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Electronic Supplementary Information

An Aqueous Molecular Tube with Polyaromatic Frameworks Capable of Binding Fluorescent Dyes

Keita Hagiwara, Munetaka Akita, Michito Yoshizawa*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
Fax: (+81)45-924-5230, E-mail: yoshizawa.m.ac@m.titech.ac.jp

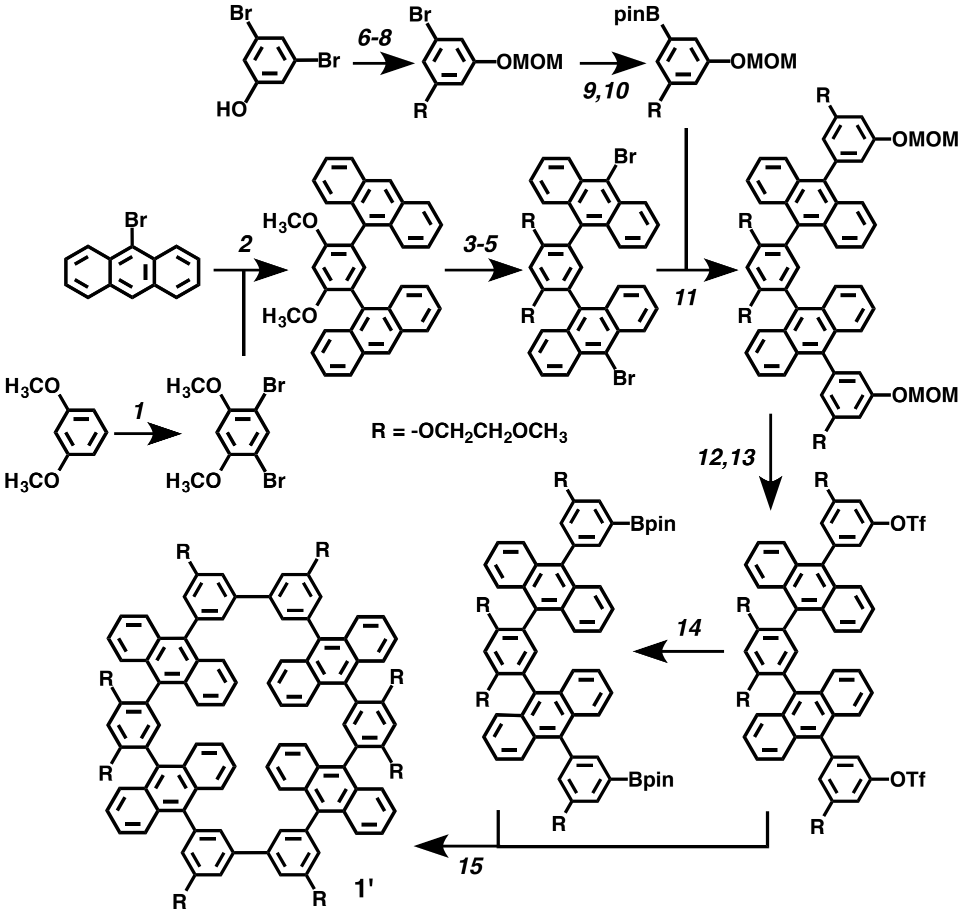
Contents

Materials and methods

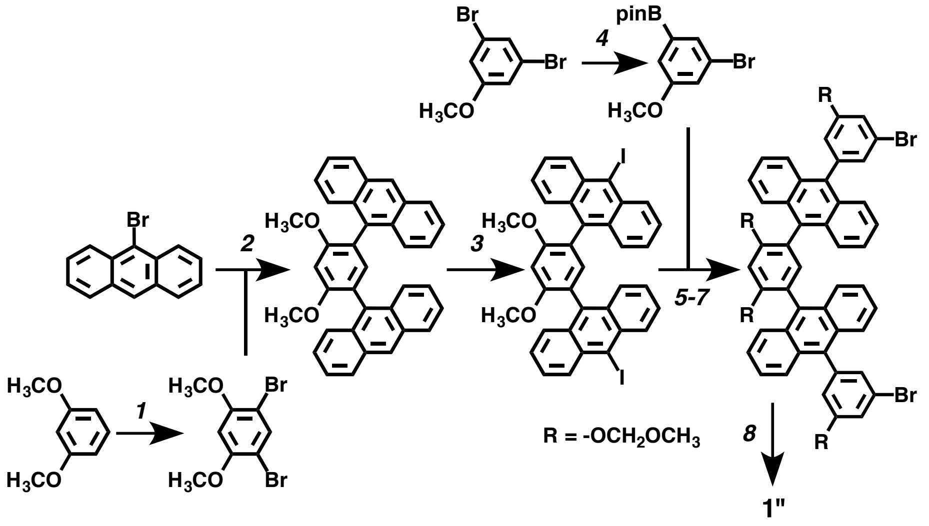
NMR: Bruker AVANCE-400 (400 MHz), GC MS: Shimadzu Parvum2/ULBON HR-1, MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, FT IR: JASCO FT/IR-4200, UV-vis: JASCO V-670DS, Fluorescence: SHIMADZU RF-5300PC, Elemental analysis: LECO CHNS-932 VTF-900, Absolute PL quantum yield: Hamamatsu C9920-02G with an integration sphere, Fluorescence lifetime: Hamamatsu C11367-01, Recycled GPC: JAI LC-9225NEXT, DLS: Wyatt Technology DynaPro NanoStar, Force-field calculation: Materials Studio version 5.0 (Accelrys Software Inc., San Diego, CA).

Solvents and reagents: TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO CHEMICAL CO., INC., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. Anthracene dimers **3a** and **3b** were synthesized according to previously reported procedures (M. Yoshizawa *et al*., *J. Am. Chem. Soc*., **2011**, *133*, 11438–11441 and *Chem. Asian J.,* **2014**, *9*, 1016–1019).

Scheme S1. Previous synthetic route of tube **1'**.

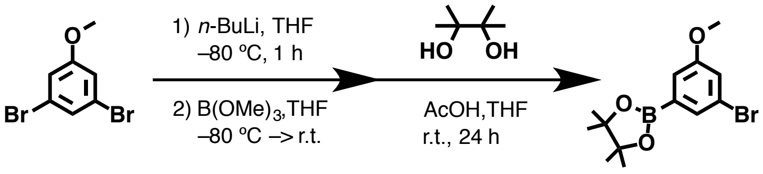


Scheme S2. New synthetic route of tube **1”**.



Synthesis of 3-bromo-5-methoxyphenylboronic acid pinacol ester

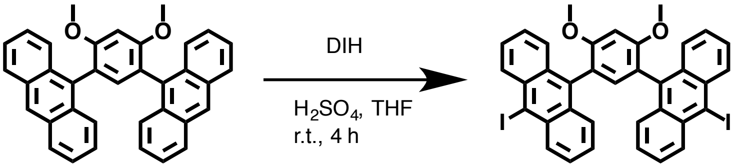
KH-268, (283, 296)



1,3-Dibromo-5-methoxybenzene (2.010 g, 7.558 mmol) and dry THF (100 mL) were added to a 2-necked 200 mL glass flask filled with N_2. A hexane solution (2.69 M) of *n*-butyllithium (3.0 mL, 7.8 mmol) was then added dropwise to this flask at –80 ºC under N_2. After the mixture was stirred at –80 ºC for 1 h, a dry THF solution (5 mL) of $B(OCH_3)_3$ (1.0 mL, 9.0 mmol) was added to the solution. The resultant mixture was further stirred at –80 ºC for 1 h and then warmed to r.t. for 1 h. Pinacol (1.280 g, 1.083 mmol) and AcOH (1 mL) were added to the solution and the resultant solution was stirred at r.t. for 24 h. The products were extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford 3-bromo-5-methoxyphenylboronic acid pinacol ester as a yellow solution (1.975 g, 6.310 mmol, 83%).

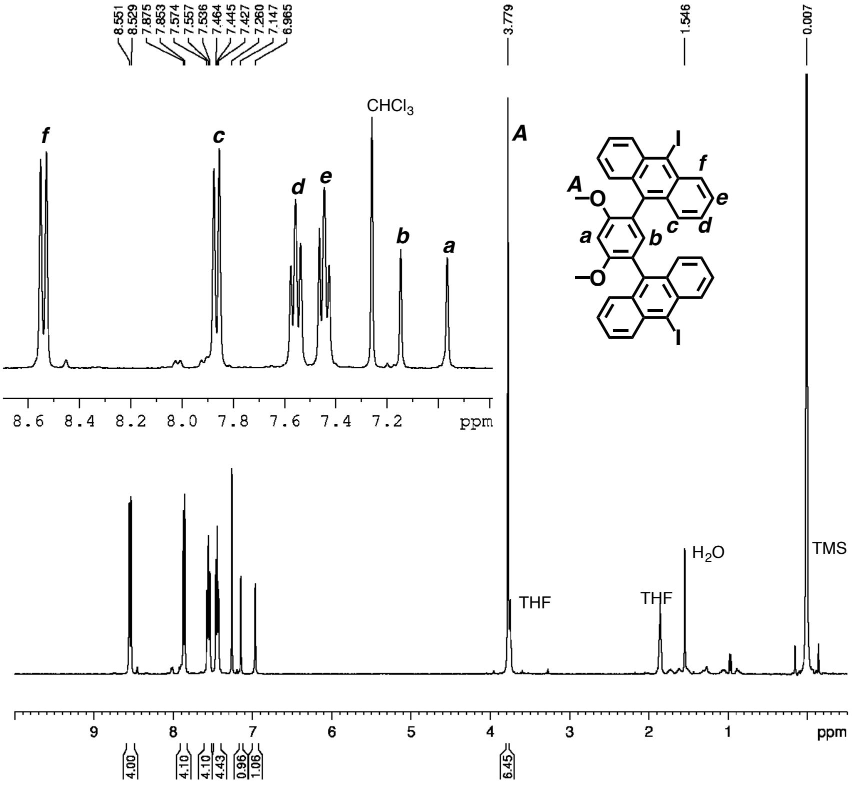
^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 7.52 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.15 (dd, J = 2.0, 2.0 Hz, 1H), 3.81 (s, 3H), 1.34 (s, 12H). GC-MS: *m/z* Calcd. for $C_{13}H_{18}BBrO_3$ 312, Found 312 $[M]^+$.

Synthesis of anthracene dimer 3b KH-287, (267, 283)



Anthracene dimer **3a** (7.762 g, 15.82 mmol) and THF (100 mL) were added to a 200 mL glass flask. 1,3-Diiodo-5,5-dimethylhydantoin (DIH; 8.036 g, 20.43 mmol) was added to the solution at 0 ºC and then concentrated H_2SO_4 (0.5 mL) was added to the solution. The resultant mixture was stirred at r.t. for 1 d. A precipitated crude product was washed with CH_3OH, H_2O, and hexane to afford **3b** as a yellow solid (7.679 g, 10.34 mmol; 65%).

^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.54 (d, J = 8.8 Hz, 4H), 7.86 (d, J = 8.8 Hz, 4H), 7.57-7.52 (m, 4H), 7.46-7.43 (m, 4H), 7.15 (s, 1H), 6.97 (s, 1H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ 159.1 (C_q), 136.5 (CH), 135.5 (C_q), 134.0 (CH), 133.8 (C_q), 131.7 (C_q), 127.6 (CH), 127.5 (CH), 125.8 (CH), 119.2 (C_q), 105.9 (C_q), 96.3 (CH), 56.2 (CH_3). FT-IR (KBr, cm^{-1}): 3440, 3068, 2942, 2836, 1606, 1506, 1450, 1330, 1261, 1201, 1157, 1029, 866, 752. MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{36}H_{24}I_2O_2$ $[M]^+$ 741.99, Found 741.80.



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D1            1.00000000 sec
TD0                    1

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WDW                   EM
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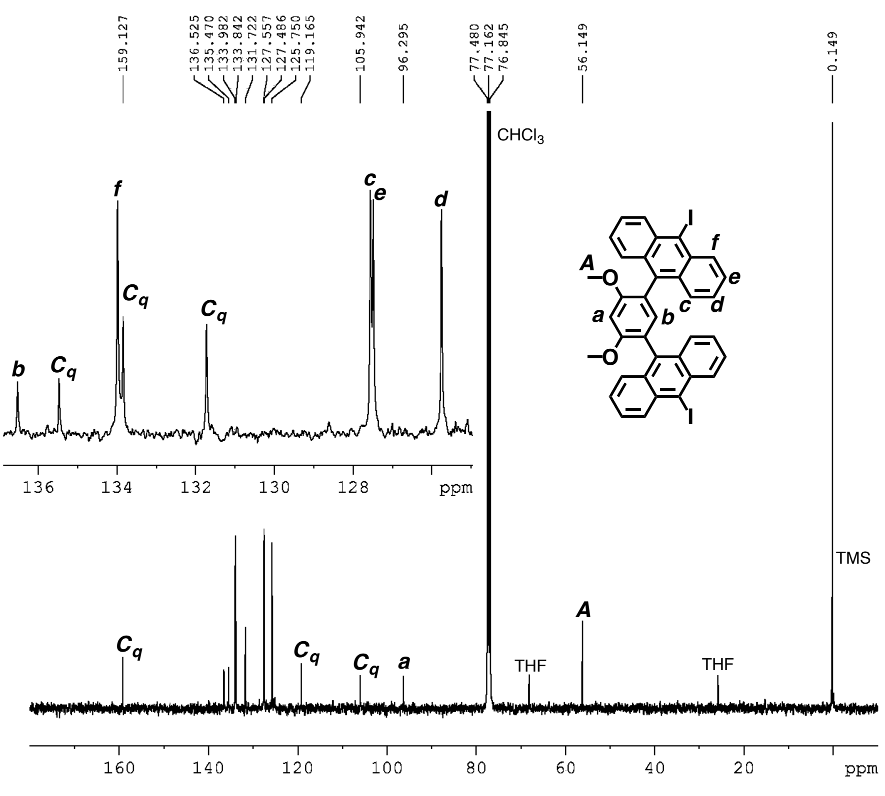
Figure S1. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, r.t.) of **3b**.



