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Electronic Supplementary Information

Synthesis and Optoelectronic Properties of Radical Conjugated Polyfluorenes

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Instrumentation

NMR: ^{1}H NMR data for samples measured in $CDCl_3$ are referenced to internal residual $CHCl_3$ (δ 7.26). ^{13}C NMR data for samples measured in $CDCl_3$ are referenced to internal $CDCl_3$ (δ 77.16). Samples were measured on either a 500 MHz Agilent DD2 or 400 MHz Bruker Avance III spectrometer. All spectra were acquired at room temperature.

GPC: Size exclusion chromatography (SEC) analysis was carried out on a Tosoh EcoSEC instrument with a dual-flow refractive-index detector. HPLC grade THF stabilized with 250 ppm BHT and 2.5 g/L tetrabutylammonium bromide was used as eluent at 40 ºC with a flow rate of 0.6 mL/min. Calibration curves for SEC analysis were obtained with polystyrene standards. Data processing was performed using the EcoSEC Data Analysis software.

Cyclic Voltammetry: CV was performed using a BioLogic SP-200 Potentiostat/ Galvanostat/ Frequency Response Analyzer with a platinum button working electrode, silver wire pseudoreference electrode, and a platinum mesh counter electrode. Experiments were conducted under an argon atmosphere in dry dichloromethane (10 mM polymer, 100 mM tetrabutylammonium hexafluorophosphate electrolyte) at a scan rate of 100 mV/s and referenced to the Fc/ Fc+ redox couple.

Electron Paramagnetic Resonance: EPR spectra were collected on a Bruker CW X-Band ECS-EMXplus EPR spectrometer. Samples were dissolved in THF under inert atmosphere and measured at room temperature.

Time-Resolved Spectroscopy: Time-resolved photoluminescence (TRPL) measurements of polymer samples in solution were acquired using excitation from a λ: 470 nm pulsed diode laser (PicoQuant, LDH-D-C-470), and data was collected using a single photon avalanche diode (Micro Photon Devices, $PD-050-CTD) and PicoQuant HydraHarp 400 event timer. The emission set-up used an off-axis parabolic collimating mirror to collect photoluminescence, which was coupled through free space to the detector. Laser scatter was rejected using a dielectric long-pass filter (FELH0500, Thorlabs) All normalized TRPL traces are fit to three-component exponential functions with the weighted average lifetime reported. An excitation irradiance of 0.6 $\mu J/cm^2$/pulse was used in the measurements presented in the main text. (Figure 6, 7, ESI 17)

Atomic Force Microscopy: Layer thickness measurements and AFM height profiles were conducted using a 10 nm tip on a Bruker Dimension Icon microscope. Slides were scratched to expose the glass substrate, allowing for layer thickness of the polymer films to be measured.

Melting Point: Melting points were recorded under ambient conditions using a Mel-Temp digital melting point apparatus, and are uncorrected.

Experimental Procedures

General Considerations

All reagents were purchased from Sigma and used without further purification.

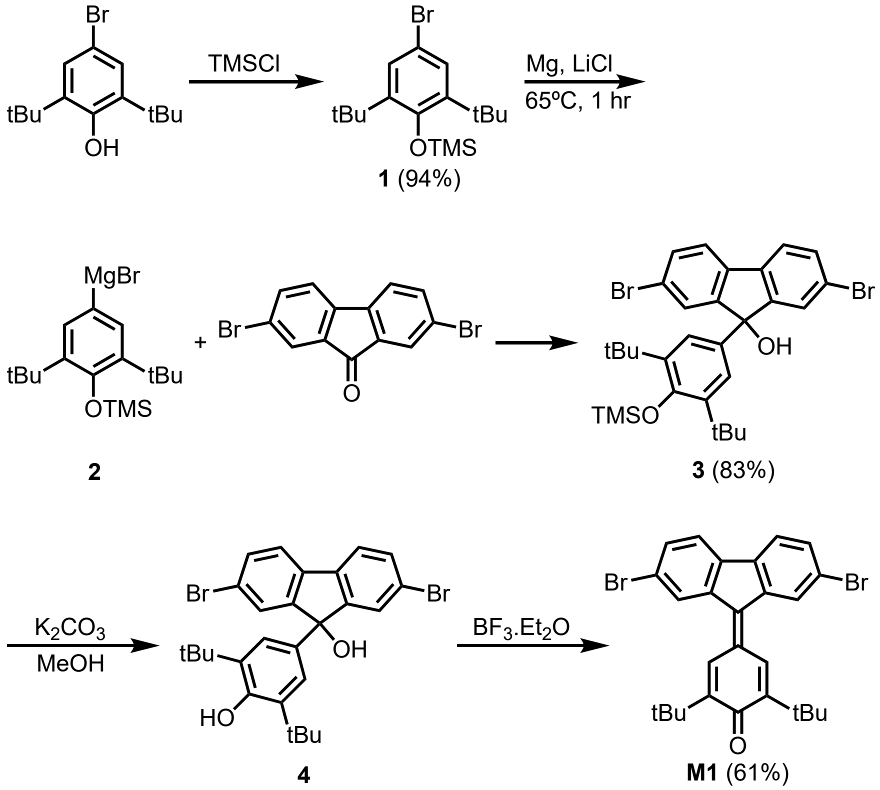


Figure ESI 1. Synthesis of monomers via protected phenol route.

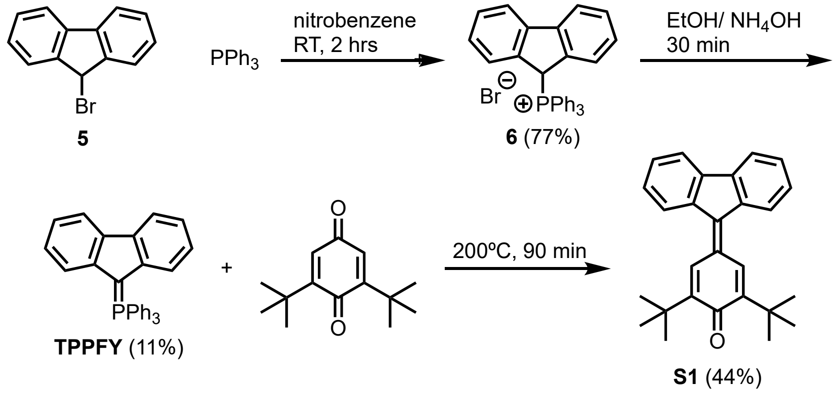


Figure ESI 2. Synthesis of small molecule test compound S1.

2,6-Di-*tert*-butyl-4-bromophenoxytrimethyl silane (1): All glass apparatus was dried before use and the reaction was carried out under inert atmosphere. 2,6-Di-*tert*-butyl-4-bromophenol (5.0 g, 17.5 mmol) was dissolved in THF (60 mL) in a Schlenk flask and cooled to -78 ºC. *n*-Butyllithium (1.5 eq.) was added dropwise and the resulting solution was stirred at -78 ºC for 1 hr. Trimethylsilyl chloride (3.8 mL, 29.6 mmol) was added via syringe and the reaction mixture was stirred and allowed to warm to room temperature over 1 hr. Water was added via syringe to quench the reaction and the mixture was stirred for another 30 minutes. The organic layer was separated and the aqueous layer was extracted with hexanes. The combined organic layers were washed with water and dried over magnesium sulfate. Purification by silica gel column chromatography with hexanes as eluent yielded the product as clear, hexagonal crystals (5.9 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2H), 1.38 (s, 18H), 0.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.58, 143.28, 128.81, 113.93, 35.44, 31.18, 4.01. Melting range: 146 – 149 ºC.

[2,6-Di-*tert*-butyl-4-(2,7-dibromofluoren-9-yl)phenoxy]trimethyl silane (3): All glass apparatus were dried before use and the reaction was carried out under inert atmosphere. **1** (1.0 g, 2.8 mmol), Mg turnings (0.68 g, 28 mmol), and a small amount (approx. 50 mg) of flame-dried lithium chloride were added to a Schlenk flask. THF (14 mL) was added and the mixture was stirred at 65 ºC for an hour to generate the 2,6-di-*tert*-butyl-phenoxytrimethyl silane Grignard. 2,7-Dibromo-9-fluorenone (0.47 g, 1.40 mmol) was dissolved in THF (12 mL) in a separate Schlenk flask. The Grignard solution was transferred via cannula to the solution of 2,7-dibromo-9-fluorenone and the resulting mixture was stirred for 20 hrs. The reaction mixture was quenched with water and extracted with chloroform. The organic fractions were washed with saturated brine solution and dried over magnesium sulfate. Purification was carried out by silica gel column chromatography with 4% acetone in hexanes as eluent. On silica, the product decomposes to form a bright yellow by-product when exposed to UV light, but is stable otherwise. The product is collected as a viscous yellow oil that foams vigorously upon drying (0.717 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, J = 1.2 Hz, 2H), 7.49 (d, J = 1.2 Hz, 4H), 7.22 (s, 2H), 1.33 (s, 18H), 0.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.07, 152.26, 140.78, 137.61, 132.86, 132.28, 128.55, 123.05, 122.35, 121.62, 83.86, 35.40, 31.29, 4.16.

Synthesis of M1: Procedures are adapted from Nishiyama and coworkers.[3] **3** (1.28 g, 2.08 mmol) and potassium carbonate (1.15 g, 8.34 mmol) were stirred in methanol (20 mL) for 10 minutes at room temperature, then concentrated under reduced pressure. The residue was redissolved in chloroform, washed with ammonium chloride and saturated brine solution, then dried over magnesium sulfate and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (70 mL) and cooled to 0 ºC. Boron trifluoride etherate (0.26 mL, 2.08 mmol) was added via syringe and the resulting solution was stirred for 1 hr. The reaction mixture was quenched with water, extracted with chloroform, washed with brine, and dried over magnesium sulfate. Purification by silica gel column chromatography with hexanes as eluent yielded the product as dark red, needle-shaped crystals (0.6728 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 1.4 Hz, 2H), 7.93 (s, 2H), 7.51 (dd, J = 1.8, 1.0 Hz, 4H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.36, 139.62, 139.45, 134.81, 132.63, 130.74, 128.84, 121.79, 121.65, 36.20, 29.90. Melting range: 237 – 241 ºC.

