

Supporting Information for

Shifting Electronic Structure by Inherent Tension in Molecular Bottlebrushes with Polythiophene Backbones

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1. Equipment and Methods

Atomic force microscope. AFM measurements were collected using a multimode Atomic Force Microscopy (AFM) with a NanoScope V controller (Bruker) in PeakForce QNM mode. We used silicon probes with a resonance frequency of 50-90 kHz and a spring constant of ~ 0.4 N/m. The samples were prepared by either spin-casting from a dilute solution in chloroform or Langmuir-Blodgett deposition on a freshly cleaved mica substrate. The analysis of digital images was performed using a custom software program developed in-house.

Fluorescence spectroscopy. Fluorescence spectra of sub-monolayers were recorded by a spectrograph (Acton SP2300, Princeton Instruments) with a CCD camera (eXcelon, Princeton Instruments) on a Langmuir-Blodgett (LB) trough (Minimicro, KSV) with a quartz window in the center as shown in Figure 2a. The excitation wavelength is 405 nm. The substrate in the trough was a mixture of water (Milli-Q double-distilled, $\rho=18.2$ M Ω) and 2-propanol (Aldrich, 99%) which allows accurate control of the spreading parameter of PT bottlebrushes. A direct emitting semiconductor laser (405nm, Coherent) was used as the excitation source. The laser beam passed through the objective (Olympus Uplan FLN 10 $\times$, NA 0.3) of an inverted microscope (Olympus X71), and excited the PT bottlebrushes on the liquid substrate. The filter cube used in the experiment includes a 390 nm (40 nm bandpass) excitation filter, a 405 nm single-edge laser-flat dichroic filter, and a 450 longpass emission filter. The pressure of the monolayer was controlled by LB control software. Each spectrum was the average of 3 scans with exposure time of 30 s.

DFT calculations. B3LYP/6-311++G** basis set implemented in the G09 software package¹ was used to perform the DFT calculations. The geometry of the model compound of an oligothiophene consisting of three monomers was optimized during the 1-dimensional stretching process in which two end carbon atoms were stretched with the scan step size of 0.02 Å in the gas phase.

As show in Figure 4a, we illustrate how the HOMO-LUMO gap can be changed when stretching two end carbon atoms in the gas phase. The HOMO-LUMO gap is first decreased from 3.5 eV to 3.43 eV when the tension is increased from 0 to 1.7 nN. After this tension point, the gap increases monotonically with applied tension. The changes in HOMO-LUMO gap strongly correlate with planarity of the model oligothiophene molecule. Without tension, the molecule is distorted and nonplanar. With increasing tension, the dihedral angles between the neighboring thiophene rings increase gradually to 180 ° at 1.7 nN where the HOMO-LUMO gap reaches its minimum. Further increase in tension leads to an increase in the HOMO-LUMO gap without affecting the planarity. This “V” shape phenomenon of the HOMO-LUMO gap change agrees qualitatively with the observed trend for the energy of maximum emission.

2. Synthesis of 2,5-Poly(3-[1-ethyl-2(2-(poly(butyl acrylate))]thiophene) (PEBBT-g-PBA).

Typical procedure is as follows: A clean and dry 25 ml Schlenk flask was charged with 2,5-Poly(3-[1-ethyl-2(2-bromoisobutyrate)]thiophene) (PEBBT, 0.0278 g, 0.100 mmol, prepared by following a previously published procedure),² butyl acrylate (18.0 mL, 140 mmol), N,N,N',N'',N'''-pentamethyldiethylenetriamine (8.63 µg, 0.050 mmol), CuBr₂ (0.0006 g, 0.0025 mmol), and anisole (2.00 mL). The flask was deoxygenated by two freeze-pump-thaw cycles. During the last cycle, the flask was filled with nitrogen and CuBr (0.0068 g, 0.0475

mmol) was added to the frozen mixture. The flask was sealed, evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 50° C. During the reaction, fractions of aliquot were taken out via syringe to obtain molecular bottlebrushes with a series of molecular weights.

