Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

New electroactive macromonomers and multi-responsive PEDOT graft copolymers

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Table of Contents

1. General Information

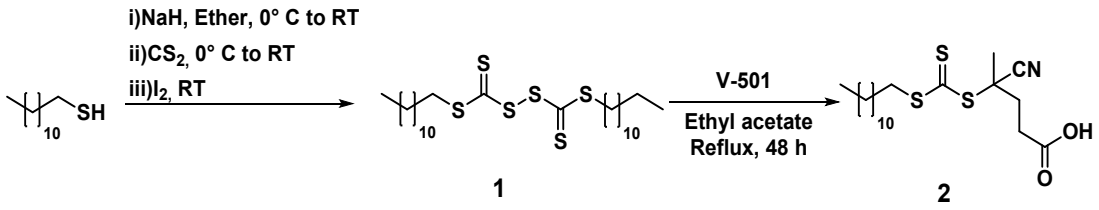
In the 1D and 2D-NMRs the following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet, dd = doublet of doublets. Coupling constants (J) are reported in Hertz (Hz). TLC were carried out on aluminum precoated plates (silica gel 40-60Å 400mesh, F254, Aldrich) using hexane:ethyl acetate (Hex:AcOEt) (v/v) as eluent. Silica gel high-purity grade, pore size 60 Å, 230-400 mesh particle size 40-63 µm was use for flash column chromatography. High-resolution mass spectrometry (HRMS) has been measured by direct injection in a Waters modelo SYNAPTTM G2 HDMSTM, using a Q-TOF detector and positive electrospray ionization ESI+.

2. Synthetic procedures

As cited in the main text, the macro-RAFT chain transfer agent was synthesized following the methodology developed by Thang et Al.,[1] and Moad et Al.[2] as shown in **Scheme S1**. The resulted molecules (**1**, **2**) matched the literature data.

2: ^{1}H NMR (400 MHz, Chloroform-d) δ 3.33 (t, J = 7.5 Hz, 2H), 2.74 – 2.64 (m, 2H), 2.60 – 2.49 (m, 1H), 2.45 – 2.34 (m, 1H), 1.88 (s, 3H), 1.69 (p, J = 7.8, 7.4 Hz, 2H), 1.45 – 1.26 (s, 18H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 216.93 , 176.74 , 119.03 , 46.36 , 37.25 , 33.67 , 32.05 , 29.76 , 29.68 , 29.56 , 29.48 , 29.21 , 29.07 , 27.81 , 25.02 , 22.83 , 14.26 .

