Rapid Photo-Oxidation Reaction of Imidazole Derivatives Accelerated by Planar Quinoid Oxidation State

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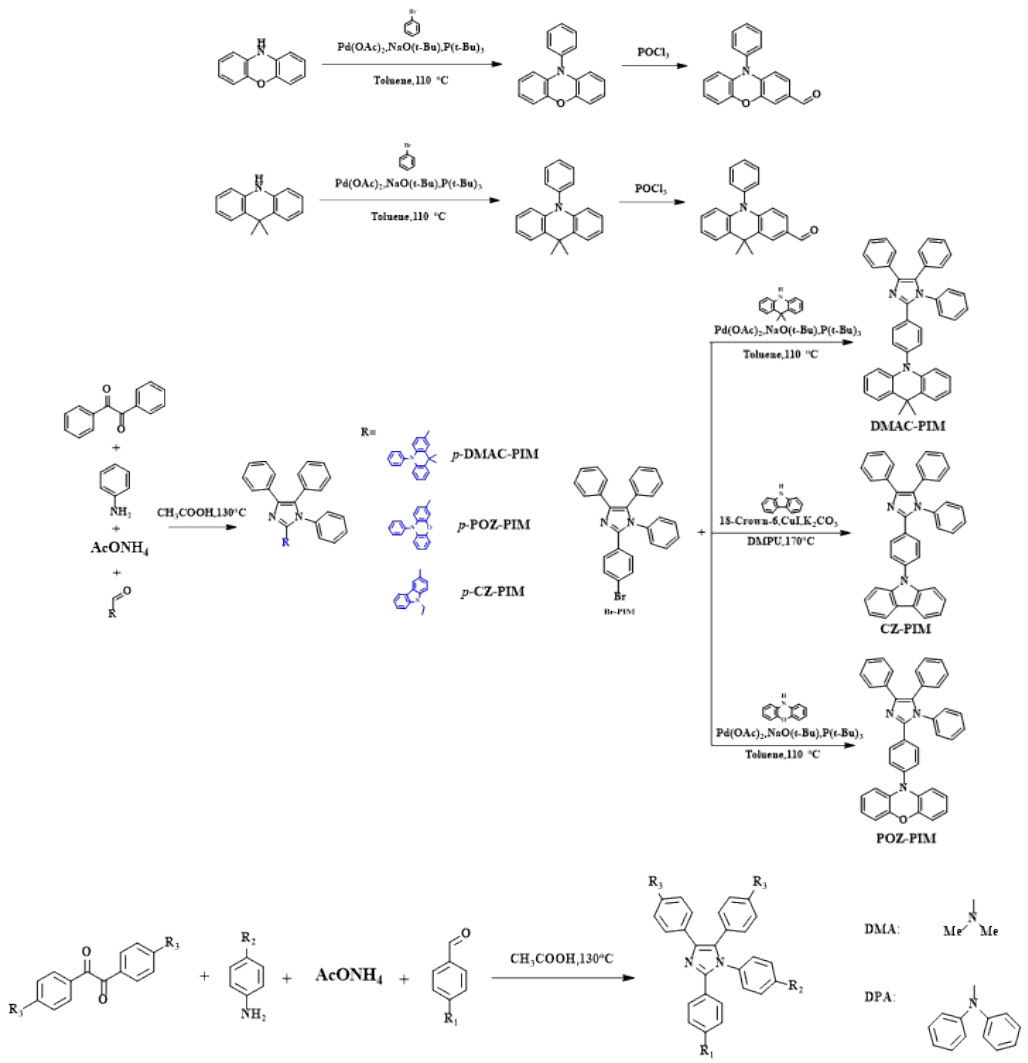
1. Materials and character

All of the reagents and solvents used for the syntheses were purchased from Energy used without further purification. All of the reactions were performed under a dry-nitrogen atmosphere. The ^{1}H 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 electrochemical measurements were performed on CHI 760D electrochemical workstation. The spin trapping-ESR tests were carried out with Bruker A300-10/12 electron paramagnetic resonance. 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

The benzene-substituted lophine derivatives were mainly synthesized by the cyclization reaction between aryl aldehyde and arylamine derivatives as well as benzil. Some other ones such as carbazole, 9,9-dimethyl-9,10- dihydroacridine and phenoxazine-based lophine derivatives were synthesized by the coupling reaction. The detail of the synthesis route was listed in the following Scheme S1.



Compound	R1	R2	R3	Compound	R1	R2	R3
1(PIM)	H	H	H	15	Br	DMA	Br
2	H	CN	H	16	Br	H	OCH3
3	H	DMA	H	17	Br	Br	OCH3
4	H	H	Br	18	Br	DMA	OCH3
5	H	Br	Br	19(DPA-PIM)	DPA	H	H
6	H	DMA	Br	20	DPA	Br	H
7	H	H	OCH3	21	DPA	DMA	H
8	H	Br	OCH3	22	DPA	H	Br
9	H	DMA	OCH3	23	DPA	Br	Br
10	Br	H	H	24	DPA	DMA	Br
11	Br	Br	H	25	DPA	H	OCH3
12	Br	DMA	H	26	DPA	Br	OCH3
13	Br	H	Br	27	DPA	DMA	OCH3
14	Br	Br	Br				

Scheme S1. The detailed synthesis route of all the benzene substituted lophine derivatives molecules

Synthesis of 1,2,4,5-tetraphenyl-1H-imidazole (Compoud 1, PIM):

A mixture of aniline (931 mg, 10.0 mmol), benzil (420 mg, 2.0 mmol), benzaldehyde (212 mg, 2.0 mmol), ammonium acetate (617 mg, 8.0 mmol), and acetic acid (15 mL) was stirred at 120 °C for 14h 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 (670 mg, 90%). ^{1}H NMR (500 MHz, DMSO) δ 7.52 – 7.47 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.23 (m, 15H), 7.18 (t, *J* = 7.3 Hz, 1H). MS (ESI): MW 372.4, *m/z* 373.2 (M+).

Synthesis of 4-(2,4,5-triphenyl-1H-imidazol-1-yl) benzonitrile (Compound 2):

The synthesis process of compound 2 was the same as PIM only by using 4-aminobenzonitrile (1.08 g, 10.0 mmol) to replace aniline. Compound 2 was obtained as a white solid (635 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.52 – 7.45 (m, 4H), 7.38 – 7.30 (m, 8H), 7.29 – 7.23 (m, 4H), 7.19 (t, *J* = 7.3 Hz, 1H). MS (ESI): MW 397.48, m/z 398.2 (M+).

Synthesis of N,N-dimethyl-4-(2,4,5-triphenyl-1H-imidazol-1-yl) aniline (Compound 3):

The synthesis process of compound 3 was the same as PIM only by using N, N-dimethylbenzene-1,4-diamine (1.36 g, 10.0 mmol) to replace aniline. Compound 3 was obtained as a white solid (747 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.33 – 7.26 (m, 6H), 7.26 – 7.20 (m, 4H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.56 (d, *J* = 9.0 Hz, 2H), 2.86 (s, 6H). MS (ESI): MW 415.54, *m/z* 416.2 (M+).

