Supplementary Information

Luminescent core-isolated solvent-free liquids as a soft material platform for optical gas sensing

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Contents

1. Materials

$PtCl_2$, benzonitrile, and spectroscopic grade solvents like dichloromethane and toluene were purchased from FUJIFILM Wako Pure Chemical Corp. NMR-solvent $CDCl_3$, common reagents for chromatographic purification such as dichloromethane, *n*-hexane, and silica gel 60 N (spherical, neutral) of 40–50 μm were supplied by Kanto Chemical. All chemicals and solvents were used as received. Poly(1-trimethylsilyl-1-propyne) (**PTMSP**) was prepared via the polymerization of 1-trimethylsilyl-1-propyne in the presence of $TaCl_5$ as the catalyst.[S1] Liquid pyrene (**PyL**) was prepared according to our previous report.[S2] Pt(II)-tetraphenyl porphyrin (**PtTPP**) was prepared according to the literature procedure.[S3] Standard gas containing diluted O_2 in N_2 (0.1%, 1%, 10%) were purchased from Suzuki Shokan Co., Ltd.

2. General methods

^{1}H-NMR and ^{13}C-NMR spectra were obtained using a JNM-ECS 400 spectrometer (400 MHz, JEOL, Japan), and NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS). High resolution electrospray ionization mass spectrometry (ESI-MS) was performed using a Thermo Scientific Q-Exactive Plus with samples dissolved in CH_2Cl_2/CH_3OH. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed using a Shimadzu MALDI-8030 with dithranol as the matrix. UV-Vis absorption and emission spectra were recorded on a JASCO V-670 spectrophotometer and a JASCO FP-8300 spectrophotometer, respectively. For typical luminescent analyses of solutions, a sample solution (10^{-6} M in toluene) was taken into a quartz cuvette (optical length = 1.0 cm) with a rubber septum cap. Two thin needles were inserted into the septum from the top, acting as an inlet and outlet. The solution was slowly bubbled with dry Ar or N_2 for 15 minutes to degas. Although evaporation of toluene was negligible, a few drops of excess toluene may be added beforehand to compensate for evaporation. For luminescent analyses of films, quartz substrates (W × D × H = 25 mm × 10 mm × 1 mm) were used to mount porphyrin films, and placed into a quartz cell (W × D × H = 10 mm × 10 mm × 45 mm) with a rubber septum cap as illustrated in **Figure S1**. Before mounting samples, quartz substrates were sonicated in acetone for 5 min, and then dried with flowing N_2. Optical microscopy images under polarized and cross-polarized light were obtained using an Olympus BX51 optical microscopy system. Fluorescence microscopy images were obtained using a Leica TCS SP5 confocal laser scanning microscope. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a Hitachi TG/DTA 6200 and Hitachi DSC7000X instruments, respectively. The heating rate of TGA and the heating-cooling rate of DSC were both set to 10 K per minute under N_2 gas flow. Phosphorescence lifetime spectroscopies were carried out using a nanosecond laser at 420 nm (10 Hz, 5–8 ns duration, incident photon density = 9.0×10^{15} photons cm^{-2}) from an optical parametric oscillator (OPO, Continuum Inc., Panther) seeded by a Nd:YAG laser (Continuum Inc., Surelite II).[S4] The phosphorescence spectra through an undercut filter (520 nm) at delayed times (1 μs gate, 1 μs step) were monitored by using an Andor model iStar image-intensifier ICCD camera equipped with a Solar TII model MS2004 monochromator. Absolute quantum yields were determined on a Hamamatsu Photonics Quantaurus C11347.

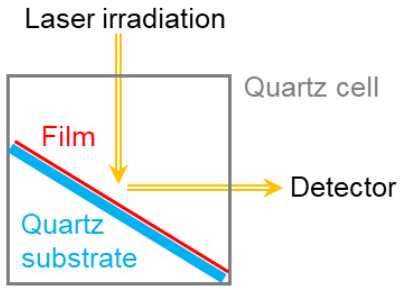


Figure S1. Top-view positioning of a sample substrate in a quartz cell.

