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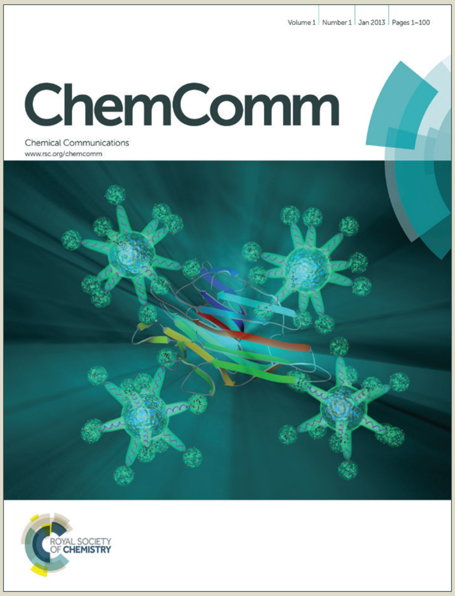

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NIR Light-Directing Self-Organized 3D Photonic Superstructures Loaded with Anisotropic Plasmonic Hybrid Nanorods †

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Self-organized 3D photonic superstructures loaded with plasmonic hybrid nanorods were found to undergo structural transformations from body-centered cubic to simple cubic upon NIR-light irradiation resulting from the "photothermal effect" of nanorods. Furthermore, dynamic NIR light-directed red, green and blue reflections of the nanocomposites were demonstrated.

Endowing remote and dynamic controllability to self-organized three-dimensional (3D) photonic nanostructures with tunable functionality is a principal driving force in the bottom-up nanofabrication of intelligent stimuli-responsive materials and devices.[1] Liquid crystalline blue phases (BPs) capable of self-organizing into periodic cubic superstructures undoubtedly represent such an appealing functional system due to their unique photonic band gap with selective reflection of incident light and the consequent potential for device applications.[2] BPs are among the most attractive self-organized liquid crystal (LC) superstructures, which exist between the isotropic phase and cholesteric phase in highly chiral nematic LCs and generally over a very narrow range of temperature. Depending on the temperature and chirality, the LC molecules usually tend to self-organize into two distinct periodic 3D nanostructures with body-centered or simple cubic symmetry, called blue phase I (BP I) or blue phase II (BP II), respectively.[3] In contrast to the conventional photonic crystals fabricated via expensive and scale-prohibitive manufacturing, the inherent self-organization of these soft materials makes them quite advantageous for cost-effective production of 3D periodic nanostructures. Importantly, being "soft" makes them responsive to various stimuli, resulting in the tunability of photonic band gaps that holds immense potential for use in all-optical integrated circuits and next-generation communication systems.[4] Among various external stimuli such as electric field, magnetic field, temperature and chemical reactions, light stimulus is particularly fascinating because of its remote, spatial, and temporal controllability in different environments.[5] Recently, we have demonstrated reversible manipulation of the photonic band gap in photoresponsive BP nanostructures under the UV or visible light irradiation and achieved dynamic optical-tuning of the reflected color across the visible spectrum.[2a] Unfortunately, the use of high-energy UV light in these systems might result in materials damage, photochemical contamination, and poor penetration through the container walls. Utilizing near infrared (NIR) light would be much preferred in areas of life sciences, materials science, and aerospace applications owing to its invisibility and superior penetration for remote activation.[6] Therefore, there are multitude incentives to explore the novel strategy to develop materials systems with NIR-light-responsive properties and functions.

Recently, plasmonic gold nanorods (GNRs) are attracting increasing attentions especially in biomedical applications due to their appealing "photothermal effect", converting NIR light into heat through a non-radiative relaxation process of longitudinal surface plasmon resonances (LSPR).[7] It is also noteworthy in this context that the characteristic wavelength of the LSPR signal corresponding to NIR absorption can be expediently tuned on demand by suitably altering the aspect ratio of GNRs,[8] and GNRs have been proposed for use in a new triggering systems where UV or visible light are not favorable. However, adequate and homogeneous dispersion of conventional GNRs into complex LC medium with self-organized 3D photonic superstructures has always been a challenging task due to their bad miscibility in LCs and destabilization of the 3D lattices. Herein, we have judiciously designed and synthesized new mesogen-functionalized anisotropic plasmonic GNRs (M-GNRs), and incorporated them

