

Supporting Information

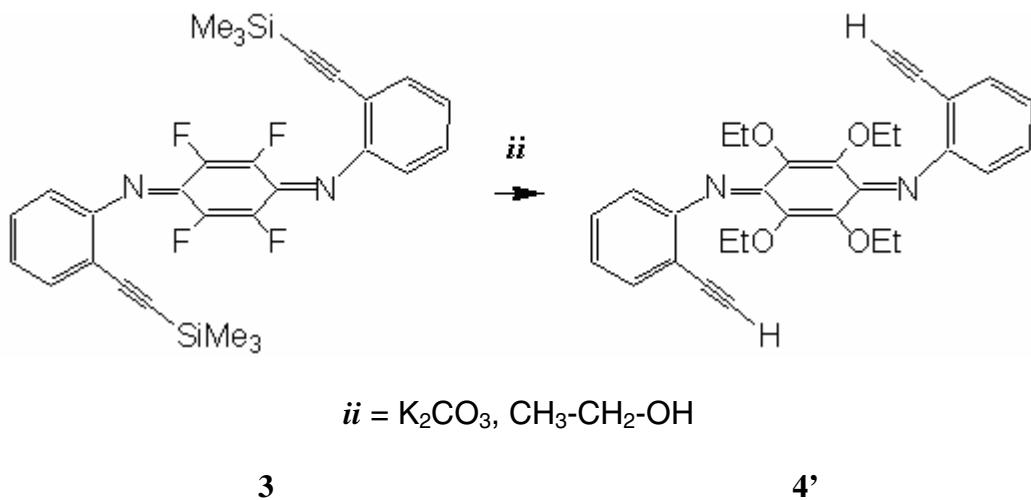
π -Conjugated Oligomers and Polymers of *cis*- and *trans*-Platinum(II)-*para*- and *ortho*-Bis(ethynylbenzene)quinone Diimine: Astonishing Materials With Only Upper Excited State Emissions

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Synthesis of 4'.



Bis(ortho-ethynylbenzene)-2,3,5,6-tetraethoxyquinone diimine (4') 0.0922 g (0.176 mmol) of **3** was placed in a 250 mL round-bottomed flask and 7 g of K_2CO_3 was added to the flask as well as 180 mL of $\text{CH}_3\text{CH}_2\text{OH}$. The reaction was stirred under Ar overnight until the solution had become orange. The excess K_2CO_3 was filtered and the remaining solvent was evaporated and the product then dissolved in CH_2Cl_2 and washed 3 times with water. The DCM solution was then dried with K_2CO_3 and filtered. Red crystals were obtained by slow evaporation a CH_2Cl_2 solution. Yield: 38% (0.0322). ^1H NMR δ (CD_2Cl_2): 7.42 (d, 4H, CH aro., $J_{\text{H-H}}=7.75$); 7.27 (t, 4 H, CH aro., $^3J_{\text{H-H}}=7.70$); 6.96 (t, 4H, CH aro., $^3J_{\text{H-H}}=7.57$); 6.72 (d, 4H, CH aro., $J_{\text{H-H}}=8.06$); 3.81 (broad m, 8H, CH_2); 3.13 (s, 2 H, CH); 1.52 (s, 12 H, CH_3) ppm. IR (KBr) δ : 2099 cm^{-1} ($\text{C}\equiv\text{C}$). Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4 \bullet 0.04 \text{H}_2\text{O}$ (482.57): C, 74.56; H, 6.27; N, 5.80. Found: C, 74.55; H, 6.52; N, 5.84. Mass spectrometry (mass m/e): 482 + 2H (M+).

Table S1. Crystals data and structure refinements:

	1	2
Empirical formula	C ₃₄ H ₅₂ P ₂ Pt	C ₃₄ H ₅₂ P ₂ Pt
Formula weight	717.79	717.79
Acquisition temperature (K)	293 (2)	293 (2)
Wavelength (Å)	1.54176	1.54176
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/n
Unit cell dimensions (Å)	a = 8.950 (7) b = 22.465 (10) c = 9.389 (8) 90° 110.83 (7)° 90°	a = 12.376 (8) b = 10.107 (7) c = 14.314 (13) 90° 103.83 (6)° 90°
Volume (Å ³)	1765 (2)	1739 (2)
Z	2	2
Density (calculated) (Mg/m ³)	1.351	1.371
Absorption coefficient (mm ⁻¹)	8.416	8.541
F(000)	728	728
Crystal size (mm ³)	0.40 X 0.20 X 0.10	0.20 X 0.20 X 0.30
Crystal color	Colorless	Yellow
Theta range	3.94 to 69.95°	4.25 to 69.78°
Index ranges	-10 ≤ h ≤ 10, 0 ≤ k ≤ 27, 0 ≤ l ≤ 11	-15 ≤ h ≤ 14, 0 ≤ k ≤ 12, 0 ≤ l ≤ 17
Reflections collected	3261	3184
Independent reflections	3261 [R(int) = 0.0000]	3184 [R(int) = 0.0000]
Completeness to theta = 70.04°	97.6%	96.8%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.1691 and 0.0445	0.1596 and 0.0506
Refinement method	Full matrix least squares on F ²	Full matrix least squares on F ²
Data / restraints / parameters	3261 / 1 / 178	3184 / 0 / 170
Goodness of fit on F ²	1.089	1.147
Final R indices [I > 2 sigma (I)]	R1 = 0.0556, wR ² = 0.1514	R1 = 0.0689, wR ² = 0.2159
R indices (all data)	R1 = 0.0828, wR ² = 0.1638	R1 = 0.0872, wR ² = 0.2306
Absolute structure parameter	Irrelevant	Irrelevant
Extinction coefficient	0.0041 (3)	0.0102 (9)
Largest diff. Peak and hole (e/Å ³)	1.322 and -1.652	1.064 and -2.279

Table 1. Crystals data and structure refinements (continued)...

Identification code	3	4
Empirical formula	$C_{28}H_{26}F_4N_2Si_2$	$C_{26}H_{22}N_2O_4$
Formula weight	522.69	426.46
Acquisition temperature (K)	293 (2)	198 (2)
Wavelength (Å)	1.54176	1.54176
Crystal system	Monoclinic	Orthorhombic
Space group	I 2/a	P21ab
Unit cell dimensions (Å)	$a = 28.982 (8)$ $b = 9.341 (9)$ $c = 33.031 (8)$ 90° $107.76 (8)^\circ$ 90°	$a = 8.065 (4)$ $b = 10.516 (12)$ $c = 25.711 (7)$ 90° 90° 90°
Volume (Å ³)	8515 (9)	2181 (3)
Z	12	4
Density (calculated) (Mg/m ³)	1.223	1.299
Absorption coefficient (mm ⁻¹)	1.524	0.718
F(000)	3264	896
Crystal size (mm ³)	0.40 X 0.25 X 0.20	0.40 X 0.40 X 0.30
Crystal color	Violet	Red
Theta range	2.81 to 74.73 ⁰	1.72 to 69.78 ⁰
Index ranges	-35 ≤ h ≤ 33, 0 ≤ k ≤ 11, 0 ≤ l ≤ 41	0 ≤ h ≤ 9, 0 ≤ k ≤ 12, 0 ≤ l ≤ 31
Reflections collected	8070	2189
Independent reflections	8070 [R(int) = 0.0000]	2189 [R(int) = 0.0000]
Completeness to theta = 70.04 ⁰	92.4%	98.6%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.8138 and 0.7270	0.9945 and 0.8048
Refinement method	Full matrix least squares on F ²	Full matrix least squares on F ²
Data / restraints / parameters	8070 / 9 / 500	2189 / 1 / 294
Goodness of fit on F ²	0.839	0.950
Final R indices [I > 2 sigma (I)]	R1 = 0.0958, wR ² = 0.2079	R1 = 0.0648, wR ² = 0.1488
R indices (all data)	R1 = 0.3185, wR ² = 0.2763	R1 = 0.1607, wR ² = 0.1828
Absolute structure parameter	Irrelevant	-0.2 (7)
Extinction coefficient	0.00104 (9)	0.0029 (9)
Largest diff. Peak and hole (e/Å ³)	0.268 and -0.262	0.217 and -0.166

Table 1. Crystals data and structure refinements (contd.)

	4'	5
Empirical formula	$C_{30}H_{30}N_2O_4$	$C_{28}H_{26}F_4N_2Si_2$
Formula weight	482.56	522.69
Acquisition temperature (K)	198 (2)	293 (2)
Wavelength (Å)	1.54176	1.54176
Crystal system	Monoclinic	Monoclinic
Space group	Pc	P21/C
Unit cell dimensions (Å)	$a = 7.941$ (4) $b = 6.900$ (6) $c = 23.58$ (4) 90° 99.54 (9) $^\circ$ 90°	$a = 5.867$ (3) $b = 5.788$ (3) $c = 40.37$ (2) 90° 91.53 (4) $^\circ$ 90°
Volume (Å ³)	1274 (2)	1370.5 (13)
Z	2	2
Density (calculated) (Mg/m ³)	1.258	1.267
Absorption coefficient (mm ⁻¹)	0.672	1.578
F(000)	512	544
Crystal size (mm ³)	0.40 X 0.40 X 0.40	0.30 X 0.30 X 0.02
Crystal color	Red	Violet
Theta range	3.80 to 70.26 $^\circ$	2.19 to 70.00 $^\circ$
Index ranges	-9 \leq h \leq 9, 0 \leq k \leq 8, 0 \leq l \leq 28	-7 \leq h \leq 7, 0 \leq k \leq 7, 0 \leq l \leq 49
Reflections collected	2328	2460
Independent reflections	2328 [R(int) = 0.0000]	2460 [R(int) = 0.0000]
Completeness to theta = 70.04 $^\circ$	95.8%	95.4%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.6800 and 0.4400	0.7976 and 0.9912
Refinement method	Full matrix least squares on F ²	Full matrix least squares on F ²
Data / restraints / parameters	2328 / 2 / 330	2460 / 0 / 167
Goodness of fit on F ²	1.026	0.921
Final R indices [I > 2 sigma (I)]	R1 = 0.0617, wR ² = 0.1751	R1 = 0.0887, wR ² = 0.2274
R indices (all data)	R1 = 0.0863, wR ² = 0.1929	R1 = 0.2223, wR ² = 0.2867
Absolute structure parameter	Irrelevant	Irrelevant
Extinction coefficient	Irrelevant	0.0048 (11)
Largest diff. Peak and hole (e/Å ³)	0.293 and -0.220	0.265 and -0.262

Table 1. Crystals data and structure refinements (contd.)

