# *Electronic Supplementary Information (ESI)*

## Materials and Instruments

In this work, all the chemicals and reagents were purchased from commercial sources and used as received without further purification. $^{1}H$ and $^{13}C$ NMR spectra were measured on a Bruker AV 500 spectrometer in deuterated solvent ($CDCl_3$ or $CD_2Cl_2$) at room temperature, and the tetramethylsilane (TMS) was tested as internal standard. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single crystal X-ray diffraction intensity data were collected at 170 K on Bruker-Nonices Smart Apex CCD detector diffractometer with graphite monochromated MoKα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields ($\Phi_F$) were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The compression experimentation was carried out by Sapphire-anvil cell, and the corresponding PL spectra were collected using Quanta Master 40 spectrometer that under reflection mode, and excitation wavelength was 380 nm.

## X-Ray crystallography

**Crystal data for Py-BP-PTZ (CB, CCDC 1838711):** $C_{35}H_{21}NOS$, $M_W$ = 503.59, monoclinic, $P2_1/c$, $a$ = 18.1738(15), $b$ = 11.7952(10), $c$ = 11.7756(10) Å, $\beta$ = 101.034(3)°, $V$ = 2477.6(4) Å$^3$, $Z$ =

4, *D*c = 1.350 g cm$^{-3}$, $\mu$ = 0.161 mm$^{-1}$ (MoKα, $\lambda$ = 0.71073), *F*(000) = 1048, *T* = 172(2) K, $2\theta_{max}$ = 25.36˚(98.5%), 12904 measured reflections, 4477 independent reflections ($R_{int}$ = 0.0679), GOF on $F^2$ = 1.081, $R_1$ = 0.1119, w$R_2$ = 0.1799 (all data), $\Delta$e 0.513 and –0.317 eÅ$^3$.

**Crystal data for Py-BP-PTZ (CG, CCDC 1838713):** $C_{35}H_{21}NOS$, $M_W$ = 503.59, monoclinic, $P2_1/c$, *a* = 17.840(3), *b* = 11.7145(16), *c* = 11.7425(15) Å, $\beta$ = 98.217(6)˚, *V* = 2428.8(6) Å$^3$, *Z* = 4, *D*c = 1.377 g cm$^{-3}$, $\mu$ = 0.165 mm$^{-1}$ (MoKα, $\lambda$ = 0.71073 ), *F*(000) = 1048, *T* = 173(2) K, $2\theta_{max}$ = 24.50˚(98.7%), 13784 measured reflections, 3983 independent reflections ($R_{int}$ = 0.0894), GOF on $F^2$ = 1.181, $R_1$ = 0.1334, w$R_2$ = 0.2468 (all data), $\Delta$e 0.593 and –0.415 eÅ$^3$.

