Supporting Information

Iptycene Containing Azaacenes with Tunable Luminescence

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1. General methods

Materials. Acetic acid (AcOH, glacial, Macron), Benzene-1,2,4,5-tetraamine tetrahydrochlorid (technical grade, Sigma Aldrich), tBuBrettPhos (97% Sigma Aldrich), tBuXPhos (97% Sigma Aldrich), copper(I) iodide (purum, Sigma Aldrich), 4,7-dibromobenzo[c]-1,2,5-thiadiazole (95%, Sigma Aldrich), dichloromethane (CH$_2$Cl$_2$, 99.5%, containing amylene as stabilizer, Sigma Aldrich), 3,5-dimethoxyphenylboronic acid (95%, Sigma Aldrich), dimethyl sulfoxide (DMSO, anhydrous, 99.9%, Sigma Aldrich), hexane (Macron), 2-methoxybenzeneboronic acid (Alfa Aesar), 4-methoxybenzeneboronic acid (95%, Sigma Aldrich), 3-methoxythiophen-2-boronic acid pinacol ester (Sigma Aldrich), nitric acid (HNO$_3$, fuming, 90%, Sigma Aldrich), phenylboronic acid (TCI America), potassium phosphate (K$_3$PO$_4$, tribasic, Sigma Aldrich), RuPhos (95% Sigma Aldrich), silica gel (SiO$_2$, technical grade, Sigma Aldrich), tetrakis(triphenylphosphine)palladium (Pd(PPh$_3$)$_4$, 99%, Sigma Aldrich), thianaphthene-2-boronic acid (Sigma Aldrich), 2,5-thiophen diboronic acid (Sigma Aldrich), trifluoroacetic anhydride (TFAA, 99%, Sigma Aldrich), trifluoromethanesulfonic acid (TFMS, reagent grade, Sigma Aldrich), tri(iso-propyl)silylacetylene (TIPS-acetylene, 97%, Sigma Aldrich), XPhos (97%, Sigma Aldrich) and zinc powder (purum, Sigma Aldrich) were purchased commercially and used without any further purification. 9,10-dihydro-9,10-ethanoanthracene-11,12-diole (3) was already present in the group. Dry solvents were obtained from a solvent purification system and stored under argon atmosphere. High Resolution Mass Spectrometry (HRMS) experiments were executed with a Bruker Daltonics APEX IV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Nuclear Magnetic Resonance (NMR) experiments were carried out using a Varian Mercury 300, a Bruker Avance III-400 or a JEOL ECZ-500 NMR. Optical Measurements were carried out in a quartz cuvette (1 cm x 1 cm) filled with 3 ml hexane and a solution of the optical active compound in hexane/CH$_2$Cl$_2$. Absorption spectra were collected with a Cary 4000 UV-Vis spectrophotometer from Agilent Technologies and fluorescence spectra were collected with a Jobin Yvon FL3-21 system.

2. Synthesis and analytical data

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\begin{align*}
\text{Br} & \quad \text{CF}_3\text{SO}_2\text{H} \quad \text{HNO}_3 \quad 50 \degree C, 16 h \\ 
\text{Br} & \quad \text{NO}_2 \quad \text{NO}_2
\end{align*}
\]

According to a literature procedure,[1] TFMS (26.0 mL, 294 mmol) was added under stirring and ice cooling dropwise to fuming nitric acid (3.4 mL, 81.5 mmol). Next, 4,7-dibromobenzo[c][1,2,5]thiadiazole (7.5 g, 25.5 mmol) was added in small portions over 20 min. The reaction mixture was stirred at 50°C for 16 h, quenched by pouring on ice water and neutralized by addition of 4M NaOH (95 mL). The reaction mixture was filtered and the precipitate washed with
water and recrystallized from ethanol (300 mL). The product 5 (5.25 g 13.6 mmol, 54%) was obtained as off-white crystals. Further product (920 mg, 2.4 mmol, 9%) was obtained as light brown crystals by evaporating the mother lye and recrystallizing the residue.

