Supplementary Information

Self-assembling 1D core/shell microrods by the introduction of additives: a one-pot and shell-tunable method

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1. Results and Discussion

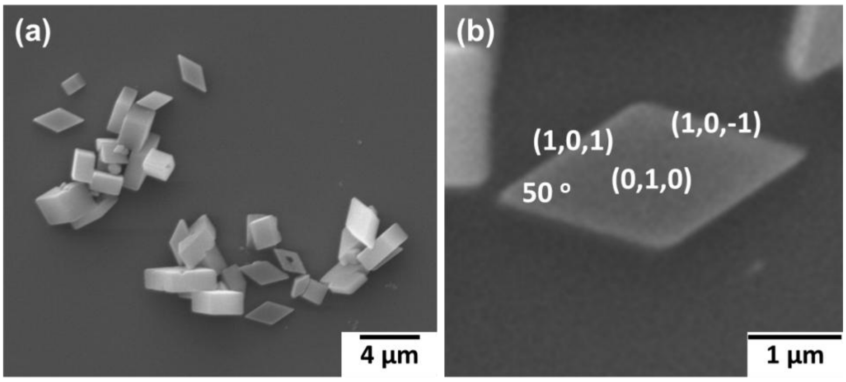


Figure S1. (a) SEM image of Mela-DM•HCl. (b) Enlarged SEM image of Mela-DM•HCl microstructure showing rhombus-shaped base with a vertex angle of 50^{o}, the exposed crystal faces are (0,1,0), (1,0,1) and (1,0,-1).

The exposed crystal faces of Mela-DM•HCl microstructures were determined according to the crystal structure of Mela-DM•HCl.

For the orthorhombic crystal system ($\alpha=\beta=\gamma=90^{o}$, $a\neq b\neq c$), the interfacial angle ϕ of crystal faces (h_1, k_1, l_1) and (h_2, k_2, l_2) can be calculated according to the following formula:

$$\cos\emptyset = \left(\frac{h_1h_2}{a^2}+\frac{k_1k_2}{b^2}+\frac{l_1l_2}{c^2}\right)\Big/\sqrt{\left(\frac{h_1^2}{a^2}+\frac{k_1^2}{b^2}+\frac{l_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2}+\frac{k_2^2}{b^2}+\frac{l_2^2}{c^2}\right)}$$

For Mela-DM•HCl crystal, $\alpha=\beta=\gamma=90^{o}$, a=6.4782(Å), b=9.5193(Å), c=14.311(Å).

The Mela-DM•HCl microstructures show two rhombus-shaped bases with vertex angles of 50^{o} ($\phi_1=50^{o}$), and the four sides are perpendicular to the bases ($\phi_2=\phi_3=90^{o}$).

Therefore, according to the previous formula, the bases correspond to the (0,1,0) crystal face, while the sides correspond to the (1,0,1) and (1,0,-1) faces.

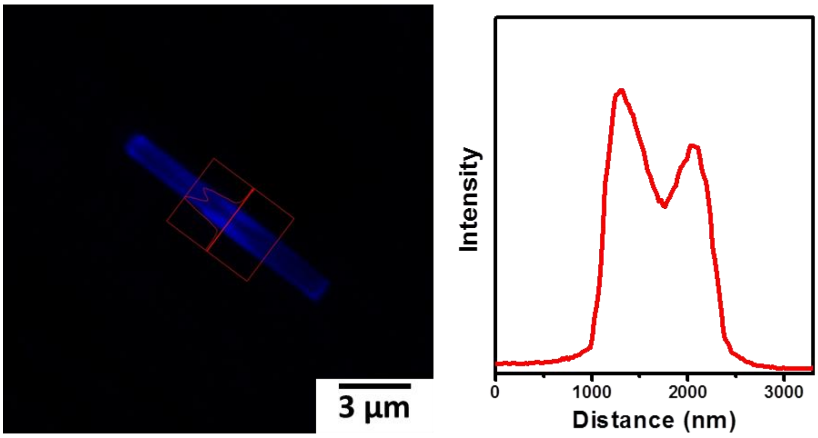


Figure S2. Confocal fluorescence microscopy image of Mela-DM/Mela-M-Pym(5%)•HCl (1 mM). The fluorescence intensity in the periphery of the microrod is stronger than the middle. The microrods of Mela-DM/Mela-M-Pym(10%)•HCl (1 mM) are too narrow to differentiate the periphery from the middle.

