

# Direct (Hetero)Arylation Polymerization: An Effective Route to 3,4-Propylenedioxythiophene-Based Polymers With Low Residual Metal Content.

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## **S1. General**

Commercially available reagents were used as received from the chemical suppliers. Reactions that required anhydrous conditions were carried out under an inert atmosphere of argon in flame-dried glassware. Toluene and THF were dried using a solvent purification system (MBraun MB Auto-SPS). The rest of solvents used for synthetic purposes were purified using conventional protocols,<sup>1</sup> except glacial acetic acid which was used as received. All reactions were monitored using F250 silica gel 60 M analytical TLC plates, with UV detection ( $\lambda = 254$  and 365 nm). Silica gel (60Å, 40–63  $\mu\text{m}$ ) was used as stationary phase for column chromatography. NMR experiments were acquired with working frequencies of 300 MHz for <sup>1</sup>H, and 75.5 MHz for <sup>13</sup>C experiments. The shifts were reported in parts per million (ppm) and referenced to the residual resonance signals of commercially available deuterated chloroform:  $\delta_{\text{H}}=7.26$  ppm,  $\delta_{\text{C}}=77.0$  ppm.<sup>2</sup> High-resolution mass spectra were recorded on a quadrupole mass analyzer instrument equipped with a direct insertion probe (ionization 70 eV) and an electron spray ionizer. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography with is internal differential refractive index detector at 40 °C, using two Waters Styragel HR-5E column (10 mm PD, 7.8 mm i.d., 300 mm length) with HPLC grade THF as the mobile phase at flow rate of 1.0 mL/min. The polymer was dissolved initially in THF (2 mg/mL), and allowed to solubilize for 24-48 hour period, in which the solution was filtered through a Millipore 0.5  $\mu\text{m}$  filter. Injections of ~200  $\mu\text{L}$  were performed and retention times were calibrated against narrow molecular weight polystyrene standards.

All reagents used for ICP-MS elemental analyses were Optima-grade and the sample preparation was done under a clean lab environment in the Department of Geological Sciences at the University of Florida. Polymer samples were

digested in pre-cleaned Savillex PFA vials (<http://www.savillex.com>) with aqua regia (3 mL HCl and 1 mL HNO<sub>3</sub>) overnight on a hot plate at 120°C. During the aqua regia digestion the polymer samples turn into a yellowish transparent mass. Although not complete dissolution of the polymer is achieved, it is expected that the elements of interest will be transferred quantitatively in solution. After digestion, part of the aqua regia solution is further diluted with 5% HNO<sub>3</sub> and loaded in the ICP-MS for analysis. Elemental analyses were performed on a ThermoFinnigan Element2 HR-ICP-MS in medium resolution mode. Quantification of results was done by external calibration using a combination of commercially available standards (<http://www.exaxol.com> and <http://www.qcdanalysts.com>) gravimetrically diluted to appropriate concentrations. All concentrations are reported in ppm in the polymer.

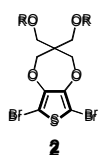
Electrochemistry was carried out in 0.1 M TBAPF<sub>6</sub>/propylene carbonate solutions, using a standard 3-electrode system: the reference electrode was Ag|Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>/0.5 M TBAPF<sub>6</sub>/ACN solution) calibrated against the Fc|Fc<sup>+</sup> ( $V_{Fc/Fc^+} = 81$  mV), the counter electrode was a Pt-wire, and the working electrode was an ITO-coated glass slide (7×50×0.7 mm<sup>3</sup>, 20 Ω/sq) from Delta Technologies Ltd. Propylene carbonate was dried using a Vacuum Atmospheres SPS. All electrochemical measurements were carried out using an EG&G PAR galvanostat/potentiostat PC-controlled using Scribner Associates 169 CorrWare II software. Absorption spectra were recorded in a double-beam Varian Cary 5000 UV-Vis-NIR spectrophotometer; the baseline correction included solution, ITO-slide, and glass cuvette. Fluorescence spectra were recorded in a Fluorolog-1057 from Horiba-Jovin-Yvon: the samples were excited using a standard 450 W xenon CW lamp and the fluorescence was detected using a multialkali PMT (250-850 nm). Correction factors for lamp signal and detector dark counts were applied using the FluorEssence® software from HJY.

## S2. Synthetic Procedures and Characterization of Products

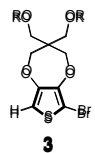
### S2.1. Materials

Write here the details about the synthesis of the materials, including monomers and synthetic intermediates (if any). Include pertinent references.

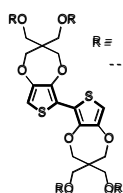
**6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (2) and 6-bromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (3):** 3,3-bis((2-ethylhexyloxy) methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**1**, 12.1 g, 27.5 mmol) was dissolved in chloroform (50 mL) and covered from light using aluminum foil. After cooling the mixture in an ice/water bath, N-bromosuccinimide (5.4 g, 30.2 mmol) was added in small portions. The bath was removed, and the mixture was allowed to react for 8 hours at room temperature. Water (25 mL) was added at once and the heterogeneous mixture was transferred to a separation funnel. After shaking, the layers were separated and the aqueous mixture was further extracted with DCM (3×50 mL). The organic mixtures were combined, dried over MgSO<sub>4</sub>, filtered and evaporated to dryness. The residual light yellow oil was purified via column chromatography in hexanes where the monobrominated and dibrominated product were collected separately. Their fractions were evaporated to dryness and the residual oils were dried under vacuum at 50-60 °C overnight.



6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**1**): Light yellow oil. 6.4 g, 39% yield. This compound has been reported previously.<sup>3</sup> Characterization data agreed accordingly (MS, <sup>1</sup>H NMR) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 4.09 (s, 4H), 3.47 (s, 4H), 3.24 (d, 4H), 1.2-1.6 (m, 18H), 0.8-1.0 (m, 12H). LRMS: [M<sup>+</sup>] 598.51, expected for C<sub>25</sub>H<sub>42</sub>O<sub>4</sub>SBr<sub>2</sub>: 598.47.



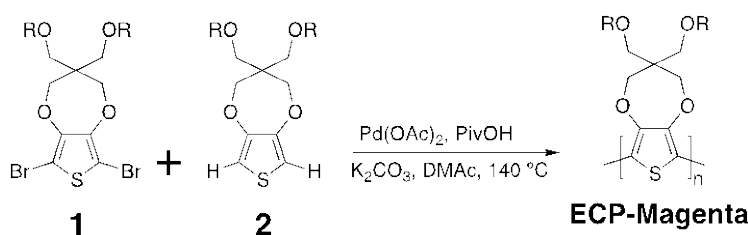
6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**3**): Light yellow oil. 4.7 g, 33% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 6.44 (s, 1H), 3.98-4.10 (d, *J* = 2.4 Hz, 4H), 3.47 (s, 4H), 3.24-3.30 (d, *J* = 0.6 Hz, 4H), 1.15-1.55 (m, 18H), 0.80-0.95 (m, 12H). HRMS: [M<sup>+</sup>] 518.2052, expected for C<sub>25</sub>H<sub>43</sub>O<sub>4</sub>SBr: 518.2065.



**3,3,3',3'-tetrakis(((2-ethylhexyl)oxy)methyl)-3,3',4,4'-tetrahydro-2H,2'H-6,6'-bithieno[3,4-b][1,4]dioxepine (**6**):** 3,3-bis((2-ethylhexyloxy) methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**1**, 2.0 g, 4.5 mmol) was dissolved in anhydrous THF (25 mL) under argon. The mixture was cooled in a dry ice/acetone bath followed by dropwise addition of *n*-BuLi (2.89 M in hexanes, 1.6 mL, 0.5 mmol). The yellow mixture was warmed up in an ice/water bath and once

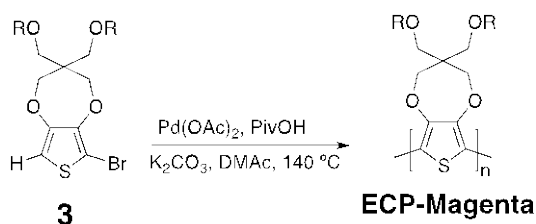
equilibrated, it was slowly transferred to a suspension of Fe(acac)<sub>3</sub> in THF at room temperature via cannula. The mixture was heated to gentle reflux and allowed to stir overnight. The resulting suspension was filtered through a pad of silica gel and eluted with hexanes until no product was found in the filtrate (monitored by TLC). The resulting organic solution was evaporated to dryness and purified via flash chromatography using hexanes as eluant. Colorless oil was obtained (1.35 g, 68 % yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 6.36 (s, 2H), 4.00-4.12 (d, *J* = 2.4 Hz, 8H), 3.50 (s, 8H), 3.25-3.31 (d, *J* = 0.6 Hz), 1.42-1.54 (m, 4H), 1.20-1.42 (m, 36H), 0.80-1.00 (m, 24H). HRMS: [M<sup>+</sup>] 878.5743, expected for C<sub>50</sub>H<sub>86</sub>O<sub>8</sub>S<sub>2</sub>: 878.5764.

## S2.2. Polymerization Procedures

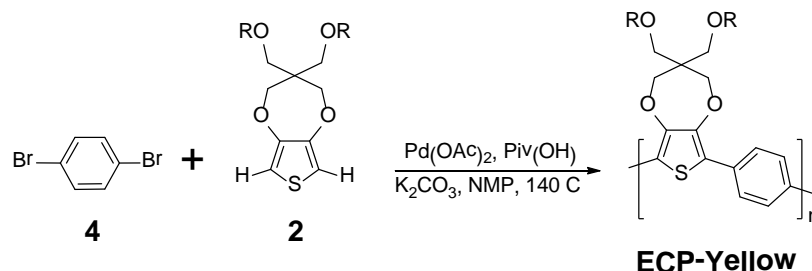


**ECP-Magenta (A):** To a oven dried Schlenk tube fitted with a magnetic stir bar Pd(OAc)<sub>2</sub> (2.25 mg, 2 mol%), K<sub>2</sub>CO<sub>3</sub> (173 mg, 1.3 mmol), and Pivalic Acid (0.01 g, 0.15 mmol) were added sequentially. The reaction flask was evacuated for a total of ten minutes, and purged with anhydrous argon. This evacuation/gas filling procedure was repeated three times. A separate vial was loaded with 6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**1**, 299 mg, 0.5 mmol), and 3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**2**, 220mg, 0.5 mmol). After evacuating for 10 minutes, argon saturated DMAc (2 mL) was added via argon flushed syringe. The resulting solution was transferred to the mother Schlenk tube via syringe in one portion. The

vial was then washed twice with 2 mL of Ar-saturated DMAc where each washing was transferred to the reaction flask. Afterward, the combined reagents were put into a 140 °C oil bath and allowed to stir for three hours. Upon cooling to room temperature, the mixture was poured into 50 mL of a 1:1 MeOH/1M HCl aqueous solution with vigorous stirring. The resulting precipitate was filtered, washed with water (5 × 10 mL), then MeOH (3 × 10 mL), and finally suction dried for 15 minutes. The resulting solid was suspended in 50 mL of chlorobenzene and heated to 60 °C. Once the solids dissolved completely, diethyl dithiocarbamic acid diethylammonium salt (Pd-scavenger, 2.0 mg, ~ 4 eq of Pd content) and 18-crown-6 (1.3 g, 5 mmol) were added and the solution was stirred for 4 hours. The reaction mixture was cooled to room temperature, and precipitated into MeOH. The precipitate was filtered by gravity filtration, washed with MeOH (5 × 10 mL), then hexanes (3 × 5 mL) and dried under vacuum overnight. A total of 388 mg of dark maroon powder was obtained (88% yield). This polymer has been previously reported.<sup>3</sup> Characterization data agreed accordingly. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 4.15 (bs, 4H), 3.60 (bs, 4H), 3.33 (bs, 4H), 1.52 (bs, 4H), 1.20-1.45 (m, 18H), 0.82-0.94 (m, 12H). GPC (THF, PS): M<sub>n</sub> = 9,980 g/mol, Đ = 1.74.

