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Electronic Supplementary Information

Synthesis of high molar extinction coefficient push-pull tricyanofuran-based disperse dyes: Biological activity and dyeing performance

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Synthetic approaches

Synthesis of 1-(3-cyano-2-dicyanomethylen-5,5-dimethyl-2,5-dihydrofuran-4-yl)-2-[5-(N,N-dipentyl)aminothien-2-yl]ethene 3

In a 250 ml round bottom flask; a mixture of 2-bromo-5-formylthiophene (2.0 g, 10.5 mmol), dipentylamine (5 g, 31.5 mmol) and *p*-toluene sulfonic acid (20 mg) was stirred at 120 ^{o}C for 18 h. An admixture of 4-chloroaniline (1.35 g, 10.6 mmol), acetic acid (2.4 g) and ethanol (30 ml) was then added. After stirring at 80 ºC for 15 hours, the admixture was cooled under ambient conditions and another addition of TCF (1.6 g, 8.0 mmol) and pyridine (15 ml) was made. The admixture was maintained under stirring under ambient conditions for 48 hours and then poured into 75 ml dichloromethane. The produced solution poured slowly into 200 ml 0.5 M HCl, washed with water (3 × 50), and dried with $MgSO_4$. After evaporating the solvent; the collected precipitate was purified through column chromatography (EtOAc : hexane = 1 : 1), re-crystallized from chloroform/methanol, and filtered thru a Millipore filter to afford a dark blue crystals 200 mg (overall reaction yield 36 %). This product is clean by TLC and NMR. DSC: mp: 216 ^{o}C; Decomposition at 289ºC; TGA: Decomposition starts at 285ºC, reaches 89% at 300ºC, 52% at 325ºC, 43% at 400ºC and 32% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (s-broad, 1 H), 7.37 (s-broad, 1 H), 6.15 (d, 1 H, J = 4.4 Hz), 5.97 (s-broad, 1 H), 3.46 (t, 4 H, J = 7.8 Hz), 1.73 (m, 10 H), 1.40 (m, 8 H), 0.97 (t, 6 H, J = 7.0 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 14.16, 22.68, 26.67, 27.20, 27.32, 31.58, 49.39, 55.11, 86.24 (br), 95.53, 103.76, 109.50, 113.69 (br), 113.94, 114.64, 125.37, 140.08, 145.09, 170.24, 171.78, 177.21 ppm; IR (neat, cm^{-1}) 2218 (CN), 1595, 1539, 1514. UV-Vis (CH_2Cl_2) λ_{max} =624 nm, ε_{max} = 166787 L mol^{-1} cm^{-1}; UV-Vis. (CH_3CN) λ_{max} = 617 nm, ε_{max} = 178717 L mol^{-1} cm^{-1}

Synthesis of 1-(3-cyano-2-dicyanomethylen-5,5-dimethyl-2,5-dihydrofuran-4-yl)-2-[5-(N,N-dihexyl)aminothien-2-yl]ethene 4

A mixture of 2-bromo-5-formylthiophene (500 mg, 2.61 mmol), dihexylamine (1.45 g, 7.8 mmol) and p-toluenesulfonic acid (5 mg) was stirred at 120^{o}C for 22 h. A mixture of 4-chloroaniline (335 mg, 2.65 mmol), acetic acid (600 mg) and ethanol (5 ml) was then added. After stirring at 100 ^{o}C for 12 hours, the admixture was cooled under ambient conditions and another addition of TCF (250 mg, 1.25 mmol) and dry pyridine (3 ml) was made. The admixture was kept stirring under ambient conditions for 10 h and then poured into 25 ml dichloromethane. The produced solution poured slowly into 100 ml 0.5 M HCl, washed with water (3×40), and

