

## Supporting Information

# Generation of 2D Organic Microsheets from Protonated Melamine Derivatives: Suppression of the Self Assembly of a Particular Dimension by Introduction of Alkyl Chains

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## 1. Experimental Section

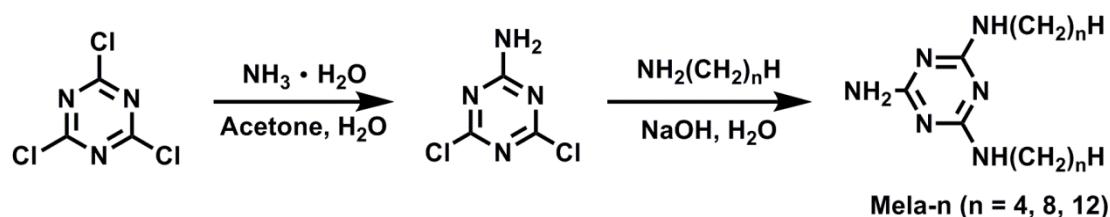
### 1.1 Materials

Cyanuric chloride (Sigma-Aldrich, 99%), 1-dodecylamine (Aladdin, 98%), 1-octylamine (Aladdin, 99%), n-butylamine (Aladdin, 99%), hydrochloric acid (Beijing Chemical Works, AR), hydrobromic acid (Alfa Aesar, ACS), triethylamine (Aladdin, 99.5%) and dichloromethane (Aladdin, Super dry, H<sub>2</sub>O ≤ 0.004%) were used as received.

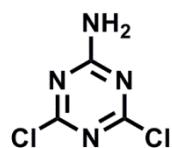
### 1.2 Synthesis and instrumentation

The synthetic route of Mela-n ( $n=4, 8, 12$ ) is shown in Scheme S1.

**Scheme S1:** The synthetic route of Mela-n ( $n=4, 8, 12$ ).



### 2-Amine-4,6-dichloro-1,3,5-triazine

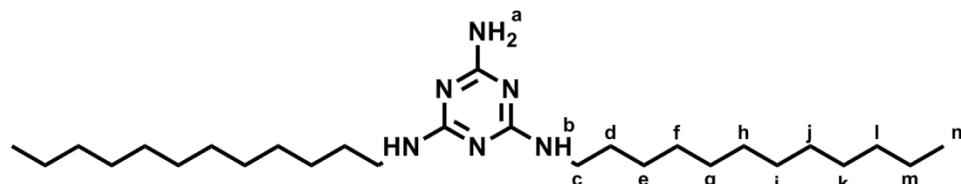


The synthesis of 2-amino-4,6-dichloro-1,3,5-triazine was performed according to a standard procedure. [J. Am. Chem. Soc., 1951, 73, 2981] A solution of cyanuric chloride (2.3676 g, 12.8 mmol) in 20 mL of acetone was added dropwise to 20 mL of well-stirred ice water to get a white slurry. 26 mL of 1.0 M ammonia water (26 mmol) was added dropwise at 0 °C for 1.5 h. After

stirring at room temperature for another 0.5 h, the white precipitate was filtered and washed chloride-free with cold water. The product was dried to a constant weight in vacuum to get a white powder (1.4 g, 67%).

ESI-MS: 165.3, 167.2 ([M+H]<sup>+</sup>, calcd:165.0, 167.0).

### N2,N4-didodecyl-1,3,5-triazine-2,4,6-triamine (Mela-12)



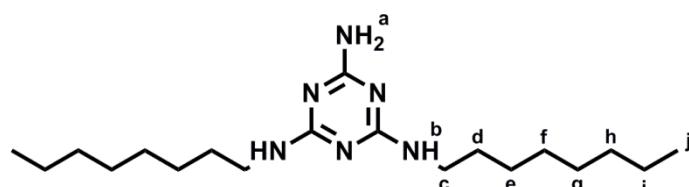
The synthesis of Mela-12 was performed according to a standard procedure. [J. Am. Chem. Soc., 1998, **120**, 4094] 2-Amino-4,6-dichloro-1,3,5-triazine (0.94 g, 5.7 mmol) and 1-dodecanamine (4.2 g, 23 mmol) was mixed in 20 mL of water. After stirring for 0.5 h, sodium hydroxide (0.46 g, 12 mmol) in 20 mL of water was added, and the mixture was refluxed at 120 °C for 16 h. After cooling, the crude product was extracted with chloroform, the organic layer was washed with water three times and dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed in vacuum. The crude product was purified by column chromatography (20:1 dichloromethane/methanol) to afford a white powder (1.8 g, 68%).

