Host–guest complexation induced emission: a pillar[6]arene-based complex with intense fluorescence in dilute solution

Pi Wang, Xuzhou Yan and Feihe Huang*

State Key Laboratory of Chemical Engineering,
Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China;
Fax and Tel: +86-571-8795-3189; Email address: fhuang@zju.edu.cn.

Electronic Supplementary Information (13 pages)

1. Materials and methods
2. Synthesis of compound 1
3. Synthesis of compound 2
4. NOESY NMR spectra of WP6 with 1 and 2 in D2O
5. Stoichiometry and association constant determination for WP6\(\supset\)2 in H2O

Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2014
1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound 1 was synthesized by a published literature procedure. $^1$H NMR spectra were collected on a temperature-controlled 400 MHz or 500 MHz spectrometer. $^{13}$C NMR spectra were recorded on a Bruker AVANCE DMX-400 or DMX-500 spectrometer. Low-resolution electrospray ionization mass spectra (LRESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization mass spectra (HRESI-MS) were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Transmission electron microscopy (TEM) investigations were carried out on a JEM-1200EX instrument. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Atomic force microscopy (AFM) investigations were carried out on a Multi-Mode 8 instrument.
2. Synthesis of compound 1

Compound 3\(^{S1}\) (0.450 g, 0.500 mmol) and trimethylamine (33 % in ethanol, 6.50 mL, 25.1 mmol) were added to ethanol (50.0 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation and deionized water (20.0 mL) was added. After filtration, a clear solution was got. Then water was removed by evaporation to obtain 1 as a colorless solid (0.53 g, 95 %). The \(^1\)H NMR spectrum of 1 is shown in Fig. S1. \(^1\)H NMR (400 MHz, D\(_2\)O, 298 K) \(\delta\) (ppm): 6.91 (s, 8H), 6.60 (s, 8H), 3.83 (s, 8H), 3.25 (s, 8H), 2.99 (s, 36H), 1.71 (d, \(J = 32\) Hz, 16H). The \(^{13}\)C NMR spectrum of 1 is shown in Fig. S2. \(^{13}\)C NMR (125 MHz, D\(_2\)O, 298 K) \(\delta\) (ppm): 156.51, 138.95, 137.24, 132.42, 114.03, 67.31, 66.10, 52.81, 25.25, 19.36. LRESIMS is shown in Fig. S3: \(m/z\) 1702.5 [M – 4Br]\(^{4+}\) (100%).

Fig. S1. \(^1\)H NMR spectrum (400 MHz, D\(_2\)O, 298 K) of 1.
**Fig. S2.** $^{13}$C NMR spectrum (125 MHz, D$_2$O, 298 K) of 1.

**Fig. S3.** Electrospray ionization mass spectrum of 1. The peak at m/z 213.2 corresponding to [M − 4Br]$^{4+}$ was clearly observed.
3. Synthesis of compound 2

A mixture of phenol (0.473 g, 5.00 mmol), 1,4-dibromo butane (1.32 g, 6.00 mmol) and K$_2$CO$_3$ (1.53 g, 11.0 mmol) in 35.0 mL of dry acetonitrile was refluxed under N$_2$ atmosphere for 24 h. Then the crude product was purified by a silica gel column using petroleum ether-dichloromethane (2:1, v/v) as the eluent. Compound 4 was obtained in 75% yield (1.33 g). The $^1$H NMR spectrum of 4 is shown in Fig. S4. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.21–7.18 (m, 2H), 6.87 (t, J = 16 Hz, H), 6.82 (t, J = 8 Hz, 2H), 3.93 (t, J = 12 Hz, 2H), 3.43 (t, J = 12 Hz, 2H), 2.04–1.97 (m, 2H), 1.91–1.84 (m, 2H). The $^{13}$C NMR spectrum of 4 is shown in Fig. S5. $^{13}$C NMR (125 MHz, CDCl$_3$, 298 K) δ (ppm): 158.86, 129.48, 120.75, 116.46, 66.70, 33.51, 29.52, 27.94.