dried with $MgSO_4$. After evaporating the solvent, the collected precipitate was purified by column chromatography (EtOAc : hexane = 1 : 1), re-crystallized from chloroform/methanol, and filtered thru a Millipore filter to afford a purple solid 165 mg (yield 27 %). This product is clean by TLC and NMR. DSC: mp: 173 ºC; Decomposition at 286ºC; TGA: Decomposition starts at 288ºC , reaches 88% at 300ºC, 49% at 350ºC, 38% at 400ºC and 28% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (s-broad, 1 H), 7.37 (s-broad, 1 H), 6.14 (d, 1 H, *J* = 4.4 Hz), 5.97 (s-broad, 1 H), 3.46 (t, 4 H, *J* = 7.8 Hz), 1.72 (m, 10 H), 1.39 (m, 12 H), 0.97 (t, 6 H, *J* = 7.0 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 14.18, 22.68, 26.67, 27.20, 27.32, 31.58, 49.39, 55.11, 86.24 (br), 95.53, 103.76, 110.50, 113.69, 113.94, 114.64, 125.37, 140.08, 145.09, 170.24, 171.78, 177.21; IR (neat, cm^{-1}) 2218 (CN), 1588, 1530, 1514. UV-Vis (CH_2Cl_2) λ_{max} =624 nm, ε_{max} =151217 L mol^{-1} cm^{-1}; UV-Vis (CH_3CN) λ_{max} = 618 nm, ε_{max} = 171477 L mol^{-1} cm^{-1}

Synthesis of 1-(3-cyano-2-dicyanomethylen-5,5-dimethyl-2,5-dihydrofuran-4-yl)-2-[5-(N,N-dioctyl)aminothien-2-yl]ethene 5

In a 250 ml round bottom flask a mixture of 2-bromo-5-formylthiophene (4.0 g, 21.0 mmol), dioctylamine (15 g, 63.0 mmol) and p-toluenesulfonic acid (40 mg) was stirred at 120 ºC for 12 h. A mixture of 4-chloroaniline (2.68 g, 21.2 mmol), acetic acid (4.8 g) and ethanol (40 ml) was then added. After stirring at 80-90 ºC for 9 hours, the admixture was cooled under ambient conditions and another addition of TCF (3 g, 15.0 mmol) and pyridine (25 ml) was made. The admixture was kept stirring under ambient conditions for 12 h and then poured into 100 ml dichloromethane. The produced solution poured slowly into 200 ml 1 M HCl, washed with water (3×50), and dried with $MgSO_4$. After evaporating the solvent; the collected precipitate was purified through column chromatography (EtOAc : hexane = 1 : 2), re-crystallized from chloroform/methanol, and filtered thru a Millipore filter to afford a purple powder 1.20 g (overall reaction yield 48 %). This product is clean by TLC and NMR. DSC: mp: 148 ºC; Decomposition at 288ºC; TGA: Decomposition starts at 288ºC, reaches 92% at 300ºC, 49% at 350ºC, 39% at 400ºC and 25% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (s-broad, 1 H), 7.37 (s-broad, 1 H), 6.15 (d, 1 H, *J* = 4.8 Hz), 5.97 (s-broad, 1 H), 3.46 (t, 4 H, *J* = 7.8 Hz), 1.72 (m, 10 H), 1.34 (m, 20 H), 0.91 (t, 6 H, *J* = 6.8 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 169.09, 139.85, 114.00, 113.22, 108.06, 103.99, 95.34, 54.71, 31.72, 29.26, 29.14, 27.18, 26.89, 22.60, 14.06; IR (neat, cm^{-1}) 2228 (CN), 1598, 1542, 1520. UV-Vis (CH_2Cl_2) λ_{max} =624 nm, ε_{max} = 194024 L mol^{-1} cm^{-1}; UV-Vis (CH_3CN) λ_{max} = 617 nm, ε_{max} = 216150 L mol^{-1} cm^{-1}

Synthesis of 4-(4-hydroxypiperidin-1-yl)benzaldehyde 6

A mixture of 4-fluorobenzaldehyde (1.0 g, 8.0 mmol), 4-hydroxypiperidine (0.80 g, 8.0 mmol), potassium carbonate (1.2 g, 8.8 mmol), DMSO (10 mL) and distilled water (1.0 mL) was stirred at 100ºC for 18 hrs. TLC showed consumption of the starting aldehyde. The mixture was cooled and poured into 50 ml of cold water. The generated solid was filtered off, washed with excess of distilled water and then hexane. The product was re-crystallized from ethanol to afford a yellow solid (0.95 g; 60 % yield). This material product is clean by TLC and NMR. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 9.78 (s, 1 H), 7.74 (d, 2 H, *J* = 8.4 Hz), 6.92 (d, 2 H, *J* = 8.8 Hz), 3.98 (m, 1 H), 3.70 (m, 2 H), 3.19 (m, 2 H), 2.02 (m, 2 H), 1.74.(s, 1 H), 1.68 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 188.3 (CHO), 168.6, 145.9, 131.6, 125.2, 74.4, 25.9, 24.8 IR (neat, cm^{-1}) 3430 (OH), 1610 (CHO).