Scheme S1 Reaction scheme to synthetize the macro-RAFT



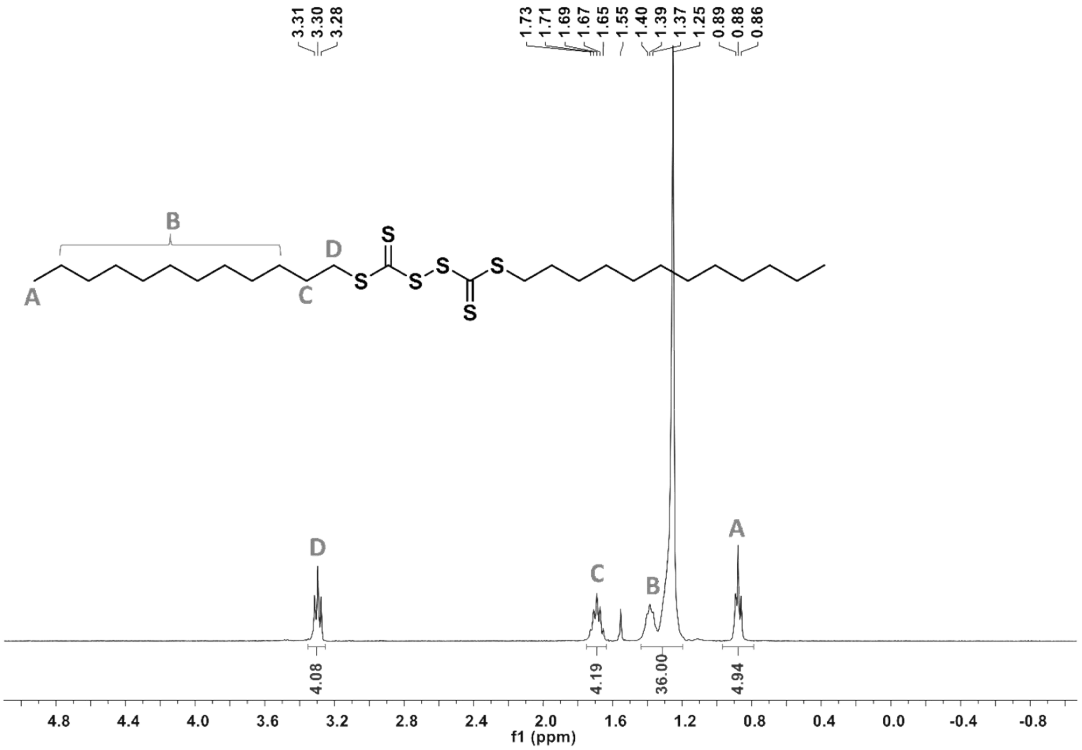


Fig. S1 ^{1}H NMR of **1** in $CDCl_3$

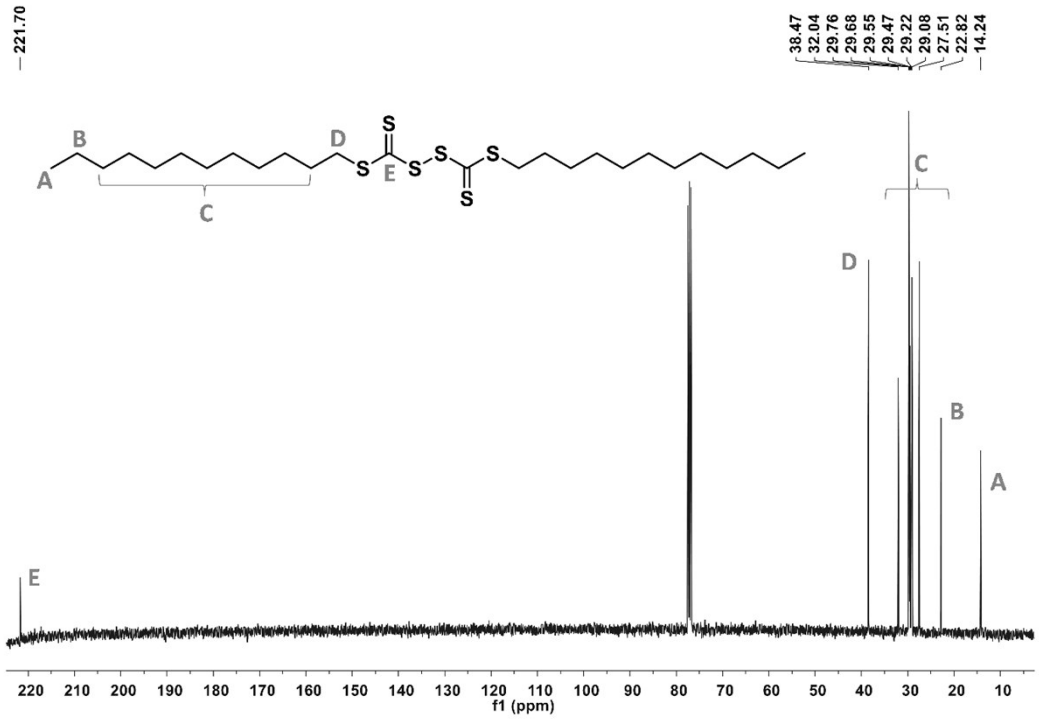


Fig. S2 ^{13}C NMR of **1** in $CDCl_3$

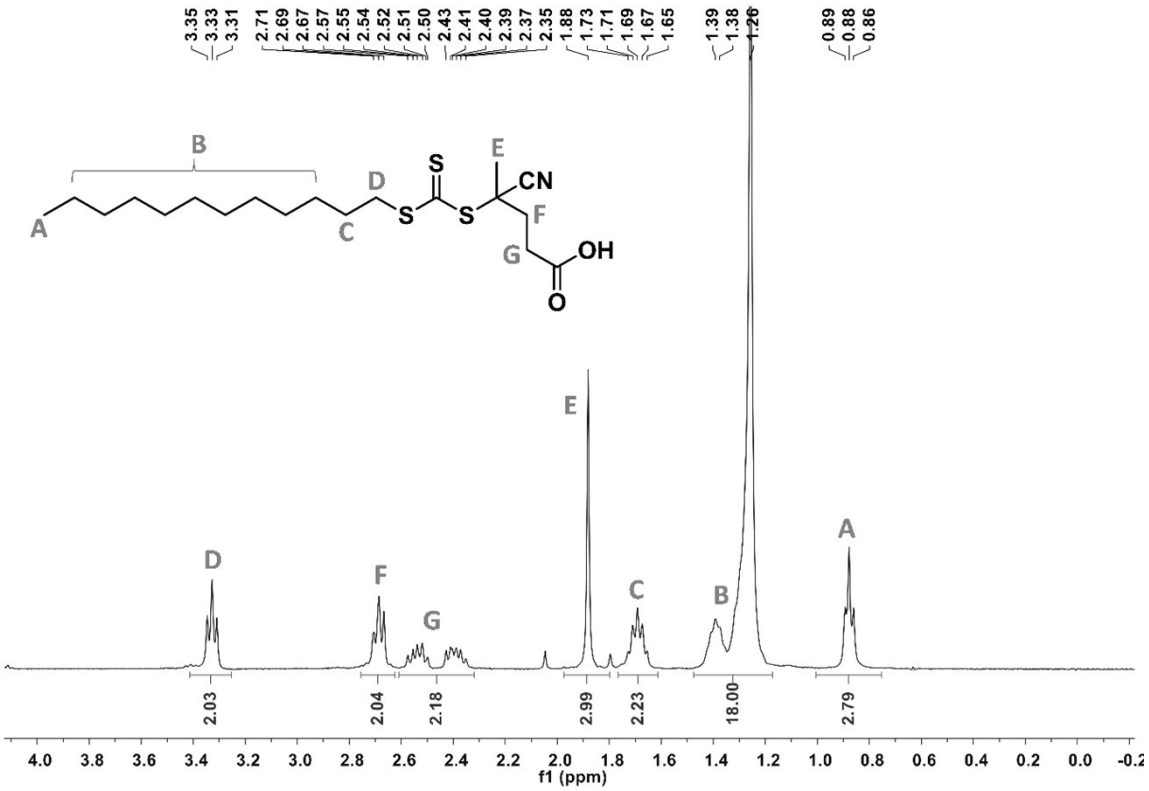


Fig. S3 ^{1}H NMR of **2** in $CDCl_3$

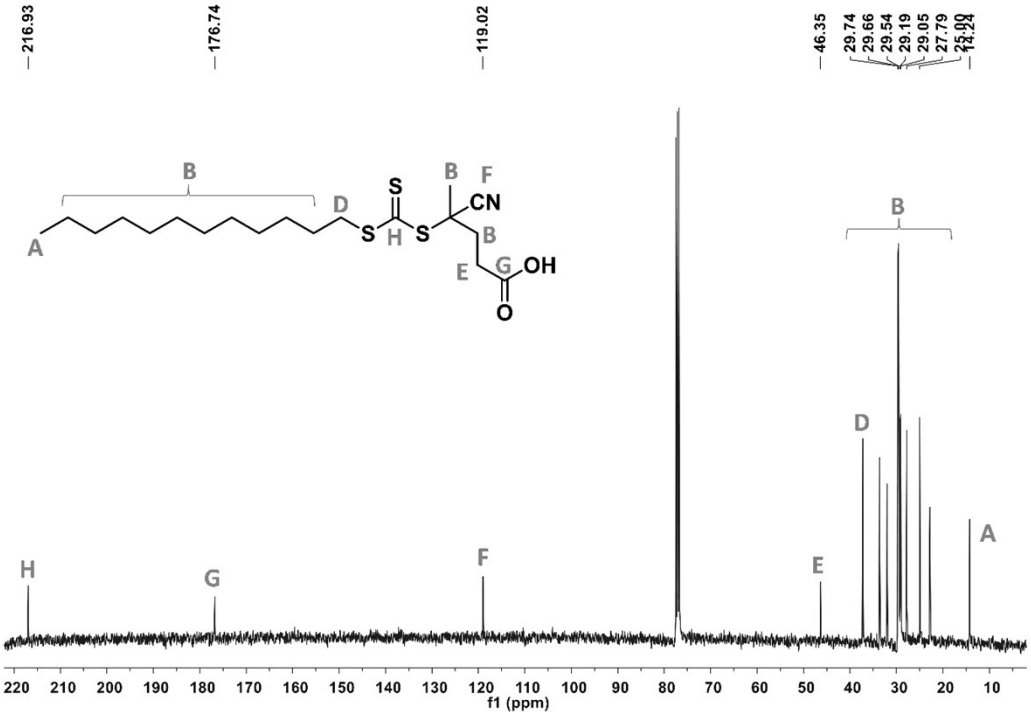
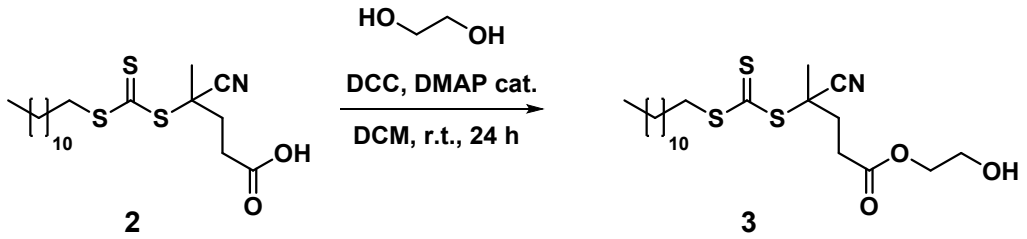


Fig. S4 ^{13}C NMR of **2** in $CDCl_3$

A similar procedure reported by Cortez-Lemus[3] was used to perform the last transterification step for the preparation of the macro-CTA. The reaction is shown in **Scheme S2**.



Scheme S2 Reaction scheme to synthetize the macro-RAFT.

To a solution of macro-CTA-COOH (**2**) 0.5g (1.24 mmol, 1 eq) in 50 mL of dry DCM, DCC 0.28 g (1.36 mmol, 1.1 eq) was added and let stirring for 30 minutes. Afterwards, ethylene glycol 173 µL (2.80 mmol, 2.5 eq, 0.192g) and DMAP 0.015 g (0.12 mmol, 0.1 eq) were added and the reaction mixture was kept 24 h at room temperature. After the reaction completion, monitored by TLC, the reaction mixture was filtered, to eliminate the urea salts precipitated during the reaction. The product containing filtrate was diluted with extra 250 mL of DCM and rinsed 3 times with 100 mL of water. The organic phase was dried over Na_2SO_4, and concentrated. The concentrated product was loaded onto a silica gel column and purified by flash column chromatography using a mixture of hexane:EtOAc 9:1 (Rf=0.86 hexane:EtOAc 9:1) to give **3** as an orange viscous oil (0.52 g, 94 %). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.25 (t, J = 4.6 Hz, 2H), 3.84 (t, J = 4.5 Hz, 2H), 3.32 (t, J = 7.4 Hz, 2H), 2.68 (t, J = 7.9 Hz, 2H), 2.54 (dt, J = 16.0, 8.0 Hz, 1H), 2.38 (dt, J = 14.9, 8.0 Hz, 1H), 1.88 (s, 3H), 1.68 (p, J = 7.3 Hz, 2H), 1.42 – 1.18 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 217.19 , 172.06 , 119.30 , 66.92 , 61.23 , 46.61 , 37.38 , 34.10 , 32.20 , 30.04 , 29.91 , 29.83 , 29.71 , 29.63 , 29.36 , 29.22 , 27.96 , 25.22 , 25.17 , 22.98 , 14.54 , 14.31 .

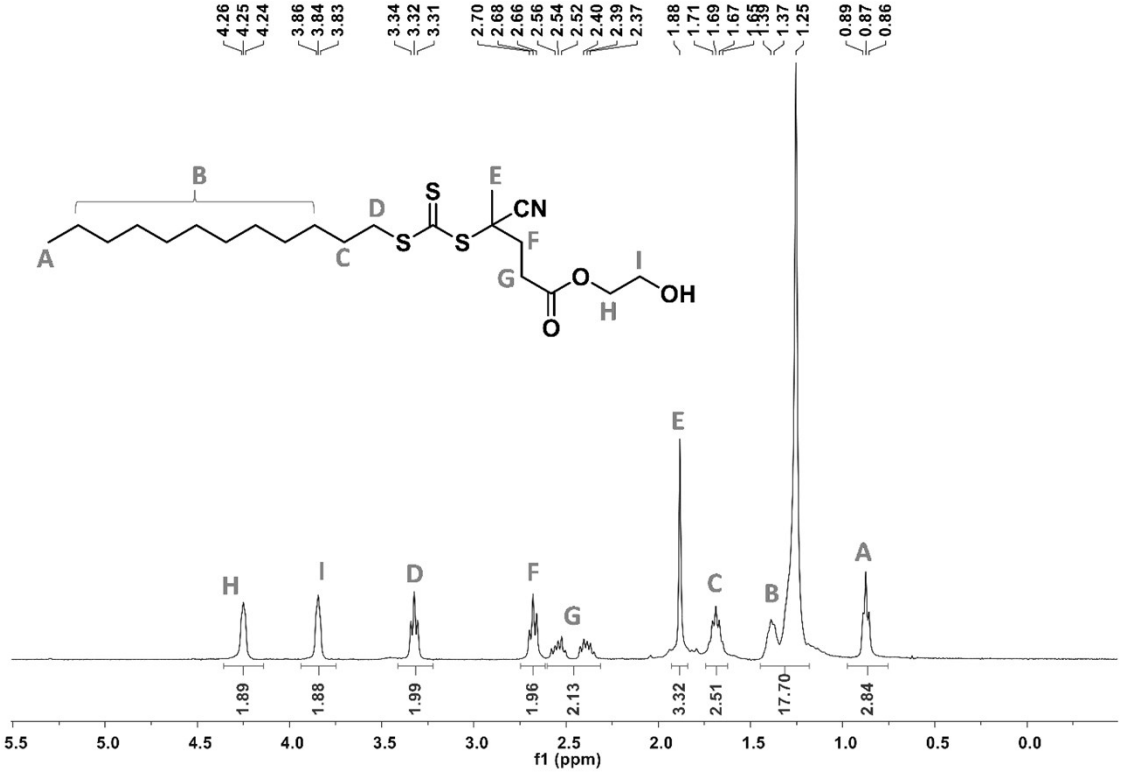


Fig. S5 ^{1}H NMR of **3** in $CDCl_3$.

