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Conjugated copolymers that shouldn't be

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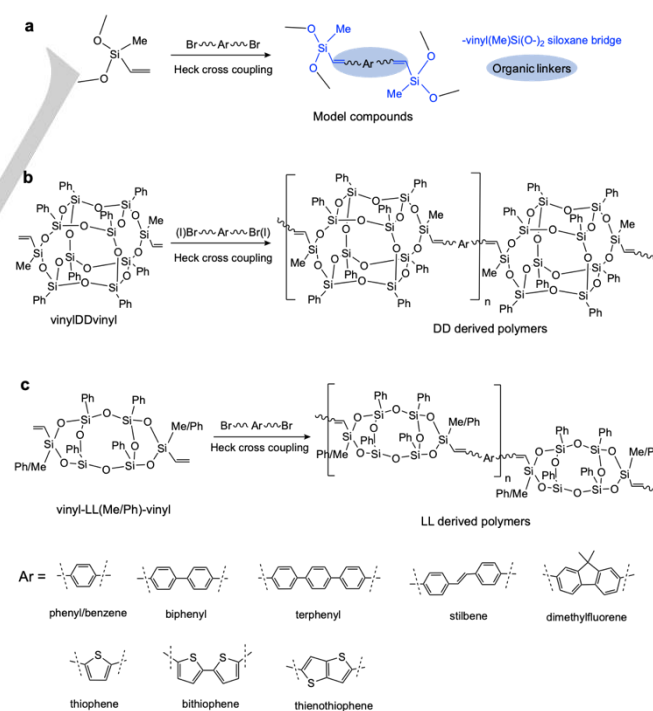
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Abstract: Multiple studies have explored using cage silsesquioxanes (SQs) as backbone elements in hybrid polymers motivated by their well-defined structures, physical and mechanical properties. As part of this general exploration, we reported unexpected photophysical properties of copolymers derived from divinyl double decker (DD) SQs, [vinyl(Me)Si(O_{0.5})₂][PhSiO_{1.5}]₈[(O_{0.5})₂Si(Me)vinyl] (vinylDDvinyl). These copolymers exhibit strong emission red-shifts from model compounds and implying unconventional conjugation, despite vinyl(Me)Si(O-)₂ siloxane bridges. In an effort to identify minimum SQ structures that do/do not offer extended conjugation; we explored Heck catalyzed co-polymerization of vinyl-ladder(LL)-vinyl compounds, vinyl(Me/Ph)Si(O_{0.5})₂[PhSiO_{1.5}]₄(O_{0.5})₂Si(Me/Ph)vinyl, with Br-Ar-Br where Br-Ar-Br = 1,4-dibromobenzene, 4,4'-dibromo-1,1'-biphenyl, 4,4''-dibromo-*p*-terphenyl, 4,4'-dibromo-*trans*-stilbene, 2,7-dibromo-9,9-dimethyl-9H-fluorene, 2,5-dibromothiophene, 5,5'-dibromo-2,2'-bithiophene and 2,5-dibromo-thieno[3,2-*b*]thiophene. Most surprising, the resulting oligomers show 30-60 nm emission red-shifts *beyond* those seen with vinylDDvinyl analogs *despite lacking a true cage*. Further evidence for unconventional conjugation includes apparent integer charge transfer (ICT) between LL-co-thiophene, bithiophene and thienothiophene with 10 mol% F₄TCNQ, suggesting potential as p-type doped organic/inorganic semiconductors. Brominating DD/LL-co-phenyl polymer vinyl groups eliminates emission red-shifts. Zn debromination thereafter restores vinyl groups and emission red-shifts but brominated phenyls remain providing potential access to families of "hairy" conjugated SQ polymers.