Scheme S1. Synthesis of PEBBT-g-PBA molecular bottlebrushes

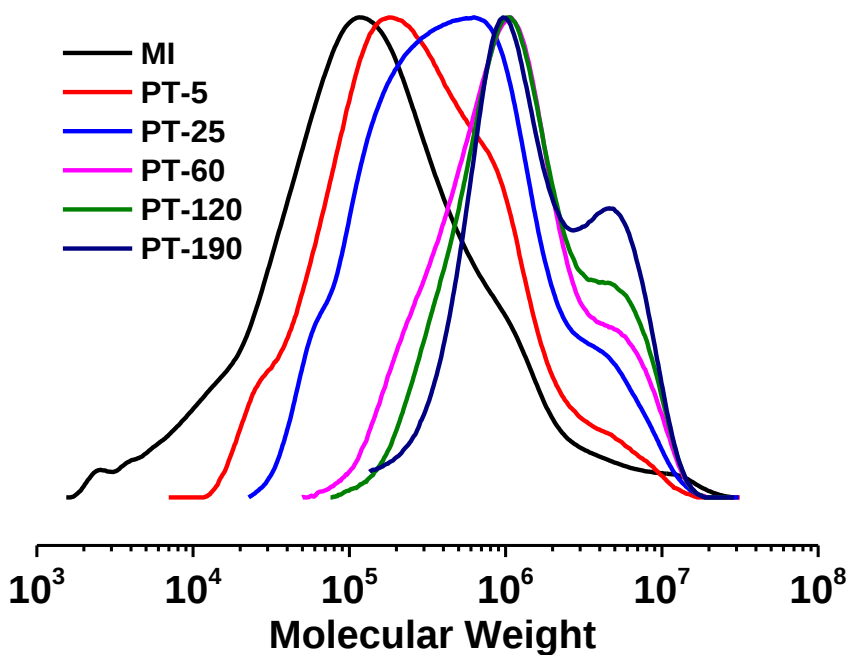
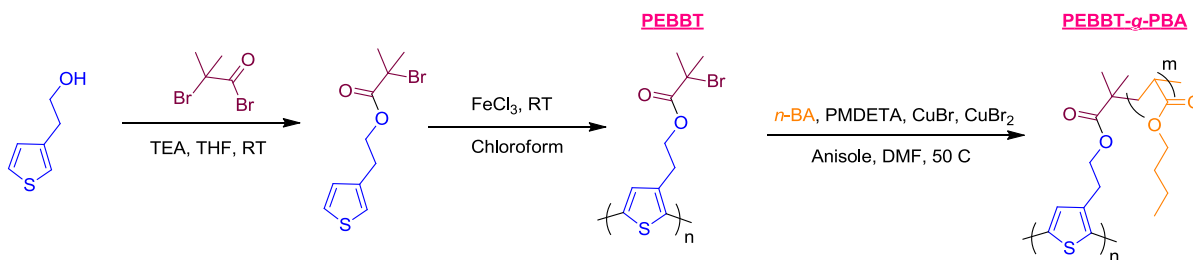


Figure S0. GPC traces of PEBBT backbone and the PT bottlebrushes.

- Synthesis of bottlebrushes with regioregular P3HT backbone.** The monomer *tert*-butyl((6-(2,5-dibromothiophen-3-yl)hexyl)oxy)dimethylsilane and functionalized polymer poly(6-(thiophen-3-yl)hexyl 2-bromo-2-methylpropanoate) were synthesized similar to related products in literature reports.^{3,4} In a flame dried, argon filled flask, *n*-BuLi was added

