |
| ν B-O (A′) | 873, 903 | 872, 895 |
| Melamine mode ($A_2''$) | 725, 807 | 718, 799 |
| $BO_3$ bend (A′′) | 655 | 642 |
| OBO bend (E′) | 539, 596 | 536, 594 |

*E′* Modes (Degenerate In-Plane Vibrations), *A′* Modes (In-Plane Vibrations), $A_1'$ high-symmetry in-plane stretching and $A_2''$ Mode (Out-of-Plane Bending, C3h), and *A″* Mode (Out-of-Plane Bending, C3h, C2v)

**Table S2b.** FTIR spectral data of sample B and assigned vibrations

| | Wave number ($cm^{-1}$) | |
|---|---|---|
| **Vibrations** | **Melamine cyanuric acid [10]** | **Sample B** |
| $\nu_{sym}$ $NH_2$ | 3396 | 3337 |
| $\nu_{sym}$ N-H | 3234 | 3206 |
| ν N-H···N | 3041 | 3067 |
| N-H deformation | 2825 | 2843 |
| $\nu_{asym}$ $NH_2$ | 2698 | 2714 |
| C=O | 1782 | 1724 |
| δ($NH_2$) | 1667 | 1661 |
| C=N | 1528 | 1539 |
| C-N | 1449 | 1431 |
| ring breathing mode | 1036 | 1039 |
| ring breathing mode | | 974 |
| ring sextant out-of-plane bending | 924 | 878 |
| ring sextant out-of-plane bending (oop) | 771 | 766, |
| Ring bending plane | 596 | 584 |
| Side chain in plane C-N bending | 529 | 527 |

Table S3. Lattice parameters of MCA and MBA from simulations and experiments.

| Compounds | Space group | Lattice parameters | | | | |
|---|---|---|---|---|---|---|
| | | | a (Å) | b (Å) | c (Å) | β (°) |
| MBA | $P2_1/c$ | Theo. | 3.346 | 19.172 | 13.702 | 93.21 |
| | | Exp. | 3.596 | 20.111 | 14.109 | 92.12 |
| MCA | I2/m | Theo. | 14.540 | 9.538 | 7.140 | 93.31 |
| | | Exp. | 14.815 | 9.635 | 7.041 | 93.19 |

## References

(1) Kawasaki, T.; Kuroda, Y.; Nishikawa, H. The crystal structure of melamine diborate. *Journal of the Ceramic Society of Japan* **1996**, *104* (1214), 935-938.

(2) Prior, T.J.; Armstrong, J. A.; Benoit, D. M.; Marshall, K. L. The structure of the melamine–cyanuric acid co-crystal. *CrystEngComm*, **2013**, *15*, 5838–5843.

(3) Panicker. C.Y.; Varghese, H.T.; John, A.; Philip, D.; Nogueira, H.I.S. Vibrational spectra of melamine diborate, $C_3N_6H_62H_3BO_3$. *Spectrochimica Acta Part A*. **2002**, *58*, 1545–1551.

(4) Sangeetha, V.; Kanagathara, N.; Sumathi, R.; Sivakumar, N.; Anbalagan, G. Spectral and thermal degradation of melamine cyanurate. *Journal of Materials* **2013**, 262094.