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Tetrakis-(4-thiyphenyl)methane: Origin of a Reversible 3D-Homopolymer

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The efficient syntheses of tetrakis(thiophenol)methane and of a new poly(disulfide) hyper-crosslinked polymer based on the former monomer are described. Controlled de-polymerization as well as surface post-functionalization are successfully conducted on this novel material. Direct prove of post-functionalization is obtained through solid-state fluorescence emission spectroscopy, and the number of unreacted thiol-functions on the surface of the polymeric material is indirectly quantified by de-polymerization of the post-functionalized material.

1. Introduction

Among the wide variety of macromolecular architectures that can be generated, a sub-class comprising connecting links deriving from sulfur-based chemistry can be distinguished.[1] These polymers have gained interest due to the propensity of the sulfur atom to undergo various oxidation states,[2] which offers the possibility of further modifications, leading to an alteration in the physical behavior of the so-generated macromolecular assemblies.[3] Although sulfoxyde –SO-,[2b,4] sulfonic acid $-SO_3H$,[5] thioester,[6] thiocarbonate, and thiourethane[7] are already largely employed,[8] the use of the sulfide linkage remains marginal.[9]

Herein, we report the synthesis of the first reversible three-dimensional polymer based on a disulfide linkage and its post-functionalization.

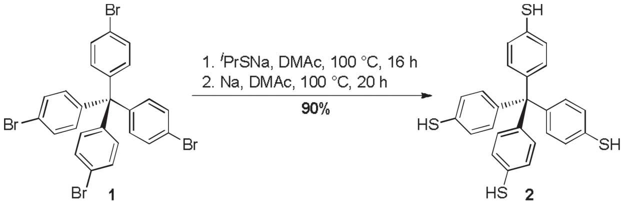
2. Results and Discussion

2.1. Preparation of the Monomer

Tetraphenylmethane (TPM)[10] has been largely used in the generation of hyper-crosslinked polymers (HCPs)[11] and dendrimers[12] due to the tetrahedral geometry and the rigidity imposed by the core. One can already cite triazoles,[2b,13] boroxine rings,[14] imines,[15] or simple carbon–carbon bonds[16] as classical junctions for the generation of the deriving polymers. The targeted TPM-SH monomer 2 for the envisioned poly(disulfide) HCP 3 has already been described in a Japanese patent with a global yield of 10%, obtained by sulfonylation of the original TPM, and further reduction in the presence of $LiAlH_4$ or $NaBH_4$.[17] Starting from tetrakis(bromophenyl)methane (1, TPM-Br),[10] the corresponding tetrakis-(thiophenol)methane (2, TPM-SH) was prepared in two steps, including a nucleophilic substitution in dimethylacetamide (DMAc) followed by reduction with sodium (**Scheme 1**).[18] The synthesis occurs under milder conditions and leads in high yield to the desired compound **2** in gram scale. The molecular structure of **2** resulting from an X-ray diffraction study is depicted in **Figure 1**.[19] The crystal structure exhibits six molecules in the unit cell showing two types of crystallographic symmetry: S_4-symmetry (1/4 molecule in the asymmetric unit) and C_2-symmetry (1/2 molecule in the asymmetric unit), which may be attributed to weak S–S interactions and hydrogen bonds between the thiol functions of neighboring molecules (3.47–3.87 Å).

2.2. Generation of the 3D-Homopolymer

Tetrakis-thiophenol **2** was further oxidized to the corresponding disulfide HCP **3** in ethyl acetate in presence of hydrogen peroxide catalyzed by sodium iodide (**Scheme 2**).[20] Considering the insolubility of the generated polymer in all the common solvents, a model compound study was initiated to monitor the reaction. Commercially available p-thiocresol was oxidized to the corresponding disulfide, and FTIR spectra were recorded (see Supporting Information), showing the extinction



Scheme 1. 2-Step synthesis of tetrakis-(4-thiyphenyl)methane **2**.

