# Preparation and Optical Properties of Polyimide Films Linked with Porphyrinato Pd (II) and Pt (II) Complexes Through a Triazine Ring and Application Toward Oxygen Sensors

**Takeshi Kimura,[1] Shuichi Watanabe,[1] Shin-ichi Sawada,[2] Yuji Shibasaki,[2] Yoshiyuki Oishi[2]**

[1]Center for Instrumental Analysis, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan
[2]Department of Chemistry & Biological Sciences, Faculty of Science & Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan
Correspondence to: T. Kimura (E-mail: kimura@iwate-u.ac.jp) or Y. Shibasaki (E-mail: yshibasa@iwate-u.ac.jp) or Y. Oishi (E-mail: yoshiyu@ iwate-u.ac.jp)

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**ABSTRACT:** 5-(3-Aminophenyl)-10,15,20-tri(4-methylphenyl) porphyrinato Pd (II) and Pt (II) complexes (**2a-Pd**) and (**2a-Pt**), respectively, were prepared from 5-(3-nitrophenyl)-10,15,20-tri(4-methyl-phenyl)-porphyrin via two-step reactions, and reacted with cyanuric chloride to produce corresponding porphyrin derivatives (**3a-Pd**) and (**3a-Pt**) with a dichlorotriazine ring. Aromatic polyimides were prepared using diamine (**4**); triazine dichlorides having porphyrin units (**3a-Pd**), (**3a-Pt**), (**3c-Pd**), and (**3c-Pt**); fluoro-functionality 6-(*p*-perfluorononenyl oxyanilino)triazine-2,4-dichloride (**6**); and tetracarboxylic dianhydride (**5**) in *N*-methyl-2-pyrrolidone (NMP) at an elevated temperature up to 300 °C. The resulting viscous polymeric solution was cast on a glass plate, affording well-proportioned reddish transparent films with number-average molecular weights of 25,000–38,000. Glass transition temperatures of the polymers were ~230 °C; the films were stable up to 400 °C in air. The film emission spectra showed a broad peak ~670 nm, similar to those of porphyrins (**2a-Pd**) and (**2a-Pt**) dispersed in a polystyrene matrix. While the luminescence of these polymer films was quenched with oxygen, it rapidly recovered under a deoxygenated atmosphere. The polyimide film sensitivity to oxygen was higher under low oxygen concentrations than those of porphyrins (**2a-Pd**) and (**2a-Pt**) dispersed in polystyrene. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *55*, 1086–1094

**KEYWORDS**: gas permeation; luminescence; polyimides; porphyrin complex; thermostability

**INTRODUCTION** Porphyrins and their metalated derivatives have attracted much attention for their structural properties and potential applications in many photoelectronic materials.[1–5] In the past few decades, many porphyrin derivatives have been studied for their biological and pharmaceutical activities.[6,7] In addition to simple porphyrins, covalently linked porphyrins, multiporphyrin oligomeres, widespread porphyrine nanosheets, and related compounds have been constructed to develop new types of functional materials.[8–16] These molecules are also used to investigate the mechanism of natural photosynthetic systems and to progress development of sensors, optoelectronic devices, photovoltaic cells, and photo-catalysis of photodynamic therapies for cancer. One of the most useful characteristics of porphyrins and metalloporphyrins is strong emission in solution and solid states. Porphyrinato palladium (II) and platinum (II) complexes are known to show strong emissions that can be quenched in the presence of oxygen; hence, these compounds can be used for molecular recognition in sensor systems.[17] In order to construct sensors using porphyrin and metalloporphyrin derivatives, these luminous compounds should be deposited on a basal plate or included in polymeric compounds. In addition, polymers as supports for luminous molecules are easily shaped as thin films and possess high molecular permeability. Recently, Amao et al. reported porphyrin-oxygen sensors supported by thin polystyrene and other polymer films, which contained porphyrinato palladium (II) or platinum (II) complexes in a noncovalent manner[18–20] and used in a velocity measurement device for airplanes as pressure sensitive paint.[21]

The three chlorine atoms in cyanuric chloride are known to be able to be substituted in a step-by-step manner through a temperature-controlled reaction.[22–24] This procedure has been applied to the synthesis of polymers, dendrimers, chiral molecules, and related supramolecules.[1,25–27] Polyimide (PI) is one of the most useful polymers due to its unique properties such as thermostability, transparency, low-dielectricity, and low

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coefficient of thermal expansion.[28–30] Therefore, this polymer is widely used for films, coatings, insulating material, electronic components, and other functional applications. PI is generally prepared by the reaction of tetracarboxylic anhydrides and diamines, allowing mono-substituted triazine dichloride to be used as one of the building blocks. We have reported the synthesis and properties of triazine-containing thermoplastic[31] and thermosetting[32] PIs with unusual high solubility in organic solvents and good mechanical properties.

In the course of our study of phthalocyanine and tetraazaporphyrin derivatives,[33–36] we have thought that PI films have potential applications in sensors, optoelectronic devices, and photovoltaic cells if porphyrin derivatives could be conjugated to the PI backbone. Therefore, we designed PI directly bonded to metalloporphyrin derivatives as functional groups and, in this case, the triazine ring served as a linker between the polymer main-chains and porphyrin moieties. In this article, we report (1) the construction of porphyrinato palladium (II) and platinum (II) derivatives with a dichlorotriazine unit as building block for PIs, (2) the preparation of the aromatic PI films directly linked with porphyrin derivatives via the triazine spacer, and (3) the examination of oxygen sensitivity of the films by observing the emission of metalloporphyrins with palladium (II) and platinum (II) metals.

## EXPERIMENTAL

### Materials

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (**5**) was purchased from Aldrich and purified by sublimation prior to use. 4,4'-(Hexafluoroisopropylidene)bis(*p*-phenyleneoxy)dianiline (**4**) was kindly donated by Seika, Japan. 4,6-Dichloro-*N*-(4-((1,1,1,4,5,5,5-heptafluoro-3-(perfluoropropan-2-yl)-4-(trifluoromethyl)-pent-2-en-2-yl)oxy)phenyl)-1,3,5-triazin-2-amine (**6**) was kindly donated by NIPPON FUSSO and used as received. *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was kindly donated by Shin-Etsu Chemical and used as received.

