Supporting Information

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

Kohei Yazaki, Norifumi Kishi, Munetaka Akita, and Michito Yoshizawa*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan; *e-mail: yoshizawa.m.ac@m.titech.ac.jp

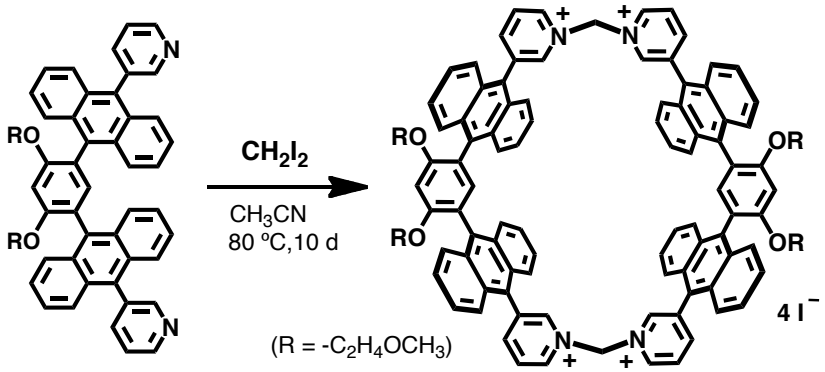
Contents

Materials and methods

NMR: Bruker AVANCE-400 (400 MHz), MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, FT-IR: JASCO FT/IR-4200, X-ray single crystal structural analysis: Bruker APEXII ULTRA/CCD diffractometer, Elemental analysis: LECO CHNS-932 VTF-900.

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 KY117



Bispyridine ligand **2** (0.101 g, 0.138 mmol), diiodomethane (2.66 g, 9.93 mmol), and MeCN (70 mL) ware added to a 2-necked 100 mL glass flask containing a magnetic stirring bar under N_2. The mixture was stirred at 80 ºC for 10 d and then concentrated under reduce pressure. The crude product was washed with MeOH, $CHCl_3$, and acetone to afford bowl **1a** as a red solid (40.7 mg, 20.3 μmol, 29% yield)

^{1}H NMR (400 MHz, DMSO-d_6, 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).

^{13}C NMR (100 MHz, DMSO-d_6, r.t.): δ 158.5 (C_q), 151.8 (CH), 146.8 (CH), 146.1 (CH), 140.1 (C_q), 136.5 (C_q), 134.4 (CH), 130.1 (CH, 2 x C_q), 127.5 (CH), 127.2 (CH, C_q), 126.2 (CH), 126.0 (CH), 118.8 (C_q), 100.5 (CH), 78.2 (CH_2), 70.6 (CH_2), 68.9 (CH_2), 58.4 (CH_3).

DOSY NMR (400 MHz, DMSO-d_6, 298 K): D = 2.40 x 10^{-10} m^2 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 (CH_3CN): m/z Calcd. 373.4, Found 373.4 $[M - 4I^-]^{4+}$.

E.A.: Calcd. for $C_{102}H_{84}O_8N_4I_7$•1.5H_2O: C, 50.85; H, 3.64; N, 2.33. Found: C, 50.57; H, 3.26; N, 2.36.

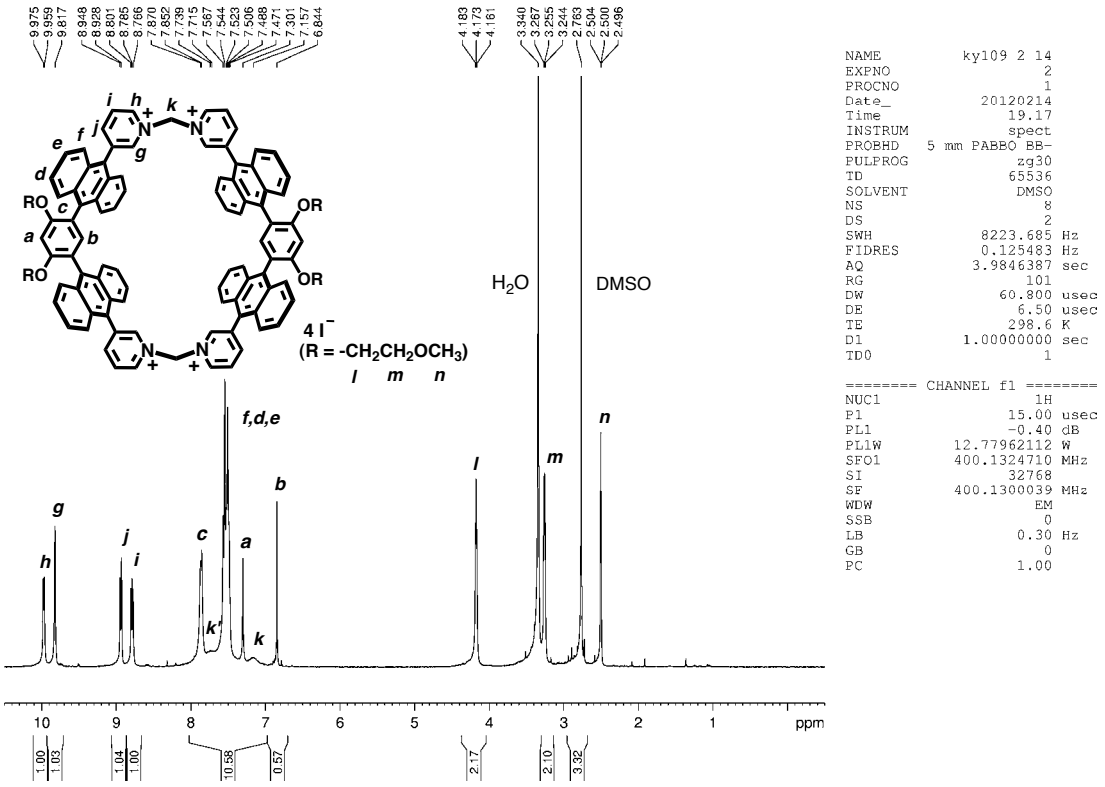


Fig. S1. [1]H NMR (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a**.

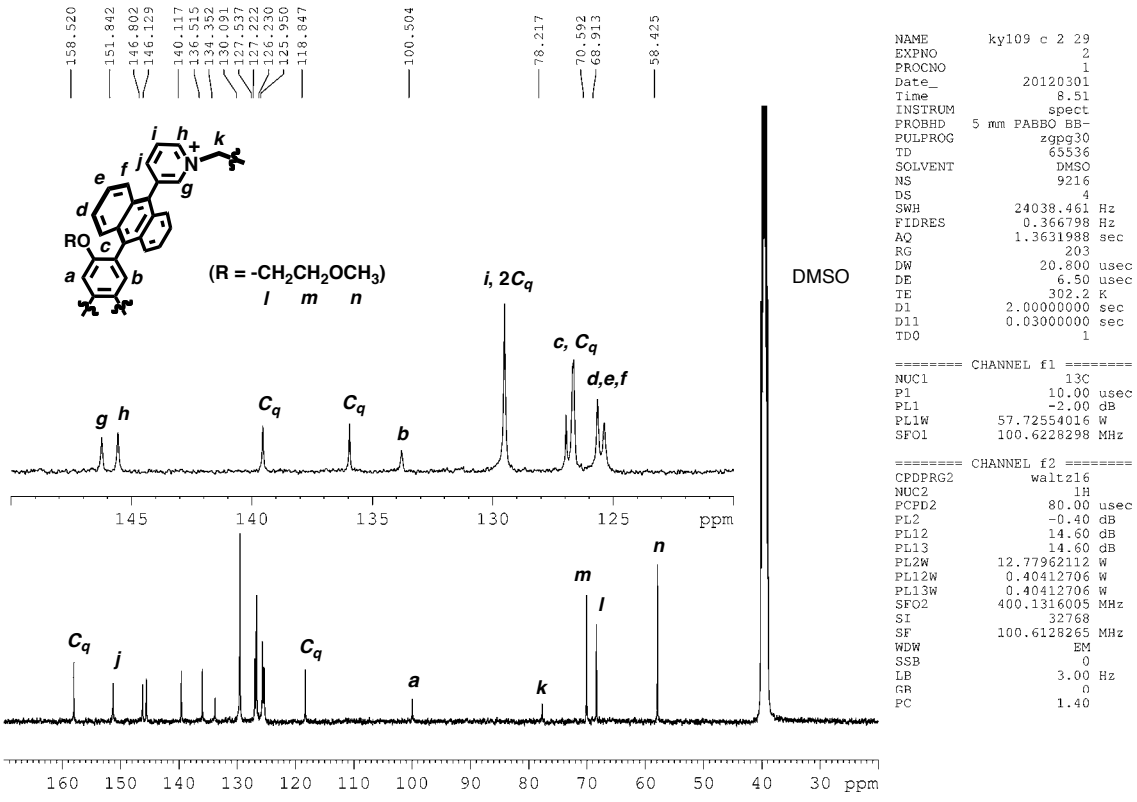


Fig. S2. [13]C NMR (100 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a**.

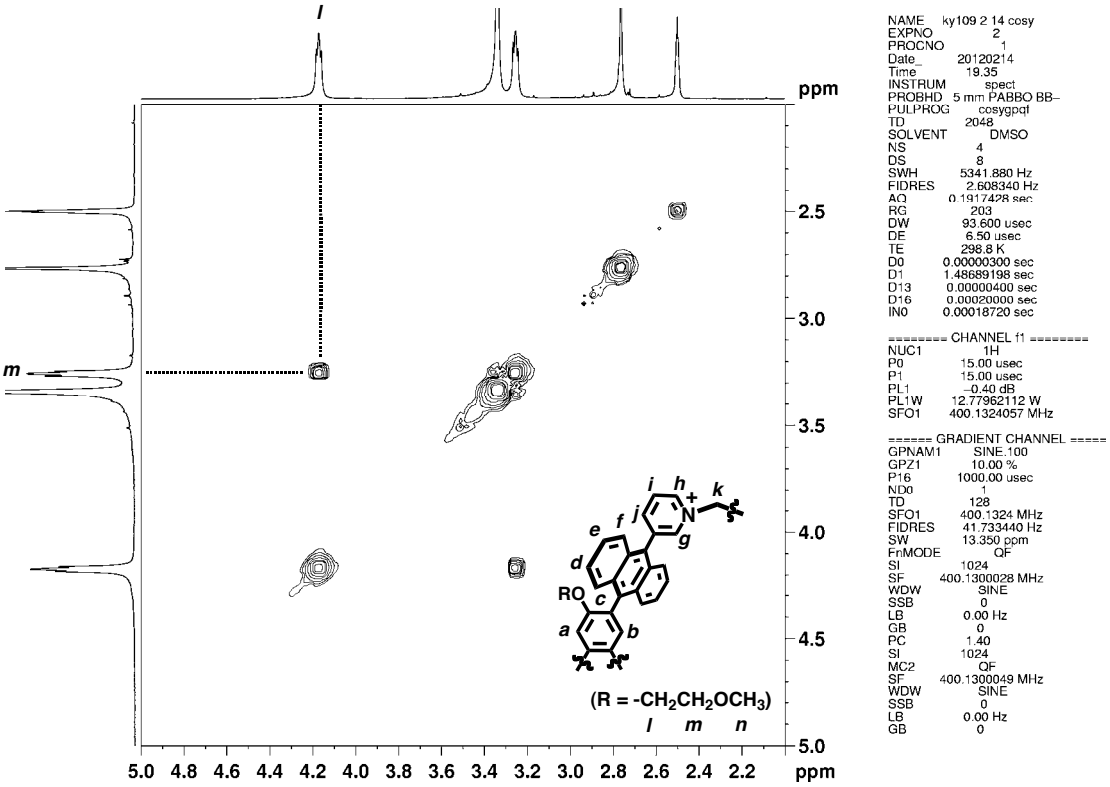


Fig. S3a. HH COSY (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a** (aliphatic region).

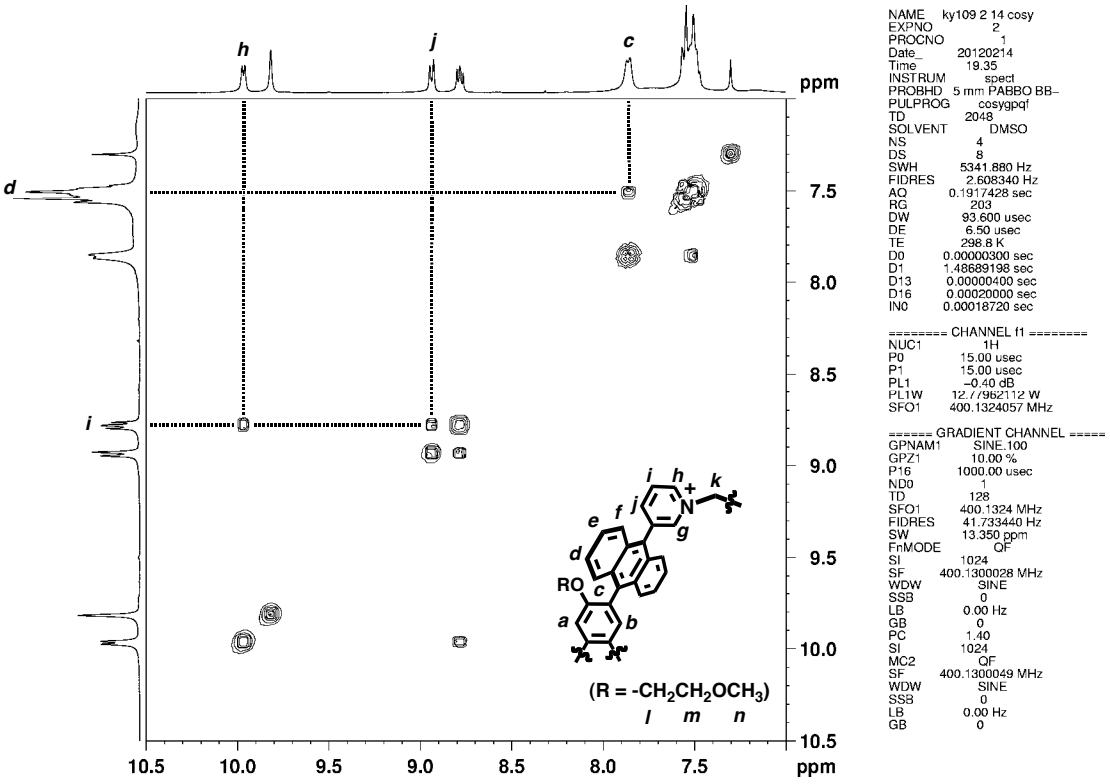
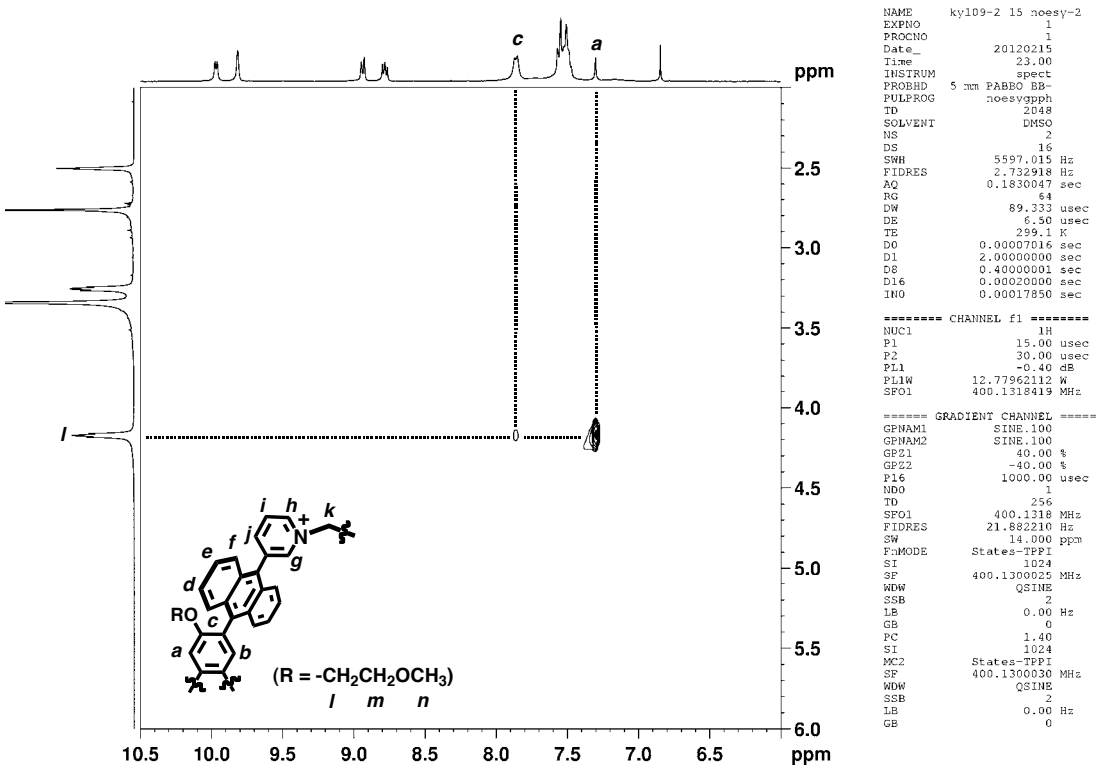


Fig. S3b. HH COSY (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a** (aromatic region).