Synthesis of 4-(3-(hydroxymethyl)piperidin-1-yl) benzaldehyde 7

A mixture of 4-fluorobenzaldehyde (1.0 g, 8.0 mmol), 3-hydroxymethylpiperidine (0.92 g, 8.0 mmol), potassium carbonate (1.2 g, 8.8 mmol), DMSO (8.0 mL) and distilled water (1.0 mL) was stirred at 100ºC for 16 hrs. TLC showed consumption of the starting aldehyde. The mixture was cooled and poured into 50 ml cold water. The product was extracted by ethyl acetate, washed with excess of water then brine, and purified by column chromatography (ethyl acetate : hexane / 2 : 8) to afford a yellow oil (820 mg; 45 % yield). This material product is clean by TLC and NMR. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 9.63 (s, 1 H), 7.61 (d, 2 H, *J* = 9.2 Hz), 6.88 (d, 2 H, *J* = 8.8 Hz), 3.98 (m, 1 H), 3.87 (m, 1 H), 3.62 (m, 1 H), 3.56 (m, 1 H), 2.98 (m, 1 H), 2.84 (m, 1 H), 2.58 (s, 1 H), 1.87 (m, 3 H), 1.66 (m, 1 H), 1.26 (m, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 190.44 (CHO), 155.15, 132.10, 125.90, 113.29, 65.21, 50.86, 74.4, 48.12, 38.25, 27.08, 24.17; IR (neat, cm^{-1}): 3412 (OH), 1610 (CHO).

Synthesis of 4-(4-(4-hydroxypiperidin-1-yl)styryl)-2-(dicyanomethylene)-2,5-dihydro-5,5-dimethylfuran-3-carbonitrile 8

A mixture of 4-(4-hydroxypiperidin-1-yl)benzaldehyde (530 mg, 2.4 mmol), TCF (480 mg, 2.4 mmol) and acetic acid (145 mg) were dissolved in dry pyridine (7 mL). The admixture was stirred for 30 minutes under ambient conditions and then poured into 30 mL ice water. The collected solied product was recrystallized from methanol/chloroform; 820 mg (yield 81%) was obtained as a purple solid. This material product is clean by TLC and NMR. DSC: mp at 229 ºC and decomposition at 231 ºC; TGA: Decomposition starts at 214ºC, reaches 83% at 300ºC, 72%

at 400ºC, and 57% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.60 (d, 1 H, *J* = 16.0 Hz), 7.55 (d, 2 H, *J* = 9.2 Hz), 6.92 (d, 2 H, *J* = 8.8 Hz), 6.81 (d, 1 H, *J* = 16.0 Hz), 4.04 (m, 1 H), 3.85 (m, 2 H), 3.31 (m, 2 H), 2.06 (m, 2 H), 1.82 (s, 6 H), 1.71 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 176.09, 174.18, 153.68, 147.78, 132.12, 123.01, 114.06, 112.44, 111.67, 111.21, 109.73, 96.91, 66.94, 44.60, 33.56, 26.74; IR (neat, cm^{-1}) 3398 (OH), 2228 (CN), 1582, 1525, 1510; UV-Vis (CH_2Cl_2) λ_{max} =554 nm, ε_{max}=50985 L mol^{-1} cm^{-1}.

