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FOCUS REVIEW

Spherical resonators from π-conjugated polymers

Yohei Yamamoto[1,2,3]

Optical resonators have an important role in optical devices; they confine, sharpen and amplify light. Self-assembled polymer resonators are advantageous for their simple fabrication processes with low cost and low energy consumption. In this focus review, we show recent advances in the self-assembly of π-conjugated polymers to form microspheres that act as optical resonators. The key factors in sphere assembly are low crystallinity of the polymers and slow diffusion of polar nonsolvent during the assembling process. Focused laser irradiation of a single isolated microsphere excites whispering gallery modes (WGMs), in which sharp and periodic lines are observed in the photoluminescence (PL) spectrum; these are characterized as transverse electric and magnetic modes. Efficient intrasphere energy transfer occurs in the case of microspheres composed of energy-donating and -accepting polymer blends. Furthermore, WGM-mediated long-range intersphere PL propagation and subsequent color conversion were observed in the case of linearly coupled microspheres. Conjugated polymer microspheres are beneficial as optical resonators in terms of their high refractive indices, high absorptivity and high PL efficiency, which are achieved by using simple fabrication processes.
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INTRODUCTION

Assembly of molecules to give a certain morphology and orientation often yields novel properties that are unexpected from the known properties of the molecules. So far, there have been a variety of research on the self-assembly of π-conjugated molecules.[1–3] By focusing on π-conjugated polymers, the assembling morphology has an important role in the performances of organic semiconductor devices. For example, highly crystalline regioregular poly(3-hexylthiophene) (**RR-P3HT**) forms two-dimensional lamellar structures with controlled macroscopic orientations,[4] whereas under certain condition of assembly, **RR-P3HT** forms a one-dimensional nanofiber structure.[5] In both cases, several factors such as π-stacking of the polymer main chains, interaction of the side chains and the solvent conditions have a crucial role for the formation of particular morphologies.

Spheres are considered to have another interesting geometry, because the spherical structure results in novel optical properties. For example, monodispersed polymer colloids with a diameter of several hundred nanometers form colloidal crystals.[6–8] The three-dimensional periodic structure results in a photonic band gap and selective reflection that depends on the periodicity. Confinement of light in the periodic structure results in nonlinear optical properties and laser oscillation.[9] Novel optical properties are also shown by single microspheres. One example is whispering gallery mode (WGM), whereby total internal reflection at the polymer/air interface results in the confinement of light inside the microspheres (Figure 1).[10,11] Optical resonance occurs when the optical path length coincides with the integer multiple of the wavelength of the light. So far, many types of WGM resonators consisting of inorganic and organic materials have been reported. Organic spherical WGM resonators consist of liquid droplets, liquid crystalline materials and nonconjugated polymers, and most of these are doped with fluorescent dyes.[12–14] Organic resonators are beneficial in terms of mechanical flexibility and color tunability, and they are often prepared by using simple fabrication processes such as molecular self-assembly. However, reports on nano and microspheres consisting of π-conjugated polymers have been limited.[15–17] One reason is high crystallinity: anisotropic crystal growth results in an aggregation that has the morphology of one-dimensional fibers and two-dimensional lamellae, not an isotropic sphere. The spherical colloids so far reported to have been formed from conjugated polymers are prepared mostly by microemulsion polymerization, dispersion polymerization or self-organized precipitation methods,[15–18] and the resultant assemblies are considered to be kinetic products.

In this focus review, we describe the self-assembly of π-conjugated polymers. The important factors for the formation of spheres are low crystallinity of the polymers and slow precipitation by vapor diffusion of polar nonsolvent. We also describe photoluminescence (PL) from single microspheres. PL contains WGMs and the Q-factor reaches several thousands. We performed intrasphere energy transfer from microspheres with energy-donating and -accepting polymer blends. Furthermore, we demonstrate long-range intersphere PL transfer and subsequent color conversion. The conjugated polymer

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microresonators that we fabricated have the following advantages: (1) because the polymers fluoresce themselves, fluorescent dyes do not need to be doped into the cavity medium; (2) conjugated polymers possess high refractive indices (n, between 1.6 and 2.0), which enhance the efficiency of light confinement; (3) microspheres are fabricated by using a simple, low-cost and low-energy self-assembly process in solution; (4) conjugated polymers are inherently redox active and electroconductive, and these properties are beneficial for future optoelectronic applications such as electrically driven WGM PL and lasing.

