Supporting Information

S_NAr as a facile method to prepare polystyrene-grafted conjugated copolymers with enhanced photoluminescence properties

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1. Methods

Thiol terminated polystyrene (average M_n 5000, $D \le 1.1$) was purchased from Sigma Aldrich and used without further purification. All other chemicals were purchased from major chemical suppliers and used as received. Synthetic reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Characterisation was carried out in air at room temperature unless stated otherwise.

¹H NMR, ¹⁹F NMR and DOSY NMR were collected either on AV-400 (MHz) or AV-500 (500 MHz) Bruker Spectrometer using the *d*-chloroform as solvent, with chemical shift values quoted relative to residual solvent signals (¹H NMR: 7.26 ppm).

Samples for DOSY NMR were prepared at 2.5 mg/mL in CDCl₃. For the blend samples, the weight ratio of polymer:PS-SH was kept at 1:5 (IDTfBT:PS-SH) or 1:10 (F8fBT/FO6-T:PS-SH) approximately the same as in graft copolymers. The DOSY experiment was measured at a temperature of 298K on a Bruker 400MHz AVANCE III HD spectrometer running TopSpin3.6.5 and equipped with a z-gradient bbfo/5mm tuneable probe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output (100%) of 53.5G/cm (5.35G/cmA).

The 1H DOSY spectrum was collected using the Bruker pulse program ledbpgp2s at a frequency of 400.05MHz with a spectral width of 4000Hz (centred on 4.0ppm) and 32768 data points giving an acquisition time of 4.1s. A relaxation delay of 3.5s was employed along with a diffusion time (large delta) of 59ms and a longitudinal eddy current delay (LED) of 5ms. Bipolar gradients pulses (little delta/2) of 2.5ms and homospoil gradient pulses of 0.6ms were used. The gradient strengths of the 2 homospoil pulses were -17.13% and -13.17%. 16 experiments of 16 transients each were collected with the bipolar gradient strength, initially at 2% (1st experiment), linearly increased to 95% (16th experiment). All gradient pulses were smoothed-square shaped (SMSQ10.100) and after each application a recovery delay of 200us used.

The data was processed using 32768 data points in the direct dimension applying an exponential function with a line broadening of 1Hz and 64 data points in the indirect dimension. Further processing was achieved using the Bruker Dynamics Center software (version 2.8.b.4) – error estimation by Monte Carlo simulation with a confidence level of 95%.

UV-vis absorption spectra were recorded on an Agilent Cary 60 UV-vis spectrophotometer at room temperature.

Photoluminescence (PL) spectra were acquired on an Agilent Cary Eclipse fluorescence spectrophotometer. Films were measured on a Fluorolog-3 spectrofluorometer (FL 3-22, Jobin Yvon, Horiba) and excited by a Xenon lamp source. The emitted photons were collected in the front face geometry with a photomultiplier tube (PMT) R928P detector with a slit width of 5 nm.

Gel permeation chromatography (GPC) measurements for polymer molecular weight analyses were carried out on an Agilent 1260 II High-Temperature GPC System fitted with three Agilent PLgel 10 μ m MIXED-B, 7.5 x 300 mm columns, RID and HTELSD detectors, using HPLC-grade 1,2,4-trichlorobenzene (with 0.0125% BHT inhibitor; TCB) as eluent at a flow rate of 1.0 mL min⁻¹ and temperature of 150 °C. Number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (*D*) values are reported relative to polystyrene standards that were run at the same temperature. Samples were prepared to a concentration of approximately 1 mg mL⁻¹ in the same solvent as the eluent.

PS-FO6-T was purified on a preparative Shimadzu GPC system running in chloroform at 40°C with an Agilent PLgel 10 µm mixed-d column, DGU-20A3 Degasser, LC-20A Pump, CTO-20A Column Oven and SPD-20A UV Detector.

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC1, heating from 25 to 750°C at 5°C/min under N₂.