![Figure S4](image-url)  
*Fig. S4.* $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of 4.
Compound 4 (1.00 g, 4.10 mmol) and trimethylamine (33 % in ethanol, 30.0 mL, 105 mmol) were added to ethanol (55.0 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation and deionized water (35.0 mL) was added. After filtration, water was removed by evaporation to obtain 2 as a colorless solid (1.13 g, 93 %). The $^1$H NMR spectrum of 2 is shown in Fig. S6. $^1$H NMR (400 MHz, D$_2$O, 298 K) $\delta$ (ppm): 7.31 (t, $J$ = 16 Hz, 2H), 7.00–6.95 (m, 3H), 4.07 (t, $J$ = 12 Hz, 2H), 3.31 (t, $J$ = 16 Hz, 2H), 3.03 (s, H), 1.90 (t, $J$ = 16 Hz, 2H), 1.80–1.75 (m, 2H). The $^{13}$C NMR spectrum of 2 is shown in Fig. S7. $^{13}$C NMR (125 MHz, D$_2$O, 298 K) $\delta$ (ppm): 157.90, 129.87, 121.51, 114.82, 67.24, 66.12, 52.73, 25.15, 19.33. LRESIMS is shown in Fig. S8: $m/z$ 208.2 [M – Br]$^+$ (100%).
**Fig. S6.** $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of 2.

**Fig. S7.** $^{13}$C NMR spectrum (125 MHz, D$_2$O, 298 K) of 2.
**Fig. S8.** Electrospray ionization mass spectrum of 2. The peak at \( m/z \) 208.2 corresponding to \([M – Br]^+\) was clearly observed.

4. NOESY NMR spectra of WP6 with 1 and 2 in D$_2$O

**Fig. S9.** Partial $^1$H NMR spectra (400 MHz, D$_2$O, 298 K): (a) 3.00 mM 1; (b) 3.00 mM 1 and WP6; (c) 3.00 mM WP6. In Fig. S9, the chemical shift differences between free guest 1 and complexed guest 1 are much smaller than those obtained for the control compound 2 (Fig. S11). This is understandable. First, both the complexation between 1 and WP6 and the complexation between 2 and WP6 are fast exchange on the proton NMR time scale. Second, there are 12.0 mM trimethyl ammonium units for 3.00 mM WP6 to bind in Fig. S9 while there are only 3.00 mM trimethyl ammonium units for 3.00 mM WP6 to bind in Fig. S11.
**Fig. S10.** Partial NOESY NMR spectrum (500 MHz, D$_2$O, 298 K) of 10.0 mM WP6 and 1.

**Fig. S11.** Partial $^1$H NMR spectra (400 MHz, D$_2$O, 298 K): (a) 3.00 mM 2; (b) 3.00 mM 2 and WP6; (c) 3.00 mM WP6.
Fig. S12. Partial NOESY NMR spectrum (500 MHz, D$_2$O, 298 K) of 10.0 mM WP6 and 2.

5. Stoichiometry and association constant determination for WP6$\supset$2 in H$_2$O

To determine the stoichiometry and association constant of WP6$\supset$2, $^1$H NMR titration was done. By a non-linear curve-fitting method, the association constant between the guest and host was calculated. By a mole ratio plot, the stoichiometry was determined.

The non-linear curve-fitting was based on the equation:$^{52}$

$$
\Delta \delta = (\Delta_\delta / [WP6]_0) \left( 0.5[2]_0 + 0.5([WP6]_0 + 1/K_a) - (0.5 ([2]_0^2 + (2[2]_0(1/K_a - [WP6]_0)) + (1/K_a + [WP6]_0)^2)^{0.5}) \right)
$$

(Eq. S1)

Where $\Delta \delta$ is the chemical shift change of H$_b$ on WP6 at [2]$_0$, $\Delta_\delta$ is the chemical shift change of H$_b$ when the host is completely complexed, [WP6]$_0$ is the fixed initial concentration of the host, and [2]$_0$ is the varying concentration of guest 2.
Fig. S13. $^1$H NMR spectra (400 MHz, D$_2$O, 293 K) of WP6 at a concentration of 1.00 mM with different concentrations of 2: (a) 0.00 mM; (b) 0.196 mM; (c) 0.385 mM; (d) 0.566 mM; (e) 0.741 mM; (f) 0.909 mM; (g) 1.07 mM; (h) 1.23 mM; (i) 1.53 mM; (j) 1.94 mM; (k) 2.48 mM; (l) 3.10 mM; (m) 3.94 mM.

Fig. S14. The chemical shift changes of H$_b$ on WP6 upon addition of 2. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.
**Fig. S15.** Mole ratio plot for the complexation between WP6 and 2, indicating a 1:1 stoichiometry.

**Fig. S16.** Complete NOESY NMR spectrum (500 MHz, D$_2$O, 298 K) of 10.0 mM WP6 and 1.
Fig. S17. AFM images of the inclusion complex between WP6 and 1. These AFM images further confirmed the wheel-like structure formation, as the TEM images showed in Fig. 3d and 3e.

References:
