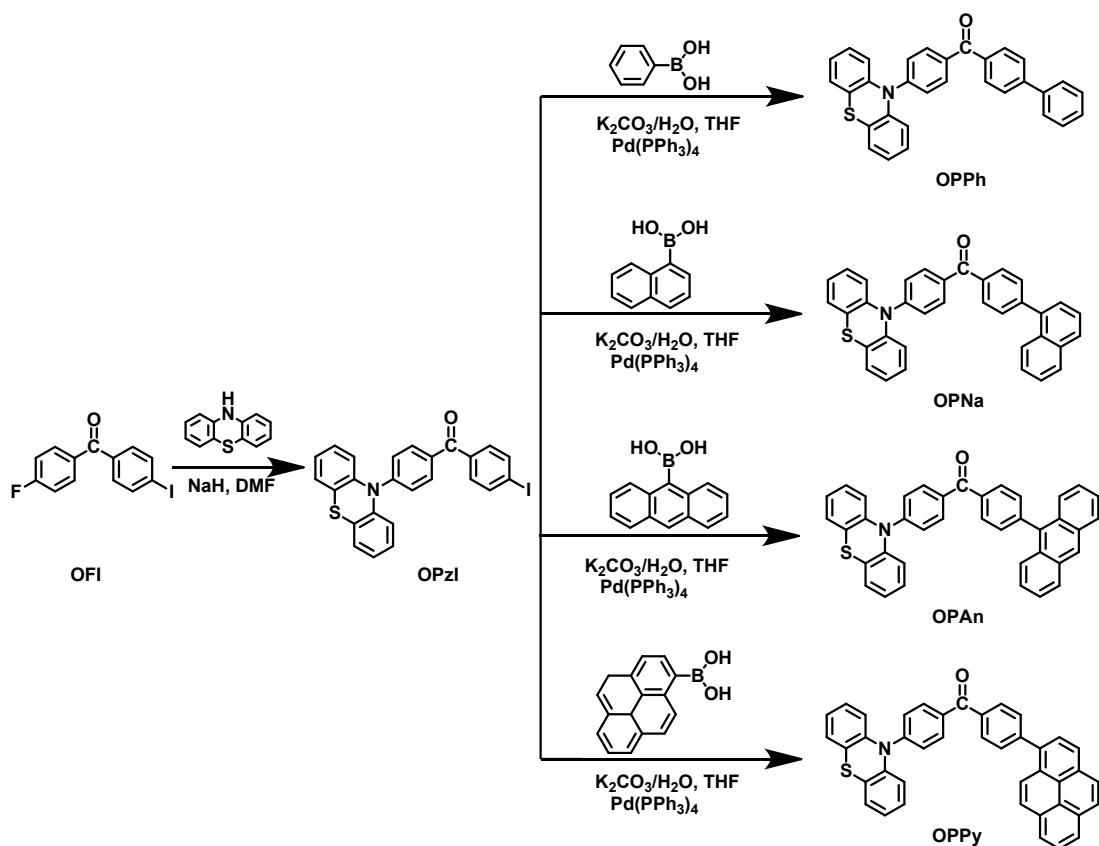


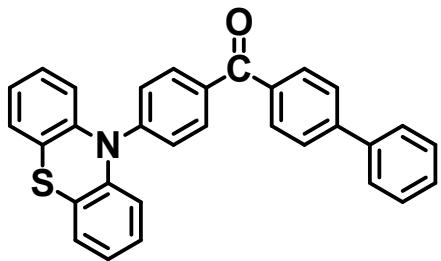
## Supporting Information

### 1 Synthesis and Characterization of Compounds

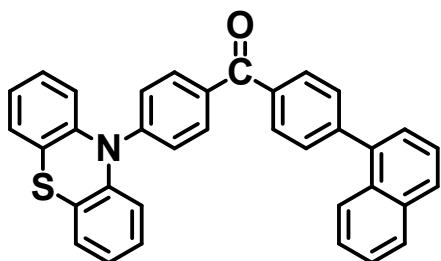
The synthetic routes of compounds OPPh, OPNa, OPAn and OPPy were described in Scheme S1. Compounds OFI, and OPzI were synthesized on the grounds of the previous literature.<sup>[1-5]</sup> <sup>1</sup>H-NMR spectroscopy and high-resolution mass spectroscopy were used to confirmed the chemical structures of all the intermediate compounds in Scheme S1. Final compounds were characterized by elemental analyses, <sup>1</sup>H NMR spectroscopy and high-resolution mass spectrometry.



**Scheme S1** Synthetic routes for the aromatic ring and phenothiazine containing unsymmetrical diphenylketone derivatives.



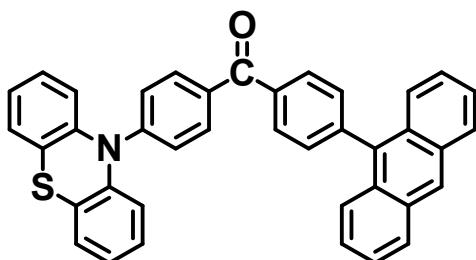
**(4-(10H-phenothiazin-10-yl)phenyl)([1,1'-biphenyl]-4-yl)methanone (OPPh)** To a mixture of OPzI (1.50 g, 2.97 mmol) and Phenylboronic acid (0.54 g, 4.45 mmol) in degassed tetrahydrofuran (THF) (50 mL) solution, 2M. aqueous  $\text{K}_2\text{CO}_3$  solution (4.5 mL) was added under an argon atmosphere. The mixture was stirred for 20 min at room temperature.  $\text{Pd}(\text{PPh}_3)_4$  catalyst was added, and then the resulting mixture was stirred at 75 °C for 16h. After cooling to room temperature, the product was concentrated and then purified by chromatography on silica gel with dichloromethane/*n*-hexane (v/v=1:1) as eluent. Yield: 0.95 g (70.3%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.88 (dd, 4H), 7.70 (d, 2H), 7.65 (d, 2H), 7.48 (t, 2H), 7.40 (t, 1H), 7.31 (dd, 2H), 7.27 (d, 2H), 7.18 (t, 2H), 7.08 (t, 2H), 7.00 (d, 2H). High-resolution MS: m/z found: 455.1336 [M]<sup>+</sup>; calcd for  $\text{C}_{31}\text{H}_{21}\text{NOS}$ : 455.1338. Elemental analyses (%) calcd for  $\text{C}_{31}\text{H}_{21}\text{NOS}$ : C 81.73, H 4.65, N 3.07; found: C 82.21, H 4.87, N 2.89.



**(4-(10H-phenothiazin-10-yl)phenyl)(4-(naphthalen-1-yl)phenyl)methanone (OPNa)** Compound OPNa was achieved according to the aforementioned procedure for OPPh with 1-Naphthylboronic acid (0.77 g, 4.45 mmol) in place of Phenylboronic acid. Yield: 1.03 g (68.6%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.98–7.87 (m, 7H), 7.62 (d, 2H), 7.57–7.50 (m, 2H), 7.46 (t, 2H), 7.33 (dd, 2H), 7.28 (d, 2H), 7.19 (t, 2H), 7.09 (t, 2H), 7.03 (d, 2H). High-resolution MS: m/z found: 505.1498 [M]<sup>+</sup>; calcd

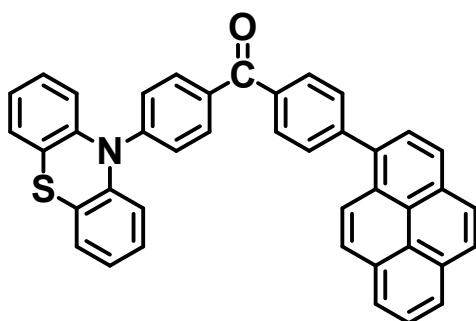
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for C<sub>35</sub>H<sub>23</sub>NOS: 505.1495. Elemental analyses (%) calcd for C<sub>35</sub>H<sub>23</sub>NOS: C 83.14, H 4.58, N 2.77; found: C 83.31, H 4.67, N 2.63.



