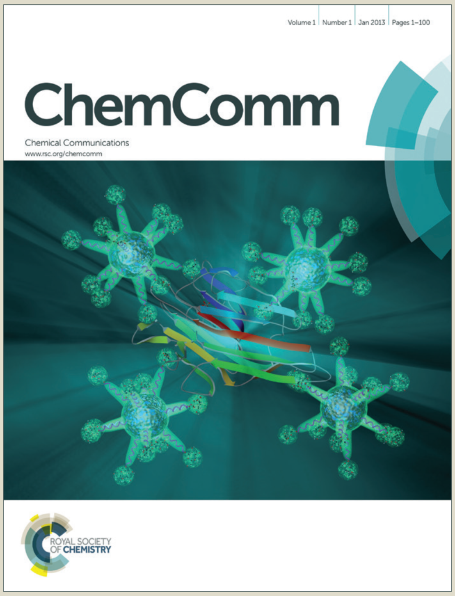
ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Tuning Structural Asymmetries of Three-Dimensional Gold Nanorod Assemblies

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

ChenqiShen, Xiang Lan, Xuxing Lu, Weihai Ni and Qiangbin Wang*

A series of 3D AuNR dimers and trimers were fabricated under the guidance of DNA origami. By tuning size, number and spatial configuration of AuNRs, their structural and componential asymmetries were rationally designed. Circular dichrosim measurements showed that resultant plasmonic chiroptical activities of these nanorod assemblies can be precisely tailored.

Structural asymmetry plays an essential role in distinct functions of numerous molecular systems, such as chiral drugs[1,2], proteins[3,4] and membranes[5,6], etc. Recently, the structural asymmetry in artificial nanostructures has attracted growing interests[7-13], keeping pace with the advancement of fabricating methods on nanometer length scale. For instance, structure-property feedback mechanism was used to assemble symmetry-breaking gold nanorod metamaterials with a longitudinal offset, which determines their electromagnetic responses[14]. Discrete nanopyramids made of gold, silver and semiconductor nanoparticles with designed asymmetry resulted in tailored optical activities in the visible regime[15]. Scissor-shaped noble metal nanoparticle dimers which can rotate the polarization of light were assembled to strongly amplify the existence of bridging biomolecules between neighboring particles[16]. Thus, novel physical properties or practical functionalities of nanostructures are expected by engineering their intrinsic structural asymmetry in a controllable way.

At present, self-assembled nanostructures composing spherical metallic nanoparticles with adjustable structural asymmetry have been widely studied, such as dimers[17], pyramids[18], single helices[19,20] and double helices[21]. Distinct optical properties, especially plasmonic chirality, were observed from these artificial nanostructures. In comparison with spherical metallic nanoparticles, nonspherical counterparts such as gold nanorod (AuNR) display unique geometric and optical characteristics[22]. AuNRs possess two surface plasmon resonance modes, which are transverse and longitudinal to the length axis, respectively. Complex plasmonic coupling and plasmon-mediated antenna effect are responsible for the optical activities of AuNR assemblies[23]. On the other hand, double geometric axis of AuNR enables easy fulfillment of asymmetric configurations. For example, as few as two AuNRs are needed to build a symmetry-breaking architecture[24]. Besides, as the development of colloidal synthesis, seed-mediated method also provides the ability to conveniently acquire AuNRs with different size[25,26]. Therefore, new insights into plasmonic chirality might be achieved through designing the structural asymmetry of AuNR nanostructures by tuning the AuNR number, size and spatial configurations, which have been rarely investigated yet.

In our previous work, we realized DNA origami-directed assembly of three-dimensional (3D) AuNR dimers[27] and double helices[28], which are featured by the designed interparticle separation and spatial configuration. We also explored the role of curvature of DNA origami in induced chirality of quasi two-dimensional AuNR dimers[29]. Whereas, the AuNRs used are of the same size, thus lead to homogeneous structures. Herein, we constructed a series of heterogeneous AuNR 3D dimers and trimers under the guidance of DNA origami, in which differently-sized AuNRs were used to create heterogeneous structures, in addition that the AuNR number and 3D configuration were tuned as well. Circular dichrosim (CD) measurements showed that resultant plasmonic chiroptical activities could be rationally tailored by designing the structural asymmetries of these AuNR nanostructures.

