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## Communications

### Two Luminescent Coordination Polymers with a Triple-Helix Structure: $\text{HgX}_2(\text{C}_{31}\text{H}_{24}\text{N}_2)\cdot\text{CH}_2\text{Cl}_2$ (X = Cl and Br)

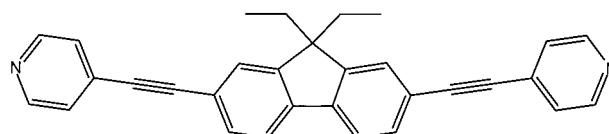
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An exciting advance in optoelectronic materials chemistry has been the development of diverse types of fluorescent organic materials for use in electroluminescent devices.<sup>1</sup> Aromatic organic molecules, conjugated organic polymers, organometallic compounds,<sup>2,3</sup> and metal–chelate complexes all have been investigated for fluorescence properties and for potential applications as light-emitting diodes (LEDs).<sup>4,5</sup> The emission properties of many of these organic materials are tunable via chemical modifications of a base structure, an approach that has been extensively explored.<sup>1</sup> An alternative route for controlling the emission wavelength of organic materials is to incorporate them into a polymeric structure, such as an all-organic polymer,<sup>6</sup> or into a



**Figure 1.** Structure of the fluorene-based fluorescent ligand 9,9-bis-ethyl-2,7-di-(4-pyridyl)ethynylfluorene.

mixed inorganic/organic coordination polymer.<sup>7,8</sup> Indeed, incorporation of fluorescent organic molecules into coordination polymers has, in some cases, led to significant enhancements of fluorescent intensities compared to the free organic molecule.<sup>9</sup> Functionalization of the organic molecule (addition of a donor atom, e.g., N) to allow incorporation into inorganic/organic coordination polymers can offer the advantages of higher thermal stability and solvent resistance compared to the all-organic materials.<sup>4</sup> Consequently, solid-state coordination polymers could significantly impact the field of electroluminescent devices in the future<sup>10</sup> as one can affect the emission color and stability by the judicious choice of metal linkers and the coordination environment around the metal center.

We have been investigating fluorene-based materials for their luminescent properties and have reported on the properties of fluorene-based, all-organic polymer systems using 9,9-dialkyl-2,7-dipropylfluorene as the monomer.<sup>6</sup> A synthetic modification of this monomer has led to the preparation of the 9,9-bis-ethyl-2,7-di-(4-pyridyl)ethynylfluorene ligand. This long *N,N*-bidentate ligand (Figure 1) has already been successfully incorporated into copper-containing square grid polymer structures having extremely large (16 Å<sup>2</sup>) accessible

