Electronic Supplementary Information (ESI)

Thermally triggered optical tuning of π-conjugated graft copolymers based on reversible Diels-Alder reaction

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Content

Materials and Instrumentation

Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), copper(I) iodide, copper(I) bromide, iodine, potassium iodate, methyl methacrylate (MMA), furfuryl methacrylate (FMA), 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA), 2,2-azobis(4-methoxy-2,4-dimethylvaleronite) and methyl α-bromoisobutyrate (MB*i*B) were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, TCI, VWR and Wako Pure Chemical Industries, Ltd. and were used without further purifications. Dry methanol, trimethylamine, tetrahydrofuran, toluene and *N*-*N*-dimethylformamide were purchased from Sigma-Aldrich. NMR spectra were recorded on a 300 MHz NMR spectrometer (Fourier 300) at 298 K and in deuterated solvents. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the deuterated solvent. Diffusion-ordered NMR spectroscopy (DOSY) was carried out on a Bruker 400 MHz Avance I NMR system equipped with a BBO z-gradient probehead. 2D spectra were recorded using a pulse programm (Bruker: "ledbpgp2s") with bipolar gradient pulses and 2 spoil gradients Experimental parameter were optimized once using a 1D version of the aforementioned pulse sequence and then kept constant for all experiments: 8 number of scans, recycle delay of 2 sec, acquisition time of 1.4 sec, diffusion time (d20) of 50 msec, a gradient pulse length (p30) of 3 msec and a linear gradient amplitude ramp ranging from 5% to 95% (with respect to the maximum strength of 53.5 G/cm) with 64 increments. Sample temperature was set to 25°C. Standard DOSY processing algorithms provides by TopSpin were utilized to obtain the final DOSY spectra and to extract the diffusion coefficients. Elemental analyses were performed on a λ EuroVector EuroEA3000 elemental analyzer. The reaction progress was monitored by thin layer chromatography (TLC) using precoated aluminum sheets (silica gel 60 F254, Merck). Column chromatography was performed on silicagel 60 (pore size 60 Å, 70-230 mesh, 63-200 μm). ESI-TOF MS measurements were performed using micrOTOF (Bruker Daltonics) mass spectrometer, which was equipped with a syringe pump for sample injection and a standard electrospray ion source. The mass spectrometer was operating in the positive ion mode and the data were processed with micrOTOF control Version 3.0 and Data Analysis Version 4.0 SP2. CH_2Cl_2, acetonitrile and chloroform were used as solvents and the concentrations ranged from 1 to 10 μg/mL. The instrument was calibrated by a tunemix solution (m/z 50 to 3,000) from Agilent. Preparative size exclusion chromatography was performed using Bio Beads® (S-X1, chloroform). SEC measurements of the copolymers were performed using a Shimadzu SCL-10A VP, DGU-14A as degasser, LC-10AD VP as the pump, a CTO-10A VP oven with 40 °C oven temperature, a

SPD-10MA VP UV-detector, a RID-10A RI-detector, a Phenomenex Phenogel guard/10^5 Å/10^3 Å column, a flow rate of 1 mL/min, DMAc + 0.08% NH_4PF_6 as the eluent and a polystyrene calibration. Vapor pressure osmometry measurements were carried out in toluene using a Knauer apparatus and benzile as standard calibration.

UV-Vis absorption spectra were recorded on Varian Cary 5000 UV/Vis spectrometer in 1 cm quartz cuvettes using a cuvette filled with chloroform as a reference. Steady-state emission spectra were recorded on a Jasco FP-6500 Spectrofluorometer. The absorbance of the samples was set below 0.05 and quantum yields Φ were calculated using quinine sulfate in a 0.1 M H_2SO_4 solution as a reference ($\Phi_R = 0.53$[1]) according to[2]

$$\Phi = \Phi_R \cdot \frac{I}{I_R} \cdot \frac{OD_R}{OD} \cdot \frac{n^2}{n_R^2}$$

with the integrated intensity I, the optical density at the excitation wavelength OD and the refractive index n. The subscript R refers to quinine sulfate. All fluorescence spectra were corrected for the solvent background and for the spectral sensitivity of the set-up relying on the data supplied by the manufacturer. Emission spectra are reported as photons per wavelength interval. From the steady-state absorption and emission spectra, the Förster radius R_0 in Å was calculated according to

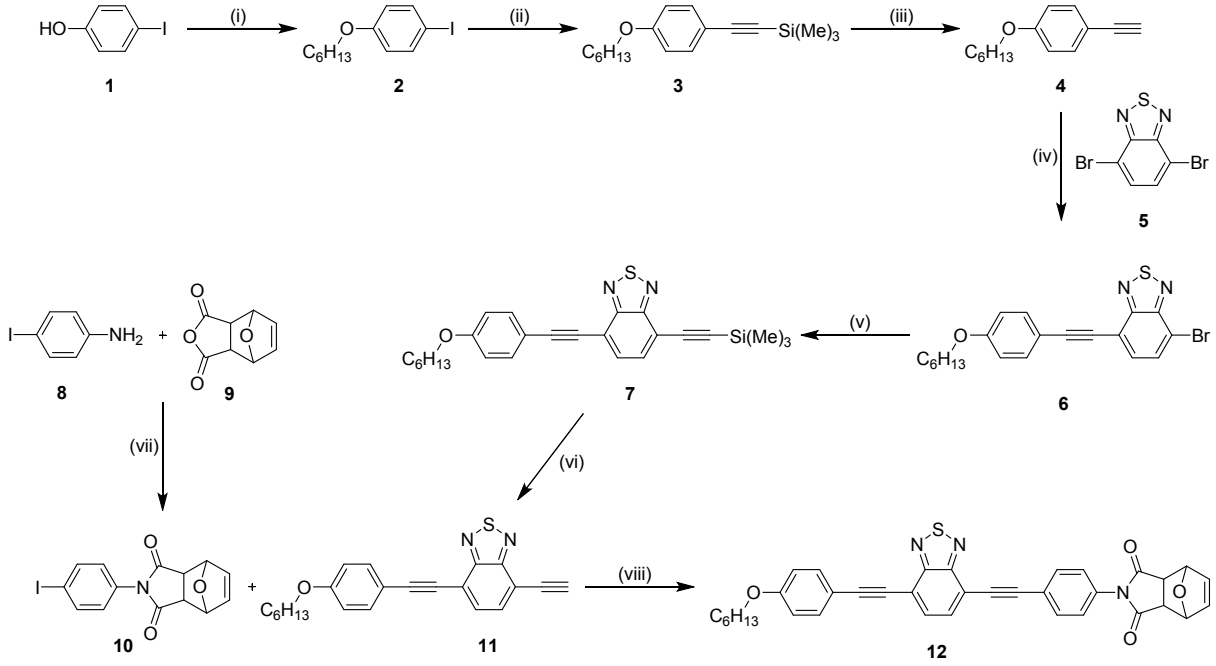
$$R_0 = 0.211\left(\frac{\kappa^2 \Phi_D}{n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda\right)^{\frac{1}{6}}$$

where Φ_D is the quantum yield of the donor in the absence of acceptor, n is the refractive index of the medium, $F_D(\lambda)$ is the corrected fluorescence intensity of the donor the total intensity normalized to unity, $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ, and κ^2 is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor, which is assumed to be equal to 2/3 (dynamic random averaging of the donor and acceptor).[2]

