

Supporting Information

Sulphur-induced structural rearrangement in the self-sensitization photo-oxidation behaviour of phenothiazine-imidazole molecules

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1. Materials and character

All of the reagents and solvents used for the syntheses were purchased from Energy without further purification. The ^1H NMR spectra were recorded on Bruker AVANCE III instrument (Bruker, Switzerland) by utilizing deuterated dimethyl sulfoxide (DMSO) or CDCl_3 as solvents and tetramethylsilane (TMS) as a standard. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus instrument. UV-vis absorption spectra were recorded on a UV-1800 spectrophotometer. Fluorescence measurements were carried out with a HORIBA fluorolog-3 instrument. The UV light we used in the photo-chemical reaction is the common ZF-7 portable UV light (6W, 365nm). All measurements were carried out at room temperature under ambient conditions.

2. Synthesis

Synthesis of 4,5-bis(4-bromophenyl)-1,2-diphenyl-1*H*-imidazole (Br-PIM):

A mixture of aniline (931 mg, 10.0 mmol), benzil (420 mg, 2.0 mmol), 4-bromobenzaldehyde (370 mg, 2 mmol), ammonium acetate (617 mg, 8.0 mmol), and acetic acid (15 mL) was stirred at 120 °C for 14 h under nitrogen. Then, some water was added to the resulting solution and the mixture was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the liquid was purified by column chromatography using petroleum ether/ CH_2Cl_2 as the eluent to afford a white solid (901 mg, 85%). ^1H NMR (500 MHz, DMSO- d_6), δ 7.51 (dd, $J = 12.2, 5.4$ Hz, 4H), 7.35 (dd, $J = 7.2, 2.9$ Hz, 3H), 7.31 (dd, $J = 5.6, 2.6$ Hz, 5H), 7.27 (ddd, $J = 15.8, 4.8, 2.6$ Hz, 6H), 7.19 (t, $J = 7.3$ Hz, 1H). MS (ESI): MW 451.37, m/z 453.1 (M^+).

Synthesis of 10-(4-(1,4,5-triphenyl-1*H*-imidazol-2-yl)phenyl)-10*H*-phenothiazine (PTZ-PIM):

A mixture of phenothiazine (199 mg, 1.0 mmol), Br-PIM (451 mg, 1.0 mmol), palladium acetate (22.4 mg, 0.1 mmol), sodium tert-butoxide (480 mg, 5 mmol), Tert-butylphosphine (101.2 mg, 0.5 mmol) in toluene (15 mL) was heated at 100 °C for 14

h under nitrogen. After cooling to room temperature, dichloromethane was added and the mixture was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. Then the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with dichloromethane as eluent. White powder (yield: 80%). ^1H NMR (500 MHz, DMSO- d_6), δ 7.61-7.56 (m, 2H), 7.54-7.50 (m, 2H), 7.39-7.37 (m, 1H), 7.36 (d, $J = 2.1$ Hz, 2H), 7.34-7.30 (m, 5H), 7.29-7.24 (m, 6H), 7.19 (dd, $J = 8.3, 6.3$ Hz, 1H), 7.15 (dd, $J = 7.6, 1.5$ Hz, 2H), 7.01 (td, $J = 7.9, 1.5$ Hz, 2H), 6.93 (td, $J = 7.5, 1.1$ Hz, 2H), 6.34 (dd, $J = 8.2, 0.9$ Hz, 2H). MS (ESI): MW 595.6, m/z 595.7 (M^+).

Synthesis of 10-(4-(1,4,5-triphenyl-1*H*-imidazol-2-yl)phenyl)-10*H*-phenoxazine (POZ-PIM):

A mixture of phenoxazine (366.0 mg, 2.0 mmol), Br-PIM (902.0 mg, 2.0 mmol), palladium acetate (22.4 mg, 0.1 mmol), sodium tert-butoxide (480 mg, 5 mmol), tri-tert-butylphosphine (101.2 mg, 0.5 mmol) and toluene (15 mL) was stirred at 100 °C for 14 h under nitrogen in an oil bath. Then, some water was added to the resulting solution and the mixture was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the liquid was purified by column chromatography using petroleum ether/ CH_2Cl_2 as the eluent to afford a white solid (940.1 mg, 87%). ^1H NMR (500 MHz, DMSO) δ 7.67-7.63 (m, 2H), 7.55-7.50 (m, 2H), 7.40-7.31 (m, 10H), 7.31-7.25 (m, 4H), 7.20 (t, $J = 7.3$ Hz, 1H), 6.76-6.72 (m, 2H), 6.70- 6.64 (m, 4H), 5.84-5.80 (m, 2H). MS (ESI): MW 553.67, m/z 555.7 (M^+).

