

# FRET-mediated near infrared whispering gallery modes: studies on the relevance of intracavity energy transfer with Q-factors

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journal or publication title	Materials Chemistry Frontiers
volume	2
number	2
page range	270-274
year	2018-02
権利	This journal is (C) The Royal Society of Chemistry and the Chinese Chemical Society 2018
URL	<a href="http://hdl.handle.net/2241/00153567">http://hdl.handle.net/2241/00153567</a>

doi: 10.1039/C7QM00498B

## FRET-mediated near infrared whispering gallery modes: Studies on the relevance of intracavity energy transfer with Q-factor

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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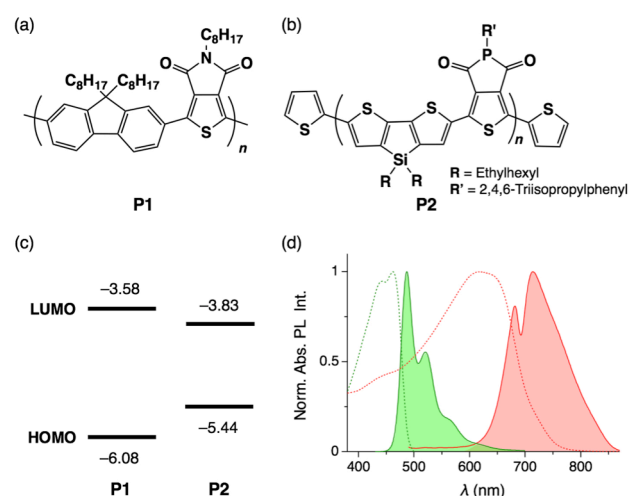
**Near infrared (NIR) optical microsphere resonators are prepared by coassembly of energy-donating and accepting conjugated polymers. In the microspheres, fluorescence resonance energy transfer occurs, leading to sharp and periodic photoluminescence from whispering gallery modes in the NIR region with Q-factors as high as 600.**

Near infrared (NIR) emitting materials represent powerful tools for biosensing and light source for bioimaging due to the high transparency of biological organisms in this spectral window.<sup>1</sup> Therein, NIR luminescent colloidal probes with sharp emission lines are often utilized. Recently, polymer whispering gallery mode (WGM) microresonators with narrow luminescence and laser emission have been reported.<sup>2</sup> Furthermore,  $\pi$ -conjugated organic and polymer microparticles, in some cases doped with rare-earth metals, were shown to exhibit resonant emission and lasing in the visible and NIR region.<sup>2,3</sup> Such organic microresonators find applications for barcoding in live cells, where lasing with a unique spectral profile makes it possible to distinguish each cell.<sup>4</sup> However, NIR emitters often suffer from low luminescence efficiency because of the small energy gap between highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO, respectively) that causes non-radiative thermal deactivation.<sup>5</sup> Furthermore, aggregation of molecules often causes serious quenching of the NIR emission.

The absence of high-performance organic and polymeric lasers in the NIR spectral regime hinders the development of new biomedical imaging probes as well as NIR communication sources. Advancing polymeric microsphere lasers into the NIR spectral region would open up numerous applications in biological systems.

Fluorescence resonance energy transfer (FRET) is an energy transfer mechanism that yields down-converted photoluminescence (PL) with high efficiency.<sup>6</sup> Because the effective distance of FRET is typically within 10 nm,<sup>6</sup> molecules that interchange energy have to be blended homogeneously without macroscopic phase separation.<sup>7</sup> Recently, we reported color conversion of WGM PL in microsphere resonators consisting of two blended  $\pi$ -conjugated polymers. By utilizing FRET, effective red-shifted WGM PL was achieved in the microsphere resonators.<sup>8</sup>

In this communication, we realize FRET in blended conjugated polymer microspheres that leads to NIR emission



**Fig. 1.** Chemical structures of **P1** (a) and **P2** (b). (c) HOMO and LUMO energy levels of **P1** and **P2** with respect to the vacuum level. (d) Photoabsorption (broken lines) and PL (solid lines) spectra of **P1** (green) and **P2** (red) in CHCl<sub>3</sub>.

