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Electronic Supplementary Information

Tunable room temperature phosphorescence and energy transfer in ratiometric cocrystals

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1. Experimental Procedures

Materials and Reagents. All the reagents (1,2,4-benzenetricarboxylic acid and melamine) were purchased from the Sigma Chemistry Co. Ltd. and used without further purification. Distilled water is prepared in our lab.

Synthesis. Cocrystal BTA-ME-1 was prepared by mixing starting materials 1,2,4-benzenetricarboxylic acid (0.6 mmol, 0.1261 g), melamine (0.6 mmol, 0.0756 g) and distilled water (15 mL) in poly(tetrafluoroethylene)-lined autoclaves. After heating at 120 °C for 2 h and cooling down to room temperature naturally, block-like transparent cocrystals are obtained (Yield: 85%). The block-like cocrystal BTA-ME-2 was synthesized by using the same method but with different amount of BTA (1.2 mmol, 0.2552 g) (Yield: 72%).

Characterization. Single-crystal X-ray diffraction data of these samples were carried out on Rigaku Oxford Diffraction Supernova X-ray source diffractometer equipped with monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. PXRD patterns of these samples were measured on a Rigaku Ultima-IV automated diffraction system with Cu Kα radiation (λ = 1.5406 Å). The measurements were made in a 2θ range of 5°–50° at room temperature with a step of 0.02° (2θ), a scan speed of 5° min^{-1}, while the working voltage was 40 kV and the working current was 30 mA. TGA tests were collected from room temperature to 1000 K on a Perkin-Elmer Diamond SII thermal analyzer under the atmosphere of nitrogen with a heating rate of 10 K min^{-1}. DSC thermograms were performed on the METTLER TOLEDO DSC 1 calorimeter under the atmosphere of nitrogen with a heating rate of 10 K min^{-1}. All the relevant photoluminescence (PL) tests and time-resolved lifetime were conducted on an Edinburgh FLS980 fluorescence spectrometer. The PLQY were reckoned by using a Teflon-lined integrating sphere (F-M101, Edinburgh, diameter: 150 mm and weight: 2 kg) accessory in FLS980 fluorescence spectrometer. PL microscope images of crystals were taken under OLYMPUS IXTI fluorescence microscope. Photographs for the long-afterglow imaging were captured under iphone X.

Electronic structure calculations of BTA-ME-1 and BTA-ME-2. All calculations were performed with the periodic density functional theory (DFT) method by using Dmol3 module in Material Studio software package.[1-3] The initial configurations were fully optimized by the Perdew-Wang (PW91) generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP).[4] The self-consistent field (SCF) converged criterion was within 1.0×10^{-5} hartree per atom and the converged criterion of the structure optimization was 1.0×10^{-3} hartree per bohr. The Brillouin zone was sampled by $1 \times 1 \times 1$ *k*-points, and calculation tests reveal that the increase in *k*-points does not affect the results.

