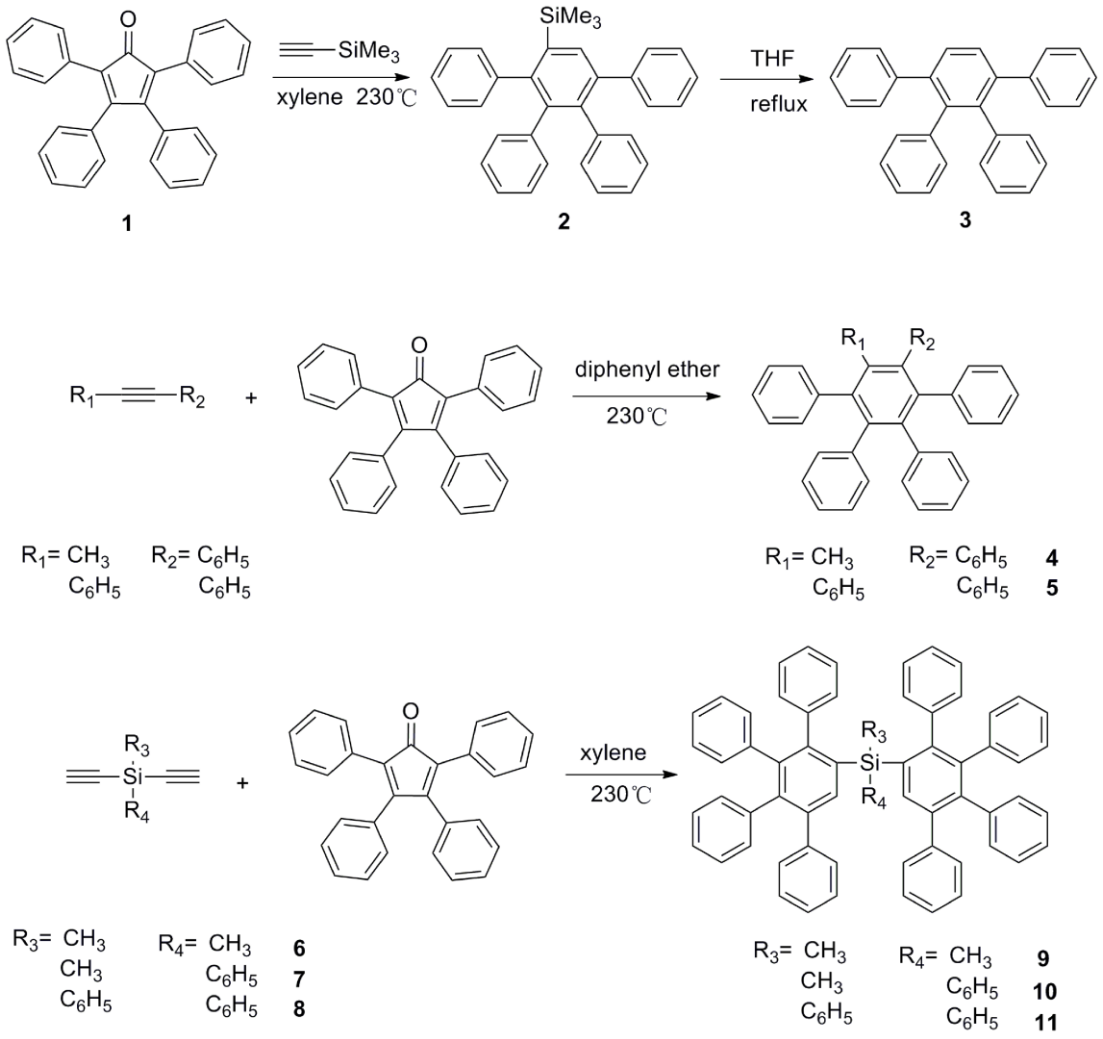
Supporting Information

Experimental section

Materials

Benzil and 1,3-diphenylacetone were obtained from the Sinopharm Chemical Reagent Company. Diphenylacetylene was purchased from Aladdin Industrial Company. Ethynyltrimethylsilane and chlorosilanes were obtained from Beijing HWRK Chem. Co. Ltd and Zibo Yuxing Chemical Engineering Company, respectively, and used after fractionation.