Fluorenyl-9-triphenylphosphonium bromide (6): The synthetic procedures reported by Anthony and coworkers was followed.[1] Triphenylphosphine (7.0 g, 26.6 mmol) was dissolved in

65 mL of nitrobenzene in a round bottom flask. 9-Bromofluorene (6.5 g, 26.6 mmol) was dissolved separately in 33 mL of nitrobenzene and added dropwise to the triphenylphosphine solution. The reaction mixture was stirred at room temperature for 2 hrs, yielding **2** as a white precipitate in a yellow solution. The precipitate was collected by vacuum filtration, washed with nitrobenzene, and used in subsequent steps without further purification (10.4 g, 77%).

Triphenylphosphoniumfluorenylide (TPPFY): The synthetic procedures reported by Anthony and coworkers was followed.[1] **2** was suspended in 200 mL of ethanol. 100 mL of ammonium hydroxide was added to the solution, resulting in immediate formation of a bright yellow solution. The reaction mixture was heated at gentle reflux for 30 minutes, then cooled to room temperature. The crude product was isolated as a yellow powder by vacuum filtration, then redissolved in 1 L acetonitrile for recrystallization. After leaving the solution overnight, small needle-like crystals were formed and isolated by vacuum filtration (1.22 g, 11%). Attempts to recover further crops of crystals from the mother liquor were unsuccessful; repeated heating and cooling resulted in decomposition of the product, as indicated by the solution turning from a bright yellow to dark brown colour. ^{31}P NMR indicates the presence of triphenylphosphine oxide (referenced to δ 29.26). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.8 Hz, 2H), 7.84–7.42 (m, 15H), 6.99 (t, J = 7.3 Hz, 2H), 6.88 (t, J = 7.5 Hz, 2H), 6.33 (d, J = 8.1 Hz, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 6.56 (s). Melting range: 264 – 270 ºC.

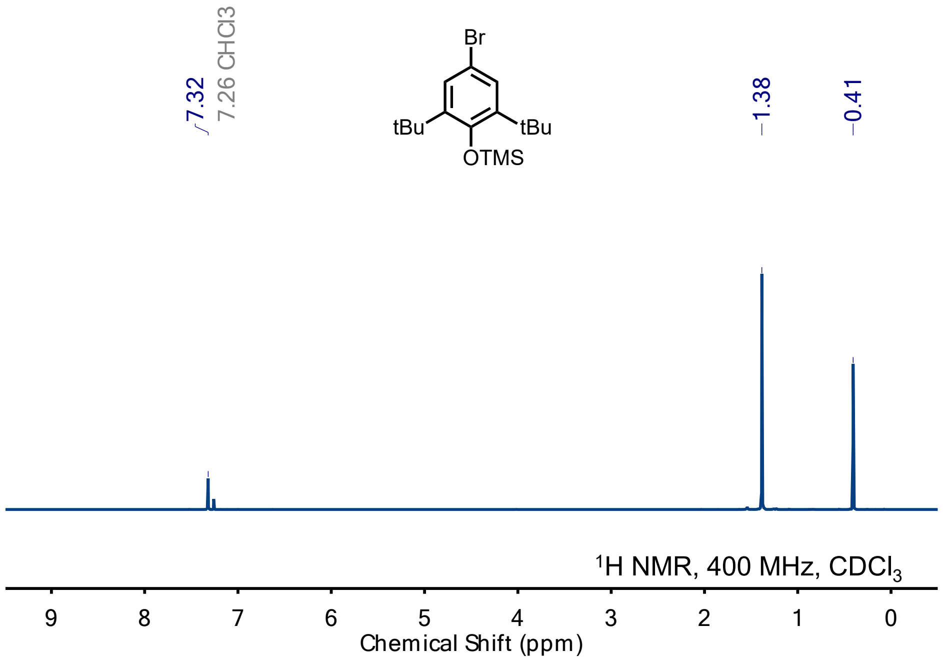
2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (S1): The synthetic procedures reported by Becker and Gustafsson was followed.[2] TPPFY (0.100 g, 0.23 mmol) and 2,6-di-*tert*-butylbenzoquinone (0.103 g, 0.47 mmol) were weighed into a glass vial with a stir bar, capped, and stirred at 200 ºC in a sand bath for 90 minutes, resulting in a deep red melt. Upon cooling, the solid residue was dissolved in CH_2Cl_2 and precipitated into methanol. The precipitate was vacuum filtered, then redissolved in a 2:1 mixture of hexanes and CH_2Cl_2. Purification was attempted by silica gel column chromatography. The yield was minimal, but enough to obtain an ^{1}H NMR spectrum. (0.040 g, 44%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.73–7.65 (m, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 1.27 (s, 18H). Melting range: 198 – 202 ºC.

Synthesis of P-alt: The reaction was conducted under inert atmosphere and all solvents were deoxygenated prior to use. **M1** (1 eq.), **M2** (1 eq.), sodium hydroxide (4 eq.), and $Pd(PPh_3)_4$ (0.05 eq.) were weighed into a Schlenk flask. Toluene (8.4 mL), water (0.76 L), and Aliquat 336 were added via syringe. The reaction mixture was heated to 90 ºC and stirred for 48 hrs. Phenylboronic acid (2.2 eq.) was added to the reaction mixture under positive argon pressure and stirred for 2 hrs. Bromobenzene (2.2 eq.) was added to the reaction mixture via syringe and stirred for an additional 2 hrs. The polymerization was quenched with 6 M HCl and precipitated into methanol. The polymer was purified by Soxhlet extraction with methanol, acetone, and hexanes, before being collected with chloroform. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33, 7.85, 7.81, 7.75, 7.71, 7.67, 7.62, 3.49, 2.10, 1.57, 1.53, 1.45, 1.26, 1.08, 0.78, 0.77, 0.75.. ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.75, 151.98, 149.34, 141.39, 140.84, 140.08, 139.08, 133.40, 129.71, 129.44, 128.95, 127.36, 126.75, 126.20, 124.98, 124.21, 121.17, 120.87, 120.48, 55.75, 40.86, 36.21, 34.63, 31.93, 30.60, 30.16, 29.86, 29.40, 24.09, 23.34, 22.74, 14.19.

Synthesis of P-ter: The same polymerization and purification procedures as above was followed, using 1:1:2 equivalents of **M1**, **M3**, and **M2**. Equivalents of other reagents are calculated relative to **M2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34, 8.09, 8.04, 7.99, 7.95, 7.82, 7.76, 7.71, 7.68, 1.55, 1.53, 1.46, 1.43, 1.26, 1.16, 1.12, 0.80, 0.79, 0.77, 0.07. ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.97, 30.29, 30.18, 29.42, 22.76, 14.21.

NMR Spectra

a) 2,6-Di-*tert*-butyl-4-bromophenoxytrimethyl silane (**1**)



b) 2,6-Di-*tert*-butyl-4-bromophenoxytrimethyl silane (**1**)

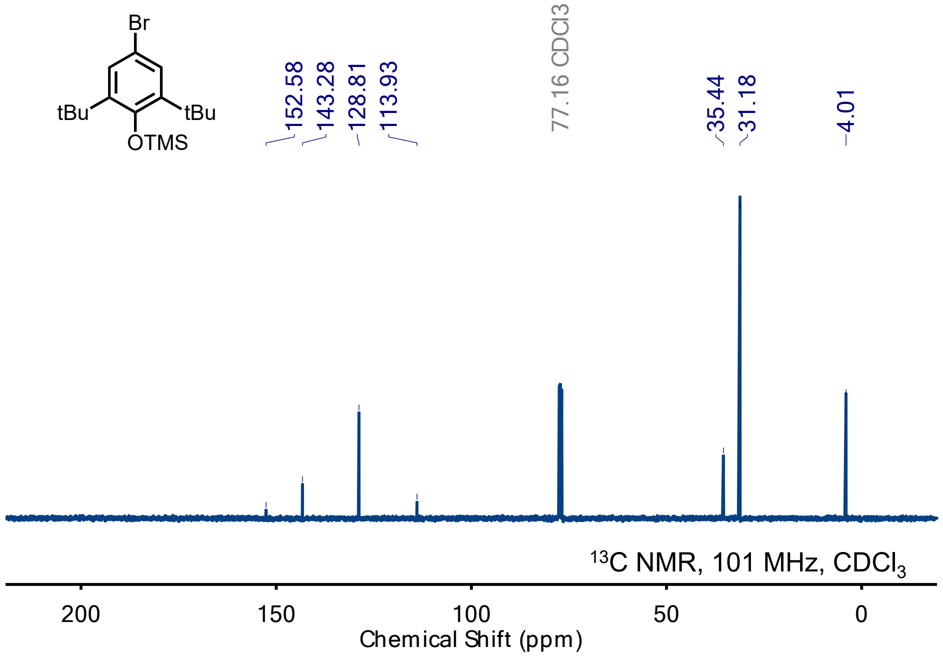
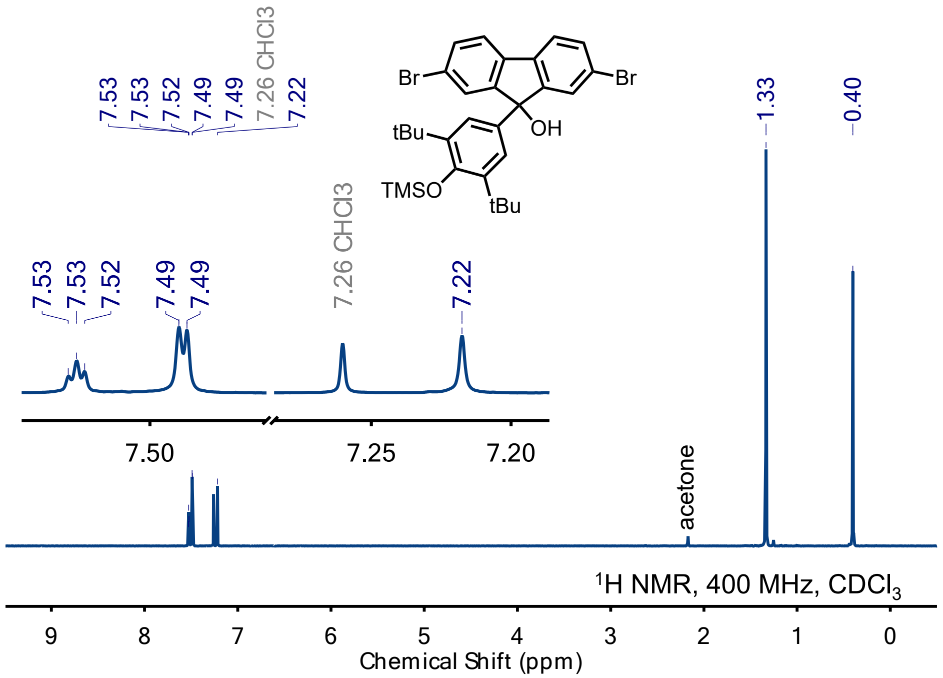


