Unconventional conjugation via vinylMeSi(O-)<sub>2</sub> siloxane bridges may imbue semiconducting properties in [vinyl(Me)SiO(PhSiO<sub>1.5</sub>)<sub>8</sub>OSi(Me)vinyl-Ar] double-decker (DD) copolymers.

J. Guan,<sup>1</sup> J. J. R. Arias,<sup>1,2</sup> K. Tomobe,<sup>3</sup> R. Ansari,<sup>4</sup> M. de F. V. Marques,<sup>2</sup> A. Rebane,<sup>5</sup> S. Mahbub,<sup>6</sup> J. C. Furgal,<sup>6</sup> N. Yodsin,<sup>7</sup> S. Jungsuttiwong,<sup>7</sup> D. Hashemi,<sup>1</sup> J. Kieffer,<sup>1</sup> R. M. Laine<sup>\*1,8</sup>

Dept of Materials Science and Engineering, University of Michigan;<sup>1</sup> Instituto de Macromoléculas Professora Eloisa Mano, Federal University of Rio De Janeiro;<sup>2</sup> Dept of Chemistry,<sup>3</sup> Chemical Engineering, University of Michigan,<sup>4</sup> Dept of Physics, Montana State University, and National Institute of Chemical Physics and Biophysics, Tallinn 12618, Estonia;<sup>5</sup> Dept. of Chemistry and Center for Photochemical Sciences, Bowling Green State University;<sup>6</sup> Dept of Chemistry and Center of Excellence for Innovation in Chemistry, Ubon Ratchathani University;<sup>7</sup> and Macromolecular Science and Engineering, University of Michigan,<sup>8</sup> Ann Arbor, MI 48109-2136 talsdad@umich.edu

Compound	<sup>1</sup> H-NMR peaks (ppm)				
	7.39 (d, 4H, Ph); 7.17 (d, 2H, vinyl); 6.31 (d, 2H, vinyl);				
1,4-[(MeO) <sub>2</sub> Sivinyi] <sub>2</sub> benzene	3.62 (s, 12H, MeO); 0.30 (s, 6H, Me)				
4 4' [(Mac) Sining I high and	7.64 (d, 4H, Ph); 7.41 (d, 4H, Ph); 7.09 (d, 2H, vinyl); 6.22				
4,4 -[(MeO)2Sivinyi]2biphenyi	(d, 2H, vinyl); 3.60 (s, 12H, MeO); 0.27 (s, 6H, Me)				
	7.69 (d, 4H, Ph); 7.63 (d, 4H, Ph); 7.57 (d, 4H, Ph); 7.16				
4,4"-[(MeO) <sub>2</sub> Sivinyl] <sub>2</sub> terphenyl	(d, 2H, vinyl); 6.33 (d, 2H, vinyl); 3.60 (s, 12H, MeO); 0.30				
	(s, 6H, Me)				
4.4' [(MaQ)aSiviny]astilbong	7.52 (d, 4H, Ph); 7.44 (d, 4H, Ph); 7.20 (m, 4H, vinyl); 6.33				
4,4 -[(WeO)23WIIYI]2Stilberie	(d, 2H, vinyl); 3.62 (s, 12H, MeO); 0.33 (s, 6H, Me)				
2.5. [(MaQ)-SivinvII-thionhona	7.22 (d, 2H, thiophene); 7.21 (d, 2H, vinyl); 6.40 (d, 2H,				
2,3-[(MeO)23Minyi]2tillophene	vinyl); 3.70 (s, 12H, MeO); 0.30 (s, 6H, Me)				
	7.61 (m, 2H, thiophene); 7.22 (m, 2H, thiophene); 7.11 (d,				
5,5'-[(MeO)2Sivinyl]2bithiophene	2H, vinyl); 6.23 (d, 2H, vinyl); 3.61 (s, 12H, MeO); 0.29 (s,				
	6H, Me)				
2,5-	7.49 (s, 2H, thiophene); 7.21 (d, 2H, vinyl); 6.41 (d, 2H,				
[(MeO) <sub>2</sub> Sivinyl] <sub>2</sub> thienothiophene	vinyl); 3.70 (s, 12H, MeO); 0.30 (s, 6H, Me)				
2.7	7.98 (m, 2H, fluorene); 7.74 (m, 2H, fluorene); 7.52 (m,				
Z, I -	2H, fluorene); 7.23 (d, 2H, vinyl); 6.30 (d, 2H, vinyl); 3.63				
	(s, 12H, MeO); 1.78 (s, 6H, Me); 0.32 (s, 6H, Me)				
	7.68 (m, 2H, BTH); 7.26 (d, 2H, vinyl); 7.08 (d, 2H, vinyl);				
4,7-[(NeO)2SIVIIIyI]2BTH	3.62 (s, 12H, MeO); 0.34 (s, 6H, Me)				
	11.7 (s, 1H, carbazole); 8.41 (s, 2H, carbazole); 7.59 (m,				
3,6-[(MeO) <sub>2</sub> Sivinyl] <sub>2</sub> carbazole	4H, carbazole); 7.40 (m, 2H, vinyl); 6.38 (d, 2H, vinyl);				
	3.63 (s, 12H, MeO); 0.32 (s, 6H, Me)				