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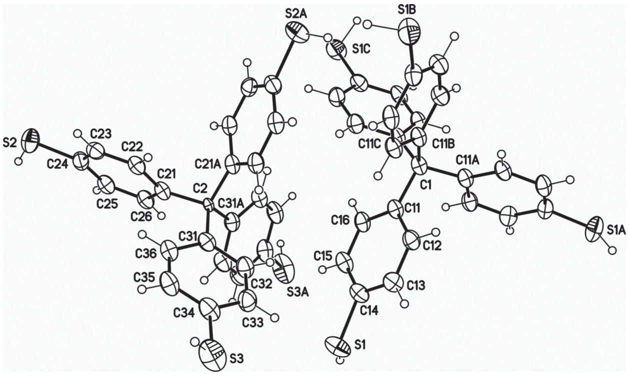


Figure 1. Molecular structures of **29**. Left: the molecule with crystallographic C_2-symmetry. Right: the molecule with crystallographic S_4-symmetry. Displacement parameters are drawn at 50% probability level (see Supporting Information).

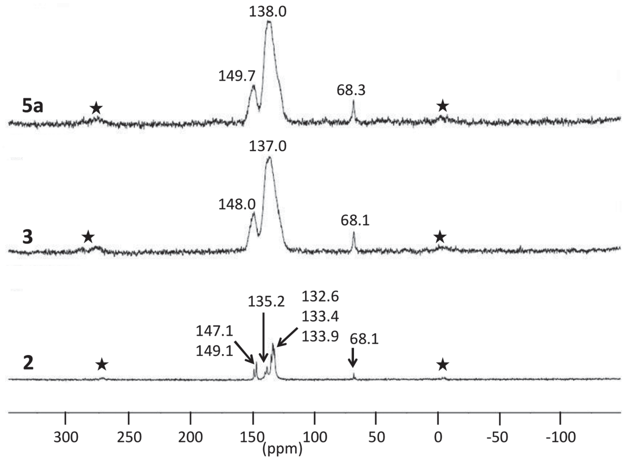


Figure 2. Solid-state ^{13}C CP/MAS NMR of **2**, **3**, and **5a**. * indicates spinning sidebands.

of the thiol stretching band in parallel to the appearance of the disulfide band (confirmed by ^1H NMR).

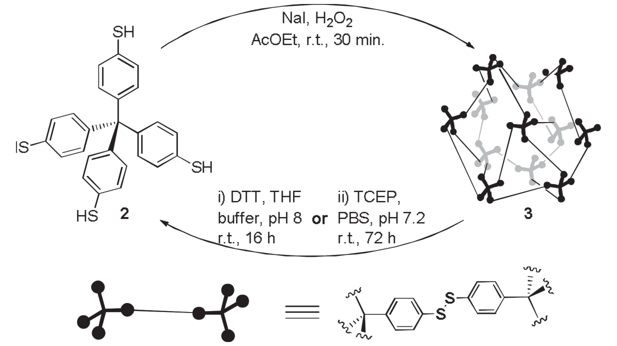
Applying these reaction conditions to TPM-SH **2**, a precipitate formed nearly instantaneously. The topology of **3** was then investigated by FTIR, solid-state ^{13}C cross-polarization with magic angle spinning (^{13}C CP/MAS NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), powder-X-ray diffraction (PXRD), and scanning electron microscopy (SEM) analysis. No stretching band of the thiol function was detected in the FTIR spectra of **3**, whereas its solid-sate ^{13}C CP/MAS NMR spectroscopic signature was similar to the one of **2**, with the presence of broader signals in the case of **3**, inherent to its polymeric structure (**Figure 2**). Elemental analysis was in good accordance with the theoretical values, discarding any hypothesis of a higher oxidation state of the thiophenol moiety, all these analysis confirming the structure of **3**. The DSC thermogram showed no glass transition temperature (T_g) which is in accordance with a high number of crosslinks.[4] No fusion peak was recorded either and decomposition starts around 200 °C. TGA data confirm that **3** possess a good thermal stability by achieving complete loss of sulfur content at 750 °C in a nitrogen atmosphere and the PXRD patterns evidenced some area of cristallinity (see Supporting Information). The SEM analysis of **3** reveals condensed spherical particles, with a non-uniform size distribution and diameters ranging from 0.5 to 1.7 µm (**Figure 3**). Investigation of nitrogen adsorption and desorption at 77.3 K indicates that **3** is a non-porous network, exhibiting a negative value for its surface area (Brunauer-Emmett-Teller method) whatever the reaction conditions employed for its generation (see Supporting Information).