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into a BP LC medium composed of commercially available components. Because of the optimized mesogenic functionalization, the resulting M-GNRs can be homogeneously dispersed in the LC medium. Interestingly, the resultant GNRs-impregnated 3D photonic superstructure was found to be stable and undergo structural transformations from body-centered cubic to simple cubic symmetry upon the irradiation of a NIR laser, resulting from the "photothermal effect" of M-GNRs, whereas its reverse process takes place upon removal of the laser irradiation. Furthermore, dynamic NIR light-directed red, green and blue reflections of the light-driven 3D photonic nanocomposites have been demonstrated. To the best of our knowledge, reversible or irreversible NIR-light directed transitions of 3D photonic superstructures have not been reported so far.

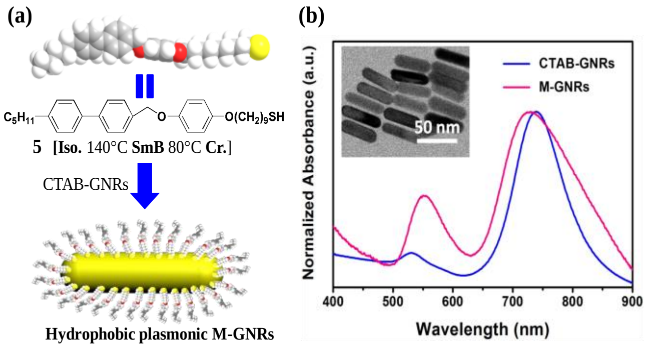

Figure 1. (a) Schematic representation on new mesomorphic surfactant **5** grafted on the GNR by covalent Au-S linkage to form hydrophobic anisotropic plasmonic M-GNRs; (b) UV-vis-near-IR spectra of CTAB-GNRs dispersed in an aqueous solution and M-GNRs in the chloroform solution. The inset shows the TEM image of M-GNRs.

The new LC surfactant **5** was prepared by a straightforward synthesis, its chemical structure was well-identified by ^{1}H and ^{13}C NMR, and the detailed mesophase behaviors were confirmed by polarizing optical microscope (POM), and the temperature-variable X-ray diffraction (XRD) studies (see Supporting Information Figure 1a and Figures S3-S5). For GNRs, the water-soluble precursor cetyltrimethylammonium bromide-capped GNRs (CTAB-GNRs) were firstly synthesized by the seed-mediated growth method,[10] and then organosoluble M-GNRs were subsequently obtained by the thiol exchange reaction with mesomorphic surfactant **5** in tetrahydrofuran, where the surface of GNRs is covalently coated by the mesogen monolayer. As expected, the resultant M-GNRs were highly soluble in organic media because of the optimized mesogen functionalization (Figure S6). The UV-Vis-NIR spectrum of as-prepared M-GNRs exhibits the characteristic longitudinal and transverse absorption signals, which are similar to the CTAB-GNRs (**Figure 1b**).[11] The transmission electron microscopy (TEM) image clearly indicates the nearly uniform size and morphology of M-GNRs with an average aspect ratio of ~ 3.1 (length 44.9 ± 4.9 nm; width 14.8 ± 1.9 nm).

Figure 2a shows the temperature dependence of the selective reflection wavelength in pure BP medium upon cooling at a rate of 0.1 °C/min. The reflection wavelength abruptly jumps from 494 nm to 551 nm at the BP II to BP I phase transition at 43.5 °C. The maximum wavelength of ~610 nm was observed at 40.7 °C. When doped with M-GNRs at concentrations ranging from 0.03 wt% to 0.07 wt% (**Figure 2b**), the mixtures showed an increasing BP I temperature range with a maximum width of 6.9 °C. Further addition of the GNRs suppressed the range, whereas the BP II temperature range is almost independent of M-GNRs' concentration. It was also observed that the maximum reflection wavelength of BPs red-shifted to ~650 nm when doping with 0.07 wt% M-GNRs, which may be attributed to the increase in the unit cell lattice constant of BPs.