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FIDRES          0.366798 Hz
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RG                  90.5
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DE                  6.50 usec
TE                 299.1 K
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D11           0.03000000 sec
TD0                    1

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PL1                -2.00 dB
PL1W         57.72554016 W
SFO1         100.6228298 MHz

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NUC2                  1H
PCPD2              80.00 usec
PL2                -0.40 dB
PL12               14.60 dB
PL13               14.60 dB
PL2W         12.77962112 W
PL12W         0.40412706 W
PL13W         0.40412706 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127524 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.40
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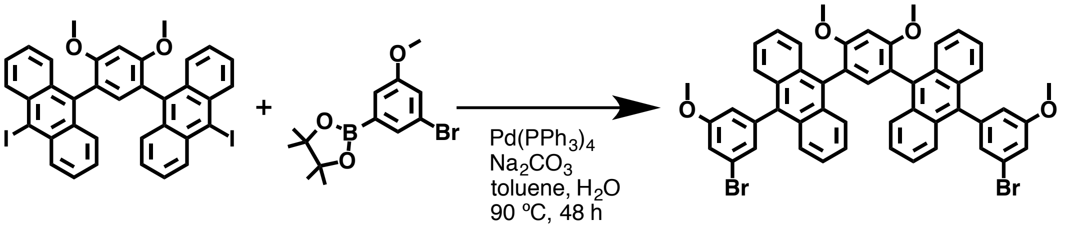
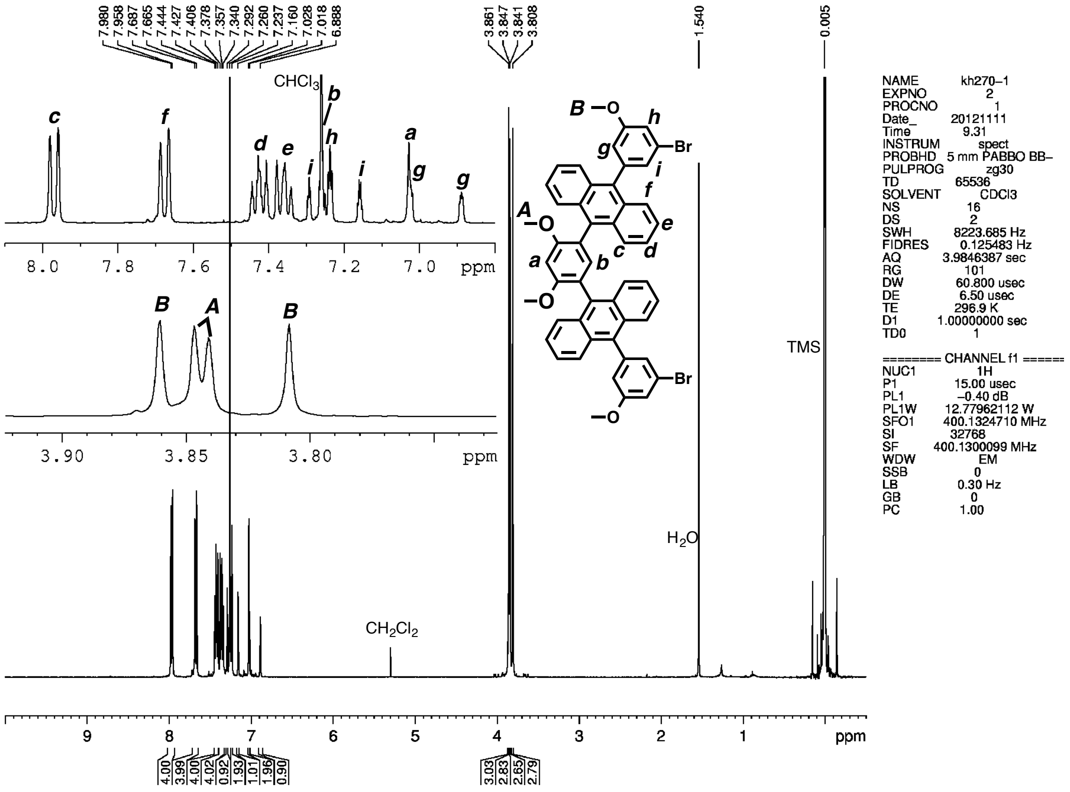
Figure S2. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, r.t.) of **3b**.

Synthesis of half-tube 2a

KH-270, (286)



Anthracene dimer **3b** (1.952 g, 2.629 mmol), 3-bromo-5-methoxyphenylboronic acid pinacol ester (1.975 g, 6.310 mmol), $Pd(PPh_3)_4$ (0.154 g, 0.133 mmol), and toluene (150 mL) were added to a 2-necked 100 mL glass flask filled with N_2. A degassed aqueous solution (25 mL) of Na_2CO_3 (3.824 g, 36.07 mmol) was added to this flask and the resultant mixture was stirred at 100 °C for 48 h. The mixture was concentrated under reduce pressure and the crude product was extracted with $CHCl_3$. The obtained crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) and GPC ($CHCl_3$) to afford half-tube **2a** as a yellow solid (1.233 g, 1.432 mmol; 54%). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 7.97 (d, J = 8.8 Hz, 4H), 7.68 (d, J = 8.8 Hz, 4H), 7.43 (dd, J = 8.8, 7.6 Hz, 4H), 7.36 (dd, J = 8.8, 7.6 Hz, 4H), 7.29 (s, 1H), 7.26 (s, 1H, overlapped by $CHCl_3$), 7.24 (s, 2H), 7.16 (s, 1H), 7.03-7.02 (m, 2H), 6.89 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ 160.4 (C_q), 159.1 (C_q), 142.4 (C_q), 137.1 (CH), 135.2 (C_q), 134.1 (C_q), 130.5 (C_q), 129.9 (C_q), 127.1 (CH), 126.9 (CH), 126.8 (CH), 125.4 (CH), 125.2 (CH), 123.0 (C_q), 119.5 (C_q), 116.7 (CH), 116.1 (CH), 96.3 (CH), 56.2 (CH_3), 55.8 (CH_3). FT-IR (KBr, cm^{-1}): 3068, 3007, 2941, 2837, 1597, 1454, 1371, 1259, 1201, 1041, 847, 766. MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{50}H_{36}Br_2O_4$ $[M]^+$ 860.10, Found 859.88. E.A.: Calcd. for $C_{50}H_{36}Br_2O_4 \bullet 0.5CH_2Cl_2$: C, 67.16; H, 4.13. Found: C, 67.27; H, 4.00.



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FIDRES      0.125483 Hz
AQ         3.9846387 sec
RG               101
DW            60.800 usec
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TE             296.9 K
D1        1.00000000 sec
TD0                1

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SI             32768
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WDW               EM
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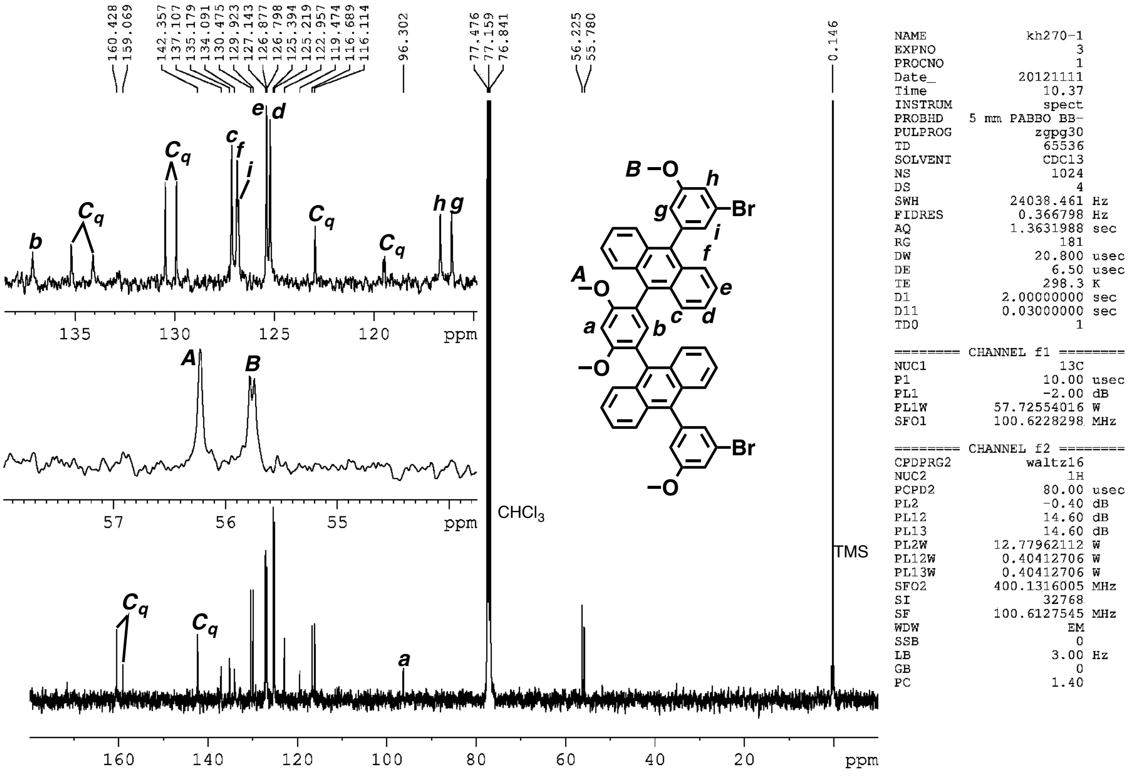
Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, r.t.) of **2a**.



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TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    181
DW                 20.800 usec
DE                   6.50 usec
TE                  298.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                 -2.00 dB
PL1W          57.72554016 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
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PL12                14.60 dB
PL13                14.60 dB
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PL12W          0.40412706 W
PL13W          0.40412706 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127545 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40
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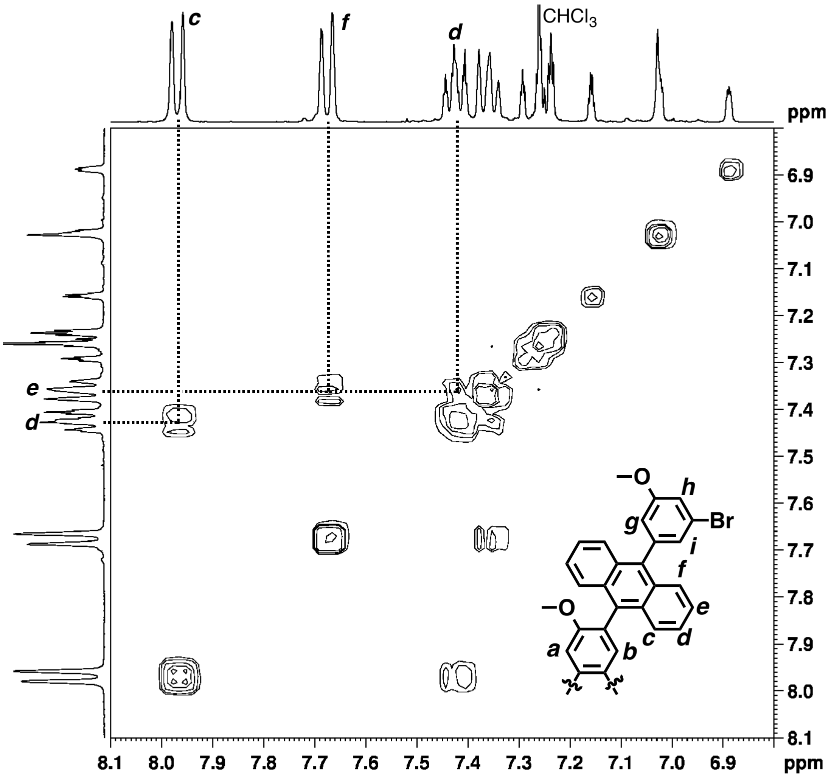
Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, r.t.) of **2a**.



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TD                   2048
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DS                      8
SWH              5341.880 Hz
FIDRES           2.608340 Hz
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RG                    203
DW                 93.600 usec
DE                   6.50 usec
TE                  297.2 K
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D1             1.48689198 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00018720 sec

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P1                  15.00 usec
PL1                 -0.40 dB
PL1W          12.77962112 W
SFO1          400.1324057 MHz

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FIDRES          41.733440 Hz
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SF            400.1300093 MHz
WDW                  SINE
SSB                     0
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GB                      0
PC                   1.40
SI                   1024
MC2                    QF
SF            400.1300072 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
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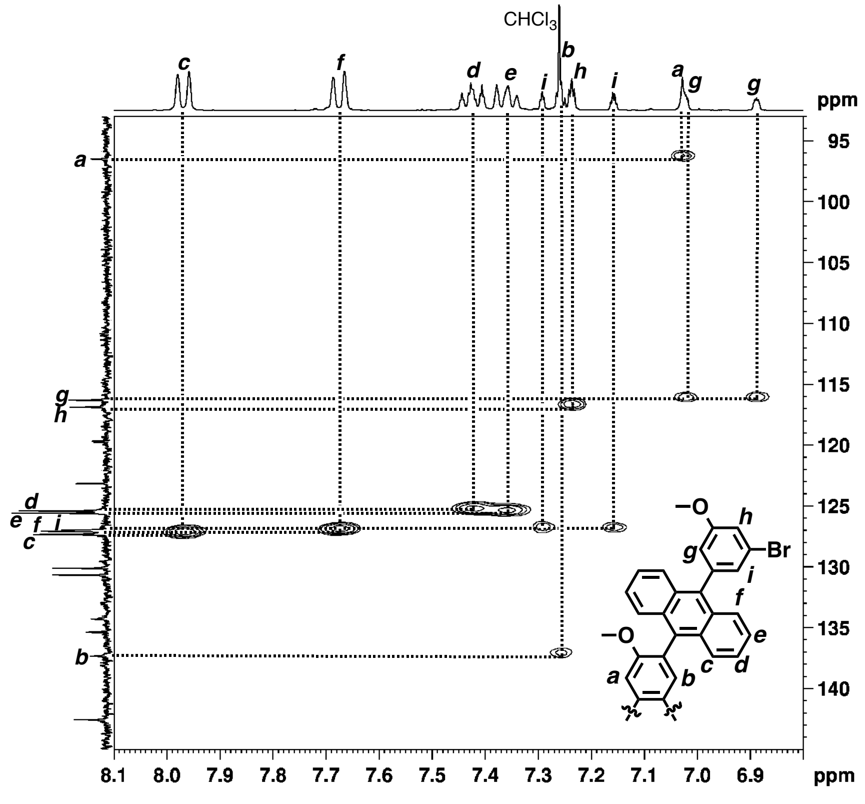
Figure S5. ^{1}H-^{1}H COSY spectrum (400 MHz, $CDCl_3$, r.t.) of **2a** (aromatic region).



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FIDRES           5.205557 Hz
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RG                    203
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TE                  297.3 K
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IN0            0.00003000 sec
ZGOPTNS

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P2                  30.00 usec
P28                  0.00 usec
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SFO1          400.1324057 MHz

======== CHANNEL f2 ========
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NUC2                  13C
P3                  10.00 usec
P4                  20.00 usec
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                16.06 dB
PL2W          57.72554016 W
PL12W          0.90233552 W
SFO2          100.6203124 MHz

====== GRADIENT CHANNEL =====
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GPNAM2           SINE.100
GPNAM3           SINE.100
GPNAM4           SINE.100
GPZ1                80.00 %
GPZ2                20.10 %
GPZ3                11.00 %
GPZ4                -5.00 %
P16               1000.00 usec
P19                600.00 usec
ND0                     2
TD                    256
SFO1             100.6203 MHz
FIDRES          65.108421 Hz
SW                165.650 ppm
FnMODE      Echo-Antiecho
SI                   1024
SF            400.1300084 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2         echo-antiecho
SF            100.6127553 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
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Figure S6. HSQC spectrum (400 MHz, $CDCl_3$, r.t.) of **2a** (aromatic region).

