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Supporting Information for

Synthesis, photovoltaic performances and TD-DFT quantum modeling of push-pull diacetylide platinum complexes in TiO_2 based dye-sensitized solar cells†

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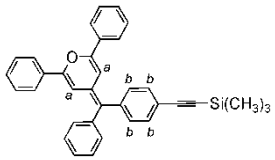
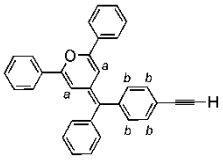
1. Synthesis and Characterization

Compound 3: 

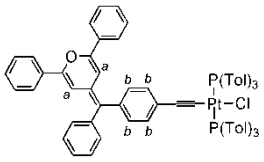
A Schlenk flask was charged with tributyl(2,6-diphenyl-4H-pyran-4-yl)phosphonium tetrafluoroborate (**1**) (600 mg, 1.15 mmol), 30 mL of anhydrous THF and *n*-BuLi in hexane solution (0.5 mL, 1.16 mmol) at -78°C under argon protection. The solution was stirred at -78°C for 15 min and 4-(2-trimethylsilylethynyl)benzophenone (**2**) (320 mg, 1.15 mmol) dissolved in dry THF (10 mL) was added dropwise. The solution was stirred at -78°C under argon 30 min and then moved to room temperature and stirred overnight. After the reaction, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 5/1) to give a yellow solid. Yield: 398 mg, 70%.

NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 7.70-7.68 (m, 4H, Ph), 7.52-7.37 (m, 10H, Ph, H_b), 7.33–7.25 (m, 5H, Ph), 6.74 (d, $^4J_{HH}$ = 1.8 Hz, 1H, H_a), 6.72 (d, $^4J_{HH}$ = 1.8 Hz, 1H, H_a), 0.32 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ (75 MHz): 151.7, 142.9, 142.0, 133.5, 133.5, 133.0, 132.1, 130.6, 130.3, 129.1, 129.0, 128.6, 128.6, 128.4, 126.9, 126.7, 125.3, 124.7, 124.7, 120.8, 105.4, 105.1, 104.8, 94.5, 0.08. Anal. Calcd for $C_{35}H_{30}OSi$: C, 84.98; H, 6.11. Found: C, 85.10; H, 6.22.

Compound 4: 

In a round bottom flask, to a methanol (10 mL) and dichloromethane (20 mL) solution of compound (**3**) (400 mg, 0.81 mmol) was added K_2CO_3 (335 mg, 2.43 mmol), and the reaction mixture was stirred at room temperature overnight. Deionized water was used to quench the reaction, dichloromethane was added to extract the product. The organic layer as dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 5/1) to give a yellow solid. Yield: 315 mg, 92%.

NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 7.70-7.69 (m, 4H, Ph), 7.67-7.50 (m, 10H, Ph, CH_b), 7.35–7.25 (m, 5H, Ph), 6.72 (d, $^4J_{HH}$ = 2.0 Hz, 1H, CH_a), 6.69 (d, $^4J_{HH}$ = 2.0 Hz, 1H, CH_a), 3.14 (s, 1H, CH). $^{13}C\{^1H\}$ (75 MHz): 151.7, 151.6, 143.2, 141.9, 133.5, 133.4, 132.1, 130.6, 130.4, 129.1, 129.0, 128.6, 128.5, 128.4, 127.0, 126.7, 125.2, 124.7, 119.8, 105.0, 104.7, 84.0. Anal. Calcd for $C_{32}H_{22}O$: C, 90.97; H, 5.25. Found: C, 90.60; H, 5.12.

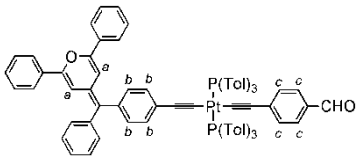
Complex 5: 

A 250 ml Schlenk flask, charged with **4** (600 mg, 1.42 mmol), *cis*-dichlorobis(*para*-tolylphosphine)platinum (1.50 g, 1.71 mmol), and cuprous iodide (27.0 mg, 10 mol%), was degassed and back-filled with argon three times. Then diethylamine (50 mL) and dried THF (100 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under argon protection at 60 °C for 2.5 h. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on Alumina (dichloromethane/petroleum ether 1/5) to give **5** as a yellow solid. Yield: 1.13 g, 74%.

NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 7.68-7.64 (m, 12H, *o* to P), 7.63-7.61 (m, 4H, Ph), 7.42-7.29 (m, 8H, Ph), 7.24-7.20 (m, 3H, Ph), 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 12H, *m* to P), 6.77 (d, $^3J_{HH}$= 8.4 Hz, 2H, CH_b), 6.61 (d, $^4J_{HH}$= 2.0 Hz, 1H, CH_a), 6.60 (d, $^4J_{HH}$= 2.0 Hz, 1H, CH_a), 6.04 (d, $^3J_{HH}$= 8.4 Hz, 2H, CH_b), 2.35 (s, 18H, CH_3). ^{13}C{^{1}H} (125 MHz): 151.0, 150.9, 142.4, 140.4, 138.6, 135.2, 135.1, 135.0, 133.7, 130.9, 130.5, 129.0, 128.8, 128.7, 128.6, 125.6, 128.5, 127.7, 127.3, 126.9, 126.6, 126.5, 126.4, 125.6, 124.5, 105.3, 105.2, 87.5. ^{31}P (202 MHz): 20.34 (s, $^1J_{PtP}$ = 2626 Hz).[s1] Anal. Calcd for $C_{74}H_{63}OClP_2Pt$: C, 70.50; H, 5.04. Found: C, 70.26; H, 5.01. MALDI-MS for $C_{74}H_{63}OClP_2Pt$ ([M + H]$^+$): 1260.7.

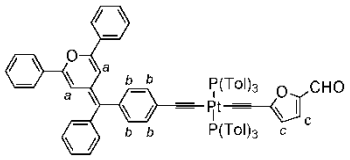
General procedure for the synthesis of Compounds 7a–e.

A 100 ml Schlenk flask, charged with chloro complex **5** (400 mg, 0.32 mmol), aldehyde **6a** (41.2 mg, 0.32 mmol), and cuprous iodide (6.0 mg, 10 mol%), was degassed and back-filled with argon three times. Then diethylamine (20 mL) and dried THF (20 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under argon protection at room temperature overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane: 1/2) to give **7a** as a yellow solid. A similar procedure was followed to prepare compounds **7b**, **7c**, **7d** and **7e**.

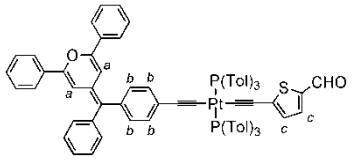
7a. 

Yield: 390 mg (yellow solid), 90%. NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 9.82 (s, 1H, CHO), 7.72-7.56 (m, 16H, *o* to P, Ph), 7.46-7.37 (m, 10H, Ph, CH_c), 7.34-7.31 (m, 3H, Ph), 7.19 (d, $^3J_{HH}$ = 7.8 Hz, 12H, *m* to P), 6.84 (d, $^3J_{HH}$= 8.0 Hz, 2H, CH_b), 6.65 (s, 1H, CH_a), 6.63 (s, 1H, CH_a), 6.36 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH_c), 6.25 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_b), 2.38 (s, 18H, CH_3). ^{13}C{^{1}H} (75 MHz): 191.7, 167.8, 151.1, 151.0, 142.4, 140.3, 138.5, 135.1, 135.0, 134.9, 133.7, 123.5, 132.3, 131.3, 130.9, 130.5, 129.2, 128.7, 128.6, 128.5, 128.4, 128.2, 126.6, 126.4, 125.6, 124.6, 105.3, 105.2, 21.4. ^{31}P (202 MHz): 17.31

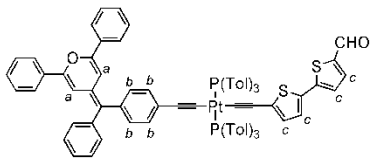
(s, $^{1}J_{PtP}$ = 2584 Hz).[s1] Anal. Calcd for $C_{83}H_{68}O_2P_2Pt$: C, 73.60; H, 5.06. Found: C, 73.34; H, 5.18. MALDI-MS for $C_{83}H_{68}O_2P_2Pt$ ($[M + H]^+$): 1354.3.

7b. 

Yield: 280 mg (orange solid), 65%. NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 9.33 (s, 1H, CHO), 7.68-7.63 (m, 12H, *o* to P), 7.62-7.60 (m, 3H, Ph), 7.42-7.23 (m, 10H, Ph), 7.24-7.21 (m, 2H, Ph), 7.19 (d, $^{3}J_{HH}$ = 7.3 Hz, 12H, *m* to P), 6.95 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, CH_c), 6.80 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_b), 6.61 (d, $^{4}J_{HH}$ = 2.0 Hz, 1H, CH_a), 6.62 (d, $^{4}J_{HH}$ = 2.0 Hz, 1H, CH_a), 6.18 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_b), 5.43 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, CH_c), 2.36 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ (75 MHz): 181.6, 151.1, 151.0, 142.4, 140.5, 140.4, 138.7, 135.0, 135.0, 134.9, 133.7, 130.8, 130.7, 130.5, 129.2, 128.8, 128.7, 128.6, 128.5, 128.1, 126.5, 125.7, 112.7, 105.3, 105.2, 21.4. ^{31}P (202 MHz): 16.70 (s, $^{1}J_{PtP}$ = 2574 Hz).[s1] Anal. Calcd for $C_{81}H_{66}O_3P_2Pt$: C, 72.36; H, 4.95. Found: C, 72.73; H, 4.86. MALDI-MS for $C_{81}H_{66}O_3P_2Pt$ ($[M + H]^+$): 1344.7.