Differential scanning calorimetry (DSC) was carried out using a Mettler Toledo DSC1, heating from 25°C to 300°C (or 280°C) at 10°C/min under N₂.

Dynamic light scattering (DLS) was performed using a Malvern Panalytical Zetasizer Ultra. Nanoparticle suspensions were directly used for analysis after preparation.

Cryo-TEM: For cryo-transmission electron microscopy (cryo-TEM) measurements, 3 μ L of each nanoparticle suspension was applied to glow-discharged (EMS 100x Glow Discharge Unit, 20mA, 1 min) holey carbon grid (Quantifoil R2/2 on gold or copper 300 mesh support), blotted for 3.5 seconds with Vitrobot filter paper (Electron Microscopy Sciences), and plunge frozen into liquid ethane cooled by liquid nitrogen using a Vitrobot (Thermo Fisher Scientific) operated at 4 or 22 °C and 100% humidity. Samples were imaged on a Titan Krios G4 (Thermo Fisher Scientific) operated at 300 kV and equipped with Falcon 4i direct electron detector (Thermo Fisher Scientific). Electron micrographs were acquired with EPU software (Thermo Fischer Scientific) at a magnification of 215'000x, corresponding to a physical pixel size of 0.575 Å. A nominal defocus range of -2.0 to -4.0 μ m was used with a total exposure time of 5 sec with a total dose of 40 e-/Å2 at a dose rate of 6 e-/pix/s.

PLQY: Photoluminescence quantum yield (PLQY) measurements were carried out on a Horiba Fluorolog with a Labsphere integrating sphere attachment at a data interval of 1 nm with equal excitation and emission slits maximized while ensuring that the blank excitation signal did not exceed the detector limit of 2 million counts / s. PLQY and CIE colour space values were calculated with Horiba FluorEssence software using the four spectra method (excitation and emission for both the blank and sample). For solution measurements, samples were prepared to a concentration of 1 mg mL⁻¹ in CHCl₃. For film measurements, samples were prepared by spin coating 15 mg mL⁻¹ CHCl₃ solutions on glass substrates. For nanoparticle suspension measurements, samples were prepared via the standard nanoparticle preparation protocol (detailed below).

2. Experimental

Synthesis of polymer F8fBT (according to A. Creamer et al.)¹



9,9-Dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacol) ester (2.39 g, 3.72 mmol, 1.0 eq.), 4,7dibromo-5-fluoro-2,1,3-benzothiadiazole (1.15 g, 3.68 mmol, 0.99 eq.), Pd(PPh₃)₄ (86.0 mg, 0.0744 mmol) and a stirrer bar were placed in a 100 mL round bottom flask and flushed with N₂ three times. Priorly degassed toluene (32 mL) was added *via* septum, followed by aq. 2M Na₂CO₃ (20 mL) and 3 drops of Aliquat 336. The reaction mixture was degassed for 1 h before it was heated to 120 °C for 3 days. The reaction was cooled to room temperature, precipitated in methanol (250 mL), stirred for 10 min and filtered through a Soxhlet thimble. The polymer was then extracted (Soxhlet) using methanol, acetone, hexane and chloroform in that order for ca. 2 h each (or until the extract was no longer coloured). The chloroform fraction was concentrated to ~20 mL before precipitation into methanol (250 mL). The suspension was stirred for 30 min and filtered to yield p(F8fBT) as a yellow solid (1.92 g, 96%).

¹H NMR (400 MHz, CDCl₃) δ 8.34 – 7.69 (m, 7H), 2.45 – 1.78 (m, 4H), 1.32 – 1.04 (m, 20H), 0.95 (s, 4H), 0.90 – 0.76 (m, 6H).

¹⁹F-NMR (377 MHz, CDCl₃) δ -114.56.

GPC (1,2,4-TCB): M_n: 45 kDa, M_w: 133 kDa, M_w/M_n (*D*): 2.99.

