Supplementary informations

Spiral Designed Surface Based on Amino-Perylene Grafted Polyacrylic Acid

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Methods

1- Polymerization of acrylic acid on polyethylene film

Polyethylene films (low density polyethylene (PE) substrates without additives and with a width of 0.5 mm). were activated by plasma treatment. The plasma treatment was performed using a Plasma NT-1 supplied by DIGIT CONCEPT, operating at 13.56 MHz. The treatment time was 1 min at 300 W. The discharge gas was Argon and the gas flow was set at 10 sccm.

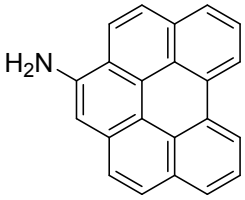
After plasma activation the polyethylene film was put in an aqueous solution containing 20 % (V/V) of acrylic acid 99 % and 0.2% of monomethyl ether hydroquinone as inhibitor. The reaction was carried out at 70°C for 2 h under nitrogen atmosphere. After reaction, the film was extensively washed with distilled water

2- Grafting of 6-amino[g,h,i]perylene on acrylic acid functionalized polyethylene

The grafting of 6-amino[g,h,i]perylene onto Polyethylene film was realized via coupling reaction between carboxylic groups of poly(acrylic acid) and amino groups 6-amino[g,h,i]perylene. The coupling reaction was carried out by means of a coupling agent and in presence of a catalyst. The reaction was carried out using N-(dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, from Aldrich) as coupling agent and in presence of N-hydroxysuccinimide (NHS, from Aldrich). EDC 0.01M and NHS 0.01M were prepared in absolute ethanol. Then the acrylic acid grafted polyethylene film (about 2 cm^2) was added in and the closed flask was put under stirring for 2 hours at room temperature. Finally 6-amino[g,h,i]perylene was added at 0.4 mM. The reaction time was 10 days. Then the film was rinsed with ethanol and let dry under ambient conditions. The reaction was also carried out in the same conditions but 6-amino[g,h,i]perylene concentration was 0.04 mM.

Dye characterization

6-Aminobenzo[g,h,i]perylene (AP)



Chemical Formula: $C_{22}H_{13}N$
Molecular Weight: 291,35

mp: 256 °C

^{1}H NMR (δ ppm, CD_2Cl_2, 300K, 300 MHz): 8.94 (d, *J* = 8.2 Hz, 1H), 8.92 (d, *J* = 8.2 Hz, 1H), 8.20 – 7.8 (m, 8H), 7.61 (s, 1H), 4.58 (s_{br}, 2H).

^{13}C NMR (δ ppm, CD_2Cl_2, 300K, 75 MHz): 149.1, 141.3, 134.0, 132.3, 130.8, 130.4, 128.9, 127.6, 126.6, 126.5, 126.3, 126.0, 125.8, 124.9, 124.7, 124.0, 120.6, 120.5, 120.1, 118.6, 117.9, 109.4.

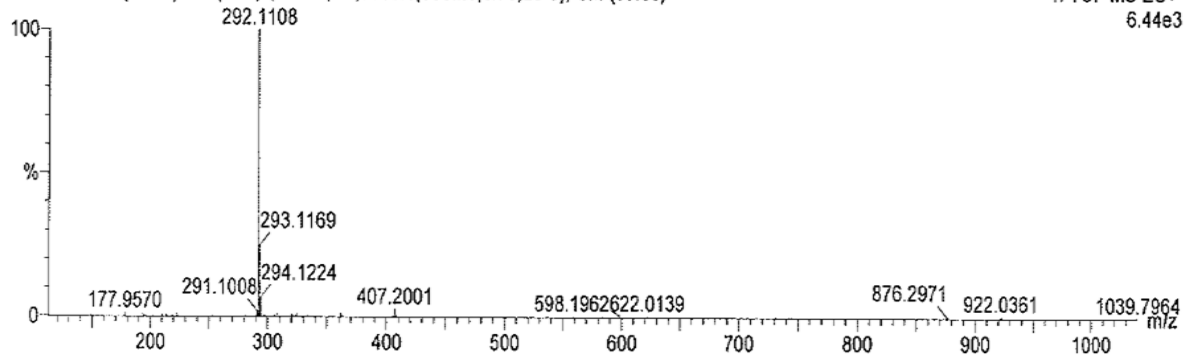
HRMS (ESI): *m/z* calculated for $C_{22}H_{14}N$ ($[M+H]^+$): 292.1126 found: 292.1108.

