# **Inorganic Chemistry**

# Tunable Fluorescent/Phosphorescent Platinum(II) Porphyrin− Fluorene Copolymers for Ratiometric Dual Emissive Oxygen Sensing

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**S** Supporting Information

[AB](#page-4-0)STRACT: [A series o](#page-4-0)f new platinum(II) 5,15-bis- (pentafluorophenyl)-10,20-bis(phenyl)porphyrin−9,9-dioctylfluorene copolymers, in which the relative intensities of the blue fluorescence and red phosphorescence can be easily tuned by the initial feed ratio of the two monomers or energy transfer between the fluorescent and phosphorescent units, have been designed and prepared for the application in



ratiometric dual emissive oxygen sensing. To the best of our knowledge, this is the first example of a ratiometric oxygen sensor based on dual fluorescent/phosphorescent polymers or copolymers containing transition-metal complexes. It also provides an alternative and easy way to achieve dual emissive oxygen sensing.

# **■ INTRODUCTION**

Conjugated polymers have been received great attention in a variety of applications, such as optoelectronic devices,<sup>1</sup> sensors,<sup>2</sup> and biomedical applications.<sup>2,3</sup> However, these  $\pi$ conjugated polymers mainly are fluorescent materials, whos[e](#page-4-0) fluoresc[en](#page-4-0)ce is generated from excited [sing](#page-4-0)let state. One of the most attractive systems is that of conjugated-polymercontaining phosphorescent transition-metal complexes. As a result, by introduction of phosphorescent transition-metal complexes into  $\pi$ -conjugated polymers, it is possible to tune the photosensitivity, charge transport, absorption, and luminescence of the polymers.<sup>4</sup>

Since the determination of oxygen concentration in solution is essential for a variety of [a](#page-4-0)pplications ranging from life sciences to environmental sciences, optical sensing of oxygen concentrations has attracted a great deal of scientific attention.<sup>5</sup> Intensely phosphorescent transition-metal complexes such as  $Pt(II)$  porphyrin and  $Ru(II)$  polypyridyl complexes<sup>5</sup> exhib[it](#page-4-0) very desirable features in terms of their optical spectra, excitedstate lifetimes, luminescence quantum yields, and high [s](#page-4-0)tability, for the purpose of oxygen sensing, $6$  because the ground state of  $O<sub>2</sub>$  is the triplet state and can quench the triplet phosphorescence. Moreover, rati[om](#page-4-0)etric  $O_2$  sensors are more desired, due to their advantages of eliminating photobleaching and excitation power fluctuation.<sup>7</sup> Usually, most of the reported ratiometric  $O_2$  sensors adopted the method of mixing two different dyes,<sup>8</sup> whose applicati[on](#page-4-0)s were limited by disadvantages, including unequal stability, reliability, and photobleaching of the two diff[e](#page-4-0)rent dyes. Another more efficient way to achieve ratiometric  $O_2$  sensors is to design and synthesize uniluminophores<sup>9</sup> with dual fluorescence/phosphorescence emission, but it is difficult to design such dual fluorescent/phosphorescent lumin[op](#page-4-0)hores from a photophysical perspective because a delicate balance between the  $S_1$  and  $T_1$  excited states has to be kept. Nonefficient intersystem crossing (ISC) will lead to

fluorescence; as a result, no phosphorescence can be observed. Conversely, an efficient ISC will eliminate the fluorescence and only phosphorescence can be observed. Only those luminophores with moderate ISC effects can display the fluorescence and phosphorescence dual emission.<sup>9g</sup> However, this is not a problem for the copolymers containing transition-metal complexes, because the relative inte[nsi](#page-4-0)ties of the fluorescence and phosphorescence can be easily tuned by modifying the composition of the phosphorescent transition-metal complex monomer and fluorescent monomer in the polymer.<sup>4b,c,e,f</sup>

