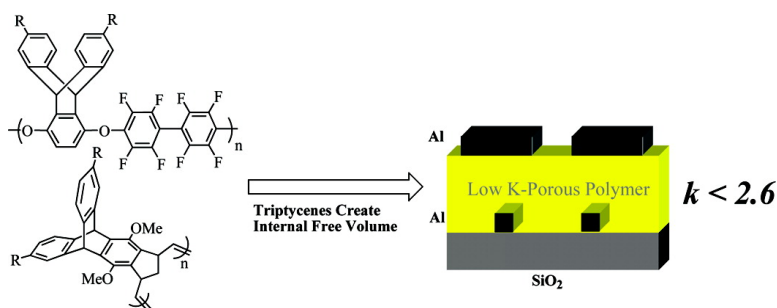Article

Molecular Design of Free Volume as a Route to Low-□ Dielectric Materials

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Molecular Design of Free Volume as a Route to Low-κ Dielectric Materials

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Abstract: Polymers incorporating the triptycene subunit were prepared for the molecular-level design of low dielectric constant (low-κ) materials that can be used to manufacture faster integrated circuits. Triptycenes having restricted rotation by multiple point attachment to the polymer backbone are shown to introduce free volume into the films, thereby lowering their dielectric constants. The triptycene containing polymers exhibit a number of desirable properties including low-water absorption and high thermal stability. Systematic studies wherein comparisons are made between two separate classes of triptycene polymers and their non-triptycene containing analogues demonstrate that proper insertion of triptycenes into a polymer backbone can give rise to a reduction in the material's dielectric constant while also improving its mechanical properties. These characteristics are desired by the semiconductor industry for the next generation of microprocessors and memory to provide insulation of the increasingly shrinking features.

Introduction

Currently, the fastest microprocessors are based on an architecture feature size (technology node) of 0.13 μm, but this node is just reaching application; currently, Intel Pentium 4 processors are based on 0.18 μm feature sizes.[1] As the demand for faster and, therefore, denser computer processors and memory increases, the semiconductor field is pushed to continually decrease the feature size used in their production. This requires improved interconnect dielectric materials to minimize resistive-capacitance (RC) elements that give rise to propagation delays, crosstalk noise, and power dissipation.[2–4] The interconnect delay caused by RC crosstalk can be calculated from[5]

$$D = 2\rho\epsilon\epsilon_0 [(4L^2/P^2) + (L^2/T^2)]$$

where D is the signal delay time, ρ is the specific resistance of the conductor (metal), ϵ and ϵ_0 are the dielectric constant of the interconnect dielectric and vacuum, respectively, L is the length of the conductor, T is the thickness of the conductor, and P is the distance between conducting lines.

This delay can be minimized in a number of ways. First, and most recently realized, is to shift from the use of aluminum (ρ = 2.66 $\mu\Omega$ cm) to copper (ρ = 1.65 $\mu\Omega$ cm) for the interconnecting lines.[6] Another method involves changes in the device design and feature size to decrease the size and spacing of the lines.[7–10] Finally, a gain can be realized with the reduction

in the dielectric constant of the inter- and intralayer insulator, and projected targets for the 0.10 μm feature size are ϵ = 2.0–2.5, with the 0.08 μm features requiring ϵ < 2.0.[11–17]

Two methods to apply dielectric materials have become prominent: spin-on application of soluble organic and inorganic dielectric polymers or their precursors (plus an annealing step) and chemical vapor deposition (CVD) applications. A limited number of materials may be applied by CVD, and it remains difficult to control the thickness, morphologies, and uniformity of the applied layer.[18] Spin-coating of soluble monomers and polymers allows for greater control of the structure of the material, and a wider breadth of materials may be applied in a uniform manner.

There are many considerations in developing a dielectric. The dielectric constant must remain low under operating conditions (currently < 3.1 GHz). Care must be taken to minimize polarizable electronic components by either avoiding extended π-systems or by incorporating highly electronegative atoms, such as fluorine, to localize electrons in σ-bonds. Due to subsequent metallization and annealing steps, the material must be stable at 450 °C for several hours with a minimal change in volume.[19] The material should have an isotropic dielectric constant since many devices are multilayered. Finally, the material must display low water absorption, since introduction of a small amount of water (ϵ = 78) into a material will greatly

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Scheme 1. Synthesis of Compounds **1**−**7**
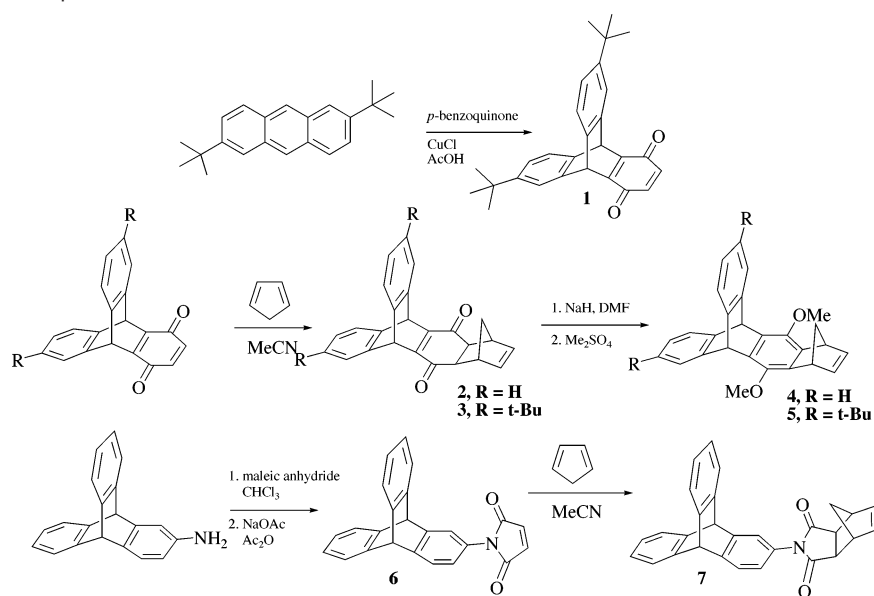
increase its bulk dielectric constant. Other requirements for low dielectric candidates include metal adhesion, planarization, metal content, etch rate, stress, gap-fill, film integrity, and cost.[11] Currently, one of the leading organic dielectric materials is SiLK, a highly cross-linked polyphenylene ($\epsilon = 2.65$) produced by a collaboration between IBM and Dow Chemcal.[20] SiLK is formulated as a mixture of soluble cyclopentadienone and acetylenic monomers that are spin-coated and cured on wafer to produce the polymer via Diels−Alder reaction followed by thermal elimination of CO.

