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

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Solvent-free functional molecular liquids have attracted great interest as a new class of stimuli-responsive soft materials, yet their potential as optical gas sensors remains unexplored. Conventionally, luminescent organic molecules are employed in combination with a solid support or matrix. However, their performance in chemical sensing and optoelectronic devices is often hindered by adverse phenomena such as aggregation, concentration quenching, and photodegradation. In this study, we employ a strategy to isolate and wrap a phosphorescent Pt(II)-porphyrin core with bulky yet flexible branched alkyl chains, resulting in a solvent-free liquid at room temperature that demonstrates excellent properties for sensing oxygen (O_2) gas. Compared to reference material composed of Pt(II)-tetraphenylporphyrin and a highly gas-permeable polymer matrix, our Pt(II)-porphyrin liquid shows comparable sensitivity ($I_0/I_{100} = 75 \sim 90$), better linearity, and greater photostability in its O_2 -responsive phosphorescence. This is attributed to the high homogeneity and gas solubility of the liquids, as well as to the shielding of luminescent-core units by bulky alkyl chains. The liquid nature of the materials allows for ratiometric sensing, where the compatibility of a phosphorescent Pt(II)-porphyrin liquid (O_2 -sensitive) and a fluorescent alkyl-pyrene liquid (O_2 -insensitive) enables reproducible monitoring of O_2 concentration without specific calibration. Indeed, these results highlight the significant benefits of core-isolated luminescent liquids in diverse sensing applications.

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Introduction

Functional molecular liquids (FMLs) have recently become a transformative category in soft functional materials.¹ Within this group, alkyl- π liquids—solvent-free systems with π -conjugated molecular units isolated and wrapped by bulky yet flexible branched alkyl chains—provide tunable optoelectronic

properties and liquid-phase behaviors that differ from traditional solid-state frameworks.^{2–4} These alkyl- π liquids have unique physical properties: molecular uniformity, fluidity, deformability, miscibility, and guest solubility, *etc.* Owing to their abundant designability for functional core units, various types of FMLs have been developed to date (*e.g.*, tunable luminescence including phosphorescence,^{5–9} triplet-mediated photochemical functions,^{10,11} optoelectronic- and energy-related functions,^{12–14} permanent porosity and gas adsorption,^{15,16} and guest- and mechano-responsiveness^{17–21}). Among those intriguing FMLs, although alkyl- π liquids have been developed as stimuli-responsive liquid materials, to the best of our knowledge, no reports have demonstrated the utility of their liquid properties for optical gas sensing. In related works, Isoda *et al.* reported alkylated *N*-heteroacene liquids that change their fluorescence color upon exposure to HCl vapor, where the vapor responsiveness is accompanied by protonation-induced solidification of the liquids.^{20,21} Unique aspects of alkyl- π liquids include their ability to provide a distinct mode of operation as stable liquid media that retain responsiveness and miscibility. According to Henry's law, the dissolution of gas molecules into liquids is proportional to their partial pressure.²² This motivated us to elucidate the potential of alkyl- π luminescent liquids as optical gas sensors and unveil any fundamental

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aspects distinct from conventional solid support or matrix systems.

Luminescent organic molecules (LOMs) have been utilized for optical sensing of physical, chemical, and biological events.^{23–26} In particular, oxygen (O_2) is a vital target analyte^{27–29} due to strong connections with the atmospheric environment, energy, and life, as exemplified by the spatiotemporal visualization of aerodynamics,³⁰ fuel cell operation,³¹ and hypoxia in cancer cells.^{32,33} Among the various optical detection modes (*e.g.*, wavelength, intensity, ratiometric, frequency, upconversion, lifetime, *etc.*), monitoring of luminescence intensity is widely utilized in O_2 sensing due to the low cost and simplicity of the devices.^{24,29} Triplet photo-excited states of LOMs can be effectively quenched by O_2 , which makes their phosphorescence intensity sensitive to O_2 levels. The interaction dynamics and correlation between luminescence intensity and a quencher's concentration are described by the Stern–Volmer equation (eqn (1)).²⁷

$$I_0/I_x - 1 = K_{SV}[Q] \quad (1)$$

where I_0 and I_x are, respectively, the emission intensity in the absence (0%) and the presence ($x\%$) of a quencher (herein, O_2), and K_{SV} is the Stern–Volmer constant.

Since the luminescence of LOMs is generally maximized in their discrete (*i.e.*, non-aggregated) states except for rare cases where molecular motion is restricted within the aggregate or confinement,³⁴ optical sensing is often performed in a solution (dissolved in water or organic solvent) or a composite with solid support or matrix (*e.g.*, polymers,^{35–37} oxides,^{38,39} porous materials,^{40–42} and nanoparticles^{43–45}). Consequently, the performance of optical O_2 sensors is influenced not only by LOMs but

also by the compatibility and O_2 permeability of the solid support or matrix. Among various phosphorophores (*e.g.*, polycyclic aromatic carbons, transition metal complexes, and fullerenes), Pt(II) and Pd(II)-porphyrins are extensively studied for optical O_2 sensing because of their intense phosphorescence at room temperature.^{27,46–48} For example, Amao *et al.* found that Pt(II)-octaethylporphyrin (**PtOEP**) embedded in a highly gas-permeable poly(1-trimethylsilyl-1-propyne) (**PTMSP**)⁴⁹ shows considerable sensitivity to O_2 ($I_0/I_{100} = 225$).⁵⁰ In contrast, the same Pt(II)-porphyrin embedded in polystyrene or poly-(dimethylsiloxane) exhibits only moderate sensitivity ($I_0/I_{100} = \sim 5$).

