

Thorpe-Ingold Effect on the Conformation and Photophysical Properties of Dialkylsilylene-Spaced Divinylarene Copolymers.

Mei-Yu Yeh,^a Hsin-Chieh Lin,^a Shern-Long Lee,^a Chun-hsien Chen,^{ac} Tsong-Shin Lim,^b Wunshain Fann,^b and Tien-Yau Luh^{*a}

Supporting Information

Experimental details and the ¹H NMR spectra of new compounds

Experimental Section

General. Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate= 1.0 mLmin⁻¹). Waters styragel HR2, HR3, HR4 (7.8 x 300 mm) were employed using polystyrene as standard (M_n values range from 375 to 3.5 x 10⁶). Absorption spectra and emission spectra (1x 10⁻⁵ M) were measured with Hitachi U-3310 and Hitachi F-4500 fluorescence spectrophotometers, respectively. Quantum yield was obtained using coumarin-I in EtOAc as reference (Φ = 0.99).

1,4-Bis-(2-di[isopropyl]silylvinyl)benzene (3b). Under N₂, to a solution of **5**⁸ (0.58 g, 2.0 mmol) in THF (50 mL) cooled at -78 °C was added slowly ^tBuLi (5.4 mL, 1.55 M in pentane, 8.4 mmol). After stirring for 30 min at -78 °C, chlorodiisopropylsilane (0.7 mL, 4.2 mmol) was added and the mixture was gradually warmed to rt, stirred for 3 h, and quenched with H₂O (5.0 mL). The aqueous layer was extracted with Et₂O (3 × 20 mL), and the organic layer was washed with brine (20 mL), dried (MgSO₄), filtered, and evaporated in vacuo to give the residue which was chromatographed on silica gel (CH₂Cl₂/hexane 1 : 4) to afford **3b** (0.60 g, 82 %) as a white solid: mp 45-46 °C (pentane); ¹H NMR (400 MHz, CDCl₃): δ 1.04-1.08 (m, 28 H), 3.73-3.75 (m, 2 H), 6.39 (dd, *J* = 19.1 Hz, 4.7 Hz, 2 H), 7.03 (d, *J* = 19.1 Hz, 2 H),

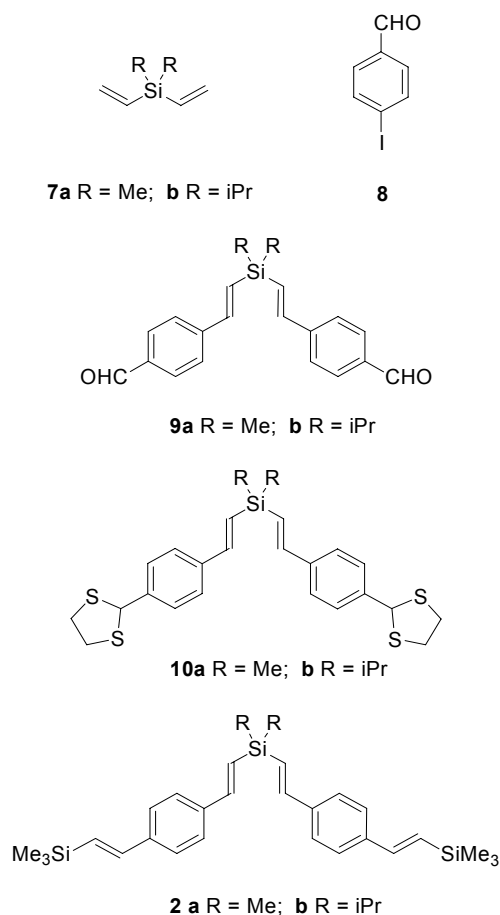
7.42 (s, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 10.8, 18.6, 18.8, 122.0, 126.6, 138.0, 147.1; IR (KBr): ν 2941, 2890, 2863, 2100, 1601, 1499, 1462, 997, 986, 881, 769, 768, 669, 655 cm^{-1} ; HRMS (FAB $^+$) (M^+ , $\text{C}_{22}\text{H}_{38}\text{Si}_2$): calcd: 358.2512; found: 358.2520.

