

Supporting Information on

Innovative Method for Controlled Synthesis of Bicomponent Monolayer Films Obtained by Reduction of Diazonium

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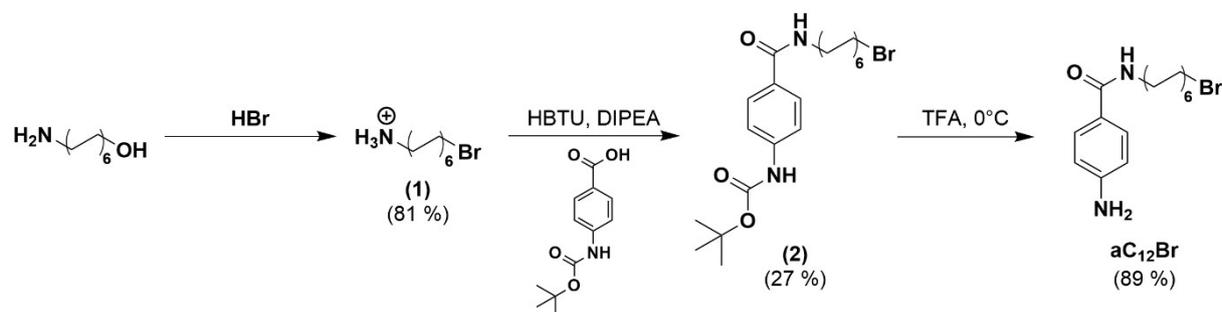
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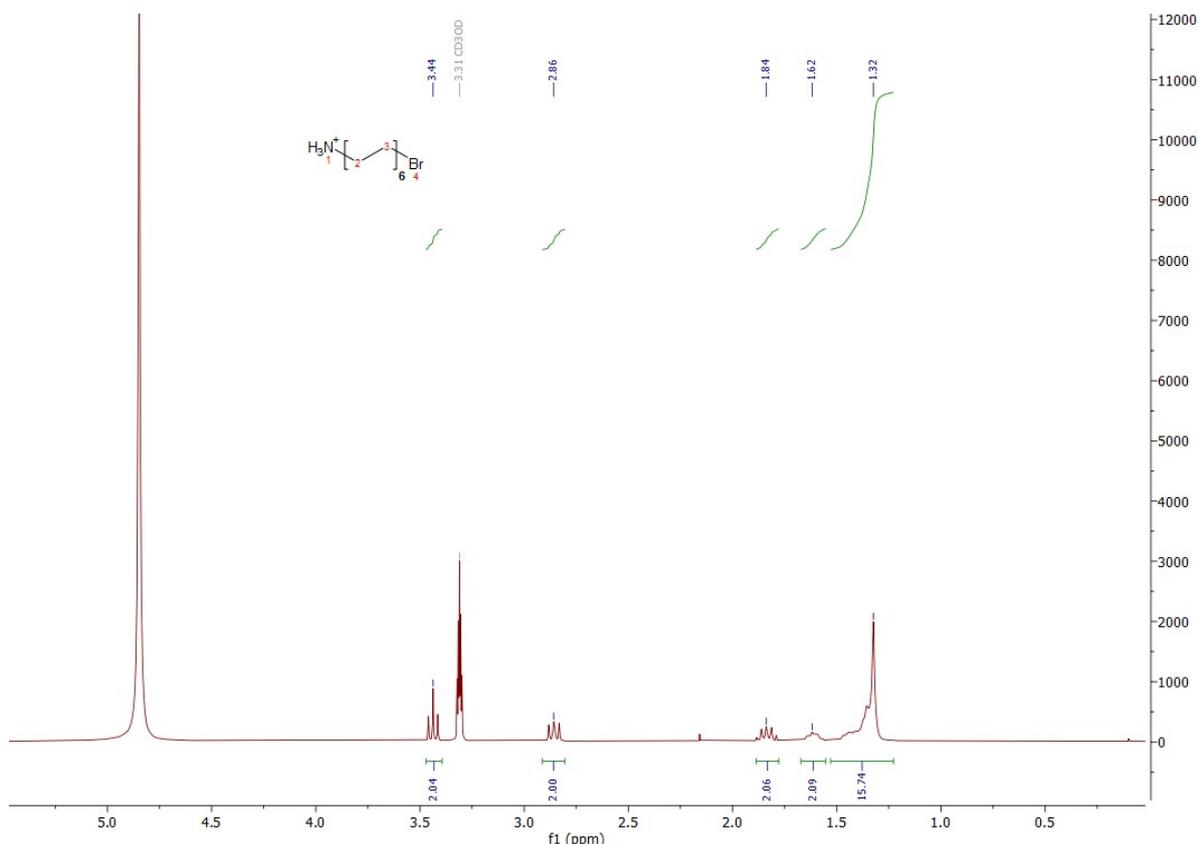
SI-1 Synthesis and characterization of aC₁₂Br compound