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

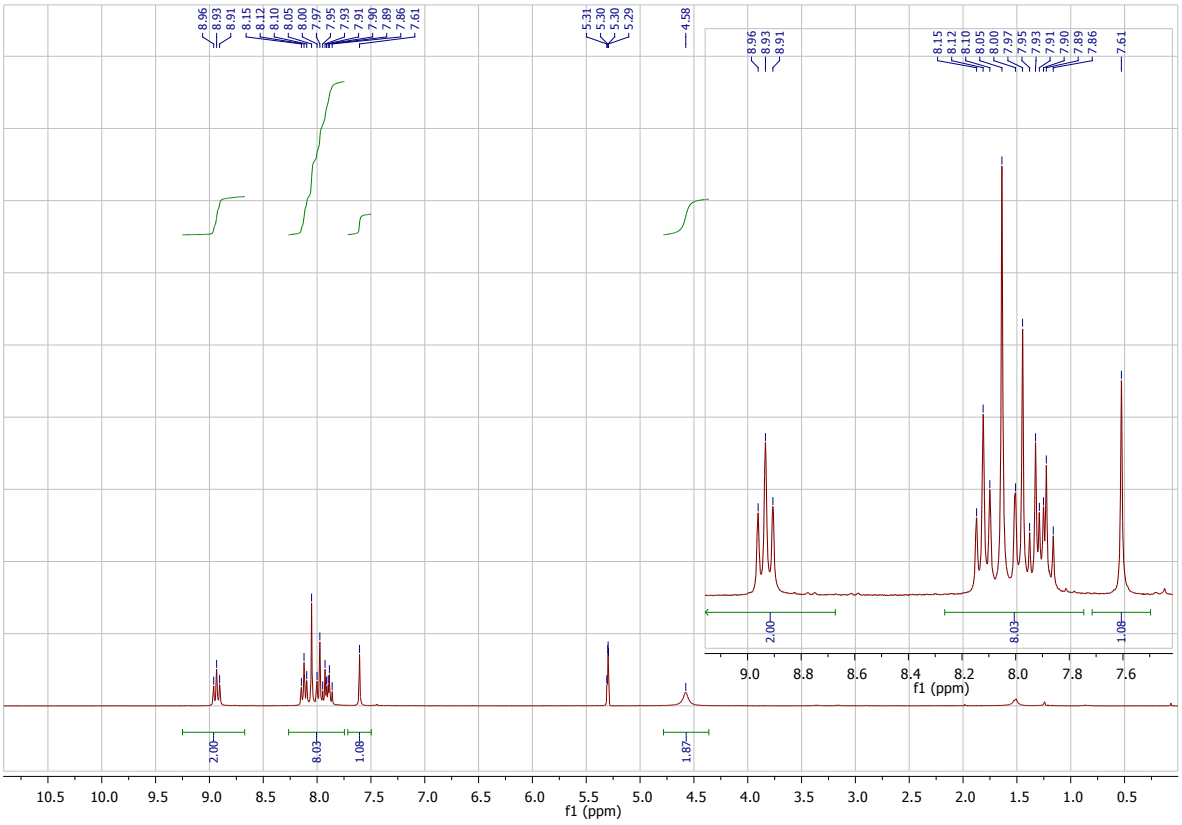
Monoisotopic Mass, Odd and Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

