Electronic Supplementary Information

Influence of alkoxy chains envelope on the interfacial photoinduced processes in tetraarylporphyrin-sensitized solar cells

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Synthesis of 1

2-butyloxybenzaldehyde

In a dry Schlenk tube 2.16 g of K_2CO_3 (15.6 mmol, 1.2 equiv.) were suspended in 17 ml of DMF anhydrous over molecular sieves. Under stirring 1.59 g of 2-hydroxybenzaldehyde (13 mmol, 1 equiv.) and 1.77 ml of 1-iodobutane (15.6 mmol, 1.2 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about -94 °C, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at 130 °C under nitrogen atmosphere for 24 h. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 170 ml of H_2O and extracted with of AcOEt (3 × 75 ml). The combined organic phase was washed with 100 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 1.88 g of product (yield 98%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.53 (1H, s), 7.83 (1H, d), 7.53 (1H, t), 6.99 (2H, m), 4.10 (2H, t), 1.84 (2H, m), 1.55 (2H, m), 1.0 (3H, m).

5,10,15,20-Tetrakis(2-butyloxyphenyl)porphyrin

In an anhydrous 3 l round-bottom flask, to a solution 1.88 g of 2-butiloxybenzaldehyde (10.56 mmol, 1.0 equiv.) in 1 l of CH_2Cl_2, 0.73 ml of pyrrole (10.56 mmol, 1.0 equiv.) were added and N_2 was bubbling for 15 min. Under vigorous stirring 0.73 ml of trifluoroacetic acid CF_3COOH (9.5 mmol, 0.9 equiv.). Under nitrogen atmosphere the reaction was stirred for 3 h in the dark. Then 3.59 g of DDQ (15.8 mmol, 1.5 equiv.) and the reaction was stirred under light for 1 h. Finally 3.85 ml of Et_3N (38 mmol, 3.6 equiv.) were added and the stirring was maintained overnight. The solution were concentrated and filtrated onto chromatographic column with CH_2Cl_2 obtaining 0.72 g of product (yield 30%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 8.76 (8H, s), 7.98 (4H, m), 7.75 (4H, m), 7.34 (8H, m), 3.91 (8H, m), 1.05 (8H, m), 0.64 (8H, m), 0.30 (12H, m), -2.60 (2H, s).

MS-FAB(+) *m/z*: ca1cd for $C_{60}H_{62}N_4O_4$ 902, found 903 $[M+H]^+$.

2-Bromo-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrin

In a 100 ml round-bottom flask, equipped with an Allihn condenser ending with a $CaCl_2$ valve, 200 mg of 5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrin were dissolved in 50 ml of $CHCl_3$. Under stirring 47 mg of NBS (0.266 mmol, 1.2 equiv.) were added and then the reaction mixture was refluxed at 70 °C for 18 h. The solvent was removed at the rotary evaporator obtaining 210 mg of crude product.

The mass spectrometry analysis has revealed just trace amounts of di-bromo derivative and unreacted porphyrin, thus the cure product was used for the successive step of the synthesis without other purification.

MS-FAB(+) *m/z*: ca1cd for $C_{60}H_{61}BrN_4O_4$ 982, found 982 $[M]^+$.

[2-Bromo-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrinate]Zn^{II}

In a two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 200 mg of 2-bromo-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrin (0.221 mmol, 1 equiv.) were dissolved in 50 ml of $CHCl_3$ and the resulting solution was heated to reflux. Under stirring a solution of 121 mg of $Zn(OAc)_2{\cdot}2H_2O$ (0.554 mmol, 2.5 equiv.) in 6 ml of CH_3OH was added dropwise, then the reaction mixture was refluxed for additional 1.5 h. The solvent was removed *in vacuo* and the crude product was dissolved in 30 ml di $CHCl_3$ again and washed with H_2O (3 × 50 ml), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. 226 mg of product were obtained (quantitative yield).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.00 (1H, m), 8.82 (6H, m), 8.02 (4H, m), 7.74 (4H, m), 7.34 (8H, m), 3.92 (8H, m), 1.06 (8H, m), 0.50 (8H, m), 0.30 (12H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 14.4 mg of 4-ethynylbenzaldehyde (1.11 mmol, 5 equiv.), 25.5 mg of $Pd(PPh_3)_4$ (22.1 μmol, 0.1 equiv.) and 226.3 mg of [2-bromo-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrinate]Zn^{II} (221 μmol, 1 equiv.) were dissolved in 5 ml of DMF anhydrous over molecular sieves and 15 ml of Et_3N. The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90 °C, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 6.3 mg of CuI (33.1 μmol, 0.15 equiv.) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120 °C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/AcOEt 90:10), obtaining 115.9 mg of product (yield 45.4%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.03 (1H, s), 9.21 (1H, m), 8.83 (5H, m), 8.76 (1H, m), 8.01 (4H, m), 7.86 (2H, d), 7.75 (4H, m), 7.57 (2H, d), 7.34 (7H, m), 7.23 (1H, m), 3.91 (8H, m), 1.07 (8H, m), 0.62 (8H, m), 0.33 (12H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{69}H_{64}N_4O_5Zn$ 1092, found 1093 $[M+H]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrinate]Zn^{II} ***1***

In a dry Schlenk tube 110 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-butyloxyphenyl)porphyrinate]Zn^{II} (95.2 μmol, 1 equiv.) were dissolved in 8 ml di $CHCl_3$. A solution of 162 mg of cyanoacetic acid (1.905 mmol, 20 equiv.) in 3 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85 °C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di $CHCl_3$ and washed with 20 ml of brine. The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2/MeOH 85:15), obtaining 76 mg of product (yield 68.7 %).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.04 (1H, m), 8.67 (6H, m), 8.17 (1H, s), 7.92 (6H, m), 7.71 (3H, m), 7.59 (2H, m), 7.46 (3H, m), 7.31 (5H, m), 7.22 (1H, m), 3.89 (8H, m), 1.06 (8H, m), 0.60 (8H, m), 0.31 (12H, m).

Elemental analysis calcd (%) for $C_{72}H_{65}N_5O_6Zn$: C 74.44, H 5.64, N 6.03; found C 74.73, H 5.66, N 6.01.

MS-ESI(-) *m/z*: ca1cd for $C_{72}H_{64}N_5O_6Zn$ (-1) 1158.41535, found 1158.41535 $[M-H]^-$.

Synthesis of 2

2-hexyloxybenzaldehyde

In a dry Schlenk tube 2.15 g of K_2CO_3 (15.6 mmol, 1.2 equiv.) were suspended in 17 ml of DMF anhydrous over molecular sieves. Under stirring 1.59 g of 2-hydroxybenzaldehyde (13 mmol, 1 equiv.) and 2.30 ml of 1-iodohexane (15.6 mmol, 1.2 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about -94 °C, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at 130 °C under nitrogen atmosphere for 24 h. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 170 ml of H_2O and extracted with of AcOEt (3 × 100 ml). The combined organic phase was washed with 100 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 2.63 g of product (yield 98%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.43 (1H, s), 7.71 (1H, dd), 7.41 (1H, dt), 6.89 (4H, m), 3.97 (2H, t), 1.74 (2H, m), 1.40 (2H, m), 1.27 (4H, m), 0.83 (3H, t).

5,10,15,20-Tetrakis(2-hexyloxyphenyl)porphyrin

In an anhydrous 3 l round-bottom flask, to a solution 2.46 g of 2-hexyloxybenzaldehyde (11.9 mmol, 1.0 equiv.) in 1.5 l of CH_2Cl_2, 0.82 ml of pyrrole (11.9 mmol, 1.0 equiv.) were added and N_2 was bubbling for 15 min. Under vigorous stirring 0.82 ml of trifluoroacetic acid CF_3COOH (10.73 mmol, 0.9 equiv.). Under nitrogen atmosphere the reaction was stirred for 3 h in the dark. Then 4.06 g of DDQ (17.9 mmol, 1.5 equiv.) and the reaction was stirred under light for 1 h. Finally 5.98 ml of Et_3N (42.9 mmol, 3.6 equiv.) were added and the stirring was maintained overnight. The solution were concentrated and filtrated onto chromatographic column with CH_2Cl_2 obtaining 1.06 g of product (yield 35.2%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 8.75 (8H, s), 7.98 (4H, m), 7.74 (4H, m), 7.32 (8H, m), 3.89 (8H, m), 1.05 (8H, m), 0.65 (24H, m), 0.38 (12H, m), -2.62 (2H, s).

MS-FAB(+) *m/z*: ca1cd for $C_{68}H_{78}N_4O_4$ 1014, found 1015 $[M+H]^+$.

2-Bromo-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrin

In a 100 ml round-bottom flask, equipped with an Allihn condenser ending with a $CaCl_2$ valve, 200 mg of 5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrin were dissolved in 50 ml of $CHCl_3$. Under stirring 38.6 mg of NBS (0.217 mmol, 1.1 equiv.) were added and then the reaction mixture was

refluxed at 70 °C for 18 h. The solvent was removed at the rotary evaporator obtaining 215 mg of crude product.

