

Organic Core/Diffused-Shell Nanorod: Fabrication, Characterization and Energy Transfer

Longtian Kang^{a,b}, Yu Chen^a, Debao Xiao^a, Aidong Peng^a, Fugang Shen^a, Xun Kuang^a,
Hongbing Fu^{*a} and Jiannian Yao^{*}

1. Synthesis and characterization of the Dye1 and DPNP:

The 2,5-bis(2-(N-hexadecyl pyridinium-4-yl)-vinyl)-pyrrole (C₅₀H₈₁I₂N₃, labeled Dye1) was synthesized as follows: 61.5mg(0.5mmol) 2,5 dialhyd-pyrrole and 445mg (1mmol) 4-methy-N-hexadecyl pyridine iodide were dissolved in 10ml ethanol. After adding 5 drops of hexahydro-pyridine, the reactants were refluxed for 20 hours. After filtrated, the product was thoroughly washed with ethanol and ether. The pure product was dried under vacuum and collected. Yield: 60%

¹HNMR (d, ppm, DMSO-d₆): 0.86 (t, 6H, CH₃); 1.25 (m, 52H, (CH₂)₁₃); 1.90 (t, 4H, (pyridinio-CH₂)-CH₂); 4.50 (t, 4H, pyridinio-CH₂-); 6.83 (m, 2H, pyrrole-H); 7.30 (d, 2H, CH=CH); 7.80 (d, 2H, CH=CH); 8.0 (m, 4H, pyridinio-H); 8.8 (m, 4H, pyridinio-H); 12.2 (s, 1H, pyrrole-N-H). ESI-MS : m/z = 361.9 [(M⁺-2I)²].

1,5-diphenyl-3-(naphthalene-4-yl)-1H-pyrazoline (C₂₅H₂₀N₂, DPNP) was synthesized as follows: 2.69g (10mmol) 1-(naphthalene-5-yl)-3-phenyl prop-2-en-one and 1.08g (10mmol) phenylhydrazine were refluxed in 25ml acetic acid for 5 hours. After the crude product was filtrated and recrystallized from benzene/MeOH, we can get pure product 1.4g. Yield: 40%

¹HNMR (d, ppm, CDCl₃): 3.29(m, 1H, J= 6.9Hz); 3.69(m, 1H, J= 12.8); 5.33(d, 1H, J= 7.32Hz); 6.80(t, 1H, J= 7Hz); 6.97(d, 2H, J= 8.4Hz); 7.00-7.50(m, 9H); 7.80(t, 1H, J= 8.6Hz); 7.84(d, 1H, J= 8.52Hz); 7.92(d, 1H, J= 8.60Hz); 8.14(d, 1H, J= 8.8Hz); 8.17(d, 1H, J= 8.8Hz); EI-MS (LC-MS 1020): m/z = 348.2

2. Experiment detail

The DPNP and Dye1 were synthesized and confirmed by 400MHz ¹H-NMR (Bruker ARX400 spectrometer) and ESI-MS (LC-MS 1020). During the preparation of DPNP-Dye1 core-shell nanostructure, firstly 100ul DPNP/acetonitrile (99.99%) solution (10⁻³M) was rapidly injected into 4 ml ultrapure water (18.2MΩ, produced by Milli-Q apparatus, Millipore) at room temperature with vigorous stirring. After 2 hours, 100ul Dye1/ethonal solution (5*10⁻⁴M) was quickly added into the above solution then aged 3 hours. Then a drop of solution was dropped on a carbon-coated copper grid to prepare sample of TEM (Hitach HF2000) and observed core-shell nanostructure. TEM-assisted EDS line analysis was measured with the help of high-resolution TEM (HRTEM, Philips Tecnsi, F30). Finally, the solution was filtrated with alumina membrane with average porous size of 100nm and radius of 13mm (Whatman International Ltd.). After drying alumina membrane at room temperature, steady-state fluorescence spectra were measured by steady-state fluorescent spectroscopy (Hitachi F-4500), then morphologies and sizes of core/shell nanostructure were examined by field emission SEM (FESEM, Hitach, S-4300). The surface electric ξ-potentials were measured by dynamic light scattering (DLS, BI-90plus, Brookhaven Instruments Corp., Holtsville, NY) using the ZetaPALS (Phase analysis light scattering) technique at room temperature (25°C). The fluorescence lifetime was analyzed by England Edinburge Analytical Instruments FLS-920.

