

Figure S1. TEM (a) and SAED pattern (b) of DG.

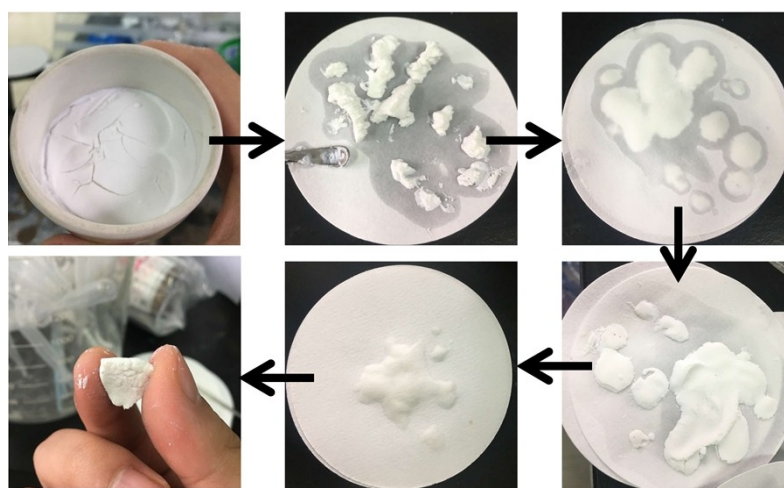


Figure S2. HAmG with about 50 wt% water obtained after removing free water by using filter paper, which was applied for ssNMR characterization.

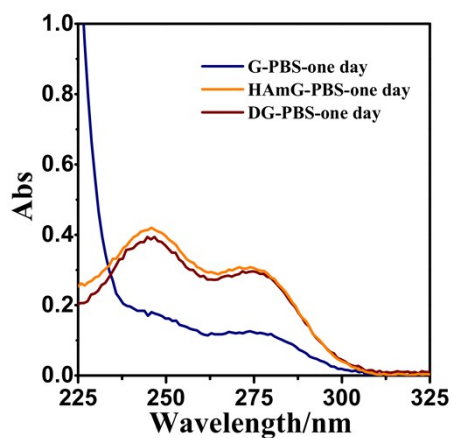


Figure S3. UV-vis spectra for the saturated PBS solutions of HAmG, DG and commercial guanine particles (G).

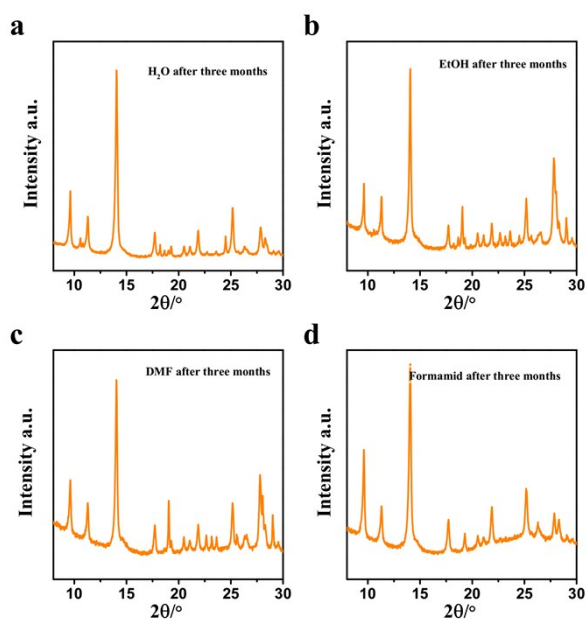


Figure S4. PXRD of the guanine samples crystallized via HAmG precursor in other solvents such as water, ethanol, DMF and formamid after three months.

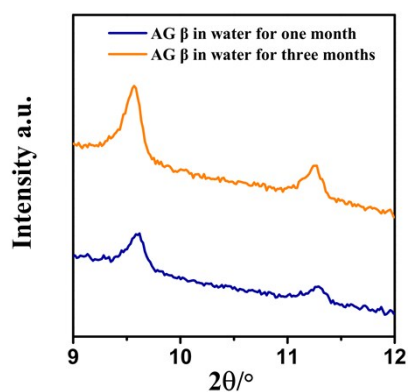


Figure S5. PXRD of AG  $\beta$  crystals which were formed in DMSO (Figure 1) and then redispersed in water for one month and three months.

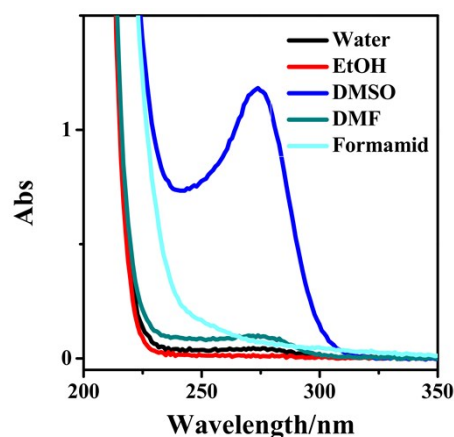


Figure S6. UV-vis spectra exhibit the solubility of guanine in different solvents. The UV-vis spectrum of the guanine solution in formamid was different from the other spectra due to the decomposition of formamid, and the guanine concentration in formamid was not comparable with the other saturated solution in this work.

