

Supporting Information

Amphiphilic Tribranched Scaffolds with Polyaromatic Panels That Wrap Perylene Stacks Displaying Unusual Emissions

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Materials and methods

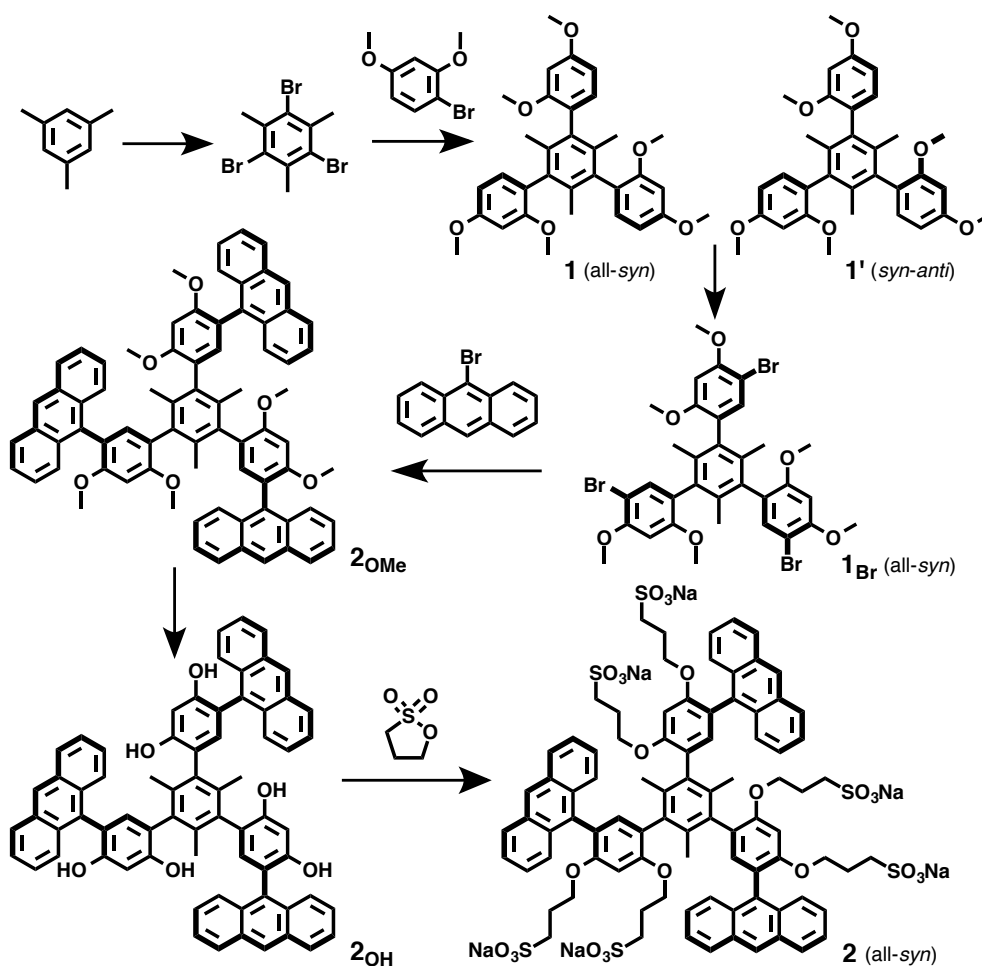
NMR: Bruker AVANCE-500 (500 MHz), MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, Size Analysis (DLS): Wyatt Technology DynaPro NanoStar, FT IR: JASCO FT/IR-4200, UV-vis: JASCO V-670DS, Fluorescence: HITACHI F-7000, Absolute PL quantum yield: Hamamatsu Quantaaurus-QY C11347-01, 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.

References

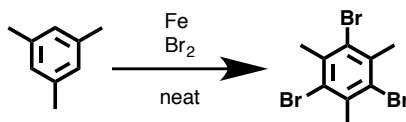
- [S1] D. Bruns, H. Miura, K. P. C. Vollhardt, *Org. Lett.* **2003**, *5*, 549–552.
[S2] A. Suzuki, K. Kondo, M. Akita, M. Yoshizawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 8120–8123.

Scheme S1. Synthetic route of tribranched scaffold **2**.



Synthesis of 1,3,5-tribromo-2,4,6-trimethylbenzene

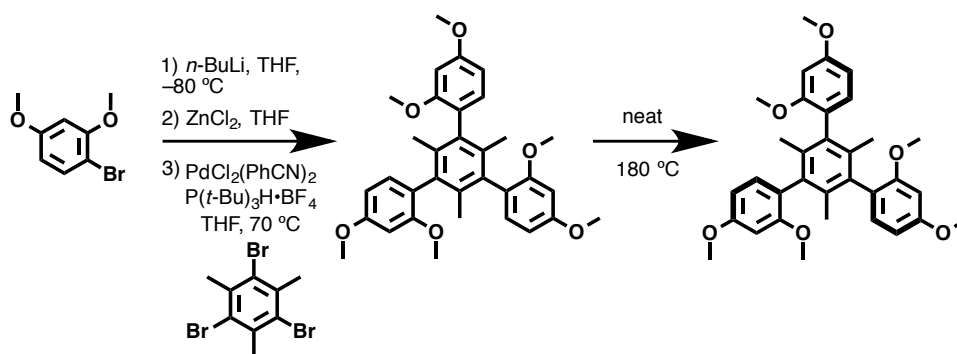
AS504



Bromine (25.0 mL, 0.485 mol) and iron powder (1.477 g, 26.45 mmol) were added to a 2-necked 200 mL glass flask. 1,3,5-Trimethylbenzene (10.011 g, 83.29 mmol) was then added dropwise to the flask for 30 min at r.t. The reaction mixture was stirred at r.t. for 1 week. After addition of an aqueous NaHSO₃ solution, the resultant mixture was extracted with CHCl₃ and the resultant organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was crystallized from CHCl₃ to afford 1,3,5-tribromo-2,4,6-trimethylbenzene^[S1] (8.936 g, 25.04 mmol, 30%) as colorless fine crystals. ¹H NMR (500 MHz, CDCl₃, r.t.): δ 2.66 (s, 9H). GC MS: *m/z* Calcd. for C₉H₉Br 356, Found 356 [M]⁺.

Synthesis of 1

AS479



1-Bromo-2,4-dimethoxybenzene (3.716 g, 17.12 mmol) and dry THF (100 mL) were added to a 2-necked 300 mL glass flask filled with N₂. A hexane solution (2.6 M) of *n*-butyllithium (6.5 mL, 17 mmol) was then added dropwise to this flask at -80 °C under N₂. After the mixture was stirred at -80 °C for 1 h, a dry THF solution (40 mL) of ZnCl₂ (3.774 g, 27.70 mmol) was added to the solution. The resultant mixture was further stirred at -80 °C and then the solution was warmed to r.t. for 1 h to obtain 2,4-dimethoxyphenylzinc chloride. 1,3,5-Tribromo-2,4,6-trimethylbenzene (1.000 g, 2.803 mmol), PdCl₂(PhCN)₂ (0.055 g, 0.14 mmol), P(*t*-Bu)₃H•BF₄ (0.124 g, 0.428 mmol), and dry THF (50 mL) were added to a 50 mL glass flask filled with N₂. After stirring at r.t. for

30 min, the mixture was added to the 300 mL flask. The resulted solution was further stirred at 70 °C for 1 d. The crude product was extracted with CH₂Cl₂, and then combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduce pressure. The crude product was purified by gel permeation chromatography (CHCl₃) to afford isomeric mixture of 1,3,5-tris(2,4-dimethoxyphenyl)-2,4,6-trimethylbenzene (**1** and **1'**; 1.370 g, 2.592 mmol, 92%). The solid was heated under neat condition at 180 °C for 5 h, and then the resultant product was washed with CH₃OH to afford single isomer **1** (all-*syn*) (1.124 g, 2.126 mmol, 76%) as a white solid. ¹H NMR (500 MHz, CDCl₃, r.t.): δ 1.71 (s, 9H), 3.70 (s, 9H), 3.84 (s, 9H), 6.55-6.56 (m, 6H), 7.01 (d, *J* = 9.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃, r.t.): δ 18.7 (CH), 55.3 (CH₃), 55.7 (CH₃), 99.3 (CH), 104.5 (CH), 123.9 (C_q), 131.6 (CH), 135.0 (C_q), 135.3 (C_q), 157.9 (C_q), 159.7 (C_q). FT-IR (KBr, cm⁻¹): 2931, 2362, 1609, 1579, 1465, 1415, 1300, 1207, 1157, 1042, 961, 833. MALDI-TOF MS (dithranol): *m/z* Calcd. for C₃₃H₃₆O₆: 528.25, Found 527.61 [M]⁺. HR MS (ESI): Calcd. For C₃₃H₃₆O₆Na 551.2404, Found 551.2404 [M+Na]⁺.

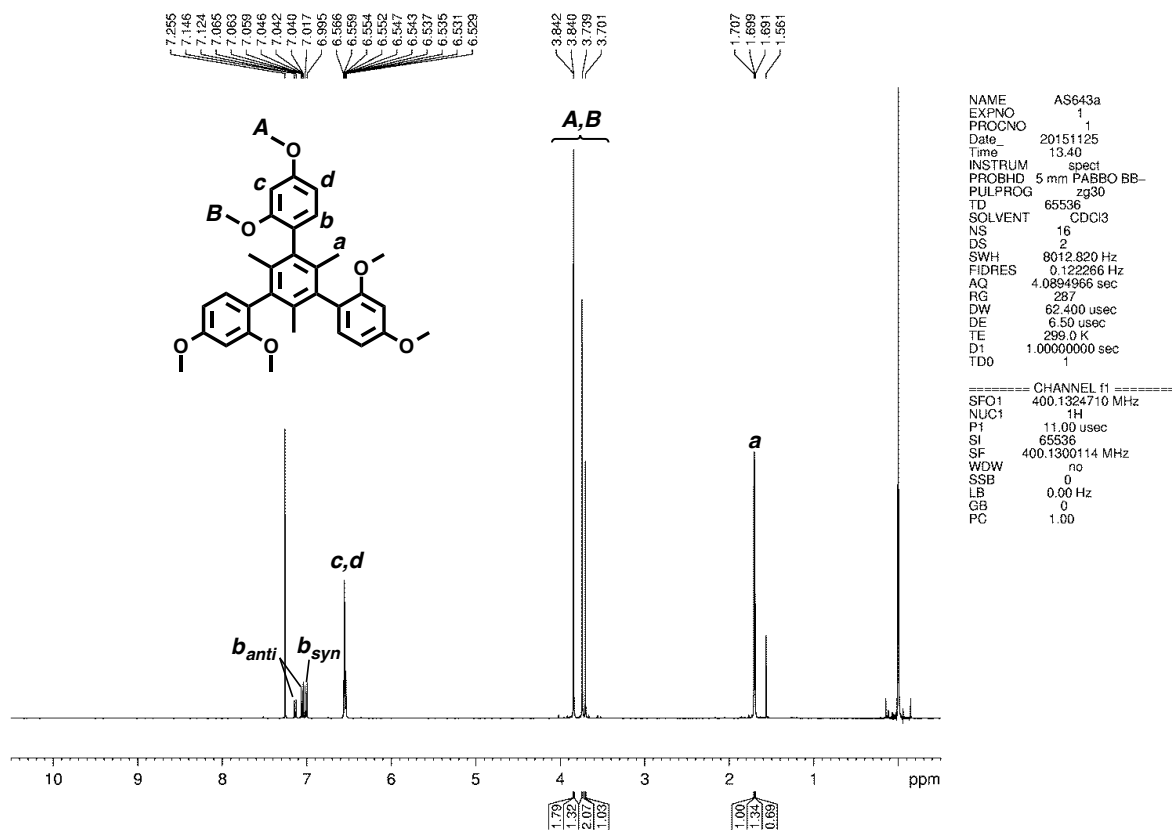


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, r.t.) of a mixture of **1** and **1'**.

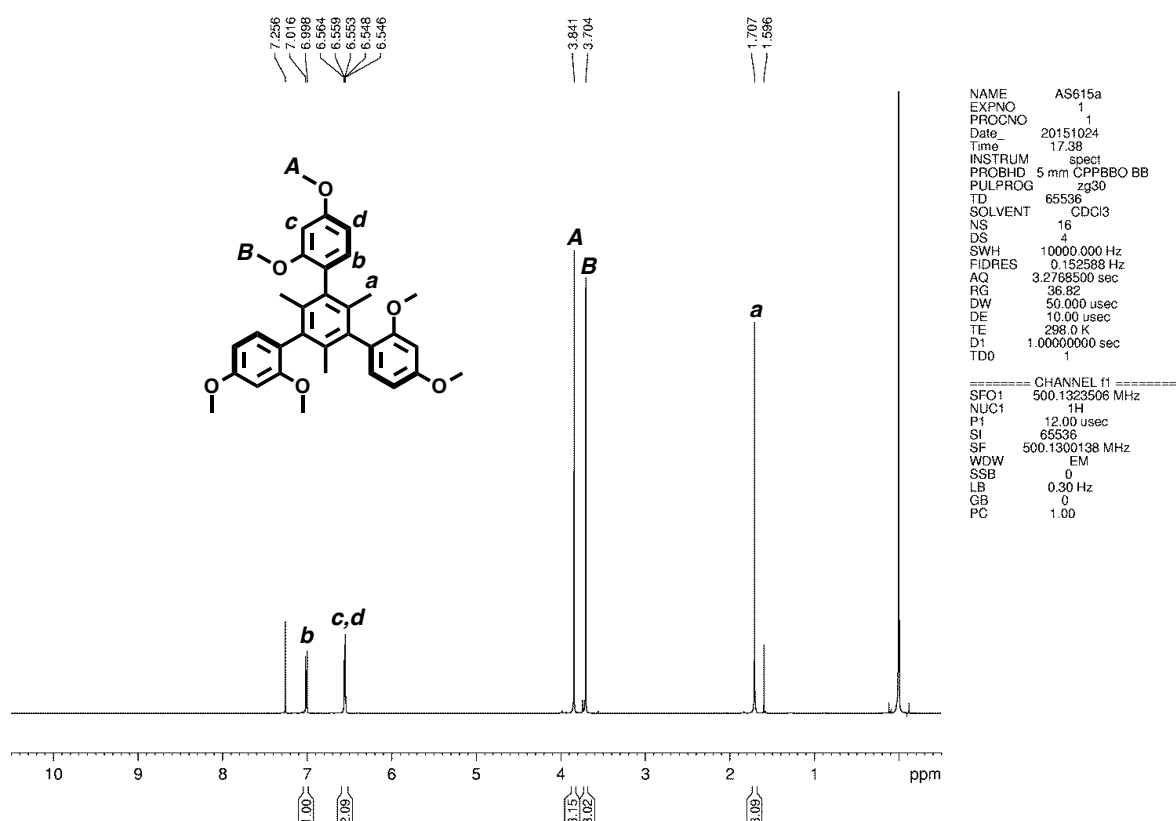


Figure S2. ¹H NMR spectrum (500 MHz, CDCl₃, r.t.) of **1**.

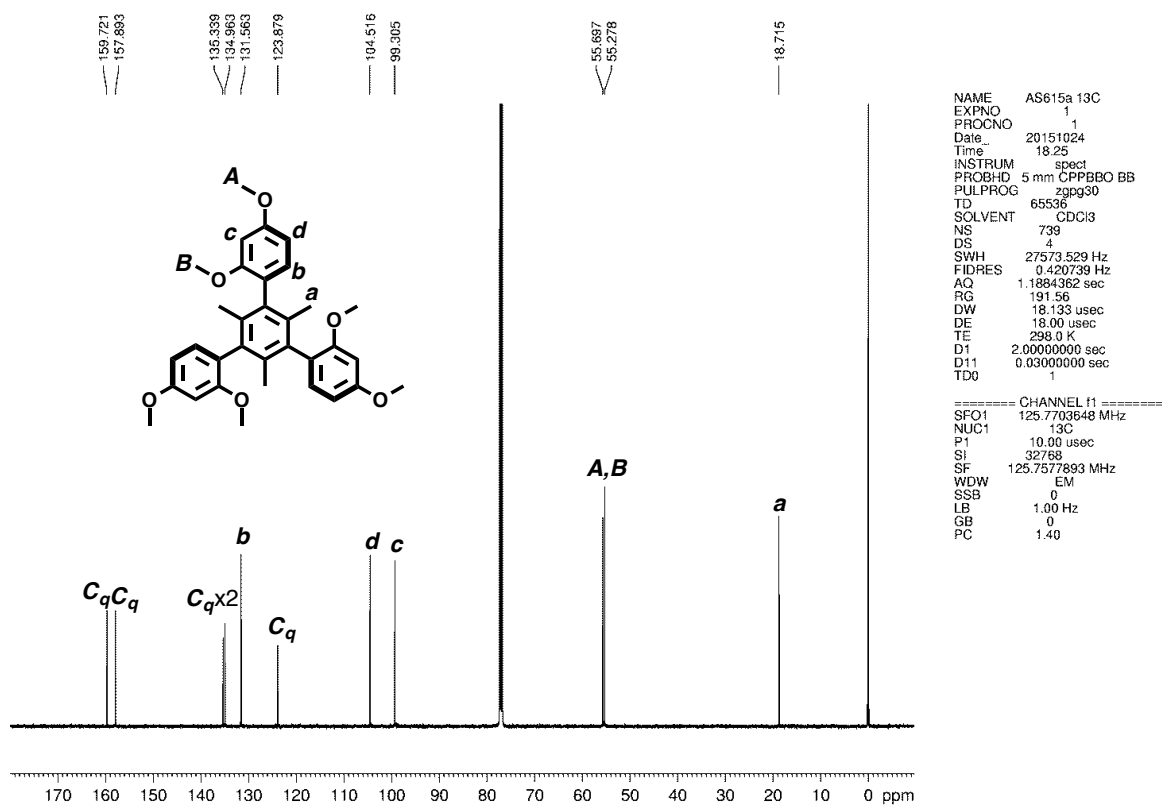


Figure S3. ¹³C NMR spectrum (125 MHz, CDCl₃, r.t.) of **1**.

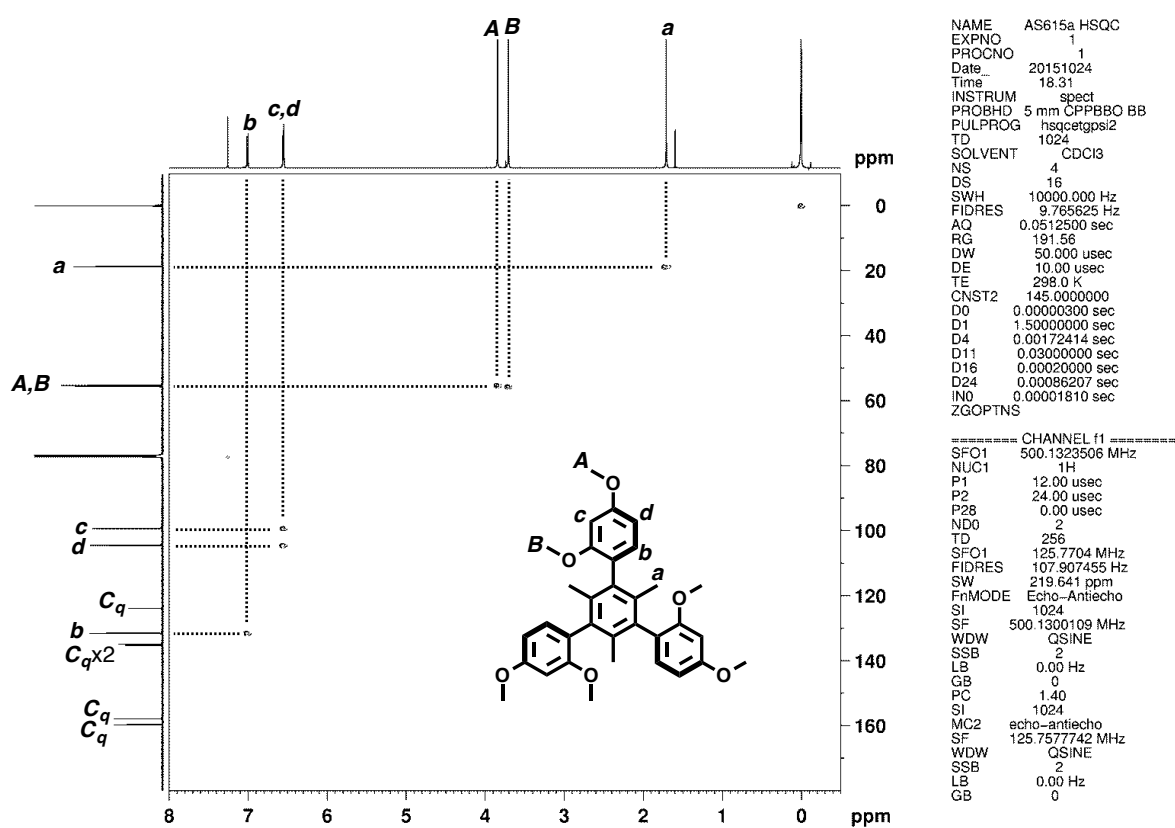


Figure S4. HSQC spectrum (500 MHz, CDCl_3 , r.t.) of **1**.

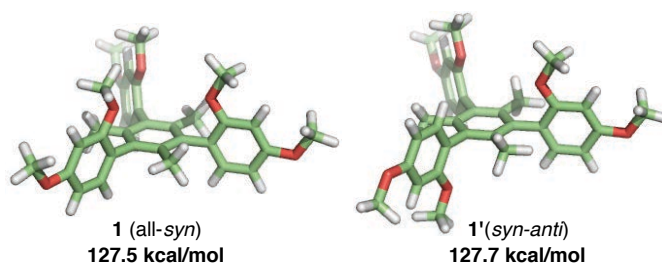


Figure S5. Optimized structure of **1** (all-syn) and **1'** (syn-anti).

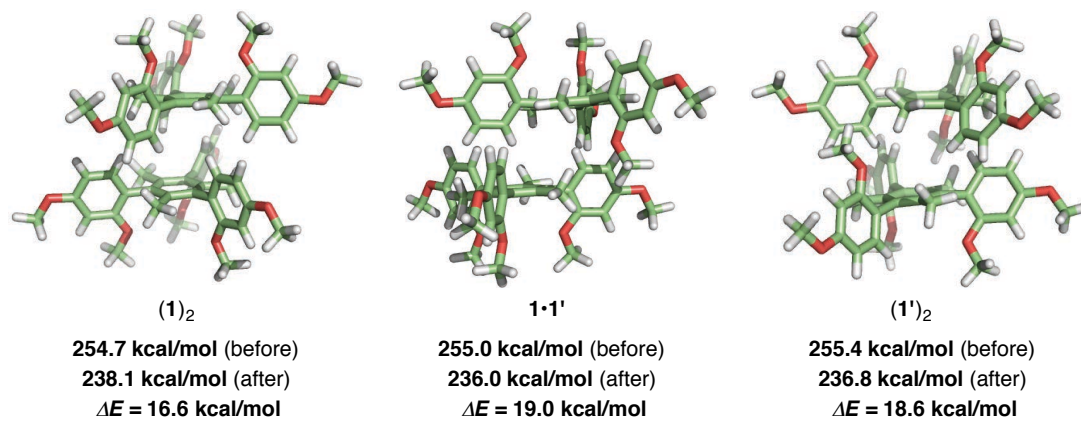
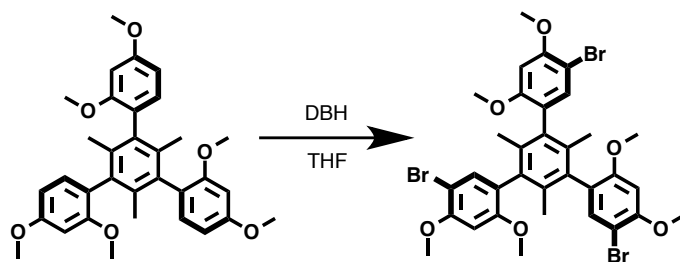


Figure S6. Optimized structure of **(1)₂**, **1•1'**, and **(1')₂**.

