

Electronic Supplementary Information

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Experimental details. Samples for the χ - T binary phase diagram of creatine and citric acid were prepared by grinding both citric acid anhydrous and creatine anhydrous (CA) with separate mortars and pestles to prevent the unintentional mechanosynthesis of either coamorphous or cocrystalline creatine-citric acid. Appropriate amounts of both components (yielding the desired χ (CA)) were weighed out, transferred to vials, and capped. Vials were thoroughly shaken to obtain a solid mixture that was as close to homogenous as possible. These solid mixtures were then transferred to hermetically sealed aluminum DSC pans for measurement. Solid mixtures used in the samples for the χ - T binary phase diagram of 1:1 creatine:citric acid and water were prepared by the same method. Once 1:1 creatine:citric acid solid mixtures had been made, appropriate amounts of deionized water (yielding the desired χ (H₂O)) were added via micropipette. Once again, vials were thoroughly shaken and sealed with electrical tape to prevent water loss due to vaporization. Samples were then embedded into a sand bath inside an oven, both of which had equilibrated to between 348 and 353 K before adding samples. Samples were left inside the oven for 24-48 h and occasionally shaken to expedite DES formation and complete dissolution. Following this period, samples were removed from the oven and allowed to cool to room temperature before being transferred to hermetically sealed aluminum DSC pans for measurement.

DSC measurements. DSC measurements for both binary phase diagrams were performed on a Netzsch DSC 214 Polyma instrument. All samples were measured under a constant flow of nitrogen. For the binary phase diagram of anhydrous creatine and citric acid, samples were heated from 298 to 408 K at a heating rate of 5 K/min, and samples were then held at 408 K for 10 min, then cooled to 223 K at a rate of 5 K/min. This cycle of heating, holding, and cooling was repeated once more immediately after. For the binary phase diagram of 1:1 creatine:citric acid and water samples were brought up to 323 K before being cooled to 163 K and then heated back to 323 K at a rate of 5 K/min.

TGA measurements. Thermogravimetric analysis was performed with a Netzsch TG 209 F3 Tarsus instrument. The sample used for the analysis was taken from the 0 χ (H₂O) DES made for the χ - T binary phase diagram of 1:1 creatine:citric acid and water. The sample was placed in an alumina crucible and heated from 303 to 773 K at a heating rate of 5 K/min under a constant flow of nitrogen.

Chemicals and reagents. Pyrene (*puriss.*, \geq 99.0%), Nile Red (\geq 98.0%), and 4-nitroaniline (\geq 99%) were from MilliporeSigma. *N,N*-Diethyl-4-nitroaniline (98 \pm %) and 1,3-bis(1-pyrenyl)propane (BPP) were purchased from Invitrogen. Citric acid anhydrous (\geq 99.5%) was purchased from Fisher Chemical. Creatine monohydrate was purchased from GNC. Creatine anhydrous was prepared by dehydration of creatine monohydrate at 373 K for 3h and confirmed with TGA.

Optical probe measurements. Spectra were collected in 1.0 cm path length quartz cuvettes (Starna). Absorbance measurements were performed on a Cary-60 UV-Vis spectrophotometer. Absorbance spectra were appropriately blank corrected. All steady-state fluorescence measurements were performed with a T-format FluoroLog®-3 spectrofluorimeter (HORIBA Scientific; model FL3-22) using a Xe lamp as the excitation source and equipped with double-grating monochromators in the excitation and emission channels. Emission spectra were background subtracted and corrected for detector and monochromator transmission non-linearities. The following parameters were used for the different fluorescent probes:

Nile Red: excitation wavelength: 550 nm; excitation/emission bandpass set at 2 nm and 1.0 nm, respectively.

pyrene: excitation wavelength: 337 nm; excitation/emission bandpass set at 2 nm and 0.5 nm, respectively.

1,3-bis(1-pyrenyl)propane (BPP): excitation wavelength: 337 nm; excitation/emission bandpass set at 1.5 nm and 1.0 nm, respectively.

Viscosity measurements. Viscosities were determined using a Brookfield DV-III Ultra Programmable Rheometer (cone-plate viscometer). The temperature of samples was controlled to within ± 0.05 K using a thermostatic water bath (Fisher Scientific Isotemp). The display on the viscometer was verified with certified viscosity standards (Cannon) at 298 ± 0.05 K. The standard uncertainty of viscosity measurement was better than 1%.

Synthesis of dicyano-bis(1,10-phenanthroline)iron(II) complex.

