

Supporting Materials and Methods

General. Unless otherwise noted, all commercial reagents and solvents were used as received. CH_2Cl_2 was dried over CaH_2 under argon and freshly distilled prior to use. Tetrahydrofuran (THF) was refluxed over a mixture of Na and benzophenone ketyl under argon and distilled just before use. ^1H and ^{13}C NMR spectra were recorded at 298 K on a JEOL model NM-Excalibur 500 spectrometer, operating at 500 and 125 MHz, respectively, using partially or nondeuterated solvent residues as internal references. Electronic absorption spectra were recorded on a JASCO model V-560 UV/VIS spectrophotometer. Circular dichroism (CD) spectra were recorded on a JASCO model J-820 spectropolarimeter by using a quartz cell of 0.1-mm path length. Infrared (IR) spectra were recorded at 20°C on a JASCO model FT/IR-660_{plus} Fourier transform IR spectrometer. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo model DSC 822° differential scanning calorimeter, where temperature and enthalpy were calibrated with In (430 K, 3.3 J•mol⁻¹) and Zn (692.7 K, 12 J•mol⁻¹) standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler–Toledo STAR° software system. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on an Applied Biosystems BioSpectrometry Workstation model Voyager-DE STR spectrometer using dithranol as a matrix. Fluorescence microscopy was performed on an OLYMPUS model BX51 fluorescence microscope. Scanning electron microscopy (SEM) was performed on a JEOL model JSM-6700F FE-SEM operating at 5 kV. Transmission electron micrographs (TEM) were recorded on a Philips model Tecnai F20 electron microscope operating at 120 kV.

as colorless oil (1.5 g, 4.51 mmol) in 73% yield. Likewise, enantiomeric counterpart (*R*)-**4** was obtained in 80% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.96–3.88 (m, 2H), 3.69–3.49 (d, 9H), 3.33 (s, 3H), 2.41, (s, 3H), 1.09 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 144.60, 132.86, 129.67, 127.78, 73.42, 72.54, 71.86, 70.65, 70.47, 68.82, 58.95, 21.64, 16.78. MALDI-TOF-MS: calcd for C₁₅H₂₄O₆S [M + Na]⁺: *m/z* = 355.40; found: 355.07; [M + K]⁺: *m/z* = 371.51; found: 370.99.

1,2-Bis(4'-methoxy-4-biphenyl)ethyne (5). Trimethylsilylacetylene (0.71 ml, 496 mg, 5.05 mmol) and water (70 μl) were successively added to a benzene solution (20 ml) of a mixture of 4-bromo-4-methoxybiphenyl (2.7 g, 10.12 mmol), DBU (9.2 g, 60.43 mmol), PdCl₂(PPh₃)₂ (425 mg, 0.61 mmol), and CuI (191 mg, 1.00 mmol). Then, the mixture was heated at 60°C for 24 h, and a precipitate formed was isolated by filtration, washed with ice-cooled CH₂Cl₂, and then recrystallized from toluene, affording **5** as pale brown solid (1.4 g, 3.51 mmol) in 69% yield. ¹H NMR (500 MHz, THF-*d*₈): δ 7.56 (t, *J* = 8.5 Hz, 8H), 7.50 (d, *J* = 8.5 Hz, 4H), 6.93 (d, *J* = 8.5 Hz, 4H), 3.76 (s, 6H). MALDI-TOF-MS: calcd for C₂₈H₂₂O₂ [M + H]⁺: *m/z* = 390.47; found: 390.13.

2,3-Bis(4'-methoxy-4-biphenyl)-5,6-di(4-dodecylphenyl)-1,4-diphenylbenzene (6).