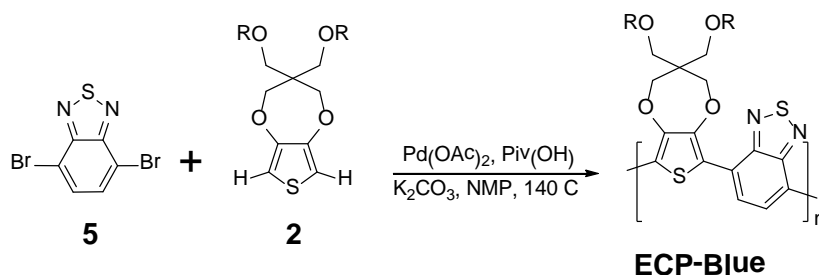


**ECP-Magenta (B):** This material was prepared following exactly the procedure described for ECP-Magenta with the following modifications: all solid materials were loaded into the over dried Schlenk. In a separate vial, 6-bromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**3**, 299 mg, 0.5 mmol) was weighed. The sequences of evacuation/purging, plus reactant mixing are the same as the general procedure. Once all reactants were mixed altogether, the tube was inserted into the oil bath preheated at 140 °C. After 3 hours, the resulting yellow mixture was worked up and the resulting polymer was isolated as previously described for ECP-Magenta. A total of 210 mg of dark purple-colored powder was obtained (95% yield). All characterization data matched the ones previously described for ECP-Magenta. GPC (THF, PS): M<sub>n</sub> = 9,440 g/mol, Đ = 1.42.

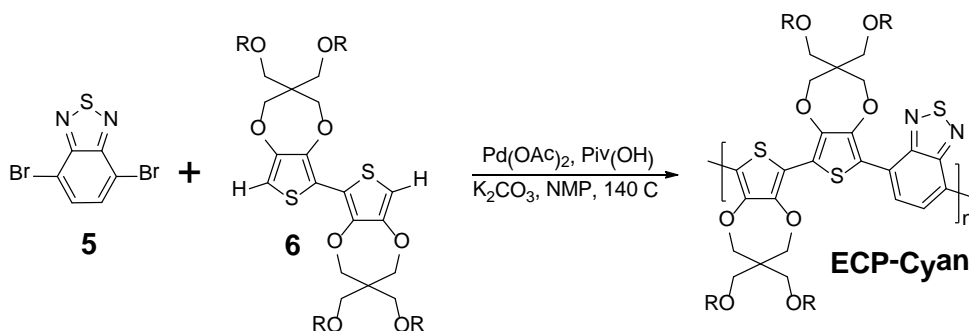


**ECP-Yellow:** This material was prepared following exactly the procedure described for ECP-Magenta with the following modifications: all solid materials were loaded into the over dried Schlenk tube including this time 1,4-

dibromobenzene (**3**, 118 mg, 0.5 mmol). In a separate vial, 3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**2**, 220 mg, 0.5 mmol) was weighed. The sequences of evacuation/purging, plus reactant mixing using NMP as solvent are exactly the as the general procedure. Once all reactants were mixed altogether, the tube was inserted into the oil bath preheated at 140 °C. After 3 hours, the resulting yellow mixture was worked up and the resulting polymer was isolated as previously described for ECP-Magenta. A total of 210 mg of dark orange-colored powder was obtained (76% yield). This polymer has been previously reported.<sup>4</sup> Characterization data agreed accordingly. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.75 (bs, 4H), 4.19 (bs, 4H), 3.60 (bs, 4H), 1.52 (bs, 4H), 1.22-1.44 (m, 18H), 0.82-0.98 (m, 12H). GPC (THF, PS): M<sub>n</sub> = 27,500 g/mol, Đ = 1.19.

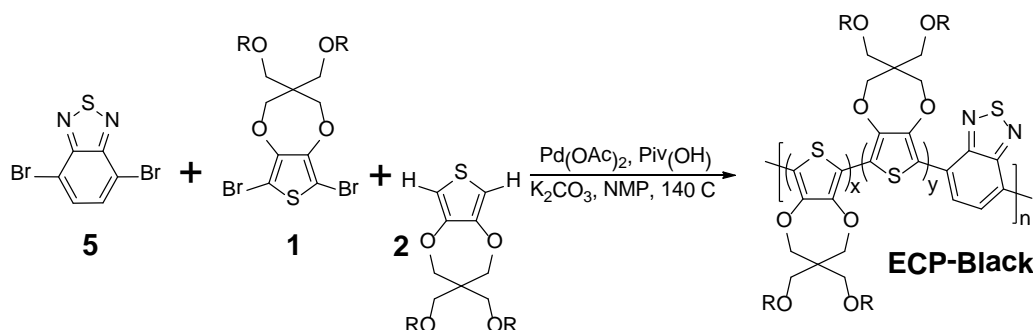


**ECP-Blue:** This material was prepared following exactly the procedure described for ECP-Magenta with the following modifications: all solid materials were loaded into the over dried Schlenk tube including this time 4,7-dibromo-2,1,3-benzothiadiazole (**4**, 147 mg, 0.5 mmol). In a separate vial, 3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**2**, 220 mg, 0.5 mmol) was weighed. The sequences of evacuation/purging, plus reactant mixing using NMP as solvent are the same as the general procedure. Once all reactants were mixed altogether, the tube was inserted into the oil bath preheated at 140 °C. After 3 hours, the resulting dark blue mixture was worked up and the resulting polymer was isolated as previously described for ECP-Magenta. A total of 375 mg of dark blue-colored (almost black) powder was obtained (81% yield). This polymer has been previously reported.<sup>5</sup> Characterization data agreed accordingly. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.42 (bs, 2H), 4.33 (bs, 4H), 3.65 (bs, 4H), 3.35 (bs, 4H), 1.20-1.60 (m, 22H), 0.85-0.98 (m, 12H). GPC (THF, PS): M<sub>n</sub> = 9,440 g/mol, Đ = 1.54.



**ECP-Cyan:** This material was prepared following exactly the procedure described for ECP-Magenta with the following modifications: all solid materials were loaded into the over dried Schlenk tube including this time 4,7-

dibromo-2,1,3-benzothiadiazole (**4**, 147 mg, 0.5 mmol). In a separate vial, 3,3,3',3'-tetrakis(2-ethylhexyloxymethyl)-3,3',4,4'-tetrahydro-2H,2'H-6,6'-bithieno[3,4-b][1,4]dioxepine (**2**, 440 mg, 0.5 mmol) was weighed. The sequences of evacuation/purging, plus reactant mixing using NMP as solvent are the same as the general procedure. Once all reactants were mixed altogether, the tube was inserted into the oil bath preheated at 140 °C. After 3 hours, the resulting dark cyan mixture was worked up and the resulting polymer was isolated as previously described for ECP-Magenta. A total of 410 mg of dark blue-colored powder was obtained (89 % yield). This polymer has been previously reported.<sup>6</sup> Characterization data agreed accordingly. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.38 (bs, 2H), 4.26 (bs, 8H), 3.62 (bs, 8H), 3.36 (bs, 8H), 1.16-1.60 (m, 44H), 0.90-0.99 (m, 24H). The sample was sparingly soluble in THF, which precluded its characterization via GPC.

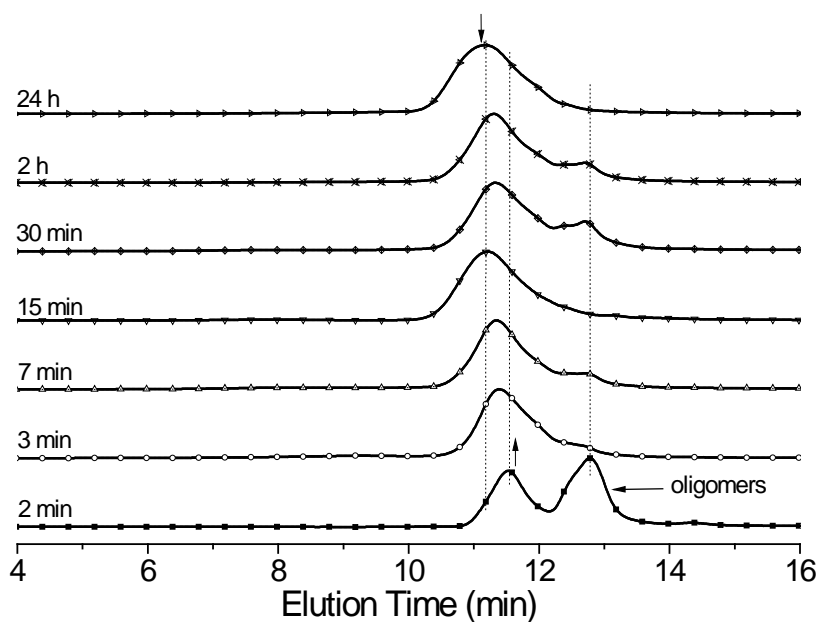


**ECP-Black:** This material was prepared following the procedure described for ECP-Magenta with the following modifications: all solid materials were loaded into the over dried Schlenk tube including this time 4,7-dibromo-2,1,3-benzothiadiazole (**4**, 74 mg, 0.25 mmol). In a separate vial, 6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**1**, 150 mg, 0.25 mmol), and 3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**2**, 220 mg, 0.50 mmol) were weighed. The sequences of evacuation/purging, plus reactant mixing using NMP as solvent are the same as the general procedure. Once all reactants were mixed altogether, the tube was inserted into the oil bath preheated at 140 °C. After 3 hours, the resulting black mixture was worked up and the resulting polymer was isolated as previously described for ECP-Magenta. A total of 395 mg of black-colored powder was obtained (78 % yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.38 (bs, 2H), 4.20 (bs, 8H), 3.62 (bs, 8H), 3.36 (bs, 8H), 1.16-1.60 (m, 44H), 0.90-0.99 (m, 24H). GPC (THF, PS): M<sub>n</sub> = 11,000 Đ = 2.03.