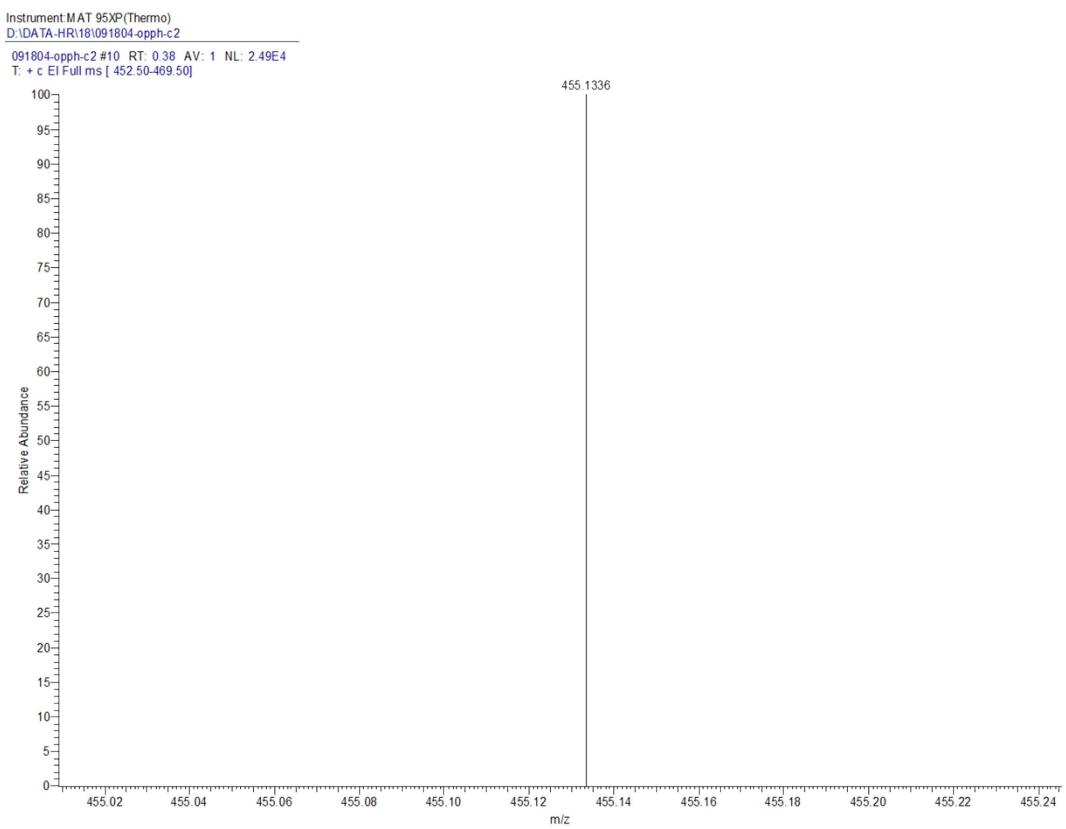
**(4-(10H-phenothiazin-10-yl)phenyl)(4-(anthracen-9-yl)phenyl)methanone**

**(OPAn)** Compound OPAn was achieved according to the aforementioned procedure for OPPh with 9-Anthraceneboronic acid (0.99 g, 4.45 mmol) in place of Phenylboronic acid. Yield: 1.14 g (69.1%). <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 8.53 (s, 1H), 8.08–7.98 (m, 6H), 7.65 (d, 2H), 7.56 (d, 2H), 7.50–7.46 (m, 2H), 7.40–7.29 (m, 6H), 7.21 (td, 2H), 7.13–7.07 (m, 4H). High-resolution MS: m/z found: 555.1655 [M]<sup>+</sup>; calcd for C<sub>39</sub>H<sub>25</sub>NOS: 555.1651. Elemental analyses (%) calcd for C<sub>39</sub>H<sub>25</sub>NOS: C 84.30, H 4.53, N 2.52; found: C 84.13, H 4.61, N 2.49.



**(4-(10H-phenothiazin-10-yl)phenyl)(4-(pyren-1-yl)phenyl)methanone (OPPy)**

Compound OPPy was achieved according to the aforementioned procedure for OPPh with 1-pyrenylboronic acid (1.10 g, 4.45 mmol) in place of Phenylboronic acid. Yield: 1.19 g (68.9%). <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 8.27–8.17 (m, 4H), 8.13 (s, 2H), 8.08–7.95 (m, 7H), 7.76 (d, 2H), 7.36–7.29 (m, 4H), 7.20 (t, 2H), 7.08 (dd, 4H). High-resolution MS: m/z found: 579.1656 [M]<sup>+</sup>; calcd for C<sub>41</sub>H<sub>25</sub>NOS: 579.1651. Elemental analyses (%) calcd for C<sub>41</sub>H<sub>25</sub>NOS: C 84.95, H 4.35, N 2.42; found: C 85.03, H 4.30, N 2.54.

