Supplementary Information

Molecular-level Insight into the Low-*k* Properties and Regulatory Mechanisms of Polybenzoxazines

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S1. Experimental Procedures

S1.1 Materials. Trichloromethane and hydrochloric acid (35.0–38.0 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,3-bis(aminopropyl)tetramethyl disiloxane (aptmds), 4,4'-cyclohexylidenebisphenol, and N.N-dimethylformamide were obtained from Shanghai Macklin Biochemical Co., Ltd. Paraformaldehyde, 4-cyclohexylphenol, hexane, and sodium hydroxide were obtained from Shanghai Titan Scientific Co., Ltd. All chemicals were of analytical grade and used as received.

S1.2 Synthesis of benzoxazine prepolymer C-aptmds. Paraformaldehyde (2.40 g, 80 mmol), 1,3-bis(aminopropyl)tetramethyl disiloxane (4.97 g, 20 mmol), and trichloromethane were introduced in a flask mixed with a mechanical agitator and heated to 60 °C. Then, 4-cyclohexylphenol (7.05 g, 40 mmol) dissolved in trichlomethane was added to the mixture. The crude product was obtained after maintaining the reaction at 80 °C for 6 h. Then, the crude product was washed sequentially with NaOH aqueous, HCl aqueous, and deionized water. The solvent was removed using a rotary evaporator and the residual water was removed using freeze drying, obtaining a viscous reddish-brown liquid named C-aptmds (yield 89.6%).

S1.3 Synthesis of benzoxazine prepolymer BZ-aptmds. Paraformaldehyde (2.40 g, 80 mmol), 1,3-bis(aminopropyl)tetramethyl disiloxane (4.97 g, 20 mmol), 4,4'-cyclohexylidenebisphenol (5.37 g, 20 mmol) and trichloromethane were introduced in a flask mixed with a mechanical agitator and heated to 80 °C. The crude product was obtained after maintaining the reaction for 6 h. After the same washing process as C-aptmds, the crude product was added to hexane to precipitate. The precipitate was then dried to obtain a yellow powder named BZ-aptmds (yield 76.8%).

S1.4 Synthesis of benzoxazine prepolymer CBZ-aptmds. Paraformaldehyde (3.60 g, 120 mmol), 4-cyclohexylphenol (3.52 g, 20 mmol), 1,3-bis(aminopropyl)tetramethyl disiloxane (7.46 g, 30 mmol), 4,4'-cyclohexylidenebisphenol (5.37 g, 20 mmol) and trichloromethane were introduced in a flask mixed with a mechanical agitator and heated to 80 °C. The crude product was obtained after maintaining the reaction for 6 h. After the same washing process as C-aptmds, the crude product was added to hexane. The precipitate was filtered off and the solvent was removed to obtain a viscous yellow liquid named CBZ-aptmds (yield 58.3%).

S1.5 Preparation of polybenzoxazines. Polybenzoxazines were all prepared by mold casting. C-aptmds and CBZ-aptmds were poured directly into the mold and heated for 1 h in a vacuum drying oven at 70 °C. Then, PC-aptmds and PCBZ-aptmds were obtained after the following curing process: 120 °C (1 h), 150 °C (1 h), 180 °C (1 h), 200 °C (1 h), 210 °C (1 h), and 220 °C (6 h). BZ-aptmds was dissolved in N.N-dimethylformamide first and poured into the mold. PBZ-aptmds was obtained after the following curing process: 120 °C (1 h), 150 °C (1 h), and 180 °C (6 h).