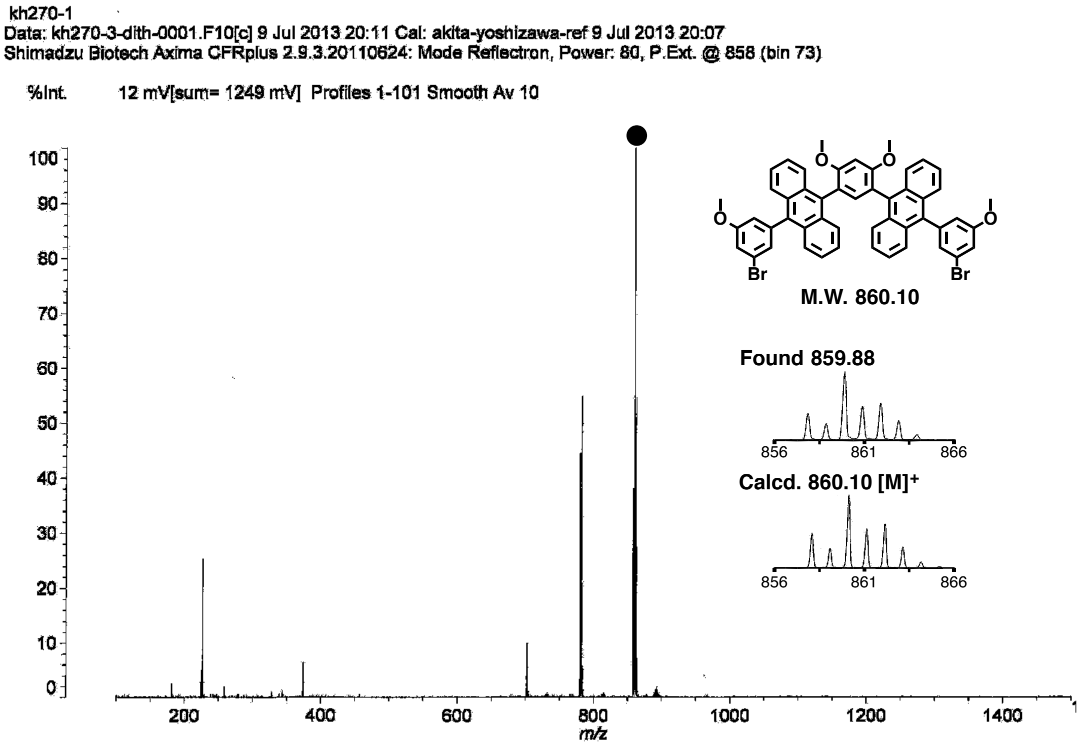
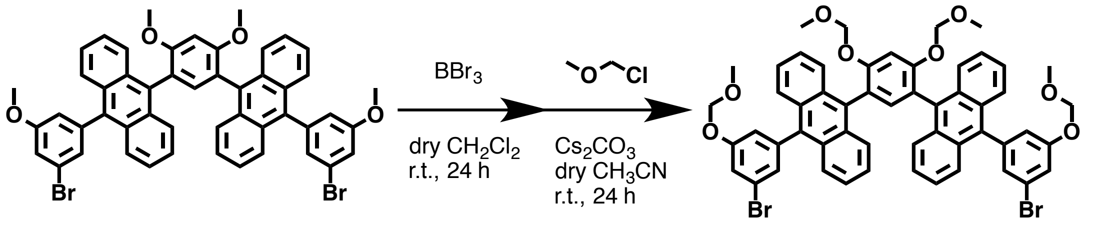


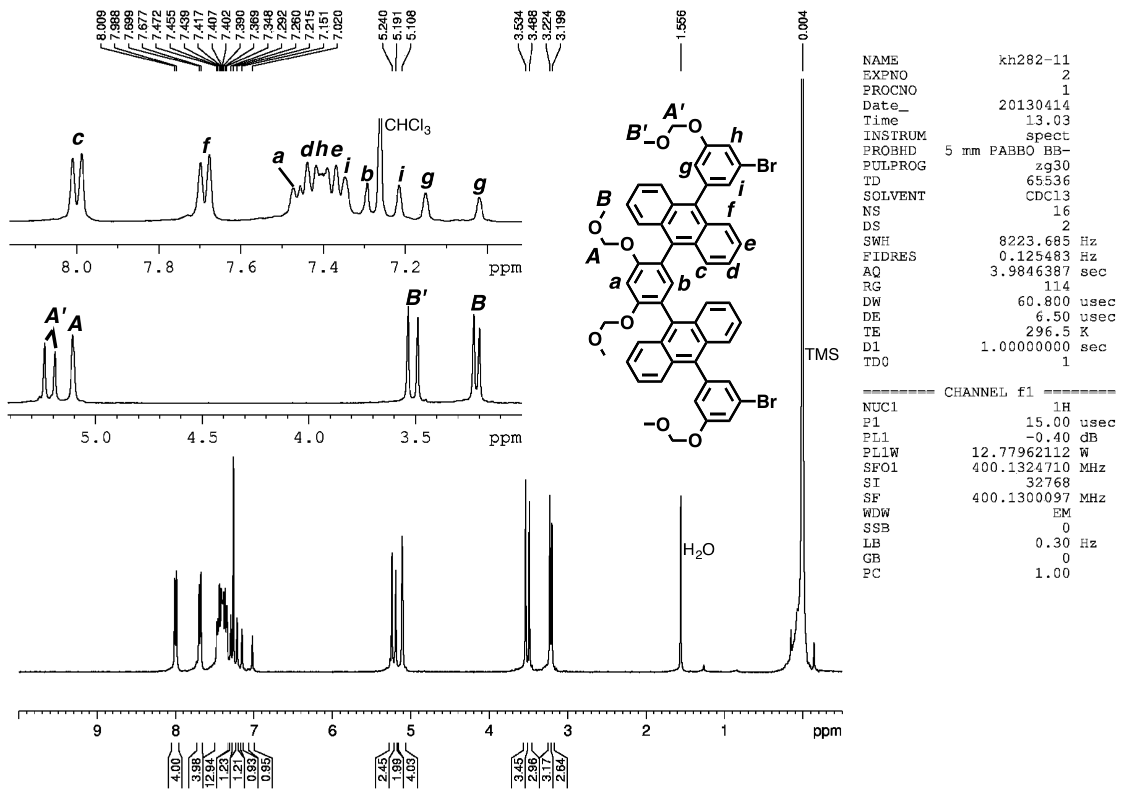
Figure S7. MALDI-TOF MS spectrum (dithranol) of **2a**.

Synthesis of half-tube 2b KH-279, (286, 298)



Dry CH_2Cl_2 (50 mL) and half-tube **2a** (0.500 g, 0.581 mmol) were added to a 2-necked 200 mL glass flask filled with N_2. A CH_2Cl_2 solution (1.0 M) of BBr_3 (5.4 mL, 5.4 mmol) was slowly added to the solution at 0 °C and then the combined solution was stirred at 40 °C for 12 h. The reaction was quenched with H_2O. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The resultant solid was washed with H_2O and hexane to afford a yellow solid. The resulted solid, Cs_2CO_3 (1.21 g, 3.73 mmol), and dry CH_3CN (30 mL) were added to a 2-necked 300 mL glass flask filled with N_2. After the mixture was stirred at r.t. for 30 min, chloromethyl methyl ether (0.45 g, 5.7 mmol) was added to the solution. The resultant solution was stirred at r.t. for 16 h. The reaction was quenched with H_2O. The crude product was extracted with CH_2Cl_2 and the combined organic phase was dried over $MgSO_4$, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give **2b** as a yellow solid (0.400 g, 0.408 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.00 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 7.47-7.35 (m, 12H), 7.29 (s, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.02 (s, 1H), 5.24 (s, 2H), 5.19 (s, 2H), 5.11 (s, 4H), 3.53 (s, 3H), 3.49 (s, 3H), 3.22 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ 158.2 (C_q), 156.6 (C_q), 142.4 (C_q), 137.0 (CH), 135.1 (C_q), 134.1 (C_q), 130.5 (C_q), 129.9 (C_q), 128.1 (CH), 127.2 (CH), 126.8 (CH), 125.5 (CH), 125.3 (CH), 122.9 (C_q), 122.2 (C_q), 118.9 (CH), 118.8 (CH), 118.5 (CH), 103.4 (CH), 95.0 (CH_2), 56.4 (CH_3). FT-IR (KBr, cm^{-1}): 3438, 3068, 2949, 2916, 2839, 1597, 1566, 1371, 1248, 1151, 1072, 1018, 920, 766. MALDI-TOF MS (dithranol): m/z Calcd. for $C_{54}H_{44}Br_2O_8$ $[M]^+$ 980.14, Found 979.93. E.A.: Calcd. for $C_{54}H_{44}Br_2O_8$: C, 66.13; H, 4.52. Found: C, 66.13; H, 4.25.



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RG                 114
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TE               296.5 K
D1          1.00000000 sec
TD0                  1

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SI               32768
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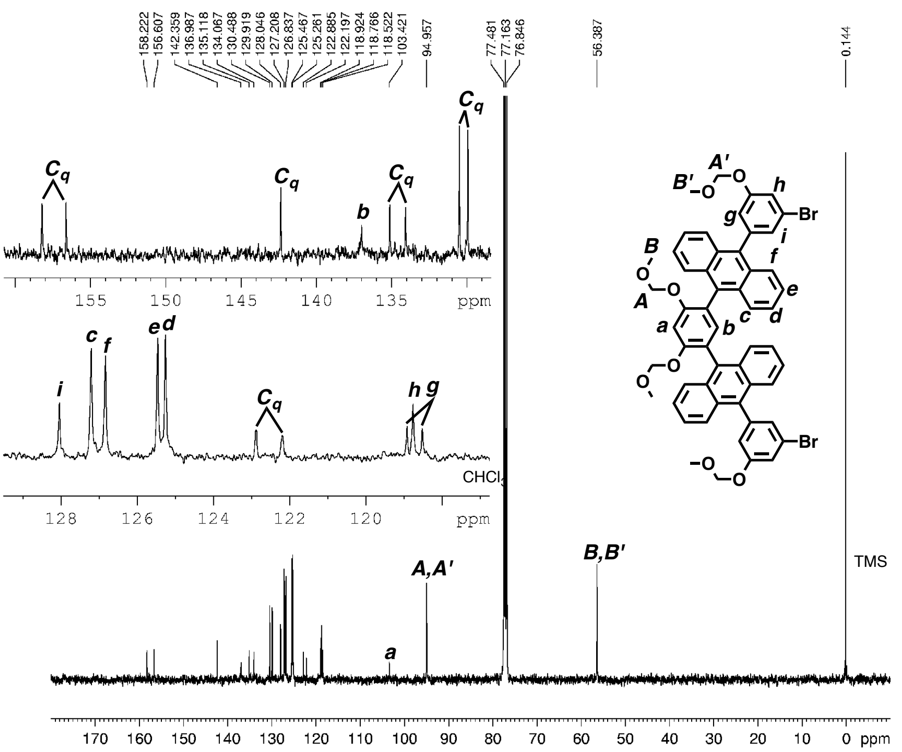
Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, r.t.) of **2b**.



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TD             65536
SOLVENT         CDCl3
NS              2048
DS                 4
SWH      24038.461 Hz
FIDRES    0.366798 Hz
AQ      1.3631988 sec
RG               128
DW        20.800 usec
DE          6.50 usec
TE           301.1 K
D1     2.00000000 sec
D11    0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1             13C
P1        10.00 usec
PL1         -2.00 dB
PL1W   57.72554016 W
SFO1  100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2      waltz16
NUC2              1H
PCPD2     80.00 usec
PL2         -0.40 dB
PL12        14.60 dB
PL13        14.60 dB
PL2W   12.77962112 W
PL12W   0.40412706 W
PL13W   0.40412706 W
SFO2  400.1316005 MHz
SI             32768
SF    100.6127509 MHz
WDW               EM
SSB                0
LB           3.00 Hz
GB                 0
PC              1.40
```

Figure S9. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, r.t.) of **2b**.

```
KH286
Data: kh286-1-dith-0001.F11[c] 9 Jul 2013 20:12 Cal: akita-yoshizawa-ref 9 Jul 2013 20:07
Shimadzu Biotech Axima CFRplus 2.9.3.20110624: Mode Reflectron, Power: 80, P.Ext. @ 978 (bin 78)
%Int.    840 mV[sum= 88148 mV]  Profiles 1-105 Smooth Av 10
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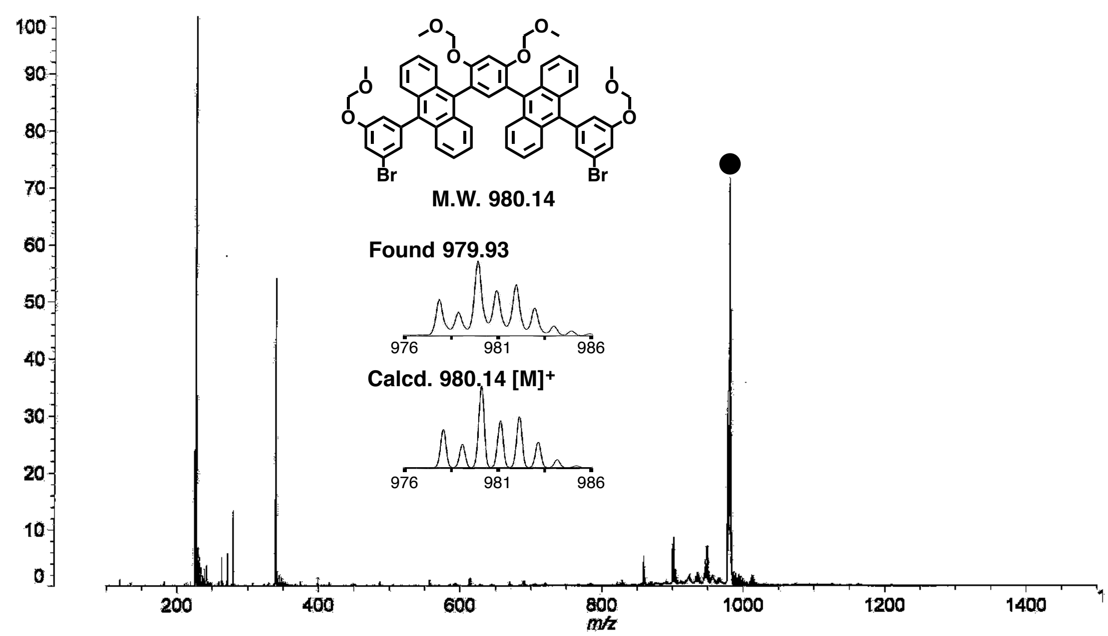
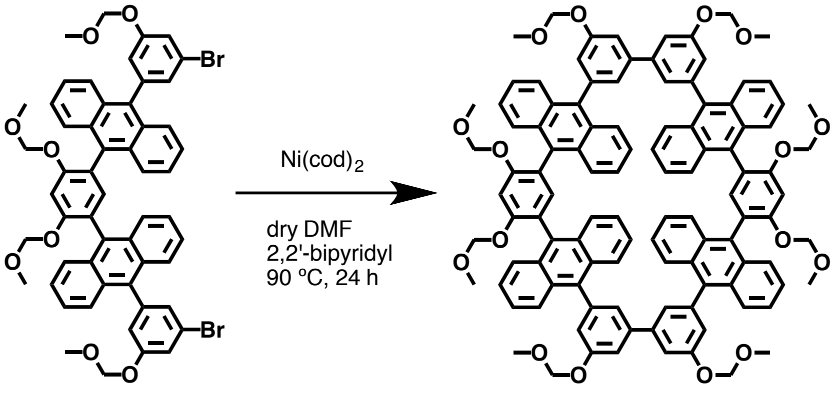


Figure S10. MALDI-TOF MS spectrum (dithranol) of **2b**.

Synthesis of tube 1” KH-304, (282, 289, 313)



Half-tube **2b** (0.150 g, 0.153 mmol), Ni(cod)$_2$ (0.098 g, 0.36 mmol), 2,2’-bipyridyl (0.064 g, 0.41 mmol), and dry DMF (50 mL) were added to a 2-necked 100 mL glass flask filled with N_2 and the resultant mixture was stirred at 90 °C for 24 h. The reaction was quenched with H_2O. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated under reduced pressure and washed with H_2O, CH_3OH, and acetone. The crude product was purified by silica-gel column chromatography (hexane:$CHCl_3$ = 10:1) to give **1”** as a yellow solid (0.037 g, 0.023 mmol, 30%).

