Analyzing Structure-Photophysical Property Relationships for Isolated T₈, T₁₀ and T₁₂ Stilbenevinyl Silsesquioxanes

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Supporting Information



Figure S1. Solvent study and MALDI-ToF analysis of separating mixed stilbenevinylSQ.



Figure S2. ²⁹Si NMR of T₁₀ stilbenevinylSQ in CDCl₃.



Figure S3. ²⁹Si NMR of T_{12} stilbenevinylSQ in CDCl₃.



Figure S4. Absorption, emission (335 nm) and excitation spectrum (380 nm) of *p*-triethoxysilylvinylstilbene in THF.



Figure S5. Absorption, emission (335 nm) and excitation spectrum (380 nm) of *p*-triethoxysilylvinylstilbene in THF.



Figure S6a. Emission/excitation wavelength of $T_{10/12}$ and **b**. T_{12} stilbenevinyISQ in THF.



Figure S7. Emission/excitation wavelength comparison of T₈ stilbenevinylSQ in THF.



Figure S8. Absorption, excitation and emission spectra of 10^{-7} M *p*-vinylstilbene in THF.



Figure S9. Absorption, excitation and emission spectra of *p*-vinylstilbene in solid-state film.



Figure S10a. Absorption spectra of stilbenevinylSQs w/film.



Figure S10b. Emission spectra of stilbenevinylSQs w/film.





Figure S11. Log-Log plot for TPA cross-sections at 740 nm (SI).

Figure S12. MATLAB modeling of T₁₂ stilbenevinylSQ showing fits with and without rise time inclusion.



Figure S13. MATLAB modeling of T₁₀ stilbenevinylSQ showing fits with and without rise time inclusion.



Figure S14. MATLAB modeling of $T_{10/12}$ stilbenevinylSQ showing fits with and without rise time inclusion.



Figure S15. MATLAB modeling of $T_{10/12}$ stilbenevinylSQ showing fits with and without rise time inclusion.



Figure S16. Fluorescence decay of T_{10/12} (H) at 400 nm excitation, and 450 nm collection.
Table S1. Fluorescence lifetimes of the stilbenevinyl based SQ systems using fluorescence upconversion spectroscopy from excitation at 400 nm and collection at 450 nm.



Figure S17. GPC comparison of separated T_{10} and T_{12} stilbenevinylSQs with M_{ns} and PDI's of 3367, 1.02 and 3758, 1.03 respectively.

29

30

Time (min)

31

33

32

0.0

27

28







Figure S20. ¹H NMR of T₁₂ stilbenevinylSQ in CDCl₃.



Figure S21. ¹³C NMR of T₁₂ stilbenevinylSQ in CDCl₃.



Figure S22. FTIR comparison of separated T_{10} and T_{12} stilbenevinylSQs.



Figure S23. Excitation spectrum of $T_{10/12}$ stilbenevinylSQ.



Scheme S1. Synthesis of triethoxysilylvinylstilbene by metathesis/Heck cross-coupling reactions.

Synthesis of triethoxysilylvinylstilbene: To a dry 25 mL Schlenk flask under N₂ was added 2.00 mL (0.0094 mol) of vinyltriethoxysilane and 10.0 mg (0.012 mmol) of first generation Grubbs catalyst. Dry CH₂Cl₂ (30 mL) was added by syringe followed by 1.23 mL (0.0094 mol) 4-bromostyrene. The mixture was stirred at 40 °C for 72 h. The reaction was then filtered through 2 cm of Celite, and solvent removed under high vacuum. The resulting oil was then vacuum distilled for purification. The final product yield was 1.58 g (49 %). The resulting oil (1.58 g, (0.0046 mol) was then added to a dry 25 mL Schlenk flask under N₂, 82 mg (0.184 mmol) of Pd[P(t-Bu)₃]₂, and 83 mg (0.092 mmol) of Pd₂(dba)₃. Dry 1,4-dioxane (15 mL) was added by syringe, followed by NCy₂Me (1.07 mL, 0.00506 mol) and 618 µL (0.0054 mol) of styrene. The resulting solution was allowed to stir at room temperature for 24 h. The reaction mixture was filtered through 2 cm Celite to remove ammonium bromide precipitate. Methylene chloride (50 mL) was then added to the filtered product, and washed 3x with deionized water. The organic layer was then dried over Na₂SO₄ and filtered. Solvent was then removed in-vacuo, and the product was redissolved in toluene and N-acetyl-L-cysteine was added to comple the remaining catalyst. The mixture was then filtered again through a 2 cm Celite to remove any remaining Pd particles and then partially precipitated to remove impurities. The solution was then filtered and concentrated to yield the final product (724 mg). See characterization below in Figures S22-S25.





Figure S23. ¹³C NMR of *p*-triethoxysilylvinylstilbene in CDCl₃.



Figure S24. FTIR of *p*-triethoxysilylvinylstilbene.



Figure S25. GPC of *p*-triethoxysilylvinylstilbene, Mn: 711, Mw: 753, PDI: 1.06 . <u>FRET Calculations</u>⁶⁵⁻⁶⁸

Förster radius determination:

k = dipole orientation in radians, n = refractive index of solvent, Q_D = fluorescence quantum yield, J is the overlap integral between absorption and emission.



$$= 9.9 \text{ Å T}_{10/12}$$

Calculations of theoretical Rise Times:

$$\tau_{hop} = \tau_{ET} = T_D \left[\frac{R_0}{r}\right]^6$$

Where τ_{hop} is the expected rise time, T_D is the lifetime of the free donor system, R_0 is the FRET radius and r is the distance between chromophores.

Table S2. Approximate distances for (r) in Å and hopping time estimate based on (r) value

		U			
	Distance		Chrom-		
	between		ophore	(r) Å used	
	first	Phenyl	Centroid	in $ au_{hop}$	$\tau_{\rm hop}(fs)$
	carbons	Centroid	Distances	calculation	
Т8	5.2	6.6	16	9.5	720
T10	5.1	6.4	14	8.2	880
T12	4.9	5.9	12	7.3	1080

given.28