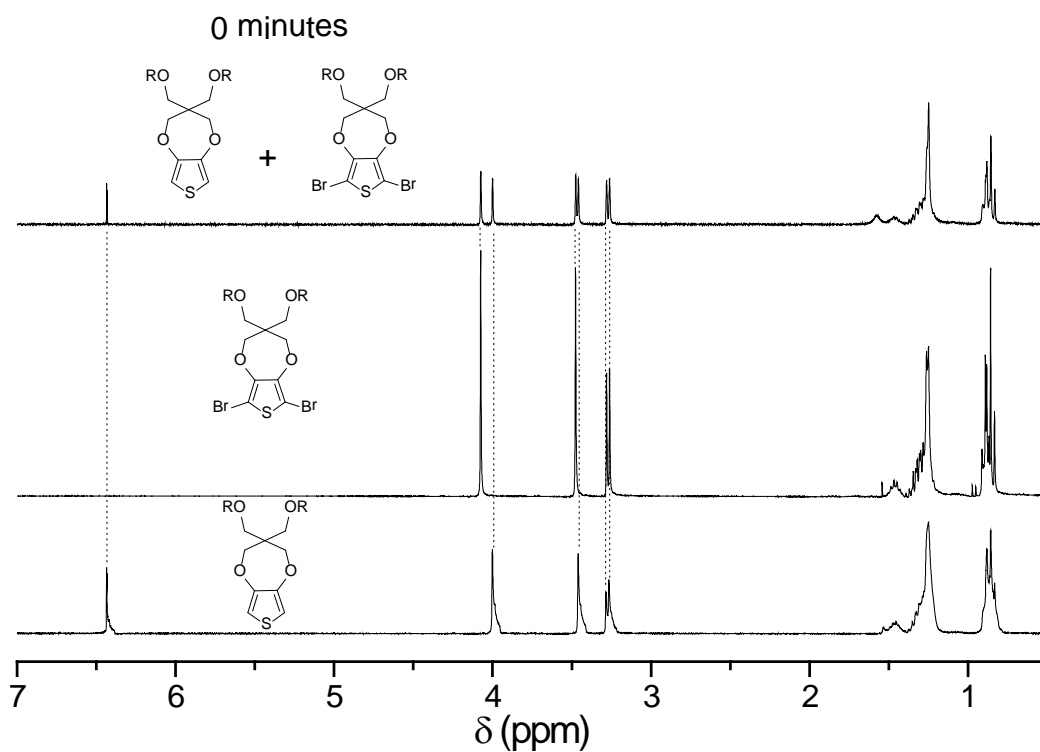
**Kinetic Experiments:** The procedures for ECP Magenta in either cases (**A,B** – *vide supra*) were repeated with the addition of 2-5 eq. of dodecane as internal standard for GCMS analyses. The aliquots were withdrawn using a 1 mL syringe in volumes of 0.1-0.2 mL at the appropriate sampling time (see manuscript, Figure 2) and transferred to a 4 mL vial with 1:1 DCM/1M HCl mixture. The organic layer was separated, and the aqueous layer was extracted twice with DCM (1 mL). The organic extracts were combined with the first organic layer, dried over MgSO<sub>4</sub>, filtered, and concentrated to V ~ 1-2 mL. The samples analyzed via <sup>1</sup>H NMR were prepared exactly as described above, without the addition of dodecane as internal standard. For the GPC analysis, the corresponding aliquot (0.5-1 mL) was instead precipitated in acidic MeOH, filtered, washed with water, MeOH and ether, and finally air-dried.

### S3. Supporting Figures and Tables

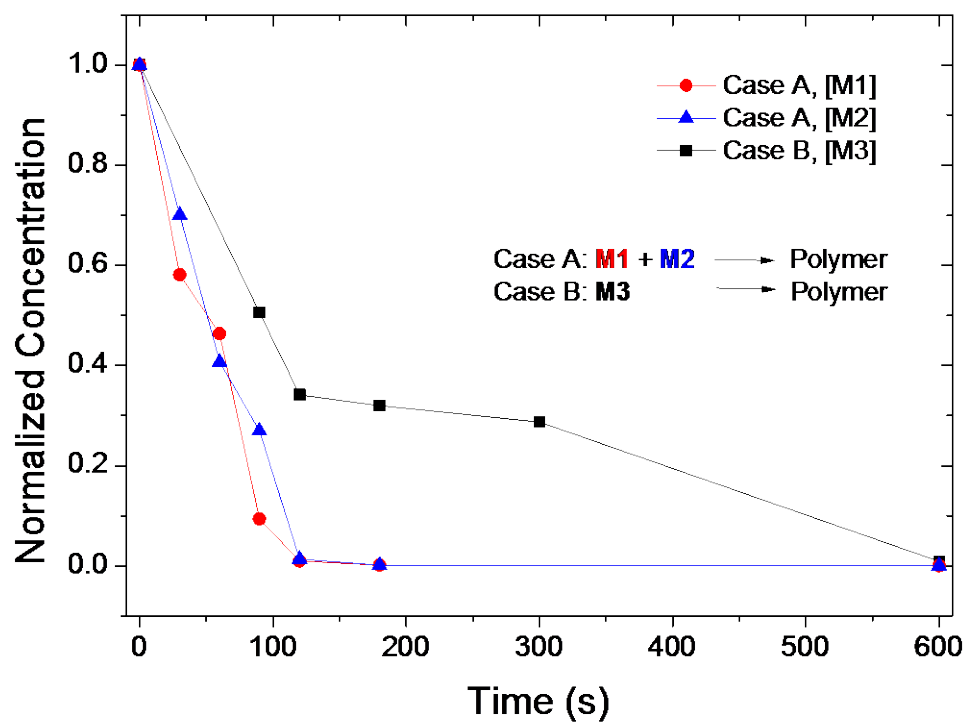
#### S3.1. Polymerization Studies



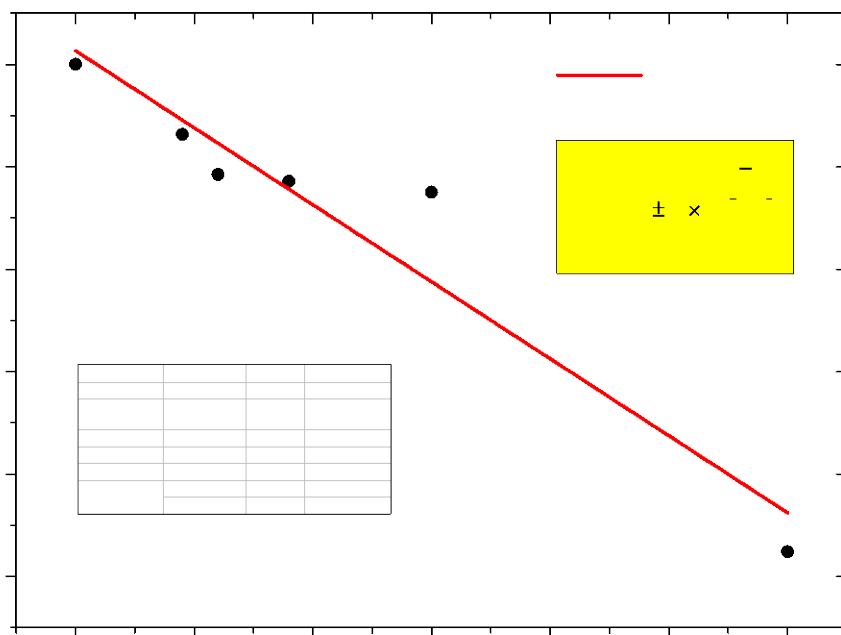
**Figure S1.** Evolution of the GPC traces for the DiHAr reaction for the generation of ECP-Magenta.



**Figure S2.** Spectral comparison of the  $^1\text{H}$  NMR signals of compounds (1) and (2) individually and as mixture.

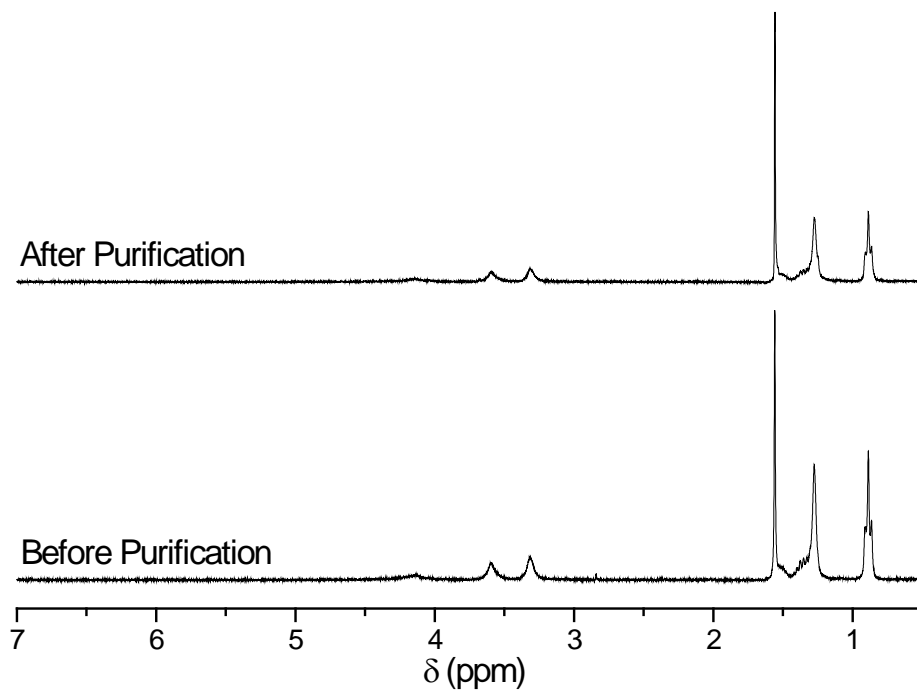


**Figure S3.** Plot of  $[X]$  vs. time under DHAP conditions where  $X = M1/M2$  for case A, and  $M3$  for case B. For case A, the consumption of the starting materials is faster than for case B.



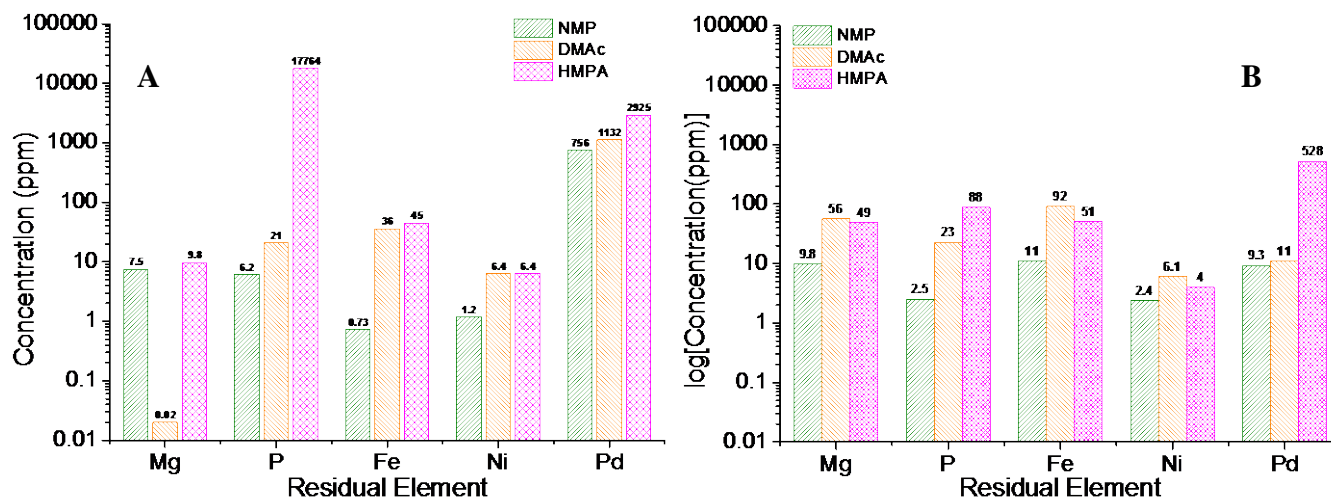
**Figure S4.** Plot of  $\ln[M3]$  vs. time under DHAP conditions. The linear model implies that the reaction follow 1<sup>st</sup> order kinetics for  $t < 10$  min (600 s).





