

Support

DNA-Ag Cluster as the Sensor of BODIPY Isomers and HepG-2 cells

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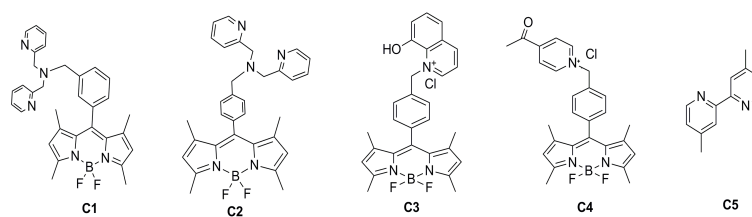
Synthesis of 8-(N-benzyl-8-hydroxyquinolinium)-4,4-difluoro-1, 3, 5, 7-tetramethyl-4-bora-3a, 4a-diaza-s-indacene (C3)

30 mL BODIPY (120 mg, 0.23 mmol) in tetrahydrofuran solution and 5 mL 8-hydroxyquinoline (100 mg, 0.70 mmol) tetrahydrofuran were mixed together in the three flask, and K₂CO₃(96 mg, 0.70 mmol) and KI (116 mg, 0.70 mmol) were added into the mixture. The result solution was stirred under N₂ for 72 h at 60 °C. After the solution was concentrated in vacuum distillation, the residues were redissolved in 20 mL DCM (dichloromethane) and washed three times with 20 mL saturated sodium bicarbonate solution. The organic phase was dried over anhydrous Na₂SO₄. The residues were purified by silica gel column chromatography (petroleum ether : ethyl acetate (2:1)) to afford to white crystal product (93.4 mg, 56.3%) (Found: C, 67.24; H, 5.27; N, 8.10. Calcd. for C₂₉H₂₇BClF₂N₃O: C, 67.27; H, 5.26; N, 8.12 %); ¹HNMR (400 MHz, CDCl₃) δ_H 9.00 (1H, m), 8.19 (1H, d), 7.68 (2H, d), 7.50 (1H, q), 7.43 (1H, m), 7.38 (1H, t), 7.30 (2H, d), 7.02 (1H, m), 5.98 (2H, s), 5.60 (2H, s), 3.54 (1H, s), 2.57 (6H, s), 1.37 (6H, s). MS(ESI) Calcd. for C₂₉H₂₇BClF₂N₃O ([C3-Cl]) =482.35, found: m/z =482.23, (100%).

Synthesis of 8-(N-benzyl-4-acetylpyridium)-4,4-difluoro-1, 3,5,7-tetramethyl-4-bora-3a, 4a-diaza- s-indacene chloride (C4)

4-Acetylpyridine (64 mg, 0.54 mmol) dichloromethane (2 mL) were added into 6 mL BODIPY (100 mg, 0.27 mmol) dichloromethane solution. This was transferred into a stainless steel autoclave with Teflon liner of 30 mL capacity, and heated in an oven at 90°C for 8 h. After the autoclave was cooled to room temperature, excess ethyl acetate was added into the solution and the black solid precipitates was obtained. After filtration, the solid was

crystallized with solvents (petroleum ether : ethyl acetate (1:1)) to afford to red crystal product (30 mg, 19.74%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ_{H} 7.72(2 H, d), 7.51 (2H, d), 6.07(2H, s), 6.18(2H, s), 1.26(5.97H, s), 2.5(6H, s), 2.44(2.95H, s), 9.15(2.02H, d), 8.86(1.93H, d). IR(KBr, v/cm^{-1}): 2919, 1303, 666 w, 1419, 1140, 511 m, 3403, 1637, 1569 s. UV-vis(MeCN/nm) ($\epsilon \times 10^{-4} / \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$): 230($\epsilon=24.6$), 270($\epsilon=9.18$), 315 ($\epsilon=6.25$), 499 ($\epsilon=32.7$). Anal. Found: C, 65.56; H, 5.15; N, 8.87; Calcd. (%) for $\text{C}_{27}\text{H}_{27}\text{BClF}_2\text{N}_3\text{O}$ (C4): C, 65.67; H, 5.51; N, 8.51. ES-MS (ESI / methanol) Calcd. for $[\text{C4}-\text{Cl}]^+=458.21$, found: $m/z=458.45(40\%)$, Calcd. for $[\text{C4}-\text{Cl}+\text{CH}_3\text{OH}]^+=490.21$, found: $m/z=490.45(100\%)$.



