

**Electronic Supplementary Information :**

Supramolecular surface adhesion mediated by azobenzene polymer brushes

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### **Supramolecular surface adhesion mediated by azobenzene polymer brushes**

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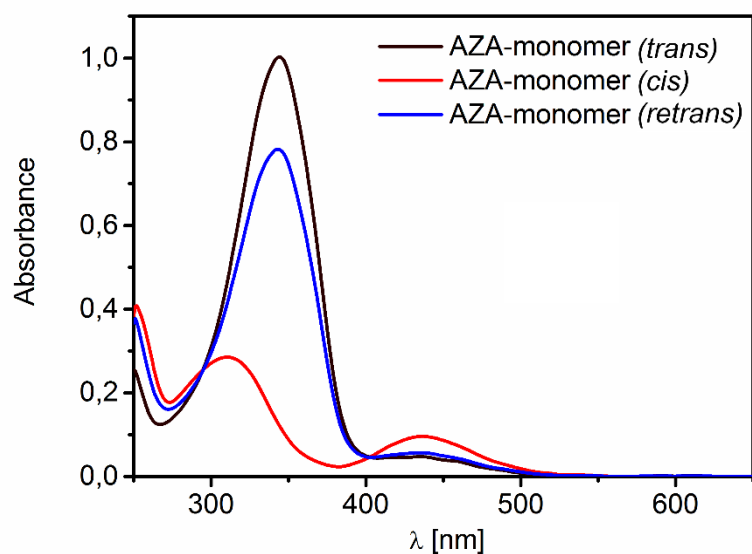
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## General

All commercially available chemicals were purchased and used without further purification, if not mentioned otherwise.  $\beta$ -cyclodextrin polymer powder (2-300 kDa) was purchased from Sigma Aldrich. Reactions which were moisture or air sensitive were performed under inert conditions using standard Schlenk-technique and dry solvents. Solvents were dried with standard methods. Analytical thin layer chromatography was done on silica coated aluminium foils with fluorescence indicator *Silica gel 60 F254* (Merck KGaA, Darmstadt). The spots were visualized by UV light of 254 nm with a *Dual Wavelength UV Lamp (254 nm and 366 nm)* (CAMAG, Muttenz, Switzerland) or by dyeing with a basic permanganate solution. Preparative silica gel column chromatography was done using *Geduran® Si 60* (Merck KGaA, Darmstadt) with a grain size of 0.040 – 0.063 mm and different eluents which are mentioned for each component. The composition of the eluents is always given in volumetric ratios. The NMR spectra were recorded on a *AV-300*-spectrometer with 300.1 Hz ( $^1\text{H}$ ), 75.5 Hz ( $^{13}\text{C}$ ) and a *AV-400* spectrometer with 400.1 Hz ( $^1\text{H}$ ), 100.1 Hz ( $^{13}\text{C}$ ) (Bruker, Karlsruhe, Germany). All measurements were performed in deuterated solvents. The chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and relative to the residual solvent signals. The measured coupling constants are given in Hertz (Hz).

## Methods

**UV/Vis spectroscopy and UV irradiation** UV/Vis spectra were recorded with a *JASCO V-650* double-beam spectrophotometer (JASCO Labor- und Datentechnik GmbH, Gross-Umstadt) at 25 °C using 1 mL low-volume disposable PMMA cuvettes (*BRAND GMBH & CO KG*, Wertheim) for measurements in aqueous medium and quartz-glass cuvettes (*111F-QS*, 10.00 mm, *Hellma Analytics*, Müllheim, Germany) for organic solvents. The spectrometer was controlled with *Spectra Manager* version 2.08.04 (JASCO Labor- und Datentechnik GmbH, Gross-Umstadt). The samples were dissolved in an appropriate solvent and measured against the same solvent. Data analysis was done using *OriginPro 9.1* (ORIGINLAB COOPERATION, Northampton, USA). For the photo isomerisation of azobenzene from *trans* to *cis*, four power LEDs from SEOUL OPTODEVICE (P8D2,  $\lambda = 365$  nm) for UV light irradiation were used. For the reverse isomerisation process, a *Philips Lumileds Royal Blue LUXEON K2 emitter* (LXK2-PR14-Q00) emitting light at a wavelength of 465 nm was used. The samples were irradiated for 30 minutes.



