Electronic Supplementary Information

for

A Perylene Bisimide Derivative with Pyrene and Cholesterol as Modifying Structures: Synthesis and Fluorescence Behavior

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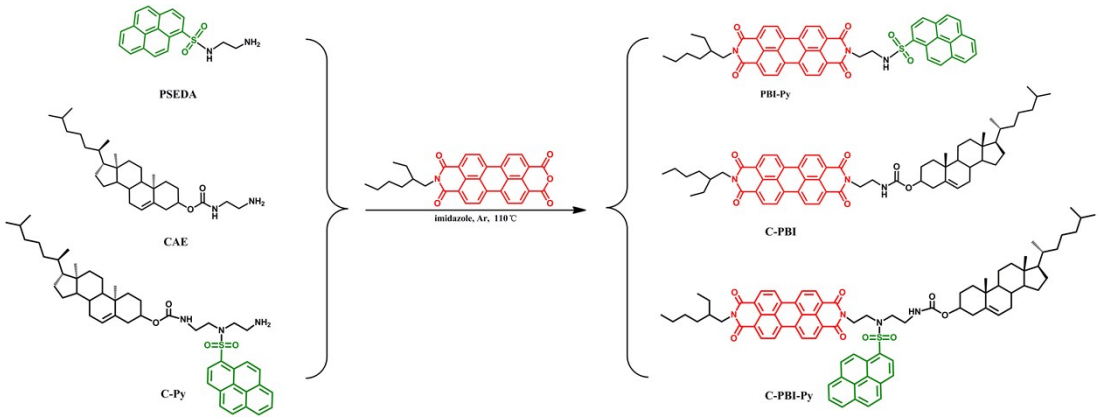
1. Synthesis strategy of the compounds



Scheme S1. The synthesis strategy of C-PBI-Py, PBI-Py and C-PBI

2. Synthesis and characterization

Preparation of C-PBI-Py

EHPMI (0.036 g, 0.072 mmol), C-Py (0.071 g, 0.091 mmol) and imidazole (2.00 g) were heated under argon atmosphere at 110 ℃ for 4 h, and then cooled to room temperature. The reaction mixture was dispersed in 50 mL ethanol and stirred rapidly for 2 h at room temperature. The resulting suspension was filtrated and washed with ethanol to give a red solid. Subsequently, the mixture as obtained was purified by column chromatography on silica gel column with CH_2Cl_2/CH_3OH (v/v, 20:l) to yield a deep red solid product. ^1H NMR ($CDCl_3/Me_4Si$, 600 MHz, Fig. S21), δ (ppm): 8.75 (d, J=8.4, 2H, perylene), 8.61 (d, J=7.8, 1H, pyrene), 8.38-8.42 (m, 3H, perylene & pyrene), 7.90-7.94 (m, 3H, perylene & pyrene), 7.85 (d, J=7.8, 2H, perylene), 7.74-7.77 (m, 2H, pyrene), 7.57 (d, *J*=9.0, 1H, pyrene), 7.35 (d, *J*=8.4, 1H, pyrene), 7.18 (t, *J*=7.2, 1H, pyrene), 7.05 (d, *J*=7.2, 1H, pyrene), 5.42 (s, 1H, *H*-C=C), 5.29 (t, *J*=6.6, 1H, N*H*), 4.61 (m, 1H, OC*H*), 4.18-4.27 (m, 6H, CH_2NS & CHCH_2N), 3.92 (s, 2H, CH_2CH_2NH), 3.75 (m, 2H, CH_2CH_2NS), 0.68-2.47 (m, 58H, cholesteryl protons & CH_3 $(CH_2)_3CHCH_2CH_3$); IR (KBr), ν_{max} (cm^{-1}): 3387 (NH), 2930 (CH_2), 1695 (O=C-O), 1659 (O=C-N), 1595 (C=C), 1157 (S=O); MS (m/z), Calcd for [(M+ $Na)^+$]: 1287.62, found: 1287.51.

Preparation of PBI-Py

A similar procedure was employed for synthesis of PBI-Py by using PSEDA instead of EHPMI. ^{1}H NMR ($(CD_3)_2SO/Me_4Si$, 600 MHz, Fig. S22), δ (ppm): 8.43 (d, *J*=9.0, 1H, pyrene), 8.29-8.34 (m, 3H, perylene & pyrene), 8.22 (d, *J*=7.8, 2H, perylene), 7.92 (d, *J*=7.8, 1H, pyrene), 7.84 (d, *J*=9.0, 1H, pyrene), 7.79 (d, *J*=7.8, 1H, pyrene), 7.69 (d, *J*=7.2, 2H, perylene), 7.35-7.39 (m, 4H, perylene & pyrene), 7.10-7.12 (m, 2H, pyrene), 3.97-4.05 (m, 2H, CHC*H*$_2$N), 3.92 (s, 2H, C*H*$_2$NH), 3.52 (s, 2H, C*H*$_2$CH$_2$NH), 1.92 (m, 1H, C*H*CH$_2$N), 1.33-1.43 (m, 8H, (C*H*$_2$)$_3$CHC*H*$_2$), 0.90-0.96 (m, 6H, CH$_2$C*H*$_3$); IR (KBr), ν_{max} (cm^{-1}): 3296 (NH), 3040 (ArH), 2926 (CH$_2$), 1693 (O=C-O), 1655 (O=C-N), 1593 (C=C); MS (m/z), Calcd for [(M+ Na)$^+$]: 832.25, found: 832.27.

Preparation of C-PBI

A similar procedure was adopted for synthesis of C-PBI by using CAE instead of EHPMI. ^{1}H NMR ($CDCl_3/Me_4Si$, 600 MHz, Fig. S23), δ (ppm): 8.54-8.66 (m, 8H, perylene), 5.12 (t, *J*=5.4, 1H, *H*-C=C)), 5.07 (s, 1H, N*H*), 4.41 (m, 2H, CH$_2$C*H*$_2$NH), 4.30 (m, 1H, OC*H*), 4.11-4.20 (m, 2H, CHC*H*$_2$N), 3.59 (s, 2H, C*H*$_2$CH$_2$NH), 0.62-2.07 (m, 58H, cholesteryl protons & C*H*$_3$ (C*H*$_2$)$_3$C*H*C*H*$_2$C*H*$_3$); IR (KBr), ν_{max} (cm^{-1}): 3371 (NH), 2934 (CH$_2$), 1697 (O=C-O), 1657 (O=C-N), 1595 (C=C); MS (m/z), Calcd for [(M+ Na)$^+$]: 957.57, found: 957.72.