2. Figure S1-Figure S10 and Table S1-Table S3

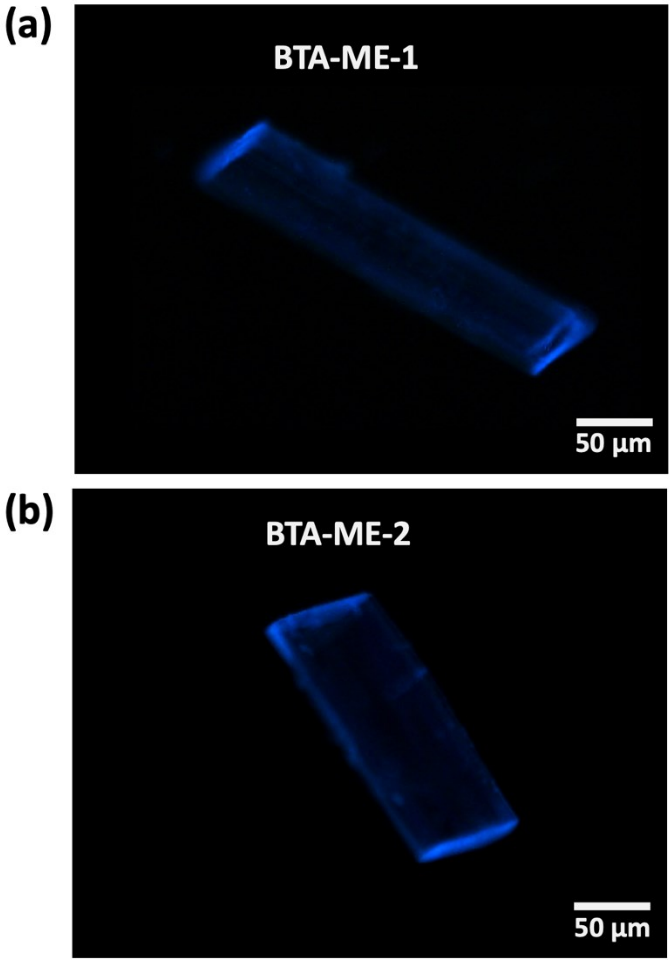


Fig. S1. The fluorescence microscopy images of the prepared cocrystals.

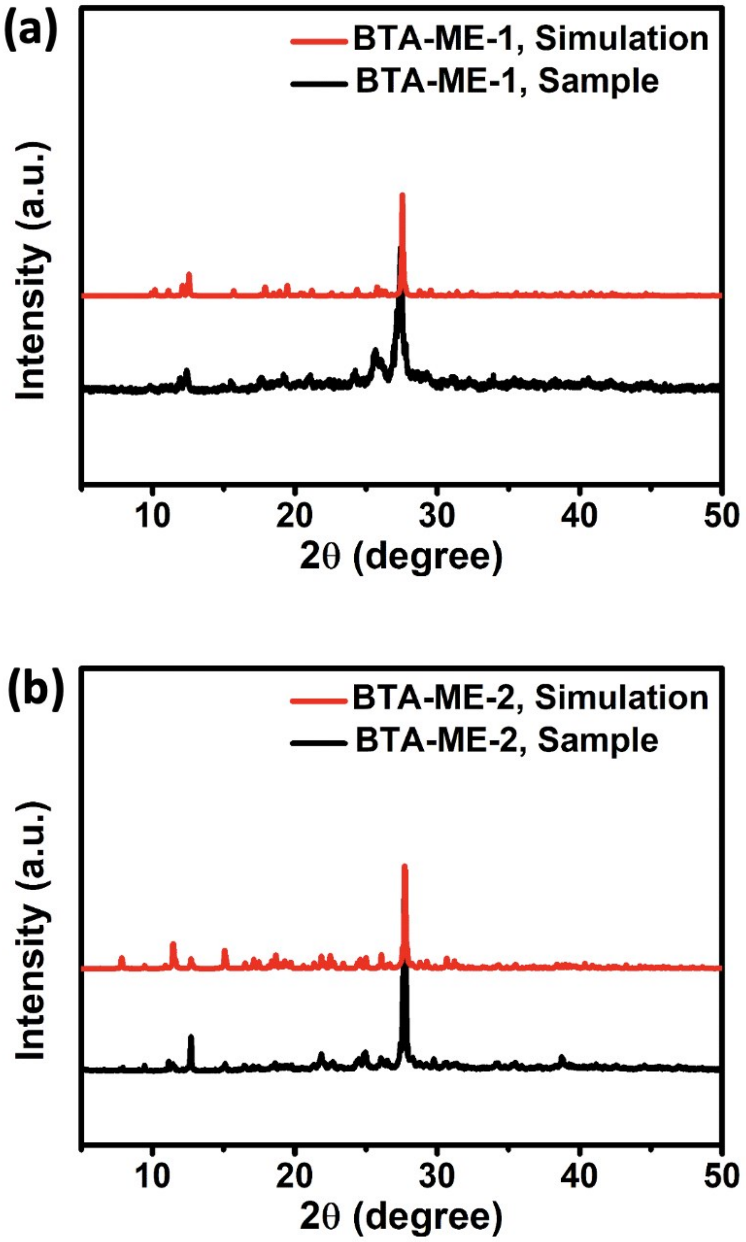
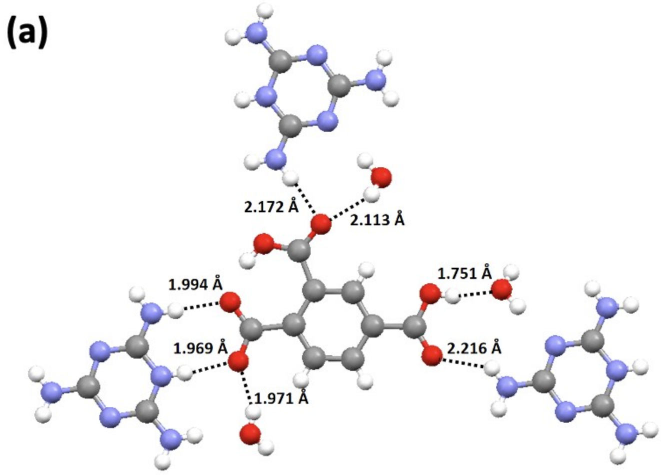
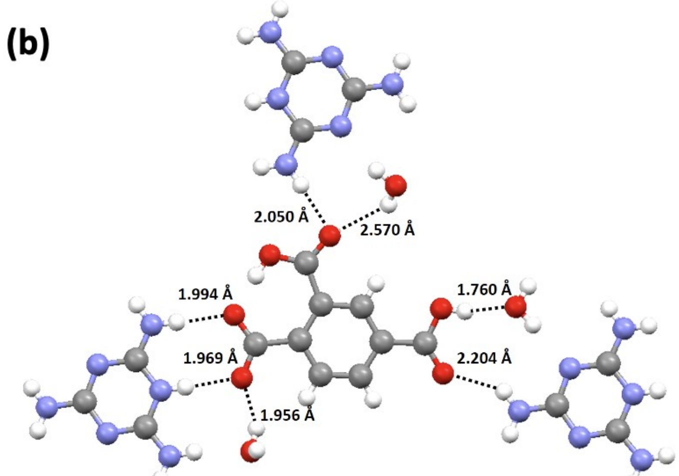


