

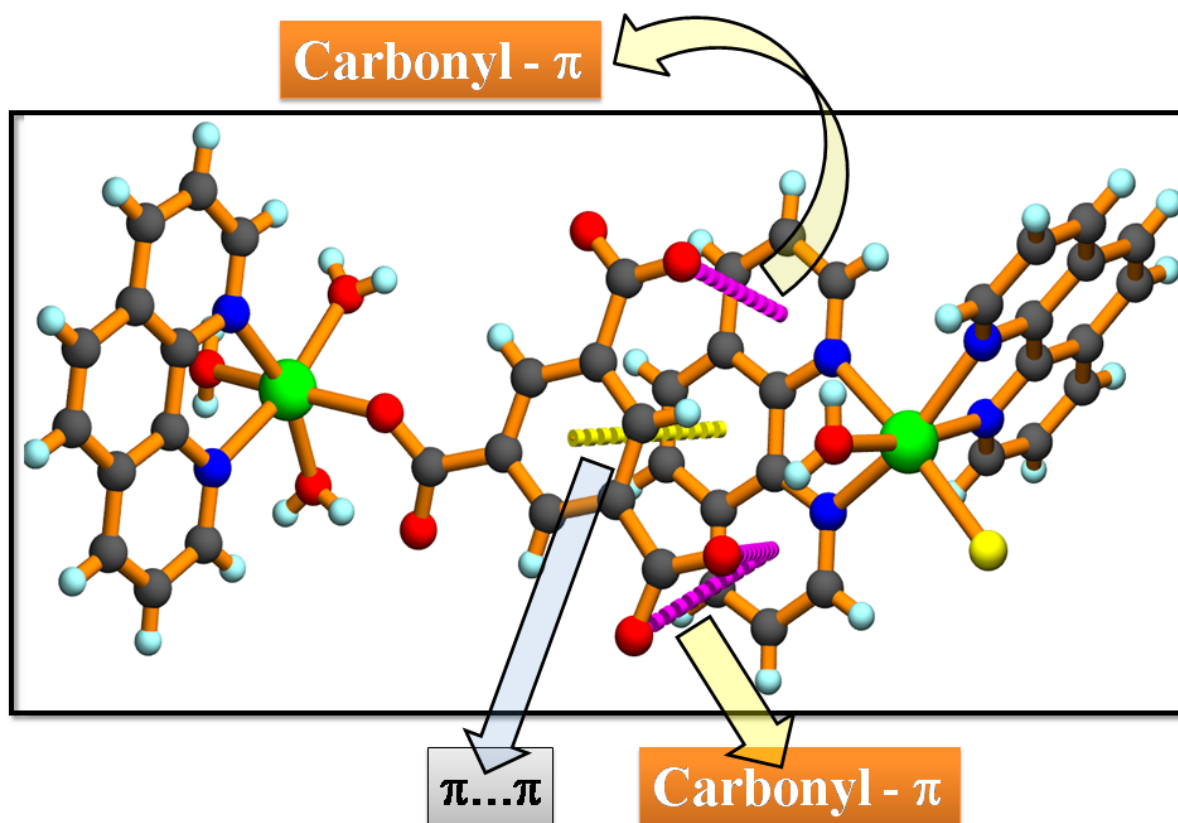
### Supplementary information

**A rare supramolecular assembly involving ion pairs of coordination complexes with a host-guest relationship: synthesis, crystal structure, photoluminescence and thermal study**

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**Fig. S1** Cooperative  $\pi$ ... $\pi$  and carbonyl lone pair... $\pi$  interaction between anionic and cationic units.

## Infrared spectroscopy

IR spectra (KBr pellet,  $400 - 4000 \text{ cm}^{-1}$ ) (Fig. S2) of complex **1** shows the characteristic bands of the carboxylate groups of 1, 3, 5- benzenetricarboxylate ligands at  $1613 - 1567 \text{ cm}^{-1}$  for the asymmetric vibration and at  $1427 - 1366 \text{ cm}^{-1}$  for the symmetric vibration. Complex **1** exhibits very strong and sharp band at  $1613$ ,  $1567$ ,  $1427$  and  $1366 \text{ cm}^{-1}$ . The bands at  $1613$  and  $1366 \text{ cm}^{-1}$  corresponding to stretching vibrations of  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$  bands respectively for unidentate carboxylate group. The separation between two  $\nu(\text{CO})$  is  $274 \text{ cm}^{-1}$  which also support the presence of monodentate carboxylate group. The bands at  $1567$  and  $1427 \text{ cm}^{-1}$  corresponds to the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$  stretching frequency respectively for free carboxylate groups of btc. The absence of the characteristic bands at  $1730 - 1690 \text{ cm}^{-1}$  for protonated carboxylate groups indicates the presence of complete deprotonated form of the 1, 3, 5- benzenetricarboxylic acid. The broad band ( $3500 - 3200 \text{ cm}^{-1}$ ) confirms the presence of water molecules. The IR spectra also show bands corresponding  $\rho_r(\text{H}_2\text{O})$  ( $726 \text{ cm}^{-1}$ ) and  $\rho_w(\text{H}_2\text{O})$  ( $637 \text{ cm}^{-1}$ ) which indicate the presence of coordinated water molecules.