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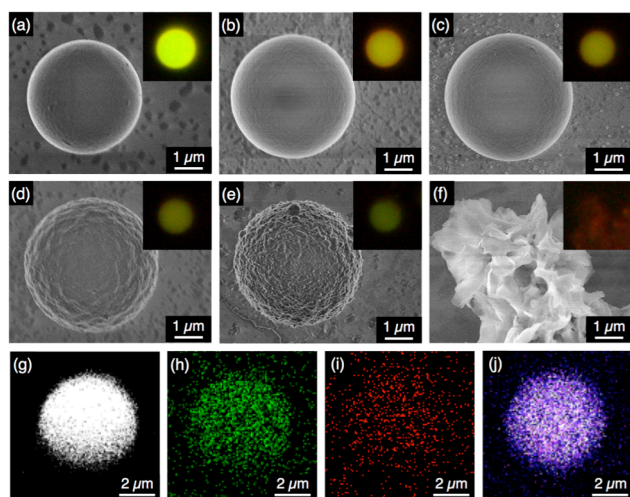
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

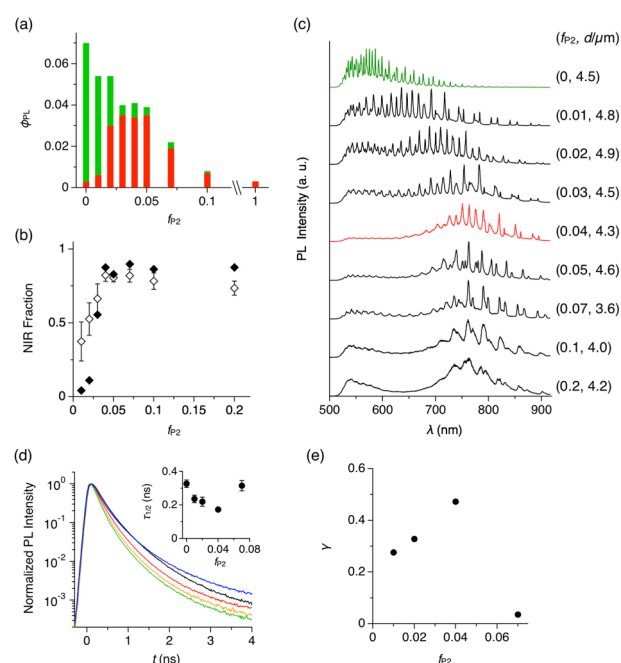


**Fig. 2.** (a–f) SEM micrographs of the self-assembled precipitates of **P1** and **P2** with  $f_{P2} = 0$  (a), 0.03 (b), 0.04 (c), 0.07 (d), 0.1 (e), and 1 (f). Insets show fluorescent micrographs of the precipitates. Image size: 10 x 10  $\mu\text{m}$ .  $\lambda_{\text{ex}} = 400\text{--}440$  nm. (g–j) EDS mapping images of the self-assembled microsphere with  $f_{P2} = 0.04$  on an aluminum stage. (g) C  $K\alpha_1$  and  $K\alpha_2$ , (h) Si  $K\alpha_1$ , (i) P  $K\alpha_1$ , (j) S  $K\alpha_1$ .

from a WGM cavity. The polymers we used in this study, named **P1** and **P2**, act as an energy donor and acceptor, respectively. **P2** displays PL at red-to-NIR region in solution but hardly fluoresces in the solid state because of the aggregation quenching. By contrast, microspheres formed by coassembly of **P1** and small fraction of **P2** exhibit clear WGM PL in the NIR spectral region, resulting from efficient intrasphere FRET from **P1** to **P2**. The utilization of FRET inside a microresonator is useful to efficiently extract NIR light with narrow line width.