Synthesis of 4-(4-(3-(hydroxymethyl)piperidin-1-yl)styryl)-2-(dicyanomethylene)-2,5-dihydro-5,5-dimethylfuran-3-carbonitrile 9

A mixture of 4-(3-(hydroxymethyl)piperidin-1-yl) benzaldehyde (500 mg, 2.4 mmol), TCF (480 mg, 2.4 mmol) and acetic acid (145 mg) were dissolved in dry pyridine (5 mL). The admixture was stirred for 30 minutes under ambient conditions and then poured into 30 mL ice-water. The collected solid product was recrystallized from methanol/chloroform; 870 mg (yield 87%) was obtained as a purple solid. This material product is clean by TLC and NMR. DSC: mp at 241 ºC and decomposition at 243 ºC; TGA: Decomposition starts at 222 ºC, reaches 83% at 300ºC, 68% at 400ºC, and 52% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.62 (d, 1 H, *J* = 16.8 Hz), 7.56 (d, 2 H, *J* = 9.2 Hz), 6.94 (d, 2 H, *J* = 8.8 Hz), 6.77 (d, 1 H, *J* = 16.0 Hz), 4.05 (m, 1 H), 3.88 (m, 1 H), 3.68 (m, 1 H), 3.58 (m, 1 H), 3.09 (m, 1 H), 2.96 (m, 1 H), 1.86 (m, 3 H), 1.78 (s, 6 H), 1.38 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 187.32, 164.76, 148.75, 134.45, 132.76, 127.45, 122.43, 116.88, 114.12, 100.05, 94.54, 66.76, 52.76, 54.12, 44.00, 42.22, 28.90, 26.22, 23.45; IR (neat, cm^{-1}) 3429 (OH), 2218 (CN), 1572, 1523, 1514; UV-Vis (CH_2Cl_2) λ_{max} =579 nm, ε_{max} = 61200 L mol^{-1} cm^{-1}.

Synthesis of 5-(4-hydroxypiperidin-1-yl)thiophene-2-carbaldehyde 10

A mixture of 2-bromothiophenecarboxaldehyde (500 mg, 2.63 mmol), 4-hydroxypiperidine (260 mg, 2.63 mmol), triethylamine (2 mL) and water (5 mL) was refluxed at 90 ºC for 9 hrs. TLC showed consumption of the starting aldehyde. The mixture was cooled and poured into 10 mL cold water. The solid product was filtered off, washed with excess of distilled water then hexane. The product recrystallized from ethanol to afford a green solid (420 mg; 73 % yield). This material product is clean by TLC and NMR. Melting point is 66-68 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 9.52 (s, 1 H), 7.48 (d, 1 H, *J* = 6.8 Hz), 6.09 (d, 1 H, *J* = 7.2 Hz), 3.98 (m, 1 H), 3.67 (m, 2 H), 3.23 (m, 2 H), 2.02 (m, 3 H), 1.73 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm:

192.3 (CHO), 163.3, 136.9, 126.4, 120.2, 54.4 (NCH_2), 25.9, 23.8; IR (neat, cm^{-1}) 3445 (OH), 1640 (CHO).

Synthesis of 5-(3-hydroxymethylpiperidin-1-yl)thiophene-2-carbaldehyde 11

A mixture of 2-bromothiophenecarboxaldehyde (500 mg, 2.63 mmol), 3-hydroxymethylpiperidine (300 mg, 2.63 mmol), triethylamine (2 mL) and water (5 mL) was refluxed at 90 ºC for 11 hrs. TLC showed consumption of the starting aldehyde. The admixture was cooled and poured into 20 ml cold water. The product was extracted by dichloromethane and washed with excess of water then brine. A flash column chromatography was applied using ethyl acetate to afford orange oil (360 mg; 59 % yield). This material product is clean by TLC and NMR. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 9.52 (s, 1 H), 7.47 (d, 1 H, J = 6.6 Hz), 6.12 (d, 1 H, J = 7.0 Hz), 3.83 (d, 1 H), 3.65 (m, 2 H), 3.58 (m, 1 H), 3.09 (m, 1 H), 2.95 (m, 1 H), 2.32 (s, 1 H), 1.98 (m, 2 H), 1.72 (m, 2 H), 1.29 (m, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 184.3 (CHO), 153.6, 136.9, 120.6, 120.2, 68.9 (OCH_2), 54.4 (NCH_2), 25.9, 23.8; IR (neat, cm^{-1}) 3380 (OH), 1635 (CHO).

