Supporting Information

Chromogenic and fluorogenic detection of a nerve agent simulant with a rhodamine-deoxylactam based sensor

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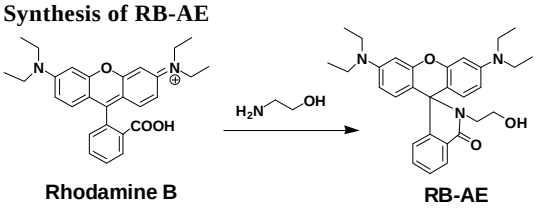
Experimental Procedures

Diethyl chlorophosphate was purchased from Acros. All other reagents were obtained from Alfa Aesar and used without further purification. Column chromatography was performed on silica gel (300-400 mesh). NMR spectra (^{1}H at 400 MHz and ^{13}C at 100 MHz) were recorded on a Bruker instrument using tetramethyl silane as the internal reference. The mass analysis was performed in Bruker En Apex ultra 7.0T FT-MS. The fluorescence spectra and Uv-vis absorption spectra were performed on a spectrofluorimeter (Spectamax M5, Molecular Device) using the excitation wavelength (λex) of 560 nm.

Synthesis of RB-AE

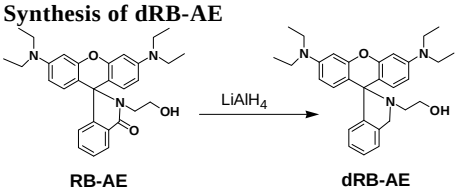


Rhodamine B RB-AE

Scheme S1: synthesis of RB-EDA

Rhodamine B (10 g) and 2-aminoethanol (25 ml) were added to a flask containing methanol (15 ml). The mixture was stirred at 70 ^{o}C until the red color of rhodamine B disappeared. The mixture was extracted with ethyl acetate (200 ml) over water (200 ml). The organic layer was collected, dried over sodium sulfate, and then concentrated to remove the solvent. The residue was purified by silica gel column chromatography using ethyl acetate/ hexanes/ triethylamine (10: 10: 1，v/v/v) as the eluent to give 6.5 g of solid as the desired product in 60 % yield. ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.92 (m, 1H) 7.46 (m, 2H), 7.09 (m,1H), 6.52 (d, 2H, J = 8.76 Hz), 6.40 (s, 2H), 6.32 (d, 2H, J = 8.32 Hz), 3.49 (broad, 2H) 3.36 (q, 8H, J= 7.03 Hz) 3.30 (t, 2H, J= 4.82 Hz), 1.19 (t, 12H, J = 7.04 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$), δ:170.08, 153.90, 153.26, 148.89, 132.70, 130.44, 128.50, 128.14, 123.80, 122.90, 108.24, 104.79, 97.79, 65.85, 62.64, 44.64, 44.36, 12.59 ppm; HRMS ($C_{30}H_{35}N_3O_3$): calculated (MH^+): 486.2751, found: 486.2752.

Synthesis of dRB-AE



RB-AE dRB-AE

Scheme S2: synthesis of dRB-EDA

N-(rhodamine B)-lactam-2-aminoethanol (2 g) was dissolved in anhydrous THF (30 ml). To the solution was added lithium aluminium hydride (1g). The mixture was stirred at rt under argon overnight. 1-Butanol (200 ml) was added gradually to the solution to quench residual lithium aluminium hydride, and then the mixture was washed with water (200 ml). The organic layer was collected, dried over sodium sulfate, and then concentrated to remove the solvent. The residue was purified by silica gel column chromatography using dichloromethane/hexanes/triethylamine (10:10:1 v/v/v) as the eluent to give 0.8 g of pale yellow solid as the

desired product (40% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.36 (d, 1H, J = 7.36 Hz), 7.30 (m, 1H) 7.22 (t, 1H, J = 7.42 Hz), 6.95 (d, 1H, J= 7.48 Hz), 6.68 (d, 2H, J= 8.72 Hz), 6.37 (d, 2H, J= 2.52 Hz), 6.35 (d, 1H, J = 2.64 Hz), 6.33 (d, 1H, J=6.24 Hz), 4.22 (s, 2H), 3.45 (t, 2H, J = 5.32 Hz), 3.35 (q, 8H, J= 7.06 Hz), 2.49 (t, 2H, J= 5.32 Hz), 1.19 (t, 12H, J = 7.04 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ:152.89, 149.14, 148.08, 138.82, 130.00, 127.72, 126.94, 124.71, 121.79, 111.26, 107.71, 97.57, 68.10, 59.06, 55.84, 50.39, 44.31, 12.73 ppm; HRMS ($C_{30}H_{37}N_3O2_{):}$ calculated (MH^+): 472.2959, found: 472.2954.

