Supplementary Materials

Luminescent Alkynylplatinum(II) Terpyridine-Containing Conjugated Polymers: Synthesis, Characterization and Photophysical Studies

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Materials

Potassium tetrachloroplatinate ($K_2[PtCl_4]$) (Chem. Pur., 98 %), 4,4′,4″-tri-*tert*-butyl-2,2,′:6′,2″-terpyridine (^{t}Bu$_3$tpy) (Sigma-Aldrich Co. Ltd.), triethylamine (Apollo Scientific Ltd.), *N*,*N*,*N*′,*N*″,*N*″-pentamethyl- diethylenetriamine (PMDETA) (Sigma-Aldrich Co. Ltd.), copper(I) bromide (CuBr) (AK Scientific Ltd.), ammonium trifluoromethanesulfonate (NH_4OTf) (Sigma-Aldrich Co. Ltd.), 1,6-dibromofluorene (Alfa Aesar Chemical Co. Ltd.), sodium ascorbate (Sigma-Aldrich Co. Ltd.), 1,6-dibromohexane (AK Scientific Ltd.), sodium azide (NaN_3) (Sigma-Aldrich Co. Ltd.), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (Sigma-Aldrich Co. Ltd.) and 2,5-dibromo-3-hexylthiophene (AK Scientific Ltd.) were purchased from the respective companies. 2,7-Dibromo-9,9-bis(6-bromohexyl)fluorene,[1] 1,4-diethynylbenzne,[2] 9,9-bis(6′-bromohexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol) ester,[3] and 1-azidohexane[4] were synthesized according to previous literatures. All other reagents were of analytical grade and were used without further purification. The reactions were performed under N_2 atmosphere using standard Schlenk techniques unless specified otherwise.

Physical Measurements and Instrumentation

Nuclear Magnetic Resonance Spectroscopic Measurements

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker AVANCE 400 (400 MHz) or DPX-300 (300 MHz) Fourier transform NMR spectrometer at room temperature with tetramethylsilane (Me_4Si) as the internal reference.

Mass Spectrometric Measurements

Positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Thermo Scientific DFS high-resolution magnetic sector mass spectrometer.

Infrared Spectroscopic Measurements

IR spectra were obtained as KBr disks by using a Bio-Rad FTS-7 Fourier-transform infrared spectrometer (4000–400 cm^{-1}).

Elemental Analyses

Elemental analyses of the platinum(II) complexes were performed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

UV-Vis Absorption and Emission Spectroscopic Measurements

The UV-vis spectra were obtained using a Cary 50 (Varian) spectrophotometer equipped with a Xenon flash lamp. Steady-state excitation and emission spectra were recorded on a SPEX Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with an R2658P PMT detector. The concentrations of the solution samples for UV-vis absorption and emission studies were adjusted to 0.1 mg mL^{-1}. All solutions for photophysical studies were freshly prepared in a 10-cm^3 round-bottomed flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. The solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with at least four successive freeze-pump-thaw cycles.

Luminescence Lifetime Measurements

Emission lifetime measurements were recorded on a conventional pulsed laser system. The excitation source used was a 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCP-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 PMT and recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS s^{-1}) digital oscilloscope. The luminescence traces were analyzed by single exponential fits with the model, $I(t) = I_0 \times e^{-t/\tau}$ to obtain the lifetime (τ), where $I(t)$ and I_0 represent the luminescence intensity at time = t and time = 0, respectively. The sample solutions for luminescence lifetime studies were rigorously degassed under high vacuum with a least four successive freeze-pump-thaw cycles.

Relative Luminescence Quantum Yield Measurements

Relative luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.[5-6] The relative luminescence quantum yield of the sample was determined according to the following equation:

$$\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$$

where the subscripts s and r refer to the sample and reference solutions, respectively, $B = 1 - 10^{-AL}$, A is the absorbance at the excitation wavelength, L is the path length, n is the refractive index of the solvent used and D is the integrated emission intensity in wavenumber. A degassed solution of quinine sulfate in 0.5 M sulfuric acid ($\phi = 0.546$ with excitation wavelength = 365 nm) or $[Ru(bpy)_3]Cl_2$ in acetonitrile ($\phi = 0.094$ with excitation wavelength = 436 nm) was used as the reference.[7] The sample solutions for luminescence quantum yield measurements were rigorously degassed under high vacuum with a least four successive freeze-pump-thaw cycles.

Gel Permeation Chromatography Measurements

Measurements of molecular mass and molecular mass distribution of the organic conjugated polymers were performed at 30°C on a gel permeation chromatography (GPC) system equipped with two Waters 515 HPLC pumps, a Waters 2414 refractive index detector, a 2998 photodiode array detector and a Styragel HR 3 THF column. Polystyrenes with narrow molecular weight distribution were used as calibration standards. THF was used as an eluent at a flow-rate of 0.4 mL min^{-1}. Measurements of molecular mass and molecular mass distribution of the platinum(II)-containing conjugated polymers (**3**–**5**) were performed at 30°C on a gel permeation chromatography (GPC) system equipped with two Waters 515 HPLC pumps, a Waters 2414 refractive index detector, a 2998 photodiode array detector and a Styragel HR 3 DMF column. Polystyrenes with narrow molecular weight distribution were used as calibration standards. DMF with 0.1 M KPF_6 was used as an eluent at a flow-rate of 0.4 mL min^{-1}.

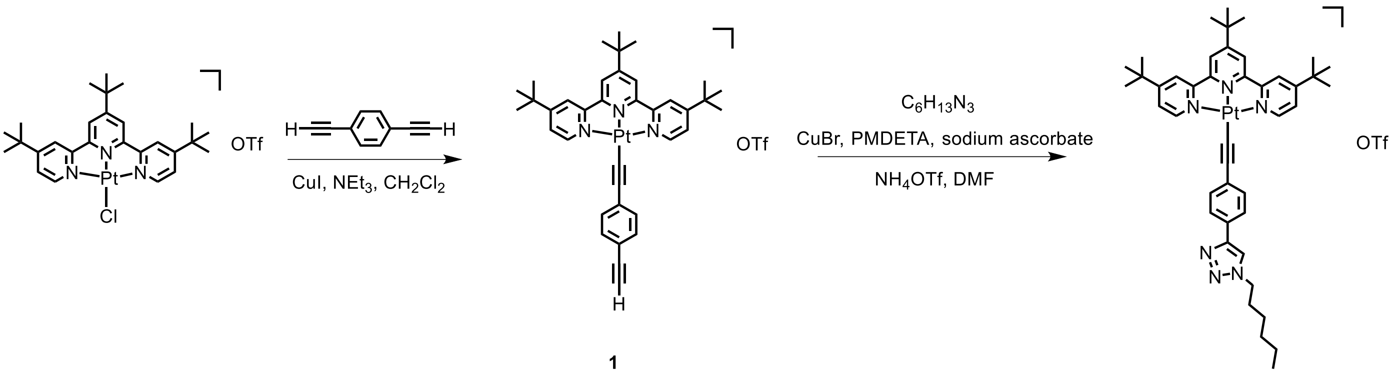
Determination of Förster Radius (R_0) of Platinum(II)-Containing Conjugated Polymers (3–5)

The Förster radius, R_0 was calculated from the following equation:[8-10]

$$R_0 = 0.211[\kappa^2 n^{-4} \Phi_D J(\lambda)]^{1/6}$$

where κ is the relative orientation of the transition dipoles of the chromophores of the donor and the acceptor ($\kappa^2 = 2/3$ for randomly oriented dipoles), n is the refractive index of the solvent, Φ_D is the luminescence quantum yield of the donor, $J(\lambda)$ is the spectral overlap integral of the emission spectrum of the donor and the UV-vis absorption spectrum of the acceptor, which was calculated as $J(\lambda) = \int f_d(\lambda)\varepsilon_a(\lambda)\lambda^4 \, d\lambda$, where $f_d(\lambda)$ is the normalized emission intensity of the donor and $\varepsilon_a(\lambda)$ is the product of the maximum molar extinction coefficient and the normalized absorbance of the acceptor.

