

Supplementary Information

A Fluorescent Molecular Capsule with a Flexible Polyaromatic Shell for Detecting Monoterpene Compounds in Water

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Contents

- Materials and methods
- Synthetic route of *cis,cis-1a*
- Synthesis of 9-(2,4-dimethoxyphenyl)anthracene (**5_H**; ¹H & ¹³C-NMR spectra)
- Synthesis of 9-(5-bromo-2,4-dimethoxyphenyl)anthracene (**5_{Br}**; ¹H & ¹³C-NMR spectra)
- Synthesis of **5_{pin}** (¹H & ¹³C-NMR spectra)
- Synthesis of **1b** (MALDI-TOF MS spectrum)
- Synthesis of **1c** (¹H, ¹³C-NMR, HH-COSY & HSQC spectra)
- Synthesis of *trans,trans-1c* (¹H, ¹³C-NMR, HH-COSY & HSQC spectra)
- Synthesis of *cis,cis-1c* (¹H, ¹³C-NMR, HH-COSY & HSQC spectra)
- Synthesis of *cis,cis-1a* (¹H, ¹³C-NMR, HH-COSY, HSQC & ESI-TOF MS spectra)
- Formation of capsule **2** (¹H NMR, ESI-TOF MS, UV-vis & Fluorescence spectra; AFM & DLS analyses)
- Preparation of **2•(3a)₂** (¹H, DOSY, and NOESY NMR spectra & Fluorescence data)
- Preparation of **2•(3b-c)₂** (¹H NMR spectra & Fluorescence data)
- Preparation of **2•(4e)_n** (¹H and DOSY NMR spectra)
- Detection of natural fragrance compounds **4a-l** by capsule **2** (Fluorescence data)

Materials and methods

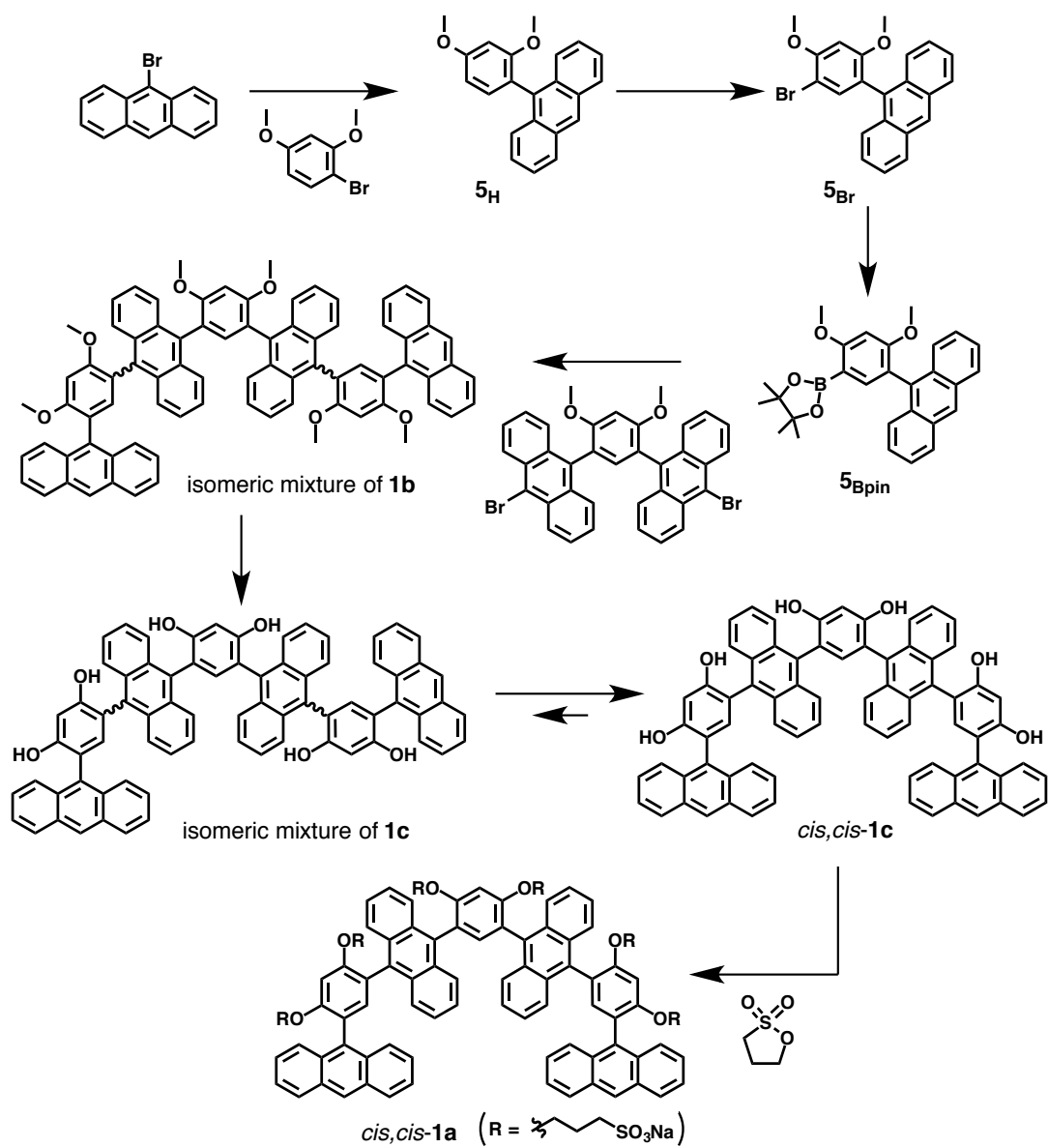
NMR: Bruker AVANCE-400 (400 MHz) & AVANCE-500 (500 MHz), MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, AFM: Asylum Research Cypher S, Size Analysis (DLS): Wyatt Technology DynaPro NanoStar, FT IR: JASCO FT/IR-4200, UV-vis: JASCO V-670DS, Fluorescence: HITACHI F-7000, Absolute PL quantum yield: Hamamatsu Quantaurus-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.

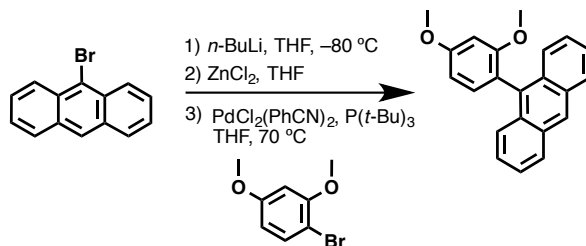
References

- [1] N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441.
- [2] A. Suzuki, K. Kondo, M. Akita, M. Yoshizawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 8120–8123.

Scheme S1. Synthetic route of *cis,cis*-1a.



Synthesis of 9-(2,4-dimethoxyphenyl)anthracene (**5_H**) AS264



9-Bromoanthracene (14.221 g, 55.307 mmol) and dry THF (200 mL) were added to a 2-necked 500 mL glass flask filled with N₂. A hexane solution (2.6 M) of *n*-butyllithium (21.0 mL, 54.6 mmol) was then added dropwise to this flask at -80 °C under N₂. After the mixture was stirred at -80 °C for 2 h, a dry THF solution (100 mL) of ZnCl₂ (10.630 g, 78.001 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 17 h to obtain 9-anthrylzinc chloride. 1-Bromo-2,4-dimethoxybenzene (8.129 g, 37.45 mmol), PdCl₂(PhCN)₂ (0.141 g, 0.370 mmol), and dry THF (50 mL) were added to a 100 mL glass flask and the flask was filled with N₂. A hexane solution (1.1 M) of tri-*tert*-butylphosphine (0.72 mL, 0.79 mmol) was added to this flask. After stirring at r.t. for 2 h, the mixture was added to the 500 mL flask. The resulted solution was further stirred at 70 °C for 3 d. H₂O was added to the solution and then the precipitate was collected and washed with CHCl₃ and hexane to afford 9-(2,4-dimethoxyphenyl)anthracene (**5_H**; 10.338 g, 32.884 mmol, 87%) as a white solid.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 3.59 (s, 3H), 3.95 (s, 3H), 6.69-6.72 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.31-7.35 (m, 2H), 7.41-7.45 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.46 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, r.t.): δ 55.5 (CH₃), 55.7 (CH₃), 99.1 (CH), 104.7 (CH), 119.9 (C_q), 125.0 (CH), 125.1 (CH), 126.4 (CH), 126.9 (CH), 128.4 (CH), 130.8 (C_q), 131.6 (C_q), 133.2 (CH), 133.7 (C_q), 159.1 (C_q), 160.9 (C_q). FT-IR (KBr, cm⁻¹): 3050, 3014, 2933, 2836, 2360, 1610, 1508, 1306, 1209, 1157, 1121, 1043, 901, 829, 736. MALDI-TOF MS (dithranol): *m/z* Calcd. for C₂₂H₁₈O₂: 314.38, Found 314.08 [M]⁺. E.A.: Calcd. for C₂₂H₁₈O₂•0.45CHCl₃: C, 73.25; H, 5.05. Found: C, 73.20; H, 5.13.

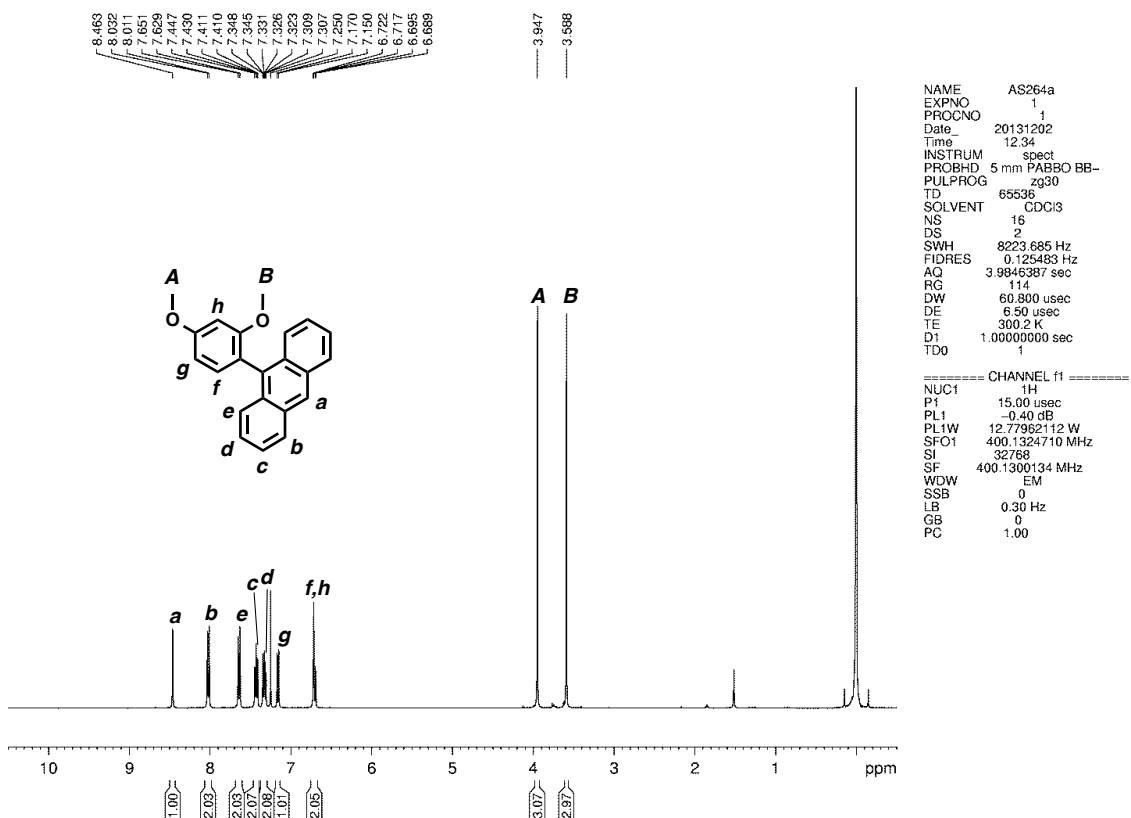


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, r.t.) of **5_H**.

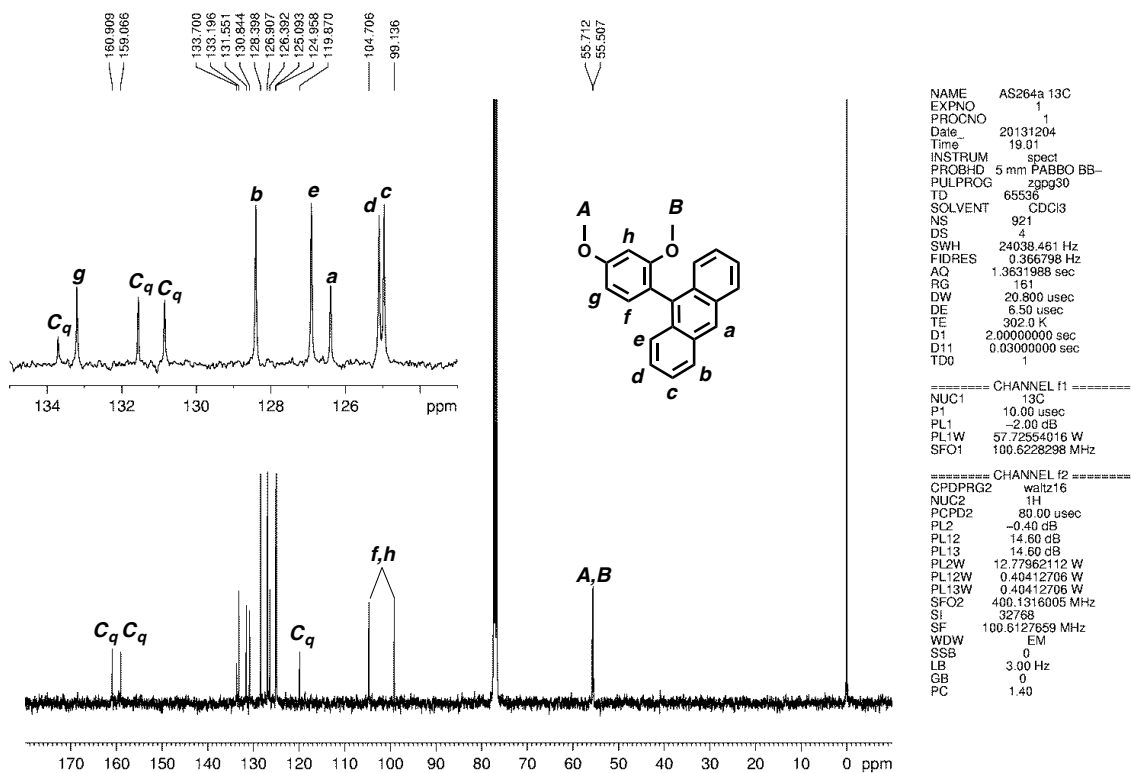
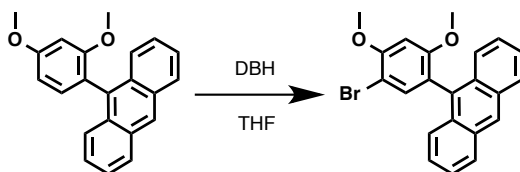


Figure S2. ¹³C NMR spectrum (100 MHz, CDCl₃, r.t.) of **5_H**.

Synthesis of 9-(5-bromo-2,4-dimethoxyphenyl)anthracene (**5_{Br}**) AS266



9-(2,4-Dimethoxyphenyl)anthracene (**5_H**; 8.005 g, 25.46 mmol) and THF (100 mL) were added to a 200 mL glass flask. A THF solution (50 mL) of 1,3-dibromo-5,5-dimethylhydantoin (DBH; 3.626 g, 12.68 mmol) was added to the solution at 0 °C and the resultant mixture was stirred at r.t. for 1 d. H₂O was added into the mixture. The precipitate was collected and washed with H₂O and CH₃OH to afford 9-(5-bromo-2,4-dimethoxyphenyl)anthracene (**5_{Br}**; 6.130 g, 15.59 mmol, 61%) as a white solid.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 3.61 (s, 3H), 4.06 (s, 3H), 6.73 (s, 1H), 7.34-7.38 (m, 2H), 7.43-7.46 (m, 3H), 7.61 (d, 2H, *J* = 8.8 Hz), 8.03 (d, 2H, *J* = 8.8 Hz), 8.48 (s, 1H).

¹³C NMR (100 MHz, CDCl₃, r.t.): δ 56.2 (CH₃), 56.5 (CH₃), 97.3 (CH), 102.3 (C_q), 121.1 (C_q), 125.1 (CH), 125.5 (CH), 126.5 (CH), 126.9 (CH), 128.5 (CH), 130.7 (C_q), 131.5 (C_q), 132.0 (C_q), 136.3 (CH), 156.7 (C_q), 158.5 (C_q). FT-IR (KBr, cm⁻¹): 3055, 2999, 2962, 2940, 2842, 2359, 1598, 1504, 1350, 1292, 1208, 1033, 889, 738, 526. MALDI-TOF MS (dithranol): *m/z* Calcd. for C₂₂H₁₇O₂Br: 392.04, Found 391.82 [M]⁺. HR MS (ESI): Calcd. For C₂₂H₁₇BrO₂ 392.0406, Found 392.0405 [M]⁺.

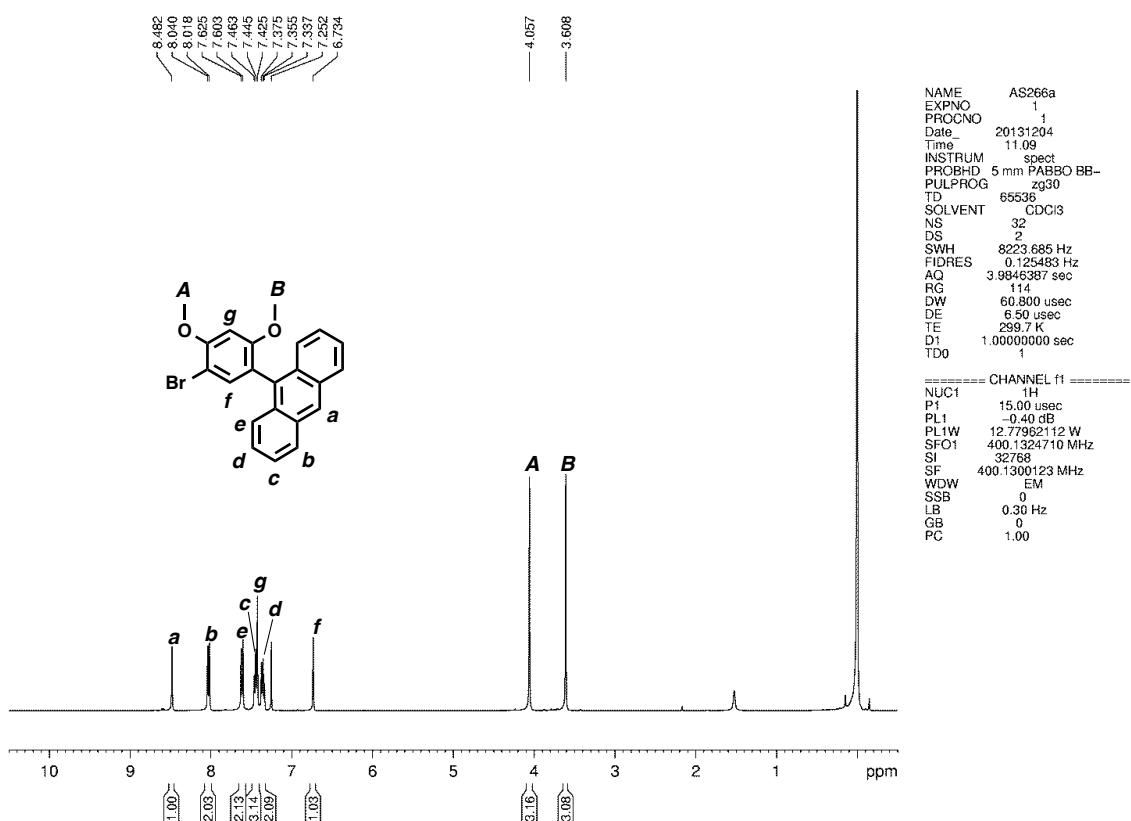


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , r.t.) of **5_{Br}**.