Here, we present the first demonstration of an optical oxygen (O_2) sensing based on a phosphorescent core-isolated solvent-free liquid, utilizing a Pt(II)-porphyrin core ([5,10,15,20-tetrakis(3,5-bis((2-hexyldecyl)oxy)phenyl)porphyrinato]platinum(II) **PtPL**, Fig. 1). The liquid exhibits benchmark-level sensitivity ($I_0/I_{100} = 75 \sim 90$), superior linearity, and improved photostability compared to conventional reference materials composed of Pt(II)-tetraphenylporphyrin (**PtTPP**)⁵¹ and **PTMSP**. Additionally, by mixing **PtPL** with a fluorescent alkyl-pyrene liquid, we develop a robust ratiometric sensing that operates without specific calibration. This work provides novel insights into optical gas sensing, establishing luminescent solvent-free liquids not only as responsive FMLs but also as active media, opening a versatile pathway toward a future soft sensing platform.

Results and discussion

To obtain Pt(II)-porphyrin liquid **PtPL**, a free-base liquid porphyrin with 2-hexyldecyl branched alkyl chains¹³ was reacted

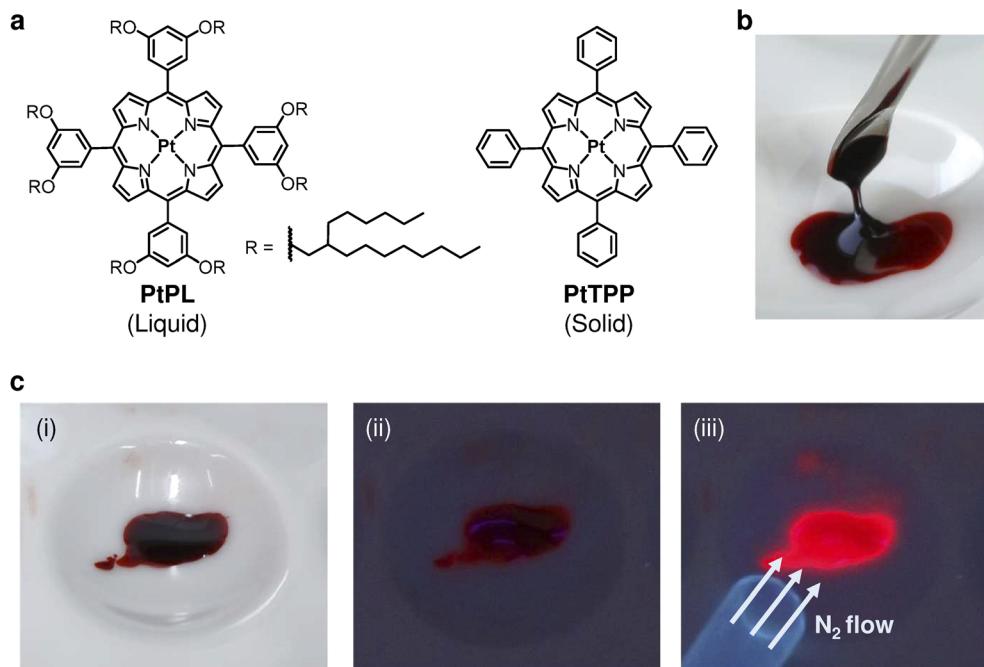


Fig. 1 (a) Chemical structures of Pt(II) porphyrins; alkylated liquid (PtPL) and solid PtTPP used in this study. (b) Photograph of PtPL at 20 °C showing solvent-free liquid appearance. (c) Phosphorescent property of PtPL observed under daylight in air (i), under UV light in air (ii), and under UV light with N_2 flow (iii).



with $\text{Pt}(\text{II})\text{Cl}_2$ in refluxing benzonitrile for 4–5 h under argon (Ar) (Fig. 1a).⁵¹ After purification and drying under vacuum, **PtPL** was obtained as a viscous red-orange liquid (Fig. 1b). Disappearance of the inner pyrrolic protons in the ^1H NMR spectrum of **PtPL** indicates the successful insertion of a $\text{Pt}(\text{II})$ ion into the porphyrin core, and the high-resolution mass spectrum of **PtPL** is in agreement with its chemical formula, $[\text{C}_{172}\text{H}_{285}\text{O}_8\text{N}_4\text{Pt}]^+$ (Fig. S2–S5). Under ultraviolet (UV) irradiation, an intense red emission was observed from **PtPL** when under an N_2 or Ar atmosphere (Fig. 1c). The emission was largely quenched in air due to energy transfer from photo-excited **PtPL** to O_2 . Thus, **PtPL** exhibits the expected phosphorescent properties for a long-lived triplet excited state. Even though branched alkyl chains surround the $\text{Pt}(\text{II})$ porphyrin core, small gas molecules can access the core through a mechanism akin to the facilitation of pyridine vapor into $\text{Zn}(\text{II})$ liquid porphyrin,¹³ which is structurally similar to **PtPL** (see Fig. S6–9 and 21).

