

Supporting Information

Solvent Effect on the Supramolecular Patterns and Luminescent Properties
of Organic Salts Comprising Naphthalene-1,5-disulfonic Acid and
Triphenylmethyllamine

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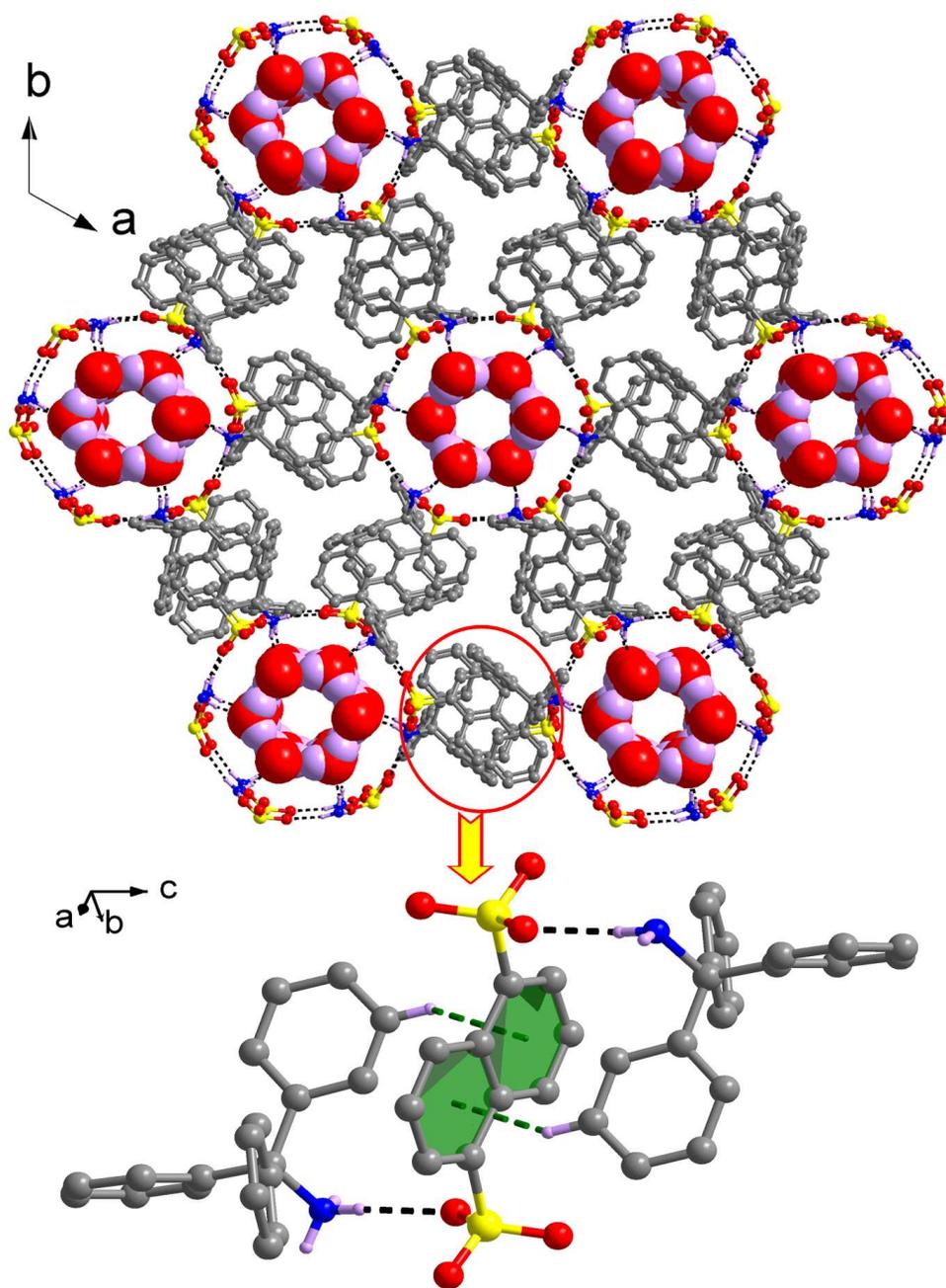


Figure S3 3-D porous hydrogen-bonding organic framework of salt 9, showing the two different channels and C-H... π interactions.