Synthesis of Platinum(II) Precursor and Reference Complex



1

2

Scheme S1 Synthetic routes for platinum(II) precursor complex **1** and platinum(II) reference complex **2**.

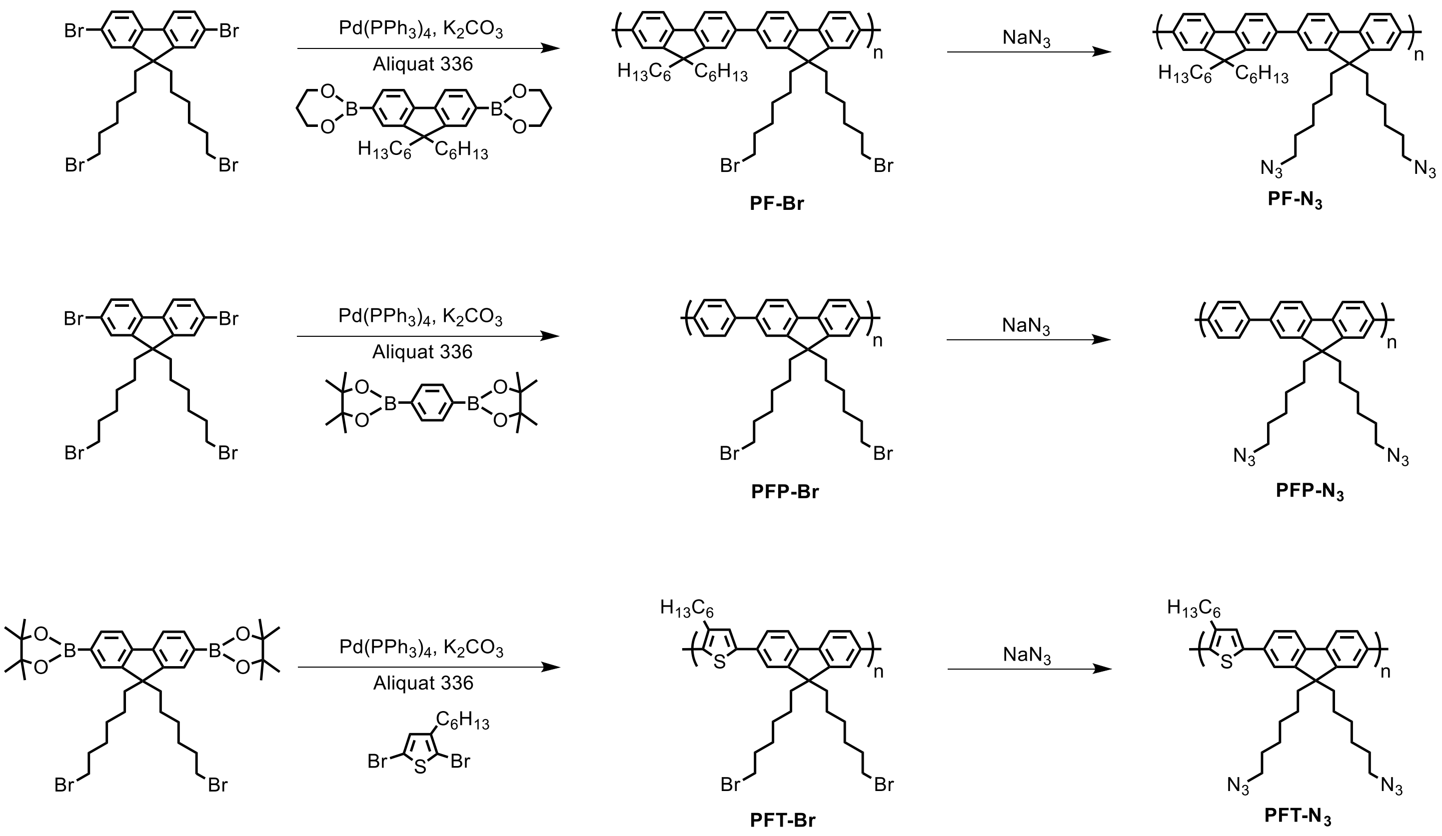
[Pt(^{t}Bu$_3$tpy)(C≡CC$_6$H$_4$C≡CH)]OTf (1)

This was synthesized by dehydrohalogenation reaction of [Pt(^{t}Bu$_3$tpy)Cl](OTf) (0.15 g, 0.17 mmol) and 1,4-diethynylbenzne (0.12 g, 0.86 mmol)) in the presence of CuI as the catalyst in dichloromethane (10 mL) and distilled triethylamine (1 mL) using modification of a literature procedure for [Pt(tpy)(C≡CC$_6$H$_5$)](OTf).[11] After overnight reaction, the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane and then purified by column chromatography on silica gel using dichloromethane-acetone (2:1, v/v) as eluent. Subsequent recrystallization by the slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of the complex gave **1** as an orange solid. Yield: 0.12 g (81 %). ^{1}H NMR (400 MHz, acetone-d_6, 298 K, relative to Me$_4$Si, δ / ppm): δ 1.48 (s, 18H, –^{t}Bu), 1.54 (s, 9H, –^{t}Bu), 3.77 (s, 1H, –C≡CH), 7.46 (m, 4H, –C$_6$H$_4$–), 7.97 (d, 2H, J = 8.0 Hz, tpy), 8.74 (d, 2H, J = 8.0 Hz, tpy), 8.78 (s, 2H, tpy), 9.18 (d, 2H, J = 6.0 Hz, tpy). IR (KBr disk, ν/cm^{-1}): 2118 (w) ν(C≡C), 2105 (w) ν(C≡C). Elemental analysis calcd (%) for $C_{38}H_{40}F_3N_3O_3PtS\bullet H_2O$: C, 51.34; H, 4.76; N, 4.73. Found: C, 51.19; H, 4.41; N, 4.57. Positive FAB-MS: *m*/*z* = 719 [M–OTf]$^+$.

[Pt(^{t}Bu$_3$tpy)(C≡CC$_6$H$_4$C$_2$HN$_3$C$_6$H$_{13}$)]OTf (2)

1 (50 mg, 0.06 mmol), 1-azidohexane (36, 0.28 mmol), sodium ascorbate (12 mg, 0.06 mmol), PMDETA (11 mg, 0.06 mmol) and NH_4OTf (96 mg, 0.57 mmol) were added into dry DMF (10 mL). This mixture was purged with nitrogen for 30 min. To this mixture was added CuBr (9 mg, 0.06 mmol) under nitrogen. This mixture was stirred at room temperature for 48 h under nitrogen atmosphere. Precipitation was achieved by adding the solution mixture into deionized water (500 mL) containing NH_4OTf (0.5 g). The resulting orange precipitate was collected and washed with water and diethyl ether. The crude product was purified by column chromatography using dichloromethane-acetone (4:1, v/v) as the eluent. Recrystallization through slow diffusion of diethyl ether vapor into a dichloromethane solution of the complex gave **2** as a red solid. Yield: 20 mg, (35%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.89 (t, 3H, *J* = 7.0 Hz, $-CH_3$), 1.34 (m, 6H, $-CH_2-$), 1.50 (s, 18H, –^{t}Bu), 1.64 (s, 9H, –^{t}Bu), 1.97 (m, 2H, $-CH_2-$), 4,42 (t, 2H, *J* = 7.6 Hz, $-CH_2N-$), 7.55 (d, 2H, *J* = 8.1 Hz, $-C_6H_4-$), 7.64 (dd, 2H, *J* = 8.0 Hz and 1.8 Hz, tpy), 7.77 (s, 1H, $-C_2HN_3-$), 7.81 (d, 2H, *J* = 8.1 Hz, $-C_6H_4-$), 8.40 (s, 2H, tpy), 8.47 (s, 2H, tpy), 9.18 (d, 2H, *J* = 5.9 Hz, tpy). IR (KBr disk, ν/cm^{-1}): 2116 (w) ν(C≡C). Elemental analysis calcd (%) for $C_{44}H_{53}F_3N_6O_3PtS\bullet H_2O$: C, 52.01; H, 5.46; N, 8.27. Found: C, 52.30; H, 5.18; N, 8.29. Positive FAB-MS: *m*/*z* = 848 [M–OTf]$^+$.