Synthesis of **1_{Br}**

AS510



1,3,5-Tris(2,4-dimethoxyphenyl)-2,4,6-trimethylbenzene (**1**; 1.702 g, 3.220 mmol) and THF (30 mL) were added to a 50 mL glass flask. A THF solution (20 mL) of 1,3-dibromo-5,5-dimethylhydantoin (DBH; 1.572 g, 5.496 mmol) was added to the solution at r.t. and the resultant mixture was stirred at r.t. for 1 d. After addition of H₂O, the resultant mixture was extracted with CHCl₃ and the obtained organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was washed with CH₃OH to afford **1_{Br}** (2.212 g, 2.890 mmol, 90%) as a white solid.

¹H NMR (500 MHz, CDCl₃, r.t.): δ 1.70 (s, 9H), 3.73 (s, 9H), 3.94 (s, 9H), 6.57 (s, 3H), 7.23 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, r.t.): δ 18.7 (CH₃), 56.1 (CH₃), 56.3 (CH₃), 97.5 (CH), 102.1 (C_q), 124.6 (C_q), 134.4 (C_q), 134.9 (C_q), 135.0 (CH), 155.6 (C_q), 157.1 (C_q). FT-IR (KBr, cm⁻¹): 2941, 2844, 2362, 1600, 1502, 1464, 1383, 1286, 1206, 1033, 893, 817, 669, 608. MALDI-TOF MS (dithranol): *m/z* Calcd. for C₃₃H₃₄Br₃O₆ 762.98, Found 763.17 [M+H]⁺. HR MS (ESI): Calcd. For C₃₃H₃₃O₆Br₃Na 784.9719, Found 784.9714 [M+Na]⁺.

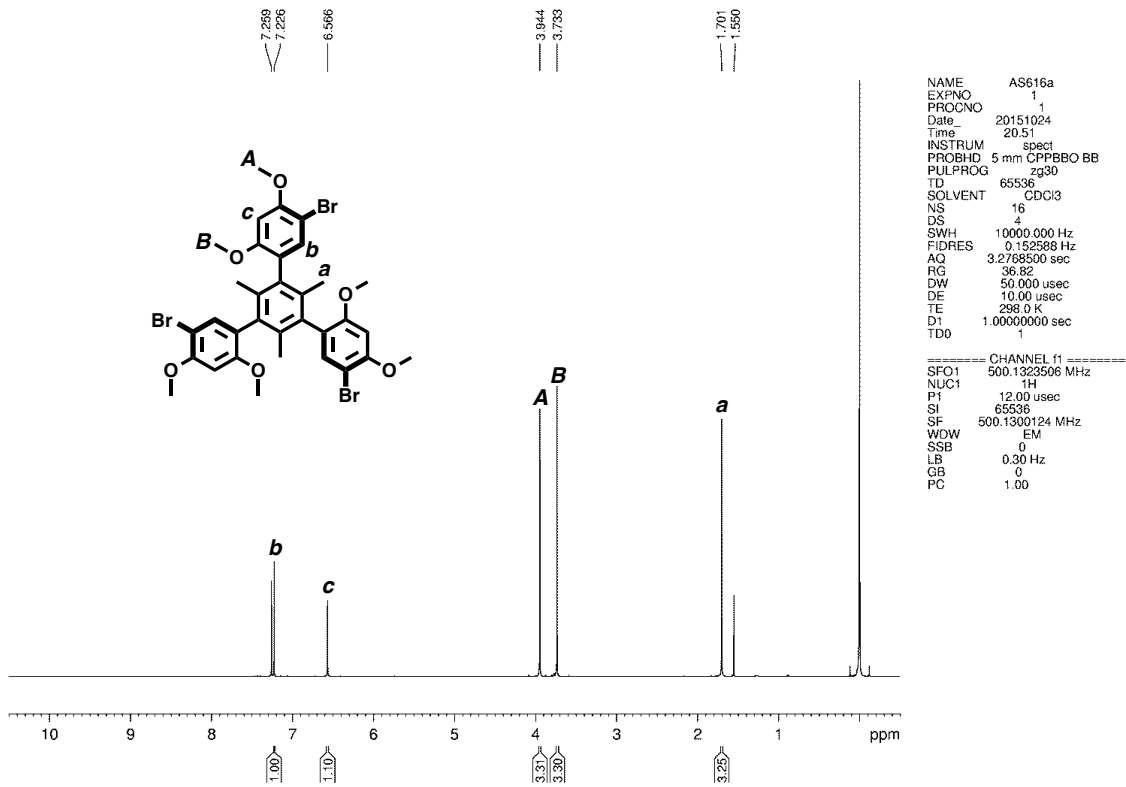


Figure S7. ¹H NMR spectrum (500 MHz, CDCl₃, r.t.) of **1_{Br}**.

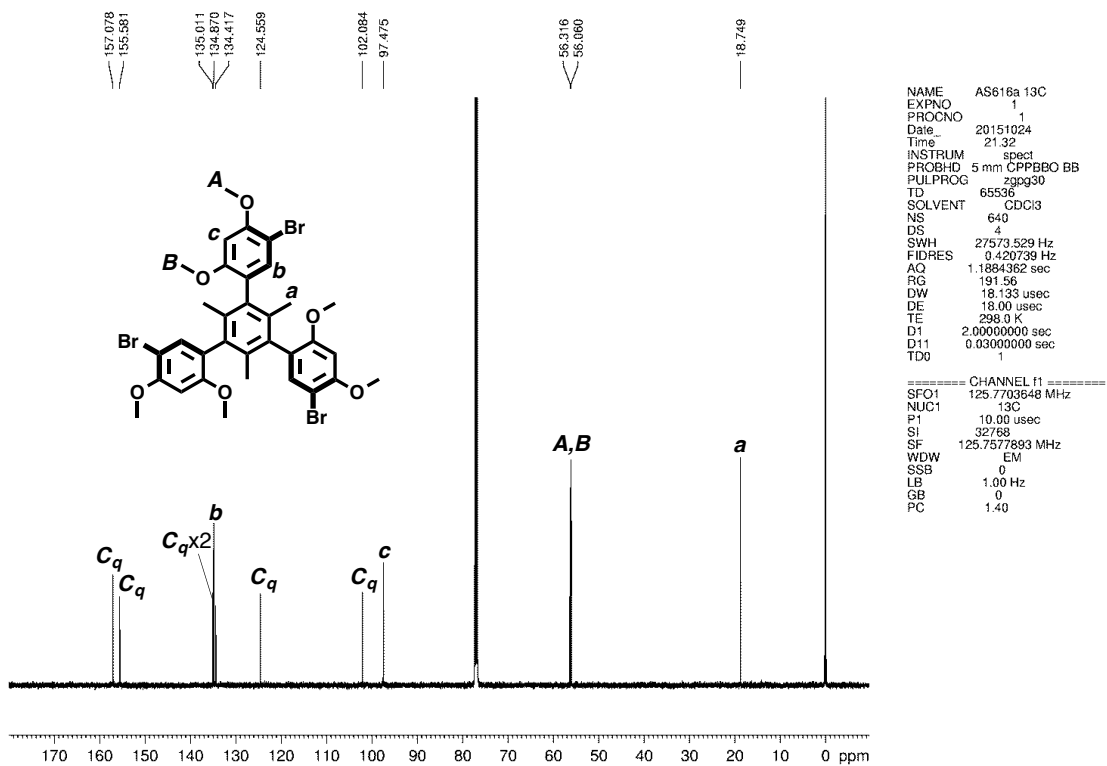


Figure S8. ¹³C NMR spectrum (125 MHz, CDCl₃, r.t.) of **1_{Br}**.

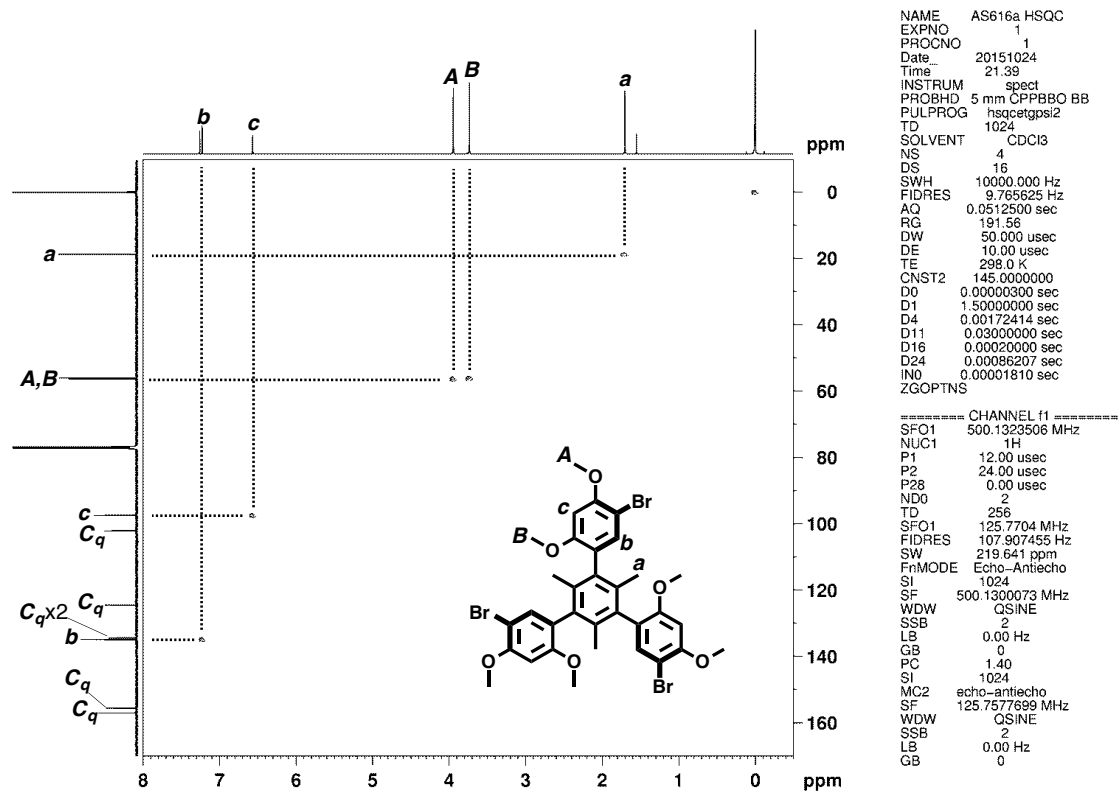
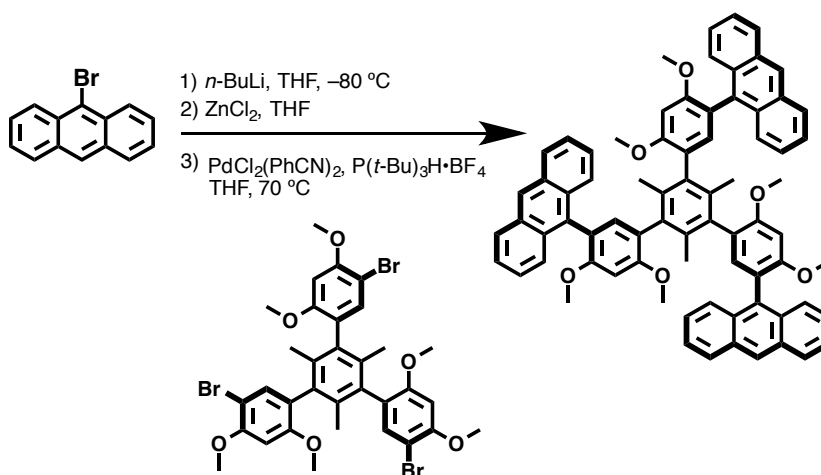


Figure S9. HSQC spectrum (500 MHz, CDCl₃, r.t.) of **1_{Br}**.

Synthesis of anthracene trimer **2_{OMe}**

AS512



9-Bromoanthracene (3.430 g, 13.34 mmol) and dry THF (200 mL) were added to a 2-necked 300 mL glass flask filled with N₂. A hexane solution (2.6 M) of *n*-butyllithium (5.0 mL, 13 mmol) was then added dropwise to this flask at -80 °C under N₂. After the mixture was stirred at -80 °C for 1 h, a dry THF solution (40 mL) of ZnCl₂ (2.573 g, 18.88 mmol) was added to the solution. The resultant mixture was further stirred at -80 °C and

then the solution was warmed to r.t. for 1.5 h to obtain 9-anthrylzinc chloride. Compound **1_{Br}** (1.708 g, 2.232 mmol), PdCl₂(PhCN)₂ (0.062 g, 0.16 mmol), P(*t*-Bu)₃H•BF₄ (0.188 g, 0.647 mmol), and dry THF (50 mL) were added to a 100 mL glass flask filled with N₂. After stirring at r.t. for 1 h, the mixture was added to the 300 mL flask. The resulted solution was further stirred at 70 °C for 2 d. After addition of H₂O, the resultant precipitate was collected and washed with CHCl₃ and hexane to afford anthracene trimer **2_{OMe}** (1.734 g, 1.640 mmol, 74%) as a pale yellow solid.

¹H NMR (500 MHz, CDCl₃, r.t.): δ 2.00 (s, 9H), 3.65 (s, 9H), 3.97 (s, 9H), 6.79 (s, 3H), 6.82 (s, 3H), 7.21-7.24 (m, 6H), 7.30-7.33 (m, 6H), 7.65 (d, *J* = 9.0 Hz, 6H), 7.90 (d, *J* = 8.5 Hz, 6H), 8.32 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, r.t.): δ 19.1 (CH₃), 55.9 (CH₃), 56.0 (CH₃), 96.6 (CH), 119.2 (C_q), 123.3 (C_q), 124.7 (CH), 125.0 (CH), 126.2 (CH), 126.8 (CH), 128.3 (CH), 130.7 (C_q), 131.4 (C_q), 133.5 (C_q), 134.7 (C_q), 135.2 (C_q), 135.5 (CH), 157.6 (C_q), 157.7 (C_q). FT-IR (KBr, cm⁻¹): 2931, 2838, 2363, 1605, 1504, 1463, 1348, 1258, 1204, 1110, 1034, 882, 843, 793, 735. MALDI-TOF MS (dithranol): *m/z* Calcd. for C₇₅H₆₀O₆ 1056.44, Found 1056.41 [M]⁺. HR MS (ESI): Calcd. For C₇₅H₆₀O₆Na 1079.4282, Found 1079.4272 [M+Na]⁺.

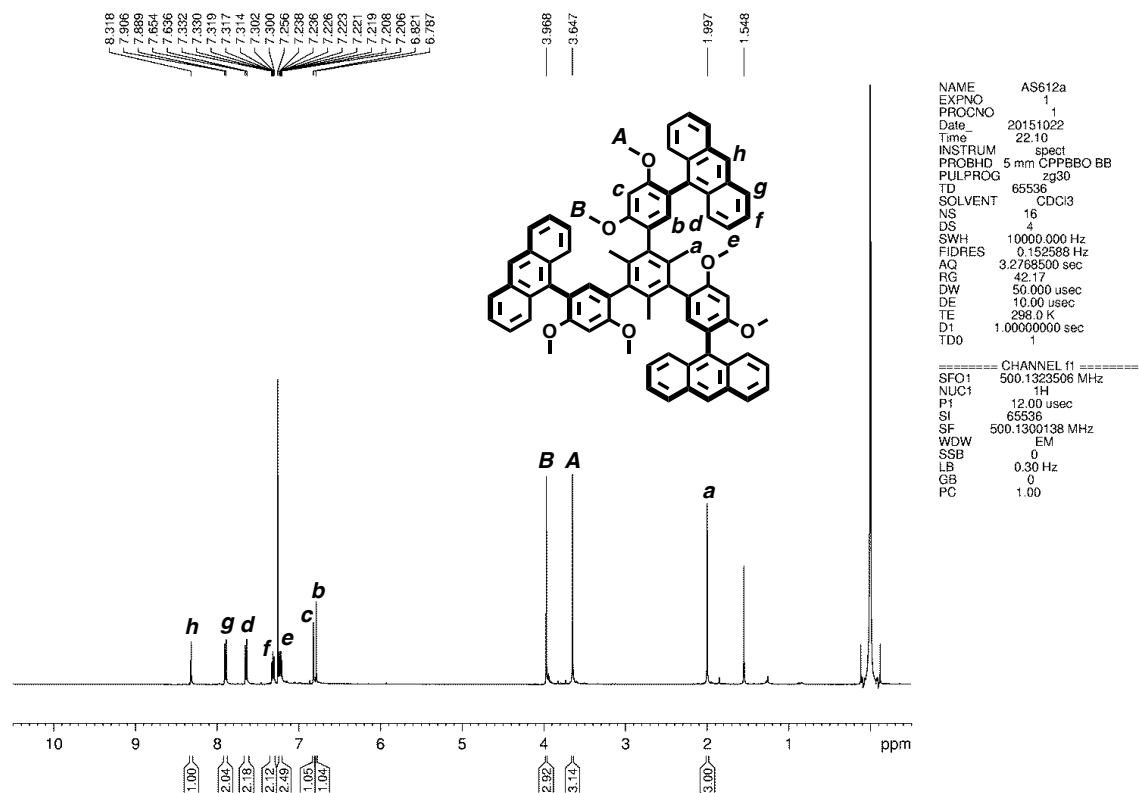


Figure S10. ¹H NMR spectrum (500 MHz, CDCl₃, r.t.) of **2_{OMe}**.

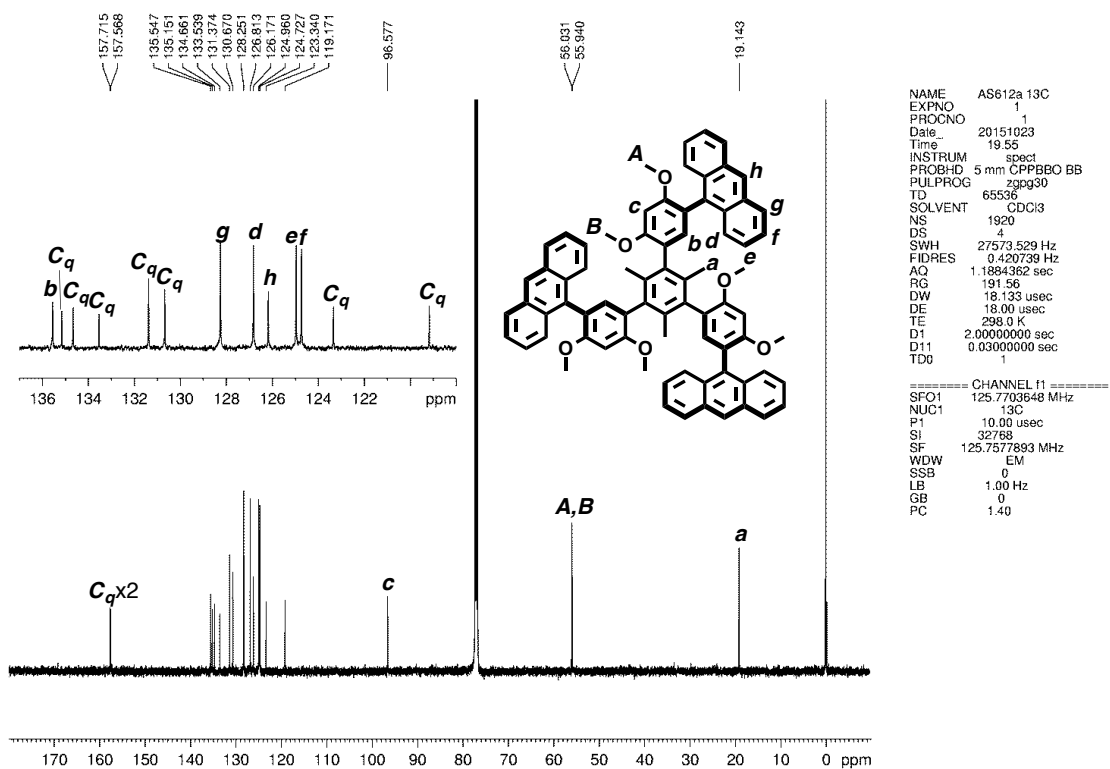


Figure S11. ^{13}C NMR spectrum (125 MHz, CDCl_3 , r.t.) of 2_{OME} .

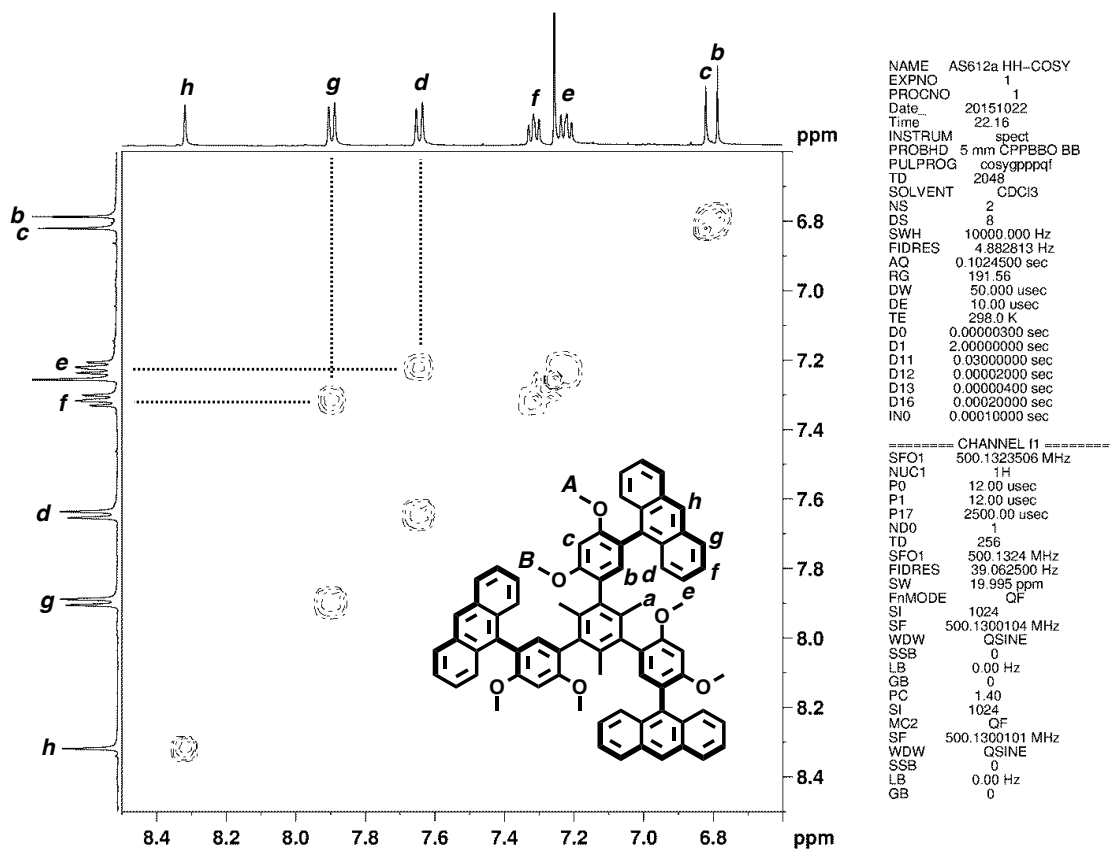


Figure S12. HH-COSY spectrum (500 MHz, CDCl_3 , r.t.) of 2_{OME} .