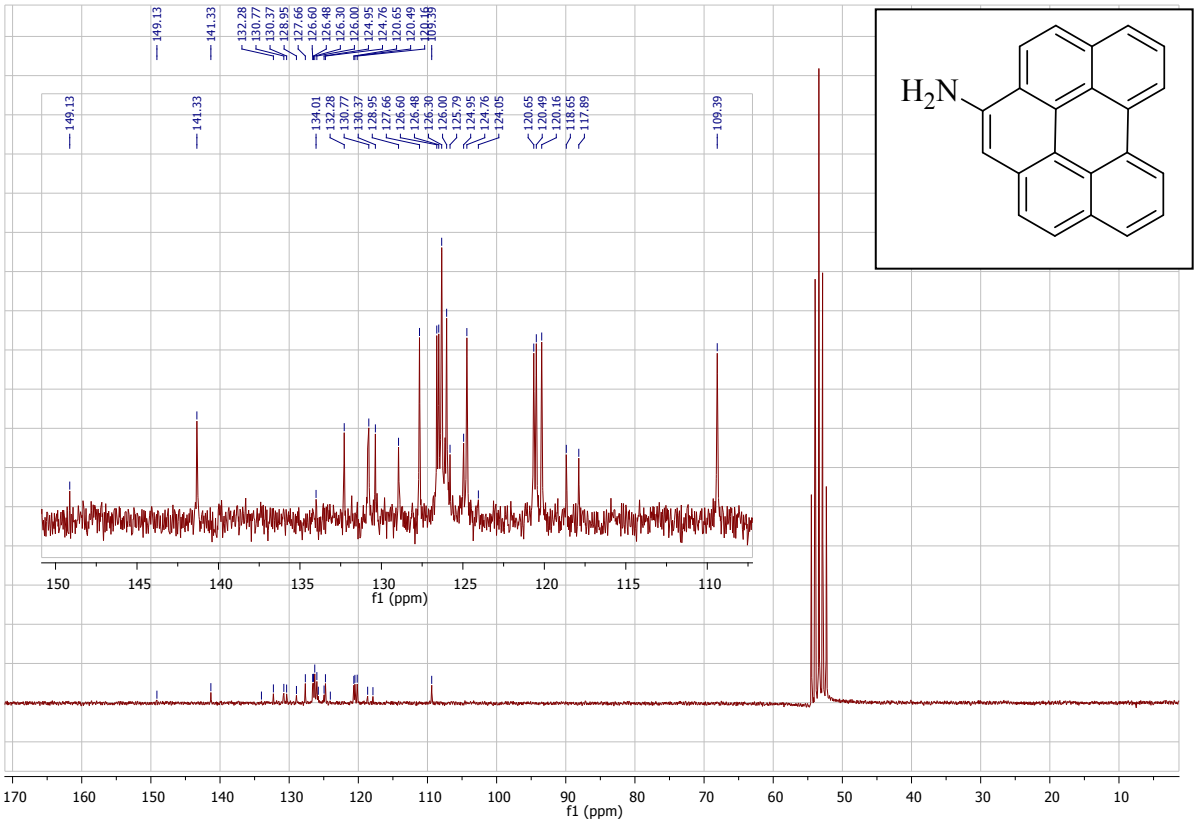
G249
HR202223 59 (1.911) AM (Cen,4, 70.00, Ar,5000.0,556.28,0.70,LS 3); Cm (59:63) 1: TOF MS ES+ 6.44e3



Minimum:				-1.5		
Maximum:		2.1	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
292.1108	292.1126	-1.8	-6.2	16.5	1	C22 H14 N

^{1}H NMR and ^{13}C NMR of 6-aminobenzo[g,h,i]perylene (AP)


8.96
8.93
8.91
8.15
8.12
8.10
8.05
8.00
7.97
7.95
7.93
7.91
7.90
7.89
7.86
7.61
5.31
5.30
5.30
5.29
4.58
2.00
8.03
1.08
1.87
f1 (ppm)


149.13
141.33
132.28
130.77
130.37
128.95
127.66
126.60
126.48
126.30
126.00
124.95
124.76
120.65
120.49
109.39
134.01
130.37
125.79
124.05
120.16
118.65
117.89
H_2N
f1 (ppm)

Surface characterization

a. *Water contact angle measurements*

Contact angles were measured using the sessile drop method by a Krüss DSA goniometer which was interfaced to an image capture-software. All samples were dried at room conditions before analysis.

b. *AFM imaging*

A diInnova SPM microscope from Veeco was used to take AFM images of samples. We worked in tapping mode using RTESPA-CP probes by Veeco. All samples were dried at room conditions before analysis.

c. *SEM imaging*

JEOL 6700F microscope was used to obtain SEM images of samples. The surface of samples was metallized by sputtering 1nm coating of Pt. All samples were dried at room conditions before analysis.

