Electronic Supplementary Information (ESI) for

Synthesis and Peptide Functionalization of Hyperbranched Poly(arylene oxindole) towards Versatile Biomaterials

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Table of Contents

I. GPC analyses of HBPs

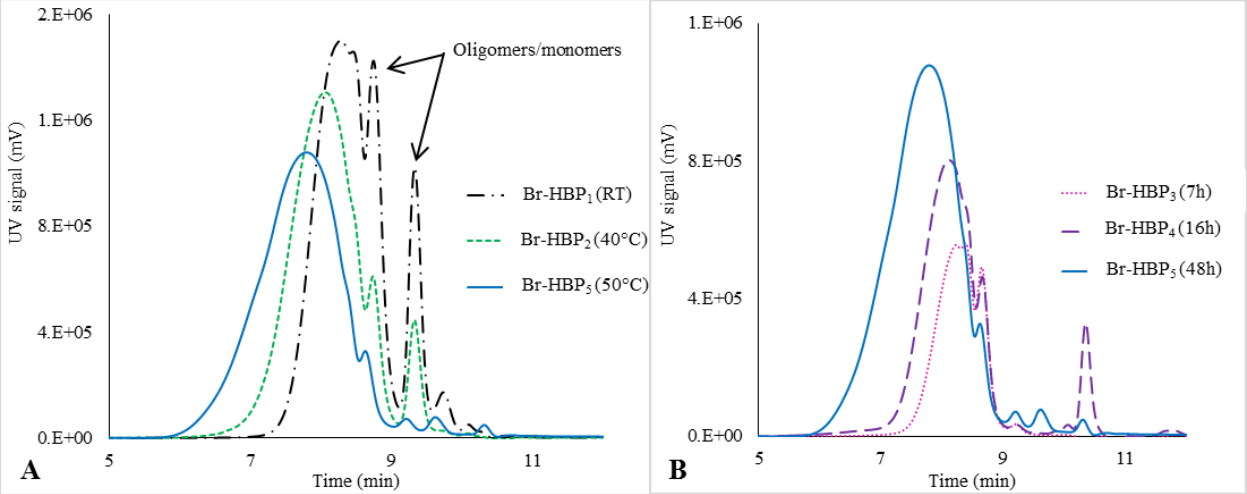

Fig. S1 Gel permeation chromatograms for Br-HBPs (see Table 1 in main text for synthesis conditions). (A) Br-HBP_1 (in black, RT), Br-HBP_2 (in green, 40 °C), and Br-HBP_5 (in blue, 50 °C) after 48h. Significant peaks of oligomers and/or monomers were observed at 8.70 and 9.30 min and decreased with increasing reaction temperature and/or time. (B) Br-HBP_3 (in pink, 7 h, 50 °C), Br-HBP_4 (in purple, 16 h, 50 °C), and Br-HBP_5 (in blue, 48 h, 50 °C).

II. Synthesis and NMR analyses

a. *Compound C (1-(3-bromopropyl)indoline-2,3-dione or bromopropylisatin)*

In a flame-dried nitrogen-flushed two-necked round-bottomed flask, isatin (Compound A: 2.0 g, 13.6 mmol) and potassium carbonate (3.8 g, 27.2 mmol) were dissolved in dry DMF (40 ml) under nitrogen atmosphere. 1,3-dibromopropane (Compound B: 5.5 ml, 54.4 mmol) was added, the reaction mixture was stirred at room temperature, and the reaction was followed via TLC (DCM/MeOH 99/1). The reaction mixture was concentrated and then partitioned in DCM/H_2O. The water layer was extracted with DCM (3X). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The concentrate was purified by MPLC (DCM/MeOH 99/1) yielding 1-(3-bromopropyl)indoline-2,3-dione (2.8 g, 78 %) as an orange powder. Mp 50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 – 7.55 (m, 2H), 7.14 (m, 1H), 7.03 (d,

J = 8.2 Hz, 1H), 3.91 (t, *J* = 7.1 Hz, 2H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.36 – 2.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.18, 158.38, 150.80, 138.62, 125.58, 124.13, 117.53, 109.94, 38.82, 30.30, 30.05; IR: ν = 1730, 1608, 1464, 1352, 1270, 757, 548, 468 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{11}H_{10}BrNO_2$, 289.98; found, 289.98

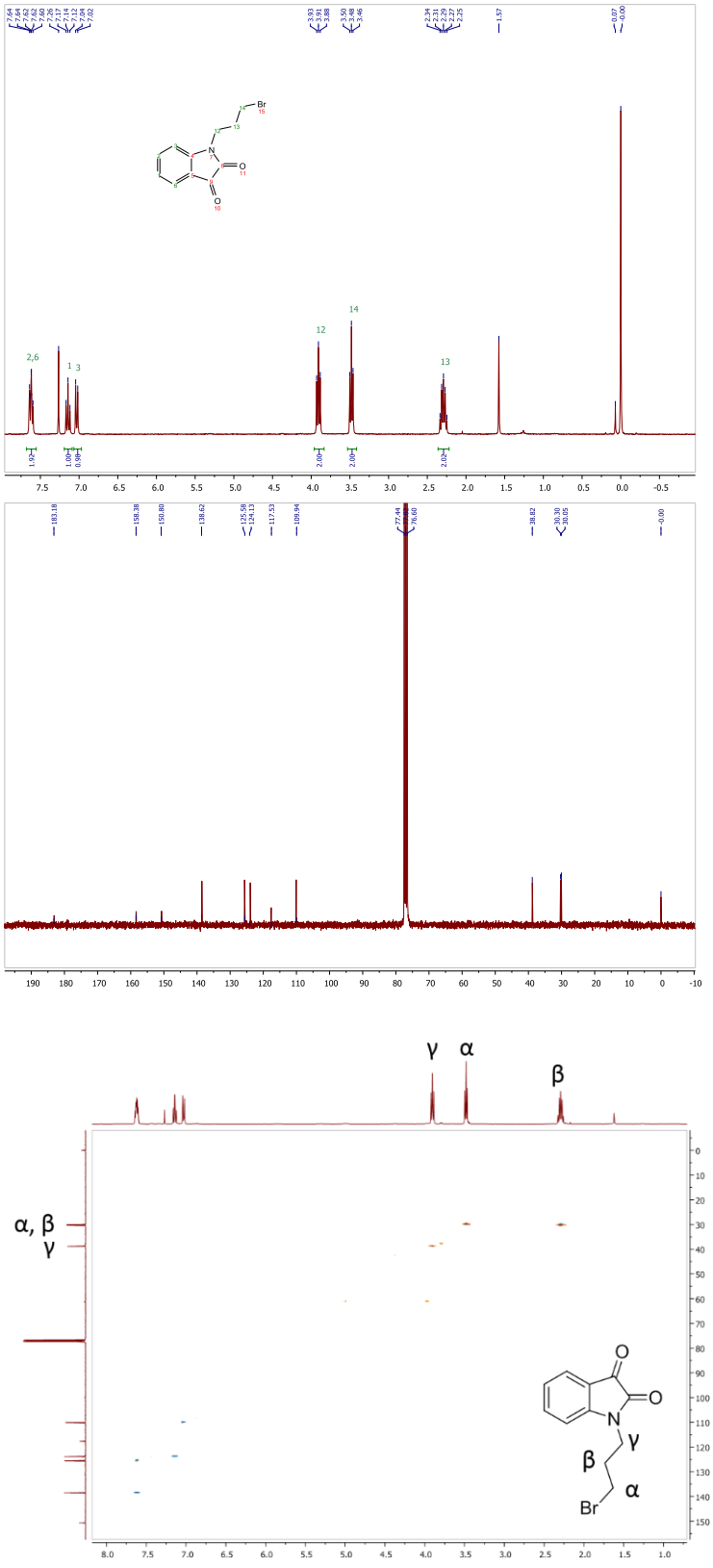

Fig. S2 ^{1}H (top panel), ^{13}C (middle panel), and HSQC (bottom panel) NMR spectra of Compound C in $CDCl_3$

b. *Compound F (Benzene-1,3,5-triyltris(4-phenoxyphenyl)methanone or benzenetricarbonyl derived B_3)*

