Supporting Information

Photoisomerization-controlled wavelength-tunable plasmonic lasers

Shuang Wen,^{a,b} Wu Zhou,^{a,b} Zhiyuan Tian,^b Yongli Yan,^{*a} and Yong Sheng Zhao^{*a,b}

^a Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 101408, China

Corresponding authors: *ylyan@iccas.ac.cn; *yszhao@iccas.ac.cn

Contents

i. **Experimental details.**

- 1). Materials.
- 2). Preparation of BIPS@PMMA film-covered Ag nanoparticle arrays.
- 3). Characterizations.
- 4). Finite-difference time-domain simulations.
- ii. **Fig. S1.** Emission spectra of the UV and white LED lights.
- iii. **Fig. S2.** Color evolution of a typical BIPS@PMMA film upon UV and Vis light exposure.
- iv. **Fig. S3.** Photoluminescence spectra of BIPS-MC@PMMA films with different doping concentrations.
- v. **Fig. S4.** Evolution of the absorbance from a 20 wt% BIPS@PMMA film upon programmed exposures to UV and Vis light.
- vi. **Fig. S5.** Relationship between the formed BIPS-MC amounts and the refractive index variations in BIPS@PMMA films under the irradiation of UV light.
- vii. **Fig. S6.** Plot of photoluminescence wavelengths of a 20 wt% BIPS@PMMA film versus UV and Vis exposure cycles.
- viii. **Fig. S7.** Schematic diagram of the fabrication flow of Ag nanoparticle arrays covered with BIPS@PMMA films.
- ix. **Fig. S8.** SEM image of an Ag nanoparticle array.
- Fig. S9. Plots of the absorbance at 578 nm of 20 wt% BIPS@PMMA films with different thicknesses versus UV exposure time.
- xi. **Fig. S10.** Schematic illustration of a home-built far-field micro-photoluminescence measurement system.
- xii. **Fig. S11.** Emission intensity of four plasmonic laser devices with different SiO₂ thicknesses as a function of pump fluence.

- xiii. **Fig. S12.** Plot of the laser wavelength as a function of programmed exposures to UV and Vis light.
- xiv. **Fig. S13.** Plot of the laser intensities at 697.5 nm versus UV and Vis exposure cycles.

Experimental details

Materials: Poly(methyl methacrylate) (PMMA M.W.=996,000) was purchased commercially (Sigma-Aldrich). 1',3'-Dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] (BIPS) was attained from TCI (Shanghai). Silver (Ag, 99.999%) and chromium (Cr, 99.999%) were from VNANO Technology Co. Ltd. Silicon dioxide (SiO₂) was purchased from J&K Scientific Ltd. (Beijing, China). Organic solvents, including isopropanol (IPA, 99.9%), methyl isobutyl ketone (MIBK, 99.9%), acetone (99.9%) and chlorobenzene (99.9%) were acquired from Beijing Chemical Reagent Co. Ltd. All chemicals were used as received.

Preparation of BIPS@PMMA film-covered Ag nanoparticle arrays: The proposed devices for wavelength-tunable plasmonic lasers consist of cylindrical Ag nanoparticle arrays covered with BIPS-doped PMMA (BIPS@PMMA) films. Ag nanoparticle arrays were fabricated on silica substrates by standard electron beam lithography (EBL).¹ In a typical preparation, a solution of PMMA in chlorobenzene [~3 weight % (wt%)] was spin-coated onto a substrate at 5000 rpm for 30 s and annealed at 180 °C for 120 s to form a 120-nm-thick resist layer. Then, the PMMA layer was patterned through electron-beam direct writing which was carried out with a scanning electron microscope (Vistec EBPG 5000plus ES, electron acceleration voltage at 100 kV, beam current of 500 pA). After that, the PMMA layer was developed in a 1:3 mixture of MIBK and IPA solution at room temperature for 30 s, followed by a thorough rinse in IPA and blow drying by compressed nitrogen gas to obtain PMMA template layer with well-defined nanohole arrays. Next, a 2-nm-thick chromium adhesion layer and a 50-nm-thick silver layer were deposited through thermal evaporation on the PMMA template layer, and followed by lift-off to get Ag nanoparticle arrays. Afterward, a 5nm-thick SiO₂ layer, which exhibits a satisfactory balance between the interactions of Ag nanoparticles and BIPS-MC molecules, was covered onto the Ag nanoparticle arrays by electron beam evaporation to protect Ag from oxidation. Finally, 20 wt% BIPS@PMMA dissolved in chlorobenzene was spin-coated to construct plasmonic lasers consisting of Ag nanoparticle arrays covered by 300-nm-thick BIPS@PMMA film, which is thin enough to ensure the full photoisomerization of BIPS molecules around Ag nanoparticles.

