

The Reduced and Oxidized Forms of the Pt-Organometallic Version of Polyaniline.

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Supporting Information

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Experimental Section.

Materials. All starting materials were obtained from Aldrich and were used as received. All solvents, unless otherwise stated, were obtained from Fisher and dried prior use. Compound **5b** was prepared as previously reported.^{S1}

Synthesis.

N,N'-bis(para-iodophenyl)benzoquinone diimine (2a) 4-iodoaniline (1.75 g, 8.0 mmol) and 2.69 g (24.0 mmol) of DABCO (1,4-diazabicyclo[2.2.2]octane) were dissolved in 25 mL of chlorobenzene while heating to 90°C. Titanium tetrachloride (0.88 mL, 8.0 mmol) was added dropwise followed by the addition of benzoquinone (0.43 g, 4.0 mmol). Quantitative transfer of benzoquinone was achieved by rinsing with 20 mL of chlorobenzene. The solution was stirred at 120°C for 12 hours. The precipitate was isolated by filtration and washed with hot chlorobenzene (2 x 20 mL). The solution was evaporated. The solid was dissolved in CH₂Cl₂, washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated to dryness. The product was purified on a silica column with CH₂Cl₂ as the solvent to give compound **2a**. Yield: 0.71 g (35%); ¹H NMR (δ 300 MHz, CDCl₃): 7.70 (4 H, dd appearing as a pseudo triplet, *J*=8.5), 7.09-6.62 (8 H, m); *m/z* (EI): 510 (M⁺).

N,N'-bis(para-Iodophenyl)tetrafluorobenzoquinone diimine (2b) 4-iodoaniline (4.87 g, 22.2 mmol) and 3.73 g (33.3 mmol) of DABCO were dissolved in (25 mL) of chlorobenzene while heating to 60°C. Titanium tetrachloride (2.41 mL, 22.2 mmol) was added dropwise, followed by the addition of p-fluoranil (2.00 g, 11.1 mmol). Quantitative transfer of benzoquinone was achieved by rinsing with 20 mL of chlorobenzene. The solution was stirred at 60°C for 5 hours. The product was isolated by filtration, washed with hot chlorobenzene (2 x 40 mL). The solution was evaporated. The filtrate was dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was evaporated. The crude product was purified on an alumina column with CHCl₃ as the eluent to give compound **2b**. Yield: 2.45 g (38%). IR (KBr)/cm⁻¹ ν : 1630 (C=N). ¹H NMR δ(400 MHz CDCl₃): 7.68 (4 H, m, C-H aro), 6.67 (4 H, m, CH aro.), ppm; λ_{max}(2-MeTHF)/nm 260 nm (ε/dm³.mol⁻¹.cm⁻¹ 27992), 295 (48860), 515 (13694)); *m/z* (EI): 582 (M⁺).

N,N'-bis(*para*-iodophenyl)tetrachlorobenzoquinone diimine (2c) 4-iodoaniline (1.75 g, 8.0 mmol) and 2.69 g (24.0 mmol) of DABCO were dissolved in 50 mL of chlorobenzene while heating to 90°C. Titanium tetrachloride (0.88 mL, 8.0 mmol) was added dropwise, followed by the addition of tetrachlorobenzoquinone (0.98 g, 4.0 mmol). Quantitative transfer of benzoquinone was achieved by rinsing with 20 mL of chlorobenzene. The solution was stirred at 60°C for 10 hours. The precipitate was isolated by filtration and washed with hot chlorobenzene (2 x 20 mL). The solution was evaporated. The solid was dissolved in CH₂Cl₂, 2.0 g (8.0 mmol) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added while stirring for 30 min. The solution was washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The crude product was purified on a silica column with 7:3 hexane/CHCl₃ as the solvent to give compound **2c**. Yield: 1.43 (55.2 %) ¹H NMR (δ 400MHz CDCl₃): 7.61 (4H, m, CH aro), 6.56 (4H, m, CH aro); m/z (EI): 648 (M⁺).

N,N'-bis(*para*-bromophenyl)benzoquinone diimine (2'a) 4-bromoaniline (1.38 g, 8.0 mmol) and 2.69 g (24.0 mmol) of DABCO were dissolved in 25 mL of chlorobenzene while heating to 90°C. Titanium tetrachloride (0.88 mL, 8.0 mmol) was added dropwise, followed by the addition of benzoquinone (0.43 g, 4.0 mmol). Quantitative transfer of benzoquinone was achieved by rinsing with 20 mL of chlorobenzene. The solution was stirred at 120°C for 12 hours. The precipitate was isolated by filtration and washed with hot chlorobenzene (2 x 20 mL). The solution was evaporated. The solid was dissolved in CH₂Cl₂, washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The crude product was purified on a silica column with CH₂Cl₂ as the solvent to give dibromide compound **2'a**. Yield: 1.33 (40%) IR (KBr)/cm⁻¹ ν : 1583 (C=N); ¹H NMR (CDCl₃): 7.50(4 H, m), 6.92 (4 H, m), 6.76 (4 H, m); m/z (EI): 416 (M⁺).

N,N'-bis(*para*-bromophenyl)tetrachlorobenzoquinone diimine (2'c) 4-bromoaniline (1.38 g, 8.0 mmol) and 2.69 g (24.0 mmol) of DABCO were dissolved in 25 mL of chlorobenzene while heating at 90°C. Titanium tetrachloride (0.88 mL, 8.0 mmol) was added dropwise, followed by the addition of tetrachlorobenzoquinone (0.98 g, 4.0 mmol). Quantitative transfer of benzoquinone was achieved by rinsing with 20 mL of chlorobenzene. The solution was stirred at 60°C for 10 hours. The precipitate was

isolated by filtration and washed with hot chlorobenzene (2 x 20 mL). The solution was evaporated. The solid was dissolved in CH₂Cl₂, 2.0 g (8 mmol) of DDQ was added with stirring for 10 min. The solution was washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The crude product was purified on a silica column with CHCl₃ as eluent to give compound **2'c**. Yield: 1.11 g (50.3 %). ¹H NMR (CDCl₃): 7.51 (4H, m, CH aro), 6.69 (4 H, m, CH aro); m/z (EI): 554 (M⁺).

N,N'-bis(para-iodophenyl)benzoquinone diamine (3a) 0.38 g (0.75 mmol) of **2a** was dissolved in 20 ml CH₂Cl₂. 0.143 g (3.75 mmol) sodium borohydride was dissolved in 20 ml anhydrous ethanol and added to the CH₂Cl₂ solution. The solution was stirred for 60 min, the solvent was evaporated. The product was dissolved in CHCl₃ and washed with water (3 x 30 ml) and dried over anhydrous MgSO₄. The solution was evaporated and the solid was purified using silica chromatography with CH₂Cl₂/Hexane (30:70) as the solvent. Product **3a** was recovered as a light orange powder. Yield: 0.36 g (95%). IR (KBr)/cm⁻¹ v: 3402 (H-N); ¹H NMR (CD₂Cl₂): 7.46 (4 H, m), 7.03 (4 H, s), 6.74 (4 H, m), 5.58 (2 H, s).

N,N'-bis(para-iodophenyl)tetrafluorobenzoquinone diamine (3b) **3b** was formed *in situ* in the reaction forming **2b** and was separated by alumina column chromatography using CHCl₃ as the eluent leading to the white product **3b** (0.77 g, 12%); IR (KBr)/cm⁻¹ v : 3416 (N-H). ¹H NMR (CDCl₃) 7.55 (d, *J*=8.8 Hz, 4H, C-H aro), 6.61 (d, *J*=8.6 Hz, 4H, C-H aro), 5.46 (s, 2H, N-H); m/z (EI): 584 (M⁺).

N,N'-bis(para-iodophenyl)tetrachlorobenzoquinone diamine (3c) 0.39 g (0.60 mmol) of **2c** was dissolved in 20 ml CH₂Cl₂. 0.095g sodium borohydride was dissolved in 20 ml anhydrous ethanol and added to the CH₂Cl₂ solution. The solution was stirred for 60 min, the solvent was evaporated, the product dissolved in chloroform and washed with water (3 x 30 ml) and dried over anhydrous MgSO₄. The solution was evaporated and the crude solid was purified using silica chromatography with CH₂Cl₂/Hexane (50:50) as the solvent. Product **3c** was recovered as a light grey powder. Yield: 0.36 g (94 %). IR (KBr)/cm⁻¹ v: 1620 (H-N). ¹H NMR δ(400 MHz CDCl₃): 5.85 (2 H, s, N-H), 6.59 (4 H, m, CH aro.), 7.36 (4 H, m, CH aro); m/z (EI): 650 (M⁺).

N,N'-bis(*para*-bromophenyl)benzoquinone diamine (3'a). Two methods were used. **a)** 1.0 g (2.4 mmol) of **2'a** was dissolved in 100 ml CH₂Cl₂. 10 ml of water was added to the solution. 1.5 ml (30%) NH₃ was added dropwise and the solution was allowed to stir for 30 min. The product was extracted with CH₂Cl₂ and washed with water (3 x 75 ml) and dried over anhydrous MgSO₄. The solution was evaporated and the solid was purified using silica chromatography with CH₂Cl₂/Hexane (30:70) as the solvent. Product **3'a** was recovered as a light orange powder. Yield: 0.82 g (82%). **b)** 0.235 g (0.57 mmol) of **2'a** was dissolved in 20 ml CH₂Cl₂. 0.095g sodium borohydride was dissolved in 20 ml anhydrous ethanol and added to the CH₂Cl₂ solution. The solution was stirred for 60 min, the solvent was evaporated, the product was dissolved in CHCl₃ and washed with water (3 x 30 ml) and dried over anhydrous MgSO₄. The solution was evaporated and the solid was purified using silica chromatography with CH₂Cl₂/Hexane (30:70) as the solvent. Product **3'a** was recovered as a light orange powder. Yield: 0.22 g (94%) IR (KBr)/cm⁻¹ v: 3402 (H-N), 1587 (C=N); ¹H NMR (CD₂Cl₂): 7.30 (4 H, m), 7.05 (4 H, m), 6.86 (4 H, m), 5.71 (2 H, s); λ_{max}(2-MeTHF)/nm 243 (ε/dm³.mol⁻¹.cm⁻¹ 13000), 313 (27000); m/z (EI): 418 (M⁺).

N,N'-bis(*para*-bromophenyl)tetrachlorobenzoquinone diamine (3'c) 0.33 g (0.60 mmol) of **2'c** was dissolved in 20 ml CH₂Cl₂. 0.095g sodium borohydride was dissolved in 20 ml anhydrous ethanol and added to the CH₂Cl₂ solution. The solution was stirred for 60 min, the solvent was evaporated, the product dissolved in CHCl₃ and washed with water (3 x 30 ml) and dried over anhydrous MgSO₄. The solution was evaporated and the solid was purified using silica chromatography with CH₂Cl₂/Hexane (50:50) as eluent. Product **3'c** was recovered as a light grey powder. Yield: 0.32 g (96 %). ¹H NMR δ(400 MHz CDCl₃): 5.85 (2 H, s, N-H), 6.59 (4 H, m, CH aro.), 7.36 (4 H, m, CH aro); m/z (EI): 556 (M⁺).

N,N'-bis(*para*-trimethylsilylethynylphenyl)benzoquinone diamine (4a) 0.42 (1.0 mmol) of N,N'-bis(*para*-bromophenyl)benzoquinone diimine, **2a**, was dissolved in 40 ml toluene, 0.052 g (0.2 mmol) PPh₃, 0.070 g (0.1 mmol) PdCl₂(PPh₃)₂ and 0.19 g (0.1 mmol) CuI were added and stirred under Ar for 30 min. 15 ml of diisopropylamine was added. Using a syringe, ethynyltrimethylsilane (0.55 ml, 4 mmol) was added dropwise.

The solution was heated at 60°C for 12 hours. The solvent was evaporated and the product was dissolved in CH₂Cl₂, washed with water (3 x 30 ml) and dried over anhydrous MgSO₄. The crude solid was purified using silica chromatography with CH₂Cl₂/Hexane (30:70) as eluent. The product was isolated as a light orange powder. Yield: 0.37 g (82%). IR (KBr)/cm⁻¹ ν : 3410 (H-N), 2139 (C $\equiv$ C); ¹H NMR (CDCl₃): 7.34 (4 H, d, *J*=8.6 Hz CH aro), 7.07 (4 H, s, CH aro), 6.86 (4 H, d, *J*=8.6 Hz CH aro), 5.70 (2 H, s, N-H), 0.24 (18 H, s, Si(CH₃)₃); *m/z* (EI): 452 (M⁺).

N,N'-bis(*para*-ethynyltrimethylsilylphenyl)tetrafluorobenzoquinone diamine (4b)

Compound **2b** (0.50 g, 0.86 mmol), PdCl₂(PPh₃)₂ (5% eq., 0.0215 mmol), PPh₃ (10% eq., 0.043 mmol) CuI (10% eq., 0.043 mmol) were dissolved in 60 mL of toluene and 30 mL of diisopropylamine while bubbling with Ar and heating at 60°C. Trimethylsilylacetylene (0.356 mL, 2.60 mmol) was added using a syringe. The resulting mixture was stirred at 60°C overnight. The solution was evaporated to dryness. The solid was dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was evaporated. The crude product was purified on an alumina column with CHCl₃/Hexanes (1/1) as eluent to give a white product, compound **4b**. Yield: (0.351 g, 78%). Found: C, 64.09; H, 5.24; N, 5.31 C₂₈H₂₈F₄N₂Si₂ requires C, 64.09; H, 5.38; N, 5.34; IR (KBr)/cm⁻¹ ν : 3414 (N-H), 2151 (C $\equiv$ C). ¹H NMR δ (400 MHz CDCl₃): 7.38 (4 H, d, *J*= 8.6Hz, CH aro), 6.73 (4 H, d, *J*= 8.6Hz, CH aro.), 5.55 (2 H, s, N-H), 0.24 (18 H, s, Si(CH₃)₃), ppm; ¹³C{¹H} NMR δ (75 MHz CDCl₃): δ 143.4, 142.6, 140.3, 133.1, 115.7, 115.5, 105.1, 92.8, 0.0; λ_{max} (2-MeTHF)/nm 323 nm (ϵ /dm³.mol⁻¹.cm⁻¹ 61889); *m/z* (EI): 524 (M⁺).

N,N'-bis(*para*-trimethylsilylethynylphenyl)tetrachlorobenzoquinone diamine (4c)

0.56 g (1.0 mmol) of **2c'**, was dissolved in 40 ml toluene. 15 ml of 0.052 g (0.20 mmol) of PPh₃, 0.070 g (0.1 mmol) of PdCl₂(PPh₃)₂ and 0.19 g (0.1 mmol) CuI was added and stirred under Ar for 30 min. 15 ml of diisopropylamine was added. Using a syringe, ethynyltrimethylsilane (0.55 ml, 4 mmol) was added dropwise. The solution was heated at 60°C for 12 hours. The solvent was evaporated and the product was dissolved in CH₂Cl₂, washed with water (3 x 30 ml) and dried over anhydrous MgSO₄. The crude solid was purified using silica chromatography with CH₂Cl₂/Hexane (30:70) as eluent.

The product was isolated as a white powder. Yield: 0.42 g (72%). IR (KBr)/cm⁻¹ ν : 2153 (C $\equiv$ C), 3390 (H-N); ¹H NMR (CDCl₃): 7.37 (4 H, d, *J* = 8.7 CH aro.); 6.61 (4 H, d, *J* = 8.7 CH aro.); 5.93 (2 H, s, N-H), 0.23 (18H, s, Si(CH₃)₃); m/z (EI): 590 (M⁺).

N,N'-bis(*para*-trimethylsilylethynylphenyl)benzoquinone diimine (5a). Two methods were used. **a)** Thirty milliliters of chlorobenzene was placed in a three-necked round bottomed flask. A 0.757 g quantity (4.0 mmol) of 4-[(trimethylsilyl)ethynyl]aniline, 1.35 g (12.0 mmol) of DABCO, and 0.44 ml (4.0 mmol) of TiCl₄ were added to the flask using a syringe. A 0.216 g quantity (2.0 mmol) of 1,4-benzoquinone was dissolved in a minimum amount of chlorobenzene and added dropwise to the solution and was stirred at 60°C for 4 h. The mixture was filtered while hot, and washed with hot chlorobenzene (2 x 20 ml). The solution was evaporated. The solid was dissolved in CH₂Cl₂, 0.90 g (4.0 mmol) 2,3-dichloro-5,6-dicyanobenzoquinone was added and stirred for 10 min. The resulting solution was washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The crude product was purified on a silica column with CH₂Cl₂/hexane (70:30) as eluent to give the compound **5a**. Yield: 0.26g (28.9%). **b)** 0.20 g (0.4 mmol) **4a** was dissolved in 30 ml CH₂Cl₂. 0.90 g (4.0 mmol) 2,3-dichloro-5,6-dicyanobenzoquinone was added and stirred for 10 min. The resulting solution was washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The product was purified on a silica column with CH₂Cl₂/hexane (70:30) as the solvent to give compound **5a**. Yield: 0.19 g (96 %). IR (KBr)/cm⁻¹ ν : 2155 (C $\equiv$ C), 1581 (N=C); ¹H NMR (CDCl₃): 7.49 (4 H, m), 7.10 (1 H, m), 6.97 (1 H, m), 6.84 (5 H, m), 6.70 (1 H, m), 0.28 (18 H, m); m/z (EI): 450 (M⁺).

N,N'-bis(*para*-trimethylsilylethynylphenyl)tetrachloro-1,4-benzoquinone diimine (5c). Two methods were used. **a)** Thirty milliliters of chlorobenzene was placed in a three-necked round bottomed flask. A 0.757 g quantity (4.0 mmol) of 4-[(trimethylsilyl)ethynyl]aniline, 1.35 g (12.0 mmol) of DABCO, and 0.44 ml (4.0 mmol) of TiCl₄ were added to the flask using a syringe. A 0.492 g quantity (2.0 mmol) of tetrachloro-1,4-benzoquinone was dissolved in a minimum amount of chlorobenzene and added dropwise to the solution. The solution was stirred at 60°C for 4 hours. The mixture was filtered while hot, and washed with hot chlorobenzene (2 x 20 ml). The solution was evaporated.

The solid was dissolved in CH₂Cl₂, 0.90 g (4.0 mmol) 2,3-dichloro-5,6-dicyano-benzoquinone was added and stirred for 10 min. The resulting solution was washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The product was purified on a silica column with CH₂Cl₂/hexane (50:50) as eluent to give compound **5c**. Yield: 0.80g (68.0%). **b**) 0.20 g (0.34 mmol) **4c** was dissolved in 30 ml CH₂Cl₂. 0.90 g (4.0 mmol), DDQ was added and stirred for 10 min. The resulting solution was washed three times with water, dried with MgSO₄, and filtered. The CH₂Cl₂ was evaporated. The product was purified on a silica column with CH₂Cl₂/hexane (50:50) as eluent to give compound **5c**. Yield: 0.19 g (94 %). IR (KBr)/cm⁻¹ ν : 2157(C $\equiv$ C); ¹H NMR (CDCl₃): 7.49 (4 H, d, *J*=8.5 Hz), 6.74 (4 H, d, *J*=8.5 Hz), 0.26 (18 H, s); *m/z* (EI): 588 (M⁺).

N,N'-bis(para-ethynylphenyl)phenylene diamine (6a). 0.222 g (0.50 mmol) of **4a** was placed in a 250 mL round-bottomed flask, and 1.4 g (10 mmol) of K₂CO₃ was added to the flask and 100 mL of CH₃OH. The reaction was stirred under Ar for 6 hours. The excess K₂CO₃ was filtered, and the remaining solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The CH₂Cl₂ solution was dried with K₂CO₃ and filtered through a sintered glass funnel. The product was purified on a silica column with CH₂Cl₂/Hexanes (50:50) as eluent to give **6a** recovered as a white powder. Yield: 0.14g (90%) IR (KBr)/cm⁻¹ ν : 3390 (H-N), 3280 (CC-H); 2093 (C $\equiv$ C); ¹H NMR (CDCl₃): 7.34 (4 H, d, *J*=8.7 Hz, CH-aro), 7.11 (4 H, s, CH-bz), 6.90 (4 H, d, *J*=8.6 Hz, CH-aro), 5.89 (2H, s, NH) 3.04 (2 H, s); *m/z* (EI): 308 (M⁺).

N,N'-bis(para-ethynylphenyl)tetrafluorobenzoquinone diamine (6b). Compound **4b** (0.20 g, 0.38 mmol) was dissolved in 60 mL of THF and 20 mL of NaOH 0.1M in water (2 mmol) and stirred overnight at room temperature. The THF was evaporated, the white solid was dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was evaporated to give compound **6b** as a white solid. Yield: (0.139 g, 96%). IR (KBr)/cm⁻¹ ν : 3402 (N-H), 3276 (C $\equiv$ C-H), 2099 (C $\equiv$ C). ¹H NMR δ (300 MHz CDCl₃): 7.42 (4 H, d, *J*= 8.6Hz, CH aro), 6.76 (4 H, d, *J*= 8.4Hz, CH aro.), 5.57 (2 H, s, N-H), 3.02 (2 H, s, C $\equiv$ C-H); *m/z* (EI): 380 (M⁺).

N,N'-bis(*para*-ethynylphenyl)tetrachlorophenylene diamine (6c). 0.3 g (0.5 mmol) of compound **4c** was placed in a 250 mL round-bottomed flask, and 1.4 g (10 mmol) of K₂CO₃ was added with 100 mL of CH₃OH. The reaction was stirred under Ar for 6 hours. The excess K₂CO₃ was filtered, and the solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The CH₂Cl₂ solution was dried with K₂CO₃ and filtered through a sintered glass funnel. The product was purified on a silica column with CH₂Cl₂/hexanes (50:50) as eluent to give **6c** as a white powder. Yield: 0.2 g (88%) IR (KBr)/cm⁻¹ ν : 3410 (H-N), 2139 (C $\equiv$ C); ¹H NMR (400 MHz CDCl₃): 7.39 (4 H, m, CH-aro), 6.63 (4 H, m, CH-aro), 5.89 (2H, m, NH) 3.02 (2 H, s); m/z (EI): 446 (M⁺).

N,N'-bis(*para*-ethynylphenyl)benzoquinone diimine (7a). 0.222 g (0.5 mmol) of *N,N'*-bis(*para*-(trimethylsilyl)ethynylbenzene)-1,4-benzoquinone diimine (**5a**) was placed in a 50 mL CH₂Cl₂ in a 100 mL round-bottomed flask. 0.4 g (1.5 mmol) of TBAF, tetrabutylammonium fluoride, was added to the flask and the reaction was stirred under Ar for 4 hours. The solution was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The CH₂Cl₂ solution was dried with MgSO₄ and filtered through a sintered glass funnel. The product was purified on a silica column with CHCl₃ as eluent to give **7a** recovered as an orange powder. Yield: 0.14 g (92%); IR (KBr)/cm⁻¹ ν : 3290 (CC-H), 2100 (C $\equiv$ C); ¹H NMR (CDCl₃): 7.51 (4 H, dd, *J*=12.1, 8.5 Hz), 7.13-6.67 (8 H, m), 3.10 (2 H, s); m/z (EI): 306 (M⁺).

N,N'-bis(*para*-ethynylphenyl)tetrafluorobenzoquinone diimine (7b) 0.090 g (0.23 mmol) of **6b** was dissolved in 20 mL of CHCl₃, DDQ (0.208 g, 4 eqs., 0.92 mmol) was added and stirred 20 min at room temperature. The mixture was separated by a pad of alumina with CHCl₃ as eluent. Yield: Not calculated. IR (KBr)/cm⁻¹ ν : 1633 (C=N), absent (C $\equiv$ C), 3280 (C $\equiv$ C-H). ¹H NMR δ (400 MHz CDCl₃): 7.50 (4 H, t, *J*= 6.6 Hz CH aro), 6.87 (4 H, t, *J*= 6.6 Hz CH aro.), 3.12 (2 H, d, C $\equiv$ C-H); m/z (EI): 378 (M⁺).

N,N'-bis(*para*-ethynylphenyl)tetrachloroquinone diimine (7c). 0.3 g (0.5 mmol) of **5c** was placed in a 50 mL CH₂Cl₂ in a 100 mL round-bottomed flask. 0.4 g (1.5 mmol) of TBAF was added to the flask and the reaction was stirred under Ar for 4 hours. The

solution was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The CH₂Cl₂ solution was dried with MgSO₄ and filtered through a sintered glass funnel. The product was purified on a silica column with CHCl₃ as eluent to give **7c** recovered as a dark purple blue solid. Yield: 0.19 g (85%); IR (KBr)/cm⁻¹ v: 3290 (CC-H), 2104 (C≡C); ¹H NMR (CDCl₃): 7.49 (4 H, m), 6.81 (4 H, m), 3.09 (2 H, m); m/z (EI): 444 (M⁺).

Polymer poly(bis(para-ethynylphenyl)tetrafluorobenzoquinonediaimine)-trans-bis-(tri-n-butylphosphine)platinum(II) (8b) 6b (0.057 g, 0.150 mmol), *trans*-Pt(PBu₃)₂Cl₂ (1 eq, 0.150 mmol, 0.100 g), CuI (10% eq, 0.015 mmol), 120 ml of CH₂Cl₂ and 40 mL of (iPr)₂NH were added under Ar. The mixture was stirred overnight at room temperature under Ar. The crude solid was evaporated to dryness, dissolved by CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was completely evaporated. White polymer **8b** was obtained. The compound changed to blue due to facile oxidation in air. Yield: 0.132 g (88%). Found: C, 56.09; H, 6.57; N, 2.85. HCl[C₄₆H₆₄F₄N₂P₂Pt]_n requires C, 55.97; H, 6.56; N, 2.84; IR (KBr)/cm⁻¹ v: 3420 (N-H), 2101 (C≡C). ³¹P{¹H} NMR (CDCl₃): δ = 3.96 (s, ¹J_{Pt-P} = 2365). ¹H NMR (400 MHz, CDCl₃) δ = 7.19 (d, *J*=8.2, 4H), 6.71 (d, *J*=8.2, 4H), 5.41 (s, 2H), 2.27–2.00 (m, 12H), 1.73–1.52 (m, 12H), 1.52–1.35 (m, 12H), 0.92 (t, *J*=7.3, 18H) ppm; λ_{max}(2-MeTHF)/nm 260 nm (ε/dm³.mol⁻¹.cm⁻¹ 48966), 290 (27970), 350(70245)); GPC: *M*_n(14572), *M*_w(38042), PD 2.61.