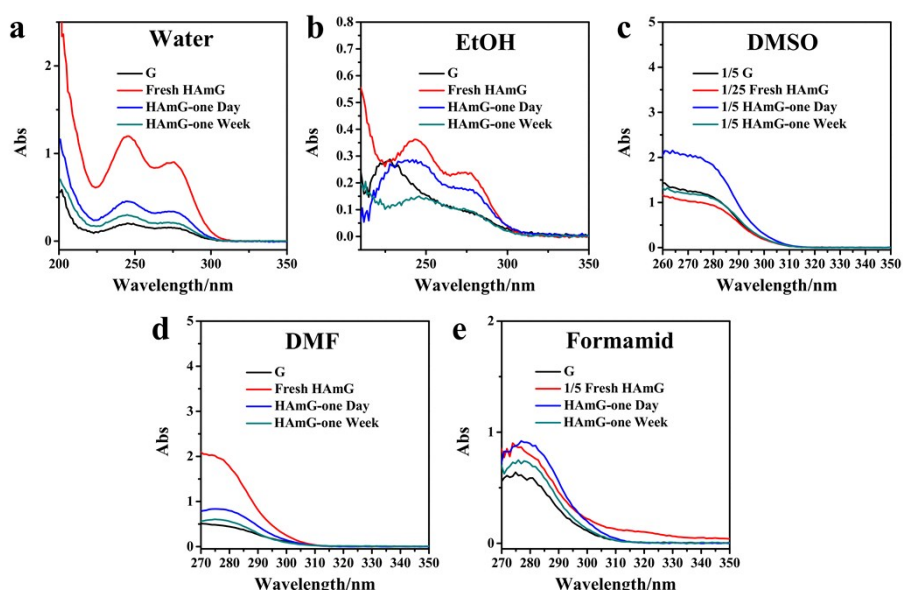


Figure S7. UV-vis spectra of HAMG solutions kept in different solvents for a certain time. saturated solution of guanine was obtained by using commercial guanine powders (mixture of AG □ and □□□shortened as G in the spectra). (a) water; (b) ethanol; (c) DMSO G (Commercial guanine) and HAMG soaked after one day and one week were diluted to one fifth. Freshly prepared HAMG solution was diluted to one twenty fifth; (d) DMF; (e) formamid (freshly prepared HAMG solution was

diluted to one fifth).

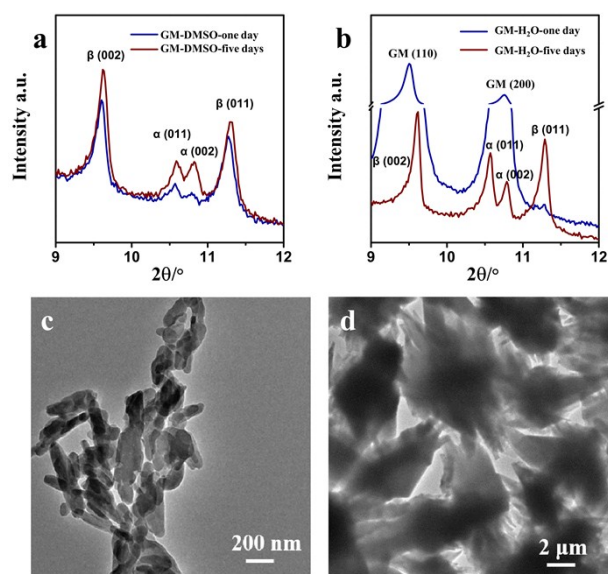


Figure S8. Characterizations on the guanine samples crystallized in water or DMSO after one or five days at room temperature while using GM as guanine precursor. (a, b) PXRD; (c, d) TEM images of samples obtained in DMSO (c) and water (d) after five days.

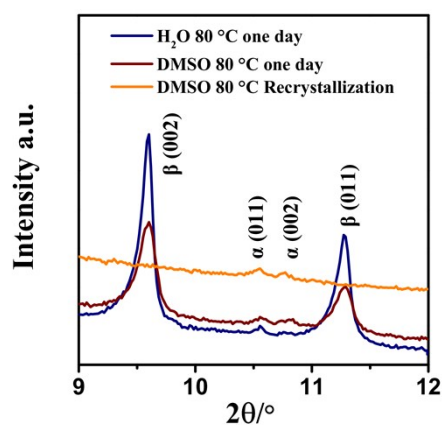


Figure S9. Characterizations on the guanine samples obtained while keeping HAMG precursor in water or DMSO at 80 °C for one day. In comparison, AG  $\alpha$  in pure phase was obtained through a similar recrystallization process by decreasing the temperature from 80 °C to RT in DMSO by using commercial guanine (mixture of AG  $\alpha$  and  $\beta$ ) as reaction precursor.

Table S1 <sup>13</sup>C Solid-state NMR shifts of HAmG, DG, AG α and β.

Samples	C <sub>6</sub> , C <sub>2</sub> , C <sub>4</sub> (ppm) <sup>a</sup>			C <sub>8</sub> (ppm)	C <sub>5</sub> (ppm)
HAmG	160.1	157.2	155.2	141.0	106.9
DG	160.4	157.4	155.4	141.3	107.1
AG β	160.4	157.4	155.5	141.2	107.1
AG α	160.3	157.3	155.1	142.4	106.7

a: the NMR shifts of C<sub>6</sub>, C<sub>2</sub>, C<sub>4</sub> of guanine samples were referenced according to the NMR shifts of guanosine in literature,<sup>1</sup>. However, it is still difficult to distinguish the NMR shifts of C<sub>6</sub>, C<sub>2</sub>, C<sub>4</sub> of guanine samples from each other since they are close to each other.

(1) Webber, A. L.; Masiero, S.; Pieraccini, S.; Burley, J. C.; Tatton, A. S.; Iuga, D.; Pham, T. N.; Spada, G. P.; Brown, S. P. Identifying guanosine self assembly at natural isotopic abundance by high-resolution <sup>1</sup>h and <sup>13</sup>c solid-state nmr spectroscopy. *J. Am. Chem. Soc.* **2011**, *133*, 19777.