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2	Supporting Information
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5	Self-assembly of Supramolecular Nanotubes/Microtubes from 3,5-Dimethyl-4-
6	iodopyrazole for Plasmonic Nanoparticle Organization
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8	Shasha Li, Rui Liu, Deribachew Bekana, Yujian Lai, and Jingfu Liu*
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24 Materials and methods

Materials. 3,5-Dimethyl-4-iodopyrazole (DMIP) was purchased from TCI (Shanghai) Development Co., Ltd. Sodium citrate, ascorbic acid, AgNO₃, polyvinyl pyrrolidone (PVP, average molecular weight 10,000), mercaptopropyltriethoxysilane (MPTES) and crystal violet were obtained from Sigma-Aldrich. HAuCl₄·4H₂O, ethanol and isopropanol were supplied by Sinopharm Chemical Reagent Co. (Beijing). All the other reagents were used as received.

Synthesis of Ag@SiO₂ NPs. Ag@SiO₂ NPs were synthesized according to a modified literature method.¹ The 110 nm Ag ananoparticles synthesized above were used as cores of Ag@SiO₂ NPs. In a typical synthesis, 0.54 ml of mercaptopropyltriethoxysilane (MPTES) solution (10%) was added to 90 ml Ag colloid and then stirred at 50 °C. The reaction proceeded for 1 h and then was cooled down. Afterwards, 0.54 ml aqueous 0.054% sodium silicate solution was added and stirred at 90 °C for 1h. The mixture was centrifugated and re-suspended in ethanol.

Theoretical calculation. We perform ab-initio molecular dynamics (AIMD) for the single molecule and three-molecule system. The canonical ensemble (NVT) has been performed at 300K using Nose-Hoover chain thermostat² with the time step of 0.5 fs. The system was equilibrated for 5 ps and the production run used 10 ps.

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38 **Results and Discussion**

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Figure S2. AFM images(a) and Height profiles (b) of DMIP assemblies.





Figure S3. ESEM image (a) and Raman spectra (b) of xerogel of DMIP assemblies in methanol/water.





from 20 to 80 °C. (c) The temperature-dependent changes of the iodine-bound carbon atom of DMIP, DMP and DMBrP.

52 The small upfield shift observed with increasing temperature was possibly attributed to the breaking of surrounding

53 intermolecular hydrogen bond interactions (between DMBrP/DMP or DMBrP/DMP and solvent). However, compared with

54 that of DMIP, variations in chemical shifts for DMBrP / DMP could almost be negligible (Figure S5c). Therefore, the control

experiment with DMBrP / DMP could further prove the involvement of iodine in halogen bond.



Figure S5. The interaction energy per molecule for different interaction configurations.



60 Figure S6. Enlarged FESEM images of DMIP tubules shaped Au NPs array, showing that small Au NPs could also be

attached to DMIP microtubes.

1 pm

65 Figure S7. FESEM images of Au NPs attached to DMIP tubules. The arrows show the visible organic tubules.



68 Figure S8. FESEM of Au NPs array (a). ESEM images of DMIP tubules shaped Au NPs arrays before (b) and after (c)



removal of the organic template.





- 72 Figure S9. ESEM images and XPS spectra that prove the removal of organic DMIP assemblies by heating. ESEM images of
- 73 DMIP tubules shaped Au NPs arrays before (a) and after (b) heating at 100 °C; (c) XPS spectra of I *3d* for DMIP after heating.



Figure S10. FESEM images of Ag NPs attached to DMIP tubules at different magnifications.





- Figure S11. HAADF-STEM images (a), the corresponding STEM-EDS elemental mappings (b) and STEM-EDS (c) of DMIP
 assemblies shaped Au NPs arrays.
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83 Figure S12. HAADF-STEM images (a), the corresponding STEM-EDS elemental mappings (b) and STEM-EDS (c) of DMIP

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assemblies shaped Ag NPs arrays.



Figure S13. XPS spectra of Au 4f (a) and Ag 4d (b). The binding energy of Au increased slightly by 0.2 eV, compared with the reference of metallic Au, which was in line with the change of Au-I (ads) complex reported in the previous literatures.³ Meanwhile, the binding energy values of Ag 3d shifted from 368.09 eV to 367.84 eV also demonstrating the chemisorption of Ag with iodine in DMIP.^{4, 5}



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Figure S14. FESEM image of organic tubules-shaped Ag@SiO2.

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