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

The synthesis process of compound 4 was the same as PIM only by using 1,2-bis(4-bromophenyl) ethane-1,2-dione (730mg, 2.0 mmol) to replace benzil. Compound 4 was obtained as a white solid (901mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.40 (dd, *J* = 7.4, 4.7 Hz, 4H), 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H), 7.06 – 7.02 (m, 2H), 7.00 – 6.96 (m, 2H). MS (ESI): MW 530.26, m/z 531.0 (M+).

Synthesis of 1,4,5-tris(4-bromophenyl)-2-phenyl-1H-imidazole (Compound 5):

The synthesis process of compound 5 was the same as 4 only by using 4-bromoaniline (1.70 g, 10.0 mmol) to replace aniline. Compound 5 was obtained as a white solid (852 mg, 70%). ^{1}H NMR (500 MHz, DMSO) δ 7.59 – 7.54 (m, 4H), 7.53 – 7.48 (m, 2H), 7.44 – 7.40 (m, 2H), 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 3H), 7.28 – 7.23 (m, 2H), 7.23 – 7.19 (m, 2H). MS (ESI): MW 609.16, *m/z* 610.9 (M+).

Synthesis of 4-(4,5-bis(4-bromophenyl)-2-phenyl-1H-imidazol-1-yl)-N,N-dimethylaniline (Compound 6):

The synthesis process of compound 6 was the same as 4 only by using N1, N1-dimethylbenzene-1,4-diamine (1.36 g, 10.0 mmol) to replace aniline. Compound 6 was obtained as a white solid (916 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.33 – 7.26 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 2.88 (s, 6H). MS (ESI): MW 573.33, *m/z* 574.0 (M+).

Synthesis of 4,5-bis(4-methoxyphenyl)-1,2-diphenyl-1H-imidazole (Compound 7):

The synthesis process of compound 7 was the same as PIM only by using 1,2-bis(4-methoxyphenyl)ethane-1,2-dione (540mg, 2.0 mmol) to replace benzil. Compound 7 was obtained as a white solid (697mg, 80%). ^{1}H NMR (500 MHz, CDCl3) δ 7.52 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.33 – 7.26 (m, 3H), 7.20 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 9.0 Hz, 2H), 2.88 (s, 6H). MS (ESI): MW 432.2, *m/z* 433.2 (M+).

Synthesis of 1-(4-bromophenyl)-4,5-bis(4-methoxyphenyl)-2-phenyl-1H-imidazole (Compound 8):

The synthesis process of compound 8 was the same as 7 only by using 4-bromoaniline (1.72g, 10.0 mmol) to replace aniline. Compound 8 was obtained as a white solid (919mg, 90%). ^{1}H NMR (500 MHz, DMSO) δ 7.57 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 7.35 – 7.30 (m, 3H), 7.24 – 7.19 (m, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H). MS (ESI): MW 511.42, *m/z* 513.1 (M+).

Synthesis of 4-(4,5-bis(4-methoxyphenyl)-2-phenyl-1H-imidazol-1-yl)-N,N-dimethylaniline (Compound 9):

The synthesis process of compound 9 was the same as 7 only by using N, N-dimethylbenzene-1,4-diamine (1.36 g, 10.0 mmol) to replace aniline. Compound 9 was obtained as a white solid (808.5mg, 90%). ^{1}H NMR (500 MHz, DMSO) δ 7.44 – 7.37 (m, 4H), 7.32 – 7.24 (m, 3H), 7.18 – 7.13 (m, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 3.73 (d, *J* = 8.4 Hz, 6H), 2.88 (s, 6H). MS (ESI): MW 475.59, *m/z* 476.2 (M+).

Synthesis of 2-(4-bromophenyl)-1,4,5-triphenyl-1H-imidazole (Compound 10):

The synthesis process of compound 10 was the same as PIM only by using 4-bromobenzaldehyde (370 mg, 2 mmol) to replace benzaldehyde. Compound 10 was obtained as a white solid (635 mg, 80%). ^{1}H NMR (500 MHz, DMSO) 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 1,2-bis(4-bromophenyl)-4,5-diphenyl-1H-imidazole (Compound 11):

The synthesis process of compound 11 was the same as 10 only by using 4-bromoaniline (1.72 g, 10 mmol) to replace aniline. Compound 11 was obtained as a white solid (635 mg, 80%).^{1}H NMR (500 MHz, DMSO) δ 10.06 (s, 2H), 7.56 (d, *J* = 8.8 Hz, 6H), 7.48 (t, *J* = 8.7 Hz, 6H), 7.34 (dd, *J* = 10.4, 5.9 Hz, 2H), 7.26 (dd, *J* = 7.5, 6.2 Hz, 2H). MS (ESI): MW 530.26, m/z 531.0 (M+).

Synthesis of 4-(2-(4-bromophenyl)-4,5-diphenyl-1H-imidazol-1-yl)-N,N-dimethylaniline (Compound 12):

The synthesis process of compound 12 was the same as 10 only by using N, N-dimethylbenzene-1,4-diamine (1.36 g, 10 mmol) to replace aniline. Compound 12 was obtained as a white solid (741 mg, 75%). ^{1}H NMR (500 MHz, DMSO) 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), 2.87 (s, 6H). MS (ESI): MW 494.44, *m/z* 496.1 (M+).

Synthesis of 2,4,5-tris(4-bromophenyl)-1-phenyl-1H-imidazole (Compound 13):

The synthesis process of compound 13 was the same as 10 only by using 1,2-bis(4-bromophenyl)ethane-1,2-dione (730 mg, 2.0 mmol) to replace benzil. Compound 13 was obtained as a white solid (1.09 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 6H), 7.44 – 7.39 (m, 2H), 7.40 – 7.34 (m, 3H), 7.32 – 7.26 (m, 4H), 7.18 (d, *J* = 8.4 Hz, 2H). MS (ESI): MW 609.16, *m/z* 610.9 (M+).

Synthesis of 1,2,4,5-tetrakis(4-bromophenyl)-1H-imidazole (Compound 14):

The synthesis process of compound 14 was the same as 13 only by using 4-bromoaniline (1.72 g, 10 mmol) to replace aniline. Compound 14 was obtained as a white solid (1.10 g, 80%). ^{1}H NMR (500 MHz, DMSO) δ 7.61 – 7.52 (m, 6H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). MS (ESI): MW 688.06, *m/z* 688.8 (M+).

Synthesis of N,N-dimethyl-4-(2,4,5-tris(4-bromophenyl)-1H-imidazol-1-yl)aniline (Compound 15):

The synthesis process of compound 15 was the same as 13 only by using N, N-dimethylbenzene-1,4-diamine (1.36 g, 10 mmol) to replace aniline. Compound 15 was obtained as a white solid (1.10 g, 80%). ^{1}H NMR (500 MHz, DMSO) δ 7.53 (dd, *J* = 8.4, 6.4 Hz, 4H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 9.1 Hz, 2H), 2.90 (s, 6H). MS (ESI): MW 652.23, *m/z* 653.9 (M+).

