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**Experimental Section**

**General Methods**

NMR experiments (¹H NMR, ¹³C NMR) were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. The UV/Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell used), respectively.

**Materials**

Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures of the unknown compounds were confirmed via ¹H NMR, ¹³C NMR and High Resolution ESI mass spectroscopy. Compound 2, 3, 4, 6 were synthesized and purified according to the references 1-4, respectively.
Synthesis

Scheme 1. Synthesis of compound 5

Synthesis of compound 5

A mixture of compound 6 (1.00 g, 3.15 mmol) and 4-hydroxybenzaldehyde (0.58 g, 4.75 mmol) in dry N, N-dimethylformamide (30 mL) was refluxed overnight under argon atmosphere. After removal of the solvent, water (30 mL) was added, the mixture was extracted by CH$_2$Cl$_2$ (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The crude product was purified via column chromatography (SiO$_2$, PE/EA = 3/1) to give compound 5 (0.84 g, 74%) as a yellow solid.

$^1$H NMR (CDCl$_3$, 400 MHz, 298 K): $\delta$ 10.01 (s, 1H), 8.67 (dd, $J =1.2$ Hz, 7.6Hz, 1H), 8.57-8.51 (m, 2H), 8.01-7.92 (m, 2H), 7.79 (dd, $J =7.6$, 8.4 Hz, 1H), 7.31-7.23 (m, 3H), 7.13 (d, $J = 8.0$ Hz, 1H), 4.18-4.12 (m, 2H), 1.86-1.69 (m, 2H), 1.02 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K): $\delta$ 190.51, 164.02, 163.42, 160.80, 157.51, 133.09, 132.31, 132.21, 131.97, 129.68, 128.09, 126.98, 124.36, 122.82, 119.80, 118.31, 113.38, 41.90, 21.38, 11.52. HRMS (ESI) (m/z): [M+H]$^+$ calcd for C$_{22}$H$_{18}$NO$_4$, 360.1236; found, 360.1237.
**Scheme 2. Synthesis of compound 1**

**Synthesis of compound 1**

A mixture of compound 5 (0.50 g, 1.4 mmol) and 4 (0.53 g, 1.67 mmol) in dry toluene (20 mL) was refluxed overnight under argon atmosphere. The solvent was removed under vacuum, and the residue was dissolved in MeOH (25 mL). To the solution was added NaBH₄ (0.21 g, 5.5 mmol) in portion under ice bath. After the mixture was stirred for 4 h, the solution was poured into water, and the mixture was extracted by CH₂Cl₂ (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated to give the free amine compound. The residue was dissolved in MeOH (25 mL), and then added saturated NH₄PF₆ (10 mL). After the mixture was stirred at room temperature for 2 h, the solvent was removed under vacuum, and then water (30 mL) was added, the mixture was extracted by CH₂Cl₂ (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The crude product was purified via column chromatography (SiO₂, CH₂Cl₂/MeOH = 30/1) to give compound 1 (0.88 g, 72%) as a pale solid. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 8.69 (d, J = 8.4 Hz, 1H), 8.65 (d, J = 6.4 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.34-7.22 (m, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.89 (t, J = 8.4 Hz, 3H), 4.20-4.10 (m, 4H), 3.95 (t, J = 6.4 Hz, 2H), 3.85 (s, 2H), 3.80 (s, 2H), 3.51 (t, J = 6.4 Hz, 2H), 2.42 (t, J = 2.4 Hz, 1H), 1.83-1.74 (m, 5H), 1.63-1.55 (m, 2H), 1.52-1.42 (m, 2H), 1.38-1.26 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, 298 K): δ 164.41, 163.78, 159.97, 158.32, 153.69, 137.84, 132.77, 131.93, 131.83, 130.12, 129.68, 129.32, 128.52, 126.44, 123.89, 122.66, 120.69, 116.67, 116.55, 114.47, 110.48, 80.08, 74.07, 70.30, 68.05, 58.01, 53.44, 52.73, 52.39, 41.85, 29.51, 29.49, 29.41, 29.38, 29.31, 26.08, 21.43, 11.54.