Effects of reaction media on the assay kenetics

dRB-AE was added to DMF, acetonitrile or aqueous DMF (H_2O: DMF = 1:50, v/v) containing diethyl chlorophosphate (100 ppm) and triethylamine (3%, v/v) to a final concentration of 1 mg ml^{-1}. dRB-EA (1 mg ml^{-1}) in DMF containing TEA (3%, v/v) was used as the control. The rates of color development in the reaction solutions were directly recorded by UV-vis absorbance at 560 nm on Spectamax-M5 (Molecular Devices).

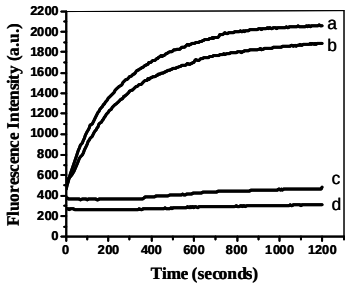


Fig. S1 Kinetic profile of the reaction rate between dRB-AE (1 mg ml^{-1}) and diethyl chlorophosphate (170 ppm) in DMF (a), DMF containing 2% of water (b) and acetonitrile (c) as compared to the control (d). Color formation was monitored by Uv-vis absorption at 560 nm.

Comparison of the fluorescent spectral properties of the colored species in the assay solution with rhodamine B

Diethyl chlorophosphate (2 µL) was added into 20 ml of DMF solutions containing dRB-AE (1 mg ml^{-1}). The solution was incubated at room temperature for 10 minutes and then an aliquot was taken for the fluorescence excitation spectrum (Em@590 nm) and fluorescence emission spectrum as compared to rhodamine B in DMF solution.

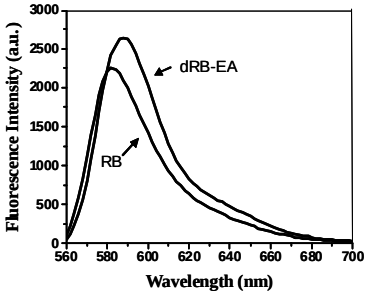


Fig. S2 Fluorescence emission spectra of of the assay solution containing dRB-EA (1 mg ml^{-1}) and diethyl chlorophosphate (500 ppm) as compared to rhodamine B (1 mg ml^{-1}) in DMF

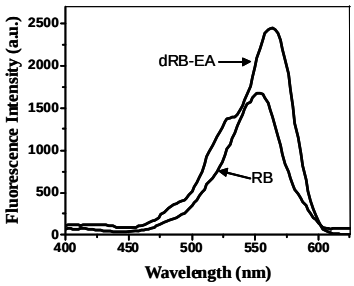


Fig. S3 Fluorescence excitation spectrum of the assay solution containing dRB-EA (1 mg ml^{-1}) and diethyl

chlorophosphate (500 ppm) as compared to rhodamine B (1 mg ml^{-1}) in DMF

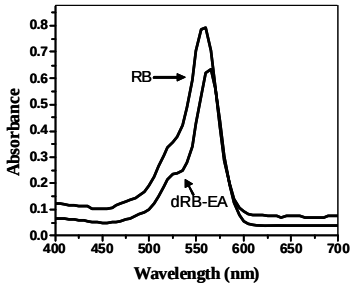


Fig. S4 Absorption spectra of the assay solution containing dRB-EA (1 mg ml^{-1}) and diethyl chlorophosphate (500 ppm) as compared to rhodamine B (1 mg ml^{-1}) in DMF.

Assay sensitivity

Diethyl chlorophosphate (5 uL) were added into a serial of DMF solutions of different volumes containing dRB-AE (1 mg ml^{-1}) to a final concentration of 500, 250, 170, 125, 100, 75, 50, 25, or 0 ppm. The reaction solutions incubated at room temperature for 10 minutes and then directly analyzed for UV-vis absorption spectra or fluorescence emission spectra.