Spectrally resolved emission decay curves were determined employing a Hamamatsu HPDTA streak camera. Samples were excited by pulses centered at 380 nm created by frequency-doubling the output of a Ti:sapphire laser (Tsunami, Newport Spectra-Physics GmbH). The repetition rate of the fundamental is reduced to 400 kHz by a pulse selector (model 3980, Newport Spectra-Physics GmbH). Emission was collected for solutions from a 1 cm cuvette in a 90° angle and spectrally dispersed on the detector using a CHROMEX spectrograph. Measurements were performed with a polarizer set to magic angle, *i.e.* set to 54.7° with respect to the excitation polarization, in the detection path. Analysis of the time-resolved emission data and FRET analysis was performed using DecayFit software.[3]

Synthesis of monomers and oligomers

1-(Hexyloxy)-4-iodobenzene (**2**), ((4-(hexyloxy)phenyl)ethynyl)trimethylsilane (**3**), 1-ethynyl-4-(hexyloxy)benzene (**4**), 4,7-dibromobenzo[c][1,2,5]thiadiazole (**5**), 4-bromo-7-((4-(hexyloxy)phenyl)ethynyl)benzo[c][1,2,5]thiadiazole (**6**), 4-((4-(hexyloxy)phenyl)-ethynyl)-7-((trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole (**7**), 4-ethynyl-7-((4-(hexyl-oxy)phenyl)ethynyl)benzo[c][1,2,5]thiadiazole (**11**), 1,4-bis(hexyloxy)benzene (**13**), ((4-bromo-2,5-bis(hexyloxy)phenyl)ethynyl)trimethylsilane (**16**), ((2,5-bis(hexyloxy)-4-((4-(hexyloxy)phenyl)ethynyl)phenyl)ethynyl)trimethylsilane (**17**), 1-ethynyl-2,5-bis(hexyloxy)-4-((4-(hexyloxy)phenyl)ethynyl)benzene (**18**), were synthesized according to literature.[4]



Supplementary Scheme 1. Schematic representation of conjugated acceptor oligomer synthesis by multiple sequential Sonogashira cross-coupling reaction. Reagents and conditions: (i) Hexyl bromide/K_2CO_3/acetonitrile/80 °C; (ii) TMSA/$Pd(PPh_3)_4$/CuI/Et_3N/tetrahydrofuran(THF)/40 °C; (iii) K_2CO_3/THF/methanol(MeOH)/25 °C; (iv) $Pd(PPh_3)_4$/CuI/Et_3N/THF/25 °C; (v) TMSA/$Pd(PPh_3)_4$/CuI/Et_3N/THF/50 °C; (vi) K_2CO_3/THF/MeOH/25 °C; (vii) Et_3N/MeOH/67 °C; (viii) $Pd(PPh_3)_4$/CuI/Et_3N/THF/25 °C.

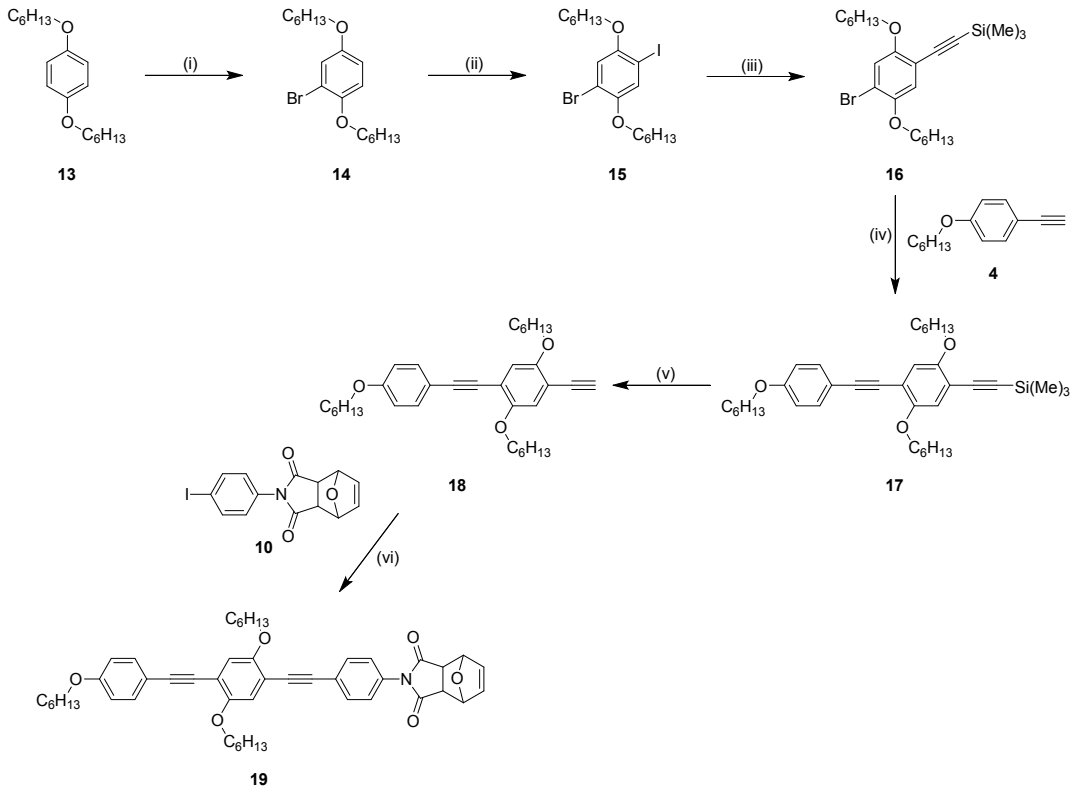
2-(4-Iodophenyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (10)

Compound **8** (2.98 g, 13.62 mmol) and **9** (4.52 g, 27.24 mmol) were dissolved in 30 mL dry methanol. Subsequently, dry triethylamine (3.78 mL, 27.24 mmol) was added and the reaction mixture was stirred overnight at 67 °C under nitrogen atmosphere. The resulting precipitate was filtered and washed three times with 10 mL methanol and dried under vacuum. Compound **10** was obtained as a white solid with a yield of 2.40 g (48%). **^{1}H NMR** ($CDCl_3$, δ): 3.01 (m, 2H, O=C-CH), 5.39 (m, 2H, O-CH), 6.57 (m, 2H, CH=CH), 7.06 (d, J = 8.6 Hz,

2H, phenyl), 7.80 (d, 2H, *J* = 8.6 Hz, phenyl) ppm; **^{13}C NMR** ($CDCl_3$, *δ*): 47.6, 81.4, 94.2, 128.2, 131.4, 136.7, 138.3, 174.9 ppm; **ESI-TOF MS**: M = 366.97 g/mol; m/z = 389.97 ($[M + Na]^+$); **HR-ESI-TOF MS**: $[C_{14}H_{10}INO_3]^{Na+}$ calcd.: m/z = 389.9598; found: m/z = 389.9587; error: 2.7 ppm.

