Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

An Efficient Room-Temperature Synthesis of Highly Phosphorescent Styrenic Pt(II) Complexes and their Polymerization by ATRP

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Table of Contents

Abbreviations

EBiB: ethyl α-bromoisobutyrate

dFppy: 2-(2,4-difluorophenyl)pyridine

PMDETA: N,N,N′,N″,N″-pentamethyldiethylenetriamine

piq: 1-phenylisoquinoline

ppy: 2-phenylpyridine

MeOppy: 2-(3-methoxyphenyl)pyridine

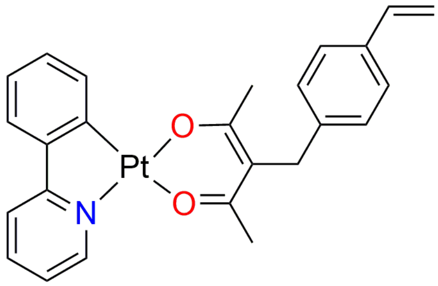
stacac: 3-((4-vinylphenyl)methyl)pentane-2,4-dione

VBCz: 4-vinylbenzyl-9H-carbazole

Additional Synthetic Procedures

Preparation of Polystyrene

Prepared according to a modified literature procedure.[1] Into a 20 mL vial with a Teflon-lined lid, CuBr (5.4 mg, 0.038 mmol, 0.29 eq) was weighed, and the vial was taken into a glovebox with nitrogen atmosphere. In the glovebox, styrene monomer (4.80 mL, 422 mmol, 320 eq), PMDETA (7.6 µL, 0.036 mmol, 0.28 eq), and a magnetic stir bar were added to the reaction vial, and the contents were stirred at ambient temperature for five minutes to ensure CuBr/PMDETA complexation. Lastly, EBiB (19 µL, 0.13 mmol, 1.0 eq) was added, and the vial was placed into a pre-heated aluminum heat block (100 °C) with vigorous stirring (700 rpm). Upon reaching 20% conversion as determined by ^{1}H NMR, the reaction vial was removed from the glovebox, cooled quickly with liquid nitrogen, followed by the addition of CH_2Cl_2 (1 mL) with vigorous shaking. The crude sample was flushed through a neutral alumina plug with CH_2Cl_2, and the collected eluent was concentrated *in vacuo*. The residue was purified by two reprecipitations from CH_2Cl_2 into MeOH. M_n (SEC) = 6,700, Đ = 1.10. ^{1}H NMR in $CDCl_3$ was used to quantify the proportion of living chain ends (96%) by direct comparison of integrals corresponding to the ω-hydrogen (0.96H, 4.45 ppm) and the hydrogens adjacent to the EBiB oxygen (2H, 3.55 ppm).



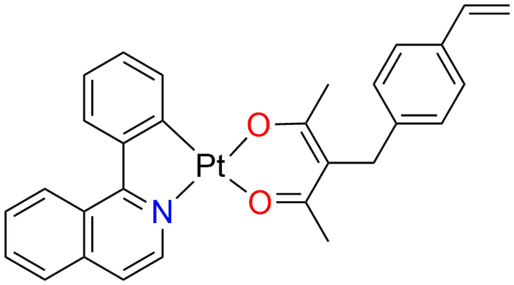
Pt(ppy)(stacac) (M1)

Purified over silica (3:2 CH_2Cl_2:hexanes) resulting in a yellow solid. Yield 1.12 g, 57 %.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.97 (d, sat, $J_{Pt\text{-}H}$ = 39.7 Hz, J = 5.8 Hz, 1H), 7.84 (td, J = 8.2, 1.6 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.56 (dd, J = 7.5, 1.3 Hz, 1H), 7.48 (dd, J = 7.7, 1.4 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.18 – 7.08 (m, 3H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 5.72 (dd, J = 17.7, 1.1 Hz, 1H), 5.20 (dd, J = 10.9, 1.0 Hz, 1H), 3.83 (s, 2H), 2.05 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 186.54, 184.18, 168.87, 147.67, 145.53, 141.37, 140.56, 138.88, 137.15, 136.03, 131.19, 129.58, 128.25, 126.89, 123.96, 123.56, 121.99, 119.06, 113.39, 109.76, 36.42, 28.55, 27.76.

TOF MS (ES+) *m/z*: [MH^+] calc'd for $[C_{25}H_{23}N_1O_2Pt_1]^+$, 563.13554; found, 563.13465.



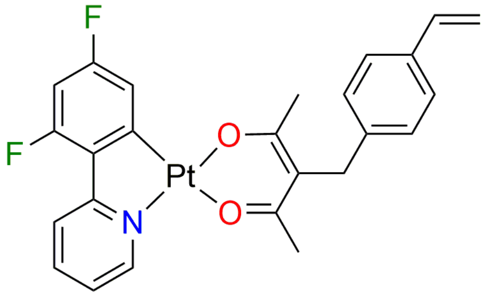
Pt(piq)(stacac) (M2)

Purified over silica (3:2 CH_2Cl_2:hexanes) resuling in a red solid. Yield 0.697 g, 33 %.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.94 (d, J = 6.5 Hz, 1H), 8.91 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 7.5, 1H), 7.88 (d, J = 8.0, 1H), 7.73 (m, 3H), 7.48 (d, J = 6.5 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.22 (m, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (dd, J = 17.6, 1.1 Hz, 1H), 5.20 (dd, J = 10.9, 1.0 Hz, 1H), 3.84 (s, 2H), 2.08 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 186.74, 184.30, 169.11, 147.05, 143.35, 141.38, 139.62, 138.01, 137.15, 136.02, 131.79, 131.21, 129.73, 129.06, 128.96, 128.27, 128.13, 126.89, 126.60, 126.58, 123.65, 120.34, 113.39, 109.82, 36.37, 28.58, 27.79.

TOF MS (ES+) *m/z*: [MH^+] calc'd for $[C_{29}H_{25}N_1O_2Pt_1]^+$, 613.15119; found, 613.14956.



Pt(dFppy)(stacac) (M3)

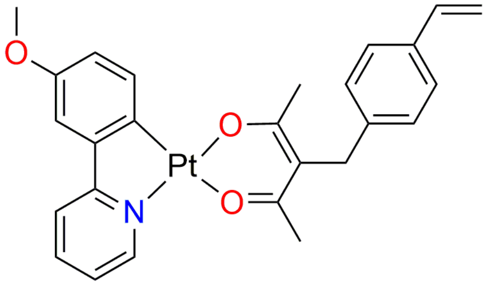
Purified over silica (1:1 CH_2Cl_2:hexanes) resulting in a yellow solid. Yield 0.446 g, 66 %.

^{1}H NMR (400 MHz, CD_2Cl_2): 9.01 (d, sat, $J_{Pt\text{-}H}$ = 39.0 Hz, J = 5.9 Hz, 1H), 8.07 – 7.94 (m, 1H), 7.88 (dddd, J = 8.2, 7.5, 1.7, 0.7 Hz, 1H), 7.36 (d, J = 8.1 Hz, 3H), 7.23 – 7.17 (m, 2H), 7.18 (d, J

= 8.1 Hz, 1H) 7.08 (dd, J = 8.6, 2.4 Hz, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 6.60 (ddd, J = 12.3, 9.3, 2.4 Hz, 1H), 5.72 (dd, J = 17.6, 1.0 Hz, 1H), 5.20 (dd, J = 10.9, 1.0 Hz, 1H), 3.83 (s, 2H), 2.07 (s, 3H), 2.05 (s, 3H).

^{19}F NMR (377 MHz, CD_2Cl_2): δ -107.53 (q, J = 9.2 Hz), -112.39 (t, J = 11.2 Hz).

TOF MS (ES+) *m/z*: [MH^+] calc'd for $[C_{25}H_{21}F_2N_1O_2Pt_1]^+$, 599.11670; found, 599.11529.



Pt(MeOppy)(stacac) (M4)

Purified over silica (3:1hexanes:EtOAc) resulting in an orange solid. Yield 0.454 g, 52 %.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.96 (d, sat, $J_{Pt\text{-}H}$ = 38.7 Hz, J = 5.7 Hz, 1H), 7.84 (td, J = 7.8, 1.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.13 (ddd, J = 7.4, 5.8, 1.5 Hz, 1H), 7.06 (d, J = 2.6 Hz, 1H), 6.87 (dd, J = 8.3, 2.7 Hz, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 5.72 (dd, J = 17.6, 1.1 Hz, 1H), 5.19 (dd, J = 10.9, 1.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 2H), 2.03 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 186.36, 183.96, 168.63, 157.71, 147.70, 145.89, 141.39, 138.83, 137.15, 136.02, 131.70, 130.38, 128.24, 126.88, 122.14, 119.10, 116.08, 113.38, 109.72, 109.15, 55.94, 36.42, 28.56, 27.72.

TOF MS (ES+) *m/z*: [MH^+] calc'd for $[C_{26}H_{25}N_1O_3Pt_1]^+$, 593.14611; found, 593.14483.

Preparation of thin films:

To prepare thin films, 10 mg/mL solutions of each polymer were prepared in chloroform. Using a spin coater, 2.5 cm x 2.5 cm glass microscope slides were coated with approximately 400 µL of polymer solution, then spun with the following sequence: 0→1400 rpm (4 sec), 2000 rpm (30 sec), 2000→1000 rpm (2 sec). The films were allowed to dry and then placed in a vacuum oven at 60 °C for 10 minutes before photophysical measurements were taken.

Calculating $k_p$app for P1-P5

For each reaction aliquot sampled for ^{1}H NMR analysis, the internal standard (1,3,5-trimethoxybenzene) was used to determine the amount of unreacted monomer $[M]_n$ remaining at t_n relative to the initial amount of monomer $[M]_0$ present at t_0. For each aliquot, $\ln([M]_0/[M]_n)$ was plotted as a function of time, yielding data that could be analyzed using linear regression due to the first-order kinetics observed in the time frame of these polymerizations. The calculated slope of the linear trendline for a given plot yields $k_p$app.

Table S1. Molecular weight and dispersities for PS-*b*-(**M5**-*co*-**M1**) polymer **P6**.