Scheme 1 Synthesis of multiphenylbezene compounds and silicon-containing polyphenyl derivatives

Synthesis

2,3,4,5-Tetraphenylcyclopenta-2,4-diene-1-one (1). About 6.30 g (0.03 mol) of benzil and 6.30 g (0.03 mol) of 1,3-diphenylacetone were dispersed in 60 mL of ethanol in 250 mL three-necked round-bottomed flask, and the mixture was then heated to 78 ℃. Approximately 0.8 g of KOH in 8 mL of ethanol was slowly added to the mixture. The mixture was stirred at 78 ℃ for 15 minutes and subsequently cooled to room temperature. Solid product was filtered and washed three times with ethanol.

After drying, bright black solid was obtained with a yield of about 90% (10.4 g).

(2,3,4,5-Tetraphenylphenyl)trimethylsilane (TPB-TMS) (2). Approximately 1.48 g (15 mmol) of ethynyltrimethylsilane and 3.84 g (10 mmol) of compound 1 were dispersed in 30 mL of xylene in a 50 mL sealed stainless steel reactor, and the mixture was run for 8 h at 230 ℃ under nitrogen atmosphere. Subsequently, the mixture was cooled to room temperature, and xylene was removed under reduced pressure. The crude product was precipitated in methanol and further purified via silica gel column chromatography. About 74% white solid powder was obtained. 1H NMR ($CDCl_3$, 400MHZ, ppm): δ 0.02 (s, 9H), 6.77-6.91(m, 12H), 7.10-7.19(m, 8H) 7.74(s, 1H). 13C NMR($CDCl_3$, 100$MH_{Z,}$ ppm): δ 0.57(Si-CH_3), 0.59, 125.18, 125.55, 126.12, 126.35, 126.51, 126.86, 126.94, 127.62, 130.01, 131.00, 131.35, 131.37, 135.61, 138.48, 139.68, 140.02, 140.27, 140.57, 140.98, 142.25, 142.48, 147.16. ^{29}Si NMR ($CDCl_{3,}$ 80$MH_{Z,}$ ppm): δ -3.41.

1,2,3,4-Tetraphenylbenzene (TPB) (3). About 1.00 g (2.2 mmol) of TPB-TMS and 2 mL of concentrated hydrochloric acid were dissolved in 30 mL of THF. The mixture was refluxed for 10 h with stirring. The solvent was then removed under reduced pressure. The crude product was precipitated in methanol and purified with silica gel column chromatography. About 93% white solid powder was obtained.^{1}H NMR ($CDCl_{3,}$ 400$MH_{Z,}$ ppm): δ6.85-6.87(m, 2H), 6.96-6.98(m, 3H), 7.16-7.21(m, 5H), 7.56(s, 1H). ^{13}C NMR ($CDCl_3$, 100$MH_{Z,}$ ppm): δ125.6, 126.2, 126.9, 127.5, 129.4, 129.9, 131.5, 139.9, 140.3, 140.9, 141.9.

1,2,3,4,5-Petaphenylbenzene (PPB) (4). Approximately 1.00 g (10mmol) of

phenylacetylene and 3.07 g (8 mmol) of compound 1 were dispersed in 10 mL diphenyl ether. The mixture was stirred 2 h at 250℃ under argon. When the system was cooled to room temperature, the mixture was poured to 100 mL of methanol and further purified via silica gel column chromatography. About 74% white solid was obtained. ^{1}H NMR ($CDCl_3$, 400MH_Z, ppm): δ6.80-6.88(m, 9H), 6.94-7.18(m, 16H), 7.59(s, 1H). ^{13}C NMR ($CDCl_3$, 100MH_Z, ppm): δ125.35, 125.62, 126.27, 126.65, 126.95, 127.62, 129.99, 131.43, 131.50, 131.56, 139.30, 139.98, 140.35, 140.77, 141.72, 141.77.

