Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

Perdeuteration of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (d-MEH-PPV): control of microscopic charge-carrier spin-spin coupling and of magnetic-field effects in optoelectronic devices

Dani M. Stoltzfus, Gajadhar Joshi, Henna Popli, Shirin Jamali, Marzieh Kavand, Sebastian Milster, Tobias Grünbaum, Sebastian Bange, Adnan Nahlawi, Mandefro Y. Teferi, Sabastian I. Atwood, Anna E. Leung, Tamim A. Darwish, Hans Malissa*, Paul L. Burn*, John M. Lupton*, and Christoph Boehme*

S1. Supporting figures



Fig. S1 GPC trace of d-MEH-PPV.



Fig. S2 Film UV-visible spectrum of d-MEH-PPV and h-MEH-PPV. The localized (at \approx 210 nm) to the delocalized (at \approx 500 nm) π - π * transitions for both materials are essentially the same indicating that they have similarly delocalized chromophores.



Fig. S3 Infrared spectrum of d-MEH-PPV.



Fig. S4 a) Monomer: 1,4-bis[chloromethyl]-2-[(2-ethylhexyl)oxy]-5-methoxybenzene-d₂₆ b) Polymer: poly[2-(2-ethylhexyloxy-d₁₇)-5-methoxy-d₃-1,4-phenylenevinylene-d₄] (d-MEH-PPV).

S2. Synthesis of d-MEH-PPV

Monomer: Chemicals, including paraformaldehyde-d₂ (98% isotopic purity), iodomethane-d₃ (99.5% isotopic purity) and LiAlD₄ (98% isotopic purity) were used as received from Sigma-Aldrich. Solvents were used as received from Sigma Aldrich or were dried following literature methods. NMR spectroscopy solvents were used as received from Cambridge Isotope Laboratories Inc. D₂O (99.8%) was purchased from AECL, Canada. ¹H NMR (400 MHz), ²H NMR (61.4 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker 400 MHz spectrometer at 298 K. Chemical shifts were referenced to the residual signal of the solvent. ²H NMR spectroscopy was performed using the lock channel of the probe for direct observation. Electrospray ionization mass spectra were recorded on a 4000 QTrap AB SCIEX mass spectrometer. The overall deuteration of 2-ethylhexanoic acid was calculated by ER MS (enhanced resolution-MS) using the isotope distribution of the different isotopologues by analyzing the area under each MS peak, which corresponds to a defined number of deuterium atoms. The contribution of the carbon 13 (natural abundance) to the value of the area under each [X+1] MS signal was subtracted based on the relative amount found in the unlabelled version. The deuteration of hydroquinone was calculated using ¹³C NMR spectroscopy according to the method reported by Darwish et al.^{S1}

Polymer: All reagents were used as received unless otherwise stated. Tetrahydrofuran was dried on an LC systems solvent purification system prior to use. UV-visible spectrophotometry was performed using a Cary 5000 UV-VIS spectrophotometer. The thin film of the polymer was spin-coated onto a fused silica substrate from chlorobenzene. FT-IR spectroscopy was performed on a solid sample using a Perkin-Elmer Spectrum 100 FT-IR spectrometer with an ATR attachment. Gel Permeation Chromatography (GPC) of the polymer was carried out on a Waters GPC 1515 system equipped with Empower software. The instrument was connected to a refractive index (RI) and an UV-vis detector, and the two columns [Styragel HT-3 and Styragel HT-6E (300 mm + 300 mm lengths, 7.8 mm diameter)] were kept at 40°C with a flow rate of 1 mL/min. No flow marker was used during the analysis. Narrow polystyrene standards in the M_w range of 1350 Da to 1300000 Da were used to create a calibration curve. The sample was prepared in tetrahydrofuran at a concentration of 1 mg/mL and filtered through a 0.45 micron PTFE filter before injection.

*Synthesis of monomer 1,4-bis[chloromethyl]-2-[(2-ethylhexyl)oxy]-5-methoxybenzene-d*₂₆: the structure is shown in Fig. S4a.

