

Supporting Information for

Water-Soluble Anionic Poly(*p*-phenylene vinylenes) with High Luminescence

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Section S1: Synthesis of Side Chains

Methyl 6-bromohexanoate (**1**)

To a stirred solution of 6-bromohexanoic acid (1.00 g, 5.12 mmol) in methanol (14 mL) at 0 °C, thionyl chloride (0.67 g, 5.63 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 24 h. Methanol was removed *in vacuo* and the residue dissolved in ethyl acetate (7 mL) and then washed in order with water (3 mL), sodium bicarbonate (3 mL), water (3 mL), brine (3 mL) and dried (MgSO₄). The solvent was then removed *in vacuo* to yield the title compound **1** (1.05 g, 96%) as a yellow oil.

δ_{H} (300 MHz; CDCl₃; Me₄Si): 3.67 (3H, s, CH₃), 3.41 (2H, t, J = 6.0 Hz, CH₂), 2.33 (2H, t, J = 3.0 Hz, CH₂), 1.90-1.85 (2H, m, CH₂), 1.66-1.56 (2H, m, CH₂), 1.52-1.42 (2H, m, CH₂). IR: ν_{max} (neat)/cm⁻¹: 3463 (CH, aromatic), 1720 (C=O), 1253, 1170 and 1196 (C-O, ether) and 560 (C-Br). HRMS (ESI): found (MNa⁺): 230.9990 C₇H₁₃NaO₂⁷⁹Br requires 230.9991. The ¹H NMR data was in agreement with literature values.¹

1-Chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane (**3**)

To a solution of 2-(2-(2-methoxyethoxy)ethoxy)ethanol (5.00 g, 30.4 mmol) and pyridine (2.40 g, 30.4 mmol) in chloroform (20 mL) at 0 °C was added dropwise a solution of thionyl chloride (4.70 g, 39.5 mmol) in chloroform (5 mL). The mixture was then stirred at reflux for 3 h, under an atmosphere of nitrogen. The mixture was then cooled and washed with water (3 x 50 mL), brine (50 mL) and dried (MgSO₄). The solvent was removed *in vacuo* to yield the title compound **3** (5.50 g, 92 %) as a pale yellow oil.

δ_{H} (300 MHz; CDCl₃; Me₄Si): 4.18-4.09 (2H, m, CH₂Cl), 3.77-3.70 (2H, m, CH₂), 3.69-3.65 (4H, m, OCH₂), 3.55-3.48 (4H, m, OCH₂), 3.39 (3H, s, OCH₃). IR: ν_{max} (neat)/cm⁻¹: 2875 (CH, aromatic), 1299, 1245, 1199 and 1102 (C-O, ether) and 749 (C-Cl). HRMS (ESI): found (MNa⁺): 205.0610 C₇H₁₅NaO₃³⁵Cl requires 205.0602. ¹H NMR data was in agreement with

literature values.²

1-Chloro-2-(2-methoxyethoxy)ethane (**4**)

Using the same method as for alkyl chloride **3**, 2-(2-methoxyethoxy)ethanol gave the title compound **4** in 90 % yield.

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 3.74 (2H, t, $J = 6.0$ Hz, CH_2Cl), 3.68-3.64 (4H, m, OCH_2), 3.58-3.56 (2H, m, OCH_2), 3.39 (3H, s, OCH_3). IR: $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$: 2878 (CH, aromatic), 1299, 1245, 1198 and 1102 (C-O, ether) and 751 (C-Cl). HRMS (ESI): found (MNa^+): 161.0346 $\text{C}_5\text{H}_{11}\text{NaO}_2^{35}\text{Cl}$ requires 161.0340. The ^1H NMR data was in agreement with literature values.²

Section S2: Synthesis of Monomers

1,4-Diiodo-2,5-dimethoxybenzene (**5**)

To a solution of 1,4-dimethoxybenzene (10.5 g, 75.9 mmol) in 90:7:3 glacial acetic acid/water/concentrated sulfuric acid (100 mL), iodine (23.7 g, 91.02 mmol) and potassium iodate (20.93 g, 91.02 mmol) were added. The mixture was then heated at 70 °C, under an atmosphere of nitrogen, for 24 h. The mixture was allowed to cool and poured onto water (500 mL). The crude solid was collected by filtration and recrystallized from THF/H₂O to give the title compound **5** (24.01 g, 81%) as a purple solid. δ_{H} (300 MHz; CDCl₃; Me₄Si): 7.19 (2H, s, ArH), 3.81 (6H, s, OCH₃). IR: ν_{max} (neat)/cm⁻¹; 1482 (C=C, aromatic), 1063 (C-O, ether), 395 (C-I). HRMS (ESI): found (MNa⁺) 412.8496 C₈H₈O₂NaI₂ requires 412.8496. The ¹H NMR data was in agreement with the literature values.³

2,5-Diiodo-1,4-benzoquinone (**6'**) and 2,5-Diiodobenzene-1,4-diol (**6**)

To a solution of 2,5-dimethoxy-1,4-diiodobenzene **5** (5.00 g, 12 mmol) in dichloromethane (50 mL), under an atmosphere nitrogen at -78 °C, was added dropwise a solution of boron tribromide (13.25 g, 52 mmol) in dichloromethane (15 mL). After stirring at -78 °C for 30 min the mixture was stirred at room temperature for 18 h. The mixture was then poured slowly onto ice water (300 mL) and the resultant precipitate filtered and recrystallized from THF/H₂O to give the title compound **6'** (3.00 g, 60% yield) as orange crystals, which were used immediately. δ_{H} (300 MHz; CDCl₃; Me₄Si): 7.98 (2H, s, Ar-CH). HRMS (ESI): found (MH⁺): 360.8239 C₆H₃O₂I₂ requires 360.8228.