### Measurements

NMR spectra were measured with a Bruker AVANCE 500 III spectrometer and a Bruker AC 400 spectrometer. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer and a Hitachi M2000 mass spectrometer. Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry was examined with a Bruker BIFLEX (III) mass spectrometer. UV–vis spectra were recorded with a JASCO Ubest V-570 spectrophotometer. For IR measurements, a JASCO FT/IR-4200 spectrometer was employed. Emission spectra were measured by a JASCO FP-6500 spectrometer. The number-average molecular weights ($M_n$), weight-average molecular weights ($M_w$), and dispersities ($M_w/M_n$) were determined using a Tosoh HLC-8220 gel permeation chromatograph (GPC) equipped with refractive index and UV detectors, and a consecutive polystyrene gel column (TSK-GEL $\alpha$-M × 2) at 40 °C and eluted with *N*-methylpyrollidone (NMP) at a flow rate of 1.0 mL/min. The inherent viscosities of the polymers were determined for solutions of 0.1 g/20 mL in NMP at 30 °C using an Ostwald viscometer. Thermal analyses were performed on a Seiko thermal analyzer (SCC 5200 system) at a heating rate of 10 °C/min for thermogravimetric analysis (TGA by TG/DTA 320) under air or nitrogen. Differential scanning calorimetry (DSC) was analyzed on a Shimadzu DSC-60 at a heating rate of 20 °C/min under nitrogen.

### Aminophenylporphyrin Derivatives

5-(3-Aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (**2a**),[37] 5-(4-aminophenyl)-10,15,20- tris-(4-methylphenyl)-porphyrin (**2b**),[40] and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**2c**)[41] were prepared by the methods reported previously.

### Pt(II)-5-(3-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (2a-Pt)

5-(3-Aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (**2a**) (0.1342 g, 0.2000 mmol), platinum bis(acetylacetonate) (0.0463 g, 0.150 mmol), and phenol (20 mL) were placed in a glass reactor and the mixture was refluxed for 24 h. After cooling to room temperature, hot water and aqueous sodium hydroxide solution were added and the precipitate was filtered. The residue was dissolved in $CHCl_3$ and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The product was purified by column chromatography (silica gel, $CHCl_3$) to afford orange crystals of the title compound in 52% yield (0.0897 g).

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.67 (s, 9H, $CH_3$), 3.87 (bs, 2H, $NH_2$), 7.04 (d, $J = 7.9$ Hz, 2H, Ar-H), 7.43–7.49 (m, 2H, Ar-H), 7.51 (d, $J = 7.4$ Hz, 6H, Ar-H), 7.56 (d, $J = 7.4$ Hz, 1H, Ar-H), 8.03 (d, $J = 7.4$ Hz, 6H, Ar-H), 8.80 (d, $J = 4.9$ Hz, 2H, Por-H), 8.81 (s, 4H, Por-H), 8.88 ppm (d, $J = 4.9$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 403, 511 nm ($CHCl_3$); IR (KBr) 3324, 3028, 1617, 801 $cm^{-1}$; FABMS ($m/z$) 864 ($M^+$).

### Pt(II)-5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (2b-Pt)

Orange crystals; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.69 (s, 9H, $CH_3$), 4.00 (bs, 2H, $NH_2$), 7.04 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.53 (d, $J = 7.7$ Hz, 6H, Ar-H), 7.91 (d, $J = 8.1$ Hz, 2H, Ar-H), 8.02 (d, $J = 7.7$ Hz, 6H, Ar-H), 8.75 (bs, 4H, Por-H), 8.76 (d, $J = 4.9$ Hz, 2H, Por-H), 8.83 ppm (d, $J = 4.9$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 403, 512 nm ($CHCl_3$); IR (KBr) 3320, 1616, 800 $cm^{-1}$; FABMS ($m/z$) 864 ($M^+$).

### Pt(II)-5-(4-aminophenyl)-10,15,20-tetraphenylporphyrin (2c-Pt)

Orange crystals; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.99 (bs, 2H, $NH_2$), 7.03 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.66–7.80 (m, 9H, Ar-H), 7.91 (d, $J = 8.2$ Hz, 6H, Ar-H), 8.12–8.18 (m, 6H, Ar-H), 8.73 (bs, 4H, Por-H), 8.74 (d, $J = 4.7$ Hz, 2H, Por-H), 8.85 ppm (d, $J = 4.7$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 407, 511 nm ($CHCl_3$); IR (KBr) 3025, 1618, 796 $cm^{-1}$ ($NH_2$); FABMS (m/s) 822 ($M^+$).

### Pd(II)-5-(3-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (2a-Pd)

Orange crystals; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.69 (s, 9H, $CH_3$), 3.90 (bs, 2H, $NH_2$), 7.04–7.09 (m, 1H, Ar-H), 7.45–7.59

(m, 9H, Ar-H), 8.01–8.06 (m, 6H, Ar-H), 8.811 (s, 4H, Por-H), 8.814 (d, $J = 4.9$ Hz, 2H), 8.88 ppm (d, $J = 4.9$ Hz, 2H, Ar-H); UV ($\lambda_{max}$) 419, 487, 525, 556 nm ($CHCl_3$); IR (KBr) 3324, 3028, 1617, 801 cm$^{-1}$; SIMS ($m/z$) 775 ($M^+$).

### Pd(II)-5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (2b-Pd)

Orange crystals; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.69 (s, 9H, $CH_3$), 4.01 (bs, 2H, $NH_2$), 7.04 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.53 (d, $J = 7.7$ Hz, 6H, Ar-H), 7.93 (d, $J = 8.3$ Hz, 2H, Ar-H), 8.04 (d, $J = 7.7$ Hz, 6H, Ar-H), 8.807 (bs, 4H, Por-H), 8.813 (d, $J = 4.8$ Hz, 2H, Por-H), 8.89 ppm (d, $J = 4.8$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 414, 525 nm ($CHCl_3$); IR (KBr) 3323, 3028, 1618, 800 cm$^{-1}$; FABMS ($m/z$) 775 ($M^+$).

### Pd(II)-5-(4-aminophenyl)-10,15,20-tetraphenylporphyrin (2c-Pd)

Orange crystals; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.01 (bs, 2H, $NH_2$), 7.04 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.68–7.80 (m, 9H, Ar-H), 7.94 (d, $J = 8.3$ Hz, 6H, Ar-H), 8.13–8.20 (m, 6H, Ar-H), 8.79 (bs, 4H, Por-H), 8.80 (d, $J = 4.9$ Hz, 2H, Por-H), 8.91 ppm (d, $J = 4.9$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 416, 525 nm ($CHCl_3$); IR (KBr) 3025, 1617 cm$^{-1}$ ($NH_2$); FABMS (m/s) 733 ($M^+$).