to 3-bromothiophene in anhydrous hexanes at -78°C and let stir for 20 min. A small amount of dry THF was added to precipitate the salt, and let stir for 1 hour at -5°C . Dibromohexane was added in large excess and the solution was stirred for three hours at RT. The distilled product was then dissolved in wet DMF and reacted overnight with excess sodium acetate. The collected residue from this reaction was refluxed in a methanol solution of 20 wt% KOH for 1 hour. The solvent was removed, and the crude product was dissolved in THF and reacted overnight with 2 equivalents of NBS. The product was flashed through a short silica plug with hexanes to yield pure product. The product was then dissolved in DMF and excess imidazole was added to deprotonate the alcohol. After 1 hour of stirring, excess *tert*-butyldimethylsiloxane was added and the solution was stirred overnight. The product was extracted with hexanes and flashed through a silica column in (2:1 hexanes : ethyl acetate) to yield pure *tert*-butyl((6-(2,5-dibromothiophen-3-yl)hexyl)oxy)dimethylsilane as a colorless oil. The polymer was synthesized via KCTP. To a flame dried, argon filled flask fitted with a reflux condensor, the monomer was added and dissolved in dry THF. To this solution 0.9 equivalents of isopropylmagnesium chloride was added at 0°C and was stirred for 30 minutes. Ni(dppp)Cl_2 was added and the solution was refluxed overnight. The polymerization was terminated by adding 6M HCl to the reaction, then precipitating the polymer in methanol. The polymer was Soxhlet extracted with methanol, hexanes, then pure polymer was collected in the chloroform fraction. The molecular weight of the polymer was measured by GPC vs PS styrene standard to verify low PDI (1.2) with high M_n (127kDa), and H-NMR confirms high regioregularity (>99%). The polymer was then dissolved in THF, to which a large excess of 2-isobutyl bromide and slight excess of triethyl amine were added. Over the course of 2 hours, a slight excess of TBAF is added and the solution is

stirred overnight. The resulting polymer was precipitated in methanol and washed with acetone to yield pure poly(6-(thiophen-3-yl)hexyl 2-bromo-2-methylpropanoate). H-NMR confirmed complete removal of protecting siloxane groups and functionalization. Then the functionalized polymer was used as macroinitiator to grow poly(*n*-butyl acrylate) side chains to prepare molecular bottlebrushes by ATRP.