To a solution of 2,5-diiodo-1,4-benzoquinone **6'** (0.50 g, 2.70 mmol) in diethyl ether (30 mL) was added a solution of Na₂S₂O₄ (15.00 g, 83.33 mmol) in water (10 mL) and the mixture was vigorously stirred for 1 h at room temperature. The mixture was then diluted with water

(30 mL) and extracted with diethyl ether (3 x 20 mL). The combined extracts were dried (Na_2SO_4) and the solvent removed *in vacuo* to give the title compound **6** (0.95 g, 97%) as a white solid. δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 8.70 (2H, s, OH), 7.29 (2H, s, Ar-H). The ^1H NMR data was in agreement with literature values.⁴

Dimethyl 6,6'-(2,5-diiodo-1,4-phenylene)bis(oxy)dihexanoate (**7**)

Freshly powdered potassium hydroxide (0.23 g, 4.14 mmol) was added to a solution of 1,4-diiodo-2,5-hydroquinone **6** (0.50 g, 1.38 mmol) and methyl 6-bromohexanoate **1** (0.79 g, 4.14 mmol) in DMSO (8 mL). The mixture was stirred at room temperature for 24 h and then partitioned between dichloromethane (30 mL) and water (100 mL). The organic layer was separated, dried (MgSO_4) and evaporated *in vacuo* to give the crude product which was purified using flash chromatography (2:1 dichloromethane, hexanes) to give the title compound **7** (0.34 g, 73 %) as a white solid. δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 7.20 (2H, s, ArH), 3.99 (4H, t, $J = 6.0$ Hz, OCH_2), 3.71 (6H, s, OCH_3), 2.39 (4H, t, $J = 6.0$ Hz, $\text{CH}_2\text{CO}_2\text{Me}$), 1.80-1.59 (12H, m, CH_2). IR: $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$: 2938 (CH, aromatic), 1718 (C=O, carbonyl), 1490 (C=C, aromatic), 1052 (C-O, ether), 595 (C-I). HRMS (ESI): found (MNa^+) 640.9870 $\text{C}_{20}\text{H}_{28}\text{I}_2\text{NaO}_6$ requires 640.9867. The ^1H NMR data was in agreement with literature values.⁵

1,4-Bis(2-methoxyethoxy)benzene (**9**)

Freshly powdered potassium hydroxide (2.60 g, 45.4 mmol) was added to a solution of 1,4-hydroquinone (1.00 g, 9.08 mmol), 2-bromoethylmethyl ether (3.00 g, 22.7 mmol) and potassium iodide (0.30 g, 1.08 mmol) in ethanol (15 mL). The mixture was stirred at room temperature for 10 min after which it was heated at reflux for 5 days, under a nitrogen atmosphere. The reaction mixture was concentrated *in vacuo* and partitioned between dichloromethane (100 mL) and 1M aqueous sodium hydroxide (100 mL). The separated

organic layer was washed with water (2 x 100 mL), brine (100 mL), dried (Na₂SO₄) and concentrated to yield the crude product which was purified using flash chromatography (2:1 ethyl acetate: hexanes) to give the title compound **9** (1.20 g, 55%) as a yellow oil. δ_{H} (300 MHz; CDCl₃; Me₄Si): 6.84 (4H, s, ArH), 4.04 (4H, t, $J = 6.0$ Hz, OCH₂), 3.72 (4H, t, $J = 6.0$ Hz, OCH₂), 3.42 (6H, s, OCH₃). IR: ν_{max} (neat)/cm⁻¹; 2875 (CH, aromatic), 1352 (C-O, ether), 1242 (C-O, ether), 1176 (C-O, ether), 1096 (C-O, ether). HRMS (ESI): found (MNa⁺) 249.1106: C₁₂H₁₈NaO₄ requires 249.1097. The ¹H NMR data was in agreement with literature values.⁶

1,4-Bis(2-(2-methoxyethoxy)ethoxy)benzene (**11**)

Anhydrous potassium carbonate (4.50 g, 36.30 mmol) was added to a solution of 1,4-hydroquinone (1.00 g, 9.08 mmol), 1-chloro-2-(2-methoxyethoxy)ethane **4** (3.70 g, 22.70 mmol) and potassium iodide (0.30 g, 1.08 mmol) in DMF (10 mL). The mixture was heated at 100 °C for 24 h, under a nitrogen atmosphere. The mixture was cooled, filtered, poured onto water (30 mL), acidified with 3 M HCl and extracted with diethyl ether (100 mL). The organic extract was washed with 5% NaOH (v/v, 100 mL), water (150 mL), brine (100 mL) and dried (Na₂SO₄) to yield the title compound **11** (1.30 g, 60%) as a yellow oil.

δ_{H} (300 MHz; CDCl₃; Me₄Si): 6.83 (4H, s, ArH), 4.08 (4H, t, $J = 3.0$ Hz, OCH₂), 3.83 (4H, m, OCH₂), 3.70 (4H, m, OCH₂), 3.58 (4H, m, OCH₂), 3.38 (6H, s, OCH₃). IR: ν_{max} (neat)/cm⁻¹; 2875 (CH, aromatic), 1352 (C-O, ether), 1242 (C-O, ether), 1176 (C-O, ether), 1096 (C-O, ether) 595. HRMS (ESI): found (MH⁺): 315.1807 C₁₆H₂₇O₆ requires 315.1802. The ¹H NMR data was in agreement with literature values.⁶

1,4-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**14**)

Freshly powdered potassium hydroxide (1.50 g, 27.00 mmol) was added to a solution of 1,4-

hydroquinone (0.60 g, 5.40 mmol), 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane **3** (2.50 g, 13.60 mmol) and potassium iodide (0.2 g, 1.08 mmol) in ethanol (15 mL). The mixture stirred at room temperature for 10 min after which it was heated at reflux for 5 days under a nitrogen atmosphere. The mixture was then cooled, concentrated *in vacuo*, partitioned between dichloromethane (100 mL) and 1M aqueous sodium hydroxide (100 mL). The organic layer was washed with water (2 x 100 mL), brine (100 mL), dried (Na₂SO₄) and concentrated to yield the crude product which was purified by flash chromatography (2:1 ethyl acetate: hexanes) giving the title compound **14** (1.20 g, 50%) as a yellow oil. δ_{H} (300 MHz; CDCl₃; Me₄Si): 6.83 (4H, s, ArH), 4.08-4.04 (4H, m, OCH₂), 3.83 (4H, t, *J* = 6.0 Hz, OCH₂), 3.71-3.70 (4H, m, OCH₂), 3.66-3.62 (8H, m, OCH₂), 3.54-3.52 (4H, m, OCH₂), 3.36 (6H, s, CH₃)

IR: ν_{max} (neat)/cm⁻¹: 2875 (CH, aromatic), 1352 (C-O, ether), 1242 (C-O, ether), 1176 (C-O, ether), 1096 (C-O, ether). HRMS (ESI): found (MNa⁺) 421.4704 C₂₀H₃₄Na⁺O₈ requires 421.47.06

The ¹H NMR data was in agreement with literature values.⁶

General method of iodination of ethylene glycol monomers

To a solution of iodine monochloride (1.61 g, 9.95 mmol) in methanol (20 mL) at 0 °C was added dropwise, the corresponding ethylene glycol monomer (1.99 mmol). The mixture was then heated at reflux for 4 h. The resultant precipitate was filtered and washed with methanol to yield the title compound. If needed recrystallization was conducted using hexanes.