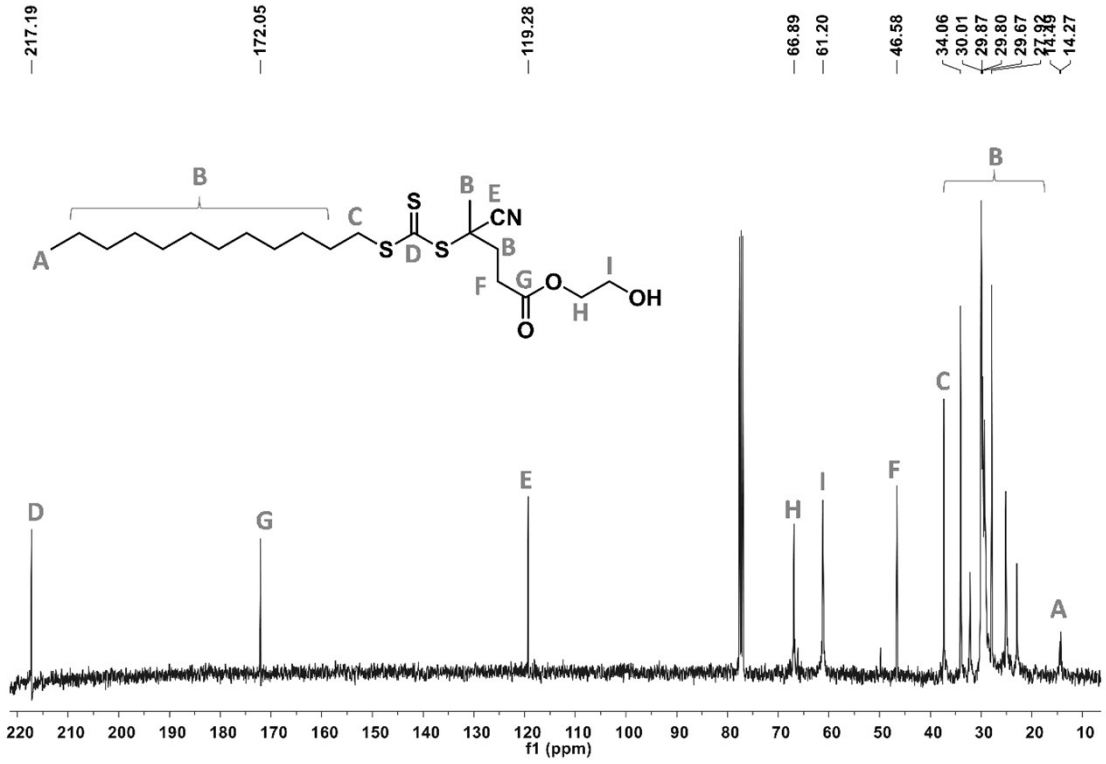
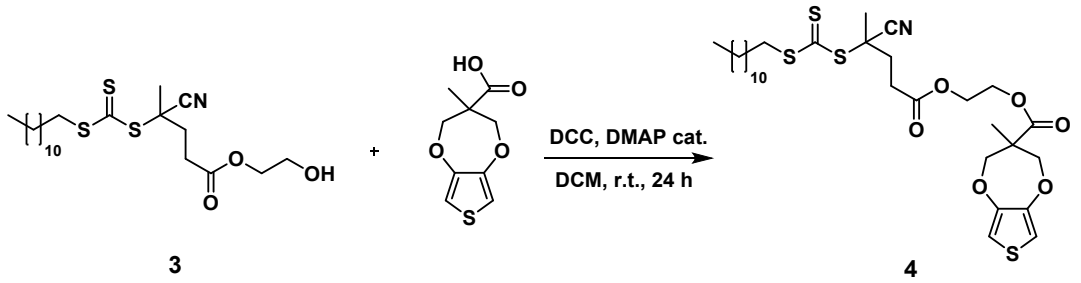


Fig. S6^{13}C NMR of **3** in $CDCl_3$

For the connection of the ProDOT moiety the same Steglich transesterification reaction has been used, putting an excess of the ProDOT-COOH for an easy work-up[4]. For that reaction the ProDOT-COOH has been prepared as previously reported in our group.[4]



Scheme S3 Reaction scheme to synthetize the ProDOT-CTA.

To a solution of ProDOT-COOH 0.3g (1.40 mmol, 1 eq) in 25 mL of dry DCM, DCC 0.32 g (1.54 mmol, 1.1 eq) was added and let stirring for 30 minutes. Afterwards, macro-CTA-OH (**3**) 0.56 g (1.26 mmol, 0.9 eq) and DMAP 0.017 g (0.14 mmol, 0.1 eq) were added and the reaction mixture was kept 24 h at room temperature. After the reaction completion, monitored by TLC, the reaction mixture was filtered, to eliminate the urea salts precipitated during the reaction. The product containing filtrate was diluted with extra 100 mL of DCM and rinsed 3 times with 50 mL of water. The organic phase was dried over Na_2SO_4, and concentrated. The concentrated product was loaded onto a silica gel column and purified by flash column chromatography using a mixture of hexane:EtOAc 8:2 (Rf=0.46, the spots containing the CTA appear bright yellow with bare eyes) to give **4** as an orange viscous oil (0.66 g, 81 %). FT-IR vmax/cm^{-1} 2973, 2851, 1735, 1481, 1451, 1383, 1247, 1190, 1140, 1030, 776. ^{1}H NMR (400 MHz, Acetone-d6) δ 6.64 (s, 1H), 4.48 (d, J =

12.3 Hz, 2H), 4.41 (m, 4H), 3.93 (d, J = 12.2 Hz, 2H), 3.45 (t, J = 7.4 Hz, 2H), 2.71 – 2.41 (m, 4H), 1.93 (s, 3H), 1.79 – 1.68 (m, 2H), 1.50 - 1.25 (m, 21H), 0.90 (t, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d6) δ 219.34 , 173.69 , 171.80 , 150.55 , 119.71 , 106.27 , 76.11 , 63.43 , 63.10 , 51.20 , 47.67 , 37.50 , 34.31 , 32.64 , 28.52 , 24.75 , 23.33 , 18.84 , 14.35 .. HRMS m/z [MNa]$^+$ theoretical 666.2027, detected 666.2025.

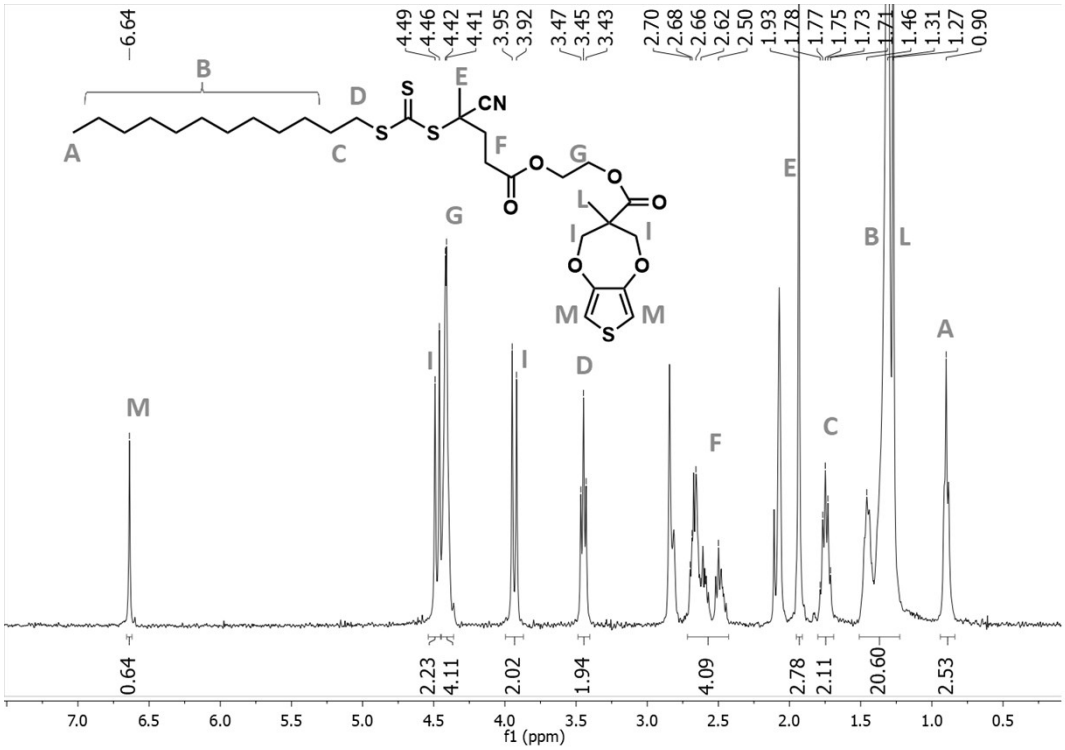


Fig. S7 ^{1}H NMR of **4** in $(CD_3)_2CO$.