3. ^{1}H-^{1}H NOESY spectroscopy of C-PBI-Py in $CDCl_3$

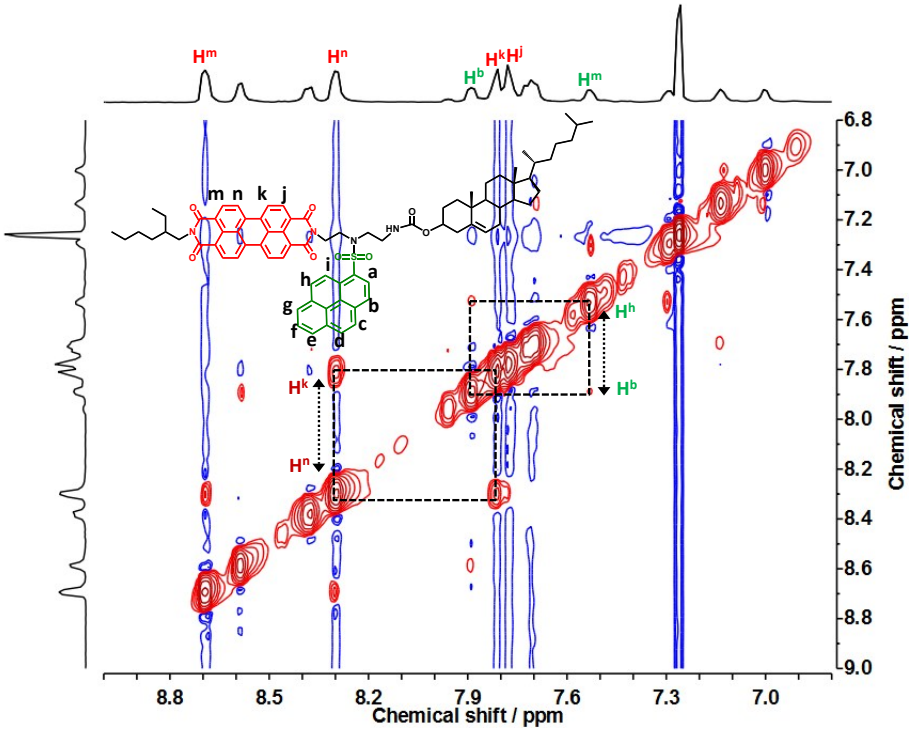


Fig. S1 ^{1}H-^{1}H NOESY spectroscopy of C-PBI-Py in $CDCl_3$.

4. ^{1}H-^{1}H COSY spectroscopy of C-PBI-Py in $CDCl_3$

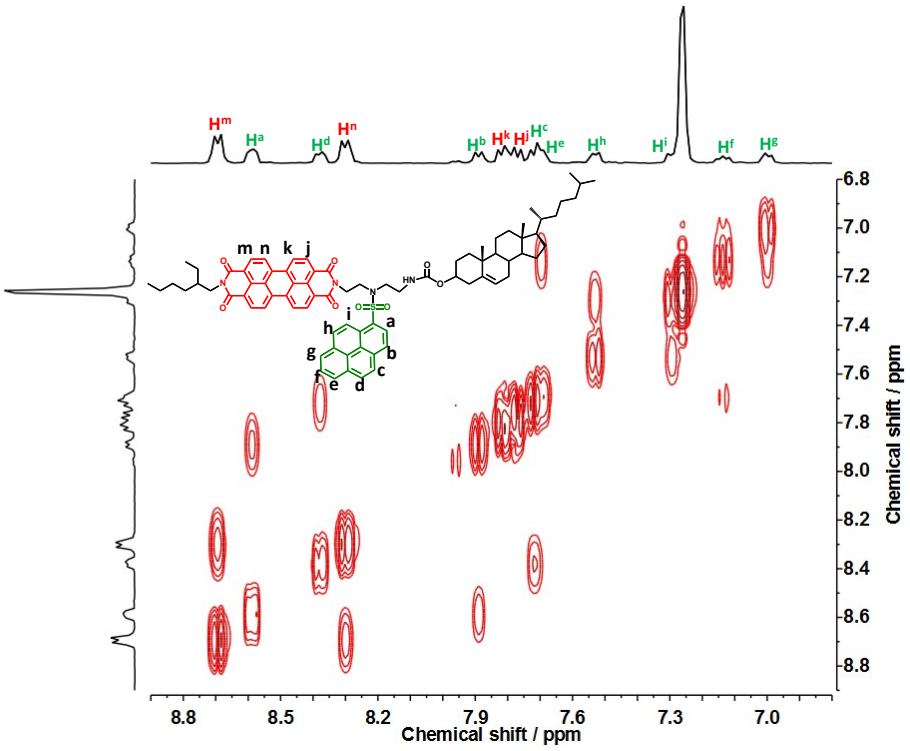


Fig. S2 ^{1}H-^{1}H COSY spectroscopy of C-PBI-Py in $CDCl_3$.

5. Cyclic voltammograms of C-Py, C-PBI and C-PBI-Py in CH_2Cl_2

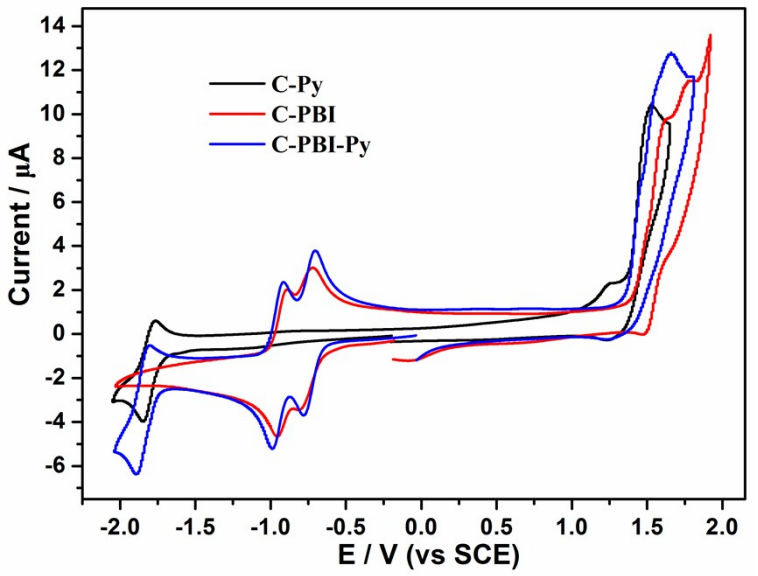


Fig. S3 CV traces of C-Py (black solid), C-PBI (red solid) and C-PBI-Py (blue solid) in dichloromethane at a concentration of 5.0×10^{-4} mol/L with 2.0×10^{-4} mol/L tetrabutylammonium hexafluorophosphate as supporting electrolyte, the scan rate was 100 mVs^{-1}.

