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Nature of reactant and influence of water on the supramolecular patterns and luminescent properties of organic salts comprising (1,1'-biphenyl)-4,4'-disulfonate and triphenylmethanaminium

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Fig. S1 Structures of salts 1-14 with the hydrogen-bonding interactions denoted as black dashed lines.



Fig. S2 Type I packing diagram tuned by H₂O in salt **1** (a) and MeOH in salt **2** (b) (pale blue ball-andstick: HTPMA⁺; green space filling: solvent molecules).



Fig. S3 Type III packing diagram tuned by *n*-BuOH in salt **5** (a) and *n*-PeOH in salt **6** (b) (pale blue balland-stick: HTPMA⁺; green space filling: solvent molecules).



Fig. S4 Type V packing diagram tuned by H₂O and *n*-PrOH in salt **11** (a), *n*-BuOH in salt **12** (b) and *n*-PeOH in salt **13** (c) (pale blue ball-and-stick: HTPMA⁺; turquoise and green space filling: solvenst and H₂O molecules).



Fig. S5 Side-to-plane $\pi \cdots \pi$ interactions (green dashed lines) in salt 14.



Fig. S6. PXRD patterns of salts 1-10 and 12-14 at room temperature.

Thermogravimetric analysis. To examine the thermal stability, powder X-ray diffraction (PXRD) patterns for solid samples of salts **1-10** and **12-14** are firstly measured at room temperature as illustrated in Fig. S6. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding

samples. Their stabilities were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 600 °C at a rate of 10 °C min⁻¹, under air. As shown in Fig. S7, salts **1-10** and **12-14** exhibit the similar weight loss with the first step corresponding to the release of solvent molecules which occurred in the range of 70-103, 80-116, 102-156, 92-115, 101-136, 107-146, 94-124, 70-135, 154-



Fig. S7 TG curves of salts 1-10 and 12-14.

240, 57-100, 69-115, 70-113, and 80-112 °C, respectively. The observed weight loss of 2.34% in 1, 3.58% in 2, 5.32% in 3, 17.52% in 4, 15.36% in 5, 17.61% in 6, 25.61% in 7, 27.04% in 8, 9.72% in 9, 10.87% in 10, 16.43% in 12, 18.71% in 13, and 20.95% in 14 is reasonably close to their calculated value (2.12% in 1, 3.70% in 2, 5.24% in 3, 17.79% in 4, 15.11% in 5, 17.47% in 6, 25.98% in 7, 27.28% in 8, 9.57% in 9, 10.73% in 10, 16.64% in 12, 18.92% in 13, and 21.12% in 14). Then, the following weight losses for salts 1-10 and 12-14 indicated the decomposition of the organic components. Totally, the pure solvent salts, especially, the *n*-PrOH, *n*-BuOH and *n*-PeOH induced salts 4-6, exhibit higher decomposition temperature than those of the mixed solvent salts 12 and 13. This result is mainly originated from their supramolecular structures. As shown in Fig. S4, the mixed solvents in salts 12 and 13 filled in the channels without any hindrance of host network, which may reduce the binding force to the solvents. On the contrary, the

solvents in salts **5** and **6** are apparently intersecting with the $-SO_3$ groups of BPDSA²⁻ dianions (Fig. S3). Such arrangement restricts the removal of solvent molecules to some extent, thus enhancing the decomposition temperature of these salts. Likewise, the high decomposition temperature of 154 °C for salt **9** is also caused by such reason.



Fig S8. Photographs for sample of H₂BPDSA, TPMA, salts 1-10 and 12-14 under UV source.