

Supporting Information

Plasmonic random lasing and amplified spontaneous emission from Donor-Acceptor-Donor dyes covered biocompatible silk fibroin film

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The syntheses of the target chromophores

The synthetic procedures for the preparation of these three chromophores are illustrated in the following Schemes. The yield for each of the synthetic step is also indicated in the Scheme. As one can see, the methodologies for the syntheses of the target dye structures are relatively straightforward. In brief, for the preparation of the end-groups, we have selected commercially available fluorene (**1**) as the starting material and perform functionalization including bromination at C2 and C7 (i.e. from compound **1** to compounds **2** and **6**), alkylation at C9 (i.e. **2**→**3** and **6**→**7**) and nitration at C7 (i.e. **7**→**9**), which are followed by a series of transformation of functional groups on the obtained precursors. The nitro group of **9** was reduced by tin chloride to form an amino group (as in compound **10**), which was transformed into a bis(4-methoxyphenyl)amino group (as in compound **11**) through Ullmann coupling condition; The diphenylamino group of compound **4** was accomplished by utilizing Pd-catalyzed Buchwald-Hartwig amination protocol. All the obtained functionalized arylbromides (i.e. **4**, **7**, and **11**) were then transformed into pinacol arylboronates (i.e. **5**, **8**, and **12**) through Miyaura reaction condition. As for the synthesis of target central core unit (i.e. compound **16**), consecutive functional group transformations were applied to the commercialized 1,2-diaminobenzene (**13**) including the formation of heterocyclic 2*H*-benzo[*d*][1,2,3]triazole (**14**), alkylation at N2 position to form compound **15**, and bromination at C4 and C7 to form compound **16**. Finally, the Pd-catalyzed Suzuki reaction condition was followed to synthesize the target chromophores (D-I, D-II, and D-III).

The spreading of the toluene drops on the PVA and SF film

Figures S1 (a) and (b) show the spreading of toluene drops on the PVA and SF film. Owing to the slightly uneven surface on PVA, the shape of toluene drop shows some distortion. On the contrary, the disspreading area (dashed line) of the blotting on SF film is relatively large, which is attributed to capillary phenomenon from the porous surface of the SF film.

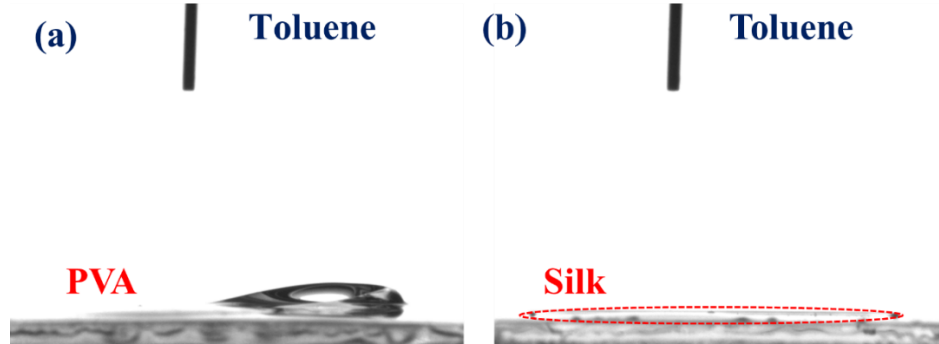


Fig. S1 The spreading of toluene drops on the (a) PVA (left), and (b) SF film (right).

AFM images

In contrast to the DC-SF film with RMS of 38.24 nm, the surface roughness of DC-PVA film is higher with RMS of 286.98 nm is shown in Fig. S2. This result demonstrated that the higher quality DC-SF film will provide a good basis for more excellent optical performance.

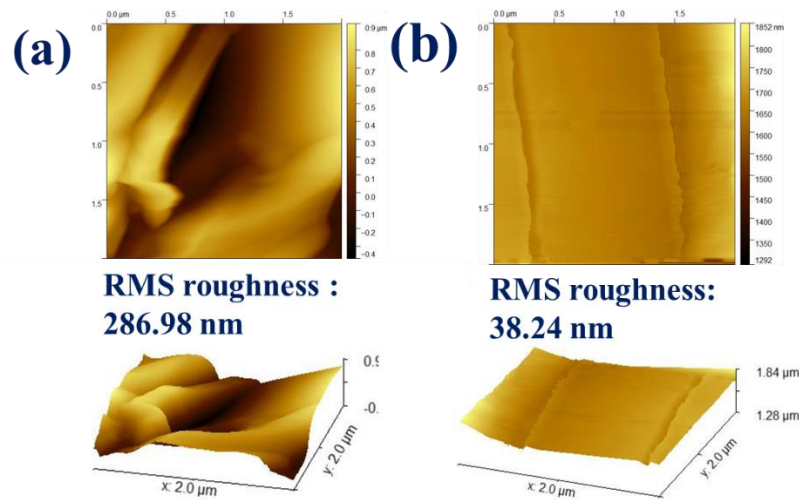


Fig. S2 The AFM and 3D-AFM images of the (a) DC-PVA film and (b) DC-SF film corresponding to panels

