Supporting Information

Experimental Section

Synthesis

The tetraphenyl benzene derivatives were synthesized via the Knoevenagel/ Diels–Alder method from commercial starting materials, such as benzil, diphenylacetone, and phenylacetylene, using only ethanol (EtOH) and (optionally) xylenes for solvents; all are inexpensive and readily available.(**Figure S1**)

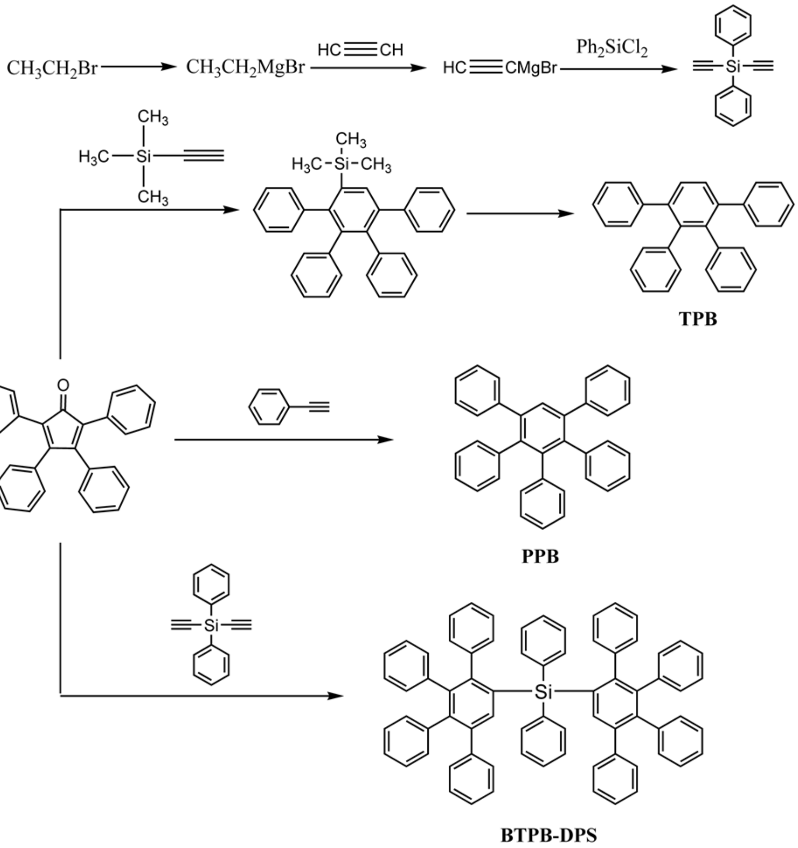

Figure S1. The synthesis of **TPB, PPB** and **BTPB-DPS**

2,3,4,5-tetraphenylcyclopenta-2,4-dienone

6.30 g benzil (0.03 mol) and 6.30 g 1,3-diphenylacetone (0.03 mol) were dissolved in 60 mL ethanol, and the mixture was heated to 78℃. A solution of 0.8g KOH in 8 mL ethanol was added slowly to the mixture. The reaction mixture was stirred at 78℃ for 15 min, and then cooled to room temperature. Solid product was filtrated and washed several times with ethanol. After drying, bright black solid was obtained. The total yield was 90%.

1,2,3,4-tetraphenylbenzeneyl trimethylsilane

1.48 g (15 mmol) ethynyltrimethylsilane and 3.84 g (10 mmol) 1 were dissolved in 30 mL xylene in a sealed stainless steel reactor, and the reaction was run for 8 h at 230℃ under a nitrogen atmosphere. Then xylene was removed under reduced pressure. The product was precipitated in methanol and purified with silica gel column chromatography. White solid powder was obtained with yield 74%.^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 0.03 (s, 9H), 6.77 (m, 2H), 6.84(m, 5H), 6.91(m, 3H), 7.07-7.20 (m, 10H), 7.74 (s, 1H). Anal.calcd for $C_{33}H_{30}Si$: C 87.17%, H 6.65%; found: C 87.54%, H 6.38%.

1,2,3,4-tetraphenylbenzene (TPB)

1.00 g **2** (2.2 mmol) and 2 mL concentrated hydrochloric acid was dissolved in 30 mL THF. The mixture was refluxed for 10 h with stirring. And then the solvent was distilled off. The product was precipitated in methanol and purified with silica gel column chromatography. White crystal was obtained. The yield was 93%. ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 6.82 (m, 4H), 6.94 (m, 6H), 7.12-7.21 (m, 10H), 7.53 (s, 2H). ^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 125.6, 126.2, 126.9, 127.5, 129.4, 129.9, 131.6, 139.9, 140.4, 140.9, 141.9. Anal.calcd for $C_{30}H_{22}$: C 94.20%, H 5.80%; found: C 94.33%, H 5.74%.