Identification code	6	7
Empirical formula	C ₂₆ H ₂₂ N ₂ O ₄	C ₃₈ H ₅₀ N ₂ O ₄ P ₂ Pt
Formula weight	426.47	855.86
Acquisition temperature (K)	198 (2)	198 (2)
Wavelength (Å)	1.54176	1.54176
Crystal system	Monoclinic	Triclinic
Space group	P21	P1
Unit cell dimensions (Å)	a = 11.732 (8) b = 7.499 (9) c = 13.186 (19) 90° 109.86 (8)° 90°	a = 9.818 (4) b = 11.012 (5) c = 18.127 (11) 87.29 (5)° 76.40 (4)° 77.93 (4)°
Volume (Å ³)	1091 (2)	1862.8 (16)
Z	2	2
Density (calculated) (Mg/m ³)	1.298	1.526
Absorption coefficient (mm ⁻¹)	0.717	8.178
F(000)	448	864
Crystal size (mm ³)	0.40 X 0.30 X 0.30	0.40 X 0.30 X 0.10
Crystal color	Orange	Purple
Theta range	3.56 to 70.22°	2.51 to 70.04°
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16	-11 ≤ h ≤ 11, 0 ≤ k ≤ 13, -21 ≤ l ≤ 22
Reflections collected	2141	6396
Independent reflections	2141 [R(int) = 0.0000]	6396 [R(int) = 0.0000]
Completeness to theta = 70.04°	95.2%	90.6%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9979 and 0.8803	0.9957 and 0.3639
Refinement method	Full matrix least squares on F ²	Full matrix least squares on F ²
Data / restraints / parameters	2141 / 1 / 295	6396 / 0 / 629
Goodness of fit on F ²	1.064	1.196
Final R indices [I > 2 sigma (I)]	R1 = 0.0573, wR ² = 0.1478	R1 = 0.0970, wR ² = 0.2521
R indices (all data)	R1 = 0.0758, wR ² = 0.1591	R1 = 0.1118, wR ² = 0.2706
Absolute structure parameter	0.0000 (17)	0.22 (6)
Extinction coefficient	0.0027 (8)	0.0087 (9)
Largest diff. Peak and hole (e/Å ³)	0.279 and -0.263	3.096 and -2.484

Table 1. Crystals data and structure refinements (contd.)

Identification code	8	9
Empirical formula	C ₂₆ H ₂₀ N ₂ O ₄	C ₅₀ H ₈₀ Cl ₂ N ₂ O ₄ P ₄ Pd ₂
Formula weight	424.46	1180.84
Acquisition temperature (K)	293 (2)	293 (2)
Wavelength (Å)	1.54176	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21
Unit cell dimensions (Å)	$a = 7.158$ (6) $b = 13.803$ (9) $c = 21.535$ (19) 90° 94.11 (8) $^\circ$ 90°	$a = 9.402$ (3) $b = 24.927$ (9) $c = 13.103$ (4) 90° 102.43 (3) $^\circ$ 90°
Volume (Å ³)	2122 (3)	2999 (2)
Z	4	2
Density (calculated) (Mg/m ³)	1.328	1.308
Absorption coefficient (mm ⁻¹)	0.737	0.834
F(000)	888	1224
Crystal size (mm ³)	0.45 X 0.25 X 0.20	0.45 X 0.20 X 0.15
Crystal color	Red	Purple
Theta range	3.81 to 70.77 $^\circ$	1.59 to 25.52 $^\circ$
Index ranges	-8 ≤ h ≤ 8, 0 ≤ k ≤ 16, 0 ≤ l ≤ 26	-11 ≤ h ≤ 11, 0 ≤ k ≤ 30, 0 ≤ l ≤ 15
Reflections collected	3893	5710
Independent reflections	3893 [R(int) = 0.0000]	5710 [R(int) = 0.0000]
Completeness to theta = (a) 70.04 $^\circ$, (b) 25.00	95.5% (a)	99.5% (b)
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9934 and 0.5183	0.9986 and 0.9209
Refinement method	Full matrix least squares on F ²	Full matrix least squares on F ²
Data / restraints / parameters	3893 / 0 / 294	5710 / 1 / 462
Goodness of fit on F ²	1.010	0.924
Final R indices [I > 2 sigma (I)]	R1 = 0.0787, wR ² = 0.2206	R1 = 0.0736, wR ² = 0.1494
R indices (all data)	R1 = 0.1462, wR ² = 0.2552	R1 = 0.1832, wR ² = 0.1771
Absolute structure parameter	Irrelevant	Irrelevant
Extinction coefficient	0.0066 (9)	Irrelevant
Largest diff. Peak and hole (e/Å ³)	0.195 and -0.313	0.681 and -0.608

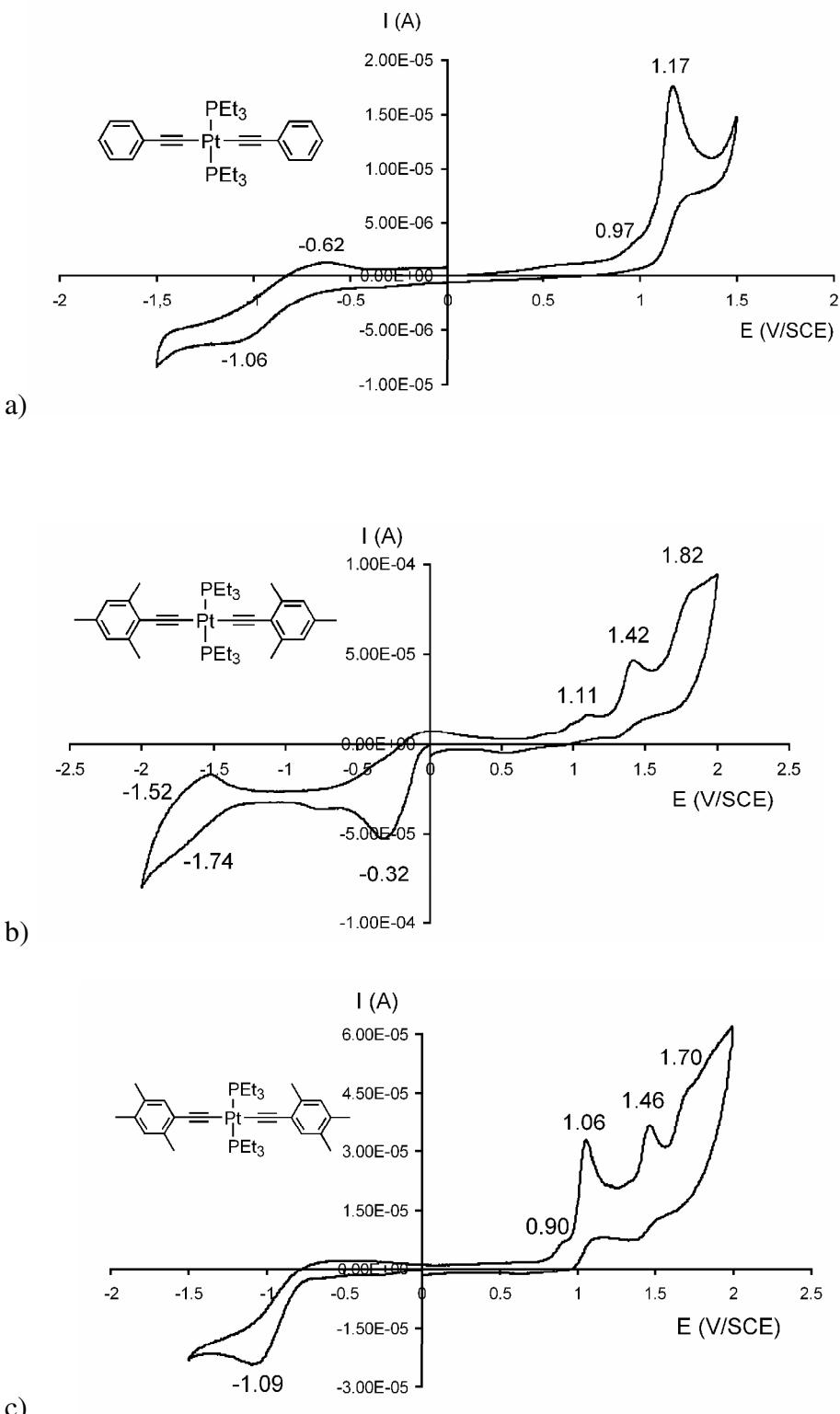
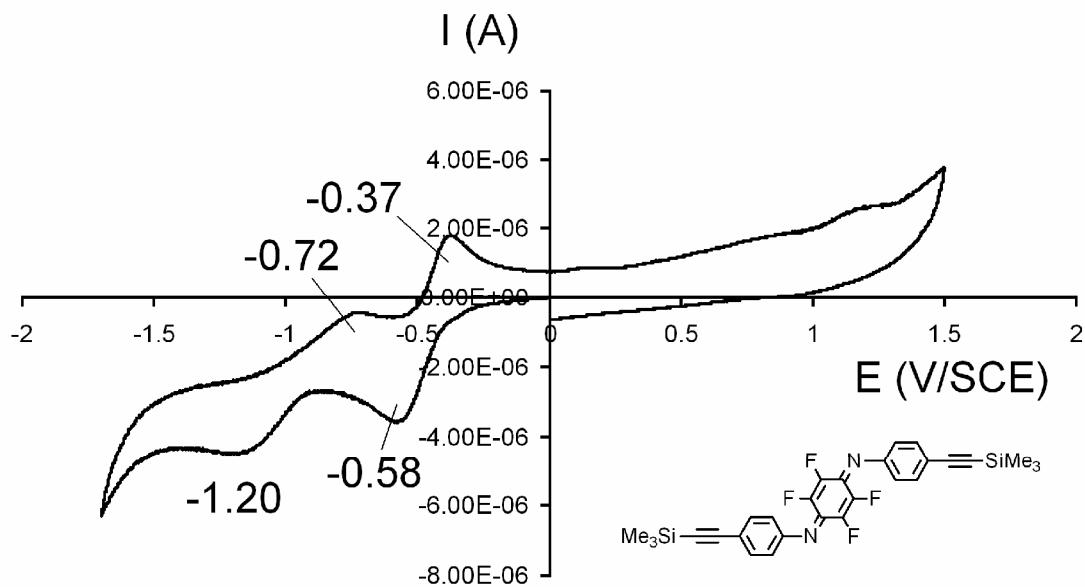
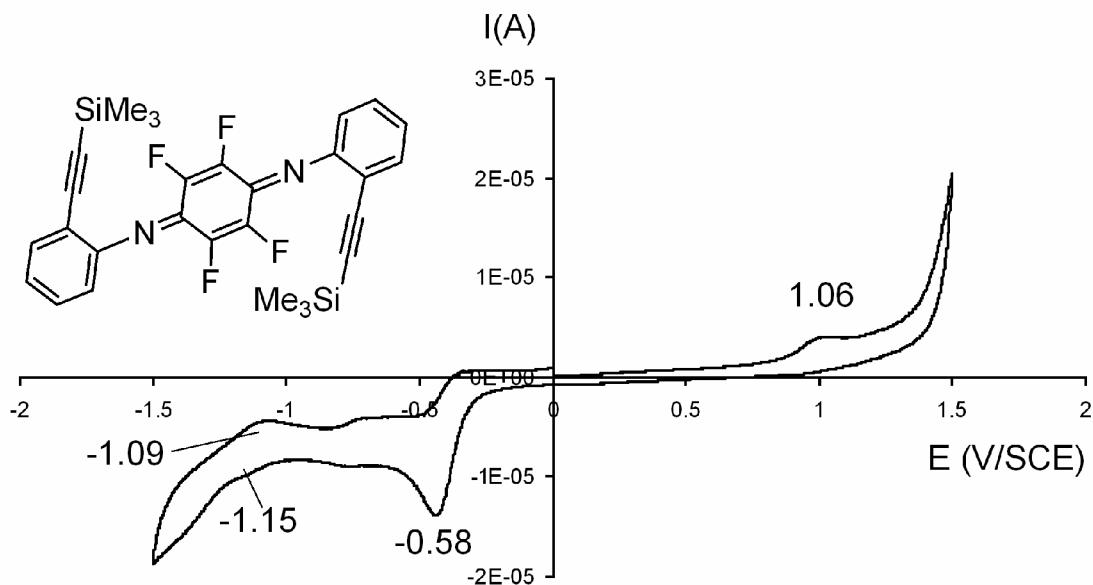


