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A stimuli-responsive and chemically tunable organic microcrystal laser switch[†]

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We demonstrated a stimuli-responsive and chemically switchable organic microbelt laser through reversible protonation-deprotonation reactions. The parent microbelt cavity together with the optically allowed 0-1 transition of H-aggregates enables a microlaser to operate at 585 nm. Upon HCl vapor treatment, the protonation of surface molecules shifts the lasing wavelength to 560 nm, generating an intensity contrast ratio $>10^5$, accompanied by a sharp color change from orange (deprotonated) to green (protonated). When treated with HCl-NH₃ vapor, the protonation-deprotonation reactions lead to a reversible microlaser switch between 585 nm and 560 nm with good reproducibility and photostablity, making them attractive in high-throughput chemical and biological sensing applications.

Microlasers that can generate intense coherent light on the micro/nanoscale have attracted extensive research interest, because of their applications in high-throughput chemical and biological sensing, on-chip data communication and color laser displays.¹⁻⁶ Output wavelength tunability is an important figure-of-merit for developing microlasers. To integrate wavelength-tunable multicolor lasers, several gain media with different bandgaps have to be assembled on a single photonic circuit.⁷⁻¹² This, however, remains difficult, because monolithic growth and patterning of II–VI and III–V semiconductors onto a silicon substrate are not easy tasks because of material lattice mismatch and incompatible growth temperatures.

As compared with inorganic counterparts which are usually hard and fragile and difficult to process in solution, organic semiconductors are soft materials with a low melting point and soluble in organic solvents which are well suitable for low-cost, low-temperature processing.¹³ On the one hand, self-assembled organic microcrystals provide well-defined crystal facets to form built-in cavities for laser applications, such as nanowire Fabry–Pérot (FP)^{14,15} and microdisk whispering-gallery mode (WGM)^{16–19} microlasers. On the other hand, organic semiconductors exhibit rich excited-state dynamics, such as excited-state intramolecular proton transfer (ESIPT)^{20–22} and twisted intramolecular charge transfer (CT) processes,^{23–28} which provide great opportunities to realize tunable laser performances. Nonetheless, reversible switch between different outputs from a single laser device upon exposure to external stimuli is still a challenge.

Many fluorescent molecules can reversibly interact with external stimuli through chemical reactions, such as protonationdeprotonation, complexation-decomplexation, and reductionoxidation reversible reactions.²⁹ Following our interest in the design of reversibly switchable microlasers, we chose 4-(4-(4-(4-(4-(dimethylamino)styryl)-2,5-dimethoxystyryl)-2,5-dimethylstyryl)-2,5-dimethoxystyryl)-N,N-dimethylbenzenamine (OPV-DMBA) as the model compound, which can undergo reversible protonationdeprotonation reactions. (i) Self-assembly of OPV-DMBA generates single-crystalline microbelts (MBs), which constitute a high-quality built-in FP microresonator. Together with the emissive H-aggregates as a superior gain medium, low-threshold microlasers were realized with a narrow output at 585 nm (full width at half maximum, FWHM = 8 nm). (ii) The chemo-reactive OPV-DMBA molecules on the surface layers of microbelts can be protonated upon exposure to HCl vapor, providing a different gain medium for microlasers, shifting the lasing wavelength to 560 nm. (iii) When treated with the HCl-NH₃ vapor, the protonation-deprotonation reactions lead to a reversible microlaser switch between 585 (orange) and 560 nm (green). With good reproducibility and photostability, our chemically tunable microlasers provide guidance for high throughput chemical and biological sensing applications.