2.3. De-Polymerization

With **3** in hands, the physical and chemical properties of the HCP were investigated by firstly exploring its controlled de-polymerization. Disulfide bonds are usually considered as weak covalent links as they can be easily cleaved by appropriate reagents.[21] Two main routes were explored in depth, using i) dithiothreitol (DTT) in slightly basic conditions,[22] or ii) the water-soluble tris(2-carboxyethyl)phosphine (TCEP) at neutral pH[23] (Scheme 2). Under both conditions, the monomer **2** was recovered after 16 h and 72 h, respectively, in almost quantitative yields, showing the reversible character of this 3D-polymer.

2.4. Post-Functionalization

Considering the size of the polymeric particles observed by SEM, a non-negligible amount of unreacted termini of the



Scheme 2. Formation and reduction of the disulfide HCP **3**.

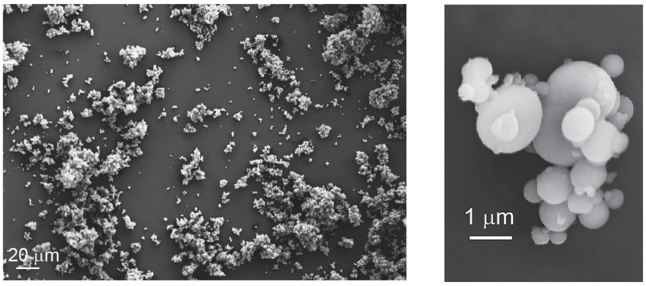
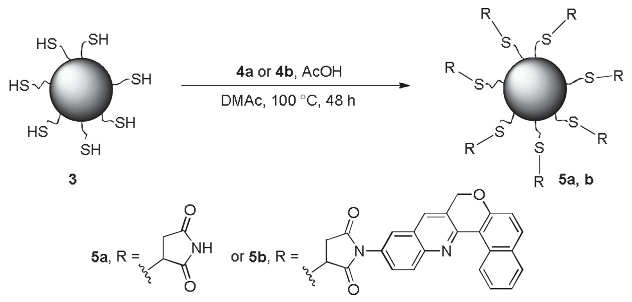


Figure 3. SEM pictures of **3**.



Scheme 3. Post-functionalization of **3** with maleimides **4a** and **4b**.

monomer should be present at the surface of the particles. Post-functionalization[24] was therefore explored next, taking advantage of the reversible nature of the S–S bond to recover the discrete molecules and thus quantifying the number of the modified end groups. To facilitate the post-functionalization, reaction conditions affording no by-products and high yields were sought and firstly optimized on a discrete molecule model. Nucleophilic addition was envisaged with maleimide **4a**, as the latter is an excellent substrate for the Thia-Michael reaction. Quantitative conversion between *p*-thiocresol and **4a** was observed in DMAc in the presence of a small amount of acetic acid, at room temperature or at 100 °C. Upon completion of the reaction, both maleimide carbonyls became unequivalent, which was confirmed in FTIR by a split of the initial carbonyl stretching band into two distinct signals.

