Supporting Information for

Synthesis, photovoltaic performances and TD-DFT quantum modeling of push-pull diacetylide platinum complexes in TiO₂ 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-trimethylsilyl)ethynylbenzophenone (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), CDCl₃):**

- ¹H (300 MHz): 7.70-7.68 (m, 4H, Ph), 7.52-7.37 (m, 10H, Ph), 7.33–7.25 (m, 5H, Ph), 6.74 (d, J_HH = 1.8 Hz, 1H, H_a), 6.72 (d, J_HH = 1.8 Hz, 1H, H_a), 0.32 (s, 9H, Si(CH₃)₃).
- ¹³C{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 C₃₅H₃₀OSi: 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 K₂CO₃ (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 MgSO₄, 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), CDCl₃):**

- ¹H (300 MHz): 7.70-7.69 (m, 4H, Ph), 7.67-7.50 (m, 10H, Ph), 7.35–7.25 (m, 5H, Ph), 6.72 (d, J_HH = 2.0 Hz, 1H, H_a), 6.69 (d, J_HH = 2.0 Hz, 1H, H_a), 3.14 (s, 1H, CH).
- ¹³C{¹H} (75 MHz): 151.7, 151.6, 143.2, 141.9, 133.5, 133.4, 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 C₃₂H₂₂O: 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, 0.10 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), CDCl₃): ¹H (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, 3JHH = 7.3 Hz, 12H, m to P), 6.77 (d, 3JHH = 8.4 Hz, 2H, CH₃), 6.61 (d, 4JHH = 2.0 Hz, 1H, CH₂), 6.60 (d, 4JHH = 2.0 Hz, 1H, CH₂), 6.04 (d, 3JHH = 8.4 Hz, 2H, CH₃), 2.35 (s, 18H, CH₃). ¹³C{¹H} (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. ³¹P (202 MHz): 20.34 (s, 1JPP = 2626 Hz). Anal. Calcd for C₇₄H₆₃OClP₂Pt: C, 70.50; H, 5.04. Found: C, 70.26; H, 5.01. MALDI-MS for C₇₄H₆₃OClP₂Pt ([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, 0.10 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.

Yield: 390 mg (yellow solid), 90%. NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 9.82 (s, 1H, CHO), 7.72-7.56 (m, 16H, o to P, Ph), 7.46-7.37 (m, 10H, Ph, CH₂), 7.34-7.31 (m, 3H, Ph), 7.19 (d, 3JHH = 7.8 Hz, 12H, m to P), 6.84 (d, 3JHH = 8.0 Hz, 2H, CH₂), 6.65 (s, 1H, CH₂), 6.63 (s, 1H, CH₂), 6.36 (d, 3JHH = 7.8 Hz, 2H, CH₂), 6.25 (d, 3JHH = 8.0 Hz, 2H, CH₂), 2.38 (s, 18H, CH₃). ¹³C{¹H} (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. ³¹P (202 MHz): 17.31
(s, $^{1}J_{PP} = 2584$ Hz).\textsuperscript{31} Anal. Calcd for $C_{83}H_{68}O_{2}P_{2}$Pt: C, 73.60; H, 5.06. Found: C, 73.34; H, 5.18. MALDI-MS for $C_{83}H_{68}O_{2}P_{2}$Pt ($[M + H]^{+}$): 1354.3.

7b.

Yield: 280 mg (orange solid), 65%. NMR ($\delta$ 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$_{a}$), 6.80 (d, $^{3}J_{HH} = 8.2$ Hz, 2H, CH$_{b}$), 6.61 (d, $^{3}J_{HH} = 2.0$ Hz, 1H, CH$_{c}$), 6.62 (d, $^{3}J_{HH} = 2.0$ 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, 130.7, 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, $^{1}J_{PP} = 2574$ Hz).\textsuperscript{31} Anal. Calcd for $C_{83}H_{66}O_{3}P_{2}$PtS: C, 72.82; H, 4.89; S, 2.36. Found: C, 72.82; H, 4.89; S, 2.36. MALDI-MS for $C_{83}H_{66}O_{3}P_{2}$PtS ($[M + H]^{+}$): 1344.7.