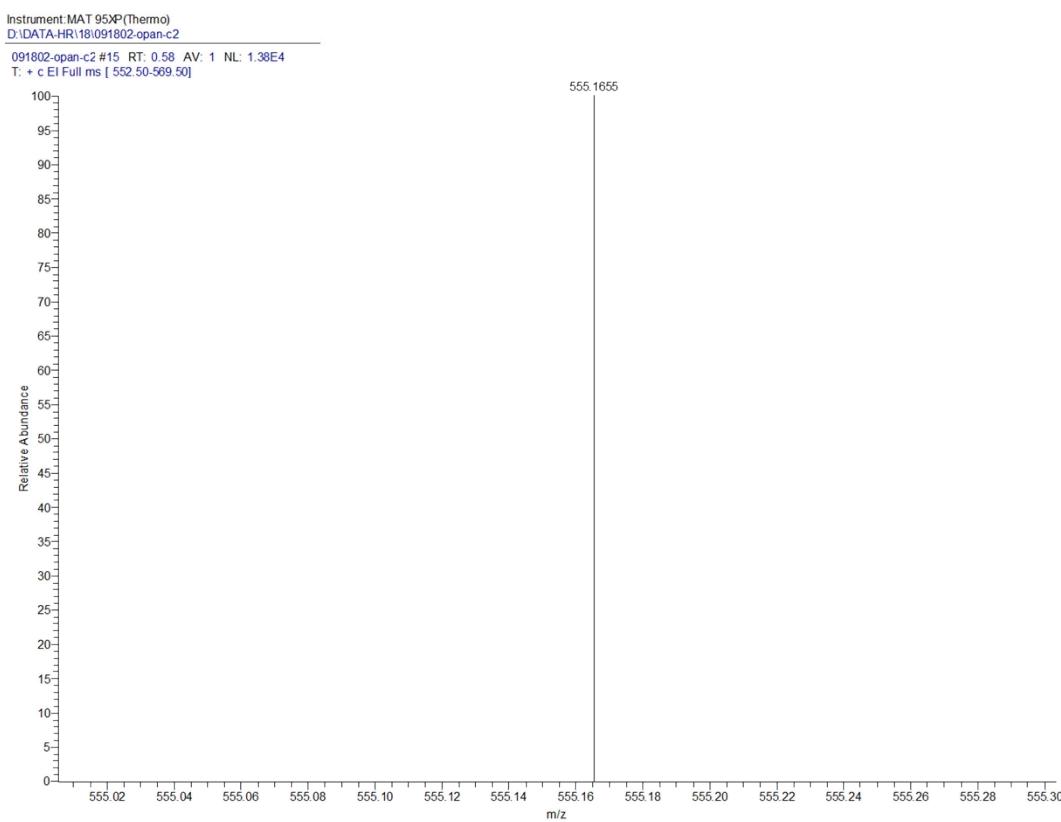


**Figure S1** High-resolution Mass Spectrum of OOPPh.

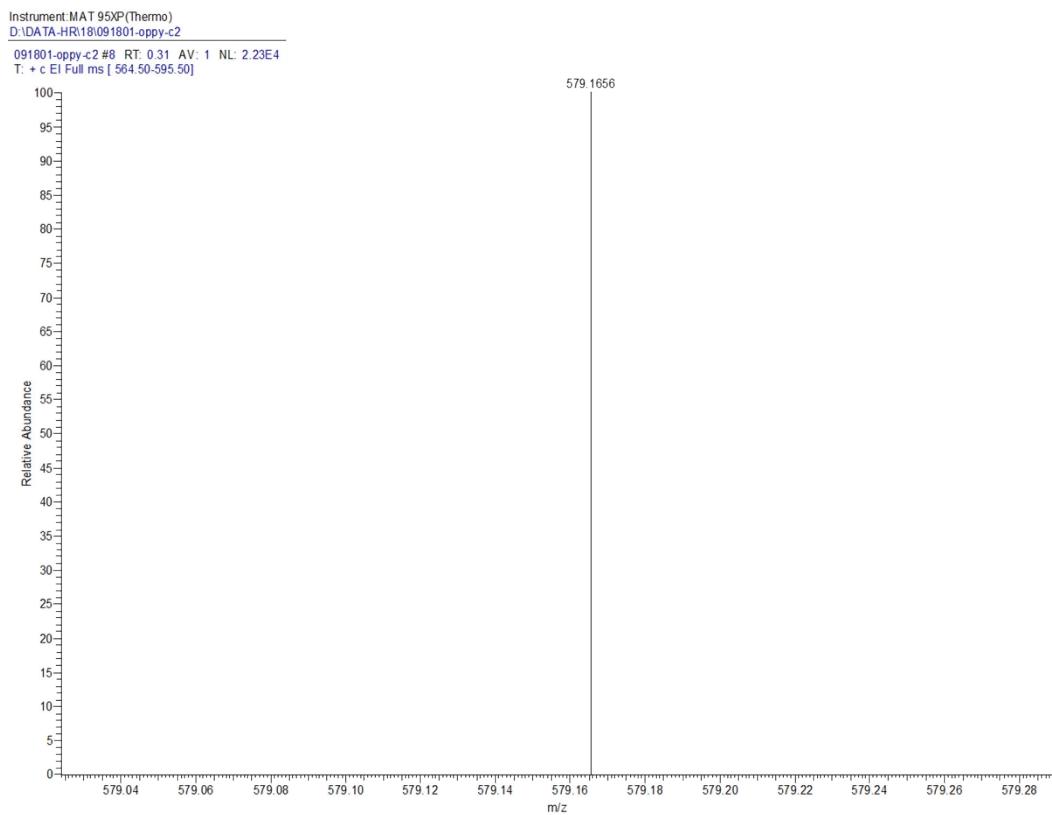


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**Figure S2** High-resolution Mass Spectrum of OPNa.



**Figure S3** High-resolution Mass Spectrum of OPAn.



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**Figure S4** High-resolution Mass Spectrum of OPPy.

## 2 Physical measurements and instrumentations

<sup>1</sup>H NMR spectra of this series were carried out on a Bruker Avance III 500 Nuclear Magnetic Resonance Spectrometer, in which the chemical shifts were relative to tetramethylsilane (TMS). Thermo MAT95XP high-resolution mass spectrometer was used to obtain the positive ion EI mass spectra. The elemental analysis studies were recorded on a Vario EL analyzer. Uv-vis absorption and photoluminescence (PL) spectra were performed with a Hitachi U-3900 spectrophotometer, a Shimadzu RF-5301PC spectrometer and an Ocean Optic QE 65Pro spectrometer with Ocean Optic reflection probes R600-125F, respectively. CIE coordinates were obtained on SpectraScan PR655 of PHOTO REASEARCH. PXRD data were collected on a Rigaku X-ray diffractometer (D/max-2200) with an X-ray source of Cu K $\alpha$  ( $\lambda = 0.154184$  nm) at 40 kV and 30 mA, at a scan rate of 10° (2 $\theta$ ) per 1 min. Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Gemini S Ultra X-ray Single Crystal Diffractometer with a (Cu) X-ray source. Temperature-dependent transient emission decay studies were performed on a Horiba Scientific Fluorolog-3 spectrofluorometer equipped with a Cryocon 22C temperature controller.

## 3 Single crystal data of OOPh, OPNa, and OPPy.

Single crystals of OOPh, OPNa, and OPPy were isolated by slow evaporation from the dichloromethane-hexane, toluene-hexane and dichloromethane-methanol mixed solvent solutions, respectively. The single crystal X-ray data for all these single crystals was collected on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer with graphite-monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å). Olex2 program and expanded with Fourier techniques was used to solve the single crystal structures. All non-H atoms of these compounds were refined with anisotropic thermal parameters. The hydrogen atoms were added in idealized positions and

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further refined with fixed geometry with respect to their carrier atoms. CCDC numbers for these single crystals of OPPh, OPNa and OPPy are 1878944, 1878945 and 1878946, respectively.

**Crystal data for OPPh:**  $C_{31}H_{21}NOS$ , Formula Weight = 455.55 g/mol, monoclinic, space group  $P2_1/n$ ,  $T = 150.00(10)$  K,  $Z = 4$ ,  $a = 13.8029(4)$  Å,  $b = 9.9367(2)$  Å,  $c = 16.9651(5)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 07.887(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2214.38(11)$  Å<sup>3</sup>,  $\rho_c = 1.366$  g cm<sup>-3</sup>,  $\mu(Cu_{K\alpha}) = 1.490$  mm<sup>-1</sup>,  $F(000) = 952.0$ . Reflections collected 8861, Independent reflections 4358 ( $R_{\text{int}} = 0.0284$ ).  $R_1 = 0.0399$  ( $I > 2\sigma(I)$ ) and  $wR_2 = 0.1110$ , GOF = 1.026.

**Table S1.** Bond distances (Å) for OPPh

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C13	1.7621(17)	C25	C24	1.385(2)
S1	C14	1.7590(16)	C20	C21	1.398(2)
O1	C1	1.219(2)	C20	C1	1.498(2)
N1	C5	1.4406(19)	C6	C7	1.393(2)
N1	C19	1.4163(19)	C8	C13	1.398(2)
N1	C8	1.4233(18)	C8	C9	1.394(2)
C5	C6	1.389(2)	C13	C12	1.392(2)
C5	C4	1.391(2)	C21	C22	1.391(2)
C19	C14	1.402(2)	C14	C15	1.394(2)
C19	C18	1.397(2)	C18	C17	1.391(2)
C2	C3	1.397(2)	C27	C28	1.389(2)
C2	C1	1.502(2)	C9	C10	1.390(2)
C2	C7	1.397(2)	C17	C16	1.384(2)
C26	C23	1.485(2)	C15	C16	1.386(2)
C26	C27	1.400(2)	C31	C30	1.387(2)
C26	C31	1.396(2)	C12	C11	1.385(3)
C23	C24	1.398(2)	C30	C29	1.380(3)
C23	C22	1.395(2)	C28	C29	1.389(3)
C3	C4	1.386(2)	C10	C11	1.381(3)
C25	C20	1.398(2)			