### Pd(II)-5-[3-amino(triazine-2,4-dichloride)phenyl]-10,15,20-tris(4-methylphenyl)porphyrin (3a-Pd)

Orange crystals; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.63 (s, 9H, $CH_3$), 7.46 (d, $J = 7.9$ Hz, 6H, Ar-H), 7.620 (s, 1H, NH), 7.621 (dd, $J = 8.3$, 7.6 Hz, 1H, Ar-H), 7.83 (dd, $J = 8.3$, 1.6 Hz, 1H, Ar-H), 7.95 (dd, $J = 7.6$, 1.6 Hz, 1H, Ar-H), 8.00 (d, $J = 7.9$ Hz, 6HAr-H), 8.10 (t, $J = 1.6$ Hz, 1H, Ar-H), 8.79 (d, $J = 5.0$ Hz, 2H, Por-H), 8.81 (s, 4H, Por-H), 8.82 ppm (d, $J = 5.0$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 418, 525 nm ($CHCl_3$); IR (KBr) 3286, 2923, 1610, 1542, 1166, 1015, 799 cm$^{-1}$; MALDI-TOFMS ($m/z$) 921.853 ($M^+$).

### Pt(II)-5-[3-amino(triazine-2,4-dichloride)phenyl]-10,15,20-tris(4-methylphenyl)porphyrin (3a-Pt)

To a solution of cyanuric chloride (0.0374 g, 0.200 mmol) in tetrahydrofuran (THF) (15 mL), Pt(II)-5-(3-amino-phenyl)-10,15,20-tris(4-methylphenyl)porphyrin (**2a-Pt**) (0.1286 g, 0.1500 mmol) in THF was slowly added at 0 °C and the solution was stirred for 2 h. An aqueous potassium carbonate solution was added slowly, and the solution was stirred for another 3 h. The organic layer was dried over $MgSO_4$ and the solvent was concentrated. The product was purified by column chromatography (silica gel, $CH_2Cl_2$) to afford orange crystals of the title compound in 90% yield (0.1356 g).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.67 (s, 9H, $CH_3$), 7.52 (d, J = 7.7 Hz, 6H, Ar-H), 7.66 (bs, 1H, NH), 7.73 (t, J = 7.5 Hz, 1H, Ar-H), 7.94–8.03 (m, 2H, Ar-H), 8.01 (d, J = 7.7, 6H, Ar-H), 8.17 (bs, 1H, Ar-H), 8.76 (d, $J = 5.1$ Hz, 2H, Por-H), 8.77 (s, 4H, Por-H), 8.79 ppm (d, $J = 5.1$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 405, 510 nm ($CHCl_3$); IR (KBr) 2918, 1540, 1166, 1017, 797 cm$^{-1}$; FABMS ($m/z$) 1012 ($MH^+$).

### Pd(II)-5-[4-amino(1,3,5-triazine-2,4-dichloride)phenyl]-10,15,20-triphenylporphyrin (3c-Pd)

Orange crystals; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69–7.80 (m, 9H, Ar-H), 7.83 (bs, 1H, NH), 7.88 (d, $J = 8.3$ Hz, 2H, Ar-H), 8.13–8.21 (m, 8H,), 8.80 (d, J = 5.0 Hz, 2H, Por-H), 8.81(s, 4H, Por-H), 8.82 ppm (d, $J = 5.0$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 416, 525 nm ($CHCl_3$); IR (KBr) 3286, 2923, 1610, 1542, 1166, 799 cm$^{-1}$; FABMS ($m/z$) 881 ($MH^+$).

### Pt(II)-5-[4-amino(1,3,5-triazine-2,4-dichloride)phenyl]-10,15,20-triphenylporphyrin (3c-Pt)

Orange crystals; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66–7.79 (m, 10H, NH, Ar-H), 7.83 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.09–8.18 (m, 8H, Ar-H), 8.23 (d, $J = 5.2$ Hz, 2H, Por-H), 8.75 (s, 4H, Por-H), 8.76 ppm (d, $J = 5.2$ Hz, 2H, Por-H); UV ($\lambda_{max}$) 405, 510 nm ($CHCl_3$); FABMS ($m/z$) 970 ($MH^+$).

### Synthesis of PIs and the Film Fabrication

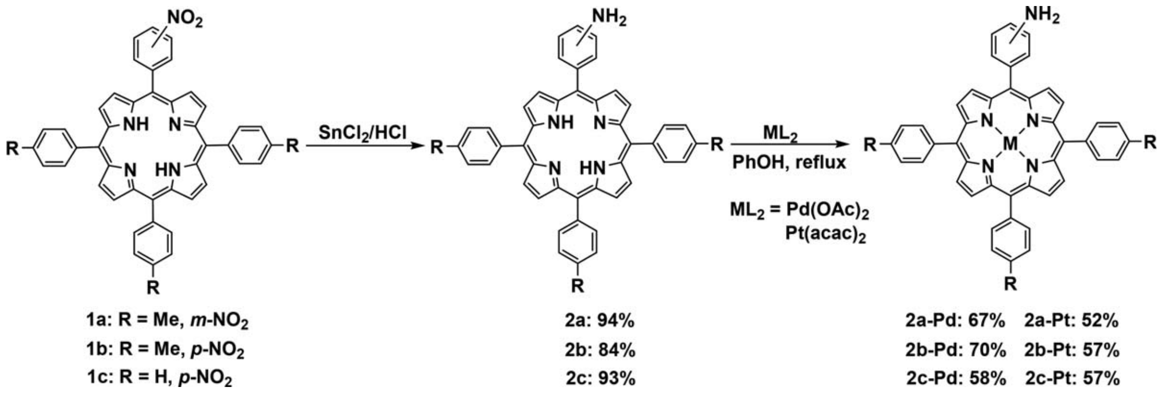
#### *Typical Procedure for 0.5 mol % 3a-Pd PI*

To a solution of compound (**4**) (2.092 g, 5.000 mmol) in dry NMP (12.5 mmol) cooled with an ice bath, *N,O*-bis(trimethylsilyl)trifluoroacetoamide (BSTFA) (3.20 mL, 10.0 mmol) was added through a syringe and the solution was stirred at 0 °C for 0.5 h and 20 °C for 15 min. 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (**5**) (2.221 g, 2.500 mmol), 6-(*p*-perfluorononenyloxy anilino)-1,3-triazine-2,4-dichloride (**6**) (1.709 g, 2.488 mmol) and the porphyrin complex (**3a-Pd**) (0.0230 g, 0.0249 mmol) were simultaneously added at 0 °C and the solution was stirred at 20 °C for 4 h, then stirred at 160 °C for 24 h. The resulting viscous mixture was poured into methanol to precipitate the polymer, which was dried at 80 °C under vacuum for 9 h (quantitative yield). The polymer was dissolved in NMP, cast on a glass plate, dried at 20, 100, 150, 200, 250, and 300 °C for 6 h each under reduced pressure to produce a reddish transparent self-standing film. IR (KBr) 3500 (NH), 2950 ($C\text{-}H_{Ar}$), 1786 (imide C=O), 1731 (imide C=O), 1500 ($C{=}C_{Ar}$), 1417 (imide C—N), 1250 (ether) cm$^{-1}$; elemental analysis ($C_{228.5}H_{118.3}F_{87.30}N_{20.18}O_{22.49}Pd_{0.0249}$) calcd (%) C: 53.07, H: 2.33, N: 5.45; found (%) C: 52.59, H: 2.39, N: 5.98.