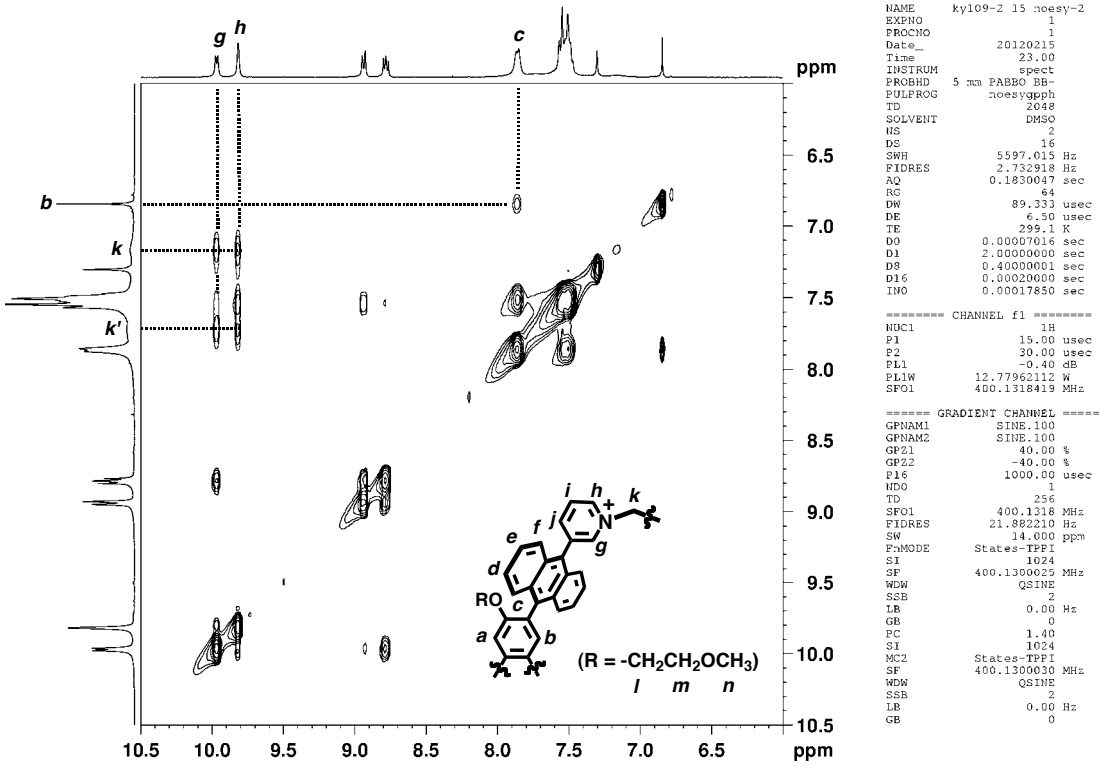



```
NAME        ky109-2 15 noesy-2
EXPNO                        1
PROCNO                       1
Date_                 20120215
Time                     23.00
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG           noesygpph
TD                        2048
SOLVENT                   DMSO
NS                           2
DS                          16
SWH                  5597.015 Hz
FIDRES               2.732918 Hz
AQ                   0.1830047 sec
RG                          64
DW                     89.333 usec
DE                       6.50 usec
TE                      299.1 K
D0                   0.00007016 sec
D1                   2.00000000 sec
D8                   0.40000001 sec
D16                  0.00020000 sec
IN0                  0.00017850 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       15.00 usec
P2                       30.00 usec
PL1                      -0.40 dB
PL1W                12.77962112 W
SFO1                400.1318419 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPZ1                     40.00 %
GPZ2                    -40.00 %
P16                    1000.00 usec
NDO                          1
TD                         256
SFO1                400.1318 MHz
FIDRES              21.882210 Hz
SW                     14.000 ppm
FnMODE             States-TPPI
SI                        1024
SF                  400.1300025 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
PC                        1.40
SI                        1024
MC2                States-TPPI
SF                  400.1300030 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
```

Fig. S4a. NOESY (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a**.




```
NAME        ky109-2 15 noesy-2
EXPNO                        1
PROCNO                       1
Date_                 20120215
Time                     23.00
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG           noesygpph
TD                        2048
SOLVENT                   DMSO
NS                           2
DS                          16
SWH                  5597.015 Hz
FIDRES               2.732918 Hz
AQ                   0.1830047 sec
RG                          64
DW                     89.333 usec
DE                       6.50 usec
TE                      299.1 K
D0                   0.00007016 sec
D1                   2.00000000 sec
D8                   0.40000001 sec
D16                  0.00020000 sec
IN0                  0.00017850 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       15.00 usec
P2                       30.00 usec
PL1                      -0.40 dB
PL1W                12.77962112 W
SFO1                400.1318419 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPZ1                     40.00 %
GPZ2                    -40.00 %
P16                    1000.00 usec
NDO                          1
TD                         256
SFO1                400.1318 MHz
FIDRES              21.882210 Hz
SW                     14.000 ppm
FnMODE             States-TPPI
SI                        1024
SF                  400.1300025 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
PC                        1.40
SI                        1024
MC2                States-TPPI
SF                  400.1300030 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
```

Fig. S4b. NOESY (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a** (aromatic region).

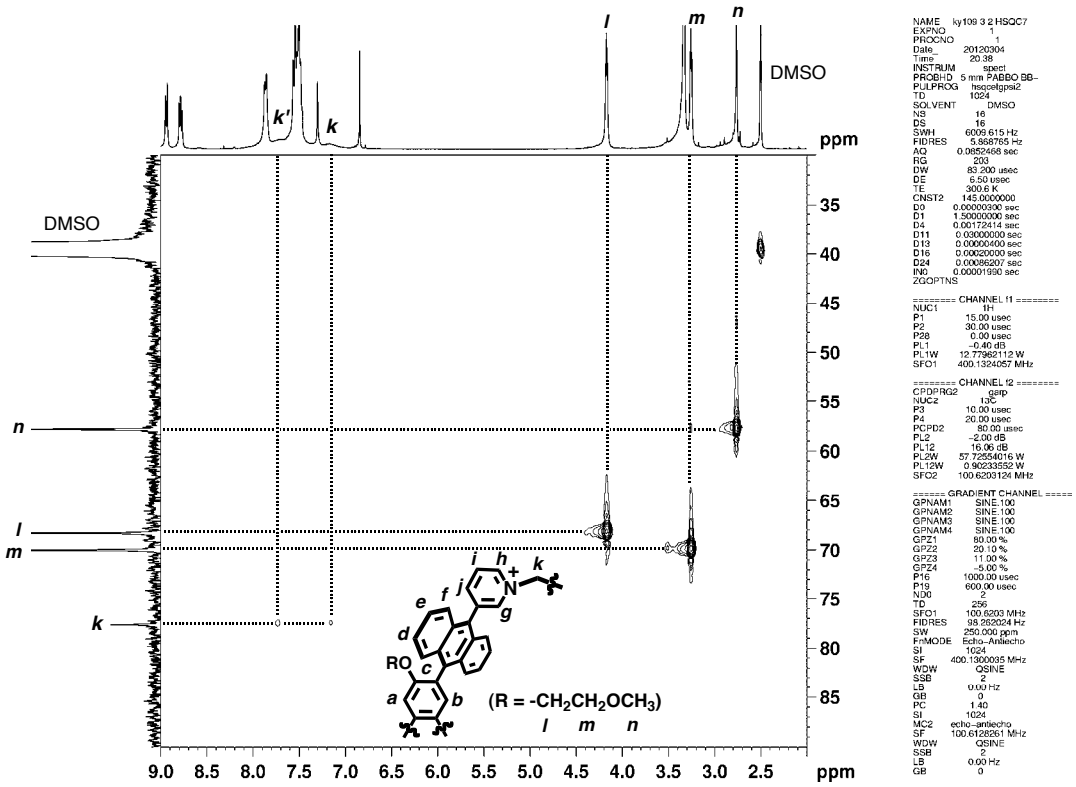


Fig. S5a. HSQC (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a** (aliphatic region).

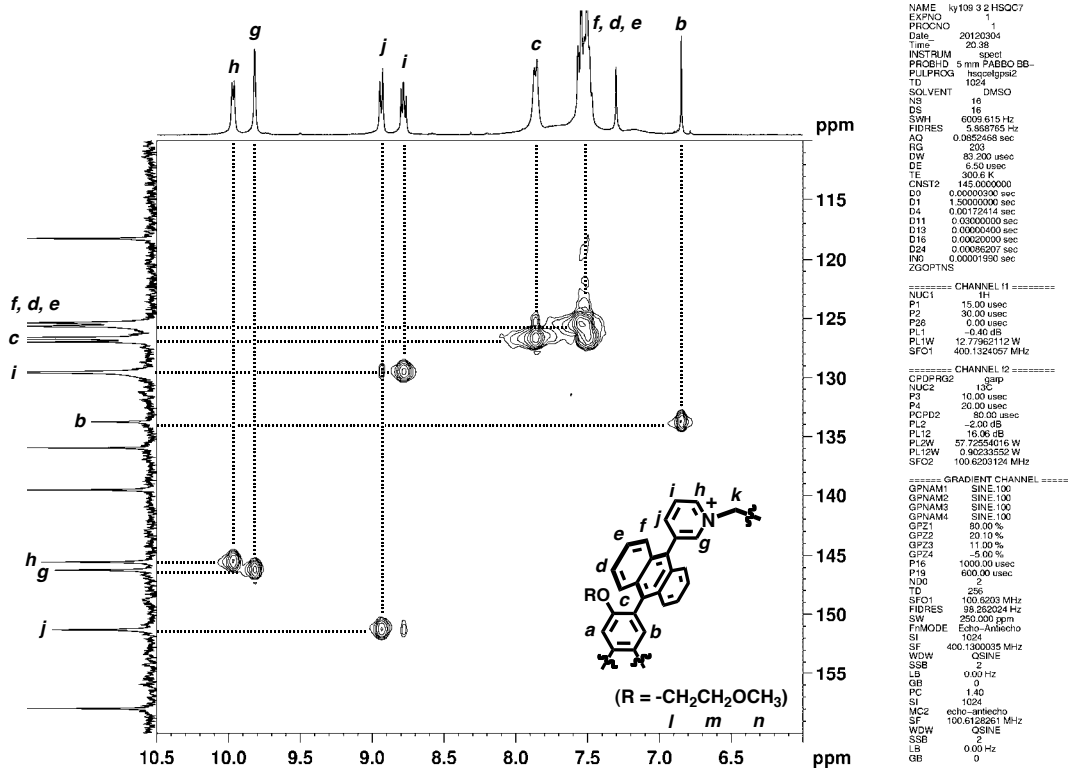


Fig. S5b. HSQC (400 MHz, DMSO-d_6, 10 mM, r.t.) spectrum of **1a** (aromatic region).

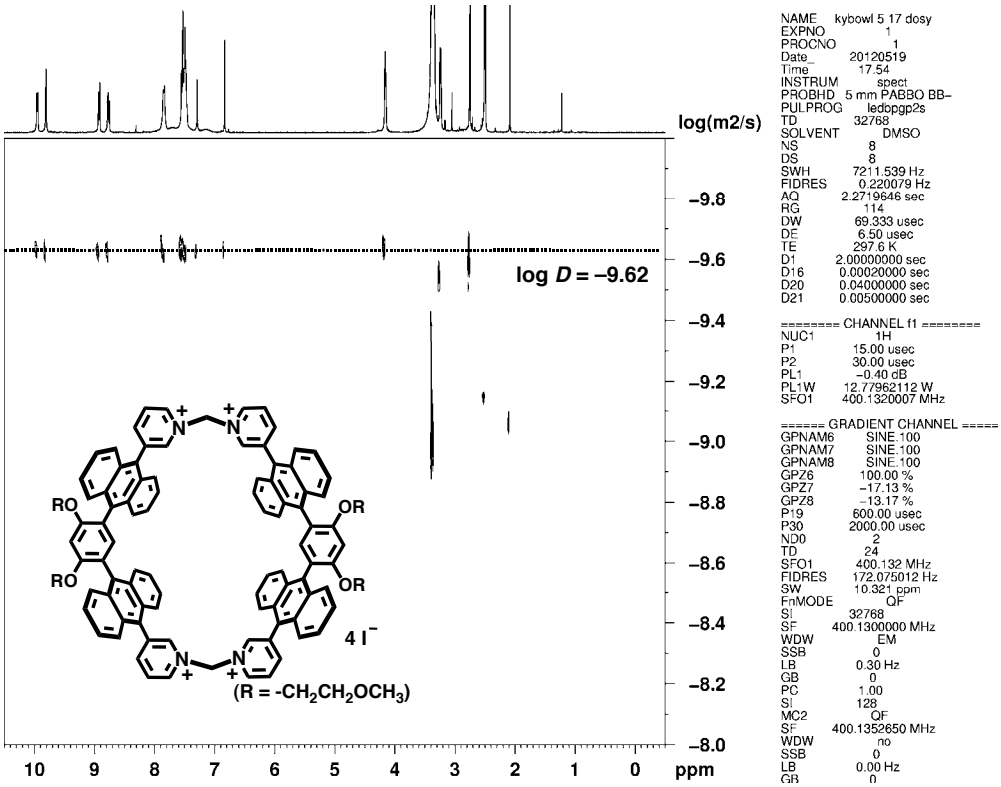


Fig. S6. DOSY NMR (400 MHz, DMSO-d_6, 10 mM, 298 K) spectrum of bowl **1a**.