12-bromododecan-1-aminium (1)

500 mg of 1-aminododecanol (2.49 mmol) were added to 10 ml of HBr in a refluxing flask with stirring and heated for 18 hours. After cooling to room temperature, the mixture was filtered using Büchner funnel and the resulting solid was washed with water. Upon drying, a mass of 700 mg of a silver-grey solid was obtained in 81% yield.

NMR¹H (300 MHz, CD₃OD): δ = 3.44 ppm (t, J = 6.6 Hz, 2H), 2.86 ppm (t, J = 7.6 Hz, 2H), 1.84 ppm (m, 2H), 1.62 ppm (m, 2H), 1.47-1.32 ppm (m, 16H).

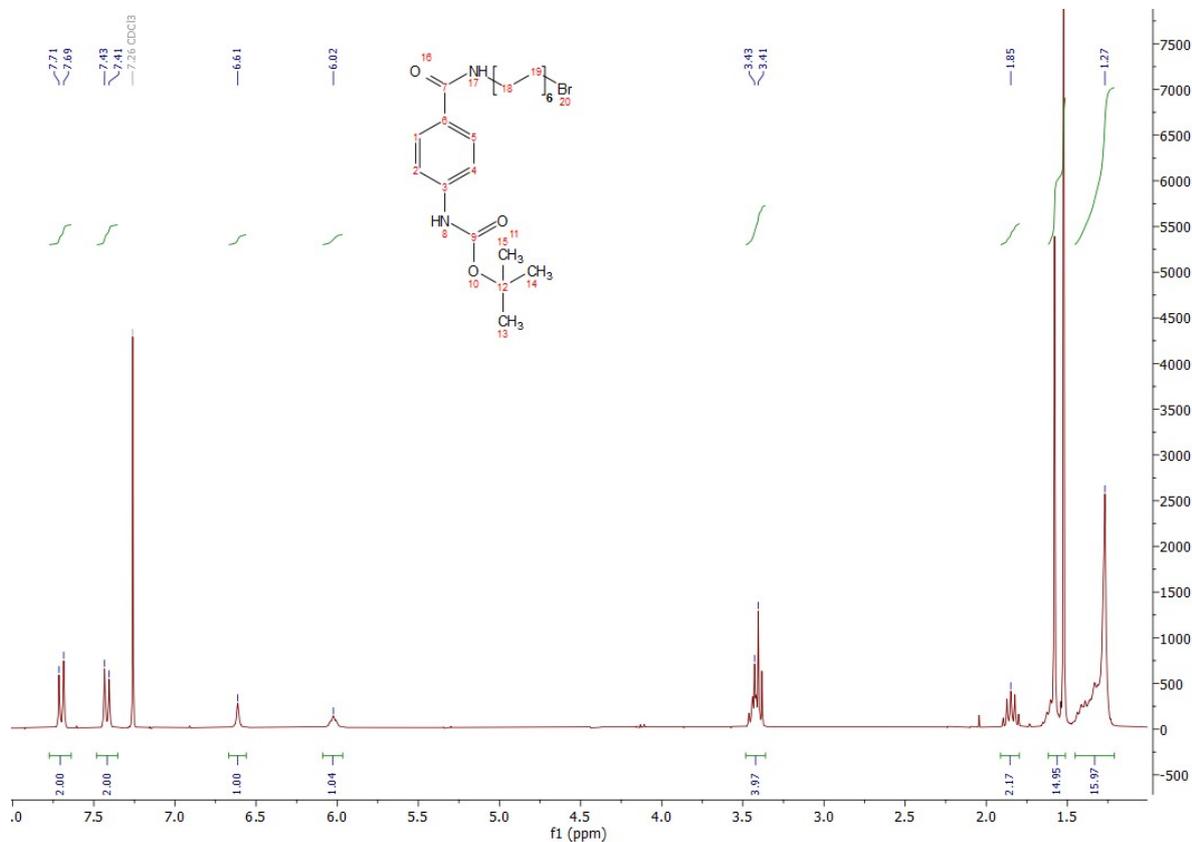


tert-butyl (4-((12-bromododecyl)carbamoyl)phenyl)carbamate (2)

In 60 mL of DCM, 344 mg of Boc-4-Abz-OH (1.45 mmol), 606 μ L of triethylamine (4.35 mmol - 3 eq), 196 mg of 12% hydrated 1-hydroxybenzotriazole (1.45 mmol - 1 eq) and 550 mg