Polymer 1b. A mixture of **3b** (110 mg, 0.3 mmol), **4** (40 mg, 0.3 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (0.0015-0.002 mmol) in THF (5 mL) was treated under different conditions (See Table below). After reaction, methanol was added. The precipitate was collected and redissolved in THF and then precipitated again with methanol. The product was collected by filtration and washed with methanol to give polymer **1b**: ^1H NMR (400 MHz, CDCl_3): δ 1.0-1.3 (m, 14 H), 6.4-6.6 (d, 2 H), 6.9-7.1 (d, 2 H), 7.5 (s, 4 H) ; IR (KBr): ν 2955, 2922, 2854, 1593, 1462, 1454, 1295, 1176, 976, 841, 805, 776, 743, 686 cm^{-1} .

Table S1. The reaction conditions of polymers **1a** and **1b**.

Substrate	M_n (PDI)	N^a	$\text{RhCl}(\text{PPh}_3)_3$ ($\text{Mx } 10^{-3}$)	Time (h)	Temp. ($^\circ\text{C}$)	Yield (%)
1a₁	3800 (2.0)	20	2.0	6	40	80
1a₂	8400 (1.8)	45	2.0	6	60	78
1a₃	13000 (2.0)	69	1.5	10	60	81
1b₁	4000 (1.5)	17	2.0	16	60	60
1b₂	5900 (1.6)	24	1.5	16	60	70
1b₃	8700 (1.8)	36	1.5	48	100 ^b	67

^a Number average of degree of polymerisation. ^bThe reaction was carried out in toluene.



Bis-β-(4-formylstyryl)dimethylsilane (9a). Under N₂, a mixture of **8** (2.32 g, 10 mmol), **7a** (0.67 g, 6 mmol), Pd(OAc)₂ (0.11 g, 0.5 mmol), Bu₄NOAc (6.03 g, 20 mmol) and molecular sieves (4 Å) in dry DMF (150 mL) was stirred at 80 °C for 24 h. After filtration over celite, the solvent was evaporated in vacuo to give the residue which was chromatographed on silica gel (Et₃N-treated) using CH₂Cl₂/hexane 1 : 4 as eluent to afford **9a** as an oil (0.93 g, 58 %): ¹H NMR (400 MHz, CDCl₃): δ 0.27 (s, 6 H), 6.67 (d, *J* = 19.1 Hz, 2 H), 6.95 (d, *J* = 19.1 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 4 H), 7.84 (d, *J* = 8.0 Hz, 4 H), 9.99 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ -2.9, 126.8, 130.0, 132.2, 132.7, 137.4, 143.2, 191.5; IR (KBr): ν 3047, 2993, 2961, 2901, 2822, 2787, 2718, 1704, 1600, 1407, 1378, 1302, 1258, 1211, 1166, 1105, 1040, 1005, 979, 951, 831, 793, 764, 688 cm⁻¹; HRMS (EI) (C₂₀H₂₀O₂ Si): calcd: 320.1233; found: 320.1240.

Bis-β-(4-{2-(1,3-dithiolanyl)}styryl)dimethylsilane (10a). An ether/CH₂Cl₂ (30

mL, 1: 1) solution of the **9a** (320 mg, 1 mmol), ZnI₂ (1 mg, 0.003 mol) and 1,2-ethanedithiol (0.26 mL, 3 mmol) was stirred at rt for 24 h. The mixture was poured into 10% NaOH and two layers were separated. The organic layer was washed 10% NaOH (10 mL x 3) and brine (20 mL), and dried (MgSO₄). The solvent was removed in vacuo to give **10a** as an oil (0.39 g, 83 %): ¹H NMR (400 MHz, CDCl₃): δ 0.32 (s, 6 H), 3.35-3.39 (m, 4 H), 3.50-3.54 (m, 4 H), 5.64 (s, 2 H), 6.50 (d, *J* = 19.1 Hz, 2 H), 6.91 (d, *J* = 19.1 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 4 H), 7.48 (d, *J* = 8.3 Hz, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ -2.4, 40.4, 56.1, 126.4, 127.1, 127.6, 128.0, 137.9, 144.1; IR (KBr): ν 2958, 2933, 2911, 1673, 1660, 1610, 1559, 1505, 1413, 1394, 1252, 1217, 1192, 1163, 986, 913, 884, 745 cm⁻¹; HRMS (EI) (C₂₄H₂₈S₄ Si): calcd: 472.0838; found: 472.0843.