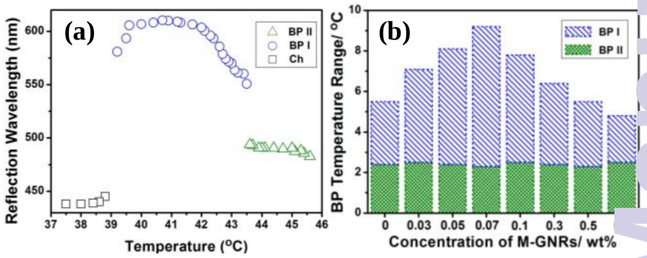

Figure 2. (a) Reflection wavelengths of the newly developed BP medium as a function of temperature; (b) Effect of the concentration of M-GNRs on the temperature range of BPs.

As is well known, the narrow temperature range of BPs is caused by their frustrated structure, in which the regions of double twist tile space through lattice of disclinations; the high energy cost of the disclination cores with reduced orientational order makes the BPs stable only in the vicinity of the isotropic melt.[3] This is why one of the approaches to expand the temperature range of the BPs is based on attracting foreign particles such as polymers to the disclination core that replace the costly misaligned LC regions.[12] Extensive studies have indicated that not only polymers but also metal and inorganic nanomaterials may act in a similar fashion to reduce the energy cost of the disclination cores and hence enhance the stability of BPs.[13] Herein, a possible mechanism for the stabilization of the BP I could be depicted as in **Figure 3**. The introduction of M-GNRs in the BPs might not only suppress the volume and the free energy around the disclination region of the lattices, but also result in stronger intermolecular interactions between LC components, especially when the temperature was close to BP I-cholesteric phase transition, consequently stabilizing nanostructure over a wider temperature range. However, the cubic superstructures of BP I may be disrupted after the critical concentration of M-GNRs was reached, thus at higher doping level, on the contrary, restrained the BP I temperature range.

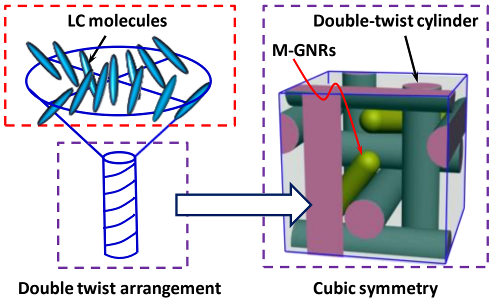

Figure 3. Schematic illustration of self-organized body-centered cubic nanostructure in BP I stabilized by anisotropic plasmonic M-GNRs.

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Figure 4a illustrates the typical textures of BPs doped with 0.07 wt% M-GNRs in 10 μm thick untreated cell at a cooling rate of 0.1 °C/min, which were captured by using a crossed POM in transmission mode. On cooling from isotropic phase, BP II firstly appeared at 46.4 °C and then transformed into BP I at 44.1 °C. As the temperature was further decreased to 37.2 °C, the phase completely changed into the cholesteric phase. Additionally, the BPs formed the characteristic platelet textures, and the reflection color gradually changed to a longer wavelength with decreasing temperature. According to the Bragg's law, the photonic reflection of BPs occurs in particular directions due to their periodic cubic nanostructures when illuminated by a monochromatic light with the wavelength comparable to lattice constant.Different from the X-ray diffraction technique applied for chacterizing the structure of conventional crystals, optical Kossel diffraction diagrams have been typically used to index the types of cubic BP lattices (more details in Supporting Information).[14] To further verify the BP lattice structures, Kossel diagram of BPs with 0.07 wt% M-GNRs in 10 μm thick planar cell was observed as shown in **Figure 4b**. As expected, the isotropic phase does not yield any Kossel diagram. A prominent circular pattern appeared in the temperature range of BP II, which resulted from the (100) lattice of the simple cubic BP II. As the temperature decreased from BP II to BP I, the diffraction ring switched to characteristic diamond-shaped pattern corresponding to (110) lattice of body-centered cubic BP I. Here we note that the BP II superstructure reappeared before transforming into the isotropic phase if the temperature was increased from the BP I state.

