

## *Supporting Information for*

# Electronic Resonant Stimulated Raman Scattering Micro-Spectroscopy

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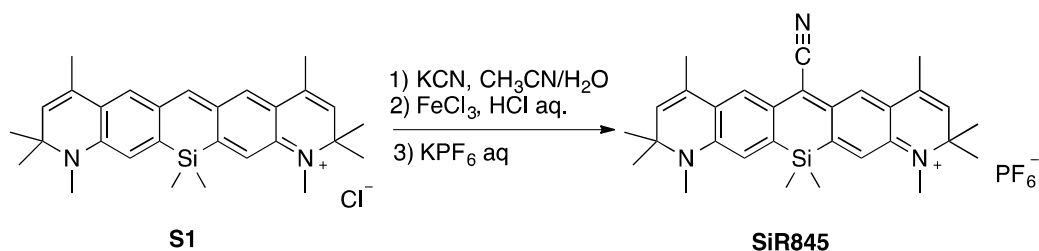
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## **S1. Synthesis of SiR845**

**General Methods.** Reagents and solvents were purchased from Sigma-Aldrich at the highest commercial quality and used without further purification, unless otherwise stated. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on glass backed silica gel TLC plates (250  $\mu\text{m}$ ) from Silicycle; visualization by UV light, an ethanolic solution of phosphomolybdic acid as staining agent. NMR spectra were recorded on either a Brüker Advance 400 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz). Brüker Advance 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz). High resolution mass spectrometric (HRMS) data were obtained using JMS-HX110A mass spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

### **Synthesis of SiR845:**

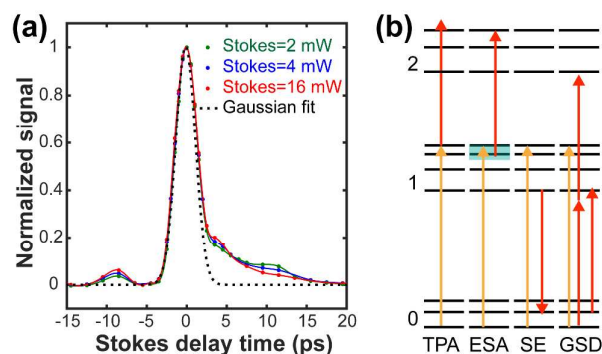


Synthesis of **S1** follows the same procedures as reported in *J. Am. Chem. Soc.* 2012, 134, 5029-5031. To a solution of **S1** (6.0 mg, 12.6  $\mu\text{mol}$ ) in 5 mL acetonitrile and 1 mL water was added KCN solution in  $\text{H}_2\text{O}$  (0.1 M, 250  $\mu\text{L}$ , 25  $\mu\text{mol}$ ). The solution was stirred for 30 min before  $\text{FeCl}_3$  solution in  $\text{HCl}/\text{H}_2\text{O}$  (0.5 M in 1 N HCl, 100  $\mu\text{L}$ , 50  $\mu\text{mol}$ ) was added. The solution was stirred for another 1 h before 2 mL 5%  $\text{KPF}_6$  aq. solution was added. Then the system was extracted with  $3 \times 3$  mL DCM. The organic layers were combined, dried over  $\text{Na}_2\text{SO}_4$  before the solvent was removed *in vacuo*. The product was purified via neutral aluminum oxide flash chromatography (DCM to DCM/MeOH = 9/1) to yield pure **SiR845** (1.3 mg, 2.14  $\mu\text{mol}$ , 17%).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  ppm: 7.75 (s, 2H), 7.28 (s, 2H), 5.77 (d,  $J = 1.4$  Hz, 2H), 3.40 (s, 6H), 2.09 (d,  $J = 1.4$  Hz, 6H), 1.57 (s, 12H), 0.57 (s, 6H)