Synthesis of polymer IDTfBT (according to J. Ponder et al.)²



IDT(n-hexadecyl) (1.20 g, 1.03 mmol, 1.0 eq.), 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole (0.322 g, 1.03 mmol, 1.0 eq.), $Pd_2(dba)_3$ (10.7 mg, 0.01 mmol, 0.01 eq.), tris(o-methoxyphenyl)phosphine (14.5 mg, 0.04 mmol, 0.04 eq.), pivalic acid (105 mg, 1.03 mmol, 1.0 eq.), and cesium carbonate (1.00 g, 3.09 mmol, 3.0 eq.) were added to an oven-dried 20 mL microwave vial equipped with a stirrer bar, sealed with a rubber septum and purged with three times with N₂. Mesitylene (12 mL) was added via syringe and the resulting solution was degassed with N₂ for 30 min. The vial was placed in a preheated heating block at 110 °C and stirred overnight. After the highly viscous reaction mixture was filtered through a Soxhlet thimble and extracted using methanol, acetone, hexane, ethyl acetate and chloroform in that order for ca. 2 h each, or until the extract was no longer coloured. The chloroform fraction was concentrated to ~20 mL and the polymer precipitated into methanol (250 mL). After filtering and washing with acetone on the filter, followed by drying under vacuum, p(IDTfBT) was obtained as a blue solid (1.11 g, 82%).

¹H-NMR: (500 MHz, CDCl₃) δ 8.24 (s, 1H), 8.11 (s, 1H), 7.85 (s, 1H), 7.44 (d, 2H), 2.13 (s, 4H), 1.99 (s, 4H), 1.38 – 1.09 (br), 0.87 (t, 12H).

¹⁹F-NMR (471 MHz, CDCl₃) δ -108.34.

GPC (1,2,4-TCB): M_n: 16 kDa, M_w: 36 kDa, M_w/M_n (*D*): 2.26.

Synthesis of FO6-T (as recently published)³

4,7-Dibromo-5-fluoro-2,1,3-benzothiadiazole (0.276 g, 0.5 mmol,2,5-1.0 eq.), bis(trimethylstannyl)thiophene (0.204 g, 0.5 mmol, 1.0 eq.), Pd₂(dba)₃·CHCl₃ (10.4 mg, 0.01 mmol, 0.02 eq.) and P(o-tol)₃ (12.2 mg, 0.04 mmol, 0.08 eq.) were placed in an oven-dried 20 mL microwave vial, sealed with a septum and flushed with three times with N_2 . Dry chlorobenzene (CB) (10 mL) was degassed for approx. 30 min and added to the reaction vial via syringe. The reaction mixture was degassed for a further 20 min, and the vial was transferred to a microwave reactor and heated stepwise to 180 °C (120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, and 180 °C for 40 min). Afterwards, the blue viscous solution was precipitated into methanol (250 mL), followed by filtration to isolate the crude polymer. Purification was carried out via Soxhlet extraction using methanol, acetone, hexane, ethyl acetate and chloroform in that order for ca. 2 h each, or until the extract was no longer coloured. The chloroform fraction was concentrated to ~ 10 mL and precipitated in methanol (250 mL). The suspension was stirred for 20 min and FO6-T was isolated after filtration and drying under vacuum as a blue solid (0.234 g, 98%).

¹H NMR (500 MHz, CDCl₃) δ 8.97 – 7.64 (m, 1H), 4.65 – 3.52 (m, 1H), 2.57 – 0.15 (m, 8H).

¹⁹F NMR (471 MHz, CDCl₃) δ -117.76.