6. UV-Vis absorption spectra of C-PBI, C-Py and their mixture

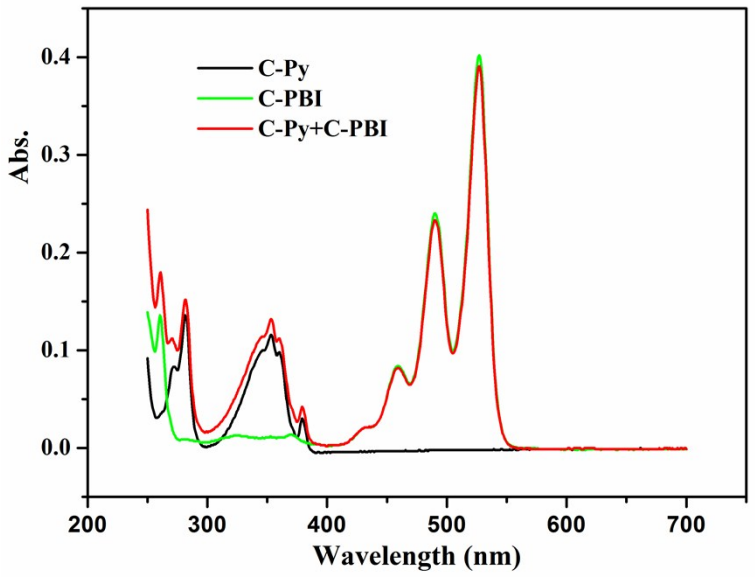


Fig. S4 UV-Vis absorption spectra of C-Py (black solid), C-PBI (green solid) and their mixture (red solid) in chloroform at a concentration of 5.0×10^{-6} mol/L.

7. Fluorescence emission spectra of C-Py, C-PBI and their mixture

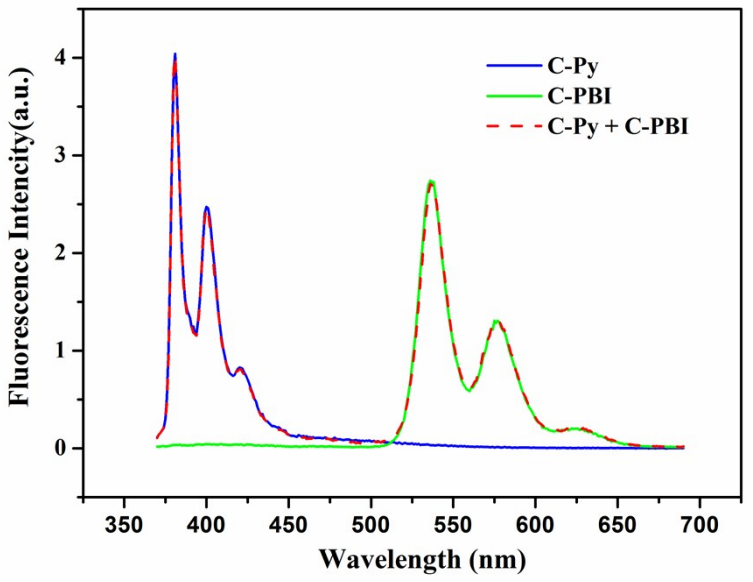


Fig. S5 Fluorescence emission spectra of C-Py (blue solid), C-PBI (green solid) and their mixture (red dash) in chloroform at a concentration of 5.0×10^{-6} mol/L upon the excitation at 353 nm.

8. Normalized fluorescence excitation and emission spectra of C-PBI-Py

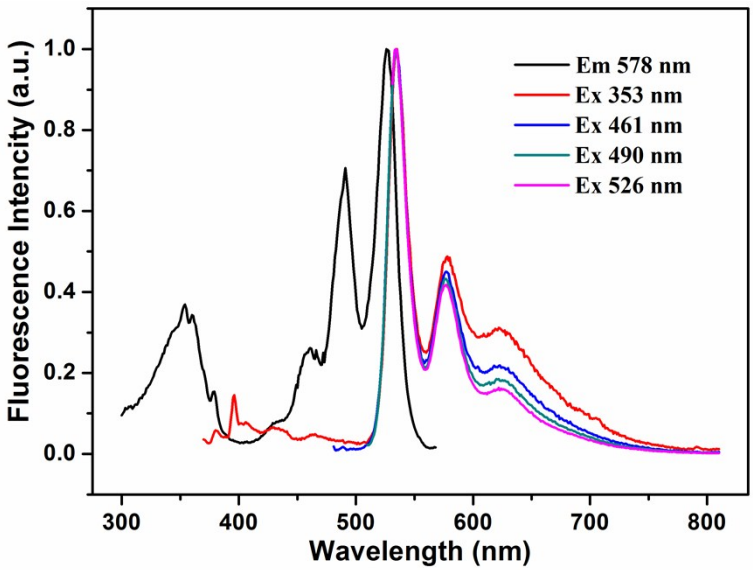


Fig. S6 Normalized fluorescence excitation and emission spectra of C-PBI-Py in chloroform at a concentration of 2.0×10^{-7} mol/L. The monitoring wavelength is 578 nm, and the excitation wavelengths are 353, 461, 490 and 526 nm, respectively.