There is growing impetus to explore silsesquioxanes (SQs) due to their ease of synthesis and purification, well-defined 3-D nanostructures, robust nature as well as high compatibility with multiple types of organics leading to large families of hybrid materials. The major story still centers on properties that can be typified as organic decorated silica moieties. In contrast, we find that cage SQs {[RSiO_{1.5}]_{8,10,12} (R=R'phenyl, R'vinyl, R=conjugated moiety, R'=H, Me, MeO, NH₂, CN, etc)} offer photophysical properties not at all reflective of organic decorated silicas but commensurate with cage centered LUMOs.¹⁻⁵ We recently extended this concept of excited-state 3-D conjugation to sets of incomplete and modified cages including corner-missing T₈, [R'StilbeneSiO_{1.5}]₇[O_{1.5}SiMe/nPr], [R'StilbeneSiO_{1.5}]₇[O_{0.5}SiMe₃]₃,⁶ and newly developed double decker (DD) [R'StilbeneSiO_{1.5}]₈[OSiMe₂]₂ and [R'StilbeneSiO_{1.5}]₈[O_{0.5}SiMe₃]₄.⁷ Recent efforts on double decker SQs follow two parallel paths in their development exploring either

molecular or macromolecular hybrid materials.⁸ In the latter area, we recently synthesized a series of DD SQ based oligomers and polymers {vinyl(Me)Si(O_{0.5})₂[PhSiO_{1.5}]₈(O_{0.5})₂Si(Me)vinyl-Ar, vinylDDvinyl-Ar} that unexpectedly exhibit conjugation that appears to involve two vinyl(Me)Si(O-)₂ bridges evidenced by significant emission red-shifts from corresponding model compounds.⁹ Schemes 1a,b provide general synthetic routes and structures. In all systems, conjugation presents in the form of emission red-shifts of 50-120 nm from model compounds without cage components. Such novel combinations of structural, thermal, mechanical and photophysical properties, such as tunable broadband UV-Vis fluorescence, may be important for applications as emissive layers in OLEDs,¹⁰ multi-functional nano-drugs, in photothermal and photodynamic therapies for cancer, etc.¹¹⁻¹³



Scheme 1. Heck cross coupling of a) model compounds, b) vinylDDvinyl derived copolymers and c) vinyl-LL-vinyl derived copolymers.

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With the recent discovery of routes to ladder SQs (vinyl-LL-vinyl),¹⁴ we can now explore vinyl-LL-vinyl equivalent systems of the type suggested in Scheme 1c. The motivation is to ascertain the nature of LUMO formation in ladder SQs where the structure appears to be approximately one-half that of relatively complete double-deckers. Our initial presumption was that these compounds should represent the limiting case where not only is there no 3-D cage, but there are also two vinyl(Me/Ph)Si(O)₂ bridges per cage in any oligomers/polymers we might synthesize. Contrary to our original thoughts, the resulting compounds actually offer emission *further red-shifted* than any analogous compounds previously studied,^{1-7,9} seeming to imply conjugation and semiconducting behavior *where there should be none*. In the following sections, we begin by characterizing a set of ladder copolymers and thereafter assess their photophysical properties.

Two structurally similar ladder SQs [vinyl-(Me)LL(Me)-vinyl and vinyl-(Ph)LL(Ph)-vinyl] were explored, with only the end groups differing. Analytical characterization and photophysical behavior are essentially identical as expected, thus only data for vinyl-LL(Me)-vinyl co-polymers are presented. Spectra for vinyl-LL(Ph)-vinyl derived copolymers are shown in Figures S9-14. Both co-polymers were characterized by MALDI-TOF, GPC, FTIR, ¹H and ¹³C NMR, and the starting ladder SQs were also characterized by ²⁹Si NMR as recorded in Table S1-3 and Figure S1-8. MALDI-TOF shows the expected m/z, consistent with GPC determined molar masses of the ladder SQs. The GPC retention time for vinyl-LL(Ph)-vinyl is ~0.3 min earlier than that for vinyl-LL(Me)-vinyl due to the slightly bulkier phenyl groups. Table 1 GPC data for the ladder copolymers indicates **degrees of polymerization (DPs)** of 3-18 units. MALDI-TOF analyses always show peaks every m/z for the co-monomer unit vinyl-LL-vinyl-Ar, suggesting no di-substitution of aromatic groups on any given vinyl and successful copolymerization.