Hydroquinone-d4: Hydroquinone (10.19 g, 92.54 mmol), NaOD (40% wt. in D₂O, 5.65 mL, 80.5 mmol), D₂O (120 mL), Pt/C (10% wt., 200 mg) and Pd/C (10% wt., 200 mg) were placed into a 600 mL Parr reactor, which was purged with nitrogen whilst stirring, then hydrogen whilst stirring, and then sealed. The vessel was heated to 150°C (maximum pressure observed: 4 bar) for 24 h, then the vessel was cooled and the contents removed. The reaction mixture was filtered through Celite to remove the catalysts and the filtrate was acidified to pH 2 with aqueous sulfuric acid (1 M). The mixture was extracted into diethyl ether (3×150 ml) and the combined organic extracts were filtered through a short silica plug using ether as eluent. The filtrate was collected and the solvent removed to provide an orange solid, which was suspended in cold ethylacetate:petroleum ether (3:7) and then filtered through a Buchner funnel to afford an off-white solid. The filtrate was collected and the solvent removed with the solid re-suspended in cold ethylacetate:petroleum ether (3:7). The mixture was filtered through a Buchner funnel to provide a second crop of an off-white solid, which was combined with the first to give hydroquinone-d₄ (6.01 g, 53%). ¹H NMR (DMSO-d₆, 400 MHz) δ 6.55 (s, residual), 8.60 (s, OH). ²H NMR (DMSO-d₆, 61.4 MHz) δ 6.58 (s, 4 D). ^{13}C NMR {1H-decoupled} (DMSO-d_6, 100 MHz) δ 115.3 (m), 149.6 (s). ^{13}C NMR {1H and ²H-decoupled} (DMSO-d₆, 100 MHz) δ 115.3 (s), 149.6 (s).

*4-Methoxyphenol-d*₇: A mixture of potassium carbonate (2.67 g, 19.3 mmol) and hydroquinone-d₄ (2.00 g, 17.5 mmol) in anhydrous acetone (50 mL) was stirred at room temperature for 1.5 h before methyliodide-d₃ (1.38 mL, 22.2 mmol) was added dropwise. The mixture was stirred for 2 h at room temperature and then potassium carbonate (702 mg, 5.08 mmol) and methyliodide-d₃ (970 µL, 16.0 mmol) (dropwise) were added sequentially. The mixture was allowed to stir at room temperature overnight and then filtered. The filtrate was collected and the solvent removed before the residue was dissolved in water (20 ml). The solution was acidified to pH 1 with hydrochloric acid (1 M) before being extracted with ethylacetate (3×100 mL). The combined organic extracts were filtered through a short silica plug using ethylacetate as eluent. The filtrate was collected and the solvent removed. The residue was purified by flash column chromatography over silica using ethylacetate:petroleum ether mixtures (1:4 to 3:7) as eluent, with the fractions containing the product visualized with iodine to afford 4-methoxyphenol-d₇ as a yellow crystalline solid (725 mg, 32%). ¹H NMR (CDCl₃, 400 MHz) δ 3.73 (s, residual), 4.59 (br s, OH), 6.77 (s, residual), 6.79 (s, residual).

²H NMR (CDCl₃, 61.4 MHz) δ 3.74 (s, 3 D), 6.83 (s, 4 D). ¹³C NMR {¹H-decoupled} (CDCl₃, 100 MHz) δ 55.1 (m), 114.6 (m), 115.8 (m), 149.5 (s), 153.8 (s). ¹³C NMR {¹H and ²H-decoupled} (CDCl₃, 100 MHz) δ 55.1, 114.6, 115.8, 149.5, 153.8.