S1.6 Measurements and characterizations. Fourier transform infrared spectroscopy (FT-IR) was obtained on a Thermo Fisher Scientific Nicolet IS10 analyzer using the KBr pellet method. Nuclear magnetic resistance spectroscopy (NMR) was recorded on a German Bruker AVANCE at a proton frequency of 600 MHz Gel permeation chromatography (GPC) was recorded on an Agilent PL-GPC220. Differential scanning calorimetry (DSC) was carried out on a Q2000 TA instrument with a temperature rate of 10 °C/min and a nitrogen flow rate of 40 mL min^{-1}. A TA Q500 thermogravimetric analyzer (TGA) was employed to characterize the mass loss from 40 to 800 °C at a temperature rate of 10 °C min^{-1}. A Mettler-Toledo DMA1 dynamic mechanical analyzer (DMA) was used to determine the storage modulus E' and the loss factor Tan(δ) using double cantilever mode at a temperature rate of 3 °C min^{-1}. Surface morphologies of the polybenzoxazines were observed with an FEI Nova NanoSEM 450 scanning electron microscopy (SEM). Wettability data were obtained through a Dataphysics OCA20 optical goniometer operating at room temperature. The water absorption test was conducted by IP-TM650-2.6.2.1. The dielectric properties in the range of 100 Hz to 1 MHz were tested at room temperature using a Novocontrol concept 40 broadband dielectric spectrometer.

S1.7 Computational Methods. MD simulation was carried out with COMPASS force field using the Forcite module in Materials Studio. Several benzoxazine monomer chains were packed in the periodic simulated box to ensure the total number of atoms was around 10000. The initial density of the periodic simulated box was set as 0.1 g cm^{-3} to prevent ring spearing. NPT molecular dynamics equilibrium was performed by applying pressures of 0.5 GPa and 0.1 MPa to the box in turn. Then the Perl programming language was applied to realize the automated crosslinking reaction. The flowchart is shown in Figure S6 (Supporting Information), where Rn is the cutoff radius, Rmax is the max cutoff radius, R1 is the carbon atom in the ortho position of the phenoxy group and R2 is the carbon atom attached to the Oxygen atom in the oxazine ring. Rn was set as 2.0 Å and Rmax was set as 9.0 Å. The calculations of electronic and Van der Waals interactions using Ewald summation and atom-based method, respectively. Then, MD optimizations were employed according to the following procedures: (1) Anneal the box from 298 to 598 K; (2) Optimize the box by a 1 ns NPT ensemble; (3) Optimize the box by a 10 ns NVT ensemble.

Quantum chemical simulation was carried out with the Gaussian program. Firstly, geometric optimization and frequency analysis of repeating units were performed by the DFT method on the B3LYP theory level with 6-31G (d, p) as the basis set. Then, the B3LYP functional with 6-311G (d, p) was employed to analyze the energy, and the CAM-B3LYP functional with 6-311G++(d, p) was used to calculate polarizability. DFT-D3(BJ) was used for dispersion correction in all DFT simulations.

S2. Results and Discussion

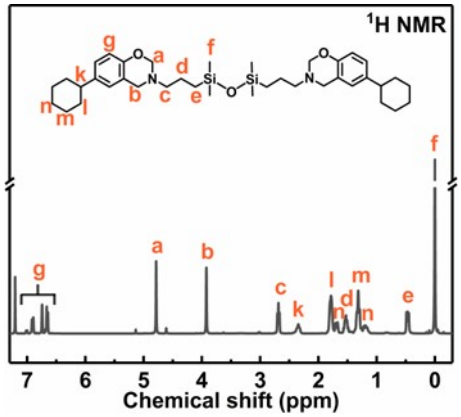

Figure S1. ^{1}H NMR spectrum of C-aptmds.

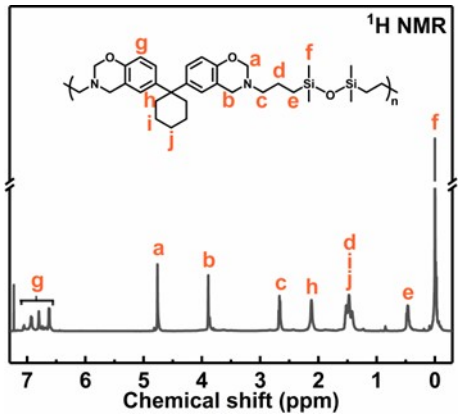

Figure S2 ^{1}H NMR spectrum of BZ-aptmds.