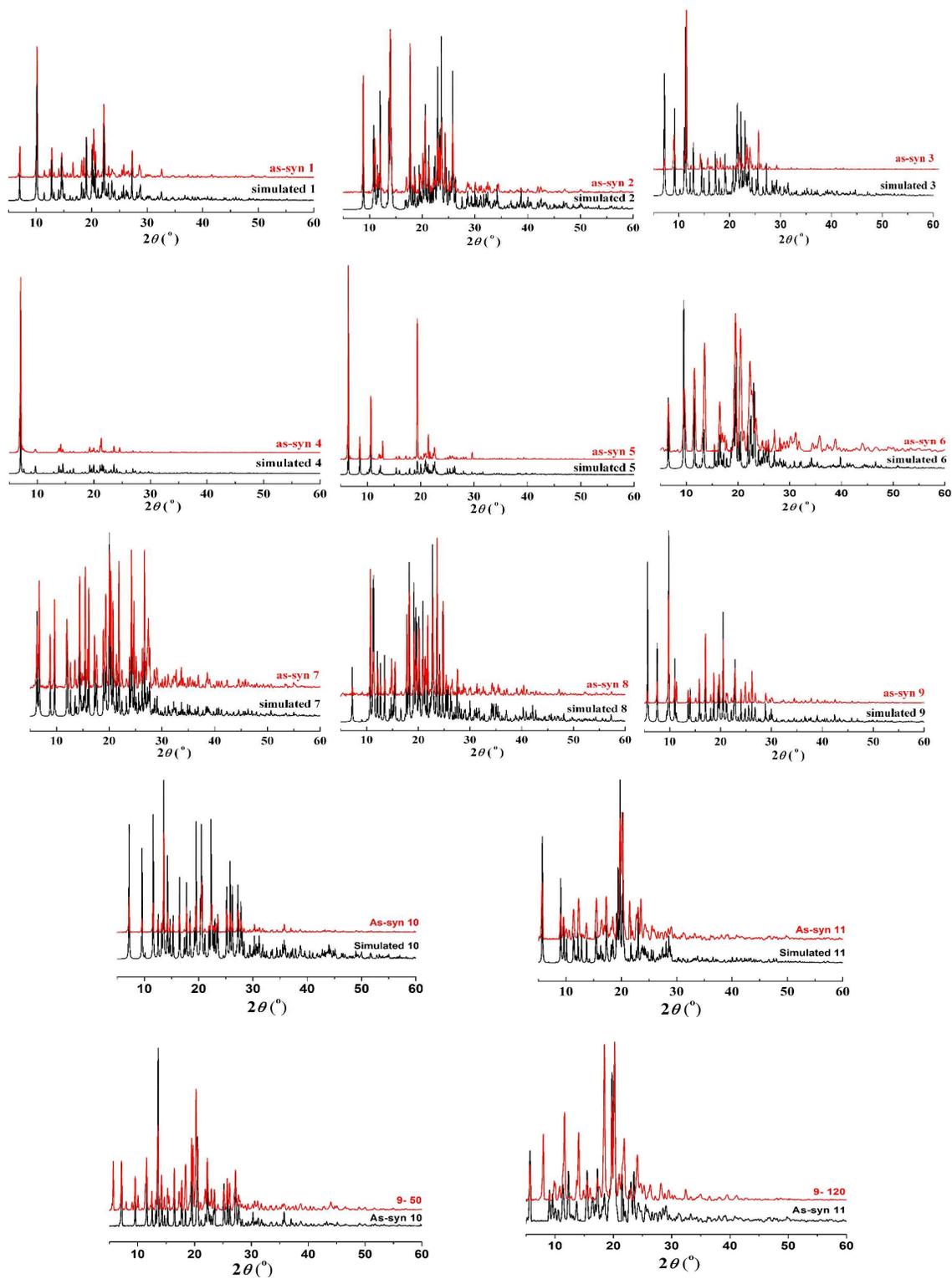


Figure S4. PXRD patterns of salts **1-11**. Last line: comparison of PXRD patterns between **10** and **9-50**, **11** and **9-120** at room temperature.

