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Energy Transfer-Assisted Whispering Gallery Mode Lasing in Conjugated Polymer/Europium Hybrid Microsphere Resonators

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Abstract: Lanthanide metal complexes display luminescence with narrow bandwidth. Here, we present coupling of the luminescence from europium ion (Eu^{3+}) with whispering gallery modes (WGMs) in conjugated polymer microsphere resonators. Self-assembly of fluorene–terpyridine alternating copolymer, coordinated by Eu^{3+} (F8tpy-Eu^{3+}), forms well-defined microspheres with an average diameter of 3.2 μm. Upon focused laser excitation, a microsphere of F8tpy copolymer displays WGM photoluminescence (PL) at a wide spectral range from 420 to 680 nm. In contrast, F8tpy-Eu^{3+} hybrid microspheres exhibit sharp WGM PL at a narrow spectral range of 615–630 nm, which is characteristic of luminescence from Eu^{3+}. The PL behavior indicates that photoinduced energy transfer from F8tpy to Eu^{3+} occurs efficiently. Furthermore, the intensity of the PL peak increases nonlinearly upon strong pumping, indicating that a lasing action appears with the threshold of 1.85 mJ cm^{-2}. These results will pave the way for developing microlasers and photonic devices from soft organic materials.

Conjugated polymers are attracted increasing attentions because of their inherent conducting and luminescent properties. These properties are beneficial for organic devices such as solar cells, light-emitting diodes (LEDs), electrochemical cells, and so forth. However, the broad bandwidth of photoluminescence (PL) from conjugated polymers limits their applications such as high-color-purity displays.[1,2] Meanwhile, lanthanide metal complexes show PL with narrow bandwidth originated from the f-f transition.[2–4] However, free lanthanide ions have small absorption coefficient because of its forbidden f-f transitions followed by the odd parity.[2,5]

To overcome this contradiction, one strategy can be referred to as hybridization of a conjugated polymer with lanthanide metal complex:[2] Excitation of a conjugated polymer and subsequent energy transfer from polymer to lanthanide metal ion would result in PL with narrow bandwidth. Indeed, previous reports show that combination of lanthanide complexes with conjugated polymers exhibit PL with narrow width,[2,4] long lifetime,[6] and high efficiency.[1] Because of these benefits, blends of lanthanide metal complex with conjugated polymer in thin film has been adopted for polymer solar cells,[7–9] organic LEDs,[10,11] and optical fibers.[12] Furthermore, if self-assembly of lanthanide metal-coordinated conjugated polymers form microstructures such as spheres, disks, rings, etc, the microstructures would act as whispering gallery mode (WGM) resonators.[13,14] In WGM resonators, luminescence is confined inside the microstructures via total internal reflection at the medium/atmosphere interface. The microcavities function as optical resonators, which can be utilized as micrometer-scale laser sources,[15–19] tools for chemical and bio-sensing[20,21], optical fibers,[22] optical waveguide resonators[23] and other photonic devices.

So far, several WGM resonators from self-assembled conjugated polymers have been reported.[13,24–29] However, reports on WGM resonators from conjugated polymer-lanthanide complex hybrids are very limited: Only one paper by Narayana et al. demonstrated WGM PL from polystyrene (PS) microspheres containing conjugated polymers and terbium(III) complex. Therein, energy transfer occurs from Tb^{3+} to conjugated polymer. However, the observed WGM was in a broad spectral range because the PL is basically from the conjugated polymers.[30] For polymer WGM lasers utilizing lanthanide metals, Fernandez-Bravo et al.[18] fabricated PS microspheres coated with thulium (Tm^{3+})-doped sodium yttrium fluoride (NaYF$_4$) nanoparticle to demonstrate upconversion WGM lasing. The observed lasing at 470 nm is produced by direct excitation of Tm^{3+} ion in the PS microsphere without energy transfer processes.

In this Communication, we investigate WGMs with narrow spectral range from self-assembled conjugated polymer-lanthanide complex hybrid microspheres. For this purpose, we choose fluorene-terpyridine alternating copolymer as an energy donor[6] and europium (Eu) complex as an energy acceptor.[6,31] Self-assembly of the Eu-coordinated conjugated polymers yields well-defined microspheres with several micrometer diameters. A single microsphere of polymer-Eu hybrid acts as an optical resonator, where sharp WGM PL appears at the red-color region, indicating that energy transfer takes place efficiently from polymer to Eu complex. The sharp emis-

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sion from lanthanide metal in a microcavity will be utilized as active materials in organic optoelectronic devices such as lasers, sensors, and LEDs.

