

Self-assembled polycarbazole microspheres as single-component, white-colour resonant photoemitters

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Self-assembled polycarbazole (PCz) microspheres exhibit whispering gallery mode photoluminescence (PL), where resonant PL lines appear at the whole visible spectral range. The ultra-wide-range PL results from a partial oxidation of PCz upon strong photoexcitation. The single component micro-photoemitters, preparable with simple and inexpensive process, is applicable as full-colour, narrow-width light emission sources.

White-colour photoemitters with high brightness and low fabrication cost are demanded for a practical use of light sources.¹ A sufficient condition to display white-colour photoluminescence (PL) is that the PL band covers with wide wavelength range over the visible region (400–800 nm) like sunlight. However, for organic molecules and polymers, the PL line-width is generally in the wavelength range of ca. 50–100 nm. Therefore, binary (complementary colour) or ternary (red, green and blue colour) fluorophores are utilized for realizing white-colour luminescence.¹ Therein, a delicate optimization of the partial donor-to-acceptor energy transfer by changing the mixing ratio and the mixed state of the fluorophores is requisite. Such fine optimization of the mixing is not necessary if a single component material exhibits white PL.²

Optical microcavities play important roles for sharpening and amplifying emission.³ Lasers are widely utilized as highly monochromatic, directional, and coherent light sources. Recently, white-colour laser is demonstrated from monolithic

inorganic crystals.⁴ Nevertheless, the fabrication process is rather complicated with a difficulty in controlling the devices with micrometer-scale accuracy. Therefore, multi-mode microresonators with a sharp emission lines in a wide spectral range will be useful not only for high brightness white-colour light sources but also for multi-colour sharp emitters by sorting the desired emission lines.

In this communication, we report on white-colour whispering gallery mode (WGM) photoemitters from single-component polycarbazole (PCz) microspheres. A simple self-assembly process prepares the micrometer-scale polymeric resonators. Upon weak photoexcitation with stationary light, the PCz microspheres show blue PL. In contrast, strong photoexcitation by a focused laser beam to a single microsphere results in sharp and periodic PL lines from whole wavelength range of the visible region (400–800 nm). The single component white-colour resonant micro-photoemitters are beneficial for low-cost, multi-colour and high brightness light sources.

The PCzs we used in this study are poly(2,7-carbazole) derivatives **P1** and **P2** (Fig. 1a), which are synthesized by Yamamoto coupling reaction from the corresponding 2,7-dibromocarbazole precursors (see ESI† and ref. 5). The wavelengths of the photoabsorption maxima (λ_{abs}) of **P1** and **P2** in CHCl₃ are 391 and 383 nm, respectively, while those of the PL maxima (λ_{em}) in CHCl₃ are 420 and 418 nm with PL quantum yield (ϕ_{PL}) of 0.80 and 0.78, respectively (Table S1, ESI†).

Self-assembly of **P1** and **P2** was carried out by vapour diffusion method.⁶ Typically, a 5-mL vial containing 1 mL of CHCl₃ solution of the polymer (0.5 mg mL⁻¹) 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 MeOH vapour was slowly diffused into the CHCl₃ solutions, resulting in a white suspension. Scanning electron microscopy (SEM) micrographs of air-dried suspensions of the precipitates displayed the formation of microspheres (Fig. 1b and c). The average diameters (d_{av}) of the microspheres of **P1** and **P2** are 2.88 and 2.11 μm with the standard deviations (σ) of 0.99 and

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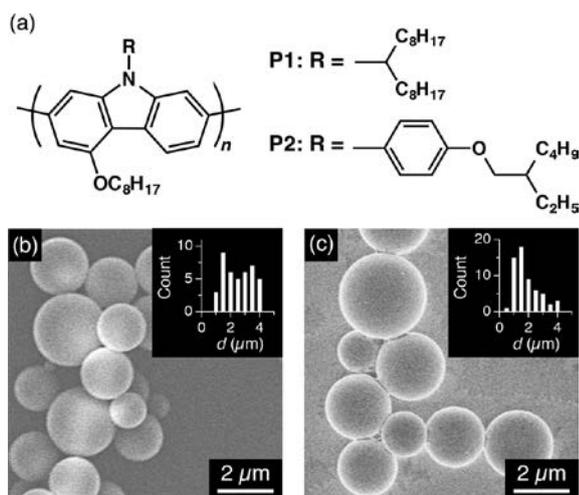


Fig. 1. (a) Molecular structures of poly(2,7-carbazole) **P1** and **P2**. (b, c) SEM micrographs of self-assembled microspheres of **P1** (b) and **P2** (c). Insets show histograms of d of the microspheres.

