

Aggregation Suppression and Enhanced Blue Emission of Perylene in Zinc-Based Coordination Polymer Glass

Supplementary Information

METHOD

Materials and Methods

Chemicals

All chemicals and solvent were purchased from Sigma Aldrich and used without further purification. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, >98%), benzimidazole ($\text{C}_7\text{H}_6\text{N}_2$, >98%), phosphoric acid (H_3PO_4) and dichloromethane (99.9%) were used for zinc coordination polymer fabrication. Perylene ($\text{C}_{20}\text{H}_{12}$, >99%) was used to make hybrid composite.

Synthesis of Zn-P-blm

Zinc acetate dihydrate (219.5 mg, 1 mmol), benzimidazole (236.3 mg, 2 mmol), and phosphoric acid (210 μL , 3 mmol) were placed in a mortar and manually ground for 10 minutes until a slimy mixture formed. The mixture was then washed with dichloromethane three times and dried in a vacuum oven at 60°C for 12 hours.

Synthesis of P-agZn-P-blm composite

Prepared Zn-P-blm powder and perylene crystals were gently mixed manually using a mortar. The mixture was then melted on glass slides using a hot plate at the melting temperature. The composites were obtained after cooling to room temperature.

Photoluminescence measurements

Photoluminescence (PL) emission spectra were measured at room temperature using a Horiba FluoroMax fluorescence spectrophotometer. The steady-state PL spectra were acquired with a xenon arc lamp as the light source, and the collected data were analyzed using the FluorEssence software powered by Origin. Absolute PLQY measurements were conducted with a pre-calibrated Quanta- ϕ integrating sphere (15 cm in diameter), with all samples and the blank excited at 375 nm.

Time-resolved PL (TRPL) decay data were collected at room temperature using a 375 nm pulsed diode laser excitation source on an Edinburgh Instruments FLSP-900 fluorescence spectrophotometer.

Stability test

All the stability tests were performed with 5.0 mm diameter 10 mg pellet high stored in the lab cabinet under ambient condition.

Differential scanning calorimetry analysis

Differential scanning calorimetry (DCS) analysis was collected separately using a Mettler Toledo 1 STARe system. ca. 8 mg of each sample was placed in an aluminium crucible and heated with nitrogen flow (20 ml/min). To determine the calorimetric features samples were heated at 20°C/min rate to designated temperature.

X-ray Powder Diffraction (XRD) analysis

Room temperature and in situ powder XRD analysis were conducted with a Rigaku MiniFlex600-C using Cu K α radiation with divergent (Gragg-Brentano) geometries. The 2 θ range was 5 to 60°, with a step size of 0.02° and a step rate of 0.02/sec

X-ray photoelectron spectroscopy (XPS)

Kratos Axis Ultra XPS with mono Al K α (1486.6 eV) at 150 W (15 kV, 10 mA) has been used to analyze the surface chemistry of samples. The instrument was equipped with a 165 mm hemispherical electron energy analyzer. The C1s peak position was set to 284.8 eV and utilized as an internal standard.

Scanning electron microscopy (SEM)

High resolution scanning electron microscope, JOEL JSM7800F has been used for the surface morphology investigation. Secondary electron modes was measured at 15.0 kV. All samples were dried in 60°C vacuum oven for 8 hours followed by surface platinum coating.

Synchrotron Tera-Hz Far – Infrared (THz-FarIR) absorption spectroscopy and DFT calculations

The THz/Far-IR beamline at the Australian Synchrotron with a Bruker IFS 125/HR Fourier Transform (FT) spectrometer was used to obtain THz-FarIR absorption data. To reduce noise from the signal, the bolometer was kept in a cryogenic condition using liquid helium and 15 a 6 μ m thick Multilayer Mylar beam splitter was used. An attenuated total reflection (ATR) was used to analyze the samples which were clamped on the diamond crystal window surface. Temperature-resolved in situ spectra were collected with installed ATR heating plate under continuous Ar flowing (ca. 20 mL/min). The OPUS 8.0 software was used for spectral data analysis.