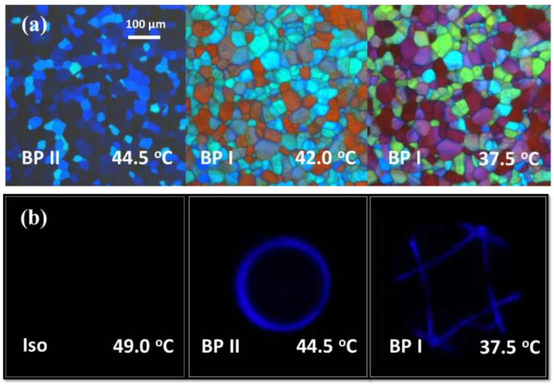

Figure 4. (a) Typical textures of BPs doped with 0.07 wt% M-GNRs in 10 μm thick cell without alignment at a cooling rate of 0.1 °C/min; (b) The Kossel diagrams of BPs doped with 0.07 wt% M-GNRs in 10 μm thick cell with planar alignment upon cooling, where the typical diagrams indicate phase transitions from isotropic to BP II followed by BP II to BP I transition.

To explore the NIR-light responsive properties of the self-organized photonic superstructures loaded with M-GNRs, the hybrid BP mixtures in the 10 μm thick untreated cells were cooled down from the isotropic phase to a stable BP I state and then irradiated with a 808 nm NIR laser (2 W). **Figure 5a** shows the typical texture changes of BPs doped with 0.3 wt% M-GNRs under the NIR irradiation at a temperature (T) below the isotropic clearing point (T_{Iso}), where ΔT = T_{Iso}-T = 5 °C and the characteristic BP I texture was observed. Upon irradiation with 808 nm NIR laser, the platelet textures initially changed from BP I to BP II in 30 s and then cleared into the isotropic state within 60 s, whereas the reverse process occurred upon removing the NIR irradiation. This combined photoirradiation and subsequent thermal relaxation process was reversible and reproducible for many cycles without noticeable degradation. By contrast, the above BP I without M-GNRs, *i.e.* pure BP host, did not transform into the isotropic phase upon the NIR irradiation even for more than five minutes. Such a significant difference is believed to result from the localized heating caused by photothermal effect of M-GNRs under the NIR laser irradiation. **Figure 5b** schematically illustrates the possible transformation of self-organized photonic superstructures. The 3D soft nanostructure transforms from body-centered cubic to simple cubic symmetry and finally changes into the isotropic phase upon the NIR laser irradiation, and it would relax back to the initial state on removal of the NIR-light owing to the bulk heat diffusion.

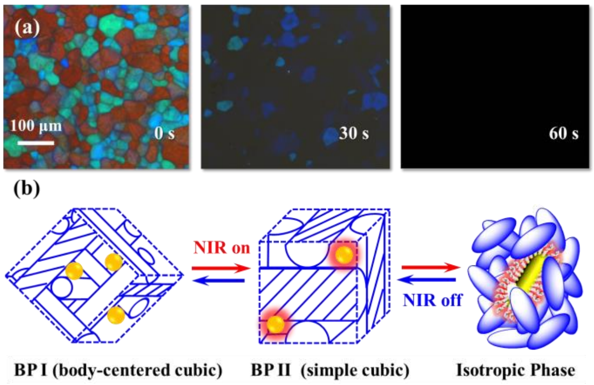

Figure 5. (a) Typical POM images of BPs doped with 0.3 wt% M-GNRs in 10 μm thick untreated cell upon irradiation with 808 nm NIR laser (2 W); (b) Schematic illustration of the NIR-light tunable self-organized soft photonic superstructures. The yellow dots represent the cross section of GNR in the BP matrices.