^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 7.82 (d, J = 8.4 Hz, 8H), 7.65 (m, 4H), 7.61 (d, J = 8.4 Hz, 4H), 7.40 (s, 2H), 7.27-7.18 (m, 24H), 7.03 (s, 2H), 5.34 (s, 8H), 5.04 (s, 8H), 3.60 (s, 12H), 3.19 (s, 12H). FT-IR (KBr, cm^{-1}): 3460, 3063, 2952, 2925, 2851, 2827, 1587, 1379, 1150, 1082, 1000, 923, 768. MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{108}H_{88}O_{16}$ [M]$^+$ 1641.61, Found 1641.44. HR MS (ESI): *m/z* Calcd. for $C_{108}H_{88}O_{16}$ [M]$^+$ 1641.6106, Found 1641.6082.

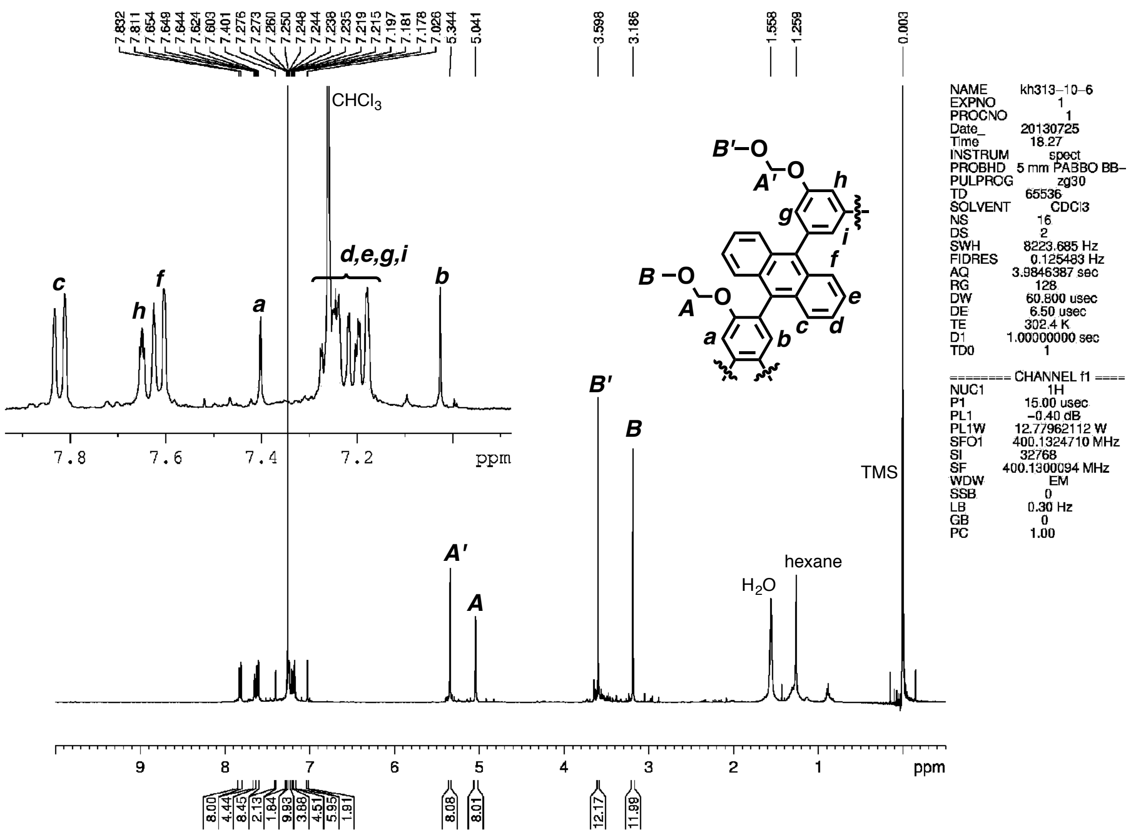


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, r.t.) of **1**”.

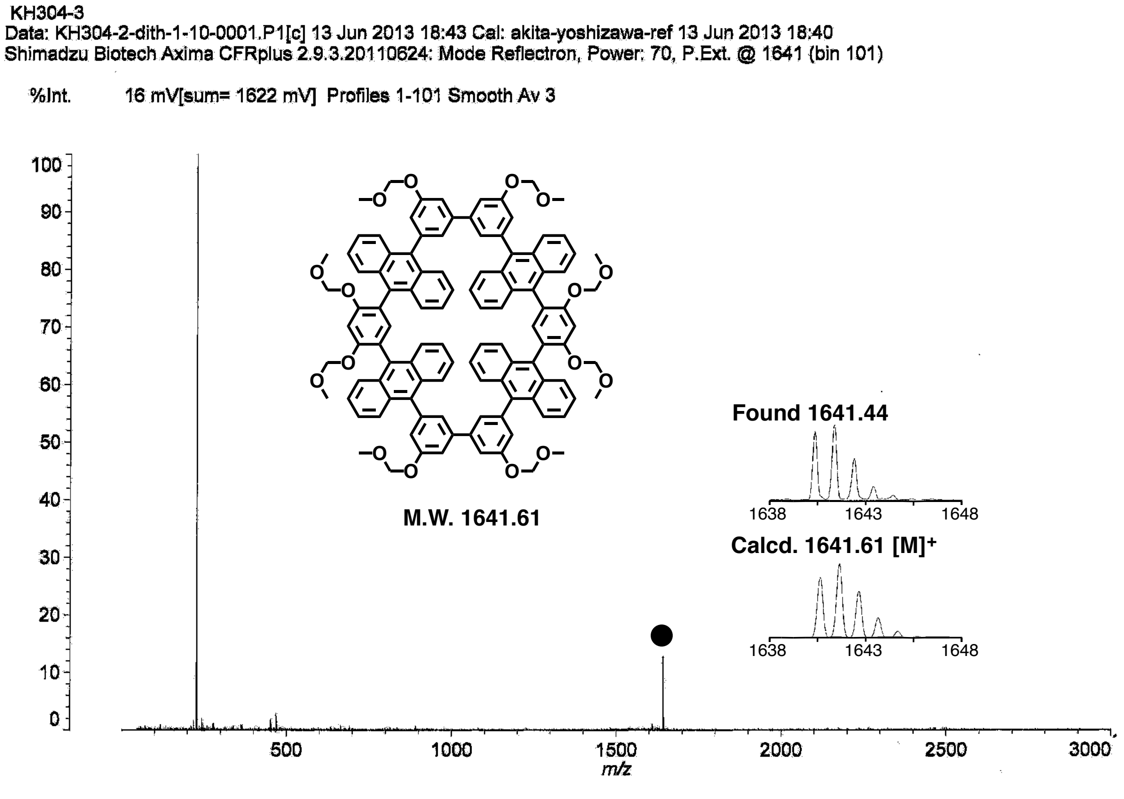
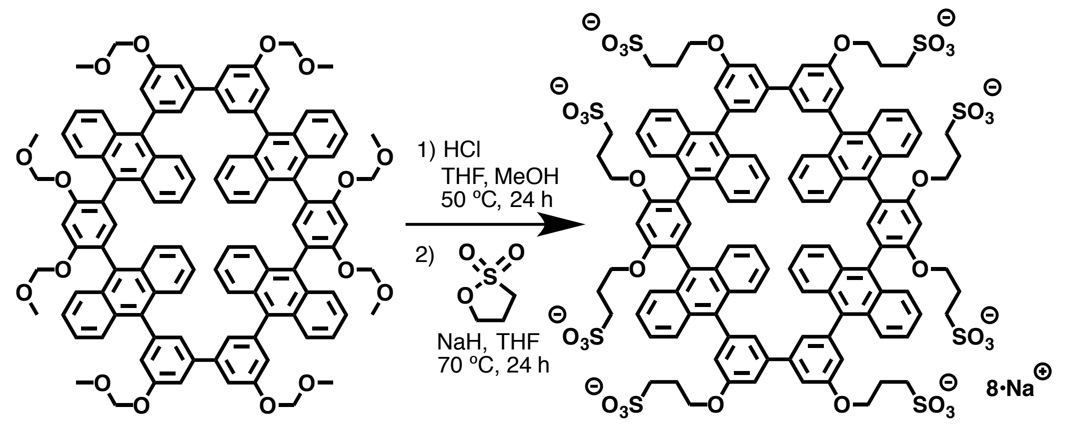


Figure S12. MALDI-TOF MS spectrum (dithranol) of **1**”.

Synthesis of tube 1 KH-349, (282, 295, 306, 322)



Tube **1”** (74.3 mg, 0.0452 mmol), THF (40 mL), and methanol (10 mL) were added to a 100 mL glass flask. Concentrated hydrochloric acid (50 mL) was added to this flask and stirred at 50 ºC for 24 h. The mixture was concentrated under reduce pressure. The crude product was washed with H_2O and $CHCl_3$, and purified by silica-gel column chromatography (hexane:acetone = 1:1) to give a deprotected tube as a white solid. NaH (60% in oil; 44.5 mg, 1.11 mmol) was added to a 100 mL glass flask and washed with hexane under N_2. The resultant deprotected tube and dry THF (20 mL) were added to this flask and stirred at r.t. for 1 h. 1,3-Propanesultone (0.135 g, 1.11 mmol) was added dropwise to this flask. The resultant mixture was stirred overnight at 80 ºC. The mixture was concentrated under reduce pressure and the crude product was washed with ether, acetone, and 1-propanol to afford **1** as a yellow solid (54.9 mg, 0.0225 mmol, 50%).

^{1}H NMR (400 MHz, CD_3OD, r.t.): δ 7.79 (d, J = 8.4 Hz, 8H), 7.65 (s, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.31-7.22 (m, 18H), 7.12 (s, 4H), 7.09 (m, 4H), 6.83 (s, 2H), 4.33 (t, J = 6.0 Hz, 8H), 4.23 (t, J = 6.0 Hz, 8H), 3.12 (t, J = 7.6 Hz, 8H), 2.47 (t, J = 7.6 Hz, 8H), 2.37 (q, J = 7.2 Hz, 8H), 1.95 (q, J = 7.2 Hz, 8H). ^{13}C NMR (100 MHz, CD_3OD, r.t.): δ 161.2 (C_q), 159.4 (C_q), 142.7 (C_q), 142.5 (C_q), 137.9 (CH), 137.5 (C_q), 134.9 (C_q), 131.5 (C_q), 131.0 (C_q), 127.9 (CH), 127.8 (CH), 126.1 (CH), 125.9 (CH), 123.0 (CH), 121.1 (C_q), 118.1 (CH), 113.4 (CH), 99.9 (CH), 68.6 (CH_2), 68.2 (CH_2), 49.4-48.6 (overlapped with MeOH), 26.5 (CH_2), 26.1 (CH_2). FT-IR (KBr, cm^{-1}): 3451, 1504, 1440, 1380, 1311, 1190, 1101, 1046, 801, 770, 606, 528. ESI-TOF MS (CH_3OH): m/z 383.8 [**1** – $6Na^+]^{6-}$, 465.2 [**1** – $5Na^+]^{5-}$, 587.2 [**1** – $4Na^+]^{4-}$, 791.0 [**1** – $3Na^+]^{3-}$.

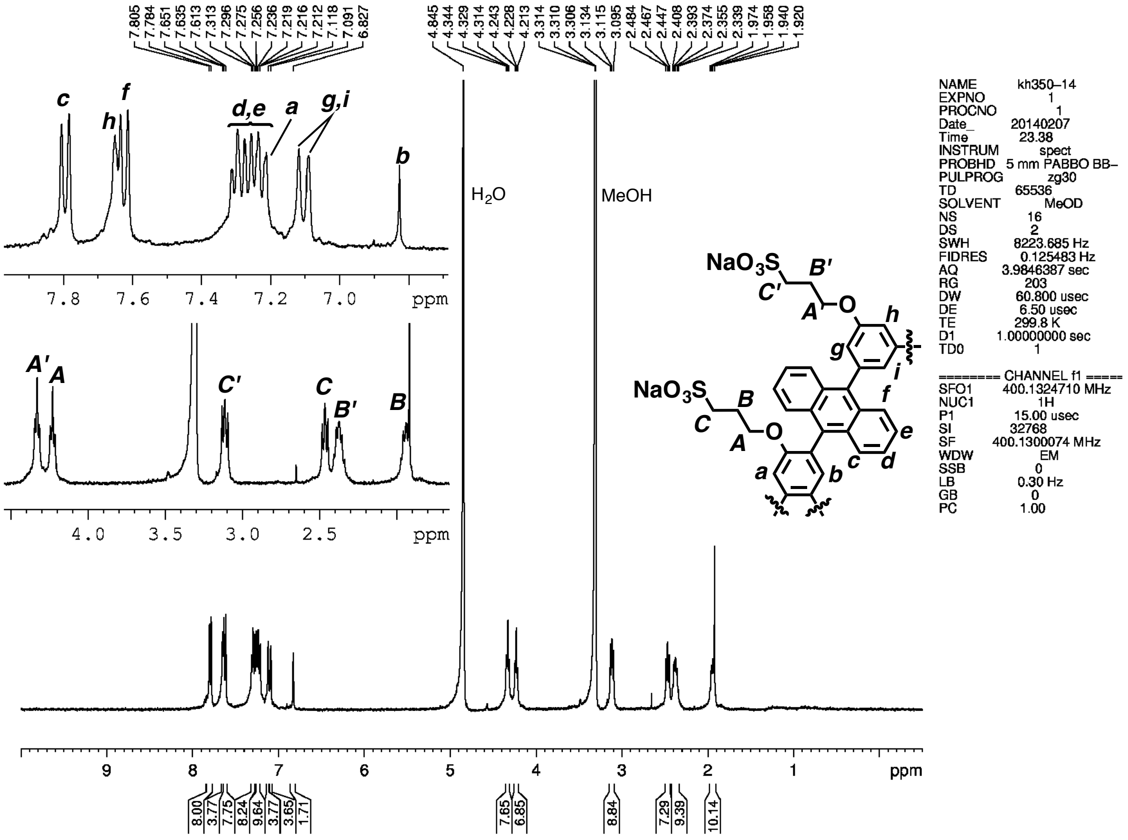


Figure S13. ^{1}H NMR spectrum (400 MHz, CD_3OD, r.t.) of **1**.