of O-(Benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (1.45 mmol - 1 eq) were dissolved. The mixture was stirred at room temperature for one hour and then 500 mg of 12-bromododecan-1-aminium (1.45 mmol - 1 eq) were added. After two days of stirring at room temperature, the precipitate was

collected on Büchner funnel. The product was subsequently purified by a chromatographic column with a 3% DCM/MeOH mixture. 190 mg of product were recovered as a white powder with a yield of 27%.

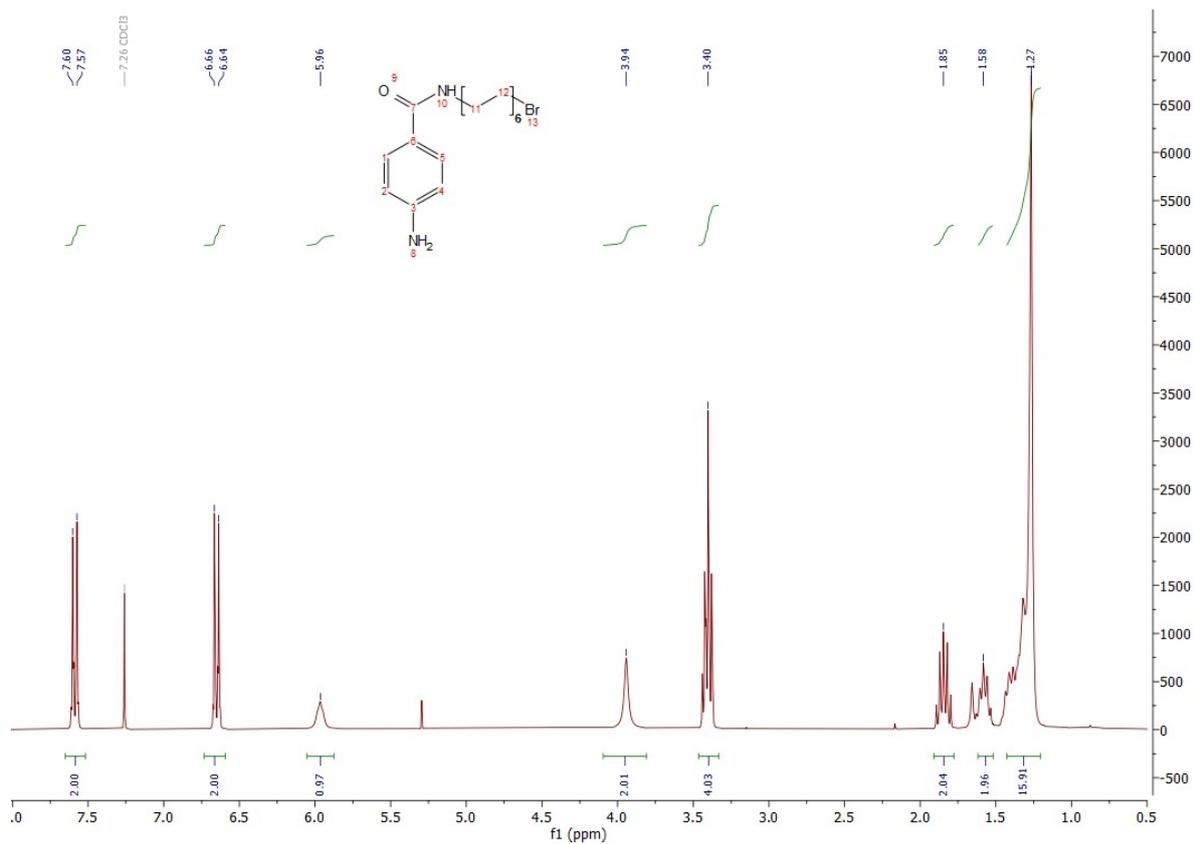
NMR¹H (400 MHz, CDCl₃): δ = 7.70 ppm (d, J = 11.6 Hz, 2H), 7.42 ppm (d, J = 11.6 Hz, 2H), 6.61 ppm (s, 1H), 6.02 ppm (s, 1H), 3.43 ppm (q, 2H), 3.41 ppm (t, 2H), 1.85 ppm (quint, J = 9.2 Hz, 2H), 1.61 ppm (quint, 2H), 1.52 ppm (s, 9H), 1.44-1.27 ppm (m, 16H).