Time resolved PL (TRPL) from DC-SF film

Figures S3 (a)-(c) illustrate the time resolved PL (TRPL) of DC-SF film (S-I, S-II and S-III). The integrated PL of three samples are shown in Fig. S4(d). Through time integration at certain wavelength ranges (S-I: 466 to 470 nm, S-II: 513 to 517 nm, and S-III: 510 to 514 nm), the photon decay trace of DC-SF films (SI: 468 nm, S-II: 515 nm and S-III: 512 nm) are shown in Fig. S4 (e) which can be ascribed by using the biexponential formula

$$F(t) = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2), \quad (S1)$$

where $F(t)$ is the time-varied intensity, τ_1 and τ_2 are the fast and slow time constant, and A_1 and A_2 are the corresponding weighting factor. The average PL lifetime τ_{ave} was calculated based on intensity weight ratios

$$\tau_{ave} = (A_1 \tau_1 + A_2 \tau_2) / (A_1 + A_2), \quad (S2)$$

By the well-fitting using Eq.(S1), the fitting parameters are listed in table S1. The average decay constant from DC-SF film S-I, S-II and S-III are around 0.83, 0.68, and 0.59 ns, respectively.

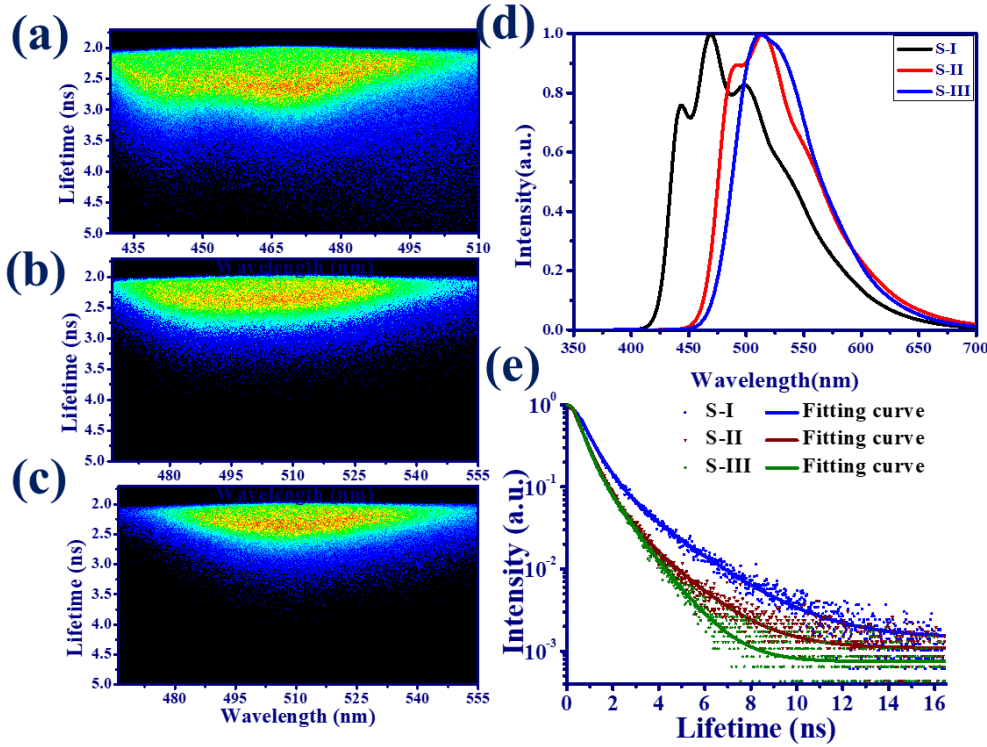


Figure S3 The 2D mapping of TRPL from sample (a) S-I, (b) S-II, and (c) S-III grabbed by the streak camera. (d) The photon decay trace of DC-SF film S-I, S-II and S-III.