Table 1. GPC and steady-state photophysical data for vinylDDvinyl derived polymers⁹ and vinyl-LL(Me)-vinyl derived polymers.

	DP ^[a]	Abs. λ_{\max} (nm)	Em. λ_{\max} (nm) ^[b]	Φ_F
Vinyl(Me)DD(Me)vinyl	1	264	281	
DD-co-phenyl	15	298	390, 412	0.08±0.001
DD-co-biphenyl	10	314	357, 373	0.66±0.05
DD-co-terphenyl	11	321	374, 392	0.87±0.04
DD-co-stilbene	7	357	412, 436	0.61±0.04
Co-dimethylfluorene	15	339, 353	424, 448	0.34±0.003
DD-co-thiophene	20	340	478, 505	0.09±0.001
DD-co-bithiophene	3	391	505, 538	0.17±0.02
Co-thienothiophene	4	358	496, 526	0.13±0.01
Vinyl-LL(Me/Ph)-vinyl	1	264	283	
LL-co-phenyl	8	298	392, 415	0.16±0.02
LL-co-biphenyl	6	312	412, 430	0.46±0.04
LL-co-terphenyl	18	321	418, 437	0.61±0.02

LL-co-stilbene	8	356	448, 472	0.35±0.03
Co-dimethylfluorene	7	337, 353	426, 451	0.68±0.02
LL-co-thiophene	4	343	540	0.07±0.01
LL-co-bithiophene	6	392	550	0.07±0.01
Co-thienothiophene	6	356, 371	530	0.09±0.01

[a] Degree of polymerization. **[b]** Excitation wavelength at Abs. λ_{\max}

The steady-state absorption and emission behavior of ladder polymers are shown in Table 1 and Figures 1 and 2, compared with data for vinylDDvinyl derived polymers from our previous study.⁹ All emission spectra were measured with excitation wavelength at corresponding absorption λ_{\max} . The Table 1 data for vinyl(Me)DD(Me)vinyl and vinyl-LL(Me)-vinyl indicates that all exhibit absorption $\lambda_{\max} \approx 265$ nm and emission $\lambda_{\max} \approx 280$ nm, typical for phenyl rings. Vinyl-LL(Ph)-vinyl is slightly red-shifted with phenyls at two ends. Polymers were synthesized from both vinyl-LL-vinyl compounds. No essential spectral differences were observed as expected.

Divinylbenzene is the simplest organic linker tested. The steady-state data in Table 1 for LL-co-phenyl are essentially identical to those of DD-co-phenyl. The red shift of 70 nm in emission compared to 1,4-[(MeO)₂Sivinyl]₂benzene suggests formation of a LUMO even with a half cage and conjugation to co-phenyl in the excited state. Based on all our previous work, it appears that a LUMO does form and these results greatly extend the families of SQs that appear to offer extended conjugation. Even though the shifts are not significant in the absorption and emission λ_{\max} of LL-co-phenyl from its DD analogue, there are significant changes in the shape of steady-state spectra as seen in Figure 1. First, LL-co-phenyl with a DP of 8 displays distinct absorption shoulders around 355 nm compared to model compound and DD-co-phenyl with a DP of 15. Additionally, its emission is slightly red-shifted beyond DD-co-phenyl, along with the disappearance of the emission peak near 340 nm and a significant shoulder at ≈ 450 nm.

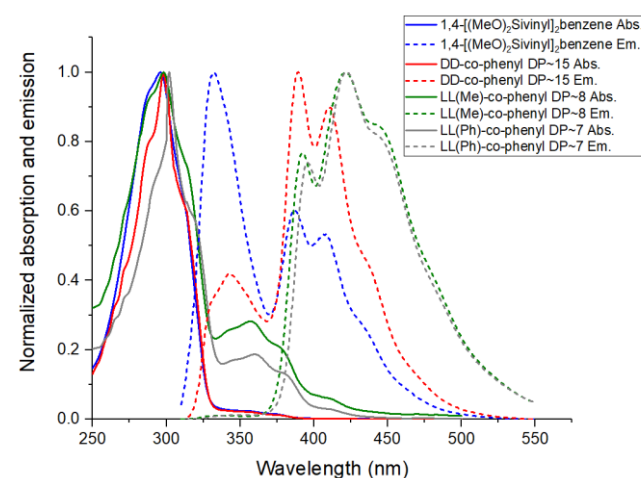


Figure 1. Normalized steady-state absorption and emission spectra of 1,4-[(MeO)₂Sivinyl]₂benzene, DD-co-phenyl and LL-co-phenyl in CH₂Cl₂.

