Supporting Information

A Bowl-Shaped Organic Host Using Bispyridine Ligands: Selective Encapsulation of Carbonyl Guests in Water

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Materials and methods

Solvents and reagents: TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO CHEMICAL CO., INC., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. Bispyridine ligand 2 was synthesized according to previously reported procedures (M. Yoshizawa et al., J. Am. Chem. Soc. 2011, 133, 11438–11441).

**Synthesis of Bowl-shaped Host 1a**

Bispyridine ligand 2 (0.101 g, 0.138 mmol), diiodomethane (2.66 g, 9.93 mmol), and MeCN (70 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar under N₂. The mixture was stirred at 80 °C for 10 d and then concentrated under reduce pressure. The crude product was washed with MeOH, CHCl₃, and acetone to afford bowl 1a as a red solid (40.7 mg, 20.3 µmol, 29% yield).

**1H NMR (400 MHz, DMSO-<d₆>, r.t.):** δ 9.97 (d, J = 6.4 Hz, 4H), 9.81 (s, 4H), 8.94 (d, J = 8.0 Hz, 4H), 8.79 (dd, J = 6.4, 8.0 Hz, 4H), 7.86 (d, J = 7.2 Hz, 8H), 7.72 (br, 2H) 7.56–7.47 (m, 24H), 7.30 (s, 2H), 7.16 (br, 2H), 6.84 (s, 2H), 4.17 (t, J = 4.5 Hz, 8H), 3.26 (t, J = 4.5 Hz, 8H), 2.76 (s, 12H).

**13C NMR (100 MHz, DMSO-<d₆>, r.t.):** δ 158.5 (Cₗ), 151.8 (CH), 146.8 (CH), 146.1 (CH), 140.1 (Cₓ), 136.5 (Cₓ), 134.4 (CH), 130.1 (CH, 2 x Cₓ), 127.5 (CH), 127.2 (CH, Cₓ), 126.2 (CH), 126.0 (CH), 118.8 (Cₓ), 100.5 (CH), 78.2 (CH₂), 70.6 (CH₂), 68.9 (CH₂), 58.4 (CH₃).

**DOSY NMR (400 MHz, DMSO-<d₆>, 298 K):** D = 2.40 x 10⁻¹⁰ m² s⁻¹.

**FT-IR (KBr, cm⁻¹):** 3047, 3012, 2929, 1607, 1576, 1506, 1457, 1456, 1387, 1312, 1267, 1194, 1157, 1127, 1102, 1053, 1028, 982, 950, 905, 852.

**ESI-TOF MS (CH₃CN):** m/z Calcd. 373.4, Found 373.4 [M – 4I]⁺⁺.

**E.A.:** Calcd. for C₁₀₂H₈₂O₈N₄I₇•1.5H₂O: C, 50.85; H, 3.64; N, 2.33. Found: C, 50.57; H, 3.26; N, 2.36.
Fig. S1. $^1$H NMR (400 MHz, DMSO-$d_6$, 10 mM, r.t.) spectrum of 1a.

Fig. S2. $^{13}$C NMR (100 MHz, DMSO-$d_6$, 10 mM, r.t.) spectrum of 1a.
Fig. S3a. HH COSY (400 MHz, DMSO-$d_6$, 10 mM, r.t.) spectrum of 1a (aliphatic region).

Fig. S3b. HH COSY (400 MHz, DMSO-$d_6$, 10 mM, r.t.) spectrum of 1a (aromatic region).
Fig. S4a. NOESY (400 MHz, DMSO-d$_6$, 10 mM, r.t.) spectrum of 1a.

Fig. S4b. NOESY (400 MHz, DMSO-d$_6$, 10 mM, r.t.) spectrum of 1a (aromatic region).
Fig. S5a. HSQC (400 MHz, DMSO-\textit{d}_6, 10 mM, r.t.) spectrum of 1a (aliphatic region).

Fig. S5b. HSQC (400 MHz, DMSO-\textit{d}_6, 10 mM, r.t.) spectrum of 1a (aromatic region).
**Fig. S6.** DOSY NMR (400 MHz, DMSO-\textit{d}_6, 10 mM, 298 K) spectrum of bowl 1a.