For materials, poly[(9,9′-dioctyl-9H-fluoren-2,7-yl)-5,5′-(2,2′:6′,2″-terpyridine) (F8tpy) (**1**) was purchased from ADS Inc., and europium(III) thenoyltrifluoroacetonate trihydrate, [Eu(tta)₃]·3H₂O (**2**) was purchased from Aldrich Co Ltd (Figure 1). A cast film of **1** from CHCl₃ solution showed photoabsorption in the UV region with the absorption edge at 380 nm (Figure 2 a, blue).[6] When **1** and **2** were mixed together in THF (equimolar amount of **2** and the repeating unit of **1**), and the solvent was evaporated, the color of the resultant powders changed from white to pale yellow (Figure 2 a inset). A cast film of the solution of a mixture of **1** and **2** showed red-shifted, broaden pho-
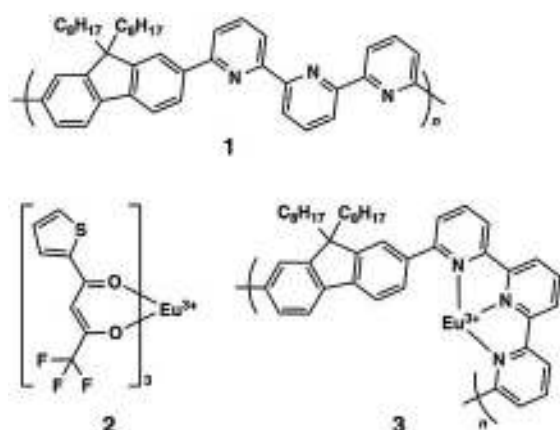
toabsorption band (Figure 2 a, red), indicating that the pyridyl groups of **1** coordinates to **2**, forming polymer-Eu complex **3** (Figure 1).

A CHCl₃ solution of **1** showed blue PL upon photoirradiation at $\lambda_{ex} = 365$ nm with the wavelength of the PL maximum (λ_{em}) of 404 nm (Figure 2 b, blue). By addition of **2**, the PL color of the solution of **1** drastically changed to pink (Figure 2 b inset, right). The PL spectrum of a cast film of the resultant solution showed narrow PL bands at $\lambda_{em} = 577$, 593, 612 and 650 nm, which correspond to $^5D_0 \rightarrow {}^7F_J$ (J=0–3) transitions of Eu³⁺. The full-width at the half maximum (fwhm) of the PL with the highest intensity at $\lambda_{em} = 612$ nm ($^5D_0 \rightarrow {}^7F_2$) was as narrow as 12 nm (Figure 2 b, red). These results indicate that energy transfer from F8tpy to Eu³⁺ takes place efficiently.[1,6,31–34] To authenticate energy transfer takes place from F8tpy polymer to Eu³⁺, excitation spectra of **1** and **3** were measured by monitoring PL at 404 nm for **1** and 612 nm for **3**. As shown in Figure S1 a, absorption bands at 314 nm and 350 nm for **1** and **3**, respectively, correspond well with their absorption spectra (Figure 2 a). Furthermore, the PL spectrum of **1** overlaps well with the absorption spectrum of **3** (Figure S1 b), indicating that energy transfer should takes place from polymer to Eu³⁺. The energy transfer efficiency from polymer to Eu³⁺ ion is evaluated as 0.90, using the following equation, $\eta_{DA} = 1 - (I_{DA}/I_D)$ where I_{DA} and I_D are the PL intensity with and without energy acceptor, respectively.[35,36]

Microspheres of **1** were prepared by a vapor diffusion method (Figure S2 a, in details, see the Experimental Section).[13] Scanning electron microscopy (SEM) image of the drop-cast film of the resultant suspension clearly shows the formation of microspheres (Figure 3 a inset). The average diameter (d_{av}) and the standard deviation (σ) of the resultant microspheres are 4.54 and 2.14 μm, respectively (Figure S3 a). The microsphere of **1** displays blue-color PL upon photoexcitation at 355 nm (Figure 3 a).