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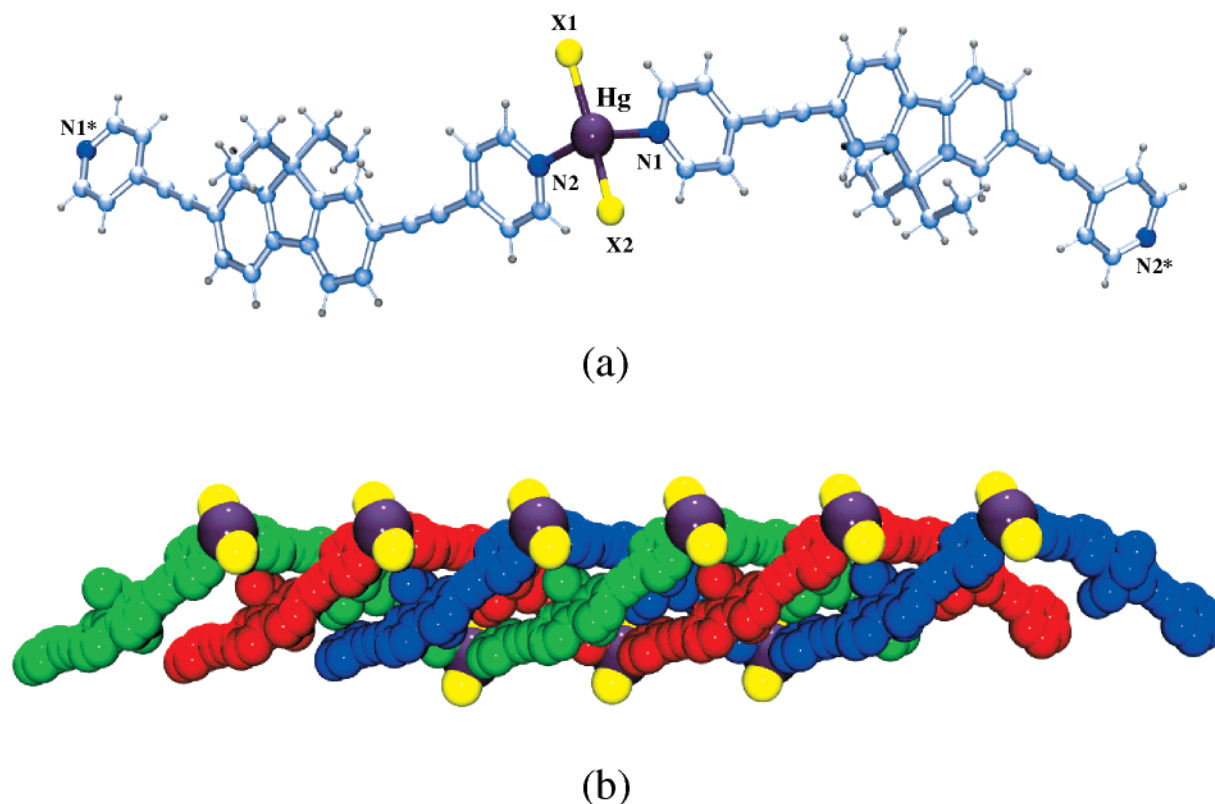
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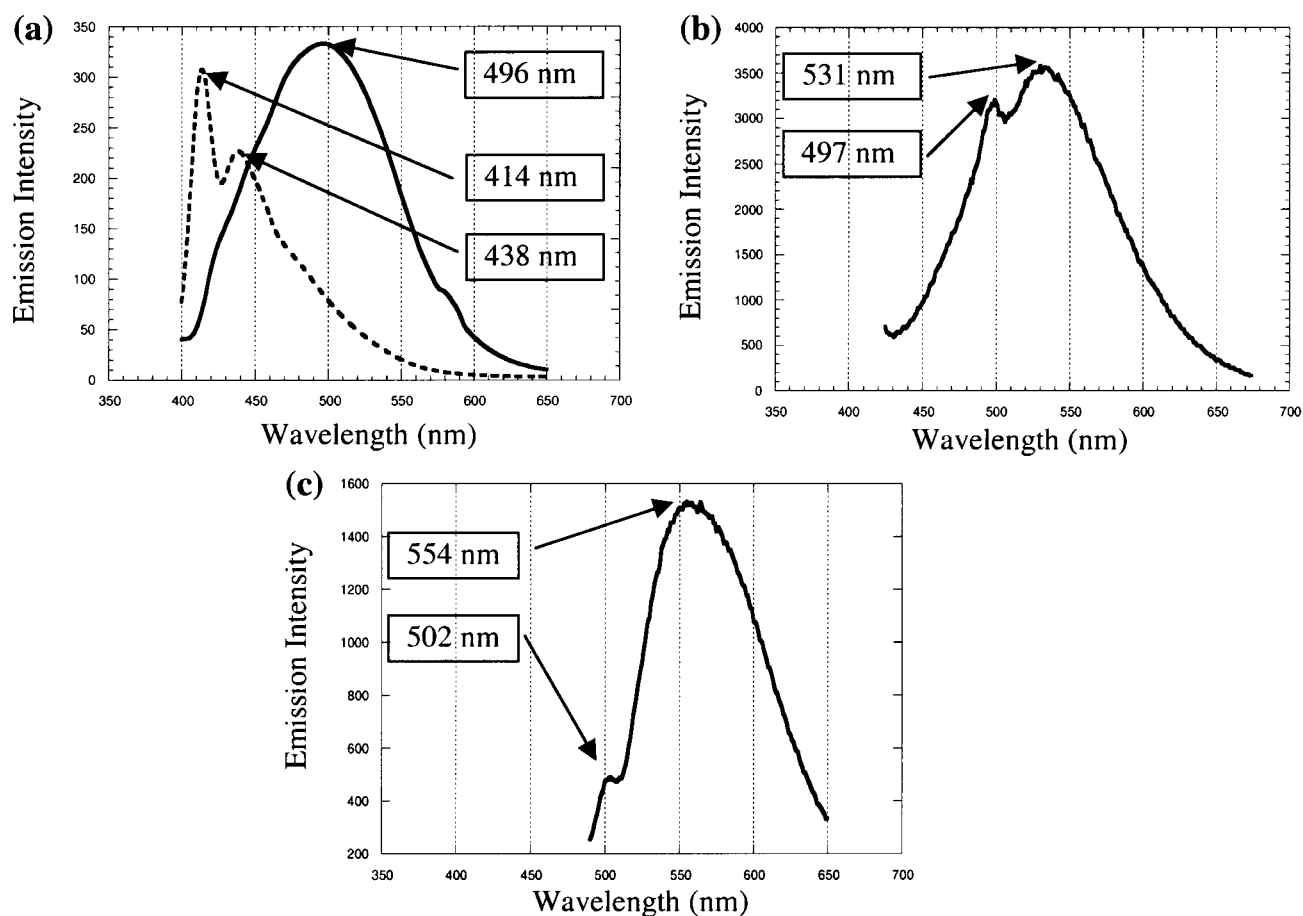
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**Figure 2.** Structure of  $\text{HgX}_2(\text{C}_{31}\text{H}_{24}\text{N}_2)\cdot\text{CH}_2\text{Cl}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ). (a) Distorted tetrahedral environment around Hg. (b) Triple-helix structure. The three intertwined helical chains are crystallographically equivalent, but are shown in red, green, and blue for clarity. Mercury and halogen atoms are purple and yellow, respectively.



