

MEH-PPV by Microwave Assisted Ring Opening Metathesis Polymerisation

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Supplementary Information

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Experimental

General Methods

The monomer, 4,12-di-2'-ethylhexyloxy-7,15-dimethoxy-[2.2]paracyclophane-1,9-diene, was synthesised by a modification of established procedures.^{S1}

The Gilch synthesised MEH-PPV was purchased from Sigma-Aldrich and used without further purification, the GPC as used for all other polymers gave an M_n of 106,800 with a PDI of 6.96. All experiments were performed under an argon atmosphere using standard Schlenk techniques. The reactions were conducted in sealed 10 mL tube by microwave dielectric heating in a CEM Explorer or CEM Discover instrument with a maximum power output of 300 W. The reaction temperature (80 °C) was reached in 100 s for all reactions and the time recorded is the time at which the reaction was held at 80 °C. Polymer molecular weight was determined by GPC in tetrahydrofuran (THF) solution using a Viscotek GPCmax VE2001 and a Viscotek VE3580 RI detector (referenced to polystyrene standards). ¹H NMR spectra were obtained using a Bruker 400 MHz spectrometer. UV-Vis absorption spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and fluorescence spectra were recorded on a Varian Cary Eclipse fluorimeter. CV was performed at 100 mV s⁻¹ in a BASI Epsilon electrochemical workstation with a three-electrode cell, Ag/AgNO₃ as reference electrode, platinum wire as counter electrode and polymer film on a platinum plate as the working electrode in argon-purged anhydrous 0.10 M tetrabutylammonium hexafluorophosphate acetonitrile solution at room temperature.

Synthesis of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (3d MEH-PPV) n =20

A microwave reactor tube was filled with 4,12-di-2'-ethylhexyloxy-7,15-dimethoxy-[2.2]paracyclophane-1,9-diene, (20 mg, 0.038 mmol), and the sealed tube was purged with vacuum and filled with argon via needle. A stock solution of third generation Grubbs catalyst (8.50 mg, 0.0096 mmols) was dissolved in 2.5 ml of anhydrous 1,2-dichloroethane under an argon atmosphere. Precisely 0.5 ml of this catalyst solution was injected into the tube containing the monomer. The tube was placed on a vortex mixer for 1 minute to ensure homogeneous mixing. The tube was then transferred to the CEM microwave reactor and heated at a temperature of 80 °C for 1 hour. After this period the reaction mixture was cooled to room temperature and excess ethyl vinyl ether (2 ml, 20.8 mmol) was injected into the tube to quench the reaction. After stirring for an additional 20 hours at room temperature the

reaction mixture was evaporated in vacuo. The crude polymer was then redissolved in the minimum amount of dichloromethane (DCM) and transferred to a Celite plug filled with methanol. This resulted in precipitation of the polymer, which was washed with excess methanol and then redissolved in DCM and collected. The solvent was removed under reduced pressure allowing the isolation of polymer **3d** as a film. Recovered yield of polymer **3d** was 17 mg (85%).

Polymer **3a**: ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.35 (m, 4H, Ar), 7.20-7.12 (m, 2H, cis vinyl), 6.88-6.64 (m, 2H, trans vinyl), 3.97 (s, 3H, trans OCH_3), 3.89 (m, 2H, trans OCH_2), 3.50 (s, 3H, cis OCH_3), 3.49 (m, 2H, cis, OCH_2), 1.84 (m, 1H, trans CH), 1.76 (m, 1H, cis CH), 1.56-1.26 (m, 16H, CH_2), 1.04-0.83 (m, 12H, CH_3) ppm. GPC: $M_n = 34100$; $M_w/M_n = 1.28$. UV-vis: $\lambda_{\text{max}} = 456$ nm, $\varepsilon = 31400$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF, and $\lambda_{\text{max}} = 458$ nm in film. PL: $\lambda_{\text{PL}} = 552$ nm (THF) and 592 nm (film).