2-(4-((7-((4-(Hexyloxy)phenyl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)ethynyl)phenyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (12)

Compound **10** (0.51 g, 1.39 mmol), compound **11** (0.50 g, 1.39 mmol), 3 mol% $Pd(PPh_3)_4$ and 3 mol% CuI were dissolved in 16 mL of a dry mixture of tetrahydrofuran/triethylamine (7/3) and stirred overnight at 40 °C under nitrogen atmosphere. After 50 mL $CHCl_3$ was added, the aqueous phase was extracted two times with 20 mL $CHCl_3$. The combined organic phase were washed two times with 50 mL distilled water and brine. Subsequently, the organic phase was dried over Na_2SO_4 and the crude product was purified by column chromatography (eluent: EtOAc/$CHCl_3$, 1/7). Compound **12** was obtained as a yellow solid with a yield of 0.71 g (85%). **^{1}H NMR** ($CDCl_3$, *δ*): 0.92 (m, 3H, CH_3), 1.30−1.55 (m, 6H, CH_2), 1.80 (m, 2H, CH_2), 3.03 (m, 2H, O=C-CH), 4.00 (m, 2H, O-CH_2), 5.37 (m, 2H, O-CH), 6.58 (m, 2H, C=CH), 6.93 (d, *J* = 8.8 Hz, 2H, phenyl), 7.36 (d, *J* = 8.6 Hz, 2H, phenyl), 7.58 (d, *J* = 8.8 Hz, 2H, phenyl), 7.70−7.85 (m, 4H, phenyl) ppm; **^{13}C NMR** ($CDCl_3$, *δ*): 14.0, 22.6, 25.7, 29.1, 31.5, 47.6, 68.1, 81.5, 84.2, 86.4, 96.1, 98.3, 114.2, 114.6, 116.2, 118.0, 123.0, 126.4, 128.2, 131.9, 132.6, 133.6, 136.7, 138.3, 154.4, 159.9, 175.0 ppm; **ESI-TOF MS**: M = 599.19 g/mol; m/z = 622.17 ($[M + Na]^+$); **HR-ESI-TOF MS**: $[C_{36}H_{29}N_3O_4S]^{Na+}$ calcd.: m/z = 622.1771; found: m/z = 622.1748; error: 3.7 ppm.



Supplementary Scheme 2. Schematic representation of conjugated donor oligomer synthesis by multiple sequential Sonogashira cross-coupling reaction. Reagents and conditions: (i) $Br_2/CHCl_3$/25 °C; (ii) $I_2/KIO_3/CHCl_3/CH_3COOH/H_2SO_4/H_2O$/80 °C; (iii) TMSA/$Pd(PPh_3)_4$/CuI/$Et_3N$/THF/40 °C; (iv) $Pd(PPh_3)_4$/CuI/Et_3N/THF/70 °C; (v) K_2CO_3/THF/methanol(MeOH)/25 °C; (vi) $Pd(PPh_3)_4$/CuI/Et_3N/THF/40 °C.

2-Bromo-1,4-bis(hexyloxy)benzene (14)

Compound **13** (8.00 g, 28.73 mmol) was dissolved in 50 mL $CHCl_3$. Subsequently, bromine (1.47 mL, 28.73 mmol) dissolved in 2 mL $CHCl_3$ was added dropwise at 0 °C. After the reaction mixture was stirred overnight at room temperature, 50 mL of a saturated solution of Na_2SO_3 was added. The resulting aqueous phase was extracted two times with 20 mL $CHCl_3$ and the combined organic phases were washed two times with 50 mL distilled water and brine. Subsequently, the organic phase was dried over Na_2SO_4 and the crude product was purified by column chromatography (eluent: dichloromethane/hexane, 1/7). Compound **14** was obtained as a colorless liquid with a yield of 5.91 g (58%). **^{1}H NMR** ($CDCl_3$, δ): 0.92 (m, 6H, CH_3), 1.30−1.55 (m, 12H, CH_2), 1.78 (m, 4H, CH_2), 3.89 (t, J = 6.5 Hz, 2H, O-CH_2), 3.96 (t, J = 6.5 Hz, 2H, O-CH_2), 6.75−6.86 (m, 2H, phenyl), 7.11 (m, 1H, phenyl) ppm; **^{13}C NMR** ($CDCl_3$, δ): 14.0, 22.6, 25.7, 29.2, 31.6, 68.8, 70.2, 112.8, 114.4, 114.7, 119.5, 149.8, 153.6 ppm.

1-Bromo-2,5-bis(hexyloxy)-4-iodobenzene (15)

Compound **14** (5.00 g, 13.99 mmol), iodine (3.34 g, 13.15 mmol), potassium iodate (1.23 g, 5.74 mmol) were stirred overnight in a mixture of 20 mL acetic acid, 1.2 mL sulfuric acid, 0.7 mL distilled water and 6 mL $CHCl_3$ at 80 °C. The resulting reaction mixture was poured on 50 mL saturated Na_2SO_3 solution and ice. After stirring for 30 min, 100 mL dichloromethane was added. The aqueous phase was extracted two times with 20 mL dichloromethane and subsequently, the combined organic phases were washed two times with 30 mL 1 M $NaHCO_3$ solution and brine. The organic phase was dried over Na_2SO_4 and the crude product was purified by column chromatography (eluent: dichloromethane/hexane, 1/9). Compound **15** was obtained as a white solid with a yield of 4.51 g (67%). **^{1}H NMR** ($CDCl_3$, δ): 0.92 (m, 6H, CH_3), 1.30-1.55 (m, 12H, CH_2), 1.81 (m, 4H, CH_2), 3.94 (m, 4H, O-CH_2), 6.99 (s, 1H, phenyl), 7.29 (s, 1H, phenyl) ppm; **^{13}C NMR** ($CDCl_3$, δ): 14.0, 22.6, 25.6, 25.7, 29.1, 70.4, 84.8, 112.5, 117.1, 124.2, 150.4, 152.5 ppm.