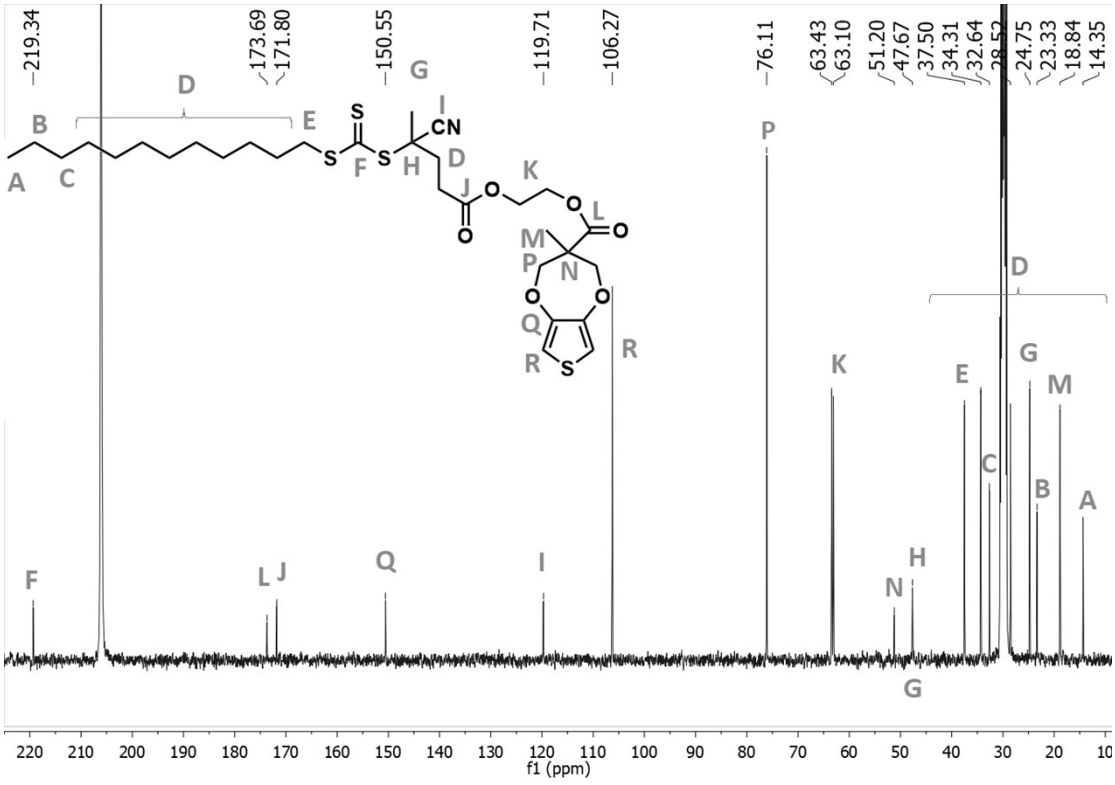


Fig. S8 ^{13}C NMR of **4** in $(CD_3)_2CO$

3. Synthesis of ProDOT end capped functional electroactive macromonomers

3.1. ProDOT-POEGMA macromonomer

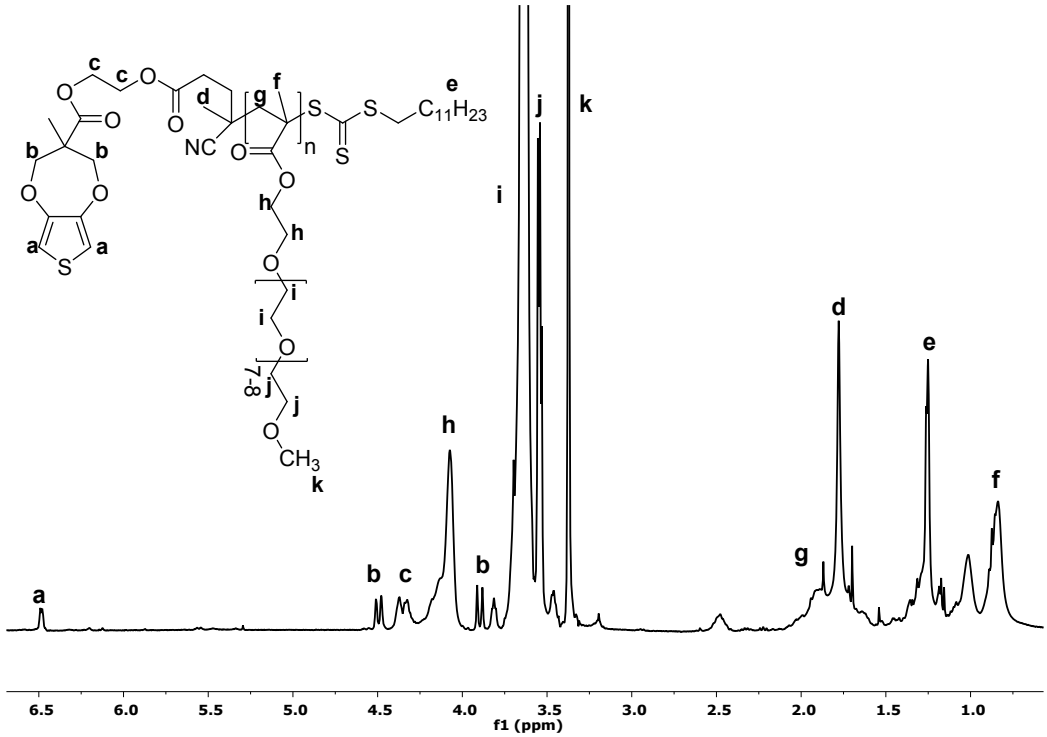


Fig. S9 ^{1}H-NMR spectrum of ProDOT-POEGMA [M]/[I]/[CTA] ratio (10:1:1) macromonomer.

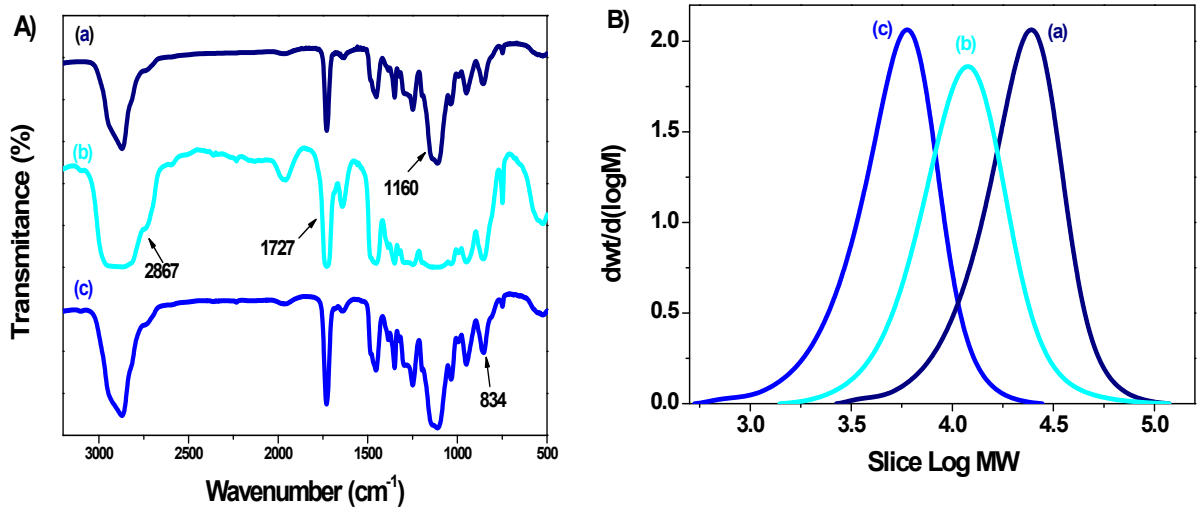


Fig. S10 A) FTIR spectra and **B)** SEC traces in THF of ProDOT- POEGMA macromonomer of different [M]/[I]/[CTA] ratios: (a) ProDOT-POEGMA (150:1:1); (b) ProDOT-POEGMA (50:1:1); and (c) ProDOT-POEGMA (10:1:1).