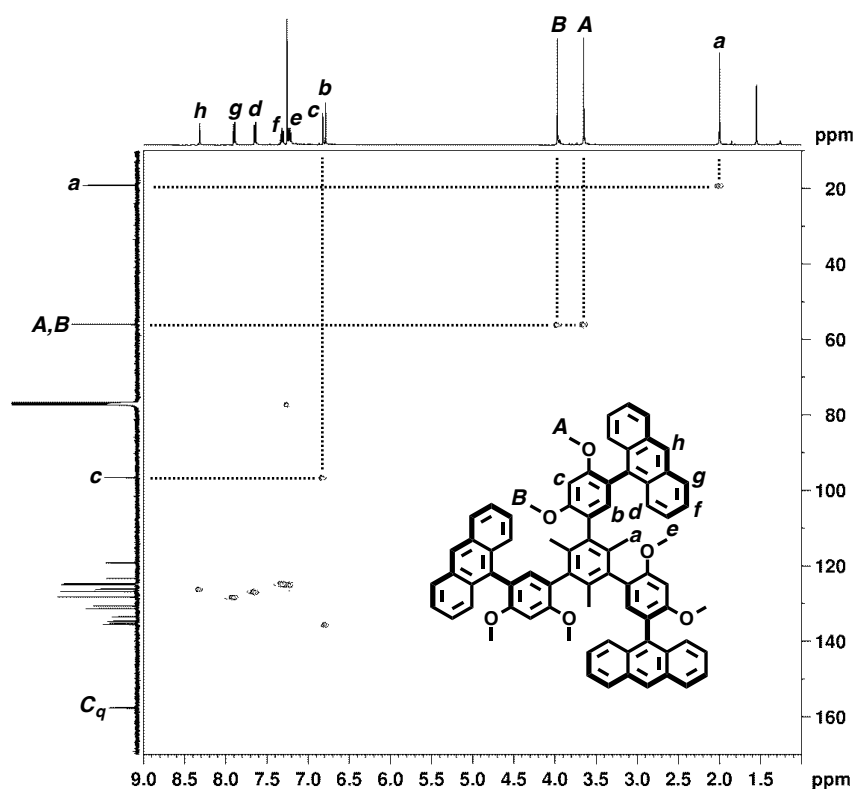


Figure S13a. HSQC spectrum (500 MHz, CDCl₃, r.t.) of 2_{OMe}.

```

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PROCNO 1
Date_ 20151022
Time 22.40
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PULPROG hsqcetgpsi2
TD 1024
SOLVENT CDCl3
NS 2
DS 16
SWH 10000.000 Hz
FIDRES 9.765625 Hz
AQ 0.0512500 sec
RG 191.56
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
CNST2 145.000000
D0 0.0000300 sec
D1 1.5000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00020000 sec
D24 0.00086207 sec
IN0 0.00001810 sec
ZGPTNS

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NUC1 1H
P1 12.00 usec
P2 24.00 usec
P28 0.00 usec
ND0 2
TD 256
SFO1 125.7704 MHz
FIDRES 107.907455 Hz
SW 219.641 ppm
FnMODE Echo-Antiecho
SI 1024
SF 500.1300088 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
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SF 125.7577751 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

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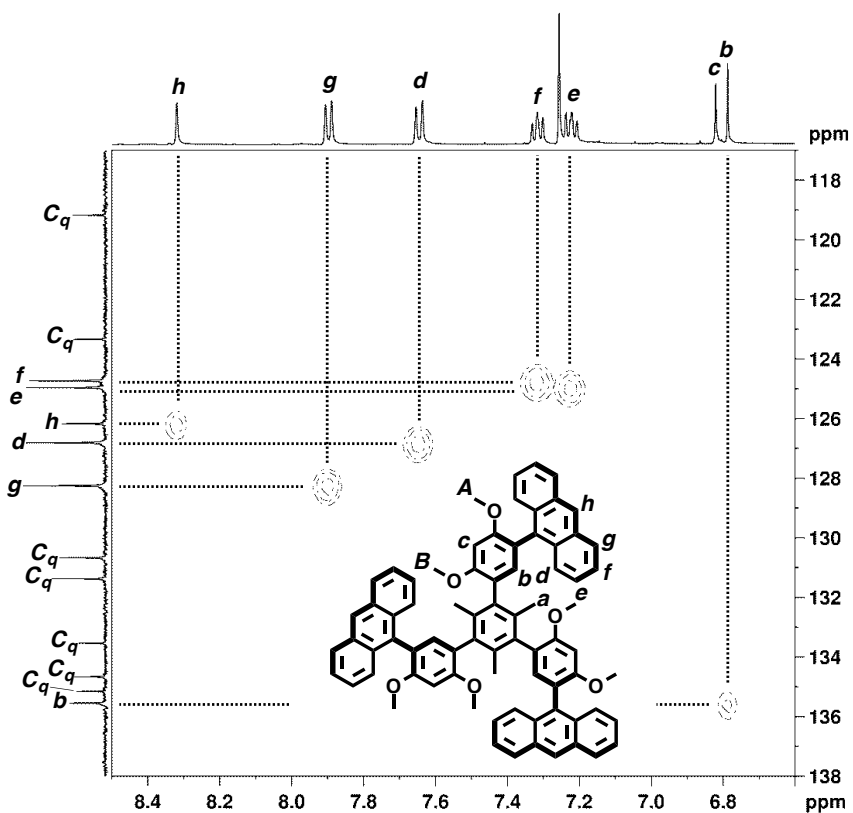


Figure S13b. HSQC spectrum (500 MHz, CDCl₃, r.t.) of 2_{OMe}.

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PROCNO 1
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Time 22.40
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG hsqcetgpsi2
TD 1024
SOLVENT CDCl3
NS 2
DS 16
SWH 10000.000 Hz
FIDRES 9.765625 Hz
AQ 0.0512500 sec
RG 191.56
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
CNST2 145.000000
D0 0.0000300 sec
D1 1.5000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00020000 sec
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ZGPTNS

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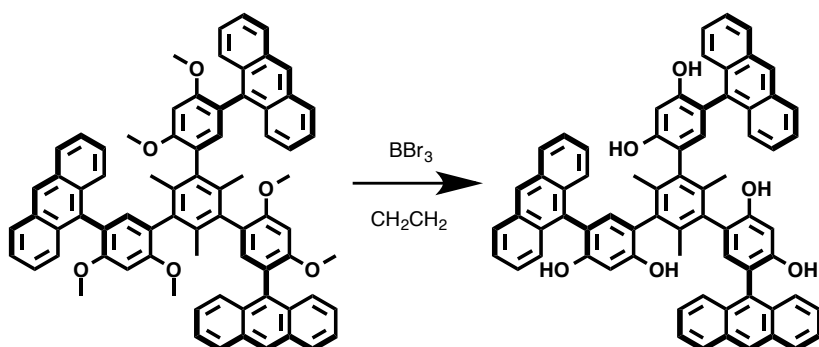
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NUC1 1H
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P2 24.00 usec
P28 0.00 usec
ND0 2
TD 256
SFO1 125.7704 MHz
FIDRES 107.907455 Hz
SW 219.641 ppm
FnMODE Echo-Antiecho
SI 1024
SF 500.1300088 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 echo-antiecho
SF 125.7577751 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

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Synthesis of anthracene trimer **2_{OH}**

AS515



Anthracene trimer **1_{OMe}** (0.501 g, 0.474 mmol) and dry CH₂Cl₂ (30 mL) were added to a 100 mL glass flask. A CH₂Cl₂ solution (1.0 M) of BBr₃ (15 mL, 15 mmol) was added dropwise to this flask under N₂. The reaction mixture was stirred at r.t. for 1 d. The reaction was quenched with H₂O (20 mL). The product was extracted with EtOAc and the resultant organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was washed with CHCl₃ and hexane to afford anthracene trimer **2_{OH}** (0.400 g, 0.411 mmol, 87%) as a pale yellow solid.

¹H NMR (500 MHz, Acetone-*d*₆, r.t.): δ 2.19 (s, 9H), 5.75 (s, 2H), 6.71 (s, 3H), 6.83 (s, 3H), 7.31-7.34 (m, 6H), 7.36-7.39 (m, 6H), 7.80 (m, 8H), 7.89 (s, 2H), 7.95 (d, *J* = 8.5 Hz, 6H), 8.40 (s, 3H). ¹³C NMR (125 MHz, Acetone-*d*₆, r.t.): δ 19.3 (CH₃), 103.9 (CH), 117.4 (C_q), 120.8 (C_q), 125.8 (CH), 126.0 (CH), 127.1 (CH), 127.6 (CH), 129.1 (CH), 131.9 (C_q), 132.5 (C_q), 134.2 (C_q), 135.0 (CH), 136.0 (C_q), 137.7 (C_q), 155.9 (C_q), 156.6 (C_q). FT-IR (KBr, cm⁻¹): 2362, 1624, 1503, 1406, 1258, 1146, 1102, 1014, 888, 849, 795, 737, 607, 540. MALDI-TOF MS (dithranol): *m/z*. Calcd. for C₆₉H₄₈O₆ 972.35, Found 971.52 [M]⁺. HR MS (ESI): Calcd. For C₆₉H₄₈O₆Na 995.3343, Found 995.3319 [M+Na]⁺.

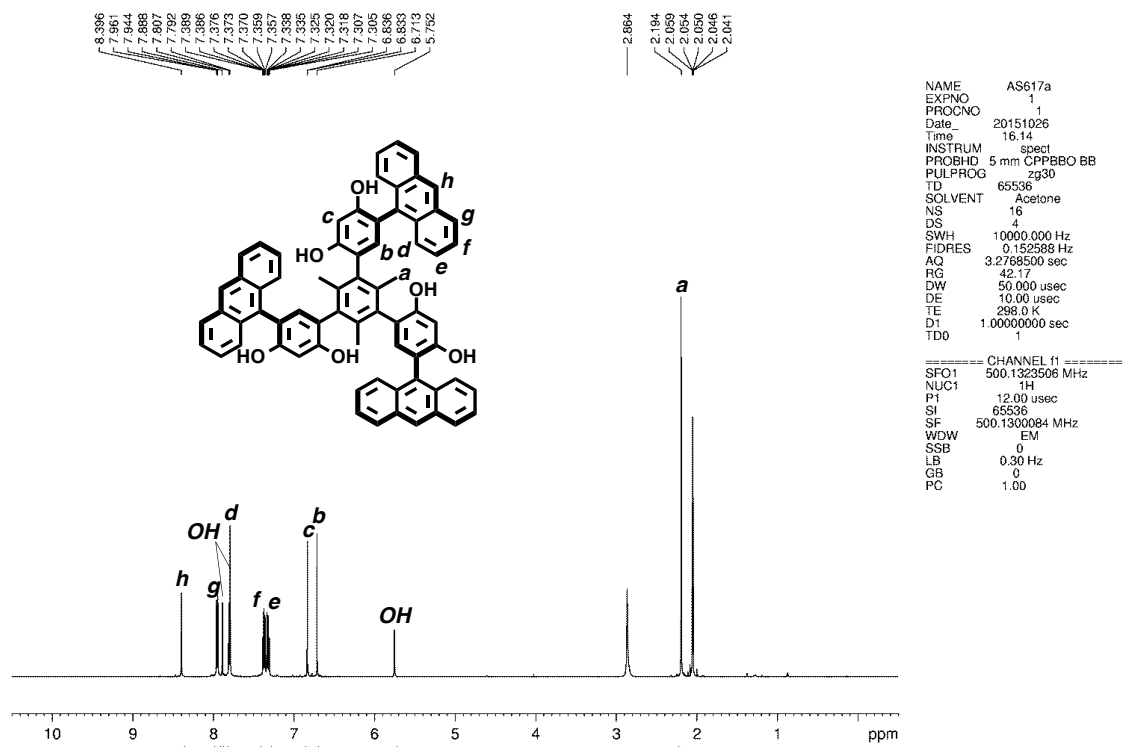


Figure S14. ¹H NMR spectrum (500 MHz, Acetone-*d*₆, r.t.) of **2OH**.

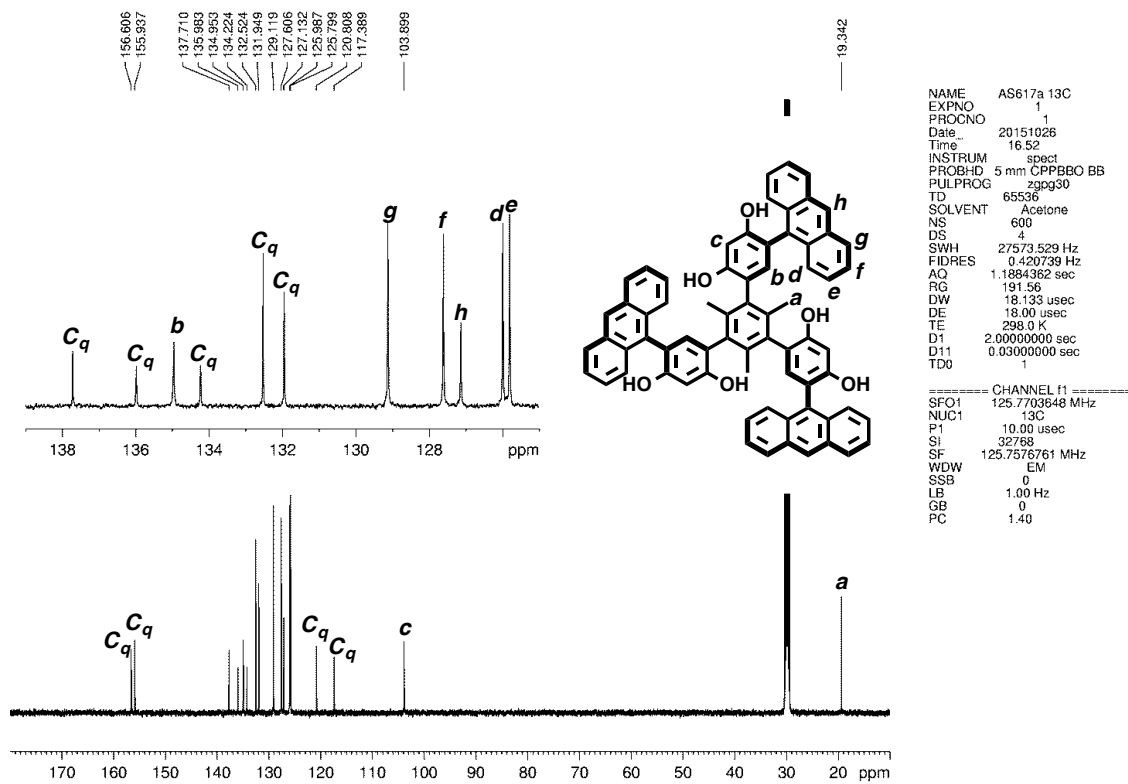


Figure S15. ¹³C NMR spectrum (125 MHz, Acetone-*d*₆, r.t.) of **2OH**.

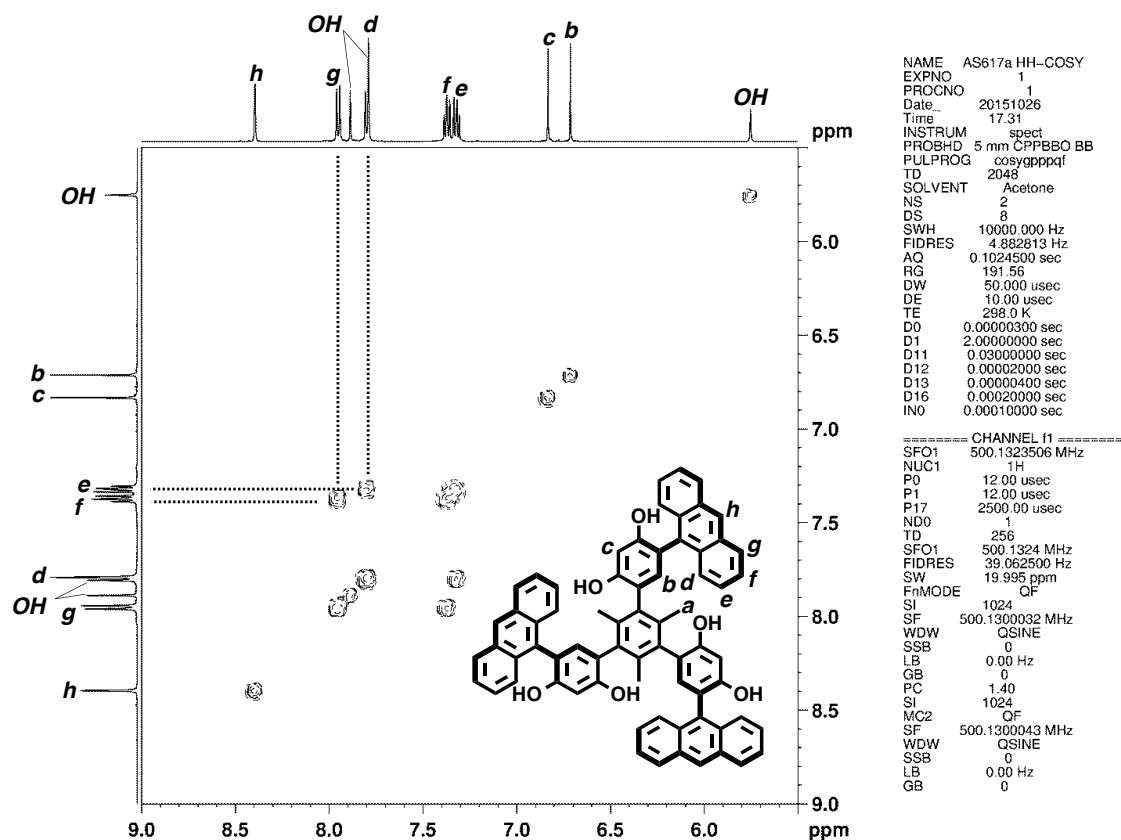


Figure S16. HH-COSY spectrum (500 MHz, Acetone- d_6 , r.t.) of 2_{OH} .

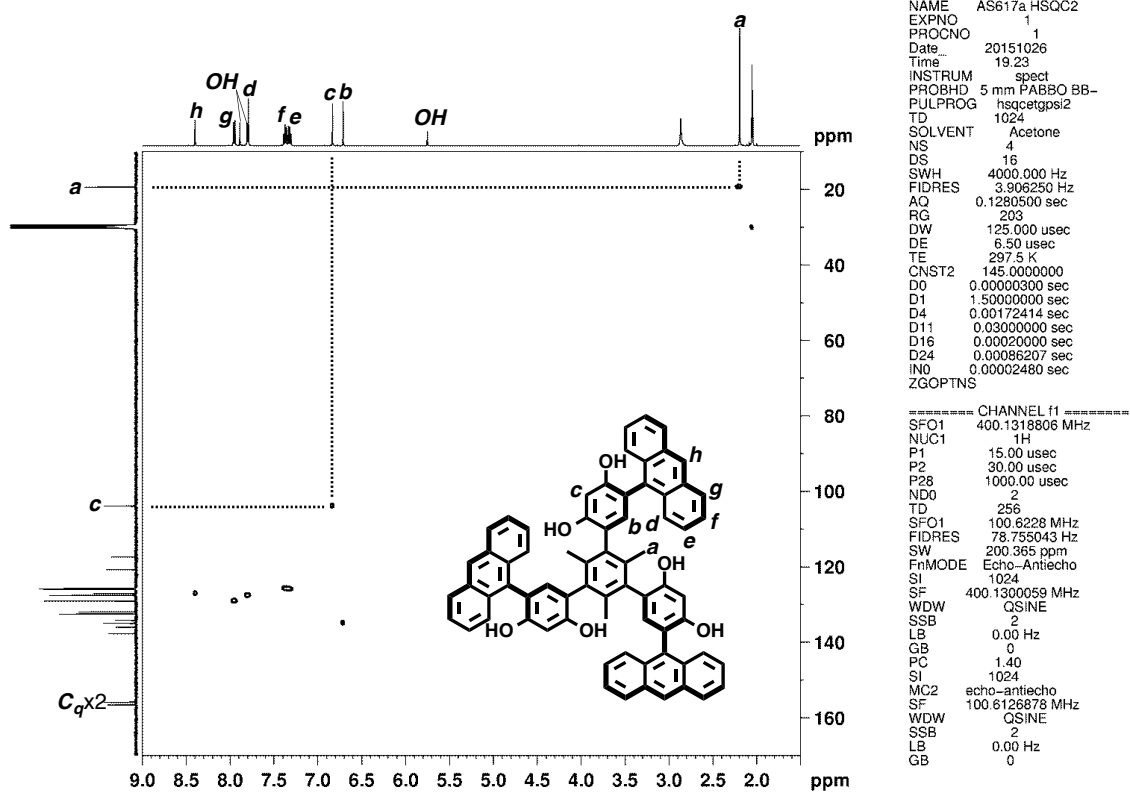


