Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

A red to blue series of push-pull dyes for NiO-based p-DSSCs

Supporting Information

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Organic synthesis of the compounds

All reagents and chemicals were purchased from Aldrich and were used as received. Characterization techniques: NMR spectra were recorded with a Bruker AVANCE DRX 400 (^{1}H, 400 MHz and ^{13}C, 100 MHz). Chemical shifts δ are expressed in ppm relative to tetramethylsilane (TMS). FTIR spectra were recorded with a Bruker Alpha-P. UV-Vis spectra were recorded with a Perkin Elmer Lambda 650 spectrometer. Mass spectra analyses were performed on SYNAPT G2 HDMS (Waters). For microwave assisted synthesis, a Microsynth Milestone laboratory microwave oven was used.

N,N-Di(4-benzoic acid tert-butyl ester)phenylamine (1)

This reaction was carried out in an inert atmosphere. Aniline (0.99 g, 10.65 mmol, 1.00 eq.), 4-Bromo-benzoic acid *tert*-butyl ester (5.99 g, 23.31 mmol, 2.19 eq.), $Pd_2(dba)_3$ (282 mg, 0.31 mmol, 0.03 eq.), $[HP(^tBu)_3]BF_4$ (150 mg, 0.52 mmol, 0.05 eq.), NaO^tBu (2.52 g, 26.25 mmol, 2.46 eq.) and 60 mL of dry toluene ($[H_2O]$=5 ppm, KF) were introduced into a 100 mL three necked flask, topped with a refrigerant. A spontaneous exothermic process was noticed. The solution was then stirred for 2 hours at 110 °C, under argon protection. The color, initially dark red, finally turned yellowish. A white precipitate (NaBr) was also noticed. Dichloromethane was added to the mixture which was then washed three times with brine. The organic phase was dried over $MgSO_4$. So as to remove the catalytic residues, the solution was filtered over a short celite pad. After removal of the solvents, brown oil was obtained. Upon the addition of boiling MeOH (25 mL), a white precipitate rapidly appeared and after one night at 4°C it was collected. The solid **1** was dried under vacuum (3.45 g, 72 % yield). **M.p.**: 138°C. **^{1}H NMR** ($CDCl_3$, ppm): 7.87 (d, ^3J = 9.0 Hz, 4H), 7.33 (t, ^3J = 7.3 Hz, 2H), 7.18 (d, ^3J = 7.3 Hz, 1H), 7.13 (d, ^3J = 8.6 Hz, 2H), 7.07 (d, ^3J = 9.0 Hz, 4H), 1.58 (s, 18H).

N,N-Di(4-benzoic acid tert-butyl ester)-4-iodo-phenylamine (2)

This synthesis was performed according to the work of Weidelener et al.[1] Iodine chloride (2.80 g, 17.28 mmol, 2.40 eq.) and zinc acetate (1.90 g, 10.38 mmol, 1.44 eq.) were introduced into 13 mL of 1,4-dioxane. The mixture was stirred for one hour, zinc acetate did not dissolve entirely. Triphenylamine **1** (3.20 g, 7.19 mmol, 1.00 eq.) was mixed with 13 mL of 1,4-dioxane and 2 mL of dichloromethane. After heating, **1** was totally dissolved into the solvent, and was added dropwise, with a syringe, to the reaction mixture (it took 20 min). After four hours of stirring at room temperature, the mixture was poured into 100 mL of a saturated sodium thiosulfate aqueous solution. This aqueous phase was extracted three times with dichloromethane. The organic phase was then dried over magnesium sulfate. Solvents were removed under reduced pressure and brown oil was obtained. Upon the addition of boiling MeOH (50 mL), a white, snow flake like, precipitate rapidly appeared. After filtration and drying, a white solid **2** was obtained (3.58 g, 85% yield). **M.p.:** 172°C. **^{1}H NMR** ($CDCl_3$, ppm): 7.87 (d, ^3J = 8.8 Hz, 4H), 7.61 (d, ^3J = 8.8 Hz, 2H), 7.06 (d, ^3J = 8.8 Hz, 4H), 6.88 (d, ^3J = 8.8 Hz, 2H), 1.59 (s, 18H).

N,N-Di(4-benzoic acid tert-butyl ester)-4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-phenyl-amine (3)

This synthesis was inspired from Cremer's protocol.[2] Care was taken to employ strictly inert conditions. In a 50 ml one-necked flask the iodine derivative **2** (1.00 g, 1.75 mmol, 1.00 eq.), the bis(pinacolato)diboron (489 mg, 1.97 mmol, 1.10 eq., *Frontier chemicals*), $PdCl_2$(dppf) (66 mg, 0.09 mmol, 0.05 eq.) and potassium acetate (515 mg, 5.25 mmol, 3.00 eq.) were mixed with 13 mL of DMSO ([H_2O]=2 ppm, KF). An orange suspension was obtained and after a few minutes, it turned greenish. Then it was stirred at room temperature for one hour (the iodine derivative solubility in DMSO was poor). The resulting brown suspension was heated for an additional hour at 80°C. After cooling at room temperature (ten minutes), it was poured into a large volume of water (300 mL). A white precipitate appeared. After 30 min at 4°C, the solid was collected, generously washed with water and finally re-solubilized into dichloromethane. A filtration over a short $MgSO_4$ pad was performed and after solvent removal under reduced pressure, a brown solid was obtained. The remaining iodine derivative was removed with the help of a short silica-gel chromatography column (dichloromethane as the eluent). After solvent removal and upon the addition of hot MeOH (50 mL), a white solid appeared. **3** was finally collected and dried under vacuum (553 mg, 55% yield). **M.p.**: 240°C. **^{1}H NMR** ($CDCl_3$, ppm): 7.86 (d, ^3J = 8.8 Hz, 4H), 7.74 (d, ^3J = 8.4 Hz, 2H), 7.09 (m, 6H), 1.58 (s, 18H), 1.34 (s, 12H). **FTIR** (ν/cm^{-1}): 2970, 2931, 1709, 1595, 1505, 1477, 1457, 1391, 1360, 1306, 1286, 1158, 1143, 1116, 1104, 1091, 1013, 963, 848, 769, 702, 653, 531, 465, 410.

4-Bromo-N-(2,6-diisopropylphenyl)-naphthalene-1,8-dicarboximide (4)

This reaction was inspired from literature.[3] In a one-necked flask, 4-Bromo-1,8-naphtalic anhydride (7.66 g, 0.028 mol, 1.00 eq.), 2,6-diisopropylaniline (4.90 g, 0.028 mol, 1.00 eq.) were mixed with acetic acid (120 mL) and the resulting yellow suspension was stirred for 3 days at reflux. After cooling at room temperature, a pale yellow precipitate was collected, washed with water and then ethanol. After one night of drying at 60°C in vacuum, the remaining brominated derivative was removed thanks to a chromatography column on Silica-gel (dichloromethane as the eluent). **4** was obtained as white solid (8.99g, 75% yield). **^{1}H NMR** ($CDCl_3$, ppm): 8.75 (dd, ^3J = 7.3 Hz, ^2J = 1.1 Hz, 1H), 8.68 (dd, ^3J = 8.6 Hz, ^2J = 1.1 Hz, 1H), 8.51 (d, ^3J = 7.9 Hz, 1H), 8.11 (d, ^3J = 7.9 Hz, 1H), 7.92 (dd, $^3J_1$ = $^3J_2$ = 7.3 Hz, 1H), 7.50 (t, ^3J = 8.1 Hz, 1H), 7.35 (d, ^3J = 7.7 Hz, 2H), 2.73 (sept, ^3J = 6.8 Hz, 2H), 1.17 (d, ^3J = 6.8 Hz, 12H). **FTIR** (ν/cm^{-1}): 2963, 2867, 1710, 1671, 1615, 1586, 1567, 1584, 1458, 1444, 1398, 1356, 1342, 1238, 1225, 1188, 1143, 1129, 1056, 1042, 963, 902847, 832, 800, 786, 755, 716, 588, 530, 444, 420.

5-(N-(2,6-diisopropylphenyl)-naphthalene-1,8-dicarboximide-4-yl)-2,2’-bithiophene (5)

In a 250 mL two necked flask, 2,2’-Bithiophene-5-boronic acid pinacol ester (543 mg, 1.86 mmol, 1.20 eq.), **4** (675 mg, 1.55 mmol, 1.00 eq.), Pd(dba)$_2$ (89 mg, 0.16 mmol, 0.10 eq.), [HP(^{t}Bu)$_3$]BF$_4$ (45 mg, 0.16 mmol, 0.10 eq.) and grinded potassium phosphate (987 mg, 4.65 mmol, 3.00 eq.) were introduced. The flask was placed in a microwave oven and carefully degassed with nitrogen. Hence, 110 mL of the solvent (a THF/H$_2$O (1/0.1) mixture, which has been carefully degassed before) was introduced into the flask. The solution was heated and stirred for 35 min under microwave irradiation. The reaction conditions were the following: t = 0 to t = 5min, P = 150 W, from room temperature to 65°C; t = 5min to t = 35 min, P = 100W, T = 65°C. After cooling at room temperature, the solvent was removed under reduced pressure. The solid obtained was solubilized into dichloromethane and washed three times with brine. The organic phases were dried over MgSO$_4$. After solvent removal, the residue was purified over silica gel column (eluent gradient, from dichloromethane/petroleum ether (1/1) mixture, to reach 100% dichloromethane). A pure orange solid **5** (672 mg, 83% yield) was finally obtained. **^{1}H NMR** (CDCl$_3$, ppm): 8.81 (dd, ^3J = 8.5 Hz, ^4J = 0.6 Hz, 1H), 8.74 (dd, $^3J_1$ = 7.1 Hz, ^4J = 0.6 Hz , 1H), 8.69 (d, ^3J = 7.6 Hz, 1H), 7.91 (d, ^3J = 7.6 Hz, 1H), 7.85 (dd, ^3J = 8.4 Hz, ^3J = 7.5 Hz, 1H), 7.49 (t, ^3J = 7.8 Hz, 1H), 7.36 to 7.31 (m, 6H), 7.09 (dd, ^3J = 5.3 Hz, ^3J = 3.6 Hz, 1H), 2.77 (sept, ^3J = 6.7 Hz, 2H), 1.17 (d, ^3J = 6.8 Hz, 12H). **FTIR** (ν/cm^{-1}): 2961, 2866, 1700, 1660, 1580, 1511, 1463, 1354, 1236, 1188, 1132, 1058, 1016, 938, 902, 833, 800, 766, 755, 723, 666, 649, 513, 443, 404.

5-Bromo-5’-(N-(2,6-diisopropylphenyl)-naphthalene-1,8-dicarboximide-4-yl)-2,2’-bithiophene (6)

In a 50 mL three necked flask, containing **5** (700 mg, 1.34 mmol, 1.00 eq.) and 10 mL of DMF, NBS (286.6 mg, 1.61 mmol, 1.2 eq., diluted into 4 mL of DMF) was added slowly, in the dark, at room temperature. The mixture was stirred overnight in these conditions. After concentration under vacuum, water was added and the precipitate was collected. Then it was purified over a short silica-gel pad (dichloromethane as the eluent). After solvent removal, **6** was obtained as an orange solid (685 mg, 85% yield). **^{1}H NMR** (CDCl$_3$, ppm): 8.78 (d, ^3J = 8.4 Hz, 1H), 8.74 (d, ^3J = 7.2 Hz, 1H), 8.69 (d, ^3J = 7.7 Hz, 1H), 7.90 (d, ^3J = 7.7 Hz, 1H), 7.51 (dd, ^3J = 8.2 Hz, ^3J = 7.6 Hz, 1H), 7.50 (t, ^3J = 7.8 Hz, 1H), 7.35 (d, ^3J = 7.7 Hz, 2H), 7.31 (d, ^3J = 3.9 Hz, 1H), 7.27 (d, ^3J = 3.9 Hz, 1H), 7.05 (s, 2H), 2.77 (sept, ^3J = 6.9 Hz, 2H), 1.18 (d, ^3J = 6.8 Hz, 12H). **FTIR** (ν/cm^{-1}): 2958, 2925, 2867, 1703, 1662, 1581, 1513, 1463, 1430, 1357, 1236, 1190, 1132, 1085, 1054, 1015, 970, 937, 899, 833, 803, 790, 755, 724, 647, 539, 486.

General procedure of acid-catalysed Knoevanagel condensation

To a mixture of 5′-Bromo-2,2′-bithiophene-5-carboxaldehyde (1.0 eq) and active methylenes (1,3-Indandione, 1,3-Diethyl-2-thiobarbituric acid, 2-(3-Oxo-indan-1-ylidene)-malonitrile) (1.0 eq) was added excess of acetic anhydride (~40 V) and heated at 80°C for 24 h. Then it was cooled to room temperature and the solid was filtered and washed with ice-cold ethanol. The solid was dried under vacuum at 40° C for 24 h to afford pure bithiophene adducts.

5-Bromo-5’-[(indan-1,3-dion-2-ylidene)methyl]-2,2’-bithiophene (7)

Stoichiometric ratio of 5′-Bromo-2,2′-bithiophene-5-carboxaldehyde (1g, 3.67 mmol, 1.0 eq) and 1H-indene-1,3(2*H*)-dione (537 mg, 3.67 mmol, 1.0 eq) was used to afford **7** as an orange powder (235 mg, 16% yield). **^{1}H NMR** (DMSO-d_6, ppm): 8.21 (d, ^3J = 4.0 Hz, 1H), 8.07 (s, 1H), 7.98-7.94 (m, 4H), 7.61 (d, ^3J = 4.0 Hz, 1H), 7.52 (d, ^3J = 4.0 Hz, 1H), 7.38 (d, ^3J = 4.0 Hz, 1H). **FTIR** (v/cm^{-1}): 3085, 1719, 1688, 1622, 1593, 1581, 1533, 1434, 1421, 1372, 1347, 1325, 1285, 1236, 1216, 1189, 1162, 1088, 1068, 1049, 1014, 978, 937, 896, 883, 829, 795, 732, 596.