3.2. ProDOT-PNIPAM macromonomer

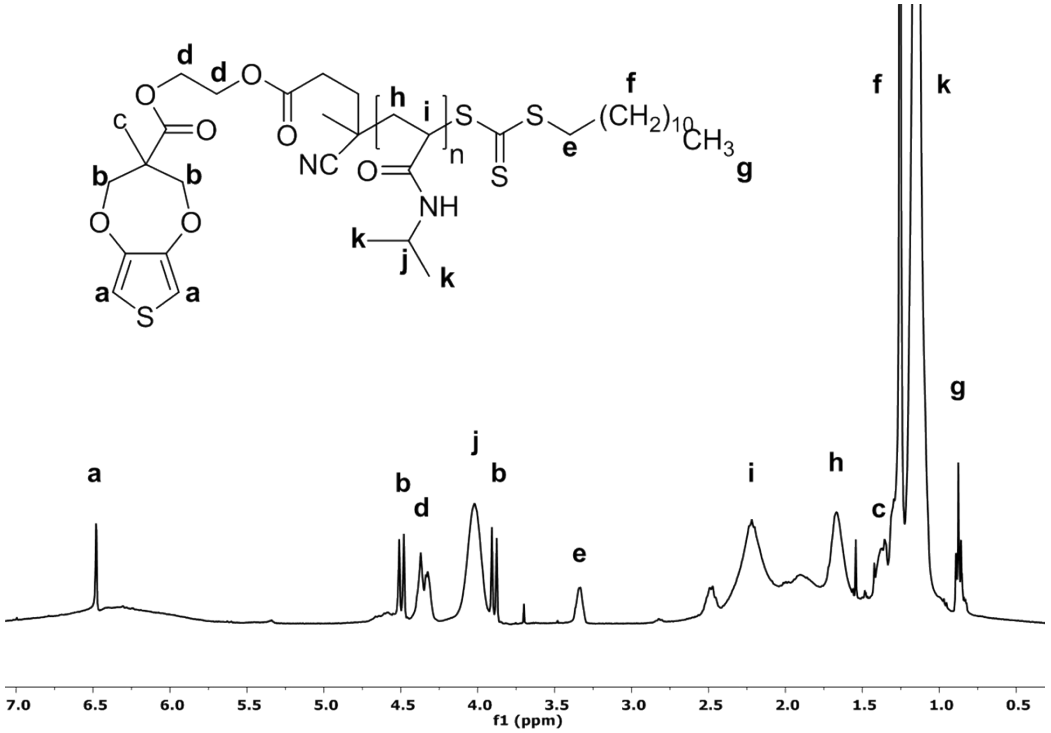


Fig. S11 ^{1}H-NMR spectrum of ProDOT-PNIPAM [M]/[I]/[CTA] ratio (10:1:1) macromonomer.

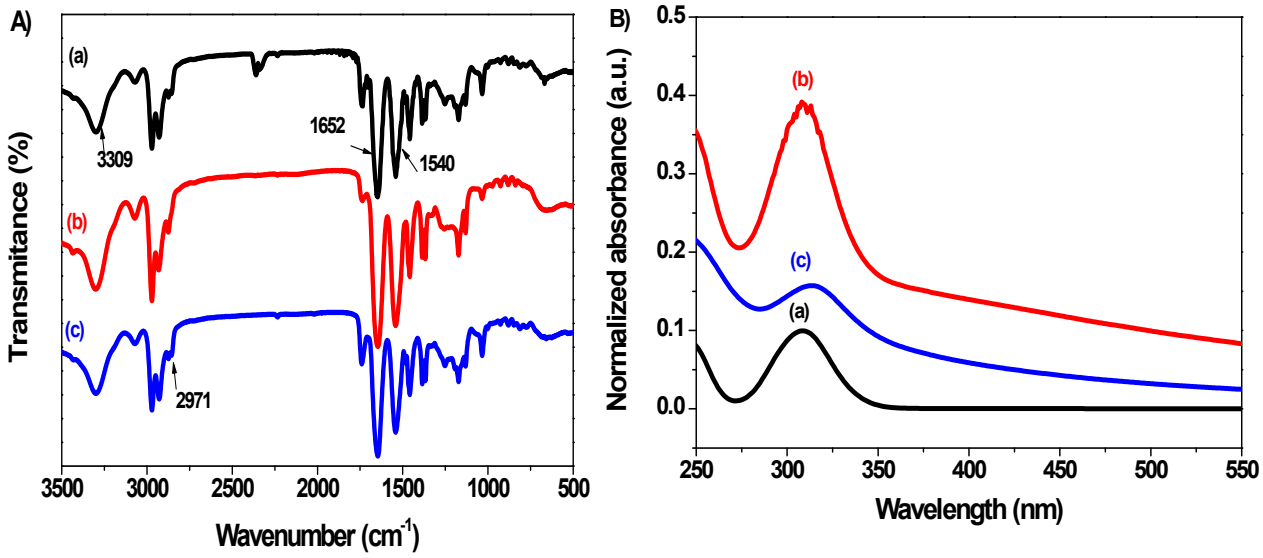


Fig. S12 (A) FTIR and **(B)** UV-vis in water spectra of ProDOT-PNIPAM macromonomers of different monomer/initiator/CTA [M]/[I]/[CTA] ratios. (a) ProDOT-PNIPAM (150:1:1); (b) ProDOT-PNIPAM (50:1:1); and (c) ProDOT-PNIPAM (10:1:1).

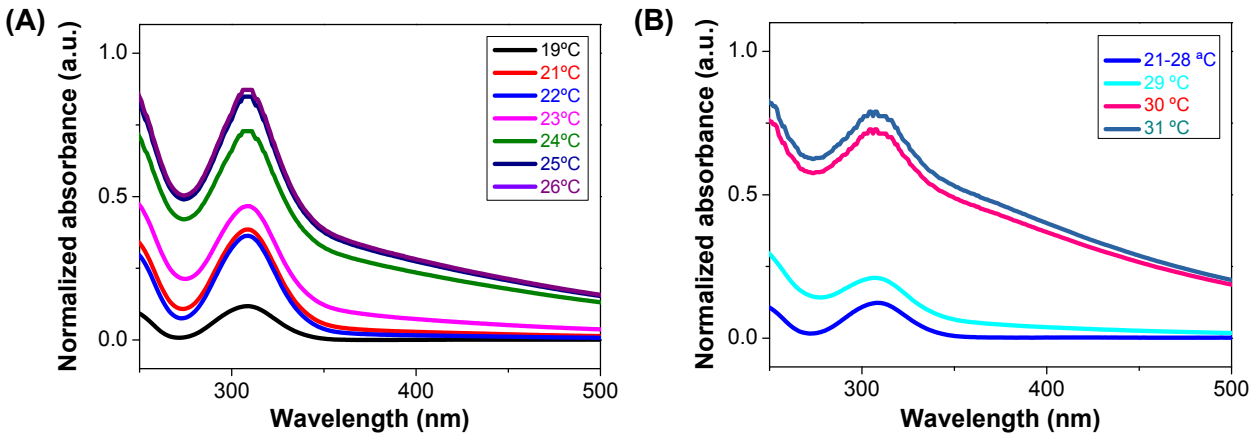


Fig. S13 (A) UV-vis absorption spectra of ProDOT-PNIPAM macromonomer of [M]/[I]/[CTA] mass ratio (50:1:1) in Milli Q water at different temperature, **(B)** UV-vis absorption spectra of ProDOT-PNIPAM of [M]/[I]/[CTA] mass ratio (150:1:1) in pure water at different temperatures.

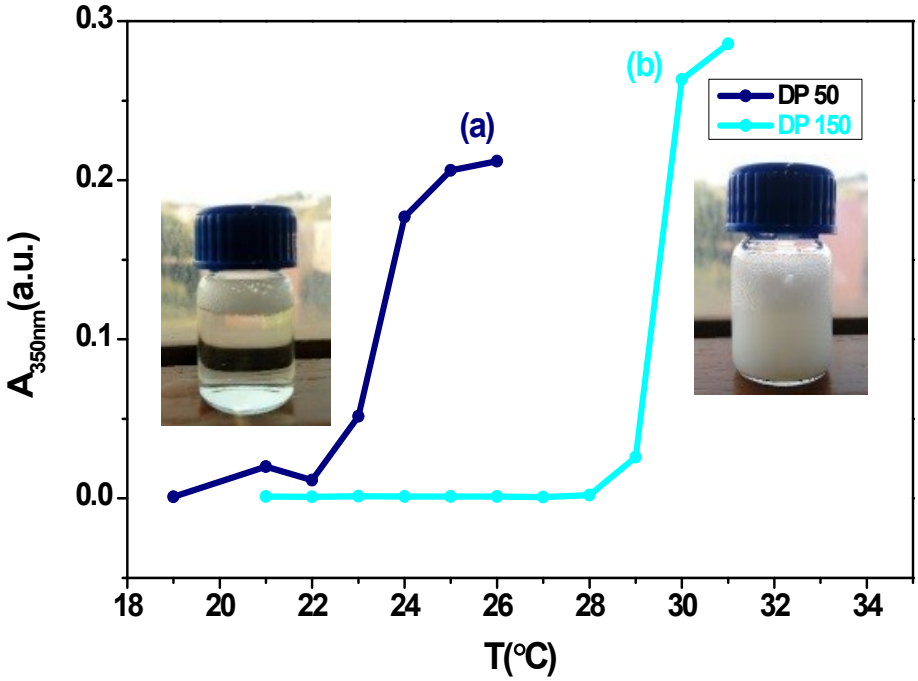


Fig. S14 UV-Vis absorption spectra at constant wavelength (350nm) of ProDOT-PNIPAM macromonomers of different [M]/[I]/[CTA] ratios (a) ProDOT-PNIPAM (50:1:1); and (b) ProDOT-PNIPAM (150:1:1).

