Supporting information for

First fluorescent photoinduced electron transfer (PET) reagent for hydroperoxides

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General. Melting points (Mp), determined on a Yanagimoto Micro Point Apparatus, are uncorrected. ^{1}H-NMR (500 Hz) spectra were determined on a JEOL LA-500 spectrometer. Chemical shifts were reported in parts per million (ppm) relative to the line of a singlet at 7.24 ppm for deuteriochloroform and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. Mass spectra (MS) were obtained on a Hitachi M-1200H mass spectrometer (atmospheric pressure chemical ionization (APCI) system). UV-vis absorption spectra were obtained on a JASCO Ubest-50 spectrometer. Fluorescence spectra were obtained on a Hitachi F-4010 fluorescence spectrometer. Analytical thin layer chromatography (TLC) was performed on 25 HPTLC aluminium sheets, silica gel 60 F_{254} (Merck). Open column chromatography was performed on Merck silica gel 60 (70-230 mesh). Reagents and solvents were commercial grades and were used as supplied. 2-Diphenylphosphinoethylamine was purchased from Fulka. 4-Fluoro-7-nitro-2,1,3-benzoxadiazole (NBD-F) was purchased from Dojin. (4-Diphenylphosphino)benzoic acid was purchased from Sigma-Aldrich, Co. Phosphonitrilic chloride trimer was purchased from Tokyo Kasei Kogyo Co., Ltd.

4-(2-Diphenylphosphinoethylamino)-7-nitro-2,1,3-benzoxadiazole (1). To a solution of 2-diphenylphosphinoethylamine (100 mg, 0.437 mmol) in acetonitrile (50 mL) at room temperature was slowly added acetonitrile (20 mL) solution of NBD-F (50.0 mg, 0.273 mmol). After stirring at room temperature for 10 min, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel (*n*-hexane–ethyl acetate, 3:1) to afford **1** (39.4 mg, 0.101

mmol, 37%) as orange crystals. APCI-MS: m/z 393 ($(M+H)^+$); Mp: 135-136 °C; ^{1}H-NMR ($CDCl_3$): δ 2.54 (t, 2H, *J* = 8.6 Hz), 3.65 (br, 2H), 5.95 (d, 1H, *J* = 8.6 Hz), 6.39 (br, 1H), 7.32-7.33 (m, 6H), 7.41-7.44 (m, 4H), 8.37 (d, 1H, *J* = 8.6 Hz). Anal. Calcd for $C_{20}H_{17}N_4O_3P$: C, 61.22; H, 4.37; N, 14.28. Found: C, 61.14; H, 4.66; N, 14.24.

4-(2-Diphenylphosphinylethylamino)-7-nitro-2,1,3-benzoxadiazole (2). To a solution of **1** (15.0 mg, 0.0383 mmol) in acetonitrile (5 mL) at room temperature was added acetonitrile (5 mL) solution of MCPBA (12.0 mg, 0.0488 mmol). After stirring at room temperature for 30 min, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel (ethyl acetate–methanol, 25:1) to afford **2** (14.5 mg, 0.0355 mmol, 93%) as yellow crystals. APCI-MS: m/z 409 ($(M+H)^+$); Mp: 219-220 °C; ^{1}H-NMR ($CDCl_3$): δ 2.74 (m, 2H), 3.92 (br, 2H), 6.07 (d, 1H, *J*=8.6 Hz), 7.43-7.52 (m, 6H), 7.71-7.75 (m, 4H), 8.40 (d, 1H, *J* = 8.6 Hz). Anal. Calcd for $C_{20}H_{17}N_4O_4P$: C, 58.83; H, 4.20; N, 13.72. Found: C, 58.86; H, 4.42; N, 13.66.