Scheme 3. Synthesis of compound 1-R and 2-R

Synthesis of 2-R

A mixture of 1 (102 mg, 0.126 mmol), 2 (49 mg, 0.25 mmol) and [Cu(CH₃CN)₄]PF₆ (71 mg, 0.19 mmol) were stirred in dry CH₂Cl₂ (4 ml) at room temperature for three days. After removal of the solvent, the residue was dissolved in iodomethane (6 mL), and the mixture was stirred for 1 d at 40 °C. The excess iodomethane was evaporated, and the solid was washed with CH₂Cl₂ to give a yellow solid. To a suspension of the solid was then added saturated NH₄PF₆ (10 mL) and CH₃OH (6 mL), respectively. The resulted mixture was vigorously stirred at room temperature for 2 h. The aqueous
layer was extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The residue was purified via column chromatography (SiO₂, CH₂Cl₂/MeOH = 20/1) to give compound 2-R (103 mg, 70 %) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 8.69 (d, J = 8.4 Hz, 1H), 8.66 (d, J = 6.0 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.23 (s, 1H), 7.77 (dd, J =7.2, 7.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 2.0 Hz, 2H), 6.49 (t, J = 2.0 Hz, 1H), 5.55 (s, 2H), 4.66 (s, 2H), 4.28 (s, 3H), 4.20-4.10 (m, 2H), 3.94 (t, J = 6.4 Hz, 2H), 3.80 (s, 6H), 3.61-3.51 (m, 6H), 3.49 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz, 298 K): δ 164.44, 163.82, 161.70, 140.93, 132.79, 132.18, 131.87, 130.98, 130.26, 129.93, 129.71, 128.87, 128.55, 126.48, 123.94, 122.68, 120.55, 116.60, 114.35, 110.59, 107.30, 102.23, 72.27, 68.00, 61.23, 60.73, 60.08, 57.83, 55.63, 53.42, 41.85, 29.78, 29.70, 29.53, 29.48, 29.42, 29.39, 29.32, 29.27, 27.22, 26.02, 25.91, 25.54, 21.43, 11.52. HRMS (ESI) (m/z): [M–2PF₆]²⁺ calcd for C₁₀₀H₁₁₅Fe₂N₅O₁₉, 434.7358; found, 434.7346.

**Synthesis of 1-R**

A mixture of 1 (102 mg, 0.126 mmol) and crown ether 3 (234 mg, 0.25 mmol) were stirred in dry CH₂Cl₂ (5 mL) at room temperature for 1 h. Then 2 (49 mg, 0.25 mmol) and [Cu(CH₃CN)₄]PF₆ (70.6 mg, 0.19 mmol) were added to the solution, the mixture was stirred for three days. After removal of the solvent, the residue was dissolved in iodomethane (6 mL), and the mixture was stirred for 1 d at 40°C. The excess iodomethane was evaporated, and the solid was washed with CH₂Cl₂ to give a yellow solid. To a suspension of the solid was then added saturated NH₄PF₆ (10 mL) and CH₃OH (6 mL), respectively. The resulted mixture was vigorously stirred at room temperature for 2 h. The aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The organic layer was dried over anhydrous sodium sulfate, and then concentrated. The residue was purified via column chromatography (SiO₂, CH₂Cl₂/MeOH = 20/1) to give compound 1-R (47 mg, 40 %) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 8.63 (d, J = 7.2 Hz, 1H), 8.59 (dd, J = 1.2, 8.4Hz, 1H), 8.41 (dd, J = 1.6, 8.4 Hz, 1H), 8.23 (s, 1H), 7.776 (t, J = 8.4 Hz, 1H), 7.31 (dd, J =2.8, 8.8Hz, 2H), 7.24 (d, J =
SUPPLEMENTARY INFORMATION