<sup>1</sup>H-NMR spectra were recorded on a JOEL JNM-ECA300 spectrometer (300 MHz, CDCl<sub>3</sub>, ppm): δ 4.95-4.50 (br, 4H, NH<sup>a</sup>, NH<sup>b</sup>), 3.45-3.25 (m, 4H, CH<sub>2</sub><sup>c</sup>), 1.63-1.45 (m, 4H, CH<sub>2</sub><sup>d</sup>), 1.41-1.01 (m, 36H, CH<sub>2</sub><sup>e+f+g+h+i+j+k+l+m</sup>), 0.88 (t, 6.7 Hz, 6H, CH<sub>3</sub><sup>n</sup>).

<sup>13</sup>C-NMR spectra were recorded on a JOEL JNM-ECX400 spectrometer (100 MHz, CDCl<sub>3</sub>, ppm): δ 40.83, 32.06, 29.91, 29.81, 29.78, 29.77, 29.74, 29.51, 29.50, 27.05, 22.84, 14.27 (The three quaternary carbons of the triazine ring do not appear in the <sup>13</sup>C-NMR spectra for Mela-12, Mela-8, or Mela-4).

ESI-MS: 463.5 ([M+H]<sup>+</sup>, calcd:463.4).

### N2,N4-dioctyl-1,3,5-triazine-2,4,6-triamine (Mela-8)

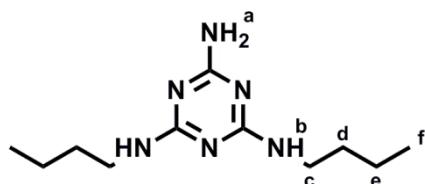


This compound was synthesized by adopting a similar procedure used for Mela-12. White powder; Yield: 31%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 4.93-4.52 (br, 4H, NH<sup>a</sup>, NH<sup>b</sup>), 3.48-3.18 (m, 4H, CH<sub>2</sub><sup>c</sup>),

1.63-1.44 (m, 4H, CH<sub>2</sub><sup>d</sup>), 1.43-1.01 (m, 20H, CH<sub>2</sub><sup>e+f+g+h+i</sup>), 0.88 (t, 6.7 Hz, 6H, CH<sub>3</sub><sup>j</sup>).  
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 40.87, 31.96, 29.86, 29.45, 29.39, 27.03, 22.80, 14.25.  
ESI-MS: 351.4 ([M+H]<sup>+</sup>, calcd: 351.3).

### N2,N4-dibutyl-1,3,5-triazine-2,4,6-triamine (Mela-4)



This compound was synthesized by adopting a similar procedure used for Mela-12. White powder; Yield: 77%.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 5.32-4.68 (br, 4H, NH<sub>2</sub><sup>a</sup>, NH<sup>b</sup>), 3.52-3.21 (m, 4H, CH<sub>2</sub><sup>c</sup>), 1.68-1.47 (m, 4H, CH<sub>2</sub><sup>d</sup>), 1.47-1.22 (m, 4H, CH<sub>2</sub><sup>e</sup>), 0.94 (t, 7.2 Hz, 6H, CH<sub>3</sub><sup>f</sup>).  
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 40.53, 31.98, 20.17, 13.96.  
ESI-MS: 239.2 ([M+H]<sup>+</sup>, calcd: 239.2).

### Transmission electron microscopy (TEM)

TEM experiments were performed at 80 kV with a HITACHI H-7650B transmission electron microscope. The samples were prepared by dripping 5 μL of 1.0 mM Mela-n•HCl (n=4, 8, 12) assembly suspensions on carbon-coated copper grids and drying in air.