Synthesis of 2-(4-bromophenyl)-4,5-bis(4-methoxyphenyl)-1-phenyl-1H-imidazole (Compound 16):

The synthesis process of compound 16 was the same as 7 only by using 4-bromobenzaldehyde (370 mg, 2mmol) to replace benzaldehyde. Compound 16 was obtained as a white solid (818 mg, 80%). ^{1}H NMR (500 MHz, DMSO) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.31 – 7.23 (m, 4H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.85 (dd, *J* = 8.8, 6.8 Hz, 4H), 3.72 (s, 6H). MS (ESI): MW 511.42, *m/z* 513.1 (M+).

Synthesis of 1,2-bis(4-bromophenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazole (Compound 17):

The synthesis process of compound 17 was the same as 16 only by using 4-bromoaniline (1.72 g, 10 mmol) to replace aniline. Compound 17 was obtained as a white solid (885 mg, 75%). ^{1}H NMR (500 MHz, DMSO) δ 7.55 (dd, *J* = 11.5, 5.0 Hz, 4H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 7.18 – 7.12 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.86 – 6.81 (m, 2H), 3.73 (d, *J* = 10.7 Hz, 6H). MS (ESI): MW 590.32, *m/z* 591.0 (M+).

Synthesis of 4-(2-(4-bromophenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazol-1-yl)-N,N-dimethylaniline (Compound 18):

The synthesis process of compound 18 was the same as 16 only by using N, N-dimethylbenzene-1,4-diamine (1.36 g, 10 mmol) to replace aniline. Compound 18 was obtained as a white solid (1.05 g, 95%). ^{1}H NMR (500 MHz, DMSO) δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.83 (d,

J = 8.9 Hz, 2H), 6.60 (d, *J* = 9.1 Hz, 2H), 3.73 (d, *J* = 8.7 Hz, 6H), 2.89 (s, 6H). MS (ESI): MW 554.49, *m/z* 556.1 (M+).

Synthesis of N, N-diphenyl-4-(1,4,5-triphenyl-1H-imidazol-2-yl)aniline (Compound 19, DPA-PIM):

The synthesis process of Compound 19 was the same as 1 only by using 4-(N, N-Diphenylamino) benzaldehyde (546mg, 2.0 mmol) to replace benzaldehyde. Compound 19 was obtained as a white solid (916 mg, 85%). ^{1}H NMR (500 MHz, Tol) δ 8.07 – 8.02 (m, 2H), 7.57 – 7.51 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.99 (dd, *J* = 4.2, 2.9 Hz, 8H), 6.92 (ddd, *J* = 6.2, 5.8, 2.2 Hz, 5H), 6.90 – 6.82 (m, 1H), 6.83 – 6.72 (m, 7H). MS (ESI): MW 539.68, *m/z* 540.2 (M+).

Synthesis of 4-(1-(4-bromophenyl)-4,5-diphenyl-1H-imidazol-2-yl)-N,N-diphenylaniline (Compound 20):

The synthesis process of compound 20 was the same as 19 only by using 4-bromoaniline (1.72 g, 10 mmol) to replace aniline. Compound 20 was obtained as a white solid (741 mg, 60%). 1H NMR (500 MHz, DMSO) δ 7.54 (d, J = 8.6 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.33 (dd, J = 10.2, 5.5 Hz, 8H), 7.24 (dt, J = 5.1, 3.1 Hz, 6H), 7.09 (dt, J = 13.2, 6.6 Hz, 4H), 7.04 (dd, J = 8.1, 4.3 Hz, 4H), 6.84 (d, J = 8.8 Hz, 2H). MS (ESI): MW 618.58, *m/z* 620.2 (M+).

Synthesis of 4-(1-(4-(dimethylamino)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)-N,N-diphenylaniline (Compound 21):

The synthesis process of compound 21 was the same as 19 only by using N, N-dimethylbenzene-1,4-diamine (1.36g, 10 mmol) to replace aniline. Compound 21 was obtained as a white solid (874 mg, 75%). ^{1}H NMR (500 MHz, DMSO) δ 7.48 – 7.44 (m, 2H), 7.36 – 7.32 (m, 6H), 7.32 – 7.28 (m, 4H), 7.26 – 7.22 (m, 3H), 7.08 (dd, *J* = 12.8, 5.4 Hz, 4H), 7.04 (dd, *J* = 6.5, 5.4 Hz, 5H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 2.87 (s, 6H). MS (ESI): MW 582.75, *m/z* 583.3 (M+).

Synthesis of 4-(4,5-bis(4-bromophenyl)-1-phenyl-1H-imidazol-2-yl)-N,N-diphenylamine (Compound 22):

The synthesis process of compound 22 was the same as 19 only by using 1,2-bis(4-bromophenyl)ethane-1,2-dione (730 mg, 2.0 mmol) to replace benzil. Compound 22 was obtained as a white solid (976 mg, 70%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 4H), 7.43 – 7.39 (m, 2H), 7.39 – 7.35 (m, 3H), 7.33 (d, *J* = 8.3 Hz, 3H), 7.31 – 7.27 (m, 3H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 4H), 6.78 (d, *J* = 8.8 Hz, 2H). MS (ESI): MW 697.47, *m/z* 698.1 (M+).

Synthesis of N, N-diphenyl-4-(1,4,5-tris(4-bromophenyl)-1H-imidazol-2-yl)aniline (Compound 23):

The synthesis process of compound 23 was the same as 22 only by using 4-bromoaniline (1.72 g, 10 mmol) to replace aniline. Compound 23 was obtained as a white solid (931 mg, 60%).^{1}H NMR (500 MHz, DMSO) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.42 – 7.38 (m, 2H), 7.34 (dd, *J* = 8.3, 7.5 Hz, 4H), 7.26 (dd, *J* = 8.8, 2.1 Hz, 4H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.06 – 7.01 (m, 4H), 6.83 (d, *J* = 8.9 Hz, 2H). MS (ESI): MW 776.37, *m/z* 778.0 (M+)

Synthesis of 4-(4,5-bis(4-bromophenyl)-1-(4-(dimethylamino)phenyl)-1H-imidazol-2-yl)-N,N-diphenylaniline (Compound 24):

The synthesis process of compound 24 was the same as 22 only by using N,N-dimethylbenzene-1,4-diamine (1.36 g, 10 mmol) to replace aniline. Compound 24 was obtained as a white solid (889 mg, 60%).^{1}H NMR (500 MHz, DMSO) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.29 (m, 6H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.08 (dd, *J* = 14.8, 8.2 Hz, 4H), 7.03 (d, *J* = 7.5 Hz, 4H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 2.89 (s, 6H). MS (ESI): MW 740.54, m/z 741.1 (M+).

Synthesis of 4-(4,5-bis(4-methoxyphenyl)-1-phenyl-1H-imidazol-2-yl)-N,N-diphenylaniline (Compound 25):

The synthesis process of compound 25 was the same as 19 only by using 1,2-bis(4-methoxyphenyl)ethane-1,2-dione (540mg, 2.0 mmol) to replace benzil. Compound 25 was obtained as a white solid (720 mg, 60%). ^{1}H NMR (500 MHz, DMSO) δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.39 (dd, *J* = 16.9, 9.1 Hz, 6H), 7.26 (d, *J* = 3.2 Hz, 3H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 4H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H). MS (ESI): MW 599.73, *m/z* 600.3 (M+).