3. The fluorescence decay lifetime of different samples in water at room temperature.

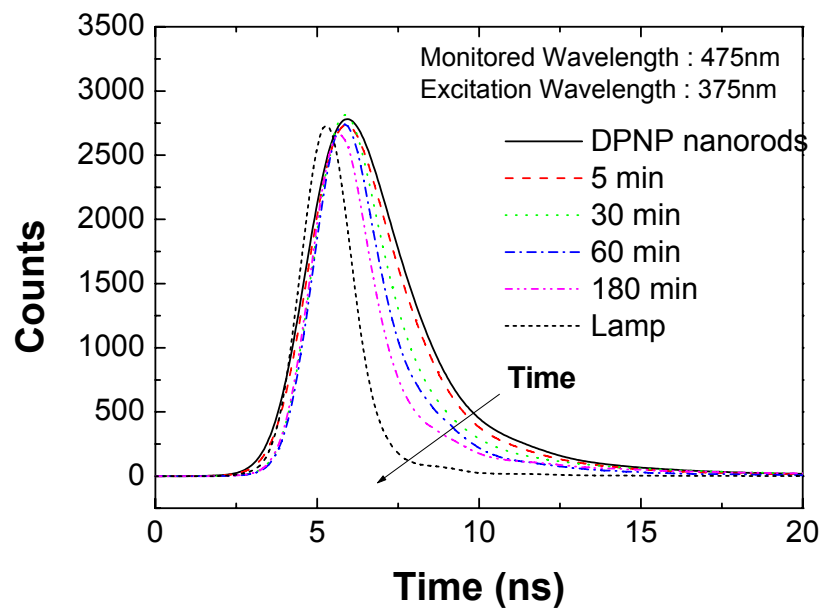


Figure S1. Fluorescence decay profiles of the aqueous dispersed system of DPNP nanorod and core/shell nanorods at different aging intervals. The nanodispersed system was monitored at 475 nm and the excitation wavelength was 375 nm. The measurements were carried out at the room temperature on a Horiba NAES-1100 PC time-resolved spectrometer by using time-correlated single-photon counting method.

4. The UV-vis spectrum of DPNP/acetonitrile dilute solution

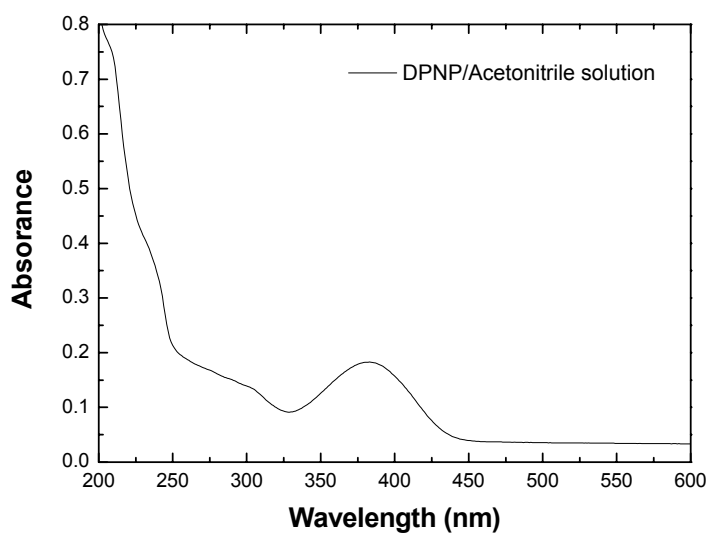


Figure S2 The UV-vis spectrum of DPNP in acetonitrile (10^{-5} M)