Polymer **3b**: ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.35 (m, 4H, Ar), 7.20-7.12 (m, 2H, cis vinyl), 6.88-6.64 (m, 2H, trans vinyl), 3.97 (s, 3H, trans OCH_3), 3.89 (m, 2H, trans OCH_2), 3.50 (s, 3H, cis OCH_3), 3.49 (m, 2H, cis, OCH_2), 1.84 (m, 1H, trans CH), 1.76 (m, 1H, cis CH), 1.56-1.26 (m, 16H, CH_2), 1.04-0.83 (m, 12H, CH_3) ppm. GPC: $M_n = 23800$; $M_w/M_n = 1.21$. UV-vis: $\lambda_{\text{max}} = 467$ nm, $\varepsilon = 26400$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF, and $\lambda_{\text{max}} = 462$ nm in film. PL: $\lambda_{\text{PL}} = 552$ nm (THF) and 592 nm (film).

Polymer **3c**: ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.35 (m, 4H, Ar), 7.20-7.12 (m, 2H, cis vinyl), 6.88-6.64 (m, 2H, trans vinyl), 3.97 (s, 3H, trans OCH_3), 3.89 (m, 2H, trans OCH_2), 3.50 (s, 3H, cis OCH_3), 3.49 (m, 2H, cis, OCH_2), 1.84 (m, 1H, trans CH), 1.76 (m, 1H, cis CH), 1.56-1.26 (m, 16H, CH_2), 1.04-0.83 (m, 12H, CH_3) ppm. GPC: $M_n = 16000$; $M_w/M_n = 1.22$. UV-vis: $\lambda_{\text{max}} = 455$ nm, $\varepsilon = 26600$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF, and $\lambda_{\text{max}} = 458$ nm in film. PL: $\lambda_{\text{PL}} = 552$ nm (THF) and 592 nm (film).

Polymer **3d**: ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.35 (m, 4H, Ar), 7.20-7.12 (m, 2H, cis vinyl), 6.88-6.64 (m, 2H, trans vinyl), 3.97 (s, 3H, trans OCH_3), 3.89 (m, 2H, trans OCH_2), 3.50 (s, 3H, cis OCH_3), 3.49 (m, 2H, cis, OCH_2), 1.84 (m, 1H, trans CH), 1.76 (m, 1H, cis CH), 1.56-1.26 (m, 16H, CH_2), 1.04-0.83 (m, 12H, CH_3) ppm. GPC: $M_n = 11200$; $M_w/M_n = 1.18$. UV-vis: $\lambda_{\text{max}} = 444$ nm, $\varepsilon = 32500$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in

THF, and $\lambda_{\max} = 444$ nm in film. PL: $\lambda_{\text{PL}} = 550$ nm (THF) and 592 nm (film).

Photoisomerisation of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV 3)

Polymer **3d** prepared as above (20 mg) was dissolved in THF (10 ml). The solution was irradiated with a SYNGENE GLLS-6 UV lamp (LF-206LS 6W tube) at 365 nm. The polymer solution was placed in a quartz vessel under Ar and irradiated at a distance of 10 cm from the lamp. The ^1H NMR spectrum of the polymer was recorded every 12 hours until complete conversion was achieved after 36 hours. After isomerisation the solvent was removed under reduced pressure and polymer **4d** isolated as a film.

Polymer **4a**: ^1H NMR (400 MHz, CDCl_3): δ 7.55 (m, 4H, Ar), 7.20 (m, 4H, vinyl), 3.97 (s, 6H, OCH_3), 3.95 (s, 4H, OCH_2), 1.84 (m, 6H, CH), 1.57-1.38 (m, 16H, CH_2), 1.02 (t, $J = 7.2\text{Hz}$, 6H, CH_3), 0.92 (t, $J = 6.7$ Hz, 6H, CH_3) ppm. GPC: $M_n = 90600$; $M_w/M_n = 1.32$. UV-vis: $\lambda_{\max} = 510$ nm, $\epsilon = 45000$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF and 537 nm in film. PL: $\lambda_{\text{PL}} = 555$ nm (THF) and 596 nm (film).