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(2-(5-(4-hydroxypiperidin-1-yl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-3-carbonitrile 12

A mixture of 5-(4-hydroxypiperidin-1-yl)thiophene-2-carbaldehyde (500 mg, 2.4 mmol), TCF (480 mg, 2.4 mmol) and acetic acid (145 mg) were dissolved in dry pyridine (3 mL). The admixture was stirred for 3 days under ambient conditions. TLC showed no change in the formation of more product or consumption of the reactants after the first one hour. The mixture was then poured into a 30 mL ice-water. The collected solid product was recrystallized from chloroform; 200 mg (yield 21 %) was obtained as a purple solid. This material product is clean by TLC and NMR. DSC: decomposition at 312 ºC; TGA: Decomposition starts at 316ºC, reaches 73% at 400ºC, 42% at 600ºC. ^{1}H NMR (400 MHz, DMSO) ppm: 8.01 (d, 1 H, J = 14.4 Hz), 7.85 (s, 1 H), 6.84 (d, 1 H, J = 4.8 Hz), 5.93 (d, 1 H, J = 11.6 Hz), 3.84 (m, 3 H), 3.58 (m, 2 H), 3.17 (s, 1 H), 1.89 (m, 2 H), 1.67 (s, 6 H), 1.58 (m, 2 H); ^{13}C NMR (400 MHz, DMSO) ppm: 177.16, 172.18, 171.18, 140.56, 126.34, 115.41, 114.63, 113.95, 112.69, 103.05, 96.15, 64.16, 55.37, 49.35, 33.73, 26.77; IR (neat, cm^{-1}) 3466 (OH), 2224 (CN), 1582, 1524, 1518; UV-Vis. (CH_2Cl_2) λ_{max} = 621 nm, ε_{max} = 94191 L mol^{-1} cm^{-1}.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(2-(5-(3-(hydroxymethyl)piperidin-1-yl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-3-carbonitrile 13

A mixture of 5-(3-hydroxymethylpiperidin-1-yl)thiophene-2-carbaldehyde (550 mg, 2.4 mmol), TCF (480 mg, 2.4 mmol) and acetic acid (145 mg) were dissolved in dry pyridine (3 mL). The admixture was stirred for 48 hrs under ambient conditions. TLC showed no change in the formation of more product or consumption of the reactants after the first one hour. The reaction system was then poured into 30 mL ice-water. The collected solid product was recrystallized from methanol/chloroform; 180 mg (yield 18 %) was obtained as a purple solid. This material product is clean by TLC and NMR; DSC: decomposition at 261ºC; TGA: Decomposition starts at 262ºC , reaches 88% at 300ºC, 59% at 400ºC, and 29% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 8.09 (d, 1 H), 7.84 (s-broad, 1 H), 6.94 (s, 1 H), 5.93 (s-broad, 1 H), 3.81 (m, 3 H), 3.25 (m, 2 H), 2.24 (m, 2 H), 1.83 (m, 2 H), 1.66 (s, 6 H), 1.52 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 177.16, 172.18, 171.75, 140.45, 133.67, 126.34, 115.45, 114.63, 113.95, 112.61, 103.05, 96.14, 64.16, 55.37, 49.35, 33.73, 26.77; IR (neat, cm^{-1}) 3429 (OH), 2232 (CN), 1572, 1528, 1519; UV-Vis. (CH_2Cl_2) λ_{max} = 641 nm, ε_{max} = 116491 L mol^{-1} cm^{-1}.

Synthesis of Bis(1-(4-(2-(4-cyano-5-(dicyanomethylene)-2,5-dihydro-2,2-dimethylfuran-3-yl)vinyl)phenyl)piperidin-4-yl) adipate 15