3. Characterizations of PtPL and ZnPL

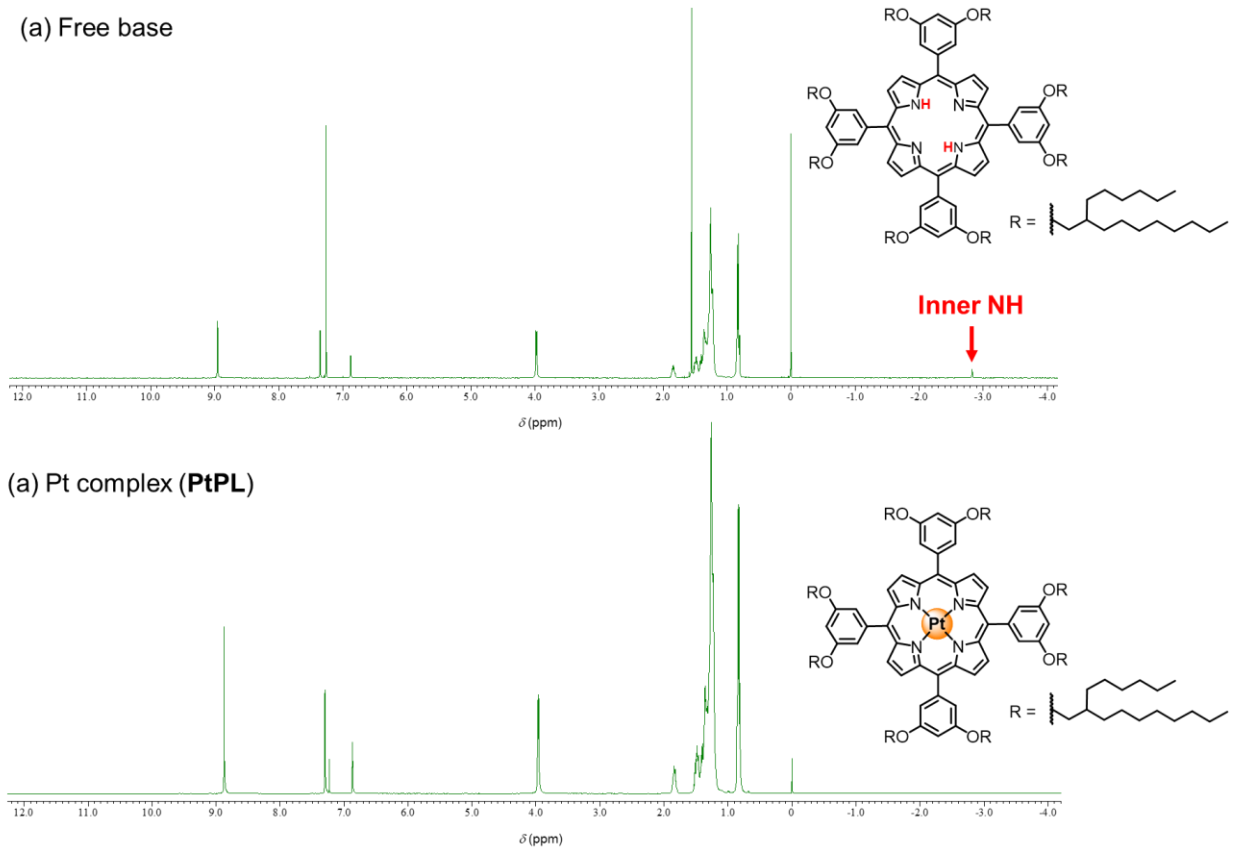


Figure S2. ^{1}H NMR spectra of the porphyrin liquid (a) before and (b) after insertion of Pt(II) into the core. Note that the inner NH proton signal at −2.83 ppm, characteristic of the free-base porphyrin, disappears after insertion of Pt(II).

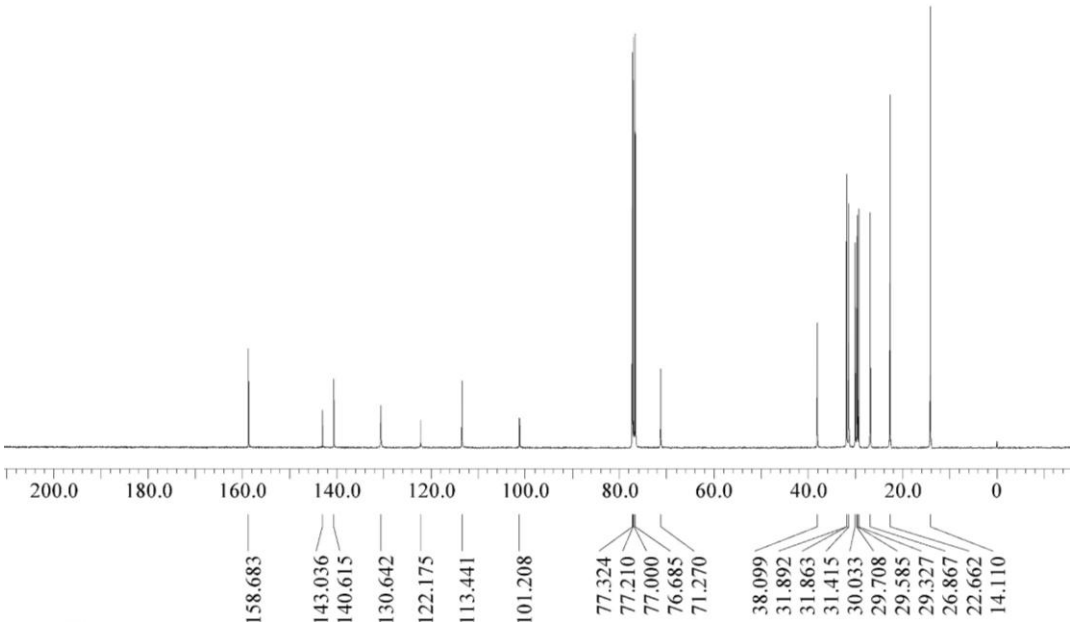


Figure S3. ^{13}C NMR spectrum of **PtPL** in $CDCl_3$.

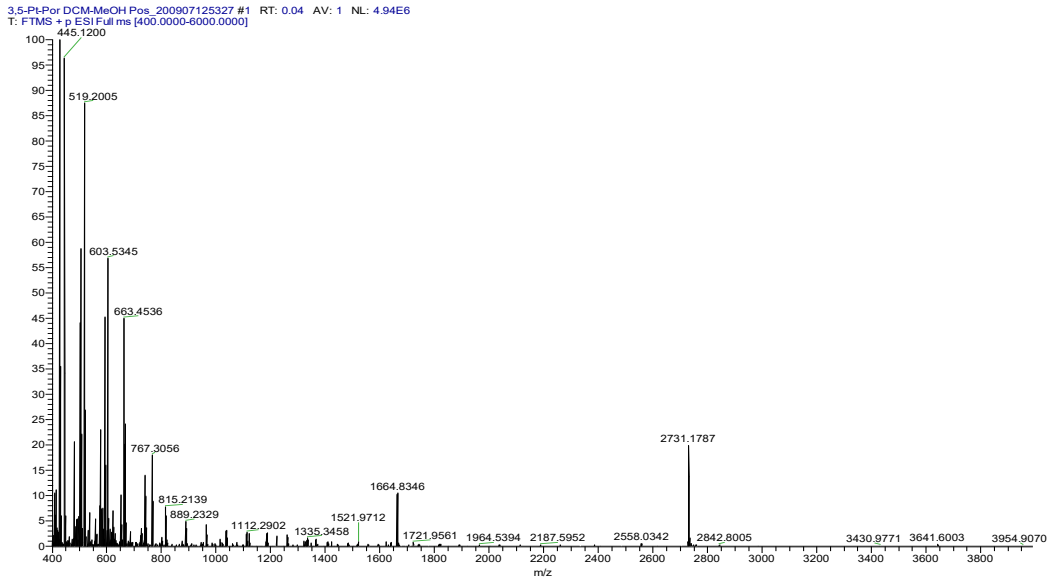


Figure S4. HR-ESI-MS spectrum of **PtPL** in CH_2Cl_2/CH_3OH mixture (9:1 in volume).