Scheme S1 The structure of C1, C2, C3, C4, C5.

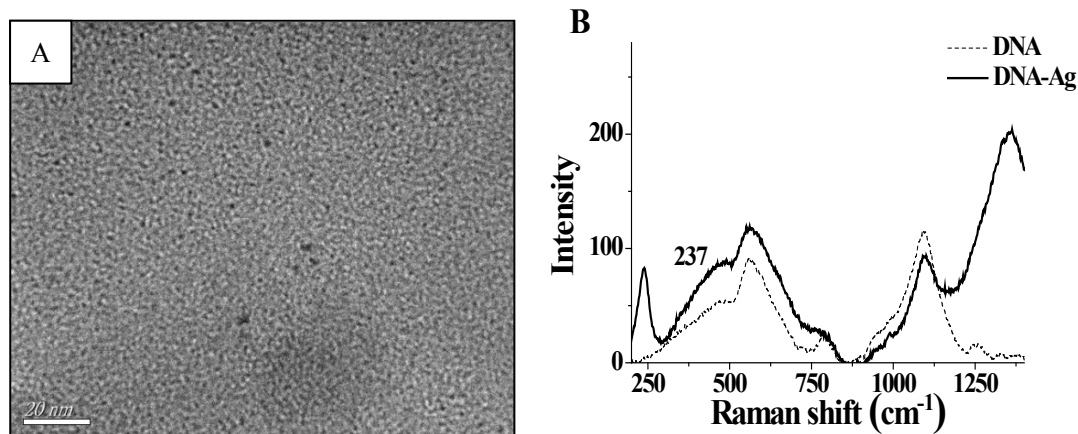


Fig. S1 (A) The TEM image of DNA-AgNCs; (B) Raman spectra of DNA (solid line) and DNA-AgNCs (dash line) with an excitation wavelength of 532 nm

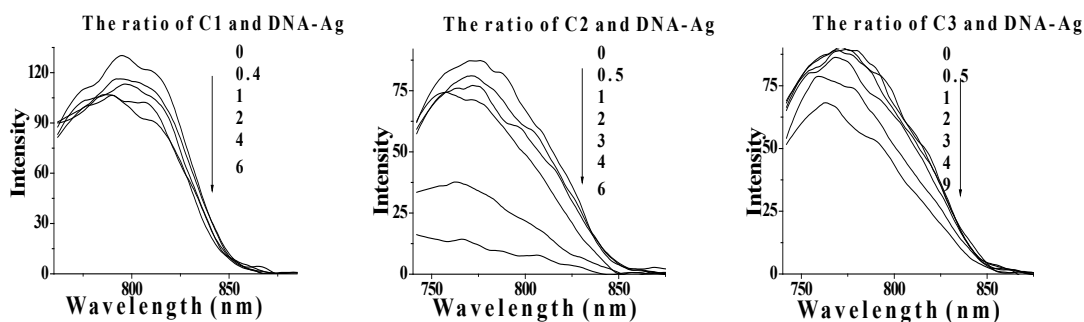


Fig. S2 The emission of 1 μ M DNA1-AgNCs in the presence of various concentration of C1, C2, C3.

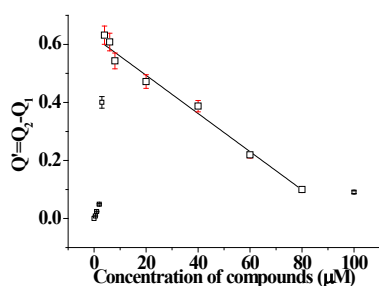


Fig. S3 Relationship of fluorescence quenching constant (Q) with varying concentration of compounds. A linear equation between the value of quenching constant difference (Q') and the concentrations (C) is $Q' = (-6.580 \pm 0.223) \times 10^{-3} C + (0.6251 \pm 0.0160)$ ($4 \sim 80 \mu\text{M}$). Q_1 is the quenching constant of C1 for DNA-AgNCs; Q_2 is the quenching constant of C2 for DNA-AgNCs; $Q' = Q_2 - Q_1$