Standard computational chemistry calculations were carried out with Gaussian 16. The default options, including integration grid and algorithms, were used in the calculations. Geometries and vibrational frequencies were obtained with the B3LYP density functional theory method and the 6-31G(d) basis set. The frequencies were inspected to confirm the optimized structures correspond to minima. The simulated spectrum was produced assuming a Gaussian shape for each peak and a halfwidth of 5 cm⁻¹.¹⁻³

Synchrotron X-ray small/wide angle-angle scattering (SAXS/WAXS)

WAXS data was collected at the SAXS/WAXS beamline of the Australian Synchrotron facility. Detector calibrations were performed using silver behenate standards on the Dectris PILATUS3 X 2M. Scattering intensity normalization was carried out using a diode embedded in the beamstop. Scattering data were collected with an beam energy of 16 keV. Data was reduced to one dimensional using the in-house developed Scatterbrain software package.

X-ray absorption spectroscopy (XAS)

Zn K-edge XAS measurements were captured at Australian Synchrotron (part of ANSTO) XAS beamline. The samples were measured using transmission geometry and probed from 9460 eV to 10890 eV. Zn foil has been probed as a reference.

Data processing and fitting were performed using the Demeter XAS software package. Followed by background normalization, k2 weighting, and Fourier transform on the Athena program, EXAFS fittings were then conducted in the Artemis program. The scattering paths Zn-N, Zn-C, and Zn-O from ZIF-7 and Zinc phosphate models were used to evaluate the structures of the samples.

Solid-state NMR

The solid state ³¹P NMR spectra were acquired from a 300 MHz Bruker Advance III spectrometer using 4 mm zirconia rotors spinning at 7 kHz. The SSNMR experiments were conducted at the Centre for Advanced Imaging, The University of Queensland.

Epifluorescence Microscope

Nikon Eclipse Ti2 inverted microscope was used for epifluorescence microscope analysis with 40x objectives. The sample has been prepared on a microscope slide glass then excited with 380 nm led light. The 3D modelling has been restructured using measurements taken in 0.5 μm increments.

UV-Vis absorption

UV-Vis absorption spectroscopy of powder mixture and composites after thermal treatment were measured with a Jasco V-650 UV-Vis spectrophotometer at solid state in ambient conditions.

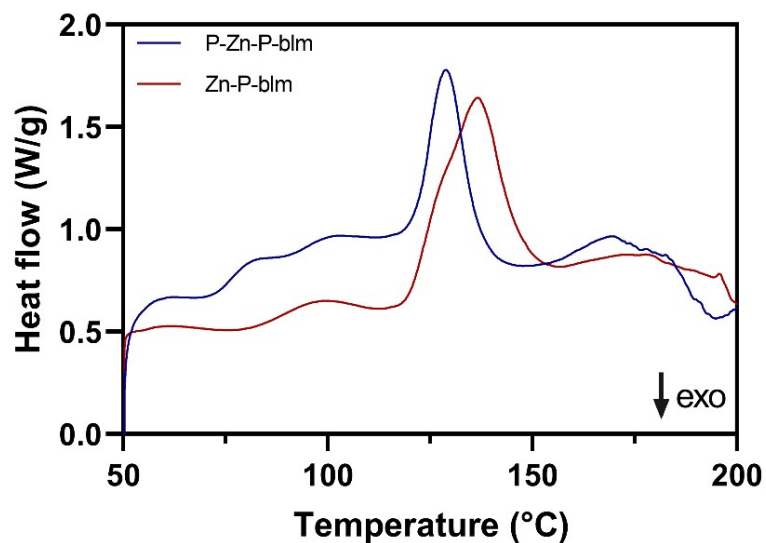


Figure.S1 DSC of Zn-P-blm and P-Zn-P-blm at a rate of 20°C/min in nitrogen environment.