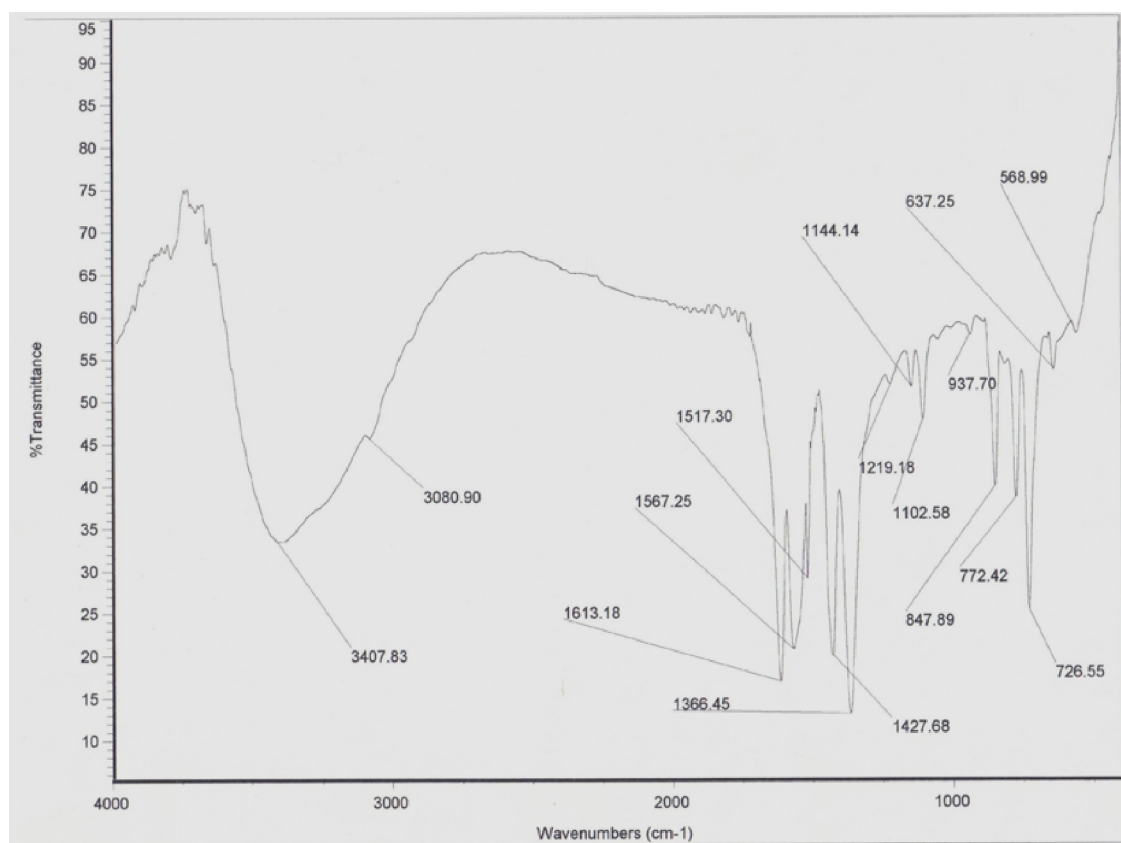
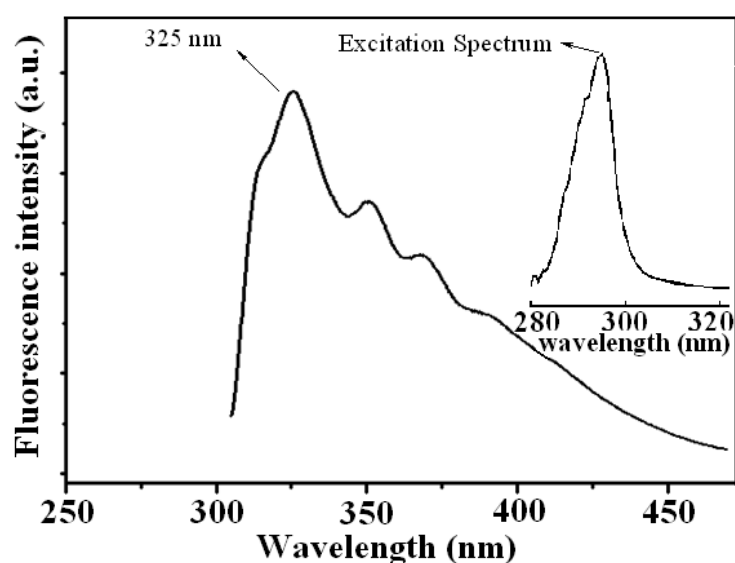