**Display Report**

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- **Method:** Pd_complex.m
- **Sample Name:**
- **Comment:**

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- **Waste**

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- **Calcd. 373.4075**

*Fig. S7.** ESI-TOF MS spectrum of bowl 1a.
Bowl 1a (250.6 mg, 125.2 µmol), Amberlite IRA-400 (8.11 g), MeOH (50 mL), and H₂O (20 mL) were added to a 200 mL glass flask containing a magnetic stirring bar. The mixture was stirred at r.t. for 8 h and then filtrated. The filtrate was concentrated under reduce pressure. An excess amount of HCl aq. was added to the solution. The obtained precipitates were collected and then dissolved in water. An excess amount of acetone was added to the solution to yield a yellow solid. The solid was washed with acetone to afford bowl 1b as a yellow solid (108.8 mg, 66.52 µmol, 53% yield).

\[ ^1H \text{ NMR (400 MHz, } D_2O, \text{ r.t.)}: \delta 9.89 (br, 4H), 9.48 (br, 4H), 8.96 (br, 4H), 8.71 (br, 4H), 7.93–7.23 (br, 38H), 6.95 (br, 2H), 4.09 (br, 8H), 3.23 (br, 8H), 2.57 (br, 12H). \]

\[ ^13C \text{ NMR (100 MHz, } D_2O, \text{ r.t.)}: \delta 158.1 (C_q), 153.2 (CH), 145.9 (CH), 141.3 (CH), 136.3 (C_p), 130.6 (C_p), 129.8, 127.5, 126.8, 126.4, 126.0, 124.8, 119.9, 101.2 (CH), 78.5 (CH_2), 70.5 (CH_2), 68.9 (CH_2), 57.8 (CH_3). \]

DOSY NMR (400 MHz, DMSO, 300 K): \(D = 7.4 \times 10^{-10} \text{ m}^2 \text{s}^{-1}.\)

FT-IR (KBr, cm⁻¹): 3410, 3060, 2935, 1627, 1605, 1574, 1505, 1443, 1387, 1312, 1268, 1197, 1160, 1126, 1103, 1054, 1031, 982, 906, 852, 817, 771.

ESI-TOF MS (H₂O): \(m/z 373.4[1b – 4Cl^-]^{4+}, 509.5[1b – 3Cl^-]^{3+}, 782.3[1b – 2Cl^-]^{2+}.\)

E.A.: Calcd. for C₁₀₂H₈₄O₈N₄Cl₄•2CHCl₃•3H₂O: C, 64.77; H, 4.81; N, 2.91. Found: C, 64.49; H, 4.72; N, 3.05.
Fig. S8. $^1$H NMR (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b.

Fig. S9. DOSY NMR (400 MHz, D$_2$O, 4 mM, 300 K) spectrum of bowl 1b.
Encapsulation of Benzoin (3) by Bowl 1b

Benzoin (3; 2.1 mg, 9.9 µmol) was added to a D$_2$O solution (0.3 mL) of bowl 1b (2.0 mg, 1.2 µmol) and the mixture was stirred at r.t. for 3 h. After filtration, the quantitative formation of a 1b⊃3 compound was confirmed by NMR and ESI-TOF MS analyses.

$^1$H NMR (400 MHz, D$_2$O, r.t.): $\delta$ 9.93 (d, $J$ = 6.2 Hz, 4H), 9.72 (s, 4H), 8.99 (d, $J$ = 7.0 Hz, 4H), 8.72 (dd, $J$ = 6.2, 7.0 Hz, 4H), 7.85–7.49 (br, 38H), 7.22 (br, 2H), 6.25 (br, 2H), 5.88 (br, 1H), 5.69 (br, 2H), 5.64 (br, 1H), 5.47 (br, 4H), 5.27 (br, 2H), 4.10 (br, 8H), 3.25 (br, 8H), 2.57 (br, 12H).

$^{13}$C NMR (100 MHz, D$_2$O, r.t.): $\delta$ 197.6 (C=O), 158.2 (C$_q$), 153.3 (CH), 145.9 (CH), 145.7 (CH), 141.6 (C$_q$), 137.0 (3), 136.4 (C$_q$), 135.3 (3), 131.9 (3), 130.6 (CH), 129.8, 128.0, 127.6, 127.1, 126.6, 126.4, 126.0, 125.8, 124.8, 119.9 (C$_q$), 101.1 (CH), 78.9 (CH$_2$), 75.4 (3), 70.2 (CH$_2$), 69.2 (CH$_2$), 57.9 (CH$_3$).

DOSY NMR (400 MHz, D$_2$O, 300 K): $D = 5.89 \times 10^{-10}$ m$^2$ s$^{-1}$.

FT-IR (KBr, cm$^{-1}$): 3409, 3061, 2934, 1683 (C=O), 1627, 1605, 1577, 1505, 1445, 1388, 1313, 1268, 1196, 1160, 1127, 1103, 1056, 1030, 974, 905, 852, 817,770.