5-Bromo-5’-[(1,3-Diaza-1,3-diethyl-4,6-dioxo-2-thioxocyclohex-5-ylidene)methyl]-2,2’-bithiophene (8)

Stoichiometric ratio of 5′-Bromo-2,2′-bithiophene-5-carboxaldehyde (1g, 3.67 mmol, 1.0 eq) and 1,3-diethyl-2-thiobarbituric acid (734 mg, 3.67 mmol, 1.0 eq) was used to afford **8** as brown solid (1.08g, 65% yield). **^{1}H NMR** (DMSO-d_6, ppm): 8.67 (s, 1H), 8.29 (d, ^3J = 4.0 Hz, 1H), 7.70 (d, ^3J = 4.0 Hz, 1H), 7.62 (d, ^3J = 4.0 Hz, 1H), 7.39 (d, ^3J = 4.0 Hz, 1H), 4.46 (q, ^3J = 6.7 Hz, 4H), 1.22 (t, ^3J = 7.0 Hz, 6H). **FTIR** (v /cm^{-1}): 3088, 3060, 2976, 2926, 1684, 1650, 1544, 1518, 1485, 1439, 1416, 1370, 1347, 1293, 1261, 1241, 1228, 1148, 1099, 1073, 1056, 999, 973, 894, 806, 792, 781, 751.

5-Bromo-5’-[3-dicyanomethylidene-1-indanon-2-ylidene)methyl]-2,2’-bithiophene (9)

Stoichiometric ratio of 5′-Bromo-2,2′-bithiophene-5-carboxaldehyde (1g, 3.67 mmol, 1.0 eq) and 2-(3-oxo-indan-1-ylidene)-malonitrile (712 mg, 3.67 mmol, 1.0 eq) was used to afford **9** as greenish blue solid (198 mg, 12% yield). **^{1}H NMR** (DMSO-d_6, ppm): 8.82 (s, 1H), 8.66 (d, ^3J = 8.2 Hz, 1H), 8.06-8.11 (m, 4H), 7.77 (d, ^3J = 4.5 Hz, 1H), 7.71 (d, ^3J = 4.2 Hz, 1H), 7.51 (d, 3J = 4.0 Hz, 1H). **FTIR** (v /cm^{-1}): 3098, 2218, 2202, 1704, 1589, 1561, 1526, 1434, 1391, 1350, 1333, 1319, 1301, 1222, 1156, 1133, 1097, 1069, 1059, 1028, 992, 973, 915, 893, 838, 788, 771, 751, 723.

N,N-Di(4-benzoic acid tert-butyl ester)-4-(5'-(N-(2,6-diisopropylphenyl)-naphthalene-1,8-dicarboximide-4-yl)-2,2'-bithien-5-yl)-phenylamine (RBG-174-P)

In a 100 mL three necked flask, **6** (556 mg, 0.93 mmol, 1.00 eq.), **3** (557 mg, 1.01 mmol, 1.09 eq.), $Pd(dba)_2$ (26 mg, 0.05 mmol, 0.05 eq.), $[HP(^tBu)_3]BF_4$ (15 mg, 0.05 mmol, 0.05 eq.) and K_3PO_4 (579 mg, 2.76 mmol, 2.98 eq., previously grinded) were introduced. Then, 50 mL of degassed THF/H_2O (1/0.1) solvent mixture were added, under nitrogen. The flask was heated and stirred in a microwave oven, and the following parameters were employed: 5 min at 150 W, from room temperature to 49°C; 55 min at 100W at 49°C. The initial orange color turned to deep red. After solvent removal under reduced pressure, dichloromethane was added and the mixture was washed three times with water. The combined organic phases were dried over $MgSO_4$ and filtered over a short celite pad. After solvent removal, a red solid was obtained. **7** could be recrystallized from cyclohexane to give a sharp-orange solid (710 mg, 80% yield). **M.p.**: 248°C. **^{1}H NMR** ($CDCl_3$, ppm): 8.82 (d, ^3J = 8.6 Hz, 1H), 8.74 (d, ^3J = 7.1 Hz, 1H), 8.70 (d, 1H), 7.93 to 7.84 (m, 6H), 7.58 (d, ^3J = 8.2 Hz, 2H), 7.49 (t, ^3J = 7.9 Hz, 1H), 7.25-7.37 (m, 6 H), 7.14 (m, 6H), 2.77 (sept, 2H, ^3J = 6.7 Hz), 1.61 (s, 18H), 1.18 (d, ^3J = 6.8 Hz, 12H). **^{13}C NMR** ($CDCl_3$, ppm): 168.19, 166.78, 153.23, 148.78, 148.49, 146.17, 142.79, 141.8, 141.26, 138.46, 135.39, 134.89, 134.12, 133.78, 133.62, 133.05, 132.90, 132.74, 132.46, 132.43, 132.29, 130.25, 129.72, 129.39, 128.88, 128.27, 127.21, 126.92, 126.67, 125.70, 124.8, 83.72, 32.04, 31.12, 29.79, 26.87. **UV/Vis** (λ_{max}, nm; molar extinction coefficient $mol^{-1}.L.cm^{-1}$), in methylene chloride: 442 (27100), 364 (47970). **FTIR** (ν/cm^{-1}): 3067, 2963, 2928, 2868, 1703, 1664, 1584, 1504, 1469, 1362, 1313, 1207, 1240, 1195, 1160, 1105, 1015, 901, 833, 800, 788, 771, 756, 724, 705, 602, 517, 410. **HRMS** (m/z) for $[M+H]^+$: theoretical 965.3653, found: 965.3656.

N,N-Di(4-benzoicacid)-4-(5'-(N-(2,6-diisopropylphenyl)-naphthalene-1,8-dicarboximide-4-yl)-2,2'-bithien-5-yl)-phenylamine (RBG-174)

In a 10 mL one necked flask, **10** (300 mg, 0.31 mmol, 1.00 eq.) was dissolved into 5 mL of dichloromethane. Then, trifluoroacetic acid (TFA) (1.77 g, 15.5 mmol, 50 eq.) was added in the dark. After 5 hours of stirring, the mixture was poured into a large volume of water, and additional dichloromethane was added. The orange organic phase was separated, washed three times with water and dried over $MgSO_4$. After solvent removal under reduced pressure and drying with high vacuum, the solid was washed with hot cyclohexane to give **RBG-174** as a crystalline orange powder (245 mg, 0.29 mmol, 94% yield). **M.p.**: 220-225°C. **^{1}H NMR** (DMF-d_7, ppm): 8.95 (d, ^3J = 8.6 Hz, 1H), 8.72 (d, ^3J = 8.1 Hz, 1H), 8.68 (d, ^3J = 8.7 Hz, 1H), 8.13 (d, ^3J =7.7 Hz, 1H), 8.09 (t, ^3J = 7.3 Hz, 1H), 8.02 (d, ^3J = 8.4 Hz, 4H), 7.85 (d, ^3J = 8.6 Hz, 2H), 7.71 - 7.65 (m, 3H), 7.59 (d, ^3J = 3.8 Hz, 1H), 7.52 (t, ^3J =

8.1 Hz, 1H), 7.42 (d, ^3J = 7.5 Hz, 2H), 7.30 (d, ^3J = 8.6 Hz, 2H), 7.25 (d, ^3J = 8.8 Hz, 4H), 2.88 (sept, ^3J = 6.8 Hz, 2H), 1.15 (d, ^3J = 6.8 Hz, 12H). **^{13}C NMR** (DMF-d_7, ppm): 164.40, 164.10, 150.87, 146.28, 143.25, 139.77, 138.89, 138.45, 135.60, 132.98, 131.94, 131.82, 131.51, 131.21, 129.97, 129.67, 129.59, 129.09, 128.45, 127.20, 126.77, 126.50, 125.51, 125.17, 124.15, 123.31, 123.25, 122.23, 26.93, 23.73. **UV/Vis** (λ_{max}, nm; molar extinction coefficient mol^{-1}.L.cm^{-1}), in acetonitrile: 429 (22740), 356 (37680). **FTIR** (v/cm^{-1}): 3066, 2961, 2924, 2869, 1703, 1663, 1613, 1584, 1524, 1502, 1466, 1426, 1359, 1315, 1237, 1169, 1104, 937, 901, 833, 790, 719, 702, 505. **HRMS** (m/z) for [M+H]$^+$: theoretical 853.2401, found: 853.2403.

N,N-Di(4-benzoic acid tert-butyl ester)-4-(5’-[(indan-1,3-dion-2-ylidene)methyl]-2,2’-bithien-5-yl)-phenylamine (COCO-P)

In a 10 mL three necked flask, **7** (26 mg, 0.06 mmol, 1.00 eq.), **3** (40 mg, 0.07 mmol, 1.17 eq.), Pd(dba)$_2$ (2 mg, 0.003 mmol, 0.05 eq.), [HP(^{t}Bu)$_3$][BF$_4$] (1 mg, 0.003 mol, 0.05 eq.) and K_3PO_4 (40 mg, 0.19 mmol, 3.17 eq., previously grinded) were introduced. The set-up was degassed with nitrogen. Then, 2.5 mL of a degassed THF/H_2O (1/0.1) solvent mixture, were introduced. This mixture was stirred and heated in the microwave, following these parameters: 5 min at 150 W, from room temperature to 49°C; 55 min at 100W at 49°C. The color of the mixture rapidly turned bloody-red. After solvent removal under reduce pressure, dichloromethane was added and the mixture was washed three times with water. The combined organic phases were dried over $MgSO_4$ and filtered over a short celite pad. After solvent removal, a Parma-red solid was obtained. The recrystallization of this solid from cyclohexane gave a pure fuchsia powder (40 mg, 87% yield). **M.p.**: 210 - 212 °C. **^{1}H NMR** ($CDCl_3$, ppm): 7.97 to 7.86 (m, 8H), 7.78 (m, 2H), 7.56 (d, ^3J = 8.42 Hz, 2H), 7.47 (d, ^3J = 3.84 Hz, 1H), 7.32 (d, 1H, ^3J=3.6 Hz), 7.28 (d, ^3J = 3.84 Hz, 1H), 7.13 (m, 6H), 1.61 (s, 18H). **UV/Vis** (λ_{max}, nm; molar extinction coefficient mol^{-1}.L.cm^{-1}), in methylene chloride: 519 (43700), 361 (36200). **FTIR** (v/cm^{-1}): 3075, 2972, 2924, 2853, 1702, 1671, 1593, 1581, 1541, 1505, 1489, 1435, 1413, 1389, 1366, 1282, 1231, 1205, 1154, 1103, 1075, 1014, 991, 845, 801, 791, 769, 730, 707, 697, 648. **HRMS** (m/z) for [M+H]$^+$: theoretical 766.2292, found: 766.2294.

N,N-Di(4-benzoicacid)-4-(5’-[(indan-1,3-dion-2-ylidene)methyl]-2,2’-bithien-5-yl)-phenylamine (COCO)

In a vial, **11** (37 mg, 0.045 mmol, 1.00 eq.) was dissolved into 1 mL of dichloromethane. Then TFA (243 mg, 2.1mmol, 47 eq.) was added in the dark. After 18 hours of stirring, dichloromethane was added and solvents were removed under reduced pressure and drying with high vacuum was operated during 36h. **11** was obtained as a pure dark powder (31 mg, 99% yield). **M.p.**: > 300°C. **^{1}H**

NMR (DMSO-d_6, ppm): 8.12 (d, ^3J = 4.2 Hz, 1H), 7.96 (s, 1H), 7.88 (m, 8H), 7.70 (d, ^3J = 8.4 Hz, 2H), 7.61 (d, ^3J = 3.8 Hz, 1H), 7.54 (d, ^3J = 3.8 Hz, 1H), 7.53 (d, ^3J = 3.7 Hz, 1H), 7.12 (m, 6H). **FTIR** (ν/cm^{-1}): 3172, 2922, 2852, 1710, 1667, 1592, 1573, 1538, 1507, 1444, 1429, 1373, 1350, 1314, 1264, 1214, 1158, 1127, 1044, 1023, 981, 884, 822, 790, 729, 673, 639, 621, 555, 524. **HRMS** (m/z) for $[M+H]^+$: theoretical 654.1040, found: 654.1039.

N,N-Di(4-benzoic acid tert-butyl ester)-4-(5'-[(1,3-Diaza-1,3-diethyl-4,6-dioxo-2-thioxocyclohex-5-ylidene)methyl]-2,2'-bithien-5-yl)-phenylamine (BBTX-P)

In a 10 mL three necked flask, **8** (76 mg, 0.17 mmol, 1.00 eq.), **3** (107 mg, 0.19 mmol, 1.12 eq.), $Pd(dba)_2$ (5 mg, 0.009 mmol, 0.05 eq.), $[HP(^tBu)_3][BF_4]$ (3 mg, 0.010 mol, 0.06 eq.) and K_3PO_4 (115 mg, 0.55 mmol, 3.24 eq., previously grinded) were introduced, the set-up was degassed with nitrogen. Then, 7 mL of previously degassed with nitrogen THF/H_2O (1/0.1) solvent mixture were introduced. The flask was heated and stirred in a microwave oven. The following parameters were employed: 5 min at 150 W, from room temperature to 49°C; 55 min at 100W at 49°C. From red, the color of the mixture rapidly turned to fuchsia. After solvent removal under reduce pressure, dichloromethane was added and the mixture was washed three times with water. The combined organic phases were dried over $MgSO_4$. The obtained powder was purified over a silica-gel chromatography column (initial eluent: cyclohexane/dichloromethane: 0.55/0.45, a gradient of eluent was then applied to reach 100% dichloromethane). The purest fraction was recrystallized from hexane to give a highly pure dark purple solid (21 mg, 15% yield). **M.p.**: > 250 °C. **^{1}H NMR** ($CDCl_3$, ppm): 8.62 (s, 1H), 7.91 (s, ^3J = 8.8 Hz, 4H), 7.80 (d, ^3J = 4.4 Hz, 1H), 7.57 - 7.55 (m, 3H), 7.38 (d, ^3J = 4.2 Hz, 1H), 7.29 (d, ^3J = 4.0 Hz, 1H), 7.13 (m, 6H), 4.6 (qd, ^3J = 6.9 Hz, 2H), 4.59 (qd, ^3J = 6.9 Hz, 2H), 1.60 (s, 18H), 1.37 (t, ^3J = 6.9 Hz, 3H), 1.32 (t, ^3J=6.9 Hz, 3H). **UV/Vis** (λ_{max}, nm; molar extinction coefficient mol^{-1}.L.cm^{-1}), in methylene chloride: 542 (64500), 430 (13000), 359 (50700). **FTIR** (ν/cm^{-1}): 2973, 2924, 2851, 1709, 1659, 1596, 1558, 1536, 1507, 1485, 1444, 1409, 1389, 1311, 1289, 1266, 1233, 1197, 1159, 1116, 1105, 1077, 795, 771. **HRMS** (m/z) for $[M+H]^+$: theoretical 820.2543, found: 820.2546.

