Formation Mechanism and Fluorescence Characterization of a Transient Assembly of Nanoparticles Generated by Femtosecond Laser Trapping

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Supplemental Information

1. Synthesis of asymmetrical perylene diimide dyes

The synthesis of asymmetrical perylene diimide dyes was carried out basically following the method introduced by Tröster.\(^1\) A perylene-3,4,9,10-tetracarboxylic dianhydride (I) (3g) was dissolved in a potassium hydroxide aqua solution (5% wt, 50 mL) and heated at 90 °C for 4 hr with stirring. The mixture solution was then acidulated by adding dropwisely 10% ortho-phosphoric acid until the pH value became 5.5-6.5.\(^2\) After further stirring it at 90°C, the precipitate was filtered, washed and dried to obtain perylene-3,4,9,10-tetracarboxylic acid monopotassium salt (II). To synthesize monoimide (III), the monopotassium salt (II) was added in aqueous solution with five molar ratio of n-butylamine and its solution was stirred at room temperature for 5hr and further for 2 hr at 90°C. The reacted solution was precipitated by acidizing it with hydrochloric acid, washed by water and dried to give monoimide (III). The monoimide (III) was then reacted with 5 molar ratio of (3-aminopropyl)triethoxysilane in isoquinolin at 140°C for 72 hr. This reacted mixture solution was washed by hexane to remove isoquinolin and extra amine. The remaining precipitate was finally purified by chromatography with eluent composed of dichloromethane and ethanol with the volume ratio of 10/1, which yields N-butyl-N’-propyl triethoxysilane perylenediimide (IV).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.59 (2H, d), 8.58 (2H, d), 8.48 (2H, s), 8.47 (2H, s), 4.19 (4H, q), 3.83 (6H, q), 1.88 (2H, quin), 1.76 (2H, quin), 1.48 (2H, sex), 1.23 (9H, t), 1.01 (3H, t), 0.78 (2H, t).

Figure S 1 (I) perylene-3,4,9,10-tetracarboxylic dianhydride. (II) perylene-3,4,9,10-tetracarboxylic acid monopotassium salt. (III) N-butyl-3,4,9,10-perylenetetracarboxylic monoanhydride monoimide. (IV) N-butyl-N’-propyl triethoxysilane perylenediimide.
2. Zeta potential measurement of viscosity dependence

![Zeta potential measurement](image)

Figure S 2 The Zeta potential of silica nanoparticles was not changed by adding EG into water. This indicates that the surface condition of nanoparticles is unchanged and the nanoparticles are well distributed in solution.

3. Preparation of PDI-silica nanoparticles

3 g of dried 100 nm silica nanoparticles was dispersed in 5 mL of 50 mM of PDI/chloroform solution. The solution was sonicated for 1 h and stirred in room temperature for 12 h to synthesize PDI-silica nanoparticles. PDI-silica nanoparticles were washed with chloroform for 3 times to remove unreactive PDI molecules and finally dispersed in pure water. The nanoparticle density is controlled to be $3.8 \times 10^2$ nanoparticles/μm$^3$.

The preparation of Low-PDI and High-PDI were similar to above one. Low-PDI was 3 g of dried 500 nm silica nanoparticles dispersed in 5 mL of 10 mM of PDI/chloroform solution. High-PDI was 3 g of dried 500 nm silica nanoparticles dispersed in 5 mL of 500 mM of PDI/chloroform solution. Both of the solutions were sonicated for 1 h and stirred in room temperature for 12 h to synthesize PDI-silica nanoparticles. PDI-silica nanoparticles were washed with chloroform for 3 times to remove unreactive PDI molecules and finally dispersed in pure water.

References