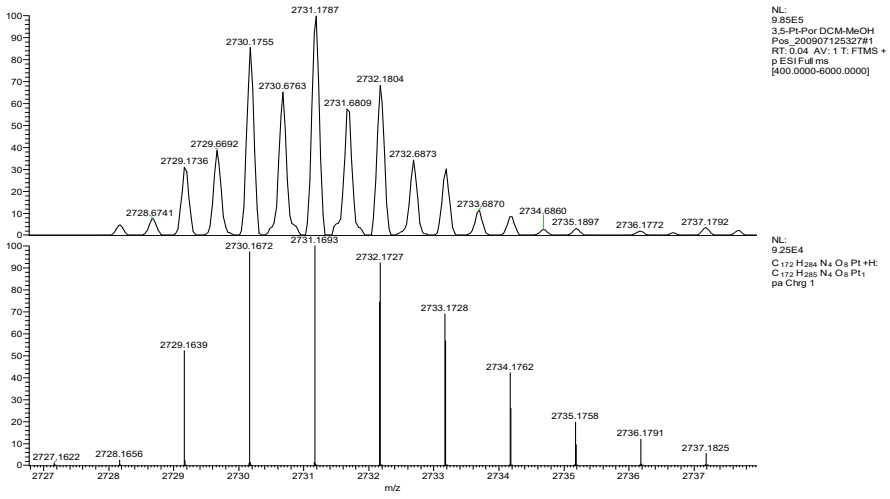
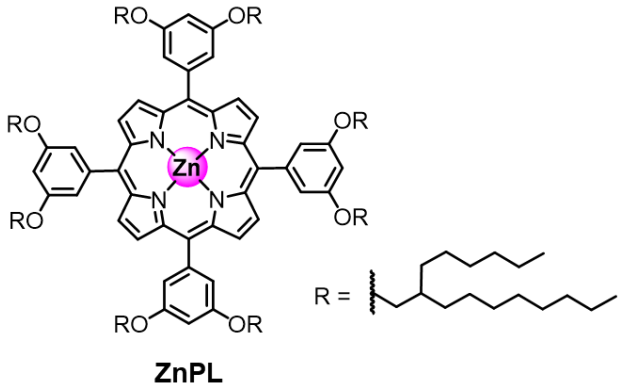


Figure S5. Experimental (up) and simulated (down) HR-ESI-MS spectrum of **PtPL** ($[C_{172}H_{285}O_8N_4{}^{194}Pt]^+$). Note that the mass signals appear to contain double-charged dimers (z = 2).



ZnPL

Figure S6. Chemical structure of **ZnPL**, an analogue of **PtPL**.

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: 9.06 (s, 8H, pyrrole β-H), 7.37 (d, J = 2.4 Hz, 8H, Ar-H), 6.88 (t, J = 2.4 Hz, 4H, Ar-H), 3.98 (d, J = 6.0 Hz, 16H, OCH_2), 1.84 (m, 8H, CH), 1.54-1.20 (m, 192H, CH_2), 0.82 (m, 48H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: 158.60, 150.17, 144.58, 132.11, 121.21, 114.23, 101.17, 71.43, 38.26, 32.02, 32.00, 31.59, 30.18, 29.85, 29.72, 29.46, 27.01, 22.81, 14.23. MALDI-TOF MS (m/z): calculated for $[C_{172}H_{285}O_8N_4Zn]^+$ = 2599.1264 m/z, found 2599.7963 m/z.

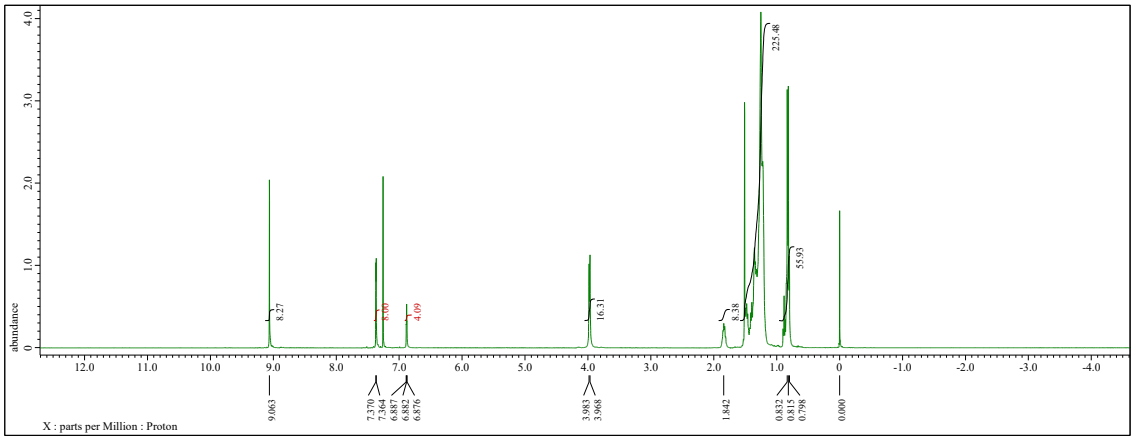


Figure S7. ^{1}H NMR spectrum of **ZnPL** in $CDCl_3$.