$AlCl_3$ (7.8 g, 58.8 mmol) was dissolved in DCE (70 ml) in a flame-dried nitrogen-flushed 250 ml two-necked round-bottomed flask under nitrogen atmosphere. Diphenyl ether (Compound E: 23.4 ml, 147 mmol) was added to the reaction mixture in one portion. A solution of benzene-1,3,5-tricarbonyl trichloride (Compound D: 2.6 g, 9.8 mmol) in DCE (30 ml) was added dropwise at room temperature over 1 h. The reaction mixture was refluxed for 2 h. Then, the reaction mixture was quenched with a cold solution of H_2O/HCl (1M) (1/1). The quenched mixture was extracted with DCM (3X). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The concentrate was further purified via precipitation from DCM/heptane and DCM/MeOH. The product was obtained as a white powder (4.8 g, 74 %). Mp 149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (s, 3H), 7.84 (d, J = 8.8 Hz, 6H), 7.45 – 7.39 (m, 6H), 7.21 (t, J = 7.4 Hz, 3H), 7.11 (d, J = 7.6 Hz, 6H), 7.04 (d, J = 8.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.70, 162.41, 155.15, 138.51, 133.49, 132.57, 130.71, 130.15, 124.90, 120.39, 117.25; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{45}H_{30}O_6$, 667.20; found, 667.60

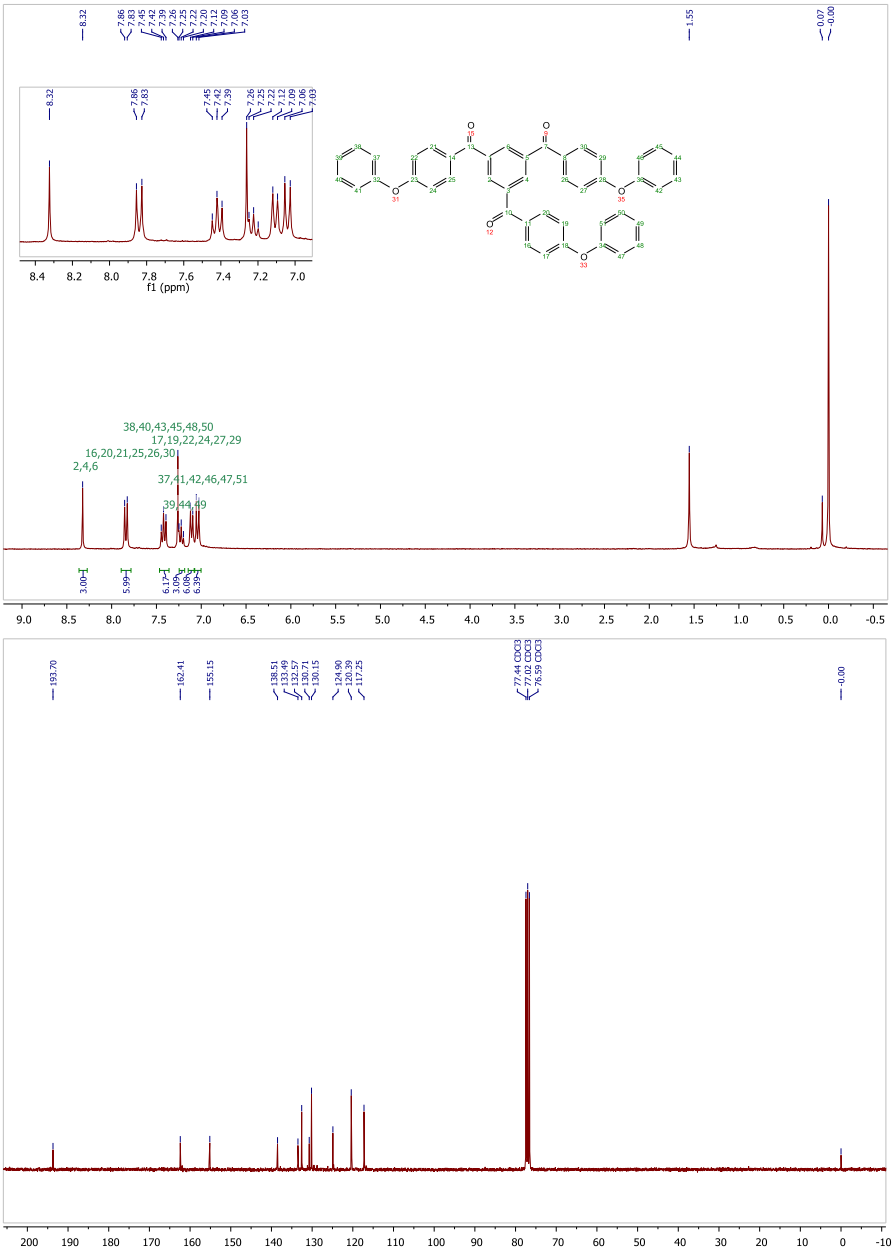

Fig. S3 ^{1}H (top panel) and ^{13}C (bottom panel) NMR spectra of Compound F in $CDCl_3$

c. *5-Hexynoic-RGDS$_{(p)}$-OH (5-Hexynoic-Arg(Pbf)-Gly-Asp(OtBu)-Ser(tBu)-OH)*

The *5-Hexynoic*-RGDS$_{(p)}$-OH peptide [(p) indicates the presence of protecting groups] was synthesized manually by conventional solid phase peptide synthesis (SPPS) using an Fmoc/tBu strategy. Fmoc-Ser(tBu)-OH was anchored on a 2-chlorotrityl chloride resin (1.6 mmol g^{-1}) in the

presence of N,N-diisopropylethylamine (DIPEA). Peptide chain elongation was performed by successive steps of deprotection with a solution of piperidine (20 % v/v in DMF) for 30 min and coupling with N,N,N′,N′-Tetramethyl-O-(1H-benzotriazol-1-yl)uronium hexafluorophosphate, (HBTU; 3 eq.) as coupling reagent and DIPEA (5 eq.) as base for 3 h. After the last coupling step, the Fmoc protecting group was removed, and 5-hexynoic acid was coupled to the arginine using HBTU (3 eq.) and DIPEA (5 eq.) to provide the reactive alkyne group. The resulting peptide was then treated with a solution of trifluoroacetic acid (TFA; 1%) in DCM for 45 min. The cleaved resin was removed by filtration, and the filtrate was evaporated under reduced pressure followed by precipitation of the protected peptide in diethyl ether to give a white powder (yield: 65 %; purity: 95 %). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{42}H_{65}N_7O_{12}S$, 892.44; found, 892.30

d. *Br-HBP$_5$*

A flame-dried nitrogen-flushed vial was filled with C and F monomers (equimolar). MsOH (0.05 M) was added in one portion. The reaction mixture was heated and stirred at 50 °C for 48 h and then quenched in distilled H_2O. The suspension was centrifuged (5 min at 4000 rpm), and the supernatant was removed. The polymer was further isolated by precipitation and centrifugation (THF/H_2O 1X, THF/Et_2O 2X, THF/MeOH 2X). The precipitate was dissolved in DCM and reprecipitated/purified in MeOH under vigorous stirring (DCM/MeOH 1/100) yielding Br-HBP$_5$ as a yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (br. s, 2H), 7.89 – 7.72 (m, 6H), 7.45 – 7.28 (m, 5H), 7.24 – 6.79 (m, 18H), 3.94 (br. s, 2H), 3.41 (br. s, 2H), 2.28 (br. s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.62, 177.49, 162.42, 161.91, 155.17, 154.67, 142.06, 138.47, 133.48, 132.57, 130.72, 130.16, 124.91, 123.20, 120.39, 120.19, 117.57, 117.27, 93.72, 61.35, 39.09, 30.59, 30.14; IR: *v* = 1713, 1658, 1586, 1490, 1234, 1161, 844, 748 cm^{-1}