**Table S2.** Bond angles for OPPh





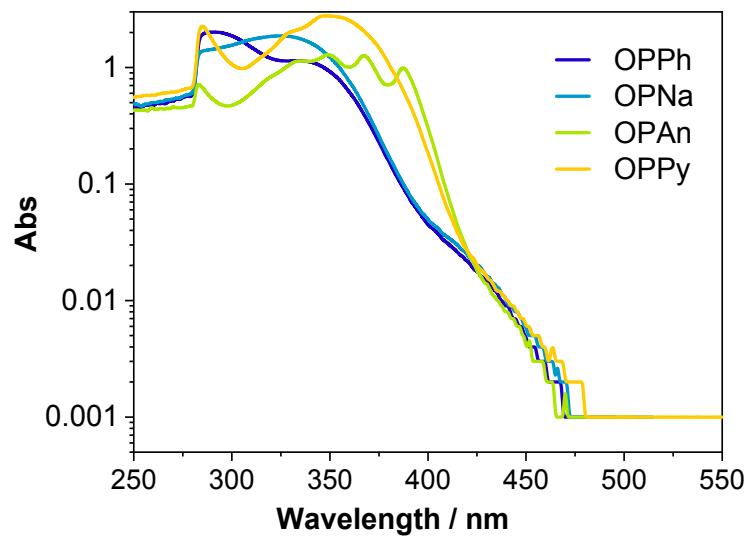




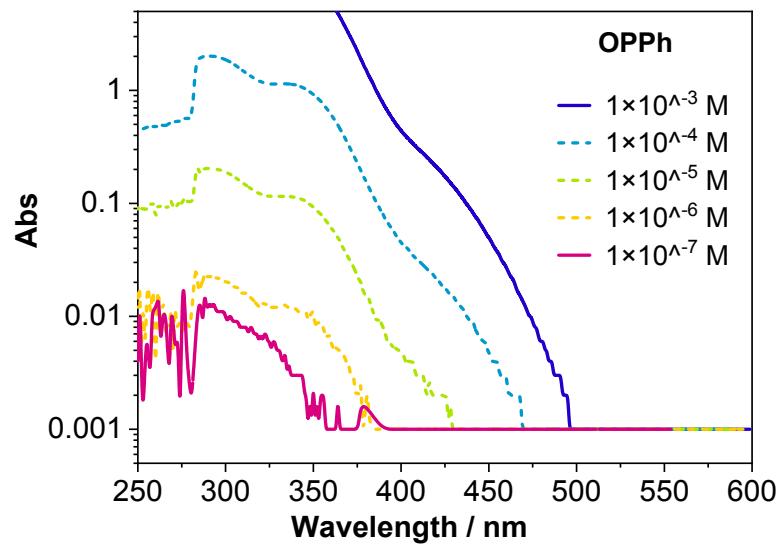
C19	C18	C21	119.25(16)	C4	C3	C2	121.81(17)
C17	C18	C19	118.58(17)	C13	C14	C1	121.49(18)
C17	C18	C21	122.00(16)	C3	C4	C5	121.50(17)
C20	C19	C18	120.66(17)	C31	C26	N25	118.94(17)
C41	C42	C21	123.75(17)	C31	C26	C27	119.98(17)
C41	C42	C43	117.50(16)	C27	C26	N25	121.05(17)
C43	C42	C21	118.74(16)	C36	C37	C38	119.67(18)
C17	C16	C15	121.00(17)	C26	C31	S32	119.29(14)
N25	C39	C40	120.98(16)	C26	C31	C30	120.34(18)
N25	C39	C44	121.05(16)	C30	C31	S32	120.31(15)
C44	C39	C40	117.97(16)	C35	C34	C33	119.94(18)
C16	C15	C1	120.62(16)	C7	C6	C5	120.5(2)
C16	C15	C20	118.20(17)	C34	C35	C36	120.23(18)
C20	C15	C1	121.14(16)	C35	C36	C37	120.26(18)
C2	C1	C15	122.10(16)	C23	C24	C12	121.29(19)
C14	C1	C2	119.23(17)	C28	C27	C26	119.82(19)
C14	C1	C15	118.66(17)	C14	C13	C12	120.79(17)
O22	C21	C18	118.90(17)	C24	C23	C9	121.65(18)
O22	C21	C42	120.46(17)	C7	C8	C9	120.73(19)
C42	C21	C18	120.62(16)	C30	C29	C28	120.51(18)
C44	C43	C42	121.80(16)	C8	C7	C6	120.68(19)
C19	C20	C15	120.97(17)	C29	C30	C31	119.25(19)
C43	C44	C39	120.48(17)	C27	C28	C29	119.94(19)
C11	C12	C24	118.72(18)	Cl2	C46	Cl1	111.92(17)

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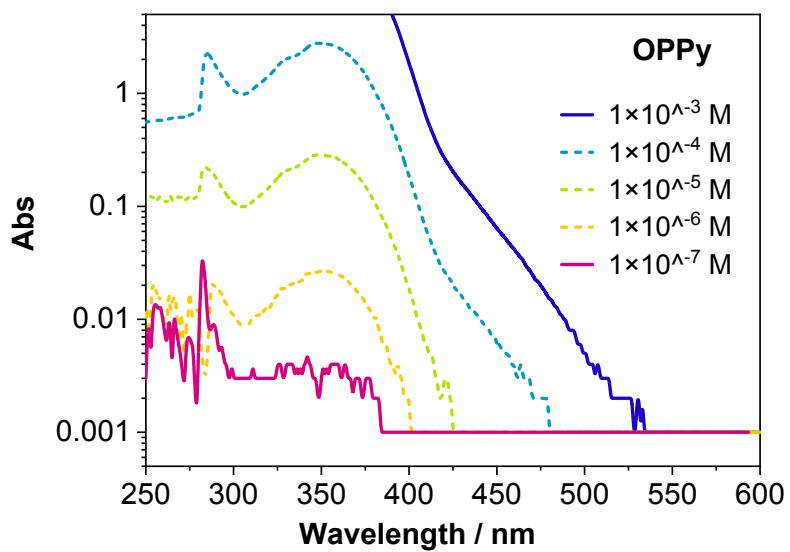
## 4 Photophysical data and spectra



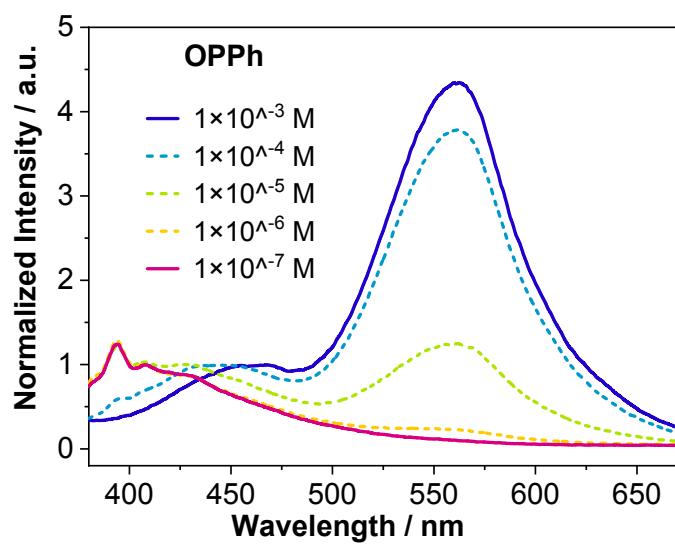
**Figure S1.** Electronic absorption spectra of compounds OPPh, OPNa, OPAn and OPPy in toluene solution with the concentration of  $1.0 \times 10^{-4}$  mol/L at room temperature.