Characterizations: The morphology of plasmonic arrays were characterized by scanning electron microscopy (SEM, Hitachi S-4800). The absorption and photoluminescence (PL) spectra were measured with Hitachi UH-4150 spectrophotometer and Hitachi F-7000, respectively. The refractive indices were obtained with SE 850 DUV spectroscopic ellipsometer. Bright-field microscopy images were taken with an inverted fluorescence microscope (Nikon Ti-U) equipped with halogen and

mercury lamps. The optically pumped lasing measurements were carried out using a home-built farfield micro-photoluminescence system. The samples were excited under the excitation of a pulsed laser beam at normal incidence. The excitation pulses (400 nm) were generated from the second harmonic of the fundamental output of a regenerative amplifier (Solstice Spectra Physics, 800 nm, 120 fs, 1 kHz), which was in turn seeded by a mode-locked Ti:sapphire laser (Mai Tai, Spectra Physics, 800 nm, 100 fs, 80 MHz). The input power was altered with neutral density filters. The PL signal from BIPS@PMMA covered on the top of Ag nanoparticle arrays were collected though an objective (Olympus LMPLFLN, $50\times$, N.A. = 0.5) and analyzed with a spectrometer (Princeton Instrument Acton SP-2358) connected with an EMCCD (Princeton Instruments ProEM 1600B). A flashlight was used to deliver ultraviolet (UV) light (13.62 mW/cm²) and visible (Vis) light (12.82 mW/cm²) to induce reversible spiropyran photoisomerization in PMMA films.

Finite-difference time-domain (FDTD) simulations: The simulations of transmission spectrum and near-field distribution of BIPS@PMMA film-covered Ag nanoparticle arrays were performed using the FDTD method. The optical constants of Ag were taken from Johnson and Christy.² The sample was illuminated with a broadband plane wave source. Periodic boundary conditions were set in the *x*-and *y*-directions to reproduce the periodic lattice, and perfectly matched layers were applied at the *z*-boundary conditions to absorb the excitation and scattered waves. A uniform mesh size of 2 nm (*x*, *y* and *z*-directions) was used to ensure the accuracy of electric field calculations within the metal region.



Fig. S1. Emission spectra of the UV and visible lights.

Fig. S1 shows the emission spectra of the UV and Vis lights. The UV light shows a narrow emission band at 365 nm (purple line, 13.62 mW/cm²) and the visible light exhibits a broadband emission covering the entire visible region (green line, 12.82 mW/cm²). The UV and visible lights were used to control reversible isomerization of BIPS molecules in PMMA films.



Fig. S2. Color evolution of a typical BIPS@PMMA film upon UV and Vis light exposure. Scale bars: 1cm.

Fig. S2a and S2b shows the images of a typical BIPS@PMMA film under the exposure to Vis and UV light, respectively. The color change indicates a reversible transformation between photochromic compound BIPS and its merocyanine isomer (BIPS-MC), which suggests a concomitant change of refractive index in the host PMMA film since BIPS and BIPS-MC have different refractive indices.



Fig. S3. PL spectra of BIPS-MC@PMMA films with different doping concentrations.

BIPS molecules incorporated in PMMA would fully transform into BIPS-MC isomers upon sufficient exposure to UV light. Fig. S3 shows PL spectra of BIPS-MC@PMMA films with different doping concentrations under 400 nm excitation. A clear bathochromic shift is observed as the doping ratio increases, which should be reasonably attributed to a polarization effect.³ As a typical ICT compound, BIPS-MC possesses strong self-polarization properties.⁴ Therefore, as the BIPS-MC concentration increases, the distance between the neighboring BIPS-MC molecules decreases, leading to the redshift of BIPS-MC emissions due to the increased local polarization field. The concentration-dependence PL spectra affords us a way to qualitatively explore the transformation between BIPS and BIPS-MC through analyzing the emission shift of BIPS@PMMA films.



Fig. S4. Evolution of the absorbance of a typical 20 wt% BIPS@PMMA film upon programmed exposures to UV and Vis light. (a) Absorption spectra of the BIPS@PMMA film with increasing exposure time to UV light. (b) Absorption spectra of the identical film with subsequent exposure to Vis light of various time. (c) Plot of the absorbance of the BIPS@PMMA film at 578 nm as a function of programmed exposures to UV and Vis light.