 Table S1. <sup>1</sup>H-NMR peaks of model silane compounds.







**Figure S2.** GPC of 3,6-[(MeO)<sub>2</sub>Sivinyl]<sub>2</sub>carbazole, 3,6-dibromocarbazole and vinylMeSi(OMe)<sub>2</sub>.



Figure S3. FTIR of 5,5'-[(MeO)<sub>2</sub>Sivinyl]<sub>2</sub>bithiophene and vinylMeSi(OMe)<sub>2</sub>.

Compound	ν	Wavenumber	Intensity
		(cm <sup>-1</sup> )	
VinylMeSi(OMe) <sub>2</sub>		778	Weak, sharp
		816	Medium, sharp
		836	Weak, sharp
	Si-O-Si	1087	Strong, sharp
	C=C	1260	Weak, sharp
	C=C	1407	Weak, sharp
	C=C	1596	Weak, sharp
	C-H	2837	Weak, sharp
	C-H	2950	Weak, broad
1,4-		789	Weak, sharp
[(MeO) <sub>2</sub> Sivinyl] <sub>2</sub> benzene		835	Medium, sharp
		991	Weak, sharp
	Si-O-Si	1087	Strong, sharp
	Si-O-Si	1133	Medium, sharp
	C=C	1410	Weak, sharp
	C=C	1452	Weak, sharp
	C=C	1508	Weak, sharp
	C=C	1600	Weak, sharp
	C-H	2836	Weak, broad
	C-H	2937	Weak, broad

**Table S2.** Representative FTIR data of selected compounds.

VinyIDDvinyI		698	Weak, sharp
		731	Weak, sharp
		811	Weak, sharp
	Si-O-Si	1029	Weak, sharp
	Si-O-Si	1132	Strong, sharp
	C=C	1261	Weak, sharp
	C=C	1430	Weak, sharp
	C=C	1594	Weak, sharp
	C-H	2875	Weak, broad
	C-H	2923	Weak, broad
	C-H	3072	Weak, broad
DD-co-phenyl		697	Weak, sharp
		729	Weak, sharp
		814	Weak, sharp
	Si-O-Si	1029	Weak, sharp
	Si-O-Si	1132	Strong, sharp
	C=C	1262	Weak, sharp
	C=C	1430	Weak, sharp
	C=C	1594	Weak, sharp
	C-H	2875	Weak, broad
	C-H	2923	Weak, broad
	C-H	3072	Weak, broad
(Styryl)2DD		698	Weak, sharp
		734	Weak, sharp
		820	Weak, sharp
	Si-O-Si	1029	Weak, sharp
	Si-O-Si	1132	Strong, sharp
	C=C	1262	Weak, sharp
	C=C	1430	Weak, sharp
	C=C	1594	Weak, sharp
	C-H	2875	Weak, broad
	C-H	2923	Weak, broad
	C-H	3072	Weak, broad



Figure S4. <sup>1</sup>H NMR of pure *trans*-vinylDDvinyl.





