Supporting Information

Morphological Evolution of Two Dimensional Porous Hexagonal Trimesic Acid Framework

Srinu Tothadi ^a, Kalipada Koner ^c, Kaushik Dey ^c, Matthew Addicoat ^b and Rahul Banerjee ^c *.

^a Organic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India.

^b Nottingham Trent University, 50 Shakespeare Street, Nottingham NG1 4FQ, UK

^c Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur Campus, Mohanpur, 741246 India.

*Correspondence to <u>*r.banerjee@ncl.res.in*</u>

Sr. No.	Contents	Page Numbers
Section S1	General information	3
Section S2	Single crystal synthesis of Trimesic acid (TMA) Form II	5
Section S3	Solvents used for TMA screening	6
Section S4	Single crystal data of Trimesic acid Form II table and crystal structure	7-9
Section S5	PXRD of Trimesic acid Form I and II	10
Section S6	TGA of Trimesic acid Form I and II	11
Section S7	DSC of Trimesic acid Form I and II	12
Section S8	SSNMR and FTIR of Trimesic acid	13-14
Section S9	SEM Images	15
Section S10	TEM Images	15
Section S11	FESEM Images for Ostwald ripening	16
Section S12	Nitrogen adsorption analysis	17
Section S13	PXRD after dye adsorption	18
Section S14	Variable temperature measurement of TMA (Form II) Single Crystal	19
Section S15	Lattice energy calculations	20-22
Section S16	Protocol is used for binding energy calculations	23-25
Section S17	Hot Stage Microscopy	26
Section S18	Variable temperature PXRD	27
	References	28

Section S1: General Information

Materials: The used Trimesic acid was purchased from Sigma Aldrich and was used without further purification. All the solvents were commercially available and used as received.

Instrumental details

Single crystal X-ray crystallography. Single crystal data of Trimesic acid Form II was collected Bruker SMART APEX IIsingle crystal X-ray CCD diffractometer having graphitemonochromatized (Mo-K α = 0.71073 Å) radiation at 100 K. The unit cell parameters of Trimesic acid Form II also were collected at various temperatures form 100-400 K with 50 K intervals. The X-ray data acquisition was monitored by the APEX2 program suit.¹The data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs which are an integral part of the APEX2 package. The structures were solved by direct methods and refined by full-matrix least-squares, based on F^2 , using SHELXL². Crystal structures were refined using Olex²-1.0 software³. PLATON⁴was used to prepare material for publication, and Mercury software was utilized for molecular representations and packing diagrams. The refinement of coordinates and anisotropic thermal parameters of nonhydrogen atoms were performed with the full-matrix least-squares method. The hydrogen atoms in OH groups were located from the difference in Fourier maps. The hydrogen atoms of CH were calculated using the riding model. We try to model the residual electron density (0.6), it leads to lager and unusual ellipsoids(size). Hence, the electron density was not taken in the refinement.

Powder X-ray diffraction (PXRD) data were collected using a Rigaku, MicroMax-007HF with high-intensity Microfocus rotating anode X-ray generator. All the crystals were recorded and the data was collected with the help of Control Win software. In the 2θ range between 2–40 The

radiation used was Cu K α (α = 1.54 Å) with a Ni filter, and the data collection was carried out using an Aluminium holder at a scan speed of 1° min⁻¹ and a step size of 0.02°.

Differential scanning calorimetry DSC was performed on DSC Q100 V8.2 Build 268 instrument. For all samples (Trimesic acid Form I and Form II)<5 mg ware taken in aluminum pan closed with a lid and then run from 27°C to 380°C with 10° per min was performed

TGA instrument details: TGA was performed on a Perkin Elmer, TGA 7 analyzer. For all samples (Trimesic acid Form I and Form II) ~5 mg sample was recorded on Alumina crucibles under nitrogen atmosphere at a scan rate of 10 °C min⁻¹ from 30°C to 900°C (nitrogen flow rate 50 mL min⁻¹).

Solid-state NMR instrument details:¹³C CP MAS Solid-state NMR (SSNMR) was collected on Bruker 300MHzNMR spectrometer. 50 mg sample was used for solid-state NMR data.

¹H-NMR instrument details: ¹H-NMR data was collected on BrukerAC-200 with Narrow bore (52mm) instrument. It is equipped with two solution probes (5mm H, C, P, and F, QNP)

FESEM: FESEM images were recorded with the Carl Zeiss SUPRA 55VP FESEM instrument.