The probe dicyano-bis(1,10-phenanthroline)iron(II), $[\text{Fe}(\text{phen})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$, was prepared following a modification of the original procedure reported by Schilt.¹ Ferrous ammonium sulfate hexahydrate, sodium cyanide, and sulfuric acid were sourced from Fisher Scientific and 1,10-phenanthroline monohydrate was purchased from Sigma. On a Schlenk line, a 500 mL three-neck flask equipped with a reflux condenser was charged with deionized water (200 mL), 1,10-phenanthroline monohydrate (3.00 g, 15.1 mmol) and ferrous ammonium sulfate hexahydrate (1.95 g, 4.97 mmol). The resulting deep red solution was heated to 95 °C and a solution of sodium cyanide (3.76 g, 76.7 mmol) in water (10 mL) was added via syringe. The reaction mixture was stirred for 5 min at 95 °C and cooled without stirring overnight to room temperature. Formation of deep violet precipitates was observed during the cooling period. The crude product was collected on a fritted funnel and dried on the rotary evaporator. The crude product was dissolved in concentrated sulfuric acid (10 mL) and the resulting orange solution was placed in a 1000 mL Erlenmeyer flask. Deionized water (500 mL) was slowly added to the orange solution while stirring, resulting in a color change from orange to deep violet. The product was collected on a fritted funnel and washed with water until no acid was left and the only color observed was purple. The product was dried on the rotary evaporator to yield a dark purple powder (2.37 g, 94% yield).

1. Schilt, A. A., Mixed Ligand Complexes of Iron(II) and (III) with Cyanide and Aromatic Di-imines. *J. Am. Chem. Soc.* 1960, 82 (12), 3000-3005.

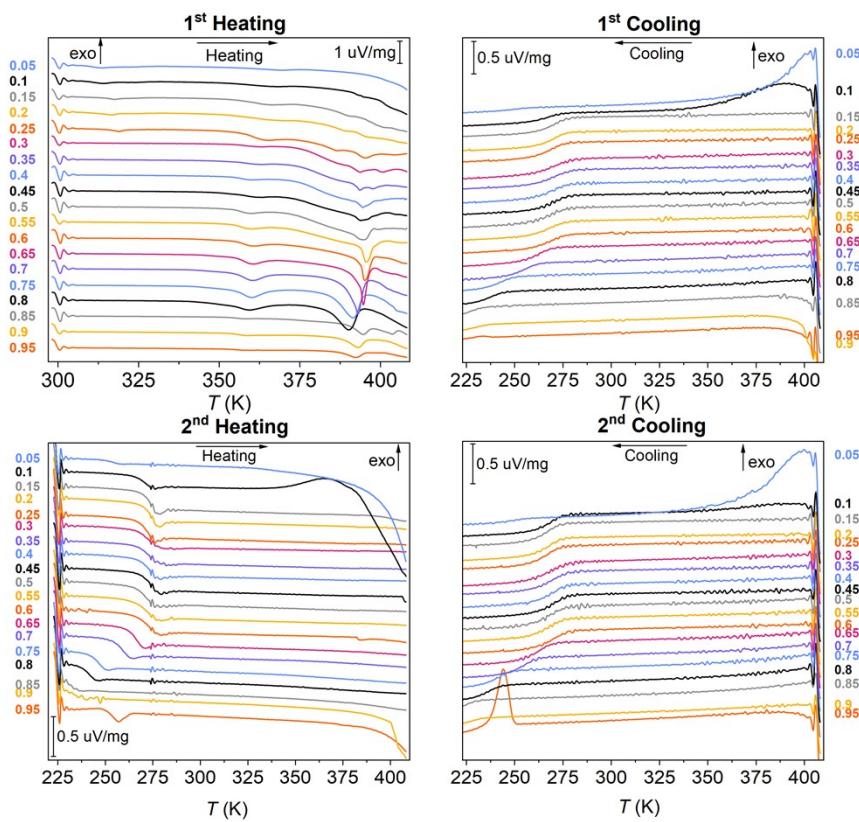


Fig. S1. DSC curves of the samples used for the construction of the creatine – citric acid phase diagram. The curves were measured upon heating and cooling, during two cycles.

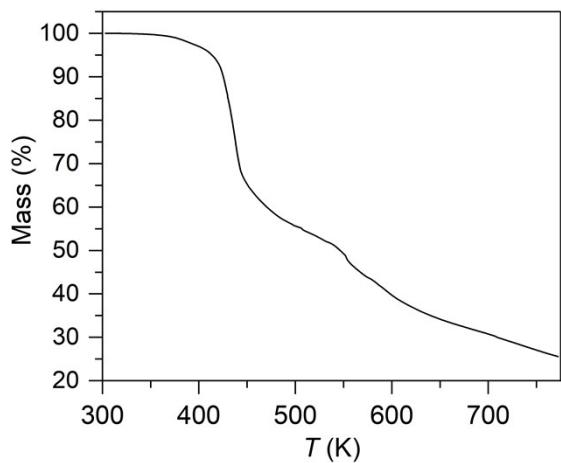


Fig. S2. TGA curve of one representative DES.