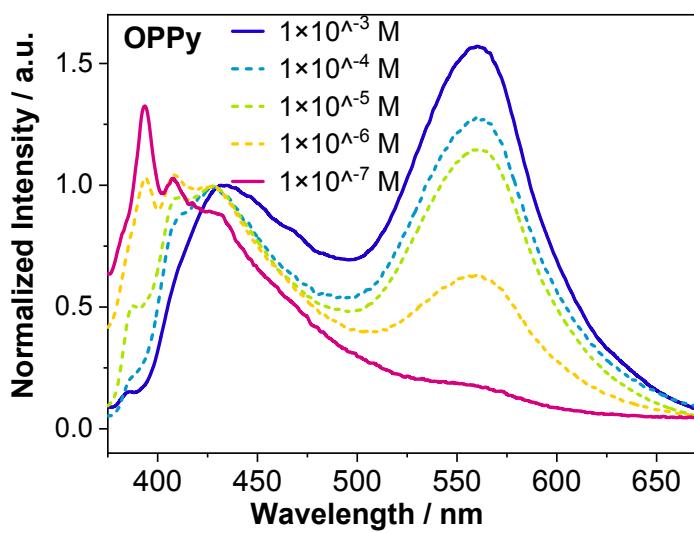
**Figure S2.** Concentration dependent electronic absorption spectra of compound OPPh in toluene solution.



**Figure S3.** Concentration dependent electronic absorption spectra of compound OPNa in toluene solution.



**Figure S4.** Concentration-dependent emission spectra of OPPh in toluene solution.



**Figure S5.** Concentration-dependent emission spectra of OPPy in toluene solution.

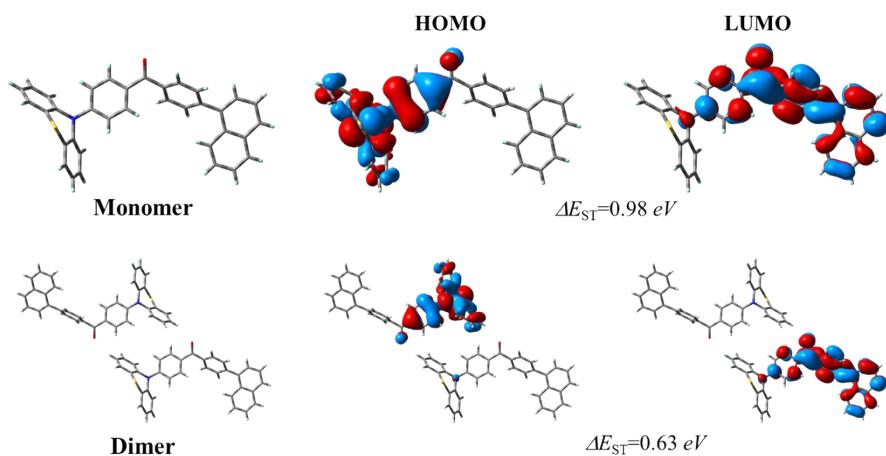


Figure S6. The HOMO, LUMO and conformations of OPNa in monomer and dimer state.

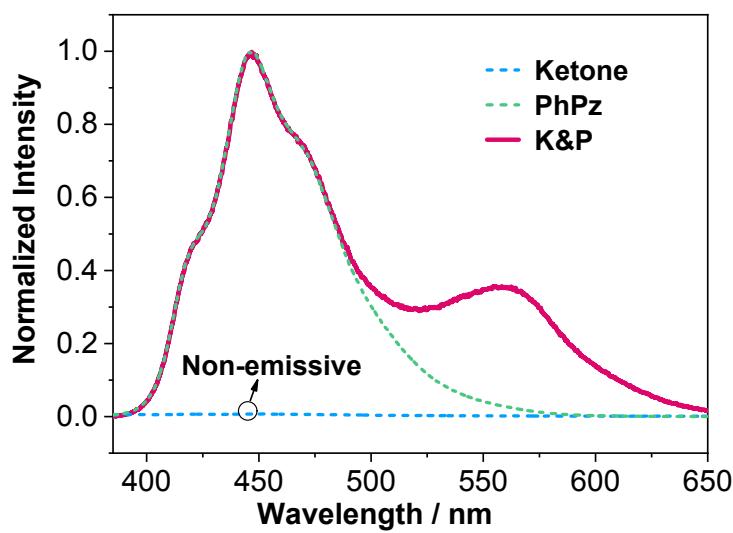


Figure S7. Emission spectra of benzophenone, 10-phenyl-10H-phenotheniazine and their mixture in toluene solution (at the concentration of  $1 \times 10^{-1}$  mol/L).

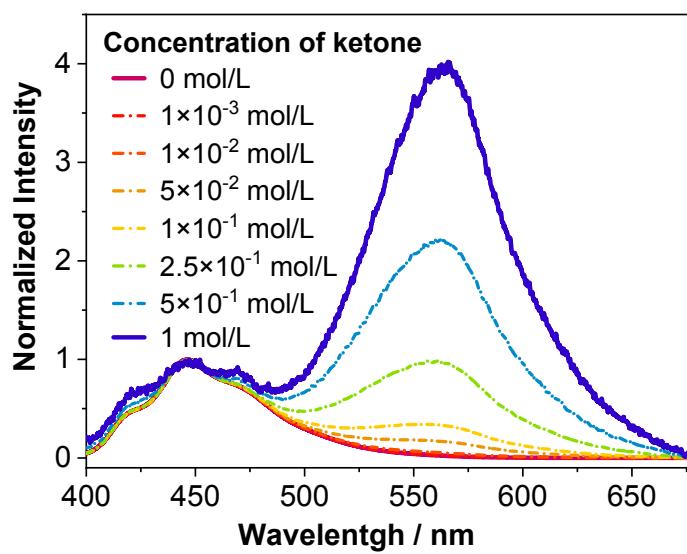


Figure S8. Emission spectra of the 10-phenyl-10H-phenotheniazine in toluene solution with varies of concentration of benzophenone.

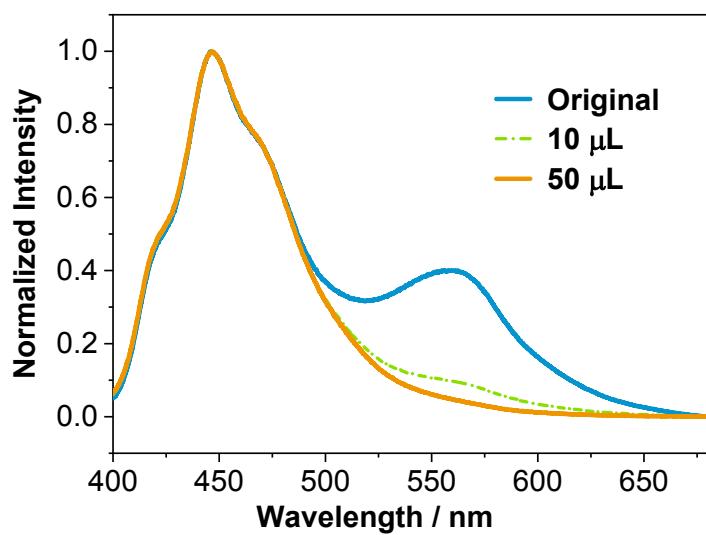


Figure S9. Changes in the emission spectra for the mixture of benzophenone and 10-phenyl-10H-phenothiazine by gradual addition of methanol in toluene solution.