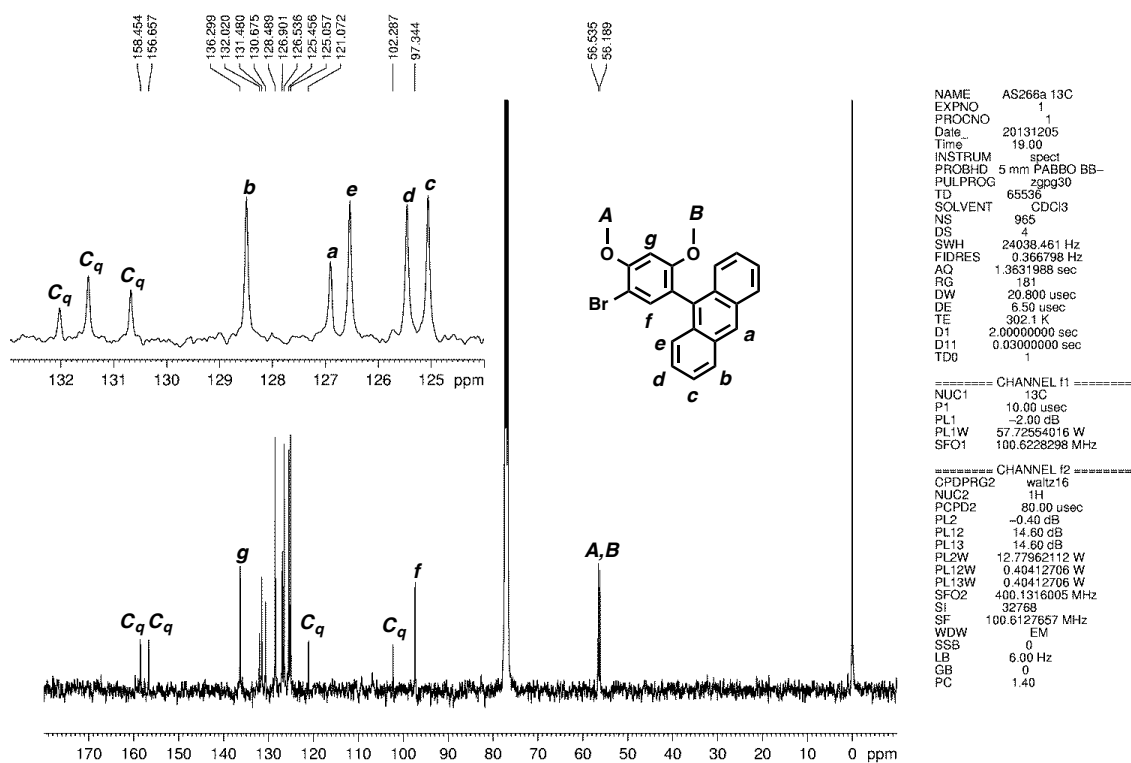
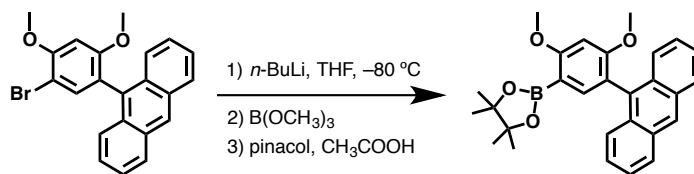


Figure S4. ^{13}C NMR spectrum (100 MHz, CDCl_3 , r.t.) of **5_{Br}**.

Synthesis of **5_{Bpin}**

AS247



9-(5-Bromo-2,4-dimethoxyphenyl)anthracene (**5_{Br}**; 6.004 g, 15.27 mmol) and dry THF (400 mL) were added to a 500 mL glass flask. A hexane solution (2.6 M) of *n*-butyllithium (5.9 mL, 15 mmol) was added dropwise to this flask at -78 °C under N₂. The reaction mixture was stirred at -78 °C for 2 h and then trimethoxyborane (2.4 mL, 21 mmol) was slowly added to the mixture at same temperature. When the reaction mixture was warmed to r.t. for 1 d, pinacol (3.623 g, 30.66 mmol) and acetic acid (7.0 mL, 0.12 mol) were added to the reaction mixture and then the resultant mixture was stirred for 13 h at r.t. After the evaporation of the solvents, the crude product was washed with water, methanol, and hexane to afford **5_{Bpin}** (4.961 g, 11.27 mmol, 74%) as a white solid.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 1.30 (s, 12H), 3.63 (s, 3H), 4.00 (s, 3H), 6.66 (s, 1H), 7.30-7.34 (m, 2H), 7.41-7.44 (m, 2H), 7.55 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.45 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, r.t.): δ 24.8 (CH₃), 55.7 (CH₃), 56.3 (CH₃), 83.2 (C_q), 95.4 (CH), 119.1 (C_q), 124.9 (CH), 125.0 (CH), 126.3 (CH), 127.1 (CH), 128.3 (CH), 130.9 (C_q), 131.5 (C_q), 133.8 (C_q), 141.0 (CH), 161.7 (C_q), 166.3 (C_q). FT-IR (KBr, cm⁻¹): 2978, 2359, 1602, 1574, 1397, 1352, 1335, 1306, 1255, 1207, 1146, 1132, 1032, 862, 740. MALDI-TOF MS (dithranol): *m/z* Calcd. for C₂₈H₂₉O₄B: 440.22, Found 439.98 [M]⁺. HR MS (ESI): Calcd. For C₂₈H₂₉BO₄Na 463.2056, Found 463.2058 [M+Na]⁺.

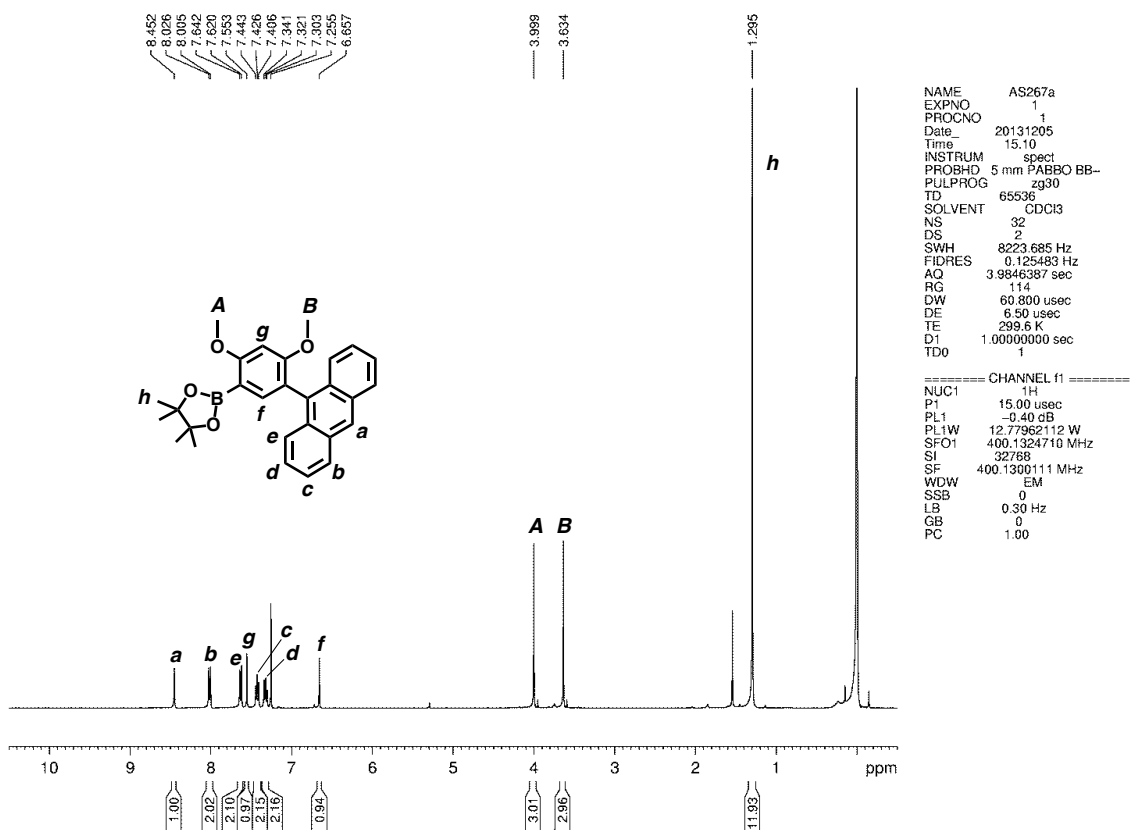


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3 , r.t.) of 5_{Bpin} .

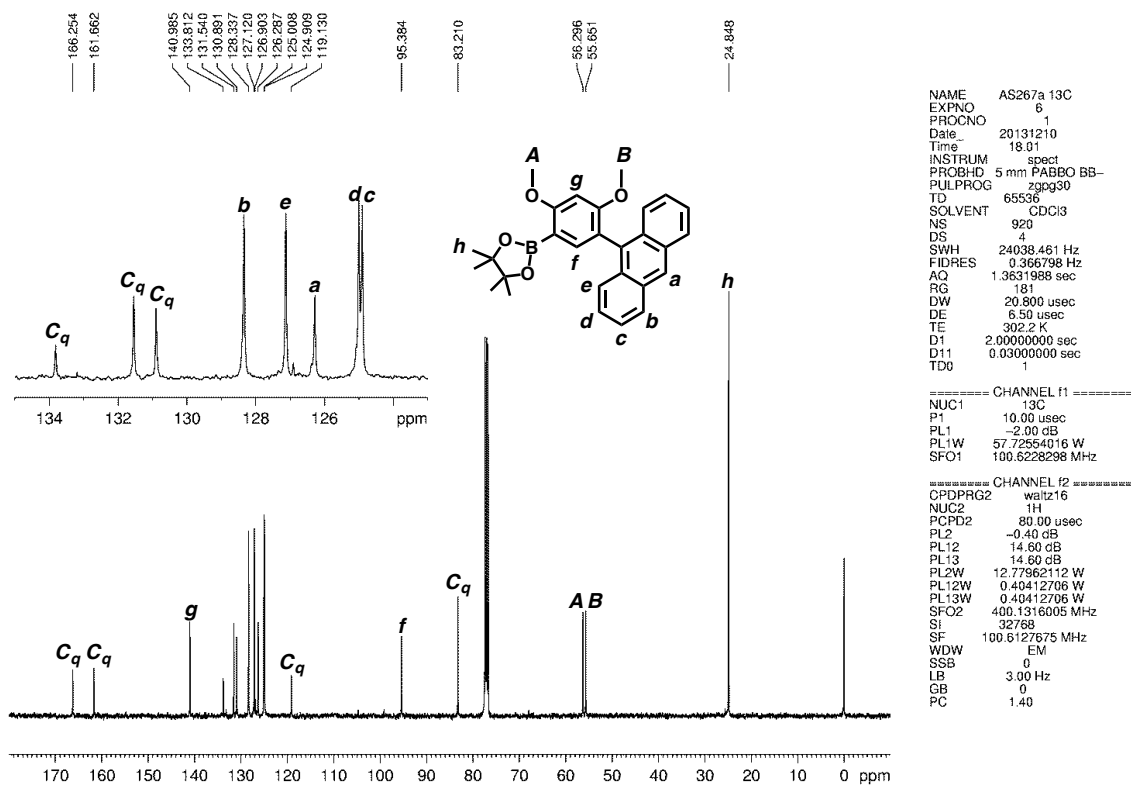
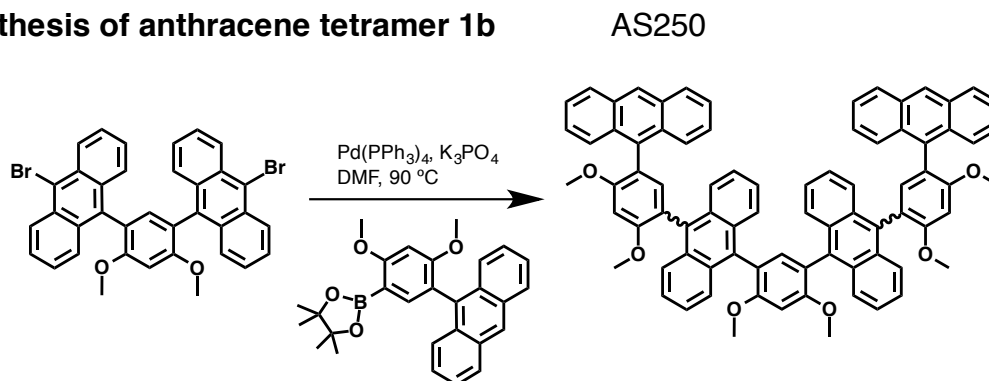


Figure S6. ^{13}C NMR spectrum (100 MHz, CDCl_3 , r.t.) of 5_{Bpin} .

Synthesis of anthracene tetramer **1b**



1,5-Di(10-bromoanthracen-9-yl)-2,4-dimethoxybenzene (0.735 g, 1.13 mmol), **5**_{Bpin} (2.001 g, 4.543 mmol), K_3PO_4 (2.414 g, 11.37 mmol), and dry DMF (80 mL) were added to a 2-necked 200 mL glass flask filled with N_2 . The DMF solution (40 mL) of $\text{Pd(PPh}_3)_4$ (0.276 g, 0.239 mmol) was added to the 200 mL flask and then the reaction mixture was stirred at 90 °C for 2 d. After water was added to the reaction mixture, the precipitate was collected by filtration. The residue was washed with CH_3OH , THF, and hexane to afford anthracene tetramer **1b** (0.701 g, 0.628 mmol, 55%) as a white solid. Product **1b** was characterized only by MALDI-TOF MS analysis due to the low solubility in various organic solvents.

MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{80}\text{H}_{58}\text{O}_6$: 1114.42, Found 1114.98 $[\text{M}]^+$.
FT-IR (KBr, cm^{-1}): 3058, 2937, 2838, 2360, 1604, 1504, 1463, 1350, 1267, 1205, 1160, 1097, 1033, 770, 736.

Data: AS268-3-dith-1-10-0001.A11[c] 12 Dec 2013 10:51 Cal: akita-yoshizawa-ref 12 Dec 2013 10:51
Shimadzu Biotech Axima CFRplus 2.9.3.20110624: Mode Reflectron, Power: 60, P.Ext. @ 1114 (bin 83)
%Int. 616 mV[sum= 64714 mV] Profiles 1-105 Smooth Av 3

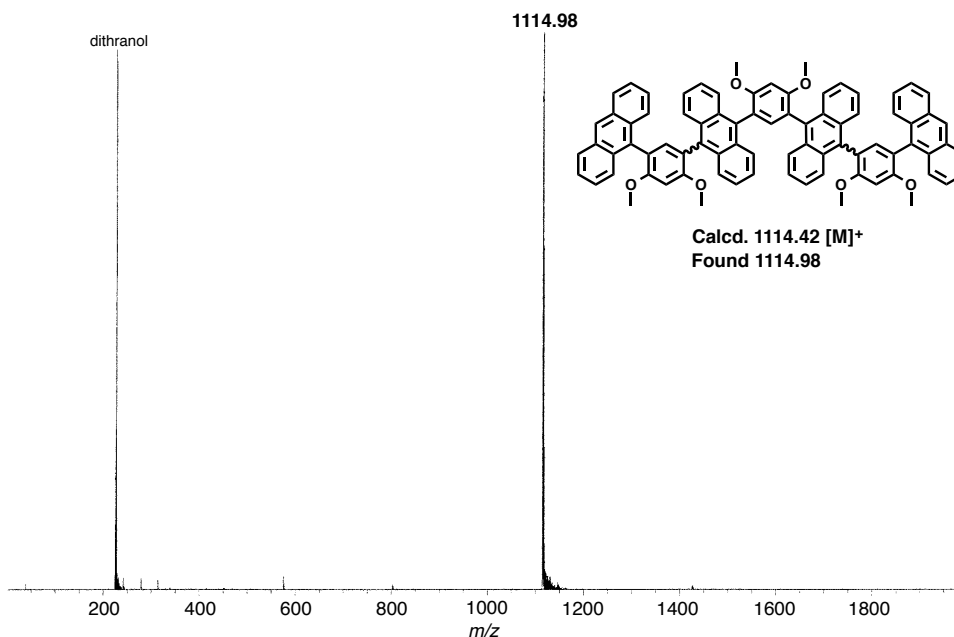
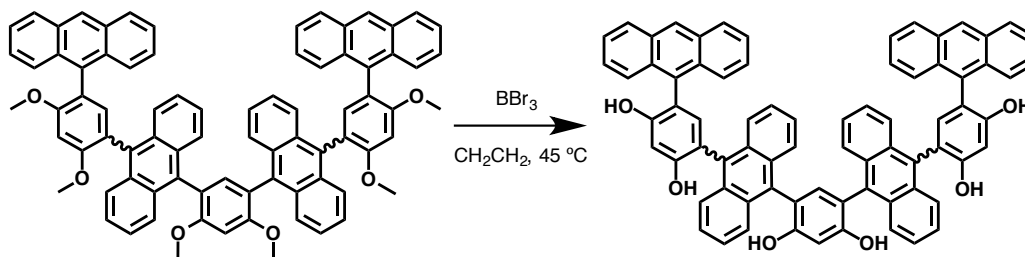


Figure S7. MALDI-TOF MS spectrum (dithranol) of **1b**.

Synthesis of anthracene tetramer **1c** (isomeric mixture)

AS339



Anthracene tetramer **1b** (1.007 g, 0.9031 mmol) and dry CH_2Cl_2 (200 mL) were added to a 300 mL glass flask. A CH_2Cl_2 solution (1.0 M) of BBr_3 (28.0 mL, 28.0 mmol) was added dropwise to this flask under N_2 . The reaction mixture was stirred at 45 °C for 2 d. The reaction was quenched with H_2O (ca. 50 mL). The product was extracted with CH_2Cl_2 and the resultant organic layer was dried over MgSO_4 , filtered, and concentrated. The crude product was washed with acetone and hexane to afford an isomeric mixture of anthracene tetramer **1c** (0.821 g, 0.796 mmol, 88%) as a pale yellow solid. ^1H NMR spectrum of the products revealed that the presence of *cis,cis-1c*, *cis,trans-1c*, and *trans,trans-1c* is a 1:2:2 ratio.

^1H NMR (500 MHz, CDCl_3 , r.t.): δ 4.67-5.01 (m, 6H), 6.97, 7.02 and 7.18 (s, 2H), 7.00,

7.04 and 7.05 (s, 1H), 7.12, 7.24, 7.27 and 7.33 (s, 2H), 7.13, 7.23 and 7.27 (s, 1H), 7.44-7.57 (m, 16H), 7.93-8.10 (m, 16H), 8.48, 8.53, 8.55 and 8.57 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3 , r.t.): δ 103.0(C_q), 103.1(C_q), 103.2 ($\text{C}_q \times 2$), 116.8 (C_q), 116.9 ($\text{C}_q \times 2$), 117.0 ($\text{C}_q \times 2$), 125.3 (CH), 125.5 (CH $\times 2$), 126.0 (CH $\times 2$), 126.5 (CH $\times 3$), 126.6 (CH $\times 2$), 126.7 (CH), 128.1 (CH), 128.2 (CH), 128.7 (CH), 128.8 (CH), 129.0 ($\text{C}_q \times 2$), 129.1 (C_q), 130.8 (C_q), 131.0 ($\text{C}_q \times 2$), 131.1 (C_q), 131.2 (C_q), 131.3 ($\text{C}_q \times 3$), 131.6 ($\text{C}_q \times 3$), 131.7 (C_q), 135.4 (C_q), 135.5 (C_q), 155.2 ($\text{C}_q \times 3$), 155.3 ($\text{C}_q \times 3$), 155.4 (C_q). FT-IR (KBr, cm^{-1}): 3060, 2360, 1622, 1502, 1441, 1356, 1267, 1222, 1166, 1083, 885, 848, 772, 738, 609. MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{74}\text{H}_{46}\text{O}_6$: 1030.33, Found 1030.21 $[\text{M}]^+$. HR MS (ESI): Calcd. for $\text{C}_{74}\text{H}_{46}\text{O}_6\text{K}$ 1069.2926, Found 1069.2926 $[\text{M}+\text{K}]^+$.