Synthesis of 10-phenyl-3-(1,4,5-triphenyl-1*H*-imidazol-2-yl)-10*H*-phenoxazine (*p*-POZ-PIM):

The synthesis process of *p*-POZ-PIM was the same as Br-PIM only by using 10-phenyl-10*H*-phenoxazine-3-carbaldehyde (574 mg, 2.0 mmol) to replace benzaldehyde, *p*-POZ-PIM was obtained as a white solid (685 mg, 62%). ^1H NMR (500 MHz, DMSO) δ 7.67 (t, $J = 7.8$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 2H), 7.46 (d, $J = 7.2$ Hz, 2H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.38-7.33 (m, 2H), 7.33-7.19 (m, 8H), 7.17 (d, $J = 7.3$ Hz, 1H), 6.74-

6.60 (m, 4H), 5.84-5.78 (m, 1H), 5.71 (d, $J = 8.5$ Hz, 1H), 5.33 (t, $J = 4.7$ Hz, 2H). MS (ESI): MW 553.6, m/z 554.2 (M^+).

Synthesis of 10-phenyl-3-(1,4,5-triphenyl-1*H*-imidazol-2-yl)-10*H* phenothiazine (*p*-PTZ-PIM):

The synthesis process of *p*-PTZ-PIM was the same as Br-PIM only by using 10-phenyl-10*H*-phenothiazine -3-carbaldehyde (574 mg, 2.0 mmol) to replace 4-bromobenzaldehyde, *p*-PTZ-PIM was obtained as a white solid (785 mg, 49%). ^1H NMR (600 MHz, DMSO), δ 7.67 (t, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.49-7.14 (m, 16H), 7.09-6.99 (m, 2H), 6.96-6.82 (m, 4H), 6.07 (dd, $J = 8.2, 1.1$ Hz, 1H), 5.97 (d, $J = 8.7$ Hz, 1H). MS (ESI): MW 569.7, m/z 570.1 (M^+).

The photo-oxidation reaction product (PTZ-DYZ):

Compound PTZ-PIM (100 mg, 0.17 mmol) is dissolved in toluene and irradiated by a 365 nm UV lamp for about 72 h. After evaporation, the resulting solution was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to afford the product as an orange solid (23 mg, 24%). ^1H NMR (500 MHz, DMSO), δ 7.59 (dd, $J = 17.5, 8.0$ Hz, 6H), 7.49-7.33 (m, 9H), 7.31-7.19 (m, 6H), 7.15-7.11 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 2H), 6.65 (d, $J = 8.1$ Hz, 2H). MS (ESI): MW 569.7, m/z 571.2 (M^+).

The photo-oxidation reaction product (*p*-POZ-PYZ):