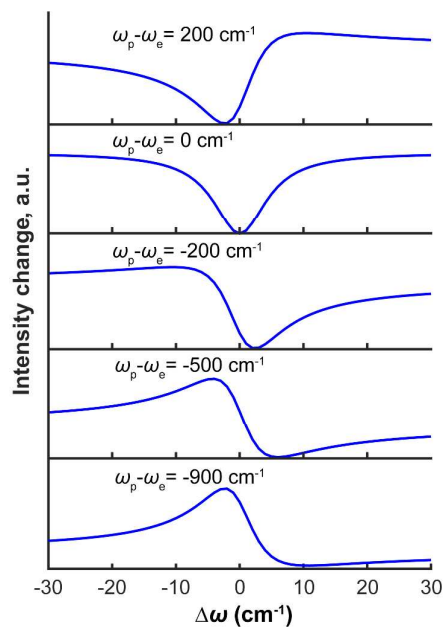
HRMS (ESI+)  $m/z$  Calcd. for  $\text{C}_{30}\text{H}_{36}\text{N}_3\text{Si}^+ [\text{M}]^+$ : 466.2679. Found: 466.2682

## Supporting Figure S1



**Figure S1. Electronic background is from competing pump-probe processes.** (a) Unsymmetrical time delay dependence of the background under different power combinations. Pump was fixed at 4 mW. (b) Energy diagram of possible pump-probe processes.

## Supporting Figure S2



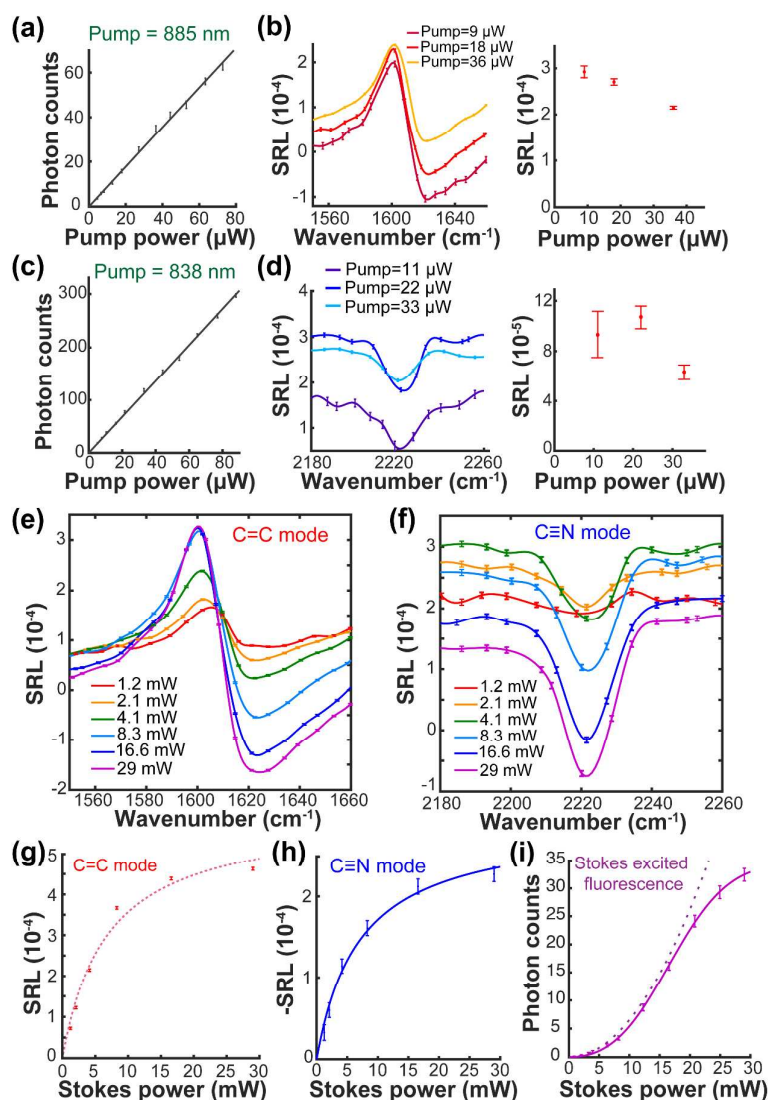
**Figure S2. Simulations of er-SRS band shapes using eq 1.**  $\Delta\omega = \omega_R - (\omega_p - \omega_e)$ .