9. Fluorescence emission spectra of C-PBI in different solvents

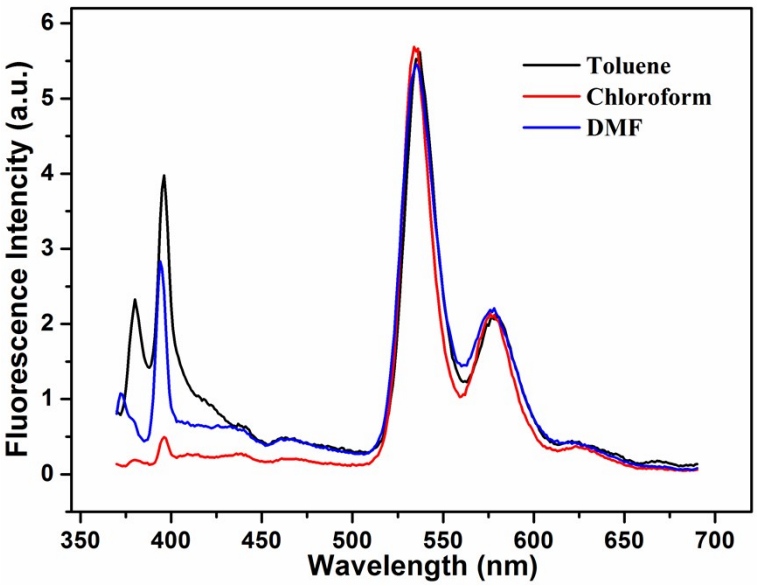


Fig. S7 Fluorescence emission spectra of C-PBI in toluene (black solid), chloroform (red solid) and DMF (blue solid) at a concentration of 5.0×10^{-8} mol/L upon the excitation at 353 nm.

10. Concentration-dependent fluorescence emission spectra of C-PBI-Py in chloroform

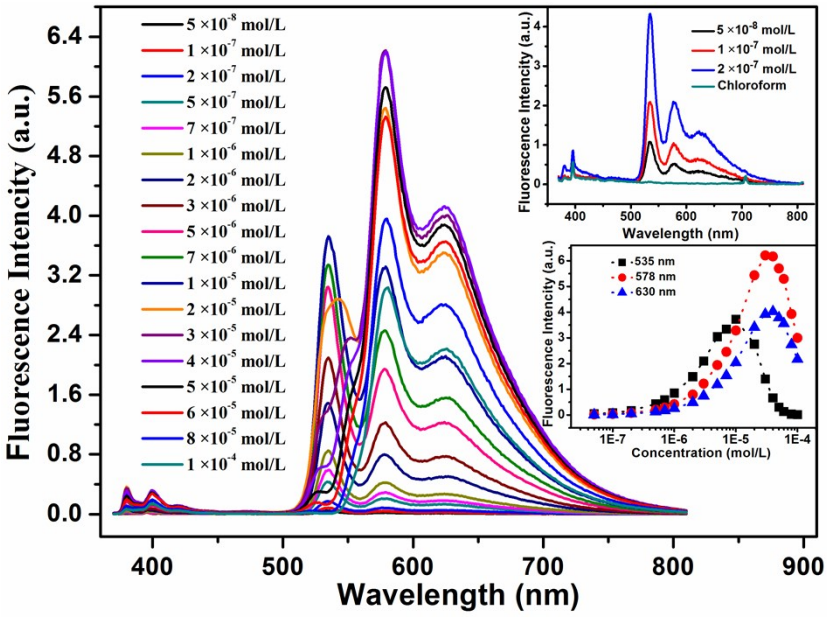


Fig. S8 Concentration-dependent fluorescence emission spectra of C-PBI-Py in chloroform in the concentration range from 5.0×10^{-8} mol/L to 1.0×10^{-4} mol/L, of which the adopted excitation wavelength is 353 nm. Inset: Fluorescence emission spectra of C-PBI-Py in chloroform at concentrations between 5.0×10^{-8} mol/L and 2.0×10^{-7} mol/L, and the excitation wavelength is 353 nm (left top), Plot of the fluorescence intensity at 535 nm, 578 nm, 630 nm, respectively, against the concentration of C-PBI-Py in chloroform (left bottom).

11. Lifetime of C-PBI-Py in chloroform

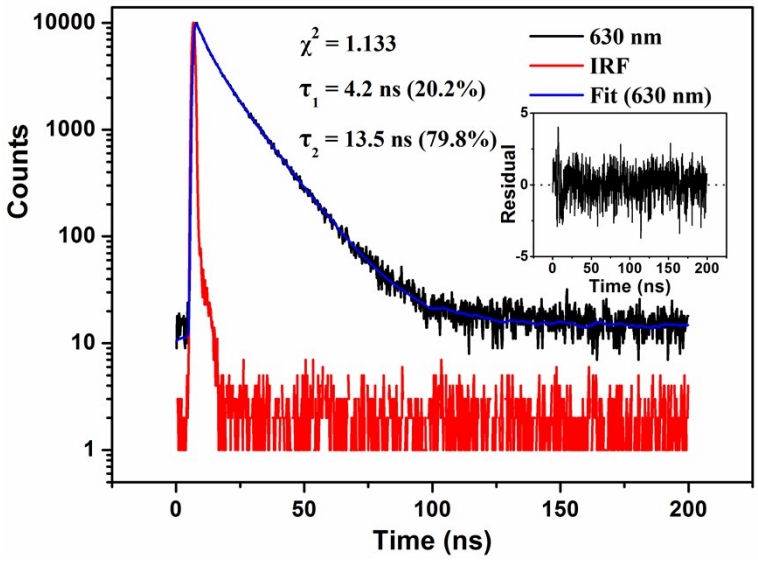


Fig. S9 Lifetime at 630 nm of C-PBI-Py in chloroform at a concentration of 5.0×10^{-6} mol/L using picosecond pulsed diode laser (EPLED-340) as an excitation source. The red trace is the instrumental response function (IRF). The inset is the corresponding residual-distribution. Note: Chi-square (χ^2) is a parameter to quantify the fitting quality.