The  $\pi$ -conjugated polymers, **P1** (poly[(9,9-dioctylfluorene-2,7-diyl)-*alt*-(5-octylthieno[3,4-c]pyrrole-4,6-dione-1,3-diyl)] with number-average molecular weight ( $M_n$ ) of 24 kg mol $^{-1}$ , Fig. 1a) and **P2** (poly[(5-(2,4,6-triisopropylphenyl)thieno[3,4-c]phosphole-4,6-dione)-*alt*-(4,4-bis(2-ethylhexyl)-silolo-[3,2-*b*:4,5-*b'*]dithiophene)],  $M_n = 6.5$  kg mol $^{-1}$ , Fig. 1b) were synthesized according to reported procedures.<sup>9</sup> The HOMO and LUMO energy levels are  $-6.08$  and  $-3.58$  eV for **P1** and  $-5.44$  and  $-3.83$  eV for **P2**, respectively, with respect to the vacuum level (Fig. 1c). As shown in the photoabsorption and PL spectra of **P1** and **P2** in  $\text{CHCl}_3$ , the PL band of **P1** largely overlaps with the absorption band of **P2**, indicating that efficient FRET from **P1** to **P2** is possible (Fig. 1d). Indeed, in cast films prepared by spin coating of **P1** and **P2** in  $\text{CHCl}_3$  solution, PL from **P1** is mostly quenched even when the weight fraction of **P2** ( $f_{P2}$ ) is only 0.02 (Fig. S1).

Self-assembly of **P1** and **P2** and coassembly of their blends into WGM microsphere resonators were carried out by slow diffusion of MeOH vapour into their  $\text{CHCl}_3$  solutions (see the experimental section).<sup>2,10</sup> The total initial concentration of polymers **P1** and/or **P2** was set at 0.5 mg mL $^{-1}$ . After three days of vapour diffusion at 25  $^\circ\text{C}$ , the solution changed to a suspension, and the polymers were precipitated. Scanning



**Fig. 3.** (a) Bar graph of  $\phi_{\text{PL}}$  ( $\lambda_{\text{PL}} = 500\text{--}900$  nm) and its red-to-NIR fraction ( $\lambda_{\text{PL}} = 650\text{--}900$  nm, red) versus  $f_{P2}$  of cast films of the self-assembled precipitates (microspheres for  $f_{P2} = 0\text{--}0.1$  and irregular aggregates for  $f_{P2} = 1$ ).  $\lambda_{\text{ex}} = 470$  nm. (b) Plots of the fraction of NIR PL to PL at all the wavelength region versus  $f_{P2}$  for cast films of the microspheres (closed squares) and a single microsphere (open squares). (c) PL spectra of a single microsphere of **P1** and **P1/P2** blends with  $f_{P2} = 0\text{--}0.2$  upon focused laser irradiation at 470 nm. (d) PL decay profiles at  $\lambda_{\text{PL}} = 540$  nm ( $\pm 2.5$  nm range) of a single microsphere with  $f_{P2} = 0$  (black), 0.01 (red), 0.02 (orange), 0.04 (green), and 0.07 (blue).  $\lambda_{\text{ex}} = 470$  nm. Insets show plots of  $\tau_{1/2}$  versus  $f_{P2}$  at  $\lambda_{\text{PL}} = 540$  nm ( $\pm 2.5$  nm range). The plots are the average value with the measurements of 5–7 isolated microspheres. (e) Plot of  $\gamma$  versus  $f_{P2}$ .