GPC (1,2,4-TCB): M_n: 24 kDa, M_w: 69 kDa, M_w/M_n (*Đ*): 2.85

Synthesis of 2S-F8BT



To a 5 mL microwave vial under nitrogen, F8fBT (10 mg, 0.018 mmol) and K_2CO_3 (210 mg, 1.44 mmol, 80 eq.) were added, sealed with a septum, and flushed three times with N₂. To the degassed mixture 2-butanethiol (0.04 mL, 0.36 mmol, 20 eq.), anhydrous chlorobenzene (1.5 mL) and DMAc (0.5 mL) were added and degassed for a further 10 minutes. The solution was heated to 120 °C in the microwave for 1.5 After cooling to room temperature, the mixture was precipitatedinto methanol and filtered into a Soxhlet thimble. The product was washed (Soxhlet) withmethanol, acetone and hexane (in that order) and finally extracted with chloroform. The solution then concentrated to a minimum amount and precipitated in methanol (100 mL). The product was filtered off and dried in vacuum and obtained as a yellow solid (10.4 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.98 (m, 5H), 7.64 – 7.62 (m, 2H), 3.29 (s, 1H), 2.12 (s, 2H), 1.73 – 1.63 (m, 4H), 1.32 – 1.25 (m, 2H), 1.22 – 1.16 (m, 22H), 1.01 – 0.92 (m, 6H), 0.81 (dt, *J* = 7.0, 3.4, 3.4 Hz, 6H).



General procedure of post-polymerisation modification for graft copolymer preparation¹

The respective polymer (1 eq., equivalence is based on the mass of the repeat unit), an excess of K_2CO_3 (20 eq.) and thiol terminated polystyrene (1.2 eq., equivalence based on mass of whole polymer) were added to an oven-dried microwave vial equipped with a stirrer bar. The vial was sealed and purged three times with N₂. CB (3 mL) and DMAc (1 mL) were added via syringe and the resulting solution was degassed with N₂ for 10 min. The resulting solution was heated to 120 °C in a heating block while stirring for 3 days. The resulting mixture was slowly dropped into methanol (100 mL) in order to precipitate the polymer. After filtration through a Soxhlet extraction thimble, the excess thiol was removed by washing with acetone for 24 h. The product was extracted with chloroform, the solution concentrated to a minimum amount and precipitate in methanol (100 mL). The product was filtered off and dried in vacuum.

PS-F8BT: F8fBT (20.0 mg, 0.037 mmol), PS-SH (222 mg, 0.044), K₂CO₃ (409 mg, 2.96 mmol); Yielded yellow polymer (101 mg, 49%).

¹H NMR (400 MHz, CDCl₃) δ 7.22 – 6.86 (m), 6.74 – 6.21 (m), 2.00 – 1.64 (m), 1.51 – 1.19 (m), 1.22 – 1.01 (m), 0.92 – 0.66 (m).

GPC (1,2,4-TCB): M_n: 98 kDa, M_w: 222 kDa, M_w/M_n (*D*): 2.26

PS-IDTBT: IDTfBT (30.0 mg, 0.023 mmol), PS-SH (137 mg, 0.027 mmol), K₂CO₃ (63 mg, 0.456 mmol); Yielded blue polymer (49 mg, 34%).

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 6.81 (m), 6.77 – 5.98 (m), 1.85 (m), 1.46 – 1.32 (m), 1.32 – 1.00 (m), 1.00 – 0.64 (m).

GPC (1,2,4-TCB): Mn: 34.4 kDa, Mw: 51 kDa, Mw/Mn (D): 1.48

PS-FO6-T: FO6-T (15.0 mg, 0.032 mmol), PS-SH (190 mg, 0.038 mmol), K₂CO₃ (87 mg, 0.632 mmol); Yielded purple polymer (154.4 mg, 88%).

¹H NMR (400 MHz, CDCl₃) δ 7.20 – 6.81 (m, 1H), 6.81 – 6.15 (m), 2.04 – 1.69 (m, 1.69 – 0.94 (m). GPC (1,2,4-TCB): M_n: 46 kDa, M_w: 73 kDa, M_w/M_n (*D*): 1.59

General procedure for the nanoparticle fabrication

Solutions (0.1 mg/mL) of the respective PS-substituted polymers in THF were prepared. 1 mL of each solution was filtered through a 0.2 μ m syringe filter (PTFE membrane) and injected into water (9 mL) while sonicating, and the suspension was sonicated for a further 3 min. N₂ was bubbled through the resulting suspension while heated to 60 °C for 1 h to remove the THF.