Polymer poly(bis(para-ethynylphenyl)tetrachlorobenzoquinonediaimine)-trans-bis-(tributylphosphine)platinum(II) (8c) A 0.116 g quantity (0.26 mmol) of **6c**, and 0.015 g of CuI were dissolved in 10 mL of CH₂Cl₂ in a 25 mL round bottomed flask. Ten milliliters of iPr₂NH were added. 0.17 g (0.26 mmol) of *trans*-Pt(PBu₃)₂Cl₂ was dissolved in a minimum amount of CH₂Cl₂ in 10 mL round bottomed flask. The Pt solution was added dropwise using a syringe to the 25 mL round-bottomed flask containing the mixture and the reaction was stirred under Ar overnight. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was evaporated. The polymer was isolated as a blue film material. The polymer was reprecipitated in CH₂Cl₂ and hexane. (0.25 g, 92 %); IR (KBr)/cm⁻¹ v: 3390 (N-H), 2102 (C≡C). ³¹P{¹H} NMR (162

MHz CDCl₃): 4.51 (2 P, s, $^1J_{\text{Pt-P}} = 2261.9$ Hz), 1.19 (2 P, s, $^1J_{\text{Pt-P}} = 2309.3$ Hz). ^1H NMR (400 MHz CDCl₃): 7.17 (4H, s, br, CH aro), 6.59 (4H, d, $J=7.7$ Hz, CH aro); 5.84 (2H, s, N-H), 2.12 (12 H, t, nBu), 1.44 (24H, m, nBu), 0.92 (18 H, t, $J=7.2$ Hz, nBu).

***Trans*-bis[chlorobis(*n*-butylphosphine)platinum(II)]*N,N'*-bis(*para*-ethynylphenyl)-tetrafluorobenzenediamine (9b)** *Trans*-dichlorobis(tri-*n*-butylphosphine)platinum(II), *trans*-Pt(PBu₃)₂Cl₂ (8 eq, 0.740 mmol, 0.494g), CuI (10% 0.01 mmol), 40 ml of CH₂Cl₂ and 40 mL of (iPr)₂NH were added under argon flux. **6b** (0.035 g, 0.09 mmol) was dissolved in CH₂Cl₂ and placed in an addition funnel. The solution of diethynyl was added dropwise at room temperature for 6 hours. The mixture was stirred overnight at room temperature under Ar. The crude product was evaporated to dryness, dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was evaporated and the product was purified on an alumina column with CH₂Cl₂/Hexanes (1/1) as the eluent to remove oligomers and excess of platinum. White product **9b** was isolated but changed to blue color due to oxidation in air, and was stored under N₂ at all time. Yield: 0.053 g (36%). Found: C, 58.19; H, 7.22; N, 1.65. C₇₀H₁₁₈Cl₂F₄N₂P₄Pt₂ requires C, 58.03; H, 7.25; N, 1.57; IR (KBr)/cm⁻¹ v: 3311 (N-H), 2120 (C≡C). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 7.87$ (s, $^1J_{\text{Pt-P}} = 2378$). ^1H NMR δ (400 MHz CDCl₃): 7.15(4 H, d, $J=8.4$, CH aro), 6.70 (4 H, d, $J=8.4$, CH aro.), 5.40 (2 H, s, N-H), 2.01(24 H, m, CH₂) 1.50-1.38 (48 H, m, CH₂) 0.92 (36 H, t, $J=7.2$, CH₃); λ_{max} (2-MeTHF)/nm 244 nm ($\epsilon/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ 52951), 340 (101424)).

***Trans*-bis[chlorobis(*n*-butylphosphine)platinum(II)]*N,N'*-bis(*para*-ethynylphenyl)-tetrachlorobenzenediamine (9c).** 1.40 g (2.0 mmol) of *trans*-Pt(PBu₃)₂Cl₂ and 0.015 g of CuI were dissolved in 20 mL of CH₂Cl₂ in a 250 mL round bottomed flask. 20 ml of iPr₂NH were added. 0.089 g (0.2 mmol) of **6c** was dissolved in a 100 ml amount of 1:1 solution of CH₂Cl₂/iPr₂NH in an addition funnel. The **6c** solution was added dropwise for 12 hours using an addition funnel to the 250 mL round-bottomed flask containing the reacting mixture. The reaction was stirred overnight under Ar. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was evaporated. The product was purified on a silica gel column using (50/50) CH₂Cl₂/Hexane. Compound **9c**

was isolated as a blue material. Yield: (0.18 g, 53 %); Found: C, 48.49; H, 6.65; N, 1.81. $C_{70}H_{118}Cl_6N_2P_4Pt_2$ requires C, 49.10; H, 6.83; N, 1.64. IR (KBr)/ cm^{-1} v: 1620 (C=N), 2098 (C≡C). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 7.8 (2 P, s, $^1J_{Pt-P} = 2378.3$ Hz) ppm. 1H NMR ($CDCl_3$): 7.18-7.08 (m, 4H, Ph), 6.63-6.50 (m, 4H, Ph), 5.58-5.80 (m, 2H, NH), 2.00 (td, $J=7.8, 3.7$ Hz, 24H, nBu), 1.60-1.39 (m, 48H, nBu), 0.98-0.86 (m, 36H, nBu).

Polymer poly(bis(*para*-ethynylphenyl)benzoquinonediimine)-*trans*-bis(tri-*n*-butylphosphine)platinum(II) (10a) 0.077 g (0.3 mmol) of **7a** and 0.017 g of CuI were dissolved in 10 mL of CH_2Cl_2 in a 25 mL round bottomed flask. Ten milliliters of iPr_2NH were added. 0.17 g (0.3 mmol) of *trans*-Pt(PBu_3) $_2Cl_2$ was dissolved in a minimum amount of CH_2Cl_2 in 10 mL round bottomed flask. The Pt solution was added dropwise using a syringe to the 25 mL round-bottomed flask containing the mixture and the reaction was stirred overnight under Ar. The solvent was evaporated. The residue was dissolved in CH_2Cl_2 and washed three times with water. The solution of CH_2Cl_2 was dried with K_2CO_3 and filtered. The solvent was then evaporated. The polymer was isolated as a purple bright film. The polymer was reprecipitated in CH_2Cl_2 and hexane. (0.22 g, 81 %); Found: C, 60.95; H, 7.48; N, 3.19. $C_{46}H_{66}N_2P_2Pt$ requires C, 61.11; H, 7.36; N, 3.10. IR (KBr)/ cm^{-1} v : 1591 (C=N), 2114 (C≡C). $^{31}P\{^1H\}$ NMR (162 MHz $CDCl_3$): 4.15 (2 P, s, $^1J_{Pt-P} = 2360.1$ Hz), 0.65 (2 P, s, $^1J_{Pt-P} = 2513.7$ Hz). 1H NMR (400 MHz, $CDCl_3$): 7.40-7.20 (m, 4H, Ph), 7.16-6.69 (m, 8H, Ph + C_6H_4), 2.17 (m, 12H, CH_2), 1.63-1.42 (m, 24 H, CH_2), 0.93 (m, 18 H, $P(CH_2)_3CH_3$).

Polymer poly(((*para*-ethynylphenyl)tetrafluorobenzoquinone diimine)-*trans*-bis(tri-*n*-butylphosphine)platinum(II)) (10b). *Trans*-dichlorobis(tri-*n*-butylphosphine)-platinum(II) *trans*-Pt(PBu_3) $_2Cl_2$ (1 eq, 0.180 mmol, 0.120 g), CuI (10% eq, 0.02 mmol), **7b** (0.068 g, 0.180 mmol) in solution in CH_2Cl_2 , 90 ml of CH_2Cl_2 and 40 mL of $(iPr)_2NH$ were added under Ar. The mixture was stirred overnight at room temperature under Ar. The crude solid was evaporated to dryness, dissolved by $CHCl_3$, washed three times with water, dried with $MgSO_4$, and filtered. The solvent was evaporated and **10b** was isolated as a blue solid. Yield: 0.12 g (67%). Found: C, 54.39; H, 6.29; N, 2.76. $HCl[C_{46}H_{62}F_4N_2P_2Pt]_n$ requires C, 54.57; H, 6.27; N, 2.77; IR (KBr)/ cm^{-1} v: 1604 (C=N), 2095 (C≡C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 4.15$ (m, $^1J_{Pt-P} = 2360$), 7.95 (m, $^1J_{Pt-P} = 2370$).

^1H NMR (400 MHz, CDCl_3) δ = 7.23 (m, 4H), 6.87 (m, 4H), 2.17-2.06 (m, 12H), 1.59 (m, 12H), 1.50-1.36 (m, 12H), 0.92 (t, $J=7.3$, 18H). $\lambda_{\text{max}}(2\text{-MeTHF})/\text{nm}$ 247 nm ($\epsilon/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ 20296), 265 (22199), 350 (22241), 630 (5638.9)); GPC $M_n(14317)$, $M_w(23393)$, PD 1.63.

Polymer poly(((*para*-ethynylphenyl)tetrachlorobenzoquinone diimine)-*trans*-bis(tributylphosphine)platinum(II)) (10c) 0.133 g (0.3 mmol) of **7c** and 0.017 g of CuI were dissolved in 10 mL of CH_2Cl_2 in a 25 mL round bottomed flask. Ten milliliters of $i\text{Pr}_2\text{NH}$ were added. 0.17 g (0.30 mmol) of *trans*-Pt(PBu₃)₂Cl₂ was dissolved in a minimum amount of CH_2Cl_2 in 10 mL round bottomed flask. The Pt solution was added dropwise using a syringe to the 25 mL round-bottomed flask containing the mixture. The reaction was stirred overnight under Ar. The solvent was evaporated. The residue was dissolved in CH_2Cl_2 and washed three times with water. The solution of CH_2Cl_2 was dried with K_2CO_3 and filtered. The solvent was evaporated. The polymer was isolated as a bright blue film. The polymer was reprecipitated in CH_2Cl_2 and hexane. (0.29 g, 92 %); IR (KBr)/ cm^{-1} v: 1604 (C=N), 2099 (C $\equiv$ C). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 5.32 (2 P, s, $^1J_{\text{Pt-P}} = 2215.1$ Hz) 1.91 (2 P, s, $^1J_{\text{Pt-P}} = 2312.5$ Hz). ^1H NMR (400 MHz CDCl_3) δ 7.25 (s, br., 4H Ph), 6.7 (m, 4H Ph), 2.12 (s, 12H, CH₂); 1.52 (m, 24H CH₂), 0.91 (s, 18 H, P(CH₂)₃CH₃).

Bis-(*Para*-ethynylphenyl)(benzoquinone diimine)bis[*trans*-chlorobis(tributylphosphine)platinum(II)] (11a) 1.34 g (2.00 mmol) of *trans*-Pt(PBu₃)₂Cl₂ and 0.013 g of CuI were dissolved in 10 mL of CH_2Cl_2 in a 25 mL round bottomed flask. Ten milliliters of $i\text{Pr}_2\text{NH}$ were added. 0.057 g (0.2 mmol) of **7a** was dissolved in a 100 mL amount of 1:1 solution of $\text{CH}_2\text{Cl}_2/i\text{Pr}_2\text{NH}$ in an addition funnel. The **7a** solution was added dropwise for 12 hours using an addition funnel to the 250 mL L round-bottomed flask containing the mixture. The reaction was stirred overnight under Ar. The solvent was evaporated. The residue was dissolved in CH_2Cl_2 and washed three times with water. The CH_2Cl_2 solution was dried with K_2CO_3 and filtered. The solvent was evaporated. The product was purified on a silica gel column using CHCl_3 and was isolated as a bright purple glassy material. Yield: 0.15 g (47 %); Found: C, 52.96; H, 7.73; N, 1.86. $\text{C}_{70}\text{H}_{120}\text{Cl}_2\text{N}_2\text{P}_4\text{Pt}_2$: requires C, 53.39; H, 7.68, N, 1.78. IR (KBr)/ cm^{-1} v: 1590 (C=N), 2113 (C $\equiv$ C). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz CDCl_3): 8.0 (2 P, s, $^1J_{\text{Pt-P}} = 2366.9$ Hz) ppm. ^1H NMR (400 MHz CDCl_3)

δ 7.35-7.12 (m, 4 H, Ph), 7.11-6.70 (m, 8H, Ph + C₆H₄), 2.38-1.71 (m, 24H, CH₂), 1.66-1.34 (m, 48H, CH₂), 1.34-0.54 (m, 36H, P(CH₂)₃CH₃); m/z (maldi tof): 1574.8 requires 1574.7.

Bis-(Para-ethynylphenyl)(tetrafluorobenzoquinone diimine)bis[trans-chlorobis(tributylphosphine)platinum(II)] (11b) *trans*-Pt(PBu₃)₂Cl₂, (8 eqs, 0.740 mmol, 0.494g), CuI (10% eq, 0.01 mmol), 40 ml of CH₂Cl₂ and 40 mL of (iPr)₂NH were added under Ar. A solution of **7b** (0.034 g 0.09 mmol) in CH₂Cl₂ was placed in an addition funnel. The solution of diethynyl was added dropwise at room temperature for 6 h. The mixture was stirred overnight at room temperature under Ar. The crude was evaporated to dryness, dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was evaporated and the product was purified on an alumina column with CH₂Cl₂/Hexanes (1/1) as the eluent to remove oligomers the excess of *trans*-Pt(PBu₃)₂Cl₂. A blue product, **11b**, was obtained. Yield: 0.035 g (24%). IR (KBr)/cm⁻¹ ν : 1597 (C=N), 2111 (C $\equiv$ C). ³¹P{¹H} NMR (CDCl₃): δ = 8.07 (s, ¹J_{Pt-P} = 2361). ¹H NMR δ (400 MHz CDCl₃): 7.22(4 H, dd, J=8.1, 4.1Hz, CH aro), 6.86 (4 H, d, 8.1Hz, CH aro.), 2.01(24 H, m, CH₂) 1.50-1.38 (48 H, m, CH₂) 0.92 (36 H, t, J=7.0 Hz, CH₃); m/z (maldi tof): 1647.5 requires 1646.6.

Bis-(Para-ethynylphenyl)(tetrachlorobenzoquinone diimine)bis[trans-chlorobis(tributylphosphine)platinum(II)] (11c) 1.34 g (2.0 mmol) of *trans*-Pt(PBu₃)₂Cl₂ and 0.013 g of CuI were dissolved in 10 mL of CH₂Cl₂ in a 25 mL round bottomed flask. Ten milliliters of iPr₂NH were added. 0.088 g (0.20 mmol) of **7c** was dissolved in 100 mL of a 1:1 solution of CH₂Cl₂/iPr₂NH in an addition funnel. The **7c** solution was added dropwise for 12 hours using an addition funnel to the 250 mL round-bottomed flask containing the mixture. The reaction was stirred overnight under Ar. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed three times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was evaporated. The product was purified on a silica gel column using (50/50) CH₂Cl₂/Hexane. Compound **11c** was isolated as a bright blue glassy material. Yield: (0.19 g, 55 %); IR (KBr)/cm⁻¹ ν : 1597 (C=N), 2112 (C $\equiv$ C). ³¹P{¹H} NMR (CDCl₃): 7.84 (2 P, s, ¹J_{Pt-P} = 2379.0 Hz) ppm. ¹H NMR (300 MHz CDCl₃) δ 7.32 (d, J=8.3Hz, 4H, Ph), 6.79 (d, J=8.4Hz, 4H, Ph),

2,12-1.90 (m, 24H, CH₂), 1.55 (m, 24H, CH₂), 1.44 (m, 24H, CH₂), 0.93 (t, 36 H, P(CH₂)₃CH₃, ³J_{H-H} = 7.2 Hz).

Instruments. All NMR spectra were acquired on a Bruker AC-300 spectrometer (¹H 300.15 MHz, ¹³C 75.48 MHz, ³¹P 121.50 MHz) or a Varian AS-400 (¹H 400.15 MHz, ³¹P 162.0 MHz) using the solvent as chemical shift standard, except in ³¹P NMR, where the chemical shifts are relative to D₃PO₄ 85% in D₂O. All chemical shifts (δ) and coupling constants (J) are given in ppm and Hertz, respectively. MALDI-TOF mass spectrometry was carried out with a Waters MALDI SYNAPT HDMS using dithranol as a matrix. The IR spectra were acquired on a Bomem FT-IR MB series spectrometer equipped with a baseline-diffused reflectance. Molecular weights and molecular weight distributions of all polymers were determined by using gel permeation chromatography (GPC). The GPC set-up consisted of a Waters 515 HPLC pump, a Waters 996 Photodiode Array Detector and a Waters 410 Differential Refractometer, with a Styragel HR4E column (7.8*300 mm). The GPC eluent was HPLC grade THF, at a flow rate of 0.5ml.min⁻¹. Calibration curve was obtained using seven PS standards (Aldrich), with *M_n* ranging from 3400 to 382 000 g.mol⁻¹. TGA were acquired on a Perkin-Elmer TGA 7 between 50 and 950 °C at 3°C/ min under a nitrogen atmosphere. The UV-visible spectra were recorded on a Hewlett-Packard diode array model 8452A. The mass spectra were collected on a VG ZAB-1F spectrometer in EI mode at 70eV.

Computations. Calculations were performed with Gaussian 09^{S2} at the Université de Sherbrooke with Mammouth super computer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT^{S3-S6} and TD-DFT^{S7-S9} were calculated with the B3LYP^{S10-S12} method. 3-21G*^{S13-S18} basis sets were used for C, H, N, F and Cl, polarized basis sets for P^{S19-S21}, and VDZ (valence double ζ) with SBKJC effective core potentials^{S22-S24} for platinum. The predicted phosphorescence wavelengths were obtained by energy differences between the triplet and singlet optimized states.^{S25} The calculated absorption spectra and related MO contributions were obtained from the TD-DFT/singlets output file and gausssum2.1.^{S26} A THF polarizable continuum solvation model was used.^{S27}

Electrochemistry. Electrochemical measurements were carried out at room temperature under a flow of argon gas. DMF (Fischer) was distilled under vacuum but otherwise used as received. Trifluoroacetic acid (Aldrich, 99%), TFA, was used as received. Solutions were made 0.1 M in NBu_4PF_6 , which had been purchased from Aldrich, recrystallized from ethanol, and vacuum-dried. Electrochemical experiments were carried out using a standard three-electrode cell configuration, where the counter electrode was a Pt mesh and the reference electrode saturated calomel. A PARC 273A potentiostat was interfaced to a personal computer. Cyclic voltammetry (CV) scans were carried out at a Pt disk of 5 mm diameter (Pine Chem) which had been polished with Buehler alumina paste of 0.5 micron and place in an ultrasonic bath for few minutes before each series of experiments. All the potentials are reported versus the saturated calomel electrode (SCE).

Crystallography. Experimental: For all crystals, data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC^{S28} program was used for centering, indexing, and data collection. Data were corrected for absorption by empirical methods based on psi scans and reduced with the NRCVAX^{S29} programs. They were solved using SHELXS-97^{S30} and refined by full-matrix least squares on F^2 with SHELXL-97^{S31}. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model.

2a: The crystals were grown in by slow vapor diffusion of EtOH on a CHCl₃ solution at room temperature. One single crystal of 0.10 X 0.30 X 0.30 mm³ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, 12% intensity decay was observed during data collection.

Table S1. Crystal data and structure refinement for **2a**.

Empirical formula	c18 h12 i2 n2	
Formula weight	510.10	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	pnaa	
Unit cell dimensions	a = 5.926(3) Å	α = 90°.
	b = 7.516(7) Å	β = 90°.
	c = 37.051(16) Å	γ = 90°.
Volume	1650.3(19) Å ³	
Z	4	
Density (calculated)	2.053 Mg/m ³	
Absorption coefficient	3.809 mm ⁻¹	
F(000)	960	
Crystal size	0.30 x 0.30 x 0.10 mm ³	
Theta range for data collection	2.20 to 25.55°.	
Index ranges	0 ≤ h ≤ 7, 0 ≤ k ≤ 9, 0 ≤ l ≤ 44	
Reflections collected	1393	
Independent reflections	1393 [R(int) = 0.0000]	
Completeness to theta = 25.50°	90.5 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.7019 and 0.3945	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1393 / 0 / 59	
Goodness-of-fit on F ²	0.979	
Final R indices [I > 2σ(I)]	R1 = 0.0834, wR2 = 0.2195	
R indices (all data)	R1 = 0.1826, wR2 = 0.2660	
Extinction coefficient	0.0026(9)	
Largest diff. peak and hole	1.467 and -2.787 e.Å ⁻³	

2'a: The crystals were grown by slow evaporation of a CH₂Cl₂ solution. One single crystal of 0.25 X 0.30 X 0.30 mm³ was mounted using a glass fiber on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S2. Crystal data and structure refinement for **2'a**.

Empirical formula	C ₉ H ₈ Br N O	
Formula weight	226.07	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Orthorhombic	
Space group	Pnab	
Unit cell dimensions	a = 7.174(2) Å	α = 90°.
	b = 10.884(7) Å	β = 90°.
	c = 23.910(8) Å	γ = 90°.
Volume	1867.0(15) Å ³	
Z	8	
Density (calculated)	1.609 Mg/m ³	
Absorption coefficient	5.609 mm ⁻¹	
F(000)	896	
Crystal size	0.30 x 0.30 x 0.25 mm ³	
Theta range for data collection	7.62 to 69.82°.	
Index ranges	0 ≤ h ≤ 8, 0 ≤ k ≤ 13, 0 ≤ l ≤ 29	
Reflections collected	1717	
Independent reflections	1717 [R(int) = 0.0000]	
Completeness to theta = 25.50°	90.5 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.3345 and 0.2839	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1717 / 3 / 106	
Goodness-of-fit on F ²	0.852	
Final R indices [I > 2σ(I)]	R1 = 0.0894, wR2 = 0.2261	
R indices (all data)	R1 = 0.2136, wR2 = 0.2792	
Extinction coefficient	0.0008(4)	
Largest diff. peak and hole	0.493 and -0.488 e.Å ⁻³	

2b: The crystals were grown by slow evaporation of THF at room temperature. One single crystal of 0.03 X 0.30 X 0.35 mm³ was mounted using a glass fiber at 193(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S3. Crystal data and structure refinement for **2b**.

Empirical formula	C18 H8 F4 I2 N2	
Formula weight	582.06	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna21	
Unit cell dimensions	a = 5.887(2) Å	α = 90°.
	b = 7.940(2) Å	β = 90°.
	c = 36.911(11) Å	γ = 90°.
Volume	1725.2(10) Å ³	
Z	4	
Density (calculated)	2.241 Mg/m ³	
Absorption coefficient	3.690 mm ⁻¹	
F(000)	1088	
Crystal size	0.35 x 0.30 x 0.03 mm ³	
Theta range for data collection	2.62 to 25.55°.	
Index ranges	0 ≤ h ≤ 7, 0 ≤ k ≤ 9, 0 ≤ l ≤ 44	
Reflections collected	1589	
Independent reflections	1589 [R(int) = 0.0000]	
Completeness to theta = 25.50°	97.2 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.8973 and 0.3583	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1589 / 4 / 69	
Goodness-of-fit on F ²	0.886	
Final R indices [I > 2σ(I)]	R1 = 0.0549, wR2 = 0.1179	
R indices (all data)	R1 = 0.1687, wR2 = 0.1492	
Absolute structure parameter	0.0(5)	
Extinction coefficient	0.0009(2)	
Largest diff. peak and hole	1.726 and -1.267 e.Å ⁻³	

2c: The crystals were grown in by slow vapor diffusion of EtOH on a CHCl₃ solution at room temperature. One single crystal of 0.025 X 0.20 X 0.20 mm³ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S4. Crystal data and structure refinement for **2c**.

Empirical formula	C18 H8 Cl4 I2 N2	
Formula weight	647.90	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pcan	
Unit cell dimensions	a = 6.232(3) Å	α = 90°.
	b = 15.450(5) Å	β = 90°.
	c = 20.624(5) Å	γ = 90°.
Volume	1985.9(12) Å ³	
Z	4	
Density (calculated)	2.167 Mg/m ³	
Absorption coefficient	3.711 mm ⁻¹	
F(000)	1216	
Crystal size	0.20 x 0.20 x 0.03 mm ³	
Theta range for data collection	2.37 to 25.59°.	
Index ranges	0 ≤ h ≤ 4, 0 ≤ k ≤ 18, 0 ≤ l ≤ 25	
Reflections collected	1373	
Independent reflections	1373 [R(int) = 0.0000]	
Completeness to theta = 25.50°	73.5 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.8968 and 0.5240	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1373 / 0 / 64	
Goodness-of-fit on F ²	0.768	
Final R indices [I > 2σ(I)]	R1 = 0.0821, wR2 = 0.1353	
R indices (all data)	R1 = 0.3495, wR2 = 0.1862	
Largest diff. peak and hole	0.724 and -0.866 e.Å ⁻³	

3b: The crystals were grown by slow evaporation of a CH₂Cl₂/MeOH (75/25) solution at room temperature. One single crystal of 0.15 X 0.30 X 0.55 mm³ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S5. Crystal data and structure refinement for **3b**.

Empirical formula	C18 H10 F4 I2 N2	
Formula weight	584.08	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnaa	
Unit cell dimensions	a = 5.793(2) Å	α = 90°.
	b = 8.312(5) Å	β = 90°.
	c = 36.680(13) Å	γ = 90°.
Volume	1766.0(14) Å ³	
Z	4	
Density (calculated)	2.197 Mg/m ³	
Absorption coefficient	3.606 mm ⁻¹	
F(000)	1096	
Crystal size	0.55 x 0.30 x 0.15 mm ³	
Theta range for data collection	1.11 to 25.56°.	
Index ranges	0 ≤ h ≤ 7, 0 ≤ k ≤ 10, 0 ≤ l ≤ 44	
Reflections collected	1654	
Independent reflections	1654 [R(int) = 0.0000]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.6138 and 0.2417	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1654 / 0 / 119	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0503, wR2 = 0.1172	
R indices (all data)	R1 = 0.1149, wR2 = 0.1330	
Extinction coefficient	0.0016(3)	
Largest diff. peak and hole	0.748 and -0.614 e.Å ⁻³	

3'c: The crystals were grown by slow evaporation of a CH₂Cl₂ solution at room temperature. One single crystal of 0.20 X 0.30 X 0.60 mm³ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S6. Crystal data and structure refinement for **3'c**.