Bis-β-[4-{2-(trimethylsilyl)vinyl}styryl]}dimethylsilane (2a). A THF solution of Me₃SiCH₂MgCl (10 equiv) was evacuated as much as possible and benzene (30 mL) was introduced. Under N₂, to this mixture was added a solution of **10a** (0.95 g, 2.0 mmol) and NiCl₂(PPh₃)₂ (0.14 g, 0.2 mmol) in benzene (50 mL). The mixture was refluxed under N₂ for 16 h and then poured into saturated NH₄Cl. The organic layer was separated and the aqueous layer was extracted twice (20 mL x 2) with ether. The combined organic portions were washed with 10% NaOH (20 mL x 3) and brine (30 mL), and dried (MgSO₄). The crude product was purified by flash chromatography (Et₃N-treated) using hexane as eluent to afford **2a** as an oil (0.57 g, 62 %): ¹H NMR (400 MHz, CDCl₃): δ 0.18 (s, 18 H), 0.33 (s, 6 H), 6.49 (d, *J* = 19.1 Hz, 2 H), 6.52 (d, *J* = 19.1 Hz, 2 H), 6.86 (d, *J* = 19.1 Hz, 2 H), 6.93 (d, *J* = 19.1 Hz, 2 H), 7.41 (s, 8 H); ¹³C NMR (100 MHz, CDCl₃): δ -2.4, -1.0, 126.4, 126.5, 126.7, 126.8, 127.2, 129.6, 142.9, 144.3; IR (KBr): ν 3028, 2984, 2955, 2920, 2892, 2851, 1603, 1413, 1242, 1201, 979, 862, 843, 789, 729 cm⁻¹; HRMS (EI) (C₂₈H₄₀Si₃): calcd: 460.2438; found: 460.2447.

Bis-β-(4-formylstyryl)]diisopropylsilane (9b). In a manner similar to that described for the preparation of **9a**, a mixture of **8** (2.32 g, 10 mmol), **7b** (1.01 g, 6

mmol), Pd(OAc)₂ (0.11 g, 0.5 mmol), Bu₄NOAc (6.03 g, 20 mmol) and molecular sieves (4 Å) in dry DMF (150 mL) was transformed into **9b** as an oil (1.03 g, 55%): ¹H NMR (400 MHz, CDCl₃): δ 1.10-1.30 (m, 14 H), 6.69 (d, *J* = 19.0 Hz, 2 H), 7.09 (d, *J* = 19.0 Hz, 2 H), 7.63 (d, *J* = 8.6 Hz, 4 H), 7.88 (d, *J* = 8.6 Hz, 4 H), 10.01 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 11.5, 18.2, 126.8, 127.3, 130.0, 135.7, 143.6, 145.7, 191.5; IR (KBr): ν 2955, 2889, 2854, 2730, 1685, 1597, 1565, 1458, 1388, 1299, 1213, 1154, 992, 881, 859, 777, 656 cm⁻¹; HRMS (EI) (C₂₄H₂₈O₂ Si): calcd: 376.1853; found: 376.1860.

Bis-β-(4-{2-(1,3-dithiolanyl)}styryl)]diisopropylsilane (10b). In a manner similar to that described for the preparation of **10a**, a mixture of **9b** (376 mg, 1 mmol), ZnI₂ (1 mg, 0.003 mol) and 1,2-ethanedithiol (0.26 mL, 3 mmol) was transformed into **10b** as an oil (0.42 g, 80 %): ¹H NMR (400 MHz, CDCl₃): δ 1.05-1.22 (m, 14 H), 3.36-3.40 (m, 4 H), 3.50-3.53 (m, 4 H), 5.65 (s, 2 H), 6.46 (d, *J* = 19.0 Hz, 2 H), 6.99 (d, *J* = 19.0 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 4 H), 7.50 (d, *J* = 8.0 Hz, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 11.5, 18.2, 40.4, 56.0, 123.0, 126.4, 126.5, 128.0, 140.0, 146.1; IR (KBr): ν 2930, 2855, 1647, 1654, 1603, 1558, 1541, 1508, 1458, 1201, 1173, 1052, 989, 913, 786 cm⁻¹; HRMS (EI) (C₂₈H₃₆S₄Si): calcd: 528.1464; found: 528.1475.