Under argon atmosphere, DMSO (3.8 mL, 53.4 mmol) was dissolved in CH₂Cl₂ (215 mL) and cooled to -78°C where TFAA (6.5 mL, 45.9 mmol) was added over a period of 15 min. Then a solution of diol 3 (3.6 g, 15.1 mmol) in CH₂Cl₂ (81 mL) and DMSO (40.5 mL) was added over 30 min. After stirring for 1 h at -78°C, NEt₃ (14.6 mL, 105 mmol) the reaction was slowly warmed to room temperature over the course of 20 h. At this point, the reaction was quenched by the addition 2M hydrochloric acid (540 mL). The aqueous phase was extracted with CH₂Cl₂ (100 mL) eight times and the combined organic extracts were washed with water and dried over MgSO₄. Next, the solvent was evaporated and the residue was purified by column chromatography (SiO₂, CH₂Cl₂). The product (4, 2.86 g, 12.2 mmol, 80%) was obtained as yellow solid.

**NMR:** ¹H (400 MHz, CDCl₃) δ [ppm] = 7.48 (dd, J₃ = 5.5 Hz, J₄ = 3.2 Hz, 4H, CH), 7.38 (dd, J₃ = 5.5 Hz, J₄ = 3.2 Hz, 4H, CH), 5.00 (s, 2H, CH).

The optimized reaction was carried out in a 20 ml vial, containing zinc powder (470 mg, 7.2 mmol) suspended in AcOH (3.5 mL). Under stirring 5 (138 mg, 358 μmol) was added and the reaction mixture heated to 60°C for 60 min. The reduced colorless intermediate 6 was separated from the zinc powder by filtration through a pad of celite and added dropwise to a solution of 4 (61 mg, 260 μmol) in AcOH (1.5 mL) over 60 min. Immediately, a yellow precipitate was formed. The solution was stirred for further 60 min and then extracted several times with CH₂Cl₂ (20 mL) until the organic phase was colorless. The combined organic layers were washed with an aqueous NaHCO₃ solution (100 mL) and
water (100mL). After evaporation of the solvent, the crude product was purified via column chromatography (SiO₂, hexane/CH₂Cl₂ 3:1 → 0:1). The product (7, 65 mg, 93.8 μmol, 72%) was obtained as yellow powder.

**NMR:** 1H (400 MHz, CDCl₃) δ [ppm] = 7.59 (dd, J₃ = 5.4 Hz, J₄ = 3.2 Hz, 4H, CH), 7.17 (dd, J₃ = 5.4 Hz, J₄ = 3.2 Hz, 4H, CH), 5.84 (s, 4H, CH).

**Preparation of Compounds 8 – 13**

Preparation of compounds 8 – 13 (GP1): A Schlenk flask was filled with 7 (10 mg, 14.4 μmol), arylboronic acid (2.2 equiv., 31.7 μmol) and K₃PO₄ (12.3 mg, 57.8 μmol), evacuated and purged with argon. A mixture of water/toluene/1,4-dioxane (1:1.8:5.5, 0.5 mL) was added and the resulting suspension degassed with argon for 15 min. Subsequently, Pd₂(dba)₃ (0.4 mg, 0.437 μmol) and P(o-tol)₃ (1.1 mg, 3.61 μmol) were added, and the reaction was heated to 60 °C for 14 h. Upon full conversion of the starting material, the reaction was diluted with CH₂Cl₂ (10 mL) and washed with water (15 mL) three times. The organic phase was dried over MgSO₄, the solvent evaporated under reduced pressure and the crude purified by column chromatography (SiO₂, gradient of hexane/CH₂Cl₂).

Preparation of 8: According to GP1, 7 (10 mg) was coupled with 3,5- dimethoxybenzeneboronic acid (5.5 mg). The crude was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 2:1 → 0:1). The product (11, 11.6 mg, 14.4 μmol, 99%) was obtained as a yellow powder. ¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 7.47 (dd, J₃ = 5.4 Hz, J₄ = 3.2Hz, 8H, CH), 7.10 (dd, J₃=5.4Hz, J₄ =3.2 Hz, 8H, CH), 6.65 (t, J=2.3 Hz, 2H, CH), 6.62 (d, J = 2.3 Hz, 4H, CH), 5.58 (s, 4H, CH), 3.85 (s, 12H, CH₃). HRMS (ESI) m/z: [M + H]⁺: 807.2966; found 807.2954.