Fig. S2. The simulated (red) and as-synthesized (black) PXRD patterns for BTA-ME-1and BTA-ME-2.



BTA-ME-1



BTA-ME-2

Fig. S3. The hydrogen bonding networks of BTA-ME-1 and BTA-ME-2 in each layer.

It is shown that some hydrogen bonds of two ratiometric cocrystals are the same (such as the N-H···O: 1.994 Å, 1.969 Å). some hydrogen bonds of BTA-ME-1 are slightly longer than that of BTA-ME-2, and the remaining hydrogens bonds of BTA-ME-1 are slightly shorter than that of BTA-ME-2. The different stacking modes, relative orientations and aggregation states of molecules in ratiometric cocrystals can lead to different lengths of hydrogen bonds, since the hydrogen bonds (including the lengths and angles) are highly flexible and adjustable in a relative wide range in molecular crystals.

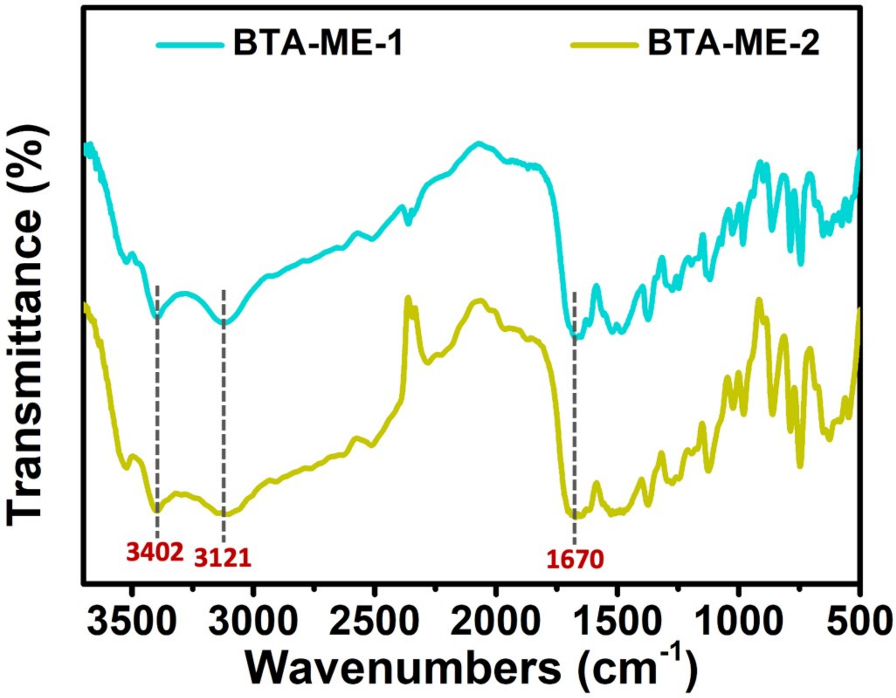


Fig. S4. The FT-IR spectra of BTA-ME-1 and BTA-ME-2 at room temperature.