It is revealed that **PtPL** is a stable liquid at room temperature and shows optical properties in neat state almost identical to **PtTPP** in a diluted toluene solution (Fig. 2). A sample of **PtPL** sandwiched between glass plates is fluidic, and its cross-polarized optical microscopy (POM) image shows no birefringence, supporting the absence of long-range ordered domains (Fig. 2a). Differential scanning calorimetry (DSC) thermogram of **PtPL** shows only a reversible glass transition temperature (T_g)

at around $-40\text{ }^\circ\text{C}$; thus, **PtPL** maintains a liquid state above that temperature (Fig. 2b). Absorption and emission spectra of **PtPL** in neat liquid are similar to those of **PtPL** and **PtTPP** in toluene due to the bulky alkyl chains isolating the $\text{Pt}(\text{II})$ -porphyrin core from the surrounding environment (Fig. 2c and d). Note that the luminescent lifetime and quantum yield of **PtPL** were slightly longer and larger than those of **PtTPP** in toluene (Fig. S11 and Table S1).

As shown in Fig. 3a–c, the emission from neat film **PtPL** is quenched (signal intensity is reduced) as the concentration of O_2 in the atmosphere increases from 0% to 100%. There is a certain response to 0.03% O_2 , and the emission intensity halved at an O_2 concentration of 1% (Fig. 3a). The Stern–Volmer plot of neat film **PtPL** shows linear correlations between O_2 concentration (x-axis) and $I_0/I_x - 1$ (y-axis). The value of I_0/I_{100} is often used in the literature to represent O_2 sensitivity, and $I_0/I_{100} = \sim 90$ is much greater than most phosphorescent O_2 sensing materials ($I_0/I_{100} = 5 \sim 10$).^{27,35,42} As described above, Amao *et al.* reported that **PtOEP** embedded in polystyrene or poly-(dimethylsiloxane) shows modest sensitivity ($I_0/I_{100} = \sim 5$).⁵⁰ Whereas, significant sensitivity to O_2 ($I_0/I_{100} = 225$) was obtained when **PtOEP** was embedded in a highly gas-permeable **PTMSP** polymer. Thus, our solvent-free liquid **PtPL** is a suitable medium for accommodating O_2 molecules from the gas phase. The higher sensitivity of Amao's film could be ascribed to

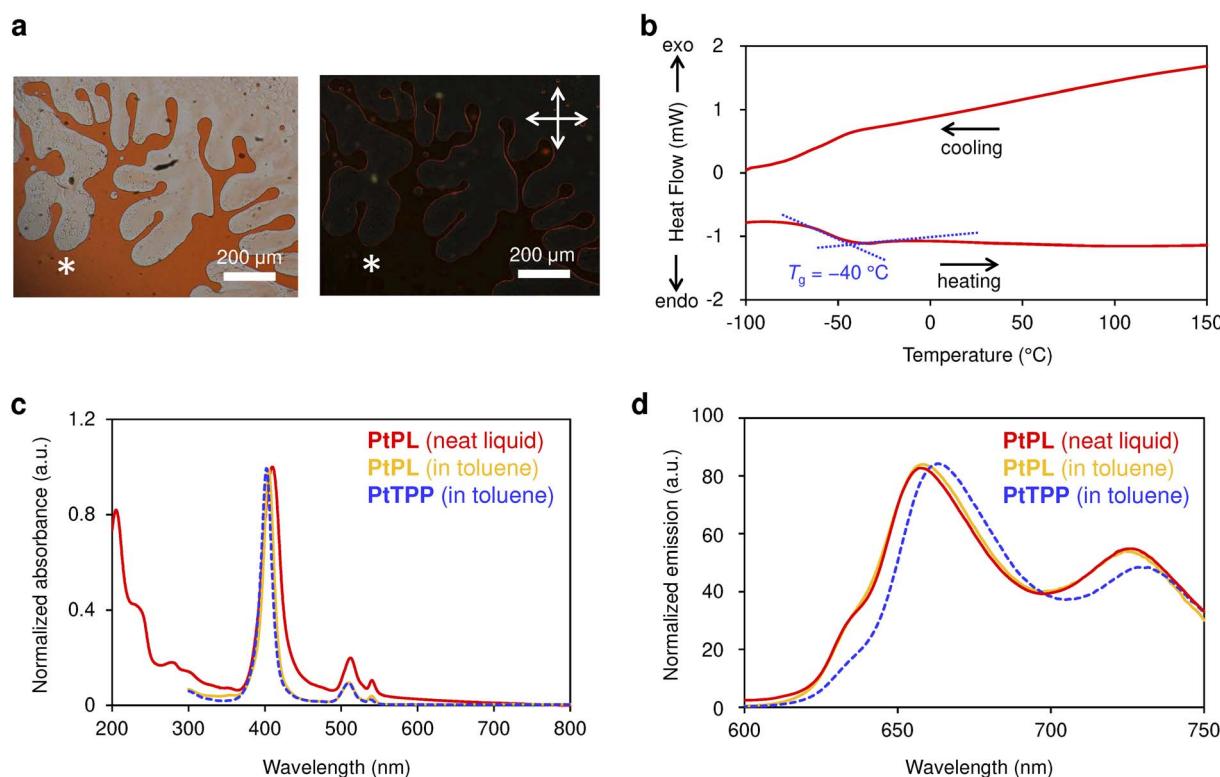


Fig. 2 (a) Optical microscopy images of **PtPL** sandwiched between glass plates without (left) and with (right) cross polarizers. Asterisks (*) represent the identical positions within the samples. (b) DSC thermogram in the 2nd heating and cooling trace of **PtPL** recorded under N_2 at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$. (c) Absorption spectra of **PtPL** in neat liquid state. The absorption spectra of **PtPL** and **PtTPP** in toluene (10^{-6} M) are shown for comparison. (d) Emission spectra of **PtPL** in neat liquid state ($\lambda_{\text{ex}} = 410\text{ nm}$) under argon (Ar). The emission spectra of **PtPL** and **PtTPP** in toluene (10^{-6} M) under Ar are shown for comparison. Note that these emissions were largely quenched under air (see Fig. S12–14).