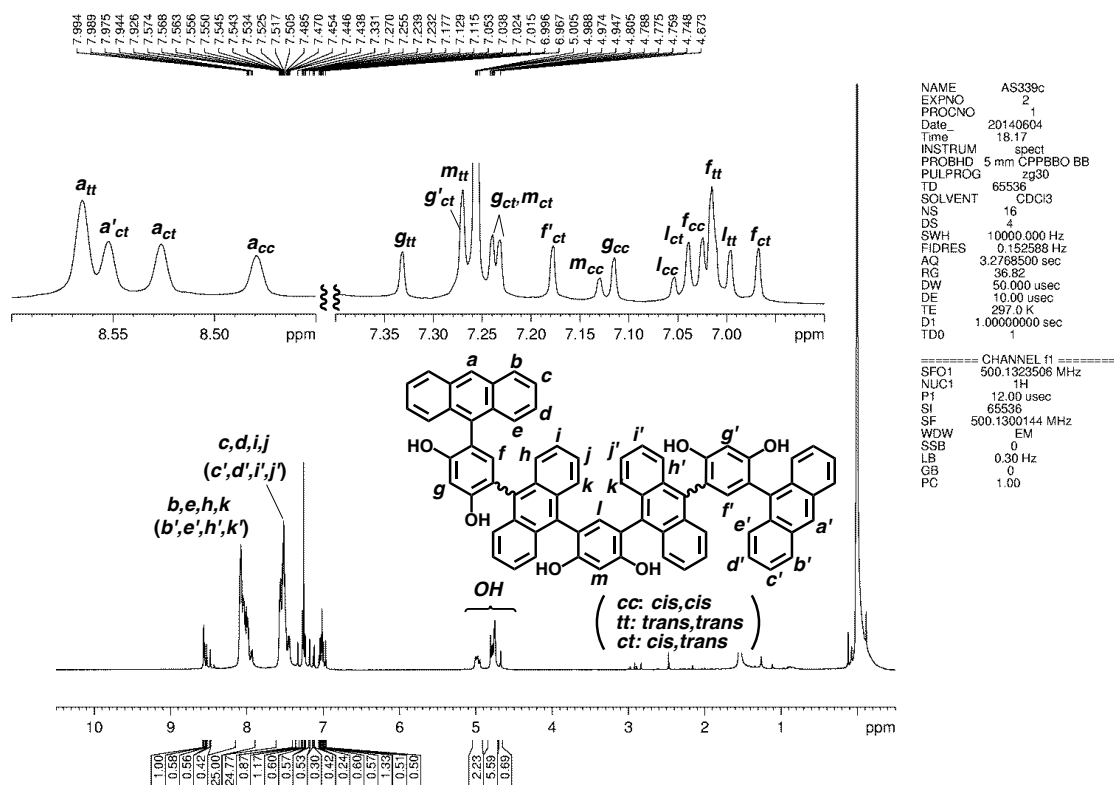


Figure S8. ^1H NMR (500 MHz, CDCl_3 , r.t.) spectrum of **1c** (isomeric mixture).

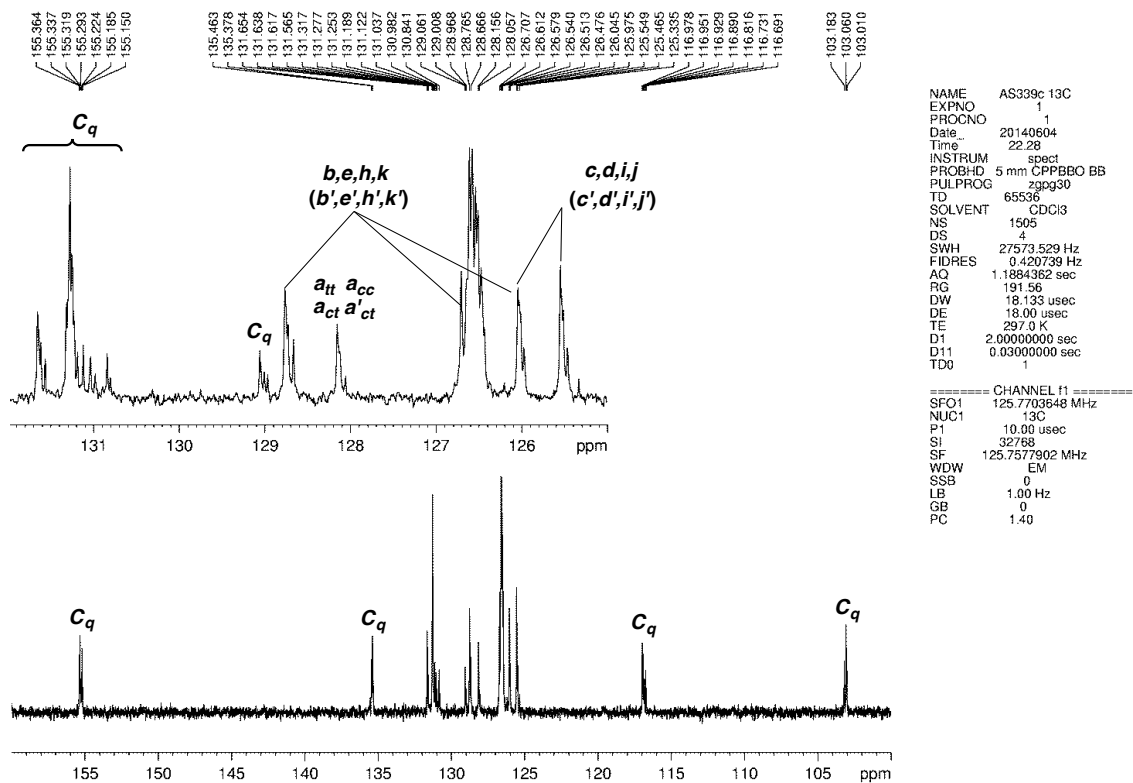


Figure S9. ¹³C NMR (125 MHz, CDCl₃, r.t.) spectrum of **1c** (isomeric mixture).

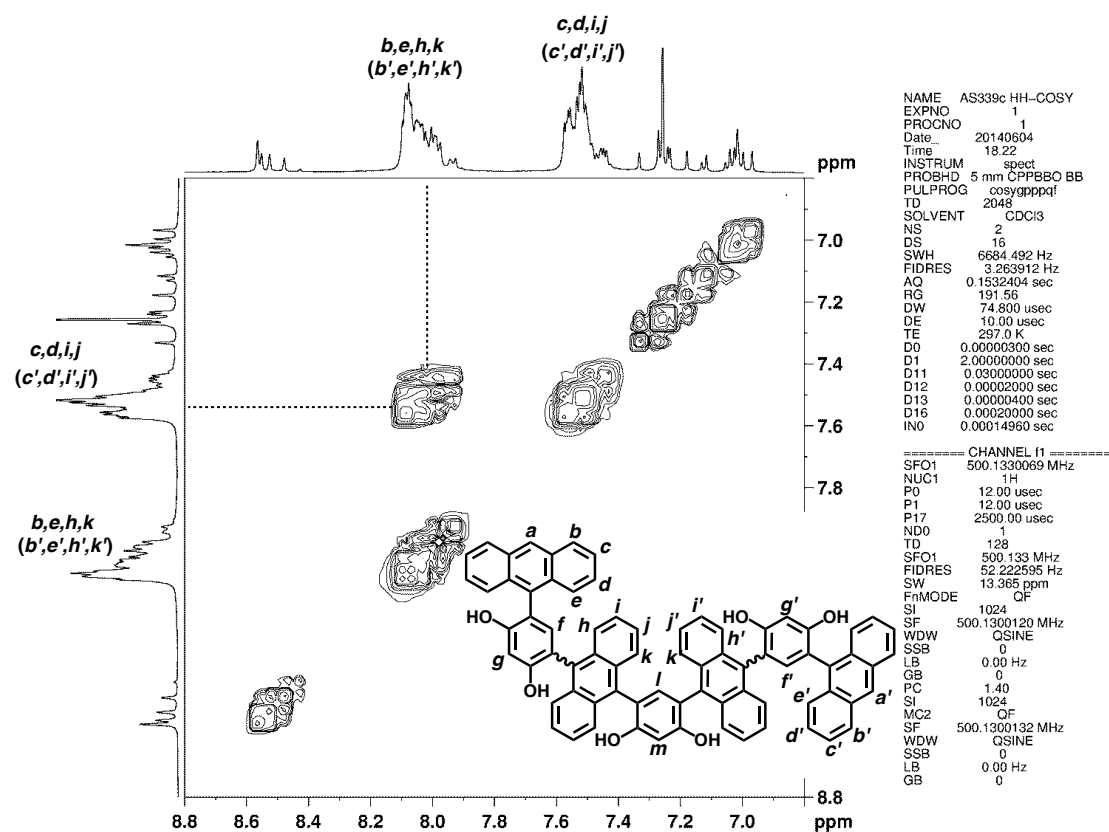


Figure S10. ¹H-¹H COSY (500 MHz, CDCl₃, r.t.) spectrum of **1c** (isomeric mixture).

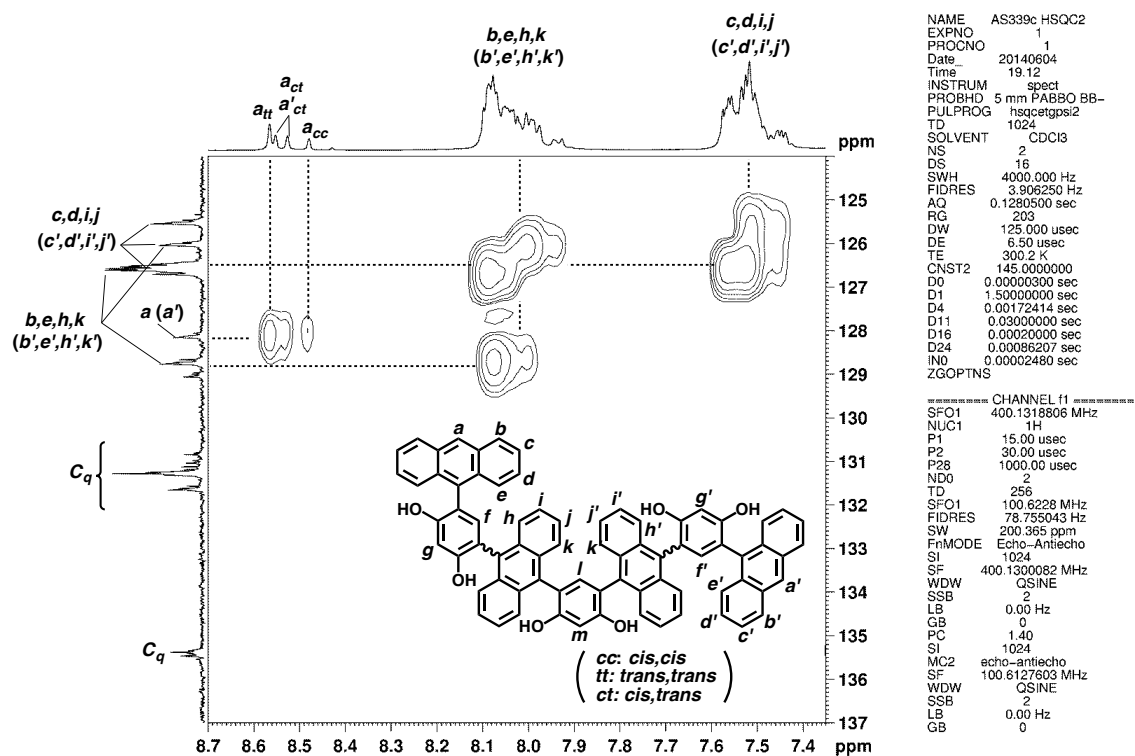


Figure S11a. HSQC (400 MHz, CDCl₃, r.t.) spectrum of **1c** (isomeric mixture).

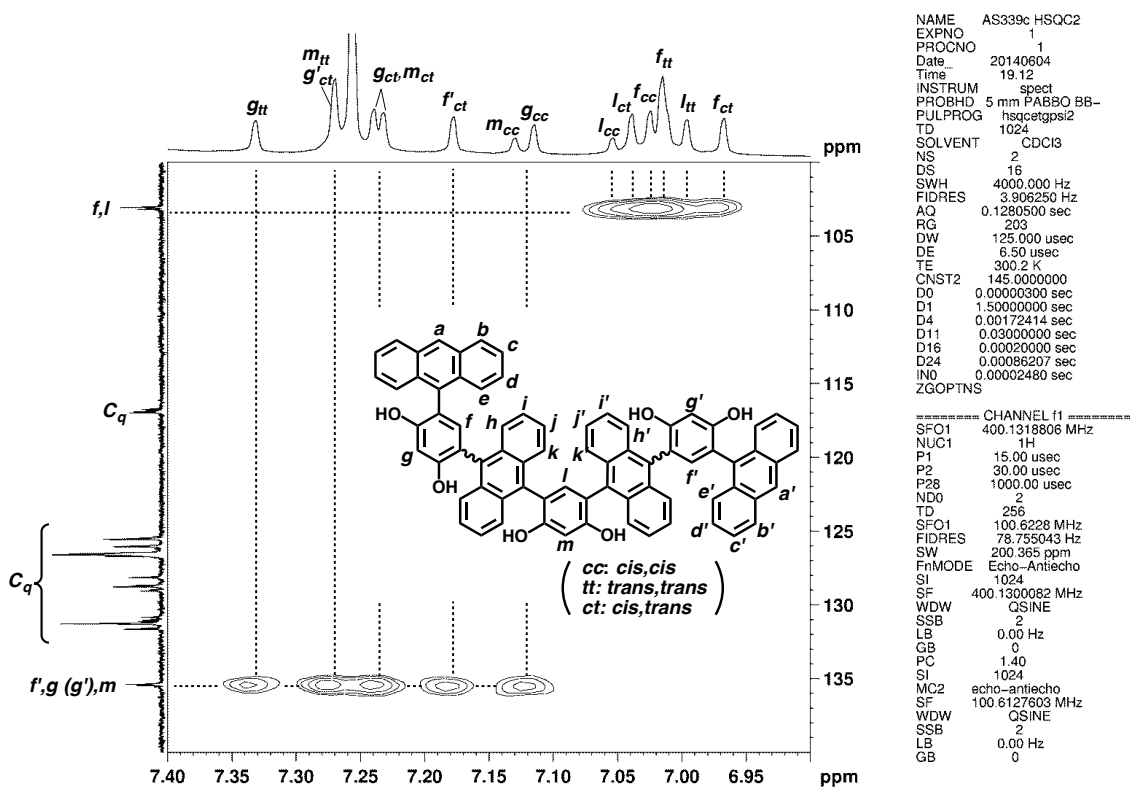
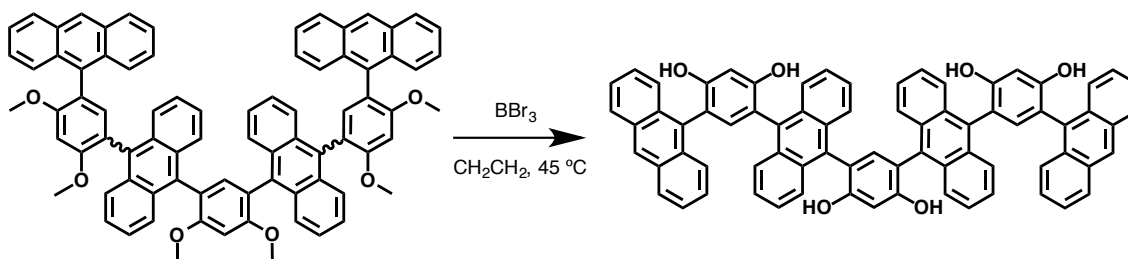


Figure S11b. HSQC (400 MHz, CDCl₃, r.t.) spectrum of **1c** (isomeric mixture).

Synthesis of anthracene tetramer *trans,trans*-1c

AS252



Anthracene tetramer **1b** (0.701 g, 0.628 mmol) and dry CH_2Cl_2 (30 mL) were added to a 200 mL glass flask. A CH_2Cl_2 solution (1.0 M) of BBr_3 (19.0 mL, 19.0 mmol) was added dropwise to this flask at $0\text{ }^\circ\text{C}$ under N_2 . The reaction mixture was stirred at $45\text{ }^\circ\text{C}$ for 1 d. The reaction was quenched with H_2O (40 mL). The product was extracted with CH_2Cl_2 and the resultant organic layer was dried over MgSO_4 , filtered, and concentrated. The crude product was washed with CH_3OH and hexane to afford a pure *trans-trans* isomer of anthracene tetramer **1c** (0.352 g, 0.341 mmol, 54%) as a pale yellow solid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$, r.t.): δ 6.88-6.95 (m, 6H), 7.50 (br, 16H), 7.96 (br, 12H), 8.10 (br, 4H), 8.58 (s, 2H), 9.32 (s, 2H), 9.37 (s, 2H), 9.43 (s, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, r.t.): δ 103.1 (CH \times 2), 115.4 (C_q), 115.7 (C_q), 115.8 (C_q), 124.8 (CH), 125.0 (CH), 125.2 (C_q), 125.7 (CH), 126.6 (C_q), 126.8 (CH), 128.2 (CH), 130.2 (C_q), 130.3 (C_q), 131.1 (C_q), 133.4 (C_q), 134.0 (C_q), 135.6 (CH \times 2), 156.1 (C_q), 156.2 (C_q), 156.3 (C_q). MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{74}\text{H}_{46}\text{O}_6$: 1030.33, Found 1029.99 $[\text{M}]^+$.

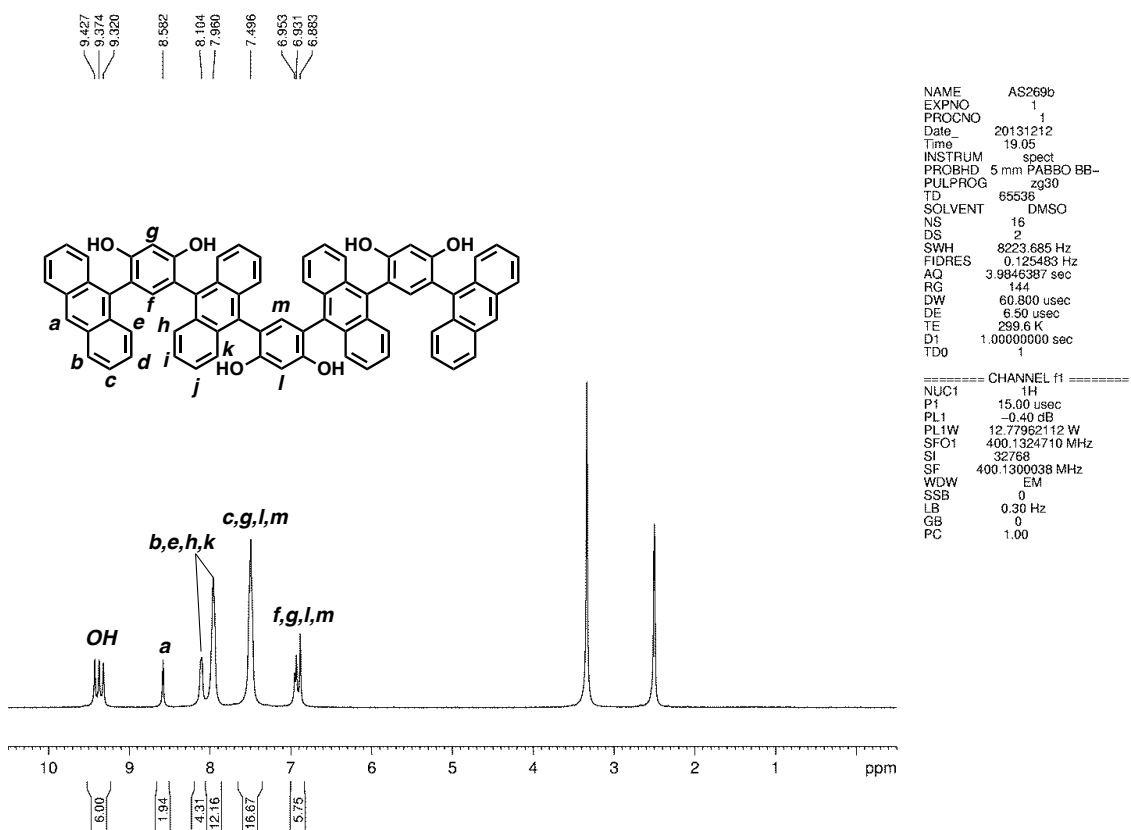


Figure S12. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, r.t.) of *trans,trans*-**1c**.

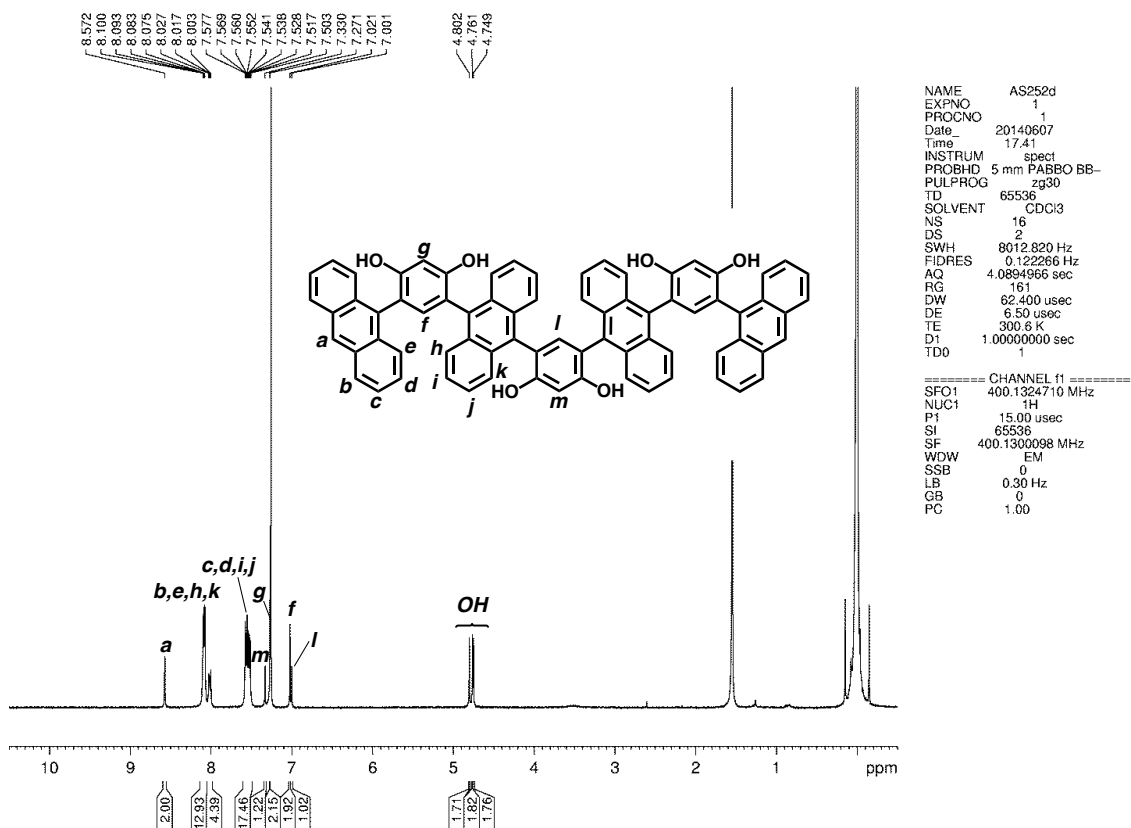


Figure S13. ^1H NMR spectrum (400 MHz, CDCl_3 , r.t.) of *trans,trans*-**1c**.