Bis-β-[4-{2-(trimethylsilyl)vinyl}styryl)]diisopropylsilane (2b). In a manner similar to that described for the preparation of **2a**, a mixture of **10b** (1.06 g, 2.0 mmol) and NiCl₂(PPh₃)₂ (0.14 g, 0.2 mmol) in benzene (50 mL) was converted to **2b** as an oil (0.61 g, 59 %): ¹H NMR (400 MHz, CDCl₃): δ 0.18 (s, 18 H), 1.05-1.22 (m, 14 H), 6.48 (d, *J* = 19.1 Hz, 2 H), 6.49 (d, *J* = 19.1 Hz, 2 H), 6.87 (d, *J* = 19.1 Hz, 2 H), 7.01 (d, *J* = 19.1 Hz, 2 H), 7.43 (s, 8 H); ¹³C NMR (100 MHz, CDCl₃): δ -1.0, 11.6, 18.2, 122.7, 126.4, 126.5, 128.4, 129.6, 138.0, 142.9, 146.3; IR (KBr): ν 3018, 2946, 2914, 2892, 2863, 1606, 1458, 1391, 1242, 1185, 986, 853, 840, 805, 774, 729 cm⁻¹; HRMS (EI) (C₃₂H₄₈Si₃): calcd: 516.3058; found: 516.3047.

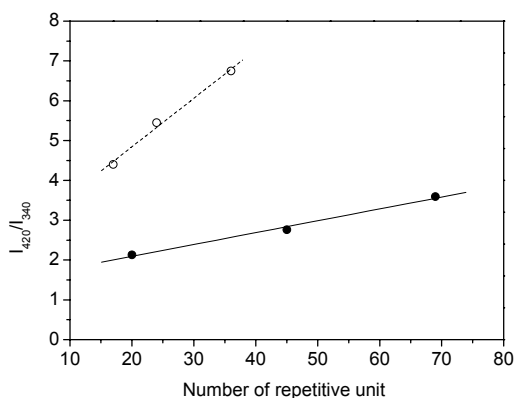


Fig. S1 Molecular weight-dependent emission intensity ratio (I_{420}/I_{340}) for polymers **1a** (solid circle) and **1b** (open circle).

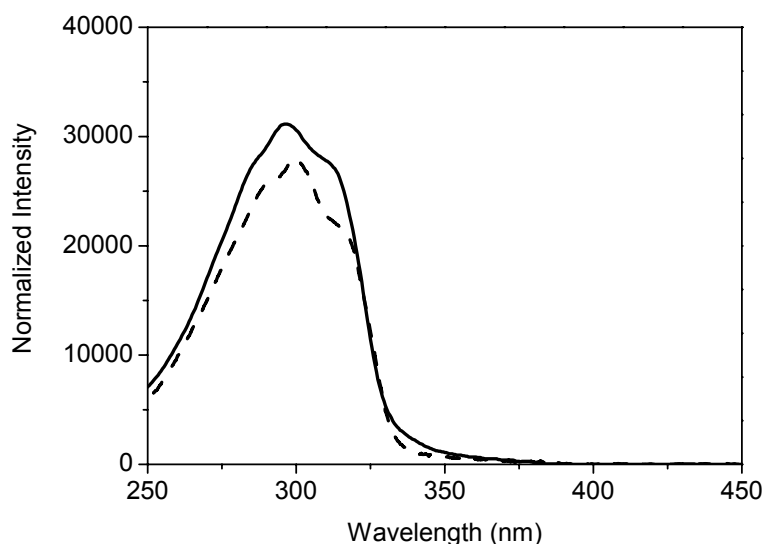


Fig. S2 Absorption spectra of **2a** (dash line) and **2b** (solid line) in CHCl_3 (1×10^{-5} M).

Time Resolved Fluorescence Measurements. A mode-locked tunable Ti:sapphire laser (Coherent, Mira 900 operating at $\lambda = 900$ nm, 76 MHz pulse rate) was passed through a third harmonic generator to generate the $\lambda = 300$ nm as the excitation light source. The fluorescence of sample was reflected by a grating (150g/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 5 ps.