On the other hand, Eu³⁺-coordinated polymer **3** hardly formed microspheres by the vapor diffusion method. Therefore, we adopted miniemulsion method to prepare microspheres from **3** (Figure S2 b, in details, see the Experimental Section).[21,37] SEM image of an air-dried suspension of **3** shows microspheres with d_{av} and σ of 3.17 and 1.12 μm, respectively (Figure 3 b inset and Figure S3 b). Due to energy transfer from F8tpy to Eu³⁺, microspheres of **3** display red-color PL (Fig-

Figure 1. Molecular structures of F8tpy (**1**), Eu(tta)₃ (**2**), and F8tpy-Eu(tta)₃ complex (**3**).
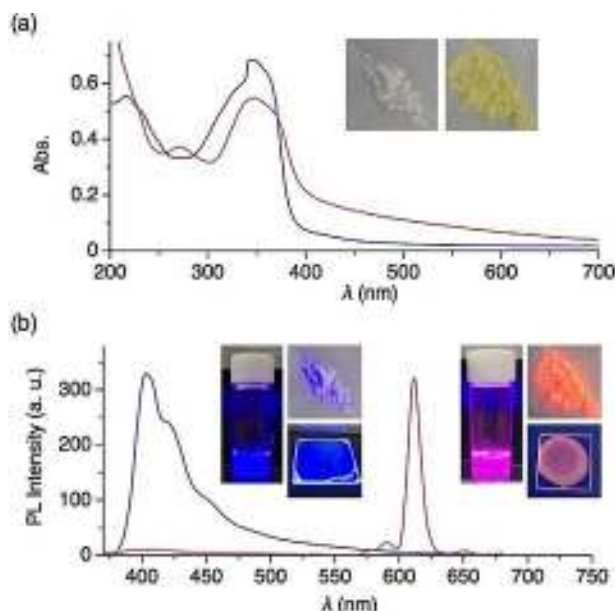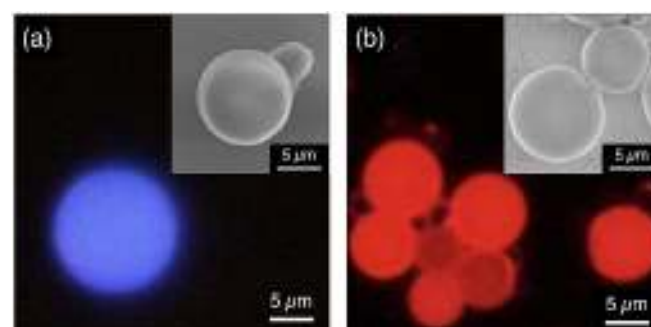

Figure 2. (a) Photoabsorption spectra of cast films of **1** (blue) and **3** (red). Insets show photographs of powder samples of **1** (left) and **3** (right). (b) PL spectra of cast films of **1** (blue) and **3** (red). $\lambda_{ex} = 350$ nm. Insets show photographs of solutions, powders, and thin films of **1** (left) and **3** (right) under UV irradiation at 365 nm.

Figure 3. Fluorescent micrographs of microspheres from **1** (a) and **3** (b). $\lambda_{ex} = 350–390$ nm. Insets show SEM images of the microspheres.

ure 3b). Energy dispersive X-ray spectrometry (EDX) measurements clearly indicate the presence of Eu in the microsphere (Figure S4).

Upon photoexcitation with focused laser ($\lambda = 355$ nm, Figure S5), a microsphere of **1** displays PL with sharp and periodic lines at a wide spectral range from 420 to 680 nm (Figure 4 blue). These PL lines are attributed to WGMs with transverse electric (TE) and magnetic (TM) modes (Figure S6a). The plot of $1/\lambda$ versus l, where λ is the peak wavelengths of the TE mode and l is the angular momentum number,[13] shows almost linear relationship (Figure S6b). From the slope of the plot, the refractive index n is evaluated as 1.76 using an [Equation (1)][13]

$$\lambda^{-1} = (n\pi d)^{-1} \cdot l \tag{1}$$

The n value is nearly identical with that evaluated by spectroscopic ellipsometry measurement of a thin film of **1** (≈ 1.70, Figure S6c).