RESULTS AND DISCUSSION

Sphere formation from π-conjugated polymers

We used a vapor diffusion method for the self-assembly of π-conjugated polymers (Figure 2a). Typically, a 5 ml vial containing polymers dissolved in a good solvent, such as chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) or tetrahydrofuran (amount: 2 ml, concentration: 0.5–2.0 mg ml^{-1}), is placed into a 50 ml vial that contains a poor solvent such as methanol, acetone or acetonitrile (amount: 5 ml). The 50 ml vial is then capped and allowed to stand for several days at a constant temperature (typically 3 days at 25 °C).

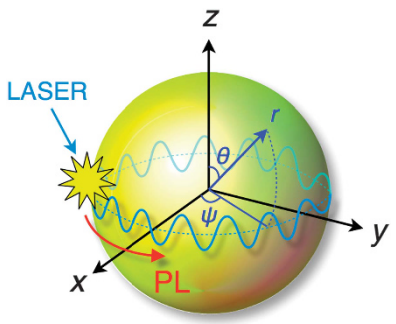

Figure 1 Schematic representation of WGM inside a microsphere. PL, photoluminescence; WGM, whispering gallery mode.

Low crystallinity is an important factor for spherical assembly. For example, the alternating copolymer **F8T2**, comprising 8,8-dioctyl-fluorene (F8) and bithiophene (T2)-repeating units, gives only irregular aggregates. In contrast, **F8TMT2**, comprising F8 and tetra-methylbithiophene (TMT2)-repeating units, forms well-defined microspheres under identical self-assembly conditions (Figure 2b).[19] The four methyl groups in **F8TMT2** induce a twist between two thiophene rings with a dihedral angle of ~66°, thus preventing π-stacking of the polymer main chains and the production of amorphous aggregates.[20] Another example is that of **RR-P3HT** and regiorandom poly(3-hexylthiophene) (**RRa-P3HT**); the former forms only irregular aggregates, whereas the latter forms well-defined microspheres.[19] Typical single-component conjugated polymers such as 8,8-dioctyl-polyfluorene (**F8**), as well as alternating copolymers with planar main chains, highly linear copolymers and donor–acceptor copolymers, tend to form irregular aggregates. On the other hand, alternating copolymers with highly twisted main chains tend to form well-defined microspheres. The TMT2 unit, in particular, is a powerful structural component for the formation of spherical assemblies.[20] We found that, as counterparts of TMT2 in alternating copolymers, not only F8, but also 2,7- and 3,6-carbazole (**2,7-CzTMT2** and **3,6-CzTMT2**), dioctylphenylene (**DOPTMT2**), and phenothiazine (**PTTMT2**) units form well-defined microspheres. The only exception is **DPPTMT2** with diketopyrrolopyrrole (DPP) and a TMT2-repeating unit, whereby strong donor–acceptor interaction induces π-stacking of the polymer main chains, affording one-dimensional nanofibers. Powder X-ray diffraction studies have revealed that no diffraction peaks appear from microspheres, whereas irregular aggregates of **F8T2** and nanofibrous assemblies of **DPPTMT2** display diffraction peaks associated with the crystalline domains in the aggregates.[20]

Figure 2c summarizes the conjugated polymers that form microspheres by the vapor diffusion method. So far, a dozen of π-conjugated polymers have been found to form well-defined microspheres.