Reaction of HCP **3** with **4a** in DMAc at 100 °C for 48 h afforded a pale yellow insoluble polymer (**Scheme 3**), whose FTIR spectrum showed a band relative to a carbonyl function (see Supporting Information). At this stage, however, there was no convincing evidence for post-functionalization of HCP **3** as some remaining starting maleimide could have been trapped within **3** during its swelling in DMAc. Moreover, solid-sate ^{13}C CP/MAS NMR did not show any signals related to a functionalized maleimide (Figure 2, **5a**), and the DSC and TGA analysis did not indicate any difference in the thermal behavior of the post-functionalized polymer compared to the starting HCP **3**. In order to prove post-functionalization, de-polymerization conditions (i) depicted in Scheme 2 were applied to HCP **5a**. The reaction sequence was conducted on gram scale in order to detect also minor side products. After the efficient cleavage of the polymer, only mono-functionalized TPM-SH bearing one maleimide unit (**S6**, 25%) and tetrakis-(thiyphenyl)methane (**2**) (75%) were isolated, which corresponds to 6% of free thiophenol functions present in the initial 3D-polymer **3**. One can assume that the amount of free thiol functions is actually higher taking into account inaccessible free thiophenol functions within the polymer matrix. The total ratio was, however, still beneath the detection threshold of solid-state ^{13}C CP/MAS NMR (Figure 2, **5a**).

Aiming at a straightforward characterization method for monitoring the outcome of a post-functionalization reaction, fluorescence was investigated next. Post-functionalization was thus realized with the fluorescent dye **4b**, reported to operate as an efficient on/off probe for the detection of thiol moieties (Scheme 3).[25] Nucleophilic addition of **3** to **4b** was conducted under the conditions used to obtain **5a**. After washing with water, the intense yellow-colored insoluble material **5b** showed two carbonyl stretching bands in FTIR, whereas nor change in the thermal behavior nor structural rearrangement compared to **3** were observed by DSC and TGA analysis and PXRD study, respectively. Solid-state fluorescence emission spectroscopy of HCP **5b** displayed two emissive bands located around 440 and 540 nm, respectively, when the sample was irradiated at 350 nm (see Supporting Information). The photo-physical properties of **3** and **4b** were also investigated, and no fluorescence emission was detected in the solid-state for both of them, proving that post-functionalization was properly performed. The fluorescence intensity of **5b** was evaluated by a solid-state emission quantum yield (PLQY) of 0.014, a relatively low value eventually due to fluorescence quenching by neighboring molecules.[26]

3. Conclusion

We have reported the synthesis of a tetrahedral thiophenol monomer that was further polymerized under mild conditions and short reaction times to afford a poly(disulfide) hyper-crosslinked polymer in excellent yields. Two conditions were used to decompose this macromolecular architecture in a controlled fashion and to recover almost quantitatively the composing monomer. Post-functionalization of the polymeric material was realized using the Thia-Michael reaction with maleimide moieties. The degree of functionalization was indirectly quantified taking advantage of the de-polymerization of **5a** and post-functionalization was directly proven on polymer **5b** through solid-state fluorescence emission spectroscopy. To the best of our knowledge, this contribution exemplifies, for the first time, a precise estimation of end termini, a feature usually excluding from the characterization of such polymers due to the quasi impossible character to access to this type of information.

The presented, completely reversible[27] HCP, based on disulfide bridges, combines the robustness of hyper-crossed-linked polymer with the dynamic behavior of supramolecular architectures held together by H- or coordination- bonding and opens the door to innovative applications such as specific drug transport[21b] and release or rapid access to functional sulfur tripods for surface coatings. We are currently exploring some of these options.

