Supporting Information

Versatile solid modifications of Icariin: structure, properties and form transformation

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All the crystals that obtained from the ICA organic solutions presented very similar XRPD patterns (Figure S1) and crystal habits (Figure S2). The hydrogen bonds of different ICA solvates are summarized in Table S1. The two-dimensional packing patterns of the solvates and hydrates are presented in Figure S3. In solvates S3-S6, there are two different types of guest molecules and they are combined to two different host molecules by hydrogen bonds O_{7A} -H···O_{1s} and O_{2s} -H···O₃, respectively (Figure S4). Solvates S1-S8 were subjected to thermal analysis and the overlaid DSC and TGA profiles are summarized in Figure S5. The desolvation and phase transformation process are monitored by XRPD (Figure S6). All the residual samples of the ICA solid forms after DVS experiments were determined by XRPD (Figure S7). The transition process of *t*-pentanol ICA solvate was also recorded by XRPD (Figure S8) The phase transformation process of hydrate H2 was also determined by XRPD (Figure S9).



Figure S1. XRPD of crystals that obtained from the ICA organic solutions.



Figure S2. HSM photograhs of ICA solvates, S1~S8.

| | $O_9\text{-}H^{\dots}O_{14A}$ | O _{14A} -H…O ₁₃ | O ₁₄ -H…O _{13A} | O_{15A} - H ···O ₉ | O_{8A} -H \cdots O_{14} | O_{9A} - H ···O_{15} |
|------------|-------------------------------|-------------------------------------|-------------------------------------|-----------------------------------|-----------------------------|--------------------------|
| H1 | 2.804(3) | 2.713(3) | 2.715(3) | 3.081(3) | 2.743(3) | 2.774(3) |
| S 1 | 3.070(4) | 2.746(4) | 2.735(4) | 2.822(4) | 2.840(4) | 3.139(4) |
| S2 | 2.843(3) | 2.728(3) | 2.742(3) | 3.044(3) | 2.764(3) | 2.790(3) |
| S3 | 3.082(4) | 2.735(4) | 2.707(4) | 2.837(4) | 2.785(4) | 3.170(4) |
| S4 | 2.881(3) | 2.719(3) | 2.725(3) | 3.162(4) | 2.769(3) | 2.813(3) |
| S5 | 2.826(4) | 2.754(4) | 2.717(4) | 3.089(4) | 2.857(4) | 3.012(4) |
| S6 | 2.815(4) | 2.703(4) | 2.743(4) | 3.095(4) | 2.779(4) | 2.825(4) |
| S 7 | 2.876(4) | 2.731(4) | 2.721(4) | 3.131(4) | 2.742(4) | 2.834(4) |
| S 8 | 3.104(4) | 2.703(4) | 2.736(4) | 2.850(4) | 2.821(4) | 3.127(4) |

Table S1 The hydrogen bonds of different ICA solvates, $d(D \cdots A)(A)$.





Figure S3. The two-dimensional packing patterns of the solvates and hydrates H1 of ICA.



(a)





Figure S4. Host-guest interactions in (a) S4, (b) S5, (c) S6.



(a)



(b)



(c)



(d)





(f)



(g)

Figure S5. The overlaid DSC and TGA profiles of (a) S1, (b) S2, (c) S3, (d) S5, (e) S6, (f) S7, (g) S8.



(a)



(b)



(c)



(d)



(e)



(f)



(g)

Figure S6. The desolvation and phase transformation process of different solvates under variable temperature (a) S1, (b) S2, (c) S3, (d) S5, (e) S6, (f) S7, (g) S8.





(b)



(c)



(d)



(e)



(f)



(g)



(h)



(i)



(j)



(k)



(1)

Figure S7. XRPD patterns of ICA solid forms before after DVS cycles, (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6, (g) S7, (h) S8, (i) H1 (j),H2 (k) form α, (l) form β.



Figure S8. The HSM photographs of S8 at different temprature.



Figure S9. The XRPD pattern of hydrate H2 during phase transformation process.