**Additional Spectra**

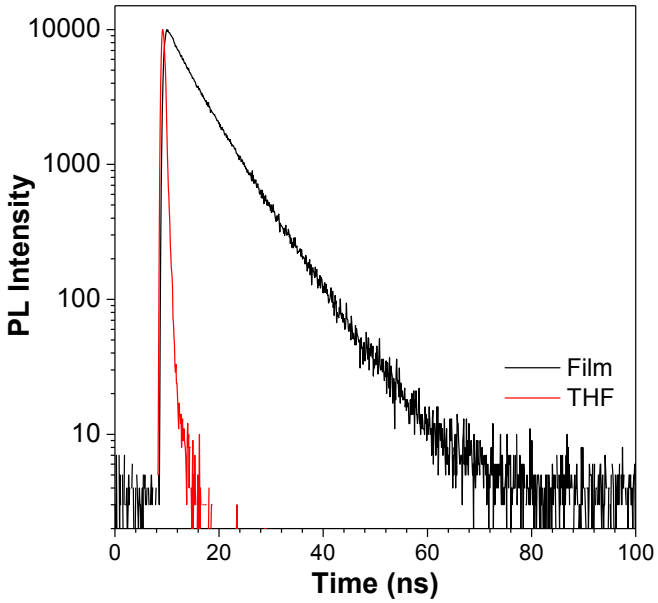


**Fig. S1** PL decay profiles of Py-BP-PTZ in THF solutions and in neat films.

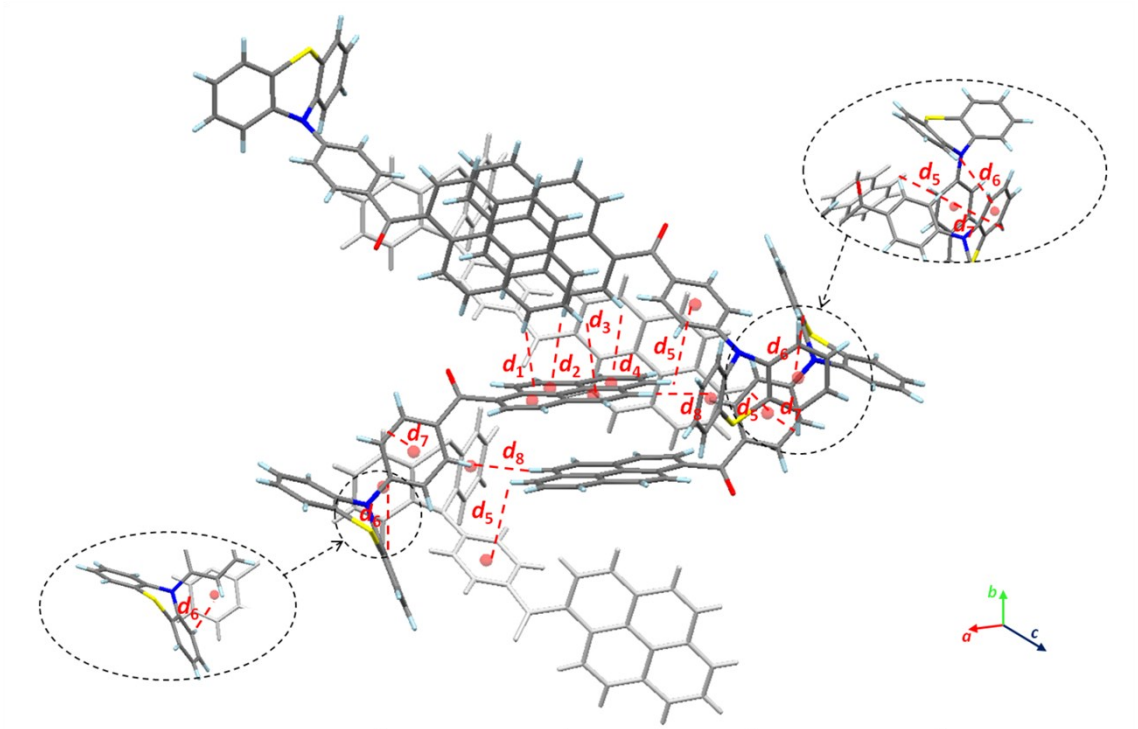


**Fig. S2** The packing pattern and weak interactions of CB in the crystal.

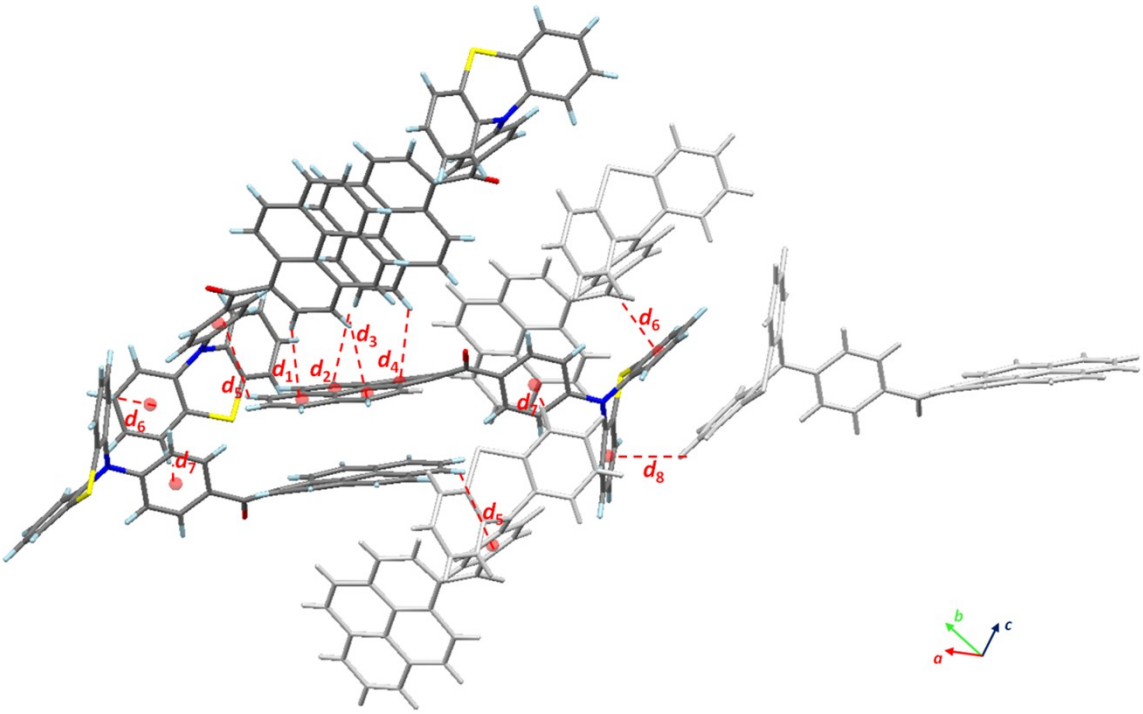


**Fig. S3** The packing pattern and weak interactions of CG in the crystal.

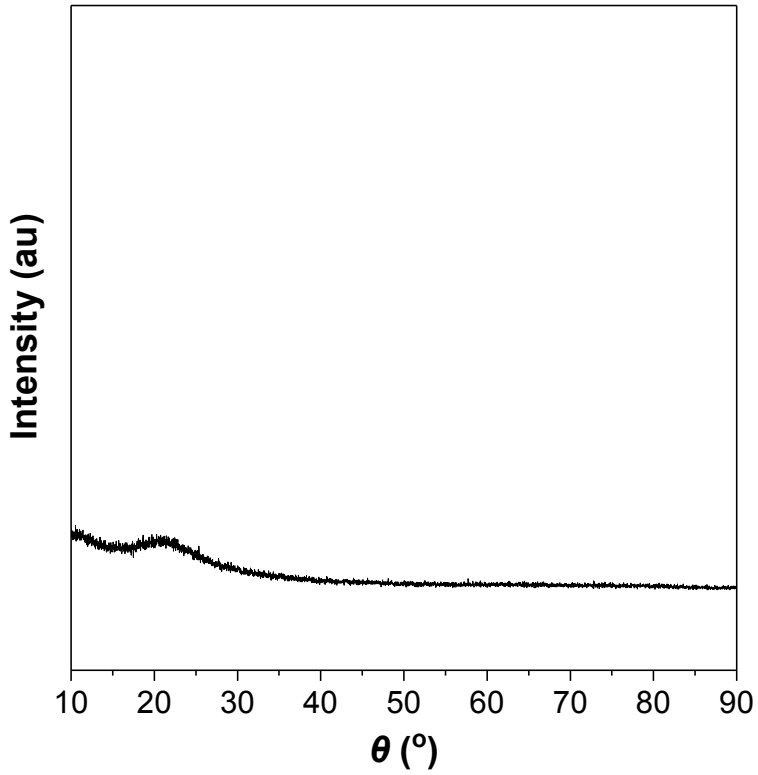


**Fig. S4** The PXRD diffractogram of the amorphous film of Py-BP-PTZ.

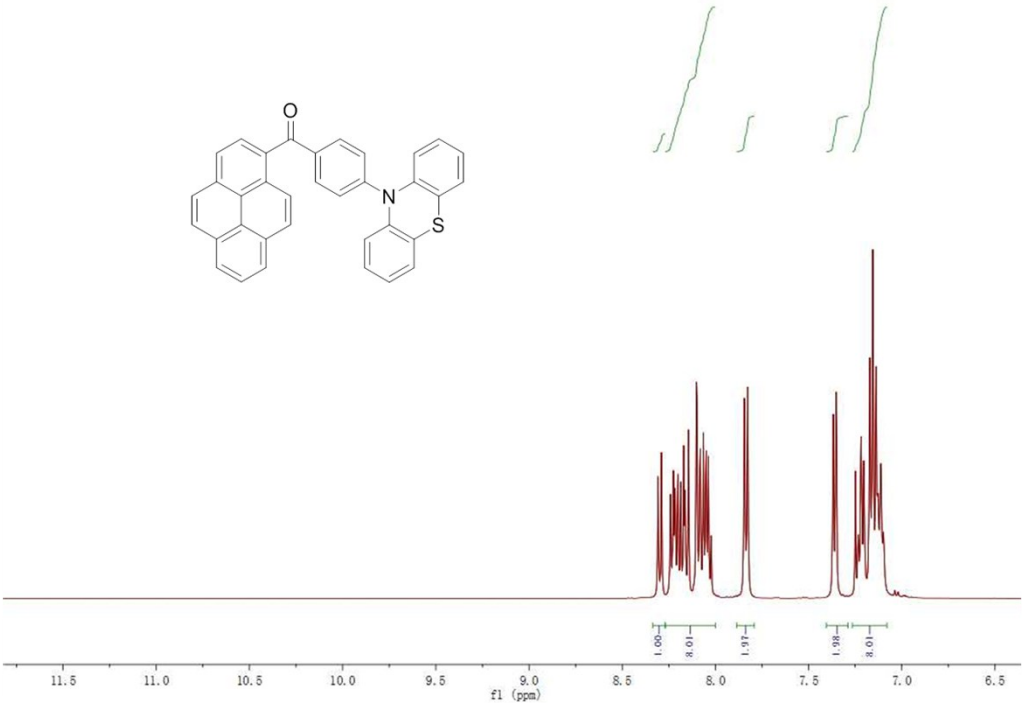


**Fig. S5** $^{1}H$ NMR spectrum of Py-BP-PTZ in $CDCl_3$.

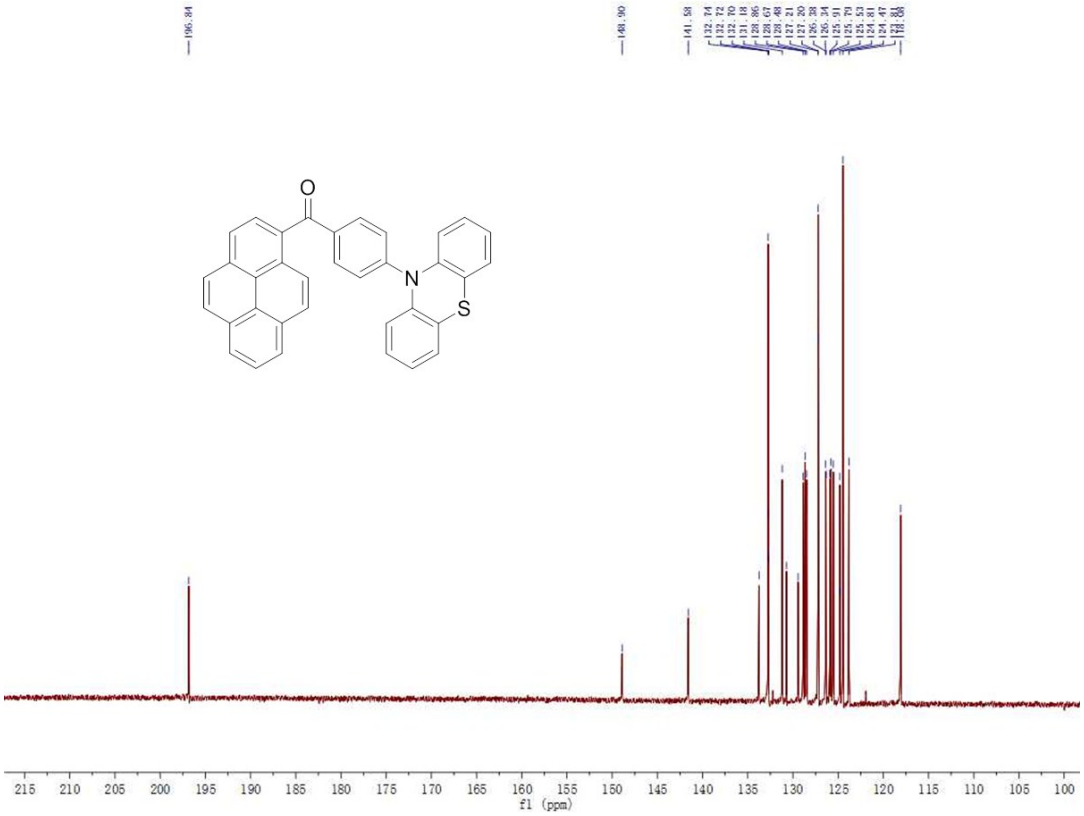