The process of constructing AuNR dimes and trimers is illustrated in Figure 1. Employed as a template for these assemblies, a rectangular bifacial DNA origami (90 nm×60 nm×2 nm) was self-assembled from a long single-stranded M13 viral genomic DNA as well as a series of ~200 short staple strands which could hybridize with the M13 DNA in specific sites through annealing. Three groups of capturing strands were rationally designed on opposite sides of the rectangular DNA origami. Every group contained seven capturing strands to precisely link a complementary-DNA-modified AuNR on specific location of the bifacial origami. As is demonstrated in theoretical studies, the optical activities of chiral structures are

---

Key Laboratory of Nano-Bio Interface, Division of Nanobiomedicine and i-Lab, Suzhou Institute ofNano-Tech and Nano-Bionics, Chinese Academy of Sciences,Suzhou 215123, China.
E-mail: qbwang2008@sinano.ac.cn
Fax: +86-0512-62872620; Tel: +86-0512-62872620

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ChemComm Accepted Manuscript

ChemComm Accepted Manuscript

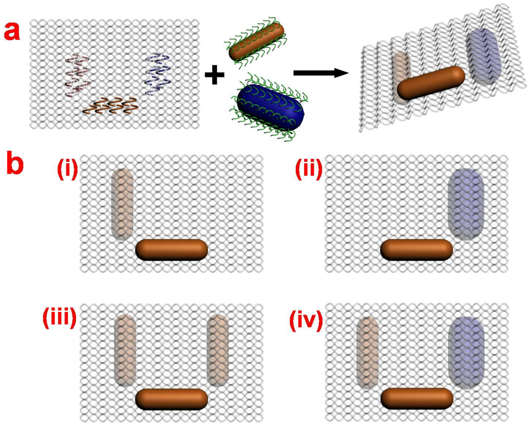


Figure 1. Schematic illustration of (a) DNA origami-directed self-assembly of AuNR nanostructures and (b) four types of AuNR assemblies (i) dimer1; (ii) dimer2; (iii) trimer1; (iv) trimer2. The brown rod represents 10×36 nm AuNR, while the blue rod represents 20×40 nm AuNR.

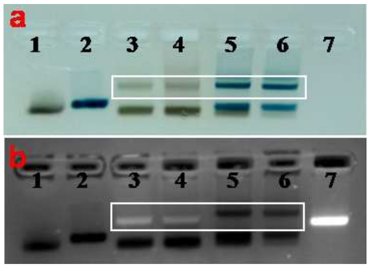


Figure 2. SYBR Green-stained agarose gel electrophoresis images of the AuNR assemblies under daylight (a) and UV light (b). Lane 1: 10×36 nm AuNRs. Lane 2: 20×40 nm AuNRs. Lanes 3–6: dimer1, trimer1, trimer2, dimer2, respectively. Lane 7: bare rectangular DNA origami.

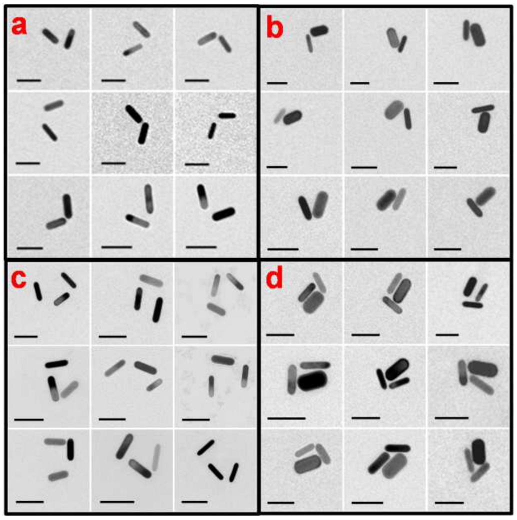


Figure 3. Characterization of the AuNR dimers and trimers assembled on rectangular DNA origami. (a–d) TEM images of the four obtained AuNR assemblies. All scale bars are 50nm.