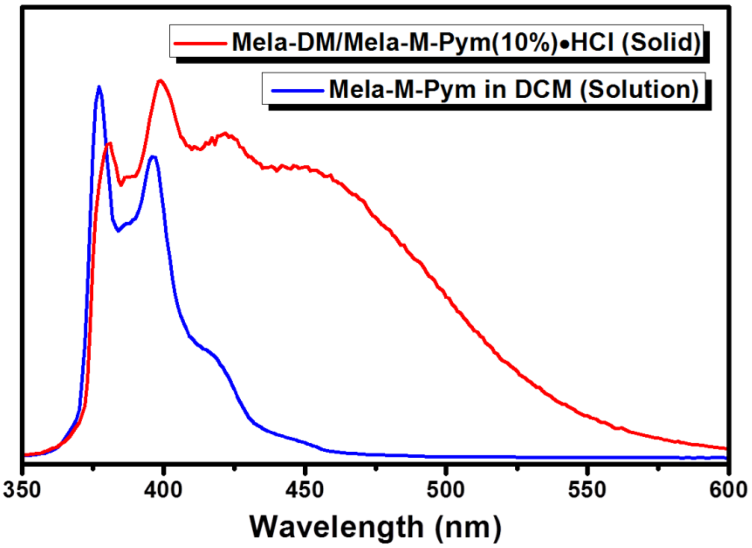


Figure S3. Fluorescence spectra of Mela-DM/Mela-M-Pym(10%)•HCl microrods and Mela-M-Pym solution in DCM (0.02 mM).

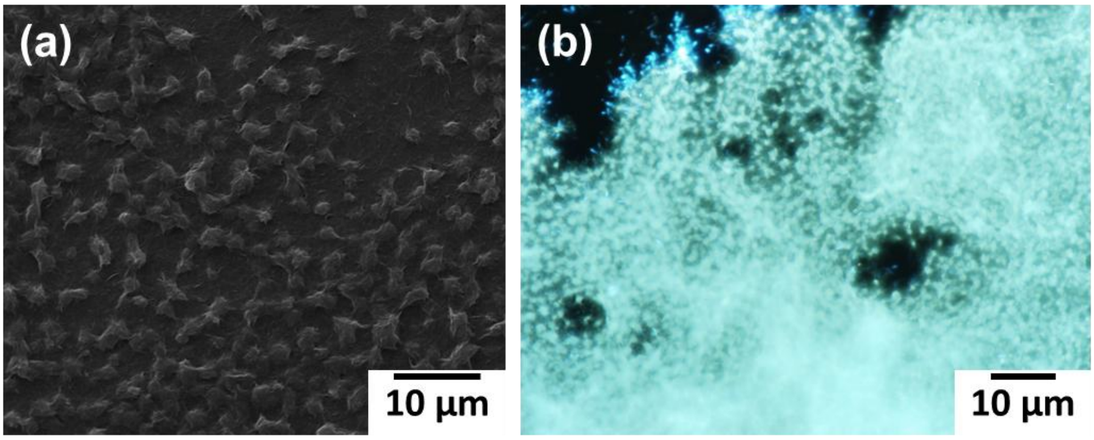


Figure S4. (a) SEM and (b) fluorescence microscopy images of Mela-M-Pym•HCl (0.5 mM).

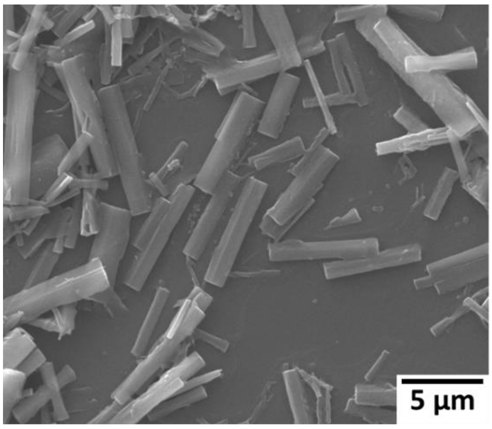


Figure S5. SEM image of Mela-DM/Mela-M-Pym(10%)•HCl (1 mM) microrods prepared at -20 ^{o}C.