In a 50 ml round bottom flask; At 0ºC an adipoyl dichloride solution (100 mg, 0.60 mmol) in CH_2Cl_2 was added dropwise into a solution of compound **8** (500 mg, 1.29 mmol) and triethylamine (0.5 mL) in dichloromethane (10 mL). The mixture then refluxed at 50ºC for 14 hrs. The admixture was then allowed to cool, filtered off and washed with diethyl ether. The combined solutions of dichloromethane and ether were concentrated under reduced pressure. The collected precipitate was recrystallized from methanol to give 375 mg (yield 33 %) was obtained as a blue solid. DSC: decomposition at 218 ºC; TGA: Decomposition starts at 215 ºC, reaches 79% at 300 ºC, 45% at 400 ºC, 36% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.62 (d, 2 H, *J* = 16.8 Hz), 7.57 (d, 4 H, *J* = 9.2 Hz), 6.92 (d, 4 H, *J* = 8.8 Hz), 6.82 (d, 2 H, *J* = 16.0 Hz), 5.06 (m, 2 H), 3.74 (m, 4 H), 3.39 (m, 4 H), 2.39 (m, 4 H), 2.04 (m, 4 H), 1.81 (m, 16 H), 1.72 (m, 4 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 188.62, 178.24, 161.26, 146.55, 143.55, 132.77, 125.45, 122.11, 117.43, 115.16, 101.55, 96.24, 67.45, 54.66, 45.87, 41.43, 29.92, 25.22, 23.91, 23.45; IR (neat, cm^{-1}) 2225 (CN), 1698 (CO), 1585, 1535, 1517; UV-Vis (CH_2Cl_2) λ_{max} = 550 nm, ε_{max} = 87206 L mol^{-1} cm^{-1}.

Synthesis of Bis((1-(4-(2-(4-cyano-5-(dicyanomethylene)-2,5-dihydro-2,2-dimethylfuran-3-yl)vinyl)phenyl)piperidin-3-yl)methyl) adipate 16

A mixture of adipic acid (50 mg, 0.35 mmol), 4-(4-(3-(hydroxymethyl)piperidin-1-yl)styryl)-2-(dicyanomethylene)-2,5-dihydro-5,5-dimethylfura--n-3-carbonitrile (300 mg, 0.75 mmol), DMAP (5 mg, 0.04 mmol) and DCC (140 mg, 0.68 mmol) was stirred in dichloromethane (10 mL) for 20 hrs. The admixture was concentrated under reduced pressure, purified through column chromatography (ethyl acetate : hexane; 1 : 5) and then re-crystallized from methanol to afford 270 mg (Yield 39 %) of the product as a blue solid. DSC: decomposition at 227ºC; TGA: Decomposition starts at 232ºC, reaches 81% at 300 ºC, 55% at 400ºC, 31% at 600ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.61 (d, 2 H, J = 16.0 Hz), 7.56 (d, 4 H, J = 8.8 Hz), 6.89 (d, 4 H, J = 8.8 Hz), 6.79 (d, 2 H, J = 16.0 Hz), 4.11 (dd, 2 H, J = 5.2 Hz, 11.2 Hz), 3.91 (m, 6 H), 3.14 (t, 2H, J = 12.2 Hz), 2.94 (t, 2 H, J = 11.6 Hz), 2.43 (m, 4 H), 2.04 (m, 2 H), 1.77 (m, 22 H), 1.39 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 181.32, 166.76, 148.15, 135.45, 132.70, 127.45, 122.43, 116.88, 114.12, 101.05, 94.54, 66.76, 52.76, 54.12, 44.00, 42.22, 31.46, 28.90, 26.22, 25.44, 24.65, 23.45; IR (neat, cm^{-1}) 2234 (CN), 1688 (CO), 1565, 1543, 1510; UV-Vis (CH_2Cl_2) λ_{max} = 448 nm, ε_{max} = 114578 L mol^{-1} cm^{-1}

Synthesis of 1,4-di-(*p*-benzaldehyde) piperazine 17

A mixture of 4-fluorobenzaldehyde (1.0 g, 8.0 mmol), piperazine (300 mg, 3.5 mmol), K_2CO_3 (1.2 g, 8.8 mmol), DMSO (8.0 mL) and distilled water (1.0 mL) was stirred at 100 ºC for 19 hrs. TLC showed consumption of the starting aldehyde. The mixture was cooled and poured into 50 ml cold water. The solid product was filtered off, washed with excess of water then hexane. The product recrystallized from chloroform-methanol (1 : 1) to afford a yellow solid (1.90 g; 79 % yield). This material product is clean by TLC and NMR. ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 9.81 (s, 2 H), 7.79 (d, 4 H, J = 8.8 Hz), 6.94 (d, 4 H, J = 8.4 Hz), 3.63 (s, 8 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 186.10 (2CHO), 132.93, 114.04, 112.55, 110.31, 46.04.74; IR (neat, cm^{-1}): 1645 (CHO).