PS Block		**5% M1-Doped Block**			**Block Copolymer**	
M_n[a]	**Đ**	$\mathbf{DP_n}$	M_n[b]	$\mathbf{DP_n}$	M_n[b]	**Đ**
6,700	1.10	64	11,000	39	17,700	1.24

[a]Determined by SEC in THF. [b]Determined by ^{1}H NMR

Additional Figures

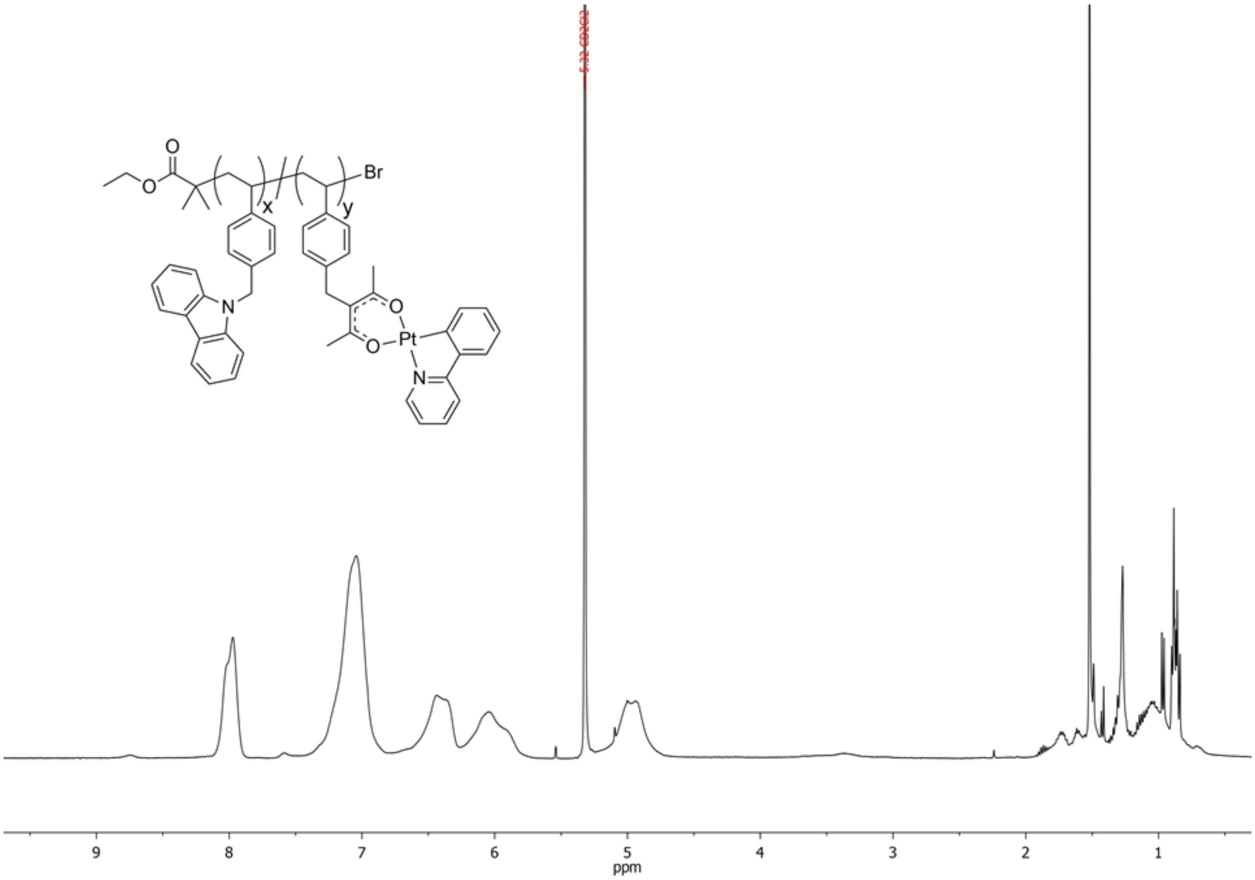


Figure S1. ^{1}H NMR in CD_2Cl_2 of copolymer **P1**, reprecipitated twice from hexanes.

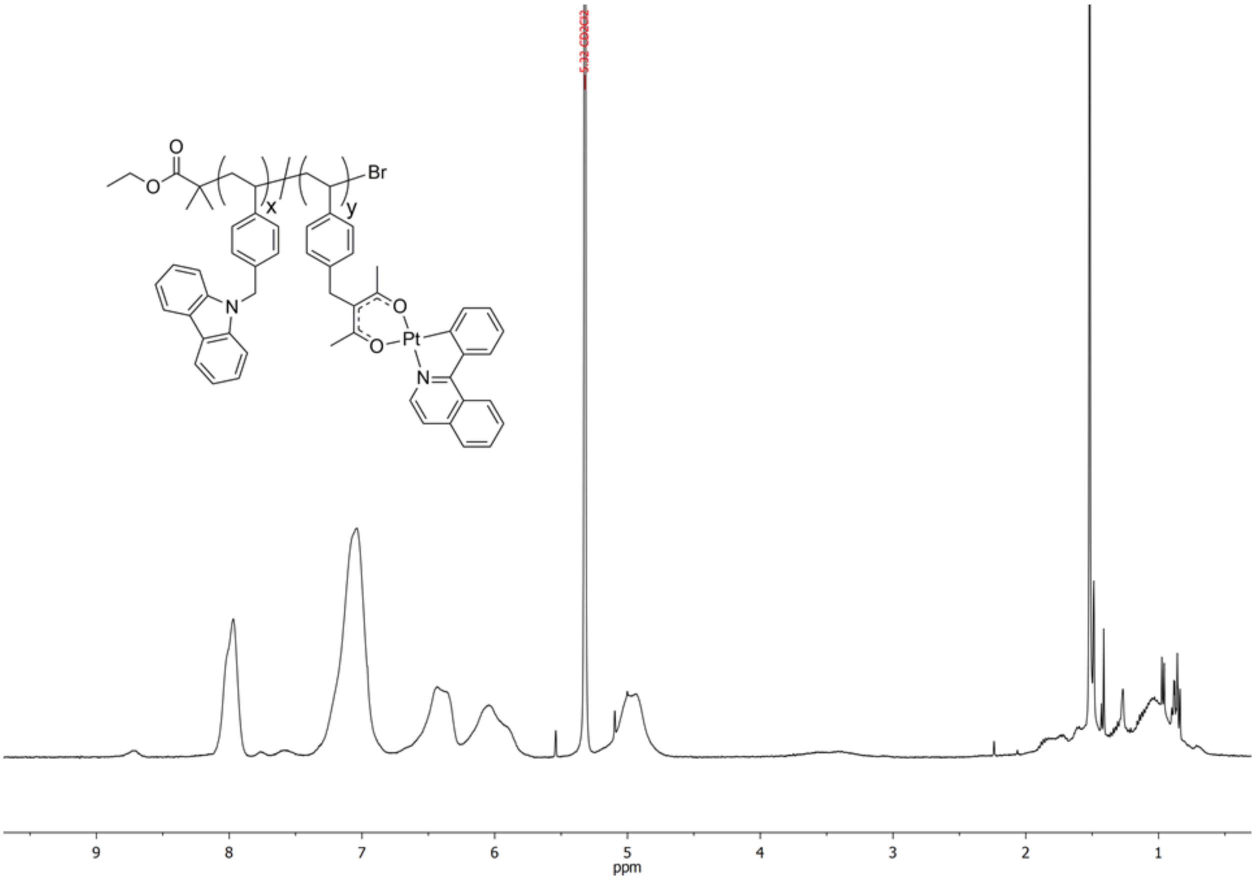


Figure S2. ^{1}H NMR in CD_2Cl_2 of copolymer **P2**, reprecipitated twice from hexanes.

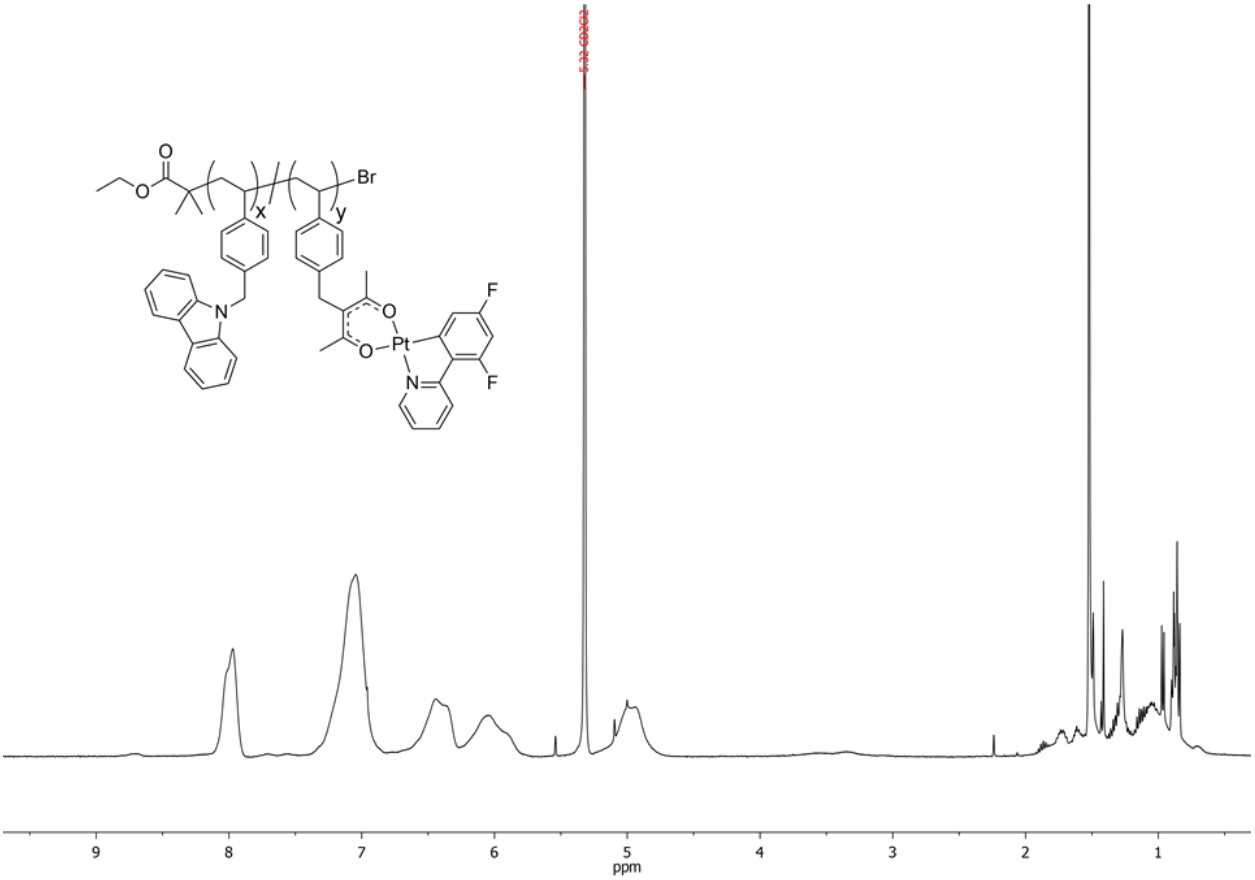


Figure S3. ^{1}H NMR in CD_2Cl_2 of copolymer **P3**, reprecipitated twice from hexanes.

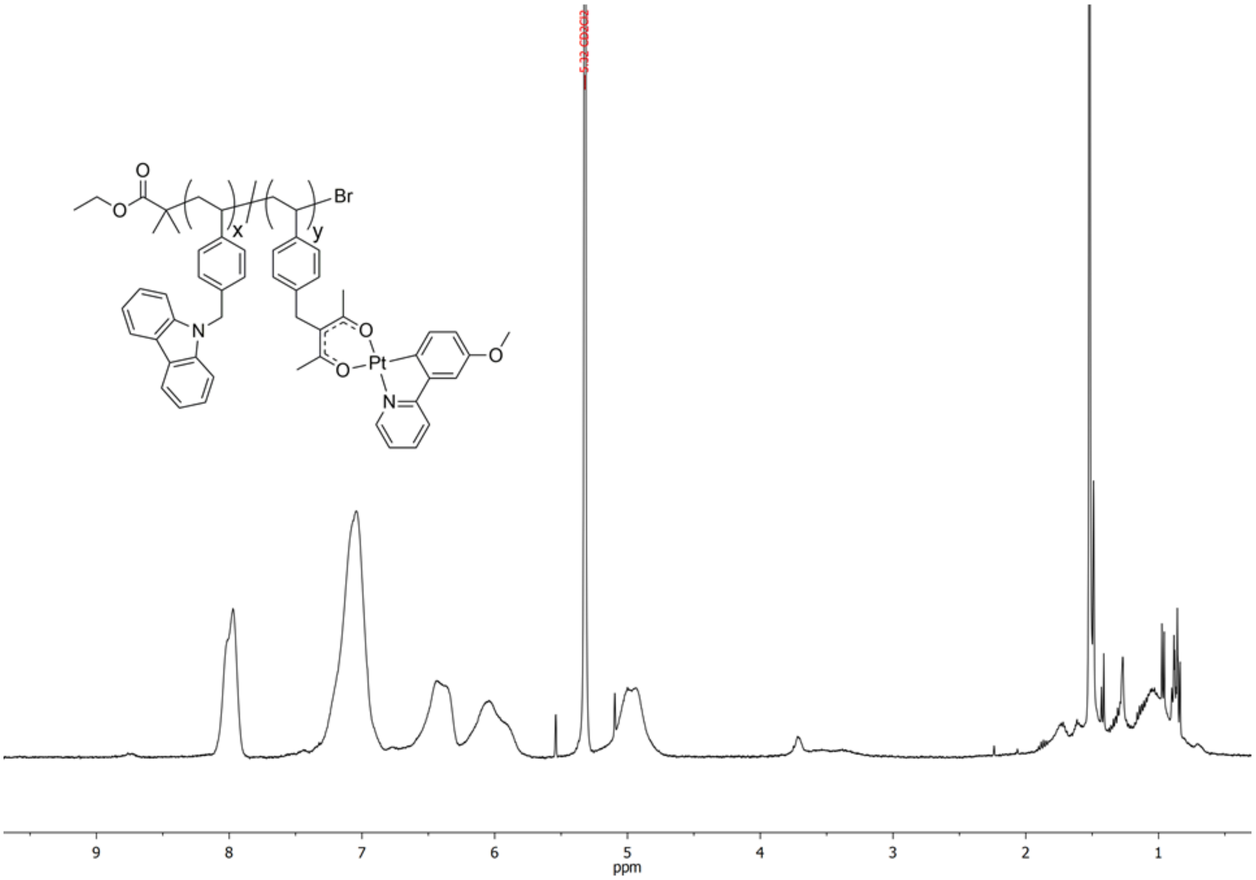


Figure S4. ^{1}H NMR in CD_2Cl_2 of copolymer **P4**, reprecipitated twice from hexanes.