12. Lifetime of C-PBI in chloroform

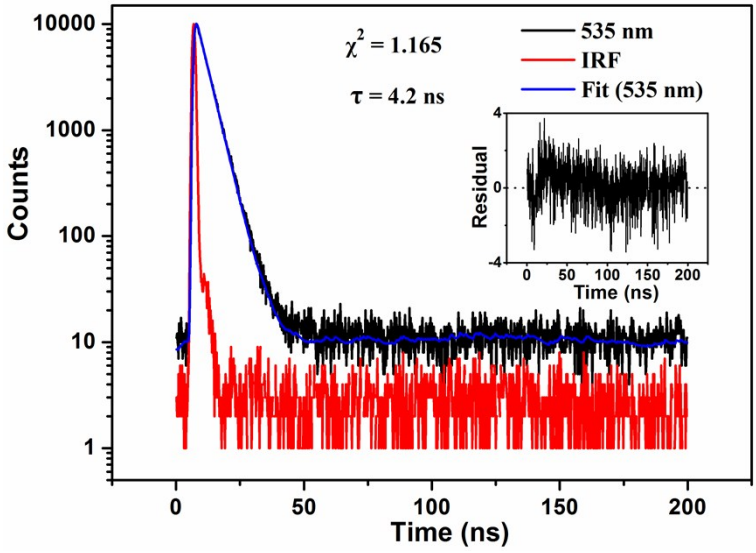


Fig. S10 Lifetime at 535 nm of C-PBI in chloroform at a concentration of 5.0×10^{-6} mol/L using picosecond pulsed diode laser (EPLED-340) as an excitation source. The red trace is the instrumental response function (IRF). The inset is the corresponding residual-distribution. Note: Chi-square (χ^2) is a parameter to quantify the fitting quality.

13. Summary of the fluorescence quantum yields of C-PBI-Py and C-PBI in chloroform

Table S1. Summary of the fluorescence quantum yields of C-PBI-Py and C-PBI in chloroform

Compound	C-PBI-Py (Φ_{pe}) [a]	C-PBI [b]
Fluorescence quantum yields	13.2%	97.3%

Note: [a] Φ_{pe} represents the fluorescence quantum yield of the PBI unit of C-PBI-Py, of which the integral range of the emission spectrum of C-PBI-Py is from 505 to 690 nm and the excitation wavelength is 353 nm. [b] The integral range for this compound is from 505 to 700 nm, and the excitation wavelength is 490 nm.

14. Concentration-dependent UV-Vis absorption spectra of C-PBI-Py in chloroform

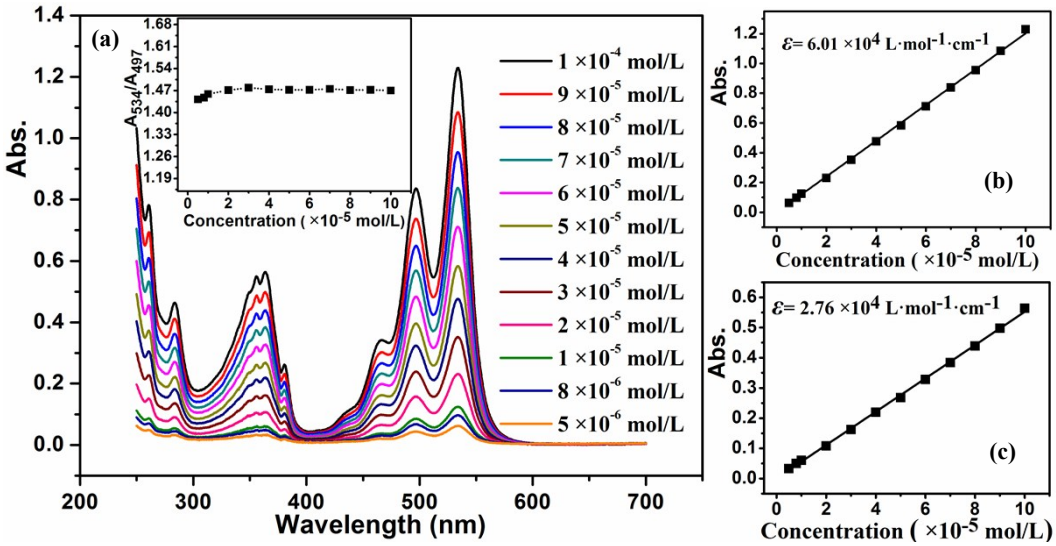


Fig. S11 Concentration-dependent UV-Vis absorption spectra of C-PBI-Py in chloroform ranging from 5.0×10^{-6} mol/L to 1.0×10^{-4} mol/L, the inset is a plot of A_{534}/A_{497} of C-PBI-Py in chloroform as a function of concentration (a); Plot of the absorbance of the C-PBI-Py solution in chloroform as a function of concentration, recorded at 534 nm (b) and 364 nm (c), respectively.

15. UV-Vis absorption spectra of C-PBI-Py in chloroform and the mixture solvent

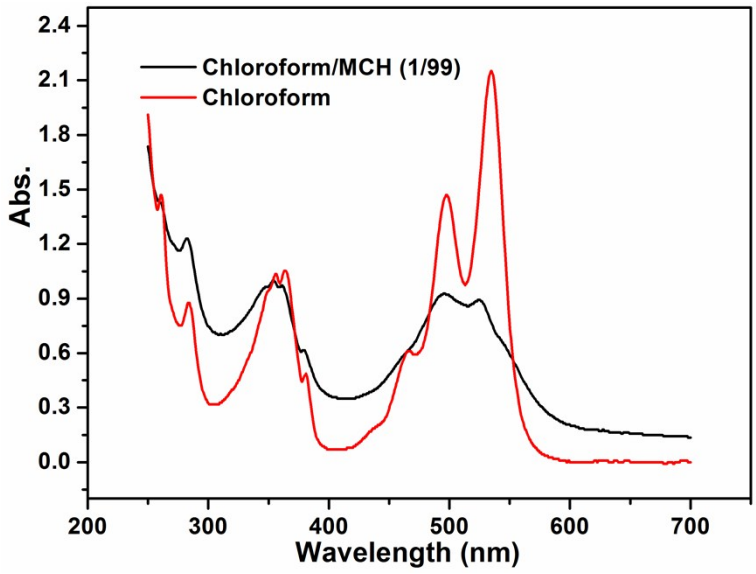


Fig. S12 UV-Vis absorption spectra of C-PBI-Py in chloroform and the mixture solvent (chloroform / Methylcyclohexane, v/v, 1/99) normalized at 354 nm at a concentration of 5.0×10^{-6} mol/L.

