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MATERIALS

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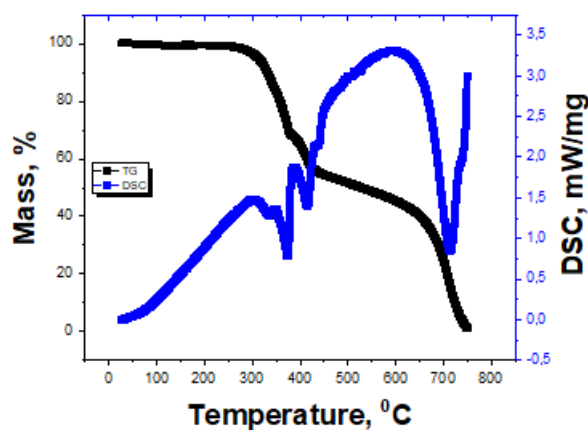
**Supporting information for article:**

**Accessing the rich carbon nitride materials chemistry by heat treatments of ammonium thiocyanate, NH<sub>4</sub>SCN**

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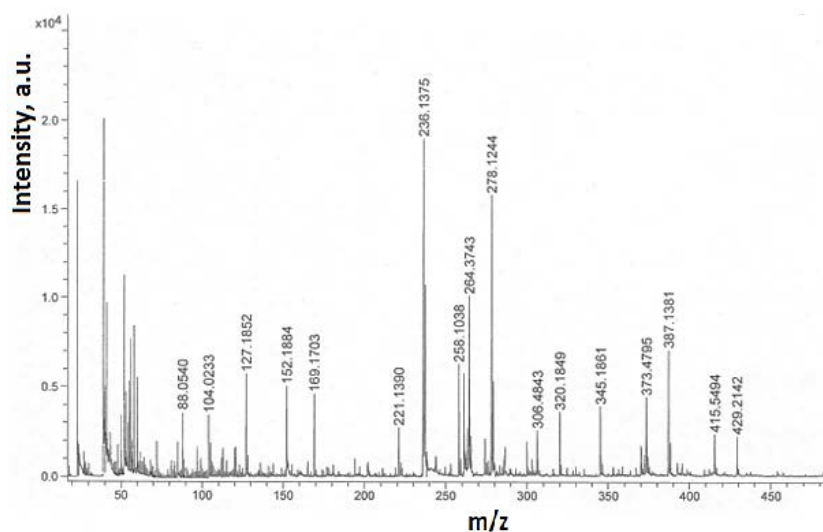
## S1. Thermal analysis

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) was measured on product **2** using a Netzsch STA 449 C using alumina (corundum) crucibles with lids and a heating/cooling rate of 10 K/min. The experiments were performed in an Ar atmosphere using gaseous nitrogen for cooling rather than liquid nitrogen since this resulted in more stable conditions. The instrument was calibrated against the melting points of In, Sn, Bi, Zn, Al, Ag and Au before use. The sets of endothermic events between 305 and 399°C are interpreted as transformation between products **2** and **3** and those between 399 and 433°C correspond to transformation between products **3** and **4**. The endothermic deflection between 433 and about 450 °C may be due to the transformation between product **4** and the pyrolysis end product.



**Figure S1** TGA /DSC measurements of product **2**, melamine melamium thiocyanate,  $([\text{H}_6\text{C}_3\text{N}_6] \cdot [\text{H}_{10}\text{C}_6\text{N}_{11}]^+ \cdot [\text{SCN}]^-)$  in the temperature interval from room temperature to past 700 °C.

