Supporting Information

Growth and Characterization of Melem Hydrate Crystals with Hydrogen-Bonded Heptazine Framework

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Experimental and calculation methods

Polarized light microscope images were observed and recorded under the crossed Nicol condition using a microscope (SMZ1000, Nikon).

The energy band and partial density of states (PDOS) were calculated based on the density functional theory (DFT). The band and PDOS calculations were performed using the CASTEP[1] plane wave basis set and general gradient approximation (GGA) applying Perdew-Burke-Ernzerhof (PBE) as correlation functional[2] (Dassault Systèmes BIOVIA)[3]. The details of the

calculation are as follows, energy cutoff: 789.1000eV, SCF tolerance threshold: 2.0×10^{-6} eV/atom, *k*-point set in reciprocal space: (separation: 0.08 $Å^{-1}$, Monkhorst-Pack Grids: 1 × 1 × 2), pseudopotentials: norm conserving, finite basis set correction: not used, and dispersion correction: not used. The calculations were performed using the c-melem and Mhr structures reported in previous studies[4,5]; for the Mhr structure, the c-axis was adjusted to be 0.13 Å longer to better reproduce the XRD data. The obtained atomic coordinates of Mhr are shown in Table S1.

The sample for fluorescence lifetime measurements was prepared by sandwiching a powder sample between two quartz plates. The measurements were carried out using a compact fluorescence lifetime measurement system (Quantaurus-Tau, C11367-01, Hamamatsu Photonics Ltd.)

The thermogravimetry-differential thermal analysis (TG-DTA) measurements were performed using TG-DTA2010SA (Bruker XS). The TG-DTA curves were acquired in a dry N_2 atmosphere at a heating rate of 5°C/min.

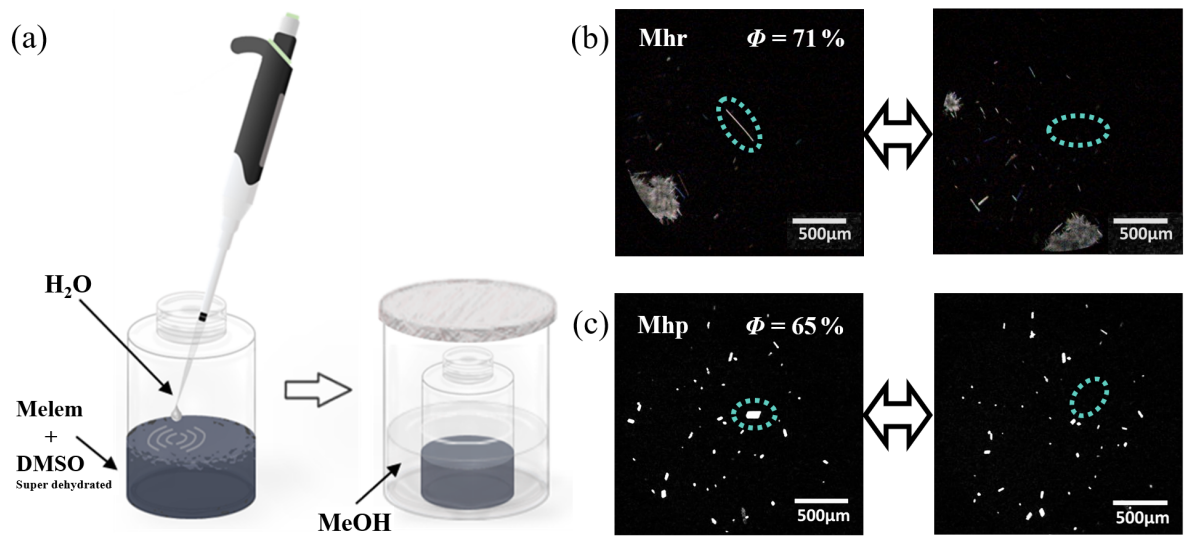

Fig. S1 (a) Schematic of the Mh single crystal growth method: a drop of pure water was added to the super dehydrated DMSO in which melem was dissolved or dispersed in (left), the screw tube was placed in a methanol-filled snap cup and covered with a lid, and the poor solvent was allowed to vapor diffuse in the dark for 7 d (right). Polarized light micrographs of (b) Mhr and (c) Mhp in the crossed Nicol state. The photograph on the right was taken by rotating the sample 45° from the state shown in the photograph on the left. The sample circled by the dashed line in the photograph was completely quenched when the sample was rotated by 45°. The complete quenching of light indicated that both Mhr and Mhp were single crystals.

