Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

A highly emissive and stable Zinc(II) metal-organic framework as a host-guest chemopalette for approaching white-light-emission

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Experimental

Materials and physical measurements:

Commercially available chemicals were used without further purification.

Elemental analyses of C, H, and N were determined using an Elementar Vario EL cube CHNS analyzer. Thermogravimetric analyses (TGA) were performed using a TA Instruments Q50 thermogravimetric analyzer under nitrogen flow (40 mL/min) at a typical heating rate of 10 °C min^{-1}. Power X-ray diffraction (PXRD) experiments were performed using a D8 Advance X-ray diffractometer. (Cu-Kα, λ = 1.5406 Å). Liquid state UV-Vis absorption spectra were recorded on an Agilent 8453 spectrometer. Solid-state UV-Vis absorption spectra were performed on a MOS 450 UV/Vis Spectrometer with KCl pellets (200−800 nm). Solid-state UV-Vis diffuse reflection spectra were performed on a Lambda 950 UV/Vis Spectrometer with $BaSO_4$ pellets (4000−400 cm^{-1}). Quantum yields were measured on HAMAMATSU absolute PL quantum yield spectrometer C11347.

The steady-state photoluminescence spectra (PL) for all samples were recorded at room temperature on a PTI QM/TM spectrofluorometer (Birmingham, NJ, USA). Corrections of excitation and emission for the detector response were performed ranging from 200-900 nm. The decay curves and time-resolved fluorescence spectra of ZnBDCA emission at 410 nm excited by a N_2 laser at 337 nm were recorded on the same instrument, and the lifetimes were calculated using the FelixGX advanced photoluminescence fluorescence software. Lifetime data were fitted with exponential decay function by Origin8.5 The absolute quantum yields were measured at room temperature by employing a S3 barium sulfate coated integrating sphere.

Single crystal X-ray data collections and structure determination. The determination of the unit cell parameters and data collection for the crystal of ZnBDCA were performed on an Oxford Diffraction Gemini E (Enhance Cu X-Ray source, Kα, λ = 1.54184 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at 100 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure of ZnBDCA was solved by direct methods, and refined by full-matrix least-square methods with the SHELX-97 program package. The solvent molecules in ZnBDCA are highly disordered, SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the high disordered guest molecules. The resulting new files were used to further refine the structure. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The isophthalic acid and adenine are disordered, which were cleaved into two parts with half occupancy. The H atoms on C atoms were generated geometrically.

Preparation of ZnBDCA

Adenine (0.125 mmol), isophthalic acid (ipa) (0.25 mmol), zinc nitrate hexahydrate (0.375 mmol), nitric acid (1 mmol), DMF (13.5 mL), and water (1 mL) were added to a 20.0 mL vial. The vial was capped and the resulting solution was heated (120°C; 24h). After cooling down to room temperature, solid sample formed，and was washed with DMF, then dried in the vacuum oven before use. Yield: *ca*. 80% based on metal. C H N elemental analyses, Found: C 40.585, N 17.97;

H 3.02%. Calculate: $C_{64}H_{60}N_{24}O_{21}Zn_6$ (that is **[(Zn_4O) (ade)$_4$(BDC)$_4$ Zn_2] ·4DMF**): C, 40.59; N, 17.75; H, 3.19%. IR data (KBr, cm^{-1}): 3363m, 3188s, 1660m，1611s，1562s, 1468m, 1385m, 1280w，1211s, 1154s, 1197w, 1000w，940m，828m，798m, 749m，726s, 661m, 579m，512s, 443w.

Table S1. Crystal data and structure refinement for ZnBDCA

Identification code	
Empirical formula	$C_{52}H_{32}N_{20}O_{17}Zn_6$
Formula weight	1601.20
Temperature/K	100.15
Crystal system	tetragonal
Space group	$P\bar{4}2_1c$
a/Å	12.42670(10)
b/Å	12.42670(10)
c/Å	27.1577(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	4193.77(7)
Z	2
$\rho_{calc}mg/mm^3$	1.268
m/mm^{-1}	2.435
F(000)	1600.0
Crystal size/mm^3	0.2 × 0.16 × 0.16
2Θ range for data collection	6.5 to 148.34°
Index ranges	$-11 \le h \le 15$, $-14 \le k \le 15$, $-30 \le l \le 33$
Reflections collected	30015
Independent reflections	4255[R(int) = 0.0290]
Data/restraints/parameters	4255/196/240
Goodness-of-fit on F^2	1.640
Final R indexes [I>=2σ (I)]	R_1 = 0.0999, wR_2 = 0.3191
Final R indexes [all data]	R_1 = 0.1018, wR_2 = 0.3269
Largest diff. peak/hole / e $Å^{-3}$	3.19/-0.68
Flack parameter	0.04(10)

[a] $R_1=\sum(||F_0|-|F_c||)/\sum|F_0|$; $wR_2=[\sum_w(F_0^2-F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