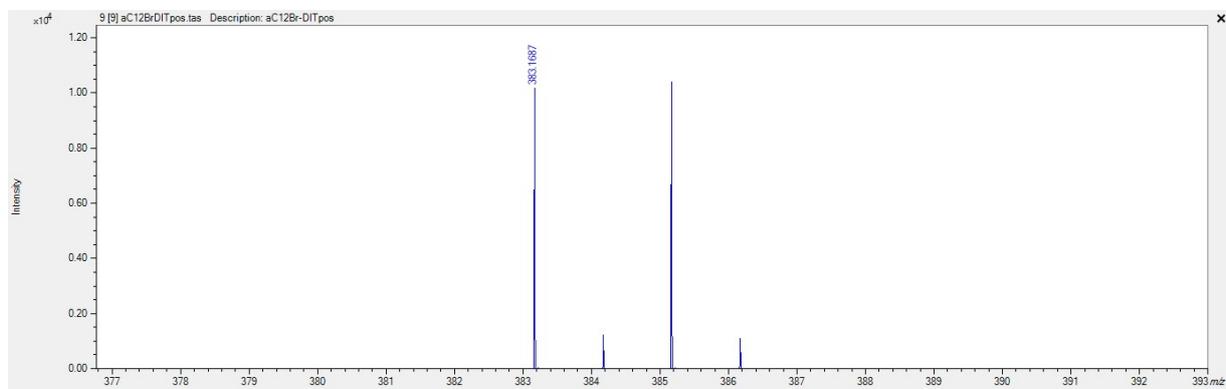
aC₁₂Br

100 mg of 4-amino-N-(12-bromododecyl)benzamide were dissolved in 5 mL of trifluoroacetic acid at 0°C. The mixture was stirred for 30 min, still at 0°C. The acid was then neutralized by adding K₂CO₃ and the mixture was diluted beforehand with 100 mL. The product was then extracted three times with 50 mL of chloroform and the organic phase was dried over MgSO₄. The solvent was evaporated under vacuum, and a white solid of 70 mg was obtained in 89% yield.

NMR¹H (400 MHz, CDCl₃): δ = 7.58 ppm (d, J = 9 Hz, 2H), 6.65 ppm (d, J = 9 Hz, 2H), 5.96 ppm (s, 1H), 3.94 ppm (s, 2H), 3.40 ppm (m, 4H), 1.85 ppm (q, J = 6 Hz, 2H), 1.58 ppm (m, 2H), 1.20-1.45 ppm (m, 16H).



HRMS (MALDI-TOF, DIT): $m/z = 383.1687$ (MH^+), calculated for $C_{19}H_{32}BrN_2O^+$: 383.17.