N,N-Di(4-benzoicacid)-4-(5'-[(1,3-Diaza-1,3-diethyl-4,6-dioxo-2-thioxocyclohex-5-ylidene)methyl]-2,2'-bithien-5-yl)-phenylamine (BBTX)

In a vial, **12** (33 mg, 0.04 mmol, 1.00 eq.) was dissolved with 1 mL of dichloromethane. Then TFA (230 mg, 2.0 mmol, 50 eq.) was added in the dark. After 18 hours of stirring, dichloromethane was added and solvents were removed under reduced pressure and drying with high vacuum was operated. The obtained solid was washed with hot cyclohexane. **BBTX** was obtained as a dark powder (27 mg, 95% yield). **M.p.**: 210 (dec) °C. **^{1}H NMR** (DMSO-d_6, ppm): 8.60 (s, 1H), 8.23 (d, ^3J = 4.6 Hz, 1H), 7.90 (d, ^3J =

8.8 Hz, 4H), 7.78 (m, 3H), 7.70 (d, ^3J = 4.2 Hz, 1H), 7.61 (d, ^3J = 4.0 Hz, 1H), 7.14 (m, 6H), 4.42 (m, 4H), 1.23 (t, ^3J = 6.9 Hz, 3H), 1.20 (t, ^3J = 7.1 Hz, 3H). **FTIR** (ν/cm^{-1}): 3073, 2980, 2929, 1689, 1658, 1592, 1553, 1533, 1507, 1446, 1428, 1408, 1381, 1317, 1266, 1226, 1171, 1154, 1103, 1075, 952, 901, 852, 833, 784, 672, 647. **HRMS** (m/z) for [M+H]$^+$: theoretical 708.1291, found: 708.1292.

N,N-Di(4-benzoic acid tert-butyl ester)-4-(5'-[3-dicyanomethylidene-1-indanon-2-ylidene)methyl]-2,2'-bithien-5-yl)-phenylamine (COCN-P)

In a 10 mL three necked flask, **9** (31 mg, 0.06 mmol, 1.00 eq.), **3** (40 mg, 0.07 mmol, 1.16 eq.), Pd(dba)$_2$ (3 mg, 0.005 mmol, 0.04 eq.), [HP(^{t}Bu)$_3$][BF$_4$] (1 mg, 0.003 mol, 0.05 eq.) and K_3PO_4 (40 mg, 0.19 mmol, 3.17 eq., previously grinded) were introduced. The set-up was degassed with nitrogen. Then, 3 mL of a previously nitrogen degassed THF/H_2O (1/0.1) solvent mixture were introduced. The flask was heated and stirred in a microwave oven. The following parameters were employed: 5 min at 150 W, from room temperature to 49°C; 55 min at 100W at 49°C. Initially wine, the mixture was dark blue at the end of the reaction. After solvent removal under reduce pressure, dichloromethane was added and the mixture was washed three times with brine. The combined organic phases were dried over $MgSO_4$ and filtered on a short celite pad. After solvent removal, the blue powder was washed with large amounts of hot cyclohexane. A careful recrystallization from toluene (cyclohexane could be used to recuperate the remaining product in the flask) enabled the getting of a pure crystalline dark green powder (35 mg, 71% yield). **M.p.**: 179 - 181 °C. **^{1}H NMR** (CDCl$_3$, ppm): 8.86 (s, 1H), 8.70 (d, ^3J = 6.9 Hz, 1H), 7.95 (d, ^3J = 7.9 Hz, 1H), 7.91 (d, ^3J = 8.8 Hz, 4H), 7.81 - 7.74 (m, 3H), 7.56 (d, ^3J = 8.6 Hz, 2H), 7.53 (d, ^3J = 3.8 Hz, 1H), 7.36 (d, ^3J = 4.0 Hz, 1H), 7.30 (d, ^3J = 4.0 Hz), 7.14 (m, 6H), 1.60 (s, 18H). **UV/Vis** (λ_{max}, nm; molar extinction coefficient mol^{-1}.L.cm^{-1}), in methylene chloride: 590 (53400), 440 (9000), 358 (45000). **FTIR** (ν/cm^{-1}): 2974, 2923, 2216, 1699, 1591, 1562, 1534, 1505, 1481, 1437, 1390, 1367, 1340, 1308, 1279, 1225, 1156, 1103, 1062, 1013, 989, 919, 847, 788, 769, 719, 708, 600, 520, 493. **HRMS** (m/z) for [M+H]$^+$: theoretical 814.2404, found: 814.2404.

N,N-Di(4-benzoicacid)-4-(5'-[3-dicyanomethylidene-1-indanon-2-ylidene)methyl]-2,2'-bithien-5-yl)-phenylamine (COCN)

In a vial, **13** (37 mg, 0.045 mmol, 1.00 eq.) was dissolved in 1 mL of dichloromethane. Then, TFA (242 mg, 2.12 mmol, 42.0 eq.) was added in the dark and the mixture was stirred overnight. Dichloromethane helped rinsing the vial and after solvent removal and drying. **13** was obtained after recrystallization from dichloromethane, as a pure black, with blue reflects, powder (31 mg, 98% yield). **M.p.**: 260°C (Decomposition). **^{1}H NMR** (DMSO-d$_6$, ppm): 8.61 (s, 1H), 8.70 (d, ^3J = 6.7 Hz, 1H), 7.85 - 7.91 (m, 8H), 7.73 (m, 3H), 7.63 (d, ^3J = 4.0 Hz, 1H), 7.58 (d, ^3J = 3.8 Hz, 1H), 7.15 (m, 6H). **FTIR**

(ν/cm^{-1}): 2971, 2217, 1681, 1590, 1532, 1507, 1483, 1431, 1387, 1341, 1387, 1341, 1315, 1269, 1225, 1171, 1132, 989, 916, 834, 791, 769, 652, 498. **HRMS** (m/z) for [M+H]$^+$: theoretical 702.1152, found: 702.1152.