Since few matrix materials have been developed with $\epsilon <$ 2.5, the introduction of pores into a matrix material, such as silsesquioxane thermosetting resins have become a focus.[21] Typically, an organic polymer is introduced as a pore generator in a blend with a thermosetting silsequioxane resin. After spin casting, heating the composite causes a cross-linking of the silsequioxane network, after which, a further increase in temperature eliminates the organic polymer resulting in a porous network.[22,23] The dielectric constant of these porous materials can be predicted by the Bruggeman effective medium approximation:[24]

$$f_1[(\kappa_1 - \kappa_e)/(\kappa_1 + 2\kappa_e)] + f_2[(\kappa_2 - \kappa_e)/(\kappa_2 + 2\kappa_e)] = 0$$

where $f_{1,2}$ are the percentages of each component, $\kappa_{1,2}$ are the dielectric constants for each component, and κ_e is the dielectric constant of the composite. The dielectric constant of the matrix material is extremely important for creating low-κ materials with $\epsilon <$ 2.0. For example, if silica ($\epsilon = 3.9-4.5$) is used as a matrix material, 70% porosity is needed for $\epsilon <$ 2.0; however, when methylsilsesquioxane (MSSQ, $\epsilon = 2.6-2.8$) is used, only 25% porosity is necessary.

Problems arise in the control of pore size due to polydispersities in the pore generators.[25] Too large of pores allow for metal diffusion through the film, resulting in short-circuiting. Also, as the percentage of pores in a network increases, the overall mechanical integrity of the material decreases until the material collapses on itself, destroying the pores entirely. Hawker et al.[26] have made great strides toward producing polymeric pore generators of uniform size; however, at higher pore generator

loadings, coalescence of pores from polymer aggregation and the loss of structural integrity remain problematic.

In this contribution, we describe the use of the triptycene moiety as a rigid and shape-persistent component as a method to introduce molecular-scale free volume into a polymer film. This approach produces bulk polymers with overall lower dielectric constants than those of polymers lacking triptycene without necessitating the introduction of pore generators, thus eliminating some of the problems inherent to microporous polymers. Herein, we introduce a new methodology for a molecular-level approach to low-κ dielectric films. We believe this is the first detailed investigation into the introduction of pores at the molecular level through targeted synthetic design.

Results and Discussion

We have previously shown that the unique three-dimensional and 3-fold symmetric shape-persistent structure of triptycene can be used to introduce free volume into supramolecular systems as well as induce novel or increased molecular alignments.[27,28] To ensure that our free volume approach to low-κ dielectric coatings was general, we have investigated two completely different classes of triptycene containing polymers and have made comparisons with nontriptycene containing analogues.

We began our investigations by synthesizing polymers by a ring-opening olefin metathesis polymerization (ROMP) of strained cyclic olefinic monomers (Scheme 1).[29,30] This method was particularly interesting to us because it allowed for the formation of two critical structural types of monomers. A first type, **4** and **5**, has the triptycene group fused to the 2.2.1-ring system of the monomer. This leads to a polymer structure

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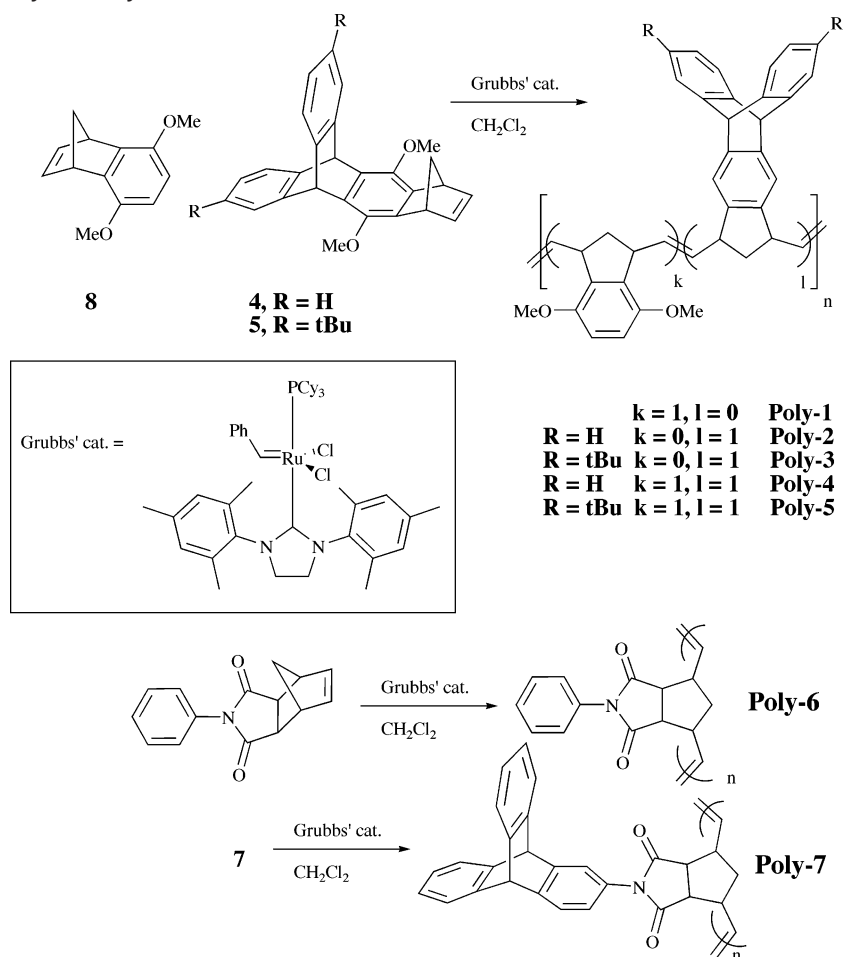(25) Treichel, H. *J. Electron. Mater.* **2001**, *30*, 290.
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Scheme 2. Synthesis of **Poly-1** to **Poly-7**

k = 1, l = 0   **Poly-1**
R = H   k = 0, l = 1   **Poly-2**
R = tBu   k = 0, l = 1   **Poly-3**
R = H   k = 1, l = 1   **Poly-4**
R = tBu   k = 1, l = 1   **Poly-5**