Polyfluorenes (PFO) are an important class of blue fluorescent conjugated polymers for optoelectronic [devi](#page-4-0)ces,<sup>1</sup> owing to their good solubility, processability, and photophysical properties. Previously, we reported the applications of [mesotetrakis(pentafluorophenyl)porphyrinato]platinum(II) in lightemitting diodes.<sup>10</sup> This fluorinated Pt $(II)$  porphyrin is highly soluble and stable toward oxidative deterioration and photodegradation. He[rei](#page-4-0)n, the synthesis and photophysical properties of poly([5,15-bis(pentafluorophenyl)-10,20-bis(phenyl) porphyrinato]platinum(II)−9,9-dioctylfluorene] copolymers PtP1−PtP3 (Figure 1) are described. The relative intensities of the fluorescence and phosphorescence of copolymers can be easily tuned by the i[ni](#page-1-0)tial feed ratio of two monomers, which are suitable for ratiometric dual emissive oxygen sensing. To the best of our knowledge, there are a number of examples of ratiometric oxygen sensing based on dual fluorescent/ phosphorescent molecules, but ratiometric oxygen sensors based on dual fluorescent/phosphorescent polymers or copolymers containing transition-metal complexes are still rare, despite the fact that they are widely used in optoelectronic devices.<sup>1d,4</sup>

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Figure 1. Synthetic route of the monomers and the polymers.

# ■ RESULTS AND DISCUSSION

The polymers PFO and PtP1−PtP3 (Figure 1) were prepared through Yamamoto coupling between various platinum(II) 5,15-bis(pentafluorophenyl)-10,20-bis(4-bromophenyl) porphyrin complexes and 2,7-dibromo-9,9-dioctylfluorene (see the Experimental Section), as shown in Figure 1. Pentafluorophenyl groups in the Pt(II) porphyrin complex can increase its solu[bility and stability.](#page-3-0)<sup>10</sup> Introduction of the 9,9-dioctylfluorene group improves its solubility and reduces aggregation and steric hindrance between th[e P](#page-4-0)t(II) porphyrin units. However, PtP4 could not be prepared by this method due to steric hindrance, which disturbed the formation of an extended  $\pi$ -conjugated system, when the porphyrin units were directly bonded to form the polymer.<sup>11</sup> The level of  $Pt(II)$  porphyrin incorporation into the final copolymers may be quite different from the initial feed ratios and [was](#page-4-0) measured by  $^{1}H$  NMR analysis (Table 1 and Figure S1 in the Supporting Information). All the polymers have good thermal stability, with thermogravimetry analysis temperatures of 418−422 °C.

The photophysi[cal](#page-4-0) [properties](#page-4-0) [of](#page-4-0) PFO and PtP1−PtP3 are summarized in Table 2. The UV/vis absorption of PFO consists of a strong featureless  $\pi-\pi^*$  transition centered at 376 nm (3.2 eV) that has [a](#page-2-0) relatively broad bandwidth (halfbandwidth 60 nm), consistent with previous reports on polyfluorenes.<sup>1</sup> PtP1 exhibits a near-UV band (the mixture of

#### Table 1. Results of the Polymers



 $a$ mol % of monomer Pt(II) porphyrin from feed ratio.  $b$ mol % of  $Pt(II)$  porphyrin units calculated by  ${}^{1}H$  NMR.  ${}^{6}No$  value obtained, since the signal for  $Pt(II)$  porphyrin units was too weak.

Soret bands of Pt(II) porphyrin and fluorene units) at  $\lambda_{\text{max}}$  394 nm and two broad absorption peaks at 510 and 542 nm corresponding to  $Q(1,0)$  and  $Q(0,0)$  of the Pt(II) porphyrin moiety (Figure 2). An increase in the concentration of  $Pt(II)$ porphyrin moieties in the polymers led to slight shifting of the  $\lambda_{\text{max}}$  $\lambda_{\text{max}}$  $\lambda_{\text{max}}$  value of the near-UV band from 394 nm in PtP1 to 400 nm in PtP3.