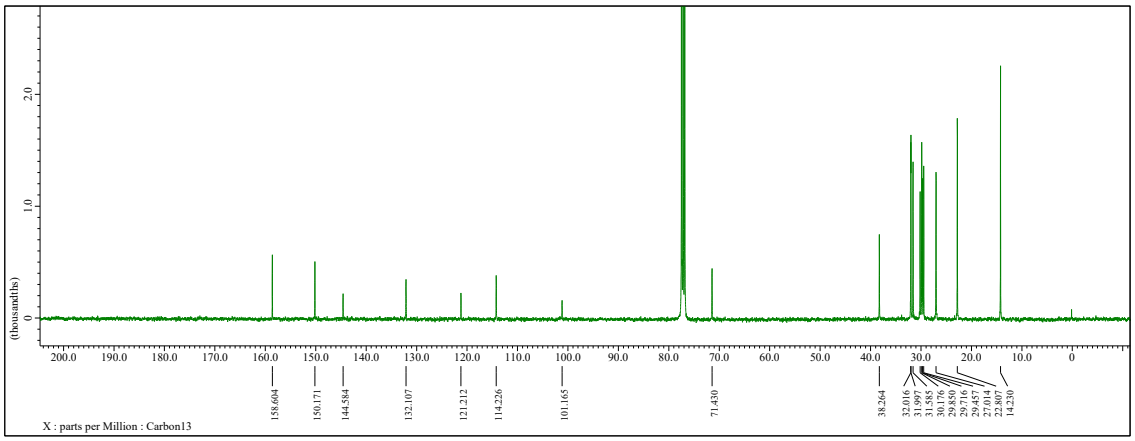


Figure S8. ^{13}C NMR spectrum of **ZnPL** in $CDCl_3$.

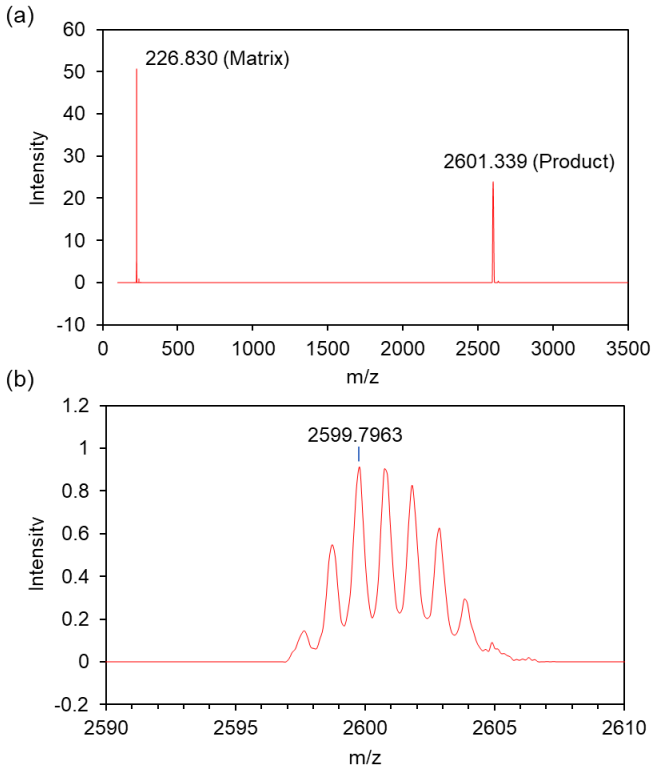


Figure S9. MALDI-TOF MS spectra of **ZnPL** measured over (a) a wide m/z range and (b) a narrow m/z range.

4. Photophysical properties of PtPL, PtTPP, and PyL

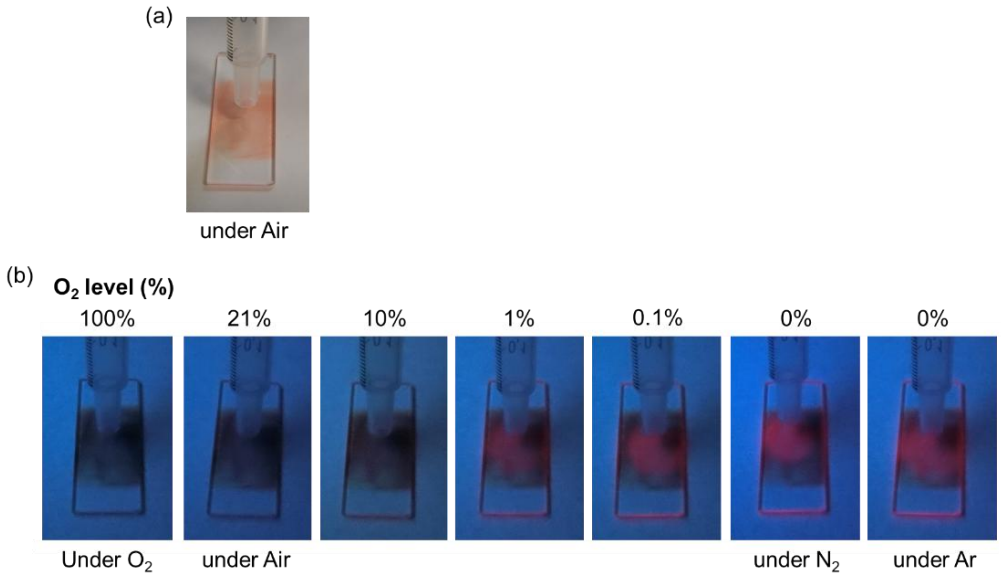


Figure S10. (a) Photograph of a neat **PtPL** film on a glass plate observed under daylight in ambient air. (b) Photographs of the same neat **PtPL** film observed under UV light (254 nm) with various O_2 levels (0–100%). A high-flow gas (5 L min^{-1}) with predefined O_2 levels was blown onto the film in ambient air. All photographs were taken individually using identical camera settings (sensitivity, focus, and exposure time). The results are consistent with those shown in **Figure 3c**, in which the emission intensity decreases exponentially with increasing O_2 levels. Under these conditions, the phosphorescence at 1% O_2 appears slightly weaker to the naked eye than that observed at 0 and 0.1% O_2. The phosphorescence becomes hardly visible when the O_2 level exceeds 10%.

Table S1. Quantum yields of **PtPL** and **PtTPP** recorded at room temperature.

