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Supporting Information

Polylutidines: Multifunctional Surfaces through Vapor-Based Polymerization of Substituted Pyridinophanes

Florence Bally-Le Gall[+],[a, b] Christoph Hussal[+],[a] Joshua Kramer,[c] Kenneth Cheng,[d] Ramya Kumar,[d] Thomas Eyster,[d] Amy Baek,[d] Vanessa Trouillet,[e] Martin Nieger,[f] Stefan Bräse,*[c, g] and Joerg Lahann*[a, d]

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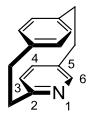
Experimental section

General information:

Solvents, reagents and chemicals were purchased from Acros, Merck, Celeres, Rockland, ABCR, Alfa Aesar or Sigma-Aldrich. Dry tetrahydrofuran was distilled prior to use from sodium/potassium under argon using benzophenone as indicator. Dry dichloromethane was distilled from calcium hydride prior to use. All other solvents, reagents and chemicals were used as purchased, unless stated otherwise. All reactions involving moisture sensitive reactants were executed under argon atmosphere using oven dried or flame dried glassware.

Routine monitoring of reactions were performed using silica gel coated aluminium plates (Merck, silica gel 60, F254), which were analysed under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. Melting points (m.p.) were determined using a *Stanford Research Systems Optimelt* melting point apparatus and are uncorrected. All values are given as single points measured by the apparatus according to the starting point of melting or decomposition.

^{1}H NMR spectra were recorded on a *Bruker* AC 250 (250 MHz), a *Bruker* Avance AM 400 (400 MHz) or a *Bruker* Avance DRX 500 (500 MHz) spectrometer as solutions in $CDCl_3$. For the classification of the signals following abbreviations were used:



H_{Pyp} = hydrogen atoms of the ethylene bridge of the pyridinophane, Ar-H = aromatic hydrogen atoms of the benzene ring, Py-H4 = hydrogen atom of pyridine or the dihydropyridine at position 4 or respectively of the mentioned number, C-Ar/Py = aromatic carbon atoms of the benzene/pyridine ring.

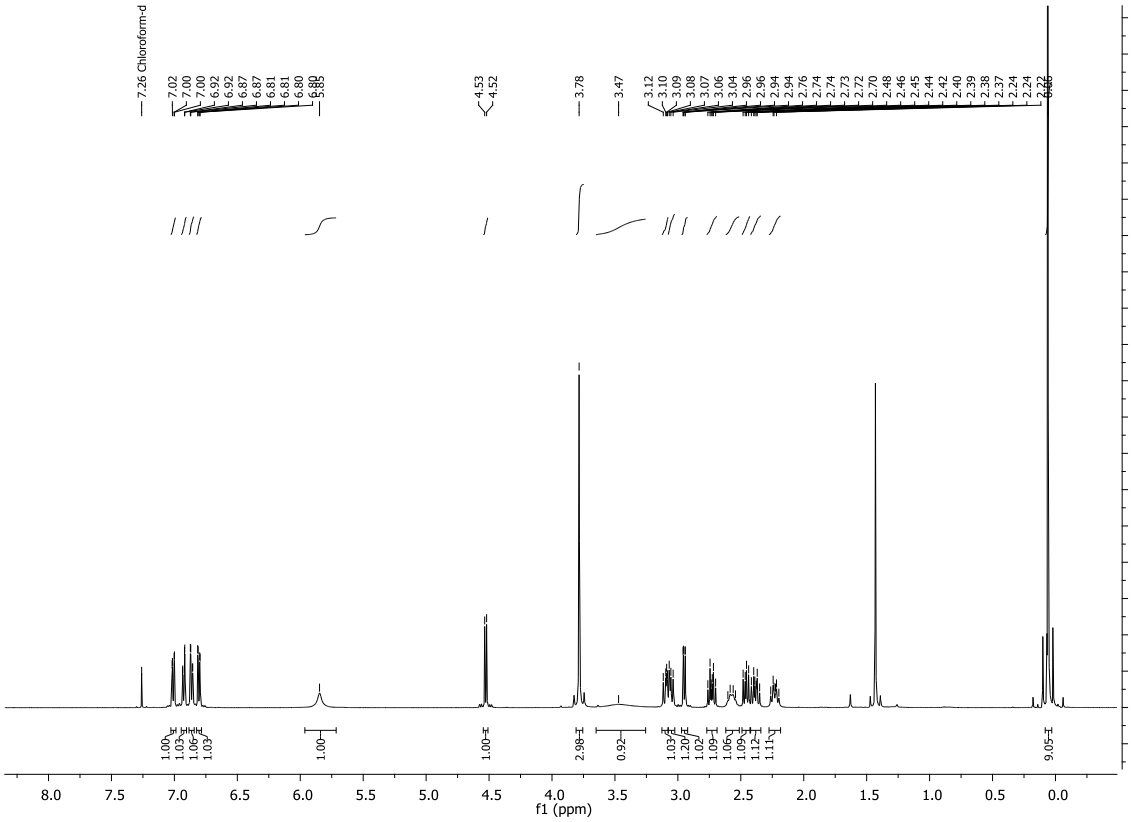
^{13}C NMR spectra were recorded on a *Bruker* Avance AM 400 (100 MHz) or a *Bruker* Avance DRX 500 (125 MHz) spectrometer as solutions in $CDCl_3$. The signal structure was analysed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal) – = secondary C-atom (negative signal) and C_q = quaternary C-atom (no signal).