Figure S1. Cyclic voltammograms for model compounds (a) $\text{Ph}-\text{C}\equiv\text{C}-\text{Pt}(\text{PEt}_3)_2$, (b) **1** and (c) **2**, in acetonitrile / TBAPtF_6 (0.1M), working electrode: Pt, auxiliary electrode: Pt, reference electrode: SCE, scan rate: 100mV/s.

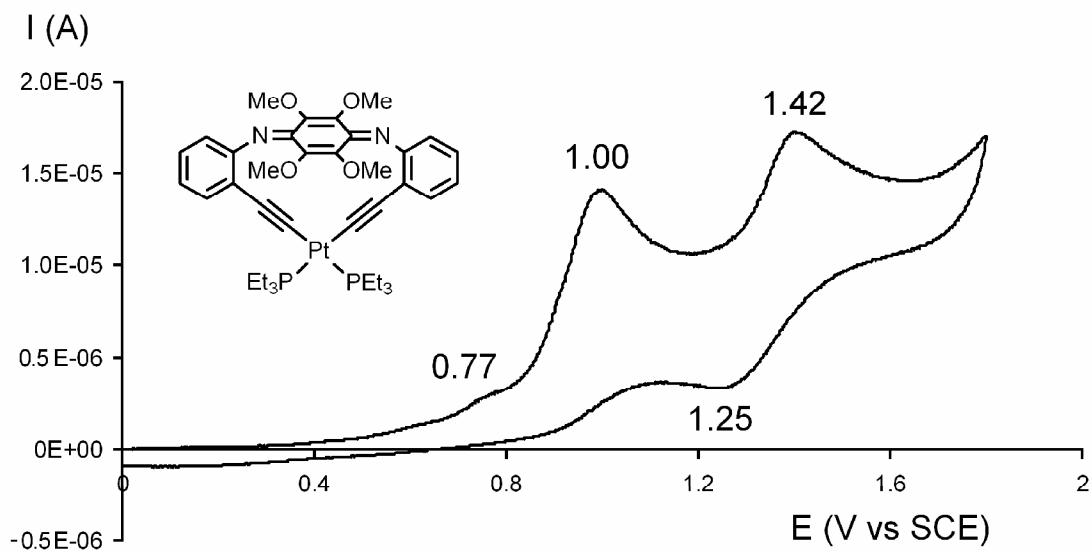


a)

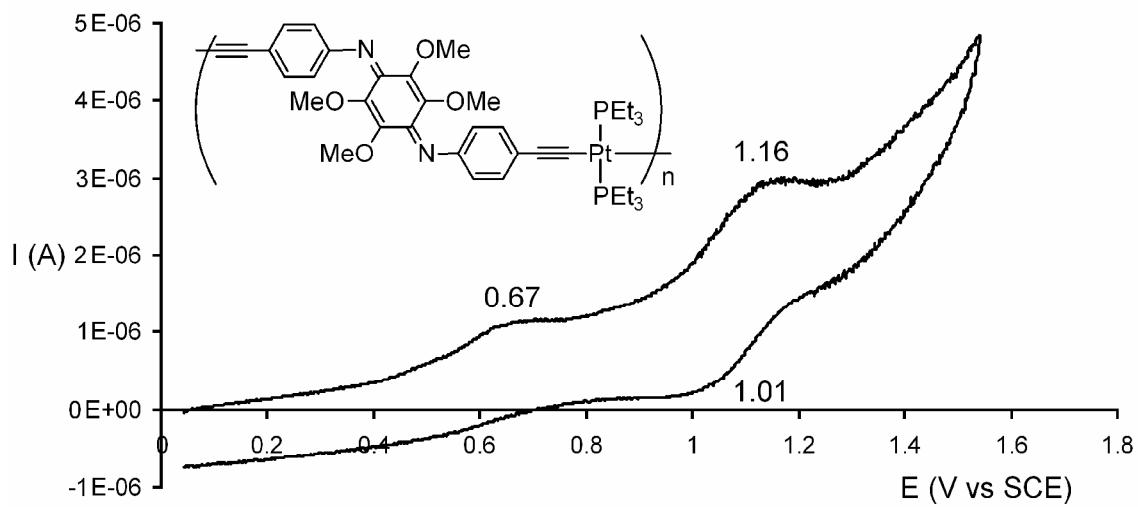


b)

Figure S2. Cyclic voltammograms for compounds (a) **5** and (b) **3**, in acetonitrile / TBAPF₆ (0.1M), working electrode: Pt, auxiliary electrode: Pt, reference electrode: SCE, scan rate: 100mV/s.

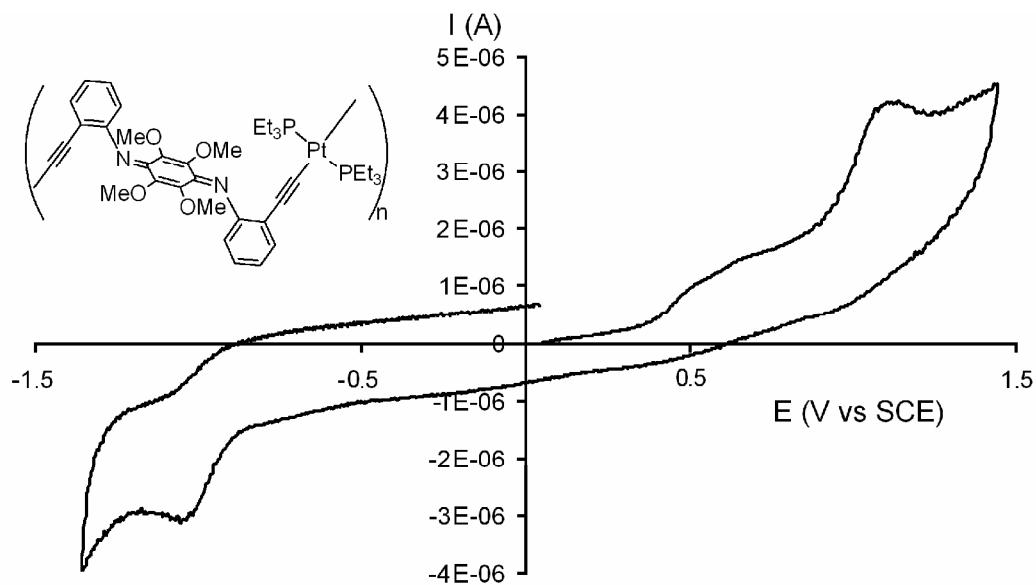


a)

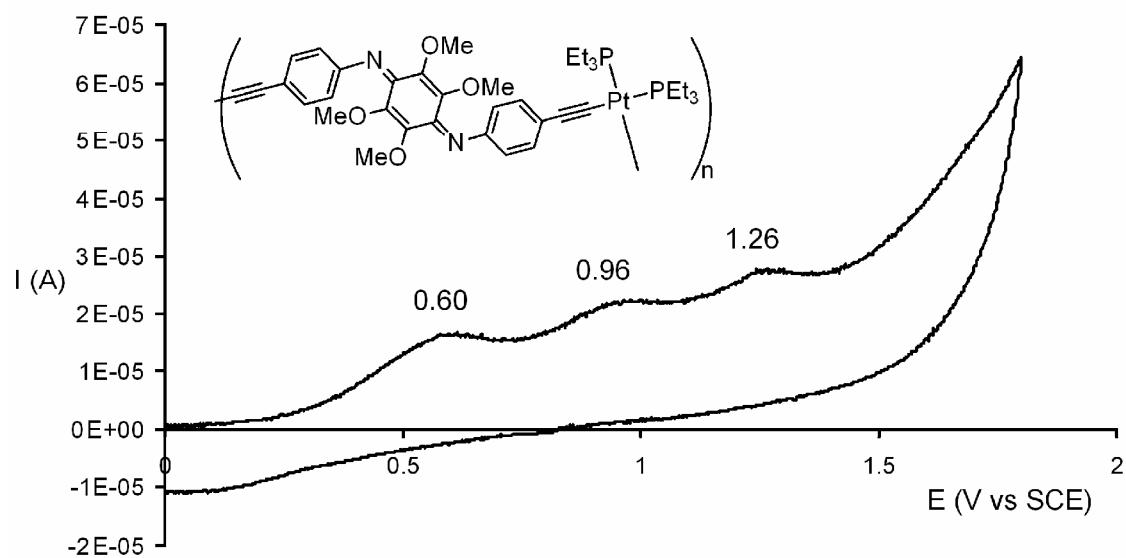


b)

Figure S3. Cyclic voltammograms for (a) compound **7** (b) polymer **10**, in acetonitrile / TBAPF₆ (0.1M), working electrode: Pt, auxiliary electrode: Pt, reference electrode: SCE, scan rate: 100mV/s



a)



b)

Figure S4. Cyclic voltammograms for polymers (a) **12** and (b) **11**, in acetonitrile / TBAPF₆ (0.1M), working electrode: Pt, auxiliary electrode: Pt, reference electrode: SCE, scan rate: 100mV/s.