$\Gamma_e = 430$  cm<sup>-1</sup>,  $\Gamma_R = 5$  cm<sup>-1</sup> and excitation condition  $(\omega_p - \omega_e)$  was indicated inside figure.

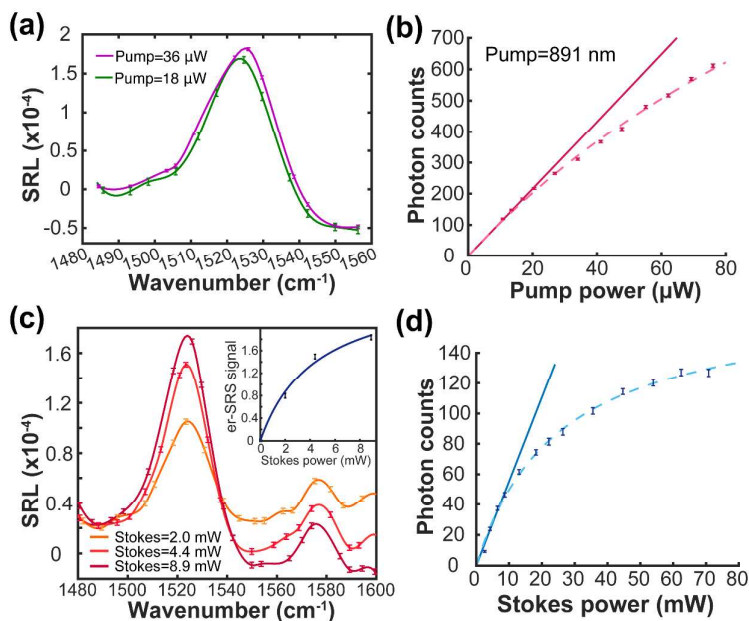
## Supporting Figure S3-S5

Study of power dependence and saturation effect:

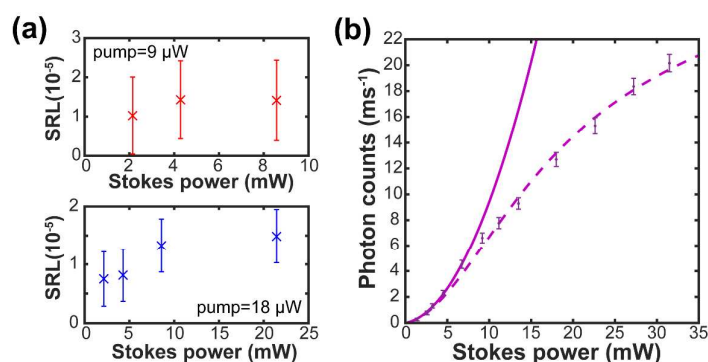
**Figure S3-S5** illustrate the power dependence and saturation effect on SiR845, IR820 and IR895, respectively. Taking SiR845 as an example (**Figure S3**). Firstly, for pump power dependence, pump-beam excited fluorescence was first measured to confirm no nonlinear absorption happened for the pump beam. As a result, **Figure S3a** and **Figure S3c** present good linear correlation at pump wavelength either for C=C mode ( $1609\text{ cm}^{-1}$ ) or C $\equiv$ N modes using laser power below  $100\ \mu\text{W}$ . For er-SRS signal, during this pump power region ( $P_{\text{pump}} < 100\ \mu\text{W}$ ), it presents relatively earlier saturation effect starting at  $P_{\text{pump}} \approx 20\ \mu\text{W}$  under relative low Stokes power ( $P_{\text{Stokes}} \approx 4\ \text{mW}$ ) (**Figures S3b** and **Figure S3d**). er-SRS signals were all calculated as the subtraction of ‘Raman resonance on’ and ‘Raman resonance off’ (by tuning the pump wavelength 2-3 nm away from the Raman peak position). Secondly, Stokes power dependence was then determined at 20-30  $\mu\text{W}$  pump power. For Stokes power dependence, er-SRS first presents linear power dependence then starts to saturate after  $P_{\text{Stokes}} > 5\ \text{mW}$  (**Figure S3e-h**). In addition, Stokes-beam excited fluorescence was also measured which is mainly from two-photon excitation for SiR845 and presents similar saturation trend as er-SRS (**Figure S3i**). This indicates the existence of ground-state depletion effect caused by competed Stokes one-photon and two-photon absorption. This result explains the Stokes power saturation of er-SRS. Similar saturation effects on either pump or Stokes beams were observed for IR820 (**Figure S4**) and IR895 (**Figure S5**).