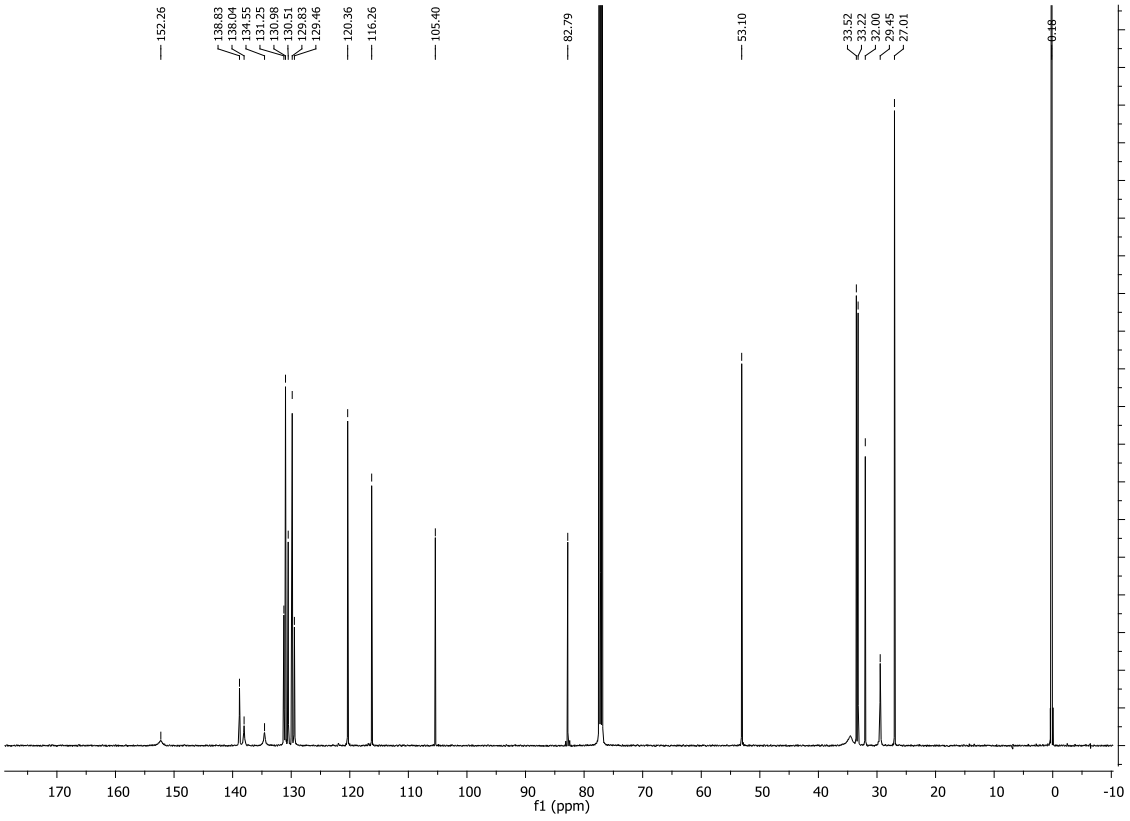
EI-MS (electron impact mass spectrometry), FAB-MS (fast atom bombardment mass spectrometry) and HRMS (high resolution mass spectrometry) spectra were recorded with a *Finnigan* MAT 90 (70 eV) spectrometer.