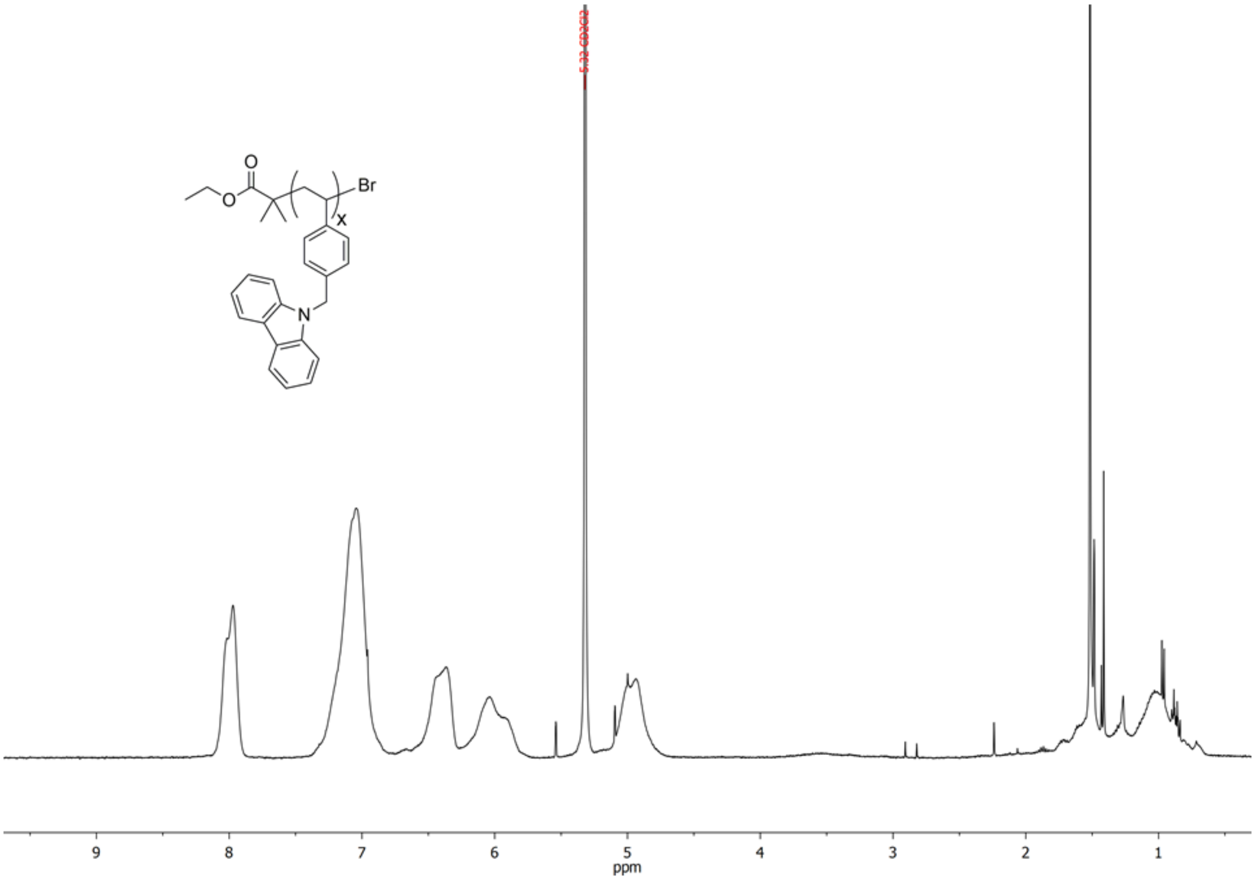


Figure S5. ^{1}H NMR in CD_2Cl_2 of homopolymer **P5**, reprecipitated twice from hexanes.

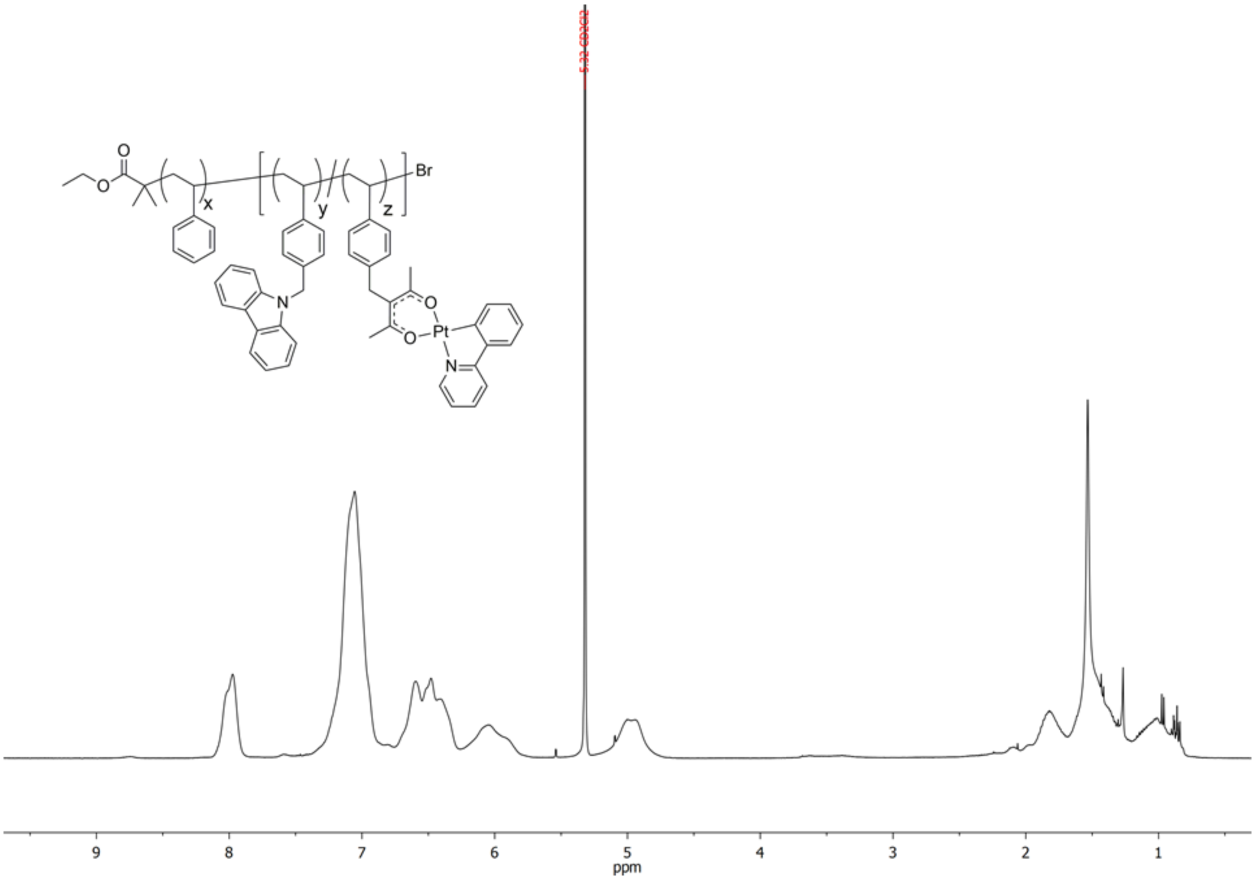


Figure S6. ^{1}H NMR in CD_2Cl_2 of **P6** diblock copolymer.

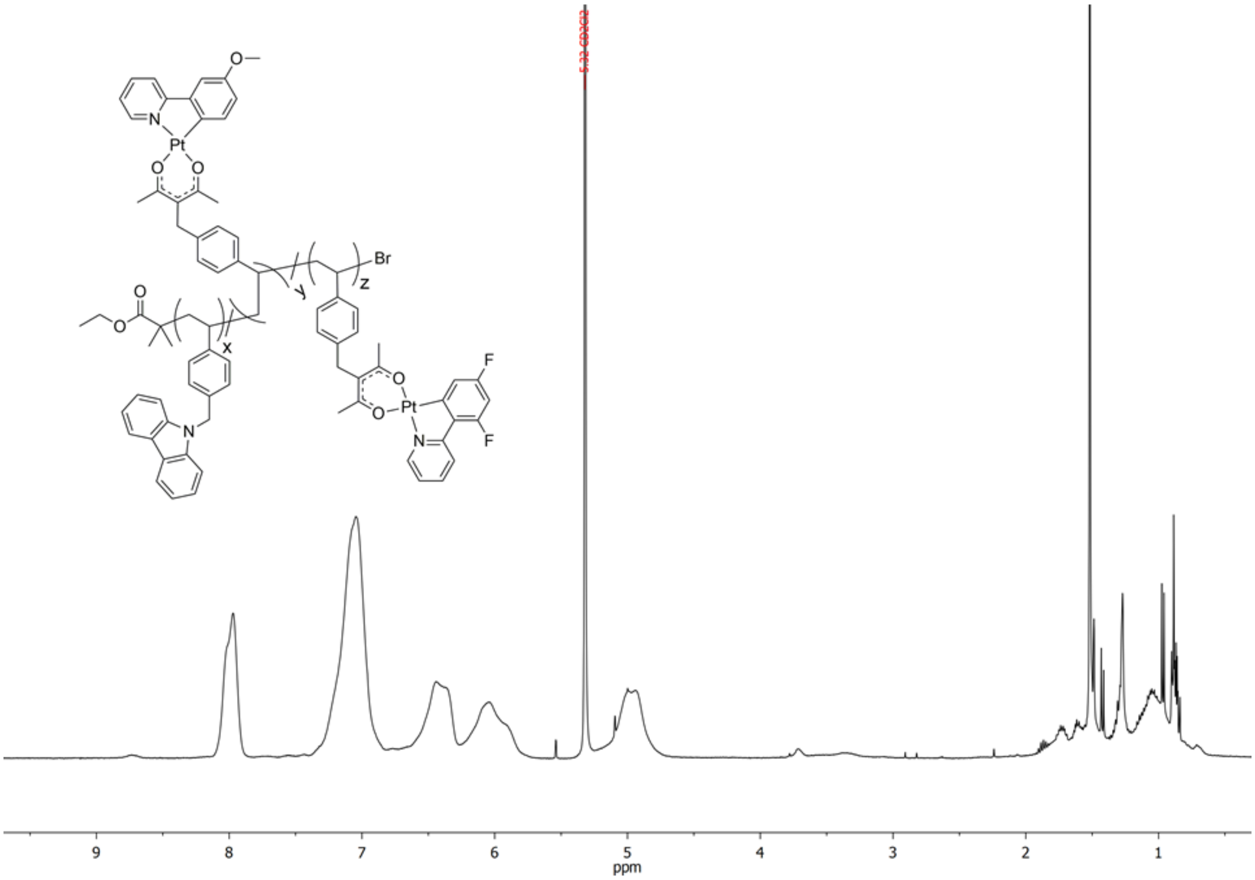


Figure S7. ^{1}H NMR in CD_2Cl_2 of copolymer **P7**, reprecipitated twice from hexanes.