## RESULTS AND DISCUSSION

### Preparation of Aminophenylporphyrin Derivatives

As a typical procedure for preparation of unsymmetrically substituted porphyrins, the statistical reaction of pyrrole with *p*-tolaldehyde and *m*-nitrobenzaldehyde (reaction ratio = 4:3:1 in mol) was conducted in chloroform at room temperature under nitrogen in the presence of trifluoroborane-etherate. The reaction mixture was treated with chloranil, according to a method previously reported.[37–40] The reaction gave symmetricand unsymmetrical five porphyrin isomers, together with the desired 5-(3-nitrophenyl)-10,15,20-tri(4-methylphenyl)porphyrin (**1a**), which was isolated from by column chromatography. Mono(4-nitrophenyl)porphyrin (**1b**) was prepared by a similar procedure using *p*-nitrobenzaldehyde. Subsequently, the nitro group of the products was reduced by tin(II) chloride in concentrated hydrochloric acid and the reaction gave 5-(3-



**SCHEME 1** Preparation of aminophenylporphyrinato Pd (II) and Pt (II) derivatives.

aminophenyl)- and 5-(4-aminophenyl)-10,15,20-tri (4-methylphenyl)porphyrin derivatives (**2a**) and (**2b**) in 94 and 84% yields, respectively (Scheme 1). 5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (**2c**) was successfully prepared using Kruper's procedure.[41] To introduce palladium and platinum atoms to the free base porphyrins, we treated **2a**, **2b**, and **2c** with palladium (II) acetate or platinum (II) acetylacetonate in phenol at reflux temperature. These reactions produced the corresponding palladium (II) or platinum (II) complexes in 67 (**2a-Pd**), 70 (**2b-Pd**), 58 (**2c-Pd**), 52 (**2a-Pt**), 57 (**2b-Pt**), and 57% (**2c-Pt**) yields.

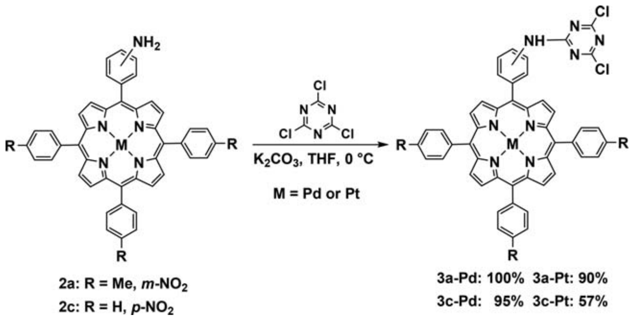
The structure of the products was determined by $^1$H NMR spectra and MS spectrometry. $^1$H NMR signals for the amino groups of **2a-Pd** and **2a-Pt** were observed as a broad singlet together with a singlet from the methyl groups; **2a-Pd** $\delta = 2.69$ ($CH_3$, 9H) and 3.90 ($NH_2$, 2H) ppm; **2a-Pt** $\delta = 2.67$ ($CH_3$, 9H) and 3.87 ($NH_2$, 2H) ppm. The peripheral pyrrole protons were observed as one singlet peak and two doublet peaks. The mass spectrometry showed molecular ion peaks; SIMS for **2a-Pd** $m/z = 775$ ($M^+$), FABMS for **2b-Pd** $m/z = 775$ ($M^+$), FABMS for **2c-Pd** $m/z = 733$ ($M^+$), FABMS for **2a-Pt** $m/z = 864$ ($M^+$), FABMS for **2b-Pt** $m/z = 864$ ($M^+$), and FABMS for **2c-Pt** $m/z = 823$ ($MH^+$). The UV–vis spectra of **2a-Pd** and **2a-Pt** measured in chloroform showed the Soret band at 419 nm and the Q bands at 487, 525, and 556 nm for **2a-Pd** and the Soret band at 403 nm and a Q band at 511 nm for **2a-Pt**.

### *Reaction of Monoaminophenylporphyrin Derivatives with Cyanuric Chloride*

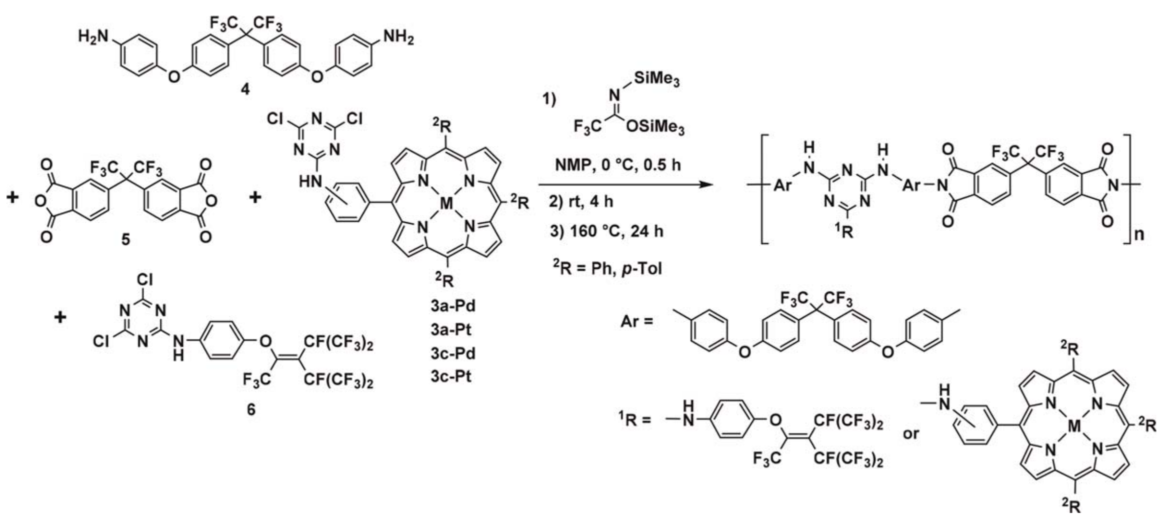
To prepare a triazine derivative containing only one porphyrin group on the ring, we reacted cyanuric chloride with porphyrins **2a-Pd**, **2b-Pd**, **2c-Pd**, **2a-Pt**, **2b-Pt**, and **2c-Pt** at low temperature; however, for these compounds, the solubility of **2b-Pd** and **2b-Pt**, with three 4-methylphenyl groups and one 4-aminophenyl group, was lower than that of **2a-Pd**, **2c-Pd**, **2a-Pt**, and **2c-Pt**. For this reason, compounds **2a-Pd**, **2c-Pd**, **2a-Pt**, and **2c-Pt** were reacted with 1 equivalent of cyanuric chloride in THF at 0 °C under nitrogen and an aqueous potassium carbonate solution was added slowly (Scheme 2). The reaction produced porphyrin derivatives with one dichlorotriazine group in 100 (**3a-Pd**), 90 (**3a-Pt**), 95 (**3c-Pd**), and 89% (**3c-Pt**) yields. The structure of the products was confirmed by $^1$H NMR spectroscopy and mass spectrometry. While the $^1$H NMR spectra showed the amino groups of **3a-Pd** and **3a-Pt** in the aromatic region at $\delta = 7.62$ and $\delta = 7.66$ ppm, respectively, a singlet assigned to the methyl groups was observed at $\delta = 2.63$ ppm (**3a-Pd**) and $\delta = 2.67$ ppm (**3a-Pt**). The spectra showed the peripheral pyrrole protons as one singlet peak and two doublet peaks. In the mass spectra of the products, the corresponding molecular ion peaks were observed for the respective compounds; MALDI TOF MS for **3a-Pd** $m/z = 921.853$ ($M^+$), FABMS for **3a-Pt** $m/z = 1012$ ($MH^+$), FABMS for **3c-Pd** $m/z = 881$ ($MH^+$), and FABMS for **3c-Pt** $m/z = 970$ ($MH^+$).