Comparison of the time-dependant fluorescence emission of dRB-AE based assay as compared to rhodamine-hydroxamate

To the solution of dRB-AE (1 mg ml^{-1}) or rhodamine-hydroxamate (1 mg ml^{-1}) in DMF containing TEA (3%, v/v) was respectively added diethyl chlorophosphate to a final concentration of 170 ppm. The fluorescence emission at 590 nm of the solution was recorded as a funtion of time using an excitation wavelength of 560 nm.

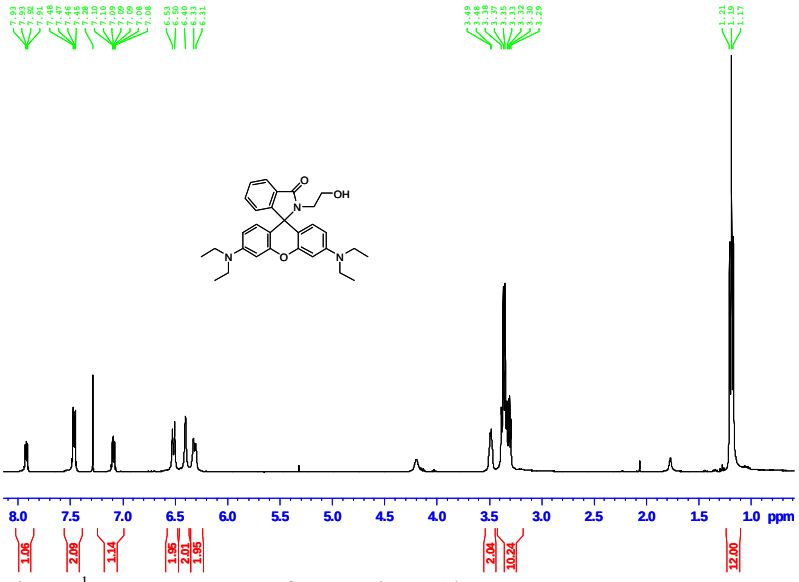


Fig. S5 ^{1}H-NMR spectrum of RB-AE in $CDCl_3$.

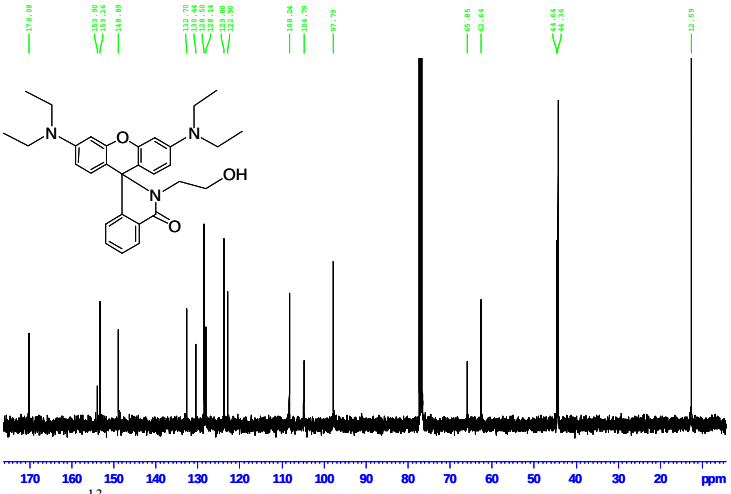


Fig. S6 ^{13}C-NMR spectrum of RB-AE in $CDCl_3$.

Fig. S7 HRMS analysis of RB-AE.