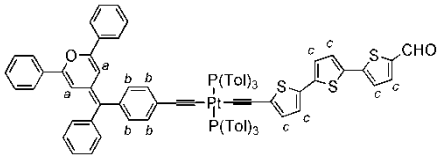
7c. 

Yield: 370 mg (orange solid), 85%. NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 9.60 (s, 1H, CHO), 7.67-7.61 (m, 15H, *o* to P, Ph), 7.42-7.23 (m, 11H, Ph, CH_c), 7.24-7.21 (m, 2H, Ph), 7.18 (d, $^{3}J_{HH}$ = 7.4 Hz, 12H, *m* to P), 6.81 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, CH_b), 6.62 (s, 1H, CH_a), 6.61 (s, 1H, CH_a), 6.21 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, CH_b), 5.97 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, CH_c), 2.37 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ (75 MHz): 182.0, 151.1, 151.0, 142.4, 140.5, 140.4, 139.3, 138.7, 136.6, 134.8, 133.7, 130.9, 130.5, 129.2, 128.8, 128.6, 126.6, 125.7, 125.3, 125.6, 105.3, 105.2, 21.4. ^{31}P (202 MHz): 17.05 (s, $^{1}J_{PtP}$ = 2590 Hz).[s1] Anal. Calcd for $C_{81}H_{66}O_2P_2PtS$: C, 71.51; H, 4.89; S, 2.36. Found: C, 71.75; H, 4.96; S, 2.09. MALDI-MS for $C_{81}H_{66}O_2P_2PtS$ ($[M + H]^+$): 1360.8.

7d. 

Yield: 425 mg (orange solid), 91%. NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 9.79 (s, 1H, CHO), 7.70-7.66 (m, 12H, *o* to P), 7.65-7.61 (m, 4H, Ph), 7.58 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, CH_c), 7.41-7.29 (m, 8H, Ph), 7.24-7.22 (m, 3H, Ph), 7.19 (d, $^{3}J_{HH}$ = 7.7 Hz, 12H, *m* to P), 7.00 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, CH_c), 6.92 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, CH_c), 6.81 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_b), 6.63 (d, $^{4}J_{HH}$= 2.0 Hz, 1H, CH_a), 6.60 (d, $^{4}J_{HH}$= 2.0 Hz, 1H, CH_a), 6.22 (d, ^{3}J= 8.4 Hz, 2H, CH_b), 5.90 (d, $^{3}J_{HH}$= 3.8 Hz, 1H, CH_c), 2.37 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ (75 MHz): 182.3, 151.1, 151.0, 148.4, 142.3, 140.3, 138.5, 137.6, 135.0, 134.9, 134.8,

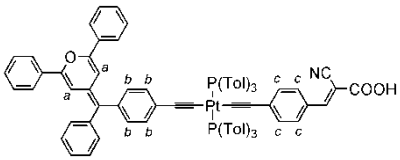
133.6, 133.5, 131.7, 130.8, 130.5, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 126.3, 125.5, 124.5, 124.4, 122.6, 105.3, 105.2, 21.5. ^{31}P (202 MHz): 17.05 (s, $^{1}J_{PtP}$ = 2595 Hz).[s1] Anal. Calcd for $C_{85}H_{68}O_2P_2PtS_2$: C, 70.77; H, 4.75; S, 4.45. Found: C, 70.90; H, 4.72; S, 4.27. MALDI-MS for $C_{85}H_{68}O_2P_2PtS_2$ ([M + H]$^+$): 1442.9.

7e. 

