**Supporting Information**

# Irradiation Induced Fluorescence Enhancement in PEGylated Cyanine-Based NIR Nano- and Mesoscale GUMBOS

Chengfei Lu, Susmita Das, Paul K. S. Magut, Min Li, Bilal El-Zahab, Isiah M. Warner*

Department of Chemistry, Baton Rouge, Louisiana 70803, Louisiana State University, United States

Email: iwarner@lsu.edu, Telephone: 225-578-2829

**Characterization of [IR786AA][I]**

$^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were acquired by use of a Bruker Avance 400 NMR spectrometer. The $^{1}$H and $^{13}$C chemical shifts are given in parts per million (δ) with TMS as an internal standard.

Triethylamine (198 μL, 1.42 mmol) and 6-aminohexanoic acid (126 mg, 1.42 mmol) were added to a solution of [IR786][I] (0.283 mmol) in anhydrous DMF (10 mL) under nitrogen atmosphere. The green solution was stirred for 3 hours at 85°C and it turned blue. Flash chromatography (AcOEt/MeOH 70/30 to 0/100) was used to obtain a pure blue product-[IR786AA][I].

[IR786AA][I] characterization: $^{1}$HNMR ($CDCl_3$): δ (ppm) 10.0 (1H), 8.02 (s, 2H), 7.37 (s, 2H), 7.05 (t, 2H), 6.87 (d, 4H), 5.60 (m, 2H), 3.84 (t, 3H), 3.28 (s, 3H), 2.96 (s, 4H), 2.49 (t, 2H), 1.99 (t, 1H), 1.69 (m, 8H), 1.44 (m, 4H), 1.38 (s, 6H), 1.26 (m, 2H); $^{13}$C NMR($CDCl_3$): 137.92, 128.07, 122.58, 122.05, 120.43, 49.71, 33.81, 30.71, 29.02, 26.01, 25.32,24.25,21.51; ESI-MS: Calculated *m/z* =578.80 , Found *m/z* =578.38