The photoluminescence (PL) spectra (excited at 375 nm) of PtP1−PtP3 in degassed  $CH<sub>2</sub>Cl<sub>2</sub>$  at room temperature are depicted in Figure 2. PtP1−PtP3 show blue fluorescence (emission decay lifetime,  $\tau$  < 100 ns) attributed to the  $\pi-\pi^*$ emission of the fluo[re](#page-2-0)ne ring, as well as the red phosphorescence of Pt(II) porphyrin moieties. The relative intensities of the fluorescence and phosphorescence of copolymers can be

#### <span id="page-2-0"></span>Table 2. Optical Data of the Polymers



"Lifetime of fluorene units <100 ns. <sup>b</sup>With quinine sulfate ( $\Phi$  = 0.55, quinine in 0.05 mol dm<sup>-3</sup> sulfate) as the standard.



Figure 2. Absorption (top) and PL spectra (bottom) of PFO and PtP1−PtP3 in  $CH<sub>2</sub>Cl<sub>2</sub>$ .

easily tuned by the initial feed ratio of the two monomers. The PL of PtP1 is dominated by fluorescence; on the other hand, the PL of PtP3 is dominated by phosphorescence. In additional, there is a spectral overlap between the absorption spectrum of Pt(II) porphyrin monomer ( $\lambda_{\text{max}} \sim 400 \text{ nm}$ ) (Figure S2, Supporting Information) and PL spectrum of PFO  $(\lambda_{\text{max}}$  ~415 nm), which provides a possibility of energy transfer from fluorene units to  $Pt(II)$  porphyrin units in the copolymers. At a Pt(II) porphyrin moiety concentration of 20 mol % (calculated by  ${}^{1}$ H NMR), there was a small blue emission from fluorene units in PtP3, indicating a good energy transfer from fluorene units to Pt(II) porphyrin units. Long emission decay lifetimes of the excited state of Pt(II) porphyrin units were founded to be 39–51  $\mu$ s in PtP1–PtP3 (Table 2), indicating their triplet transition nature. All the polymers have bright PL in degassed  $\text{CH}_2\text{Cl}_2$  with quantum yields ( $\Phi$ ) of 0.70, 0.62, 0.14, and 0.070 for PFO and PtP1−PtP3, respectively.

The PL spectra (excited at 375 nm) of PtP3 in 1,2 dichloroethane at room temperature under various oxygen concentrations are shown in Figure 3. Under an atmosphere of 100% oxygen, PtP3 produces blue fluorescence with weak red phosphorescence. The blue fluorescence intensities show little change with decreasing oxygen contents, but at the same time,



Figure 3. PL spectra of PtP3 in 1,2-dichloroethane at room temperature at various oxygen concentrations.

the red phosphorescence intensities grow with decreasing oxygen contents, which is in agreement with the reported data based on  $Pt(II)$  porphyrin complexes.<sup>5</sup> The color of the emission changes from blue to red with decreasing oxygen content and could be seen by the n[a](#page-4-0)ked eye under UV excitation.

The oxygen quenching of red phosphorescence intensity at 655 nm in PtP3 can be interpreted in terms of the Stern− Volmer relation  $(I_{\text{p0}}/I_{\text{p}} = 1 + K_{\text{SV}} [O_2]$ ; where  $I_{\text{p0}}$  and  $I_{\text{p}}$  are phosphorescence intensities in the absence and in the presence of oxygen, respectively,  $[O_2]$  is the concentration of oxygen, and  $K_{SV}$  is the Stern–Volmer quenching constant), as shown in Figure 4. A good linearity (correlation coefficient  $R^2 = 0.997$ , n = 7) of  $I_{\text{p0}}/I_{\text{p}}$  as the function of the concentration of O<sub>2</sub> between 0 and 100% is established. The calculated  $K_{SV}$  value is found to be 402  $\pm$  12 bar<sup>-1</sup>. In order to achieve ratiometric dual emissive oxygen sensing, the relationship between  $I_F/I_P$  ( $I_F$ is blue fluorescence intensity at 416 nm) and oxygen concentration is depicted in Figure 4. A good linearity  $(R^2 =$ 



Figure 4. Stern−Volmer plot (black line) and linear correlation between the ratiometric fluorescent/phosphorescent response toward O2 partial pressure (red line) of PtP3.

