Supporting Information

For

A highly selective fluorescent probe for pyrophosphate in aqueous solution

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Experimental

N-butyl-4-hydrazino-1,8-naphthalimide[1] (**3**) and 5-(Guanidiniocarbonyl)-1H-pyrrole-2-carboxylate[2] (**4**) were synthesized according to the literature.

Methyl 5-[(N-butyl-1,8-naphthalimide-4-amino))carbamoyl]pyrrole-2-carboxylate (6): Compound **4** (510 mg, 3 mmol) was suspended in dry CH_2Cl_2 (20 ml). Dry DMF (three drops), and oxalyl chloride (760 mg, 6mmol, 2 equiv) were added and the reaction mixture was refluxed for four hours. The slightly yellow solution was evaporated to get rid of the excess oxalyl chloride. The residue (**5**) was dissolved in dry CH_2Cl_2 (10 ml), and added dropwise to the reaction mixture of N-butyl-4-hydrazino-1,8-naphthalimide **3** (850 mg, 3 mmol) and triethylamine (6 mmol, 2 equiv) in CH_2Cl_2 at 0 ºC, then the reaction mixture was stirred at room temperature overnight. The CH_2Cl_2 was removed under reduced pressure and water (50 ml) was added. The solution was acidified to pH<7 with hydrochloric acid and extracted with chloroform (3×30 ml). The collected organic layers were dried with $MgSO_4$, and the chloroform was removed in vacuo. The crude product was purified by column chromatography on silica gel (chloroform-methanol 100:5) to

give **6** (720 mg, 55%) as a red solid (Found: C, 63.39; H, 5.16; N, 12.80; O, 18.64. Calc. for $C_{23}H_{22}N_4O_5$: C, 63.59; H, 5.10; N, 12.90; O, 18.41 %); mp 264-266 °C.; δ_H (300 MHz; DMSO-d_6) 0.92 (3 H, m, butyl CH_3), 1.32 (2 H, m, butyl CH_2), 1.58 (2 H, m, butyl CH_2), 3.80 (3 H, s, OCH_3), 4.03 (2 H, m, NCH_2), 6.68 (1 H, s, pyrrole CH), 6.87 (1 H, s, pyrrole CH), 7.76 (1 H, dd, J (H, H)=7.8, 7.5 Hz, Naph(3)H), 7.85 (1 H, d, J = 8.7 Hz, Naph(6)H), 8.34 (2 H, d, Naph(2)H, Naph-NH), 8.45 (1 H, d, J = 7.5 Hz, Naph(7)H), 8.78 (1 H, d, J=7.8 Hz, Naph(5)H), 11.50 (1 H, s, carbamoyl NH), 12.50 (1 H, s, pyrrole NH); δ_C (75 MHz; DMSO-d_6) 14.4, 20.5, 30.4, 52.0, 107.9, 111.0, 111.4, 117.1, 119.2, 122.6, 124.4, 125.4, 128.9, 129.7, 131.4, 133.9, 134.1, 136.1, 147.0, 161.3, 163.6, 164.3; m/z (HPLC-MS) 435 (M+1).

5-[(N-butyl-1,8-naphthalimide-4-amino)carbamoyl]-1H-pyrrole-2-carbonylguanidinium picrate (1): Ester **6** (434 mg, 1 mmol) and guanidine (5 equiv, prepared from guanidinium hydrochloride with sodium methoxide) were refluxed in 20 ml dry DMF for 36h under nitrogen. The orange solution was poured into water, upon acidification with hydrochloric acid (2 M), the crude product precipitated. It was filtered off and washed thoroughly with methanol to provide hydrochloride salt of **1** (199 mg, 40%) as dark red solid. The picrate salt **1** was obtained by dissolving the hydrochloride salt in an aqueous picric acid solution, and recrystallized from methanol as dark red solid (Found: C, 50.81; H, 3.87; N, 20.24; O, 24.55. Calc. for $C_{29}H_{26}N_{10}O_{11}$: C, 50.44; H, 3.79; N, 20.28; O, 25.48 %); mp > 250 °C; δ_H (300 MHz; DMSO-d_6) 0.91 (3 H, m, butyl CH_3), 1.37 (2 H, m, butyl CH_2), 1.58 (2 H, m, butyl CH_2), 4.01 (2 H, m, NCH_2), 6.80 (1 H, s, pyrrole CH), 7.25 (1 H, s, pyrrole CH), 7.77 (1 H, dd, J (H, H)=7.2, 8.1Hz, Naph(3)H), 7.83 (1 H, d, J = 8.7 Hz, Naph(6)H), 8.23 (4 H, s, guanidinium), 8.34 (1 H, d, J = 8.1 Hz, Naph(2)H), 8.39 (1 H, s, Naph-NH), 8.45 (1 H, d, J = 7.2 Hz, Naph(7)H), 8.56 (2 H, s, picrate), 8.79 (1 H, d, J=8.7 Hz,

