Electronic supplementary information

Induce Chirality Sensing through Formation and Aggregation of the Chiral Imines Double Winged with Pyrenes or Perylenes

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1. Materials and methods

All the chemicals were of analytically pure grade and were used as received. Solvents were dried and distilled before using for the synthesis. \(^1\)H and \(^13\)C NMR spectra were recorded at room temperature on a Bruker AMX–400 (operating at 400 MHz for \(^1\)H NMR and 101 MHz for \(^13\)C NMR) in CDCl\(_3\) with TMS as an internal standard. HRMS were measured in a Waters Q–TOF Premiers (ESI). UV/Vis spectral studies were done on a JASCO V-650 spectrophotometer. Steady-state emission spectral studies were done on a FluoroMax-4 spectrofluorometer (Horiba Scientific), and the data obtained were analyzed with Origin (v8.1) integrated software FluoroEssence (v2.2). Circular Dichroism (CD) studies were done on a JASCO CD spectropolarimeter (model-J1500). Dynamic light scattering (DLS) studies were done on a Zetasizer Nano ZS90. Scanning electron microscope (SEM) studies were done on a Hitachi Su500 instrument.

2. Synthetic procedures for sensors 1 and 2

2.1 Synthesis of 3,5-diethynylbenzaldehyde

Under an argon atmosphere, 3, 5-dibromobenzaldehyde (1.96 g, 7.42 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (260 mg, 0.37 mmol), CuI (70 mg, 0.37 mmol) and PPh\(_3\) (193 mg, 0.74 mmol) were dissolved in 80 mL anhydrous THF/Et\(_3\)N (1:1, v:v). The flask was vacuumed and back-filled with argon for several times and the mixture was stirred for ca. 15 min at room temperature, then trimethylsilylacetylene (2.19 g, 22.26 mmol) was added via syringe. The solution was refluxed for 7 h. Then the solvent was removed under a reduced pressure, and the residue was purified by column chromatography on silica gel (hexane as the eluent) to give 3,5-bis(trimethylsilyl)ethynyl)benzaldehyde 2.0 g (yield: 90.9%) as a colorless oil.

The above trimethylsilane protected intermediate (2.0 g, 6.70 mmol) was dissolved in methanol (30 mL), to which K\(_2\)CO\(_3\) (500 mg, 3.62 mmol) was added and the mixture was stirred for 2 h at room temperature. The reaction mixture was then concentrated under vacuum, and the residue 1.6 H was purified by silica gel chromatography to give 3,5-diethynylbenzaldehyde (750 mg, 70% yield) as white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.0 (s, 1H), 8.0 (d, \(J=1.6\) Hz, 2H), 7.8 (t, \(J=1.6\) Hz, 1H), 3.0 (s, 2H). Literature data\(^1\), \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 9.97 (s, 1 H), 7.95 (d, 2 H, \(J=1.5\) Hz), 7.82 (t, 1 H, \(J=1.5\) Hz), 3.19 (s, 2 H).

2.2 Synthesis of compound 1
Under an argon atmosphere, 3,5-diethynylbenzaldehyde (200 mg, 1.30 mmol) and 1-bromopyrene (911 mg, 3.24 mmol) were dissolved in 60 mL anhydrous THF/Et3N (2:1, v:v). Then, a mixture of Pd(PPh3)2Cl2 (45.62 mg, 0.065 mmol), PPh3 (34.08 mg, 0.13 mmol) and CuI (24.74 mg, 0.13 mmol, 10 mol %) were added. The mixture was refluxed for 24 h, and then the solvent was evaporated under a reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/CH2Cl2 (1:1) eluent) to give compound 1 (60 mg, 8.35% yield) as light yellow solid. 1H NMR (CDCl3, 400 MHz), δ 10.12 (s, 1H), 8.70 (d, J = 9.1 Hz, 2H), 8.28–8.25 (m, 9H), 8.20–8.11 (m, 6H), 8.08 (dd, J = 8.3, 4.4 Hz, 4 H). 13C NMR (CDCl3, 100 MHz) δ 191.3, 139.7, 137.1, 132.6, 132.5, 132.4, 132.2, 132.0, 131.5, 131.3, 130.1, 128.9, 128.8, 128.7, 127.4, 126.6, 126.2, 126.1, 125.6, 125.5, 124.8, 124.7, 124.5, 117.0, 93.1, 91.2. HRMS (ESI): calcd ([C43H22O]+), [M+Na]+: 557.1671; found: [M+Na]+: 557.1800.

2.2 Synthesis of compound 2

Under an argon atmosphere, 3,5-diethynylbenzaldehyde (60.0 mg, 0.38 mmol) and 1-bromoperylene (308.5 mg, 0.93 mmol) were dissolved in anhydrous THF/Et3N (2:1, 80 mL) solution. Then, a catalyst mixture of Pd(PPh3)2Cl2 (45.6 mg, 0.065 mmol, 5 mol %), PPh3 (34.1 mg, 0.13 mmol 10 mol %), and CuI (24.7 mg, 0.13 mmol, 10 mol %) was added under argon. The mixture was refluxed for 24 h at 90 ºC. The solvent was evaporated under a reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/CH2Cl2 = 1/1 as the eluent) to give 15 mg light yellow solid (Yield: 5.89%). 1H NMR (CDCl3, 400 MHz) δ 10.02 (s, 1H), 8.36–7.86 (m, 12H), 7.84–7.38 (m, 10H), 7.35 (d, J = 2.3 Hz, 1H), 7.13 (dd, J = 8.6, 2.5 Hz, 2H). 13C NMR (CDCl3, 100 MHz) δ 190.8, 140.1, 136.8, 134.7, 132.6, 132.5, 131.6, 128.4, 127.7, 126.9, 126.8, 126.0, 125.2, 124.6, 124.4, 123.9, 121.3, 121.0, 120.9, 119.7, 119.3, 81.6, 79.6. ESI-HRMS: calcd ([C51H26O]+): 654.1984; found: 654.0506.
3. Structure characterization data

Fig. S1 $^1$H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of 3,5-diethynylbenzaldehyde.