**Figure 3.** Fluorescence data for (a) the ligand 9,9-bis-ethyl-2,7-di-(4-pyridyl)ethynylfluorene. Dashed line corresponds to the ligand in chloroform and the solid line corresponds to the ligand in the solid state, (b) a single crystal of  $\text{HgCl}_2(\text{C}_{31}\text{H}_{24}\text{N}_2)\cdot\text{CH}_2\text{Cl}_2$  (**1**), and (c) a single crystal of  $\text{HgBr}_2(\text{C}_{31}\text{H}_{24}\text{N}_2)\cdot\text{CH}_2\text{Cl}_2$  (**2**).

channels, establishing its suitability as a ligand for inorganic/organic coordination polymers. In this coordination environment, however, the coordination polymer did not fluoresce.<sup>11</sup> In this communication we wish to report on the use of this ligand in the synthesis of two new mercury-containing helical coordination polymers,  $\text{HgCl}_2(\text{C}_{31}\text{H}_{24}\text{N}_2)\cdot\text{CH}_2\text{Cl}_2$  (**1**) and  $\text{HgBr}_2(\text{C}_{31}\text{H}_{24}\text{N}_2)\cdot\text{CH}_2\text{Cl}_2$  (**2**), that fluoresce in the visible and that mark the beginning of new fluorescent inorganic/organic materials containing fluorene-based fluorescent ligands.

The synthesis and structure of the fluorescent ligand has been reported previously.<sup>11</sup> In short, the synthesis involves the in situ deprotection of 9,9-bis-ethyl-2,7-di-(trimethylsilylethynyl)fluorene (KOH/EtOH), and the subsequent Sonigashira coupling (1% Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 3% CuI) with 3 equiv of 4-bromopyridine in triethylamine at 70 °C (24 h). Column chromatography (dichloromethane/methanol) afforded a yellow powder in 96% yield.

Single crystals of **1** and **2** were obtained by slowly diffusing a solution of  $\text{HgX}_2$  (X = Cl, Br) (3.93 mg, 0.01425 mmol of  $\text{HgCl}_2$ , 6.16 mg, 0.0171 mmol of  $\text{HgBr}_2$ , respectively) in ethanol into a solution of 9,9-bis-ethyl-2,7-di-(4-pyridyl)ethynylfluorene (12.1 mg, 0.0285 mmol, 14.5 mg, 0.0342 mmol, respectively) in dichloromethane. Yellow transparent crystals of **1** and **2** were isolated after the solution was left at room temperature for several days.

The structures of both compounds were determined by standard single-crystal X-ray diffraction techniques.<sup>12</sup> **1** and **2** are isostructural and form infinite one-dimensional chains. As shown in Figure 2a, the mercury atom is in a distorted tetrahedral environment, coordinated by two chlorine (**1**) or bromine (**2**) atoms and two fluorene ligands (**1**: Hg–N1 = 2.427(6) Å, Hg–N2 = 2.429(6) Å, Hg–Cl1 = 2.352(2) Å, Hg–Cl2 = 2.351(2) Å; N1–Hg–N2 = 96.6(2)°, Cl1–Hg–Cl2 = 154.38(9)°. **2**: Hg–N1 = 2.423(6) Å, Hg–N2 = 2.423(5) Å, Hg–Br1 = 2.474(1) Å, Hg–Br2 = 2.470(1) Å; N1–Hg–N2 = 96.4(2)°, Br1–Hg–Br2 = 151.76(3)°). The bending of the ligand and its coordination at the Hg center results in zigzag chains that adopt a helical twist. Three such

helical zigzag chains intertwine to form the triple-helix structure shown in Figure 2b. In the crystal, the triple-helix bundles pack parallel to one another along the monoclinic *b* direction.