### Atomic force microscopy (AFM)

AFM images were obtained on a commercial MultiMode 8 Atomic Force Microscope with ScanAsyst mode on glass substrate, using silicon cantilevers (ScanAsyst-Air from Bruker). The sample was prepared by dripping 15 μL of 1.0 mM Mela-12•HCl assembly suspension on glass substrate and drying in air.

### Wide-angle X-ray diffraction (WAXD)

WAXD data was collected at room temperature on a Rigaku D/max 2500 diffractometer with Cu Kα radiation. The samples were prepared by successively dripping 15 μL of 1.0 mM Mela-n•HCl (n=4, 8, 12) assembly suspensions on glass substrates and drying in air for dozens of times.

### X-ray crystallography

The X-ray crystallography experiment was performed on an Oxford Diffraction Gemini E diffractometer. The single crystal of Mela-4•HCl was obtained by evaporation of HCl (6 M)

into a solution of Mela-4 (10 mM) in dichloromethane.

### FT-IR spectra

FT-IR spectra were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer and the results were collected at 16 scans with a spectral resolution of  $1\text{ cm}^{-1}$ . The samples were prepared by dripping 15  $\mu\text{L}$  of 1.0 mM Mela-12 solution or 15  $\mu\text{L}$  of 1.0 mM Mela-12•HCl assembly suspension on KBr substrates and drying in air for several times.

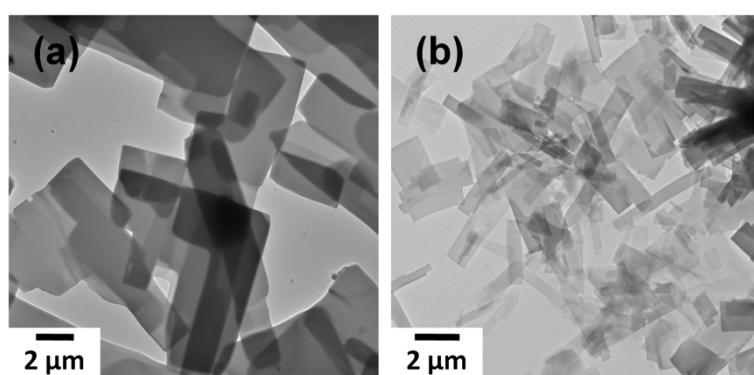
### UV-Vis spectra

UV-Vis spectra were obtained using a HITACHI U-3010 Spectrophotometer.

## 2. Results and Discussion

### 2.1 Microsheets formed by Mela-8•HCl and Mela-4•HCl

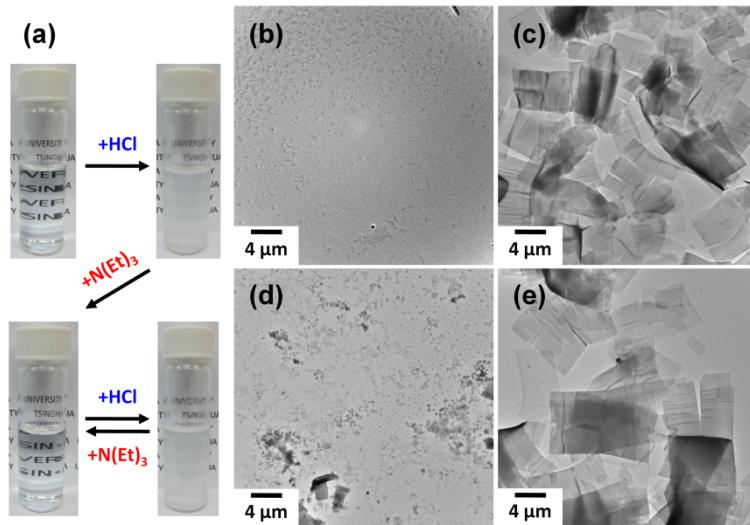
The self-assembly of Mela-n•HCl ( $n=8, 4$ ) leads to the formation of 2D microsheets. The TEM images of the prepared microsheets with rectangular shape are shown in Fig. S1.