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Such changes in steady-state behavior are more apparent in LL-co-biphenyl, terphenyl, stilbene and thiophene as witnessed by 30–60 nm red-shifts beyond their DD analogues even with shorter chains, again suggesting LUMO formation even in ladder structures but also more efficient communication between the ladder SQ and the conjugated organic moieties in the excited state as compared to full and double-decker SQs. This finding is quite important in that it completely changes our assumptions about ladder SQs. To further probe such structure-property relationships, a shorter fraction of LL-co-thiophene was separated via TLC (silica, 1:1 DCM:hexane) and characterized by GPC and MALDI-TOF in Figure S15 and Table 2.

Table 2. MALDI-TOF and GPC data for DD-co-thiophene, short LL-co-thiophene isolated by TLC and long LL-co-thiophene.

	GPC		MALDI-TOF		
	M_n	M_w	\bar{D} ^[a]	Oligomers ^[b]	M/z
LL-co-thiophene DP-3	2540	3630	1.12	Dimer	1896 ^[c]
LL-co-thiophene DP-7	5600	8000	1.42	Trimer	2797 ^[c]
DD-co-thiophene DP-20	22540	43250	1.92	Decamer	13010 ^[c]

[a] Polydispersity. [b] Largest oligomers identifiable. [c] As Ag⁺ adduct.

The GPC of the starting vinyl-LL-vinyl, short LL-co-thiophene separated by TLC (DP-3) and long LL-co-thiophene (DP-7) are shown in Figure S15. The GPC trace of the LL-co-thiophene with DP ~7 shows a broad peak around 27.5 min with a \bar{D} of 1.43 for relatively long oligomers as well as a quite narrow peak at 33.2 min overlapping with vinyl-LL-vinyl with polydispersity (\bar{D}) of 1.02, suggesting presence of unreacted starting material during copolymerization. The short LL-co-thiophene with DP-3 comes at 31.5 min with a small \bar{D} of 1.12, dominated by dimers and trimers following removal of longer oligomers via TLC. The GPC and MALDI-TOF data are shown in Table 2. The largest oligomers identifiable by MALDI-TOF with corresponding masses are presented. It is known that the peak intensities in MALDI corresponds to the ionization efficiencies of the species and are not necessarily representative of the quantity of each component. High M_w oligomers are not as readily ionizable as monomers thus even though the GPC shows even higher M_w oligomers, they are not necessarily “seen” in MALDI. Data for DD-co-thiophene with DP ~20 are also presented here. Since LL-co-thiophene is shorter than its DD analogue, it is safe to say that its red-shifted emission comes from more efficient electronic communication between LL SQs in the excited state rather than longer chains with extended conjugation lengths. extend the families of SQs that appear to offer extended conjugation.

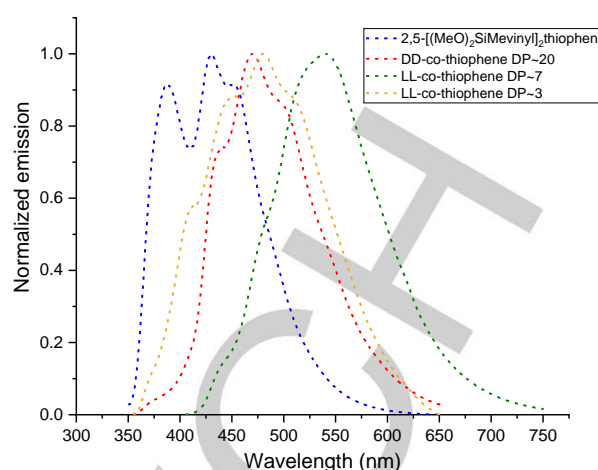


Figure 2. Normalized progressive emission spectra of 2,5-[(MeO)₂Siviny]₂thiophene, DD-co-thiophene, short (DP-3) and long (DP-7) LL-co-thiophene in CH₂Cl₂.