Figure ESI 3. a) ^{1}H NMR (400 MHz) and b) ^{13}C NMR (101 MHz) spectra of 1 in CDCl$_3$.

a) 2,6-Di-*tert*-butyl-4-(2,7-dibromofluoren-9-yl)phenoxy]trimethyl silane (**3**)



b) 2,6-Di-*tert*-butyl-4-(2,7-dibromofluoren-9-yl)phenoxy]trimethyl silane (**3**)

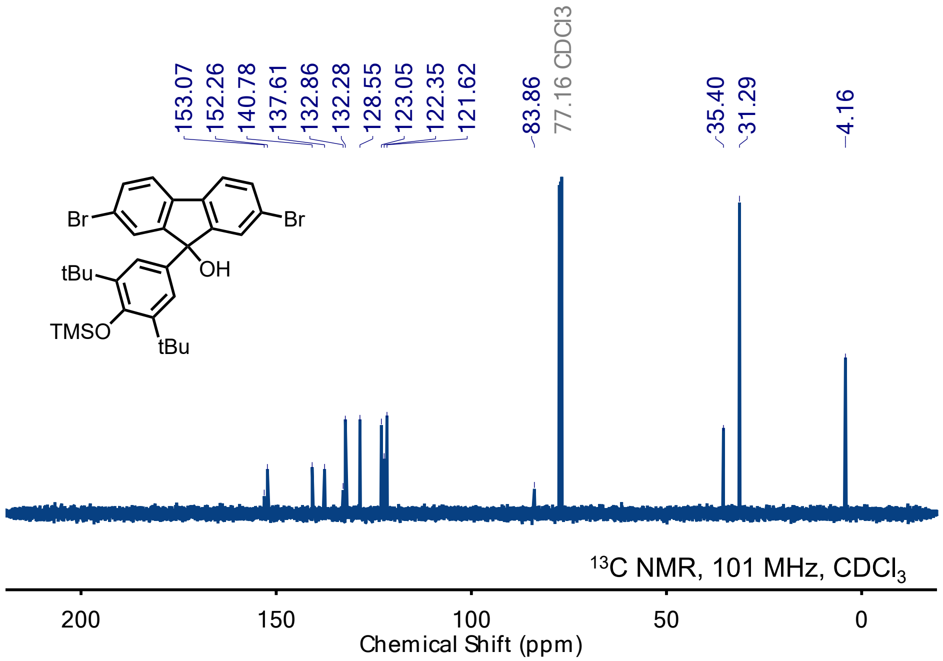
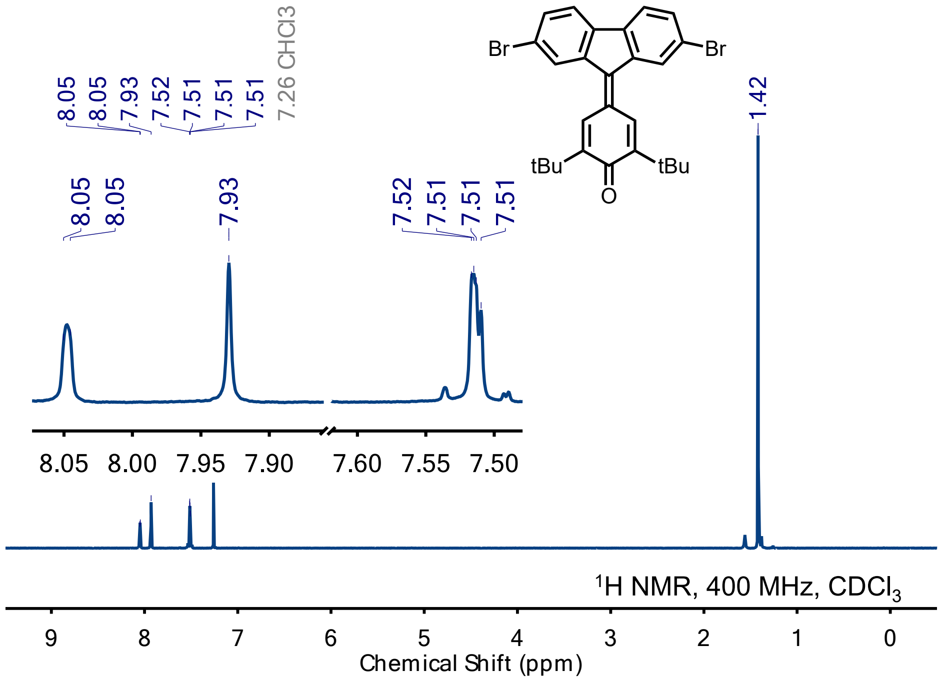


Figure ESI 4. a) ^{1}H NMR (400 MHz) and b) ^{13}C NMR (101 MHz) spectra of 3 in CDCl$_3$.

a) Compound **M1**



b) Compound **M1**

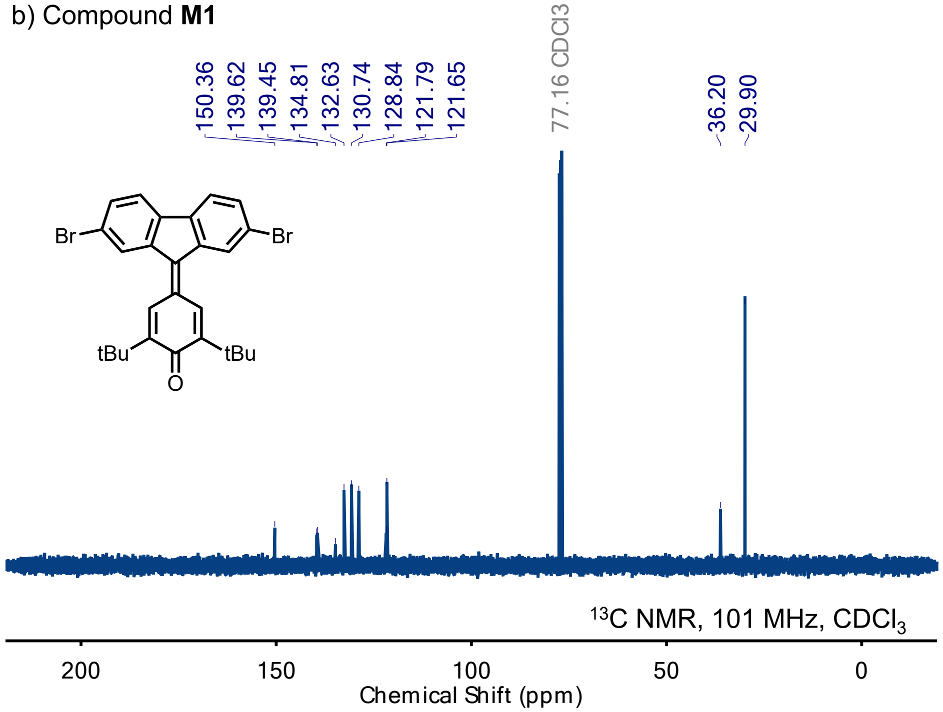
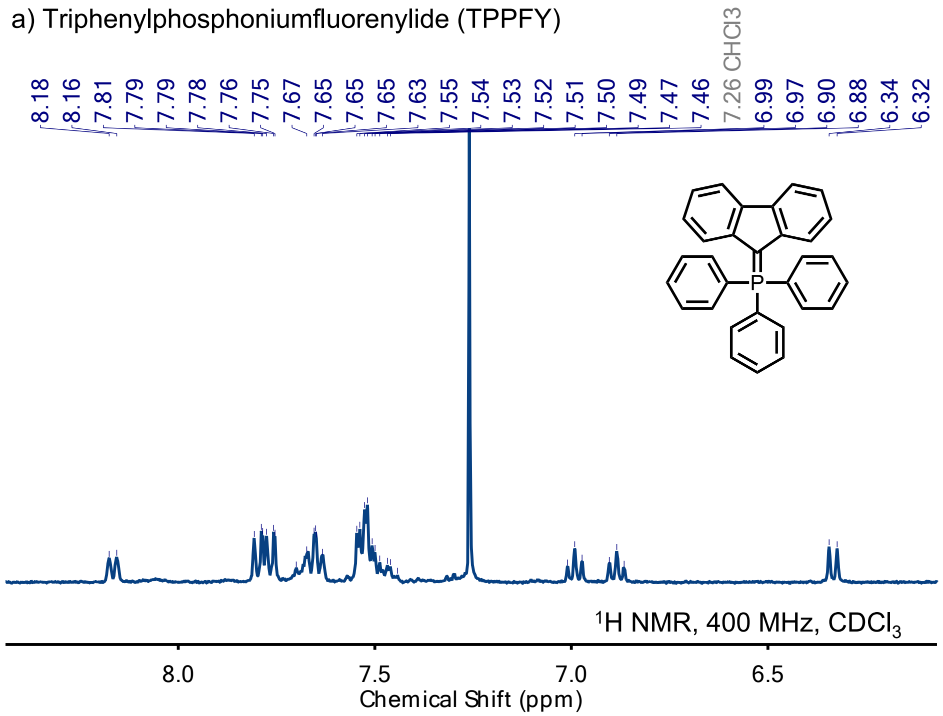