Fig. S2 $^1$H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of compound 1.
Fig. S3 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound 1.

Fig. S4 HRMS of compound 1.

Fig. S5 $^1$H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of compound 2.
**Fig. S6** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound 2.

**Fig. S7** HRMS of compound 2.
4. Photophysical properties of sensors 1 and 2

**Fig. S8.** UV–vis spectra of pyrene (black) and sensor 1 (red) (1 \times 10^{-5} \text{ M}) in DMF at 25 °C.
Fig. S9. Fluorescence spectra of pyrene (black) and sensor I (red) (3.0 × 10⁻⁶ M) in DMF at 25 °C; λ<sub>ex</sub> = 370 nm.
**Fig. S10.** UV–vis absorption spectra of perylene (black) and sensor 2 (red) ($1 \times 10^{-5}$ M) in DMF at 25 °C.

**Fig. S11.** Fluorescence spectra of perylene (black) and sensor 2 (red) ($3.0 \times 10^{-6}$ M) in DMF at 25 °C; $\lambda_{ex} = 440$ nm.
5. Characterization of the formation of imine from 1 and (R)-A2

Fig. S12. Partial $^1$H NMR spectra (400 MHz, CDCl$_3$) for the formation of imine from 1 and (R)-A2.
6. The characterization of aggregates of imine formed by 2 with A6

![UV–vis spectra](image1)

**Fig. S13.** Water content-dependent UV–vis spectra of the chiral imine (40 μM) derived from the reaction of 2 with A6 in DMF for 30 min.

![Fluorescence spectra](image2)

**Fig. S14.** Water content-dependent fluorescence of the chiral imine (40 μM) derived from the reaction of 2 with A6 in DMF for 30 min.
**Fig. S15.** Water content-dependent CD spectra of the chiral imine (40 μM) derived from the reaction of 2 with (S)-A6 in DMF for 30 min.

**Fig. S16.** Light scattering of the chiral imine (40 μM) derived from 2 and A6 in DMF (left) and in 1:1 (v/v) DMF/H₂O (right).
Fig. S17 Emission of the chiral imine (40 μM) derived from 2 and A6 in DMF (left) and 1:1 (v/v) DMF/H₂O (right).

Fig. S18. SEM image of the imine derived from 2 and A6 aggregated in 1:1 (v/v) DMF/H₂O.
**Fig. S19.** DLS measurements of the imine derived from 2 and A6 aggregated in 1:1 (v/v) DMF/H₂O.

7. Chiroptical sensing with sensors 1 and 2

**Fig. S20.** CD spectra of 50 μM chiral imines derived from 1 and A2 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.
**Fig. S21.** CD spectra of 50 μM chiral imines derived from 1 and A3 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H2O, respectively.

**Fig. S22.** CD spectra of 50 μM chiral imines derived from 1 and A4 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H2O, respectively.
Fig. S23. CD spectra of 50 μM chiral imines derived from I and A6 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H2O, respectively.

Fig. S24. CD spectra of 50 μM chiral imines derived from I and A7 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H2O, respectively.
**Fig. S25** CD spectra of 50 μM chiral imines derived from 1 and A8 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.

**Fig. S26** CD spectra of 50 μM chiral imines derived from 1 and A9 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.
**Fig. S27** CD spectra of 50 μM chiral imines derived from 1 and A10 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.

**Fig. S28**. CD spectra of 50 μM chiral imines derived from 2 and A1 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.
**Fig. S29.** CD spectra of 50 μM chiral imines derived from 2 and A2 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H2O, respectively.

**Fig. S30.** CD spectra of 50 μM chiral imines derived from 2 and A3 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H2O, respectively.
**Fig. S31.** CD spectra of 50 μM chiral imines derived from 2 and A4 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.

**Fig. S32.** CD spectra of 50 μM chiral imines derived from 2 and A5 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.
**Fig. S33** CD spectra of 50 μM chiral imines derived from 2 and A9 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.

**Fig. S34** CD spectra of 50 μM chiral imines derived from 2 and A10 at 25 °C. Red and black lines represent the CD spectra of chiral imines derived from (R)- and (S)-amines, respectively, while broken and solid lines represent the CD spectra measured in DMF and in 1:1 (v/v) DMF/H₂O, respectively.
**Fig. S35** CD spectra of 50 μM chiral imines obtained by reacting 2 with (S)-A10 in the presence of 0-30% achiral n-butylamine in DMF; measured in 1:1 (v/v) DMF/H₂O at 25 °C.

**Fig. S36** CD spectra of the imines (40 μM) obtained by reacting 1 with A1 of different ee’s in DMF; measured in 1:1 (v/v) DMF/H₂O at 25 °C. Inset: Plot of the ellipticity at 390 nm as a function of ee.
Fig. S37 CD spectra of the imine (40 μM) obtained by reacting 2 with A4 of different ee’s in DMF; measured in 1:1 (v/v) DMF/H₂O at 25 °C. Inset: Plot of the ellipticity at 390 nm as a function of ee.

Fig. S38 CD spectra of the imine (20 μM) obtained by reacting 2 with A3 of different ee’s in DMF; measured in 1:1 (v/v) DMF/H₂O at 25 °C. Insert: Plot of the ellipticity at 390 nm as a function of ee.
Table S1. The ee determination of amines A1 and A5 with sensor 1 and of A3 and A4 with 2 using the calibration line for each analyte (Figs. 3 and S37-S39)

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8. Reference