Polymer **4b**: ^1H NMR (400 MHz, CDCl_3): δ 7.55 (m, 4H, Ar), 7.20 (m, 4H, vinyl), 3.97 (s, 6H, OCH_3), 3.95 (s, 4H, OCH_2), 1.84 (m, 6H, CH), 1.57-1.38 (m, 16H, CH_2), 1.02 (t, $J = 7.2\text{Hz}$, 6H, CH_3), 0.92 (t, $J = 6.7$ Hz, 6H, CH_3) ppm. GPC: $M_n = 57000$; $M_w/M_n = 1.34$. UV-vis: $\lambda_{\max} = 508$ nm, $\epsilon = 52500$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF and 537 nm in film. PL: $\lambda_{\text{PL}} = 554$ nm (THF) and 596 nm (film).

Polymer **4c**: ^1H NMR (400 MHz, CDCl_3): δ 7.55 (m, 4H, Ar), 7.20 (m, 4H, vinyl), 3.97 (s, 6H, OCH_3), 3.95 (s, 4H, OCH_2), 1.84 (m, 6H, CH), 1.57-1.38 (m, 16H, CH_2), 1.02 (t, $J = 7.2\text{Hz}$, 6H, CH_3), 0.92 (t, $J = 6.7$ Hz, 6H, CH_3) ppm. GPC: $M_n = 38800$; $M_w/M_n = 1.27$. UV-vis: $\lambda_{\max} = 502$ nm, $\epsilon = 49600$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF and 530 nm in film. PL: $\lambda_{\text{PL}} = 554$ nm (THF) and 596 nm (film).

Polymer **4d**: ^1H NMR (400 MHz, CDCl_3): δ 7.55 (m, 4H, Ar), 7.20 (m, 4H, vinyl), 3.97 (s, 6H, OCH_3), 3.95 (s, 4H, OCH_2), 1.84 (m, 6H, CH), 1.57-1.38 (m, 16H, CH_2), 1.02 (t, $J = 7.2\text{Hz}$, 6H, CH_3), 0.92 (t, $J = 6.7$ Hz, 6H, CH_3) ppm. GPC: $M_n = 28800$; $M_w/M_n = 1.30$. UV-vis: $\lambda_{\max} = 502$ nm, $\epsilon = 49200$ $\text{M}^{-1} \text{cm}^{-1}$ (based on repeating unit, $-\text{C}_{34}\text{H}_{48}\text{O}_4-$) in THF and 528

nm in film. PL: $\lambda_{\text{PL}} = 554$ nm (THF) and 595 nm (film).

Reference

- S1 a) V. Boekelheide, P.H. Anderson and T. A. Hylton, *J. Am. Chem. Soc.*, 1974, **96**, 1558; b) R. H. Mitchell, T. Otsubo, V. Boekelheide, *Tetrahedron Lett.*, 1975, **16**, 219; c) S. E. Potter, I. O. Sutherland, *J. Chem. Soc. Chem. Commun.*, 1973, 520.

Table S11 Physical, optical and electronic properties of MEH-PPV (**3**, **4** and **5**)

Polymer	λ_{max} /nm		λ_{PL} /nm		ϕ_{PL}^a	$E_{\text{g-opt}}^b$ /nm		$E_{1/2}$ /V vs Ag/AgNO ₃ ^c		HOMO /eV ^d	LUMO /eV ^e	$E_{\text{g-ec}}$ /eV ^f
	solution	film	solution	film		solution	film	oxidation	reduction			
3a	456	458	552	592	0.07	2.24	2.06	0.56	-2.09	-5.08	-2.66	2.42
3b	467	462	552	592	0.08	2.24	2.07	0.50	-2.13	-5.09	-2.64	2.44
3c	455	458	552	592	0.07	2.25	2.08	0.51	-2.10	-5.08	-2.62	2.46
3d	444	444	550	592	0.06	2.25	2.08	0.55	-2.11	-5.08	-2.62	2.46
4a	510	537	555	596	0.10	2.23	2.05	0.45	-2.01	-5.03	-2.71	2.31
4b	508	537	554	596	0.10	2.23	2.05	0.43	-2.09	-5.02	-2.64	2.38
4c	502	530	554	596	0.10	2.23	2.05	0.46	-2.12	-5.05	-2.63	2.42
4d	502	528	554	595	0.10	2.23	2.05	0.43	-2.08	-5.04	-2.64	2.40
5 (Gilch)	498	530	554	592	0.10	2.24	2.03	0.53	-2.14	-4.99	-2.63	2.36

^a PL quantum yields were calculated using quinine sulfate standards; ^b $E_{\text{g-opt}}$ = optical band gap; ^c CV of polymer films on Pt plate were measured in MeCN solution containing 0.10 M *n*-Bu₄NPF₆.