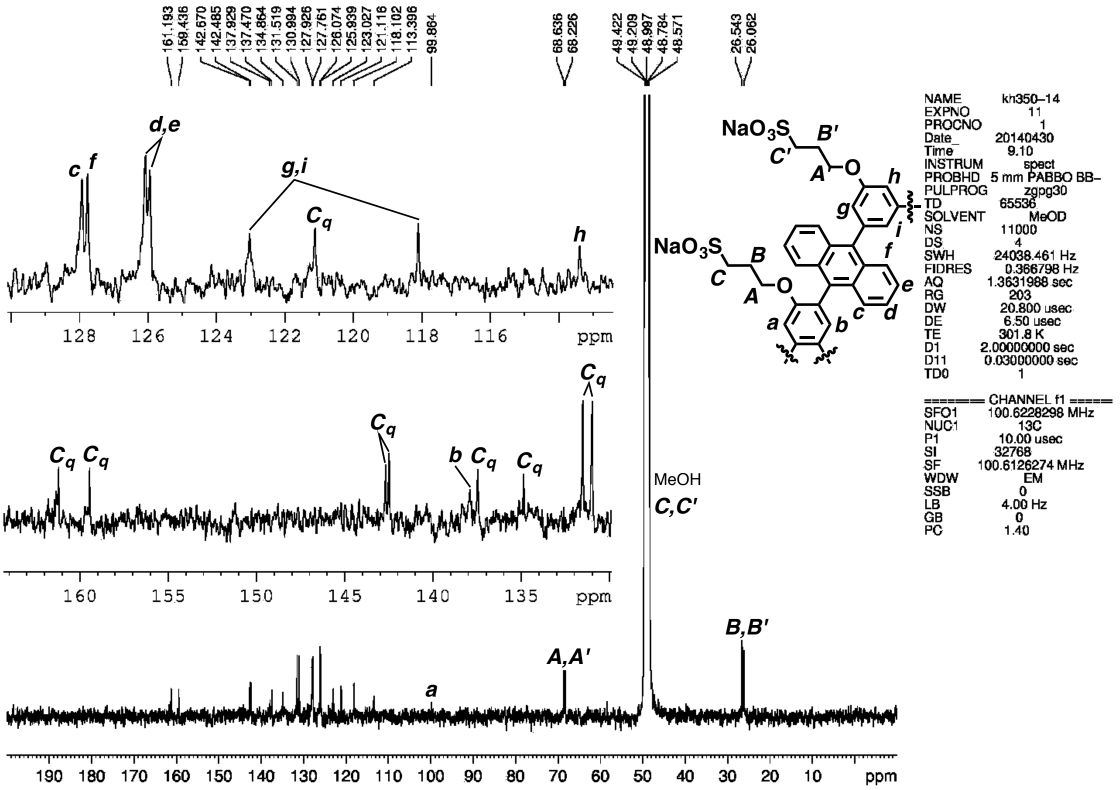
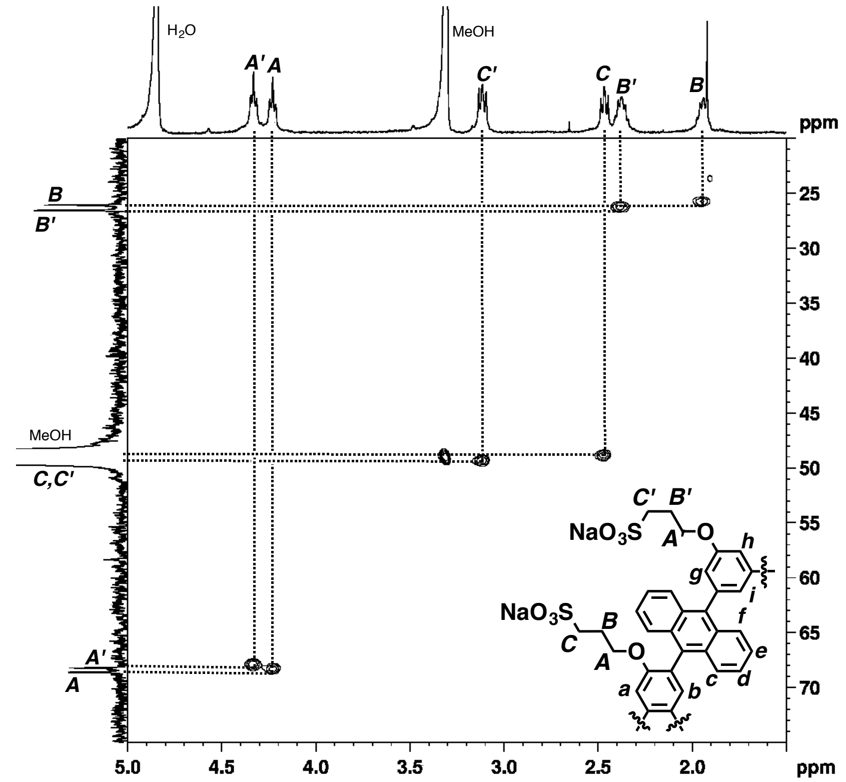


Figure S14. ^{13}C NMR spectrum (100 MHz, CD_3OD, r.t.) of **1**.



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NS                 2
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FIDRES    5.205557 Hz
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RG               203
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DE          6.50 usec
TE           300.6 K
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WDW            QSINE
SSB                2
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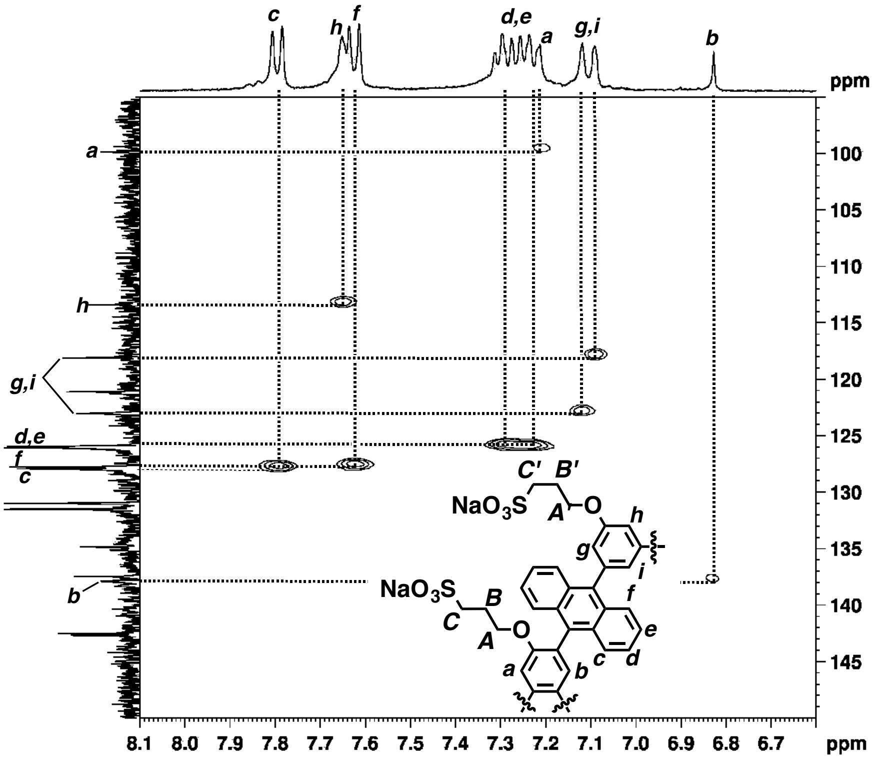
Figure S15. HSQC spectrum (400 MHz, CD_3OD, r.t.) of **1** (aliphatic region).



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TD              1024
SOLVENT         MeOD
NS                 2
DS                16
SWH       5330.490 Hz
FIDRES    5.205557 Hz
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RG               203
DW        93.800 usec
DE          6.50 usec
TE           300.6 K
CNST2    145.0000000
D0     0.00000300 sec
D1     1.50000000 sec
D4     0.00172414 sec
D11    0.03000000 sec
D16    0.00020000 sec
D24    0.00086207 sec
IN0    0.00003000 sec
ZGOPTNS

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NUC1              1H
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P2         30.00 usec
P28      1000.00 usec
ND0                2
TD               256
SFO1    100.6203 MHz
FIDRES  65.104164 Hz
SW       165.639 ppm
FnMODE Echo-Antiecho
SI              1024
SF     400.1300062 MHz
WDW            QSINE
SSB                2
LB           0.00 Hz
GB                 0
PC              1.40
SI              1024
MC2   echo-antiecho
SF     100.6126552 MHz
WDW            QSINE
SSB                2
LB           0.00 Hz
GB                 0
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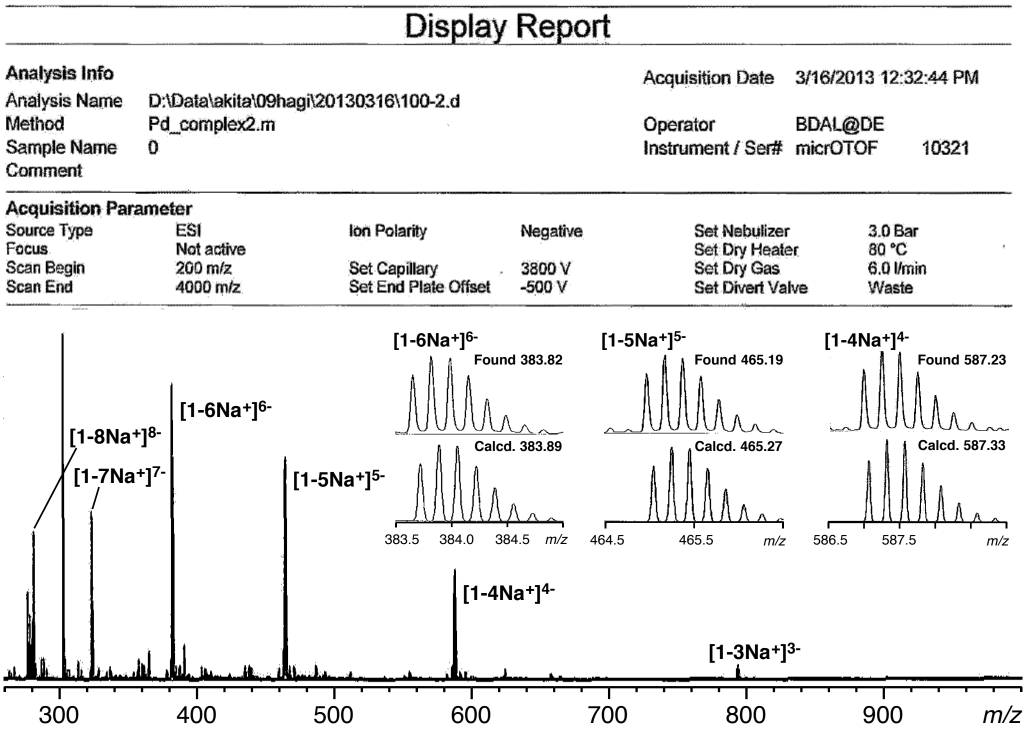
Figure S16. HSQC spectrum (400 MHz, CD_3OD, r.t.) of **1** (aromatic region).



Display Report

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Comment			

Acquisition Parameter

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Figure S17. ESI-TOF MS spectrum (CH_3OH) of **1**.

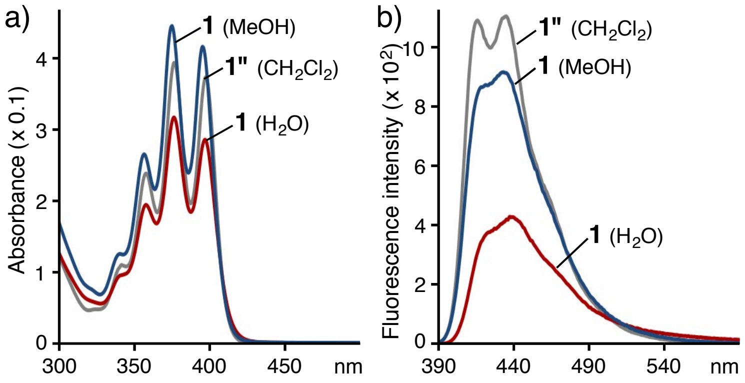
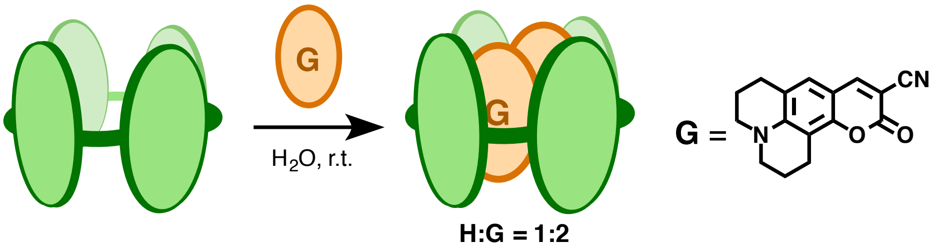


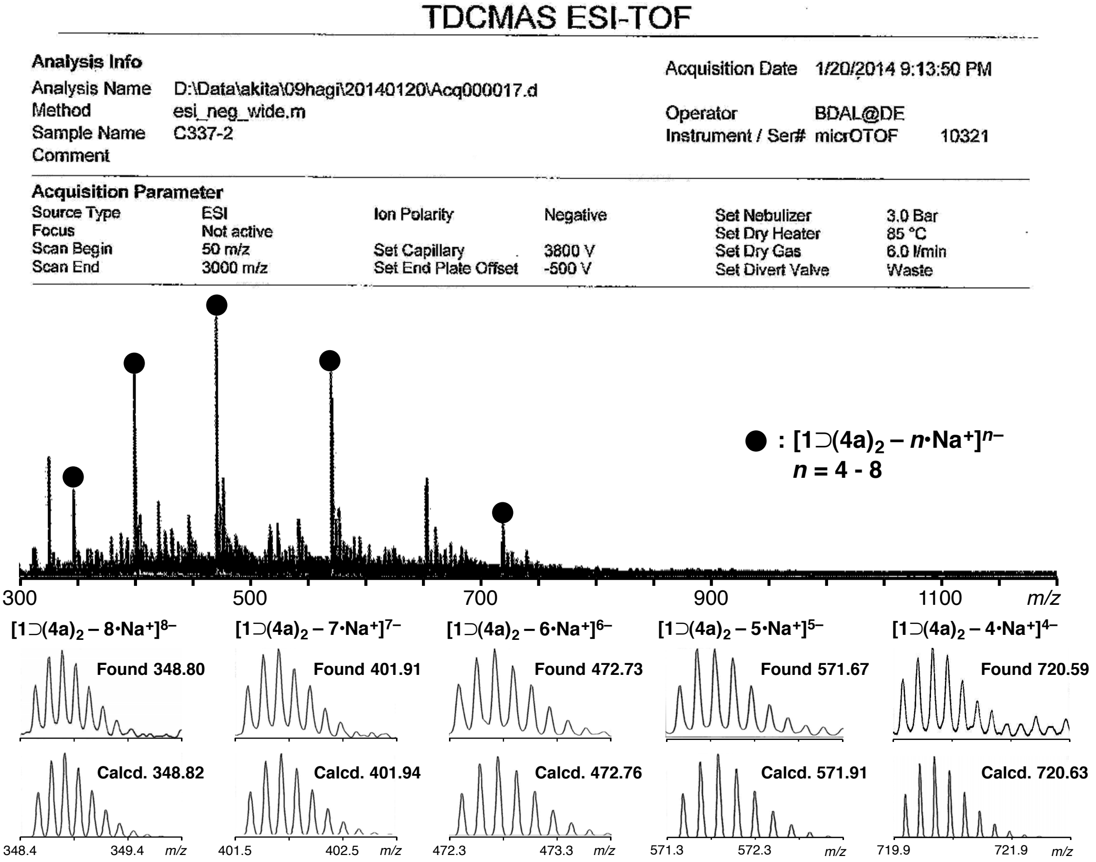
Figure S18. (a) UV-vis (10 μM, r.t.) and (b) fluorescence spectra (λ_{ex} = 377 nm, 10 μM, r.t.) of **1”** in CH_2Cl_2 and **1** in H_2O and CH_3OH.

Synthesis and properties of $1\supset(4a)_2$ KH-347



Coumarin 337 (**4a**; 0.05 mg, 0.2 μmol) was added to an H_2O solution (0.5 mL) of tube **1** (0.25 mg, 0.10 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the quantitative formation of a $\mathbf{1}\supset(\mathbf{4a})_2$ complex was confirmed by UV-vis, fluorescence, DLS, and MS analyses.

ESI-TOF MS (H_2O): *m/z* 348.8 $[\mathbf{1}\supset(\mathbf{4a})_2 - 8\mathrm{Na}^+]^{8-}$, 401.9 $[\mathbf{1}\supset(\mathbf{4a})_2 - 7\mathrm{Na}^+]^{7-}$, 472.7 $[\mathbf{1}\supset(\mathbf{4a})_2 - 6\mathrm{Na}^+]^{6-}$, 571.7 $[\mathbf{1}\supset(\mathbf{4a})_2 - 5\mathrm{Na}^+]^{5-}$, 720.6 $[\mathbf{1}\supset(\mathbf{4a})_2 - 4\mathrm{Na}^+]^{4-}$.