- *NMR analysis*

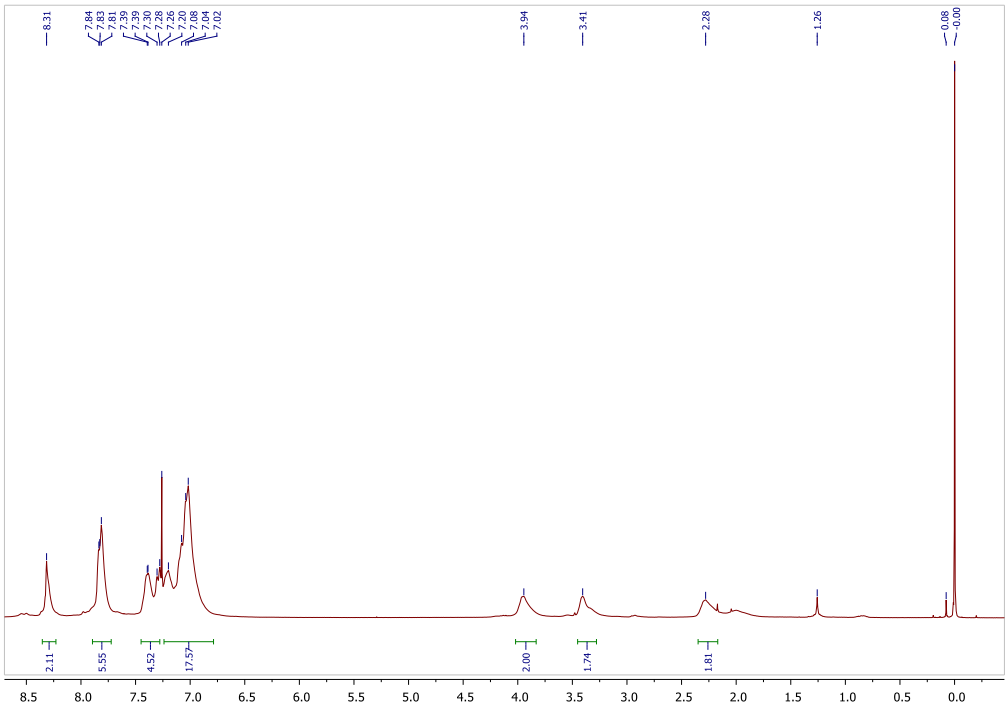

Fig. S4 ^{1}H NMR spectrum of Br-HBP$_5$ in $CDCl_3$

- *Loading determination of Br-HBP$_5$ via quantitative NMR (qNMR)*

The loading of Br-HBP$_5$ was determined by qNMR with an internal standard (IS). An appropriate IS satisfies several requirements, such as being highly pure and stabile, non-hygroscopic, non-volatile, non-toxic, and extremely dry, and most importantly the signal of the IS may not cover areas in the spectra where the critical signals from the compound of interest appear.[1] Piperonal has all of the above mentioned criteria with two different signals [aldehyde (Ald) and methylene (CH_2) groups] that do not overlap with the signals from Br-HBP$_5$ (**Figure S5**). Thus, piperonal was selected as an IS to determine the loading of Br-HBP$_5$.

A NMR tube was filled with a defined amount of piperonal and Br-HBP$_5$ (see **Table S1**). Br-HBP$_5$ and the IS were dissolved in $CDCl_3$ (700 µl) and measured by ^{1}H-NMR (600 MHz, d1 = 1 sec). An example spectrum is shown in Figure S5.This process was repeated three times, and the

results are summarized in Table S1. The loading of Br-HBP$_5$ was calculated to be 1.30 mmol g^{-1} by using an average of the values determined by qNMR.

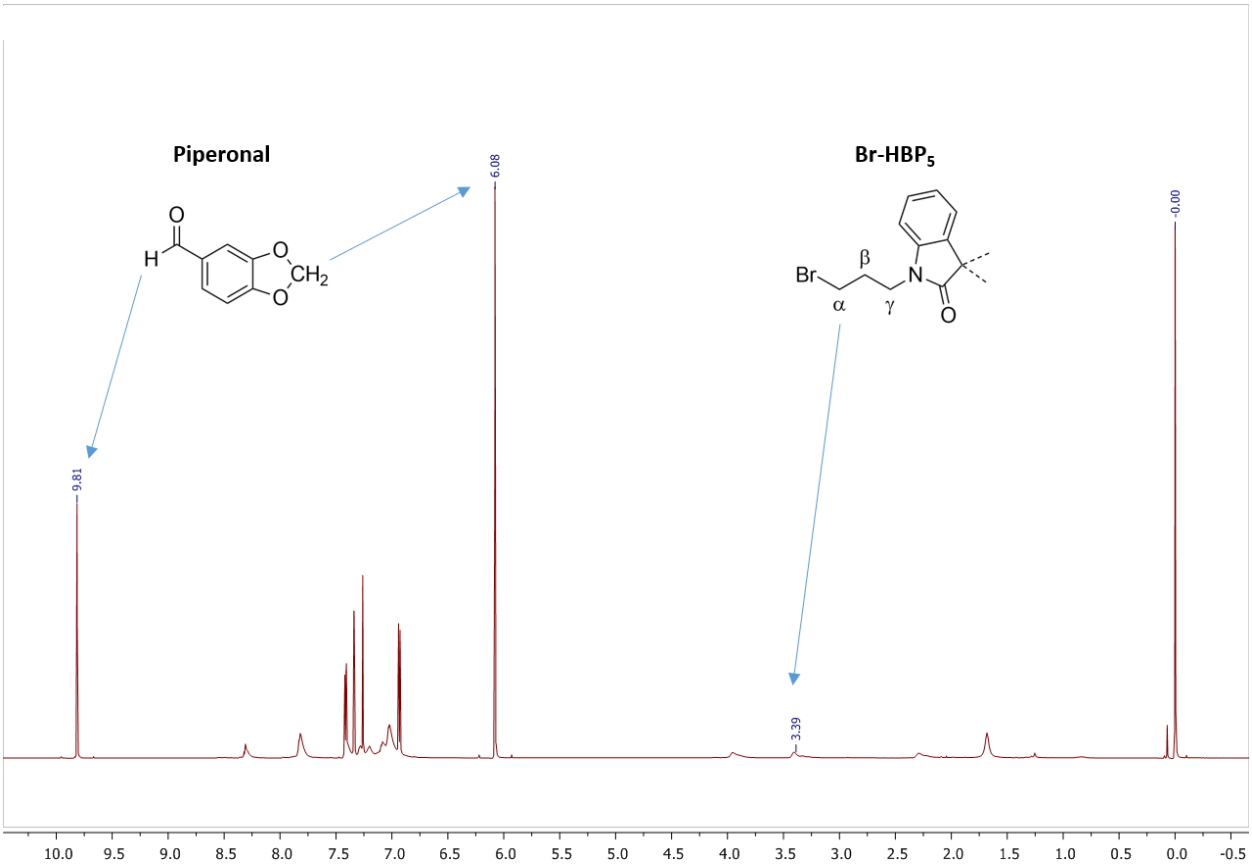

Fig. S5 ^{1}H NMR spectrum of Br-HBP$_5$ and piperonal

Table S1. Summarized results of qNMR data: [a] mmol piperonal. [b] For each NMR spectrum, a comparison of the α-CH_2 integration value of Br-HBP$_5$ to both the Ald and CH_2 signals of the IS was performed.