Table S1 The obtained parameters of DC-SF film S-I, S-II and S-III from the TRPL measurement.

DC-SF film	$A_1(\%)$	$\tau_1(\text{ns})$	$A_2(\%)$	$\tau_2(\text{ns})$	$\tau_{\text{ave}}(\text{ns})$	$k_f \times 10^9(\text{s}^{-1})$
S-I	86.22	0.63	13.78	2.12	0.83	1.20
S-II	89.14	0.56	10.86	1.69	0.68	1.47
S-III	78.40	0.43	21.6	1.17	0.59	1.69

Stability test of RL from DC-SF film

In order to prevent the photo-oxidation of sample, I sealed the DC-SF film inside glass cell and investigated the photo stability through the excitation of Q-switched laser. As shown in Fig. S4 (a), the sample was produced by sealing DC-SF film (S-II) between two glass plates in glove box. Figure S4 (b) shows the five hours monitoring of emission intensity from sample S-II every twenty minutes to confirm the stability of the RL under the excited energy density of $48.38 \mu\text{J}/\text{cm}^2$. After five hours continuous excitation of the pulsed lasers, it is seen that the intensity drop is around the 77% of the initial output intensity of RL.

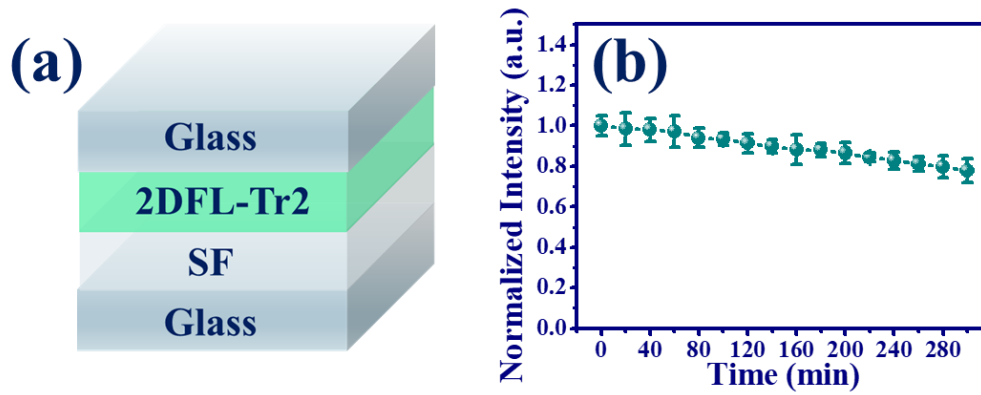


Figure S4 (a) The structure of DC-SF film (S-II) sealing between two glass substrate, (b) the plots of stability monitoring of the RL from sample S-II under five hours excitation of pulsed laser.

Gain coefficient

Figure S5 (a) and (b) show the plots of the ASE peak intensity (black squares) as a function of the stripe length. The stripe length dependent emission spectra of sample S-I and S-II are shown in the inset of Figs. S5 (a) and (b). By the best fitting (shown by red lines) according to Eq. (1) in the main text, the optical gain coefficients of sample S-I and S-II are 73.4 and 75.1 cm^{-1} , respectively.