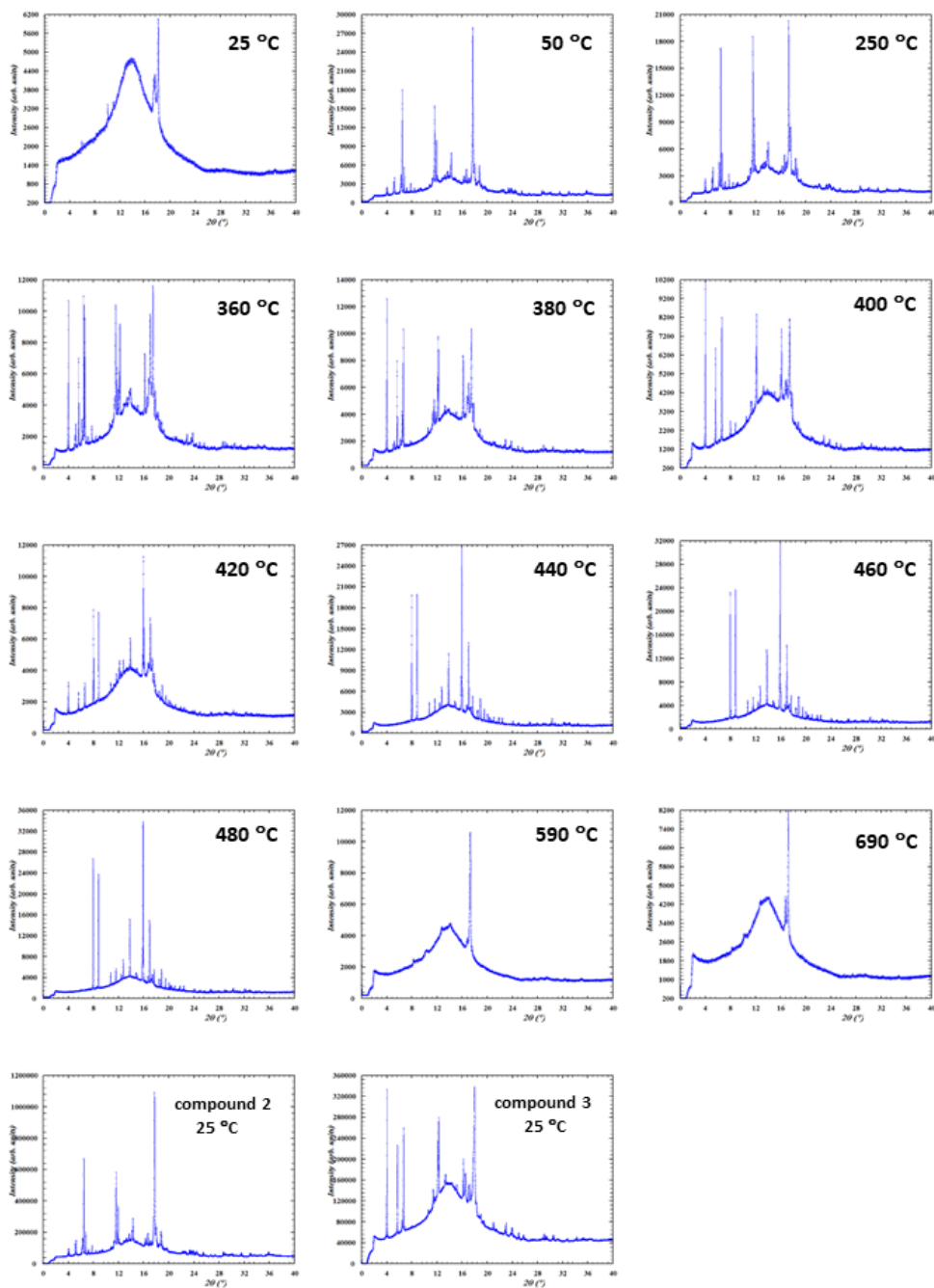
## S2. Mass spectrometry



**Figure S2** Mass spectrum of product **2**, melamine melamium thiocyanate, ( $[\text{H}_6\text{C}_3\text{N}_6] \cdot [\text{H}_{10}\text{C}_6\text{N}_{11}]^+ \cdot [\text{SCN}]^-$ )

**Table S1** Potential interpretation of mass spectrum lines for product **2**, melamine melamium thiocyanate, ( $[\text{H}_6\text{C}_3\text{N}_6] \cdot [\text{H}_{10}\text{C}_6\text{N}_{11}]^+ \cdot [\text{SCN}]^-$ ) in terms of formula and abbreviated fragment name (mth = melamium thiocyanate ( $\text{C}_6\text{H}_{10}\text{N}_{11}^+\text{SCN}^-$ ), tria.rep.= triazine repeat unit, ( $\text{C}_3\text{H}_3\text{N}_5$ ))

m/z (observed)	Formula	fragments	m/z(calculated)
127.19	$\text{C}_3\text{H}_7\text{N}_6^+$	melamine+ $\text{H}^+$	127.15
169.17	$\text{C}_3\text{H}_5\text{N}_5^+\text{SCN}^-$	guanamine-thiocyanate	169.20
221.14	$\text{C}_6\text{H}_9\text{N}_{10}^+$	diguanamine+ $\text{H}^+$	221.23
236.14	$\text{C}_6\text{H}_{10}\text{N}_{11}^+$	melam+ $\text{H}^+$	236.25
264.37	$\text{C}_6\text{H}_8\text{N}_9^+\text{SCN}^-$	mth -2NH	264.29
278.12	$\text{C}_6\text{H}_8\text{N}_{10}^+\text{SCN}^-$	mth - $\text{NH}_2$	278.30
306.48	$\text{C}_8\text{H}_6\text{N}_{10}\text{S}_2$	mth + $\text{SCN}^-$ - $\text{NH}_2$ -2NH	306.34
320.18	$\text{C}_8\text{H}_6\text{N}_{11}\text{S}_2$	mth + $\text{SCN}^-$ -2 $\text{NH}_2$	320.35
345.19	$\text{C}_9\text{H}_{13}\text{N}_{16}^+$	melam+ $\text{H}^+$ + tria.rep.	345.35
373.48	$\text{C}_9\text{H}_{11}\text{N}_{14}^+\text{SCN}^-$	mth-2NH + tria.rep.	373.40
387.14	$\text{C}_9\text{H}_{11}\text{N}_{15}^+\text{SCN}^-$	mth - $\text{NH}_2$ + tria.rep.	387.41
415.55	$\text{C}_{11}\text{H}_9\text{N}_{15}\text{S}_2$	mth + $\text{SCN}^-$ + tria.rep. - $\text{NH}_2$ -2NH	415.45
429.21	$\text{C}_{11}\text{H}_9\text{N}_{16}\text{S}_2$	mth + $\text{SCN}^-$ + tria.rep. - 2 $\text{NH}_2$	429.46



**Figure S3** Multi-temperature synchrotron PXRD data ( $\lambda = 1.00254 \text{ \AA}$ ) of product 2, melamine melamium thiocyanate,  $[\text{H}_6\text{C}_3\text{N}_6] \cdot [\text{H}_{10}\text{C}_6\text{N}_{11}]^+ \cdot [\text{SCN}]^-$  collected at beamline BL02B2, Spring-8, Japan (Nishibori *et al.*, 2001)