0.82 μm , respectively. We recently reported that π -conjugated polymers with amorphous aggregation tend to form spherical assembly when a polar nonsolvent is slowly diffused into the solution of the polymers.⁶ The branched alkyl chain or alkoxyphenyl substituent at 9-position of the carbazole (Cz) moiety in **P1** and **P2**, as well as the octyloxy group at the 4-position, possibly results in a steric hindrance, which disturbs the interchain π -stacking of the Cz moiety,⁵ leading to the spherical aggregation. In fact, PCz **P3** without octyloxy group and **P4** and **P5** with branched alkyl chain and alkoxyphenyl substituents at 9-position, separated by one methylene group, hardly formed well-defined microspheres under the identical self-assembling conditions but only gave irregular or harsh aggregates (Fig. S1, ESI[†]). There are several methods to prepare microspheres from conjugated polymers such as self-organized precipitation (SORP) method, emulsion polymerization method, and so forth.⁷ However, the vapor diffusion method has a high advantage to obtain well-defined, high-sphericity microspheres quantitatively.⁶ Below 80 °C, the microspheres maintain their shapes, while further heating results in a melting of the microspheres above 95 °C with a slight PL color change (Fig. S2, ESI[†]).

Cast films of the microspheres of **P1** and **P2**, upon photoexcitation with stationary light ($\lambda_{\text{ex}} = 380 \text{ nm}$) displayed PL with λ_{em} of 445 and 447 nm, respectively (Fig. 2a, black), which are slightly red-shifted in comparison with the PL spectra in CHCl_3 (Table S1, ESI[†]). The ϕ_{PL} values for **P1** and **P2** in the solid state are 0.21 and 0.16, respectively. In contrast with the photoexcitation with stationary light, focused laser excitation ($\lambda_{\text{ex}} = 405 \text{ nm}$) to a single microsphere of **P1** and **P2** results in sharp and periodic PL lines at the whole visible spectral range (Fig. 2a and b, red). The sharp and periodic PL lines are attributed to WGMs, where PL, generated inside the microsphere, is confined and resonates through propagation at the circumference.^{8,9} The average refractive indices (n) of