<span id="page-3-0"></span>0.997) is also found. Thin films of the polymers, prepared by the spin-coating method, have optical properties similar to those of polymer solutions (Figure S3, Supporting Information). Ratiometric dual emissive oxygen sensing based on the thin films of polymers is now under way.

#### [■](#page-4-0) **CONCLUSIONS**

In conclusion, we have demonstrated a ratiometric dual emissive oxygen sensing system based on fluorescent/ phosphorescent platinum(II) porphyrin−fluorene copolymers with only one excitation wavelength. The relative intensities of the fluorescence and phosphorescence of the copolymers can be tuned by the initial feed ratio of two monomers or energy transfer between two fluorescent and phosphorescent units. It also provides an alternative and easy way to achieve dual emissive oxygen sensing.

#### **EXPERIMENTAL SECTION**

Characterization Techniques for Materials. Mass spectra were recorded with a high-resolution Finnigan MAT-95 mass spectrometer. UV−vis absorption spectra were measured with a PerkinElmer UV/ vis/near-IR Lambda 900 spectrophotometer. All emissive measurements were detected by a Fluorolog 3 spectrofluorometer. Emissive lifetimes were measured with a HoribaJobin Yvon fluorescence lifetime spectrophotometer. Thermal analyses were measured on a PerkinElmer DSC7 and a TGA7 thermal analyzer with heating rates of 10 and 15 °C/min, respectively. The number-average molecular weight  $(M_n)$  and weight-average molecular weight  $(M_w)$  of the polymers were characterized in THF by gel permeation chromatography at 35 °C (polystyrene as standard). The  $n/m$  ratios of the polymers were determined by  ${}^{1}H$  NMR (in CDCl<sub>3</sub>). Elemental analyses were performed at the Institute of Chemistry of the Chinese Academy of Sciences, Beijing, People's Republic of China. All  $^1\mathrm{H}$  and  $^{19}\mathrm{F}$  NMR (in CDCl3) spectra were collected on Bruker 300 and 400 NMR spectrometers, respectively. For oxygen sensing, standard gas mixtures containing 0, 10, 21, 40, 60, 80, and 100% of  $O_2$  balanced with  $N_2$ (100, 90, 79, 60, 40, 20, and 0%, respectively) were passed through the cuvette to equilibrate the oxygen content to the respective concentrations and to monitor the changes of sensor luminescence.

Materials. The polymers PFO and PtP1−PtP3 were prepared by the method shown in Figure  $1.^{12}$ 

Synthesis of 5-(Pentafluorophenyl)dipyrromethane.<sup>12a</sup> Pyrrole (50.0 mL, 720 mmol) [and](#page-4-0) 2,3,4,5,6-pentafluorobenzaldehyde (5.34 g, 27.2 mmol) were a[dd](#page-1-0)ed to a dry round-bottomed [100](#page-4-0) mL flask and degassed with a stream of  $N_2$  for 10 min. Trifluoroacetic acid (210  $\mu$ L, 2.72 mmol) was then added, and the solution was stirred under  $N_2$  at room temperature for 5 min and then quenched with 0.1 M NaOH (20 mL). A 100 mL portion of ethyl acetate was then added. The organic phase was washed with  $4 \times 80$  mL of water and dried  $(Na<sub>2</sub>SO<sub>4</sub>)$ , and the solvent was removed under vacuum to afford an orange oil. Bulb-to-bulb distillation typically gave an oil which crystallized upon standing (distilled at 150−160 °C (0.03 mmHg)). The resulting oil was difficult to recrystallize directly; therefore, it was dissolved by ethyl acetate. Removal of the solvent under vacuum gave a solid that was recrystallized two times from ethanol/water  $(1/1, v/v)$ to give 5.50 g of 5-(pentafluorophenyl)dipyrromethane as colorless crystals (yield 65%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.15 (br s, 2 H), 6.74−6.73 (m, 2 H), 6.16 (q, 2 H), 6.02 (m, 2 H), 5.90 (s, 1 H), MS (EI): calcd for  $C_{15}H_9N_2F_5$  312.24, found: 312.32. Anal. Calcd: C, 57.70; H, 2.90; N, 8.97. Found: C, 57.69; H, 2.87; N, 9.01.