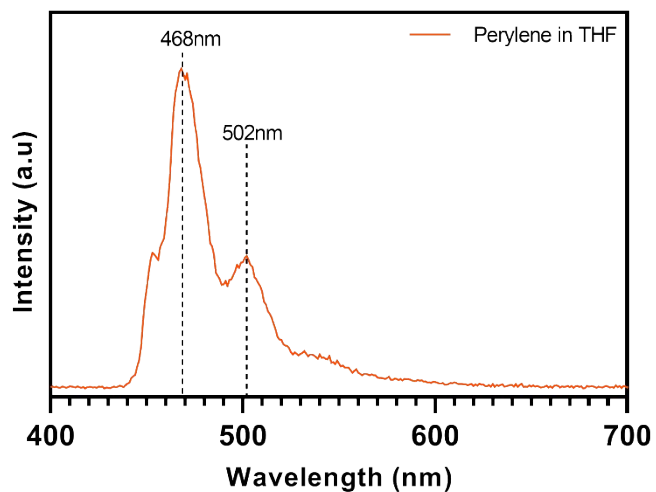


Figure.S2 PL spectra of 1mM perylene solution in THF, at excitation wavelength of 375nm.

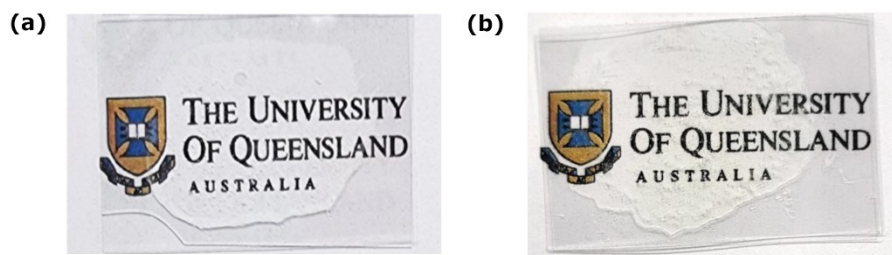


Figure.S3 Photograph under bright field of (a) $a_g\text{Zn-P-blm}$ and (b) $\text{P-}a_g\text{Zn-P-blm}$.