electron microscopy (SEM) shows that **P1** ( $f_{P2} = 0$ ) forms well-defined microspheres with a typical diameter of 5  $\mu\text{m}$  (Fig. 2a),<sup>2a,8,11</sup> while **P2** ( $f_{P2} = 1$ ) gave irregular aggregates (Fig. 2f). For **P1/P2** blend, well-defined microspheres with smooth surface morphology could be obtained within a  $f_{P2}$  range of 0.01–0.05 (Fig. 2b, c). However, in case of the coassembly with  $f_{P2}$  greater than 0.06, the surface morphology of the resulting spheres deteriorated (Fig. 2d, e). Polymer blends tend to phase separate due to their small mixing entropy.<sup>7</sup> In case of  $f_{P2} \geq 0.06$ , microspheres with rough surfaces are obtained with characteristic features inherent to phase segregation. On the other hand, in case of  $f_{P2} \leq 0.05$ , **P1** and **P2** are well mixed, and segregation of **P2** is suppressed due to its small fraction. In fact, energy dispersive X-ray spectrometry (EDS) mapping of the microsphere with  $f_{P2} = 0.04$  shows that signals of Si and P from **P2** are homogeneously distributed throughout the entire microsphere. This result indicates that **P2** is well dispersed in a single microsphere (Figure 2g–j). The signals of each element

are much clearer for microspheres with  $f_{P2} = 0.07$ , yet it is hard to recognize the phase separation of **P1** and **P2**, because the resolution of the apparatus is not sufficient (Fig. S3).

The change of PL quantum yield ( $\phi_{PL}$ ) with  $f_{P2}$  further indicates that **P2** is well dispersed in the **P1** matrix. Upon excitation at 470 nm,  $\phi_{PL}$  of the microspheres decreases monotonically with increasing  $f_{P2}$  (Fig. 3a). However, the fraction of the PL in the red and NIR region ( $\lambda = 650\text{--}950$  nm) increases with increasing  $f_{P2}$ , and at  $f_{P2} \geq 0.03$ , the PL spectrum is same as for pure **P2** (Fig. 3b, closed squares). These results show that efficient energy transfer takes place from **P1** to **P2**. When  $f_{P2}$  is greater than 0.07,  $\phi_{PL}$  decreases largely, indicating that the aggregation of **P2** causes concentration quenching of the NIR PL from **P2**. Excitation spectrum of a cast film of microspheres ( $f_{P2} = 0.05$ ) shows that PL at 650 nm is mostly generated by photoabsorption of **P1**, further supporting that efficient energy transfer from **P1** to **P2** occurs inside the microsphere (Fig. S2).

To quantify the energy transfer, we measure PL spectra of individual microspheres ( $\lambda_{ex} = 470$  nm, see the experimental section and Fig. S4). For microspheres with  $f_{P2} = 0\text{--}0.2$ , characteristic spectral modulation from the WGM cavity can be observed, indicating that the generated PL is confined inside of the microspheres and self-interferes (Fig. 3c).<sup>2,8,12</sup> As  $f_{P2}$  increases, the spectral series of WGM modes shift from the visible to the NIR region, and at  $f_{P2} = 0.04$ , WGM PL is observed mostly in the NIR region at 700–900 nm (Fig. 3c, red). According to the area intensity, more than 80% of the PL originates from **P2** in the microsphere with  $f_{P2}$  of 0.04 (Fig. 3b, open circles). At  $f_{P2}$  greater than 0.07, the NIR PL slightly decreases and the PL in the visible region reappears (Fig. 3c), possibly caused by the meso- and macroscopic phase segregation of **P1** and **P2** in the microsphere (Fig. 2d and e).

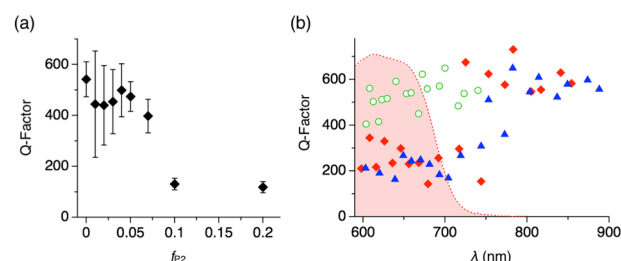
We performed time-resolved PL spectroscopy, which further supports the intrasphere energy transfer. As  $f_{P2}$  increases from 0 to 0.04, the PL half lifetime ( $\tau_{1/2}$ ) at 540 nm (PL from **P1**) monotonically decreases from 0.327 to 0.172 ns (Fig. 3d), while  $\tau_{1/2}$  at 675–730 nm (PL from **P2**) is almost constant at around 0.6 ns (Fig. S5). Further increase of  $f_{P2}$  to 0.07 results in an increase of  $\tau_{1/2}$  at 540 nm to 0.315 ns.

