

Towards chemosensing phosphorescent conjugated polymers: cyclometalated platinum(II) poly(phenylene)s†

Samuel W. Thomas III, Shigeyuki Yagi and Timothy M. Swager*

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The synthesis and optical properties of several phosphorescent conjugated poly(phenylene)s containing cyclometalated square-planar platinum (II) complexes are reported. These electronic polymers were synthesized *via* Suzuki cross-coupling of a dibromophenylpyridine-ligated Pt(II) complex with a fluorene diboronic ester. Their optical properties are characterized by relatively strong orange room-temperature phosphorescence with well-resolved vibronic structure in both frozen 2-methyltetrahydrofuran glass and room-temperature fluid solution. Time-resolved phosphorescence spectroscopy has shown that the polymers have excited state lifetimes of approximately 14 μ s. These optical properties of the oligomers and polymers are contrasted with those of small model complexes, the optical properties of which have a strong dependence on the identity of the β -diketonate ligand used. The potential utility of phosphorescent conjugated polymers is illustrated by examination of the diffusive quenching due to oxygen as a function of molecular structure.

Introduction

The use of fluorescent conjugated polymers is an established method for achieving a large degree of amplification for the chemosensing of analytes in both solution and solid states.¹ This approach has been successfully applied to biological binding events *via* Förster energy transfer,² as well as nitroaromatics and quinones, including 2,4,6-trinitrotoluene (TNT), *via* photoinduced electron transfer from the excited polymer to the bound analyte.³ We have sought to investigate the potential of phosphorescent conjugated polymers as chemosensing materials. The longer lifetimes of triplet excitons in conjugated materials may lead to increased sensitivity to trace analytes. This is an important goal for the purposes of detecting dangerous analytes with much smaller vapor pressures than TNT, such as the high explosives RDX and PETN.⁴

There are numerous examples of the incorporation of transition metal complexes into conjugated systems.⁵ Research into highly phosphorescent conjugated polymers with high loading of transition-metal complexes has focused on the platinum acetylide class of materials.⁶ These polymers incorporate the phosphine-substituted platinum atoms as part of the conjugated backbone, the significant spin-orbit coupling of which partially allows the intrinsically spin-forbidden processes of intersystem crossing and phosphorescence.⁷ However, one of the major advantages of working with organic conjugated materials is the modularity of material design, and this feature is limited in the platinum acetylide polymers.

Highly phosphorescent late-transition metal complexes and materials incorporating these moieties have received increasing attention of late. This is principally due to the utility of

phosphorescent materials in increasing the efficiency of organic light-emitting diodes by harnessing the large percentage of triplet excitons created upon electron-hole recombination.⁸ Principal amongst these are cyclometalated complexes of iridium (III)⁹ and platinum (II),¹⁰ which are attractive due to their modular synthesis and high luminescence efficiencies. Related work in the field of phosphorescent materials has recently included the use of these phosphors as pendant groups on both traditional vinyl and conjugated polymer backbones,¹¹ the preparation and study of an electrophosphorescent fluorene-based conjugated polymer with a small percentage of cyclometalated Ir complex in the backbone,¹² as well as the detailed photophysical study of several different π -conjugated oligo(arylene ethynylene)s containing transition metal complexes.¹³

We have directed our attention and efforts towards conjugated polymers based on cyclometalated transition metal complexes for their modularity in both the choice of central metal atom as well as ligand environment around the metal center. We report herein the synthesis and optical characteristics of a poly(phenylene) type of conjugated polymer in which the phenylpyridine ligand of a square planar Pt(II) complex constitutes one of the two repeat units. The stark contrast between the optical properties of the polymeric systems and several model complexes are highlighted and rationalized. The increased sensitivity of the polymeric system to dissolved oxygen demonstrates the conjugated nature of the system as well as the potential for using phosphorescent conjugated polymers as chemosensing materials.

Experimental

All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. NMR (¹H and ¹³C) spectra were recorded on a

† Electronic supplementary information (ESI) available: Synthetic procedures for **P1** and associated model complexes. See <http://www.rsc.org/suppdata/jm/b5/b503539b/>
*tswager@mit.edu

Varian 300 MHz spectrometer. NMR chemical shifts are referenced to residual protonated solvent. Polymer molecular weights were determined by gel-permeation chromatography (GPC) using an HP series 1100 GPC system running at 1.0 mL min⁻¹ in THF equipped with a diode array detector (254 and 450 nm) and a refractive index detector. Molecular weights are reported relative to poly(styrene) standards. Preparative GPC was performed in THF using a 10 μm PLgel preparative GPC column. The flow was supplied by a Rainin HPXL solvent delivery system at 10 mL min⁻¹. Absorbance was monitored with a Dynamax UV-1 absorbance detector. MALDI-TOF data was collected using a Bruker Omniflex instrument with 2,5-dihydroxybenzoic acid as the matrix. The instrument was calibrated with the Sequazyme Peptide Mass Standards Kit (Applied Biosystems).