2-(4-((2,5-Bis(hexyloxy)-4-((4-(hexyloxy)phenyl)ethynyl)phenyl)ethynyl)phenyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (19)

Compound **18** (0.53 g, 1.05 mmol), compound **10** (0.39 g, 1.05 mmol), 3 mol% $Pd(PPh_3)_4$ and 3 mol% CuI were dissolved in 12 mL of a mixture of dry tetrahydrofuran/triethylamine (7/3) and stirred overnight at 40 °C under nitrogen atmosphere. After 50 mL $CHCl_3$ was added, the aqueous phase was extracted two times with 20 mL $CHCl_3$. The combined organic phases were washed two times with 50 mL distilled water and brine. Subsequently, the organic phase was dried over Na_2SO_4 and the crude product was purified by column chromatography (eluent: EtOAc/$CHCl_3$, 3/2). Compound **19** was obtained as a light yellow solid with a yield of 0.61 g (77%). **^{1}H NMR** (CD_2Cl_2, δ): 0.91 (m, 9H, CH_3), 1.30−1.55 (m, 18H, CH_2), 1.82 (m, 6H, CH_2), 3.03 (m, 2H, O=C-CH), 4.00 (m, 6H, O-CH_2), 5.41 (m, 2H, O-CH), 6.58 (m, 2H, CH=CH), 6.87 (d, J = 8.8 Hz, 2H, phenyl), 7.01 (s, 2H, phenyl), 7.31 (d, J = 8.6 Hz, 2H, phenyl), 7.47 (d, J = 8.8 Hz, 2H, phenyl), 7.61 (d, J = 8.6 Hz, 2H, phenyl) ppm; **^{13}C NMR** ($CDCl_3$, δ): 14.0, 22.6, 25.7, 29.1, 29.3, 47.5, 68.1, 69.6, 69.7, 81.4, 84.5, 87.2, 93.7, 95.3, 113.0, 114.5, 115.3, 116.7, 117.0, 124.1, 126.3, 131.2, 132.1, 133.0, 136.6, 153.4, 153.8, 159.3, 175.1 ppm; **ESI-TOF MS**: M = 741.40 g/mol; m/z = 764.39 ($[M + Na]^+$); **Elemental analysis**: calcd. for $C_{48}H_{55}NO_6$: C 77.70, H 7.47, N 1.89; found: C 77.74, H 7.42, N 1.89.

(2-(4-((7-((4-(Hexyloxy)phenyl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)ethynyl)phenyl)-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methyl methacrylate (20)

Compound **12** (0.30 g, 0.50 mmol) was dissolved in 2 mL chlorobenzene and stirred at 120 °C for four hours. Subsequently, the solvent was removed by vacuum. Furan-2-ylmethyl methacrylate (0.17 g, 1.00 mmol) and 1 mL $CHCl_3$ were added. The reaction mixture was stirred at 55 °C overnight. The resulting crude product was purified by column chromatography (eluent: EtOAc/$CHCl_3$, 1/9). Compound **20** was obtained as a yellow solid with a yield of 0.29 g (82%). **^{1}H NMR** ($CDCl_3$, δ): 0.92 (t, J = 6.9 Hz, 3H, CH_3), 1.23−1.55 (m, 6H, CH_2), 1.81 (m, 2H, CH_2), 1.96 (s, 3H, CH_2=C-CH_3), 3.10 (d, J = 6.5 Hz, 1H, O=C-CH), 3.18 (d, J = 6.5 Hz, 1H, O=C-CH), 4.00 (m, 2H, O-CH_2), 4.65 (d, J = 12.9 Hz, 1H, O=C-O-CH_2), 5.07 (d, J = 13.0 Hz, 1H, O=C-O-CH_2), 5.43 (m, 1H, CH=CH-C*H*), 5.60 (m, 1H, C*H*=CH-CH), 6.14 (m, 1H, CH=C*H*-CH), 6.52 (d, J = 5.6 Hz, 1H, C=CH), 6.63 (d, J = 5.8 Hz, 1H, C=CH), 6.92 (d, J = 8.6 Hz, 2H, phenyl), 7.36 (d, J = 8.6 Hz, 2H, phenyl), 7.60 (d, J = 8.8 Hz, 2H, phenyl), 7.71 (m, 4H, phenyl + thiadiazol) ppm; **^{13}C NMR** ($CDCl_3$, δ): 14.0, 18.3, 22.6, 25.7, 29.1, 31.5, 48.5, 50.0, 61.5, 68.1, 81.6, 84.2, 86.5, 90.1, 96.1, 98.3, 114.2, 114.6, 116.2, 118.0, 123.1, 126.4, 131.8, 131.9, 132.5, 132.8, 133.6, 135.7, 137.3, 137.6, 154.3, 154.4, 159.9, 172.9, 174.4 ppm; **ESI-TOF MS**: M = 697.22 g/mol; m/z = 720.22 ([M + Na]$^+$); **HR-ESI-TOF MS**: $[C_{41}H_{35}N_3O_6S]^{Na+}$ calcd.: m/z = 720.2139; found: m/z = 720.2120; error: 2.6 ppm.

(2-(4-((2,5-Bis(hexyloxy)-4-((4-(hexyloxy)phenyl)ethynyl)phenyl)ethynyl)phenyl)-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methyl methacrylate (21)

Compound 19 (0.30 g, 0.40 mmol) was dissolved in 2 mL chlorobenzene and stirred at 120 °C for four hours. Subsequently, the solvent was removed by vacuum. Furan-2-ylmethyl methacrylate (0.13 g, 0.80 mmol) and 1 mL $CHCl_3$ were added. The reaction mixture was stirred at 55 °C overnight. The resulting crude product was purified by column chromatography (eluent: EtOAc/$CHCl_3$, 2/3). Compound **21** was obtained as a light yellow solid with a yield of 0.24 g (69%). **^{1}H NMR** ($CDCl_3$, δ): 0.91 (m, 9H, CH_3), 1.23−1.55 (m, 18H, CH_2), 1.82 (m, 6H, CH_2), 1.96 (s, 3H, CH_2=C-CH_3), 3.09 (d, J = 6.5 Hz, 1H, O=C-CH), 3.17 (d, J = 6.5 Hz, 1H, O=C-CH), 4.00 (m, 6H, O-CH_2), 4.63 (d, J = 12.9 Hz, 1H, O=C-O-CH_2), 5.07 (d, J = 13.0 Hz, 1H, O=C-O-CH_2), 5.42 (m, 1H, CH=CH-C*H*), 5.60 (m, 1H, C*H*=CH-CH), 6.14 (m, 1H, CH=C*H*-CH), 6.52 (d, J = 5.6 Hz, 1H, C=CH), 6.63 (d, J = 5.8 Hz, 1H, C=CH), 6.87 (d, J = 8.8 Hz, 2H, phenyl), 7.01 (s, 2H, phenyl), 7.30 (d, J = 8.6 Hz, 2H, phenyl), 7.46 (d, J = 8.8 Hz, 2H, phenyl), 7.61 (m, J = 8.6 Hz, 2H, phenyl)

ppm; **^{13}C NMR** ($CDCl_3$, δ): 14.0, 18.3, 22.6, 25.7, 29.1, 29.3, 31.6, 48.5, 50.0, 61.5, 68.1, 69.6, 69.7, 81.6, 84.5, 87.3, 93.6, 95.3, 113.0, 114.5, 114.9, 115.3, 116.1, 116.8, 117.0, 124.2, 126.3, 126.4, 131.1, 132.1, 133.0, 135.7, 137.4, 137.6, 153.4, 153.8, 159.3, 166.8, 173.0, 174.6 ppm; **ESI-TOF MS**: M = 839.44 g/mol; m/z = 862.42 ($[M + Na]^+$); **Elemental analysis**: calcd. for $C_{53}H_{61}NO_8$: C 75.78, H 7.32, N 1.67; found: C 75.72, H 7.48, N 1.58.