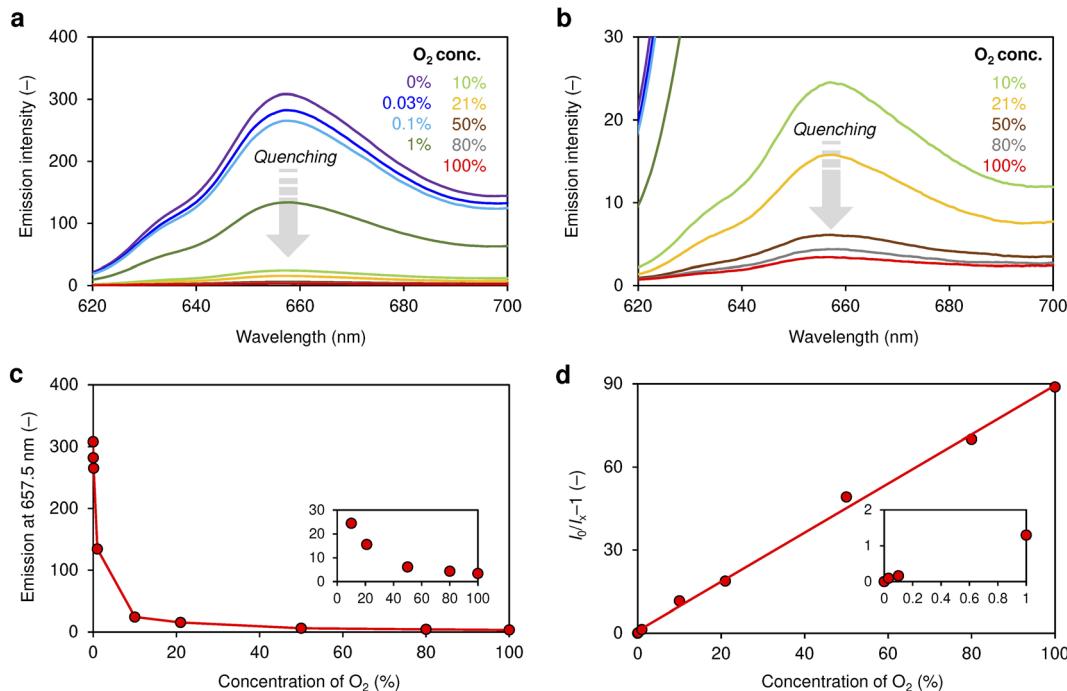


Fig. 3 (a and b) Emission spectra of a neat film PtPL ($\lambda_{\text{ex}} = 412$ nm) measured under various O₂ concentrations (a; with higher emission intensities, b; emission intensities lower than 30). See Fig. S10 for photographs illustrating the emission changes of neat PtPL films at different O₂ levels. (c) Plot of O₂ concentration vs. emission intensity ($\lambda_{\text{em}} = 657.5$ nm) in a neat film PtPL. Inset shows intensities lower than 30. (d) Stern–Volmer plot of a neat film PtPL ($\lambda_{\text{em}} = 657.5$ nm) for O₂ sensing. Inset shows the plot for lower O₂ concentration than 1%. It is worth noting that the phosphorescence of PtPL shows little sensitivity to humidity, whereas it is sensitive to temperature and air pressure (see Fig. S15–17).

the excellent gas permeability of **PTMSP** as well as minimum substituents around the Pt(II)-porphyrin unit, enabling efficient energy transfer to proximal O₂. However, it should be noted that the porphyrin concentration in the Amao's film was very dilute (*ca.* 2.9×10^{-5} mol dm⁻³, estimated as *ca.* 0.003 wt% based on molecular weight of the **PtOEP** (727.8 g mol⁻¹) and density of **PTMSP** (0.7 g cm⁻³)⁵²), presumably for preventing undesirable aggregation of porphyrins in the polymer matrix. Therefore, compared to the neat liquid **PtPL**, the brightness of the **PtOEP-PTMSP** film should be modest.

To investigate the effect of the bulky alkyl side chains compared to a porous polymer matrix, the O₂ sensing performance of the neat liquid **PtPL** was compared with **PtTPP-PTMSP** and **PtPL-PTMSP** composites. A solution of **PtTPP** and **PTMSP** was spin-coated on a quartz substrate, and the optical properties of the thin films were investigated (Fig. 4a). Absorption signals corresponding to the Soret-band ($\lambda_{\text{max}} = 401$ nm) of **PtTPP** linearly increased when the amount of **PtTPP** was increased from 0.2 to 20 wt% (Fig. 4b). However, the absorption signals did not grow beyond 20 wt%, suggesting aggregation or precipitation of **PtTPP** either within or outside the polymer matrix. In contrast, absorption signals of **PtPL** blended into **PTMSP** ($\lambda_{\text{max}} = 406$ nm) did not saturate even at 80 wt% owing to the absence of aggregation of **PtPL** in the **PtPL-PTMSP** composite (Fig. 4c). Composite films of **PtTPP-PTMSP** (1, 5, 20, and 50 wt%) exhibited slightly better sensitivity to O₂ ($I_0/I_{100} = \sim 120$) than a neat liquid film of **PtPL** ($I_0/I_{100} = \sim 90$), which can be attributed to the higher gas permeability of **PTMSP**.

