Electronic Supplementary Material (ESI) for CrystEngComm

Co-crystallization turned on the phosphorescence of phenanthrene by C-Br···π halogen bonding, π-hole···π bonding and other assisting interactions

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Supporting information

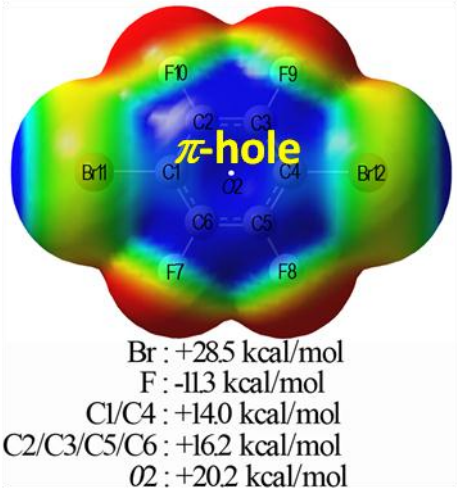

Figure S1 The molecular surface electrostatic potential of 1,4-DBrTFB was generated by mapping the MP2/6-311++G** electrostatic potential onto surface of molecular electron density (0.001 electron/bohr3) (kcal/mol)

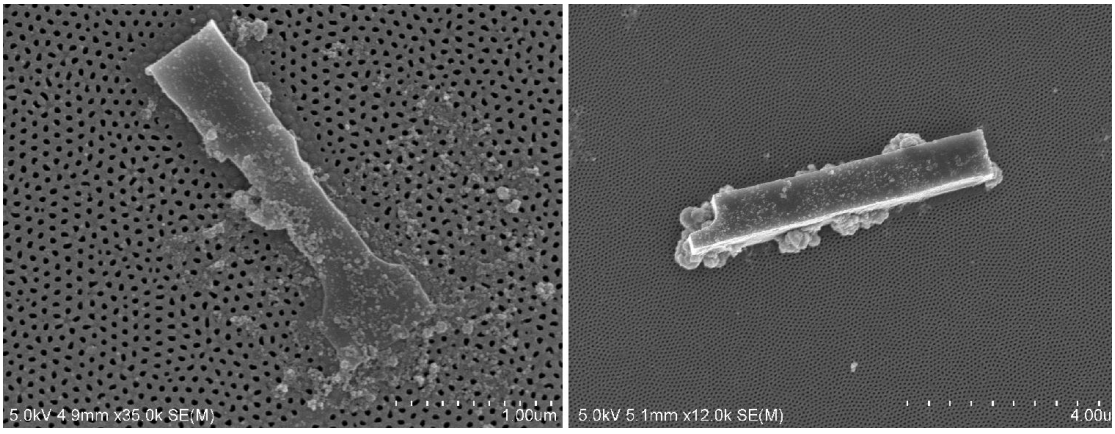

Figure S2 SEM of 1,4-DBrTFB (left) and Phe (right)

Phosphorescent properties of suspension of cocrystal microparticles

The mixture of Phe and 1,4-DBrTFB are not phosphorescent in ethanol solution but they become highly emissive in the suspension of microparticle cocrystal. Figure S2 depicts luminescent/phosphorescent spectra of Phe/1,4-DBrTFB mixture in ethanol and an ethanol/water mixture (2% ethanol, v/v), respectively. The excitation and emission wavelengths are somewhat different from the cocrystal grown from organic solvent. It is most possibly due to the effect of polar hydration layer wrapping the cocrystal

microparticles in suspension.

In addition, although the excitation spectrum appears different from that of cocrystal, the emission at 673 nm has close intensity to 0-0 band, it is agreement with cocrystal. And interval of 50-74 nm between vibrational bands displays the consistency with cocrystal. For cocrystal reported previously[sR1], the difference in phosphorescent intensity of Phe between 0-0 and third bands (therein at 675 nm) is obvious and the phosphorescence lifetime of Phe is 1.4 ms. So, it should be believed that the cocrystal microparticles in suspension should has the same crystal structure with 1,4-DBrTFB/Phe cocrystal prepared from organic solution.

Decay of cocrystal microparticle suspension is also investigated. As shown as Figure S2 and Table S1, the decay behaviors also are somewhat different from the cocrystal grown from organic solvent due to the reason mentioned above.

Table S1. Phosphorescent character of cocrystal microparticles in suspension

Phosphorescence spectra		decay			
λ_{ex}/nm	λ_{em}/nm	$\lambda_{ex}/\lambda_{em}$/nm	τ_1/ms (f_1 /%)	τ_2/ms (f_2 /%)	$\tau_{average}$/ms
290, 330	565, 612, 673, 741	290-565	5.254 (74.7)	2.364 (25.3)	4.523
290, 330	565, 612, 673, 741	290-673	6.523 (39.4)	3.266 (60.6)	4.549

