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## Influence of solvents and assembly methods on the supramolecular patterns and luminescent properties of organic salts comprising 4,4'-dihydroxybiphenyl-3,3'-disulfonate and triphenylmethanaminium

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Fig. S1 Structures of  $2(H_3O)^+ \cdot (H_2M)^{2-}$  and salts 1-12 with the hydrogen-bonding interactions denoted as black dashed lines.





**Fig. S3** Side-to-plane (blue dashed lines) and plane-to-plane (green dashed lines)  $\pi^{...}\pi$  interactions between HTPMA<sup>+</sup> cations and H<sub>2</sub>M<sup>2-</sup> dianions in salts **4** (top) and **6** (down).



Fig. S4 Side-to-plane  $\pi^{...}\pi$  interactions (green dashed lines) between HTPMA<sup>+</sup> cations and H<sub>2</sub>M<sup>2-</sup> dianions in salts 10 (left) and 12(right).



Fig. S5 PXRD patterns of  $2({\rm H_3O})^{+} \cdot ({\rm H_2M})^{2\text{-}}$  and salts 1-12.



Fig. S6 TG curves of  $2(H_3O)^+ (H_2M)^{2-}$  (a), salts 1, 2 (b), 3-6 (c), 7-9 (d) and 10-12 (e).

## Thermogravimetric analysis (TGA)

To examine the thermal stability, powder X-ray diffraction (PXRD) patterns for solid samples of  $2(H_3O)^+$   $(H_2M)^{2-}$  and salts 1-12 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<sup>-1</sup>, under air. As shown in Fig. S6,  $2(H_3O)^+ (H_2M)^{2-}$  and salts 1-12 exhibit the similar weight loss with the first step corresponding to the release of solvent molecules which occurred in the range of 70-156, 50-98, 80-120, 50-102, 58-147, 50-130, 110-160, 115-168, 128-180, 80-187, 75-173 and 66-168 °C, respectively. The observed weight loss of 9.92% in  $2(H_3O)^+$   $(H_2M)^2$ , 7.81% in 1, 3.87% in 2, 8.53% in 3, 12.83% in 4, 12.98% in **6**, 12.07% in **7**, 14.77% in **8**, 17.05% in **9**, 16.82% in **10**, 10.72% in **11** and 15.41% in **12** is reasonably close to their calculated value  $(9.94\% \text{ in } 2(\text{H}_3\text{O})^+ (\text{H}_2\text{M})^{2-}, 7.69\% \text{ in } 1, 3.92\% \text{ in } 2, 8.67\% \text{ in } 3, 12.90\%$ in 4 and 6, 12.20% in 7, 14.63% in 8, 16.93% in 9, 16.92% in 10, 10.89% in 11 and 15.30% in 12). Then, the following weight losses for  $2(H_3O)^+ (H_2M)^{2-}$  and the eleven salts indicated the decomposition of the organic components. Different from the above twelve salts, salt 5 exhibits nearly one loss step from 182 to 556 °C, in which all the organic components decomposed gradually.



Fig. S7 Emission spectrum of TPMA in the solid-state at room temperature.