1,4-Diiodo-2,5-bis(2-methoxyethoxy)benzene (**10**)

Using the general method, 1,4-bis(2-methoxyethoxy)benzene **9** gave the title compound **10** (0.50 g, 55%) as a white solid. δ_{H} (400 MHz; CDCl₃; Me₄Si): 7.23 (2H, s, ArH), 4.08 (4H, t,

$J = 5.0$ Hz, OCH₂), 3.78 (4H, t, $J = 5.0$ Hz, OCH₂), 3.48 (6H, s, OCH₃). IR: $\nu_{\max}(\text{neat})/\text{cm}^{-1}$; 2875 (CH, aromatic), 1352 (C-O, ether), 1242 (C-O, ether), 1176 (C-O, ether), 1096 (C-O, ether) 595 (C-I). HRMS (ESI): found (MNa⁺) 500.9044 C₁₂H₁₆I₂Na⁺O₄ requires 500.9030. The ¹H NMR data was in agreement with literature values.⁷

1,4-Diiodo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (**12**)

Using the general method, 1,4-bis(2-(2-methoxyethoxy)ethoxy)benzene (**11**) gave the title compound **12** (0.480 g, 50%) as a pale yellow solid. δ_{H} (300 MHz; CDCl₃; Me₄Si): 7.24 (2H, s, ArH), 4.10 (4H, t, $J = 3.0$ Hz, OCH₂), 3.88 (4H, t, $J = 6.0$ Hz, OCH₂), 3.76 (4H, m, OCH₂), 3.58 (4H, m, OCH₂), 3.40 (6H, s, OCH₃). IR: $\nu_{\max}(\text{neat})/\text{cm}^{-1}$; 2875 (CH, aromatic), 1352 (C-O, ether), 1242 (C-O, ether), 1176 (C-O, ether), 1096 (C-O, ether) 595 (C-I). m/z (CI⁺) 566 (MH⁺, 100 %).

HRMS (ESI): found (MH⁺) 566.9735 C₁₆H₂₅I₂O₆ requires 566.9735. The ¹H NMR data was in agreement with literature values.⁷

1,4-Diiodo-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**13**)

Using the general method, 1,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**14**) gave a crude oil after concentrating *in vacuo*, which was partitioned between dichloromethane (100 mL) and saturated aqueous sodium thiosulfate (100 mL). The separated organic layer was washed with water (2 x 100 mL), brine (100 mL), dried (Na₂SO₄) and concentrated to yield the title compound **13** (0.40 g, 43%) as a yellow solid. δ_{H} (300 MHz; CDCl₃; Me₄Si): 7.25 (2H, s, ArH), 4.18 (4H, t, $J = 6.0$ Hz, CH₂), 3.82 (4H, t, $J = 6.0$ Hz, CH₂), 3.80-3.75 (4H, m, CH₂), 3.74-3.68 (8H, m, CH₂), 3.66-3.49 (4H, m, CH₂), 3.38 (6H, s, OCH₃). IR: $\nu_{\max}(\text{neat})/\text{cm}^{-1}$; 2875 (CH, aromatic), 1352 (C-O, ether), 1242 (C-O, ether), 1176 (C-O, ether), 1096 (C-O, ether) 395 (C-I). HRMS (ESI): found (MH⁺) 677.0099 C₂₀H₃₂O₈I₂

requires 677.0103. The ^1H NMR data was in agreement with literature values.⁷

Dimethyl 6,6'-((2,5-divinyl-1,4-phenylene)bis(oxy))dihexanoate (**16**)

A solution of dimethyl 6,6'-((2,5-diiodo-1,4-phenylene)bis(oxy))dihexanoate **7** (0.40 g, 0.77 mmol), vinyltributyltin (0.49 g, 1.55 mmol) and tetrakis(triphenylphosphine)palladium(0) catalyst (46.00 mg, 0.04 mmol) in dimethylformamide (8 mL) was heated at 100 °C, under an atmosphere of nitrogen, for 5 h. The mixture was filtered and poured onto water (30 mL). Dichloromethane (30 mL) was added, and then the separated organic layer was washed with water (3 x 30 mL), brine (2 x 30 mL), dried (MgSO_4) and reduced *in vacuo* to yield the crude product which was purified by flash chromatography (1:2 hexanes: dichloromethane) to give the title compound **16** (0.20 g, 62%) as pale yellow crystals. δ_{H} (300 MHz; CDCl_3 ; Me_4Si): 7.00 (2H, s, ArH), 6.97 (2H, t, $J = 3.0$ Hz, $\text{HC}=\text{CH}_2$), 5.68 (2H, d, $J = 18.0$ Hz, $\text{CH}=\text{CH}_2$), 5.26 (2H, d, $J = 12.0$ Hz, $\text{CH}=\text{CH}_2$), 3.96 (4H, t, $J = 3.0$ Hz, OCH_2), 3.67 (6H, s, OCH_3), 2.35 (4H, t, $J = 8.0$ Hz, CH_2), 1.82 -1.54 (12H, m, CH_2) δ_{C} (100 MHz; CDCl_3 ; Me_4Si): 174.1 (C=O), 150.5 (Ar-C), 131.4 (Ar-C), 127.1 ($\text{CH}=\text{CH}_2$), 114.1 ($\text{CH}=\text{CH}_2$), 110.4 (Ar-C), 68.9 (Ar- OCH_2), 51.4 (CH_2), 33.9 (OCH_3), 29.1 (CH_2). IR: ν_{max} (neat)/ cm^{-1} ; 2938 (CH, aromatic), 1718 (C=O, carbonyl), 1490 (C=C, aromatic), 1052 (C-O, ether), 919 (C=CH, vinylene)

HRMS (ESI): found (MNa^+) 441.2237 $\text{C}_{24}\text{H}_{34}\text{NaO}_6$ requires 441.2248.