Synthesis of copolymers

Synthesis of copolymer P(MMA-*co*-FMA) (P1)

HMTETA (44 mg; 2 eq.), MMA (253 mg; 25 eq.) and FMA (415 mg; 25 eq.) were dissolved in 2 mL of dry toluene under nitrogen atmosphere. The resulting reaction mixture was purged with nitrogen for additional 15 min. Subsequently, CuBr (29 mg; 2 eq.) was added and the mixture was stirred for 10 min at room temperature. The polymerization was started by adding MB*i*B (13 µL; 1 eq.) and was carried out at 70 °C under a nitrogen atmosphere. The reaction was stopped after four hours. The polymer was purified by passing the solution through an alumina column to remove the catalyst, precipitation in ice-cold methanol and further drying under reduced pressure. Furthermore, purification by preparative size exclusion chromatography using a Biobeads® S-X1 column ($CHCl_3$) was performed. The combined polymer samples were analyzed by size exclusion chromatography (**SEC**: DMAc + 0.08% NH_4PF_6 as solvent, PS as calibration standard) to determine the molar mass M_n of 10,000 g/mol and molar mass distribution (Đ) of 1.3. **^{1}H NMR** ($CDCl_3$, δ): 0.5−2.3 (m, backbone), 3.57 (s, MMA), 4.93 (s, FMA), 6.37 (d, FMA), 7.43 (s, FMA) ppm; **Elemental analysis**: anal. calcd. for repeating units and monomer ratio based on NMR and SEC: C: 62.40, H: 6.78, Br: 1.17, found: C: 63.24, H: 6.86, Br: 0.80.

Synthesis of copolymer P(MMA-*co*-FMA-*co*-20) (P2)

Compound **12** (90 mg, 2 eq.) was dissolved in 2 mL chlorobenzene and stirred at 120 °C for four hours. Subsequently, the solvent was removed by vacuum. Copolymer **P1** (20 mg, 1 eq. calcd. for 1 repeating unit) and 0.4 mL chlorobenzene were added. The reaction mixture was drop casted and the resulting polymer film was heated up to 55 °C for about four days. Furthermore, purification by preparative size exclusion chromatography using a Biobeads® S-X1 column ($CHCl_3$) was performed to separate the non-converted monomers. The combined polymer samples were analyzed by size exclusion chromatography (**SEC**: DMAc + 0.08% NH_4PF_6 as solvent, PS as calibration) to determine the molar mass M_n of 23,100 g/mol

and molar mass distribution (Đ) of 1.8. **^{1}H NMR** ($CDCl_3$, δ): 0.5−2.3 (m, backbone, alkyl chains), 3.08 (m, O=C-CH), 3.58 (s, MMA), 3.97 (m, O-CH_2), 4.20-4.90 (m, O-CH_2-21), 4.97 (m, O-CH_2-furan), 5.39 (m, O-CH), 6.20−6.70 (m, CH=CH + furan), 6.88 (m, phenyl), 7.34 (m, phenyl), 7.42 (m, furan), 7.57 (m, phenyl), 7.71 (m, phenyl + thiadiazol) ppm; **Elemental analysis**: anal. calcd. for repeating units and monomer ratio based on NMR and SEC: C: 68.63, H: 5.57, N: 4.74, S: 3.62, found: C: 64.84, H: 5.49, N: 4.27, S: 2.98.

Synthesis of copolymer P(MMA-*co*-FMA-*co*-21) (P3)

Compound **19** (111 mg, 2 eq.) was dissolved in 2 mL chlorobenzene and stirred at 120 °C for four hours. Subsequently, the solvent was removed by vacuum. Copolymer **P1** (20 mg, 1 eq. calcd. for 1 repeating unit) and 0.4 mL chlorobenzene were added. The reaction mixture was drop casted and the resulting polymer film was heated up to 55 °C for about four days. Furthermore, purification by preparative size exclusion chromatography using a Biobeads® S-X1 column ($CHCl_3$) was performed to separate the non-converted monomers. The combined polymer samples were analyzed by size exclusion chromatography (**SEC**: DMAc + 0.08% NH_4PF_6 as solvent, PS as calibration) to determine the molar mass M_n of 17,100 g/mol and molar mass distribution (Đ) of 1.5. **^{1}H NMR** ($CDCl_3$, δ): 0.5−2.3 (m, backbone, alkyl chains), 3.10 (m, O=C-CH), 3.59 (s, MMA), 4.00 (m, O-CH_2), 4.20−4.90 (m, O-CH_2-C), 4.97 (m, O-CH_2-furan), 5.39 (m, O-CH), 6.20−6.70 (m, CH=CH + furan), 6.86 (m, phenyl), 7.00 (s, phenyl), 7.30 (m, 2H, phenyl), 7.42 (m, furan), 7.46 (m, phenyl), 7.59 (m, phenyl) ppm; **Elemental analysis**: anal. calcd. for repeating units and monomer ratio based on NMR and SEC: C: 72.65, H: 7.28, N: 1.31, found: C: 72.43, H: 7.29, N: 1.35.

Synthesis of copolymer P(MMA-*co*-20) (P4)

The initiator 2,2-azobis(4-methoxy-2,4-dimethylvaleronite) (7 mg; 3 eq.) was added to a vial containing a stirring bar *via* continuous cooling. A solution of compound **20** (80 mg; 15 eq.) and MMA (65 mg; 85 eq.) in dry DMF (1 mL) was added to the vial at 0 °C. The polymerization was carried out at 40 °C under a nitrogen atmosphere overnight. The polymer was purified by preparative size exclusion chromatography using a Biobeads® S-X1 column ($CHCl_3$). The combined polymer samples were analyzed by size exclusion chromatography (**SEC**: DMAc + 0.08% NH_4PF_6 as solvent, PS as calibration) to determine the molar mass M_n of 8,100 g/mol and molar mass distribution (Đ) of 1.5. **^{1}H NMR** ($CDCl_3$, δ): 0.5−2.3 (m, backbone, alkyl chains), 3.13 (m, 2H, O=C-CH), 3.59 (s, 13H, MMA), 3.99 (m, 2H, O-CH_2), 4.20−4.90 (m, 2H, O-CH_2-C), 5.42 (m, 1H, O-CH), 6.62 (m, 2H, CH=CH), 6.90 (m, 2H,

phenyl), 7.36 (m, 2H, phenyl), 7.60 (m, 2H, phenyl), 7.75 (m, 4H, phenyl + thiadiazole) ppm; **Elemental analysis**: anal. calcd. for repeating units and monomer ratio based on NMR and SEC: C: 68.07, H: 5.66, N: 4.72, S: 3.60, found: C: 63.32, H: 6.12, N: 3.52, S: 2.24.

