Supplementary Material (ESI) for *PCCP*

Are the Silyl Group Hydrogens in peri-Substituted-9-Silyltriptycenes Engaged in Blue-Shifting Hydrogen Bonds?

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In this supplementary material, ^{1}H NMR characteristics at room temperature of 1,4-dichloro-, 1,4-dibromo-, and 1,4-dimethyl-9-silyltriptycene, **1, 2** and **3**, respectively, are given. Moreover, ^{1}H COSY spectrum of **3** documenting the occurence of *J*-couplings between the silyl and methyl group protons is shown.

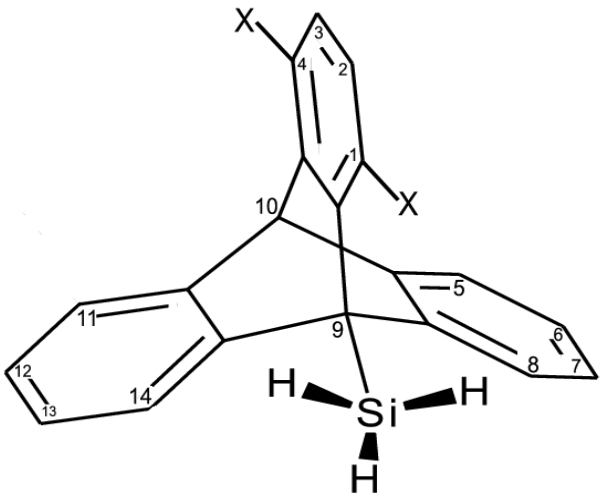

Fig. S1. Labelling of the skeleton positions in **1-3**.

Experimental details

1,4-dichloro-, 1,4-dibromo-, and 1,4-dimethyl-9-silyltriptycene, **1**, **2**, and **3**, respectively, were synthesized by adapting the literature procedures.[12] The details of these rather cumbersome syntheses will be published elsewhere. The structures of the compounds

were confirmed by room-temperature ^{1}H NMR spectra (500 MHz, $CDCl_3$, δ, see Fig. S1 for the position labelling); **1**: 4.45 (1H, br s, Si<u>H</u>H_2), 4.98 (2H, br s, SiH<u>H_2</u>), 5.970 (1H, s, C10-<u>H</u>), 6.900 (1H, d, C2-<u>H</u> or C3-<u>H</u>), 6.955 (1H, d, C3-<u>H</u> or C2-<u>H</u>), 7.07 - 7.11 (4H, m, C6-<u>H</u>,C7-<u>H</u>,C12-<u>H</u>,C13-<u>H</u>), 7.46 - 7.49 (2H, m, C5-<u>H</u>, C11-<u>H</u>), 7.60 - 7.63 (2H, m, C8-<u>H</u>, C14-<u>H</u>); **2**: 4.50 (1H, br s, Si<u>H</u>H_2), 5.18 (2H, br s, SiH<u>H_2</u>), 6.030 (1H, s, C10-<u>H</u>), 7.04 (1H, d, J = 8.60 Hz, C2-<u>H</u> or C3-<u>H</u>), 7.07 (1H, d, J = 8.60 Hz, C3-<u>H</u> or C2-<u>H</u>), 7.09 - 7.14 (4H, m, C6-<u>H</u>,C7-<u>H</u>,C12-<u>H</u>,C13-<u>H</u>), 7.49 - 7.52 (2H, m, C5-<u>H</u>, C11-<u>H</u>), 7.65 - 7.69 (2H, m, C8-<u>H</u>, C14-<u>H</u>); **3:** 2.49 (3H, s, C3-C<u>H_3</u>), 2.64 (3H, s, C2-C<u>H_3</u>), 4.75 (3H, br s, Si<u>H_3</u>), 5.66 (1H, s, C10-<u>H</u>), 6.65 (1H, d, J = 7.80 Hz, C2-<u>H</u> or C3-<u>H</u>), 6.72 (1H, d, J = 7.8 Hz, C3-<u>H</u> or C2-<u>H</u>), 7.01 - 7.06 (4H, m, C6-<u>H</u>,C7-<u>H</u>,C12-<u>H</u>,C13-<u>H</u>), 7.38 - 7.43 (2H, m, C5-<u>H</u>, C11-<u>H</u>), 7.54 - 7.59 (2H, m, C8-<u>H</u>, C14-<u>H</u>).