Synthesis of Conjugated Polymers



Scheme S2 Synthetic routes for conjugated polymers.

Poly[fluorene($C_6H_{12}Br$)$_2$-*co*-fluorene(C_6H_{13})$_2$] (PF-Br)

The polymer was synthesized according to a reported method.[12] 2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene (0.52 g, 0.80 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.40 g, 0.80 mmol), aliquat 336 (few drops), and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) were added into toluene (10 mL). This mixture was purged with nitrogen for 30 min. To this mixture was added a degassed aqueous K_2CO_3 solution (2.00 M, 2 mL). This mixture was stirred at 90°C for 48 h under nitrogen atmosphere. 1-Bromobenzene (0.14 g, 0.88 mmol) was added and the mixture was stirred at 90°C for 6 h for the end-capping reaction. Phenylboronic acid (0.11 gg, 0.88 mmol) was added and stirred at 90°C for another 6 h for another end-capping reaction. The mixture was diluted with dichloromethane (50 mL), and the organic layer was washed with brine, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was then dissolved in a small amount of dichloromethane. The concentrated solution was added into an excess amount of cold methanol with vigorous stirring. The precipitate was collected and redissolved in dichloromethane. The precipitation was repeated for two more times. A grey solid was obtained. Yield: 0.55 g (83 %). ^1H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.63–1.35 (br, 34H, $-CH_2-$), 1.56–1.78 (br, 4H, $-CH_2-$), 1.80–2.20 (br, 8H, $-CH_2-$), 3.30 (br, 4H, $-CH_2Br$), 7.47–8.11 (br, 12H, fluorene). GPC (versus polystyrene in THF): M_n = 5.6 kDa, M_w = 7.4 kDa, PDI = 1.30.

Poly[fluorene($C_6H_{12}N_3$)$_2$-*co*-fluorene(C_6H_{13})$_2$] (PF-N_3)

The polymer was synthesized according to a reported procedure.[13] To a solution of **PF-Br** (0.50 g, 5.86 mmol per repeating unit) in a mixture of dry THF (20 mL) and dry DMF (10 mL) was added NaN_3 (0.15 g, 23.0 mmol). The reaction mixture was stirred overnight at 40°C. The reaction was cooled to room temperature and diluted with dichloromethane. The solution was washed with deionized water for three times to remove any unreacted NaN_3, and then dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure. The concentrated solution was added into an excess amount of methanol with vigorous stirring. The precipitate was collected and then redissolved in dichloromethane. The precipitation was repeated for two more times. A grey solid was obtained. Yield: 0.45 g (94 %). ^1H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.63–1.35 (br, 34H), 1.56–1.78 (br, 4H, $-CH_2-$), 1.80–2.20 (br, 8H, $-CH_2-$), 3.14 (br, 4H, $-CH_2N_3$), 7.47–8.11 (br, 12H, fluorene). IR (KBr disk, ν/cm^{-1}): 2093 (s) ν(N=N=N). GPC (versus polystyrene in THF): M_n = 5.8 kDa, M_w = 8.0 kDa, PDI = 1.39.

Poly[fluorene($C_6H_{12}Br$)$_2$-*co*-phenylene] (PFP-Br)

The procedure was similar to that for **PF-Br** except that 1,4-benzenediboronic acid bis(pinacol)ester (0.52 g, 1.58 mmol) was used instead of 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. The product was obtained as a grey solid. Yield: 0.56 g (63 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.77 (br, 4H, $-CH_2-$), 1.13–1.23 (br, 8H, $-CH_2-$), 1.67 (br, 4H, $-CH_2-$), 2.09 (br, 4H, $-CH_2-$), 3.28 (br, 4H, $-CH_2Br$), 7.47–8.00 (br, 10H, fluorene and phenylene). GPC (versus polystyrene in THF): M_n = 11.2 kDa, M_w = 43.1 kDa, PDI = 3.85.

Poly[fluorene($C_6H_{12}N_3$)$_2$-*co*-phenylene] (PFP-N_3)

The procedure was similar to that for **PF-N_3** except that **PFP-Br** (75 mg, 0.13 mmol per repeating unit) was used instead of **PF-Br**. The product was obtained as a grey solid. Yield: 60 mg (94 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.78 (br, 4H, $-CH_2-$), 1.01–1.70 (br, 12H, $-CH_2-$), 2.11 (br, 4H, $-CH_2-$), 3.13 (br, 4H, $-CH_2N_3$), 7.47–8.00 (br, 10H, fluorene and phenylene). IR (KBr disk, ν/cm^{-1}): 2093 (s) ν(N=N=N). GPC (versus polystyrene in THF): M_n = 8.3 kDa, M_w = 26.9 kDa, PDI = 3.24.

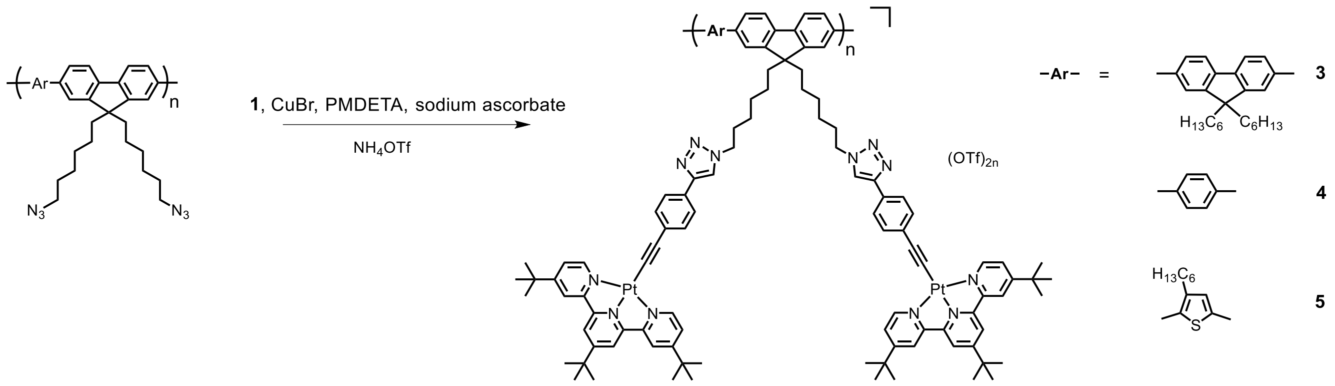
Poly[fluorene($C_6H_{12}Br$)$_2$-*co*-thiophene(C_6H_{13})] (PFT-Br)

The procedure was similar to that for **PF-Br** except that 9,9-bis(6′-bromohexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.64 g, 0.86 mmol) and 2,5-dibromo-3-hexylthiophene (0.28 g, 0.86 mmol) were used instead of 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and 2,7-dibromo-9,9-bis(6′-bromohexyl)fluorene. The product was obtained as a greenish yellow solid. Yield: 0.35 g (63 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.71 (br, 4H, $-CH_2-$), 1.00–1.48 (br, 16H, $-CH_2-$), 1.68 (br, 7H, $-CH_2-$ and $-CH_3$), 2.06 (br, 4H, $-CH_2-$), 2.75 (br, 2H, $-CH_2-$), 3.32 (br, 4H, $-CH_2Br$), 7.40–7.80 (br, 7H, fluorene and thiophene). GPC (versus polystyrene in THF): M_n = 5.1 kDa, M_w = 11.6 kDa, PDI = 2.27.