Hexaphenylbenzene (HPB) (5). This compound was prepared by a procedure similar to that for **4**. About 68% white solid powder was obtained. ^{1}H NMR ($CDCl_3$, 400MH_Z, ppm): δ7.41 (m, 30H). ^{13}C NMR ($CDCl_3$, 100MH_Z, ppm): δ127.6, 127.9, 129.0, 133.6, 134.3.

Diethynylsilanes (6–8). Diethynyldimethylsilane (**6**), diethynylmethylphenylsilane (**7**) and diethynyldiphenylsilane (**8**) were prepared according to the published method[1]. Approximately 4.8 g (0.2 mol) of magnesium powder and 50 mL of dry THF were mixed into a 250 mL three-necked round-bottomed flask under an argon atmosphere with stirring. Approximately 22.0 g (0.2 mol) of bromoethane in 50 mL of dry THF were slowly dropped into the mixture. When the magnesium powder disappeared, the mixture was allowed to boil for 2 h. After cooling to room temperature, the bromoethane Grignard reagent was obtained.

Acetylene, which was cooled at −78 ℃, was bubbled into 150 mL of dry THF for 1 h to obtain acetylene-saturated solution. Subsequently, the bromoethane Grignard

reagent was dropwise added into the acetylene-saturated solution. In this process, acetylene was maintained bubbling into the mixture. The reaction was kept for 3 h after the complete addition of bromoethane Grignard reagent, and the ethynylmagnesium chloride was then obtained.

A 1 L three-necked round-bottomed flask was equipped with a reflux condenser and a Teflon-covered magnetic stirring bar. The flask was charged with ethynylmagnesium chloride obtained at the last step under argon atmosphere. Dimethyldichlorosilane (7.80 g, 60 mmol) and THF (50 mL) were placed into the addition funnel and added dropwise to the well-stirred reaction mixture over 1 h. The mixture was quenched by adding saturated aqueous ammonium chloride (10 mL), and THF (30 mL) was then added. The organic layer was washed with water, dried with anhydrous $MgSO_4$, filtered, and concentrated at reduced pressure. The residue was fractionally distilled to obtain 6 (colorless liquid with 34% yield); bp 86.5 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.48 (s, 2H, –C≡C*H*), 0.35 (s, 6H, –SiCH_3).

Compound 7 was prepared in a similar manner. Methylphenyldichlorosilane (11.5 g, 60.0 mmol) was used to obtain the colorless liquid with 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.76 (m, 2H, Ar*H*), 7.28–7.46 (m, 3H, Ar*H*), 2.75 (s, 2H, –C≡C*H*), 0.64 (s, 3H, –SiCH_3).

Compound 8 was prepared in a similar manner to the synthesis of compound 6. Diphenyldichlorosilane (15.2 g, 60.0 mmol) was used to obtain the straw-yellow crystal with 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.75 (m, 4H, Ar*H*), 7.26–7.50 (m, 6H, Ar*H*), 2.75 (s, 2H, –C≡C*H*).

Bis(2,3,4,5-tetraphenyl)dimethylsilane (BTPB-DMS) (9) Approximately 3.84 g (10 mmol) of compound 1 and 1.16 g (5 mmol) of compound 6 were dispersed in 30 mL xylene in a 50 mL sealed stainless steel reactor. The mixture was run for 10 h at 230 ℃ under nitrogen atmosphere. Subsequently, the mixture was cooled to room temperature, and xylene was removed under reduced pressure. The crude product was precipitated in methanol and further purified by silica gel column chromatography. About 48% of yellow solid powder was obtained. 1H NMR ($CDCl_3$, 400MHZ, ppm): δ 0.02 (s, 9H), 6.77-6.91(m, 12H), 7.10-7.19(m, 8H) 7.74(s, 1H). 13C NMR($CDCl_3$, $100MH_{Z,}$ ppm): δ 0.57(Si-CH_3), 125.1, 125.5, 125.6, 126.1, 126.3, 126.4, 126.8, 126.9, 127.5, 127.6, 129.3, 129.9, 130.0, 130.9, 131.1, 131.3, 131.5, 135.6, 138.4, 139.6, 139.9, 140.0, 140.2, 140.3, 140.5, 140.9, 141.9, 142.2, 142.4, 147.1. ^{29}Si NMR ($CDCl_{3,}$ $80MH_{Z,}$ ppm):δ -3.41.