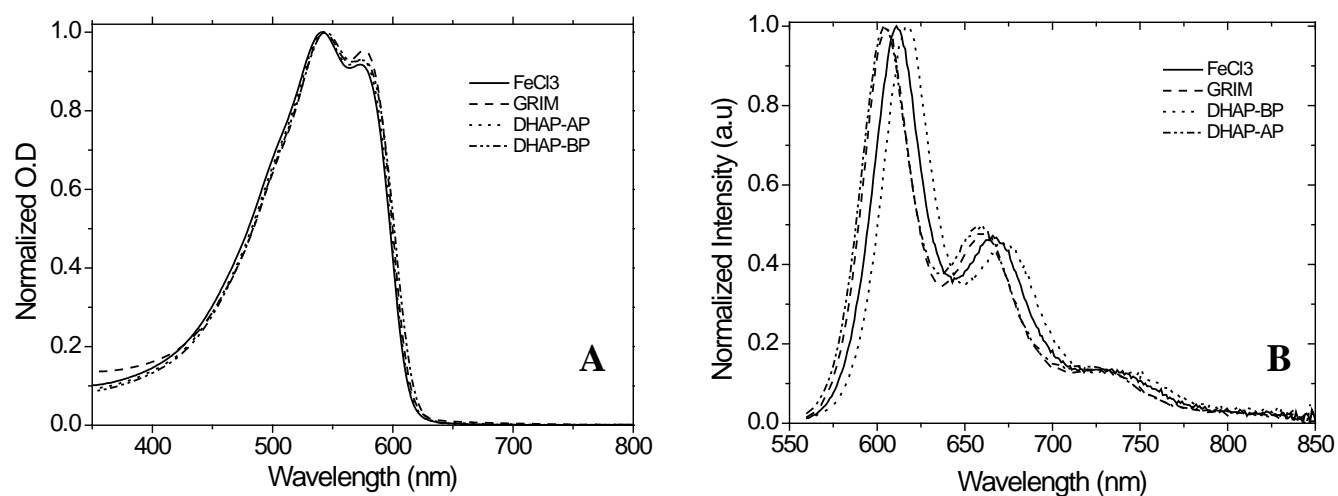
**Figure S5.** Spectral comparison of the  $^1\text{H}$  NMR signals of ECP-Magenta before and after purification.

### S3.2. ICP/MS Studies

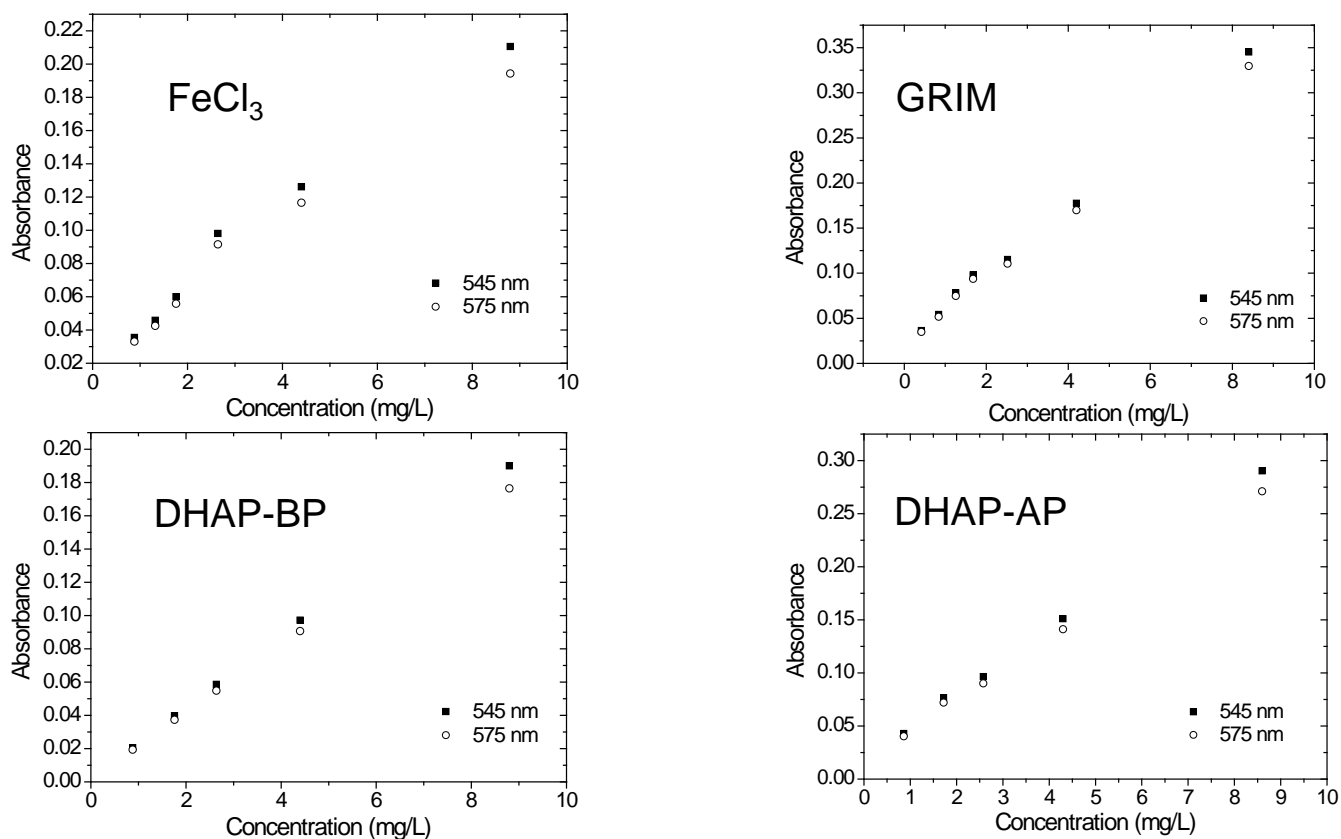


**Figure S6.** Residual content of selected elements for ECP-Magenta obtained via DHAP from different solvents through the ICP-MS technique. (A) Before purification. (B) After purification.