Fig. S4 shows the evolution of the absorbance from a 20 wt% BIPS@PMMA film under the programmed exposure to UV and Vis light. Here, the BIPS@PMMA film was illuminated with UV light for 120 s, followed by an exposure to Vis light for 600 s. As shown in Fig. S4a, the BIPS@PMMA film (t = 0 s) exhibits a small absorbance over the wavelength of 470 – 680 nm, indicating a trace amount of BIPS-MC in the film. These BIPS-MC molecules may originate from photoisomerization caused by thermal annealing during fabrication processes. With the increasing of UV exposure time, the absorbance is enhanced due to the conversion from BIPS to BIPS-MC. When the exposure time was up to 60 s, the absorbance of the film remains almost constant with further increasing the exposure time, suggesting that the BIPS molecules had fully transformed to BIPS-MC. Subsequently, the absorbance gradually decreased under the irradiation of Vis light, demonstrating that BIPS-MC transformed back to BIPS. After 120 s-Vis exposure, the absorbance dropped to 0.020, indicating only 2.6 wt% BIPS-MC molecules remained in the PMMA film. According to the Lambert–Beer law, the absorbance value is related to the amounts of BIPS-MC, which provides us a way to quantitatively analyze the formation of BIPS-MC.



Fig. S5. Relationship between the formed BIPS-MC amounts and the refractive index variations in BIPS@PMMA films under the irradiation of UV light. (a) Plot of the absorbance of BIPS-MC@PMMA films as a function of the doping concentration. (b) Plots of the formed BIPS-MC amounts and refractive index of a 20 wt% BIPS@PMMA film versus time of exposure to UV light.

To recognize the exact relationship between the formation of BIPS-MC and the change of refractive index, it is necessary to explore the formed BIPS-MC amounts by UV irradiation. Fig. S5a summarizes the absorbance of BIPS-MC@PMMA films with different doping concentrations. A linear fitting was established between the absorbance and the concentration, which helps us to quantitatively analyze the formed BIPS-MC amounts through the absorbance measured by the UV– Vis spectrophotometer. According to the absorbance in Fig. S4b, we calculated the formed BIPS-MC amounts of a 20 wt% BIPS@PMMA film upon different UV exposure time (Fig. S5b). It is shown that the formed BIPS-MC amounts and the refractive index change synchronously with the UV exposure time (Fig. S5b), demonstrating the photoisomerization-induced change of the refractive index.



Fig. S6. Plot of the PL wavelength of a 20 wt% BIPS@PMMA film versus UV and Vis exposure cycles.

The robustness of BIPS upon photoexcitation is essential to the steady operation of plasmonic lasers. Therefore, we examined the stability of the photoisomerization of BIPS molecules by recording PL emission wavelength after multiple cycles of alternating UV and Vis irradiation for 40 s and 120 s, respectively. Fig. S6 shows that the PL wavelength remains almost unchanged after a dozen of programmed UV and Vis exposure cycles, manifesting excellent stability and reversibility of BIPS and BIPS-MC, which are beneficial for a continuous tuning of refractive index.



Fig. S7. Schematic diagram of the fabrication flow of Ag nanoparticle arrays covered with BIPS@PMMA films.

The fabrication flow of Ag nanoparticle arrays covered with BIPS@PMMA films is shown in Fig. S7. Ag nanoparticle arrays were fabricated on silica substrate through a standard electron beam lithography. A PMMA resist layer was patterned by exposing to an electron beam, developing, and fixing. The patterned PMMA layer was subsequently covered with a chromium adhesion layer and an aluminum layer by thermal evaporation and followed by lift-off to get the Ag nanoparticle arrays. Then, an ultrathin SiO₂ film was deposited on the Ag nanoparticle arrays by electron beam evaporation to protect Ag from oxidation. Finally, a thin BIPS@PMMA film was integrated onto the arrays through spin-coating to construct wavelength-tunable plasmonic lasers.



Fig. S8. SEM image of an Ag nanoparticle array. Scale bar: 1 μ m.

Fig. S8 shows the SEM image of a fabricated plasmonic lattice with a period of 460 nm. Ag nanoparticles, with a particle diameter of 80 nm and a height of 50 nm, were periodically arrayed on the predesigned sites of the silica surface to support the high-quality surface lattice resonance (SLR) modes, which is important for the realization of plasmonic lasing.



Fig. S9. Plots of the absorbance at 578 nm of 20 wt% BIPS@PMMA films with different thicknesses versus UV exposure time.

Considering that the light penetration depth strongly relates to the BIPS-MC formation around bottom Ag nanoparticles, we investigate the BIPS@PMMA film thickness dependence for the UV-induced BIPS-MC formation by analyzing the absorbance of 20 wt% BIPS@PMMA film with different thicknesses at different UV exposure time. As shown in Fig. S9, the absorbance is substantially enhanced with increasing the film thickness, and the time to reach the absorption saturation increases dramatically, indicating that BIPS molecules in the film bottom can transform into BIPS-MC. Moreover, the penetration depth of the used 365 nm-UV light was estimated to be 2 µm based on the Lambert–Beer law.⁵ Therefore, for the fabricated plasmonic laser devices consisting of 300 nm BIPS@PMMA film-covered Ag nanoparticle arrays, the photoisomerization of BIPS around Ag nanoparticles can occur to induce a change of refractive index and thus a shift of lasing wavelength.