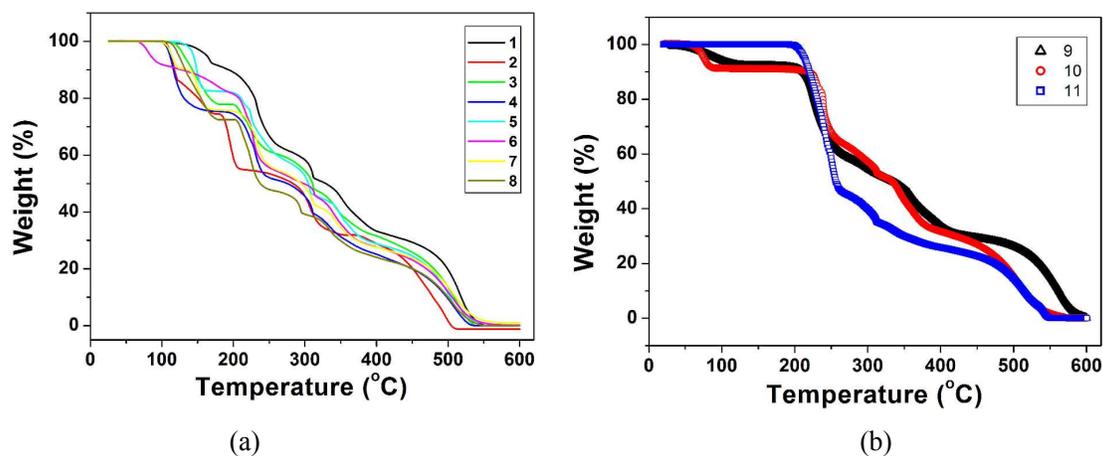


Figure S5 TG curves of salts **1-8** (a) and **9-11** (b).

Thermogravimetric analysis. To examine the thermal stability, powder X-ray diffraction (PXRD) patterns for solid samples of salts **1-11** are firstly measured at room temperature as illustrated in Figure S4 (*Supporting Information*). 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 Figure S5 (*Supporting Information*), salts **1-10** exhibit the similar weight loss with the first step corresponding to the release of solvent molecules which occurred in the range of 125-175, 110-169, 110-176, 106-162, 120-163, 67-190, 107-173, 110-178, 50-120 and 54-96 °C, respectively. The observed weight loss of 7.22% in **1**, 25.43% in **2**, 22.73% in **3**, 26.91% in **4**, 18.06% in **5**, 19.11% in **6**, 26.41% in **7**, 28.04% in **8**, 7.93% in **9**, and 8.36% in **10** is reasonably close to their calculated value (7.36% in **1**, 25.61% in **2**, 22.95% in **3**, 26.87% in **4**, 17.93% in **5**, 19.17% in **6**, 26.59% in **7**, 27.91% in **8**, and 8.20% in **9** and **10**). Then, the following weight losses for salts

1-11 indicated the decomposition of the organic components. Salt **11** exhibits only one loss step from 200 °C corresponding to the decomposition of the organic components.

