

pH Responded Reversible Supramolecular Self-assembly of Water-soluble

Amino-imidazole-armed Perylene Diimide Dye for Biological Application

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Supporting Information Available

***N,N*-bis-(1-propylimidazole)-3,4,9,10-perylene tetracarboxylic acid diimide synthesis.**

3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA, 3.923 g, 10 mmol) and *N*-(3-Aminopropyl)-imidazole (3.75 g, 30 mmol) were added to isobutanol (200 mL) and heated at 90 °C for 24 h with stirring under N₂ atmosphere. The crude product was filtered, washed with ultrapure water and ethanol. The obtained residue was treated with 150 mL 5% aqueous NaOH solution at 90 °C for 30 min to remove the unreacted PTCDA. The mixture was filtered, washed with ultrapure water and ethanol and dried under vacuum (5.40 g, 89%). ¹H NMR (CF₃COOD, 400 MHz, 25 °C), δ/ppm: 2.33-2.37 (t, 4H), 4.24-4.27 (t, 4H), 4.3-4.33 (t, 4H), 7.27 (s, 2H), 7.36 (s, 2H), 8.60-8.66 (m, 8H), 8.75 (s, 2H). ¹³C NMR (CF₃COOD, 400 MHz, 25 °C), δ/ppm: 29.1, 38.7, 48.5, 111.1, 113.9, 119.6, 121.1, 122.7, 125.0, 133.6, 135.3, 136.6, 166.4.

***N,N*-bis-(1-aminopropyl-3-propylimidazol salt)-3,4,9,10-perylene tetracarboxylic acid diimide (PDI) synthesis.** The obtained *N,N*-bis-(1-propylimidazole)-3,4,9,10-perylene tetracarboxylic acid diimide (3.03 g, 10 mmol) and 3-bromopropylamine hydrobromide (0.438 g, 20 mmol) were added to ethanol (100 mL), refluxed for 24 h under N₂ atmosphere. After the mixture was cooled to room temperature, the precipitate was filtered and washed with ethanol. The resulting mixture was purified by re-crystallization from ethanol and dried under vacuum to give a red product (3.2 g, 93%). ¹H NMR (DMSO, 400 MHz, 25 °C), δ/ppm: 1.23 (t, 4H), 2.26-2.30 (t, 4H), 4.11 (s, 4H), 4.33-4.37 (s, 4H), 7.75 (s, 2H), 7.86 (s, 2H), 8.34-8.36 (d, 4H), 8.61-8.63 (d, 4H), 9.19 (s, 2H). ¹³C NMR (CF₃COOD, 400 MHz, 25 °C), δ/ppm: 29.21, 38.78, 48.59, 111.03, 113.85, 119.48, 120.84, 122.50, 122.74, 124.88, 126.19, 129.46, 133.24, 135.72, 135.79, 165.91.

Table S1. The final pH values of the reaction mixture containing GOx and different concentrations of glucose.

Glucose concentration(mM)	0	0.3	0.5	1	1.5	2
pH	7.1	6.83	6.61	5.85	4.60	4.13

^a Footnote text.

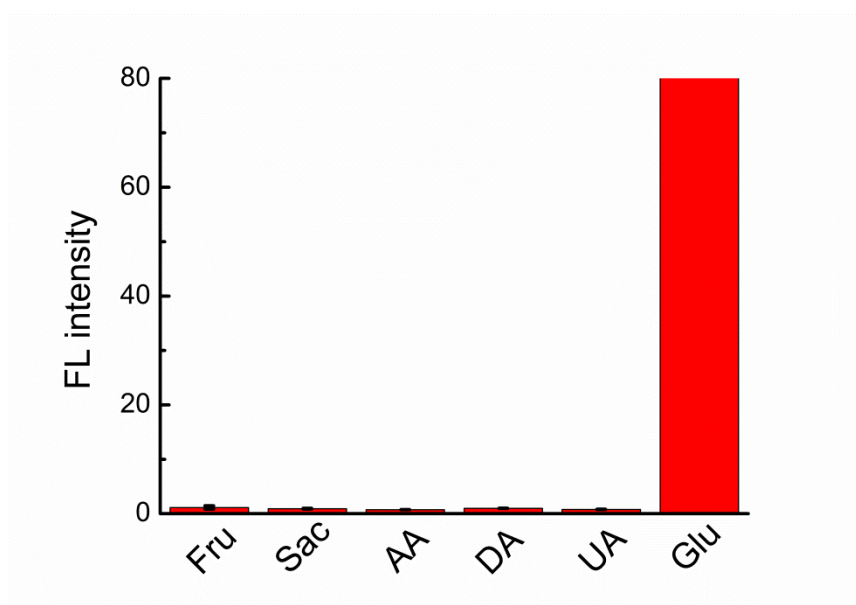


Fig. S1 the relative fluorescence spectra change of AIA-PDI in the presence of different interferents (after incubation with GOx); the final concentrations of the relative species were: fructose (Fru) 20 mM, saccharose (Sac) 20 mM, ascorbic acid (AA) 0.1 mM, dopamine (DA) 0.1 mM, uric acid (UA) 0.1 mM and glucose (Glu) 2 mM.

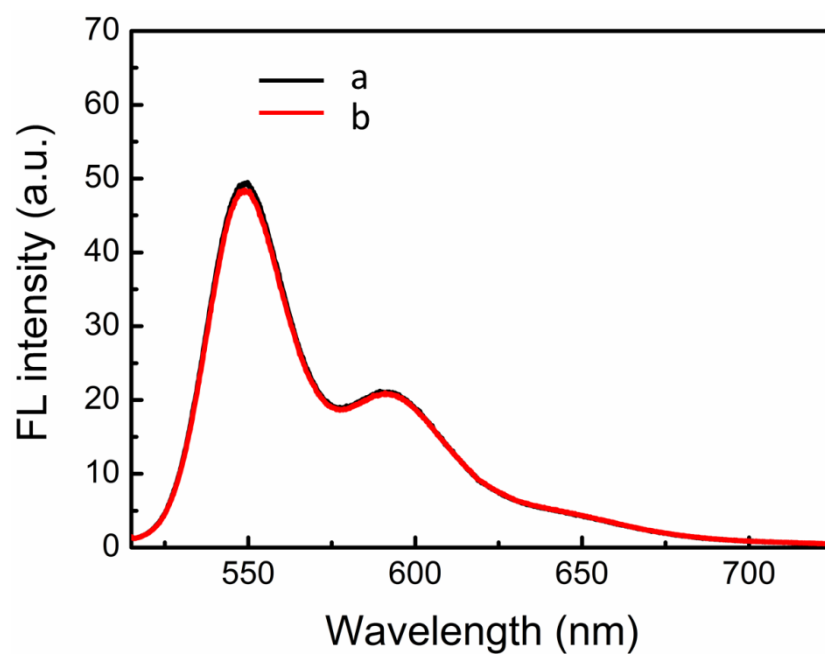


Fig. S2 the stability measurement of glucose detection, the fluorescence spectra of AIA-PDI incubated in reaction mixture of GOx and glucose (a) and 20 minutes later (b).