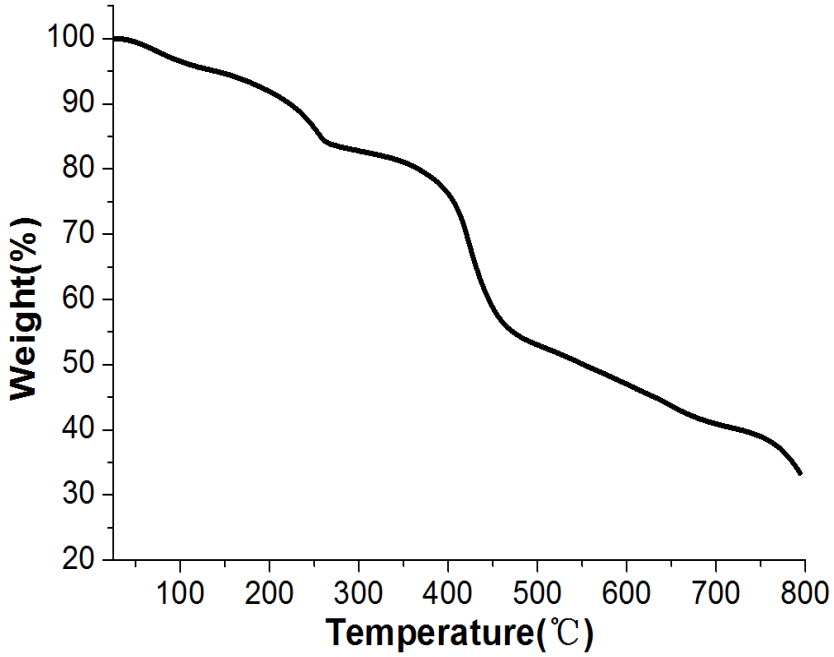


Fig. S1 Thermogravimetric analysis of ZnBDCA

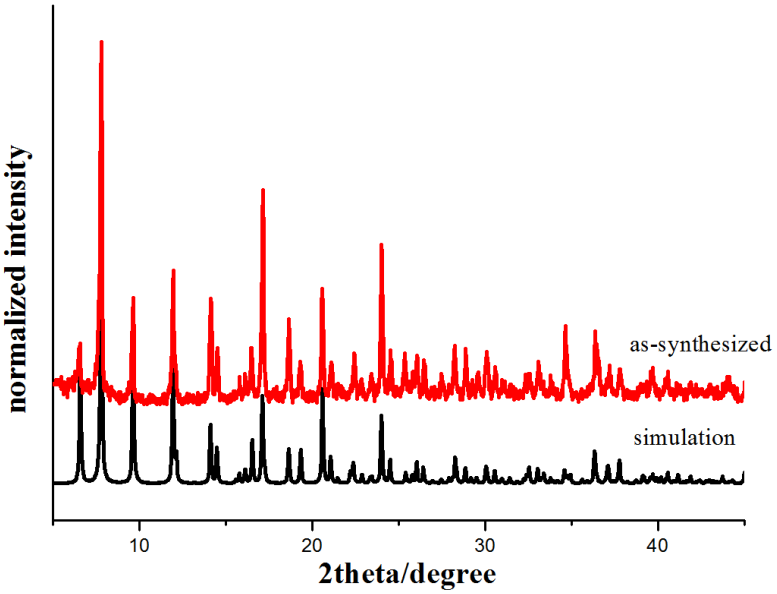


Fig. S2 Powder X-ray Diffraction Pattern of the ZnBDCA.

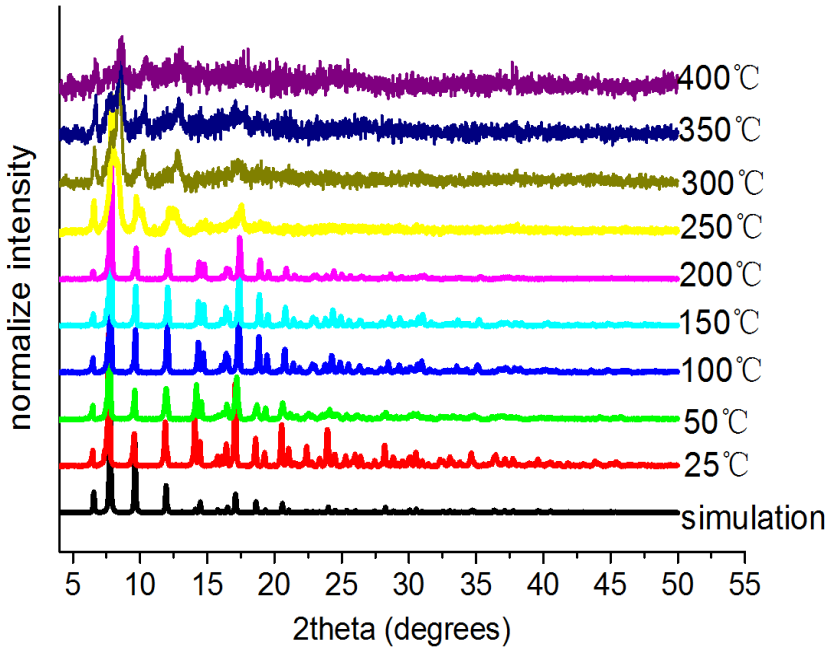


Fig. S3 Powder X-ray Diffraction Pattern of ZnBDCA as-synthesized sample heated in air at different temperatures.