The broad peaks from 3500 cm^{-1} to 3000 cm^{-1} can indicate the existence of intense hydrogen bonding. In addition, due to the formation of strong hydrogen bonds, vibrational peaks of aromatic carboxylic acid undergo red-shift to 1670 cm^{-1}.

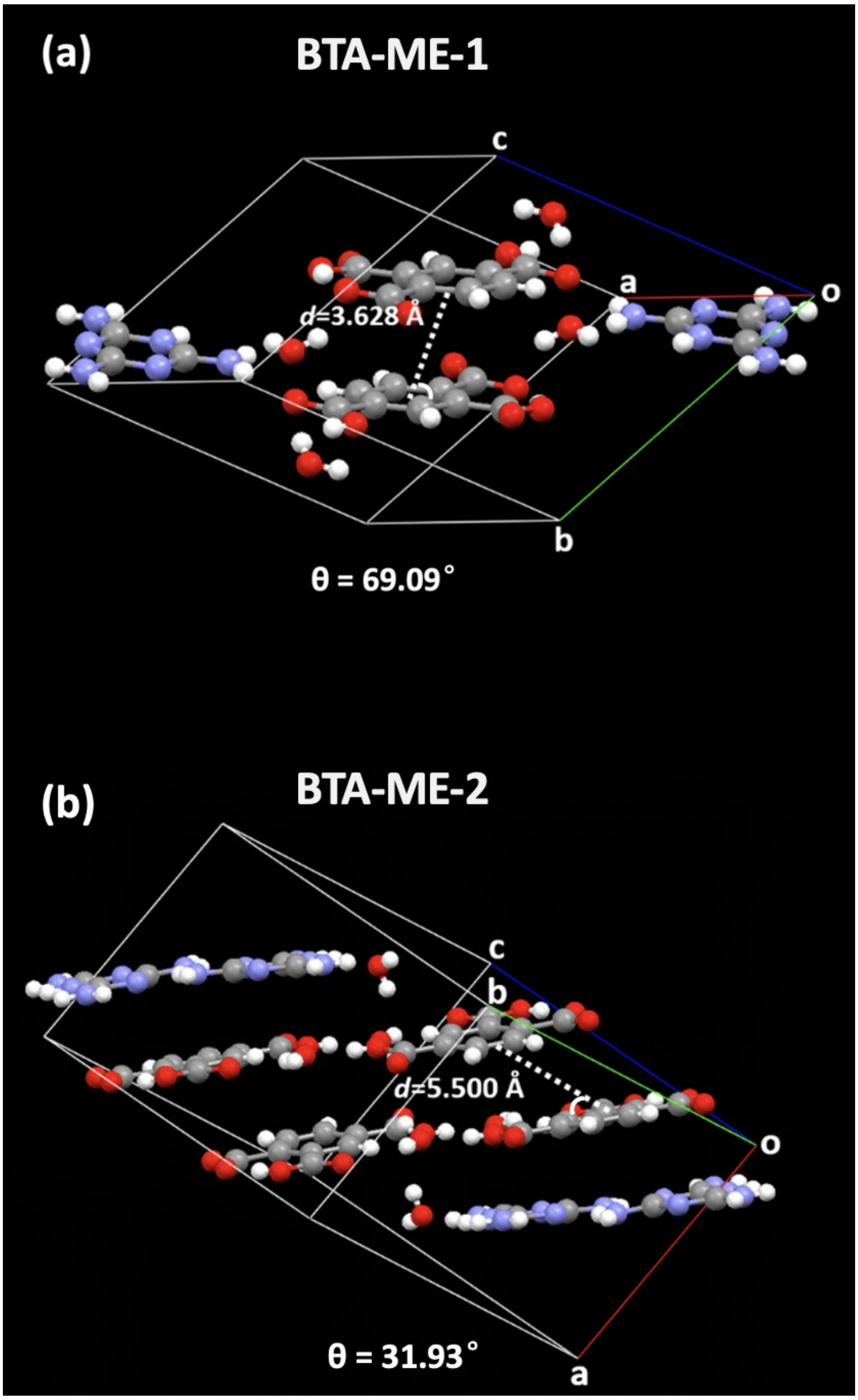


Fig. S5. The stacking modes of BTA-ME-1 and BTA-ME-2 between adjacent layers.