The mass spectrometry analysis has revealed just trace amounts of di-bromo derivative and unreacted porphyrin, thus the cure product was used for the successive step of the synthesis without other purification.

MS-FAB(+) *m/z*: ca1cd for $C_{68}H_{77}BrN_4O_4$ 1092, found 1092 $[M]^+$.

[2-Bromo-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II}

In a two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 200 mg of 2-bromo-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrin (0.183 mmol, 1 equiv.) were dissolved in 50 ml of $CHCl_3$ and the resulting solution was heated to reflux. Under stirring a solution of 100 mg of $Zn(OAc)_2{\cdot}2H_2O$ (0.457 mmol, 2.5 equiv.) in 6 ml of CH_3OH was added dropwise, then the reaction mixture was refluxed for additional 1.5 h. The solvent was removed *in vacuo* and the crude product was dissolved in 30 ml di $CHCl_3$ again and washed with H_2O (3 × 50 ml), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. 211 mg of product were obtained (quantitative yield).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.00 (1H, m), 8.83 (6H, m), 8.02 (4H, m), 7.74 (4H, m), 7.32 (8H, m), 3.88 (8H, m), 1.03 (8H, m), 0.57 (24H, m), 0.31 (12H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 11.9 mg of 4-ethynylbenzaldehyde (0.914 mmol, 5 equiv.), 21.1 mg of $Pd(PPh_3)_4$ (18.3 μmol, 0.1 equiv.) and 226.3 mg of [2-bromo-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II} (221 μmol, 1 equiv.) were dissolved in 5 ml of DMF anhydrous over molecular sieves and 15 ml of Et_3N. The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90 °C, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 5.2 mg of CuI (27.4 μmol, 0.15 equiv.) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120 °C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/AcOEt 90:10), obtaining 81.7 mg of product (yield 37%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.07 (1H, s), 9.19 (1H, m), 8.78 (6H, m), 8.01 (4H, m), 7.87 (2H, d), 7.75 (4H, m), 7.57 (2H, d), 7.33 (8H, m), 3.88 (8H, m), 1.03 (8H, m), 0.57 (24H, m), 0.30 (12H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{77}H_{80}N_4O_5Zn$ 1204, found 1205 $[M+H]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II} ***2***

In a dry Schlenk tube 81.7 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II} (67.7 μmol, 1 equiv.) were dissolved in 5 ml di $CHCl_3$. A solution of 115.1 mg of cyanoacetic acid (1.35 mmol, 20 equiv.) in 1.5 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85 °C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di $CHCl_3$ and washed with 20 ml of brine. The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2/MeOH 95:5 gradient to 80:20), obtaining 89.9 mg of product (yield 100%).

^{1}H-NMR (400.1 MHz, THF-d_8) δ, *ppm*: 9.08 (1H, s), 8.67 (6H, m), 8.48 (1H, br s), 8.15 (2H, d), 7.95 (4H, m), 7.66 (6H, m), 7.33 (8H, m), 3.92 (8H, m), 1.03-0.46 (44H, m).

Elemental analysis calcd (%) for $C_{80}H_{81}N_5O_6Zn$: C 75.43, H 6.41, N 5.50; found C 75.14, H 6.43, 5.48.

MS-ESI(-) *m/z*: ca1cd for $C_{80}H_{80}N_5O_6Zn$ (-1) 1270.53946, found 1270.53877 $[M-H]^-$.

Synthesis of 4

2-(dodecyloxy)benzaldehyde

In a dry Schlenk tube 2.16 g of K_2CO_3 (15.6 mmol, 1.2 equiv.) were suspended in 17 ml of DMF anhydrous over molecular sieves. Under stirring 1.59 g of 2-hydroxybenzaldehyde (13 mmol, 1 equiv.) and 3.85 ml of 1-iododododecane (15.6 mmol, 1.2 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about -94 °C, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at 130 °C under nitrogen atmosphere for 24 h. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 170 ml of H_2O and extracted with of AcOEt (3 × 75 ml). The combined organic phase was washed with 100 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 3.70 g of product (yield 98%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.53 (1H, s), 7.83 (1H, dd), 7.52 (1H, m), 6.99 (2H, m), 4.07 (2H, t), 1.86 (2H, m), 1.50 (2H, m), 1.36 (16H, m), 0.89 (3H, t).

5,10,15,20-Tetrakis(2-(dodecyloxyphenyl)porphyrin

In an anhydrous 3 l round-bottom flask, to a solution 3.77 g of 2-dodecyloxybenzaldehyde (13.0 mmol, 1.0 equiv.) in 1 l of CH_2Cl_2, 0.90 ml of pyrrole (13.0 mmol, 1.0 equiv.) were added and N_2 was bubbling for 15 min. Under vigorous stirring 0.90 ml of trifluoroacetic acid CF_3COOH

(11.7 mmol, 0.9 equiv.). Under nitrogen atmosphere the reaction was stirred for 3 h in the dark. Then 4.43 g of DDQ (19.5 mmol, 1.5 equiv.) and the reaction was stirred under light for 1 h. Finally 6.53 ml of Et_3N (46.8 mmol, 3.6 equiv.) were added and the stirring was maintained overnight. The solution were concentrated and filtrated onto chromatographic column with CH_2Cl_2 obtaining 0.72 g of product (yield 30%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 8.80 (8H, s), 8.04 (4H, m), 7.78 (4H, m), 7.37 (8H, d), 3.93 (8H, m), 1.50-0.50 (92H, m), -2.56 (2H, s).

MS-FAB(+) *m/z*: ca1cd for $C_{92}H_{126}N_4O_4$ 1350, found 1352 $[M+H]^+$.

2-Bromo-5,10,15,20-tetrakis(2-dodecyloxyphenyl)porphyrin

In a 100 ml round-bottom flask, equipped with an Allihn condenser ending with a $CaCl_2$ valve, 200 mg of 5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrin were dissolved in 50 ml of $CHCl_3$. Under stirring 47 mg of NBS (0.266 mmol, 1.2 equiv.) were added and then the reaction mixture was refluxed at 70 °C for 18 h. The solvent was removed at the rotary evaporator obtaining 210 mg of crude product.

The mass spectrometry analysis has revealed just trace amounts of di-bromo derivative and unreacted porphyrin, thus the cure product was used for the successive step of the synthesis without other purification.

MS-FAB(+) *m/z*: ca1cd for $C_{92}H_{125}BrN_4O_4$ 1428, found 1429 $[M+H]^+$.

[2-Bromo-5,10,15,20-tetrakis(2-dodecyloxyphenyl)porphyrinate]Zn^{II}

In a two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 200 mg of 2-bromo-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrin (0.221 mmol, 1 equiv.) were dissolved in 50 ml of $CHCl_3$ and the resulting solution was heated to reflux. Under stirring a solution of 121 mg of $Zn(OAc)_2{\cdot}2H_2O$ (0.554 mmol, 2.5 equiv.) in 6 ml of CH_3OH was added dropwise, then the reaction mixture was refluxed for additional 1.5 h. The solvent was removed *in vacuo* and the crude product was dissolved in 30 ml di $CHCl_3$ again and washed with H_2O (3 × 50 ml), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. 226 mg of product were obtained (quantitative yield).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 8.99 (1H, m), 8.81 (6H, m), 8.00 (4H, m), 7.74 (4H, m), 7.32 (8H, m), 3.88 (8H, m), 1.49-0.5 (92H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-dodecyloxyphenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 14.4 mg of 4-ethynylbenzaldehyde (1.11 mmol, 5 equiv.), 25.5 mg of $Pd(PPh_3)_4$ (22.1 μmol, 0.1 equiv.) and 226.3 mg of [2-bromo-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II} (221 μmol, 1 equiv.) were dissolved in 5 ml of DMF anhydrous over molecular sieves and 15 ml of Et_3N. The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90 °C, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 6.3 mg of CuI (33.1 μmol, 0.15 equiv.) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120 °C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/AcOEt 90:10), obtaining 115.9 mg of product (yield 45.4%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.07 (1H, s), 9.19 (1H, m), 8.82 (5H, m), 8.74 (1H, m), 8.02 (4H, m), 7.88 (2H, d), 7.75 (3H, m), 7.59 (4H, m), 7.45 (1H, m), 7.34 (5H, m), 7.23 (1H, m), 3.88 (8H, m), 1.40-0.5 (92H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{101}H_{128}N_4O_5Zn$ 1540, found 1541 $[M+H]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2-dodecyloxyphenyl)porphyrinate]Zn^{II} ***4***

In a dry Schlenk tube 65.0 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-hexyloxyphenyl)porphyrinate]Zn^{II} (36.0 μmol, 1 equiv.) were dissolved in 3 ml di $CHCl_3$. A solution of 90.6 mg of cyanoacetic acid (1.064 mmol, 30 equiv.) in 3 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85 °C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di $CHCl_3$ and washed with 20 ml of brine. The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2/MeOH 95:5 gradient to 80:20), obtaining 49.9 mg of product (yield 73%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.19 (1H, m), 8.76 (6H, m), 8.09 (6H, m), 7.67 (6H, m), 7.26 (9H, m), 3.84 (8H, m), 1.40-0.25 (92H, m).