Figure ESI 5. a) ^{1}H NMR (400 MHz) and b) ^{13}C NMR (101 MHz) spectra of M1 in $CDCl_3$.


a) Triphenylphosphoniumfluorenylide (TPPFY)

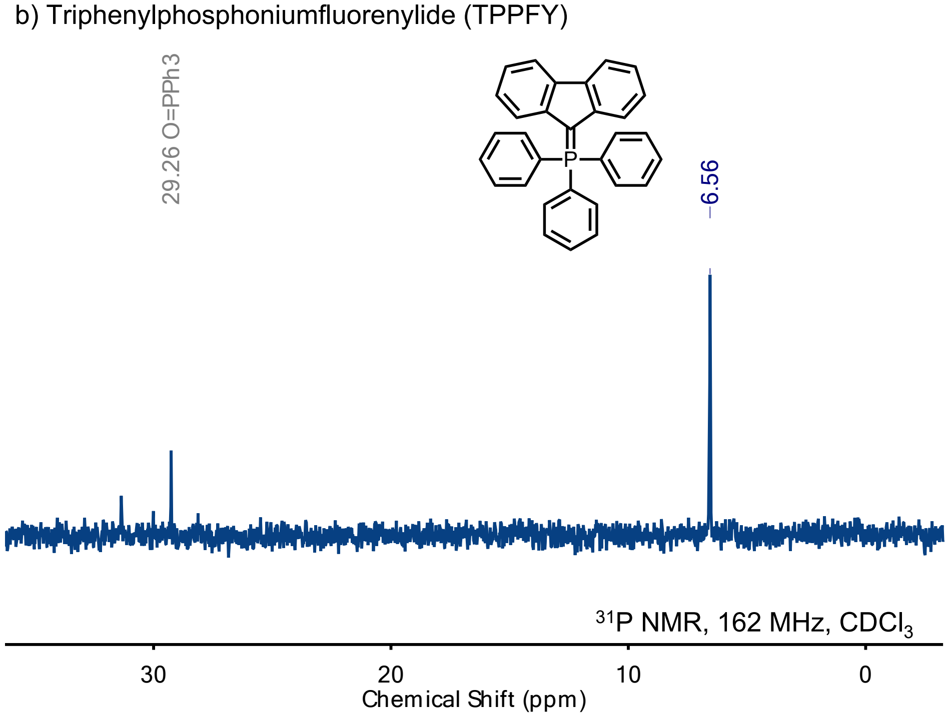

b) Triphenylphosphoniumfluorenylide (TPPFY)

Figure ESI 6. a) ^{1}H NMR (400 MHz) and b) ^{31}P NMR (162 MHz) spectra of TPPFY in CDCl$_3$.

2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (**S1**)

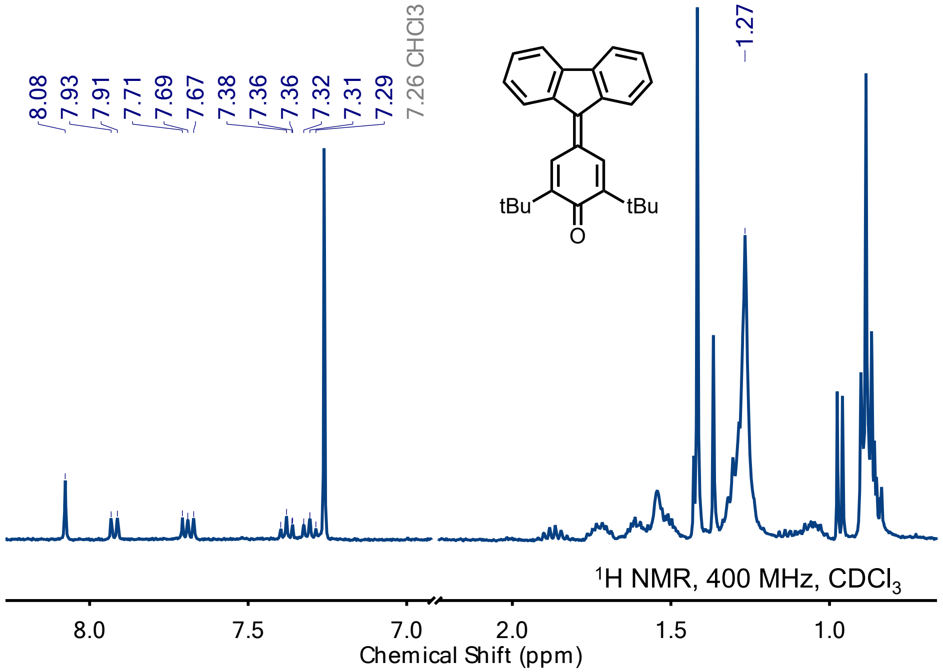
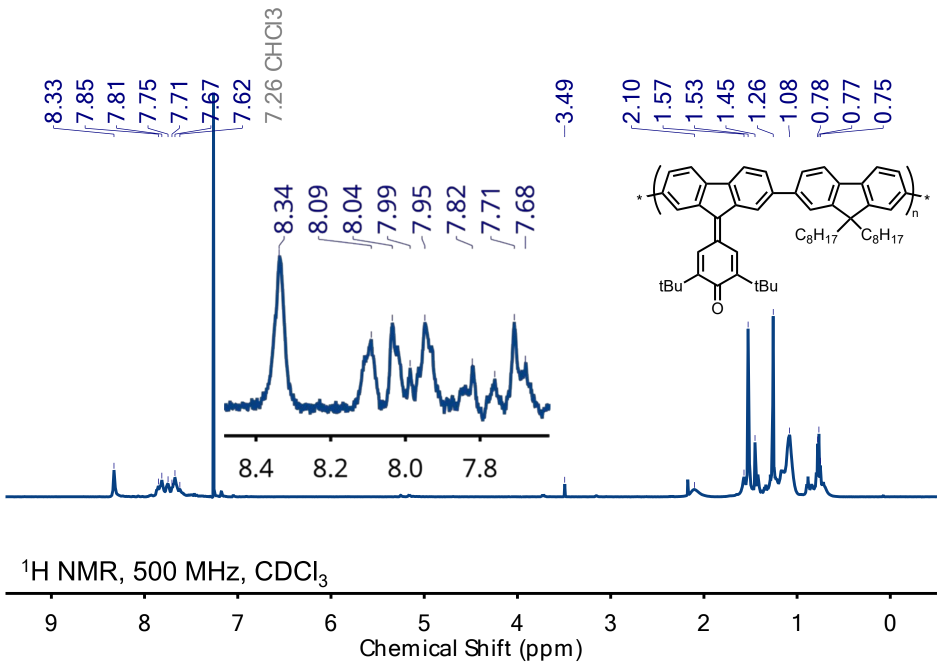


Figure ESI 7. ^{1}H NMR (400 MHz) spectrum of S1 in CDCl$_3$.