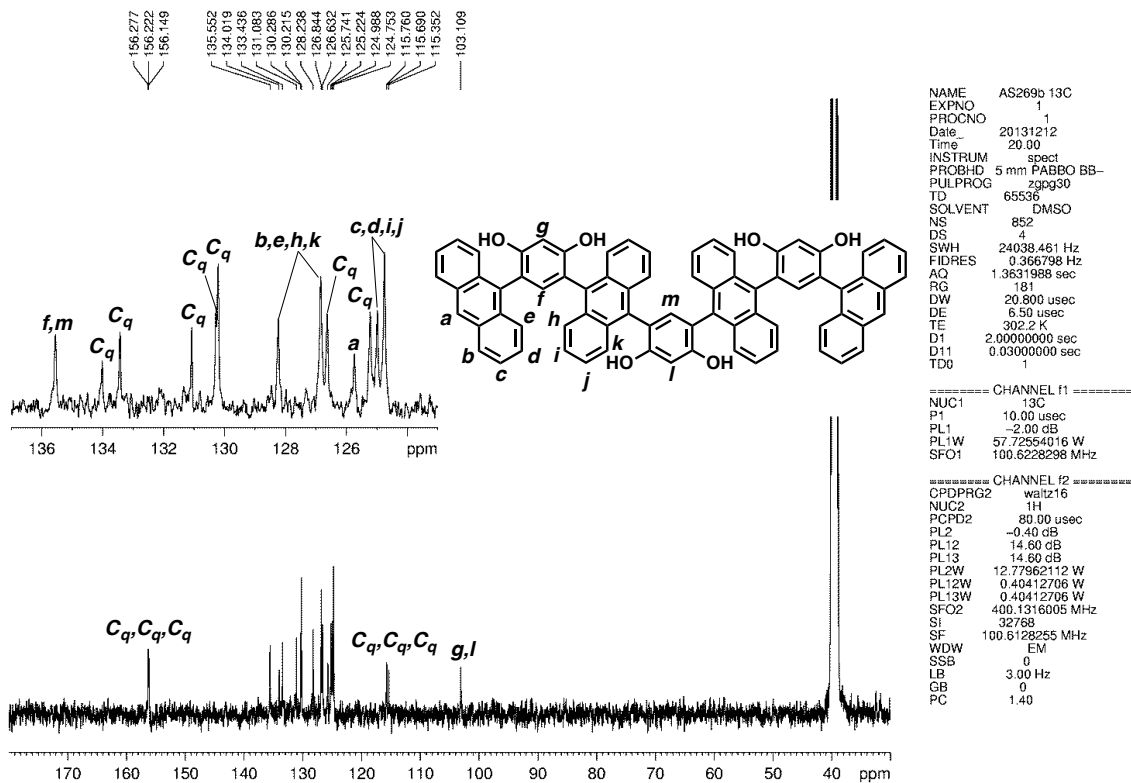


Figure S14. ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$, r.t.) of *trans,trans-1c*.

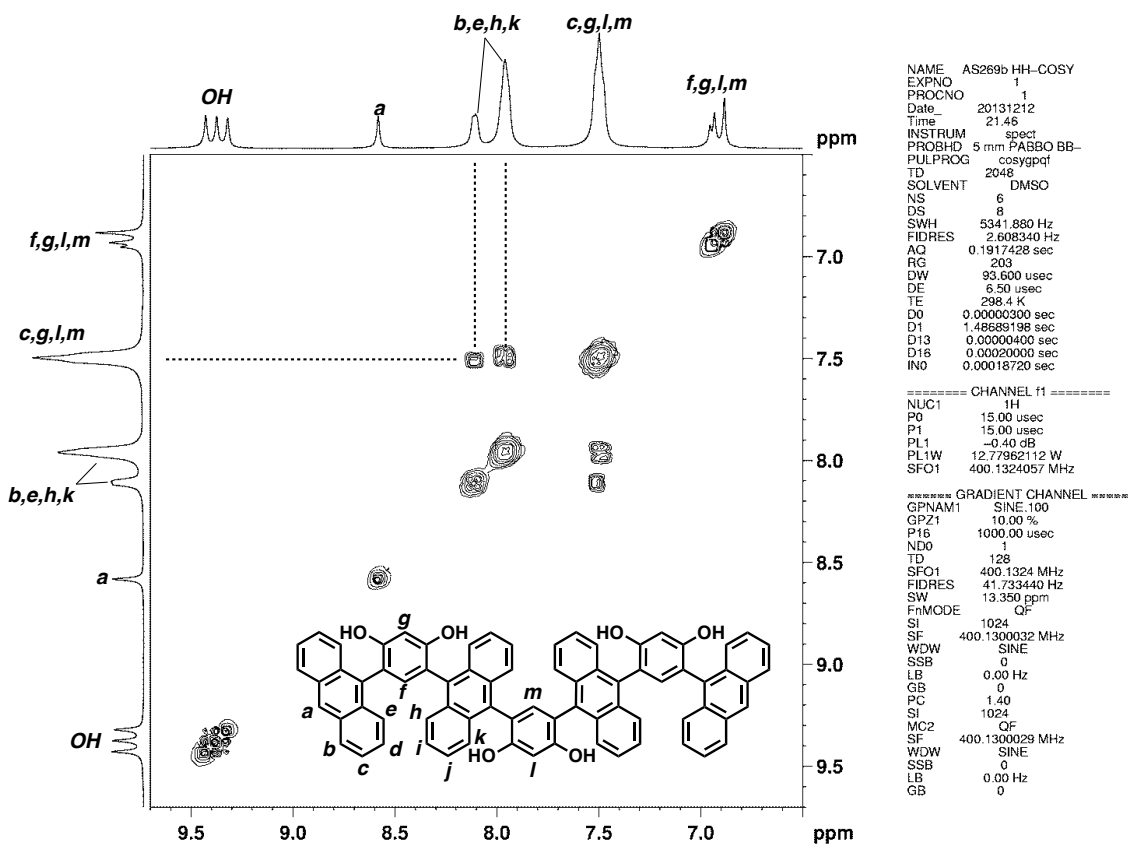


Figure S15. $^1\text{H-}^1\text{H}$ COSY spectrum (400 MHz, $\text{DMSO-}d_6$, r.t.) of *trans,trans-1c*.

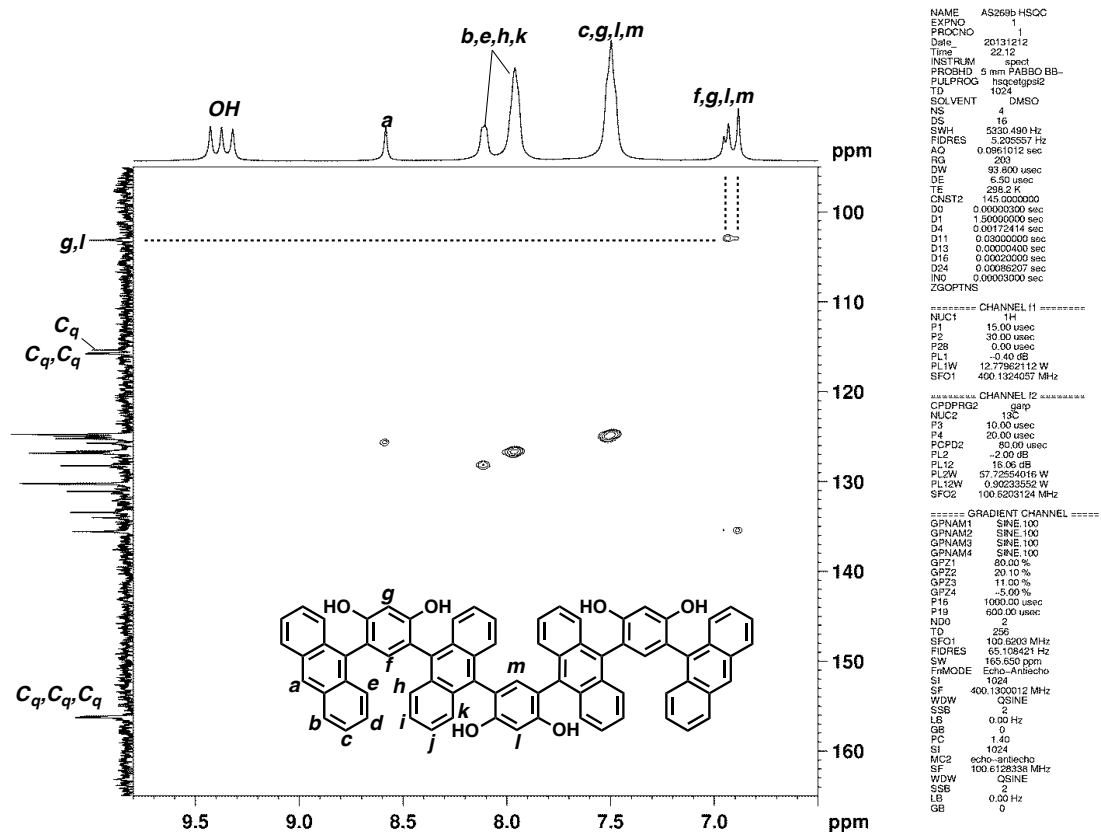


Figure 16a. HSQC spectrum (400 MHz, DMSO-*d*₆, r.t.) of *trans,trans*-1c.

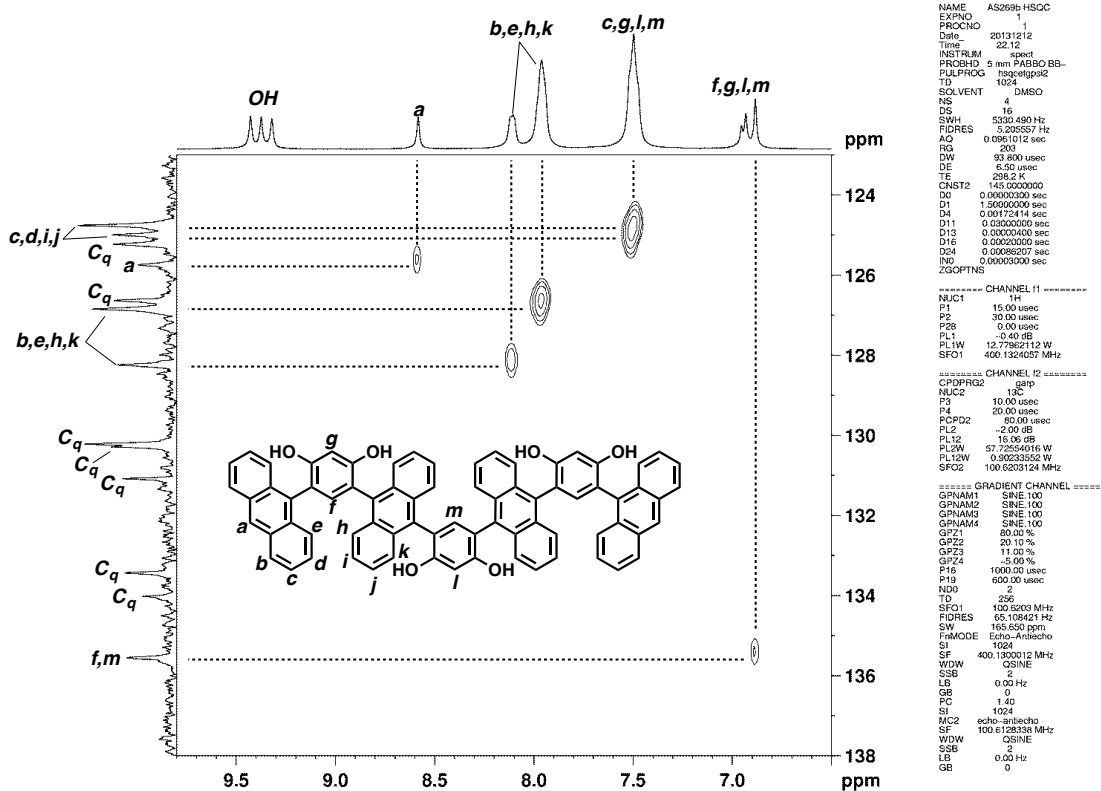
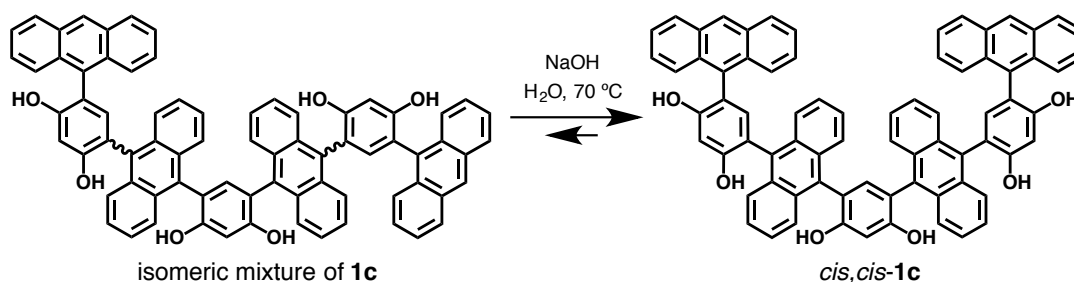


Figure 16b. HSQC spectrum (400 MHz, DMSO-*d*₆, r.t.) of *trans,trans*-1c.

Synthesis of anthracene tetramer *cis,cis-1c*

AS349, 350



An isomeric mixture of anthracene tetramer **1c** (0.102 g, 98.5 μmol), NaOH (0.298 g, 7.45 mmol), and degassed H_2O (15 mL) were added to a 2-necked 50 mL glass flask filled with N_2 . The resultant mixture was stirred at 70 $^\circ\text{C}$ for 1 d. ^1H NMR analysis of the aliquot revealed that the thermodynamic equilibrium ratio of *cis,cis-1c*, *cis,trans-1c*, and *trans,trans-1c* is 1:0:0. The aqueous solution was neutralized with HCl(aq. (ca. 2 mL) and then the products were extracted by CHCl_3 . The resultant organic layer was dried over MgSO_4 , filtered, and concentrated. The crude product was washed with hexane to afford a pure *cis,cis* isomer of anthracene tetramer **1c** (89 mg, 86 μmol , 87%) as a gray solid.

^1H NMR (400 MHz, CDCl_3 , r.t.): δ 4.75 (s, 2H), 4.92 (s, 2H), 4.96 (s, 2H), 7.01 (s, 2H), 7.05 (s, 1H), 7.11 (s, 2H), 7.13 (s, 1H), 7.42-7.53 (m, 16H), 7.92-8.05 (m, 16H), 8.48 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , r.t.): δ 103.2(CH), 103.4(CH), 116.9 (C_q), 117.1 ($\text{C}_q \times 2$), 125.6 (CH), 126.1 (CH), 126.6 ($\text{CH} \times 2$), 126.7 (CH), 126.8 (C_q), 128.2 (CH), 128.8 (CH), 129.1 (C_q), 131.1 (C_q), 131.3 (C_q), 131.4 ($\text{C}_q \times 2$), 131.7 (C_q), 135.6 (CH), 135.7 (CH), 155.3 (C_q), 155.4 (C_q), 155.5 (C_q).

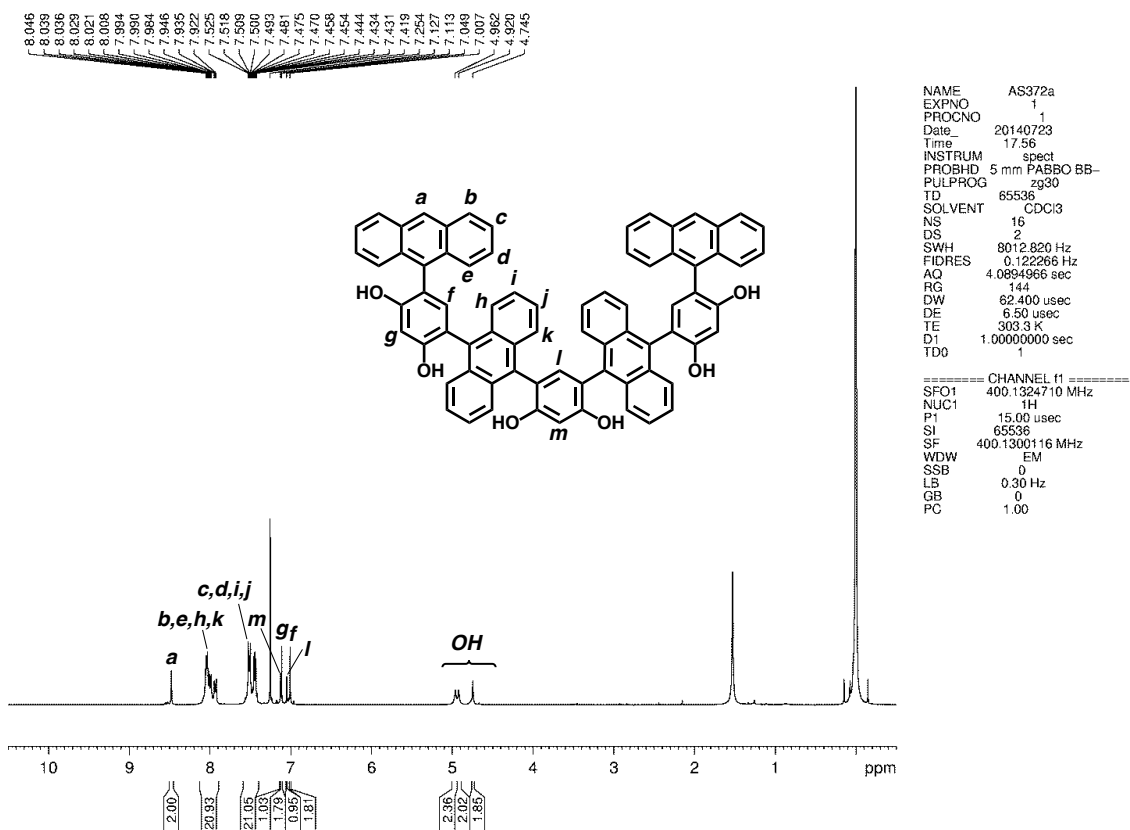


Figure S17. ¹H NMR (400 MHz, CDCl₃, r.t.) spectrum of *cis,cis*-1c.