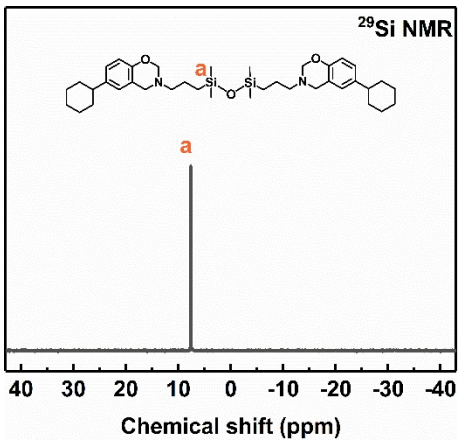

Figure S3 ^{29}Si NMR spectrum of C-aptmds.

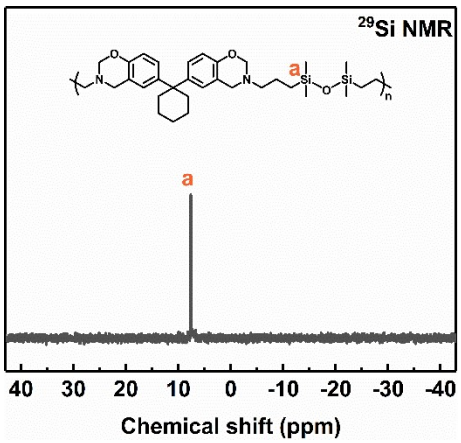

Figure S4 ^{29}Si NMR spectrum of BZ-aptmds.

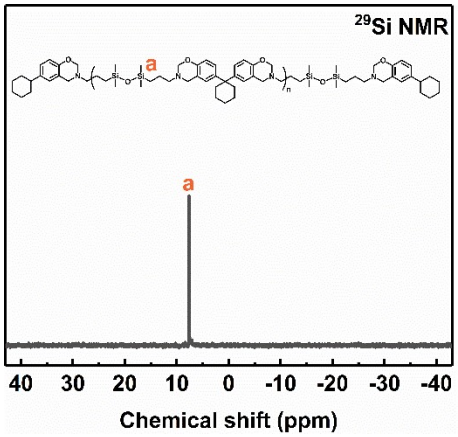

Figure S5 ^{29}Si NMR spectrum of CBZ-aptmds.

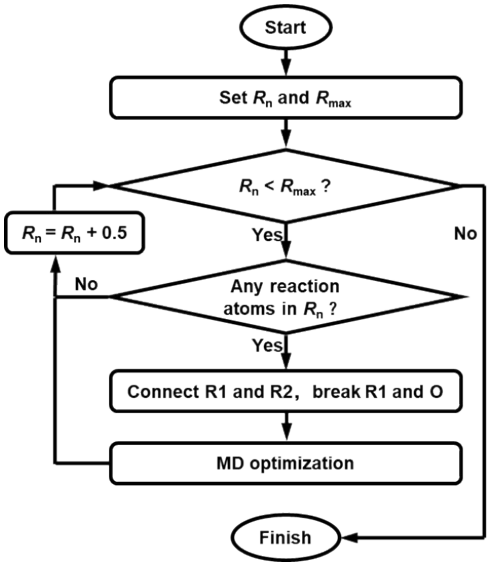

Figure S6. Flowchart for implementing ring-opening polymerization of benzoxazine using perl language.

Table S1. Summary of TGA and DMA results of polybenzoxazines.

Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	CY (%)	E' (GPa)	ρ_x (mol/cm^3)	T_g (°C)	T_{gDFT} (°C)
PC-aptmds	306	338	8.66	2.5	2.15E-3	95	90
PBZ-aptmds	300	342	21.36	3.8	2.99E-3	179	187
PCBZ-aptmds	314	344	12.70	3.0	2.95E-3	132	115

Table S2. Polarizability of each atom in PC-aptmds.