Bis(2,3,4,5-tetraphenyl)methylphenylsilane(BTPB-MPS) (10) This compound was prepared by a procedure similar to that for **9**. About 40% white solid powder was obtained as yield. ^{1}H NMR ($CDCl_3$, 400MHZ, ppm): δ -0.53 (s, 3H), 6.73-6.76(m, 4H), 6.81-6.99(m, 26H), 7.04-7.07(m, 4H), 7.13-7.15(m, 6H), 7.41-7.43(m, 3H), 7.56(s, 2H), 7.63-7.65 (q, 2H). ^{13}C NMR($CDCl_3$, $100MH_{Z,}$ ppm): δ -2.07(Si-CH_3), 125.1, 125.5, 125.9, 126.0, 126.4, 126.5, 126.6, 126.9, 127.4, 127.6, 130.0, 131.0, 131.1, 131.3, 131.50, 131.53, 135.53, 136.4, 138.2, 138.9, 140.2, 140.4, 140.7, 141.2, 141.9, 142.0, 147.1. ^{29}Si NMR ($CDCl_{3,}$ $80MH_{Z,}$ ppm): δ -8.44.

Bis(2,3,4,5-tetraphenyl)diphenylsilane(BTPB-DPS) (11) This compound was prepared by a procedure similar to that for **9**. White solid powder was obtained. The

yield was 33%. ^{1}H NMR ($CDCl_3$, 400MHZ, ppm): δ 6.63-6.70(m, 6H), 6.79-6.86(m, 6H), 6.94-9.95(t, 3H), 7.07-7.20(m, 7H), 7.24-7.38(m, 3H), 7.77(s, 1H). ^{13}C NMR ($CDCl_3$, $100MH_Z$, ppm): δ 124.9, 125.5, 125.9, 126.0, 126.3, 126.4, 126.8, 127.0.9, 127.4, 128.3, 130.1, 131.3, 131.4, 136.0, 136.9, 139.6, 138.7, 139.0, 140.2, 140.5, 140.8, 141.5, 141.7, 142.0, 147.3. ^{29}Si NMR ($CDCl_3$, $80MH_Z$, ppm): δ -14.87.