Figure S5. (a) <sup>29</sup>Si NMR of pure *trans*-vinylDDvinyl; (b) zoom-in.





Figure S6. (a) <sup>29</sup>Si NMR of mixed cis-, *trans*-vinylDDvinyl; (b) zoom-in.

Table S3. N	ALDI-TOF,	GPC and TGA	data for vinyll	DDvinyl and	derived polymers.
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Compound	MALDI-TO	)F m/z		GPC		TGA		
	Monomer	Theor	Mn	Mw	Ð	Ceramic	Theor	Td5% °C
						yield %	yield %	(air)
VinylDDvinyl	1315ª	1314 <sup>a</sup>	1010	1080	1.07	49.3	49.7	540
-phenyl	1280	1280	19550	49410	2.53	46.3	46.9	460
-biphenyl	1355	1356	11690	24480	2.09	43.2	44.1	400
-terphenyl	1430	1432	15780	34770	2.20	41.7	41.8	410
-stilbene	1380	1382	9210	25390	2.76	42.8	43.3	400
-thiophene	1290	1286	22540	43250	1.92	46.5	46.7	540
-bithiophene	1370	1368	3580	7200	2.01	42.2	43.8	520
-thienothiophene	1340	1342	4480	10040	2.24	42.7	44.4	500
-dimethylfluorene	1400	1396	20790	46100	2.22	41.4	43.0	510
-BTH	1335	1338	8390	17380	2.07	44.0	44.8	540
-carbazole	1370	1369	13680	33850	2.47	42.8	43.8	540

<sup>a</sup> As Ag<sup>+</sup> adduct.

Auto-Scaled Chromatogram



Figure S7. GPC of vinylDDvinyl.



Figure S8. GPC of DD-co-benzene.





Figure S9. GPC of DD-co-biphenyl.



Figure S10. GPC of DD-co-terphenyl.





Figure S11. GPC of DD-co-stilbene.



Figure S12. GPC of DD-co-thiophene.

Auto-Scaled Chromatogram



Figure S13. GPC of DD-co-bithiophene.



Auto-Scaled Chromatogram

Figure S14. GPC of DD-co-thienothiophene.

Auto-Scaled Chromatogram







Figure S16. GPC of DD-co-BTH.

Auto-Scaled Chromatogram



Figure	<b>S17</b> .	GPC	of DD	-co-carb	azole.

<b>Table S4.</b> MALDI-TOF, GPC and	TGA d	data foi	vinylDDv	vinyl derive	d model	cage
	compo	ounds.				

	MALDI-TOF			GPC		TGA			
	m	/z							
	Actual	Theor	Mn	Mw	Ð	Ceramic	Theor	Td5% ℃	
						yield %	yield %	(air)	
(Styryl)₂DD	1467ª	1466ª	1121	1129	1.01	42.9	44.2	431	
(Styryl)₃DD	1543ª	1542ª	1126	1149	1.02	41.8	41.8	435	
(ThiophenevinyI)2DD	1480ª	1478ª	1149	1161	1.01	43.2	43.8	445	
(Dimethylfluorenevinyl)2DD	1697ª	1698ª	1545	1663	1.07	36.2	37.7	358	
(Dimethylfluorenevinyl) <sub>4</sub> DD	1977 <sup>ь</sup>	1976 <sup>ь</sup>	1715	1828	1.07	30.3	30.3	400	

 $^{\rm a}$  As Ag  $^{\scriptscriptstyle +}$  adduct.  $^{\rm b}$  As  ${\rm H}^{\scriptscriptstyle +}$  adduct.





Figure S21. FTIR of DD-co-dimethylfluorene and (Dimethylfluorenevinyl)2DD.