NMR spectra of the final compounds

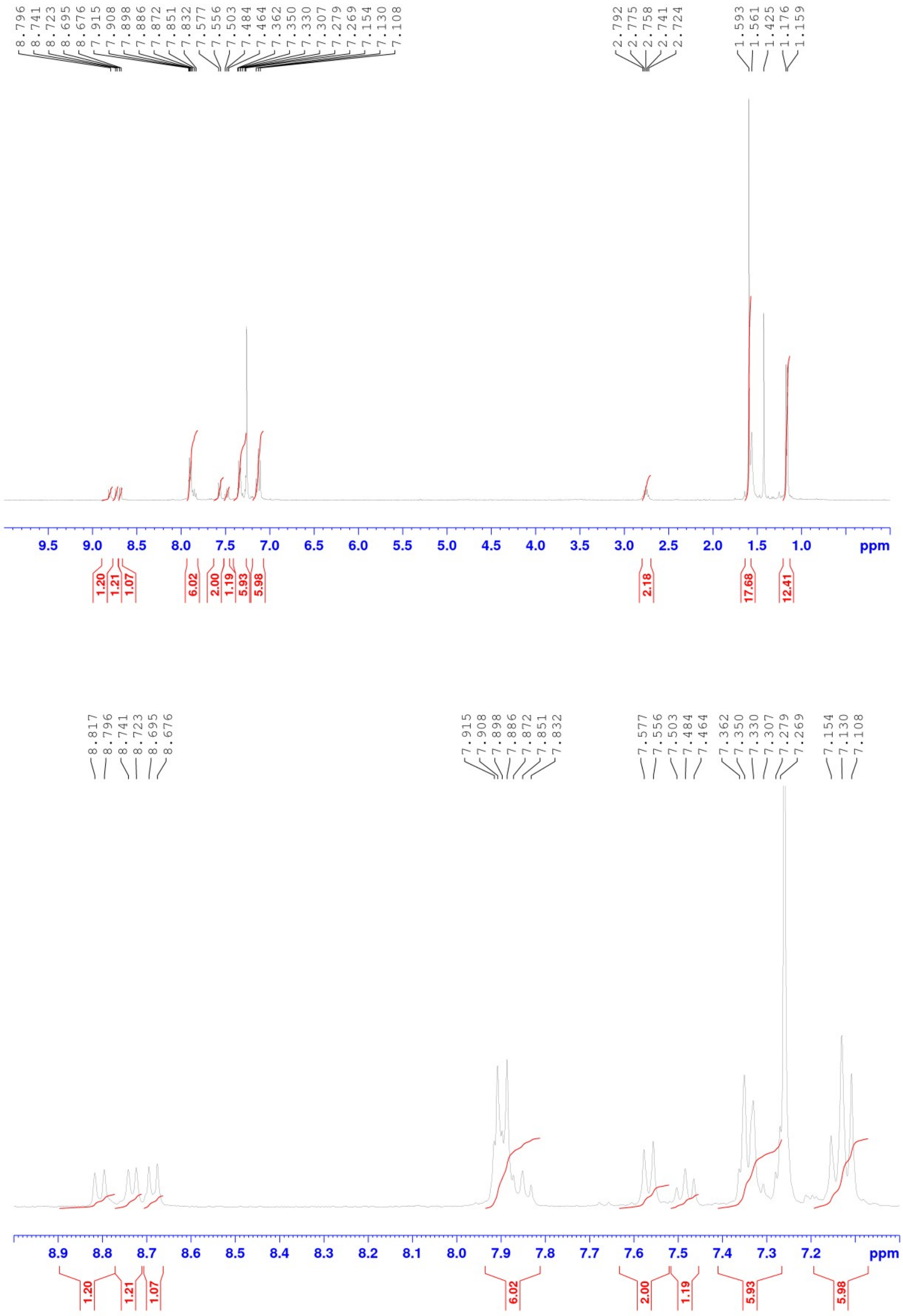


Figure S1- 1H NMR spectrum of RBG-174-P

RBG-174

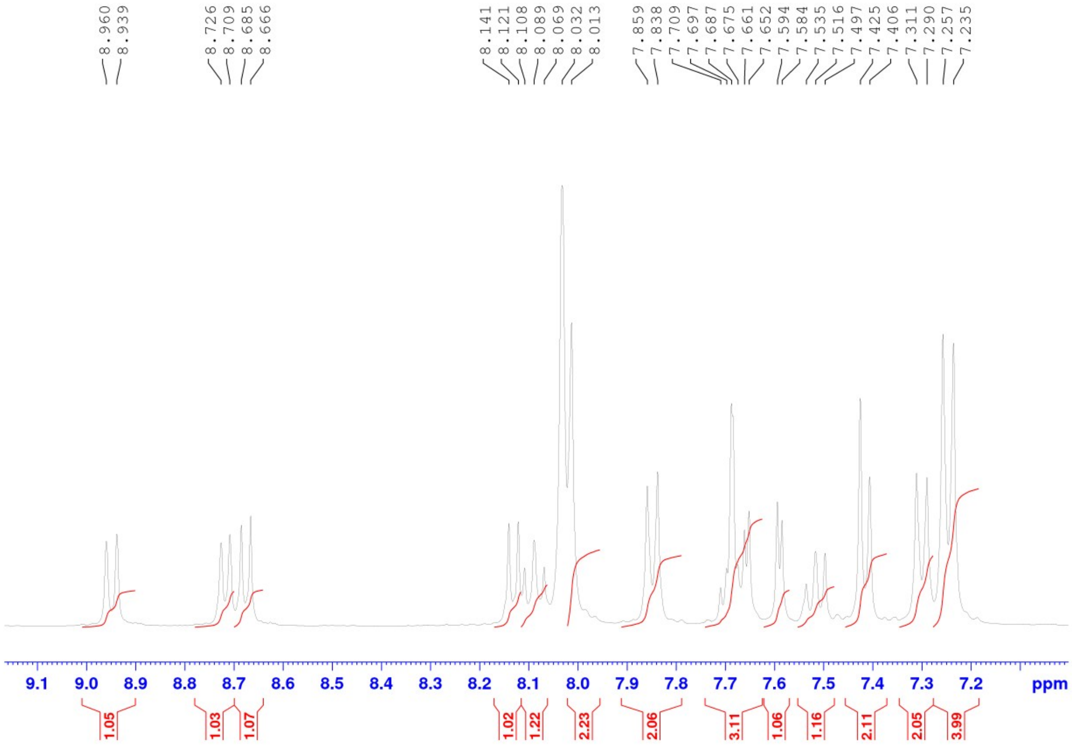


Figure S2- 1H NMR spectrum of RBG-174

COCO-P

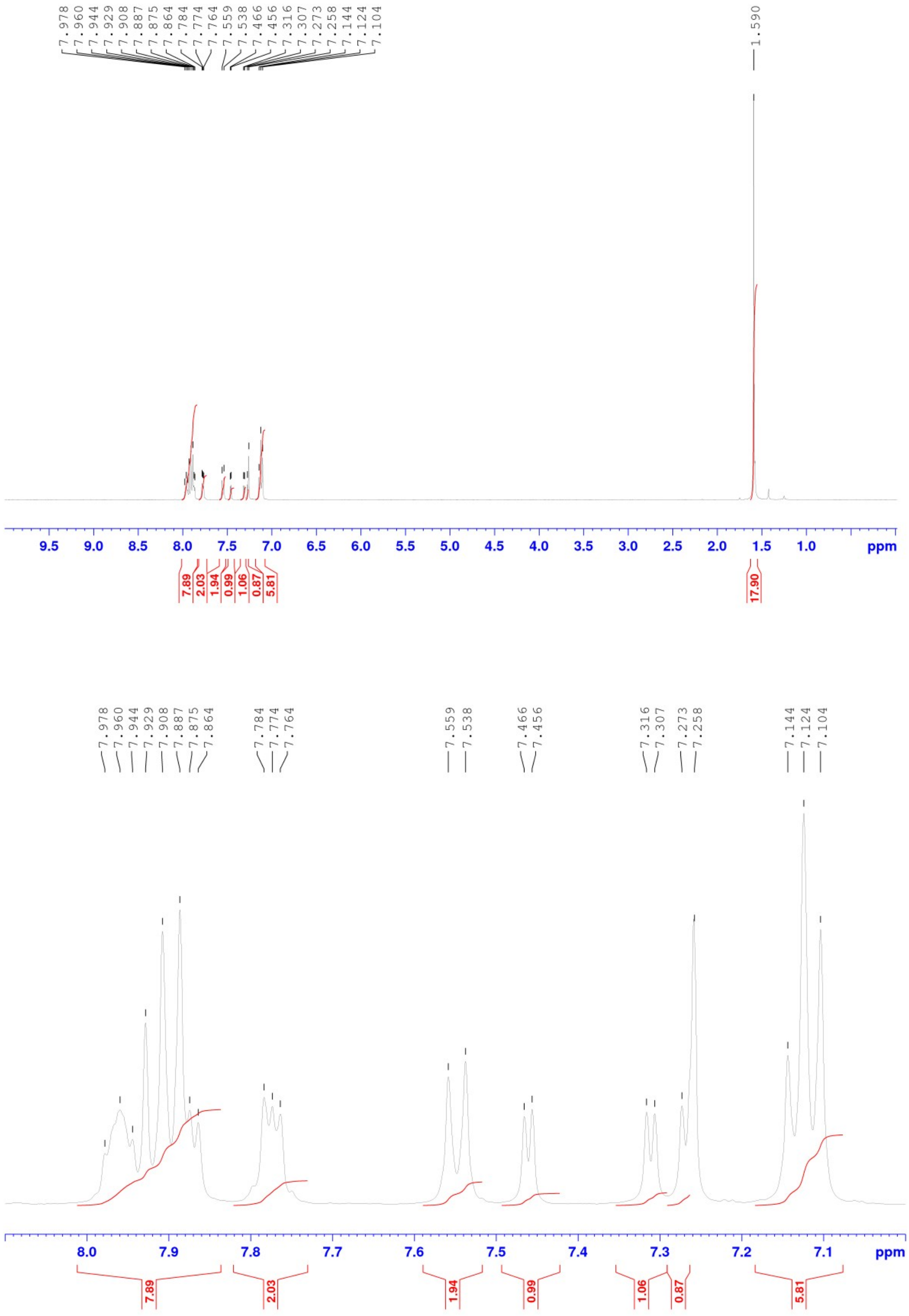


Figure S3- 1H NMR spectrum of COCO-P

COCO

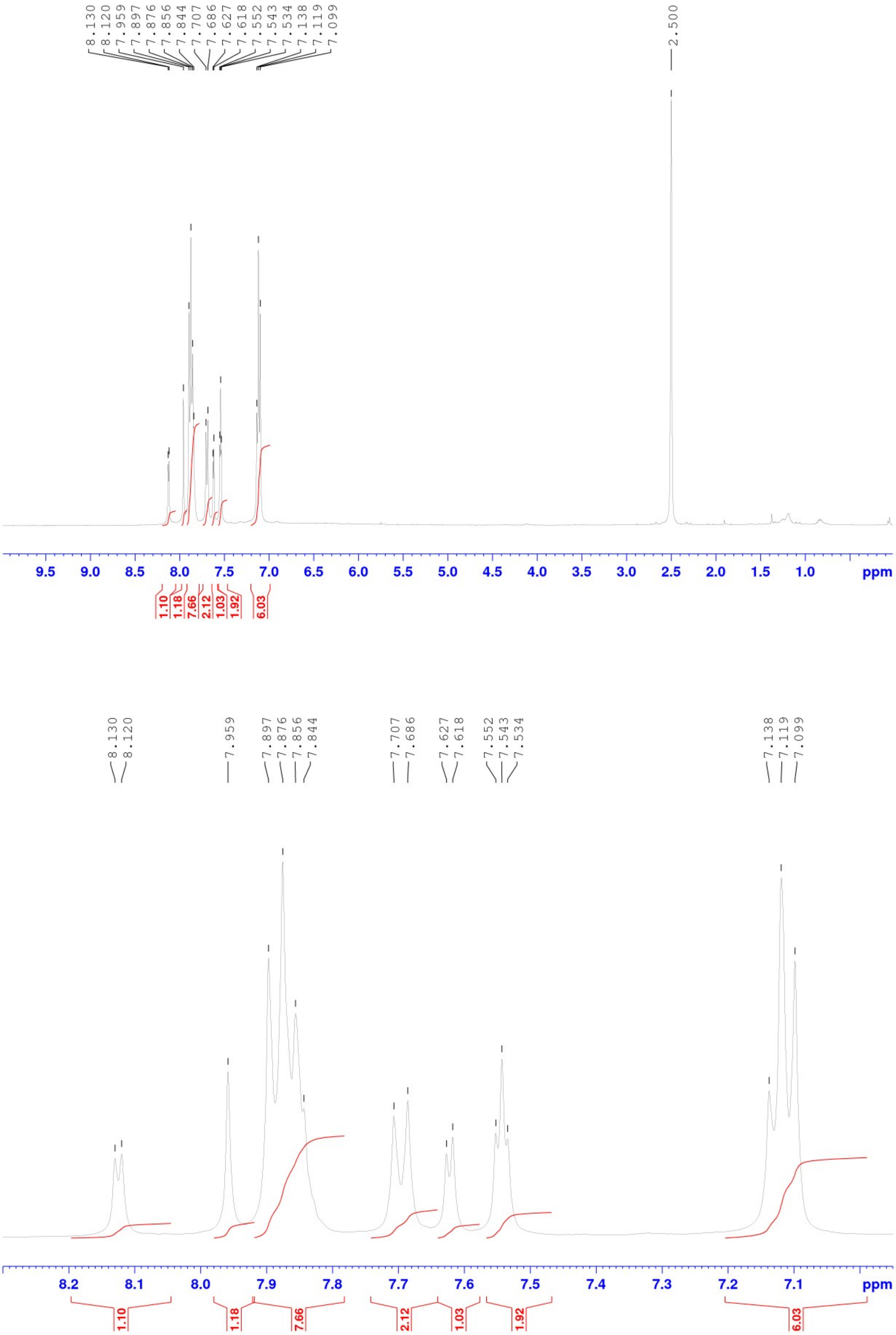
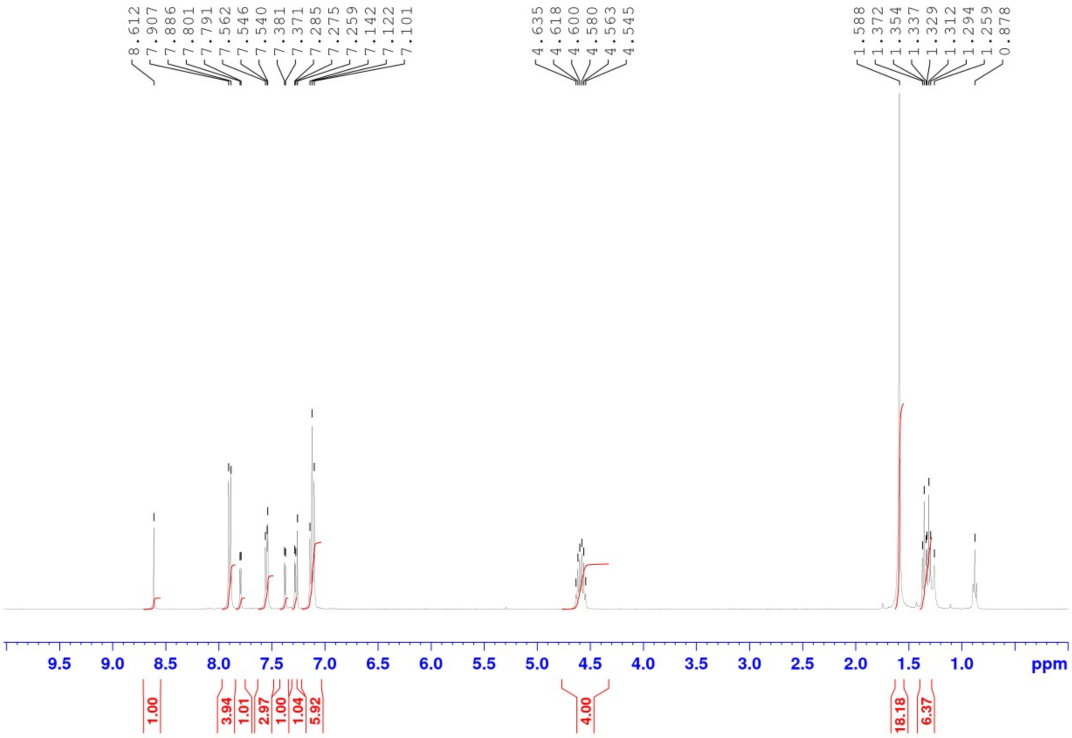


Figure S4- 1H NMR spectrum of COCO

BBTX-P



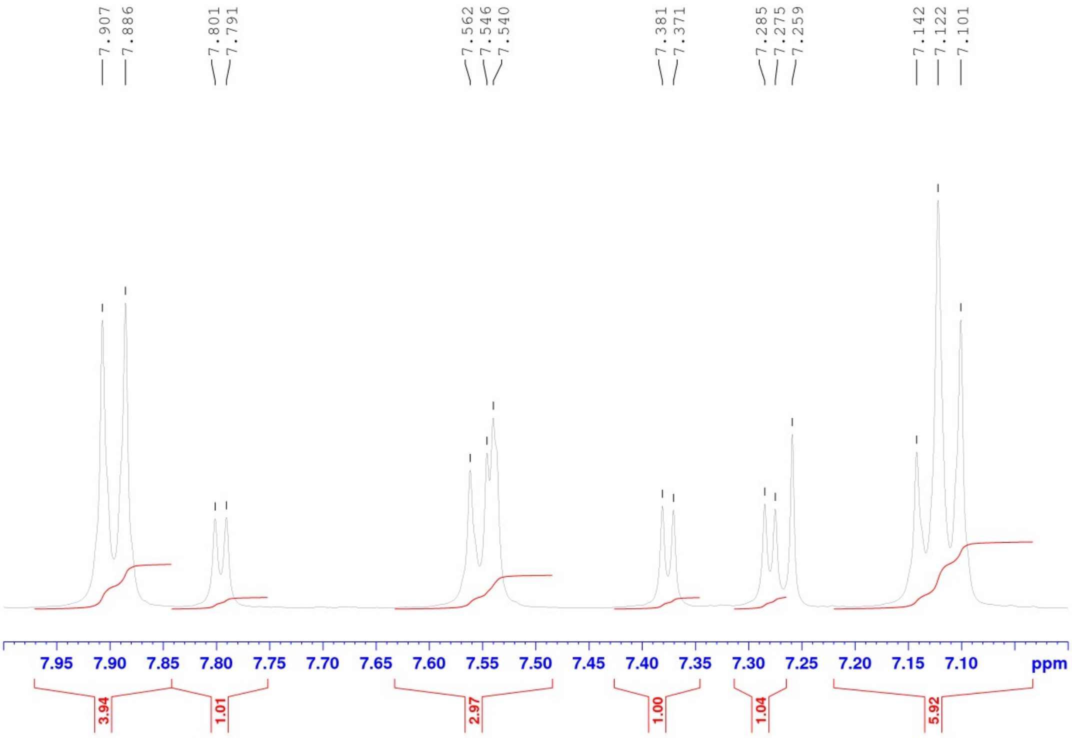
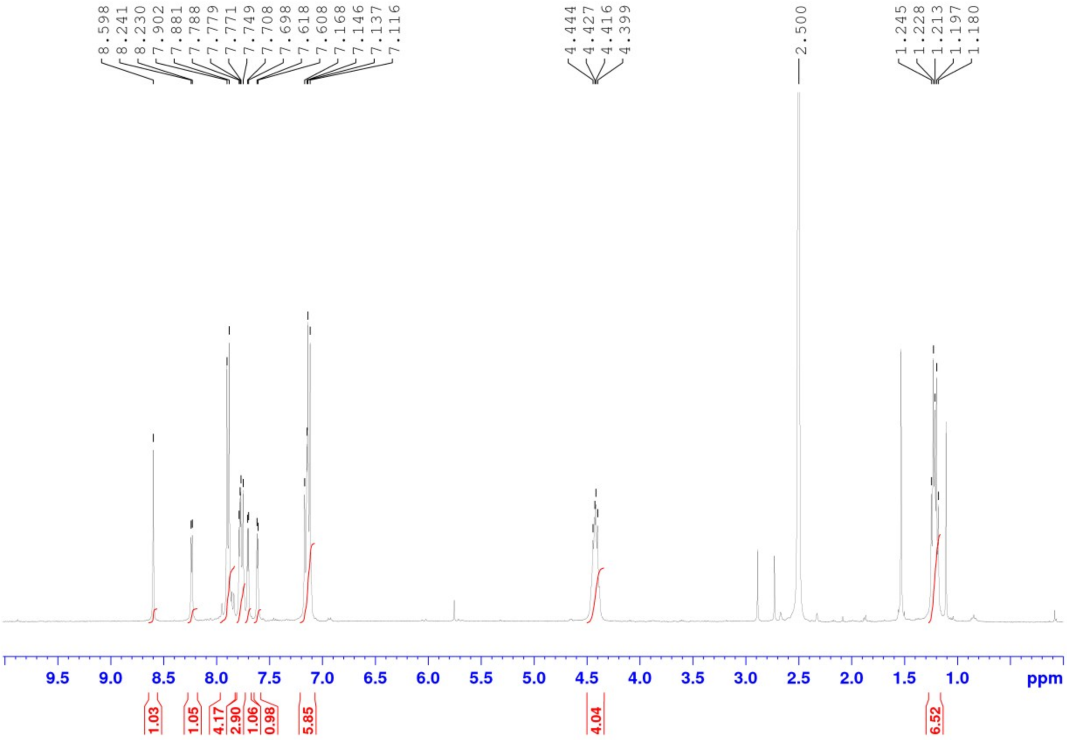