UV-vis spectra were recorded on an Agilent 8453 diode-array spectrophotometer and corrected for background signal with a solvent-filled cuvette. Emission spectra were acquired on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using right angle detection. All samples were degassed by at least three freeze-pump-thaw cycles in an anaerobic cuvette and were repressurized with Ar following each cycle. The absorbance of all samples was kept below 0.1 OD in order to minimize reabsorption artifacts. Quantum yields of emission were determined by comparison to appropriate standards and are corrected for solvent refractive index and absorption differences at the excitation wavelength. Emission spectra at 77 K were acquired in frozen 2-methylpentane glass. All solvents used in photophysical experiments were of spectral grade or better.

Phosphorescence lifetimes were determined by time-resolved phosphorescence spectroscopy. The irradiation source was an Oriel nitrogen laser (Model 79111) with a 5 ns pulsewidth operating at approximately 25 Hz. The emitted light was dispersed in an Oriel MS-260i spectrograph with a 300 lines mm⁻¹ grating. The detector was an Andor Technologies Intensified CCD camera (1024 × 128 pixels) with an onboard delay generator and a minimum gate width of 5 ns operating in full vertical binning mode and triggered by a TTL prepulse from the nitrogen laser. Data taken of 77 K glasses were subjected to no horizontal binning, while solution data was acquired with a horizontal binning of 2 or 3. 10–15 spectra at different delay times after the laser pulse were taken per lifetime measurement, the integrated intensities of which were fit to a single-exponential function. The detector was calibrated with a Hg(Ar)pencil-style calibration lamp.

Gas mixing was performed by flowing air and nitrogen through two separate Sierra mass flow controllers that were coordinated and controlled with a Sable Systems MFC-4 Gas Mixer. The controlled gas flows were led into the bottom of a round bottom flask equipped with a magnetic stirring bar. The gas mixture was led out of the top of the flask and introduced to the vacuum-degassed sample.

Results and discussion

Synthesis of Pt(II) polymer and model complexes

The synthesis of the Pt(II) polymerization monomer used is illustrated in Scheme 1. The dihalophenylpyridine ligand was