The model compound of OPV-DMBA was synthesized by a classical Horner–Wadsworth–Emmons coupling reaction with a yield of 58% (Scheme S1, ESI†) OPV-DMBA is an oligo(phenylenevinylene) derivative with two *N*,*N*-dimethyl end-groups as chemical

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Fig. 1 (a) The reversible chemical reaction between molecule OPV-DMBA and OPV-DMBA⁺·HCl⁻. (b) Theoretically calculated frontier orbitals. (c) Normalized UV-Vis absorption and PL spectra of OPV-DMBA in THF solution (upper panel) and then adding with excess HCl (lower panel). The concentrations of dyes are all 1.0×10^{-5} M.

reaction sites, which can undergo reversible protonation/deprotonation reactions (Fig. 1a). We calculated the frontier molecular orbitals of parent OPV-DMBA and protonated OPV-DMBA⁺·HCl⁻ forms by Gaussian 03 programs at the B3LYP/6-31g* level. As shown in Fig. 1b, the HOMO (-4.29 eV) of OPV-DMBA is distributed on the whole molecule, while the LUMO (-1.66 eV) is concentrated on the distyrylbenzene core. Upon protonation by HCl, OPV-DMBA⁺·HCl⁻ possesses a deeper HOMO at -5.06 eV and a LUMO at -2.32 eV. Different from most investigations on the decreased band gap of functional chromophores containing nitrogen atoms under the proton trigger,³⁰ the calculation results predict that the band gap increases from OPV-DMBA (2.63 eV) to OPV-DMBA⁺·HCl⁻ (2.74 eV). This case is similar to the reported 1,1'-(2,5-distyryl-1,4-phenylene)-dipiperidine molecule.³¹

Fig. 1c presents the UV-Vis absorption (dashed) and fluorescence (solid) spectra. The maximum absorption peak of the OPV-DMBA monomer is at 444 nm with a molar extinction coefficient of $\varepsilon = 107\ 200\ M^{-1}\ cm^{-1}$, while its emission spectrum exhibits a vibronic progression with the maximum at 541 nm (CIE: 0.40, 0.57, Fig. S1, ESI†) and a fluorescence quantum yield of $\Phi = 0.80$. Upon protonation, the absorption band of OPV-DMBA⁺·HCl⁻ was shifted to 432 nm with $\varepsilon = 55\ 000\ M^{-1}\ cm^{-1}$. Meanwhile, its emission maximum was blue-shifted to 500 nm (CIE: 0.25, 0.58, Fig. S1, ESI†) with $\Phi = 0.90$. The blue-shift observed in the emission maxima from OPV-DMBA to OPV-DMBA⁺·HCl⁻ is consistent with the calculation results in Fig. 1b. Notably, upon addition of NH₃·H₂O into OPV-DMBA⁺·HCl⁻solution in THF, the fluorescence emission color was recovered to yellow-green instantly (Fig. S1–S4, ESI†). Moreover, the switch is reversible.

The MBs of OPV-DMBA were prepared by drop-casting a 0.5 M THF solution on the glass substrate at room temperature. The as-prepared MBs have a well-defined belt-like morphology (Fig. 2a), with a width (*W*) of 0.3–10 µm uniformly distributed along the entire length (*L*) of 5–50 µm. The thickness of the MBs is about 170 nm (Fig. S5, ESI†). Triclinic OPV-DMBA crystals (CCDC no. 1845245†) belong to the space group of $P\bar{1}$, with cell parameters of a = 5.97 Å, b = 8.15 Å, c = 20.83 Å, $\alpha = 81.49^{\circ}$, $\beta = 88.64^{\circ}$ and $\gamma = 79.85^{\circ}$. Therefore, the squared and circled sets of spots in the SAED pattern are due to {100} and {020} Bragg reflections. This is consistent with X-ray diffraction (XRD) measurements, in which only the diffraction peaks



Fig. 2 (a) SEM images of ensemble MBs placed on a glass substrate. (b) The SAED pattern of a single microbelt. (c) XRD profiles of MBs and the simulated powder spectrum using MECURY software. (d) The molecular arrangement in the MBs. (e) Intensity normalized absorption (dashed lines) and PL (solid lines) spectra of random MBs mat on the glass substrate.

corresponding to crystal planes with k = 0, such as {002} and high-order {004}, are observed (Fig. 2c). The OPV-DMBA molecules stack in a face-to-face configuration along the crystal *b*-axis, leaving the dimethylamino group exposed on the surface layers of microbelts which can be protonated upon exposure to HCl vapor (Fig. 2d and Fig. S6, ESI†).