Empirical formula	C18 H10 Br2 Cl4 N2	
Formula weight	555.90	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/C	
Unit cell dimensions	a = 4.5815(15) Å	α = 90°.
	b = 9.242(4) Å	β = 95.06(2)°.
	c = 22.912(4) Å	γ = 90°.
Volume	966.3(5) Å ³	
Z	2	
Density (calculated)	1.911 Mg/m ³	
Absorption coefficient	4.753 mm ⁻¹	
F(000)	540	
Crystal size	0.60 x 0.30 x 0.20 mm ³	
Theta range for data collection	1.78 to 25.59°.	
Index ranges	-5 ≤ h ≤ 5, 0 ≤ k ≤ 11, 0 ≤ l ≤ 27	
Reflections collected	1805	
Independent reflections	1805 [R(int) = 0.0000]	
Completeness to theta = 25.50°	99.8 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.4499 and 0.1627	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1805 / 0 / 76	
Goodness-of-fit on F ²	0.857	
Final R indices [I > 2σ(I)]	R1 = 0.0675, wR2 = 0.1444	
R indices (all data)	R1 = 0.2129, wR2 = 0.1798	
Largest diff. peak and hole	0.535 and -0.793 e.Å ⁻³	

3d: The crystals were grown by slow evaporation of a CHCl_3 solution at room temperature. One single crystal of $0.20 \times 0.30 \times 0.40 \text{ mm}^3$ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S7. Crystal data and structure refinement for **3d**.

Empirical formula	C ₂₂ H ₂₂ I ₂ N ₂	
Formula weight	568.22	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	p-1	
Unit cell dimensions	a = 8.632(2) Å	$\alpha = 72.46(4)^\circ$.
	b = 10.136(5) Å	$\beta = 78.12(3)^\circ$.
	c = 13.097(6) Å	$\gamma = 79.22(4)^\circ$.
Volume	1059.5(7) Å ³	
Z	2	
Density (calculated)	1.781 Mg/m ³	
Absorption coefficient	2.976 mm ⁻¹	
F(000)	548	
Crystal size	0.40 x 0.30 x 0.20 mm ³	
Theta range for data collection	1.65 to 25.54°.	
Index ranges	-10 ≤ h ≤ 10, 0 ≤ k ≤ 12, -14 ≤ l ≤ 15	
Reflections collected	3953	
Independent reflections	3953 [R(int) = 0.0000]	
Completeness to theta = 25.50°	99.9 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.5875 and 0.3823	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3953 / 0 / 236	
Goodness-of-fit on F ²	1.014	
Final R indices [I > 2σ(I)]	R1 = 0.0593, wR2 = 0.1439	
R indices (all data)	R1 = 0.1141, wR2 = 0.1639	
Extinction coefficient	0.0026(10)	
Largest diff. peak and hole	1.048 and -1.108 e.Å ⁻³	

4a: The crystals were grown by slow evaporation of a CH₂Cl₂ solution. One single crystal of 0.10 X 0.20 X 0.40 mm³ was mounted using a glass fiber on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S8. Crystal data and structure refinement for **4a**.

Empirical formula	C ₂₈ H ₃₂ N ₂ Si ₂	
Formula weight	452.74	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.1972(11) Å	α = 103.779(17)°.
	b = 8.5180(14) Å	β = 100.711(18)°.
	c = 13.484(3) Å	γ = 94.252(15)°.
Volume	674.0(2) Å ³	
Z	1	
Density (calculated)	1.115 Mg/m ³	
Absorption coefficient	1.309 mm ⁻¹	
F(000)	242	
Crystal size	0.40 x 0.20 x 0.10 mm ³	
Theta range for data collection	3.45 to 69.96°.	
Index ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 10, -16 ≤ l ≤ 15	
Reflections collected	2520	
Independent reflections	2520 [R(int) = 0.0000]	
Completeness to theta = 69.96°	97.9 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.8802 and 0.6225	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2520 / 0 / 146	
Goodness-of-fit on F ²	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0842, wR2 = 0.2297	
R indices (all data)	R1 = 0.1486, wR2 = 0.2632	
Extinction coefficient	0.070(9)	
Largest diff. peak and hole	0.268 and -0.220 e.Å ⁻³	

4b: The crystals were grown by slow evaporation of CH₂Cl₂ at room temperature. One single crystal of 0.10 X 0.40 X 0.50 mm³ was mounted using a glass fiber at 193(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S9. Crystal data and structure refinement for **4b**.

Empirical formula	C ₂₈ H ₂₈ F ₄ N ₂ Si ₂	
Formula weight	524.71	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 5.647(7) Å	α = 90°.
	b = 5.670(8) Å	β = 92.41(12)°.
	c = 41.2(7) Å	γ = 90°.
Volume	1318(23) Å ³	
Z	2	
Density (calculated)	1.323 Mg/m ³	
Absorption coefficient	0.183 mm ⁻¹	
F(000)	548	
Crystal size	0.50 x 0.40 x 0.10 mm ³	
Theta range for data collection	1.98 to 25.55°.	
Index ranges	-6 ≤ h ≤ 6, 0 ≤ k ≤ 6, 0 ≤ l ≤ 49	
Reflections collected	2278	
Independent reflections	2278 [R(int) = 0.0000]	
Completeness to theta = 25.50°	92.8 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.9819 and 0.9141	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2278 / 0 / 163	
Goodness-of-fit on F ²	0.921	
Final R indices [I > 2σ(I)]	R ₁ = 0.0844, wR ₂ = 0.1296	
R indices (all data)	R ₁ = 0.2393, wR ₂ = 0.1640	
Largest diff. peak and hole	0.364 and -0.396 e.Å ⁻³	

4c: The crystals were grown by slow evaporation of CHCl₃ at room temperature. One single crystal of 0.05 X 0.40 X 0.50 mm³ was mounted using a glass fiber at 298(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S10. Crystal data and structure refinement for **4c**.

Empirical formula	C ₂₈ H ₂₈ Cl ₄ N ₂ Si ₂	
Formula weight	590.50	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 5.9752(19) Å	α = 90°.
	b = 50.52(3) Å	β = 93.96(3)°.
	c = 10.226(6) Å	γ = 90°.
Volume	3080(3) Å ³	
Z	4	
Density (calculated)	1.274 Mg/m ³	
Absorption coefficient	4.388 mm ⁻¹	
F(000)	1224	
Crystal size	0.50 x 0.40 x 0.05 mm ³	
Theta range for data collection	3.50 to 69.99°.	
Index ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 61, 0 ≤ l ≤ 12	
Reflections collected	5582	
Independent reflections	5582 [R(int) = 0.0000]	
Completeness to theta = 69.99°	95.5 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.8105 and 0.2177	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5582 / 3 / 329	
Goodness-of-fit on F ²	0.850	
Final R indices [I > 2σ(I)]	R1 = 0.1046, wR2 = 0.2133	
R indices (all data)	R1 = 0.3464, wR2 = 0.2865	
Largest diff. peak and hole	0.380 and -0.471 e.Å ⁻³	

5a: The crystals were grown by slow vapor evaporation of a mixture 70:30 DMF:MeOH solution. One single crystal of 0.10 X 0.10 X 0.30 mm³ was mounted using a glass fiber on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S11. Crystal data and structure refinement for **5a**.

Empirical formula	C ₂₈ H ₃₀ N ₂ Si ₂	
Formula weight	450.72	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /C	
Unit cell dimensions	a = 6.091(5) Å	α = 90°.
	b = 25.289(13) Å	β = 102.69(7)°.
	c = 8.863(7) Å	γ = 90°.
Volume	1332.0(16) Å ³	
Z	2	
Density (calculated)	1.124 Mg/m ³	
Absorption coefficient	1.325 mm ⁻¹	
F(000)	480	
Crystal size	0.30 x 0.10 x 0.10 mm ³	
Theta range for data collection	3.50 to 69.94°.	
Index ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 30, 0 ≤ l ≤ 10	
Reflections collected	2427	
Independent reflections	2427 [R(int) = 0.0000]	
Completeness to theta = 69.94°	95.8 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.8789 and 0.6920	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2427 / 0 / 145	
Goodness-of-fit on F ²	0.800	
Final R indices [I > 2σ(I)]	R ₁ = 0.0783, wR ₂ = 0.1393	
R indices (all data)	R ₁ = 0.2912, wR ₂ = 0.1908	
Largest diff. peak and hole	0.189 and -0.260 e.Å ⁻³	

5b: The crystals were grown by slow evaporation of a CH₂Cl₂/MeOH (75/25) solution at room temperature. One single crystal of 0.300 X 0.300 X 0.025 mm was mounted using a glass fiber on the goniometer at 293(2) K. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S12. Crystal data and structure refinement for **5b**.

Empirical formula	C ₂₈ H ₂₆ F ₄ N ₂ Si ₂	
Formula weight	522.69	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /C	
Unit cell dimensions	a = 5.867(3) Å	α = 90°.
	b = 5.788(3) Å	β = 91.53(4)°.
	c = 40.37(2) Å	γ = 90°.
Volume	1370.5(13) Å ³	
Z	2	
Density (calculated)	1.267 Mg/m ³	
Absorption coefficient	1.578 mm ⁻¹	
F(000)	544	
Crystal size	0.300 x 0.300 x 0.025 mm ³	
Theta range for data collection	2.19 to 70.00°.	
Index ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 7, 0 ≤ l ≤ 49	
Reflections collected	2460	
Independent reflections	2460 [R(int) = 0.0000]	
Completeness to theta = 70.00°	95.4 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2460 / 0 / 167	
Goodness-of-fit on F ²	0.921	
Final R indices [I > 2σ(I)]	R ₁ = 0.0887, wR ₂ = 0.2274	
R indices (all data)	R ₁ = 0.2223, wR ₂ = 0.2867	
Extinction coefficient	0.0048(11)	
Largest diff. peak and hole	0.265 and -0.262 e.Å ⁻³	

5c: The crystals were grown by slow evaporation of a CH₂Cl₂/MeOH (75/25) at room temperature. One single crystal of 0.05 X 0.70 X 0.80 mm³ was mounted on a glass fiber and mounted on the goniometer at 298(2) K. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S13. Crystal data and structure refinement for **5c**.

Empirical formula	C ₂₈ H ₂₆ Cl ₄ F ₀ N ₂ Si ₂	
Formula weight	588.49	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /a	
Unit cell dimensions	a = 11.181(6) Å	α = 90°.
	b = 5.613(3) Å	β = 102.47(4)°.
	c = 24.414(14) Å	γ = 90°.
Volume	1496.0(13) Å ³	
Z	2	
Density (calculated)	1.306 Mg/m ³	
Absorption coefficient	4.516 mm ⁻¹	
F(000)	608	
Crystal size	0.80 x 0.70 x 0.05 mm ³	
Theta range for data collection	1.85 to 70.09°.	
Index ranges	-13 ≤ h ≤ 13, 0 ≤ k ≤ 6, 0 ≤ l ≤ 29	
Reflections collected	2787	
Independent reflections	2787 [R(int) = 0.0000]	
Completeness to theta = 70.00°	98.2 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.8057 and 0.1228	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2787 / 0 / 164	
Goodness-of-fit on F ²	0.987	
Final R indices [I > 2σ(I)]	R ₁ = 0.0839, wR ₂ = 0.2248	
R indices (all data)	R ₁ = 0.1265, wR ₂ = 0.2573	
Extinction coefficient	0.0125(17)	
Largest diff. peak and hole	0.526 and -0.501 e.Å ⁻³	

6b: The crystals were grown by slow evaporation of an ethyl acetate solution at room temperature. One single crystal of 0.05 X 0.30 X 0.60 mm³ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S14. Crystal data and structure refinement for **6b**.

Empirical formula	C ₂₂ H ₁₂ F ₄ N ₂	
Formula weight	380.34	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 7.7079(10) Å	α = 90°.
	b = 5.7966(9) Å	β = 90.594(12)°.
	c = 19.243(3) Å	γ = 90°.
Volume	859.7(2) Å ³	
Z	2	
Density (calculated)	1.469 Mg/m ³	
Absorption coefficient	1.006 mm ⁻¹	
F(000)	388	
Crystal size	0.60 x 0.30 x 0.05 mm ³	
Theta range for data collection	6.16 to 69.90°.	
Index ranges	-9 ≤ h ≤ 9, 0 ≤ k ≤ 7, 0 ≤ l ≤ 23	
Reflections collected	1605	
Independent reflections	1605 [R(int) = 0.0000]	
Completeness to theta = 69.90°	98.8 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.9514 and 0.5836	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1605 / 0 / 128	
Goodness-of-fit on F ²	0.946	
Final R indices [I > 2σ(I)]	R1 = 0.0740, wR2 = 0.1863	
R indices (all data)	R1 = 0.1488, wR2 = 0.2182	
Extinction coefficient	0.039(4)	
Largest diff. peak and hole	0.231 and -0.222 e.Å ⁻³	

6c: The crystals were grown by slow evaporation of CHCl_3 at room temperature. One single crystal of $0.11 \times 0.40 \times 0.40 \text{ mm}^3$ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S15. Crystal data and structure refinement for **6c**.

Empirical formula	C ₂₂ H ₁₂ Cl ₄ N ₂	
Formula weight	446.14	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 5.576(3) Å	$\alpha = 90^\circ$.
	b = 10.283(7) Å	$\beta = 96.69(5)^\circ$.
	c = 17.257(11) Å	$\gamma = 90^\circ$.
Volume	982.7(10) Å ³	
Z	2	
Density (calculated)	1.508 Mg/m ³	
Absorption coefficient	0.613 mm ⁻¹	
F(000)	452	
Crystal size	0.40 x 0.40 x 0.11 mm ³	
Theta range for data collection	2.31 to 25.54°.	
Index ranges	-6 ≤ h ≤ 6, 0 ≤ k ≤ 12, 0 ≤ l ≤ 20	
Reflections collected	1825	
Independent reflections	1825 [R(int) = 0.0000]	
Completeness to theta = 25.50°	99.4 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.9356 and 0.7916	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1825 / 0 / 127	
Goodness-of-fit on F ²	0.947	
Final R indices [I > 2σ(I)]	R1 = 0.0628, wR2 = 0.1169	
R indices (all data)	R1 = 0.1602, wR2 = 0.1369	
Largest diff. peak and hole	0.227 and -0.285 e.Å ⁻³	

7a: The crystals were grown by slow evaporation of a CHCl_3 solution at room temperature. One single crystal of $0.10 \times 0.40 \times 0.50 \text{ mm}^3$ was mounted using a glass fiber on the goniometer at 293(2) K.

Table 16. Crystal data and structure refinement for **7a**.

Identification code	tkbxx3	
Empirical formula	C ₂₂ H ₁₄ N ₂	
Formula weight	306.35	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 5.6880(13) Å	$\alpha = 90^\circ$.
	b = 37.790(16) Å	$\beta = 93.264(18)^\circ$.
	c = 7.7896(16) Å	$\gamma = 90^\circ$.
Volume	1671.7(9) Å ³	
Z	4	
Density (calculated)	1.217 Mg/m ³	
Absorption coefficient	0.558 mm ⁻¹	
F(000)	640	
Crystal size	0.50 x 0.40 x 0.10 mm ³	
Theta range for data collection	2.34 to 70.06°.	
Index ranges	-6 ≤ h ≤ 6, 0 ≤ k ≤ 46, 0 ≤ l ≤ 9	
Reflections collected	3168	
Independent reflections	3168 [R(int) = 0.0000]	
Completeness to theta = 70.00°	100.0 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.9463 and 0.7677	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3168 / 0 / 218	
Goodness-of-fit on F ²	1.065	
Final R indices [I > 2σ(I)]	R ₁ = 0.0692, wR ₂ = 0.1878	
R indices (all data)	R ₁ = 0.1301, wR ₂ = 0.2176	
Extinction coefficient	0.0073(10)	
Largest diff. peak and hole	0.198 and -0.203 e.Å ⁻³	

7b: The crystals were grown in by slow evaporation of dioxane at room temperature. One single crystal of 0.20 X 0.20 X 0.50 mm³ was mounted using a glass fiber at 293(2) K on the goniometer.

Table 17. Crystal data and structure refinement for **7b**.

Empirical formula	C22 H8 F4 N2	
Formula weight	376.31	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Orthorhombic	
Space group	pb $\bar{c}$ 21	
Unit cell dimensions	a = 6.067(4) Å	$\alpha = 90^\circ$.
	b = 11.96(2) Å	$\beta = 90^\circ$.
	c = 24.27(4) Å	$\gamma = 90^\circ$.
Volume	1761(5) Å ³	
Z	4	
Density (calculated)	1.419 Mg/m ³	
Absorption coefficient	0.982 mm ⁻¹	
F(000)	760	
Crystal size	0.50 x 0.20 x 0.20 mm ³	
Theta range for data collection	3.64 to 70.10°.	
Index ranges	0 ≤ h ≤ 7, 0 ≤ k ≤ 14, 0 ≤ l ≤ 29	
Reflections collected	1650	
Independent reflections	1650 [R(int) = 0.0000]	
Completeness to theta = 70.00°	96.0 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.8279 and 0.6396	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1650 / 1 / 254	
Goodness-of-fit on F ²	0.873	
Final R indices [I > 2σ(I)]	R1 = 0.0793, wR2 = 0.1898	
R indices (all data)	R1 = 0.1919, wR2 = 0.2411	
Absolute structure parameter	0.0(6)	
Extinction coefficient	0.0034(9)	
Largest diff. peak and hole	0.447 and -0.213 e.Å ⁻³	

9b: The crystals were grown by slow evaporation of a CHCl₃ solution at room temperature. One single crystal of 0.10 X 0.20 X 0.30 mm³ was mounted using a glass fiber at 293(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S18. Crystal data and structure refinement for **9b**.

Empirical formula	C70 H118 Cl2 F4 N2 P4 Pt2	
Formula weight	1648.68	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.307(4) Å	α = 90°.
	b = 23.926(4) Å	β = 114.10(2)°.
	c = 14.694(5) Å	γ = 90°.
Volume	3949.8(18) Å ³	
Z	2	
Density (calculated)	1.386 Mg/m ³	
Absorption coefficient	8.279 mm ⁻¹	
F(000)	1676	
Crystal size	0.30 x 0.20 x 0.10 mm ³	
Theta range for data collection	3.69 to 69.77°.	
Index ranges	-14 ≤ h ≤ 13, 0 ≤ k ≤ 29, 0 ≤ l ≤ 17	
Reflections collected	7310	
Independent reflections	7310 [R(int) = 0.0000]	
Completeness to theta = 69.77°	98.3 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.4915 and 0.1902	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7310 / 2 / 260	
Goodness-of-fit on F ²	0.989	
Final R indices [I > 2σ(I)]	R1 = 0.0850, wR2 = 0.2110	
R indices (all data)	R1 = 0.1709, wR2 = 0.2465	
Extinction coefficient	0.00143(12)	
Largest diff. peak and hole	0.949 and -1.112 e.Å ⁻³	

9c: The crystals were grown by slow evaporation of a CH₂Cl₂:Hexanes solvent mixture at room temperature. One single crystal of 0.10 X 0.15 X 0.60 mm³ was mounted using a glass fiber at 193(2) K on the goniometer. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection.

Table S19. Crystal data and structure refinement for **9c**.

Empirical formula	C70 H118 Cl6 N2 P4 Pt2	
Formula weight	1714.42	
Temperature	193(2) K	
Wavelength	0.70930 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 14.294(5) Å	α = 90°.
	b = 12.545(5) Å	β = 98.48(3)°.
	c = 23.197(9) Å	γ = 90°.
Volume	4114(3) Å ³	
Z	2	
Density (calculated)	1.384 Mg/m ³	
Absorption coefficient	3.706 mm ⁻¹	
F(000)	1740	
Crystal size	0.60 x 0.15 x 0.10 mm ³	
Theta range for data collection	1.57 to 25.48°.	
Index ranges	-17 ≤ h ≤ 17, 0 ≤ k ≤ 15, 0 ≤ l ≤ 28	
Reflections collected	7306	
Independent reflections	7306 [R(int) = 0.0000]	
Completeness to theta = 25.48°	95.0 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.7082 and 0.2146	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7306 / 0 / 187	
Goodness-of-fit on F ²	0.830	
Final R indices [I > 2σ(I)]	R1 = 0.0859, wR2 = 0.1211	
R indices (all data)	R1 = 0.2789, wR2 = 0.1551	
Largest diff. peak and hole	0.951 and -1.656 e.Å ⁻³	

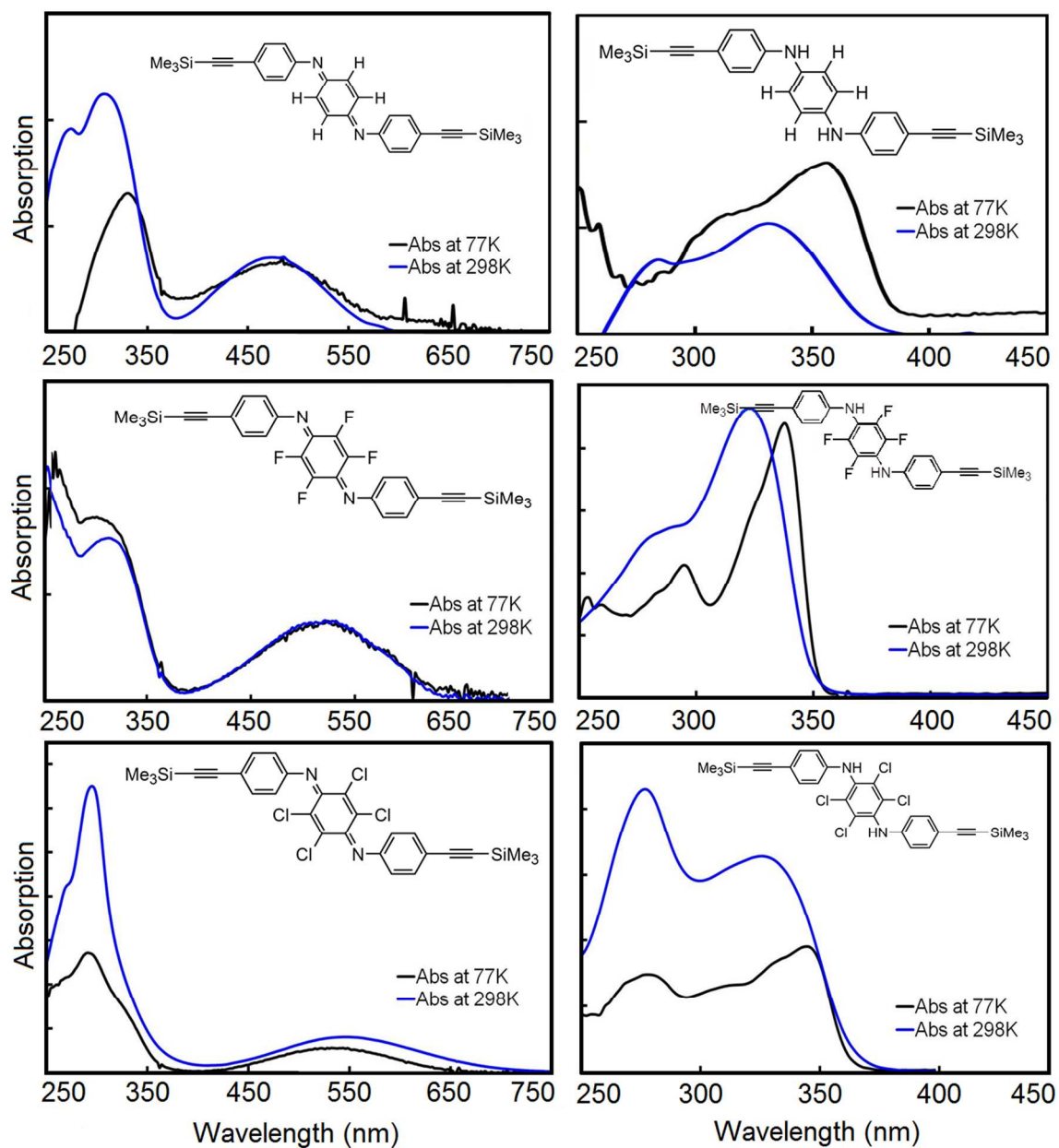


Figure S1. Absorption spectra of compounds **4a,b,c** and **5a,b,c** in 2MeTHF at 298 (blue) and 77 K (black).

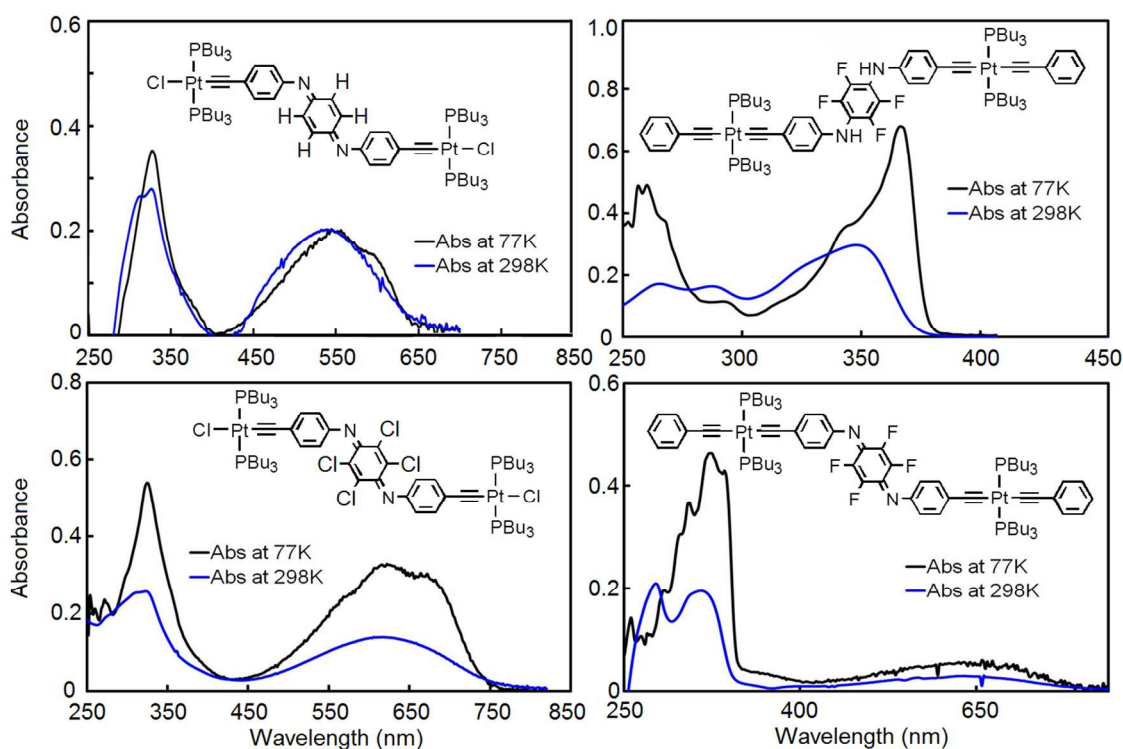


Figure S2. Absorption spectra of compounds **11a,c** in 2MeTHF at 298 (blue) and 77 K (black), along with $\text{PhC}\equiv\text{C-Pt(PBu}_3)_2\text{-C}\equiv\text{CC}_6\text{H}_4\text{-NH-C}_6\text{F}_4\text{-NH-C}_6\text{H}_4\text{C}\equiv\text{C-Pt(PBu}_3)_2\text{-C}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{C-Pt(PBu}_3)_2\text{-C}\equiv\text{CC}_6\text{H}_4\text{-N=C}_6\text{F}_4\text{=N-C}_6\text{H}_4\text{C}\equiv\text{C-Pt(PBu}_3)_2\text{-C}\equiv\text{CPh}$.