Confocal laser scanning microscopy (CLSM): CLSM was done by Axio observer microscope, Clsm 710, Carl Zeiss.

FTIR: FTIR spectra were obtained using a Bruker Optics ALPHAE spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory. IR data are reported with a wavenumber (cm^{-1}) scale.

Activation and gas sorption studies of Form II: N2 adsorption analyses were performed at 77K using a liquid nitrogen bath (77 K) on a QuantachromeQuadrasorb automatic volumetric instrument. Form II (hexagonal) crystals were taken in a glass tube and heated it at 80 °C in vacuum for 5 hours to remove all the gases adsorbed in the pore of Form II (Hexagonal). After that, we have measured the BET surface are

Section S2: Single crystal synthesis of Trimesic acid Form II

Single crystal of Trimesic acid Form II: 50 mg of Trimesic acid was dissolved in 5 ml of THF in 15 ml vial. The homogenous solution was kept for slow evaporation at room temperature (27 °C and humidity 38%). Good quality single crystals, suitable for diffraction, were obtained within 5 days.

	Solvent	Solubility
1	EtOH	Yes
2	МеОН	Yes
3	CHCl ₃	No
4	CH ₃ CN	No
5	DCM	No
6	THF	Yes
7	Propanol	No
8	DMSO	Yes
9	DMF	Yes
10	1,4-Dioxane	Yes (After gentle heating)
11	Benzene	No
12	Toluene	No
13	Hexane	No
14	Nitromethane	No
15	Pyridine	Yes
16	H ₂ O	Yes partially

Section S3: Solvents used for TMA crystallisation

Section S4: Single crystal data of Trimesic acid Form II table and crystal structure

Parameter	Trimesic acid Form II
empirical formula	C ₉ H ₆ O ₆
Formula weight	210.14
CrystalSystem	Trigonal
SpaceGroup	P3 ₁ 21
T (K)	100
<i>a</i> (Å)	16.5042(5)
<i>b</i> (Å)	16.5042(5)
<i>c</i> (Å)	9.6802(3)
α (°)	90
β (°)	90
γ (°)	120
$V(\text{\AA}^3)$	2283.51(16)
$D_{\rm cal}({\rm g~cm}^{-3})$	0.917
Z	6
$R_1[I > 2\sigma(I)]$	0.0772
R int	0.033
wR_2 (all)	0.2819
measured reflections	39403
independent reflections	4841
reflections with $I > 2\sigma(I)$	3931
Goodness of fit	1.178
X-ray diffractometer	BRUKER
CCDC number	1916955



Figure S1: Trimesic acid (Form II), the hexagonal pore diameter is about 14.5 Å



Figure S2: Trimesic acid (Form I), the interpenetrated structure having no pore channel.



Figure S3: Trimesic acid (Form II), the distance between two consecutive layers of the hexagonal framework shows 3.291 Å. It is basically less than two consecutive layers of graphite structure⁵, (an allotrope of carbon).

This structure is patented

Application Number: 16/401,664

Filed date: May 2, 2019 (US patent office)

Publication Number: US2019/0337879A1

Publication date: November 7, 2019



Figure S4: Experimental PXRD of trimesic acid Form I and Form II



Section S6: TGA of Trimesic acid Form I and II

Figure S5: TGA of form I shows 60 % weight loss after 300 °C. Form II shows initial weight loss 10% started at 98 °C till 150 °C then it follows the same path as Form I



Figure S6: DSC of form I shows two endotherms at 309 °C and 368 °C. Form II shows one exotherm at 150 °C and three endotherms at 160 °C, 309 °C and 368 °C.

(a) SSNMR

Form II



Figure S7: SSNMR of Trimesic acid Form II and Form I(* * corresponds to sidebands)

(b) FTIR of Trimesic acid



Figure S8 (a): FTIR of Trimesic acid Form I and II. The IR spectra show a sharp peak at 1706 cm-1 which corresponds to the carbonyl bond (-C=O). The other two stretching frequency at 1412 cm-1 and 1279 cm-1 indicates the presence of C=C bond and C-O bond. The IR graph is similar for two forms which indicate similar bonding between trimesic acid moieties i.e., hydrogen bonding.