Elemental analysis calcd (%) for $C_{104}H_{129}N_5O_6Zn$: C 77.56, H 8.07, N 4.35; found C 76.27, H 8.07, N 4.31.

MS-ESI(-)*m/z*: ca1cd for $C_{104}H_{128}N_5O_6Zn$ (-1) 1606.91616, found 1606.91997 $[M-H]^-$.

Synthesis of 5

2-(2-ethylhexyloxy)benzaldehyde

In a dry Schlenk tube 2.16 g of K_2CO_3 (15.6 mmol, 1.2 equiv.) were suspended in 17 ml of DMF anhydrous over molecular sieves. Under stirring 1.59 g of 2-hydroxybenzaldehyde (13 mmol, 1 equiv.) and 2.77 ml of 2-ethylhexylbromide (15.6 mmol, 1.2 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about -94 °C, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at 130 °C under nitrogen atmosphere for 24 h. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 170 ml of H_2O and extracted with of AcOEt (3 × 100 ml). The combined organic phase was washed with 100 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 2.41 g of product (yield 79.3%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.41 (1H, s), 7.69 (1H, d), 7.40 (1H, t), 6.87 (2H, m), 3.85 (2H, d), 1.67 (1H, m), 1.37 (4H, m), 1.21 (4H, m), 0.81 (6H, m).

5,10,15,20-Tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrin

In an anhydrous 3 l round-bottom flask, to a solution 2.41 g of 2-(2-ethylhexyloxy)benzaldehyde (10.3 mmol, 1.0 equiv.) in 1 l of CH_2Cl_2, 0.71 ml of pyrrole (10.3 mmol, 1.0 equiv.) were added and N_2 was bubbling for 15 min. Under vigorous stirring 0.71 ml of trifluoroacetic acid CF_3COOH (9.27 mmol, 0.9 equiv.). Under nitrogen atmosphere the reaction was stirred for 3 h in the dark. Then 3.51 g of DDQ (15.5 mmol, 1.5 equiv.) and the reaction was stirred under light for 1 h. Finally 5.17 ml of Et_3N (37 mmol, 3.6 equiv.) were added and the stirring was maintained overnight. The solution were concentrated and filtrated onto chromatographic column with CH_2Cl_2 obtaining 1.48 g of product (yield 51.1%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 8.75 (8H, m), 7.96 (4H, m), 7.76 (4H, m), 7.34 (8H, m), 3.84 (8H, m), 1.00 (4H, m), 0.75-0.20 (56H, m), -2.59 (2H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{76}H_{94}N_4O_4$ 1126, found 1128 $[M+H]^+$.

2-Bromo-5,10,15,20-tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrin

In a 100 ml round-bottom flask, equipped with an Allihn condenser ending with a $CaCl_2$ valve, 200 mg of 5,10,15,20-tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrin were dissolved in 50 ml of $CHCl_3$. Under stirring 38 mg of NBS (0.213 mmol, 1.2 equiv.) were added and then the reaction

mixture was refluxed at 70 °C for 18 h. The solvent was removed at the rotary evaporator obtaining 210 mg of crude product.

The mass spectrometry analysis has revealed just trace amounts of di-bromo derivative and unreacted porphyrin, thus the cure product was used for the successive step of the synthesis without other purification.

MS-FAB(+) *m/z*: ca1cd for $C_{76}H_{93}BrN_4O_4$ 1204, found 1204 $[M]^+$.

[2-Bromo-5,10,15,20-tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrinateyl]Zn^{II}

In a two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 255 mg of 2-Bromo-5,10,15,20-tetrakis(2-(2-ethhexyloxy)phenyl)porphyrin (0.228 mmol, 1 equiv.) were dissolved in 50 ml of $CHCl_3$ and the resulting solution was heated to reflux. Under stirring a solution of 125 mg of $Zn(OAc)_2 \cdot 2H_2O$ (0.554 mmol, 2.5 equiv.) in 6 ml of CH_3OH was added dropwise, then the reaction mixture was refluxed for additional 1.5 h. The solvent was removed *in vacuo* and the crude product was dissolved in 30 ml di $CHCl_3$ again and washed with H_2O (3 × 50 ml), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. 226 mg of product were obtained (quantitative yield).

^{1}H-NMR (400.1 MHz, $CDCl_3$) *δ*, *ppm*: 8.99 (1H, m), 8.82 (6H, m), 7.99 (3H, m), 7.84 (1H, m), 7.75 (4H, m), 7.30 (8H, m), 3.78 (8H, t), 0.93 (4H, m), 0.70-0.00 (56H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 14.4 mg of 4-ethynylbenzaldehyde (0.917 mmol, 5 equiv.), 21.2 mg of $Pd(PPh_3)_4$ (18.3 μmol, 0.1 equiv.) and 232.8 mg of 2-bromo-5,10,15,20-tetrakis(2-(2-ethhexyloxy)phenyl)porphyrinateyl]Zn^{II} (0.183 mmol, 1 equiv.) were dissolved in 5 ml of DMF anhydrous over molecular sieves and 15 ml of Et_3N. The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90 °C, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 5.2 mg of CuI (27.5 μmol, 0.15 equiv.) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120 °C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/AcOEt 90:10), obtaining 130.6 mg of product (yield 54.1%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) *δ*, *ppm*: 10.06 (1H, s), 9.18 (1H, m), 8.78 (6H, m), 7.99 (4H, m), 7.87 (2H, d), 7.76 (3H, m), 7.55 (3H, m), 7.33 (7H, m), 7.18 (1H, m), 3.79 (8H, m), 0.92 (4H, m), 0.70-0.10 (56H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{85}H_{96}N_4O_5Zn$ 1316, found 1316 $[M]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrinate]Zn^{II} ***5***

In a dry Schlenk tube 130.6 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-(2-ethylhexyloxy)phenyl)porphyrinate]Zn^{II} (99.0 μmol, 1 equiv.) were dissolved in 3 ml di $CHCl_3$. A solution of 42.1 mg of cyanoacetic acid (0.495 mmol, 5 equiv.) in 1.5 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85 °C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di $CHCl_3$ and washed with 20 ml of brine. The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2/MeOH 95:5 gradient to 80:20), obtaining 123.1 mg of product (yield 89.7 %).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.16 (1H, m), 8.74 (7H, m), 8.15 (2H, m), 7.93 (4H, m), 7.62 (6H, m), 7.26 (8H, m), 3.74 (8H, m), 0.89 (4H. m), 0.65-0.00 (56H, m).

Elemental analysis calcd (%) for $C_{88}H_{97}N_5O_6Zn$: C 76.25, H 7.05, N 5.05; found C 75.96, H 7.09, N 4.99.

MS-ESI(-)*m/z*: ca1cd for $C_{88}H_{96}N_5O_6Zn$ (-1) 1382.66576, found 1382.66751 $[M-H]^-$.

Synthesis of 6

2-(cyclohexyloxy)benzaldehyde

In a dry Schlenk tube 7.19 g of K_2CO_3 (52 mmol, 4 equiv.) were suspended in 20 ml of DMF anhydrous over molecular sieves. Under stirring 1.59 g of 2-hydroxybenzaldehyde (13 mmol, 1 equiv.) and 3.36 ml of iodocyclohexane (15.6 mmol, 2 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about -94 °C, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at 130 °C under nitrogen atmosphere for 3 days. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 170 ml of H_2O and extracted with of AcOEt (3 × 100 ml). The combined organic phase was washed with 100 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 0.33 g of product (yield 12.4 %).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.53 (1H, s), 7.84 (1H, d), 7.53 (1H, t), 7.00 (2H, t), 4.44 (1H, m), 1.98 (2H, m), 1.83 (2H, m), 1.65 (3H, m), 1.45 (3H, m).

5,10,15,20-Tetrakis(2-(cyclohexyloxy)phenyl)porphyrin

In an anhydrous 0.5 l round-bottom flask, to a solution 0.45 g of 2-(cyclohexyloxy)benzaldehyde (2.2 mmol, 1.0 equiv.) in 200 l of CH_2Cl_2, 0.15 ml of pyrrole (2.2 mmol, 1.0 equiv.) were added and N_2

was bubbling for 15 min. Under vigorous stirring 0.15 ml of trifluoroacetic acid CF_3COOH (2.0 mmol, 0.9 equiv.). Under nitrogen atmosphere the reaction was stirred for 3 h in the dark. Then 0.75 g of DDQ (3.3 mmol, 1.5 equiv.) and the reaction was stirred under light for 1 h. Finally 1.11 ml of Et_3N (7.9 mmol, 3.6 equiv.) were added and the stirring was maintained overnight. The solution were concentrated and filtrated onto chromatographic column with CH_2Cl_2 obtaining 0.058 g of product (yield 10.6%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 8.77 (8H, m,), 7.98 (4H, m), 7.71 (4H, m), 7.34 (8H, m), 4.17 (4H, m), 1.59-0.72 (40H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{68}H_{70}N_4O_4$ 1006, found 1007 $[M+H]^+$.