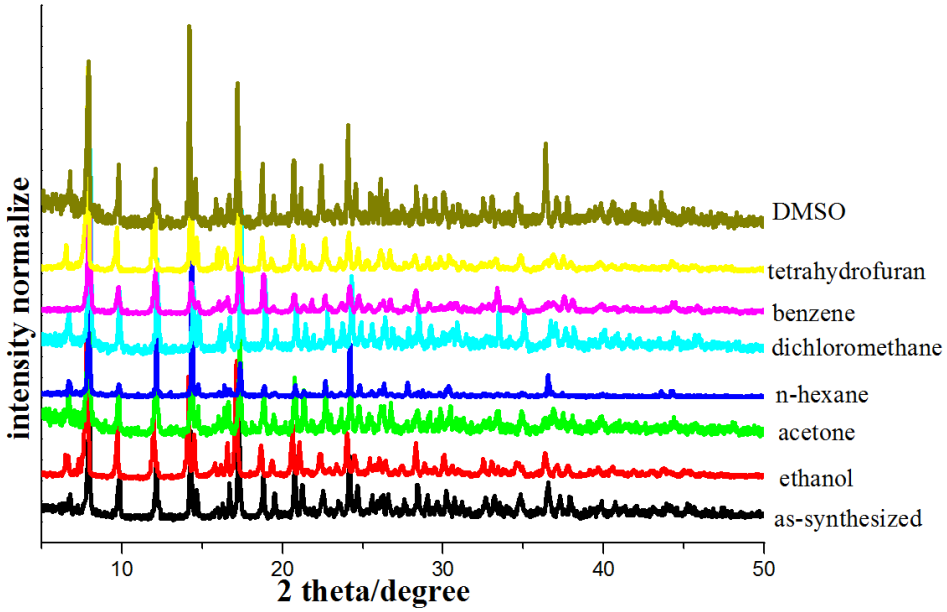
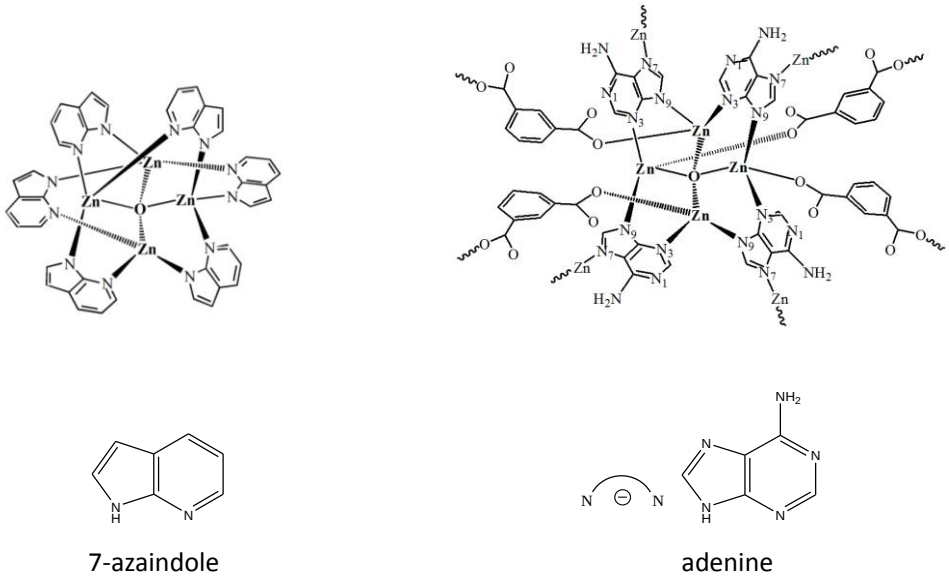
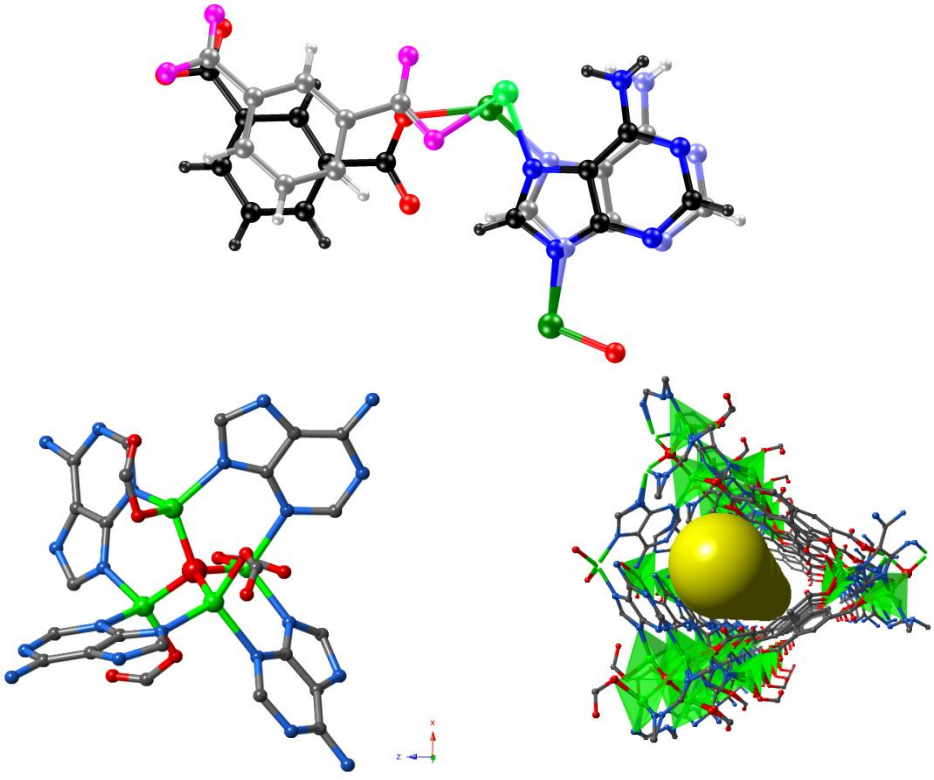