Atom	Polarizability (a.u.)	Proportion of polarizability (%)
1(C)	5.29108359	1.306925
2(C)	-6.06758028	-1.498724
3(C)	-6.97774559	-1.723539
4(C)	2.90900887	0.71854
5(C)	23.09754639	5.705214
6(C)	25.12534141	6.206089
7(H)	-4.61003055	-1.138701
8(H)	23.8811899	5.898778
9(H)	24.14710491	5.96446
10(C)	-0.07817413	-0.019309
11(C)	0.41063286	0.101428
12(C)	5.42634498	1.340335
13(H)	-6.74408533	-1.665824
14(C)	0.25145148	0.06211
15(H)	11.55776828	2.854829
16(H)	-8.97873429	-2.217794
17(C)	6.44730217	1.592517
18(H)	21.70620267	5.361544
19(H)	8.32898519	2.057302
20(C)	4.92145927	1.215626
21(H)	-1.90519599	-0.470593
22(H)	-8.09784828	-2.00021
23(H)	27.85433719	6.880166
24(H)	-7.77102018	-1.919482
25(H)	5.40592872	1.335292
26(H)	23.43131575	5.787656
27(O)	13.26298798	3.276027
28(H)	-3.75490488	-0.927481
29(C)	1.55448896	0.383967
30(H)	1.19873571	0.296094
31(H)	0.02162154	0.005341
32(N)	1.80080792	0.444809
33(C)	1.63855132	0.404731
34(H)	3.17384152	0.783955
35(H)	2.91503657	0.720029
36(C)	1.90562518	0.470699
37(H)	1.96659987	0.48576
38(H)	3.87908052	0.958153
39(C)	1.99924592	0.493824

40(H)	6.02408768	1.487981
41(H)	1.2694155	0.313552
42(C)	2.55088258	0.630081
43(H)	2.50024147	0.617573
44(H)	4.79040663	1.183255
45(H)	0.61230037	0.151241
46(Si)	2.74566638	0.678194
47(O)	0.24691103	0.060988
48(Si)	1.64906148	0.407327
49(C)	5.44417674	1.34474
50(H)	29.3760484	7.256036
51(H)	3.21723481	0.794674
52(C)	1.65369131	0.40847
53(H)	-8.95106647	-2.21096
54(H)	1.6459596	0.406561
55(C)	3.84003628	0.948509
56(H)	3.98096445	0.983319
57(H)	30.09372748	7.433307
58(N)	-8.42059934	-2.079932
59(C)	2.79806273	0.691136
60(H)	-6.96786507	-1.721099
61(H)	25.96963919	6.414635
62(H)	1.69679267	0.419117
63(C)	1.5504495	0.382969
64(H)	21.27498874	5.255032
65(H)	-6.10737448	-1.508553
66(H)	-4.49437045	-1.110133
67(C)	4.78313348	1.181459
68(H)	-1.93271294	-0.47739
69(H)	28.50544642	7.040993
70(H)	-5.5652566	-1.374647
71(C)	6.92226163	1.709834
72(H)	-2.33697451	-0.577245
73(H)	0.76162383	0.188125
74(H)	32.37848595	7.997654
75(C)	2.40349302	0.593675
76(H)	2.75005295	0.679277
77(H)	4.94525695	1.221504
78(H)	1.07442082	0.265388
79(C)	2.77923986	0.686487
80(H)	5.13555394	1.268508
81(H)	0.83365774	0.205918
82(H)	0.89835226	0.221898
Sum	404.84981115	100

Table S3. Polarizability of each atom in PBZ-aptmds.