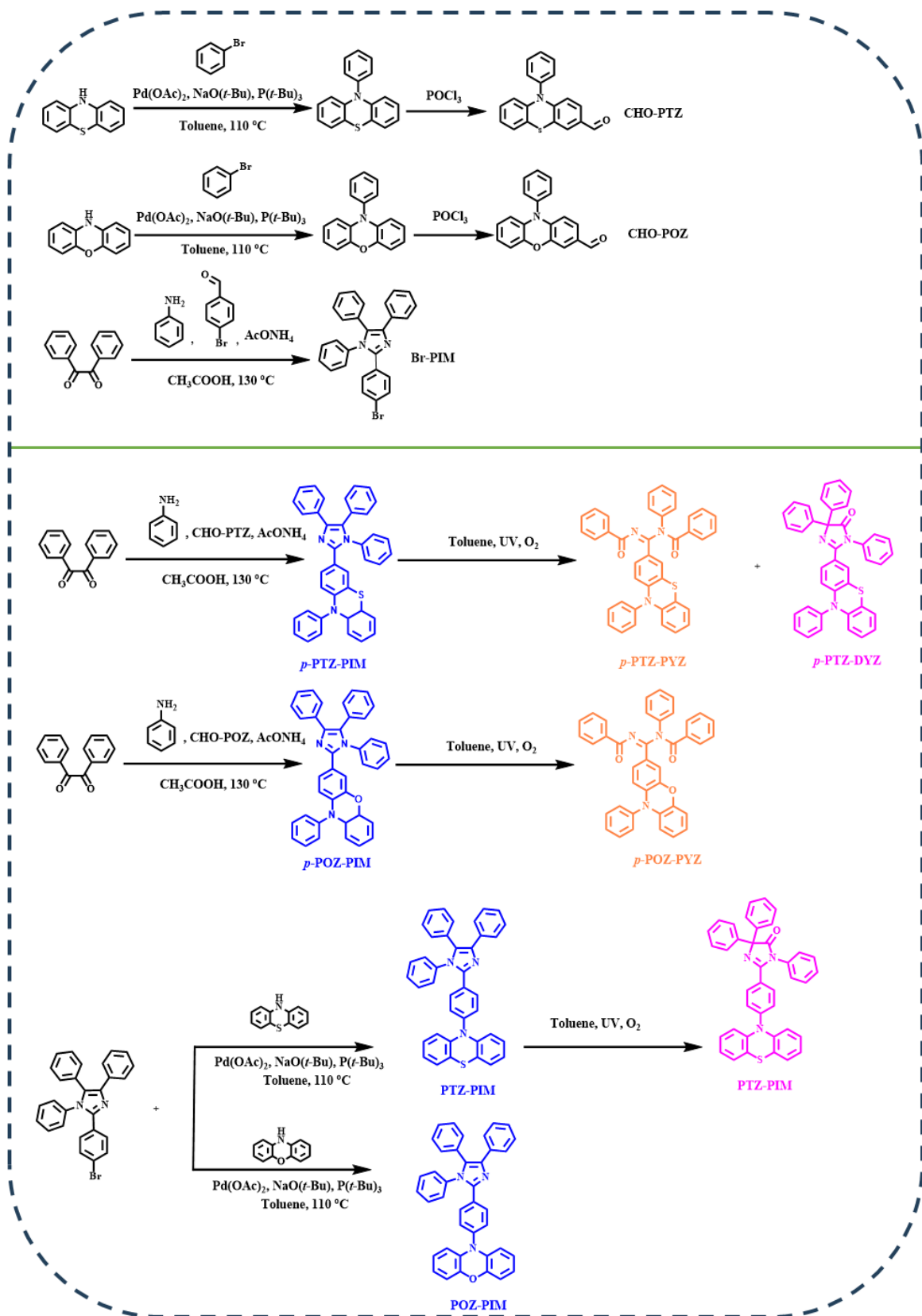
Compound *p*-POZ-PIM (100 mg, 0.18 mmol) is dissolved in toluene and irradiated by a 365 nm UV lamp for about 24 h. After evaporation, the resulting solution was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to afford the product as an orange solid (60 mg, 57%). ^1H NMR (500 MHz, DMSO) δ 7.67 (t, $J = 7.7$ Hz, 2H), 7.61 (d, $J = 7.2$ Hz, 2H), 7.55 (m, $J = 26.0, 7.5$ Hz, 4H), 7.44 -7.33 (m, 5H), 7.28 (td, $J = 15.5, 8.2$ Hz, 6H), 7.18 (m, $J = 8.4, 2.1$ Hz, 1H), 7.14-7.10 (m, 1H), 7.05 (d, $J = 2.1$ Hz, 1H), 6.73 (m, $J = 9.1, 7.1$ Hz, 3H), (d, $J = 7.6$ Hz, 1H), 5.78 (d, $J = 8.5$ Hz, 1H). MS (ESI): MW 585.6, m/z 586.2 (M^+).

The photo-oxidation reaction product (*p*-PTZ-PYZ):

Compound *p*-PTZ-PIM (100 mg, 0.18 mmol) is dissolved in toluene and irradiated by a 365 nm UV lamp for about 72 h. After evaporation, the resulting solution was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to afford the product as an orange solid (20 mg, 18%). ¹H NMR (400 MHz, DMSO), δ 7.96 (d, *J* = 7.1 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 2H), 7.57 (dt, *J* = 26.9, 8.8 Hz, 5H), 7.49-7.33 (m, 6H), 7.32-7.19 (m, 4H), 7.15-7.01 (m, 3H), 6.90 (dt, *J* = 14.7, 6.6 Hz, 2H), 6.73-6.67 (m, 1H), 6.02 (dd, *J* = 14.3, 8.2 Hz, 2H), 5.33 (s, 1H). MS (ESI): MW 601.1, *m/z* 602.2 (M⁺).

The photo-oxidation reaction product (*p*-PTZ-DYZ):

Compound *p*-PTZ-PIM (100 mg, 0.18 mmol) is dissolved in toluene and irradiated by a 365 nm UV lamp for about 72 h. After evaporation, the resulting solution was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to afford the product as an orange solid (21 mg, 19%). ¹H NMR (600 MHz, DMSO), δ 7.68 (t, *J* = 7.8 Hz, 1H), 7.59-7.50 (m, 2H), 7.43 (dddd, *J* = 18.2, 15.1, 8.4, 4.7 Hz, 4H), 7.34 (ddd, *J* = 7.3, 6.0, 1.2 Hz, 1H), 7.25-7.21 (m, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.96 - 6.85 (m, 2H), 6.05 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.97 (d, *J* = 8.7 Hz, 1H). MS (ESI): MW 585.7, *m/z* 586.2 (M⁺).



Scheme S1. The detailed synthesis route of imidazolinone and benzoylamino-benzamide derivatives molecules.

