Supporting information for

Synthesis and Characterization of the Ground and Excited States of Tripodal-like Oligothienyl-imidazoles

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Synthesis and Characterization

Materials and Instrumentation: All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh). IR spectra were determined on a BOMEM MB 104 spectrophotometer. NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR using the solvent peak as internal reference at 25 ºC. All chemical shifts are given in ppm using δ_H Me_4Si = 0 ppm as reference and *J* values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. Mass spectrometry analyses were performed at the "C.A.C.T.I. - Unidad de Espectrometria de Masas", at the University of Vigo, Spain. Thermogravimetric analysis of samples was carried out using a TGA instrument model Q500 from TA Instruments, under high purity nitrogen supplied at a constant 50 mL min^{-1} flow rate. All samples were subjected to a 20 ºC min^{-1} heating rate and were characterized between 25 and 800 ºC. 2-Formylthiophene **1a**, 5-formyl-2,2'-bithiophene **1b** and di-2-thienylethanedione were commercially available and the synthesis of 5-formyl-5'-ethoxy-bithiophene **1c**,[33] 5-formyl-2,2':5'2''-terthiophene **1d**,[34] 5,5'-diformyl-2,2'-bithiophene **1e**[29] and 2-formyl-5-(4'-formylphenyl)-thiophene **2**[35] were described elsewhere. All reagents were used as received.

General procedure for the synthesis of 2,4,5-tri(2-thienyl)-imidazoles 3-5

A mixture of (di)formylated (oligo)thiophene **1a-e** or diformylated arylthiophene **2** (1 mmol), NH_4OAc (20 mmol) and di-2-thienylethanedione (1 mmol) in glacial acetic acid (20 mL) was stirred and heated at reflux for 15h. The mixture was then cooled to room temperature and the product precipitated during neutralization with NH_4OH 5 M. The precipitate was filtrated, washed with water and diethyl ether, recrystalized from dichloromethane and dried at 50 ºC in *vacuo* to give the pure product.

2,4,5-Tri(2'-thienyl)imidazole (3a): light yellow solid (80 mg; 84%). Mp = 270.1-272.4 °C (lit.[32] 248-249 ºC). UV (EtOH): λ_{max} nm (ε/M^{-1} cm^{-1}) 322.0 (27910). IR (KBr disc), ν (cm^{-1}): 3400, 3070, 2813, 2755, 1601, 1505, 1417, 1384, 1332, 1252, 1211, 1103, 1076, 1042, 1005, 932, 906, 841, 691. ^{1}H NMR (300 MHz, DMSO-d_6 and a drop of TFA) [δ (ppm)]: 7.09-7.13 (m, 2H, 2 x 4''-H), 7.14-7.17 (m, 1H, 4'-H), 7.30 (d, 2H, J = 3.3 Hz, 2 x 3''-H), 7.56 (d, 2H, J = 4.2 Hz, 2 x 5''-H), 7.61 (dd, 1H, J = 4.9 and 0.9 Hz, 5'-H), 7.70 (dd, 1H, J = 3.6 and 0.9 Hz, 3'-H), 12.95 (s, 1H, N*H*). ^{13}C NMR (75.4 MHz, DMSO-d_6 and a drop of TFA) [δ (ppm)]: 125.28 (C3'), 126.25 (2 x C3" + C4), 126.50 (2 x C5"), 127.23 (C5'), 127.53 (2 x C4"), 128.07 (C4'), 132.53 (C2'), 133.29 (2 x C2" + C5), 141.61 (C2). MS (FAB), *m/z* (%): 315 ([M+H]$^+$, 100), 314 (M^+, 74), 307 (28), 289 (13), 282 (12), 155 (21), 154 (68). HRMS: *m/z* (FAB) calcd for $C_{15}H_{11}N_2S_3$ 315.0084, found 315.0082.

4,5-Bi(2'-thienyl)-2-(2''-bithienyl)imidazole (3b): light green solid (87 mg; 90%). Mp = 279.0-282.0 °C. UV (EtOH): λ_{max} nm (ε/M^{-1} cm^{-1}) 367.0 (27330). IR (KBr disc), ν (cm^{-1}): 3430, 3095, 3067, 2824, 1659, 1601, 1502, 1420, 1347, 1209, 1102, 1080, 1043, 1006, 932, 843, 807, 691. ^{1}H NMR (400 MHz, DMSO-d_6) [δ (ppm)]: 7.08-7.13 (m, 3H,