In sharp contrast, a microsphere of **3** displays WGM PL in a very narrow spectral range at 615–630 nm with almost no emission at 420–570 nm (Figure 4a red, orange, and green). These PL are characteristic of the emission from Eu^{3+}, indicating that energy transfer takes place from F8tpy to Eu^{3+} in the microsphere cavities. The number of WGM peaks increases from one to three as d increases from 3.24 to 4.86 μm (Fig-
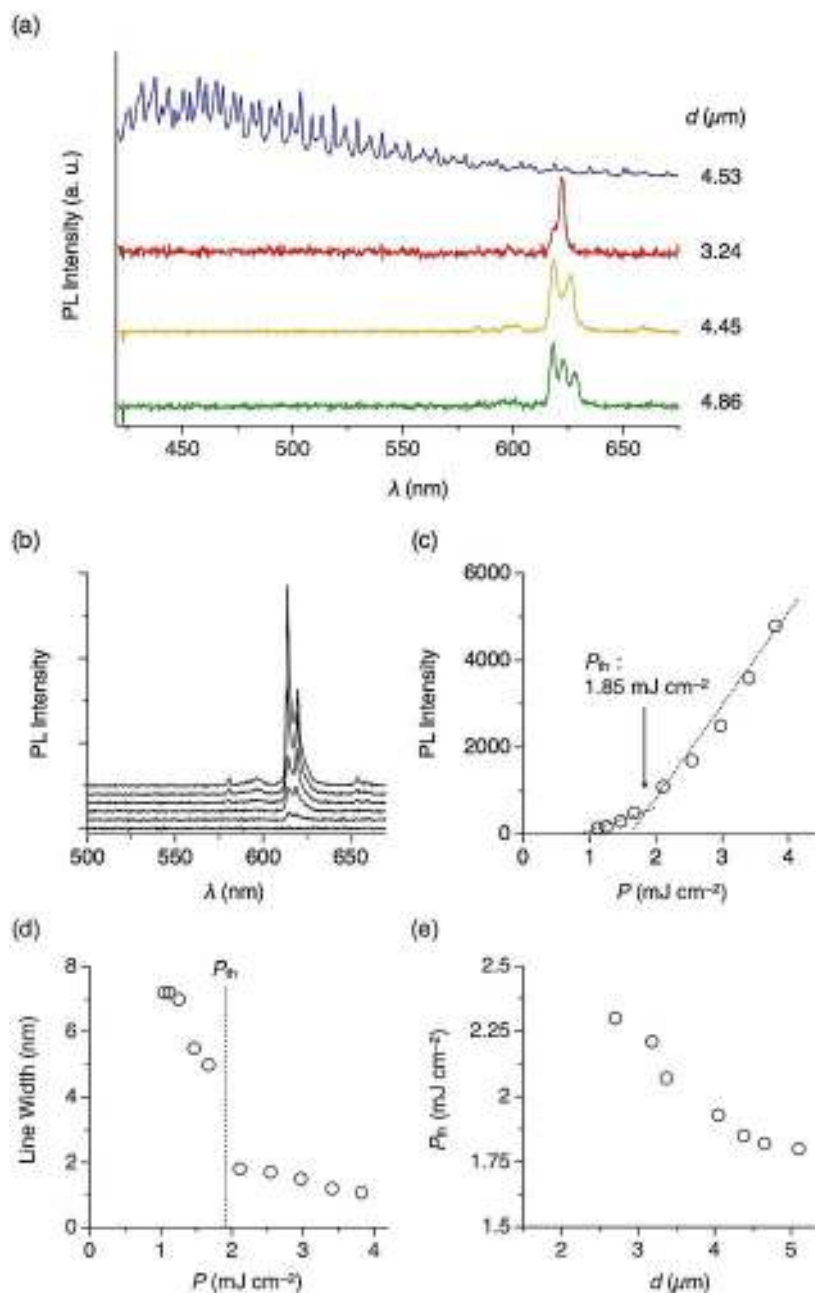

Figure 4. (a) PL spectra of a single microsphere of **1** (blue, $d = 4.53$ μm) and **3** with d of 3.24 (red), 4.45 (orange), and 4.86 μm (green). (b) PL spectra of a single microsphere of **3** with d of 4.38 μm with P of 1.04, 1.25, 1.67, 2.11, 2.97 and 3.82 mJ cm^{-2} (from bottom to top). (c) Plot of the PL intensity at 615 nm versus P. (d) Plot of the line width of the PL peak at around 615 nm versus P. (e) Plot of P_{th} versus d.

ure 4a). The fwhm of the WGM peaks are 1.3–2.7 nm, which are roughly 10 times smaller than that of a cast film from the solution of **3** (12 nm, Figure S7).

As the pumping power (P) increases, the intensity of the PL peak at 615 nm increases non-linearly, which are characteristic of lasing (Figure 4b). The intensity dependence is fitted to a power law x^S where S is the slope of power-law fit in the log-log plot.[15, 16, 18] From Figure 4c, the S values in the linear and the superlinear regions are 0.93 ± 0.04 and 2.46 ± 0.34, respectively. The presence of superlinear region confirms the lasing action from the microsphere. According to the plot of the PL intensity versus P, the lasing threshold (P_{th}) is evaluated as 1.85 mJ cm^{-2} (Figure 4c). Above P_{th}, the line width of the PL peak becomes narrow with less than 2 nm (Figure 4d). The lasing property also depends on d of the microspheres: As d increased from 2.6 to 5.1 µm, P_{th} decreased from 2.3 to 1.8 mJ cm^{-2}, possibly because the scattering loss is small for the larger sphere due to the small curvature (Figure 4e).[28, 29] Furthermore, the line width becomes narrow as d increases on the same P value, also indicating the small leakage loss for microspheres with large d (Figure S6).