Figure S23. TGA of vinylDDvinyl.



Figure S25. TGA of DD-co-biphenyl, DD-co-terphenyl and DD-co-stilbene.



Figure S26. TGA of DD-co-thiophene and (Thiophenevinyl)2DD.



Figure S27. TGA of DD-co-bithiophene and DD-co-thienothiophene.



Figure S28. TGA of DD-co-dimethylfluorene, (Dimethylfluorene)<sub>2</sub>DD and (Dimethylfluorene)<sub>4</sub>DD.



Figure S29. TGA of DD-co-BTH and DD-co-carbazole.



Figure S30. Normalized steady-state spectra of 2,7-[(MeO)2Sivinyl]2dimethylfluorene, DD-co-dimethylfluorene and (Dimethylfluorene)2DD inserted with amplification of absorption shoulders around 389 nm.

Table S5. Two photon absorption (2PA) cross section values of polymers DD-cophenyl, -thiophene, -dimethylfluorene, -BTH and -carbazole and model cage

••••••••••••••••••••••••••••••••••••••				-0
		2PA-δ	(GM)	
λ <sub>ΤΡΑ</sub> (nm)	550	600	650	700
DD-co-phenyl		2.0	1.1	0.6
DD-co-thiophene		31	24	12
DD-co-dimethylfluorene		50	49	20
DD-co-BTH	13	4.4	3.4	0.38
DD-co-carbazole		10.2	2.5	2.4
(StyryI) <sub>2</sub> DD	4.6	0.64	0.54	0.62

compound (Styryl)2DD at discrete excitation wavelength.

Modeling studies. Previous modeling studies of SQ cage compounds focused on the addition of simple substituents to the T<sub>8,10,12</sub> cage including H, OH, and F. The first studies with H substitution found cage-centered LUMOs.<sup>50</sup> In modeling studies in previous papers,<sup>44,45</sup> we introduced methyl groups to completely/incompletelycondensed cages including corner-missing and double-decker compounds, again finding cage-centered LUMOs, which correlate well with experimental data. However, multiple previous attempts to model stilbene-functionalized cages were unsuccessful,<sup>44,45</sup> finding stilbene-localized HOMOs and LUMOs, which is inconsistent with experimental absorption and emission results for both single and two

photon experiments done in two separate laboratories. These studies were also inconsistent with magnetic field generation studies which also show formation of cage centered magnetic fields. Modeling studies done on vinylDDvinyl and its derived copolymers by Professor Jungsuttiwong's group at Ubon Ratchathani University, Thailand are shown in Figure **S31**. Modeling indicates that cage centered LUMOs occur inside the cage with methyl substituents on cage corners for both *cis* and *trans* configurations. With phenyl substituents, LUMOs reside on phenyl groups, which is consistent with published modeling results. The *trans* structure is more stable than the *cis* according to their HOMO, LUMO levels, which may explain why in the synthesis of vinylDDvinyl the majority product is always *trans*.





Figure S31. HOMO and LUMO modeling of vinylDDvinyl.

However, the introduction of co-monomer units as shown in Figure **S32** below, again places the LUMO on the organic co-monomer.







**Figure S32**. HOMO and LUMO modeling of *trans*-vinylDDvinyl derived polymers DD-co-phenyl, -thiophene, -dimethylfluorene, -BTH and carbazole.

Modeling indicates LUMOs of *trans*-vinylDDvinyl derived copolymers sit on the organic linkers only, without involving SQ cages. Calculated absorption spectra and date are presented below in Figure S33 and Table S6, and experimental data are shown for comparison. There is some similarity in the shape of experimental and calculated absorption spectra; as might be expected given the comments made above, but the calculated absorption  $\lambda_{max}$  is always blue-shifted from experimental by 35–68 nm.

One might choose to argue that current modeling methods are unable to successfully address the interaction of cage centered LUMOs with conjugated moieties. Hence efforts to model the unique structures developed with the DD polymers wherein

cage centered LUMOs must interact with co-monomer LUMOs through vinylMeSi(O-)<sub>2</sub> bridges (assuming our arguments are valid) must search for new modeling approaches.