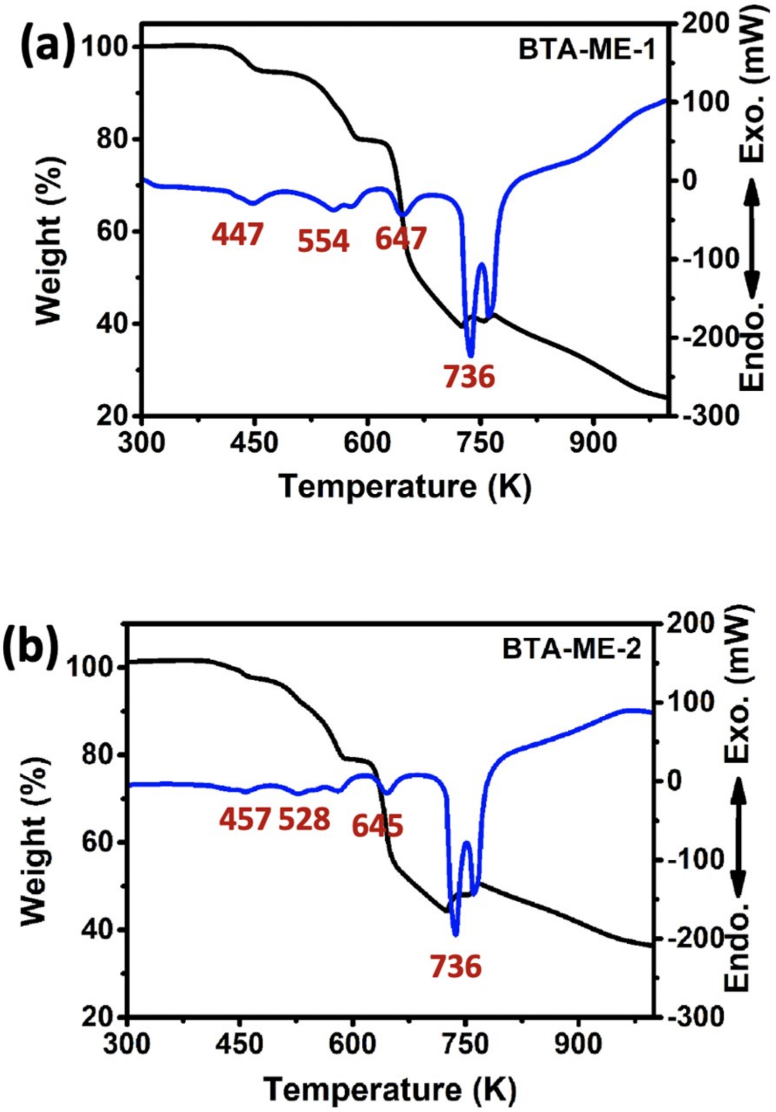


Fig. S6. The TGA-DSC curves of BTA-ME-1 and BTA-ME-2.