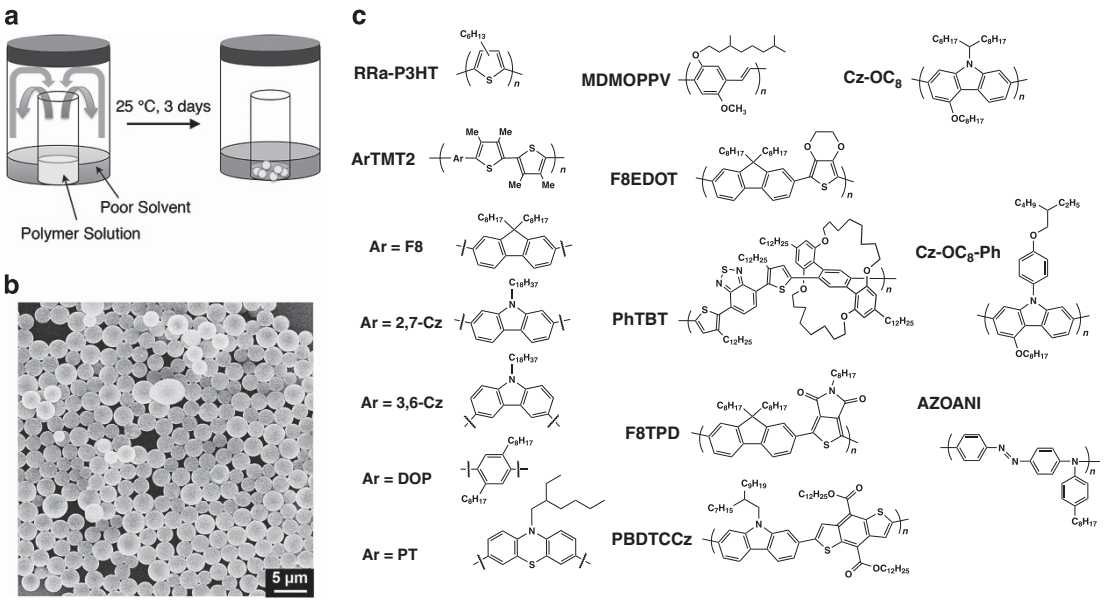

Figure 2 (**a**) Schematic representation of the vapor diffusion method. (**b**) Scanning electron microscopic micrograph of the resultant microspheres formed from self-assembly of π-conjugated polymers. (**c**) Summary of π-conjugated polymers that form microspheres by vapor diffusion method. A full color version of this figure is available at the *Polymer Journal* journal online.

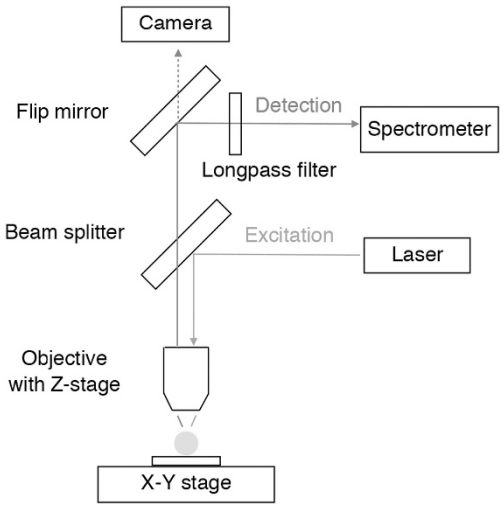

Figure 3 Schematic representation of experimental setup of μ-PL measurement. PL, photoluminescence. A full color version of this figure is available at the *Polymer Journal* journal online.

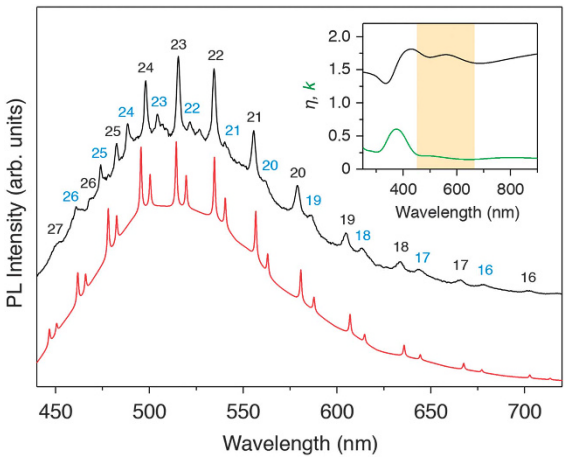

Figure 4 PL spectrum from a single isolated microsphere of **F8TMT2** with 2.6 μm diameter. Black and blue numeric represents TE and TM mode WGM indices, respectively. The red curves indicate the simulated spectrum, superimposed on the broad background emission. Inset shows real (η, black) and imaginary (k, green) parts of refractive indices of the corresponding polymers with respect to the wavelength (Reproduced with permission from.[21] Copyright 2014 Nature Publishing Group). PL, photoluminescence; TE, transverse electric; TM, transverse magnetic; WGM, whispering gallery mode.