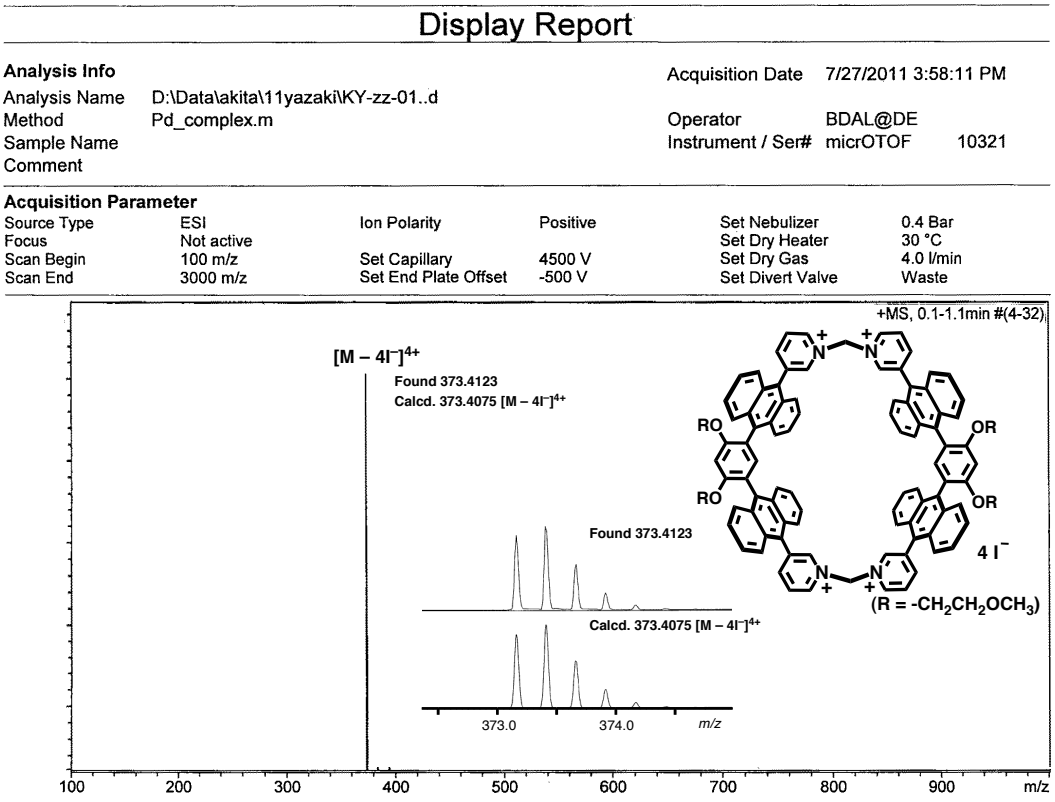
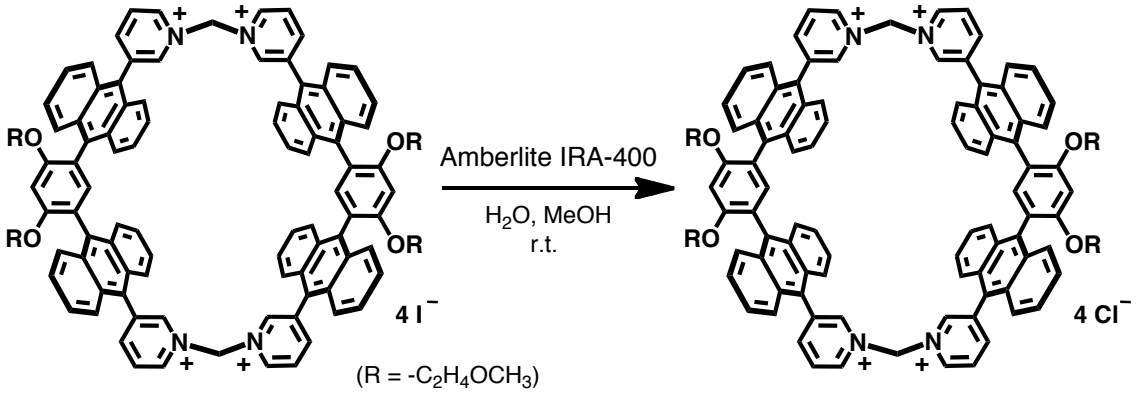


Fig. S7. ESI-TOF MS spectrum of bowl **1a**.

Synthesis of Bowl-shaped Host 1b KY215



Bowl **1a** (250.6 mg, 125.2 μmol), Amberlite IRA-400 (8.11 g), MeOH (50 mL), and H_2O (20 mL) ware 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 obatined 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).

^{1}H NMR (400 MHz, D_2O, r.t.): δ 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).

^{13}C NMR (100 MHz, D_2O, r.t.): δ 158.1 (C_q), 153.2 (CH), 145.9 (CH), 141.3 (CH), 136.3 (C_q), 130.6 (C_q), 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): $D = 7.4 \times 10^{-10}$ m^2 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 (H_2O): *m/z* 373.4 [**1b** – 4Cl$^-$]$^{4+}$, 509.5 [**1b** – 3Cl$^-$]$^{3+}$, 782.3 [**1b** – 2Cl$^-$]$^{2+}$.

E.A.: Calcd. for $C_{102}H_{84}O_8N_4Cl_4$•2$CHCl_3$•3H_2O: C, 64.77; H, 4.81; N, 2.91. Found: C, 64.49; H, 4.72; N, 3.05.

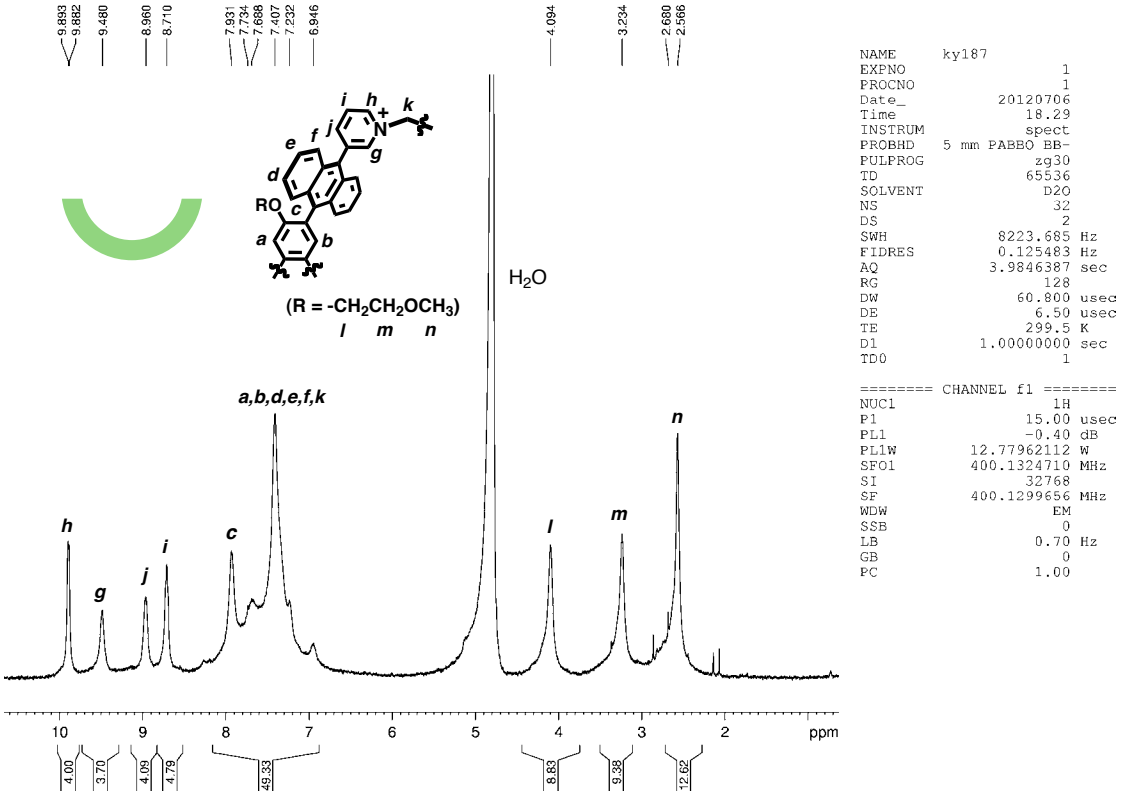


Fig. S8. ^{1}H NMR (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**.

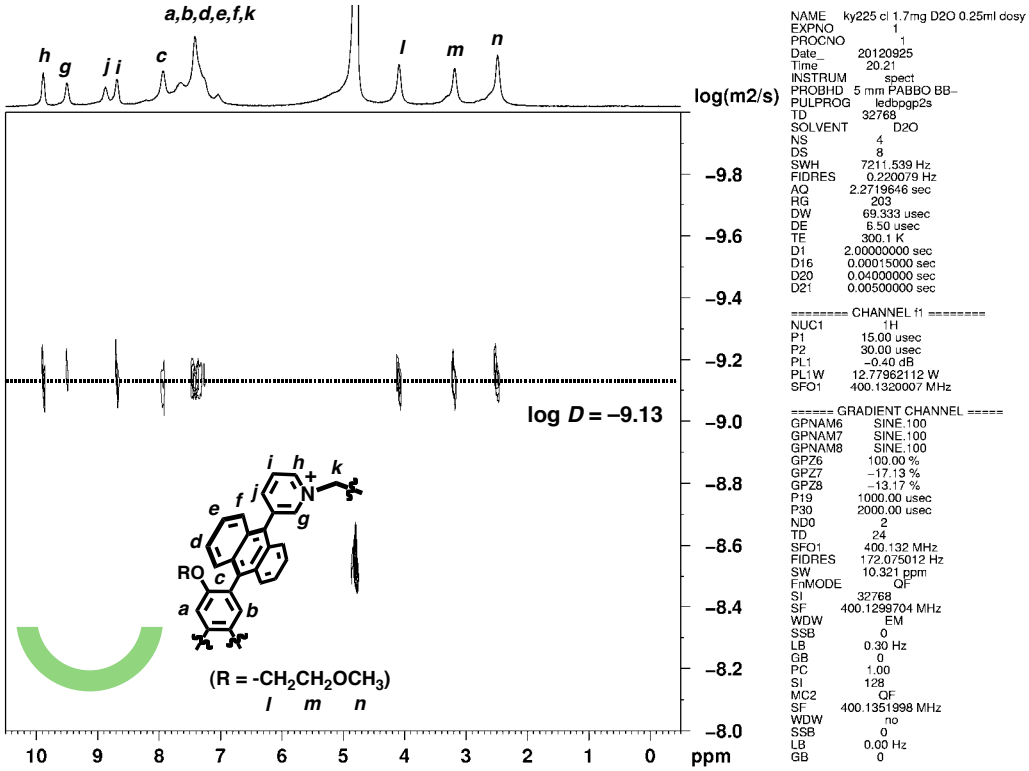
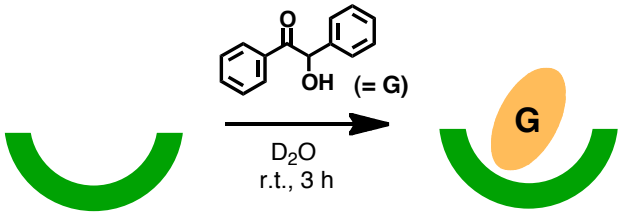


Fig. S9. DOSY NMR (400 MHz, D_2O, 4 mM, 300 K) spectrum of bowl **1b**.

Encapsulation of Benzoin (3) by Bowl 1b KY211, 249



Benzoin (**3**; 2.1 mg, 9.9 μmol) was added to a D_2O 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_2O, r.t.): δ 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_2O, r.t.): δ 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_2O, 300 K): D = 5.89 x 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_2O): m/z 426.4 [**1b**⊃**3** – $4Cl^-$]$^{4+}$.

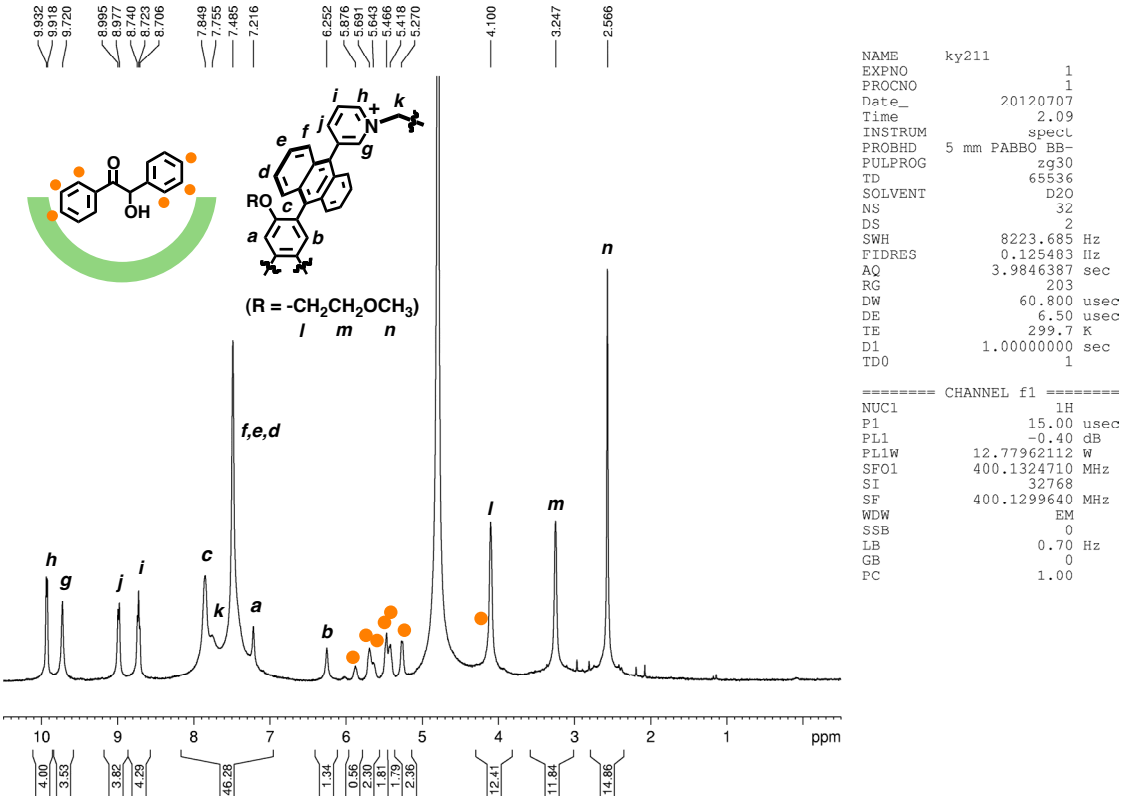


Fig. S10. ^{1}H NMR (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃3**.