4’’-H + 2 x 4’’’-H), 7.27-7.31 (m, 3H, 3’-H + 2 x 3’’’-H), 7.39 (dd, 1H, *J* = 3.9 and 0.9 Hz, 3’’-H), 7.51 (m, 3H, 5’’-H + 2 x 5’’’-H), 7.60 (d, 1H, *J* = 3.9 Hz, 4’-H), 12.99 (s, 1H, N*H*). ^{13}C NMR (100 MHz, DMSO-d_6) [δ (ppm)]: 123.74 (C4), 124.48 (C3”), 124.59 (C3’ + 2 x C3’’’), 125.49 (C4’), 125.83 (C5’’ + 2 x C5’’’), 127.50 (2 x C4’’’), 128.47 (C4’’), 131.68 (C2’), 133.20 (C5), 136.12 (C2’’), 136.68 (C5’ and C2’’’), 141.23 (C2). MS (FAB), *m/z* (%): 397 ([M+H]$^+$, 100), 396 (M$^+$, 87), 307 (30), 289 (12), 155 (24), 154 (77). HRMS: *m/z* (FAB) calcd for $C_{19}H_{13}N_2S_4$ 396.9962, found 396.9969.

4,5-Bi(2’-thienyl)-2-(5’’’-ethoxy-2’’-bithienyl)imidazole (3c): green solid (80 mg; 89%). Mp = 258.2-259.3 °C. UV (EtOH): λ_{max} nm (ε/M^{-1} cm^{-1}) 378.0 (9970). IR (KBr disc), ν (cm^{-1}): 3410, 3074, 2974, 1604, 1557, 1510, 1468, 1434, 1409, 1389, 1300, 1244, 1208, 1098, 1040, 932, 844, 765, 699. ^{1}H NMR (300 MHz, DMSO-d_6) [δ (ppm)]: 1.34 (t, 3H, *J* = 7.2 Hz, OCH_2CH_3), 4.14 (q, 2H, *J* = 6.9 Hz, OCH_2CH_3), 6.30 (d, 1H, *J* = 3.9 Hz, 4’’-H), 6.97-7.01 (m, 1H, 4’’’-H_a), 7.03 (d, 1H, *J* = 3.9 Hz, 3’’-H), 7.10 (d, 1H, *J* = 3.9 Hz, 3’-H), 7.15 (d, 1H, *J* = 3.6 Hz, 5’’’-H_a), 7.19-7.22 (m, 1H, 4’’’-H_b), 7.39-7.43 (m, 2H, 3’’’-H_{a+b}), 7.54 (d, 1H, *J* = 3.9 Hz, 4’-H), 7.69 (d, 1H, *J* = 4.8 Hz, 5’’’-H_b), 12.97 (s, 1H, N*H*). ^{13}C NMR (75.4 MHz, DMSO-d_6) [δ (ppm)]: 14.46 (OCH_2CH_3), 69.32 (OCH_2CH_3), 105.93 (C4”), 120.50 (C4), 122.22 (C2”), 122.54 (C3’’), 122.88 (C3’), 123.58 (C5’’’$_a$), 125.02 (C3’’’$_a$), 125.41 (C4’), 127.35 (C4’’’$_a$), 127.53 (C5’’’$_b$), 127.66 (C4’’’$_b$), 128.44 (C3’’’$_b$), 130.36 (C2’), 130.47 (C2’’’$_a$), 133.32 (C5), 136.90 (C2’’’$_b$), 137.44 (C5’), 141.35 (C2), 164.07 (C5”). MS (FAB), *m/z* (%): 441 ([M+H]$^+$, 97), 440 (M$^+$, 100), 411 (29), 307 (22), 155 (24), 154 (79). HRMS: *m/z* (FAB) calcd for $C_{21}H_{17}N_2OS_4$ 441.0224, found 441.0200.

4,5-Bi(2'-thienyl)-2-(5''-terthienyl)imidazole (3d): dark green solid (61 mg; 67%). Mp = 298.0-301.0 °C. UV (EtOH): λ_{max} nm (ε/M^{-1} cm^{-1}) 400.0 (10285). IR (nujol), ν (cm^{-1}): 2969, 1465, 1377, 1212, 1104, 1042, 934, 844, 787, 701. ^{1}H NMR (300 MHz, DMSO-d_6) [δ (ppm)]: 6.97-700 (m, 1H, 4'''-H), 7.07-7.10 (m, 1H, Ar-H), 7.16 (dd, 1H, J = 3.5 and 1.2 Hz, Ar-H), 7.19-7.23 (m, 1H, Ar-H), 7.27-7.30 (m, 2H, 2 x Ar-H), 7.38-7.39 (m, 2H, 2 x Ar-H), 7.40-7.45 (m, 2H, 2 x Ar-H), 7.52-7.55 (m, 1H, Ar-H), 7.60 (d, 1H, J = 3.9 Hz, Ar-H), 7.65 (dd, 1H, J = 5.2 and 1.2 Hz, Ar-H), 13.06 (s, 1H, N*H*). ^{13}C NMR (75.4 MHz, DMSO-d_6) [δ (ppm)]: 123.63, 124.21, 124.64, 124.80, 124.86, 125.49, 125.61, 126.05, 127.21, 127.35, 127.52, 128.31, 130.47, 131.96, 133.46, 134.71, 135.73, 136.83, 141.14. MS (FAB), *m/z* (%): 479 ($[M+H]^+$, 9), 478 ($[M]^+$, 9), 307 (43), 289 (18), 282 (12), 155 (33), 154 (100). HRMS: *m/z* (FAB) calcd for $C_{23}H_{15}N_2S_5$ 478.9839, found 478.9816.