1,4-Divinylbenzene (**17**)

Potassium tert-butoxide (8.89 g, 79.2 mmol) was added to a solution of methyltriphenylphosphonium bromide (27.15 g, 76 mmol) in dry tetrahydrofuran (110 mL) and the mixture was stirred for 20 min at room temperature under an atmosphere of nitrogen. A solution of terephthalaldehyde (5.00 g, 37.00 mmol) in dry tetrahydrofuran (50 mL) was

then added dropwise. After stirring for 1 h the mixture was poured onto iced water (120 mL). The organic layer was separated and the aqueous phase was extracted with hexane (3 x 50 mL). The combined organic layers were washed with brine (200 mL), dried (MgSO₄) and concentrated *in vacuo* after adding 1,4-hydroquinone (5 mg) as an inhibitor to give the crude product which was purified using flash chromatography (hexanes), to give the title compound **17** (3.00 g, 63%) as a yellow oil. δ_{H} (300 MHz; CDCl₃; Me₄Si): 7.35 (4H, s, ArH), 6.61 (2H, dd, $J = 9.0$ Hz, 9.0 Hz, CH=CH₂), 5.76 (2H, d, $J = 18.0$ Hz, HC=CH₂), 5.24 (2H, d, $J = 12.0$ Hz, HC=CH₂). IR: ν_{max} (neat)/cm⁻¹; 3008 (CH, aromatic), 1264 (CH, aromatic), 989 (C=C, vinylenes). The ¹H NMR data was in agreement with values presented in the literature.⁸

6,6'-((2,5-divinyl-1,4-phenylene)bis(oxy))dihexanoic acid (**18**)

A solution of NaOH (4M, 5 mL) was added dropwise to a solution of dimethyl 6,6'-((2,5-divinyl-1,4-phenylene)bis(oxy))dihexanoate **16** (0.05 g, 0.119 mmol), in THF (5 mL) and methanol (10 mL). The mixture was then stirred at room temperature, under an atmosphere of nitrogen for 24 h. The mixture was acidified with conc hydrochloric acid and concentrated *in vacuo* to yield the title compound **18** (0.03 g, 90%) as pale yellow crystals. δ_{H} (300 MHz; DMSO-d₆): 7.10 (2H, s, ArH), 6.87 (2H, t, $J = 9.0$ Hz, HC=CH₂), 5.82 (2H, d, $J = 15.0$ Hz, CH=CH₂), 5.22 (2H, d, $J = 12.0$ Hz, CH=CH₂), 3.93 (4H, t, $J = 6.0$ Hz, OCH₂), 2.22 (4H, t, $J = 6.0$ Hz, CH₂), 1.73 -1.40 (12H, m, CH₂). δ_{C} (100 MHz; DMSO): 174.9 (C=O), 168.5 (Ar-C), 143.4 (Ar-C), 131.5 (CH=CH₂), 126.8 (CH=CH₂), 110.9 (Ar-C), 68.9 (Ar-OCH₂), 29.1 (CH₂), 24.7 (CH₂). IR: ν_{max} (neat)/cm⁻¹; 2935 (CH, aromatic), 1701 (C=O, carbonyl), 1498 (C=C, aromatic), 1052 (C-O, ether), 978 (C=CH, vinylenes)

HRMS (ESI): found (MNa⁺) 413.1935 C₂₂H₃₀NaO₆ requires 413.1867.

Section S3: Solubilities of novel PPVs synthesized

	Hexane (P = 0.009)	THF (P = 0.207)	Chloroform (P = 0.259)	Acetone (P = 0.355)	Methanol (P = 5.1)	Water (pH = 7) (P = 10.2)
PMDH						
COOMe	-	*	+	+	-	-
COOH	-	*	*	+	-	*
PDDMe						
COOMe	-	*	+	+	-	-
COOH	-	*	*	+	-	*
PDMonoG						
COOMe	-	*	+	+	-	-
COOH	-	*	*	+	*	0.0525 mg/mL
PDDiG						
COOMe	-	*	+	+	-	-
COOH	-	*	*	+	*	*
PDTriG						
COOH	-	-	+	+	-	0.09 mg/mL

Table S3.1: Overview of observed solubilities of synthesized PPVs in selected solvents (- completely insoluble (particles observed in solution and solution did not fluoresce), * partially soluble (particles observed in fluorescent solution as polymers did not dissolve fully), + completely soluble (no particles were visible in the fluorescent solution)).