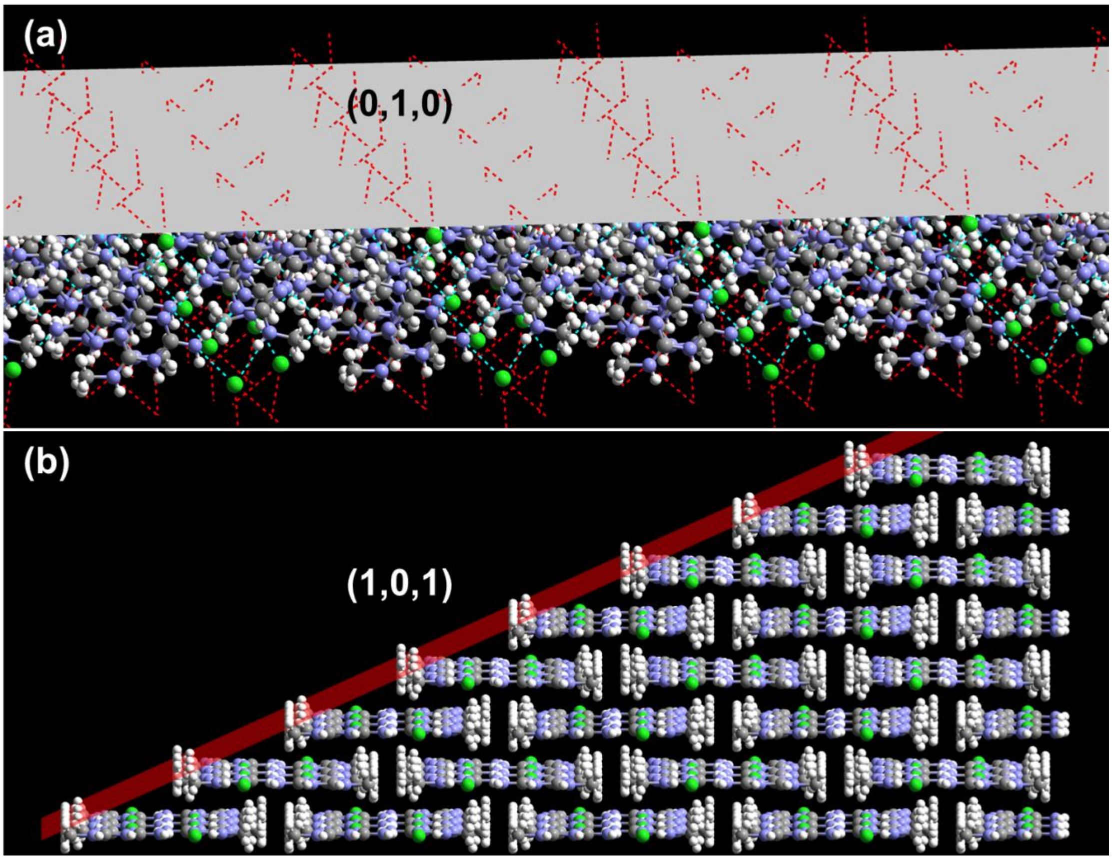


Figure S6. Crystal faces of (a) (0,1,0) and (b) (1,0,1). Abundant hydrogen bonding sites (red dashed lines) are exposed on (0,1,0) face (grey plane), while only methyl groups are exposed on (1,0,1) face (red plane).

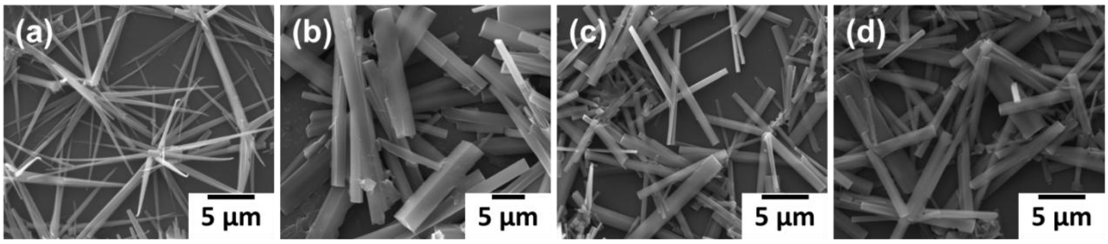


Figure S7. SEM images of (a) Mela-DM/Mela-M-DNI4(10%)•HCl (1 mM); (b) Mela-DM/Mela-M-Pm(10%)•HCl (1 mM); (c) Mela-DM/Mela-M-2Nm(10%)•HCl (1 mM); (d) Mela-DM/Mela-M-3Tm(10%)•HCl (1 mM).

Table S1. Length/width ratio of microrods prepared with different additives.

Additives*	Mela-M-Pym	Mela-M-Pm	Mela-M-2Nm	Mela-M-3Tm
Length/width ratio	29.7 ±11.4	12.0 ±5.1	15.7 ±6.3	15.5 ±5.0

*The width of microrods prepared with Mela-M-NDI4 is not uniform, so the length/width ratio cannot be calculated.