FT-IR spectra were recorded with a FT-IR *Bruker* IFS 88 or a *Bruker* Alpha T spectrometer. IR spectra were recorded using the DRIFT technique (diffused reflectance infrared Fourier transform-spectroscopy) or ATR Diamant (attenuated total reflection) for solids. IR spectra of oils were determined as KBr plates.

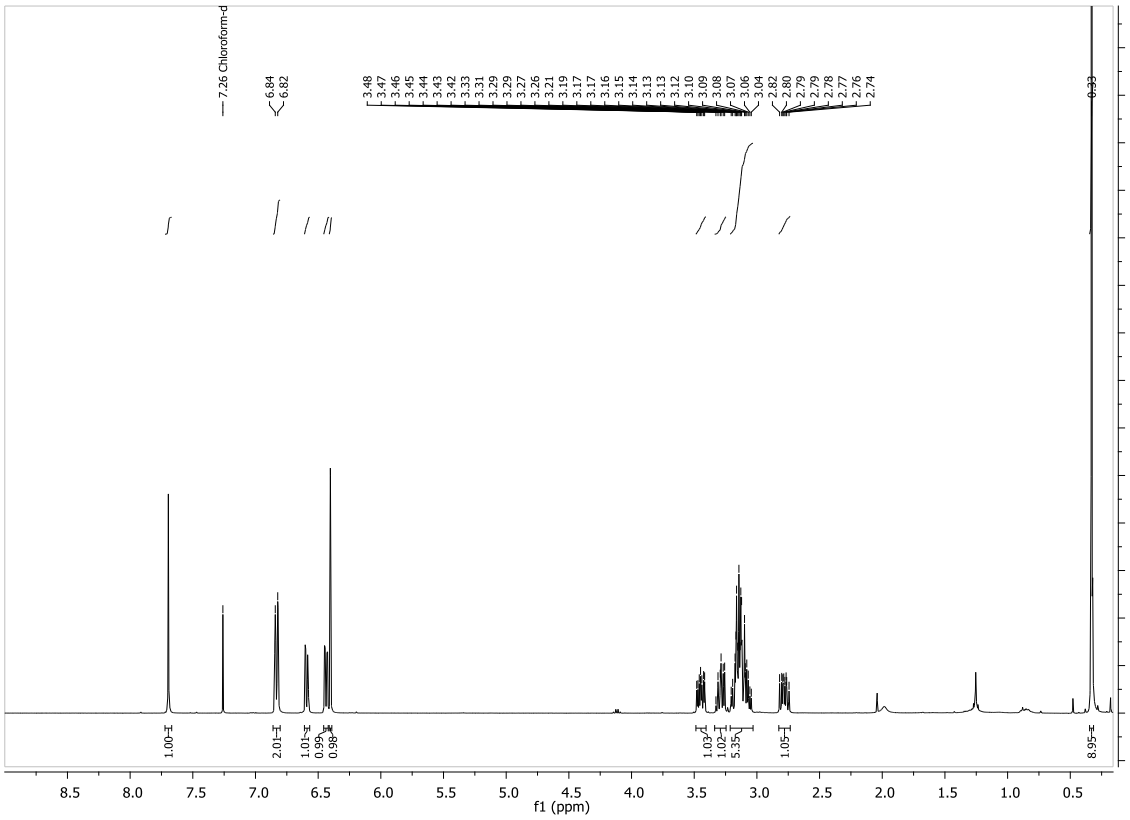
NMR spectra

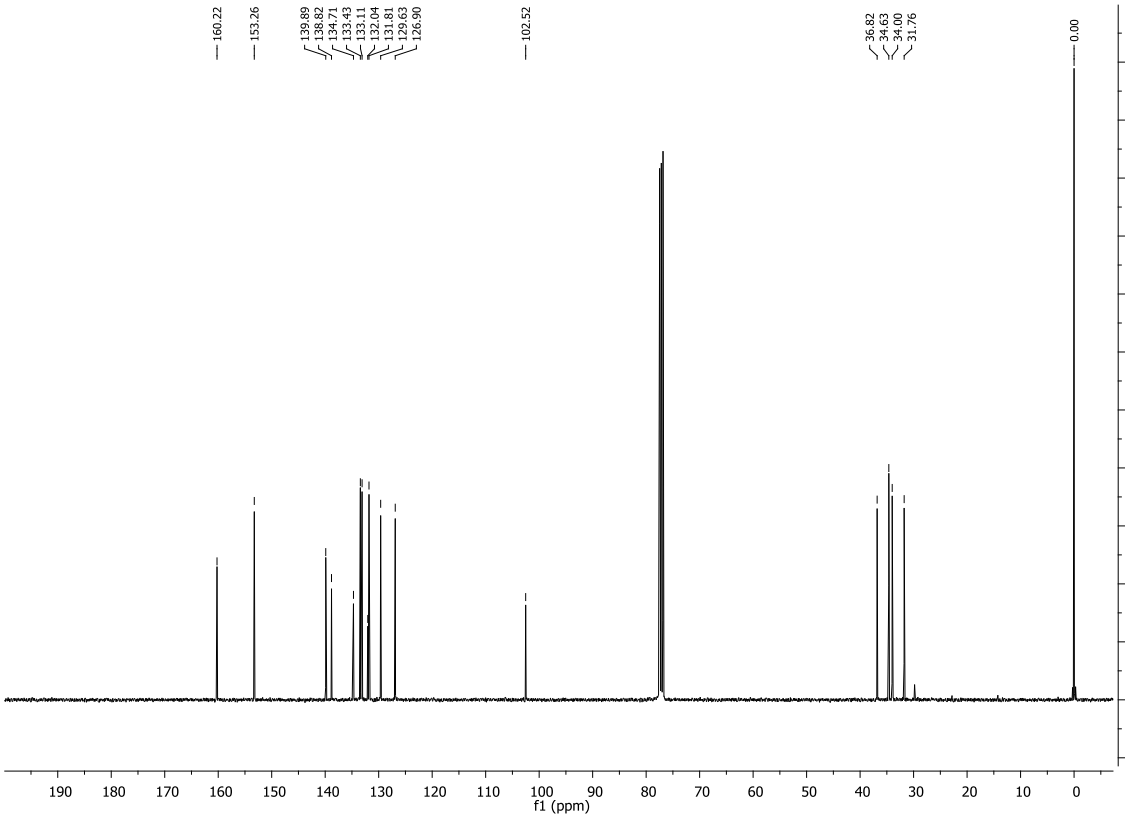
(rac)-N-Methoxycarbonyl-4-((trimethylsilyl)ethynyl)[2](1,4)benzeno[2](2,5)-4(2H)-pyridinophane **2**



