

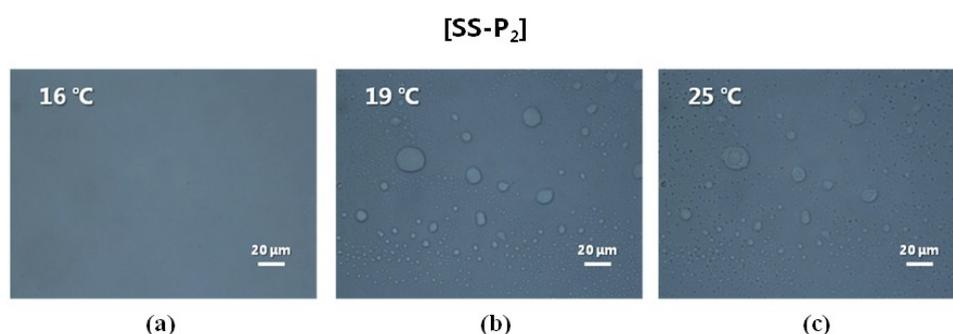
Supporting Information (SI)

**Insights Into the Thermal Phase Transition Behavior of A Gemini  
Dicationic Polyelectrolyte in Aqueous Solution**

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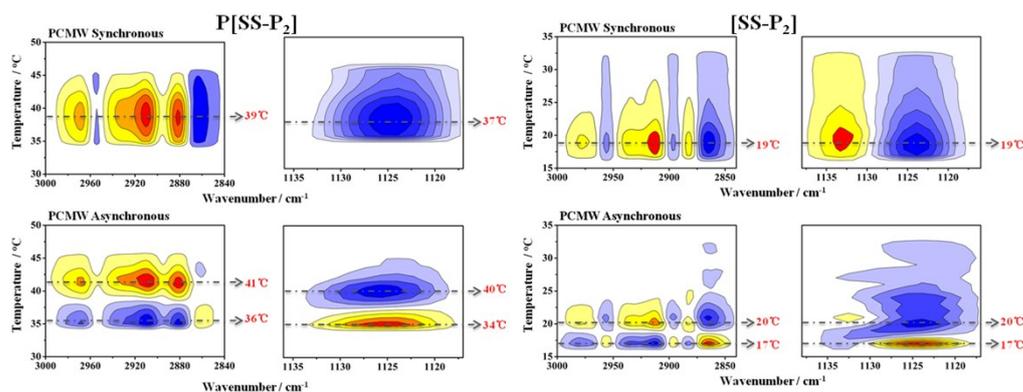
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**Optical microscopy**



**Fig. S1** Optical micrographs of [SS-P<sub>2</sub>] aqueous solutions (10 wt%) during heating process.

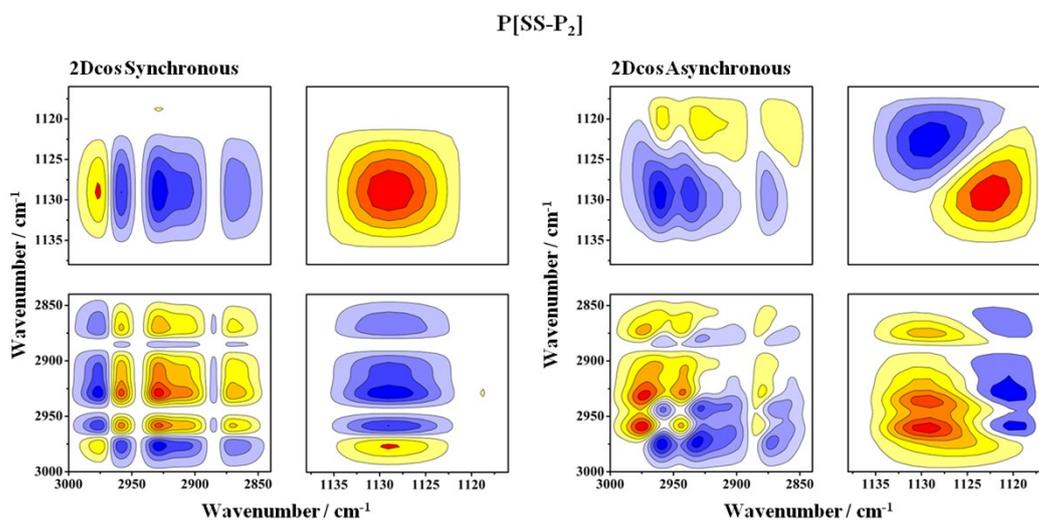
**Perturbation Correlation Moving Window (PCMw) Analysis**