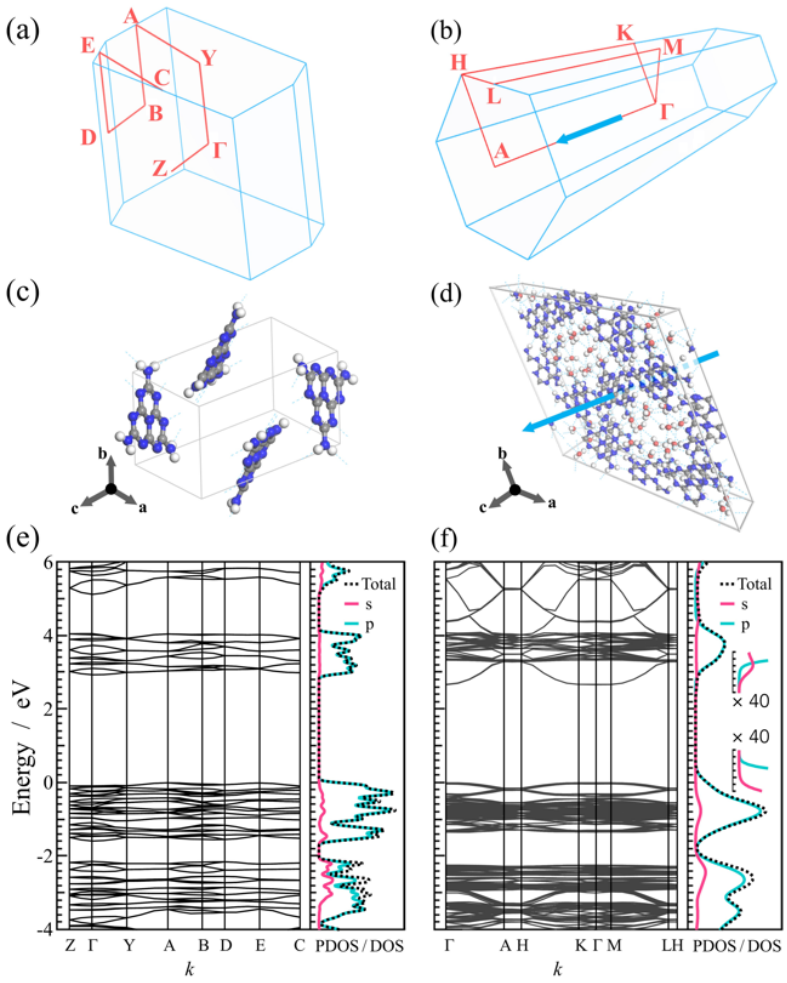

Fig. S2 Brillouin zones of (a) c-melem and (b) Mh, unit cells of (c) c-melem and (d) Mh used in the DFT calculations, and energy band structure and PDOS of (e) c-melem and (f) Mh determined by DFT calculations. The red and green lines represent the PDOS of the s and p orbitals, respectively, and the black dotted curve represents the total DOS. The left axis represents the energy measured from the top of the valence band. The symbols on the bottom axes indicate the high symmetry points corresponding to the Brillouin zones in (a) and (b). The free-electron-like bands that appeared in the unoccupied states of Mh, were the H 1s bands of water molecules aligned in the channels of Mh.

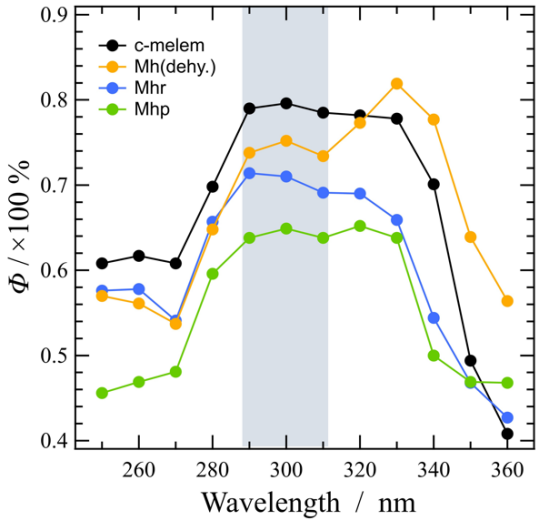

Fig. S3 Excitation wavelength dependence of the absolute quantum yields Φ of c-melem, Mh(dehy.), Mhr, and Mhp. The average quantum yields $\Phi_{average}$ which are the average values of Φ in the excitation wavelength range of 290–310 nm represented by the blue band in the figure are given in Table S2.