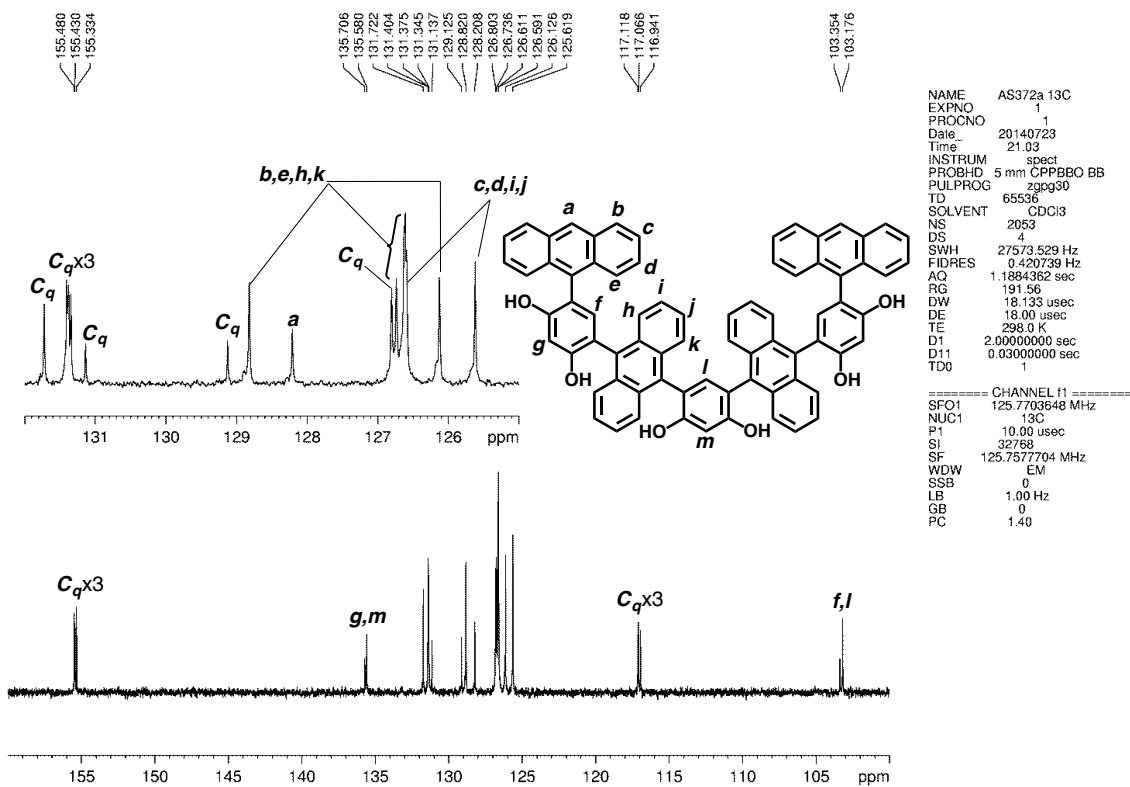


Figure S18. ¹³C NMR (125 MHz, CDCl₃, r.t.) spectrum of *cis,cis*-1c.

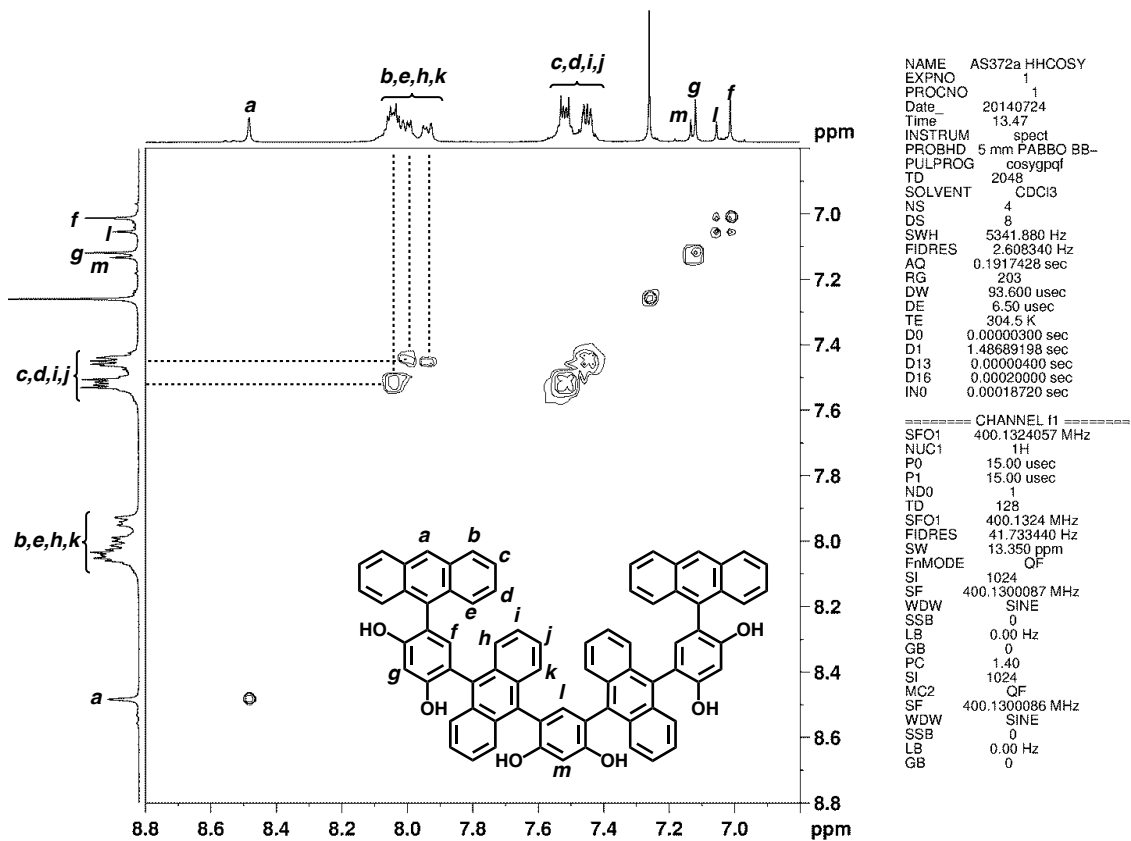


Figure S19. ^1H - ^1H COSY spectrum (400 MHz, CDCl_3 , r.t.) of *cis,cis*-1c.

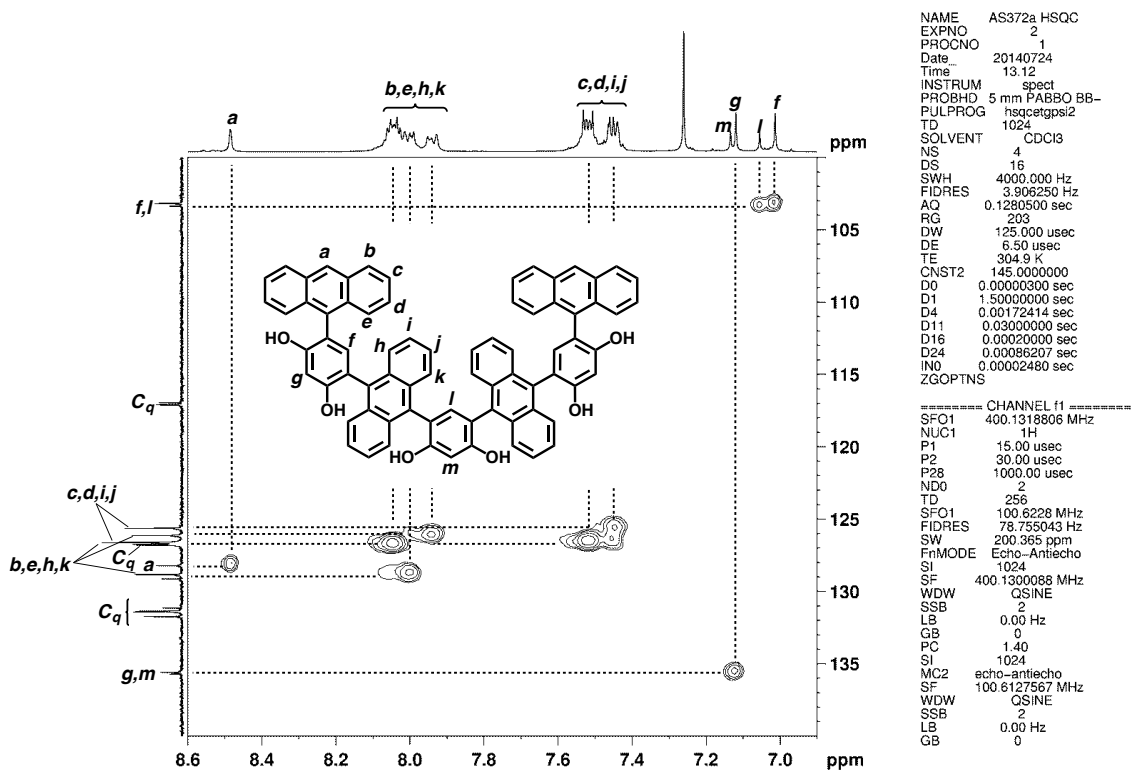


Figure S20. HSQC spectrum (400 MHz, CDCl_3 , r.t.) of *cis,cis*-1c.

Table S1. Crystal data and structure refinement for *cis,cis-1c*.

| | |
|-----------------------------------|---|
| Identification code | AS257 |
| Empirical formula | C78 H40 O11 |
| Formula weight | 1153.10 |
| Temperature | 90 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P21/c |
| Unit cell dimensions | $a = 17.323(3)$ Å $\alpha = 90^\circ$ $b = 22.428(4)$ Å $\beta = 95.051(3)^\circ$ $c = 15.591(3)$ Å $\gamma = 90^\circ$ |
| Volume | 6033.8(17) Å ³ |
| Z | 4 |
| Density (calculated) | 1.269 Mg/m ³ |
| Absorption coefficient | 0.085 mm ⁻¹ |
| F(000) | 2384 |
| Crystal size | 0.35 x 0.14 x 0.09 mm ³ |
| Theta range for data collection | 1.489 to 20.469°. |
| Index ranges | -17 < h < 16, -22 < k < 19, -15 < l < 15 |
| Reflections collected | 18523 |
| Independent reflections | 5991 [R(int) = 0.0926] |
| Completeness to theta = 25.03° | 99.6 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.971 and 0.992 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 5991 / 1371 / 802 |
| Goodness-of-fit on F ² | 0.945 |
| Final R indices [I > 2sigma(I)] | R ₁ = 0.0806, wR ₂ = 0.2219 |
| R indices (all data) | R ₁ = 0.1437, wR ₂ = 0.2691 |
| Largest diff. peak and hole | 0.613 and -0.649 e.Å ⁻³ |

The supplementary crystallographic data (CCDC 985689) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

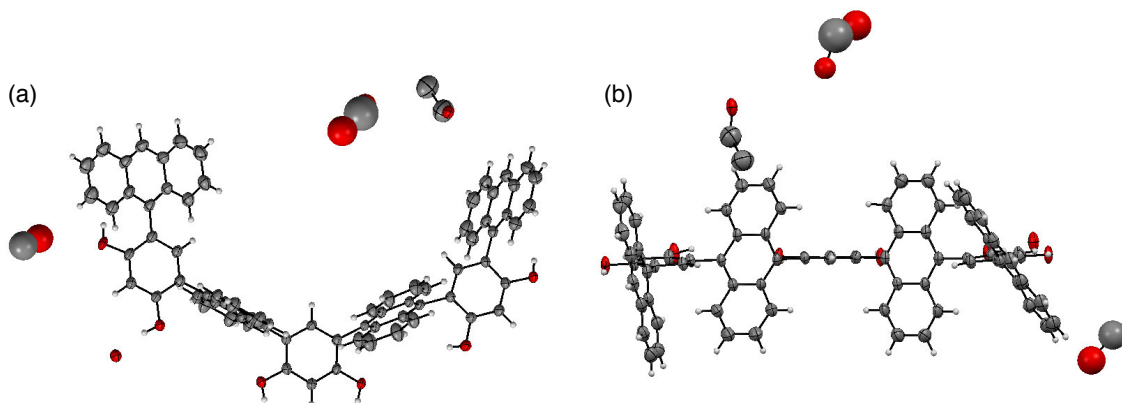


Figure S21. ORTEP drawing of *cis,cis-1c*.

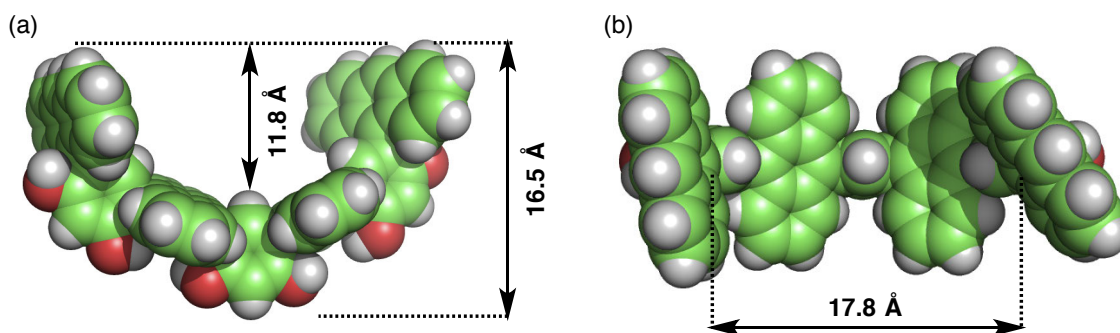


Figure S22. CPK representation of the crystal structure of *cis,cis-1c*.

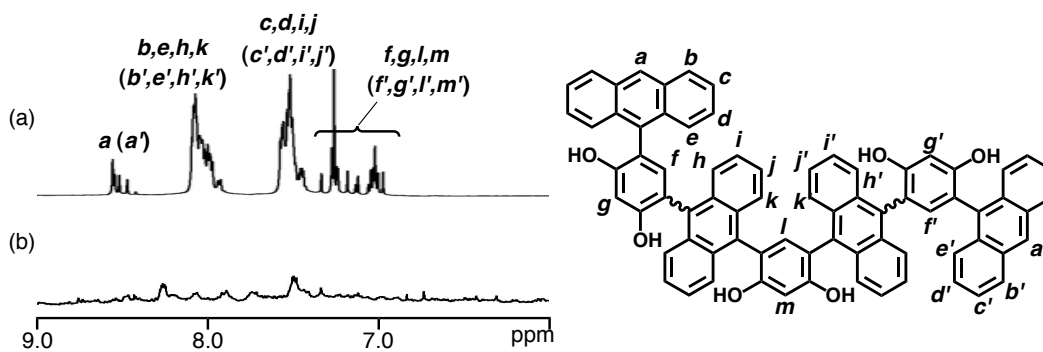
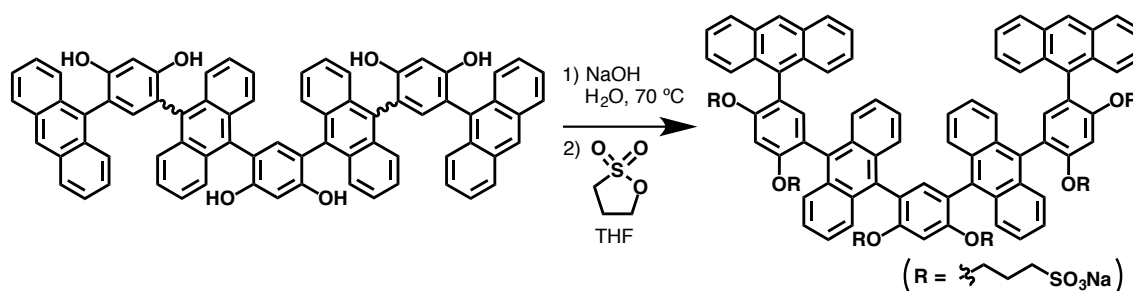


Figure S23. ^1H NMR spectra (400 MHz, r.t.) of **1c** (isomeric mixture) in (a) CDCl_3 and (b) $\text{NaOD}/\text{D}_2\text{O}$ after heating at $70\text{ }^\circ\text{C}$ for 1 d.

Synthesis of anthracene tetramer *cis,cis-1a*

AS257



An isomeric mixture of **1c** (0.151 g, 0.146 mmol), NaOH (0.318 g, 7.95 mmol), and H₂O (15 mL) were added to a 2-necked 50 mL glass flask filled with N₂. The resultant mixture was stirred at 70 °C for 21 h. A THF solution (20 mL) of 1,3-propanesultone (0.554 g, 4.53 mmol) was added to the reaction mixture and then the solution was further stirred at 70 °C for 2 d. After the evaporation of the resultant solution, the crude product was dissolved in water (1.0 mL). When 1-propanol (10 mL) was added to the aqueous solution, yellow precipitate was generated. The precipitate was collected by centrifugation and dried under vacuum and then pure *cis,cis-1a* (0.232 g, 0.122 mmol, 84%) was obtained as a yellow solid.^[1]

¹H NMR (400 MHz, CD₃OD, r.t.): δ 1.83-1.87 (m, 4H), 2.01-2.06 (m, 8H), 2.28-2.31 (m, 4H), 2.61-2.66 (m, 8H), 4.18 (t, 4H, $J = 6.0$ Hz), 4.26-4.31 (m, 8H), 6.93 (s, 2H), 6.96 (s, 1H), 7.22 (s, 2H), 7.28 (s, 1H), 7.34-7.44 (m, 16H), 7.81-7.96 (m, 16H), 8.37 (s, 2H). ¹³C NMR (125 MHz, CD₃OD, r.t.): δ 25.9 (CH₂), 26.0 (CH₂), 26.1 (CH₂), 49.1-49.7 (CH₂ × 3), 68.4 (CH₂), 68.5 (CH₂), 68.6 (CH₂), 99.8 (CH × 2), 120.6 (C_q), 121.0 (C_q), 121.2 (C_q), 126.0 (CH × 4), 126.3 (C_q), 127.3 (CH), 127.7 (CH), 128.0 (CH), 128.1 (CH), 129.4 (CH), 131.8 (C_q × 2), 132.0 (C_q), 132.9 (C_q), 134.5 (C_q), 134.6 (C_q × 2), 137.5 (CH × 2), 159.4 (C_q), 159.5 (C_q). ¹H DOSY NMR (400 MHz, CD₃OD, 1.0 mM, 300 K): $D = 6.17 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. FT-IR (KBr, cm⁻¹): 3087, 2974, 2947, 2887, 2359, 1631, 1503, 1470, 1441, 1350, 1193, 1046, 737, 608, 528. ESI-TOF MS (CH₃OH): m/z 450.7 [M-4Na⁺]⁴⁻, 608.7 [M-3Na⁺]³⁻, 924.5 [M-2Na⁺]²⁻.

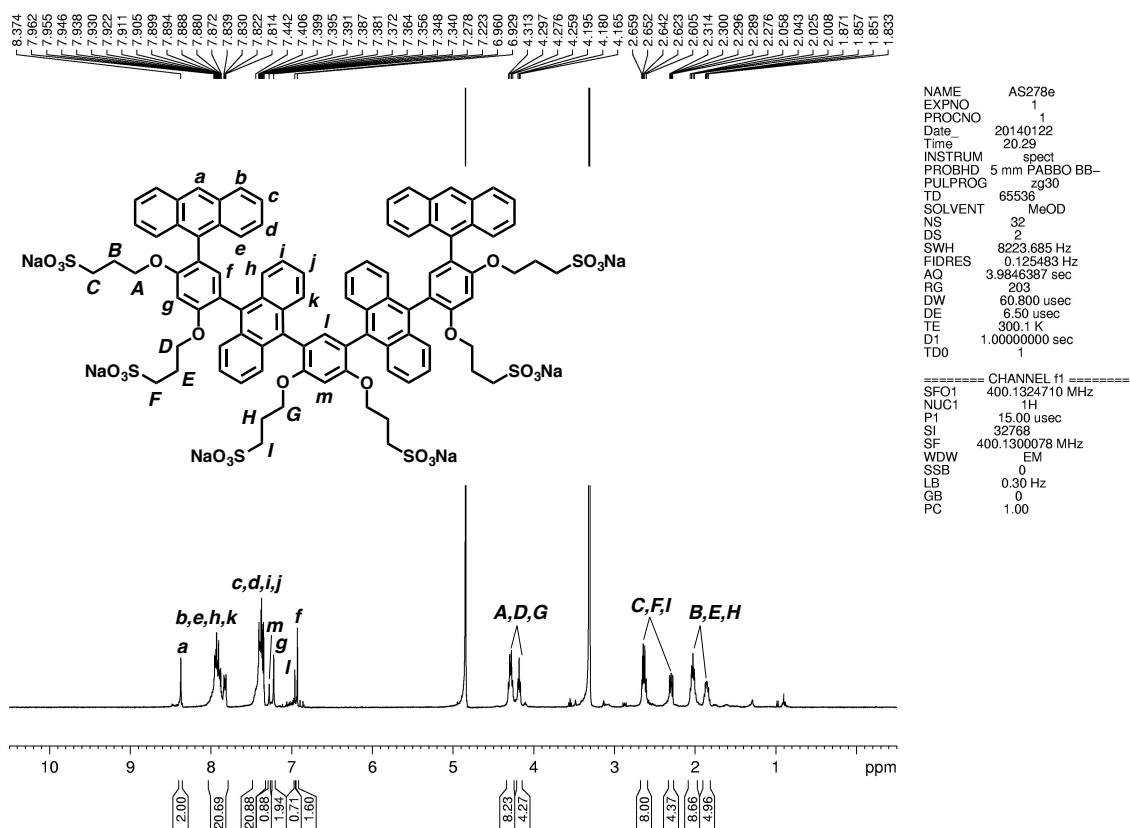


Figure S24. ^1H NMR spectrum (400 MHz, CD_3OD , r.t.) of *cis,cis*-1a.