Atmosphere	**Quantum yield (%)**		
	PtPL neat liquid	**PtPL** in toluene	**PtTPP** in toluene
Air	1.2	0.6	1.2
Ar	18.2	18.6	14.1

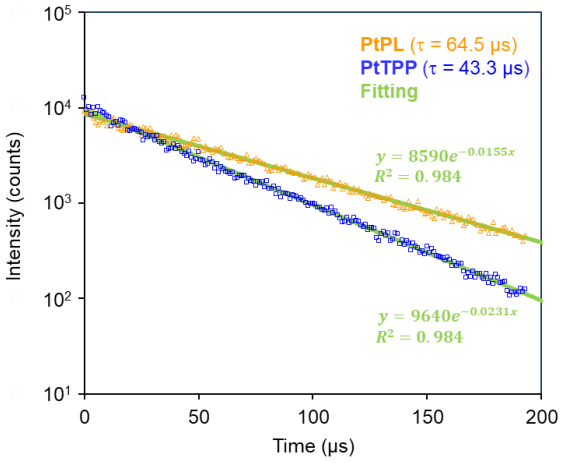


Figure S11. Phosphorescence decay profile of **PtPL** and **PtTPP** (10^{-6} M in toluene, λ_{ex} = 420 nm, ns laser with I_0 = 9.0 x 10^{15} photons/cm^2) after degassing with Ar for 15 min. See **Figure 2** for corresponding absorption and emission spectra. The decay curves were fitted by exponential function. Note that the intensity is plotted on a logarithmic scale and is approaching a plateau when represented on a linear scale.

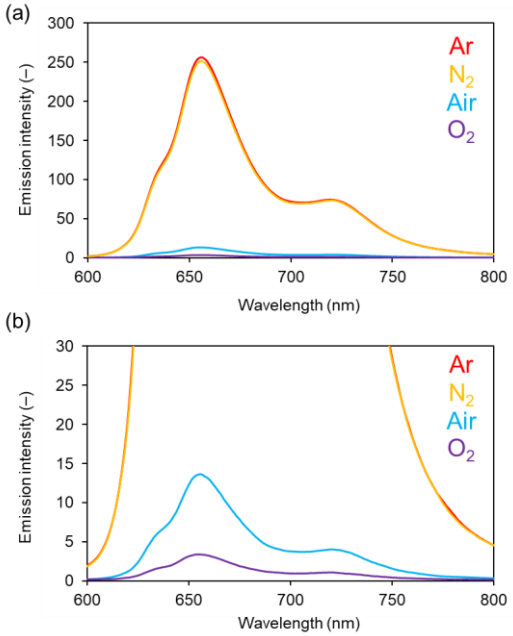


Figure S12. Emission spectra of **PtPL** in the neat liquid state measured under Ar, N_2, air, and O_2 (λ_{ex} = 412 nm): (a) full scale and (b) magnified view.

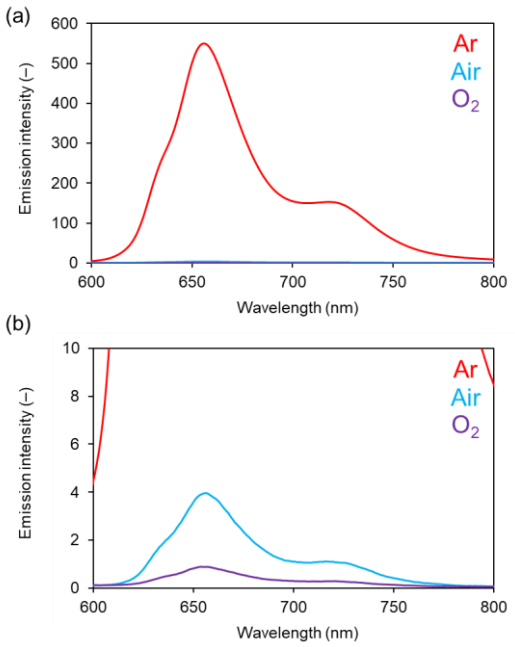


Figure S13. Emission spectra of **PtPL** in toluene (10^{-6} M) measured under Ar, air, and O_2 (λ_{ex} = 405 nm): (a) full scale and (b) magnified view.

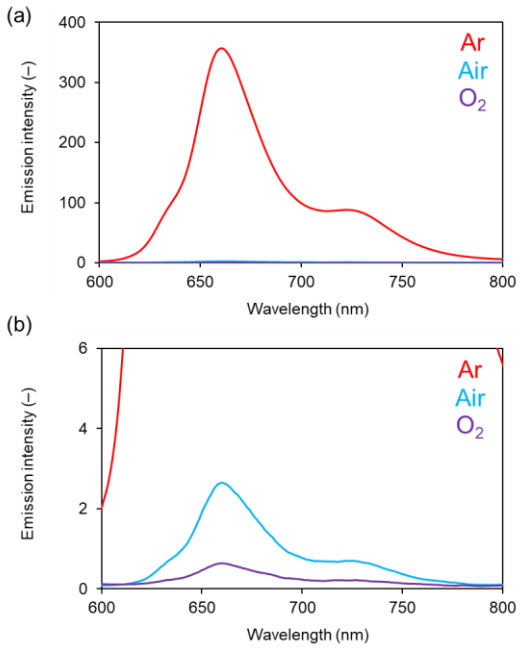


Figure S14. Emission spectra of **PtTPP** in toluene (10^{-6} M) measured under Ar, air, and O_2 (λ_{ex} = 402 nm): (a) full scale and (b) magnified view.