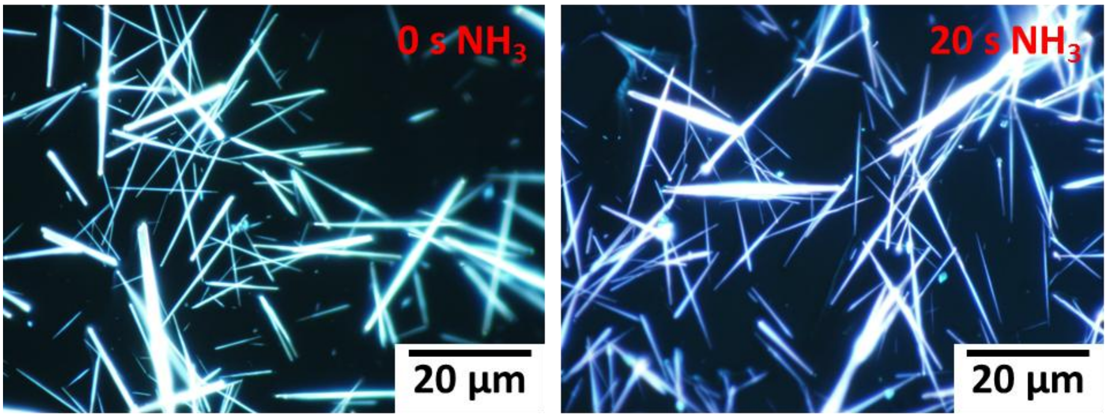


Figure S8. Fluorescence microscopy images of Mela-DM/Mela-M-Pym(10%)•HCl (1 mM) before and after exposure to ammonia for 20 s.

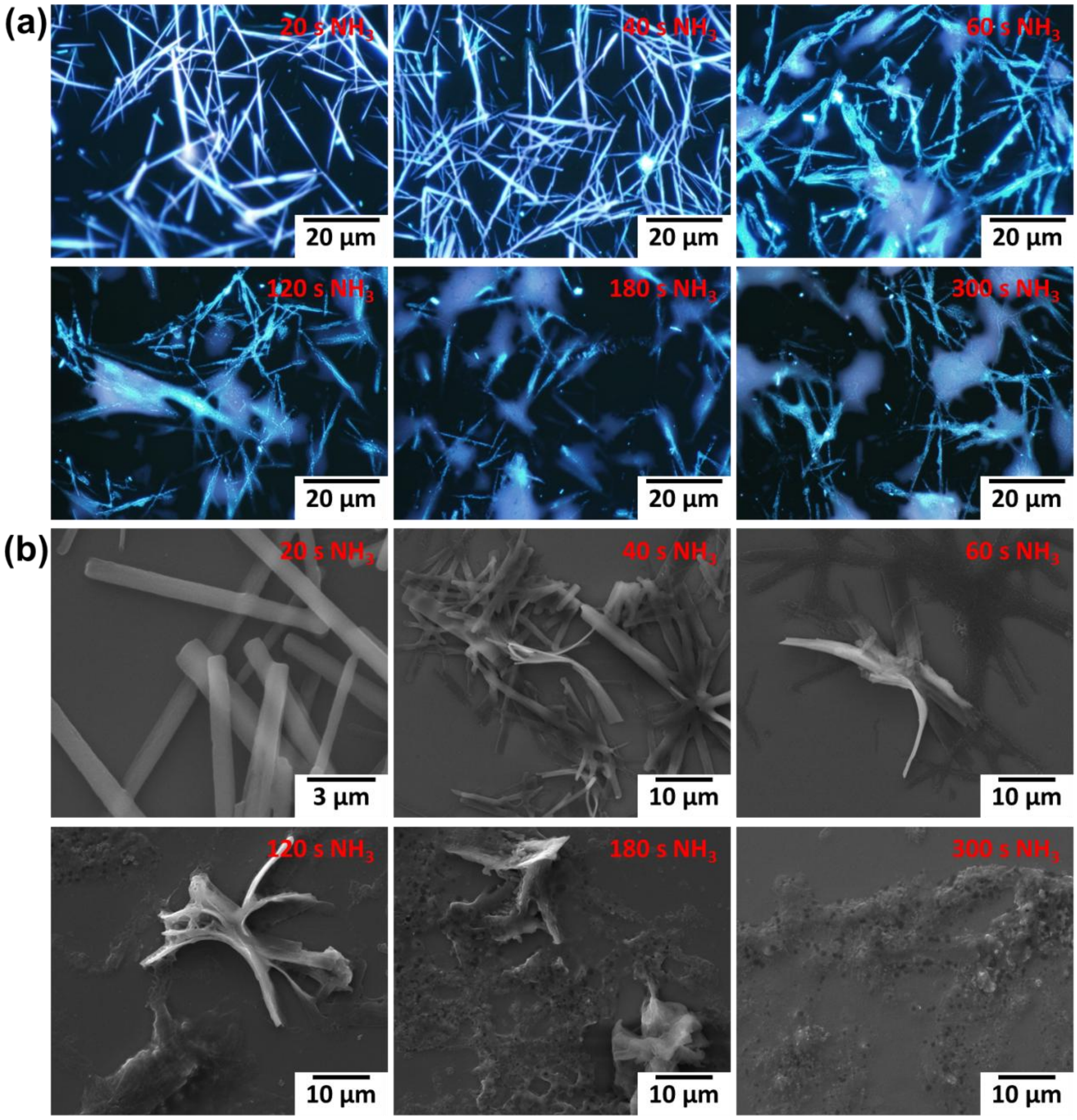


Figure S9. (a) Fluorescence microscopy images and (b) SEM images of Mela-DM/Mela-M-Pym(10%)•HCl (1 mM) with increased exposure time to ammonia.