4. Experimental Section

Materials: NMR spectra were recorded on a Bruker AM 300 (300 MHz) as solutions in CDCl$_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to CHCl$_3$ (7.26 ppm), as internal standard. All coupling constants (J) are absolute values. The description of signals includes: s = singlet, d = doublet, t = triplet, m = multiplet, and dd = doublets of doublets. The spectra were analyzed according to first order. The signal structure in ^{13}C NMR was analyzed by DEPT. The solid-state NMR spectra were measured on a Bruker Avance 400 spectrometer operating at 100.6 MHz for ^{13}C. The ^{13}C CP/MAS experiments were carried out at MAS rates of 14 kHz using densely packed powders of the compounds in 4 mm ZrO$_2$ rotors. The ^{1}H $\Pi/_2$ pulse was 4 µs and decoupling was used during the acquisition. The Hartmann-Hahn condition was optimized with adamantane at a rotational speed of 5 kHz. All spectra were measured using a contact time of 1.5 ms and a relaxation delay of 10.0 s, and 6000 FIDs were accumulated. The microstructure of **3** was investigated by scanning electron microscopy (SEM, Zeiss Supra S5) after metallization. The dynamic DSC was measured on a METTLER Toledo DSC 30, in a sealed aluminium 40 µL pan under argon atmosphere. The obtained data was analyzed electronically with the software program STAR ^{e}SW 8.10 and plotted in a diagram. The enthalpy changing ΔH [mW] was plotted against the temperature (–50 °C to 250 °C) of the heating rate of 10 °C min^{-1}. Infrared spectra were recorded with a FT-IR Bruker IFS 88 spectrometer with OPUS software using the attenuated total reflection technique (ATR). The deposit of the absorption band was given in wave numbers ν in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs = very strong 0–10% T, s = strong 11–40% T, m = medium 41–70% T, w = weak 71–90% T, vw = very weak, 91–100% T, br = broad. MS (EI) (electron impact mass spectrometry) was performed by using a Finnigan MAT 90 (70 eV). The EA measurements were performed on an Elementar vario MICRO device using a Sartorius M2P precision balance. The following abbreviations were used: calc. = calculated data, found = measured data. TGA was performed under N_2 on a Shimadzu TGA-50 thermogravimetric analyzer, with a heat rate of 10 °C min^{-1}. Emission and excitation spectra in the solid-state were measured with a Horiba Scientific FluoroMax-4 spectrofluorometer using a JX monochromator and a R928P PMT detector. For the determination of PLQY, an absolute PL quantum yield measurement system from Hamamatsu Photonics was used. The system consisted of a photonic multichannel analyzer PMA-12, a model C99200–02G calibrated integrating sphere, and a monochromatic light source L9799–02 (150 W Xe- and Hg-Xe-lamps). Data analysis was done with the PLQY measurement software U6039–05, provided by Hamamatsu Photonics. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, ABCR and Acros Organics. All solvents, reagents and chemicals were used as purchased unless stated otherwise. Tetrakis(4-bromophenyl) methane (**1**)[23] and 1-(8H-benzo[5,6]chromeno[4,3b]quinolin-11-yl)-1H-pyrrole-2,5-dione (**4**)[24] were obtained according to literature procedures.

