Spectral and Photophysical Characterization of Donor-π -Acceptor Arylthienyl- and Bithienyl-Benzothiazole Derivatives in Solution and Solid State

Supplementary Information

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Synthesis and Characterization

General. All reagents were obtained from Sigma-Aldrich Co. and used as received. All the solvents used were of spectroscopic or equivalent grade. For the absorption and emission experiments in ethanol, the concentrations of the solutions ranged from 1×10^{-5} to 10^{-6} M. Thin layer chromatography was carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$). All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 25 °C in $CDCl_3$ or DMSO-d_6 on a Varian 300 Unity Plus spectrometer at 300 MHz; chemical shifts are given in δ (ppm) using TMS as standard and *J*-values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicity and *J*-values.^{13}C NMR spectra were recorded with the same instrument at 75.4 MHz and using the solvent peak as internal reference; assignments were carried out by the DEPT 135, HMQC and HMBC techniques. IR spectra were run on a FTIR Perkin-Elmer 1600 spectrophotometer. Elemental analyses were carried out on a Leco CHNS 932 instrument. Mass spectrometry analyses were performed at the C.A.C.T.I. -Unidad de Espectrometria de Masas of the University of Vigo, Spain.

The Suzuki coupling was carried out under an argon atmosphere.

Synthesis. The preparation of derivatives T1,[1] T2[2] and benzothiazoles BzT1a-b[2] and BZT2b[3] were recently described. For bithienyl-benzothiazoles BzT2a and BzT2c, which have also been communicated in the literature,[3] more details of its synthesis are given here.

General procedure for the synthesis of BzT2a and BzT2c. The corresponding formyl-bithiophenes[4] (1.0 eq) and *o*-aminobenzenethiol (1.1 eq) were heated in DMSO (0.5 ml/ mmol) at 120 ºC with stirring for 30-60 min. The reaction was followed by TLC using chloroform/ hexane 1:1 as eluent. When the reaction was complete, the reaction mixture was allowed to cool and poured into water and extracted with ethyl acetate (3 × 30 ml/ mmol). The organic layer was dried with magnesium sulphate and evaporated under vacuum. The crude residue was submitted to silica gel column chromatography using mixtures of hexane and chloroform of increasing polarity. The fractions containing the purified product were collected and evaporated under vacuum.

2-(2’,2’’-Bithienyl)-1,3-benzothiazole (BzT2a). Yellow solid (92%). Mp 169.9-171.2 ºC. ^{1}H NMR ($CDCl_3$) δ 7.06 (t_{ap}, J = 4.0 Hz, 1H, 4’’-H), 7.17 (d, J = 4 Hz, 1H, 3’-H), 7.28-7.31 (m, 2H, 3’’ and 5’’-H), 7.38 (dt, J = 7.0, 1.2 Hz, 1H, 6-H), 7.48 (dt, J = 7.0, 1.2 Hz, 1H, 5-H), 7.53 (d, J = 4 Hz, 1H, 4’-H), 7.84 (dd, J = 7.0, 1.2 Hz, 1H, 7-H), 8.03 (dd, J = 7.0, 1.2 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$) δ 121.39 (C7), 122.83 (C4), 124.18 (C3’), 124.79 (C3’’), 125.17 (C6), 125.60 (C5’’), 126.44 (C5), 128.10 (C4’’), 129.20 (C4’), 134.60 (C7a), 135.41 (C5’), 136.51 (C2’’), 141.17 (C2’), 153.63 (C3a), 160.90 (C2). IR (KBr disc) ν 1587, 1518, 1478, 1445, 1308, 1256, 1122, 1037, 911, 803, 758, 699 cm^{-1}. Anal. Calcd for $C_{15}H_9NS_3$: C, 60.17; H, 3.03; N, 4.67; S, 32.12. Found: C, 60.16; H, 3.10; N, 4.70; S, 31.68.