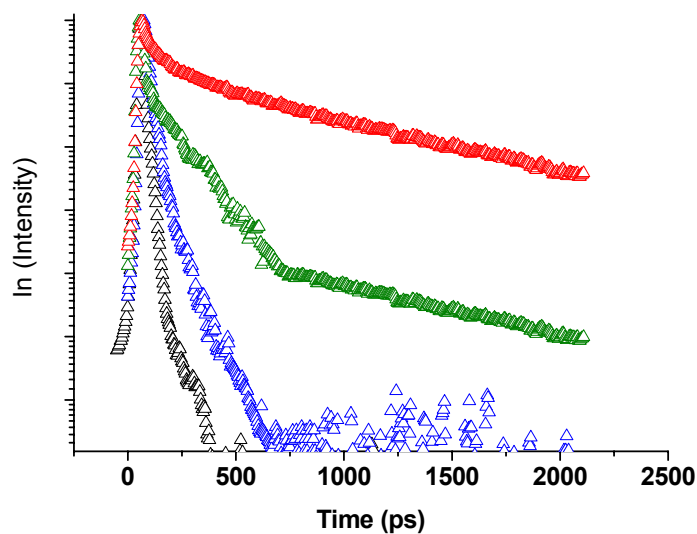


Fig. S3 Time-Resolved Fluorescence decays of polymer **1a₁** (detection at 340 nm, blue open up triangle; detection at 420 nm, red open up triangle) and the corresponding monomer **3a** (detection at 340 nm, black open up triangle), dimer **2a** (detection at 390 nm, green open up triangle) in CHCl₃ excitation at 300 nm.

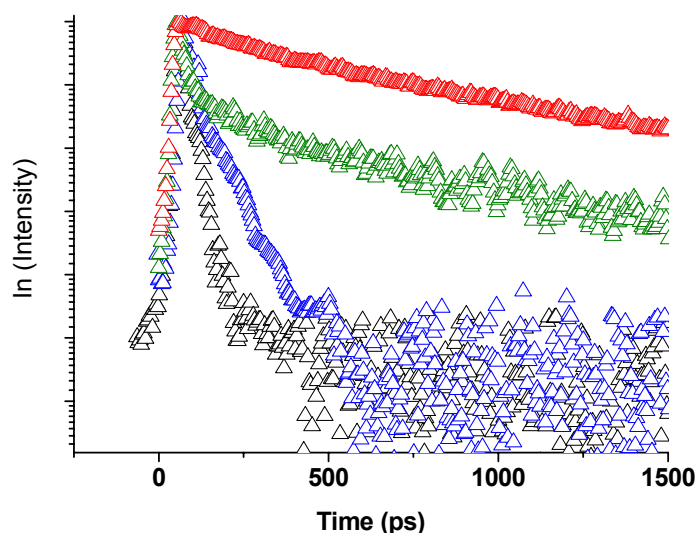


Fig. S4 Time-Resolved Fluorescence decays of polymer **1b₁** (detection at 340 nm, blue open up triangle; detection at 420 nm, red open up triangle) and the corresponding monomers **3b** (detection at 340 nm, black open up triangle), dimer **2b** (detection at 390 nm, green open up triangle) in CHCl₃ excitation at 300 nm.

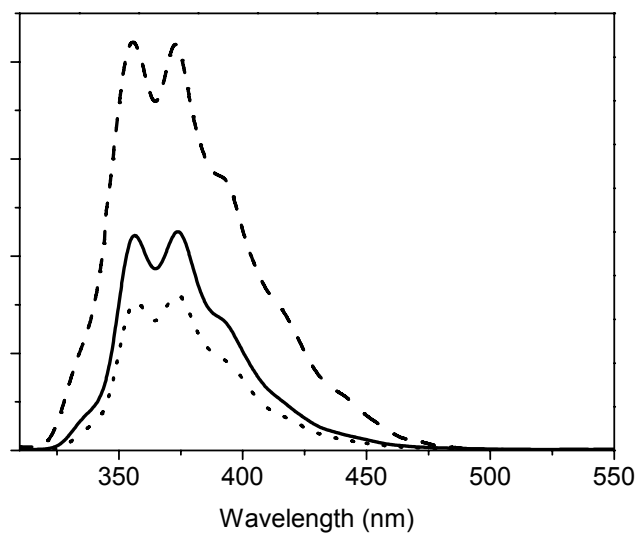


Fig.e S5 Emission spectra of **2a** in CHCl₃. 1x 10⁻³ M (dash line), 1x 10⁻⁵ M (solid line), 1x 10⁻⁶ M (dotted line).