The energy transfer efficiency ( $\gamma$ ) in the single microsphere is evaluated with equation (1),

$$\gamma = 1 - \tau_B / \tau_D \quad (1)$$

where  $\tau_D$  and  $\tau_B$  represent the PL half lifetime of the energy donating polymer ( $\lambda_{PL} = 540$  nm) in the microspheres of **P1** and **P1/P2** blend, respectively.<sup>6b</sup> We find that  $\gamma$  increases from 0.276 to 0.473 with increasing  $f_{P2}$  from 0.01 to 0.04 (Fig. 3e). However, further increase of  $f_{P2}$  to 0.07 greatly suppresses  $\gamma$ . The phase separation of **P1** and **P2** in the microsphere starts to occur at this blending fraction, which also reduces the donor-acceptor interface area in the microsphere.

We further carry on to determine the performance of the WGM resonator by evaluating the Q-factor. The average Q-factor is defined as the peak wavelength divided by the full-width at the half maximum of the observed WGM PL peaks ( $Q_{av}$ ). For the microspheres with  $f_{P2} \leq 0.07$  and  $d \sim 5$   $\mu\text{m}$ ,  $Q_{av}$  is around 400 (Fig. 4a). With increasing  $f_{P2} \geq 0.1$ ,  $Q_{av}$  decreases



**Fig. 4.** (a) Plot of the average Q-factor versus  $f_{P2}$ . (b) Plots of Q-factors of each WGM PL line for microspheres with  $f_{P2} = 0$  (circle), 0.01 (square), and 0.02 (triangle). The red-colored area indicates photoabsorption spectrum of a  $\text{CHCl}_3$  solution of **P2**.

greatly to  $\sim 100$ , which results from the increased surface roughness that causes scattering losses of the confined PL. It is noteworthy that the Q-factor shows wavelength dependency. The WGM PL lines of the microspheres with  $f_{P2} = 0$  display Q-factors around 500 (Figs. 4b and S6, green).<sup>13</sup> By contrast, WGMs of the microspheres with  $f_{P2} = 0.01$  and 0.02 exhibit Q-factors around 200 in the visible range (600–750 nm) and as large as 600 in the NIR region ( $> 800$  nm, Figs. 4b and S6, red and blue). Q-factor is described as follows:

$$Q^{-1} = Q_{\text{rad}}^{-1} + Q_{\text{scat}}^{-1} + Q_{\text{abs}}^{-1} \quad (2)$$

where  $Q_{\text{rad}}^{-1}$  is leakage loss for the internal reflection,  $Q_{\text{scat}}^{-1}$  is scattering loss by the surface roughness, and  $Q_{\text{abs}}^{-1}$  is absorption loss by the resonator medium.<sup>13</sup>  $Q_{\text{abs}}^{-1}$  is shown as

$$Q_{\text{abs}}^{-1} = \alpha \lambda / 2n\pi \quad (3)$$

where  $\alpha$  is absorption coefficient and  $n$  is refractive index of the medium.<sup>14</sup>  $Q_{\text{abs}}^{-1}$  increases when  $\lambda$  overlaps with the absorption wavelength, thereby resulting in the decrease of Q. As shown in Figure 4b, the increase of the Q-factor is observed at wavelengths higher than 750 nm. This wavelength coincides with the absorption edge of the doped **P2** (Fig. 4b, blue and red). Using equation (3), we simulate the wavelength dependency of  $Q_{\text{abs}}$ , and the tendency of the experimental plot in Figure 4b matches well with the simulated plots (Fig. S7).