Figure S5- 1H NMR spectrum of BBTX-P

BBTX



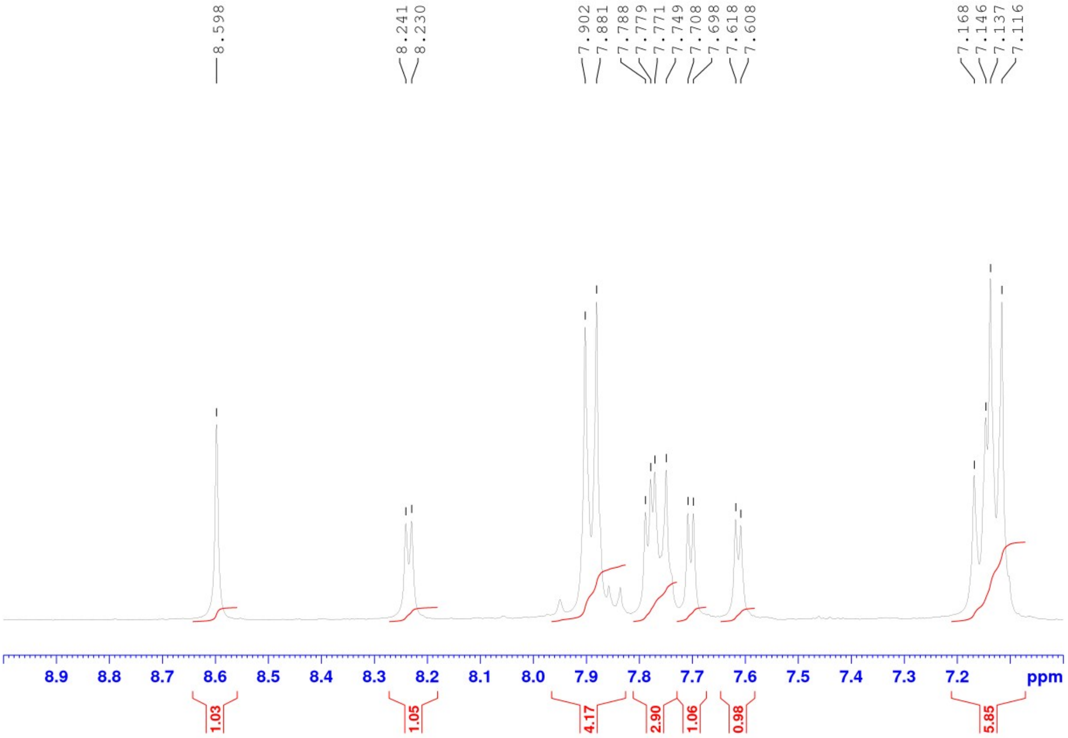


Figure S6- 1H NMR spectrum of BBTX

COCN-P

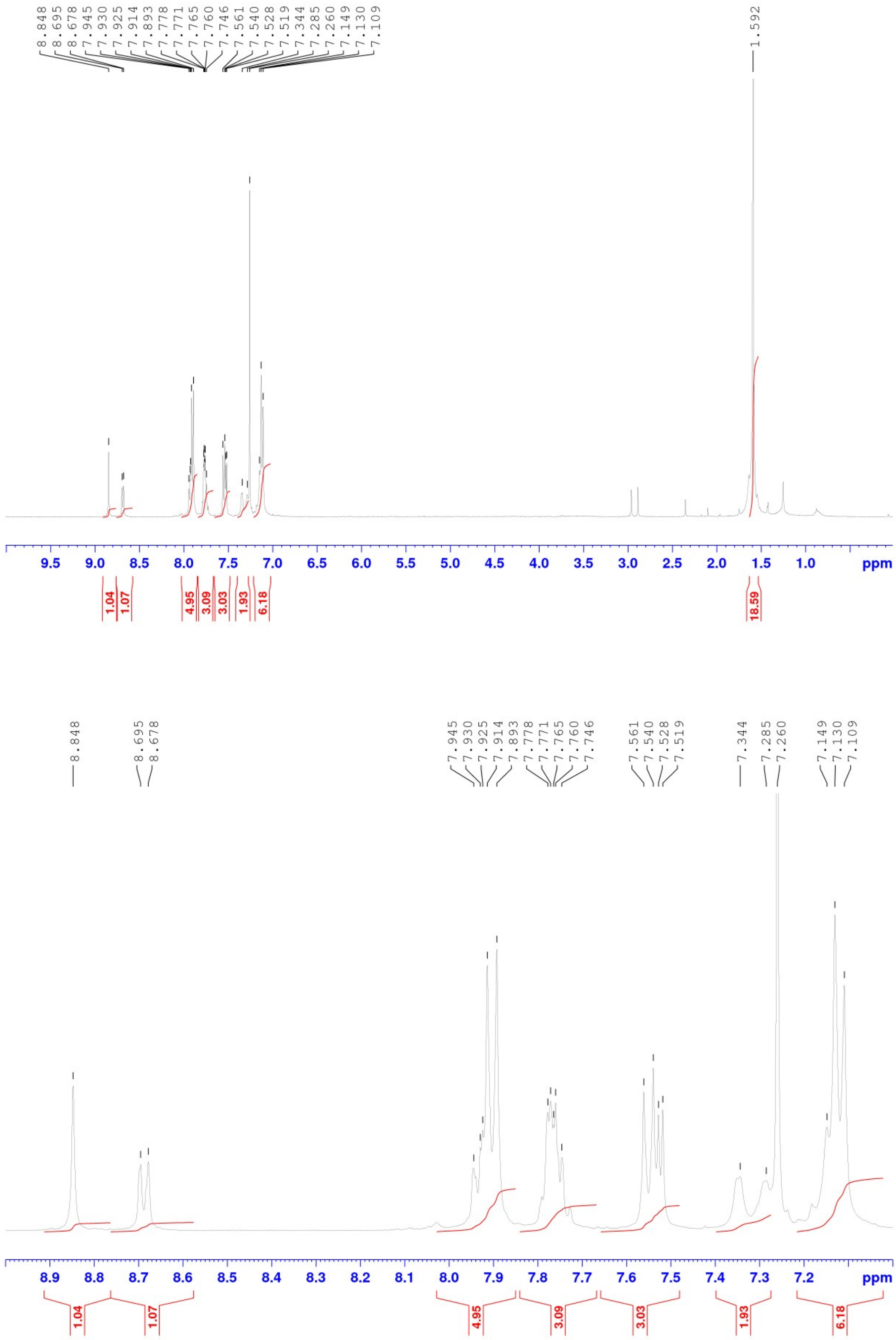


Figure S7- 1H NMR spectrum of COCN-P

COCN

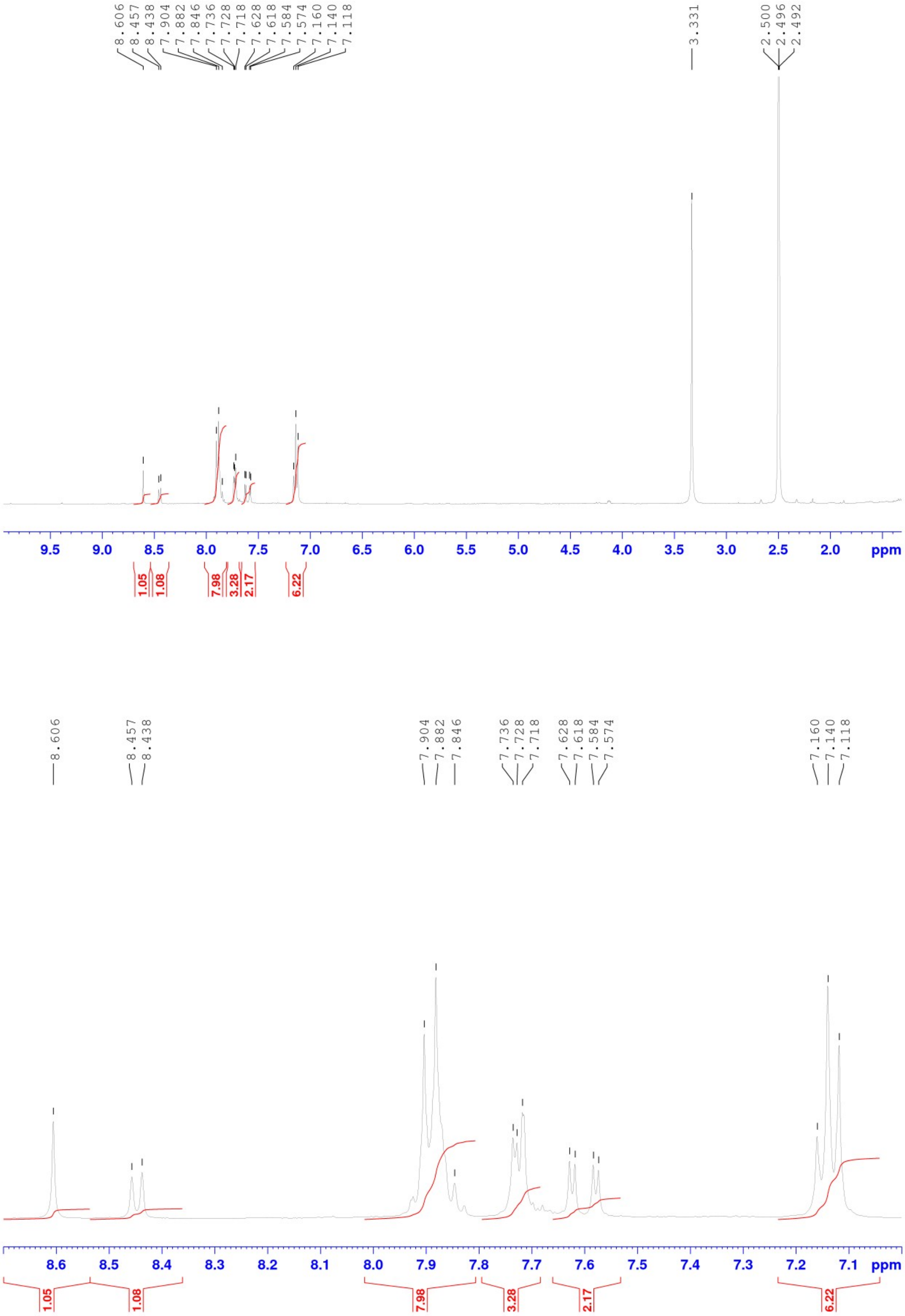


Figure S8- 1H NMR spectrum of COCN

Physical characterisation and quantum calculation

Optical properties

The solvent used for steady-state solution-based optical properties was spectrophotometric grade DCM. Solid-state spectra were acquired on one-layer ink-jet printed 320 nm NiO.[3] The absorption spectra were recorded with a double-beam UV-visible spectrophotometer (Perkin Elmer lambda 900). Steady-state solution fluorescence spectra were acquired with a spectrofluorometer (SPEX Fluorolog 3, Horiba Jobin Yvon) in 1 cm optical path quartz cells. The fluorescence spectra were first corrected by subtraction of the pure solvent contribution. Then, they were also corrected for the wavelength-dependent response of the instrument (using an adapted correction curve) and for the re-absorption process. The absorbance of the samples at the excitation wavelength was kept below 0.1. The molar absorption coefficients of the final dyes, in their protected *tert*-butyl ester versions, **RBG-174-P**, **COCO-P**, **BBTX-P** and **COCN-P**, were measured precisely by weighting each dye with an error below 5%. Then, solutions were prepared using only one volumetric flask and the absorption spectrum was recorded.

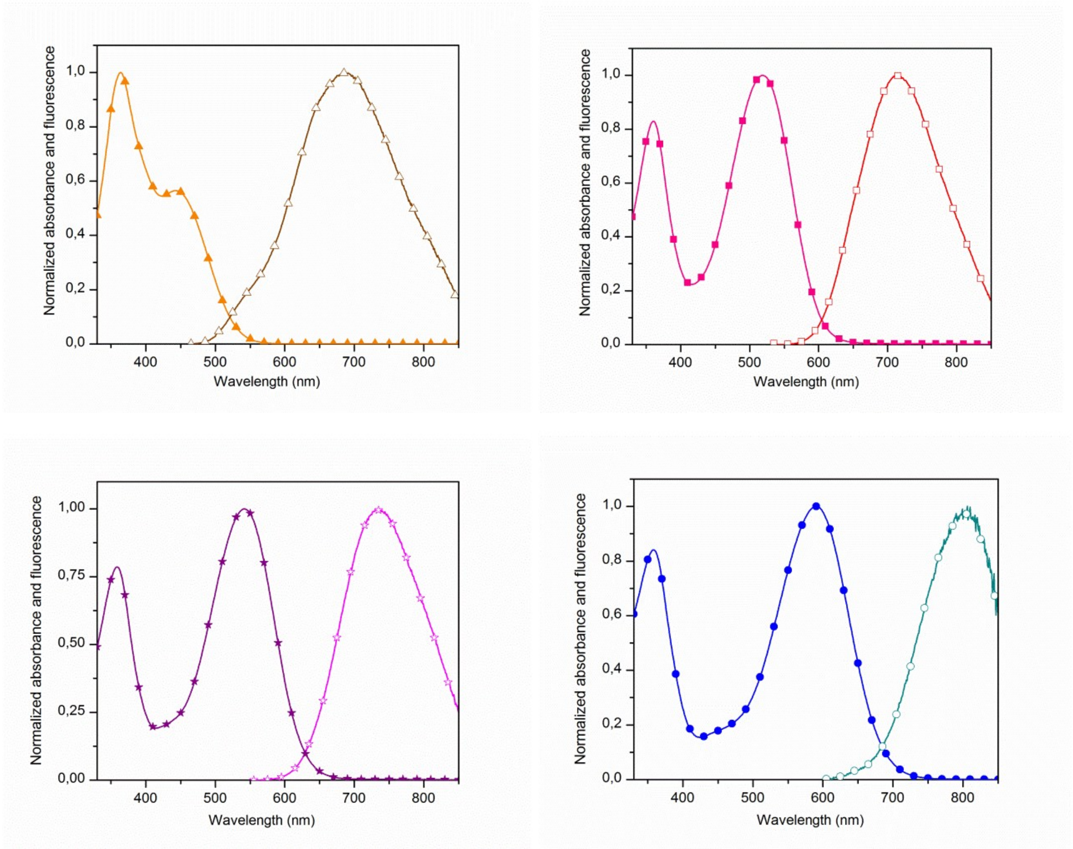


Figure S9- Steady state normalized absorption (filled shapes) and fluorescence (empty shapes) solution spectra of RBG-174-P (top-left), COCO-P (top right), BBTX-P (bottom left), COCN-P (bottom right). Fluorescence excitation wavelength: RBG-174-P: 450 nm; COCO-P: 520 nm; BBTX-P: 540 nm; COCN: 590 nm.