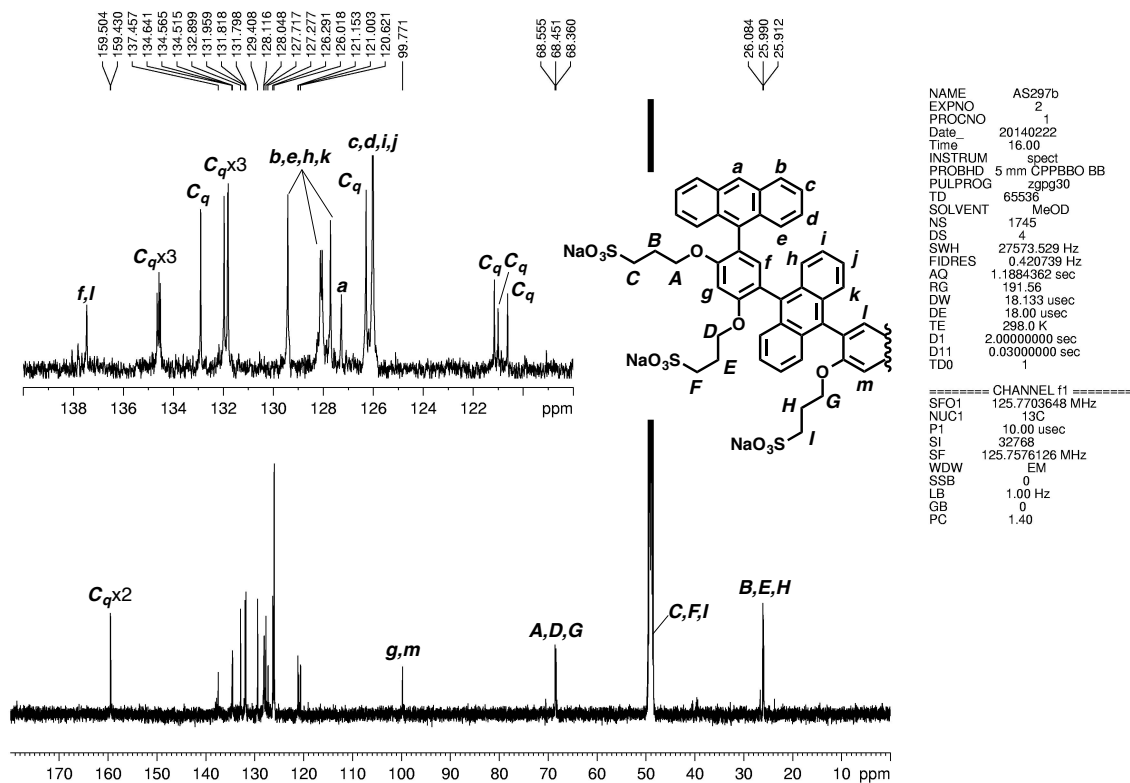


Figure S25. ^{13}C NMR spectrum (125 MHz, CD_3OD , r.t.) of *cis,cis*-1a.

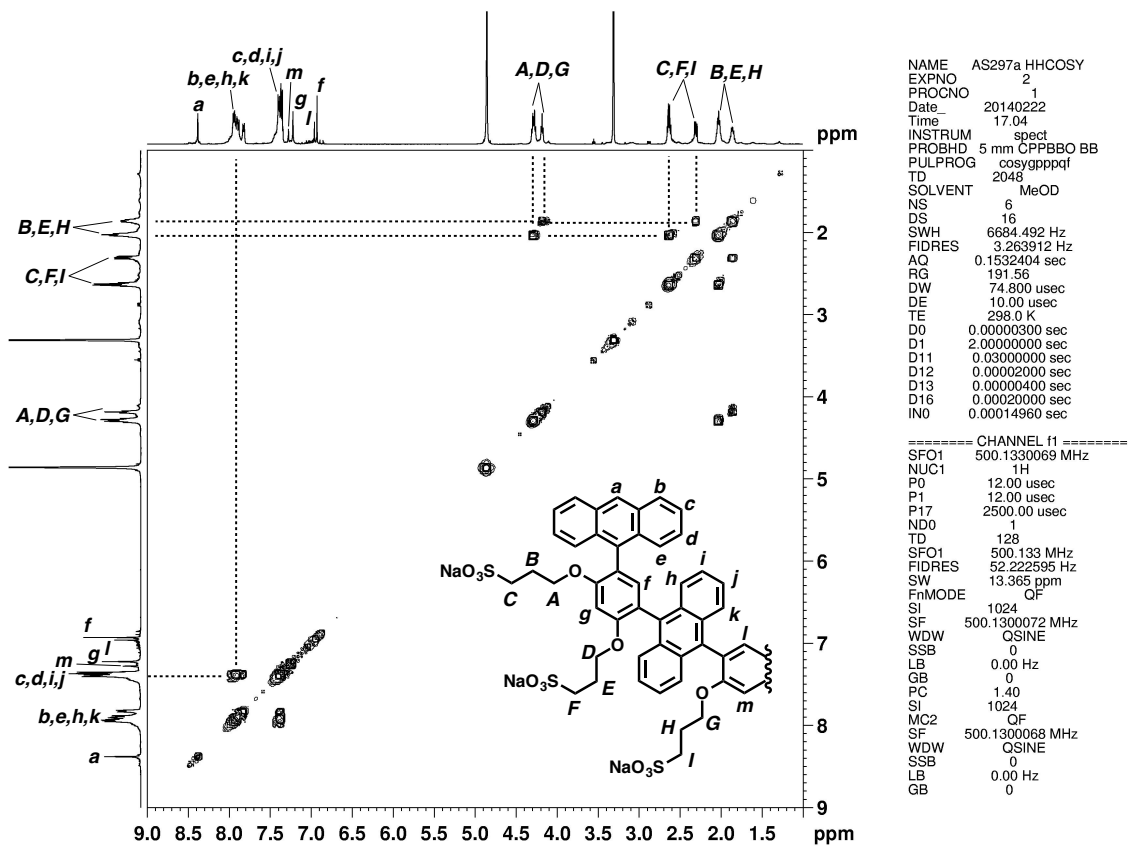


Figure S26. ^1H - ^1H COSY spectrum (500 MHz, CD_3OD , r.t.) of *cis,cis*-**1a**.

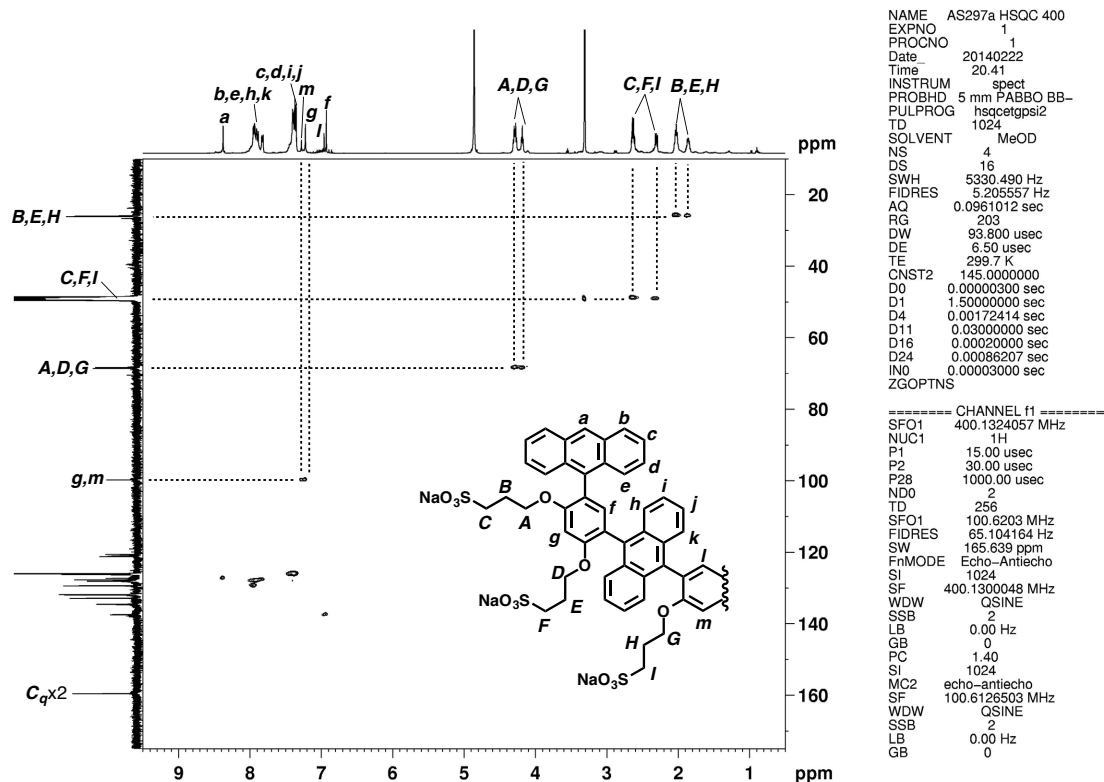


Figure S27a. HSQC spectrum (400 MHz, CD_3OD , r.t.) of *cis,cis*-**1a**.

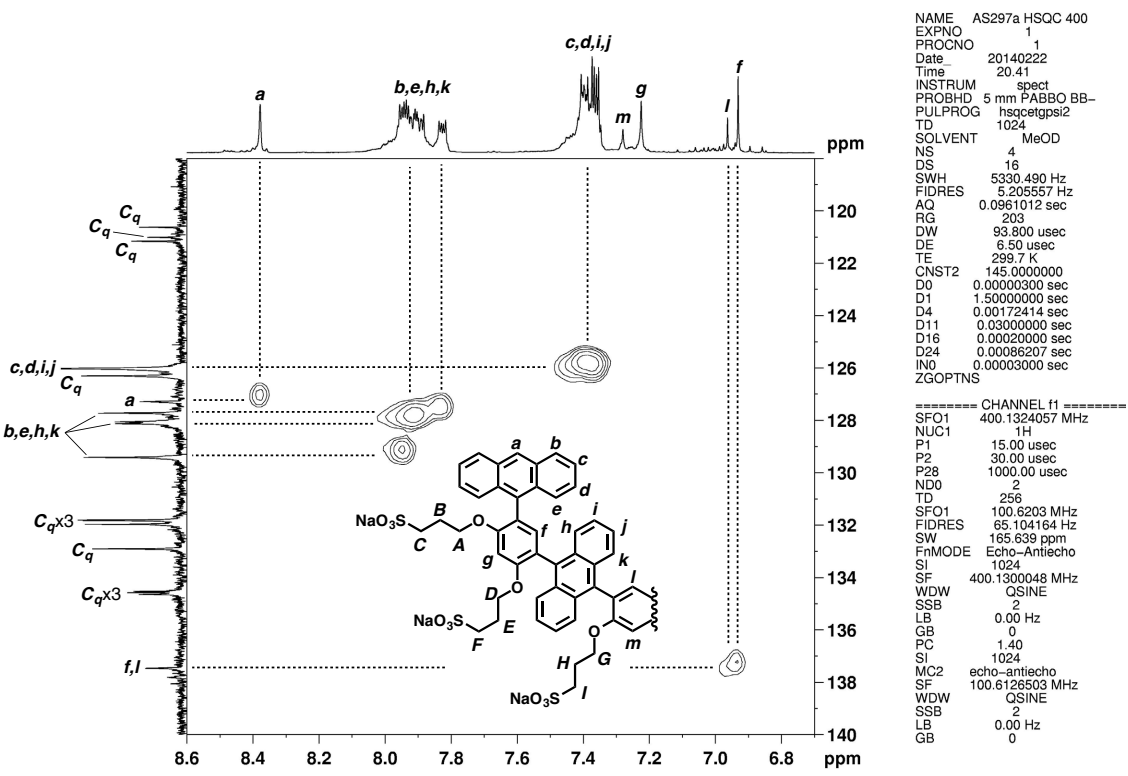


Figure S27b. HSQC spectrum (400 MHz, CD₃OD, r.t.) of *cis,cis-1a*.

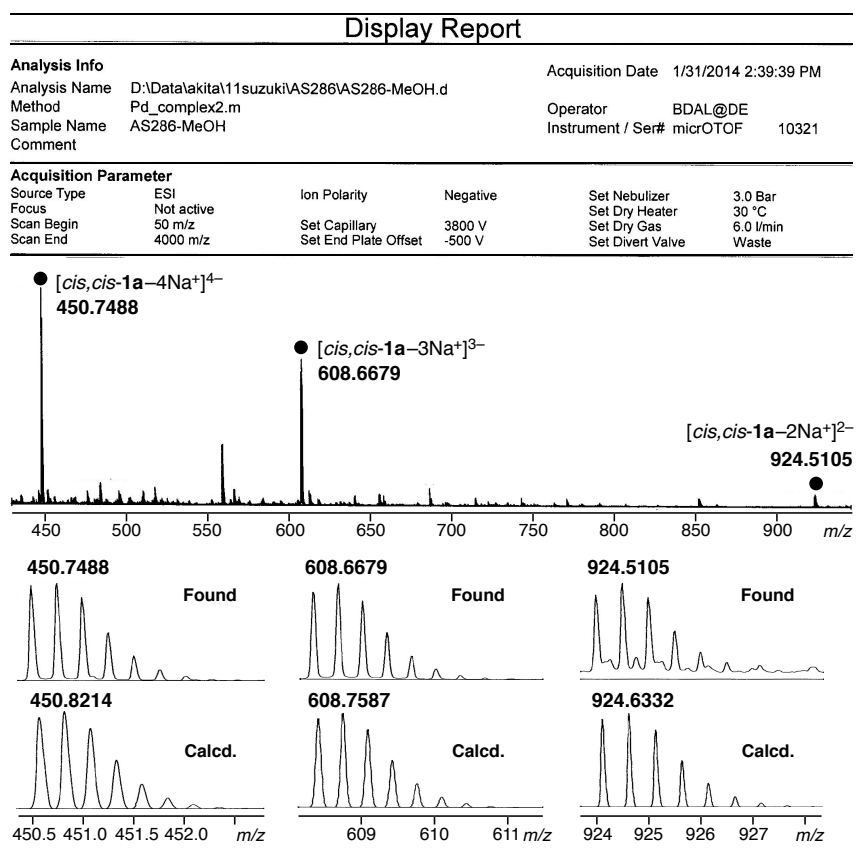
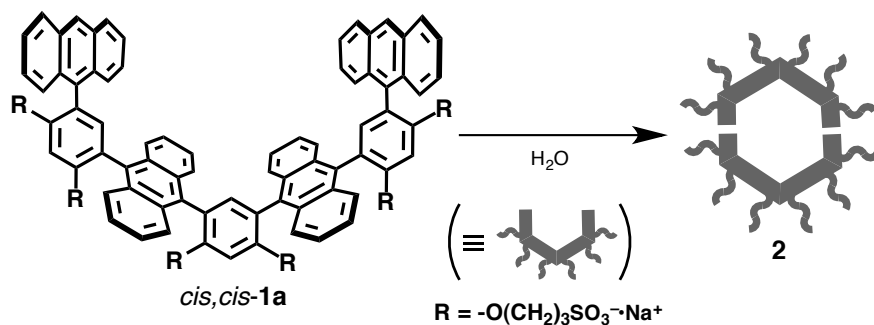


Figure S28. ESI-TOF MS spectrum (CH₃OH) of *cis,cis-1a*.

Formation of molecular capsule 2

AS258



Compound *cis,cis-1a* (19.1 mg, 10.1 μmol) was dissolved in water (1.0 mL) and then the solution was stirred at r.t. for 1 min. The formation of molecular capsule **2** was confirmed by NMR, ESI-TOF MS, DLS, and AFM analyses.

Display Report

| Analysis Info | | Acquisition Date 1/31/2014 4:24:10 PM | | | |
|-----------------------|--|---------------------------------------|----------------|------------------|-----------|
| Analysis Name | D:\Data\akita\11suzuki\AS286\AS286-H2O-4.d | Operator | BDAL@DE | | |
| Method | Pd_complex2.m | Instrument / Ser# | microTOF 10321 | | |
| Sample Name | AS286-H2O-4 | Comment | | | |
| Acquisition Parameter | | | | | |
| Source Type | ESI | Ion Polarity | Negative | Set Nebulizer | 3.0 Bar |
| Focus | Not active | Set Capillary | 3800 V | Set Dry Heater | 30 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 6.0 l/min |
| Scan End | 4000 m/z | Set Divert Valve | | Set Divert Valve | Waste |

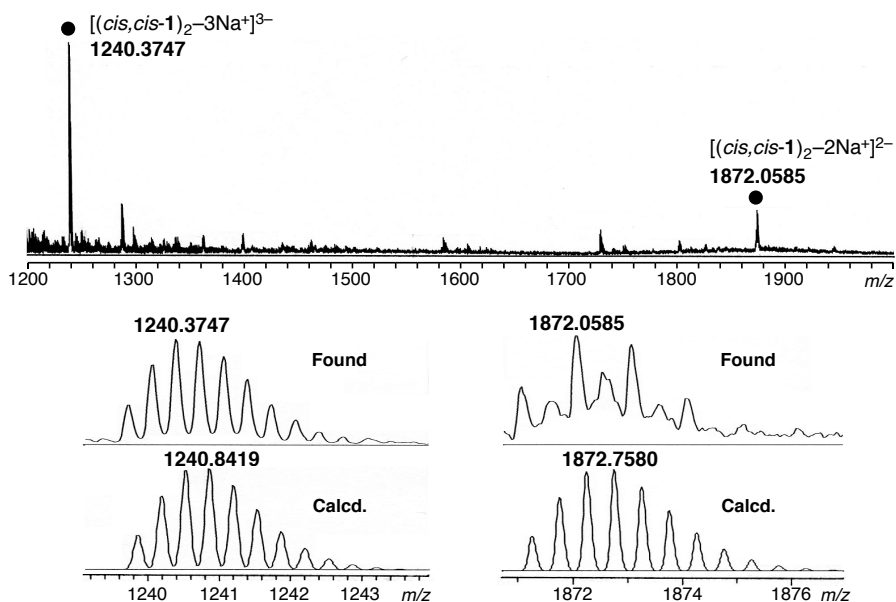


Figure S29. ESI-TOF MS spectrum (H₂O) of capsule **2**.

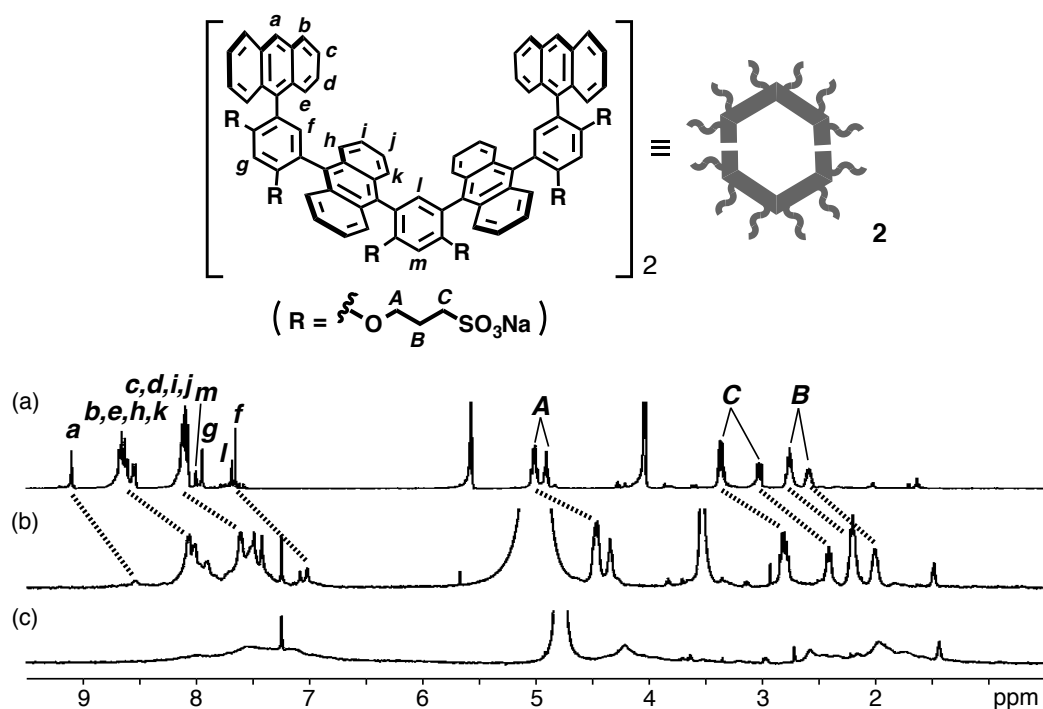


Figure S30. ^1H NMR spectra (400 MHz, r.t., TMS as an external standard) of *cis,cis*-**1a** (1 mM) in (a) CD_3OD , (b) $\text{CD}_3\text{OD}/\text{D}_2\text{O} = 4:6$ (v/v), and (c) D_2O .