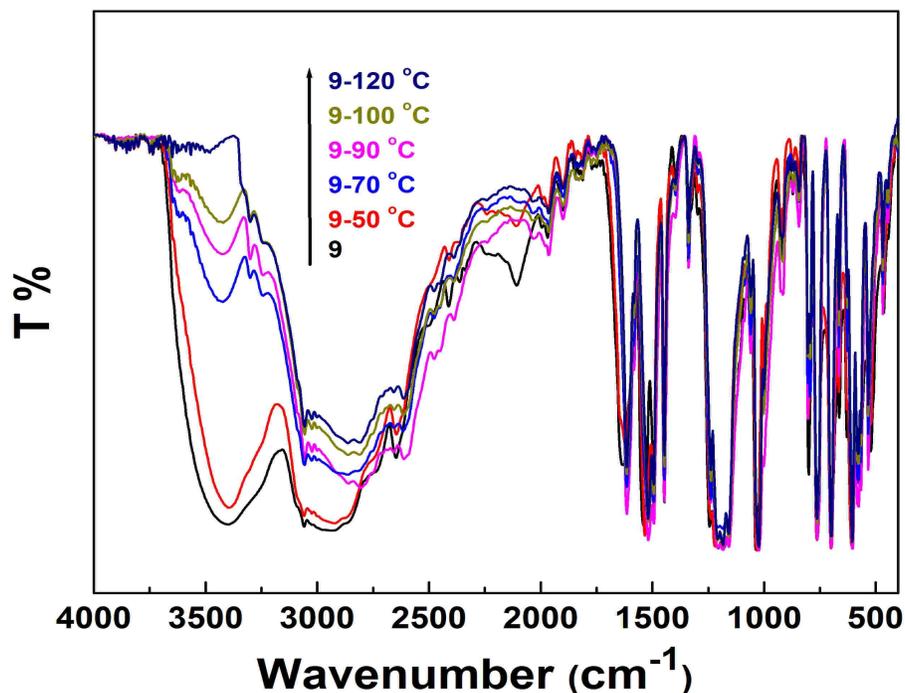


Figure S6 Temperature-dependent IR spectra of **9**.

Temperature-dependent IR Spectra. As shown in Figure S6, the stretching bands around 3406 cm^{-1} in the IR spectra can be attributed to water molecules and extensive hydrogen-bonding interactions. The sharp stretching band appearing around 3190 cm^{-1} corresponds to the existence of the N-H group. The bands appearing in the range of 1633 ~ 1449 cm^{-1} and 1338 cm^{-1} are ascribed to the $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}-\text{N}}$ stretching vibrations of the NDS^{2-} anion and HTPMA^+ cation. The characteristic vibrations of $\nu_{\text{as}}(\text{SO}_3^-)$ are in the range of 1253 ~ 1141 cm^{-1} , whereas the $\nu_{\text{s}}(\text{SO}_3^-)$ absorptions locate at 1037 cm^{-1} . With the increasing of temperature, the intensity around 3406 cm^{-1} is gradually decreased from 50 to 120 °C.



Figure S7 Pictures of single crystals of salts **9-11**.