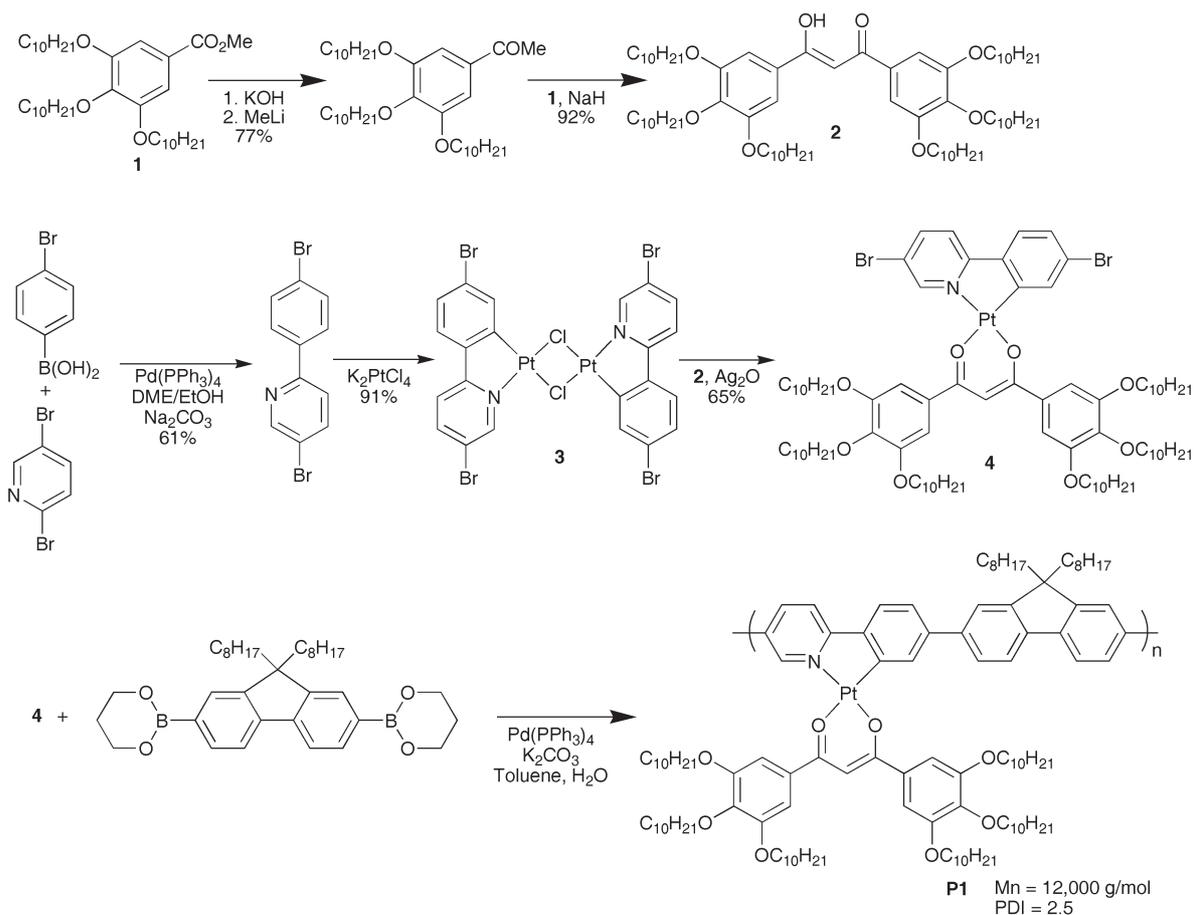
synthesized in one step *via* a regiospecific palladium-mediated Suzuki cross-coupling reaction between 2,5-dibromopyridine and 4-bromophenylboronic acid in good yield following chromatography and recrystallization from hexanes. The higher reactivity of the 2-position of the 2,5-dibromopyridine has been identified previously to make regiospecific poly(pyridyl vinylene)s.¹⁴ The insoluble dichloride-bridged platinum dimer was isolated from the reaction between the phenylpyridine ligand and K₂PtCl₄ in good yield as a yellow powder after Soxhlet extraction with dichloromethane.

The β-diketonate ligand **2** was obtained in good yield following a procedure that involved alkylation of the triol derivative followed by a Claisen-type condensation in the presence of sodium hydride in THF.¹⁵ The methyl ketone was prepared by methyllithium monoreduction of the carboxylic acid. This particular ligand was chosen to help improve the solubility of any polymers made from this material, especially given the square planar geometry of Pt(II) complexes. The monomeric complex **4** could be readily obtained by fragmenting the chloride-bridged platinum dimer in the presence of the dihalophenylpyridine and Ag₂O. Column chromatography allowed for the isolation of pure platinum monomer. This known procedure is highly suitable for making these halogen-containing monomers,¹⁰ in contrast to that for homoleptic biscyclometalated complexes which require the prior formation of organolithium phenylpyridines and intermediates.¹⁶

In addition to monomer **4**, several different model complexes were synthesized for comparison with the platinated conjugated polymer. These are illustrated in Chart 1. Dialkylated phenylpyridine (Scheme 2) could be prepared from the dibromo derivative in the two-step sequence of Sonogashira coupling with the corresponding terminal acetylene, followed by catalytic hydrogenation in ethyl acetate at 45 psi H₂ in the presence of palladium on carbon. All cyclometalated Pt(II) complexes were made following the same procedure described above. Polymerization of **4** was accomplished by standard Suzuki polymerization with the commercially available 2,7-diboronate ester of fluorene as a comonomer. The number average molecular weight of **P1**, as determined by gel-permeation chromatography (*versus* polystyrene standards), was 12000 g mol⁻¹ with a polydispersity index of approximately 2.5. In addition, model complex **5**, a short oligomeric model of the platinum-containing polymer, was synthesized as shown in Scheme 3 by dialkylation of 2-bromofluorene, followed by formation of the boronic acid and Suzuki coupling with **4**.

Solution and frozen glass optical properties

Table 1 displays some of the critical optical properties of the polymers and model complexes synthesized in both deoxygenated tetrahydrofuran (THF) or cyclohexane (CHX) fluid solution, as well as in frozen 2-methyltetrahydrofuran glass at 77 K. The absorbance and emission spectra of **P1** at room temperature, as well as the 77 K emission spectrum are shown in Fig. 1. The absorbance spectrum of this material reflects the conjugated nature of the backbone. As the length of the phenylene backbone increases from two phenylene units, (**6**) to six phenylenes (**5**), and ultimately to the polymeric species (**P1**)



Scheme 1 Synthesis of P1.