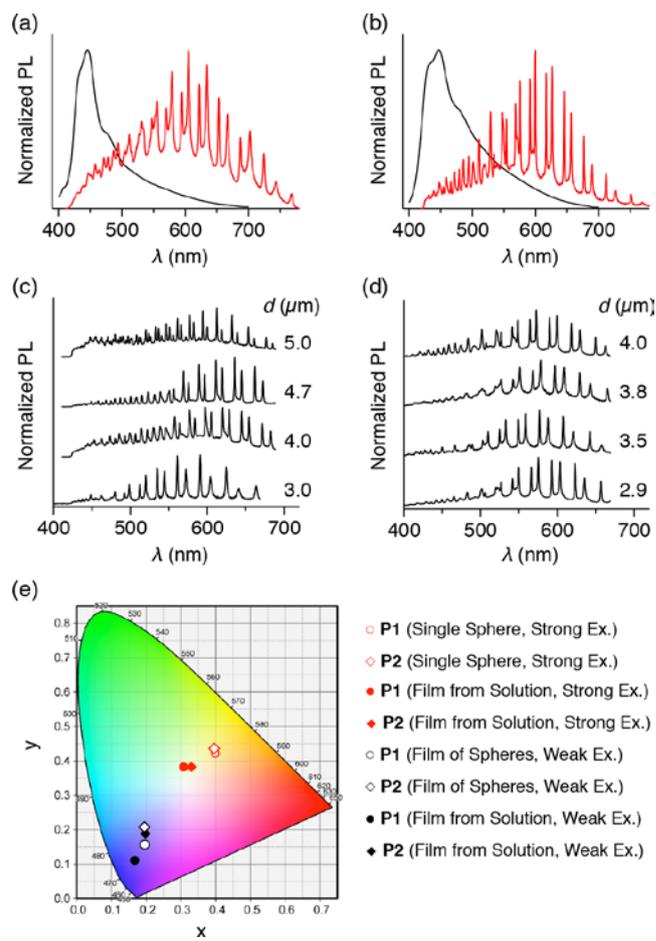


Fig. 2. (a, b) PL spectra of microspheres of **P1** (a) and **P2** (b). Black spectra show PL of a thin film of the microspheres upon excitation with stationary light ($\lambda_{\text{ex}} = 380 \text{ nm}$), while red spectra shows PL from a single microsphere upon focused laser excitation ($\lambda_{\text{ex}} = 405 \text{ nm}$). (c, d) PL spectra of a single microsphere of **P1** (c) and **P2** (d) with different d . (e) CIE coordinates of **P1** (circles) and **P2** (squares) upon excitation with stationary light (black) and focused laser (red) to microspheres (open symbols) and cast films from solution (closed symbols).

P1 and **P2** at the wavelength range of 500–700 nm are 1.55 and 1.58, respectively (Fig. S3, ESI[†]), which are high enough to confine PL via total internal reflection (TIR) at the polymer/air interface. As the diameter (d) of the microspheres increased, the intervals of the PL lines become narrow due to the increase of the optical path length (Fig. 2c and d). Using the n and d values, each PL line is assigned as transverse electric (TE) and magnetic (TM) modes of WGM (Fig. S4, ESI[†]).⁸ As d increased from 2.9 to 5.0 μm , the Q-factor enhanced from 290 to 520 due to the increase of the efficiency of TIR by the decrease of the curvature (Fig. S5, ESI[†]).¹⁰

Similar to the microspheres, spin-cast films from solutions of these polymers displayed large differences in PL spectra between weak and strong excitation. Upon weak excitation with stationary light, spin-cast films of **P1** and **P2** from CHCl_3