Atom	Polarizability (a.u.)	Proportion of polarizability (%)
1(C)	5.10992903	1.172712
2(C)	2.70562981	0.620933
3(C)	2.89140100	0.663567
4(C)	2.87721618	0.660312
5(C)	3.04269805	0.698289
6(C)	5.96278663	1.368440
7(H)	0.44927197	0.103106
8(H)	0.60480649	0.138801
9(H)	4.30007133	0.986852
10(C)	0.32367177	0.074282
11(C)	1.36047557	0.312225
12(C)	2.41790861	0.554902
13(C)	1.26899495	0.291230
14(H)	-0.01903293	-0.004368
15(H)	-0.36467386	-0.083691
16(C)	6.08803855	1.397185
17(H)	-3.16979822	-0.727458
18(H)	9.16246739	2.102757
19(C)	2.62789041	0.603092
20(H)	-1.53353153	-0.351941
21(H)	6.01922688	1.381393
22(H)	13.53155506	3.105448
23(H)	15.34110074	3.520733
24(H)	7.12562440	1.635308
25(H)	-2.65034218	-0.608245
26(O)	7.79104466	1.788019
27(H)	5.27939329	1.211604
28(C)	1.44436412	0.331477
29(H)	0.27594483	0.063328
30(H)	10.42693219	2.392947
31(N)	-0.38005154	-0.087221
32(C)	2.86549554	0.657622
33(H)	17.52820006	4.022665
34(H)	1.87282657	0.429808
35(H)	-1.31713219	-0.302278
36(C)	2.53270363	0.581247
37(H)	16.54722358	3.797534
38(H)	-1.14199199	-0.262083
39(C)	2.10735130	0.483630
40(H)	4.67573698	1.073066
41(H)	-1.03911623	-0.238474
42(C)	2.52391078	0.579229
43(H)	12.67365175	2.908562
44(H)	-1.27257235	-0.292051
45(Si)	0.60172174	0.138093
46(O)	-0.01083737	-0.002487

47(Si)	1.47522100	0.338558
48(C)	4.33598526	0.995095
49(H)	10.80076987	2.478742
50(H)	11.44455356	2.626488
51(C)	1.25357579	0.287692
52(H)	-1.74854802	-0.401286
53(H)	-1.27680382	-0.293022
54(C)	3.24695286	0.745165
55(H)	13.84150219	3.176580
56(H)	8.20910036	1.883962
57(N)	-1.24987009	-0.286841
58(C)	3.29546980	0.756300
59(H)	-2.48333081	-0.569916
60(H)	14.77863076	3.391648
61(H)	6.63175025	1.521965
62(C)	1.30987124	0.300611
63(H)	3.78776753	0.869280
64(H)	-0.06457566	-0.014820
65(H)	0.04387854	0.010070
66(C)	5.46794387	1.254875
67(H)	-1.61978834	-0.371736
68(H)	14.74452840	3.383821
69(H)	9.00462371	2.066532
70(C)	5.66935586	1.301099
71(H)	16.54151592	3.796224
72(H)	0.42526887	0.097598
73(H)	5.66739989	1.300650
74(C)	2.14270163	0.491743
75(H)	1.07499356	0.246708
76(H)	1.85773678	0.426345
77(H)	2.20122546	0.505174
78(C)	2.81357561	0.645706
79(H)	2.33855067	0.536690
80(H)	3.82142455	0.877005
81(H)	0.86878274	0.199383
82(C)	-8.10434971	-1.859922
83(C)	5.25524933	1.206063
84(C)	-5.73228736	-1.315541
85(C)	24.31636546	5.580527
86(H)	2.86255225	0.656946
87(C)	3.52253831	0.808411
88(H)	-4.69726562	-1.078007
89(C)	18.93166899	4.344757
90(H)	25.83403751	5.928828
91(H)	1.57983647	0.362567
92(O)	29.44013990	6.756417
93(H)	22.41760179	5.144767
Sum	435.73601262	100

Table S4. Polarizability of each atom in PCBZ-aptmds.