Figure 6a illustrates the response time dependence of photonic nanostructures on the temperature and the concentration of M-GNRs. It was found that the response time from the BP I to isotropic phase decreased significantly with increasing the doped concentration of M-GNRs, and raising the initial temperature also contributed to a reduction in the response time. To be specific, it takes nearly five minutes for the BPs with 0.01 wt% M-GNRs to transform from the BP I where ΔT = 5 °C to isotropic phase, whereas the response time decreased apparently to 1 minute for 0.3 wt% M-GNRs. Furthermore, the response time of the BPs with 0.3 wt% M-GNRs decreased from 60 to 10 s when ΔT was reduced from 5 to 1 °C. The shift in the photonic bandgap upon NIR-light irradiation was recorded using a spectrometer incorporated into the POM under the reflection mode. The BP photonic nanostructures loaded with 0.3 wt% M-GNRs were found to exhibit the tunable NIR-light directed reflections as shown in **Figure 6b**. A strong and narrow reflection centered at a wavelength of 607 nm (red) was observed in the initial BP I state, where ΔT = 5 °C. The reflection exhibited a significant blue-shift while its intensity decreased apparently upon irradiation with 808 nm NIR laser, and the center wavelength

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shifted to 560 nm (green) in 10 s. Interestingly, the reflection abruptly jumped to 491 nm (blue) around 15 s because of the phase transition from BP I to BP II. Thus dynamic red, green and blue color reflections were achieved from the BP by NIR laser irradiation for the first time. Longer irradiation with NIR-light only resulted in a continuous decrease in reflection intensity at the BP II state and, as expected, the reflection completely disappeared after the sample transformed into the isotropic phase.

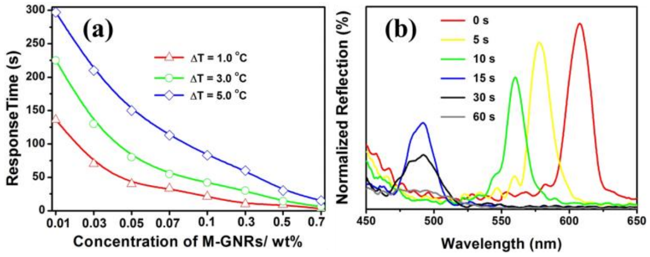

Figure 6. (a) Response time-dependence on the temperature and the concentration of M-GNRs. Note: $\Delta T = T_{Iso}-T$, where T_{Iso} is the isotropic clearing point of LCs; (b) Reflection spectra of BPs doped with 0.3 wt% M-GNRs upon irradiation with 808 nm NIR laser.

In conclusion, a NIR-light-responsive self-organized 3D photonic superstructure was fabricated by incorporating new hydrophobic mesogen-functionized GNRs into a BP LC medium composed of commercially available components. The introduction of M-GNRs was found to be beneficial in stabilizing the cubic nanostructure. Importantly, the resultant 3D photonic nanostructures could be switched between body-centered cubic and simple cubic symmetry under the irradiation of 808 nm NIR laser due to the significant photothermal effect from M-GNRs. The reverse process occurs upon removal of the NIR laser irradiation. This is the first observation of BP phase transition enabled by NIR light. Furthermore, reversible dynamic NIR-light-directed red, green, blue (RGB) reflections of the light-driven 3D soft photonic crystals were for the first time demonstrated. The results of this research reported here are expected to provide a route to spatially and temporally manipulate the 3D self-organized nanostructures and their dynamic photonic properties, thus paving way to cost-effective large-scale 3D photonic crystals in a remotely programmable technique and leading to applications in areas of optical devices and critical components for next-generation of optical communication technology.

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Notes and references

1 a) Q. Li (Ed.), Intelligent Stimuli-Responsive Materials: From Well-Defined Nanostructures to Applications, John Wiley & Sons, Hoboken, New Jersey, 2013; b) L. Wang, Q. Li, *Adv. Funct. Mater.* 2015, **25**, DOI: 10.1002/adfm.201502071.