Results and discussion

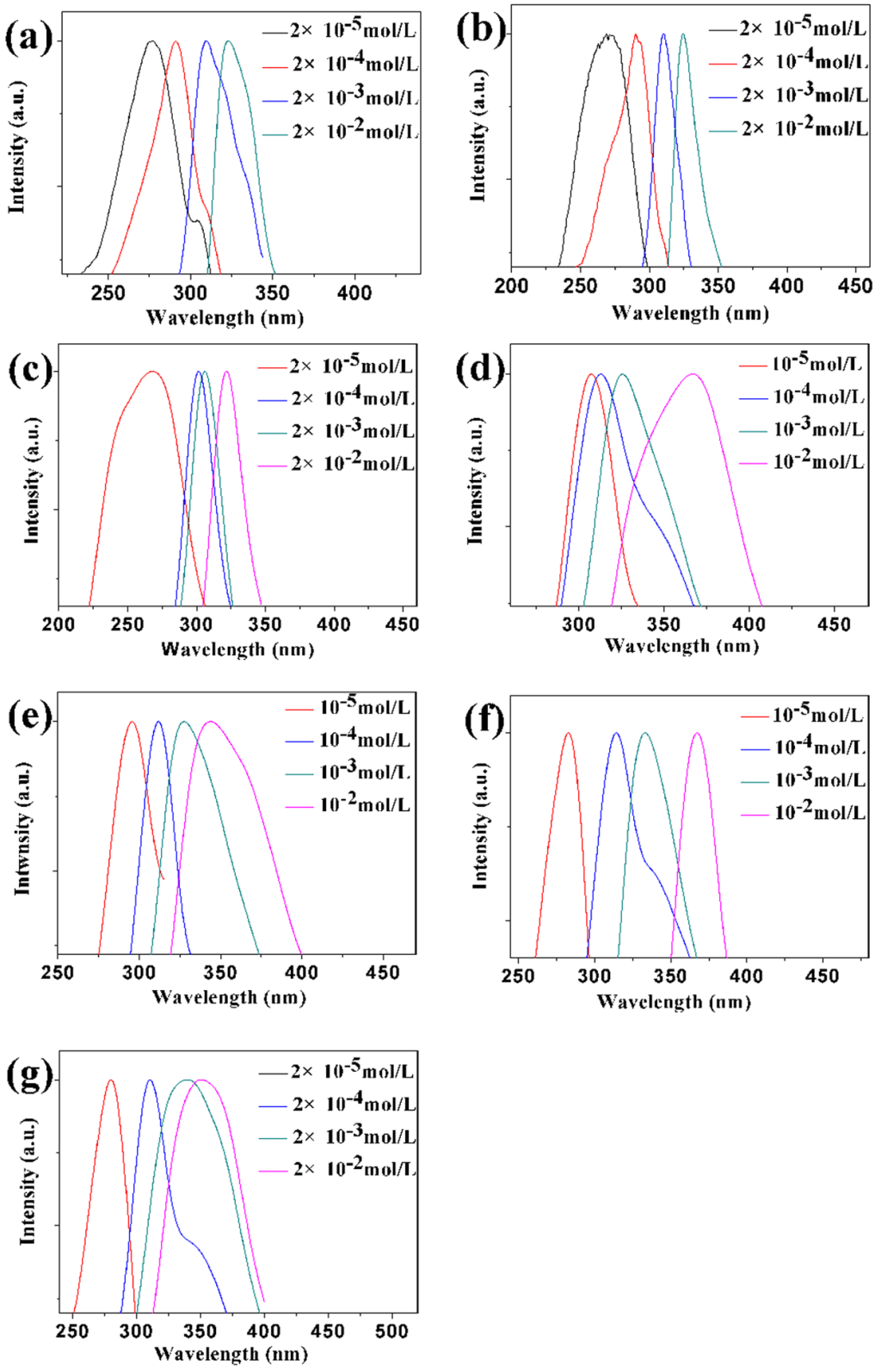


Fig.S1 Normalized fluorescence excitation spectra of **3(a)**, **4(b)**, **5(c)**, **9(d)**, **10(e)**, **11(f)** and **2(g)** in THF solutions with different concentrations.