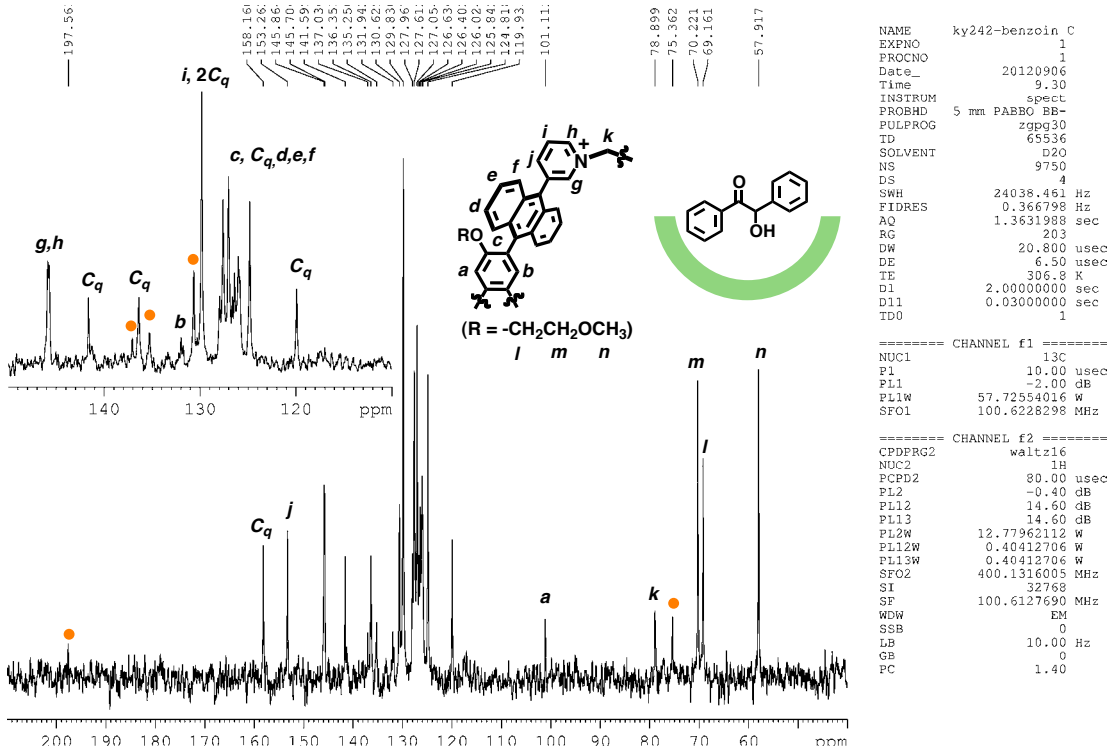


Fig. S11. ^{13}C NMR (100 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃3**.

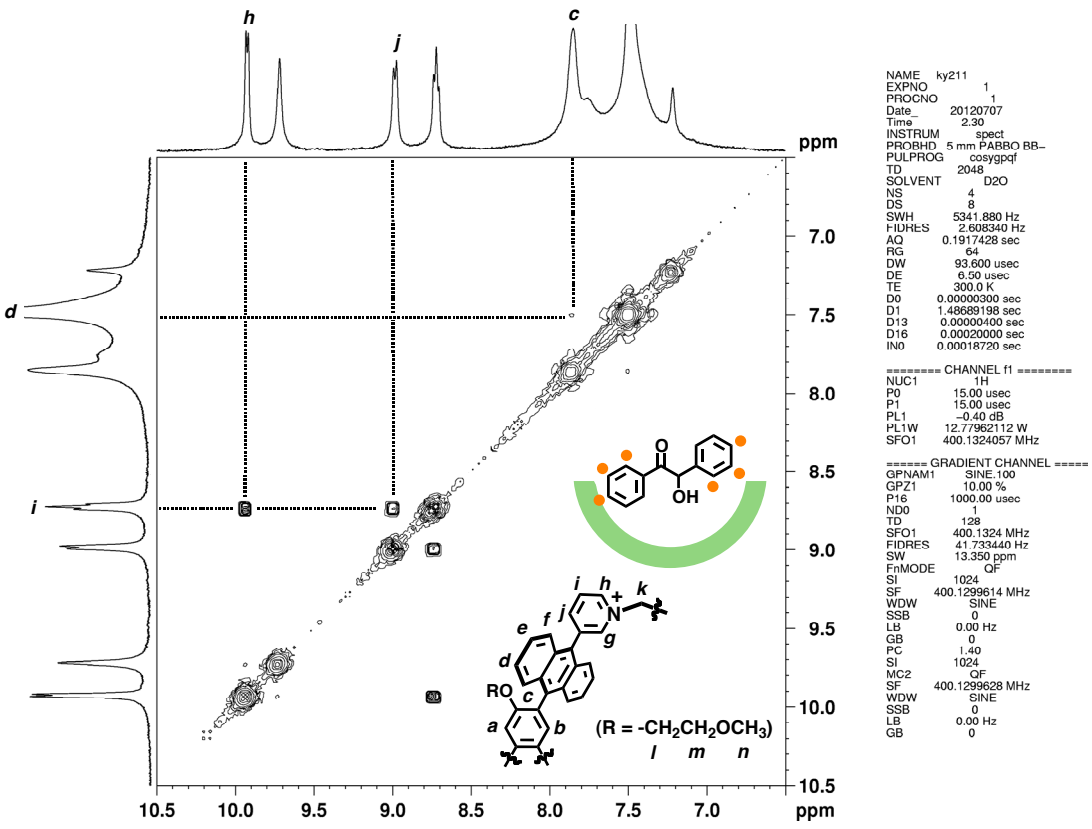


Fig. S12a. HH-COSY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃3** (aromatic region).

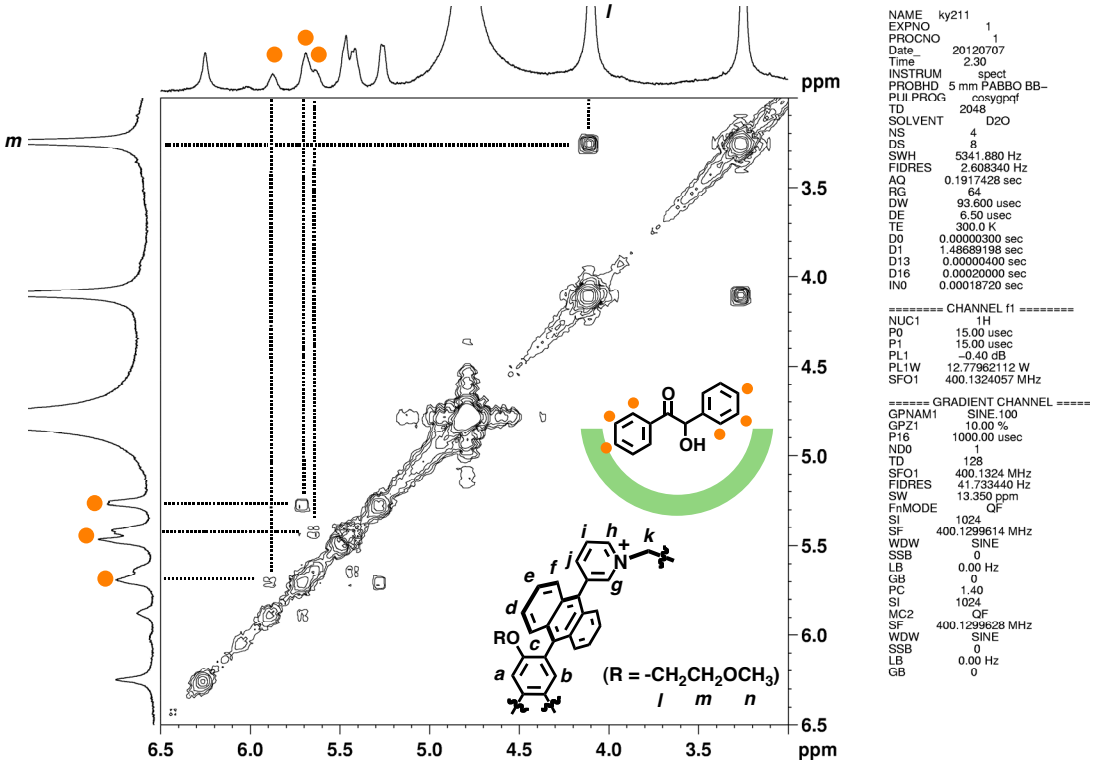


Fig. S12b. HH-COSY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃3** (aromatic region).

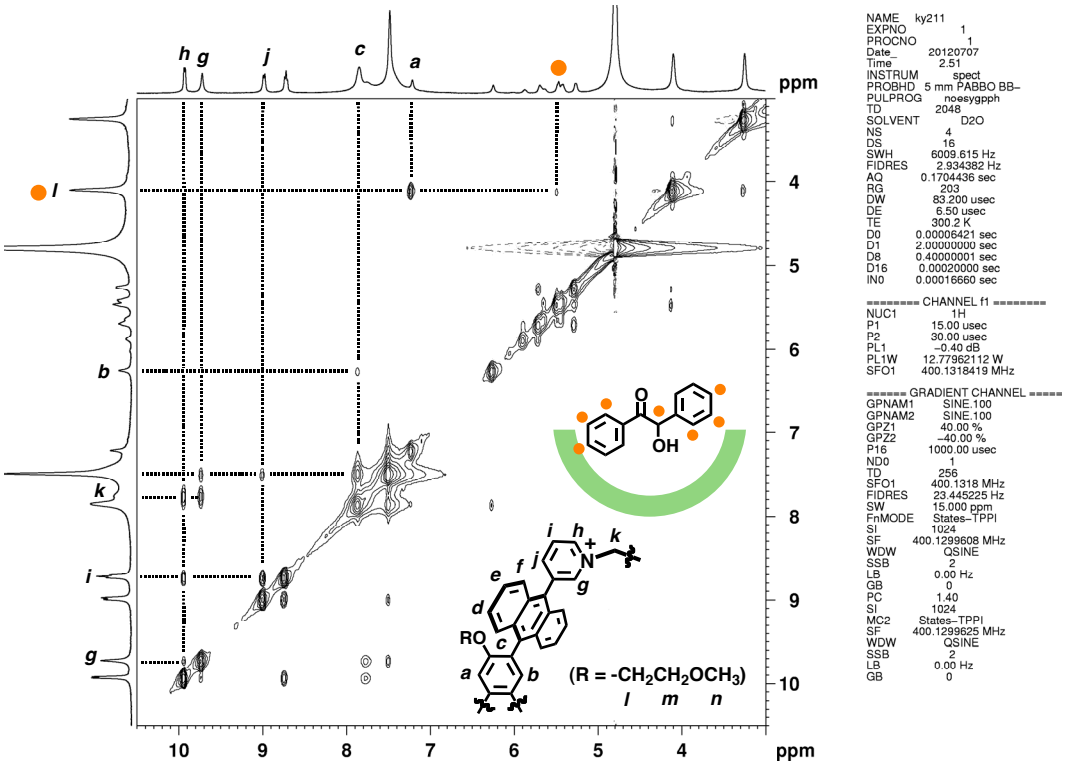


Fig. S13a. NOESY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃3**.

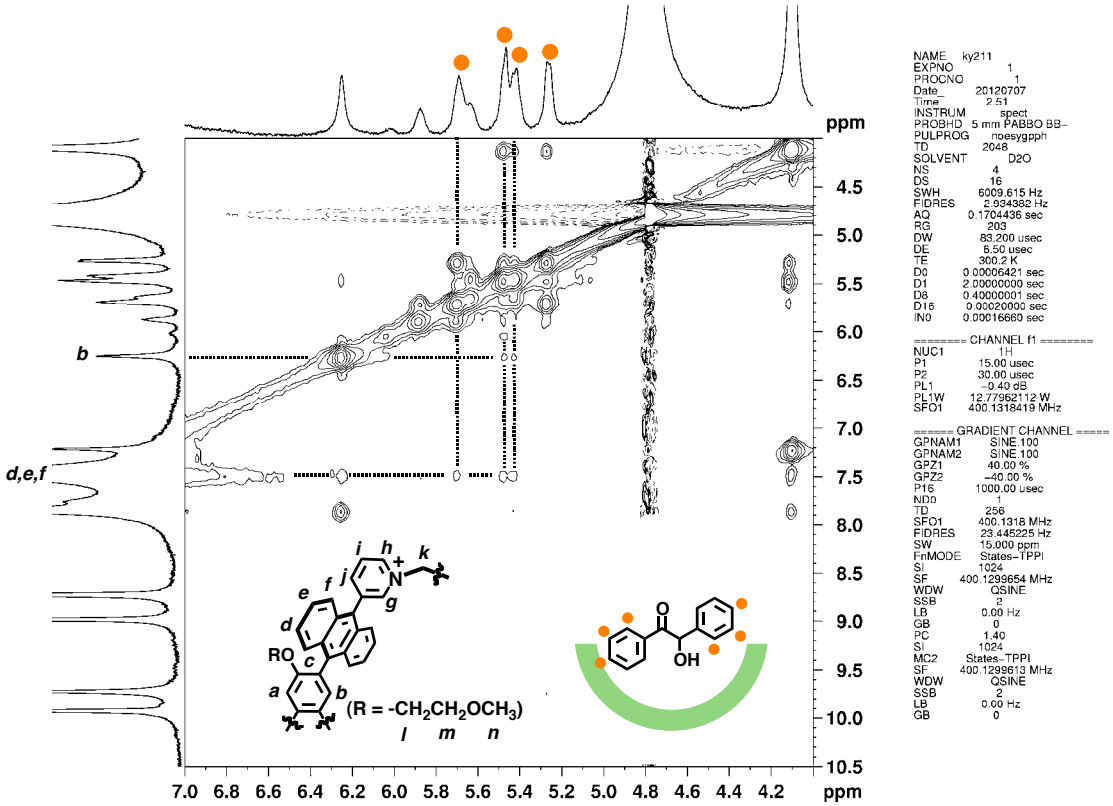


Fig. S13b. NOESY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃3**. (host-guest region).

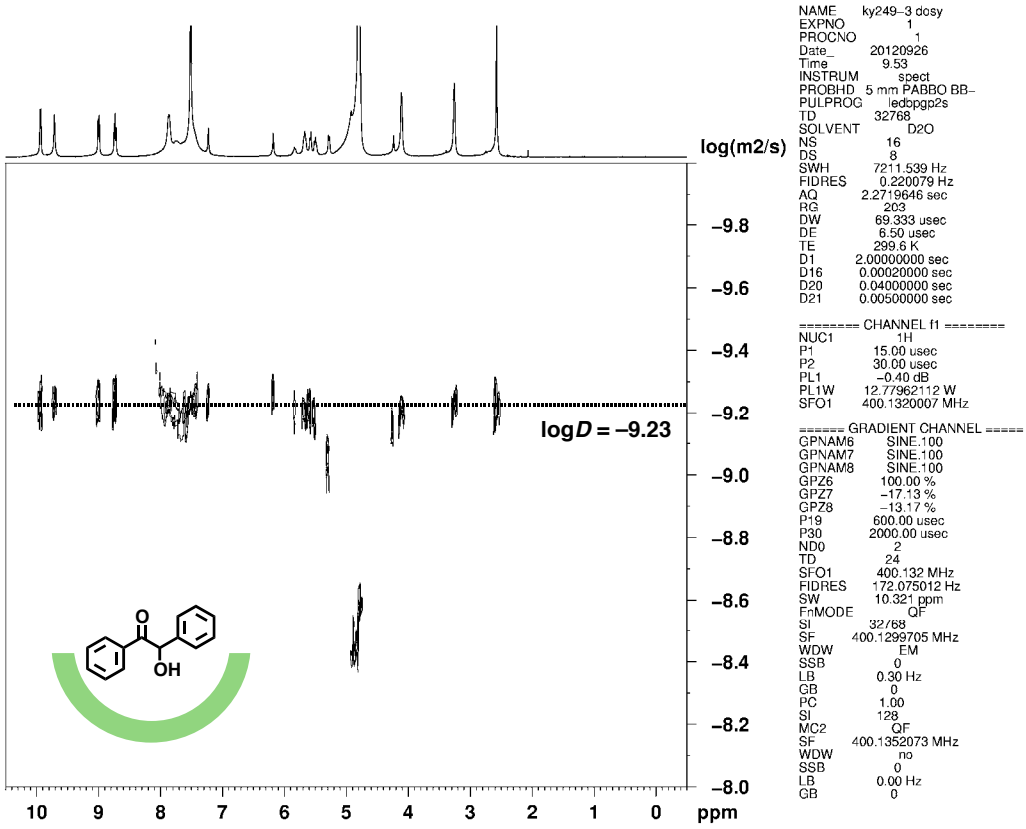
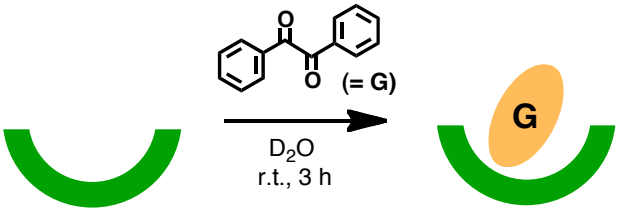


Fig. S14. DOSY (400 MHz, D_2O, 4 mM, 300 K) spectrum of **1b⊃3**.

