Novel Heterocycle-Based Two-Photon Absorbing Dyes

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Supporting Information

Experimental

^1H and ^{13}C NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 500 and 125.70 MHz, respectively. The spectral parameters and calibrations have been previously reported.¹ Coupling constants are presented in Hertz. Anhydrous *N,N*-dimethylformamide (DMF) was supplied by Fluka and stored over molecular sieves. Anhydrous acetonitrile was supplied by Aldrich and stored under nitrogen. Melting points are uncorrected.

1-(*N*-Methylpyrid-4-yl)-2-(5-formyl-*N*-methylpyrrol-2-yl)ethene triflate (4). Freshly distilled POCl_3 (0.449 g, 2.93 mmol) was added dropwise to anhyd DMF (0.214 g, 2.93 mmol) under nitrogen at 5 °C. A solution of 1-(*N*-methylpyrid-4-yl)-2-(*N*-methylpyrrol-2-yl)ethylene triflate² (0.700 g, 2.01 mmol) in anhyd acetonitrile (15 mL) was added dropwise to the reaction mixture at 5 °C. After the mixture was stirred for 4 h at room temperature, the formed precipitate was filtered off under reduced pressure and washed with aq K_2CO_3 (5 mL), to give the product as a yellow solid (0.530 g, 1.41 mmol, 70%): mp = 189 - 191 °C (H_2O); ^1H NMR ($\text{DMSO}-d_6$) 9.63 (s, 1H), 8.85 (d, 2H, $J = 6.7$), 8.27 (d, 2H, $J = 6.8$), 8.01 (d, 1H, $J = 16.1$), 7.50 (d, 1H, $J = 16.1$), 7.14 (d, 1H, $J = 4.4$), 6.99 (d, 1H, $J = 4.4$), 4.24 (s, 3H), 4.08 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$) 180.0, 151.2, 145.0, 140.0, 135.0, 127.0, 125.0, 123.5, 111.0, 48.5, 31.5. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_4\text{S}$: C, 47.87; H, 4.02; N, 7.44. Found: C, 47.68; H, 4.21; N, 7.80.

2,5-Bis[1-(4-*N*-methylpyridinium)ethen-2-yl]-*N*-methylpyrrole ditriflate (1). Methyl triflate (2.87 g, 17.5 mmol) was added dropwise to a solution of 4-picoline (1.63 g, 17.5 mmol) in dry benzene (18 mL) at room temperature under dry atmosphere. After stirring for 20 h the precipitate was isolated to give practically pure *N*-methyl-4-picolinium triflate as a white solid (4.38 g, 17.0 mmol, 97%): mp 110-111 °C; ¹H NMR (DMSO-*d*₆) δ 8.82 (d, 2H, *J* = 7.1), 7.94 (d, 2H, *J* = 7.1), 4.26 (s, 3H), 2.59 (s, 3H). A solution of *N*-methyl-4-picolinium triflate (0.424 g, 1.65 mmol) in EtOH (8 mL) and a few drops of piperidine were added to a solution of **4** (0.621 g, 1.65 mmol) in the same solvent (12 mL). The reaction mixture was refluxed and then cooled to room temperature. The formed precipitate was filtered off under reduced pressure and washed with absolute EtOH (4 mL) to give the product as a dark solid (0.680 g, 1.13 mmol, 68%): mp 300-304 °C (H₂O); ¹H NMR (DMSO-*d*₆) 8.66 (d, 4H, *J* = 6.8), 8.08 (d, 4H, *J* = 6.9), 7.91 (d, 2H, *J* = 15.9), 7.20 (d, 2H, *J* = 15.9), 7.02 (s, 2H), 4.15 (s, 6H), 3.80 (s, 3H); ¹³C NMR (DMSO-*d*₆) 152.5, 144.5, 135.6, 128.0, 121.2, 122.7, 113.5, 46.5, 30.8. Anal. Calcd for C₂₃H₂₃N₃F₆S₂O₆: C, 44.88; H, 3.77; N, 6.83. Found: C, 44.24; H, 3.77; N, 6.41.

