Chemical Communications
Electronic supplementary information

Arylene–hexaynylene and –octaynylene macrocycles: Extending the polyyne chains drives self-association by enhanced dispersion forces

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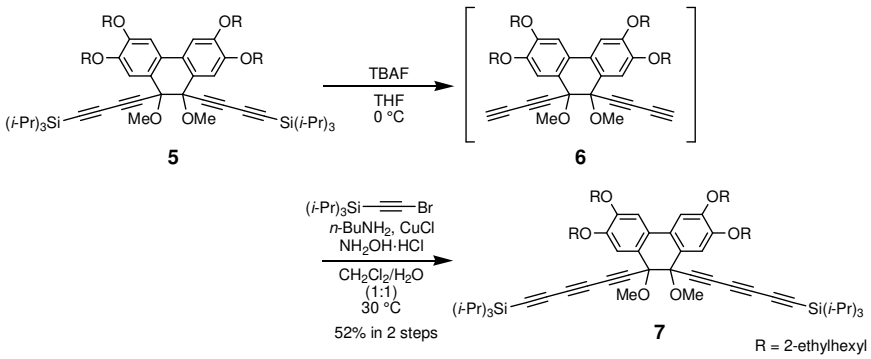
1. Experimental Details

A. Synthesis of Compounds

Commercially available reagents and solvents were used as received: THF was distilled from Na/benzophenone. Compound **5** was prepared according to the literature procedures.[1] Oil bath was used as the heat source. Column chromatography and plug filtrations were carried out with SiO_2. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254}. Melting points (M.p.) were measured with a hot-stage apparatus (Yanako MP-S3) and are uncorrected. Recycling gel-permeation chromatography (JAIGEL LC-918) was performed with UV detectors using 1H and 2H polystyrene columns eluting with $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded on a spectrometer (JEOL JNM-ECA600, JNM-ECS400, or JNM-ECS300) at 600 or 400 MHz for ^1H and 150 or 75 MHz for ^{13}C, respectively. Residual solvent signal ($CHCl_3$) in the ^1H and ^{13}C NMR spectra was used as an internal reference. MALDI-TOF-MS (Shimadzu Biotech Axima Performance) and FT-MS (Thermo Fisher Scientific LTQ Orbitrap XL) spectrometric analyses were conducted in a positive mode.

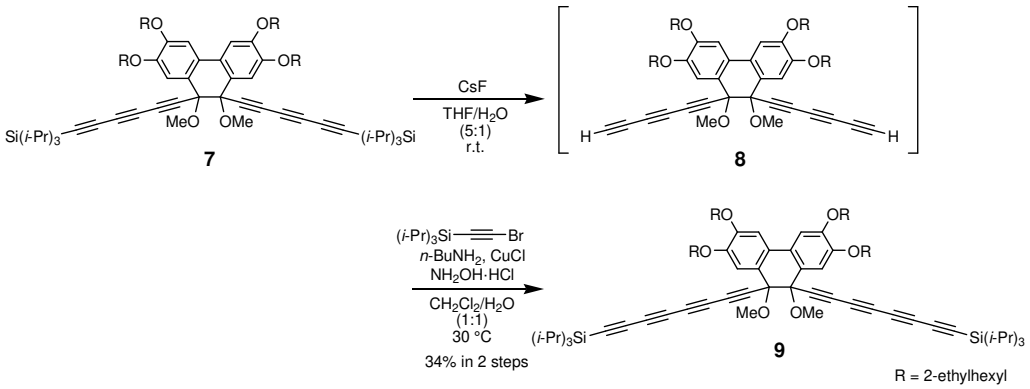
Preparation of hexatriynyl-substituted dihydrophenanthrene 7



To a solution of butadiynyl-substituted dihydrophenanthrene **5** (3.58 g, 3.08 mmol, probably *trans* isomer) in THF (200 mL) was added dropwise a tetrabutylammonium fluoride THF solution (1.0 mol L^{-1}, 15.4 mL, 15.4 mmol) at 0 °C. After the mixture was stirring for 15 min, the resulting mixture was diluted with CH_2Cl_2. The mixture was concentrated under reduced pressure to approximately 1 mL. The resulting mixture was subjected to silica gel column chromatography (CH_2Cl_2) to give a yellow solution of desilyated alkyne **6**, which was used in the next coupling reaction without further purification due to the instability. To a suspension of desilylated alkyne **6**, CuCl (304 mg, 3.08 mmol), and *n*-$BuNH_2$ (10.6 mL, 108 mmol) in H_2O (50 mL) and CH_2Cl_2 (50 mL) was added $NH_2OH{\cdot}HCl$ at 0 °C under an argon atmosphere until the original blue color of the suspension disappeared. A solution of (2-bromoethynyl)triisopropylsilane (3.21 g, 12.3 mmol) in CH_2Cl_2 (10 mL) was then added dropwise to the mixture. After the mixture was stirred at 30 °C for 12 h, H_2O was added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure.

The residue was purified by silica gel column chromatography (hexane/EtOAc, 40:1) to afford hexatriynyl-substituted dihydrophenanthrene **7** (2.03 g, 1.68 mmol, 52%) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, probably *trans* isomer): δ 7.24 (s, 2H), 7.11 (s, 2H), 3.97–3.95 (m, 8H), 3.14 (s, 6H), 1.82–1.74 (m, 4H), 1.61–1.32 (m, 32H), 1.11 (brs, 42H), 0.99–0.89 (m, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 150.53, 150.50, 148.34, 125.02, 122.98, 115.60, 115.59, 110.00, 89.85, 85.61, 82.00, 75.56, 74.14, 72.08, 72.03, 71.74, 64.40, 60.67, 52.91, 39.80, 39.71, 30.80, 30.74, 29.25, 24.08, 23.25, 18.67, 14.27, 11.41 (29 signals out of 32 expected); UV–vis (CH_2Cl_2): λ_{max} = 432 nm; HR-APCI-MS (FT, positive): *m*/*z* calcd for $C_{78}H_{120}O_6Si_2$: 1208.8618, found: 1208.8629 [M^+].

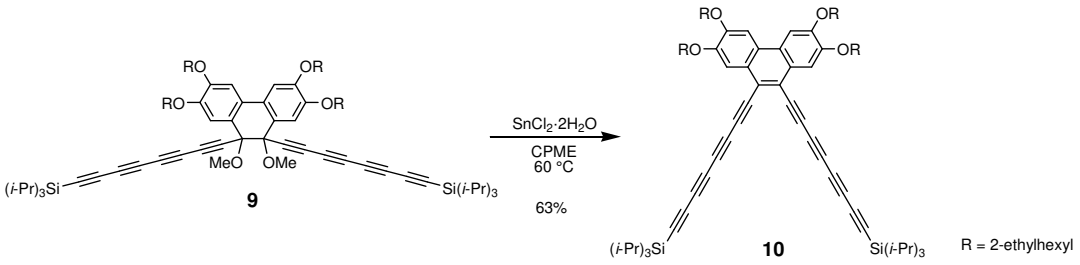
Preparation of octatetraynyl-substituted dihydrophenanthrene 9



A solution of **7** (260 mg, 0.215 mmol) and cesium fluoride (78 mg, 0.52 mmol) in THF/H_2O (5:1, 12 mL) was stirred at room temperature for 15 h. Then, CH_2Cl_2 (10 mL) and H_2O (10 mL) were added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to approximately 1 mL. The resulting mixture was subjected to silica gel column chromatography (CH_2Cl_2) to give a yellow solution of desilylated alkyne **8**, which was used in the next coupling reaction without further purification due to the instability. To a suspension of desilylated alkyne **8**, CuCl (21 mg, 0.22 mmol), and *n*-$BuNH_2$ (0.75 mL, 7.5 mmol) in H_2O (5 mL) and CH_2Cl_2 (5 mL) was added $NH_2OH{\cdot}HCl$ at 0 °C under an argon atmosphere until the original blue color of the suspension disappeared. A solution of (2-bromoethynyl)triisopropylsilane (225 mg, 0.865 mmol) in CH_2Cl_2 (5 mL) was then added dropwise to the mixture. After the mixture was stirred at 30 °C for 3 h, H_2O was added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 40:1) to afford octatetraynyl-substituted dihydrophenanthrene **9** (93 mg, 0.074 mmol, 34%) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, probably *trans* isomer): δ 7.21 (s, 2H), 7.11 (s, 2H), 3.97–3.95 (m, 8H), 3.15 (s, 6H), 1.79–1.76 (m, 4H), 1.60–1.28 (m, 32H), 1.10 (brs, 42H), 0.99–0.89 (m, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 150.62, 149.38, 148.42, 149.01, 145.82, 125.03, 122.63, 115.57, 110.05, 89.68, 86.32, 82.14, 82.94, 74.10, 72.05, 71.73, 64.62, 63.21, 61.35, 53.09, 39.79, 39.72, 30.85, 30.80,

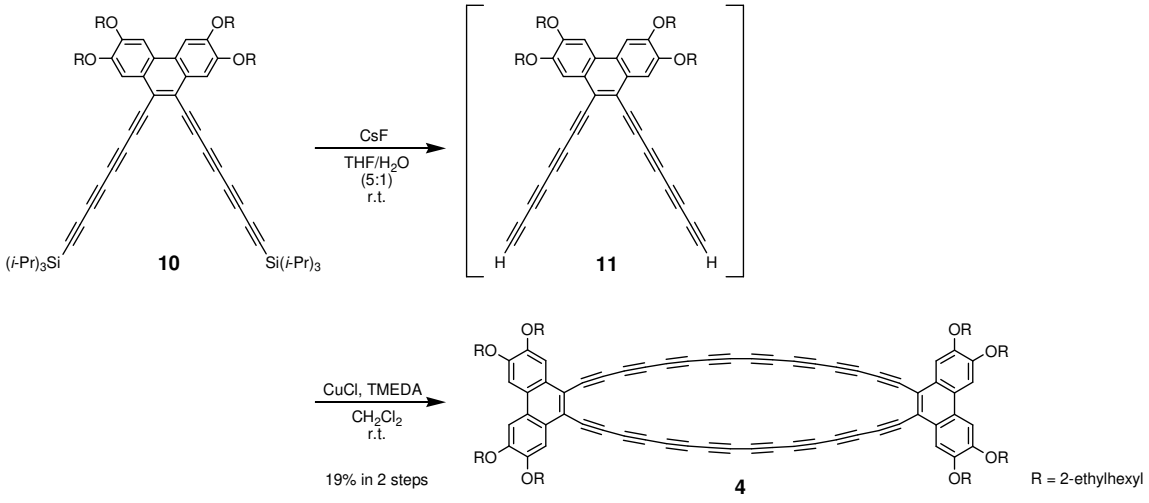
30.75, 24.08, 23.28, 18.67, 14.27, 11.42 (30 signals out of 34 expected); UV–vis (CH_2Cl_2): λ_{max} = 459 nm; HR-APCI-MS (FT, positive): *m/z* calcd for $C_{82}H_{120}O_6Si_2$: 1256.8618, found: 1256.8621 [M^+].

Preparation of octatetraynyl-substituted phenanthrene 10



A solution of octatetraynyl-substituted dihydrophenanthrene **9** (93 mg, 0.074 mmol) and $SnCl_2 \cdot H_2O$ (83 mg, 0.37 mmol) in CPME (5 mL) was bubbled with argon with stirring for 30 min. After the mixture was stirred at 60 °C for 24 h, H_2O was added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column (hexane/CH_2Cl_2, 5:1) to afford octatetraynyl-substituted phenanthrene **10** (55 mg, 0.046 mmol, 63%) as orange solids. M.p. 149–151 °C; ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.66 (s, 2H), 7.51 (s, 2H), 4.12 (d, 4H, *J* = 7.2 Hz), 4.06 (d, 4H, *J* = 7.2 Hz), 1.92–1.82 (m, 4H), 1.62–1.32 (m, 32H), 1.11 (brs, 42H), 1.03–0.90 (m, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 153.76, 151.47, 150.38, 149.01, 145.82, 126.02, 124.85, 120.89, 107.65, 104.48, 90.20, 89.86, 82.94, 75.22, 71.67, 71.21, 70.49, 66.19, 61.80, 61.58, 39.67, 39.51, 31.04, 24.16, 23.27, 18.96, 14.27, 11.54, 11.45 (29 signals out of 33 expected); UV–vis (CH_2Cl_2): λ_{max} = 462 nm; HR-APCI-MS (FT, positive): *m/z* calcd for $C_{80}H_{114}O_4Si_2$: 1194.8250, found: 1194.8265 [M^+].

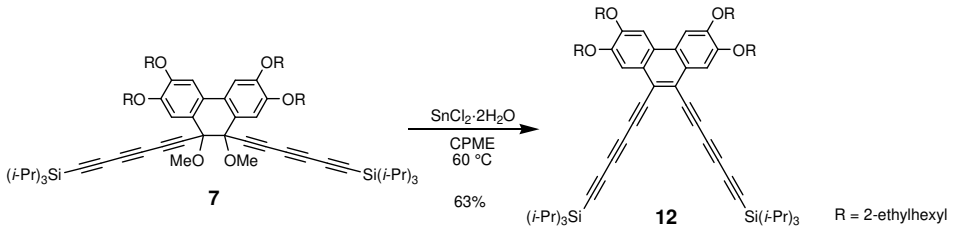
Preparation of macrocycle 4



A solution of octatetraynyl-substituted phenanthrene **10** (95 mg, 0.079 mmol) and cesium fluoride (29 mg, 0.19 mmol) in THF/H_2O (5:1, 25 mL) was stirred at room temperature for 8 h. Then, CH_2Cl_2 (10

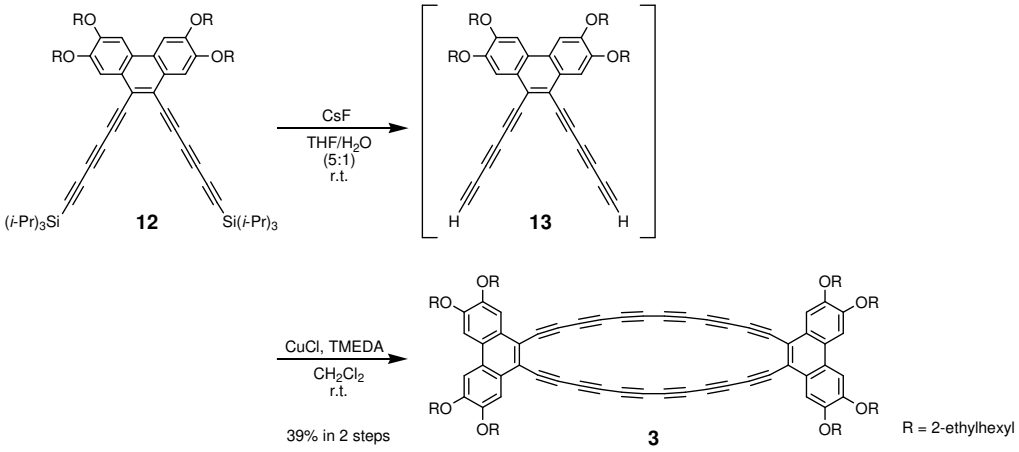
mL) and H_2O (10 mL) were added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to approximately 1 mL. The resulting mixture was subjected to silica gel column chromatography (CH_2Cl_2) to give to a yellow solution of desilylated alkyne **11,** which was used in the next coupling reaction without further purification due to the instability. To a mixture of the desilylated alkyne **11** and TMEDA (59 μL, 0.40 mmol) in CH_2Cl_2 (7.9 mL) was added CuCl (39 mg, 0.40 mmol) at room temperature, and the resulting mixture was stirred for 10 min. The mixture was filtrated through a bed of silica gel and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2, 5:1) and recycling GPC eluting with $CHCl_3$ to afford macrocycle **4** (13 mg, 0.0074 mmol, 19%) as deep red solids. M.p. Not clear (decomp.); ^{1}H NMR ($CDCl_3$, 600 MHz, 1.89 mmol L^{-1}): δ 7.37 (s, 4H), 7.24 (s, 4H), 3.96–3.91 (m, 16H), 1.84–1.79 (m, 8H), 1.61–1.32 (m, 64H), 0.99–0.90 (m, 48H); ^{13}C NMR ($CDCl_3$, 150 MHz): 151.25, 150.04, 125.12, 124.52, 124.02, 101.38, 84.56, 71.93, 71.42, 71.08, 67.99, 66.19, 65.48, 65.10, 64.29, 39.45, 39.40, 30.78, 29.67, 29.38, 29.23, 24.12, 23.98, 23.32, 23.27, 14.31, 14.27, 11.47 (28 signals out of 31 expected); UV–vis ($CHCl_3$): λ_{max} (ε) = 276 (174000), 292 (168000), 337 (227000), 382 (55800), 412 (63000), 467 (53200), 506 (53800), 554 (20000) nm; HR-ESI-MS (FT, positive): $C_{124}H_{144}O_8$: 1761.0855, found: 1761.0867 [M^+].

Preparation of hexatriynyl-substituted phenanthrene 12



A solution of hexatriynyl-substituted dihydrophenanthrene **7** (2.00 g, 1.65 mmol) and $SnCl_2{\cdot}2H_2O$ (1.86 g, 8.26 mmol) in CPME (150 mL) was bubbled with argon with stirring for 30 min. After the mixture was stirred at 60 °C for 24 h, H_2O was added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2, 5:1) to afford hexatriynyl-substituted phenanthrene **12** (1.21 g, 1.05 mmol, 63%) as yellow solids. M.p. 145–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (s, 2H), 7.57 (s, 2H), 4.12–4.07 (m, 8H), 1.90–1.81 (m, 4H), 1.61–1.34 (m, 32H), 1.13 (brs, 42H), 1.03–0.90 (m, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 151.28, 151.03, 150.03, 126.05, 124.71, 120.99, 107.79, 104,55, 90.12, 88.32, 74.63, 71.68, 71.22, 70.12, 61.12, 48.54, 39.67, 39.52, 30.31, 24.25, 24.13, 23.28, 23.24, 18.72, 14.27, 11.51, 11.48 (27 signals out of 31 expected); UV–vis (CH_2Cl_2): λ_{max} = 432 nm; HR-APCI-MS (FT, positive): *m/z* calcd for $C_{76}H_{114}O_4Si_2$: 1146.8250, found: 1146.8271 [M^+].

Preparation of macrocycle 3



A solution of hexatriynyl-substituted phenanthrene **12** (88 mg, 0.077 mmol) and cesium fluoride (28 mg, 0.18 mmol) in THF/H_2O (5:1, 25 mL) was stirred at room temperature for 15 h. Then, CH_2Cl_2 (10 ml) and H_2O (10 mL) were added to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to approximately 1 mL. The resulting mixture was subjected to silica gel column chromatography (CH_2Cl_2) to give a yellow solution of desilylated alkyne **13**, which was used in the next coupling reaction without further purification due to the instability. To a mixture of the desilylated alkyne **13** and TMEDA (58 μL, 0.38 mmol) in CH_2Cl_2 (7.6 mL) was added CuCl (38 mg, 0.38 mmol) at room temperature, and the resulting mixture was stirred for 1 h. The mixture was filtrated through a bed of silica gel, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/toluene, 3:1) to afford macrocycle **3** (25 mg, 0.023 mmol, 39%) as deep red solids. M.p. Not clear (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, 1.94 mmol L^{-1}): δ 7.53 (s, 4H), 7.28 (s, 4H), 4.04 (d, 8H, J = 7.2 Hz), 3.99 (d, 8H, J = 7.2 Hz), 1.88–1.78 (m, 8H), 1.60–1.31 (m, 64H), 1.01–0.89 (m, 48H); ^{13}C NMR ($CDCl_3$, 150 MHz): 151.39, 150.19, 125.07, 124.68, 124.45, 107.58, 104.07, 84.75, 80.02, 71.78, 71.53, 71.14, 67.86, 66.02, 64.92, 39.52, 30.82, 29.37, 29.29, 24.14, 24.06, 23.27, 14.29, 11.48 (24 signals out of 29 expected); UV–vis ($CHCl_3$): λ_{max} (ε) = 276 (135000), 291 (129000), 336 (165000), 382 (41800), 411 (46600), 466 (39000), 506 (39600), 554 (14800) nm; HR-ESI-MS (FT, positive): *m/z* calcd for $C_{116}H_{144}O_8$: 1665.0855, found: 1665.0865 [M^+].

B. UV–vis Spectroscopy and Cyclic Voltammetry

Electronic absorption spectra (JASCO JV-550 or HITACHI U-3000) were measured in a cuvette of 1 cm or 0.1 cm at room temperature. Cyclic voltammetry and differential pulse voltammetry (EC Frontier ECstat-100) were performed by using a cell equipped with platinum as a working electrode, a platinum wire as counter electrodes, and $Ag/AgNO_3$ as a referential electrode. All electrochemical measurements were performed in CH_2Cl_2 solution (*ca.* 5×10^{-4} mol L^{-1}) containing 0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6] at room temperature. All potentials are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple, used as a standard.

C. Evaluation of Self-Association

Electronic absorption spectra (JASCO JV-550 or HITACHI U-3000) were measured in a cuvette of 1 cm or 0.1 cm at room temperature: the spectroscopic measurements in methylcyclohexane at various temperature were carried out with a Peltier-type temperature controller.

Monomer–Dimer Model:[2] The monomer–dimer model is the one for the description of dimerization. The ^{1}H NMR spectra were measured at various concentrations. According to the monomer–dimer model, the relationship between the observed chemical shifts (δ_{obs}) and the total concentration (C_T) is expressed as:

$$\delta_{obs} = \delta_{mon} + (\delta_{agg} - \delta_{mon})\ (4KC_T + 1 - (8KC_T + 1)^{1/2})\ /\ 4KC_T$$

where K is the association constant, δ_{agg} is chemical shifts of aggregated species, δ_{mon} is chemical shifts of monomer. The observed chemical-shift data were analyzed by a nonlinear least-squares method fit to Kaleida Graph Program[3] give best-fit values for variables K, δ_{mon}, and δ_{agg}.

Isodesmic Model:[4] The isodesmic model is the model for the description of extended aggregates. In this model, the aggregates are assumed to be one-dimensional. For all the binding events *i.e.* the addition of one monomer to another monomer or any aggregated species, the equilibrium constants are equal. The UV–vis spectra were measured at various concentrations or temperatures. According to the isodesmic model, the relationship between observed molar excitation coefficient (ε_{obs}) and C_T is expressed as:

$$\varepsilon_{obs} = \varepsilon_{mon} + (\varepsilon_{agg} - \varepsilon_{mon})\ (1 - (2KC_T + 1 - (4KC_T + 1)^{1/2})\ /\ 2K^2C_T^2)$$

where K is association constant, ε_{agg} and ε_{mon} are the molar excitation coefficients for the monomer and the aggregated species, respectively. The observed chemical-shift or molar excitation coefficients data were analyzed by a nonlinear least-squares method fit to Kaleida Graph Program[3] to give best-fit values for variables K, ε_{mon}, and ε_{agg}.

D. Theoretical Calculations

Quantum Chemical Calculations. All DFT calculations were performed by using the restricted DFT (RDFT) implemented in the Gaussian16 program package.[5] Pair interaction energy decomposition analyses (PIEDA)[6,7] were carried out for **1′**$_2$–**4′**$_2$ at the HF/6-31G(d) level of theory. The interaction energies were calculated by using the ab initio fragment molecular orbital method[8] at the HF/6-31G(d) level of theory. To estimate E_{DISP}, calculated HF energies were corrected for dispersion interactions by using Grimme's dispersion correction scheme D3,[9–11] which is computationally inexpensive and can reasonably account for E_{DISP}.[12,13] Based on the optimized geometries of the dimer models, PIEDA implemented in the GAMESS program package[14] was carried out to determine the energetic components governing the molecular interactions. The total interaction energy (E_{INT}) can be partitioned into the electrostatic (E_{ES}), exchange-repulsion (E_{EX}), charge-transfer (E_{CT}), and dispersion (E_{DISP}) contributions:

$$E_{INT} = E_{ES} + E_{EX} + E_{CT} + E_{DISP}$$

where E_{EX} is repulsive while others are attractive. E_{CT} includes higher-order mixed terms because it is calculated by subtracting the other two (electrostatic + exchange) components from the total pair interaction energy.

Molecular Dynamics Simulations. The BIOVIA Materials Studio 2020 (ver. 20.1.0.2728) was used for calculations.[15] Parameters for the molecular dynamics simulations were: COMPASS III force field as implemented, ultra-fine quality, NVE ensemble, temperature 298 K, time step 1.0 fs, total simulation time 100 ps. 201 structures were sampled over the simulation time (output every 500 frames/100000 steps).

2. Supporting Figures and Tables

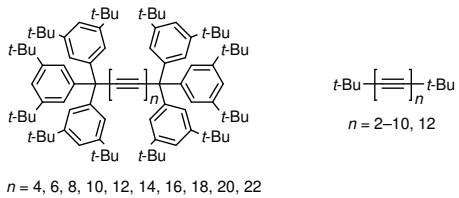
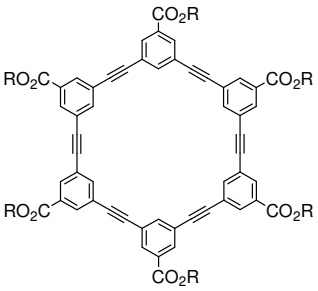
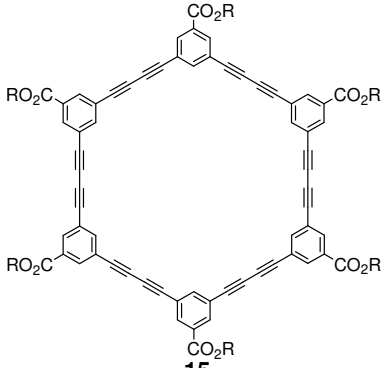


Figure S1. Chemical structures of Tykwinski's polyynes mentioned in this paper.[16,17] It should be noticed that Tykwinski and co-workers have very recently isolated a polyyne featuring 24 contiguous C≡C bonds; for details, see: Y. Gao, Y. Hou, F. G. Gámez, M. J. Ferguson, J. Casado, R. R. Tykwinski, *Nat. Chem.*, 10.1038/s41557-020-0550-0.