Poly[fluorene($C_6H_{12}N_3$)$_2$-*co*-thiophene(C_6H_{13})] (PFT-N_3)

The procedure was similar to that for **PF-N$_3$** except that **PFT-Br** (0.13 g, 0.20 mmol per repeating unit) was used instead of **PF-Br**. The product was obtained as a greenish yellow solid. Yield: 95 mg (84 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.73 (br, 4H, $-CH_2-$), 1.00–1.50 (br, 16H, $-CH_2-$), 1.66 (br, 7H, $-CH_2-$ and $-CH_3$), 2.05 (br, 4H, $-CH_2-$), 2.75 (br, 2H, $-CH_2-$), 3.13 (br, 4H, $-CH_2N_3$), 7.40–7.80 (br, 7H, fluorene and thiophene). IR (KBr disk, ν/cm^{-1}): 2091 (s) ν(N=N=N). GPC (versus polystyrene in THF): M_n = 5.8 kDa, M_w = 12.8 kDa, PDI = 2.21.

Synthesis of Platinum(II)-Containing Conjugated Polymers



Scheme S3 Synthetic routes for platinum(II)-containing conjugated polymers (**3**–**5**).

[PF–{N_3C_2H–$C_6H_4C{\equiv}CPt(^tBu_3tpy)$}$_2$](OTf)$_{2n}$ (3)

1 (80 mg, 0.09 mmol), **PF-N$_3$** (33 mg, 0.04 mmol per repeating unit), sodium ascorbate (21 mg, 0.11 mmol), PMDETA (18 mg, 0.11 mmol) and NH_4OTf (73 mg, 0.44 mmol) were added into a mixture of dry DMF (4 mL) and dry THF (10 mL). This mixture was purged with nitrogen for 30 min. To this mixture was added CuBr (15 mg, 0.11 mmol) under the protection of nitrogen. This mixture was stirred at 45°C for 48 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and subjected to a gentle flow of compressed air to evaporate THF. Precipitation was achieved by adding the remaining solution into deionized water (500 mL) containing NH_4OTf (0.5 g) with vigorous stirring. The resulting precipitate was collected by vacuum filtration, and then dissolved into acetonitrile. Any insoluble impurities were removed by filtration. The solvent was removed and the residue was then dissolved in acetonitrile (20 mL) with NH_4OTf (0.5 g) and PMDETA (0.5 mL). The solution was then stirred for 30 min and followed by addition of deionized water (250 mL). The orange precipitate was collected by vacuum filtration, washed with deionized water, methanol, THF and diethyl ether and dried under vacuum. An orange solid was finally obtained. Yield: 55 mg (50 %). ^{1}H NMR (400 MHz, CD_3CN, 298 K, δ / ppm): δ 0.50–1.50 (br), 4.25 (br), 7.49 (br), 7.40–8.00 (br), 8.00–8.25 (br), 8.75–9.00 (br). IR (KBr disk, ν/cm^{-1}): 2114 (w) ν(C≡C), 1156 (s) ν(S=O), 1030 (s) ν(C–F). GPC (versus polystyrene in DMF): M_n = 34.8 kDa, M_w = 41.0 kDa, PDI = 1.19.

[PFP–{N_3C_2H–$C_6H_4C{\equiv}CPt(^t Bu_3tpy)\}_2](OTf)_{2n}$ (4)

The procedure was similar to that for **3** except that **PFP-N_3** (20 mg, 0.04 mmol) was used instead of **PF-N_3**. The product was obtained as an orange solid. Yield = 35 mg (45 %). ^{1}H NMR (300 MHz, CD_3CN, 298 K, δ / ppm): δ 0.80–1.80 (br), 4.24 (br), 7.00–7.80 (br), 7.80–8.20 (br). 8.40–9.00 (br). IR (KBr disk, ν/cm^{-1}): 2112 (w) ν(C≡C), 1155 (s) ν(S=O), 1030 (s) ν(C–F). GPC (versus polystyrene in DMF): M_n = 45.1 kDa, M_w = 53.6 kDa, PDI = 1.19.

[PFT–{N_3C_2H–$C_6H_4C{\equiv}CPt(^tBu_3tpy)$}$_2$](OTf)$_{2n}$ (5)

The procedure was similar to that for **3** except that **PFT-N_3** (43 mg, 0.07 mmol) was used instead of **PF-N_3**. The product was obtained as an orange solid. Yield: 50 mg (35 %). ^{1}H NMR (400 MHz, CD_3CN, 298 K, δ / ppm): δ 0.20–0.80 (br), 4.25 (br), 6.80–7.80 (br), 7.80–8.20 (br), 8.25–9.00 (br). IR (KBr disk, ν/cm^{-1}): 2112 (w) ν(C≡C), 1152 (s) ν(S=O), 1028 (s) ν(C–F)b. GPC (versus polystyrene in DMF): M_n = 42.9 kDa, M_w = 51.5 kDa, PDI = 1.20.

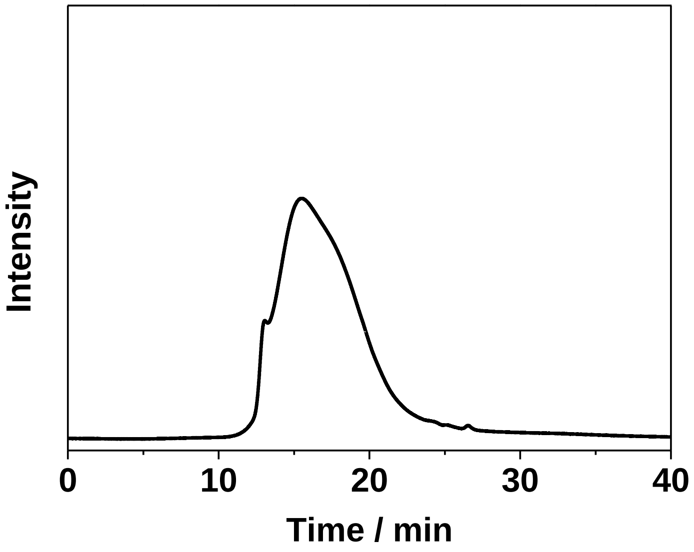


Figure S1 GPC data of **5** in dimethylformamide at 298 K.