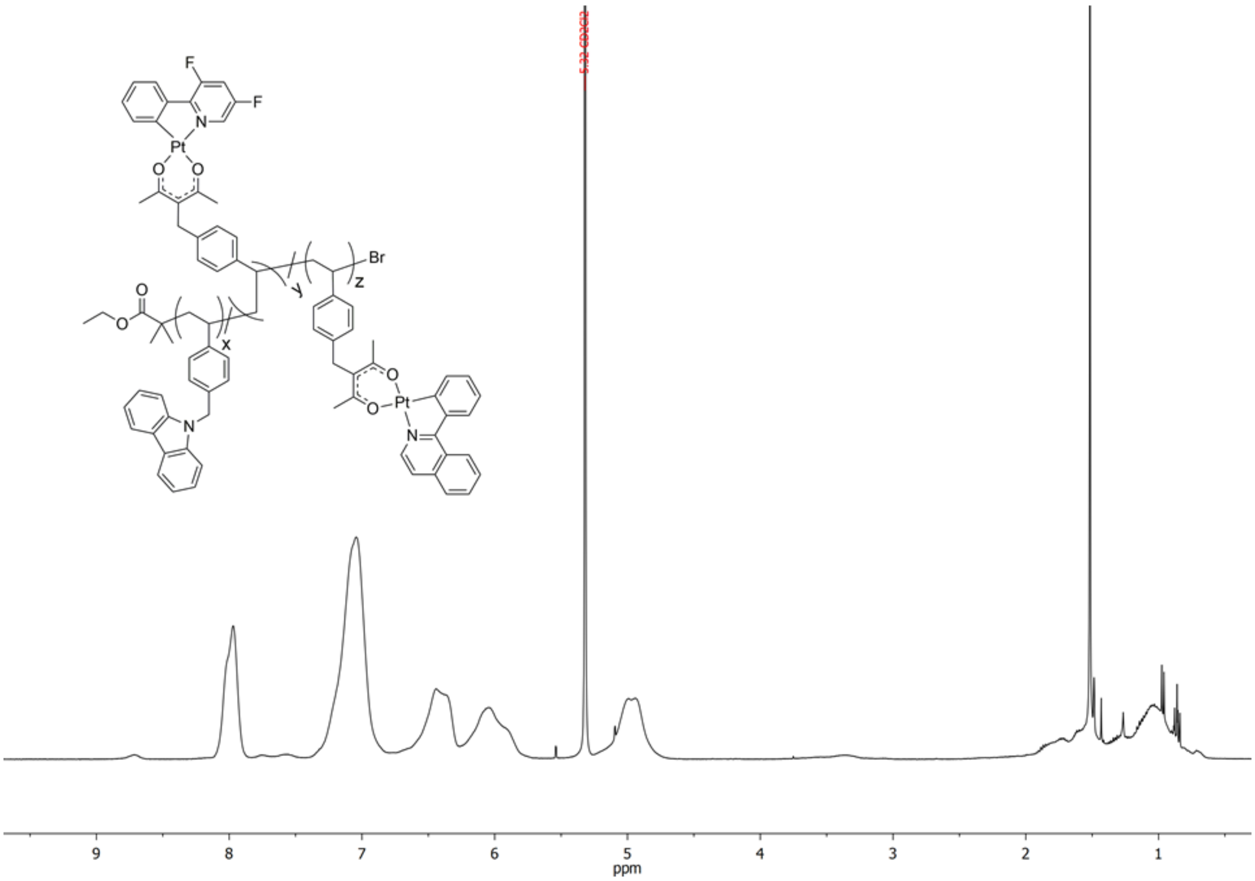


Figure S8. ^{1}H NMR in CD_2Cl_2 of copolymer **P8**, reprecipitated twice from hexanes.

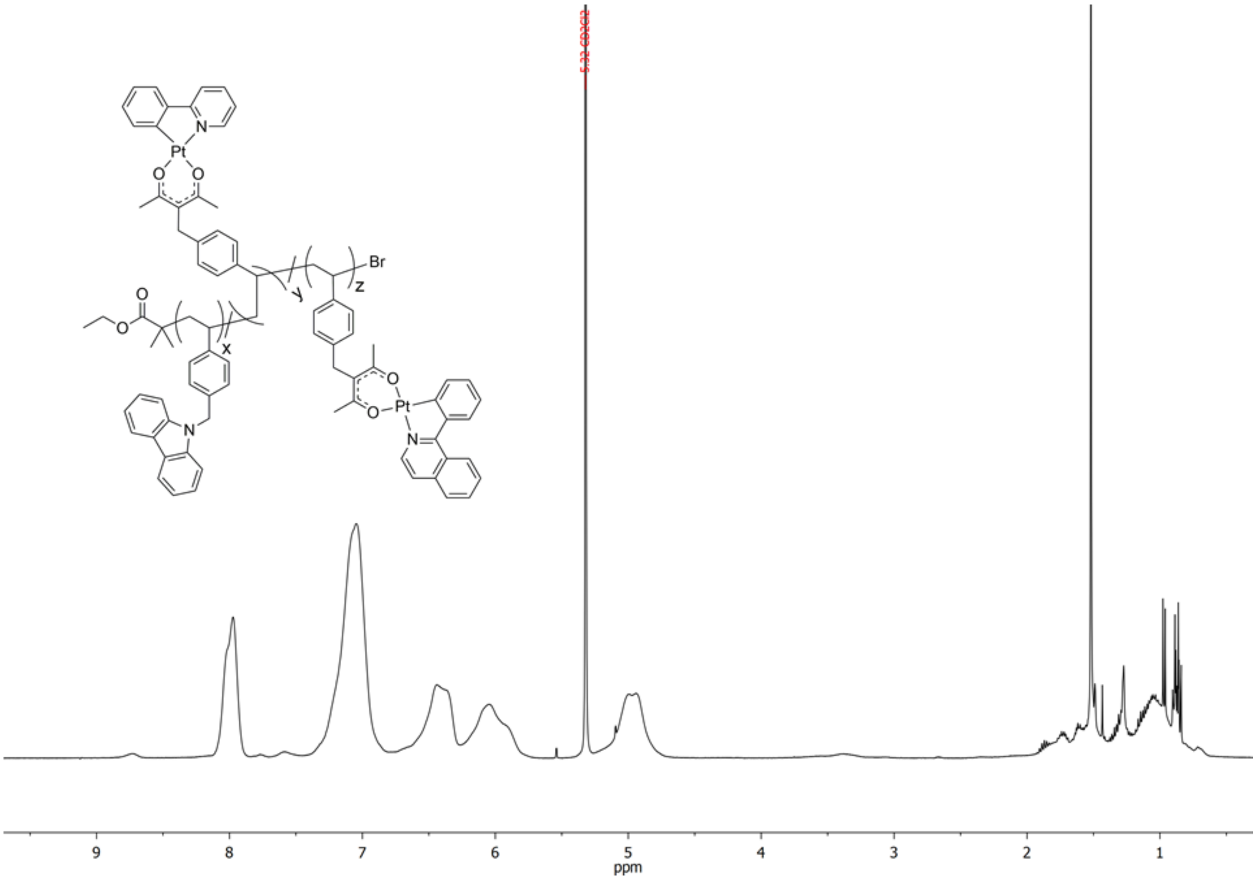


Figure S9. ^{1}H NMR in CD_2Cl_2 of copolymer **P9**, reprecipitated twice from hexanes.

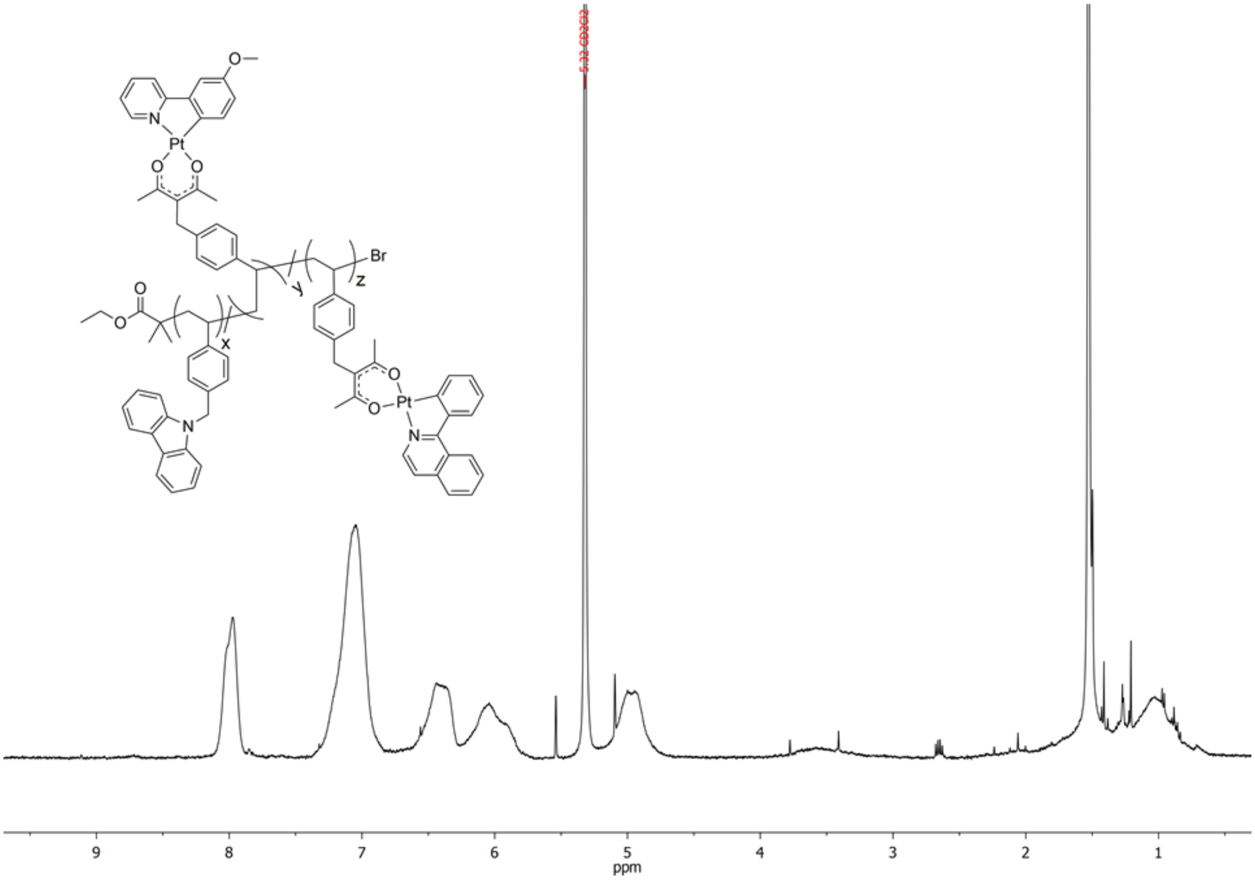


Figure S10. ^{1}H NMR in CD_2Cl_2 of copolymer **P10**, reprecipitated twice from hexanes.

