Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

EXPERIMENTAL SECTION

Materials and Measurements:

Silver nitrate ($AgNO_3$), 99.9995%, and sodium borohydride ($NaBH_4$), 98%, were purchased from Alfa Aesar and used without further purification. DNA oligonucleotides were purchased from Sangon (Shanghai, China). Polyethylene glycols (PEGs) with molecular weights of 200, 400, 1000, 3400, 6000, and 8000 were purchased from Sigma (St. Louis, MO). All other reagents were all of analytical reagent grade and used as received. Fluorescence measurements were carried out by using a JASCO FP-6500 spectrofluorometer (Jasco International Co., Japan). Absorption spectra were acquired using a CARY 300 UV/Visible spectrophotometer (Varian Inc., CA). Circular dichroism (CD) spectra were measured on a Jasco J-810 spectropolarimeter (Jasco International Co., LTD., Japan) with a computer-controlled water bath. The optical chamber of CD spectrometer was deoxygenated with dry purified nitrogen (99.99%) for 45min before use and kept the nitrogen atmosphere during experiments. Three scans were accumulated and automatically averaged. Nanopure water (18.2 MΩ; Millpore Co., USA) was used in all experiments.

Preparation of fluorescent Ag nanoclusters (AgNCs):

PEGs were dissolved in the appropriate buffer for combination with DNA solutions. The AgNCs were synthesized by first cooling the solution of DNA and $AgNO_3$ to 0 °C and then adding $NaBH_4$ followed by vigorous shaking for 2 min. Final concentrations were 15 μM in DNA template, 90μM in $AgNO_3$ and 90μM in $NaBH_4$. Unless otherwise noted, experiments were carried out in phosphate buffer (25 mM, pH7.0).

Figure

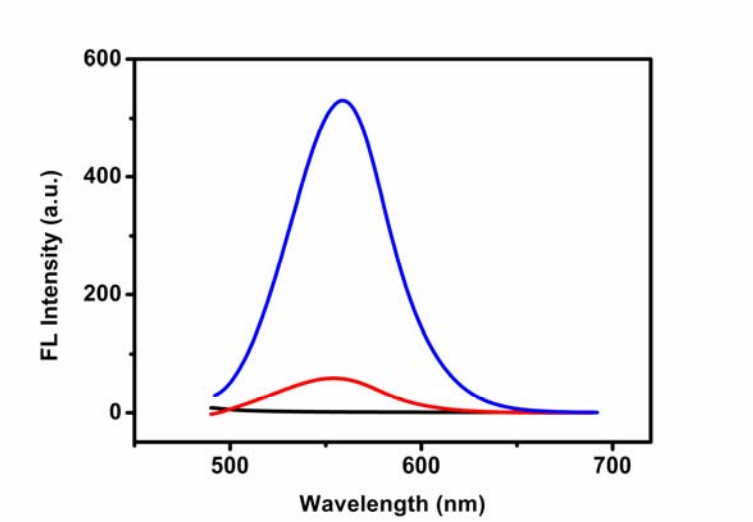

Figure S1 Ag (I) ions were reduced in 25mM phosphate buffer (pH 7.0) containing 30% PEG 200 in the absence of DNA template (black line). Fluorescent spectra of DNA 1-AgNCs synthesized with (red line) and without (blue line) 30% PEG 200 in 25mM phosphate buffer (pH7.0).

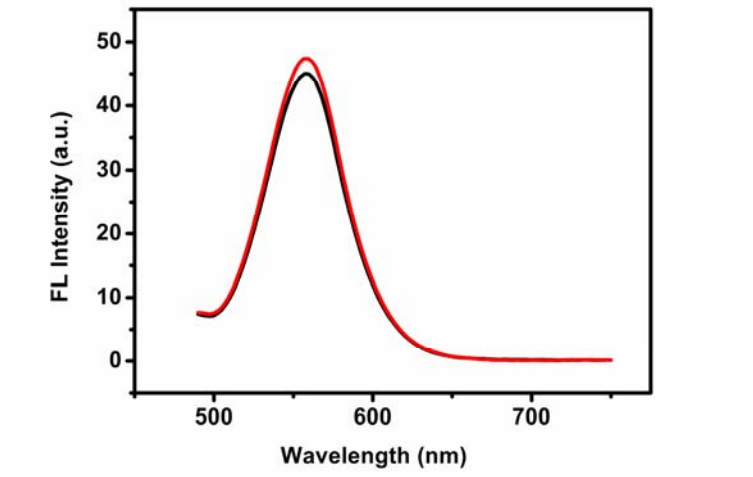

Figure S2 Fluorescent spectra of DNA 1-AgNCs synthesized under noncrowded condition after adding same amount of phosphate buffer (black line) and PEG 200 (to 30% ,w/w, red line).