Yield: 450 mg (red solid), 90%. NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 9.83 (s, 1H, CHO), 7.70-7.66 (m, 12H, *o* to P), 7.65-7.61 (m, 5H, Ph, CH, CH_c), 7.41-7.29 (m, 10H, Ph, CH_c), 7.22-7.17 (m, 15H, *m* to P, Ph, CH_c), 6.90 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, CH_c), 6.82 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_b), 6.78 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, CH_c), 6.64 (s, 1H, CH_a), 6.61 (s, 1H, CH_a), 6.23 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_b), 5.90 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, CH_c), 2.38 (s, 18H, CH_3). ^{13}C{^{1}H} (75 MHz): 182.3, 151.1, 151.0, 147.2, 142.4, 140.3, 138.6, 137.5, 135.1, 134.9, 133.7, 133.2, 132.4, 130.9, 130.6, 129.2, 128.7, 128.6, 128.5, 128.4, 127.0, 126.7, 126.4, 125.7, 124.6, 124.5, 123.7, 123.1, 105.3, 105.2; 21.5. ^{31}P (202 MHz): 17.04 (s, $^{1}J_{PtP}$ = 2605 Hz).[s1] Anal. Calcd for $C_{89}H_{70}O_2P_2PtS_3$: C, 70.11; H, 4.63; S, 6.31. Found: C, 70.20; H, 4.70; S, 6.20. MALDI-MS for $C_{89}H_{70}O_2P_2PtS_3$ ([M + H]$^+$): 1524.2.

General procedure for the synthesis of Compounds 8a–e.

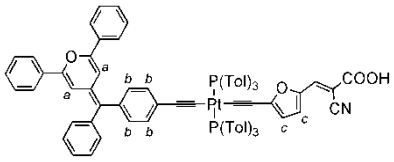
A solution of complex **7a** (150 mg, 0.055 mmol) and cyanoacetic acid (37.6 mg, 0.44 mmol) in $CHCl_3$ (20 mL) was refluxed in the presence of 4 drops of piperidine for 12 hours. After removing the solvent, the residue was purified by column chromatography on silica gel to give **8a** as a yellow solid. The residue was purified by column chromatography on silica gel (dichloromethane/methanol: 9/1) to give **8a** as a yellow solid. A similar procedure was followed to prepare final products **8b**, **8c**, **8d** and **8e**.

8a. 

Yield: 142 mg (yellow solid), 91%. IR (ATR, cm-1) 2160 w ($\nu_{C\equiv N}$), 2097 m ($\nu_{C\equiv C}$), 1659 w ($\nu_{C=O}$), 1579 s ($\nu_{C=C}$). NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 8.04 (s, 1H, NCC=C*H*), 7.67-7.56 (m, 16H, *o* to P, CH_c), 7.40-7.35 (m, 10H, Ph), 7.34-7.22 (m, 3H, Ph), 7.14 (d, $^{3}J_{HH}$ = 7.8 Hz, 12H, *m* to P), 6.84 (d, $^{3}J_{HH}$= 8.0 Hz, 2H, CH_b), 6.62 (s, 1H, CH_a), 6.60 (s, 1H, CH_a), 6.28 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, CH_c),

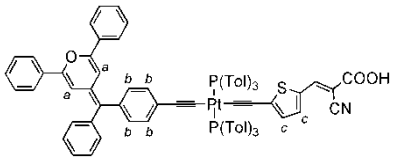
6.22 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_b), 2.32 (s, 18H, CH_3).[s2] $^{13}C\{^1H\}$ (125 MHz): 151.0, 151.9, 142.4, 140.3, 138.5, 135.0, 134.9, 134.8, 133.6, 131.4, 130.9, 130.5, 129.1, 128.6, 128.5, 128.4, 128.1, 126.6, 126.3, 126.1, 125.6, 115.9, 105.3, 105.2, 21.4.[s3] ^{31}P (202 MHz): 17.39 (s, $^1J_{PtP}$ = 2596 Hz).[s1] Anal. Calcd for $C_{86}H_{69}NO_3P_2Pt$: C, 72,66; H, 4.89; N, 0.99. Found: C, 72.84; H, 4.83; N, 1.06. MALDI-MS for $C_{86}H_{69}NO_3P_2Pt$ ($[M + H]^+$): 1421.8.

8b.