compared to **PtPL** (Fig. 4d). The linearity of each plot was quantitatively assessed using the coefficient of determination (R^2) obtained from linear fitting, showing moderate linearity ($R^2 = 0.84$ –0.97). In contrast, **PtPL-PTMSP** displays clear composition-dependent behavior (Fig. 4e). At low loadings (1, 5, and 20 wt%), a nonlinear response with high sensitivity is observed. This high sensitivity can be attributed to the high gas permeability of the **PTMSP** matrix as well as the increased number of O₂ molecules available per **PtPL** molecule. Another possible interpretation is that **PtPL**, bearing branched alkyl chains reminiscent of those typically present in plasticizers, may slightly modify the local polymer environment, potentially facilitating O₂ diffusion. By contrast, at higher loadings (50 and 100 wt%), the Stern–Volmer plots exhibit excellent linearity ($R^2 > 0.99$), while maintaining a sufficiently high level of sensitivity compared with other materials, despite some reduction. Such excellent linearity is advantageous for the quantification of a wide O₂ range based on two-point calibration. Downward-curved Stern–Volmer plots are commonly observed in sensor films and are often attributed to the presence of multiple emissive states with different luminescence lifetimes and/or quenching efficiencies within heterogeneous matrices.^{27,53–56} Thus, the improvement of linearity is likely due to the increased homogeneity of the sensing phase upon reducing the influence of the polymer matrix, which suppresses microenvironmental heterogeneity. Although neat liquid **PtPL** shows the lowest sensitivity among the samples in Fig. 4e, this limitation is addressed in the blended liquid system discussed in a later