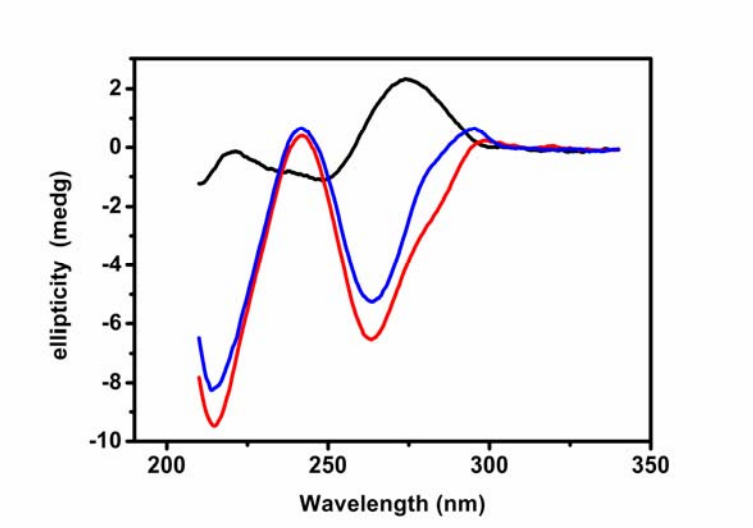

Figure S3 CD spectra of DNA 1 alone (black line), DNA 1 with Ag (I) ions (red line) and DNA 1-AgNCs under molecular crowded conditions (PEG 200, 30%, blue line).

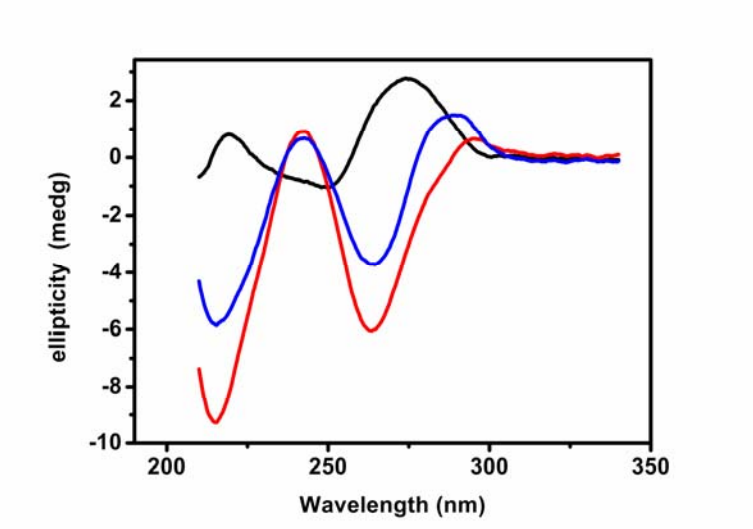

Figure S4 CD spectra of DNA 1 alone (black line), DNA 1 with Ag (I) ions (red line) and DNA 1-AgNCs under noncrowded conditions.

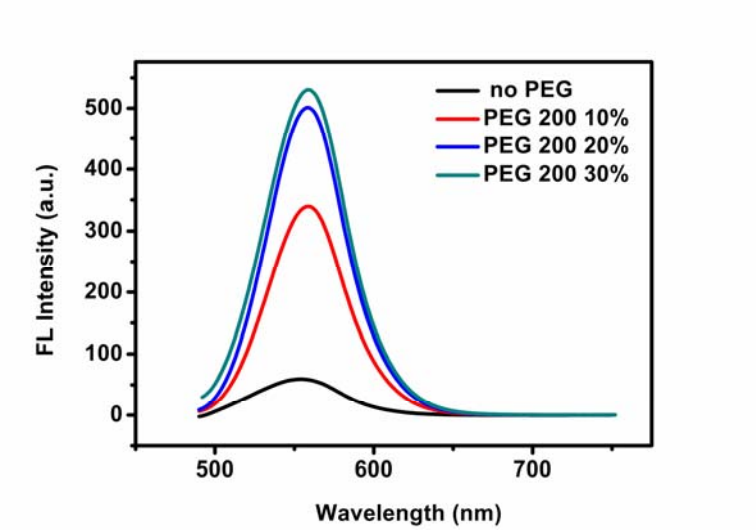

Figure S5 Fluorescence spectra of DNA 1-AgNCs synthesized in the absence and presence of 10%, 20% and 30% PEG 200, respectively.