a) **P-alt**



b) **P-alt**

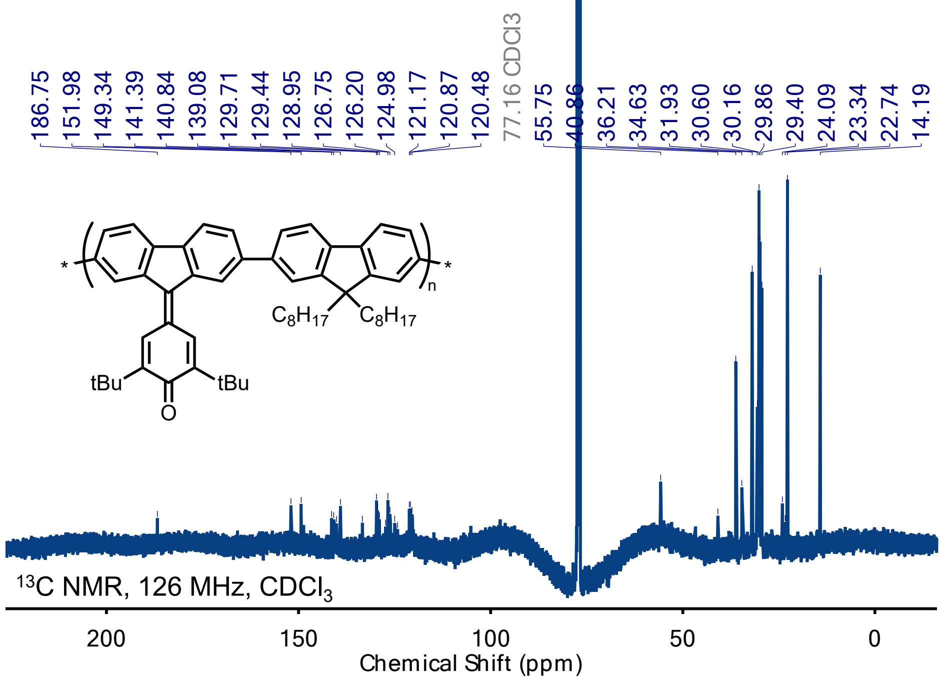
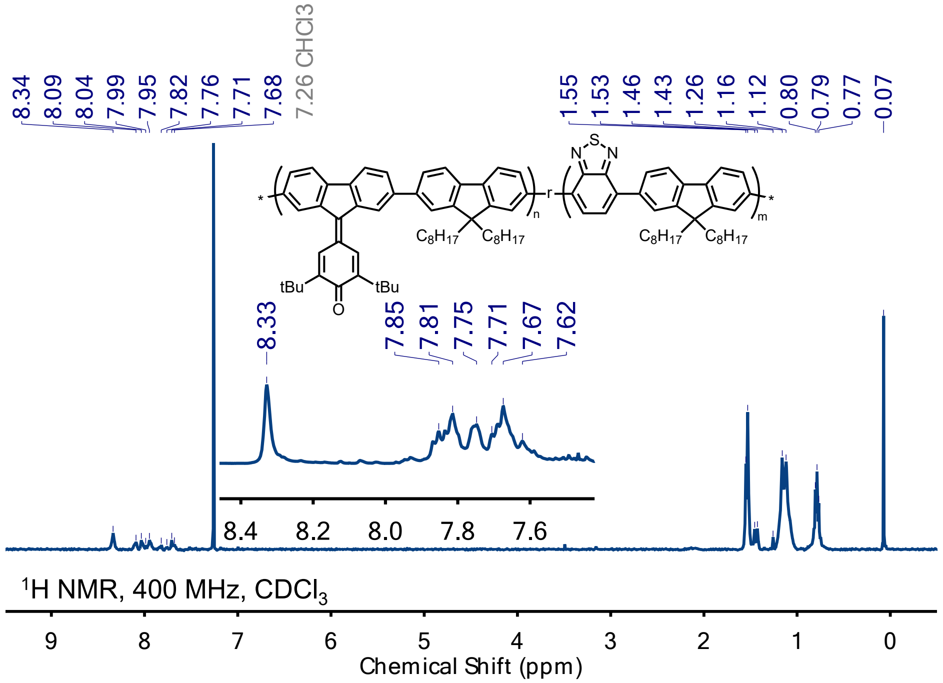
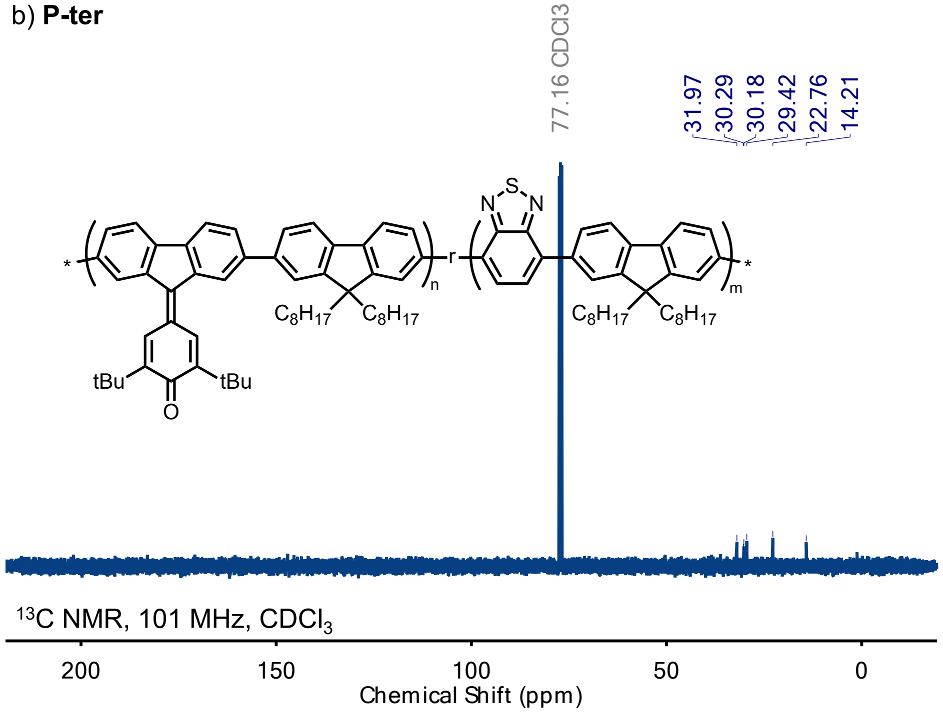


Figure ESI 8. a) ^{1}H NMR (500 MHz) and b) ^{13}C NMR (126 MHz) spectra of P-alt in CDCl$_3$.



a) **P-ter**



b) **P-ter**

Figure ESI 9. a) ^{1}H NMR (400 MHz) and b) ^{13}C NMR (101 MHz) spectra of P-ter in $CDCl_3$.

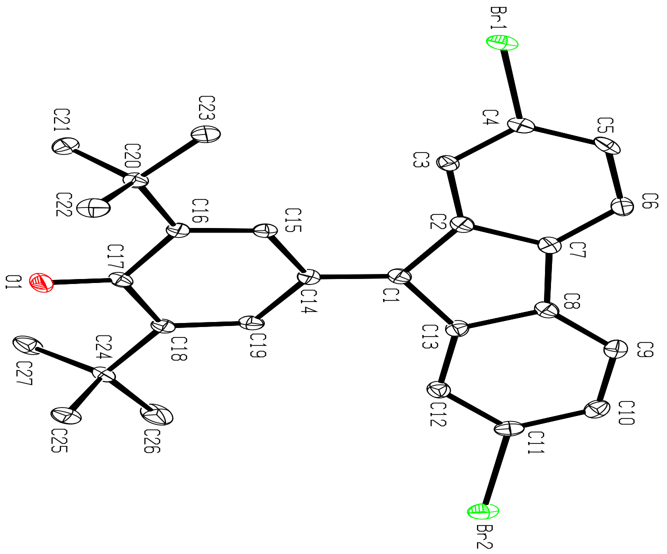


Figure ESI 10. Structure of M1 obtained from single crystal x-ray diffraction. Compound crystallized by slow evaporation from a mixture of CH_2Cl_2 and hexanes.

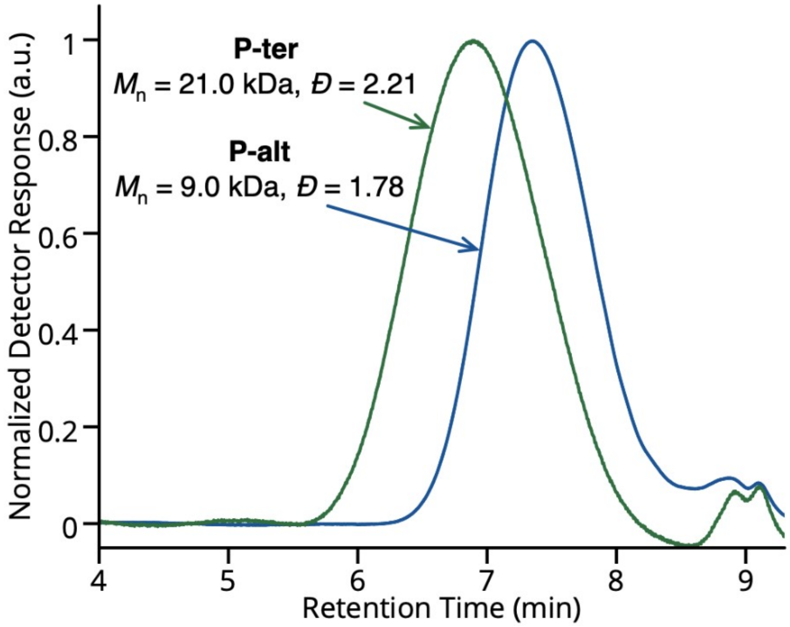


Figure ESI 11. GPC traces of P-alt and P-ter (eluent: THF, 40 ºC). Values are calculated relative to polystyrene calibration standards.

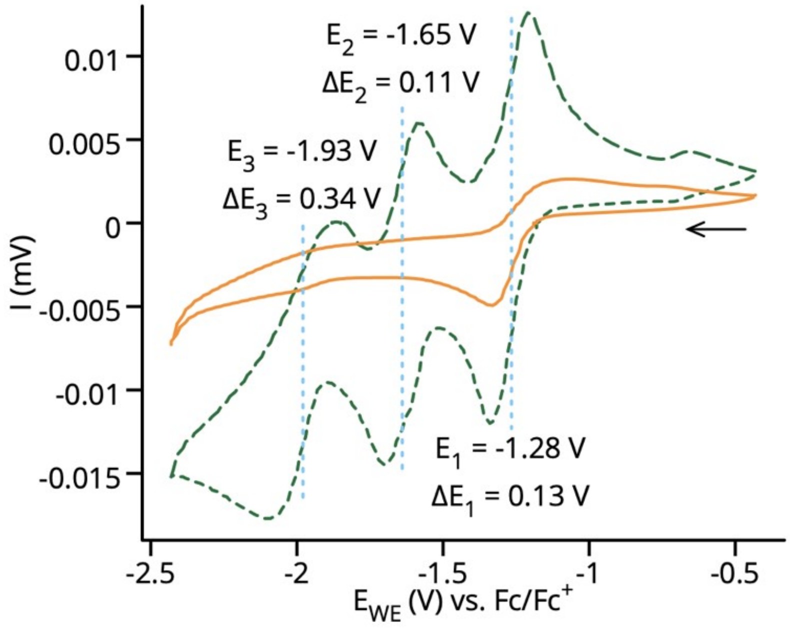


Figure ESI 12. CV measurement of P-ter copolymer (10 mM) in dichloromethane referenced to Fc/Fc$^+$ at scan rate of 100 mV/s. Counterion from TBAPF$_6$ (100 mM). The dashed trace represents the first measurement (second scan) in which peaks show distinct redox events, and the orange solid trace represents a subsequent measurement in which loss of redox features is attributed to fouling of the electrodes.