Synthesis of 5,15-Bis(pentafluorophenyl)-10,20-bis(4 **bromophenyl)porphyrin.**<sup>12b</sup> 4-Bromobenzaldehyde  $(0.925 \text{ g}, 5.00$ mmol) and 5-(pentafluorophenyl)dipyrromethane (1.56 g, 5.00 mmol) were added to a dr[y ro](#page-4-0)und-bottomed 1 L flask with 500 mL of  $CH_2Cl_2$  and degassed with a stream of N<sub>2</sub> for 10 min. BF<sub>3</sub>·O(Et)<sub>2</sub> (0.418 mL, 1.65 mmol) was then added, the solution was stirred under  $N_2$  at room temperature for 1 h, and then 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ; 860 mg, 3.80 mmol) was added. The mixture

was stirred at room temperature for an additional 1 h, and then the solvent was removed. Column chromatography (silica,  $1/2$  CH<sub>2</sub>Cl<sub>2</sub>/ hexane v/v) afforded the porphyrin as the first moving band. Removal of the solvent under vacuum gave 0.728 g of 5,15-free base porphyrin as a purple solid (yield 31%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.97−8.80 (dd, 8 H), 8.07 (m, 4 H), 7.94 (m, 4 H), −2.87 (br s, 2 H). MS (FAB): calcd for C<sub>44</sub>H<sub>18</sub>N<sub>4</sub>F<sub>10</sub>Br<sub>2</sub> 952.45, Found: 952.89. Anal. Calcd: C, 55.49; H, 1.90; N, 5.88. Found: C, 55.68; H, 2.02; N, 5.81. UV-vis absorption: 413, 508, 586 nm (CH<sub>2</sub>Cl<sub>2</sub>); 418, 512, 589 nm (thin film). Photoluminescence (fluorescence): 655, 709 nm  $(CH_2Cl_2)$ ; 642, 708 nm (thin film).

Synthesis of Platinum(II) 5,15-Bis(pentafluorophenyl)-10,20 bis(4-bromophenyl)porphyrin.<sup>12c,d</sup>  $K_2[PtCl_4]$  (0.937 g, 2.26 mmol) and 5,15-bis(pentafluorophenyl)-10,20-bis(4-bromophenyl) porphyrin (0.717 g, 0.753 mmo[l\) we](#page-4-0)re added to a dry roundbottomed 100 mL flask with 50 mL of anhydrous benzonitrile and degassed with a stream of  $N_2$  for 10 min. The solution was stirred and refluxed under  $N_2$  at 180 °C for 2 days, the mixture was cooled, and the solvent was removed under vacuum. Column chromatography (silica,  $1/2$  CH<sub>2</sub>Cl<sub>2</sub>/hexane v/v) afforded the Pt(II) porphyrin complex as the first moving band. Removal of the solvent under vacuum gave a solid that was recrystallized to give  $0.620$  g of  $Pt(II)$ porphyrin complex as brown-red crystals (yield 72%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.90–8.70 (dd, 8 H), 8.01 (m, 4 H), 7.90 (m, 4 H). MS (FAB): calcd for  $C_{44}H_{16}N_{4}F_{10}Br_{2}Pt$  1145.51, found 1146.32. Anal. Calcd: C, 46.14; H, 1.41; N, 4.89. Found: C, 46.31; H, 1.52; N, 4.90. UV–vis absorption: 395, 508, 541 nm (CH<sub>2</sub>Cl<sub>2</sub>); 399, 510, 541 nm (thin film). Photoluminescence (phosphorescence): 650, 713 nm  $(CH_2Cl_2)$ ; 650, 710 nm (thin film).