**Fig. S1** TEM images of Mela-8•HCl (a) and Mela-4•HCl (b) microsheets with rectangular shape.

### 2.2 The assembly and disassembly of microsheets

The formation and decomposition of Mela-12•HCl assemblies can be tuned by successive addition of HCl and triethylamine, and this process can be directly observed from the turbidity change of the solution (Fig. S2a). The assembly and disassembly of microsheets can be further demonstrated by TEM (Fig. S2b-S2e).

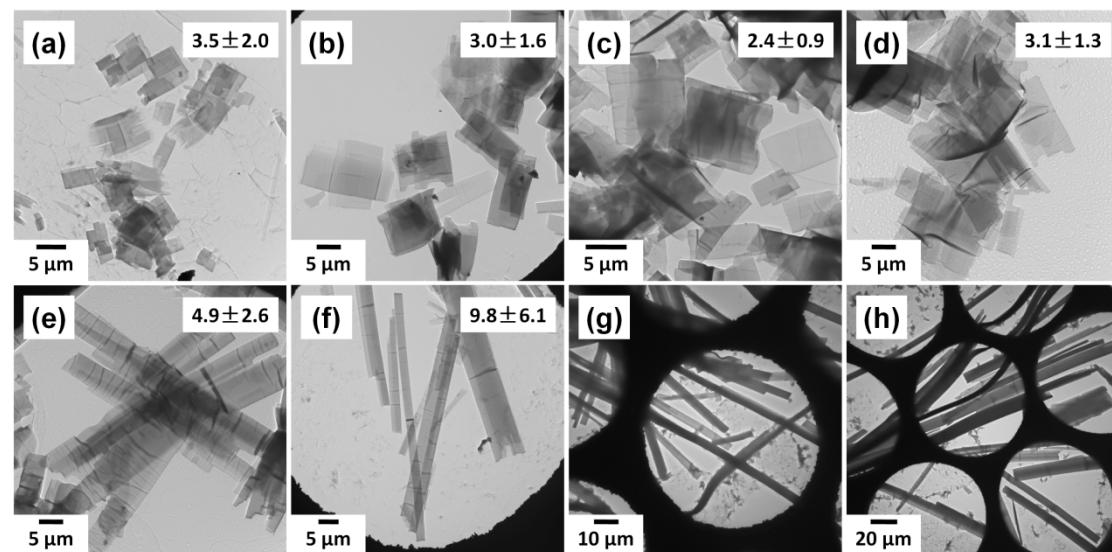


**Fig. S2** (a) The turbidity of Mela-12 solution changes with addition of HCl and triethylamine. (b) TEM image of Mela-12. (c) Microsheets formed after addition of HCl. (d) Microsheets disappeared after addition of triethylamine. (e) Microsheets formed again after addition of HCl.

### 2.3 Microsheets formed with different molar ratio of HCl and Mela-12

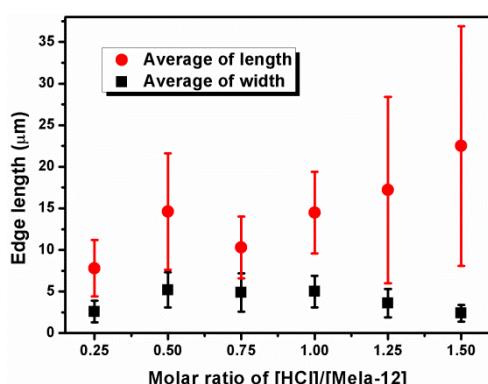
The aspect ratio of the rectangular microsheets formed by Mela-12•HCl changes with different molar ratio of Mela-12 and HCl, as indicated by TEM results in Fig. S3.

Excess amount of HCl increases the length of the rectangular microsheets and decreases the width of the microsheets, as shown in Fig. S4.