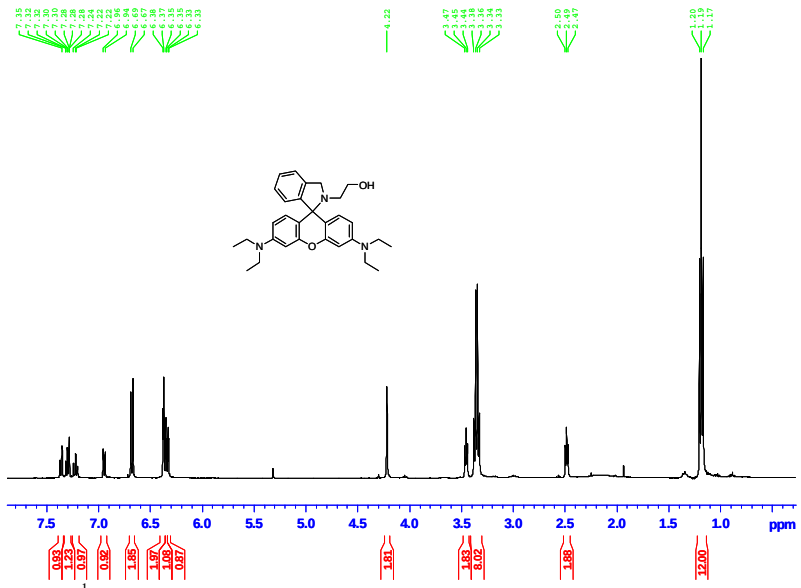


Fig. S8 ^{1}H-NMR spectrum of dRB-AE in $CDCl_3$.

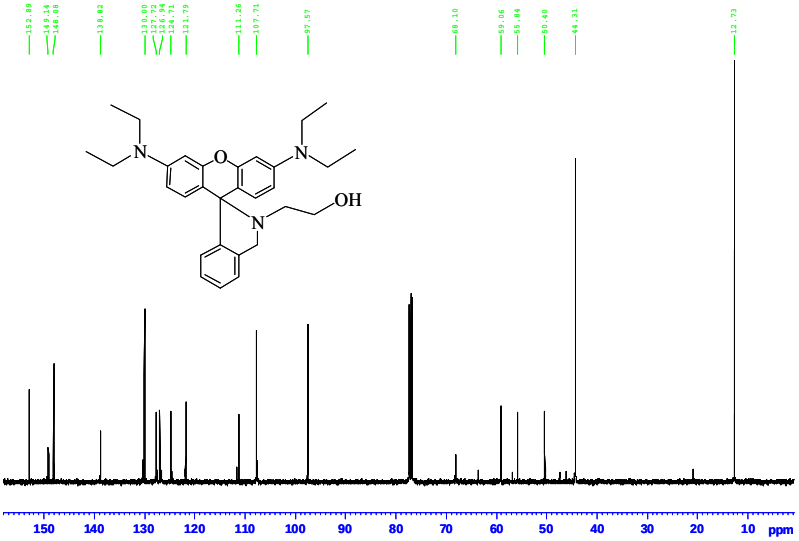


Fig. S9 ^{13}C-NMR spectrum of dRB-AE in $CDCl_3$.

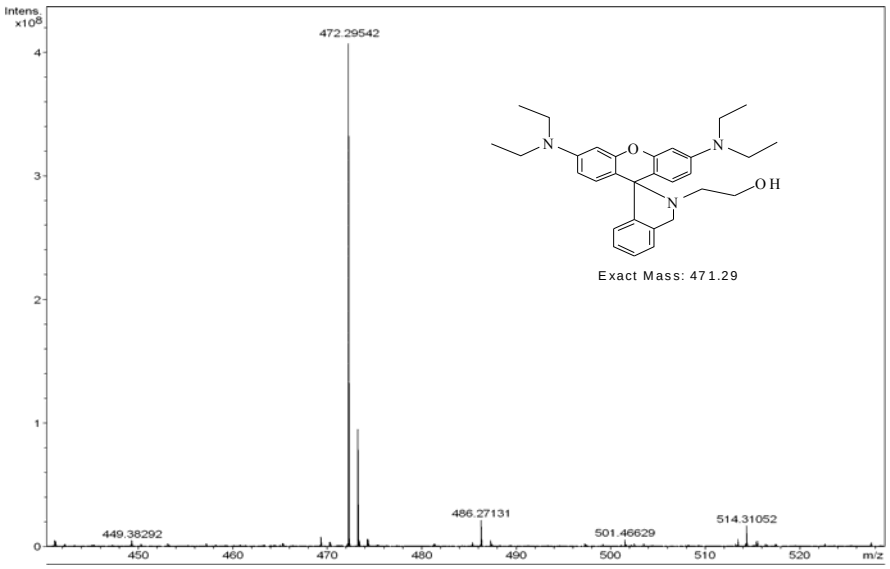


Fig. S10 HRMS analysis of dRB-AE.