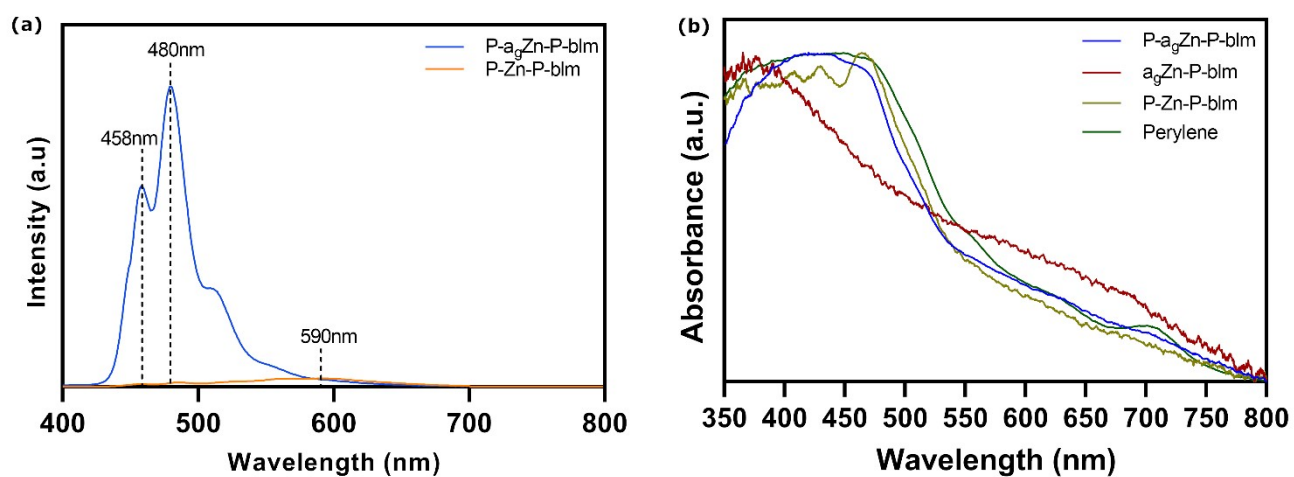


Figure.S4 (a) PL spectra of $\text{P-}a_g\text{Zn-P-blm}$ and P-Zn-P-blm at excitation wavelength of 375nm. (b) Normalized UV-vis absorption spectra of $\text{P-}a_g\text{Zn-P-blm}$, $a_g\text{Zn-P-blm}$, P-Zn-P-blm and perylene. All UV-Vis samples were measured in the solid state under ambient conditions.

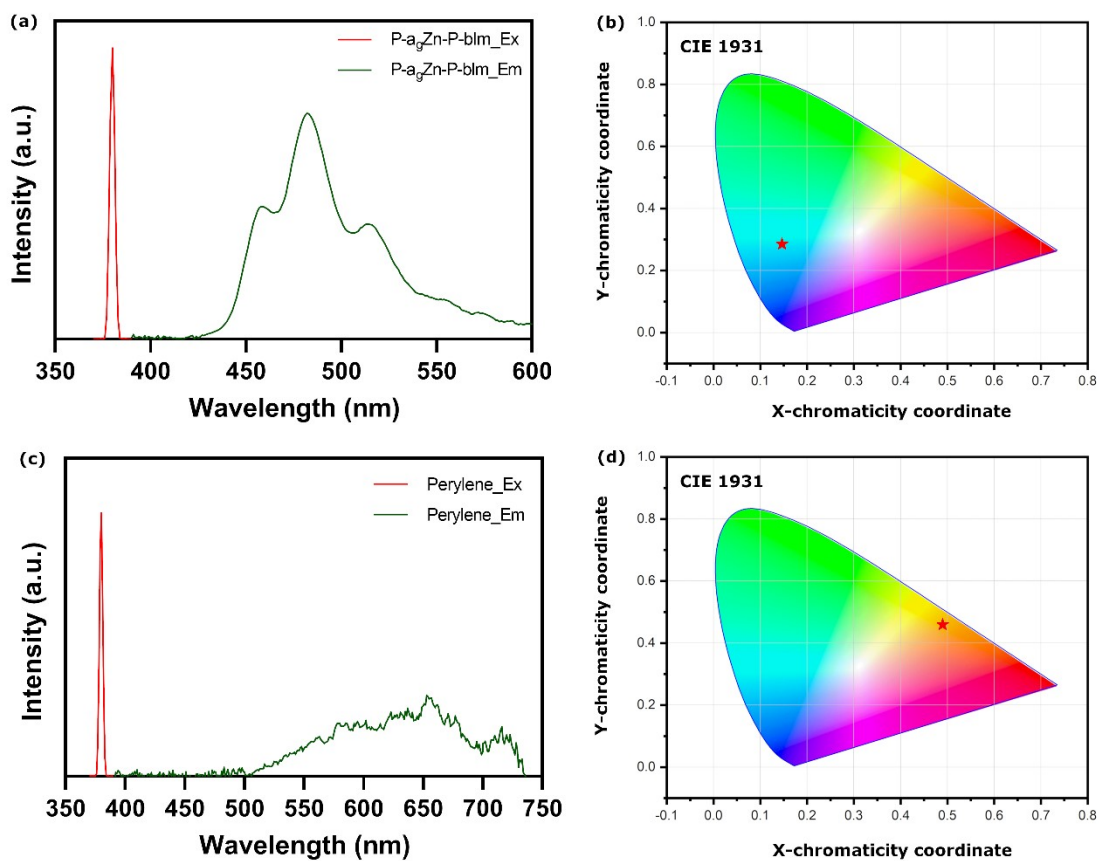


Figure.S5 Photoluminescence analysis: (a) PLQY and (b) CIE coordination of P-a_gZn-P-blm; (c) PLQY and (d) CIE coordination of Perylene.