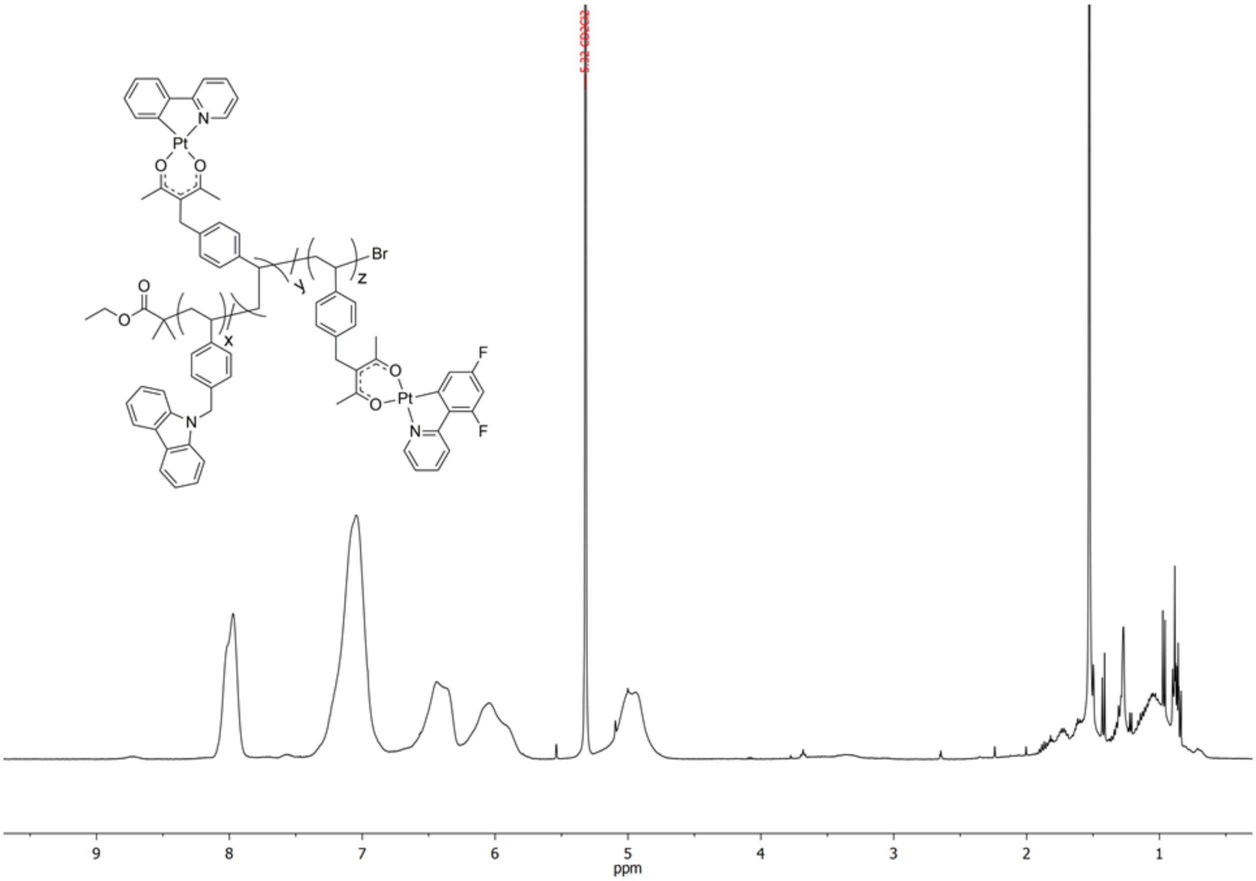


Figure S11. ^{1}H NMR in CD_2Cl_2 of copolymer **P11**, reprecipitated twice from hexanes.

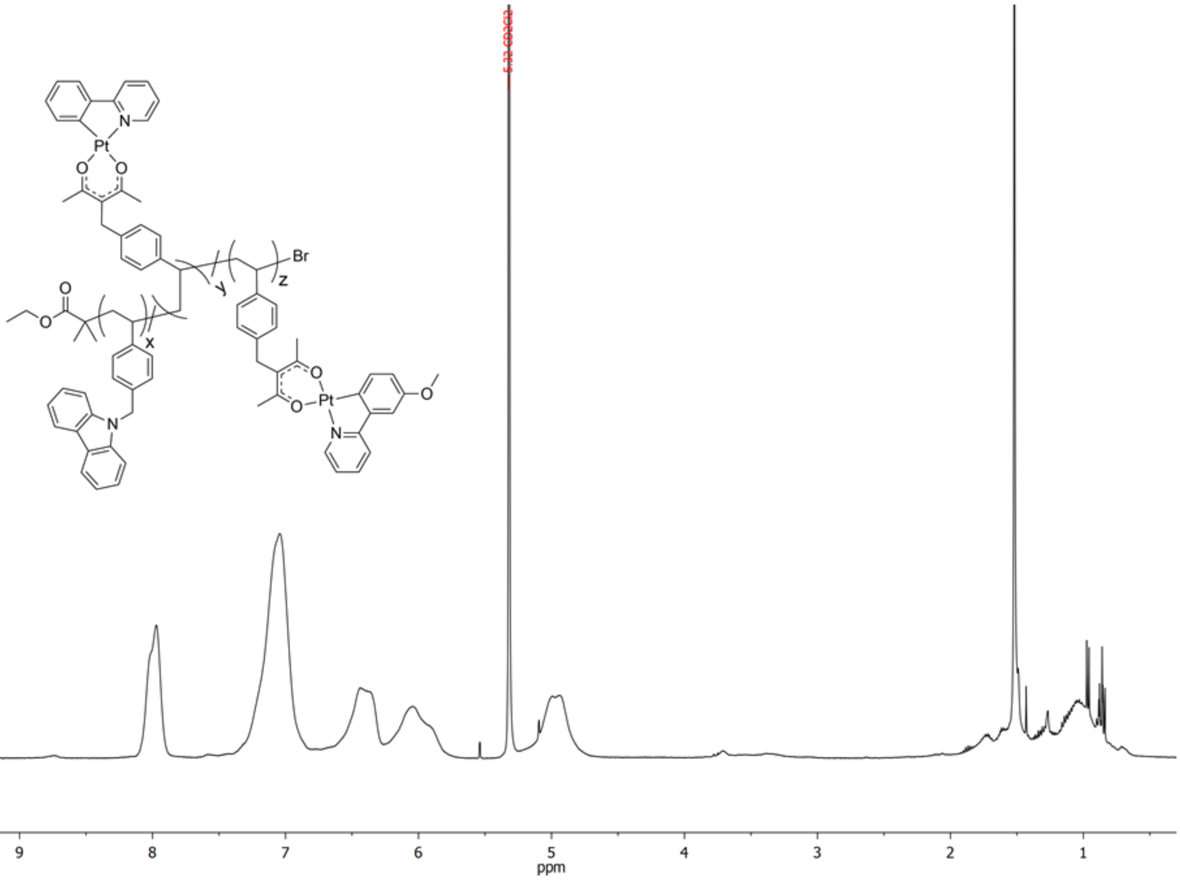


Figure S12. ^{1}H NMR in CD_2Cl_2 of copolymer **P12**, reprecipitated twice from hexanes.

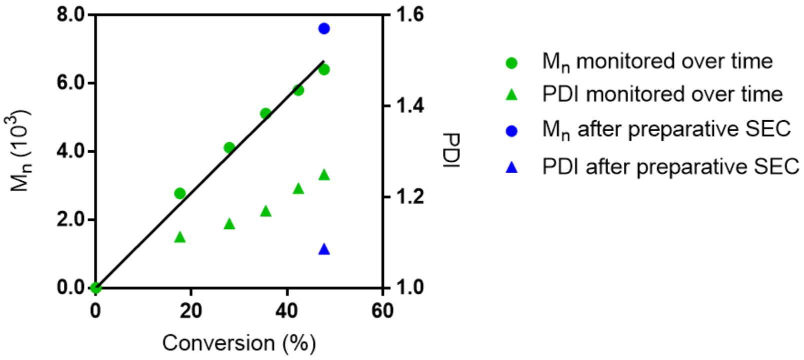


Figure S13. An example of the evolution of M_n and PDI as a function of conversion for the synthesis of a 5 mol% **M1**-doped copolymer. Crude reaction aliquots (green) were sampled for GPC and ^{1}H NMR analysis every 15 minutes for a total of 75 minutes. Data indicating the final polymer M_n and PDI after preparative SEC purification is included for comparison (blue).

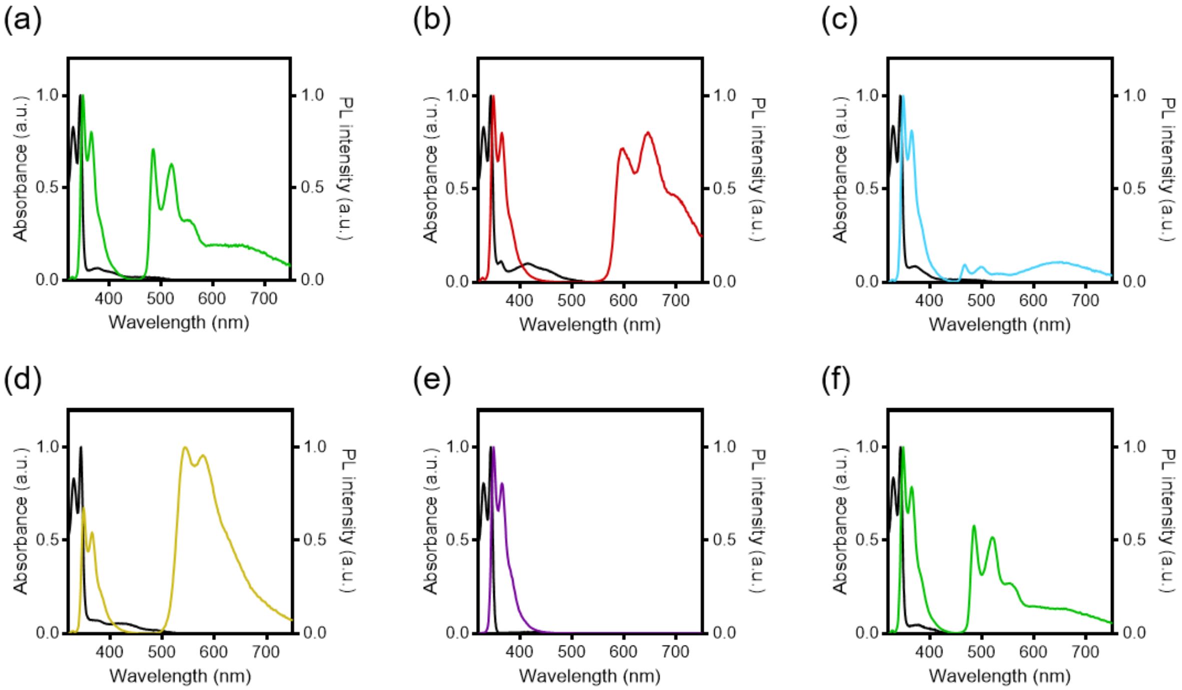


Figure S14. Normalized absorbance (black) and photoluminescence (colored) spectra for copolymers **P1-P4** (a-d, respectively). Homopolymer **P5** (e), and diblock copolymer **P6** (f) are also shown. Dopant concentrations = 5 mol% for **P1-P4** and **P6**. Recorded in toluene at 0.01 mg mL^{-1}.