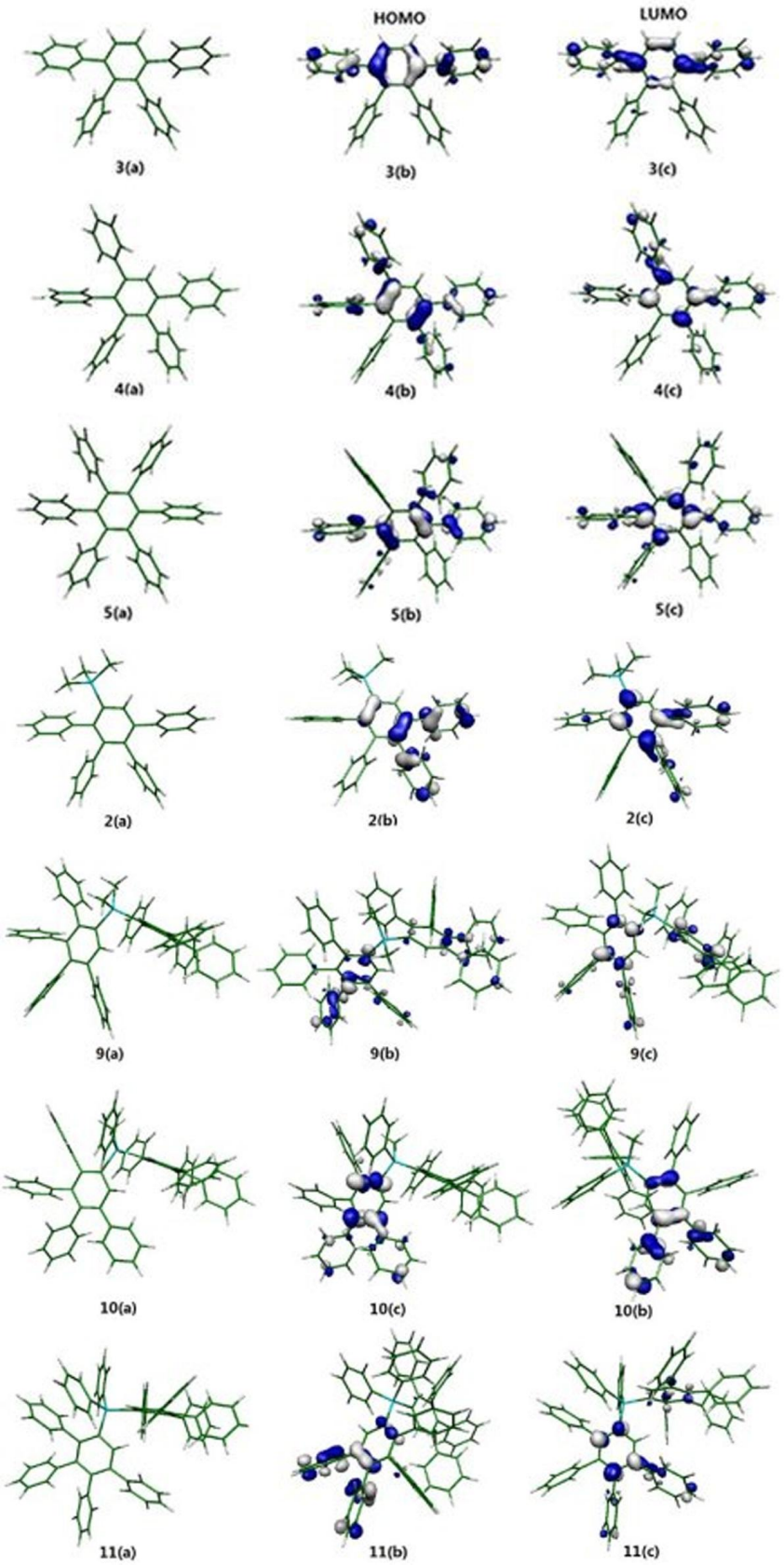


Fig. S2 Optimized geometries and calculated HOMO and LUMO density maps, of

2, **3**, **4**, **5**, **9**, **10** and **11**

Table S1 Excitation peak dates of multiphenylbezene compounds (**3**, **4 and 5**) and their silicon-containing derivatives (**2**, **9**, **10 and 11**) in different concentrations.

Concentration/ mol L-1	**1×10^{-5}**	**2×10^{-5}**	**1×10^{-4}**	**2×10^{-4}**	**1×10^{-3}**	**2×10^{-3}**	**1×10^{-2}**	**2×10^{-2}**
TPB-TMS	-	280	-	310	-	340	-	351
TPB	-	277	-	291	-	309	-	323
PPB	-	269	-	290	-	310	-	325
HPB	-	268	-	301	-	306	-	321
BTPB-DMS	307	-	313	-	325	-	367	-
BTPB-MPS	295	-	311	-	327	-	344	-
BTPB-DPS	283	-	314	-	333	-	367	-

Table S2. HOMO**,** LUMO and band gap energy of hydrocarbon polyphenyl compounds (**3**, **4**, **5**) and their silicon-containing derivatives (**2**, **9**, **10**, **11**).

Compound	HOMO/ ev	LUMO/ ev	Band gap / ev
2	-5.89	-0.80	5.09
3	-5.83	-0.84	4.99
4	-5.79	-0.89	4.90
5	-5.87	-0.74	5.13
9	-5.89	-0.70	5.19
10	-5.86	-0.79	5.07
11	-5.90	-0.81	5.09

[1] ***Organic Syntheses*** **1987, *65*, 61.**