firmly dependent on their asymmetric geometry[30-32]. Previous experimental work has proved "L"-shaped AuNR dimers show strong CD signals. On this basis, a left-handed dimer1 composed of two 10×36 nm AuNRs (Figure S1a) was firstly assembled. We then introduced a larger size 20×40 nm AuNR (Figure S1b) to our system to acquire a heterogeneous right-handed dimer2. To further tailor their spatial asymmetry, a third 10×36 nm AuNR was added to dimer1 and dimer2 respectively, which is parallel to the vertical AuNR on the same side of DNA origami template, forming trimer1 and trimer2.

The AuNR-origami complexes were purified by agarose gel electrophoresis and characterized by transmission electron microscopy (TEM). The gel images (stained with SYBR Green) under daylight and UV light are presented in Figure 2a,b. After conjugation with AuNRs, all four AuNR-origami complexes showed less mobility than bare rectangular DNA origami. Heterogeneous dimer2 and trimer2 (lane 6 and 5) moved at similar speed and slower than dimer1 and trimer1 (lane 3 and 4) owing to the introduction of larger-sized 20×40 nm AuNR. As shown in Figure 3, we obtained high yield production of the four designed AuNR nanostructures (see Figure S2 for more TEM images). Although some deformation existed during the drying process of TEM sampling and 2D imaging, the observed nanostructures can still be easily recognized, proving the successful creation of the AuNR assemblies. It is notable that dimer1 and trimer1 kept better configurations in comparison with dimer2 and trimer2. This morphological difference mainly arose from the deformation effect caused by the drying effect of DNA origami and building blocks linked to DNA origami, which is proved to be a flexible template.[29] Compared to the AuNR in dimer1 and trimer1, the larger-sized AuNR in dimer2 and trimer2 caused more obvious deformation, forming more compact assemblies under TEM characterization.

We then carefully investigated the optical properties of the four AuNR nanostructures. Absorption spectra of AuNR dimers and trimers are presented in Figure S3. No obvious peak shift is observed in comparison with that of free AuNRs, which indicates very weak surface plasmon coupling between AuNRs inside the assemblies. Especially in spectra of dimer2 and trimer2, both peaks of 10×36 nm and 20×40 nm AuNRs can be identified. The chiroptical responses of the assemblies were experimentally characterized by CD spectroscopy. "L"-shaped dimer1 displays a characteristic left-handed bisignate CD signal (Figure 4a). The symmetric center of the chiral signal is around 720 nm, consistent with the extinction spectra peak of 10×36 nm AuNR. With utilization of a larger-sized 20×40 nm AuNR, the right-handed CD signal of dimer2 showed much higher intensity than that of dimer1, as well as broadening of both positive and negative peaks. Such a spectral change mainly arises from the strong surface plasmon resonance of 20×40 nm AuNR, which strikingly increases the optical extinction section and determines the electromagnetic responses of AuNR dimers, causing an increase in asymmetry. Besides, blue-shift in CD spectra of dimer2 was also observed due to the higher plasmon resonance frequency of 20×40 nm AuNR. This indicates the strong impact of

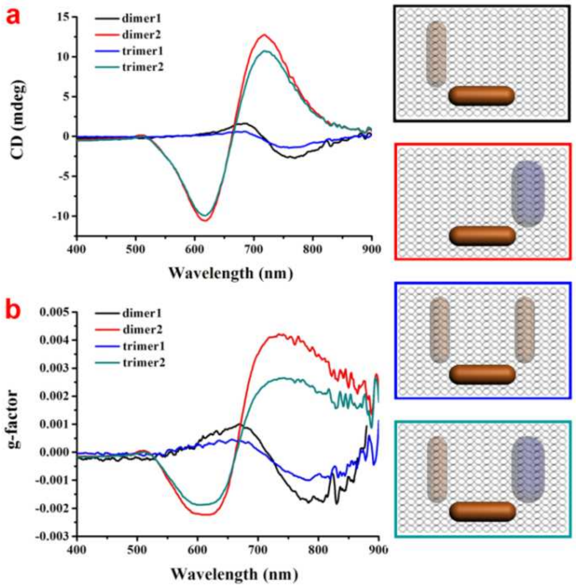


Figure 4. Circular dichroism spectra and anisotropy factors of the AuNR dimers and trimers: (a) measured CD spectra of dimer1, dimer2, trimer1, trimer2; (b) measured g-factors of AuNR assemblies corresponding to the nanostructures in (a).

larger-sized AuNR on the chiroptical responses of heterogeneous AuNR nanostructures.