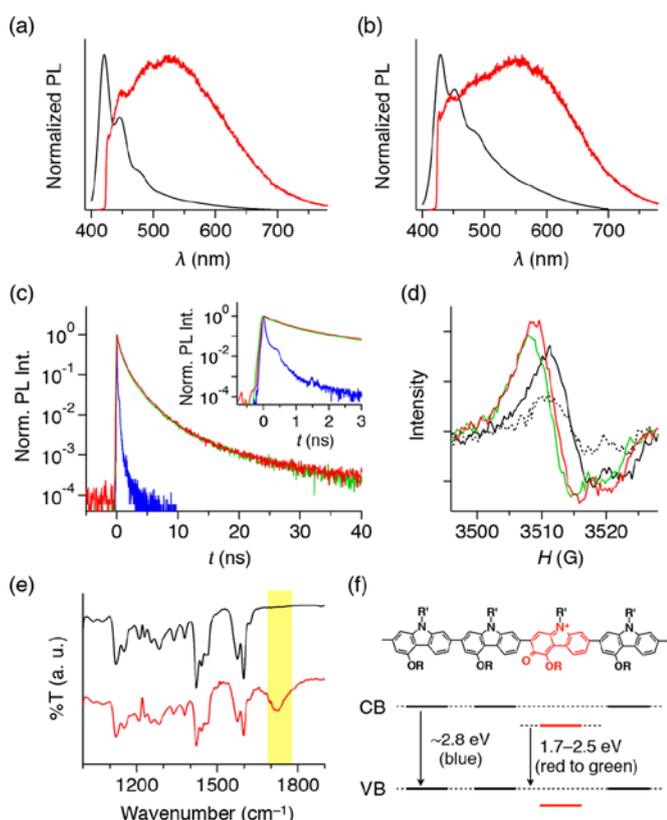


Fig. 3. (a, b) PL spectra of thin films of **P1** (a) and **P2** (b), prepared by drop-cast from CHCl_3 solutions, upon excitation with stationary light (black, $\lambda_{\text{ex}} = 380$ nm) and focused laser excitation (red, $\lambda_{\text{ex}} = 405$ nm). (c) Fluorescence decay profiles of a cast film of microspheres of **P1** at 450 (blue), 550 (green), and 650 nm (red). Inset shows decay profiles with the shorter time range (< 3 ns). (d) ESR spectra of **P1** in dark (black, dotted), upon laser irradiation in N_2 (black, solid) and in air (red), and after laser irradiation (green). $\lambda_{\text{ex}} = 355$ nm. (e) FT-IR spectra of a cast film of **P1** before (black) and after (red) laser irradiation ($\lambda_{\text{ex}} = 355$ nm) in air. (f) Schematic representation of the possible structure of the partly oxidized PCz (top) and its electronic state (bottom). CB; conduction band, VB; valence band.

solutions show PL with λ_{em} of 427 and 430 nm, respectively (Fig. 3a and b, black, and Table S1, ESI[†]). In contrast, PL spectra of these films, upon focused laser excitation, displayed broad PL bands at 500–700 nm, in addition to the PL band at around 450 nm (Fig. 3a and b, red). The Commission Internationale de L'éclairage (CIE) coordinates of the spectra are plotted in Fig. 2e. For weak excitations, the CIE coordinates of the films of **P1** (circles) and **P2** (squares), prepared by spin-cast from their solutions, are (0.17, 0.11) and (0.20, 0.19), respectively (black, filled). The thin films of the microspheres of **P1** and **P2**, with weak excitation, still show the CIE coordinates in the blue region of (0.19, 0.16) and (0.20, 0.20), respectively (black, open). Contrastively, upon strong excitation, CIE coordinates of the spin-cast films of **P1** and **P2** shift to the white region of (0.31, 0.38) and (0.33, 0.38), respectively (red, closed). The

points further shift to (0.40, 0.42) and (0.40, 0.43) for a single microsphere of **P1** and **P2**, respectively (red, open).

The PL lifetime of the microspheres show clear differences depending on the PL wavelength (Fig. 3c). Upon pulsed laser excitation ($\lambda_{\text{ex}} = 377$ nm) of a thin film of microspheres of **P1**, average PL lifetime (τ_{av}) at 450 nm is 0.191 ns. In contrast, τ_{av} at $\lambda = 550$ and 650 nm are 1.23 and 2.25 ns, which are roughly one order of magnitude longer than that at 450 nm (Table S2, ESI[†]). Similar tendency was observed for a thin film of microspheres of **P1** and spin-cast films of **P1** and **P2** from their solutions (Fig. S6 and Table S2, ESI[†]). The results indicate the presence of the low energy-lying chromophore that has narrower energy gap than that of the original PCz. It is known that poly(*N*-vinylcarbazole) shows PL with long lifetime (~20 ns) at room temperature, originating from the excimer state.¹¹ However, poly(2,7-carbazole) has been reported to show pure blue PL without excimer emission.¹² Accordingly, it is plausible that PL at the long wavelength region observed from **P1** and **P2** is not derived from the excimer state.

Electron spin resonance (ESR) spectra displayed the irreversible spectral change upon strong photoexcitation. Before laser irradiation, a thin film of **P1** showed weak ESR signal (Fig. 3d, black dotted) with g -factor of 2.0048, which possibly originates from the naturally oxidized species. The intensity of the ESR signal was enhanced upon laser irradiation in N_2 atmosphere (Fig. 3d, black), while the g -factor was almost intact (2.0047). The shape of the ESR signal is analogous with that of **P1** upon exposure to an iodine vapour ($g = 2.0048$, Fig. S7, ESI[†]), indicating that laser irradiation in N_2 results in a generation of cation radical species steadily in the π -conjugate system.¹³ On the other hand, under laser irradiation in ambient atmosphere, ESR signal was much enhanced, accompanying a shift of the spectrum to the lower magnetic field side with the g -factor of 2.0061 (Fig. 3d, red). After the laser irradiation, the ESR spectrum hardly recovered to the initial state (Fig. 3d, green). PL spectrum of the thin film of **P1**, after the laser irradiation, involved broad PL band at the longer wavelength region (Fig. S8a, ESI[†]), indicating that irreversible change occurs in the polymers by the laser irradiation.¹³