Naph(5)H), 11.11 (1 H, s, carbamoyl NH), 11.60 (1 H, s, guanidinium amide NH), 12.72 (1 H, s, pyrrole NH); δ_C (75 MHz; DMSO-d_6) 14.4, 20.5, 30.4, 49.3, 108.0, 111.3, 111.8, 117.4, 119.3, 122.6, 124.8, 125.9, 129.0, 129.7, 131.5, 133.9, 135.5, 136.4, 142.5, 146.8, 155.8, 160.0, 161.5, 163.6, 164.3; m/z (HPLC-MS) 462 (M+1).

References

1 T. Gunnlaugsson, P. E. Kruger, P. Jensen, J. Tierney, H. D. P. Ali and G. H. Hussey, *J. Org. Chem.*, 2005, **70**, 10875-10878.

2 P. Barker, P. Gendler and H. Rapoport, *J. Org. Chem.*, 1978, **43**, 4849-4853.

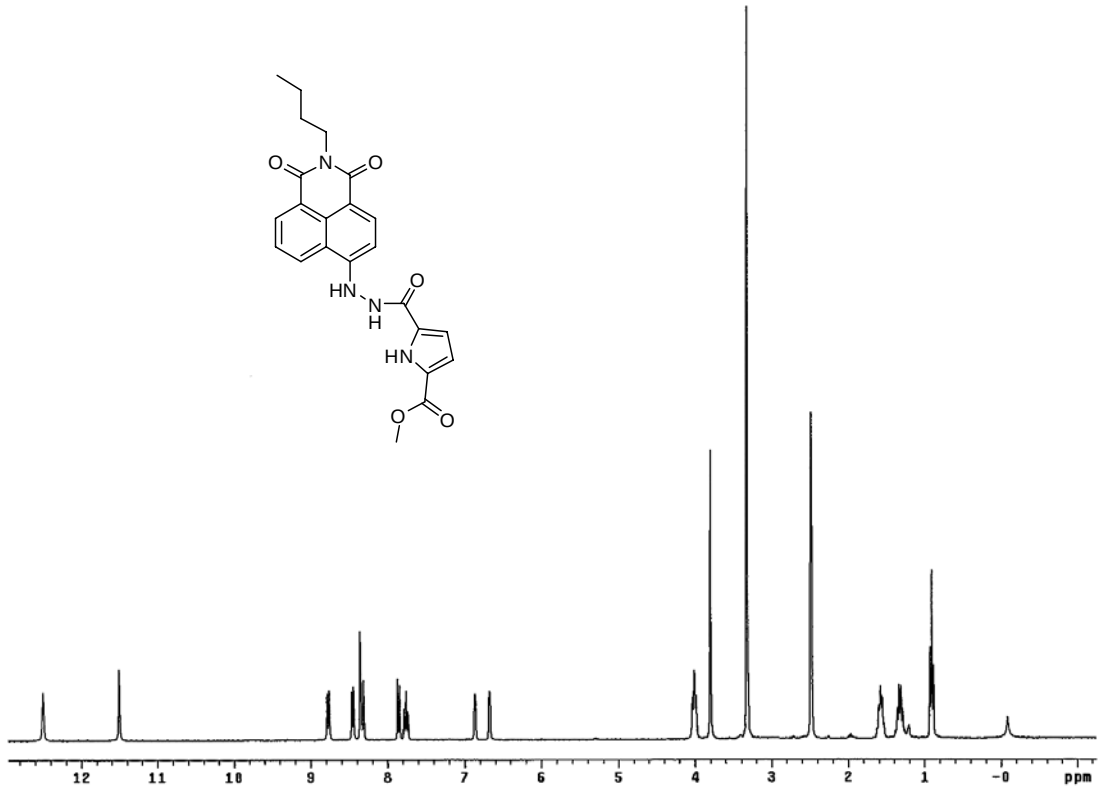

Figure S1. ^{1}H NMR spectra of compound **6** in DMSO-d_6.