Encapsulation of Benzil (4) by Bowl 1b KY251



Benzil (**4**; 1.1 mg, 5.2 μmol) was added to a D_2O 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.

^{1}H NMR (400 MHz, D_2O, 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, D_2O, 301 K): D = 6.5 x 10^{-10} m^2 s^{-1}.

FT-IR (KBr, cm^{-1}): 3399, 3062, 2934, 1960, 1680 (C=O), 1662 (C=O), 1628, 1604, 1577, 1505, 1448, 1388, 1313, 1268, 1197, 1160, 1127, 1103, 1055, 1030, 982, 905, 853, 815, 770, 725. ESI-TOF MS (H_2O): m/z 425.9 [**1b⊃4** – $4Cl^-$]$^{4+}$.

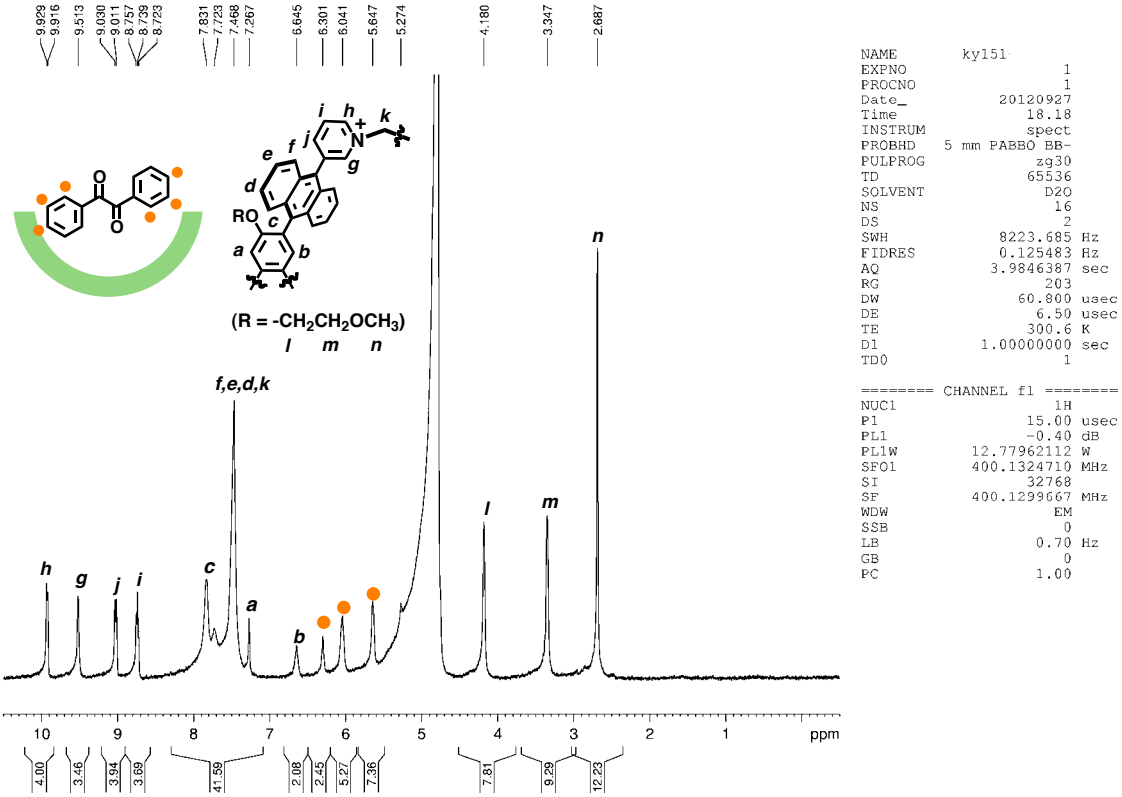


Fig. S15. ^{1}H NMR (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃4**.

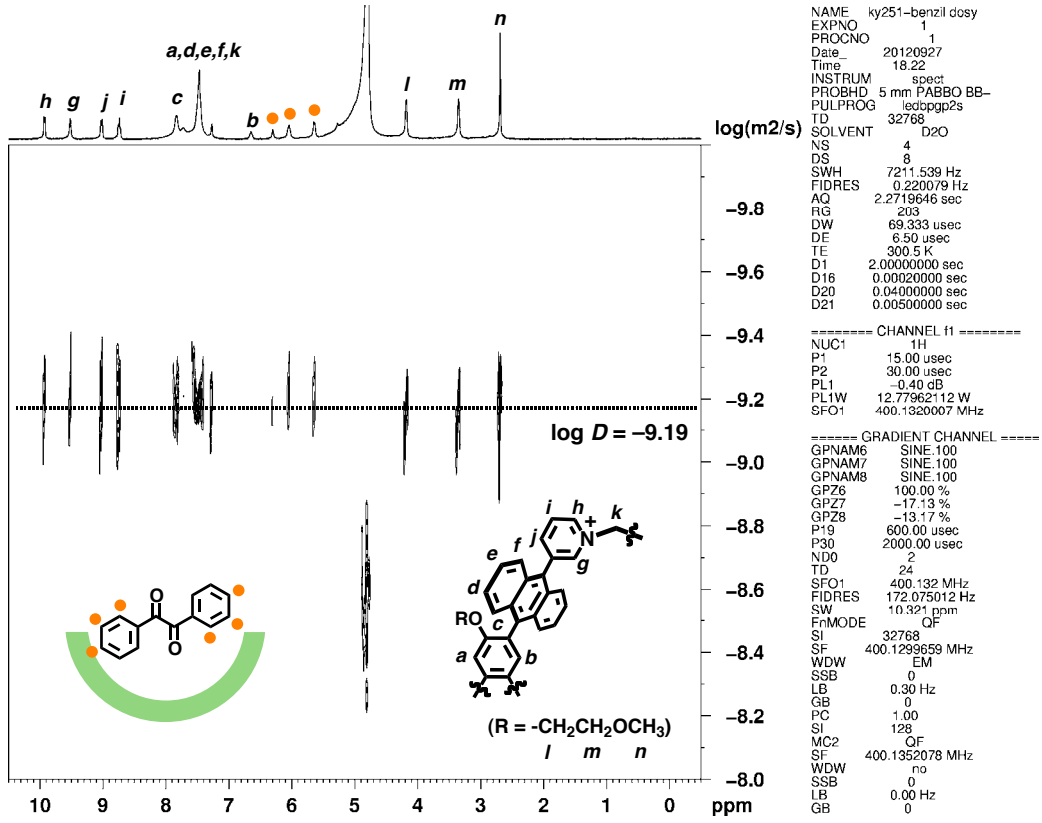
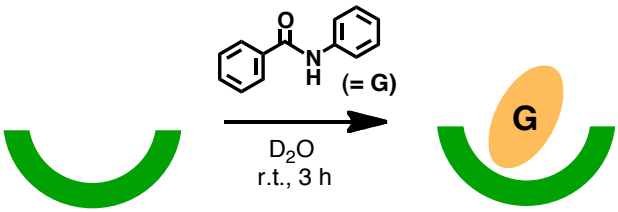


Fig. S16. DOSY (400 MHz, D_2O, 4 mM, 301 K) spectrum of **1b⊃4**.

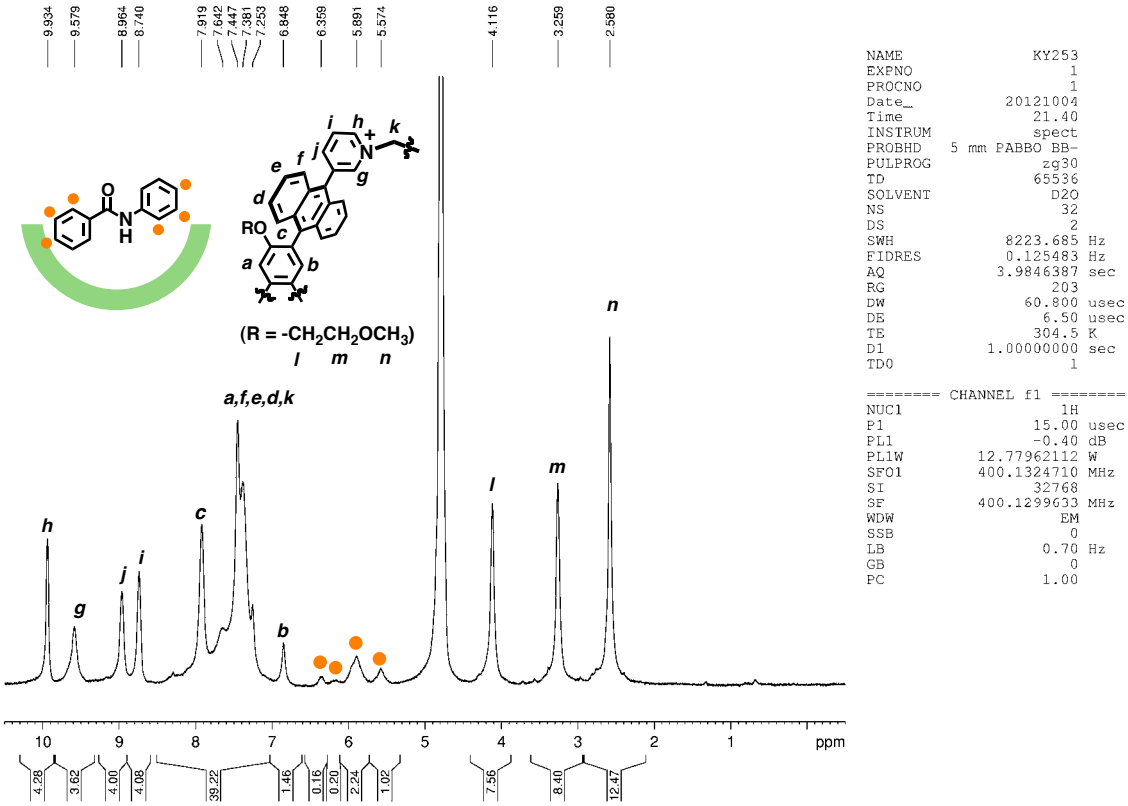
Encapsulation of Benzanilide (5) by Bowl 1b KY253



Benzanilide (**5**; 1.5 mg, 7.6 μmol) was added to a D_2O 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).

^{1}H NMR (400 MHz, D_2O, 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, D_2O, 305 K): D = 6.6 x 10^{-10} m^2 s^{-1}.




```
NAME                 KY253
EXPNO                    1
PROCNO                   1
Date_             20121004
Time                 21.40
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                       32
DS                        2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     203
DW                  60.800 usec
DE                   6.50 usec
TE                  304.5 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  15.00 usec
PL1                 -0.40 dB
PL1W          12.77962112 W
SFO1          400.1324710 MHz
SI                   32768
SF            400.1299633 MHz
WDW                    EM
SSB                     0
LB                   0.70 Hz
GB                      0
PC                   1.00
```

Fig. S17a. ^{1}H NMR (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b⊃5**.

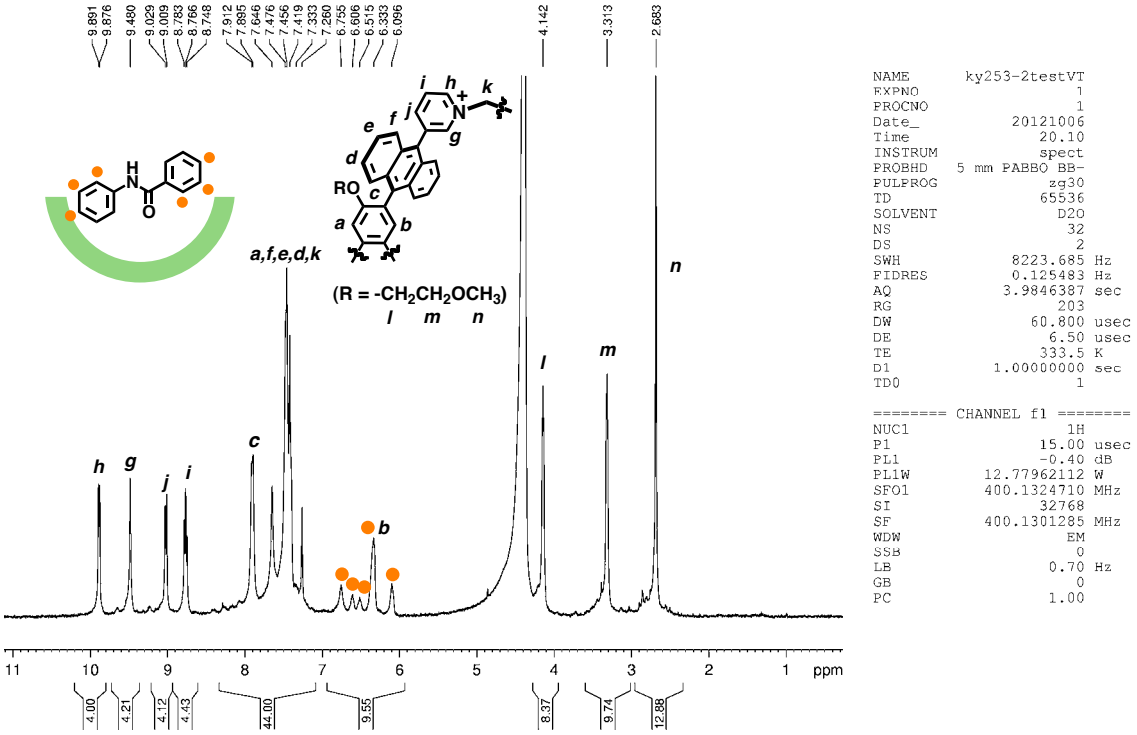


Fig. S17b. ^{1}H NMR (400 MHz, D_2O, 4 mM, 333 K) spectrum of **1b⊃5**.