The PL spectral change was examined upon continuous laser irradiation. At the initial excitation, the WGM peaks covered whole visible spectral range. Further irradiation gradually suppressed the PL intensity, and after 2 min. of irradiation, the intensity becomes less than one sixth of the initial PL intensity (Fig. S9a and c, ESI[†]). However, the WGM spectral shape does not change by laser irradiation (Fig. S9b, ESI[†]), indicating that the spherical shape does not become deformed.

Fourier-transform infrared (FT-IR) spectrum of **P1**, after laser irradiation, showed a broad absorption band centered at 1720 cm^{-1} (Fig. 3e). This band possibly derives from the stretching vibration of a carbonyl group.† Because the 3-position of the carbazole moiety in **P1** is the most electron-rich part¹⁴ with an influence of the electron-pushing alkoxy group at the 4-position,⁴ the 3-position is possibly photooxidized (possible structure is drawn in Fig. 3f).‡ As a result of the

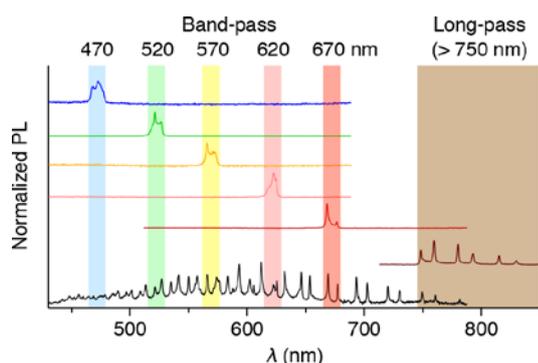


Fig. 4. PL spectra of a single microsphere of **P1**, upon focused laser excitation ($\lambda_{\text{ex}} = 405 \text{ nm}$), without an optical filter (black), with band-pass filters centered at 470 (blue), 520 (green), 570 (orange), 620 (pale-red) and 670 nm (deep red) and with a long-pass filter ($> 750 \text{ nm}$, brown).

electron-withdrawing carbonyl group, π -system at the oxidized moiety is stabilized to some extent, which induces a narrow band gap region in the polymer main chain (Fig. 3f bottom), analogous to donor-acceptor polymers.¹⁵

Finally, by virtue of the wide-range resonant PL over visible region, PL lines of any colours can be picked out from a single microsphere. Using band-pass filters centered at 470, 520, 570, 620, and 670 nm (full-widths at the half maximum of all the filters: 10 nm), single or double resonant PL lines of blue, green, yellow, red, and deep red can be sorted out, respectively, while a use of long-pass filter of $> 750 \text{ nm}$ can extract resonant PL lines at the near infrared region (Fig. 4). Such full-colour selectivity of resonant PL from a single-component microsphere is valuable for application to a light source with multi-colour compatibility.

In summary, white-colour resonant photoluminescence was achieved from self-assembled microspheres composed of single-component polycarbazoles. The extremely wide photoluminescence window results from the photoinduced partial oxidation of the polymers by a strong photoexcitation. Generation of the electron-withdrawing carbonyl group results in narrow band gap spots in the polymer. The high brightness resonant photoemitter is valuable for micrometer-scale, white-colour light source and will further be applied as full-colour light sources by sorting the necessary emission lines.

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Notes and references

‡Judging from the FT-IR spectrum of Poly(3,6-Cz) in ref. 16, the photocrosslink of the interpolymer Cz moiety is not plausible.

‡‡ In case of **P3** without alkoxy group, λ_{em} shifted to 500 nm after laser irradiation with the PL color change from blue to green, not to white (Fig. 8b, ES†).

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