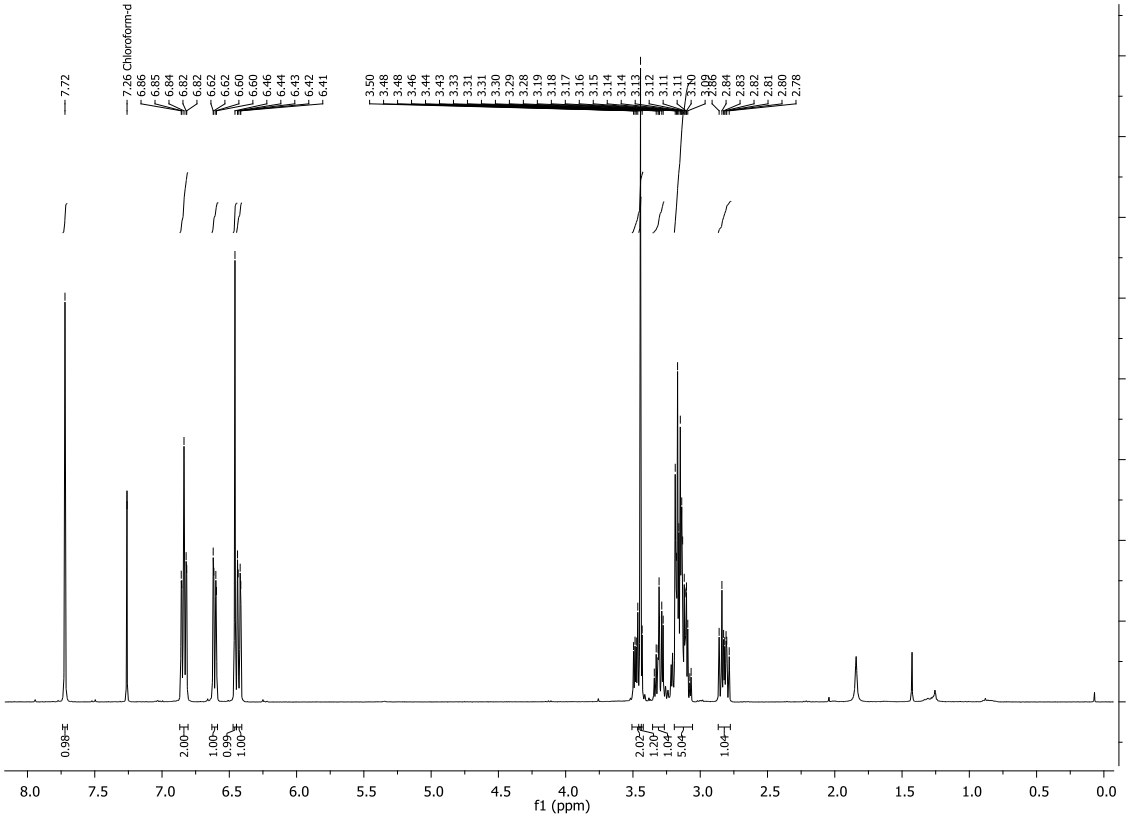


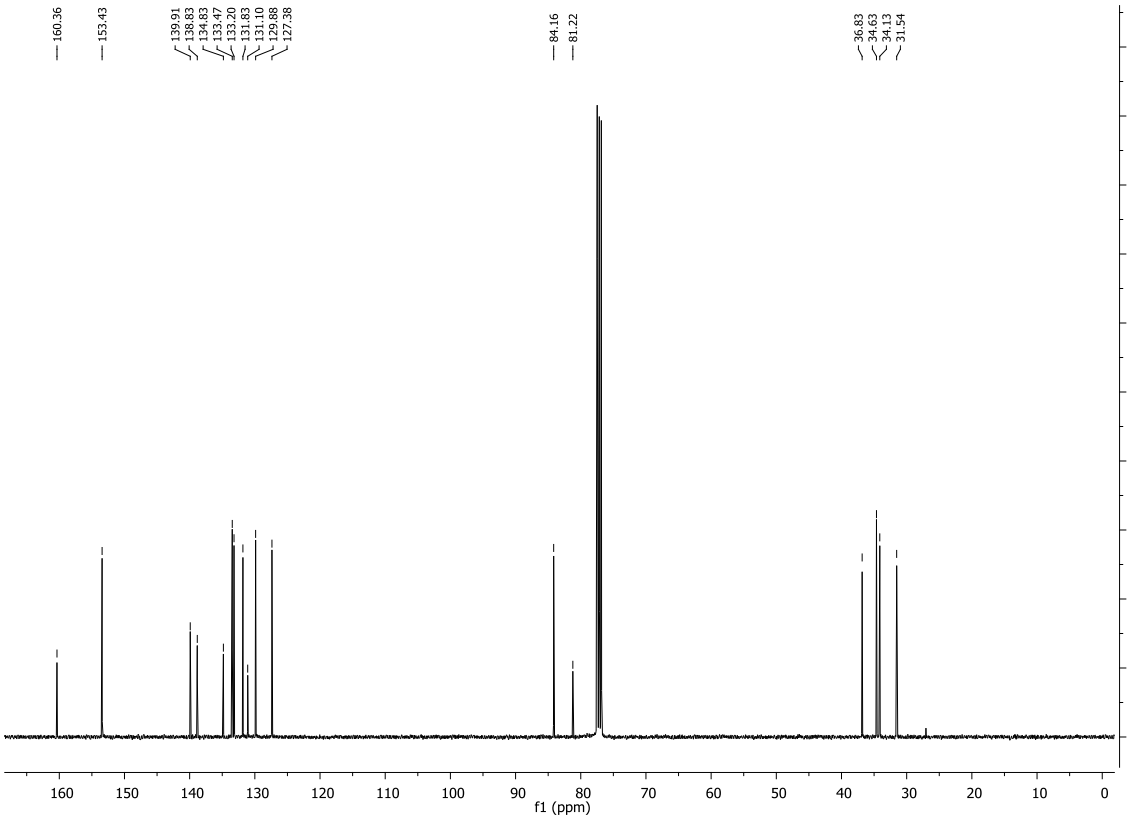
(rac)-4-((Trimethylsilyl)ethynyl)[2](1,4)benzeno[2](2,5)pyridinophane ***3***