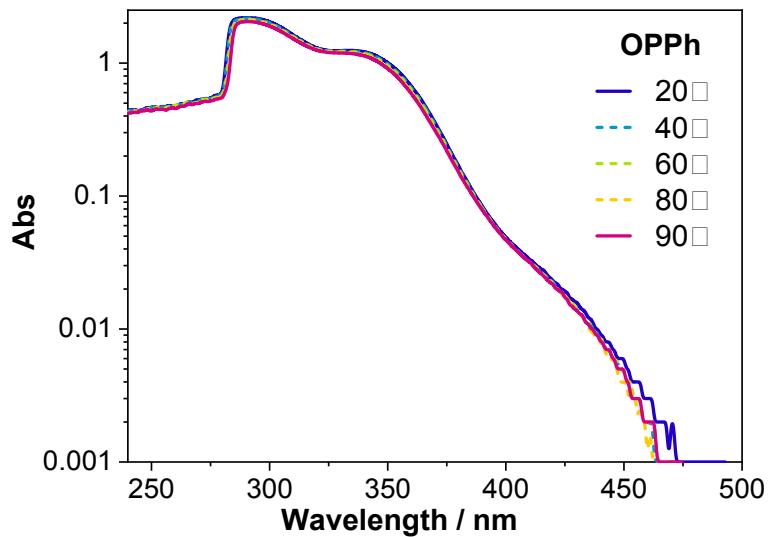
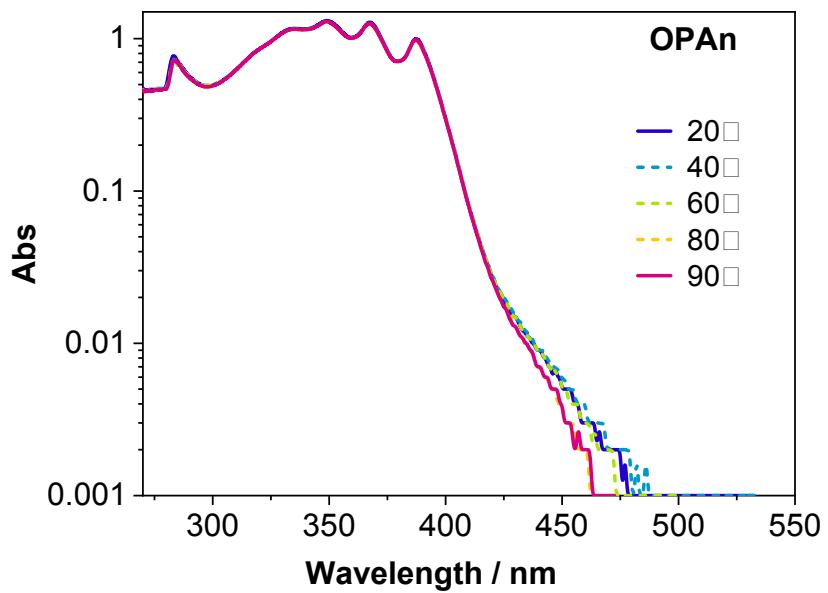
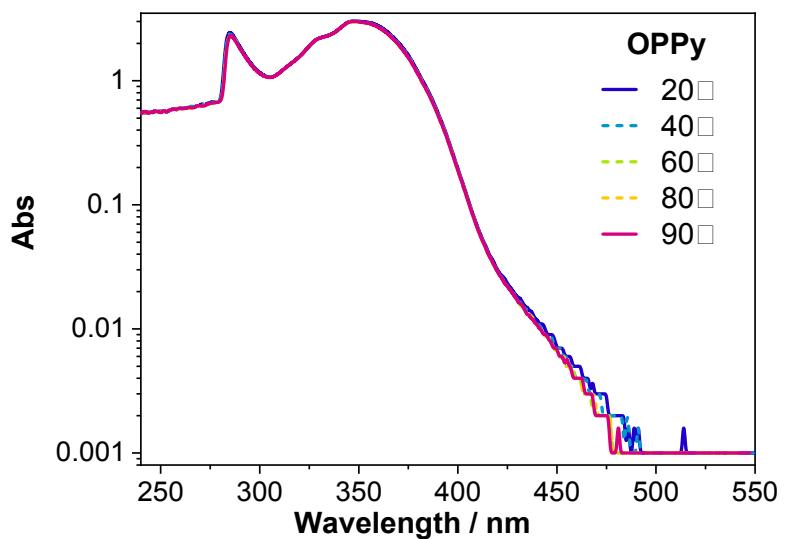


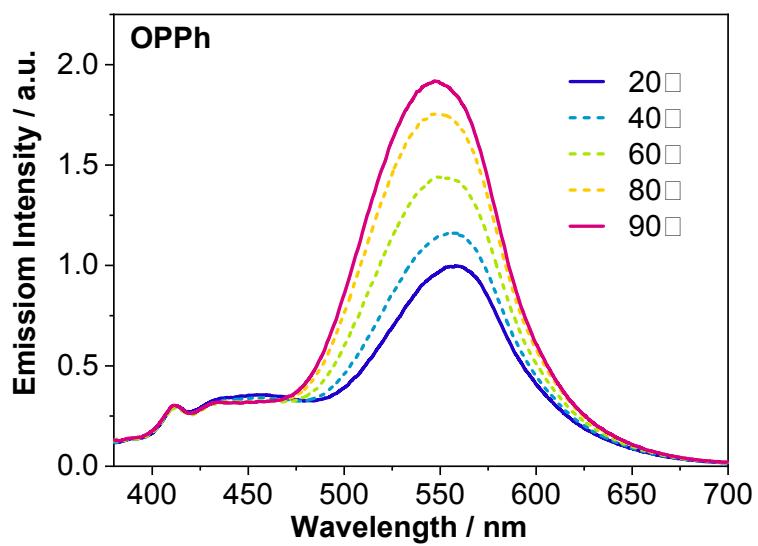
Figure S10. Temperature-dependent absorption spectra of OPPh in toluene solution.



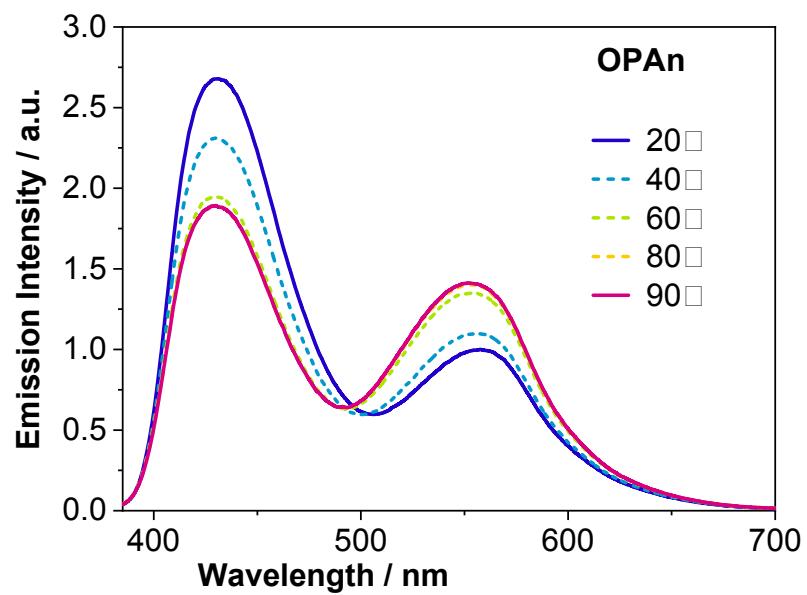
**Figure S11.** Temperature-dependent absorption spectra of OPAn in toluene solution.