(Scheme 2) wherein the triptycene group cannot undergo free rotation and its orientation is fixed by the orientation of the polymer backbone. These monomers were efficiently synthesized directly from triptycene-1,4-quinone derivatives (for example, intermediate **1**, was prepared by reaction of 2,6-di-(*tert*-butyl)anthracene[31] and *p*-benzoquinone in acetic acid in the presence of CuCl, Scheme 2) by Diels−Alder reactions with an excess of cyclopentadiene to give **2** and **3**.[32] These intermediates were tautomerized and methylated in one pot to give monomers **4** and **5**.

To determine if the restricted orientation of the triptycene group was necessary to produce the desired reduction in dielectric constant, a second monomer **7** was synthesized containing a pendant triptycene. In this case, the attachment through a single bond allows for free rotation of the triptycene group. Monomer **7** was prepared by condensation of 2-amino-triptycene[33] with maleic anhydride to give malimide, **6**. This compound undergoes a facile Diels−Alder reaction with cyclopentadiene to produce monomer **7**.

All monomers were readily polymerized by a "second generation" Grubbs catalyst[34] (Scheme 2) in dichloromethane

and were isolated by precipitation into methanol. For the purposes of this study, homopolymers of monomers **4**, **5**, and **7** were prepared as well as 1:1 random copolymers of **4** and **5** with their parent monomer, **8**, as shown in Scheme 2. Non-triptycene containing polymers, **Poly-1** and **Poly-6**, were prepared from literature monomers[35,36] for comparison to **Poly-2**−**5** and **Poly-7**, respectively. These ROMP polymers were subjected to a series of tests to determine the effect of triptycene substitution on properties relevant to dielectric applications, and these results are summarized in Table 1.

We were principally interested in determining if we had succeeded in lowering the dielectric constant. The dielectric constant was determined by two independent methods. Simple metal−insulator−metal capacitor devices were fabricated on by spin-coating polymers onto a glass substrate with a pattern of two strip aluminum bottom electrodes followed by evaporation of 10 smaller top aluminum electrodes (300−600 Å, shadow mask, 0.5 Å/s) to give 10 working devices, each with a working electrode area of 2.52×10^{-6} m^2. Electrical connections were made by sharp contact probes, and the thickness of the applied polymers were determined by profilometry. We also determined the refractive index by optical methods which, when squared, provides the dielectric constant at optical frequencies. The

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Table 1. Physical and Thermal Characterization for **Poly-1**−**Poly-11**

polymer	M_n	Pdi	ϵ (10 kHz)[a]	n (633 nm)	$\epsilon - n^2$	water abs (wt %)	water contact angle (advancing)	water contact angle (receding)	T_g (°C)	decomp temp °C
					ROMP					
Poly-1	71 650	2.61	3.35 (0.15)	1.592	0.81	1.0	71	63	none	399
Poly-2	44 000[b]	c	2.78 (0.09)	1.606	0.19	1.0	82	71	none	416
Poly-3	29 200	1.51	2.59 (0.08)	1.567	0.13	1.1	90	84	none	473
Poly-4	43 900	2.58	2.82 (0.06)	1.602	0.25	0.9	69	61	none	410
Poly-5	47 600	2.20	2.69 (0.06)	1.577	0.20	0.8	69	58	none	407
Poly-6	48 700	2.44	3.00 (0.11)	1.597	0.45	5.1	56	23	none	451
Poly-7	66 400[b]	c	2.98 (0.13)	1.613	0.38	3.7	64	37	none	464
					PAEs					
Poly-8	11 400	2.67	2.41 (0.10)	1.546	0.02	0.9	91	86	none	504
Poly-9	10 100	2.54	d	d		1.1	d	d	none	594
Poly-10	9600	2.11	2.47 (0.07)	1.568	0.01	0.3	95	88	none	521
Poly-11	11 100	2.70	2.42 (0.07)	1.569	0.00[e]	0.4	91	90	none	501

[a] Error limits in parentheses. [b] From ^{1}H NMR end group analysis. [c] Insoluble in THF. [d] Sparingly soluble in common organic solvents. [e] $n^2 = 2.46$ is within the error range for ϵ of **Poly-11**.

general agreement in the dielectric constant determined by these two methods provides an additional check of our determinations.

The ROMP polymers provide a clear trend in the dielectric constant. Incorporation of triptycenes into the backbone (**Poly-2** vs **Poly-1**) decreased the dielectric constant of the polymer by nearly 0.6, from 3.35 to 2.78, respectively. The dielectric constant was further decreased by adding *tert*-butyl groups at the periphery of the triptycene core thereby increasing its size. For **Poly-3**, the dielectric constant decreased to 2.59. These examples illustrate the effect of adding "internal free volume" from triptycenes into the polymer film. To further confirm this trend, we investigated the random copolymers **Poly-4** and **Poly-5** of triptycene monomers **4** and **5** with the parent monomer **8**. These polymers exhibited intermediate dielectric constants of 2.82 and 2.69, respectively, relative to their parent homopolymers. The presence of free volume in these materials was further confirmed by BET gas absorption studies that revealed a surface area for powders of **Poly-3** of approximately 400 m²/g with a median pore diameter of 13.2 Å. Of the polymer free volume, 90% is contained within pores with a diameter of less than 45 Å.