Synthesis of 4-(1-(4-bromophenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazol-2-yl)-N,N-diphenylaniline (Compound 26):

The synthesis process of compound 26 was the same as 25 only by using 4-bromoaniline (1.72 g, 10 mmol) to replace aniline. Compound 26 was obtained as a white solid (745 mg, 55%).^{1}H NMR (500 MHz, DMSO) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 4H), 7.24 (dd, *J* = 15.8, 8.7 Hz, 4H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 4H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 4H), 3.74 (s, 3H), 3.72 (s, 3H). MS (ESI): MW 678.63, *m/z* 680.2 (M+).

Synthesis of 4-(1-(4-(dimethylamino)phenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazol-2-yl)-N,N-diphenylaniline (Compound 27):

The synthesis process of compound 27 was the same as 25 only by using N, N-dimethylbenzene-1,4-diamine (1.36 g, 10 mmol) to replace aniline. Compound 27 was obtained as a white solid (771 mg, 60%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.26 (m, 6H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 6H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 9.1 Hz, 4H), 6.59 (d, *J* = 9.0 Hz, 2H), 3.72 (d, *J* = 8.2 Hz, 6H), 2.87 (s, 6H). MS (ESI): MW 642.80, m/z 643.3 (M+).

Synthesis of N, N-diphenyl-4-(1, 4, 5-triphenyl-1H-imidazol-2-yl) aniline (DMA-PIM):

The synthesis process of DMA-PIM was the same as PIM only by using 4-Dimethylaminobenzaldehyde (298 mg, 2.0 mmol) to replace benzaldehyde. DMA-PIM was obtained as a white solid (732 mg, 88%). ^{1}H NMR (500 MHz, DMSO) δ 7.51 – 7.45 (m, 2H), 7.33 (dd, *J* = 6.6, 3.9 Hz, 3H), 7.31 – 7.26 (m, 3H), 7.27 – 7.21 (m, 6H), 7.20 – 7.14 (m, 3H), 6.58 (d, *J* = 9.0 Hz, 2H), 2.88 (s, 6H). MS (ESI): MW 415.5, *m/z* 414.5 (M+)

Synthesis of 9-ethyl-3-(1,4,5-triphenyl-1H-imidazol-2-yl)-9H-carbazole (*p*-CZ-PIM):

The synthesis process of *p*-CZ-PIM was the same as PIM only by using 9-ethyl-9H-carbazole-3-carbaldehyde (446 mg, 2.0 mmol) to replace benzaldehyde, *p*-CZ-BM was obtained as a white solid (500 mg, 51%). ^{1}H NMR (500 MHz, DMSO) δ 8.13 (d, *J* = 1.1 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.44 (m, 5H), 7.33 (qd, *J* = 6.4, 3.7 Hz, 8H), 7.30 – 7.25 (m, 4H), 7.19 (t, *J* = 7.6 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). MS (ESI): MW 489.6, *m/z* 490.3 (M+).

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

The synthesis process of *p*-POZ-PIM was the same as PIM only by using 10-phenyl-10H-phenoxazine-3-carbaldehyde (574 mg, 2.0 mmol) to replace benzaldehyde, *p*-POZ-PIM was obtained as a white solid (685 mg, 62%). ^{1}H 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 9,9-dimethyl-10-phenyl-2-(1,4,5-triphenyl-1H-imidazol-2-yl)-9,10-dihydroacridine (*p*-DMAC-PIM):

The synthesis process of *p*-DMAC-PIM was the same as PIM only by using 9,9-dimethyl-10-phenyl-9,10-dihydroacridine-2-carbaldehyde (616 mg, 2.0 mmol) to replace benzaldehyde, *p*-DMAC-PIM was obtained as a white solid (522 mg, 45%). ^{1}H NMR (500 MHz, DMSO) δ 7.71 (t, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.27 (m, 12H), 7.27 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 7.00 – 6.92 (m, 1H), 6.89 (t, *J* = 6.9 Hz, 1H), 6.17 – 6.06 (m, 2H). MS (ESI): MW 579.7, *m/z* 580.3 (M+).

Synthesis of 9-(4-(1,4,5-triphenyl-1H-imidazol-2-yl)phenyl)-9H-carbazole (CZ-PIM):

A mixture of carbazole (450 mg, 1.0 mmol), Br-PIM (451 mg, 1.0 mmol), CuI (10.0 mg, 0.05 mmol), 18-crown-6 (13.2 mg, 0.05 mmol), and K_2CO_3 (0.83 g, 6.0 mmol) in 1,3-dimethyltetrahydropyrimidin-2(1H)-one (DMPU) (2.0 mL) was heated at 170 °C for 48 h under nitrogen. After cooling to room temperature, dichloromethane was added and the mixture was extracted with chloroform for 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: 84%). ^{1}H NMR (400 MHz, DMSO) δ 7.79 – 7.62 (m, 3H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.30 (m, 10H), 7.27 (t, *J* = 6.6 Hz, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.74 (dd, *J* = 6.0, 3.4 Hz, 2H), 6.72 – 6.62 (m, 4H), 5.82 (dd, *J* = 5.9, 3.5 Hz, 2H).MS (ESI): MW 537.67, *m/z* 539.6 (M+).

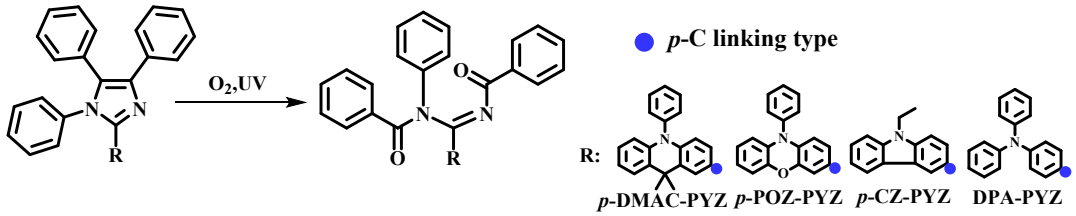
Synthesis of 9,9-dimethyl-10-(4-(1,4,5-triphenyl-1H-imidazol-2-yl)phenyl)-9,10-dihydroacridine (DMAC-PIM):

A mixture of 9,9-dimethyl-9,10-dihydroacridine (418 mg, 2.0 mmol), Br-PIM (902.0 mg, 2.0 mmol), palladium acetate (22.4 mg, 0.1mmol), sodium tert-butoxide (480mg, 5mmol), tri-tert-butylphosphine (101.2 mg, 0.5 mmol) and toluene(15 mL) was stirred at 100^{o}C for 14h 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 (464mg, 40%). ^{1}H NMR (500 MHz, DMSO) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.35 (m, 5H), 7.35 – 7.31 (m,3H), 7.31 – 7.24 (m, 6H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.97 (dd, *J* = 11.2, 4.2 Hz, 2H), 6.90 (t, *J* = 7.0 Hz, 2H), 6.10 (d, *J* = 8.0 Hz, 2H), 1.59 (s, 6H). MS (ESI): MW 579.7, *m/z* 580.4 (M+).