On the other hand,  $Q_{\text{rad}}^{-1}$  and  $Q_{\text{scat}}^{-1}$  of the compared microspheres are assumed not differ greatly, because microspheres with identical diameters ( $\sim 5$   $\mu\text{m}$ ) and similar degree of surface roughness are applied here.  $Q_{\text{rad}}$  is indeed size dependent,<sup>14b</sup> which is clearly visible when plotting Q versus the particle diameter (Fig. S8). As a result of the reabsorption loss, WGM lines in the visible range display smaller Q values ( $\sim 200$ ) than those in the NIR range, where they reach as high as 600. This value is of similar level as previously reported NIR WGMs of self-assembled organic resonators.<sup>3</sup>

## Conclusions

We fabricate whispering gallery mode (WGM) microresonators by self-assembly of energy donating conjugated polymer doped with a small portion of energy accepting, NIR-emitting polymer. Due to efficient energy transfer (FRET) from donor to

acceptor polymers inside the microspheres, WGM in the NIR region appears upon photoexcitation at the perimeter of the microsphere. The observed Q-factor is as high as 600 in the NIR region, at which the absorption loss by the energy-accepting polymer is almost dismissed. The NIR WGM resonators will be valuable for applications as sensing and imaging in the biological system.<sup>15</sup>

## Experimental section

**Self-assembly of P1, P2 and coassembly of their blends.** Typically, a 5 mL vial containing a CHCl<sub>3</sub> solution of P1, P2 or their blends with a total concentration and amount of 0.5 mg mL<sup>-1</sup> and 2 mL, respectively, was placed in a 50 mL vial containing 5 mL of MeOH. The outside vial was capped and then allowed to stand for 3 days at 25 °C. The vapour of the nonsolvent was slowly diffused into the solution, resulting in a precipitation of the polymers through the supersaturated state.

**μ-PL Measurements.** μ-PL measurements were carried out using a μ-PL measurement system (Fig. S4).<sup>8</sup> An optical microscope was used with a long-distance 100x objective (NA = 0.8) to identify suitable particles and determine their diameters. For measurements, a WITec μ-PL system was used with a model Alpha 300S microscope combined with a Princeton Instruments model Action SP2300 monochromator (grating: 300 grooves mm<sup>-1</sup>) and an Andor iDus model DU-401A BR-DD-352 CCD camera cooled to -60 °C. The PL spectrum was measured at a resolution of 0.27 nm. The edge of a single sphere was photoexcited at 25 °C under ambient conditions by a diode pulsed laser (a PicoQuant model LDH-D-C-470B with a PDL 828 'Sepia II' driver) with the wavelength, power, integration time, frequency, pulse duration and spot size of 470 nm, 1.5 μW, 1 s, 2.5 MHz, 70 ps, and ~1 μm, respectively. Time-resolved PL decay experiments on individual isolated microspheres were carried out on the samples sealed under nitrogen in a glove box using a PicoHarp 300 TCSPC module from PicoQuant hooked to a Leica TCS SP8 microscope equipped with a pulsed White Light Laser.

## Acknowledgements

The authors acknowledge Prof. Tatsuya Nabeshima, Masaki Yamamura, and Takashi Nakamura for PL quantum yield experiments. This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas "π-System Figuration" (JP17H05141, JP17H05142, JP17H05155), Scientific Research (A) (JP16H02081), and Joint International Research (JP15KK0182) from Japan Society for the Promotion of Science (JSPS), University of Tsukuba Pre-strategic initiative "Ensemble of light with matters and life", Asahi Glass Foundation, and the Deutsche Forschungsgemeinschaft DFG (KU 2738/3-2).

## Conflicts of interest

There are no conflicts to declare.

## Author Contribution

YY and YT designed experiment, KH, YT, SM, JK, TK synthesized polymers, OO and SK conducted self-assembly, OO, AM, TD, SI, TN, AK, FD, RF conducted μ-PL and time-resolved PL measurements, YY and OO prepared manuscript.

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