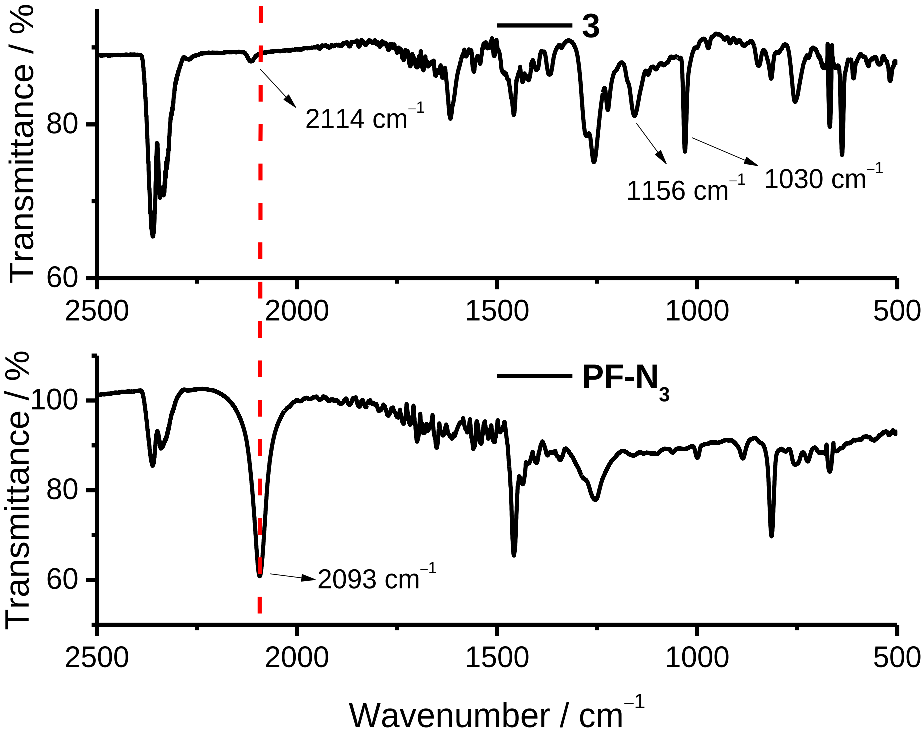


Figure S2 IR spectra of $[PF–\{N_3C_2H–C_6H_4C\equiv CPt(^tBu_3tpy)\}_2](OTf)_{2n}$ (**3**) and its corresponding precursor polymer, poly[fluorene$(C_6H_{12}N_3)_2$-*co*-fluorene$(C_6H_{13})_2$] (**PF-N$_3$**).

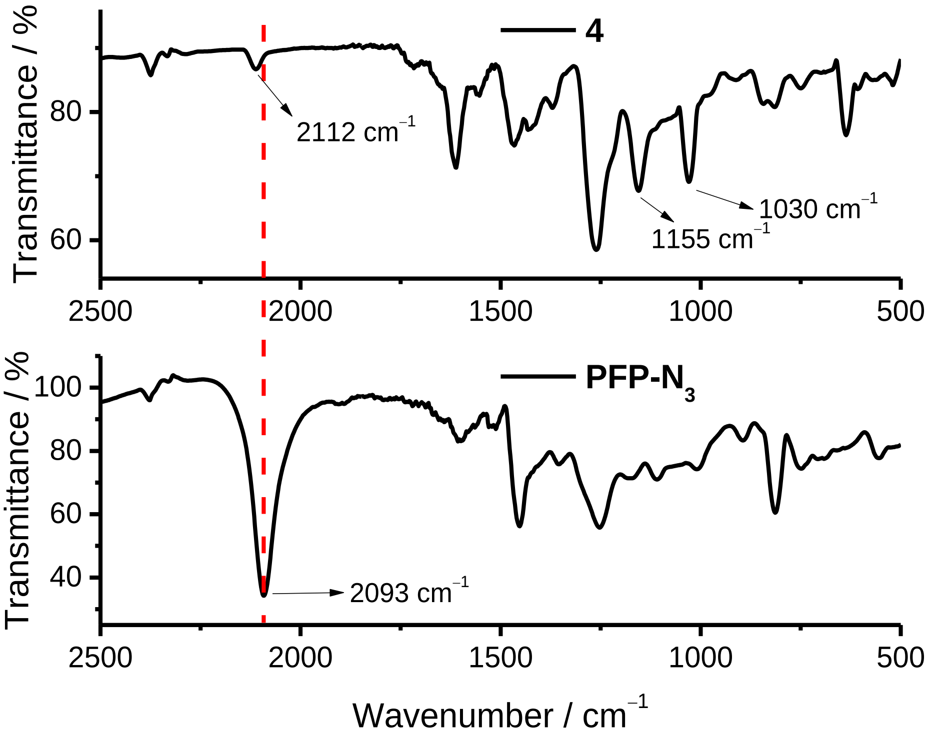


Figure S3 IR spectra of [PFP–{N_3C_2H–C_6H_4C≡CPt(^{t}Bu$_3$tpy)}$_2$](OTf)$_{2n}$ (**4**) and its corresponding precursor polymer, poly[fluorene($C_6H_{12}N_3$)$_2$-*co*-phenylene] (**PFP-N$_3$**).

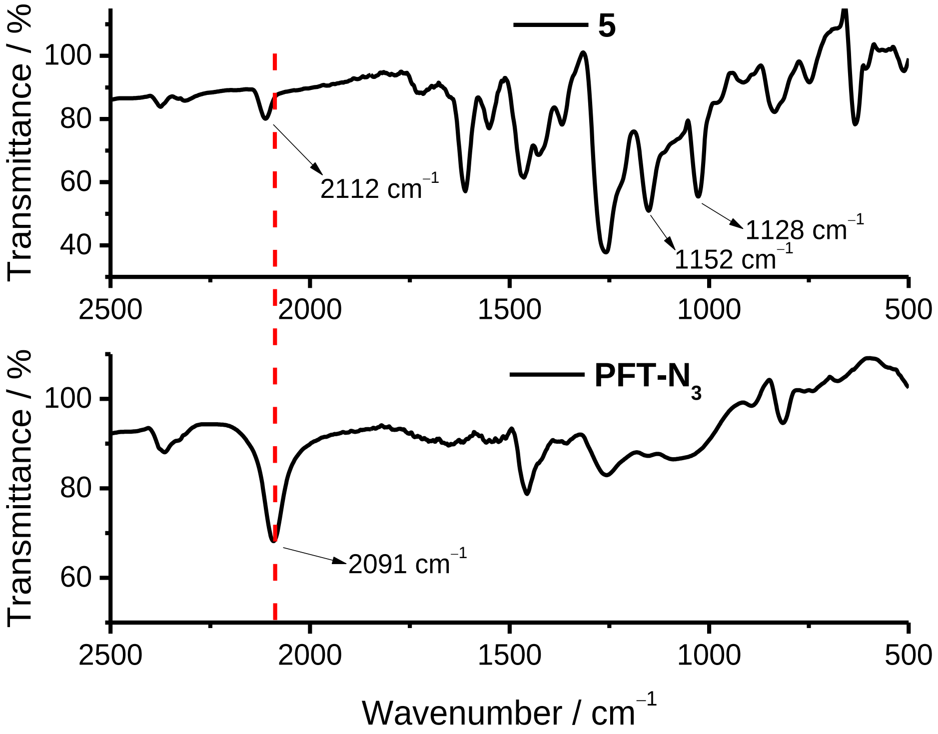


Figure S4 IR spectra of [PFT–{N_3C_2H–$C_6H_4C{\equiv}CPt(^tBu_3tpy)$}$_2$](OTf)$_{2n}$ (**5**) and its corresponding precursor polymer, poly[fluorene($C_6H_{12}N_3$)$_2$-*co*-thiophene(C_6H_{13})] (**PFT-N$_3$**).