Synthesis of 10-(4-(1,4,5-triphenyl-1H-imidazol-2-yl)phenyl)-10H-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, 0.1mmol), sodium tert-butoxide (480mg, 5mmol), tri-tert-butylphosphine (101.2 mg, 0.5 mmol) and toluene(15 mL) was stirred at 100°C for 14h 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%). ^{1}H 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+).



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

Compound *p*-DMAC-PIM (100 mg, 0.17 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 (60mg, 58%). ^{1}H NMR (500 MHz, DMSO) δ 7.92 (t, *J* = 12.7 Hz, 2H), 7.74 (d, *J* = 7.1 Hz, 2H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.61 – 7.23 (m, 14H), 7.16 (d, *J* = 6.6 Hz, 1H), 6.96 (dd, *J* = 26.3, 7.1 Hz, 4H), 5.86 – 5.74 (m, 2H), 1.59 (s, 6H). MS (ESI): MW 611.75, *m/z* 612.3 (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 (60mg, 57%). ^{1}H 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+).

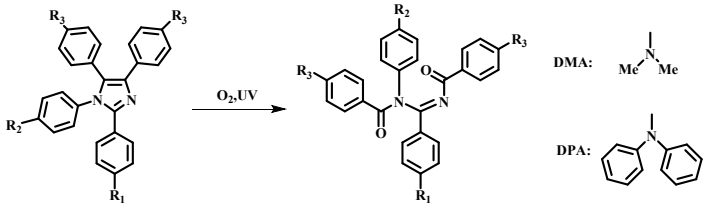
The photo-oxidation reaction product (*p*-CZ-PYZ):

Compound *p*-CZ-PIM (100 mg, 0.2 mmol) is dissolved in toluene and irradiated by a 365 nm UV lamp for about 24h. 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 (40mg, 38%). ^{1}H NMR (500 MHz, DMSO) δ 8.69 (d, *J* = 1.7 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.65 – 7.60 (m, 2H), 7.52 (ddd, *J* = 11.9, 9.2, 4.3 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.37 (dd, *J* = 15.2, 7.7 Hz, 3H), 7.30 – 7.22 (m, 5H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.33 – 1.25 (m, 3H). MS (ESI): MW 521.6, *m/z* 522.2 (M+).

The photo-oxidation reaction product (DPA-PYZ):

Compound DPA-PIM (100 mg, 0.18 mmol) is dissolved in toluene and irradiated by a 365nm UV lamp for about 24h. 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 (70mg, 67%). ^{1}H NMR (500 MHz, DMSO) δ 7.60 (ddd, *J* = 15.4, 12.3, 5.1 Hz, 9H), 7.52 (dd, *J* = 15.3, 7.9 Hz, 2H), 7.44 – 7.28 (m, 14H), 7.28 – 7.15 (m, 9H), 7.09 (dd, *J* = 7.4, 6.3 Hz, 7H), 6.75 (d, *J* = 8.9 Hz, 3H). MS (ESI): MW 571.6, m/z 573.6 (M+).

Table S1. Benzene substituted lophine derivatives studies.



Compound	R1	R2	R3	Reaction condition[a]	Whether react[b]
1(PIM)	H	H	H	O_2, UV (330nm, 365 nm)	Not Observed
2	H	CN	H	O_2, UV (330nm, 365 nm)	Not Observed
3	H	DMA	H	O_2, UV (330nm, 365 nm)	Not Observed
4	H	H	Br	O_2, UV (330nm, 365 nm)	Not Observed
5	H	Br	Br	O_2, UV (330nm, 365 nm)	Not Observed
6	H	DMA	Br	O_2, UV (330nm, 365 nm)	Not Observed
7	H	H	OCH3	O_2, UV (330nm, 365 nm)	Not Observed
8	H	Br	OCH3	O_2, UV (330nm, 365 nm)	Not Observed
9	H	DMA	OCH3	O_2, UV (330nm, 365 nm)	Not Observed
10	Br	H	H	O_2, UV (330nm, 365 nm)	Not Observed
11	Br	Br	H	O_2, UV (330nm, 365 nm)	Not Observed
12	Br	DMA	H	O_2, UV (330nm, 365 nm)	Not Observed
13	Br	H	Br	O_2, UV (330nm, 365 nm)	Not Observed
14	Br	Br	Br	O_2, UV (330nm, 365 nm)	Not Observed
15	Br	DMA	Br	O_2, UV (330nm, 365 nm)	Not Observed
16	Br	H	OCH3	O_2, UV (330nm, 365 nm)	Not Observed
17	Br	Br	OCH3	O_2, UV (330nm, 365 nm)	Not Observed
18	Br	DMA	OCH3	O_2, UV (330nm, 365 nm)	Not Observed
19(DPA-PIM)	DPA	H	H	O_2, UV (365 nm)	Yes
20	DPA	Br	H	O_2, UV (365 nm)	Yes
21	DPA	DMA	H	O_2, UV (365 nm)	Yes

22	DPA	H	Br	O_2, UV (365 nm)	Yes
23	DPA	Br	Br	O_2, UV (365 nm)	Yes
24	DPA	DMA	Br	O_2, UV (365 nm)	Yes
25	DPA	H	OCH3	O_2, UV (365 nm)	Yes
26	DPA	Br	OCH3	O_2, UV (365 nm)	Yes
27	DPA	DMA	OCH3	O_2, UV (365 nm)	Yes

[a] The wavelength of irradiation source is determined by the absorption spectra of analogue compounds. [b] Determined by the changement of absorption spectra for analogue compounds under UV irradiation in air for 60 min.

