

## Electronic supplementary information

### Recoverable fluorescence chemosensors for Ni<sup>2+</sup> ions based on hydrogen-bonded side-chain copolymers presenting pendent benzoic acid and pyridyl receptor units

Po-Jen Yang, Hsuan-Chih Chu, Te-Cheng Chen and Hong-Cheu Lin\*

*Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan (ROC)*

**\*Author for correspondence:**

Prof. Hong-Cheu Lin, Department of Materials Sci. and Eng., National Chiao Tung University, Hsinchu, Taiwan (ROC). Tel: 8863-5712121 ext.55305; Fax: 8863-5724727; E-mail: [linhc@cc.nctu.edu.tw](mailto:linhc@cc.nctu.edu.tw).

#### *Electronic supplementary information (ESI)*

##### **General synthetic procedures and characterization of monomer (M2).**

*2-(4-Bromo-phenoxy)-tetrahydro-pyran (1)*. To a solution of 4-bromophenol (10.0 g, 57.8 mmol) and 3,4-dihydro-2H-pyran (DHP) (9.72 g, 115.6 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (250 mL) at 0 °C, pyridinium *p*-toluenesulfonate (PPTS) (0.29 g, 1.16 mmol) was added under nitrogen, and the mixture was stirred at room temperature for 24 h. The reaction mixture was washed with a saturated aqueous NaHCO<sub>3</sub> solution and water several times, and then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residual product was purified by flash column chromatography (silica gel, hexane/ethyl acetate = 60:1 v/v) to give a colorless crystal. Yield: 14.0 g (95%). <sup>1</sup>H

NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.36 (d,  $J = 9.0$  Hz, 2H), 6.93 (d,  $J = 9.0$  Hz, 2H), 5.36 (t,  $J = 3.0$  Hz, 1H), 3.86 (m, 1H), 3.61 (m, 1H), 2.10–1.50 (m, 6H).

*4-((Tetrahydro-2H-pyran-2-yl)oxy)phenylboronic acid (2)*. To a solution of **1** (10.0 g, 38.9 mmol) in anhydrous THF, 23.3 mL (58.35 mmol) of *n*-butyllithium (2.5 M in hexane) was added dropwise at  $-78$  °C under nitrogen. After the mixture was stirred for 1.5 h at  $-78$  °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14.5 g, 77.8 mmol) was added to the solution. The mixture was warmed to room temperature and stirred overnight. The resulting mixture was quenched by water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residual product was purified by flash column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 2:1 v/v) to give a white solid. Yield: 9.7 g (82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.72 (d, 2H,  $J = 8.7$  Hz), 6.91 (d, 2H,  $J = 8.7$  Hz), 5.42 (t, 1H,  $J = 3.2$  Hz), 3.76 (m, 1H), 3.55 (m, 1H), 1.78 (m, 2H), 1.55 (m, 2H), 1.25 (m, 2H).

*2-((4'-Bromo-2',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)tetrahydro-2H-pyran (3)*. A solution of **2** (5.0 g, 10.3 mmol), 1,4-dibromo-2,5-dimethoxy-benzene (3.67 g, 12.4 mmol), and anhydrous potassium carbonate (1.89 g, 13.7 mmol) in 160 mL of toluene/ethanol (3:1, v/v) were purged with nitrogen for 10 min at room temperature. After 10 min, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.177 g, 0.154 mmol) was added, and then the reaction mixture was stirred to react at  $90$  °C for 6 h under nitrogen. After cooling to room

temperature, the solvent was removed under reduced pressure, and the residue was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4:1 v/v) to give a white solid. Yield: 3.0 g (75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.43 (d, *J* = 9.0 Hz, 2H), 7.15 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 6.88 (s, 1H), 5.46 (t, *J* = 9.0 Hz, 1H), 3.89 (m, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 3.63 (m, 1H), 2.06–1.56 (m, 6H).