[c] $n(BrHBP_5) = \left(Peak\ area\ BrHBP_5 \cdot n(IS)\right) \cdot \left(\frac{1000}{m_{BrHBP_5}}\right)$

[d] $n(BrHBP_5) = \left(\frac{Peak\ area\ BrHBP_5}{2} \cdot n(IS)\right) \cdot \left(\frac{1000}{m_{BrHBP_5}}\right)$

Sample	m(Br-HBP$_5$) (mg)	m(IS) (mg)	n(IS) (mmol)[a]	Signal IS[b]	Peak area IS	Peak area Br-HBP$_5$	n(Br-HBP$_5$) (mmol g^{-1})
1	6.5	4.2	0.028	CH_2	1	0.28	1.21[c]
1	6.5	4.2	0.028	Ald	1	0.57	1.23[d]
2	4.8	3.4	0.023	CH_2	1	0.28	1.34[c]
2	4.8	3.4	0.023	Ald	1	0.58	1.39[d]
3	5.1	4.0	0.027	CH_2	1	0.25	1.32[c]
3	5.1	4.0	0.027	Ald	1	0.50	1.32[d]

- *Loading determination of Br-HBP$_5$ via quantitative Total Reflection X-Ray Fluorescence (TXRF)*

A copper standard of 1000 ppm Cu in 3 % HNO_3 was diluted to 500 ppm in an ammonia (25 %) water solution to prepare the copper IS solution. An Eppendorf tube was filled with an exactly determined amount of Br-HBP$_5$ (see **Table S2**). The sample was dissolved in THF (900 µl). The copper IS solution (100 µl) was added, and the mixture was sonicated. A small amount of this prepared solution (5 µl) was put on a small quartz plate, which was pre-coated with a hydrophobic silicone solution (about 10 µl), and dried in an oven at 60 °C. The samples were measured on a Bruker S2 Picofox TXRF spectrometer after evaporation of the solvent. The results obtained from TXRF are summarized in Table S2.

Table S2. Summarized results of TXRF data for the determination of the loading of Br-HBP$_5$

[a] determined by TXRF

[b] calculated via: $Loading\ \left[\frac{mmol}{g}\right] = \left(\frac{c_{TXRF}\left[\frac{mg}{L}\right] \cdot 0.001L}{A_r\left[\frac{g}{mol}\right] \cdot m_{Br-HBP}[mg]}\right) \cdot\ 1000\ \left[\frac{mmol}{mol}\right]$ with A_r the standard atomic weight of bromine and a factor 1000 to convert mol to mmol.

Sample	m (mg)	C_1 (mg L^{-1})[a]	Loading (mmol g^{-1})[b]
Br-HBP$_5$	1.23	125.437	1.27
Br-HBP$_5$	1.44	160.809	1.39
Br-HBP$_5$	1.21	132.024	1.36

e. *N_3-HBP*

Br-HBP$_5$ (1.0 g, 1.3 mmol) and NaN_3 (0.4 g, 5.4 mmol) were dissolved in dry DMF (20 ml) in a flame-dried vial under nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight and then concentrated the next day. The concentrated residue was purified by precipitation and centrifugation steps (5 min at 4000 rpm) (THF/H_2O 2X, THF/Et_2O 2X) yielding N_3-HBP as a yellow powder (functionalization 100 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (br.

s, 2H), 7.86 – 7.77 (m, 5H), 7.46 – 7.27 (m, 5H), 7.25 – 6.82 (m, 17H), 3.90 (br. s, 2H), 3.37 (br. s, 2H), 1.99 (br. s, 2H); IR: ν = 2092, 1711, 1656, 1585, 1488, 1231, 1159, 841, 744 cm^{-1}

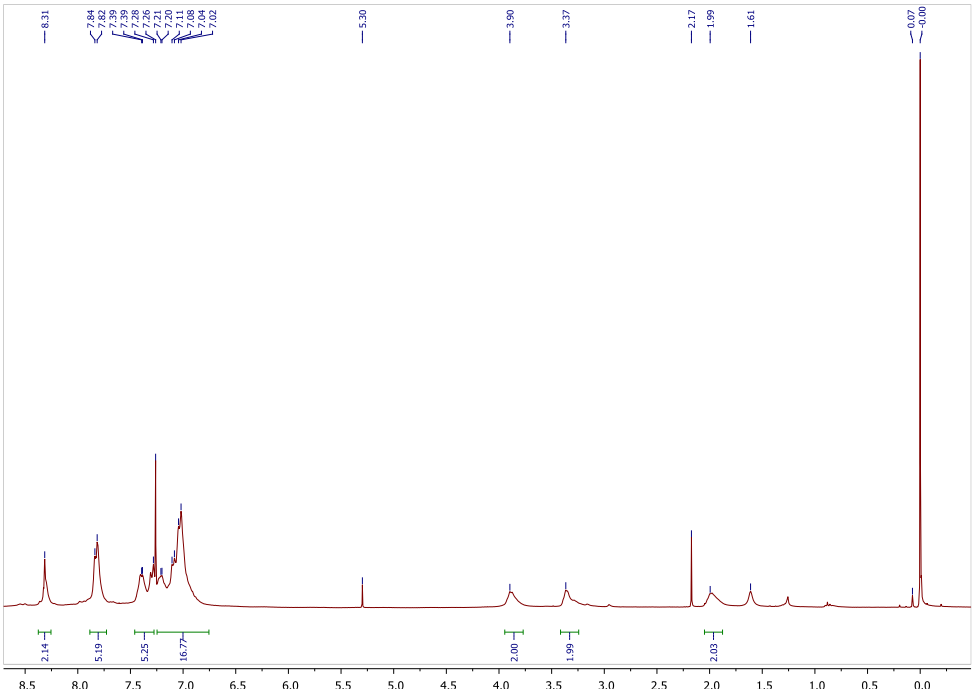

Fig. S6 ^{1}H NMR spectrum of N_3-HBP in $CDCl_3$

f. *Phe-trz-HBP*

N_3-HBP (100 mg, 0.1 mmol) was dissolved in THF (5 ml) in a flask. Phenylacetylene (22 µl, 0.2 mmol), CuI (2.5 mg, 10 mol%), and Et_3N (22 µl, 0.2 mmol) were added. The reaction mixture was stirred at room temperature overnight and then concentrated the next day. The concentrated residue was purified by precipitation (THF/H_2O 2X, THF/Et_2O 2X, THF/MeOH 2X), centrifuged (5 min at 4000 rpm), and washed with acetone to obtain Phe-trz-HBP as a gray powder (functionalization 100 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (br. S, 2H), 7.94 – 7.60 (m, 8H), 7.46 – 7.27 (m, 6H), 7.23 – 6.80 (m, 17H), 4.37 (br. S, 2H), 3.89 (br. S, 2H), 2.41 (br. S, 2H); IR: ν = 1712, 1659, 1588, 1493, 1237, 1163, 845, 752, 693, 495 cm^{-1}

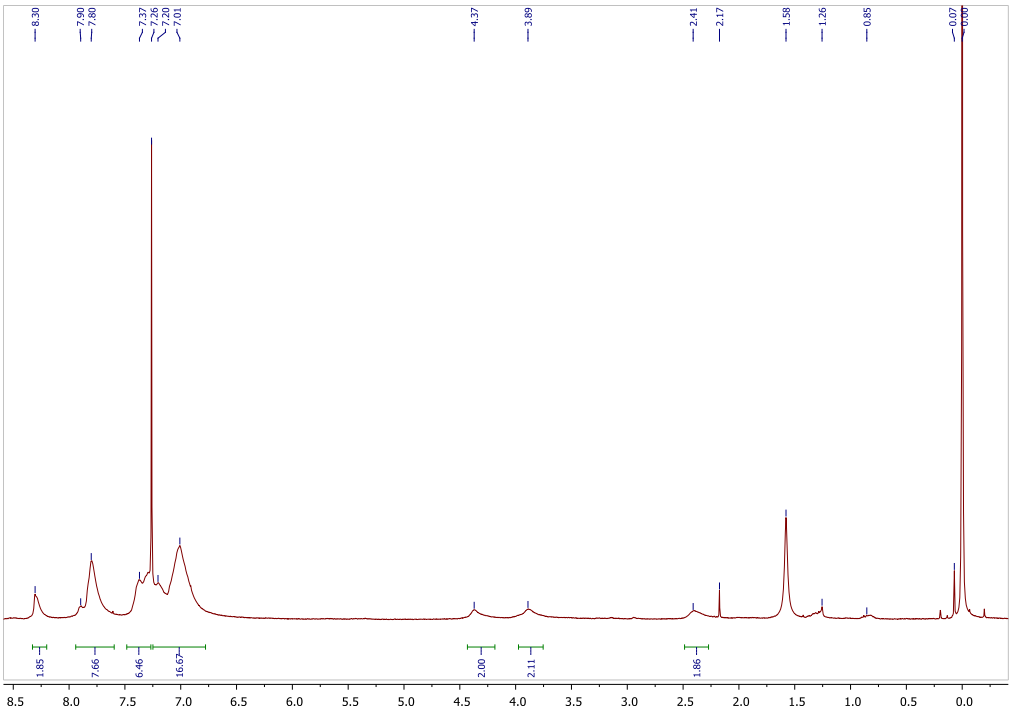

Fig. S7 ^{1}H NMR spectrum of Phe-trz-HBP in $CDCl_3$, isolated after postgrafting

g. *Annotation of propylene signals based on model compound*s

In order to identify the peaks, especially those from the propyl linker, in the spectra of the different polymers, two model compounds (MC1 and MC2) were prepared, following the synthesis given in **Figure S8**, and peaks were assigned via ^{1}H NMR, ^{13}C NMR, and 2D NMR (HSQC). Assignment of the propylene peaks in the spectra of the HBP was based on the comparison of ^{1}H NMR spectra of the starting monomer and model compounds (C, MC1, and MC2) and the corresponding HBPs (Br-HBP$_5$, N$_3$-HBP, and Phe-trz-HBP).