### Preparation of PI and the Film

Cyanuric chloride and its mono-substituted dichloro derivatives can be utilized as building blocks of PI; hence, we used porphyrin derivatives **3a-Pd**, **3a-Pt**, **3c-Pd**, and **3c-Pt** as starting compounds for PI synthesis (Scheme 3). Importantly, oxygen sensors using thin polymer films are affected by the characteristics of the polymeric materials, so they need high oxygen permeability. In order to increase oxygen permeability of the polymer film, we introduced fluorinated substituents on the polymer chain by selecting a fluorine-based dichloride monomer (**6**) as a building block, in addition to the aromatic diamine (**4**) and aromatic tetracarboxylic anhydride (**5**). In advance of polymerization, compound **6** was prepared by reaction of *p*-perfluorononenyloxy aniline with cyanuric chloride.



**SCHEME 2** Reaction of aminophenylporphyrins **2a** and **2c** with cyanuric chloride.



**SCHEME 3** Preparation of PI with aminophenylporphyrins.

To prepare the aromatic PIs, we utilized an *in situ* N-silylated method (Scheme 3). Thus, aromatic diamine (**4**), aromatic tetracarboxylic anhydride (**5**), dichlorotriazine (**6**), and porphyrin complexes **3a-Pd**, **3a-Pt**, **3c-Pd**, and **3c-Pt** were simultaneously mixed in NMP at room temperature for 4 h in the presence of the silylation reagent BSTFA, then at 160 °C for 24 h to afford the corresponding poly(amic acid) solution. The feed of porphyrins **3a-Pt**, **3c-Pd**, and **3c-Pt** was fixed at 1 mol % against **6**, and the concentration of **3a-Pd** varied from 0.5 to 3 mol %. The polymer solution was cast on a glass plate and successively heated under reduced pressure to give the PI film. The formation of PI was confirmed by IR spectroscopy (Supporting Information Fig. 1S). Since the polymerization temperature was very high at 160 °C for 24 h, the dried film at 100 °C for 1 h did not have the characteristic amide absorptions at 1640 $cm^{-1}$. With the curing temperature, an absorption assignable to the imide ring at 1786 and 1731 $cm^{-1}$ became stronger, then saturated after 1 h at 250 °C. In order to ensure imidization, the curing temperature was up to 300 °C (see Experimental section). The formation of the PI was also supported by elemental analysis.

Table 1 summarizes the results of the polymerization. All polymers were obtained quantitatively after precipitation from methanol, and the viscosity was sufficiently high, from 0.28 to 0.75 (dL/g) in NMP, to fabricate homogeneous thin films. Molecular weights of lower viscosity samples were estimated by GPC from 25,000 to 56,000 for $M_n$ with reasonable $M_w/M_n$ values (1.7–3.0). The resulting PI samples all show high thermostability of $T_{d5}$ around 420 °C in air, and the $T_g$ values were around 230 °C as estimated by DSC. Since the introduction of the porphyrin unit in this experiment is less than 3 mol % (2 wt %), there does not seem to be a significant influence on the thermal properties of the polymers. The $M_n$ and $M_w/M_n$ values of the **3a-Pt** derivative are higher than those of the **3c-Pt** derivative, which may result from their structures.

**TABLE 1** Viscosity and Thermal Properties of Porphyrin-PIs

| Dichloride Monomer | Conc. (mol %) | $M_n$[a] × $10^{-3}$ | $M_w/M_n$[a] | $\eta_{inh}$[b] (dL/g) | $T_g$[c] (°C) | $T_{d5}$ (°C)[d] Air | $T_{d5}$ (°C)[d] $N_2$ | $T_{d10}$ (°C)[d] Air | $T_{d10}$ (°C)[d] $N_2$ |
|---|---|---|---|---|---|---|---|---|---|
| **3a-Pd** | 0.5 | –[e] | -[e] | 0.75 | 233 | 415 | 420 | 435 | 440 |
| **3a-Pd** | 1.0 | -[e] | -[e] | 0.62 | 229 | 420 | 425 | 435 | 440 |
| **3a-Pd** | 2.0 | -[e] | -[e] | 0.63 | 230 | 415 | 420 | 435 | 435 |
| **3a-Pd** | 3.0 | 25.0 | 1.7 | 0.28 | 227 | 410 | 425 | 430 | 430 |
| **3a-Pt** | 1.0 | 56.0 | 3.0 | 0.42 | 231 | 430 | 435 | 450 | 455 |
| **3c-Pd** | 1.0 | 38.0 | 2.6 | 0.51 | 231 | 425 | 430 | 450 | 450 |
| **3c-Pt** | 1.0 | 29.0 | 1.6 | 0.44 | 235 | 415 | 420 | 435 | 440 |

[a] Determined by GPC (NMP with LiBr, PSt).

[b] Measured in NMP (0.5 g/dL) at 30 °C.

[c] Determined by DSC (20 °C/min).

[d] $T_{d5}$ and $T_{d10}$ are the temperatures for 5% and 10% decomposition, respectively (10 °C/min).

[e] Insoluble in NMP.