3. In-situ absorption spectra and NMR

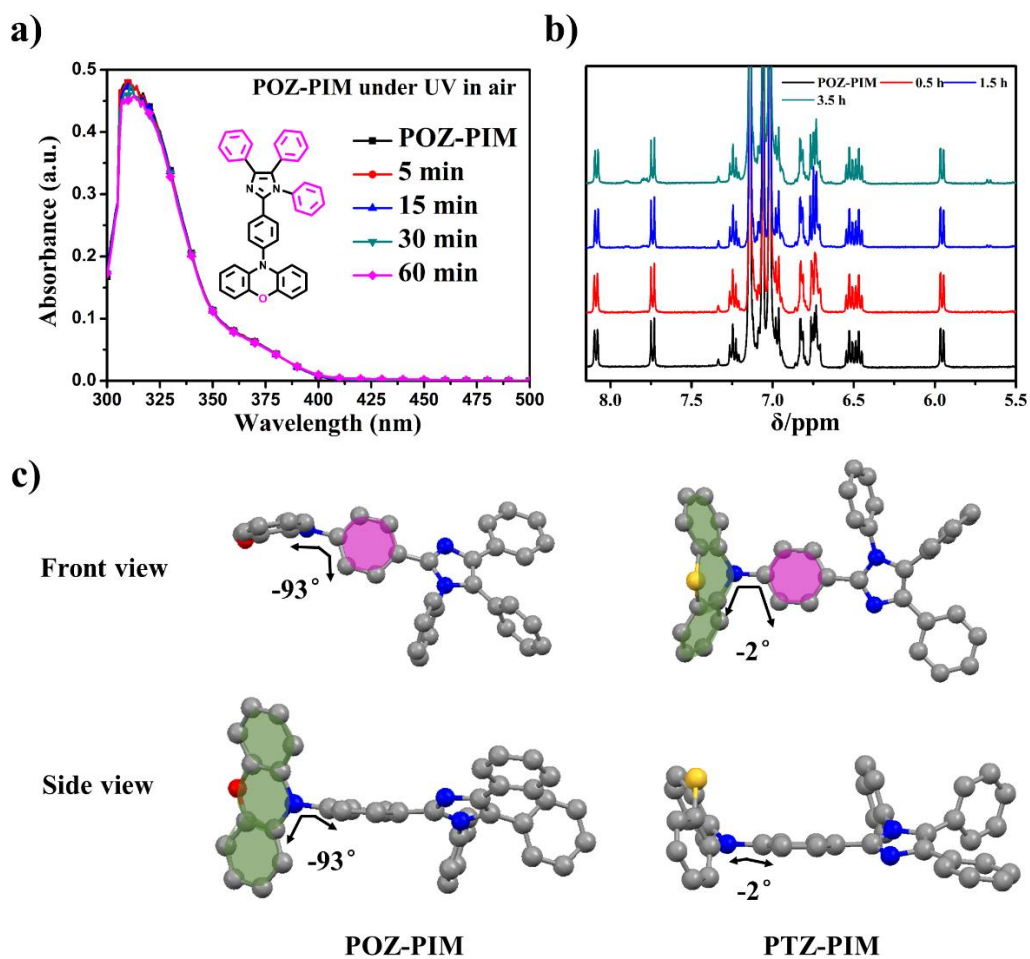


Figure S1. a) In-situ absorption spectra of POZ-PIM in toluene solvent at 10^{-5} mol L $^{-1}$ under different UV irradiation (365 nm, 6 w) time in air (O_2). b) The in-situ 1H NMR spectra of PTZ-PIM in toluene- d_8 solvents under UV irradiation at different times. c) Single crystal structures of PTZ-PIM and POZ-PIM.