It is particularly noteworthy that **Poly-7** showed no improvement in dielectric constant, with respect to parent **Poly-6** (3.00 versus 2.98). This can be attributed to the attachment of the triptycene via a single bond. Evidently, the rotational freedom of the triptycene group in **Poly-7** allows for denser packing and thus does not efficiently lower the bulk dielectric constant. It is evident that ring fusion of the triptycenes is essential to create the desired free volume.

Given the successful systematic lowering of the dielectric constants in fused ring polymers produced by ROMP, we sought to determine the generality of this concept by demonstrating it in a completely different class of polymers. We were particularly interested in poly(aryl ether) materials (PAEs) as these materials
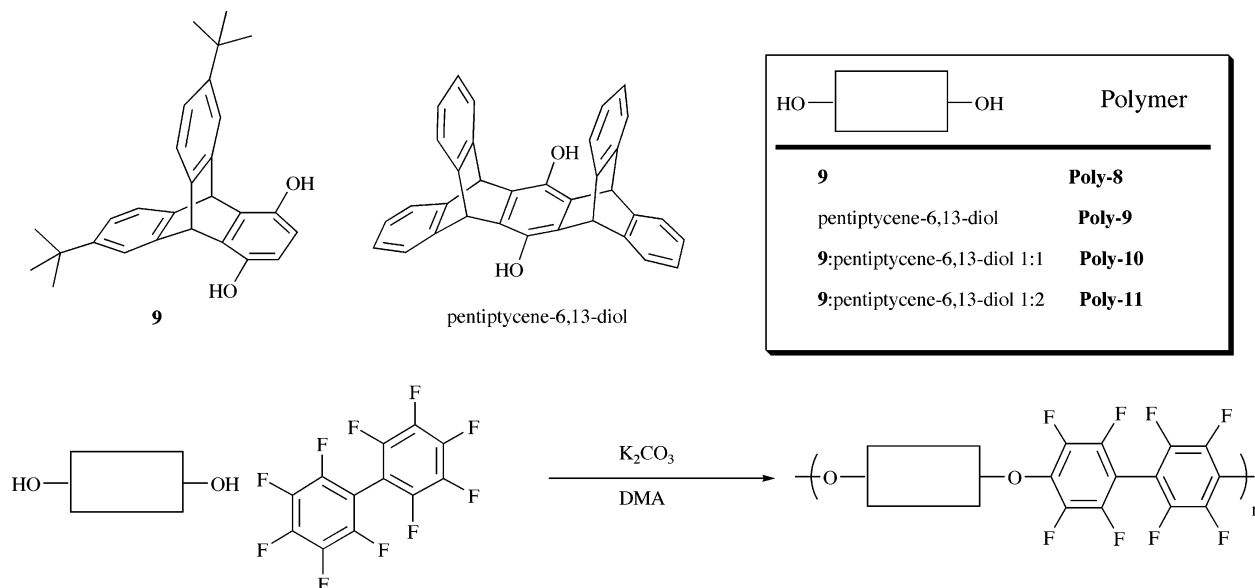
are known to have excellent stability and have been used as interlayer dielectrics. An additional attractive aspect of these systems is that they can be synthesized by condensation of readily available triptycene and pentiptycene monomers having 1,4-dihydroxy-arene (i.e., hydroquinone) groups with electron deficient comonomers such as bis(4-fluorophenyl)sulfone and decafluorobiphenyl, among others.[37,38] As shown in Scheme 3, we decided to produce PAEs by condensation of triptycene with decafluorobiphenyl to give alternating copolymers that are triptycene homologues of commercially based FLARE polymers.[5] In these materials, we endeavored to increase the amount of free volume by using a triptycene-1,4-hydroquinone bearing bulky *t*-butyl groups (**9**)[39] and by using a pentiptycene monomer. The incorporation of *tert*-butyl groups on the exterior of the triptycene also aided in the solubility and processability of the polymers.

Physical Characterization

Dielectric studies of these PAEs again showed that the insertion of ring fused triptycene moieties produced a lower dielectric constant. In fact, these materials displayed even lower dielectric constants than those of the materials produced by ROMP. Among these, **Poly-8** had the lowest, with a value of 2.41. This polymer compares nicely to FLARE 1.0, a commercial PAE (Honeywell), which is reported to have a $\epsilon = 2.62$, which rises to $\epsilon = 2.66$ at 60% relative humidity.[40]

As mentioned earlier, a successful interlayer dielectric must possess a number of other desirable properties in addition to a low κ, and other relevant properties are summarized in Table

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Scheme 3. Synthesis of **Poly-8**−**Poly-11**

HO—☐—OH	Polymer
9	**Poly-8**
pentiptycene-6,13-diol	**Poly-9**
9:pentiptycene-6,13-diol 1:1	**Poly-10**
9:pentiptycene-6,13-diol 1:2	**Poly-11**

1. Fortunately, we also found that triptycene substitution produces desirable improvements in all of the categories investigated. The dimensional and chemical stability of the materials to high temperatures is critical. A survey of all of the materials (**Poly-1**−**Poly-14**) by differential scanning calorimetry (DSC) revealed no sign of a glass transition (T_g) before reaching their thermal decomposition temperature (Table 1). Their thermal decomposition temperatures (T_d = temperature at 5% mass loss) were measured via thermogravimetric analysis (TGA) and showed that the introduction of triptycenes into polymer backbones increased thermal stability. This is apparent in the ROMP materials by comparing **Poly-1** (T_d = 399 °C) to **Poly-2** (T_d = 416 °C) and **Poly-3** (T_d = 473 °C). There is a also an improvement in the stability of **Poly-7** (T_d = 464 °C) with respect to **Poly-6** (T_d = 451 °C). Since these two materials have similar dielectric constants, the effect may not be directly related to triptycene induced free volume. Preliminary thermal mechanical analysis (TMA) data for **Poly-2** and **Poly-3** gave thermal expansion coefficients of 272 and 167 ppm/°C, respectively. While these are on the high end for commercially viable matrix materials, well-established cross-linking methods should provide the ability to readily adjust these values as necessary.[41]

We found **Poly-9** had an extremely impressive thermal stability (T_d = 594 °C); however, this polymer has limited utility because it is insoluble in common organic solvents. A two-step weight loss by **Poly-8**, **Poly-10**, and **Poly-11** indicated that the most likely decomposition pathways for PAEs studied here are initial decomposition of the *tert*-butyl groups via loss of isobutylene followed by chain scission above 500 °C. TMA of **Poly-10** indicated that the PAEs were generally more acceptable for integration into semiconductor devices, with a thermal expansion coefficient of 30 ppm/°C.