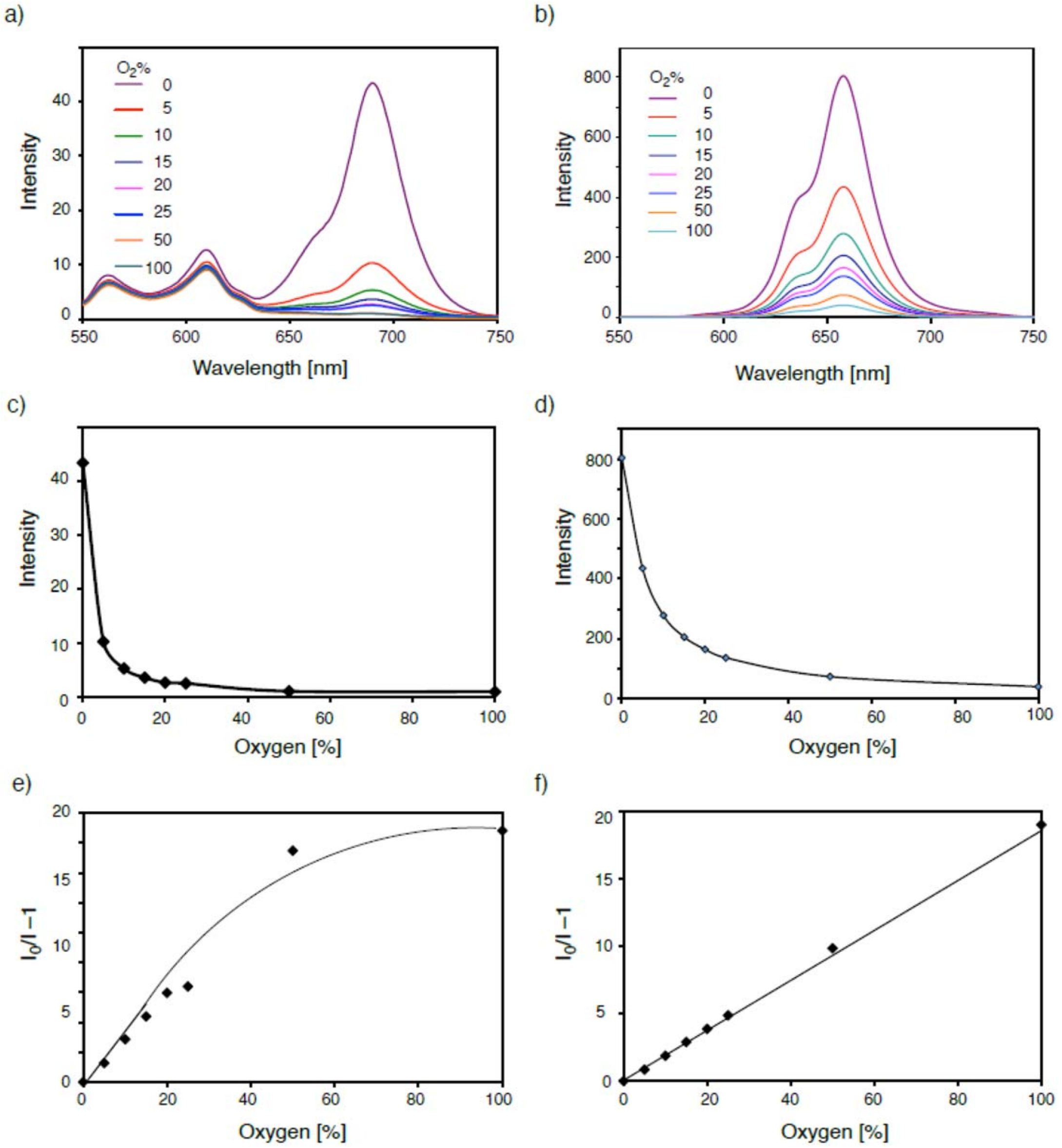


**FIGURE 1** The emission spectra, $\lambda_{\max}$ intensity relative to oxygen concentration, and Stern-Volmer plots of the porphyrin-polystyrene films 2a-Pd (1 wt %) (left) and 2a-Pt (1 wt %) (right). [Color figure can be viewed at wileyonlinelibrary.com]

### *Optical Properties of Porphyrin Derivatives Contained in a Polystyrene Film*

The porphyrin derivatives (**2a-Pd** and **2a-Pt**) were dispersed into a polystyrene matrix by mixing the porphyrin compounds with polystyrene in chloroform, followed by casting the film.[18–20] The porphyrin content was fixed to be 1 wt % against the matrix polymer. The emission spectra of the prepared film were measured under oxygen concentrations of 0, 5, 10, 15, 20, 25, 50, and 100% at room temperature. As shown in Figure 1(a), the spectra showed emission around 690 nm (excited with 418.5 nm light) for a **2a-Pd** film dispersed in polystyrene matrix. When the oxygen concentration was 0%, the emission showed maximum intensity. The emission intensity of the spectra decreased with an increase in oxygen concentration [Fig. 1(c)]. In these cases, the Stern-Volmer plot of the spectra showed a curved line [Fig. 1(e)].

The polystyrene film of the platinum derivative **2a-Pt** was excited with 403.5 nm light [Fig. 1(b)]. When the oxygen concentration was 0%, the film showed strong emission around 660 nm. The intensity of the emission also decreased with an increase in oxygen concentration [Fig. 1(d)]. In these cases, the Stern-Volmer plot of the spectra showed a linear correlation [Fig. 1(f)]. As a result, the polystyrene film of the platinum derivative **2a-Pt** exhibited stronger emission at an oxygen concentration of 0% compared to the palladium derivative **2a-Pd**.

Since the Stern-Volmer plot did not show a linear relationship for the polystyrene film of **2a-Pd**, palladium derivatives could be only used as sensors at low concentrations of oxygen. On the other hand, the polystyrene film of platinum derivative **2a-Pt** could be utilized as an oxygen sensor under