16. Concentration-dependent ^{1}H NMR spectra of C-PBI-Py

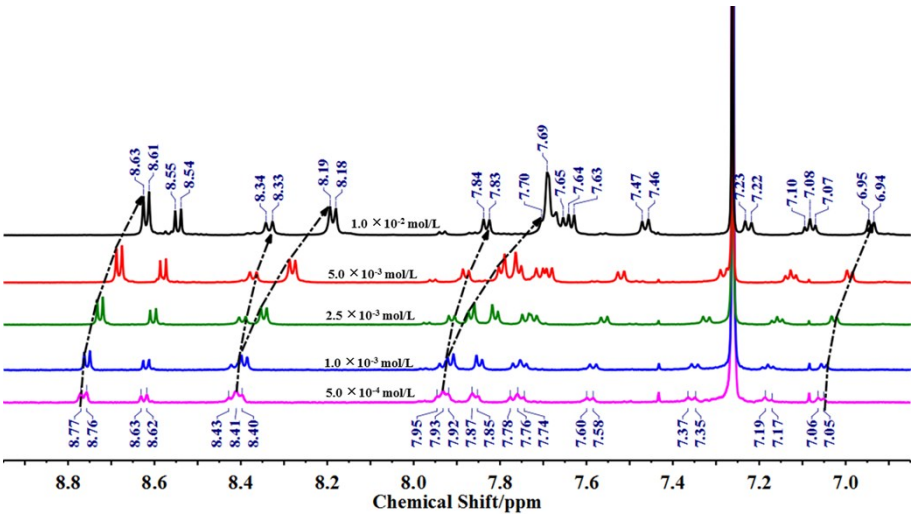


Fig. S13 Concentration-dependent partial ^{1}H NMR spectra of C-PBI-Py in deuterated chloroform ranging from 5.0×10^{-4} mol/L to 1.0×10^{-2} mol/L.

17. Time-resolved emission spectra of C-PBI-Py in chloroform at a concentration of 1.0×10^{-4} mol/L

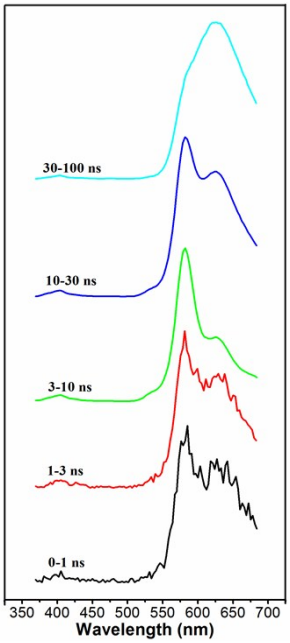


Fig. S14 Time-resolved emission spectra of C-PBI-Py in chloroform at a concentration of 1.0×10^{-4} mol/L using picosecond pulsed diode laser (EPLED-340) as an excitation source.

18. Time-resolved emission spectra of PBI-Py in chloroform at a concentration of 5.0×10^{-6} mol/L

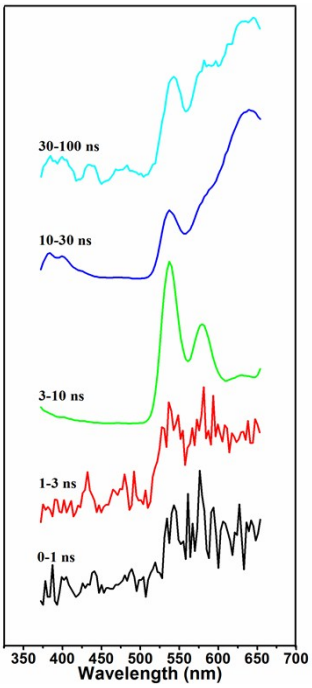


Fig. S15 Time-resolved emission spectra of PBI-Py in chloroform at a concentration of 5.0×10^{-6} mol/L using picosecond pulsed diode laser (EPLED-340) as an excitation source.

19. Fluorescence emission spectra of C-PBI in chloroform at a concentration of 5.0×10^{-6} mol/L at two different temperatures

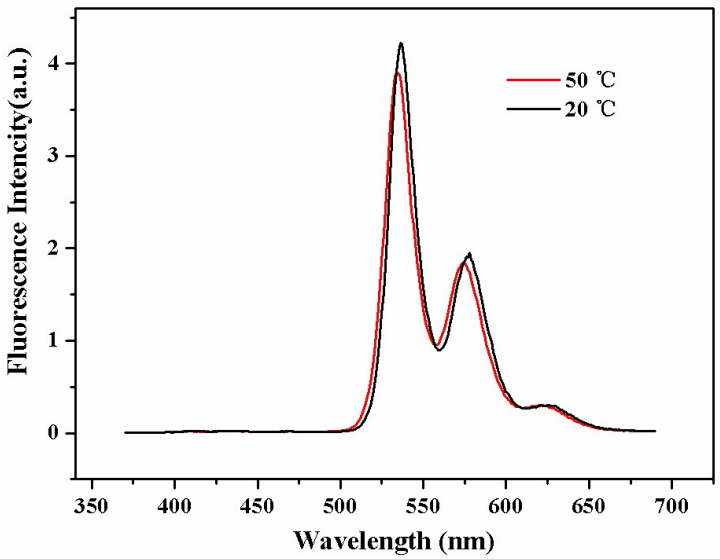


Fig. S16 Fluorescence emission spectra of C-PBI in chloroform at a concentration of 5.0×10^{-6} mol/L at two different temperatures.

20. Temperature-dependent fluorescence emission spectra of C-PBI-Py in chloroform at 2.0×10^{-5} mol/L

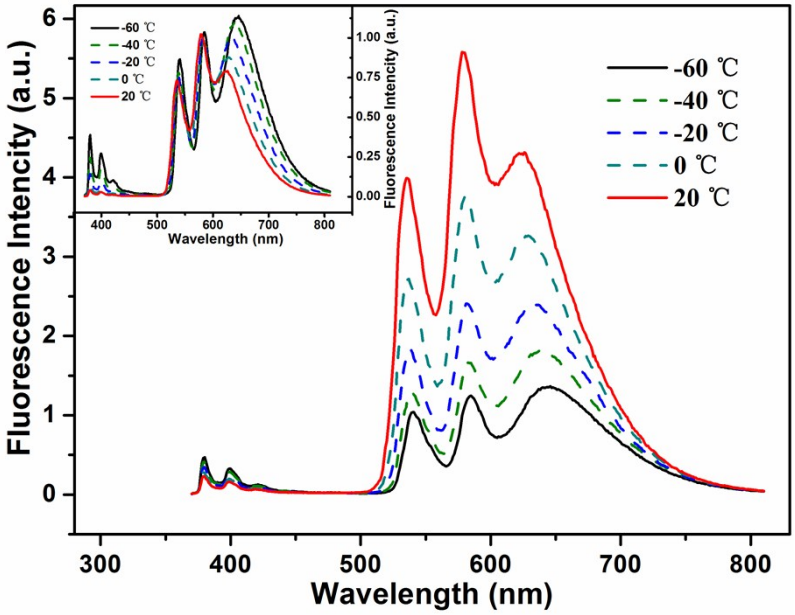


Fig. S17 Temperature-dependent fluorescence emission spectra of C-PBI-Py solution in chloroform (2.0×10^{-5} mol/L) ranging from 20 ℃ to -60 ℃, of which the excitation wavelength is 353 nm. The inset is the emission spectra normalized at 582 nm.