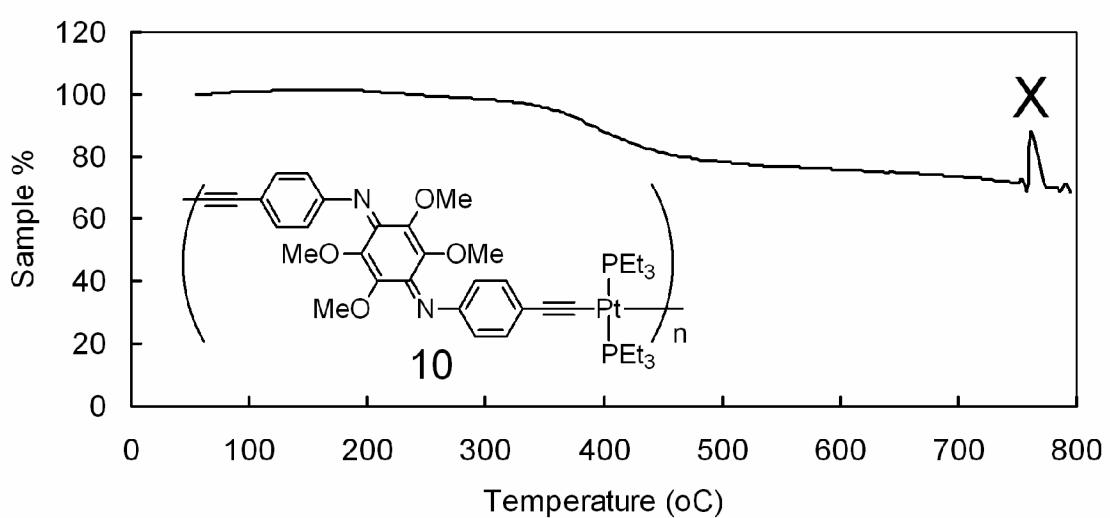
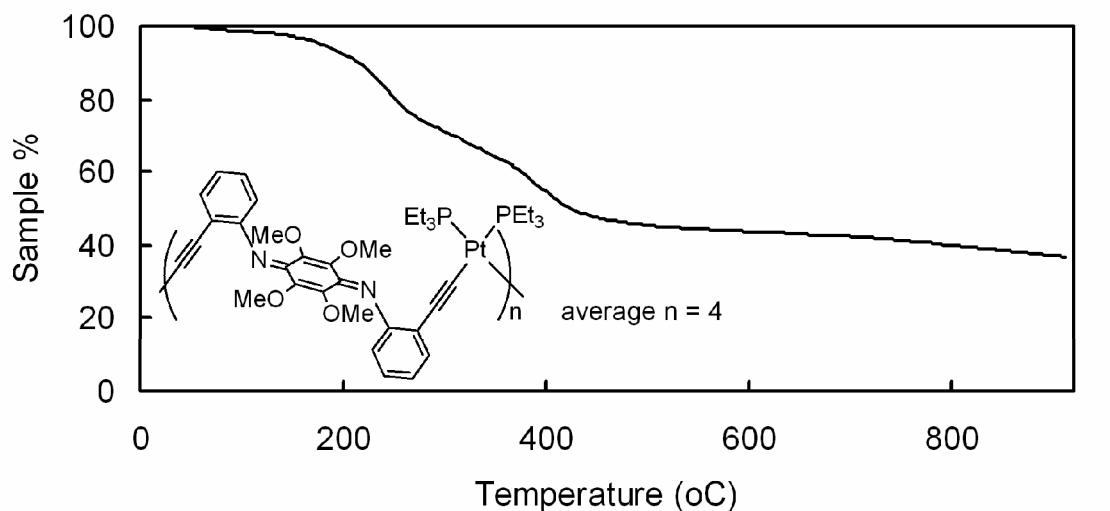


Figure S5. TGA traces for the oligomers and polymers **7'**, **10-12**.

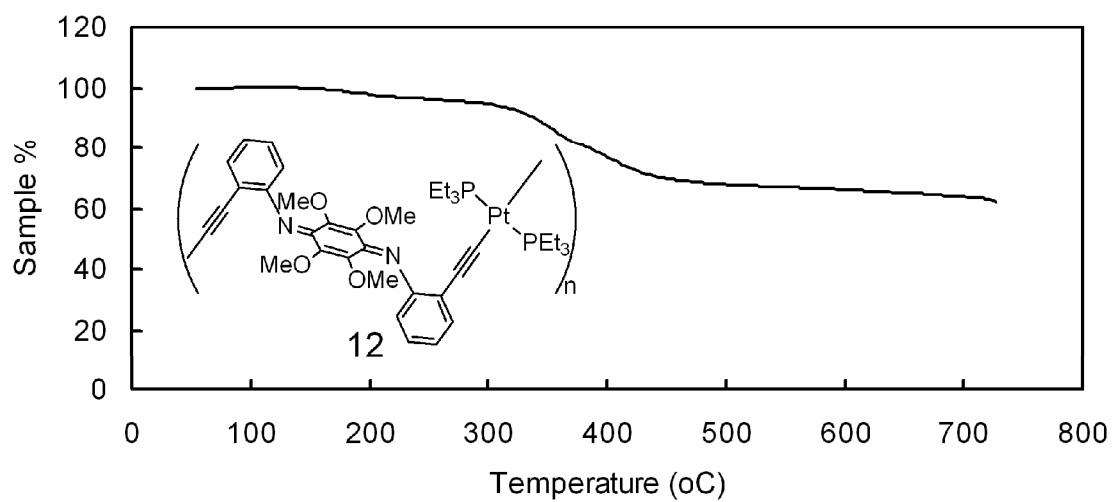
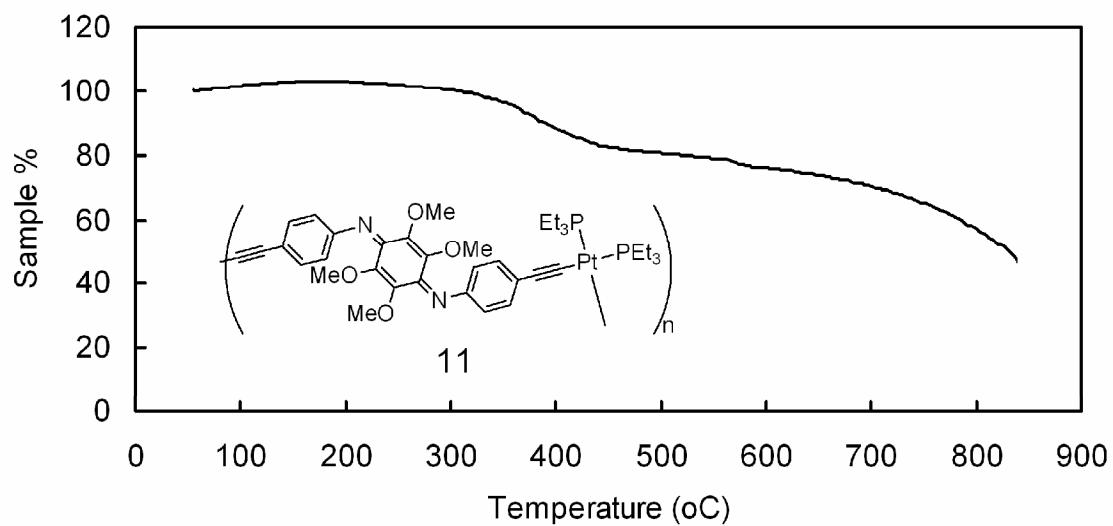


Figure S5. TGA traces for the oligomers and polymers **7'**, **10-12**. (Continued)

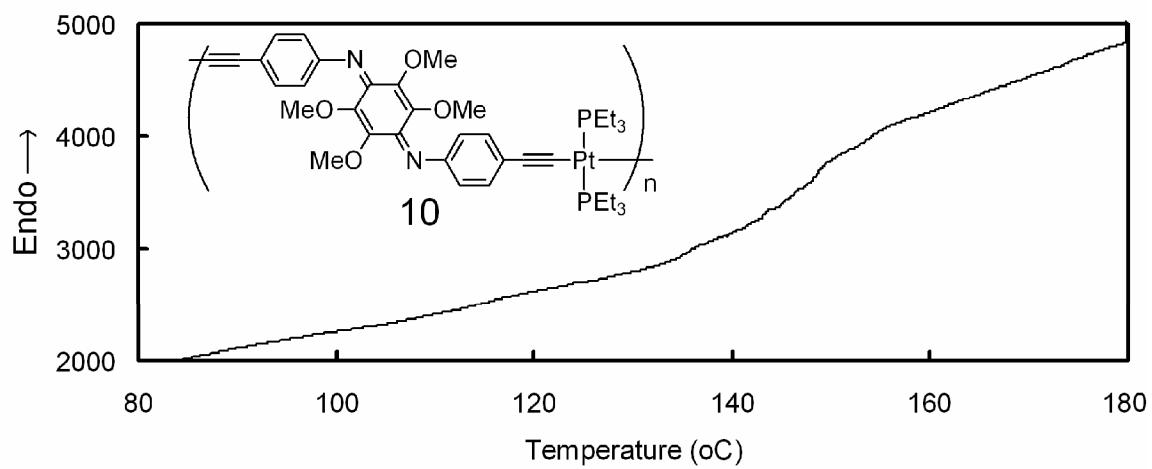


Figure S6. DSC trace for polymer **10** in the 80-180 °C window.



Figure S7. Picture of stand-alone polymer **10**.

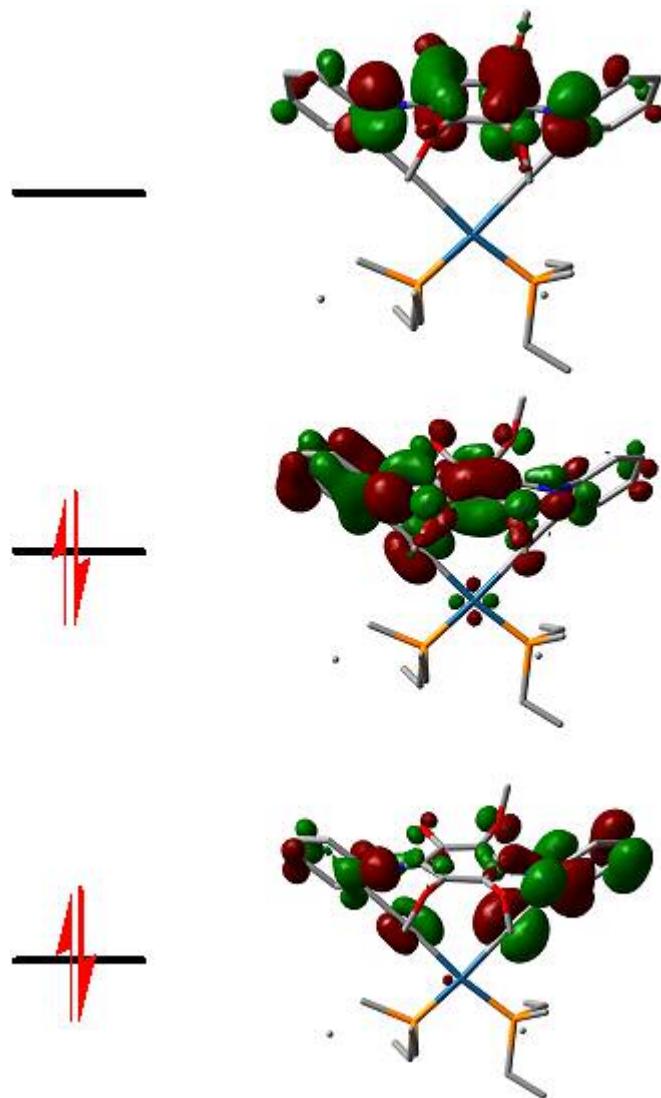


Figure S8. Frontier MO's for the cyclic compound **7**. The respective MO energies are from bottom to top: -0.067, -0.177, -0.187 a.u., respectively. The points beside the P atoms are C atoms of the PEt₃ ligands not drawn by the program.