3,4-(4-Didodecylphenyl)-2,5-diphenylcyclopentadienen-1-one (6.7 g, 9.22 mmol) (**2**) and **5** (3.6 g, 9.22 mmol) were mixed in diphenyl ether (10 ml), and the resulting suspension was refluxed for 24 h. After being allowed to cool to room temperature, ethanol (300 ml) was added to the reaction mixture, and a brown precipitate formed was isolated by filtration and subjected to column chromatography (SiO₂, ethyl acetate/hexane 1/7) to allow isolation of **6** as colorless solid (8.0 g, 7.38 mmol) in 80% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.34 (d, *J* = 8.5 Hz, 4H), 7.06 (d, *J* = 7.5 Hz, 4H), 6.89–6.80 (m, 18H), 6.68 (d, *J* = 8.0 Hz, 4H), 6.62 (d, *J* = 8.0 Hz, 4H), 3.77, (s, 6H), 2.33 (t, *J* = 7.5 Hz, 4H), 1.41–1.35 (m, 4H), 1.31–1.20 (m, 32H), 1.09 (br., 4H), 0.87 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 158.69, 140.77, 140.59, 140.34, 139.68, 139.19, 137.82, 136.83, 133.31, 131.83, 131.46, 131.18, 127.60, 126.50, 126.48, 124.91, 124.59, 113.90,

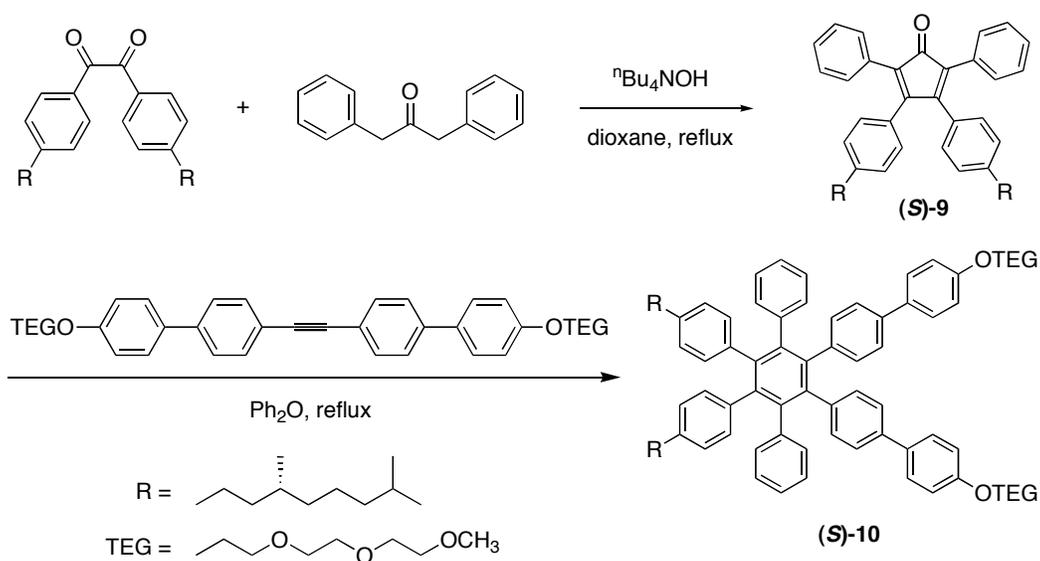
55.34, 35.38, 32.01, 32.00, 31.23, 29.81, 29.76, 29.60, 29.46, 28.88, 22.79, 14.21. MALDI-TOF-MS: calcd for C₈₀H₉₀O₂ [M + H]⁺: *m/z* = 1083.57; found: 1083.81.