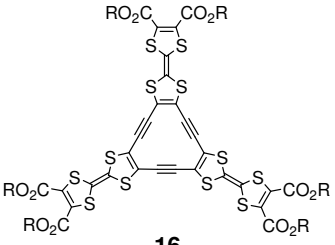
14 R = *n*-Oct

K = 39 L mol^{-1}
(In $CDCl_3$) [18]



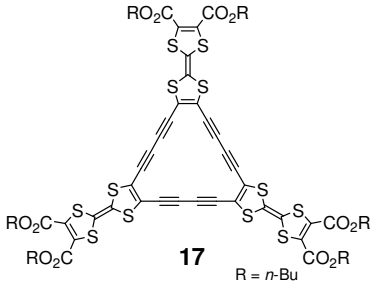
15 R = *n*-Oct

K = 173 L mol^{-1}
(In $CDCl_3$) [19]



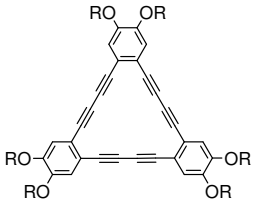
16 R = *n*-Bu

K = 176 L mol^{-1}
(In toluene-d_8) [20]



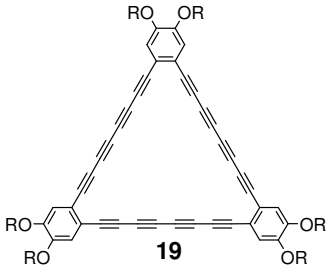
17 R = *n*-Bu

K = 522 L mol^{-1}
(In toluene-d_8) [20]



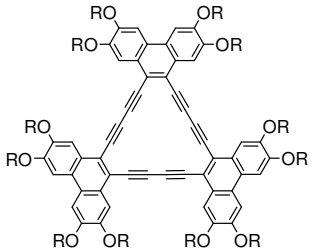
18 R = *n*-Bu

Almost no self-association
(In $CDCl_3$) [21]



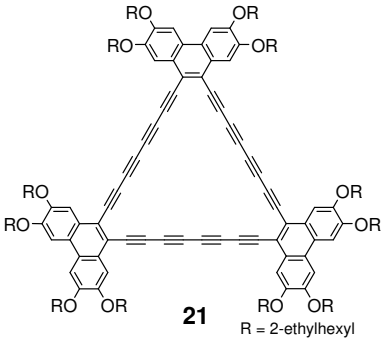
19 R = *n*-Bu

K = 4 L mol^{-1}
(In $CDCl_3$) [22]



20 R = 2-ethylhexyl

K = 16 L mol^{-1}
(In methylcyclohexane) [1]



21 R = 2-ethylhexyl

K = 33000 L mol^{-1}
(In methylcyclohexane) [1]

Figure S2. Chemical structures of selected arylene–alkynylene macrocycles and self-association constants (K).

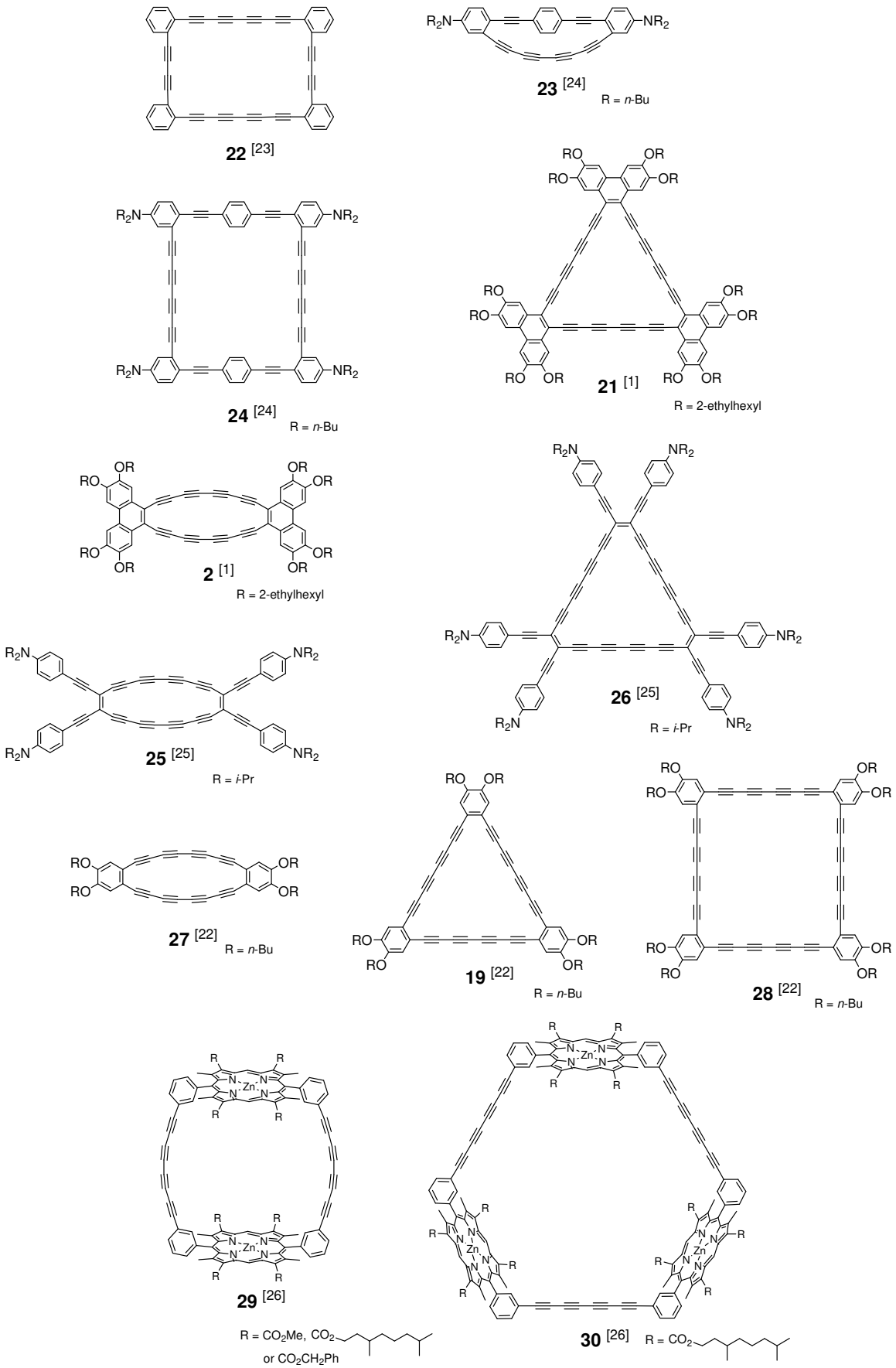


Figure S3. Chemical structures of arylene–alkynylene macrocycles possessing tetrayne moieties. Macrocycles **22**, **24**, **28**, **29**, and **30** are nonplanar.

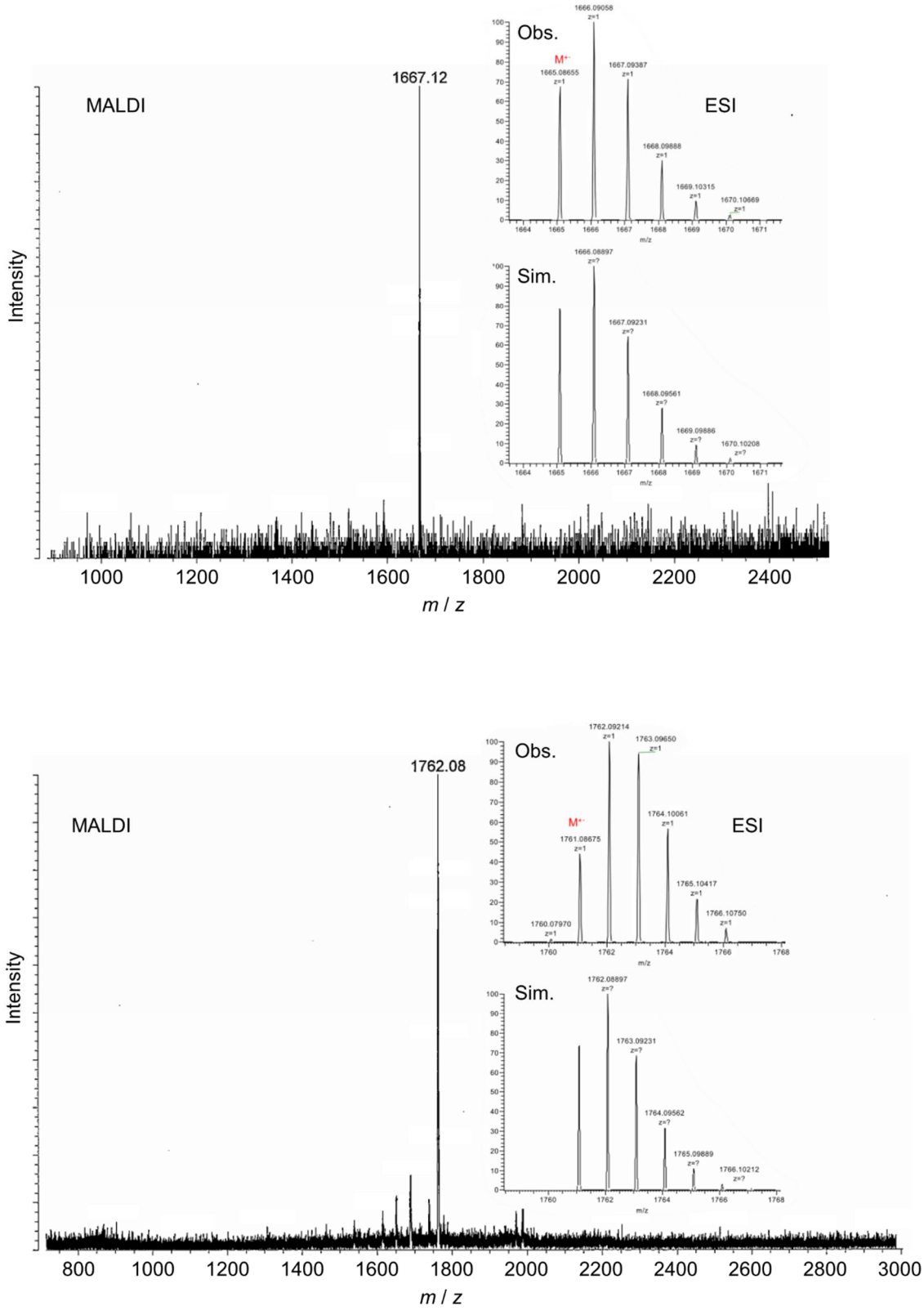


Figure S4. MALDI-TOF-MS (dithranol, positive) of **3** (top) and **4** (bottom).
The parent [$(M+H)^+$] ion peaks were observed. Inset: HR-ESI-MS.

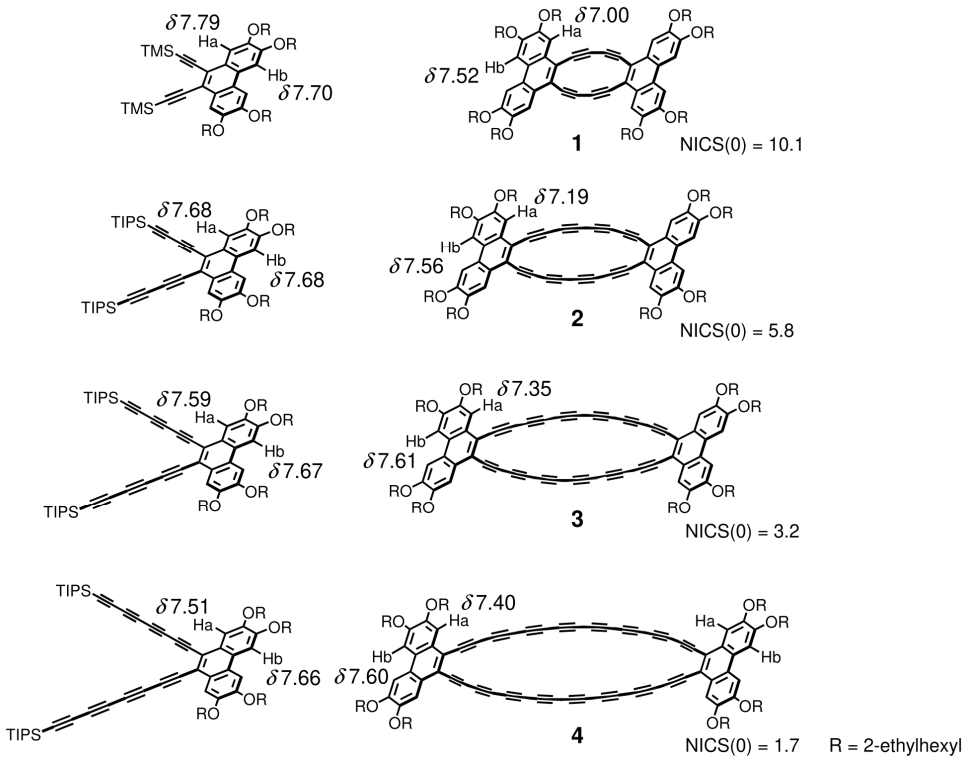


Figure S5. Summary of chemical shifts (ppm) in ^{1}H NMR spectra of **1**–**4** in $CDCl_3$. NICS calculations were performed in **1′**–**4′**, in which the 2-ethylhexyl groups in **1**–**4** were replaced with methyl groups, at the GIAO-B3LYP/6-311+G(d)//B3LYP/6-31G(d) level of theory.

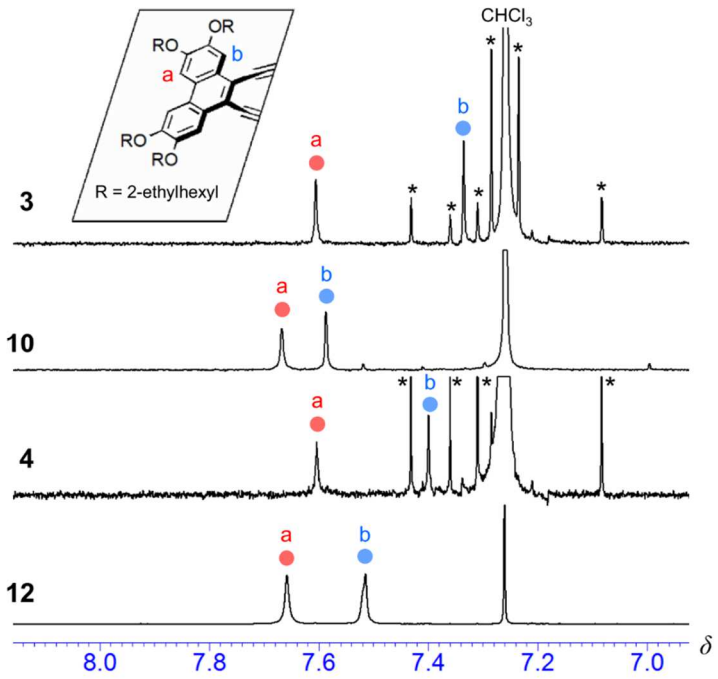


Figure S6. Partial ^{1}H NMR spectra of **3**, **4**, **10**, and **12** in $CDCl_3$. The peaks attributed to carbon satellites, spinning sidebands, and impurities included in $CDCl_3$ are labeled in asterisks. The spectra of highly diluted solutions of **3** and **4** were measured to estimate the chemical shifts of their monomeric species.

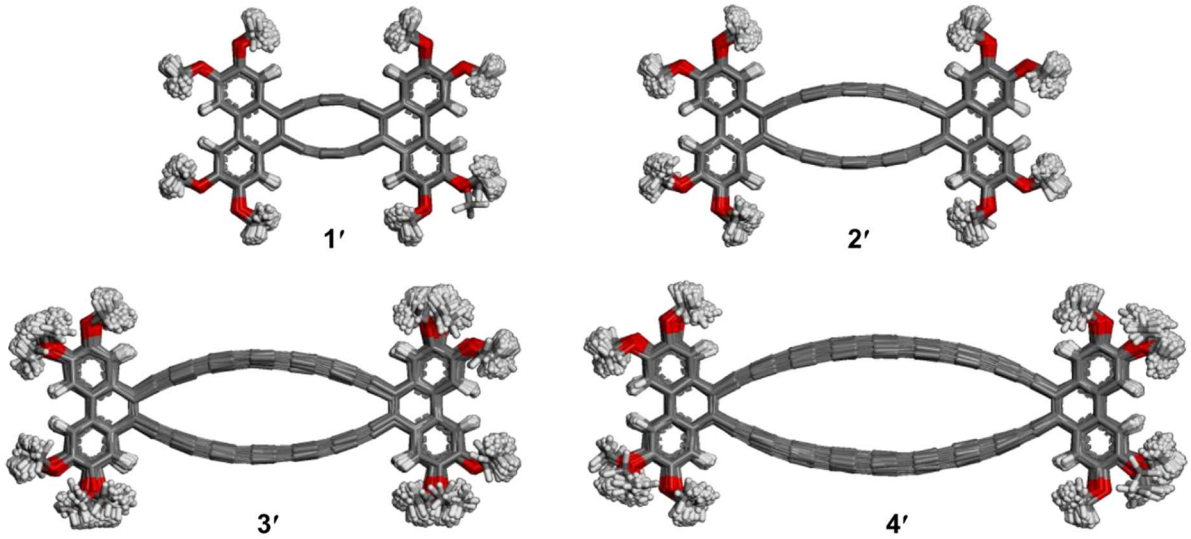


Figure S7. Overlays of 201 structures of **1′**–**4′**, in which the 2-ethylhexyloxy groups in **1**–**4** were replaced with methoxy groups, obtained by molecular dynamics simulations. The range of macrocyclic motion slightly increases with extending the polyyne moieties.

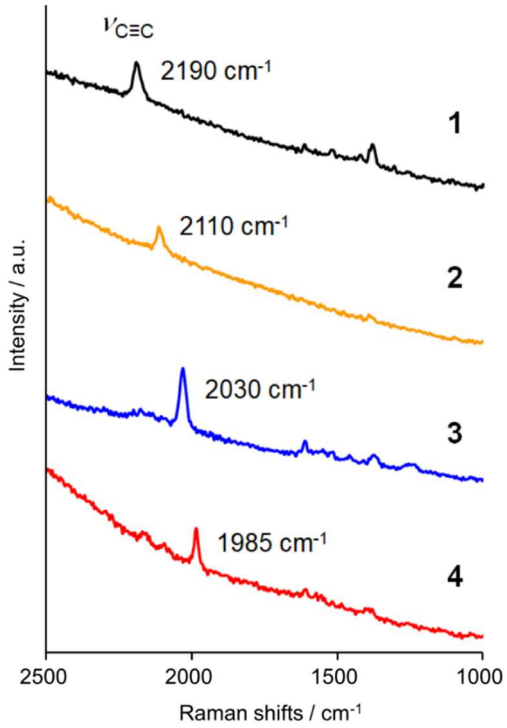
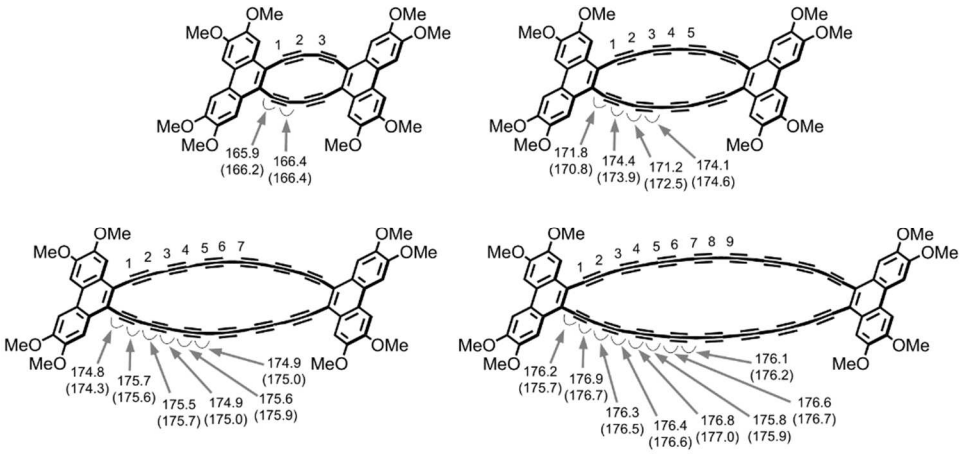


Figure S8. Raman spectra of solid samples of **1**–**4**. The Raman spectra of the samples were acquired with a 100X objective, which reduced the spatial resolution to 1 μm.

Table S1. Selected Bond Lengths (Å) and Angles (°) Tabulated for DFT-Optimized Structures of **1′**–**4′**[a]



Bond	**1′**	**2′**	**3′**	**4′**
C1–C2	1.223 (1.216)	1.226 (1.217)	1.228 (1.217)	1.228 (1.218)
C2–C3	1.364 (1.376)	1.350 (1.366)	1.346 (1.364)	1.345 (1.363)
C3–C4		1.233 (1.220)	1.235 (1.222)	1.236 (1.221)
C4–C5		1.344 (1.362)	1.340 (1.359)	1.337 (1.358)
C5–C6			1.236 (1.223)	1.238 (1.223)
C6–C7			1.338 (1.358)	1.335 (1.357)
C7–C8				1.239 (1.223)
C8–C9				1.334 (1.358)

[a] Values obtained at the B3LYP/6-31G(d) level of theory (values in parentheses refers to bond lengths and angles obtained at the M06-2X/6-31G(d) level of theory)

Table S2. Summary of BLA Data for DFT-Optimized Structures of **1′**–**4′**[a]

	1′	**2′**	**3′**	**4′**
BLA[b]	0.141 (0.160)	0.111 (0.142)	0.102 (0.135)	0.095 (0.135)
BLA_{avg}[c]	0.141 (0.160)	0.118 (0.146)	0.108 (0.140)	0.103 (0.138)

[a] Values obtained at the B3LYP/6-31G(d) level of theory (values in parentheses refers to bond lengths and angles obtained at the M06-2X/6-31G(d) level of theory) [b] The bond-length alternation (BLA) is defined as the bond length difference between the central single and the central triple bonds. [c] The averaged bond-length alternation (BLA_{avg}) is defined as the difference between the average of all single bonds of the alkyne segment (excluding the terminal C–C bond) and triple bonds.