Fig. 2e depicts the emission and absorption spectra of OPV-DMBA MBs. Table S1 (ESI[†]) summarizes the related photophysical parameters. As compared with monomers, the absorption spectrum of these microcrystals exhibits a strongly blue-shifted maximum around 401 nm, suggesting that OPV-DMBA molecules form H-aggregates in these crystals. This is consistent with the face-to-face packing in the molecular arrangement (Fig. 2d).^{12,16} The PL spectrum of these microcrystals is dominated by the 0–1 transition at 585 nm. The fact that the radiation transition rate k_r of the crystals is slower than that of the monomers is the fingerprint of the H-aggregation model (Fig. S7 and S8, ESI†).

As reported previously, H-aggregated organic semiconductors can be superior gain materials for laser applications, in which the optically allowed 0–1 transitions naturally provide a four-level scheme.^{12,16} Optically pumped lasing measurements were performed by using our homemade PL setup in Scheme S2 (ESI†). Representative μ -PL spectra of the selected microbelt with width $W = 10.3 \ \mu\text{m}$ and $L = 19.4 \ \mu\text{m}$ at different pump densities (*P*) are shown in Fig. 3c and Fig. S9 (ESI†). With the increase of pump intensity, the PL intensity of the 0–1 transition at 585 nm was dramatically amplified and strong laser emissions emerge as a set of multiple sharp peaks with a spacing of $\Delta\lambda = 1.18 \ \text{nm}$. Simultaneously, the PL spectra become sharp peaks with FWHMs from 40 nm to 8 nm. The integrated intensities of the 0–1 peaks as a function of *P* show clearly a threshold at $P_{\text{th}} = 12.8 \ \mu\text{J} \ \text{cm}^{-2}$.

Considering the sensitivity to the HCl molecule of OPV-DMBA, we study the chemically tunable microlasers utilizing a gas flowing system based on a confocal dish (Fig. 3a). As shown in Fig. 3b, after adding a small amount of HCl vapor (≥ 10 ppm), the MBs on the glass substrate exhibit a maximum emission blueshifted to 560 nm. The ion chromatography results show that the mole fraction of OPV-DMBA⁺·HCl⁻ in MBs@HCl is ~0.03, which verifies the formation of a unilayer of DMBA⁺·HCl⁻ on the surface



Fig. 3 (a) Schematic of the microlaser sensor measurement. (b) Relative PL spectra of a single MB (orange line) and MB@HCl (green line) placed on a glass substrate below the threshold. (c and d) PL spectra of a single MB (c) and MB@HCl (d). (e and f) The integrated area of the 0–1 peak for MB (e) and MB@HCl (f) as a function of pump density. (g) The mode spacing $\Delta \lambda$ at $\lambda = 585$ nm for MBs (orange) and 560 nm (green) for MB@HCl *versus* 1/L. The scale bar is 10 μ m.

of the microbelts through the chemical adsorption process (ESI†). However, the MB microlaser can still operate around 560 nm with a threshold at 14.3 μ J cm⁻² and a spacing of $\Delta \lambda$ = 1.11 nm, which are both close to them without HCl vapors (Fig. 3d).

Correspondingly, the PL-color of the microbelts below the threshold becomes a little greenish without an obvious change, owing to broad spontaneous emissions (FWHM > 40 nm) overlapping with each other (Fig. 3 and Fig. S9, ESI⁺). However, when the optical pumping exceeds the threshold, a sharp colour change from orange (CIE = 0.54, 0.46) to green (CIE = 0.39, 0.61) occurred, consistent with the strong laser emission with FWHM < 10 nm centered from 585 nm to 560 nm. Moreover, they all exhibit two impressive spots on the two end facets along the length of the MBs, which is a typical characteristic of FP type resonators with nearly all the electric field $|E|^2$ intensities limited inside on the surface of four edges of MBs (Fig. S10, ESI[†]). For the FP-type resonance, the mode spacing $(\Delta \lambda)$ at λ is given by equation, $\Delta \lambda = \lambda^2 / 2L [n - \lambda (dn/d\lambda)]$, where $[n - \lambda(dn/d\lambda)]$ is the group velocity refractive index. As shown in Fig. 3g and Fig. S11 (ESI[†]), two plots of the mode spacing $\Delta \lambda$ at λ = 585 nm for MBs (yellow line) and λ = 560 nm for MB@HCl (green line) versus 1/L of the length of the MBs, respectively, demonstrate a clear linear relationship. Moreover, the group refractive index $[n - \lambda(dn/d\lambda)]$ at 585 nm and 560 nm were calculated to be 7.73 and 7.53, respectively. Moreover, the morphology of the microbelts also remains the same after exposure to HCl (Fig. S12-S14, ESI†). However, the laser switch MBs might be achieved through the competition light amplification from the two kinds of gain medium.