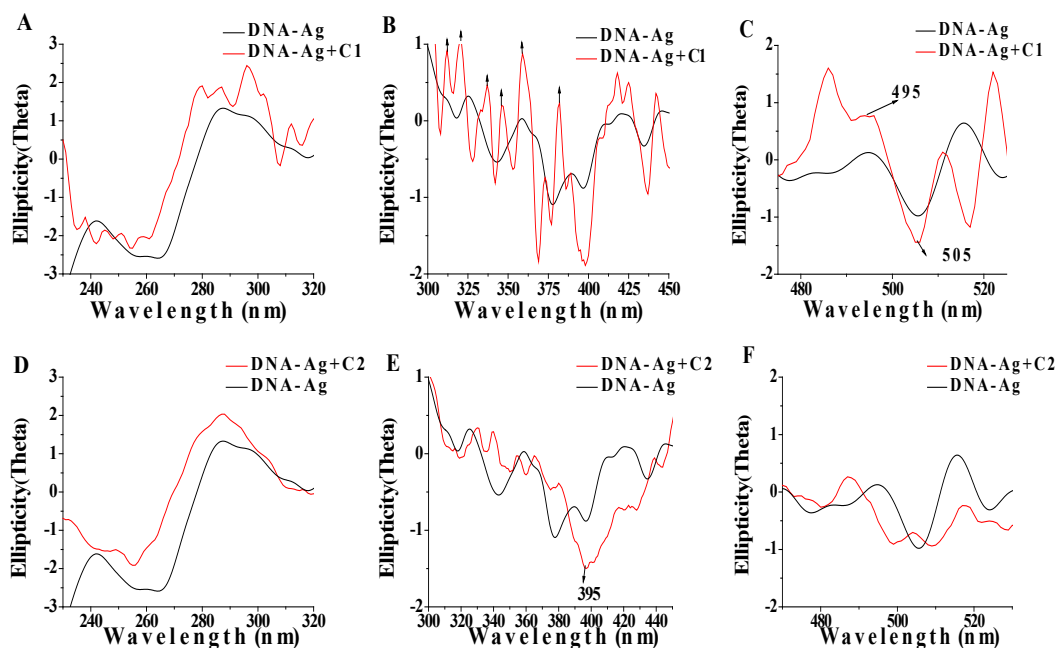


Fig. S4 CD spectra of DNA-Ag and DNA-Ag –compound (the ratio of compound and DNA1-Ag is 6: 1). (A), (B), (C) are the CD spectra of DNA-AgNCs with C1; (D), (E), (F) are the CD spectra of DNA-AgNCs with C2. (A), (D)

are at 230~320nm; (B), (E) are at 300~450nm; (C), (F) are at 475~530nm. (B), (C), (E), (F) are the ICD spectra for C1 and C2

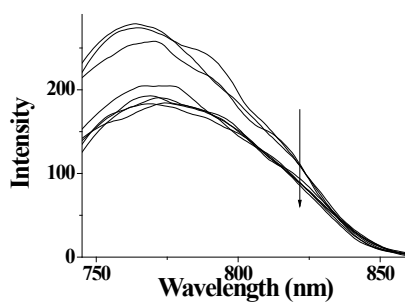


Fig. S5 Emission spectra of fluorescence 1uM DNA-AgNCs in the presence of various concentration of total protein from HepG-2 (H-Pro), the concentration of H-Pro from top: 0, 2, 6, 10, 16, 24 μ g/mL

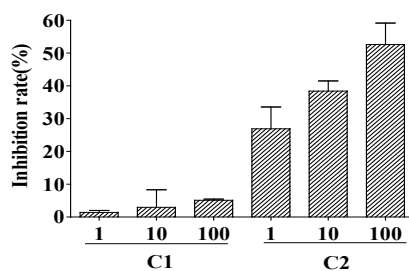


Fig. S6 Inhibition activities of C1, C2 to HepG-2 at different concentrations (1 μ M, 10 μ M and 100 μ M).