SI-2 AFM measurements

dC₁₂PDI 100%

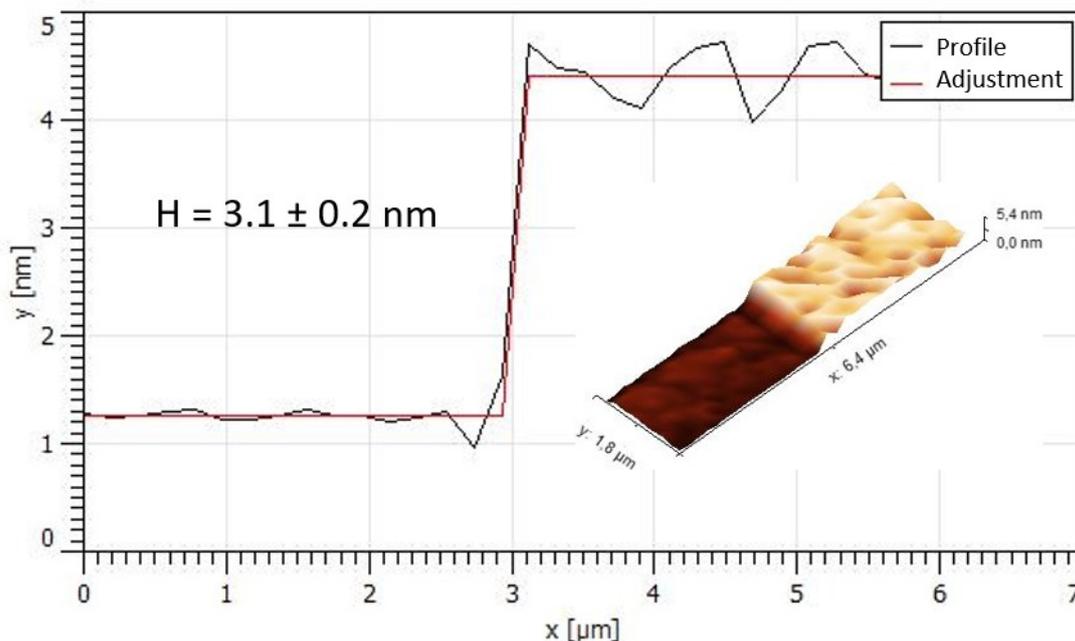


Figure SI-2. A. Depth profile of an area formed by AFM scratching of a C₁₂PDI layer obtained on a PPF substrate by reduction at 0 V for 5 min in a DCM solution containing 10⁻³M dC₁₂PDI + 0.1 M nBu₄NPF₆. Insert: corresponding AFM image of the scratched area.