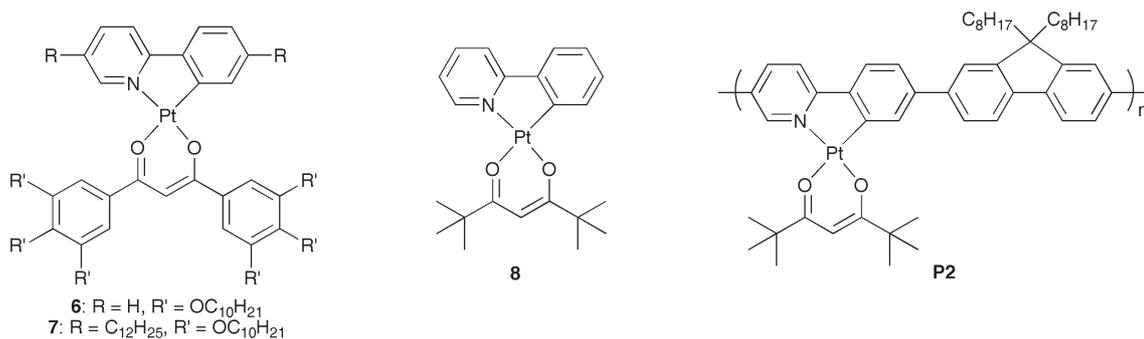


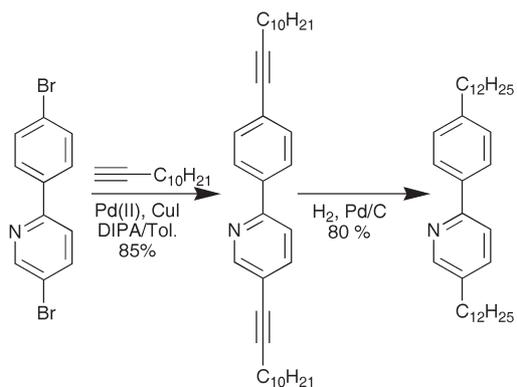
Chart 1 Other model complexes studied.

there is a corresponding extension of the absorbance spectrum to the red. For **P1** onset of absorption begins at 480 nm and there is a local maximum at 450 nm. Intensity-normalized absorbance spectra of these three species are illustrated in Fig. 2.

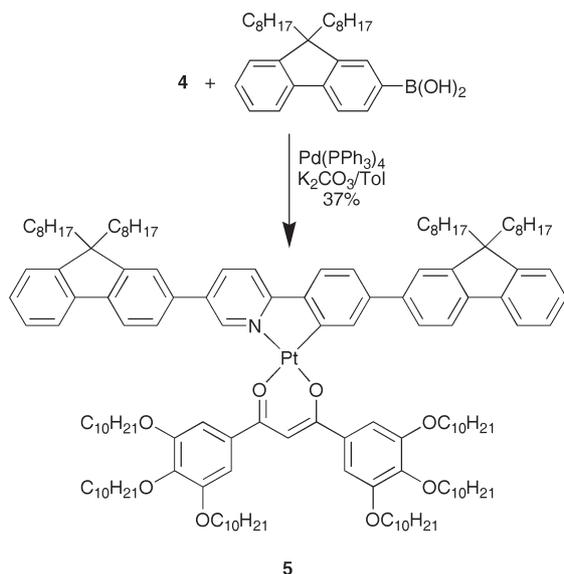
The emission spectrum is dominated by a strong phosphorescence peak at about 585 nm, with a Stokes shift of more than 200 nm. This large difference between the absorbance and emission energies is indicative of phosphorescence, due to the approximately 0.7 eV singlet–triplet energy gap that is curiously characteristic of all phosphorescent conjugated polymers.¹⁷ Another noteworthy feature of the phosphorescence spectra is

the well-resolved vibronic structure observable even in the room temperature sample. The energy difference between the vibronic bands is approximately 1350 wavenumbers, a value typically observed in the fluorescence spectra of phenylene-based conjugated polymers. In addition, the pattern of relative Frank–Condon factors of this material, with the 0,0 band being the most intense and smaller intensities with decreasing energy, is also a common feature in the emission spectra of conjugated polymers.¹⁸

There is little contrast between the 77 K spectrum of **P1** and the spectrum at ambient temperature, save for the typical small rigidochromic blue shift and more highly resolved vibronic



Scheme 2 Synthesis of alkyl substituted *ppy*.