2-Ethylhexanoic acid-d₁₅: to each of two 600 mL Parr reactors was added 2-ethylhexanoic acid (13.0 g, 90.1 mmol), D₂O (120 mL), NaOD (40% wt. in D₂O, 7.00 mL, 99.7 mmol) and Pt/C (10% wt., 400 mg). The vessels were purged with nitrogen whilst stirring, then sealed and heated to 220°C for 3 d (maximum pressure observed: 22 bar). The vessels were cooled and the contents were filtered through Celite to remove the catalyst. The filtrate was collected and acidified to pH 2 with hydrochloric acid (1 M). The aqueous mixture was then extracted with ethylacetate (3×200 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and the solvent removed to afford 2-ethylhexanoic acid-d₁₅ (27.04 g, 90.5% D by MS, 95%). The material was subjected to a second deuteration cycle as follows: to each of two 600 mL Parr reactors were added 2-ethylhexanoic acid-d₁₅ (13.50 g, 90.5% D by MS, 85.3 mmol), D₂O (120 mL), NaOD 40% wt. in D₂O, 6.60 ml, 94.0 mmol) and Pt/C (10% wt., 400 mg). The vessels were purged with nitrogen whilst stirring, then sealed and heated to 220°C for 3 d (maximum pressure observed: 22 bar). The vessels were cooled and the contents were filtered through Celite to remove the catalyst. The filtrate was acidified to pH 2 with hydrochloric acid (1 M) then extracted with ethylacetate (3×200 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and the solvent removed to afford 2-ethylhexanoic acid-d₁₅ (25.8 g, 96.1% D by MS, 96%). ¹H NMR (CDCl₃, 400 MHz) δ 0.83 (s, residual), 0.88 (s, residual), 1.26 (s, residual), 1.43 (s, residual), 1.50 (s, residual), 1.58-1.59 (complex, residual), 2.25 (s, residual). ²H NMR (CDCl₃, 61.4 MHz) δ 0.84-0.90 (complex, 6 D), 1.25 (s, 4 D), 1.45-1.59 (complex, 4 D), 2.25 (s, 1 D). ¹³C NMR {¹H-decoupled} (CDCl₃, 100 MHz) δ 10.8 (m), 12.9 (m), 21.5 (m), 24.4 (m), 28.3 (m), 30.7 (m), 46.4 (m), 183.1 (s). ¹³C NMR {¹H and ²H-decoupled} (CDCl₃, 100 MHz) δ 10.9, 13.0, 21.6, 24.3, 28.4, 30.6, 46.5, 183.2. MS (ESI-) m/z calculated for C₈D₁₅O₂ [M-H]⁻ as 158.2; found: 158.2. Deuteration: 96.1% by MS: isotope distribution: *d*₁₂ 2.0%, *d*₁₃ 8.6%, *d*₁₄ 34.0%, d_{15} 55.4%.

*2-Ethylhexan-1-ol-d*₁₇: A solution of 2-ethylhexanoic acid-d₁₅ (13.00 g, 96.1% D by MS, 81.6 mmol) in dry tetrahydrofuran (50 mL) was added dropwise over 2 h to an ice-cold suspension of LiAlD₄ (4.70 g, 112 mmol) in dry tetrahydrofuran (150 mL) that had been placed under a nitrogen flow. When the addition was complete, the mixture was allowed to

warm to room temperature before being heated at reflux overnight. The mixture was cooled in an ice bath and water was added slowly and cautiously to quench the remaining LiAlD₄. Aqueous sulfuric acid (1 M, 100 mL) was added and the mixture was extracted with diethyl ether (3×200 mL). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (150 mL), dried over anhydrous sodium sulfate, filtered, and the solvent removed to provide 2-ethylhexan-1-ol-d₁₇ as a clear oil (11.50 g, 96%), which required no further purification. ¹H NMR (CDCl₃, 400 MHz) δ 0.83 (s, residual), 1.21-1.35 (complex, residual), 3.50 (s, residual). ²H NMR (CDCl₃, 61.4 MHz) δ 0.85 (s, 6 D), 1.22-1.53 (complex, 9 D), 3.52 (s, 2 D). ¹³C NMR {¹H-decoupled} (CDCl₃, 100 MHz) δ 10.0 (m), 13.1 (m), 21.9 (m), 22.2 (m), 27.9 (m), 29.0 (m), 40.9 (m), 64.6 (m). ¹³C NMR {¹H and ²Hdecoupled} (CDCl₃, 100 MHz) δ 10.1, 13.0, 21.9, 22.2, 27.9, 29.0, 40.9, 64.6.