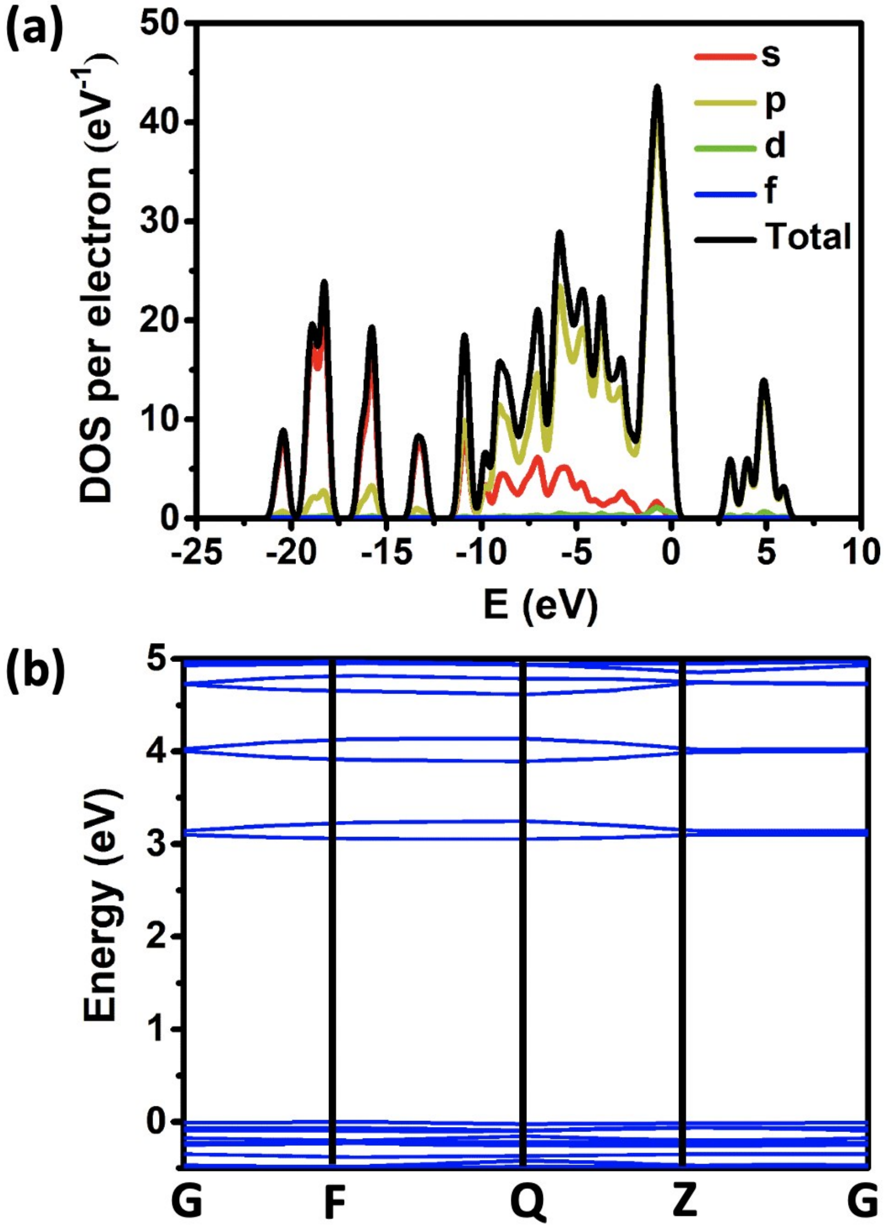


Fig. S7. Calculated band structures around Fermi energy level of BTA-ME-1.