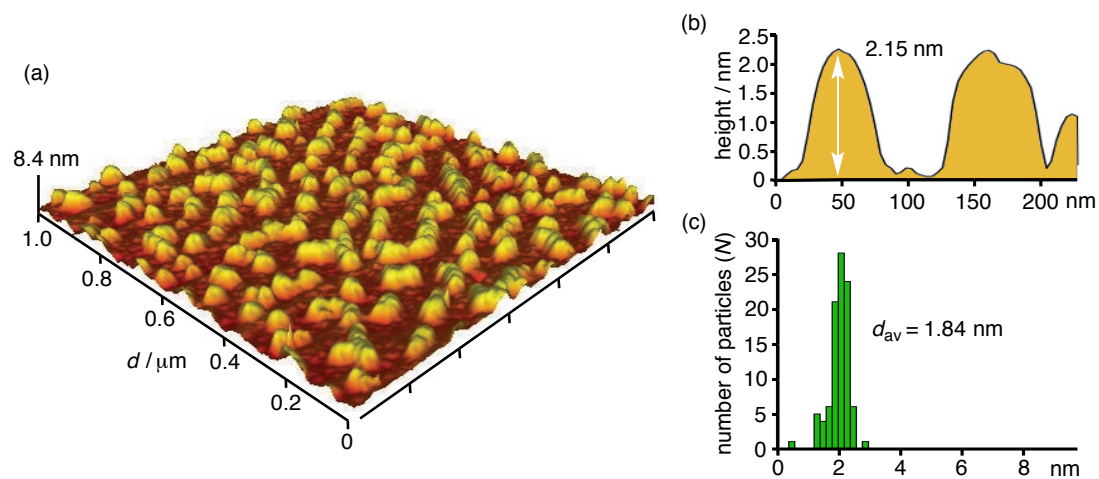


Figure S31. (a) AFM image of capsule **2** on mica and (b) the height profile of selected features of **2**. (c) Size and number (N) distribution of the AFM image of **2**.

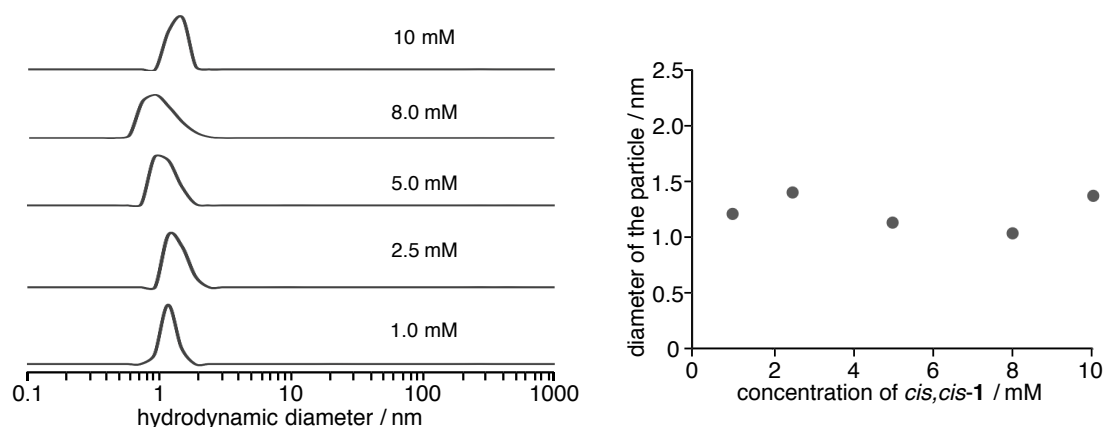


Figure S32. Particle size distribution of capsule **2** by DLS analysis (H_2O , r.t., 1.0-10.0 mM based on *cis,cis*-**1a**).

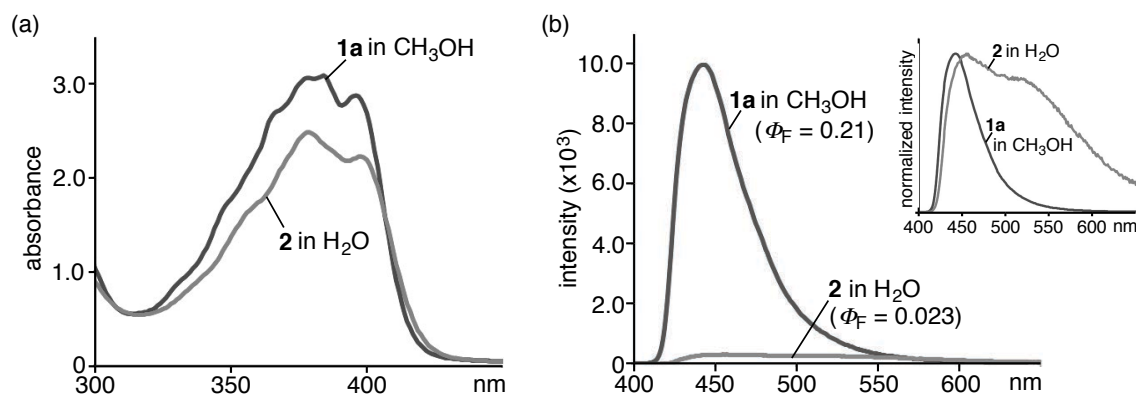
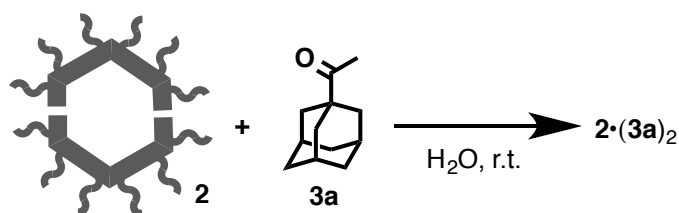


Figure S33. (a) UV-vis spectra and (b) fluorescence spectra ($\lambda_{\text{ex}} = 370 \text{ nm}$, r.t.) of *cis,cis*-**1a** in CH_3OH and capsule **2** in H_2O (1.0 mM based on *cis,cis*-**1a**). Absolute fluorescence quantum yields are given in brackets.

Preparation of $2 \cdot (3a)_2$ AS390, 565



An excess amount of 1-acetyladamantane (**3a**; 1.3 mg, 7.0 μmol) was added to a H_2O solution (0.7 mL) of capsule **2** (1.3 mg, 0.70 μmol based on *cis,cis*-**1a**) in a test tube. The suspended mixture was stirred at r.t. for 1 h. The resultant solution was centrifuged and filtered by a membrane filter (0.20 μm) to give a solution of $2 \cdot (3a)_2$. The formation of $2 \cdot (3a)_2$ was confirmed by ^1H NMR, DOSY NMR, and fluorescence analyses.

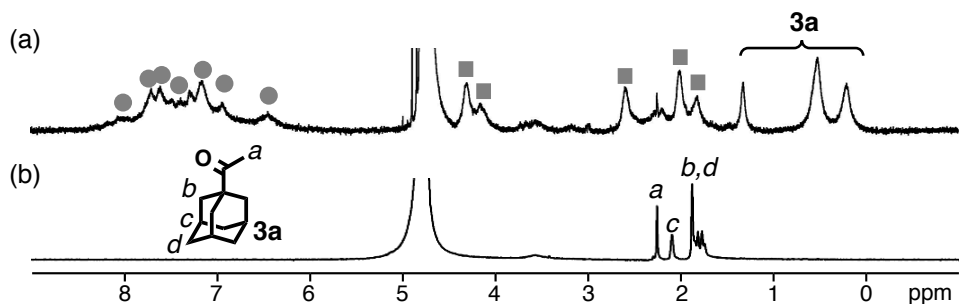


Figure S34a. ¹H NMR spectra (400 MHz, D₂O, r.t.) of (a) **2•(3a)₂** and (b) 1-acetyladamantane (**3a**). The gray circles and squares indicate the aromatic moieties and hydrophilic chains of **2**, respectively.

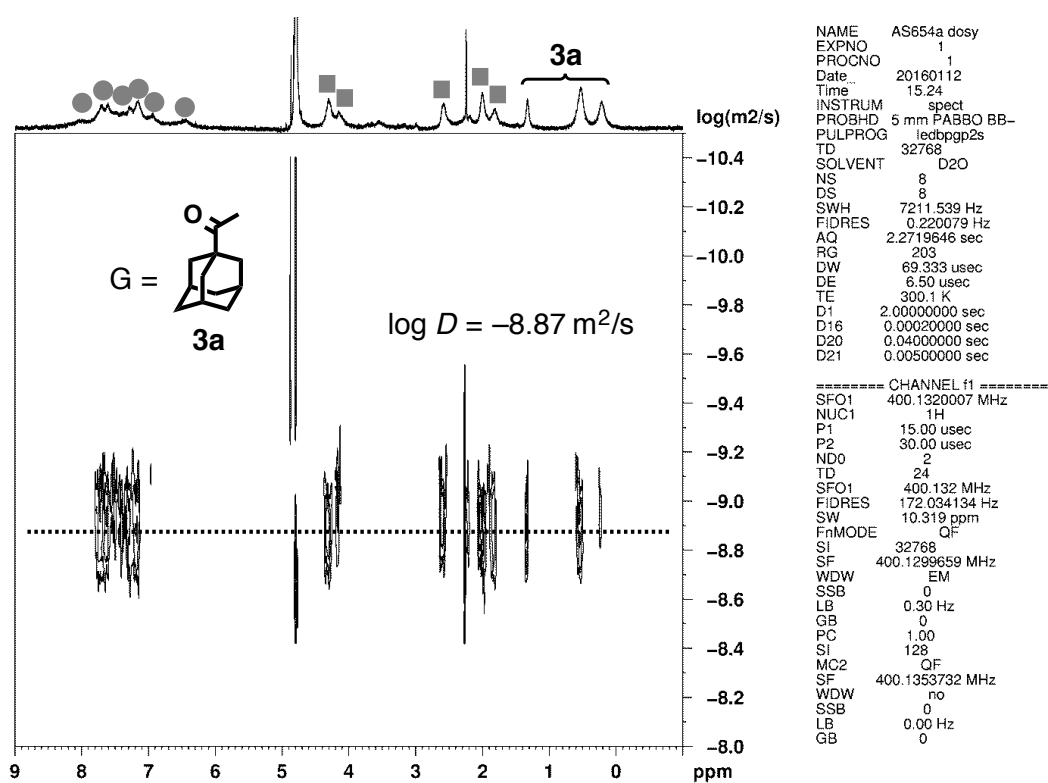


Figure S34b. DOSY NMR spectrum (400 MHz, D₂O, r.t.) of **2•(3a)₂**. The gray circles and squares indicate the aromatic moieties and hydrophilic chains of **2**, respectively.

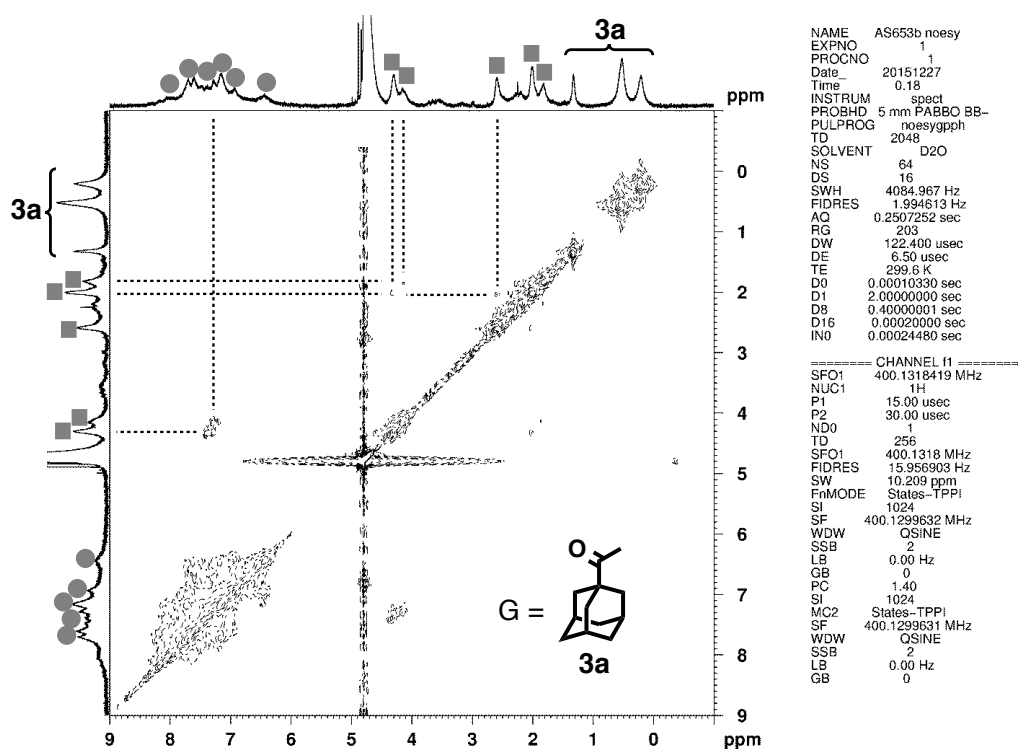


Figure S34c. NOESY NMR spectrum (400 MHz, D₂O, r.t.) of **2•(3a)₂**. The gray circles and squares indicate the aromatic moieties and hydrophilic chains of **2**, respectively.

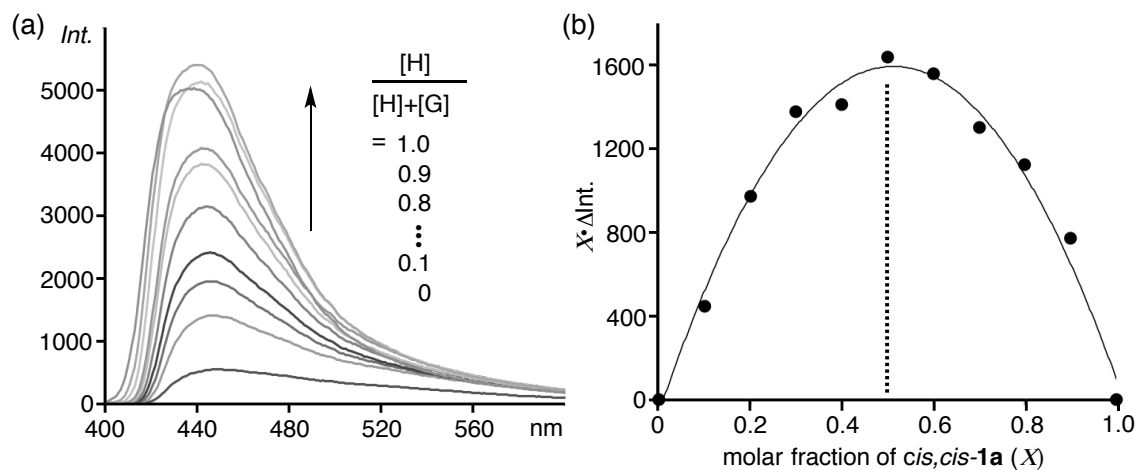
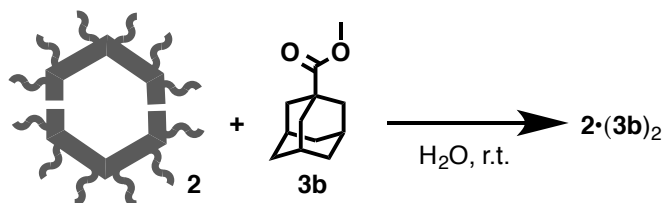


Figure S35. (a) Fluorescence spectra (H₂O, r.t., $\lambda_{\text{ex}} = 370$ nm) and (b) Job's plot for **3a** with *cis,cis*-**1a**.

Preparation of $2 \cdot (3b)_2$

AS371, 565



An excess amount of methyl 1-adamantane carboxylate (**3b**; 1.4 mg, 6.9 μmol) was added to a H₂O solution (0.7 mL) of capsule **2** (1.3 mg, 0.70 μmol based on *cis,cis*-**1a**) in a test tube. The suspended mixture was stirred at r.t. for 1 h. The resultant solution was centrifuged and filtered by a membrane filter (0.20 μm) to give a solution of $2 \cdot (3b)_2$. The fluorescence properties of $2 \cdot (3b)_2$ were analyzed by optical spectrometers. The host-guest composition of $2 \cdot (3b)_2$ was confirmed by the ¹H NMR spectrum in DMSO-*d*₆ after vacuum freeze-drying.

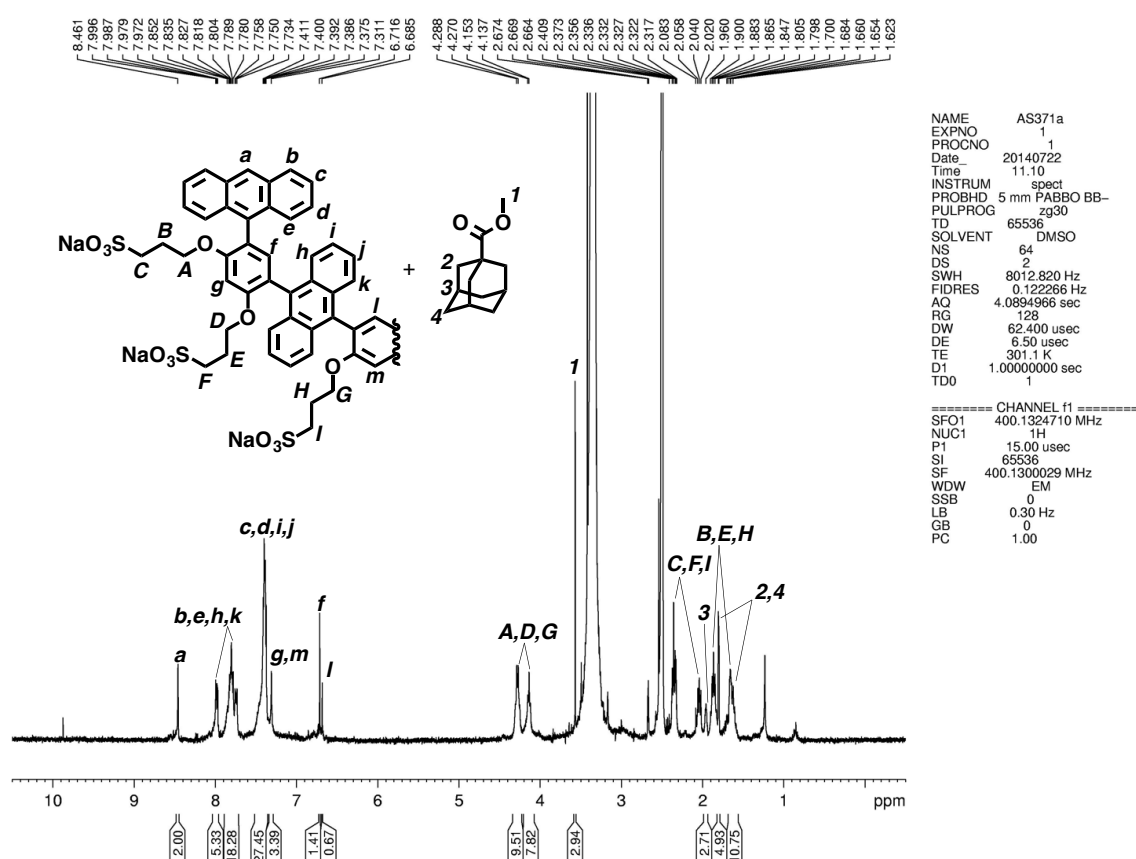
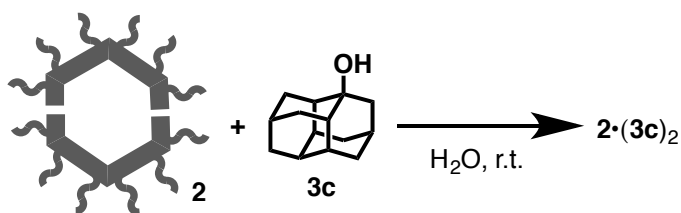


Figure S36. ¹H NMR spectra (400 MHz, DMSO-*d*₆, r.t.) of $2 \cdot (3b)_2$.

Preparation of $2 \cdot (3c)_2$

AS370, 565



An excess amount of methyl 1-diamantanol (**3c**; 1.5 mg, 7.1 μmol) was added to a H₂O solution (0.7 mL) of capsule **2** (1.3 mg, 0.70 μmol based on *cis,cis*-**1a**) in a test tube. The suspended mixture was stirred at r.t. for 1 h. The resultant solution was centrifuged and filtered by a membrane filter (0.20 μm) to give a solution of $2 \cdot (3c)_2$. The fluorescence properties of $2 \cdot (3c)_2$ were analyzed by optical spectrometers. The host-guest composition of $2 \cdot (3c)_2$ was confirmed by the ¹H NMR spectrum in DMSO-*d*₆ after vacuum freeze-drying.