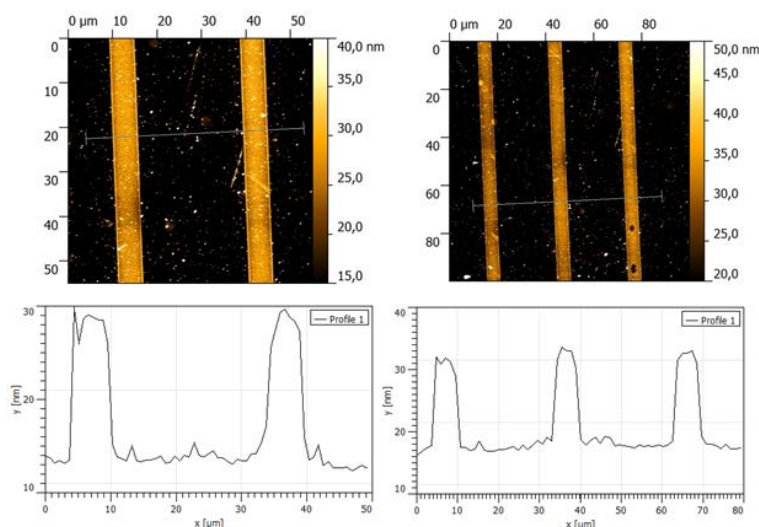
**Fig.S1:** UV-Vis spectra of the AZA-monomer (1) and its switching ability under UV light irradiation.

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**X-ray photoelectron spectroscopy:** XPS measurements were performed with an Axis Ultra DLD (Kratos Analytical Ltd, UK). A monochromatic Al K $\alpha$  source ( $h\nu = 1486.6$  eV) at 10 mA filament current and 12 kV filament voltage source energy was used. The pass energy was set to 20 eV for high resolution scans and to 160 eV for survey scans. The charge neutralizer was used to compensate for sample charging. All measurements were carried out in the “hybrid mode”. The data were evaluated with CasaXPS (version 2.3.15, Casa Software Ltd, UK) and the spectra were calibrated to aliphatic carbon (C1s = 285 eV).

**Atomic Force Microscopy:** AFM imaging was performed using a NanoWizard 3 from JPK Instruments operated in tapping mode with Veeco RTESP-Tapping Mode etched silicon probes. The AFM was typically operated at a scan rate of 1.00 Hz and a set point of 0.900 V. Images were recorded with a resolution of 512 x 512 pixels and data evaluation was done with gwyddion version 2.38.



**Fig.S2:** AFM images of the patterned AZA-brushes and the corresponding height profile.

Preparation of ATRP initiator functionalized substrates was done as recently reported.<sup>1</sup>

**Stamp Preparation** Poly(dimethyl siloxane) (PDMS) stamps were prepared from Sylgard 184 provided by Dow Corning. PDMS and curing agent are mixed in a 10:1 ratio (v/v) and thoroughly stirred by hand for 10 minutes. The precursor mixture is casted onto a structured or unstructured silicon master, degassed and cured in an oven at 80 °C overnight. The cured stamps were cut out with a knife and treated with a UV ozonizer (PSD-UV, Novascan Technologies Inc.) for 55 minutes prior to use.

**Preparation of glass supported Undecenyl SAMs** Glass slides were cut into pieces of approximately 2.5 x 1.4 cm<sup>2</sup> and cleaned by sonication in pentane, acetone and deionised water. The substrates were dried in a stream of argon and immersed into a freshly prepared piranha solution (conc. H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (30%), 3:1 (v/v)). After 30 minutes the substrates were thoroughly washed with deionised water, dried in a stream of argon and put into a freshly prepared solution of 10-undecenyl trichlorosilane in toluene (0.1vol%). After 45 minutes the substrates were taken of the solution, immersed in toluene, washed with ethanol and deionised water and dried in a stream of argon. These substrates were used for surface functionalisations with ATRP-TAD.

**$\mu$ CC Procedure** Flat or structured oxidised PDMS stamps were covered with approximately 30-60  $\mu$ L of a 50 mM solution of ATRP-TAD in acetonitrile. After an incubation time of 1 minute, the stamps were dried in a stream of argon and placed onto glass supported 10-undecenyltrichlorosilane SAMs. After a reaction time of 10 minutes, the stamps were lifted off and the substrates washed with DCM and acetone. After sonication in DCM these substrates were ready for SI-ATRP.