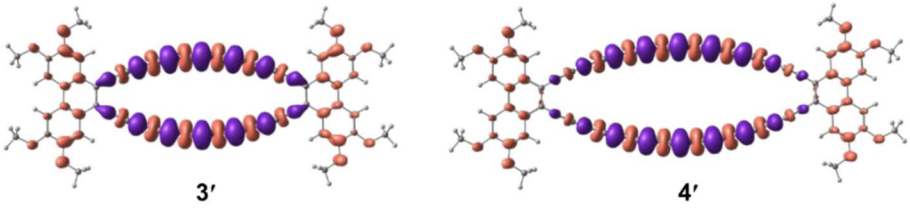


Figure S9. Electron density difference maps (EDDM) of the first electronic transitions of **3′** and **4′** at the TD-CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

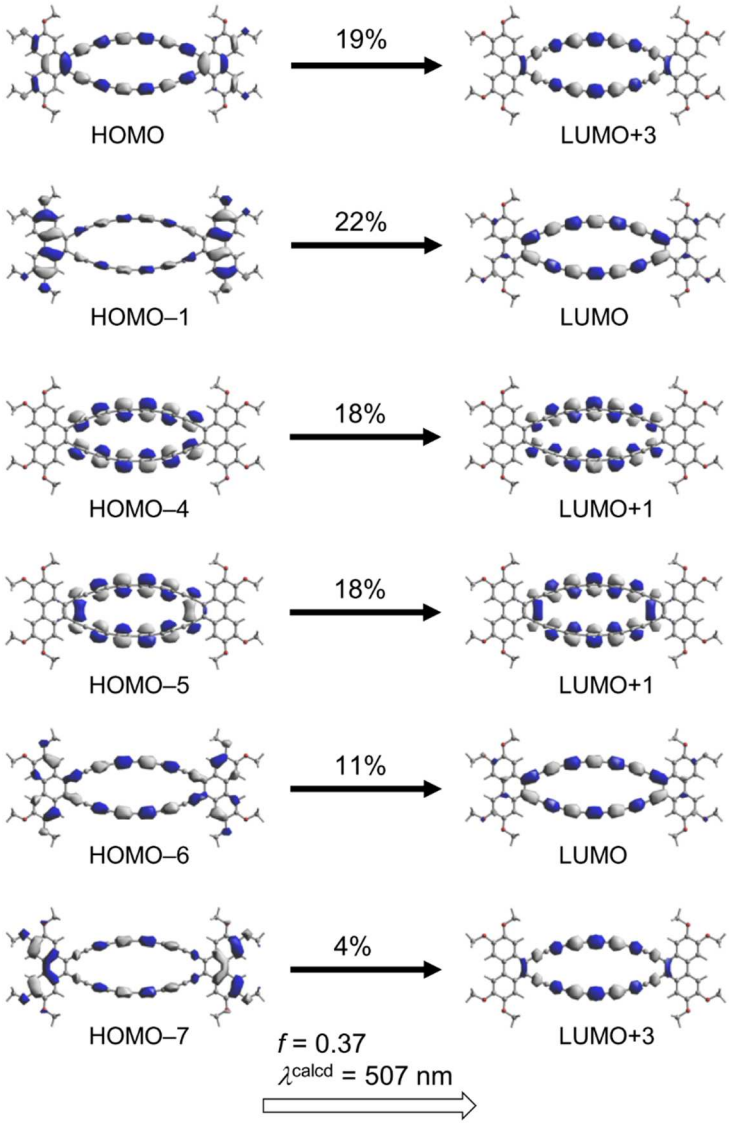


Figure S10. FMOs and the calculated absorption wavelength (λ^{calcd}) and oscillator strengths (*f*) of **3′** at the TD-CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

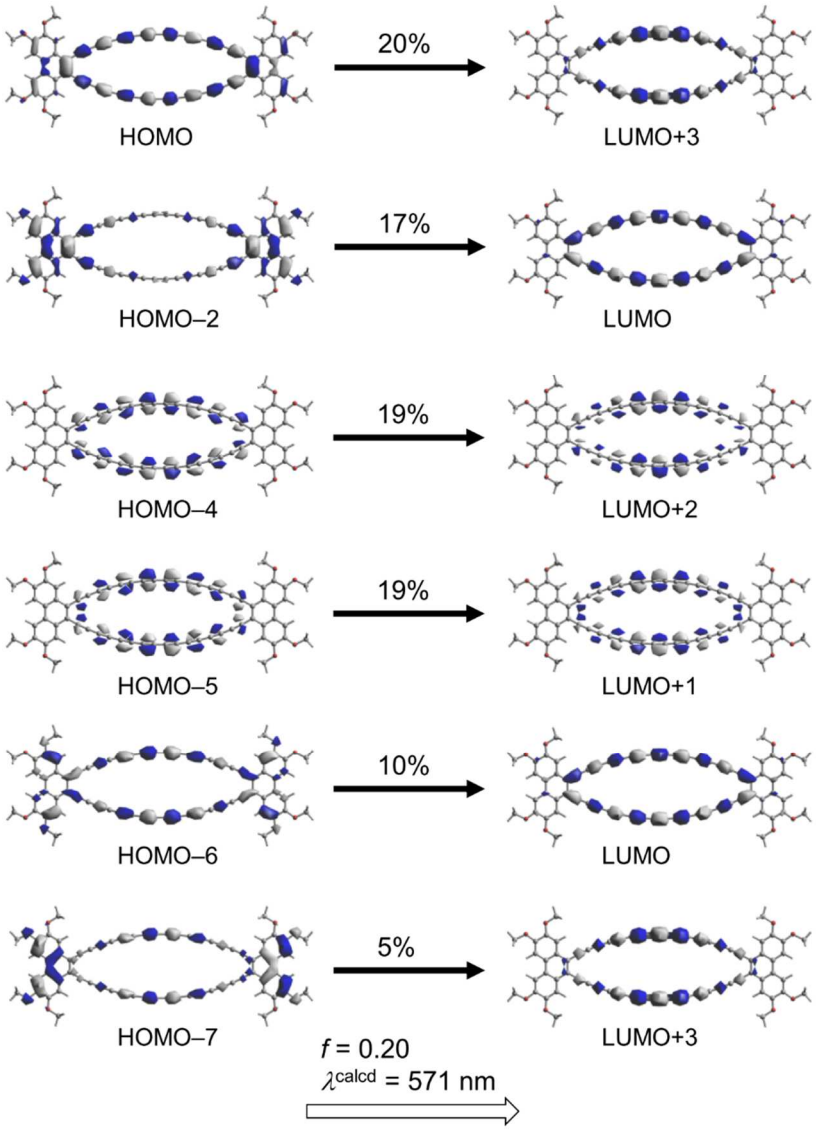


Figure S11. FMOs and the calculated absorption wavelength (λ^{calcd}) and oscillator strengths (*f*) of **4′** at the TD-CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

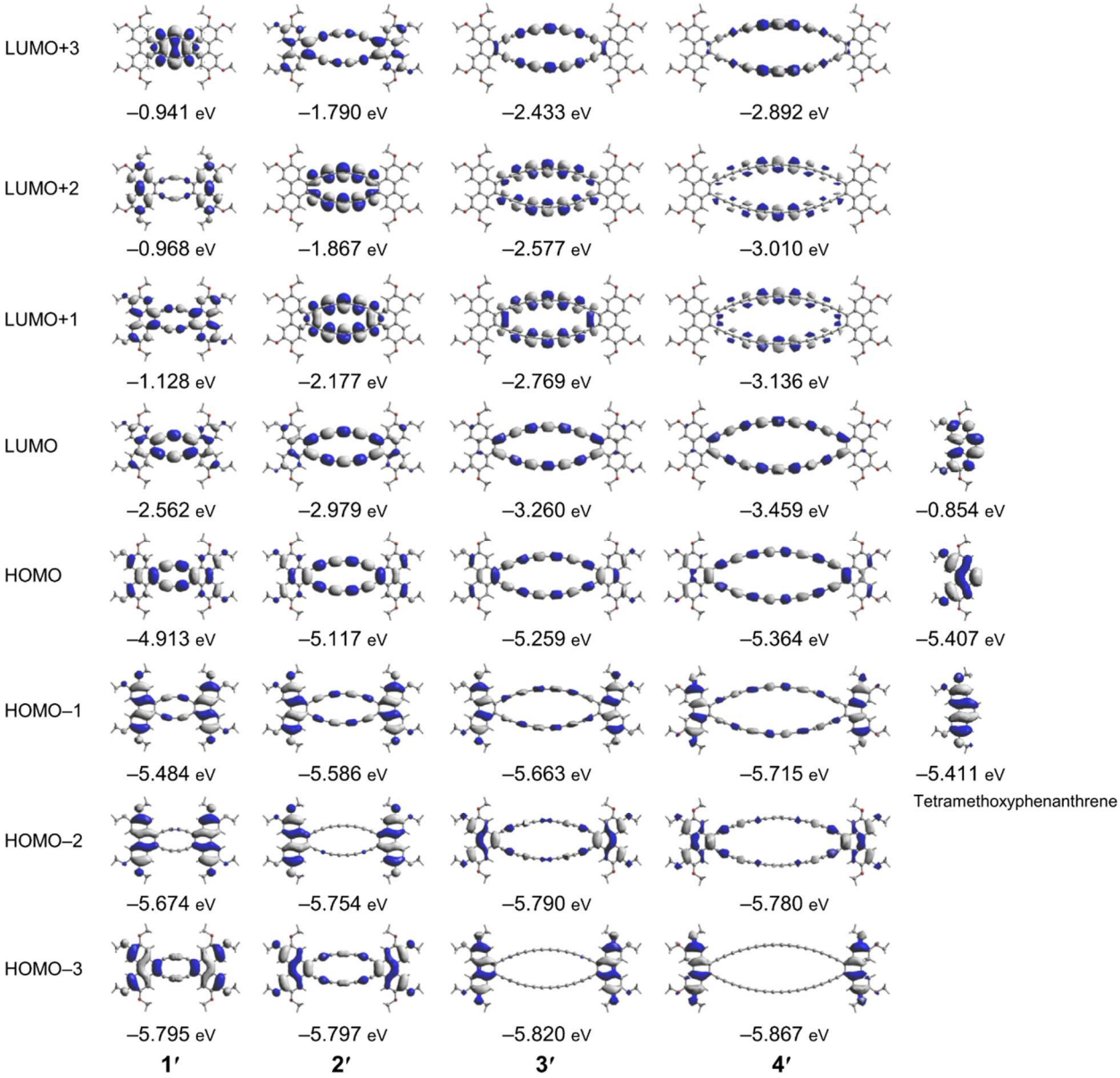


Figure S12. FMOs of **1′**–**4′** and tetramethoxyphenanthrene at the B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) level of theory.

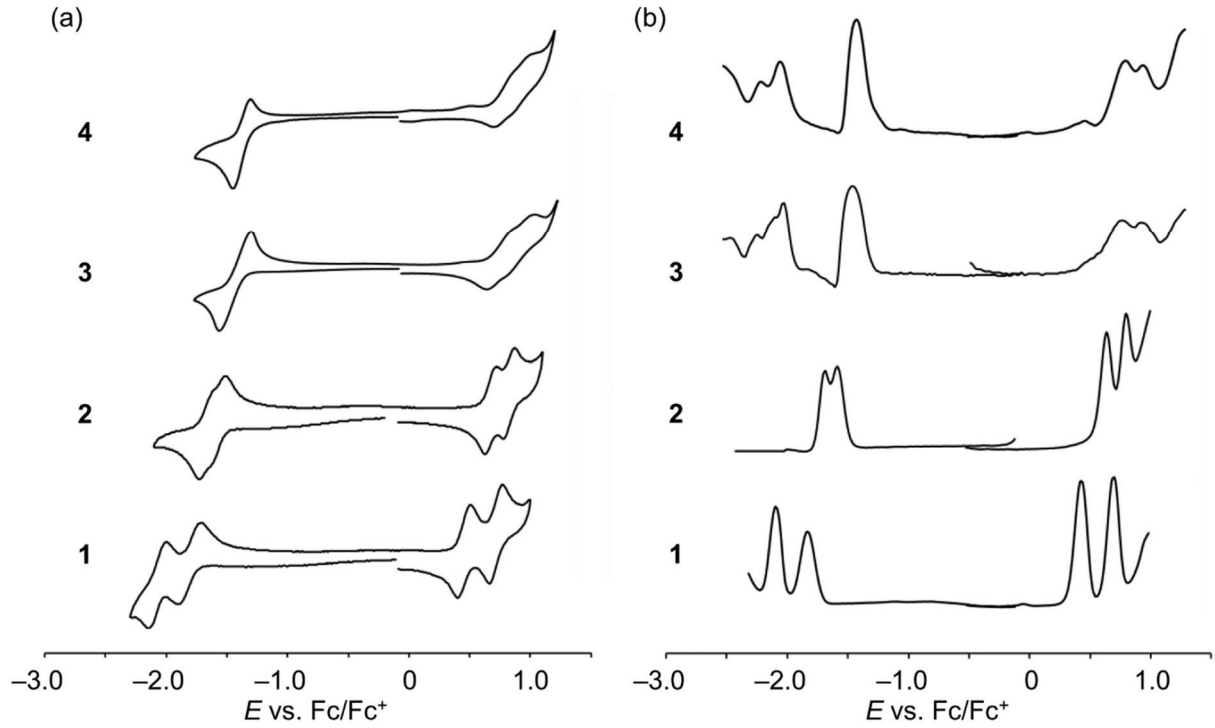


Figure S13. (a) Cyclic voltammograms of **1**–**4** at scan rate 100 mV s^{-1} in *o*-dichlorobenzene (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]). (b) Differential pulse voltammograms of **1**–**4** at a pulse width of 0.1 s over a period of 0.2 s in *o*-dichlorobenzene (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]).

Table S3. Differential Pulse Voltammetry Data of **1**–**4** in *o*-dichlorobenzene (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6])

Compound	E_{red}/V	E_{ox}/V	ΔE_{redox}/V
1	−1.84, −2.10	+0.42, +0.70	2.26
2	−1.58, −1.68	+0.64, +0.80	2.22
3	−1.46	+0.77, +0.93	2.23
4	−1.43	+0.80, +0.95	2.23

Cyclic voltammetry measurements showed that **3** and **4** exhibit reversible or quasi-reversible oxidation and reduction waves as well as **1** and **2** (Figure S13); both the difference between the first and second oxidation potentials and the difference between the first and second reduction potentials became progressively smaller upon extending the polyyne chains.

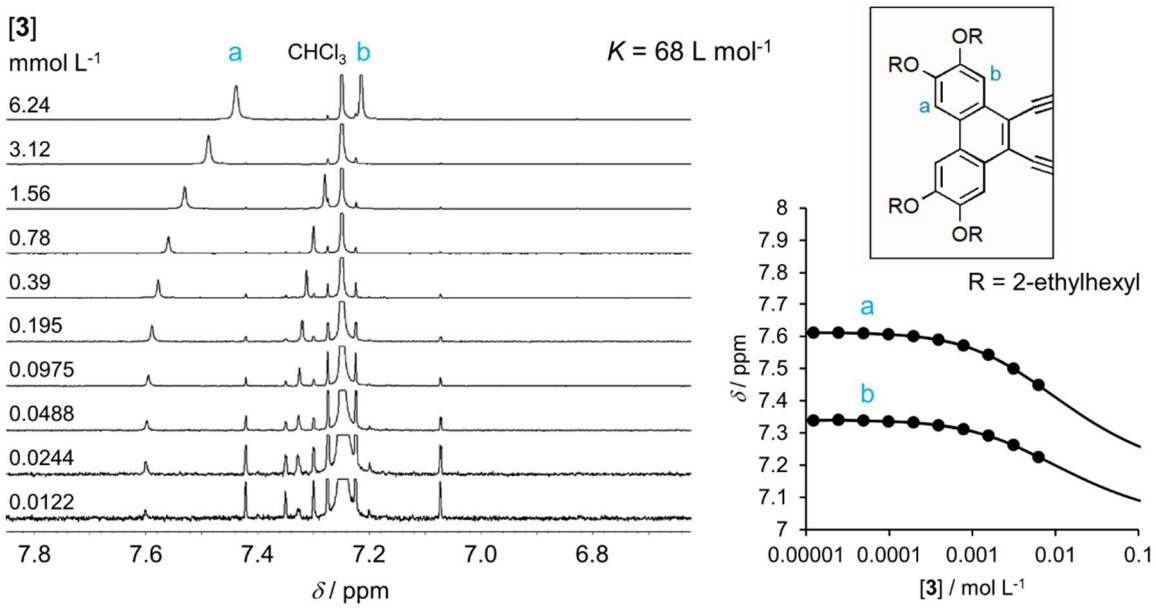


Figure S14. ^{1}H NMR spectra of **3** in $CDCl_3$ at different concentrations at 293 K (left) and fitting of the changes in the chemical shifts of the aromatic protons of **3** (right). The aromatic proton signals were tentatively assigned by DFT calculations at the GIAO-PCM (chloroform)-B3LYP/6-311++G(2df,2pd)//B3LYP-D3/6-31G(d) level.

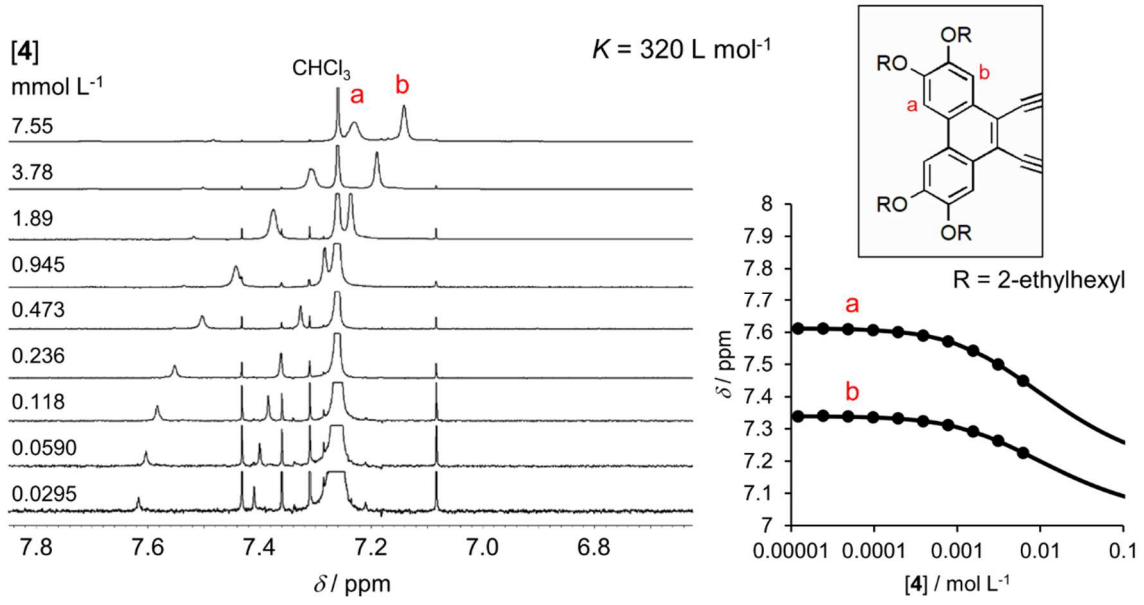


Figure S15. ^{1}H NMR spectra of **4** in $CDCl_3$ at different concentrations at 293 K (left) and fitting of the changes in the chemical shifts of the aromatic protons of **4** (right). The aromatic proton signals were tentatively assigned by DFT calculations at the GIAO-PCM (chloroform)-B3LYP/6-311++G(2df,2pd)//B3LYP-D3/6-31G(d) level.

Table S4. Association Constants (K) of **1**–**4** [a]

	$CDCl_3$ [b,c]	Methylcyclohexane [d]
	K [L mol^{-1}]	K [L mol^{-1}]
1	N/A	400 ± 30 [c]
2	9 ± 1	1600 ± 100 [e]
3	68 ± 2	8500 ± 1600 [e]
4	320 ± 22	15500 ± 3100 [e]

[a] At 20 °C. [b] Monomer–dimer model. [c] Concentration-dependent ^{1}H NMR experiments. [d] Isodesmic model. [e] Concentration-dependent UV–vis experiments.

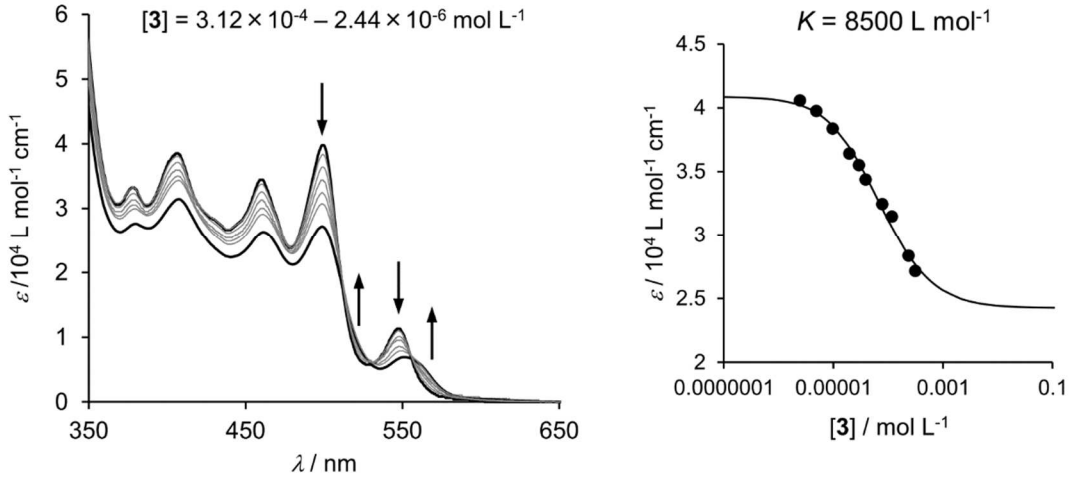


Figure S16. Absorption spectra of **3** in methylcyclohexane at different concentrations at 293 K (left) and fitting of the changes in the molar absorptivity at 499 nm to the isodesmic model (right). Arrows indicate the spectral change with increasing concentration.

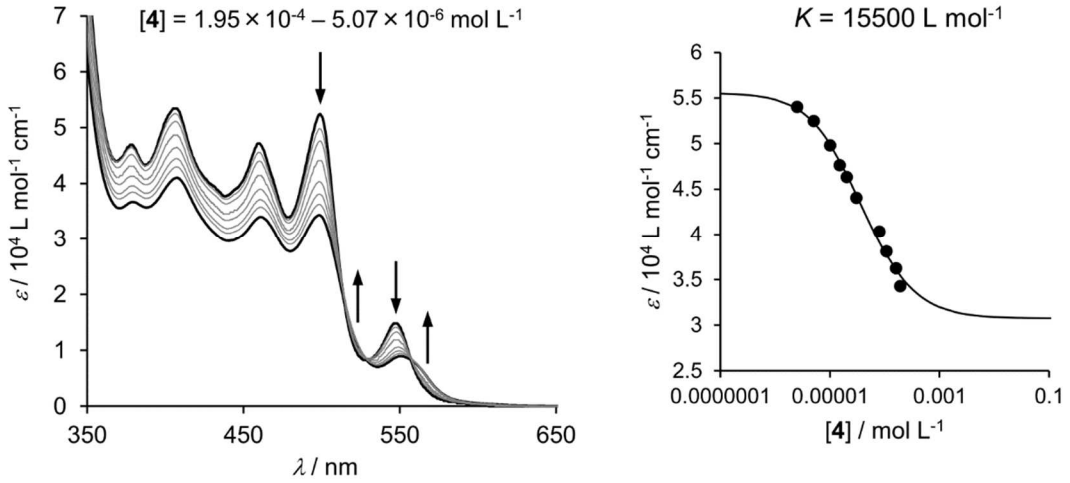


Figure S17. Absorption spectra of **4** in methylcyclohexane at different concentrations at 293 K (left) and fitting of the changes in the molar absorptivity at 500 nm to the isodesmic model (right). Arrows indicate the spectral change with increasing concentration.

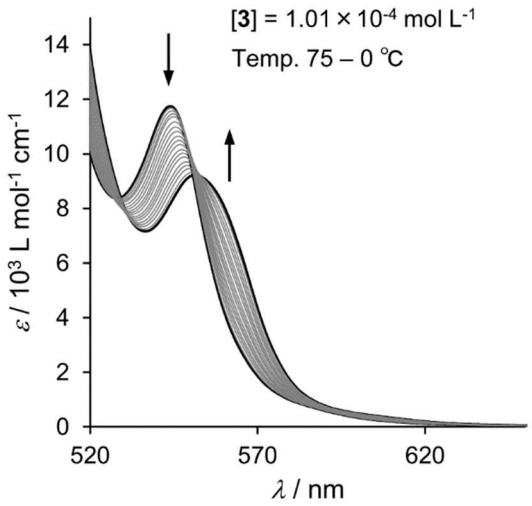


Figure S18. Absorption spectra of **3** in methylcyclohexane at different temperatures. Arrows indicate the spectral changes with decreasing temperature.

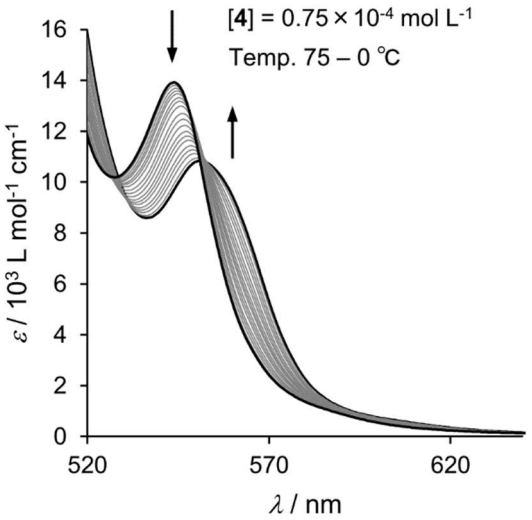


Figure S19. Absorption spectra of **4** in methylcyclohexane at different temperatures Arrows indicate the spectral changes with decreasing temperature.

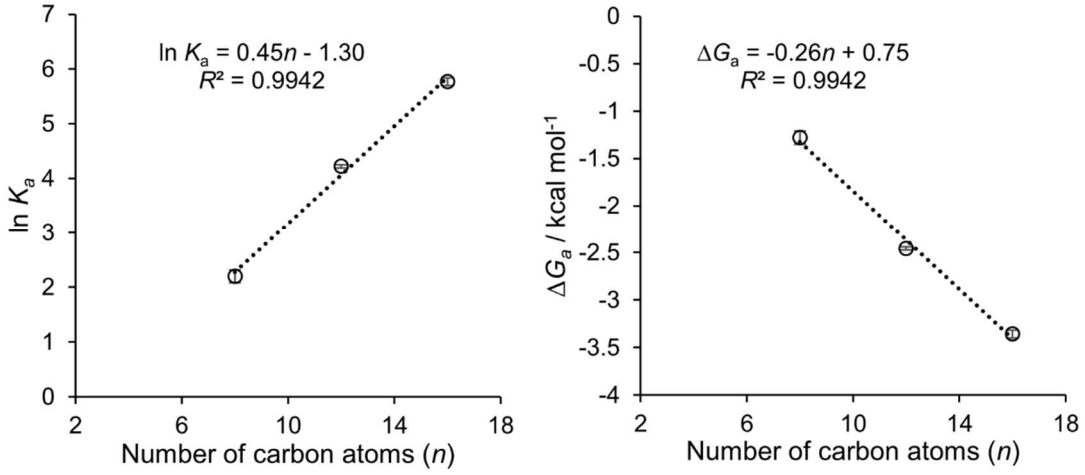


Figure S20. (Left) The plot of the logarithm of K_a in $CDCl_3$ against the number of carbon atoms (n) in each polyyne chain. (Right) Gibbs free energy of self-association in $CDCl_3$ against the number of carbon atoms in each polyyne chain for **1**–**4**. The dotted line denotes the best-fit line by linear regression. Because **1**–**4** have two polyyne chains, the C≡C unit increases by one when n is incremented by one.