2-Bromo-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrin

In a 100 ml round-bottom flask, equipped with an Allihn condenser ending with a $CaCl_2$ valve, 200 mg of 5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrin (0.198 mmol, 1 equiv.) were dissolved in 50 ml of $CHCl_3$. Under stirring 42 mg of NBS (0.238 mmol, 1.2 equiv.) were added and then the reaction mixture was refluxed at 70 °C for 18 h. The solvent was removed at the rotary evaporator obtaining 210 mg of crude product.

The mass spectrometry analysis has revealed just trace amounts of di-bromo derivative and unreacted porphyrin, thus the cure product was used for the successive step of the synthesis without other purification.

MS-FAB(+) *m/z*: ca1cd for $C_{68}H_{69}BrN_4O_4$ 1084, found 1085 $[M+H]^+$.

[2-Bromo-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrinate]Zn^{II}

In a two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 200 mg of 2-bromo-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrin (0.221 mmol, 1 equiv.) were dissolved in 50 ml of $CHCl_3$ and the resulting solution was heated to reflux. Under stirring a solution of 121 mg of $Zn(OAc)_2{\cdot}2H_2O$ (0.554 mmol, 2.5 equiv.) in 6 ml of CH_3OH was added dropwise, then the reaction mixture was refluxed for additional 1.5 h. The solvent was removed *in vacuo* and the crude product was dissolved in 30 ml di $CHCl_3$ again and washed with H_2O (3 × 50 ml), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. 226 mg of product were obtained (quantitative yield).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.03 (1H, m), 8.84 (6H, m), 8.02 (4H, m), 7.83 (1H, m), 7.74 (4H, m), 7.31 (8H, m), 4.16 (4H, m), 1.70-0.40 (40H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 14.4 mg of 4-ethynylbenzaldehyde (1.11 mmol, 5 equiv.), 25.5 mg of $Pd(PPh_3)_4$ (22.1 μmol, 0.1 equiv.) and 226.3 mg of [2-bromo-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrinate]Zn^{II} (221 μmol, 1 equiv.) were dissolved in 5 ml of DMF anhydrous over molecular sieves and 15 ml of Et_3N. The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90 °C, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 6.3 mg of CuI (33.1 μmol, 0.15 equiv.) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120 °C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/AcOEt 90:10), obtaining 115.9 mg of product (yield 45.4%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 10.06 (1H, s), 9.23 (1H, m), 8.81 (6H, m), 8.02 (4H, m), 7.88 (2H, d), 7.72 (4H, m), 7.57 (2H, m), 7.36 (8H, m), 4.15 (4H, m), 1.70-0.40 (40H, m).

MS-FAB(+) *m/z*: ca1cd for $C_{77}H_{72}N_4O_5Zn$ 1196, found 1196 $[M]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrinate]Zn^{II} ***6***

In a dry Schlenk tube 65.0 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-(cyclohexyloxy)phenyl)porphyrinate]Zn^{II} (36.0 μmol, 1 equiv.) were dissolved in 3 ml di $CHCl_3$. A solution of 90.6 mg of cyanoacetic acid (1.064 mmol, 30 equiv.) in 3 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85 °C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di $CHCl_3$ and washed with 20 ml of brine. The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2/MeOH 95:5 gradient to 80:20), obtaining 49.9 mg of product (yield 73%).

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ, *ppm*: 9.24 (1H, m), 8.80 (6H, m), 8.03 (6H, m), 7.64 (7H, m), 7.32 (8H, m), 4.14 (4H, m), 1.72-0.40 (40H, m).

Elemental analysis calcd (%) for $C_{80}H_{73}N_5O_6Zn$: C 75.91, H 5.81, N 5.53; found C 76.19, H 5.78, 5.49.

MS-ESI(-) *m/z*: ca1cd for $C_{80}H_{72}N_5O_6Zn$ (-1) 1262.47796, found 1262.47843 $[M-H]^-$.

Additional steady-state and time-resolved spectrofluorimetric data in THF solution

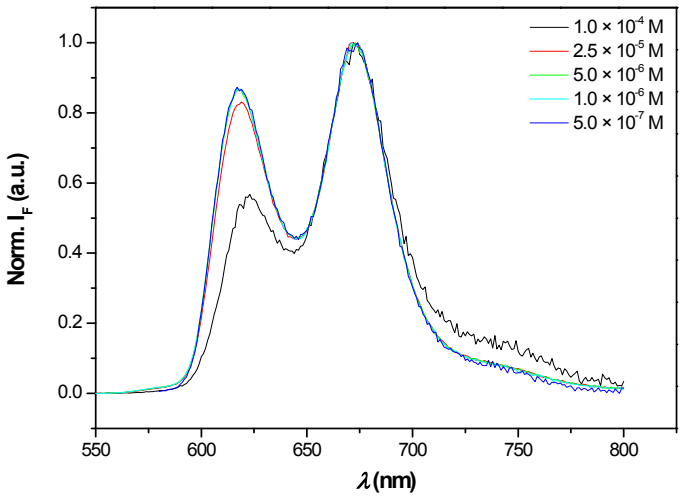

Figure S1. Fluorescent emission spectra of dye **1** at different concentrations.

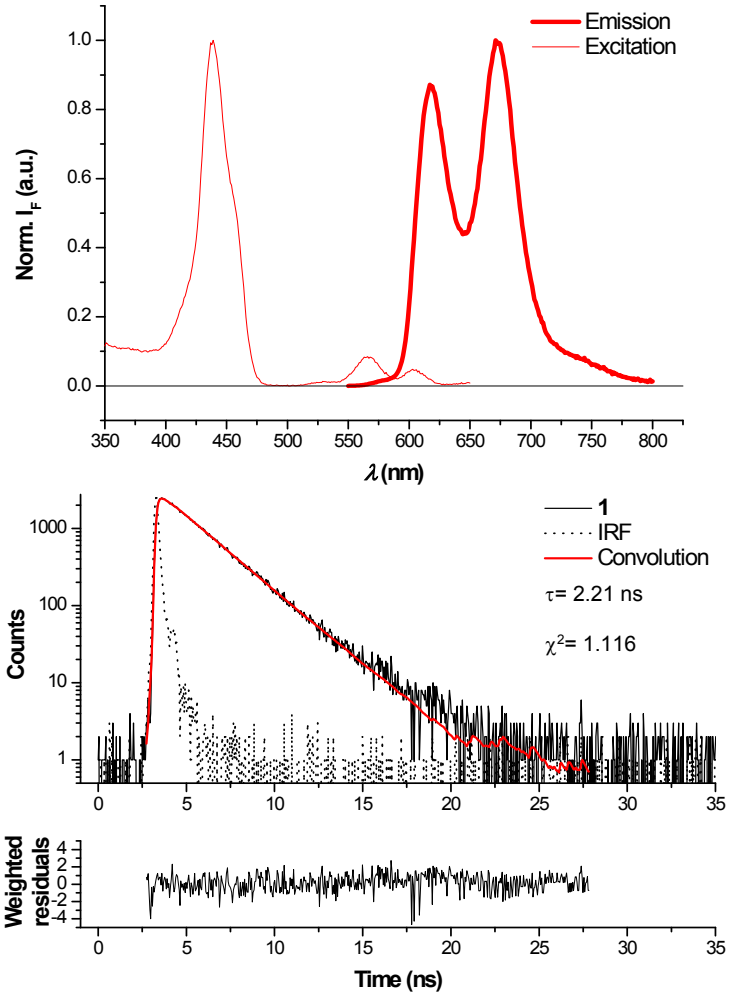

Figure S2. *Top*: emission and excitation spectra of **1**. *Bottom*: fluorescence decay of **1**, black line (λ_{exc} 445 nm; λ_{em} 618 nm). Instrument response function (IRF) and convolution fit black dotted line and red line respectively. Weighted residuals are shown under the decay curves.