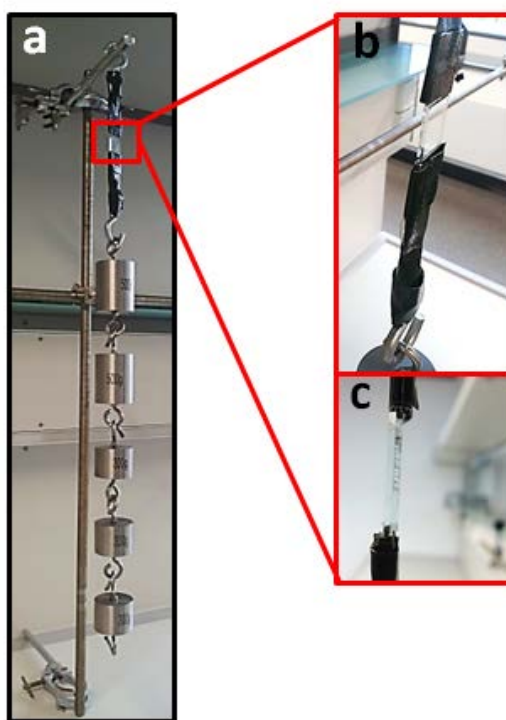
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**Polymerisation Procedure** HEA was distilled before use in order to remove the inhibitor. HEA (4.74 g, 40.8 mmol), AZA (1.42 g, 3.3 mmol) and ethyl- $\alpha$ -bromo isobutyrate (1.8 mg, 9.4  $\mu$ mol) were added to a schlenk tube containing initiator functionalised substrates. Then a vortexed solution (1 mL) of Cu(II)Br<sub>2</sub> (5 mg, 22  $\mu$ mol) and tris[2-(dimethylamino)ethyl]amine (36 mg, 110  $\mu$ mol) dissolved in DMF (10 mL) was added. Subsequently DMF (1 mL) was added, the tube purged with argon and subjected to three freeze/thaw circles with intermediate argon purges. Then ascorbic acid (24 mg, 141  $\mu$ mol) was added and the tube placed in an oil bath overnight at 75 °C. After cooling, the surfaces were cleaned by sonication in MeOH. The polymer grown in solution was dried, taken up in a minimum amount of methanol and precipitated from Et<sub>2</sub>O three times, in order to remove unreacted monomer.

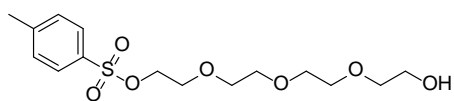
**Gluing Procedure** AZA-brush functionalised substrates were incubated with an aqueous solution of commercially available  $\beta$ -CD polymer (100 mg/mL) for 10 minutes at room temperature. The polymer solution was removed from the surface and substrates were cleaned with water in order to remove unbound  $\beta$ -CD polymer. These surfaces were brought into contact with a complementary AZA-brush functionalised substrates, pressed together by hand and left to dry at room temperature for approximately one hour. After attaching hooks, the maximum loading capacity was tested by adding weight in a step by step fashion. Following the rupture of surfaces, the substrates were sonicated in EtOH, MeOH and ultrapure water for 5 minutes each in order to remove the  $\beta$ -CD polymer and the gluing process was started over.



**Fig.S3:** a) Set up of the glued glass surfaces, (Contact area 2.24 cm<sup>2</sup>, total weight 1.9 kg), b) and c) close up photographs.

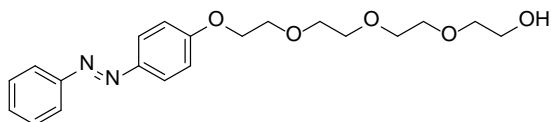
## Synthesis

### 2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl-4-methylbenzenesulfonate(1)<sup>2</sup>



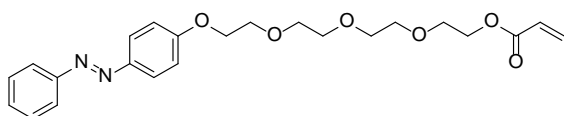
To a solution of tetraethylene glycol (22.0 g, 113 mmol, 10.3 eq.) in THF (4 mL) a solution of NaOH (690 mg, 17.1 mmol, 1.6 eq.) in water (4 mL) was added at 0 °C. At the same temperature a solution of *p*-toluenesulfonyl chloride (2.08 g, 10.9 mmol, 1 eq.) in THF (13 mL) was added dropwise over 1 hour and stirred for 2 hours at 0 °C. The solution was poured into ice-water and the layers were separated. The aqueous layer was extracted with DCM (3 × 50 mL) and the organic layers were combined, washed with water (2 × 50 mL), dried over MgSO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The desired compound was used in the next step without further purification. **Yield:** 3.50 g (10.1 mmol, 92%) as yellow oil. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 4.15 (t, *J* = 4.9 Hz, 2H), 3.72 – 3.55 (m, 14H), 2.43 (s, 3H) ppm. **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ = 144.93, 133.04, 129.93, 128.07, 72.56, 70.83, 70.74, 70.56, 70.42, 69.36, 68.79, 61.82, 21.75 ppm.