7c.

Yield: 370 mg (orange solid), 85%. NMR ($\delta$ 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$_{c}$), 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, 139.3, 138.7, 136.6, 134.8, 133.7, 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, $^{1}J_{PP} = 2590$ Hz).\textsuperscript{31} Anal. Calcd for $C_{83}H_{66}O_{2}P_{2}$PtS: C, 71.51; H, 4.89; S, 2.36. Found: C, 71.51; H, 4.89; S, 2.09. MALDI-MS for $C_{83}H_{66}O_{2}P_{2}$PtS ($[M + H]^{+}$): 1360.8.

7d.

Yield: 425 mg (orange solid), 91%. NMR ($\delta$ 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, $^{3}J_{HH} = 2.0$ Hz, 1H, CH$_{a}$), 6.60 (d, $^{3}J_{HH} = 2.0$ Hz, 1H, CH$_{b}$), 6.22 (d, $^{3}J_{HH} = 8.4$ 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, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 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, $J_{PP} = 2595$ Hz). 

Anal. Calcd for $C_{89}H_{70}O_2P_2PtS_3$: C, 70.77; H, 4.75; S, 4.45. Found: C, 70.90; H, 4.72; S, 4.27. MALDI-MS for $C_{89}H_{70}O_2P_2PtS_3$: [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$_2$), 7.41-7.29 (m, 10H, Ph, CH$_2$), 7.22-7.17 (m, 15H, m to P, Ph, CH$_2$), 6.90 (d, $J_{HH} = 3.8$ Hz, 1H, CH$_3$), 6.82 (d, $J_{HH} = 8.2$ Hz, 2H, CH$_2$), 6.78 (d, $J_{HH} = 3.7$ Hz, 1H, CH$_2$), 6.64 (s, 1H, CH$_2$), 6.61 (s, 1H, CH$_2$), 6.23 (d, $J_{HH} = 8.2$ Hz, 2H, CH$_3$), 5.90 (d, $J_{HH} = 3.7$ Hz, 1H, 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, $J_{PP} = 2605$ Hz). 

Anal. Calcd for $C_{89}H_{70}O_2P_2PtS_3$: 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 (νC=O), 2097 m (νC=O), 1659 w (νC=O), 1579 s (νC=C). NMR (δ ppm, CDCl$_3$): $^1$H (500 MHz): 8.04 (s, 1H, NCC=CH), 7.67-7.56 (m, 16H, o to P, CH$_2$), 7.40-7.35 (m, 10H, Ph), 7.34-7.22 (m, 3H, Ph), 7.14 (d, $J_{HH} = 7.8$ Hz, 12H, m to P), 6.84 (d, $J_{HH} = 8.0$ Hz, 2H, CH$_3$), 6.62 (s, 1H, CH$_2$), 6.60 (s, 1H, CH$_2$), 6.28 (d, $J_{HH} = 7.8$ Hz, 2H, CH$_3$),...
6.22 (d, $^{3}J_{HH} = 8.1$ Hz, 2H, CH$_b$), 2.32 (s, 18H, CH$_3$).$^{13}$C{$_1$H} (125 MHz): 151.0, 151.9, 142.4, 140.3, 138.5, 135.0, 134.9, 134.8, 133.6, 131.4, 130.9, 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.$^{31}$P (202 MHz): 17.39 (s, $^{1}J_{PP} = 2596$ Hz).

Anal. Calcd for C$_{86}$H$_{69}$NO$_3$P$_2$Pt: 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$_3$P$_2$Pt ([M + H$^+$]): 1421.8.

8b.