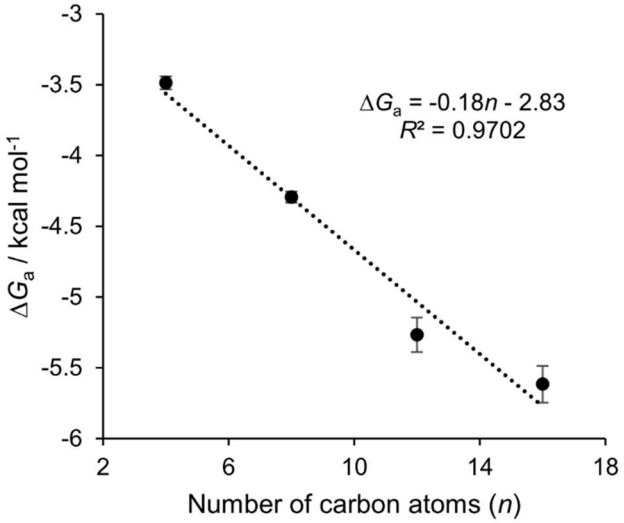


Figure S21. Gibbs free energy of self-association in MCH against the number of carbon atoms in each polyyne chain for **1**–**4**. The dotted line denotes the best-fit line by linear regression. Because **1**–**4** have two polyyne chains, the C≡C unit increases by one when n is incremented by one.

The natural logarithm of K_a in MCH was roughly dependent on the polyyne chain length linearly (Figure 3c in the main text). The relationship can be rationalized in terms of the Gibbs free energy of self-association, ΔG_a, in accordance with equation (1):

$$\Delta G_a = -RT \ln K_a \qquad (1)$$

in which R is the gas constant and T is the temperature. The ΔG_a value should reflect the energy gained by the formation of self-assemblies from the monomer in MCH. The plot of experimentally obtained

G_a value versus the number of carbon atoms in the polyyne chain is shown in Figure S21. Linear regression gives equation (2):

$$\Delta G_a = -0.18\,n - 2.83\ [\text{kcal mol}^{-1}] \qquad (2)$$

in which n is the number of carbon atoms in the polyyne chain. Because **1**–**4** have two polyyne segments, the total number of carbon atoms increased by two when n is increased by one. Therefore, equation (2) suggests that the stabilization free energy for the formation of self-assemblies from the monomer by π-stacking increases by 0.2 kcal mol^{-1} at 20 °C as a C≡C unit increases by one.

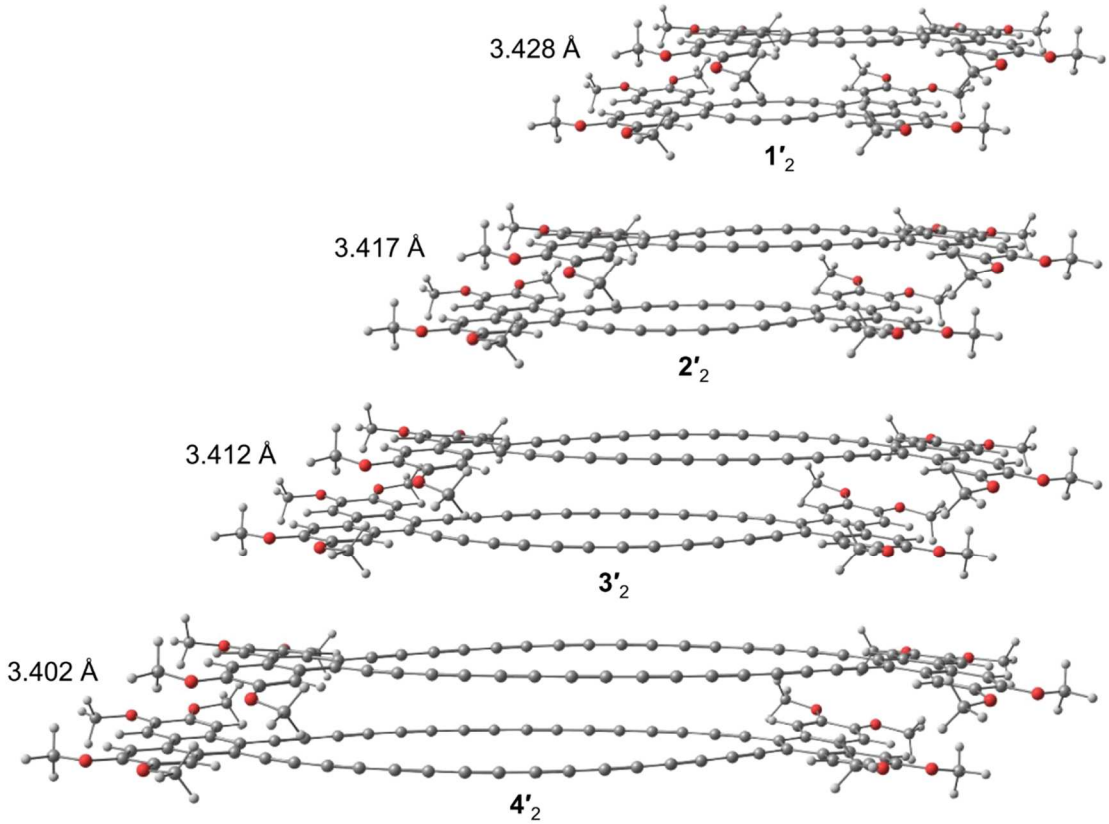


Figure S22. Optimized structures of dimers **1′**$_2$–**4′**$_2$ at the B3LYP-D3/6-31G(d) level of theory. The distance of the least-squares planes of macrocyclic rings is defined as the intermolecular distance.

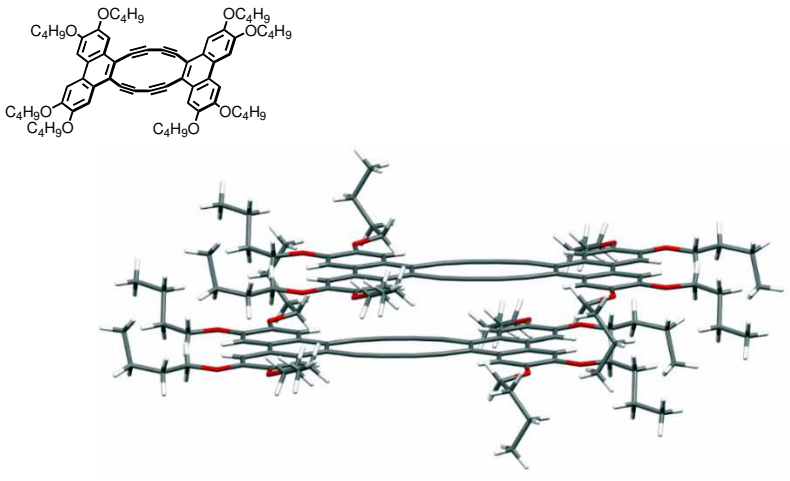


Figure S23. Crystal packing structure of **1″** with butoxy groups.[7]

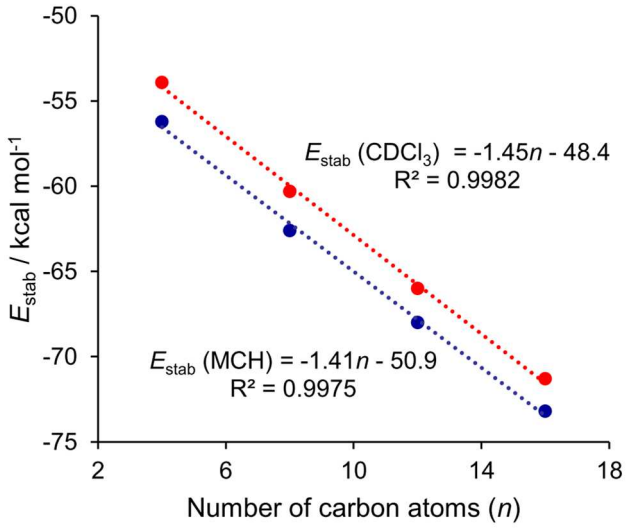


Figure S24. The stabilization energy values (E_{stab}) for the formation of **1′**$_2$–**4′**$_2$ calculated at the B3LYP-D3/6-31G(d) level of theory (PCM solvation model, $CDCl_3$ (blue) and MCH (red)) against the number of carbon atoms in each polyyne chain for **1′**–**4′**. The dotted line denotes the best-fit line by linear regression.

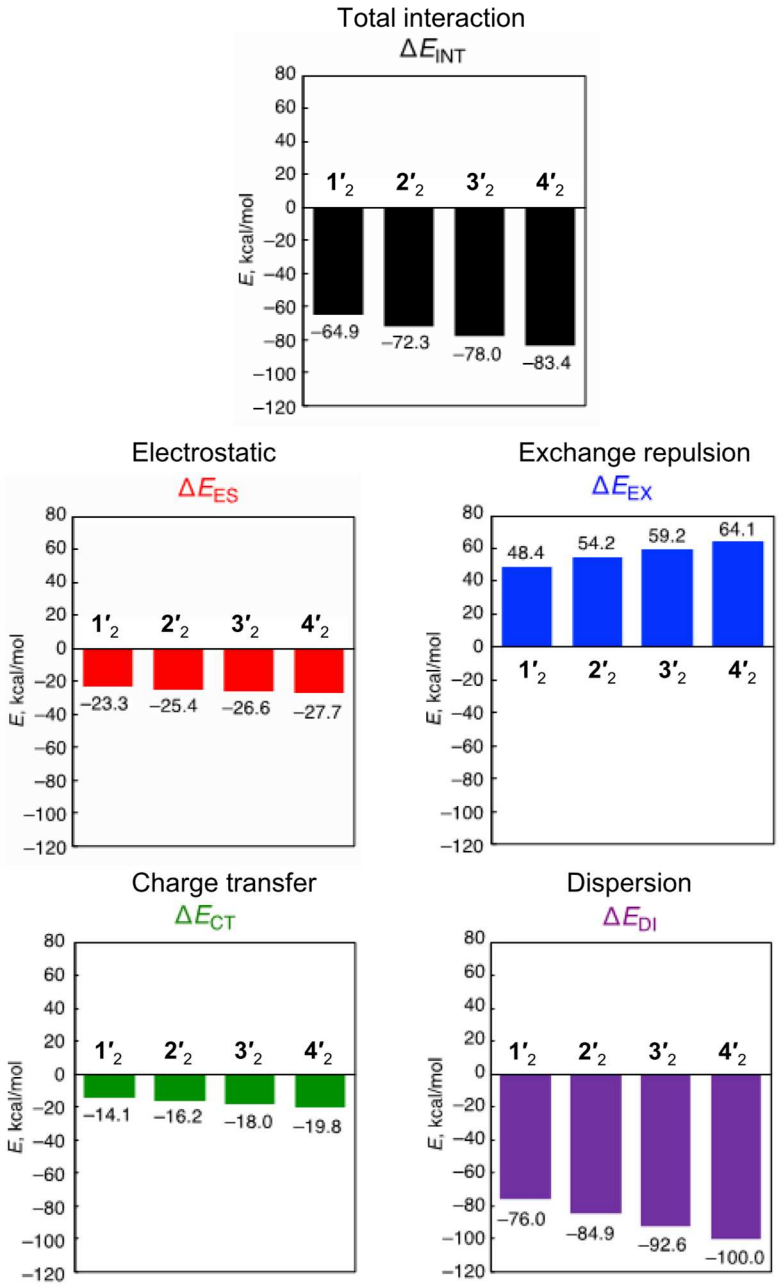


Figure S25. Decomposition of the total intermolecular interaction energy of **1′**$_2$–**4′**$_2$ calculated at the HF-GD3/6-31G(d)//B3LYP-D3/6-31G(d) level of theory.

3. Tables of Cartesian Coordinates of Molecules

Table S5. Cartesian Coordinates of **1′** at the B3LYP/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.607674	0.724311	0.000064
2	6	0	4.371187	1.426469	0.000130
3	6	0	3.131303	0.702895	0.000068
4	6	0	3.131303	-0.702895	-0.000068
5	6	0	4.371187	-1.426469	-0.000130
6	6	0	5.607674	-0.724311	-0.000064
7	6	0	6.803142	1.490472	0.000131
8	6	0	6.788059	2.870639	0.000263
9	6	0	5.538019	3.569010	0.000331
10	6	0	4.366650	2.846257	0.000265
11	6	0	4.366650	-2.846257	-0.000265
12	6	0	5.538019	-3.569010	-0.000331
13	6	0	6.788059	-2.870639	-0.000263
14	6	0	6.803142	-1.490472	-0.000131
15	6	0	1.871113	1.365214	0.000162
16	6	0	1.871113	-1.365214	-0.000162
17	6	0	0.681637	1.652059	0.000175
18	6	0	0.681637	-1.652059	-0.000175
19	6	0	-0.681637	1.652059	-0.000175
20	6	0	-0.681637	-1.652059	0.000175
21	6	0	-1.871113	-1.365214	0.000162
22	6	0	-3.131303	-0.702895	0.000068
23	6	0	-3.131303	0.702895	-0.000068
24	6	0	-4.371187	1.426469	-0.000130
25	6	0	-5.607674	0.724311	-0.000064
26	6	0	-5.607674	-0.724311	0.000064
27	6	0	-4.371187	-1.426469	0.000130
28	6	0	-1.871113	1.365214	-0.000162
29	6	0	-6.803142	-1.490472	0.000131
30	6	0	-6.788059	-2.870639	0.000263
31	6	0	-5.538019	-3.569010	0.000331
32	6	0	-4.366650	-2.846257	0.000265
33	6	0	-4.366650	2.846257	-0.000265
34	6	0	-5.538019	3.569010	-0.000331
35	6	0	-6.788059	2.870639	-0.000263
36	6	0	-6.803142	1.490472	-0.000131
37	8	0	5.632294	-4.924364	-0.000464
38	6	0	4.423664	-5.668683	-0.000506
39	8	0	7.888396	-3.668832	-0.000330
40	6	0	9.163847	-3.050804	-0.000367
41	8	0	7.888396	3.668832	0.000330
42	6	0	9.163847	3.050804	0.000367
43	8	0	5.632294	4.924364	0.000464
44	6	0	4.423664	5.668683	0.000506
45	8	0	-5.632294	-4.924364	0.000464
46	6	0	-4.423664	-5.668683	0.000506
47	8	0	-7.888396	-3.668832	0.000330
48	6	0	-9.163847	-3.050804	0.000367
49	8	0	-7.888396	3.668832	-0.000330
50	6	0	-9.163847	3.050804	-0.000367
51	8	0	-5.632294	4.924364	-0.000464
52	6	0	-4.423664	5.668683	-0.000506
53	1	0	7.758260	0.983635	0.000073
54	1	0	3.407221	3.349237	0.000318
55	1	0	3.407221	-3.349237	-0.000318
56	1	0	7.758260	-0.983635	-0.000073
57	1	0	-7.758260	-0.983635	0.000073
58	1	0	-3.407221	-3.349237	0.000318
59	1	0	-3.407221	3.349237	-0.000318
60	1	0	-7.758260	0.983635	-0.000073

61	1	0	4.721310	-6.718677	-0.000588
62	1	0	3.822814	-5.458208	-0.894896
63	1	0	3.822832	-5.458340	0.893926
64	1	0	9.889558	-3.865945	-0.000500
65	1	0	9.311609	-2.431767	-0.895507
66	1	0	9.311747	-2.431941	0.894872
67	1	0	9.889558	3.865945	0.000500
68	1	0	9.311747	2.431941	-0.894872
69	1	0	9.311609	2.431767	0.895507
70	1	0	3.822832	5.458340	-0.893926
71	1	0	4.721310	6.718677	0.000588
72	1	0	3.822814	5.458208	0.894896
73	1	0	-3.822814	-5.458208	0.894896
74	1	0	-4.721310	-6.718677	0.000588
75	1	0	-3.822832	-5.458340	-0.893926
76	1	0	-9.889558	-3.865945	0.000500
77	1	0	-9.311609	-2.431767	0.895507
78	1	0	-9.311747	-2.431941	-0.894872
79	1	0	-9.889558	3.865945	-0.000500
80	1	0	-9.311609	2.431767	-0.895507
81	1	0	-9.311747	2.431941	0.894872
82	1	0	-3.822832	5.458340	0.893926
83	1	0	-3.822814	5.458208	-0.894896
84	1	0	-4.721310	6.718677	-0.000588

No imaginary frequency.
Total energy = –2297.45869373 hartree.

Table S6. Cartesian Coordinates of **1′** at the M06-2X/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.600347	-0.723746	-0.000003
2	6	0	4.373572	-1.421483	0.000002
3	6	0	3.138210	-0.695447	0.000012
4	6	0	3.138206	0.695442	0.000019
5	6	0	4.373564	1.421484	0.000011
6	6	0	5.600343	0.723754	-0.000002
7	6	0	6.797532	-1.485578	-0.000008
8	6	0	6.777245	-2.859769	-0.000011
9	6	0	5.528252	-3.557076	-0.000009
10	6	0	4.360155	-2.839665	-0.000001
11	6	0	4.360139	2.839666	0.000017
12	6	0	5.528232	3.557085	0.000008
13	6	0	6.777228	2.859785	-0.000009
14	6	0	6.797523	1.485594	-0.000014
15	6	0	1.869900	-1.354726	0.000021
16	6	0	1.869892	1.354713	0.000035
17	6	0	0.688126	-1.642331	0.000029
18	6	0	0.688118	1.642318	0.000045
19	6	0	-0.688116	-1.642314	0.000035
20	6	0	-0.688124	1.642323	0.000031
21	6	0	-1.869901	1.354728	0.000021
22	6	0	-3.138211	0.695450	0.000013
23	6	0	-3.138205	-0.695438	0.000022
24	6	0	-4.373563	-1.421483	0.000014
25	6	0	-5.600342	-0.723754	-0.000002
26	6	0	-5.600348	0.723746	-0.000002
27	6	0	-4.373575	1.421485	0.000002
28	6	0	-1.869889	-1.354704	0.000042
29	6	0	-6.797534	1.485577	-0.000004
30	6	0	-6.777249	2.859768	-0.000007
31	6	0	-5.528257	3.557077	-0.000009
32	6	0	-4.360160	2.839667	-0.000003
33	6	0	-4.360136	-2.839665	0.000020
34	6	0	-5.528227	-3.557084	0.000009

35	6	0	-6.777225	-2.859786	-0.000013
36	6	0	-6.797522	-1.485595	-0.000019
37	8	0	5.625788	4.904786	0.000012
38	6	0	4.414298	5.628710	0.000029
39	8	0	7.868179	3.658104	-0.000021
40	6	0	9.129693	3.029974	-0.000025
41	8	0	7.868200	-3.658082	-0.000015
42	6	0	9.129710	-3.029945	-0.000029
43	8	0	5.625816	-4.904777	-0.000013
44	6	0	4.414330	-5.628708	-0.000030
45	8	0	-5.625823	4.904777	-0.000014
46	6	0	-4.414337	5.628709	-0.000047
47	8	0	-7.868206	3.658080	-0.000007
48	6	0	-9.129715	3.029941	-0.000023
49	8	0	-7.868175	-3.658107	-0.000030
50	6	0	-9.129689	-3.029979	-0.000022
51	8	0	-5.625782	-4.904786	0.000015
52	6	0	-4.414290	-5.628707	0.000021
53	1	0	7.752727	-0.978956	-0.000006
54	1	0	3.398361	-3.339441	0.000002
55	1	0	3.398342	3.339437	0.000028
56	1	0	7.752722	0.978977	-0.000031
57	1	0	-7.752729	0.978954	0.000004
58	1	0	-3.398366	3.339445	-0.000001
59	1	0	-3.398338	-3.339434	0.000035
60	1	0	-7.752721	-0.978980	-0.000044
61	1	0	4.692628	6.682162	0.000032
62	1	0	3.819783	5.404107	0.893756
63	1	0	3.819765	5.404117	-0.893689
64	1	0	9.866329	3.833041	-0.000021
65	1	0	9.264211	2.409218	0.894637
66	1	0	9.264211	2.409227	-0.894693
67	1	0	9.866351	-3.833008	-0.000040
68	1	0	9.264236	-2.409195	0.894636
69	1	0	9.264213	-2.409190	-0.894694
70	1	0	3.819801	-5.404127	0.893694
71	1	0	4.692666	-6.682159	-0.000044
72	1	0	3.819809	-5.404099	-0.893751
73	1	0	-3.819823	5.404093	-0.893772
74	1	0	-4.692674	6.682160	-0.000068
75	1	0	-3.819800	5.404137	0.893673
76	1	0	-9.866357	3.833003	-0.000036
77	1	0	-9.264215	2.409186	-0.894687
78	1	0	-9.264242	2.409192	0.894642
79	1	0	-9.866324	-3.833048	-0.000009
80	1	0	-9.264199	-2.409222	0.894640
81	1	0	-9.264218	-2.409235	-0.894690
82	1	0	-3.819761	-5.404106	-0.893697
83	1	0	-3.819772	-5.404110	0.893748
84	1	0	-4.692618	-6.682161	0.000018

No imaginary frequency.
Total energy = –2296.55219414 hartree.

Table S7. Cartesian Coordinates of **2′** at the B3LYP/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.075377	0.720205	0.000006
2	6	0	6.844459	1.430169	0.000006
3	6	0	5.598045	0.710105	0.000002
4	6	0	5.591551	-0.696411	-0.000003
5	6	0	6.831140	-1.428408	-0.000005
6	6	0	8.068628	-0.729976	-0.000001
7	6	0	9.275509	1.477821	0.000011
8	6	0	9.270108	2.858514	0.000018

9	6	0	8.024942	3.565064	0.000018
10	6	0	6.848811	2.849155	0.000012
11	6	0	6.822249	-2.847339	-0.000010
12	6	0	7.991674	-3.574189	-0.000013
13	6	0	9.243401	-2.879314	-0.000009
14	6	0	9.261671	-1.498748	-0.000002
15	8	0	10.374880	3.648180	0.000022
16	8	0	8.127396	4.918454	0.000023
17	6	0	6.923539	5.672352	0.000025
18	6	0	11.647366	3.022619	0.000059
19	8	0	10.340731	-3.679280	-0.000010
20	8	0	8.081514	-4.928452	-0.000018
21	6	0	6.870773	-5.671224	-0.000023
22	6	0	11.619058	-3.065744	-0.000043
23	6	0	4.357974	1.391424	0.000003
24	6	0	4.345141	-1.365544	-0.000006
25	6	0	3.209146	1.820982	0.000007
26	6	0	1.904123	2.165480	0.000005
27	6	0	0.677698	2.286144	0.000007
28	6	0	3.195369	-1.792812	-0.000010
29	6	0	1.888416	-2.127472	-0.000013
30	6	0	0.666640	-2.290428	-0.000013
31	6	0	-8.075411	-0.720201	0.000006
32	6	0	-6.844535	-1.430232	0.000003
33	6	0	-5.598084	-0.710246	-0.000006
34	6	0	-5.591509	0.696271	-0.000012
35	6	0	-6.831058	1.428345	-0.000010
36	6	0	-8.068585	0.729979	-0.000001
37	6	0	-9.275586	-1.477751	0.000014
38	6	0	-9.270259	-2.858447	0.000021
39	6	0	-8.025132	-3.565064	0.000017
40	6	0	-6.848963	-2.849217	0.000008
41	6	0	-6.822090	2.847277	-0.000017
42	6	0	-7.991478	3.574189	-0.000015
43	6	0	-9.243242	2.879380	-0.000006
44	6	0	-9.261586	1.498816	0.000002
45	8	0	-10.375073	-3.648050	0.000029
46	8	0	-8.127657	-4.918449	0.000024
47	6	0	-6.923840	-5.672408	0.000020
48	6	0	-11.647526	-3.022422	0.000074
49	8	0	-10.340532	3.679405	-0.000003
50	8	0	-8.081247	4.928456	-0.000022
51	6	0	-6.870469	5.671166	-0.000032
52	6	0	-11.618889	3.065932	-0.000035
53	6	0	-4.358047	-1.391635	-0.000012
54	6	0	-4.345065	1.365328	-0.000021
55	6	0	-3.209210	-1.821174	-0.000019
56	6	0	-1.904152	-2.165508	-0.000019
57	6	0	-0.677716	-2.286076	-0.000019
58	6	0	-3.195343	1.792742	-0.000028
59	6	0	-1.888395	2.127404	-0.000019
60	6	0	-0.666660	2.290635	-0.000011
61	1	0	10.227285	0.965088	0.000008
62	1	0	5.894088	3.360392	0.000013
63	1	0	5.862886	-3.349828	-0.000013
64	1	0	10.218194	-0.994896	0.000003
65	1	0	7.229561	6.719764	0.000031
66	1	0	6.321809	5.466341	-0.894572
67	1	0	6.321805	5.466332	0.894617
68	1	0	12.377268	3.833843	0.000085
69	1	0	11.791198	2.403262	-0.895327
70	1	0	11.791141	2.403252	0.895446
71	1	0	7.167150	-6.721408	-0.000029
72	1	0	6.270946	-5.459728	-0.894625
73	1	0	6.270944	-5.459738	0.894579
74	1	0	12.341262	-3.883830	-0.000067
75	1	0	11.768768	-2.447786	0.895350
76	1	0	11.768717	-2.447776	-0.895437
77	1	0	-10.227332	-0.964967	0.000013

78	1	0	-5.894267	-3.360506	0.000006
79	1	0	-5.862703	3.349717	-0.000024
80	1	0	-10.218137	0.995014	0.000013
81	1	0	-7.229913	-6.719806	0.000027
82	1	0	-6.322103	-5.466428	-0.894580
83	1	0	-6.322093	-5.466421	0.894612
84	1	0	-12.377471	-3.833607	0.000106
85	1	0	-11.791258	-2.403046	0.895462
86	1	0	-11.791328	-2.403056	-0.895310
87	1	0	-7.166793	6.721364	-0.000037
88	1	0	-6.270655	5.459639	-0.894634
89	1	0	-6.270646	5.459649	0.894568
90	1	0	-12.341054	3.884051	-0.000060
91	1	0	-11.768581	2.447970	-0.895429
92	1	0	-11.768633	2.447983	0.895359

No imaginary frequency.
Total energy = –2602.11711011 hartree.