The general ability of the triptycene to increase the stability of the polymers is interesting and may be the result of decreased interactions between the backbones of neighboring chains and/ or a rigidified solid-state structure. In our studies of semiconducting polymers containing similar functionalities, we found that triptycene residues generally reduce interactions between polymer backbones.[42] It is interesting to note that decreased interchain interactions normally decrease the T_g of a polymer; however, the rigid three-dimensional nature of the triptycenes appears to increase the rigidities of the polymer chain, increasing T_g.

Since low water absorption is important to maintaining a low dielectric constant after application of the polymer, the percent water absorbed at 100% relative humidity was determined by quartz crystal microbalance where a polymer sample was drop cast onto both sides of the quartz crystal (∼0.1 μm thick on each side of the crystal). Nearly all the polymers synthesized herein showed water absorptions of 1.1 wt % or less (Table 1). This was seen regardless of fluorine incorporation, as even ROMP polymers **Poly-2** and **Poly-3** only absorbed 1.0 and 1.1 wt %, respectively. The imide containing polymers **Poly-6** and **Poly-7** had much higher water absorptions, 5.1 and 3.7%, respectively, as would be expected from the inclusion of the hydrophilic imide functionalities. Small differences in advancing and receding contact angles of polymers **Poly-3** and **Poly-8**−**11** indicate that the spin-coated films are highly uniform and smooth.

Conclusions

We have shown that the triptycene can be used in the tailored design of polymers to introduce free volume at the molecular scale and, thereby, produce polymers with lower dielectric constants that are potentially useful to the semiconductor industry. Further, triptycene does not have a deleterious effect on bulk properties, as these triptycene containing polymers do not display any glass transitions, are highly thermally stable, and exhibit very low water absorption. All of these characteristics are desired for the next generation of microprocessors and memory for computers to provide insulation in the increasingly shrinking feature sizes of faster microprocessors. We believe these materials are viable candidates for evaluation for and incorporation into future generations of microchips.

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Experimental Section

Materials. *p*-Benzoquinone, CuCl, dimethyl sulfate, maleic anhydride, naphthacene, 1-adamantanol, *N,N*-dimethylacetamide (99%, anhydrous), *N,N*-dimethylformamide (anhydrous, sure-seal), and potassium carbonate were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Dicyclopentadiene (Aldrich) was freshly cracked prior to use. Et$_2$O (absolute) was from EM Sciences (Gibbstown, NJ) and used as received. MeCN and AcOH (glacial) were purchased from Mallinckodt Baker (Paris, KY) and used as received. Na$_2$S$_2$O$_4$ (85% technical grade) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. Dichloromethane for ROMP polymerizations was collected from a dry still (activated alumina) and stored over 4 Å sieves.

Characterization. Capacitor devices for the determination of dielectric constants were built on freshly cleaned glass via a multistep cleaning process: (1) Sonicate in aqueous detergent (1% v/v, 5 min); (2) deionized (DI) water rinse; (3) sonicate in DI water (2 min); (4) repeat steps 2 and 3; (5) sonicate in acetone 2× (2 min each); (6) heat in boiling 1,1,2-trichloroethane 2× (2 min each); (7) sonicate in acetone (2 min); (8) heat in boiling *i*PrOH (2×, 2 min each); (9) dry with stream of air; (10) clean with UV/ozone cleaner. The evaporation of maluminum was performed on a homemade evaporator setup in the labs of Prof. Vladimir Bulovic (MIT, Department of Electrical Engineering). Polymers were applied by spin-coating polymer solutions of 10−15 mg/mL polymer in chloroform at a rate of 2000 rpm for 1 min. The capacitances were measured on an HP 4192A LF Impedance Analyzer connected to a Wenthworth Labs (Brookfield, CT) model no. 001-1120 Four Point Probe Station and fit for a capacitor and resistor in parallel. Polymer thicknesses were measured on a Tencor P10 Surface Profilometer.

TGA was on a Perkin-Elmer TGA7 under N$_2$ at a rate of 10 °C /min. TMA was on pressed polymer pellets in a Perkin-Elmer TMA7 at a rate of 10 °C /min between 50 and 250 °C. DSC were performed on a Perkin-Elmer DSC7 under N$_2$ at a rate of 10 °C/min. Water contact angles were determined on a VCA2000 Video Contact Angle System on freshly prepared substrates. The glass was cleaned to ensure hydrophilicity by cleaning with (1) detergent solution (30 min sonication); (2) DI water rinse; (3) saturated NaOH/EtOH for 15 min; (4) DI water rinse; (5) HNO$_3$ (concentrated) for 15 min; (6) DI water rinse; (7) sonication in EtOH for 30 min and dried in an oven at 100 °C. The films were spin-coated as above and dried under vacuum. Ellipsometry was on a Gaertner Scientific Three Wavelength Variable Angle Ellipsometer on freshly prepared films as above.

Water absorption was on a home-built QCM setup with crystals and oscillator from the International Crystal Manufacturing Co. (10 MHz, Au electrodes). The crystal frequency was measured with a HP53131A Universal counter and collected by Lab-View 5.0 running on a Macintosh Powerbook 5300cs. Films were applied by drop casting 4 µL of a 4 mg/ml concentration solution on either side of the crystal to induce an ∼40 kHz change in frequency. Films on either side of the crystal were calculated to be ∼0.1 µm thick. Blank crystal and polymer frequencies were measured at low humidity <5%, and water was introduced by purging the system (in an enclosed desiccator) with air bubbled through water and the frequency recorded when the film became saturated. All polymer solutions were filtered through 0.45 µm syringe filters prior to use. Polymer molecular weights were determined on an HP Series 1100 GPC system in THF at room temperature versus polystyrene standards.