3.3. ProDOT-PMMA macromonomer

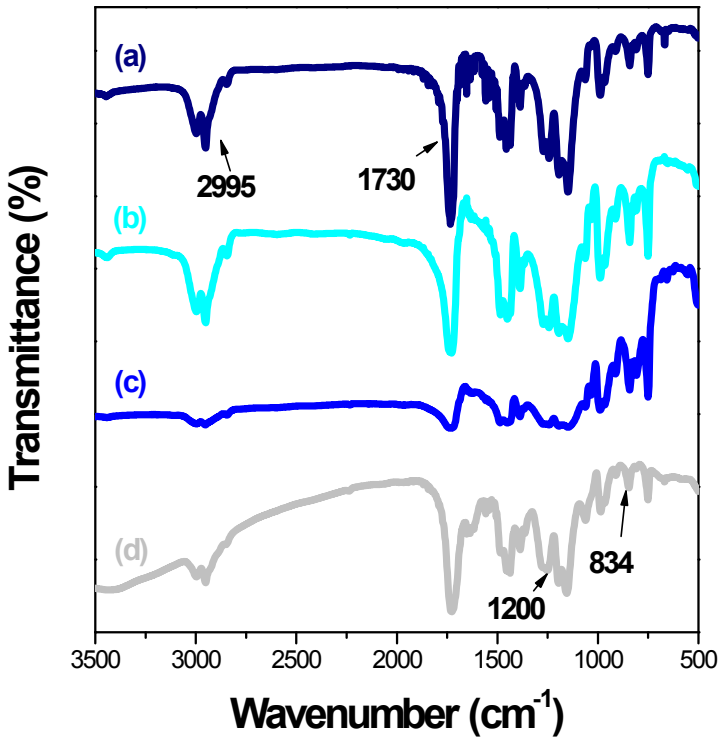


Fig. S15 FTIR spectra of ProDOT-MMA macromonomers of different [M]/[I]/[CTA] ratios: (a) 100:1:1; (b) 50:1:1; (c) 25:1:1; and (d) 10:1:1..

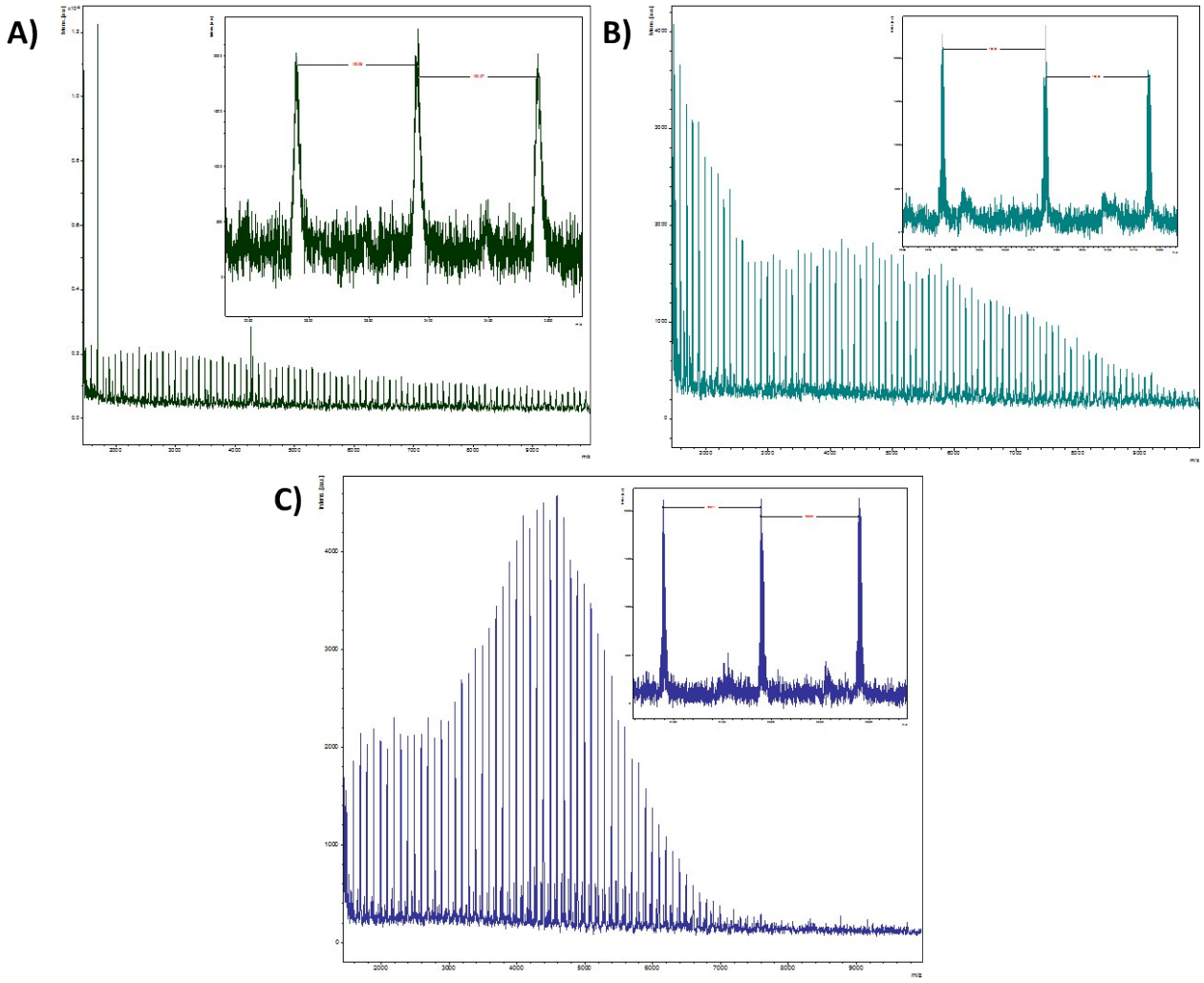


Fig. S16 MALDI-ToF-MS spectra of ProDOT-PMMA macromonomers of different mass ratios [M]/[I]/[CTA] **(A)** (25:1:1), **(B)** (50:1:1) and **(C)** (100:1:1) with the full spectra and the expanded spectral region.

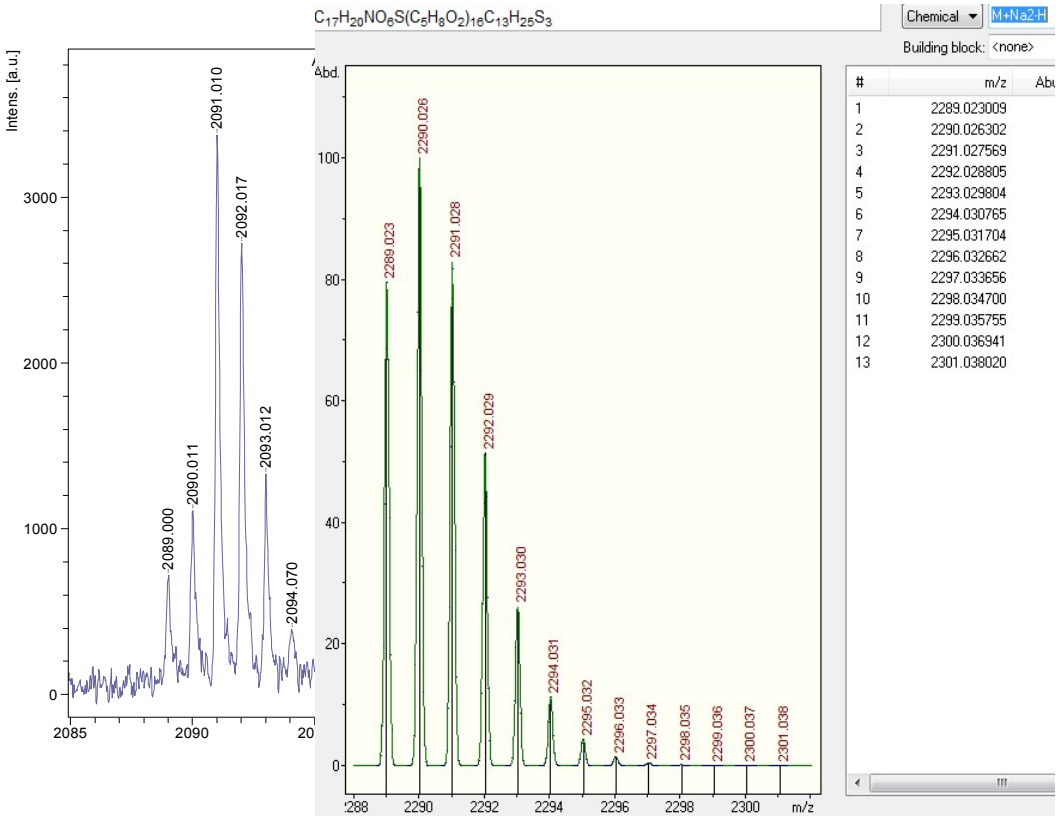


Fig.S17 Enlargements of MALDI-TOF spectrum of ProDOT-PMMA macromonomer (Table 1, entry 7) in which the exact mass and assignment of the corresponding molecule is disclosed.

4. Homopolymerization of ProDOT-PMMA macromonomers.

Table S1. Polymerization conditions used for the oxidative homopolymerization of a set of ProDOT-PMMA macromonomers.