TDCMAS ESI-TOF

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Instrument / Ser# micrOTOF 10321

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Figure S19. ESI-TOF MS spectrum (H_2O) of $\mathbf{1}\supset(\mathbf{4a})_2$.

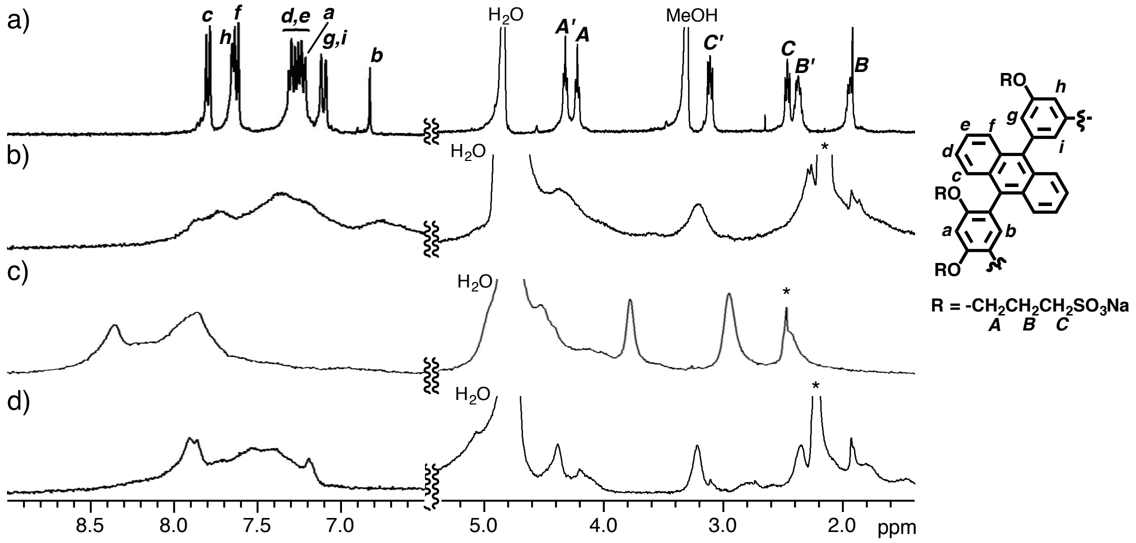


Figure S20. ^{1}H NMR spectra (400 MHz, r.t.) of tube **1** in (a) CD$_3$OD, (b) D$_2$O and (c) D$_2$O (at 80 ºC), and (d) **1**⊃(**4a**)$_2$ in D$_2$O.

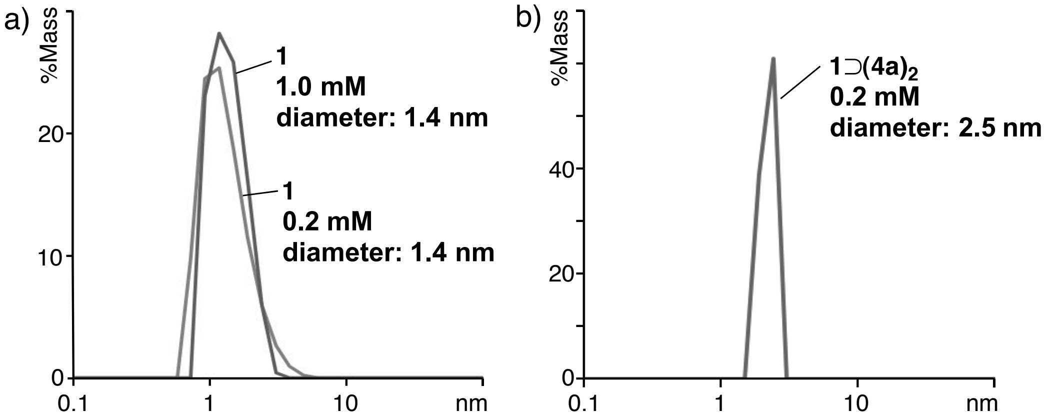


Figure S21. Particle size distribution (H$_2$O, r.t.) of (a) **1** and (b) **1**⊃(**4a**)$_2$ by DLS analysis.

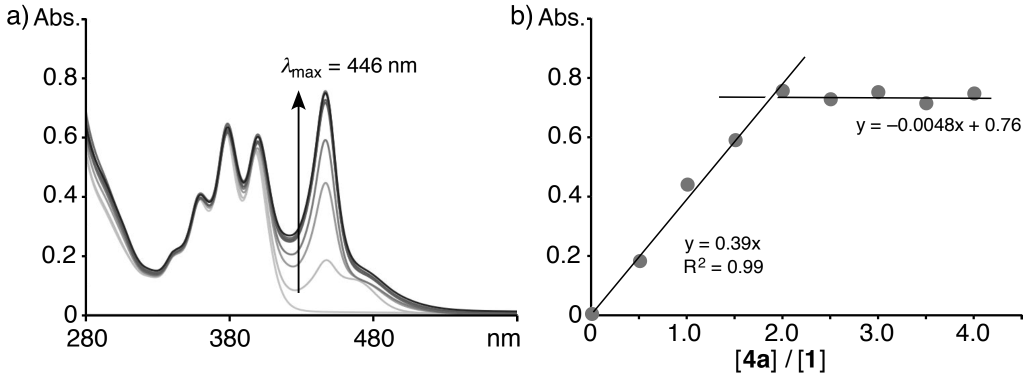


Figure S22. (a) Titration UV-vis spectra (0.2 mM, H$_2$O, r.t.) and (b) the plot (λ_{abs} = 446 nm) of **1** by the addition of **4a** ([**4a**]/[**1**] = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0).

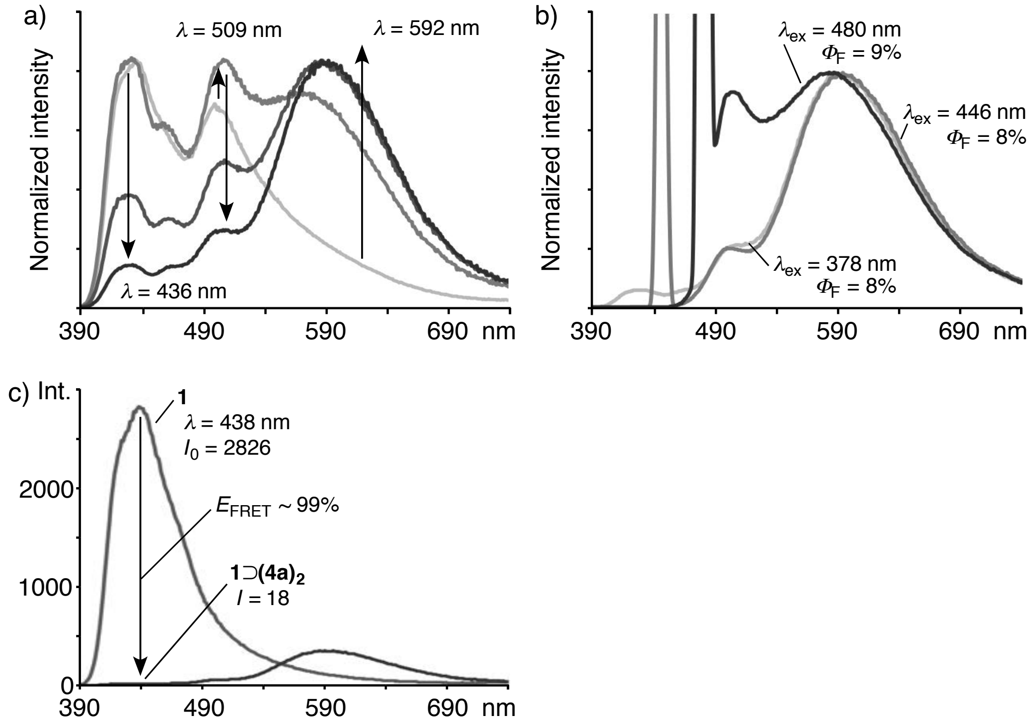


Figure S23. (a) Titration fluorescence spectra (λ_{ex} = 378 nm, 0.2 mM, H_2O, r.t.) of **1** by the addition of **4a** ([**4a**]/[**1**] = 0.5, 1.0, 1.5, 2.0), and (b) fluorescence spectra (0.2 mM, H_2O, r.t.) of **1**⊃(**4a**)$_2$ upon irradiation at λ_{ex} = 378, 446, and 480 nm, and (c) fluorescence spectra (0.2 mM, H_2O, r.t.) of **1** and **1**⊃(**4a**)$_2$ for the estimation of the FRET efficiency ($E_{FRET} = 1 - I/I_0$).

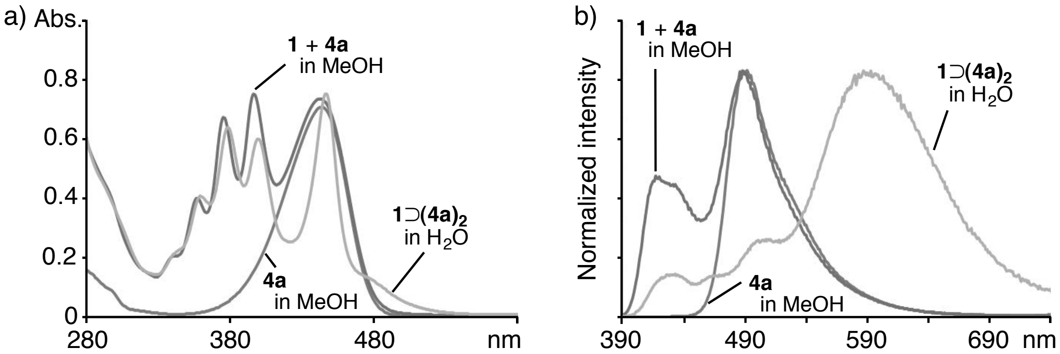


Figure S24. (a) UV-vis spectra (r.t.) and (b) fluorescence spectra (λ_{ex} = 378 nm r.t.) of **1⊃(4a)$_2$** in H_2O (0.2 mM), **1** + **4a** in CH_3OH (0.2 mM), and **4a** in CH_3OH (0.4 mM).

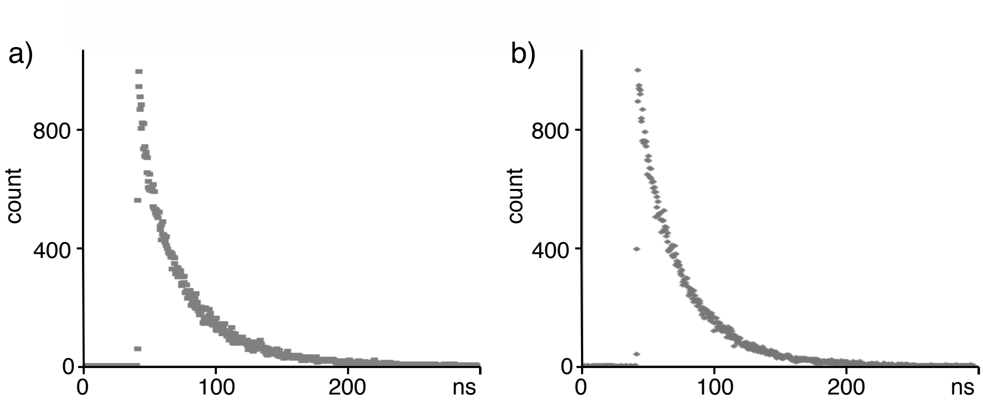


Figure S25. Fluorescent lifetime (λ_{ex} = 365 nm, 10 μM, H_2O, r.t.) of (a) **1** (λ_{em} = 440 nm) and (b) **1**⊃(**4a**)$_2$ (λ_{em} = 600 nm).

Table S1. Fluorescent lifetime of **1** and **1**⊃(**4a**)$_2$.

	τ_1 [ns]	τ_2 [ns]	τ_3 [ns]	A_1	A_2	A_3	$<\tau>^a$ [ns]
1	0.443	33.9		618	329		12.1
1⊃(**4a**)$_2$	0.288	2.61	32.4	267	82.7	357	16.7

[a] $<\tau> = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3)$

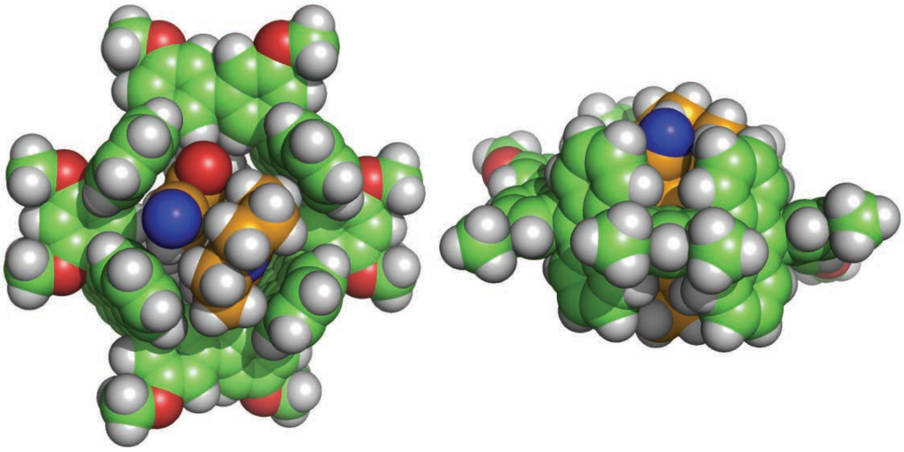
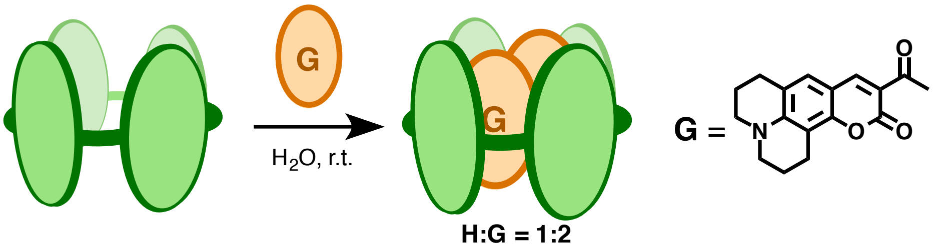


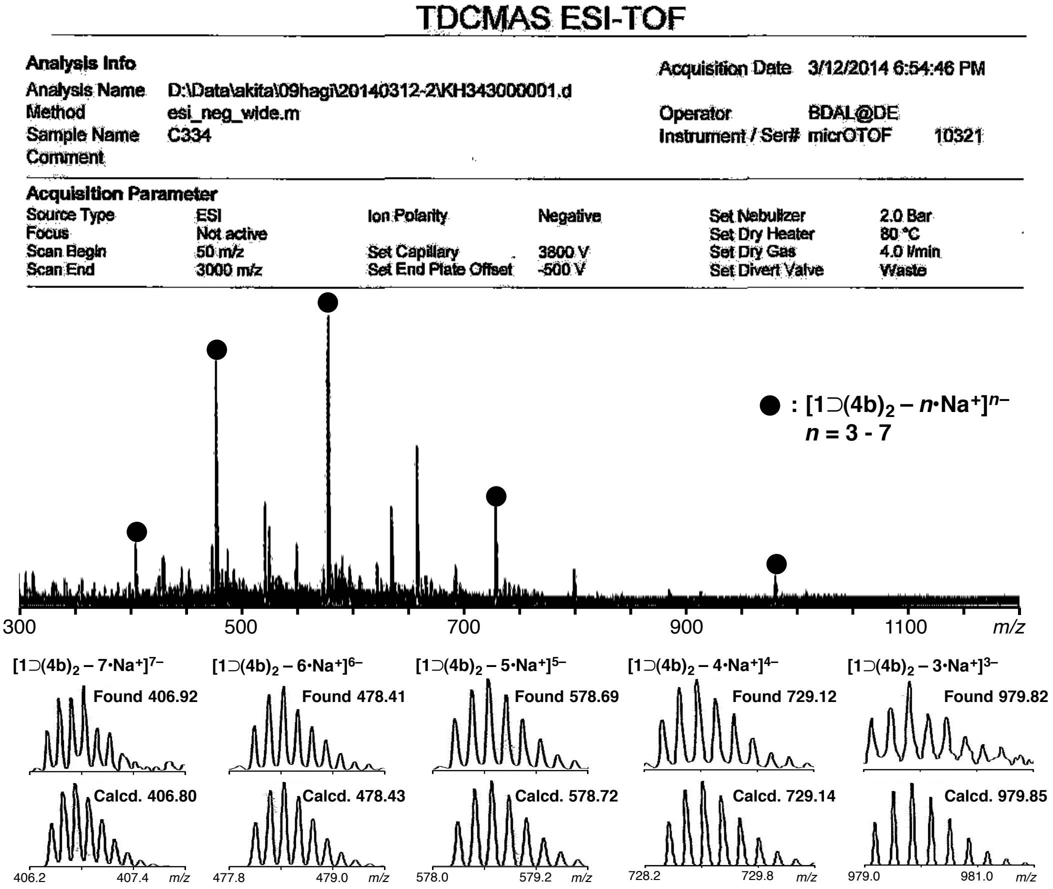
Figure S26. Optimized structure of a **1**⊃(**4a**)$_2$ complex.