21. Temperature-dependent UV-Vis absorption spectra of C-PBI-Py in chloroform

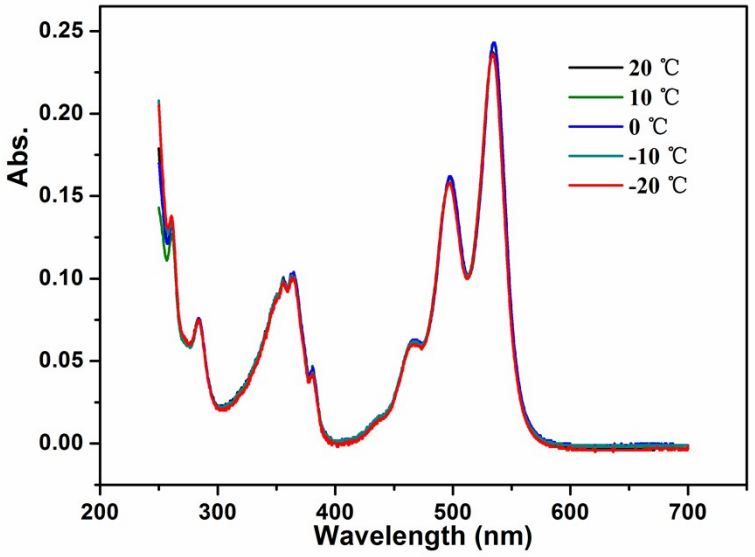


Fig. S18 Temperature-dependent UV-Vis absorption spectra of C-PBI-Py in chloroform at 5.0×10^{-6} mol/L monitored from 20 ºC to -20 ºC.

22. Lifetimes recorded at 535 nm of C-PBI-Py in chloroform at different temperatures

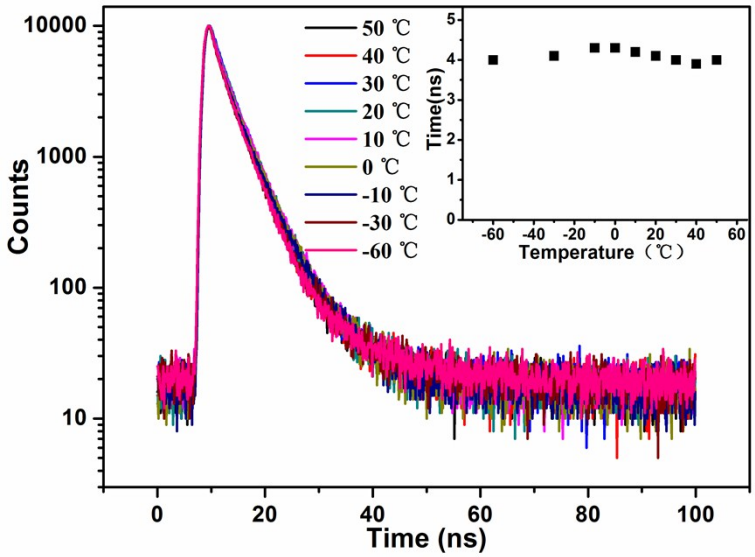


Fig. S19 Lifetimes at 535 nm of C-PBI-Py in chloroform at a concentration of 5.0×10^{-6} mol/L at different temperatures using picosecond pulsed diode laser (EPLED-340) as an excitation source. The inset is the plot of the average lifetime at 535 nm of C-PBI-Py against the temperature.

23. Lifetimes recorded at 630 nm of C-PBI-Py in chloroform at different temperatures

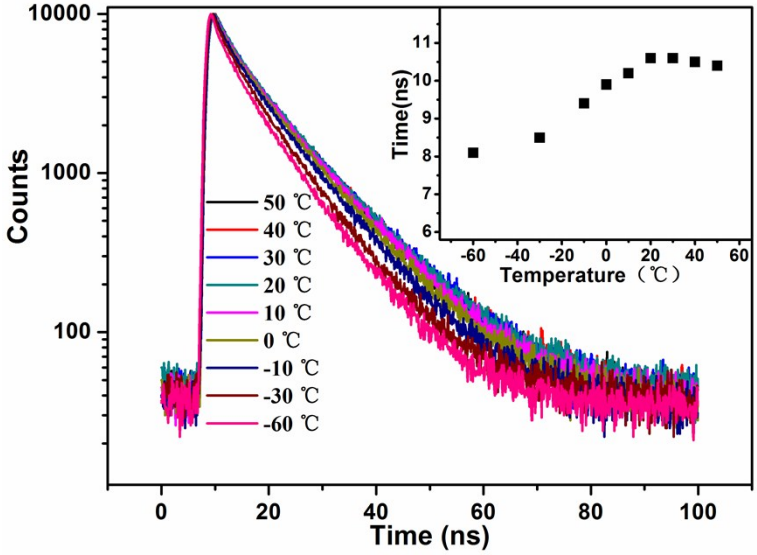


Fig. S20 Lifetimes at 630 nm of C-PBI-Py in chloroform at a concentration of 5.0×10^{-6} mol/L at different temperatures using picosecond pulsed diode laser (EPLED-340) as an excitation source. The inset is the plot of the average lifetime at 630 nm of C-PBI-Py against the temperature.