(rac)-4-(Ethynyl)[2](1,4)benzeno[2](2,5)pyridinophane ***4***





Ellipsometry results:

Polymer	*Mass of precursor (mg)*	*Thickness (nm)*
7	41	51 ± 13
8	30	64 ± 4
9	39	39 ± 1
10	30	25 ± 3

IRRAS results:

Polymer **7** (ν (cm^1)) = 3046, 3005, 2942, 2922, 2856, 1514, 1453, 1437, 1418, 1140, 824, 805.

Polymer **8** (ν (cm^1)) = 3287 [≡C-H], 2944, 2927, 2859, 2102 [C≡C], 1492, 1454, 1438, 1411, 1159, 1196, 1120, 893, 834.

Polymer **9** (ν (cm^1)) = 3033, 3004, 2941, 2923, 2856, 1600, 1567, 1488, 1452, 1437, 1420, 1394, 1142, 1030, 836.

Polymer **10** (ν (cm^1)) = 3292 [≡C-H], 3043, 3011, 2952, 2929, 2858, 2099 [C≡C], 1594, 1576, 1559, 1540, 1506, 1483, 1450, 1436, 1376, 912, 878, 804.

Contact angle measurements

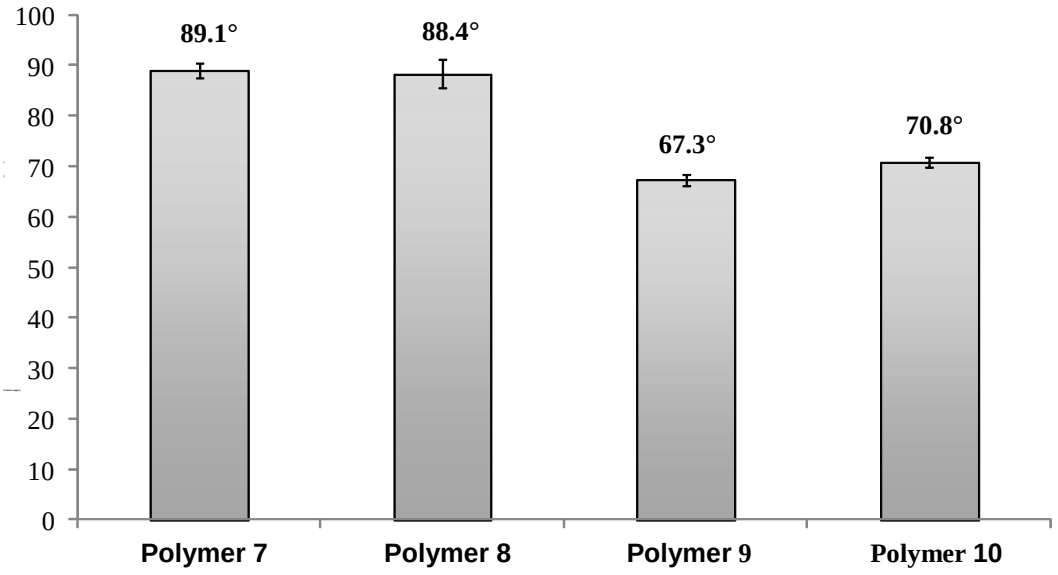


Figure 1. Contact angle measurements of the polymers **7** to **10** prepared by CVD. The contact angle decreases by the presence of a nitrogen atom in polymer back-bone.