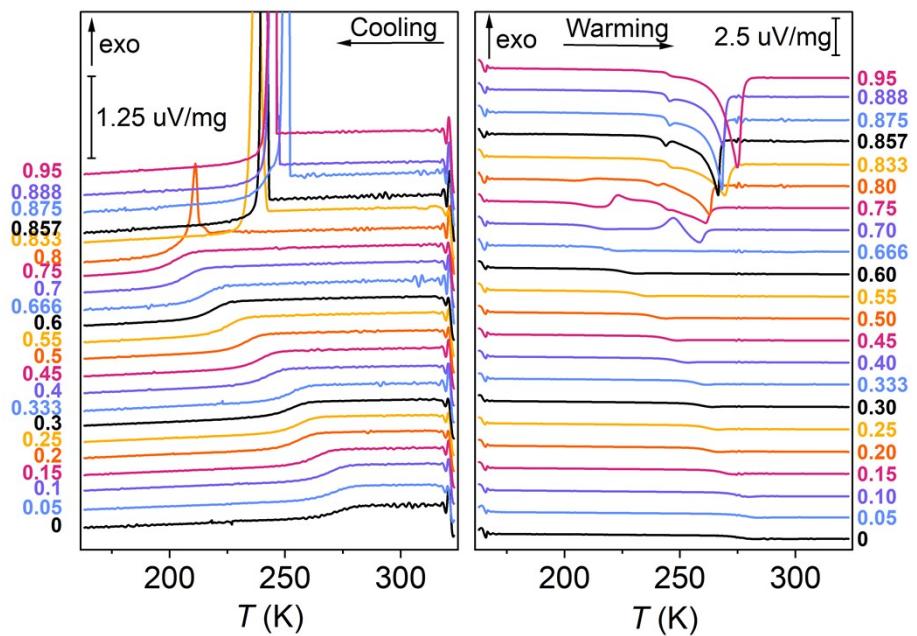


Fig. S3. DSC curves of the samples used for the construction of the creatine:citric acid (1:1) – water phase diagram. The curves were measured upon heating and cooling.

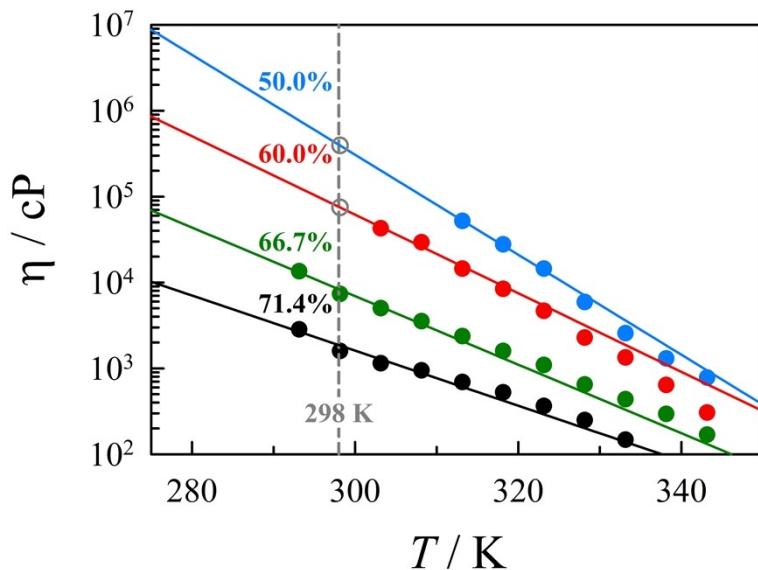


Fig S4. Semi-logarithmic plots of measured viscosity as a function of absolute temperature for the 1:1 creatine:citric acid binary system containing various mol% water, as indicated. Linear data extrapolation using such plots provides a rudimentary estimate of the viscosity at 298 K (open grey circles) for the low-water content eutectics which are too viscous to measure directly.