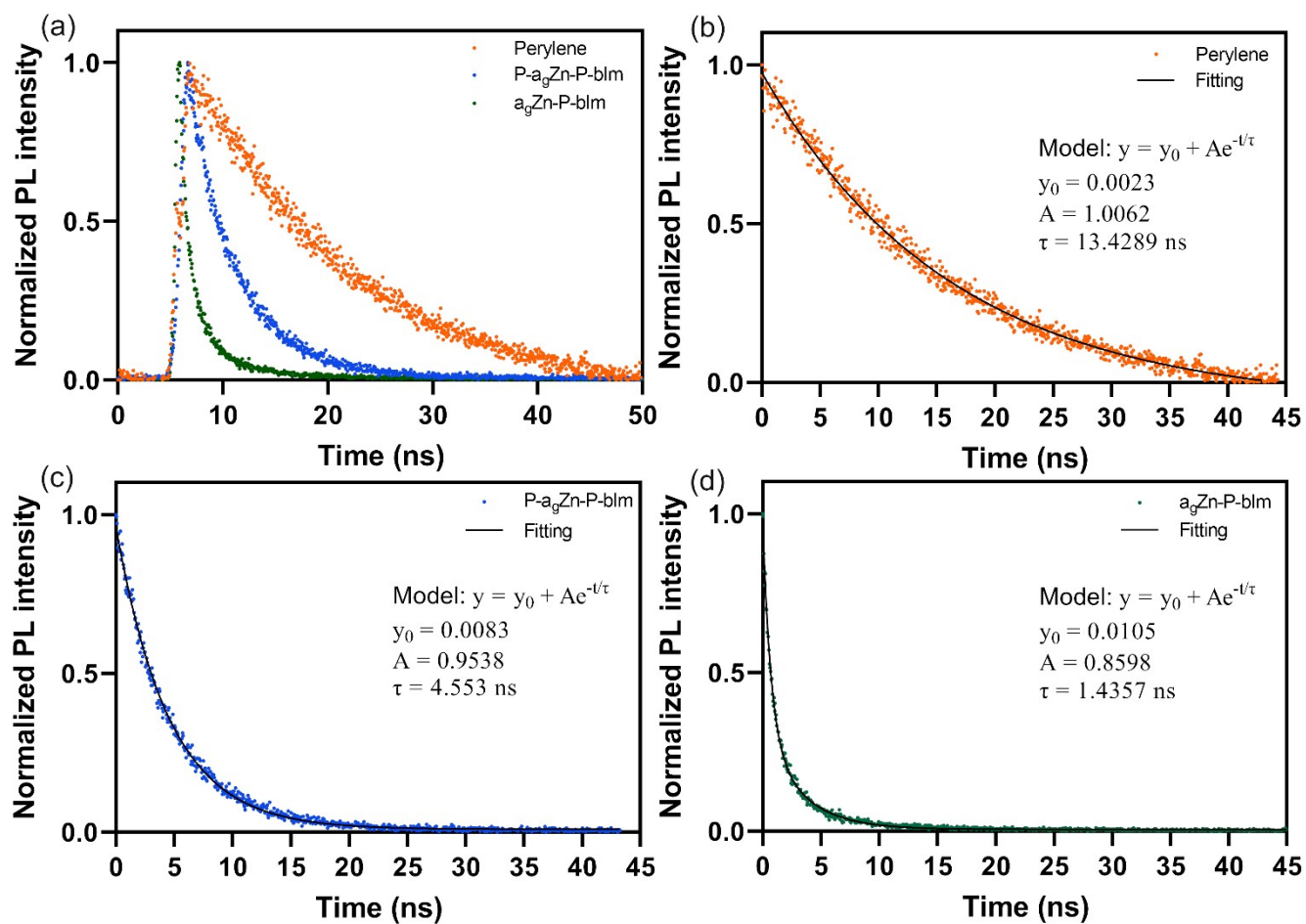


Figure.S6 (a) TRPL analysis of perylene, a_gZn-P-blm and P-a_gZn-P-blm. TRPL fitting results: (b) perylene, (c) P-a_gZn-P-blm and (d) a_gZn-P-blm.