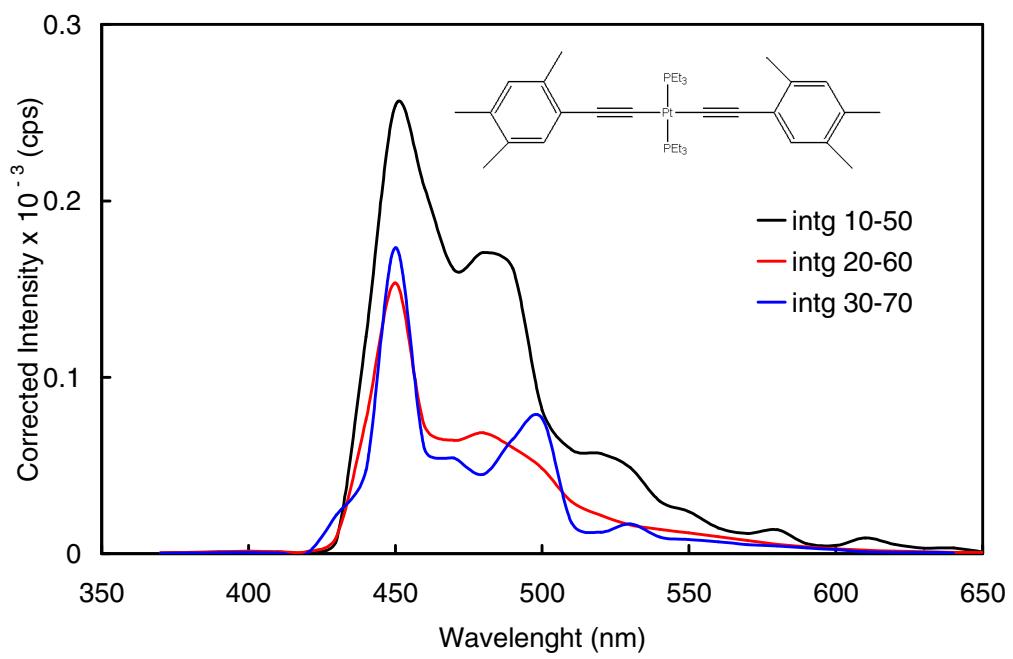
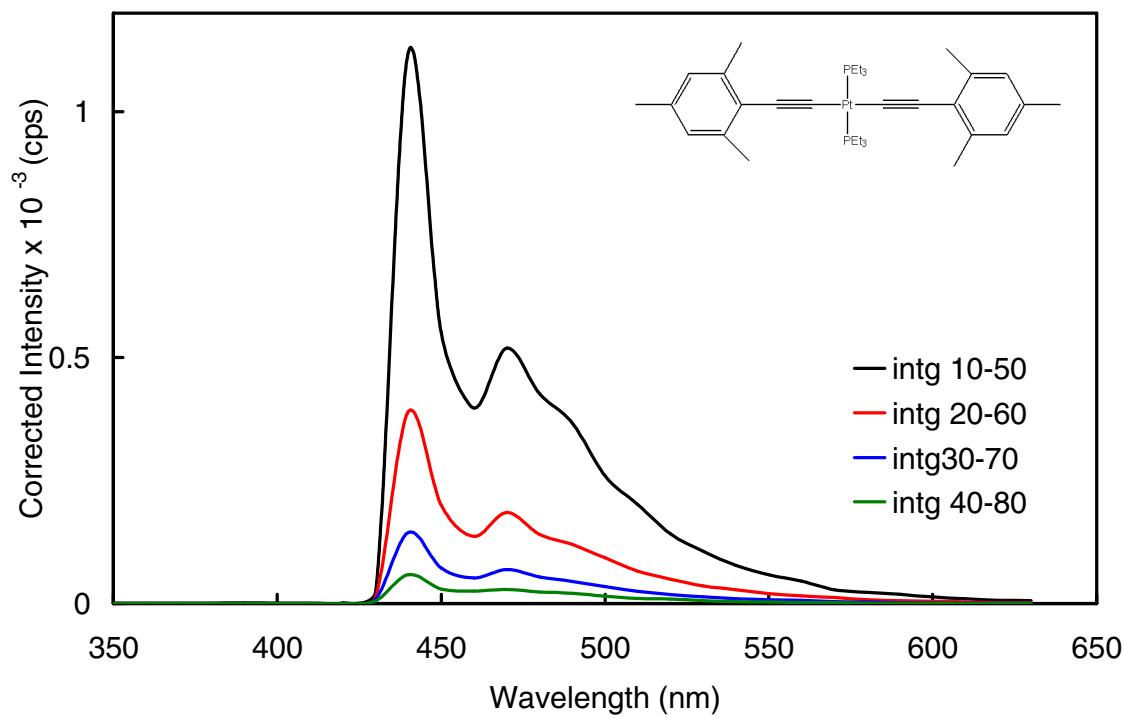


Figure S9. Time-resolved spectra of the model compounds **1** and **2** in 2MeTHF at 77K in the μ s time scale (the delay times are indicated in the figure). The spectra are smoothed due to noise.

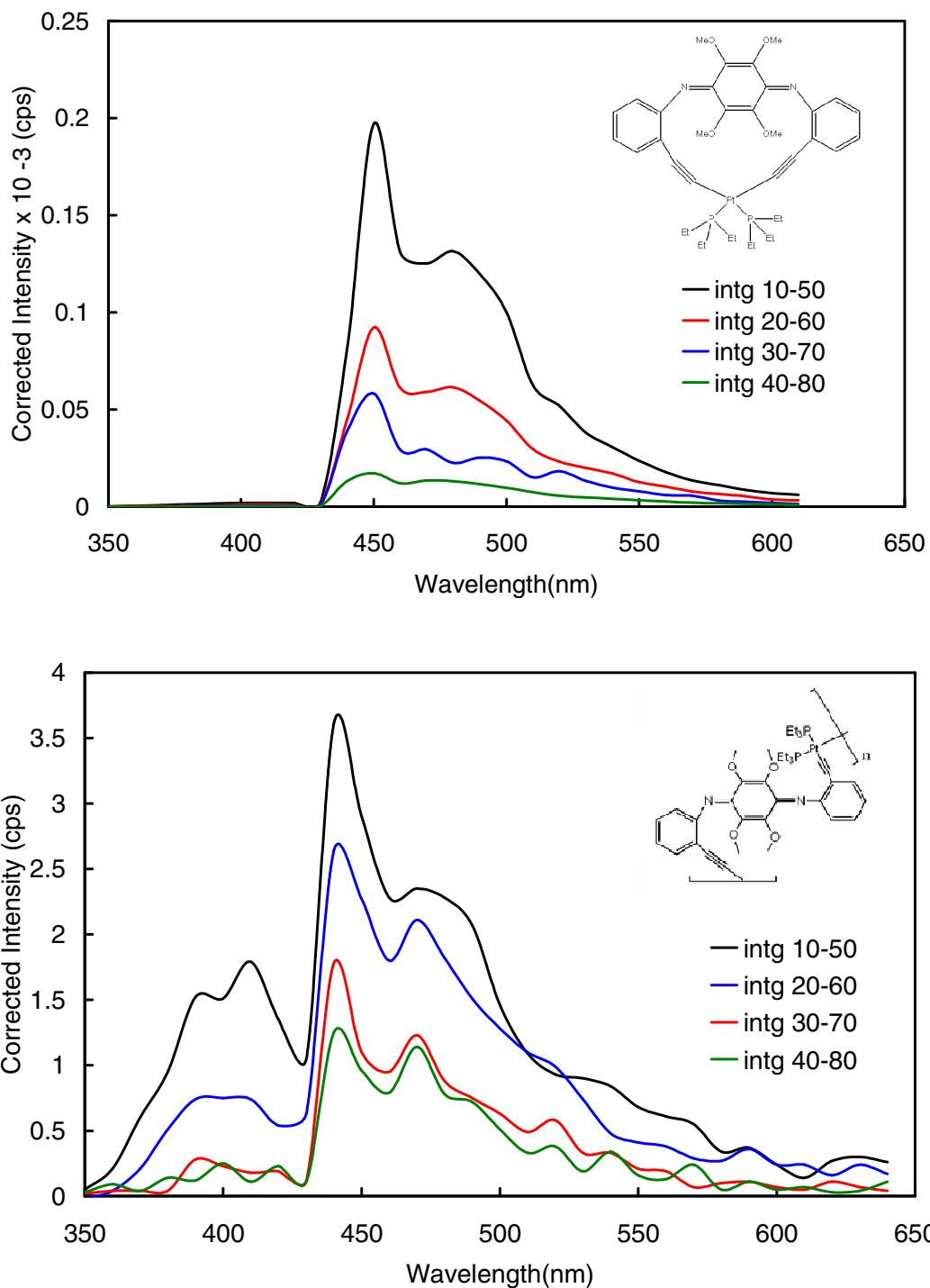


Figure S10. Time-resolved spectra of the model compound **7** (up) and oligomer **7'** (down) in 2MeTHF at 77K in the μ s time scale (the delay times are indicated in the figure). Delayed fluorescence is observed at 400nm. The spectra are smoothed due to noise.