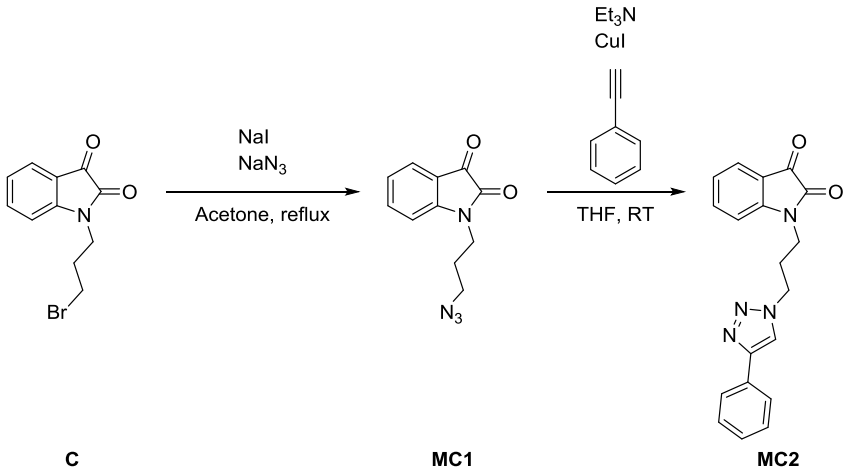

Fig. S8 Synthesis of model compounds MC1 and MC2.

Compound MC1 (1-(3-azidopropyl)indoline-2,3-dione):

In a flame-dried nitrogen-flushed two-necked round-bottomed flask, 1-(3-bromopropyl)indoline-2,3-dione (Compound C: 0.5 g, 1.9 mmol), NaI (0.3 g, 2.0 mmol), and NaN_3 (0.2 g, 2.4 mmol) were dissolved in dry acetone (40 ml) under nitrogen atmosphere. The reaction mixture was refluxed overnight. The reaction mixture was concentrated under reduced pressure and then partitioned in DCM/H_2O. The water layer was extracted with DCM (3X), and the organic layers were combined and washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The concentrate was purified by MPLC (Heptane/EtOAc 8/2) yielding 1-(3-azidopropyl)indoline-2,3-dione (0.3 g, 77 %) as an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 – 7.58 (m, 2H), 7.18 – 7.10 (m, 1H), 6.96 (d, J = 8.5 Hz, 1H), 3.83 (t, J = 7.0 Hz, 2H), 3.45 (t, J = 6.4 Hz, 2H), 1.99 (dd, J = 13.5, 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.16, 158.33, 150.68, 138.52, 125.66, 123.93, 117.62, 109.95, 48.75, 37.55, 26.85

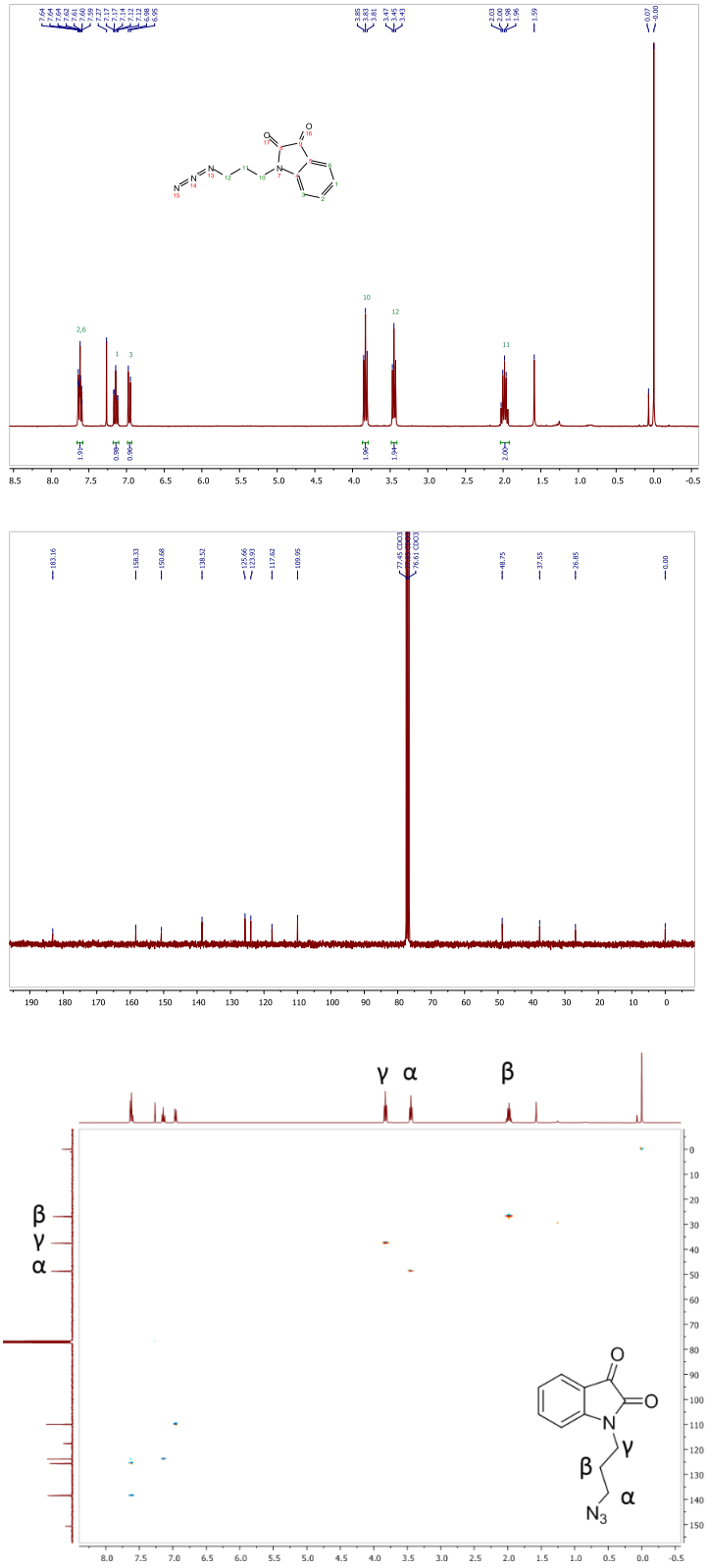

Fig. S9 ^{1}H (top panel), ^{13}C (middle panel), and HSQC (bottom panel) NMR spectra of MC1 in $CDCl_3$

Compound MC2 (1-(3-(4-phenyl-1H-1,2,3-triazol-1-yl)propyl)indoline-2,3-dione):