*Methyl 4-((2,5-dimethoxy-4'-((tetrahydro-2H-pyran-2-yl)oxy)-[1,1'-biphenyl]-4-yl)ethynyl)benzoate (4)*. A mixture of **3** (3.0 g, 9.0 mmol), 4-ethynyl-benzoic acid methyl ester (1.73 g, 10.8 mmol), PPh<sub>3</sub> (47.3 mg, 0.18 mmol), and CuI (34.2 mg, 0.18 mmol) in dry 80 mL of Et<sub>3</sub>N/THF (1:1, v/v) was degassed with nitrogen for 5 min. Then, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (63.1 mg, 0.09 mmol) was added to the solution at room temperature, and the reaction mixture was stirred to react overnight at 70 °C under nitrogen. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was taken up in water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Then, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 2:1 v/v) to give a light yellow solid. Yield: 3.1 g (72%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.02 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz,

2H), 7.09 (s, 1H), 6.88 (s, 1H), 5.48 (t,  $J = 3$  Hz, 1H), 3.97 (m, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.79 (s, 3H), 3.63 (m, 1H), 2.04–1.56 (m, 6H).

*Methyl 4-((4'-hydroxy-2,5-dimethoxy-[1,1'-biphenyl]-4-yl)ethynyl)benzoate (5)*. To a solution of **4** (3.0 g, 6.4 mmol) in 60 mL of methanol/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v), *p*-toluenesulfonic acid monohydrate (TsOH·H<sub>2</sub>O) (0.12g, 0.64 mmol) was added. The reaction was stirred overnight at room temperature. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. Then, the organic layer was separated, and then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 1:1 v/v) to give a light yellow solid. Yield: 2.2 g (90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.02 (d,  $J = 8.7$  Hz, 2H), 7.63 (d,  $J = 8.7$  Hz, 2H), 7.46 (d,  $J = 8.7$  Hz, 2H), 7.10 (s, 1H), 6.90 (d,  $J = 8.7$  Hz, 2H), 6.87 (s, 1H), 4.97 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.80 (s, 3H).

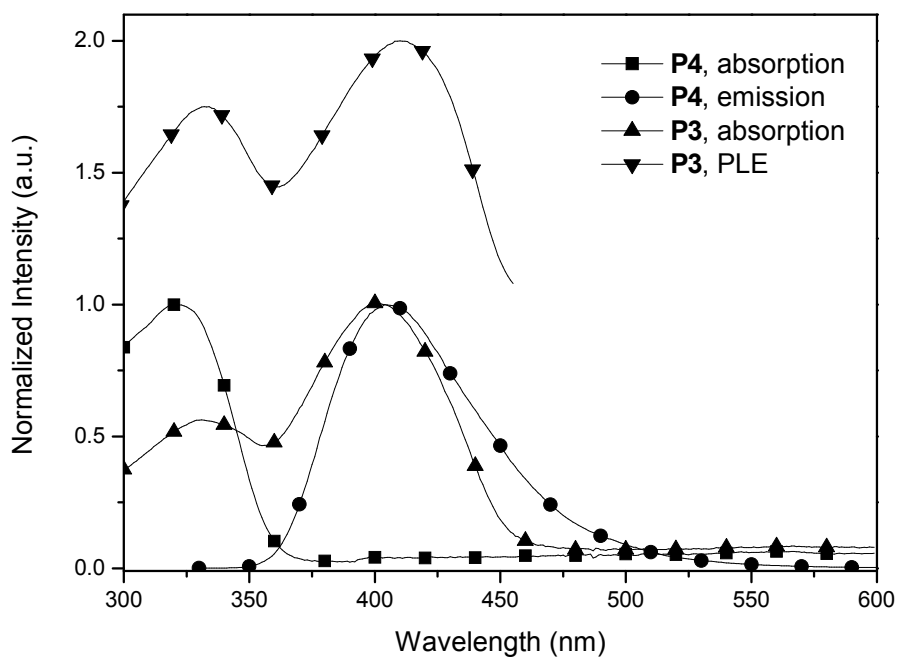
*Methyl 4-((4'-((10-hydroxydecyl)oxy)-2,5-dimethoxy-[1,1'-biphenyl]-4-yl)ethynyl)benzoate (6)*. A mixture of **5** (2.2 g, 5.66 mmol), 10-bromodecanol (1.61 g, 6.79 mmol), K<sub>2</sub>CO<sub>3</sub> (1.56 g, 11.32 mmol), and a small amount of potassium iodide (ca. 10 mg) in acetone (100 mL) was stirred and refluxed under nitrogen for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was taken up in water and extracted with ethyl acetate. Then, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by