Table S1 UV-Vis absorption data for organic polymers at 298 K

Polymer	**Medium**	**Absorption** **λ_{max} /nm**
Poly[fluorene($C_6H_{12}Br)_2$-*co*-fluorene($C_6H_{13})_2$] (**PF-Br**)	CH_2Cl_2	375
Poly[fluorene($C_6H_{12}Br)_2$-*co*-phenylene] (**PFP-Br**)	CH_2Cl_2	371
Poly[fluorene($C_6H_{12}N_3)_2$-*co*-thiophene(C_6H_{13})] (**PFT-Br**)	CH_2Cl_2	398

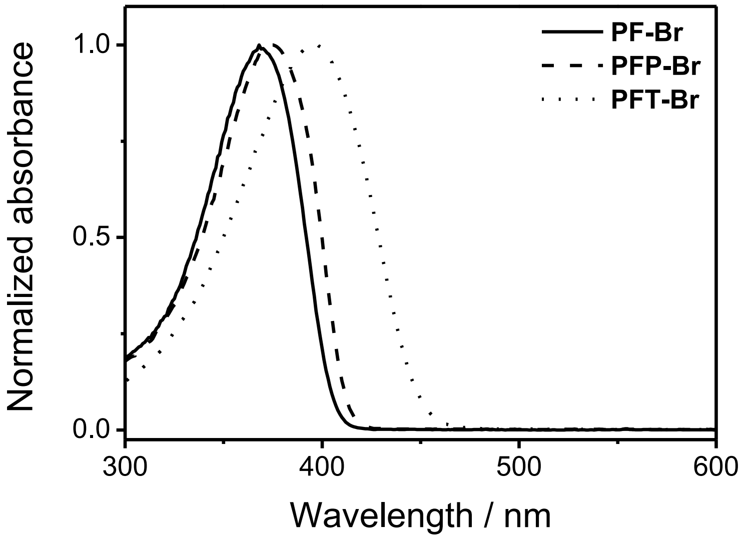


Figure S5 Normalized UV-vis absorption spectra of the organic conjugated polymers in dichloromethane at 298 K.

Table S2 Emission data for organic conjugated polymers

Polymers	**Medium**	**λ_{em} /nm**	**Φ_{lum}**
Poly[fluorene($C_6H_{12}Br$)$_2$-*co*-fluorene(C_6H_{13})$_2$] (**PF-Br**)	CH_2Cl_2	414[a]	0.92[b]
Poly[fluorene($C_6H_{12}Br$)$_2$-*co*-phenylene] (**PFP-Br**)	CH_2Cl_2	410[a]	0.90[b]
Poly[fluorene($C_6H_{12}Br$)$_2$-*co*-thiophene(C_6H_{13})] (**PFT-Br**)	CH_2Cl_2	462[a]	0.45[b]

[a] Vibronic-structured band with vibrational progessional spacings of about 1150–1340 cm^{-1}.

[b] The relative luminescence quantum yields were measured at room temperature using quinine sulfate in 0.5 M H_2SO_4 as a standard.

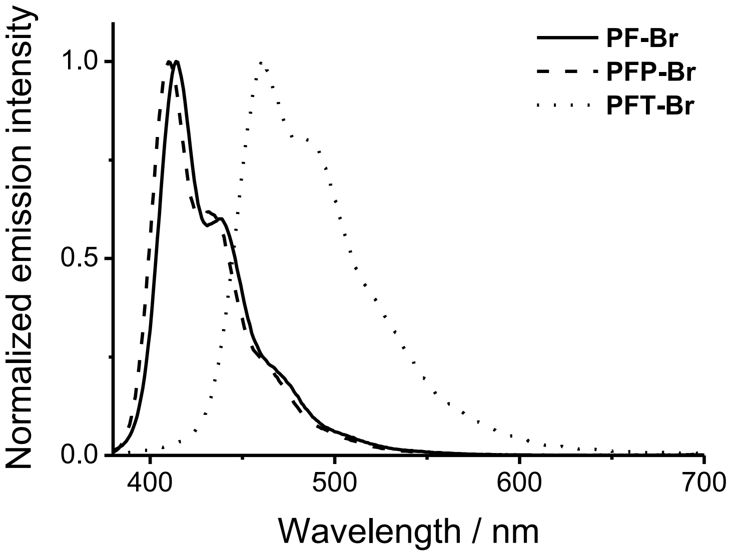


Figure S6 Normalized emission spectra of conjugated polymers in dichloromethane at 298 K.

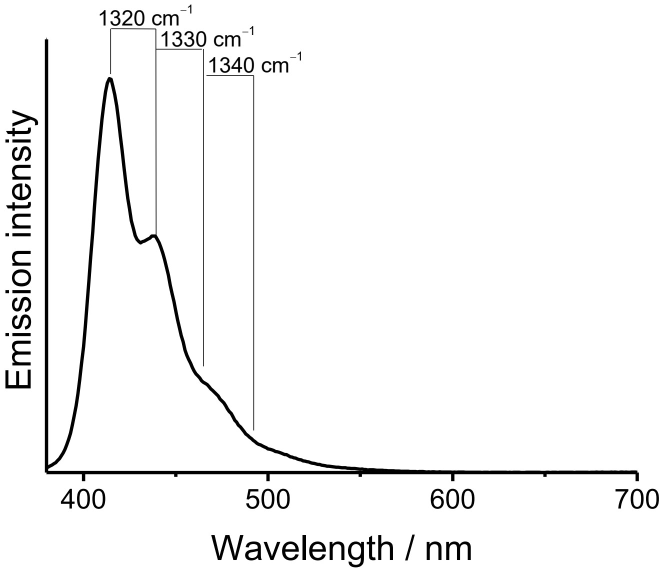


Figure S7 Emission spectrum of poly[fluorene($C_6H_{12}Br$)$_2$-*co*-fluorene(C_6H_{13})$_2$] (**PF-Br**) in dichloromethane at 298 K.

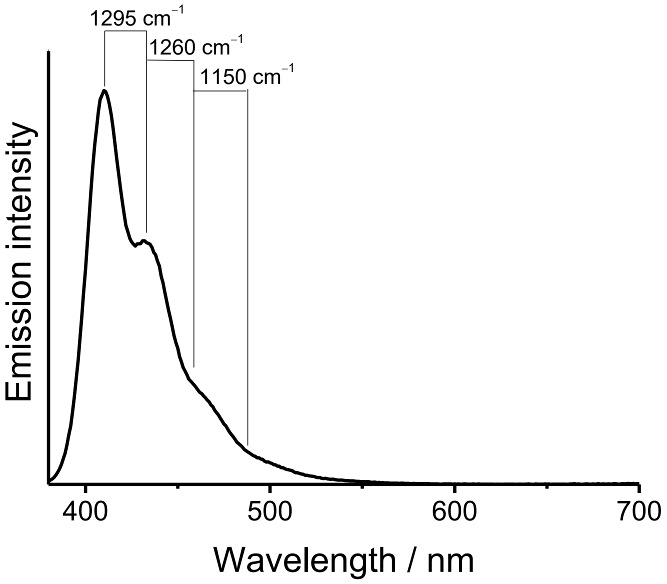


Figure S8 Emission spectrum of poly[fluorene($C_6H_{12}Br$)$_2$-*co*-phenylene] (**PFP-Br**) in dichloromethane at 298 K.

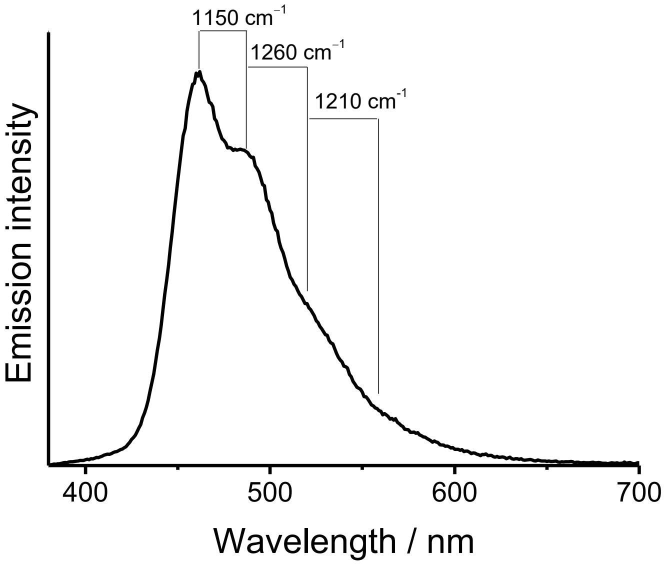


Figure S9 Emission spectrum of poly[fluorene($C_6H_{12}Br$)$_2$-*co*-thiophene(C_6H_{13})] (**PFT-Br**) in dichloromethane at 298 K.