Fig. S2 IR spectrum of complex **1**.

## Photoluminescence properties

Luminescent compounds are of great interest because of their various applications in chemical sensors, photochemistry, and electroluminescent displays.<sup>s1</sup> The absorption maxima of free Na<sub>3</sub>btc and phen appear in ultraviolet region at 295 nm and 309 nm respectively (Figs. S3 and S4), which are assigned to the  $\pi$ - $\pi^*$  transitions of the aromatic ring. Both Na<sub>3</sub>btc and phen shows photoluminescence, the maxima emission for the ligands are located at 325 nm for Na<sub>3</sub>btc and 363 and 379 nm for phen (Figs.S3 and S4). The complex has its own excitation spectrum (Fig.S5) different from those of Na<sub>3</sub>btc and phen. The strongest excitation peak of complex **1** is at 290 nm, a higher energy than those for Na<sub>3</sub>btc and phen excitation peaks, 295 and 309 nm. The fluorescence spectra of complex **1** recorded in water solution shown in Fig.S5. Upon excitation at 290 nm complex **1** displays fluorescence emission at 367 nm and 384 nm. Because two emission peaks at 363 and 380 nm appears for the free phen ligand, thus the emission bands at 366 and 383 nm of **1** should be ascribed to the intra ligand charge transfer of phen.



**Fig. S3** Emission spectra of Na<sub>3</sub>btc (recorded in water at room temperature).

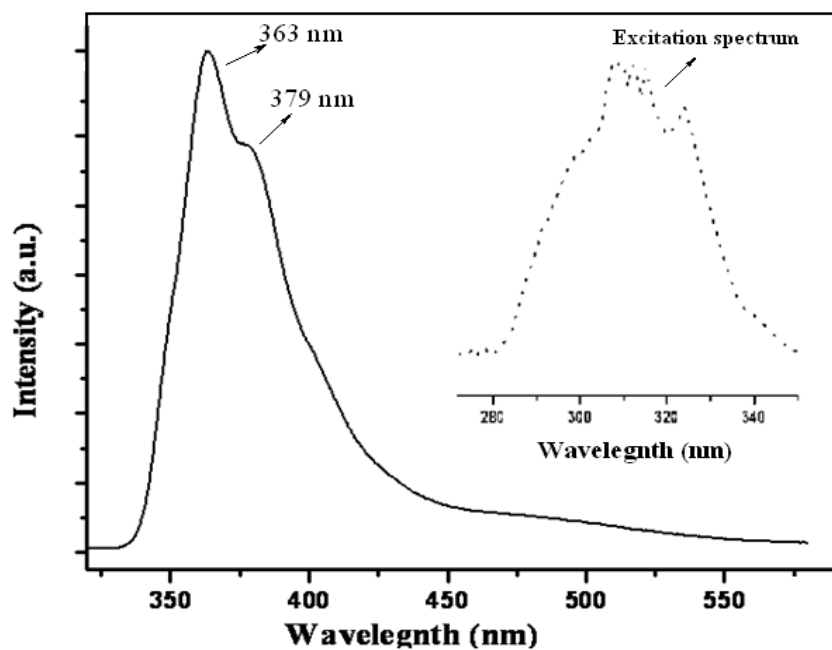


Fig. S4. Emission spectra of phen (recorded in methanol at room temperature).