Figure 2 presents the normalized steady-state emission spectra for 2,5-[(MeO)₂Siviny]₂thiophene, DD-co-thiophene, LL-co-thiophene with DPs of 3 and 7 respectively. The absorption λ_{max} is always around 340 nm and not shown here. The progressively red-shifted emission λ_{max} of short and long LL-co-thiophenes are 484 and 539 nm respectively, suggesting extended conjugation with further extensions in chain length and smaller bandgaps. Short LL-co-thiophene, consisting mostly of dimers and trimers, still shows λ_{max} emission similar to long DD-co-thiophene, which is ~50 nm red-shifted from 2,5-[(MeO)₂Siviny]₂thiophene. It has been reported that T₈ SQ cages exhibit electron-withdrawing capacities approximately equivalent to -CF₃.¹⁵ One can extend this idea to DD SQs given similar structures and presumably LL systems. It then becomes possible to argue that DD-co-thiophene oligomers and even dimers and trimers of LL-co-thiophene should offer similar properties. This further confirms the efficient semiconducting behavior of such ladder SQs polymers. Similar study has also done on LL-co-biphenyl as an example from the phenyl system of LL copolymers and the GPC and steady-state emission spectra are shown in Figure S16, 17. The progressive red-shifts in the emission of LL-co-biphenyl as a function of DPs have also been observed.

Further evidence of unconventional conjugation includes the charge-transfer studies of thiophene systems of LL SQ copolymers. Integer charge transfer (ICT) is observed between electron-acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) and DD-co-thiophene, bithiophene and thienothiophene as reported in our previous paper.⁹ Similar ICT also occurred in 10 mol%F₄TCNQ doped LL-co-thiophene, bithiophene and thienothiophene using the mixed-solution method. The original orange-red color becomes dark green immediately on mixing. The literature reports that poly(3-hexylthiophene-2,5-diyl) regioregular (P3HT) exhibits integer charge transfer interactions with F₄TCNQ and coincident nitrile-stretching mode shifts from a neutral value $\nu_0 = 2227 \text{ cm}^{-1}$ to $\nu_1 = 2194 \text{ cm}^{-1}$ on doping.^{16,17} In marked contrast, however, quaterthiophene (4T) forms partial charge transfer with F₄TCNQ and thus shows only a small shift.¹⁸ Shifts of characteristic cyano-vibrational bands from the neutral value to the anion value are observed in the FTIR for

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LL-co-bithiophene mixing with F_4TCNQ as shown in Figure 3 indicating integer charge transfer (ICT).

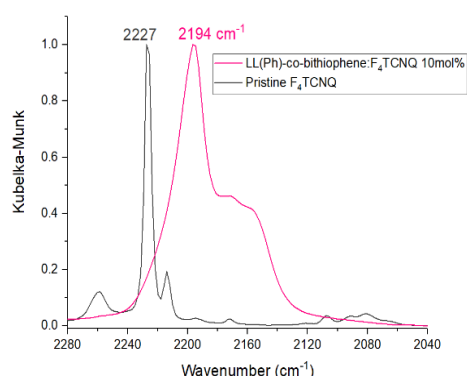


Figure 3. FTIR of vCN region for pristine F_4TCNQ and mixture of LL-co-bithiophene: F_4TCNQ 10 mol%.