**Fig. S6** $^{13}C$ NMR spectrum of Py-BP-PTZ in $CDCl_3$.

## Additional Data

**Table. S1** Photophysical properties of Py-BP-PTZ.

| Compound | $\lambda_{abs}$[a] (nm) | $\lambda_{em}$ (nm) | | $\Phi_{PL}$[c] (%) | | $\alpha_{AIE}$[d] | $\tau$[e] (ns) ($k_r$[$10^8$ $s^{-1}$], $k_{IC}$[$10^8$ $s^{-1}$]) | |
|---|---|---|---|---|---|---|---|---|
| | ($\varepsilon/10^4$) | soln[a] | film[b] | soln | film | | soln | film |
| Py-BP-PTZ | 347 (2.90) | 606 | 555 | 0.4 | 4.7 | 11.75 | 0.64 (0.063, 15.563) | 1.89 (0.249, 5.042) |

[a] In dilute THF solution ($10^{-5}$ M), $\varepsilon$ = molar absorptivity ($mol^{-1}$ L $cm^{-1}$).

[b] Spin-coated film on quartz plate. Solvent: THF.

[c] Fluorescence quantum yield, determined by a calibrated integrating sphere at room temperature in nitrogen.

[d] Values of AIE effect, calculated by $\Phi_{PL}$(film) / $\Phi_{PL}$(soln).

[e] Fluorescence lifetime, measured at room temperature in nitrogen, $k_r$ = radiative transition rate ($k_r$ = $\Phi_{PL}$ / $\tau$), $k_{IC}$ = internal conversion decay rate ($k_{IC}$ = (1 – $\Phi_{PL}$) / $\tau$).

**Table S2** Data of crystal structures for CB and CG.

| Crystal | $d_{\pi-\pi}$[a] (Å) | $\Delta x$[b] | | Overlap ratio (%) | | |
|---|---|---|---|---|---|---|
| | | horizontal | vertical | $R$[c] | $R_l$[d] | $R_s$[e] |
| CB | 3.459 | 2.058 | 0.034 | 52.32 | 70.60 | 86.20 |
| CG | 3.485 | 0.966 | 1.640 | 44.59 | 99.30 | 66.16 |

[a] Interplanar distances between the overlapped pyrene planes.

[b] Horizontal and vertical displacements between the overlapped pyrene planes, with one of the pyrene moieties as a reference.

[c] The overlapped area divided by the whole area of the mean pyrene rings.

[d] $R_l = [l - \Delta x(\text{horizontal})] / l$.

[e] $R_s = [s - \Delta x(\text{vertical})] / s$.