

Supporting Information for:

Tuning the Optical Properties of Fluorophore-hexylcarbazole Organic Nanoribbons with Dispersed Inorganic Nanocrystals (AgNCs)

Lin Kong,^a Jiaxiang Yang,^{ab} Xiaopeng Hao,^b Hongping Zhou,^a Jieying Wu,^a Fuying Hao,^a

Lin Li,^a Shengyi Zhang,^a Baokang Jin,^a Xutang Tao,^b Minhua Jiang,^b and Yupeng Tian^{*abc}

Synthesis procedures and characterization of organic materials. PL spectra of **L** in different states. Formation of pure Ag NCs. Morphologies of the mixture physically mixes **L** nanofibres and Ag NCs. EDX spectrum of Ag NCs and **L**-Ag hybrid. XPS measurement of the hybrid. Time-resolved FL result of the hybrid. Effect of reaction time and concentration of AgNO₃ on the formation of the hybrid.

1. Preparation of N-hexylcarbazole: NaH (4.08 g, 0.17 mol) and DMF (5 mL) were added to a three-necked flask equipped with a magnetic stirrer and a reflux condenser, then carbazole (16.70 g, 0.1 mol), DMF (10 mL) were added dropwisely (about 30 min), refluxed for another 20 min. Then C₆H₁₃Br (17 mL) was dropped into the mixture and refluxed for 2 h with TLC detection, during which the reaction solution turned into dark-green gradually. The pH of the solution was adjusted to acidic with hydrochloric acid then extracted the solution with 500 mL of ethyl acetate, washed three times with distilled water, and dried with anhydrous magnesium sulfate. It was then filtered and concentrated. The residual solid was recrystallized from ethanol to give white needle crystals (17.60 g, 70 % in yield). ¹H NMR

(400 MHz, CDCl_3) δ (ppm) : 8.09 (d, $J=7.6$ Hz, 2H), 7.46~7.39 (q, $J=7.2$ Hz, 4H), 7.21 (d, $J=10.8$ Hz, 2H), 4.30 (t, $J=7.2$ Hz, 2H), 1.87 (q, $J=7.6$ Hz, 2H), 1.48~1.29 (q, $J=3.2$ Hz, 6H), 0.86 (t, $J=6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 14.01, 22.55, 26.99, 28.94, 31.60, 43.10, 108.65, 118.68, 120.33, 122.83, 125.56, 140.44. FT-IR (KBr, cm^{-1}): ν = 3050 (m), 2955 (s), 2924 (s), 2855 (s), 1594 (s), 1453 (s), 1324 (s), 752 (s), 724 (s).

2. Preparation of N-hexylcarbazole-3-aldehyde: N-hexylcarbazole (12.55 g, 0.05 mol) and DMF (39 mL) were added to a three-necked flask in an ice bath equipped with a magnetic stirrer and a reflux condenser, then POCl_3 (92 mL) was added dropwisely (about 30 min), the mixture was heated in an oil bath at 80 °C and refluxed for 1 h. Then the mixture was poured into ice to get light yellow solid. The pH of the mixture was adjusted to be neutral with NaOH and extracted three times with 150 mL of ethyl acetate. The organic layer was washed with distilled water and then saturated brine. The organic extracts were dried with anhydrous magnesium sulfate. The solvent was removed in *vacuo*. The residue was purified by column chromatography on silica gel with petroleum ether as eluent to get 8.90 g N-hexylcarbazole-3-aldehyde as a white solid in 64 % yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 10.12 (s, 1H), 8.64 (d, $J=1.2$ Hz, 1H), 8.20 (d, $J=7.6$ Hz, 1H), 8.03 (q, $J=1.6$ Hz, 1H), 7.56 (d, $J=7.6$ Hz, 1H), 7.49 (t, $J=7.2$ Hz, 2H), 7.35 (t, $J=7.2$ Hz, 1H), 4.36 (t, $J=6.8$ Hz, 2H), 1.95 (q, $J=8.2$ Hz, 2H); 1.42~1.32 (q, $J=7.8$ Hz, 6H), 0.87 (t, $J=7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 13.96, 22.50, 26.91, 28.89, 31.50, 43.49, 108.94, 109.38, 120.28, 120.74, 123.01, 123.08, 123.99, 126.69, 127.16, 128.52, 141.18, 144.09, 191.76. FT-IR (KBr, cm^{-1}): ν = 2951 (m), 2925 (m), 2856 (m), 1689 (s), 1594 (m), 1131 (m), 748 (m), 729 (m).