### (E)-2-(2-(2-(2-(4-(phenyldiazenyl)phenoxy)ethoxy)ethoxy)ethoxy)ethanol (2)<sup>3</sup>



To a stirred solution of (1) (5.90 g, 6.93 mmol, 1 eq.) in 150 ml of dry acetonitrile, containing K<sub>2</sub>CO<sub>3</sub> (11.70 g, 84.65 mmol, 5 eq.) and catalytic amounts of LiBr, 4-phenylazophenol (3.96 g, 20 mmol, 1.2 eq.) dissolved in acetonitrile (50 mL) was added and the reaction mixture was refluxed for 3 days under argon. It was then allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in DCM (120 mL), washed with water (100 mL) and brine (3 × 100 mL). The organic phase was dried over MgSO<sub>4</sub> and concentrated. The residue was purified by silica gel column chromatography (eluent, DCM → DCM/methanol 99:1) to afford the title compound. **Yield:** 5.83 g (15.6 mmol, 92%) as red oil. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>) δ = 7.97 – 7.77 (m, 4H), 7.56 – 7.37 (m, 3H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.27 – 4.17 (m, 2H), 3.94 – 3.84 (m, 2H), 3.83 – 3.63 (m, 10H), 3.62 – 3.56 (m, 2H), 2.49 (s, 1H) ppm. **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>) δ = 161.39, 152.77, 147.14, 130.52, 129.15, 124.89, 122.67, 114.96, 87.44, 72.64, 70.98, 70.78, 70.70, 70.43, 69.74, 67.82, 61.86 ppm.

### (E)-2-(2-(2-(2-(4-(phenyldiazenyl)phenoxy)ethoxy)ethoxy)ethoxy)ethyl acrylate (3)



Triethylamine (4.20 mL, 30.1 mmol, 2 eq.) was added to a solution of (2) (5.80 g, 15.49 mmol, 1 eq.) in dry DCM (50 mL). To this a solution of acryloylchloride (2.52 mL, 30.1 mmol, 2 eq.) in dry DCM (30 mL) was added dropwise at 0 °C. Afterwards the solution was allowed to warm to room temperature and was stirred for 18 h. Water was added (75 mL) and the layers were separated. The organic layer was washed with brine (3 × 75 mL), dried with MgSO<sub>4</sub> and concentrated under reduced pressure. Purification via column chromatography (DCM/methanol 99.9:0.1 → 99.5:0.5) yielded the desired compound. **Yield:** 5.03 g (11.7 mmol, 76%) as red oil. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>) δ = 7.96 – 7.83 (m, 4H), 7.54 – 7.41 (m, 3H), 7.03 (d, *J* = 9.0 Hz, 3H), 6.42 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.82 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.37 – 4.24 (m, 2H), 4.26 – 4.17 (m, 2H), 3.97 – 3.77 (m, 2H), 3.80 – 3.60 (m, 10H) ppm. **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>) δ = 161.41, 152.79, 147.15, 142.03,

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141.97, 131.19, 130.53, 129.16, 128.38, 124.87, 122.68, 114.95, 71.02, 70.76, 69.76, 69.25, 67.85, 63.81 ppm.

HRMS: calculated for  $[C_{23}H_{28}N_2O_6Na]^+$ : 451.1845, found: 451.1831.