2.0 Hz, 2H), 7.02 (dd, J = 2.0, 8.4 Hz, 2H), 6.97-6.98 (m, 4H), 6.83-6.77 (m, 4H), 6.73-6.68 (m, 1H), 6.59 (d, J = 2.4 Hz, 2H), 6.45 (t, J = 2.0 Hz, 1H), 5.54 (s, 2H), 5.14 (s, 4H), 4.75-4.68 (m, 4H), 4.66 (s, 2H), 4.60-4.53 (m, 2H), 4.51-4.43 (m, 2H), 4.33-4.27 (m, 4H), 4.25 (s, 3H), 4.18 (s, 2H), 4.14-4.05 (m, 8H), 4.02 (s, 10H), 3.90 (t, J = 6.6 Hz, 2H), 3.84-3.73 (m, 14H), 3.55-3.45 (m, 10H), 1.78-1.73 (m, 2H), 1.69-1.62 (m, 5H), 1.56-1.53 (m, 2H), 1.45-1.41 (m, 2H), 1.35-1.26 (m, 10H). $^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K): δ 174.76, 170.52, 163.28, 162.62, 160.49, 158.94, 157.83, 154.56, 146.36, 139.96, 131.62, 131.47, 130.93, 130.42, 129.77, 129.20, 128.89, 128.64, 127.79, 127.76, 127.44, 125.73, 123.00, 122.03, 121.63, 121.11, 119.38, 116.16, 113.75, 112.35, 111.54, 110.15, 106.12, 101.38, 70.91, 70.45, 69.75, 69.69, 69.11, 68.67, 67.37, 67.05, 64.48, 59.00, 56.58, 54.60, 54.58, 51.35, 50.63, 40.85, 37.44, 28.76, 28.68, 28.30, 28.24, 28.18, 28.08, 28.00, 26.20, 24.79, 24.74, 21.67, 20.40, 13.10, 10.53. HRMS (ESI) (m/z): [M–2PF$_6$]$^{2+}$ calcd for C$_{100}$H$_{115}$Fe$_2$N$_5$O$_{19}$, 901.3454; found, 901.3438.

The photophysical property of 1-R

![Fig. S1](image_url) The UV/Vis absorption spectrum changes of [2]rotaxane 1-R (1×10$^{-5}$ M, CHCl$_3$, r.t.), the mixture obtained after adding 1.2 equiv. DBU to the solution of 1-R, and the mixture obtained after adding 2.0 equiv. TFA to the DBU-added solution of 1-R.
**Fig. S2** Fluorescence intensity of rotaxane 1-R (1×10⁻⁵ M, CHCl₃, r.t.) at 421 nm upon addition of alternate compound (DBU and TFA) for three cycles. The excitation wavelength is 365 nm.

**Fig. S3** Fluorescence intensity of PBI 1 (1×10⁻⁵ M, CHCl₃, r.t.) at 543 nm upon addition of alternate compound (TFA and DBU) for three cycles. The excitation wavelength is 365 nm.
Table S1. Fluorescence quantum yield of white light emission in CHCl₃ at r.t. (λₑₓ = 365 nm)

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<th>Compound</th>
<th>molar ratio</th>
<th>TFA (equiv.)</th>
<th>Φⁿ (%)</th>
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<tr>
<td>1-R -H &amp; PBI 1</td>
<td>1:1</td>
<td>2.2</td>
<td>0.52</td>
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</table>

⁻ Quantum yields were calculated using anthracene (C₂H₅OH, Φᵣ = 0.31) as reference and using the following formula $Φ = Φᵣ \times \frac{F}{Fᵣ} \times \frac{Aᵣ}{A} \times \frac{(n/nᵣ)^2}$. Where $Φ$ = quantum yield, $F$ = emission intensity, $A$ = absorbance, $n$ = refractive index of solvent, $R$ = reference.

Reference:

\(^1\)H NMR, \(^{13}\)C NMR and Mass spectra

Compound 5
SUPPLEMENTARY INFORMATION

Elemental Composition Report

**Single Mass Analysis**
- Tolerance = 5.0 PPM
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 2

**Monoisotopic Mass, Even Electron Ions**
- 6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
- Elements Used:
  - C: 0-22
  - H: 0-18
  - N: 0-1
  - O: 0-4

**Minimum:**
- Calc. Mass
- mDa
- PPM
- DBE
- i-FIT
- i-FIT (Norm)
- Formula

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<th>Mass</th>
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<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
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<td>0.1</td>
<td>0.3</td>
<td>14.5</td>
<td>45.0</td>
<td>0.0</td>
<td>C22 H10 N O4</td>
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</tbody>
</table>

**Compound 1**
**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 5.0 PPM  
DBE: min = -1.5, max = 50.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ion  
10 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 0-42  
H: 0-46  
N: 0-2  
O: 0-5

**Minimum:**  
661.3649  
**Maximum:**  
661.3641  
**Calculated Mass:**  
661.3641  
**mDa:**  
0.8  
**FPM:**  
12  
**DBE:**  
19.5  
**i-FIT:**  
19.6  
**i-FIT (Norm):**  
0.0  
**Formula:**  
c42 h40 n2 o5
Compound 2-R
Compound 1-R

[Spectroscopic data and analysis]