Scheme 3 Synthesis of model complex **5**.

structure in the glass. Metal-to-ligand charge-transfer (MLCT) based transitions often show a substantial solvent dependence because of the potentially large solvent reorganization energies in polar solvents as opposed to non-polar or rigid media.^{13a} The lack of a large blue shift in the frozen glass is consistent with the transition being primarily a triplet π - π^* ligand centered (3 LC) transition with mixing from an MLCT transition to decrease the forbidden character of the inter-system crossing and phosphorescence. The basic spectral

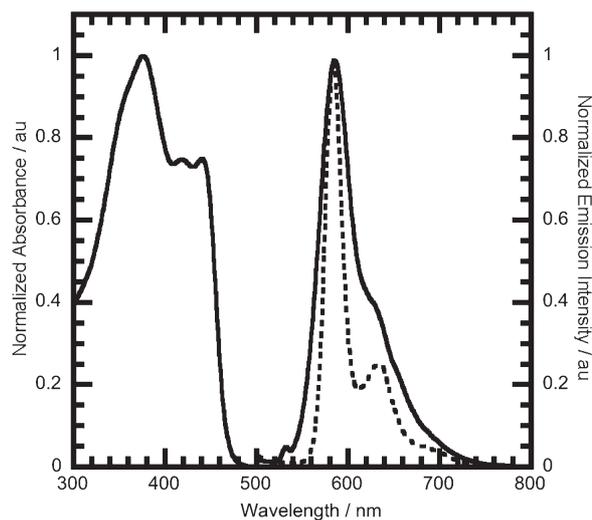


Fig. 1 **P1** room temperature absorbance and emission spectra in THF (solid lines) and 77 K emission spectrum (dotted line) in 2-methyl THF frozen glass.

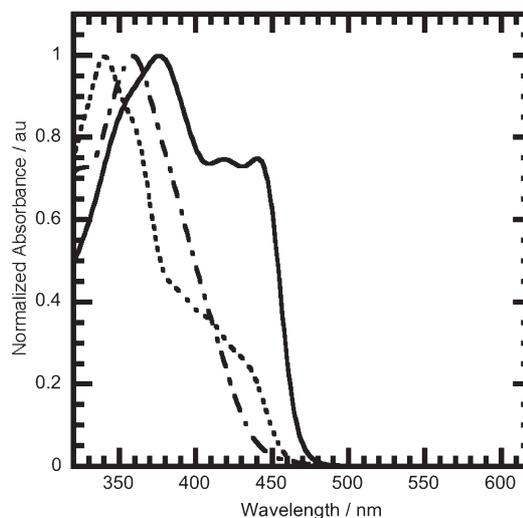


Fig. 2 Height-normalized absorption spectra of **P1** (solid line), **5** (dotted line) and **6** (dot-dash) in THF at room temperature.

characteristics discussed above also support this conclusion. This is very consistent with structurally related square planar platinum complexes previously studied.¹⁰

Table 1 Optical properties of Pt(II) complexes^a

Complex	Absorbance $\lambda_{\text{max}}/\text{nm}$ (rt)	Emission $\lambda_{\text{max}}/\text{nm}$		Φ_p (rt)	$\tau_p/\mu\text{s}$	
		rt	77 K		rt	77 K
P1	374	585	584, 634	0.05	14.4	22.3
5	336	575	560, 606	0.19	13.3	19.2
6	361	531	501, 522	<0.01	0.035	5.3
6 (CHX)	359, 381	490, 526	—	0.24	2.2	—
7	361	533	531	<0.01	0.037	7.2
7 (CHX)	359	496, 530	—	0.30	2.4	—
8	281, 317, 373	485, 519	476, 494, 513	0.16	1.4	8.9 ¹⁰

^a Room temperature data in THF unless otherwise noted as “CHX” (cyclohexane). 77 K data in 2-methyl THF glass.

Another noteworthy feature of this material is its long room temperature excited state lifetime of approximately 14 μs . This is about an order of magnitude longer than the simple model complex **8** that is very similar to the those studied by Thompson.¹⁰ This effect can be understood in terms of the relative energy levels of the ^3LC and MLCT states. Extending the conjugation length causes a lowering of the energy of the ^3LC state as is evident from the absorption and emission spectra. This leads to a decreased amount of mixing between the two states and hence the observed longer phosphorescence lifetime.