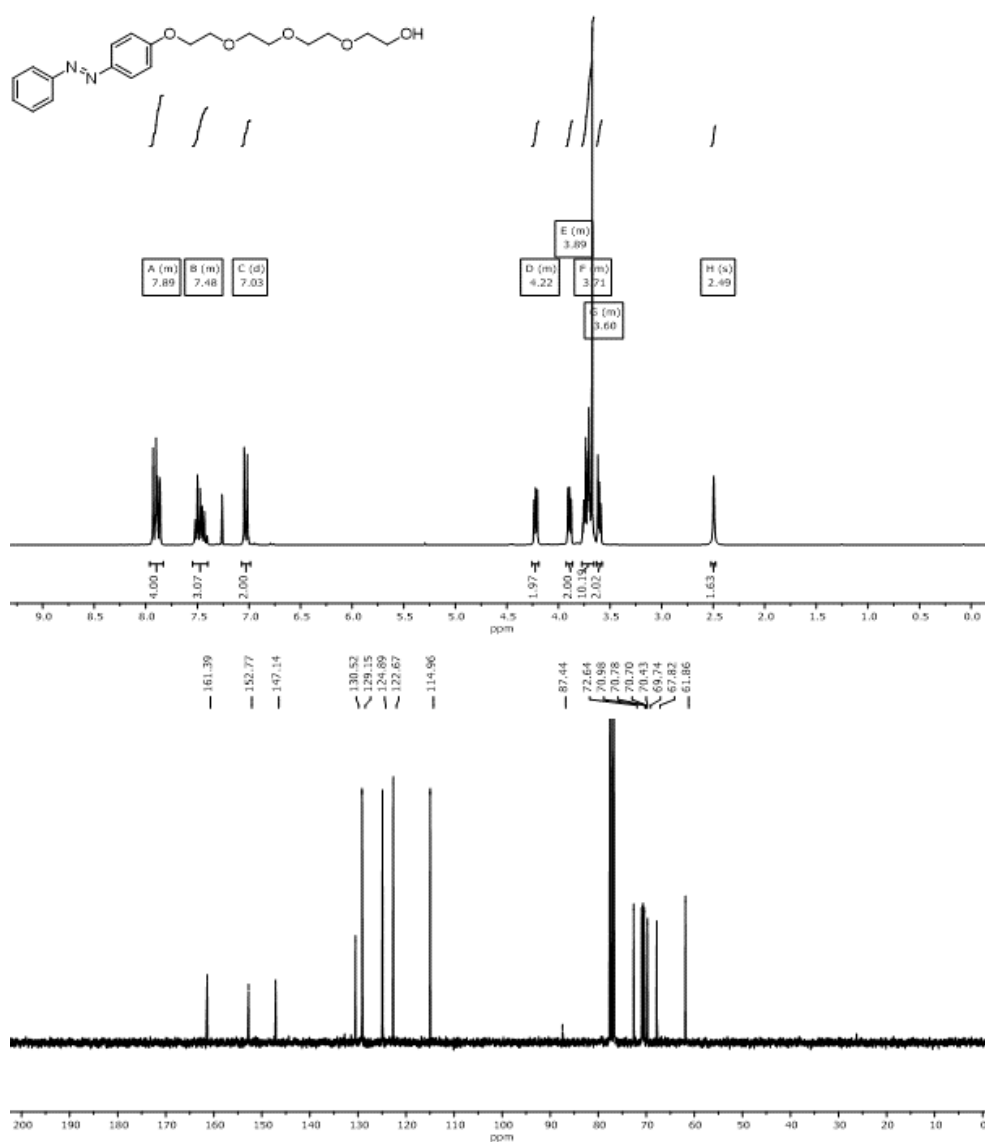


Fig.S4:  $^1H$ - and  $^{13}C$ -NMR of compound (2).