2 a) T.-H. Lin, Y. Li, C.-T. Wang, H.-C. Jau, C.-W. Chen, C.-C. , H. K. Bisoyi, T. J. Bunning, Q. Li, *Adv. Mater.* 2013, **25**, 5050-5054; b) H. J. Coles, M. N. Pivnenko, *Nature* 2005, **436**, 99-1000; c) X. Chen, L. Wang, C. Li, C. J. Xiao, H. Ding, X. Liu, X. Zhang, W. He, H. Yang, *Chem. Comm.* 2013, **49**, *10097-10*

3 a) D. C. Wright, N. D. Mermin, *Rev. Mod. Phys. 1989,* **6** 385-432; b) H. Kikuchi, *Struct. Bonding* 2008, **128**, 99-117.

4 a) Y. Xia, B. Gates, Z.-Y. Li, *Adv. Mater.* 2001, **6**, 409-413; b) Ge, Y. Yin. *Angew. Chem. Int. Ed*. 2011, **50**, 1492-1522.

5 H. K. Bisoyi, Q. Li, *Acc. Chem. Res.* 2014, **47**, 3184-3195.

6 a) L. Wang, H. Dong, Y. Li, C. Xue, L. D. Sun, C. H. Yan, Q. Li, *Am. Chem. Soc.* 2014**, 136**, 4480-4483; b) L. Wang, H. Dong, Y. Li, R. Liu, Y.-F. Wang, H. K. Bisoyi, L.-D. Sun, C.-H. Yan, Q. Li. *Adv. Mater.* 2015, **27**, 2065-2069. c) K. G. Gutiérrez-Cuevas, Wang, C. Xue, S. Gautam, S. Kumar, A. Urbas, Q. Li, *Chem Comm.* 2015, **51**, 9845-9848.

7 a) H. Yang, J. Liu, Z. Wang, L. Guo, P. Keller, B. Lin, Y. Sun, X. Zhang. *Chem. Comm.* 2015, **51**, 12126-12129; b) H. Chen, Shao, J. Wang, *Chem. Soc. Rev*. 2013, **42**, 2679-2724.

8 B. Nikoobakht, M. A. El-Sayed, *Chem. Mater.* 2003, **15**, 1957-1962.

9 a) V. Shanmugam, S. Selvakumar, C.-S. Yeh, *Chem. Soc. Rev* 2014, **43**, 6254-6287; b) I. Gorelikov, L. M. Field, Kumacheva, *J. Am. Chem. Soc.* 2004**, 126**, 15938-15939.

10 C. J. Murphy, T. K. San, A. M. Gole, C. J. Orendorff, J. X. Gao L. Gou, S. E. Hunyadi, T. Li, *J. Phys. Chem. B* 2005, **10**, 13857-13870.

11 a) M. Gluodenis, C. A. Foss, *J. Phys. Chem. B* 2002, **10** 9484-9489; b) X. Huang, S. Neretina, M. A. El-Sayed, *Ad Mater.* 2009, **21**, 4880-4910.

12 a) H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, T. Kajiyam *Nature Mater.* 2002, **1**, 64-68; b) D. Voloschenko, O. Pishnyak, S. V. Shiyanovskii, O. D. Lavrentovich, *Phys. Rev.* 2002, **65**, 060701; c) J. Xiang, O. D. Lavrentovich*, Appl. Phys. Lett.* 2013, 103, 051112; d) F. Castles, F. V. Day, S. M. Morri, D. H. Ko, D. J. Gardiner, M. M. Qasim, S. Nosheen, P. J. Hand, S. S. Choi, R. H. Friend, H. J. Coles, *Nat. Mater.* 2012, **11**, 9 603.

13 a) L. Wang, W. He, X. Xiao, F. Meng, Y. Zhang, P. Yang, L Wang, J. Xiao, H. Yang, Y. Lu, *Small.* 2012, **8***,* 2189-2193; b) M. Wong, J. Y. Hwang, L. C. Chien, *Soft Matter* 2011, **7**, 7956-7959; c) L. Wang, W. He, Q. Wang, M. Yu, X. Xiao, Y. Zhang M. Ellahi, D. Zhao, H. Yang, L. Guo, *J. Mater. Chem. C* 201 6526-6531.

14 a) P. Crooker, *in Chirality in Liquid Crystals*, Springer, New York, 2001; b) R. J. Miller, H. F. Gleeson, J. E. Lydon. *Phys. Rev E* **1999**, *59*, 1821-1827.