Fig. S10. Schematic illustration of the home-built far-field micro-photoluminescence measurement system.

The optically pumped lasing of BIPS@PMMA film-covered Ag nanoparticle arrays was studied on a home-built far-field micro-photoluminescence system (Fig. S10). A 400 nm femtosecond laser (Spectra Physics) was employed as the excitation source, and the excitation energy was altered using a neutral density filter. The PL signal was collected with an objective (Olympus LMPLFLN, $50 \times$, N.A. = 0.8). The collected emissions were dispersed with a grating (600 G/mm) and recorded by a thermal-electrically cooled CCD (Princeton Instrument ProEm: 1600 B) connected with a monochrometer (Princeton Instrument Acton SP-2358). For the two-beam irradiation, UV/Vis light and 400 nm fs-laser recombined onto a beam-splitter (BS), and then focused on the sample.



Fig. S11. Emission intensity of four plasmonic laser devices with different SiO_2 thicknesses (t = 1, 5, 10 and 20 nm) as a function of pump fluence.

The SiO₂ coating thickness which affects the energy transfer between BIPS-MC molecules and Ag nanoparticles in the arrays is an important factor to determine the lasing threshold and lasing efficiency of the fabricated devices. Here, we fabricated four plasmonic laser devices with different SiO₂ coating thicknesses (t = 1, 5, 10 and 20 nm) to investigate the impact of SiO₂ layer thickness on lasing performance. Fig. S11 presents the emission intensities of these devices as a function of pump fluences. The device with 5-nm-thick SiO₂ layer exhibits the lowest lasing threshold and the largest lasing efficiency. For devices with thinner SiO₂ layers, such as 1 nm, the non-radiative energy transfer loss is significant, and thus non-radiative quenching is increased. For devices with thicker SiO₂ layers, such as 10 nm or 20 nm, the quenching effect can be avoided, whereas the local electric field enhancement is remarkably weakened due to the evanescent nature. Therefore, the device with a 5-nm-thick SiO₂ layer exhibits a satisfactory balance between the interactions of Ag nanoparticles and BIPS-MC molecules.



Fig. S12. Plot of the laser wavelength as a function of programmed exposures to UV and Vis light.

Fig. S12 summarizes the laser wavelength as a function of programmed exposures to UV and Vis light. Here, a typical device was illuminated with UV light for 60 s, followed by an exposure to Vis light for 120 s. Accordingly, the lasing wavelength gradually shifted from 697.5 nm to 711 nm within the first 60 s due to the convension from low-refractive-index BIPS to high-refractive-index BIPS-MC. Then, the lasing peak underwent a blue-shift with increasing exposure time to Vis light because of the reduce amount of BIPS-MC. Finally, the laser wavelength returned to its initial position when Vis exposure ends. The reversible and continuous tuning of lasing wavelength in BIPS@PMMA film-covered Ag nanoparticle arrays demonstrated the realization of wavelength-tunable plasmonic laser based on the photoisomerization process.



Fig. S13. Plot of the laser intensities at 697.5 nm versus UV and Vis exposure cycles.

To investigate the laser stability, we detected the laser output intensities of BIPS@PMMA filmcovered Ag nanoparticle array after multiple cycles of alternating UV and Vis irradiation. The exposure times of UV and Vis light in every cycle were set to be 60 s and 120 s, respectively. The laser intensity maintains 92.7% of its initial intensity after a dozen of UV–Vis exposure cycles, demonstrating an excellent stability and reliability.

References:

- S. Pourjamal, T. K. Hakala, M. Necada, F. Freire-Fernandez, M. Kataja, H. Rekola, J. P. Martikainen, P. Torma and S. van Dijken, *ACS Nano*, 2019, **13**, 5686–5692.
- 2. P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370–4379.
- 3. M. Koch, K. Perumal, O. Blacque, J. A. Garg, R. Saiganesh, S. Kabilan, K. K. Balasubramanian and K. Venkatesan, *Angew. Chem. Int. Ed.*, 2014, **53**, 6378-6382.
- 4. C. Qiao, C. Zhang, Z. Zhou, H. Dong, Y. Du, J. Yao and Y. S. Zhao, *Angew. Chem. Int. Ed.*, 2020, **59**, 15992–15996.
- T. Tada, T. Asahi, M. Tsuchimori, O. Watanabe and H. Masuhara, *Jpn. J. Appl. Phys.*, 2004, 43, 5337-5346.