Changing the self-assembly conditions can control the diameter (d) and dispersion of the resultant microspheres. For example, large-molecular-weight polymers tend to form small spheres with rapid nucleation and fast growth rates. A high initial concentration of the polymers results in small spheres. The precipitation rate has an important role in determining the size of the spheres. Accordingly, when a shallow petri dish is used instead of a tall vial, the diffusion rates of solvent and nonsolvent are much more rapid, resulting in the precipitation of spheres with smaller d.[19] The size distribution (σ) depends on the assembly condition. For example, a rapid precipitation yields microspheres with small d and σ. We assume that time lag of the nucleation causes the difference in the growth time of the spheres, thereby resulting in the large deviation of the diameters. In fact, **F8TMT2** in CH_2Cl_2, upon vapor diffusion of MeOH, results in the spherical precipitates with the smaller σ value than that in THF and $CHCl_3$, where evaporation of the good solvent takes place more rapidly for CH_2Cl_2 than THF and $CHCl_3$ (boiling point of CH_2Cl_2, THF and $CHCl_3$ are 40, 66, and 61 °C, respectively).

WGM PL from single and coupled microspheres

Upon focused laser excitation of a single isolated microsphere of conjugated polymers, WGM is generated inside the microsphere. In micro-PL (μ-PL) experiments, we spin cast a suspension of self-assembled microspheres onto a SiO_2 substrate. We then used a focused laser beam with excitation wavelengths (λ_{ex}) of 405 nm (continuous wave), 532 nm (continuous wave) and 470 nm (pulse laser; frequency, 2.5 MHz; pulse duration, 70 ps) to irradiate the perimeter of an isolated microsphere. The spot size was ~0.5 μm (Figure 3).

WGM PL was first observed from microspheres of **F8TMT2**.[21] Figure 4 shows the PL spectrum from a single microsphere of **F8TMT2**; sharp and periodic PL lines are observed. As the first approximation, wavelength (λ) of the WGM PL lines follows the Equation (1)

$$n\pi d = l\lambda \tag{1}$$

where l is an integer. When optical path with one-circle propagation coincides integral multiple of λ, resonance of PL occurs. The PL spectrum observed is much more complicated; the sharp PL lines are attributable to transverse electric and magnetic modes, where electric field vectors stand perpendicular and parallel to the radial direction of the sphere, respectively. In such a case, λ of the WGM PL lines follows the simplified Oraevsky's Equations (2) and (3),[10]

$$\lambda_l^E = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[l+\frac{1}{2}+1.85576\left(l+\frac{1}{2}\right)^{\frac{1}{3}}-\frac{1}{\varepsilon}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1} \tag{2}$$

$$\lambda_l^H = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[l+\frac{1}{2}+1.85576\left(l+\frac{1}{2}\right)^{\frac{1}{3}}-\frac{1}{\mu}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1} \tag{3}$$

where λ_l^E and λ_l^H are the wavelengths of the l-th transverse electric and transverse magnetic modes, respectively, ε ($=n^2$) is the dielectric permittivity, μ ($=1$) is the magnetic permeability and r is the sphere's radius. Using the n value of 1.70 that is estimated from ellipsometry data of the thin film of **F8TMT2** (Figure 4, inset), the observed PL lines are well characterized as transverse electric and transverse magnetic mode WGM (Figure 4).[21]

The WGM PL was not observed when d of the microspheres are <2 μm. This is because the microspheres with small d results in a large curvature, which lowers the efficiency of the total internal reflection at the polymer/air interface. When d is larger than 2 μm, clear periodical WGM lines appear in the PL spectrum, and, as d is larger, the WGM lines become much more crowded because the one-circle optical path can contain the larger number of waves of light.[21]

WGM has been observed from various microspheres, including **2,7-CzTMT2**, **PTTMT2** and **AZOANI**.[21] Further investigations of self-assembly and μ-PL experiments have shown that a variety of conjugated polymer microspheres, such as the isolated conjugated polymer **PhTBT**,[22] the poly-*para*-phenylenevinylene derivative **MDMOPPV**,[23] the fluorene copolymer **F8TPD**,[24,25] and the carbazole polymers **PBDTCCz**,[25] **Cz-OC$_8$** and **Cz-OC$_8$-Ph**[26] display WGM PL.