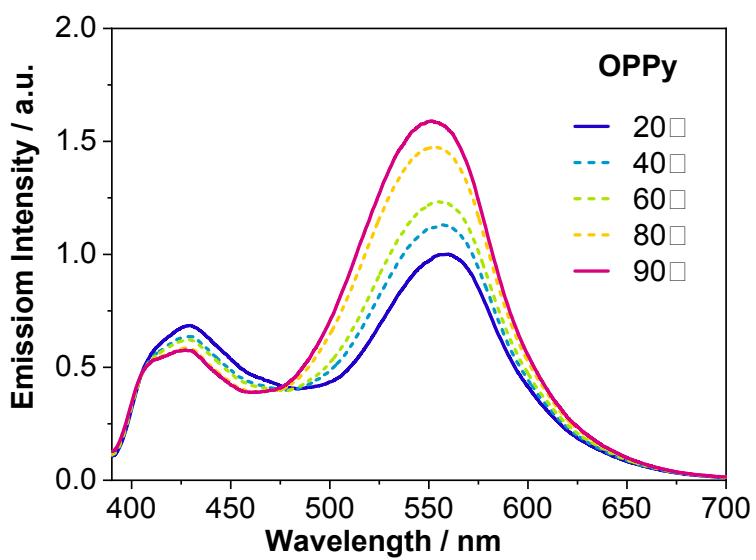
**Figure S12.** Temperature-dependent absorption spectra of OPPy in toluene solution.



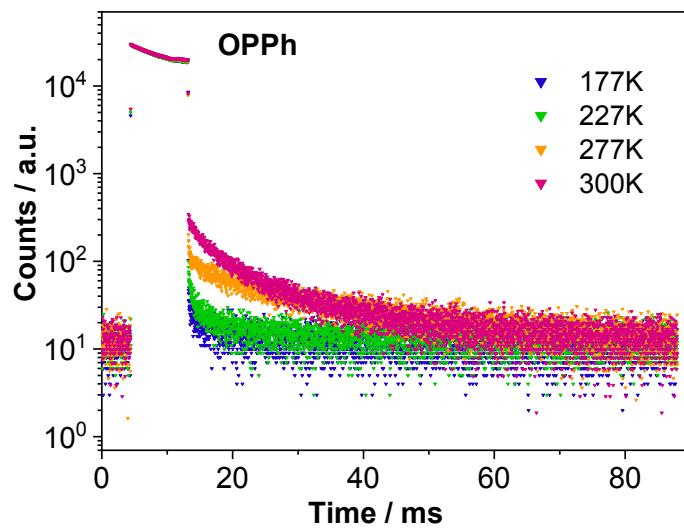
**Figure S13.** Temperature-dependent emission spectra of OPPh in toluene solution.



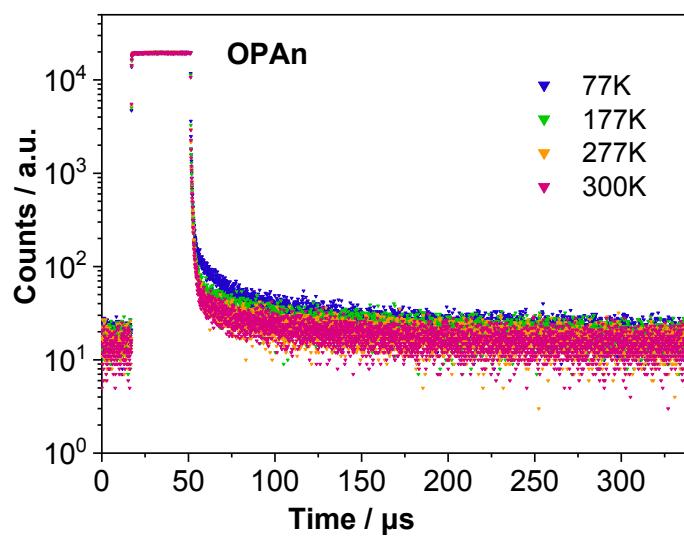
**Figure S14.** Temperature-dependent emission spectra of OPAn in toluene solution.



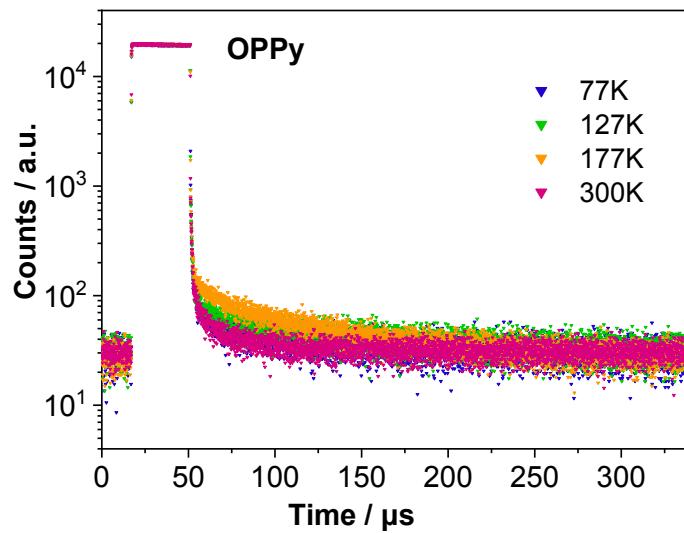
**Figure S15.** Temperature-dependent emission spectra of OPPy in toluene solution.



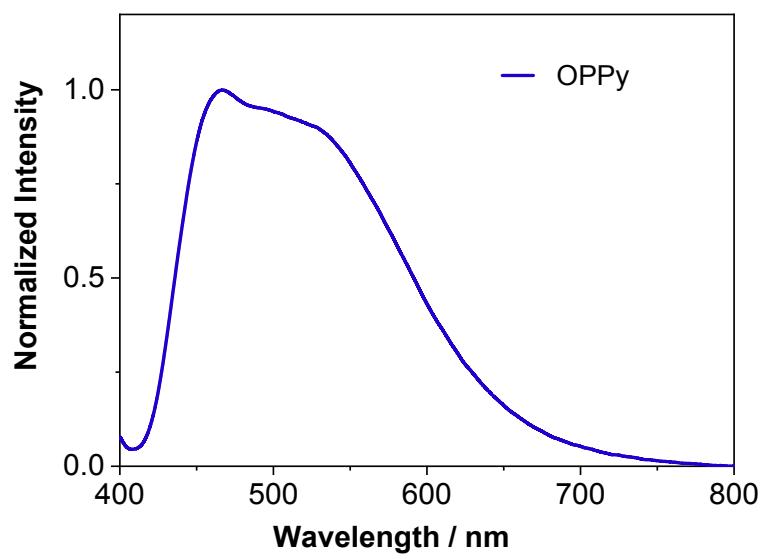
**Figure S16.** temperature-dependent emission decay spectra of OPPh at 565 nm in the crystalline state.



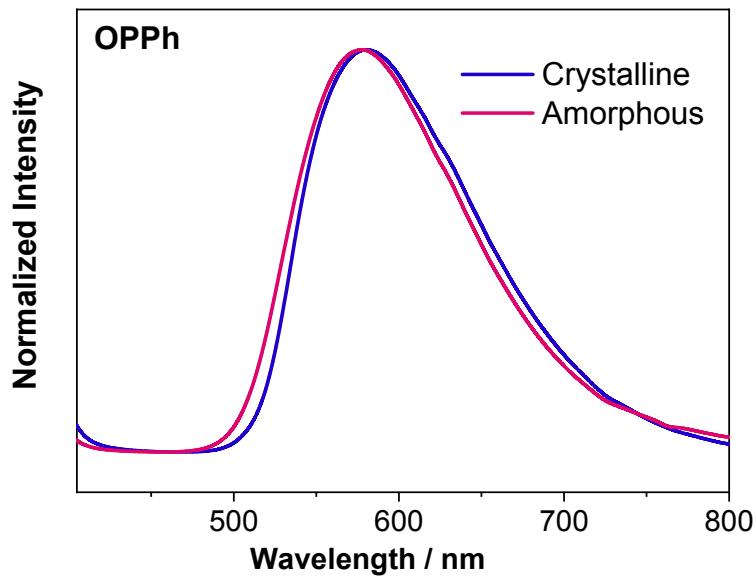
**Figure S17.** temperature-dependent emission decay spectra of OPAn at 565 nm in the crystalline state.