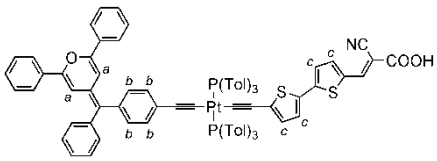


Yield: 132 mg (orange solid), 85%. IR (ATR, cm-1) 2160 w ($\nu_{C\equiv N}$), 2090 m ($\nu_{C\equiv C}$), 1662 w ($\nu_{C=O}$), 1589 s ($\nu_{C=C}$). NMR (δ (ppm), $CDCl_3$): ^1H (500 MHz): 7.75 (s, 1H, NCC=C*H*), 7.67-7.60 (m, 15H, *o* to P, Ph), 7.40-7.25 (m, 11H, Ph, CH_c), 7.23-7.20 (m, 2H, Ph), 7.19 (d, $^3J_{HH}$ = 7.6 Hz, 12H, *m* to P), 6.81 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_b), 6.62 (d, $^4J_{HH}$ = 1.8 Hz, 1H, CH_a), 6.60 (d, $^4J_{HH}$ = 1.8 Hz, 1H, CH_a), 6.19 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_b), 5.53 (d, $^3J_{HH}$ = 2.4 Hz, 1H, CH_c), 2.35 (s, 18H, CH_3).[s2] $^{13}C\{^1H\}$ (75 MHz): 151.1, 151.0, 145.9, 142.4, 140.5, 138.8, 135.0, 135.0, 134.8, 133.7, 130.8, 130.5, 129.2, 128.8, 128.7, 128.6, 128.5, 128.2, 128.0, 127.6, 126.5, 126.4, 125.7, 124.6, 115.6, 105.3, 21.4.[s3] ^{31}P (202 MHz): 16.79 (s, $^1J_{PtP}$ = 2562 Hz).[s1] Anal. Calcd for $C_{84}H_{67}NO_4P_2Pt$: C, 71.48; H, 4.78. Found: C, 71.73; H, 4.80. MALDI-MS for $C_{84}H_{67}NO_4P_2Pt$ ($[M + H]^+$): 1411.7.

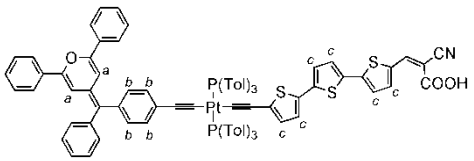
8c.



Yield: 146 mg (orange solid), 93%. IR (ATR, cm-1) 2160 w ($\nu_{C\equiv N}$), 2085 m ($\nu_{C\equiv C}$), 1654 w ($\nu_{C=O}$), 1572 s ($\nu_{C=C}$). NMR (δ (ppm), $CDCl_3$): ^1H (500 MHz): 8.04 (s, 1H, NCC=C*H*), 7.67-7.60 (m, 15H, *o* to P, Ph), 7.40-7.29 (m, 11H, Ph, CH_c), 7.23-7.20 (m, 2H, Ph), 7.19 (d, $^3J_{HH}$ = 7.7 Hz, 12H, *m* to P), 6.81 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_b), 6.62 (d, $^4J_{HH}$ = 1.6 Hz, 1H, CH_a), 6.60 (d, $^4J_{HH}$ = 1.6 Hz, 1H, CH_a), 6.21 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_b), 5.96 (d, $^3J_{HH}$ = 3.9 Hz, 1H, CH_c), 2.36 (s, 18H, CH_3).[s2] $^{13}C\{^1H\}$ (75 MHz): 151.0, 150.9, 147.1, 142.3, 140.5, 139.1, 138.7, 134.9, 134.8, 134.7, 133.6, 130.8, 130.5, 129.2, 128.8, 128.7, 128.5, 128.1, 126.3, 125.7, 124.5, 125.4, 116.5 105.1, 21.5.[s3] ^{31}P (202 MHz): 16.94 (s, $^1J_{PtP}$ = 2570 Hz).[s1] Anal. Calcd for $C_{84}H_{67}NO_3P_2PtS$: C, 70.67; H, 4.73; N, 0.98; S, 2.25. Found: C, 70.59; H, 4.73; N, 1.14; S, 2.04. MALDI-MS for $C_{84}H_{67}NO_3P_2PtS$ ($[M + H]^+$): 1427.8.

8d. 

Yield: 158 mg (red solid), 94%. IR (ATR, cm-1) 2161 w ($\nu_{C\equiv N}$), 2091 m ($\nu_{C\equiv C}$), 1659 w ($\nu_{C=O}$), 1578 s ($\nu_{C=C}$). NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 8.20 (s, 1H, NCC=C*H*), 7.67-7.61 (m, 15H, *o* to P, Ph), 7.40-7.29 (m, 11H, Ph, CH_c), 7.24-7.22 (m, 3H, Ph, CH_c), 7.19 (d, $^3J_{HH}$ = 7.4 Hz, 12H, *m* to P), 6.88 (s, 1H, CH_c), 6.81 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_b), 6.63 (s, 1H, CH_a), 6.60 (s, 1H, CH_a), 6.23 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_b), 5.84 (s, 1H, CH_c), 2.33 (s, 18H, CH_3).[s2] ^{13}C{^{1}H} (75 MHz): 151.1, 151.0, 142.4, 140.3, 138.6, 135.0, 134.9, 134.8, 133.7, 130.9, 130.6, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 126.7, 126.4, 125.7, 124.6, 114.9, 105.3, 105.2, 21.5.[s3] ^{31}P (202 MHz): 17.04 (s, $^1J_{PtP}$ = 2600 Hz).[s1] Anal. Calcd for $C_{88}H_{69}NO_3P_2PtS_2$: C, 70.01; H, 4.61; N, 0.93; S, 4.25. Found: C, 70.03; H, 4.55; N, 1.01, S, 4.08. MALDI-MS for $C_{88}H_{69}NO_3P_2PtS_2$ ([M + H]$^+$): 1509.7.