Synthesis of 4-(4-(4-(4-((1)-2-(4-cyano-5-(dicyanomethylene)-2,5-dihydro-2,2-dimethylfuran-3-yl)vinyl)phenyl)piperazin-1-yl)styryl)-2-(dicyanomethylene)-2,5-dihydro-5,5-dimethylfuran-3-carbonitrile 18

A mixture of 1,4-di-(p-benzaldehyde) piperazine (300 mg, 1 mmol), TCF (500 mg, 2.5 mmol) and acetic acid (145 mg) were dissolved in dry pyridine (8 mL). The admixture was stirred for 48

hrs at 40˚C. After cooling, the mixture was then poured into 30 mL ice-water. The product was recrystallized from methanol/chloroform; 80 mg (yield 92%) was obtained as a blue-purple solid. This material product is clean by TLC and NMR. DSC: decomposition at 326 ºC; TGA: Decomposition starts at 331ºC, reaches 68% at 400ºC, 34% at 600ºC. ^{1}H NMR (400 MHz, DMSO) ppm at 55ºC: 7.92 (d, 2 H), 7.81 (d, 4 H), 7.04 (d, 4 H), 6.96 (d, 2 H), 3.70 (s, 8 H), 1.77 (s, 12 H); ^{13}C NMR (400 MHz, DMSO) ppm at 55ºC: 190.57, 186.10, 132.93, 131.94, 114.04, 113.37, 112.55, 111.84, 110.31, 101.70, 46.04, 26.04, 23.74, 14.59; IR (neat, cm^{-1}) 2224 (CN), 1598, 1544, 1539; UV-Vis (CH_2Cl_2) Max abs.= 624 nm, ε = 67219 L mol^{-1} cm^{-1}; UV-Vis (DMF) λ_{max} = 584 nm, ε_{max} = 91748 L mol^{-1} cm^{-1}.

Synthesis of 4-(4-(1,4-diazepan-1-yl)phenyl)-2-(dicyanomethylene)-2,5-dihydro-5,5-dimethylfuran-3-carbonitrile 21

A mixture of 2-cyanomethylen-3-cyano-5,5-dimethyl-4-(4-fluorophenyl)-2,5-dihydrofuran (700 mg, 2.5 mmol), homopiperazine (1.25 g, 12.5 mmol) and 50 ml pyridine was stirred overnight under ambient conditions. The reaction progress is monitored by TLC until the 2-cyanomethylen-3-cyano-5,5-dimethyl-4-(4-fluorophenyl)-2,5-dihydrofuran was consumed. The admixture was poured into 50 mL of ice-water; the produced precipitate was filtered off and washed with 100 mL water. The produced residue was recrystallized from *n*-propanol to afford a golden orange solid (350 mg, 63%). DSC: decomposition at 321ºC; TGA: Decomposition starts at 319ºC, reaches 57% at 400ºC, and 42% at 600ºC; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 8.00 (d, 2 H, *J* = 9.6 Hz), 6.82 (d, 2 H, *J* = 9.2 Hz), 3.76 (t, 2 H, *J* = 6.2 Hz), 3.70 (t, 2 H, *J* = 5.2 Hz), 3.09 (t, 2 H, *J* = 5.4 Hz), 2.88 (t, 2 H, *J* = 6.0 Hz), 1.95 (m, 2 H), 1.85 (s, 6 H); ^{13}C NMR (400 MHz, $CDCl_3$) ppm: 176.94, 173.67, 153.34, 132.57, 113.66, 113.10, 112.89, 111.96, 111.89, 97.26, 91.28, 52.70, 48.69, 48.23, 47.85, 28.56, 27.62; IR (neat, cm^{-1}) 3318 (NH), 2221 (CN), 1565, 1543, 1518; UV-Vis (CH_2Cl_2) λ_{max} = 496 nm, ε_{max} = 87645 L mol^{-1} cm^{-1}.