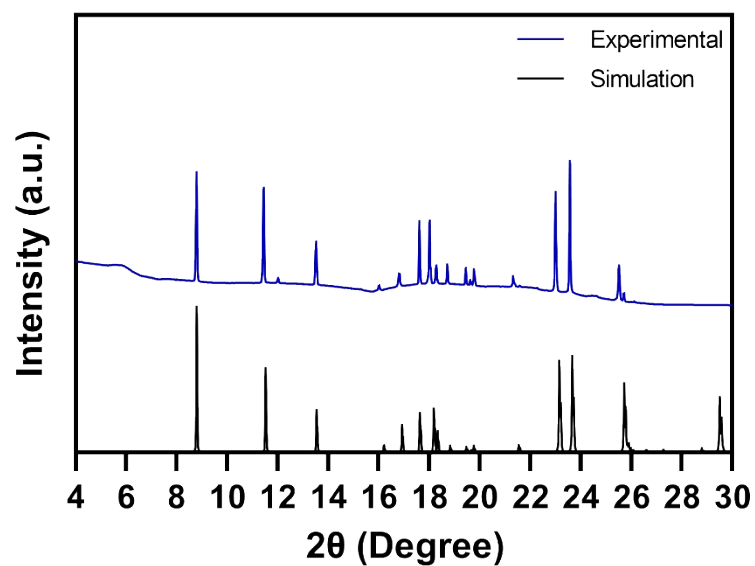


Figure.S7 WAXS experiment data of perylene crystal and simulation patterns. Powder diffraction simulations were performed using VESTA, with crystal structures and basic parameters obtained from published works.⁴

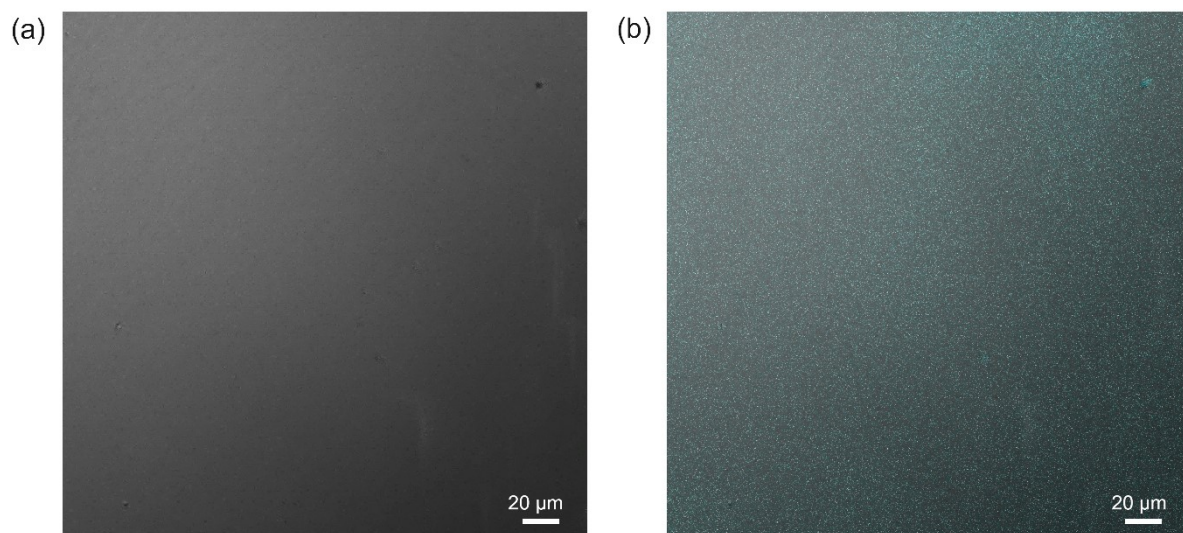


Figure.S8 Fluorescence microscopy images P-a_gZn-P-blm composite at (a) bright field (b) confocal fluorescence mode.