ESI-TOF MS (H$_2$O): $m/z$ 426.4 [1b⊃3 – 4Cl$^-$$]^{4+}$. 

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Fig. S10. $^1$H NMR (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b$\supset$3.

Fig. S11. $^{13}$C NMR (100 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b$\supset$3.
Fig. S12a. HH-COSY (400 MHz, D₂O, 4 mM, r.t.) spectrum of 1b⁻⁻３ (aromatic region).

Fig. S12b. HH-COSY (400 MHz, D₂O, 4 mM, r.t.) spectrum of 1b⁻⁻３ (aromatic region).
**Fig. S13a.** NOESY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊃3.

**Fig. S13b.** NOESY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊃3. (host-guest region).
Encapsulation of Benzil (4) by Bowl 1b

Benzil (4; 1.1 mg, 5.2 µmol) was added to a D₂O solution (0.28 mL) of capsule 1b (1.9 mg, 1.2 µmol) and the mixture was stirred at r.t. for 3 h. After filtration, the quantitative formation of a 1b⊃4 compound was confirmed by NMR.

¹H NMR (400 MHz, D₂O, r.t.): δ 9.92 (d, J = 5.8 Hz, 4H), 9.51 (s, 4H), 9.02 (d, J = 7.4 Hz, 4H), 8.74 (dd, J = 7.4, 5.8 Hz, 4H), 7.83–7.27 (br, 38H), 6.65 (br, 2H), 6.30 (br, 2H), 6.04 (br, 4H), 5.65 (br, 4H), 4.18 (br, 8H), 3.35 (br, 8H), 2.69 (br, 12H).

DOSY NMR (400 MHz, D₂O, 301 K): D = 6.5 x 10⁻¹⁰ m² s⁻¹.

FT-IR (KBr, cm⁻¹): 3399, 3062, 2934, 1960, 1680 (C=O), 1662 (C=O), 1628, 1577, 1505, 1448, 1388, 1313, 1268, 1197, 1160, 1127, 1103, 1055, 1030, 982, 905, 853, 815, 770, 725. ESI-TOF MS (H₂O): m/z 425.9 [1b⊃4 – 4Cl]⁺.

Fig. S14. DOSY (400 MHz, D₂O, 4 mM, 300 K) spectrum of 1b⊃3.
Fig. S15. $^1$H NMR (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊃4.

Fig. S16. DOSY (400 MHz, D$_2$O, 4 mM, 301 K) spectrum of 1b⊃4.
Encapsulation of Benzanilide (5) by Bowl 1b

Benzanilide (5; 1.5 mg, 7.6 µmol) was added to a D₂O solution (0.3 mL) of bowl 1b (2.1 mg, 1.3 µmol) and the mixture was stirred at r.t. for 3 h. After filtration, the selective formation of 1b⊃5 compound was confirmed by NMR (~80% yield).

¹H NMR (400 MHz, D₂O, r.t.): δ 9.93 (br, 4H), 9.96 (br, 4H), 8.86 (br, 4H), 8.74 (br, 4H), 7.92–7.25 (br, 38H), 6.85 (br, 2H), 6.36 (br), 5.98 (br), 5.57 (br), 4.12 (br, 8H), 3.26 (br, 8H), 2.58 (br, 12H).

DOSY NMR (400 MHz, D₂O, 305 K): D = 6.6 x 10⁻¹⁰ m² s⁻¹.

Fig. S17a. ¹H NMR (400 MHz, D₂O, 4 mM, r.t.) spectrum of 1b⊃5.
**Fig. S17b.** $^1$H NMR (400 MHz, D$_2$O, 4 mM, 333 K) spectrum of 1b⊃5.

**Fig. S18.** DOSY NMR (400 MHz, D$_2$O, 4 mM, 305 K) spectrum of 1b⊃5.
Encapsulation of 2-Methyl-1,4-naphthoquinone (6) by Bowl 1b

KY210

2-Methyl-1,4-naphthoquinone (6; 2.0 mg, 11.6 µmol) was added to a D$_2$O solution (0.3 mL) of bowl 1b (2.0 mg, 1.2 µmol) and the mixture was stirred at r.t. for 3 h. After filtration, the quantitative formation of a 1b⊃(6)$_2$ compound was confirmed by NMR and ESI-TOF MS analyses.