2-(2',2''-bithienyl)-*bis*[4,5-di(2'-thienyl)imidazole] (4): dark yellow solid (60 mg; 71%). Decomposition at T > 320ºC. UV (EtOH): λ_{max} nm (ε/M^{-1} cm^{-1}) 407.0 (5360). IR (KBr disc), ν (cm^{-1}): 3429, 3078, 2828, 1641, 1600, 1502, 1412, 1387, 1349, 1211, 1080, 1046, 1004, 936, 906, 845, 803, 695. ^{1}H NMR (300 MHz, DMSO-d_6) [δ (ppm)]: 7.00-703 (m, 2H, 2 x 4''-H_a), 7.16 (dd, J = 3.6 and 0.6 Hz, 2H, 2 x 5''-H_a), 7.21-7.24 (m, 2H, 2 x 4''-H_b), 7.41-7.45 (m, 6H, 2 x 3"-H_a + 2 x 3"-H_b + 2 x 3'-H), 7.63 (d, 2H, J = 3.9 Hz, 2 x 4'-H), 7.71 (dd, 2H, J = 4.5 and 0.6 Hz, 2 x 5''-H_b), 13.07 (s, 2H, 2 x N*H*). ^{13}C NMR (75.4 MHz, DMSO-d_6) [δ (ppm)]: 120.79 (2 x C4), 123.70 (2 x C5"$_a$), 125.12 (2 x C3"$_a$), 125.21 (2 x C3''$_b$), 125.64 (2 x C4'), 127.39 (2 x C4"$_a$), 127.67 (2 x C5"$_b$), 127.71 (2 x C4"$_b$), 128.59 (2 x C3'), 130.38 (2 x C2"$_b$), 132.10 (2 x C2'), 133.53 (2 x C5), 136.29 (2 x C5'), 136.80 (2 x C2"$_a$), 141.16 (2 x C2). MS (FAB), *m/z* (%): 627

([M+H]$^+$, 9), 460 (8), 308 (12), 307 (45), 289 (18), 155 (32), 154 (100). HRMS: *m/z* (FAB) calcd for $C_{30}H_{19}N_4S_6$ 626.9934, found 626.9935.

2-(4''-aryl-2''-thienyl)- bis[4,5-di(2'-thienyl)imidazole] (5): green solid (74 mg; 77%). Mp = 201.6-203.4 °C. UV (EtOH): λ_{max} nm (ε/M^{-1} cm^{-1}) 385.0 (7960). IR (KBr disc), ν (cm^{-1}): 3380, 3078, 1704, 1643, 1499, 1405, 1349, 1232, 1045, 842, 725, 695. ^{1}H NMR (400 MHz, DMSO-d_6) [δ (ppm)]: 7.00-7.03 (m, 2H, 2 x Ar-H), 7.17-7.19 (m, 2H, 2 x Ar-H), 7.21-7.23 (m, 2H, 2 x Ar-H), 7.42-7.44 (m, 4H, 4 x Ar-H), 7.64 (d, 1H, *J* = 3.9 Hz, 3'-H), 7.69-7.73 (m, 3H, 4'-H + 2 x Ar-H), 7.85 (d, 2H, *J* = 8.4 Hz, 2'-H + 6'-H), 8.10 (d, 2H, *J* = 8.4 Hz, 3'-H + 5'-H), 12.95 (s, 1H, N*H*), 13.05 (s, 1H, N*H*). ^{13}C NMR (75.4 MHz, DMSO-d_6) [δ (ppm)]: 120.62, 121.02, 123.53, 123.57, 124.84, 124.95, 125.04, 125.57, 125.84, 125.92, 127.35, 127.48, 127.68, 128.50, 128.54, 128.67, 128.79, 128.86, 130.44, 130.67, 131.41, 131.51, 132.00, 132.02, 132.19, 132.57, 133.29, 133.50, 133.83, 141.42, 142.87, 145.20. MS (FAB), *m/z* (%): 621 ([M+H]$^+$, 12), 620 ([M]$^+$, 8), 460 (7), 308 (11), 307 (41), 289 (18), 282 (29), 155 (32), 154 (100). HRMS: *m/z* (FAB) calcd for $C_{32}H_{21}N_4S_5$ 621.0370, found 621.0359.