Table S8. Cartesian Coordinates of **2′** at the M06-2X/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.096578	0.724434	-0.000004
2	6	0	6.871541	1.424041	-0.000038
3	6	0	5.634899	0.695302	-0.000047
4	6	0	5.634905	-0.695324	-0.000023
5	6	0	6.871559	-1.424048	0.000010
6	6	0	8.096586	-0.724426	0.000020
7	6	0	9.294516	1.484036	0.000003
8	6	0	9.276496	2.858643	-0.000022
9	6	0	8.028680	3.557899	-0.000057
10	6	0	6.859427	2.841660	-0.000064
11	6	0	6.859468	-2.841665	0.000033
12	6	0	8.028731	-3.557889	0.000066
13	6	0	9.276538	-2.858619	0.000077
14	6	0	9.294537	-1.484011	0.000054
15	8	0	10.367885	3.654399	-0.000018
16	8	0	8.127812	4.904307	-0.000079
17	6	0	6.917477	5.631664	-0.000111
18	6	0	11.629472	3.025340	0.000019
19	8	0	10.367940	-3.654358	0.000109
20	8	0	8.127881	-4.904297	0.000089
21	6	0	6.917559	-5.631674	0.000078
22	6	0	11.629517	-3.025276	0.000120
23	6	0	4.379351	1.364460	-0.000096
24	6	0	4.379380	-1.364522	-0.000026
25	6	0	3.227650	1.759136	-0.000145
26	6	0	1.896135	2.061441	-0.000024
27	6	0	0.680872	2.176328	-0.000038
28	6	0	3.227704	-1.759267	-0.000016
29	6	0	1.896193	-2.061596	-0.000029
30	6	0	0.680925	-2.176416	0.000016
31	6	0	-8.096582	-0.724433	-0.000001
32	6	0	-6.871556	-1.424059	-0.000031
33	6	0	-5.634902	-0.695341	-0.000037
34	6	0	-5.634889	0.695292	-0.000012
35	6	0	-6.871534	1.424031	0.000017
36	6	0	-8.096569	0.724427	0.000023
37	6	0	-9.294531	-1.484018	0.000004
38	6	0	-9.276531	-2.858626	-0.000020
39	6	0	-8.028725	-3.557899	-0.000050
40	6	0	-6.859462	-2.841676	-0.000056
41	6	0	-6.859421	2.841646	0.000040
42	6	0	-8.028674	3.557888	0.000068
43	6	0	-9.276491	2.858637	0.000076

44	6	0	-9.294510	1.484029	0.000054
45	8	0	-10.367931	-3.654366	-0.000018
46	8	0	-8.127876	-4.904306	-0.000072
47	6	0	-6.917553	-5.631681	-0.000101
48	6	0	-11.629509	-3.025288	0.000016
49	8	0	-10.367881	3.654392	0.000105
50	8	0	-8.127803	4.904297	0.000091
51	6	0	-6.917471	5.631658	0.000085
52	6	0	-11.629467	3.025329	0.000112
53	6	0	-4.379379	-1.364556	-0.000075
54	6	0	-4.379368	1.364504	-0.000016
55	6	0	-3.227711	-1.759321	-0.000113
56	6	0	-1.896148	-2.061426	-0.000089
57	6	0	-0.680889	-2.176355	-0.000093
58	6	0	-3.227721	1.759329	-0.000009
59	6	0	-1.896214	2.061671	0.000017
60	6	0	-0.680944	2.176461	0.000039
61	1	0	10.249084	0.976517	0.000027
62	1	0	5.899482	3.344577	-0.000090
63	1	0	5.899531	-3.344597	0.000025
64	1	0	10.249095	-0.976473	0.000064
65	1	0	7.198760	6.684190	-0.000125
66	1	0	6.322897	5.408554	-0.894008
67	1	0	6.322868	5.408584	0.893773
68	1	0	12.366231	3.828162	0.000020
69	1	0	11.763325	2.404841	-0.894800
70	1	0	11.763288	2.404874	0.894867
71	1	0	7.198862	-6.684194	0.000101
72	1	0	6.322975	-5.408607	-0.893826
73	1	0	6.322943	-5.408578	0.893954
74	1	0	12.366291	-3.828084	0.000146
75	1	0	11.763326	-2.404777	0.894946
76	1	0	11.763357	-2.404806	-0.894721
77	1	0	-10.249092	-0.976485	0.000025
78	1	0	-5.899523	-3.344605	-0.000078
79	1	0	-5.899475	3.344562	0.000034
80	1	0	-10.249074	0.976504	0.000060
81	1	0	-7.198851	-6.684203	-0.000114
82	1	0	-6.322967	-5.408581	-0.893995
83	1	0	-6.322942	-5.408611	0.893785
84	1	0	-12.366279	-3.828100	0.000016
85	1	0	-11.763318	-2.404820	0.894862
86	1	0	-11.763351	-2.404789	-0.894805
87	1	0	-7.198760	6.684182	0.000106
88	1	0	-6.322887	5.408583	-0.893817
89	1	0	-6.322861	5.408554	0.893963
90	1	0	-12.366229	3.828149	0.000134
91	1	0	-11.763313	2.404861	-0.894730
92	1	0	-11.763289	2.404832	0.894937

No imaginary frequency.
Total energy = –2601.07949707 hartree.

Table S9. Cartesian Coordinates of **3′** at the B3LYP/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.049938	0.703559	0.000000
2	6	0	-8.049938	-0.703559	-0.000000
3	6	0	-9.293520	-1.430705	0.000000
4	6	0	-10.526938	-0.725319	0.000000
5	6	0	-10.526938	0.725319	0.000000
6	6	0	-9.293520	1.430705	0.000000
7	6	0	-11.724013	1.487247	0.000000
8	6	0	-11.713611	2.868102	0.000000
9	6	0	-10.465731	3.570067	0.000000

10	6	0	-9.292287	2.849473	0.000000
11	6	0	-9.292287	-2.849473	-0.000000
12	6	0	-10.465731	-3.570067	-0.000000
13	6	0	-11.713611	-2.868102	-0.000000
14	6	0	-11.724013	-1.487247	-0.000000
15	6	0	-6.811761	1.382024	0.000000
16	6	0	-5.685634	1.870927	0.000000
17	6	0	-4.414814	2.314102	0.000000
18	6	0	-3.220993	2.628140	0.000000
19	6	0	-1.900350	2.850547	0.000000
20	6	0	-0.668914	2.962234	0.000000
21	6	0	0.668914	2.962234	0.000000
22	6	0	1.900350	2.850547	0.000000
23	6	0	3.220993	2.628140	0.000000
24	6	0	4.414814	2.314102	0.000000
25	6	0	5.685634	1.870927	0.000000
26	6	0	6.811761	1.382024	0.000000
27	6	0	8.049938	-0.703559	0.000000
28	6	0	8.049938	0.703559	0.000000
29	6	0	9.293520	1.430705	0.000000
30	6	0	10.526938	0.725319	0.000000
31	6	0	10.526938	-0.725319	0.000000
32	6	0	9.293520	-1.430705	0.000000
33	6	0	11.724013	-1.487247	0.000000
34	6	0	11.713611	-2.868102	0.000000
35	6	0	10.465731	-3.570067	0.000000
36	6	0	9.292287	-2.849473	0.000000
37	6	0	9.292287	2.849473	0.000000
38	6	0	10.465731	3.570067	0.000000
39	6	0	11.713611	2.868102	0.000000
40	6	0	11.724013	1.487247	0.000000
41	6	0	-6.811761	-1.382024	-0.000000
42	6	0	-5.685634	-1.870927	-0.000000
43	6	0	-4.414814	-2.314102	-0.000000
44	6	0	-3.220993	-2.628140	-0.000000
45	6	0	-1.900350	-2.850547	-0.000000
46	6	0	-0.668914	-2.962234	-0.000000
47	6	0	0.668914	-2.962234	0.000000
48	6	0	1.900350	-2.850547	0.000000
49	6	0	3.220993	-2.628140	0.000000
50	6	0	4.414814	-2.314102	0.000000
51	6	0	5.685634	-1.870927	0.000000
52	6	0	6.811761	-1.382024	0.000000
53	8	0	12.814558	3.661386	0.000000
54	6	0	14.090340	3.041620	0.000000
55	8	0	10.562893	4.922961	0.000000
56	6	0	9.356507	5.673651	0.000000
57	8	0	12.814558	-3.661386	-0.000000
58	6	0	14.090340	-3.041620	-0.000000
59	8	0	10.562893	-4.922961	-0.000000
60	6	0	9.356507	-5.673651	-0.000000
61	8	0	-10.562893	4.922961	-0.000000
62	6	0	-9.356507	5.673651	-0.000000
63	8	0	-12.814558	3.661386	-0.000000
64	6	0	-14.090340	3.041620	-0.000000
65	8	0	-12.814558	-3.661386	0.000000
66	6	0	-14.090340	-3.041620	0.000000
67	8	0	-10.562893	-4.922961	0.000000
68	6	0	-9.356507	-5.673651	0.000000
69	1	0	-12.677773	0.978373	0.000000
70	1	0	-8.336431	3.358291	0.000000
71	1	0	-8.336431	-3.358291	-0.000000
72	1	0	-12.677773	-0.978373	-0.000000
73	1	0	12.677773	-0.978373	0.000000
74	1	0	8.336431	-3.358291	0.000000
75	1	0	8.336431	3.358291	0.000000
76	1	0	12.677773	0.978373	0.000000
77	1	0	14.236735	2.423214	0.895520
78	1	0	14.236735	2.423214	-0.895520

79	1	0	14.816149	3.856398	0.000000
80	1	0	9.659779	6.721763	0.000000
81	1	0	8.755758	5.465867	-0.894752
82	1	0	8.755758	5.465867	0.894752
83	1	0	14.236735	-2.423214	0.895520
84	1	0	14.816149	-3.856398	-0.000000
85	1	0	14.236735	-2.423214	-0.895520
86	1	0	8.755758	-5.465867	-0.894752
87	1	0	8.755758	-5.465867	0.894752
88	1	0	9.659779	-6.721763	-0.000000
89	1	0	-9.659779	6.721763	-0.000000
90	1	0	-8.755758	5.465867	-0.894752
91	1	0	-8.755758	5.465867	0.894752
92	1	0	-14.816149	3.856398	-0.000000
93	1	0	-14.236735	2.423214	-0.895520
94	1	0	-14.236735	2.423214	0.895520
95	1	0	-14.816149	-3.856398	0.000000
96	1	0	-14.236735	-2.423214	0.895520
97	1	0	-14.236735	-2.423214	-0.895520
98	1	0	-9.659779	-6.721763	0.000000
99	1	0	-8.755758	-5.465867	-0.894752
100	1	0	-8.755758	-5.465867	0.894752

No imaginary frequency.
Total energy = –2906.76554668 hartree.

Table S10. Cartesian Coordinates of **3′** at the M06-2X/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.089224	0.695082	0.000000
2	6	0	-8.089224	-0.695082	-0.000000
3	6	0	-9.326116	-1.424890	0.000000
4	6	0	-10.550664	-0.724384	0.000000
5	6	0	-10.550664	0.724384	0.000000
6	6	0	-9.326116	1.424890	0.000000
7	6	0	-11.749139	1.483030	0.000000
8	6	0	-11.732412	2.857702	0.000000
9	6	0	-10.485062	3.558000	0.000000
10	6	0	-9.315218	2.842683	0.000000
11	6	0	-9.315218	-2.842683	-0.000000
12	6	0	-10.485062	-3.558000	-0.000000
13	6	0	-11.732412	-2.857702	-0.000000
14	6	0	-11.749139	-1.483030	-0.000000
15	6	0	-6.840064	1.372789	0.000000
16	6	0	-5.717582	1.845064	0.000000
17	6	0	-4.423683	2.274700	0.000000
18	6	0	-3.239211	2.572953	0.000000
19	6	0	-1.897059	2.787935	0.000000
20	6	0	-0.679324	2.893567	0.000000
21	6	0	0.679324	2.893567	0.000000
22	6	0	1.897059	2.787935	0.000000
23	6	0	3.239211	2.572953	0.000000
24	6	0	4.423683	2.274700	0.000000
25	6	0	5.717582	1.845064	0.000000
26	6	0	6.840064	1.372789	0.000000
27	6	0	8.089224	-0.695082	0.000000
28	6	0	8.089224	0.695082	0.000000
29	6	0	9.326116	1.424890	0.000000
30	6	0	10.550664	0.724384	0.000000
31	6	0	10.550664	-0.724384	0.000000
32	6	0	9.326116	-1.424890	0.000000
33	6	0	11.749139	-1.483030	0.000000
34	6	0	11.732412	-2.857702	0.000000
35	6	0	10.485062	-3.558000	0.000000
36	6	0	9.315218	-2.842683	0.000000

37	6	0	9.315218	2.842683	0.000000
38	6	0	10.485062	3.558000	0.000000
39	6	0	11.732412	2.857702	0.000000
40	6	0	11.749139	1.483030	0.000000
41	6	0	-6.840064	-1.372789	-0.000000
42	6	0	-5.717582	-1.845064	-0.000000
43	6	0	-4.423683	-2.274700	-0.000000
44	6	0	-3.239211	-2.572953	-0.000000
45	6	0	-1.897059	-2.787935	-0.000000
46	6	0	-0.679324	-2.893567	-0.000000
47	6	0	0.679324	-2.893567	0.000000
48	6	0	1.897059	-2.787935	0.000000
49	6	0	3.239211	-2.572953	0.000000
50	6	0	4.423683	-2.274700	0.000000
51	6	0	5.717582	-1.845064	0.000000
52	6	0	6.840064	-1.372789	0.000000
53	8	0	12.823449	3.652264	0.000000
54	6	0	14.085252	3.022932	0.000000
55	8	0	10.584837	4.903556	0.000000
56	6	0	9.375336	5.632921	0.000000
57	8	0	12.823449	-3.652264	-0.000000
58	6	0	14.085252	-3.022932	-0.000000
59	8	0	10.584837	-4.903556	-0.000000
60	6	0	9.375336	-5.632921	-0.000000
61	8	0	-10.584837	4.903556	-0.000000
62	6	0	-9.375336	5.632921	-0.000000
63	8	0	-12.823449	3.652264	-0.000000
64	6	0	-14.085252	3.022932	-0.000000
65	8	0	-12.823449	-3.652264	0.000000
66	6	0	-14.085252	-3.022932	0.000000
67	8	0	-10.584837	-4.903556	0.000000
68	6	0	-9.375336	-5.632921	0.000000
69	1	0	-12.703325	0.974960	0.000000
70	1	0	-8.356568	3.347729	0.000000
71	1	0	-8.356568	-3.347729	-0.000000
72	1	0	-12.703325	-0.974960	-0.000000
73	1	0	12.703325	-0.974960	0.000000
74	1	0	8.356568	-3.347729	0.000000
75	1	0	8.356568	3.347729	0.000000
76	1	0	12.703325	0.974960	0.000000
77	1	0	14.218745	2.402643	0.894944
78	1	0	14.218745	2.402643	-0.894944
79	1	0	14.821887	3.825791	0.000000
80	1	0	9.658399	6.684900	0.000000
81	1	0	8.780694	5.410709	-0.894024
82	1	0	8.780694	5.410709	0.894024
83	1	0	14.218745	-2.402643	0.894944
84	1	0	14.821887	-3.825791	-0.000000
85	1	0	14.218745	-2.402643	-0.894944
86	1	0	8.780694	-5.410709	-0.894024
87	1	0	8.780694	-5.410709	0.894024
88	1	0	9.658399	-6.684900	-0.000000
89	1	0	-9.658399	6.684900	-0.000000
90	1	0	-8.780694	5.410709	-0.894024
91	1	0	-8.780694	5.410709	0.894024
92	1	0	-14.821887	3.825791	-0.000000
93	1	0	-14.218745	2.402643	-0.894944
94	1	0	-14.218745	2.402643	0.894944
95	1	0	-14.821887	-3.825791	0.000000
96	1	0	-14.218745	-2.402643	0.894944
97	1	0	-14.218745	-2.402643	-0.894944
98	1	0	-9.658399	-6.684900	0.000000
99	1	0	-8.780694	-5.410709	-0.894024
100	1	0	-8.780694	-5.410709	0.894024

No imaginary frequency.
Total energy = –2905.59461713 hartree.

Table S11. Cartesian Coordinates of **4′** at the B3LYP/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-10.500634	0.703672	0.000000
2	6	0	-10.500634	-0.703672	-0.000000
3	6	0	-11.744429	-1.431406	0.000000
4	6	0	-12.977540	-0.725394	0.000000
5	6	0	-12.977540	0.725394	0.000000
6	6	0	-11.744429	1.431406	0.000000
7	6	0	-14.174902	1.486569	0.000000
8	6	0	-14.165326	2.867498	0.000000
9	6	0	-12.917682	3.570170	0.000000
10	6	0	-11.743898	2.850091	0.000000
11	6	0	-11.743898	-2.850091	-0.000000
12	6	0	-12.917682	-3.570170	-0.000000
13	6	0	-14.165326	-2.867498	-0.000000
14	6	0	-14.174902	-1.486569	-0.000000
15	6	0	-9.265475	1.385143	0.000000
16	6	0	-9.265475	-1.385143	-0.000000
17	6	0	-8.152972	1.905194	0.000000
18	6	0	-6.905744	2.407589	0.000000
19	6	0	-5.733311	2.795989	0.000000
20	6	0	-4.439898	3.135460	0.000000
21	6	0	-3.226966	3.381916	0.000000
22	6	0	-1.902891	3.551906	0.000000
23	6	0	-0.667178	3.636363	0.000000
24	6	0	0.667178	3.636363	0.000000
25	6	0	1.902891	3.551906	0.000000
26	6	0	3.226966	3.381916	0.000000
27	6	0	4.439898	3.135460	0.000000
28	6	0	5.733311	2.795989	0.000000
29	6	0	6.905744	2.407589	0.000000
30	6	0	8.152972	1.905194	0.000000
31	6	0	9.265475	1.385143	0.000000
32	6	0	10.500634	0.703672	0.000000
33	6	0	-8.152972	-1.905194	-0.000000
34	6	0	-6.905744	-2.407589	-0.000000
35	6	0	-5.733311	-2.795989	-0.000000
36	6	0	-4.439898	-3.135460	-0.000000
37	6	0	-3.226966	-3.381916	-0.000000
38	6	0	-1.902891	-3.551906	-0.000000
39	6	0	-0.667178	-3.636363	-0.000000
40	6	0	0.667178	-3.636363	0.000000
41	6	0	1.902891	-3.551906	0.000000
42	6	0	3.226966	-3.381916	0.000000
43	6	0	4.439898	-3.135460	0.000000
44	6	0	5.733311	-2.795989	0.000000
45	6	0	6.905744	-2.407589	0.000000
46	6	0	8.152972	-1.905194	0.000000
47	6	0	9.265475	-1.385143	0.000000
48	6	0	11.744429	1.431406	0.000000
49	6	0	12.977540	0.725394	0.000000
50	6	0	12.977540	-0.725394	0.000000
51	6	0	11.744429	-1.431406	0.000000
52	6	0	10.500634	-0.703672	0.000000
53	6	0	11.743898	2.850091	0.000000
54	6	0	12.917682	3.570170	0.000000
55	6	0	14.165326	2.867498	0.000000
56	6	0	14.174902	1.486569	0.000000
57	6	0	14.174902	-1.486569	0.000000
58	6	0	14.165326	-2.867498	0.000000
59	6	0	12.917682	-3.570170	0.000000
60	6	0	11.743898	-2.850091	0.000000
61	8	0	-13.015853	4.922590	0.000000
62	6	0	-11.810228	5.674942	0.000000

63	8	0	-15.266290	3.659930	0.000000
64	6	0	-16.542366	3.040087	0.000000
65	8	0	-15.266290	-3.659930	-0.000000
66	6	0	-16.542366	-3.040087	-0.000000
67	8	0	-13.015853	-4.922590	-0.000000
68	6	0	-11.810228	-5.674942	-0.000000
69	8	0	13.015853	4.922590	0.000000
70	6	0	11.810228	5.674942	0.000000
71	8	0	15.266290	3.659930	0.000000
72	6	0	16.542366	3.040087	0.000000
73	8	0	15.266290	-3.659930	0.000000
74	6	0	16.542366	-3.040087	0.000000
75	8	0	13.015853	-4.922590	0.000000
76	6	0	11.810228	-5.674942	0.000000
77	1	0	-15.128430	0.977376	0.000000
78	1	0	-10.788776	3.360054	0.000000
79	1	0	-10.788776	-3.360054	-0.000000
80	1	0	-15.128430	-0.977376	-0.000000
81	1	0	10.788776	3.360054	0.000000
82	1	0	15.128430	0.977376	0.000000
83	1	0	15.128430	-0.977376	0.000000
84	1	0	10.788776	-3.360054	0.000000
85	1	0	-11.209449	5.467872	0.894847
86	1	0	-11.209449	5.467872	-0.894847
87	1	0	-12.114958	6.722574	0.000000
88	1	0	-17.267925	3.855012	0.000000
89	1	0	-16.688546	2.421872	0.895610
90	1	0	-16.688546	2.421872	-0.895610
91	1	0	-17.267925	-3.855012	-0.000000
92	1	0	-16.688546	-2.421872	-0.895610
93	1	0	-16.688546	-2.421872	0.895610
94	1	0	-12.114958	-6.722574	-0.000000
95	1	0	-11.209449	-5.467872	0.894847
96	1	0	-11.209449	-5.467872	-0.894847
97	1	0	12.114958	6.722574	0.000000
98	1	0	11.209449	5.467872	0.894847
99	1	0	11.209449	5.467872	-0.894847
100	1	0	17.267925	3.855012	0.000000
101	1	0	16.688546	2.421872	-0.895610
102	1	0	16.688546	2.421872	0.895610
103	1	0	17.267925	-3.855012	0.000000
104	1	0	16.688546	-2.421872	0.895610
105	1	0	16.688546	-2.421872	-0.895610
106	1	0	11.209449	-5.467872	-0.894847
107	1	0	11.209449	-5.467872	0.894847
108	1	0	12.114958	-6.722574	0.000000

No imaginary frequency.
Total energy = –3211.41128931 hartree.