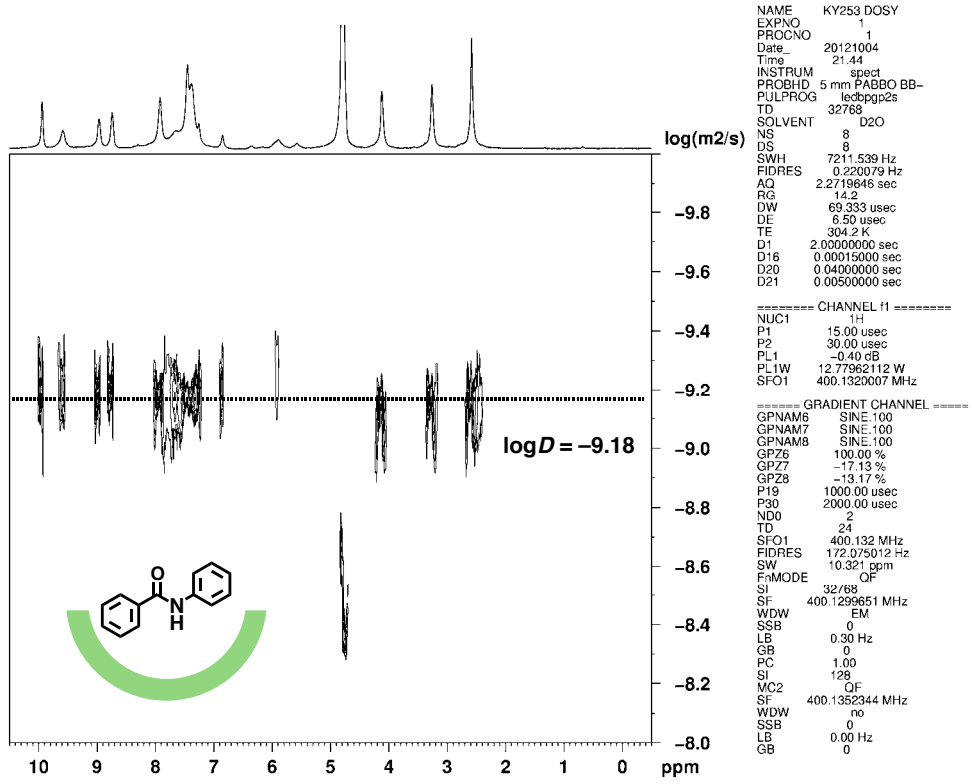
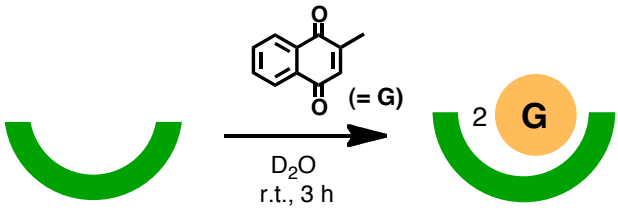


Fig. S18. DOSY NMR (400 MHz, D_2O, 4 mM, 305 K) spectrum of **1b⊃5**.

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_2O 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_2O, 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_2O, 300 K): D = 5.24 x 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_2O): m/z 416.4 [**1b**⊃**6** – 4Cl$^-$]$^{4+}$, 459.4 [**1b**⊃(**6**)$_2$ – 4Cl$^-$]$^{4+}$.

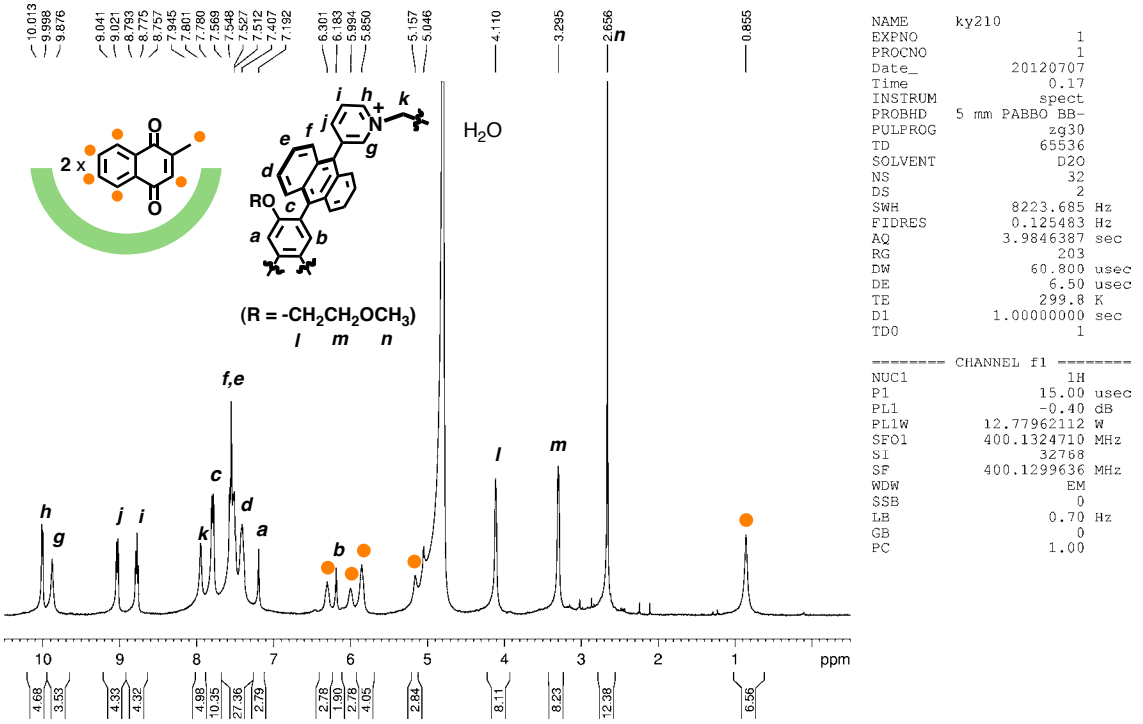


Fig. S19. ^{1}H NMR (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$.

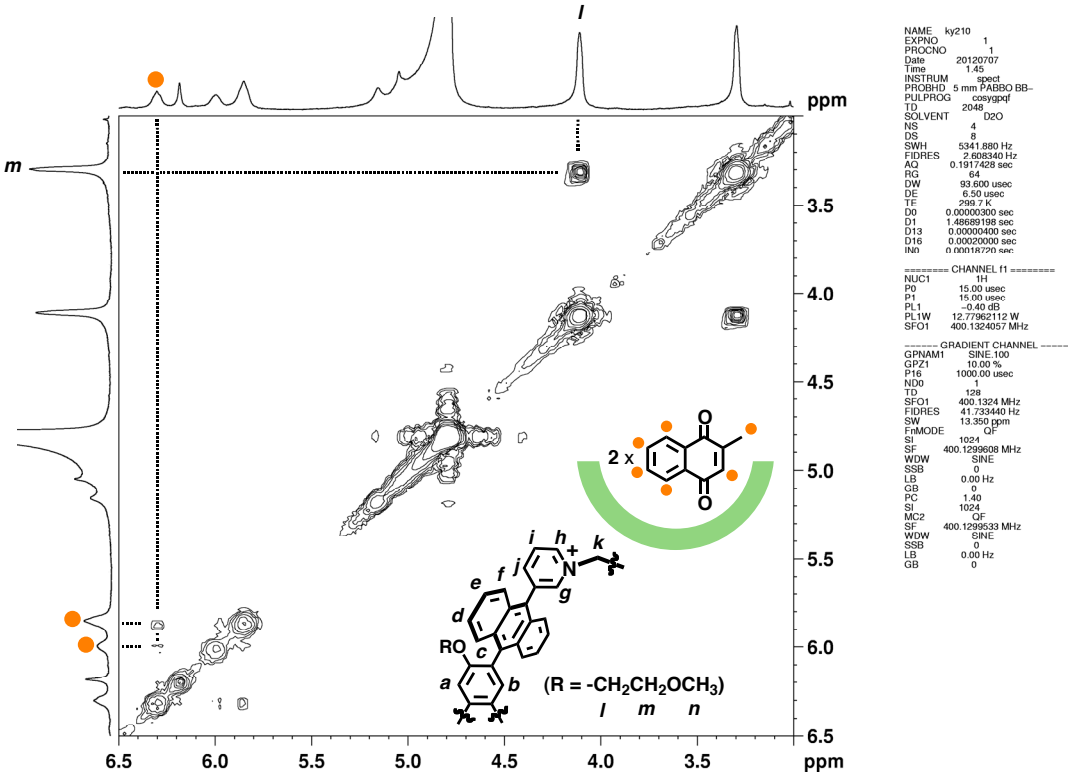


Fig. S20a. HH-COSY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$.

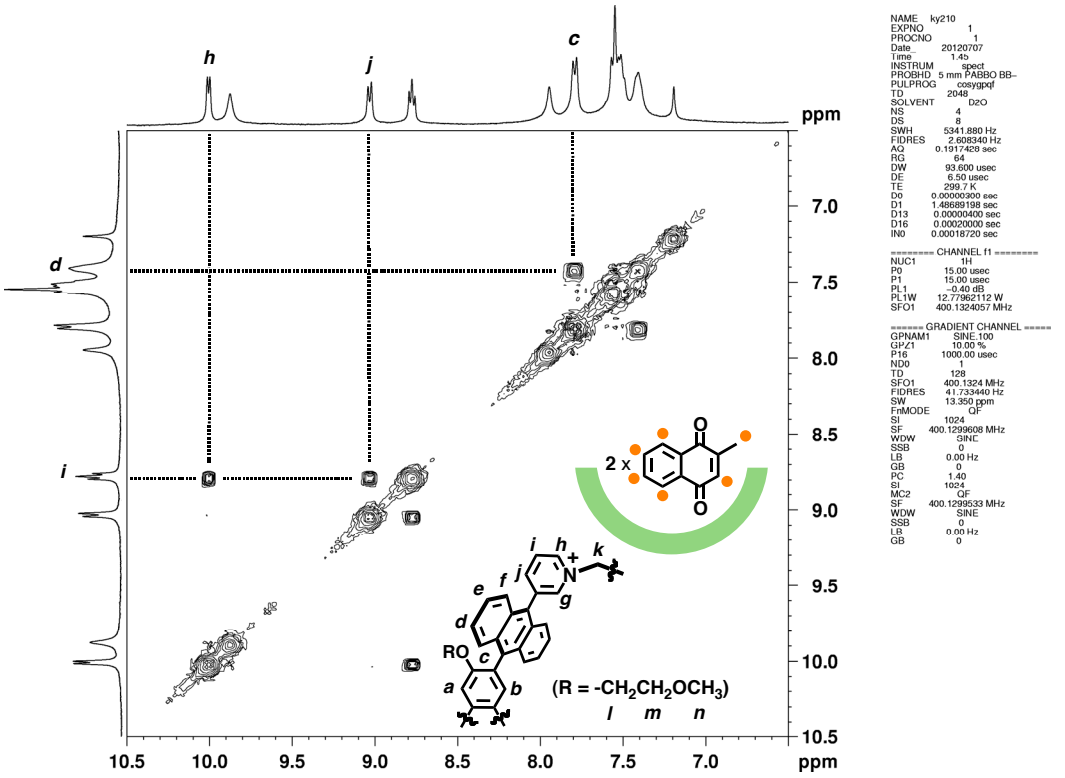


Fig. S20b. HH-COSY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$ (aromatic region).

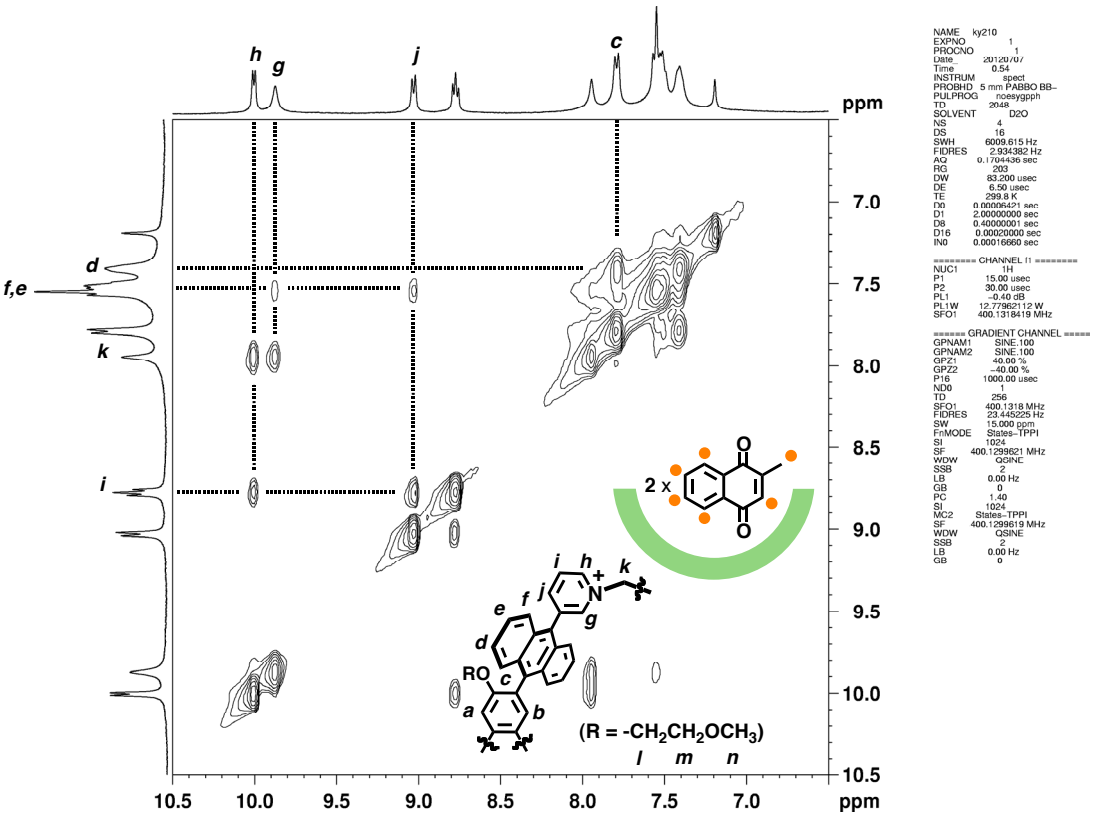


Fig. S21a. NOESY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$ (aromatic region).

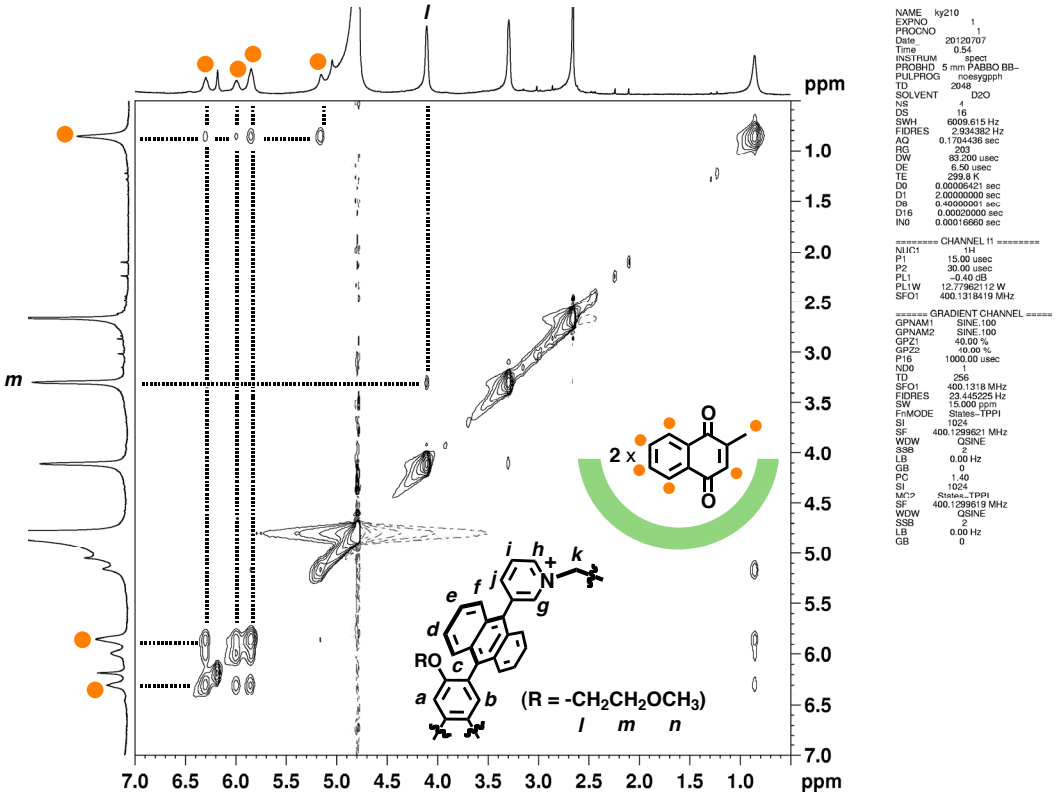


Fig. S21b. NOESY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$ (aromatic region).