dC₁₂Br 100%

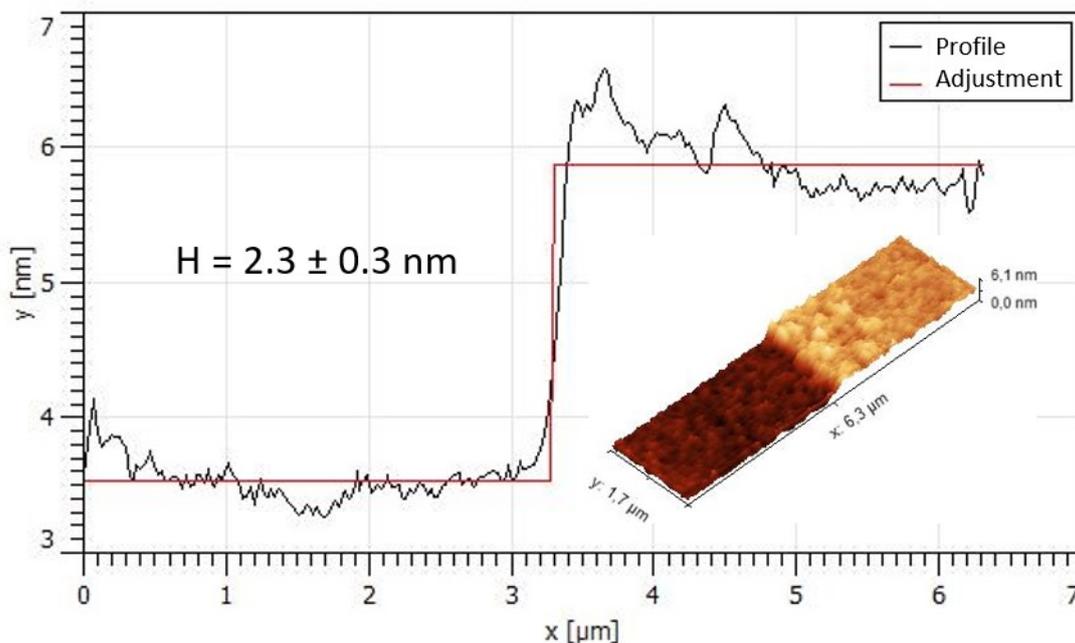


Figure SI-2. B. Depth profile of an area formed by AFM scratching of a C₁₂Br layer obtained on a PPF substrate by reduction at 0 V for 5 min in a DCM solution containing 10⁻³M dC₁₂Br + 0.1 M nBu₄NPF₆. Insert: corresponding AFM image of the scratched area.

dC₁₂PDI/dC₁₂Br 50/50

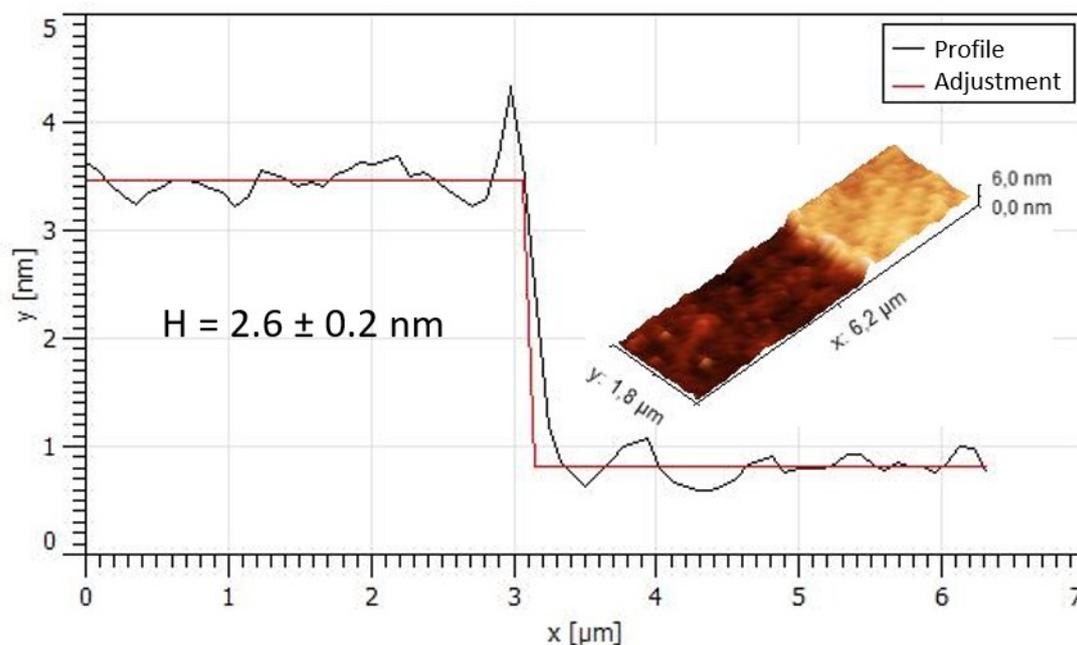


Figure SI-2. C. Depth profile of an area formed by AFM scratching of a mixed C₁₂PDI/C₁₂Br layer obtained on a PPF substrate by reduction at 0 V for 5 min in a DCM solution containing 10⁻³M dC₁₂PDI/dC₁₂Br 50/50 + 0.1 M nBu₄NPF₆. Insert: corresponding AFM image of the scratched area.