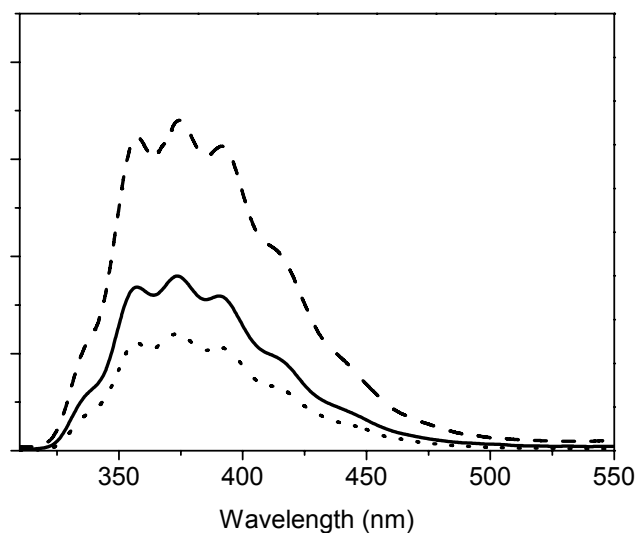


Fig. S6 Emission spectra of **2b** in CHCl₃. 1x 10⁻³ M (dash line), 1x 10⁻⁵ M (solid line), 1x 10⁻⁶ M (dotted line).

STM (scanning tunneling microscopy) Characterization.

STM imaging of polymers **1a₁** and **1b₁** was carried out with a NanoScope IIIa controller equipped with a low-current converter for experiments requiring high

tunneling impedance (Veeco Metrology Group/Digital Instruments, USA). The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments, USA). To observe individual polymers, a relatively diluted solution was prepared by dissolving 1- $\mu\text{g}/\text{mL}$ **1a**₁ or **1b**₁ in hexane (ca. 0.25 μM). The polymers were drop-cast onto freshly cleaved HOPG (highly orientated pyrolytic graphite, grade ZYD, Advanced Ceramics Corp., USA), subjected to vacuum-dry (~30 min, 120 mTorr) to remove trace amount of solvent, and rapidly transferred to a chamber where dry N₂ was purging throughout the experiments and the humidity was lower than 2%. Typical imaging conditions were 0.5~1.2 V in bias voltage and 10~50 pA in tunnelling current. The dimensions of images were calibrated by the unit cell vectors of the underlying HOPG. The large panels of Figure 4 were raw data. To better present the detail structure of polymer **1b**₁, the inset of Figure 4b was FFT-filtered (fast Fourier Transform) by removal of signal contributed from HOPG lattice. 17-20 bright spots (divinylbenzene moieties) can therefore be addressed (for example, Figure S7b) with the absence of HOPG features. Shown below is Figure S7 to demonstrate that the filtering procedure does not alter the morphological characteristics of polymer **1b**₁.

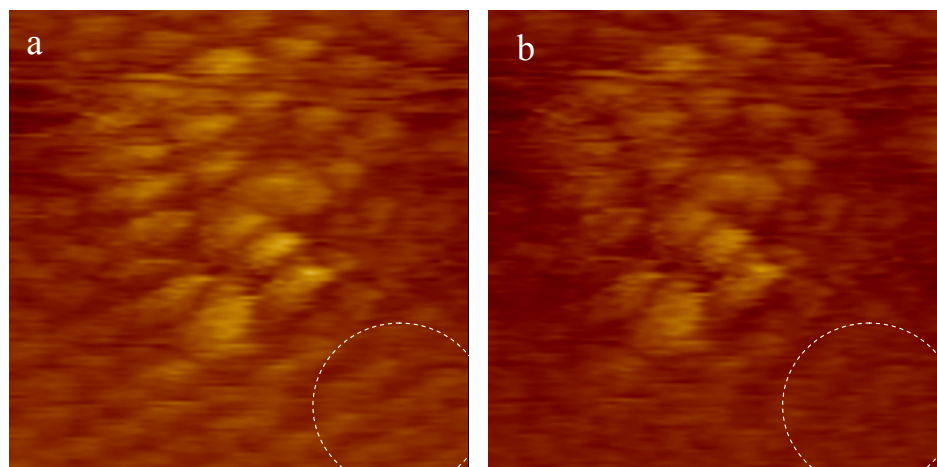


Fig. S7. STM images of **1b**₁. (a) Raw image and (b) FFT-filtered image. The white circles indicate that the removal of HOPG features facilitates counting the number of divinylbenzene moieties in the images. Conditions: image size, 3.1 x 3.1 nm; bias voltage, 0.50 V; tunnelling current, 33 pA.

