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ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for *Adv. Funct. Mater.*, DOI: 10.1002/adfm.201102486

Colorimetric Detection of Warfare Gases by Polydiacetylenes Toward Equipment-Free Detection

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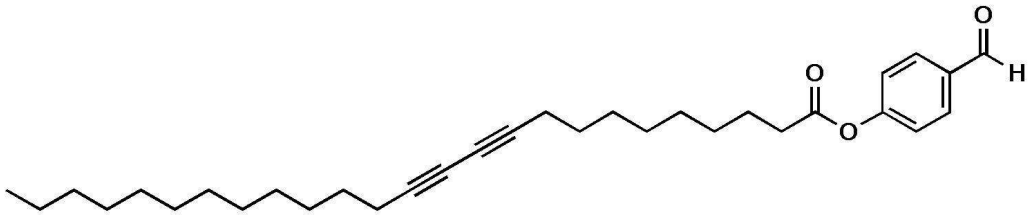
Colorimetric Detection of Warfare Gases by Polydiacetylenes toward Equipment-free detection

By *Jiseok Lee*, *Sungbaek Seo* and *Jinsang Kim**

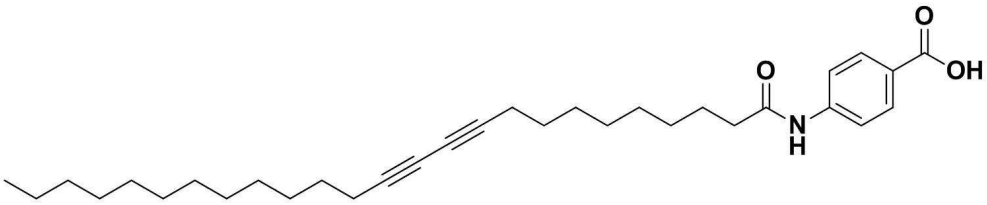
Supporting Information

Materials and Method. All solvents were purchased from Sigma-Aldrich Chemicals. 10,12-pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. Oxalyl chloride, triphenylphosphine, diethylazocarboxylate and 4-hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, hydroxylamine, sodium carbonate, tetrahydrofuran, pyridine, dichloromethane, diethylether and agarose were purchased from Sigma-Aldrich Chemical Co. Cellulose acetate membrane filter was purchased from Millipore Membranes. UV/Vis absorption spectra were measured on a Varian Cary50 UV/Vis spectrophotometer. Fluorescence spectra were obtained using PTI QuantaMasterTM spectrofluorometers equipped with an integrating sphere.

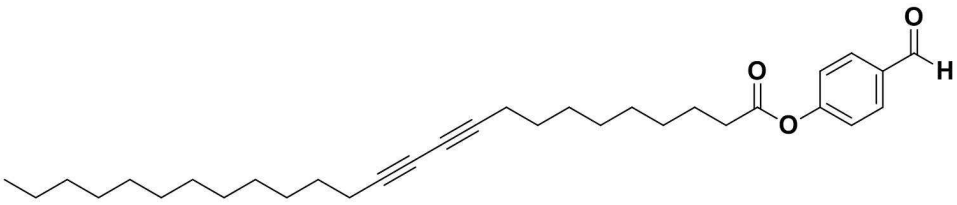
Synthesis of PCDA Derivatives



PCDA-CPE To a solution containing 1.39 g (3.70 mmol) of 10,12-pentacosadiynoic acid in 20 mL of methylene chloride was added dropwise 0.94 g (7.4 mmol) of oxalyl chloride at room temperature. The resulting solution was stirred at room temperature for 1 h. To the solution was added a catalytic amount (one drop) of DMF and stirred for an additional hour. After concentrating in vacuo, the residue was redissolved in 15 mL of methylene chloride. The resulting solution was added dropwise to the solution containing 0.66 g (4.81 mmol) of 4-hydroxybenzoic acid in 15 mL of THF. The resulting mixture was allowed to stir for overnight at room temperature. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (4:1 chloroform: methanol) to give 0.48 g (26%) of the desired diacetylene monomer PCDA-CPE as a white solid. mp 75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H), 1.20-1.80 (m, 36H), 2.22 (t, 4H), 2.35 (t, 2H), 7.07-7.55 (m, 5H), 7.18 (brs, 1H).