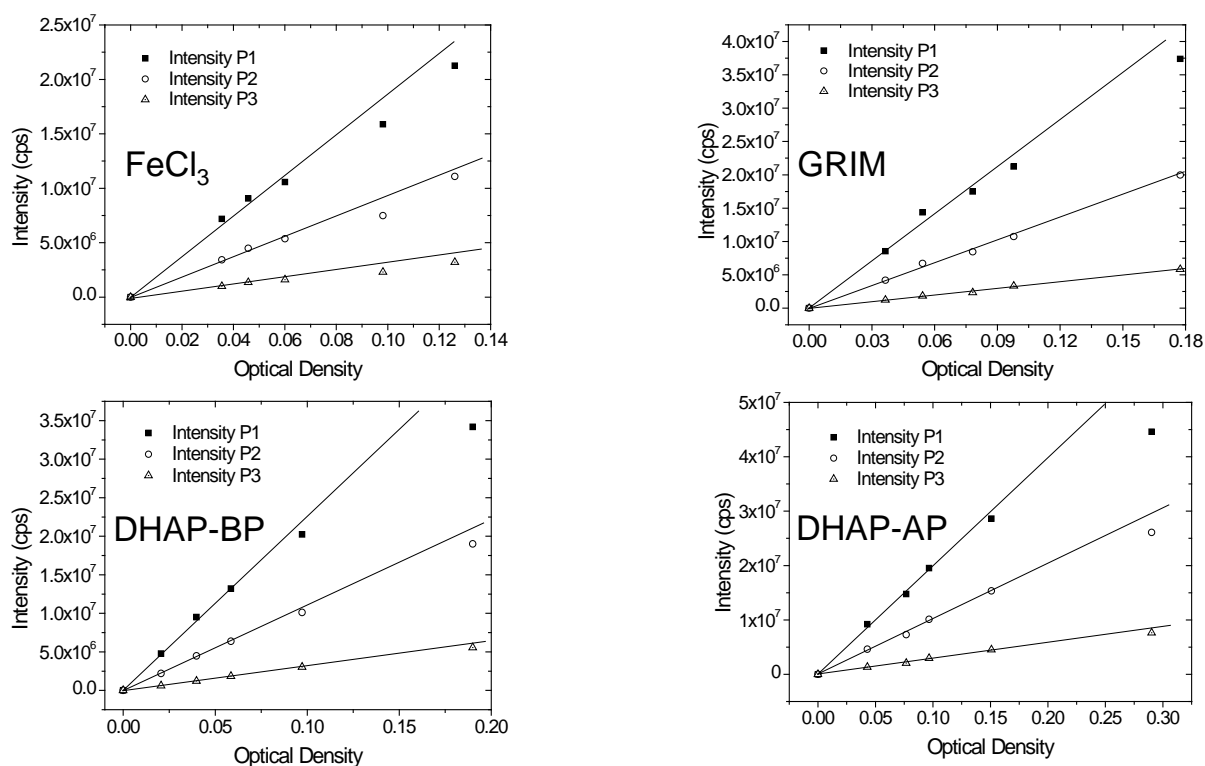
## S3.3. Optical Studies



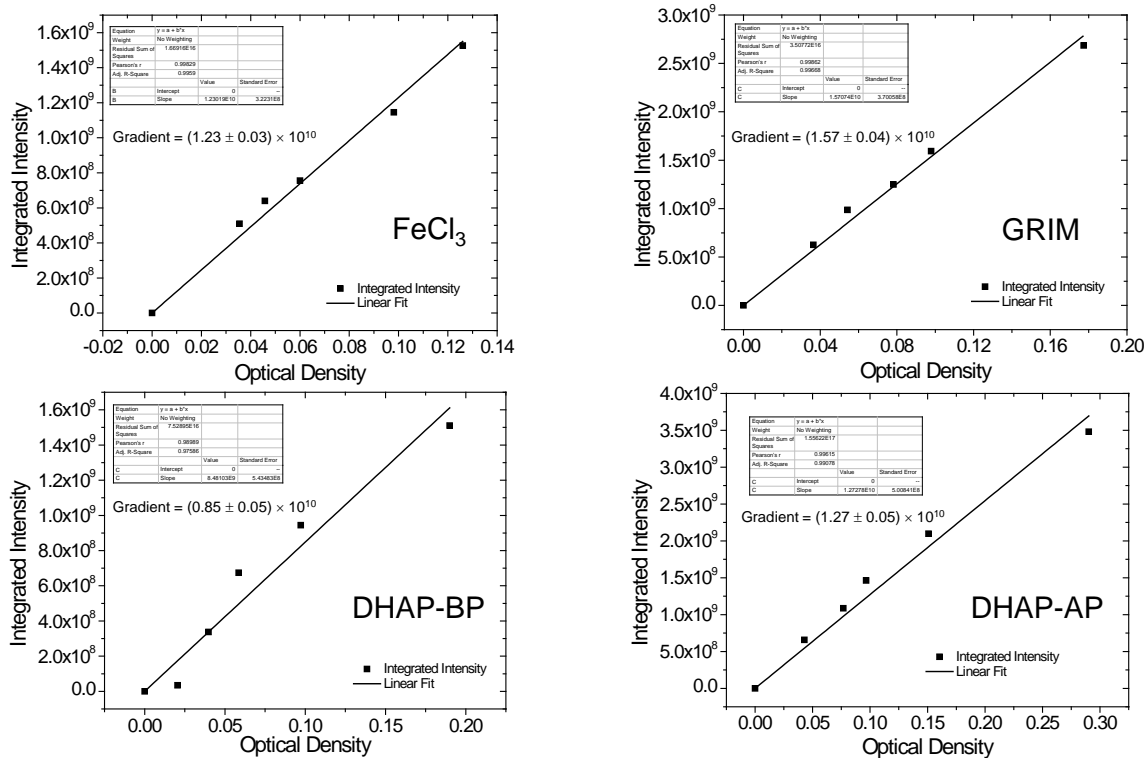
**Figure S7.** Steady state UV-Vis spectra of polymer samples (A) Absorption. (B) Fluorescence.



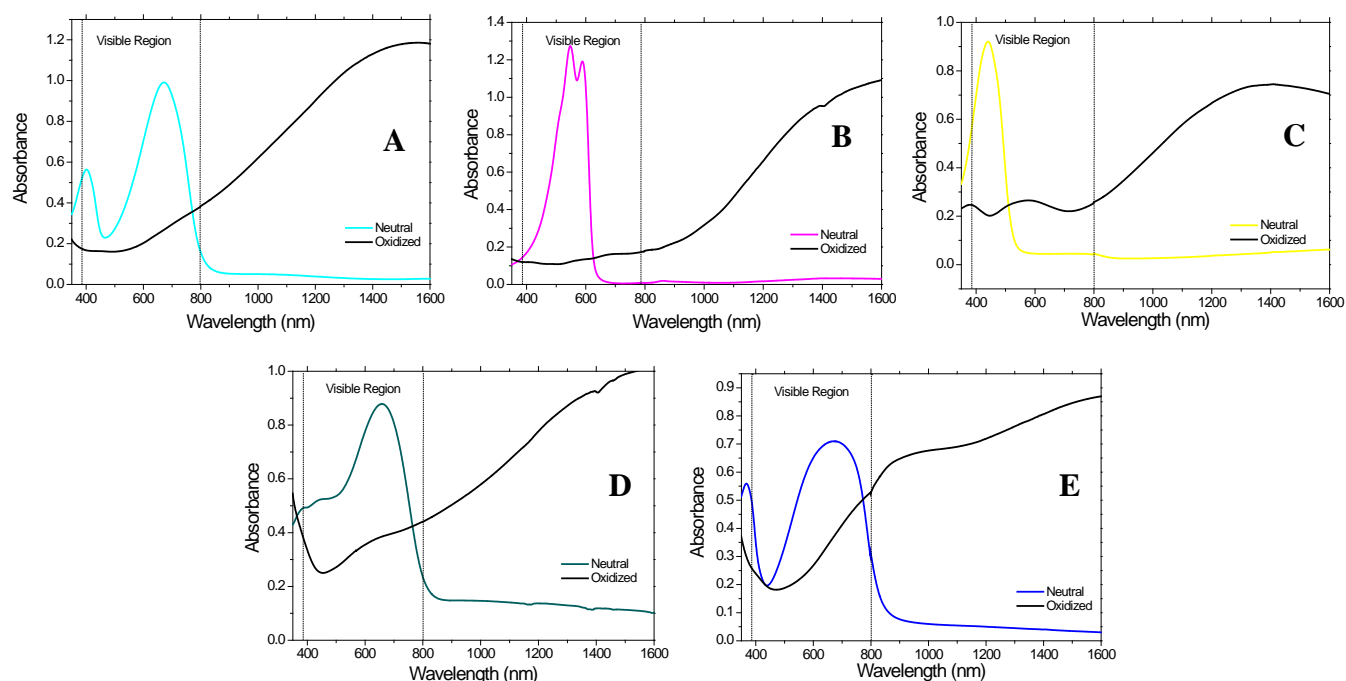
**Figure S8.** Plot of Mass Concentration vs. Absorbances for ECP-Magenta Samples synthesized through various synthetic methods (DHAP is presented before and after purification). Probe wavelengths: 454 and 575 nm.



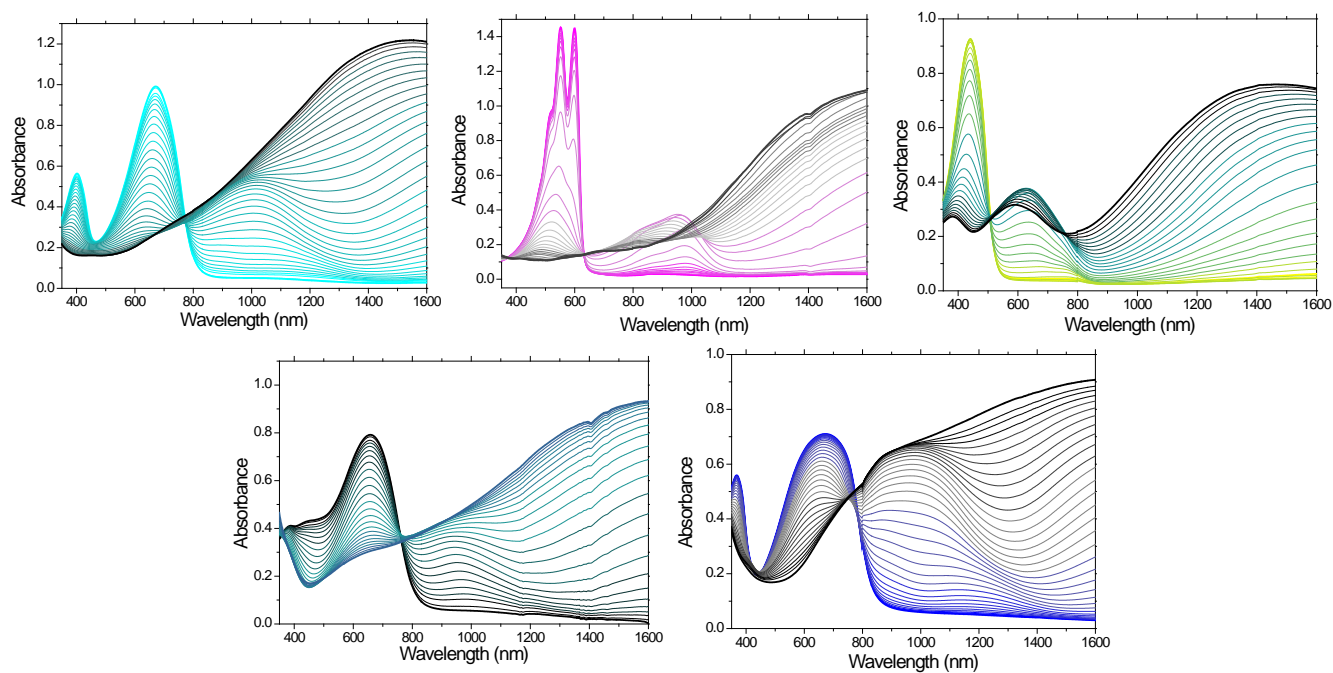
**Figure S9.** Plots of Optical Densities vs. Fluorescence Intensities for ECP-Magenta Samples (probe wavelengths: 605-610 (P1), 660-666 (P2), and 725-734 (P3) nm bands).



**Figure S10.** Plots of Fluorescence Gradients for ECP-Magenta



**Figure S11.** UV-Vis-NIR spectra of the neutral (colored line) and oxidized (black line) species of ECPs obtained via DHAP. Applied potentials vs.  $\text{Ag}|\text{Ag}^+$  were (A) ECP-Cyan:  $-0.10$  and  $0.90$  V, (B) ECP-Magenta:  $-0.10$  and  $0.80$  V, (C) ECP-Yellow:  $0.00$  and  $1.00$  V, (D) ECP-Black:  $0.00$  and  $0.65$  V (E) ECP-Blue:  $0.00$  and  $0.90$  V.



**Figure S12.** Spectral evolution for the UV-Vis-NIR absorption of ECPs obtained via DHAP with respect to potential steps of 25 mV. Applied potentials vs.  $\text{Ag}|\text{Ag}^+$  were in the range of: (A) ECP-Cyan ( $-0.10, 0.90$ ) V, (B) ECP-Magenta ( $-0.10, 0.80$ ) V, (C) ECP-Yellow ( $0.00, 1.00$ ) V, (D) ECP-Black ( $0.00, 0.65$ ) V (E) ECP-Blue ( $0.00, 0.90$ ) V.