XPS spectra

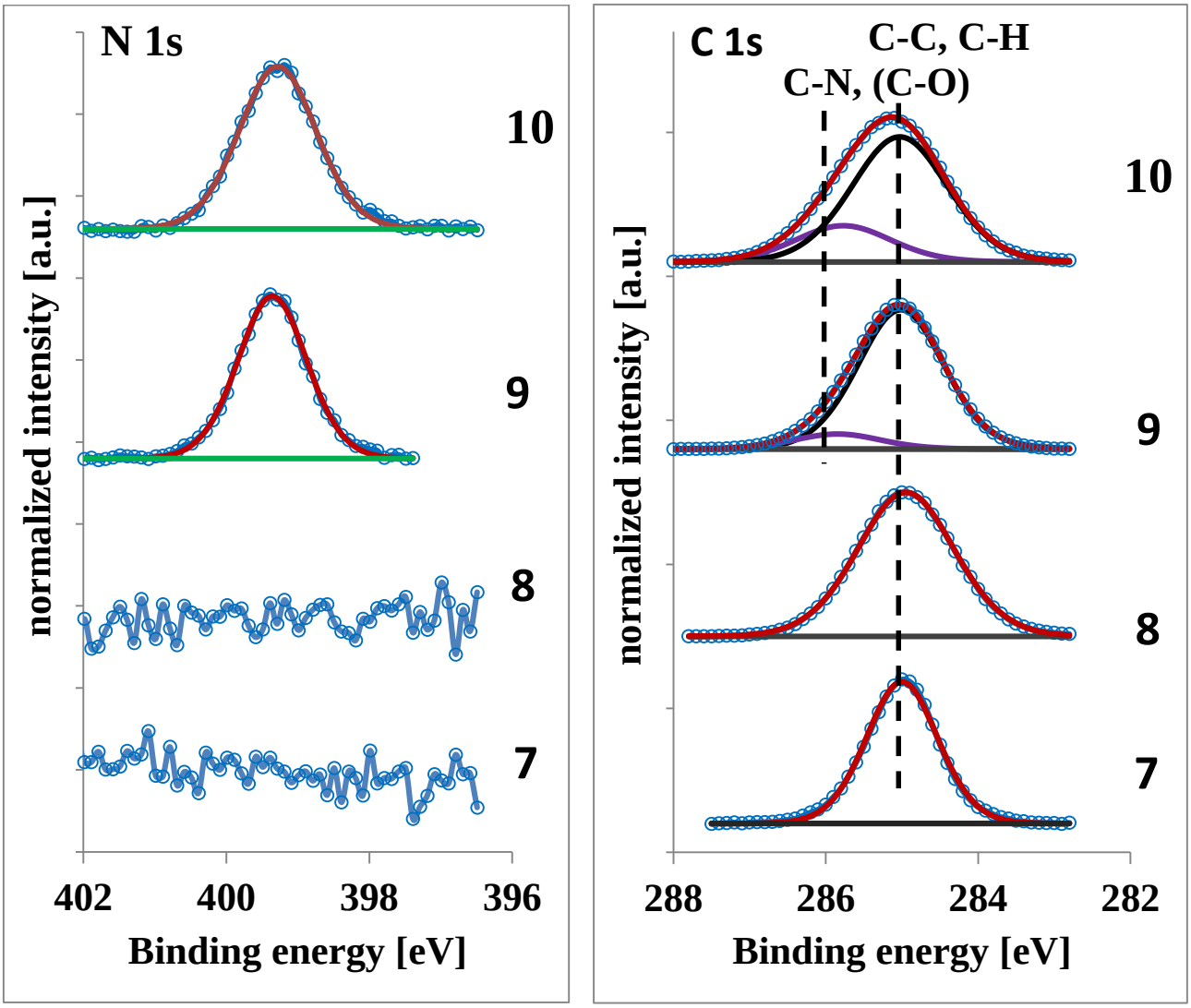


Figure 2. C 1s and N 1s XP Spectra from the polymers **7** to **10** (from the bottom to the top) (left). The presence of nitrogen in the samples **9** and **10** can be clearly seen (right). All spectra are normalized to the maximum of intensity.