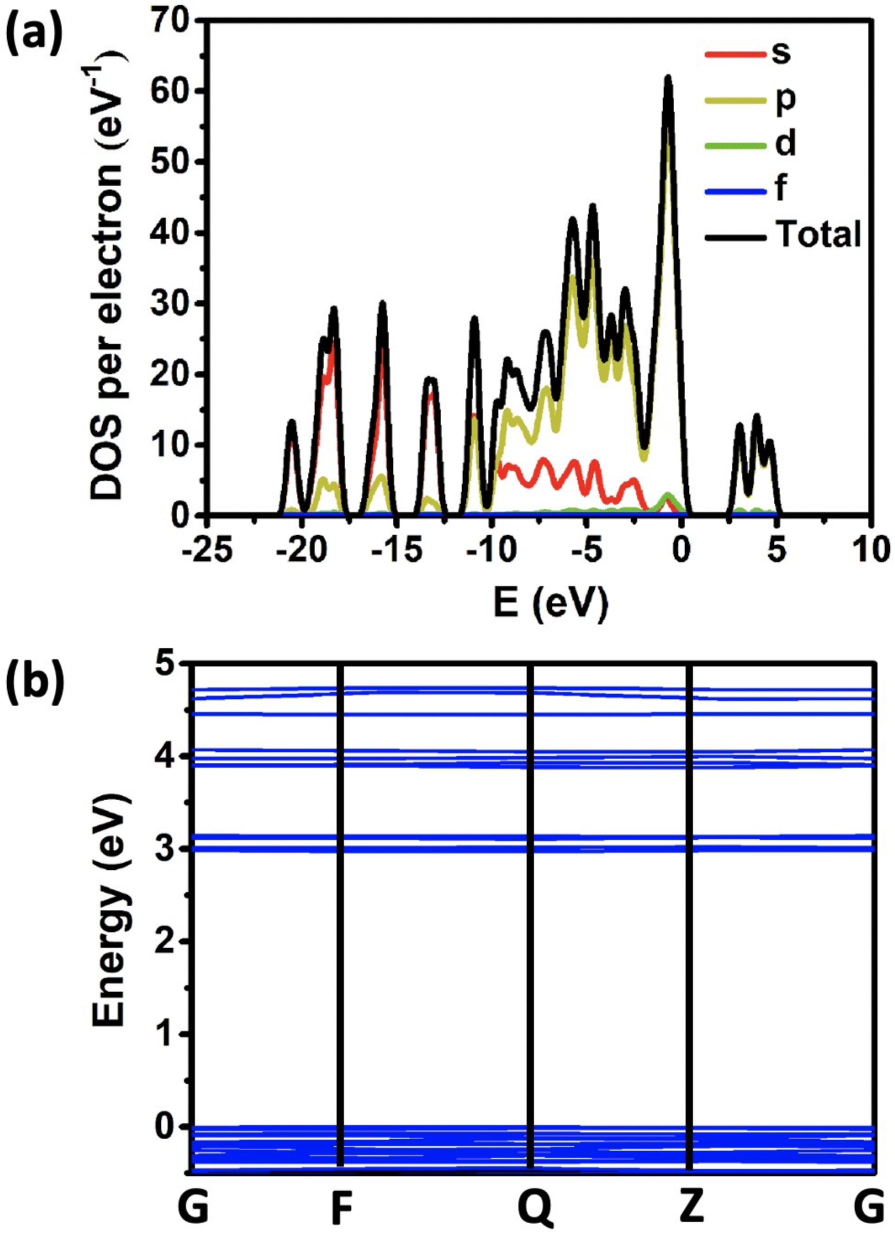


Fig. S8. Calculated band structures around Fermi energy level of BTA-ME-2.

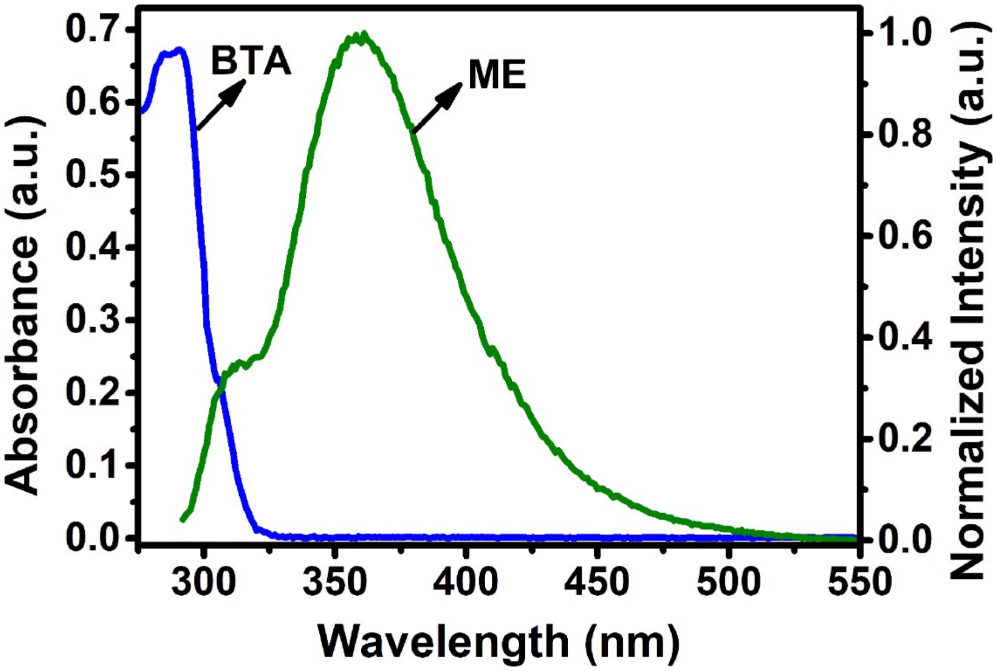


Fig. S9. UV-vis absorption spectra of BTA and the PL spectra of ME under ambient conditions.