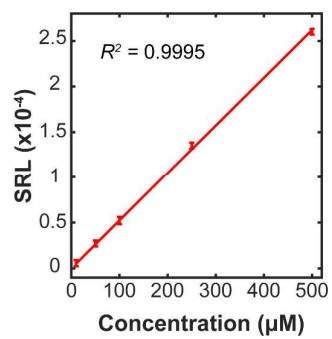
**Figure S3. Power dependence study for SiR845.** (a-b) SiR845 C=C mode ( $1609\text{ cm}^{-1}$ ) pump power dependence of (a) pump-excited fluorescence (pump set at 885 nm) and (b) er-SRS ( $P_{\text{Stokes}}=4.1\text{ mW}$ ). (c-d) C≡N mode pump power dependence of (c) pump-excited fluorescence (pump set at 838 nm) and (d) er-SRS ( $P_{\text{Stokes}}=4.1\text{ mW}$ ). (e) er-SRS spectra of a C=C mode under different Stokes powers. (f) er-SRS spectra of C≡N mode under different Stokes powers. (g) Stokes power dependence of the C=C mode plotted from measurements in (e). Curve was fitted by a two-level one-photon excitation model. (h) Stokes power dependence of the C≡N mode plotted from measurements in (f). Curve was fitted by a two-level one-photon excitation model. (i) Power dependence curve for Stokes-excited fluorescence presents similar saturation trend as er-SRS process shown in (g-h). Solid line is the fitting of all data points with a two-level two-photon excitation model; dot line is the fitting of low power data (first 5 data points) with the quadratic correlation.



**Figure S4. Pump and Stokes power dependence of C=C mode ( $1526 \text{ cm}^{-1}$ ) of IR820.** (a) er-SRS spectrum under low pump power shows no saturation effect as the SRL are almost the same for two pump power conditions. (b) Liner power dependence for pump-excited fluorescence (pump set at 891 nm) shows no nonlinear absorption happened for pump beam with  $P_{\text{pump}} < 20 \text{ } \mu\text{W}$ . (c) Stokes power saturation effect on er-SRS signal.  $P_{\text{pump}} = 18 \text{ } \mu\text{W}$ . (d) Stokes-excited fluorescence also presents saturation trend indicates the existence of ground-state depletion caused by Stokes one-photon absorption. In (b) and (d), solid lines are the fittings of low power data (first 4 data points) with the linear correlation; dashed lines are the fittings of all data points with a two-level one-photon excitation model.



**Figure S5. Pump and Stokes power dependence of C=C mode ( $1576 \text{ cm}^{-1}$ ) of IR895.** (a) current pump and Stokes power already saturate the er-SRS. Lower laser power is prevented by the laser noise and low solubility of IR895. (b) Quadratic power dependence for Stokes-excited fluorescence shows saturation trend after  $P_{\text{Stokes}} > 7 \text{ mW}$ . Solid line is the fitting of low power data (first 5 data points) with the quadratic correlation; dashed line is the fitting of all data points with a two-level two-photon excitation model.



**Figure S6. Concentration curve of IR820 solution.** Linear concentration curve for  $1526\text{ cm}^{-1}$  peak of IR820. The detection limit is  $5\ \mu\text{M}$  for  $\text{SNR}=1$  under 1-ms time constant. Pump power is about  $25\ \mu\text{W}$  and Stokes power is 50 mW.