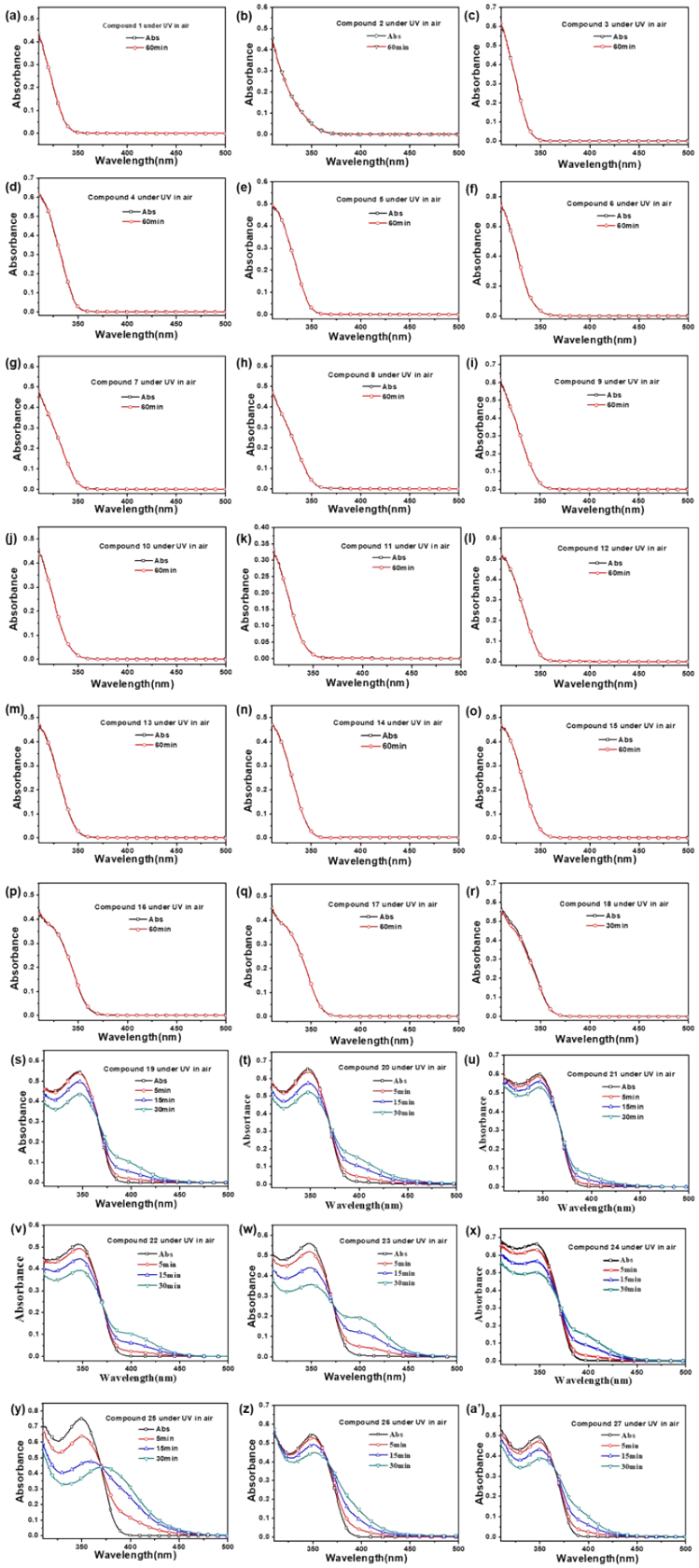


Figure S1. Absorption spectra of (a)-(a') compounds 1-27 toluene solution (10^{-5}M) in the air under UV irradiation for a different time.

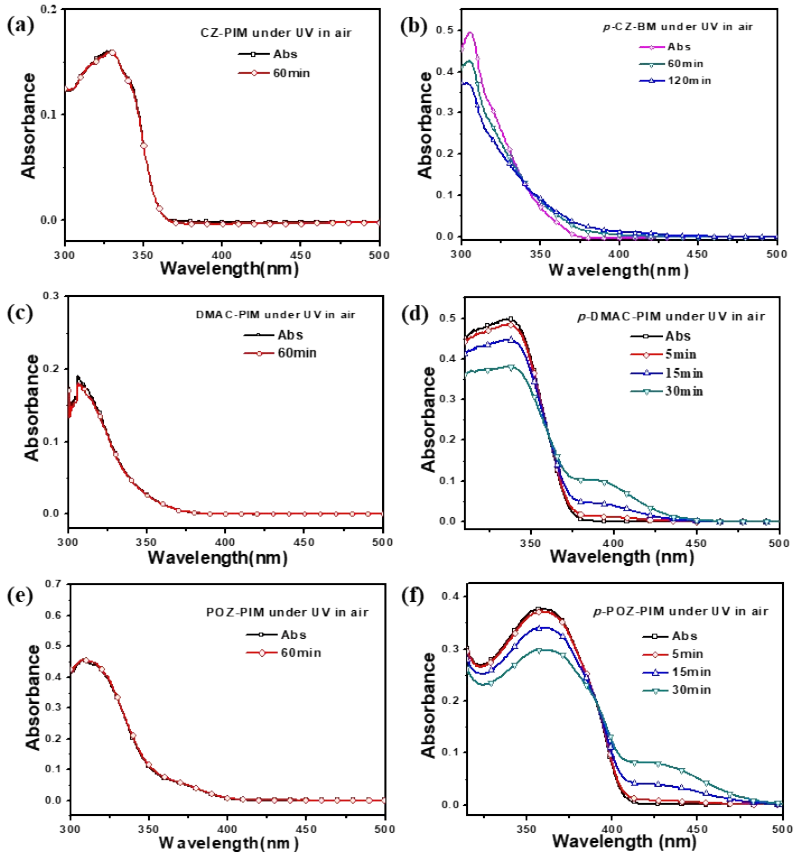


Figure S2. Absorption spectra of (a) CZ-PIM (b) *p*-CZ-PIM (c) DMAC-PIM (d) *p*-DMAC-PIM (e) POZ-PIM and (f) *p*-POZ-PIM toluene solution(10^{-5}M) in the air under UV irradiation for a different time.

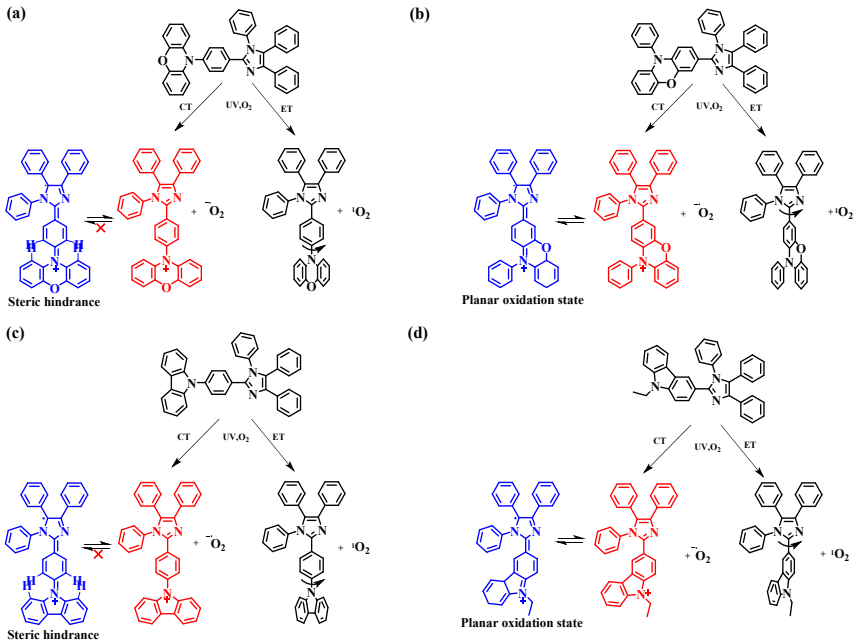


Figure S3. The possible conformation change of a) POZ-PIM b) *p*-POZ-PIM and c) CZ-PIM d) *p*-CZ-PIM under UV irradiation in the air.