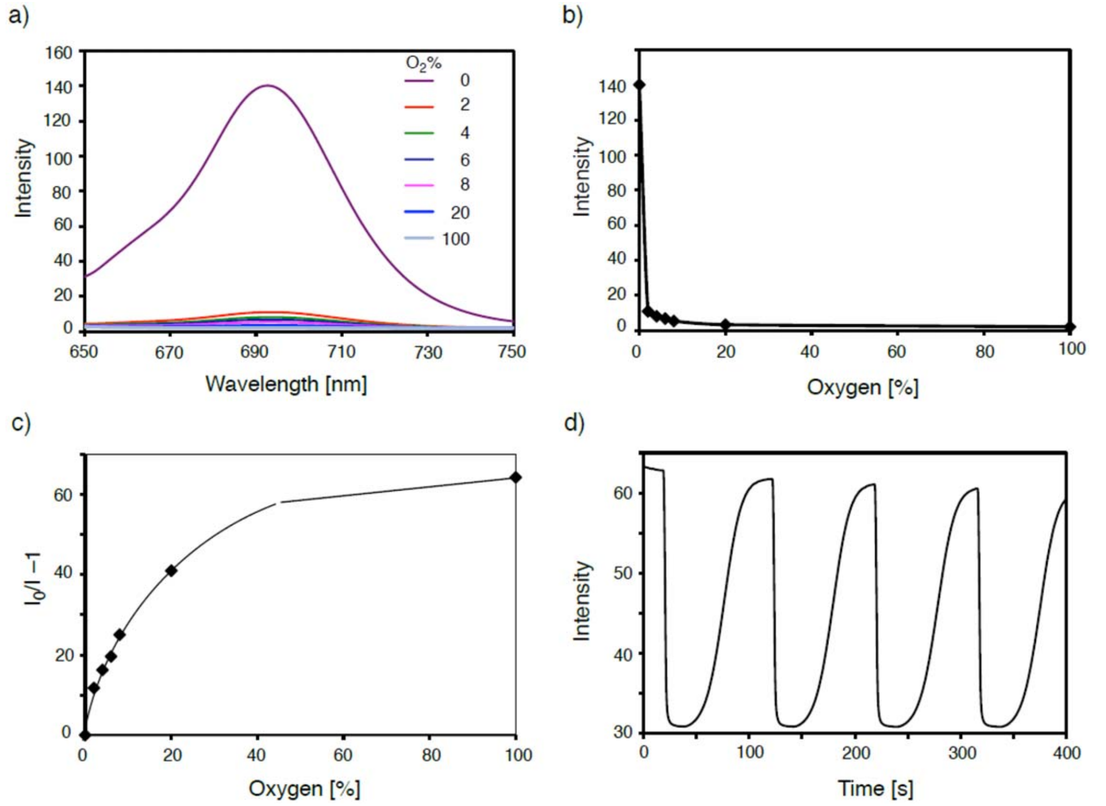


**FIGURE 2** The emission spectra, $\lambda_{max}$ intensity with respect to oxygen concentration, Stern-Volmer plot, and on/off switching property of porphyrin-PI film **3a-Pd** (3 mol %) in response to oxygen. [Color figure can be viewed at wileyonlinelibrary.com]

oxygen concentrations between 0% and 100%. Since the platinum and palladium complexes of octaethylporphyrin were reported to show strong phosphorescence at room temperature, oxygen sensing system using **2a-Pd** and **2a-Pt** are expected to quench the triplet state of these complexes.

### *Optical Properties of Porphyrin Derivatives Linked to a PI Film*

The concentration of porphyrin **3a-Pd** was varied from 0.5 to 3 mol % in the poly(amic acid) matrix by changing the feed ratio of the monomers **6** and **3** (total 2.5 mmol) in the polymerization reaction. PI films containing the porphyrin derivative **3a-Pd** were obtained by thermal treatment of the poly(amic acid) films at an elevated temperature up to 300 °C as described above. When the emission of the film containing 0.5, 1.0, and 2.0 mol % of porphyrin **3a-Pd** was measured under 0% oxygen concentration, the intensity was very low; hence, the results of the emission are shown in Figure 2 using a film containing 3.0 mol % of porphyrin **3a-Pd**. The emission spectra of the film were measured under oxygen concentrations of 0, 2, 4, 6, 8, 10, 20, and 100%, and porphyrin **3a-Pd** was excited using 418.5 nm light. Under an oxygen concentration of 0%, the spectra showed emission around 690 nm and the intensity of the emission decreased with increasing oxygen concentration [Fig. 2(a,b)]. In these cases, the Stern-Volmer plot of the spectra showed a curved line [Fig. 2(c)]. When the oxygen concentration was reduced to 0%, the strength of the emission recovered, as shown in Figure 2(d). The luminescence of this polymer film appeared to be quenched by oxygen and recovered under deoxygenated conditions. The results using **3c-Pd** are similar to that of **3a-Pd** (not shown); hence, these compounds can be utilized as sensors for low oxygen concentrations.

The emission spectra of a film of platinum derivative **3a-Pt** were measured under oxygen concentrations of 0, 2, 4, 6, 8, 10, 20, and 100%. The spectrum was obtained using 403.5 nm excitation light when the oxygen concentration was 0%. As shown in Figure 3(a), the emission spectra of **3a-Pt** (1 mol %) showed a strong emission around 660 nm, similar to the polystyrene film [Fig. 1(b)]. On the other hand, when the concentration of oxygen increased, the intensity of the emission in the spectra decreased [Fig. 3(b)]. In this case, the Stern-Volmer plot of the spectra showed a linear correlation [Fig. 3(c)]. As shown, since the intensity of the emission of the platinum derivatives were strong, 1 mol % of the porphyrin derivative is sufficient to utilize the compound in an oxygen sensor. The intensity of the emission of the film appeared strong under an oxygen concentration of 0% but weak under a 100% oxygen atmosphere; however, the intensity recovered under deoxygenated condition. As such, the film could repeatedly be used as an oxygen sensor [Fig. 3(d)]. Additionally, it appeared that the sensitivity to oxygen of the PI film is higher than that of porphyrins (**2a-Pd**) and (**2a-Pt**) contained in a polystyrene film.