2,3-Bis(4'-hydroxy-4-biphenyl)-5,6-di(4-dodecylphenyl)-1,4-diphenylbenzene (7). Boron tribromide (2.6 mL, 27.5 mmol) was added at 0°C to a CH₂Cl₂ solution of **6** (8.0 g, 7.38 mmol), and the mixture was stirred for 45 min at 0°C and then overnight at room temperature. The reaction mixture was poured into a mixture of ice–water/THF (10/9 ml) and extracted with CH₂Cl₂. The combined organic extract was washed with brine, dried over anhydrous MgSO₄, and evaporated to dryness. The residue was subjected to column chromatography (SiO₂, ethyl acetate/hexane 1/7) to allow isolation of **7** as colorless solid (7.0 g, 6.63 mmol) in 90% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.28 (d, *J* = 8.5 Hz, 4H), 7.04 (d, *J* = 8.5 Hz, 4H), 6.89–6.79 (m, 14H), 6.75 (d, *J* = 8.5 Hz, 4H), 6.67 (d, *J* = 8.5 Hz, 4H), 6.61 (d, *J* = 8.0 Hz, 4H), 2.33 (t, *J* = 7.5 Hz, 4H), 1.40–1.35 (m, 4H), 1.30–1.19 (m, 34H), 1.08 (br., 4H), 0.87 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 154.58, 140.75, 140.60, 140.33, 139.64, 139.24, 139.20, 137.80, 136.77, 133.53, 131.82, 131.44, 131.16, 127.84, 126.49, 126.47, 124.91, 124.57, 115.30, 35.37, 32.00, 31.22, 29.80, 29.75, 29.59, 29.45, 28.87, 22.77, 14.20. MALDI-TOF-MS: calcd for C₇₈H₈₆O₂ [M + H]⁺: *m/z* = 1054.66; found: 1054.89.

2,3-Bis[4'-(2*S*)-{2-[2-(2-methoxyethoxy)ethoxy]propoxy}-4-biphenyl]-5,6-di(4-dodecylphenyl)-1,4-diphenylbenzene [(*S*)-8**].** A THF solution (7 ml) of a mixture of **7** (455 mg, 0.43 mmol) and (*S*)-**4** (358 mg, 1.08 mmol) was added KOH (60.5 mg, 1.08 mmol), and the resulting suspension was refluxed for 14 h under argon. The reaction mixture was allowed to cool to room temperature and evaporated to dryness. A CH₂Cl₂ solution of the residue was washed with water, dried over anhydrous MgSO₄, and evaporated to dryness. The residue was subjected to column chromatography (SiO₂, ethyl acetate/CH₂Cl₂ 1/3) to allow isolation of (*S*)-**8** as colorless solid (440 mg, 0.32 mmol) in 74% yield. Likewise, enantiomeric counterpart (*R*)-**8** was obtained in 85% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.32 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 4H), 6.85–6.79 (m, 18H), 6.66 (d, *J* = 8.5 Hz, 4H), 6.61 (d, *J* = 8.0 Hz, 4H), 3.99–3.95 (m, 2H),

3.85–3.81 (m, 4H), 3.75–3.69 (m, 4H), 3.63–3.61 (m, 8H), 3.51–3.49 (m, 4H), 3.34 (s, 6H), 2.32 (t, $J = 7.5$ Hz, 4H), 1.40–1.34 (m, 4H), 1.30–1.19 (m, 38H), 1.07 (br, 4H), 0.86 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 157.98, 140.77, 140.59, 140.35, 139.66, 139.19, 137.82, 136.81, 133.42, 131.83, 131.46, 131.17, 127.58, 126.47, 124.90, 124.58, 114.63, 74.42, 71.97, 71.74, 70.90, 70.56, 68.88, 59.05, 35.38, 32.01, 31.23, 29.80, 29.75, 29.60, 29.46, 28.88, 22.78, 17.42, 14.21. MALDI-TOF-MS: calcd for $\text{C}_{94}\text{H}_{106}\text{O}_8$ $[\text{M} + \text{H}]^+$: $m/z = 1375.94$; found: 1375.06.