**Table S1.** Elemental concentrations (ppm) for ECP-Magenta samples made via DHAP in various solvents.

Element	NMP_BP	NMP_AP	DMAc_BP	DMAc_AP	HMPA_BP	HMPA_AP
Li	3.5	1.4	7.0	1.3	5.4	0.7
B	23.6	7.8	6.7	6.8	8.1	5.4
Na	82.2	17.9	98.1	37.9	844.8	566.3
Mg	7.49	9.75	bdl	56.08	9.83	48.93
Al	bdl	5.57	2.65	141.13	bdl	26.17
Si	401	1826	1072	15487	1446	13884
P	6.2	2.5	21.4	22.8	17764	88.3
K	bdl	bdl	bdl	bdl	bdl	bdl
Ca	357.2	217.9	162.6	383.1	254.1	320.6
Sc	0.3	0.3	0.2	0.3	0.2	0.3
Ti	0.25	0.96	bdl	1.52	bdl	2.15
V	0.27	0.28	0.21	0.39	0.21	0.31
Cr	45.59	40.96	25.31	59.76	15.87	26.41
Mn	1.89	1.82	1.43	3.14	1.42	2.19
Fe	0.73	10.64	35.76	91.95	44.98	50.68
Co	0.10	0.12	0.10	0.33	0.15	0.19
Ni	1.21	2.37	6.42	6.09	6.43	4.02
Cu	3.35	1.82	7.36	3.23	6.65	2.09
Zn	36.24	14.53	42.44	10.99	1510	24.90
Ga	0.45	0.47	0.32	0.61	0.39	0.53
Ge	6.49	8.26	5.53	11.52	6.29	8.83
Rb	0.70	0.60	1.64	0.83	1.55	0.60
Sr	3.14	3.38	2.50	5.01	4.39	4.71
Y	0.43	0.47	0.30	1.12	0.36	0.76
Zr	0.45	0.61	0.30	0.75	0.55	0.58
Nb	0.17	0.18	0.12	0.23	0.16	0.18
Mo	bdl	0.12	bdl	bdl	bdl	bdl
Ru	0.01	0.00	0.01	0.02	0.03	0.01
Pd	756.0	9.3	1132.4	11.4	2924.6	528.4
Ag	5.3	4.0	2.7	4.9	3.1	4.2
Cd	0.7	0.4	0.2	0.4	0.3	0.4
In	0.26	0.26	0.17	0.33	0.21	0.28
Sn	4.13	2.10	1.64	3.36	2.32	2.97
Sb	bdl	bdl	bdl	bdl	bdl	bdl
Te	13.24	14.27	9.30	17.48	10.99	15.15
Cs	0.34	0.33	0.20	0.51	0.92	0.46
Ba	1.79	3.44	1.67	6.07	9.08	10.20
La	0.343	0.357	0.242	0.461	0.288	0.398
Ce	0.365	0.383	0.259	0.507	0.308	0.430
Pr	0.344	0.357	0.241	0.457	0.284	0.393
Nd	0.227	0.231	0.159	0.309	0.188	0.253
Sm	0.393	0.406	0.271	0.526	0.323	0.449
Eu	0.879	0.924	0.626	1.188	0.741	1.027
Gd	0.243	0.286	0.191	0.348	0.213	0.303
Tb	0.356	0.369	0.250	0.470	0.295	0.408
Dy	0.560	0.582	0.393	0.740	0.465	0.641
Ho	0.548	0.569	0.385	0.724	0.455	0.628
Er	0.588	0.610	0.413	0.776	0.488	0.673
Tm	0.442	0.459	0.310	0.583	0.367	0.506
Yb	0.460	0.476	0.322	0.606	0.381	0.525
Lu	0.319	0.331	0.224	0.421	0.265	0.366
Hf	bdl	bdl	bdl	bdl	bdl	bdl
Ta	0.717	0.742	0.501	0.943	0.592	0.814
W	0.597	0.606	0.414	0.782	0.485	0.675
Ir	0.352	0.170	0.082	0.107	0.061	0.066
Pt	0.004	0.001	0.004	0.004	0.013	0.007
Au	0.054	0.010	0.020	0.012	0.003	0.003
Tl	bdl	bdl	bdl	bdl	bdl	bdl
Pb	bdl	bdl	bdl	bdl	bdl	bdl
Bi	0.495	0.568	0.323	1.240	0.379	0.535
Th	0.479	0.497	0.337	0.632	0.397	0.547
U	0.476	0.494	0.334	0.628	0.395	0.544

bdl: below detection limit.

**Table S2.** Elemental concentrations (ppm) for various ECP samples made via DHAP in NMP after purification (AP).

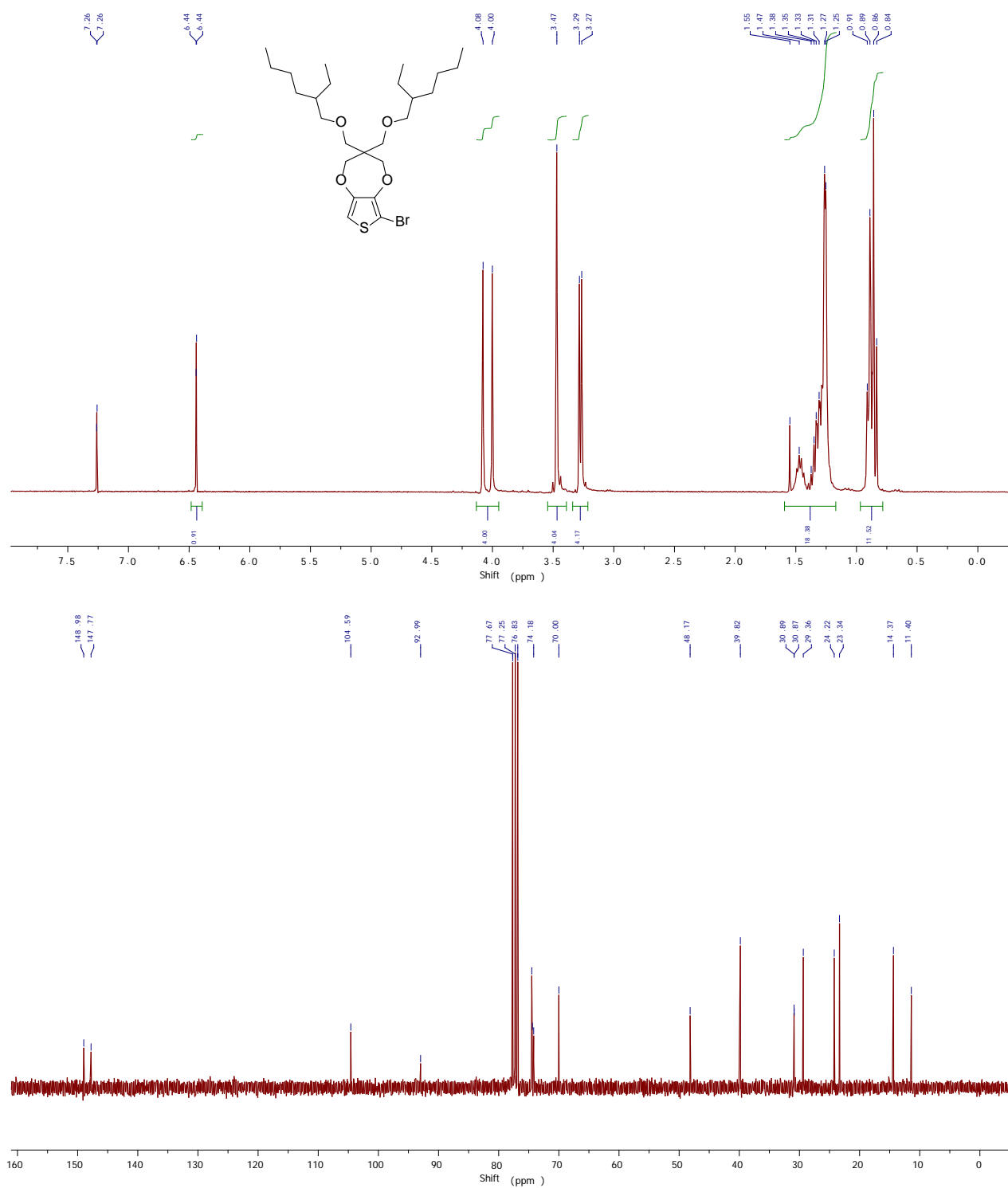
Element	Cyan_AP	Black_AP	Yellow_AP	Blue_AP
Li	35.6	79.9	39.7	45.9
B	63.6	165.6	74.0	107.6
Na	bdl	bdl	bdl	bdl
Mg	50.6	328.1	53.1	57.5
Al	89.5	241.8	99.1	118.3
Si	bdl	3294	272.6	738.1
P	5.5	23.4	-2.1	13.4
K	bdl	bdl	bdl	bdl
Ca	98.2	1322.9	413.7	385.3
Sc	bdl	bdl	bdl	bdl
Ti	21.9	52.8	23.8	30.3
V	bdl	bdl	bdl	bdl
Cr	34.2	71.7	38.0	42.9
Mn	51.7	113.3	59.5	69.3
Fe	48.5	107.5	69.4	56.6
Co	bdl	bdl	bdl	bdl
Ni	49.6	112.4	56.5	82.8
Cu	47.2	132.4	57.7	78.7
Zn	12.9	39.9	22.1	85.8
Ga	bdl	bdl	bdl	bdl
Ge	7.9	31.2	10.8	13.2
Rb	bdl	bdl	bdl	bdl
Sr	48.6	109.4	56.2	64.8
Y	bdl	bdl	bdl	bdl
Zr	bdl	bdl	bdl	bdl
Nb	bdl	bdl	bdl	bdl
Mo	17.0	36.5	19.1	22.2
Ru	bdl	0.2	bdl	bdl
Pd	214.59	118.68	216.29	230.22
Ag	61.16	133.42	69.42	80.21
Cd	39.39	86.09	44.51	51.91
In	bdl	bdl	bdl	bdl
Sn	4.71	19.99	29.67	21.26
Sb	bdl	bdl	bdl	bdl
Te	54.19	117.07	60.85	75.42
Cs	bdl	bdl	bdl	bdl
Ba	58.70	142.38	68.46	81.66
La	bdl	bdl	bdl	bdl
Ce	bdl	bdl	bdl	bdl
Pr	bdl	bdl	bdl	bdl
Nd	bdl	bdl	bdl	bdl
Sm	bdl	bdl	bdl	bdl
Eu	bdl	bdl	bdl	bdl
Gd	bdl	bdl	bdl	bdl
Tb	bdl	bdl	bdl	bdl
Dy	bdl	bdl	bdl	bdl
Ho	bdl	bdl	bdl	bdl
Er	bdl	bdl	bdl	bdl
Tm	bdl	bdl	bdl	bdl
Yb	bdl	bdl	bdl	bdl
Lu	bdl	bdl	bdl	bdl
Hf	bdl	bdl	bdl	bdl
Ta	bdl	bdl	bdl	bdl
W	bdl	bdl	bdl	bdl
Ir	0.14	0.40	0.06	0.06
Pt	0.16	0.00	0.03	0.05
Au	0.44	4.40	0.50	0.30
Tl	48.37	105.44	54.80	63.41
Pb	5.05	11.73	5.77	7.66
Bi	bdl	bdl	bdl	bdl
Th	bdl	bdl	bdl	bdl
U	bdl	bdl	bdl	bdl

bdl: below detection limit.