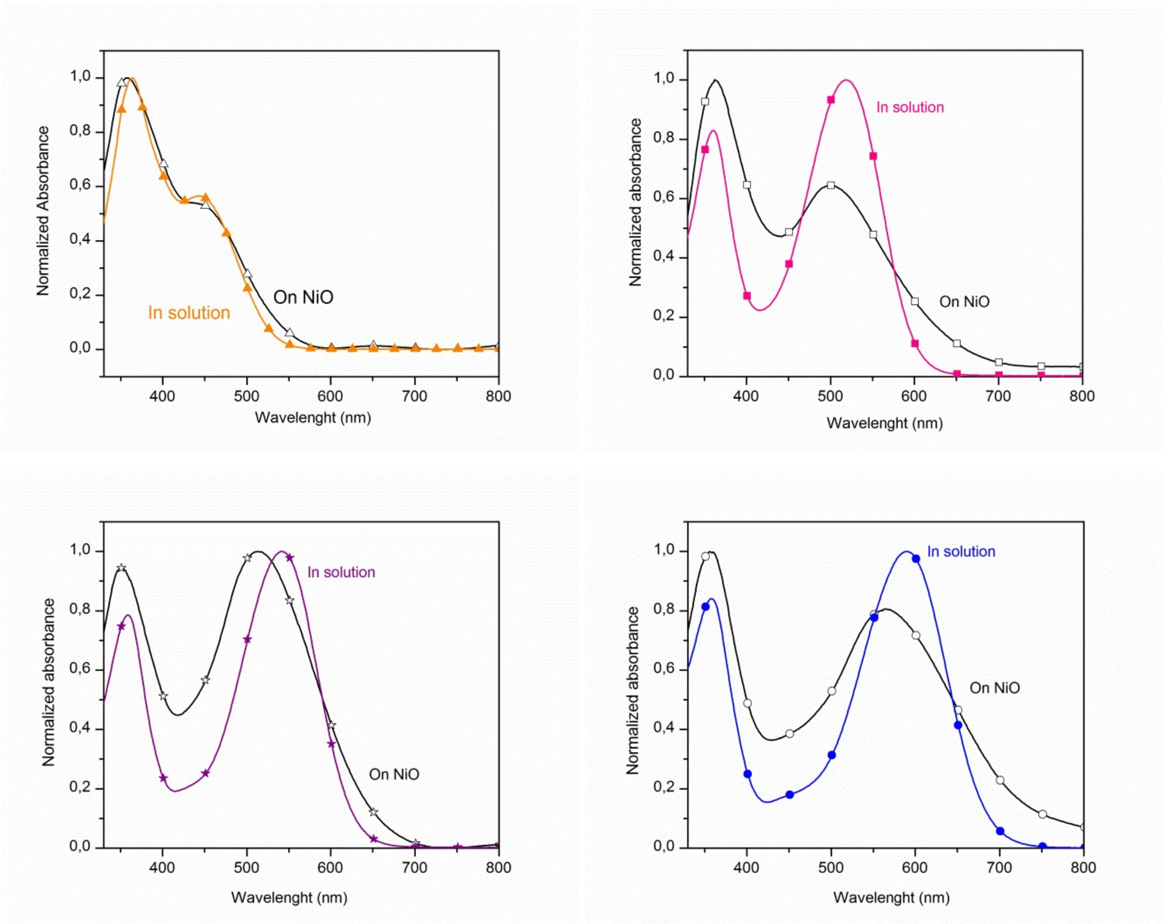


Figure S10- Comparison of the normalized absorption spectra of RBG-174 (top left, triangle), COCO (top right, squares), BBTX (bottom left, stars) and COCN (bottom right, circles) dyes after their grafting on NiO (empty shapes, black) and in solution (filled shapes, respectively orange, pink, purple and blue).

Redox properties

Electrochemical measurements were carried out in a three electrodes set-up, with a Biologic VSP potentiostat. The redox potentials of interest were determined in DCM with TBAPF$_6$ as the support salt (10^{-1}M). Cyclic-voltamperometry technique was employed, with a scan rate of 100 V.s^{-1}. A platinum wire was used in lieu of the working electrode and carbon graphite was the counter electrode. The reference electrode used was AgNO$_3$/Ag in DMF. Measurements were performed under nitrogen. For every measurement session, the redox potential of the {Fc$^+$/Fc} reference couple in DCM was measured (ex situ).

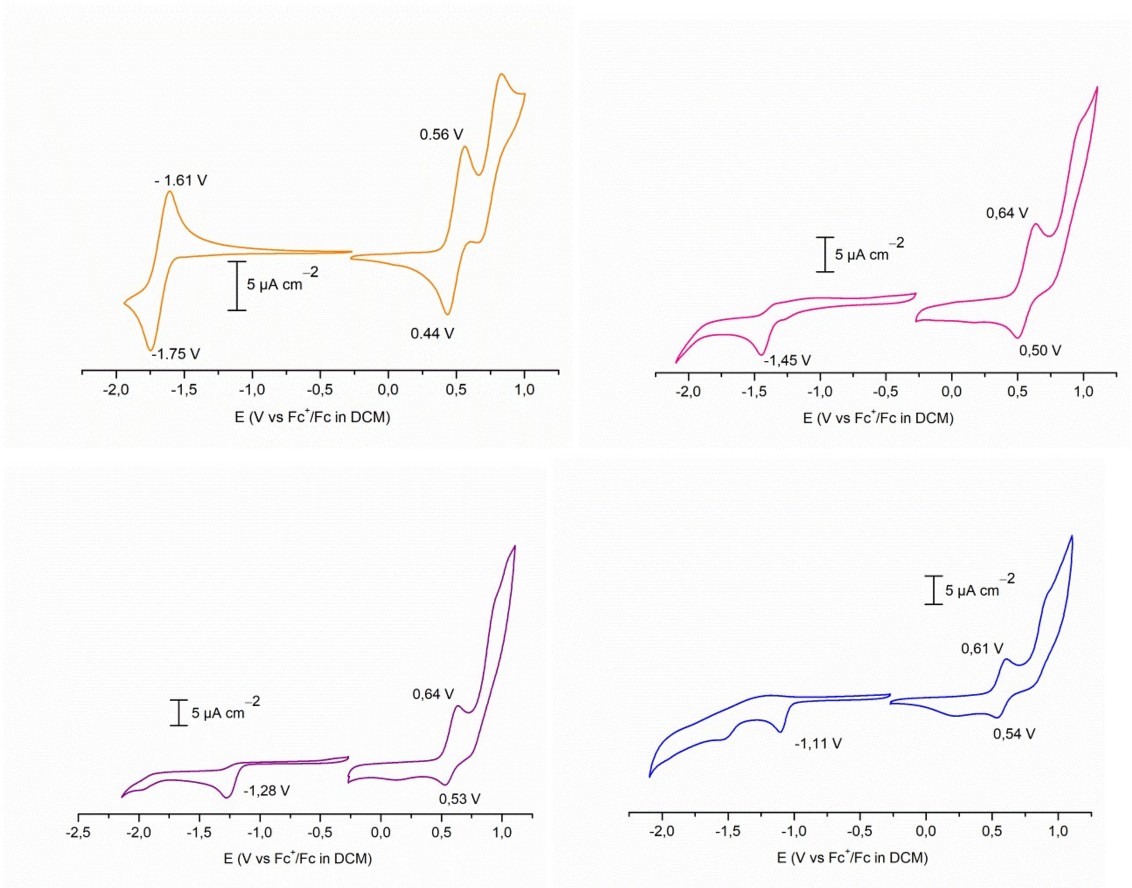


Figure S11- Cyclic voltamperometry of RBG (top left), COCO (top right), BBTX (bottom left) and COCN (bottom right) in methylene chloride. TBAPF$_6$ was used as the support salt (10^{-1}M). Scan rate: 100 mV/sec. WE: Pt wire.

Quantum calculation

Quantum calculations were carried out with the Gaussian 3 package. All the calculations were performed in vacuum, on the carboxylic-acid version of the dyes (**RBG-174**, **COCO**, **BBTX**, **COCN**). DFT calculations were done so as to optimize the geometry of the compounds and to calculate the energies of their molecular orbitals. B3LYP was used as the hybrid functional and the 6-31G (d) basis set was employed. To ensure a true energy minimum was reached, the vibration frequencies were calculated and it was ensured there was no imaginary frequency. The molecular orbitals are represented with an isodensity value of 0.02 a.u. TDDFT allowed calculating the 7 first vertical transitions energy and the UV-Visible steady state absorption spectrum could be simulated. The orbital composition of each transition was thus established and is displayed.

RBG-174

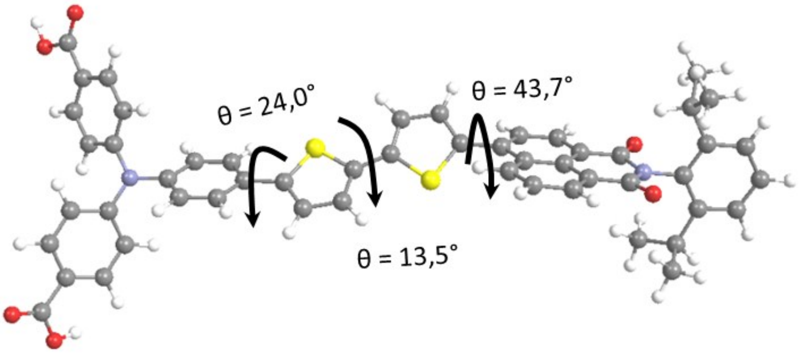


Figure S12- Optimized geometry for RBG-174 in vacuum.

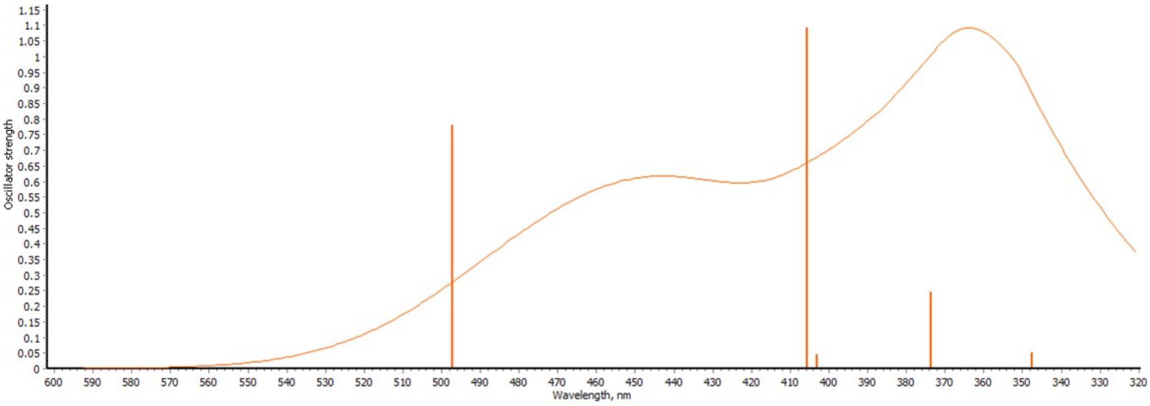


Figure S13- Computed optical transitions of RBG-174 in vacuum and the experimental spectrum of RBG-174-P in DCM.

Tab. S1- Computed transition energies (λ_{max}), their orbital contributions and the associated oscillator strength in vacuum, for RBG-174

Computed λ_{max}	**Orbitals contribution**	**Oscillator strength**	**Type of transition**
497.15 nm/ 2.4939 eV	HOMO -> LUMO (91.65 %)	0.7804	Charge Transfer (CT)
405.61 nm/ 3.0568 eV	HOMO-1 -> LUMO (26.36%) HOMO -> LUMO+1 (61.83%)	1.0930	-CT (26.36 %) -TPA-2T centered, partial CT (61.83%)
373.52 nm / 3.3193 eV	HOMO -> LUMO+2 (91.90%)	0.2440	TPA centered

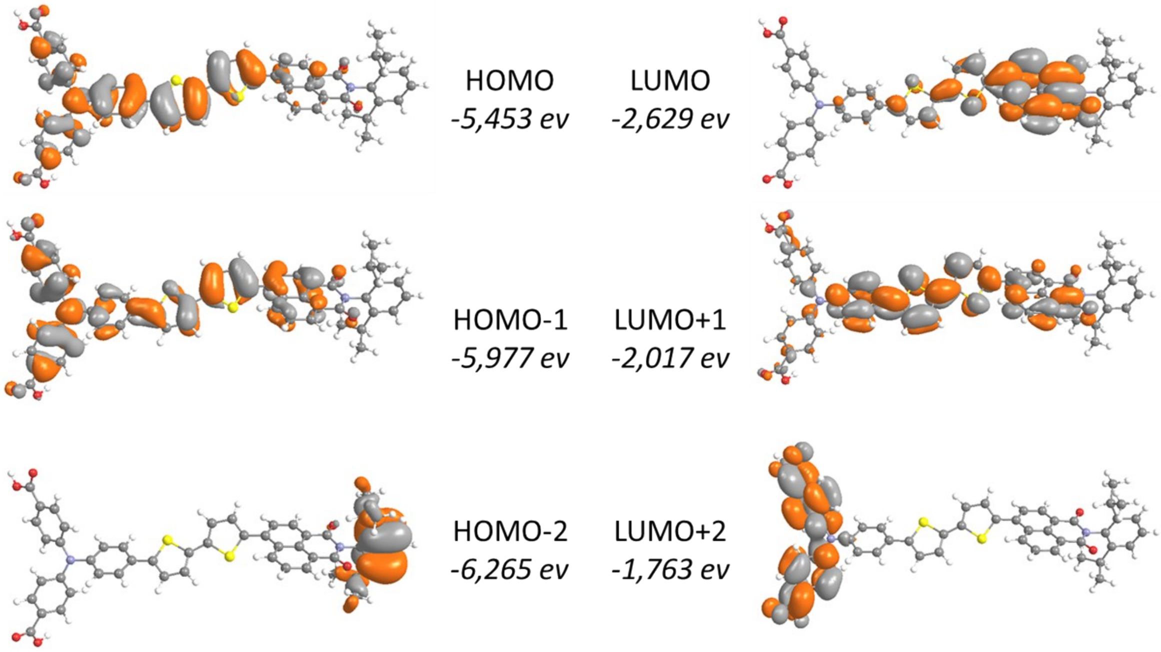


Figure S14- Computed orbitals for RBG-174 in vacuum and their energies. In orange, the positive lobes and in grey, the negative lobes.