The fluorescence of the free 9,9-bis-ethyl-2,7-di-(4-pyridyl)ethynylfluorene ligand in chloroform is shown in Figure 3a and exhibits two emission maxima at 414 and 438 nm. In the solid state, excimer formation is observed, resulting in a broad emission peak at 496 nm. The emission of **1**, collected on a single crystal, is red-shifted to 531 nm (Figure 3b), with a second, less intense band present at 497 nm. A single crystal of **2** emits at 554 nm (Figure 3c), indicating that the lower electronegativity of the bromine relative to the chlorine has an apparent effect on the fluorescent properties of the mercury-bound ligand in the polymer. A second, much less intense, emission band is also present for **2** at 502 nm. These emission bands at 497 and 502 nm (**1** and **2**, respectively) could possibly be explained by vibronic progressions, by emission from a higher excited singlet state, *S*<sub>2</sub>, or by simple emission from the ligand. Vibronic progressions were ruled out by the absence of vibrational bands in the IR spectra at 1288 and 1870 cm<sup>-1</sup> (peak spacing in **1** and **2**, respectively). We therefore attribute these higher energy bands either to emission from a higher excited singlet state, *S*<sub>2</sub>, or to emission from the ligand itself, which is certainly possible. It is, at least at the moment, not possible to differentiate between these two possibilities. Emission from the coordination polymer dominates these spectra, especially in the case of **2** where only a small shoulder at 502 nm is seen, and a narrower spectrum is observed. Overall, there is a large shift in the emission between the free ligand and the one incorporated into the polymer structure. Reasonably, the presence of the intervening mercury atoms, which exert a strong electron-withdrawing effect as a consequence of their +2 charge and attached halides, have a significant influence on the fluorescent properties of the ligand.

We have started to alter the fluorescent ligand by modifying the side chains both to change the fluorescent properties and to affect the structure of coordination polymers that form. This should, presumably, lead to new, tunable, fluorescent materials.

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**Supporting Information Available:** Complete crystallographic information available in the Supporting Information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Crystal data: Data collection, Bruker SMART APEX CCD diffractometer (Mo K $\alpha$ , 0.71073 Å), *T* = 183(2) K. 1350 raw data frames (hemisphere) of width 0.3° in omega and 10 s exposure per frame. Raw data integrated into reflection intensity files and corrected for Lp and time decay effects with the Bruker SAINT+ (v. 6.02a) program. The final unit cell parameters are based on the least-squares refinement of all reflections with *I* > 5 $\sigma$ (*I*) from the full data sets. Corrections for absorption based on the multiple measurement of equivalent reflections applied with the program SADABS. Structure solution/refinement: direct methods followed by difference Fourier synthesis using SHELXTL v. 5.1; refinement on *F*<sup>2</sup> by full-matrix least-squares. For **1**: monoclinic, *P*2<sub>1</sub>/*n*, *a* = 14.918(1) Å, *b* = 12.755(1) Å, *c* = 16.322(1) Å,  $\beta$  = 93.890(2)°, *V* = 3098.7(5) Å<sup>3</sup>, *Z* = 4, *d*(calc) = 1.674 g cm<sup>-3</sup>, 20401 refl. measured, 6359 unique, 4324 with *I* > 2 $\sigma$ (*I*) (*R*(int) = 0.0525); *R*1 (*F*) = 0.0502, *wR*2 (*F*<sup>2</sup>) = 0.1274, *GooF* = 0.992. For **2**: monoclinic, *P*2<sub>1</sub>/*n*, *a* = 15.214(1) Å, *b* = 12.738(1) Å, *c* = 16.441(1) Å,  $\beta$  = 94.706(2)°, *V* = 3175.4(5) Å<sup>3</sup>, *Z* = 4, *d*(calc) = 1.820 g cm<sup>-3</sup>, 20878 refl. measured, 6481 unique, 4565 with *I* > 2 $\sigma$ (*I*) (*R*(int) = 0.0411); *R*1(*F*) = 0.0443, *wR*2 (*F*<sup>2</sup>) = 0.1052, *GooF* = 1.002.