To further tailor the spatial configuration of the obtained homo- and hetero-nanorod dimers, we constructed trimer1 and trimer2 by adding a third vertical 10×36 nm AuNR. In the case of trimer1, we observed a slight decrease in CD intensity as compared with dimer1 (Figure 4a). Trimer1 contains two types of substructures, dimer1 and its enantimeric structure. Therefore, the mesomeric effect dominates the CD response of trimer1, generating a weaker CD signal. Principally, trimer1 was designed as an axial symmetric structure, which is supposed to exhibit no chiral signals. Owing to the size distribution of AuNRs and slight curvature of DNA origami in solution, a weak CD signal was still observed. Due to the same mesomeric effect, trimer2 also displayed a lower CD intensity in comparison with dimer2. Trimer2 can be similarly separated into homogeneous dimer1 and heterogeneous dimer2, which have reversed chiroptical properties. However, right-handed dimer2 possesses much stronger CD signal than left-handed dimer1. Hence, despite the signal offsetting produced by substructure dimer1, trimer2 still acquires a strong right-handed CD signal.

On the other hand, the chiral responses of the AuNR nanostructures can also be characterized by anisotropy factor (g-factor), defined as the ratio of molar CD to molar extinction[28]. As demonstrated in Figure 4b, dimer2 has a maximum g-factor around 0.004, much bigger than that of dimer1 due to introduction of a larger AuNR. As for the trimer systems, g-factor of trimer1 decreases in comparison with dimer1, and is the minimum among the four types of assembled nanostructures. Trimer2 shows a similar decrease compared to dimer2. These anisotropy factors of AuNR nanostructures are highly consistent with their designed structural asymmetries.

In summary, through DNA origami-directed self-assembly, we successfully fabricated a series of chiral AuNR dimers and trimers, whose structural asymmetries were tuned by modifying the AuNR size, number, and location. Mesomeric and accumulative effects of CD signals were observed by designing the structural and componential asymmetry of AuNR nanostructures. We expect that, the understanding of impact of structural and componential asymmetry on the chiroptical activities of AuNR nanostructures will inspire the future assembly of chiral nanostructures, and provide a new avenue for rational designing of functional chiral devices for versatile applications.

The authors acknowledge funding by the National Science Foundation of China (grant no. 21303249, 21301187, 21425103), and the National Science Foundation of Jiangsu Province, China (grant no. BK2012007).