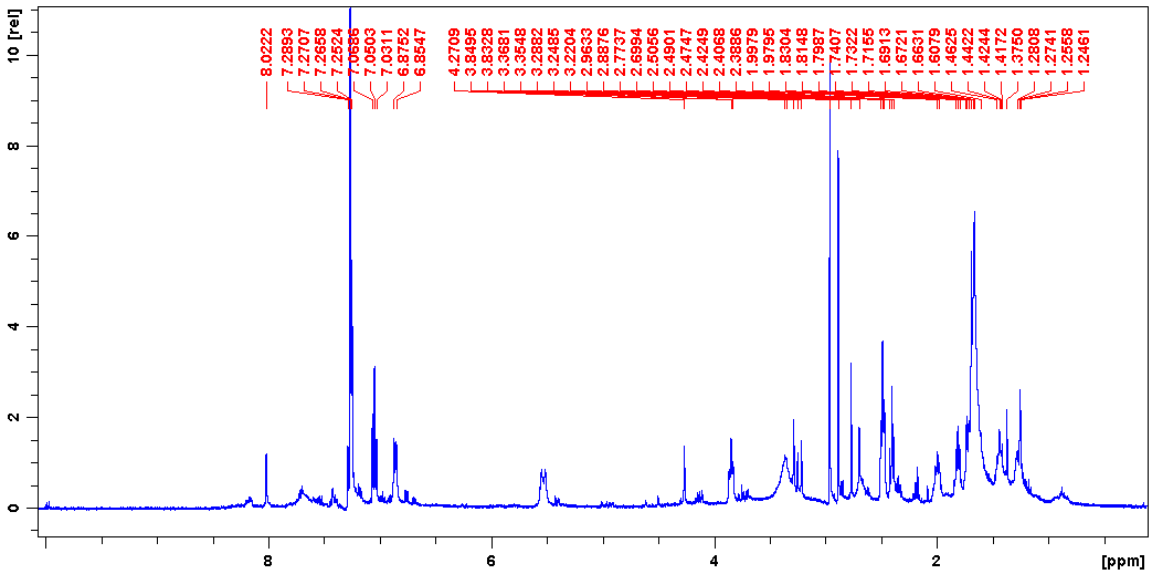



**Figure S1.** $^{1}$HNMR of [IR786AA][I]

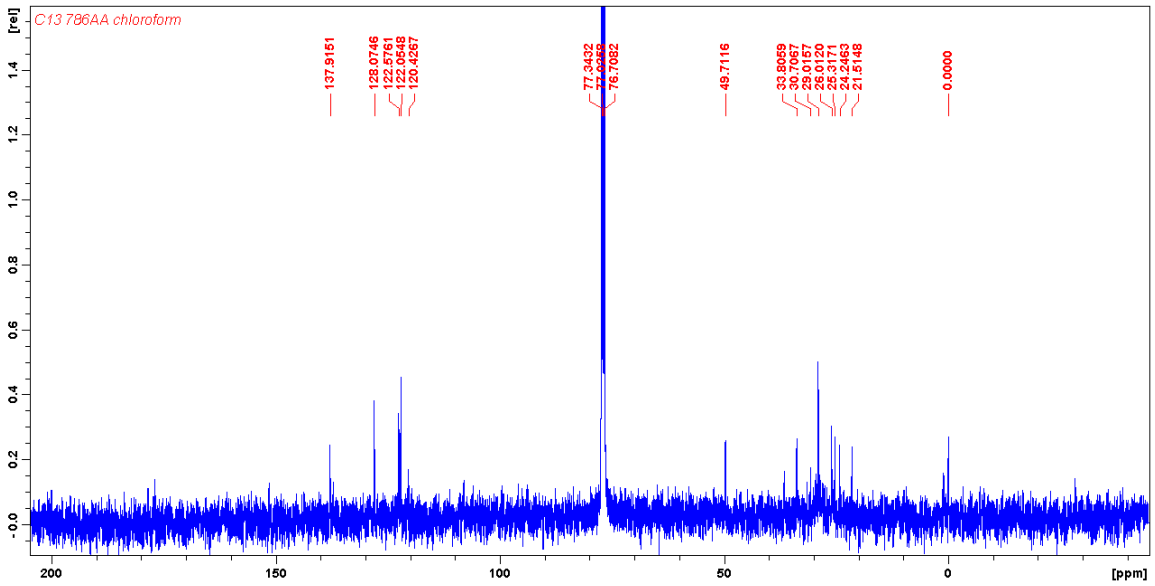



**Figure S2.** $^{13}$CNMR of [IR786AA][I]

## Characterization of PEGylated dye GUMBOS

[PEG786][I] characterization: $^{1}$HNMR ($CDCl_3$): δ (ppm) 8.12 (d, 1H), 7.65 (d, 1H), 7.22 (m, 2H), 7.16(m, 1H), 6.98 (d, 2H), 6.88 (t, 1H), 6.79 (d, 1H), 6.67(d, 1H), 5.37(t, 2H), 3.78 (m, 2H), 3.68 (m, 2H), 3.68 (s, 3H), 3.62 (m, 44H), 3.52 (s, 3H), 3.35 (s, 3H), 3.26 (m, 3H), 2.47(t, 4H), 2.35 (t, 2H), 2.14 (s, 1H), 1.67 (m, 10H), 1.27 (m, 10H). $^{13}$CNMR ($CDCl_3$): δ (ppm) 171.56, 144.62 , 139.61, 136.40, 132.69, 127.92, 127.61, 126.88, 122.09, 121.96, 121.69, 120.46, 106.39, 107.45, 72.60,71.93, 70.56, 70.29, 61.66, 58.98, 50.98, 49.95, 49.71, 46.41, 35.86, 34.33, 32.44 , 29.76, 29.25, 28.77, 26.25, 26.15, 25.86, 25.41, 25.02, 24.62, 24.32; ESI-MS: Found *m/z* =784.56

