Supporting Information for

Organic Janus Microspheres: A General Approach to All-Color Dual-Wavelength Microlasers

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**Materials and experimental details**

1. Materials.

The 1,4-bis(α-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (CNDPASDB) and cyano-substituted oligo(p-phenylenevinylene) (CNDPDSB) were synthesized via the Knoevenagel condensation reactions.\(^1\)\(^2\) The polystyrene (PS, M.W. 260,000), polymethyl methacrylate (PMMA, M.W. 35,000), coumarin 6, rhodamine 6G and rhodamine B were purchased from Acros Organics. The coumarin 153 was purchased from Sigma chemical company. The rhodamine-101 (Rh101) and sulforhodamine 101 were purchased from the Exciton company.

**Synthesis procedure of CNDPDSB:**

Step 1: Synthesis of [1,1′;4′,1″] terphenyl-2′,5′-dicarbaldehyde.\(^3\)

A mixture of 2,5-dibromobenzene-1,4-dicarbaldehyde (1.0 g), phenylboronic acid (1.1 g), Pd(PPh\(_3\))\(_4\) (0.2 g), toluene (12.5 mL) and 2 M Na\(_2\)CO\(_3\) solution (2.5 mL) was refluxed at 85 °C for 36 h under nitrogen, then poured into water and extracted using dichloromethane. The organic layer was washed with brine and water and dried over magnesium sulfate. The crude product was first purified by flash column chromatography (dichloromethane as eluent) and then recrystallized from chloroform.

Step 2: Synthesis of CNDPDSB.\(^1\)

[1,1′;4′,1″] terphenyl-2′,5′-dicarbaldehyde (0.3 mmol) and phenylacetonitrile (0.6 mmol) were dissolved in tert-butanol (2 mL) and THF (1 mL) at 40°C under nitrogen atmosphere. Potassium tert-butoxide (0.05 mmol) and tetra-n-butylammonium hydroxide (0.05mmol, 1 M solution in methanol) was added quickly, and the mixture was stirred vigorously at 50 °C. After 20 min the mixture was poured into acidified methanol. The precipitate was collected and dissolved in chloroform and then reprecipitated in methanol. The crude product was purified by column chromatography in the darkness to give the green solid.

**Synthesis procedure of CNDPASDB:**

Step1: Synthesis of 2-(cyanomethyl)-4-(diphenylamino)benzene.\(^2\)

A solution of tosyl-2-(cyanomethyl)-4-(diphenylamino)benzene methyl isocyanide (2.2 mmol) in anhydrous THF (3.4 mL) was slowly added to a solution of potassium tert-butoxide (4.6 mmol) in THF (10.2 mL) under nitrogen atmosphere. The mixture was cooled at -40 °C, and a solution of 4-(diphenylamino)benzaldehyde (2 mmol) in anhydrous THF (3.4 mL) was slowly added. The mixture was stirred at -40 °C for 45 min followed by addition of MeOH (13.6 mL). The solution was heated at 80 °C for 20 min and cooled at room temperature. The solvent was removed under reduced pressure, and 2 mL of glacial acetic acid was added to the resulting dark solid. Water (40 mL) was added and washed three times with dichloromethane. The combined organic layer was dried over magnesium sulfate, and the
solvent was removed under reduced pressure. The crude dark red viscous oil was purified by column chromatography to provide the brown solid.

Step 2: Synthesis of CNDPASDB.2

2-(Cyanomethyl)-4-(diphenylamino)benzene (0.6 mmol) and [1,1';4',1'""] terphenyl-2',5'- dicarbaldehyde (0.3 mmol) were dissolved in tert-butanol (2 mL) and THF (1 mL) under a nitrogen atmosphere. Potassium tert-butoxide (0.05 mmol) and tetra-n-butylammonium hydroxide (0.05 mmol, 1 M solution in methanol) were added quickly, and the mixture was stirred vigorously at 50 °C. After 20 min the mixture was poured into acidified methanol. The precipitate was collected and dissolved in chloroform and then reprecipitated in methanol. The crude product was purified by column chromatography under rigorous exclusion of light.