Scheme S2. Synthesis of molecular bottlebrush with regioregular P3HT backbone

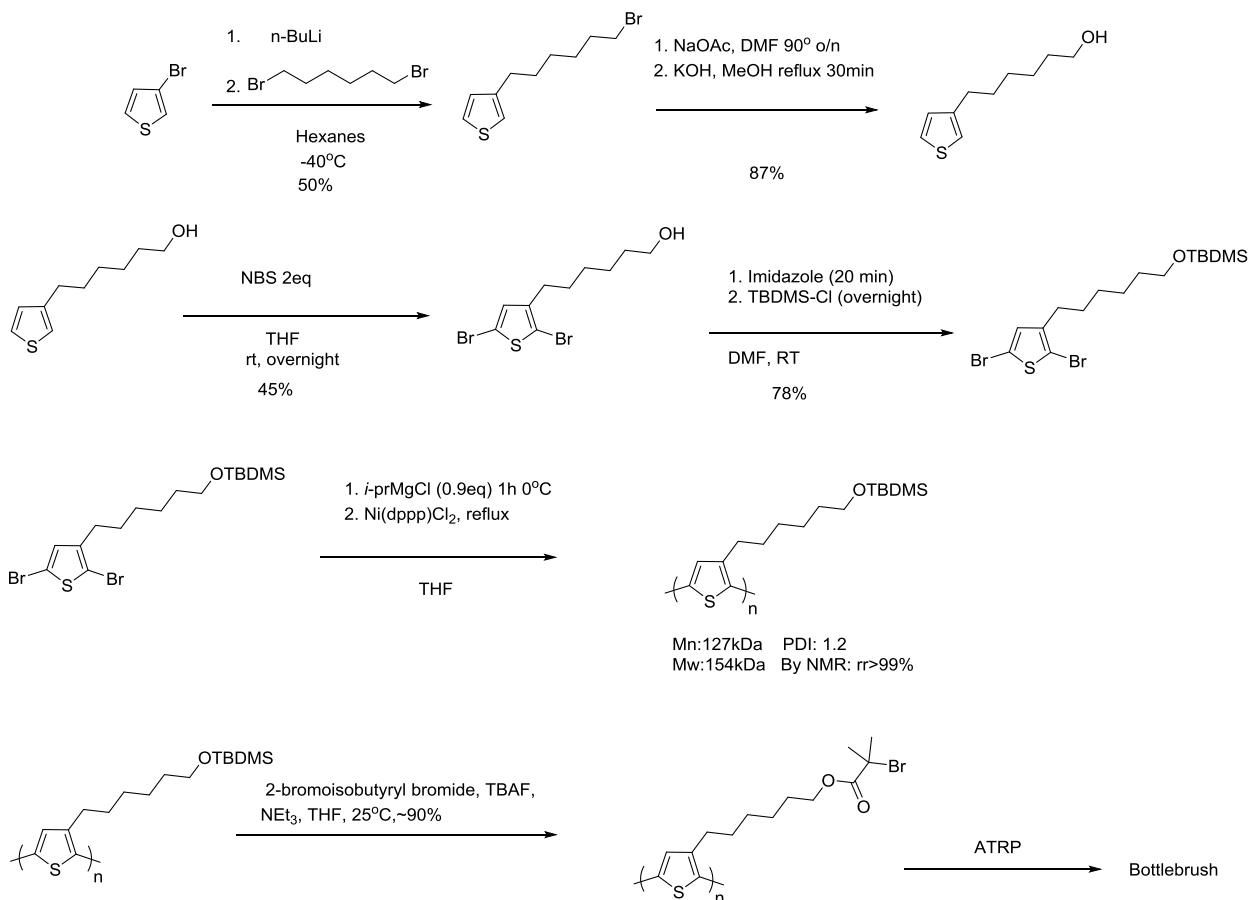


Table S1. Characterization of molecular bottlebrush with regioregular P3HT backbone.

sample	M_n^a (g/mol)	$\bar{D}^b$	d^c (nm)
rr-P3HT bottlebrush	2,460,000	1.46	60±5

^aMolecular weight determined by GPC using poly(methyl methacrylate) standard. ^bdispersity determined by GPC. ^cThe width of rr-P3HT bottlebrushes measured by AFM.

4. Supporting Figures

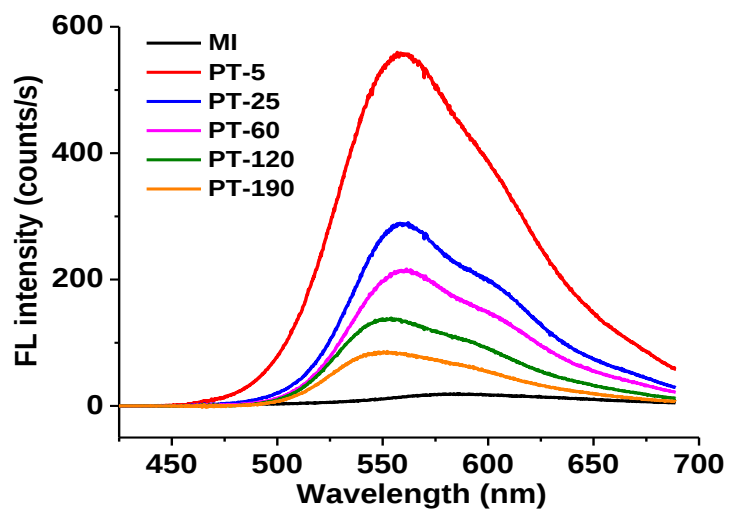


Figure S1. Fluorescence spectra of PT bottlebrushes as well as MI on a 0.5% w/w 2-propanol/water substrate at the same surface pressure of 0.2 mN/m.

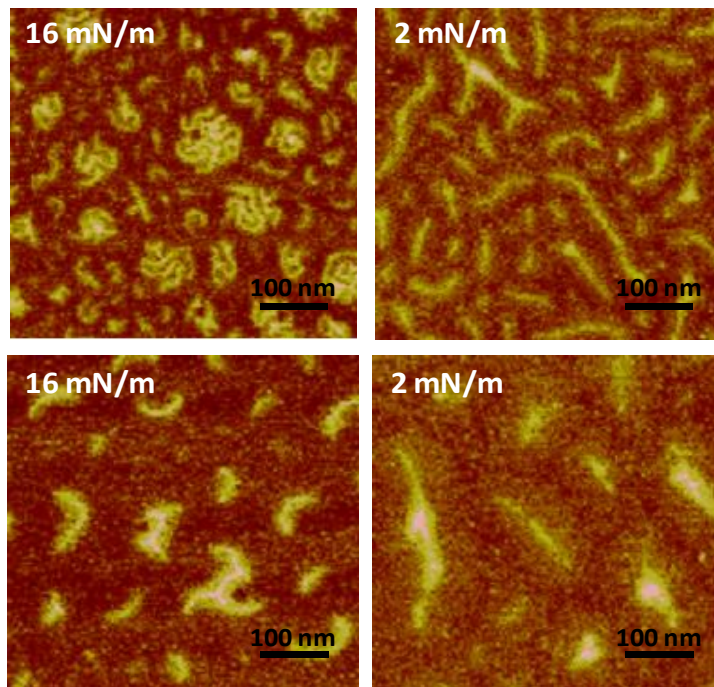


Figure S2. AFM micrographs of PT-60 (top) and PT-190 (bottom) bottlebrushes transferred to freshly cleaved mica substrates from the surface of 0.5% w/w 2-propanol/water substrate at different pressures: 16 mN/m (left) and 2 mN/m (right).