Fig. 4a exhibits the evolution of the laser emission spectra of MBs above the threshold after a small amount of HCl vapor was injected into the confocal dish. Initially, the orange MB shows a periodic interference laser peak at 585 nm with a ratio of the intensity at 560 nm and 585 nm $I_{560}/I_{585} = 0.0015 \pm 0.0002$. When the exposure time was increased to 1–3 s, the competition between two gain media would happen, and two laser peaks can simultaneously emerged. And, the band at 585 nm was quenched with the increase of the laser peak intensity at 560 nm. Upon increasing the exposure time to 5 s, the competition would disappear and only a single 560 nm laser peak exists with $I_{560}/I_{585} = 400 \pm 50$, which means that the much narrower laser emissions above the lasing threshold generate an intensity contrast ratio > 10⁵. At the same time, the PL images of the



Fig. 4 (a) Wavelength shift from to 585 nm to 560 nm of the microlaser with the different exposure times after adding HCl vapor. The scale bar is 5 μ m. (b) Cyclic switch of the microlaser wavelength.

microbelts exhibit a gradual color change from orange to green (Fig. 4a and Fig. S16, ESI†). Considering the change in the I_{560}/I_{585} ratio for PL spectra to be about 8 (Fig. 3b), the on-off ratio of our tunable microlasers is 4 orders of magnitude greater than that of the PL sensor.

Using the Gaussian03 programs at the B3LYP/6-31G^{**} level, the energy change containing zero-point vibrational energy in the OPV-DMBA + HCl \rightarrow OPV-DMBA⁺·HCl⁻ gas phase is -6.96 kcal mol⁻¹, and the change in Gibbs free energy is 1.97 kcal mol⁻¹ at normal temperature, which is very small. The results indicate that the reaction is basically reversible. In fact, the lasing peaks of the MBs can be recovered from 560 nm to 585 nm after 24 hours, as the HCl vapor in the confocal dish evaporated in air. Moreover, with N₂ introduced in the gas flowing system, the recovery time can be shortened to 2 minutes.

After introducing a small amount of N_2 gas to remove the residual HCl, adding 8 μ L of NH₃ vapor accelerates the reversed chemical reaction from OPV-DMBA⁺·HCl⁻ to OPV-DMBA, bringing on the lasing peaks recovering from 560 nm to the coexistence of the two peaks at 585 nm and 560 nm to the single 585 nm lasing peak consistent with the initial one in 5 s. (Fig. 4a and Fig. S17, ESI⁺).

Excitingly, the chemical reaction tunable switch can still work after several continuous cycles with $HCl-NH_3$ treatment using the gas flowing system, indicating high stability and reliability (Fig. 4b, Fig. S16 and S17, ESI†).

In conclusion, a stimuli-responsive and chemically tunable organic microcrystal laser switch is realized through a new chemical reaction tunable mechanism based on OPV-DMBA molecules. With HCl-NH₃ treatment, the reversible protonationdeprotonation reaction of OPV-DMBA occurs, accompanied by the changes in the emission peak from 542 nm to 500 nm. With a high-quality belt-like microcavity together with the emissive H-aggregates as superior gain materials, a microlaser at 585 nm with a low laser threshold was realized. Upon HCl-vapor treatment, the protonation of surface molecules shifts the lasing wavelength to 560 nm. Furthermore, much narrower laser emissions above the lasing threshold generate an intensity contrast ratio $>10^5$. The NH₃ vapor can tune the laser wavelength back to 585 nm. Moreover, this microlaser switch exhibits good repeatability and photostablity under several continuous chemical gas treatments, making them attractive in high-throughput chemical and biological sensing applications.

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Conflicts of interest

There are no conflicts to declare.

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