In a round-bottomed flask, 1-(3-azidopropyl)indoline-2,3-dione (Compound MC1: 55.2 mg, 0.2 mmol) and CuI (4.6 mg, 0.02 mmol) were dissolved in THF (2 ml). Et_3N (40.1 µl, 0.3 mmol) and phenylacetylene (39.5 µl, 0.4 mmol) were added in one portion, and the mixture was stirred overnight. The mixture was concentrated, dissolved in DCM, washed with saturated NH_4Cl (2X) and brine, dried over $MgSO_4$, filtered, and concentrated, yielding 1-(3-(4-phenyl-1H-1,2,3-triazol-1-yl)propyl)indoline-2,3-dione (79.0 mg, 98 %) as a beige powder. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.87 – 7.81 (m, 2H), 7.61 (m, 2H), 7.48 – 7.41 (m, 2H), 7.38 – 7.33 (m, 1H), 7.18 – 7.11 (m, 1H), 6.96 – 6.90 (m, 1H), 4.49 (t, J = 6.7 Hz, 2H), 3.85 (t, J = 6.7 Hz, 2H), 2.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.91, 158.67, 150.20, 147.82, 138.68, 130.33, 128.89, 128.29, 125.72, 125.68, 124.17, 120.72, 117.61, 110.17, 47.57, 37.44, 27.79

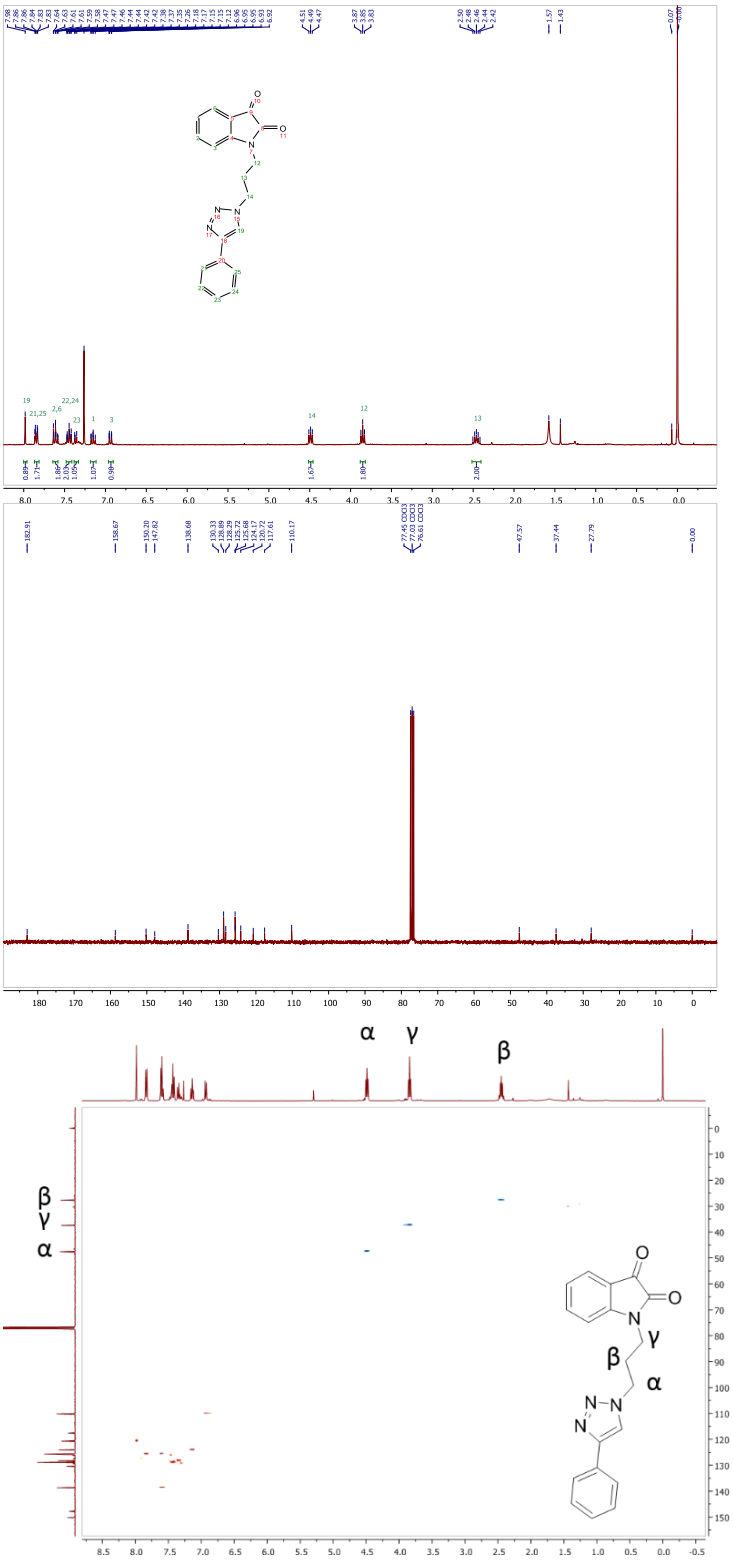

Fig. S10 ^{1}H (top panel), ^{13}C (middle panel), and HSQC (bottom panel) NMR spectra of MC2 in $CDCl_3$

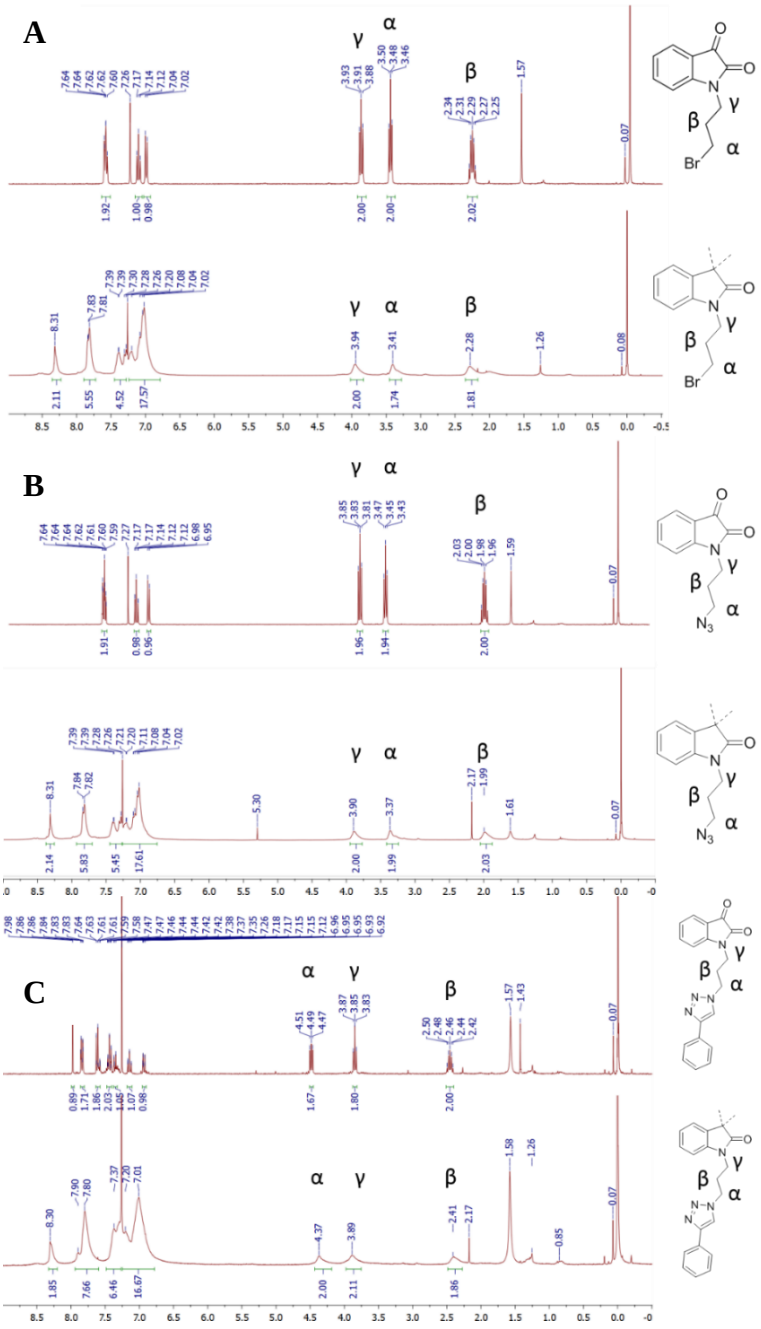

Fig. S11 ^{1}H NMR spectra in $CDCl_3$ of model compounds/starting monomers and associated HBPs. (A) Comparison of C and Br-HBP$_5$. (B) Comparison of MC1 and N_3-HBP. (C) Comparison of MC2 and Phe-trz-HBP.

h. *$RGDS_{(p)}$-trz-$HBP_{33,41,80}$*

N_3-HBP (50 mg, 0.07 mmol), *5-Hexynoic*-$RGDS_{(p)}$-OH (0.4 or 0.8 or 1.5 eq), and CuI (1.3 mg, 0.007 mmol) were dissolved in DMF (1 ml). Et_3N (47 µl, 0.3 mmol) was added, and the reaction mixture was stirred at 50 °C overnight and concentrated the following day. The white powder was further purified by precipitation and centrifugation steps (THF/H_2O 2X, THF/MeOH 2X) and finally freeze-dried to obtain $RGDS_{(p)}$-trz-$HBP_{33,41,80}$ (the final subscript indicates the percentage of functionalization of the end groups of the HBP with RGD) as a white powder.