The literature also reports that the electronic structure of F_4TCNQ anion includes doublet states because of the presence of an unpaired single electron.¹⁹ The UV-Vis spectrum of $F_4TCNQ^{\cdot-}$ contains two main absorption peaks around 400 and 800 nm. $D_0 \rightarrow D_1$ transition corresponds to the absorption band around 600-900 nm with local maxima at 754 and 856 nm while $D_0 \rightarrow D_2$ transition gives absorption band at 410 nm. The absorption spectrum of LL(Ph)-co-bithiophene: F_4TCNQ in Figure 4 clearly shows spectral signatures from $F_4TCNQ^{\cdot-}$ at 600-900 nm and LL-co-bithiophene at 350-500 nm, strongly suggesting ICT, consistent with the FTIR data.

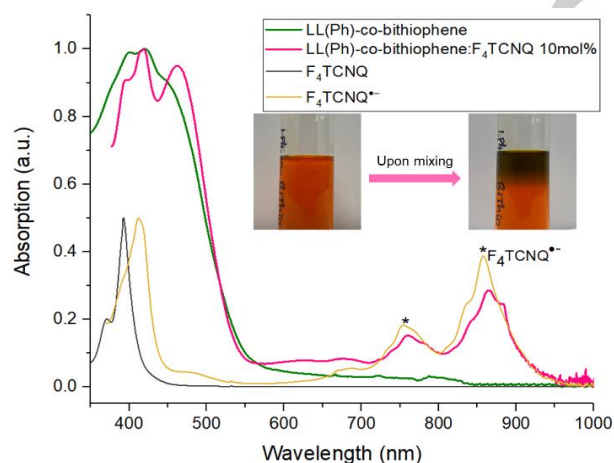


Figure 4. Absorption spectra of undoped LL-co-bithiophene and LL-co-bithiophene: F_4TCNQ 10 mol%, F_4TCNQ and $F_4TCNQ^{\cdot-}$ shown for reference.

Another evidence of unconventional conjugation comes from the breaking and restoring conjugation by brominating/debrominating vinyls. Our original objective in brominating phenyl groups in DD/LL-co-phenyl polymers was to further functionalize the phenyl groups peripherally to prepare 'hairy polymers' and explore possible 3-D conjugation. As expected, vinyl groups brominate first on as evidenced by Figure S16-19. ^{13}C and ^{29}Si NMR coincident with elimination of conjugation and partial cage cleavage as tracked by GPC. As shown in Figure 5b, brominated polymers display only characteristic phenyl absorption around 250 nm. The emission spectra are diminished and only show

CH_2Cl_2 solvent background. The photophysical behavior of both DD/LL-co-phenyl reappear after zinc debromination,²⁰ with absorption λ_{max} around 300 nm and red-shifted emission λ_{max} around 400 nm with respect to the emission of 1,4-[(MeO) $_2$ Siviny] $_2$ benzene at 332 nm. This finding further proves the presence and reproducibility of the excited-state conjugation in the DD/LL SQ derived polymers via vinylSi(O) $_2$ siloxane unit.

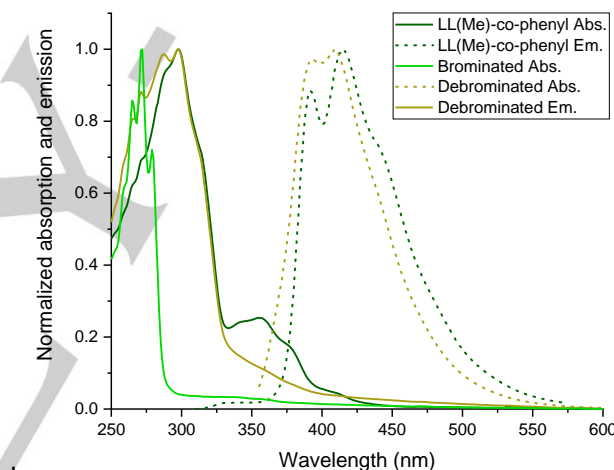
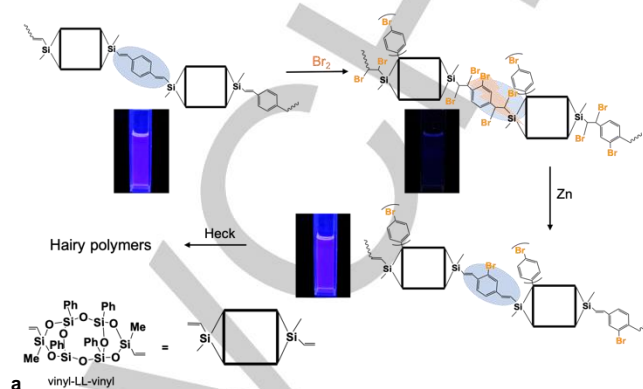


Figure 5. a) Bromination and debromination of LL-co-phenyl. b) Steady-state spectra in CH_2Cl_2 .