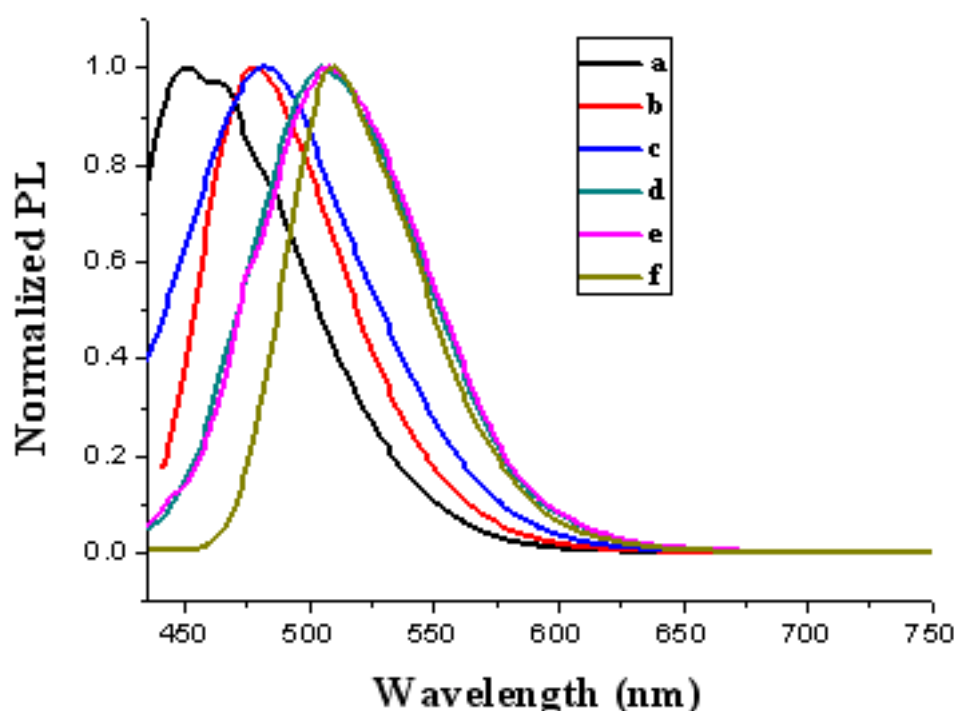


Figure S1. PL spectra of **L** samples: (a) in benzene solution (1.0×10^{-6} M); (b–e) nanocrystals prepared from different solvents: (b) benzene, (c) THF, (d) EtOH, (e) EG; (f) in solid state.

3. Formation of Ag NCs

Ag NCs are obtained by MW heating an EG solution of AgNO_3 with PVP as an additive. The XRD pattern of the NCs shows face-centered cubic structure (JCPDS card No. 04-0783) (**Fig. 2a**). The FESEM image reveals that the Ag NCs display polygon morphologies (**Fig. 3a**) with an average diameter of about 65 nm. The corresponding EDX analysis (**Fig. S2a**) verifies the presence of the Ag component. Note that the silicon and gold signals originate from silicon wafer as substrate and sputtered gold on the measured samples to improve conductivity.

In the experiments, according to reaction 1, heating of EG in air may generate GA, which is a dominant reductant for polyol synthesis of Ag nanostructures. At last, GA is oxidized into glyoxal according to reaction 2¹.



The UV-vis absorption spectra showed that Ag NCs display a wide absorption band

from 340 nm to 550 nm and centers at about 430 nm (**Fig. 5b**), which was assigned to the surface plasma resonance (SPR) band².