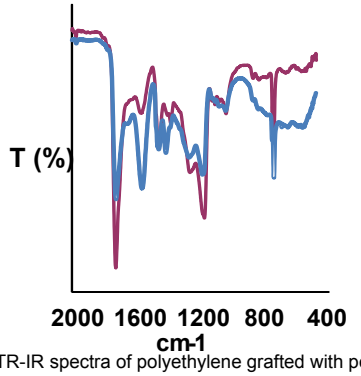


Figure 1 ATR-IR spectra of polyethylene grafted with polyacrylic acid film before (red line) and after reaction (blue line) with reaction with amino-perylene

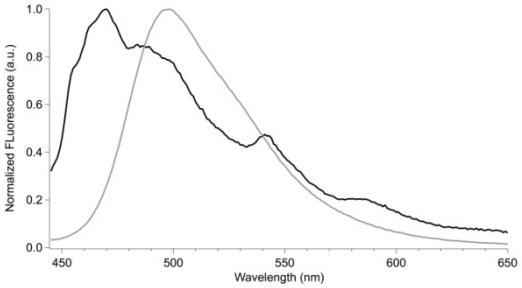


Figure 2 Fluorescence emission spectra (excitation 430 nm) of amino benzoperylene in ethanol ($3.6.10^{-4}$ M -grey line) and grafted on PAA-PE surface (black line).

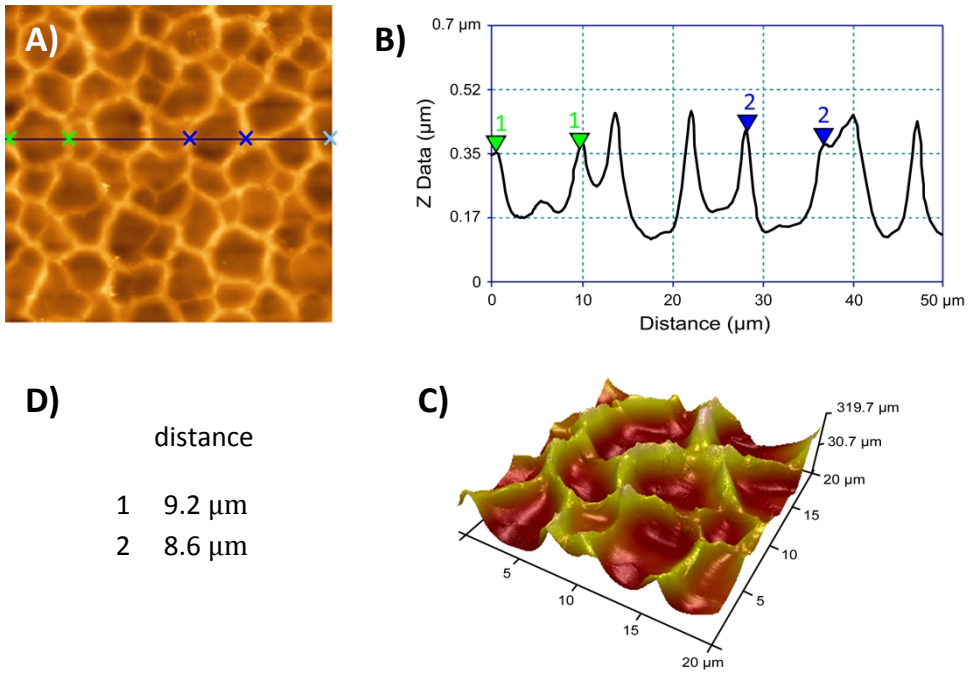
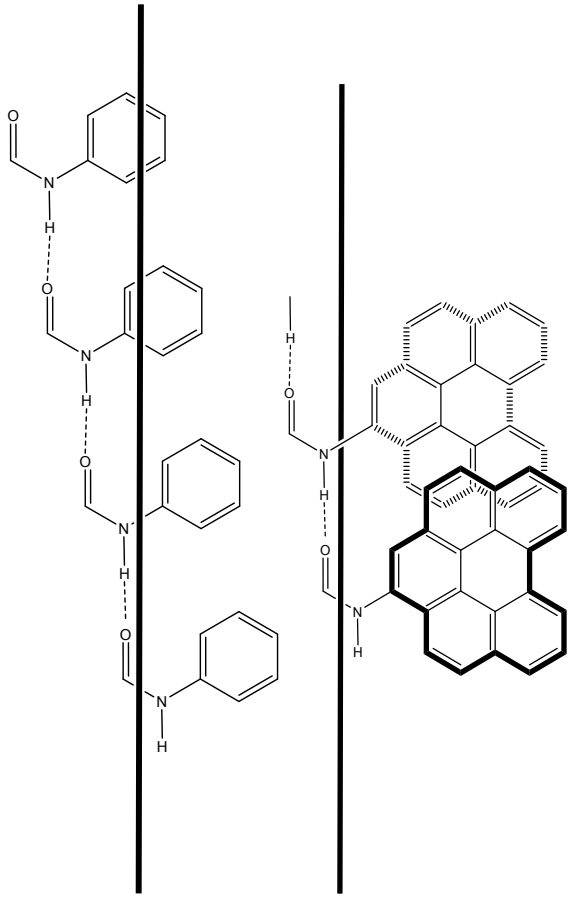


Figure 3 AFM line analysis (A) image with markers and (B) surface profile and (C) distance between markers of polyethylene grafted with poly(acrylic acid) after reaction with reaction with amino-perylene, (D) 3D-AFM image of 20x20 µm surface.