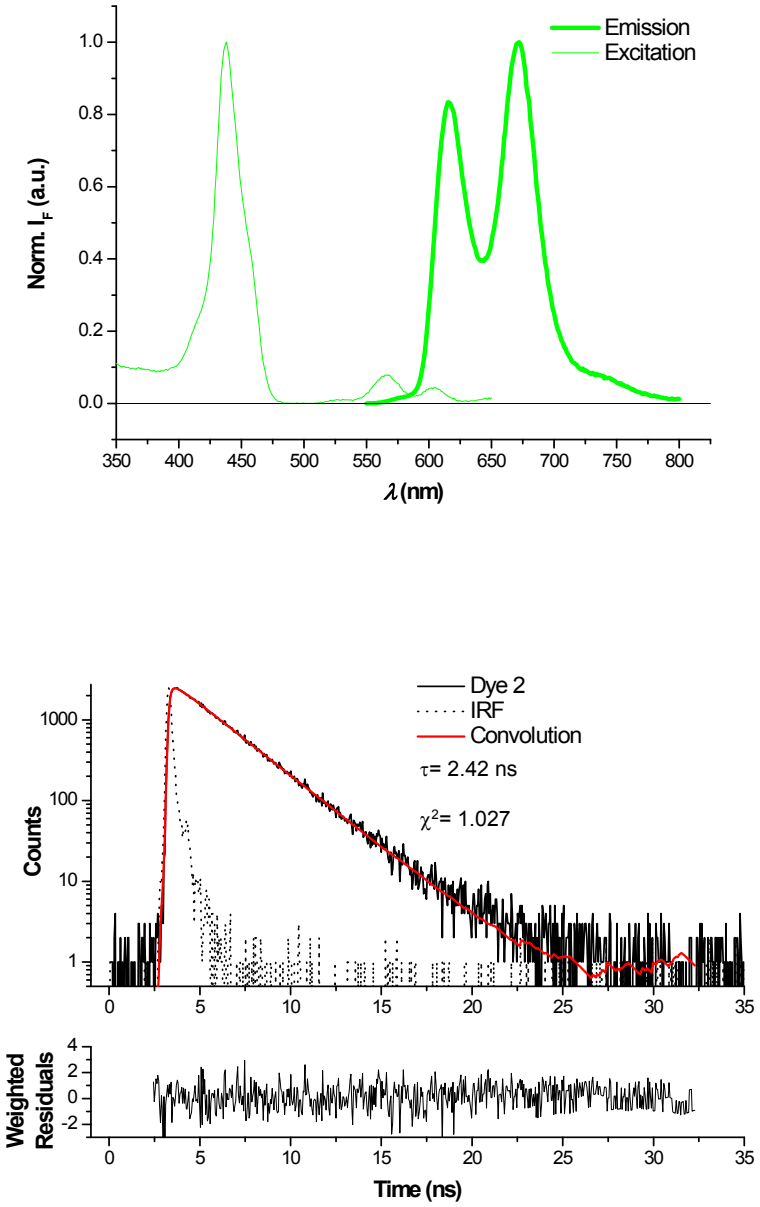

Figure S3. *Top*: emission and excitation spectra of **2**. *Bottom*: fluorescence decay of **1**, black line (λ_{exc} 445 nm; λ_{em} 616 nm). Instrument response function (IRF) and convolution fit black dotted line and red line respectively. Weighted residuals are shown under the decay curves.

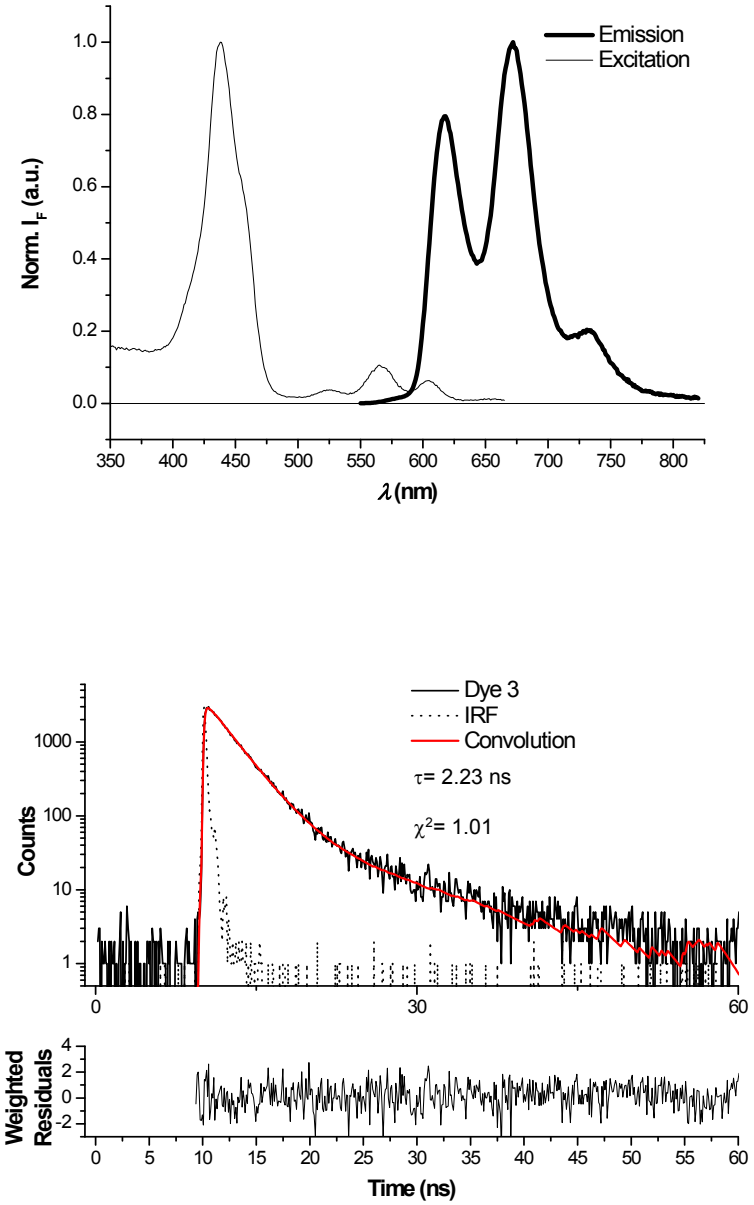

Figure S4. *Top*: emission and excitation spectra of **3**. *Bottom*: fluorescence decay of **1**, black line (λ_{exc} 445 nm; λ_{em} 616 nm). Instrument response function (IRF) and convolution fit black dotted line and red line respectively. Weighted residuals are shown under the decay curves.

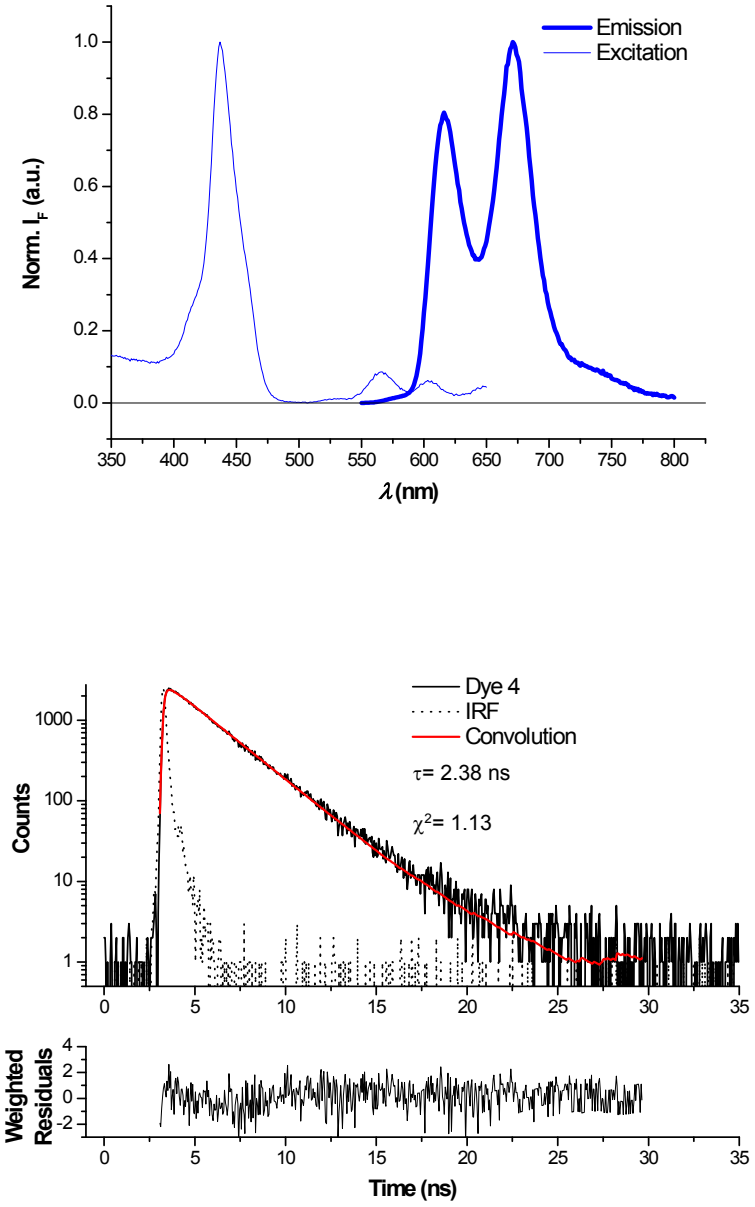

Figure S5. *Top*: emission and excitation spectra of **4**. *Bottom*: fluorescence decay of **1**, black line (λ_{exc} 445 nm; λ_{em} 616 nm). Instrument response function (IRF) and convolution fit black dotted line and red line respectively. Weighted residuals are shown under the decay curves.