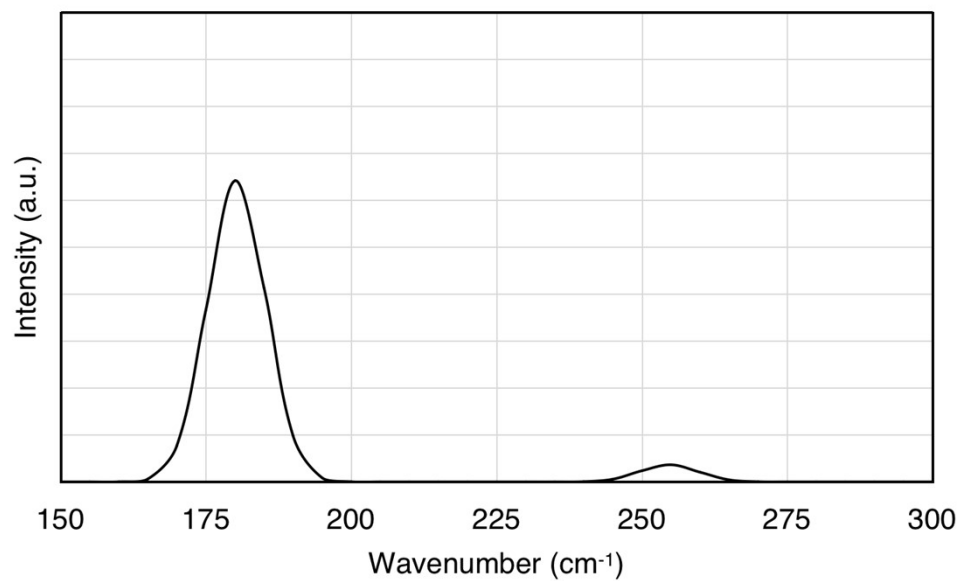


Figure.S9 DFT calculated THz spectrum of the perylene.

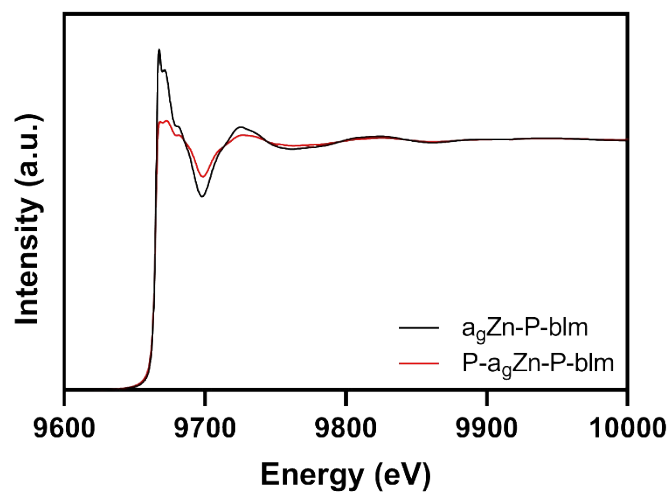


Figure.S10 Zinc XANES spectra of a_gZn-P-blm and P-a_gZn-P-blm composite.