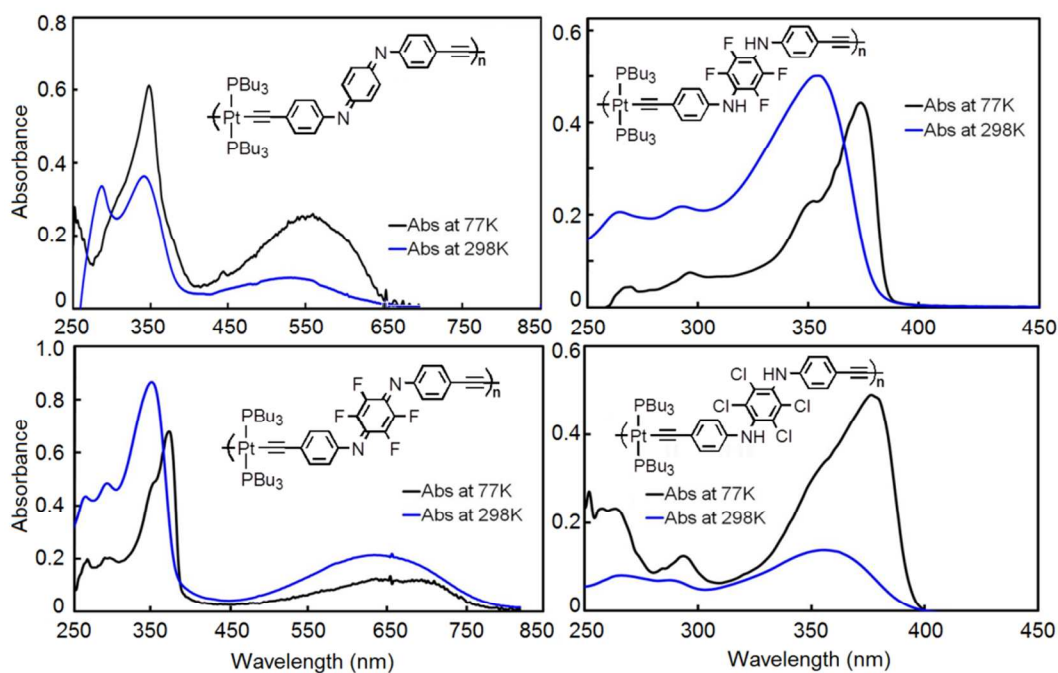


Figure S3. Absorption spectra of polymers **8b,c** and **10a,b** in 2MeTHF at 298 (blue) and 77 K (black).

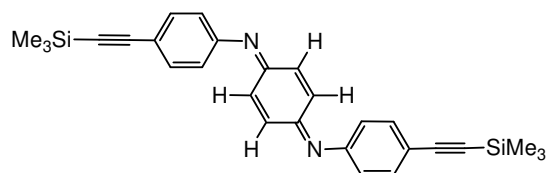


Table S20. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for compound **5a**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	17686	565	0.996	HOMO→LUMO (93)
2	19232	519	0.000	H-1→LUMO (93)
3	27823	359	0.948	H-8→LUMO (27), H-4→LUMO (15), H-2→LUMO (46)
4	28658	348	0.000	H-3→LUMO (86)
5	29617	337	0.000	H-5→LUMO (94)
6	29753	336	0.034	H-8→LUMO (36), H-4→LUMO (60)
7	31145	321	0.000	H-7→LUMO (90)
8	31167	320	0.000	H-6→LUMO (91)
9	31467	317	0.578	H-8→LUMO (26), H-4→LUMO (18), H-2→LUMO (35)
10	31976	312	0.000	H-9→LUMO (96)
11	34721	288	0.000	HOMO→L+1 (91)
12	36954	270	0.058	H-1→L+1 (72), HOMO→L+2 (23)
13	37935	263	0.363	H-11→LUMO (34), HOMO→L+2 (44)
14	38291	261	0.000	H-10→LUMO (12), HOMO→L+3 (74)
15	38376	260	0.000	H-10→LUMO (79), HOMO→L+3 (10)
16	39081	255	0.042	H-1→L+3 (11), HOMO→L+4 (67)
17	39582	252	0.000	H-1→L+2 (25), HOMO→L+5 (53)
18	39671	252	0.000	H-1→L+2 (66), HOMO→L+5 (21)
19	39986	250	0.216	H-11→LUMO (61), HOMO→L+2 (19)
20	40328	247	0.001	H-13→LUMO (28), H-12→LUMO (68)

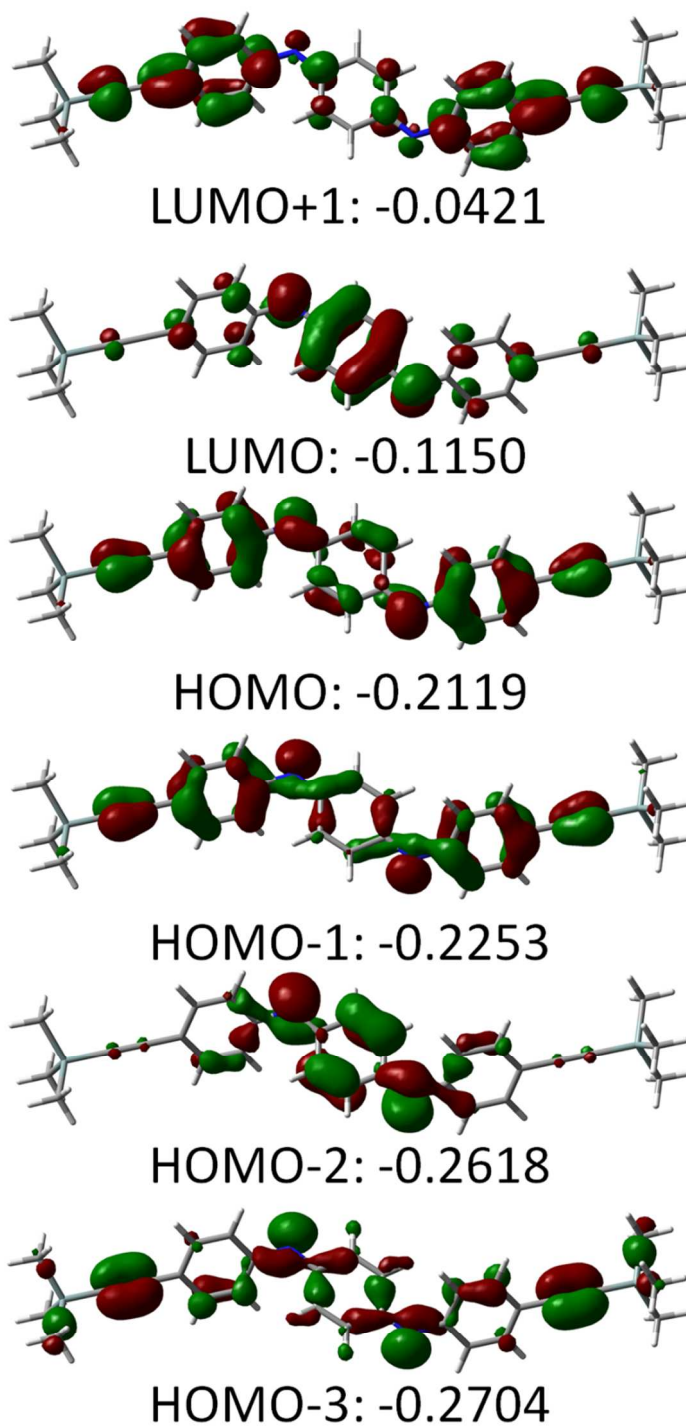


Figure S4. Representation of the frontier MOs of compound **5a**. The units are a.u.

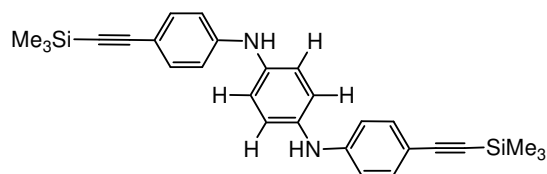


Table S21. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for compound **4a**.

1	27570	362	1.916	HOMO→LUMO (98)
2	31845	314	0.000	HOMO→L+1 (96)
3	32391	308	0.059	HOMO→L+2 (95)
4	33895	295	0.000	HOMO→L+3 (92)
5	34118	293	0.027	HOMO→L+4 (93)
6	34928	286	0.000	H-1→LUMO (93)
7	37486	266	0.590	H-1→L+1 (82), HOMO→L+5 (15)
8	38546	259	0.000	H-1→L+2 (94)
9	39840	251	0.086	H-2→LUMO (11), H-1→L+1 (14), HOMO→L+5 (68)
10	40254	248	0.006	H-1→L+3 (76)
11	40325	247	0.000	H-1→L+4 (76)
12	40590	246	0.000	H-1→L+7 (14), HOMO→L+6 (76)
13	40601	246	0.001	H-1→L+6 (15), HOMO→L+7 (77)
14	42771	233	0.164	H-2→LUMO (66)
15	42896	233	0.001	H-7→L+1 (22), H-6→LUMO (58)
16	42922	232	0.031	H-7→LUMO (30), H-6→L+1 (27), H-5→LUMO (14), H-2→LUMO (16)
17	44781	223	0.001	H-2→L+1 (69), H-1→L+5 (14)
18	44960	222	0.000	H-2→L+1 (17), H-1→L+5 (73)
19	45073	221	0.011	H-7→LUMO (18), H-5→LUMO (14), H-3→LUMO (30), H-2→L+2 (28)
20	46234	216	0.097	H-5→LUMO (17), H-3→LUMO (29), H-2→L+2 (13), H-2→L+4 (18), H-1→L+3 (15)

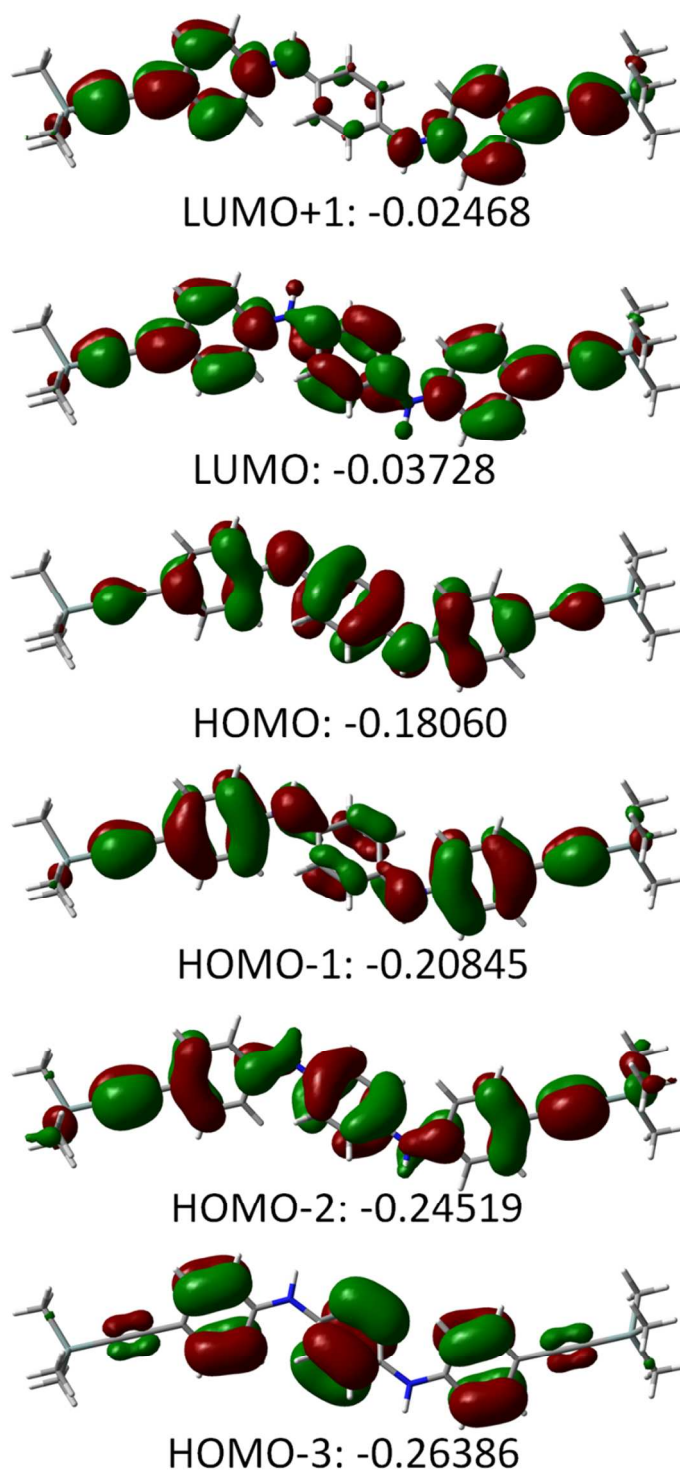


Figure S5. Representation of the frontier MOs of compound **4a**. The units are a.u.

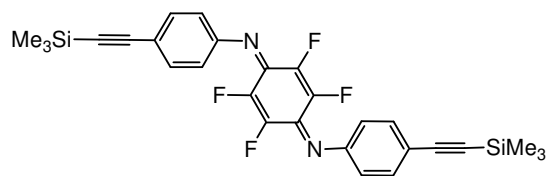


Table S22. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for compound **5b**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	16628	601	1.635	HOMO→LUMO (93)
2	19507	512	0.000	H-1→LUMO (87)
3	24634	405	0.849	H-9→LUMO (24), H-2→LUMO (64)
4	25370	394	0.000	H-3→LUMO (97)
5	26293	380	0.000	H-8→LUMO (27), H-4→LUMO (47), H-1→LUMO (10)
6	27321	366	0.021	H-5→LUMO (94)
7	27383	365	0.000	H-8→LUMO (29), H-6→LUMO (25), H-4→LUMO (42)
8	28290	353	0.000	H-7→LUMO (89)
9	28292	353	0.000	H-8→LUMO (34), H-6→LUMO (62)
10	29879	334	0.205	H-9→LUMO (61), H-2→LUMO (21)
11	33195	301	0.000	H-10→LUMO (11), HOMO→L+1 (80)
12	35777	279	0.000	H-10→LUMO (85), HOMO→L+1 (13)
13	36112	276	0.081	H-11→LUMO (81), H-1→L+1 (10)
14	37237	268	0.021	H-1→L+1 (68), HOMO→L+2 (23)
15	37318	267	0.001	H-12→LUMO (97)
16	37321	267	0.000	H-13→LUMO (97)
17	39139	255	0.420	H-11→LUMO (12), H-1→L+1 (10), HOMO→L+2 (58)
18	39506	253	0.000	H-14→LUMO (31), HOMO→L+3 (50)
19	39601	252	0.000	H-14→LUMO (59), HOMO→L+3 (27)
20	39764	251	0.039	H-4→L+1 (10), HOMO→L+4 (66)

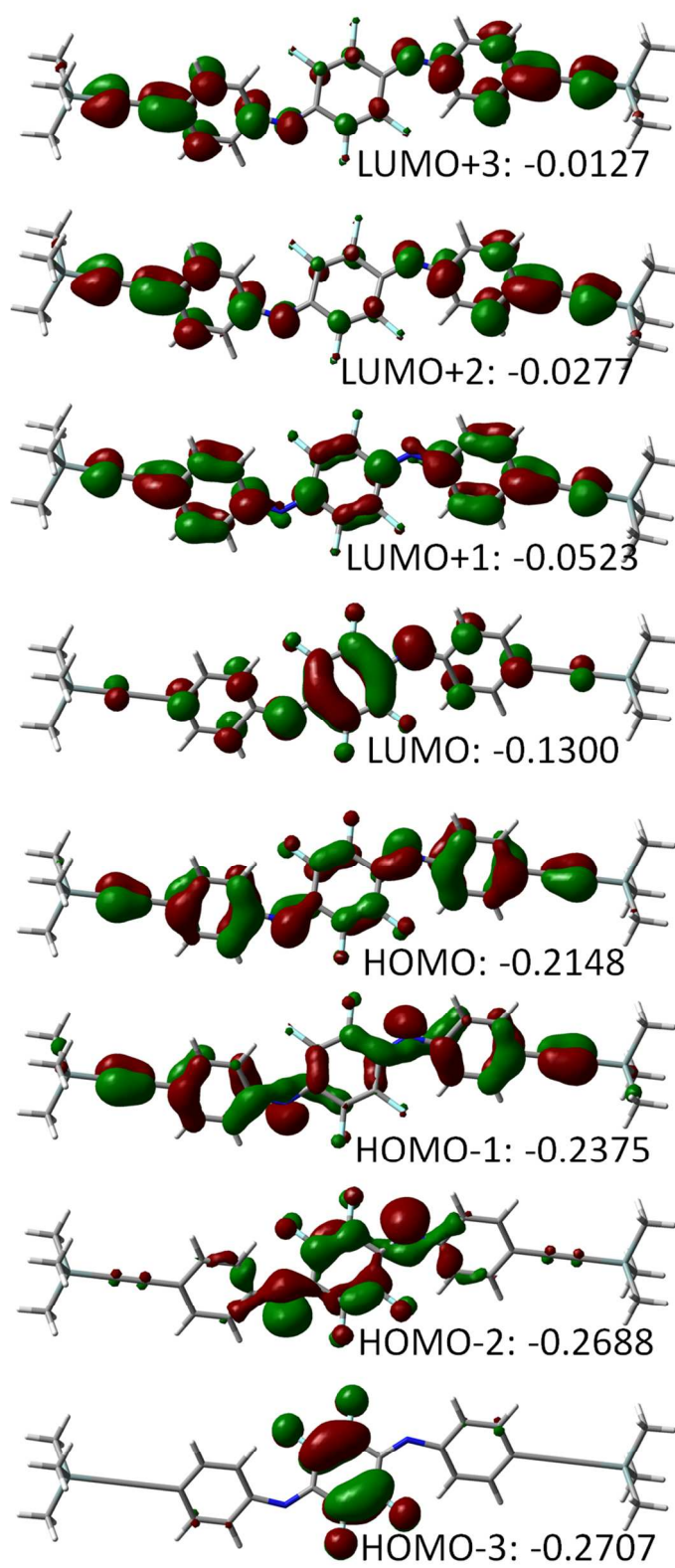


Figure S6. Representation of the frontier MOs of compound **5b**. The units are a.u.

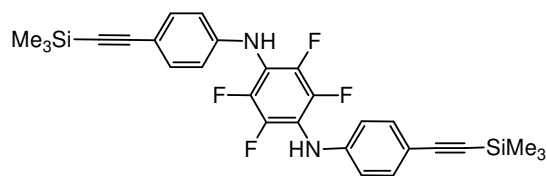


Table S23. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for compound **4b**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	28579	350	2.182	HOMO→LUMO (98)
2	33504	298	0.014	HOMO→L+2 (92)
3	33798	295	0.000	H-1→LUMO (23), HOMO→L+1 (76)
4	34904	286	0.000	H-1→LUMO (75), HOMO→L+1 (22)
5	36107	276	0.000	HOMO→L+3 (86)
6	36205	276	0.023	HOMO→L+4 (84)
7	38405	260	0.367	H-1→L+1 (66), HOMO→L+5 (29)
8	38797	257	0.000	H-1→L+2 (97)
9	39547	252	0.242	H-2→LUMO (12), H-1→L+1 (28), HOMO→L+5 (54)
10	39800	251	0.000	HOMO→L+6 (90)
11	41374	241	0.001	H-5→LUMO (11), H-1→L+3 (68), HOMO→L+4 (10)
12	41471	241	0.000	H-4→LUMO (12), H-1→L+4 (65), HOMO→L+3 (11)
13	41997	238	0.000	H-7→L+1 (19), H-6→LUMO (39), HOMO→L+8 (22)
14	41998	238	0.000	H-7→LUMO (39), H-6→L+1 (19), HOMO→L+7 (22)
15	42603	234	0.001	H-7→L+1 (10), H-6→LUMO (22), H-1→L+7 (13), HOMO→L+8 (48)
16	42609	234	0.000	H-7→LUMO (22), H-6→L+1 (10), H-1→L+8 (14), HOMO→L+7 (49)
17	42817	233	0.092	H-2→LUMO (77)
18	43253	231	0.072	H-3→LUMO (65), H-2→L+2 (15)
19	43680	228	0.000	H-1→L+5 (91)
20	45593	219	0.000	H-8→LUMO (19), H-2→L+1 (72)

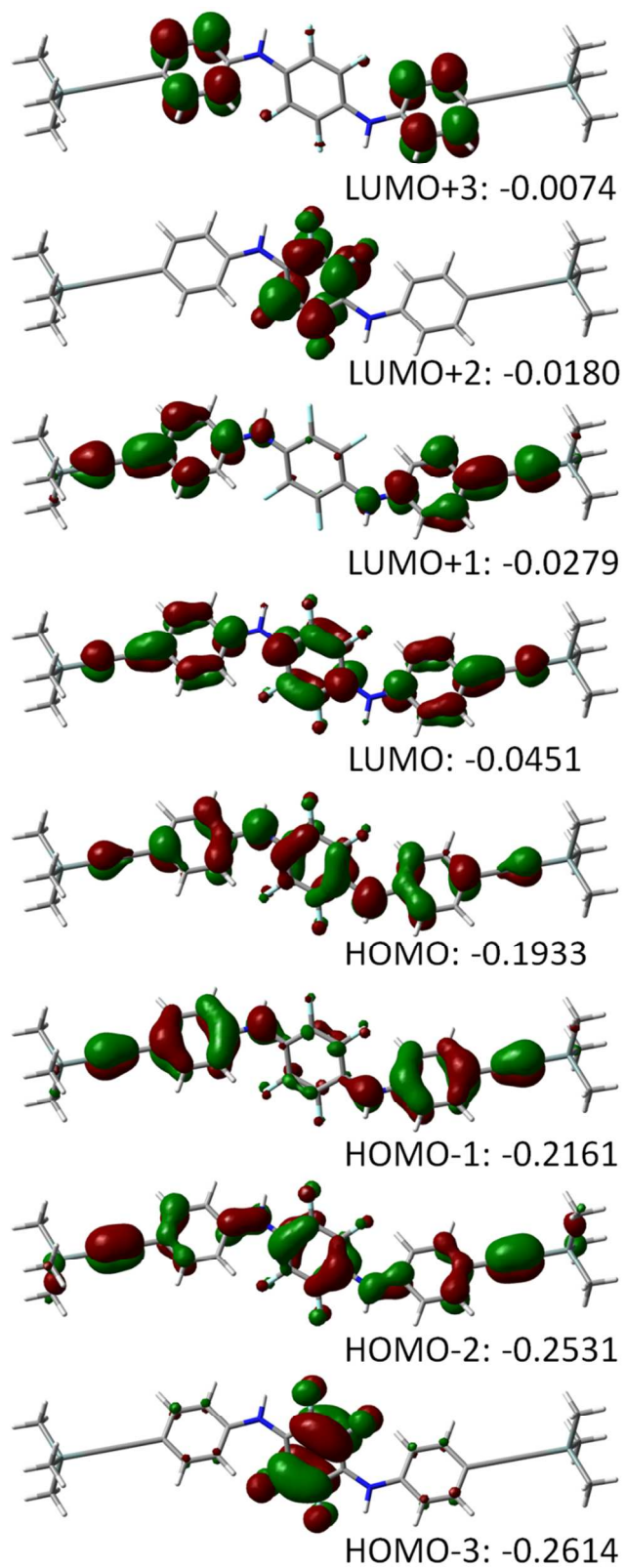


Figure S7. Representation of the frontier MOs of compound **4b**. The units are a.u.