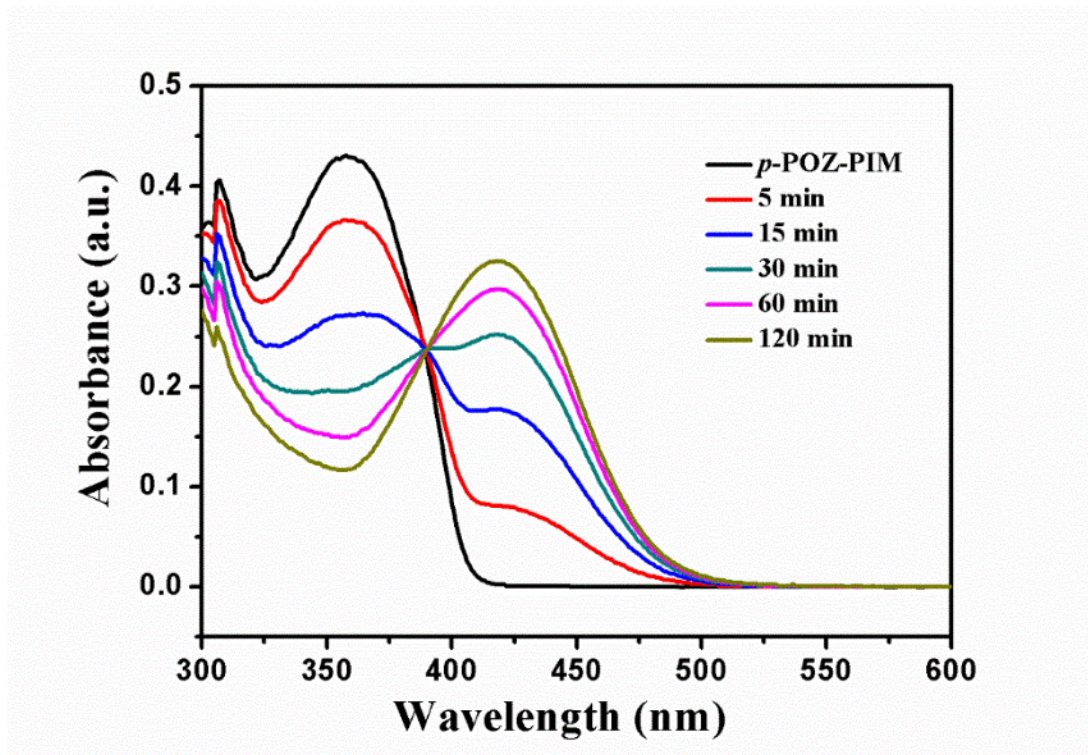


Figure S2. In-situ absorption spectra of *p*-POZ-PIM in toluene solvent at 10^{-5} mol L $^{-1}$ under different UV irradiation (365 nm, 6 w) times in the air (O $_2$).

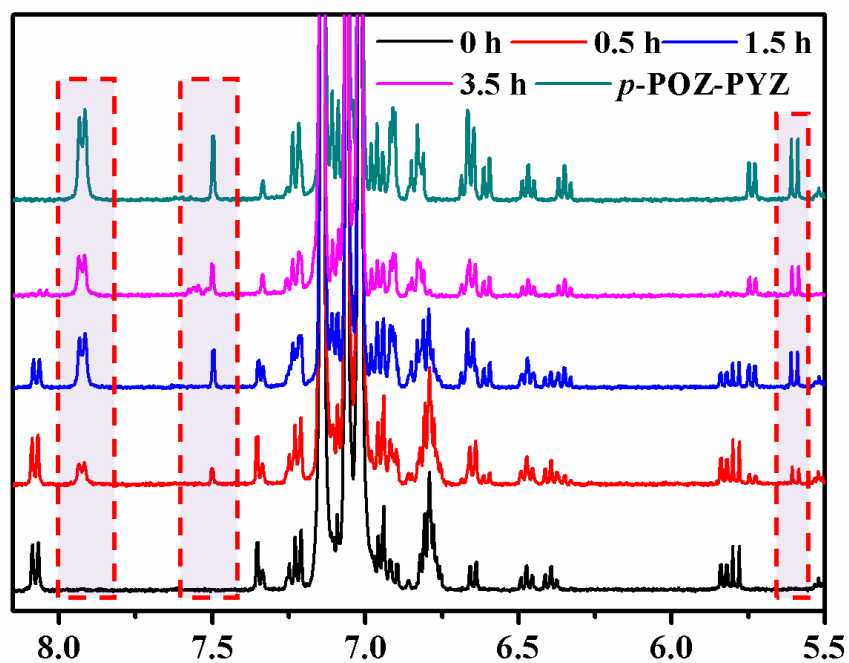


Figure S3. The in situ ^1H NMR spectra of *p*-POZ-PIM in toluene solvents under UV irradiation for a different time with that of *p*-POZ-PYZ used as reference.

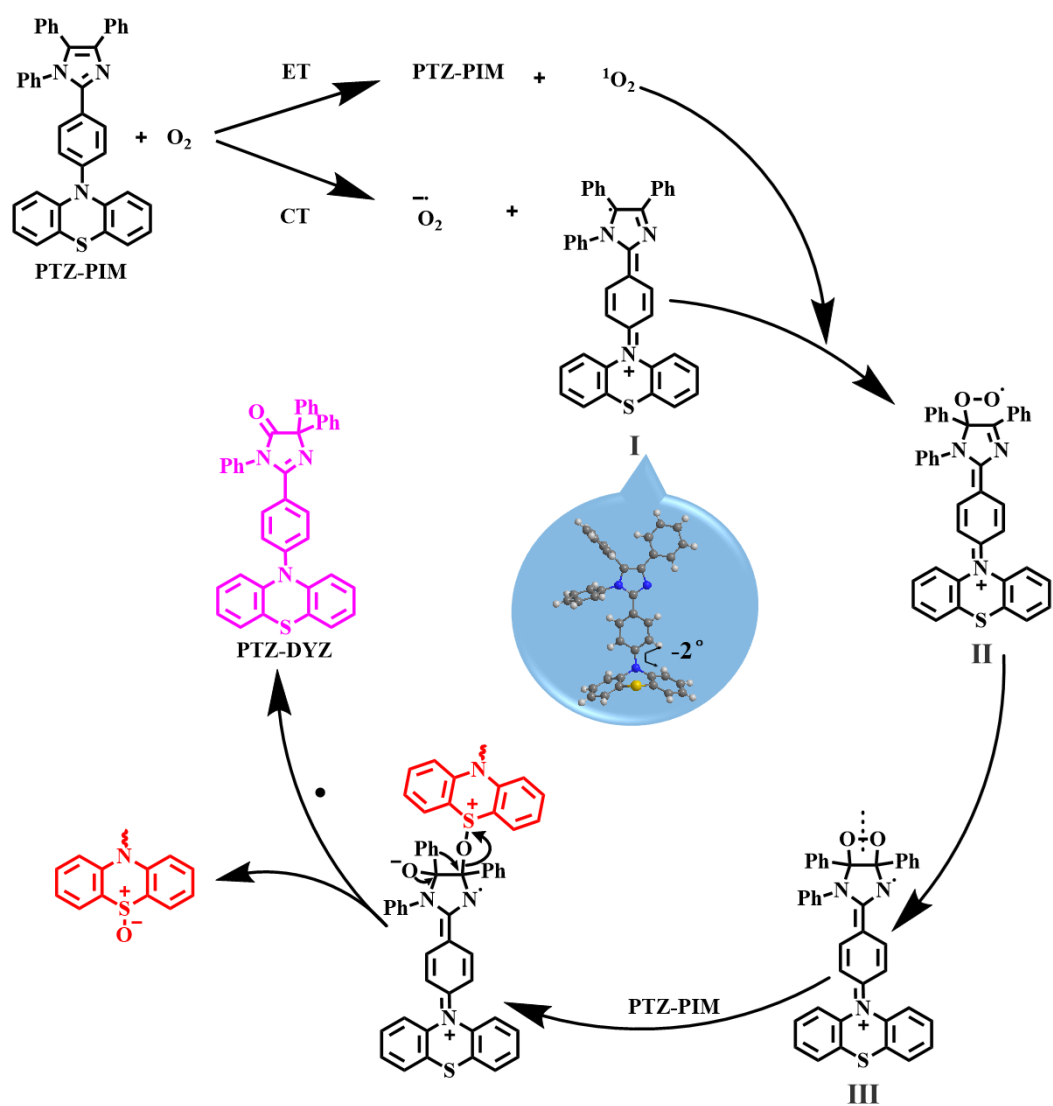


Figure S4. Proposed mechanism for the N linking PTZ-PIM photo-oxidation reaction.