3-(Bromomethyl)heptane- d_{17} (2-ethylhexyl bromide- d_{17}): Triphenylphosphine (31.2 g, 119 mmol) was added to a solution of 2-ethylhexan-1-ol-d₁₇ (11.5 g, 78.1 mmol) in dry dichloromethane (180 mL). The mixture was stirred until the triphenylphosphine dissolved, and was then cooled in an ice bath. N-Bromosuccinimide (21.20 g, 118 mmol) was added portion-wise, allowing each portion to dissolve before the next was added. At the end of the addition, the bright yellow solution was stirred with ice bath cooling for 30 min, then allowed to warm to room temperature and stirred for an additional 4.5 h. The mixture was quenched with the addition of saturated aqueous sodium thiosulfate (100 mL). The layers were separated and the aqueous portion was extracted with dichloromethane (2×150 mL). The combined organic extracts were washed with brine (100 mL), then water (100 mL) before being filtered through a short silica plug using dichloromethane as eluent. The filtrate was collected and the solvent removed to leave a pink oil containing a suspension of a white solid. Petroleum ether was added to the mixture and the suspension was filtered through a second short silica plug using petroleum ether as eluent. The filtrate was collected and the solvent removed to afford 3-(bromomethyl)heptane-d₁₇ (13.88 g, 85%) as a clear oil. ¹H NMR (CDCl₃, 400 MHz) & 0.83-0.90 (complex, residual), 1.14-1.36 (complex, residual), 1.50 (s, residual), 3.41-3.42 (complex, residual). ²H NMR (CDCl₃, 61.4 MHz) δ 0.86 (s, 6 D), 1.19-1.37 (complex, 8 D), 1.50 (s, 1 D), 3.43 (s, 2 D). ¹³C NMR {¹H-decoupled} (CDCl₃, 100 MHz) δ 9.9 (m), 13.0 (m), 21.7 (m), 24.3 (m), 27.6 (m), 30.8 (m), 38.7 (m), 40.1 (m). ¹³C NMR {¹H and ²H-decoupled} (CDCl₃, 100 MHz) δ 9.9, 13.0, 21.7, 24.1, 27.6, 30.8, 38.7, 40.1.

 $1-[(2-Ethylhexyl)oxy]-4-methoxybenzene-d_{24}:$ 3-(Bromomethyl)heptane-d₁₇ (2.31 g, 11.0 mmol) was added to a solution of 4-methoxyphenol-d₇ (1.20 g, 9.15 mmol) in dry N,Ndimethylformamide (35 mL). Sodium tert-butoxide (1.77 g, 18.4 mmol) was added and the mixture was heated at 110°C overnight, then cooled. Saturated aqueous ammonium chloride (50 mL) was added. The mixture was extracted with dichloromethane (3×50 mL) and the combined organic extracts were washed with water (6×100 mL), dried over anhydrous sodium sulfate, filtered, and the solvent removed. The residue was purified by flash column chromatography over silica using a dichloromethane:petroleum ether mixture (1:4) as eluent (visualized with UV light) to provide $1-[(2-ethylhexyl)oxy]-4-methoxybenzene-d_{24}$ as a clear oil (2.06 g, 86%). ¹H NMR (CDCl₃, 400 MHz) δ 0.846-0.864 (complex, residual), 1.26-1.37 (complex, residual), 1.66 (s, residual), 3.73-3.76 (complex, residual), 6.82-6.84 (complex, residual). ²H NMR (CDCl₃, 61.4 MHz) δ 0.86-0.88 (complex, 6 D), 1.26-1.45 (complex, 8 D), 1.66 (s, 1 D), 3.75 (complex, 5 D), 6.88 (s, 4 D). ¹³C NMR {¹H-decoupled} (CDCl₃, 100 MHz) δ 10.1 (m), 13.1 (m), 21.9 (m), 22.7 (m), 27.9 (m), 29.4 (m), 38.4 (m), 55.1 (m), 70.5 (m), 114.3 (m), 115.2 (m), 153.6 (s), 153.7 (s). ¹³C NMR {¹H and ²H-decoupled} (CDCl₃, 100 MHz) δ 10.1, 13.1, 21.9, 22.7, 27.9, 29.4, 38.4, 55.1, 70.5, 114.3, 115.2, 153.59, 153.64.