8e. 

Yield: 143 mg (red solid), 80%. IR (ATR, cm-1) 2160 w ($\nu_{C\equiv N}$), 2080 m ($\nu_{C\equiv C}$), 1658 w ($\nu_{C=O}$), 1570 s ($\nu_{C=C}$). NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 8.23 (s, 1H, NCC=C*H*), 7.67-7.61 (m, 15H, *o* to P, Ph, CH_c), 7.40-7.22 (m, 14H, Ph, CH_c), 7.19 (m, 14H, *m* to P, Ph, CH_c), 6.80 (d, $^3J_{HH}$ = 7.2 Hz, 2H, CH_b), 6.68 (s, 1H, CH_c), 6.62 (s, 1H, CH_a), 6.66 (s, 1H, CH_a), 6.21 (d, $^3J_{HH}$ = 7.2 Hz, 2H, CH_b), 5.84 (s, 1H, CH_c), 2.33 (s, 18H, CH_3).[s2] ^{13}C{^{1}H} (75 MHz): 151.2, 151.1, 142.5, 140.3, 138.6, 135.2, 135.0, 134.9, 134.8, 133.7, 130.9, 130.6, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 126.7, 126.4, 125.7, 124.6, 115.3, 105.3, 105.2, 21.5.[s3] ^{31}P (202 MHz): 17.00 (s, $^1J_{PtP}$ = 2606 Hz).[s1] Anal. Calcd for $C_{92}H_{71}NO_3P_2PtS_3$: C, 69.42; H, 4.50; N, 0.88; S, 6.04. Found: C, 69.13; H, 4.50; N, 1.01, S, 5.96. MALDI-MS for $C_{92}H_{71}NO_3P_2PtS_3$ ([M + H]$^+$): 1591.4.

2. Cyclic Voltammetry

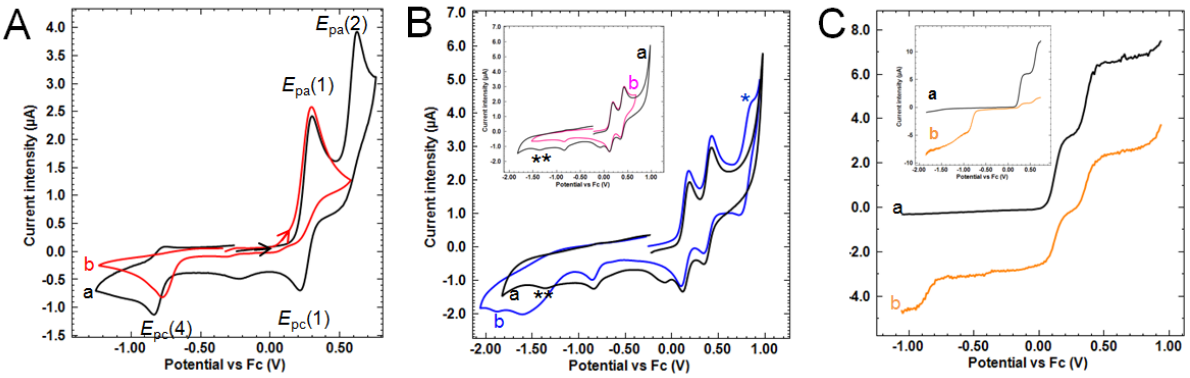


Figure S1 CVs (v = 0.1 V s^{-1}, E /V vs Fc^+/Fc) at a Pt working electrode in CH_2Cl_2/NBu_4PF_6 0.1 M of : **A**) compounds **4** (a, black curve) and **9** (b, red curve); **B**) compounds **5** (a, black curve) and **8b** (b, blue curve); Peak *: see discussion; Peak **: only appears after oxidation of pyrylidene moieties for compound **5**; Inset: CV of compound **5** for different potential windows (0.1 V s^{-1}); **C**) RDEV (600 t min^{-1}) of **5** before (a, black curve) and after (b, orange curve) electrolysis at +0.25 V. Inset: RDEV (600 t min^{-1}) of **4** before (a, black curve) and after (b, orange curve) electrolysis at +0.40 V. Concentration in electroactive species = 1 mM.