Entry	[M]/[I]/[CTA]	Mn_{SEC} [a] ($g \cdot mol^{-1}$)	Đ[b]	Yield[c] (%)
1	**25:1:1**	30200	1.7	50
2	**50:1:1**	14100	1.3	55
3	**100:1:1**	23300	1.1	60

a) Mn determined by SEC in THF using universal calibration according to PS standards, b) Đ=Mw/Mn, c) Calculated as: Yield (%) = (grams of Pi obtained/ grams of monomers in the feed) ×100.

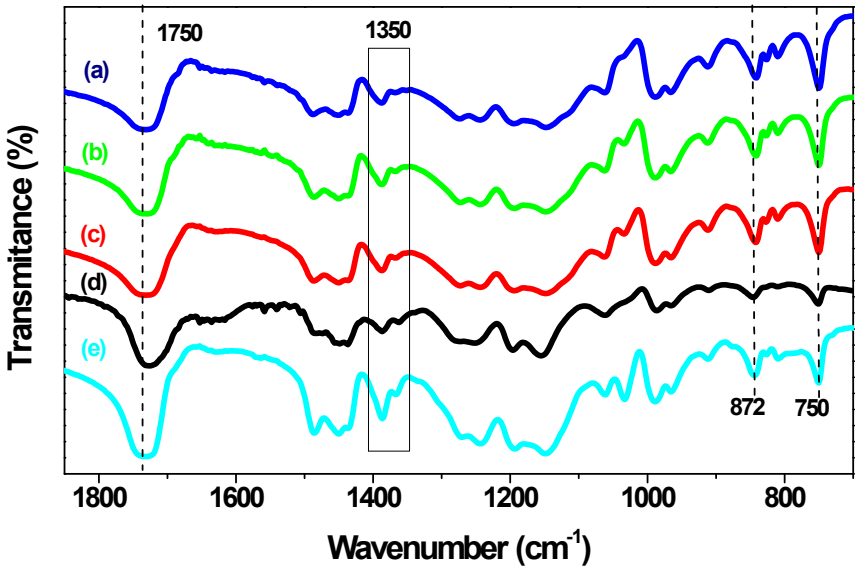


Fig. S18 FTIR spectra (e) ProDOT-PMMA (10:1:1) macromonomer and normalized PProDOT-PMMA poly(macromonomers) obtained by the homopolymerization of: (a) 10:1:1; (b) 25:1:1; (c) 50:1:1; and (d) 100:1:1 macromonomers.

5. Synthesis of PEDOT based graft copolymers

Table S2. Set of compositions used for oxidative polymerization of PEDOT-*g*-POEGMA and PEDOT-*g*-PNIPAM dispersions.

Entry	EDOT [wt%]	PolyM. [Table 1]	[M]/[I]/[CTA]	PolyM. [wt%]	*Conduct.** *[S· cm^{-1}]*
1	**20**	POEGMA	10:1:1	80	-
2	**50**	POEGMA	10:1:1	50	0.01
3	**80**	POEGMA	10:1:1	20	0.07
4	**20**	POEGMA	50:1:1	80	0.03
5	**50**	POEGMA	50:1:1	50	*
6	**80**	POEGMA	50:1:1	20	0.12
7	**20**	POEGMA	150:1:1	80	*
8	**50**	POEGMA	150:1:1	50	0.10
9	**80**	POEGMA	150:1:1	20	*
10	**20**	PNIPAM	10:1:1	80	*
11	**50**	PNIPAM	10:1:1	50	0.006
12	**80**	PNIPAM	10:1:1	20	*
13	**20**	PNIPAM	50:1:1	80	*
14	**50**	PNIPAM	50:1:1	50	*
15	**80**	PNIPAM	50:1:1	20	*
16	**20**	PNIPAM	150:1:1	80	*
17	**50**	PNIPAM	150:1:1	50	*
18	**80**	PNIPAM	150:1:1	20	*

*The heterogeneous morphology of some graft copolymer films did not allow us to obtain reliable results of conductivity.

5.1. PEDOT-*g*-POEGMA copolymer

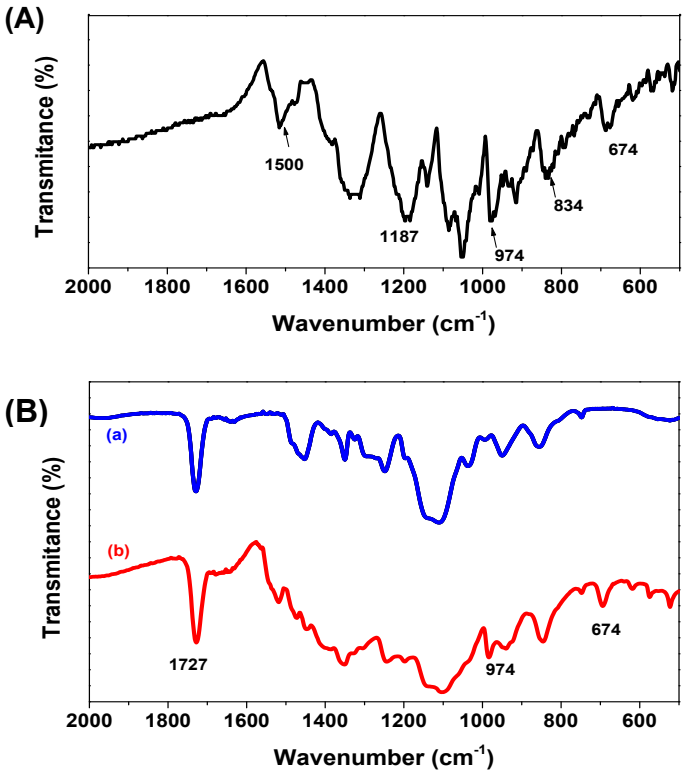


Fig. S19 (A) FTIR spectra of (a) oxidized PEDOT; **(B)** (a) ProDOT-POEGMA macromonomer ([M]/[I]/[CTA] (150:1:1); and (b), PEDOT-*g*-POEGMA dispersion 80:20 mass ratio

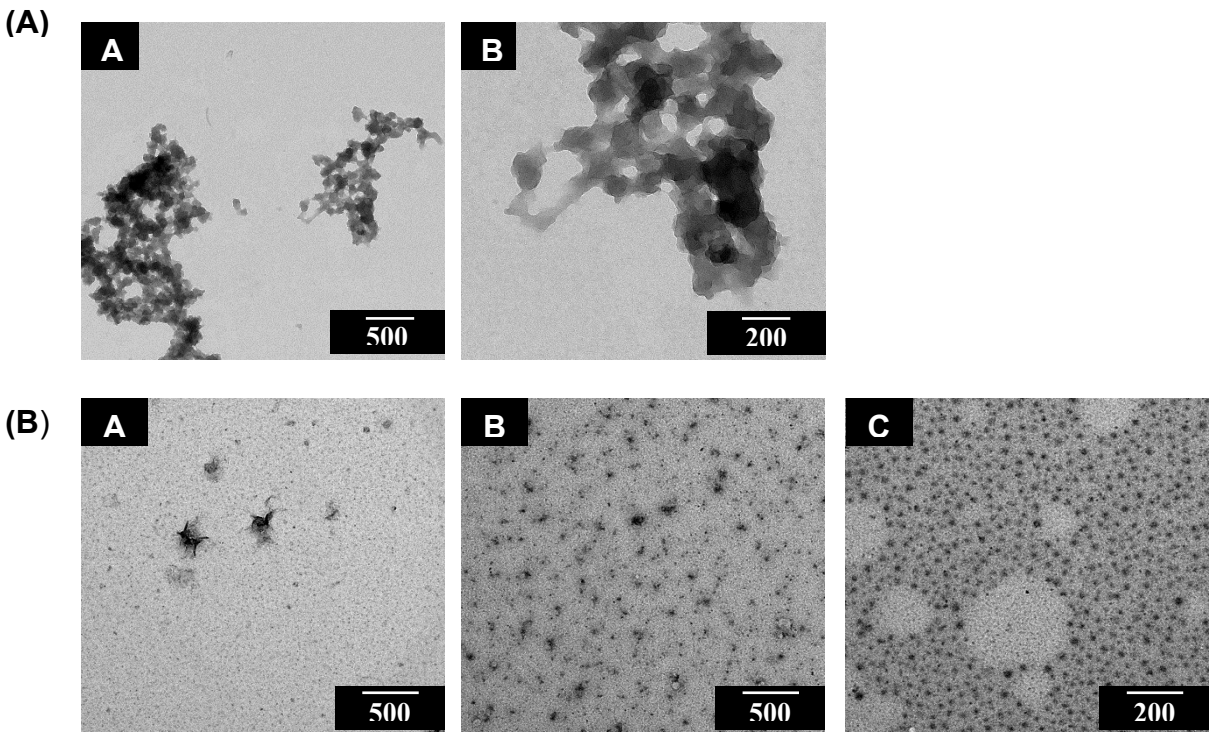


Fig. S20 (A) Transmission electron microscope (TEM) images of PEDOT- *g*- POEGMA dispersion (50:50) (ProDOT-POEGMA macromonomer of [M]/[I]/[CTA] ratio (50:1:1)) **(B)** Transmission electron microscope (TEM) images of PEDOT- *g*- PNIPAM dispersion (50:50) using macromonomers with different [M]/[I]/[CTA] ratios (A) 10:1:1; (B) 50:1:1; and (C) 150:1:1.