The contrasts between **P1** and other, more structurally related model compounds become even more dramatic upon changing the β -diketonate ligand from dipivaloylmethane to phenyl-substituted ligands such as **6**. Fig. 3 illustrates the emission spectra of **6** in several different solvents. Although this changing of the non-cyclometalating ligand does not result in a significant change in the color of emission *versus* those such as compound **8**, it has a large effect on both the quantum yield of phosphorescence and the phosphorescence lifetime in THF. Those complexes with phenyl-substituted β -diketonate ligands show much lower emission efficiencies and excited state lifetimes as low as 35 ns in THF, which are almost three orders of magnitude less than **P1**. The lifetime of complexes **6** and **7** at 77 K is about 6–7 μs , similar in magnitude to **8**.

A reasonable model that is consistent with these observations is the presence of a very weakly or non-emissive state that is in thermal equilibrium with the phenylpyridine-based ^3LC at room temperature in THF. The substitution of aromatic rings on the diketonate ligand extends its conjugation and lowers its oxidation potential (raising the local HOMO), thereby lowering the energy of a charge transfer transition from this ligand to the central platinum atom. This is consistent with previous photophysical data of fluorine-substituted Pt(II) phenylpyridine complexes with high-energy ^3LC transitions.¹⁰ These complexes also have very short lifetimes and low emission quantum yields. Equilibration of the high-energy

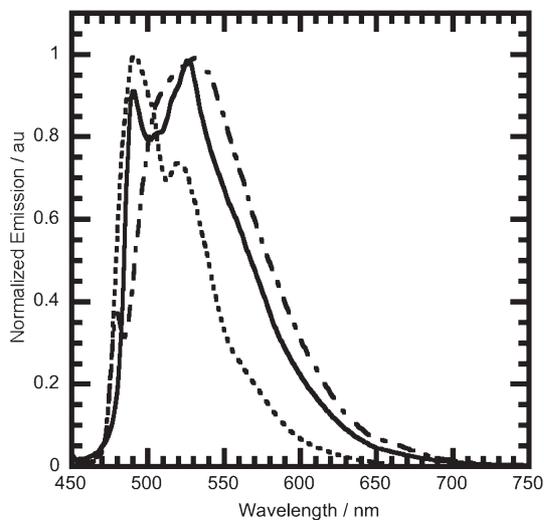


Fig. 3 Height-normalized emission spectra of **6** in room temperature THF (dot-dashed line), 77 K 2-methyl THF glass (dotted line) and room temperature cyclohexane (solid line).

LC state with a non-emissive CT state involving the β -diketonate ligand accounts for this observation as well. In addition, phenyl substituted β -diketonate ligands have been shown to dramatically reduce the phosphorescence efficiency of cyclometalated Ir(III) complexes in 2-methyl THF.^{9b}

This CT model is further supported by the very close similarities of the optical properties of **P1** and **P2**, which are identical polymer structures except for the nature of the diketonate ligand. The room temperature absorption and emission spectra of **P1** and **P2** are overlaid in Fig. 4. Extending the conjugation beyond the immediate phenylpyridine ligand shifts the emission of the based ^3LC transition by over 50 nm to longer wavelength. This lower energy nature of the polymer's emissive state prevents thermal equilibrium with the non-emissive Pt-diketonate CT state, regardless of that diketonate's chemical structure. As a result, the spectral positions, shapes, and most importantly excited state lifetimes of **P1** (14.4 μs) and **P2** (14.2 μs) are all very similar, in stark contrast to those of the corresponding model compounds **8** and **6**.

The nature of the very weakly emissive state has been probed with a solvent-dependence study. When one of the highly soluble complexes **6** or **7** is dissolved in cyclohexane (CHX) as opposed to THF, the excited state lifetime changes from approximately 35 ns to over 2 μs . In addition, the quantum yield of emission is raised from less than one percent to approximately 25–30%. Therefore, the emission from the lowest energy ^3LC state remains undisturbed in CHX, whereas the polar CT Pt-diketonate states are destabilized by the non-polar nature of CHX relative to the more polar THF. Fig. 5 summarizes the model deduced from the experimental data with a qualitative energy level diagram.