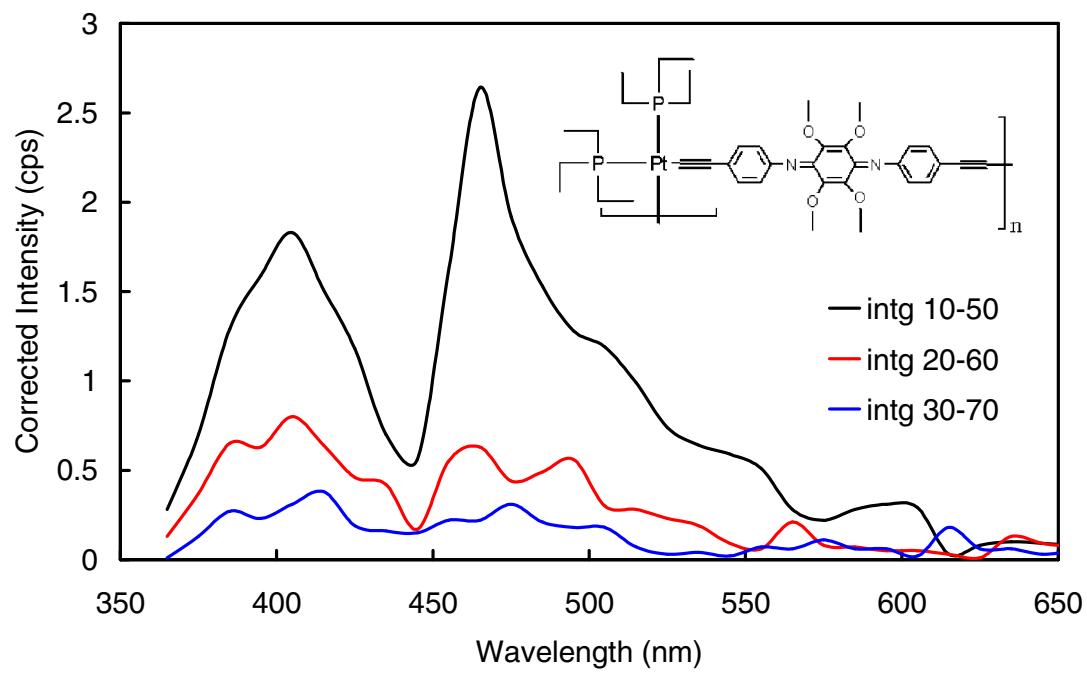
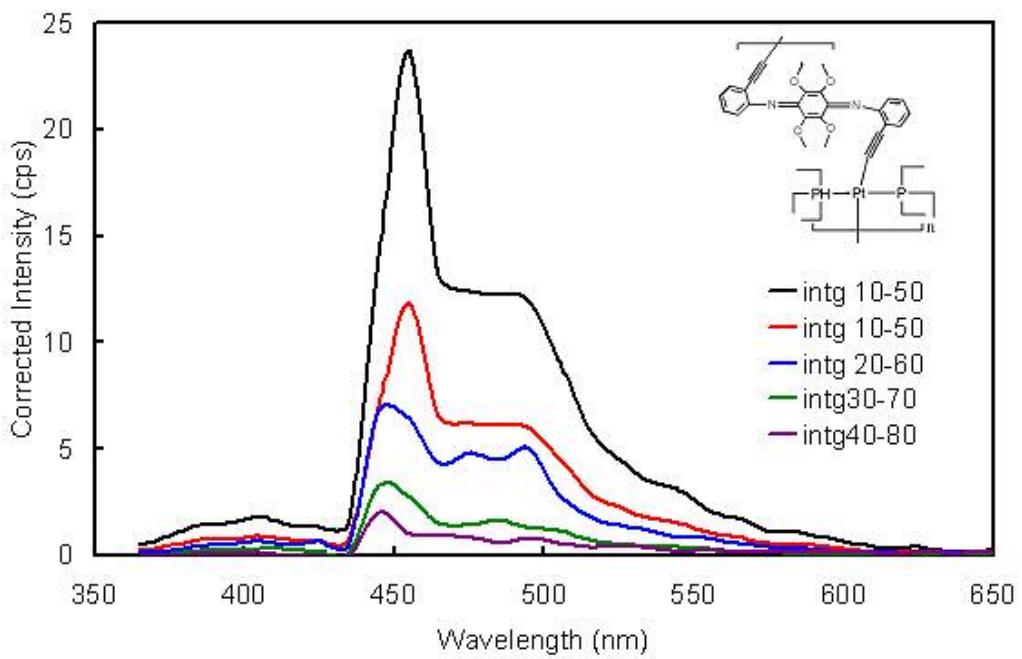


Figure S11. Time-resolved spectra of polymer **12** (up) and oligomer **11** (down) in 2MeTHF at 77K in the μ s time scale (the delay times are indicated in the figure). Delayed fluorescence is observed at 400nm. The spectra are smoothed due to noise.

Table S2. Comparison of the calculated and experimental absorption maximum with the structural parameters A1 and A2 presented in Chart 4 using optimized geometry.^{a)}

Compound or polymer	A2 ($^{\circ}$)	A1 ($^{\circ}$)	Calculated position in nm (oscillator strength)	Exp. λ_{\max} in nm (ε in M $^{-1}$ cm $^{-1}$)	Nature of the excited state
Opt. geometry					
1	–	73.9	327 (0.06) 293 (0.13)	322 (20000)	MLCT
2	–	61.7	331 (0.36)	330 (118000)	MLCT
4b (syn)	66.9	–	548 (0.11)	476 (3440)	CT
4a (anti)	73.4	–	574 (0.11)		CT
6	51.5	–	597 (0.51)	480 (4200)	CT
SOLVENT THF					
			607 (0.65)		
7	55.7	61.4	634 (0.03) 576 (0.02)	514 (2100)	CT
SOLVENT THF					
			657 (0.04)		
			593 (0.03)		
10	49.8	82.7	660 (2.1)	560 (13700)	CT

a) All angles are from optimized structure (DFT).

Experimental Section

Materials. 1-ethynyl-2,4,5-trimethylbenzene (Aldrich), 2,4,6-trimethyliodobenzene (Acros Organics), CuI (Aldrich), HP(t-Bu)₃BF₄ (Strem), trimethylsilylacetylene (Fluka), tetrafluoroquinone (Aldrich), tetramethylquinone (Aldrich), tetrachloroquinone (Aldrich), 4-bromoaniline (Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆; Fluka, puriss.), CF₃COOH (Fluka)) and 1,2-(trimethylsilane(ethynyl)aniline (Aldrich) were commercially available and were used as received. The solvents (1,2-C₂H₄Cl₂ (Aldrich), CH₂Cl₂ (EMD), CH₃CN (Anachemia), dioxane (EMD), MeOH (ACP), ethyl acetate (ACP), (iPr)₂NH (Aldrich), and butyronitrile (Aldrich), were purified according to standard procedures.¹ The complexes Pd(PhCN)₂Cl₂,² *cis*-M(PEt₃)₂Cl₂,³ *trans*-M(PEt₃)₂Cl₂⁴ (M = Pd, Pt), 1-ethynyl-2,4,6-trimethylbenzene, 1-mesityl-2-trimethylsilaneacetylene,⁵ and 1,4-trimethylsilane(ethynyl)aniline,⁶ were synthesized according to published procedures. All the syntheses were performed under Ar using Schlenk techniques. All flasks were dried under a flame to eliminate moisture. All the solvents were dried over MgSO₄ under N₂ prior to use.

trans-bis(ethynylmesityl)bis(triethylphosphine)platinum(II) (1) CuI (0.00790 g, 0.0418 mmol) was added to a mixture of *trans*-Pt(PEt₃)₂Cl₂ (0.210g, 0.418 mmol) and freshly prepared ligand, mesitylacetylene (0.121 g, 0.836 mmol) in CH₂Cl₂/iPr₂NH (50 ml, 1:1 v/v). The yellow solution was stirred for 48 hrs at room temperature, after which all volatiles were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed three times with water and dried on K₂CO₃. All solvents were removed under reduced pressure. The residue was dissolved in a minimum amount of CH₂Cl₂ and filtered through a short silica column first with pure CH₂Cl₂ followed by a 1:1 solution of

$\text{CH}_2\text{Cl}_2/\text{EtOEt}$. Further purification was accomplished from recrystallization using PhMe and MeOH. Colorless crystals were obtained by vapour diffusion of methanol on a toluene solution. Yield 50 % (0.149g). ^1H NMR (CD_2Cl_2): δ 6.79 (s, 2H, CHar.), 2.36 (s, 3H, *para*- C_6CH_3), 2.21 (s, 6H, *ortho*- C_6CH_3), 2.18-2.11 (m, 6H, CH_2CH_3) 1.22-1.11 (m, 9H, CH_2CH_3). ^{31}P NMR (CD_2Cl_2): δ , 14.7 (s + 2 sat.; $^1\text{J}(\text{P-Pt}) = 2394$). IR (KBr) ν : 2098 cm^{-1} ($\text{C}\equiv\text{C}$). Anal. Calcd for $\text{C}_{34}\text{H}_{52}\text{P}_2\text{Pt} \bullet \text{H}_2\text{O}$ (717.80): C, 54.96; H, 7.43. Found: C, 54.89; H, 7.36. Mass spectrometry (mass m/e): 717 (M+).

trans-bis(1-ethynyl-2,4,5-trimethylbenzene)bis(triethylphosphine)platinum(II) (2) CuI (0.0034 g, 0.018 mmol) was added to a mixture of *trans*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ (0.0905g, 0.180 mmol) and the ligand 1-ethynyl-2,4,5-trimethylbenzene (0.070 g, 0.360 mmol) in $\text{CH}_2\text{Cl}_2/\text{iPr}_2\text{NH}$ (50 ml, 1:1 v/v). The yellow solution was stirred for 48 hrs at room temperature, after which all volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed three times with water and dried on K_2CO_3 . All solvents were removed under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and filtered through a short silica column first with CH_2Cl_2 followed by a 1:1 solution of $\text{CH}_2\text{Cl}_2/\text{EtOEt}$. Further purification was accomplished from recrystallization using PhMe and MeOH. Yellow crystals were obtained by vapour diffusion of methanol on a toluene solution. Yield 71 % (0.092 g). ^1H NMR (CD_2Cl_2): δ 7.00 (s, 1H, CHar.), 6.88 (s, 1H, CHar.), 2.32 (s, 3H, C_6CH_3), 2.16 (s, 3H, C_6CH_3), 2.15 (s, 3H, C_6CH_3), 2.21-2.11 (m, 6H, CH_2CH_3), 1.24-1.13 (m, 9H, CH_2CH_3). ^{31}P NMR (CD_2Cl_2): δ 15.1 (s + 2 sat., $^1\text{J}(\text{P-Pt}) = 2385$). IR (KBr) ν : 2094 cm^{-1} ($\text{C}\equiv\text{C}$). Anal. Calcd for $\text{C}_{34}\text{H}_{52}\text{P}_2\text{Pt} \bullet \text{H}_2\text{O}$ (717.80): C, 55.91; H, 7.37. Found: C, 55.88; H, 7.33. Mass spectrometry (mass m/e): 717 (M+).