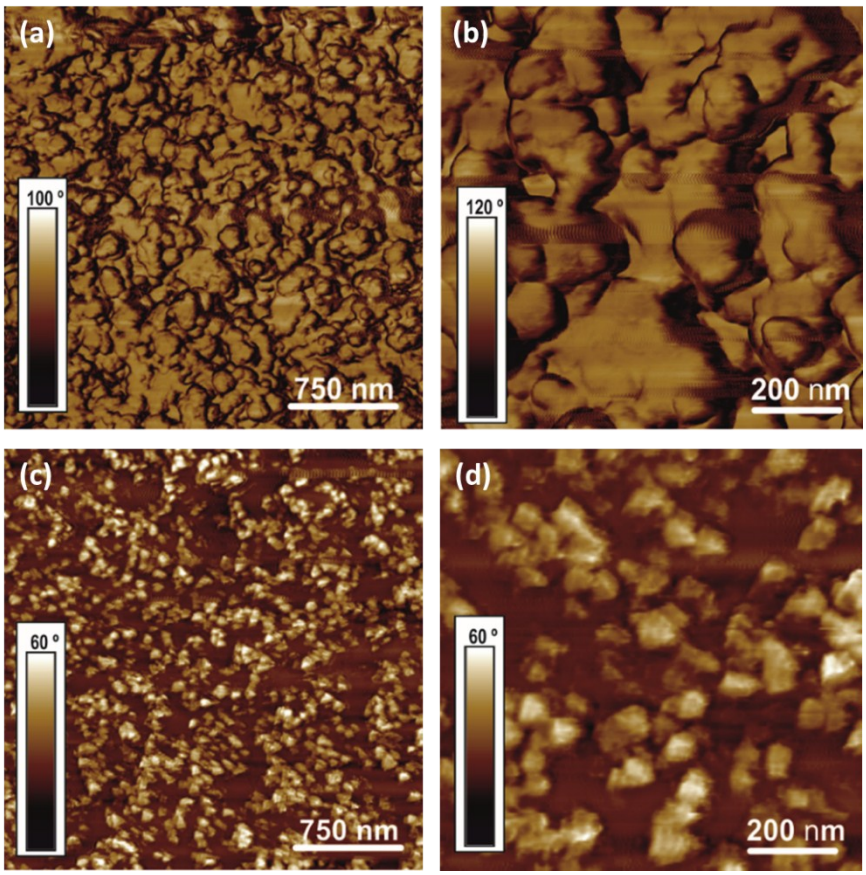


Fig. S21 AFM phase images of PEDOT-g-POEGMA (Table S1, entry 4)) with mass ratio 20:80 film based on ProDOT- POEGMA macromonomer [M]/[I]/[CTA] : 50:1:1 mass ratio (Mn=9678 , Table 1, entry 2):(a) 3 μm x 3 μm, (b) 1 μm x 1 μm (a,b). AFM phase images of PEDOT-g-POEGMA (Table S1, entry 9)) with mass ratio 80:20 film based on ProDOT- POEGMA macromonomer [M]/[I]/[CTA]: 150:1:1 mass ratio (Mn=24163 , Table 1, entry 3) (c) 3 μm x 3 μm, (d) 1 μm x 1 μm (c,d).

5.2. PEDOT-*g*-PNIPAM copolymer

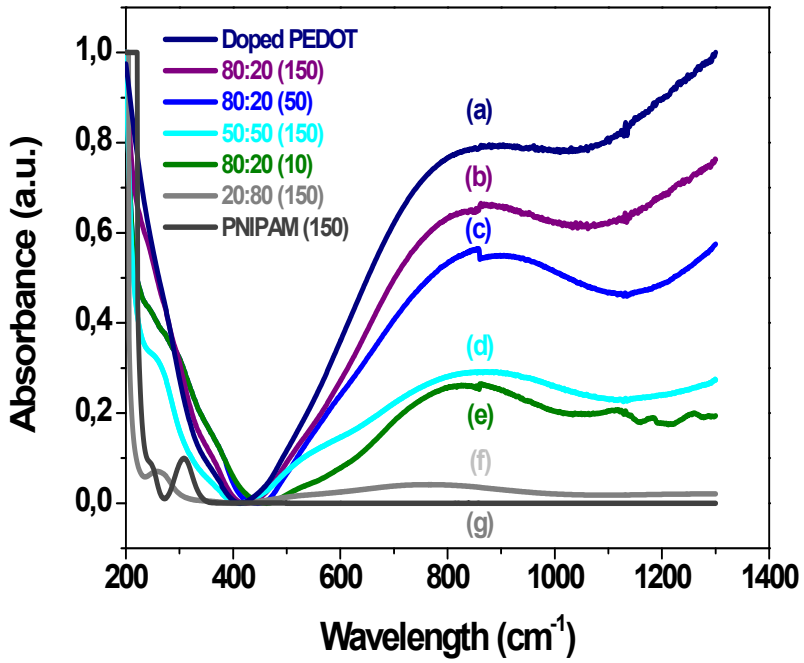


Fig. S22 UV-Vis NIR absorption spectra of (a) doped PEDOT and normalized PEDOT-*g*-PNIPAM copolymers obtained from different weight ratios EDOT:ProDOT-PNIPAM. (b) EDOT:ProDOT-PNIPAM macromonomer ([M]/[I]/[CTA] ratio 150:1:1) 80:20; (c) EDOT:ProDOT-PNIPAM (50:1:1) 80:20; (d) EDOT:ProDOT-PNIPAM (150:1:1) 50:50; (e) EDOT:ProDOT-PNIPAM (10:1:1) 80:20; (f) EDOT:ProDOT-PNIPAM (150:1:1) 20:80; and(g) ProDOT-PNIPAM (150:1:1).

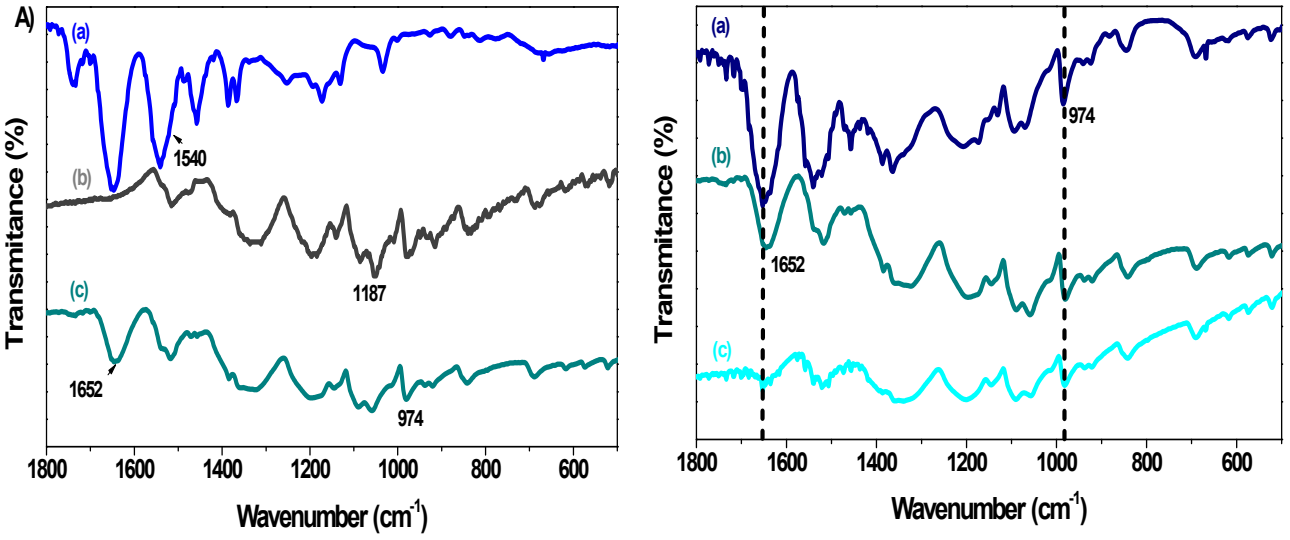


Fig. S23 (A) FTIR spectra of (a) ProDOT-PNIPAM(150:1:1) macromonomer (b) oxidized PEDOT and (c) PEDOT-*g*-PNIPAM(150) dispersion 50:50 mass ratio **(B)** FTIR spectra of PEDOT-*g*-PNIPAM(150:1:1) dispersions with different ratios of EDOT:ProDOT-PNIPAM : (a) 20:80, (b) 50:50), (c) 80:20.

Table S3. Low critical solution temperature values for PEDOT-*g*-PNIPAM copolymers with mass ratio of (20:80).

[M]/[I]/[CTA]	LCST $_{C.P.}$ (°C)[a] PEDOT-PNIPAM	LCST $_{C.P.}$ (°C)[b] PEDOT-*g*-PNIPAM	$LCST_{DSC}$ (°C)[c]
10:1:1	< 22	-	-
50:1:1	24	26	-
150:1:1	29.5	34	33.5

a) LCST (Low Critical Solution Temperature) of the macromonomers was measured by the cloud point method in UV-Vis absorption spectra at a constant wavelength (350 nm). b) Upon heating in a glycerine bath until hydrophobic behaviour was observed. c) Differential Scanning Calorimetric measurements at heating rate of 20 °C min^{-1}.

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