Explanation of the spiral shape of the grooves



As represented here, interchain connexion due to H-bonding are possibly responsible of the non strictly face to face interaction of the neighbouring benzoperylene units, inducing spiral shape grafted motives. This assistance of π- π stacking by H-bonding has already been observed by P.K. Sukul et al. (1). The H-bonding drives the molecules towards sufficient proximity enabling self-assembly.

SEM images of the PE-AA-AP sample obtained with the a 0.04 mol/L solution of AP:

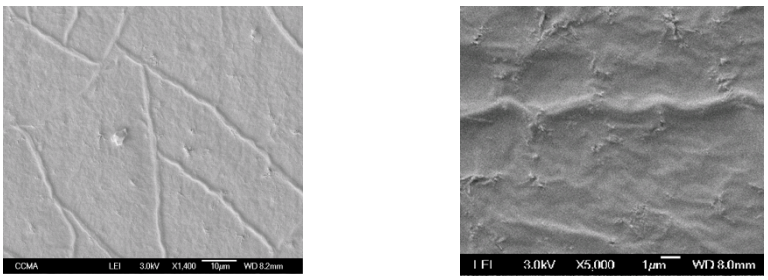
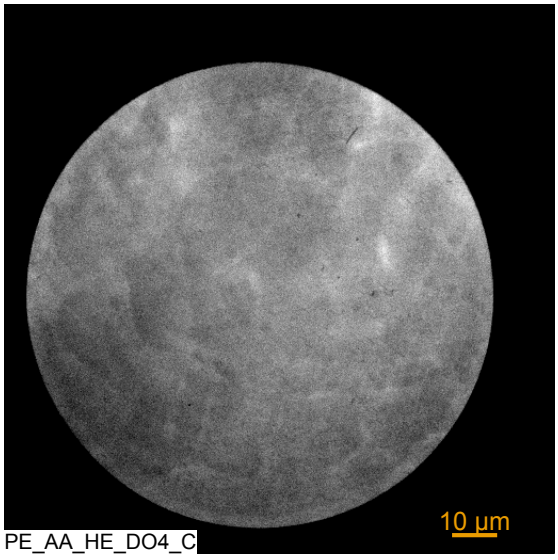


Figure 4: SEM images of the PE-AA-AP sample obtained with the a 0.04 mol/L solution of AP



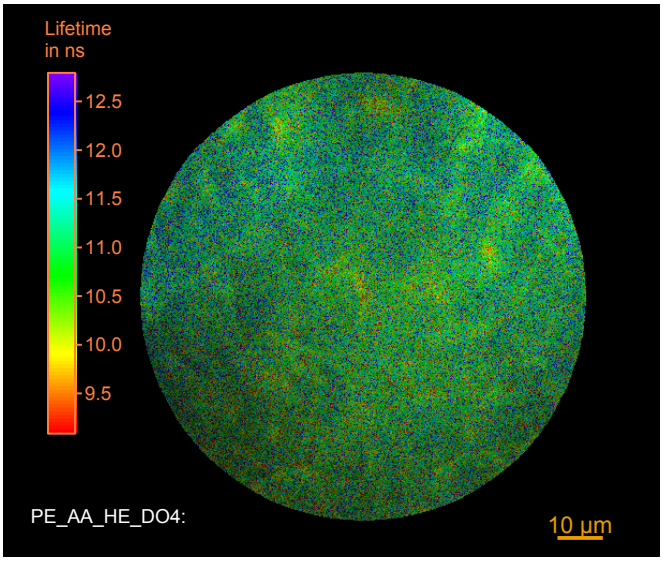


Figure 5: imaging of a PE-AA-AP film - Transmission image (left) and lifetime image (right) – excitation 515 nm – emission > 515 nm (no filtering)