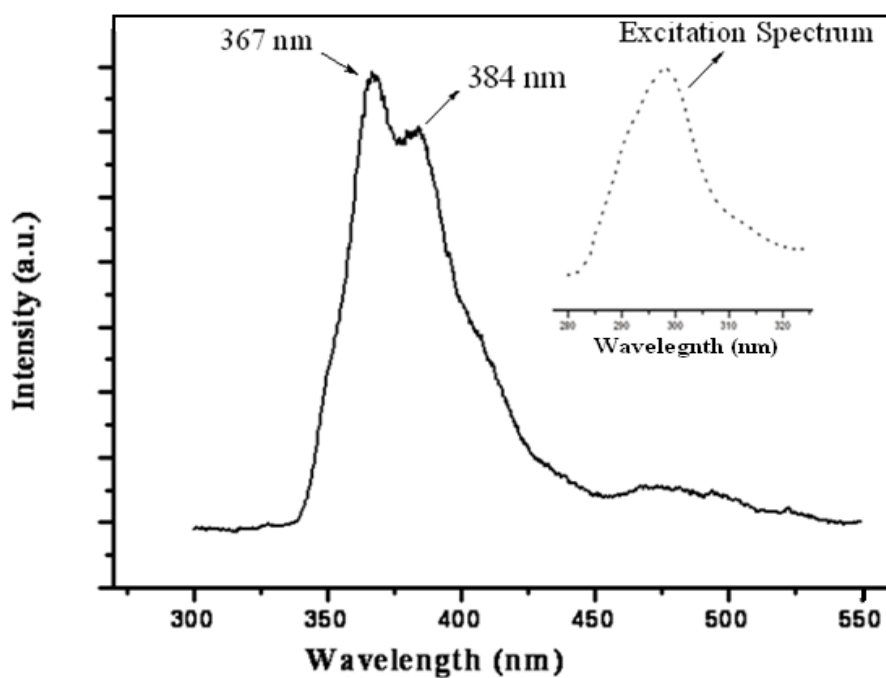
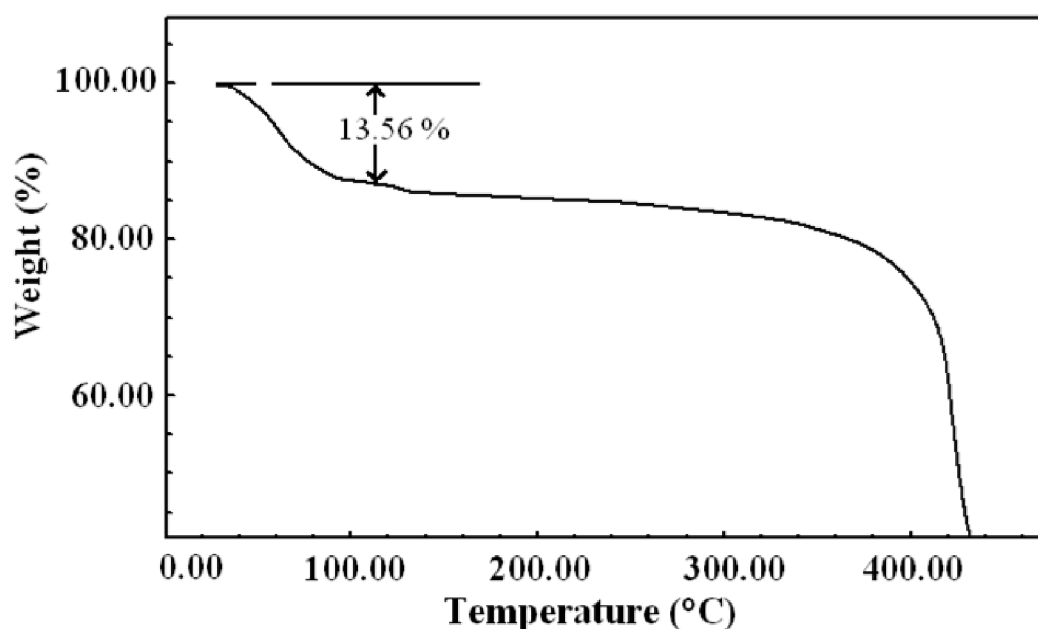


Fig.S5 Emission spectra of complex 1 (recorded in water at room temperature).

## Thermal analysis

Thermogravimetric (TG) analysis of complex **1** has been conducted at a rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere to 500 °C. The TG profile (Fig.S6) of complex **1** reveals that it starts to lose solvent molecules at ~ 27 °C and process completes at ~115 °C. The desolvated species collapses immediately upon further heating. The range of temperatures of desolvation and the collapse of the network immediately after desolvation corroborate the participation of lattice (water and methanol) and coordinated (water) solvent molecules in constructing the 3D supramolecular architecture.



**Fig.S6** Thermogravimetric analysis of complex **1**.

## References

- S1 (a) J. E. McGarrah, Y. J. Kim, M. Hissler and R. Eisenberg, *Inorg. Chem.*, 2001, **40**, 4510;  
(b) G. D. Santis, L. Fabbrizzi, M. Licchelli, A. Poggi and A. Taglietti, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 202.