In particular, microspheres of **F8TPD** have Q-factors, approximated by the peak wavelength divided by the full width at half maximum of the peak, as high as 2200,[25] and in a certain case, over 10 000 (ref. 24)

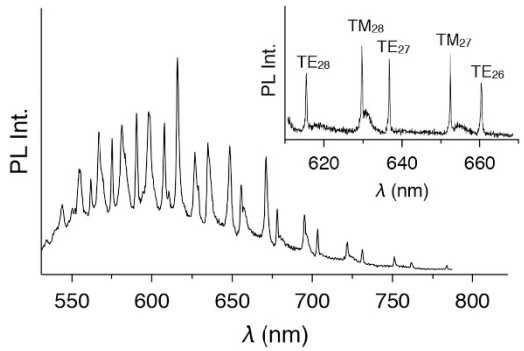

Figure 5 PL spectrum of a single microsphere of **F8TPD** upon focused laser excitation at 470 nm. Grating: 300 grooves per mm. Inset shows high-resolution PL spectrum. Grating: 1200 grooves per mm (Reproduced with permission from.[25] Copyright 2016 American Chemical Society). PL, photoluminescence; TE, transverse electric; TM, transverse magnetic.

as a result of their high sphericity and superior PL quantum yield (Figure 5). WGM is quite sensitive to the geometry and surface morphology of the spheres. For example, in the case of self-assembly of the isolated conjugated polymer **PhTBT**, microspheres form when $CHCl_3$ and CH_2Cl_2 are used as good solvents. However, only the microspheres prepared from CH_2Cl_2 exhibit WGM PL because of their high degree of sphericity.[22]

We conducted self-assembly of a binary mixture from the energy-donating polymer **F8TPD** and the energy-accepting polymer **PBDTCCz**.[25] When the molecular weights were identical and the precipitation times (that is, nucleation and growth rates) matched well, these two polymers blended well to form identical microspheres. On the other hand, when the molecular weights differed greatly, the polymers gave only irregular aggregates with macroscopic phase separation. PL spectroscopy measurements revealed that well-defined microspheres had efficient intrasphere donor-to-acceptor energy transfer, indicating that the polymers were miscible with one another in the microspheres. Intersphere energy transfer occurs when several microspheres are coupled and one side of a microsphere is photo-excited. WGM-mediated long-range energy propagation takes place (Figure 6), and energy transfer occurs at the point of contact of the