6,10-Di(*tert*-butyl)triptycene-1,4-quinone (1). In 70 mL of glacial acetic acid were added 2,6-di(*tert*-butyl)anthracene (3.87 g, 13.3 mmol), *p*-benzoquinone (7.00 g, 35 mmol), and CuCl (1.30 g, 13.1 mmol), and the solution was heated to reflux for 2 h. The reaction was cooled and quenched by pouring into water. The precipitate was filtered, washed with hot water, dissolved in dichloromethane, and flushed through a plug of silica gel with dichloromethane. Removal of the solvent in vacuo yields **1** as an orange solid (4.87 g, 92%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, 2H, *J* = 1.5 Hz), 7.34 (d, 2H, *J* = 8.0

Hz), 7.04 (dd, 2H, *J* = 7.8 Hz, *J* = 1.8 Hz), 6.56 (s, 2H), 5.74 (s, 2H), 1.25 (s, 18H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 183.9, 152.5, 149.0, 143.9, 140.9, 135.5, 124.0, 122.2, 122.0, 47.4, 34.8, 31.7; FTIR (KBr) ν/cm^{-1}: 2964, 2901, 2867, 1648, 1576, 1480, 1307, 1262, 1122, 987, 846, 822. HRMS (EI): calcd for C$_{28}$H$_{28}$O$_2$, 396.2084 (M+); found, 396.2081. Mp 249−51 °C.

6,11-[1′2′]-Benzeno-1,4-methano-1,4,6,11-tetrahydrotetracene-5,-12-dione (2). To a suspension of triptycene-1,4-quinone (1.42 g, 5.0 mmol) in 100 mL of MeCN at 0 °C was added freshly cracked cyclopentadiene (3.5 mL, 50 mmol), and the solution was stirred at 0 °C for 2.5 h. The cooling apparatus was removed, and the solution was allowed to warm to room temperature over 17 h. The solvent was removed in vacuo, and the resulting residue was titurated with MeOH to give **2** as a pale yellow solid (1.39 g, 80%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (dd, 2H, *J* = 5.5 Hz, *J* = 3.3 Hz), 7.37 (dd, 2H, *J* = 5.5 Hz, *J* = 3.3 Hz), 7.02 (dd, 2H, *J* = 5.5 Hz, *J* = 3.0 Hz), 6.99 (dd, 2H, *J* = 5.5 Hz, *J* = 3.3 Hz), 5.74 (s, 2H), 5.62 (s, 2H), 3.47 (s, 2H), 3.18 (s, 2H), 1.45 (d, 1H, *J* = 9.0 Hz), 1.37 (1H, d, *J* = 9.0 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 195.3, 157.8, 143.75, 143.68, 134.8, 125.7, 125.6, 124.6, 124.3, 49.9, 49.2, 49.1, 47.8; FTIR (KBr) ν/cm^{-1} 2960, 2862, 1753, 1733, 1658, 1458, 1274, 752, 609. HRMS (EI): calcd for C$_{25}$H$_{18}$O$_2$, 350.1301 (M+); found, 350.1311. Mp 165 °C (dec).

Compound 3. To a suspension of **1** (1.88 g, 5.0 mmol) in 50 mL of MeCN was added freshly cracked cyclopentadiene (5.0 mL, 71 mmol), and the solution was stirred at 0 °C for 3 h. The solvent was removed in vacuo, and the resulting residue was titurated with hexanes to give **3** as a pale yellow solid (1.82 g, 79%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35 (m, 4H), 7.00 (m, 2H), 5.67 (s, 2H), 5.59 (m, 2H), 3.47 (s, 2H), 3.18 (s, 2H), 1.46 (d, 1H, *J* = 8.7 Hz), 1.38 (d, 1H, *J* = 8.4 Hz), 1.31 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 159.2, 158.07, 158.04, 148.7, 148.5, 143.6, 140.7, 134.7, 134.4, 123.8, 123.5, 122.0, 121.9, 121.86, 121.5, 50.02, 49.95, 49.14, 49.10, 47.8, 34.90, 34.85, 31.8; FTIR (KBr) ν/cm^{-1} 2963, 2904, 2868, 1660, 1607, 1481, 1363, 1301, 1264, 1195. HRMS (EI): calcd for C$_{33}$H$_{34}$O$_2$, 462.2553 (M+); found, 462.2569. Mp 160 °C (dec).

6,11-[1′2′]-Benzeno-1,4-methano-5,12-dimethoxy-1,4,6,11-tetrahydrotetracene (4). To a −15 °C solution of **2** (975 mg, 2.78 mmol) in 25 mL of DMF was added NaH (60% w/w in oil, 300 mg, 7.50 mmol), and the solution was stirred at −15 °C for 1 h. Me$_2$SO$_4$ (2.4 mL, 25.0 mmol) was added, the cooling apparatus removed, and the solution warmed to room temperature over 3 h. The reaction was quenched in dilute NH$_4$Cl and extracted with dichloromethane. The combined organic extracts were washed with dilute NH$_4$Cl and saturated NaCl and dried over MgSO$_4$. After filtration, the solvent was removed in vacuo. The resulting solid can be purified by column chromatography over silica gel with 1:1 hexanes/chloroform followed by recrystallization from MeOH to yield pure **4** (617 mg, 59%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (m, 4H), 6.98 (m, 4H), 6.75 (t, 2H, *J* = 2.5 Hz), 5.72 (s, 2H), 4.07 (m, 2H), 3.84 (s, 6H), 2.19 (d, 1H, *J* = 9.0 Hz), 2.09 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 146.6, 146.2, 146.1, 143.1, 140.5, 136.3, 125.17, 125.14, 123.8, 123.7, 69.5, 62.5, 48.3, 47.6; FTIR (KBr) ν/cm^{-1} 2989, 2976, 2940, 2821, 1474, 1458, 1304, 1262, 1245, 1226, 1105, 1040, 976, 759, 612. HRMS (EI): calcd for C$_{27}$H$_{22}$O$_2$, 378.1614 (M+); found, 378.1604. Mp 210−2 °C.