1,4-Bis[chloromethyl]-2-[(2-ethylhexyl)oxy]-5-methoxybenzene-d₂₆: Concentrated hydrochloric acid (37%, 12.6 mL, 153 mmol) and then acetic anhydride (20.3 mL, 215 mmol) (dropwise as exothermic) were added to a mixture of 1-[(2-ethylhexyl)oxy]-4methoxybenzene-d₂₄ (2.02 g, 7.75 mmol) and paraformaldehyde-d₂ (650 mg, 20.3 mmol). When the addition was complete, the mixture was heated to 80°C overnight, before being allowed to cool to room temperature and diluted with water (50 mL). The mixture was extracted with ethylacetate (3×50 mL) and the combined organic extracts were washed with brine (100 mL), then saturated aqueous sodium hydrogen carbonate (100 mL), dried over anhydrous sodium sulfate, filtered, and then the solvent was removed to afford an off-white solid. The residue was purified by flash column chromatography over silica using dichloromethane:petroleum ether mixtures (0:1 to 1:9) as eluent to provide 1,4bis[chloromethyl]-2-[(2-ethylhexyl)oxy]-5-methoxybenzene-d₂₆ as a white solid (2.06 g, 74%). ¹H NMR (CDCl₃, 400 MHz) δ 0.86-0.89 (complex, residual), 1.26-1.47 (complex, residual), 1.70 (s, residual), 3.82-3.85 (complex, residual), 4.63 (d, J = 1.00 Hz, residual), 6.85 (s, residual), 6.91-6.92 (complex, residual). ²H NMR (CDCl₃, 61.4 MHz) δ 0.86-0.90 (complex, 6 D), 1.28-1.70 (complex, 9 D), 3.84 (complex, 5 D), 4.63 (s, 4 D). ¹³C NMR {¹Hdecoupled} (CDCl₃, 100 MHz) δ 10.4 (m), 13.0 (m), 21.9 (m), 22.9 (m), 27.9 (m), 29.5 (m), 38.5 (m), 41.0 (m), 55.6 (m), 70.6 (m), 113.4 (m), 114.1 (m), 126.7 (s), 126.9 (s), 150.97 (s), 151.02 (s). 13 C NMR { 1 H and 2 H-decoupled} (CDCl₃, 100 MHz) δ 10.2, 13.0, 21.9, 22.9, 27.9, 29.5, 38.5, 41.0, 55.6, 70.4, 113.1, 113.8, 126.7, 126.9, 150.97, 151.01. The integration of the 2 H NMR spectrum of the final compound, 1,4-bis[chloromethyl]-2-[(2-ethylhexyl)oxy]-5-methoxybenzene-d₂₆, demonstrates that the deuteration is consistent across the molecule, indicating that no D/H exchange occurred during any of the synthetic steps.

Synthesis of polymer, $poly[2-(2-ethylhexyloxy-d_{17})-5-methoxy-d_3-1,4-phenylenevinylene-d_4]$ (*d-MEH-PPV*): the structure is shown in Fig. S4b

Poly[2-(2-*ethylhexyloxy*-*d*₁₇)-5-*methoxy*-*d*₃-1,4-*phenylenevinylene*-*d*₄] (*d*-*MEH*-*PPV*): А solution of 1,4-bis[chloromethyl]-2-[(2-ethylhexyl)oxy]-5-methoxybenzene- d_{26} (0.500 g, 1.40 mmol) in anhydrous tetrahydrofuran (40 mL) was stirred at room temperature under argon. Freshly sublimed potassium tert-butoxide (0.98 g, 8.79 mmol) in anhydrous tetrahydrofuran (10 mL) was added in one portion, and the solution was stirred for 4 h at room temperature. The resulting gel was diluted with tetrahydrofuran (~500 mL) and chloroform (~500 mL) until the material was fully dissolved, and then methanol (~250 mL) was added. The precipitate was collected via vacuum filtration and was dissolved in tetrahydrofuran (400 mL) before methanol (~600 mL) was added. The mixture was centrifuged (10 min, 2000 rpm) and the majority of the supernatant removed before the precipitate was collected via vacuum filtration. The precipitate was then dissolved in tetrahydrofuran (400 mL) and methanol (600 mL) was added. The mixture was centrifuged (10 min, 2000 rpm) and the majority of the supernatant was removed before the precipitate was collected via vacuum filtration and was dried in vacuo to afford poly[2-(2-ethylhexyloxy d_{17})-2-methoxy- d_3 -1,4-phenylenevinylene- d_4] as a red powder (0.150 g, 36%); IR (solid) λ /cm⁻¹: 2212, 2099, 2067, 1448, 1395, 1293, 1219, 1108, 1072, 1055, 982, 851, 732, 719; $\lambda_{max}(film)/nm 208, 256sh, 326, 491; GPC (THF, 40^{\circ}C), M_w = 4.2x10^5, M_n = 1.3x10^5, D = 3.3.$ A GPC trace, UV-vis spectrum and an IR spectrum of d-MEH-PPV are shown in Figs. S1-3.

The molecular weight and polydispersity of the conventional h-MEH-PPV are $M_w = 3.8 \times 10^5$ and D = 4.7 as stated by the manufacturer.