Atom	Polarizability (a.u.)	Proportion of polarizability (%)
1(C)	-1.30069105	-0.112201
2(C)	-0.90442357	-0.078018
3(C)	-1.60040166	-0.138054
4(C)	5.52326724	0.476449
5(C)	16.35346276	1.410686
6(C)	8.74270324	0.754165
7(H)	1.97009292	0.169945
8(H)	22.20964799	1.915854
9(H)	7.71017305	0.665097
10(C)	0.88346569	0.07621
11(C)	1.348971	0.116365
12(C)	2.24879187	0.193986
13(H)	1.36047583	0.117358
14(C)	2.55895157	0.220741
15(H)	1.12697354	0.097215
16(H)	1.78724676	0.154172
17(C)	1.41069242	0.121689
18(H)	5.04982391	0.435609
19(H)	5.19951908	0.448522
20(C)	1.60223285	0.138212
21(H)	3.06117624	0.264064
22(H)	7.53702419	0.65016
23(H)	2.59615861	0.22395
24(H)	1.4451548	0.124662
25(H)	2.90428457	0.25053
26(H)	0.95856609	0.082688
27(O)	22.87856364	1.973556
28(H)	0.19512385	0.016832
29(C)	1.00815744	0.086966
30(H)	0.93132098	0.080338
31(H)	2.03105694	0.175203
32(N)	2.36806279	0.204274
33(C)	0.63739931	0.054983
34(H)	0.13434299	0.011589
35(H)	-0.1792718	-0.015464
36(C)	2.41186744	0.208053
37(H)	4.51258905	0.389266
38(H)	6.56500829	0.566312
39(C)	-0.02879152	-0.002484
40(H)	-2.27160847	-0.195954
41(H)	-2.92096516	-0.251969
42(C)	2.64653214	0.228296
43(H)	0.63152445	0.054477
44(H)	10.41957864	0.898816
45(H)	0.58002992	0.050035
46(Si)	0.45324434	0.039098
47(O)	5.08762472	0.43887
48(Si)	-0.37616147	-0.032449
49(C)	7.86951466	0.678842

50(H)	7.01578254	0.605197
51(H)	-5.77967852	-0.498568
52(H)	30.06915439	2.593832
53(C)	8.37270475	0.722248
54(H)	-3.91269543	-0.337518
55(H)	8.25336695	0.711954
56(H)	34.05552855	2.937706
57(C)	13.9140145	1.200254
58(H)	30.16661854	2.60224
59(H)	17.47362043	1.507313
60(H)	11.2220813	0.968042
61(C)	1.39528392	0.12036
62(H)	-7.31498827	-0.631007
63(H)	9.81336474	0.846523
64(H)	1.1762786	0.101468
65(C)	1.35675784	0.117037
66(H)	7.07985401	0.610724
67(H)	-2.89602836	-0.249818
68(C)	1.35072673	0.116517
69(H)	-1.35741112	-0.117093
70(H)	5.70725765	0.492321
71(C)	0.74226597	0.06403
72(H)	-0.02016657	-0.00174
73(H)	2.47696687	0.213669
74(N)	0.95558948	0.082431
75(C)	2.0445318	0.176366
76(H)	1.48054352	0.127715
77(H)	0.57284277	0.049415
78(H)	6.61994645	0.571051
79(C)	0.84020297	0.072478
80(H)	1.10547671	0.095361
81(H)	0.32942039	0.028417
82(C)	-4.12395955	-0.355742
83(C)	5.45188965	0.470292
84(C)	-4.03555532	-0.348116
85(C)	23.32358994	2.011945
86(C)	-2.56088872	-0.220908
87(H)	-1.06073655	-0.091501
88(C)	17.61694083	1.519677
89(H)	29.99773656	2.587672
90(H)	16.89718694	1.457589
91(O)	4.16899723	0.359627
92(H)	15.90669257	1.372147
93(C)	0.37936545	0.032725
94(C)	0.7567042	0.065275
95(C)	4.69437536	0.404947
96(C)	1.04548793	0.090186
97(H)	2.35837166	0.203438
98(H)	0.19338241	0.016682
99(C)	3.53162492	0.304646
100(H)	10.02613177	0.864876
101(H)	12.29843895	1.060891