$RGDS_{(p)}$-trz-HBP_{33}: ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (br. s, 2H), 7.89 – 7.69 (m, 4H), 7.48 – 7.28 (m, 4H), 7.23 – 6.70 (m, 13H), 4.77 (br. s, 1H), 4.57 – 4.19 (m, 2H), 4.02 -3.69 (m, 2H), 3.64 – 3.49 (br. s, 1H), 3.40 – 3.23 (m, 1H), 2.98 - 2.85 (m, 1H), 2.79 – 2.64 (br. s, 1H), 2.59 – 2.38 (m, 2H), 2.07 – 1.84 (m, 3H), 1.59 – 1.28 (br. s, 5H), 1.19 – 0.73 (m, 3H); IR: ν = 2094, 1711, 1658, 1585, 1494, 1235, 1161, 1107, 1015, 844, 750, 495 cm^{-1}

$RGDS_{(p)}$-trz-HBP_{41}: ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (br. s, 2H), 7.89 – 7.69 (m, 4H), 7.48 – 7.28 (m, 3H), 7.23 – 6.70 (m, 11H), 4.77 (br. s, 1H), 4.57 – 4.19 (m, 2H), 4.02 – 3.69 (m, 3H), 3.64 – 3.49 (br. s, 1H), 3.40 – 3.23 (m, 2H), 2.98 – 2.85 (m, 1H), 2.79 – 2.64 (br. s, 2H), 2.59 – 2.38 (m, 3H), 2.07 – 1.84 (m, 3H),1.59 – 1.28 (br. s, 6H), 1.19 – 0.73 (m, 4H); IR: ν = 2097, 1712, 1654, 1586, 1489, 1236, 1161, 1107, 1015, 845, 751, 495 cm^{-1}

$RGDS_{(p)}$-trz-HBP_{80}: ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (br. s, 2H), 7.89 – 7.69 (m, 5H), 7.48 – 7.28 (m, 4H), 7.23 – 6.70 (m, 14H), 4.77 (br. s, 1H), 4.57 – 4.19 (m, 2H), 4.02 – 3.69 (m, 3H), 3.64 – 3.49 (br. s, 1H), 3.40 – 3.23 (m, 2H), 2.98 – 2.85 (m, 2H), 2.79 – 2.64 (br. s, 2H), 2.59 – 2.38 (m, 7H), 2.07 – 1.84 (m, 4H), 1.59 – 1.28 (br. s, 12H), 1.19 – 0.73 (m, 7H); IR: ν = 1714, 1660, 1586, 1490, 1236, 1161, 1089, 1006, 844, 751, 495 cm^{-1}

i. *RGDS-trz-HBP$_{33,41,80}$*

In a 25 ml flask, RGDS$_{(p)}$-trz-HBP$_{33,41,80}$ was introduced, and a mixture of TFA/triisopropylsilane/H_2O (95/2.5/2.5) in DCM (10 % v/v) was added to the flask. The mixture was stirred for 30 min at room temperature and concentrated under vacuum. Et_2O was added to the concentrate, and the deprotected RGDS-trz-HBP$_{33,41,80}$ was precipitated. The precipitate was washed with Et_2O, water, and methanol to remove the salts and the triisopropylsilane, dried on a shlenk line, and freeze-dried to give RGDS-trz-HBP$_{33,41,80}$ as a white powder.

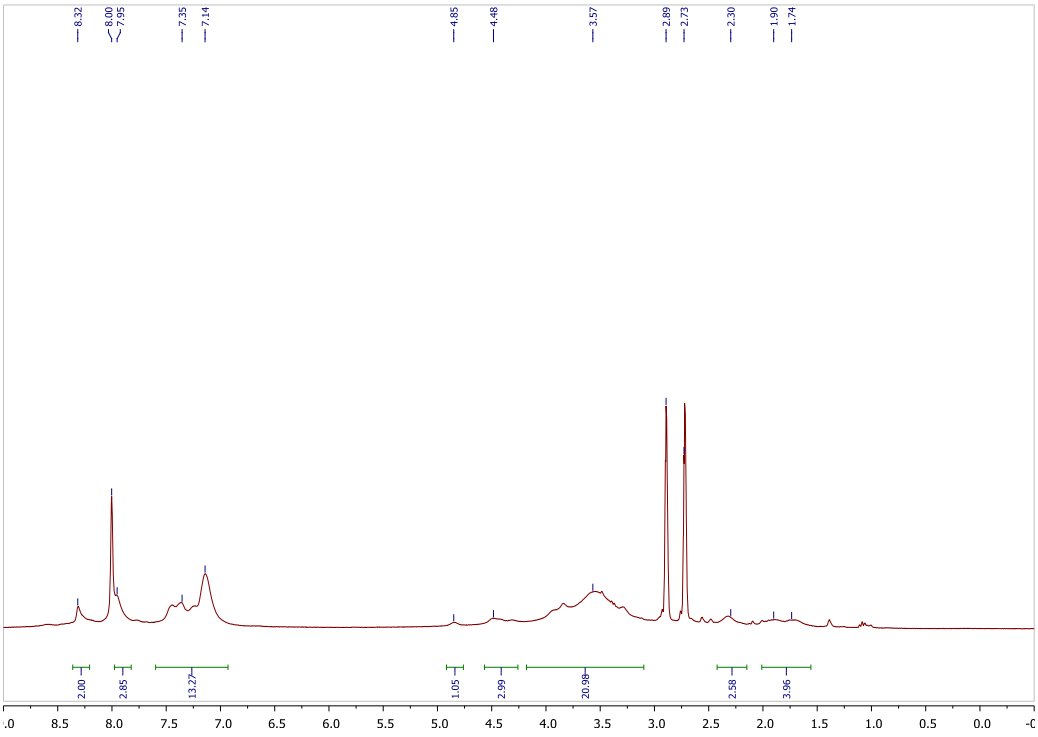

Fig. S12 ^{1}H NMR spectrum of RGDS-trz-HBP$_{80}$ in N,N-Dimethylformamide-d_7

j. *Determination of loading*

Table S3. Calculated loading of N_3-HBP, Phe-trz-HBP, or RGDS-trz-$HBP_{33,41\ and\ 80}$ based on the degree of functionalization.

HBP	Degree of functionalization	Loading of Br, N_3, Phe or RGDS
Br-HBP_5	/	1.34 mmol/g[a]
N_3-HBP	100 %	1.41 mmol/g[b]
Phe-trz-HBP	100 %	1.30 mmol/g[c]
RGDS-trz-HBP_{33}	33 %	0.39 mmol/g[d]
RGDS-trz-HBP_{41}	41 %	0.46 mmol/g[d]
RGDS-trz-HBP_{80}	80 %	0.73 mmol/g[d]

[a] Determined experimentally by TXRF and qNMR as described above.