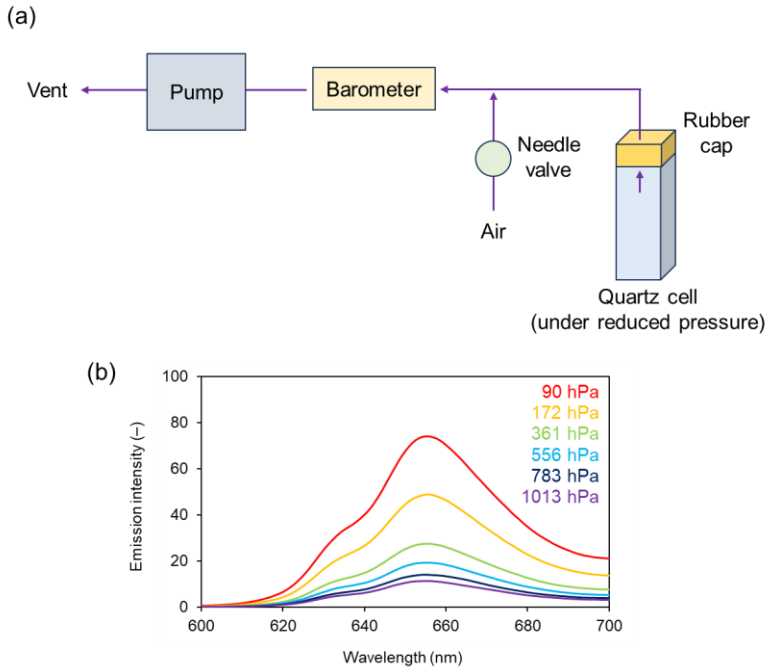


Figure S15. (a) Experimental setup for measuring emission spectra under reduced pressure. The air in the quartz cell was partially evacuated without replacement by inert gases (e.g., N_2 or Ar), thereby reducing the partial pressure of O_2. The air pressure was adjusted using a needle valve, and monitored with a digital barometer (VACUU·VIEW extended, VACUUBRAND). (b) Emission spectra of a neat **PtPL** film measured under various reduced air pressures.

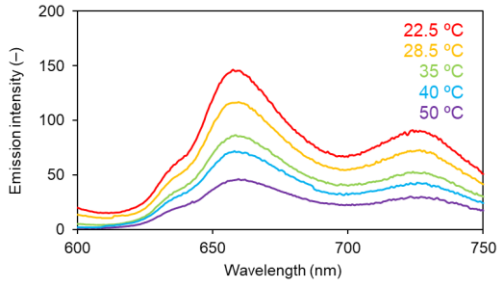


Figure S16. Emission spectra of a neat **PtPL** film measured at various temperatures in air. Temperature was controlled using a cryostat for spectrophotometer (CoolSpek USP-203-B, UNISOKU). Higher temperatures generally increase molecular motion, thereby enhancing non-radiative decay (i.e., quenching of phosphorescence).[S5]

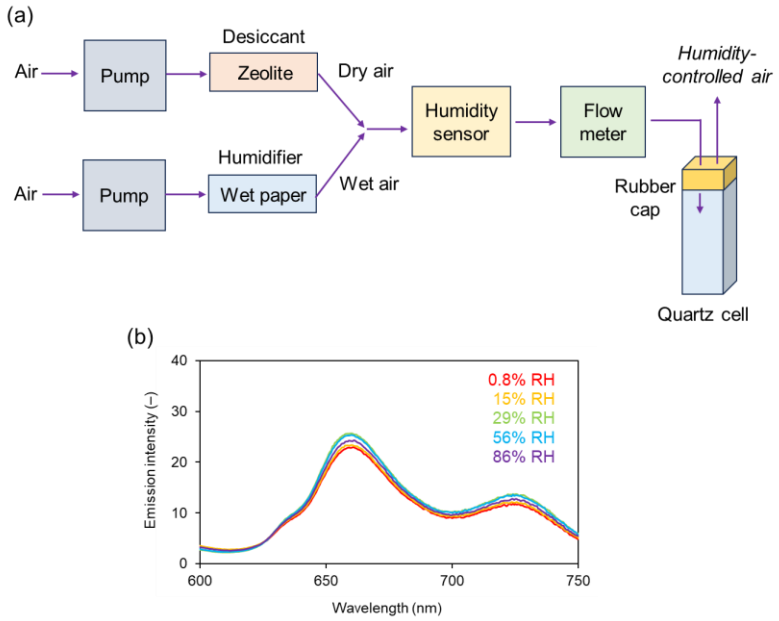


Figure S17. (a) Experimental setup for measuring emission spectra under various relative humidities (RH) in air. Ambient air was independently withdrawn using two electrically powered pumps (GSP-400FT, GASTEC) and separately processed to generate dry and humid air by passing through a desiccant (zeolite, synthetic, A-4, shot, 0.50–1.18 mm, Wako Pure Chemical Industries, Ltd.) column and a humidifier (wet paper) column, respectively. These two streams were then mixed at controlled flow rates, with the total flow rate fixed at 300 mL min^{-1}. The relative humidity was monitored using a digital humidity sensor (HMI-41, VAISALA). (b) Emission spectra of a neat **PtPL** film measured under various relative humidity conditions, showing little sensitivity to changes in relative humidity.

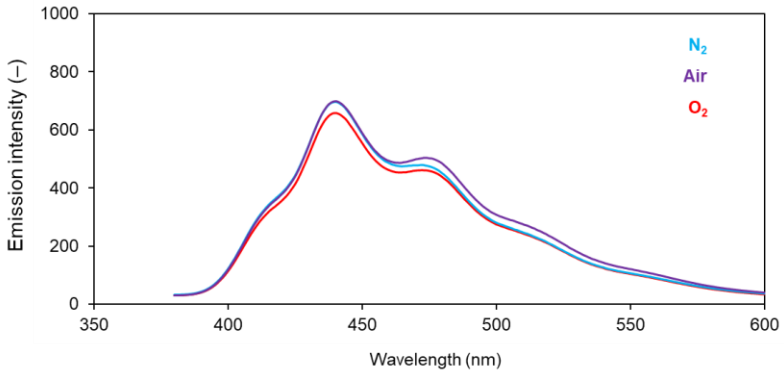


Figure S18. Emission spectra of **PyL** in the neat liquid state (λ_{ex} = 360 nm) under N_2, air, and O_2, showing little sensitivity to O_2 levels.

