Supporting Information

Surface-grafted polyacrylonitrile brushes with aggregation-induced emission properties

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Experimental section

Materials. Acrylonitrile (AN, 99%), α -bromophenylacetic acid (BPAA, 98%), tris(2pyridiylmethyl)amine (TPMA, 98%), copper (II) bromide (CuBr₂, 99%), (3aminopropyl)triethoxysilane (APTES), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), sulfuric acid (95%), hydrogen peroxide (30%) were purchased from Sigma-Aldrich. AN was passed through a column of basic alumina before polymerization to remove inhibitor. All solvents were of highest available grade, and Milli-Q water was used in all experiments.

Synthesis of PAN by photoinduced ATRP. Typical polymerization conditions for the reaction with 50 ppm of catalyst: 4.0 mL of DMSO, 0.1 mL of DMF (NMR standard), 14.90 mg (0.069 mmol, 1 equiv.) of BPAA, 13.5 μ L of CuBr₂/TPMA stock solution in DMF (c = 25.4 mg CuBr₂/mL, 1.54 × 10⁻³ mmol CuBr₂, 5.0 × 10⁻⁵ equiv., CuBr₂/TPMA 1:3) were placed in a Schlenk flask and degassed by bubbling with nitrogen for 20 minutes. In a separate vial 2.0 mL of acrylonitrile (31 mmol, 442 equiv.) was degassed and transferred into the Schlenk flask. The reaction mixture was irradiated with a UV light ($\lambda_{max} = 365$ nm) from a commercial household UV device (equipped with four 9W lamps) for 6 hours at room temperature. Samples were taken at one-hour intervals for ¹H NMR and GPC measurements. After 6 h, the polymer was precipitated in methanol/water mixture (9/1 v/v), filtered, thoroughly washed with methanol and deionized water, and dried in a vacuum oven for 24 hours.

Preparation of BPA-modified surfaces. Silicon substrates were cleaned with piranha solution, rinsed with deionized water, dried and placed in the desiccator containing a petri dish with a few drop (100 μ L) of APTES. The desiccator was placed under vacuum for 15 min. After 15 min the desiccator was fully closed. The substrates together with the APTES were left overnight under vacuum. Afterwards the substrates were rinsed with toluene, ethanol, deionized water, and ethanol to remove physically attached APTES and dried in a stream of air. The substrates functionalized with APTES were placed in a flask 20 mL of DMF. 10 mg (0.046 mmol) of BPAA and 9.0 mg (0.047 mmol) of EDC was added and left for 24 hours. Afterwards the substrates were cleaned with DMF, ethanol, milliQ water, and ethanol and dried in a stream of air.

Grafting of PAN brushes. BPA-functionalized silicon wafer was placed in a vial with 1 mL of acrylonitrile, 2 mL of DMSO and appropriate amount of $CuBr_2/TPMA$ stock solution in DMF. The catalyst concentrations used were: 50 ppm, 200 ppm and 400 ppm vs monomer. The reaction mixture was degassed and irradiated with a UV lamp ($\lambda_{max} = 365$ nm) for 6 hours. Afterwards the substrates were thoroughly rinsed with DMF, toluene, ethanol, water and ethanol and dried in a stream of nitrogen.

Characterization. Gel permeation chromatography (GPC) was performed on a Waters system (pump: Waters 515, USA, injector: Hewlett-Packard 1050 USA, detector: Waters 2414 and Waters Styragel HR3-6 columns) with DMF 50 mM LiCl as eluent at 50 °C. Molecular weights were calculated using linear PMMA calibration standards. ¹H NMR (Bruker Avance 400 MHz) was used to determine monomer conversion and real molecular weights of synthesized PAN in DMSO-*d*6. AFM topography measurements were performed in tapping mode on a Bruker Multimode 8 using a NanoScope V controller and a JV vertical engage scanner. The cantilevers (resonance frequency 70 kHz and spring constant 2N/m) were purchased from Olympus. Surface water contact angle measurements were conducted on OCA15 (Dataphysics,

Germany). After deposition the drop was left to stabilize for 10 seconds. The volume of the drop was 3 μ L. FT-IR measurements of Si wafers after APTES deposition and after grafting of PAN brushes were performed on Alpha-P spectrometer (Bruker). The spectra were averaged over 64 scans. Fluorescence microscopy measurements were performed on the Olympus IX71 microscope. The objective used was 20x magnification and the excitation wavelength was λ_{ex} = 360 nm. 460 nm emission filter was used. Film thickness of the PAN brushes was measured by spectroscopic ellipsometry (M2000, J.A. Woollam Co., Inc., USA) within the wavelength range of 370 – 1000 nm and Cauchy dispersion model was used to fit the data. The results were averaged over at least two measurements taken at different spots on the sample. Fluorescence spectroscopy was conducted on Perkin Elmer LS55 with FLWinlab software. For excitation measurements, the opening of the emission slit was set to $\lambda_{em} = 430$ nm. For the emission measurements, the opening of the emission and excitation slits were both set at 4.0 nm, and the excitation wavelength was $\lambda_{ex} = 348$ nm.



Figure S1. GPC traces of photoinduced ATRP of acrylonitrile conducted at 110 ppm and 290 ppm (vs monomer) of CuBr₂/TPMA catalyst.



Figure S2. ¹H NMR spectrum of PAN synthesized by photoinduced ATRP under conditions [AN]:[BPAA]:[CuBr₂]:[TPMA] = 442:1:0.022:0.066; AN/DMSO = 1/2 (v/v), $\lambda = 360$ nm, rt, 6h (Table 1, entry 3). M_n was calculated by integrating aromatic peaks at 7.40 ppm (peak a, 5H) and peak d at 3.21 ppm (1H). Chain-end functionality (CEF) can be estimated from the peak at 5.31 ppm, corresponding to the methane proton at the terminal carbon atom (peak e, 1H).



Figure S3. Excitation ($\lambda_{max} = 345 \text{ nm}$, $\lambda_{em} = 430 \text{ nm}$) and emission ($\lambda_{max} = 431 \text{ nm}$, $\lambda_{ex} = 348 \text{ nm}$) spectra of PAN ($M_n=12,200$; $M_w/M_n=1.17$; Table 1, entry 2) in DMF at concentrations 0.00125 M, 0.025 M, 0.5 M, 1 M and 2 M.



Figure S4. Fluorescence microscopy image of a silicon wafer after deposition of APTES.