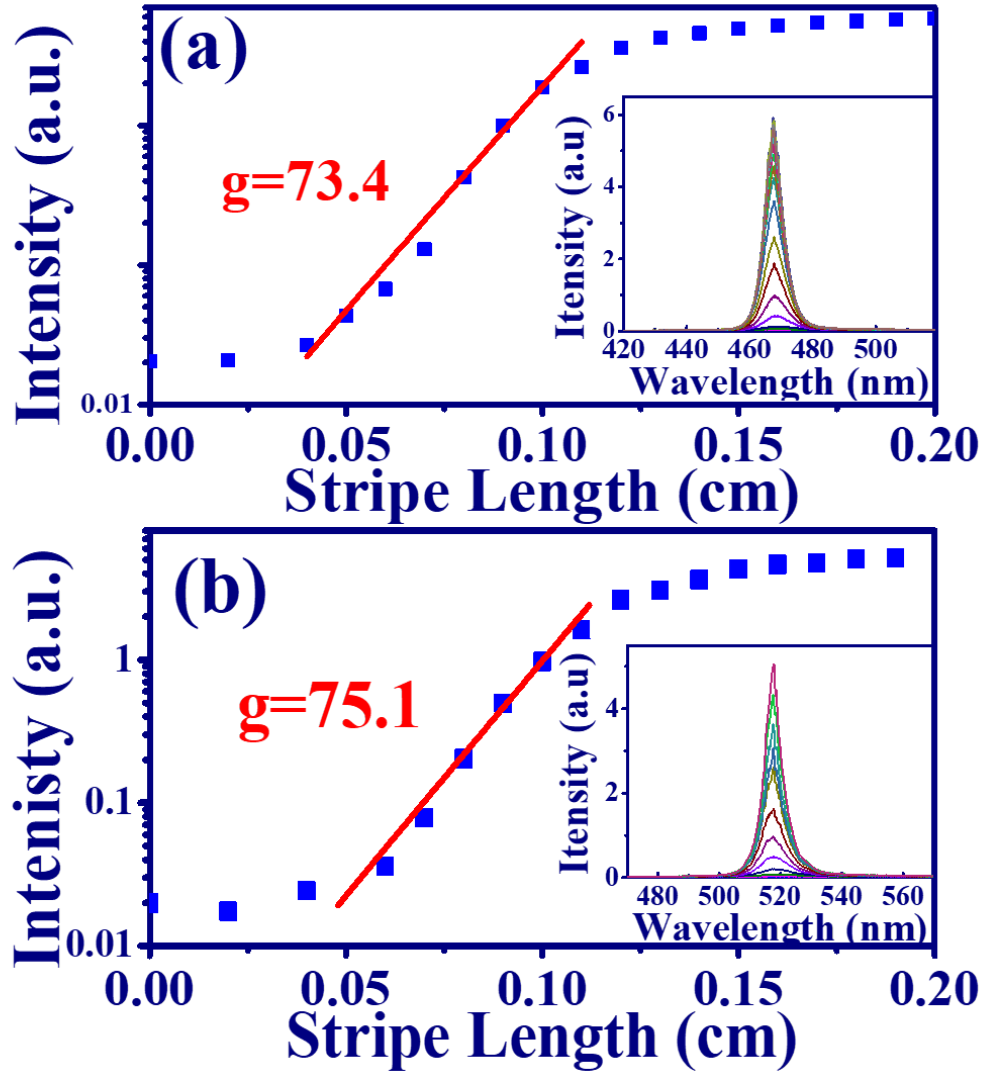


Fig. S5 Gain coefficient measurement of DC-SF films by the VSL model. The plot of ASE intensity (blue squares) as a function of stripe length and the best fitting (red solid line) according to Eq.(1) in main text for sample (a) S-I, and (b) S-II. Inset figures show the corresponding emission spectra with different stripe lengths.

Coherent back scattering (CBS)

In order to obtain the transport mean free path, the CBS was measured by using the collimated green laser beam with a central wavelength λ at 532 nm as a light source. After splitting by a beamsplitter (BS), the signal beam was reflected by the sample and recorded by a detector (D_{Sig}), which was moved by a motorized translation stage along the direction perpendicular to the incident beam. A mask with a small pinhole (0.5 mm in diameter) was placed in front of the detector. The transmitted beam through

the BS was detected by the other detector (D_{Ref}) as a reference beam. The distance between D_{Sig} and the sample was around 25 cm. To increase the signal-to-noise ratio, a mechanical chopper in cooperation with a lock-in amplifier was used. The scattering signal of the DC-SF film with and without AgNPs from $D_{\text{Sig}} / D_{\text{Ref}}$ as a function of the divergent angle θ is shown in Fig. S6 (a)-(b).

The CBS trace can be theoretically fitted by the albedo $\alpha(\theta)$ with the following formula [1]:

$$\alpha(\theta) = \frac{3}{8\pi} \left\{ 1 + \frac{2z_0}{l_t} + \frac{1}{(1+q_{\perp}l_t)^2} \left[1 + \frac{1-\exp(-2z_0q_{\perp})}{l_tq_{\perp}} \right] \right\}. \quad (\text{S3})$$

Here, $q_{\perp} = 2\pi\theta / \lambda$ is the component of q normal to the z axis, and $z_0 \cong 0.7l_t$ (for pointlike scatter). With the good fit of Eq. (S3) [red solid curves in Figs. S6 (a)–(b)], the obvious differences in l_t between the two cases of about 18.4 and 10.5 μm , respectively, were obtained.