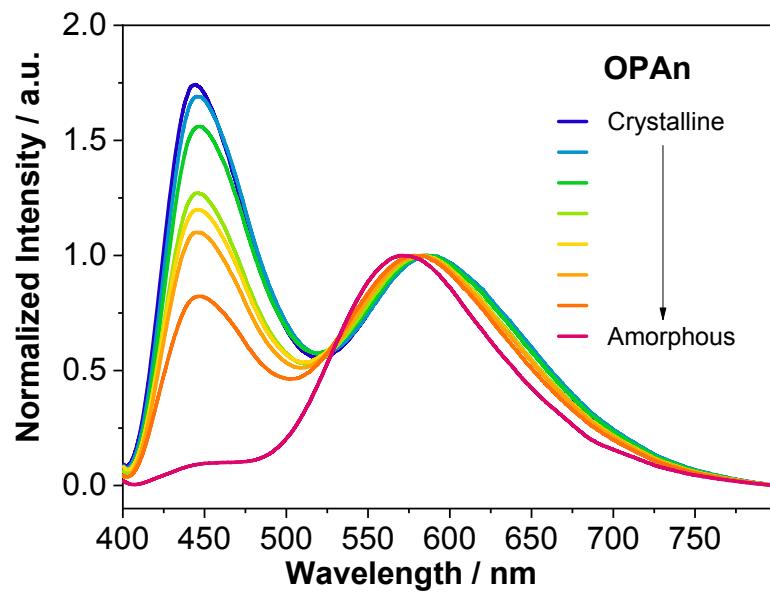
**Figure S18.** temperature-dependent emission decay spectra of OPPy at 565 nm in the crystalline state.



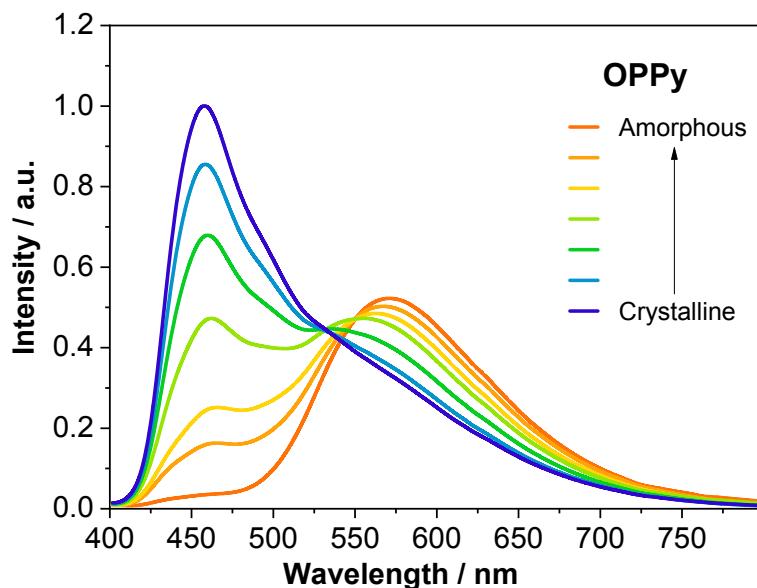
**Figure S19.** Emission spectra of single crystal of OPPy.



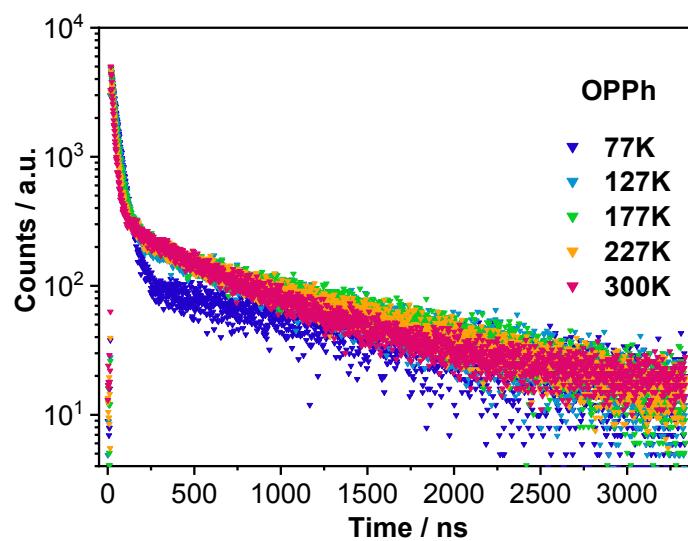
**Figure S20.** PL spectra of the crystalline powders of OOPh in solid state under grinding.



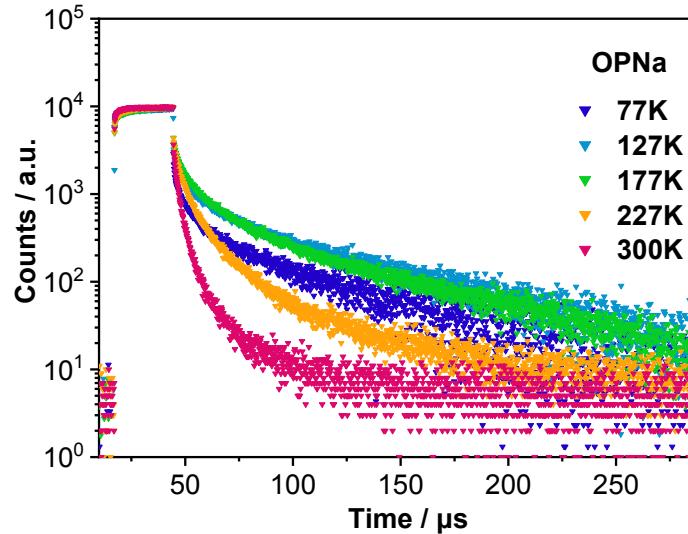
**Figure S21.** PL spectra of the crystalline powders of OPAn in solid state under grinding.



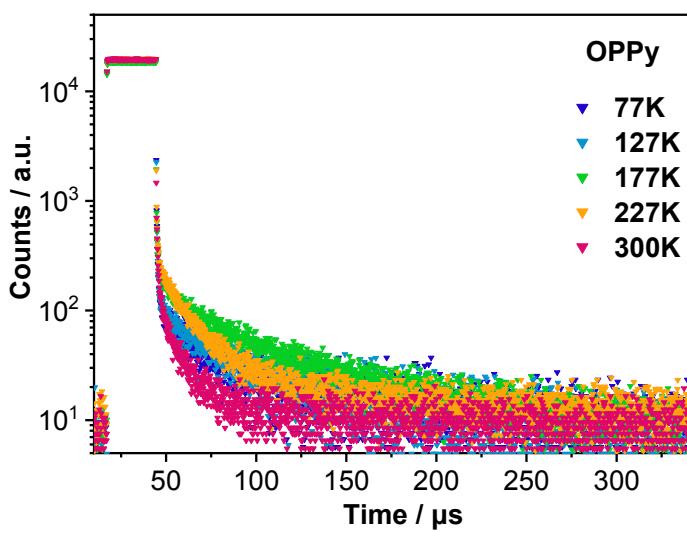
**Figure S22.** PL spectra of the crystalline powders of OPPy in solid state under grinding.



**Figure S23.** temperature-dependent emission decay spectra of OPPh at 565 nm in the amorphous state.



**Figure S24.** temperature-dependent emission decay spectra of OPNa at 565 nm in the amorphous state.



**Figure S25.** temperature-dependent emission decay spectra of OPPy at 565 nm in the amorphous state.

## References

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