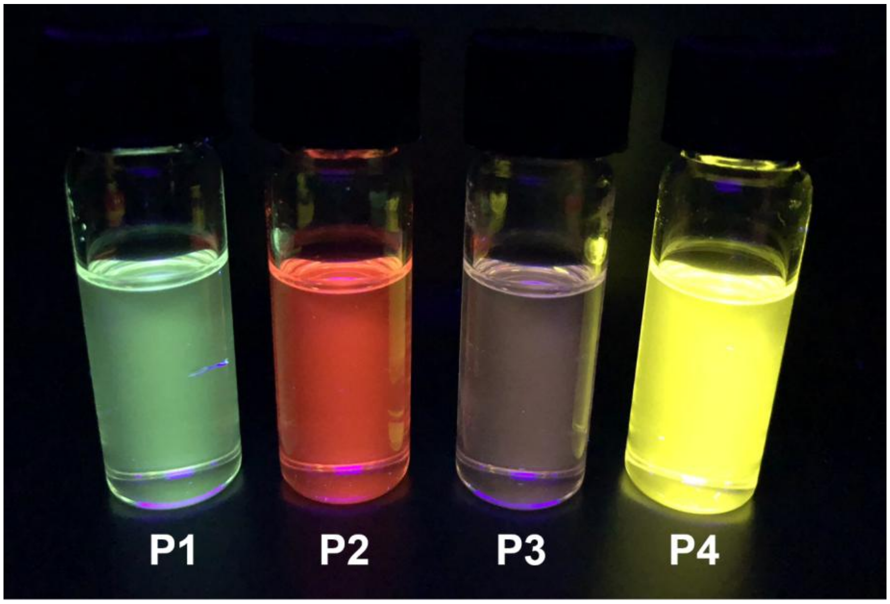


Figure S15. Nitrogen-sparged 0.01 mg mL^{-1} solutions of single-dopant copolymers **P1-P4** in toluene under UV irradiation (λ = 365 nm).

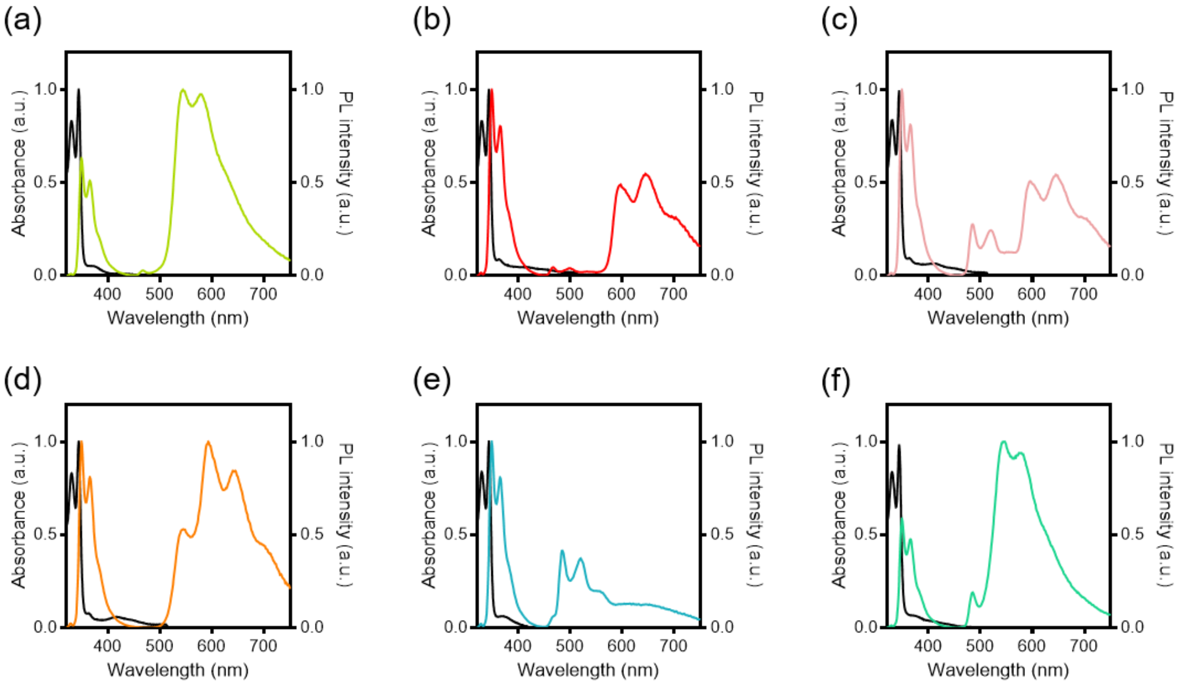


Figure S16. Normalized absorbance (black) and photoluminescence (colored) spectra for copolymers **P7-P12** (a-f, respectively). Combined dopant concentrations = 5 mol% total, with equimolar ratios of dopant pairs in each copolymer. Recorded in toluene at 0.01 mg mL^{-1}.

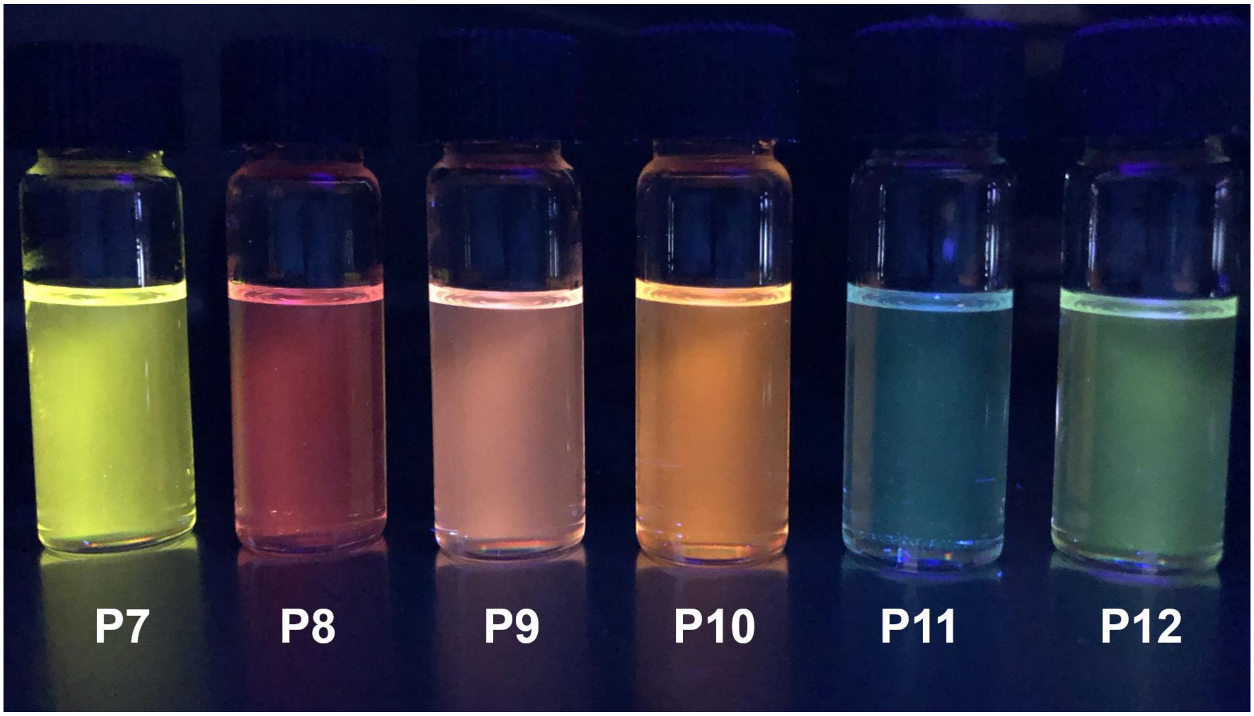


Figure S17. Nitrogen-sparged 0.01 mg mL^{-1} solutions of mixed-dopant copolymers **P7-P12** in toluene under UV irradiation (λ = 365 nm).

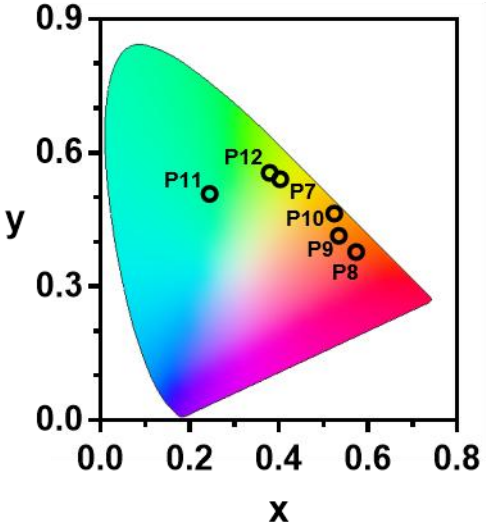


Figure S18. CIE 1931 diagram showing the solid-state emission colours of mixed-dopant copolymers **P7-P12**.

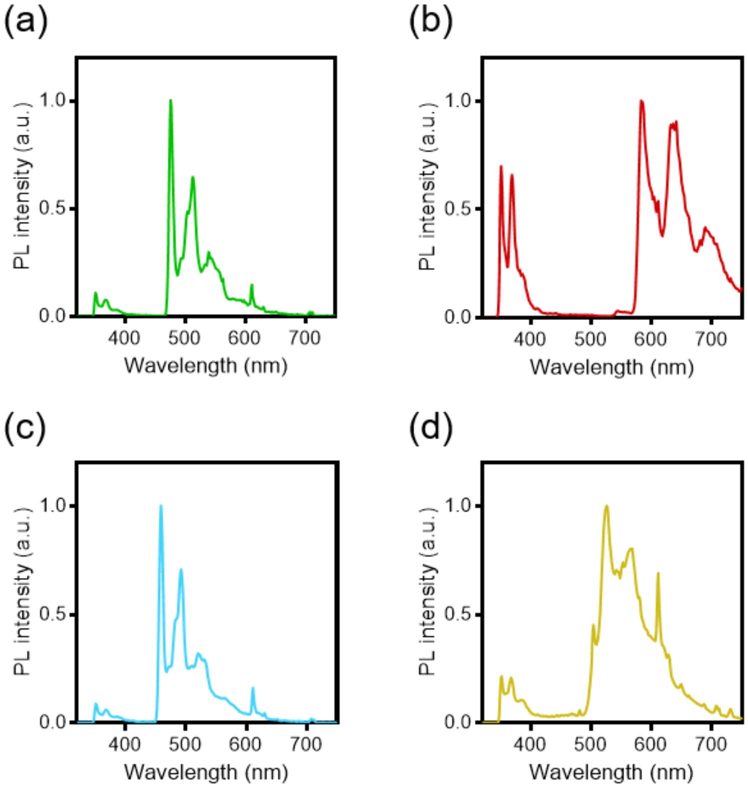


Figure S19. Normalized photoluminescence spectra at 77 K for single-dopant copolymers **P1-P4** (a-d, respectively). Recorded in 2-methyltetrahydrofuran at approximate concentrations of 0.1 mg mL^{-1}.