Synthesis and properties of $\mathbf{1}\supset(\mathbf{4b})_2$ KH-347



Coumarin 334 (**4b**; 0.06 mg, 0.2 μmol) was added to an H_2O solution (0.5 mL) of tube **1** (0.25 mg, 0.10 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the quantitative formation of a $\mathbf{1}\supset(\mathbf{4b})_2$ complex was confirmed by UV-vis, fluorescence, and ESI-TOF MS analyses.

ESI-TOF MS (H_2O): *m/z* 406.9 $[\mathbf{1}\supset(\mathbf{4b})_2 - 7Na^+]^{7-}$, 478.4 $[\mathbf{1}\supset(\mathbf{4b})_2 - 6Na^+]^{6-}$, 578.7 $[\mathbf{1}\supset(\mathbf{4b})_2 - 5Na^+]^{5-}$, 792.1 $[\mathbf{1}\supset(\mathbf{4b})_2 - 4Na^+]^{4-}$, 979.8 $[\mathbf{1}\supset(\mathbf{4b})_2 - 3Na^+]^{3-}$.



TDCMAS ESI-TOF

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Instrument / Ser# micrOTOF 10321

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Figure S27. ESI-TOF MS spectrum (H_2O) of $\mathbf{1}\supset(\mathbf{4b})_2$.

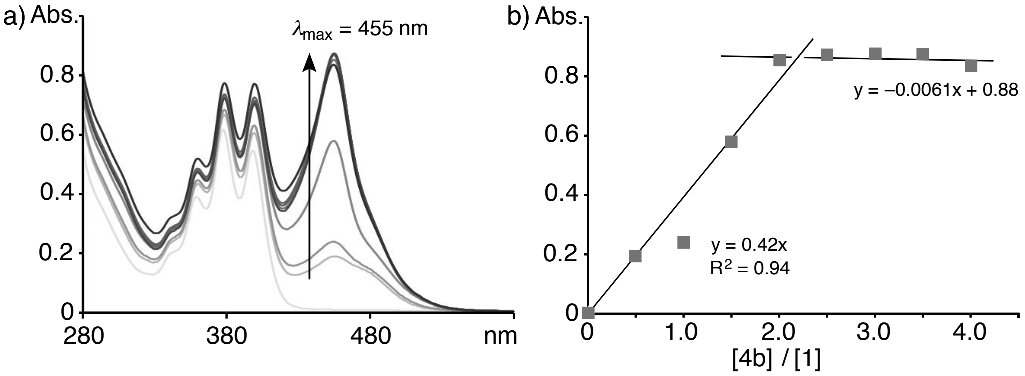


Figure S28. (a) Titration UV-vis spectra (0.2 mM, H_2O, r.t.) and (b) the plot (λ_{abs} = 455 nm) of **1** by the addition of **4b** ([**4b**]/[**1**] = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0).

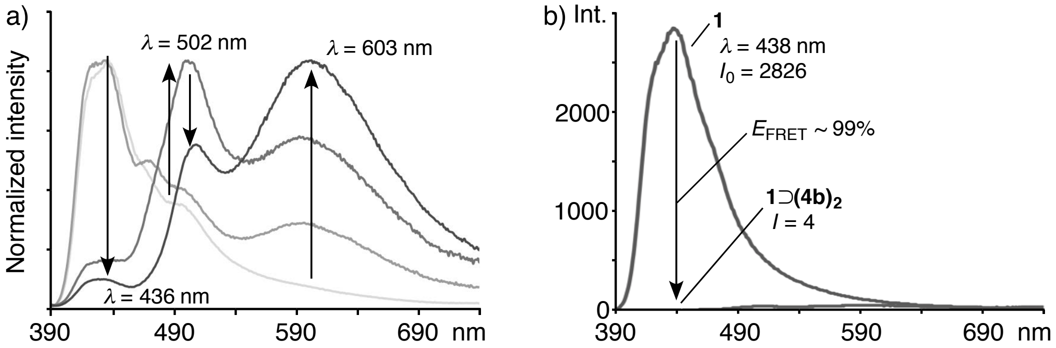


Figure S29. (a) Titration fluorescence spectra (λ_{ex} = 378 nm, 0.2 mM, H_2O, r.t.) of **1** by the addition of **4b** ([**4b**]/[**1**] = 0.5, 1.0, 1.5, 2.0), and (b) fluorescence spectra (0.2 mM, H_2O, r.t.) of **1** and **1**⊃(**4b**)$_2$ for the estimation of the FRET efficiency ($E_{FRET} = 1 - I/I_0$).

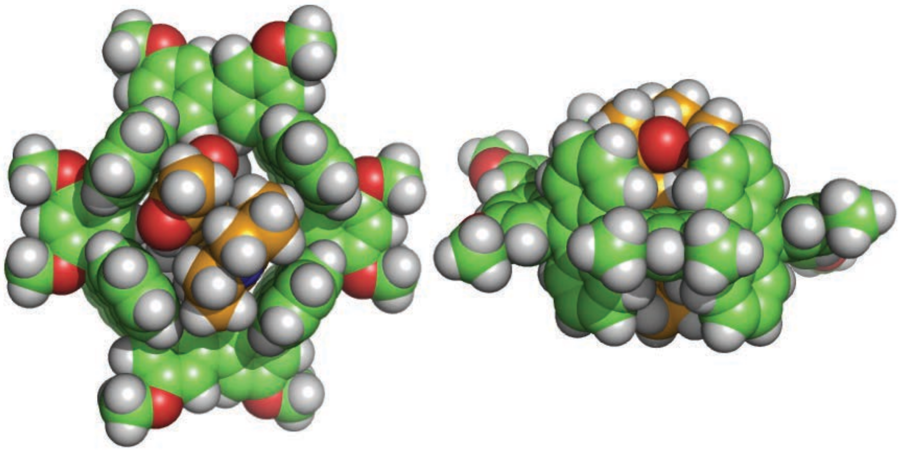
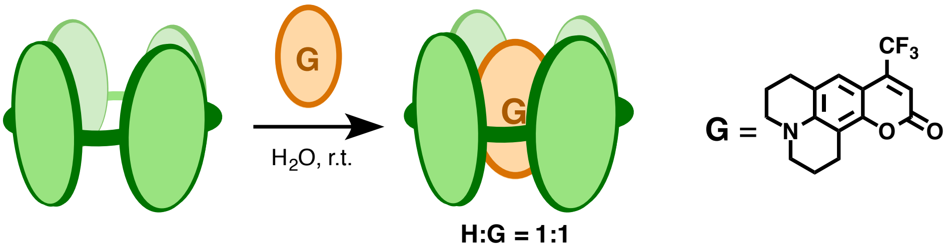


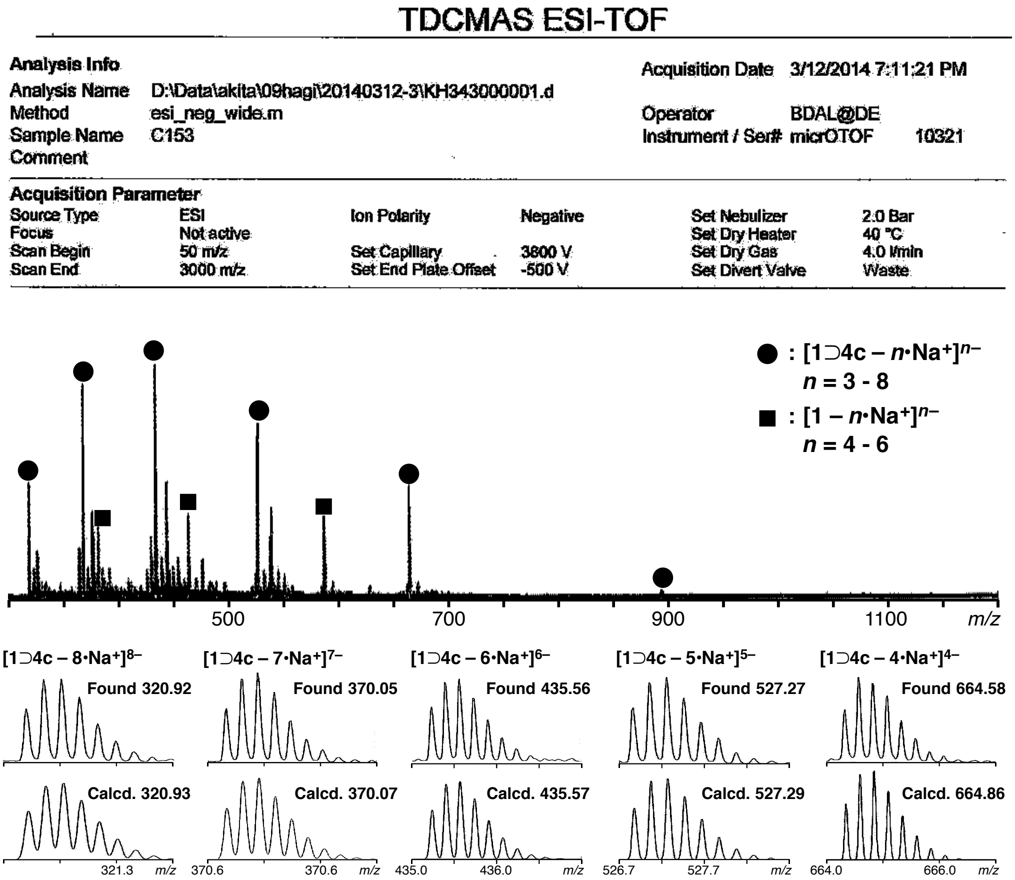
Figure S30. Optimized structure of a **1**⊃(**4b**)$_2$ complex.

Synthesis and properties of 1⊃4c KH-348



Coumarin 153 (**4c**; 0.06 mg, 0.2 μmol) was added to an H_2O solution (0.5 mL) of tube **1** (0.25 mg, 0.10 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the formation of a **1⊃4c** complex (40%) was confirmed by UV-vis, fluorescence, and ESI-TOF MS analyses.

ESI-TOF MS (H_2O): m/z 320.9 [**1⊃4c** – 8Na$^+$]$^{8-}$, 370.1 [**1⊃4c** – 7Na$^+$]$^{7-}$, 435.6 [**1⊃4c** – 6Na$^+$]$^{6-}$, 527.3 [**1⊃4c** – 5Na$^+$]$^{5-}$, 664.6 [**1⊃4c** – 4Na$^+$]$^{4-}$.



TDCMAS ESI-TOF

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Comment

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Instrument / Ser# microTOF 10321

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	2.0 Bar
Focus	Not active			Set Dry Heater	40 °C
Scan Begin	50 m/z	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Figure S31. ESI-TOF MS spectrum (H_2O) of **1⊃4c**.

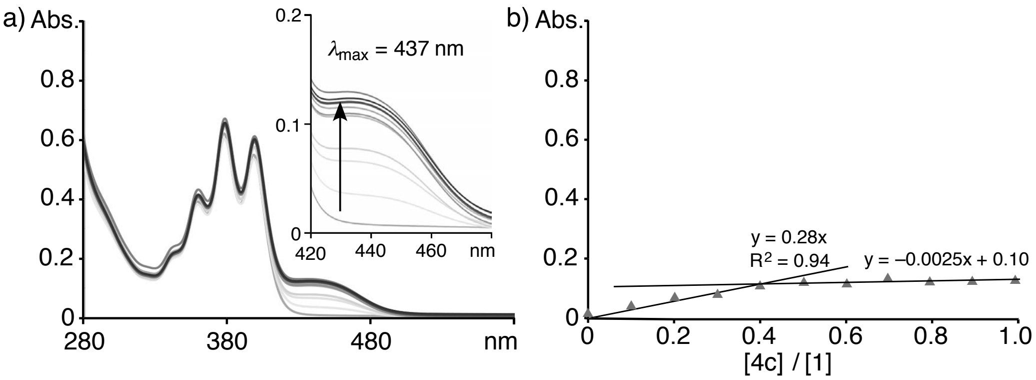


Figure S32. (a) Titration UV-vis spectra (0.2 mM, H_2O, r.t.) and (b) the plot (λ_{abs} = 437 nm) of **1** by the addition of **4c** ([**4c**]/[**1**] = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0).

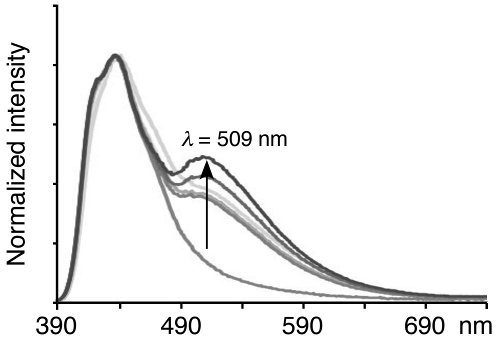


Figure S33. Titration fluorescence spectra (λ_{ex} = 378 nm, 0.2 mM, H_2O, r.t.) of **1** by the addition of **4c** ([**4c**]/[**1**] = 0.1, 0.2, 0.3, 0.4, 0.5).