For **3**, the assignements of both the methyl- and peri-protons' resonances were made on the basis of the difference NOE experiments at room temperature, with irradiation of the silyl protons' signal. The COSYLR spectrum of **3** was measured on a Bruker Avance II 300 MHz spectrometer at room temperature. Further details are given in Ref. 7.

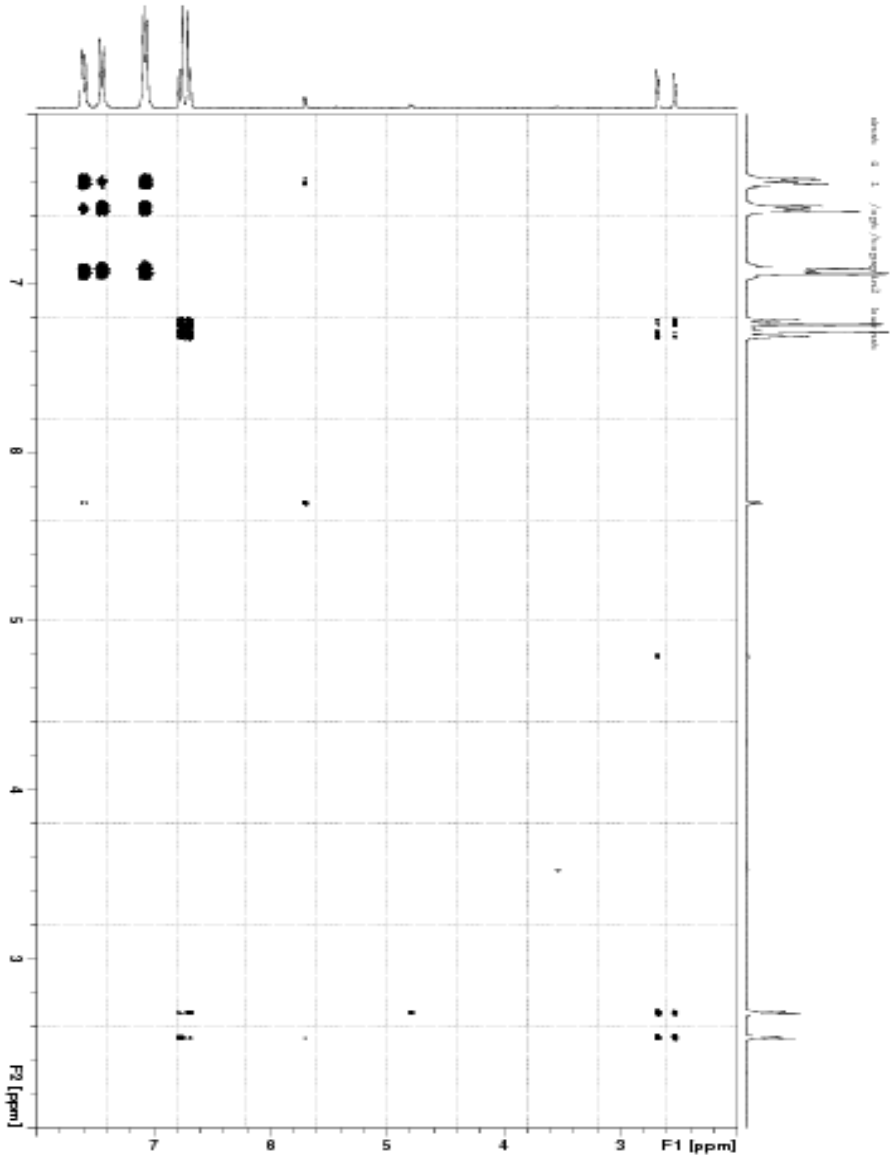

Fig. S2. ^{1}H (300 MHz) COSYLR spectrum of **3**, measured at room temperature. The Si$\underline{H}_3$ resonance appears as the small, broad peak at 4.75 ppm. The coupling to the methyl protons is represented by the crosspeak at F1=2.65 ppm and F2 = 4.75 ppm.