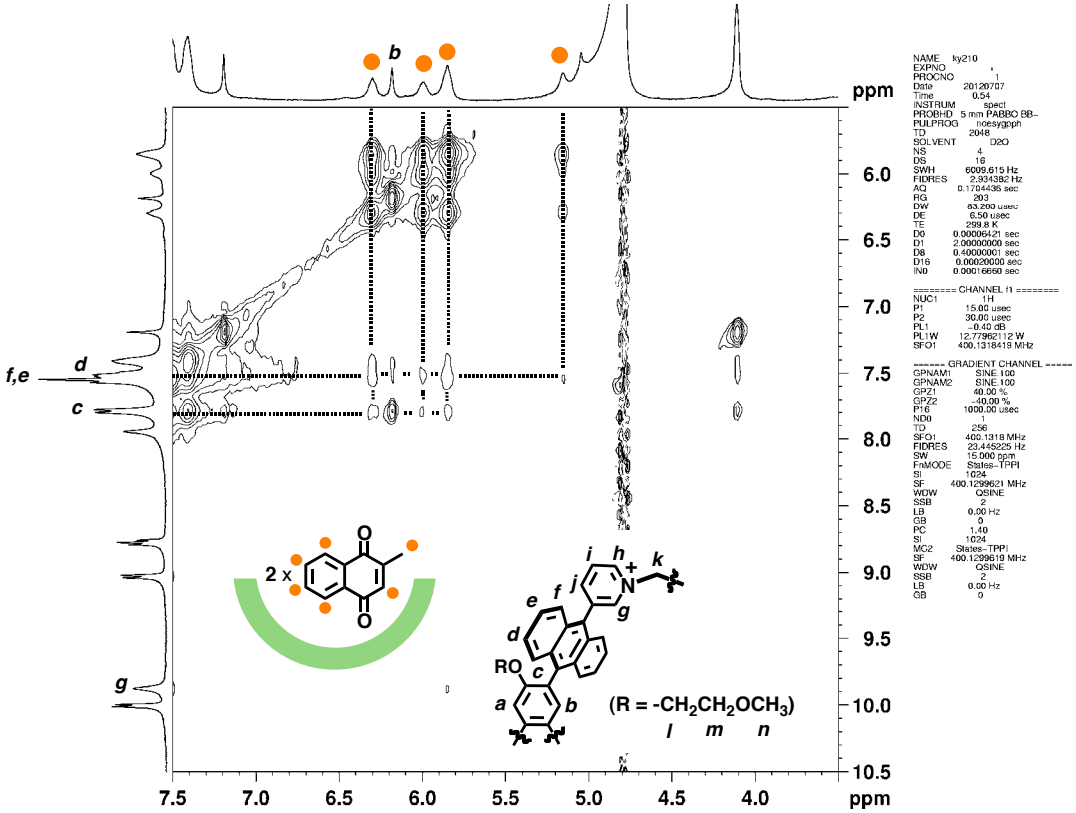


Fig. S21c. NOESY (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$ (host-guest region).

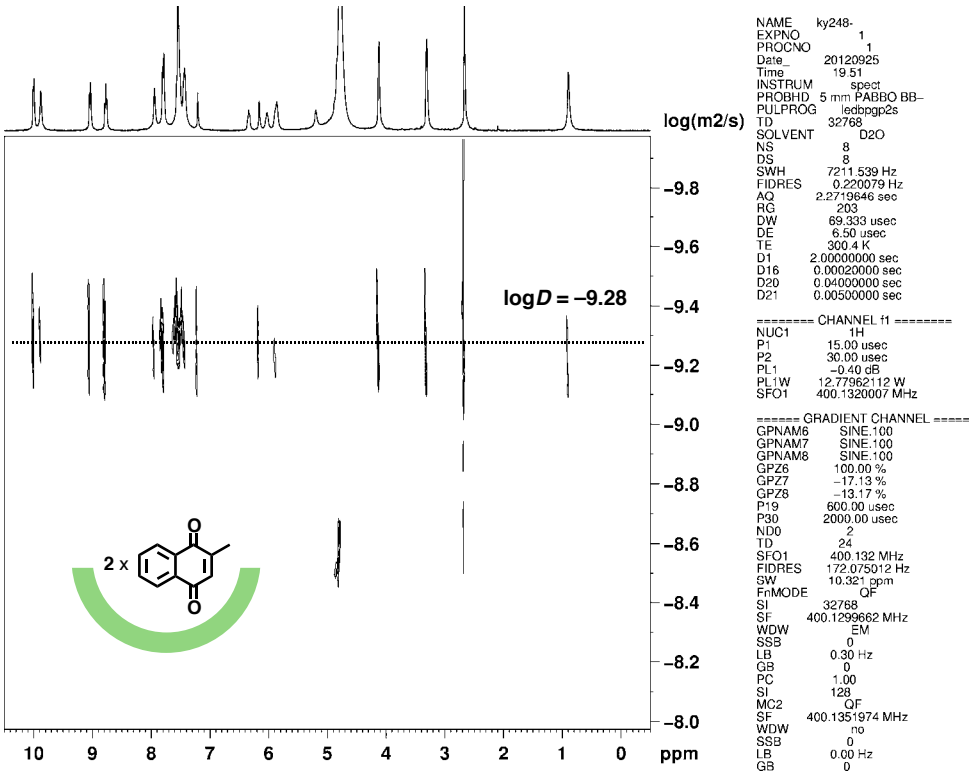


Fig. S22. DOSY (400 MHz, D_2O, 4 mM, 300 K) spectrum of **1b**⊃(**6**)$_2$.

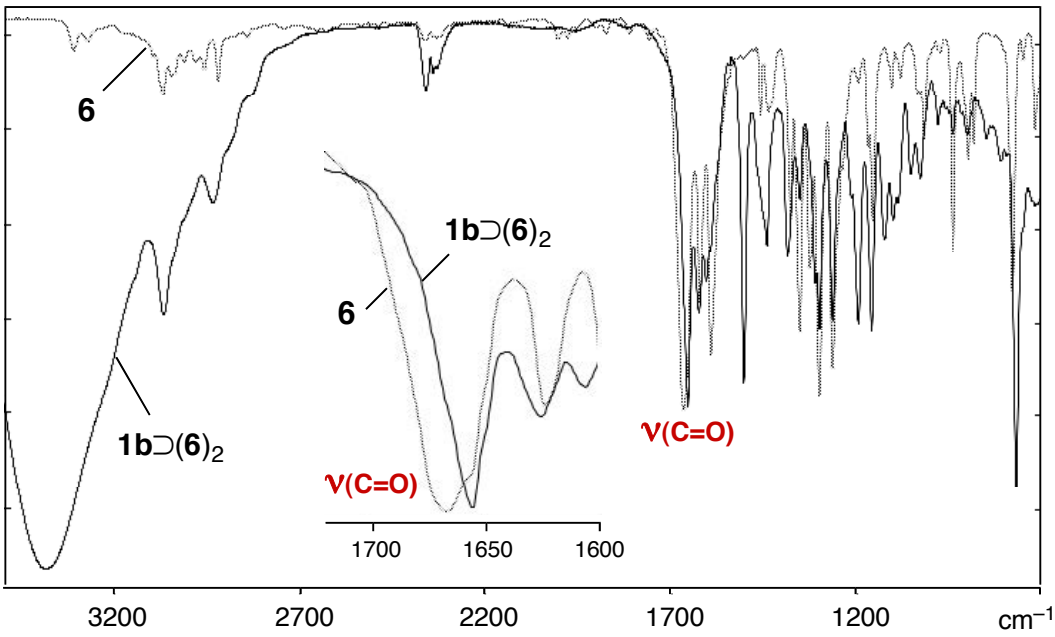
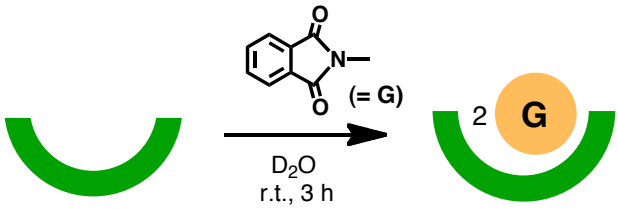


Fig. S23. FT-IR spectra (KBr) of **1b**⊃(**6**)$_2$ and **6**.

Encapsulation of *N*-methylphthalimide (7) by Bowl 1b KY243



N-Methylphthalimide (**7**; 1.0 mg, 6.2 μmol) was added to a D_2O 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.

^{1}H NMR (400 MHz, D_2O, 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, D_2O, 304 K): D = 6.9 x 10^{-10} m^2 s^{-1}.

ESI-TOF MS (H_2O): m/z 413.7 [**1b**⊃**7** – 4Cl$^-$]$^{4+}$, 453.9 [**1b**⊃(**7**)$_2$ – 4Cl$^-$]$^{4+}$.

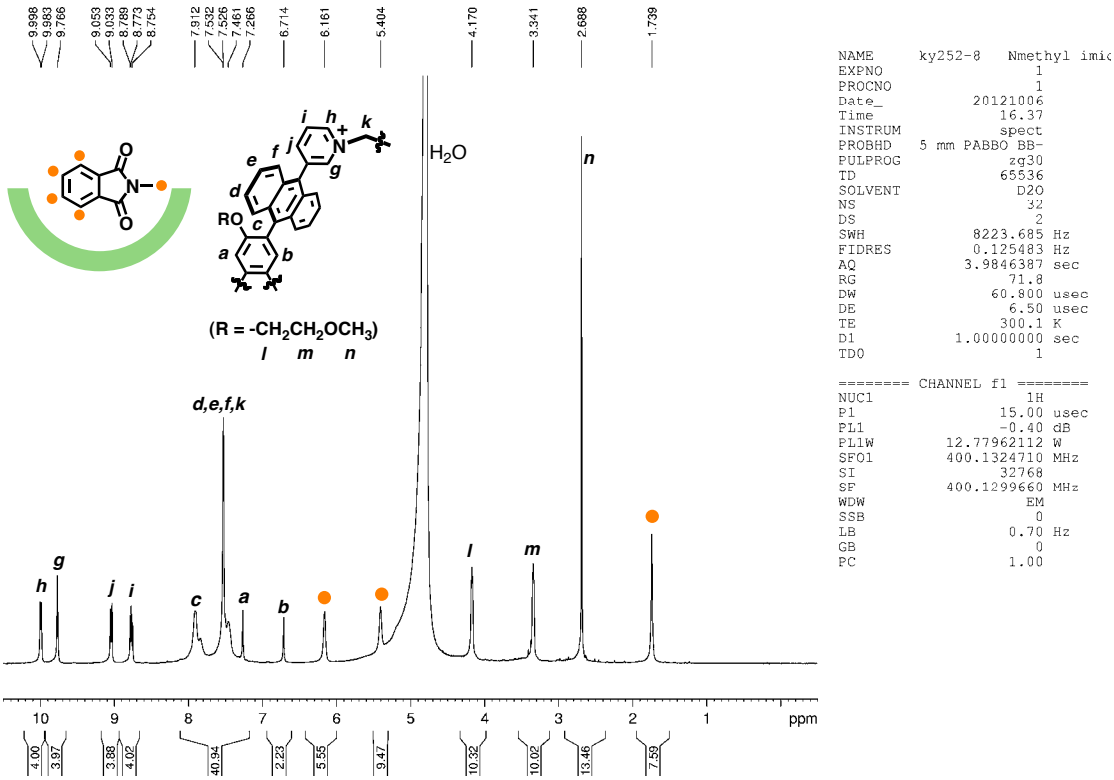


Fig. S24. ^{1}H NMR (400 MHz, D_2O, 4 mM, r.t.) spectrum of **1b**⊃(**7**)$_2$.

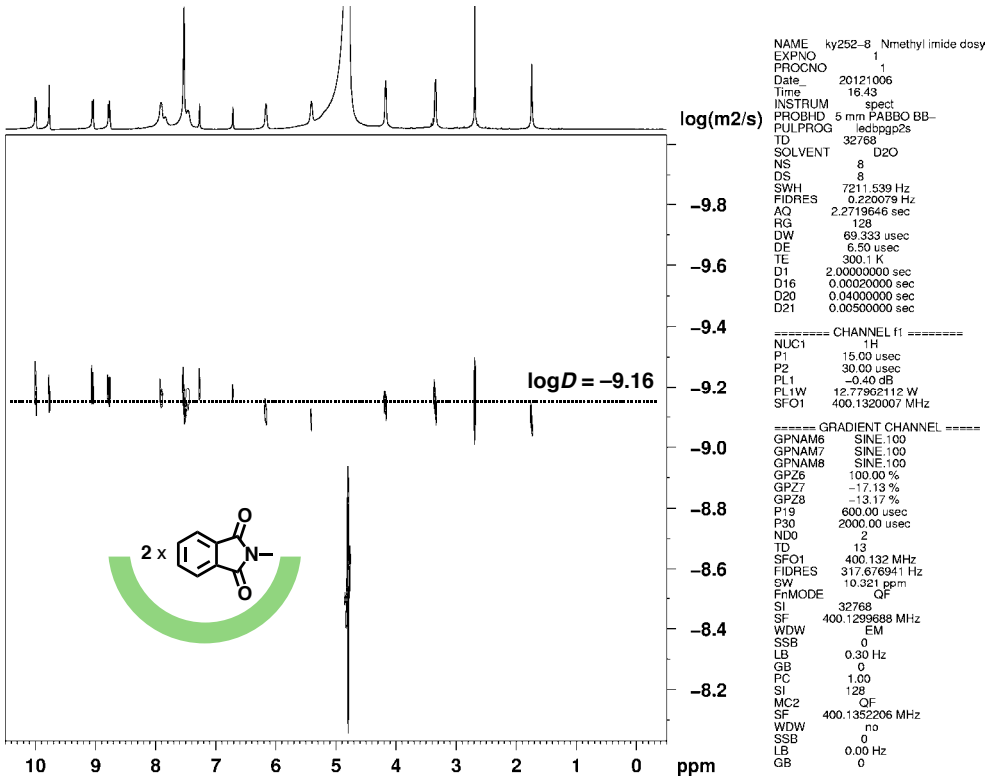


Fig. S25. DOSY (400 MHz, D_2O, 4 mM, 300 K) spectrum of **1b**⊃(**7**)$_2$.

Table. S1. Crystal data and structure refinement for **1a**

Identification code	KY84	
Empirical formula	C225 H210 I14.45 N8 O23	
Formula weight	5227.71	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 23.135(3) Å	α = 102.793(2)°
	b = 23.325(3) Å	β = 91.669(2)°
	c = 23.341(3) Å	γ = 90.170(2)°
Volume	12277.(3) Å^3	
Z	2	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	1.879 mm^{-1}	
F(000)	5132	
Crystal size	0.27 x 0.26 x 0.01 mm^3	
Theta range for data collection	2.04 to 25.03°.	
Index ranges	-27<=h<=27, -13<=k<=27, -27<=l<= 27	
Reflections collected	58449	
Independent reflections	42423 [R(int) = 0.0510]	
Completeness to theta = 25.03°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8344 and 0.7051	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	42423 / 633 / 2503	
Goodness-of-fit on F^2	1.319	
Final R indices [I>2sigma(I)]	R_1 = 0.1302, wR_2 = 0.3669	
R indices (all data)	R_1 = 0.1711, wR_2 = 0.3907	
Largest diff. peak and hole	5.669 and -2.438 e.Å^{-3}	

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.