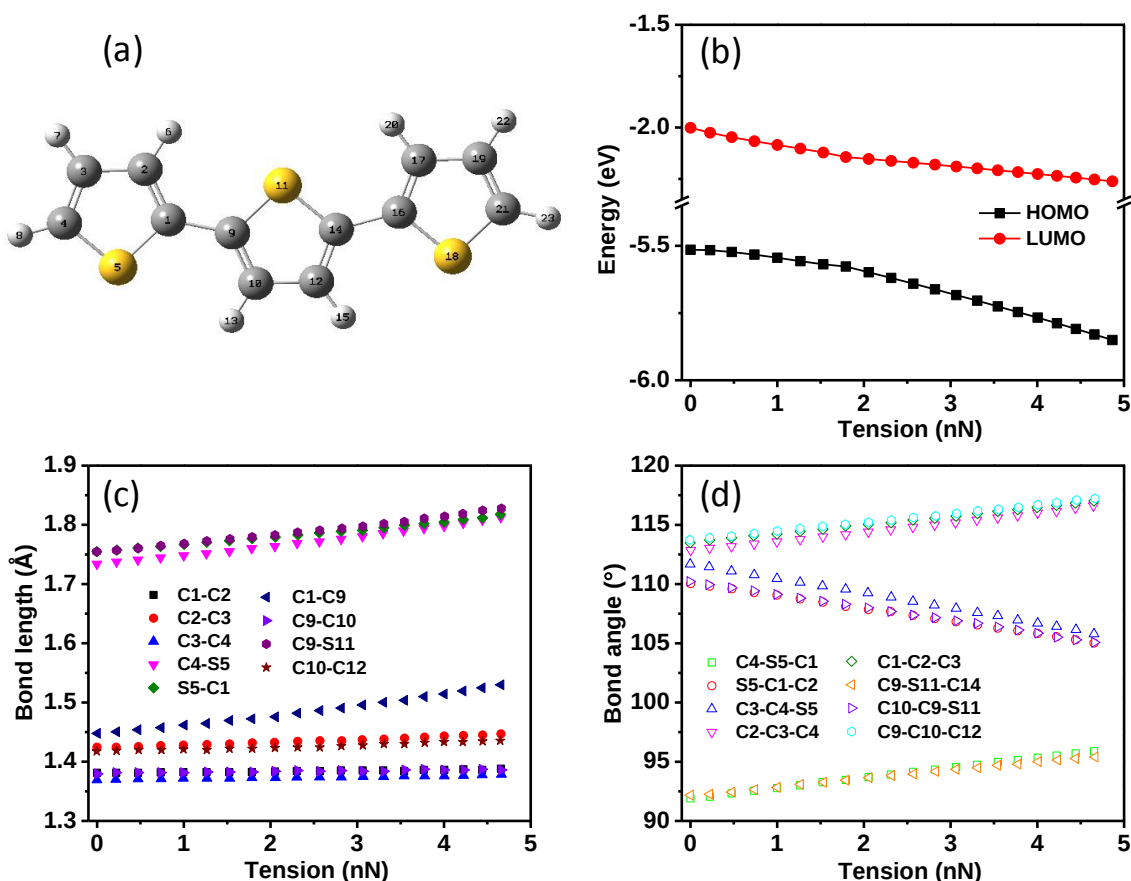


Figure S3. (a) Chemical structure of the model oligothiophene; changes in (b) HOMO/LUMO energies, (c) bond lengths and (d) angles of the model molecule with applied tension based on DFT.