The absolute quantum yields of compounds depend on the wavelength of their excitation light. The $\Phi_{average}$ values in Table S2, which represent the average of the quantum yields at an excitation wavelength of 290–310 nm, suggested that the dependence of all the samples on the excitation light wavelength was relatively small except for melem(DMSO), as shown in Fig. S3.

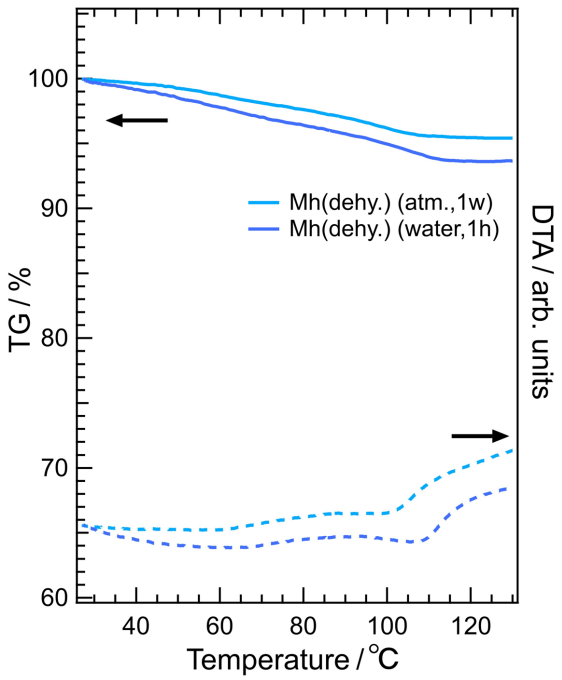

Fig. S4 TG-DTA profiles of Mh(dehy.)(atm., 1w) and Mh(dehy.)(water, 1h). The mass loss at 125°C (corresponding to the amount of water adsorbed and taken up by Mh(dehy.)) is 4.59% and 6.39% for Mh(dehy.)(atm., 1w) and Mh(dehy.)(water, 1h), respectively.

Table S1 Atomic coordinates of Mhr.

Unit cell parameters: $a = 28.79000$ Å, $b = 28.79000$ Å, $c = 6.77275$ Å, $\alpha = \beta = 90°, \gamma = 120°$.

Atom	*x*	*y*	*z*
C1	0.71469	0.86427	0.04960
C2	0.66667	0.76689	0.08333
C3	0.66667	0.90780	0.08333
C4	0.75685	0.81522	0.02330
N1	0.66667	0.81588	0.08333
N2	0.75963	0.86372	0.02140
N3	0.71399	0.91008	0.04460
N4	0.71194	0.76694	0.04980
N5	0.66667	0.95368	0.08333
N6	0.80212	0.81497	-0.00470
O1	0.86793	0.94939	0.03260
O2	0.94810	0.94810	0.25000
H1	0.69740	0.98310	0.04200
H2	0.80060	0.78450	-0.00900
H3	0.82780	0.84310	-0.01700
H4	0.85100	0.93700	0.14000
H5	0.89810	0.97530	0.00700

Table S2 PL absolute quantum yields Φ, average of absolute quantum yields $\Phi_{average}$ over excitation light wavelengths ranging from 290 to 310 nm. Average fluorescence lifetimes τ of c-melem, Mh(dehy.), Mhr, and Mhp were evaluated from the fluorescence lifetime measurement results in Fig. 8. Melem(DMSO) refers to the DMSO s. d. solution of Melem.

Sample	Φ / %[*1]	$\Phi_{average}$ / %[*2]	τ / ns[*3]
c-melem	80	79.0 ± 0.4	176
Mh (dehy.)	75	74.1 ± 0.8	287
Mhr	71	70.5 ± 0.5	365
Mhp	65	64.2 ± 0.5	370
Melem(DMSO)	19	18.1 ± 2.1	161

τ is the time when the intensity decreases to 1/e, [*1] represents the values measured using excitation light with a wavelength of 300 nm, [*2] represents the values measured using excitation light with wavelengths of 290 to 310 nm, [*3] represents the values measured using excitation light with a wavelength of 340 nm. The value of $\Phi_{average}$ for melem(DMSO) is also calculated between 290-310 nm like the other samples, but in this wavelength range, it is more wavelength dependent than the other samples. Emission wavelengths of 370 nm were used for measurements on c-melem, Mh(dehy.), Mhr, and melem(DMSO) while wavelength of 380 nm was used for the measurement on Mhp.

References

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