Two modeling groups attempted to model the vinyl-LL-vinyl SQ structure. Professor Jungstittiwong's group at Ubon Ratchathani University, Thailand, and Professor Kieffer's group at the University of Michigan, found both HOMOs and LUMOs reside on the peripheral phenyl groups of vinyl-LL(Me/Ph)-vinyl, with an energy band gap of ~ 8.9 eV. The calculated absorption λ_{max} is always ~ 60 nm blue-shifted compared to the experimental data, as shown in Table S4. In another effort from Professor Kieffer's group the peripheral phenyl groups are replaced by methyl for modeling purposes, LUMO+2 at 8.47 eV is from LL SQ core and extends out of the ladder frame, suggesting possible interaction between an SQ-centered LUMO and vinyl π^* . Orbitals. When phenyls are retained, the LUMO+10 also resides in the center of LL SQ and extends out to vinyl π^* with a lower energy level at 7.86 eV. These modeling results are presented in Figure S26-28. At this time, modeling is still not as precise as we would like but these systems are quite unique as our results demonstrate.

In summary, a series of ladder (LL) SQ copolymers were synthesized via Heck catalytic cross-coupling of vinyl-LL-vinyl with various dibromo-aromatic compounds. Compared to model silane compounds and analogs of double-decker (DD) SQ copolymers, LL derived polymers display similar absorption peaks

but with significant shoulders at longer wavelength. Furthermore, LL SQs linked with longer or more complex aromatic bridges, LL-co-biphenyl, terphenyl, stilbene and thiophene, show 30-60 nm emission red-shifts *beyond* those seen with the DD analogs and progressively red-shifted emissions with respect to longer chains were also observed. Integral charge transfer occurs in 10 mol% F₄TCNQ-doped LL-co-thiophene, bithiophene, thienothiophene, which also occur on mixing F₄TCNQ with DD analogous polymers. These results suggest not only a new perspective on the ease of formation of LUMOs in even LL SQs, but also more efficient communication of the LL SQ with conjugated organic moieties in the excited state as compared to full and double-decker SQs that potentially offer access to a wide variety of semiconducting polymers. In addition, brominating vinyl as well as phenyl groups in DD/LL derived copolymers and then debrominating vinyls not only restores through chain conjugation but also provides the potential to further peripherally functionalize these systems via a variety of catalytic cross-coupling reactions to explore 3-D conjugation in "hairy SQ polymers".

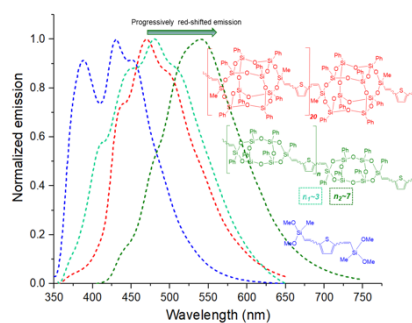
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Keywords: silsesquioxane • ladder silsesquioxanes • polymers • LUMOs • semiconducting

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Unexpected excited-state conjugation was observed in a series of ladder silsesquioxane, vinyl(Me/Ph)Si(O_{0.5})₂[PhSiO_{1.5}]₄(O_{0.5})₂Si(Me/Ph)vinyl derived copolymers, which exhibited 30-60 nm red-shifted emission from respective double-decker derived analogues with equal or larger DPs. Further studies including higher quantum yield, integer charge transfer with F₄TCNQ, conjugation cleavage and recovery were explored for potential application as semiconducting polymers.