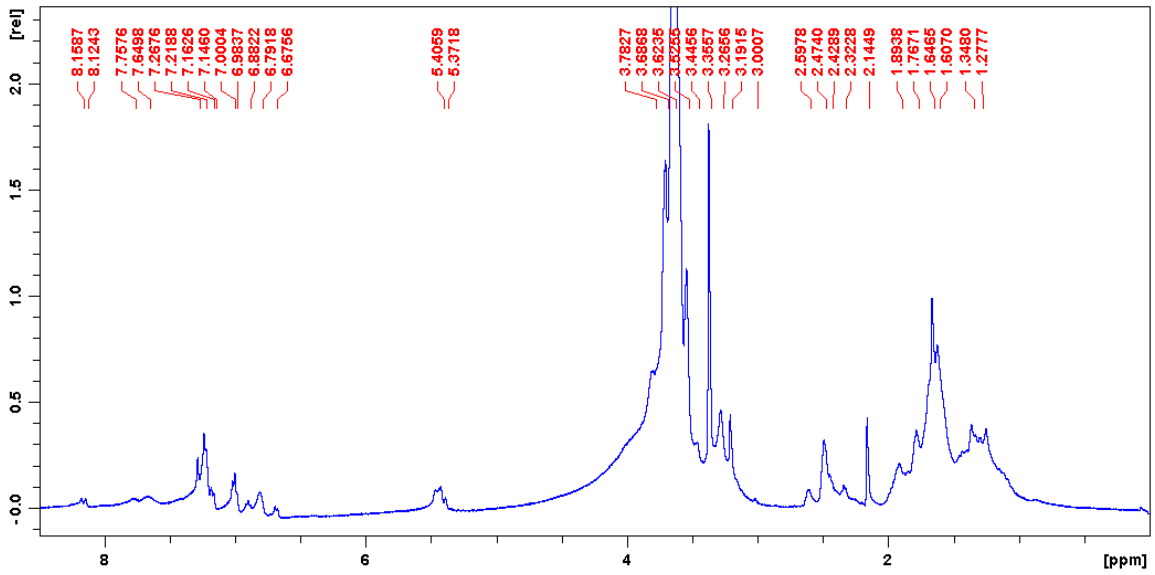



**Figure S3.** $^{1}$HNMR of [PEG786][I]

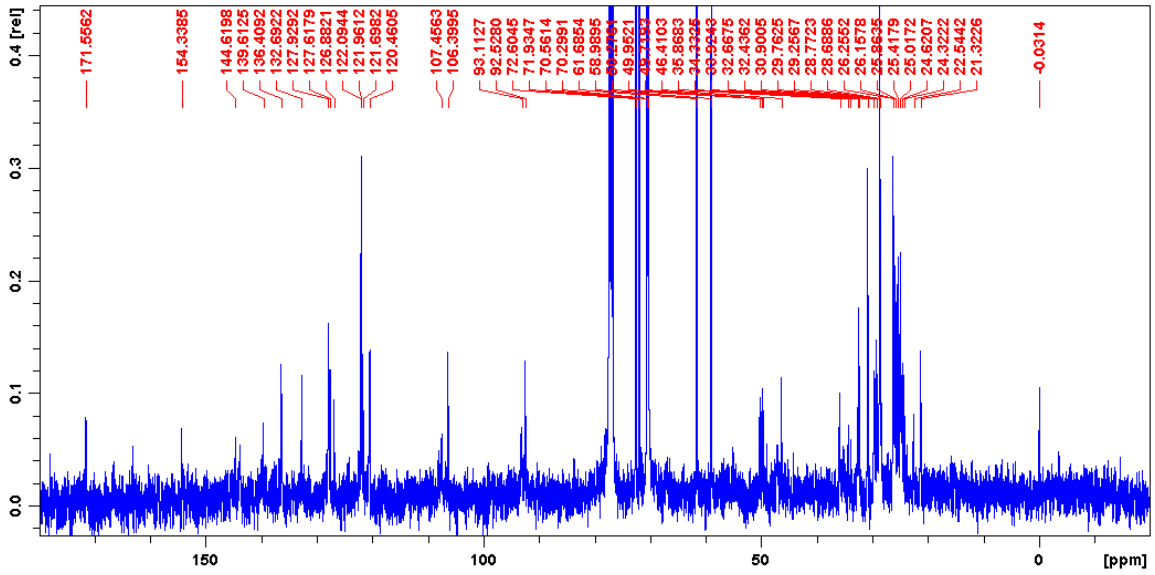
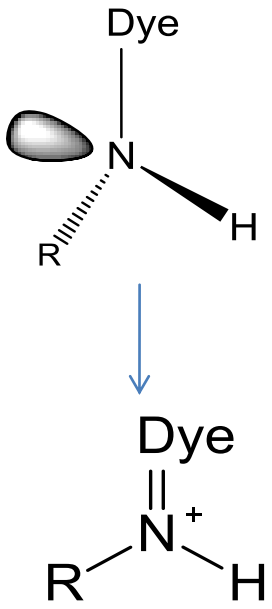