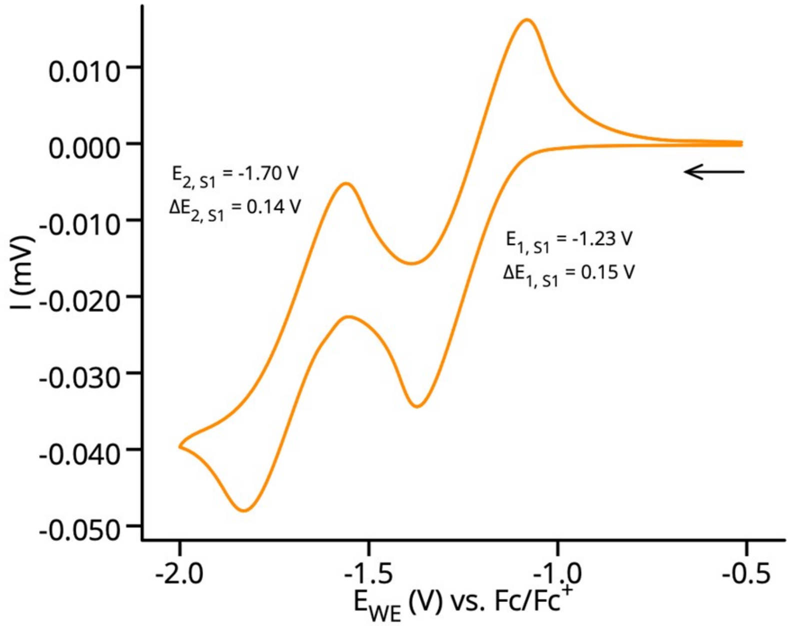


Figure ESI 13. CV measurement of S1 (10 mM) in dichloromethane referenced to Fc/Fc$^+$ at scan rate of 100 mV/s. Counterion from TBAPF$_6$ (100 mM).

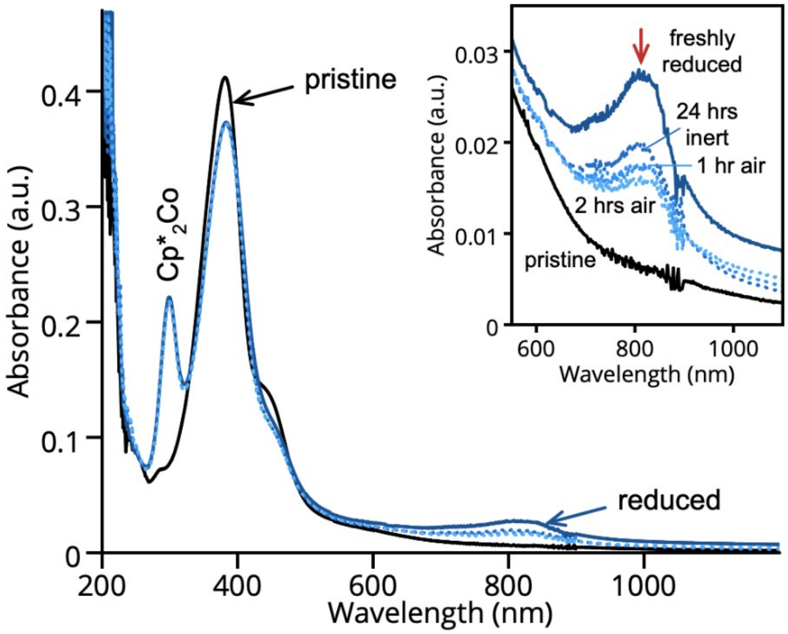


Figure ESI 14. Absorbance spectra of P-alt thin films in the pristine and reduced states. Films were reduced by immersion in a saturated solution of Cp*$_2$Co in hexanes under inert atmosphere and then exposed to air immediately prior to measurement.

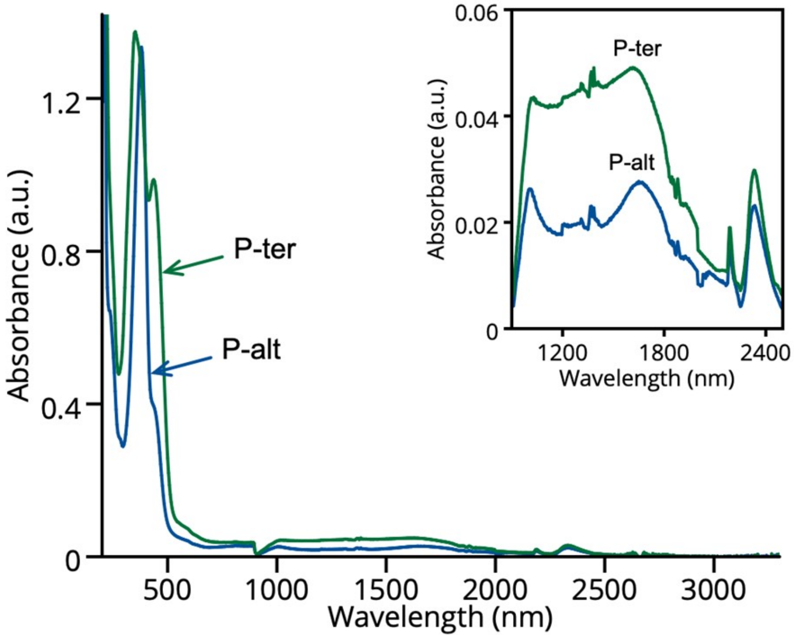


Figure ESI 15. Absorbance spectra of P-alt and P-ter thin films cast from polymer solutions in THF and then reduced with sodium metal.

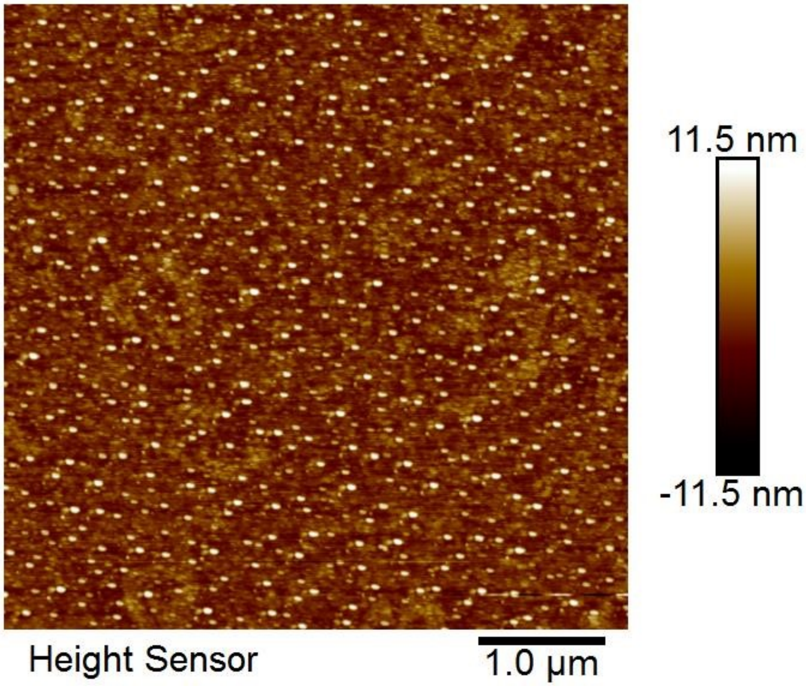


Figure ESI 16. AFM image of rP-alt film on glass substrate, reduced with saturated Cp*$_2$Co in hexanes.

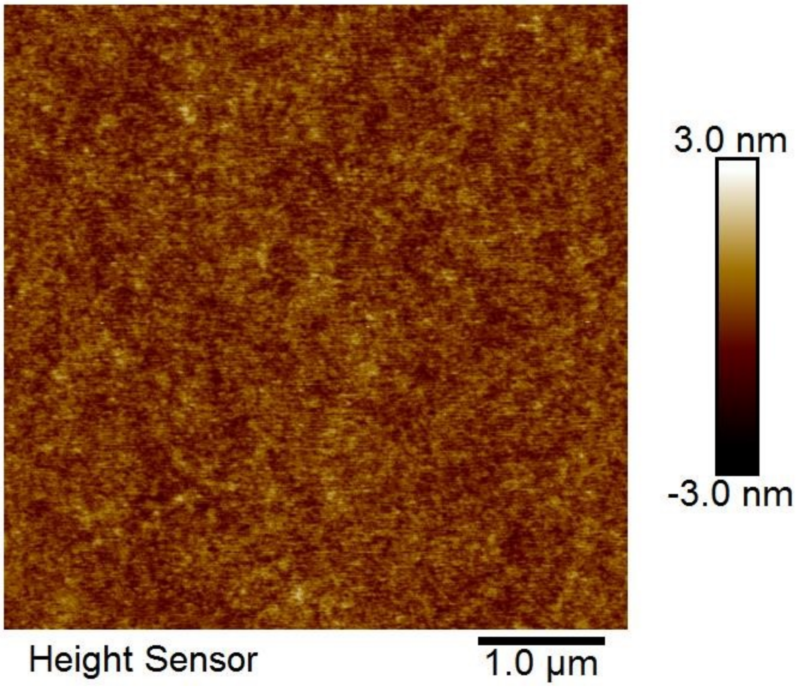


Figure ESI 17. AFM image of rP-ter film on glass substrate, reduced with saturated Cp*$_2$Co in hexanes.

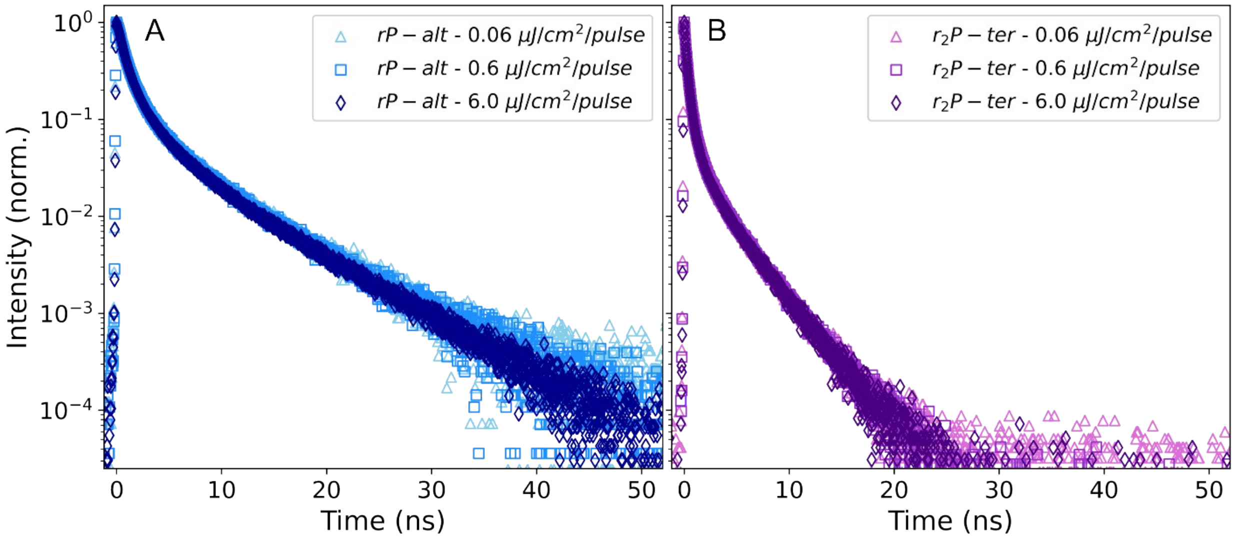


Figure ESI 17. Intensity dependence of transient photoluminescence measurements on a) rP-alt and b) r_2P-ter in solution.