3. GPC Characterisation



Figure S.1: Normalised GPC traces of parent polymers in 1,2,4-TCB.

The molecular weights of the graft copolymers were analysed using GPC in 1,2,4-TCB (Figure S.2). While **PS-IDTBT** exhibited a monomodal peak, both **PS-F8BT** and **PS-F06-T** exhibited multimodal traces with a common peak at ~16 min (Figure S.2a), although the peak was significantly more intense in the latter case. It was hypothesised that the major impurity in these polymers was unreacted PS-SH, which was incompletely removed by washing due to the large physical excess. This was strongly supported by GPC data of the PS-SH starting material which showed a peak at an identical retention time (Figure S.2b). The excess PS-SH (and is oxidised dimer PS-SS-PS) could be removed from **PS-F06-T** by preparative GPC, as demonstrated by a major reduction in the PS-SH peak in the analytical GPC data after purification (Figure S.3).



Figure S.2: Normalised GPC traces of the graft copolymers in 1,2,4-TCB.



Figure S.3: Normalised GPC traces in 1,2,4-TCB of **PS-FO6-T** before and after purification by preparative GPC.

4. NMR Spectra





Figure S.4: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of F8fBT recorded in CDCl₃ at room temperature.





Figure S.5: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of **IDTfBT** recorded in CDCl₃ at 55 °C.





Figure S.6: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of FO6-T recorded in CDCl₃ at 55 °C.





Figure S.7: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of **2S-F8BT** recorded in CDCl₃ at room temperature.





Figure S.8: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of **PS-F8BT** recorded in $CDCl_3$ at room temperature.





Figure S.9: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of **PS-IDTBT** recorded in $CDCl_3$ at room temperature.





Figure S.10: ¹H NMR (top) and ¹⁹F NMR (bottom) spectra of **PS-FO6-T** recorded in $CDCl_3$ at room temperature.



Figure S.11: DOSY NMR spectra of **PS-F8BT** (left) and PS:F8fBT blend (right).



Figure S.12: DOSY NMR spectra of **PS-IDTBT** (left) and PS:**IDTfBT** blend (right).



Figure S.13: DOSY NMR spectra of PS-FO6-T (left) and PS:FO6-T blend (right).

5. Contact angle measurements

Polymer	Water mean (°)	Ethylene glycol mean (°)	Benzylic alcohol mean (°)
F8fBT	96.95	76.25	27.38
PS-F8BT	95.59	72.81	40.94
IDTfBT	102.64	79.75	49.9
PS-IDTBT	99.92	76.07	37.44
FO6T	106.59	86.02	44.93
PS-FO6T	94.22	75.39	31.81

Table S.1: Contact angle measurements

6. Thermal Characterisation



Figure S.14: TGA traces of a) graft copolymers and b) parent polymers.



Figure S.15: DSC traces of the parent polymers.



Figure S.16: DSC traces (a, c, e), and derived heat flow (b, d, f) for **PS-F8BT**, **PS-IDTBT**, and **PS-F06-T**, respectively.

7. Nanoparticle Characterisation



Figure S.17: DLS characterisation of NPs aged over different time periods: a) **PS-F8BT** NPs were analysed over a 14 day interval, b) **PS-IDTBT** NPs after 1 day and 10 days, c) **PS-FO6-T** after 1 day and 10 days, d) parent polymers after 10 days.

8. Optical Characterisation







Figure S.19: CIE plots of PS-IDTBT



Figure S.20: CIE plots of PS-FO6-T



Figure S.21: Photos of respective graft copolymer NP suspensions under white light and under UV light (wavelength stated in brackets).

9. References

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