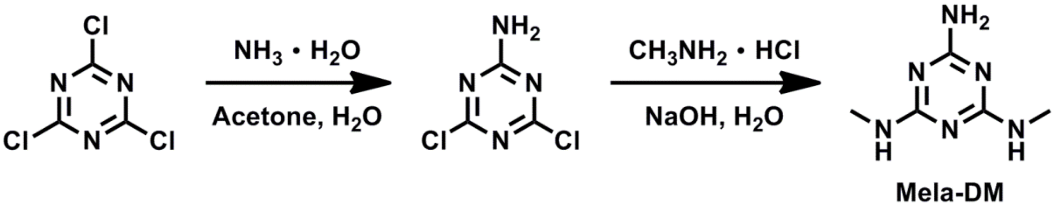
2. Experimental Section

2.1 Materials

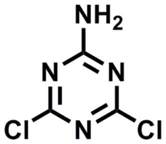
Cyanuric chloride (Sigma-Aldrich, 99%), methylamine hydrochloride (Alfa Aesar, 99%), 1-pyrenemethylamine hydrochloride (Sigma-Aldrich, 95%), benzyl amine (Aladdin, AR), 3-thiophenemethylamine (Aladdin, >97%), 2-naphthalenemethylamine hydrochloride (Bide Pharmatech, >95%), naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (Alfa Aesar, 97%), ethylenediamine (Alfa Aesar, 99%), di-tert-butyl dicarbonate (Aladdin, 99%), n-butylamine (Aladdin, 99%), trifluoroacetic acid (J&K Chemical, 99%), sodium hydroxide (Beijing Chemical Works, AR), hydrochloric acid (Beijing Chemical Works, AR), ammonia solution (25-28%, Sinopharm Chemical Reagent, AR), nitrobenzene (Beijing Chemical Works, AR) and dichloromethane (J&K Chemical, Super dry) were used as received.

2.2 Synthesis and instrumentation

Scheme S1. The synthetic route of Mela-DM.

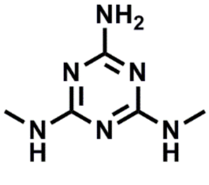


2-Amine-4,6-dichloro-1,3,5-triazine



The synthesis of 2-amino-4,6-dichloro-1,3,5-triazine was performed according to a procedure described in the literature [*J. Am. Chem. Soc.*, 1951**, 73**, 2981].

N2,N4-dimethyl-1,3,5-triazine-2,4,6-triamine (Mela-DM)



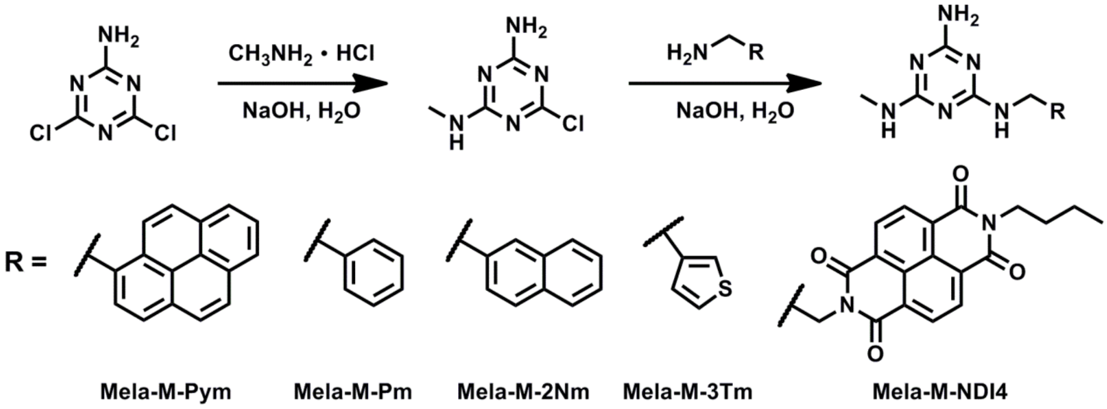
2-Amino-4,6-dichloro-1,3,5-triazine (0.25 g, 1.5 mmol) and methylamine hydrochloride (0.44 g, 6.5 mmol) was mixed in 20 mL of water, sodium hydroxide (0.26 g, 6.5 mmol) in 5 mL of water was added. After stirring at room temperature for 0.5 h, sodium hydroxide (0.12 g, 3.0 mmol) in 5 mL of water was added, and the mixture was refluxed at 110 ^{o}C for 12 h. After cooling, water was removed in vacuum. The residue was absorbed on silica gel, purified by column chromatography (15:1 dichloromethane/methanol) to afford a white powder (0.19 g, 82%).

^{1}H-NMR spectra were recorded on a JOEL JNM-ECA300 spectrometer (300 MHz, D_2O, ppm): δ 2.83 (s, 6H).