^d HOMO = $-(4.8 + E_{\text{pa-onset}} - E_{\text{Fc}})$. Half wave potential of ferrocene, E_{Fc} (= 0.105 V vs

Ag/AgNO₃), was measured in MeCN solution. ^e LUMO = $-(4.8 + E_{\text{pc-onset}} - E_{\text{Fc}})$; ^f

Electrochemical band gap was calculated from $E_{\text{g-ec}} = \text{LUMO} - \text{HOMO}$.

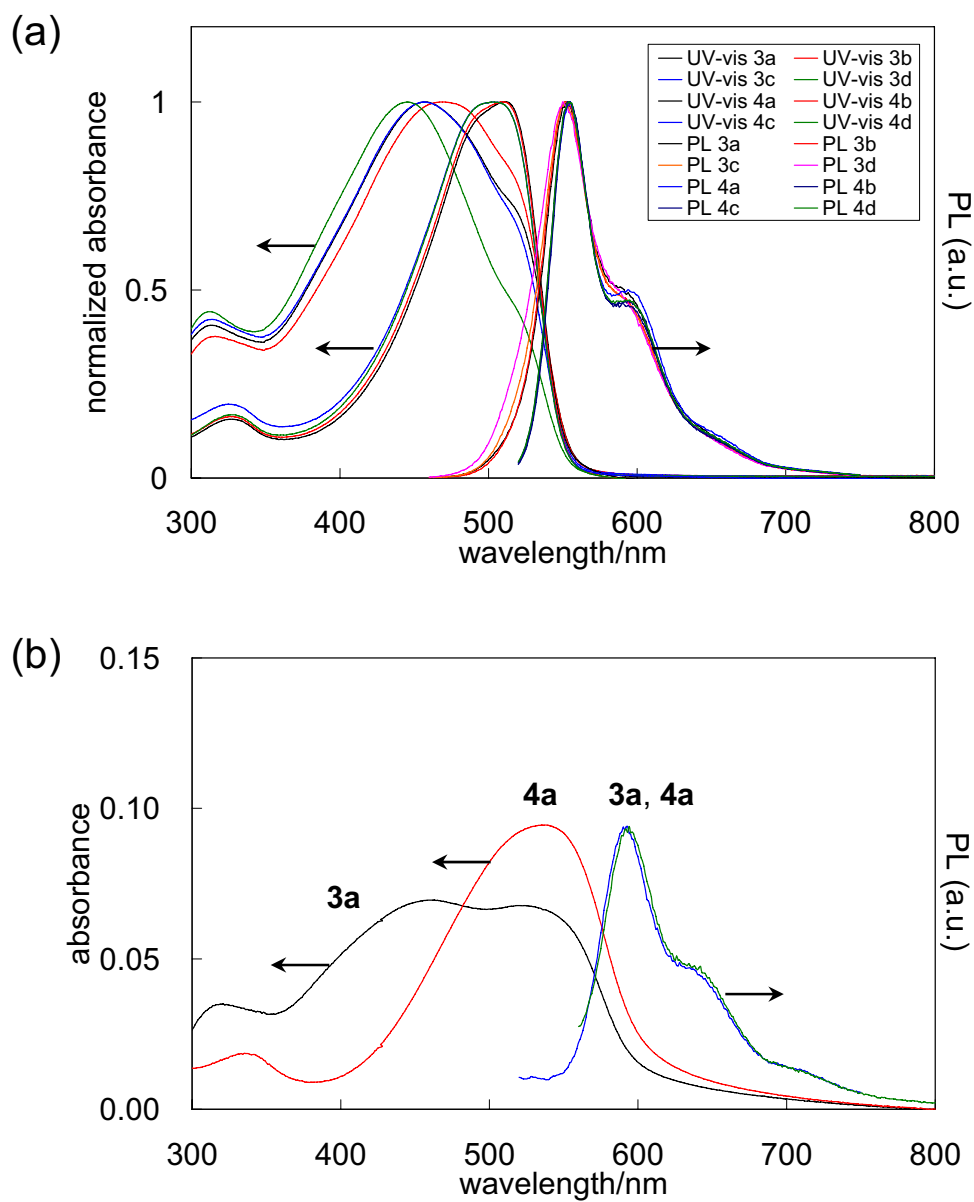


Fig. S11 UV-vis absorption and fluorescence spectra of MEH-PPV (a) in THF and (b) in a thin film (**3a** and **4a**).