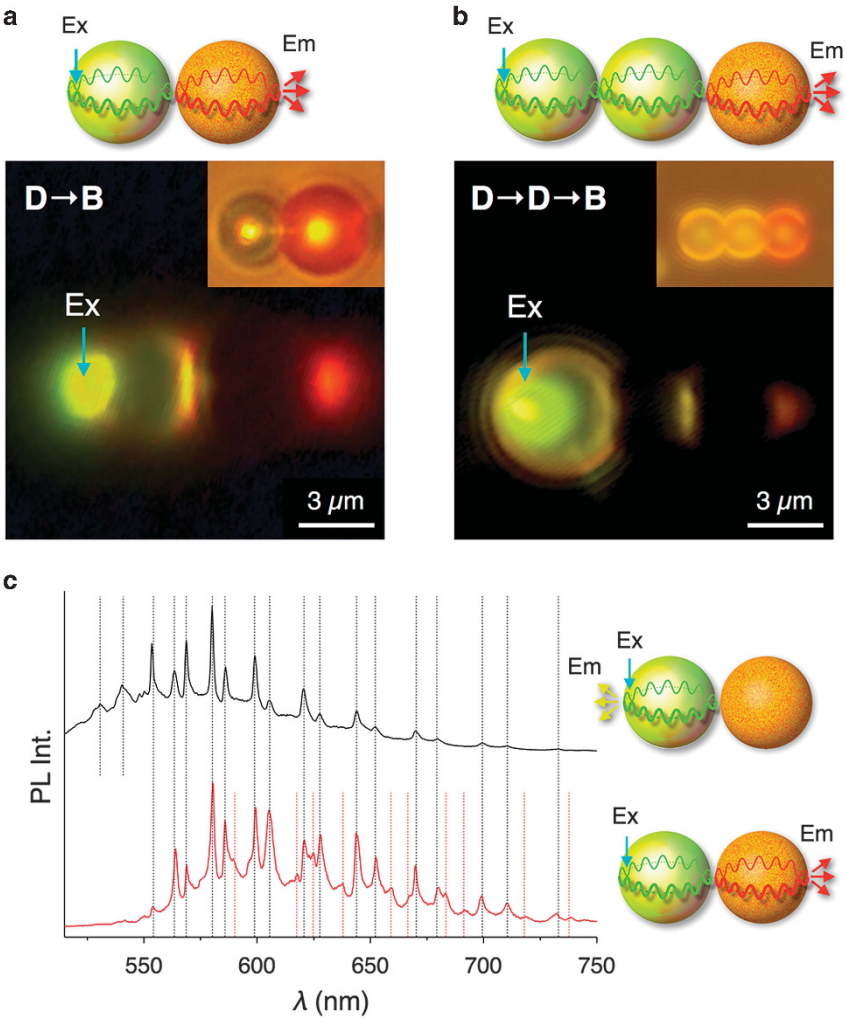

Figure 6 (**a**, **b**) Schematic representations of WGM-mediated intersphere energy transfer, and fluorescent and optical micrographs of bisphere **D**–**B** (**a**) and trisphere **D**–**D**–**B** (**b**) upon focused laser excitation at the left side of **D**. **D**: microsphere of **F8TPD**, **B**: microsphere of a blend of **F8TPD** and **PBDTCCz** (8/2 w/w). (**c**) PL spectra of a coupled **D**–**B** bisphere upon laser excitation at **D**, and PL detection at **D** (black) and **B** (red). (Reproduced with permission from.[25] Copyright (2016) American Chemical Society).

energy-donating and -accepting microspheres. WGM was observed even after energy transfer to the energy-accepting microspheres, indicating that WGM-to-WGM PL conversion took place. Furthermore, a WGM-mediated intersphere multistep energy-transfer cascade was achieved by using polystyrene microspheres doped with a single polymorphic dye (boron–dipyrrin). Multicolor (green, yellow, orange and red) WGM PL was observed from coupled microspheres.[26]

White-color WGM PL was realized from microspheres of the single-component polycarbazoles, **Cz-OC$_8$** and **Cz-OC$_8$-Ph**. The ultra-wide-range WGM PL resulted from partial oxidation of the polymer main chain. This will be useful in multicolor resonant photoemitters.[27] In addition, the production of water-dispersible conjugated polymer microspheres by enwrapping the bare microspheres with graphene oxide nanosheets have been reported.[28] Although the surface morphology of the microspheres is roughed by the graphene oxide wrapping, clear WGM PL is observed.

Summary and prospects

This review article describes self-assembly of π-conjugated polymers to form well-defined microspheres. The important factors for the formation of microspheres are the low crystallinity of the polymer main chain and slow diffusion of polar nonsolvent into the solution of the π-conjugated polymers. The size and its distribution of the microspheres are generally controlled by the self-assembly condition, where slow precipitation results in the large microspheres with broad size distribution. The conjugated polymer microspheres, upon focused laser irradiation to a single microsphere, exhibited WGM-resonant PL, involving sharp and periodic PL lines, owing to the interference of the confined photons inside the microsphere. Both intra and intersphere light energy transfers were demonstrated using microspheres with blend of energy-donating and -accepting conjugated polymers.

Conjugated polymer microresonators are advantageous in terms of their high refractive index (1.6–2.0), high absorptivity and PL efficiency, and simple and low-cost fabrication. For the practical application using the microspheres, all of these factors are important, especially simple fabrication process is inevitable. The next principal objective is to realize laser oscillation by light pumping. To achieve this, much higher photon density pumping is needed for population inversion and stimulated emission. Future prospects are electrically driven WGM PL and lasing by charge injection into conjugated polymer microresonators. For practical applications, a microsphere array needs to be formed on a substrate or electrode surface. Insight into the self-assembly mechanism of sphere formation is essential if we are to construct much more complicated hierarchically assembled structures with multiple molecular and polymer components.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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