column chromatography (silica gel, hexane/ethyl acetate = 1:2 v/v) to give a light yellow solid. Yield: 2.6 g (85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.02 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.09 (s, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.88 (s, 1H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.80 (s, 3H), 3.66 (t, *J* = 6.6 Hz, 2H), 1.81 (quint, *J* = 7.8 Hz, 2H), 1.57–1.32 (m, 14H).

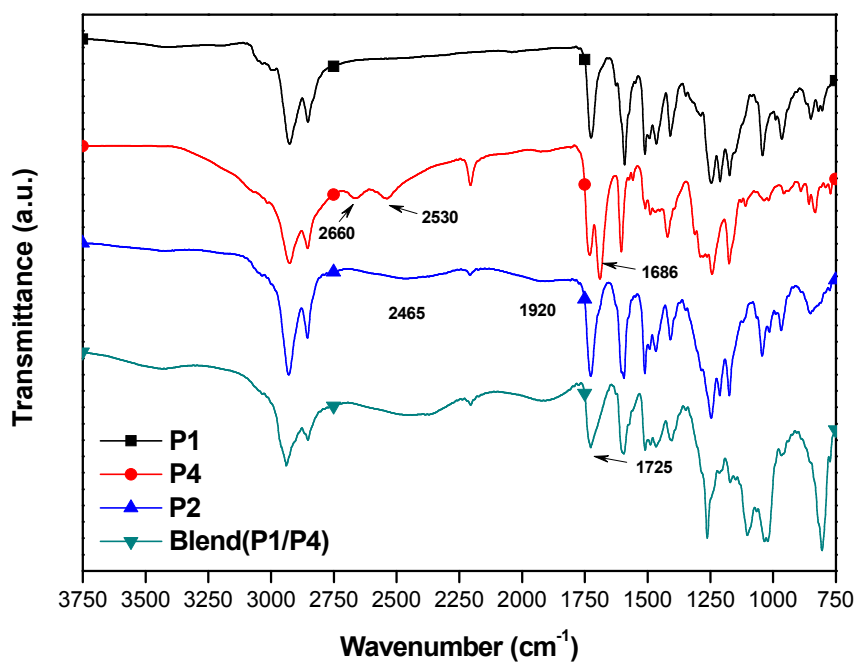
*4-((4'-((10-Hydroxydecyl)oxy)-2,5-dimethoxy-[1,1'-biphenyl]-4-yl)ethynyl)benzoic acid (7)*. To a stirred solution of **6** (2.0 g, 3.67 mmol) in 80 mL of ethanol/THF (1:1, v/v), an aqueous solution 10 mL of potassium hydroxide (0.82 g, 14.68 mmol) was added dropwise and heated to reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure, and acidified with 6 N HCl. The precipitated product was collected by filtration and recrystallization from ethanol/H<sub>2</sub>O (3:1 v/v) to give a light yellow solid. Yield: 1.75 g (90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.09 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.10 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.89 (s, 1H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 3.79 (s, 3H), 3.66 (t, *J* = 6.6 Hz, 2H), 1.81 (quint, *J* = 7.8 Hz, 2H), 1.58–1.32 (m, 14H).