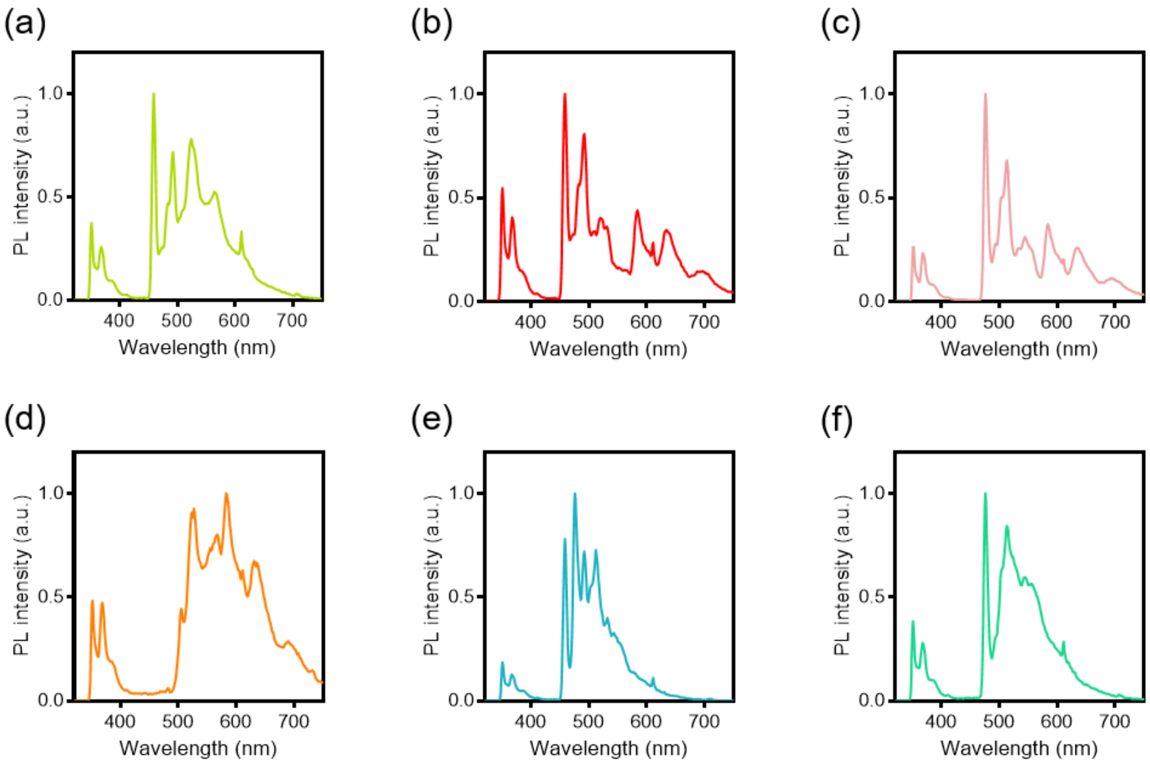


Figure S20. Normalized photoluminescence spectra at 77 K of mixed-dopant copolymers **P7-P12** (a-f, respectively). Recorded in 2-methyltetrahydrofuran at approximate concentrations of 0.1 mg mL^{-1}.

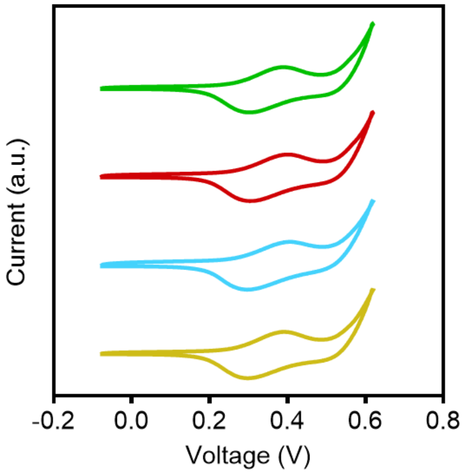


Figure S21. Cyclic voltammograms of single-dopant copolymers **P1** (green), **P2** (red), **P3** (blue), and **P4** (yellow), relative to $FeCp_2^{0/+}$. Recorded at a rate of 100 mV s^{-1} in dichloromethane under N_2 flow containing 2 mg mL^{-1} of analyte, and 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

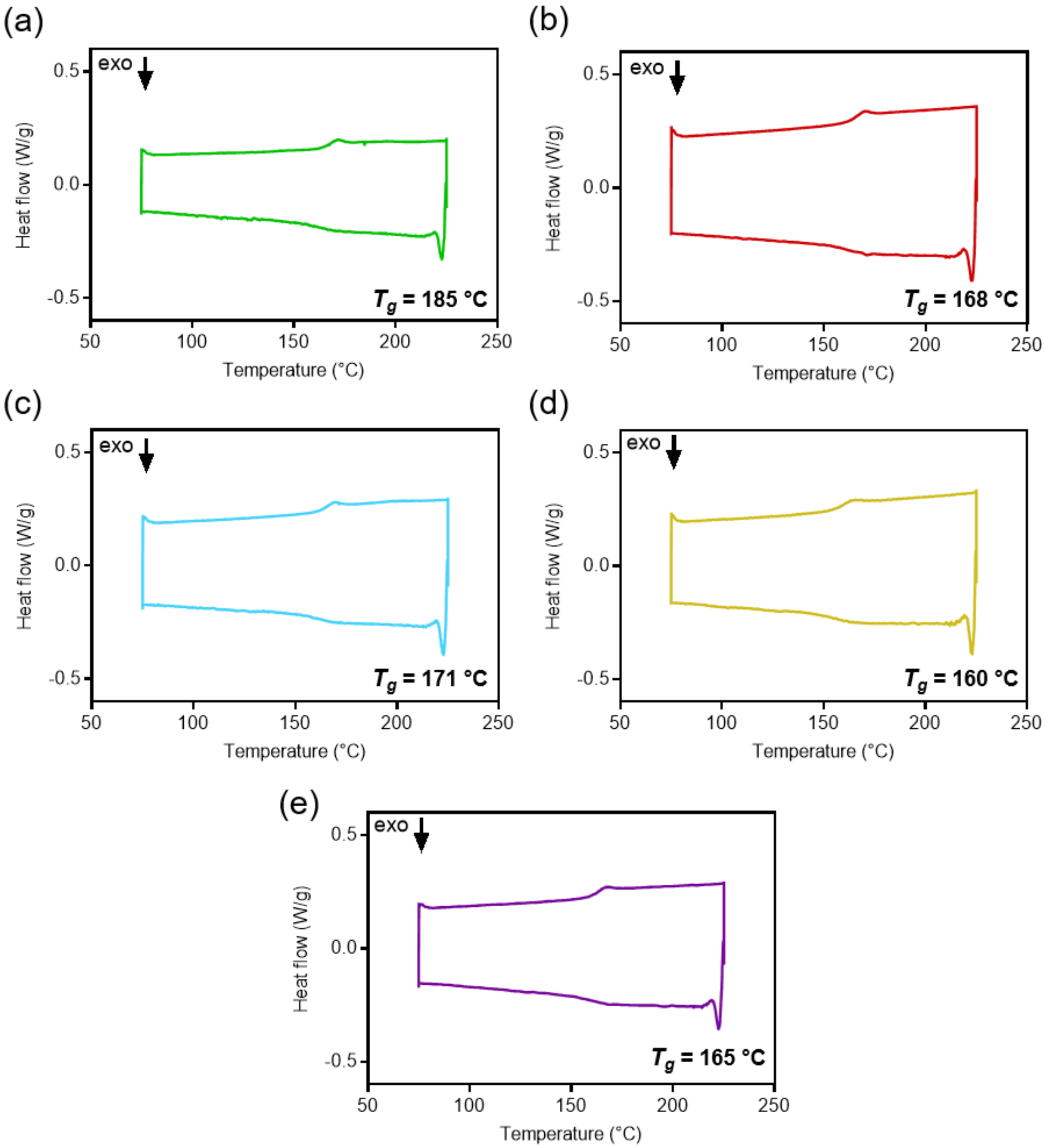
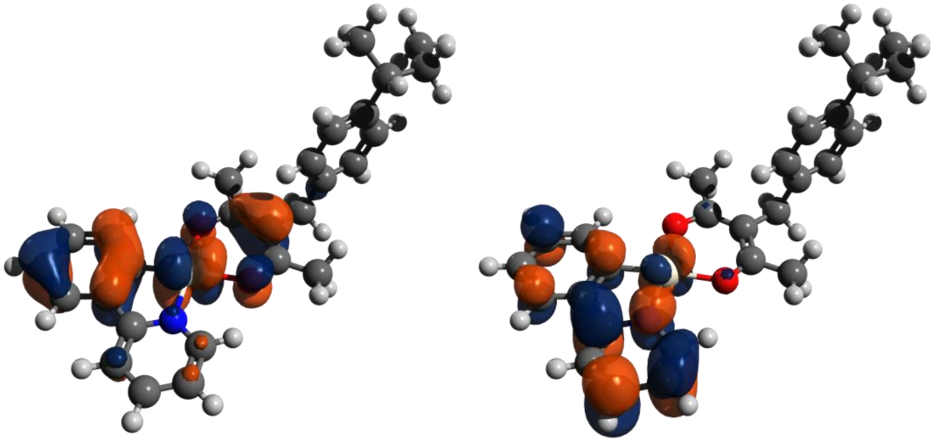
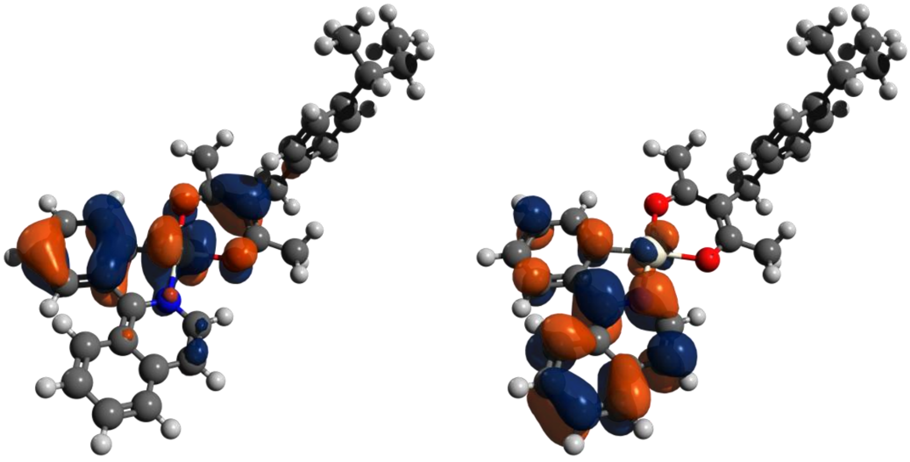


Figure S22. DSC traces of copolymers **P1-P5** (a-e, respectively). Run at a rate of 10 °C min^{-1} under a 50 mL min^{-1} flow of nitrogen. Two consecutive heating and cooling cycles were performed, and the second traces are shown.



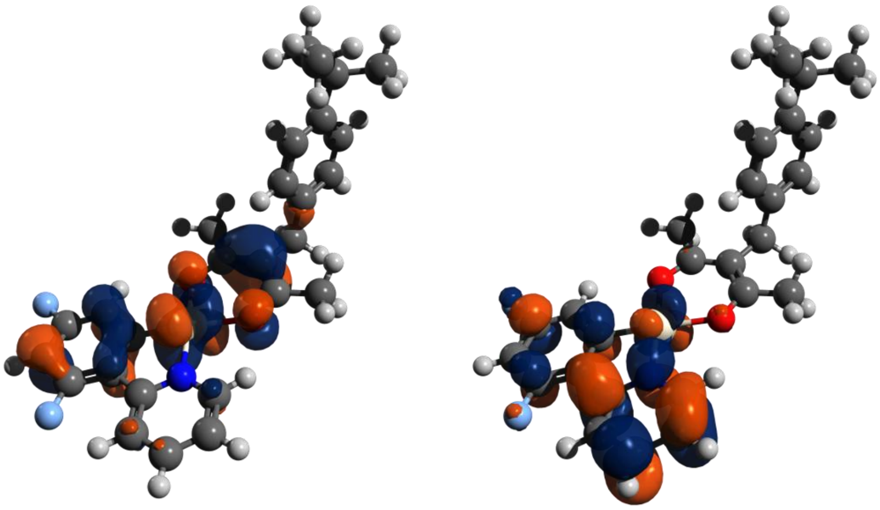
HOMO = -5.687 eV LUMO = -1.953 eV

Figure S23. Calculated HOMO and LUMO energies for the *sec*-butyl analogue of **M1**.