1-(*N*-Methylquinol-4-yl)-2-(*N*-methylpyrrol-2-yl)ethene triflate (5). A solution of 1,4-dimethylquinolinium triflate³ (1.00 g, 3.3 mmol) and piperidine (0.1 mL) in EtOH (10 mL) was added to a solution of *N*-methyl-2-pyrrolicarboxaldehyde (0.371 g, 3.4 mmol) in the same solvent (10 mL) at room temperature. The reaction mixture was stirred under reflux for 2 h and then cooled in an ice bath. A bright violet precipitate was separated by filtration and washed with ethanol (3 mL) to give the almost pure product as a violet solid (0.850 g, 2.15 mmol, 65%): mp 215-217 °C; ¹H NMR (DMSO-*d*₆) 9.10 (d, 1H, *J* = 6.7), 8.95 (d, 1H, *J* = 8.5), 8.46 (d, 1H, *J* = 8.8), 8.34 (d, 1H, *J* = 6.7), 8.20 (t, 1H, *J* = 7.5), 8.14 (d, 1H, *J* = 15.5), 7.97 (t, 1H, *J* = 7.7), 7.90 (d, 1H, *J* = 15.5), 7.35 (d, 1H, *J* = 4.0), 7.20 (m, 1H), 6.30 (m, 1H), 4.42 (s, 3H), 3.88 (s, 3H).

1-(*N*-Methylquinol-4-yl)-2-(5-formyl-*N*-methylpyrrol-2-yl)ethene triflate (6). Freshly distilled POCl₃ (0.711 g, 4.64 mmol) was added dropwise to anhyd DMF (0.339 g, 4.64 mmol)

under a nitrogen atmosphere at $-15\text{ }^{\circ}\text{C}$. Anhyd acetonitrile (4 mL) and then a solution of **5** (0.918 g, 2.32 mmol) in anhyd acetonitrile (15 mL) was added dropwise to the reaction mixture at $-15\text{ }^{\circ}\text{C}$. The mixture was stirred for 6 h at room temperature, the precipitate was collected to give the as a red fluorescent solid (0.530 g, 1.25 mmol, 54%): mp $234\text{--}235\text{ }^{\circ}\text{C}$ (EtOH); ^1H NMR (DMSO- d_6) 9.67 (s, 1H), 9.37 (d, 1H, $J = 6.3$), 9.03 (d, 1H, $J = 8.5$), 8.68 (d, 1H, $J = 6.5$), 8.46 (d, 1H, $J = 8.6$), 8.41 (d, 1H, $J = 15.5$), 8.28 (t, 1H, $J = 7.8$), 8.19 (d, 1H, $J = 15.5$), 8.06 (t, 1H, $J = 7.6$), 7.45 (d, 1H, $J = 4.3$), 7.20 (d, 1H, $J = 4.3$), 4.57 (s, 3H), 4.13 (s, 3H).

***N*-Methyl-2-[1-(*N*-methylquinol-4-yl)ethen-2-yl]-5-[1-(bis-2-benzothiazolylmethyl)ethen-2-yl]pyrrole triflate (2).** A solution of **6** (0.118 g, 0.27 mmol) in EtOH (10 mL) was added to a solution of bis-2-benzotiazolilmethane⁴ (0.077 g, 0.27 mmol) and piperidine (0.1 mL) in EtOH (8 mL). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The bright violet precipitate was collected and washed with ethanol (3mL) to give the product as a violet solid (0.090 g, 0.13 mmol, 48.5%): mp $220\text{--}221\text{ }^{\circ}\text{C}$ (EtOH); ^1H NMR (DMSO- d_6) 9.22 (d, 1H, $J = 6.7$), 8.90 (d, 1H, $J = 8.5$), 8.61 (d, 1H, $J = 6.6$), 8.37 (d, 1H, $J = 8.8$), 8.26 (d, 1H, $J = 7.5$), 8.25 (d, 1H, $J = 15.5$), 8.21 (d, 1H, $J = 7.7$), 8.20 (t, 1H, $J = 7.6$), 8.15 (s, 1H), 8.08 (d, 1H, $J = 7.9$), 8.04 (d, 1H, $J = 15.3$), 7.99 (d, 1H, $J = 8.1$), 7.98 (t, 1H, $J = 7.6$), 7.67 (t, 1H, $J = 7.2$), 7.61 (t, 1H, $J = 7.3$), 7.54 (t, 1H, $J = 7.7$), 7.64 (t, 1H, $J = 7.7$), 7.28 (d, 1H, $J = 4.5$), 5.71 (d, 1H, $J = 4.4$), 4.48 (s, 3H), 4.08 (s, 3H); ^{13}C NMR (DMSO- d_6) 166.88, 163.93, 153.25, 152.90, 151.96, 147.00, 138.80, 136.02, 135.71, 134.73, 134.67, 133.20, 128.90, 126.87, 126.72, 126.30, 126.06, 125.88, 125.50, 124.92, 124.46, 123.51, 122.75, 122.64, 122.19, 119.23, 117.69, 115.87, 115.12, 114.53, 45.03, 31.11. Anal. Calcd for $\text{C}_{34}\text{H}_{25}\text{F}_3\text{N}_4\text{O}_3\text{S}_3$: C, 59.12; H, 3.65; N, 8.11. Found: C, 60.06; H, 3.28; N, 8.46.

References.

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