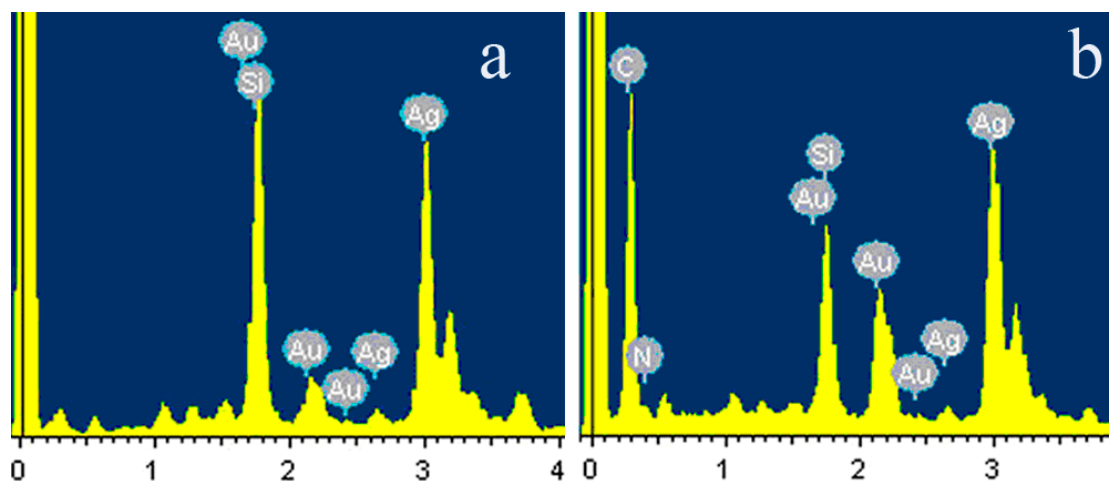


Figure S2. EDX spectra of (a) Ag NCs, (b) L-Ag nanohybrid.

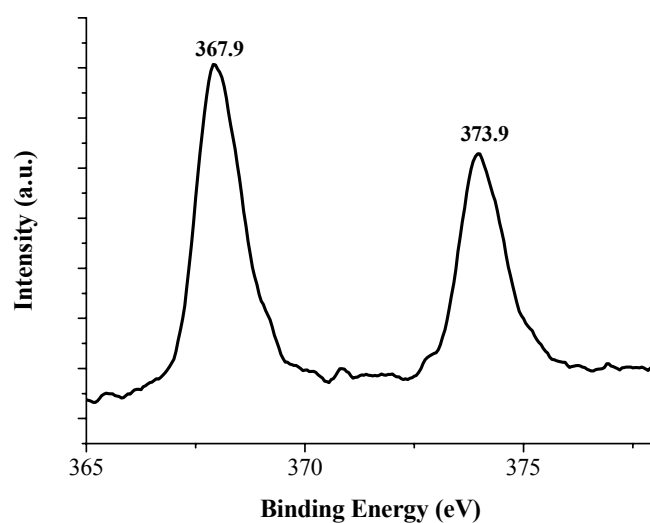


Figure S3. X-ray photoelectron spectra of the Ag 3d transition of L-Ag nanohybrid.

The XPS analysis of the hybrid showed two peaks centered at binding energy of 367.9 and 373.9 eV, which could be attributed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively^{3,4}.

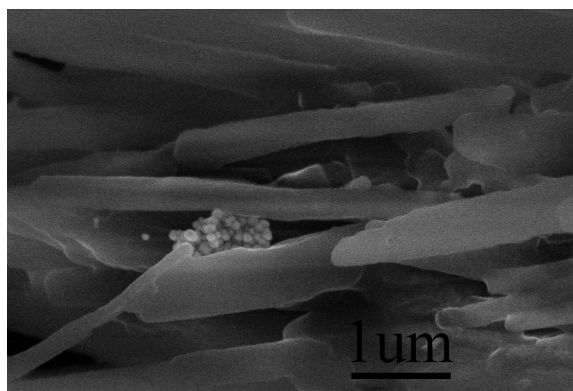


Figure S4. SEM micrograph of the mixture physically mixed **L** nanofibres and Ag NCs

Table S1. Time-resolved FL results for the nanofibres and nanohybrid.

	τ_1 (ns)	χ^2
L nanofibres	0.20	1.052
L-Ag nanohybrid	10.84	1.179

4. Effect of reaction time on the formation of the nanohybrid

The effect of the reaction time on the size and amount of Ag NCs attaching onto **L** nanoribbons is investigated. The average size of Ag NCs remains nearly unchanged as the time varied from 1.0 min to 6.5 min (**Fig. S5**), which indicates that the formation of Ag NCs is a fast process under microwave heating⁵. In the absence of **L**, Ag NCs tend to grow from 65 nm (**Fig. 3a**) to larger than 200 nm (**Fig. S6**) when the reaction time varied from 1 min to 5 min. This clearly demonstrates that **L** plays a crucial role in the growth of Ag NCs. **Fig. S5** also reveals that the amount of Ag NCs on **L** ribbons increases with the increase of the reaction time from 1.0 to 5.0 min, but decreases at the time longer than 6.5 min. Further results are obtained through thermogravimetric analysis (**Fig. S7**). The results of the experiments clearly showed that the optimum time for the coupling between **L** and Ag NCs is

5 min.

