Supporting Information

smart Porphyrin Cage for Recognizing azide anion

Jianhong Zhang\textsuperscript{a,b}, Yongjun Li\textsuperscript{*a}, Wenlong Yang\textsuperscript{a,b}, Sui-Wai Lai\textsuperscript{c}, Chunjie Zhou\textsuperscript{a,b}, Huibiao Liu\textsuperscript{a}, Chi-Ming Che\textsuperscript{c}, Yuliang Li\textsuperscript{*a}

Table of contents

1. Synthesis of 1 and 3
2. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra
3. NOESY spectrum of 1 in CD\textsubscript{2}Cl\textsubscript{2}
4. UV–vis spectrum of the cage 1 with N\textsubscript{3}– in CH\textsubscript{2}Cl\textsubscript{2}, THF, acetone
5. \textsuperscript{1}H NMR spectra of the cage 1 in d\textsubscript{6}-acetone at 298 K upon titrational addition of TBASCN
6. UV–vis spectrum of the cage 1 with SCN– in acetone
7. X-ray crystal structure of 1

1. Synthesis of 1 and 3:

\[
\begin{align*}
\text{H}_N^+ + &\text{CHO} \rightarrow \text{BBF}_{2}\text{EtO} \\
&\text{DDQ, EtN} \rightarrow \text{N}_3 \rightarrow \text{N}_3 \rightarrow \text{Zn(CHA)O}_2 \rightarrow \text{N}_3 \rightarrow 3
\end{align*}
\]

The synthesis of 3:

To a solution of 4- (azidomethyl) benzaldehyde (1.61 g, 10 mmol) and pyrrole
(0.67 g, 10 mmol) in CHCl₃ (400 mL), degassed (argon) for 30 minutes, were added
BF₃·Et₂O (356 µl, 2.8 mmol). The solution was stirred at room temperature for 1 h and
added DDQ (1.96 g, 8.6 mmol). The suspension was stirred for 0.5 h, then Et₃N
m(389 µl, 2.8 mmol) was added. Stirred for five minute, Zn(AcO)₂(4.53 g, 30 mmol)
in CH₃OH (18 ml) was added. The solution was stirred for 12 h continuously. The
solution was concentrated under reduced pressure. The residue was purified by
column chromatography to give 3 (petroleum ether : CHCl₃ 1:1 as eluent) (2.6 g, yield
= 30%). ¹H NMR (400 MHz, CDCl₃) δ 8.86 (s, 8 H), 8.25 (d, J = 7.6Hz, 8H), 7.70 (d,
J = 7.6Hz, 8H), 4.70 (s, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 149.3, 142.5, 134.9,
134.4, 131.6, 126.6, 119.9, 53.7. MALDI-TOF, Calcd for C₄₈H₃₂N₁₆Zn: 896.2; Found
896.4. Anal. Calcd for C₄₈H₃₂N₁₆Zn: C, 64.18; H, 3.59; N, 24.95; Found: C, 64.16; H,
3.60; N, 24.93.
The porphyrin 3 was prepared by the literature (1): Y. Liu, C.F Ke, H. Y.

<Diagram of 1, 2, and 3>

Synthesis of 1:
1, 8-Diaza [5.4.0] bicycloundec-7-ene (DBU) (4.0 mmol, 0.7 mL) was added to
toluene (400 mL), degassed (argon) for 30 minutes and heated to 75 °C while flushing
with argon. At 75 °C, CuI (0.05 mmol, 9.5 mg) was added to the mixture. A solution
of the 2 (89.4 mg, 0.1 mmol) and 3 (89.6 mg, 0.1 mmol) in THF (5 mL) and toluene
(50 mL) was added to the solution slowly over 12 h and stirred for another 12 h under
argon. The reaction was quenched with water and washed with H₂O (100 mL × 3),
dried over anhydrous MgSO₄ and concentrated under reduced pressure. The mixture
was concentrated in vacuo. The product was purified via chromatography (SiO₂, CHCl₃ : methanol 30 : 1) to afford 1 (104 mg, 55% yield) as a purple solid. ¹H NMR (400 MHz, (CD₃)CO  δ 8.40 (s, 8H), 8.37 (s, 8H), 8.34 (s, 4H), 8.12 (d, J = 8 Hz, 1 H), 7.88 (d, J = 8 Hz, 1H), 7.75 (d, J = 8Hz, 1H), 7.40 (d, J = 8Hz, 1H), 7.26 (d, J = 8Hz, 1H), 7.15 (m, 2H), 6.92 (d, J = 8Hz, 1H), 6.05 (s, 8H), 5.66 (s, 8H) MALDI-TOF (M), Calcd for C₁₀₄H₆₈N₂₀O₄Zn₂ (M) 1788.4; Found 1788.6.

2. ¹H NMR and ¹³C NMR

¹H NMR spectrum (400 MHz, 298 K, d₆-acetone) of 1
$^{13}$C NMR spectrum (100 MHz, 298 K, CDCl$_3$) of 3

$^1$H NMR spectrum (400 MHz, 298 K, $d_6$-acetone) of 1+pyridine
$^1$H NMR spectrum (400 MHz, 298 K, $d_6$-acetone) of 2+$\text{TAN}_3$
3. NOESY spectrum of 1 in $d_6$-acetone at 258 K
4. UV–vis spectrum of the cage 1 with $\text{N}_3^-$ in $\text{CH}_2\text{CCl}_2$, THF, acetone

UV–vis titration of the cage 1 (10 $\mu$M in $\text{CH}_2\text{Cl}_2$) with $\text{N}_3^-$ (up to 15 equal)

UV–vis titration of the cage 1 (10 $\mu$M in acetone) with $\text{N}_3^-$ (up to 9)
UV–vis titration of the cage 1 (10 μM in THF) with N₃ (up to 4 equal)
5. $^1$H NMR spectra of the cage 1 in $d_6$-acetone at 298 K upon titrational addition of TBASCN

$^1$H NMR spectra of the cage 1 in $d_6$-acetone at 298 K upon titrational addition of TBASCN
6. UV–vis spectrum of the cage 1 with SCN$^-$ in acetone

UV–vis titration of the cage 1 (10 μM in acetone) with SCN$^-$ (up to 8 equal)
7. X-ray crystal structure of 1.

The crystal A of 1 was obtained in pyidine and acetone.

The crystal B of 1 was obtained in THF