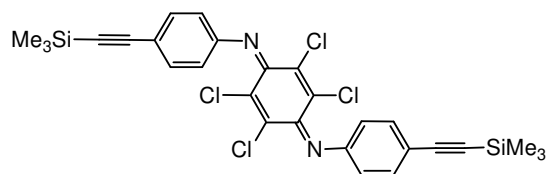


Table S24. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for compound **5c**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	13725	728	0.648	HOMO→LUMO (96)
2	15186	658	0.000	H-1→LUMO (96)
3	23951	417	0.000	H-2→LUMO (93)
4	25280	395	0.105	H-7→LUMO (14), H-3→LUMO (78)
5	25589	390	0.000	H-6→LUMO (92)
6	26299	380	0.546	H-8→LUMO (78), H-7→LUMO (12)
7	26479	377	0.000	H-9→LUMO (88)
8	27077	369	0.000	H-5→LUMO (14), H-4→LUMO (83)
9	27077	369	0.000	H-5→LUMO (77), H-4→LUMO (15)
10	28909	345	0.802	H-8→LUMO (12), H-7→LUMO (63), H-3→LUMO (13)
11	32451	308	0.000	H-14→LUMO (35), H-10→LUMO (42), HOMO→L+2 (17)
12	32976	303	0.000	H-10→LUMO (10), HOMO→L+2 (81)
13	34194	292	0.000	H-14→LUMO (10), HOMO→L+1 (81)
14	34675	288	0.231	H-11→LUMO (45), H-1→L+2 (14), HOMO→L+3 (30)
15	35063	285	0.077	H-11→LUMO (39), H-1→L+2 (36), HOMO→L+3 (15)
16	35224	283	0.030	H-1→L+2 (44), HOMO→L+3 (40)
17	35401	282	0.000	H-14→LUMO (41), H-10→LUMO (38), HOMO→L+1 (14)
18	35795	279	0.122	H-15→LUMO (68), H-1→L+1 (24)
19	36078	277	0.003	H-13→LUMO (23), H-12→LUMO (75)
20	36079	277	0.000	H-13→LUMO (75), H-12→LUMO (23)

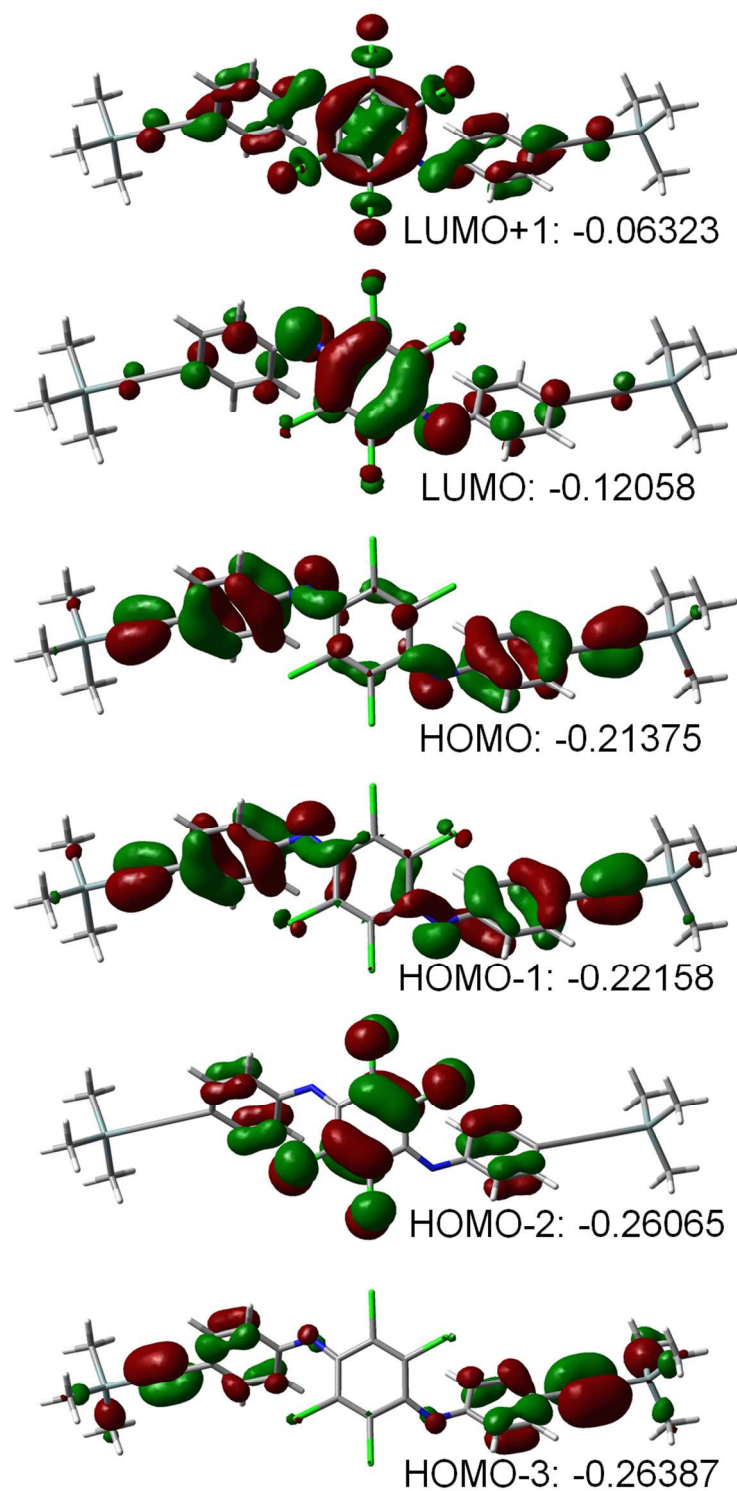


Figure S8. Representation of the frontier MOs of compound **5c**. The units are a.u.

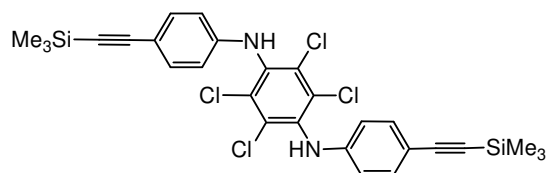


Table S25. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for compound **4c**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	28293	353	1.401	HOMO→LUMO (98)
2	28917	345	0.041	HOMO→L+1 (97)
3	31357	318	0.000	H-1→LUMO (13), H-1→L+1 (20), HOMO→L+2 (60)
4	31634	316	0.000	H-1→LUMO (70), HOMO→L+2 (21)
5	31898	313	0.000	H-1→LUMO (14%), H-1→L+1 (75)
6	34870	286	0.036	H-1→L+2 (91)
7	35762	279	0.000	HOMO→L+3 (89)
8	37462	266	0.194	HOMO→L+4 (46), HOMO→L+6 (34)
9	37533	266	0.000	H-4→LUMO (10), H-1→L+6 (15), HOMO→L+5 (67)
10	37590	266	0.217	HOMO→L+4 (44), HOMO→L+6 (31)
11	38233	261	0.721	H-1→L+3 (86)
12	39226	254	0.028	H-3→LUMO (35), H-2→L+1 (37)
13	40240	248	0.000	H-1→L+4 (95)
14	40630	246	0.002	HOMO→L+7 (93)
15	41543	240	0.046	H-2→LUMO (16), H-1→L+5 (42), HOMO→L+6 (25)
16	41567	240	0.000	H-4→LUMO (13%), H-1→L+6 (54), HOMO→L+5 (29)
17	41740	239	0.066	H-5→LUMO (15), H-2→LUMO (33), H-1→L+5 (10)
18	41809	239	0.000	H-7→L+3 (11), H-6→LUMO (53)
19	41845	238	0.000	H-3→L+2 (62)
20	41850	238	0.037	H-7→LUMO (27), H-6→L+3 (13), H-5→LUMO (13), H-2→LUMO (18)

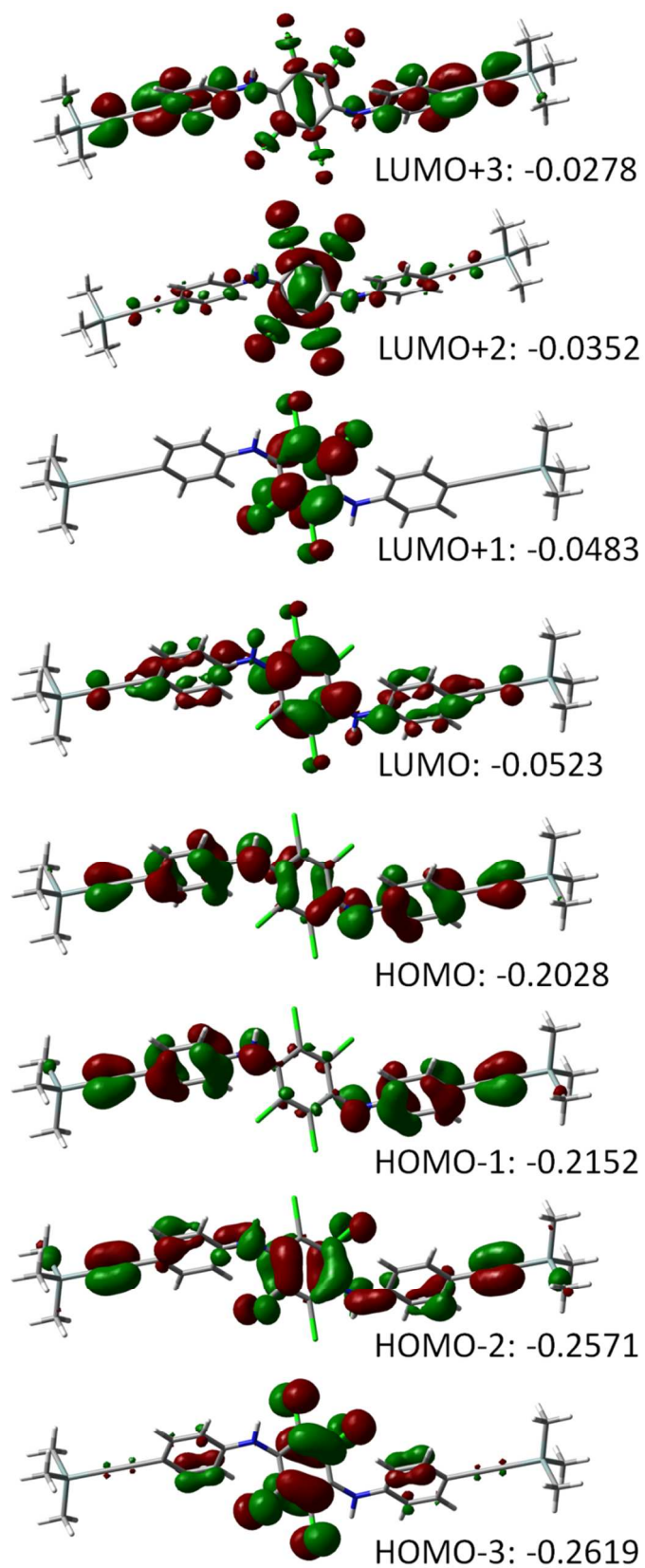


Figure S9. Representation of the frontier MOs of compound **4c**. The units are a.u.

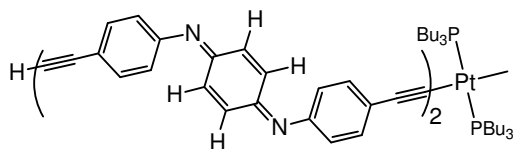
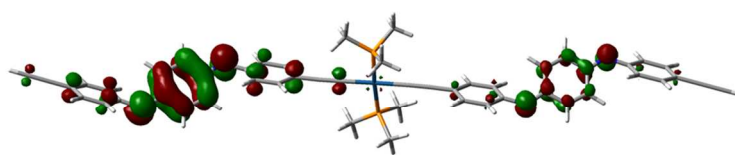
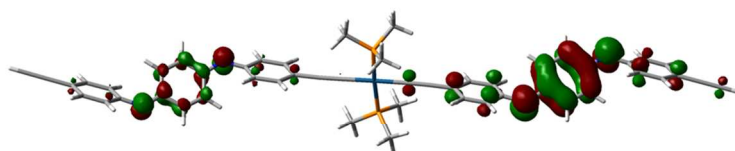


Table S26 . TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for the model **[PtL₂]**a****.

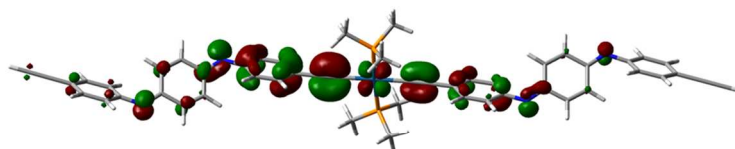
No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	15481	646	2.081	HOMO→LUMO (78), HOMO→L+1 (10)
2	16279	614	0.001	HOMO→L+1 (81)
3	17650	566	0.179	H-1→LUMO (75), HOMO→LUMO (10)
4	18246	548	0.159	H-1→LUMO (10), H-1→L+1 (80)
5	19479	513	0.201	H-4→LUMO (19), H-4→L+1 (27), H-3→LUMO (28), H-3→L+1 (11)
6	19506	512	0.002	H-4→LUMO (41), H-3→L+1 (43)
7	20536	487	0.000	H-2→LUMO (85)
8	20753	482	0.000	H-2→L+1 (87)
9	22865	437	0.001	H-4→LUMO (13), H-3→LUMO (58), H-3→L+1 (21)
10	23247	430	0.001	H-4→LUMO (18), H-4→L+1 (62), H-3→L+1 (12)
11	25103	398	0.206	H-8→L+1 (25), H-6→LUMO (17), H-6→L+1 (33)
12	25597	390	0.123	H-9→LUMO (30), H-7→LUMO (31)
13	26785	373	0.000	H-5→LUMO (100)
14	26992	370	0.000	H-5→L+1 (100)
15	28323	353	1.338	H-8→L+1 (26), H-6→LUMO (25)
16	28470	351	0.252	H-7→LUMO (25), H-6→LUMO (35), H-6→L+1 (18)
17	28544	350	0.114	H-9→LUMO (19), H-6→LUMO (10), H-6→L+1 (16)
18	29102	343	0.113	H-11→LUMO (24), H-11→L+1 (63)
19	29180	342	0.050	H-12→LUMO (31), H-7→LUMO (17), H-7→L+1 (37)
20	29222	342	0.043	H-12→LUMO (38), H-12→L+1 (11), H-7→L+1 (37)



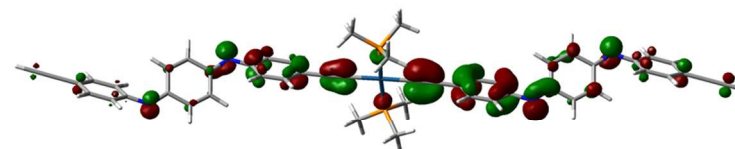
LUMO+1: -0.1107



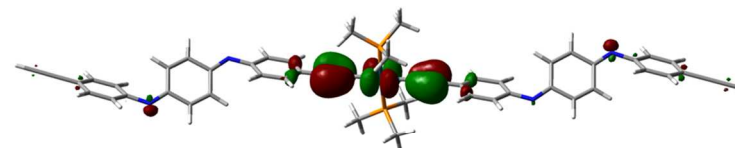
LUMO: -0.1120



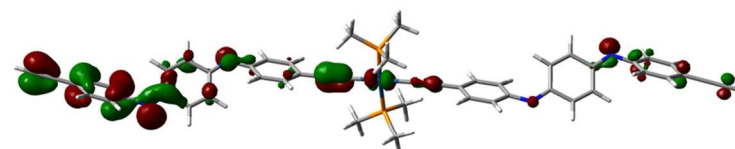
HOMO: -0.1939



HOMO+1: -0.2023



HOMO+2: -0.2182



HOMO+3: -0.2205

Figure S10. Representation of the frontier MOs of the model **[PtL₂]**a****. The units are a.u.

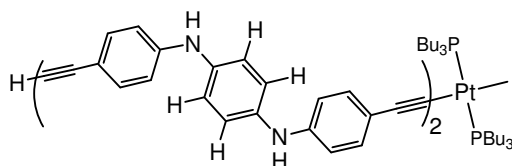


Table S27. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for the model **[PtL₂]a'**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	26556	376	3.023	H-1→L+1 (12), HOMO→LUMO (77)
2	27814	360	0.047	H-1→LUMO (47), HOMO→L+1 (48)
3	29195	342	0.380	H-1→L+1 (25), HOMO→L+2 (59)
4	29575	338	0.010	H-1→LUMO (40), H-1→L+2 (14), HOMO→L+1 (-7)
5	305062	327	0.177	H-1→L+1 (52), HOMO→LUMO (20), HOMO→L+2 (21)
6	31306	319	0.020	H-1→L+2 (44), HOMO→L+4 (28)
7	31344	319	0.044	H-1→L+2 (31), H-1→L+4 (13), HOMO→L+4 (38)
8	31484	317	0.049	H-1→L+3 (37), HOMO→L+3 (39)
9	32647	306	0.044	H-1→L+6 (18), HOMO→L+6 (58)
10	32858	304	0.156	H-1→L+7 (15), HOMO→L+5 (22), HOMO→L+7 (16)
11	33101	302	0.223	H-2→LUMO (11), H-1→L+7 (24), HOMO→L+7 (22), HOMO→L+8 (18)
12	33340	300	0.049	H-2→LUMO (25), HOMO→L+5 (20)
13	33568	297	0.035	H-1→L+9 (31), HOMO→L+9 (41)
14	33640	297	0.043	H-2→LUMO (14), H-1→L+10 (11), HOMO→L+10 (3)
15	33823	295	0.118	H-4→LUMO (26), H-4→L+2 (17), HOMO→L+10 (27)
16	34266	292	0.024	H-2→L+1 (13), H-1→L+5 (13), HOMO→L+5 (10)
17	34486	290	0.048	H-4→LUMO (14), H-2→LUMO (14), HOMO→L+8 (20)
18	34694	288	0.012	H-1→L+3 (30), H-1→L+5 (13), HOMO→L+3 (29), HOMO→L+5 (17)
19	34857	287	0.087	H-2→L+1 (34), H-1→L+5 (27)
20	35027	285	0.001	HOMO→L+11 (74)

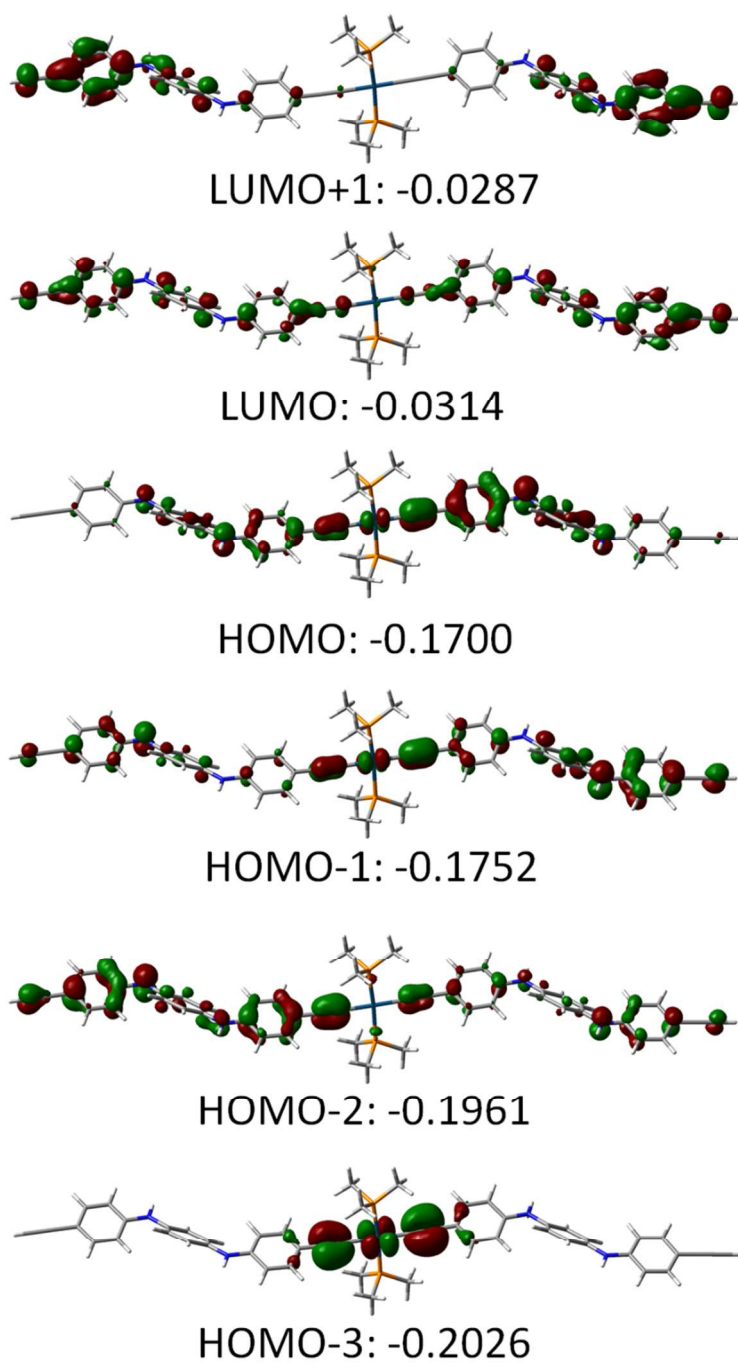


Figure S11. Representation of the frontier MOs of the model $[\text{PtL}_2]\mathbf{a}'$. The units are a.u.

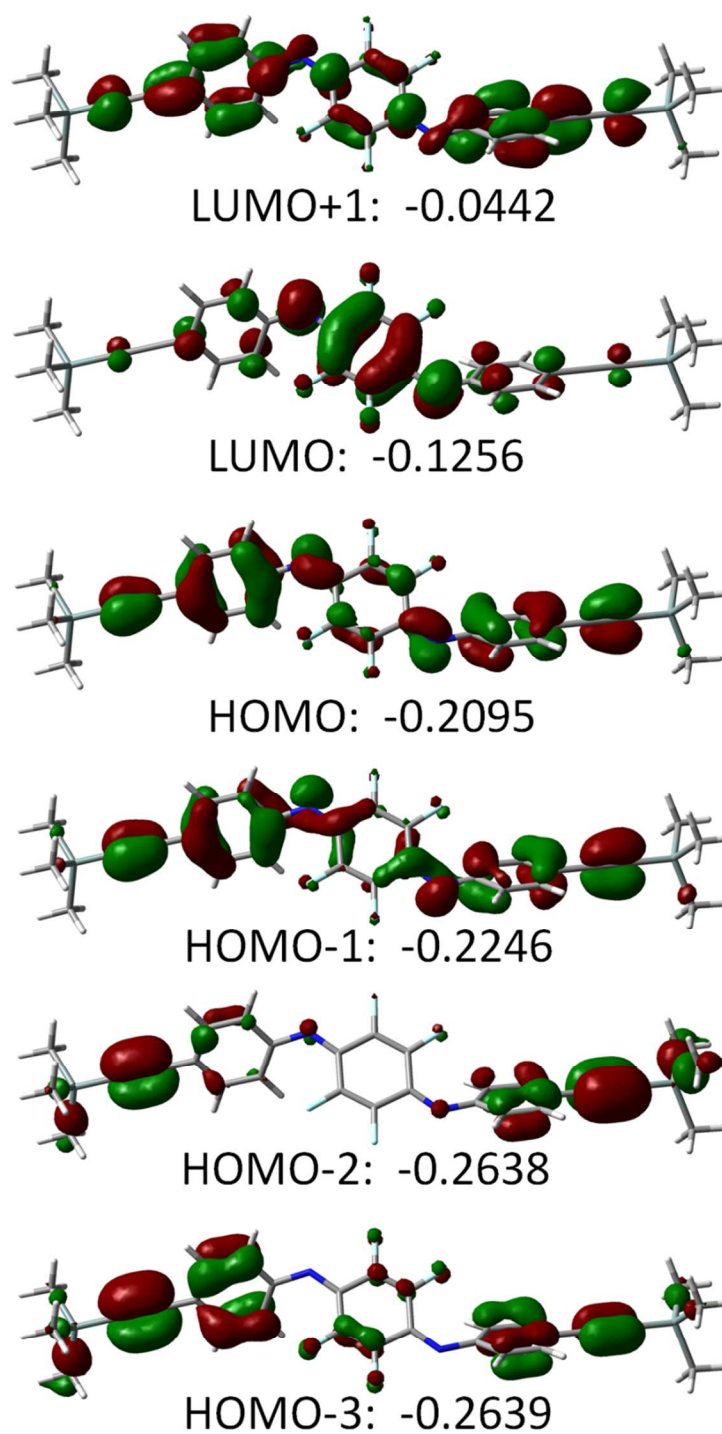


Figure S12. Representation of the frontier MOs of the model $[\text{PtL}_2]\mathbf{b}$. The units are a.u.

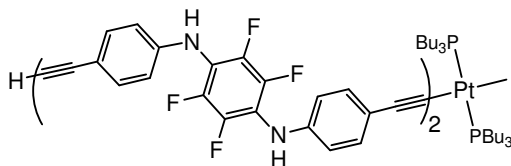


Table S29. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for the model **[PtL₂]b'**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	26983	370	3.158	H-1→L+1 (11), HOMO→LUMO (79)
2	28314	353	0.060	H-1→LUMO (27), HOMO→L+1 (69)
3	30128	331	0.154	H-1→LUMO (42), H-1→L+1 (14), HOMO→L+1 (-21), HOMO→L+2 (15)
4	30340	329	0.118	H-1→LUMO (20), H-1→L+1 (12), HOMO→L+2 (48)
5	30933	323	0.452	H-1→L+1 (57), HOMO→LUMO (19), HOMO→L+2 (16)
6	31937	313	0.011	H-1→L+3 (19), HOMO→L+3 (72)
7	32301	309	0.013	H-1→L+4 (34), HOMO→L+4 (56)
8	32847	304	0.001	H-1→L+2 (81)
9	33354	299	0.040	H-4→LUMO (34), H-4→L+2 (22), H-2→LUMO (35)
10	33579	297	0.536	H-4→LUMO (19), H-2→LUMO (33), H-2→L+1 (10)
11	33886	295	0.076	H-3→LUMO (23), H-2→L+1 (29), HOMO→L+5 (25)
12	34576	289	0.001	H-2→L+1 (20), HOMO→L+5 (39)
13	34808	287	0.016	HOMO→L+6 (57)
14	35107	284	0.015	H-1→L+10 (13%), HOMO→L+10 (70)
15	35121	284	0.001	H-1→L+7 (15), H-1→L+9 (11), HOMO→L+7 (27), HOMO→L+9 (28)
16	35221	283	0.016	H-1→L+7 (10), H-1→L+9 (11%), HOMO→L+7 (24), HOMO→L+9 (31)
17	35303	283	0.025	HOMO→L+8 (41%)
18	35329	283	0.006	H-1→L+4 (47), HOMO→L+4 (30)
19	35444	282	0.006	H-4→L+1 (18), H-3→LUMO (29), H-2→L+1 (11)
20	35591	280	0.013	H-1→L+3 (52), HOMO→L+3 (13), HOMO→L+8 (10)

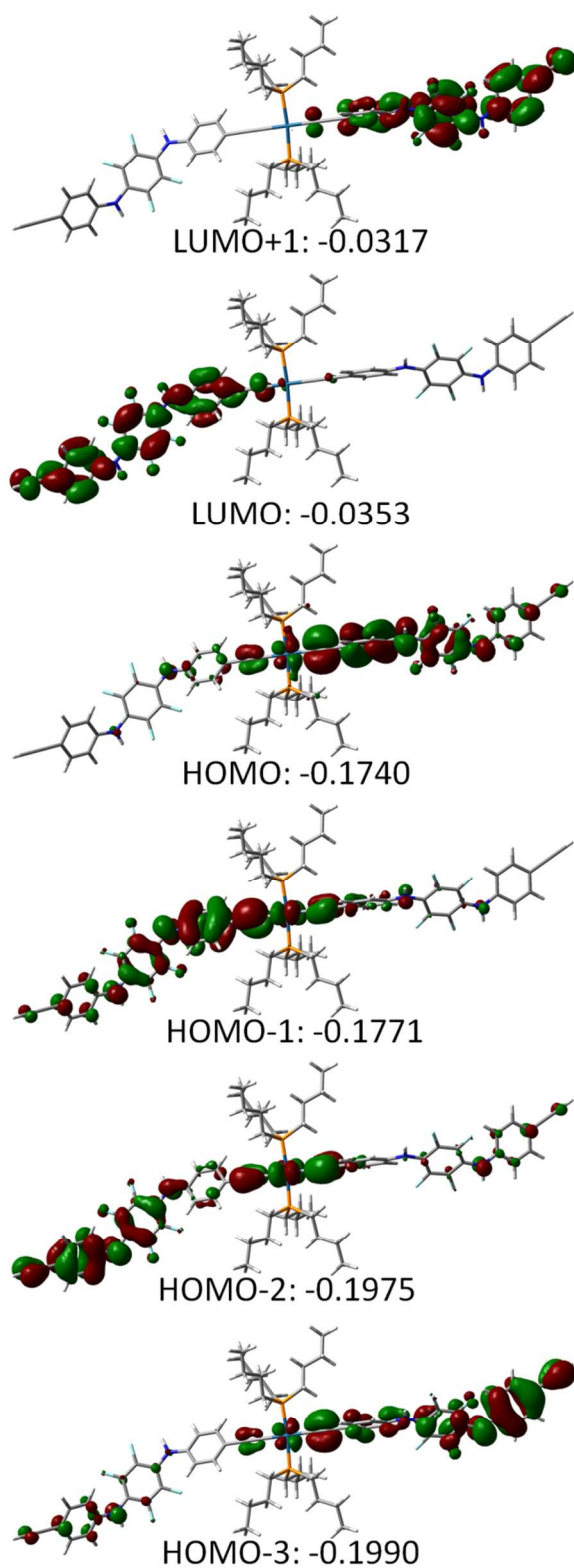


Figure S13. Representation of the frontier MOs of the model $[\text{PtL}_2]\mathbf{b}'$. The units are a.u.