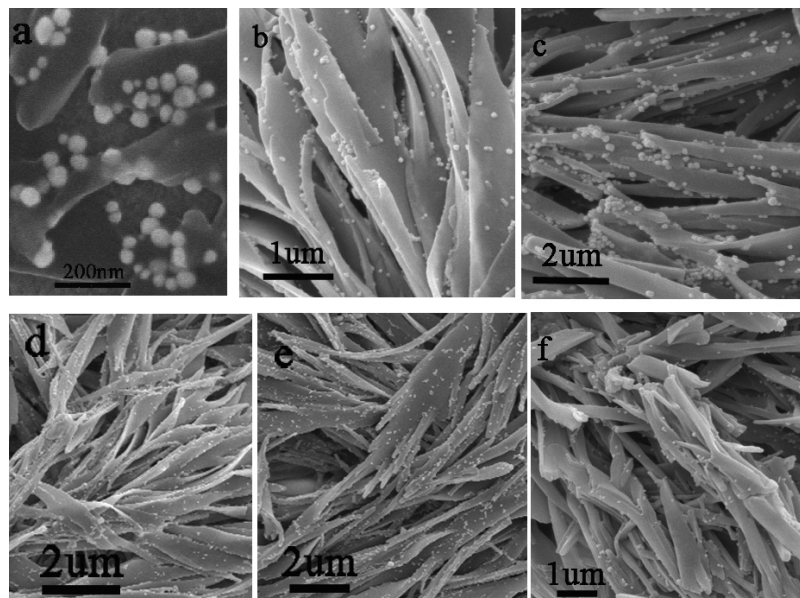


Figure S5. SEM micrograph of the L-Ag nanohybrids prepared from MW heating EG (10 mL) solution containing AgNO₃ (0.5 mmol), **L** (0.5 mmol) and PVP (0.04 g) for (a) 1 min, (b) 2 min, (c) 3 min, (d) 4 min, (e) 5 min and (f) 6.5 min.

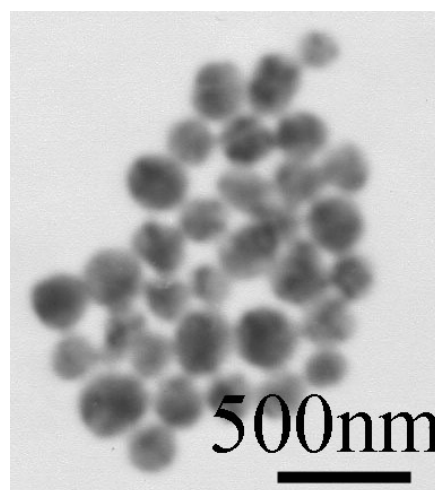


Figure S6. TEM micrograph of Ag NCs prepared by MW heating for 5 min

5. Thermogravimetric analysis of the hybrids prepared with different time

After the TG measurement, it was found that almost nothing is left for **L** nanofibres (the residual mass is 0.72 % at 700 °C, **Fig. S7a**), and black residues are left for **L-Ag** nanohybrids. The amount of the residue at 700 °C varied along the reaction time for the nanohybrid formation: they were 7.5 % (**Fig. S7b**), 13 % (**Fig. S7c**), 34 % (**Fig. S7d**), and 22.5 % (**Fig. S7e**) at the time of 2 min, 4 min, 5 min and 6.5 min, respectively.

The thermal stability of the hybrid is tunable by varying the content of Ag NCs. The thermal stability of the hybrid with low Ag contents (**Fig. S7b** and **c**) is lower than that of **L** (**Fig. S7a**). However, it increases with the increase of Ag contents (**Fig. S7d** and **e**). It was reported that the presence of small amount of Ag could reduce the dipole–dipole interactions of **L** molecules and result in the poor thermal stability⁶. As the Ag content increases, the metal–metal interactions would become dominant and increase as expected, which could improve the thermal stability of the nanohybrid⁷.