Notes and references

1 H. Caner, E. Groner, L. Levy, and I. Agranat, *Drug Discov. Today*, 2004, **9**, 105.
2 P. Etayo, and A. Vidal-Ferran, *Chem. Soc. Rev.*, 2013, **42**, 728.
3 L. Fu, J. Liu, and E. C. Y. Yan, *J. Am. Chem. Soc.*, 2011, **133**, 8094.
4 F. J. Ramírez, B. Nieto-Ortega, J. Casado, and J. T. L. Navarrete, *Chem. Comm.*, 2013, **49**, 8893.
5 C. Ma, X. Xu, P. Ai, S. Xie, Y. Lv, H. Shan and L. Yuan, *Chirality*, 2011, **23**, 379.
6 W. Xiong, W. Wang, L. Zhao, Q. Song, and L. Yuan, *J. Membrane Sci.*, 2009, **328**, 268.
7 M. Hentschel, L. Wu, M. Schäferling, P. Bai, E. P. Li, and H. Giessen, *ACS Nano*, 2012, **6**, 10355.
8 W. Liu, D. Liu, Z. Zhu, B. Han, Y. Gao, and Z. Tang,*Nanoscale*, 2014, **6**, 4498.
9 J. G. Gibbs, A. G. Mark, S. Eslami, and P. Fischer, *Appl. Phys. Lett.*, 2013, **103**, 213101.
10 B. Frank, X. Yin, M. Schäferling, J. Zhao, S. M. Hein, P. V. Braun, and H. Giessen, *ACS Nano*, 2013, **7**, 6321.
11 Y. Wang, J. Xu, Y. Wang, and H. Chen, *Chem. Soc. Rev.,* 2013, **42**, 2930.
12 V. K. Valev, J. J. Baumberg, C. Sibilia, and T. Verbiest, *Adv. Mater.*, 2013, **25**, 2517.
13 A. Ben-Moshe, B. M. Maoz, A. O. Govorov, and G. Markovich, *Chem. Soc. Rev.,* 2013, **42**, 7028.
14 S. Yang, X. Ni, X. Yin, B. Kante, P. Zhang, J. Zhu, Y. Wang, and X. Zhang, *Nature Nanotech.*, 2014, **9**, 1002.
15 W. Yan, L. Xu, C. Xu, W. Ma, H. Kuang, L. Wang, and N. A. Kotov, *J. Am. Chem. Soc.*, 2012, **134**, 15114.
16 X. Wu, L. Xu, L. Liu, W. Ma, H. Yin, H. Kuang, L. Wang, C. Xu, and N. A. Kotov, *J. Am. Chem. Soc.*, 2013, **135**, 18629.
17 X. Lu, J. Wu, Q. Zhu, J. Zhao, Q. Wang, L. Zhan, and W. Ni, *Nanoscale*, 2014, **6**, 14244.
18 A. J. Mastroianni, S. A. Claridge, and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2009, **131**, 8455.
19 X. Shen, C. Song, J. Wang, D. Shi, Z. Wang, N. Liu, and B. Ding, *J. Am. Chem. Soc.*, 2012, **134**, 146.
20 A. Kuzyk, R. Schreiber, Z. Fan, G. Pardatscher, E. Roller, A. Högele, F. C. Simmel, A. O. Govorov, and T. Liedl, *Nature*, 2012, **483**, 311.
21 J. Sharma, R. Chhabra, A. Cheng, J. Brownell, Y. Liu, and H. Yan, *Science*, 2009, **323**, 112.
22 T. K. Sau, A. L. Rogach, F. Jäckel, T. A. Klar, and J. Feldmann, *Adv. Mater.*, 2010, **22**, 1805.
23 L. M. Liz-Marzán, *Langmuir*, 2006, **22**, 32.

ChemComm Accepted Manuscript

24 W. Ma, H. Kuang, L. Wang, L. Xu, W.–S. Chang, H. Zhang, M. Sun, Y. Zhu, Y. Zhao, L. Liu, C. Xu, S. Link, and N. A. Kotov, *Scientific Reports*,2013,**3**, 1934.
25 B. Nikoobakht, and M. A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957.
26 A. Gole, and C. J. Murphy, *Chem. Mater.,*2004, **16**, 3633.
27 X. Lan, Z. Chen, G. Dai, X. Lu, W. Ni, and Q. Wang, *J.Am. Chem. Soc.,* 2013, **135**, 11441.
28 X. Lan, X. Lu, C. Shen, Y. Ke, W. Ni, and Q. Wang, *J.Am. Chem. Soc.,* 2015, **137**, 457.
29 Z. Chen, X. Lan, Y.-C. Chiu, X. Lu, W. Ni, H. Gao, and Q. Wang, *ACS Photonics*, 2015, **2**, 392.
30 Z. Fan, and A. O. Govorov, *Nano Lett.*, 2010, **10**, 2580.
31 D. N. Chigrin, C. Kremers, and S. V. Zhukovsky, *Appl. Phys. B*, 2011, **105**, 81.
32 Z. Fan, and A. O. Govorov, *Nano Lett.*, 2012, **12**, 3283.

ChemComm Accepted Manuscript