Electronic Supplementary Information (ESI) for

## Enhanced self-assembly for the solubilization of cholesterol in molecular solvent/ionic liquid mixtures



Fig. S1 WAXD patterns of the *n*-heptane/ $[P_{4444}][C_{15}H_{31}COO]$  mixture with a fixed cholesterol concentration of 0.40 as *n*-heptane's concentration from 5 wt% to 80 wt% at ambient temperature.



**Fig. S2** POM images of the *n*-heptane/ $[P_{4444}][C_{15}H_{31}COO]$  mixture with a fixed cholesterol concentration of 0.40 as *n*-heptane's concentration from 5 wt% to 80 wt% at ambient temperature. (a) 5 wt%; (b) 10 wt%; (c) 20 wt%; (d) 80 wt%. The scale bar is presented as marked above.





**Fig. S3** POM images of the DMSO/ $[P_{4444}][C_{15}H_{31}COO]$  (10 wt%) (a), methanol/ $[P_{4444}][C_{15}H_{31}COO]$  (15 wt%) (b), and EA/ $[P_{4444}][C_{15}H_{31}COO]$  (40 wt%) (c) mixtures with a fixed cholesterol concentration of 0.40 at ambient temperature. The scale bar is presented as marked above. (Note: the temperature in (a) is 35°C as the solubility is less than 0.40 at ambient temperature.)



**Fig. S4** WAXD patterns (from top to bottom) of the DMSO/ $[P_{4444}][C_{15}H_{31}COO]$  (10 wt%) (blue), methanol/ $[P_{4444}][C_{15}H_{31}COO]$  (15 wt%) (cyan), EA/ $[P_{4444}][C_{15}H_{31}COO]$  (40 wt%) (orange), *n*-heptane / $[P_{4444}][C_{15}H_{31}COO]$  (40 wt%) (green), methanol/ $[P_{4444}][CH_{3}COO]$  (15 wt%) (violet), and EA/ $[P_{4444}][CH_{3}COO]$  (40 wt%) (red), mixtures with a cholesterol concentration of 0.40 for  $[P_{4444}][C_{15}H_{31}COO]$  systems and saturated cholesterol for  $[P_{4444}][CH_{3}COO]$  systems at ambient temperature.



**Fig. S5** IR spectrum of cholesterol and cholesterol dissolved in *n*-heptane/ $[P_{4444}][C_{15}H_{31}COO]$  with *n*-heptane's concentration from 0 to 80 wt% at ambient temperature.



**Fig. S6** IR spectrum of cholesterol (blue line) and cholesterol dissolved in pure  $[P_{4444}][C_{15}H_{31}COO]$  (red line), DMSO/ $[P_{4444}][C_{15}H_{31}COO]$  (10 wt%) (green line), methanol/ $[P_{4444}][C_{15}H_{31}COO]$  (15 wt%) (magenta line), EA/ $[P_{4444}][C_{15}H_{31}COO]$  (40 wt%) (cyan line), and *n*-heptane/ $[P_{4444}][C_{15}H_{31}COO]$  (black line) respectively, at ambient temperature.



**Fig. S7** IR spectrum of cholesterol (blue line) and cholesterol dissolved in methanol/ $[P_{4444}][CH_3COO]$  (15 wt%) (red line), EA/ $[P_{4444}][CH_3COO]$  (50 wt%) (cyan line), methanol/ $[P_{4444}][C_{15}H_{31}COO]$  (15 wt%) (magenta line), and EA/ $[P_{4444}][C_{15}H_{31}COO]$  (40 wt%) (green line) respectively, at ambient temperature.

| Molecular structure of Cholesterol   | $HO = \frac{1}{4} + \frac{1}{5} + \frac{1}{6} + \frac{1}{5} + \frac{1}{6} + \frac{1}{5} +$ |        |        |        |
|--|--|--------|--------|--------|
| Mixtures   | $\Delta\delta = \delta(\text{complex}) - \delta(\text{free}) / (\text{ppm})$   |        |        |        |
|  | H2   | H3     | H4     | Н6     |
| <i>n</i> -heptane/[P <sub>4444</sub> ][C <sub>15</sub> H <sub>31</sub> COO] (20 wt%) | -0.028   | -0.03  | -0.052 | -0.029 |
| <i>n</i> -heptane/[P <sub>4444</sub> ][C <sub>15</sub> H <sub>31</sub> COO] (80 wt%) | -0.023   | -0.023 | -0.036 | -0.023 |
| EA/[P <sub>4444</sub> ][C <sub>15</sub> H <sub>31</sub> COO] (40 wt%)                | -0.027   | -0.032 | -0.051 | -0.027 |
| DMSO/[P <sub>4444</sub> ][C <sub>15</sub> H <sub>31</sub> COO] (10 wt%)              | -0.029   | -0.034 | -0.052 | -0.03  |
| methanol/[P <sub>4444</sub> ][C <sub>15</sub> H <sub>31</sub> COO] (15 wt%)          | -0.028   | -0.033 | -0.054 | -0.03  |

**Table S1** The molecular structure of cholesterol and <sup>1</sup>H NMR spectrum shift of cholesterol in molecularsolvent/[ $P_{4444}$ ][ $C_{15}H_{31}$ COO] mixtures with a fixed cholesterol concentration of 0.40