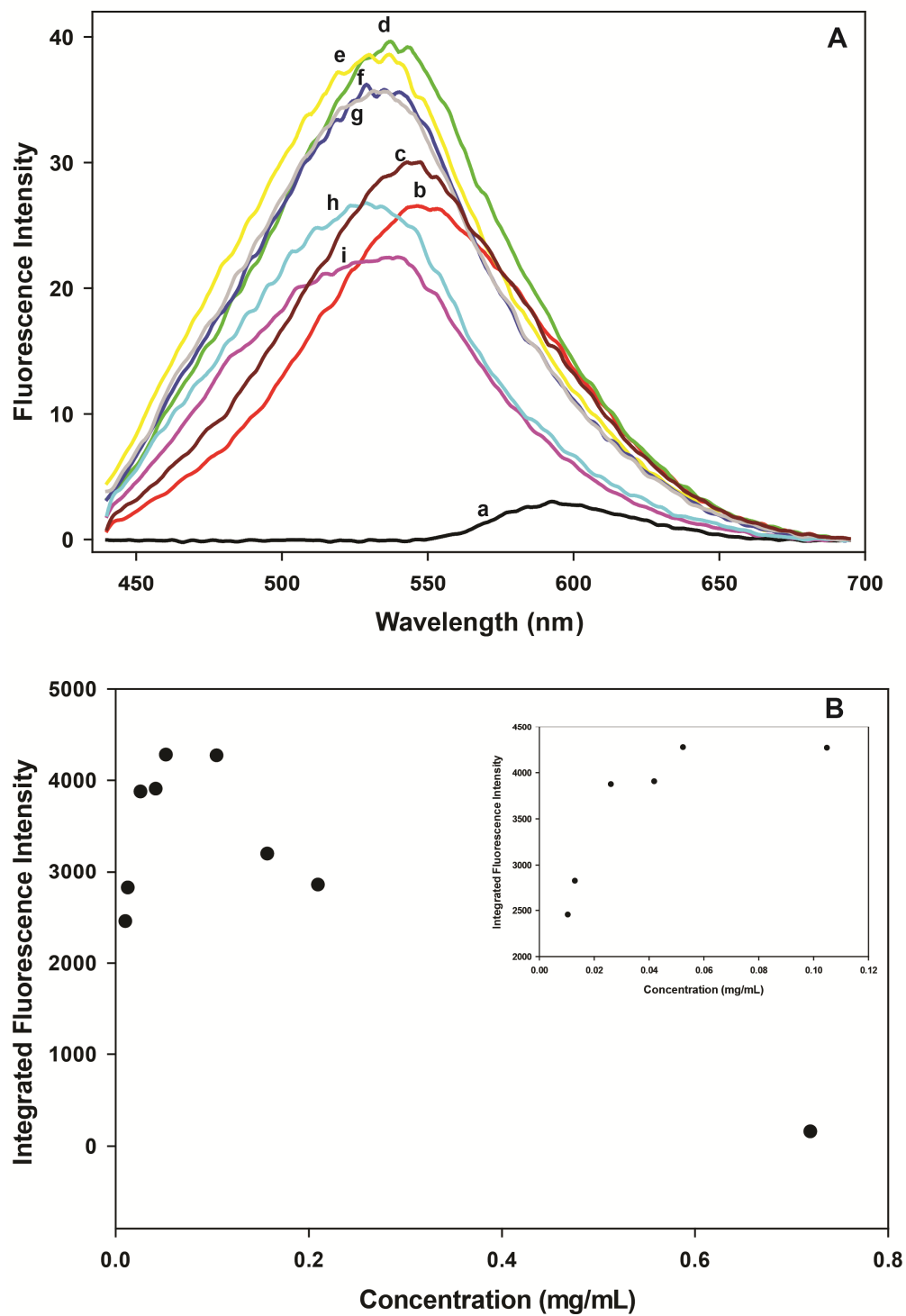


Figure S3.1: Fluorescence based solubility study of **PDMonoG** in water at pH 7 at different concentrations (A), integrated fluorescence intensity (B) and linear region between 0.0105 mg/mL – 0.105 mg/mL (Inset).

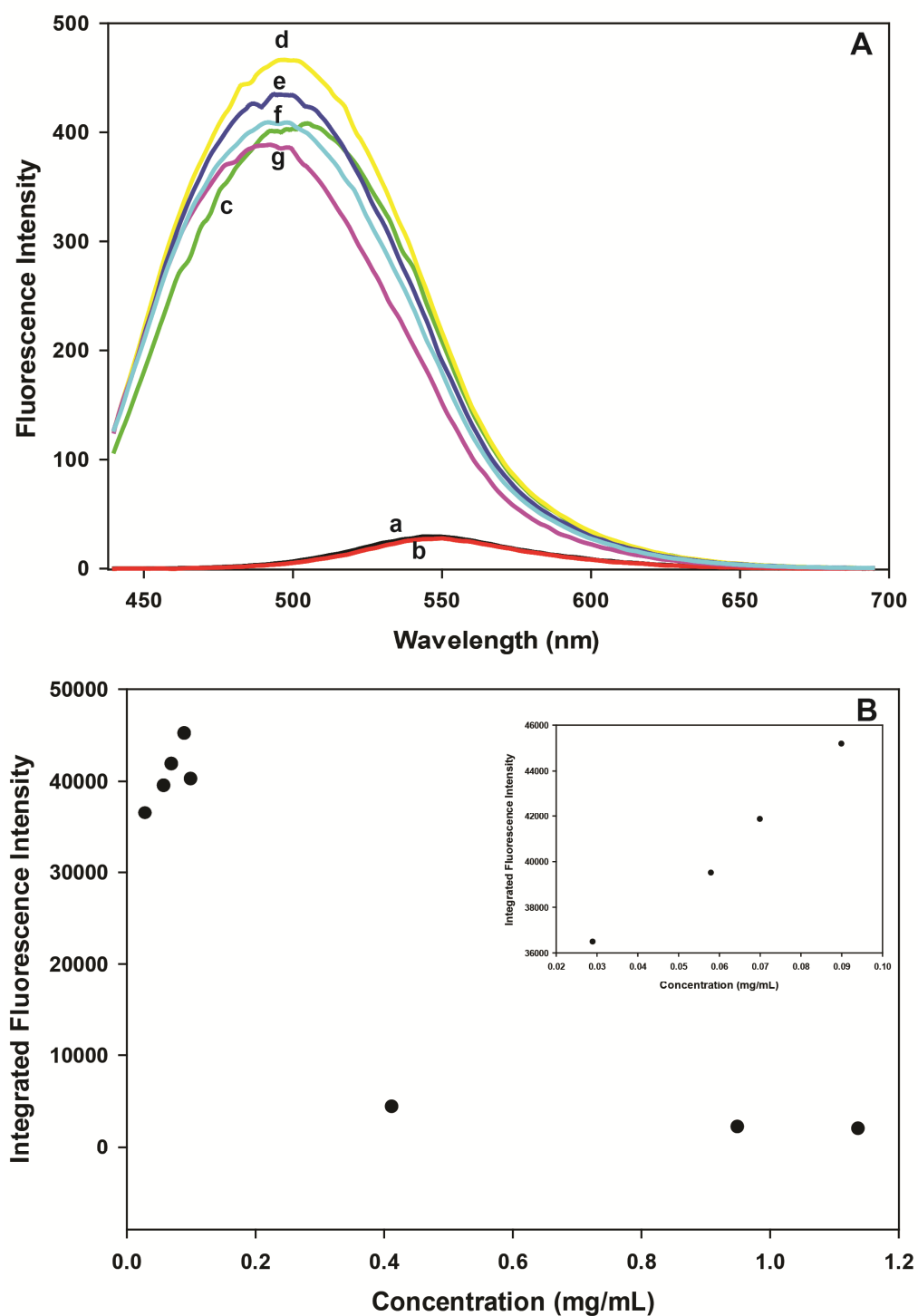


Figure S3.2: Fluorescence based solubility study of **PDTriG** in water at pH 7 at different concentrations (A), integrated fluorescence intensity (B) and linear region between 0.058 mg/mL – 0.09 mg/mL (Inset).