1,2,3,4,5-pentaphenylbenzene (PPB)

1.00 g (10 mmol) phenylacetylene and 3.07 g (8 mmol) **1** were dissolved in 10 mL diphenyl ether, and the reaction was run for 2 h at 250℃ under a nitrogen atmosphere. Then the product was precipitated in methanol and purified with silica gel column chromatography. White solid powder was obtained with yield 74%.^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 6.80 (m, 2H), 6.88 (m, 7H), 6.94(m, 6H), 7.18 (m, 10H), 7.59 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 125.3, 125.6, 126.3, 126.9, 127.6, 130.0, 131.4, 131.5, 131.6, 139.3, 140.0, 140.4, 140.8, 141.7. Anal.calcd for $C_{36}H_{26}$: C 94.29%, H 5.71%; found: C 94.53%, H 5.69%.

Diethynyldiphenylsilane

Diethynyldiphenylsilane were prepared according to the published method. [1,2]

4.8 g (0.2 mol) magnesium powder and 50 mL dry THF were mixed into a 250 mL three-necked, round bottomed flask. The mixture was under an argon atmosphere and magnetic stirring. And then 22.0 g (0.2 mol) bromoethane in 50 mL dry THF were slowly dropped into the mixture. After the magnesium powder disappeared, the mixture was kept boiling for 2h. After cooling to room temperature, the bromoethane Grignard reagent was obtained.

Acetylene which was cooled at -78 ˚C was bubbled into the dry 150 mL THF for 1 h to obtain the acetylene saturated solution. Then the bromoethane Grignard reagent was dropwise added into the acetylene saturated solution. In this process the acetylene was always kept bubbling into the mixture. The reaction was kept for 3 h after the dropping of bromoethane Grignard reagent was completed. And then the ethynylmagnesium chloride was 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 the ethynylmagnesium chloride obtained on the last step under an argon atmosphere. Diphenylyldichlorosilane (15.2g, 60.0 mmol) and THF (50 mL) were placed into the addition funnel and added drop-wise to the well stirred reaction mixture over 1h. It was quenched by addition of saturated aqueous ammonium chloride (10 mL), and THF (30 mL) was added. The organic layer was washed with water, dried with anhydrous $MgSO_4$, filtered, and concentrated at reduced pressure. The residue was then fractionally distilled to give straw yellow crystal with yield 70%. ^1H NMR(400MHz, $CDCl_3$, δ): 7.75 (m, 4H, Ar*H*), 7.26-7.50 (m, 6H, Ar*H*), 2.75 (s, 2H, $-C{\equiv}C$*H*).

Bis(1,2,3,4-tetraphenylbenzene-yl) diphenylsilane (**BTPB-DPS**).

3.84 g **1** (10 mmol) and 1.16 g diethynyldiphenylsilane (5 mmol) were dissolved in 30 mL xylene in a sealed stainless steel reactor, and the reaction was run for 10 h at 230℃ under a nitrogen atmosphere. Then xylene was removed under reduced pressure. The product was purified with silica gel column chromatography. The yield was 68%. ^1H NMR ($CDCl_3$, 400MHz, ppm): δ 6.64 (m, 12H), 6.78 (m, 12H), 6.92 (m, 6H), 7.04 (m, 4H), 7.12-7.34 (m, 16H), 7.74 (s, 2H). ^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 124.9, 125.5, 125.9, 126.0, 126.3, 126.8, 127.0, 127.4, 127.5, 128.3, 130., 130.1, 131.3, 131.4, 133.8, 136.1, 136.7, 138.7, 139.0, 140.2, 140.5, 140.8, 141.5, 141.7, 142.1. ^{29}Si NMR ($CDCl_3$, 80MHz, ppm) : δ -14.9. Anal.calcd for $C_{72}H_{52}Si$: C

91.48%, H 5.54%; found: C91. 66%, H 5.53%.

References

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(2) A. B. Holmes, C. N. Sporikou., *Org. Synth.,* 1987, **65**, 61.

(3) H. Wang, Y. Liang, Y. Wang, H. Xie, L. Feng, H. Lu and S. Feng, *RSC Advances*, 2014, **4**, 17171.