SI-3 Current versus scan rate

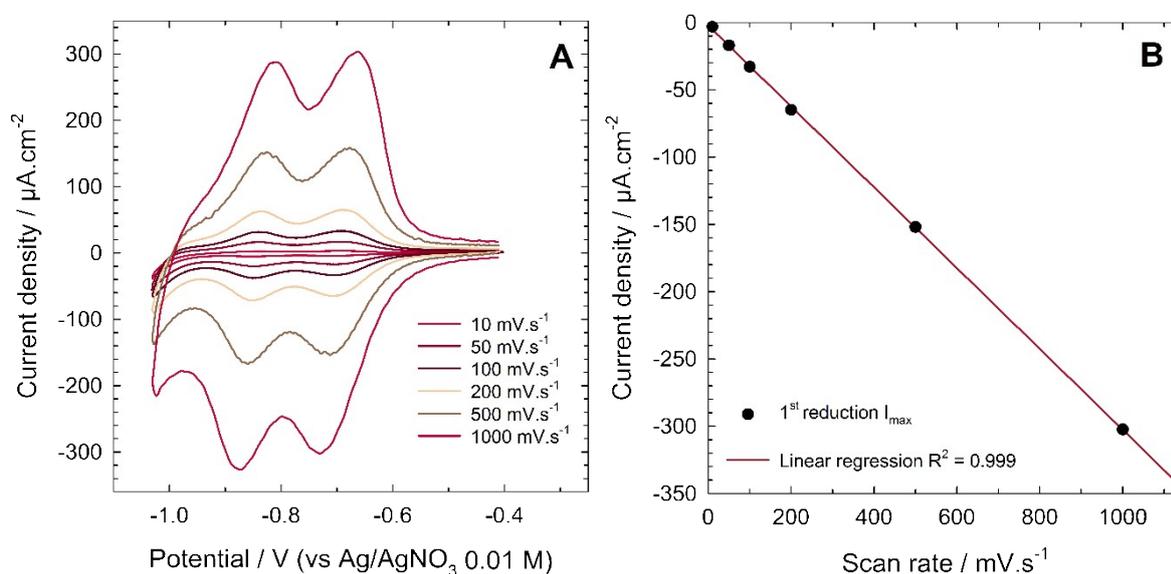


Figure SI-3. A. Cyclic voltammograms recorded in 0.1 M nBu₄NPF₆ in DCM on a glassy carbon electrode previously functionalized by a monolayer of C₁₂PDI (surface concentration of 2.3×10^{-10} mol.cm⁻²). Scan rates ranging from 10 mV.s⁻¹ to 1000 mV.s⁻¹. **B.** Maximum current recorded on the first reduction (PDI⁻ formation) as a function of the scan rate.

SI-4 Spectroscopic response recorded on aC₁₂PDI in solution and on monolayers formed by diazonium reduction on gold