Section S4: Fluorescence studies of PDMonoG and PDDiG in DMSO and water.

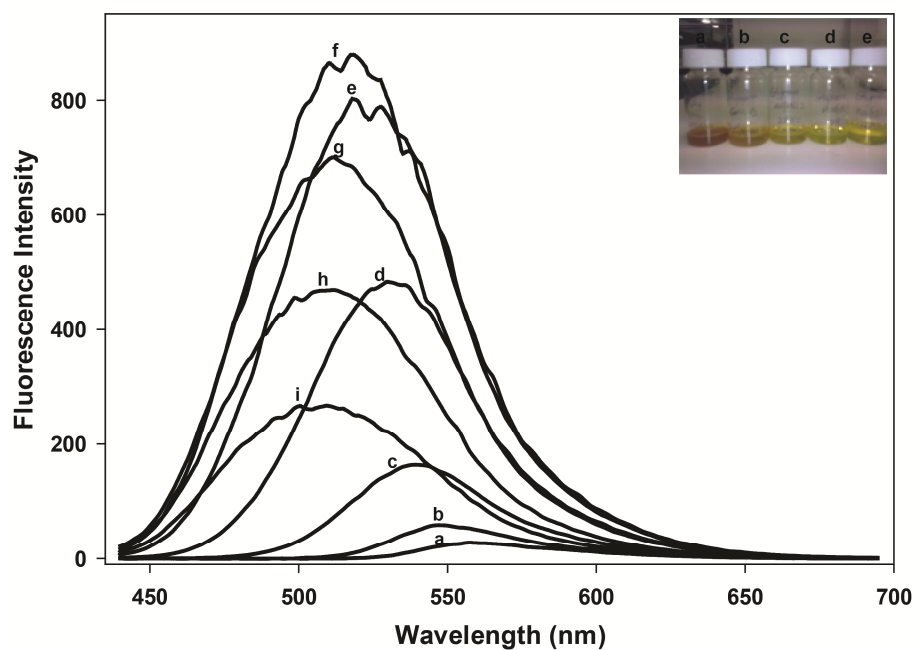


Figure S4.1 Fluorescence spectra of **PDMonoG** at (a) 2 mg/mL, (b) 1 mg/mL, (c) 0.5 mg/mL, (d) 0.25 mg/mL, (e) 0.125 mg/mL, (f) 0.062 mg/mL, (g) 0.031 mg/mL, (h) 0.015 mg/mL, and (i) 0.007 mg/mL in DMSO.

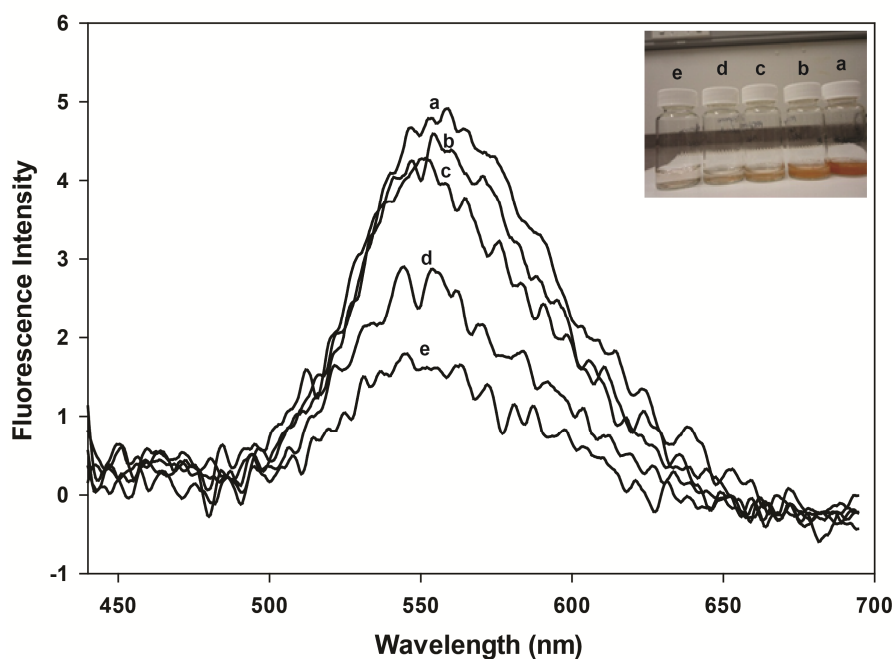


Figure S4.2 Fluorescence spectra of **PDMonoG** at (a) 0.5 mg/mL, (b) 0.25 mg/mL, (c) 0.125 mg/mL, (d) 0.062 mg/mL and (e) 0.031 mg/mL in water.