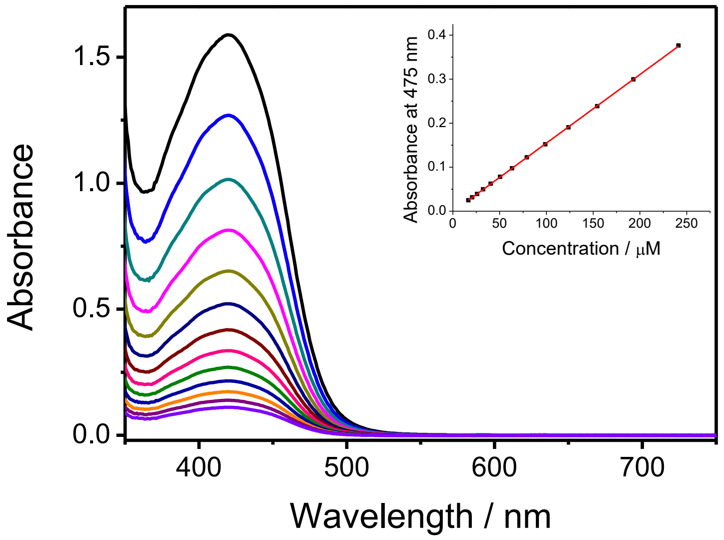


Figure S10 Concentration-dependent UV-vis absorption spectra of [Pt(^{t}Bu$_3$tpy)(C≡CC$_6$H$_4$C≡CH)]OTf (**1**) in acetonitrile (from 17 to 254 μM) at 298 K. The inset shows the apparent absorbance at 475 nm with different concentrations of **1**.

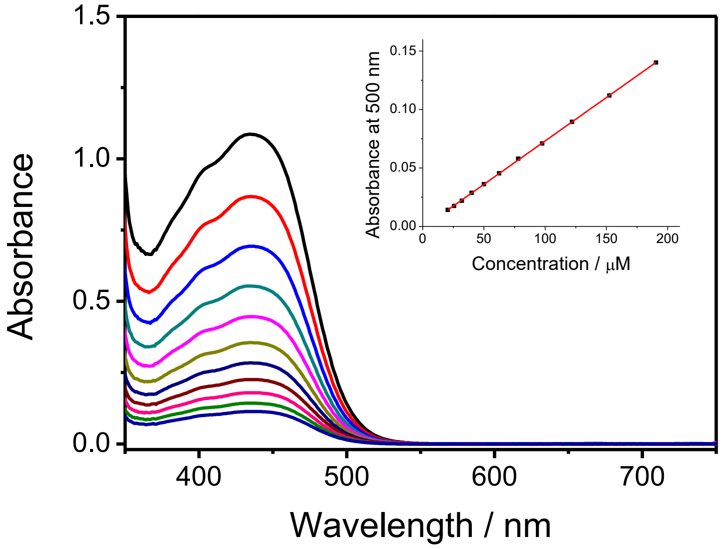


Figure S11 Concentration-dependent UV-vis absorption spectra of [Pt(^{t}Bu$_3$tpy)(C≡CC$_6$H$_4$C$_2$HN$_3$C$_6$H$_{13}$)]OTf (**2**) in acetonitrile (from 20 to 191 μM) at 298 K. The inset shows the apparent absorbance at 500 nm with different concentrations of **2**.

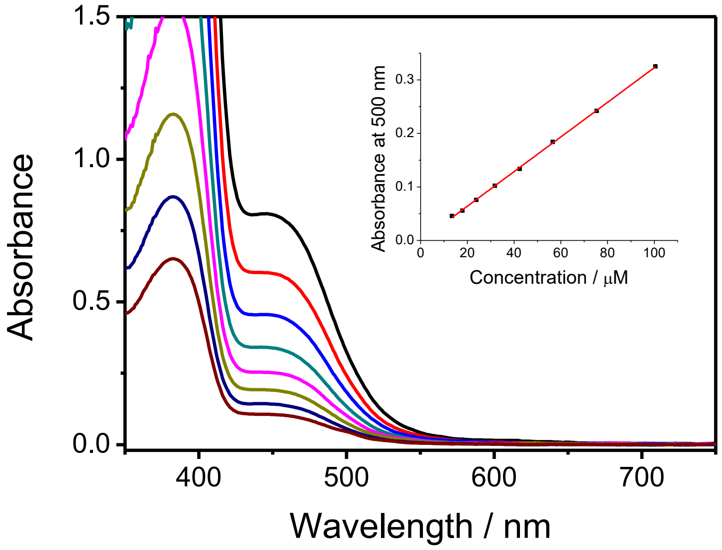


Figure S12 Concentration-dependent UV-vis absorption spectra of $[PF–\{N_3C_2H–C_6H_4C{\equiv}CPt(^tBu_3tpy)\}_2](OTf)_{2n}$ (**3**) in acetonitrile (from 13 to 101 μM per repeating unit) at 298 K. The inset shows the apparent absorbance at 500 nm with different concentrations of **3**.

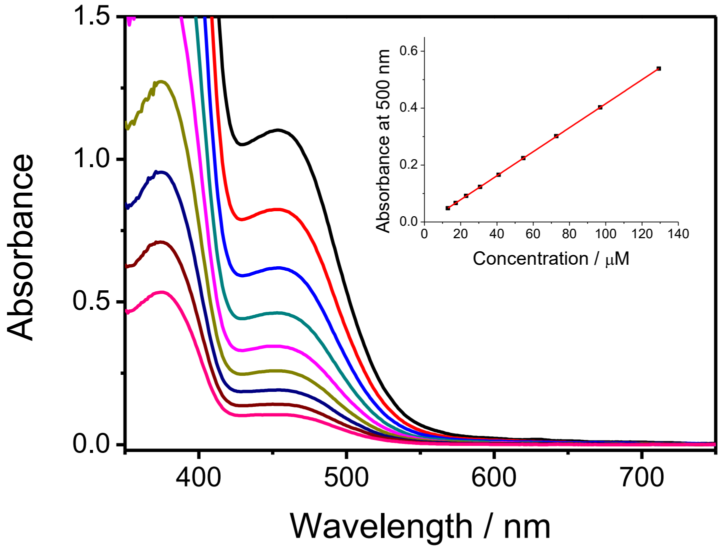


Figure S13 Concentration-dependent UV-vis absorption spectra of [PFP–{N_3C_2H–$C_6H_4C{\equiv}CPt(^t Bu_3tpy)$}$_2$](OTf)$_{2n}$ (**4**) in acetonitrile (from 13 to 129 μM per repeating unit) at 298 K. The inset shows the apparent absorbance at 500 nm with different concentrations of **4**.