Section S9: SEM Images



Figure S9: SEM Images of Form II show hollow hexagonal tube morphology.

Section S10: TEM Images



Figure S10: TEM Images of Form II show that hollow hexagonal tube morphology.

Section S11: FESEM Images of Ostwald Ripening



Figure S11: FESEM Images of Form II show that hollow hexagonal tube formation via Ostwald Ripening. a) solid hexagonal tube undergoing Ostwald ripening process with time, changing via b) to c) and finally to hollow hexagonal tube d).



Section S12: Nitrogen adsorption analysis

Figure S12: Nitrogen adsorption isotherm of Form II (hexagonal).

Section S13: PXRD after dye adsorption



Figure S13: PXRD of Form II after Rhodamine B dye adsorption indicating the intact crystal structure.

Section S14: Variable temperature measurement of TMA (Form II) Single Crystal



Figure S14: Variable temperature measurements of TMA Form II single crystal. It shows that there is a linear expansion of the *c* axis only and *a* and *b* axes remain constant. It is due to 2D hexagonal layers of TMA that are staked along only *c*-axis which are connected *via* flexible weak $\Pi \cdots \Pi$ interactions whereas in the *ab* plane molecules are connected *via* strong (rigid) acid-acid homodimer (hydrogen bonds).

Section S15: Lattice energy calculations

Beginning from crystal structures of both Form I and Form II of TMA, the hydrogen atoms were checked and manually repaired, before calculation of the lattice stabilization energies. Atomic positions and cell sizes of both forms of TMA COF were optimized using the Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB) method as implemented in DFTB+ version 18.2. Both the mio-0-1 [DOI: 10.1103/PhysRevB.58.7260] (including Lennard Jones dispersion) and 3ob-3-1 [DOI: 10.1021/ct300849w] (including DftD3 dispersion) were tested.The 3ob-3-1 parameters yield very high binding energies and so the mio-0-1 parameters were chosen to proceed. The SCC-DFTB/mio-0-1 calculations indicate that Form I is 26.5 kJ/mol more stable than Form II.

	mio			
	no lattice opt		lattice opt	
	Form I	Form II	Form I	Form II
Formula units TMA_mono Total Mermin free energy	48 -37.638471	6	48	6
Energy H0:	-1872.2181	-233.99558	-1871.6787	-233.95574
Energy SCC:	3.50762755	0.43651587	3.54300698	0.43890918
Total Electronic energy:	-1868.7105	-233.55907	-1868.1357	-233.51683
Repulsive energy:	55.9593103	6.97286426	55.2964722	6.91500244
Dispersion energy:	3.33123306	0.46926683	3.27104839	0.46203533
Total energy:	-1809.4199	-226.11694	-1809.5682	-226.13979
Total Mermin free energy:	-1809.4199	-226.11694	-1809.5682	-226.13979
DFTB Energy	-1809.4199	-226.11694	-1809.5682	-226.13979
LJ Energy	3.33123306	0.46926683	3.27104839	0.46203533
НОМО	-5.77127	-6.58502	-5.83347	-6.62233
Fermi Level	-4.505	-4.9539	-4.5051	-4.9652
LUMO	-3.23877	-3.32287	-3.17676	-3.30807

a	26.52	16.5042	26.278	16.8858	
Ь	16.42	16.5042	16.6372	16.7972	
с	26.551	9.6802	26.4001	9.9244	
α	90	90	90.8491	89.8832	
β	91.53	90	83.8793	90.0927	
γ	90	120	89.7485	119.613	
HOMO-LUMO	2.5325	3.26215	2.65671	3.31426	
Per unit stabilization(kJ/mol):	-151.69523	-125.19647	-159.80471	-135.19752	
	3ob-3-1				
	no lattice	opt	lattice opt		
	Form I	Form II	Form I	Form II	
Formula units	48	6	48	6	
TMA_mono Total Mermin free					
energy	-37.4566				
En anon 110.	1926.0	220 624	1026 71	220 592	
Energy H0:	-1830.9	-229.024	-1830./1	-229.383	
Energy SCC: Total Electronic energy	3./249/	0.448892	5./31232 1922 57	0.430401	
Populsive energy:	-1055.79	-229.247	-1055.57	-229.193	
Dispersion energy:	20.37393	0.31741	20.47098	0.33721	
Total energy:	-2.7702	-0.31/41	-5.11800	-0.55721	
Total Mermin free energy:	-1807.98	-225.955	-1808.21	-225.900	
Total Merinin free energy.	-1807.98	-223.933	-1808.21	-223.900	
DFTB Energy	-1807.98	-225.953	-1808.21	-225.966	
LJ Energy	-2.7702	-0.31741	-3.11806	-0.33721	
НОМО	-6.90943	-7.21363	-6.94339	-7.26772	
Fermi Level	-5.2959	-5.5432	-5.3412	-5.6262	
LUMO	-3.68233	-3.87284	-3.73897	-3.98477	
a	26.52	16.5042	25.3501	16.5978	
b	16.42	16.5042	16.3534	16.6636	
c	26.551	9.6802	25.5085	9.03425	
α	90	90	90.9618	90.069	
β	91.53	90	76.0728	89.9251	