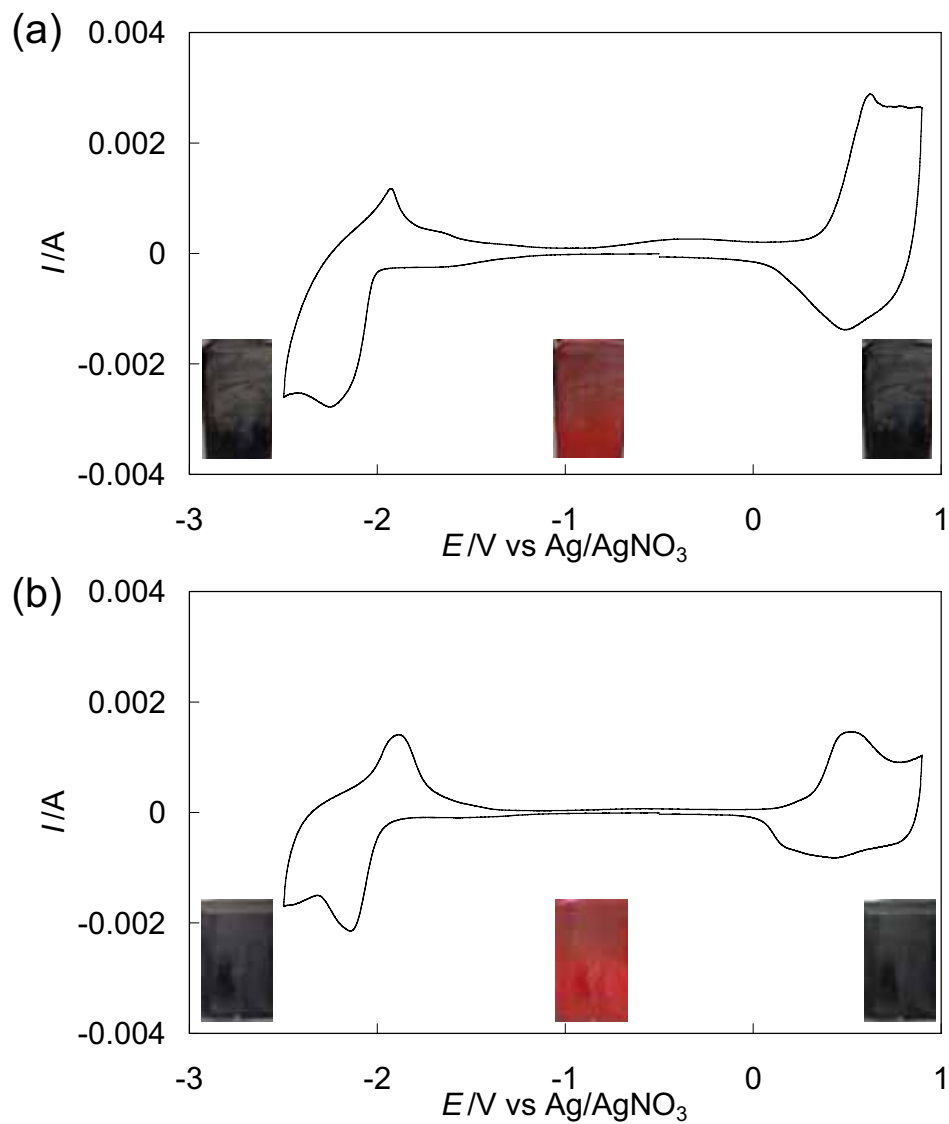


Fig. SI2 Cyclic voltammograms of films of (a) polymer 3a and (b) polymer 4a. Images of films on Pt plate at applied potential are inserted.