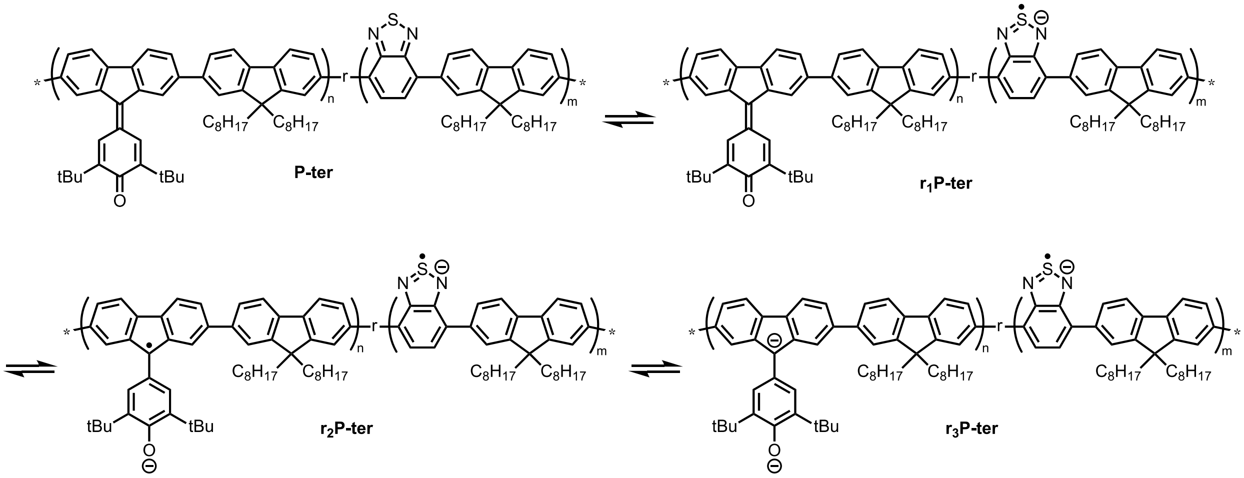


Figure ESI 18. Proposed structures of tertiary copolymer species corresponding to peaks E_1, E_2, and E_3 observed in the CV scan.

Crystallographic Data for M1 – CCDC 2168372

Table 1. Crystal data and structure refinement for d21120_a.

Identification code	d21120_a	
Empirical formula	C27 H26 Br2 O	
Formula weight	526.30	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.9449(9) Å	a= 98.128(4)°.
	b = 11.5815(17) Å	b= 96.785(4)°.
	c = 17.349(2) Å	g = 99.935(4)°.
Volume	1152.3(3) Å^3	
Z	2	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	3.534 mm^{-1}	
F(000)	532	
Crystal size	0.230 x 0.200 x 0.020 mm^3	
Theta range for data collection	1.999 to 27.458°.	
Index ranges	-7<=h<=7, -14<=k<=15, -20<=l<=22	
Reflections collected	33349	
Independent reflections	5248 [R(int) = 0.0940]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5718	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5248 / 0 / 277	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.0917	
R indices (all data)	R1 = 0.0846, wR2 = 0.1021	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.485 and -0.762 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for d21120_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	13003(1)	5302(1)	599(1)	30(1)
Br(2)	2128(1)	8570(1)	4418(1)	30(1)
O(1)	1752(5)	1254(3)	2462(2)	33(1)
C(1)	6554(6)	5768(3)	2560(2)	20(1)
C(2)	8429(6)	6162(4)	2100(2)	21(1)
C(3)	9714(6)	5533(4)	1640(2)	22(1)
C(4)	11381(6)	6163(4)	1283(2)	23(1)
C(5)	11863(7)	7385(4)	1392(2)	30(1)
C(6)	10654(7)	8030(4)	1879(2)	26(1)
C(7)	8943(7)	7411(4)	2230(2)	21(1)
C(8)	7473(6)	7862(4)	2769(2)	21(1)
C(9)	7345(7)	9018(4)	3049(2)	25(1)
C(10)	5782(7)	9233(4)	3552(2)	26(1)
C(11)	4325(7)	8280(4)	3744(2)	24(1)
C(12)	4413(7)	7106(4)	3460(2)	22(1)
C(13)	6063(7)	6888(3)	2983(2)	22(1)
C(14)	5427(6)	4627(3)	2563(2)	19(1)
C(15)	5482(6)	3664(3)	1936(2)	20(1)
C(16)	4339(6)	2549(3)	1885(2)	18(1)
C(17)	2917(6)	2252(4)	2505(2)	21(1)
C(18)	2941(6)	3210(3)	3183(2)	19(1)
C(19)	4124(6)	4305(4)	3176(2)	21(1)
C(20)	4432(6)	1569(4)	1197(2)	21(1)
C(21)	5477(7)	580(4)	1523(2)	28(1)
C(22)	2019(7)	1067(4)	738(3)	33(1)
C(23)	5962(8)	2057(4)	622(2)	31(1)
C(24)	1632(6)	2893(4)	3855(2)	21(1)
C(25)	-949(7)	2564(4)	3554(2)	29(1)

C(26)	1998(9)	3948(4)	4523(3)	44(1)
C(27)	2450(7)	1866(4)	4199(3)	33(1)

Table 3. Bond lengths [Å] and angles [°] for d21120_a.

Br(1)-C(4)	1.898(4)
Br(2)-C(11)	1.894(4)
O(1)-C(17)	1.227(5)
C(1)-C(14)	1.375(5)
C(1)-C(13)	1.490(5)
C(1)-C(2)	1.492(5)
C(2)-C(3)	1.387(5)
C(2)-C(7)	1.405(5)
C(3)-C(4)	1.386(5)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.376(6)
C(5)-C(6)	1.393(6)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.392(5)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.457(5)
C(8)-C(9)	1.377(6)
C(8)-C(13)	1.406(5)
C(9)-C(10)	1.377(6)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.386(6)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.392(5)
C(12)-C(13)	1.389(5)
C(12)-H(12A)	0.9500
C(14)-C(19)	1.441(5)
C(14)-C(15)	1.452(5)
C(15)-C(16)	1.337(5)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.486(5)
C(16)-C(20)	1.540(5)
C(17)-C(18)	1.496(5)
C(18)-C(19)	1.343(5)
C(18)-C(24)	1.528(5)

C(19)-H(19A)	0.9500
C(20)-C(23)	1.529(5)
C(20)-C(22)	1.530(5)
C(20)-C(21)	1.537(6)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.525(5)
C(24)-C(26)	1.527(6)
C(24)-C(27)	1.530(6)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800

C(14)-C(1)-C(13)	127.2(3)
C(14)-C(1)-C(2)	127.9(3)
C(13)-C(1)-C(2)	104.8(3)
C(3)-C(2)-C(7)	119.4(3)
C(3)-C(2)-C(1)	131.9(4)
C(7)-C(2)-C(1)	108.5(3)
C(4)-C(3)-C(2)	118.4(4)
C(4)-C(3)-H(3A)	120.8
C(2)-C(3)-H(3A)	120.8
C(5)-C(4)-C(3)	122.5(4)

C(5)-C(4)-Br(1)	118.9(3)
C(3)-C(4)-Br(1)	118.5(3)
C(4)-C(5)-C(6)	119.6(4)
C(4)-C(5)-H(5A)	120.2
C(6)-C(5)-H(5A)	120.2
C(7)-C(6)-C(5)	118.6(4)
C(7)-C(6)-H(6A)	120.7
C(5)-C(6)-H(6A)	120.7
C(6)-C(7)-C(2)	121.3(4)
C(6)-C(7)-C(8)	129.6(4)
C(2)-C(7)-C(8)	109.1(3)
C(9)-C(8)-C(13)	122.1(4)
C(9)-C(8)-C(7)	129.4(4)
C(13)-C(8)-C(7)	108.4(3)
C(8)-C(9)-C(10)	119.2(4)
C(8)-C(9)-H(9A)	120.4
C(10)-C(9)-H(9A)	120.4
C(9)-C(10)-C(11)	119.2(4)
C(9)-C(10)-H(10A)	120.4
C(11)-C(10)-H(10A)	120.4
C(10)-C(11)-C(12)	122.4(4)
C(10)-C(11)-Br(2)	119.4(3)
C(12)-C(11)-Br(2)	118.2(3)
C(13)-C(12)-C(11)	118.4(4)
C(13)-C(12)-H(12A)	120.8
C(11)-C(12)-H(12A)	120.8
C(12)-C(13)-C(8)	118.6(4)
C(12)-C(13)-C(1)	132.1(4)
C(8)-C(13)-C(1)	109.0(3)
C(1)-C(14)-C(19)	123.0(3)
C(1)-C(14)-C(15)	121.3(3)
C(19)-C(14)-C(15)	115.7(3)
C(16)-C(15)-C(14)	124.2(3)
C(16)-C(15)-H(15A)	117.9
C(14)-C(15)-H(15A)	117.9
C(15)-C(16)-C(17)	119.1(3)