Table S12. Cartesian Coordinates of **4′** at the M06-2X/6-31G(d) level

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-10.551948	0.694809	0.000000
2	6	0	-10.551948	-0.694809	-0.000000
3	6	0	-11.788878	-1.425430	0.000000
4	6	0	-13.013263	-0.724449	0.000000
5	6	0	-13.013263	0.724449	0.000000
6	6	0	-11.788878	1.425430	0.000000
7	6	0	-14.211999	1.482370	0.000000
8	6	0	-14.195973	2.857074	0.000000
9	6	0	-12.948791	3.557879	0.000000
10	6	0	-11.778635	2.843075	0.000000
11	6	0	-11.778635	-2.843075	-0.000000
12	6	0	-12.948791	-3.557879	-0.000000

13	6	0	-14.195973	-2.857074	-0.000000
14	6	0	-14.211999	-1.482370	-0.000000
15	6	0	-9.305707	1.376990	0.000000
16	6	0	-9.305707	-1.376990	-0.000000
17	6	0	-8.196795	1.880311	0.000000
18	6	0	-6.925130	2.370998	0.000000
19	6	0	-5.761087	2.741067	0.000000
20	6	0	-4.444646	3.074754	0.000000
21	6	0	-3.245467	3.312689	0.000000
22	6	0	-1.898733	3.481876	0.000000
23	6	0	-0.678611	3.563782	0.000000
24	6	0	0.678611	3.563782	0.000000
25	6	0	1.898733	3.481876	0.000000
26	6	0	3.245467	3.312689	0.000000
27	6	0	4.444646	3.074754	0.000000
28	6	0	5.761087	2.741067	0.000000
29	6	0	6.925130	2.370998	0.000000
30	6	0	8.196795	1.880311	0.000000
31	6	0	9.305707	1.376990	0.000000
32	6	0	10.551948	0.694809	0.000000
33	6	0	-8.196795	-1.880311	-0.000000
34	6	0	-6.925130	-2.370998	-0.000000
35	6	0	-5.761087	-2.741067	-0.000000
36	6	0	-4.444646	-3.074754	-0.000000
37	6	0	-3.245467	-3.312689	-0.000000
38	6	0	-1.898733	-3.481876	-0.000000
39	6	0	-0.678611	-3.563782	-0.000000
40	6	0	0.678611	-3.563782	0.000000
41	6	0	1.898733	-3.481876	0.000000
42	6	0	3.245467	-3.312689	0.000000
43	6	0	4.444646	-3.074754	0.000000
44	6	0	5.761087	-2.741067	0.000000
45	6	0	6.925130	-2.370998	0.000000
46	6	0	8.196795	-1.880311	0.000000
47	6	0	9.305707	-1.376990	0.000000
48	6	0	11.788878	1.425430	0.000000
49	6	0	13.013263	0.724449	0.000000
50	6	0	13.013263	-0.724449	0.000000
51	6	0	11.788878	-1.425430	0.000000
52	6	0	10.551948	-0.694809	0.000000
53	6	0	11.778635	2.843075	0.000000
54	6	0	12.948791	3.557879	0.000000
55	6	0	14.195973	2.857074	0.000000
56	6	0	14.211999	1.482370	0.000000
57	6	0	14.211999	-1.482370	0.000000
58	6	0	14.195973	-2.857074	0.000000
59	6	0	12.948791	-3.557879	0.000000
60	6	0	11.778635	-2.843075	0.000000
61	8	0	-13.049629	4.903224	0.000000
62	6	0	-11.840682	5.633732	0.000000
63	8	0	-15.287382	3.650933	0.000000
64	6	0	-16.549292	3.021426	0.000000
65	8	0	-15.287382	-3.650933	-0.000000
66	6	0	-16.549292	-3.021426	-0.000000
67	8	0	-13.049629	-4.903224	-0.000000
68	6	0	-11.840682	-5.633732	-0.000000
69	8	0	13.049629	4.903224	0.000000
70	6	0	11.840682	5.633732	0.000000
71	8	0	15.287382	3.650933	0.000000
72	6	0	16.549292	3.021426	0.000000
73	8	0	15.287382	-3.650933	0.000000
74	6	0	16.549292	-3.021426	0.000000
75	8	0	13.049629	-4.903224	0.000000
76	6	0	11.840682	-5.633732	0.000000
77	1	0	-15.165998	0.974046	0.000000
78	1	0	-10.820705	3.349262	0.000000
79	1	0	-10.820705	-3.349262	-0.000000
80	1	0	-15.165998	-0.974046	-0.000000
81	1	0	10.820705	3.349262	0.000000

82	1	0	15.165998	0.974046	0.000000
83	1	0	15.165998	-0.974046	0.000000
84	1	0	10.820705	-3.349262	0.000000
85	1	0	-11.245981	5.412015	0.894093
86	1	0	-11.245981	5.412015	-0.894093
87	1	0	-12.124746	6.685408	0.000000
88	1	0	-17.285853	3.824308	0.000000
89	1	0	-16.682618	2.401245	0.895007
90	1	0	-16.682618	2.401245	-0.895007
91	1	0	-17.285853	-3.824308	-0.000000
92	1	0	-16.682618	-2.401245	-0.895007
93	1	0	-16.682618	-2.401245	0.895007
94	1	0	-12.124746	-6.685408	-0.000000
95	1	0	-11.245981	-5.412015	0.894093
96	1	0	-11.245981	-5.412015	-0.894093
97	1	0	12.124746	6.685408	0.000000
98	1	0	11.245981	5.412015	0.894093
99	1	0	11.245981	5.412015	-0.894093
100	1	0	17.285853	3.824308	0.000000
101	1	0	16.682618	2.401245	-0.895007
102	1	0	16.682618	2.401245	0.895007
103	1	0	17.285853	-3.824308	0.000000
104	1	0	16.682618	-2.401245	0.895007
105	1	0	16.682618	-2.401245	-0.895007
106	1	0	11.245981	-5.412015	-0.894093
107	1	0	11.245981	-5.412015	0.894093
108	1	0	12.124746	-6.685408	0.000000

No imaginary frequency.
Total energy = –3210.10749326 hartree.

Table S13. Cartesian Coordinates of **1′**$_2$ at the B3LYP-D3/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.572555	0.724679	-1.042187
2	6	0	6.341911	1.425231	-1.164633
3	6	0	5.112444	0.701333	-1.321550
4	6	0	5.112480	-0.701393	-1.321530
5	6	0	6.341990	-1.425233	-1.164670
6	6	0	7.572601	-0.724621	-1.042254
7	6	0	8.756752	1.494361	-0.893246
8	6	0	8.729132	2.874294	-0.834631
9	6	0	7.480114	3.568674	-0.922415
10	6	0	6.325189	2.841492	-1.102630
11	6	0	6.325352	-2.841497	-1.102753
12	6	0	7.480334	-3.568631	-0.922704
13	6	0	8.729322	-2.874187	-0.834998
14	6	0	8.756859	-1.494247	-0.893501
15	6	0	3.862962	1.365757	-1.448562
16	6	0	3.863023	-1.365871	-1.448426
17	6	0	2.679731	1.654673	-1.549336
18	6	0	2.679799	-1.654850	-1.549072
19	6	0	1.321103	1.658892	-1.640188
20	6	0	1.321183	-1.659405	-1.640112
21	6	0	0.136387	-1.364233	-1.704055
22	6	0	-1.119789	-0.702422	-1.780624
23	6	0	-1.119820	0.701690	-1.780692
24	6	0	-2.357052	1.423839	-1.840296
25	6	0	-3.585229	0.722928	-1.977227
26	6	0	-3.585183	-0.723849	-1.977133
27	6	0	-2.356969	-1.424664	-1.840110
28	6	0	0.136349	1.363521	-1.704079
29	6	0	-4.777980	-1.484717	-2.058493
30	6	0	-4.775031	-2.860155	-1.954637
31	6	0	-3.540295	-3.551431	-1.750730

32	6	0	-2.363637	-2.838780	-1.727178
33	6	0	-2.363820	2.837971	-1.727579
34	6	0	-3.540524	3.550542	-1.751320
35	6	0	-4.775210	2.859159	-1.955073
36	6	0	-4.778079	1.483699	-2.058651
37	8	0	7.552392	-4.915146	-0.785947
38	6	0	6.323965	-5.640635	-0.743518
39	8	0	9.817450	-3.673494	-0.664006
40	6	0	11.090435	-3.057452	-0.568963
41	8	0	9.817199	3.673644	-0.663448
42	6	0	11.090210	3.057665	-0.568337
43	8	0	7.552078	4.915176	-0.785494
44	6	0	6.323584	5.640572	-0.743389
45	8	0	-3.651169	-4.900675	-1.583251
46	6	0	-2.465698	-5.621582	-1.281527
47	8	0	-5.878545	-3.652713	-2.008326
48	6	0	-7.128723	-3.040468	-2.299664
49	8	0	-5.878800	3.651619	-2.008790
50	6	0	-7.128814	3.039330	-2.300714
51	8	0	-3.651490	4.899825	-1.584141
52	6	0	-2.466322	5.620697	-1.281110
53	1	0	9.709521	0.990030	-0.809921
54	1	0	5.365768	3.339967	-1.156672
55	1	0	5.365959	-3.340030	-1.156750
56	1	0	9.709608	-0.989867	-0.810247
57	1	0	-5.725971	-0.978211	-2.166763
58	1	0	-1.413326	-3.338588	-1.586826
59	1	0	-1.413552	3.337878	-1.587287
60	1	0	-5.726058	0.977116	-2.166658
61	1	0	6.608724	-6.684162	-0.596013
62	1	0	5.775958	-5.546224	-1.690911
63	1	0	5.693969	-5.304587	0.087469
64	1	0	11.807708	-3.871239	-0.447877
65	1	0	11.333518	-2.489576	-1.477754
66	1	0	11.151260	-2.386722	0.299994
67	1	0	11.807426	3.871481	-0.447117
68	1	0	11.333408	2.489876	-1.477152
69	1	0	11.150989	2.386866	0.300570
70	1	0	5.775929	5.546267	-1.690999
71	1	0	6.608220	6.684090	-0.595601
72	1	0	5.693321	5.304319	0.087313
73	1	0	-1.993485	-5.246409	-0.363328
74	1	0	-2.775382	-6.658580	-1.138332
75	1	0	-1.741471	-5.568585	-2.105432
76	1	0	-7.866666	-3.842710	-2.250752
77	1	0	-7.386854	-2.276198	-1.558957
78	1	0	-7.120914	-2.594778	-3.303677
79	1	0	-7.866755	3.841619	-2.252534
80	1	0	-7.120396	2.593326	-3.304583
81	1	0	-7.387438	2.275309	-1.559919
82	1	0	-1.994937	5.245221	-0.362612
83	1	0	-1.741340	5.568028	-2.104372
84	1	0	-2.776184	6.657639	-1.137882
85	6	0	3.585088	0.723572	1.977767
86	6	0	2.356870	1.424416	1.840932
87	6	0	1.119682	0.702194	1.781517
88	6	0	1.119689	-0.701905	1.781589
89	6	0	2.356899	-1.424086	1.840989
90	6	0	3.585104	-0.723212	1.977778
91	6	0	4.777900	1.484437	2.058984
92	6	0	4.774939	2.859886	1.955213
93	6	0	3.540195	3.551176	1.751382
94	6	0	2.363535	2.838527	1.728007
95	6	0	2.363584	-2.838200	1.728072
96	6	0	3.540260	-3.550822	1.751428
97	6	0	4.774987	-2.859499	1.955237
98	6	0	4.777933	-1.484049	2.058970
99	6	0	-0.136487	1.363984	1.704769
100	6	0	-0.136495	-1.363684	1.704963

101	6	0	-1.321239	1.659344	1.640930
102	6	0	-1.321285	-1.658906	1.641114
103	6	0	-2.679850	1.655028	1.549930
104	6	0	-2.679915	-1.654584	1.550293
105	6	0	-3.863107	-1.365543	1.449452
106	6	0	-5.112520	-0.701069	1.322129
107	6	0	-5.112506	0.701650	1.321944
108	6	0	-6.341919	1.425497	1.164474
109	6	0	-7.572492	0.724916	1.041486
110	6	0	-7.572508	-0.724393	1.041694
111	6	0	-6.341946	-1.424966	1.164888
112	6	0	-3.863071	1.366113	1.449081
113	6	0	-8.756639	-1.494064	0.892183
114	6	0	-8.728998	-2.874003	0.833672
115	6	0	-7.480062	-3.568402	0.922320
116	6	0	-6.325230	-2.841238	1.103155
117	6	0	-6.325149	2.841741	1.102347
118	6	0	-7.479954	3.568899	0.921351
119	6	0	-8.728916	2.874513	0.832912
120	6	0	-8.756600	1.494584	0.891795
121	8	0	3.651153	-4.900042	1.583812
122	6	0	2.465646	-5.621007	1.282390
123	8	0	5.878521	-3.652019	2.009030
124	6	0	7.128711	-3.039619	2.299998
125	8	0	5.878471	3.652417	2.008990
126	6	0	7.128643	3.040039	2.300076
127	8	0	3.651034	4.900406	1.583795
128	6	0	2.465547	5.621284	1.282064
129	8	0	-7.552003	-4.914930	0.785563
130	6	0	-6.323680	-5.640705	0.746160
131	8	0	-9.816967	-3.673346	0.661778
132	6	0	-11.089896	-3.057342	0.565717
133	8	0	-9.816874	3.673847	0.660907
134	6	0	-11.089819	3.057858	0.564980
135	8	0	-7.551836	4.915380	0.784181
136	6	0	-6.323489	5.641156	0.745226
137	1	0	5.725910	0.977929	2.167092
138	1	0	1.413208	3.338347	1.587816
139	1	0	1.413268	-3.338034	1.587852
140	1	0	5.725939	-0.977523	2.167031
141	1	0	-9.709353	-0.989725	0.808287
142	1	0	-5.365860	-3.339742	1.157844
143	1	0	-5.365749	3.340216	1.156744
144	1	0	-9.709335	0.990256	0.808068
145	1	0	2.775370	-6.657958	1.138933
146	1	0	1.993088	-5.245756	0.364400
147	1	0	1.741693	-5.568184	2.106548
148	1	0	7.866632	-3.841919	2.251705
149	1	0	7.386854	-2.275835	1.558791
150	1	0	7.120907	-2.593279	3.303725
151	1	0	7.866537	3.842373	2.251951
152	1	0	7.386914	2.276340	1.558819
153	1	0	7.120722	2.593598	3.303756
154	1	0	1.993036	5.245736	0.364174
155	1	0	2.775288	6.658183	1.138276
156	1	0	1.741553	5.568733	2.106205
157	1	0	-5.777851	-5.545985	1.694789
158	1	0	-6.608371	-6.684224	0.598483
159	1	0	-5.691489	-5.305387	-0.083468
160	1	0	-11.807036	-3.871147	0.443968
161	1	0	-11.333762	-2.489546	1.474348
162	1	0	-11.150014	-2.386547	-0.303238
163	1	0	-11.806939	3.871657	0.443075
164	1	0	-11.149959	2.386892	-0.303842
165	1	0	-11.333695	2.490247	1.473724
166	1	0	-5.777879	5.546248	1.693958
167	1	0	-5.691131	5.306008	-0.084332
168	1	0	-6.608163	6.684710	0.597735

No imaginary frequency.
Total energy = –4595.18769962 hartree.

Table S14. Cartesian Coordinates of **2′**$_2$ at the B3LYP-D3/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	10.027277	0.725626	-1.146579
2	6	0	8.796830	1.428410	-1.245012
3	6	0	7.562258	0.701796	-1.379866
4	6	0	7.562300	-0.701414	-1.380101
5	6	0	8.796884	-1.428057	-1.245460
6	6	0	10.027303	-0.725268	-1.146760
7	6	0	11.215163	1.492412	-1.019343
8	6	0	11.191572	2.872741	-0.958643
9	6	0	9.942722	3.569474	-1.022440
10	6	0	8.783160	2.843780	-1.181754
11	6	0	8.783255	-2.843450	-1.182656
12	6	0	9.942826	-3.569143	-1.023447
13	6	0	11.191652	-2.872389	-0.959308
14	6	0	11.215208	-1.492046	-1.019618
15	8	0	12.283303	3.668910	-0.806994
16	8	0	10.019619	4.914504	-0.886810
17	6	0	8.794088	5.645382	-0.831372
18	6	0	13.558134	3.051739	-0.739034
19	8	0	12.283385	-3.668574	-0.807756
20	8	0	10.019755	-4.914202	-0.888202
21	6	0	8.794285	-5.645246	-0.833762
22	6	0	13.558186	-3.051385	-0.739410
23	6	0	6.324677	1.374137	-1.482493
24	6	0	6.324788	-1.373827	-1.482902
25	6	0	5.171866	1.782073	-1.554483
26	6	0	3.864205	2.105008	-1.613706
27	6	0	2.637208	2.210022	-1.653053
28	6	0	5.172089	-1.782056	-1.554923
29	6	0	3.864450	-2.105089	-1.614060
30	6	0	2.637431	-2.209901	-1.653117
31	6	0	-6.114699	-0.724216	-1.954697
32	6	0	-4.886395	-1.426344	-1.835393
33	6	0	-3.645375	-0.701834	-1.802465
34	6	0	-3.645650	0.703292	-1.802602
35	6	0	-4.886982	1.427265	-1.835817
36	6	0	-6.114990	0.724564	-1.954939
37	6	0	-7.309025	-1.484160	-2.014519
38	6	0	-7.305983	-2.859476	-1.900141
39	6	0	-6.069592	-3.550453	-1.706381
40	6	0	-4.891753	-2.838391	-1.712330
41	6	0	-4.893007	2.839352	-1.713278
42	6	0	-6.071171	3.550903	-1.707778
43	6	0	-7.307267	2.859303	-1.901198
44	6	0	-7.309644	1.483952	-2.015124
45	8	0	-8.410567	-3.650178	-1.929155
46	8	0	-6.177008	-4.894827	-1.514653
47	6	0	-4.988696	-5.606415	-1.190462
48	6	0	-9.665571	-3.039919	-2.204413
49	8	0	-8.412287	3.649410	-1.930674
50	8	0	-6.179127	4.895354	-1.516813
51	6	0	-4.991094	5.607663	-1.193208
52	6	0	-9.666942	3.038212	-2.205387
53	6	0	-2.400731	-1.369950	-1.767189
54	6	0	-2.401221	1.371835	-1.767338
55	6	0	-1.240782	-1.765167	-1.749878
56	6	0	0.070695	-2.075095	-1.725190
57	6	0	1.295055	-2.207903	-1.694242
58	6	0	-1.241204	1.766862	-1.749890
59	6	0	0.070388	2.076362	-1.725353

60	6	0	1.294829	2.208403	-1.694263
61	1	0	12.168552	0.986767	-0.954809
62	1	0	7.825010	3.345832	-1.217904
63	1	0	7.825136	-3.345544	-1.219022
64	1	0	12.168565	-0.986385	-0.954728
65	1	0	9.085139	6.687908	-0.690423
66	1	0	8.234842	5.550151	-1.771919
67	1	0	8.173206	5.314140	0.008203
68	1	0	14.277768	3.865127	-0.631071
69	1	0	13.781857	2.485874	-1.653861
70	1	0	13.635883	2.379689	0.127390
71	1	0	9.085405	-6.687815	-0.693273
72	1	0	8.235506	-5.549535	-1.774534
73	1	0	8.172880	-5.314640	0.005688
74	1	0	14.277834	-3.864785	-0.631628
75	1	0	13.635797	-2.379631	0.127256
76	1	0	13.782017	-2.485197	-1.654011
77	1	0	-8.258152	-0.977683	-2.112374
78	1	0	-3.941260	-3.339352	-1.580107
79	1	0	-3.942748	3.340817	-1.581265
80	1	0	-8.258500	0.977005	-2.113141
81	1	0	-5.299211	-6.637231	-1.010816
82	1	0	-4.268157	-5.582587	-2.018396
83	1	0	-4.514543	-5.198333	-0.288009
84	1	0	-10.402420	-3.841738	-2.136920
85	1	0	-9.910934	-2.269916	-1.465137
86	1	0	-9.674520	-2.602047	-3.211712
87	1	0	-5.302034	6.638478	-1.014304
88	1	0	-4.270583	5.583521	-2.021154
89	1	0	-4.516735	5.200445	-0.290473
90	1	0	-10.404311	3.839564	-2.137963
91	1	0	-9.675869	2.599997	-3.212540
92	1	0	-9.911602	2.268315	-1.465770
93	6	0	6.114969	0.724104	1.954097
94	6	0	4.886853	1.426554	1.834696
95	6	0	3.645667	0.702350	1.801158
96	6	0	3.645634	-0.702779	1.800957
97	6	0	4.886796	-1.427044	1.834204
98	6	0	6.114943	-0.724681	1.953850
99	6	0	7.309432	1.483759	2.014696
100	6	0	7.306797	2.859149	1.901028
101	6	0	6.070598	3.550504	1.707379
102	6	0	4.892605	2.838656	1.712380
103	6	0	4.892512	-2.839102	1.711269
104	6	0	6.070502	-3.550950	1.705864
105	6	0	7.306710	-2.859729	1.899935
106	6	0	7.309382	-1.484391	2.014200
107	8	0	8.411606	3.649514	1.931015
108	8	0	6.178274	4.895046	1.516839
109	6	0	4.990073	5.607331	1.193809
110	6	0	9.666341	3.038606	2.206031
111	8	0	8.411479	-3.650157	1.929673
112	8	0	6.178197	-4.895370	1.514500
113	6	0	4.990056	-5.607415	1.190697
114	6	0	9.666204	-3.039430	2.205145
115	6	0	2.401158	1.370719	1.765796
116	6	0	2.401082	-1.371089	1.765553
117	6	0	1.241177	1.765847	1.748356
118	6	0	-0.070312	2.075723	1.723536
119	6	0	-1.294706	2.208102	1.692203
120	6	0	1.241069	-1.766134	1.748210
121	6	0	-0.070457	-2.075911	1.723571
122	6	0	-1.294862	-2.208301	1.692514
123	6	0	-10.027423	-0.725560	1.147357
124	6	0	-8.797066	-1.428558	1.245504
125	6	0	-7.562309	-0.702097	1.379602
126	6	0	-7.562111	0.701123	1.379494
127	6	0	-8.796639	1.427955	1.245287
128	6	0	-10.027213	0.725337	1.147265

129	6	0	-11.215522	-1.492124	1.020862
130	6	0	-11.192284	-2.872487	0.960875
131	6	0	-9.943573	-3.569472	1.024553
132	6	0	-8.783740	-2.843971	1.182832
133	6	0	-8.782851	2.843350	1.182493
134	6	0	-9.942420	3.569211	1.024028
135	6	0	-11.191353	2.872621	0.960370
136	6	0	-11.215064	1.492276	1.020678
137	8	0	-12.284267	-3.668472	0.810101
138	8	0	-10.020913	-4.914578	0.889866
139	6	0	-8.795569	-5.645680	0.832499
140	6	0	-13.558982	-3.051041	0.742367
141	8	0	-12.283065	3.668933	0.809386
142	8	0	-10.019282	4.914341	0.889335
143	6	0	-8.793725	5.645108	0.832976
144	6	0	-13.557988	3.051914	0.741743
145	6	0	-6.324770	-1.374562	1.481953
146	6	0	-6.324464	1.373378	1.481749
147	6	0	-5.171926	-1.782461	1.553629
148	6	0	-3.864264	-2.105475	1.612488
149	6	0	-2.637244	-2.210377	1.651452
150	6	0	-5.171711	1.781523	1.553380
151	6	0	-3.864080	2.104636	1.612207
152	6	0	-2.637081	2.209775	1.651024
153	1	0	8.258382	0.976988	2.112715
154	1	0	3.942261	3.339922	1.580255
155	1	0	3.942163	-3.340292	1.578893
156	1	0	8.258337	-0.977696	2.112568
157	1	0	5.300841	6.638249	1.015200
158	1	0	4.515512	5.200452	0.291029
159	1	0	4.269792	5.582756	2.021945
160	1	0	10.403529	3.840139	2.138832
161	1	0	9.911366	2.268786	1.466457
162	1	0	9.675111	2.600341	3.213163
163	1	0	5.300847	-6.638217	1.011457
164	1	0	4.515717	-5.199884	0.288094
165	1	0	4.269578	-5.583413	2.018677
166	1	0	10.403372	-3.840953	2.137629
167	1	0	9.674873	-2.601684	3.212507
168	1	0	9.911332	-2.269227	1.466012
169	1	0	-12.168807	-0.986290	0.956288
170	1	0	-7.825692	-3.346253	1.218678
171	1	0	-7.824643	3.345320	1.218341
172	1	0	-12.168534	0.986757	0.956359
173	1	0	-9.087092	-6.688273	0.693087
174	1	0	-8.176523	-5.315096	-0.008674
175	1	0	-8.234281	-5.549766	1.771761
176	1	0	-14.278855	-3.864323	0.635201
177	1	0	-13.782154	-2.484596	1.656969
178	1	0	-13.636980	-2.379476	-0.124411
179	1	0	-9.084840	6.687766	0.693083
180	1	0	-8.173889	5.314343	-0.007541
181	1	0	-8.233387	5.549255	1.772808
182	1	0	-14.277576	3.865414	0.634315
183	1	0	-13.636153	2.380141	-0.124859
184	1	0	-13.781407	2.485794	1.656484

No imaginary frequency.
Total energy = –5204.52520490 hartree.