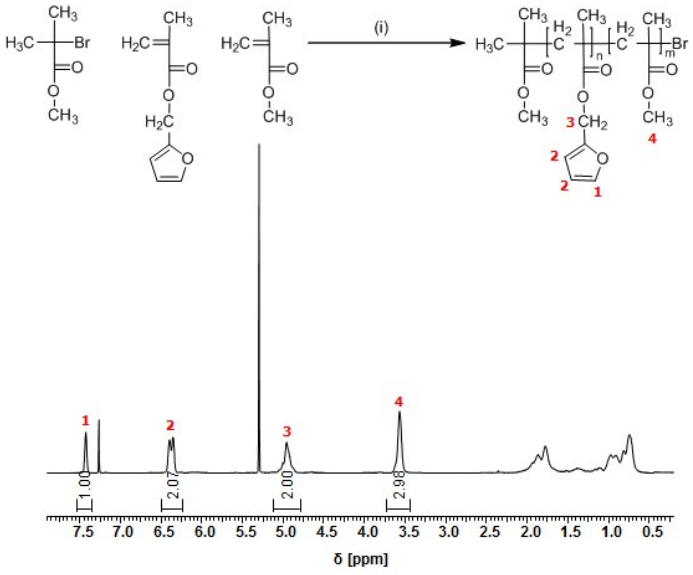
Synthesis of copolymer P(MMA-*co*-21) (P5)

The initiator 2,2-azobis(4-methoxy-2,4-dimethylvaleronite) (6 mg; 3 eq.) was added to a vial containing a stirring bar *via* continuous cooling. A solution of 21 (80 mg; 15 eq.) and MMA (56 mg; 85 eq.) in dry DMF (1 mL) was added to the vial at 0 °C. The polymerization was carried out at 40 °C under a nitrogen atmosphere overnight. The resulting polymer was purified by preparative size exclusion chromatography using a Biobeads® S-X1 column ($CHCl_3$). The combined polymer samples were analyzed by size exclusion chromatography (**SEC**: DMAc + 0.08% NH_4PF_6 as solvent, PS as calibration) to determine the molar mass M_n of 9,800 g/mol and molar mass distribution (Đ) of 1.6. **^{1}H NMR** ($CDCl_3$, δ): 0.5−2.3 (m, backbone, alkyl chains), 3.03 (m, 2H, O=C-CH), 3.60 (s, 13H, MMA), 4.00 (m, 6H, O-CH_2), 4.20−4.90 (m, 2H, O-CH_2-C), 5.41 (m, 1H, O-CH), 6.62 (m, 2H, CH=CH), 6.87 (m, 2H, phenyl), 7.00 (s, 2H, phenyl), 7.31 (m, 2H, phenyl), 7.45 (m, 2H, phenyl), 7.60 (m, 2H, phenyl) ppm; **Elemental analysis**: anal. calcd. for repeating units and monomer ratio based on NMR and SEC: C: 72.65, H: 7.41, N: 1.36, found: C: 66.97, H: 7.33, N: 1.30.

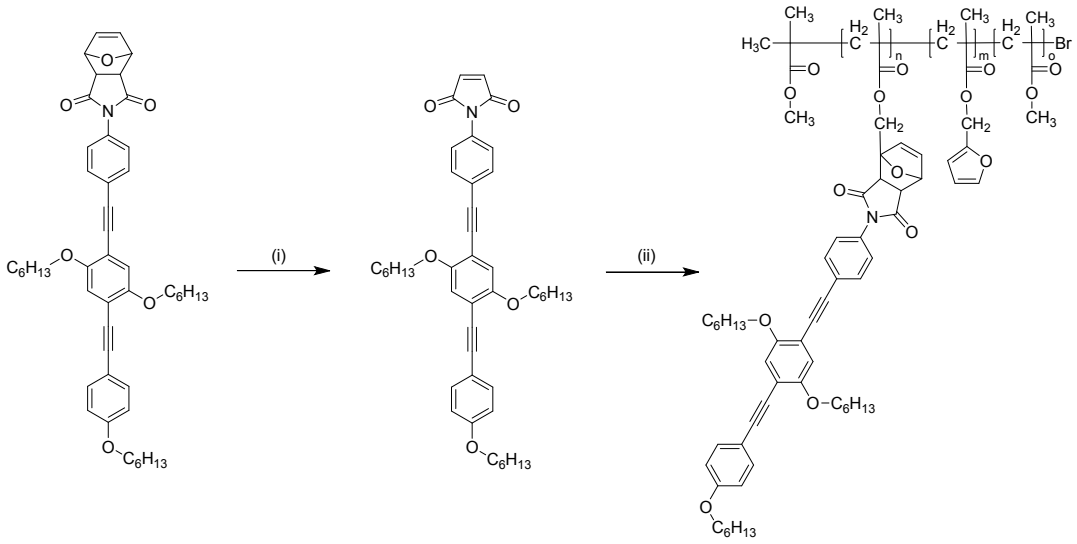
Calculation of Donor-Acceptor distance from UV-Vis and NMR data

From the steady-state UV-Vis absorption data (Fig. 1), a MMA:**20** ratio of 6.4:1 for **P4** and a MMA:**21** ratio of 3.3:1 for **P5** was calculated. For the exchange between both comb polymers, a mass ratio of 1:1 **P4**:**P5** was used, which is equal to a molar ratio of 1:1.5 (the average molar mass of repeating unit amounts to M_{P4} = 180.8 g/mol and M_{P5} = 272.0 g/mol). Thus, the exchanged graft polymer should exhibit a MMA:chromophore binding sites ratio of 4.25:1. From the NMR data of the exchanged comb polymer (Fig. 7), the ratio of free furan groups:**P4**:**P5** was determined as 14:43:43. Consequently, the MMA:furan group:**P4**:**P5** ratio is 4.25:0.14:0.43:0.43 or, alternatively, 9.9:0.33:1:1. Thus, on average, one donor and one acceptor are within 10 MMA units. Under the simplified assumption that one MMA repeating unit is 3 Å long (two carbon single bonds) and keeping in mind that the chromophores and free furan groups also incorporate a MMA unit each, an average donor-acceptor distance of 36.7 Å could be calculated.