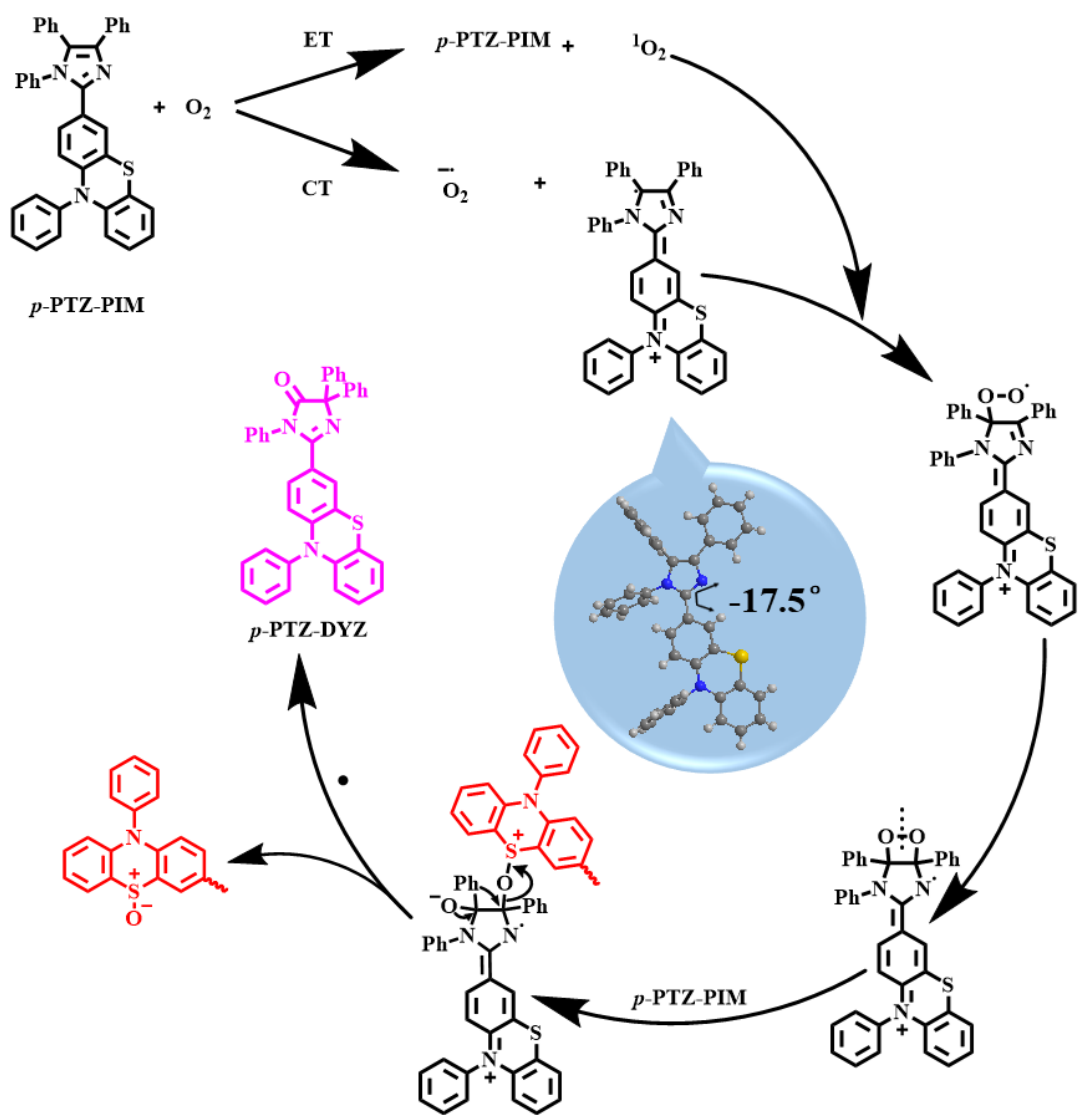


Figure S5. Proposed mechanism for the *p*-C linking type *p*-PTZ-PIM photo-oxidation reaction.

4. PL spectra and Lifetime measurement of PTZ-DYZ

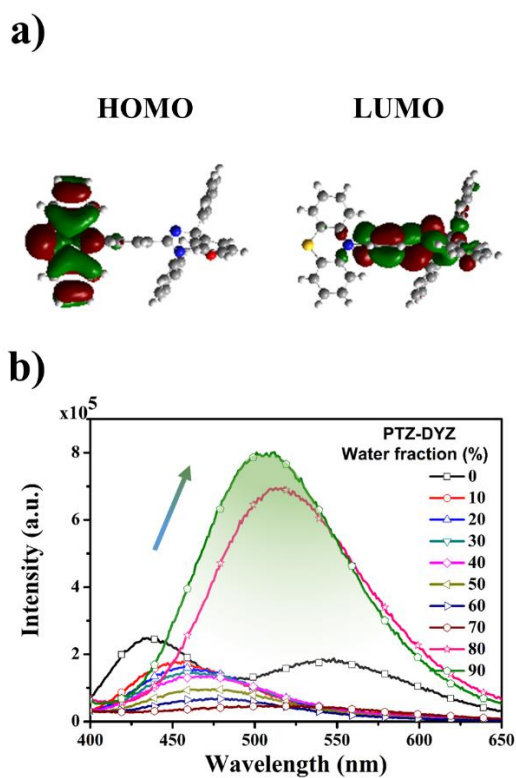


Figure S6. a) The calculated spatial distributions of HOMO and LUMO of PTZ-DYZ based on crystal structure. b) Fluorescence spectra of PTZ-DYZ in the THF/water mixtures with different fractions of water (10^{-5} M).