COCO

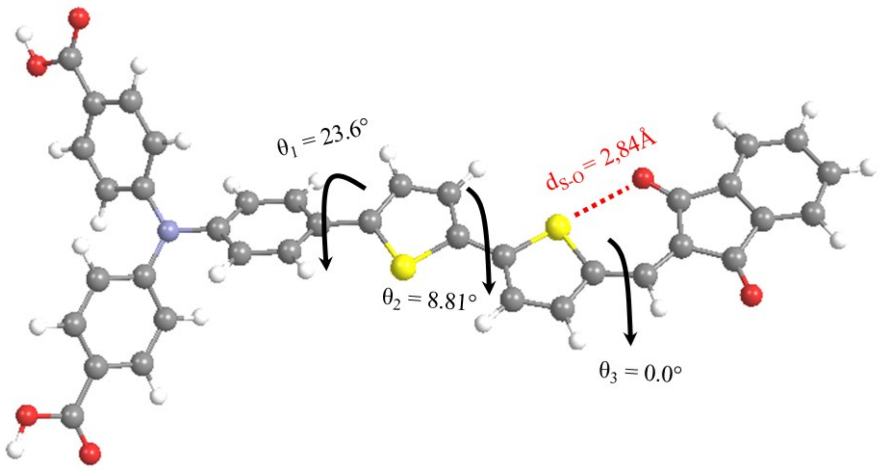


Figure S15- Optimized geometry for COCO in vacuum

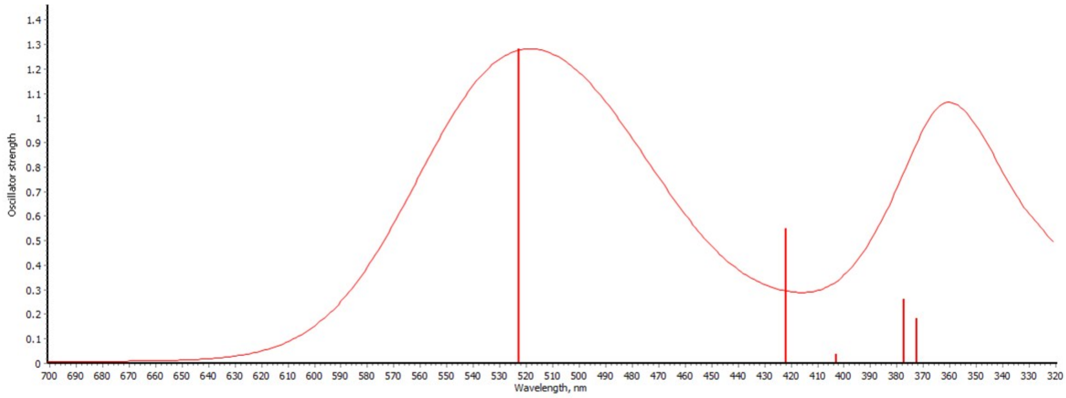


Figure S16- Computed optical transitions of COCO in vacuum and the experimental spectrum of COCO-P in DCM.

Tab. S2- Computed transition energies (λ_{max}), orbital contributions, associated oscillator strength and the calculated absorption molar extinction coefficient at λ_{max} (ε_{max}), in vacuum, for compound COCO

Computed λ_{max}	**Orbitals contribution**	**Oscillator strength**	**Type of transition**
522.62 nm/ 2.3723 eV	HOMO -> LUMO (85.83 %)	1.2833	CT
421.78 nm/ 2.9395 eV	HOMO-1 -> LUMO (84.6%)	0.5501	CT
377.50 nm / 3.2843 eV	HOMO -> LUMO+2 (91.55%)	0.2624	TPA centered
372.52 nm/ 3.3282 eV	HOMO->LUMO+3 (80.86%)	0.1845	The whole dye

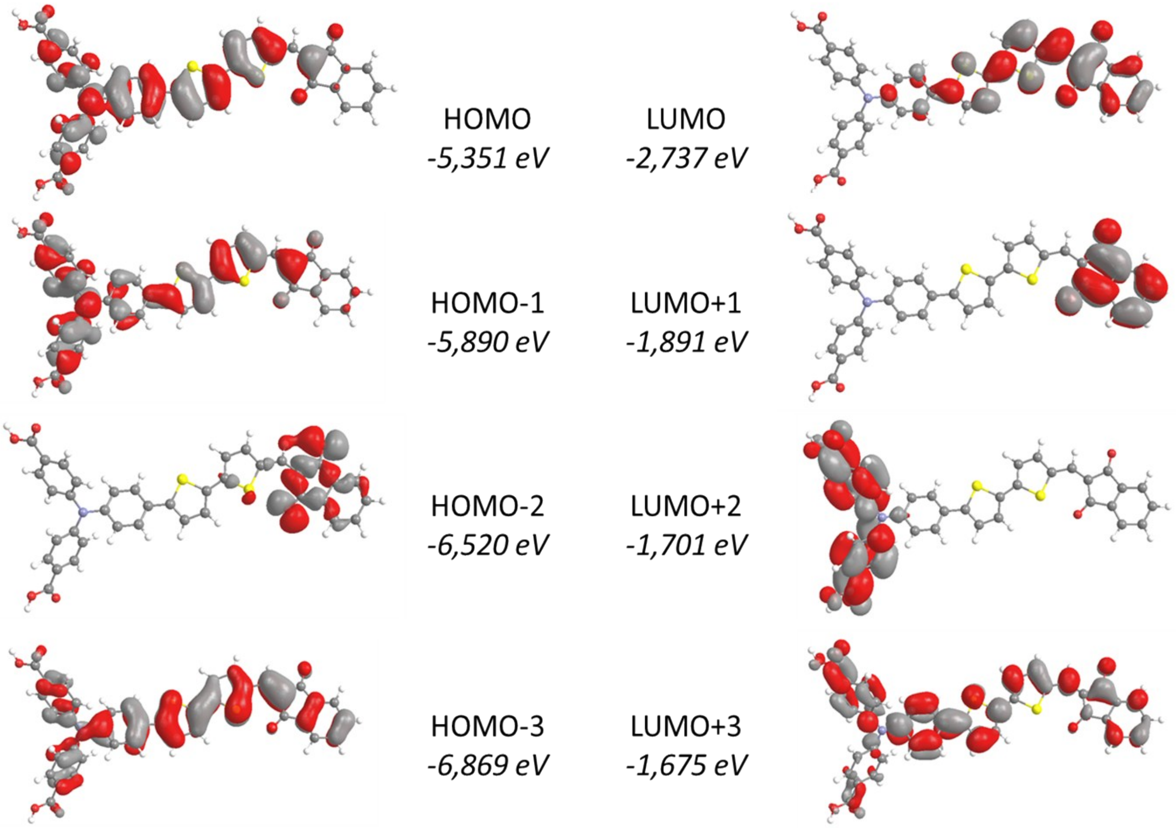


Figure S17- Computed orbitals and their energies for compound COCO in vacuum. In red, the positive lobes and in grey, the negative lobes.

BBTX

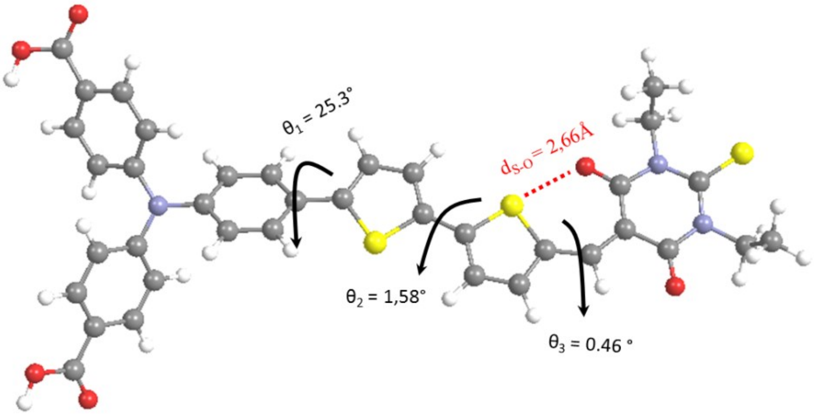


Figure S18- Optimized geometry for BBTX in vacuum

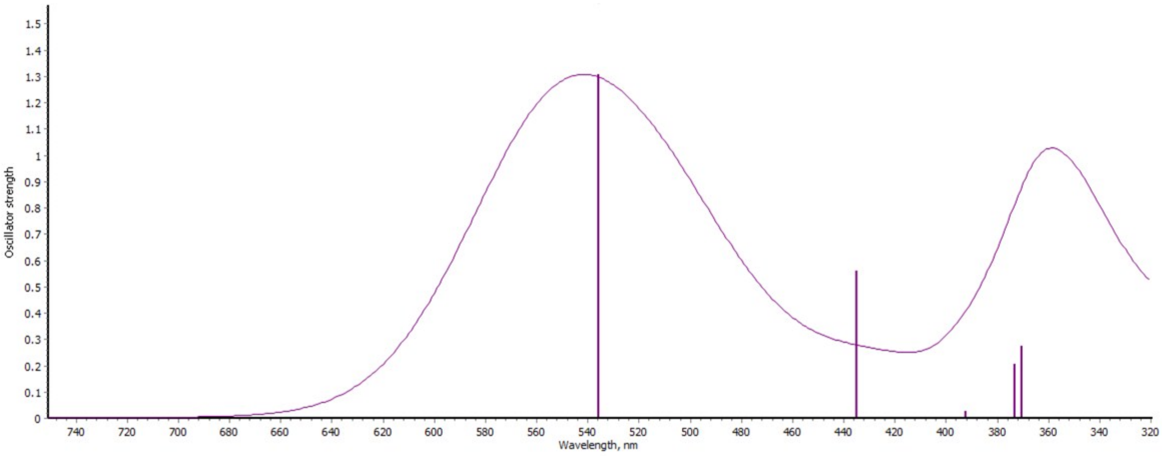


Figure S19- Computed optical transitions of BBTX in vacuum and the experimental spectrum of BBTX-P in DCM.

Tab. S3- Computed transition energies (λ_{max}), orbital contributions, associated oscillator strength and the calculated absorption molar extinction coefficient at λ_{max} (ε_{max}), in vacuum, for BBTX

Computed λ_{max}	**Orbitals contribution**	**Oscillator strength**	**Type of transition**
535.71 nm/ 2.3144 eV	HOMO -> LUMO (85.48 %)	1.3080	CT
434.89 nm/ 2.8509 eV	HOMO-2 -> LUMO (85.25%)	0.5597	CT
373.23 nm / 3.3219 eV	HOMO -> LUMO+1 (65.52 %) HOMO-> LUMO+2 (25.53 %)	0.2062	-The whole dye (65.52%) - TPA centered (25.53%)
370.54 nm/ 3.3461 eV	HOMO -> LUMO+1 (20.75 %) HOMO-> LUMO+2 (63.45 %)	0.2733	-The whole dye (20.75%) - TPA centered (63.45%)

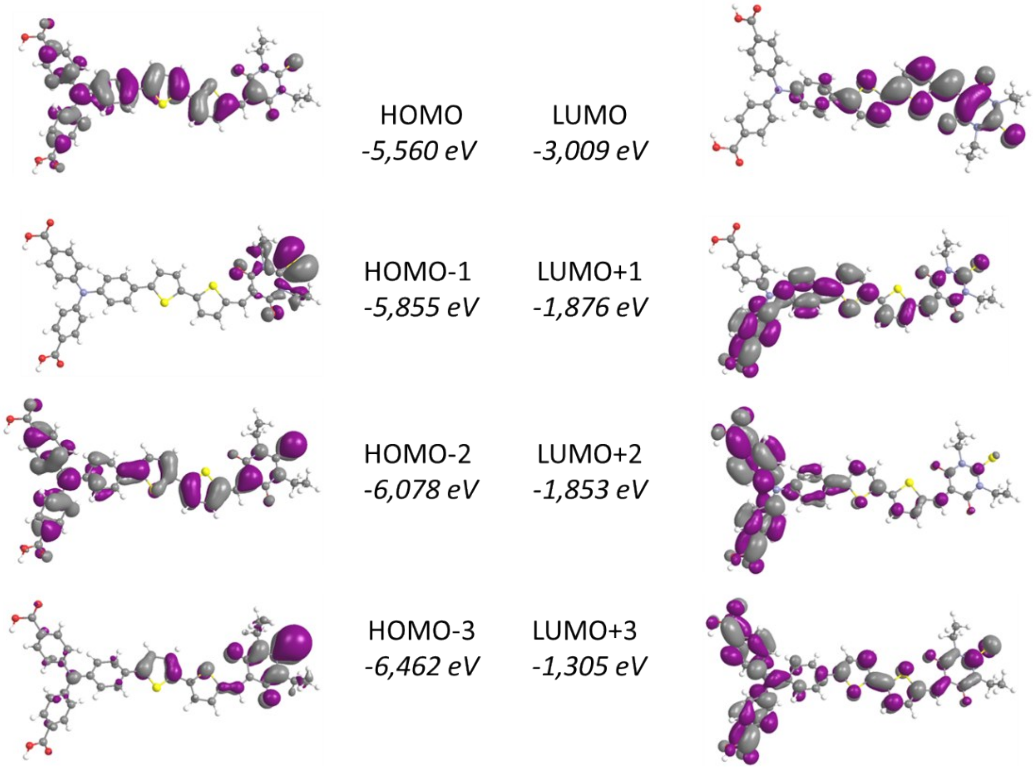


Figure S20- Computed orbitals and their energies for BBTX in vacuum. In purple, the positive lobes and in grey, the negative lobes