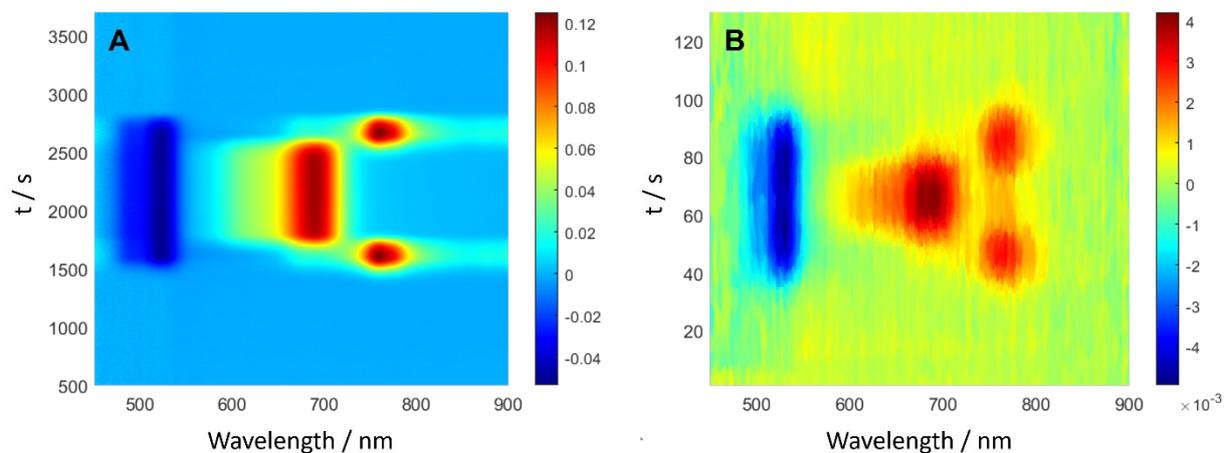


Figure SI-4. **A.** Time-dependent variation of the optical response recorded during a cyclic voltammetry measurement in a 10^{-3} M solution of aC₁₂PDI (DCM, nBu₄NPF₆ 0.1 M at $10 \text{ mV}\cdot\text{s}^{-1}$) under thin layer conditions. **B.** Time-dependent variation of the optical response recorded during cyclic voltammetry measurement (in nBu₄NPF₆ 0.1 M/DCM at $10 \text{ mV}\cdot\text{s}^{-1}$) on a gold electrode modified with a C₁₂PDI monolayer ($\Gamma_{\text{PDI}} = 1.9 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$, deposited by chronoamperometry at 0 V for 5 min in a solution of dC₁₂PDI 10^{-3} M, nBu₄NPF₆ 0.1 M/DCM).

SI-5 XPS fitting curves for Cl 2p et Br 3d components

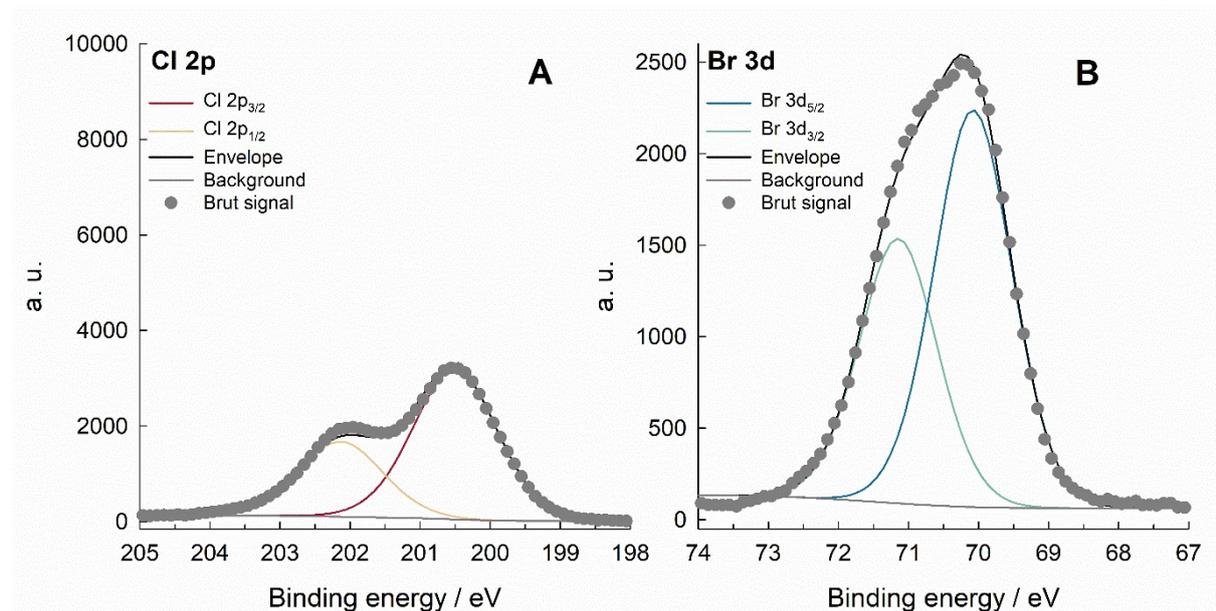


Figure SI-5. XPS core-level spectra recorded on GC plates functionalized by reduction at 0 V during 5 min in a mixture containing dC₁₂PDI/dC₁₂Br (molar ratio of 40/60 and total concentration of dC₁₂PDI+dC₁₂Br = 10^{-3} M in 0.1 M nBu₄NPF₆/DCM). **A.** Core-level spectrum and fitting curves for Cl 2p component. **B.** Core-level spectrum and fitting curves for Br 3d component.