*4-((4'-((10-(Acryloyloxy)decyl)oxy)-2,5-dimethoxy-[1,1'-biphenyl]-4-yl)ethynyl)benzoic acid (M2)*. To a solution of **7** (1.5 g, 2.82 mmol), *N,N*-dimethylaniline (0.44 g, 3.67 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (7.27 mg, 0.033 mmol) in dry dioxane (20 mL), acryloyl chloride (0.34 mL, 4.23 mmol) was added dropwise at 0 °C

under nitrogen. The reaction mixture was stirred at 50 °C for 4h. After cooling to room temperature, the mixture was poured into a dilute HCl and ice water. The precipitated product was collected by filtration and washed with water. The crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/THF = 20:1 v/v) to give a light yellow solid. Yield: 1.15 g (70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.09 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.10 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.89 (s, 1H), 6.40 (dd, *J* = 17.4 Hz, *J* = 1.5 Hz, 1H), 6.12 (dd, *J* = 17.4 Hz, *J* = 10.5 Hz, 1H), 5.82 (dd, *J* = 10.2 Hz, *J* = 1.5 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 1.81 (quint, *J* = 6.6 Hz, 2H), 1.67 (quint, *J* = 6.6 Hz, 2H), 1.58–1.32 (m, 12H). HRMS (EI): calcd for C<sub>36</sub>H<sub>40</sub>O<sub>7</sub>, 584.2774; found 581.3146. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>O<sub>7</sub>: C, 73.95; H, 6.90. Found: C, 73.96; H, 7.00.

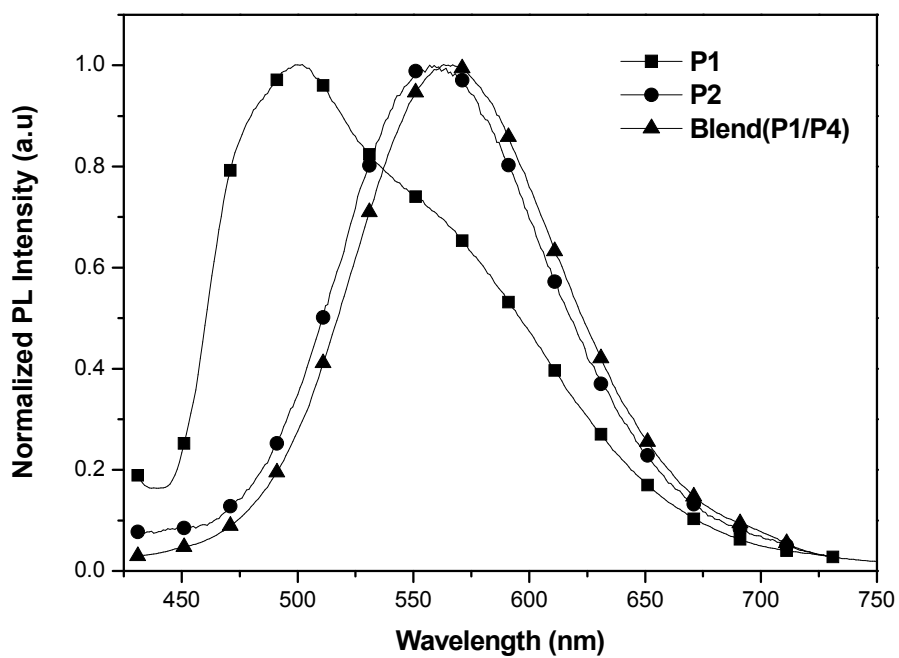


**Fig. S1** The photoluminescent excitation (PLE) and absorption spectra of copolymer **P3**, as well as the absorption and PL emission spectra of homopolymer **P4** in THF solutions, where the PLE spectrum of **P3** was monitored at the corresponding maximum PL emission. Note: PL spectrum of **P4** was excited at 320 nm and PLE spectrum of **P3** was excited at 464 nm.