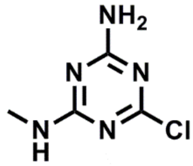
^{13}C-NMR spectra were recorded on a JOEL JNM-ECA400 spectrometer (100 MHz, D_2O, ppm): δ 26.89 (The three quaternary carbons on the triazine ring do not appeared in the ^{13}C-NMR spectra).

ESI-MS: 155.11 ($[M+H]^+$, calcd: 155.10).

Scheme S2. The synthetic route of Mela-M-R (R= Pym, Pm, 2Nm, 3Tm, NDI4).



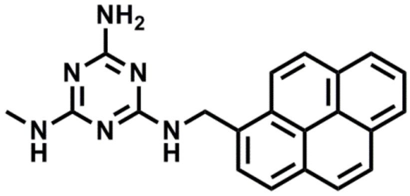
6-Chloro-N2-methyl-1,3,5-triazine-2,4-diamine



2-Amino-4,6-dichloro-1,3,5-triazine (0.35 g, 2.1 mmol) and methylamine hydrochloride (0.22 g, 3.3 mmol) was mixed in 30 mL of water, sodium hydroxide (0.13 g, 3.3 mmol) in 5 mL of water was added. After stirring at room temperature for 0.5 h, sodium hydroxide (0.09 g, 2.3 mmol) in 5 mL of water was added, and the mixture was stirred at 30 °C for 5 h. The precipitate was filtered, washed with water (3*10 mL), dried in vacuum to afford a white powder (0.32 g, 95%). The product was used for the next step without further purification.

ESI-MS: 160.04, 162.04 ($[M+H]^+$, calcd: 160.04, 162.04).

Mela-M-Pym



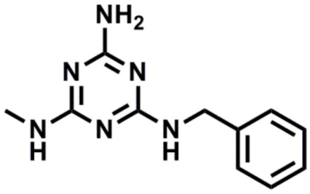
6-Chloro-N2-methyl-1,3,5-triazine-2,4-diamine (0.31 g, 1.9 mmol) and 1-pyrenemethylamine hydrochloride (0.96 g, 3.6 mmol) was mixed in 30 mL of water, sodium hydroxide (0.15 g, 3.8 mmol) in 5 mL of water was added. After stirring at room temperature for 0.5 h, sodium hydroxide (0.08 g, 2.0 mmol) in 5 mL of water was added, and the mixture was refluxed at 110 ^{o}C for 12 h. After cooling, the precipitate was filtered, absorbed on silica gel, purified by column chromatography (20:1 dichloromethane/methanol) twice to afford a white powder (0.37 g, 55%).

^{1}H-NMR (300 MHz, DMSO-d6, ppm): δ 8.55-7.95 (m, 9H), 7.45-7.05 (br, 1H), 6.55-5.90 (br, 3H), 5.18 (d, 6.0 Hz, 2H), 2.85-2.60 (br, 3H).

^{13}C-NMR (100 MHz, DMSO-d6, ppm): δ 167.08, 166.62, 166.09, 134.44, 130.83, 130.34, 129.70, 127.73, 127.45, 127.30, 127.12, 126.73, 126.14, 125.76, 125.08, 125.02, 124.66, 124.00, 123.28, 41.43, 27.24.

ESI-MS: 355.17, 356.17 ($[M+H]^+$, calcd: 355.17, 356.17).

Mela-M-Pm

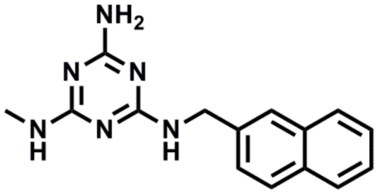


This compound was synthesized from 6-chloro-N2-methyl-1,3,5-triazine-2,4-diamine and benzyl amine following the similar procedure for Mela-M-Pym. White powder; Yield: 33%.

^{1}H-NMR (300 MHz, DMSO-d6, ppm): δ 7.40-7.10 (m, 5H), 7.08-6.82 (br, 1H), 6.50-5.90 (br, 3H), 4.42 (d, 6.0 Hz, 2H), 2.68 (d, 4.6 Hz, 3H).

ESI-MS: 231.2 ($[M+H]^+$, calcd: 231.1).

Mela-M-2Nm

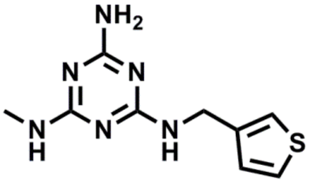


This compound was synthesized from 6-chloro-N2-methyl-1,3,5-triazine-2,4-diamine and 2-naphthalenemethylamine hydrochloride following the similar procedure for Mela-M-Pym. White powder; Yield: 83%.

^{1}H-NMR (300 MHz, CD_3OD, ppm): δ 7.88-7.68 (m, 4H), 7.50-7.35 (m, 3H), 4.70 (s, 2H), 2.84 (s, 3H).