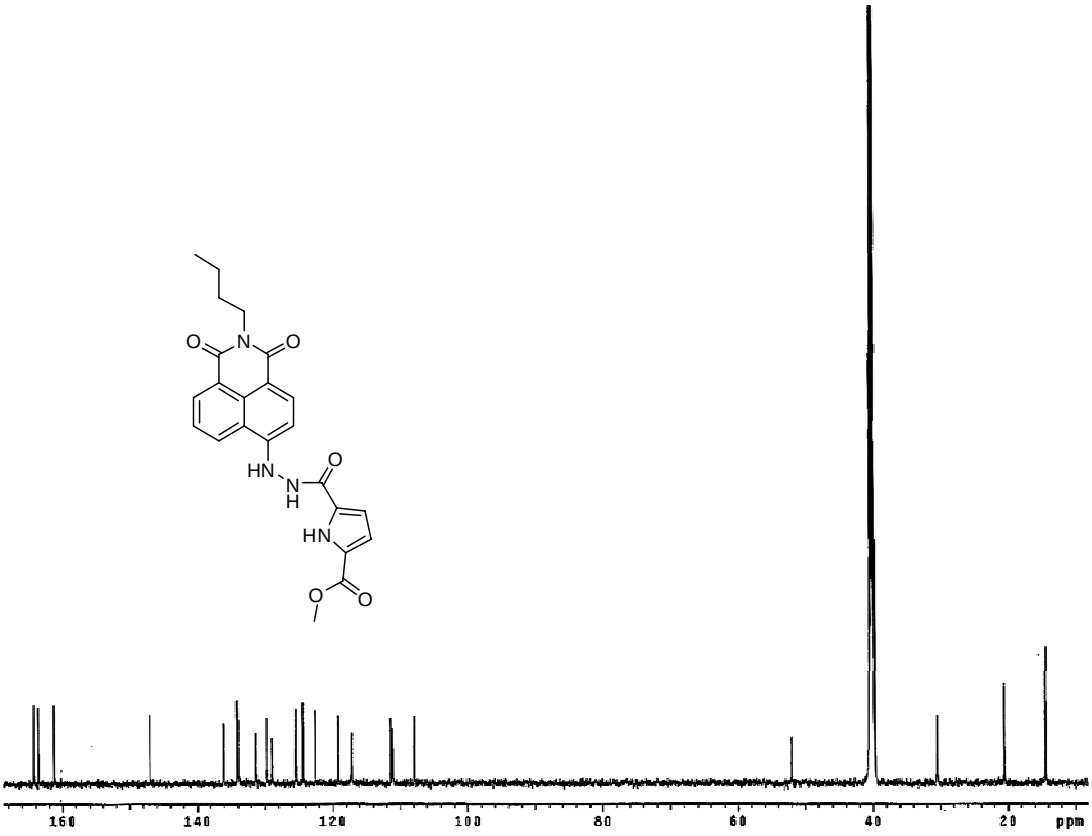

Figure S2. ^{13}C NMR spectra of compound **6** in DMSO-d_6.