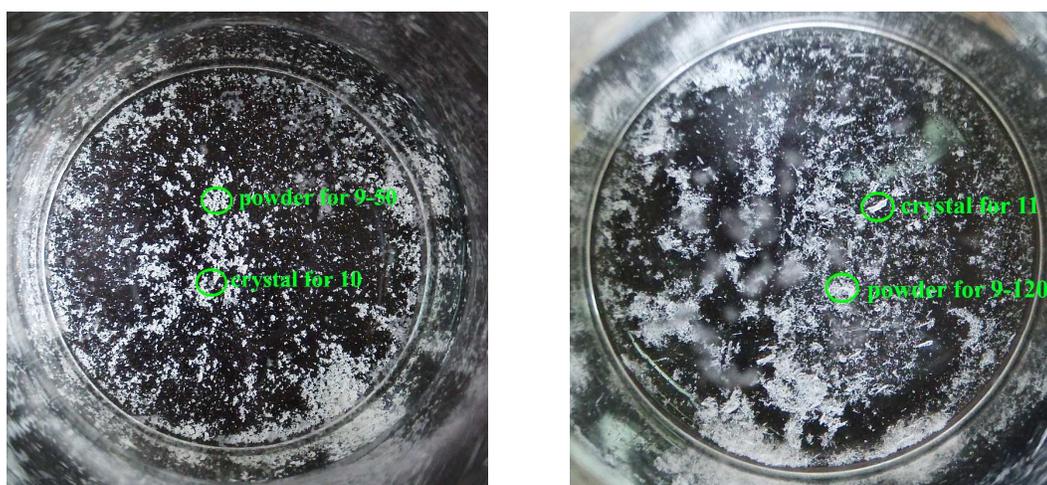
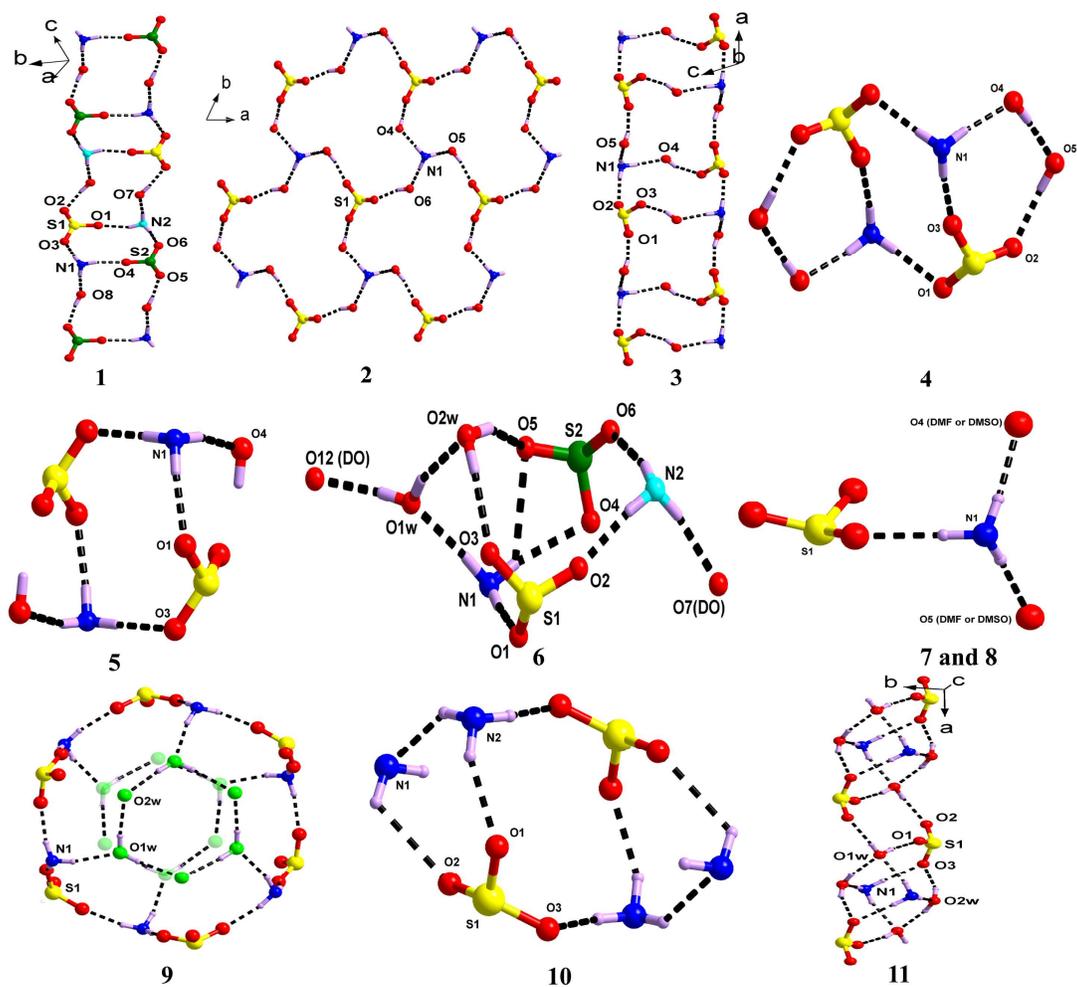


Figure S8 Recrystallization **10** (left) and **11** (right) from **9-50** and **9-120** in aqueous solution.