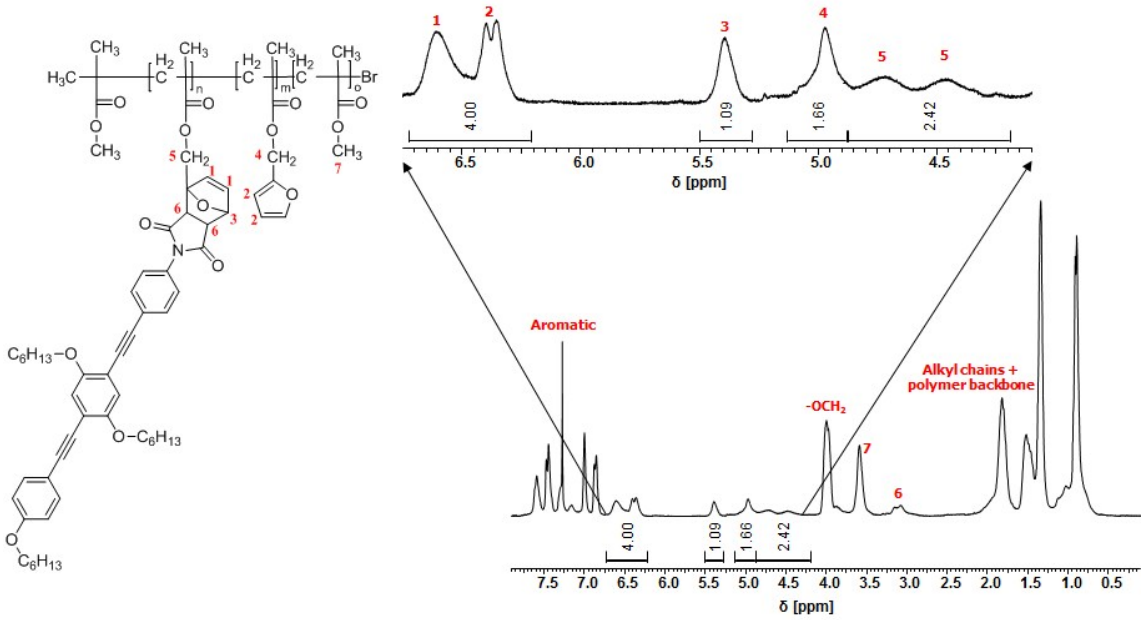
Additional schemes



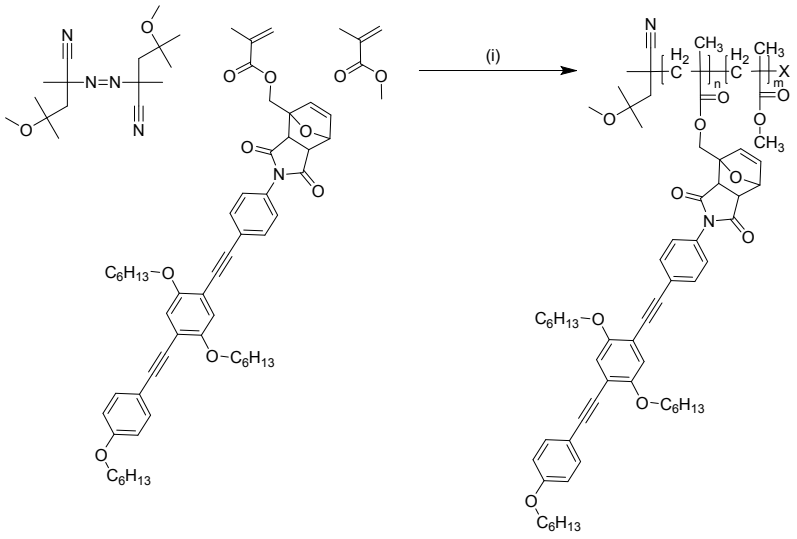
Supplementary Fig. 1. Synthesis of copolymer **P1** and quantification of monomer ratio *via* ^{1}H NMR spectrum ($CDCl_3$), Reagents and conditions: (i) CuBr/HMTETA/MB*i*B/FMA/MMA/toluene/70 °C.



Supplementary Scheme 3. Schematic representation of the polymer synthesis of **P3** *via* "grafting to" method, Reagents and conditions: (i) Chlorobenzene/120 °C; (ii) **P1**/55 °C (drop casted film).

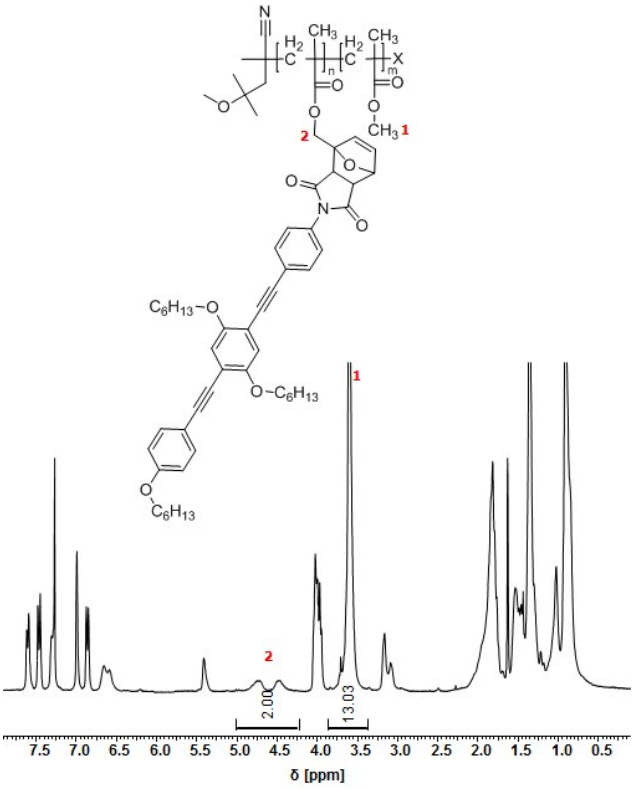


Supplementary Fig. 2 Quantification of free furan moieties in the polymer back bone *via* ^{1}H NMR spectrum ($CDCl_3$) of donor containing graft polymer **P3**.