Fig. S4 Powder X-ray Diffraction Pattern of ZnBDCA as-synthesized samples, and immersed in organic solvents. Indeed. ZnBDCA maintained its crystallinity as evidenced by powder X-ray diffraction experiments.



(a)



(b)

Fig. S5 (a) $[Zn_4O(AID)_6]$ core-shell structure and (b) $[(Zn_4O)\ (ade)_4(BDC)_4Zn_2]$ core-shell structure. (b) The asymmetric unit of the ZnBDCA. The isophthalic acid and adenine are disordered, which were cleaved into two parts with half occupancy. The binding mode of the $Zn_4O(ade)_4(COO)_4$ cluster core-cell molecular structure and 1D channel of the ZnBDCA along b axis showing the pores.

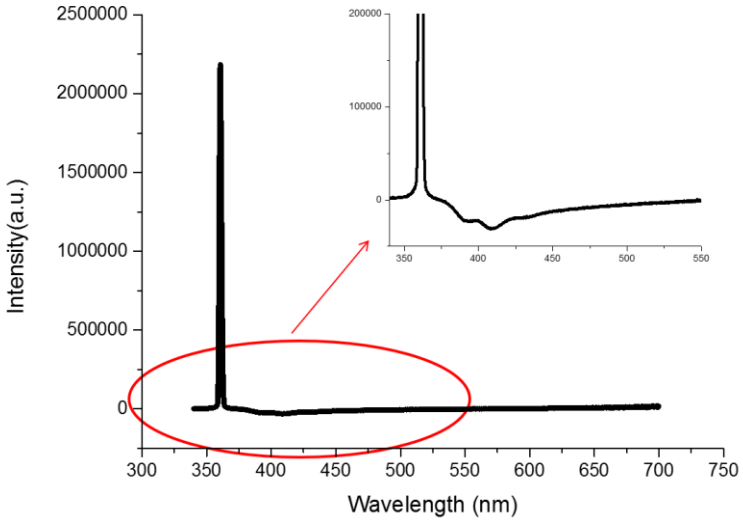


Fig. S6 The fluorescence quantum yield curve measured for the ZnBDCA powder sample at room temperture. (excited at 360 nm)

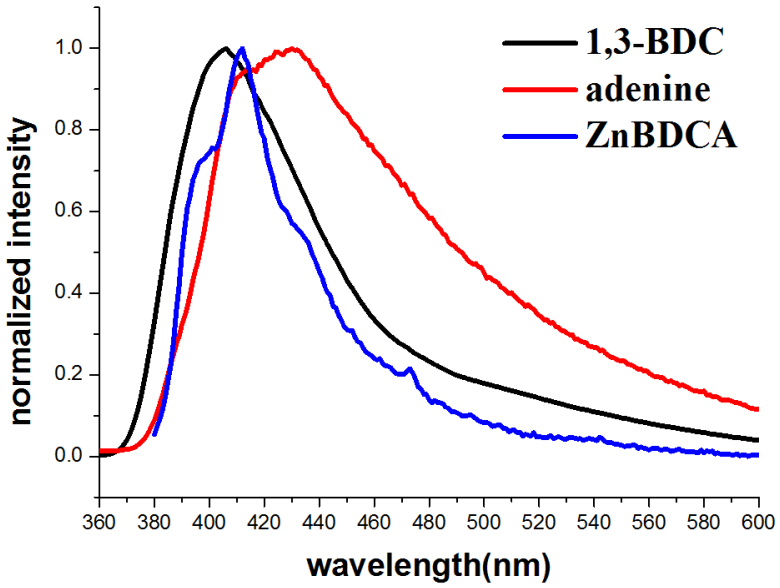


Fig. S7 The emission excited (at 365 nm) spectra of isophthalic acid (black $\lambda_{em} \approx 405$ nm), adenine (red $\lambda_{em} \approx 430$ nm) and ZnBDCA (blue, maximum emission peak at 410 nm) in the solid state at room temperature.