Figure S17a. HSQC spectrum (400 MHz, Acetone- d_6 , r.t.) of 2_{OH} .

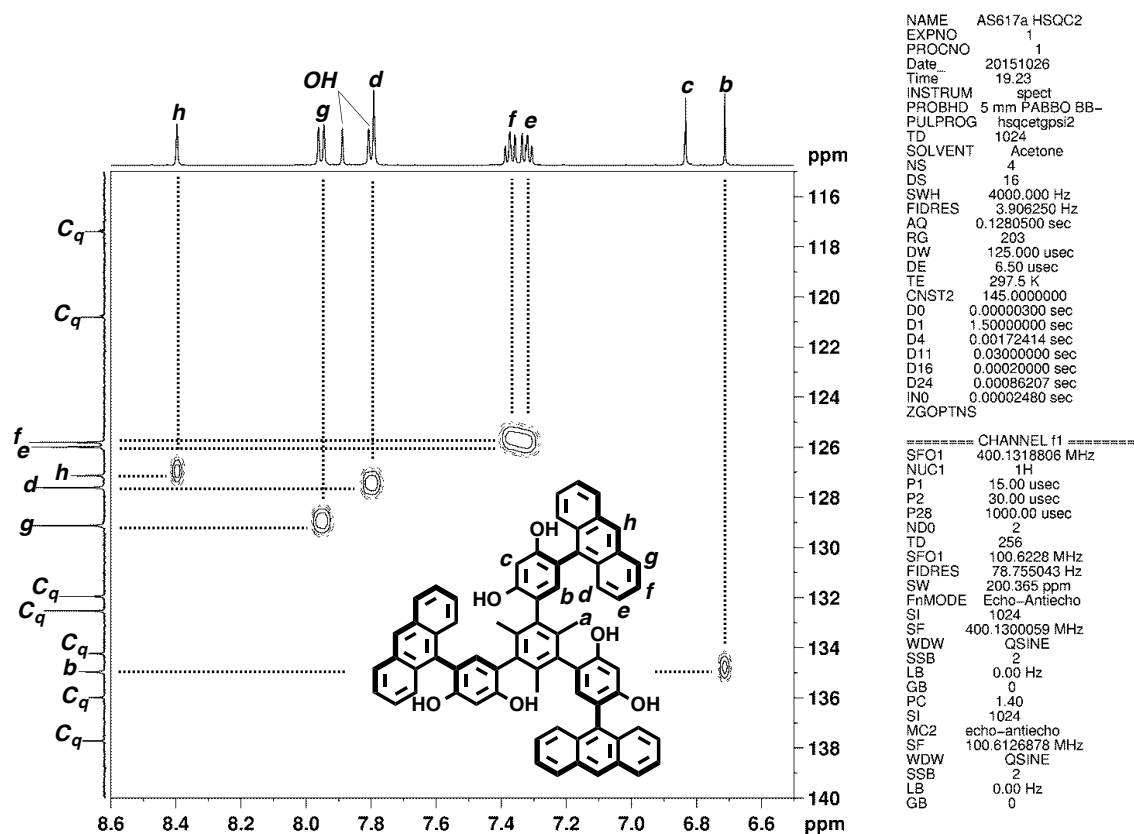
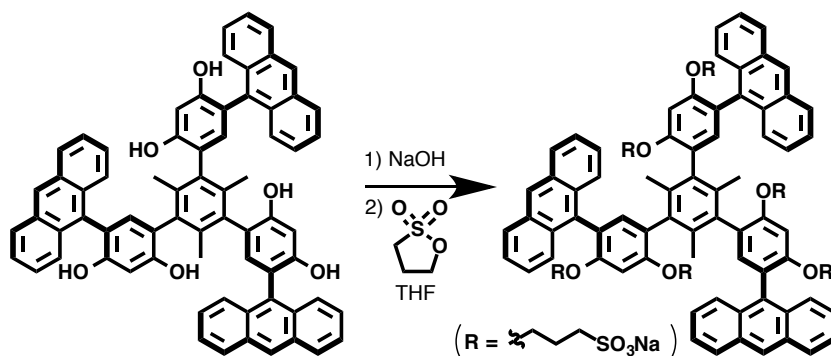


Figure S17b. HSQC spectrum (400 MHz, Acetone- d_6 , r.t.) of 2_{OH} .

Synthesis of tribranched scaffold 2

AS589



Anthracene trimer 2_{OH} (0.310 g, 0.318 mmol), NaOH (0.801 g, 20.0 mmol), and dry THF (20 mL) were added to a 2-necked 50 mL glass flask filled with N_2 . The resultant mixture was stirred at 70 °C for 1 h. A THF (10 mL) solution of 1,3-propanesultone (1.170 g, 9.582 mmol) was added to the reaction mixture and then the solution was further stirred at 70 °C for 2 d. After the evaporation, the crude product was dissolved in water (20 mL) and neutralized by an aqueous HCl solution. After evaporation, the crude product was dissolved in CH_3OH and then precipitated NaCl was removed by centrifugation. The

resultant solution was evaporated and the resultant solid was washed with small amount of cold CH₃OH to afford tribranched scaffold **2** (0.264 g, 0.143 mmol, 45%) as a pale yellow solid.

¹H NMR (500 MHz, CD₃OD, r.t.): δ 1.77-1.82 (m, 6H), 2.05 (s, 9H), 2.21-2.24 (m, 6H), 2.36 (t, *J* = 7.0 Hz, 6H), 3.11 (t, *J* = 7.0 Hz, 6H), 4.07 (t, *J* = 6.0 Hz, 9H), 4.37 (t, *J* = 7.0 Hz, 9H), 6.73 (s, 3H), 7.07 (s, 3H), 7.26-7.30 (m, 6H), 7.33-7.36 (m, 6H), 7.67 (d, *J* = 9.0 Hz, 6H), 7.92 (d, *J* = 9.0 Hz, 6H), 8.34 (s, 3H). ¹³C NMR (125 MHz, CD₃OD, r.t.): δ 19.8 (CH₃), 26.1 (CH₂), 26.6 (CH₂), 48.5-49.5 (CH₂ × 2), 68.5 (CH₂), 68.9 (CH₂), 100.8 (CH), 120.8 (C_q), 125.4 (C_q), 125.9 (CH), 126.1 (CH), 127.1 (CH), 127.8 (CH), 129.3 (CH), 131.9 (C_q), 132.9 (C_q), 135.0 (C_q), 135.5 (C_q), 135.9 (CH), 136.9 (C_q), 158.4 (C_q × 2). ¹H DOSY NMR (400 MHz, CD₃OD, 2.0 mM, 300 K): *D* = 1.35 × 10⁻⁹ m² s⁻¹. FT-IR (KBr, cm⁻¹): 3052, 2949, 2362, 1606, 1502, 1348, 1194, 1109, 1048, 795, 738, 608, 528. ESI-TOF MS (CH₃OH): *m/z* 344.4 [M-5•Na⁺]⁵⁻, 436.3 [M-4•Na⁺]⁴⁻, 589.4 [M-3•Na⁺]³⁻, 895.6 [M-2•Na⁺]²⁻.

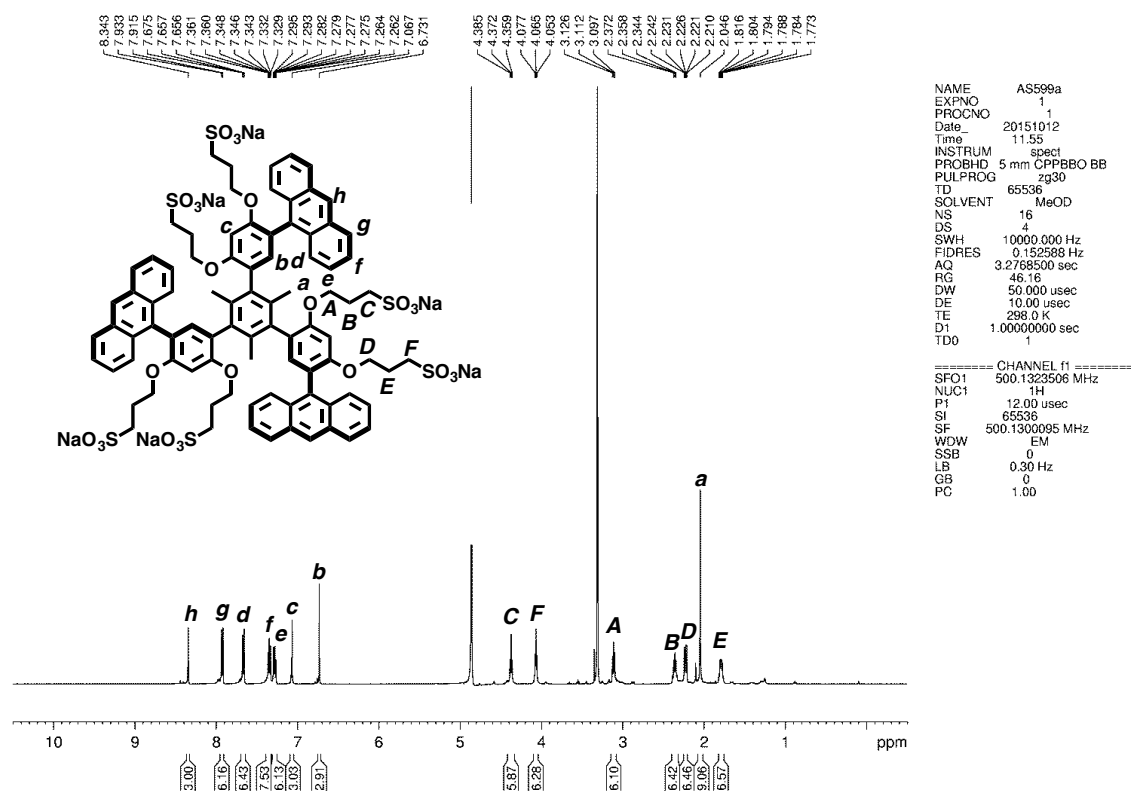


Figure S18. ¹H NMR spectrum (500 MHz, CD₃OD, r.t.) of **2**.

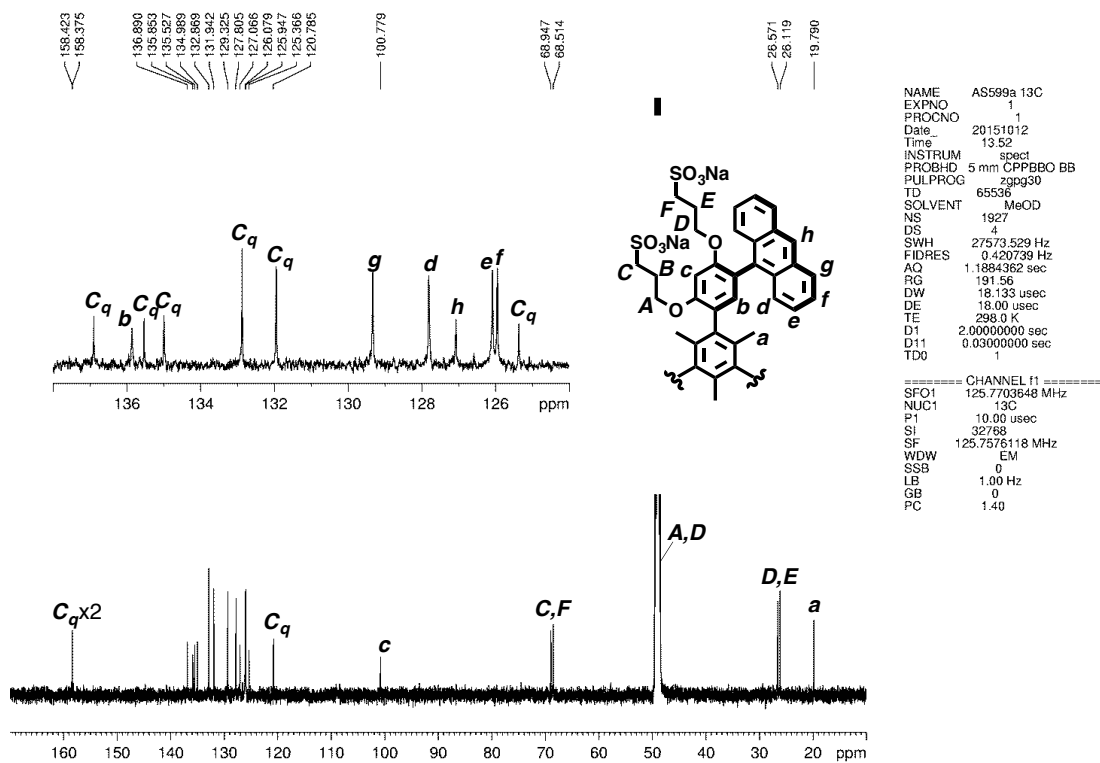


Figure S19. ^{13}C NMR spectrum (125 MHz, CD_3OD , r.t.) of **2**.

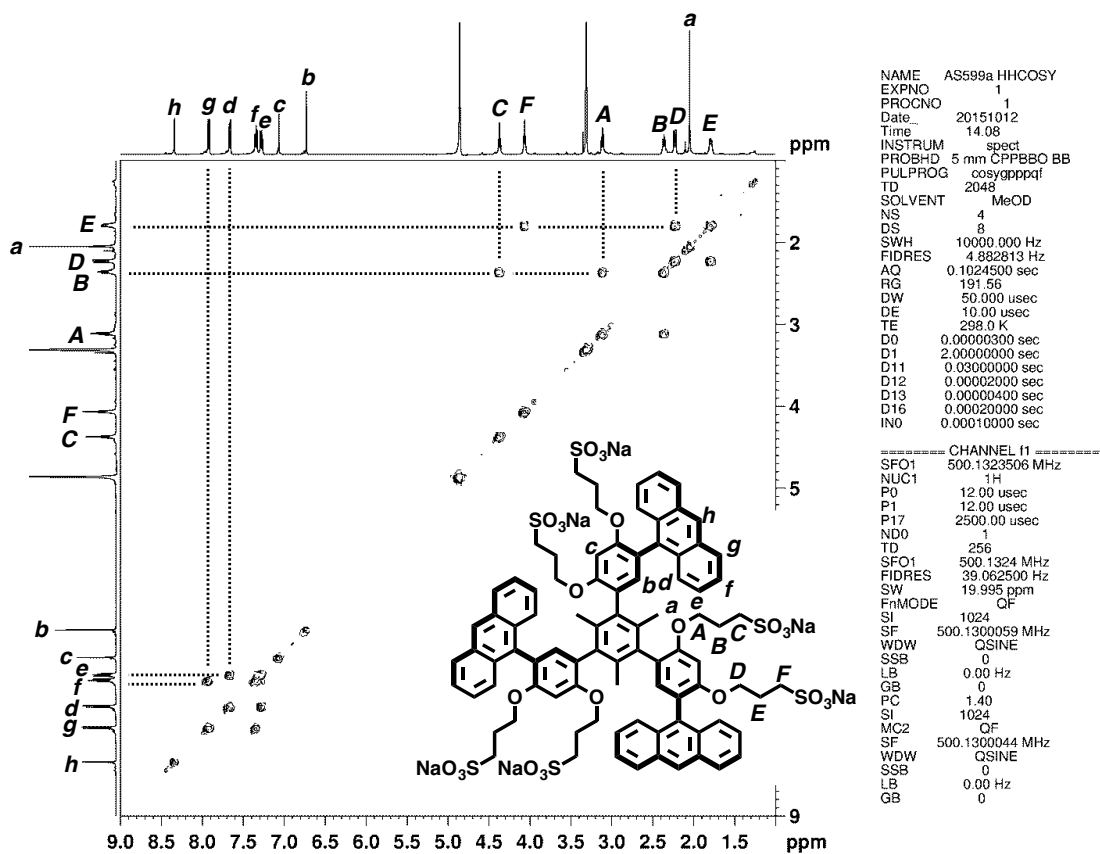


Figure S20. HH-COSY spectrum (500 MHz, CD_3OD , r.t.) of **2**.

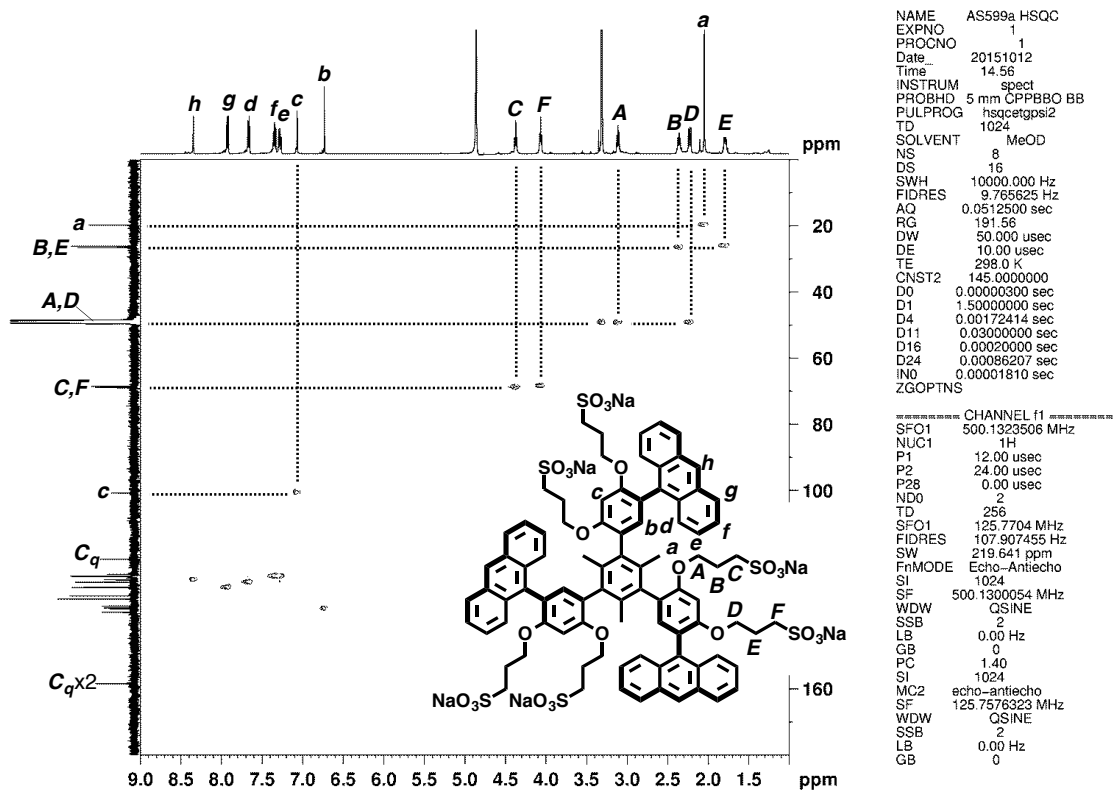


Figure S21a. HSQC spectrum (500 MHz, CD₃OD, r.t.) of **2**.

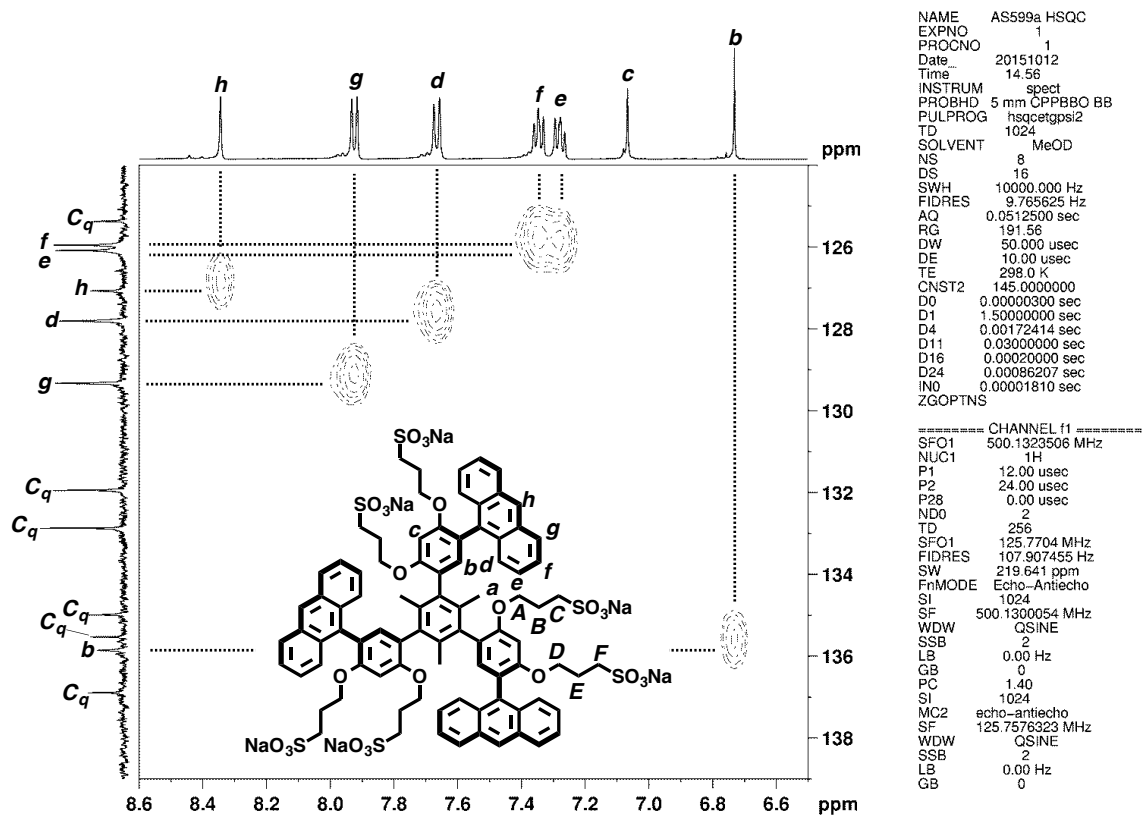


Figure S21b. HSQC spectrum (500 MHz, CD₃OD, r.t.) of **2**.

Display Report

Analysis Info

Analysis Name D:\Data\akita\11suzuki\AS651\AS651-7.d
Method esi_neg_low.m
Sample Name
Comment

Acquisition Date 12/4/2015 5:47:01 PM

Operator BDAL@DE
Instrument / Ser# micrOTOF 10321

Acquisition Parameter

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Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

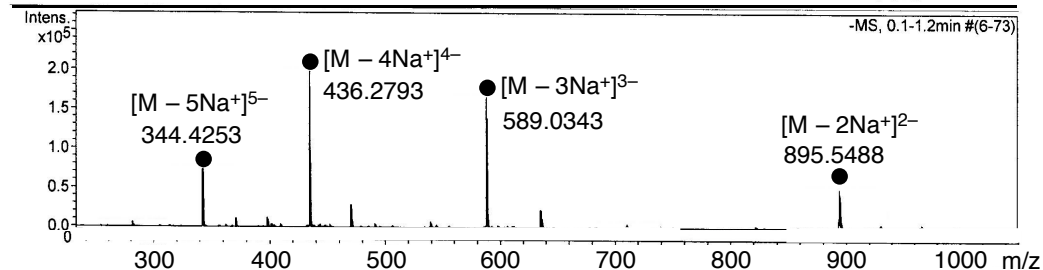
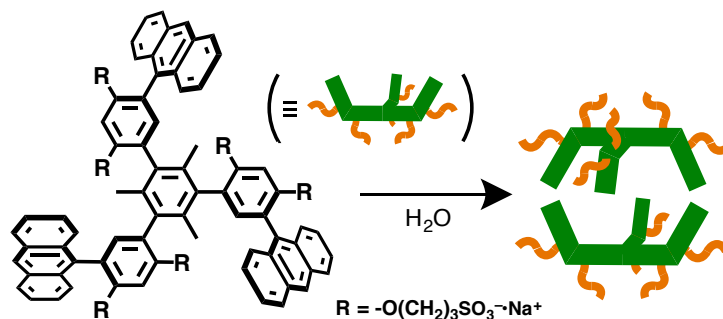


Figure S22. ESI-TOF MS spectrum (CH₃OH) of **2**.

Formation of molecular capsule (**2**)₂

AS523



Tribranched scaffold **2** (1.9 mg, 1.0 μ mol) was added to water (0.5 mL) and then the solution was stirred at r.t. for 1 min. The formation of molecular capsule (**2**)₂ was confirmed by NMR, DLS, and spectroscopic analyses.

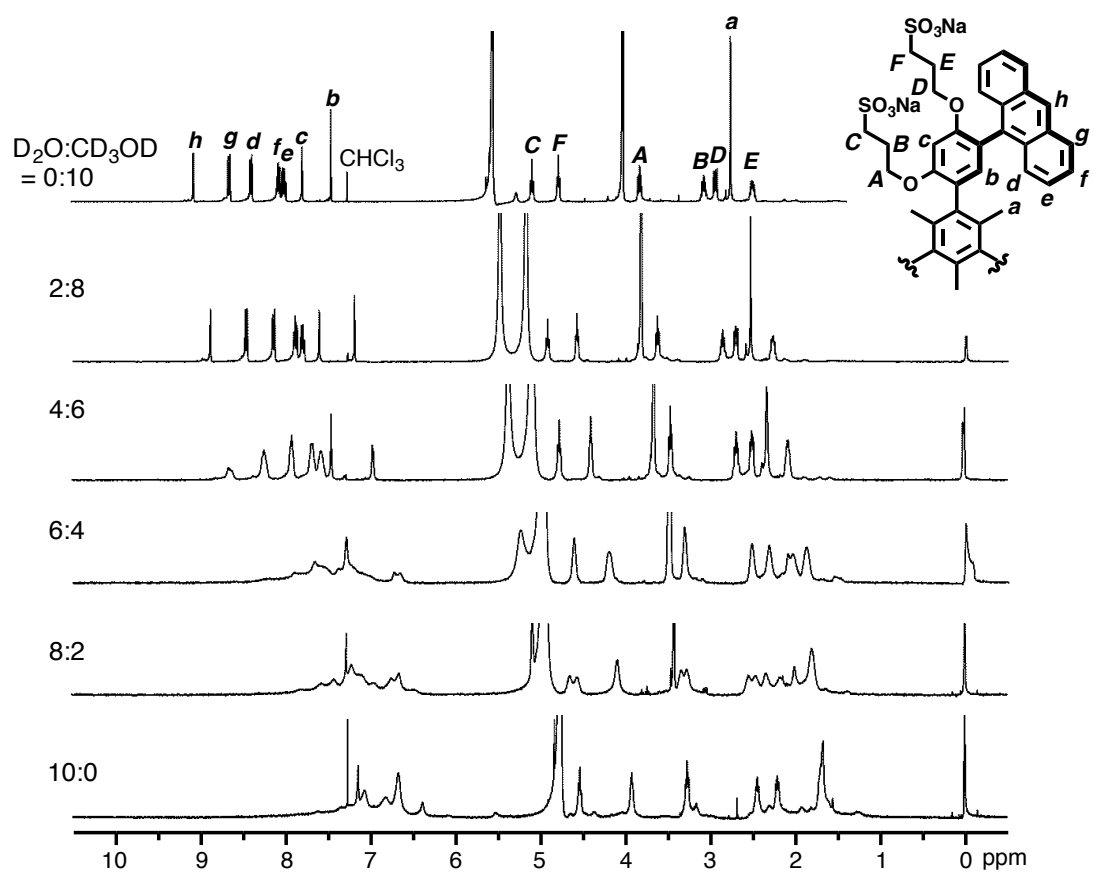


Figure S23. ^1H NMR spectra (400 MHz, r.t., TMS as an external standard) of **2** (2.0 mM) in $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ mixtures.

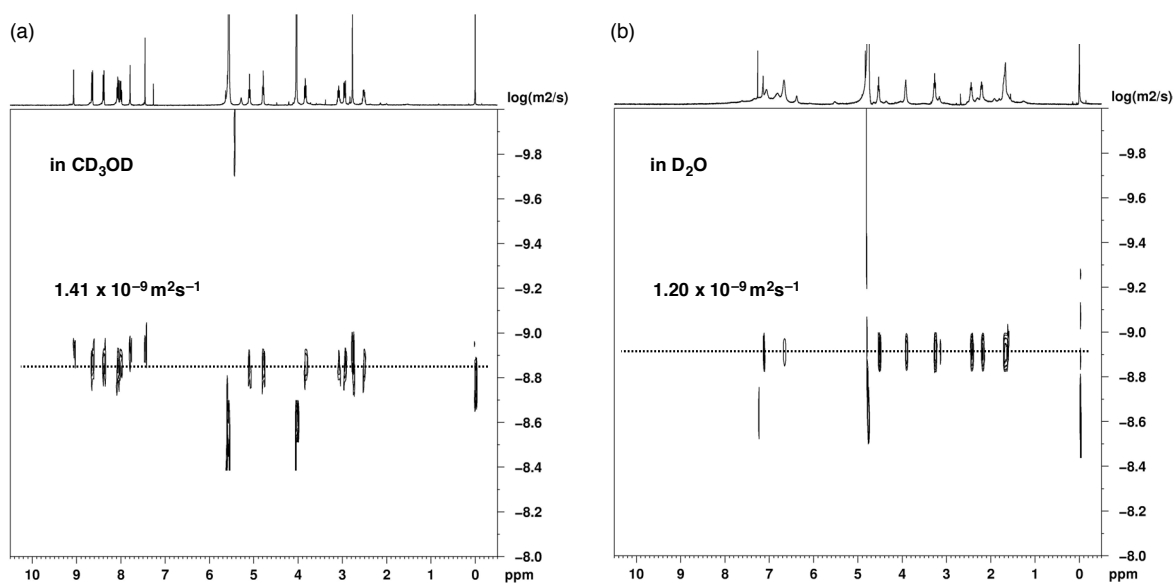


Figure S24. DOSY NMR spectra (500 MHz, r.t., TMS as an external standard) of **2** (2.0 mM) in (a) CD_3OD and (b) D_2O .

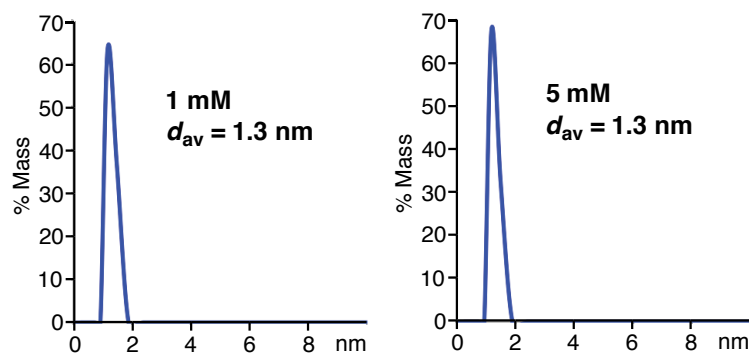


Figure S25. Particle size distribution of assembly $(2)_2$ by DLS analysis (H_2O , r.t., 1.0 and 5.0 mM based on 2).

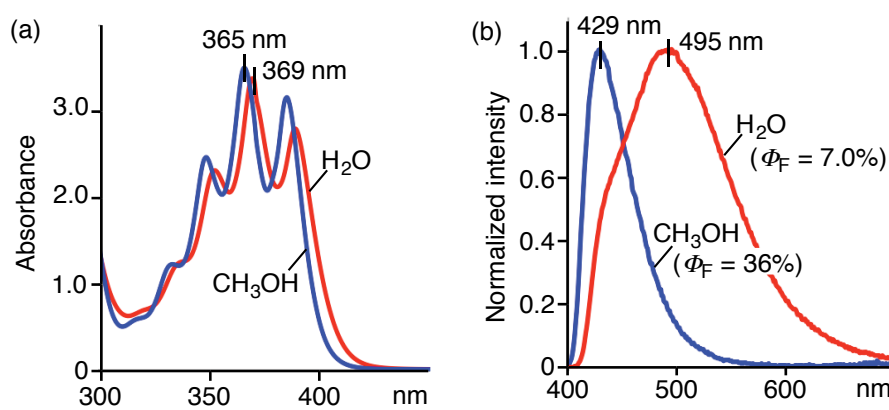