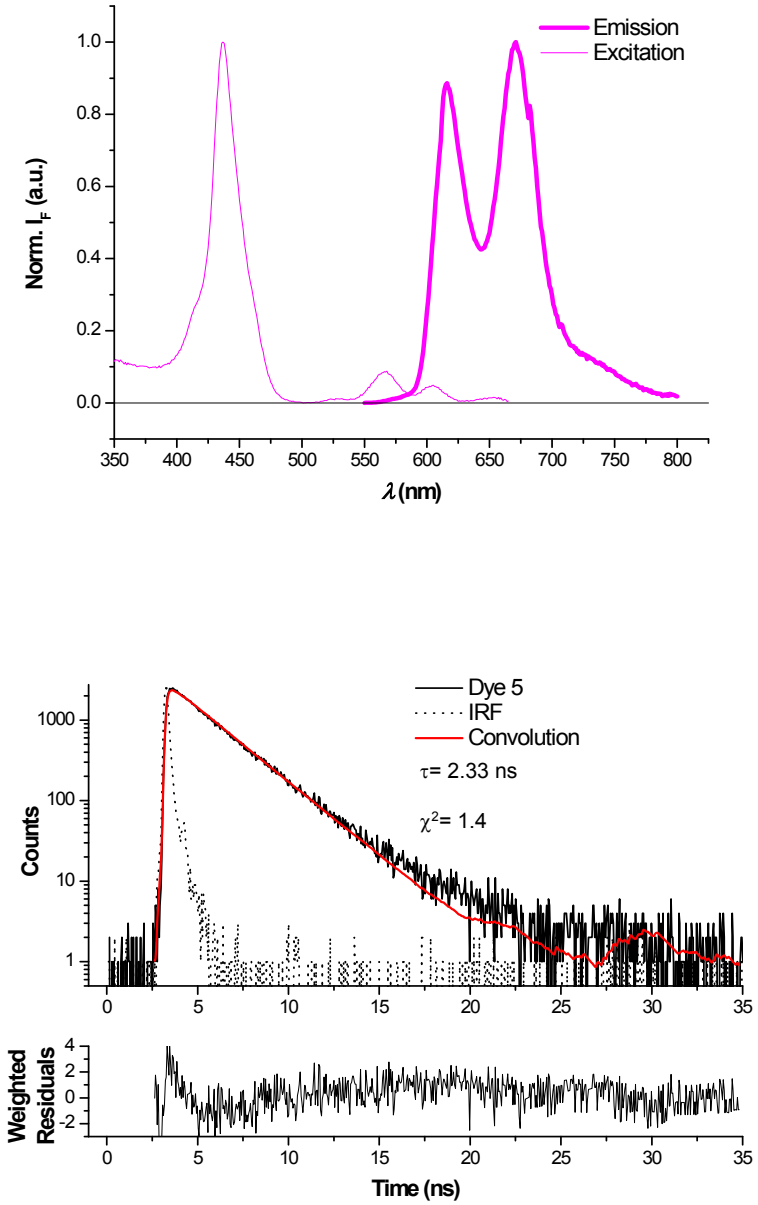

Figure S6. *Top*: emission and excitation spectra of **5**. *Bottom*: fluorescence decay of **1**, black line (λ_{exc} 445 nm; λ_{em} 616 nm). Instrument response function (IRF) and convolution fit black dotted line and red line respectively. Weighted residuals are shown under the decay curves.

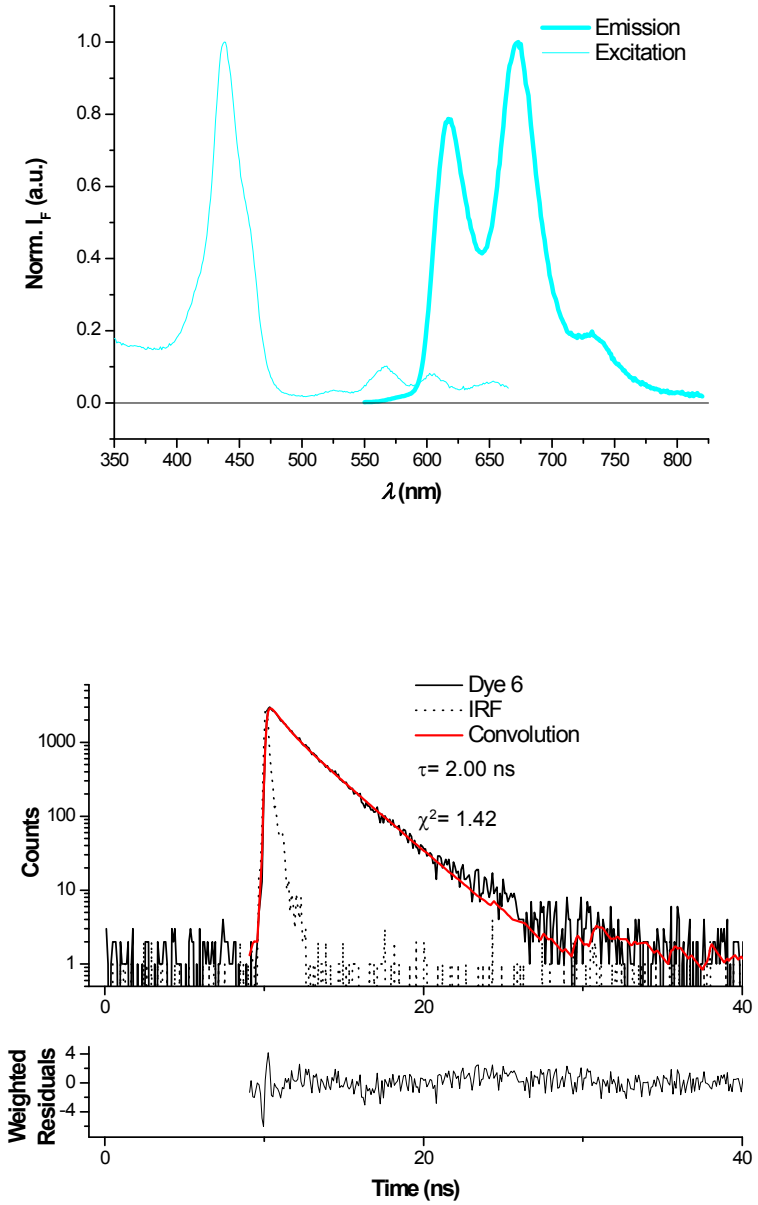

Figure S7. *Top*: emission and excitation spectra of **6**. *Bottom*: fluorescence decay of **1**, black line (λ_{exc} 445 nm; λ_{em} 616 nm). Instrument response function (IRF) and convolution fit black dotted line and red line respectively. Weighted residuals are shown under the decay curves.

Electrochemical data

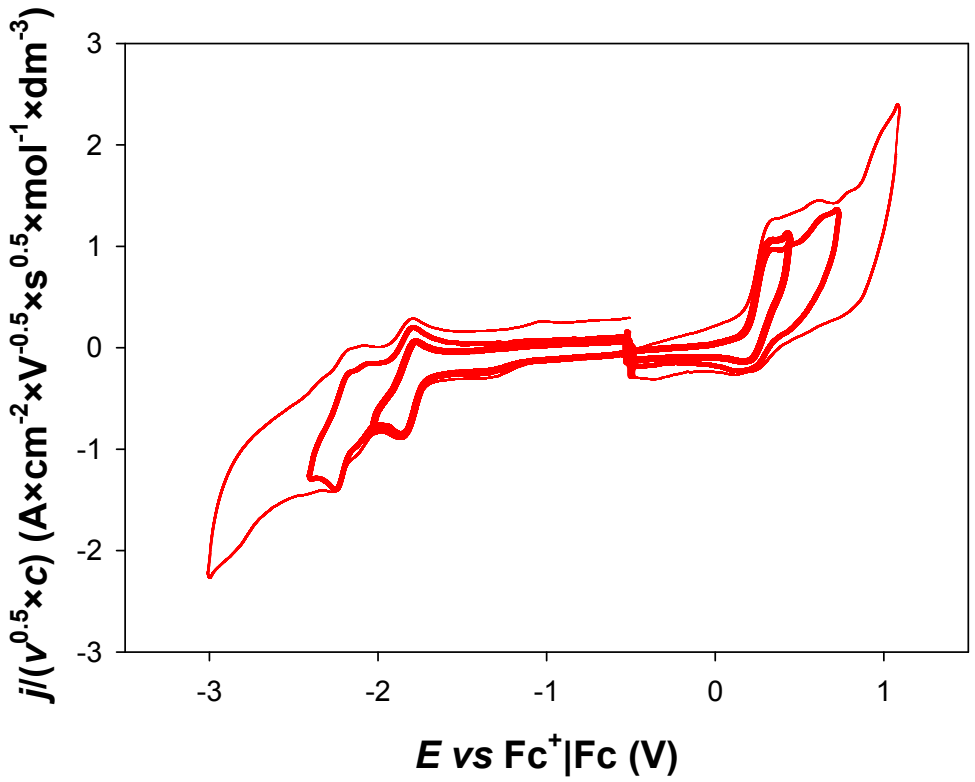

Figure S8. CV pattern of **1** on glassy carbon electrode, in DMF + 0.1 M TBAP, at 0.2 Vs^{-1}.