2. Synthesis of the dual-color Janus microspheres.

The dye doped organic Janus microspheres were prepared through an emulsion-solvent-evaporation method. In a typical preparation, 50 μL well mixed CNDPASDB/Rh101/PMMA/PS/CH₂Cl₂ solution (dye concentration was ~0.5 wt % relative to the polymer blends) was added into 500 μL cetyltrimethyl ammonium bromide (CTAB) aqueous solution (2 mmol), which was subsequently treated with vigorous stirring. After aging for 2 h, the CH₂Cl₂ was totally evaporated and dye doped Janus microspheres were obtained and dispersed in the colloid solutions. The surfactant CTAB was removed by filtration and washing. The precipitate was redispersed in the aqueous solution and was then used to prepare samples for further characterizations by drop-casting. By increasing the concentration of PS-PMMA blends from 5 to 30 mg mL⁻¹, the diameter of obtained sphere can be well tuned from 3 to 15 μm.

3. Optical measurements.

The fluorescence spectra were measured using a fluorescence spectrometer (Hitachi F-7000). Bright-field optical images and fluorescence microscopy images were taken using an inverted fluorescence microscope (Nikon Ti-U) by exciting the samples with the halogen and mercury lamps, respectively. The optically pumped lasing measurements were carried out using a homebuilt far-field microphotoluminescence system (Figure S6). A 400-nm pulsed laser (100 fs, 1000 Hz) was focused using a 50× microscope objective to excite the Janus microsphere locally. Spatial photoluminescence was collected and detected by a monochromator that was coupled with a charge-coupled device.
Figure S1. Molecular structures (a) and normalized fluorescence spectra (b) of the CNDPASDB and Rh101.

Amphiphilic PS/PMMA Janus microspheres possess polarity dependent doping behavior among their two hemispheres. Organic laser dyes with distinct polarities can be selectively encapsulated into the two hemistructures of a single Janus microsphere, providing us an effective approach to design and fabricate the dual-color luminescent heterostructures. Rh101 (ionic molecules) and CNDPASDB (nonpolar molecules) were chosen as the laser dye pair to fabricate the bicolor Janus microspheres for their divergent polarities and well-separated emission peaks (Figure S1).
Figure S2. Polarity dependent doping behavior of the Janus microspheres. PL images of the CNDPASDB (a) and Rh101 (b) doped Janus microspheres. Scale bars are 5 μm.

Single-dye doping control experiments were carried out to confirm the polarity dependent doping behavior of the amphiphilic Janus microspheres. CNDPASDB (hydrophobic dye) and Rh101 (hydrophilic dye) molecules were separately dissolved in the identical PS/PMMA/CH₂Cl₂ solutions, which were then used as the precursors for the preparation of the Janus microspheres. Under UV excitation, both the CNDPASDB and Rh101 doped Janus microspheres exhibit asymmetrical emission, with only one side luminescent and the other side dark (Figure S2), indicating that the CNDPASDB and Rh101 molecules were discriminatively encapsulated into the distinct part of the Janus microspheres. This polarity dependent doping behavior is the driving force for the formation of dual-color Janus microspheres.
Figure S3. False-color SEM images of the Janus microspheres obtained from the PS/PMMA (1:1, w:w) blend solutions with different concentrations. (a) 5 mg/mL, (b) 15 mg/mL, and (c) 30 mg/mL, respectively. All scale bars are 2 μm.

The Janus microspheres were obtained via the phase separation of PS and PMMA in a one-step emulsion self-assembly. According to the proposed assembly process (Figure 1b in the main text), the diameter of the Janus microsphere is in direct proportion to the size of the micelles in the emulsion solution, which is strongly depend on interfacial tension between water and PS/PMMA blend solution. The interfacial tension would increase with increasing concentration of the added polymer blends, and larger micelles with smaller specific surface areas will generate to reduce the interfacial energy of the whole system. As shown in Figure S3, the diameter of the Janus microspheres significantly increased by raising the concentration of PS-PMMA blends, which is well consistent with the above inference, offering us an effective way to control the geometric parameters of the Janus cavities.
**Figure S4.** False-color SEM images of the Janus microspheres obtained from the PS/PMMA blend solutions with different mixing ratios (PS:PMMA, w:w). a 3:4, b 1:1 and c 4:3, respectively. All scale bars are 2 μm.