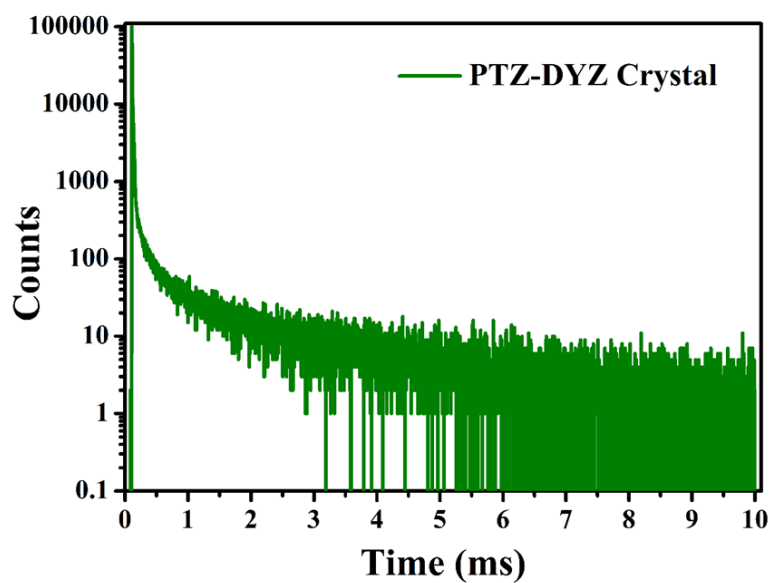


Figure S7. The time-resolved PL decay curves for the PTZ-DYZ crystal.

5. Applications

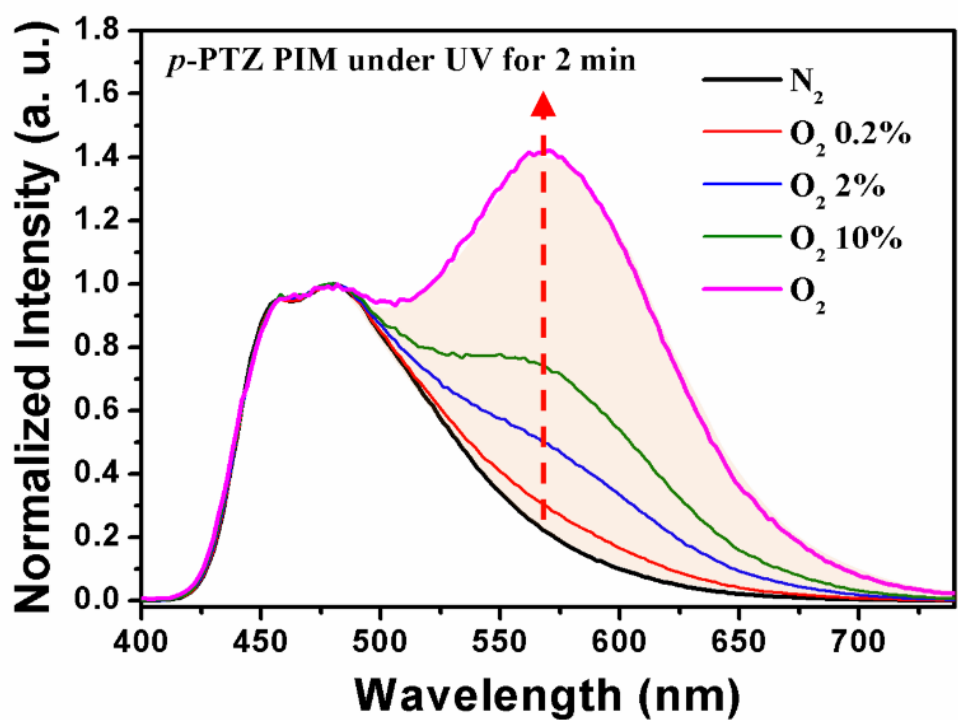
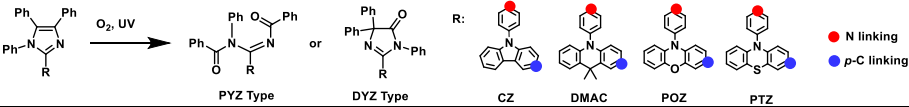


Figure S8. Normalized PL spectra of the *p*-PTZ-PIM film in the gas mixture of N₂ and O₂ (different volume ratios).

Table S1. Results of photo-oxidation reactions of imidazole derivatives

Compound	Linking type	Whether react	Product type
PTZ-PIM ^a	N linking	Yes	DYZ
<i>p</i> -PTZ -PIM ^a	<i>p</i> -C linking	Yes	DYZ and PYZ
POZ-PIM ^{ab}	N linking	Not observed	Not observed
<i>p</i> -POZ-PIM ^{ab}	<i>p</i> -C linking	Yes	PYZ
CZ-PIM ^b	N linking	Not observed	Not observed
<i>p</i> -CZ -PIM ^b	<i>p</i> -C linking	Yes	PYZ
DMAC-PIM ^b	N linking	Not observed	Not observed
<i>p</i> -DMAC-PIM ^b	<i>p</i> -C linking	Yes	PYZ

^a This work, ^b the previous work [1].

6. References

1. Y. Yu, B. Wang, J. Chen, Y. Dong, W. Zhan, S. Zhang, W. Li, B. Yang, C. Zhang and Y. Ma, *J. Mater. Chem. A*, 2023, **11**, 5067-5075.