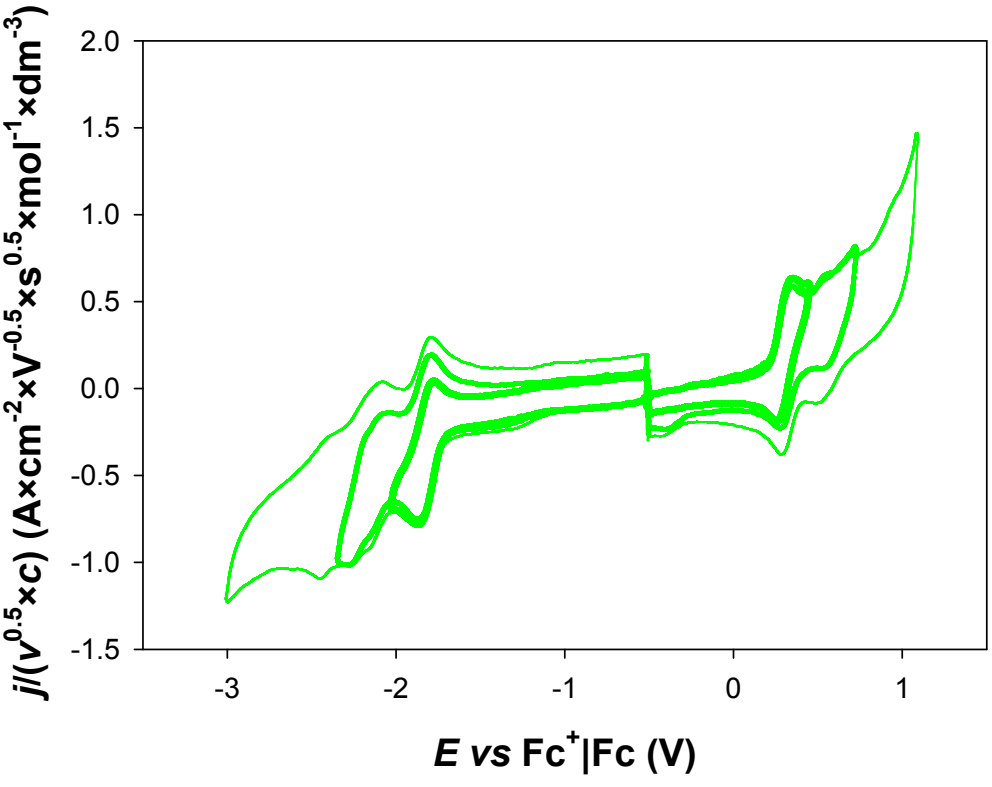

Figure S9. CV pattern of **2** on glassy carbon electrode, in DMF + 0.1 M TBAP, at 0.2 Vs^{-1}.

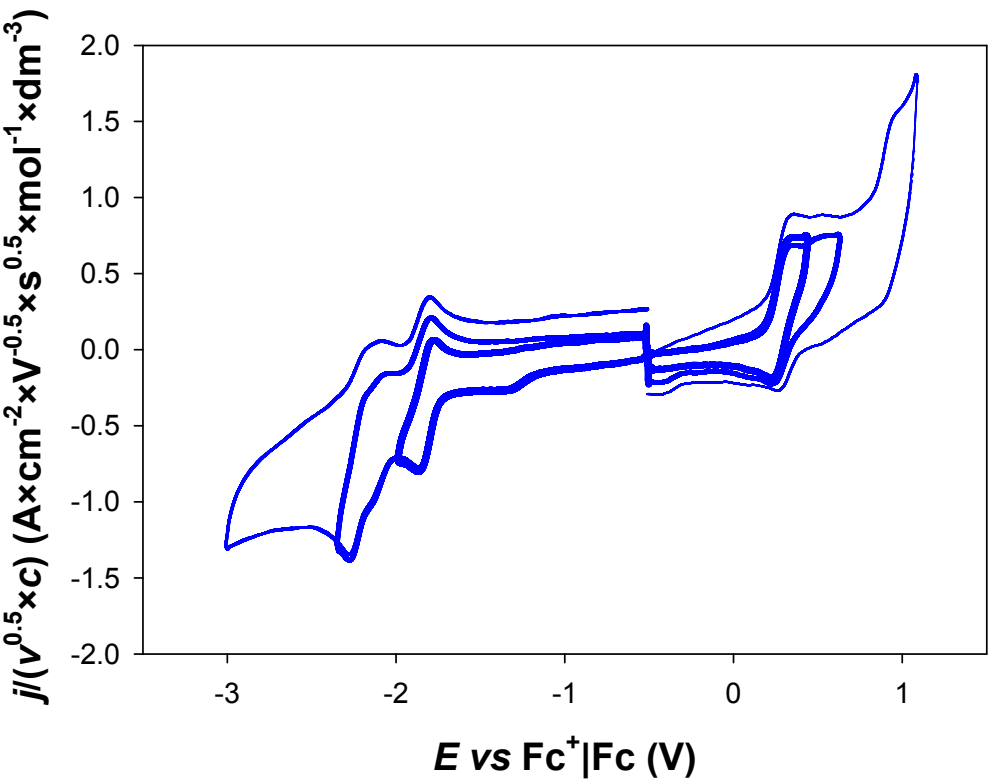

Figure S10. CV pattern of **4** on glassy carbon electrode, in DMF + 0.1 M TBAP, at 0.2 Vs^{-1}.

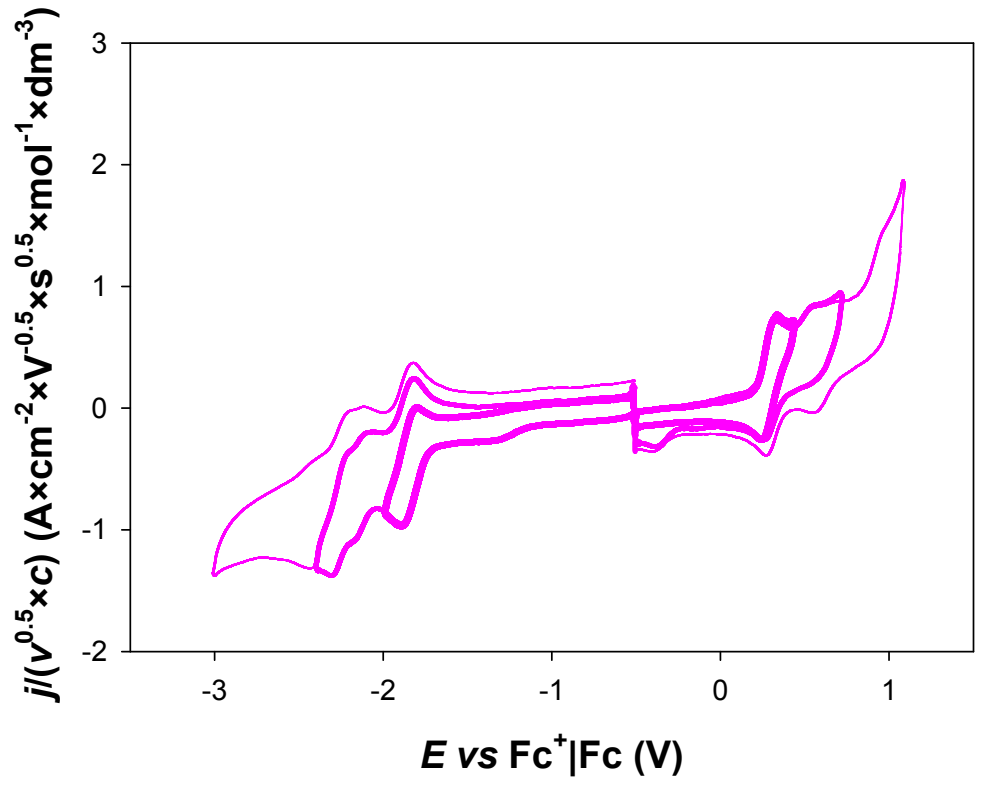

Figure S11. CV pattern of **5** on glassy carbon electrode, in DMF + 0.1 M TBAP, at 0.2 Vs^{-1}.