We note that it is conceivable that the polymerisation process incorporates traces of metal atoms into the material, which in turn could affect spin-orbit coupling. The polymerization of

d-MEH-PPV relies on the addition of a base (potassium t-butoxide in this case) and after purification we assume that the potassium salts are removed. Although potassium is certainly not a heavy metal (Z=19) and one would therefore not expect a substantial change in the spinorbit coupling strength, we undertook additional material characterization with x-ray photoelectron spectroscopy (XPS) measurements on thin films of the polymer on silicon substrates. In order to compare d-MEH-PPV and h-MEH-PPV, both materials were measured separately. The sensitivity of the XPS measurement is approximately ~0.1 atom% (i.e. 1/1000 atoms). There is no indication of an atomic K 2p signal in the XPS spectra of either material, implying that the atomic potassium concentration is definitely less than 1/1000. There are no further signatures of metallic impurities either. From these XPS results, we conclude that metal impurities do not contribute significantly to spin-orbit coupling of electronic states in either d-MEH-PPV or in h-MEH-PPV.

S3. Analysis of the degree of deuteration d-MEH-PPV

Based on the isotopic purities of LiAlD₄, methyliodide-d₃ and paraformaldehyde-d₂, and the percentage deuteration of hydroquinone-d₄ and 2-ethylhexanoic acid-d₁₅ it was calculated that the isotopic purity of the synthesized MEH-PPV-d₂₄ would be $97\pm2\%$. The analysis was determined from the following data and assumptions:

1. Paraformaldehyde-d₂ (98% isotopic purity) was purchased from Sigma-Aldrich; the percentage deuteration of the vinylene moieties is thus 98%.

2. Iodomethane-d₃ (99.5% isotopic purity) was purchased from Sigma-Aldrich; the percentage deuteration at the methoxy methyl group is thus 99.5%.

3. The percentage deuteration at the aromatic positions was calculated having determined the deuteration of hydroquinone-d₄ via ¹H and ¹³C NMR spectroscopy. The ¹³C {¹H, ²Hdecoupled} NMR spectrum of hydroquinone-d₄ was used to determine the percentage deuteration to be 95.4±0.5%, using a comparison of the integration of the analogous carbon sites at both the quaternary and tertiary positions, according to Darwish *et al.*^{S1} The quaternary sites are represented by two resonances at 149.733 and 149.684 ppm. The resonance at 149.684 ppm (arbitrary integration of 1) is assigned as the quaternary carbon flanked by a deuterated tertiary carbon on either side. The resonance at 149.733 ppm (integrating for 0.114) is assigned as the quaternary carbon flanked by one deuterated tertiary carbon and one protonated tertiary carbon. The percentage deuteration is thus calculated by:

$$(1 + 0.114 / 2) / (1 + 0.114) = 94.9\%$$

4. The tertiary sites are represented by three resonances at 115.617, 115.451 and 115.359 ppm. The resonance at 115.359 ppm is assigned at the deuterated tertiary carbon adjacent to another deuterated tertiary carbon, while the resonance at 115.451 ppm is assigned as the deuterated tertiary carbon adjacent to a protonated tertiary carbon (combined integration of 2.144). The resonance at 115.617 is assigned as the

corresponding protonated tertiary carbon adjacent to a deuterated tertiary carbon (integration of 0.094). The percentage deuteration is thus calculated by:

$$2.144 / (2.144 + 0.094) = 95.8\%$$

5. The ¹H NMR spectrum of hydroquinone-d₄ was used to determine that the minimum percentage deuteration is 94.2%, using a comparison of the integration of the four residual aromatic protons with the hydroxyl protons.

6. The percentage deuteration of the branched alkyl chain (except for the methylene group adjacent to the ether) was calculated having determined the deuteration of the starting acid, 2-ethylhexanoic acid- d_{15} , to be 96.1±2% via mass spectrometry.

7. LiAlD₄ (98% isotopic purity) was purchased from Sigma-Aldrich; the percentage deuteration at the methylene adjacent to the ether is thus 98%.