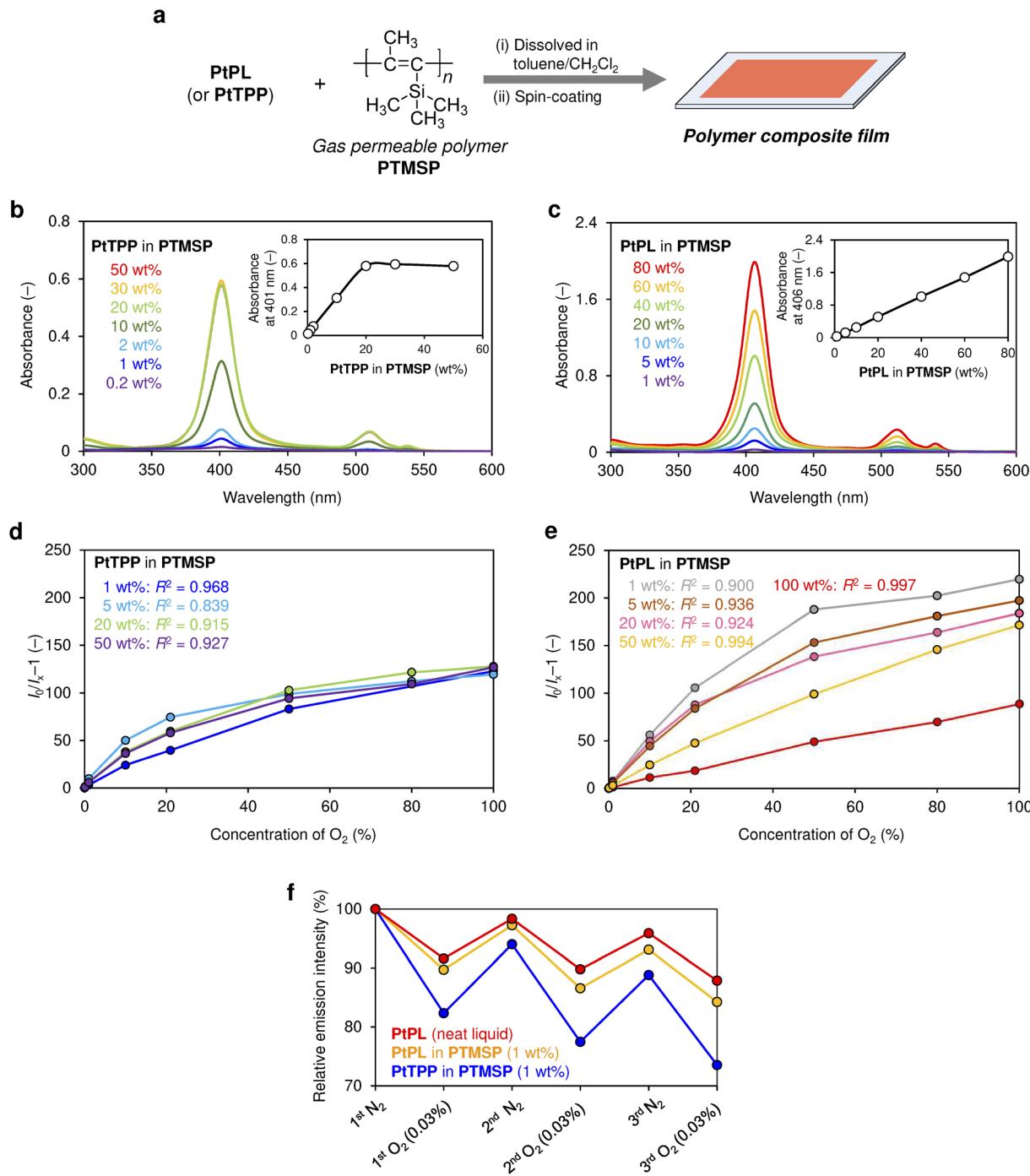


Fig. 4 (a) Preparation of polymer composite films. (b) Absorption spectra of PtTPP-PTMSP composite film with various amounts of PtTPP. (c) Absorption spectra of PtPL-PTMSP composite film with various amounts of PtPL. (d) Stern-Volmer plots of PtPL composite films (1, 5, 20, and 50 wt%). R^2 denotes the coefficient of determination for the linear fit. (e) Stern-Volmer plots of neat liquid PtPL (100 wt%) and PtPL-PTMSP composite films (1, 5, 20, and 50 wt%). (f) Decay of emission intensity upon repeated exposure to excited beam irradiations under N_2 and 0.03% O_2 .

section, where both high sensitivity and good linearity are simultaneously achieved.

Notably, neat liquid **PtPL** shows better photostability than **PtTPP-PTMSP** upon repeated measurements, which can be ascribed to protecting the Pt(II)-porphyrin unit by the bulky alkyl chains (Fig. 4f). Although fluorinated porphyrins are known to

show improved photostability,⁵⁷ fluorinated organic compounds potentially cause environmental concerns due to poor biodegradability. The core-shielding effect of phosphorescent liquids (*e.g.*, **PtPL**) by hydrocarbon alkyl chains is advantageous in this regard. Toward practical implementation, photostability could be further improved by elongating or