C(15)-C(16)-C(20)	121.8(3)
C(17)-C(16)-C(20)	119.1(3)
O(1)-C(17)-C(16)	121.3(3)
O(1)-C(17)-C(18)	120.9(3)
C(16)-C(17)-C(18)	117.8(3)
C(19)-C(18)-C(17)	118.5(3)
C(19)-C(18)-C(24)	123.0(3)
C(17)-C(18)-C(24)	118.4(3)
C(18)-C(19)-C(14)	124.5(3)
C(18)-C(19)-H(19A)	117.7
C(14)-C(19)-H(19A)	117.7
C(23)-C(20)-C(22)	107.7(3)
C(23)-C(20)-C(21)	107.9(3)
C(22)-C(20)-C(21)	110.5(3)
C(23)-C(20)-C(16)	111.0(3)
C(22)-C(20)-C(16)	110.7(3)
C(21)-C(20)-C(16)	109.1(3)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(26)	107.3(3)

C(25)-C(24)-C(18)	109.4(3)
C(26)-C(24)-C(18)	111.3(3)
C(25)-C(24)-C(27)	110.2(3)
C(26)-C(24)-C(27)	107.5(4)
C(18)-C(24)-C(27)	111.1(3)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for d21120_a. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	24(1)	42(1)	28(1)	8(1)	11(1)	11(1)
Br(2)	31(1)	36(1)	27(1)	5(1)	9(1)	15(1)
O(1)	38(2)	23(2)	34(2)	-2(1)	17(1)	-5(1)
C(1)	20(2)	23(2)	18(2)	3(2)	4(2)	4(2)
C(2)	17(2)	24(2)	20(2)	3(2)	0(2)	2(2)
C(3)	16(2)	21(2)	27(2)	2(2)	4(2)	0(2)
C(4)	18(2)	31(2)	20(2)	3(2)	4(2)	3(2)
C(5)	23(2)	37(3)	32(2)	12(2)	14(2)	0(2)
C(6)	29(2)	22(2)	26(2)	5(2)	5(2)	1(2)
C(7)	21(2)	23(2)	20(2)	4(2)	2(2)	3(2)
C(8)	17(2)	25(2)	19(2)	2(2)	1(2)	0(2)
C(9)	25(2)	22(2)	26(2)	4(2)	1(2)	3(2)
C(10)	27(2)	22(2)	27(2)	-1(2)	-1(2)	6(2)
C(11)	24(2)	32(2)	17(2)	1(2)	2(2)	11(2)
C(12)	24(2)	23(2)	21(2)	5(2)	5(2)	3(2)
C(13)	24(2)	20(2)	19(2)	0(2)	3(2)	3(2)
C(14)	19(2)	22(2)	17(2)	5(2)	2(1)	5(2)
C(15)	20(2)	23(2)	18(2)	3(2)	5(2)	7(2)
C(16)	13(2)	22(2)	18(2)	4(2)	-1(1)	4(2)
C(17)	15(2)	25(2)	20(2)	3(2)	3(2)	1(2)
C(18)	14(2)	25(2)	17(2)	5(2)	2(1)	5(2)
C(19)	18(2)	25(2)	19(2)	-1(2)	5(2)	4(2)
C(20)	20(2)	25(2)	16(2)	0(2)	3(2)	3(2)
C(21)	31(2)	25(2)	28(2)	0(2)	7(2)	7(2)
C(22)	25(2)	38(3)	29(2)	-9(2)	-2(2)	3(2)
C(23)	40(3)	30(2)	23(2)	-3(2)	14(2)	7(2)
C(24)	16(2)	25(2)	20(2)	4(2)	6(2)	0(2)
C(25)	19(2)	40(3)	31(2)	9(2)	6(2)	7(2)
C(26)	53(3)	44(3)	29(3)	-6(2)	24(2)	-5(2)
C(27)	25(2)	47(3)	35(2)	23(2)	10(2)	11(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d21120_a.

	x	y	z	U(eq)
H(3A)	9457	4690	1571	26
H(5A)	13013	7787	1135	36
H(6A)	10989	8874	1970	31
H(9A)	8321	9660	2896	30
H(10A)	5704	10025	3765	31
H(12A)	3371	6468	3590	27
H(15A)	6390	3837	1536	24
H(19A)	4102	4910	3605	25
H(21A)	5537	-48	1088	42
H(21B)	4518	247	1891	42
H(21C)	7042	910	1798	42
H(22A)	1364	1712	545	50
H(22B)	1025	701	1085	50
H(22C)	2121	468	291	50
H(23A)	5281	2656	381	46
H(23B)	6084	1407	210	46
H(23C)	7503	2420	906	46
H(25A)	-1254	1872	3134	44
H(25B)	-1461	3236	3348	44
H(25C)	-1790	2374	3987	44
H(26A)	1496	4624	4320	66
H(26B)	3639	4167	4743	66
H(26C)	1095	3728	4936	66
H(27A)	2136	1157	3793	50
H(27B)	1625	1699	4640	50
H(27C)	4112	2084	4386	50

Table 6. Torsion angles [°] for d21120_a.

C(14)-C(1)-C(2)-C(3)	-8.6(7)
C(13)-C(1)-C(2)-C(3)	174.7(4)
C(14)-C(1)-C(2)-C(7)	175.4(4)
C(13)-C(1)-C(2)-C(7)	-1.3(4)
C(7)-C(2)-C(3)-C(4)	-3.8(6)
C(1)-C(2)-C(3)-C(4)	-179.6(4)
C(2)-C(3)-C(4)-C(5)	2.4(6)
C(2)-C(3)-C(4)-Br(1)	-176.0(3)
C(3)-C(4)-C(5)-C(6)	0.3(6)
Br(1)-C(4)-C(5)-C(6)	178.7(3)
C(4)-C(5)-C(6)-C(7)	-1.5(6)
C(5)-C(6)-C(7)-C(2)	0.0(6)
C(5)-C(6)-C(7)-C(8)	178.7(4)
C(3)-C(2)-C(7)-C(6)	2.7(6)
C(1)-C(2)-C(7)-C(6)	179.4(4)
C(3)-C(2)-C(7)-C(8)	-176.2(3)
C(1)-C(2)-C(7)-C(8)	0.4(4)
C(6)-C(7)-C(8)-C(9)	2.5(7)
C(2)-C(7)-C(8)-C(9)	-178.6(4)
C(6)-C(7)-C(8)-C(13)	-178.1(4)
C(2)-C(7)-C(8)-C(13)	0.8(4)
C(13)-C(8)-C(9)-C(10)	-0.2(6)
C(7)-C(8)-C(9)-C(10)	179.2(4)
C(8)-C(9)-C(10)-C(11)	-2.1(6)
C(9)-C(10)-C(11)-C(12)	1.5(6)
C(9)-C(10)-C(11)-Br(2)	-178.7(3)
C(10)-C(11)-C(12)-C(13)	1.6(6)
Br(2)-C(11)-C(12)-C(13)	-178.3(3)
C(11)-C(12)-C(13)-C(8)	-3.8(6)
C(11)-C(12)-C(13)-C(1)	-176.9(4)
C(9)-C(8)-C(13)-C(12)	3.2(6)
C(7)-C(8)-C(13)-C(12)	-176.3(3)
C(9)-C(8)-C(13)-C(1)	177.8(4)
C(7)-C(8)-C(13)-C(1)	-1.6(4)

C(14)-C(1)-C(13)-C(12)	-1.3(7)
C(2)-C(1)-C(13)-C(12)	175.5(4)
C(14)-C(1)-C(13)-C(8)	-174.9(4)
C(2)-C(1)-C(13)-C(8)	1.8(4)
C(13)-C(1)-C(14)-C(19)	-21.9(6)
C(2)-C(1)-C(14)-C(19)	162.1(4)
C(13)-C(1)-C(14)-C(15)	158.0(4)
C(2)-C(1)-C(14)-C(15)	-18.0(6)
C(1)-C(14)-C(15)-C(16)	-176.8(4)
C(19)-C(14)-C(15)-C(16)	3.1(5)
C(14)-C(15)-C(16)-C(17)	-0.4(6)
C(14)-C(15)-C(16)-C(20)	178.9(3)
C(15)-C(16)-C(17)-O(1)	176.5(4)
C(20)-C(16)-C(17)-O(1)	-2.8(5)
C(15)-C(16)-C(17)-C(18)	-3.2(5)
C(20)-C(16)-C(17)-C(18)	177.5(3)
O(1)-C(17)-C(18)-C(19)	-175.8(4)
C(16)-C(17)-C(18)-C(19)	4.0(5)
O(1)-C(17)-C(18)-C(24)	4.8(5)
C(16)-C(17)-C(18)-C(24)	-175.5(3)
C(17)-C(18)-C(19)-C(14)	-1.2(6)
C(24)-C(18)-C(19)-C(14)	178.3(3)
C(1)-C(14)-C(19)-C(18)	177.6(4)
C(15)-C(14)-C(19)-C(18)	-2.3(5)
C(15)-C(16)-C(20)-C(23)	0.2(5)
C(17)-C(16)-C(20)-C(23)	179.5(3)
C(15)-C(16)-C(20)-C(22)	-119.3(4)
C(17)-C(16)-C(20)-C(22)	59.9(5)
C(15)-C(16)-C(20)-C(21)	118.9(4)
C(17)-C(16)-C(20)-C(21)	-61.9(4)
C(19)-C(18)-C(24)-C(25)	114.4(4)
C(17)-C(18)-C(24)-C(25)	-66.1(4)
C(19)-C(18)-C(24)-C(26)	-4.0(5)
C(17)-C(18)-C(24)-C(26)	175.5(4)
C(19)-C(18)-C(24)-C(27)	-123.7(4)
C(17)-C(18)-C(24)-C(27)	55.8(4)

Symmetry transformations used to generate equivalent atoms:

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