Bis(ortho-trimethylsilyl ethynylbenzene)-2,3,5,6-tetrafluoroquinone diimine (3) 25 ml of chlorobenzene was placed in a three-necked round bottomed flask. 0.940 g (4.97 mmol) of 2-[(trimethylsilyl)ethynyl]aniline, 1.01 g (9.93 mmol) of triethylamine, and 0.707 g (3.72 mmol) of TiCl_4 were then added to the flask using a syringe. 0.447 g (2.48 mmol) of 2,3,5,6-tetrafluoroquinone was then dissolved in a minimum amount of chlorobenzene and added dropwise to the solution. The solution was stirred at 60^0C for 4 hrs. The mixture was then left to cool to room temperature, filtered, and washed with chlorobenzene. The solution was evaporated and the solid dissolved in CH_2Cl_2 and washed three times with water, dried on K_2CO_3 , and filtered. The CH_2Cl_2 was completely evaporated leaving only the product. The product was purified on a silica column with 25% CH_2Cl_2 / 75% hexanes as the solvent. Violet crystals were obtained by slow evaporation of a CH_2Cl_2 solution. Yield: 54 % (0.70 g). ^1H NMR δ (CD_2Cl_2): 7.42 (d, 4H, CH aro., $J_{\text{H-H}}=7.56$); 7.24 (t, 4 H, CH aro., $^3J_{\text{H-H}}=7.67$); 6.87 (t, 4H, CH aro., $^3J_{\text{H-H}}=7.47$); 6.67 (d, 4H, CH aro., $J_{\text{H-H}}=8.26$); 0.29 (s, 18 H, $\text{Si}(\text{CH}_3)_3$). IR (KBr) ν : 2140 cm^{-1} ($\text{C}\equiv\text{C}$). Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{F}_4\text{Si}_2$ (522.67): C, 64.34; H, 5.01; N, 5.36. Found: C, 63.86; H, 4.88; N, 5.23. Mass spectrometry (mass m/e): 522 (M+).

Bis(ortho-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine (4) 0.281 g (0.537 mmol) of **3** was placed in a 250 ml round-bottomed flask and 7 g of K_2CO_3 was added to the flask as well as 180 ml of CH_3OH . The reaction was stirred under Ar overnight until the solution had become orange. The excess K_2CO_3 was filtered and the remaining solvent was evaporated and the product then dissolved in CH_2Cl_2 and washed 3 times with water. The CH_2Cl_2 solution was then dried with K_2CO_3 and filtered. The product

was purified on a silica column with 25% ethyl acetate and 75% hexanes as the solvent. Red crystals were obtained by slow evaporation of a CH_2Cl_2 solution. Yield: 96% (0.22 g). ^1H NMR δ (CD_2Cl_2): 7.45 (d, 4H, CH aro., $J_{\text{H-H}} = 7.68$); 7.31 (t, 4 H, CH aro., $J_{\text{H-H}} = 7.72$); 7.00 (t, 4H, CH aro., $J_{\text{H-H}} = 7.58$); 6.77 (d, 4H, CH aro., $J_{\text{H-H}} = 8.08$); 3.60 (broad m, 12H, CH_3); 3.18 (s, 2 H, CH) ppm. IR (KBr) ν : 2100 cm^{-1} (C≡C). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4 \bullet 0.06 \text{H}_2\text{O}$ (426.47): C, 73.04; H, 5.21; N, 6.55. Found: C, 73.03; H, 5.40; N, 6.59. Mass spectrometry (mass m/e): 426 + 2H (M+).

Bis(para-trimethylsilyl ethynylbenzene)-2,3,5,6-tetrafluoroquinone diimine (5) 25 ml of chlorobenzene was placed in a three-necked round bottomed flask. 1.09 g (5.74 mmol) of 4-[(trimethylsilyl)ethynyl]aniline, 1.17 g (11.5 mmol) of triethylamine, and 1.09 g (5.74 mmol) of TiCl_4 were then added to the flask using a syringe. 0.515 g (2.86 mmol) of 2,3,5,6-tetrafluoroquinone was then 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 then left to cool to room temperature, filtered, and washed with chlorobenzene. The solution was evaporated and the solid dissolved in dichloromethane and washed three times with water, dried with K_2CO_3 , and filtered. The dichloromethane was completely evaporated leaving only the product. Violet crystals were obtained by slow evaporation a of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution. Yield: 40% (1.50). ^1H NMR δ (CD_2Cl_2): 7.42 (m, 4H, CH aro.); 6.82 (m, 4H, CH aro.); 0.25 (s, 18 H, $\text{Si}(\text{CH}_3)_3$). IR (KBr) ν : 2098 cm^{-1} (C≡C). Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{F}_4\text{Si}_2$ (522.67): C, 64.34; H, 5.01; N, 5.36. Found: C, 64.49; H, 5.11; N, 5.27. Mass spectrometry (mass m/e): 522 (M+).

Bis(para-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine (6) 0.920 g (1.760 mmol) of **5** was placed in a 250 ml round-bottomed flask and 8 g of K_2CO_3 was added to the flask as well as 200 ml of CH_3OH . The reaction was stirred under Ar overnight until the solution had become orange. The excess K_2CO_3 was filtered and the remaining solvent was evaporated and the product then dissolved in CH_2Cl_2 and washed 3 times with water. The CH_2Cl_2 solution was then dried with K_2CO_3 and filtered. The product was purified on a silica column with 25% ethyl acetate and 75% hexanes as the solvent. Orange crystals were obtained by slow evaporation a CH_2Cl_2 solution. Yield: 75% (0.75). 1H NMR δ (CD_2Cl_2): 7.42 (d, 4H, CH aro., $J_{H-H} = 8.05$); 6.70 (d, 4H, CH aro., $J_{H-H} = 8.48$); 3.56 (broad m, 12H, CH_3); 3.09 (s, 2 H, CH). IR ($CHCl_3$) ν : 2098 cm^{-1} ($C\equiv C$). Anal. Calcd for $C_{26}H_{22}N_2O_4$ (426.47): C, 73.22; H, 5.20; N, 6.57. Found: C, 73.45; H, 5.01; N, 6.68. Mass spectrometry (mass m/e): 426 + 2H (M^+).

(Bis(ortho-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine) bis(triethylphosphine)-platinum(II) (7) 0.102 g (0.238 mmol) of **4** was placed in a 100 ml round-bottomed flask along with 0.120 g (0.238 mmol) of *cis*- $Pt(PEt_3)_2Cl_2$ and 0.0136 g (0.0715 mmol) of CuI . 30 ml of CH_2Cl_2 and 30 ml of (iPr)₂NH were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH_2Cl_2 and washed 3 times with water. The solution of CH_2Cl_2 was then dried with K_2CO_3 and filtered. The product was purified using a silica column where 10% ethyl acetate and 90% CH_2Cl_2 were used as solvents. Purple crystals were obtained by slow evaporation of a $CH_2Cl_2/MeOH$ solution. Yield: 50% (0.10 g). 1H NMR δ (CD_2Cl_2): 7.21 (d, 4H, CH aro., $J_{H-H} = 7.59$); 7.09 (t, 4 H, CH aro., $^3J_{H-H} = 7.60$); 6.91 (d, 4H, CH aro., $J_{H-H} = 7.78$); 6.83 (t, 4H, CH aro., $^3J_{H-H} = 7.49$); 3.94 (s, 6H, CH_3) ; 3.19 (s, 6H, CH_3); 1.93 (q, 12H, CH_2 ,

$^5J_{H-H} = 8.37$); 1.04 (q, 18H, CH_3 , $^5J_{H-H} = 7.82$) ppm. ^{31}P NMR δ (CD_2Cl_2): 8.67 s + 2 stat., $^1J(P-Pt) = 1110$). IR (KBr) ν : 2100 cm^{-1} (C≡C). Anal. Calcd for $C_{38}H_{50}N_2O_4P_2Pt \bullet 0.2 (iPr)_2NH$ (855.8402): C, 53.74; H, 6.10; N, 3.52. Found: C, 53.64; H, 6.20; N, 3.53.

Oligomers of (*Bis(ortho-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine*) *bis(triethylphosphine)platinum(II)* (**7'**). 0.102 g (0.238 mmol) of **4** was placed in a 100 ml round-bottomed flask along with 0.120 g (0.238 mmol) of *cis*- $Pt(PEt_3)_2Cl_2$ and 0.0136 g (0.0715 mmol) of CuI. 30 ml of CH_2Cl_2 and 30 ml of $(^iPr)_2NH$ were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH_2Cl_2 and washed 3 times with water. The solution of CH_2Cl_2 was then dried with K_2CO_3 and filtered. The product was purified using a silica column where 10% ethyl acetate and 90% CH_2Cl_2 were used as solvents. Yield: 27% (0.055 g). 1H NMR δ (CD_2Cl_2): 6.86 (m, 8H, CH aro.); 3.58 (m, 12H, CH aro.); 1.96 (broad s, 12H, CH_2); 1.07 (m, 18H, CH_3). ^{31}P NMR δ (CD_2Cl_2): 8.7 s + 2 sat., $^1J(P-Pt) = 1120$. IR (KBr) ν : 2100 cm^{-1} (C≡C). No satisfactory analysis was obtained. This is due to the difficulty in establishing the nature of the end group for very small oligomers.

Cyclodiethynylbis(ortho-benzene)-2,3,5,6-tetramethoxyquinone diimine (**8**) 0.106 g (0.248 mmol) of **4** was placed in a 100 ml round-bottomed flask along with 0.103 g (0.248 mmol) of *cis*- $Pd(PEt_3)_2Cl_2$ and 0.0142 g of CuI. 30 ml of CH_2Cl_2 and 30 ml of $(^iPr)_2NH$ were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH_2Cl_2 and washed 3 times with water. The solution of CH_2Cl_2 was then dried with K_2CO_3 and filtered. Red crystals were obtained by slow evaporation of a MeOH solution. Yield: 14 % (0.0271 g). 1H NMR δ (CD_2Cl_2):

7.28 (m, 8H, CH aro.); 3.63 (m, 12 H, CH₃) ppm. IR (KBr) ν : 2132, 2192 cm⁻¹ (C≡C). Anal. Calcd for C₂₆H₂₀N₂O₄ • 0.1 H₂O (424.4481): C, 73.26; H, 4.78; N, 6.57. Found: C, 73.27; H, 4.50; N, 6.46. Mass spectrometry (mass m/e): 424 (M+).