Figure S26. (a) UV-vis spectra and (b) normalized fluorescence spectra ($\lambda_{ex} = 370$ nm, r.t.) of 2 in CH_3OH and capsule $(2)_2$ in H_2O (2.0 mM based on 2).

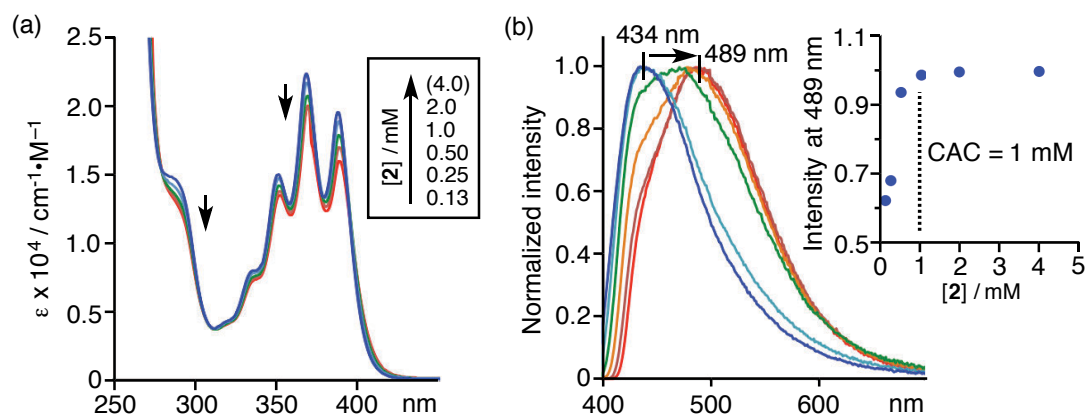
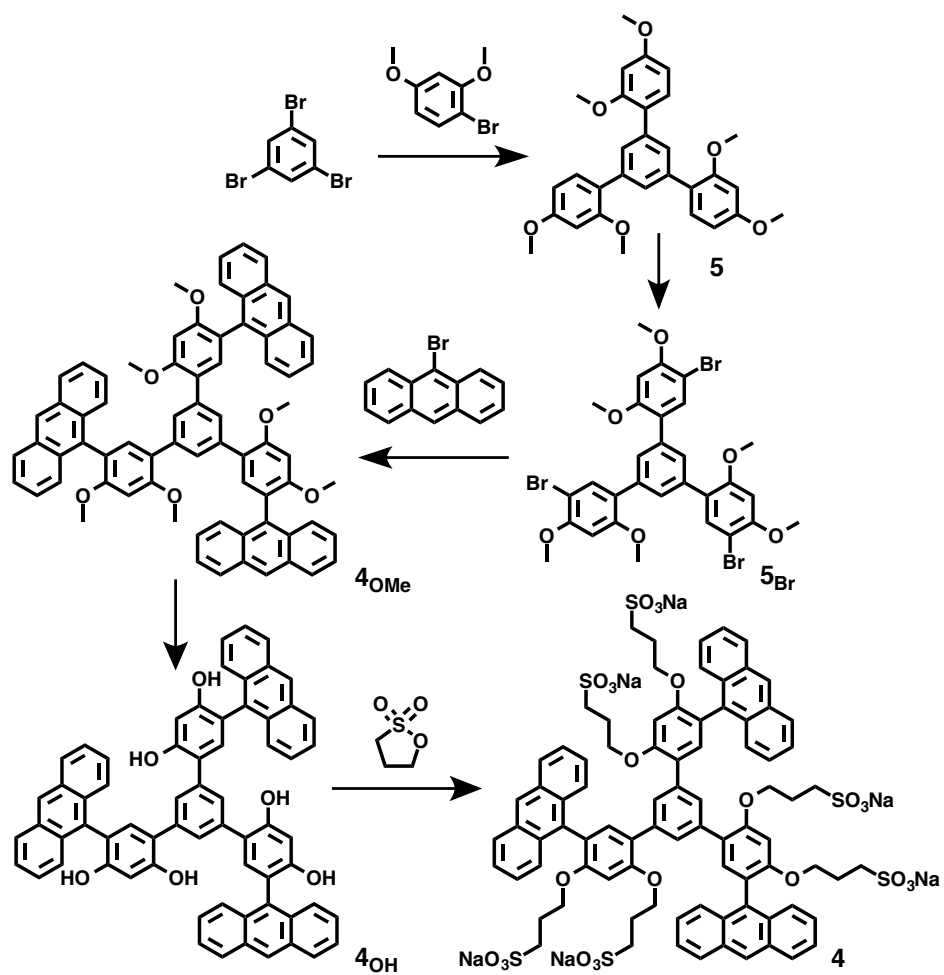


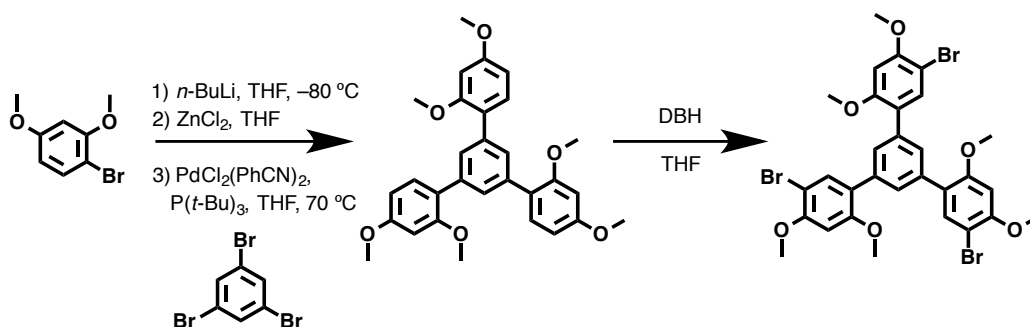
Figure S27. Concentration-dependent (a) UV-vis spectra (0.13-2.0 mM) and (b) fluorescence spectra (normalized, 0.13-4.0 mM, $\lambda_{ex} = 370$ nm, r.t.) of 2 in H_2O .

Scheme S2. Synthetic route of tribranched scaffold 4.



Synthesis of **5_{Br}**

KK401, 410



1-Bromo-2,4-dimethoxybenzene (4.136 g, 19.05 mmol) and dry THF (200 mL) were added to a 2-necked 300 mL glass flask filled with N₂. A hexane solution (2.6 M) of *n*-butyllithium (7.8 mL, 20 mmol) was then added dropwise to this flask at -80 °C under N₂. After the mixture was stirred at -80 °C for 30 min, a dry THF solution (50 mL) of ZnCl₂ (3.392 g, 24.89 mmol) was added to the solution. The resultant mixture was further stirred at -80 °C and then the solution was warmed to r.t. for 2 h to obtain 2,4-dimethoxyphenylzinc chloride. 1,3,5-Tribromobenzene (1.017 g, 3.230 mmol), PdCl₂(PhCN)₂ (0.130 g, 0.339 mmol), a hexane solution (0.95 M) of P(*t*-Bu)₃ (0.70 mL, 0.67 mmol), and dry THF (30 mL) were added to a 50 mL glass flask filled with N₂. After stirring at r.t. for 2 h, the mixture was added to the 300 mL flask. The resulted solution was further stirred at 80 °C for 1 d. After evaporation, the product was extracted with CH₂Cl₂ and the resultant organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was purified by silica-gel column chromatography (hexane/EtOAc = 1/1) to afford 1,3,5-tris(2,4-dimethoxyphenyl)benzene (**5**; 1.154 g, 2.373 mmol, 73%) as a white solid.

Compound **5** (1.558 g, 3.203 mmol) and THF (30 mL) were added to a 50 mL glass flask. DBH (2.132 g, 7.457 mmol) was added to the solution and the resultant mixture was stirred at r.t. for 12 h. After addition of H₂O, resultant precipitate was collected and washed with H₂O to afford **5_{Br}** (1.999 g, 2.764 mmol, 86%) as a white solid. ¹H NMR (500 MHz, CDCl₃, r.t.): δ 3.84 (s, 9H), 3.96 (s, 9H), 6.59 (s, 3H), 7.52 (s, 3H), 7.55 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, r.t.): δ 56.0 (CH₃), 56.5 (CH₃), 97.1 (CH), 102.2 (C_q), 124.6 (C_q), 129.1 (CH), 134.6 (CH), 136.6 (C_q), 156.0 (C_q), 156.9 (C_q). FT-IR (KBr, cm⁻¹): 2939, 2842, 2363, 1602, 1502, 1464, 1434, 1363, 1295, 1206, 1173, 1030, 876, 815, 716, 632. HR MS (ESI): Calcd. For C₃₀H₂₇Br₃O₆Na 742.9250, Found 742.9249 [M+Na]⁺.

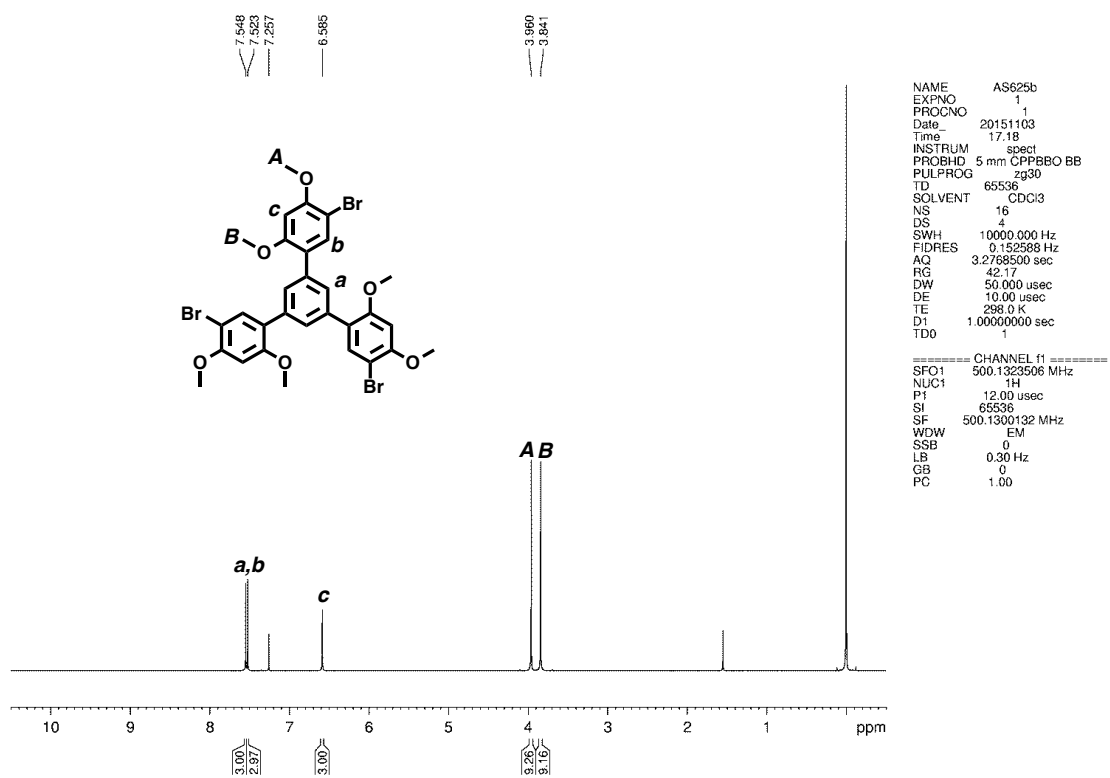


Figure S28. ^1H NMR spectrum (500 MHz, CDCl_3 , r.t.) of 5_{Br} .

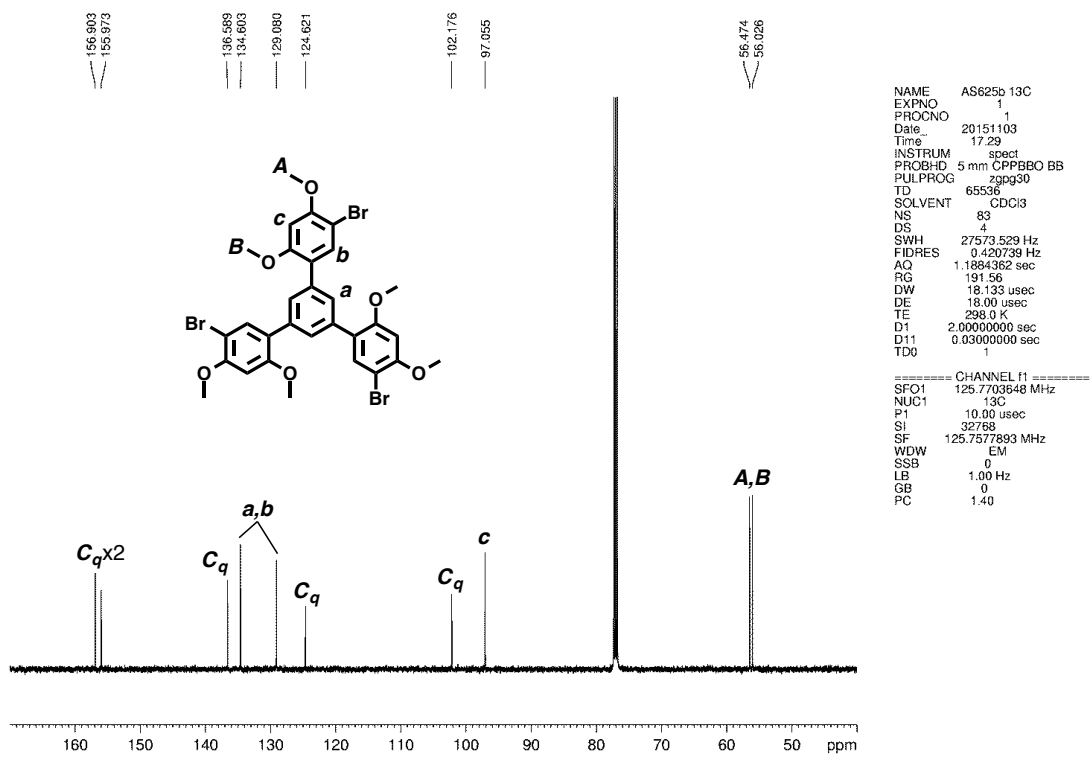


Figure S29. ^{13}C NMR spectrum (125 MHz, CDCl_3 , r.t.) of 5_{Br} .

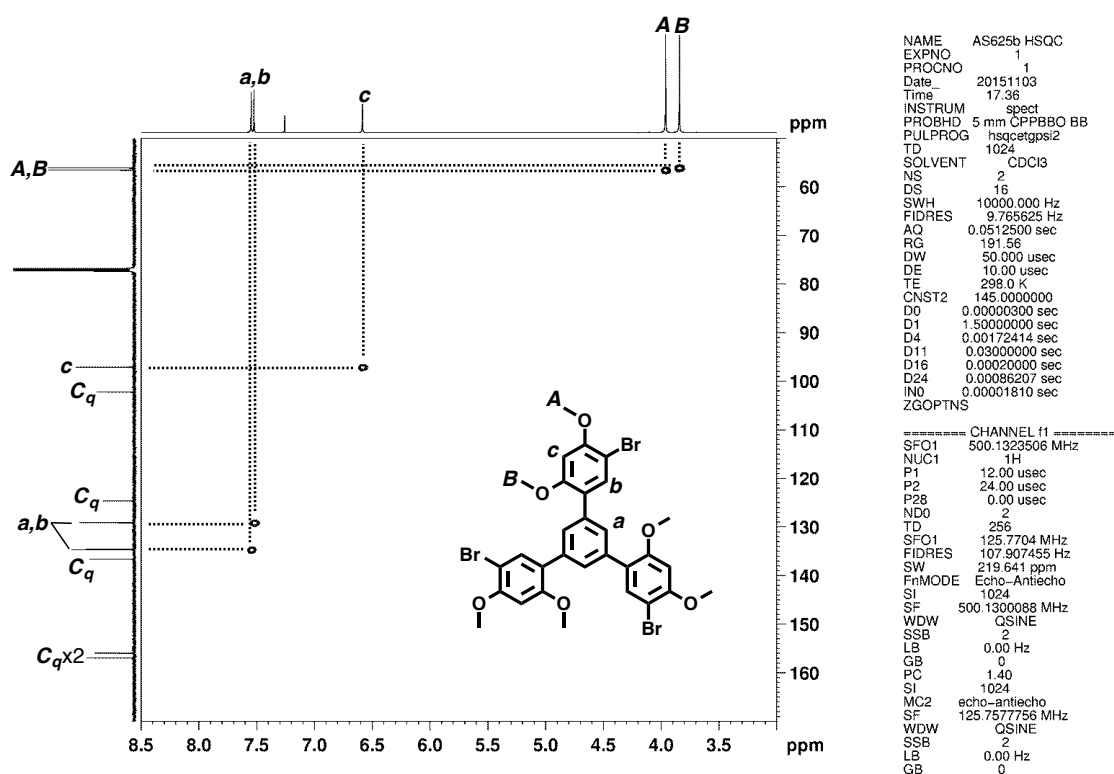
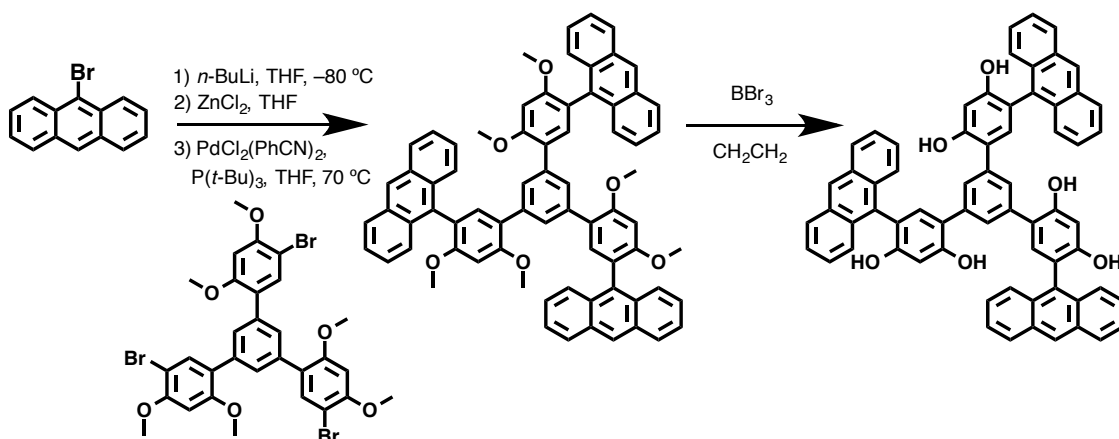


Figure S30. HSQC spectrum (500 MHz, CDCl₃, r.t.) of **5_{Br}**.

Synthesis of anthracene trimer **4_{OH}**

KK404, 409



9-Bromoanthracene (1.551 g, 6.030 mmol) and dry THF (200 mL) were added to a 2-necked 300 mL glass flask filled with N₂. A hexane solution (2.6 M) of *n*-butyllithium (2.5 mL, 6.5 mmol) was then added dropwise to this flask at -80 °C under N₂. After the mixture was stirred at -80 °C for 30 min, a dry THF solution (40 mL) of ZnCl₂ (1.082 g, 7.940 mmol) was added to the solution. The resultant mixture was further stirred at -80 °C

and then the solution was warmed to r.t. to obtain 9-anthrylzinc chloride. Compound **5_{Br}** (0.712 g, 0.985 mmol), PdCl₂(PhCN)₂ (0.039 g, 0.10 mmol), a hexane solution (0.95 M) of P(*t*-Bu)₃ (0.21 mL, 0.20 mmol), and dry THF (30 mL) were added to a 50 mL glass flask filled with N₂. After stirring at r.t. for 30 min, the mixture was added to the 300 mL flask. The resulted solution was further stirred at 80 °C for 1 d. After evaporation, the product was extracted with CH₂Cl₂ and the resultant organic layer was dried over MgSO₄, filtered, and concentrated. The resultant product was washed with hexane to afford anthracene trimer **4_{OMe}** (0.961 g, 0.946 mmol, 96%) as a white solid.