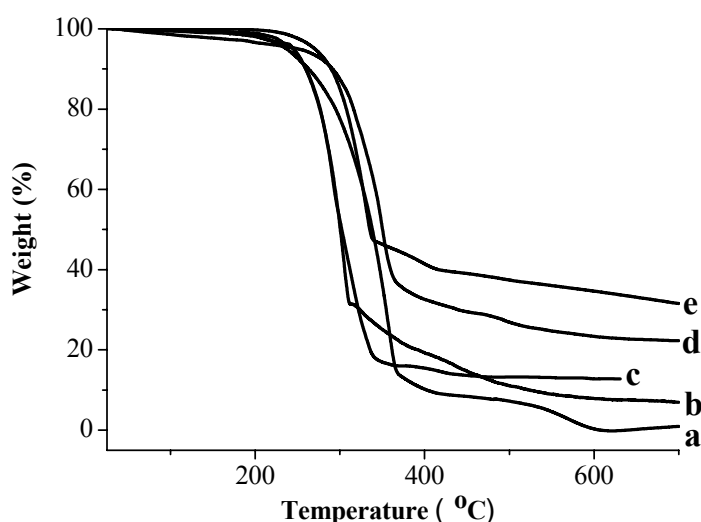


Figure S7. TG curves of samples: (a) **L**, (b)–(e) **L-Ag** nanohybrid prepared with different time: (b) 2 min, (c) 4 min, (d) 5 min, and (e) 6.5 min.

6. Effect of concentration of AgNO_3 on the formation of the nanohybrid

It is found that the number of Ag NCs attaching on the nanoribbons is also depended on the concentration of AgNO_3 used in the preparation process. When the usage increases from 0.01 mmol to 0.10 mmol (the concentration of AgNO_3 varies from 1×10^{-3} mol/L to 1×10^{-2} mol/L), the number of Ag NCs clinging to the ribbons increases along with it (**Fig. S8**), and Ag NCs tend to aggregate more and more. It can also be seen that the size of Ag NCs depositing on the surface of the organic component remains unchanged (that is about 55 nm).

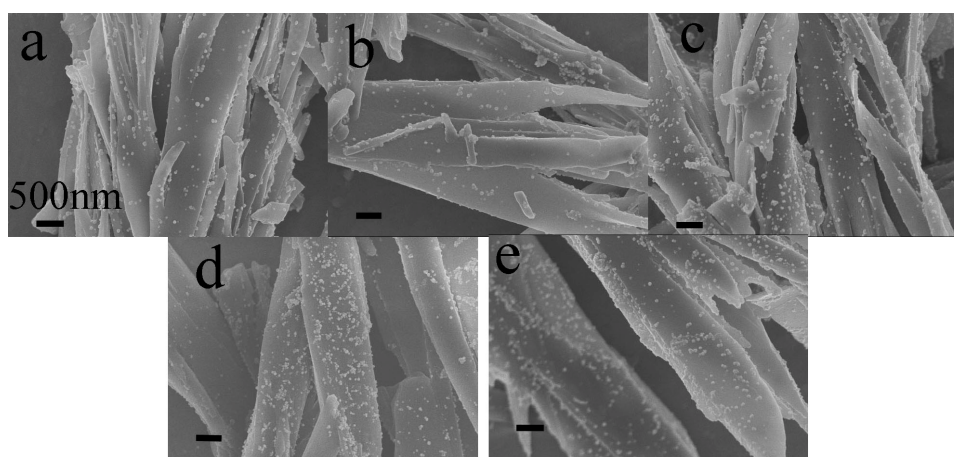


Figure S8. SEM images of the as-prepared products at various concentration of AgNO_3 :

(a) 1×10^{-3} , (b) 2×10^{-3} , (c) 6×10^{-3} , (d) 8×10^{-3} , (e) 1×10^{-2} mol/L

The results indicate that **L** is a preferable site for the nucleation and subsequent growth of Ag NCs due to their strong interactions. The organic component used here is a very important factor of the Ag NCs size coupling with it. Clearly, an optimum particle size should exist balancing the appropriate bandgap with a high surface area needed for adsorption of molecules⁸.

References

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