Yield: 132 mg (orange solid), 85%. IR (ATR, cm$^{-1}$) 2160 w (v$\text{C=O}$), 2085 m (v$\text{C=O}$). NMR (8 (ppm), CDCl$_3$): $^{1}$H (500 MHz): 7.75 (s, 1H, NCC=CH$_2$), 7.67-7.60 (m, 15H, o to P, Ph), 7.40-7.29 (m, 11H, Ph, CH$_3$), 7.23-7.20 (m, 2H, Ph), 7.19 (d, $^{3}J_{HH} = 7.6$ Hz, 12H, m to P), 6.81 (d, $^{3}J_{HH} = 8.2$ Hz, 2H, CH$_3$), 6.62 (d, $^{3}J_{HH} = 1.8$ Hz, 1H, CH$_3$), 6.60 (d, $^{3}J_{HH} = 1.8$ Hz, 1H, CH$_3$), 6.19 (d, $^{3}J_{HH} = 8.2$ Hz, 2H, CH$_3$), 5.53 (d, $^{3}J_{HH} = 2.4$ Hz, 1H, CH$_3$), 2.35 (s, 18H, CH$_3$).$^{13}$C{$_1$H} (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, 128.0, 127.6, 126.5, 126.4, 125.7, 124.6, 115.6, 105.3, 21.4.$^{31}$P (202 MHz): 16.79 (s, $^{1}J_{PP} = 2562$ Hz).

Anal. Calcd for C$_{84}$H$_{67}$NO$_4$P$_2$Pt: C, 71.48; H, 4.78. Found: C, 71.73; H, 4.80. MALDI-MS for C$_{84}$H$_{67}$NO$_4$P$_2$Pt ([M + H$^+$]): 1411.7.

8c.

Yield: 146 mg (orange solid), 93%. IR (ATR, cm$^{-1}$) 2160 w (v$\text{C=O}$), 2085 m (v$\text{C=O}$). NMR (8 (ppm), CDCl$_3$): $^{1}$H (500 MHz): 8.04 (s, 1H, NCC=CH$_2$), 7.67-7.60 (m, 15H, o to P, Ph), 7.40-7.29 (m, 11H, Ph, CH$_3$), 7.23-7.20 (m, 2H, Ph), 7.19 (d, $^{3}J_{HH} = 7.7$ Hz, 12H, m to P), 6.81 (d, $^{3}J_{HH} = 8.2$ Hz, 2H, CH$_3$), 6.62 (d, $^{3}J_{HH} = 1.6$ Hz, 1H, CH$_3$), 6.60 (d, $^{3}J_{HH} = 1.6$ Hz, 1H, CH$_3$), 6.21 (d, $^{3}J_{HH} = 8.2$ Hz, 2H, CH$_3$), 5.96 (d, $^{3}J_{HH} = 3.9$ Hz, 1H, CH$_3$), 2.36 (s, 18H, CH$_3$).$^{13}$C{$_1$H} (75 MHz): 151.0, 150.9, 147.1, 142.3, 140.5, 139.1, 138.7, 134.9, 134.8, 134.8, 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.$^{31}$P (202 MHz): 16.94 (s, $^{1}J_{PP} = 2570$ Hz).

Anal. Calcd for C$_{84}$H$_{67}$NO$_4$P$_2$PtS: 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$_4$P$_2$PtS ([M + H$^+$]): 1427.8.
Yield: 158 mg (red solid), 94%. IR (ATR, cm⁻¹) 2161 w (νC=N), 7091 m (νC=C), 1659 w (νC=O), 1578 s (νC=C). NMR (δ ppm, CDCl₃): ¹H (500 MHz): 8.20 (s, 1H, NCC=CH), 7.67-7.61 (m, 15H, o to P, Ph), 7.40-7.29 (m, 11H, Ph, CH₃), 7.24-7.22 (m, 3H, Ph, CH₃), 7.19 (d, JHH = 7.4 Hz, 12H, m to P), 6.88 (s, 1H, CH₃), 6.81 (d, JHH = 8.2 Hz, 2H, CH₃), 6.63 (s, 1H, CH₃), 6.60 (s, 1H, CH₃), 6.23 (d, JHH = 8.2 Hz, 2H, CH₃), 5.84 (s, 1H, CH₃), 2.33 (s, 18H, CH₃). ¹³C{¹H} (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. ³¹P (202 MHz): 17.04 (s, JPP = 2600 Hz). Anal. Calcd for C₈₈H₆₉NO₃P₂PtS₂: 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 C₈₈H₆₉NO₃P₂PtS₂ ([M + H]+): 1509.7.