**Figure S4.** $^{13}$CNMR of [PEG786][I]




**Scheme S1.** Transformation of pyramidal geometry to planar configuration

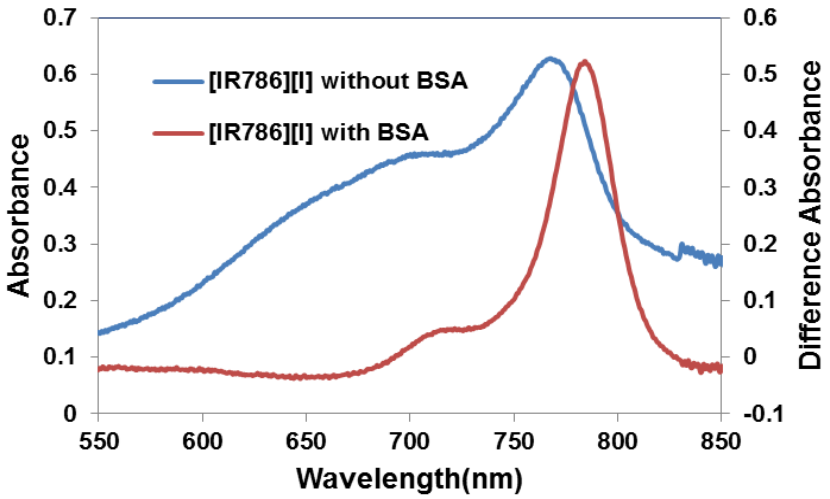



**Figure S5.** Spectrum of 20μM of [IR786][I] in 0.1 M PBS pH 7.0 (blue) and different spectrum for [IR786][I] binding to BSA in the same buffer (red). The BSA concentration in the sample cuvette was 0.5 mg/mL and the dye concentration in both the sample and reference cuvettes was 20μM

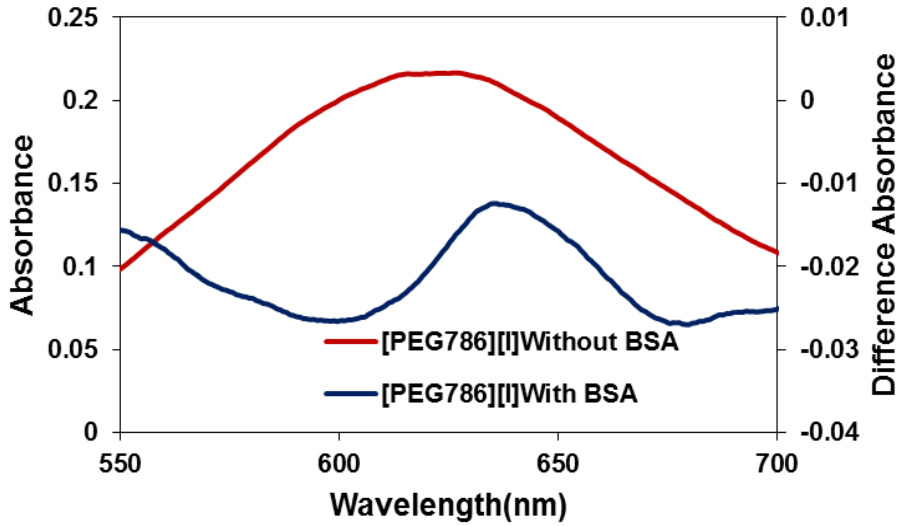



**Figure S6.** Spectrum of 20µM of [PEG786][I] in 0.1 M PBS pH 7.0 (blue) and difference spectrum for [PEG786][I] binding to BSA in the same buffer (red). The BSA concentration in the sample cuvettes was 0.5 mg/mL and the dye concentration in both the sample and reference cuvettes was 20µM