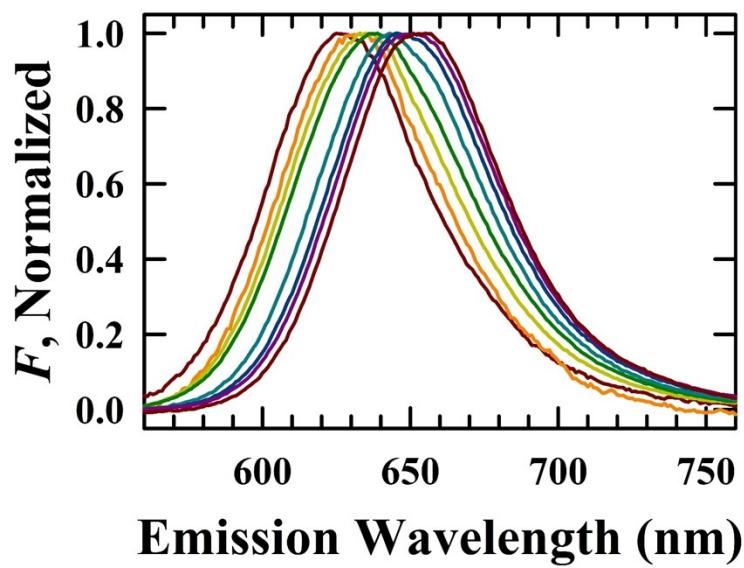


Fig S5. Normalized fluorescence emission spectra of Nile Red in the 1:1 creatine:citric acid eutectic with increasing water content, *left to right*: 33.0, 42.9, 50.0, 60.0, 66.7, 71.4, 75.0, and 77.8 mol%. Excitation wavelength: 550 nm.

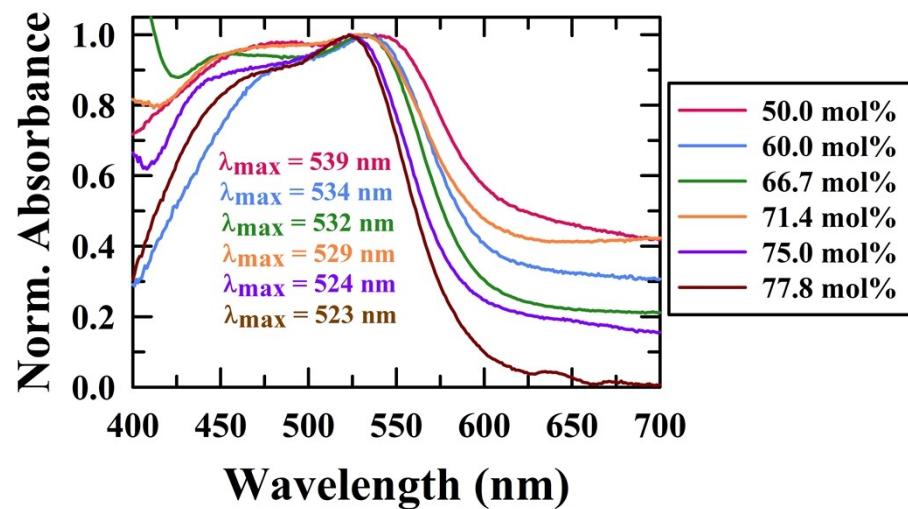


Fig S6. Normalized absorption spectra of the $[\text{Fe}(\text{phen})_2(\text{CN})_2]$ complex dissolved in 1:1 creatine:citric acid containing various mol% water.

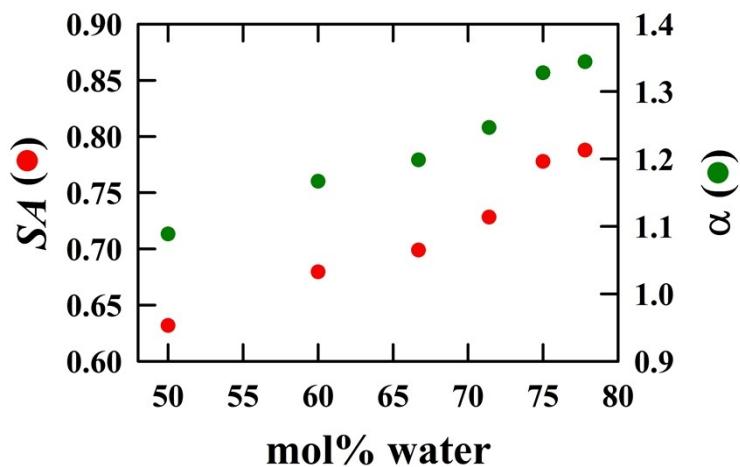


Fig S7. Summary of $[\text{Fe}(\text{phen})_2(\text{CN})_2]$ solvatochromic probe studies. Variation in the calculated (left axis) Catalán solvent acidity (SA) and (right axis) the Kamlet–Taft hydrogen bond donor (α) parameter for the 1:1 creatine:citric acid system having different water contents.