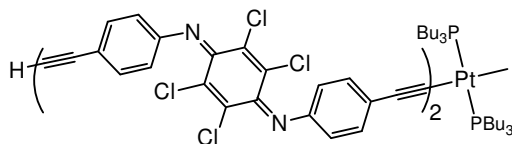


Table S30. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for the model **[PtL₂]**c****.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	12073	828	1.836	HOMO→LUMO (78)
2	12991	769	0.016	HOMO→L+1 (81)
3	14137	707	0.108	H-1→LUMO (77), HOMO→LUMO (10)
4	14791	676	0.109	H-1→L+1 (81)
5	15470	646	0.024	H-4→LUMO (57), H-4→L+1 (13), H-2→LUMO (16)
6	15609	640	0.016	H-3→LUMO (14), H-3→L+1 (59)
7	16795	595	0.001	H-4→LUMO (11), H-3→LUMO (16), H-2→LUMO (71)
8	17045	586	0.000	H-3→L+1 (14), H-2→L+1 (76)
9	18825	531	0.000	H-3→LUMO (62), H-3→L+1 (17)
10	19238	519	0.001	H-4→LUMO (12), H-4→L+1 (70), H-2→L+1 (11)
11	22641	441	0.289	H-6→LUMO (14), H-6→L+1 (52)
12	22762	439	0.001	H-5→LUMO (98)
13	23007	434	0.001	H-5→L+1 (98)
14	23123	432	0.084	H-7→LUMO (55), H-7→L+1 (12)
15	24016	416	0.000	H-9→LUMO (79), H-9→L+1 (15)
16	24041	415	0.000	H-8→LUMO (20), H-8→L+1 (75)
17	25267	395	0.001	H-6→LUMO (74), H-6→L+1 (19)
18	25368	394	0.062	H-15→LUMO (15), H-11→LUMO (54), H-11→L+1 (10)
19	25391	393	0.044	H-13→L+1 (24), H-10→LUMO (14), H-10→L+1 (49)
20	25882	386	0.013	H-7→LUMO (12), H-7→L+1 (63)

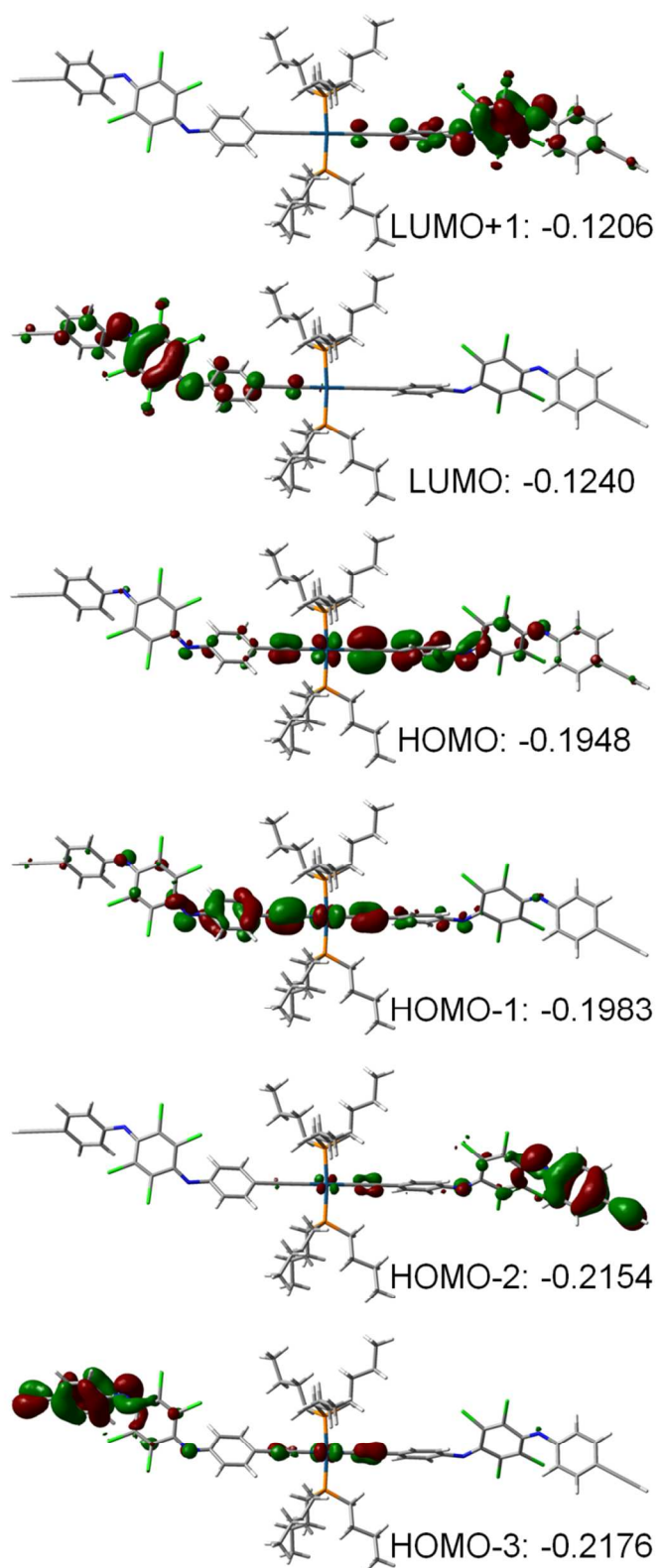


Figure S14. Representation of the frontier MOs of the model $[\text{PtL}_2]\text{c}$. The units are a.u.

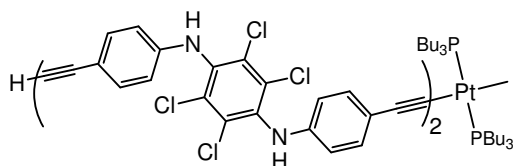


Table S31. TDDFT Calculated energy, position, oscillator strength (f) and major contributions of the first 20 singlet-singlet electronic transitions for the model **[PtL₂]c'**.

No.	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	f	Major contributions (%)
1	24700	405	0.575	HOMO→LUMO (88)
2	25672	389	0.010	HOMO→L+2 (89)
3	26515	377	0.876	H-1→L+1 (17), HOMO→L+1 (77)
4	26885	371	0.058	H-1→L+3 (25), HOMO→L+3 (72)
5	29084	343	0.068	H-1→LUMO (13), H-1→L+1 (51), HOMO→L+1 (12), HOMO→L+5 (13)
6	29168	342	0.141	HOMO→L+5 (73)
7	29412	340	0.243	H-1→LUMO (62), H-1→L+1 (14)
8	29537	338	0.035	H-1→L+3 (59), HOMO→L+3 (23)
9	29735	336	0.018	H-1→L+4 (26), HOMO→L+4 (60)
10	29918	334	0.497	HOMO→L+6 (69)
11	30295	330	0.004	H-3→L+2 (14), H-1→L+2 (69)
12	30568	327	0.167	H-3→LUMO (71)
13	31021	322	0.007	H-3→L+2 (69), H-1→L+2 (17)
14	31121	321	0.016	H-2→L+1 (38), H-2→L+3 (36)
15	31391	318	0.037	H-2→L+1 (39), H-2→L+3 (37)
16	32414	308	0.007	H-2→L+4 (10), H-1→L+4 (54), HOMO→L+4 (31)
17	32584	307	0.022	H-4→LUMO (46), H-4→L+1 (18), H-4→L+6 (12), H-2→LUMO (13)
18	33237	300	0.005	H-4→LUMO (12), H-4→L+1 (43), H-2→LUMO (24)
19	33357	299	0.004	H-1→L+5 (14), H-1→L+6 (67)
20	33669	297	0.000	HOMO→L+7 (77)

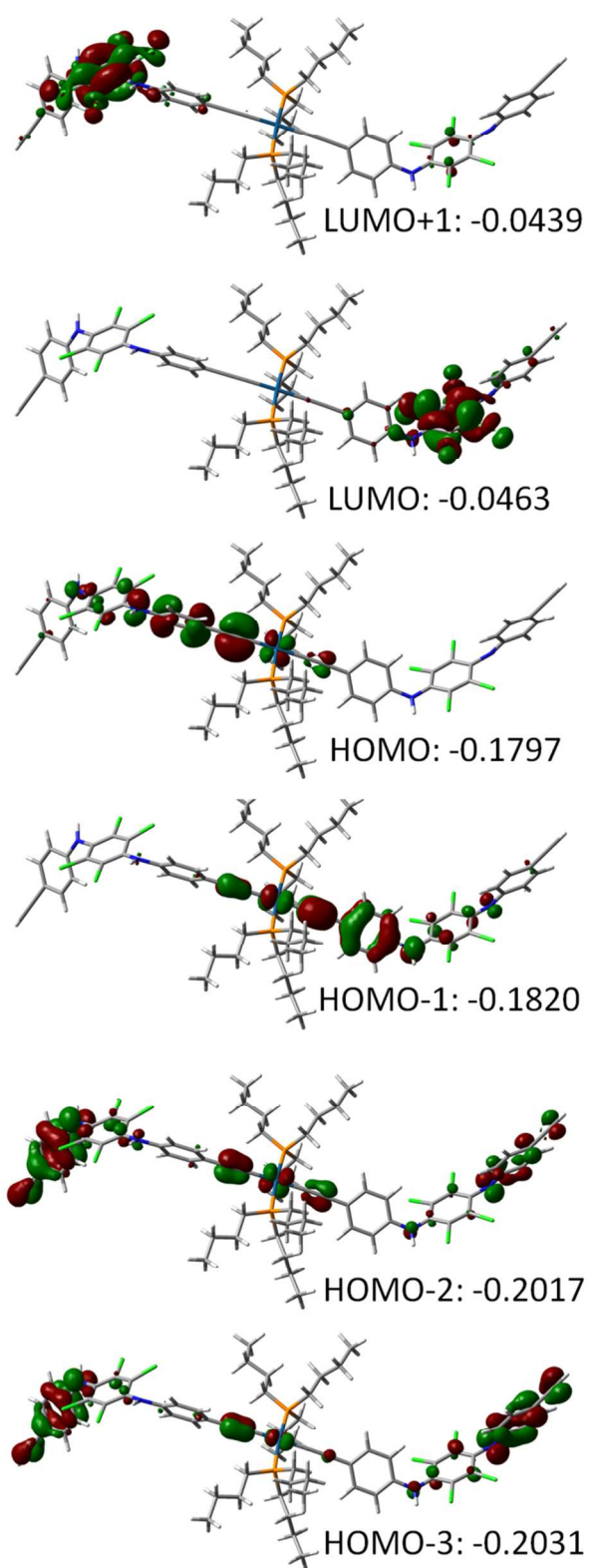


Figure S15. Representation of the frontier MOs of compound $[\text{PtL}_2]\text{c}'$. The units are a.u.

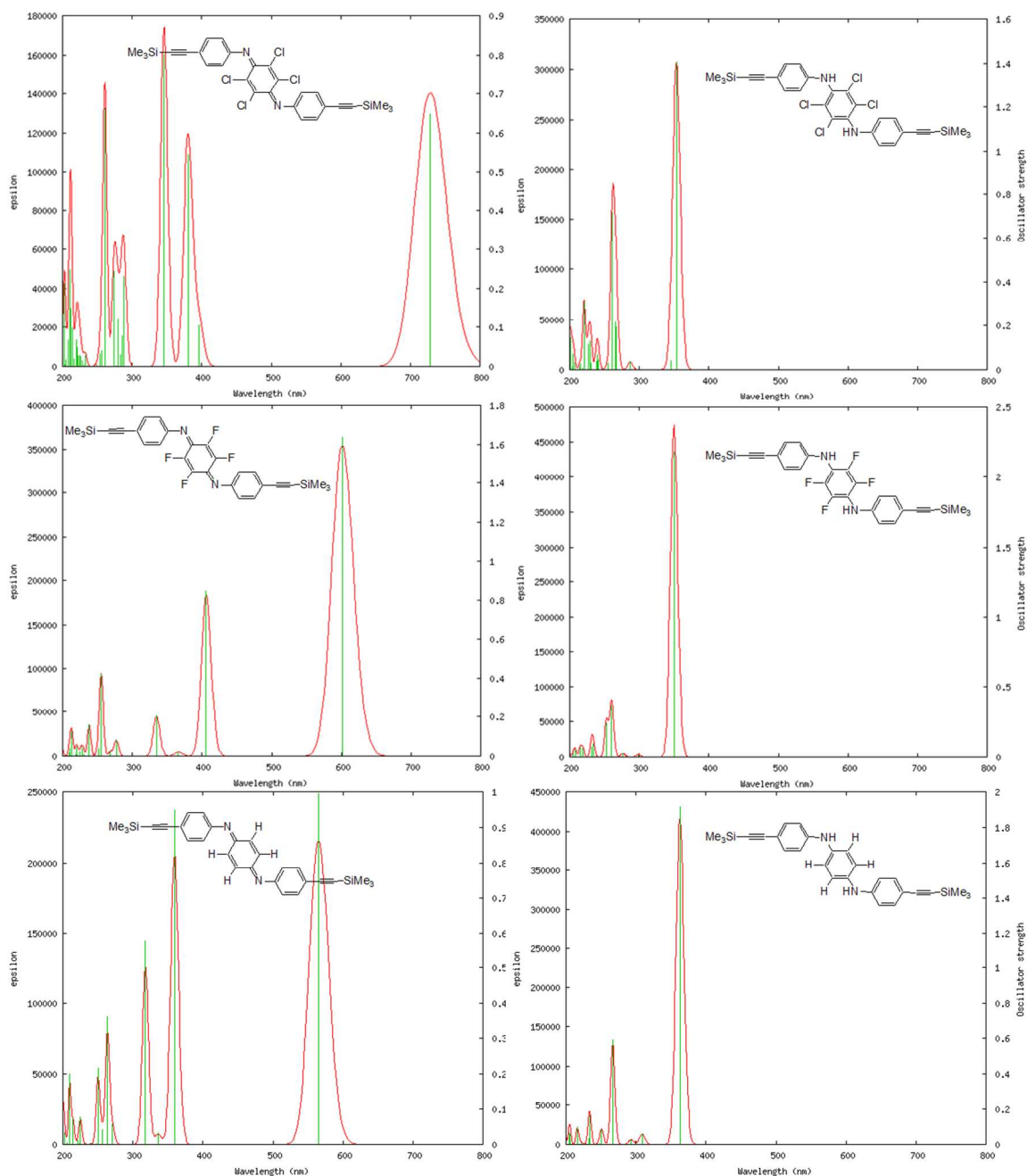


Figure S16. TDDFT calculated spectra of the spacers **4a,b,c** and **5a,b,c** using a THF polarizable continuum solvation model. The green lines represent the calculated 0-0 transitions. The red lines represent the same transitions except a thickness of 500 cm^{-1} is assigned give a shape to the absorption spectra. The vibronic components are not included.

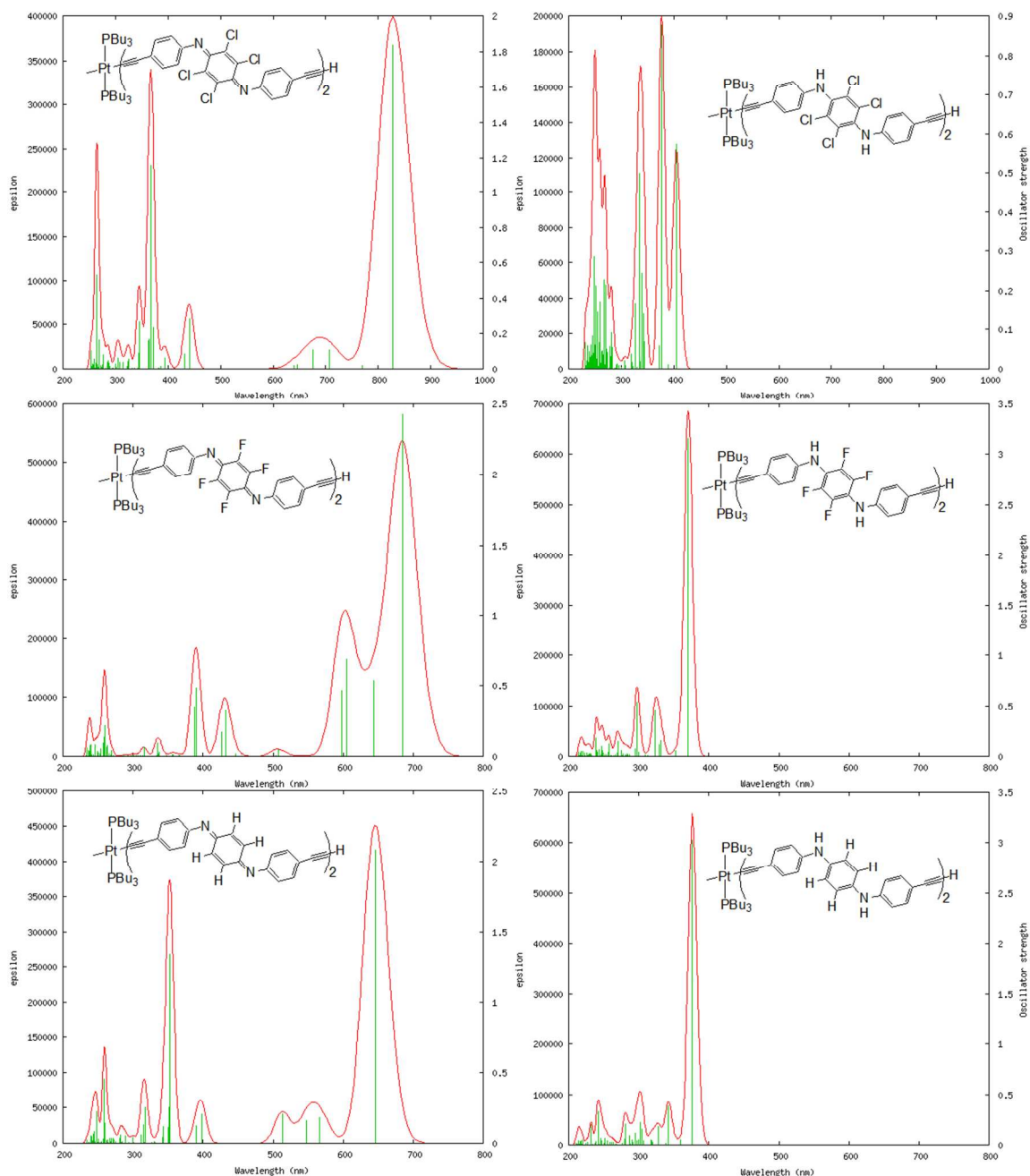


Figure S17. TDDFT calculated spectra of the Pt-containing models **[PtL₂]a,b,c** and **[PtL₂]a',b',c'** using a THF polarizable continuum solvation model. The green lines represent the calculated 0-0 transitions. The red lines represent the same transitions except a thickness of 500 cm⁻¹ is assigned give a shape to the absorption spectra. The vibronic components are not included.

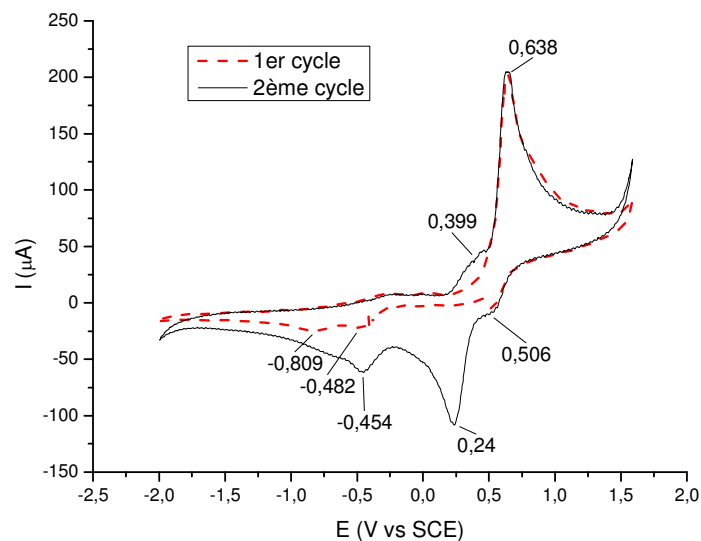
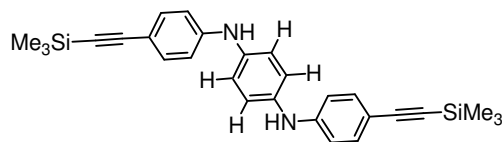


Figure S18. CV traces of compound **4a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

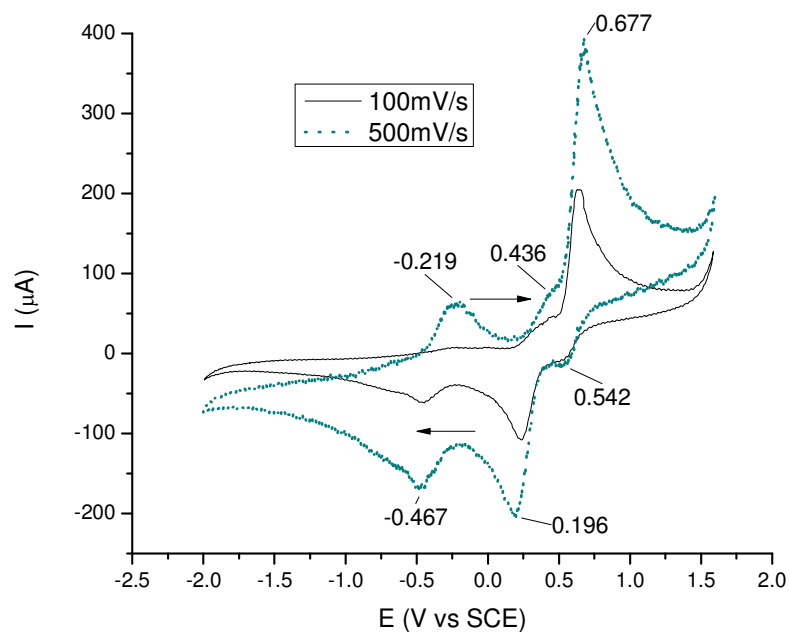


Figure S19. CV traces of compound **4a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black line) and 500mV/s (blue dotted line).

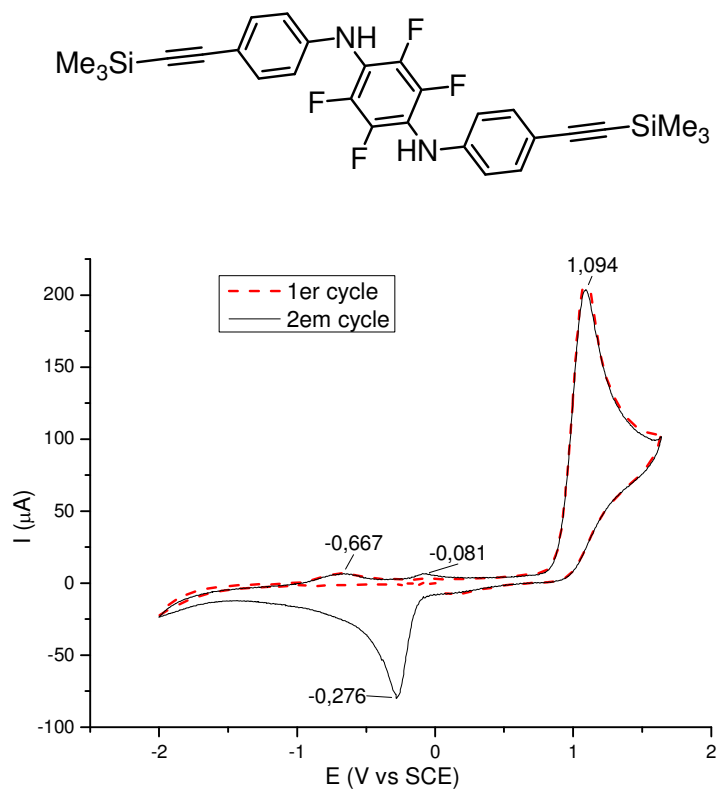


Figure S20. CV traces of compound **4b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

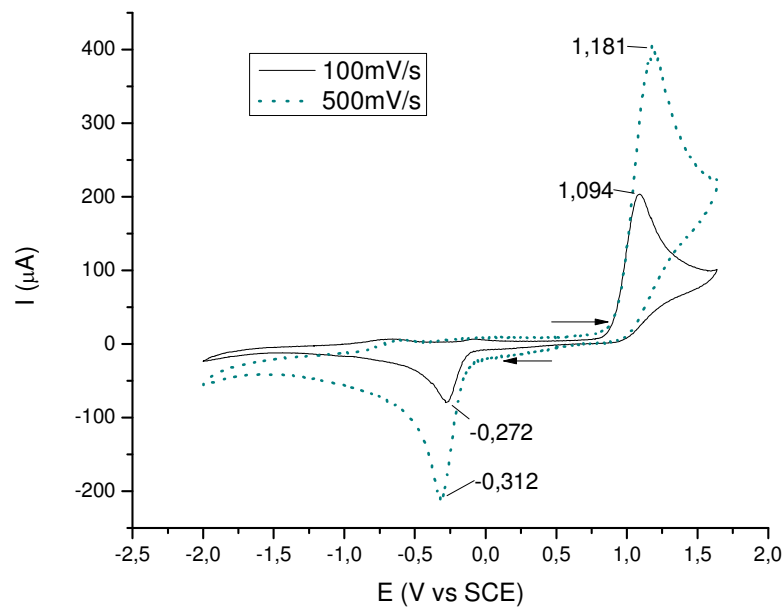


Figure S21. CV traces of compound **4b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

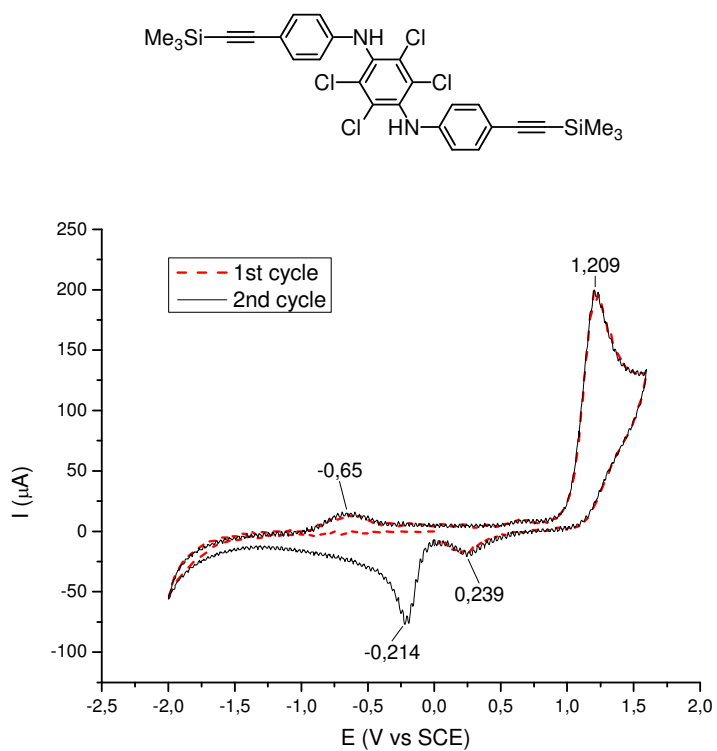


Figure S22. CV traces of compound **4c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s. 1st sweep in red broken line and 2nd sweep in black solid line.