4-((4-Diphenylphosphino)benzylamino)-7-nitro-2,1,3-benzoxadiazole (3). To a solution of (4-diphenylphosphino)benzoic acid (1.00 g, 3.27 mmol) in benzene (30 mL) at room temperature was added phosphonitrilic chloride trimer (2.20 g, 6.33 mmol). After stirring at room temperature for 1 h, the reaction mixture was added to the mixture of acetonitrile (20 mL) and 28% aqueous ammonia (30 mL) dropwise over a period of 30 min. After stirring at room temperature for 10 min, the reaction mixture was diluted with water (70 mL) and extracted with ethyl acetate (70 mL). Organic layer was concentrated under reduced pressure and the residue was chromatographed on silica gel (dichloromethane–methanol, 25:1) to afford 4-(diphenylphosphino)benzamide (558 mg, 1.83 mmol, 56%) as white crystals. APCI-MS: m/z 306 ($(M+H)^+$); ^{1}H-NMR ($CDCl_3$): δ 6.32 (br, 2H), 7.27-7.44 (m, 12H), 7.69-7.76 (m, 2H). Anal. Calcd for $C_{19}H_{16}NOP$: C, 74.74; H, 5.28; N, 4.59. Found: C, 74.46; H, 5.47; N, 4.62. To a solution of 4-(diphenylphosphino)benzamide (252 mg, 0.825 mmol) in THF (2 mL) at room temperature was carefully added lithium aluminium hydride (124 mg, 3.26 mmol). The mixture was heated at reflux for 1 h and after cooling to 0 °C, diluted with diethyl ether (60 mL). To the vigorously stirred mixture was sequentially added water (124 μL), 15% aqueous sodium hydroxide (124 μL), and water (372 μL). The resultant slurry was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The crude product was chromatographed on silica gel (*n*-hexane–ethyl acetate → dichloromethane–methanol, 9:1) to give 4-(diphenylphosphino)benzylamine (215 mg, 0.738 mmol, 89%) as a pale yellow oil. ^{1}H-NMR ($CDCl_3$): δ 3.88 (s, 2H), 7.29-7.33 (m, 14H). To a solution of 4-(diphenylphosphino)benzylamine (50.0 mg, 0.172 mmol) in acetonitrile (50 mL) at room temperature was slowly added acetonitrile (20 mL) solution of NBD-F (30.0 mg, 0.164 mmol). After stirring at room temperature for 10 min, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel (*n*-hexane–dichloromethane, 1:4) to afford **3** (31.4 mg, 0.0691 mmol, 42%) as orange crystals. APCI-MS: m/z 455 ($(M+H)^+$); Mp: 175-177 °C; ^{1}H-NMR ($CDCl_3$): δ 4.66 (br, 2H), 6.20 (d, 1H, *J*=8.5 Hz), 6.53 (br, 1H), 7.27-7.34 (m, 14H), 8.44 (d, 1H, *J*=8.5 Hz). Anal. Calcd for $C_{25}H_{19}N_4O_3P$: C, 66.08; H, 4.21; N, 12.33. Found: C, 65.88; H, 4.48; N, 12.26.

4-((4-Diphenylphosphinyl)benzylamino)-7-nitro-2,1,3-benzoxadiazole (4). To a solution of **3** (20.0 mg, 0.0441 mmol) in acetonitrile (10 mL) at room temperature was added acetonitrile (5 mL) solution of MCPBA (15.0 mg, 0.0610 mmol). After stirring at room temperature for 30 min, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel (ethyl acetate–methanol, 25:1) to afford **4** (18.8 mg, 0.0400 mmol, 91%) as yellow crystals. APCI-MS: m/z 471 ($(M+H)^+$); Mp: 202-203 °C; ^{1}H-NMR ($CDCl_3$): δ 4.76 (br, 2H), 6.15 (d, 1H, *J*=8.5), 7.39-7.65 (m, 14H), 8.40 (d, 1H, *J*=8.5). Anal. Calcd for $C_{25}H_{19}N_4O_4P$: C, 63.83; H, 4.07; N, 11.91. Found: C, 63.62; H, 4.33; N, 11.61.

Fluorescence spectra. Fluorescence spectra of **1-4** (1 μM, in acetonitrile, λ_{ex} = 460 nm) are shown in Figure 1.