Synthesis of Polymers PFO, PtP1, PtP2, and PtP3.<sup>12a,e,f</sup> Ni(COD)<sub>2</sub> (0.303 g, 1.10 mmol), 2,2'-dipyridyl (0.172 g, 1.10 mmol), and 1,5-cyclooctadiene (0.119 g, 1.10 mmol) were added in a [25 mL](#page-4-0) flask with 4.0 mL of toluene. After three freeze−thaw cycles, the catalyst was heated to 80  $^{\circ}$ C for  $^{1}/_{2}$  h to form the purple complex. 2,7-Dibromo-9,9-octylfluorene  $(0.261 \text{ g}, 0.475 \text{ mol})$  and  $Pt(II) 5,15$ bis(pentafluorophenyl)-10,20-bis(4-bromophenyl)porphyrin complex (0.0286 g, 0.025 mmol) were added to the solution and heated at 80 °C for another 4 days under  $N_2$ . After it was cooled to room temperature, the reaction mixture was poured into 100 mL of hexane. The solid was filtered and then washed with dilute NH4OH, dilute HCl, dilute NH4OH, acetone, and methanol in that order. The residue was redissolved in chloroform and precipitated in a 100 mL mixture of methanol and acetone  $(1/1, v/v)$ . The yellow-brown solid was dried under vacuum at 60 °C for 48 h to give 0.123 g of PtP1 (yellow-brown solid) (yield 52%). The ratio of the monomers was varied for the different copolymer compositions. Data for PtP1: <sup>1</sup>H NMR (300 MHz, CDCl3) δ (ppm) 7.85 (d, 2H), 7.67 (m, 4H), 2.12 (m, 4H), 1.25−1.05 (m, 24H), 0.83 (t, 6H); <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) −136.5 (4F, dd, ortho), −151.4 (2F, t, para), −161.6 (4F, m, meta). Data for PFO:  ${}^{1}H$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.85 (d, 2H), 7.68 (m, 4H), 2.13 (m, 4H), 1.25−1.05 (m, 24H), 0.83 (t, 6H); light yellow solid; yield 72%. Data for PtP2: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 9.05 (s, 0.37 H), 8.84 (d, 0.37 H), 8.29 (s, 0.37 H), 8.16 (s, 0.37 H) 7.86 (d, 2H), 7.68 (m, 4H), 2.14 (m, 4H), 1.25−1.05 (m, 24H), 0.83 (t, 6H); <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) −136.7 (4F, dd, ortho), −151.4 (2F, t, para), −161.6 (4F, m, meta); red solid; yield 40%. Data for PtP3:  $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) 9.05 (s, 1.0 H), 8.83 (d, 1.0 H), 8.30 (s, 1.0 H), 8.16 (s, 1.0 H) 7.85 (d, 2H), 7.68 (m, 4H), 2.13 (m, 4H), 1.25−1.05 (m, 24H), 0.83 (t, 6H); <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) −136.7 (4F, dd, ortho), −151.4 (2F, t, para), −161.5 (4F, m, meta); brown-red solid; yield 28%.

**Oxygen Quenching.** In this approach, the  $O_2$  dependence on the emission intensity is described by the Stern–Volmer expression,  $I_0/I$  =  $1 + K_{SV}$  [O<sub>2</sub>], where  $I_0$  and I denote the emission intensities in the absence of oxygen and at a oxygen concentration,  $[O_2]$  is the oxygen concentration or partial pressure in the solution, and  $K_{SV}$  is the Stern− Volmer quenching constant.  $[O_2]$  can be calculated by  $[O_2]$ =  $S_{\text{O}_2}[p(\text{O}_2)]$ , where the proportionality constant,  $S_{\text{O}_2}$ , is the oxygen solubility defined by Henry's law ( $S_{\text{O}_2}$  = 4.8 × 10<sup>-2</sup> for the solution of

<span id="page-4-0"></span>1,2-dichloroethane at room temperature of 25 °C; http://www.epa. gov/athens/learn2model/part-two/onsite/esthenry.html $\bar{p}$  and  $p(\bar{O_2})$ is the oxygen partial pressure above the solution.