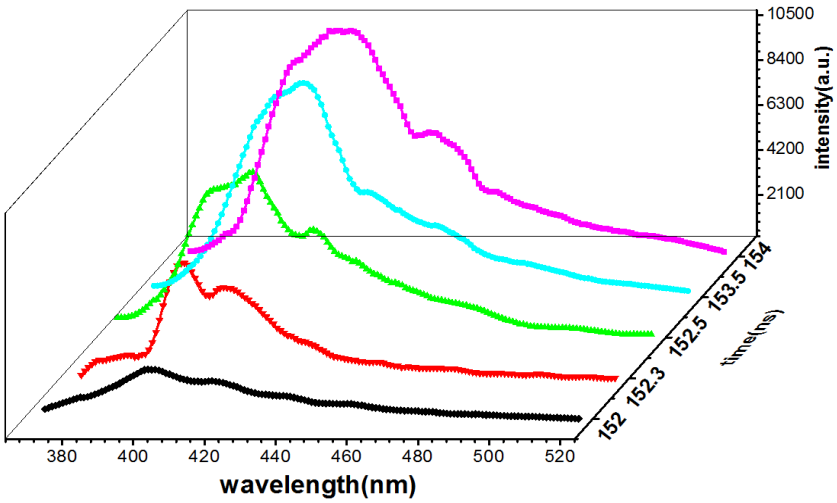
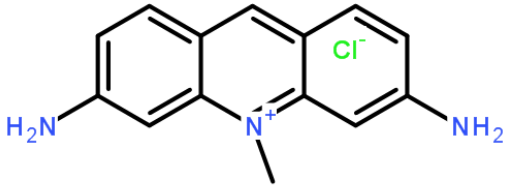
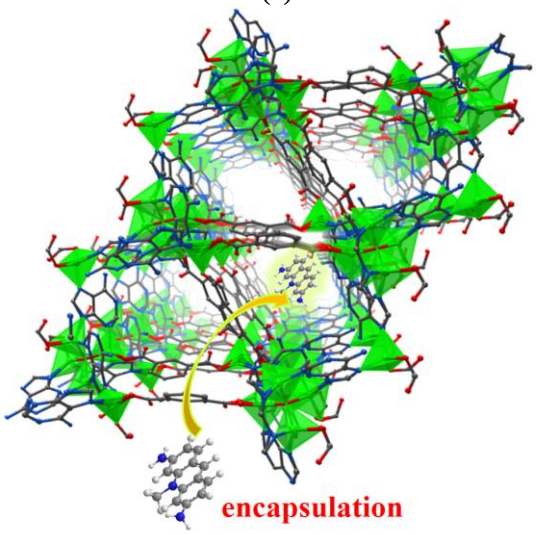


Fig. S8 Time-resolved luminescence spectra of the ZnBDCA powder sample.



(a)



(b)

Fig. S9 (a) The structure of acriflavine. (b) The schematic of acriflavine molecule was encapsulated in the channel of ZnBDCA and formed Acf@ZnBDCA system

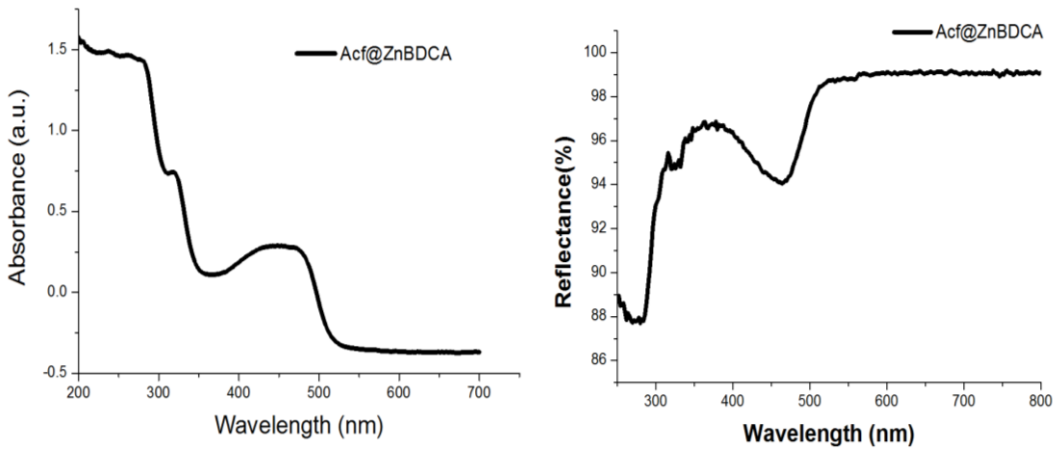


Fig. S10 (a) The solid-state UV-Vis absorption spectrum of Acf@ZnBDCA. (b) The UV-Vis diffuse reflection spectrum of Acf@ZnBDCA in the solid state.