2-(5’’-Ethoxy-2’,2’’-bithienyl)-1,3-benzothiazole (BzT2c). Yellow solid (94%). Mp 128.0-130.0 ºC. ^{1}H NMR ($CDCl_3$) δ 1.46 (t, J = 7.2 Hz, 3H, CH_3), 4.15 (q, J = 7.2 Hz, 2H, CH_2), 6.17 (d, J = 4.2 Hz, 1H, 4’’-H), 6.96 (d, J = 4.2 Hz, 1H, 3’’-H), 7.00 (d, J = 4.2 Hz, 1H, 3’-H), 7.38 (dt, J = 8.1, 1.2 Hz, 1H, 6-H), 7.48 (dt, J = 8.1, 1.2 Hz, 1H, 5-H), 7.51 (d, J = 4.2 Hz, 1H, 4’-H), 7.85 (dd, J = 8.1, 1.2 Hz, 1H, 7-H), 8.01 (dd, J = 8.1, 1.2 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$) δ 14.65 (CH_3), 69.50 (CH_2), 105.58 (C4’’), 121.34 (C7), 122.39 (C3’), 122.71 (C3’’), 122.82 (C4), 125.00 (C6), 126.36 (C5), 129.27 (C4’), 133.88 (C2’’), 134.50 (C7a), 142.17 (C2'), 153.63 (C3a), 161.03 (C5' and C2), 165.62 (C5''). IR (KBr disc) ν 3065, 1491, 1443, 1388, 1307, 1260, 1239, 1050, 911, 785, 753, 729 cm^{-1}. MS (EI) *m/z* (%): 343 (M$^+$, 33), 314 (100). HRMS: *m/z* (EI) calcd for $C_{17}H_{13}NOS_3$ 343.0159, found 343.0163.

Bithienyl-benzothiazole (BzT2d) was prepared by treatment of *ortho*-aminobenzenethiol with 5-formyl-(3,4-ethylenodioxy)-2,2'-bithiophene using the same experimental procedure described above. This in turn was synthesized by Suzuki coupling between 2-formyl-3,4-ethylenodioxy-5-bromo-thiophene with 2-thienyl boronic acid. 1-Formyl-3,4-ethylenodioxy-5-bromo-thiophene was obtained from 1-formyl-3,4-ethylenodioxythiophene[5] by bromination with NBS in DMF in 68 % yield.

2-Formyl-3,4-ethylenodioxy-5-bromo-thiophene. To a stirred solution of 2-formyl-3,4-ethylenodioxythiophene (0.1 g, 0.58 mmol) in DMF (1 mL) was added NBS (0.1 g, 0.58 mmol) in small portions at rt. The mixture was shielded from light and stirred during 4 h at -20 °C. After this time the mixture was added to ice. The yellow solid formed was filtered and washed several times with water. Recristalization of this solid from ethanol gave the pure compound as a yellow solid (68%). Mp 141.0-142.0 °C. ^{1}H NMR ($CDCl_3$) δ 4.34-4.41 (m, 4H, 2 × C*H*$_2$), 9.84 (s, 1H, C*H*O). IR (nujol) ν 1644 cm^{-1}. Anal. Calcd for $C_7H_5BrO_3S$: C, 33.72; H, 2.01; S, 12.84. Found: C, 33.84; H, 2.14; S, 12.81.

5-Formyl-(3,4-ethylenodioxy)-2,2'-bithiophene. 2-Formyl-3,4-ethylenodioxy-5-bromo-thiophene (1.2 mmol) were coupled with the 2-thienyl boronic acid (1.6 mmol), in a mixture of DME (15 ml) and aqueous 2M Na_2CO_3 (1 ml) and $Pd(PPh_3)_4$ (6 mol %) at 80 ºC under a argon atmosphere. The reaction where followed by TLC which determined the reaction time. After cooling the mixture was filtered. Ethyl acetate and a saturated solution of NaCl were added and the phases were separated. The organic phase was washed with water (3 x 50 ml) and with a solution of NaOH (10%). The organic phase obtained was dried ($MgSO_4$), filtered and solvent removal gave the crude mixture which was submitted to column chromatography affording the coupled product as a light brown solid (85%). Mp 143.2-144.4 ºC. ^{1}H NMR ($CDCl_3$) δ 4.42 (s, 4H, 2 × C*H*$_2$), 7.05-7.09 (m, 1H, 4'-H), 7.38 (dd, *J* = 4.8, 0.9 Hz, 1H, 5'-H), 7.44 (dd, *J* = 3.6, 0.9 Hz, 1H, 3'-H), 9.91 (s, 1H, C*H*O). ^{13}C NMR ($CDCl_3$) δ 64.73 (CH_2), 65.24 (CH_2), 114.71 (C5), 123.27 (C2), 125.81 (C3'), 126.87 (C5'), 127.50 (C4'), 133.35 (C2'), 136.75 (C3 or C4), 148.59 (C3 or C4), 179.36 (*C*HO). IR (KBr disc) ν