#### ■ [ASSOCIATED](http://www.epa.gov/athens/learn2model/part-two/onsite/esthenry.html) [CONTENT](http://www.epa.gov/athens/learn2model/part-two/onsite/esthenry.html)

#### **S** Supporting Information

Figures giving <sup>1</sup>H NMR spectra of the polymers, absorption, excitation and PL spectra of 5,15-bis(pentafluorophenyl)-10,20 bis(4-bromophenyl)porphyrin and its Pt(II) complex in  $CH<sub>2</sub>Cl<sub>2</sub>$ , and absorption and emission spectra of the thin films of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The aut[hors](mailto:xianghaifeng@scu.edu.cn) [declare](mailto:xianghaifeng@scu.edu.cn) [no](mailto:xianghaifeng@scu.edu.cn) [competin](mailto:xianghaifeng@scu.edu.cn)g financial interest.

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#### ■ REFERENCES

(1) (a) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. Adv. Mater. 2000, 12, 1737−1750. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. Adv. Mater. 2002, 14, 99−117. (c) McNeill, C. R.; Greenham, N. C. Adv. Mater. 2009, 21, 3840−3850. (d) Wu, H. B.; Ying, L.; Yang, W.; Cao, Y. Chem. Soc. Rev. 2009, 38, 3391−3400.

(2) (a) Leclerc, M. Adv. Mater. 1999, 11, 1491−1498. (b) Gerard, M.; Chaubey, A.; Malhotra, B. D. Biosens. Bioelectron. 2002, 17, 345− 359. (c) Adhikari, B.; Majumdar, S. Prog. Polym. Sci. 2004, 29, 699− 766.

(3) Smela, E. Adv. Mater. 2003, 15, 481−494.

(4) (a) Wang, Q.; Yu, L. P. J. Am. Chem. Soc. 2000, 122, 11806− 11811. (b) Ng, P. K.; Gong, X.; Chan, S. H.; Lam, L. S. M.; Chan, W. K. Chem. Eur. J. 2001, 7, 4358−4367. (c) Wong, W. Y.; Lu, G. L.; Choi, K. H.; Shi, J. X. Macromolecules 2002, 35, 3506−3513. (d) Chan, W. K.; Gong, X.; Ng, W. Y. Appl. Phys. Lett. 1997, 71, 2919−2921. (e) Galbrecht, F.; Yang, X. H.; Nehls, B. S.; Neher, D.; Farrella, T.; Scherf, U. Chem. Commun. 2005, 2378−2380. (f) Hou, Q.; Zhang, Y.; Li, F. Y.; Peng, J. B.; Cao, Y. Organometallics 2005, 24, 4509−4518. (5) (a) Mills, A. Platinum Met. Rev. 1997, 41, 115−127. (b) Amao, Y. Microchim. Acta 2003, 143, 1−12. (c) Ramamoorthy, R.; Dutta, P. K.; Akbar, S. A. J. Mater. Sci. 2003, 38, 4271−4282. (d) Khalil, G. E.; Gouterman, M. P.; Green, E. US Patent 4,810,655, 1989. (e) Lee, S. K.; Okura, I. Anal. Commun. 1997, 34, 185−188. (f) Obata, M.; Matsuura, N.; Mitsuo, K.; Nagai, H.; Asai, K.; Harada, M.; Hirohara, S.; Tanihara, M.; Yano, S. J. Polym. Sci., Part A 2010, 48, 663−670. (6) Chu, B. W. K.; Yam, V. W. W. Langmuir 2006, 22, 7437−7437. (7) Sanchez-Barragan, I.; Costa-Fernandez, J. M.; Valledor, M.; Campo, J. C.; Sanz-Medel, A. Trends Anal. Chem. 2006, 25, 958−967. (8) (a) Evans, R. C.; Douglas, P.; Williams, J. A. G.; Rochester, D. L. J. Fluoresc. 2006, 16, 201−206. (b) Wang, X. D.; Chen, X.; Xie, Z. X.; Wang, X. R. Angew. Chem. 2008, 120, 7560−7563. (c) Cywinski, P. J.; Moro, A, J.; Stanca, S. E.; Biskup, C.; Mohr, G. J. Sens. Actuators B 2009, 135, 472−477. (d) Amelia, M.; Lavie-Cambot, A.; McClenaghan, N. D.; Credi, A. Chem. Commun. 2011, 47, 325−327. (9) (a) Kostov, Y.; Harms, P.; Pilato, R. S.; Rao, G. Analyst 2000, 125, 1175−1178. (b) Kostov, Y.; Rao, G. Sens. Actuators B 2003, 90, 139−142. (c) Hochreiner, H.; Sanchez-Barragan, I.; Costa-Fernandez, J. M.; Sanz-Medel, A. Talanta 2005, 66, 611−618. (d) Valledor, M.; Campo, J. C.; Sanchez-Barragan, I.; Viera, J. C.; Costa-Fernandez, J. M.; Sanz-Medel, A. Sens. Actuators B 2006, 117, 266−273. (e) Zhang,