Crystal Structure Determination of ethynylpyridinophane 4.

The single-crystal X-ray diffraction study was carried out on a Nonius KappaCCD diffractometer at 123(2) K using Mo-Kα radiation (λ = 0.71073 Å. Direct Methods (SHELXS-97)[1] were used for structure solution and refinement was carried out using SHELXL-98 (full-matrix least-squares on F^2).[1] Hydrogen atoms were refined using a riding model. The absolute structure could not be determined reliably either by refinement of Flack's x-parameter x = –7(8)[2] nor using Bayesian statistics on Bijvoet differences (Hooft's y-parameter y = 0.6(14)).[3] There is a disorder of the ethynylpyridine vs. the benzene ring (approx. 2:1: (0.684(4) : 0.316(4)) about a mirror plane (for details see the cif-file).

ethynylpyridinophane: colourless crystals, $C_{17}H_{15}N$, M_r = 233.30, crystal size 0.30 × 0.20 × 0.10 mm, monoclinic, space group *C*2 (No. 5), *a* = 15.3179(9) Å, *b* = 7.5135(5) Å, *c* = 11.3255(6) Å, β = 95.508(5)°, *V* = 1297.45(13) Å^3, *Z* = 4, ρ = 1.194 Mg/m^3, μ(Mo-K$_\alpha$) = 0.069 mm^1, *F*(000) = 496, $2\theta_{max}$ = 50.0°, 6440 reflections, of which 2276 were

independent (R_{int} = 0.062), 156 parameters, 4 restraints R_1 = 0.063 (for 1935 I > 2σ(I)), wR_2 = 0.162 (all data), S = 1.03, largest diff. peak / hole = 0.255 / -0.211 e Å^3, x = –7(8), y = 0.6(14).

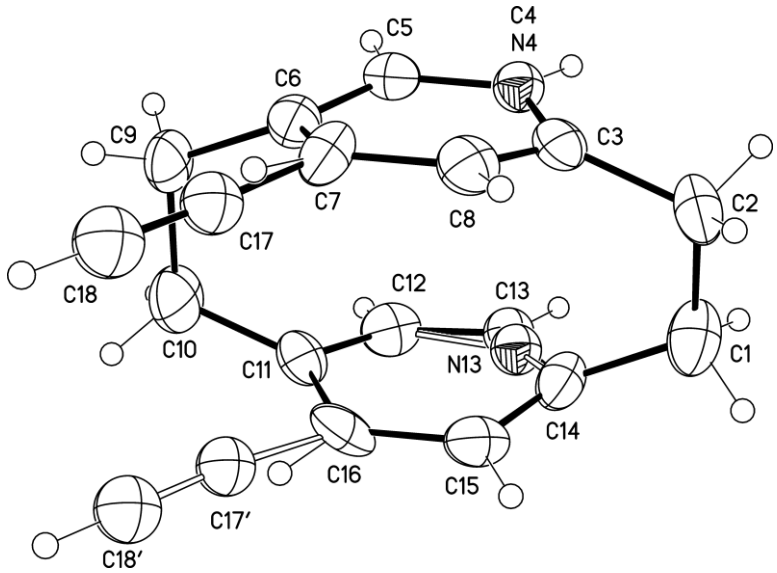


Figure. 3. Molecular structure of **4** (displacement parameters are drawn at 50 % probability level).

References

1. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
2. H. Flack, *Acta Crystallographica Section A*, 1983, **39**, 876-881.
3. R. W. W. Hooft, L. H. Straver and A. L. Spek, *J. Appl. Crystallogr.*, 2008, **41**, 96-103.