[b] Calculated via:

$$Loading\ N_3\left[\frac{mmol}{g}\right] = \frac{\left((l_{x1}.df).M_{x2}\right).\frac{1000}{\left(1000-\left((l_{x1}.M_{x1})-\left((l_{x1}.df).M_{x2}\right)\right)\right)}}{M_{x2}}$$

where l_{x1} = 1.34 mmol/g (loading of bromine), df = 1 (degree of functionalization 100% based on ^{1}H NMR), M_{x1} = 79.9 (bromine atomic mass), and M_{x2} = 42.0 (azide atomic mass).

[c] Calculated via:

$$Loading\ Phe\left[\frac{mmol}{g}\right] = \frac{\left((l_{x1}.df).M_{x2}\right).\frac{1000}{\left(1000-\left((l_{x1}.M_{x1})-\left((l_{x1}.df).M_{x2}\right)\right)\right)}}{M_{x2}}$$

where l_{x1} = 1.41 mmol/g (loading of azide), df = 1 (degree of functionalization 100% based on ^{1}H NMR), M_{x1} = 42.0 (azide atomic mass), and M_{x2} = 102.1.

[d] Calculated via:

$$Loading\ RGDS\left[\frac{mmol}{g}\right] = \frac{\left((l_{x1}.df).M_{x2}\right).\frac{1000}{\left(1000-\left((l_{x1}.M_{x1})-\left((l_{x1}.df).M_{x2}\right)\right)\right)}}{M_{x2}}$$

where l_{x1} = 1.41 mmol/g (loading of azide), df = 0-1 (degree of functionalization based on ^{1}H NMR: df = 0.33 if 33% functionalized, df = 0.41 if 41% functionalized, or df = 0.80 if 80% functionalized), M_{x1} = 42.0 (azide atomic mass), and M_{x2} = 527.5.

III. FTIR

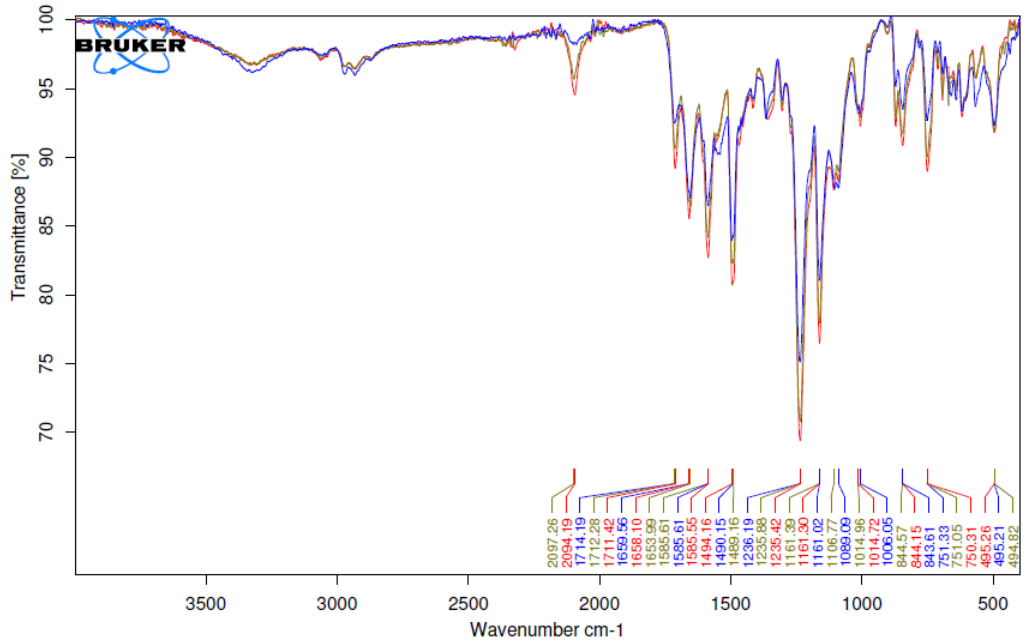

Fig. S13 FTIR spectra of RGDS-trz-HBP_{80} (blue curve), RGDS-trz-HBP_{41} (green curve), and RGDS-trz-HBP_{33} (red curve) overlaid, showing a progressive diminution of the azide signal at 2092.26 cm^{-1} associated with the increase in the amount of RGDS used for postgrafting via *CuAAC*.

IV. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

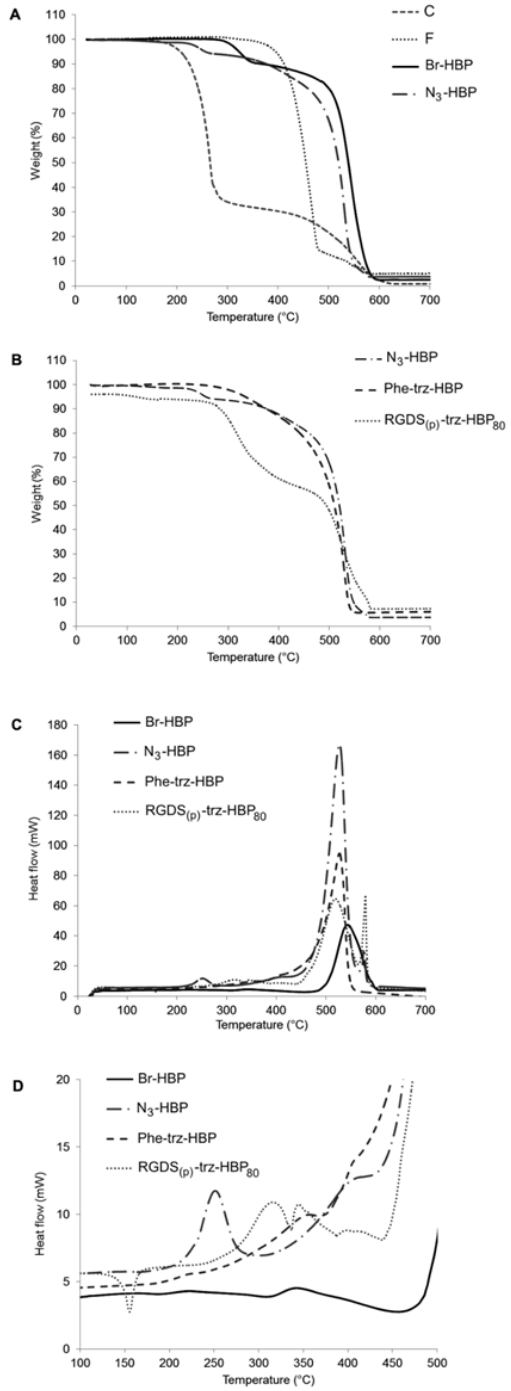

Fig. S14 TGA and DSC curves for C, F, Br-HBP$_5$, N$_3$-HBP, Phe-trz-HBP, and RGDS$_{(p)}$-trz-HBP$_{80}$. (A) TGA curves showing the differences in the degradation profiles between the monomers and Br-HBP$_5$ and between Br-HBP$_5$ and N$_3$-HBP. (B) TGA curves of N3-HBP, Phe-trz-HBP, and RGDS$_{(p)}$-trz-HBP$_{80}$. (C) DSC curves of Br-HBP$_5$, N$_3$-HBP, Phe-trz-HBP, and RGDS$_{(p)}$-trz-HBP$_{80}$. (D) Enlarged region of (C) between 100 °C and 500 °C showing the effect of the different modification/functionalization steps carried out on Br-HBP$_5$.

V. Contact angle

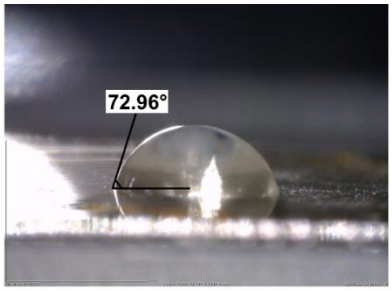

Fig. S15 Digital image showing the contact angle of water measured on Br-HBP_5

[attached as separate file]

Fig. S16 Movie of the contact angle measurement showing the complete wetting of a glass cover slip coated with RGDS-trz-HBP_{80}

ESI Reference

1. S. K. Bharti and R. Roy, *Trac-Trends Anal. Chem.*, 2012, **35**, 5-26.