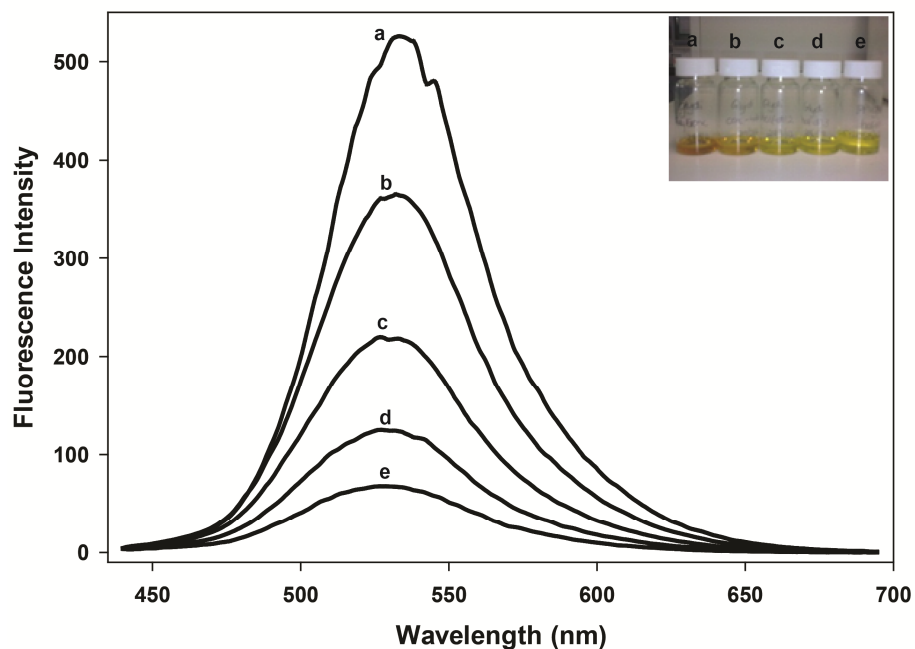


Figure S4.3 Fluorescence spectra of **PDDiG** at (a) 1 mg/mL, (b) 0.5 mg/mL, (c) 0.25 mg/mL, (d) 0.125 mg/mL and (e) 0.0625 mg/mL in DMSO.

Section S5: Quantum yield measurements of **PDMonoG** and **PDTriG** in DMSO and DMSO: water mixtures

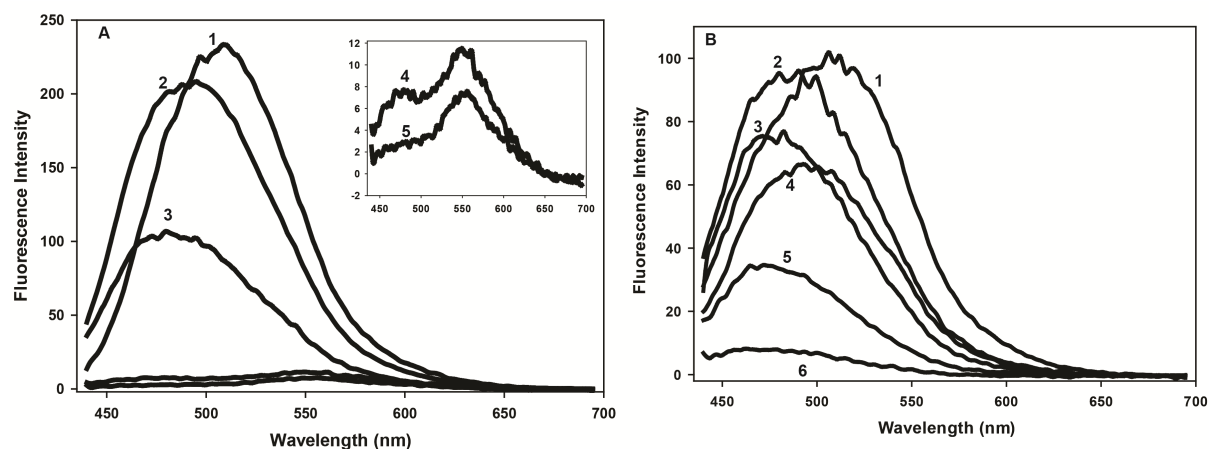


Figure S5.1 (A) Fluorescence of **PDMonoG** in DMSO (1) and DMSO-water ratios v/v (80:20 (2), 60:40 (3), 50:50 (4), 30:70 (5)). (B) Fluorescence of **PDTriG** in DMSO (1), water (6) and DMSO-water ratios v/v (80:20 (2), 60:40 (3), 50:50 (4), 30:70 (5)).

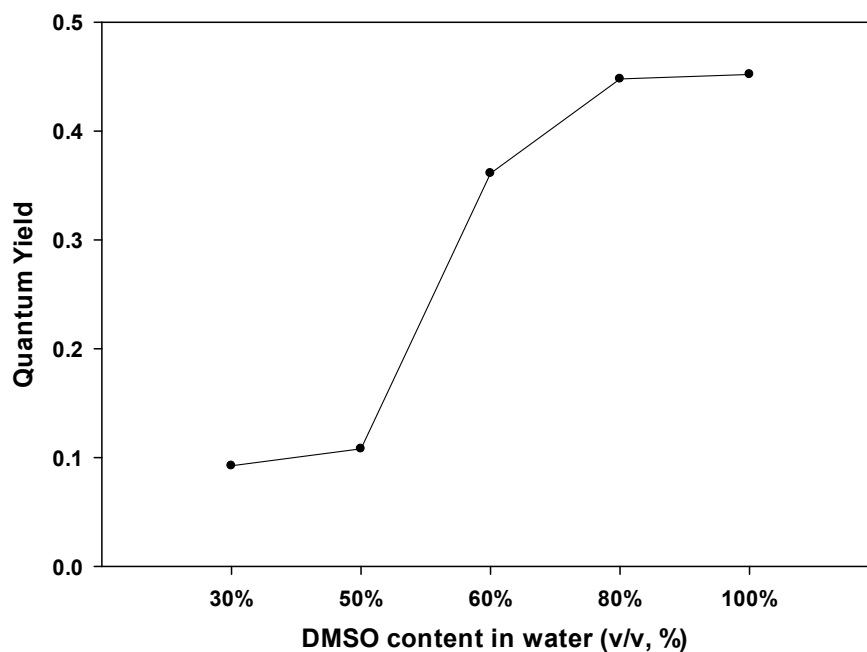


Figure S5.2 Quantum yield of **PDMonoG** in DMSO: water ratios (v/v).