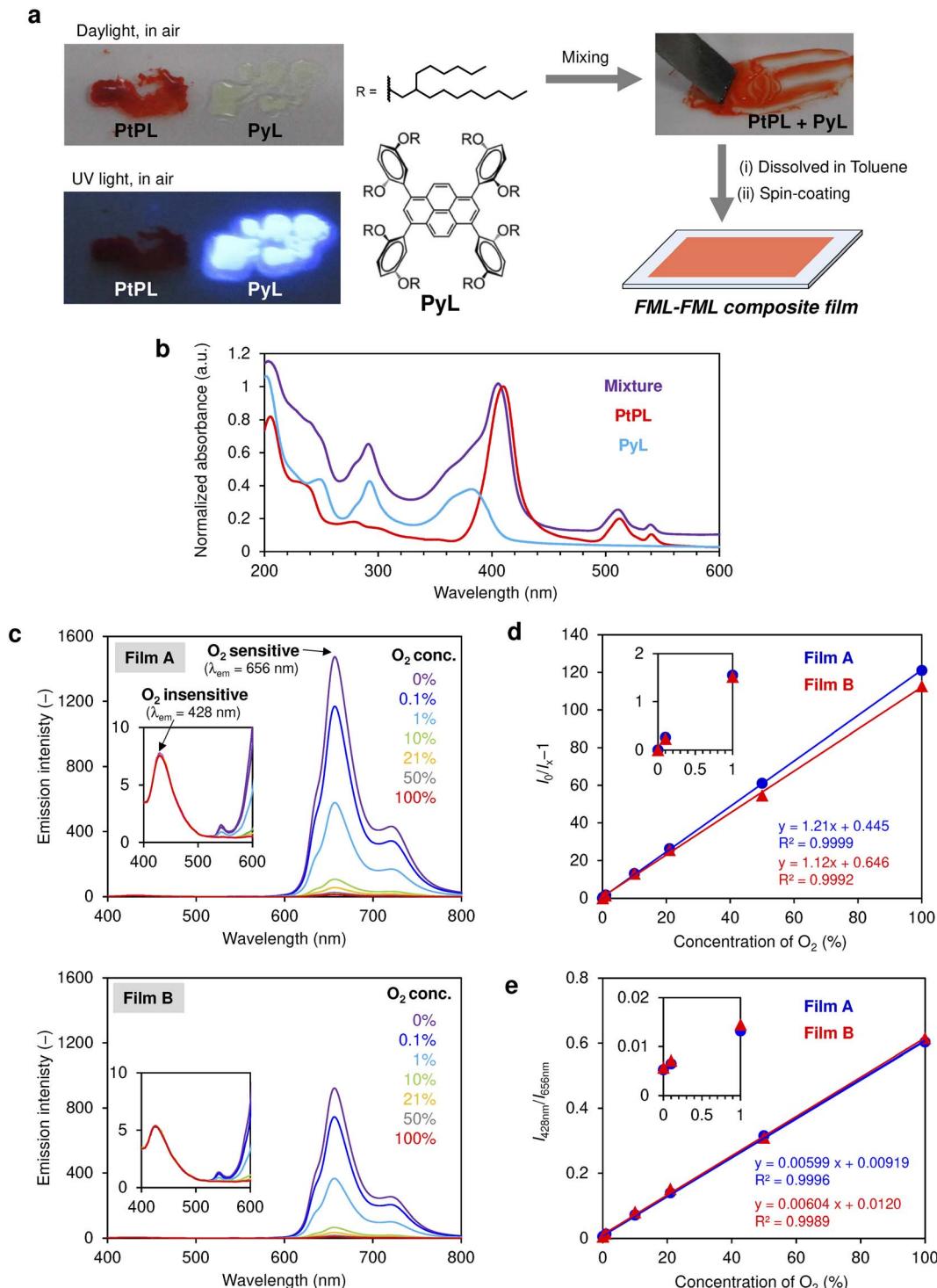


Fig. 5 (a) Blending of phosphorescent liquid PtPL and fluorescent liquid PyL. (b) Absorption spectrum of the mixed liquid film of PtPL+PyL (1 : 2, by weight) measured in air. For comparison, the absorption spectra of the individual neat liquids (PtPL and PyL), measured separately, are also shown. (c) Emission spectra ($\lambda_{\text{ex}} = 360 \text{ nm}$) of the mixed liquid film of PtPL+PyL (1 : 2, by weight) under various O_2 levels. The excitation wavelength was selected to simultaneously excite both PtPL and PyL while minimizing photobleaching caused by shorter-wavelength UV irradiation. Based on emission intensity, film A has approximately double the loading of liquids compared to film B. (d) Stern–Volmer plots obtained from phosphorescence ($\lambda_{\text{em}} = 656 \text{ nm}$) of films A and B. (e) Ratiometric plots obtained from O_2 -insensitive fluorescence ($\lambda_{\text{em}} = 428 \text{ nm}$) and O_2 -sensitive phosphorescence ($\lambda_{\text{em}} = 656 \text{ nm}$) of films A and B.

densifying the branched alkyl chains; however, this may adversely affect O_2 sensitivity because of reduced energy transfer efficiency. Therefore, photostability and sensitivity should

be balanced depending on the aim of the application. We note that the present study focused on the equilibrium response to O_2 , and response time was not evaluated due to the

unavailability of appropriate equipment. Overall, these studies elucidated, for the first time, that phosphorescent solvent-free liquids can be a promising platform for creating advanced optical gas sensors with high dye-loading amounts, excellent sensitivity, linearity, and photostability.

Finally, ratiometric optical O₂ sensing was performed simply by blending **PtPL** with an alkylated pyrene fluorescent (O₂-insensitive) liquid **PyL**⁵⁸ (Fig. 5a and S18). The emission intensity of dye-loaded polymeric films can be influenced by various factors such as beam intensity, film thickness, and homogeneity of LOMs in the polymer matrix, and the accurate determination of I_0 (*i.e.*, emission intensity in the absence of O₂) is indispensable for reliable quantification of O₂.^{24,27,59} To avoid frequent calibrations, ratiometric O₂ detection based on phosphorescent (O₂ sensitive) and fluorescent (O₂ insensitive) dyes is a promising approach.^{60–62} In the present study, ratiometric O₂ sensing was achieved simply by blending two types of liquids. Since both **PtPL** and **PyL** are hydrophobic and have similar liquid physical properties due to the same 2-hexyldecyl branched alkyl chains, the two liquids are miscible with each other,⁶³ and the blended liquid contains absorption profiles from both individual components (Fig. 5a and b). Two films (A and B) with different loadings were prepared from the blended liquid of **PtPL+PyL** (1 : 2, by weight) and investigated for ratiometric O₂ sensing (Fig. 5c). Upon excitation at 360 nm, the fluorescence ($\lambda_{\text{em}} = 428$ nm) from **PyL** is insensitive to O₂, while the phosphorescence from **PtPL** ($\lambda_{\text{em}} = 656$ nm) is sensitive to O₂. Stern–Volmer plots of the two films are highly linear ($R^2 > 0.999$), and the value of I_0/I_{100} in film A reaches ~ 120 (comparable to that of **PtPPP–PTMSP** in Fig. 4d). A increase in O₂ sensitivity in the liquid blend system (compared with a neat liquid film of **PtPL**) may originate from enhanced O₂ solubility and/or diffusion in the liquid upon blending with the relatively smaller-sized molecule **PyL**. Stern–Volmer plots of films A and B are slightly different, presumably due to differences in the loading amount of liquid or experimental errors. Nevertheless, when ratios of phosphorescence and fluorescence are plotted against O₂ levels, films A and B demonstrate almost identical linear lines despite nearly double the difference in their emission intensity. Thus, the miscibility of liquids offers reliable ratiometric O₂ sensing without the need for elaborate synthesis, fine-tuning of film loading, and frequent calibrations.

To confirm the enhanced sensitivity in the blended system, the sensitivity (I_0/I_{100}) of six independently prepared **PtPL** and **PtPL+PyL** films was statistically analyzed (Tables S2 and S3). As a result, the average sensitivity of **PtPL+PyL** ($I_0/I_{100} = 113.2$, $\sigma = 3.3$) was reproducibly higher than that of **PtPL** ($I_0/I_{100} = 75.3$, $\sigma = 1.8$). The sensitivity of **PtPL** in Fig. 3d ($I_0/I_{100} \approx 90$) is slightly higher than that shown in Table S2 ($I_0/I_{100} = 75.3$ on average). This moderate difference can be attributed to cumulative decay of the emission intensity upon repeated exposure to excitation light (see Fig. 4f). The data in Fig. 3 were obtained at multiple O₂ levels, with 100% O₂ measured at the final stage of the experiment, which likely led to a reduction in the I_{100} value compared to its actual value. In contrast, the data in Table S2 were obtained from only two measurements, namely under N₂ for I_0 and

under O₂ for I_{100} . Therefore, the values reported in Table S2 are considered to be more reliable.