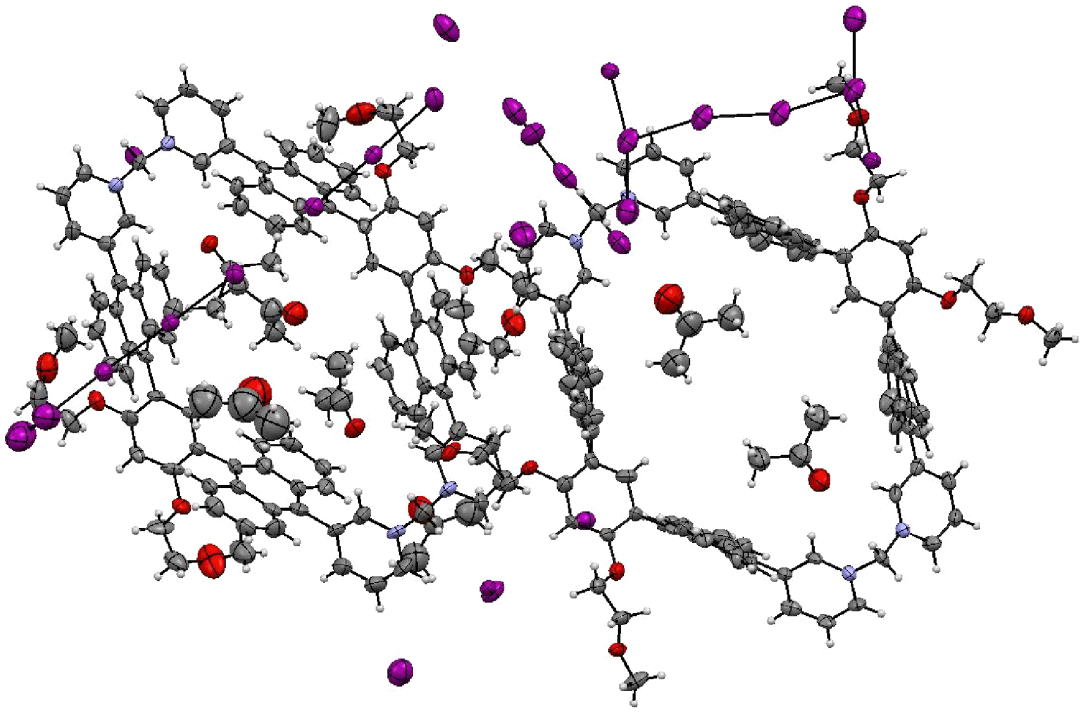


Fig. S26. ORTEP drawing of bowl **1a**.

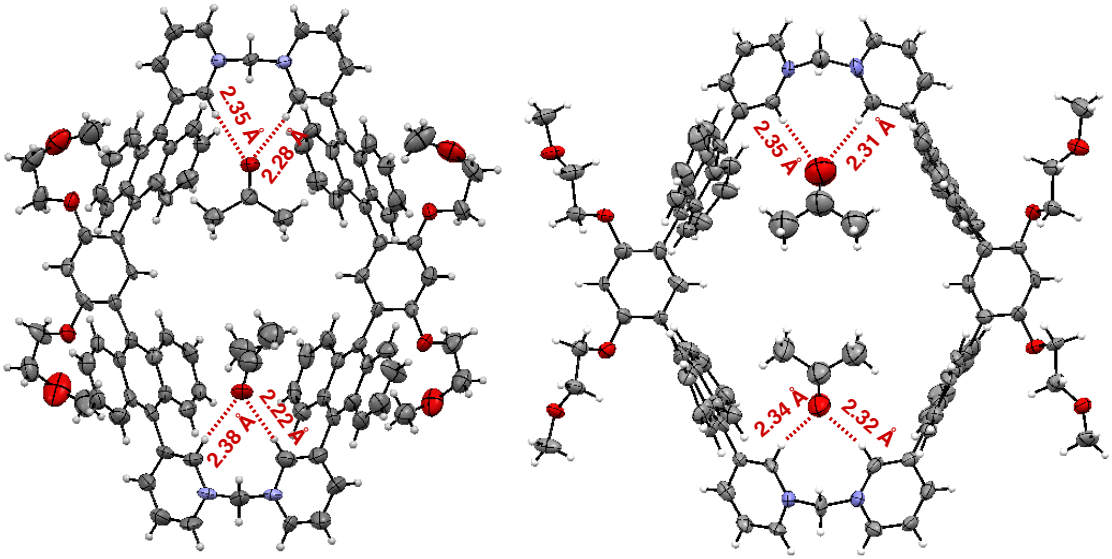


Fig. S27. Hydrogen bonding interactions between the carbonyl oxygen atoms of acetones and α-hydrogen atoms of the bispyridinium moieties of bowl **1a**.

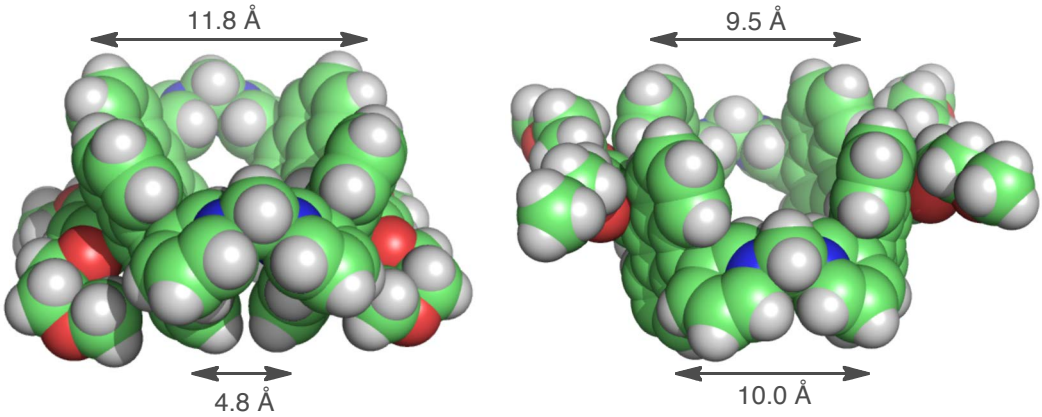
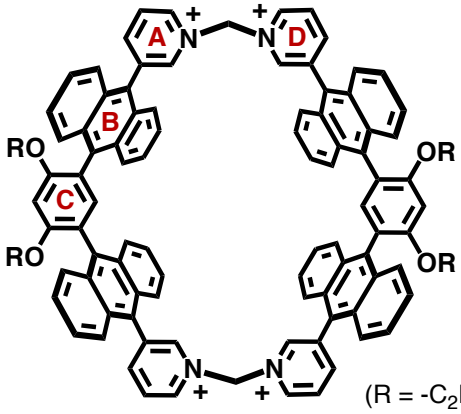


Fig. S28. Crystal structures of bowl **1a** in bowl (left) and tube-shape (right) conformations.



	bowl-shaped conformation	tube-shaped conformation	ideal
torsion angles			
ring A – ring B:	av. 83.6°	av. 57.9°	87.5°
ring B – ring C:	av. 85.8°	av. 65.3°	84.0°
bite angles			
ring A-CH_2-ring D:	av. 109.7°	av. 118.4°	111.6°

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

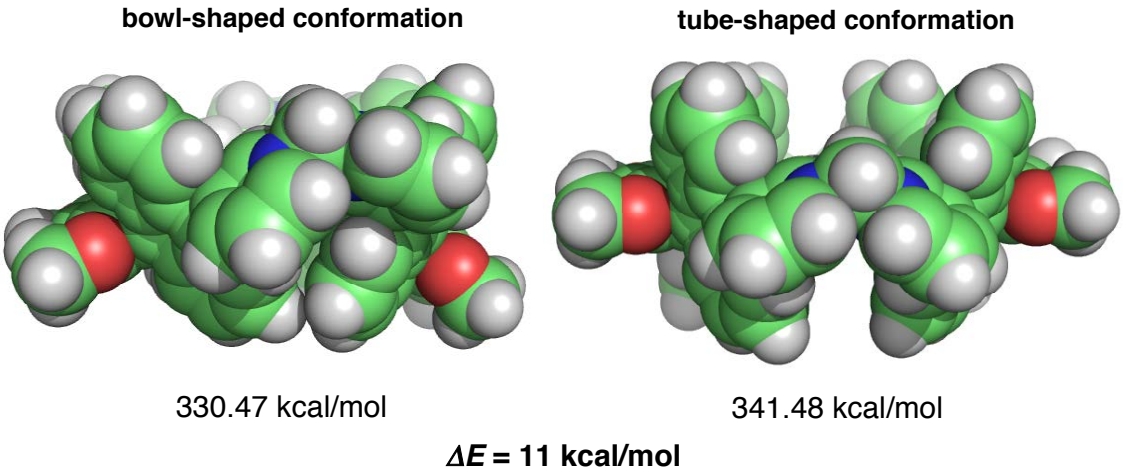


Fig. S30. Optimized structures of the bowl- and tube-shaped conformations of **1** (R = CH_3).

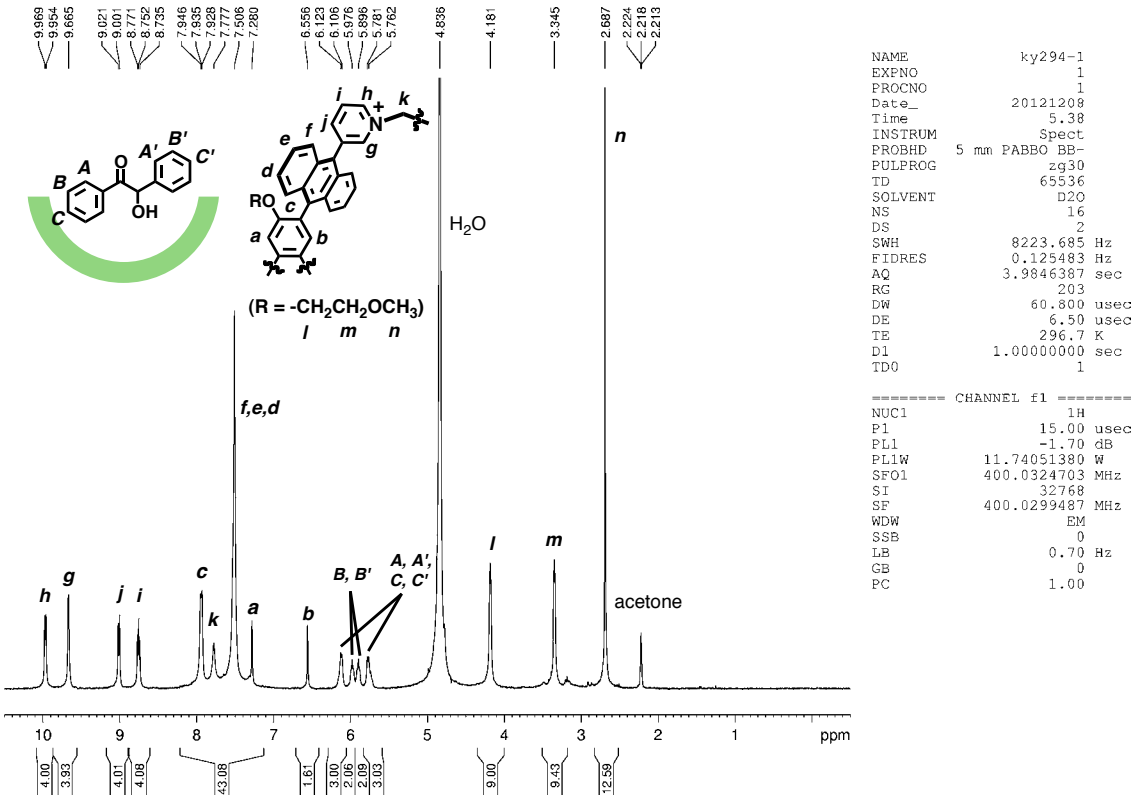


Fig. S31. ^{1}H NMR (400 MHz, D_2O:acetone-d_6 (10:1), 4 mM, r.t.) spectrum of **1b**⊃**3**.

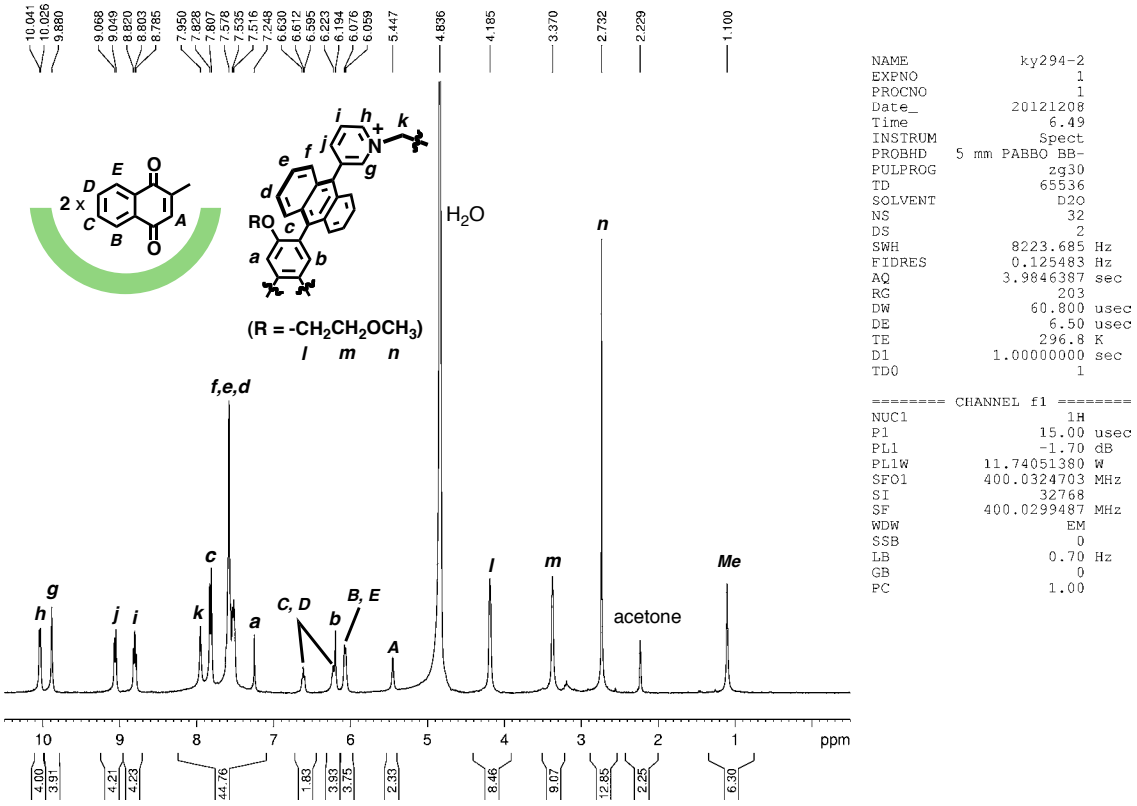


Fig. S32. ^{1}H NMR (400 MHz, D_2O:acetone-d_6 (10:1), 4 mM, r.t.) spectrum of **1b**⊃(**6**)$_2$.