Table S15. Cartesian Coordinates of **3′**$_2$ at the B3LYP-D3/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-10.035636	0.701740	1.419548
2	6	0	-10.035599	-0.701737	1.419597

3	6	0	-11.271290	-1.429728	1.293241
4	6	0	-12.501558	-0.725756	1.203503
5	6	0	-12.501594	0.725619	1.203472
6	6	0	-11.271359	1.429650	1.293162
7	6	0	-13.690793	1.491188	1.084108
8	6	0	-13.668831	2.871681	1.022694
9	6	0	-12.420075	3.569636	1.077780
10	6	0	-11.258832	2.844758	1.229432
11	6	0	-11.258696	-2.844836	1.229549
12	6	0	-12.419914	-3.569773	1.077959
13	6	0	-13.668704	-2.871874	1.022860
14	6	0	-13.690725	-1.491380	1.084171
15	6	0	-8.801325	1.375823	1.512218
16	6	0	-7.667341	1.837772	1.572489
17	6	0	-6.388635	2.252435	1.616060
18	6	0	-5.180834	2.504350	1.640960
19	6	0	-3.856363	2.694264	1.673247
20	6	0	-2.622307	2.758188	1.702496
21	6	0	-1.285999	2.748313	1.728882
22	6	0	-0.053523	2.655469	1.745007
23	6	0	1.270391	2.461772	1.751533
24	6	0	2.478507	2.211485	1.750201
25	6	0	3.763851	1.815830	1.748725
26	6	0	4.907867	1.373257	1.750709
27	6	0	6.148155	-0.702975	1.778374
28	6	0	6.148259	0.702664	1.778548
29	6	0	7.390199	1.427752	1.808971
30	6	0	8.618034	0.724395	1.923645
31	6	0	8.617930	-0.725137	1.923408
32	6	0	7.389982	-1.428270	1.808564
33	6	0	9.812740	-1.484486	1.978380
34	6	0	9.810097	-2.859983	1.862446
35	6	0	8.573239	-3.551696	1.673304
36	6	0	7.395127	-2.839988	1.686310
37	6	0	7.395572	2.839503	1.687167
38	6	0	8.573793	3.551047	1.674460
39	6	0	9.810544	2.859082	1.863317
40	6	0	9.812951	1.483552	1.978907
41	6	0	-8.801275	-1.375790	1.512282
42	6	0	-7.667348	-1.837878	1.572570
43	6	0	-6.388670	-2.252647	1.616168
44	6	0	-5.180909	-2.504759	1.641093
45	6	0	-3.856448	-2.694812	1.673204
46	6	0	-2.622395	-2.758829	1.702416
47	6	0	-1.286084	-2.749052	1.728693
48	6	0	-0.053617	-2.656085	1.744810
49	6	0	1.270268	-2.462210	1.751293
50	6	0	2.478349	-2.211752	1.749978
51	6	0	3.763657	-1.815977	1.748474
52	6	0	4.907669	-1.373394	1.750452
53	8	0	10.915471	3.648466	1.886015
54	6	0	12.172087	3.038037	2.154440
55	8	0	8.680391	4.894068	1.478940
56	6	0	7.490650	5.605361	1.155342
57	8	0	10.914862	-3.649563	1.884841
58	6	0	12.171537	-3.039555	2.153993
59	8	0	8.679663	-4.894647	1.477212
60	6	0	7.489858	-5.605595	1.153055
61	8	0	-12.499331	4.913859	0.943073
62	6	0	-11.275499	5.647801	0.882683
63	8	0	-14.761461	3.666488	0.878358
64	6	0	-16.037325	3.049424	0.820944
65	8	0	-14.761298	-3.666741	0.878607
66	6	0	-16.037187	-3.049737	0.821138
67	8	0	-12.499124	-4.914002	0.943290
68	6	0	-11.275264	-5.647869	0.882415
69	1	0	-14.644284	0.985067	1.026375
70	1	0	-10.301471	3.348521	1.259072
71	1	0	-10.301312	-3.348553	1.259173

72	1	0	-14.644234	-0.985303	1.026353
73	1	0	10.761976	-0.977752	2.073578
74	1	0	6.444868	-3.342070	1.557922
75	1	0	6.445390	3.341783	1.558972
76	1	0	10.762070	0.976646	2.074318
77	1	0	12.186846	2.601141	3.161993
78	1	0	12.412643	2.267413	1.414159
79	1	0	12.908558	3.839705	2.081933
80	1	0	7.801606	6.634729	0.969052
81	1	0	7.012977	5.192451	0.257043
82	1	0	6.773890	5.586596	1.986474
83	1	0	12.185942	-2.602935	3.161673
84	1	0	12.907816	-3.841402	2.081589
85	1	0	12.412604	-2.268771	1.414058
86	1	0	7.012349	-5.192098	0.254940
87	1	0	6.773008	-5.587206	1.984117
88	1	0	7.800693	-6.634899	0.966207
89	1	0	-11.569792	6.689781	0.745197
90	1	0	-10.658421	5.319516	0.039202
91	1	0	-10.711528	5.551980	1.820254
92	1	0	-16.757317	3.863058	0.718195
93	1	0	-16.121854	2.377078	-0.044510
94	1	0	-16.253548	2.484477	1.738022
95	1	0	-16.757146	-3.863412	0.718475
96	1	0	-16.253429	-2.484707	1.738161
97	1	0	-16.121748	-2.377482	-0.044384
98	1	0	-11.569535	-6.689850	0.744889
99	1	0	-10.658534	-5.319399	0.038755
100	1	0	-10.710975	-5.552136	1.819804
101	6	0	-6.148325	0.703147	-1.777856
102	6	0	-6.148201	-0.702497	-1.777796
103	6	0	-7.390010	-1.427803	-1.808299
104	6	0	-8.617932	-0.724664	-1.923409
105	6	0	-8.618061	0.724868	-1.923437
106	6	0	-7.390259	1.428230	-1.808414
107	6	0	-9.812992	1.484006	-1.978810
108	6	0	-9.810599	2.859519	-1.863095
109	6	0	-8.573893	3.551482	-1.673920
110	6	0	-7.395655	2.839978	-1.686422
111	6	0	-7.395162	-2.839539	-1.686192
112	6	0	-8.573277	-3.551243	-1.673638
113	6	0	-9.810090	-2.859523	-1.862996
114	6	0	-9.812726	-1.484021	-1.978815
115	6	0	-4.907940	1.373765	-1.749828
116	6	0	-3.763917	1.816321	-1.747753
117	6	0	-2.478575	2.211976	-1.749182
118	6	0	-1.270470	2.462324	-1.750479
119	6	0	0.053427	2.656108	-1.743796
120	6	0	1.285899	2.748986	-1.727592
121	6	0	2.622208	2.758776	-1.701169
122	6	0	3.856254	2.694718	-1.671929
123	6	0	5.180715	2.504674	-1.639831
124	6	0	6.388485	2.252601	-1.615096
125	6	0	7.667176	1.837863	-1.571745
126	6	0	8.801154	1.375870	-1.511711
127	6	0	10.035641	-0.701610	-1.419502
128	6	0	10.035533	0.701868	-1.419366
129	6	0	11.271230	1.429914	-1.293398
130	6	0	12.501579	0.725999	-1.204347
131	6	0	12.501674	-0.725377	-1.204330
132	6	0	11.271446	-1.429471	-1.293587
133	6	0	13.690960	-1.490892	-1.085436
134	6	0	13.669095	-2.871384	-1.024147
135	6	0	12.420349	-3.569411	-1.078743
136	6	0	11.259001	-2.844583	-1.229847
137	6	0	11.258598	2.845013	-1.229550
138	6	0	12.419865	3.570008	-1.078584
139	6	0	13.668725	2.872173	-1.024308
140	6	0	13.690777	1.491684	-1.085699

141	6	0	-4.907713	-1.372903	-1.749686
142	6	0	-3.763686	-1.815442	-1.747569
143	6	0	-2.478363	-2.211185	-1.748948
144	6	0	-1.270283	-2.461642	-1.750206
145	6	0	0.053601	-2.655526	-1.743741
146	6	0	1.286063	-2.748552	-1.727696
147	6	0	2.622373	-2.758480	-1.701387
148	6	0	3.856427	-2.694506	-1.672266
149	6	0	5.180901	-2.504521	-1.640211
150	6	0	6.388687	-2.252511	-1.615496
151	6	0	7.667377	-1.837762	-1.572093
152	6	0	8.801344	-1.375750	-1.511980
153	8	0	14.761372	3.667086	-0.880724
154	6	0	16.037339	3.050153	-0.824208
155	8	0	12.499055	4.914241	-0.943944
156	6	0	11.275082	5.647769	-0.880636
157	8	0	14.761821	-3.666151	-0.880315
158	6	0	16.037676	-3.049030	-0.823364
159	8	0	12.499746	-4.913614	-0.943967
160	6	0	11.275917	-5.647513	-0.882144
161	8	0	-8.680671	4.894483	-1.478324
162	6	0	-7.491080	5.605845	-1.154282
163	8	0	-10.915482	3.648926	-1.885682
164	6	0	-12.171920	3.038728	-2.155411
165	8	0	-10.914833	-3.649131	-1.885628
166	6	0	-12.171377	-3.039133	-2.155328
167	8	0	-8.679830	-4.894222	-1.477784
168	6	0	-7.490134	-5.605276	-1.153438
169	1	0	-10.762119	0.977110	-2.074182
170	1	0	-6.445500	3.342235	-1.557933
171	1	0	-6.444931	-3.341615	-1.557570
172	1	0	-10.761930	-0.977300	-2.074355
173	1	0	14.644434	-0.984722	-1.027861
174	1	0	10.301635	-3.348363	-1.259016
175	1	0	10.301170	3.348680	-1.258675
176	1	0	14.644354	0.985653	-1.028625
177	1	0	16.122545	2.377813	0.041184
178	1	0	16.252975	2.485234	-1.741441
179	1	0	16.757319	3.863861	-0.721961
180	1	0	11.569313	6.689741	-0.742954
181	1	0	10.709265	5.552489	-1.817146
182	1	0	10.659946	5.318530	-0.036125
183	1	0	16.122555	-2.376823	0.042163
184	1	0	16.757758	-3.862642	-0.721062
185	1	0	16.253465	-2.483923	-1.740446
186	1	0	10.710790	-5.551656	-1.819002
187	1	0	10.660026	-5.319108	-0.037851
188	1	0	11.570343	-6.689504	-0.745035
189	1	0	-7.802135	6.635236	-0.968289
190	1	0	-6.773941	5.586983	-1.985084
191	1	0	-7.013810	5.193056	-0.255715
192	1	0	-12.908374	3.840445	-2.083300
193	1	0	-12.185831	2.602116	-3.163100
194	1	0	-12.413211	2.267891	-1.415591
195	1	0	-12.907675	-3.841013	-2.083423
196	1	0	-12.412851	-2.268475	-1.415380
197	1	0	-12.185322	-2.602347	-3.162942
198	1	0	-7.800997	-6.634707	-0.967341
199	1	0	-6.772867	-5.586406	-1.984129
200	1	0	-7.013097	-5.192219	-0.254869

No imaginary frequency.
Total energy = –5813.83683312 hartree.

Table S16. Cartesian Coordinates of **4′**$_2$ at the B3LYP-D3/6-31G(d) level

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Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-12.498534	-0.702152	1.448369
2	6	0	-12.498534	0.701453	1.448583
3	6	0	-13.734618	1.430038	1.325272
4	6	0	-14.964815	0.725424	1.239634
5	6	0	-14.964808	-0.726044	1.239337
6	6	0	-13.734612	-1.430677	1.324776
7	6	0	-16.154561	-1.490958	1.122804
8	6	0	-16.133379	-2.871439	1.059580
9	6	0	-14.884544	-3.570001	1.109693
10	6	0	-13.722638	-2.845648	1.258986
11	6	0	-13.722674	2.845034	1.260029
12	6	0	-14.884607	3.569414	1.111107
13	6	0	-16.133445	2.870859	1.060841
14	6	0	-16.154600	1.490354	1.123513
15	6	0	-11.266525	-1.378684	1.536128
16	6	0	-11.266545	1.378003	1.536452
17	6	0	-10.146763	-1.875920	1.588782
18	6	0	-8.888696	-2.346435	1.620779
19	6	0	-7.702911	-2.690776	1.633749
20	6	0	-6.398770	-2.983441	1.654968
21	6	0	-5.178117	-3.183860	1.679718
22	6	0	-3.850821	-3.317848	1.706489
23	6	0	-2.614254	-3.375453	1.730041
24	6	0	-1.280794	-3.364072	1.748339
25	6	0	-0.045336	-3.282762	1.756928
26	6	0	1.280315	-3.132438	1.758427
27	6	0	2.499515	-2.921815	1.750357
28	6	0	3.803751	-2.630802	1.737540
29	6	0	4.992913	-2.299292	1.722965
30	6	0	6.259626	-1.851553	1.715870
31	6	0	7.390843	-1.375982	1.718142
32	6	0	8.628426	-0.702969	1.749819
33	6	0	-10.146823	1.875333	1.589091
34	6	0	-8.888764	2.345882	1.621008
35	6	0	-7.703001	2.690307	1.633861
36	6	0	-6.398895	2.983133	1.655168
37	6	0	-5.178263	3.183676	1.679952
38	6	0	-3.850972	3.317725	1.706768
39	6	0	-2.614408	3.375383	1.730263
40	6	0	-1.280944	3.363964	1.748351
41	6	0	-0.045487	3.282610	1.756754
42	6	0	1.280156	3.132217	1.758080
43	6	0	2.499346	2.921538	1.749919
44	6	0	3.803589	2.630567	1.737137
45	6	0	4.992746	2.299038	1.722550
46	6	0	6.259459	1.851311	1.715415
47	6	0	7.390694	1.375779	1.717721
48	6	0	9.870524	-1.428608	1.784716
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50	6	0	11.098080	0.725010	1.898447
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52	6	0	8.628369	0.702945	1.749606
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56	6	0	12.293197	-1.483638	1.953774
57	6	0	12.293056	1.483976	1.953284
58	6	0	12.290806	2.859740	1.838687
59	6	0	11.053787	3.552310	1.652870
60	6	0	9.875664	2.840631	1.666110
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62	6	0	-13.741916	-5.648936	0.909502
63	8	0	-17.226158	-3.665423	0.917850
64	6	0	-18.502714	-3.048575	0.865663
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72	6	0	14.653433	-3.037774	2.125209
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79	1	0	-12.765834	3.349805	1.286279
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83	1	0	13.242234	0.976987	2.047510
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85	1	0	-13.175395	-5.553811	1.845538
86	1	0	-13.127146	-5.321219	0.064134
87	1	0	-14.037913	-6.690462	0.772740
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92	1	0	-18.590414	2.375123	0.002732
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100	1	0	15.389379	-3.839787	2.051834
101	1	0	14.892201	-2.267968	1.383473
102	1	0	14.670576	-2.599980	3.132249
103	1	0	15.388963	3.840444	2.051384
104	1	0	14.670115	2.600240	3.131319
105	1	0	14.892158	2.268733	1.382484
106	1	0	9.489375	5.196339	0.241704
107	1	0	9.255034	5.587858	1.972577
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114	6	0	-9.870720	-1.428359	-1.784233
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119	6	0	-9.876139	2.840885	-1.665332
120	6	0	-11.054337	3.552461	-1.652337
121	6	0	-12.291252	2.859865	-1.838621
122	6	0	-12.293337	1.484109	-1.953470
123	6	0	-7.391026	-1.375564	-1.717109
124	6	0	-7.391035	1.376157	-1.716887
125	6	0	-6.259767	-1.851051	-1.714706
126	6	0	-4.992998	-2.298642	-1.721759
127	6	0	-3.803797	-2.630042	-1.736295
128	6	0	-2.499516	-2.920860	-1.749117
129	6	0	-1.280299	-3.131426	-1.757190
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131	6	0	1.280815	-3.363115	-1.747115
132	6	0	2.614279	-3.374644	-1.728823
133	6	0	3.850854	-3.317127	-1.705256
134	6	0	5.178179	-3.183334	-1.678515
135	6	0	6.398856	-2.983030	-1.653862
136	6	0	7.703050	-2.690537	-1.632829

137	6	0	8.888872	-2.346311	-1.620074
138	6	0	10.146961	-1.875820	-1.588186
139	6	0	11.266744	-1.378607	-1.535687
140	6	0	12.498732	-0.701965	-1.448357
141	6	0	-6.259819	1.851734	-1.714502
142	6	0	-4.993063	2.299354	-1.721625
143	6	0	-3.803854	2.630705	-1.736256
144	6	0	-2.499575	2.921528	-1.748963
145	6	0	-1.280353	3.132040	-1.756994
146	6	0	0.045308	3.282282	-1.755529
147	6	0	1.280774	3.363524	-1.747023
148	6	0	2.614240	3.374914	-1.728900
149	6	0	3.850807	3.317238	-1.705519
150	6	0	5.178108	3.183217	-1.678903
151	6	0	6.398750	2.982704	-1.654332
152	6	0	7.702885	2.689978	-1.633227
153	6	0	8.888672	2.345635	-1.620428
154	6	0	10.146779	1.875209	-1.588559
155	6	0	11.266603	1.378096	-1.536053
156	6	0	13.734900	-1.430466	-1.325299
157	6	0	14.965099	-0.725767	-1.240365
158	6	0	14.965049	0.725698	-1.240689
159	6	0	13.734788	1.430269	-1.325772
160	6	0	12.498680	0.701644	-1.448555
161	6	0	13.723083	-2.845453	-1.259665
162	6	0	14.885153	-3.569703	-1.111070
163	6	0	16.133952	-2.871058	-1.061372
164	6	0	16.154976	-1.490573	-1.124390
165	6	0	16.154863	1.490671	-1.125210
166	6	0	16.133706	2.871174	-1.062589
167	6	0	14.884835	3.569696	-1.112212
168	6	0	13.722834	2.845274	-1.260495
169	8	0	-11.160680	-4.894701	-1.460001
170	6	0	-9.970221	-5.607534	-1.140316
171	8	0	-13.396010	-3.648018	-1.860991
172	6	0	-14.653339	-3.037623	-2.127039
173	8	0	-13.396038	3.648621	-1.859486
174	6	0	-14.653365	3.038330	-2.125778
175	8	0	-11.160691	4.895172	-1.458219
176	6	0	-9.970203	5.607908	-1.138410
177	8	0	14.965718	-4.913181	-0.974911
178	6	0	13.742879	-5.648819	-0.911252
179	8	0	17.226852	-3.664983	-0.920250
180	6	0	18.503380	-3.048031	-0.868584
181	8	0	17.226575	3.665237	-0.921949
182	6	0	18.503176	3.048426	-0.870440
183	8	0	14.965271	4.913214	-0.976442
184	6	0	13.742263	5.648555	-0.910948
185	1	0	-13.242419	-0.976413	-2.048769
186	1	0	-8.926352	-3.343527	-1.539768
187	1	0	-8.926368	3.344062	-1.538684
188	1	0	-13.242434	0.977079	-2.048232
189	1	0	12.766266	-3.350285	-1.285444
190	1	0	17.108472	-0.984138	-1.070581
191	1	0	17.108435	0.984363	-1.071537
192	1	0	12.765953	3.349995	-1.286284
193	1	0	-9.490575	-5.196578	-0.242245
194	1	0	-9.255631	-5.587452	-1.973177
195	1	0	-10.281560	-6.636977	-0.955526
196	1	0	-15.389290	-3.839725	-2.054671
197	1	0	-14.892937	-2.268113	-1.385262
198	1	0	-14.669503	-2.599483	-3.133952
199	1	0	-15.389325	3.840392	-2.053053
200	1	0	-14.669536	2.600624	-3.132879
201	1	0	-14.892950	2.268493	-1.384335
202	1	0	-10.281521	6.637312	-0.953379
203	1	0	-9.490541	5.196725	-0.240452
204	1	0	-9.255643	5.588008	-1.971299
205	1	0	14.038959	-6.690354	-0.774742

206	1	0	13.128108	-5.321384	-0.065783
207	1	0	13.176323	-5.553469	-1.847234
208	1	0	19.223362	-3.861826	-0.767719
209	1	0	18.715839	-2.484431	-1.787280
210	1	0	18.591217	-2.374877	-0.004178
211	1	0	19.223098	3.862319	-0.769934
212	1	0	18.591290	2.375481	-0.005899
213	1	0	18.715475	2.484634	-1.789056
214	1	0	13.174421	5.553275	-1.846147
215	1	0	13.128840	5.320678	-0.064666
216	1	0	14.038331	6.690115	-0.774645

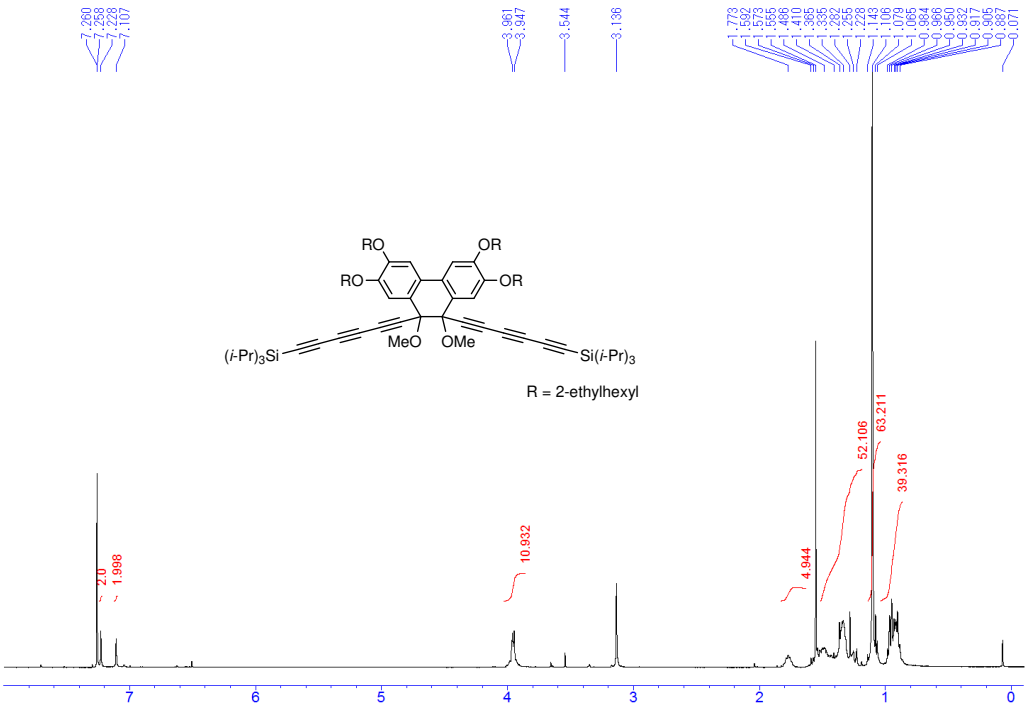
No imaginary frequency.
Total energy = –6423.14128584 hartree.

Table S17. Cartesian Coordinates of Tetramethoxyphenanthrene at the B3LYP/6-31G(d) level

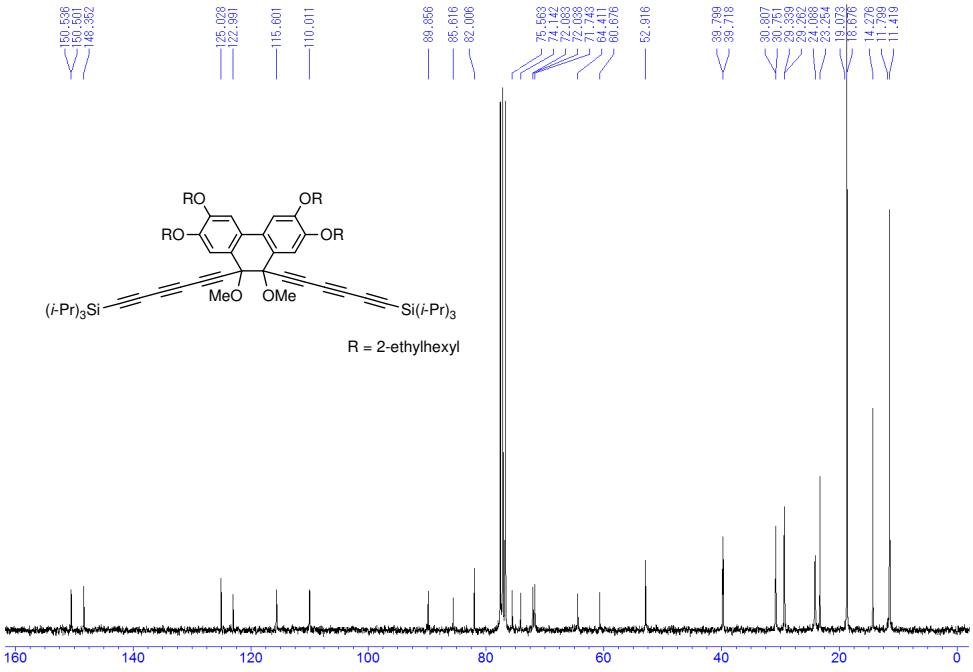
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.681901	-2.716476	-0.000060
2	6	0	0.681900	-2.716476	-0.000012
3	6	0	1.419248	-1.491305	0.000033
4	6	0	0.725413	-0.250184	0.000027
5	6	0	-0.725414	-0.250184	-0.000032
6	6	0	-1.419249	-1.491305	-0.000072
7	6	0	-1.497541	0.942331	-0.000055
8	6	0	-2.877621	0.918483	-0.000107
9	6	0	-3.569251	-0.333809	-0.000142
10	6	0	-2.838951	-1.502212	-0.000127
11	6	0	2.838950	-1.502213	0.000085
12	6	0	3.569250	-0.333810	0.000130
13	6	0	2.877621	0.918483	0.000127
14	6	0	1.497541	0.942331	0.000079
15	8	0	-4.928206	-0.245797	-0.000195
16	6	0	-5.665467	-1.455954	-0.000178
17	8	0	-3.684014	2.016802	-0.000133
18	6	0	-3.070448	3.293006	-0.000056
19	8	0	3.684016	2.016801	0.000182
20	6	0	3.070453	3.293006	0.000089
21	8	0	4.928205	-0.245798	0.000178
22	6	0	5.665465	-1.455956	0.000211
23	1	0	-0.995371	1.900480	-0.000037
24	1	0	-3.341974	-2.463117	-0.000158
25	1	0	3.341973	-2.463118	0.000086
26	1	0	0.995371	1.900479	0.000090
27	1	0	-5.453767	-2.057282	0.894311
28	1	0	-6.717540	-1.164907	-0.000180
29	1	0	-5.453772	-2.057306	-0.894653
30	1	0	-3.887411	4.017031	-0.000057
31	1	0	-2.451197	3.443984	0.894764
32	1	0	-2.451131	3.444061	-0.894819
33	1	0	3.887418	4.017029	0.000079
34	1	0	2.451200	3.443974	-0.894733
35	1	0	2.451137	3.444076	0.894850
36	1	0	5.453719	-2.057300	0.894678
37	1	0	5.453815	-2.057291	-0.894286
38	1	0	6.717538	-1.164910	0.000268
39	1	0	1.232965	-3.654237	-0.000005
40	1	0	-1.232967	-3.654237	-0.000092

No imaginary frequency.
Total energy = –997.62021079 hartree.