Yield: 143 mg (red solid), 80%. IR (ATR, cm⁻¹) 2160 w (νC=N), 2080 m (νC=C), 1658 w (νC=O), 1570 s (νC=C). NMR (δ ppm, CDCl₃): ¹H (500 MHz): 8.23 (s, 1H, NCC=CH), 7.67-7.61 (m, 15H, o to P, Ph, CH₃), 7.40-7.22 (m, 14H, Ph, CH₃), 7.19 (m, 14H, m to P, Ph, CH₃), 6.80 (d, JHH = 7.2 Hz, 2H, CH₃), 6.68 (s, 1H, CH₃), 6.62 (s, 1H, CH₃), 6.66 (s, 1H, CH₃), 6.21 (d, JHH = 7.2 Hz, 2H, CH₃), 5.84 (s, 1H, CH₃), 2.33 (s, 18H, CH₃). ¹³C{¹H} (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, 125.3, 124.5, 114.9, 105.3, 105.2, 21.5, ⁳¹P (202 MHz): 17.00 (s, JPP = 2600 Hz). Anal. Calcd for C₉₂H₇₁NO₃P₂PtS₃: 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 C₉₂H₇₁NO₃P₂PtS₃ ([M + H]+): 1591.4.
2. Cyclic Voltammetry

Figure S1 CVs ($v = 0.1$ V s$^{-1}$, $E$/V vs Fe$^3$/Fe$^2$) at a Pt working electrode in CH$_2$Cl$_2$/NBu$_4$PF$_6$ 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$_2$Pt ($M=1262.53$): triclinic, space group P-1 (no. 2), $a = 10.4357(10)$ Å, $b = 10.9498(10)$ Å, $c = 27.725(3)$ Å, $\alpha = 91.852(7)^\circ$, $\beta = 93.653(7)^\circ$, $\gamma = 110.591(7)^\circ$, $V = 2954.6(5)$ Å$^3$, $Z = 2$, $T = 110.15$ K, $\mu$(CuK$\alpha$) = 5.715 mm$^{-1}$, $D_{calc} = 1.419$ 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. Crystallographic data for compound 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{74}$H$</em>{63.2}$ClO$_{1.1}$P$_2$Pt</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1262.53</td>
</tr>
<tr>
<td>Temperature</td>
<td>110(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 10.4357(10)$ Å (\alpha = 91.852(7)^\circ). $b = 10.9498(10)$ Å (\beta = 93.653(7)^\circ). $c = 27.725(3)$ Å (\gamma = 110.591(7)^\circ).</td>
</tr>
<tr>
<td>Volume</td>
<td>2954.6(5) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.419 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>5.715 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1282</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.09 x 0.07 x 0.03 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.60 to 60.00°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11&lt;=h&lt;=11, -12&lt;=k&lt;=12, -31&lt;=l&lt;=31</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>69136</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8612 [R(int) = 0.0548]</td>
</tr>
<tr>
<td>Completeness to theta = 60.00°</td>
<td>98.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8472 and 0.6273</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8612 / 0 / 727</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.074</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>$R_1 = 0.0238$, $wR_2 = 0.0568$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0272$, $wR_2 = 0.0578$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.466 and -0.829 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
4. Density difference plots for 8b (top) and 8d (bottom)
5. Comparison between experimental and theoretical absorption for $8\epsilon$

![Graph showing comparison between experimental and theoretical absorption](image-url)
6. Photovoltaic measurements

FTO conductive glass substrates (F-doped SnO\textsubscript{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\textsubscript{2} films were prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous TiCl\textsubscript{4} solution at 80°C. Three successive layers of mesoporous TiO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsuperscript{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 COOH signal was not observed.

(s3) The COOH signal was not observed.