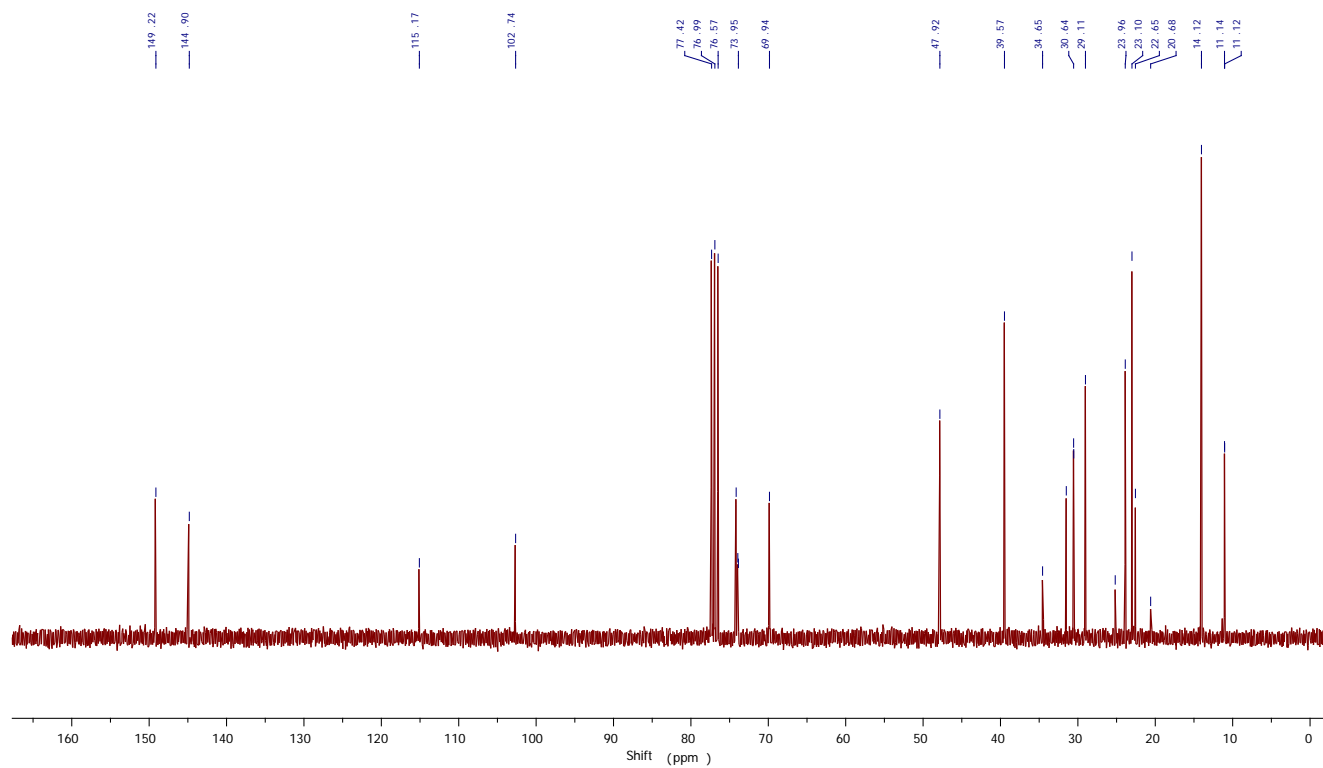
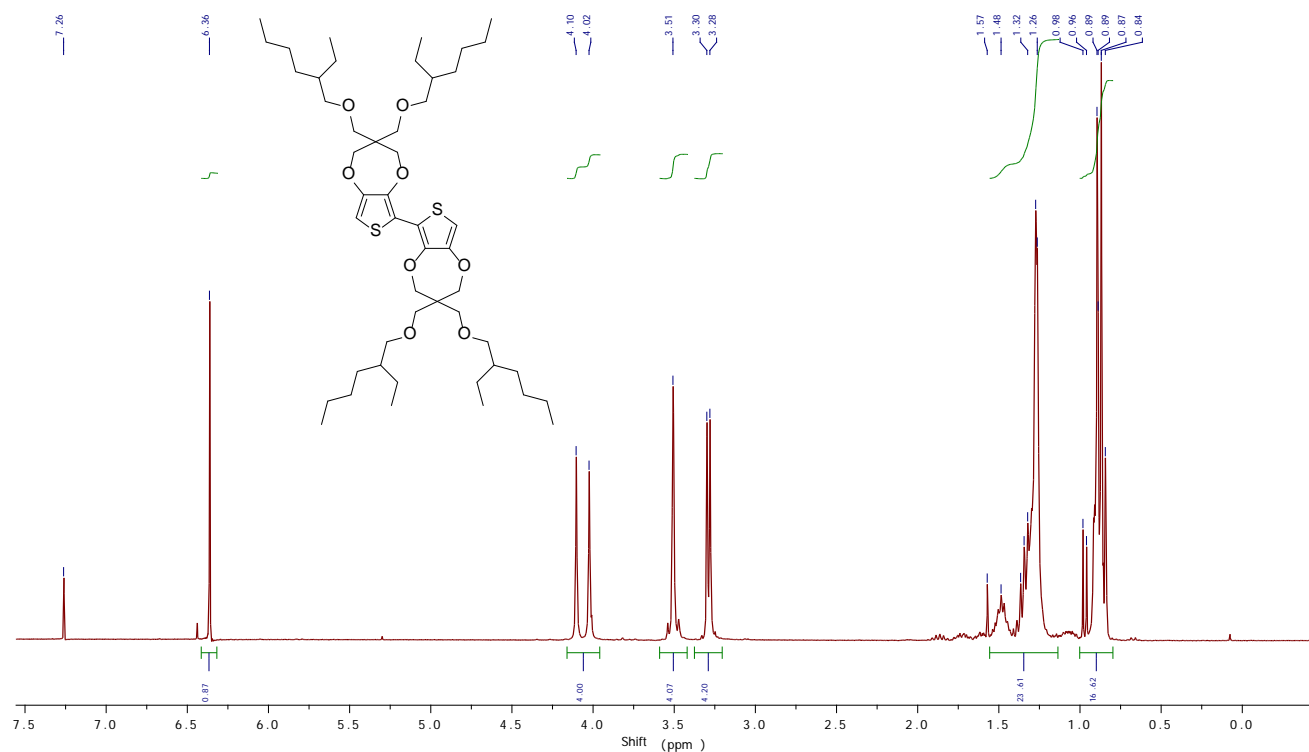
**Table S3.** Elemental concentrations (ppm) for various ECP samples made via DHAP in NMP after purification (AP).

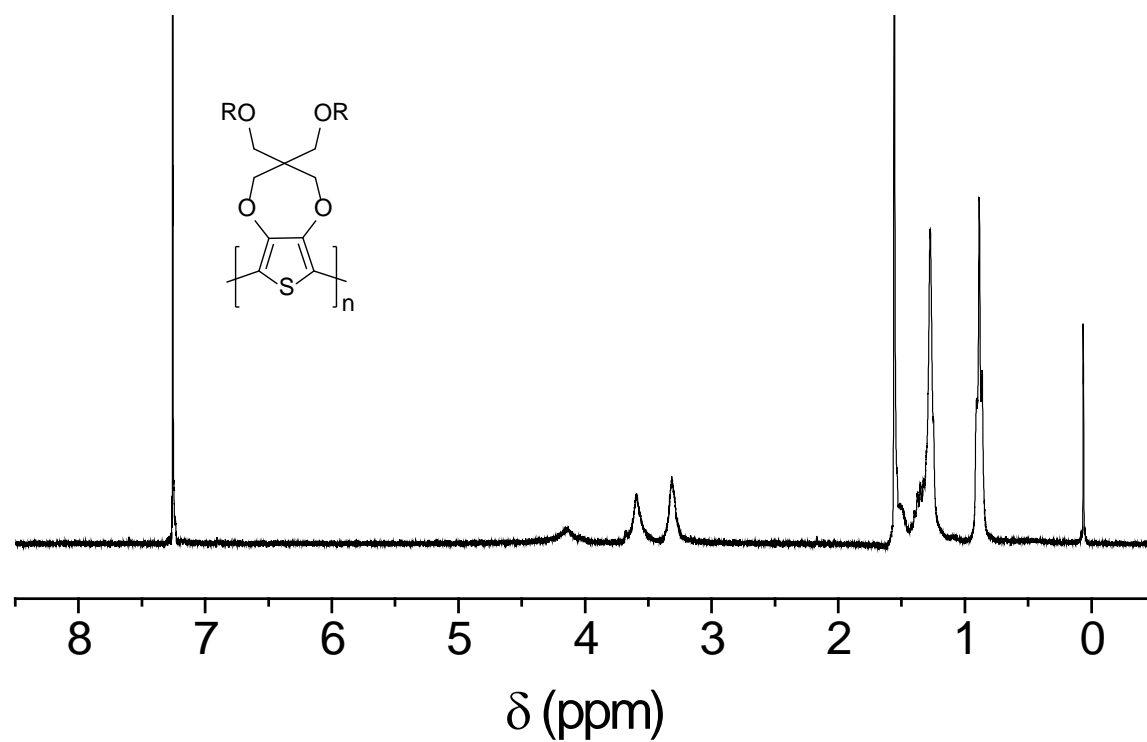
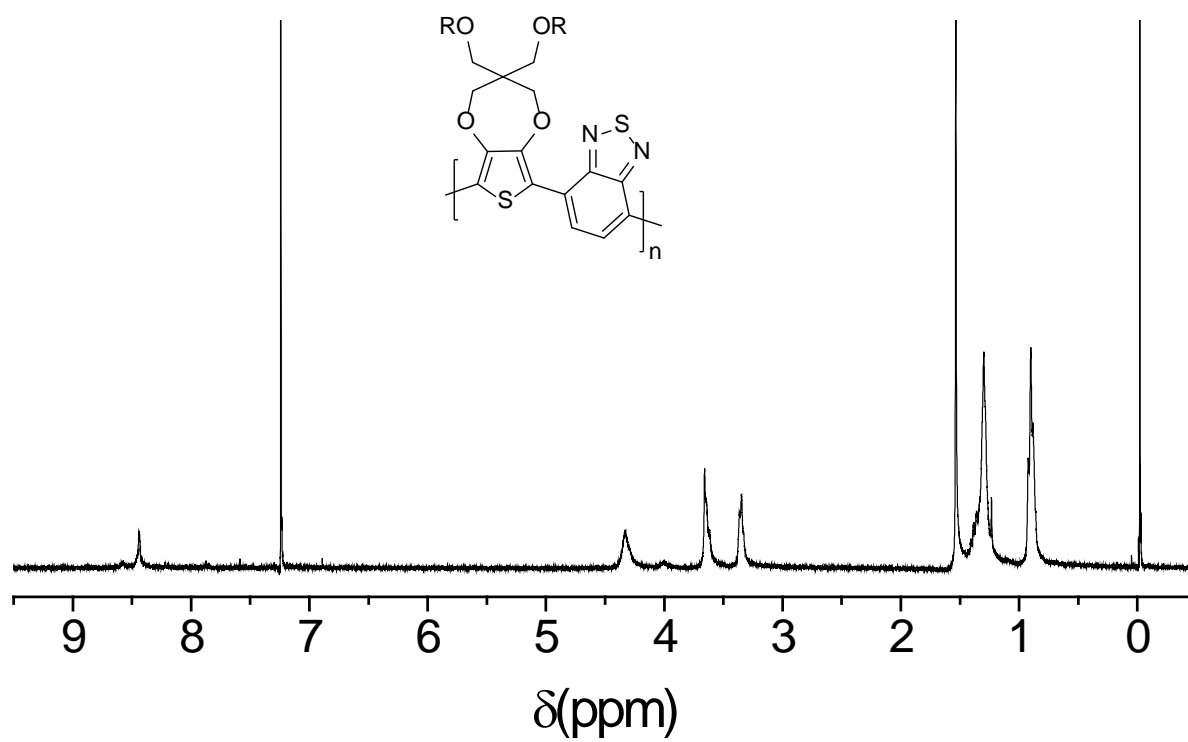
Element	OxP	GRIM	DHAP (AP)	Element	OxP	GRIM	DHAP (AP)
Li	bdl	1.49	1.4	In	0.13	0.12	0.26
B	25.30	1.55	7.8	Sn	2.13	1.39	2.10
Na	bdl	bdl	17.9	Sb	bdl	bdl	bdl
Mg	37	1636	9.75	Te	10.87	10.57	14.27
Al	61	49	5.57	Cs	0.11	0.10	0.33
Si	641	533	1826	Ba	4.41	4.77	3.44
P	5.25	29.35	2.5	La	bdl	bdl	0.357
K	bdl	bdl	bdl	Ce	0.22	0.21	0.383
Ca	130	96	217.9	Pr	0.09	0.09	0.357
Sc	0.15	0.14	0.3	Nd	bdl	bdl	0.231
Ti	1.52	0.95	0.96	Sm	0.49	0.47	0.406
V	0.66	0.47	0.28	Eu	0.01	0.01	0.924
Cr	0.60	bdl	40.96	Gd	bdl	bdl	0.286
Mn	1.34	1.61	1.82	Tb	0.52	0.51	0.369
Fe	1112	6	10.64	Dy	0.11	0.11	0.582
Co	0.05	0.00	0.12	Ho	0.19	0.19	0.569
Ni	1.74	926	2.37	Er	bdl	bdl	0.610
Cu	4.60	0.05	1.82	Tm	0.26	0.25	0.459
Zn	63.1	8.4	14.53	Yb	bdl	bdl	0.476
Ga	0.24	0.17	0.47	Lu	0.03	0.03	0.331
Ge	12.7	7.7	8.26	Hf	0.67	0.65	bdl
Rb	0.32	0.31	0.60	Ta	bdl	bdl	0.742
Sr	0.94	0.74	3.38	W	bdl	bdl	0.606
Y	0.45	0.43	0.47	Re	0.58	0.57	Not obtained
Zr	0.11	0.07	0.61	Ir	0.03	0.00	0.170
Nb	0.25	0.02	0.18	Pt	11.83	11.50	0.001
Mo	bdl	bdl	0.12	Au	0.01	0.01	0.010
Ru	0.01	0.00	0.00	Tl	bdl	bdl	bdl
Rh	0.01	0.01	0.02	Pb	0.76	bdl	bdl
Pd	0.37	0.36	9.3	Bi	0.32	0.28	0.568
Ag	bdl	bdl	4.0	Th	0.16	0.15	0.497
Cd	0.50	0.43	0.4	U	0.36	0.35	0.494