Preparation of 9: According to GP1, 7 (10 mg) was coupled with phenylboronic acid (3.9 mg). The crude was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 3:1 → 0:1). The product (9, 9.9 mg, 14.4 μmol, 99%) was obtained as a yellow powder. ¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 7.59 – 7.58 (m, 2H) 7.57 (d, J = 1.8 Hz, 4H, CH), 7.51- 7.50(m, 4H), 7.47 (dd, J₃ =5.4Hz, J₄ =3.2Hz, 8H, CH), 7.09 (dd, J₃ =5.4Hz, J₄ =3.2Hz, 8H, CH), 5.54 (s, 4H, CH). HRMS (ESI) m/z: [M + H]⁺: 687.2543; found 687.2539.

Preparation of 10: According to GP1, 7 (10 mg) was coupled with 2- methoxybenzeneboronic acid (4.8 mg). The crude was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 3:1 → 0:1). The product (10, 7.1 mg, 9.5 μmol, 66%) was obtained as a yellow powder. ¹H-NMR (300 MHz, CD₂Cl₂) δ [ppm] = 7.60 – 7.46 (m, 10H), 7.19 – 7.09 (m, 14H), 5.54 (s, 4H, CH), 3.54 (d, J = 13.5 Hz, 6H, CH) HRMS (ESI) m/z: [M + H]⁺: 747.2755; found 747.2745.
Preparation of 11: According to GP1, 7 (10 mg) was coupled with 4- methoxybenzeneboronic acid (4.8 mg). The crude was purified by column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ 2:1 $\rightarrow$ 0:1). The product (12, 10.7 mg, 14.4 μmol, 99%) was obtained as a yellow powder. $^1$H-NMR (300 MHz, CDCl$_3$) δ [ppm] = 7.49 – 7.47 (m, 8H), 7.46 (d, $J$ = 1.6 Hz, 4H, CH), 7.11 – 7.08 (m, 12H), 5.57 (s, 4H, CH), 4.00 (s, 6H, CH$_3$). HRMS (ESI) m/z: [M + H]$^+$: 747.2755; found 747.2736.

Preparation of 12: GP1 was carried out with 7 (10 mg) and 3-methoxythiophen-2- boronic acid pinacol ester (7.6 mg). The crude product was purified by column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ 2:1 $\rightarrow$ 0:1, including 10% NEt$_3$). The product (14, 7.5 mg, 9.9 μmol, 69%) was obtained as a yellow powder. HRMS (ESI) m/z: [M + H]$^+$: 759.1883; found 759.1900. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ [ppm] = 7.61 (m, 5H), 7.53 (9H, m), 7.14 (br, 13H), 5.63 (4H, br), 3.70, (br). Due to low solubility, only a poor NMR spectrum could be obtained.

Preparation of 13: According to GP1, 7 (10 mg) was coupled with thianaphthene-2- boronic acid (5.7 mg). The crude was purified by column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ 3:1 $\rightarrow$ 0:1). The product (13, 7.5 mg, 9.4 μmol, 65%) was obtained as an orange powder. Due to poor solubility, only a poor NMR spectrum could be obtained. HRMS (ESI) m/z: [M + H]$^+$: 799.1985; found 799.1967.

2.2 Analytical data

![Figure S1: $^1$H NMR of compound 4 in CD$_2$Cl$_2$.](image)
Figure S2: $^1$H NMR of compound 7 in CDCl$_3$.

Figure S3: $^1$H NMR of compound 8 in CDCl$_3$. 
Figure S4: $^1$H NMR of compound 9 in CDCl$_3$.

Figure S5: $^1$H NMR of compound 10 in CD$_2$Cl$_2$. 
Figure S4: $^1$H NMR of compound 11 in CDCl$_3$.

Figure S7: $^1$H NMR of compound 14 in CD$_2$Cl$_2$. 
Figure S8: $^1$H NMR of compound 15 in CDCl$_3$.

Figure S9: $^{13}$C ($^1$H) NMR of compound 15 in CDCl$_3$. 
3. Additional photophysical data

Figure S10: Absorption spectrum of 14 in CH₂Cl₂.

Figure S11: Absorption spectrum of 8 in hexane.

4. References