Anthracene trimer **4_{OMe}** (1.008 g, 0.993 mmol) and dry CH₂Cl₂ (100 mL) were added to a 100 mL glass flask. A CH₂Cl₂ solution (1.0 M) of BBr₃ (6.0 mL, 6.0 mmol) was added dropwise to this flask at 0 °C under N₂. The reaction mixture was stirred at r.t. for 1 d. The reaction was quenched with H₂O (50 mL). The product was extracted with CH₂Cl₂ and the resultant organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was washed with hexane to afford anthracene trimer **4_{OH}** (0.714 g, 0.767 mmol, 77%) as a pale yellow solid.

¹H NMR (500 MHz, DMSO-*d*₆, r.t.): δ 6.68 (s, 3H), 7.02 (s, 3H), 7.29-7.33 (m, 6H), 7.43-7.46 (m, 6H), 7.58 (s, 3H), 7.65 (d, *J* = 8.5 Hz, 6H), 8.07 (d, *J* = 8.5 Hz, 6H), 8.55 (s, 3H), 9.26 (s, 3H), 9.57 (s, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆, r.t.): δ 103.5 (CH), 115.9 (C_q), 119.8 (C_q), 125.2 (CH), 125.4 (CH), 125.9 (CH), 126.8 (CH), 127.5 (CH), 128.4 (CH), 130.4 (C_q), 131.2 (C_q), 133.6 (CH), 134.3 (C_q), 137.7 (C_q), 155.0 (C_q), 155.7 (C_q). FT-IR (KBr, cm⁻¹): 2362, 1623, 1507, 1358, 1261, 1220, 1157, 1062, 1014, 886, 851, 738, 607, 576. HR MS (ESI): Calcd. For C₆₆H₄₂O₆Na 953.2874, Found 953.2874 [M+Na]⁺.

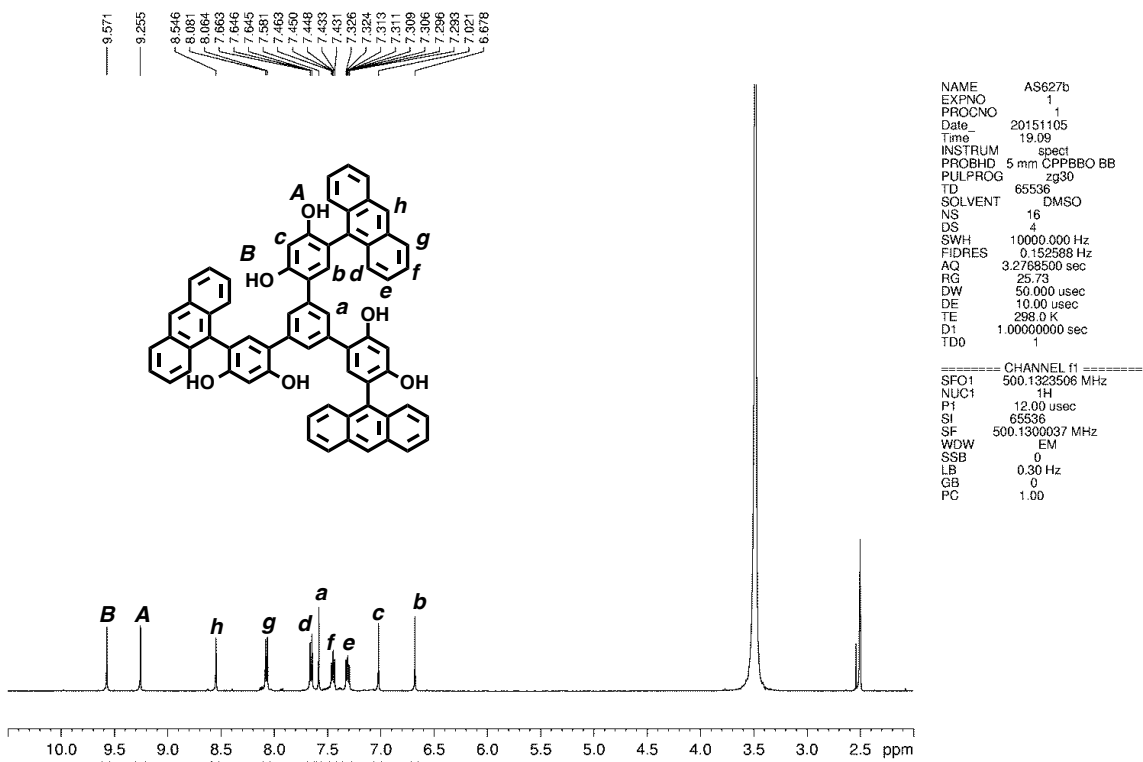


Figure S31. ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$, r.t.) of 4_{OH} .

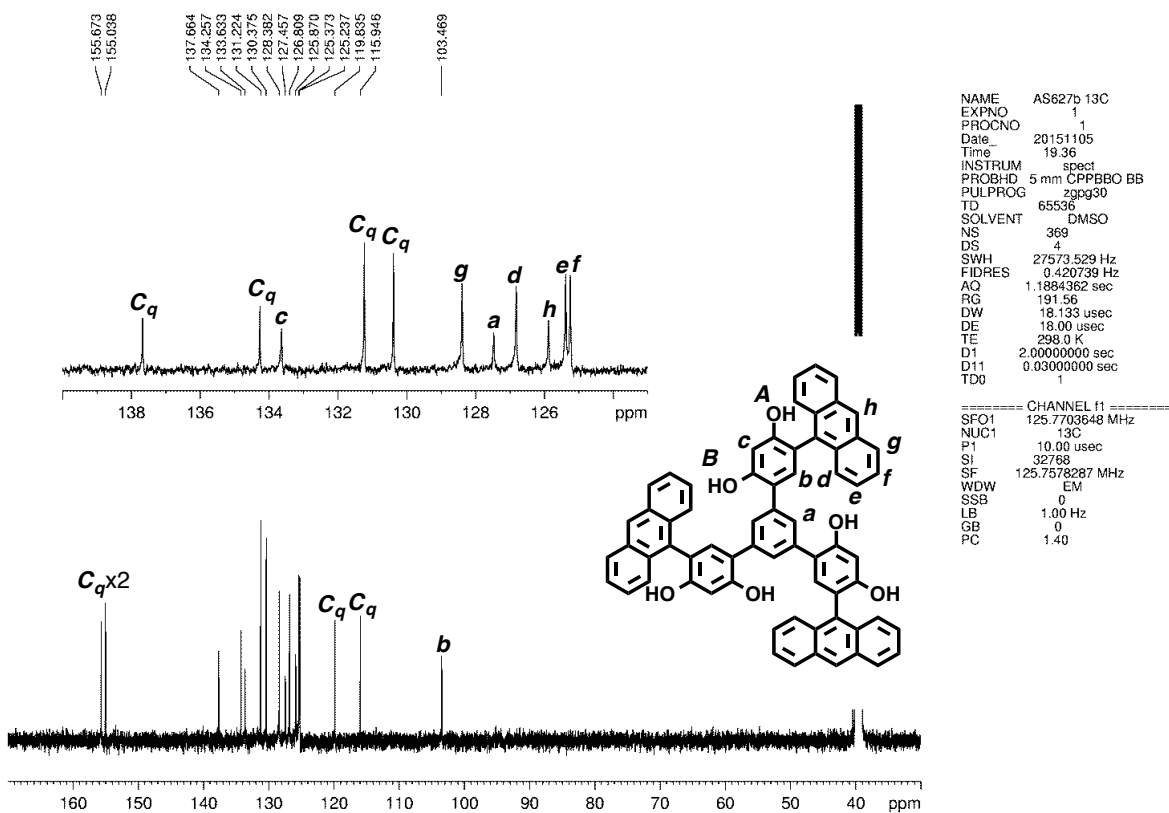


Figure S32. ^{13}C NMR spectrum (125 MHz, $\text{DMSO-}d_6$, r.t.) of 4_{OH} .

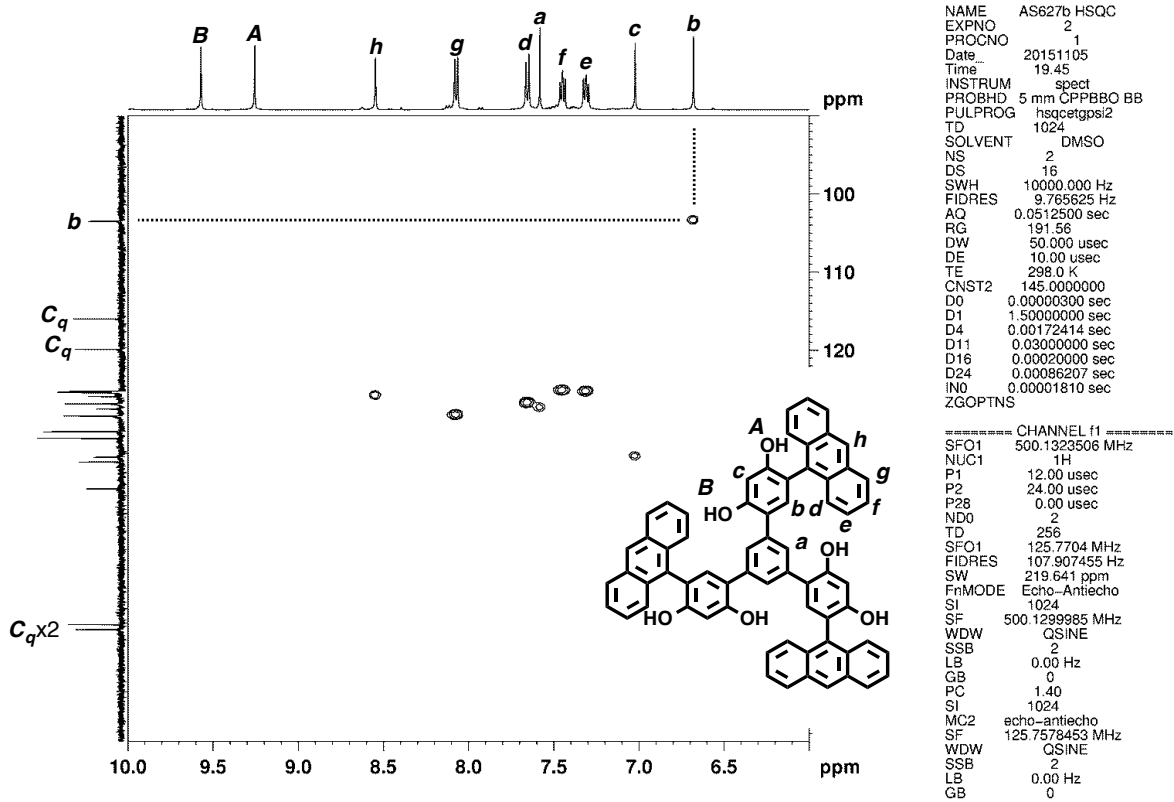


Figure S33a. HSQC spectrum (500 MHz, DMSO-*d*₆, r.t.) of 4_{OH}.

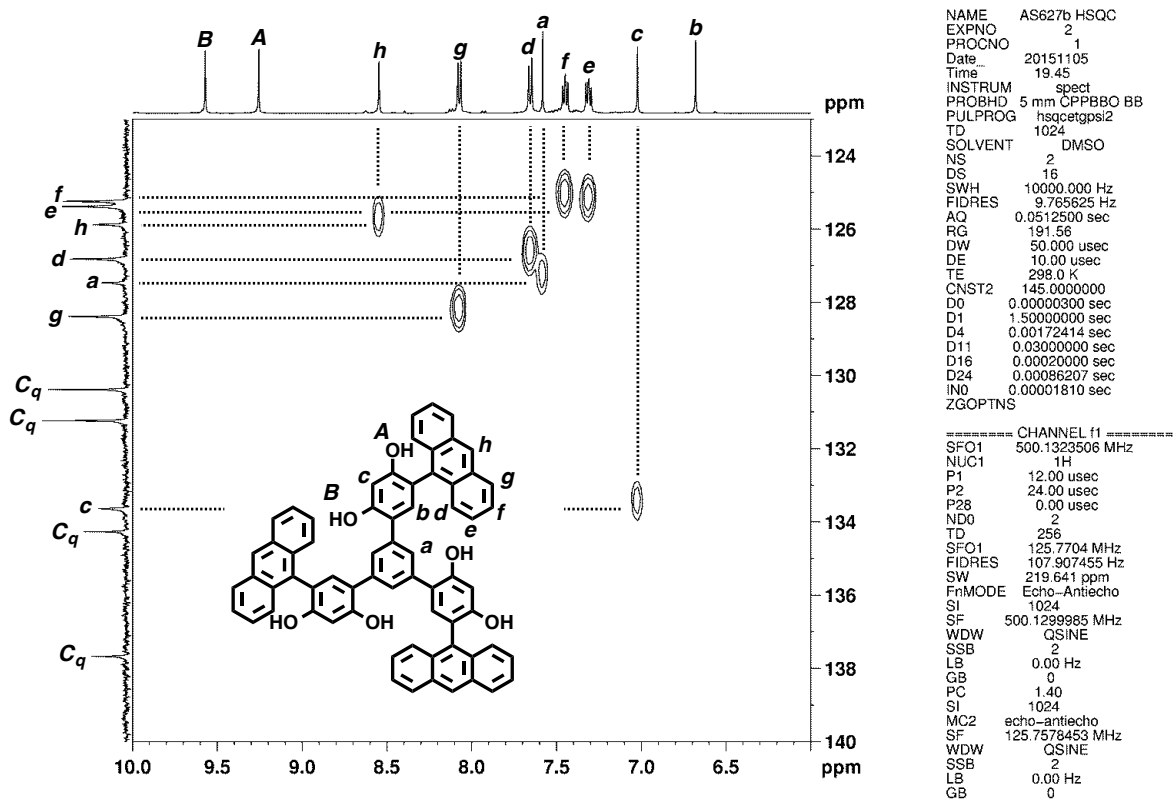
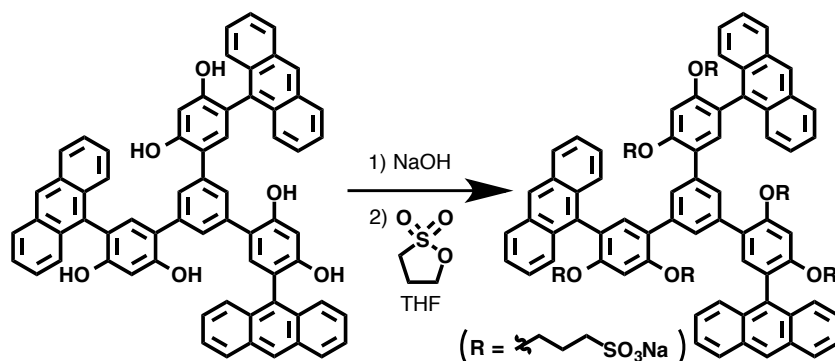


Figure S33b. HSQC spectrum (500 MHz, DMSO-*d*₆, r.t.) of 4_{OH}.

Synthesis of tribranched scaffold 4

AS652



Anthracene trimer **4_{OH}** (0.160 g, 0.254 mmol), NaOH (0.683 g, 17.1 mmol), and dry THF (20 mL) were added to a 2-necked 50 mL glass flask filled with N₂. The resultant mixture was stirred at 70 °C for 1 h. 1,3-Propanesultone (0.986 g, 8.07 mmol) was added to the reaction mixture and then the solution was further stirred at 70 °C for 17 h. After the centrifugation, the crude product was dissolved in water (20 mL) and neutralized by an aqueous HCl solution. After evaporation, the crude product was dissolved in CH₃OH and then precipitated NaCl was removed by centrifugation. The resultant solution was evaporated and the resultant solid was washed with cold CH₃OH to afford tribranched scaffold **4** (0.139 g, 0.0771 mmol, 30%) as a pale yellow solid.

¹H NMR (500 MHz, CD₃OD, r.t.): δ 1.77-1.80 (m, 6H), 1.94 (t, *J* = 7.0 Hz, 6H), 2.25-2.28 (m, 6H), 2.60 (t, *J* = 7.0 Hz, 6H), 4.04 (t, *J* = 7.0 Hz, 6H), 4.26 (t, *J* = 7.0 Hz, 6H), 6.98 (s, 3H), 7.26 (s, 3H), 7.31-7.34 (m, 6H), 7.42 (t, *J* = 7.5 Hz, 6H), 7.71 (d, *J* = 7.5 Hz, 6H), 7.75 (s, 3H), 8.03 (d, *J* = 7.5 Hz, 6H), 8.47 (s, 3H). ¹³C NMR (125 MHz, CD₃OD, r.t.): δ 26.0 (CH₂ × 2), 68.4 (CH₂), 68.6 (CH₂), 100.2 (CH), 120.9 (C_q), 124.7 (C_q), 126.1 (CH), 126.4 (CH), 127.4 (CH), 127.9 (CH), 129.4 (CH), 129.7 (CH), 131.9 (C_q), 133.0 (C_q), 134.8 (C_q), 135.7 (CH), 138.8 (C_q), 158.1 (C_q), 158.7 (C_q). ¹H DOSY NMR (500 MHz, CD₃OD, 2.0 mM, r.t.): *D* = 0.95 × 10⁻⁹ m² s⁻¹. FT-IR (KBr, cm⁻¹): 3052, 2945, 2363, 1605, 1504, 1347, 1192, 1047, 883, 793, 738, 607, 530. ESI-TOF MS (CH₃OH): *m/z* 335.8 [M-5•Na⁺]⁵⁻, 425.5 [M-4•Na⁺]⁴⁻, 575.0 [M-3•Na⁺]³⁻, 874.5 [M-2•Na⁺]²⁻.

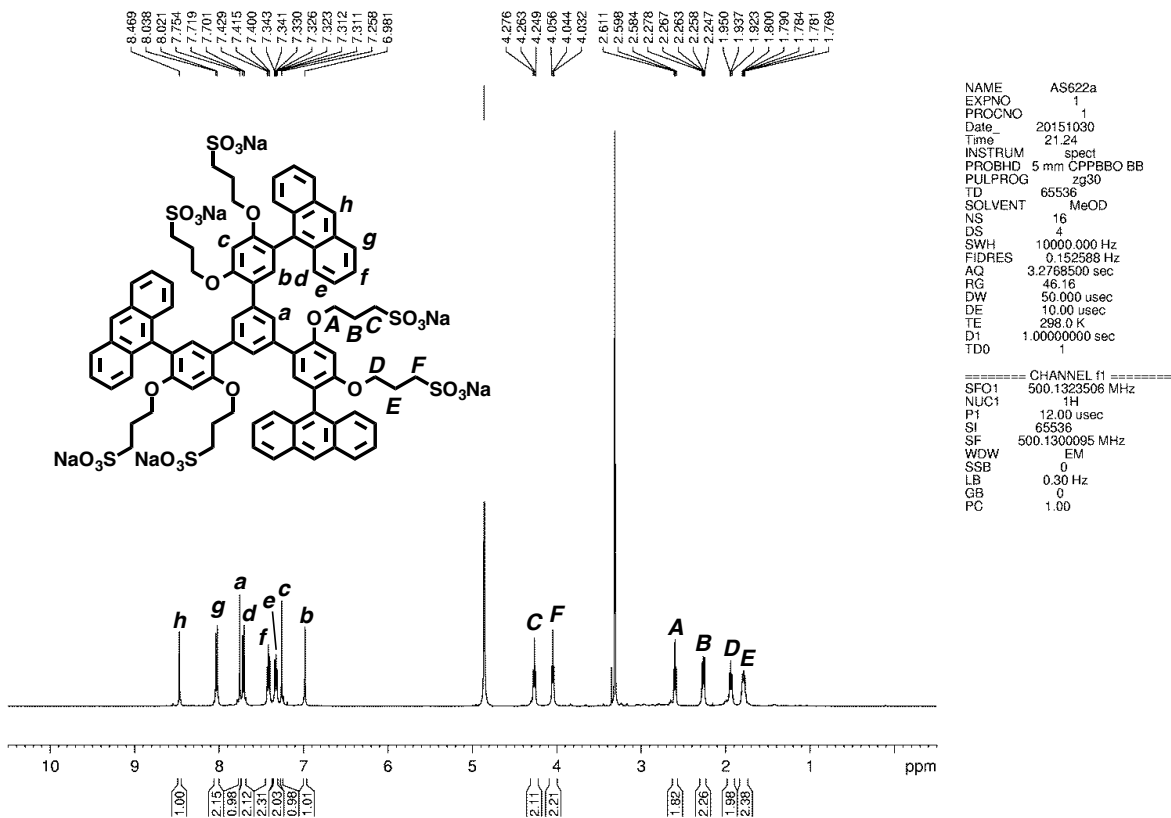


Figure S34. ¹H NMR spectrum (500 MHz, CD₃OD, r.t.) of 4.

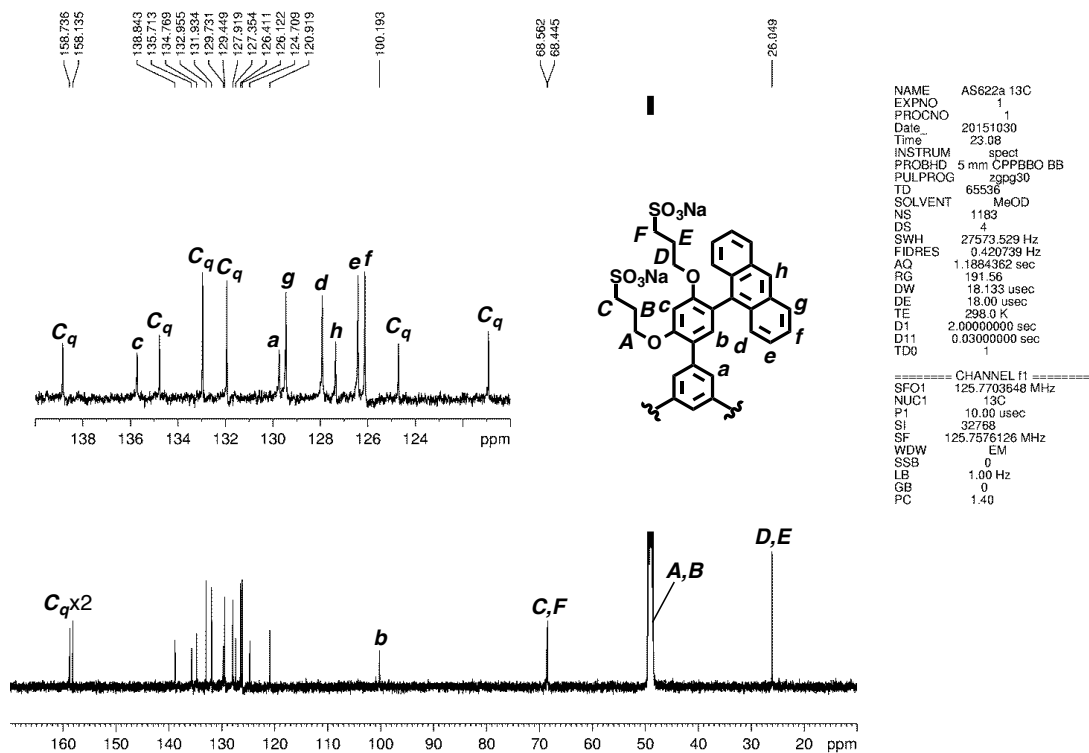