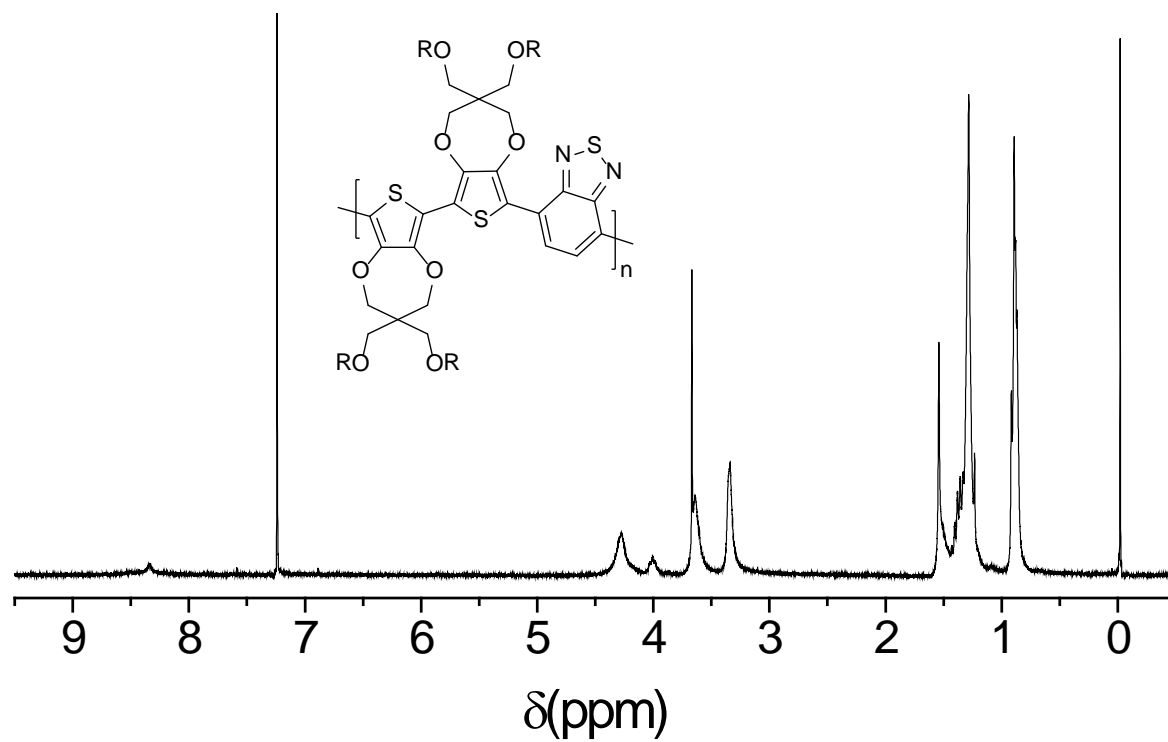
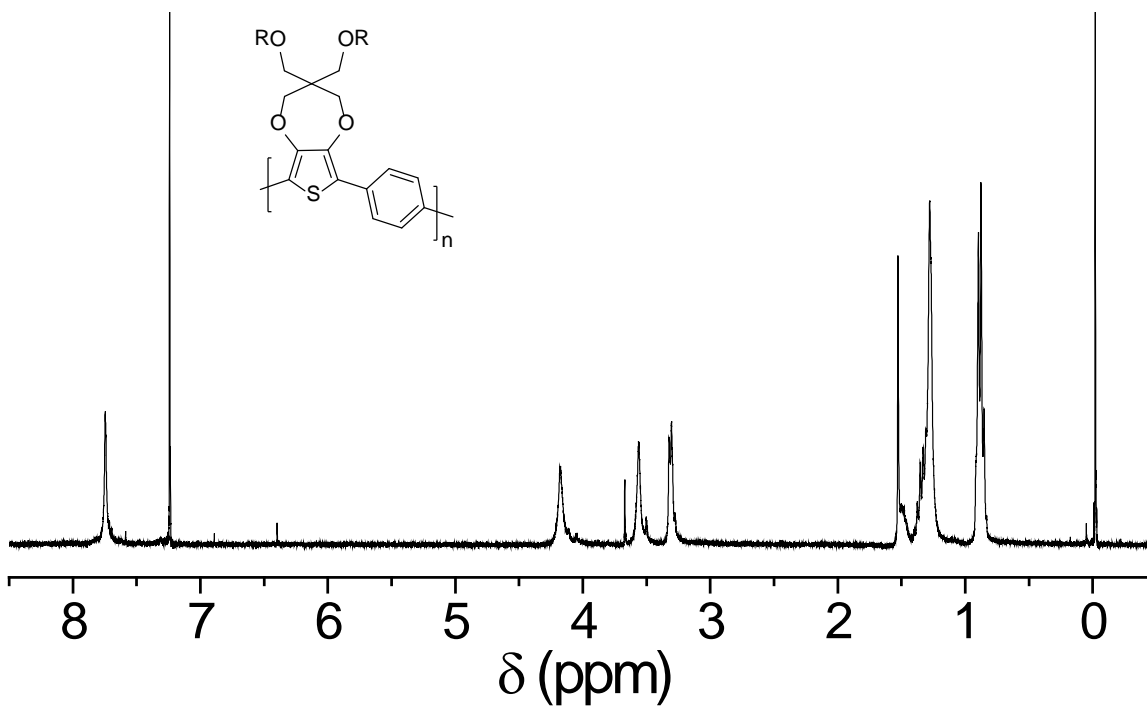
bdl: below detection limit

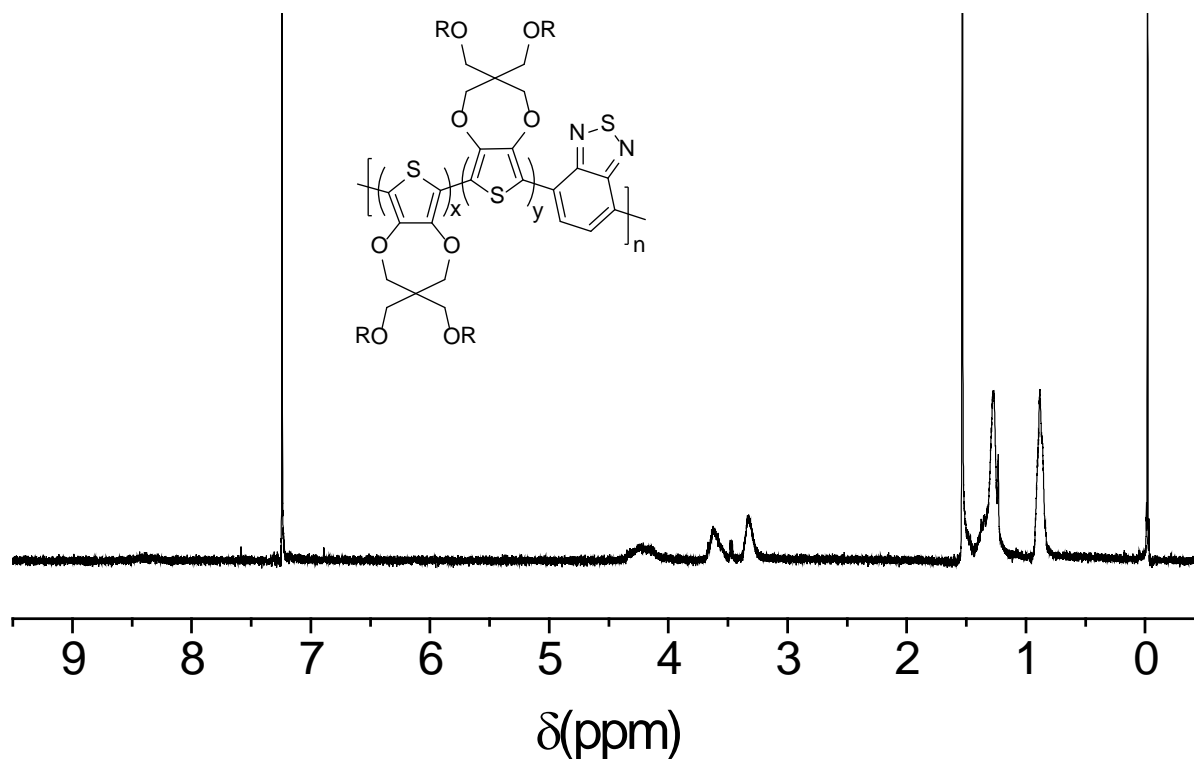
**S4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of novel compounds.****6,8-dibromo-3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (3)**



**3,3',3'-tetrakis(((2-ethylhexyl)oxy)methyl)-3,3',4,4'-tetrahydro-2H,2'H-6,6'-bithieno[3,4 -b][1,4]dioxepine (6)**

**ECP-Magenta  $^1\text{H}$  NMR****ECP-Blue  $^1\text{H}$  NMR**

**ECP-Cyan  $^1\text{H}$  NMR****ECP-Yellow  $^1\text{H}$  NMR**

ECP-Black  $^1\text{H}$  NMR

## S5. References

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