Bis(ortho-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine-trans-chlorotriethylphosphinepalladium(II) (9) 0.106 g (0.248 mmol) of **4** was placed in a 100 ml round-bottomed flask along with 0.103 g (0.248 mmol) of *cis*-Pd(PEt₃)₂Cl₂ and 0.0142 g of CuI. 30 ml of CH₂Cl₂ and 30 ml of (iPr)₂NH were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was then dried with K₂CO₃ and filtered. The product was purified on a silica column with 20% AcOEt and 80% hexanes as the solvent. Purple crystals were obtained by slow evaporation of a CH₂Cl₂ solution. Yield: 3.3% (0.0063 g). ¹H NMR δ (CD₂Cl₂): 7.26 (d, 4H, CH aro., J_{H-H} = 7.50); 7.05 (m, 4 H, CH aro.); 6.89 (t, 4H, CH aro., ³J_{H-H} = 7.50); 6.45 (d, 4H, CH aro., J_{H-H} = 7.82); 3.58 (m, 12H, CH₃); 1.91 (t, 24H, CH₂, ³J_{H-H} = 3.66); 1.14 (q, 36H, CH₃, ⁵J_{H-H} = 8.02). ³¹P NMR δ (CD₂Cl₂): 21.7. IR (KBr) ν : 2110 cm⁻¹ (C≡C). Anal. Calcd for C₅₀H₈₀N₂O₄P₄Pd₂ (1180.822): C, 50.86; H, 6.83; N, 2.37. Found: C, 51.08; H, 6.54; N, 2.37.

Polymer poly(bis(para-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine)-trans-bis(triethyl-phosphine)platinum(II) (10) 0.122 g (0.286 mmol) of **7** was placed in a 100 mL round-bottomed flask along with 0.144 g (0.286 mmol) of *trans*-Pt(PEt₃)₂Cl₂ and 0.0163 g of CuI. 30 ml of CH₂Cl₂ and 30 ml of (iPr)₂NH were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was then dried with

K_2CO_3 and filtered. Yield: 83 % (0.203 g). ^1H NMR δ (CD_2Cl_2): 7.19 (m, 4H, CH aro.); 6.67 (m, 4H, CH aro.); 3.58 (m, 12H, CH_3); 2.19 (broad s, 12H, CH_2); 1.23 (m, 18H, CH_3). ^{31}P NMR δ (CD_2Cl_2): 14.8 s + 2 sat., $^1\text{J}(\text{P-Pt}) = 1190$. IR (KBr) ν : 2099 cm^{-1} ($\text{C}\equiv\text{C}$). Anal. Calcd for $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_4\text{P}_2\text{Pt} \bullet 0.37 \text{ H}_2\text{O}$ (855.8402): C, 52.92; H, 5.93; N, 3.25. Found: C, 52.92; H, 6.06; N, 3.34. The larger polymer chains were precipitated with ether and were passed through a GPC giving the results shown in the Table 1 below.

Polymer poly(bis(para-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine)-cis-bis(triethylphosphine)platinum(II) (11) 0.129 g (0.286 mmol) of **7** was placed in a 100 ml round-bottomed flask along with 0.143 g (0.286 mmol) of *cis*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ and 0.0163 g of CuI . 30 ml of CH_2Cl_2 and 30 ml of $(^i\text{Pr})_2\text{NH}$ were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH_2Cl_2 and washed 3 times with water. The solution of CH_2Cl_2 was then dried with K_2CO_3 and filtered. Yield: 83 % (0.204 g). ^1H NMR δ (CD_2Cl_2): 6.97 (m, 8H, CH aro.); 3.56 (m, 12H, CH_3); 2.07 (broad s, 12H, CH_2); 1.17 (q, 18H, CH_3 , $^5\text{J}_{\text{H-H}} = 7.69$). ^{31}P NMR δ (CD_2Cl_2): 8.4 s + 2 sat., $^1\text{J}(\text{P-Pt}) = 1130$. IR (KBr) ν : 2102 cm^{-1} ($\text{C}\equiv\text{C}$). Anal. Calcd for $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_4\text{P}_2\text{Pt} \bullet 0.03 (\text{iPr})_2\text{NH}$ (855.8402): C, 53.39; H, 5.92; N, 3.31. Found: C, 53.45; H, 5.92; N, 2.83. The larger polymer chains were precipitated with ether and were passed through a GPC giving the results shown in the Table 1 below.

Polymer poly(bis(ortho-ethynylbenzene)-2,3,5,6-tetramethoxyquinone diimine)-trans-bis(triethylphosphine)platinum(II) (12) 0.141 g (0.330 mmol) of **4** was placed in a 100 ml round-bottomed flask along with 0.166 g (0.330 mmol) of *trans*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ and 0.0188

g of CuI. 30 ml of CH₂Cl₂ and 30 ml of (iPr)₂NH were added and the reaction was stirred under Ar overnight. The solvent was evaporated and the solid was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was then dried with K₂CO₃ and filtered. Yield: 99% (0.28 g). ¹H NMR δ (CD₂Cl₂): 7.25 (d, 4H, CH aro., J_{H-H} = 7.49); 7.00 (t, 4H, CH aro., ³J_{H-H} = 7.05); 6.86 (t, 4H, CH aro., ³J_{H-H} = 7.46); 6.42 (d, 4H, CH aro., J_{H-H} = 7.83); 3.57 (m, 12H, CH₃); 2.06 (t, 12H, CH₂, ³J_{H-H} = 3.21); 1.09 (q, 18H, CH₃, ⁵J_{H-H} = 7.89). ³¹P NMR δ (CD₂Cl₂): 15.2 s + 2 sat., ¹J(P-Pt) = 1190). IR (KBr) ν : 2098 cm⁻¹ (C≡C). Anal. Calcd for C₃₈H₅₀N₂O₄P₂Pt • 0.33 H₂O (855.8402): C, 52.96; H, 5.93; N, 3.25. Found: C, 52.96; H, 5.75; N, 3.46. The larger polymer chains were precipitated with ether and were passed through a GPC. The results are Table 1.

Instruments. All NMR spectra were acquired on a Bruker AC-300 spectrometer (¹H 300.15 MHz, ¹³C 75.48 MHz, ³¹P 121.50 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. The spectra were measured from freshly prepared samples. The IR spectra were acquired on a Bomem FT-IR MB series spectrometer equipped with a baseline-diffused reflectance. UV-visible spectra were recorded on a Hewlett-Packard diode array model 8452A. For the measurements of the absorptivity, the concentration was adjusted so that the absorbance of the investigated peaks fitted the 0-1 absorption scale (typically 10⁻⁴ to 10⁻⁵ M depending on the sample or the investigated band). Emission and excitation spectra were obtained using a double monochromator Fluorolog 2 instrument from Spex. All measurements were performed using samples for which absorbance fitted the approximate 0.1-0.3 absorbance scale at the excitation wavelength. Fluorescence

lifetimes were measured on a Timemaster Model TM-3/2003 apparatus from PTI. Some phosphorescence lifetime measurements and time-resolved spectra were also performed on a PTI LS-100 using a $1\mu\text{s}$ xenon-flash lamp. The source was nitrogen laser with high-resolution dye laser (FWHM ~ 1.5 ns) and the fluorescence lifetimes were obtained from high quality decays and deconvolution or distribution lifetimes analysis. The uncertainties were about $\pm 10\text{-}40$ ps based on multiple measurements. Again all the lifetime measurements were performed using samples for which absorbance fitted the approximate 0.1-0.3 absorbance scale at the excitation wavelength. The flash photolysis spectra and the transient lifetimes were measured with Luzchem spectrometer using the 355 nm line of a YAG laser from Continuum (Serulite), and the 355 nm line from OPO module pump by the same laser (FWHM = 13 ns). All measurements for the transient spectra were performed using samples for which absorbance was ~ 0.4 absorbance at the excitation wavelength.

Gel permeation chromatography. 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 $0.5\text{ml}\cdot\text{min}^{-1}$. Calibration curve was obtained using seven PS standards (Aldrich), with Mn ranging from 3400 to $382\,000\text{ g}\cdot\text{mol}^{-1}$.

Computations. All calculations were performed on an Intel Xeon 3.40GHz PC with the Gaussian 03 revision C.02 and Gausview 3.0 software package.⁷ The

hybrid B3LYP exchange - correlation function has been considered due to the high accuracy of the ensued results.⁸⁻¹⁰ LANL2DZ pseudo-potentials were used on platinum and phosphorus atoms, with LANL2DZ basis set for platinum and 3-21G* for all other atoms.^{11,12} The platinum cycle complex (**7**) crystal structure file was used without optimization before the TDDFT calculation. The model compound for polymer **10** was optimized before the TDDFT calculation. Only the relevant (stronger oscillator strength and wavefunction coefficients) molecular orbitals are shown. All computations were performed without symmetry constraint. For **3*** (without silyl groups) and **4**, a redundant relaxed energy scan at the Hartree Fock level was performed to explain the energy rotation barriers for syn to anti conformers.

Emission quantum yields. 9,10-diphenylanthracene ($\Phi = 1.0$)¹³ was used as comparative standard.

Electrochemistry. All the electrochemical measurements were carried out under nitrogen atmosphere at room temperature. The auxiliary electrode was a platinum grid and the reference electrode was a saturated calomel electrode (SCE). Voltammetric measurements were carried out in a three-electrode cell containing an 0.1 M supporting electrolyte solution (tetrabutylammonium hexafluorophosphate; TBAPF₆), connected to a potentio/galvanostat (EG&G Princeton Avanced Research model 273). The working electrode was a platine wire. Controlled potential coulometries were performed using the same potentio/galvanostat. A cell containing a scintered glass disk (porosity 4) was used to prevent diffusion of the electrogenerated species from working to auxiliary

compartment. The exhaustive electrolysis were carried out in a stirred and degassed solution containing a large platinum grid as a working electrode, the reference electrode was connected to the studied solution by a junction bridge filled with the corresponding solvent-supporting electrolyte solution and the auxiliary platinum grid electrode was plunged in a concentrated (0.6 M) supporting electrolyte solution.

X-ray crystallography. The crystals named **1** to **9** were all collected on an Enraf-Nonius CAD-4 automatic diffractometer using omega scans. The crystals decay observed were obtained by scanning one reflection measured every 100 reflections. The DIFRAC¹⁴ program was used for centering, indexing and data collection. The data were corrected for absorption by empirical methods based on psi scans and reduced with the NRCVAX¹⁵ programs. They were solved using SHELXS-97,¹⁶ and were refined by full-matrix least squares on F^2 with SHELXL-97.¹⁷ The non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model. Refinement details specific to each crystal: C16 and C17 on **1** were disordered on two possible sites, only the major refined occupational site is shown for clarity. **2** lost 1.3% of its diffraction intensity during data collection. **3** lost 7% of its diffraction intensity during data collection and disorder was found on the methyl groups on the trimethylsilyls; only the major occupational sites are shown for clarity. **5** one of the crystal faces is only 0.025 mm. **7** the absolute structure parameter is in between 0 and 1 typical of a twinned crystal, so the absolute structure could not be assigned.¹⁸ The absolute crystal structure (for crystal exhibiting chirality) was irrelevant for **1, 2, 3, 4', 5, 8** and **9**.

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