**Figure S33**. Experimental absorption and emission spectra (blue) and modeling absorption spectra (grey) for *trans*-vinylDDvinyl and its derived polymers DD-co-phenyl, -thiophene, -dimethylfluorene, -BTH and -carbazole calculated at TD-CAM-B3LYP/6-31G(d) level of theory.

polymers DD-co-pnenyi, -intopnene, -dimetryintuorene, -BTH and -carbazole.							
	Experimental	Modeling	Transition	НОМО	LUMO	Egap	
	Abs. $\lambda_{max}$ (nm)	Abs. $\lambda_{max}$ (nm)		(eV)	(eV)	(eV)	
Trans-	264	228	H-10 to L+9	-8.32	1.16	9.48	
vinylDDvinyl							
-phenyl	298	249	HOMO to LUMO	-7.43	0.11	7.54	
-thiophene	340	281	HOMO to LUMO	-6.94	-0.03	6.91	

**Table S6.** Experimental and modeling data for *trans*- vinylDDvinyl and its derived polymers DD-co-phenyl, -thiophene, -dimethylfluorene, -BTH and -carbazole.

-dimethyl-	<u>339</u> , 353	295	HOMO to LUMO	-6.72	-0.19	6.53
fluorene						
-BTH	392	337	HOMO to LUMO	-6.93	-0.87	6.06
-carbazole	301	254	H-1 to L+1	-7.03	0.44	7.47

Modeling studies were also explored on vinylDDvinyl with corner phenyls substituted by methyls by Professor Kieffer and Dr. Hashemi's group at University of Michigan. In these modeling studies, LUMO+4 and LUMO+5 are from SQ core and cage centered as shown in Figure S34. Furthermore, the energy difference is only ~0.6 eV between LUMO in cage and vinyl  $\pi^*$ , which makes interaction between cage LUMO and vinyl  $\pi^*$  possible. Modeling of a similar structure where two Si(O-)<sub>2</sub> units are inserted into the each opposing edge is also investigated in Figure S35. With all methyl substituents, the structure again exhibits cage centered LUMO and LUMO+1.



**Figure S34**. Energy diagram of the molecular orbitals of vinylDDvinyl showing cage centered LUMO+4 and LUMO+5, calculated using PBE potentials as implemented in VASP.



**Figure S35**. Energy diagram of the molecular orbitals of methyl substituted DD with two Si(O-)<sub>2</sub> unites per opposing edge showing cage centered LUMO and LUMO+1, calculated using PBE potentials as implemented in VASP.

Cyclic voltammetry. We have previously demonstrated that cyclic voltammetry (CV) can be used to measure HOMO LUMO energies in (RvinylT)<sub>10/12</sub> cages with conjugated moieties.<sup>61</sup> Cyclic voltammograms were run on a CHI 600C electrochemical analyzer using a three-electrode setup. A glassy carbon working electrode was used in conjunction with a platinum wire counter electrode and a silver/silver nitrate reference electrode. All scans were taken in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in acetonitrile at 0.1 V/s. Ferrocene was used for calibration. Samples were dropcast onto the working electrode from THF for each scan polarity because reversible redox behavior was not observed. The LUMO-HOMO levels were inferred from the onset of reduction/oxidation (the intercept of the slope and baseline) for each sample.<sup>61</sup> In these previous studies, we learned to manipulate HOMO LUMO energies by designing (RvinylT)<sub>10/12</sub> cages with different strongly electron donating/accepting moieties (R). The results of this study again support the existence of cage centered LUMOs and 3-D conjugation; otherwise, one would not anticipate the found energy levels based on those of the individual moieties. In the current studies, we were unable to identify (easily accessible) redox behavior either in solution using the same setup above or in the solid state for the thiophene copolymers which we believe would be most likely to be easily accessible as they show the greatest red-shifts.