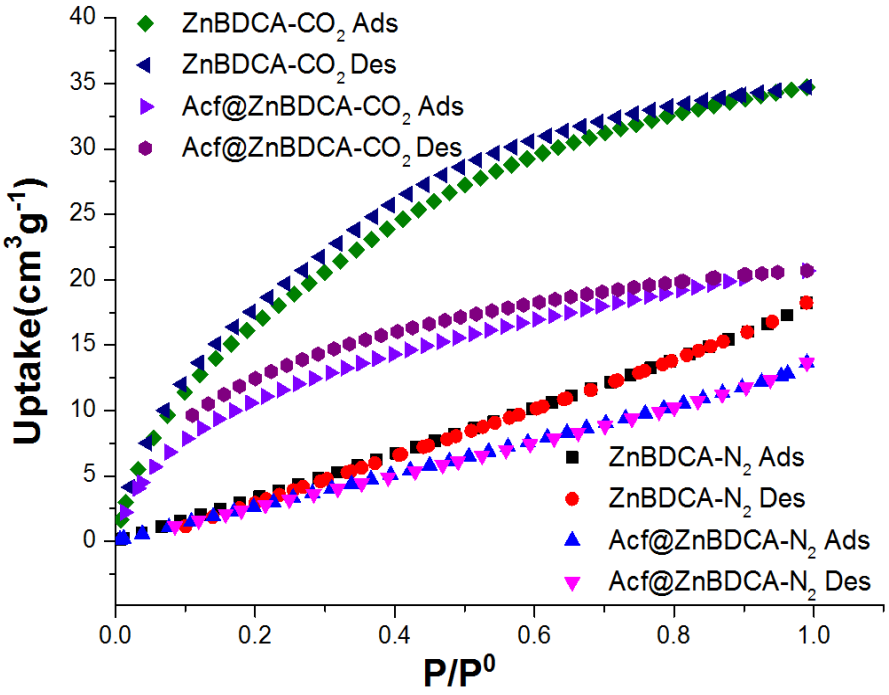


Fig. S11 Comparison of the N_2 adsorption isotherms at 77K and CO_2 adsorption isotherms at 273K for ZnBDCA and Acf@ ZnBDCA, respectively.

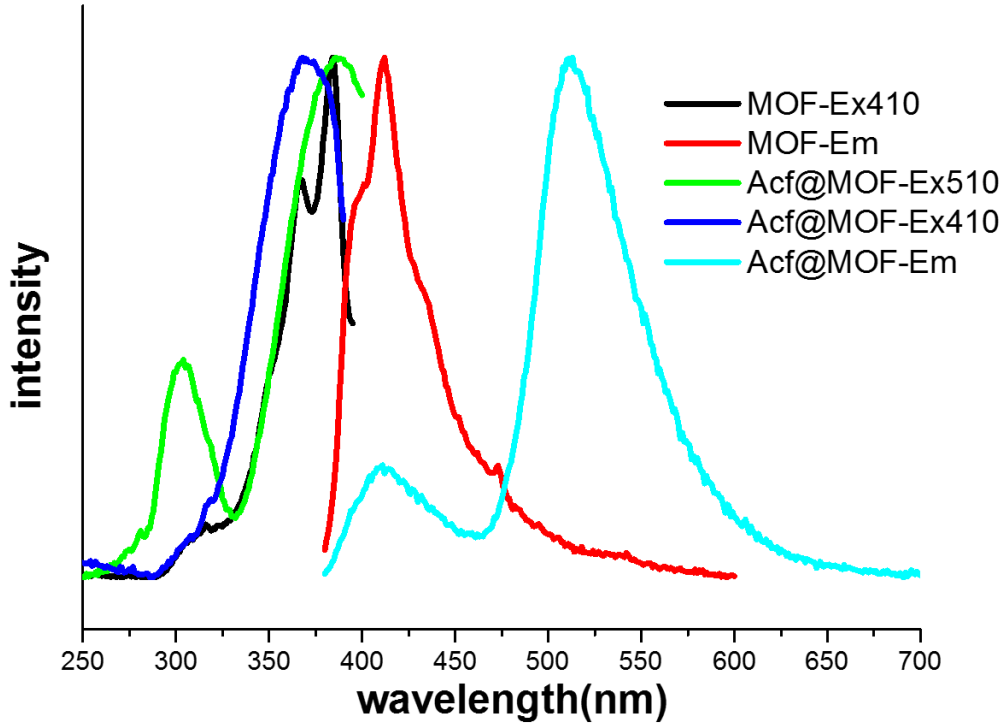
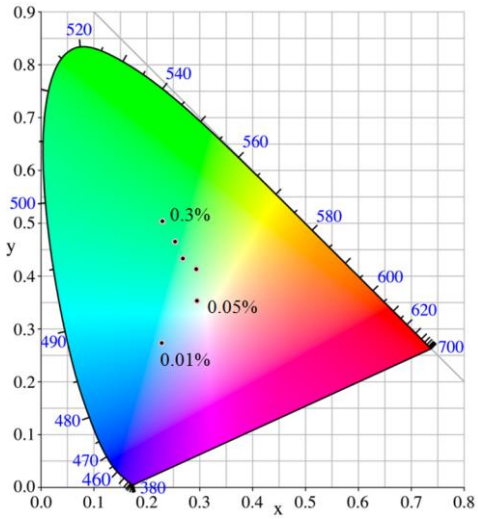
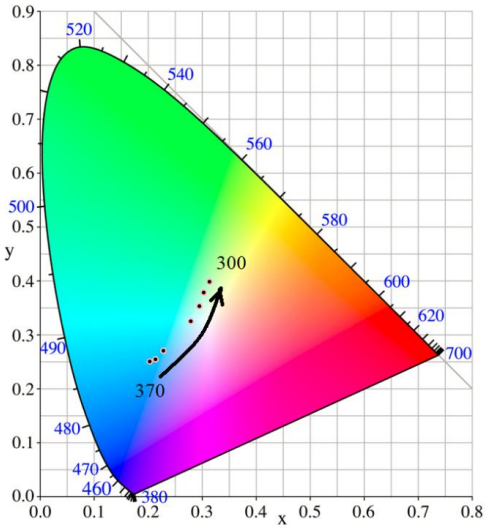