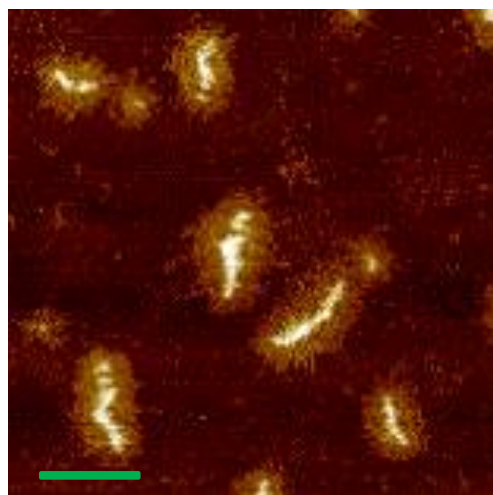


Figure S4. AFM height micrographs of rr-P3HT bottlebrushes spin-cast from dilute chloroform solution on freshly cleaved mica substrate. The scale bar is 100 nm.

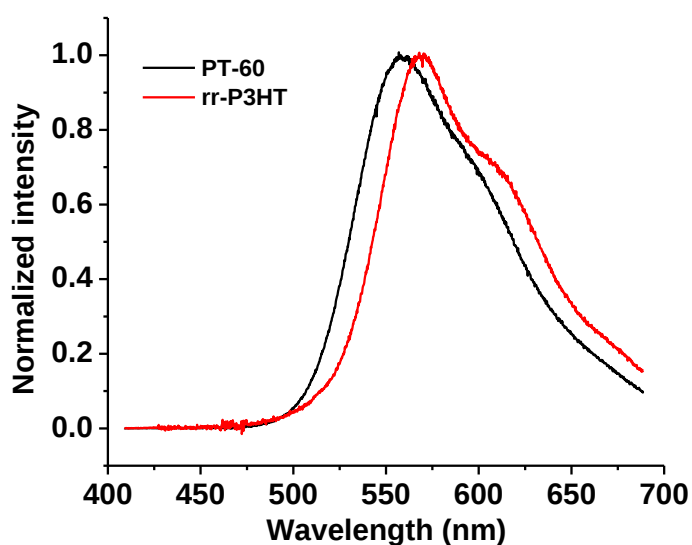


Figure S5. The wavelength of maximum emission of rr-P3HT bottlebrush with regioregular backbone is red-shifted (~ 11 nm) compared to PT-60 with regiorandom backbone (with similar side chain length of ~ 60 nm) under the same tension (~ 1.2 nN). This shift is substantially larger than that of PT-60 at different backbone tensions.

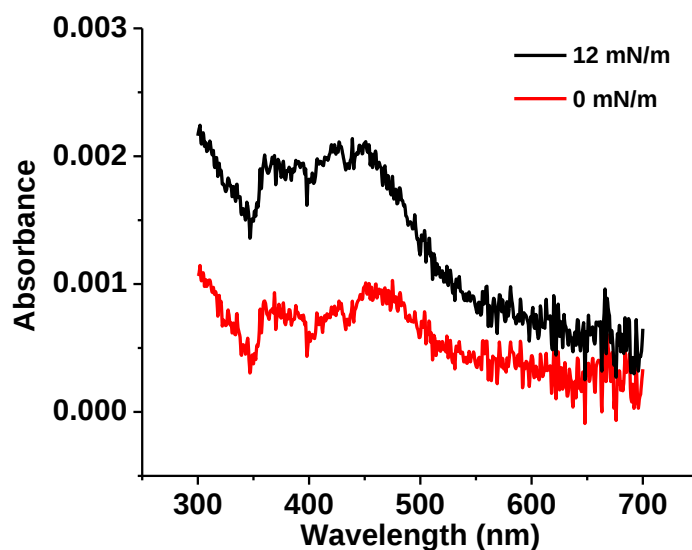


Figure S6. UV-Vis absorption spectra of PT-5 measured at different surface pressures on a LB trough with a quartz window using a Cary 60 Spectrophotometer with fiber optics. Unfortunately, the signal to noise ratio was insufficient to allow quantitative studies of tension-induced alterations of the band shifts. There could be two reasons for the low signal: (1) Due to predominated adsorption of side chains in bottlebrush monolayers, the surface fraction of thiophene monomeric units is much lower than that for the molecules in the abovementioned paper; (2) The extinction coefficient of PT is not high enough to yield measurable absorbance

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