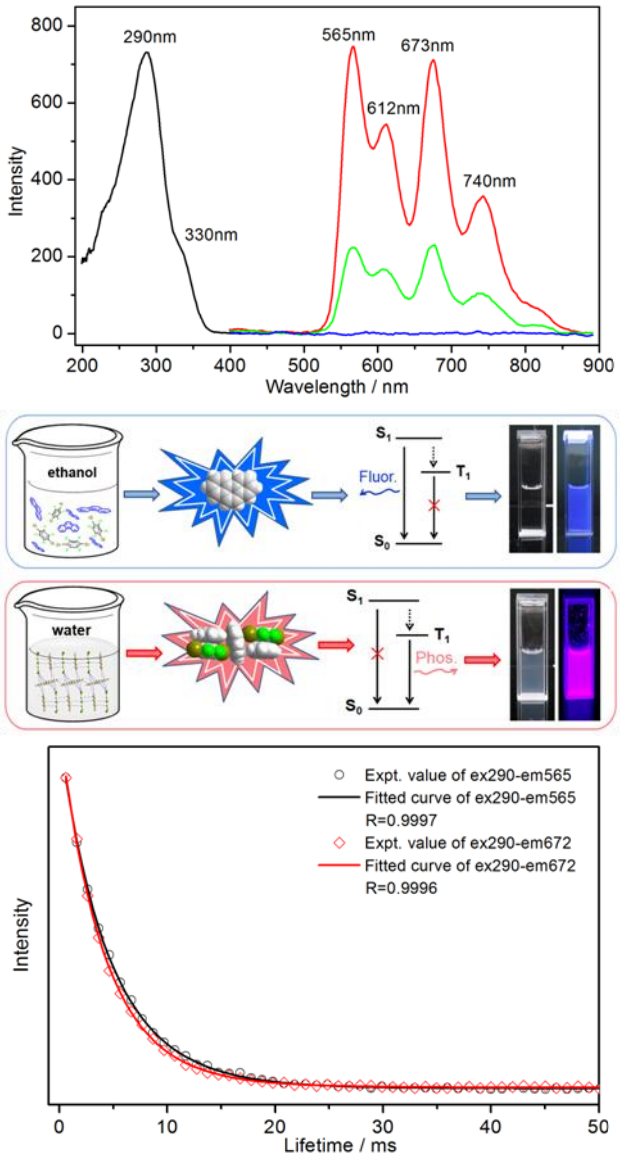

Figure S3. Phosphorescent spectra (upper) for Phe/DBrTFB mixture in pure ethanol (blue line: basically a flat line parallel to the abscissa) and ethanol/water mixture (black line: excitation spectra; red line: emission spectra when excitation is set at 290 nm; green line: emission spectra when excitation is set at 330 nm). [Phe]=3.0×10^{-4} mol/L; [DBrTFB]=2.0×10^{-4} mol/L. Luminescent scheme (middle) in ethanol solution (upper-panel): Phe is blue-fluorescent but nonphosphorescent (phosphorescence is probably quenched by dissolved oxygen); In 2% ethanl/98% water (lower-panel): the suspension of co-crystilline microparticles is phosphorescent. Phosphorescent decay of cocrystal microparticles in suspension (Lower) with di-exponential law.

Stoichiometry of suspension of cocrystal microparticles

The phosphorescent intensity increases progressively with varying 1,4-DBrTFB concentration, as shown as in Figure S3. Interestingly, when the molar ratio of Phe and 1,4-DBrTFB reaches just 3:2, the maximum phosphorescence intensity can be obtained. Then further increase of 1,4-DBrTFB concentration results in the decrease of phosphorescence. The result implies the stoichiometry of Phe and 1,4-DBrTFB may be 3:2, which is consistent with that revealed in cocrystal. Further, it may mean the microparticles of cocrystal prepared in aqueous solution have almost the same structural properties. The phosphorescent lifetime very closely consistent with that measured in cocrystal may support further the conclusion.

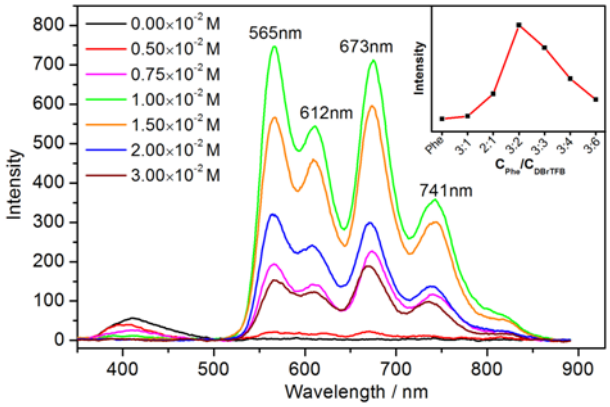

Figure S4. Evolution of phosphorescence spectra of cocrystal microparticles in suspension as increase of 1,4-DBrTFB concentration from 0.0, 0.5, 1.0, 1.5, 2.0 to 3.0×10^{-4} mol/L and inset shows the plot of phosphorescent intensity *vs*. 1,4-DBrTFB concentration. [Phe]=3.0×10^{-4} mol/L.

REFERENCES

[sR1] Q. J. Shen, X. Pang, X. R. Zhao, H. Y. Gao, H.-L. Sun, W. J. Jin, *CrystEngComm*, 2012, **14**, 5027.