γ	90	120	89.2348	118.975
HOMO-LUMO	3.2271	3.34079	3.20442	3.28295
Per unit stabilization(kJ/mol):	-550.558	-530.696	-563.184	-536.796

Section 16: Protocol is used for binding energy calculations:

To determine the likely binding motif of Rhodamine B within the pore of Form II of TMA, the Kick3 [DOI: 10.1002/jcc.23420] the procedure was used. A single Rhodamine B molecule, including a Cl⁻ counterion was inserted into a 2x2x4 supercell of TMA Form II. 100 initial starting geometries were generated and optimized using DFTB+ as above and the halorg-0-1 parameters [DOI: 10.1021/ct4001922]. The global minimum structure thus obtained has a binding energy of 314 kJmol⁻¹.

ID	E (a.u.)	delta E (kJ/mol)	Binding E (kJ/mol)
K0027	-3695.4944	0	-313.8
K0088	-3695.4914	7.86	-305.9
K0057	-3695.4905	10.36	-303.4
K0045	-3695.4896	12.70	-301.1
K0096	-3695.4886	15.22	-298.6
K0067	-3695.4885	15.38	-298.4

Energies of the 6 lowest energy stochastically generated Rhodamine B @ TMA Form II structures.

In some cases, it was noted that the Cl⁻ ion could disrupt the TMA framework, without significant energy penalty (see the below figure S13 b of FormII_K0057). However, the main binding motif in all low energy structures involved the hydrogen from the carboxyl group, with $H_{Rhodamine B}$...O_{TMA} distances of between 1.8 and 2.1Å.



Figure S15: (a) Form I has four interpenetrating lattices and each lattice is colored (red/blue/green/yellow). The interlayer distance is about 3.65 Å. (b) The dimension of the dye molecule indicates that it can fit within the pore of Form II. Form I cannot take up the dye

molecule as it does not have any continuous channels in the crystalline lattices. So the interaction of the dye absorption could be only on the crystallite surface. In Form I, there must be a lot more work to disrupt the crystal to adsorb Rhodamine-B whereas in Form II, the pore already exists and so there is less disruption to the hydrogen bond network. So, we posit that for Form I, absorption of the dye molecule is mostly on the surface of the crystals where for Form II the dye is absorbed both on the surface as well as in the pores of the crystalline lattice which are accessible. This can validate the experimental observations.



Figure **S16**: Snapshots of Rhodamine-B in the crystalline lattice of TMA (Form II) and the corresponding ID are on the top. (a) Crystal packing view along the a-axis (b) crystal packing view along the c-axis.

Section 17: Hot Stage Microscopy

Hot Stage Microscopy (HSM) TMA Form I





330°C



366°C



395°C

.

403°C

Hot Stage Microscopy (HSM) TMA Form II



Figure S17: HSM image of Form I and Form II of TMA from 35 °C to 403 °C.





Figure **S18**: PXRD of Form II (Hexagonal) at 160°C is equivalent to Form I and it is compared along with Form I and Form II.

References:

- 1. Bruker APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA. 2006.
- 2. Sheldrick, G. M. SHELXT Integrated space-group and crystal-structure determination Acta Cryst. 2015, D65, 148–155.
- Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. OLEX2: a complete structure solution, refinement and analysis program *Appl. Cryst.* 2009, 42, 339–341.
- 4. Spek, A. L. *PLATON* SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors *Acta*. *Cryst.* **2009**, *C71*, 3–8.
- 5. Ergun, S. Structure of carbon *Carbon* **1968**, *6*, 41-159.