Fig. S12 Comparison of the excitation and emission spectra of ZnBDCA and Acf@ZnBDCA in the solid state at room temperature. The black line and red line is the excitation and emission spectra of ZnBDCA, respectively. The blue line (monitored at 410 nm), yellow line (monitored at 510nm) and cyan line are the excitation and emission spectra of Acf@ZnBDCA, respectively.



(b)

Fig. S13 The CIE chromaticity diagram with different amounts of encapsulated Acriflavine (the order of Acf concentration is 0.01 wt%, 0.05 wt%, 0.1 wt%, 0.15 wt%, 0.25 wt%，0.3 wt% from bottom to top, respctively) for Acf@ZnBDCA excited at 320 nm in the solid-state at room temperature.



(b)

Fig. S14 The CIE chromaticity diagram of Acf@ZnBDCA (Acf concentration is 0.05wt%) excited at different wavelengths in the solid state at room temperature.

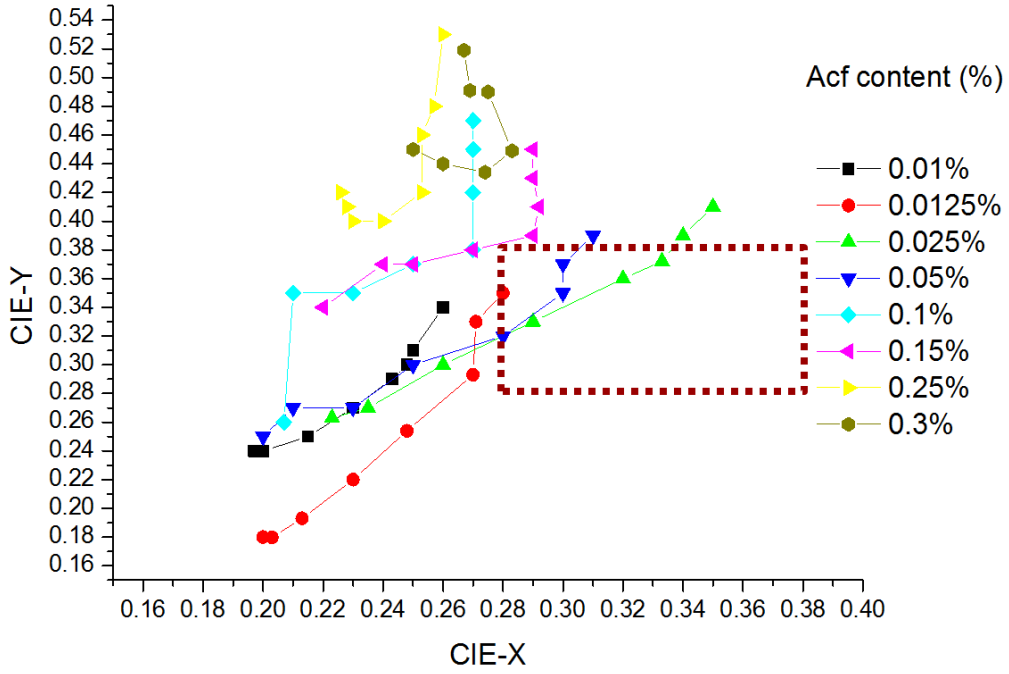


Fig. S15 CIE chromaticity coordinates with different amounts of encapsulated Acriflavine for Acf@ZnBDCA excited from 370 nm to 300 nm in the solid-state at room temperature. Dashed box in the figure includes the range of white-light-emitting (0.28,0.38).