These comparisons emphasize that the design of materials containing organometallic complexes for optical and optoelectronic applications is still a relatively unexplored field compared to purely organic materials. The presence of multiple transitions such as metal centered, MLCT and LC transitions

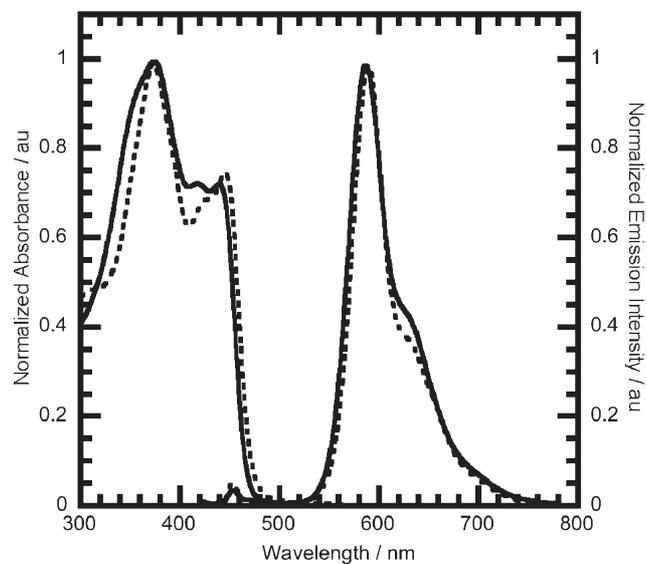


Fig. 4 Height-normalized absorption and emission spectra of **P1** (solid line) and **P2** (dotted line). These two polymers also have very similar excited state lifetimes (14.4 and 14.2 μs , respectively).

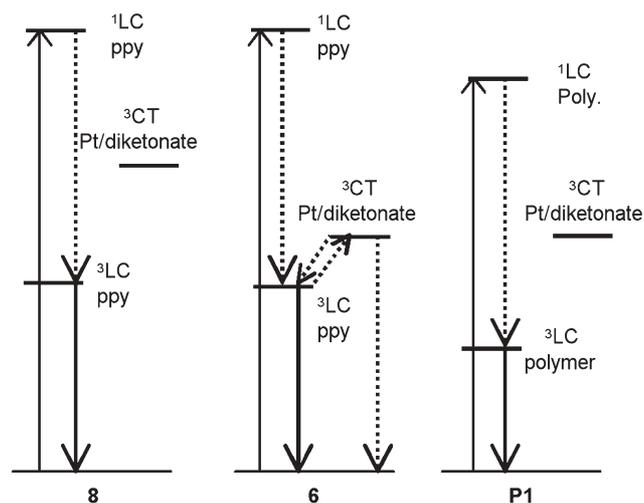


Fig. 5 Qualitative energy diagram of Pt(II) complexes, displaying the emissive ^3LC state and the non-emissive charge-transfer state involving the diketonate ligand. Lowering of the CT state energy by incorporation of phenyl groups on the diketonate group allows the LC state to be in thermal equilibrium with it (**6**). Dramatic lowering of the ^3LC energy by incorporation into a conjugated polymer (**P1**) restores the energy difference between the two states.

adds a significant amount of information to be deconvoluted for each individual metal-containing system. The wide choices of available metal atoms and ligands will not only increase the modularity of potential phosphorescent materials, but also the complexity of data and performance analysis. This being said, these features of organometallic complexes offer additional opportunities for the design and application of new sensory transduction schemes. Manipulation of excited state energy levels in these systems with environmental and chemical structure changes such as this study demonstrates can be envisioned to be critical elements of novel chemosensing mechanisms.

Oxygen induced quenching

The field of optical oxygen sensing has been dominated by phosphorescent transition metal complexes because of their reactivity towards molecular oxygen, through a combination of triplet–triplet annihilation and photoinduced electron transfer, to form singlet oxygen and their long excited state lifetime that allows for competitive diffusion of oxygen with their radiative rates.¹⁹ Oxygen detection is often performed by analyzing the reductions of the excited state lifetimes due to purely diffusive phosphorescence quenching. An advantage of this method is that it does not depend on absolute phosphorescence intensity, which can vary due to partial decomposition of the complex. Hence, lifetime analysis lowers inaccuracies in oxygen concentration measurements brought about by artifacts such as photobleaching.²⁰

Many current research efforts into oxygen detection involve the encapsulation or dispersal of monomeric transition metal complexes into an inert matrix such as poly(dimethylsiloxane) or a sol–gel.²¹ The potential for higher sensitivity brought about by conjugated polymer sensors along with their material properties and processability may make them viable candidates for the next generation in oxygen sensing materials. As a

proof of principle for this type of approach, the sensitivity of **P1** towards dissolved oxygen was compared to the fluorene-containing polymer mimic **5**.