In summary, europium complex-coordinated conjugated polymers self-assemble to form microspheres by miniemulsion method. Upon focused laser excitation, the resultant microspheres exhibit whispering gallery mode photoluminescence in a narrow spectral range of 615–630 nm, as a result of efficient energy transfer from polymer to europium. Upon strong pumping, the microspheres of **3** demonstrate lasing action. The microsphere resonators with narrow spectral range are advantageous for miniaturizing lasers and other photonic devices.

Experimental Section

Materials and Measurements

All the reagents and solvent were purchased from Aldrich Co Ltd and used without further purification. The absorbance and PL spectra of **1** and **3** were measured using JASCO model UV-570 spectrophotometer and model FP-6200 spectrofluorometer, respectively. SEM microscopy was performed on a Hitachi model SU-8000 FE-SEM operating at 10 kV. Silicon was used as a substrate and Au for coating. EDX measurements were performed on a Hitachi model S-3900N SEM equipped with an Oxford Instruments model X-Max50 silicon drift detector. Optical and fluorescent microscope observations were carried out using an Olympus model BX53 Upright Microscope. Ellipsometry measurements were carried out on a J. A. Woollam Japan model M-2000 spectroscopic ellipsometer using thin films of **1** and **3**. Attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectra were recorded at 25 °C with a JASCO model FT/IR-4200 Fourier transform infrared spectrometer equipped with a model PR0450-S ATR attachment.

Synthesis of 3

The complexation process of **1** with **2** was followed according to Ref. [38] with a small modification. Equimolar amounts of **1** (10 mg, 0.0016 mmol) and **2** (13.9 mg, 0.0016 mmol) were dissolved in dry tetrahydrofuran (THF, 10 mL) under N$_2$ in two neck round-bottomed-flask. After stirring for 24 h at 50 °C, the solvent was re-

moved by evaporation. The crude product was washed with MeOH and was collected by filtration and dried in vacuum to yield **3** as yellow powder. FT-IR spectrum: $\tilde{v} = 3114$, 2950, 2878 (C–H), 2360 (C≡C), 1600 (C=O), 1539, 1531 (C=C), 1439, 1411, 1317, 1298, 1281, 1180, 1123, 1107, 1059, 932, 859, 787, 715, 678, 640, 583 cm^{-1}.

Preparation of Microspheres of 1 by a Vapor Diffusion Method

A 5 mL vial containing CHCl$_3$ solution of **1** (1.0 mg mL^{-1}, total amount, 2.0 mL) was put in a 50 mL vial containing 5 mL of MeOH. The vial was allowed to stand for 3 days in a thermostat bath at 25 °C, then MeOH vapor was slowly diffused into the CHCl$_3$ solution of **1**, yielding white precipitates (Figure S2a).

Preparation of Microspheres of 3 by a Miniemulsion Method

A CHCl$_3$ solution of **3** (10 mg mL^{-1}, 300 µL) was added to an aqueous solution of sodium n-dodecyl sulfate (SDS, 1.0×10^{-2} M, 2.5 mL), and the water/CHCl$_3$ two-phase-separated solution was emulsified by vigorously stirring with homogenizer (30 000 rpm, 2 min). The resultant emulsion was allowed to stand for 3 days at 25 °C in an atmosphere to naturally evaporate CHCl$_3$. The excess SDS was removed by exchanging the supernatant water through centrifugation by three times (Figure S2b).

µ-PL Measurements

Suspensions of microspheres of **1** and **3** were drop-casted onto a clean quartz substrate and air-dried to immobilize microsphere on the substrate. µ-PL measurements were carried out with homemade µ-PL measurement system. A 355-nm pulsed laser (CNI model MPL-F-355-10 mW-10%, pulse duration 7 ns, frequency 1 kHz,) was passed through ×100 objective lens (NA = 0.9) set on an optical microscope (Nicon model Eclipse LD100D) and excites a single microsphere of **1** and **3**. The PL from a single microsphere was detected by a spectrometer (Lambda Vision model LV-MC3/T, grating: 300 grooves mm^{-1}) through an optical fiber with the spectral resolution of 0.12 nm with 10 µm slit. The schematic representation of the µ-PL setup is drawn in Figure S5.

Conflict of interest

The authors declare no conflict of interest.

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