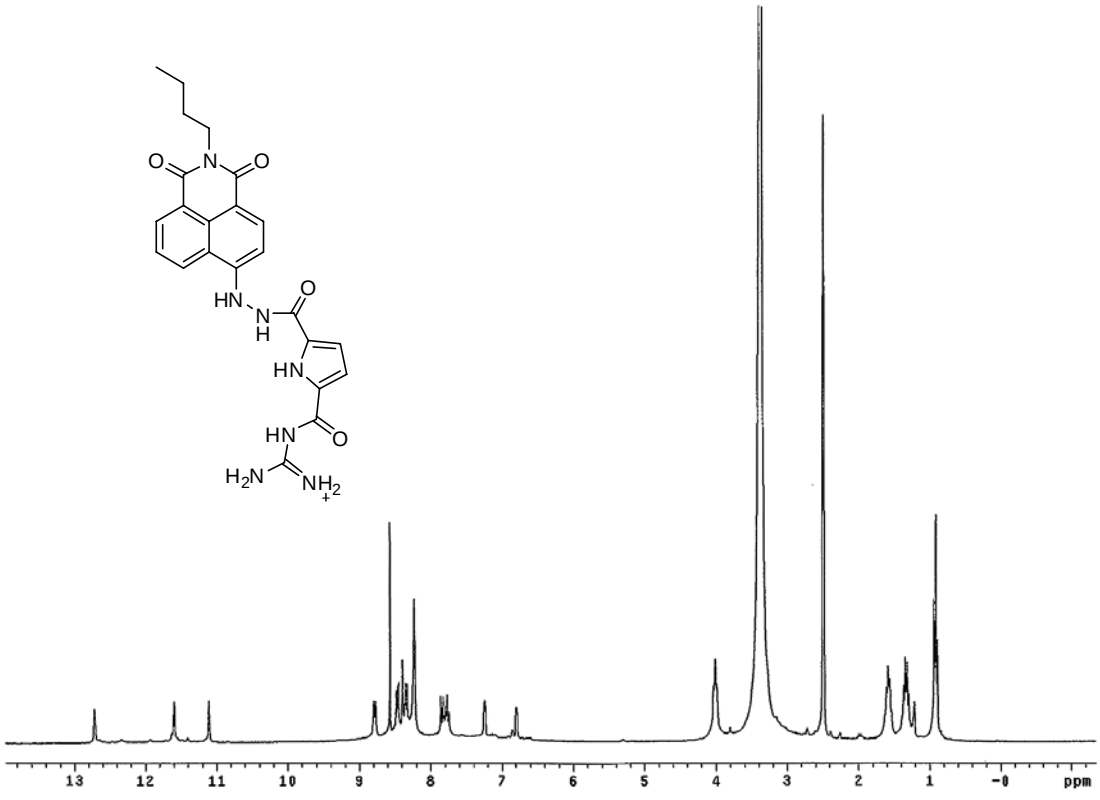

Figure S3. ^{1}H NMR spectra of compound **1** in DMSO-d_6.

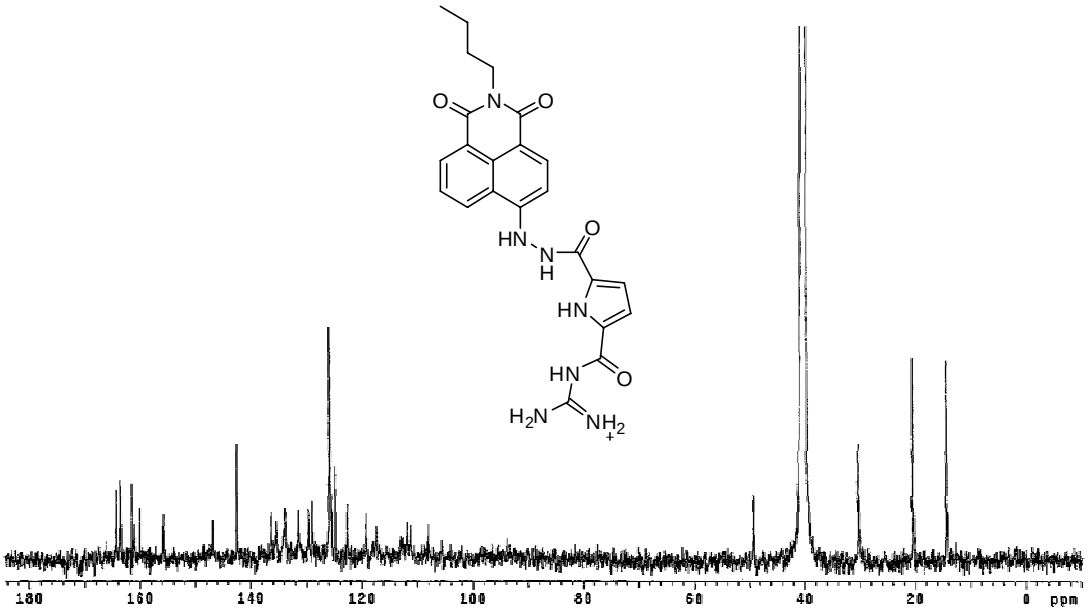

Figure S4. ^{13}C NMR spectra of compound **1** in DMSO-d_6.