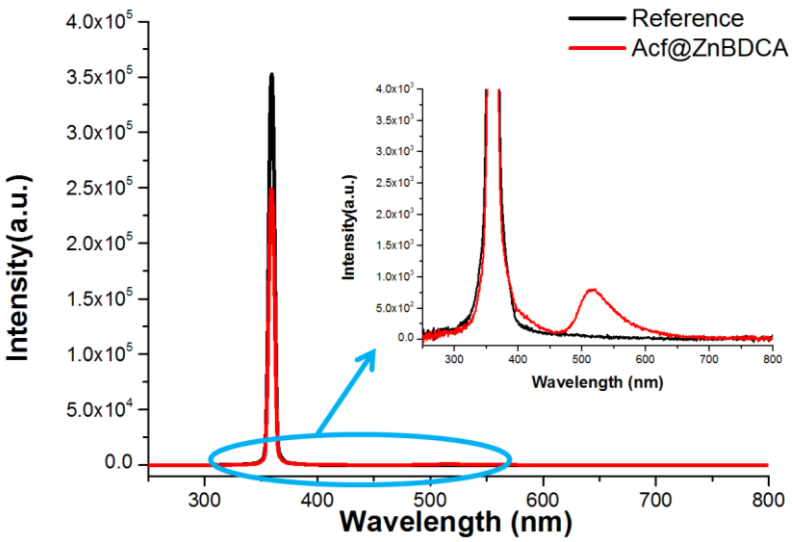


Fig. S16 The fluorescence quantum yield curve measured for the Acf@ZnBDCA powder sample at room temperture. (excited at 360 nm)

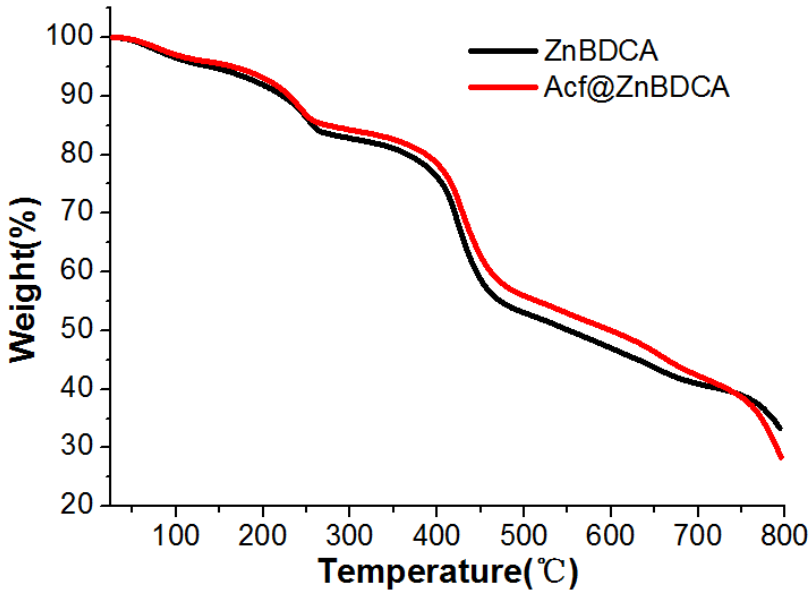


Fig S17 Comparison of TGA of ZnBDCA and Acf@ZnBDCA under the same condition.

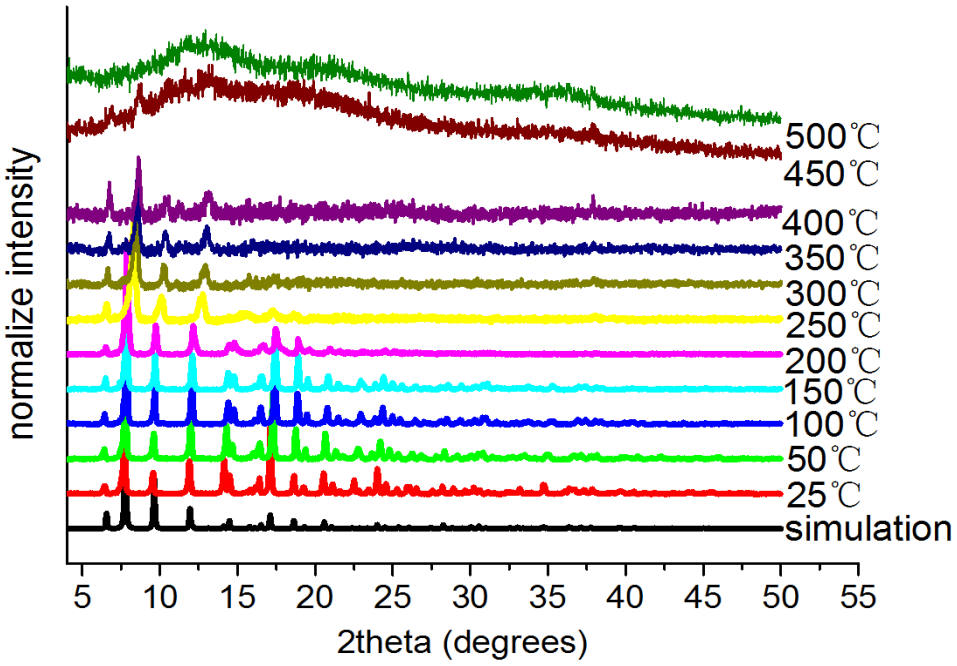


Fig S18 Powder X-ray Diffraction Pattern of Acf@ZnBDCA as-synthesized samples heated in air at different temperatures.