Conclusions

This work reveals numerous benefits of luminescent core-isolated solvent-free liquids for optical gas sensing applications. Due to the liquid characteristics (*e.g.*, homogeneity, gas solubility, diffusion, and miscibility) and the shielding effects of the phosphorescent-core units by the bulky yet flexible alkyl chains, the Pt(II) porphyrin liquid demonstrates exceptional sensitivity, linearity, photostability, and calibration-free ratiometric operations in phosphorescent O₂ sensing. The concept presented in this study is broadly applicable to other functional π -chromophores and gaseous species, paving the way for a new platform for optical sensing materials.

Methods

Synthesis of **PtPL**

A previously reported liquid free-base porphyrin¹³ was used to prepare a liquid Pt(II) porphyrin (**PtPL**). Typically, the alkylated free-base porphyrin (140 mg, 0.055 mmol) and Pt(II)Cl₂ (147 mg, 0.55 mmol) were refluxed in dry benzonitrile (15 ml) under an Ar atmosphere,⁵¹ and the progress of metalation was monitored by thin-layer chromatography (TLC) and variation in the Q-bands in the UV-vis spectrum. After the reaction (*ca.* 4–5 h) was completed, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (eluent: 10–20% CH₂Cl₂ in *n*-hexane). After drying under vacuum at 40 °C, a red-orange liquid (**PtPL**) was obtained (yield: 80%). ¹H NMR (400 MHz, CDCl₃) in ppm: 8.86 (s, 8H, pyrrole β -H), 7.29 (d, $J = 2.4$ Hz, 8H, Ar-H), 6.86 (t, $J = 2.0$ Hz, 4H, Ar-H), 3.96 (d, $J = 5.6$ Hz, 16H, OCH₂), 1.83 (m, 8H, CH), 1.35–1.23 (m, 192H, CH₂), 0.82 (m, 48H, CH₃). ¹³C NMR (100 MHz, CDCl₃) in ppm: 158.68, 143.04, 140.62, 130.64, 122.18, 113.44, 101.21, 71.27, 38.10, 31.89, 31.86, 31.42, 30.03, 29.71, 29.59, 29.33, 26.87, 22.66, 14.11. HR-ESI-MS (*m/z*): calculated for [C₁₇₂H₂₈₅O₈N₄¹⁹⁴Pt]⁺ = 2729.1639 *m/z*, found 2729.1736 *m/z*.

Preparation of liquid films

Liquid films for O₂ sensing were obtained by spin-coating a toluene solution of liquid materials onto a quartz substrate. Typically, it took 5 seconds to reach 3000 rpm, and the film was dried at 3000 rpm for 60 seconds. Thus, homogeneous liquid films were obtained. The loading amount of the liquid film was adjusted by changing the concentration of the toluene solution or repeating the spin-coating process. A blended liquid film of **PtPL+PyL** was prepared from a solution of **PtPL** and **PyL** in toluene (1 : 2, by weight). Liquid films were dried in air for more than 12 h before spectroscopic measurements. See Fig. S20 for a discussion of residual solvent in a liquid film.

Preparation of polymer films

Stock solutions of **PtPL** in dichloromethane (5.00 mg ml^{−1}) and **PTMSP**^{49,64} in toluene (10.0 mg ml^{−1}) were mixed at various



ratios. The mixed solutions were spin-coated on a quartz substrate, as described above. In the case of **PtTPP**, a more diluted stock solution (1.67 mg ml⁻¹) in dichloromethane was used due to limited solubility. See Fig. S19 for a discussion on the homogeneity of **PtPL** in polymer films.

O₂ sensing

The porphyrin film containing quartz substrate was placed in a quartz cell (1 cm × 1 cm), as illustrated in Fig. S1. The quartz cell was capped with a rubber septum, and then dry N₂ or Ar containing various concentrations of O₂ was flowed through the cell using inlet and outlet needles to measure emission spectra (FP-8300 spectrophotometer, JASCO) under controlled O₂ levels. The typical flow rate was 100 ml min⁻¹, and 5 min flow was sufficient to replace the interior gases of the small cell (~3 ml). The flow rate was adjusted and monitored using a float-ball-type flow meter (KOFLOCK) and a digital flow meter (7000 flowmeter, Ellutia). Dry N₂ and O₂ from laboratory lines were used as 0% and 100% O₂, respectively. Ambient air supplied by a battery-powered pump (GSP-400FT, GASTEC) was regarded as 21% O₂. For 0.1%, 1%, and 10% O₂, standard gases supplied from high-pressure gas cylinders were directly used. For 50% and 80% O₂, dry N₂ and O₂ from laboratory lines were mixed at appropriate flow rates (monitored by digital flow meters). Similarly, 0.1% O₂ with dry N₂ dilution yielded 0.03% O₂.

Author contributions

A. G. and T. M. synthesized porphyrins. A. G., S. I., and T. M. performed sensing experiments. M. K. C. and D. T. P. conducted material characterization. A. S. measured transient emission properties. T. H. provided PTMSP and discussed the results of O₂ sensing. S. I. wrote the manuscript with input from all other authors. All authors read and approved the final version of the manuscript. S. I. and T. N. designed and directed the research.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data presented in this study are available upon reasonable request from the corresponding authors. Supplementary information (SI) is available for materials, methods, characterizations, photophysical and statistical analyses, and miscellaneous data. See DOI: <https://doi.org/10.1039/d5sc08398b>.

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