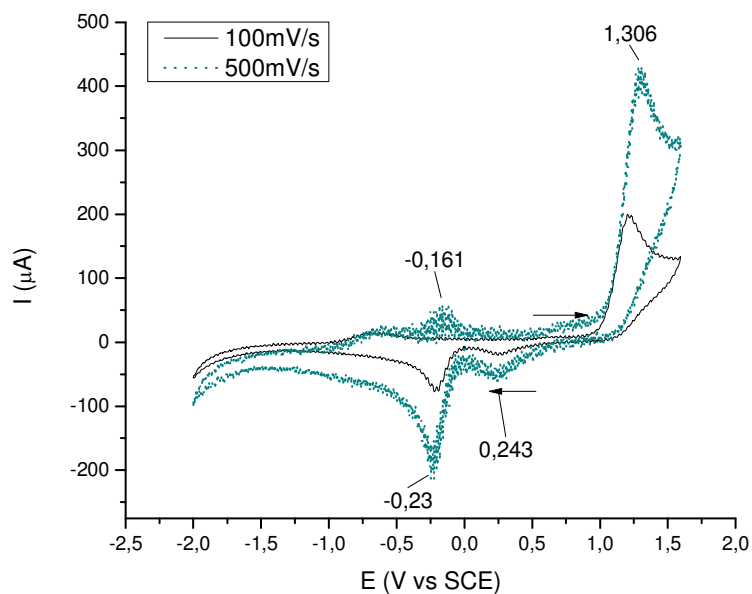


Figure S23. CV traces of compound **4c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

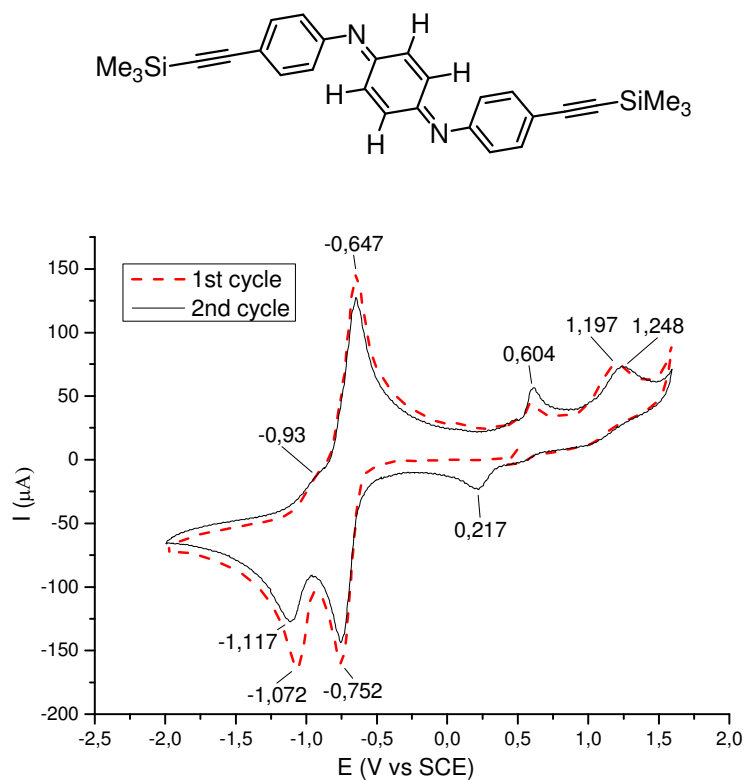


Figure S24. CV traces of compound **5a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

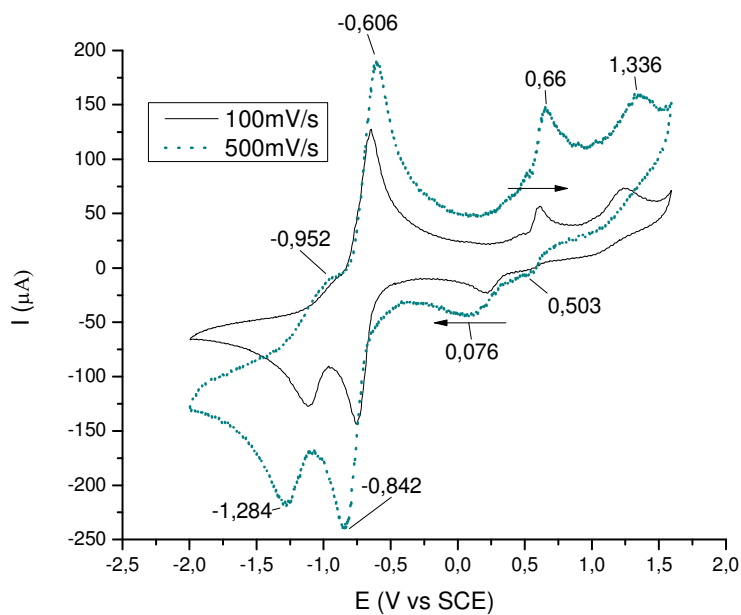


Figure S25. CV traces of compound **5a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

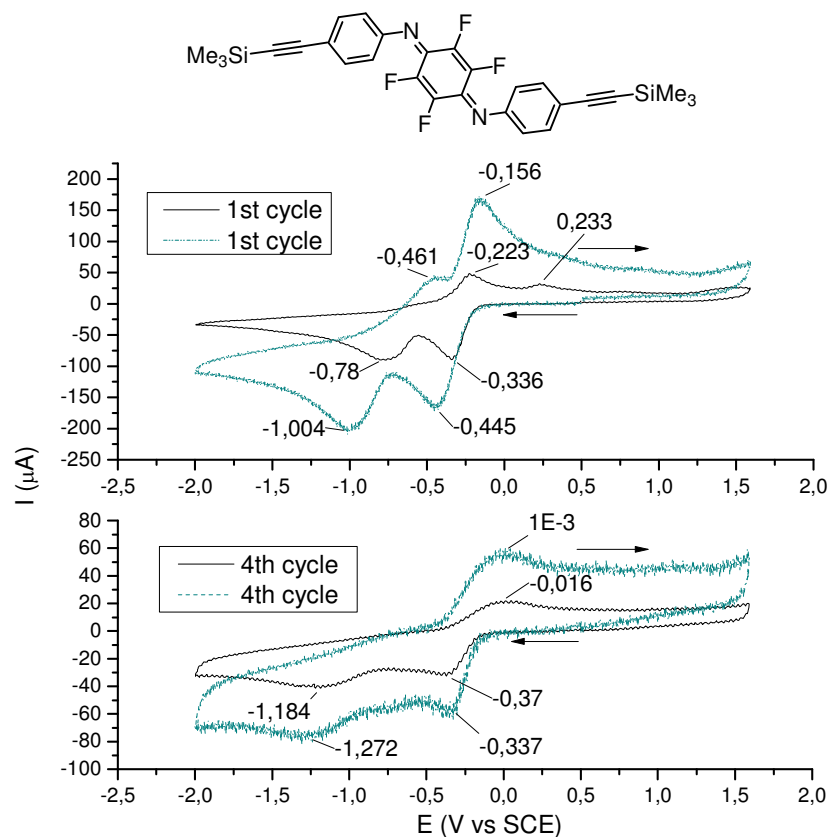


Figure S26. CV traces of compound **5b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black line) and 500mV/s (turquoise dotted line).

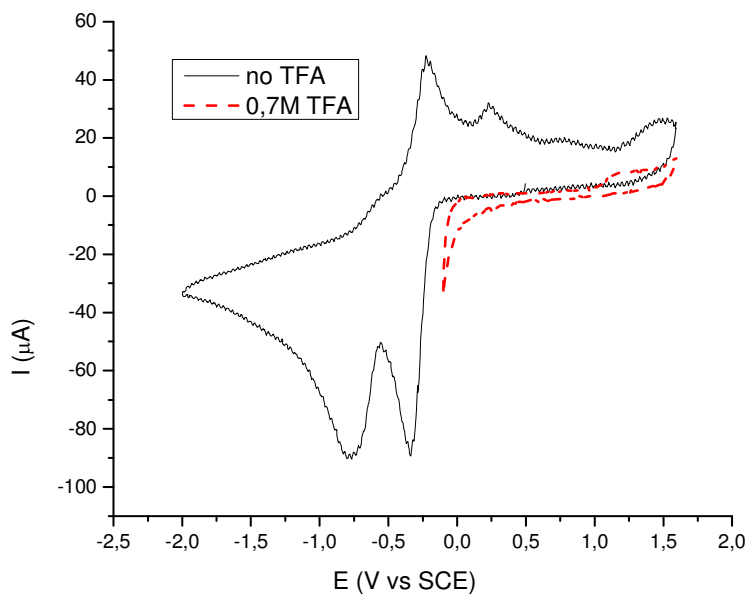


Figure S27. CV traces of compound **5b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; red dot line) and without acid (black line).

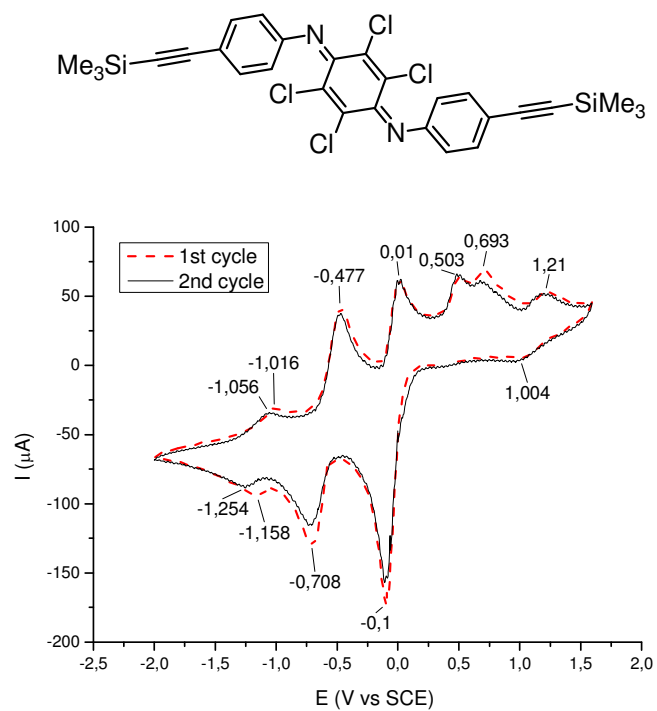


Figure S28. CV traces of compound **5c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

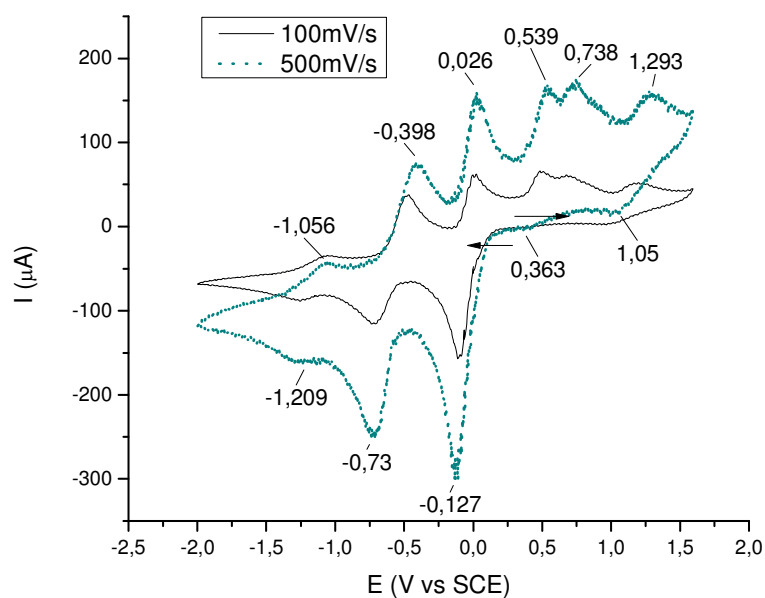


Figure S29. CV traces of ligand **5c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

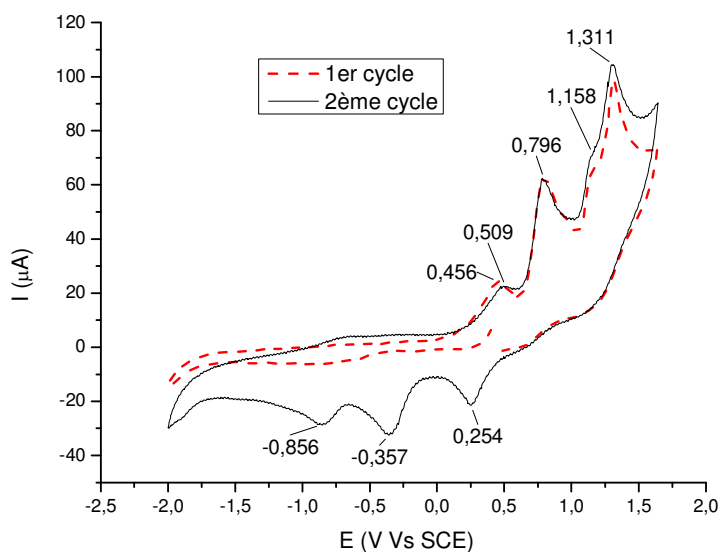
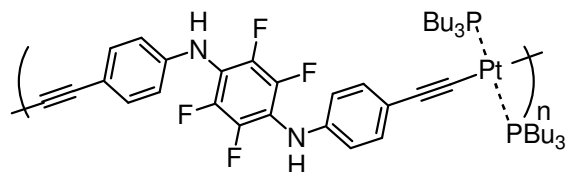


Figure S30. CV of polymer **8b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

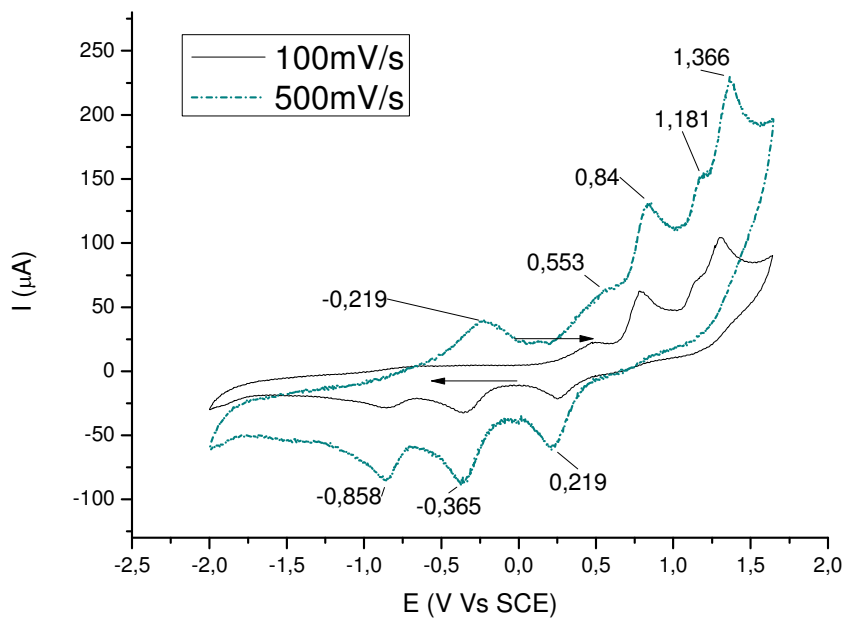


Figure S31. CV traces of polymer **8b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

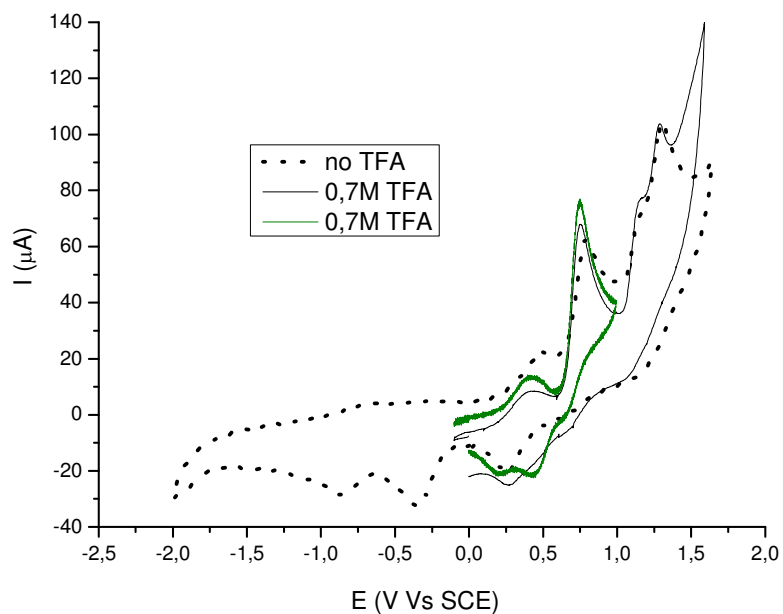


Figure S32. CV traces of polymer **8b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; solid lines) and without acid (black dotted line).

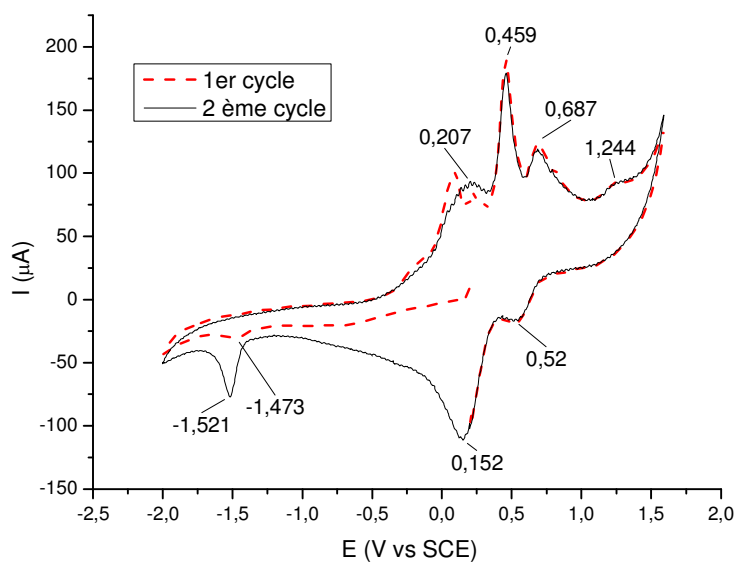
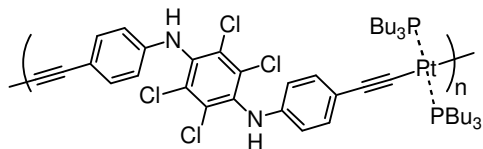


Figure S33. CV traces of polymer **8c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

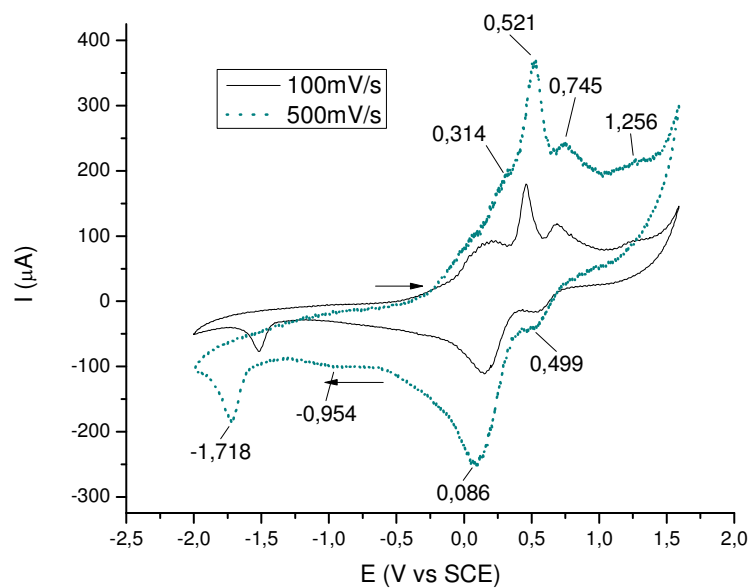


Figure S34. CV traces of polymer **8c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

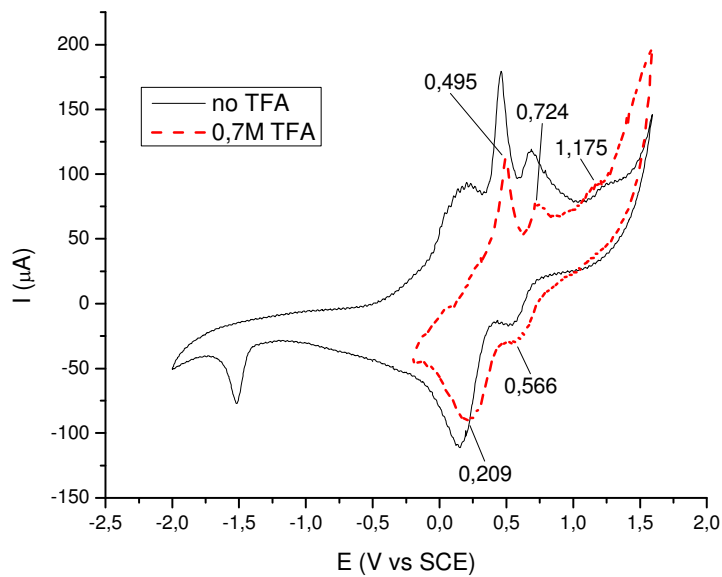


Figure S35. CV traces of polymer **8c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; broken line) and without acid (black line).

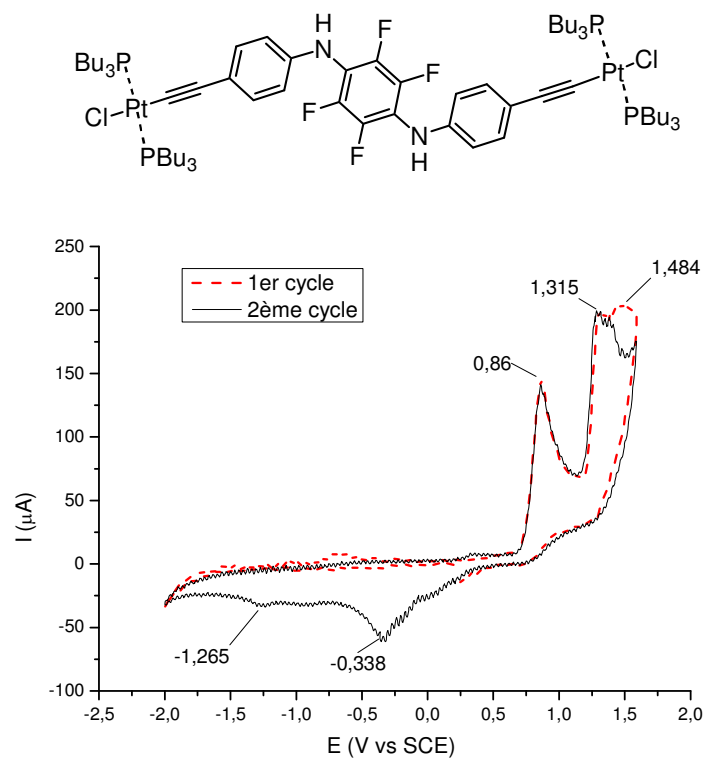


Figure S36. CV traces of model compound **9b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black solid line).

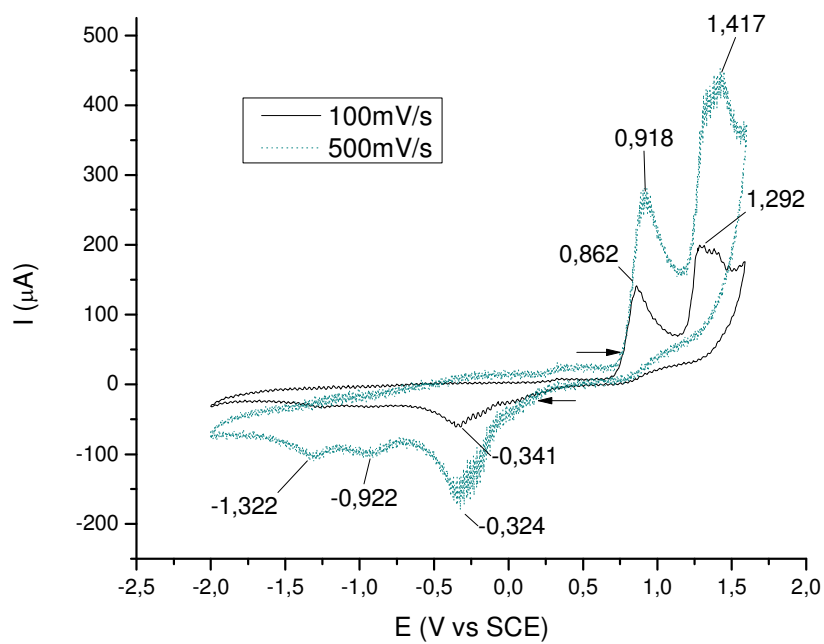


Figure S37. CV traces of model compound **9b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

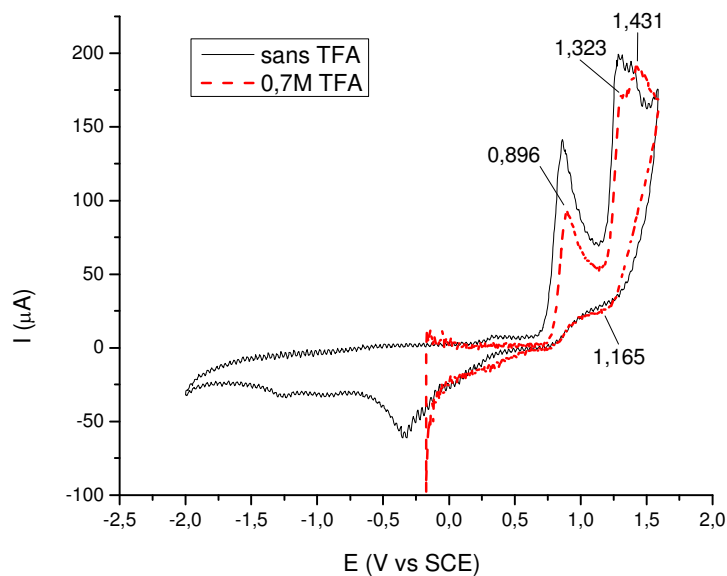


Figure S38. CV traces of model compound **9b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; red broken line) and without acid (black line).