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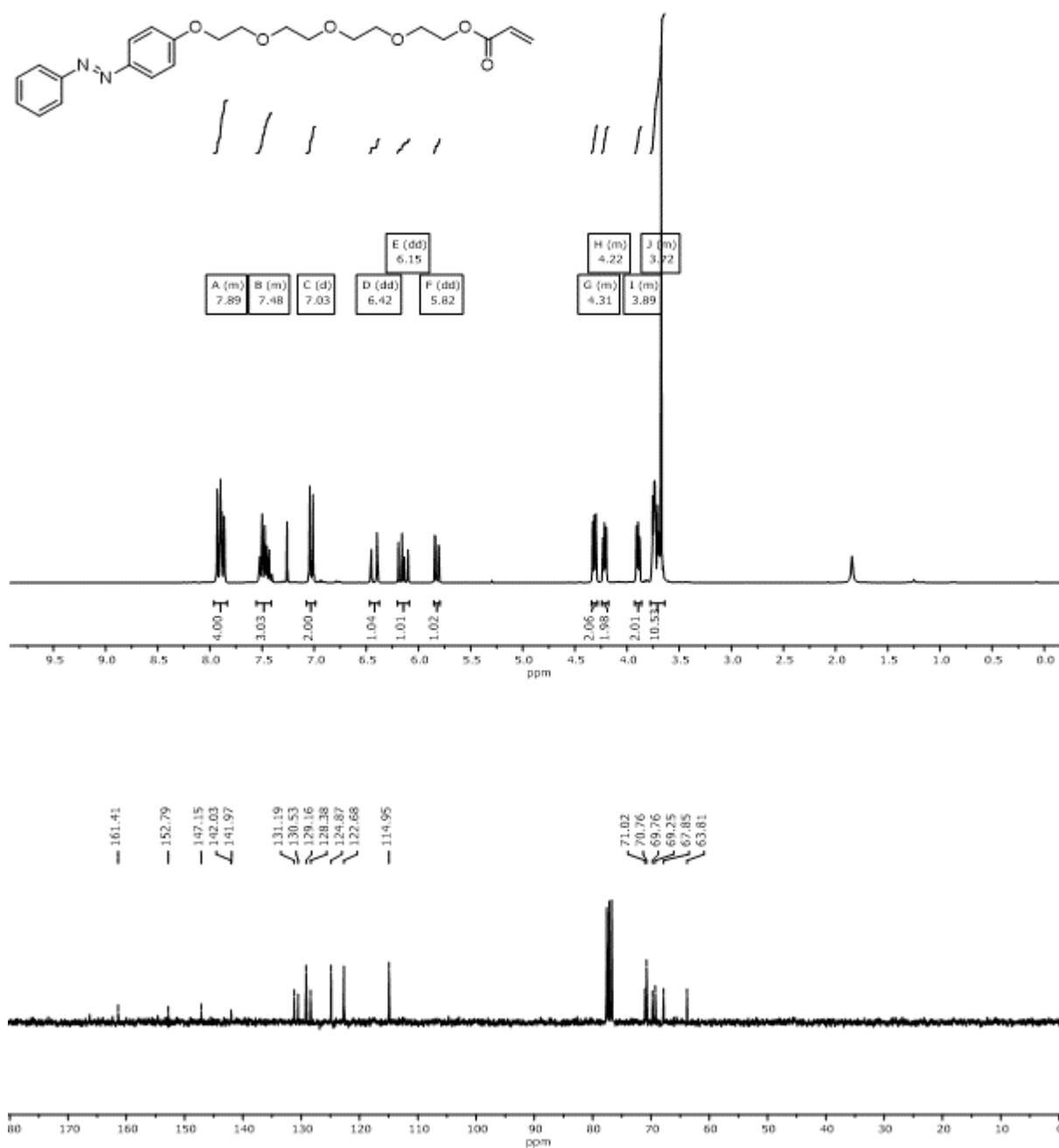
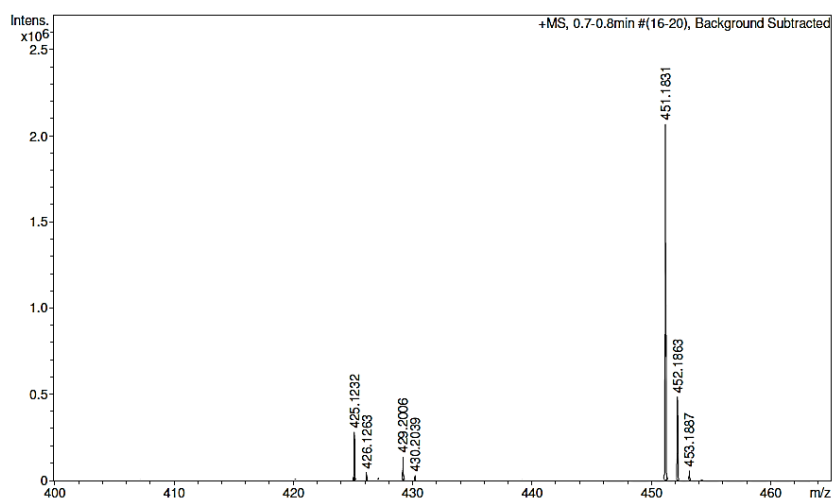


Fig.S5:  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR of compound (3).

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**Fig.S6:** Mass spectrum (ESI-MS) of compound (3).

## References

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