1631 cm^{-1}. MS (EI) *m/z* (%): 252 (M$^+$, 100). HRMS: *m/z* (EI) calcd for $C_{11}H_8O_3S_2$ 251.9915, found 251.9904.

2-(3',4'-Ethylenodioxy-2',2''-bithienyl)-1,3-benzothiazole (BzT2d). Yellow solid (84%). Mp 208.7-209.8 ºC. ^{1}H NMR ($CDCl_3$) δ 4.43-4.45 (m, 2H, C*H*$_2$), 4.48-4.51 (m, 2H, C*H*$_2$), 7.09 (m, 1H, 4''-H), 7.30 (dd, *J* = 4.7, 1.2 Hz, 1H, 5''-H), 7.32 (dt, *J* = 7.8, 1.2 Hz, 1H, 6-H), 7.38 (dd, *J* = 3.6, 1.2 Hz, 1H, 3''-H), 7.46 (dt, *J* = 7.8, 1.2 Hz, 1H, 5-H), 7.85 (dd, *J* = 7.8, 1.2 Hz, 1H, 7-H), 8.01 (dd, *J* = 7.8, 1.2 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$) δ 64.82 (CH_2), 65.43 (CH_2), 109.20 (C5'), 115.91 (C2'), 121.21 (C7), 122.26 (C4), 124.27 (C3''), 124.33 (C6), 125.32 (C5''), 126.19 (C5), 127.35 (C4''), 133.83 (C2''), 134.91 (C7a), 136.97 (C4' or C3'), 142.16 (C4' or C3'), 152.40 (C3a), 157.94 (C2). IR (KBr disc) ν 2999, 1447, 1350, 1085 cm^{-1}. MS (EI) *m/z* (%): 357 (M$^+$, 100). HRMS: *m/z* (EI) calcd for $C_{17}H_{11}NO_2S_3$ 356.9952, found 356.9964.

Spectral and Photophysical determinations

Singlet ground-state molar extinction determinations

The molar extinction coefficients (ε) were obtained at absorption maxima from the slope of the plot of the absorption *vs.* the concentration using seven solutions of different concentrations (correlation coefficients ≥0.999).

Triplet-triplet molar extinction and S_1~~→T_1 intersystem crossing yields determinations

The triplet molar absorption coefficients were obtained by the singlet depletion and energy transfer methods. In the cases where the singlet depletion method was applied the triplet molar absorption coefficients were determined according to the well-known relationship:[6]

$$\varepsilon_T = \frac{\varepsilon_S \times \Delta OD_T}{\Delta OD_S} \qquad (1)$$

where both ΔOD_S and ΔOD_T are obtained from the triplet-singlet difference transient absorption spectra. In the case of the energy transfer method[7], the triplet molar absorption coefficients were determined using anthracene (10^{-3} mol dm^{-3}), ε_T= 45500 M^{-1} cm^{-1} (430 nm)[8] or benzophenone (10^{-2} mol dm^{-3}), ε_T= 7220 M^{-1} cm^{-1} (530 nm)[8], as triplet energy donors. Concentrations of 10^{-5} mol dm^{-3} were used for the compounds that were further dissolved in methylcyclohexane solutions of anthracene or benzophenone. All solutions were degassed with argon for ≈20 minutes and sealed. The molar triplet-triplet molar absorption coefficients were then determined from equation (2):[7]