Structural Change. Powder samples of **9-50** and **9-120** were dispersed in aqueous solution. After *ca.* one month, blocky and prismatic single crystals in the two systems were formed, which were picked up for single-crystal diffraction. To our surprise, two new structures of **10** and **11** were obtained. Meanwhile, the left powders were proved to be **9-50** and **9-120** by PXRD. According to these results, we inferred that the phenomena are recrystallization rather than in aqueous solution transformation.



Scheme S1 Diverse Supramolecular Patterns of the $-\text{SO}_3$ and $-\text{NH}_3$ Groups Tuned by Solvent Molecules in Salts **1-11**.

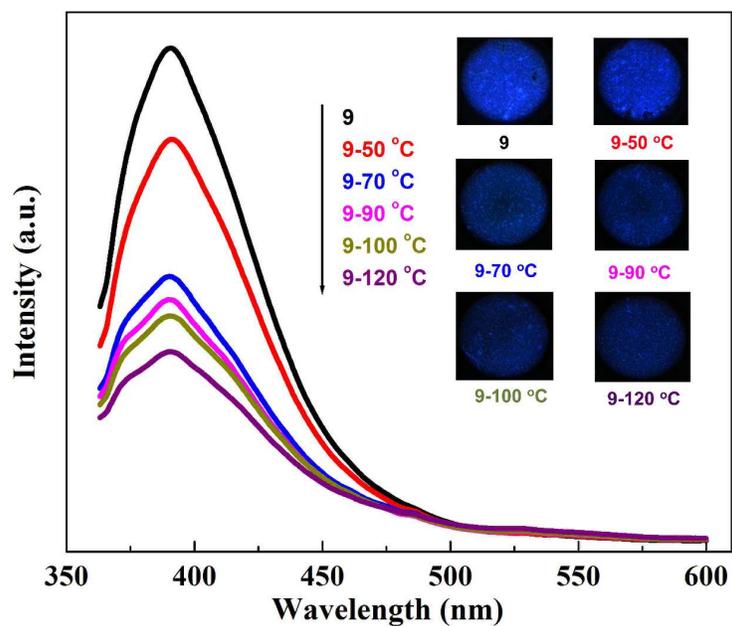


Figure S9 Temperature-dependent emission spectra for **9** in the solid-state at room temperature (insets: photographs of sample powder under UV source).

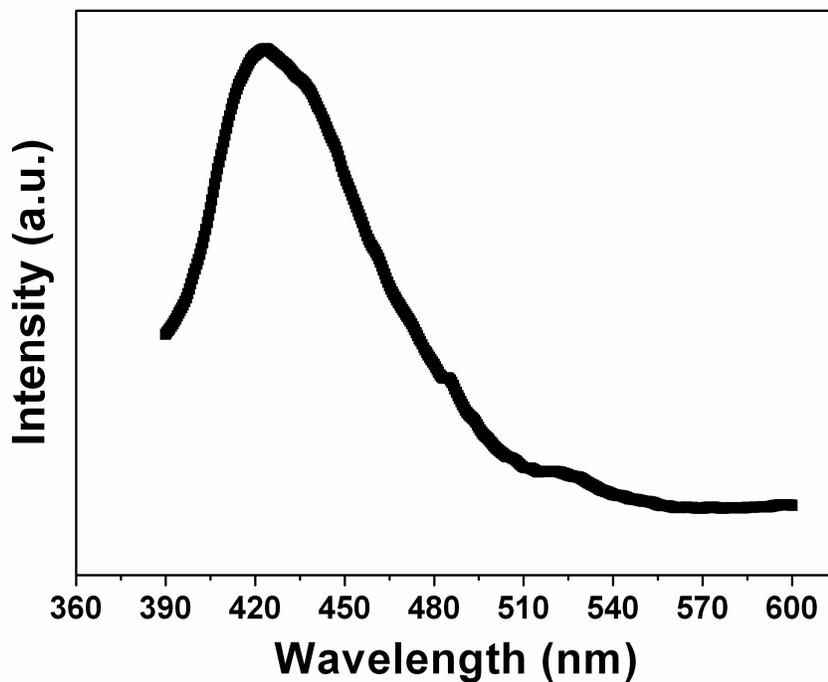


Figure S10 Emission spectrum of TPMA in the solid-state at room temperature.