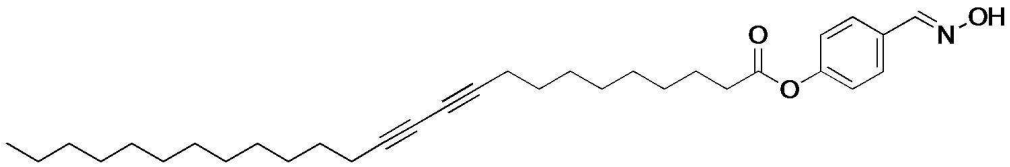


PCDA-*p*BzA To a solution of 10,12-pentacosadiynoic acid (2.00 g, 5.34 mmol) in dichloromethane (20 mL) at room temperature was added dropwise oxalyl chloride (2.03 g, 16.02 mmol). The resulting solution was stirred at room temperature for 30 min. To the solution was added a catalytic amount of dimethylformamide and stirred for an additional hour. After concentrating in vacuo, the residue was redissolved in THF (15 mL). The resulting solution was added dropwise to the solution containing 4-aminobenzoic acid (1.10 g, 8.01 mmol) and TEA (2.16 g, 21.36 mmol) in THF (15 mL). The resulting mixture was allowed to stir for overnight at room temperature, poured into the water and extracted with ethyl acetate. The organic layer was washed 3 times with water to eliminate the excess 4-aminobenzoic acid, dried with MgSO4 and filtered. The solvent was removed under vacuo. The resulting solution was recrystallized from methyl alcohol and isopropyl alchol to give 2.20 g (83 %) of desired diacetylene monomer PCDA-pBzA as a white solid. mp 190 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, 3H), 1.23-1.60 (m, 32H), 2.25-2.28 (m, 4H), 2.31-2.35 (m, 2H), 7.69 (d, 2H), 7.86 (d, 2H), 10.15 (s, 1H).

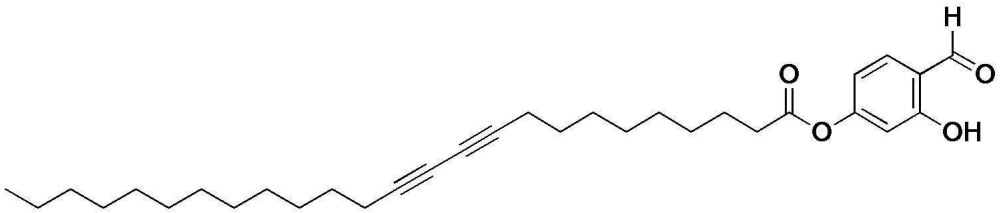


PCDA-*p*BA To a solution of 10,12-pentacosadiynoic acid (1.00 g, 1.33 mmol) in dichloromethane (20 mL) at room temperature was added dropwise oxalyl chloride (1.01 g, 7.98 mmol). The resulting solution was stirred at room temperature for 30 min. To the solution was added a catalytic amount (one drop) of dimethylforamide and stirred for an additional hour. After concentrating in vacuo, the residue was redissolved in tetrahydrofuran (15 mL) and added dropwise to the solution containing 4-hydroxybenzaldehyde (0.65 g, 5.32 mmol) in pyridine (15 mL). The resulting mixture was allowed to stir for overnight at room temperature. The residue was extracted with ethyl acetate and dried with $MgSO_4$ and filtered. The solvent was removed under vacuo. The residue was further purified by silica

gel column chromatography (hexane:ethylacetate =6:1) to give 1.00 g (86.2 %) of desired diacetylene monomer **PCDA-*p*BA** as a white solid. mp 80 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H), 1.15-1.64 (m, 32H), 2.26 (t, 4H), 7.35 (d, 2H), 7.98 (d, 2H), 9.90 (s, 1H).