**Fig. S3** TEM images of rectangular microsheets formed by Mela-12•HCl with molar ratio of  $[HCl]/[Mela-12] =$  (a) 0.25; (b) 0.50; (c) 0.75; (d) 1.00; (e) 1.25; (f) 1.50; (g) 1.75; (h) 2.00. The average values of aspect ratio are statistically analyzed and listed on the top right corner of each image. For molar ratio greater than 1.50, the assemblies are even much longer than the grid, which makes it difficult for aspect ratio analysis. The concentration of Mela-12 is 1.0 mM for

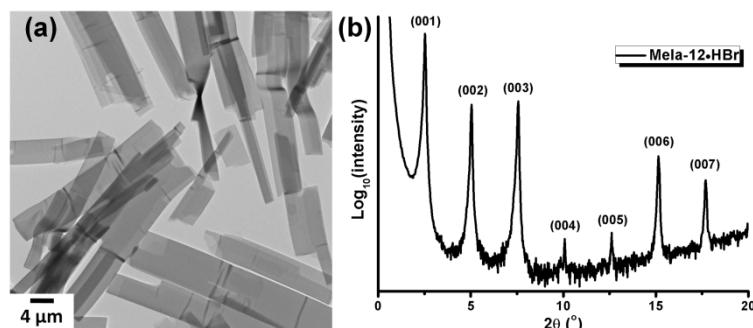
all samples.



**Fig. S4** Edge length of the rectangular microsheets generated from different molar ratio of  $[HCl]/[Mela-12]$ . For  $[HCl]/[Mela-12] > 1$ , the average length of the microsheets increases and the average width decreases.

#### 2.4 Microsheets formed by Mela-12•HBr

The self-assembly of Mela-12•HBr leads to the formation of 2D microsheets similar to Mela-12•HCl. The TEM image of the prepared microsheets is shown in Fig. S5a. WAXD pattern for the drop-cast film of Mela-12•HBr in Fig. S5b indicates the existence of lamellar structure with d-spacing of 3.50 nm.



**Fig. S5** (a) TEM image of 2D microsheets formed by Mela-12•HBr. (b) WAXD pattern for the drop-cast film of Mela-12•HBr.

## 2.5 Single crystal structure of Mela-4•HCl

**Table S1** Details of Data Collection, Processing and Structure Refinement

Sample code	<b>EXP_346</b>		
Molecular formula	C <sub>11</sub> H <sub>23</sub> N <sub>6</sub> ·Cl		
Molecular weight	274.80		
Color and habit	colorless plate		
Crystal size	0.05 × 0.3 × 0.3 mm		
Crystal system	triclinic		
Space group	P $\bar{1}$ (No. 2)		
Unit cell parameters	$a = 4.4289(4)$ Å	$\alpha = 101.395(8)$ °	
	$b = 9.6455(18)$ Å	$\beta = 95.279(8)$ °	
	$c = 17.6718(18)$ Å	$\gamma = 92.673(7)$ °	
	$V = 735.27(17)$ Å <sup>3</sup>	$Z = 2$	$F(000) = 296$
Density (calcd)	1.241 g/cm <sup>3</sup>		
Diffractometer	Bruker P4		
Radiation	graphite-monochromatized Mo K $\alpha$ , $\lambda = 0.71073$ Å		
Temperature	295±2K		
Scan type	ω-scan		
Data collection range	$-5 < h < 5$ , $-11 < k < 11$ , $-21 < l < 11$ ; $\theta_{\max} = 26.0$ °		
Reflections measured	Total: 4647	Unique ( $n$ ): 2901	Observed [ $I \geq 2\sigma(I)$ ]: 2228
Absorption coefficient	0.255 mm <sup>-1</sup>		
Minimum and maximum transmission	0.885, 1.000		
No. of variables, $p$	206		
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.001P)^2 + 1.5P}$		$P = (F_o^2 + 2F_c^2)/3$
$R1 = \frac{\sum   F_o - F_c  }{\sum  F_o }$ (for all reflections)	0.1011		0.0772 (for observed data)
$wR2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}}$ (for all reflections)	0.1493		0.1406 (for observed data)
$Goof = S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{n - p}}$	1.236		
Largest and mean $\Delta/\sigma$	0.000, 0.000		
Residual extrema in final difference map	-0.374 to 0.709 e Å <sup>-3</sup>		