102(C)	1.37500477	0.118611
103(H)	1.43020023	0.123372
104(H)	0.90541223	0.078103
105(H)	14.61554535	1.260769
106(H)	-1.61006615	-0.138888
107(H)	-0.70921382	-0.061178
108(H)	4.67502194	0.403278
109(C)	3.42243699	0.295227
110(C)	11.06845673	0.95479
111(C)	0.71839133	0.06197
112(C)	5.82723104	0.50267
113(H)	13.72200762	1.183691
114(C)	1.10630529	0.095432
115(H)	1.44507986	0.124656
116(C)	-0.32002422	-0.027606
117(H)	7.03372712	0.606745
118(O)	1.55854004	0.134443
119(H)	0.75922616	0.065493
120(C)	1.4099273	0.121623
121(H)	2.3207279	0.200191
122(H)	5.41683114	0.467268
123(N)	0.02513029	0.002168
124(C)	3.66250827	0.315936
125(H)	0.99138289	0.085519
126(H)	17.21447128	1.484959
127(C)	2.18743095	0.188693
128(H)	9.27891988	0.80042
129(H)	-2.22839356	-0.192226
130(H)	3.54727518	0.305996
131(C)	4.13897857	0.357038
132(H)	20.59760733	1.776795
133(H)	3.37868578	0.291453
134(C)	0.17320685	0.014941
135(H)	-0.02110407	-0.00182
136(H)	-4.64263362	-0.400484
137(Si)	-1.88765998	-0.162834
138(O)	-0.07902159	-0.006817
139(Si)	1.93799954	0.167176
140(C)	1.94976603	0.168191
141(H)	0.62310964	0.053751
142(H)	1.0418876	0.089876
143(H)	1.29946821	0.112095
144(C)	2.53448734	0.218631
145(H)	9.97588538	0.860542
146(H)	5.06496171	0.436915
147(C)	4.37556493	0.377446
148(H)	16.26992459	1.40348
149(H)	2.16343595	0.186623
150(H)	-1.53531039	-0.132439
151(C)	11.14387263	0.961295
152(H)	4.50708007	0.388791
153(H)	17.78159383	1.53388

154(H)	26.47042188	2.283398
155(C)	3.72931196	0.321699
156(H)	-6.99436925	-0.60335
157(H)	17.29783107	1.492149
158(H)	7.10345851	0.61276
159(C)	0.96350347	0.083114
160(H)	0.10929762	0.009428
161(H)	0.09135677	0.007881
162(C)	1.80312882	0.155542
163(H)	4.44921203	0.383799
164(H)	6.06325316	0.52303
165(N)	1.732548	0.149453
166(C)	1.36381932	0.117646
167(H)	4.32899396	0.373429
168(H)	0.1002029	0.008644
169(C)	1.8702929	0.161336
170(H)	2.49253275	0.215011
171(H)	2.82588855	0.243767
172(H)	2.8496884	0.24582
173(C)	0.47165358	0.040686
174(C)	3.91683699	0.337875
175(C)	2.80607474	0.242058
176(C)	11.15744241	0.962466
177(C)	5.9469829	0.513
178(H)	-0.99636876	-0.085949
179(C)	13.21820946	1.140232
180(H)	7.79494015	0.672409
181(H)	7.77152562	0.670389
182(O)	1.94078582	0.167417
183(H)	2.34986577	0.202705
184(C)	-0.10909049	-0.00941
185(C)	0.95220793	0.08214
186(C)	5.51856044	0.476043
187(C)	0.6589246	0.05684
188(H)	9.0218247	0.778243
189(H)	-3.39720055	-0.29305
190(C)	6.916157	0.596603
191(H)	19.39470539	1.67303
192(H)	8.21378468	0.708539
193(C)	4.89699349	0.422426
194(H)	-1.13326509	-0.097758
195(H)	-4.15117012	-0.358089
196(H)	31.43783245	2.711897
197(H)	-4.91224958	-0.423742
198(H)	6.27764694	0.541524
199(H)	21.00674734	1.812089
200(C)	6.01313491	0.518706
201(C)	0.31726496	0.027368
202(C)	8.63731556	0.745074
203(C)	0.86442584	0.074567
204(H)	0.04527999	0.003906
205(C)	2.43720107	0.210238