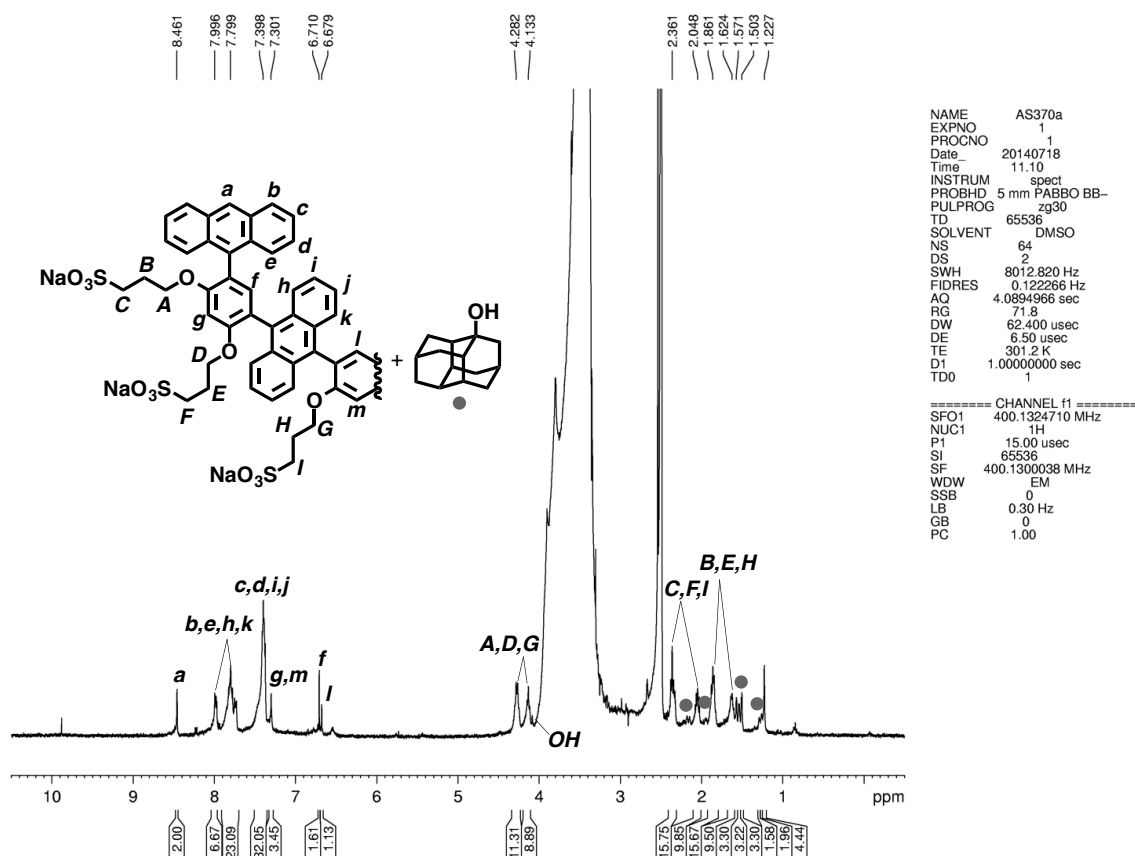


Figure S37. ¹H NMR spectra (400 MHz, DMSO-*d*₆, r.t.) of $2 \cdot (3c)_2$.

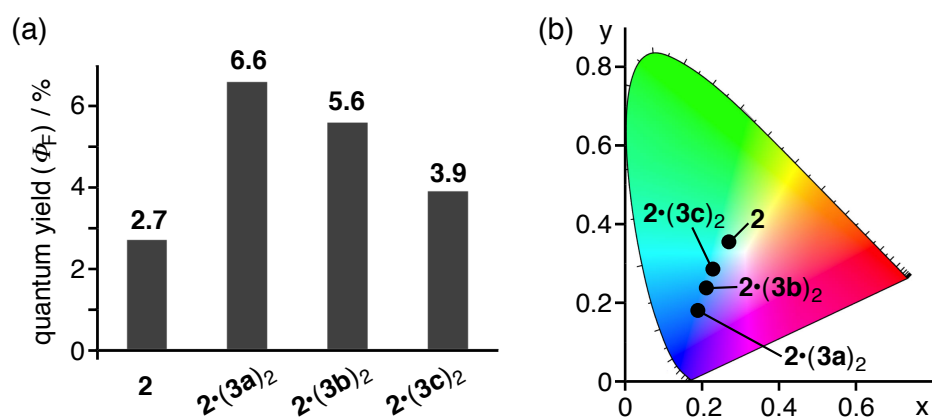


Figure S38. (a) Quantum yield (Φ_F) and (b) CIE chromaticity (x and y values) of **2·(3a-c)₂** (H₂O, 1.0 mM based on **1a**, r.t., λ_{ex} = 370 nm).

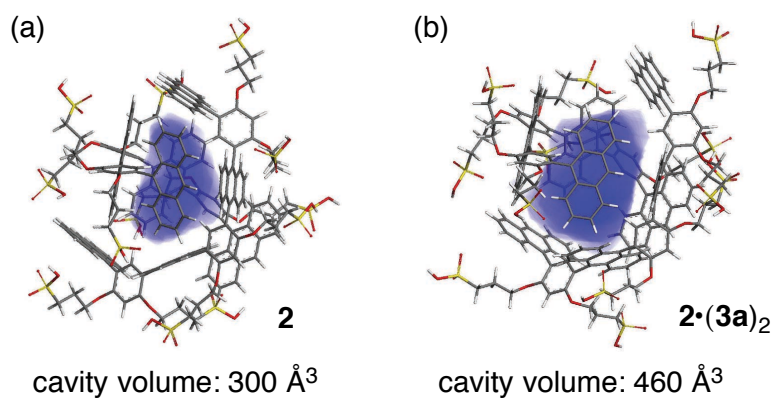
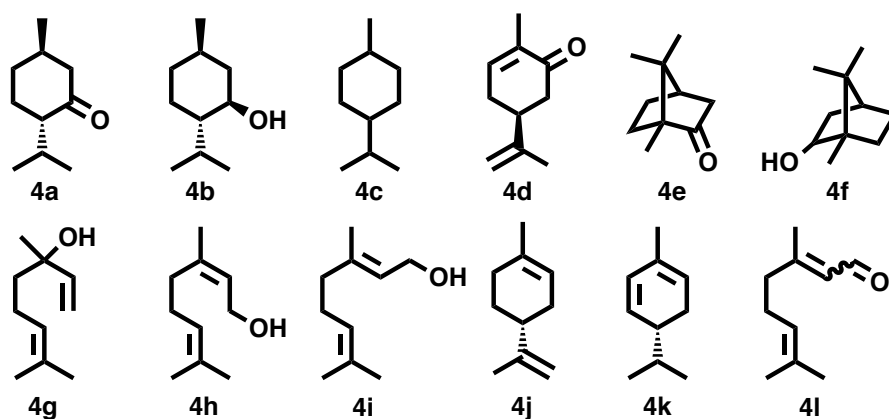
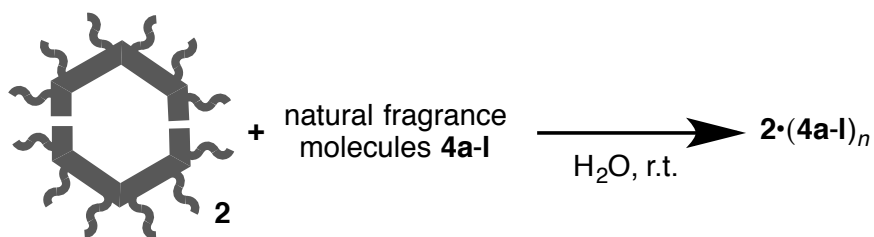


Figure S39. Cavity volumes (blue mesh) of (a) **2** and (b) **2·(3a)₂** based on the optimized structure.

Detection of natural fragrance compounds **4a-l** by capsule **2**

AS561, 562, 563, 564, 566, 567, 569



An excess amount of (-)-menthone (**4a**; 1.1 mg, 7.3 μmol) was added to a H_2O solution (0.7 mL) of capsule **2** (1.3 mg, 0.70 μmol based on *cis,cis*-**1a**) in a test tube. The suspended mixture was stirred at r.t. for 1 h. The resultant solution was centrifuged and filtered by a membrane filter (0.20 μm) to give a solution of **2·(4a)_n**. The fluorescent properties of the host-guest complex were analyzed by optical spectrometers. Host-guest composites **2·(4b-l)_n** were also prepared and analyzed by the same procedures. The experiments were conducted at least three times for each sample and the average values of Φ_{F} , x , and y were used. The error bars denote the standard deviation.

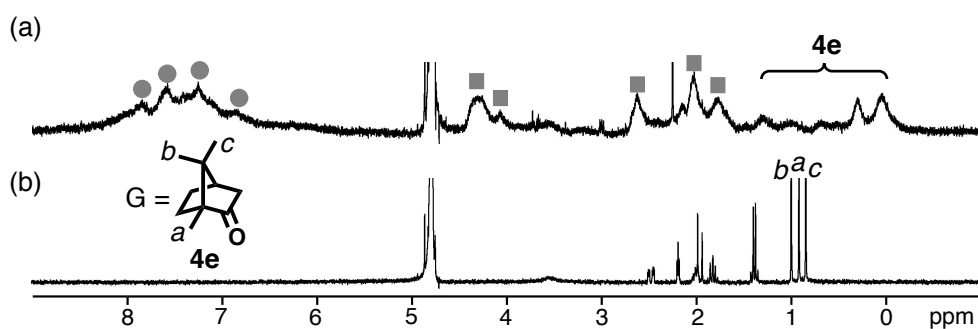


Figure S40a. ¹H NMR spectra (400 MHz, D₂O, r.t.) of (a) $2 \cdot (4e)_n$ and (b) (+)-camphor (4e). The gray circles and squares indicate the aromatic moieties and hydrophilic chains of **2**, respectively.

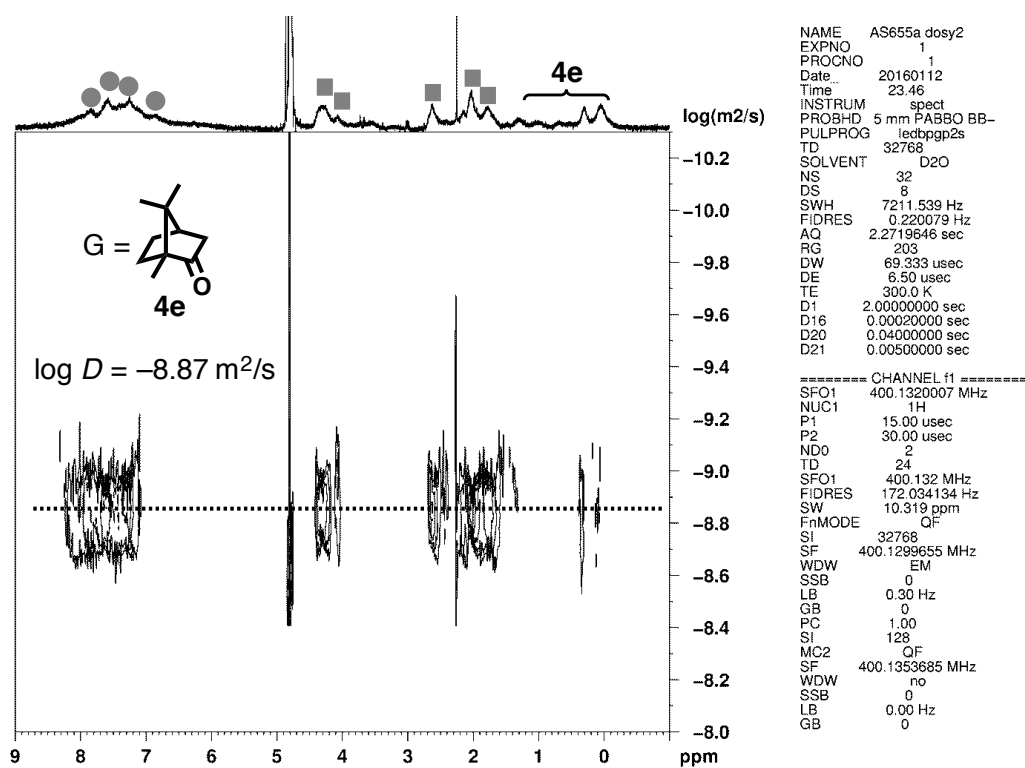


Figure S40b. DOSY NMR spectrum (400 MHz, D₂O, r.t.) of $2 \cdot (4e)_n$. The gray circles and squares indicate the aromatic moieties and hydrophilic chains of **2**, respectively.

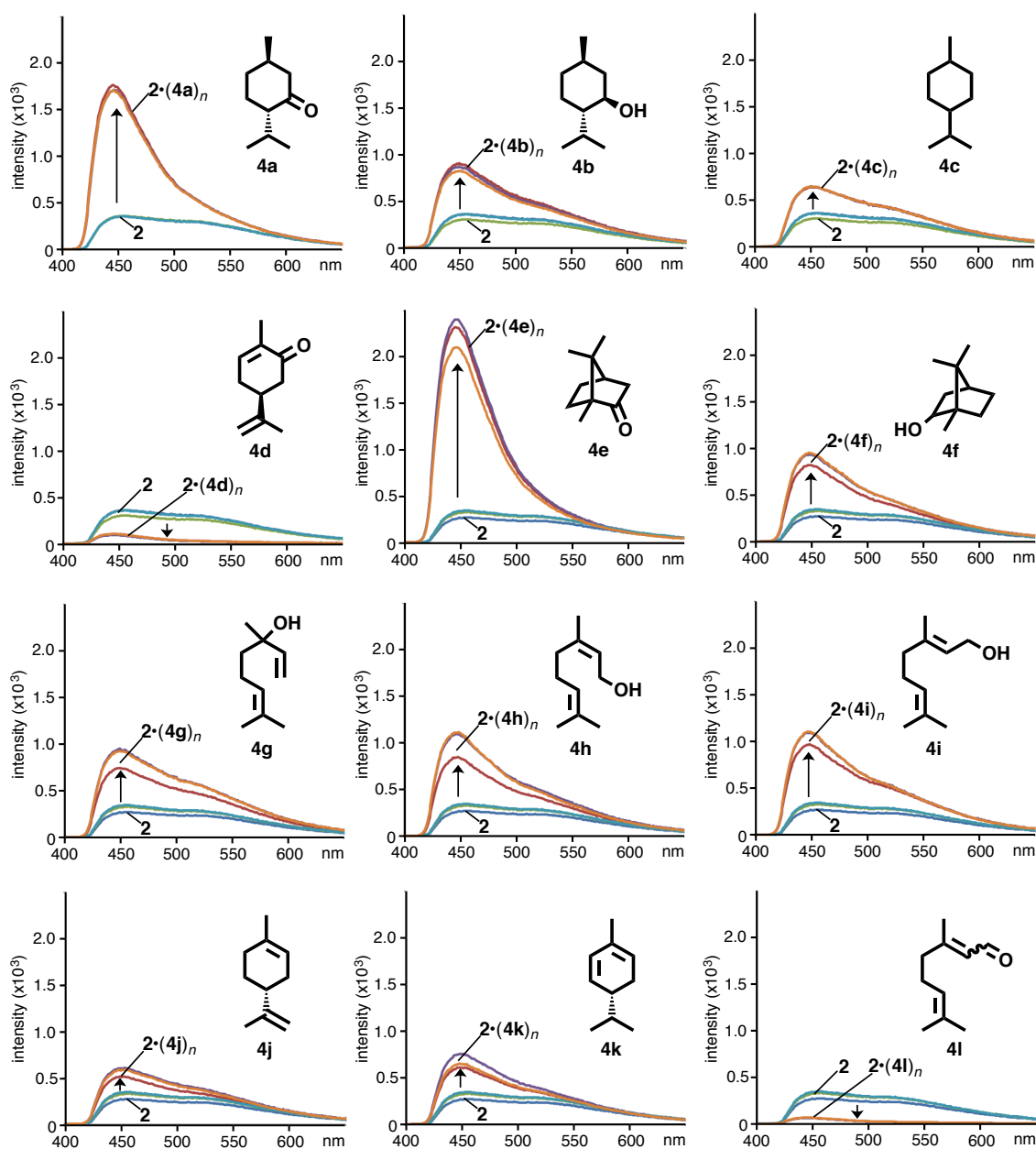


Figure S41. Fluorescence spectra (H_2O , 1.0 mM based on **1a**, r.t., $\lambda_{\text{ex}} = 370$ nm) of the host-guest complexes **2•(4a-l)_n**.

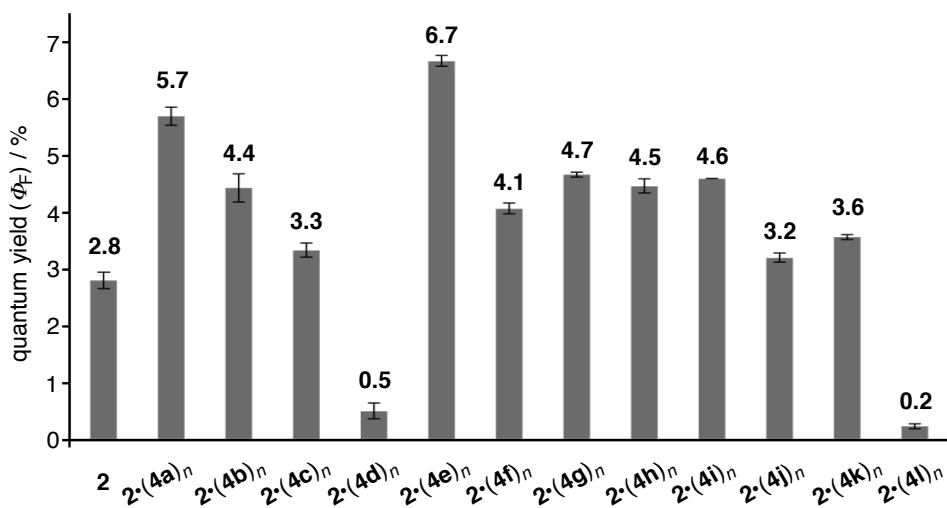


Figure S42. Quantum yields (Φ_F) of $2\bullet(4a-l)_n$ (H_2O , 1.0 mM based on **1a**, r.t., $\lambda_{ex} = 370$ nm).

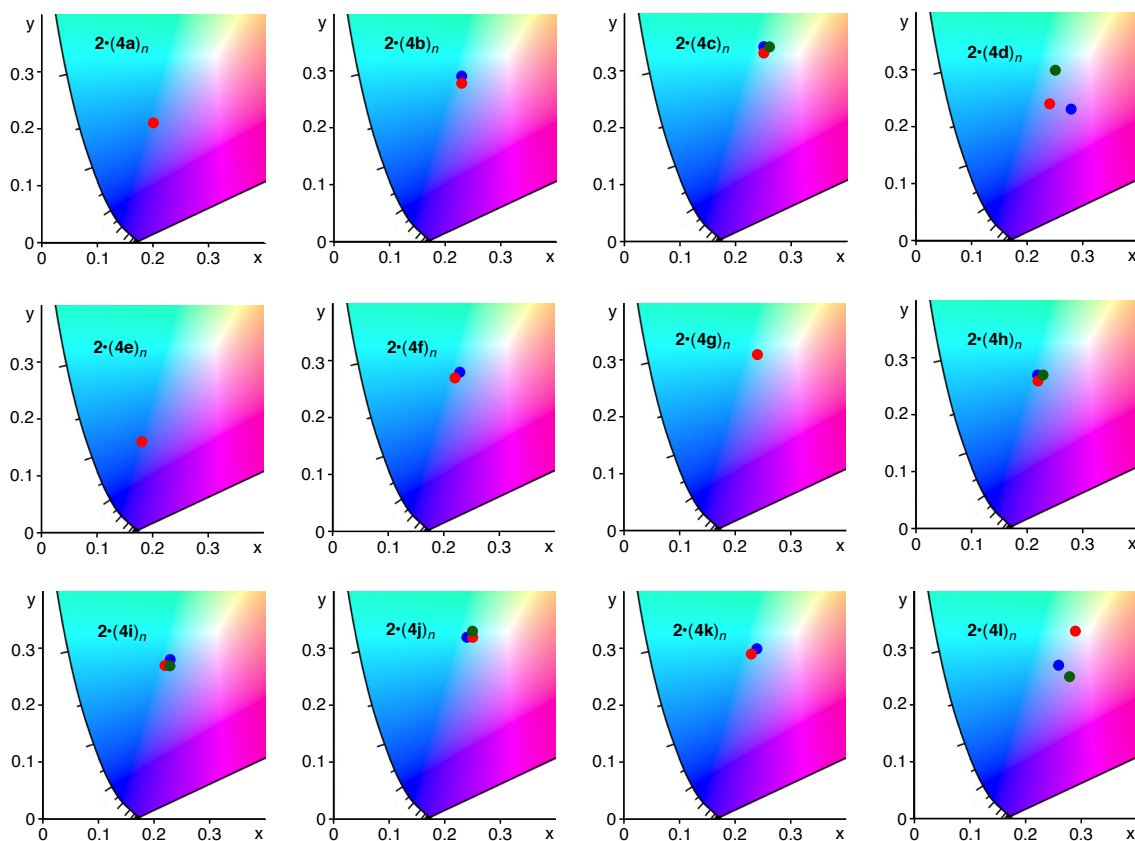


Figure S43. CIE chromaticity (x and y values) of $2\bullet(4a-l)_n$ (H_2O , 1.0 mM based on **1a**, r.t., $\lambda_{ex} = 370$ nm).