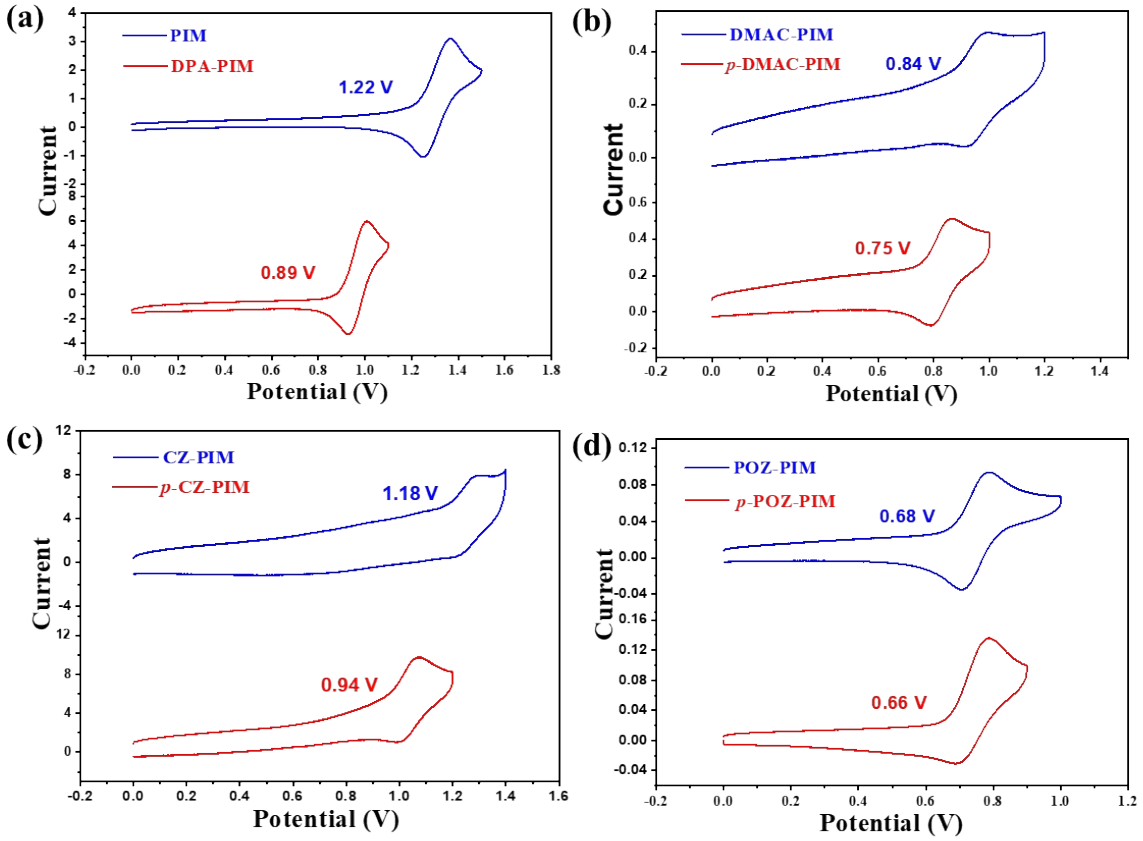


Figure S4. Cyclic voltammograms of a) PIM and DPA-PIM b) DMAC-PIM and *p*-DMAC-PIM c) CZ-PIM and *p*-CZ-PIM d) POZ-PIM and *p*-POZ-PIM.

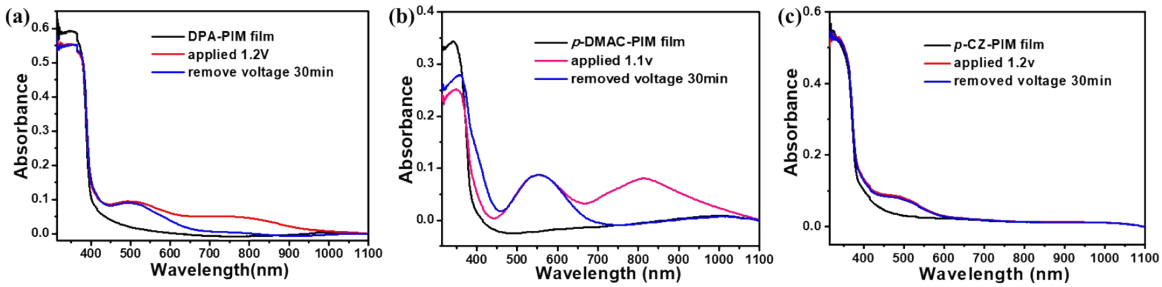


Figure S5. Absorption spectra of a) DPA-PIM and b) *p*-DMAC-PIM c) *p*-CZ-PIM film applied voltage and removed for 30min.

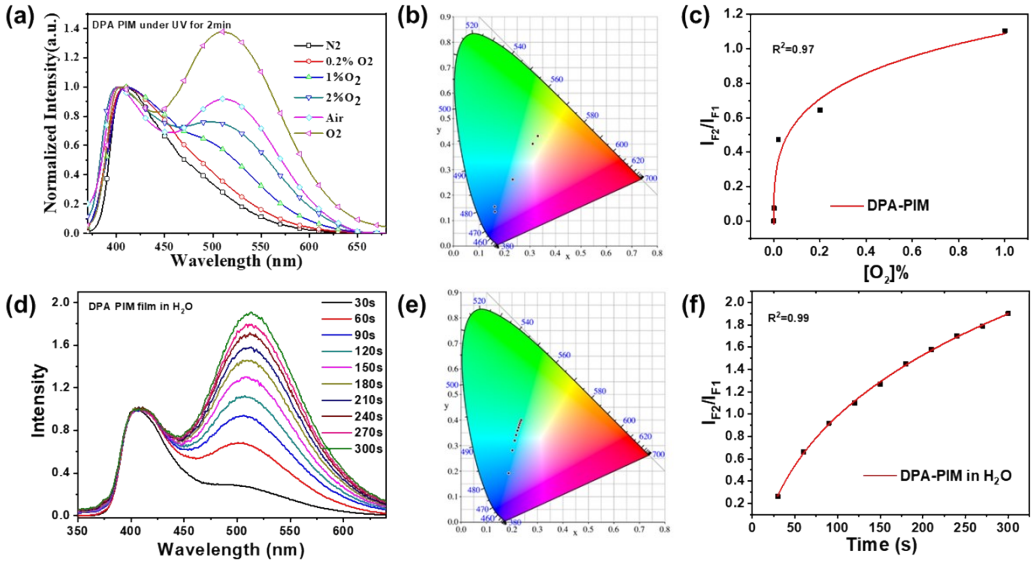


Figure S6. a) The normalized PL spectra, b) CIE colorimetry, c) plot of I_{F2}/I_{F1} against $[O_2]$ of DPA-PIM film in the gas mixture of N_2 and O_2 (different volume ratios). d) The normalized PL spectra, e) CIE colorimetry, and f) plot of I_{F2}/I_{F1} against $[O_2]$ of DPA-PIM film in H_2O after UV irradiation (365nm, 6 W) for a different time.