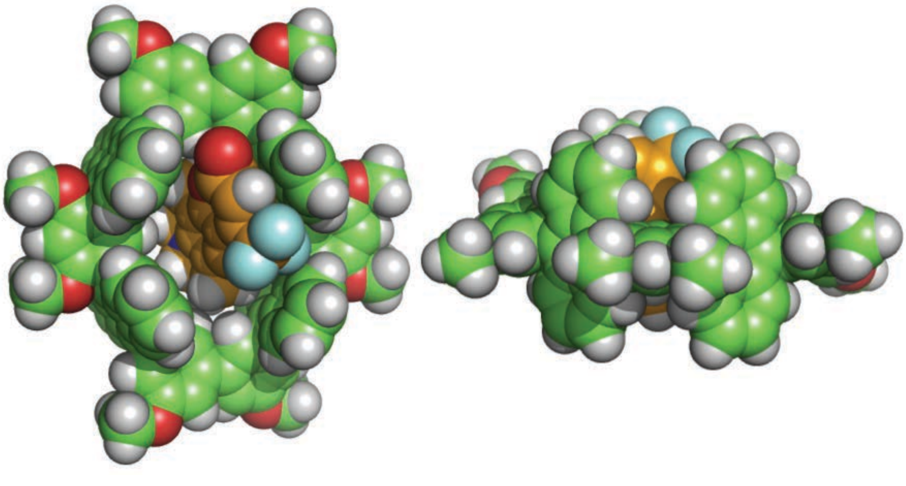
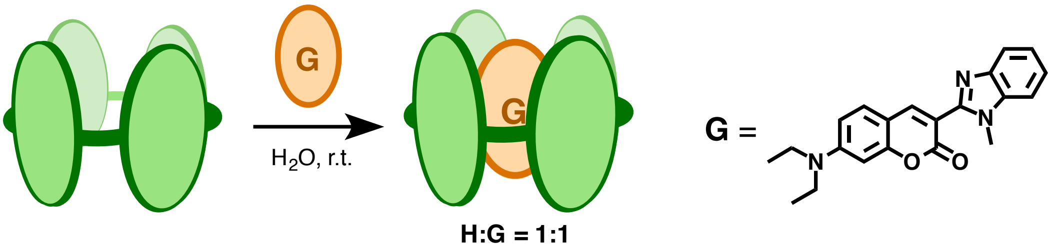


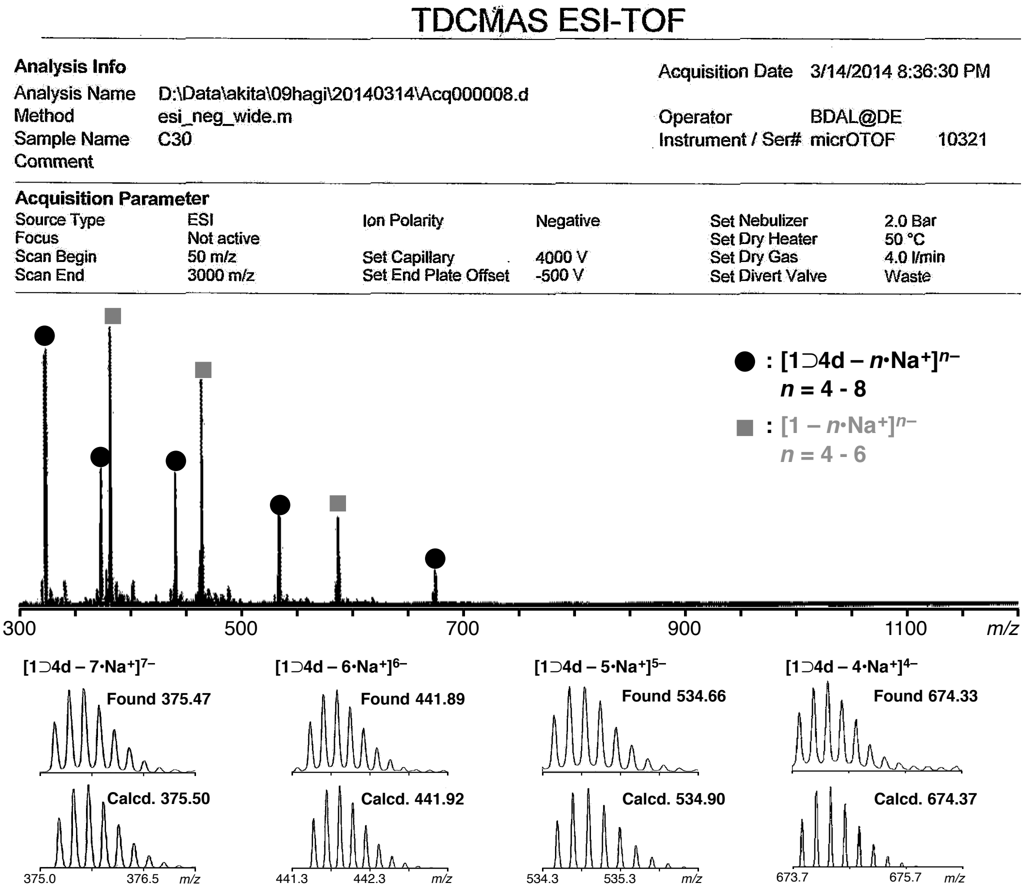
Figure S34. Optimized structure of **1**⊃**4c** complex.

Synthesis and properties of host-guest complex 1⊃4d KH-348



Coumarin 334 (**4d**; 0.07 mg, 0.2 μmol) was added to an H_2O solution (0.5 mL) of tube **1** (0.25 mg, 0.10 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the formation of a **1⊃4d** complex (30%) was confirmed by UV-vis, fluorescence, and ESI-TOF MS analyses.

ESI-TOF MS (H_2O): *m/z* 375.5 [**1⊃4d** – $7Na^+]^{7-}$, 441.9 [**1⊃4d** – $6Na^+]^{6-}$, 534.7 [**1⊃4d** – $5Na^+]^{5-}$, 674.3 [**1⊃4d** – $4Na^+]^{4-}$.


TDCMAS ESI-TOF

Analysis Info

Analysis Name	D:\Data\akita\09hagi\20140314\Acq000008.d	Acquisition Date	3/14/2014 8:36:30 PM
Method	esi_neg_wide.m	Operator	BDAL@DE
Sample Name	C30	Instrument / Ser#	micrOTOF 10321
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	2.0 Bar
Focus	Not active			Set Dry Heater	50 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Figure S35. ESI-TOF MS spectrum (H_2O) of **1⊃4d**.

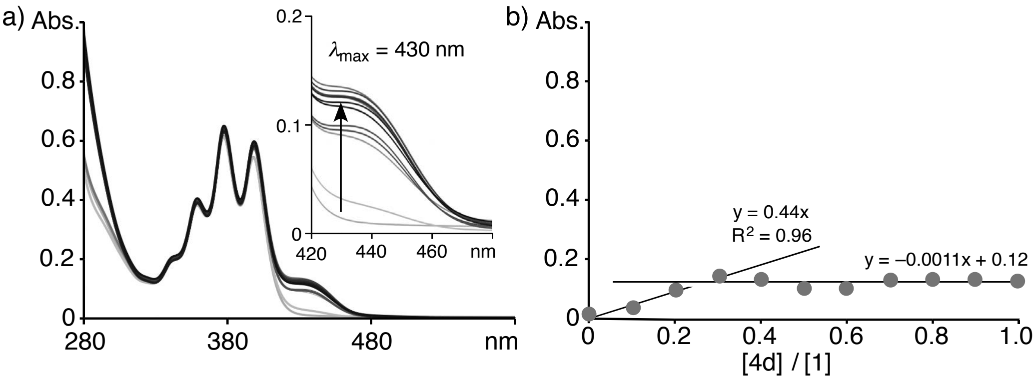


Figure S36. (a) Titration UV-vis spectra (0.2 mM, H_2O, r.t.) and (b) the plot (λ_{abs} = 430 nm) of **1** by the addition of **4d** ([**4d**]/[**1**] = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0).

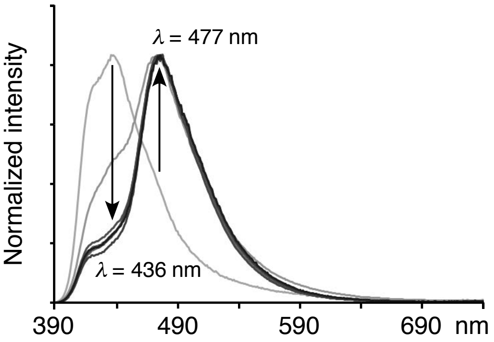


Figure S37. Titration fluorescence spectra (λ_{ex} = 378 nm, 0.2 mM, H_2O, r.t.) of **1** by the addition of **4d** ([**4d**]/[**1**] = 0.1, 0.2, 0.3, 0.4, 0.5).

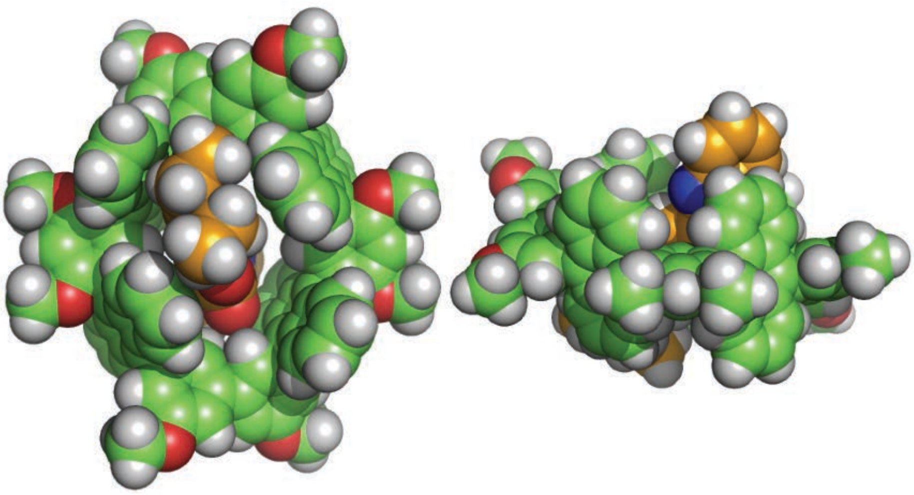


Figure S38. Optimized structure of a **1**⊃**4d** complex.

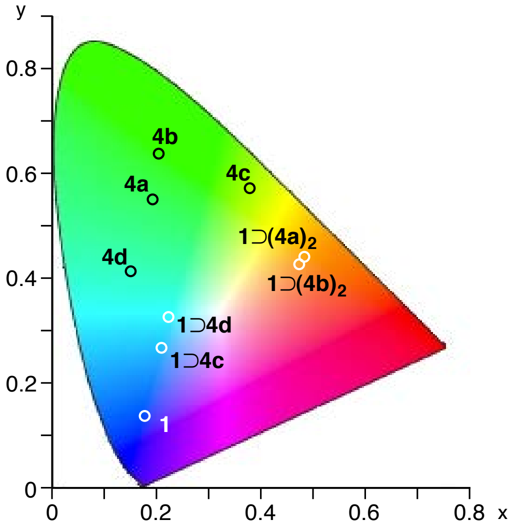
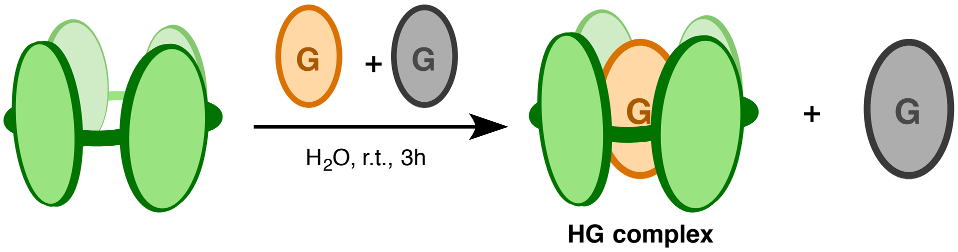


Figure S39. CIE chromaticity diagram (λ_{ex} = 378 nm, 0.2 mM, H_2O, r.t.) of **1**, **4a-d**, **1**$\supset$(**4a**)$_2$, **1**$\supset$(**4b**)$_2$, **1**$\supset$**4c**, and **1**$\supset$**4d**.

Competitive binding experiment of coumarin guests

KH-361



Coumarin dyes **4a** and **4b** (1.0 μmol each) were added to an H_2O solution (0.5 mL) of tube **1b** (0.025 mg, 0.10 μmol) in a glass test tube. The solution was stirred at r.t. for 3 h. After filtration, the formation of host-guest complexes was confirmed by UV-vis analysis. Similarly, competitive binding experiments of coumarin guests, **4a** vs. **4c**, **4a** vs. **4d**, **4b** vs. **4c**, and **4b** vs. **4d** were examined.

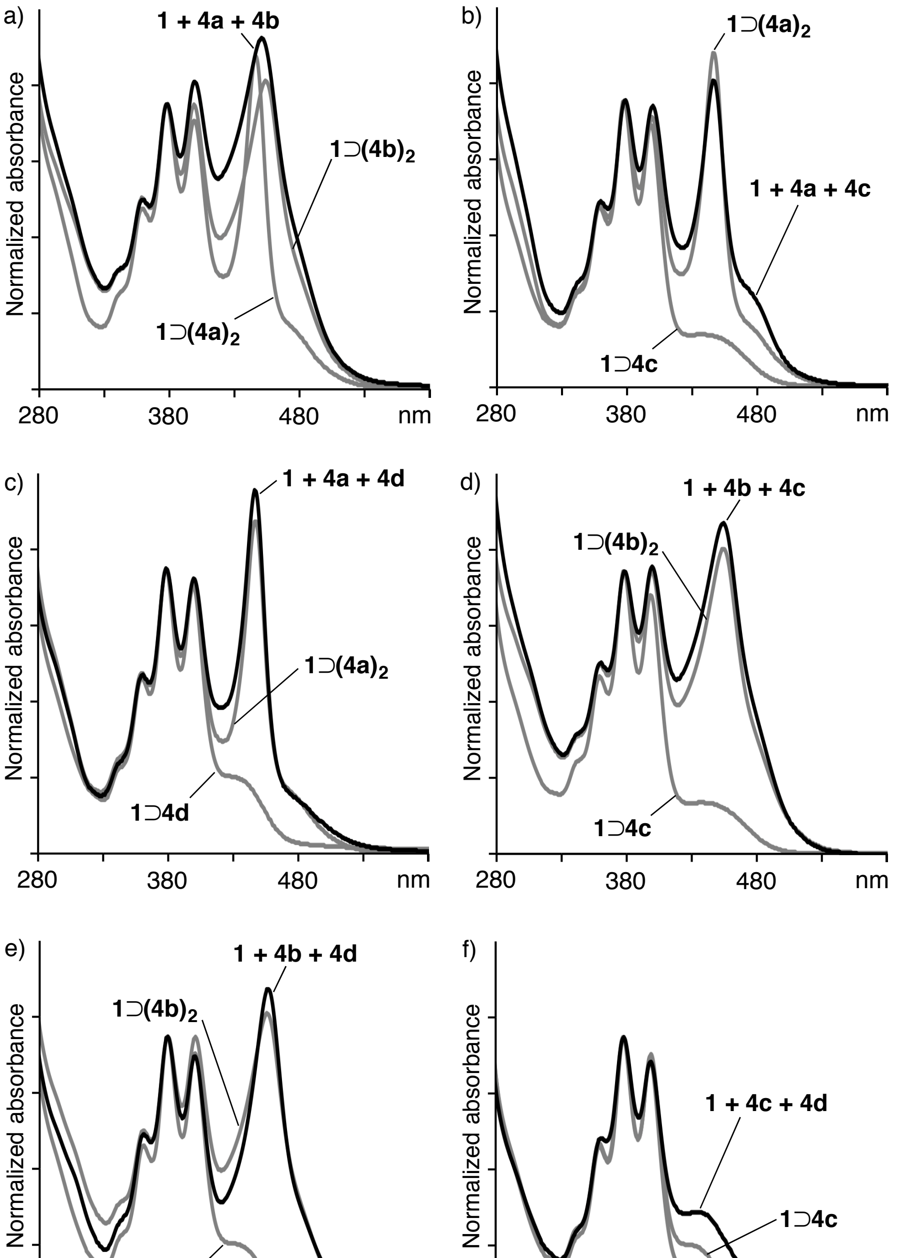


Figure S40. Fluorescent spectra (λ_{ex} = 378 nm, 0.2 mM, H_2O, r.t.) of competitive binding experiments after mixing (a) **1+4a+4b**, (b) **1+4a+4c**, (c) **1+4a+4d**, (d) **1+4b+4c**, (e) **1+4b+4d**, and (f) **1+4c+4d** in H_2O for 3 h at r.t.