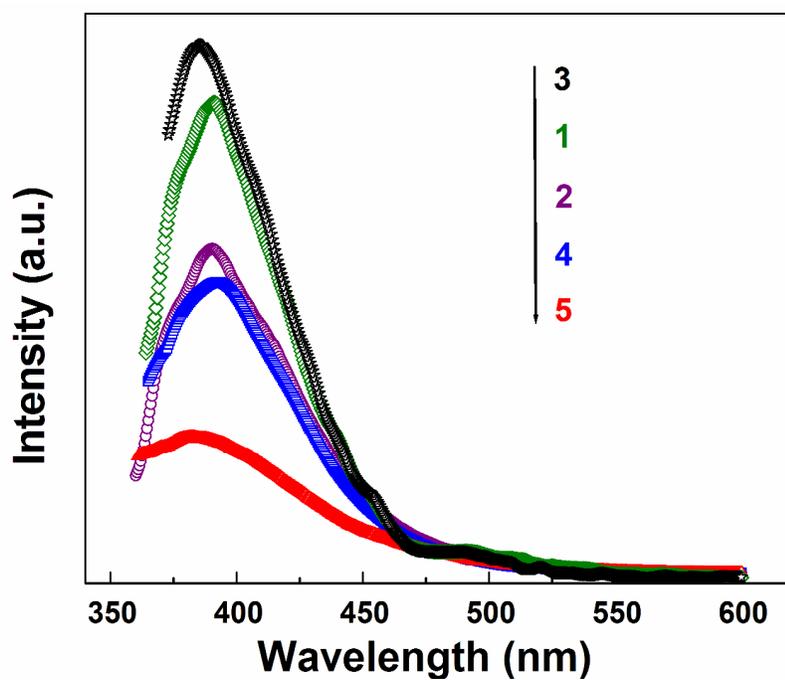


Figure S11 Emission spectra of salts 1-5 in the solid-state at room temperature.

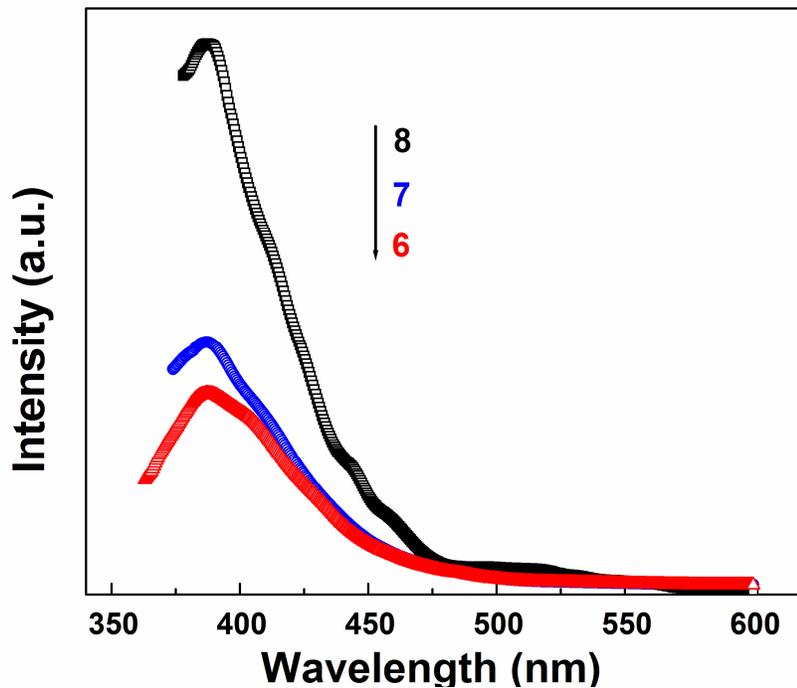


Figure S12 Emission spectra of salts 6-8 in the solid-state at room temperature.