Synthesis of a Precursor for (S)-3



3,4-Bis[4-(S)-(3,7-dimethyloctyl)phenyl]-2,5-diphenylcyclopentadienen-1-one [(S)-9]. To a 1,4-dioxane (5 ml) solution of a mixture of 1,2-bis[4-(S)-(3,7-dimethyloctyl)phenyl]-1,2-diketone (1.5 g, 3.12 mmol) and 1,3-diphenyl-2-propanone (655 mg, 3.12 mmol), upon refluxing under argon, was added a methanol solution (1.0 M) of tetrabutylammonium hydroxide (1.56 ml, 1.56 mmol). After 10 min, the reaction mixture was poured into water and extracted with CH_2Cl_2 . The combined organic extract was washed with water, dried over anhydrous MgSO_4 , and evaporated to dryness. The residue was subjected to column chromatography (SiO_2 , CH_2Cl_2 /hexane 1:2) to allow isolation of (S)-9 as purple oil (1.18 g, 1.77 mmol) in 57% yield. ^1H

NMR (500 MHz, CDCl₃): δ 7.26–7.21 (m, 10H), 6.97 (d, J = 8.0 Hz, 4H), 6.82 (d, J = 8.0 Hz, 4H), 2.61–2.52 (m, 4H), 1.61–1.12 (m, 20H), 0.96–0.87 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): 154.55, 143.60, 131.00, 130.18, 130.05, 129.30, 127.84, 127.74, 127.14, 124.84, 39.37, 38.52, 37.21, 33.39, 32.54, 28.03, 24.82, 22.79, 22.71, 19.70. MALDI-TOF-MS: Calcd for C₈₈H₉₄O₈ [M + H]⁺: m/z = 1279.68; found: 1279.68.

2,3-Bis[4-(*S*)-(3,7-dimethyloctyl)phenyl]-5,6-bis(4'-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-4-biphenyl)-1,4-diphenylbenzene [(*S*)-10]. Compound (*S*)-**9** (1.18 g, 1.77 mmol) and 1,2-bis(4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-4-biphenyl)ethyne (1.16 g, 1.77 mmol) were mixed in diphenyl ether (5 ml), and the resulting suspension was refluxed for 24 h. After allowed to cool to room temperature, the reaction mixture was subjected to column chromatography (SiO₂, ethyl acetate) to allow isolation of (*S*)-**10** as colorless solid (1.0 g, 0.77 mmol) in 44% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.32 (d, J = 8.5 Hz, 4H), 7.05 (d, J = 8.5 Hz, 4H), 6.85–6.82 (m, 18H), 6.67 (d, J = 8.0 Hz, 4H), 6.62 (d, J = 8.0 Hz, 4H), 4.09 (t, J = 5.0 Hz, 4H), 3.82, (t, J = 5.0 Hz, 4H), 3.72–3.69 (m, 4H), 3.66–3.62 (m, 8H), 3.53–3.51 (m, 4H), 3.35 (s, 6H), 2.40–2.28 (m, 4H), 1.52–1.36 (m, 4H), 1.24–1.00 (m, 16H), 0.84 (d, J = 6.5 Hz, 12H), 0.78 (d, J = 6.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 157.88, 140.74, 140.55, 140.35, 139.65, 139.43, 139.18, 137.76, 136.79, 133.47, 131.80, 131.44, 131.19, 127.55, 126.45, 126.43, 124.89, 124.57, 114.66, 71.93, 70.83, 70.66, 70.56, 69.75, 67.50, 59.04, 39.42, 38.65, 37.17, 32.92, 32.04, 28.03, 24.77, 22.79, 22.71, 19.64. MALDI-TOF-MS: calcd for C₈₈H₁₀₆O₈ [M + H]⁺: m/z = 1291.78; found: 1291.79.

References

1. Prince, R. B., Brunsveld, L., Meijer, E. W. & Moore, J. S. (2000) *Angew. Chem. Int. Ed.* **39**, 228–230.
2. Hill, J. P., Jin, W., Kosaka, A., Fukushima, T., Ichihara, H., Shimomura, T., Ito, K., Hashizume, T., Ishii, N. & Aida, T. (2004) *Science* **304**, 1481–1483.