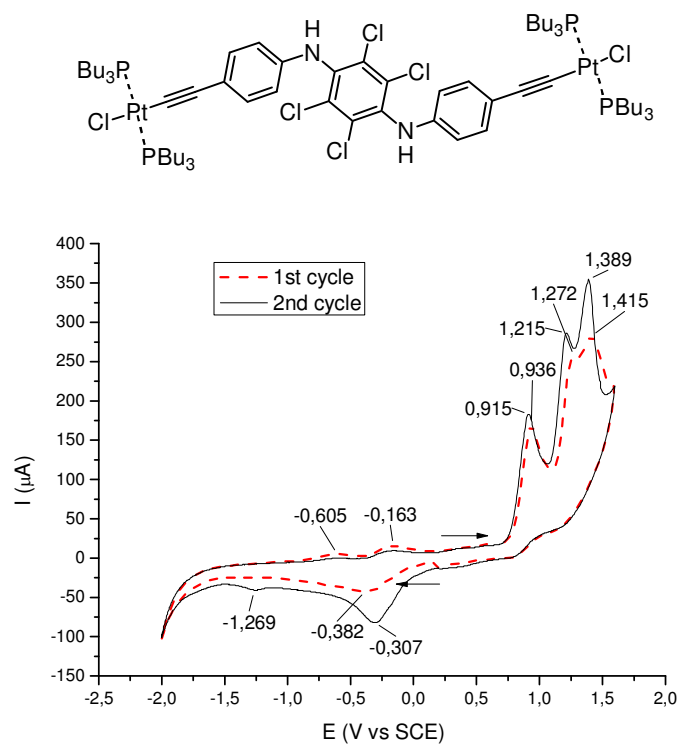


Figure S39. CV traces of model compound **9c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

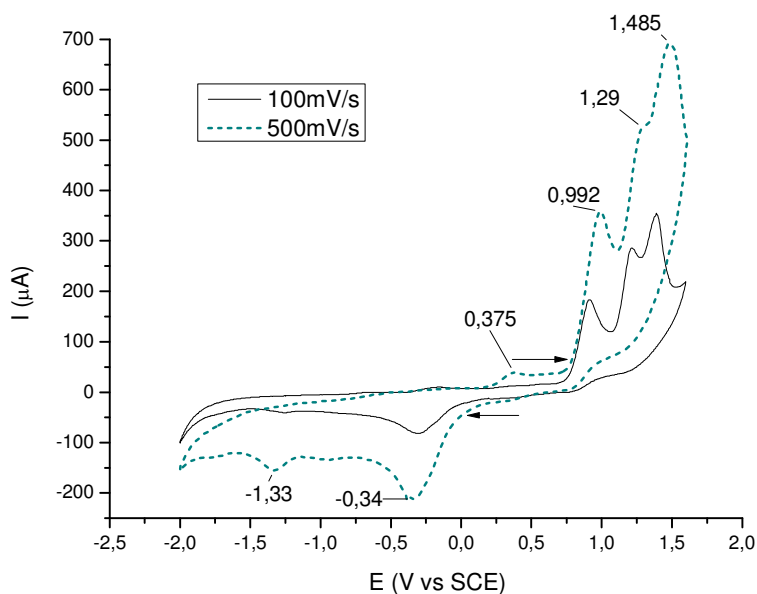


Figure S40. CV traces of model compound **9c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

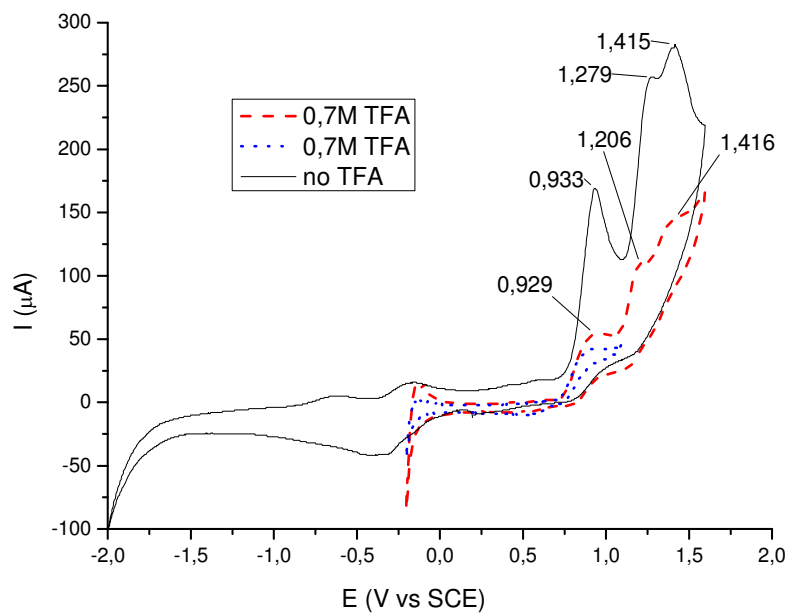


Figure S41. CV traces of model compound **9c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; broken lines) and without acid (black line).

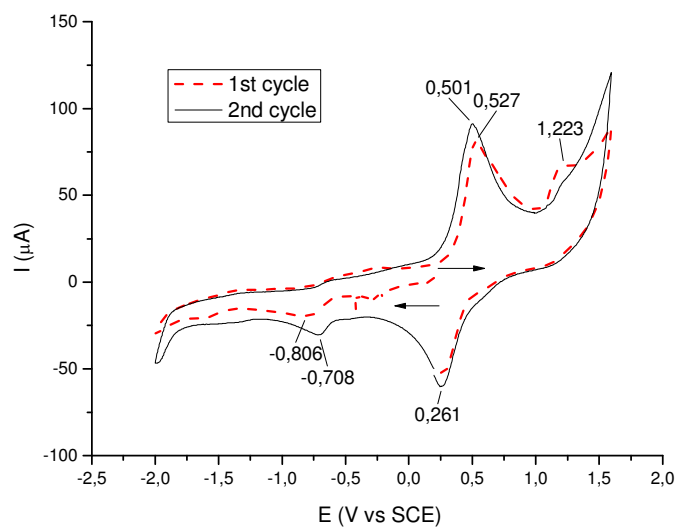
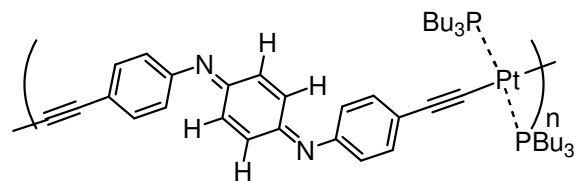


Figure S42. CV traces of polymer **10a**, 4mM in DMF containing 0,1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep in (black line).

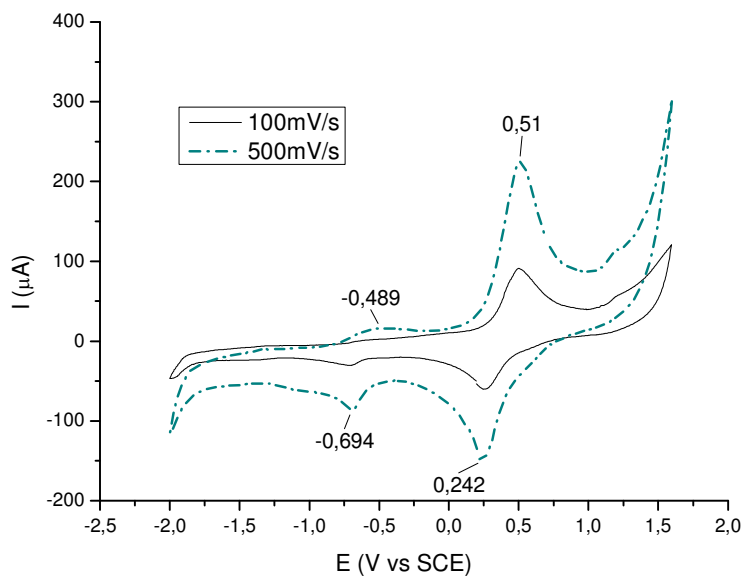


Figure S43. CV traces of polymer **10a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black) and 500mV/s (turquoise).

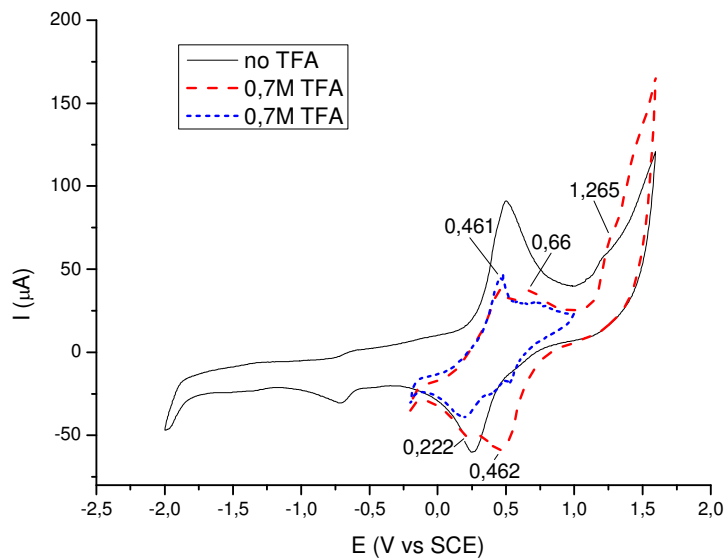


Figure S44. CV traces of polymer **10a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; broken lines) and without acid (black line).

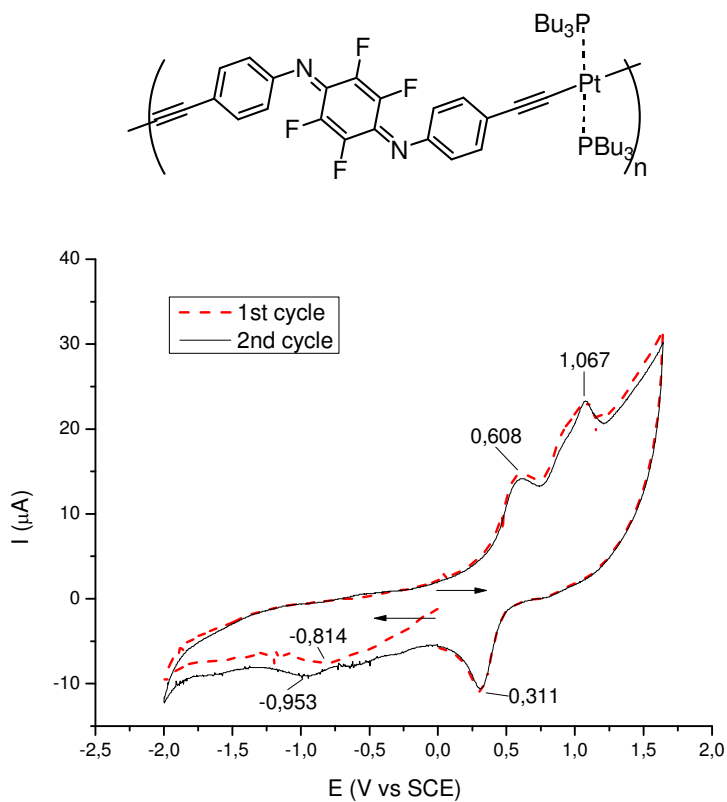


Figure S45. CV traces of polymer **10b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s. 1st sweep (red broken line) and 2nd sweep (black line).

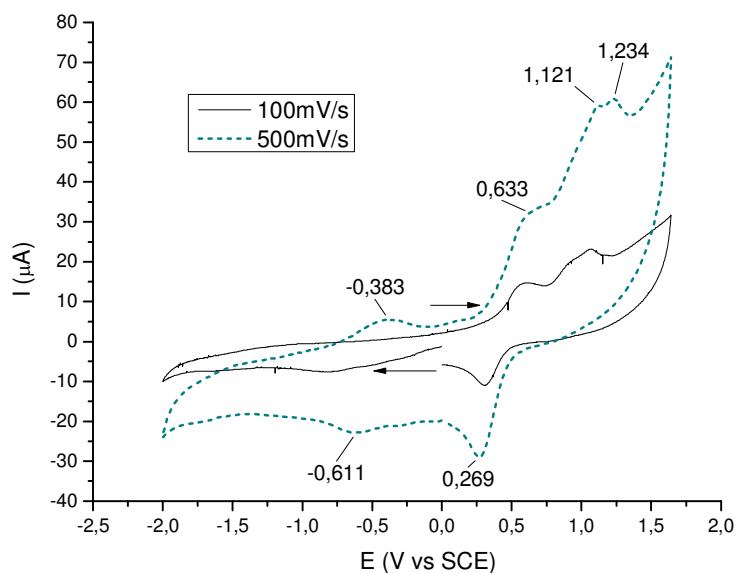


Figure S46. CV traces of polymer **10b**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black line) and 500mV/s (blue broken line).

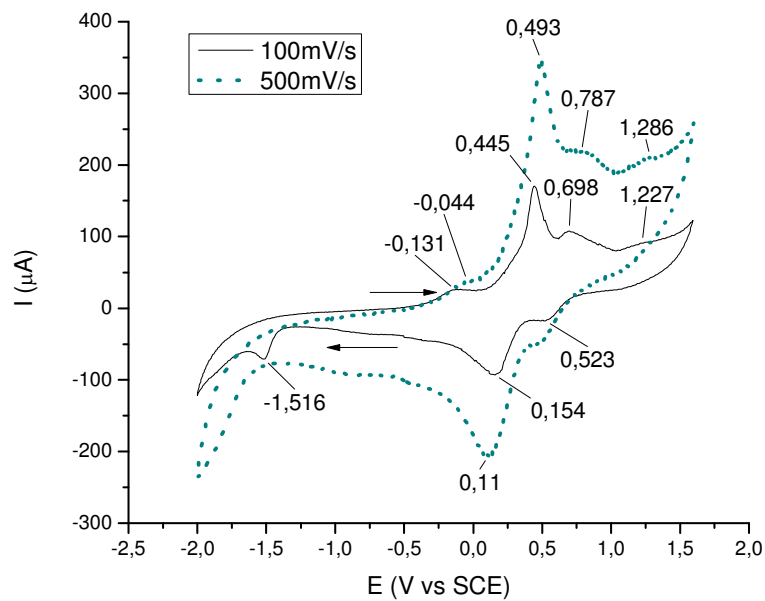
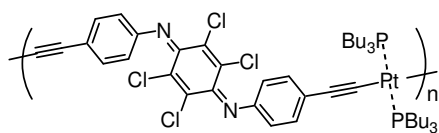


Figure S47. CV traces of polymer **10c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black and) 500mV/s (turquoise dots line).

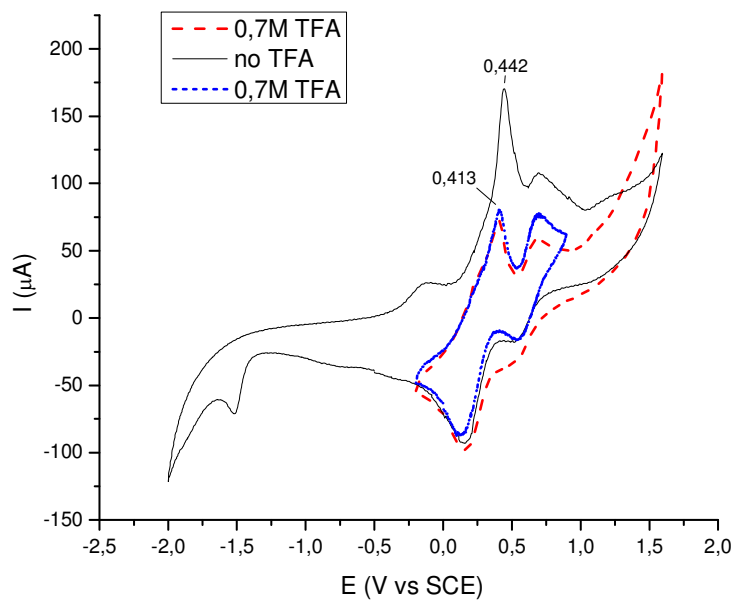


Figure S48. CV traces of polymer **10c**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA; broken lines) and without acid (black line).

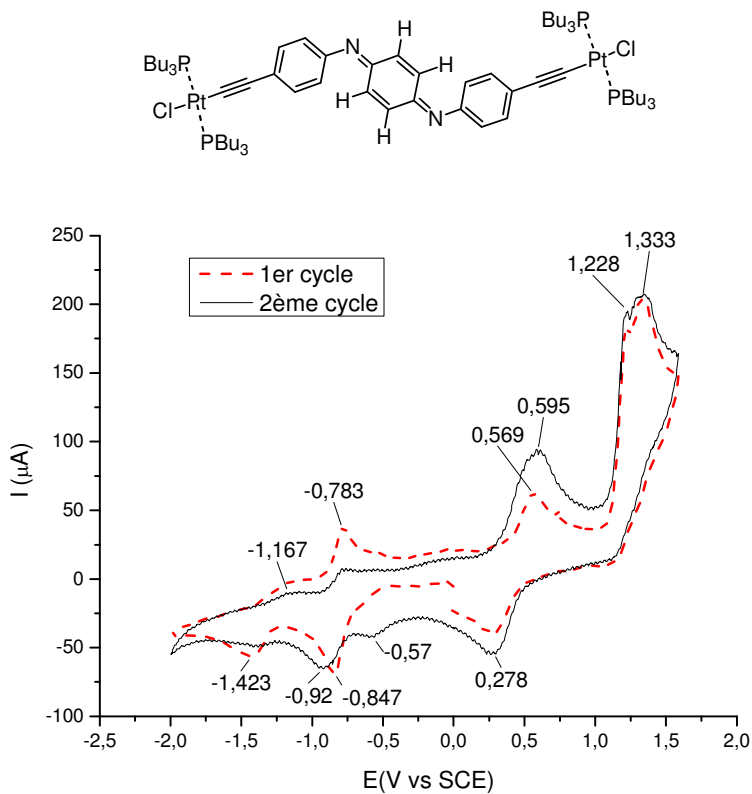


Figure S49. CV traces compound **11a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s 1st sweep (red broken line) and 2nd sweep (black line).

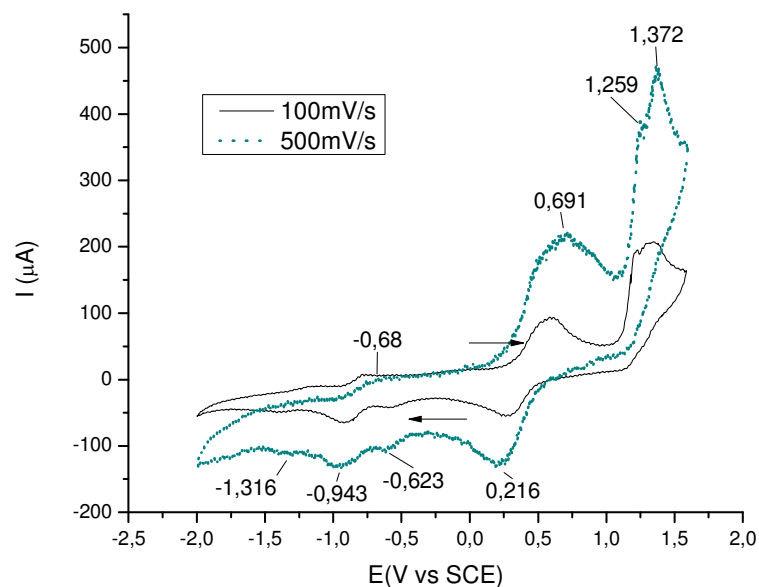


Figure S50. CV traces of model compound **11a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s (black line) and 500mV/s (turquoise dotted line).

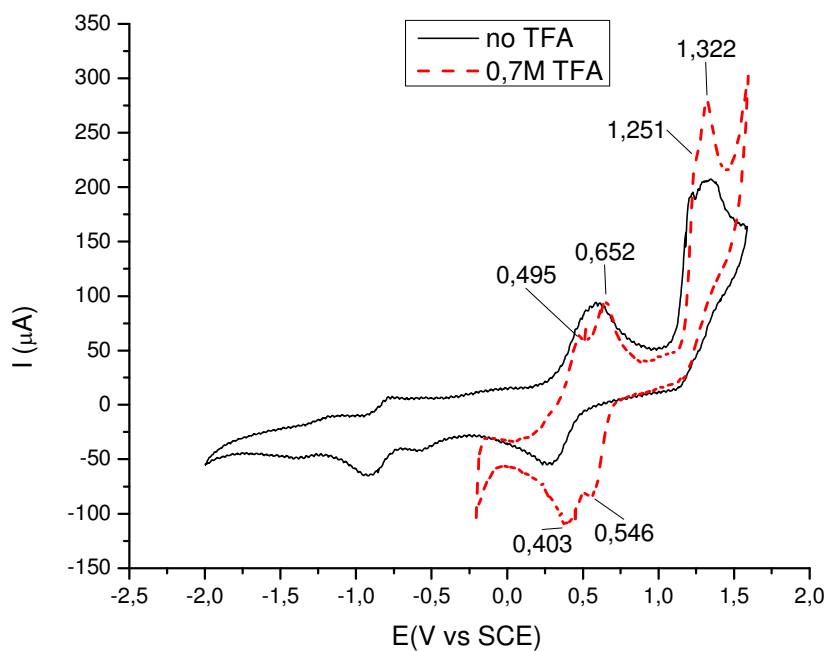


Figure S51. CV traces of model compound **11a**, 4mM in DMF containing 0.1M of TBAPF₆ at 100mV/s, with acid (0.7M TFA red broken line) and without acid (black line).

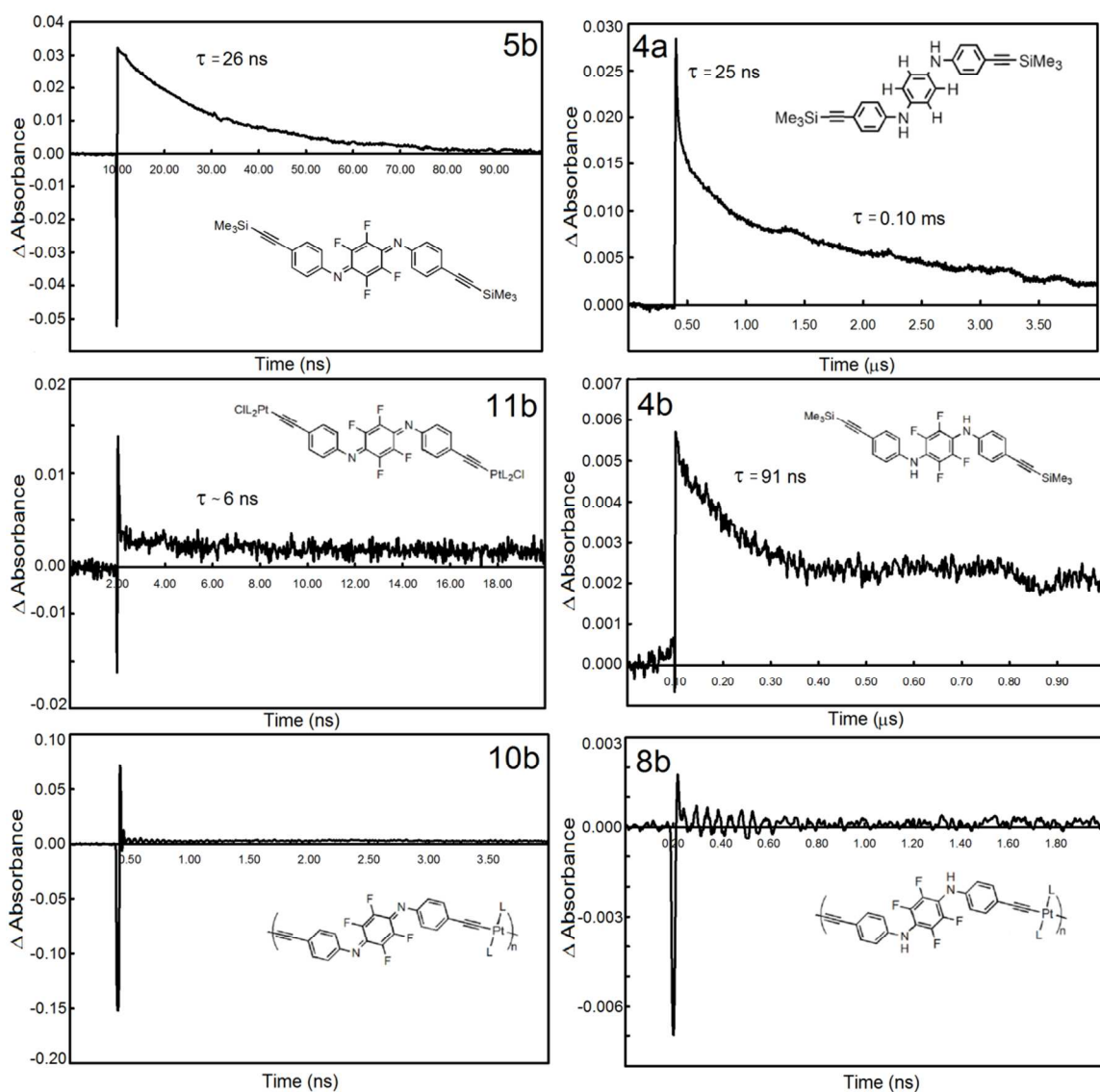


Figure S52. Comparison of the transient decay curves of **4a**, **4b**, **5b**, **8b**, **10b** and **11b** at 298 K in degassed 2MeTHF. $\lambda_{\text{exc}} = 355$ nm. Please note that **10b** is its mixed-valence form.

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