

Cite this: *M*, 2018,
14, 7045

located in assemblies will be broadened and contribute minimally to the observed spectrum, whereas proton signals of the free molecules in solution will be detected and contribute most significantly to the integrated area and intensity of signals in the NMR spectrum. This simple NMR strategy was used to monitor the relative concentration of free-state molecules in the self-assembled TTPC-nanofibers. By varying the sample temperature, the change in NMR signal intensity was monitored, which corresponded to the concentration change of free TTPC molecules as a reflection of the self-assembly process. If we consider the disassembly process as analogous to the dissolution process, the solubility of TTPC can be expressed by the Van't Hoff equation,

$$\ln(\text{solubility}) = (-\Delta H_{\text{dis}}/RT_{\text{eq}}) + \Delta S_{\text{dis}}/R$$

in which ΔH_{dis} and ΔS_{dis} denote the molar enthalpy and the molar entropy for the disassembly process (the interconversion between assembly and free molecules), T_{eq} is the equilibrium temperature, and R is the gas constant. The proton signal of the repeating methylene ($-\text{CH}_2-$) was selected to calculate the relative concentration of free TTPC molecules at different temperatures (Fig. 2c), and a typical Van't Hoff plot is shown in Fig. 2d. ΔH_{dis} and ΔS_{dis} were calculated from the slope and intercept of the plot, and the opposite values of these two thermodynamic parameters reflect the change in enthalpy and entropy in the self-assembly process of TTPC molecules ($\Delta H_{\text{as}} = -\Delta H_{\text{dis}} = -36.03 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{as}} = -\Delta S_{\text{dis}} = -50.1 \text{ J mol}^{-1} \text{ K}^{-1}$). Thus, the self-assembly of TTPC is an enthalpy-favored and entropy-disfavored process.

f

The morphology of the TTPC assembly is fibrous and has the potential to form a gel by physical entanglement of the fibers. At room temperature (20 °C), the TTPC assembly dispersion forms a gel above a critical gel concentration (CGC) of 1.3 wt%. The gel exhibits typical rheological properties of a supramolecular gel, especially self-recovery, which is a common characteristic of supramolecular gels (Fig. S3 and S4, ESI[†]). To access the sol-gel transition temperature (T_{gel}) of the TTPC supramolecular hydrogel, we carried out a vial inversion experiment on gel samples with different TTPC concentrations. The T_{gel} value increases with higher TTPC concentration (from 1.3 wt% to 4 wt% TTPC), finally reaching a plateau ($T_{\text{gel}} \equiv 55 \text{ °C}$ when TTPC% > 5 wt%) which denotes a concentration-independent T_{gel} (Fig. S5, ESI[†]).

f

At room temperature a fibrous assembly forms at the critical aggregation concentration (CAC) of TTPC in water (0.00033 wt%, Fig. S6, ESI[†]), and this fibrous assembly morphology is maintained at all concentrations till gelation (CGC). An increase of the concentration of TTPC results in the appearance of birefringence which indicates the presence of liquid crystal (LC) ordering. At room temperature, POM images show that the LC phase appears at 5 wt% TTPC (Fig. 3a and b), and that gel samples with higher TTPC-fraction exhibit stronger birefringence. The birefringence

disappeared when the temperature increased (Fig. 3c), with a concentration-dependent LC-isotropic phase transition temperature, a characteristic of lyotropic LCs. To investigate the structure of this lyotropic LC, SAXS measurements were performed on gel samples with different TTPC-fractions ranging from 5 wt% to 30 wt%. The 1D SAXS spectrum shows only one diffraction peak, which has the same Q value as that corresponding to the diameter of the TTPC nanofiber (0.5 wt%) (Fig. 3d), indicating that the LC phase in gel-samples is likely composed of bundles of TTPC fibers (Fig. 3d).

For a detailed investigation of the LC phase, the sample was observed under 2PEFPM using a 25 wt% TTPC sample labelled with fluorescent dye DiOC₁₈ (Fig. 4a). The small diameter of the fibrous assembly induces high curvature at the transversal surface and leads to rotation-prohibition of the rigid oxacarbo-cyanine structure of DiOC₁₈ in the TTPC fiber,^{†BilC ime}

should be observed. As expected, in the 2PEFPM images, ui2,67ht

structure of single TTPC fibers and the transition from fibrous bundles to the lamellar phase, it is hypothesized that the transition may involve fusion of fibers in a transversal direction (Fig. 6d), and the fusion induces phases with different periods, causing the two diffraction peaks. Although various defects appear across the fiber bundle

Boulder EM Service Core Facility in the Dept. of MCD Biology,
with the technical assistance of facility sta .

N •  •  •  •