G. Q.; Chen, J. B.; Payne, S. J.; Kooi, S. E.; Demas, J. N.; Fraser, C. L. J. Am. Chem. Soc. 2007, 129, 8942−8943. (f) Zhang, G. Q.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. S. Nat. Mater. 2009, 8, 747−751. (g) Liu, Y. F.; Guo, H. M.; Zhao, J. Z. Chem. Commun. 2011, 47, 11471−11473. (h) Van Houten, K. A.; Heath, D. C.; Barringer, C. A.; Rheingold, A. L.; Pilato, R. S. Inorg. Chem. 1998, 37, 4647−4653. (i) He, Z.; Wong, W. Y.; Yu, X. M.; Kwok, H. S.; Lin, Z. Y. Inorg. Chem. 2006, 45, 10922−10937.

(10) (a) Xiang, H. F.; Yu, S. C.; Che, C. M.; Lai, P. T. Appl. Phys. Lett. 2003, 83, 1518−1520. (b) Che, C. M.; Hou, Y. J.; Chan, M. C. W.; Guo, J. H.; Liu, Y.; Wang, Y. J. Mater. Chem. 2003, 13, 1362-1366. (c) Xiang, H. F.; Li, C. N.; Yu, S. C.; Che, C. M.; Lai, P. T.; Chui, P. C. Proc. SPIE 2004, 5519, 218−225.

(11) Yamamoto, T.; Fukushima, N.; Nakajima, H.; Maruyama, T.; Yamaguchi, I. Macromolecules 2000, 33, 5988−5994.

(12) (a) Xia, C. J.; Advincula, R. C. Macromolecules 2001, 34, 5854− 5859. (b) Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. J. Org. Chem. 1999, 64, 1391−1396. (c) Kwong, R. C.; Sibley, S.; Dubovoy, T.; Baldo, M.; Forrest, S. R.; Thompson, M. E. Chem. Mater. 1999, 11, 3709−3713. (d) Tyulyaeva, E. Y.; Lomova, T. N.; Andrianova, L. G. Russ. J. Inorg. Chem. 2001, 46, 371−375. (e) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z. H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. Macromolecules 1992, 25, 1214−1223. (f) Xiang, H. F. Ph.D. Thesis; The University of Hong Kong, Hong Kong, People's Republic of China, 2005.