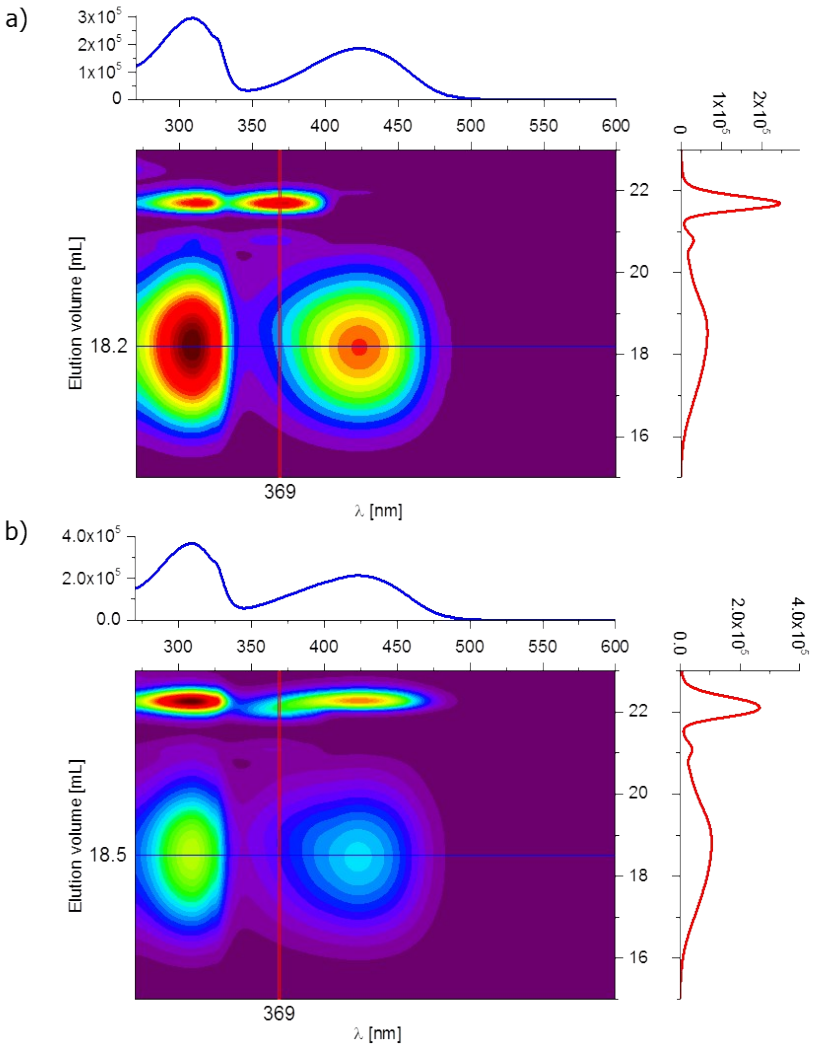


21 **P5**

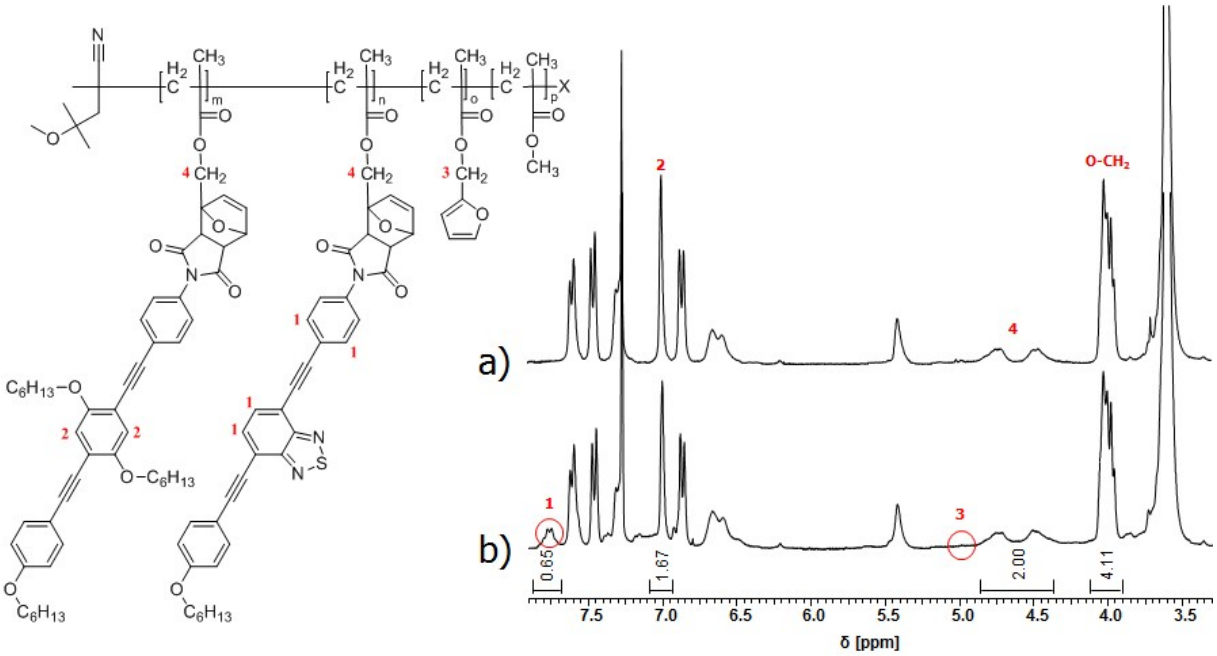
Supplementary Scheme 4. Schematic representation of the polymer synthesis of **P5**. Reagents and conditions: (i) Dimethylformamide/40 °C.



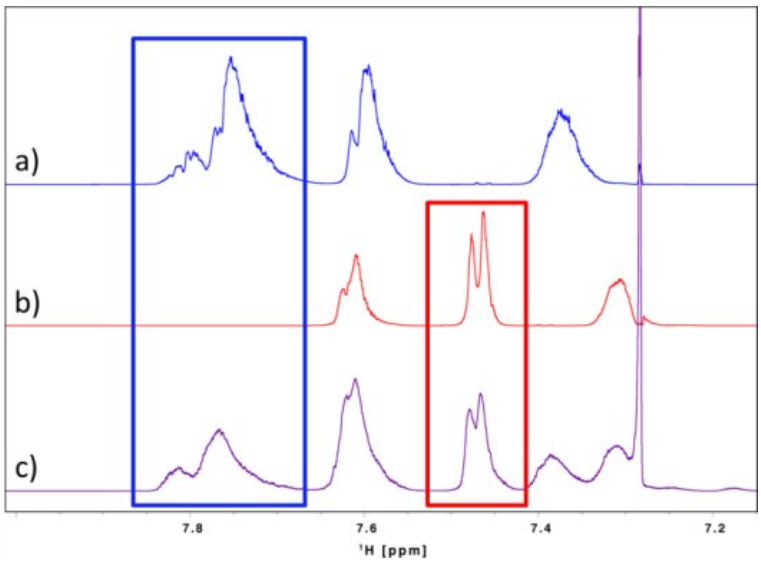
Supplementary Fig. 3. Quantification of polymerized monomer ratio and free furan groups *via* ^{1}H NMR spectrum ($CDCl_3$) of donor containing graft copolymer **P5**.



Supplementary Fig. 4. SEC measurements with diode array detector: starting points of a) acceptor graft copolymer **P4**/donor oligomer **19** and after exchange in polymer film b) mixture of acceptor-donor graft copolymer and donor/acceptor oligomer.



Supplementary Fig. 5. Quantification of donor and acceptor dye ratio and free furan groups *via* ^{1}H NMR spectrum ($CDCl_3$) a) before and b) after exchange between donor comb copolymer **P5** and acceptor oligomer **12**.



Supplementary Fig. 6. ^{1}H NMR-spectra of selected region of a) **P4**, b) **P5** and c) after exchange of **P4** and **P5** ($CDCl_3$).

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