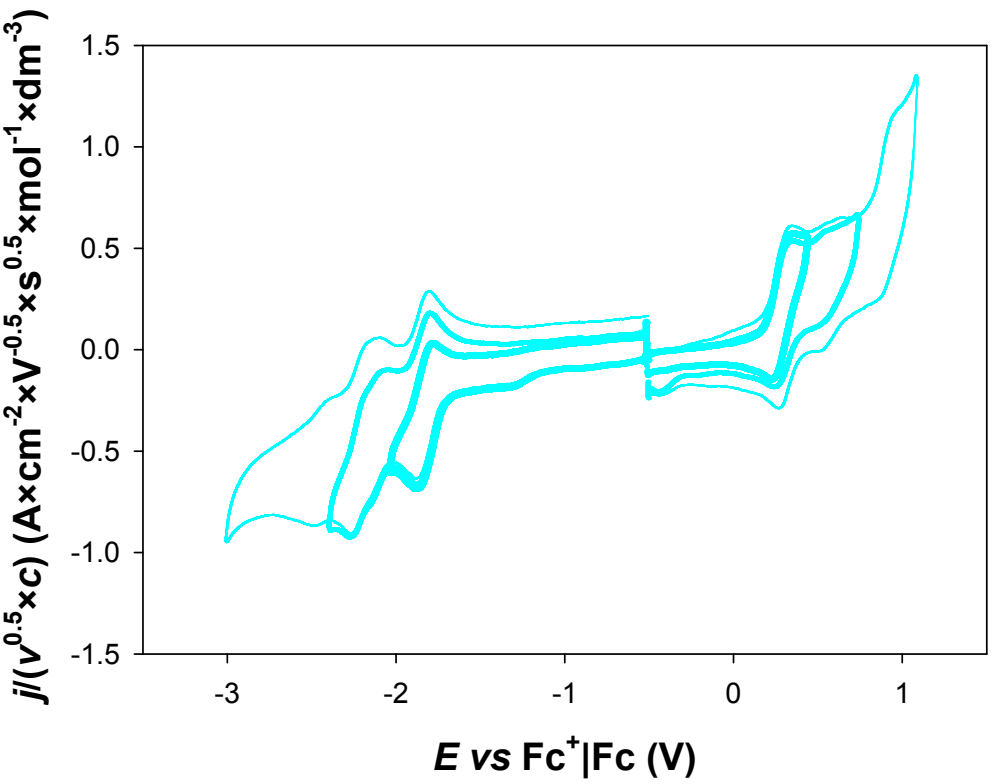

Figure S12. CV pattern of **6** on glassy carbon electrode, in DMF + 0.1 M TBAP, at 0.2 Vs^{-1}.

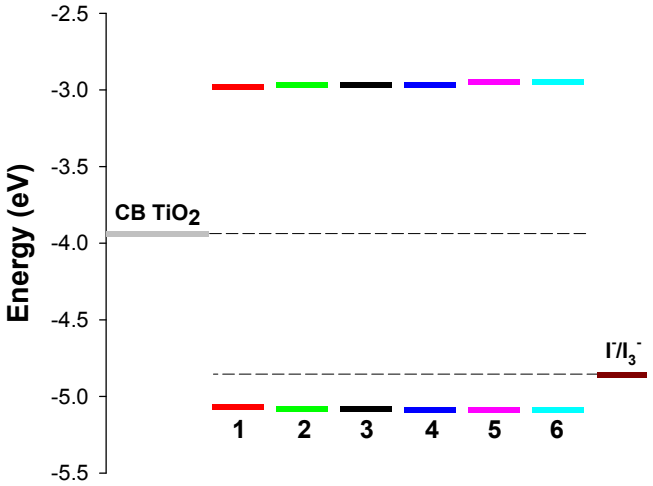

Figure S13. HOMO-LUMO levels for **1**-**6**.

Additional photoelectrochemical data

Dye-uptaking solutions employing different solvents

Considering that the aggregation could be attributed to a not perfect solubility of the dye in the solution, we fixed the amount of CDCA (1×10^{-3} M) and varied the amount of THF in the dye-uptaking solution (substrate employed: 9.0-μm TiO_2 transparent monolayer). Estimating the PV characteristics of **4** we found, in the solvent mixture THF/EtOH 1:4, the best results, as reported in Table S1.

Table S1. Photovoltaic performances of dyes **4** varying the solvent

solvent solution	J_{SC} (mA×cm^{-2})	V_{OC} (mV)	FF	PCE (%)
THF	3.50	679	0.63	1.60
THF/EtOH1:4	7.95	706	0.69	3.87
THF/EtOH 1:9	5.91	710	0.66	2.81

PV performances of photoelectrodes sensitized by NO-CDCA dye solutions

Defined this latter parameter (2×10^{-4} M solution in THF:EtOH=1:4), we decide to perform a test in which all the Zn^{II} porphyrinates **1**, **2**, **3**, **4**, **5**, **6** were tested, adsorbed onto 16 μm-thick-TiO_2 electrodes (12 μm 18NRT + 4 μm opaque layer), without the presence of CDCA, with the aim to test the real effect of the different chains. The results are reported in Table S2.

Table S2. Photovoltaic performances of dyes **1-6** without CDCA

Dye	J_{SC} (mA×cm^{-2})	V_{OC} (mV)	FF	PCE (%)
1	7.12	670	0.70	3.36
2	8.12	662	0.73	3.91
3	8.11	663	0.71	3.61
4	9.18	680	0.72	4.51
5	5.80	660	0.75	2.86
6	7.43	654	0.69	3.36

The dyes **2-4** featured by longer linear alkoxy chains show better PCE values instead of dyes **1** and **6**, which are characterized by shorter alkyl moieties, they are unable to efficiently shield the porphyrinic core. A different comment must be done on dye **5**, which is characterized by a branched chain C_6. Here, the ramification introduces limitations in the folding around the porphyrinic core, thus less flexibility involves a worst shielding effect of the central core, when compared to the dye **2**, in which the chains are linear. The same trend obtained with the addition of CDCA, among the performances of the six alkoxyl chains (Main Test Table 4), is even more pronounced in absence of CDCA: the alkyl chains C_6, C_8 and, most of all, C_{12} prevent π-interactions, producing higher open

circuit voltage and higher photocurrent, where the fill factor remains comparable. Since dye **4** leads to higher PCE values compared to dye **3** in the previously tests made, it will be now considered as a new reference in the future measures.

Additional TCSPC data

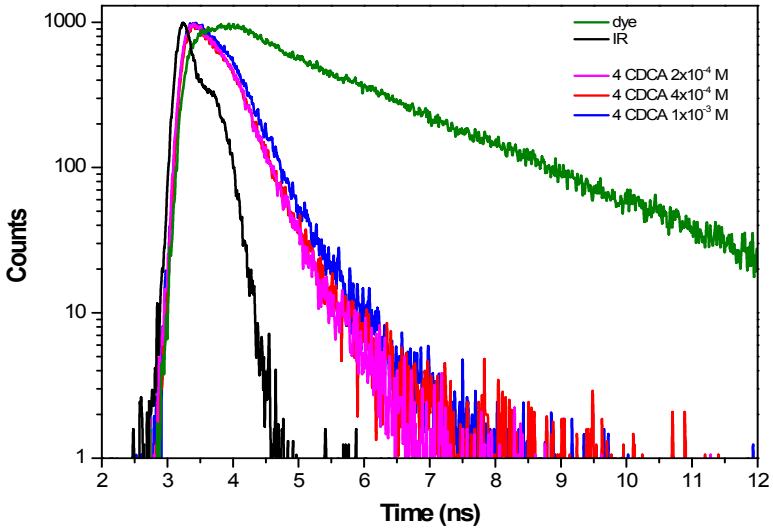

Figure S14. TCSPC analysis on Al_2O_3 films.

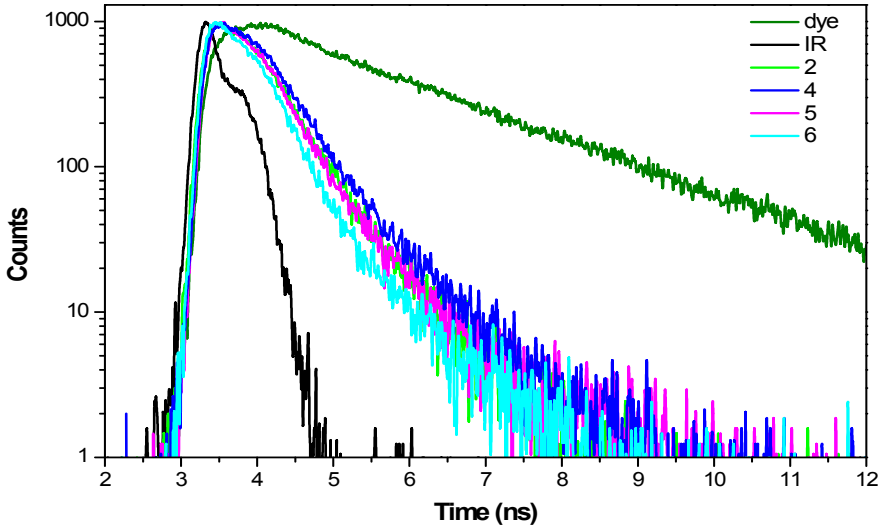

Figure S15. TCSPC analysis on Al_2O_3 films with no addiction of CDCA.