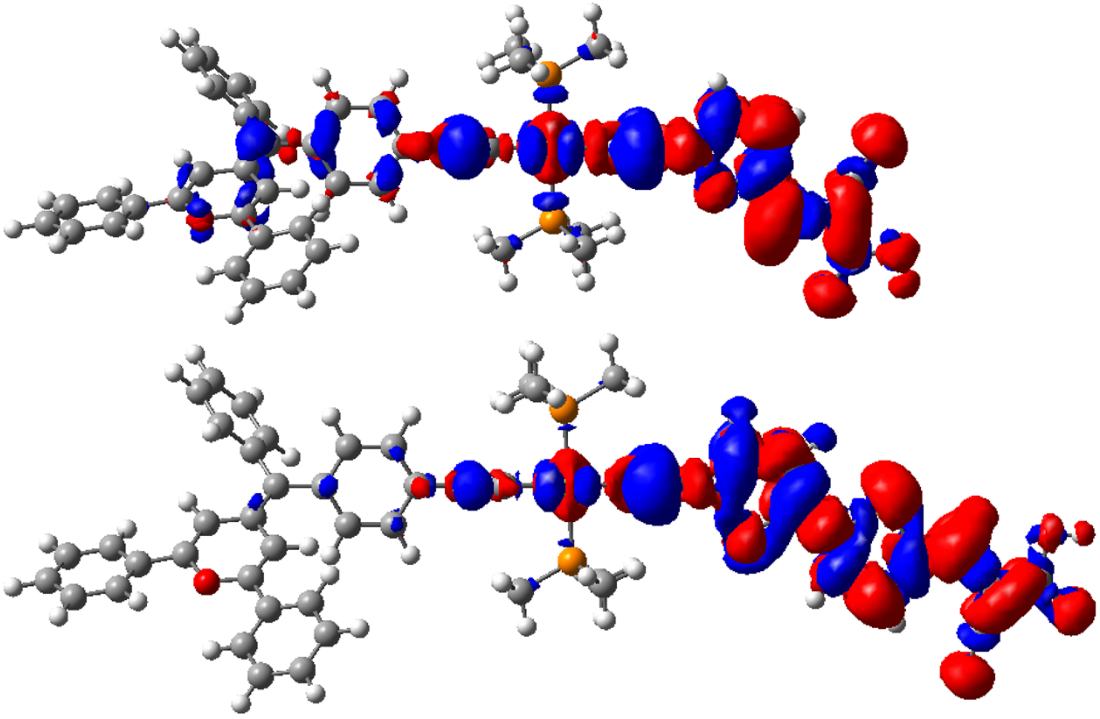
3. X-ray Crystallography Data of complex 5

Crystal Data for $C_{74}H_{63.2}ClO_{1.1}P_2Pt$ (M =1262.53): triclinic, space group P-1 (no. 2), a = 10.4357(10) Å, b = 10.9498(10) Å, c = 27.725(3) Å, α = 91.852(7)°, β = 93.653(7)°, γ = 110.591(7)°, V = 2954.6(5) Å^3, Z = 2, T = 110.15 K, μ(CuKα) = 5.715 mm^{-1}, *Dcalc* = 1.419 g/mm^3, 69136 reflections measured ($3.2 \leq 2\Theta \leq 120$), 8612 unique ($R_{int}$ = 0.0548) which were used in all calculations. The final R_1 was 0.0238 (>2sigma(I)) and wR_2 was 0.0578 (all data).

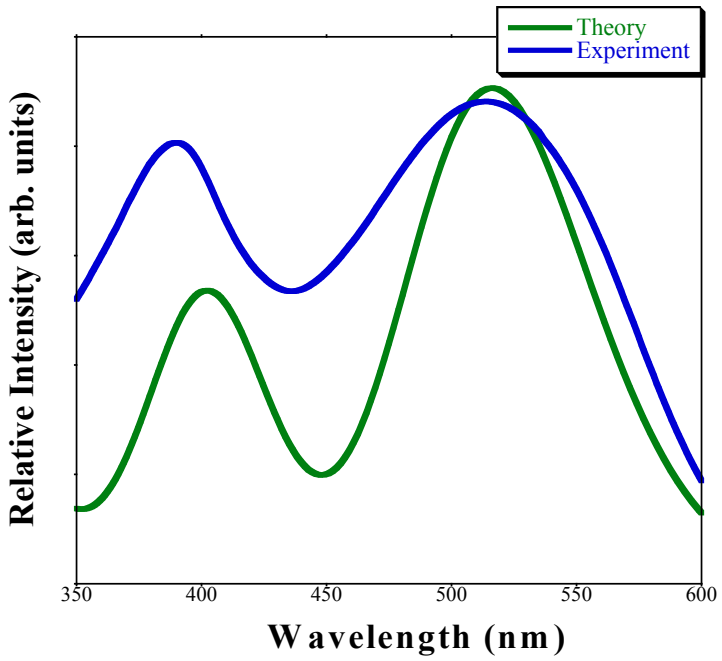
Table 1. Crystalllographic data for compound 5.