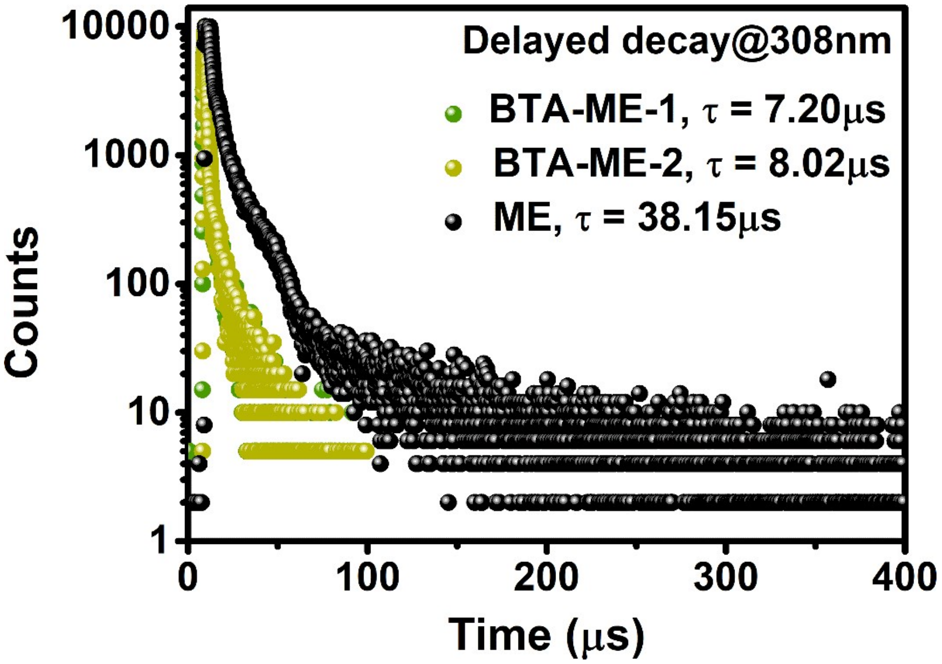


Fig. S10. The lifetime decay profiles of ME, BTA-ME-1 and BTA-ME-2.

Table S1: Crystal data for BTA-ME-1 and BTA-ME-2.

Sample	BTA-ME-1	BTA-ME-2
Molecular Formula	$C_{12}H_{16}N_6O_8$	$C_{24}H_{32}N_{12}O_{16}$
Molecular Weight	372.31	744.61
Temperature (K)	293	293
Crystal System	triclinic	triclinic
Space Group	*P*-1	*P*-1
a (Å)	9.3092 (13)	9.4813 (8)
b (Å)	9.8441(14)	11.8746 (10)
c (Å)	10.1956 (14)	14.6779 (13)
α (deg)	63.563 (14)	72.186 (7)
β (deg)	71.551 (13)	82.829 (7)
γ (deg)	73.220 (12)	81.819 (7)
V (Å^3)	781.5 (2)	1551.5 (2)
Z	2	2
GooF	1.055	1.023
R [$I > 2\sigma(I)$]	$R_1 = 0.0660$, $wR_2 = 0.1267$	$R_1 = 0.0607$, $wR_2 = 0.1229$
CCDC Number	1875915	1875919

Table S2: The hydrogen bonds of BTA-ME-1 and BTA-ME-2 in each layer.

Compound	O-H···O	N-H···O
BTA-ME-1	2.113 Å 1.971 Å 1.751 Å	2.172 Å 1.994 Å 1.969 Å 2.216 Å
BTA-ME-2	2.570 Å 1.956 Å 1.760 Å	2.050 Å 1.994 Å 1.969 Å 2.204 Å

Table S3: The photophysical properties of BTA, BTA-ME-1 and BTA-ME-2.

Compound	λ_F (nm)	λ_p (nm)	τ_F (ns)	τ_P (ms)	RTP QY (%)
BTA	384	538	3.0	0.2	—
BTA-ME-1	458	505	14.2	1.0	7.86
BTA-ME-2	379	515	3.2	0.7	5.24

"λ_F" refers to fluorescence wavelength; "λ_p" refers to phosphorescence wavelength.

3. Supporting References

[1] B. Delley and *J. Chem. Phys.*, 1990, **92**, 508-517.

[2] B. Delley and *J. Chem. Phys.*, 2000, **113**, 7756-7764.

[3] Dmol3 Module, MS Modeling, Version 2.2; Accelrys Inc.: San, Diego, 2003

[4] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B.*, 1992, **46**, 6671