ESI-MS: 281.2 ([M+H]$^+$, calcd: 281.2).

Mela-M-3Tm

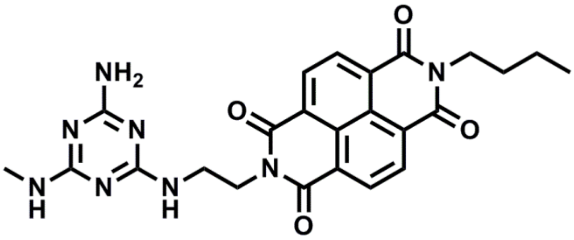


This compound was synthesized from 6-chloro-N2-methyl-1,3,5-triazine-2,4-diamine and 3-thiophenemethylamine following the similar procedure for Mela-M-Pym. White powder; Yield: 55%.

^{1}H-NMR (300 MHz, DMSO-d6, ppm): δ 7.43 (dd, 3.0 Hz, 4.9 Hz, 1H), 7.28-7.16 (br, 1H), 7.06 (d, 4.9 Hz, 1H), 6.95-6.70 (br, 1H), 6.55-6.90 (br, 3H), 4.39 (d, 5.5 Hz, 2H), 2.70 (d, 4.5 Hz, 3H).

ESI-MS: 237.09 ([M+H]$^+$, calcd: 237.09).

Mela-M-NDI4

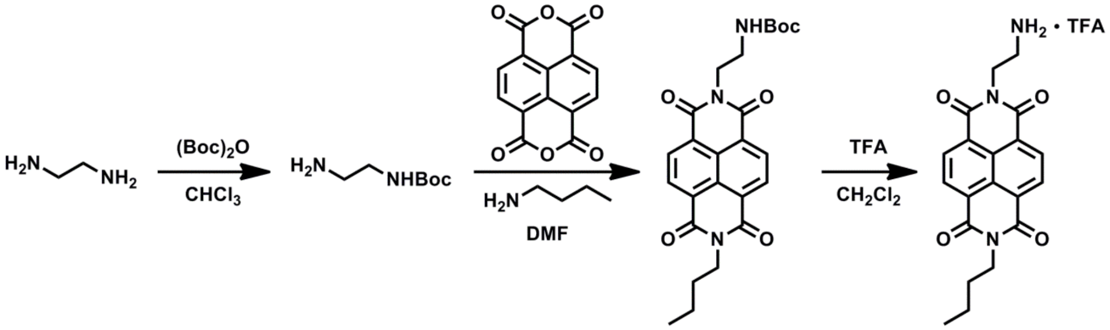


This compound was synthesized from 6-chloro-N2-methyl-1,3,5-triazine-2,4-diamine and NDI-4-NH$_2$•TFA following the similar procedure for Mela-M-Pym. Yellow powder; Yield: 36%.

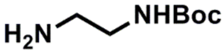
^{1}H-NMR (300 MHz, DMSO-d6, ppm): δ 8.65 (s, 4H), 6.70-5.80 (br, 4H), 4.35-4.15 (br, 2H), 4.07 (t, 7.3 Hz, 2H), 3.67-3.47 (br, 2H), 2.75-2.55 (br, 3H), 1.72-1.58 (m, 2H), 1.45-1.32 (m, 2H), 0.94 (t, 7.2 Hz, 3H).

ESI-MS: 489.20, 490.20 ([M+H]$^+$, calcd: 489.20, 490.20).

Scheme S3: The synthetic route of NDI-4-NH$_2$•TFA.



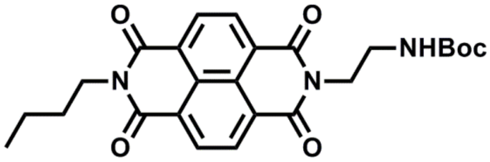
Tert-butyl (2-aminoethyl)carbamate



Di-tert-butyl dicarbonate (2.4 mL, 10.4 mmol) in 50 mL of $CHCl_3$ was added dropwise to a solution of ethylenediamine (7.0 mL, 105 mmol) in 100 mL of $CHCl_3$ at 0 ^{o}C over 3 h. After stirring at room temperature for 20 h, the precipitate was filtered. The filtrate was washed with brine (6*30 mL) and water (2*30 mL), dired over Na_2SO_4, concentrated in vacuum to afford a colorless oil (1.5 g, 90%).

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 5.25-4.95 (br, 1H), 3.32-3.18 (m, 2H), 2.95-2.80 (br, 2H), 2.75-2.50 (br, 2H), 1.45 (s, 9H).