Compound	**5**	
Empirical formula	C74 H63.20 Cl O1.10 P2 Pt	
Formula weight	1262.53	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4357(10) Å	α= 91.852(7)°.
	b = 10.9498(10) Å	β= 93.653(7)°.
	c = 27.725(3) Å	γ = 110.591(7)°.
Volume	2954.6(5) Å^3	
Z	2	
Density (calculated)	1.419 Mg/m^3	
Absorption coefficient	5.715 mm^{-1}	
F(000)	1282	
Crystal size	0.09 x 0.07 x 0.03 mm^3	
Theta range for data collection	1.60 to 60.00°.	
Index ranges	-11<=h<=11, -12<=k<=12, -31<=l<=31	
Reflections collected	69136	
Independent reflections	8612 [R(int) = 0.0548]	
Completeness to theta = 60.00°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8472 and 0.6273	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8612 / 0 / 727	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0238, wR2 = 0.0568	
R indices (all data)	R1 = 0.0272, wR2 = 0.0578	
Largest diff. peak and hole	0.466 and -0.829 e.Å^{-3}	

4. Density difference plots for 8b (top) and 8d (bottom)



5. Comparison between experimental and theoretical absorption for 8e



6. Photovoltaic measurements

FTO conductive glass substrates (F-doped SnO_2) were purchased from Pilkington (TEC8). The plates were cleaned by successive sonication in soapy water, then an ethanolic solution of HCl (0.1 M) for 10 minutes, and finally dried in air. TiO_2 films were prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous $TiCl_4$ solution at 80°C. Three successive layers of mesoporous TiO_2 were then screen printed using a transparent colloidal paste (Dyesol DSL 18NR-T) and a final light scattering layer (Dyesol DSL 18NR-AO) was affixed, with 20-minute long drying steps at 150°C between each layer. The obtained substrates were then sintered at 450°C, following a progressive heating ramp (325°C for 5 min, 375°C for 5 min, 450°C for 30 min). A second $TiCl_4$ treatment was immediately conducted afterwards and the electrodes were fired one last time at 450°C for 30 minutes. Thicknesses (16 µm) were measured by a Sloan Dektak 3 profilometer. The prepared TiO_2 electrodes were soaked while still hot (ca. 80°C) in a 0.25 mM solution of complexes **8a-e** and chenodeoxycholic acid (5 mM) in a 1:1 mixture (v:v) of dichloromethane and ethanol. After one night of dyeing, the electrodes were rinsed in ethanol and dried in air, in the dark. Platinum based counter electrodes were prepared by drop casting two drops of hexachloroplatinic acid in distilled isopropanol (2 mg per mL) on FTO plates, and subsequent firing at 380°C for 30 minutes. The photoelectrode and the counter electrode were placed on top of each other and sealed using a thin transparent film of Surlyn polymer (DuPont, 60 µm) as a spacer. The resulting chamber was filled with an iodine-based electrolyte (30 mM I_2, 0.1 M LiI, 0.1 M guanidinium thiocyanate, 0.6 M 1-ethyl-2,3-dimethylimidazolium iodide and 0.1 M 4-tertbutylpyridine when mentioned, in dry distilled acetonitrile) by vacuum back filling through a predrilled hole in the counter electrode, and the photovoltaic device was sealed afterwards with Surlyn and a cover glass. The cell had an active area of 0.25 cm^2. Photovoltaic measurements were performed with a calibrated AM 1.5 artificial solar light simulator (Oriel) and a Keithley 2400 digital source-meter; data were collected with a local software designed by Synervia (labview).

7. References

(s1) This coupling represents a satellite (d, ^{195}Pt = 33.8%), and is not reflected in the peak multiplicity given.

(s2) The COO*H* signal was not observed.

(s3) The *C*OOH signal was not observed.