$^1$H NMR (400 MHz, D$_2$O, r.t.): δ 10.01 (d, J = 6.6 Hz, 4H), 9.88 (s, 4H), 9.03 (d, J = 7.6 Hz, 4H), 8.77 (dd, J = 6.6, 7.6 Hz, 4H), 7.95 (br, 4H), 7.79 (d, J = 8.4 Hz, 8H) 7.57–7.41 (br, 24H), 7.19 (s, 2H), 6.30 (br, 2H), 6.18 (br, 2H), 5.99 (br, 2H), 5.85 (br, 4H), 5.16 (br, 2H), 4.11 (br, 8H), 3.30 (br, 8H), 2.66 (br, 12H), 0.86 (br, 6H).

DOSY NMR (400 MHz, D$_2$O, 300 K): $D = 5.24 \times 10^{-10}$ m$^2$/s$^{-1}$.

FT-IR (KBr, cm$^{-1}$): 3384, 3068, 2935, 1655 (C=O), 1626, 1606, 1505, 1442, 1387, 1355, 1302, 1266, 1196, 1160, 1030, 982, 941, 903, 770.

ESI-TOF MS (H$_2$O): $m/z$ 416.4 [1b⊃6 − 4Cl]$^{4+}$, 459.4 [1b⊃(6)$_2$ − 4Cl]$^{4+}$.

Fig. S19. $^1$H NMR (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊃(6)$_2$. 

S18
Fig. S20a. HH-COSY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b$\supset$(6)$_2$.

Fig. S20b. HH-COSY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b$\supset$(6)$_2$ (aromatic region).
**Fig. S21a.** NOESY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊂(6)$_2$ (aromatic region).

**Fig. S21b.** NOESY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊂(6)$_2$ (aromatic region).
Fig. S21c. NOESY (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊃(6)$_2$ (host-guest region).

Fig. S22. DOSY (400 MHz, D$_2$O, 4 mM, 300 K) spectrum of 1b⊃(6)$_2$.
Encapsulation of N-methylphthalimide (7) by Bowl 1b

*N*-Methylphthalimide (7; 1.0 mg, 6.2 µmol) was added to a D₂O solution (0.64 mL) of bowl 1b (4.3 mg, 2.6 µmol) and the mixture was stirred at r.t. for 3 h. After filtration, the quantitative formation of a 1b⊃(7)₂ compound was confirmed by NMR and ESI-TOF MS analyses.

1H NMR (400 MHz, D₂O, r.t.): δ 9.99 (d, J = 6.2 Hz, 4H), 9.77 (s, 4H), 9.04 (d, J = 7.8 Hz, 4H), 8.77 (dd, J = 6.2, 7.8 Hz, 4H), 7.91–7.46 (br, 36H), 7.27 (s, 2H), 6.71 (s, 2H), 6.16 (br, 4H), 5.40 (br, 4H), 4.17 (br, 8H), 3.34 (s, 8H), 2.69 (s, 12H), 1.74 (br, 6H).

DOSY NMR (400 MHz, D₂O, 304 K): D = 6.9 x 10⁻¹⁰ m² s⁻¹.

ESI-TOF MS (H₂O): m/z 413.7 [1b⊃7 – 4Cl⁻]⁺⁺, 453.9 [1b⊃(7)₂ – 4Cl⁻]⁺⁺.
Fig. S24. $^1$H NMR (400 MHz, D$_2$O, 4 mM, r.t.) spectrum of 1b⊂(7)$_2$.

Fig. S25. DOSY (400 MHz, D$_2$O, 4 mM, 300 K) spectrum of 1b⊂(7)$_2$. 
Table. S1. Crystal data and structure refinement for 1a

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The supplementary crystallographic data of bowl 1a can be obtained free of charge (under CCDC 893651) by containing the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Fig. S26. ORTEP drawing of bowl 1a.

Fig. S27. Hydrogen bonding interactions between the carbonyl oxygen atoms of acetones and α-hydrogen atoms of the bispyridinium moieties of bowl 1a.
Fig. S28. Crystal structures of bowl 1a in bowl (left) and tube-shape (right) conformations.

Fig. S29. Torsion and bite angles of the aromatic rings of 1a in the crystal structures.

Fig. S30. Optimized structures of the bowl- and tube-shaped conformations of 1 (R = CH₃).
Fig. S31. $^1$H NMR (400 MHz, D$_2$O:acetone-$d_6$ (10:1), 4 mM, r.t.) spectrum of 1b⊂3.

Fig. S32. $^1$H NMR (400 MHz, D$_2$O:acetone-$d_6$ (10:1), 4 mM, r.t.) spectrum of 1b⊂(6)$_2$.