206(H)	11.30578141	0.975262
207(C)	0.05441341	0.004694
208(H)	1.52091746	0.131198
209(O)	4.73087362	0.408096
210(H)	0.18507535	0.015965
211(C)	1.47364858	0.12712
212(H)	3.85661841	0.33268
213(H)	3.68415674	0.317804
214(N)	-0.20180536	-0.017408
215(C)	4.21982202	0.364011
216(H)	2.04789524	0.176656
217(H)	9.46254226	0.81626
218(H)	8.30563091	0.716462
219(C)	0.90784822	0.078313
220(H)	0.33563774	0.028953
221(H)	1.47736492	0.127441
222(C)	1.8207862	0.157065
223(H)	5.92151395	0.510803
224(H)	0.32981881	0.028451
225(C)	1.649458	0.142286
226(H)	1.88748948	0.162819
227(H)	0.36847965	0.031786
228(Si)	0.88460348	0.076308
229(O)	2.93433728	0.253122
230(Si)	0.77720706	0.067044
231(C)	1.44389595	0.124554
232(H)	5.60950079	0.483888
233(H)	1.11826205	0.096464
234(C)	2.4713565	0.213185
235(H)	-3.16780205	-0.273262
236(H)	5.43021367	0.468422
237(H)	4.77704089	0.412078
238(C)	11.05820176	0.953905
239(H)	17.29581725	1.491976
240(H)	4.52945825	0.390721
241(H)	18.23741187	1.5732
242(C)	3.85631611	0.332654
243(H)	12.34567255	1.064965
244(H)	2.31526677	0.19972
245(H)	-0.82441844	-0.071116
246(C)	1.88972981	0.163012
247(H)	4.42820522	0.381987
248(H)	0.03481238	0.003003
249(H)	0.05959371	0.005141
250(C)	0.91689587	0.079093
251(H)	0.48536957	0.041869
252(H)	0.68851181	0.059393
253(C)	0.82954862	0.071559
254(H)	0.31541852	0.027209
255(H)	0.73666209	0.063546
256(N)	2.19112152	0.189011
257(C)	2.61462402	0.225543

258(H)	10.3705099	0.894583
259(H)	-1.57055606	-0.13548
260(H)	0.63462202	0.054744
261(C)	4.17496862	0.360142
262(H)	16.03595567	1.383297
263(H)	2.61781279	0.225818
264(H)	1.24613468	0.107494
Sum	1159.25595625	100

Table S5. Summary of simulation results and dielectric properties.

Samples	Density[a] ($g\ cm^{-3}$)	Density[b] ($g\ cm^{-3}$)	α' (m^3)	M_{ru} ($g\ mol^{-1}$)	ε_s	$\varepsilon_{1\ Hz}$[c]	ε_∞	$\varepsilon_{1\ MHz}$[d]
PC-aptmds	1.03	1.07	5.56E-29	478.34	2.90	2.66	2.30	2.58
PBZ-aptmds	1.07	1.11	6.49E-29	570.37	3.24	3.02	2.33	2.83
PCBZ-aptmds	1.04	1.08	1.81E-28	1615.04	3.01	2.72	2.25	2.62

[a]. Calculated by molecular dynamics simulation.
[b]. Tested by the density balance.
[c]. Experimental value of dielectric constant at 1 Hz.
[d]. Experimental value of dielectric constant at 1 MHz