Figure S35. ¹³C NMR spectrum (125 MHz, CD₃OD, r.t.) of 4.

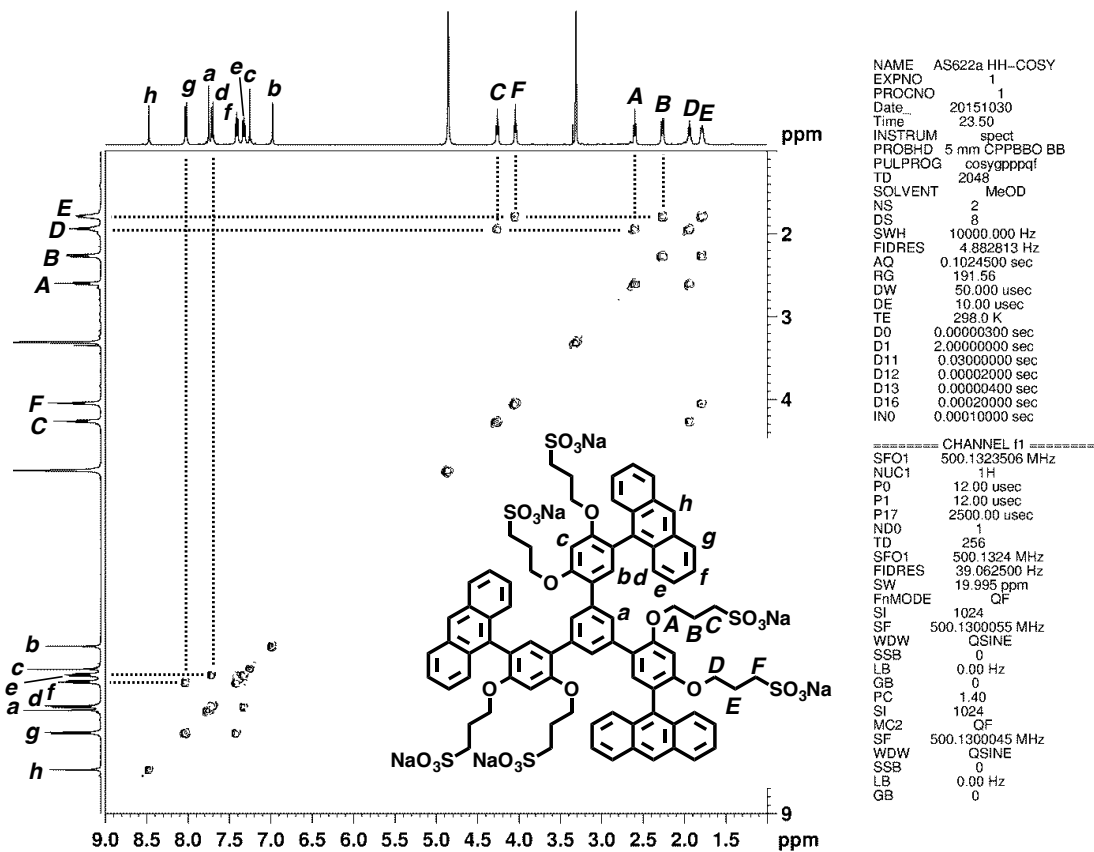


Figure S36. HH-COSY spectrum (500 MHz, CD₃OD, r.t.) of **4**.

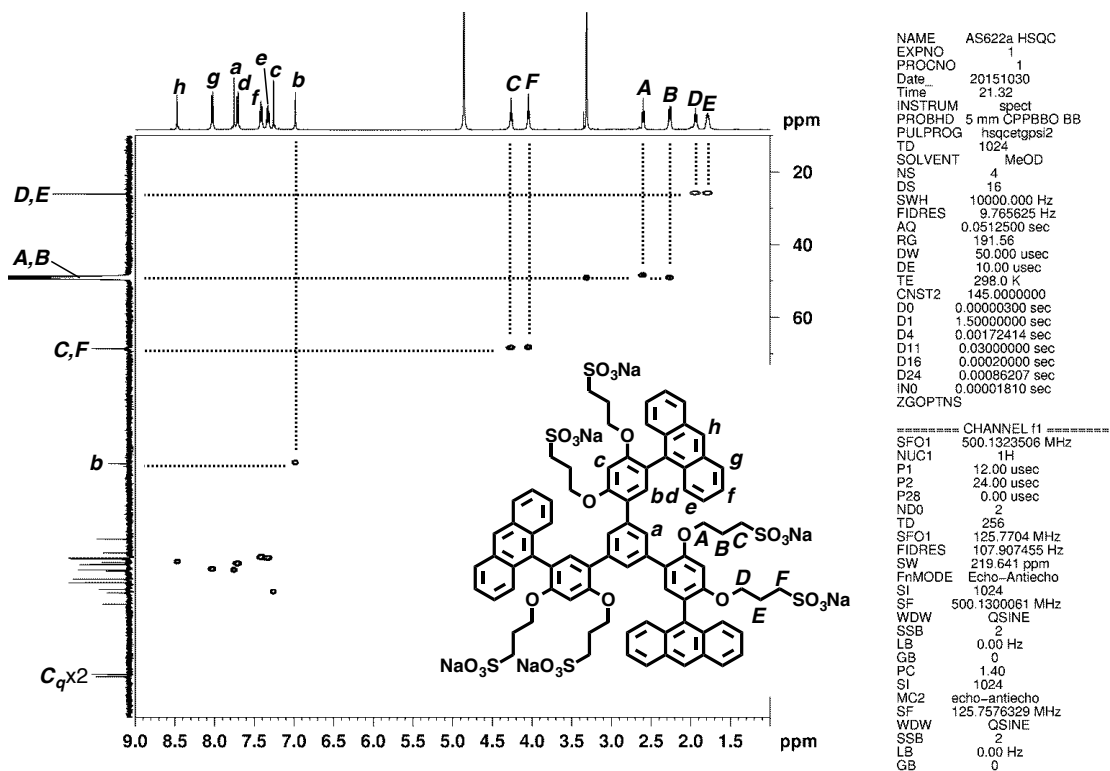


Figure S37a. HSQC spectrum (500 MHz, CD₃OD, r.t.) of **4**.

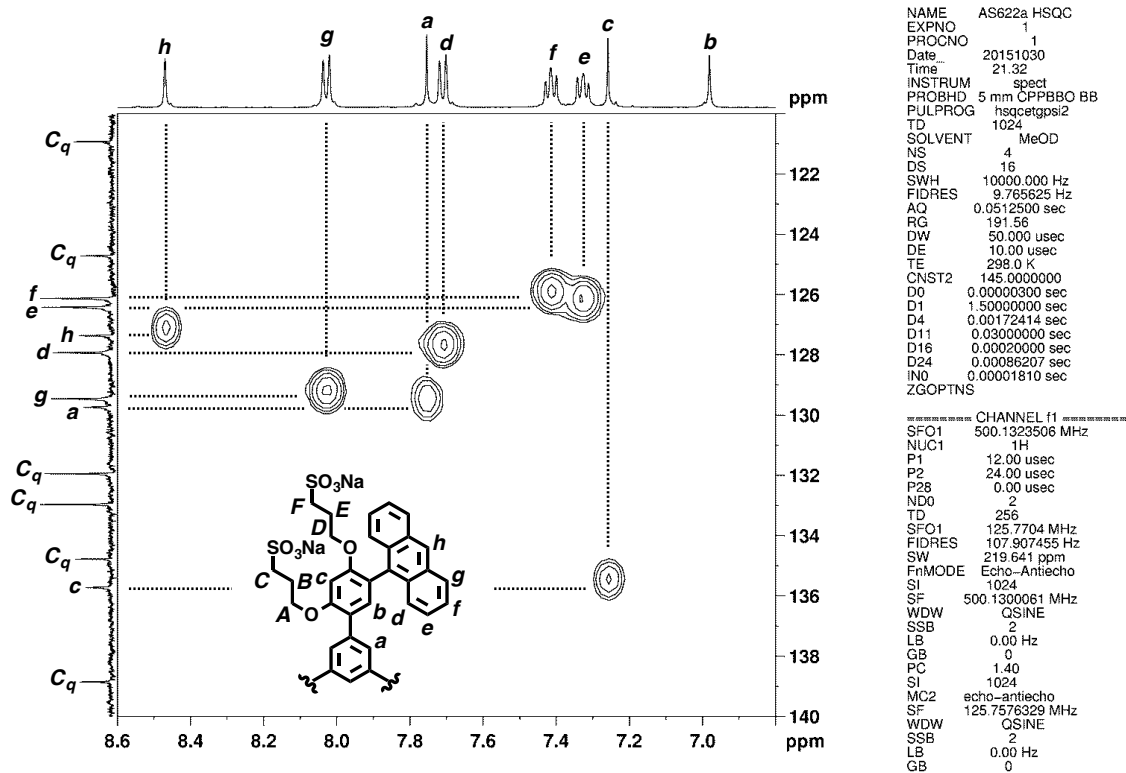


Figure S37b. HSQC spectrum (500 MHz, CD₃OD, r.t.) of 4.

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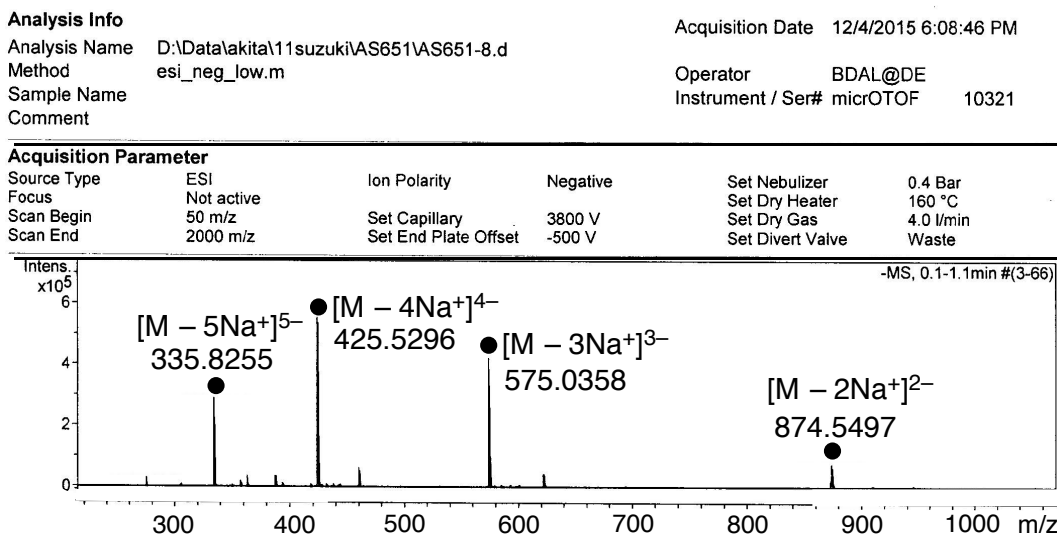
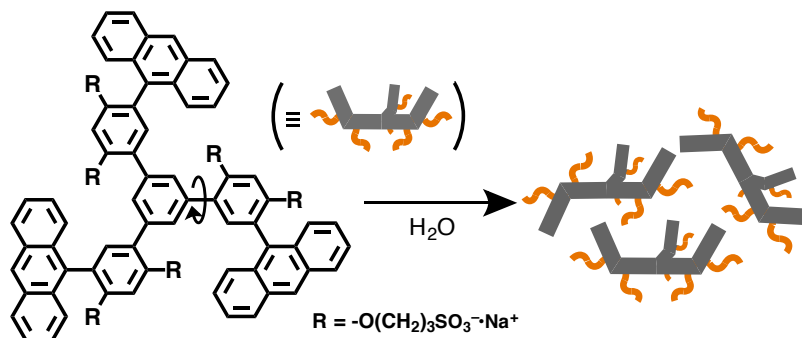


Figure S38. ESI-TOF MS spectrum (CH₃OH) of 4.

Formation of assembly (4)_n

AS529



Tribranched scaffold **4** (1.8 mg, 1.0 μ mol) was dissolved in water (0.5 mL) and then the solution was stirred at r.t. for 1 min. The formation of assembly (**4**)_n was confirmed by NMR, DLS, and spectroscopic analyses.

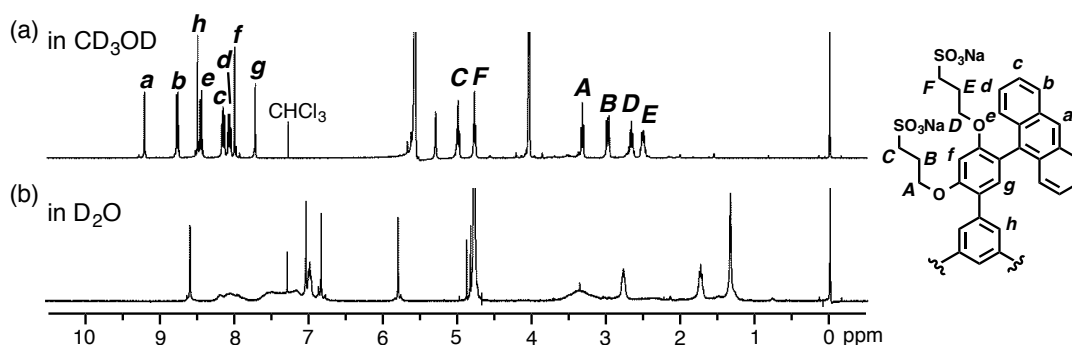


Figure S39. ¹H NMR spectra (400 MHz, r.t., TMS as an external standard) of **4** (2 mM) in (a) CD₃OD and (b) D₂O.

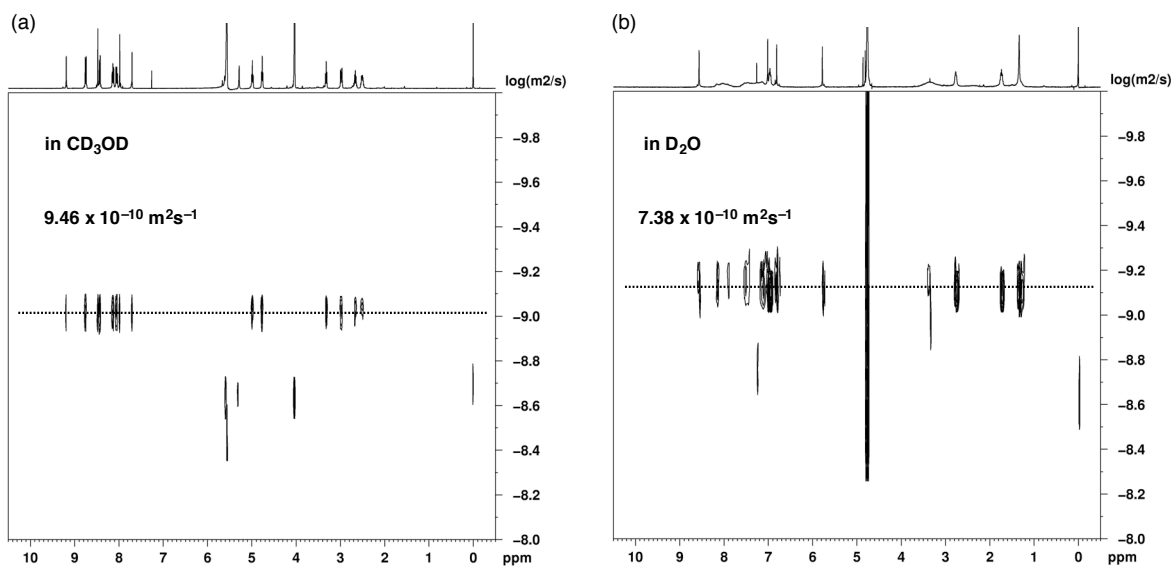


Figure S40. DOSY NMR spectra (500 MHz, r.t., TMS as an external standard) of **4** (2 mM) in (a) CD₃OD and (b) D₂O.

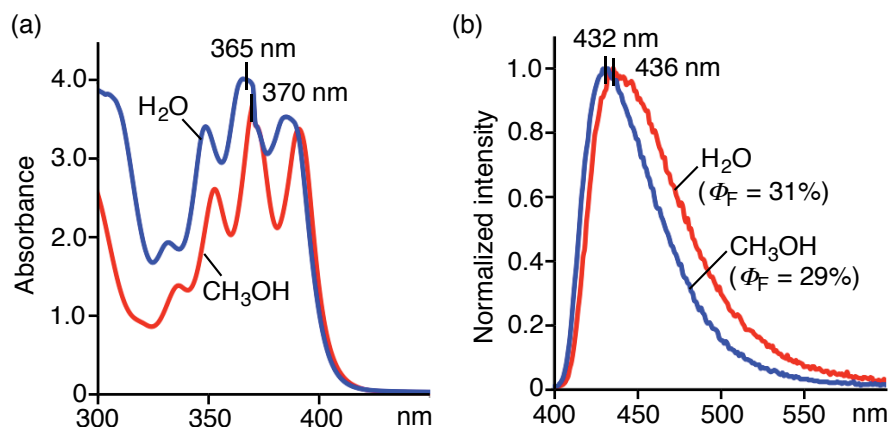


Figure S41. (a) UV-vis spectra and (b) normalized fluorescence spectra ($\lambda_{\text{ex}} = 370$ nm, r.t.) of **4** in CH_3OH and $(\mathbf{4})_n$ in H_2O (2.0 mM based on **4**).

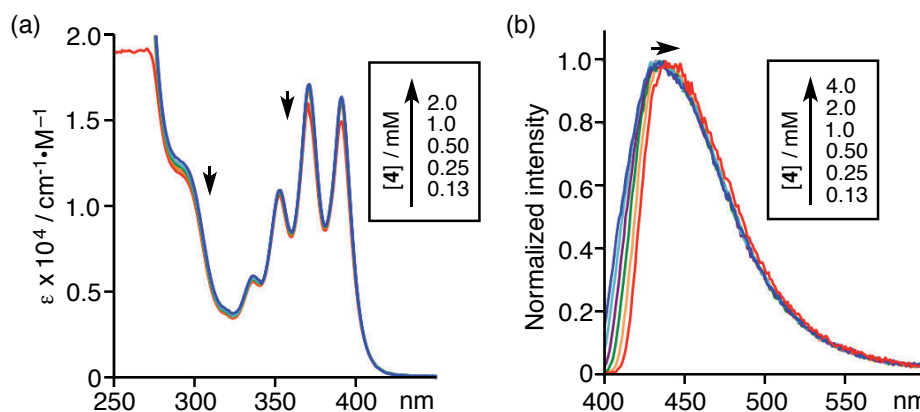


Figure S42. Concentration-dependent (a) UV-vis spectra (0.13-2.0 mM) and (b) fluorescence spectra (normalized, 0.13-4.0 mM, $\lambda_{\text{ex}} = 370$ nm, r.t.) of **4** in H_2O .

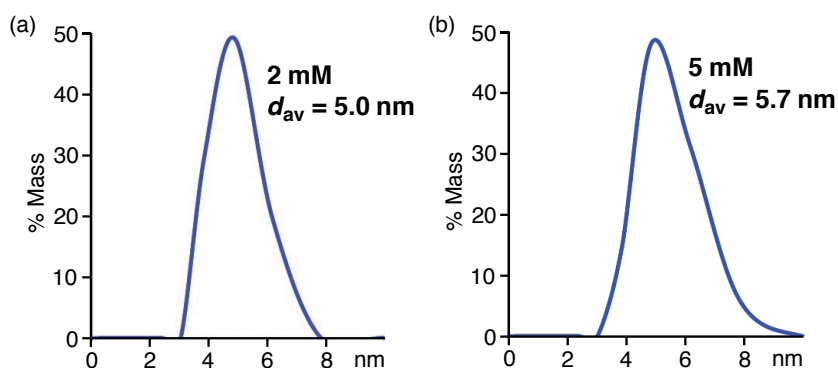
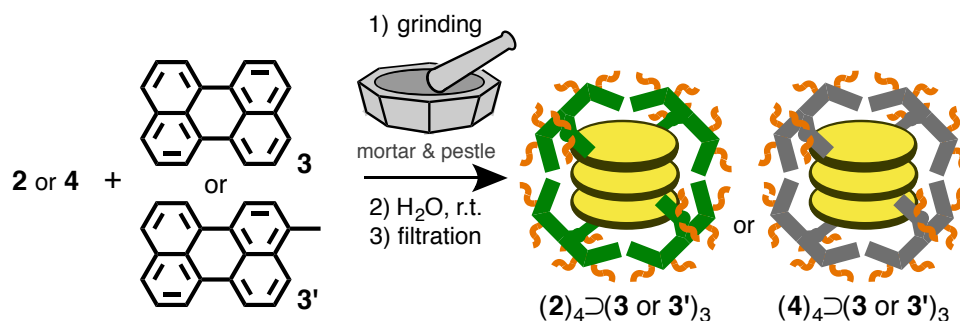


Figure S43. Particle size distribution of $(\mathbf{4})_n$ by DLS analysis (H_2O , r.t., (a) 2.0 and (b) 5.0 mM based on **4**).

General procedure for the synthesis of host-guest complex $(\mathbf{2})_4\supset(\mathbf{3})_3$



A mixture of amphiphilic compound **2** (2.2 mg, 1.2 μmol) and perylene (**3**; 1.5 mg, 6.0 μmol) was ground for 1 min using an agate mortar and pestle. After the addition of H₂O (0.6 mL), the suspension solution was centrifuged (16000 g, ~10 min) and then filtrated by a membrane filter (pore size; 200 nm) to give a clear aqueous solution of host-guest complex $(\mathbf{2})_4\supset(\mathbf{3})_3$. Host-guest complexes $(\mathbf{2})_4\supset(\mathbf{3}')_3$ and $(\mathbf{4})_4\supset(\mathbf{3} \text{ or } \mathbf{3}')_3$ were also prepared by the same procedure.

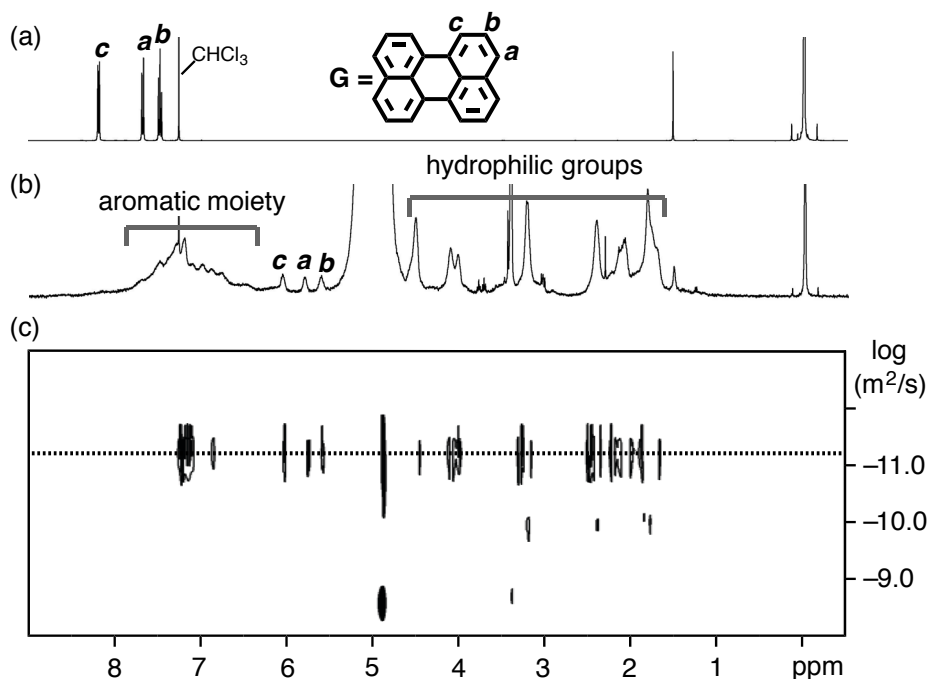


Figure S44a. ¹H NMR spectra (400 MHz, r.t., TMS as an external standard) of (a) **3** in CDCl₃, (b) $(\mathbf{2})_4\supset(\mathbf{3})_3$ in 4:1 D₂O/CD₃OD, and (c) DOSY NMR spectrum (500 MHz, r.t., TMS as an external standard) of $(\mathbf{2})_4\supset(\mathbf{3})_3$ in 4:1 D₂O/CD₃OD.

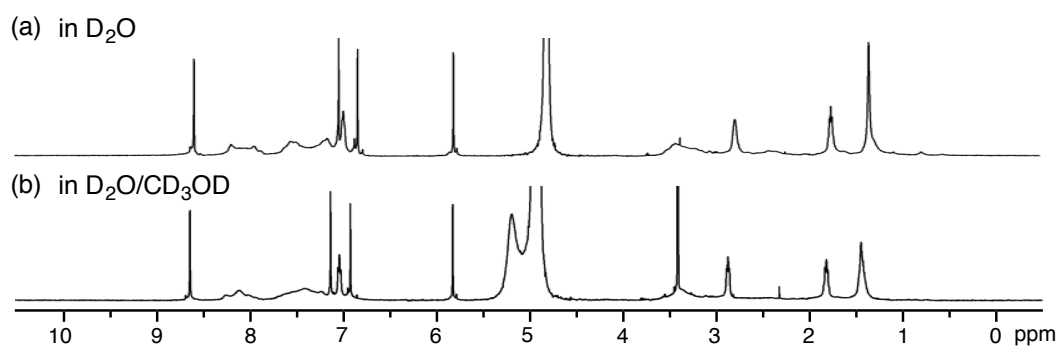


Figure S44b. ^1H NMR spectra (400 MHz, r.t., TMS as an external standard) of $(\mathbf{4})_4\supset(\mathbf{3})_3$ in (a) D_2O and (b) 4:1 $\text{D}_2\text{O}/\text{CD}_3\text{OD}$.

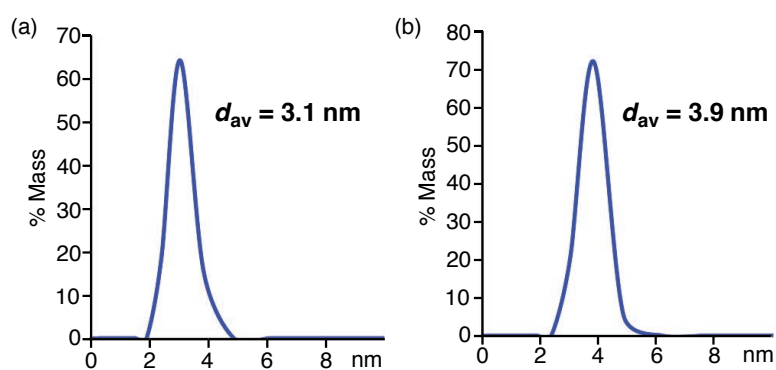


Figure S45. Particle size distribution of host-guest complexes (a) $(\mathbf{2})_4\supset(\mathbf{3})_3$ and (b) $(\mathbf{4})_4\supset(\mathbf{3})_3$ by DLS analysis (H_2O , r.t.).

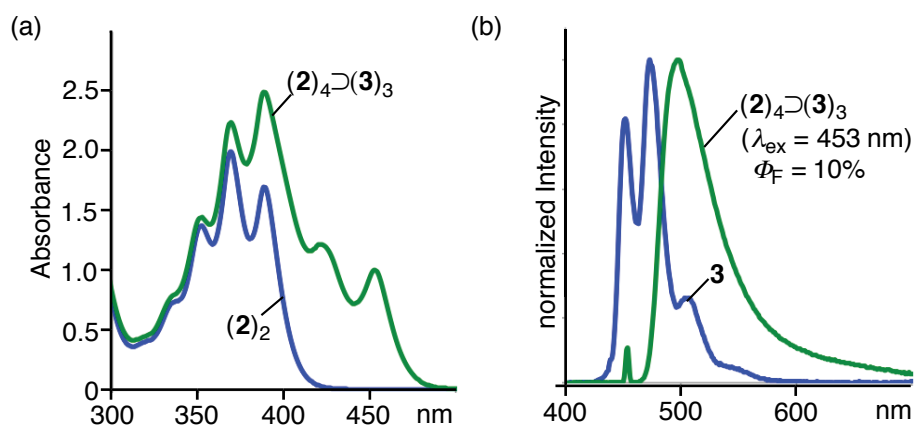


Figure S46. (a) UV-vis (H_2O , r.t., 1.0 mM based on $\mathbf{2}$) and (b) fluorescence spectra (H_2O , r.t., 2.0 mM based on $\mathbf{2}$) of $(\mathbf{2})_4\supset(\mathbf{3})_3$.

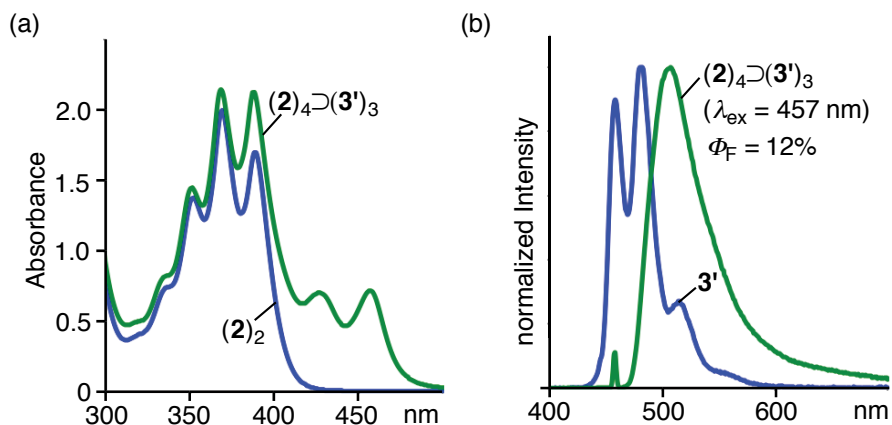


Figure S47. (a) UV-vis (H_2O , r.t., 1.0 mM based on **2**) and (b) fluorescence spectra (H_2O , r.t., 2.0 mM based on **2**) of $(2)_4 \supset (3')_3$.

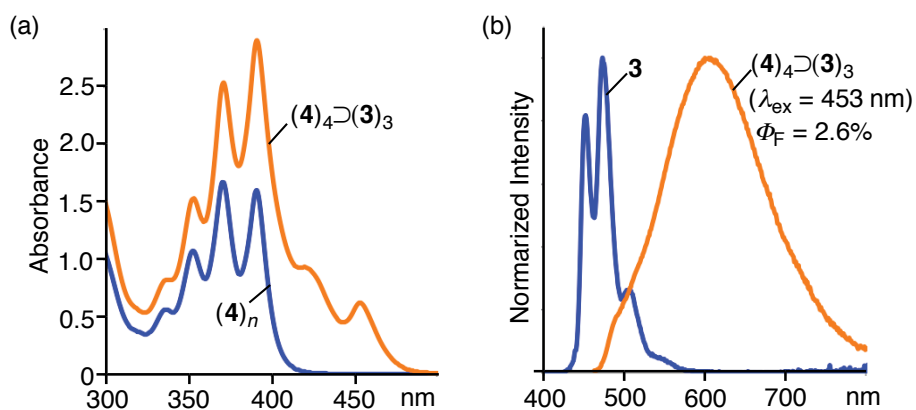


Figure S48. (a) UV-vis (H_2O , r.t., 1.0 mM based on **4**) and (b) fluorescence spectra (H_2O , r.t., 2.0 mM based on **4**) of $(4)_4 \supset (3)_3$.