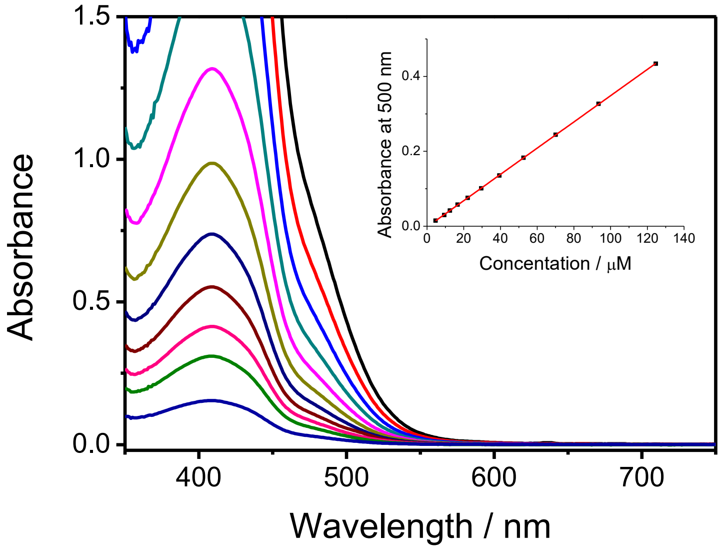


Figure S14 Concentration-dependent UV-vis absorption spectra of $[\mathrm{PFT{-}\{N_3C_2H{-}C_6H_4C{\equiv}CPt({}^{t}Bu_3tpy)\}_2](OTf)_{2n}}$ (**5**) in acetonitrile (from 5 to 125 μM per repeating unit) at 298 K. The inset shows the apparent absorbance at 500 nm with different concentrations of **5**.

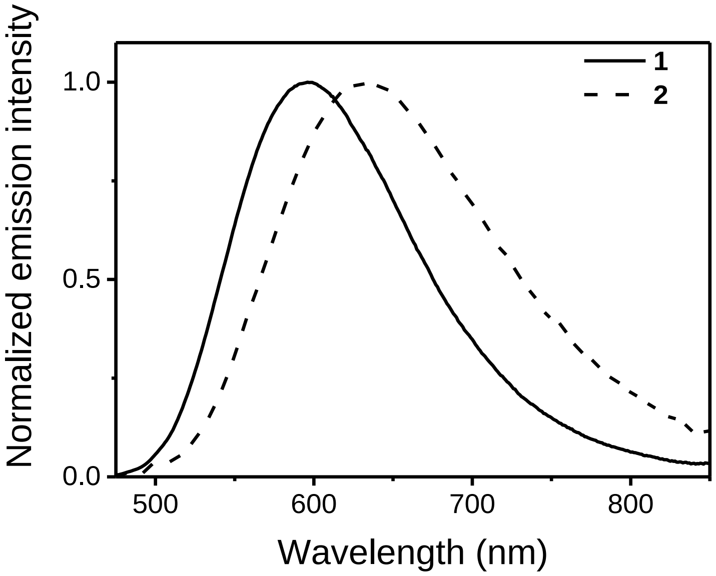


Figure S15 Normalized emission spectra of **1** and **2** in degassed acetonitrile at 298 K.

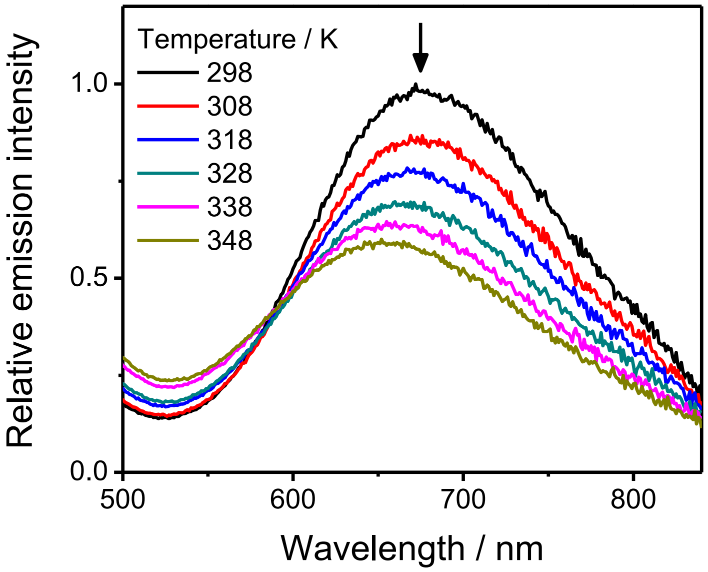


Figure S16 Emission spectra of $[PF–\{N_3C_2H–C_6H_4C{\equiv}CPt(^tBu_3tpy)\}_2](OTf)_{2n}$ (**3**) in acetonitrile with increasing temperature.

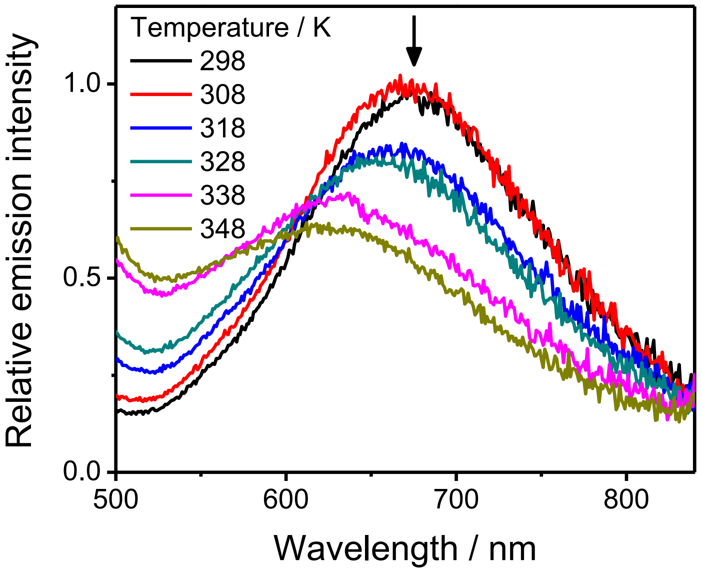


Figure S17 Emission spectra of [PFP–{N_3C_2H–$C_6H_4C{\equiv}CPt(^tBu_3tpy)$}$_2$]–(OTf)$_{2n}$ (**4**) in acetonitrile with increasing temperature.

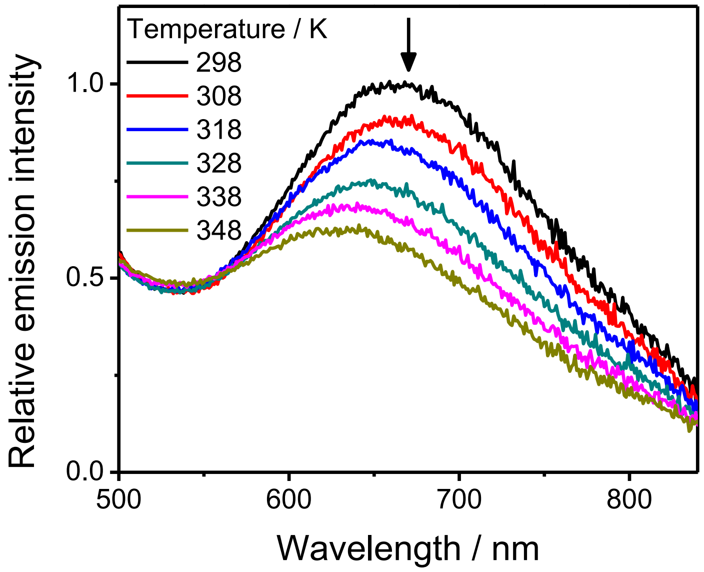


Figure S18 Emission spectra of [PFT–{N_3C_2H–C_6H_4C≡CPt(^{t}Bu_3tpy)}$_2$]–$(OTf)_{2n}$ (**5**) in acetonitrile with increasing temperature.

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