Due to their distinct polarities, PS and PMMA chains would undergo phase separation at almost arbitrary proportion. Therefore, the balance of the PS/PMMA Janus microspheres can be effectively tuned by varying the relative fraction of the added two polymers. When an equal amount (1:1 weight ratio of PS/PMMA) of polymer matrix is adopted, the obtained Janus microspheres reveal a symmetric geometry (Figure S4b). With the PS fraction is gradually reduced, Janus particles with smaller rough hemisphere and larger smooth side were obtained (Figure S4a). The rough segment of the Janus microspheres was positively correlated to the added PS content (Figure S4), indicating that the rough hemispheres are PS-rich phase while the smooth sides are PMMA-rich. These results show that the relative size of the two hemispherical cavities can be well controlled, enabling us to systematically investigate the resonance behavior of the Janus microcavities.
**Figure S5.** Asymmetrical fluorescence emission of the double-doped Janus microsphere. Spatially resolved PL spectra collected from the CNDPASDB-Rh101 doped Janus microsphere shown in inset. Scale bar is 2 μm.

Under UV excitation, CNDPASDB-Rh101 doped Janus microsphere exhibited asymmetrical PL emission, with one side of yellow emission and the other red (inset of Figure S5). The corresponding PL spectra of the two hemispheres are displayed in Figure S5. Both the two PL spectra exhibit two separate peaks, attributing to the emission of CNDPASDB and Rh101 respectively (Figure S1b). But the relative intensity of the two emission peaks varied clearly from the two hemispheres. It can be observed that the CNDPASDB emission dominates the spectrum collected from the left part, whereas the Rh101 dominates that from the right, confirming that two laser dyes were asymmetrically encapsulated in the Janus microsphere. This heterogeneously luminescent structure effectively minimizes the absorption of short-wavelength emission by narrow-gap material, which is favor for the realization of dual-wavelength lasers.  

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Figure S6. Schematic illustration of the experimental setup for the optical characterization.

A homemade micro-photoluminescence system was used to characterize the optical performance of the Janus microspheres. A 400 nm pulse laser beam (100 fs, 1000 Hz) was focused down to a 2-µm diameter spot through an objective (Nikon CFLU Plan, 50×, N.A = 0.8) to excite the Janus microsphere locally. The PL signal was collected by the same microscope objective, passed through the dichroic mirror (DM 400 nm), then a 420 nm long-pass emission filter to eliminate the exciter light, focused by a group of lenses onto a confocal iris. The output signal can be spatially selected by the iris and recorded using a spectrometer.
Figure S7. Size-dependent resonance behavior of the Janus microspheres. (a) PL spectra of the CNDPASDB-Rh101 doped Janus microspheres with three different diameters. Corresponding PL images are depicted as insets. All scale bars are 5 μm. Relationship between $\frac{\lambda}{\Delta \lambda}$ and the diameter (D) of the Janus microsphere at CNDPASDB emission band (b) and Rh101 emission band (c). The yellow and red lines are fit to the function $\frac{\lambda^2}{\Delta \lambda} = n \pi D$.

The lasing spectra of CNDPASDB-Rh101 doped Janus microspheres with different diameters were measured to study the microcavity effects. As shown in Figure S7a, the lasing mode spacing ($\Delta \lambda$) measured from the CNDPASDB emission and the Rh101 emission bands both gradually increase with decreasing the microsphere diameter (D). The mode spacing versus microsphere diameter is in reasonable agreement with the WGM resonance condition that given by the equation $\frac{\lambda^2}{\Delta \lambda} = n \pi D$ (Figure S7b-c), where $\lambda$ is the resonance wavelength and n is the group refractive index. The calculated n (1.59 at the CNDPASDB emission band, 1.58 at the Rh101 emission band) are consistent well with the intrinsic refractive index of the PS and PMMA polymer, indicating that the PL modulation in the Janus microsphere is attributed to the WGM-type optical resonance.
Figure S8. Plot of experimental quality (Q) factor vs diameter (D) of the Janus microsphere. The yellow ball is calculated from the CNDPASDB emission band and the red ball is from the Rh101 emission band.

As shown in Figure S8, the measured Q factors of the Janus microspheres were on the order of $10^3$, which is pretty high for organic resonators. The Q factor increased with increasing D because the bending radiation loss of circular resonators declines exponentially with their size.
Figure S9. Relationship between $\lambda_2^2/\Delta\lambda_1$ and $\lambda_2^2/\Delta\lambda_2$ obtained from the Figure 2c in the main text. The red line is fit to the function $y=x$.