COCN

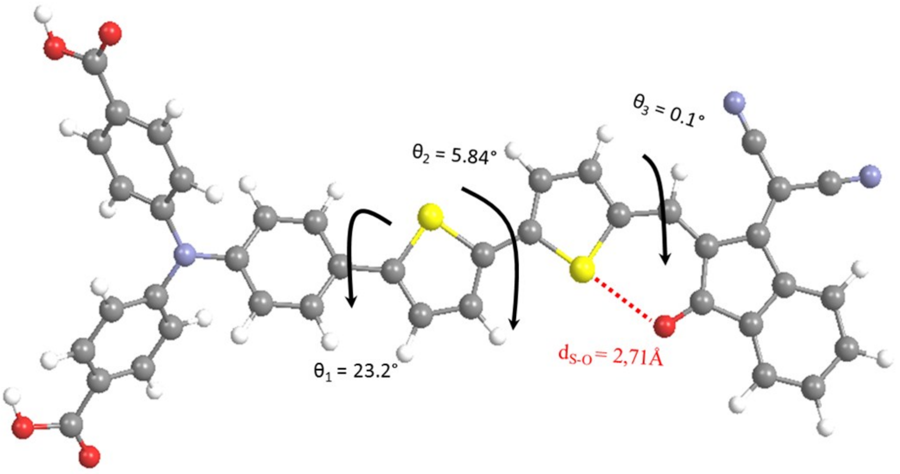


Figure S21- Optimized geometry for COCN in vacuum

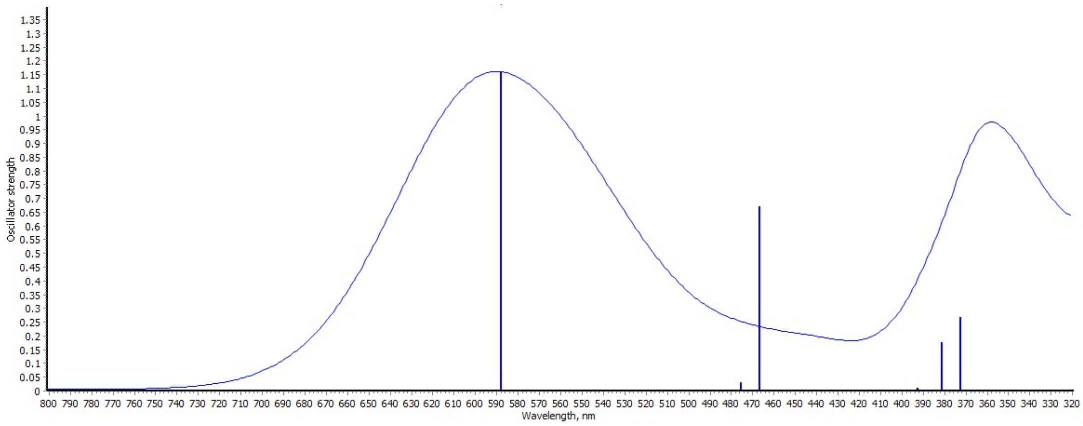


Figure S22- Computed optical transitions of COCN in vacuum and the experimental spectrum of COCN-P in DCM

Tab. S4- Computed transition energies (λ_{max}), orbital contributions, associated oscillator strength and the calculated absorption molar extinction coefficient at λ_{max} (ε_{max}), in vacuum, for COCN

Computed λ_{max}	**Orbitals contribution**	**Oscillator strength**	**Type of transition**
587.83 nm/ 2.1092 eV	HOMO -> LUMO (85.76 %)	1.1619	CT
466.72 nm/ 2.6565 eV	HOMO-1 -> LUMO (71.35%) HOMO->LUMO+1 (15.75%)	0.6709	CT
381.02 nm / 3.2540 eV	HOMO-2 -> LUMO (13.71 %) HOMO-> LUMO+2 (69.19 %)	0.1761	The whole dye
372.41 nm/ 3.3293 eV	HOMO-> LUMO+3 (89.49 %)	0.2658	TPA centered

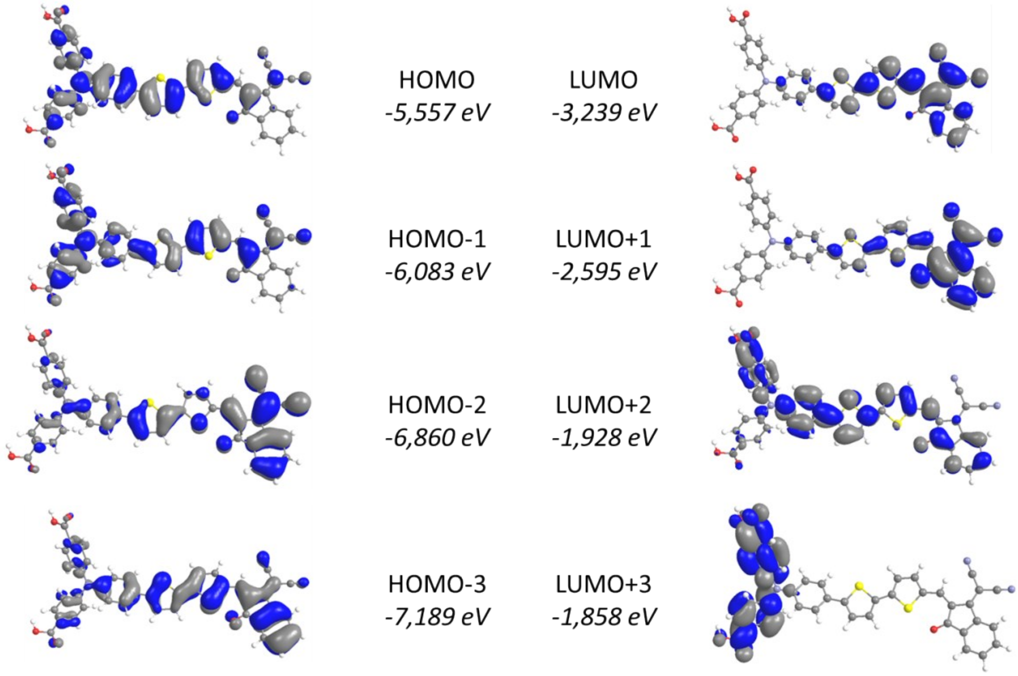


Figure S23- Computed orbitals for COCN in vacuum and their energy. In blue, the positive lobes, in grey, the negative lobes.

Solar cells

All the reagents were purchased from Aldrich and used without further purification. The water used was always deionized water (R = 18 MΩ.cm). The glass / FTO substrates were purchased from Xinyan Technology Ltd (e_{FTO} = 330 nm, ρ = 32 $\Omega.cm^{-1}$). A Dimatix DMP 2831 printer was employed in association with 10pL-16 nozzle cartridges. A Thermolyne 48 000 furnace was used as the muffle oven to perform high temperature treatments. A Novascan PSDP-UV6T UV/Ozone system was used to perform the desired UVO treatments.

NiO film formation by Inkjet printing (IJP)

The 850 nm NiO substrates were prepared according to a previously reported procedure which we recall below.[3]

Cleaning of the FTO substrates

The substrates were successively cleaned by the following media: DECON diluted in water, water, ethanol, acetone and finally isopropanol. The cleaning process was always the following: the substrates were sonicated in the desired cleaning medium at maximum power, at 60 °C for 10 minutes. A rinsing step with boiling water between each cleaning medium was also performed (three times each). After careful drying with nitrogen, the FTO substrates were transferred to the UVO cleaner, UVO treatment lasted 10 minutes.

Preparation of the polymer-templated nickel precursor sol-gel ink

Pluronic® F-127 (1 g) was mixed with water (2.19 g) and ethanol (4.85 g). When the polymer was totally dissolved, $NiCl_2,6H_2O$ (1.83 g) was added to the mixture. The green solution was diluted by one mass equivalent (*i.e.* 9.7 g) of water and aged at least 20 hours at room temperature in a sealed glass bottle, before being used.

Fabrication of mesoporous 4 layer-NiO films by IJP

The sol-gel ink was filtered (through a 200 µm PTFE filter) and transferred to the cartridge. Prior to printing, the substrate was always thermalized at the platen temperature (30°C) and before each layer deposition one "purge-spit-purge" cleaning cycle was performed. The printing parameters for the deposition of one layer of the sol-gel ink were the following: voltage applied to the piezoelectric actuator during printing set at 25 V; resolution (drop spacing) of 20 µm; platen temperature set at 30°C; nozzle-to-substrate distance of 650 µm; print-head temperature comprised between 21°C and 23°C (room temperature); Dimatix model fluid waveform; maximum jetting frequency of 3 kHz; relative humidity comprised between 35% and 45%; Four layer, 0.5 cm per 0.5 cm tinted area films were formed (cell area: 0.25 cm^2). The interlayer thermal treatment was the following: the film was dried at 30°C in the printer (1 min), then at 100°C during 3 min on a heating plate and at 450°C for 4 minutes in a preheated oven. It was finally sintered at 450°C in the oven during 30 min after the fourth layer had been deposited.

Sensitization of the NiO substrates

After the sintering step at 450°C, the substrates were cooled down and plunged still hot (60°C) into the dye solution. For all the dyes, 5.10^{-4} mol of compound per liter of solvent was employed. For **RBG-174 and BBTX**, the solvent was MeOH. For **COCO** and **COCN**, a solvent mixture was used: {1/1: DCM/MeOH}. The electrodes were kept immersed in this bath during 1 hour, in the dark, under slow orbital agitation. A picture of the sensitizing solutions is depicted on Figure S24. For the reference dye **P1**, we used a previously reported procedure to perform the sensitization.[4] The sensitized films were taken out of the bath, generously rinsed with ethanol and dried with a nitrogen flux. The as-built photocathodes were rapidly used for solar cell construction. Pictures of the obtained films are displayed on Figure S25.

Figure S24- The dye solutions that were employed for the sensitization of NiO electrodes – From left to right: COCO, RBG-174, BBTX, COCN

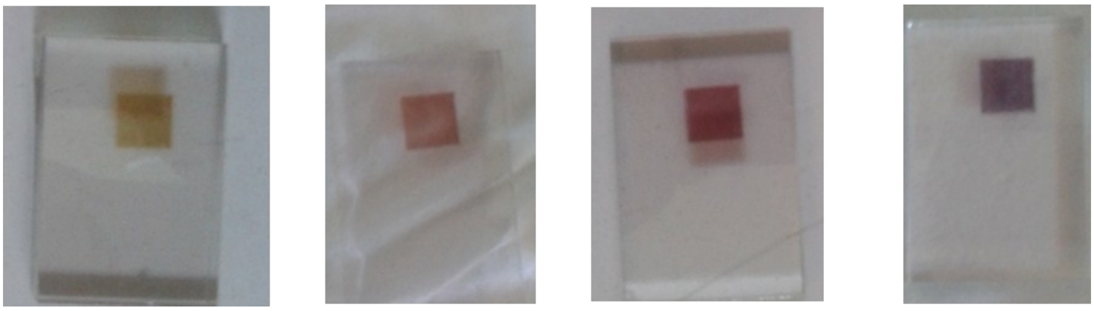


Figure S25- 850 nm NiO films, after sensitization with, from left to right: RBG-174, COCO, BBTX and COCN

Preparation of the iodine-based electrolyte

The electrolyte ([I_2] = 0.1M, [LiI] = 1M in ACN) was prepared in an oxygen and water free glove box. Dry acetonitrile (50 mL) was poured onto LiI (6.70 g, 50 mmol). Then iodine (1.27 g, 5 mmol) was added and the mixture was stirred until no solid could be distinguished.

Solar cell fabrication

The pre-drilled platinum counter electrodes (Solaronix) were sintered at 450°C for one hour. After being flushed with nitrogen, the NiO photocathodes and the Pt anodes were sealed together at 110°C with 60 µm meltonix sealer (Solaronix, 1170-60). In a nitrogen and water free glove box, the electrolyte was infiltrated between the two electrodes, with a "Vac'n'Fill" syringe (Solaronix) and the filling hole was sealed with Meltonix and a glass cap. MBR electronics USS-9210 Ultrasonic Soldering System was used to solder conducting wires, with Cerasolzer alloy, to the electrodes of the DSSC.

Photovoltaic measurements

The current-voltage characteristics of the p-DSSCs were measured under illumination using a Keithley 2635 source-measure unit and a home-made acquisition program. The light source was a AM1.5 SolarCellTest 575 from ATLAS MTT, equipped with a metal halogen lamp, 100mW.cm^{-2}. The same measurement was carried out in the dark. The step was 2 mV, from negative to positive bias, with a settling time of 250 ms. Measurement under light was performed first, then, the dark measurement was done. All the measurements were done on a series of three cells at minimum and performance was averaged on this basis.

Dark-current trace

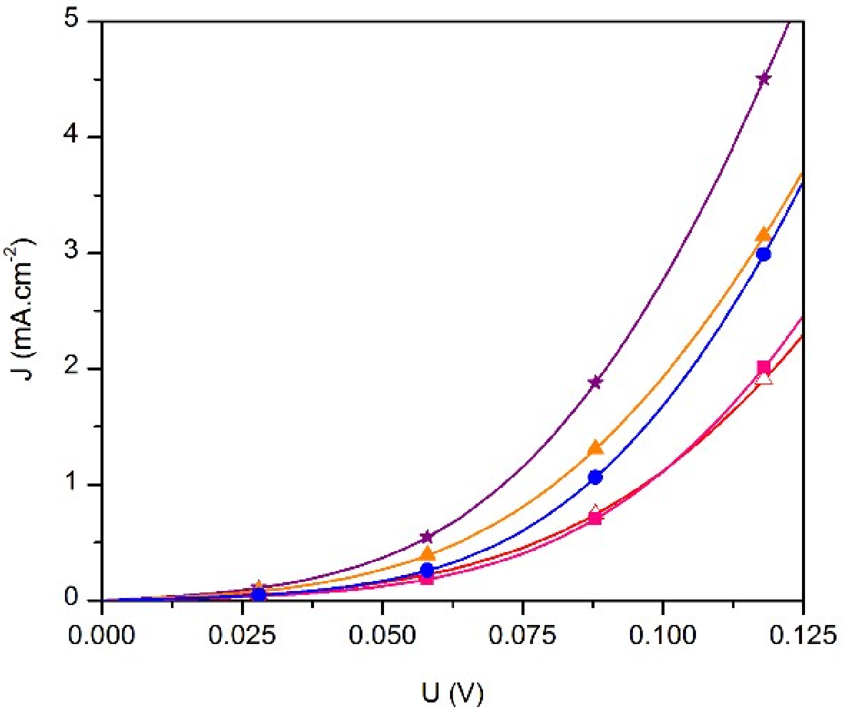


Figure S26- Example of dark current trace of the solar cells presented in this work – RBG-174: orange, filled-triangles; COCO: pink, squares, BBTX: purple, stars; COCN: blue, circles; P1: red, empty triangles

References

1 M. Weidelener, A. Mishra, A. Nattestad, S. Powar, A. J. Mozer, E. Mena-Osteritz, Y.-B. Cheng, U. Bach and P. Bäuerle, *J. Mater. Chem.*, 2012, **22**, 7366–7379.

2 J. Cremer, PhD thesis, 2005, Novel hail to tail coupled oligo(3-hexylthiophene) derivatives for photovoltaic applications.

3 R. Brisse, R. Faddoul, T. Bourgeteau, D. Tondelier, J. Leroy, S. Campidelli, T. Berthelot, B. Geffroy and B. Jousselme, *ACS Appl. Mater. Interfaces*, 2017, **9**, 2369–2377.

4 L. Li, E. A. Gibson, P. Qin, G. Boschloo, M. Gorlov, A. Hagfeldt and L. Sun, *Adv. Mater.*, 2010, **22**, 1759–1762.