*Synthesis of **2***: Tetrakis(bromophenyl)methane **1** (3.143 g, 4.6 mmol, 1.0 equiv.) and NaS^{i}Pr (5.388 g, 49.4 mmol, 10.0 equiv.) were suspended under an inert atmosphere (Ar) in dimethylacetamide (DMAc) (40 mL) and the mixture was heated for 16 h at 100 °C. Subsequently, Na (2.272 g, 98.8 mmol, 20.0 equiv.) was added under vigorous stirring and the mixture was heated for an additional 24 hour-period. The mixture was carefully hydrolyzed with H_2O (250 mL) and *tert*-butyl methyl ether (MTBE) (150 mL) was added before acidifying the mixture with conc. hydrochloric acid (pH < 1). The layers were separated and the aqueous layer was extracted with MTBE (2 × 75 mL). The combined organic layers were washed with H_2O (5 × 100 mL) and dried over Na_2SO_4. After filtration, the crude mixture was evaporated before being subjected to column chromatography (MTBE/cyclohexane: 50/50) to afford the title compound as a light yellow solid (1.874 g, 90%). R_f = 0.50 (dichloromethane/cyclohexane: 50/50). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.41 (s, 4 H), 7.00 (AA'BB', ^2J = 8.4 Hz, 8 H), 7.14 (AA'BB', ^2J = 8.4 Hz, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 63.5 (C_{quart}, *C*(Ar)$_4$), 128.8 (*C*H), 131.4 ($C_{quart,}$*C*S), 131.6 (*C*H), 143.8 (C_{quart}, C*C*); IR (ATR): ν = 3020 (vw), 2919 (vw), 2552 (S-H, vw), 2045 (vw), 1916 (vw), 1647 (vw), 1586 (w), 1561 (vw), 1483 (m), 1400 (w), 1310 (vw), 1262 (w), 1191 (w), 1118 (vw), 1100 (m), 1013 (m), 947 (w), 900 (w), 836 (vw), 806 (m), 732 (w), 632 (w), 542 (m), 523 (m), 515 (m), 444 (vw), 402(vw) cm^{-1} (m); EIMS *m/z* (%): 448 (68) [M]+, 416 (26) [M–S]+, 339 (100) [M–C_6H_5S]+, 307 (36) [M–$C_6H_5S_2$]+, 273 (23) [M–$C_6H_7S_3$] +. Anal. calcd for $C_{25}H_{20}S_4$ + 0.3 CH_2Cl_2 + 0.1 C_6H_{12}: C 64.46, H 4.55, S 26.58; found: C 64.53, H 4.55, S 26.57.

*Synthesis of **3***: To a stirred suspension of tetrakis(thiophenyl) methane **2** (1.319 g, 2.9 mmol, 1.0 equiv.) in ethyl acetate (150 mL) were added NaI (0.004 g, 0.02 mmol, 0.01 equiv.) and aq. 30% H_2O_2 (2.00 mL, 29.4 mmol, 10.0 equiv.) and the mixture was shaken at room temperature for two hours. Saturated aqueous $Na_2S_2O_3$ (15 mL) was added, and the resulting solid was filtrated and extensively washed with water (50 mL), EtOH (50 mL), MeOH (50 mL), then with EtOAc (3 × 50 mL), THF (50 mL), acetone (50 mL), and CH_2Cl_2 (50 mL). The resulting material was dried at 100 °C under vacuum during 24 h (m = 1.122 g, 93%). ^{13}C CP/MAS NMR (400 MHz, δ): 68.1 (C_{quart}, *C*(Ar)$_4$), 137.0 ($C_{quart,}$*C*S, *C*H), 148.0 (C_{quart}, C*C*) ppm; IR (ATR): ν = 3073 (vw), 3020 (vw), 2567 (S-H, vw), 1586 (vw), 1561 (vw), 1482 (w), 1398 (w), 1307 (vw), 1271 (vw), 1239 (vw), 1191 (vw), 1101 (vw), 1081 (vw), 1012 (w), 951 (vw), 912 (vw), 809 (m), 760 (vw), 737 (vw), 695 (vw), 631 (vw) cm^{-1} (m). Anal. calcd for $C_{25}H_{16}S_4$ + Na: C 64.21, H 3.45, S 27.42; found: C 64.48, H 3.61, S 27.18.