Figure S7 proved that the PL modulation in the Janus microsphere is attributed to the WGM-type optical resonance. In order to distinguish whether the lasing modes resonated along the radial direction or the longitudinal direction of the Janus microsphere, lasing spectra of the CNDPASDB-Rh101 doped Janus microspheres with different PS:PMMA size ratios were studied (Figure 2c in the main text). If the photons resonate along the longitudinal direction (vertical to the interface of the two hemispheres), the $\lambda^2/\Delta\lambda$ measured from the two frequency ranges should be approximately identical (the dispersion of the refractive index is neglected). However, as shown in Figure S9, the value of $\lambda^2/\Delta\lambda$ measured at the CNDPASDB emission band ($\lambda_1^2/\Delta\lambda_1$) are distinctly different from that measured at the Rh101 emission band ($\lambda_2^2/\Delta\lambda_2$), unless the size ratio is 1:1, suggesting that the lasing modes at the two emission bands were resulted from two separate optical cavities. This means that the parallelly aligned hemispheres in the Janus structure form a side-by-side cavity geometry, which can separately provide the optical feedback for the two incorporated organic laser dyes.
Figure S10. Spatial distributions of the WGM in the PMMA-PS Janus microspherical resonators. The electric field distribution of the resonance modes at 584 nm (a, corresponding to the lasing mode in the CNDPASDB emission band) and 623 nm (b, corresponding to the lasing mode in the Rh101 emission band) in a blank Janus microsphere ($n_{PMMA}=1.49; n_{PS}=1.52$). The electric field distribution of the resonance modes at 593 nm (c, corresponding to the lasing mode in the CNDPASDB emission band) and 634 nm (d, corresponding to the lasing mode in the Rh101 emission band) in the Janus microsphere with antisymmetric gain profile.

without optical gain at the resonance wavelengths located in the CNDPASDB (a) and Rh101 (b) emission bands when the optical gain and loss are neglected. The electric field distribution when the optical gain is introduced into the PS hemisphere at the CNDPASDB emission band (c) and when the optical gain is introduced into the PMMA hemisphere at the Rh101 emission band (d).

As shown in Figure S10a-b, in the blank PS-PMMA Janus microsphere, resonance modes at different wavelengths propagate along nearly the same optical feedback paths. The optical field is distributed at the interface of the Janus microsphere (slightly inclined to the PS side for its larger refractive index). However, when optical gain coefficient was introduced into the PS hemisphere at the CNDPASDB emission band (corresponding to the gain of the doped CNDPASDB molecules), the electric fields of the resonance mode are confined mainly in the PS
section (Figure 10c). A similar situation goes for the PMMA hemisphere (Figure 10d). This demonstrated that the asymmetric gain distribution will significantly change the cavity resonant modes and electric fields of the lasing modes are confined mainly in the corresponding amplification sections, which is well consistent with our experimental results (Figure S9). This further confirmed that the asymmetrically double-doped Janus can form two independent WGM cavities and separately provide the optical feedback for the two incorporated laser dyes.
Figure S11. PL spectra of three hydrophilic-hydrophobic dye pairs. (a) PL spectra of CNDPDSB (blue) and sulforhodamine 101 (pink). (b) PL spectra of coumarin 153 (cyan) and rhodamine 6G (red). (c) PL spectra of coumarin 6 (green) and rhodamine B (orange).

The universality of our approach was examined by fabricating double-doped Janus microspheres from three hydrophilic-hydrophobic dye pairs with different emission colors (Figure S11). Blue-pink, cyan-red and green-orange colored Janus microspheres, and corresponding dual-wavelength lasing emission were successfully achieved (Figure 4 in the main text), confirming that the polarity driven encapsulation process in amphiphilic Janus microspheres is applicable to any hydrophilic and hydrophobic dye pair.
Figure S12. Chromaticity of the lasing peaks extracted from the spectra in Figure 4c, f, i of the main text.

As shown in Figure S12, the emission color of the Janus lasers was preliminarily tuned from blue-pink to green-orange by systematically altering the encapsulated dyes, almost covering the whole visible colors. The organic Janus microspheres provide a general platform for the programmable design and construction of compact all-color dual-wavelength lasers.
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