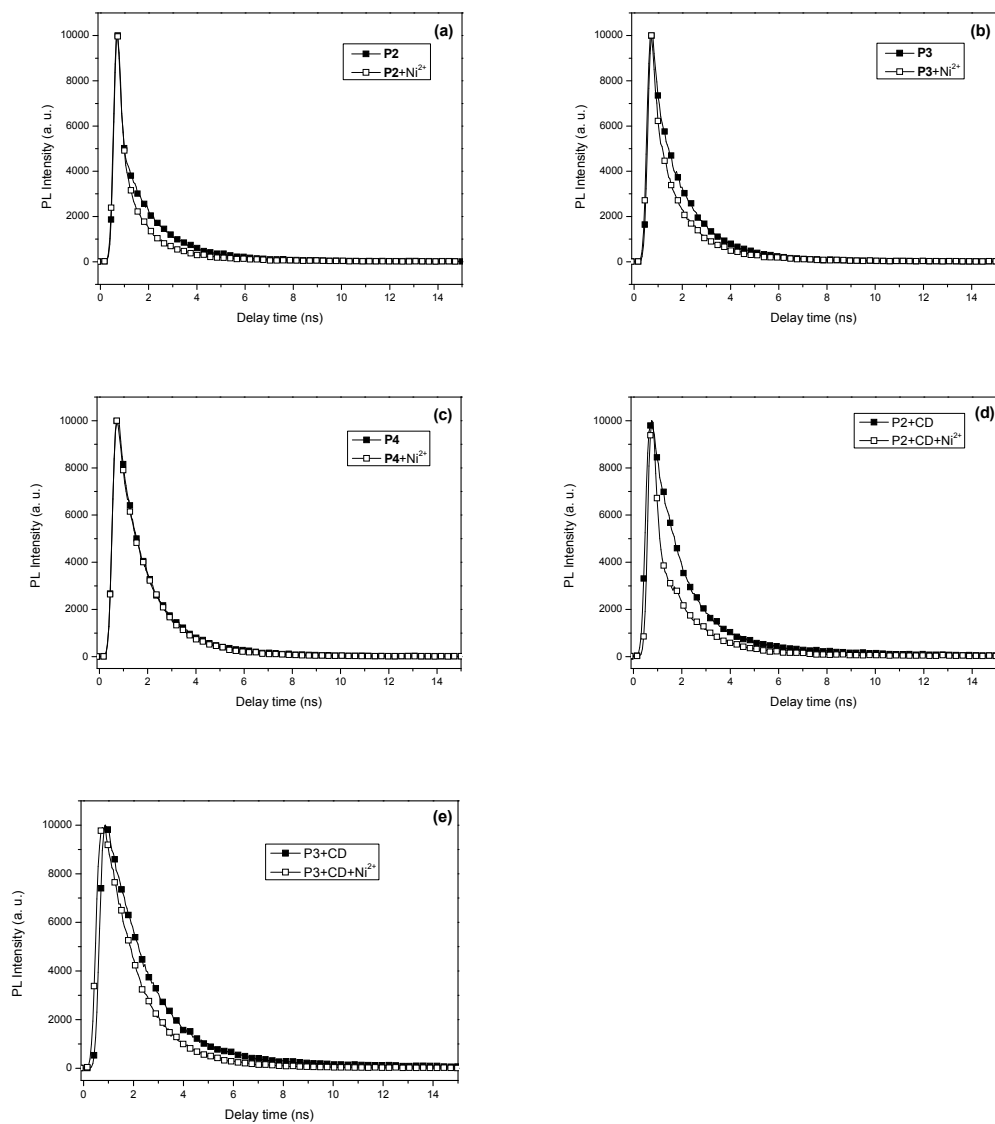


**Fig. S2** FT-IR spectra of pure H-acceptor homopolymer **P1**, H-donor homopolymer **P4**, H-bonded copolymer **P2**, and H-bonded blend(**P1/P4**) at room temperature (in the solid state).





**Fig. S3** Normalized PL spectra of polymers **P1**, **P2**, and H-bonded blend(**P1/P4**), which were excited at the maximum absorption of **M1** units in solid films.



**Fig. S4** Time-resolved fluorescence of polymers **P1-P4** (in THF with a concentration of  $5 \times 10^{-6}$  M) in the absence (solid square) and presence (empty square) of  $\text{Ni}^{2+}$  ions ( $2.5 \times 10^{-6}$  M) (a) **P2**, (b) **P3**, (c) **P4**, (d) **P2+CD**, and (e) **P3+CD**.