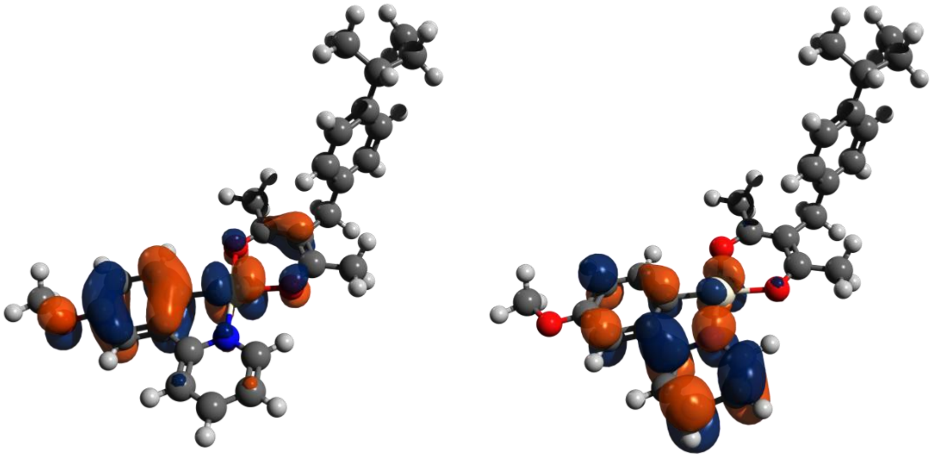
HOMO = -5.688 eV LUMO = -2.405 eV

Figure S24. Calculated HOMO and LUMO energies for the *sec*-butyl analogue of **M2**.



HOMO = -5.962 eV **LUMO = -2.095 eV**

Figure S25. Calculated HOMO and LUMO energies for the *sec*-butyl analogue of **M3**.



HOMO = -5.330 eV **LUMO = -1.919 eV**

Figure S26. Calculated HOMO and LUMO energies for the *sec*-butyl analogue of **M4**.

X-Ray Crystallography

X-ray crystallographic data for **M1**-**M4** have been deposited to the CCDC with deposition numbers 1867397-1867400.

X-Ray Crystallography Details for M1

Experimental. A yellow plate-shaped crystal with dimensions 0.16×0.11×0.02 mm^3 was mounted on a mylar loop in oil. X-ray diffraction data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 90(2) K. Data were measured using ω and ϕ scans of 0.5 ° per frame for 10 s using MoKα radiation (TRIUMPH monochromator, sealed X-ray tube, 50kV, 30mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution achieved was Θ = 30.529°. Cell parameters were retrieved using the SAINT (Bruker, V8.38A, after 2013) software and refined using SAINT (Bruker, V8.38A, after 2013) on 9988 reflections, 40 % of the observed reflections. Data reduction was performed using the SAINT (Bruker, V8.38A, after 2013) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 30.529° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR2(int) was 0.0848 before and 0.0587 after correction. The ratio of minimum to maximum transmission is 0.7979. The λ/2 correction factor is not present. The absorption coefficient μ of this material is 6.884 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.695 and 0.871. The structure was solved in the space group $Pna2_1$ (# 33) by Intrinsic Phasing using the XT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/1 of XL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Additional crystallographic data can be found in Table S2.

Table S2. Crystallographic data for M1.

Formula	$C_{25}H_{23}NO_2Pt$
$D_{calc.}$/ g cm^{-3}	1.834
μ / mm^{-1}	6.884
Formula Weight	564.53
Colour	yellow
Shape	plate
Size/mm^3	0.16×0.11×0.02
T/K	90(2)
Crystal System	orthorhombic
Space Group	$Pna2_1$
a/Å	26.595(6)
b/Å	11.416(3)
c/Å	6.7344(15)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
V/Å^3	2044.6(8)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoKα
$\theta_{min}/^\circ$	1.941
$\theta_{max}/^\circ$	30.529
Measured Refl.	25018
Independent Refl.	6227
Reflections Used	5042
R_{int}	0.0662
Parameters	264
Restraints	237
Largest Peak	0.900
Deepest Hole	-2.693
GooF	1.016
wR_2 (all data)	0.0618
wR_2	0.0572
R_1 (all data)	0.0502
R_1	0.0324

X-Ray Crystallography Details for M2

A red blade-shaped crystal with dimensions 0.20×0.06×0.02 mm^3 was mounted on a mylar loop in oil. Data were collected using a Bruker APEX II area detector diffractometer equipped with a Kryoflex low-temperature device operating at T = 100(2) K. Data were measured using ω and ϕ scans using MoKα radiation. The maximum resolution that was achieved was Θ = 26.477° (0.80 Å). The diffraction pattern was indexed and the unit cell was refined using SAINT (Bruker, V8.38A, after 2013) on 9914 reflections, 30% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, after 2013). The final completeness is 99.90 % out to 26.477° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR2(int) was 0.1636 before and 0.0621 after correction. The ratio of minimum to maximum transmission is 0.7101. The λ/2 correction factor is not present. The absorption coefficient μ of this material is 6.237 mm^{-1} at this wavelength (λ = 0.711Å) and the minimum and maximum transmissions are 0.627 and 0.883.

The structure was solved and the space group C2/c (# 15) determined by the XT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2017/1 of XL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. Additional crystallographic data can be found in Table S3.

Table S3. Crystallographic data for M2.

Formula	$C_{29}H_{25}NO_2Pt$
$D_{calc.}$/ g cm^{-3}	1.807
μ / mm^{-1}	6.237
Formula Weight	614.59
Colour	red
Shape	blade
Size/mm^3	0.20×0.06×0.02
T/K	100(2)
Crystal System	monoclinic
Space Group	C2/c
a/Å	46.3286(19)
b/Å	5.1027(2)
c/Å	20.9343(9)
$\alpha/^{\circ}$	90
$\beta/^{\circ}$	114.049(2)
$\gamma/^{\circ}$	90
V/Å^3	4519.3(3)
Z	8
Z'	1
Wavelength/Å	0.71073
Radiation type	MoKα
$\theta_{min}/^{\circ}$	2.672
$\theta_{max}/^{\circ}$	26.477
Measured Refl.	33199
Independent Refl.	4673
Reflections Used	4083
R_{int}	0.0627
Parameters	300
Restraints	0
Largest Peak	5.203
Deepest Hole	-1.683
GooF	1.115
wR_2 (all data)	0.1161
wR_2	0.1114
R_1 (all data)	0.0526
R_1	0.0458

X-Ray Crystallography Details for M3

Experimental. A green needle-shaped crystal with dimensions 0.24×0.03×0.02 mm^3 was mounted on a mylar loop in oil. X-ray diffraction data were collected using a Bruker APEX II area detector diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 90(2) K. Data were measured using ω and ϕ scans of 0.5 ° per frame for 20 s using MoKα radiation (TRIUMPH monochromator, sealed X-ray tube, 50kV, 30mA). The total number of runs and images was based on the strategy calculation from the program APEX3. The maximum resolution achieved was Θ = 30.559°. Cell parameters were retrieved using the SAINT (Bruker, V8.38A, after 2013) software and refined using SAINT (Bruker, V8.38A, after 2013) on 8147 reflections, 35 % of the observed reflections. Data reduction was performed using the SAINT (Bruker, V8.38A, after 2013) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 30.559° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR2(int) was 0.0846 before and 0.0602 after correction. The ratio of minimum to maximum transmission is 0.7409. The $\lambda/2$ correction factor is not present. The absorption coefficient μ of this material is 6.825 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.646 and 0.872. The structure was solved in the space group $Pna2_1$ (# 33) by Intrinsic Phasing using the XT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/1 of XL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Additional crystallographic data can be found in Table S4.

Table S4. Crystallographic data for M3.

Formula	$C_{25}H_{21}NO_2F_2Pt$
$D_{calc.}$/ g cm^{-3}	1.929
μ /mm^{-1}	6.825
Formula Weight	600.52
Colour	green
Shape	needle
Size/mm^3	0.24×0.03×0.02
T/K	90(2)
Crystal System	orthorhombic
Space Group	$Pna2_1$
a/Å	27.0937(13)
b/Å	11.3331(6)
c/Å	6.7354(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
V/Å^3	2068.14(17)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoKα
$\theta_{min}/^\circ$	1.503
$\theta_{max}/^\circ$	30.559
Measured Refl.	23144
Independent Refl.	5898
Reflections Used	4427
R_{int}	0.0704
Parameters	282
Restraints	255
Largest Peak	1.477
Deepest Hole	-2.987
GooF	1.012
wR_2 (all data)	0.0604
wR_2	0.0552
R_1 (all data)	0.0686
R_1	0.0393

X-Ray Crystallography Data for M4.

Experimental. An orange prism-shaped crystal with dimensions 0.29×0.24×0.06 mm^3 was mounted on a mylar loop in oil. Data were collected using an Bruker APEX DUO diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 90(2) K. Data were measured using ω and ϕ scans of 0.5 ° per frame for 2 s using MoKα radiation (TRIUMPH monochromator, sealed X-ray tube, 50kV, 30mA). The total number of runs and images was based on the strategy calculation from the program APEX3.The maximum resolution that was achieved was Θ = 30.588° (0.70 Å). The diffraction pattern was indexed and the unit cell was refined using SAINT (Bruker, V8.38A, after 2013) on 9480 reflections, 16% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, after 2013). The final completeness is 99.80 % out to 30.588° in Θ. A multi-scan absorption correction was performed using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. wR2(int) was 0.1161 before and 0.0462 after correction. The ratio of minimum to maximum transmission is 0.6927. The λ/2 correction factor is not present. The absorption coefficient μ of this material is 6.325 mm^{-1} at this wavelength (λ = 0.711Å) and the minimum and maximum transmissions are 0.474 and 0.684. The structure was solved and the space group $P2_1/c$ (# 14) determined by the XT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2017/1 of XL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. Additional crystallographic data can be found in Table S5.

Table S5. Crystallographic data for M4.

Formula	$C_{26}H_{25}NO_3Pt$
$D_{calc.}$/ g cm^{-3}	1.773
μ / mm^{-1}	6.325
Formula Weight	594.56
Colour	orange
Shape	prism
Size/mm^3	0.29×0.24×0.06
T/K	90(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	13.1943(5)
b/Å	14.6170(5)
c/Å	23.1255(9)
$\alpha/^\circ$	90
$\beta/^\circ$	92.4490(10)
$\gamma/^\circ$	90
V/Å^3	4455.9(3)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	MoKα
$\theta_{min}/^\circ$	1.545
$\theta_{max}/^\circ$	30.588
Measured Refl.	60930
Independent Refl.	13400
Reflections Used	11030
R_{int}	0.0442
Parameters	565
Restraints	0
Largest Peak	2.159
Deepest Hole	-0.943
GooF	1.004
wR_2 (all data)	0.0509
wR_2	0.0473
R_1 (all data)	0.0397

R_1	0.0259

Table S6. Platinum-oxygen bond lengths and angles for **M1**-**M4**.

Monomer	**Pt – O1 bond length (Å)**	**Pt – O2 bond length (Å)**	**O1 – Pt – O2 angle (°)**	**Pt – N1 bond length (Å)**	**Pt – C1 bond length (Å)**
M1	2.070	1.998	90.08	1.995	1.979
M2	2.088	1.991	89.42	1.974	1.962
M3	2.068	1.989	89.94	1.987	1.969
M4	2.066	1.995	90.99	1.992	1.977
Pt(ppy)(acac)[2]	2.066	2.009	92.82	1.980	1.948

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