8. The overall deuteration was determined using steps 1-5 as follows:

$$(0.98 \times 2) + (0.995 \times 3) + (0.954 \times 2) + (0.961 \times 15) + (0.98 \times 2) = x \times 24$$
$$x = (1.96 + 2.985 + 1.908 + 14.415 + 1.96)/24$$
$$x = (23.228/24)$$
$$x = 96.8\%$$

S4. Fabrication of OLEDs

d-MEH-PPV solutions were prepared inside a glove box with a N₂ atmosphere in order to avoid contamination with O₂ and H₂O. The d-MEH-PPV was dissolved in toluene at a concentration of 4.5 g/L. As the d-MEH-PPV did not dissolve easily at room temperature, the solution was heated to 50-70°C on a hot plate while stirring until it had dissolved, after several days. The OLED devices were prepared by spin-coating of the d-MEH-PPV solution on a previously deposited PEDOT:PSS/indium-tin-oxide stack on a glass substrate, as described previously.^{S2,S3} The spin-coater was operated at 550 rpm, and a time delay of 55 s was introduced between the application of the d-MEH-PPV onto the substrate and the spin-

coating procedure to ensure wetting. Thermally deposited Al/Ca electrodes were used to ensure bipolar charge-carrier injection.

S5. Experimental measurement procedures

Magnetoresistance and magneto-electroluminescence (magnetoEL) measurements were performed in a custom-made uncooled electromagnet powered by a CAEN ELS easy driver 5020 bipolar power supply. The samples were operated under a constant current of $100 \,\mu A$ using a Keithley 238 high-current source measure unit, and the change in device voltage was recorded as a function of the magnetic field and digitized with appropriate acquisition software. Note that since the devices are operated in constant current mode to be able to record the magneto-electroluminescence, the overall magnitude of magnetoresistance is smaller than that usually reported for conditions of constant voltage. The EL was collected using an optical fibre and directed onto a Femto OE-200 low-noise silicon photoreceiver, which was read out by a Keysight 34461A multimeter. We performed EDMR (using both continuous-wave excitation with magnetic field modulation and with ns-range pulsed excitation) on the same devices used for the magnetoresistance measurements in a commercial spectrometer (Bruker ElexSys 580). For X-band (~9.7 GHz) MW frequencies, we used a cylindrical dielectric resonator (Bruker FlexLine ER4118X-MD5) for magnetic resonant excitation. For other MW frequencies (between 100 MHz and 20 GHz) we used an Agilent EXG N5173B frequency generator with custom-designed EDMR probe-heads with coplanar waveguide resonators for frequencies between 1 GHz and 20 GHz, and NMR-style radiofrequency coils for frequencies between 100 MHz and 1 GHz.^{S4,S5} In all cases, EDMR was recorded by applying a constant voltage with a battery source (Stanford Research Systems SIM928), and detecting the resulting current changes at magnetic resonance with a transimpedance amplifier (SRS 570) with adjustable frequency filters, a bandpass filter for the range 100 Hz to 3 kHz for continuous wave and 100 Hz to 100 kHz for pulsed experiments. For continuous-wave measurements, the output of the current amplifier was connected to the built-in lock-in amplifier of the Bruker Elexsys E580 facility, while for pulsed measurements, it was connected to the built-in digitizer. Electrical detection of the spin echo was made by integration of the transient spin-dependent device current recorded following the echo pulse sequence, over an interval of 15 µs. This integration was achieved using a boxcar integrator (SRS 250).^{S6}

We also performed pulsed ISHE spectroscopy by measuring the electric current in the d-MEH-PPV films under ferromagnetic resonant (FMR) excitation of an adjacent ferromagnetic layer.^{S7–S9} For these measurements, dedicated devices were prepared, consisting of a 240 nm thick d-MEH-PPV layer that was located on top of two Cu electrodes and was covered with a NiFe film. FMR in the NiFe was excited by 2 μ s long MW pulses at a power of 1000 W, which caused injection of a pure spin current into the d-MEH-PPV layer for the duration of the pulse. In the polymer film, the spin current was then converted into an electromotive force through the ISHE, which in turn was detectable through a current measurement at the Cu electrodes. ISHE spectroscopy as well as details about the device structure are described in Sun *et al.*,^{S7} and a sketch of the device architecture is shown in the inset of Figure 7. The exact MW power at the position of the sample was established independently from inductively detected Rabi oscillations on a separate spin standard (a 1:1 complex of α , γ -bisdiphenylene- β -phenylallyl and benzene, BDPA, a free radical).^{S10} All of the above-described experiments were performed at room temperature.

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