The oxygen sensitivity experiments were conducted in THF solvent. All samples were degassed by at least three freeze–pump–thaw cycles and then repressurized with the appropriate mixture of nitrogen and air. In addition, the solutions were shaken for approximately 2 min before data collection to ensure equilibration between the gas and the solution. Phosphorescence lifetimes as a function of the percentage of air were acquired a minimum of two times to ensure reproducibility.

Fig. 6 shows the dependence of the excited state lifetimes of **P1** and **5** on the volume fraction of air in solution. As can be inferred from this information, the polymeric species demonstrates a noticeable increase in oxygen sensitivity *via* diffusional quenching of approximately 30–40%. The nature of the Stern–Volmer plot serves to “normalize out” any difference in lifetime since the operable quantity is τ_0/τ . This result is indicative of a somewhat larger exciton present in the excited state of **P1** as compared to **5**.

This experiment demonstrates that extension of the excited state of organometallic complexes into conjugated polymers is a potentially viable means towards improving oxygen sensing materials. Though the effect of increased conjugation length is modest in solution, it could be greatly enhanced in conjugated polymers that are highly phosphorescent in the solid state, which may allow for more sensitive amplified detection of oxygen due to intramolecular exciton migration. The current technology of dispersing small molecule phosphors in sol–gel or inert polymer hosts precludes this type of amplification. This enhancement due to the extension of the exciton length is coupled with the increase of the intrinsic excited state lifetime resulting from the lower energy of the ^3LC state relative to the MLCT (*vide supra*). The longer excited state lifetime offered by

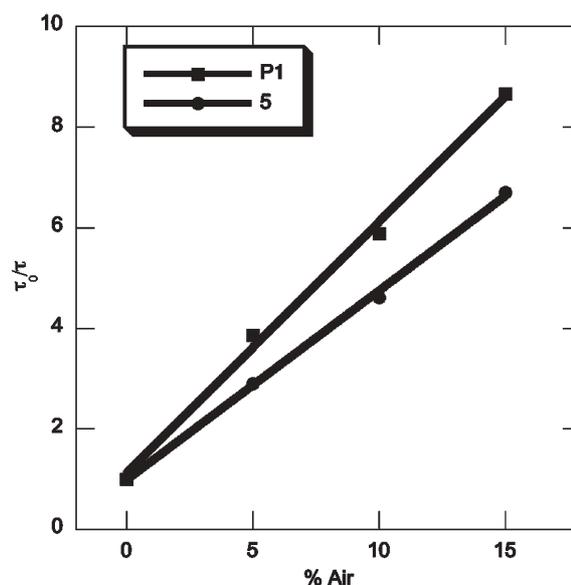


Fig. 6 Lifetime Stern–Volmer Plots for **P1** and **5** as a function of percent air in nitrogen. **P1** shows a 30–40% increased sensitivity to dissolved O_2 . The maximum error in lifetime measurements was 8%.

phosphorescent conjugated polymers should have the practical effect of increasing the dynamic range and resolution of optical oxygen sensing since a wider range of lifetimes would be available for a given range of oxygen concentrations.

Conclusion

We have synthesized and characterized the optical properties of a new organometallic poly(phenylene) conjugated polymer based on a monocyclometalated platinum (II) complex. The emission of this material is dominated by the polymeric ³LC transition, with a small contribution from the MLCT band that decreases the forbidden nature of intersystem crossing and leads to strong phosphorescence. The lower energy of the LC state, due to extension of the cyclometalated chromophore, results in a relatively long 14 μs lifetime at room temperature in THF solution. The vastly different optical properties observed between **8** and **6** or **7** are due to the latter containing the more easily oxidized phenyl-substituted ligand which increases mixing with the CT state. This difference is not apparent between **P1** and **P2**, due to the lower energy of the LC state in the polymers. The polymeric nature of this conjugated material also gives a sensitivity improvement for dissolved oxygen quantification.

Our future efforts will be focused in several different directions. These include the development of phosphorescent conjugated polymers that are highly emissive in the solid state or that are emissive under ambient conditions. In addition, we are currently investigating the unique chemistry and excited state features of organometallic complexes, such as oxidative addition, as novel transduction mechanisms for the trace detection of potentially dangerous vapor phase analytes.

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Samuel W. Thomas III, Shigeyuki Yagi and Timothy M. Swager*
Department of Chemistry, Massachusetts Institute of Technology,
77 Massachusetts Avenue, Cambridge, MA, USA.
E-mail: tswager@mit.edu; Fax: 617-253-7929; Tel: 617-253-4423

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