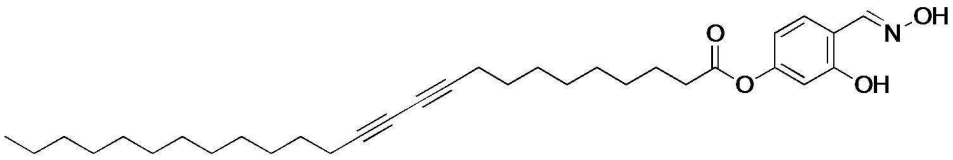


PCDA-*p*BO To a solution of PCDA-*p*BA (1.00 g, 2.09 mmol) in 2-propanol (100 mL) at room temperature was added dropwise hydroxylamine hydrochloride (0.17 g, 2.51 mmol) and sodium carbonate (0.20 g, 2.51 mmol) in 60 ml of 2-propanol/di-water (1/2). The reaction mixture was refluxed at 80 °C for 2 hours. After cooling, the reaction mixture was concentrated in vacuo and extracted with diethylether. The residue was recrystalized in 2-propanol/di-water (1/1) and further purified with gel column chromatography (ethylacetate: hexane = 1:5) to give 0.60 g (59 %) of desired diacetylene monomer **PCDA-*p*BO** as a white solid. mp 100 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.84 (t, 3H), 1.15-1.66 (m, 34H), 2.27 (t, 4H), 2.61 (t, 2H), 7.12 (d, 2H), 7.60 (d, 2H), 8.12 (s, 1H). 11.25 (s, 1H).



PCDA-HBA To a solution of 10,12-pentacosadiynoic acid (2.00 g, 5.33 mmol) in dichloromethane (20 mL) at room temperature was added dropwise oxalyl chloride (2.00 g, 15.7 mmol). The resulting solution was stirred at room temperature for 30 min. To the solution was added a catalytic amount (one drop) of dimethylforamide and stirred for an additional hour. After concentrating in vacuo, the residue was redissolved in 2-butanone (20 mL). The resulting solution was added dropwise to the solution containing 2,4-dihydroxybenzaldehyde (0.72 g, 5.27 mmol) and TEA (0.62 g, 6.17 mmol) in 2-butanone (50 mL). The resulting mixture was allowed to stir for 6 hours at room temperature. The solvent was removed under vacuo and the residue was crystallized in methanol for 40 min. The residue was further purified by silica gel column chromatography (hexane:ethyl acetate =9:1) to give 1.2 g (44 %) of desired diacetylene monomer **PCDA-HBA** as a white solid. Mp 90 °C. ^{1}H NMR (400

MHz, DMSO-d_6): δ 0.78 (t, 3H), 1.17-1.71 (m, 32H), 2.26 (t, 4H), 2.51 (t, 2H), 6.64-6.68 (m, 2H), 7.64 (s, 1H), 10.18 (s, 1H).



PCDA-HBO To a solution of PCDA-HBA (0.38 g, 0.62 mmol) in ethanol (20 mL) at room temperature was added hydroxylamine hydrochloride (0.14 g, 2.06 mmol) and sodium carbonate (0.43 g, 4.13 mmol) in 10 ml of ethanol/di-water (1/1). The reaction mixture was refluxed at 44 °C for 6 hours. After concentrating in vacuo, the residue was recrystalized in 2-propanol/water (1/1) and dichloromethane. The residue was further purified with gel column chromatography (ethyl acetate: hexane = 1:5) to give 0.30 g (73 %) of desired diacetylene monomer **PCDA-HBO** as a white solid. mp 107 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H), 1.15-1.63 (m, 32H), 2.27 (t, Hz, 4H), 2.54 (t, 2H), 6.62 (m, 2H), 7.49 (d, 1H), 8.29 (s, 1H), 10.35 (s, 1H), 11.29 (s, 1H).