24. ^{1}H NMR spectra of the target and the reference compounds

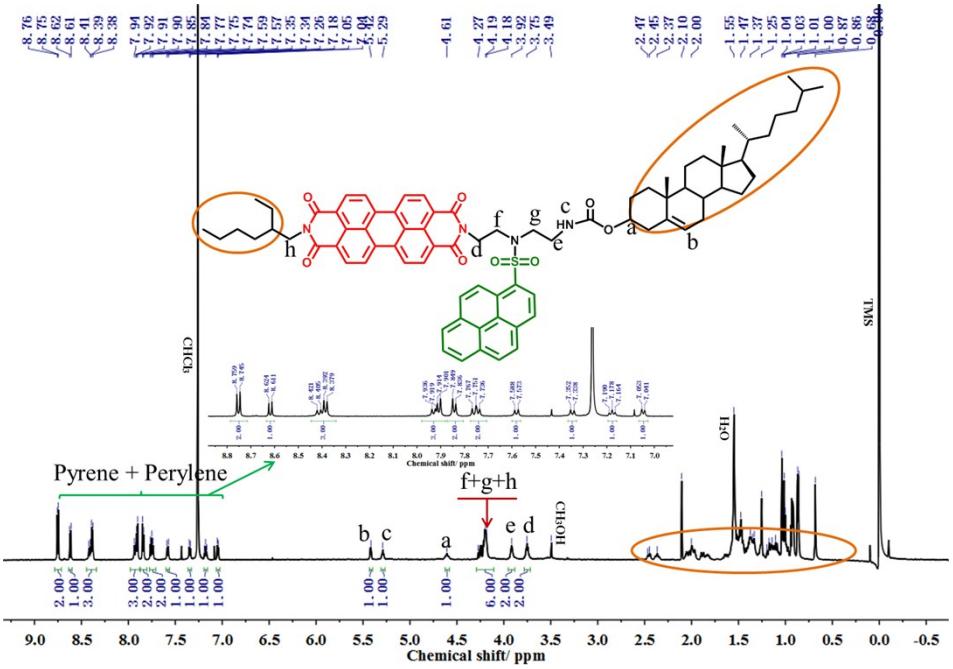


Fig. S21 ^{1}H NMR spectrum of C-PBI-Py in $CDCl_3$.

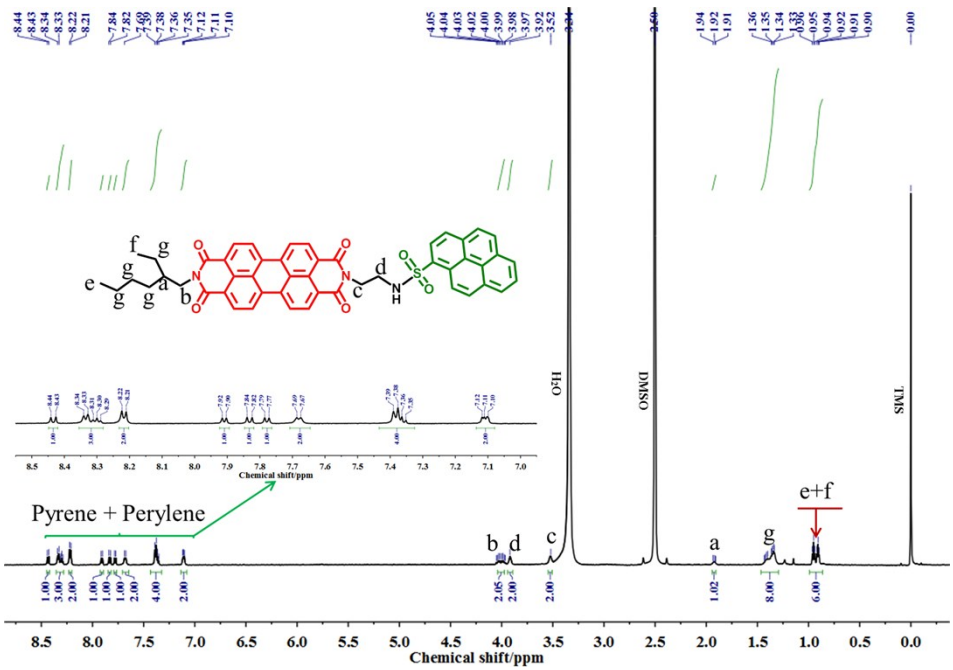


Fig. S22 ^{1}H NMR spectrum of PBI-Py in $CDCl_3$.

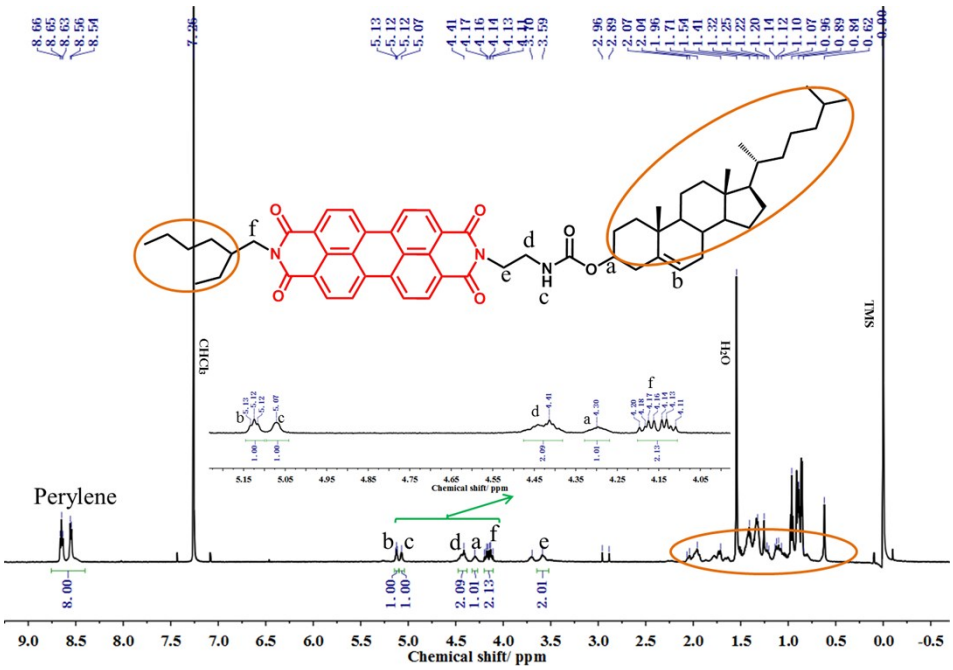


Fig. S23 ^{1}H NMR spectrum of C-PBI in $CDCl_3$.