$$\frac{\varepsilon_{TT}^{D}}{\varepsilon_{TT}^{A}} = \frac{\Delta OD^{D}}{\Delta OD^{A}} \qquad (2)$$

where ε_{TT}^{D} and ε_{TT}^{A} stand for the triplet molar absorption coefficients of donor and acceptor respectively; ΔOD^D is the maximum absorbance from the transient triplet-triplet absorption spectra of the donor in the absence of acceptor; ΔOD^A is the maximum absorbance of the acceptor triplet when both the donor and acceptor are present. For the determination of ΔOD^A value, additional corrections had to be taken into account when the acceptor decay rate constant (k_3) is not negligible. For this situation, equation 3 was applied,[7]

$$\Delta OD_{obs}^{A} = \Delta OD^{A} \exp\left[-\frac{\ln k_2/k_3}{k_2/k_3 - 1} \right] \qquad (3)$$

where k_2 is the donor decay rate constant in the presence of acceptor and ΔOD_{obs}^{A} is taken from the ΔOD maximum observed in the triplet-singlet difference spectra of the acceptor in the presence of the donor.

The intersystem crossing yields for the compounds (ϕ_T^{cp}) were obtained by comparison between the ΔOD at 525 nm of benzene solutions (optically matched at the laser excitation wavelength) of benzophenone (standard) and of the compound using equation:[9,10]

$$\phi_T^{cp} = \frac{\varepsilon_{TT}^{Benzophenone}}{\varepsilon_{TT}^{cp}} \cdot \frac{\Delta OD_{\max}^{cp}}{\Delta OD_{\max}^{Benzoph.}} \cdot \phi_T^{Benzophenone} \qquad (4)$$

Singlet Oxygen Yield determinations

Room-temperature singlet oxygen phosphorescence was detected at 1270 nm using a Hamamatsu R5509-42 photomultiplier, cooled to 193 K in a liquid nitrogen chamber (Products for Research model PC176TSCE-005), following laser excitation of aerated solutions at 355 nm (OD@355 nm = 0.20), with an adapted Applied Photophysics flash kinetic spectrometer. The modification of the spectrometer involved the interposition of a Schott RG665 filter. A 600-line diffraction grating was used instead of the standard spectrometer one to extend spectral response to the infrared. The filter employed is essential to eliminate from the infrared signal all the first harmonic contributions from the sensitizer emission in the 500–800 nm region. 1*H*-Phenalen-1-one (perinaphthenone) in ethanol (ϕ_Δ= 0.97) was used as standard.[11]

Fluorescence Quantum yields Determinations in Thin films

The fluorescence emission spectra of the thin films were obtained with a Horiba-Jobin-Yvon integrating sphere. The solid-state photoluminescence quantum yields in thin films were obtained with this integrating sphere, using the method outlined by de Mello et al.[12] and applied by Palsson and Monkman[13] to polypyridine films using a set-up similar to ours. The following equation was used to determine the fluorescence quantum yields, eq. 5,

$$\phi_F(solid) = \frac{\int^{Sample} I(\lambda)d\lambda}{\left(\int^{R\_alone} I(\lambda)d\lambda - \int^{R\_in\_sample} I(\lambda)d\lambda\right)\cdot 10^{\Delta OD(\lambda_{exc})}} \qquad (5)$$

where ϕ_F (solid) is the fluorescence quantum yield for the compounds in a thin-film, $\int^{sample} I(\lambda)d\lambda$ is the integrated area under the emission of the compound in the thin-film (which excludes the integration of Rayleigh peak), $\int^{R\_alone} I(\lambda)d\lambda$ is the integrated area under the Rayleigh peak of a sample containing only the sapphire support, and $\int^{R\_in\_sample} I(\lambda)d\lambda$ is the integrated area under the Rayleigh peak in the emission spectra of the compound in the thin-film. Since in practice the emission from the sample is much weaker than the scattered excitation light, i.e., the Rayleigh peak, the spectra are recorded with a filter that attenuates the emission intensity at the excitation wavelength. This is considered in eq. 5 with $10^{\Delta OD(\lambda exc)}$, that is, the value for the filter transmittance at the excitation wavelength.

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