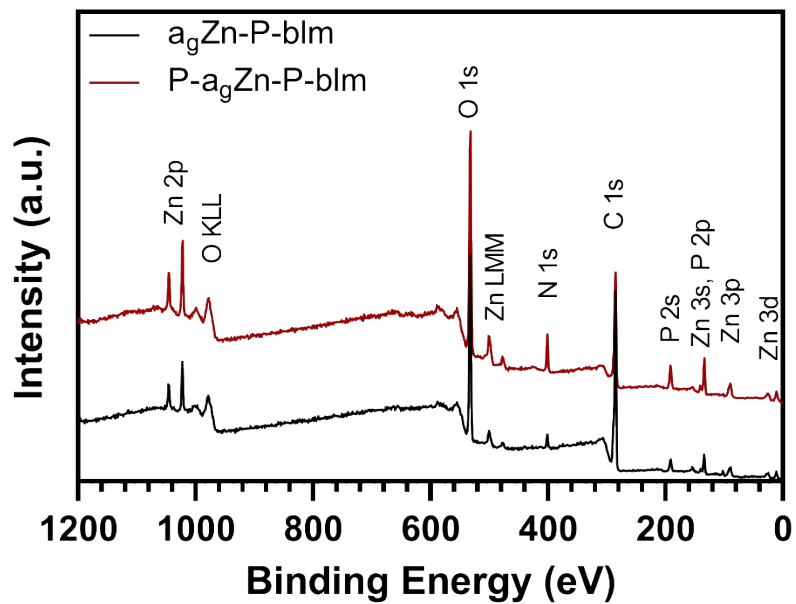


Figure.S11 XPS survey spectra of $\text{P-}a_g\text{Zn-P-blm}$ and $a_g\text{Zn-P-blm}$.

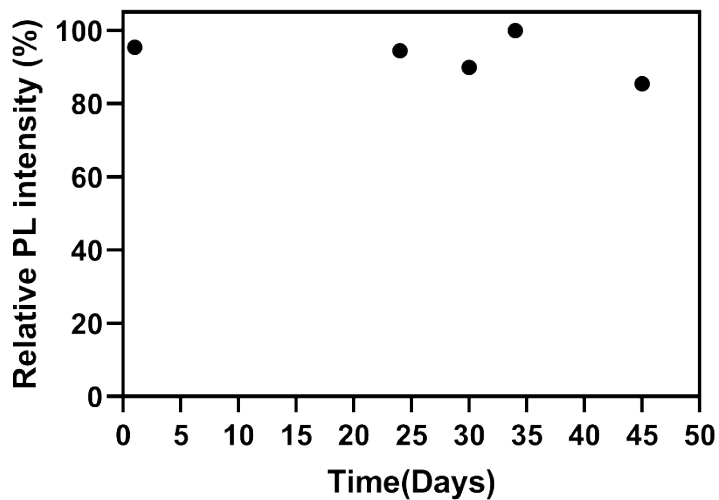


Figure.S12 Photoluminescence stability test of $\text{P-}a_g\text{Zn-P-blm}$.

Table S1 The k²-weighted Zn K-edge EXAFS fitting parameters of a_gZn-P-blm.

Zn-N coordination number	2.59
Zn-O coordination number	1.41
Zn-C1 coordination number	2.05
Zn-C2 coordination number	8.13
Zn-O1	1.326
Zn-N bond length	2.04970
Zn-O bond length	1.93211
Zn-C1 bond length	2.96887
Zn-C2 bond length	3.36983
Zn-O1 bond length	3.27407
Zn-N σ^2	0.01848
Zn-O σ^2	0.00198
Zn-C1 σ^2	0.00579
Zn-C2 σ^2	0.02464
Zn-O1 σ^2	0.00100
R factor	0.0101601

Table S2 The k²-weighted Zn K-edge EXAFS fitting parameters of P-a_gZn-P-blm.

Zn-N coordination number	2.73
Zn-O coordination number	1.27
Zn-C1 coordination number	3.62
Zn-C2 coordination number	11.3
Zn-O1	1.51
Zn-N bond length	2.08415
Zn-O bond length	1.93168
Zn-C1 bond length	2.96178
Zn-C2 bond length	3.01320
Zn-O1 bond length	3.26664
Zn-N σ^2	0.02630
Zn-O σ^2	0.00018
Zn-C1 σ^2	0.00746
Zn-C2 σ^2	0.02732
Zn-O1 σ^2	0.00488
R factor	0.0037055

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, et al., Gaussian 16, rev. C01, Gaussian Inc., Wallingford CT, 2016.
2. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* 1994, 98, 11623–11627
3. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* 1973, 28, 213–222.
4. M. Botoshansky, F. H. Herbstein and M. Kapon, *Helvetica chimica acta*, 2003, 86, 1113-1128.