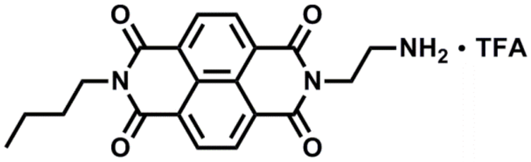
NDI-4-NHBoc



naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (0.86 g, 3.2 mmol), tert-butyl (2-aminoethyl)carbamate (0.52 g, 3.2 mmol) and n-butylamine (0.32 mL, 3.2 mmol) was mixed in 20 mL of DMF. The mixture was stirred at 110 ^{o}C for 1 d. After cooling, the mixture was added dropwise to 200 mL of water. The precipitate was filtered, absorbed on silica gel, purified by column chromatography (1:1 petroleum ether/ethyl acetate) to afford a pale yellow powder (0.47 g, 32%).

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 8.77 (s, 4H), 4.84 (s, 1H), 4.39 (t, 5.6 Hz, 2H), 4.21 (t, 7.5 Hz, 2H), 3.62-3.48 (br, 2H), 1.80-1.68 (m, 2H), 1.52-1.42 (m, 2H), 1.23 (s, 9H), 1.00 (t, 7.2 Hz, 3H).

NDI-4-NH_2•TFA



NDI-4-NHBoc (0.79 g, 1.7 mmol) was dissolved in 12 mL of CH_2Cl_2, trifluoroacetic acid (TFA, 4 mL) was added at 0 ^{o}C. The mixture was stirred at room temperature for 12 h. The solvent was removed in vacuum. The residue was washed with ether (200 mL), filtered, dried in vacuum to afford a pale yellow powder (0.67 g, 82%). The product was used for the next reaction without further characterization.

Scanning electron microscopy (SEM)

SEM experiments were performed with a FEI Quanta 200 scanning electron microscope. The samples were prepared by dripping 5 μL of the suspensions on silicon wafers and drying in air.

Fluorescence microscopy

Fluorescence microscopy images were obtained with an Olympus BX51 microscope. The samples were prepared by dripping 10 μL of the suspensions on glass substrates and drying in air.

Fluorescence spectroscopy

Fluorescence spectra were recorded using a HITACHI F-7000 apparatus (excitation wavelength: 330 nm). The samples were prepared by dripping 10 μL of the suspensions on quartz plates and drying in air for 5 times. For ammonia responsiveness experiment, the sample on a quartz plate was placed at the center of a cylindrical container (containing 200 μL of ammonia solution on the periphery) for a certain period of time before fluorescence measurement.

Confocal fluorescence microscopy

Confocal fluorescence microscopy image was obtain on a Zeiss LSM780 confocal microscope. The sample was prepared by dripping 10 μL of the suspension on glass substrate and drying in air.

X-ray crystallography

The X-ray crystallography experiment was performed on a Rigaku Saturn 724+ CCD diffractometer. The single crystal of Mela-DM•HCl was obtained by slow evaporation of Mela-DM•HCl solution in chloromethane and methanol at room temperature.

Powder X-ray diffraction (XRD)

Powder XRD data was collected at room temperature on a Rigaku D/max 2500 diffractometer with Cu Kα radiation. The samples were prepared by successively dripping 10 μL of the suspensions on glass substrates and drying in air for about 100 times.

3. Single crystal structure of Mela-DM•HCl

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

Sample code	**bo2923**	
Molecular formula	$[C_5H_{11}N_6]Cl$	
Molecular weight	190.65	
Color and habit	colorless prism	
Crystal size	0.080 × 0.085 × 0.125 mm	
Crystal system	orthorhombic	
Space group	*Pmna* (No. 53)	
Unit cell parameters	a = 6.4782(13) Å α = 90.00° b = 9.5193(19) Å β = 90.00° c = 14.311(3) Å γ = 90.00° V = 882.5(3) Å^3 Z = 4	F(000) = 400
Density (calcd)	1.435 g/cm^3	
Diffractometer	Rigaku Saturn724+	
Radiation	Mo K_α, $\lambda = 0.71073$ Å	
Temperature	163±2K	
Scan type	ω-scan	
Data collection range	$-7 < h < 8$, $-12 < k < 12$, $-19 < l < 19$; $\theta_{max} = 29.1°$	
Reflections measured	Total: 7576 Unique (n): 1283	Observed [I ≥ 2σ(I)]: 1053
Absorption coefficient	0.390 mm^{-1}	
Minimum and maximum transmission	0.906, 1.000	
No. of variables, p	85	
Weighting scheme	$w = \dfrac{1}{\sigma^2(F_o^2)+(0.06P)^2+0.7P}$	$P = (F_o^2 + 2F_c^2)/3$
$R1 = \dfrac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$ (for all reflections)	0.0476	0.0355 (for observed data)
$wR2 = \sqrt{\dfrac{\Sigma[w(F_o^2-F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.1214	0.0920 (for observed data)
Goof = S = $\sqrt{\dfrac{\Sigma[w(F_o^2-F_c^2)^2]}{n - p}}$	1.059	
Largest and mean Δ/σ	0.000, 0.000	
Residual extrema in final difference map	−0.309 to 0.329 e Å^{-3}	