5. Statistical analysis of sensitivity

Table S2. O_2 sensitivity (I_0/I_{100}) of neat **PtPL** films (n = 6).

Film	1	2	3	4	5	6	Average	σ
I_0	218.2	262.0	196.0	224.7	219.8	285.0		
I_{100}	2.85	3.36	2.65	3.00	2.89	3.95		
I_0/I_{100}	76.5	77.9	74.1	74.9	75.9	72.2	75.3	1.8

I_0: Emission intensity at 655 nm under N_2 (λ_{ex} = 412 nm)

I_{100}: Emission intensity at 655 nm under O_2 (λ_{ex} = 412 nm)

σ: Standard deviation

Table S3. O_2 sensitivity (I_0/I_{100}) of mixed liquid films of **PtPL+PyL** (1:2, by weight) (n = 6).

Film	1	2	3	4	5	6	Average	σ
I_0	206.0	175.8	223.7	166.9	278.3	197.4		
I_{100}	1.83	1.53	1.95	1.51	2.57	1.67		
I_0/I_{100}	112.8	114.8	114.6	110.3	108.3	118.4	113.2	3.3

I_0: Emission intensity at 656 nm under N_2 (λ_{ex} = 360 nm)

I_{100}: Emission intensity at 656 nm under O_2 (λ_{ex} = 360 nm)

σ: Standard deviation

6. Microscopic analysis of PtPL-PTMSP composites

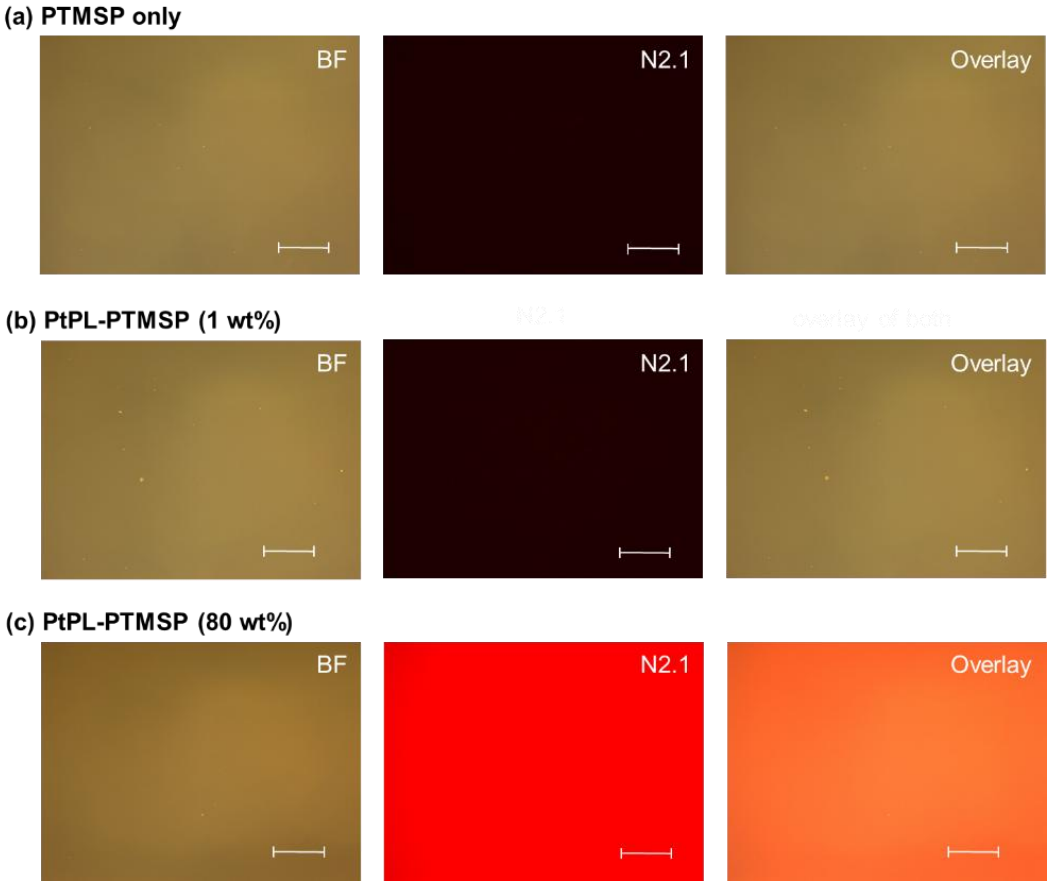


Figure S19. Fluorescence microscopy images of **PTMSP** and **PtPL-PTMSP** composite films (1 and 80 wt%). BF and N2.1 indicate bright-field and fluorescence images obtained using the N2.1 (red-channel) filter set, respectively. Scale bar: 200 μm. The obtained images show a homogeneous appearance, and no apparent phase separation was observed within the spatial resolution of this technique. These results indicate that the complexes are macroscopically well dispersed. Thus, it is likely that the emergence of multiple emissive states in the Stern–Volmer analysis originates from molecular-level heterogeneity, rather than from microscale or macroscale phase separation.