Compound 5. To a −15 °C solution of **3** (1.15 g, 2.50 mmol) in 25 mL of DMF was added NaH (60% w/w in oil, 300 mg, 7.50 mmol), and the solution was stirred at −15 °C for 1.5 h. Me$_2$SO$_4$ (2.4 mL, 25 mmol) was added, and the reaction stirred at 0 °C for 1 h. The cooling apparatuswas removed, and the solution was warmed to room temperature over 12 h. The reaction was quenched in dilute NH$_4$Cl and extracted with chloroform. The combined organic extracts are washed with dilute NH$_4$Cl and saturated NaCl and dried over MgSO$_4$. After filtration, the solvent was removed in vacuo. The resulting solid can be purified by recrystallization from CHCl$_3$/MeOH to yield **5** as a white solid (971 mg, 80%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (dd, 2H, *J* = 7.2 Hz, *J* = 1.8 Hz), 7.27 (d, 2H, *J* = 7.5 Hz), 6.97 (m, 2H), 6.74

(t, 2H, *J* = 1.8 Hz), 5.65 (s, 2H), 4.04 (m, 2H), 3.83 (pr. s, 6H), 2.17 (m, 1H), 2.09 (m, 1H), 1.24 (s, 18H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.0, 146.55, 146.50, 146.2, 146.1, 143.4, 143.3, 143.2, 143.1, 140.3, 140.2, 136.89, 136.87, 123.03, 123.01, 121.61, 121.57, 121.1, 121.0, 69.5, 62.5, 48.2, 47.6, 47.5, 34.7, 31.8; FTIR (KBr) *ν*/cm^{-1} 2961, 2862, 2827, 1478, 1425, 1302, 1267, 1050, 981, 826, 731, 609. HRMS (EI): calcd for C$_{35}$H$_{38}$O$_2$, 490.2866 (M+); found, 490.2849. Mp 240−3 °C.

***N*-(2-Triptycyl)malimide (6).** 2-Aminotriptycene (810 mg, 2.70 mmol) and maleic anhydride (294 mg, 3.00 mmol) were combined, 10 mL of chloroform was added, and the solution stirred for 1 h. The reaction was cooled in the refrigerator, and the precipitate filtered and transferred to a clean flask. Acetic anhydride (12 mL) was added, and the solution was heated to 100 °C. NaOAc (250 mg) was added and heated for another 1.5 h. After the solution was cooled, it was poured into water, stirred for 0.5 h, extracted with chloroform, washed with water, and dried over MgSO$_4$. After filtration, the solvent was removed in vacuo, and the crude solid was heated with 200 mL hexanes and filtered hot. The filtrate was cooled, and the precipitate was filtered to yield **6** as a bright yellow solid (932 mg, 98%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.41 (d, 1H, *J* = 7.8 Hz), 7.33 (m, 5H), 6.96 (m, 4H), 6.90 (dd, 1H, *J* = 7.5 Hz, *J* = 2.0 Hz), 6.60 (s, 2H), 5.43 (s, 1H), 5.42 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.6, 146.4, 145.2, 144.7, 144.6, 134.0, 127.8, 125.38, 125.35, 124.1, 123.9, 123.7, 123.0, 121.7, 54.0, 53.9; FTIR (KBr) *ν*/cm^{-1} 3477, 3064, 2958, 1713, 1490, 1470, 1398, 1379, 1224, 1201, 1143, 828, 746, 694. HRMS (EI): calcd for C$_{24}$H$_{15}$-NO$_2$, 349.1097 (M+); found, 349.1085. Mp 123 °C (dec).

Compound 7. To a suspension of **6** (698 mg, 2.0 mmol) in 20 mL of MeCN at 0 °C was added freshly cracked cyclopentadiene (1.40 mL, 20 mmol), and the solution was stirred at 0 °C for 2.5 h. The cooling apparatus was removed, and the solution was allowed to warm to room temperature over 17 h. The solvent was removed in vacuo, and the resulting residue was titurated with hexanes to give **7** as a white solid (700 mg, 84%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, 1H, *J* = 8.0 Hz), 7.35 (m, 5H), 7.12 (s, 1H), 6.98 (m, 4H), 6.75 (dd, 1H, *J* = 8.5 Hz, *J* = 2.0 Hz), 6.22 (s, 2H), 5.42 (s, 1H), 5.39 (s, 1H), 3.44 (s, 2H), 3.34 (s, 2H), 1.72 (d, 1H, *J* = 8.5 Hz), 1.53 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 177.2, 146.4, 145.9, 144.9, 144.8, 134.8, 128.6, 125.48, 125.46, 124.2, 124.0, 123.9, 123.6, 122.2, 54.0, 53.9, 52.4, 45.9, 45.6; FTIR (KBr) *ν*/cm^{-1}: 2989, 1769, 1713, 1488, 1469, 1376, 1188, 742, 722. HRMS (EI): calcd for C$_{29}$H$_{21}$NO$_2$, 415.1567 (M+); found, 415.1554. Mp 290 °C (dec).

6,11-Di(*tert*-butyl)triptycene-1,4-hydroquinone (9). To a solution of **1** (600 mg, 1.51 mmol) in 25 mL of Et$_2$O was added a solution of Na$_2$S$_2$O$_4$ (1.25 g, 6.05 mmol) in 25 mL of H$_2$O and stirred vigorously for 1 h. The organic layer was separated, the aqueous layer was extracted with Et$_2$O, and the extracts were combined. The organic layer was washed with water and saturated NaCl (aq). After drying over Mg-SO$_4$ and filtration, the solvent was removed in vacuo to yield **9** as a tan solid (446 mg, 77%). Analytically pure samples may be obtained from recrystallization from EtOAc/hexanes. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.82 (s, 2H), 7.40 (d, 2H, *J* = 2.1 Hz), 7.29 (d, 2H, *J* = 7.5 Hz), 6.95 (dd, 2H, *J* = 8.1 Hz, *J* = 1.8 Hz), 6.32 (s, 2H), 5.75 (s, 2H), 1.22 (s, 18H); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 147.3, 145.8, 144.8, 143.1, 132.4, 123.0, 121.0, 120.6, 112.8, 46.6, 34.3, 31.4; FTIR (KBr) *ν*/cm^{-1} 3334, 2961, 2869, 1606, 1487, 1365, 1264, 1214. HRMS (EI): calcd for C$_{28}$H$_{30}$O$_2$, 398.2240 (M+); found, 398.2255. Mp 338 °C (dec).