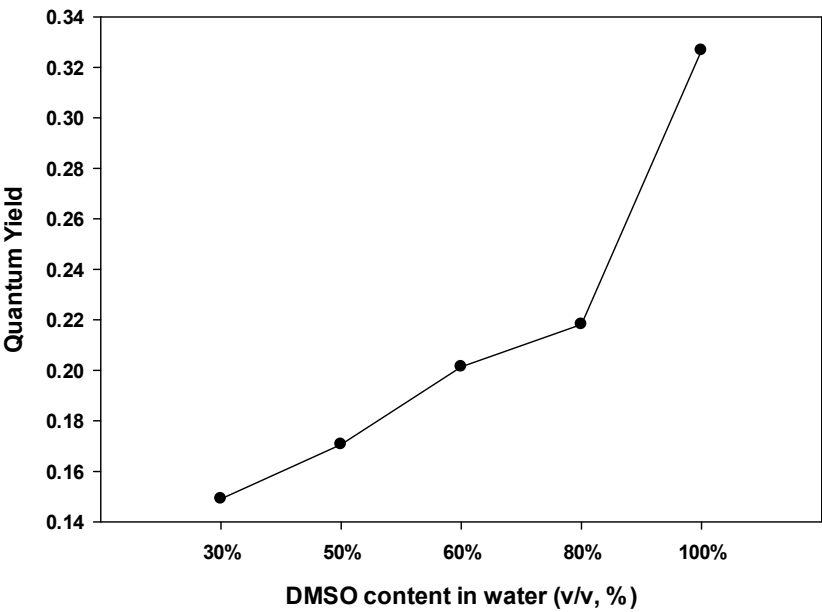


Figure S5.3 Quantum yield of **PDTriG** in DMSO: water ratios (v/v).

Section S6: Electrochemical properties and optical band gaps of the polymers

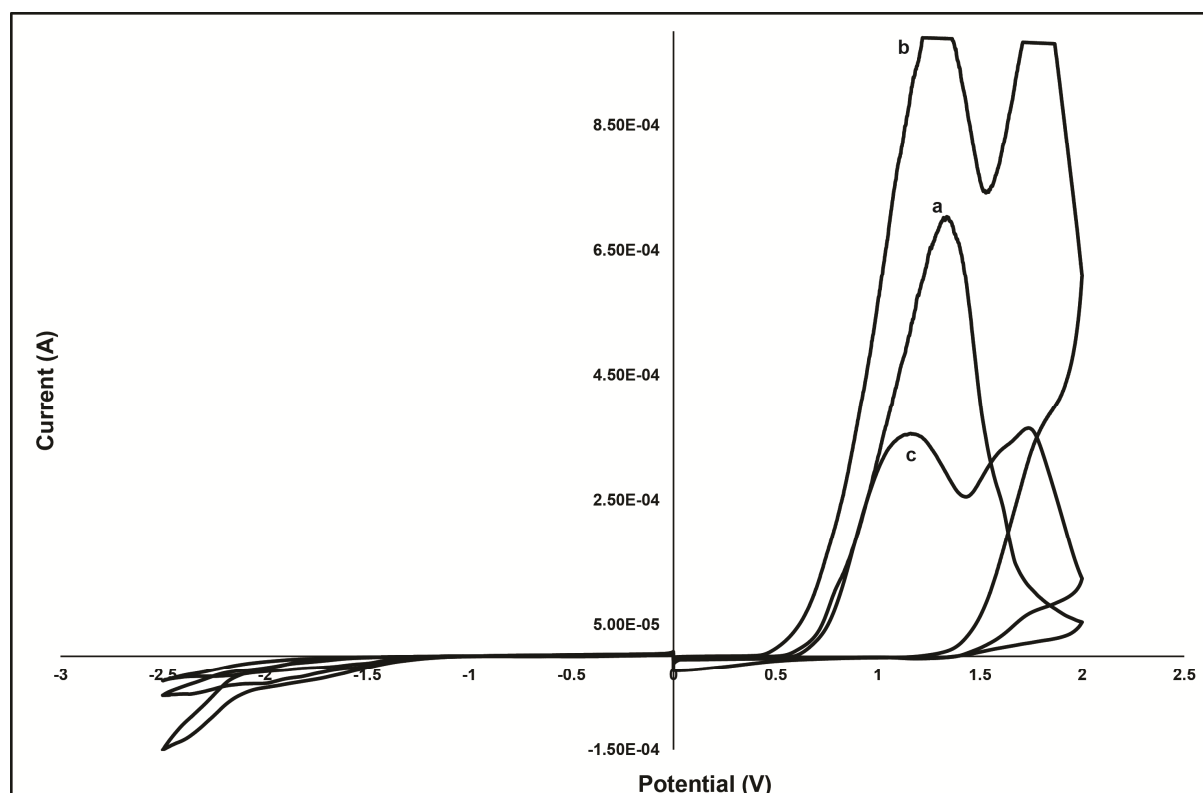


Figure S6.1 Cyclic voltammograms of **PMDH**, **PDDMe** and **PDMonoG** coated on glassy carbon electrodes in acetonitrile and 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ with a scan rate of 0.1 Vs^{-1} .

Polymer	E_{ox} vs FOC ^a (V)	E_{red} vs FOC ^a (V)	E_{HOMO} ^b (eV)	E_{LUMO} ^b (eV)	E^{elc} (eV)	E^{opt} (eV)
PMDH	0.75	-1.66	-5.46	-3.05	2.41	2.38
PDDMe	0.70	-1.85	-5.41	-2.86	2.55	2.30
PDMonoG	0.72	-1.94	-5.43	-2.77	2.66	2.44
PDDiG	-	-	-	-	-	2.34
PDTriG	-	-	-	-	-	2.25

^a $E_{\text{FOC}} = 0.47 \text{ V vs Ag/AgCl}$. ^b $E_{\text{HOMO}} = -(E_{\text{ox,FOC}} + 4.71) \text{ eV}$;

$E_{\text{LUMO}} = -(E_{\text{red,FOC}} + 4.71) \text{ eV}$. $E^{\text{elc}} = \text{Electrochemical band gap}$: $E^{\text{elc}} = \text{LUMO} - \text{HOMO}$.

$E^{\text{opt}} = \text{Optical band gap}$.

Table S6.2 Electrochemical properties of PPVs synthesized.

Monomer	MDH	DDE	MonoG	DiG	TriG
λ_{max} (nm)	352.75	376.64	378.24	382.15	374.02
E_{gap} (eV)	3.79	3.63	3.62	3.58	3.67

Table S6.1 λ_{max} obtained from the UV-Vis spectra predicted from Gaussian calculations on the monomers and the band gap calculated from the molecular orbitals from the Gaussian calculations.

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