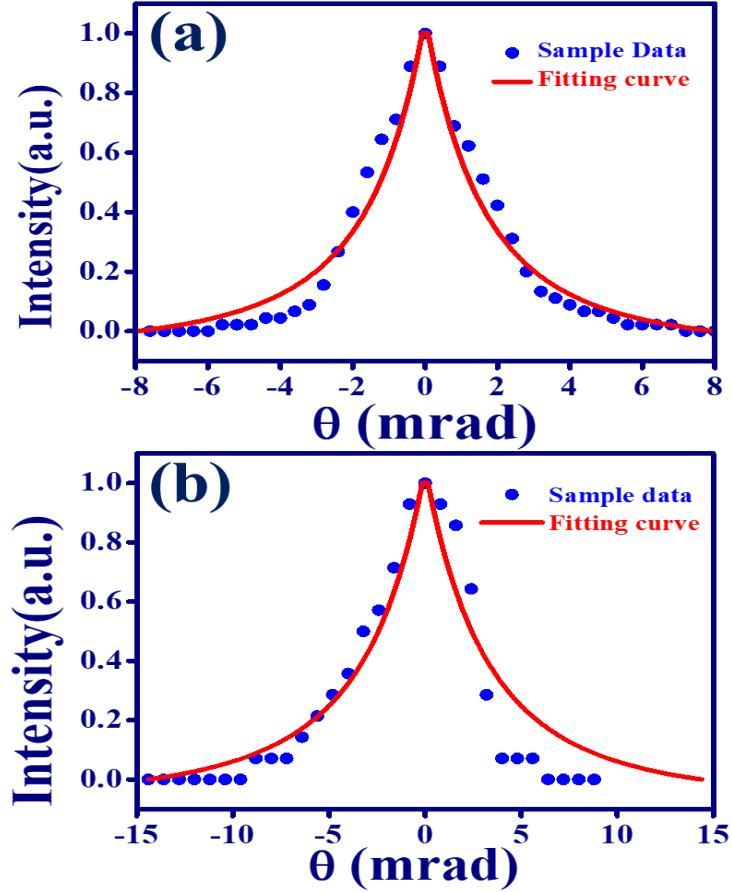


Fig. S6 The measured CBS cone from three output plates of DD-LC lasers including (a) without Ag, (c) with Ag.

Refractive index

The refractive index of D-A-D organic dye are measured by ellipsometry (Woollam M-2000VI). Figure S7 shows the refractive index of synthesized D-A-D dye as a function of wavelength. The refractive index of material varies with wavelength according to the Cauchy's relation: $n(\lambda)=A+B/\lambda^2$, where the corresponding parameters A and B are listed in Table S2.

Table S2: The parameters of A and B in Cauchy's relation.

	A	B
2FL-Tr2	1.54	0.036
2DFL-Tr2	1.61	0.028
2OMe-DFL-Tr2	1.53	0.038

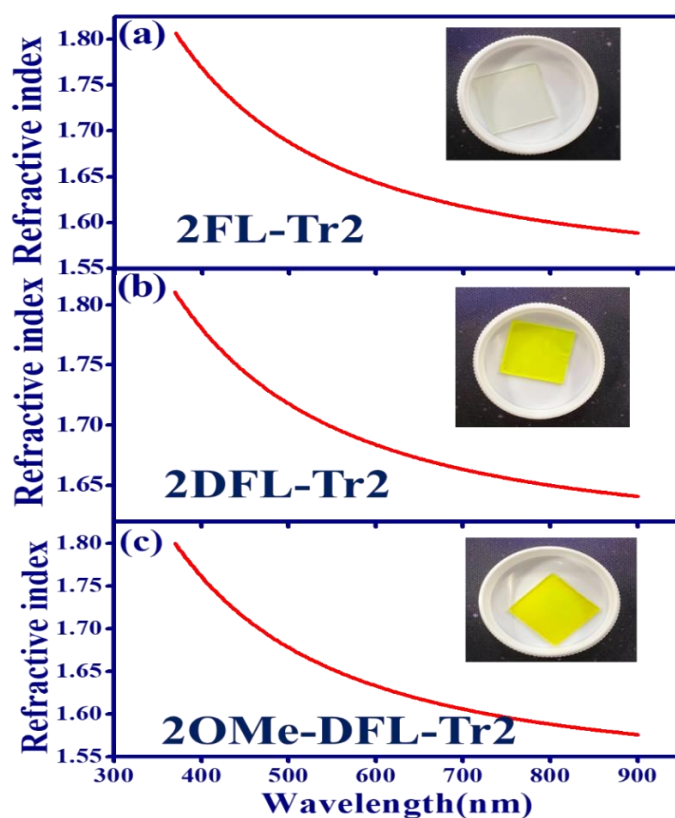


Fig. S7 Refractive index as a function of organic dyes with (a) 2FL-Tr2, (b) 2DFL-Tr2, and (c) 2OMe-DFL-Tr2.