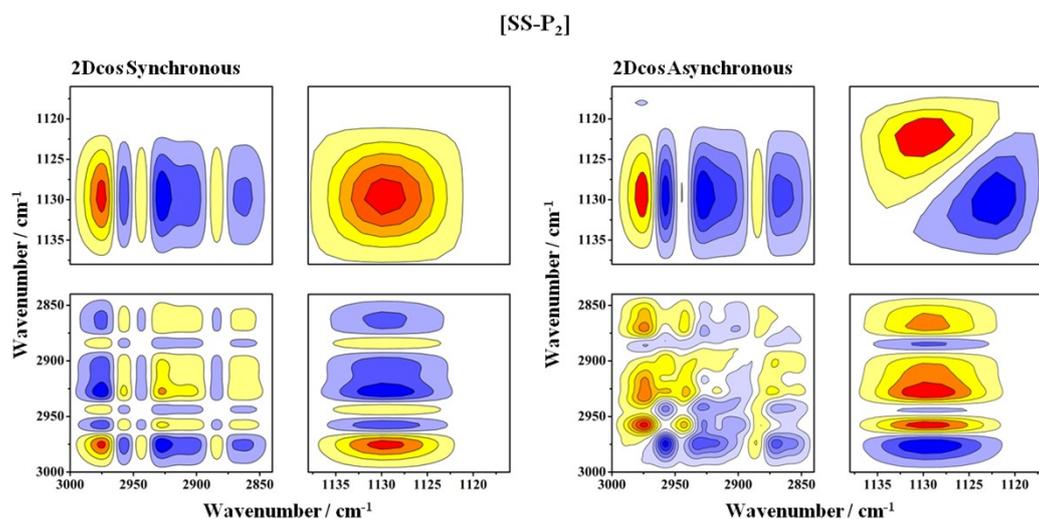
**Fig. S2** PCMw synchronous and asynchronous spectra of P[SS-P<sub>2</sub>] (left) and [SS-P<sub>2</sub>] (right) in D<sub>2</sub>O (10 wt%) between 30 to 50 °C and 15 to 35 °C, respectively. Warm

colors (red) are defined as positive intensities, whereas cool colors (blue) as negative ones.

### Two-Dimensional Correlation Analysis (2Dcos)



**Fig. S3** 2Dcos synchronous and asynchronous spectra of P[SS-P<sub>2</sub>] in D<sub>2</sub>O (10 wt%) during heating between 30 and 50 °C. Red colors are defined as positive intensities, while blue colors as negative ones.



**Fig. S4** 2Dcos synchronous and asynchronous spectra of P[SS-P<sub>2</sub>] in D<sub>2</sub>O (10 wt%) during heating between 15 and 35 °C. Red colors are defined as positive intensities, while blue colors as negative ones.

2Dcos spectra was also used to analyze the dynamic variations of various chemical groups in [SS-P<sub>2</sub>] and the sequence order of these groups during heating can be deduced as: 2872 > 2957 > 2860 > 2930 > 2883 > 2974 > 2944 > 1129 > 1122 cm<sup>-1</sup>. Or  $\nu_s(\text{dehydrated CH}_2 \text{ in dication}) > \nu_{as}(\text{dehydrated CH}_3 \text{ in diation}) > \nu_s(\text{alkyl CH}_2 \text{ chain between dication}) > \nu_{as}(\text{dehydrated CH}_2 \text{ in diation}) > \nu_s(\text{hydrated CH}_2 \text{ in diation}) > \nu_{as}(\text{hydrated CH}_3 \text{ in diation}) > \nu_{as}(\text{hydrated CH}_2 \text{ in diation}) > \nu_s(\text{SO}_3 \dots m\text{D}_2\text{O in anion}) > \nu_s(\text{SO}_3 \dots (m-n) \text{D}_2\text{O in anion})$ . It can be found that the response of hydrated C-H groups lagged behind that of dehydrated C-H groups, indicating that the dehydration process of C-H groups started when they underwent conformational changes during the phase transition.

When the differences in stretching modes can be ignored, the sequence order of [SS-P<sub>2</sub>] can be simplified as: CH<sub>2</sub> > CH<sub>3</sub> > SO<sub>3</sub> or even C-H groups > SO<sub>3</sub>, demonstrating that the driving force of the LCST transition process was hydrophobic interaction among C-H groups. Unlike the dehydration process triggered by the dehydration of SO<sub>3</sub> groups in P[SS-P<sub>2</sub>] solution, hydrophobic C-H groups in [SS-P<sub>2</sub>] solution dehydrated firstly. Afterwards, hydrogen bonds between SO<sub>3</sub> groups and water molecules fractured and SO<sub>3</sub> groups began to dehydrate. Since C-H groups and SO<sub>3</sub> groups can respectively represent dications and anions, the dynamic process of dications and anions in [SS-P<sub>2</sub>] during phase transition can be reflected by analyzing the sequence order of C-H groups and SO<sub>3</sub> groups. Apparently, dications instead of anions responded to the increasing temperature firstly and aggregated with each other. Then, driven by coulomb forces, anions dehydrated sequentially and were also involved in aggregates. In addition, diation were connected by long alkyl chains, which made it easier to achieve hydrophobic interaction and dehydrate. The process was similar to its corresponding mono-cationic IL.

Table S1. Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of P[SS-P<sub>2</sub>].

1122	-	-	-	-	-	-	-	-	-
1129	-	-	-	-	-	-	-	-	-
2860	+	+	-	-	+	+			
2872	+	+	-	-	+				
2883	+	-	-	-					
2930	+	+	-						
2944	+	+							
2957	+								
2974									
	2974	2957	2944	2930	2883	2872	2860	1129	1122

Table S2. Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of [SS-P<sub>2</sub>].

1122	+	+	+	+	+	+	+	+	+
1129	+	+	+	+	+	+	+	+	
2860	-	+	-	-	-	+			
2872	-	-	-	-	-				
2883	-	+	-	+					
2930	-	+	-						
2944	+	+							
2957	-								
2974									
	2974	2957	2944	2930	2883	2872	2860	1129	1122