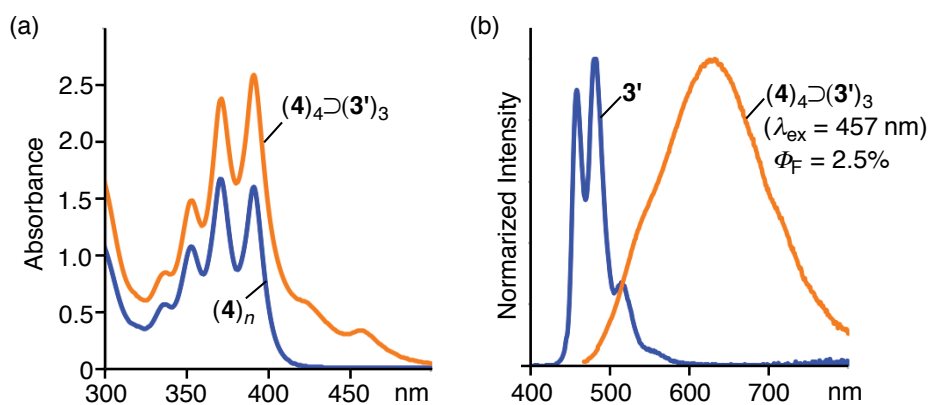


Figure S49. (a) UV-vis (H_2O , r.t., 1.0 mM based on **4**) and (b) fluorescence spectra (H_2O , r.t., 2.0 mM based on **4**) of $(4)_4 \supset (3')_3$.

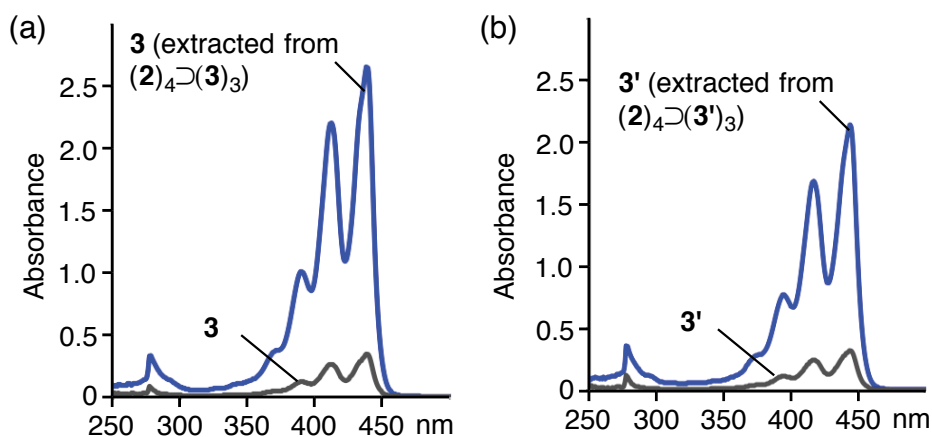


Figure S50. Estimation of host-guest ratios by UV-vis spectra (toluene, r.t., after 2-fold dilution) of the extracted guests from (a) $(2)_4\supset(3)_3$ and (b) $(2)_4\supset(3')_3$.

Table S1. Host-guest ratios of $(2)_n\supset(3 \text{ or } 3')_m$ based on the UV-vis analysis.

guest	abs. (λ / nm)	$\epsilon \times 10^4 / \text{M}^{-1}\text{cm}^{-1}$ (λ / nm) ^a	concentration of guest / mM	2 : guest
3	2.66 (438)	3.40 (438)	1.56	1 : 0.78
3'	2.14 (444)	3.18 (444)	1.35	1 : 0.68

^a Calculated by the absorption spectra of **3** and **3'** in toluene.

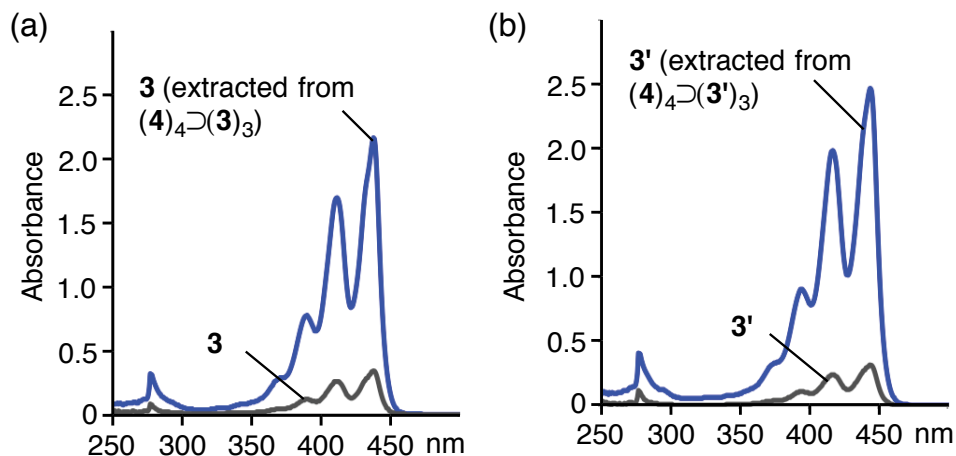


Figure S51. Estimation of host-guest ratios by UV-vis spectra (toluene, r.t., after 2-fold dilution) of the extracted guests from (a) $(4)_4\supset(3)_3$ and (b) $(4)_4\supset(3')_3$.

Table S2. Host-guest ratios of $(\mathbf{4})_n \supset (\mathbf{3} \text{ or } \mathbf{3}')_m$ based on the UV-vis analysis.

guest	abs. (λ / nm)	$\epsilon \times 10^4 / \text{M}^{-1}\text{cm}^{-1}$ (λ / nm) ^a	concentration of guest / mM ^b	4 : guest
3	2.16 (438)	3.40 (438)	1.27	1 : 0.64
3'	2.47 (444)	3.18 (444)	1.55	1 : 0.78

^a Calculated by the absorption spectra of **3** and **3'** in toluene.

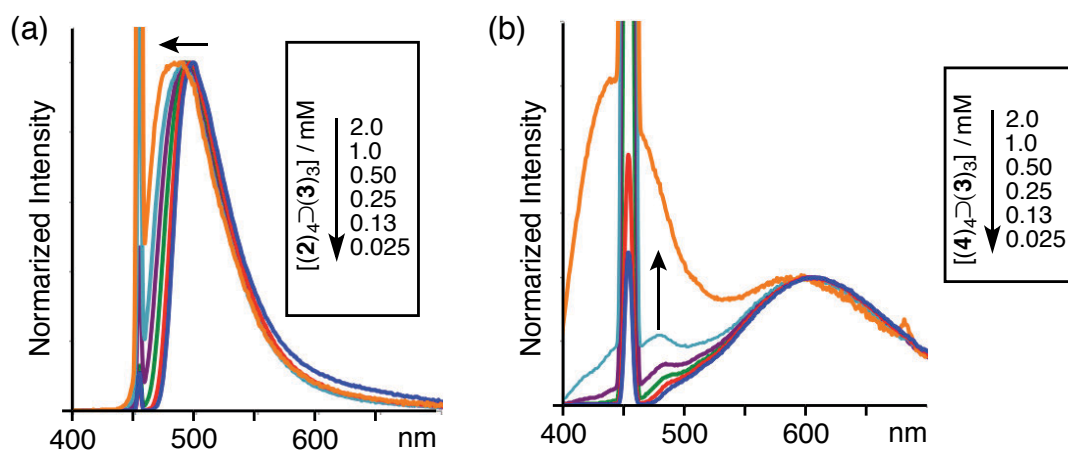


Figure S52. Concentration-dependent fluorescence spectra (0.025–2.0 mM, H₂O, λ_{ex} = 453 nm, r.t.) of (a) $(\mathbf{2})_4 \supset (\mathbf{3})_3$, and (b) $(\mathbf{4})_4 \supset (\mathbf{3})_3$.

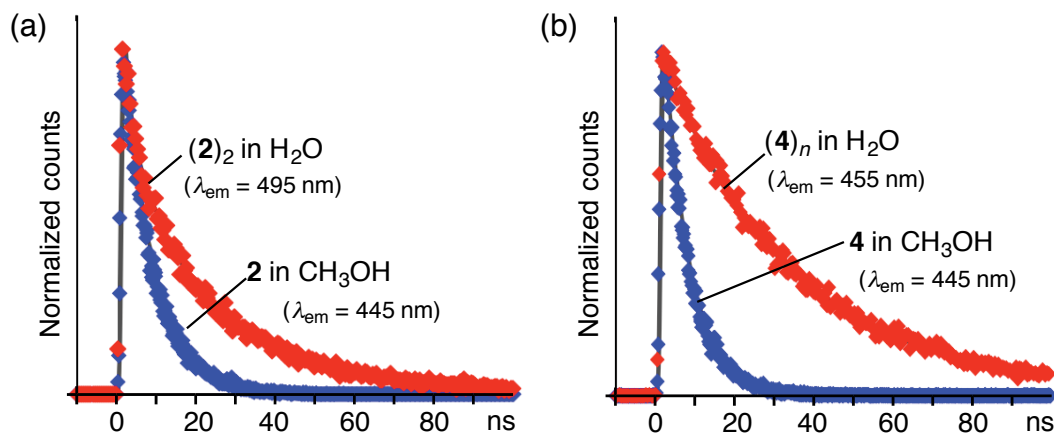
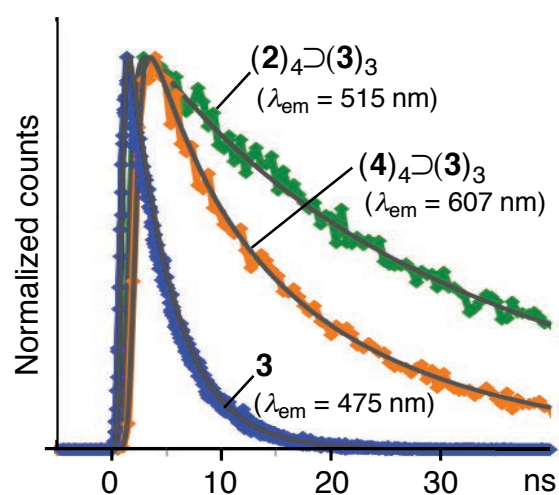


Figure S53. Fluorescence decays (λ_{ex} = 365 nm, 2.0 mM, r.t.) of (a) **2** in CH₃OH (λ_{em} = 445 nm), $(\mathbf{2})_2$ in H₂O (λ_{em} = 495 nm), (b) **4** in CH₃OH (λ_{em} = 445 nm), and $(\mathbf{4})_n$ in H₂O (λ_{em} = 455 nm).

Table S3. Summary of fluorescence lifetimes of **2**, **(2)₂**, **4**, and **(4)_n**.

	τ_1 / ns (a_1 / %)	τ_2 / ns (a_2 / %)	τ_3 / ns (a_3 / %)	χ^2
2	2.1 (3.5)	7.7 (96.5)	—	1.1
(2)₂	0.75 (3.0)	11 (26.5)	29 (70.5)	1.0
4	0.12 (0.6)	6.5 (99.3)	—	1.1
(4)_n	0.61 (0.6)	12 (3.7)	36 (95.7)	1.1

**Figure S54.** Fluorescence decays (2.0 mM based on the monomer, H₂O, λ_{ex} = 470 nm, r.t.) of **(2)₄⊃(3)₃**, **(4)₄⊃(3)₃**, and **3** (0.10 mM, toluene, λ_{ex} = 405 nm).**Table S4.** Summary of fluorescence lifetimes of **(2)₄⊃(3)₃**, **(4)₄⊃(3)₃**, and **3**.

complex (λ_{ex} / nm)	τ_1 / ns (a_1 / %)	τ_2 / ns (a_2 / %)	τ_3 / ns (a_3 / %)	χ^2
(2)₄⊃(3)₃ (470)	0.56 (0.4)	11 (5.0)	36 (94.6)	1.1
(4)₄⊃(3)₃ (470)	5.5 (15.4)	19 (84.6)	—	1.0
3 (405)	3.9 (100)	—	—	1.1

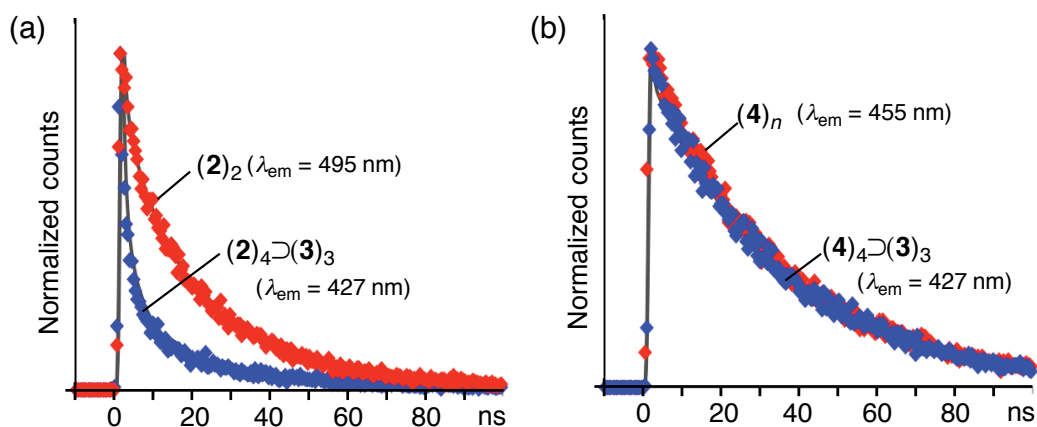


Figure S55. Fluorescence decays (2.0 mM based on the monomer, H₂O, $\lambda_{\text{ex}} = 365$ nm, r.t.) of (a) $(\mathbf{2})_2$ and $(\mathbf{2})_4\text{D}(\mathbf{3})_3$, (b) $(\mathbf{4})_n$ and $(\mathbf{4})_4\text{D}(\mathbf{3})_3$

Table S5. Summary of fluorescence lifetimes of $(\mathbf{2})_2$, $(\mathbf{2})_4\text{D}(\mathbf{3})_3$, $(\mathbf{4})_n$ and $(\mathbf{4})_4\text{D}(\mathbf{3})_3$.

	τ_1 / ns (a_1 / %)	τ_2 / ns (a_2 / %)	τ_3 / ns (a_3 / %)	χ^2
$(\mathbf{2})_2$	0.75 (3.0)	11 (26.5)	29 (70.5)	1.0
$(\mathbf{2})_4\text{D}(\mathbf{3})_3$	0.59 (11.8)	4.5 (25.0)	27 (63.2)	1.1
$(\mathbf{4})_n$	0.61 (0.6)	12 (3.7)	36 (95.7)	1.1
$(\mathbf{4})_4\text{D}(\mathbf{3})_3$	0.46 (1.3)	34 (98.7)	—	0.99

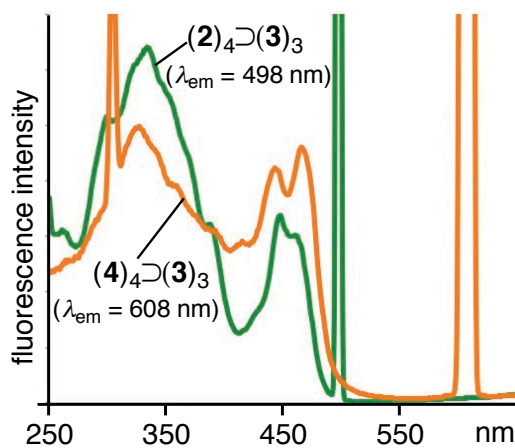


Figure S56. Excitation spectra (2.0 mM based on the monomer, H₂O, r.t.) of $(\mathbf{2})_4\text{D}(\mathbf{3})_3$ and $(\mathbf{4})_4\text{D}(\mathbf{3})_3$.

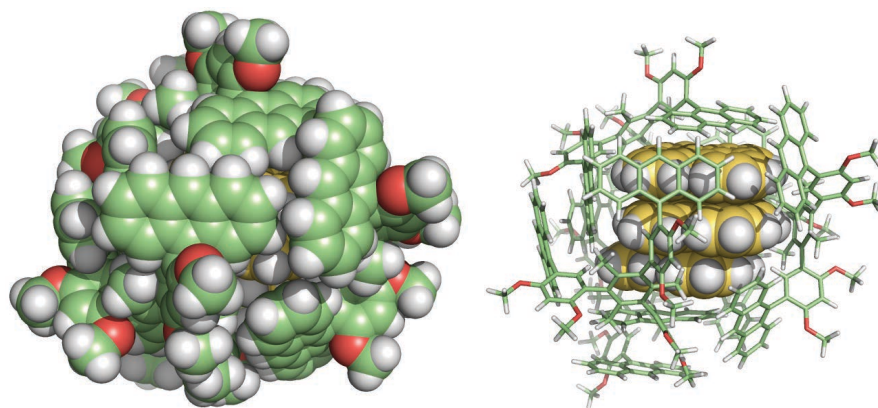


Figure S57. Molecular modeling of $(\mathbf{2})_4\supset(\mathbf{3})_3$ ($R = -OCH_3$).