General Procedure for Preparation of ROMP Polymers. In a drybox, Grubbs catalyst (Scheme 4.4) was massed in a vial and dissolved in 1 mL of dichloromethane. In a separate vial was prepared a solution of monomer in a minimum volume of dichloromethane. The monomer solution is added rapidly to the stirring solution of catalyst and stirred at room temperature for 2 h. After 2 h, the reaction was removed from the drybox, and an excess of ethyl vinyl ether was added to quench the reaction and stirred for at least 1 h. The polymer was isolated by precipitation into MeOH followed by vacuum filtration and drying in vacuo overnight.

Poly-1. 8 (82 mg), catalyst (5.0 mg), yield 68 mg (83%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.58 (br. s, 2H), 5.48 (m, 2H), 4.25 (br. s, 2H), 3.71 (s, 6H), 2.66 (m, 1H), 1.79 (m, 1H).

Poly-2. 4 (255 mg), catalyst (6.5 mg), yield 245 mg (96%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.29 (m, 4H), 6.79 (m, 4H), 5.67 (br. s, 2H), 5.41 (br. s, 2H), 3.98 (br. s, 2H), 3.68 (br. s, 6H), 2.45 (br. s, 1H), 1.67 (br. s, 1H).

Poly-3. 5 (114 mg), catalyst (3.0 mg), yield 100 mg (88%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.31 (br. s, 2H), 7.25 (br. s, 2H), 6.87 (br. s, 2H), 5.62 (br. s, 2H), 5.47 (br. s, 2H), 4.01 (br. s, 2H), 3.74 (br. s, 6H), 2.49 (br. s, 1H), 1.83 (br. s, 1H), 1.12 (br. s, 18H).

Poly-4. 8 (26 mg), **4** (47 mg), catalyst (2.8 mg), yield 52 mg (71%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36 (br. s, 4H), 6.92 (br. s, 4H), 6.39 (br. s, 2H), 5.73 (br. s, 2H), 5.38 (br. s, 4H), 4.06 (br. s, 4H), 3.73 (m, 12H), 2.50 (br. s, 2H), 1.85 (br. s, 2H).

Poly-5. 8 (27 mg), **5** (53 mg), catalyst (2.8 mg), yield 53 mg (66%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.41 (br. s, 2H), 7.27 (br. s, 2H), 6.97 (br. s, 2H), 6.45 (br. s, 2H), 5.70 (br. s, 2H), 5.43 (br. s., 4H), 4.09 (br.s, 4H), 3.68 (m, 12H), 2.50 (br. s, 2H), 1.75 (br. s, 2H), 1.24 (br. s, 18H).

Poly-6. *N*-Phenylmaleimide−cyclopentadiene adduct (123 mg), catalyst (2.9 mg), yield 112 mg (91%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50−7.00 (m, 5H), 5.80−5.60 (m, 2H), 3.33 (m, 3H), 2.96 (br. s, 1H), 1.90 (br. s, 1H), 1.42 (br. s, 1H).

Poly-7. 7 (100 mg), catalyst (3.1 mg), yield 80 mg (80%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34 (m, 7H), 6.95 (m, 5H), 5.65 (br. s, 2H), 5.43 (br. s, 2H), 3.27 (m, 3H), 2.88 (br. s, 1H), 1.85 (br. s, 1H), 1.31 (br. s, 1H)

General Procedure for Preparation of Poly(aryl ether)s. A solution of hydroquinone and decafluorobiphenyl was prepared in DMA and purged with Ar. K$_2$CO$_3$ (2.4 equiv) was added, and the solution was heated to 150 °C for 3 h. Acetic anhydride was added, and then the solution was added dropwise to 1:1 MeOH/water. The polymer was collected by vacuum filtration and dried in vacuo overnight with heating.

Poly-8. 9 (199 mg, 0.5 mmol), decafluorobiphenyl (167 mg, 0.5 mmol), K$_2$CO$_3$ (152 mg, 1.1 mmol), DMA (7.5 mL), yield (235 mg, 68%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.52 (s, 2H), 7.39 (br. d, 2H), 7.09 (br. d, 2H), 6.50 (s, 2H), 6.01 (s, 2H), 1.31 (s, 18H).

Poly-9. Pentiptycene-6,13-hydroquinone (231 mg, 0.5 mmol), decafluorobiphenyl (167 mg, 0.5 mmol), K$_2$CO$_3$ (152 mg, 1.1 mmol), DMA (7.5 mL), yield (351 mg, 90%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.12 (m, 8H), 6.92 (m, 8H), 5.59 (s, 4H).

Poly-10. Pentiptycene-6,13-hydroquinone (115 mg, 0.25 mmol), monomer **9** (99 mg, 0.25 mmol), decafluorobiphenyl (167 mg, 0.5 mmol), K$_2$CO$_3$ (152 mg, 1.1 mmol), DMA (7.5 mL), yield (353 mg, 97%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.52 (m, 2H), 7.41 (m, 2H), 7.12 (m, 10H), 6.93 (m, 8H), 6.51 (m, 2H), 6.04 (m, 2H), 5.60 (m, 4H), 1.32 (m, 18H).

Poly-11. Pentiptycene-6,13-hydroquinone (154 mg, 0.33 mmol), **9** (66 mg, 0.17 mmol), decafluorobiphenyl (167 mg, 0.5 mmol), K$_2$CO$_3$ (166 mg, 1.2 mmol), DMA (5.0 mL), yield (312 mg, 85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52 (m, 1H), 7.41 (m, 1H), 7.12 (m, 9H), 6.93 (m, 8H), 6.51 (m, 1H), 6.04 (m, 1H), 5.60 (m, 4H), 1.32 (m, 9H).