Conditions for Depolymerization: Scheme 2, i) To a stirred suspension of **3** (0.280 g, 0.6 mmol, 1.0 equiv.) in THF (5 mL) was added DTT (0.385 g, 2.5 mmol. 4.0 equiv.) in a buffer solution (V = 5 mL, pH 8) and the mixture was shaken at room temperature until complete dissolution of the solid, usually after 16 h. The mixture was then diluted in water and CH_2Cl_2 and acidified with HCl 2M until pH 1 was reached. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtrated and evaporated to dryness. Excess of DTT was removed by column chromatography to afford **2** (m = 0.252 g, 90%). Scheme 2, ii) To a stirred suspension of **3** (0.308 g, 0.7 mmol, 1.0 equiv.) in THF (5 mL) was added TCEP (0.866 g, 3.0 mmol, 4.0 equiv.) in phosphate buffer solution (V = 5 mL, pH 7.2) and the mixture was shaken at room temperature until total dissolution of the mixture, usually three days. The mixture was then diluted in water and CH_2Cl_2 and acidified with conc. HCl (a few drops). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried with Na_2SO_4, filtrated, and evaporated to dryness to afford **2** (m = 0.273 g, 88%).

*Post-Functionalization of **3** with Maleimide **4a** and Generation of **5a** and **S6***: To a suspension of **3** (1.000 g, 2.2 mmol, 1.0 equiv.) in abs. DMAc (20 mL) acidified by a few drops of acetic acid was added maleimide (0.865 g, 8.9 mmol, 4.0 equiv.), and the mixture was shaken at 100 °C for two days. After filtration and extensive washing with water, the resulting polymer was dried at 100 °C at atmospheric pressure to afford **5a** (m = 0.805g). ^{13}C CP/MAS NMR (400 MHz, δ): 68.3 (C_{quart}, *C*(Ar)$_4$), 138.0 ($C_{quart,}$*C*S, *C*H), 149.7 (C_{quart}, C*C*) ppm; IR (ATR): ν = 3054 (vw), 3020 (vw), 2306 (vw), 2163 (vw), 2050 (vw), 1915 (vw), 1786 (vw), 1728 (w), 1586 (vw), 1562 (vw), 1482 (m), 1398 (w), 1339 (vw), 1307 (vw), 1270 (vw), 1219 (vw), 1191 (w), 1156 (vw), 1117 (vw), 1081 (w), 1012 (m), 951 (vw), 913 (vw), 809 (m), 738 (w), 695 (w), 631 (w), 600 (vw), 549 (w) cm^{-1} (m). The post-functionalized polymer **5a** (0.805 g, 1.8 mmol, 1.0 equiv.) was suspended in THF (50 mL) and DTT (1.383g, 9.0 mmol, 4.0 equiv.) in a buffer solution (V = 50 mL, pH 8) was added. The resulting mixture was then shaken at room temperature until complete dissolution of the solid, usually 16 h. The mixture was then diluted in water and CH_2Cl_2, and acidified with 2 M HCl. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried with Na_2SO_4, filtrated and evaporated to dryness. The crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane: 50/50) to afford **2** (0.556 g, 75%) and mono-functionalized TPM **S6** (0.233 g, 25%).

*Post-Functionalization of **3** with the Fluorescent Dye **4b** and Generation of **5b***: To a stirred suspension of **3** (0.200 g, 0.4 mmol, 1.0 equiv.) in abs. DMAc (20 mL) acidified by a few drops of acetic acid was added 1-(8H-benzo[5,6]chromeno[4,3b]quinolin-11-yl)-1H-pyrrole-2,5-dione (0.506 g, 1.3 mmol, 3.0 equiv.) and the mixture was shaken at 100 °C for two days. The mixture was then filtrated and extensively washed with water (100 mL), acetone (50 mL) and CH_2Cl_2 (50 mL) to afford **5b**. IR (ATR): ν = 3055 (vw), 1787 (vw), 1721 (w), 1593 (vw), 1511 (vw), 1483 (w), 1437 (vw), 1396 (w), 1365 (w), 1225 (vw), 1169 (w), 1081 (vw), 1012 (w), 911 (vw), 810 (m), 749 w), 695 (vw), 630 (vw), 548 (w), 521 (w) cm^{-1} (m). Anal. found: C 67.48, H 3.81, S 20.21, N 1.60.

CCDC 929924 contains the supplementary crystallographic data for this paper.[28]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[28] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.