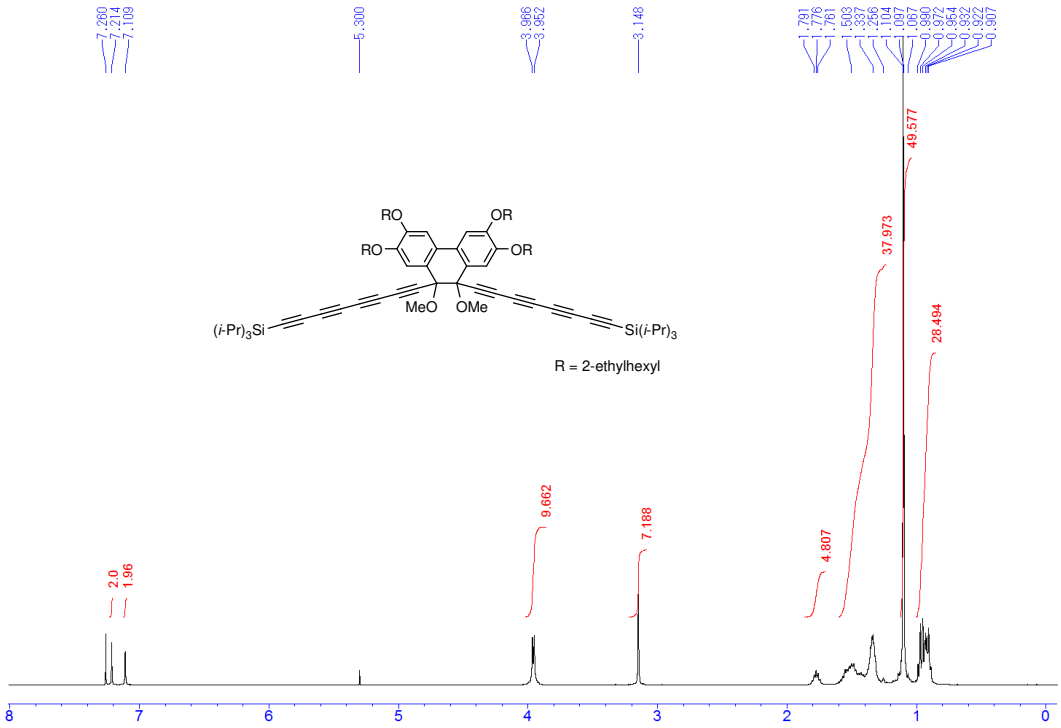
4. ^{1}H and ^{13}C NMR Spectral Data



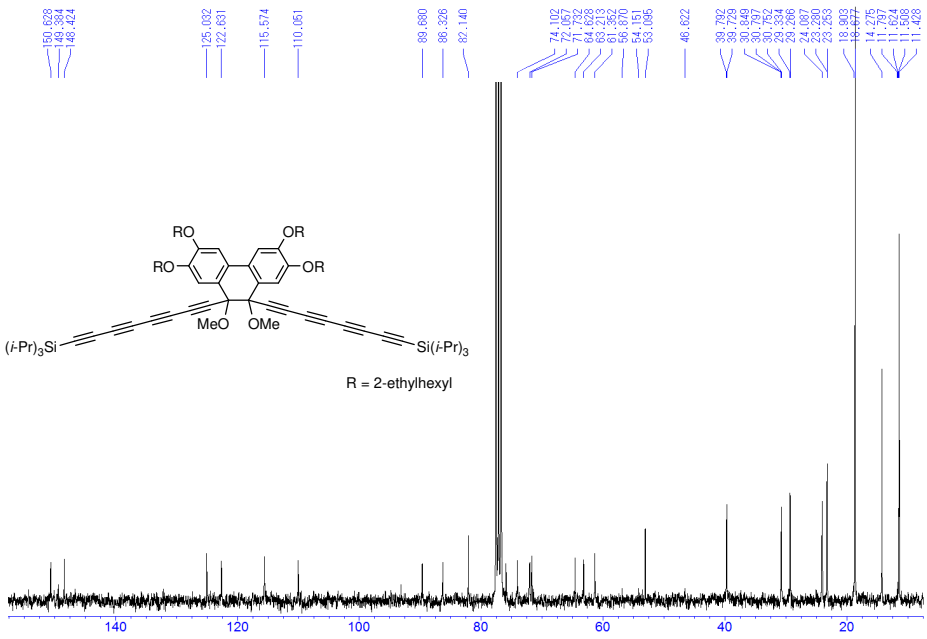
^{1}H NMR spectrum of **7** in $CDCl_3$ solution.



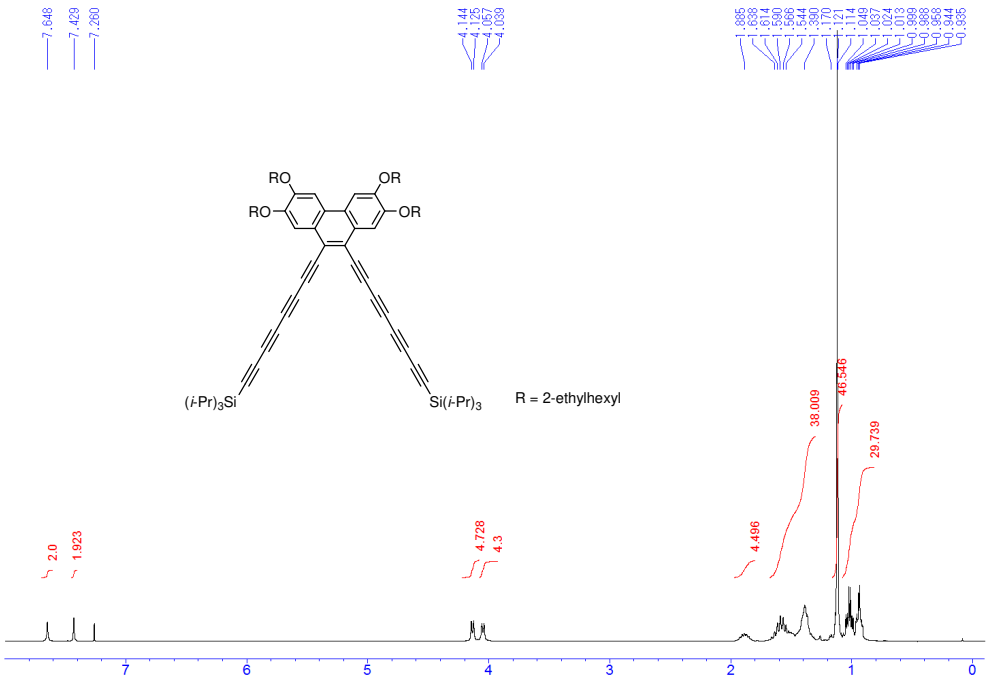
^{13}C NMR spectrum of **7** in $CDCl_3$ solution.



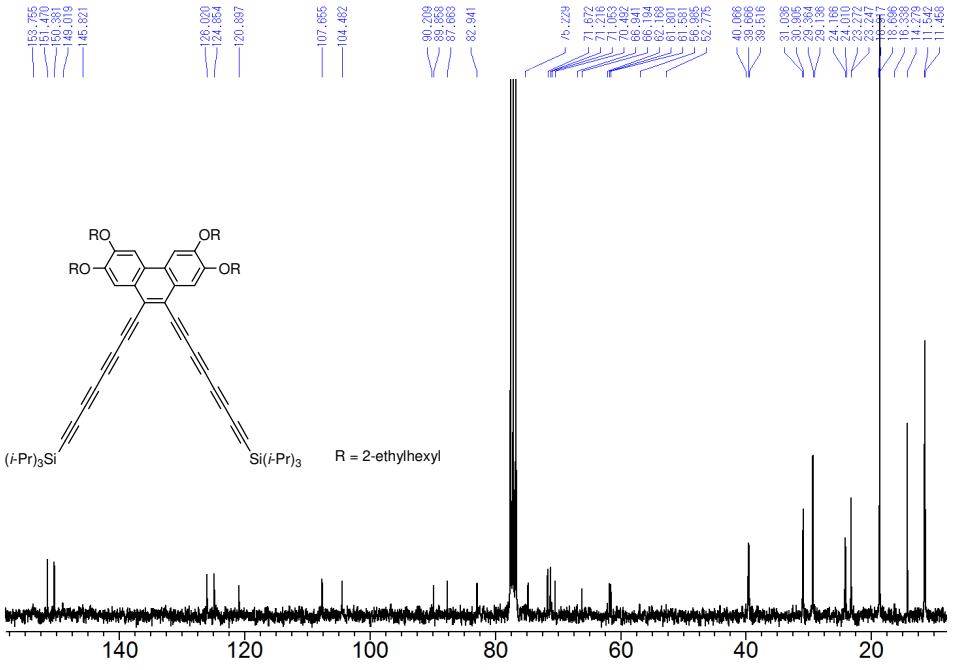
^{1}H NMR spectrum of **9** in $CDCl_3$ solution.



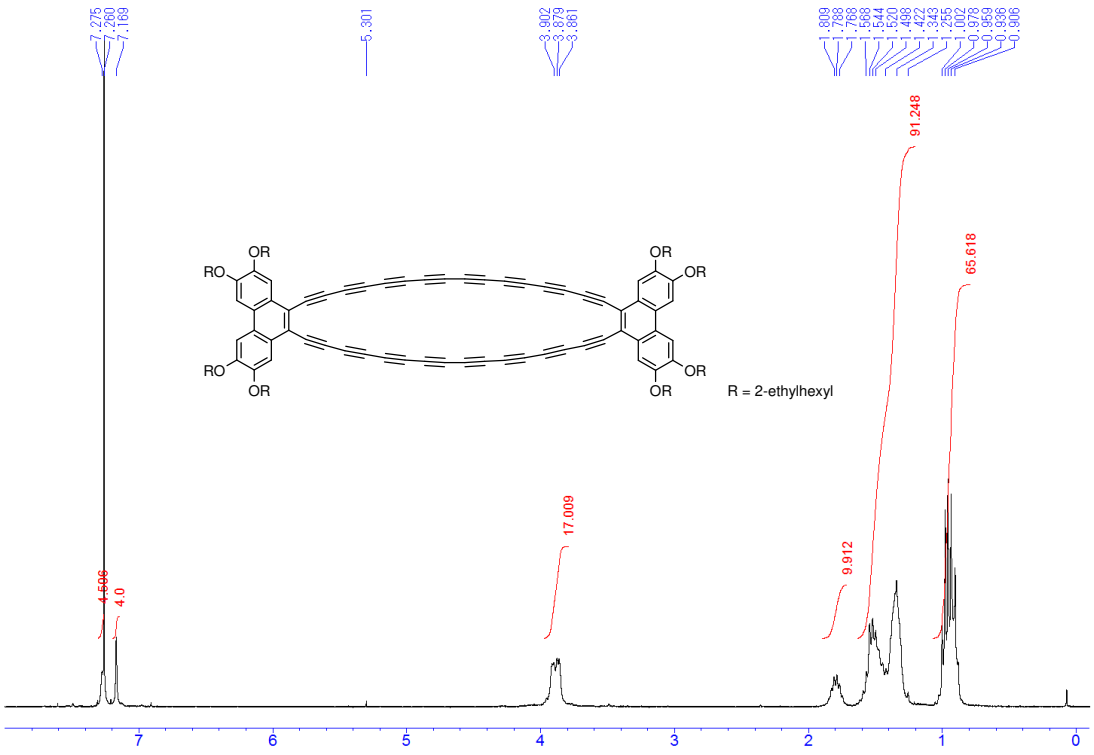
^{13}C NMR spectrum of **9** in $CDCl_3$ solution.



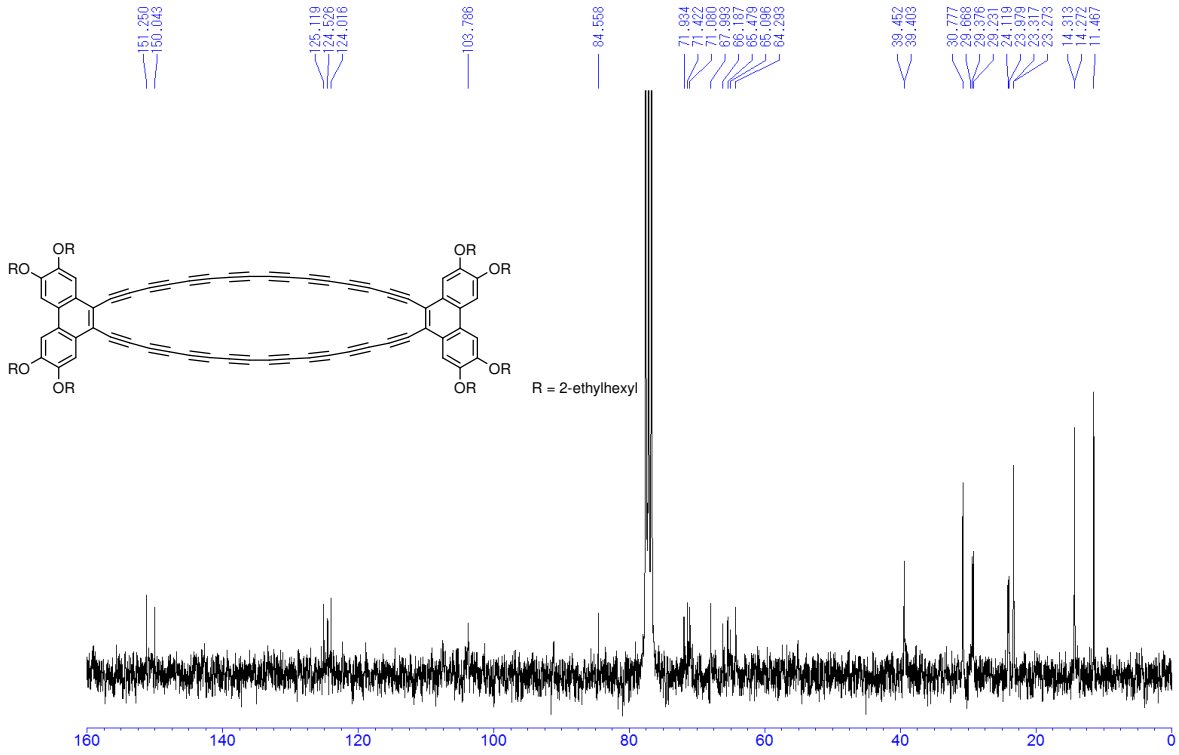
^{1}H NMR spectrum of **10** in $CDCl_3$ solution.



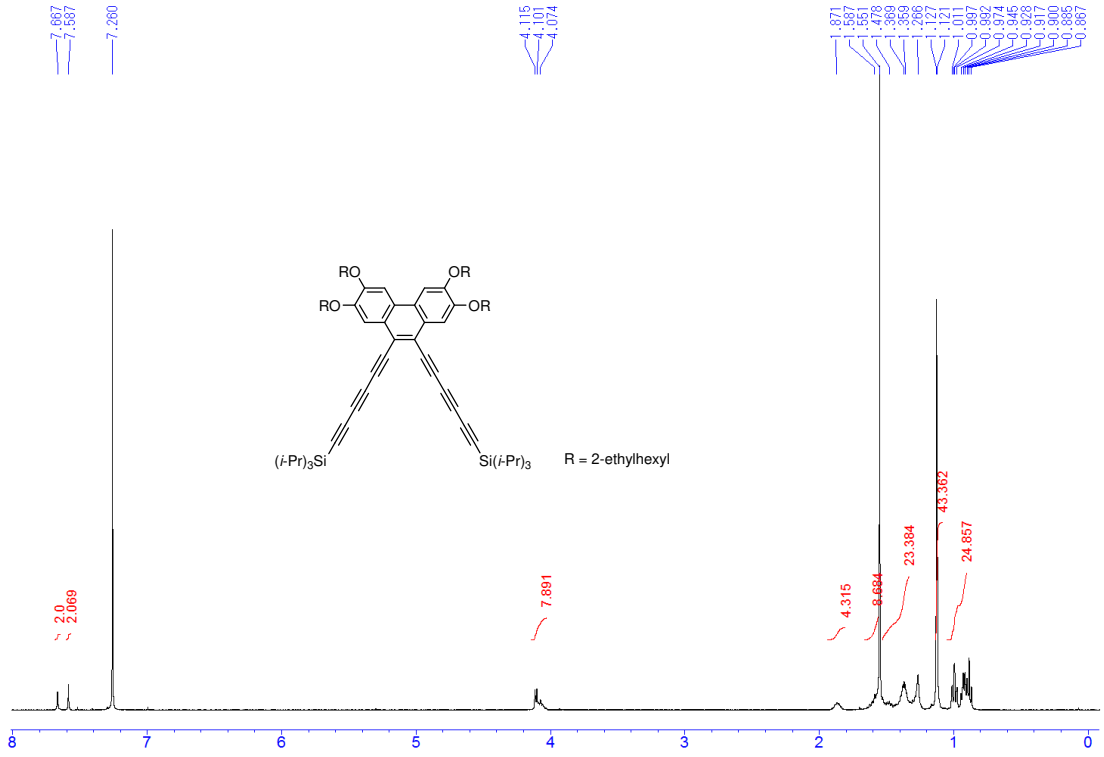
^{13}C NMR spectrum of **10** in $CDCl_3$ solution.



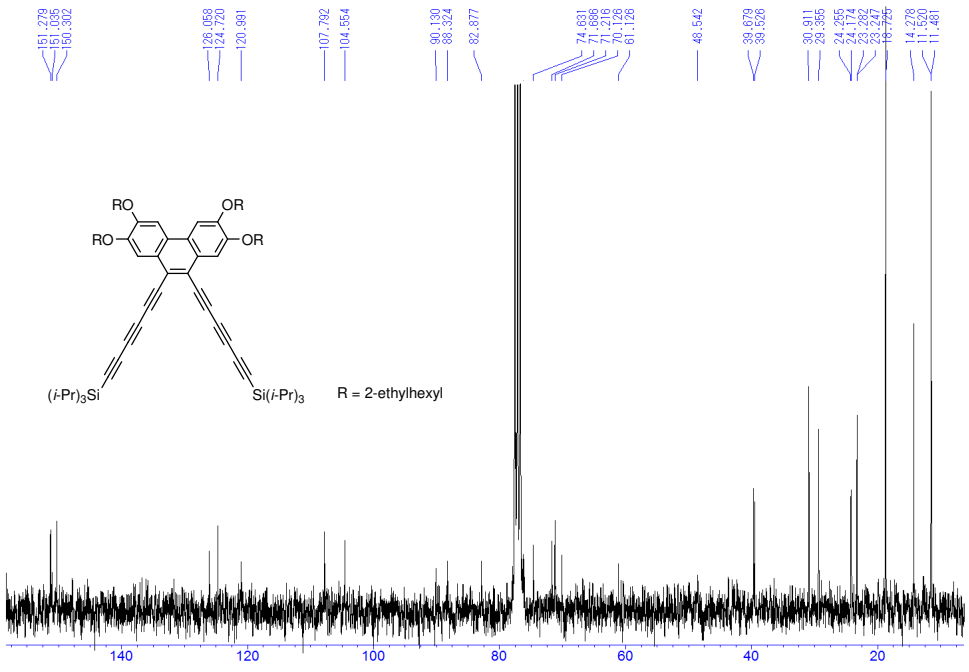
^{1}H NMR spectrum of **4** in $CDCl_3$ solution.



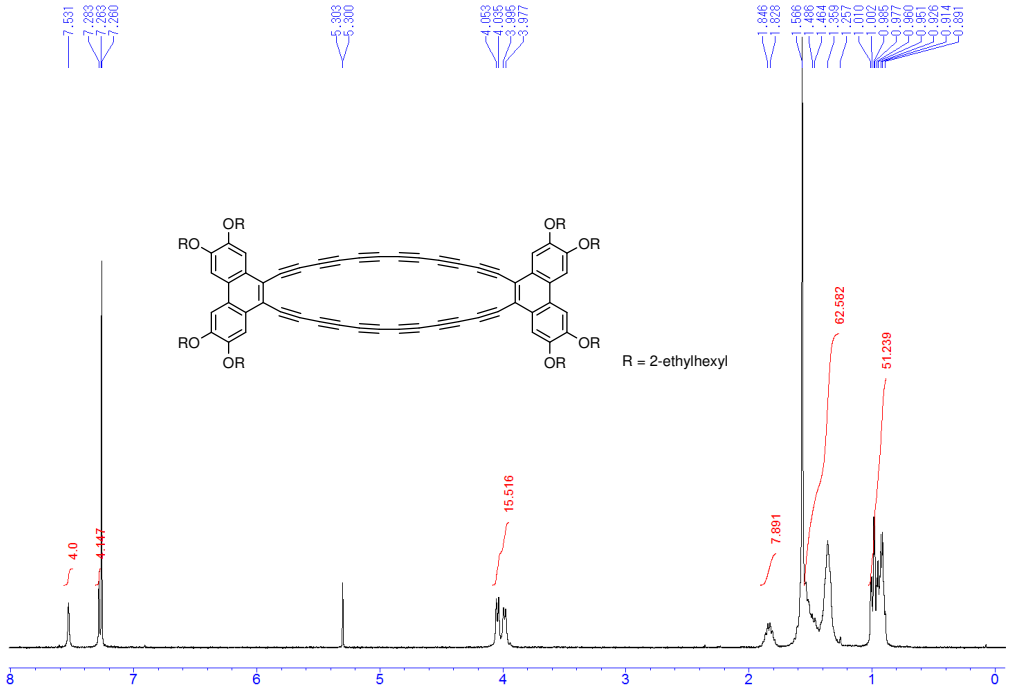
^{13}C NMR spectrum of **4** in $CDCl_3$ solution. Despite many attempts, the spectrum with a high S/N ratio was not obtained probably due to the self-association behavior.



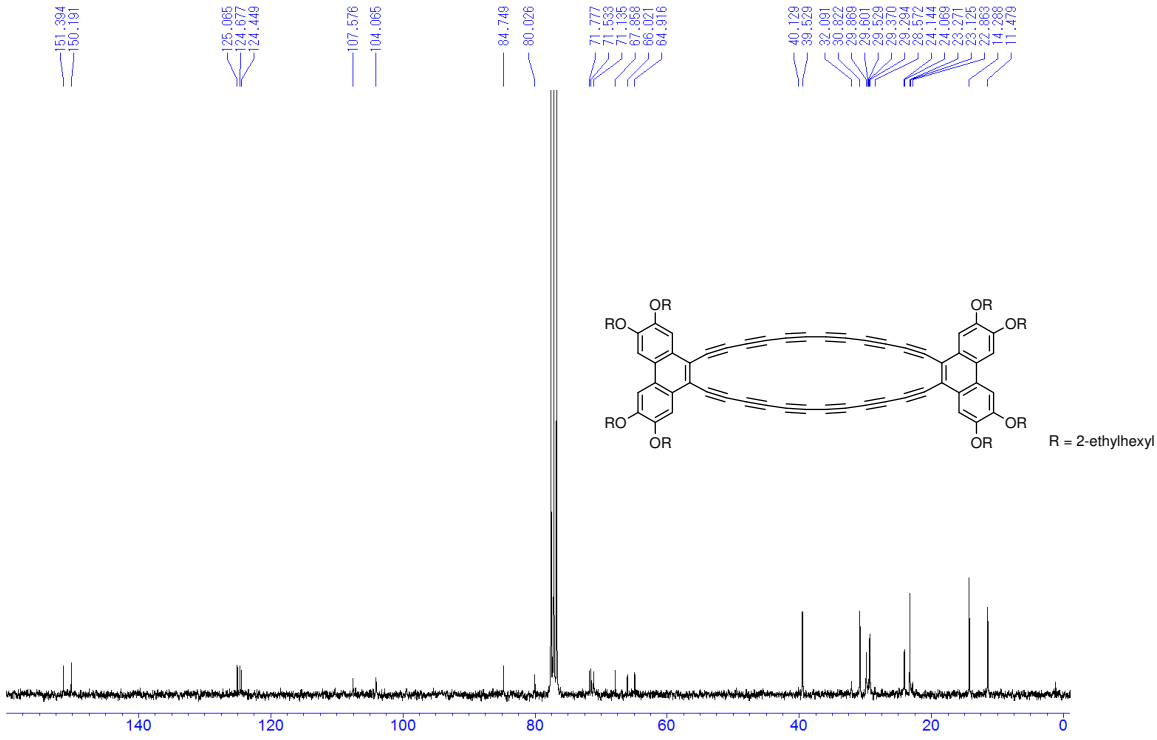
^{1}H NMR spectrum of **12** in $CDCl_3$ solution.



^{13}C NMR spectrum of **12** in $CDCl_3$ solution.



^{1}H NMR spectrum of **3** in $CDCl_3$ solution.



^{13}C NMR spectrum of **3** in $CDCl_3$ solution.

5. References

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6. Author contributions

S.-i. Kato and Y. Nakamura conceived and designed the projects; R. Kumagai synthesized the compounds and contributed on most of the experimental work; R. Kumagai, N. Takahashi, and K. Hayashi performed the investigation on self-association; S.-i. Kato, T. Abe, C. Higuchi, Y. Shiota, T. Hirose, and K. Yoshizawa performed the theoretical calculations; Md. Z. Hossain performed the Raman spectroscopic measurements; S.-i. Kato, Y. Shiota, K. Yamamoto, T. Hirose, and Y. Nakamura wrote the manuscript; S.-i. Kato played a critical role in the discussion of the experimental design, project direction, experiments and results, and preparation of the manuscript; All authors discussed the results and commented on the manuscript.