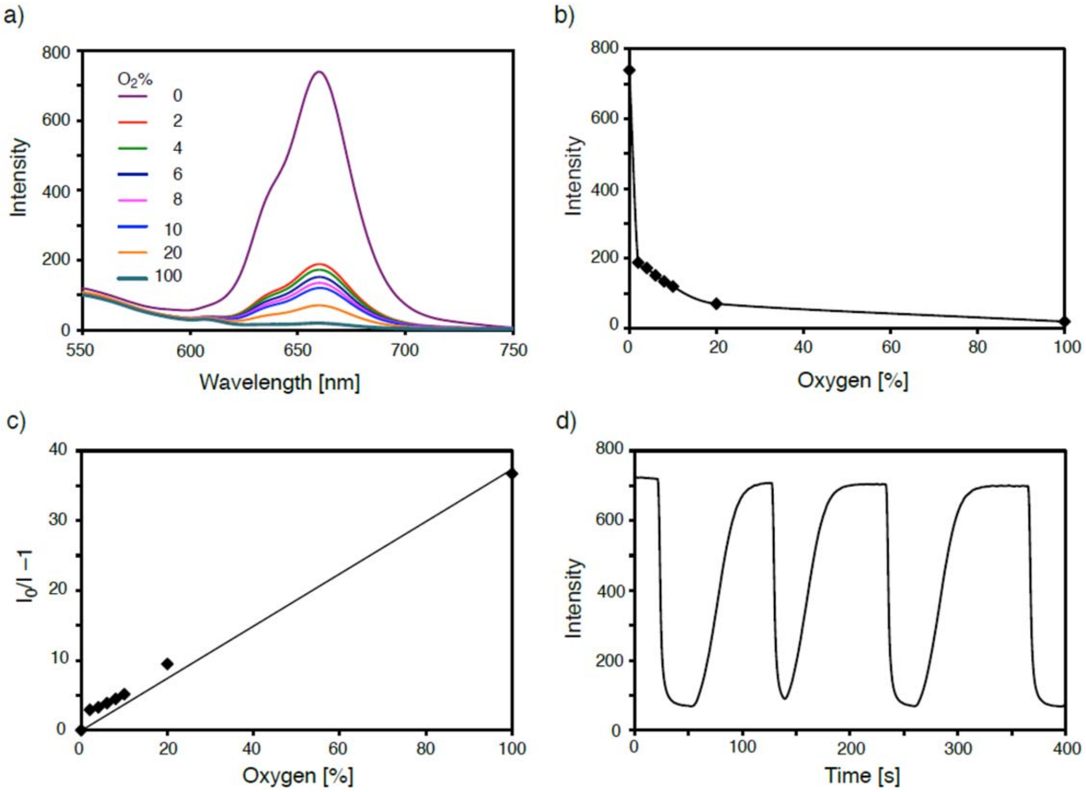


**FIGURE 3** The emission spectra, $\lambda_{max}$ intensity with respect to oxygen concentration, Stern-Volmer plot, and on/off switching property of a porphyrin-polyimide film of **3a-Pt** (1 mol %) in response to oxygen. [Color figure can be viewed at wileyonlinelibrary.com]

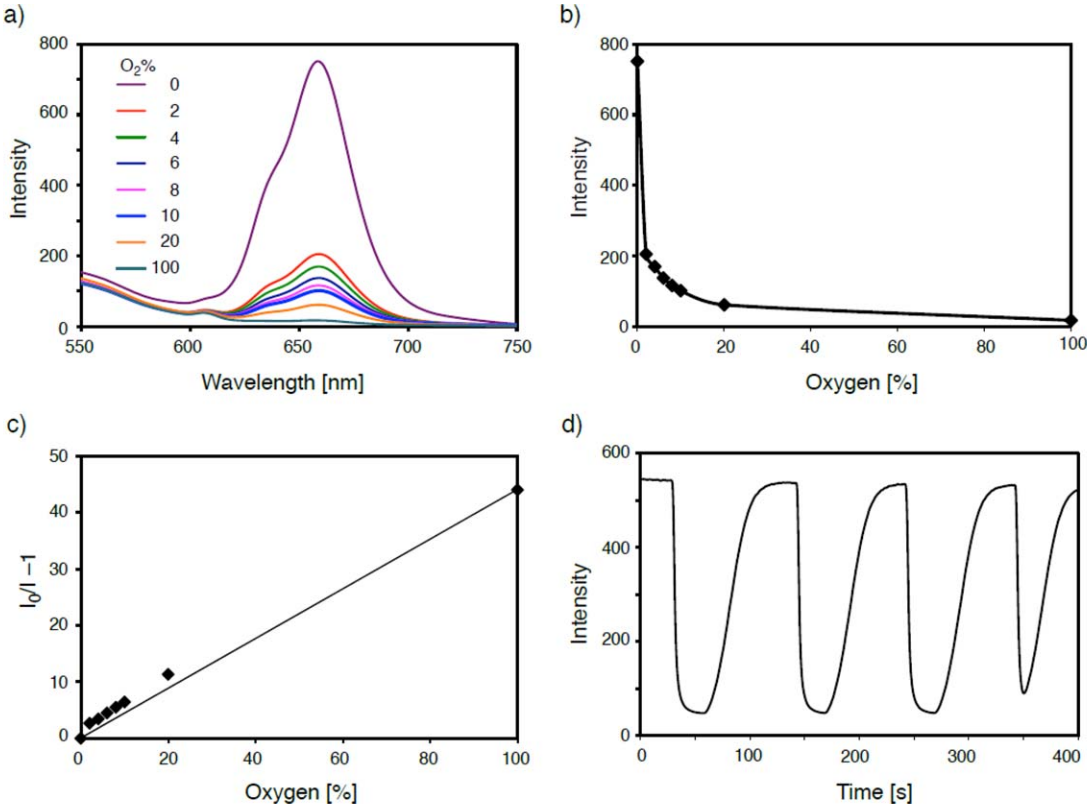


**FIGURE 4** The emission spectra, $\lambda_{max}$ intensity with respect to oxygen concentration, Stern-Volmer plot, and on/off switching property of a polyimide film of **3c-Pt** (1 mol %) in response to oxygen. [Color figure can be viewed at wileyonlinelibrary.com]

As shown in Figure 4(a), the emission spectra of **3c-Pt** (1 mol %) were also measured at room temperature. The emission spectra of a film of **3c-Pt** was measured under oxygen concentrations of 0, 2, 4, 6, 8, 10, 20, and 100%. The intensity of the emission in the spectra varied with an increase in the oxygen concentration, and the Stern-Volmer plot of the spectra showed a linear correlation [Fig. 4(b,c)]. The intensity of the emission was repeatedly varied with changing oxygen concentration [Fig. 4(d)].

## CONCLUSIONS

5-(3-Aminophenyl)-10,15,20-tristolylporphyrinato Pd (II) and Pt (II) complexes (**2a-Pd**) and (**2a-Pt**) were prepared and reacted with cyanuric chloride to produce the corresponding porphyrin derivatives (**3a-Pd**) and (**3a-Pt**) with a dichlorotriazine ring as a linker substituent. Compounds (**3a-Pd**) and (**3a-Pt**) showed a broad emission band around 670 nm and were utilized as a building block for polyimide (PI) polymers. Porphyrin units were directly linked to the PI backbone a luminous component. The emission spectra of the films were similar to those of porphyrins (**2a-Pd**) and (**2a-Pt**). The luminescence of this polymer film was quenched by oxygen. While the Stern-Volmer plot did not show a linear correlation in PI films of **3a-Pd** and **3d-Pd**, films of **3a-Pt** and **3a-Pt** exhibited a linear relationship in the plot. Films of the platinum derivatives, **3a-Pt** and **3c-Pt**, can be used as oxygen sensors at oxygen concentration between 0% and 100%, and the sensitivity of these PI films are slightly higher than that of the compounds in a polystyrene film.

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