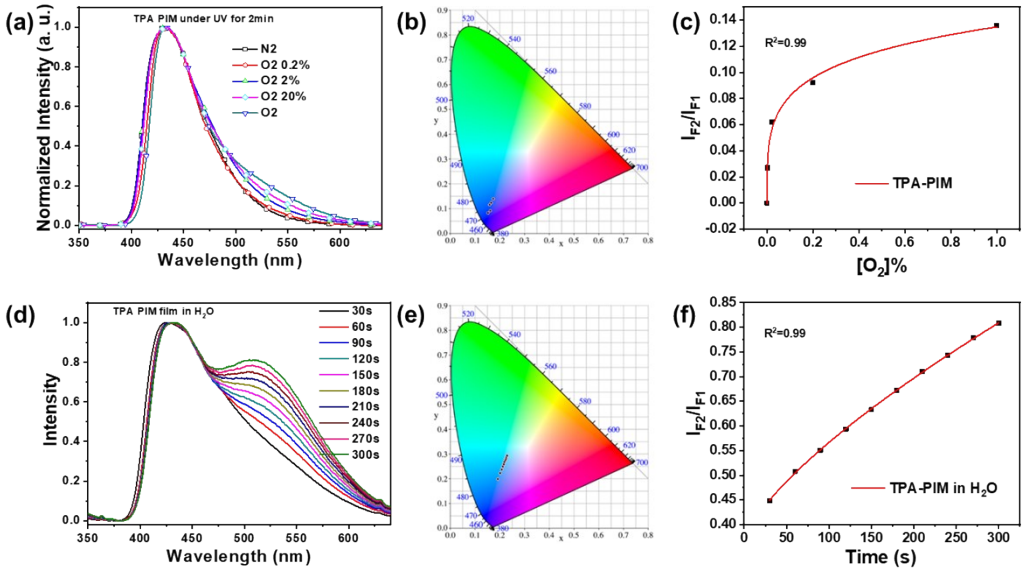


Figure S7. a) The normalized PL spectra, b) CIE colorimetry, c) plot of I_{F2}/I_{F1} against $[O_2]$ of TPA-PIM film in the gas mixture of N_2 and O_2 (different volume ratios). d) The normalized PL spectra, e) CIE colorimetry, and f) plot of I_{F2}/I_{F1} against $[O_2]$ of TPA-PIM film in H_2O after UV irradiation (365nm, 6 W) for a different time.

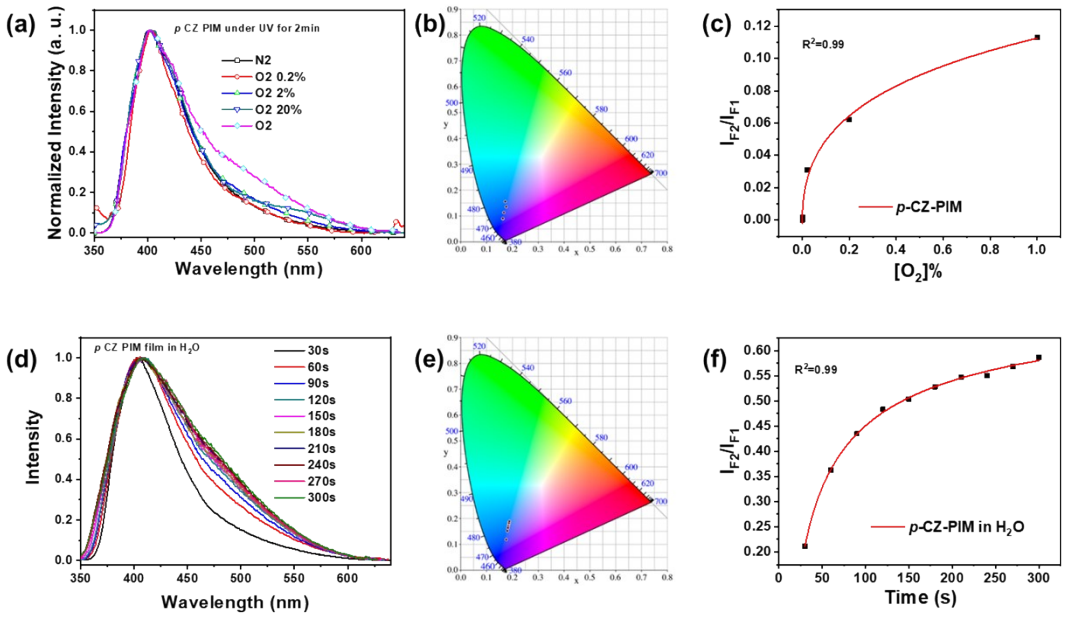


Figure S8. a) The normalized PL spectra, b) CIE colorimetry, c) plot of I_{F2}/I_{F1} against $[O_2]$ of *p*-CZ-PIM film in the gas mixture of N_2 and O_2 (different volume ratios). d) The normalized PL spectra, e) CIE colorimetry, and f) plot of I_{F2}/I_{F1} against $[O_2]$ of *p*-CZ-PIM film in H_2O after UV irradiation (365nm, 6 W) for a different time.

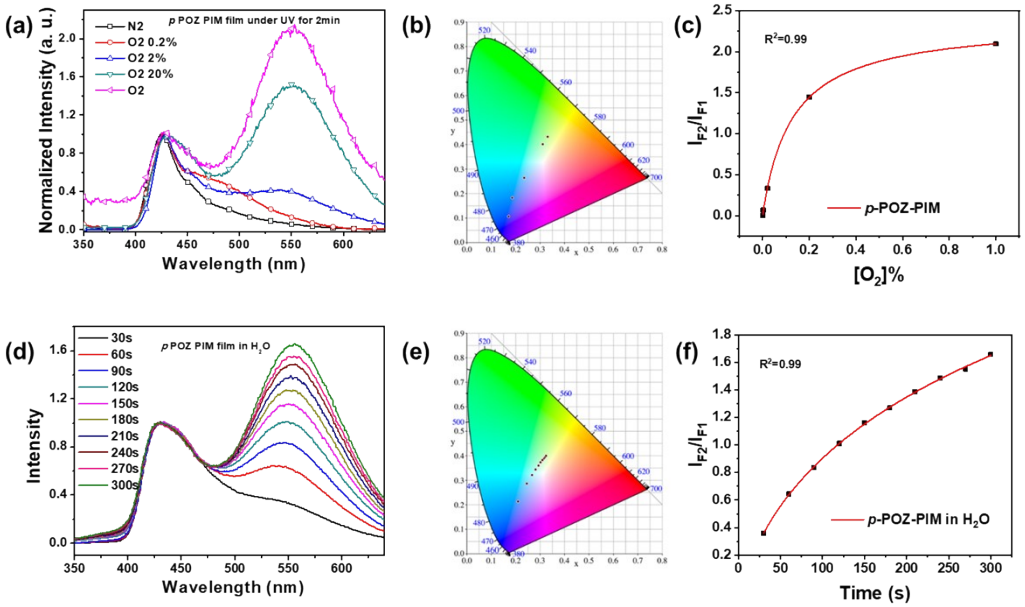


Figure S9. a) The normalized PL spectra, b) CIE colorimetry, c) plot of I_{F2}/I_{F1} against $[O_2]$ of *p*-POZ-PIM film in the gas mixture of N_2 and O_2 (different volume ratios). d) The normalized PL spectra, e) CIE colorimetry, and f) plot of I_{F2}/I_{F1} against $[O_2]$ of *p*-POZ-PIM film in H_2O after UV irradiation (365nm, 6 W) for a different time.