Random lasing characteristic of DC-SF film

We also investigated the characteristics of random lasing from the side emission of DC-SF film (S-II) by the setup shown in Fig. 8 (a). The following figure shows the evolution of emission spectra of the DC-SF film as the pump energy density increases. It can be clearly seen that the multiple emission spikes are generated owing to the recurrent light scattering. The corresponding output intensity (solid circles) and FWHM (solid triangle) as a function of pump energy are shown in Fig. S8 (b). By the intersection of two best fitting lines, the threshold is around $6.24 \mu\text{J}/\text{cm}^2$.

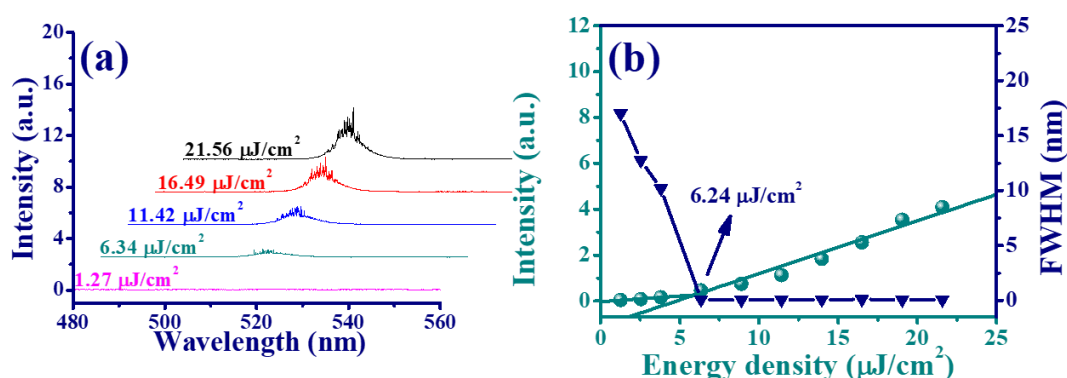


Fig. S8 (a) Evolution of random lasing spectra from the side-emission of the DC-SF film (S-II), and (b) the corresponding peak intensity and FWHM as the function of excitation energy density.

Emission property of DC-AgNPs Film without SF

The original purpose of casting dye solution on the surface of SF is to make the resulting film with high uniformity and avoid the aggregation of AgNPs. Owing to the porous surface of SF film, the dye solution could efficiently infiltrate into the SF and produce more uniform film in comparison to the sample without SF. We have tried to prepare dye covered AgNPs film (without SF as the basic matrix) and utilize the same pumping condition to measure the emission behavior of the prepared film and the result is shown in Fig. S9. It is noted that only PL emission can be observed and no ASE signals generated in this experiment. We postulate that the aggregation of AgNPs may occur in the resulting film because no appropriate matrix such as SF is used to make AgNPs distributed evenly in the film. Therefore, it can be anticipated that no ASE behavior can be observed from such a film without efficient scattering media.

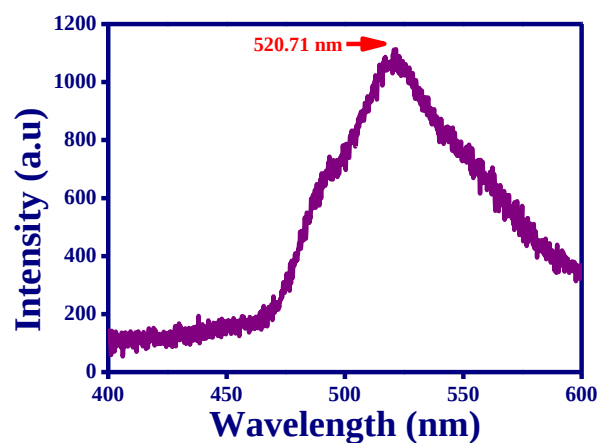


Fig. S9 The PL emission from dye covered AgNPs Film (without SF as the matrix).

1. Lin, J.-H.; Li, Y.-H.; Lin, S.-H.; Nguyen, B.-H., Configuration dependent output characteristics with Fabry–Perot and random lasers from dye-doped liquid crystals within glass cells. *Photonics Research* **2018**, *6* (5), 403-408.