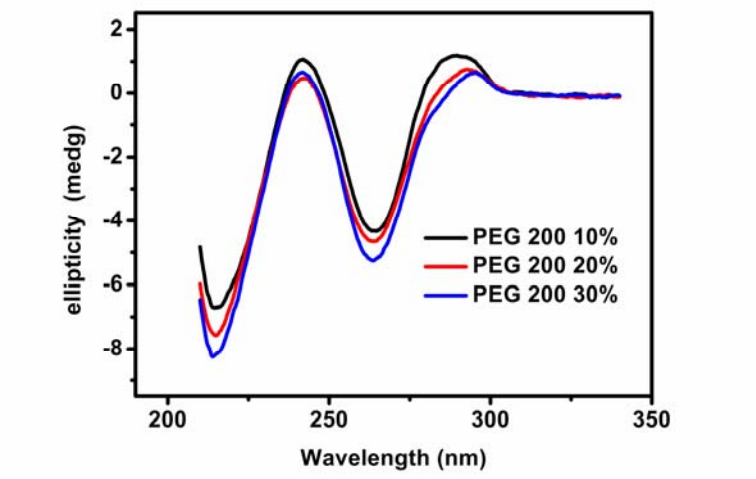

Figure S6 CD spectra of DNA 1-AgNCs synthesized in the presence of 10%, 20% and 30% PEG 200, respectively.

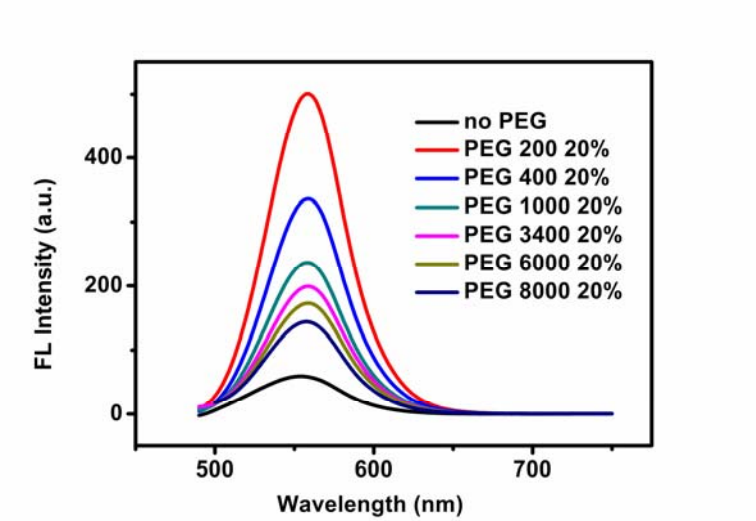

Figure S7 Fluorescence spectra of DNA 1-AgNCs synthesized in the absence and presence of 20% PEG 200, 400, 1000, 3400, 6000, 8000 respectively.

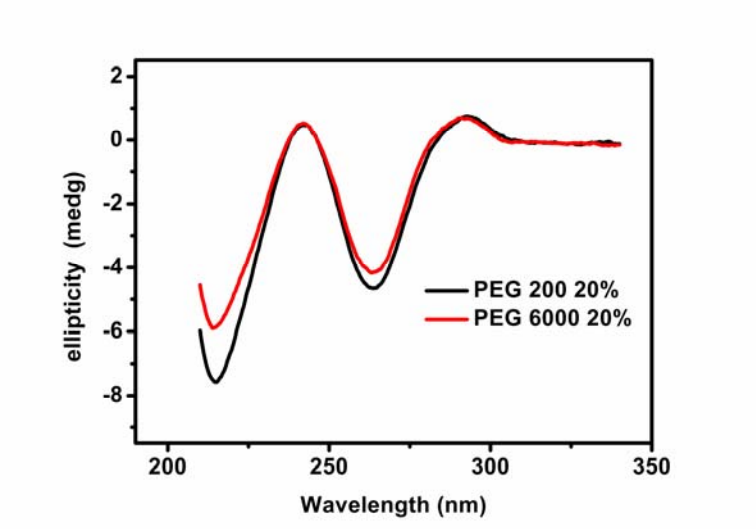

Figure S8 CD spectra of DNA 1-AgNCs synthesized in the presence of 20% PEG 200 and 6000, respectively.

Table S1 Photophysical parameters of various Ag nanoclusters prepared under noncrowding and molecular crowding conditions.

template	λ_{ex} /λ_{em} (nm)	noncrowding condition		molecular crowding condition	
		Lifetime (ns)	Φ^a (%)	Lifetime (ns)	Φ^a (%)
DNA-1	475/560	2.41±0.09	6.4[b]	2.04±0.03	66.2[b]
DNA-2	440/510	1.48±0.04	11.3[b]	1.48±0.03	38.6[b]
DNA-3	520/575	1.93±0.07	6.7[c]	2.85±0.12	34.7[c]
DNA-4	540/600	2.21±0.10	14.5[c]	2.41±0.05	32.1[c]
DNA-5	580/616	2.11±0.08	24.5[d]	2.34±0.06	67.6[d]

a: Φ represents quantum yield . *b:* relative to rhodamine 6G in water.

c: relative to rhodamine B in water. *d:* relative to cresyl violet in methanol.