7. Analysis of residual solvent in a liquid film

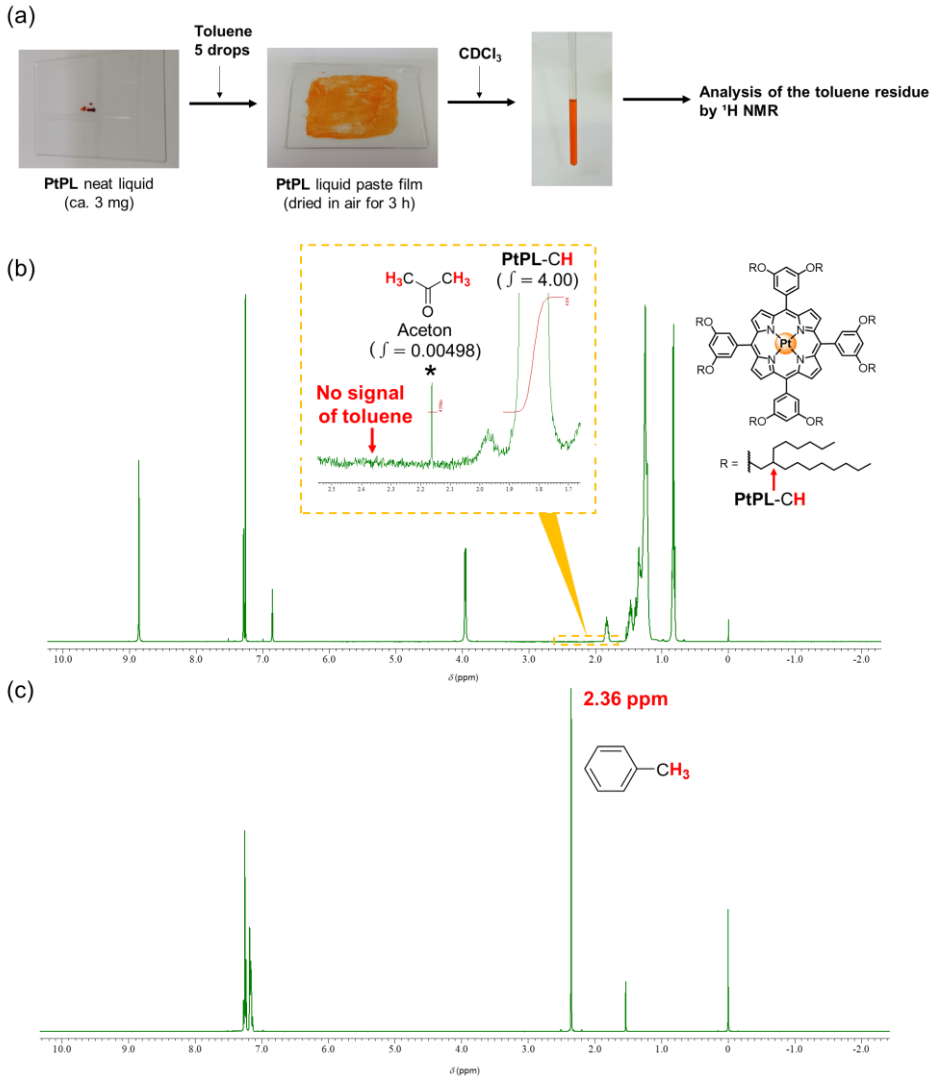
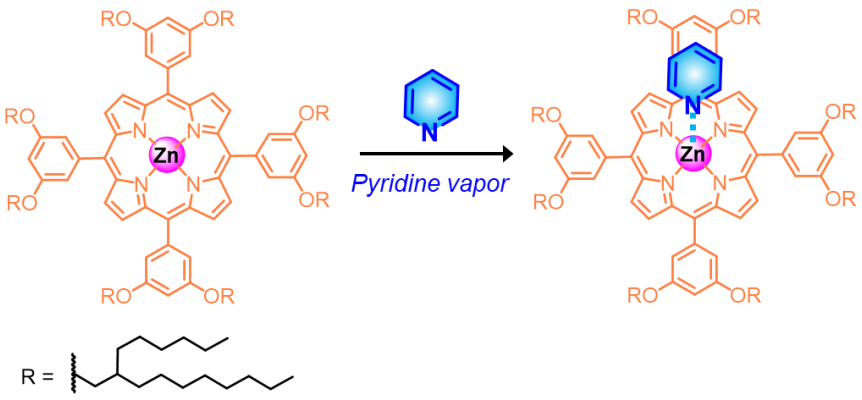


Figure S20. (a) Experimental procedure for ^{1}H NMR analysis of the toluene residue in a **PtPL** liquid film. The **PtPL** neat liquid (ca. 3 mg) was dissolved in toluene (five drops), spread on a glass plate (5.2 cm × 7.6 cm) with a spatula, and dried in air for 3 h. The resulting film was then dissolved in $CDCl_3$ for ^{1}H NMR analysis. (b) ^{1}H NMR spectrum of the **PtPL** film in $CDCl_3$, showing the absence of residual toluene. The asterisk (*) indicates the signal from residual acetone, a common contaminant in chemical laboratories; its amount was estimated by integration to be less than 0.1 mol% relative to **PtPL**. The amount of residual toluene was much smaller than this. (c) ^{1}H NMR spectrum of toluene in $CDCl_3$, showing an intense methyl proton signal at 2.36 ppm.

8. Coordination property of ZnPL



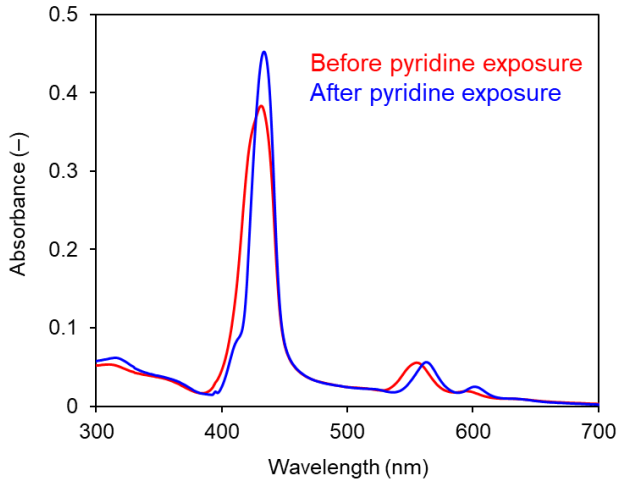


Figure S21. (a) Coordination of pyridine vapor by **ZnPL**, an analogue of the **PtPL**. (b) UV-vis absorption spectra of **ZnPL** neat film on quartz plate before and after exposure to pyridine vapor. The red-shift of Soret-band and Q-bands are characteristic to the coordination of ligand molecules on Zn(II) core.

9. References

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