Supporting Information for

A Soluble Bispentacenequinone Precursor for Creation of Directly 6,6'-Linked Bispentacenes and a Tetracyanobipentacenequinodimethane

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1. Instrumentation and Materials

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded with JEOL JNM-ECX 400 spectrometers at ambient temperature by using tetramethylsilane as an internal standard. HRMS were measured by a JEOL JMS-700 MStation spectrometer. The high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) and atmosphere pressure chemical ionization (APCI) MS were performed on a BRUKER DALTONICS micrOTOF using positive and negative ion modes, and acetonitrile as a solvent. Single-crystal diffraction analysis data were collected with a BRUKER-APEX X-Ray diffractometer equipped with a large area CCD detector for **8b** and **8c** by using graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) and X-ray crystallographic data for the others were recorded at 100 K on a Rigaku CCD detector (Saturn 724) mounted on a Rigaku rotating anode X–ray generator (MicroMax–007HF) using Mo-K α radiation from the corresponding set of confocal optics. The diffraction data were solved with the SIR-97 program and refined with the SHELX-97 program.^[S1]

UV/Vis absorption spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570. CV measurements were conducted in a solution of 0.1 M TBAPF₆ in dry acetonitrile with a scan rate of 100 mV/s at room temperature in an argon-filled cell. A glassy carbon electrode and a Pt wire were used as a working and a counter electrode, respectively. An Ag/Ag⁺ electrode was used as reference electrodes, which were normalized with the half-wave potential of ferrocene/ferrocenium⁺ (Fc/Fc⁺) redox couple. Constant potential spectro-electrochemical experiments were performed using a quartz glass cell with Pt-net as a working and an Pt wire as a counter electrode. The applied potential was fixed to 0.42 V vs Fc/Fc⁺ for electrolysis condition. Thermogravimetic analysis was performed on an SII Exstar 600 TG/DTA 6200.

TLC and gravity column chromatography were per-formed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All other solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification except as noted. For spectral measurements, spectral-grade chloroform was purchased from Nacalai Tesque.

2. Experimental Section



5: The compound **4** was synthesized according to a literature procedure.^[S2] **4** (1.23 g, 9.32 mmol) and *p*-benzoquinone (0.41 g, 3.8 mmol) in CHCl₃ (30 ml) were heated to 60 °C for 2 days with stirring. After cooled to room temperature, the reaction mixture was evaporated to remove the solvent. The residue was washed with hexane and filtrated to afford **5'** (0.880 g, 2.37 mmol, 63%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 6.21-6.30 (m, 4H), 3.26 (s, 4H), 2.92-2.86 (m, 4H), 2.57-2.25 (m, 8H), and 1.25-1.20 (m, 8H) ppm.

5' (1.74 g, 4.68 mmol) and KOH (2.63 g, 46.8 mmol) in EtOH (50 ml) were heated to 60 °C and stirred for 19 h under the air. After stirring, the reaction mixture was cooled to room temperature. The reaction mixture was poured into water and filtrated. The residue was purified by chromatography on silica gel with CHCl₃ to afford **5** (1.59 g, 4.39 mmol, 93%) as a white yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.04 (s, 2H), 6.51-6.55 (m, 4H), 4.17 (s, 4H), 1.67-1.64 (m, 4H), and 1.51-1.45 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃, 295 K): δ = 184.08, 150.71, 134.34, 131.62, 120.87, 40.60, and 25.14 ppm; HR-MS (FAB): *m*/*z*: calcd for C₂₆H₂₁O₂, 365.146 [*M*+H]⁺; found: 365.154.

6: LAH (0.20 g, 5.26 mmol) was added slowly to suspension of **5** (0.20 g, 0.571 mmol) in dry THF (20 ml) at 0 °C. After adding, the reaction mixture was refluxed for 1 h. After refluxing, the reaction mixture was cooled to 0 °C again. 6 M HCl (9 ml) was added to the mixture and refluxed for 1 h again. The precipitate was filtered off and washed with water and MeOH, Et₂O and purified by chromatography on silica gel with CHCl₃ to afford **6** (0.132 g, 0.377 mmol, 66%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.12 (s, 2H), 7.24 (s, 2H), 6.59-6.46 (m, 4H), 4.25 (s, 2H), 4.11-4.09 (m, 2H), 4.03-4.01 (m, 2H), 1.63-1.60 (m, 4H), and 1.50-1.46 (m, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃, 295 K): δ = 184.73, 149.42, 143.10, 138.40, 135.68, 133.96, 129.50, 122.32, 120.76, 40.26, 39.90, 32.55, 25.55, and 25.49 ppm; HR-MS (FAB): *m*/*z*: calcd for C₂₆H₂₂O, 350.167 [*M*]⁺; found: 350.162.

7: **6** (0.132 g, 0.377 mmol) was dissolved in a mixture of dry pyridine (8 ml) and piperidine (0.5 ml, 5.1 mmol). Pyridine-*N*-oxide (0.32 g, 3.36 mmol) and ferrous sulfate heptahydrate (20 mg, 0.072 mmol) added to the resulting solution, and the reaction mixture was heated to 100 °C under argon atmosphere for 5 h. After cooling, the reaction mixture was mixed with 5% aqueous hydrochloric acid (10 ml), a yellow precipitate was formed. The precipitate was filtered off and washed with water and ethanol to afford **7** (0.105 g, 0.151 mmol, 80%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃, mixture of isomers): δ = 7.86-7.78 (m, 4H), 6.91-6.72 (m, 4H), 6.63-6.24 (m, 8H), 4.03 (m, 4H, bridge head), 3.60-3.50 (m, 4H, bridge head), and 1.51-1.14 (m,

16H) ppm; HR-MS (FAB): m/z: calcd for C₅₂H₄₁O₂, 697.303 [M+H]⁺; found: 697.306; UV-vis (CHCl₃): λ_{max} (ε [M⁻¹ cm⁻¹]) = 414 (15800) nm.

8a: LAH (5.6 mg, 0.147 mmol) was added slowly to suspension of **7** (50 mg, 0.072 mmol) in dry THF (6 ml) at 0 °C. The reaction mixture was stirred at room temperature. for 1 h. After stirring, 6 M HCl was added slowly at room temperature. Subsequently, the reaction mixture was refluxed for 30 min. The precipitate was filtered off and washed with water. The crude product (52 mg) in dry THF (10 ml) was cooled to 0 °C. DIBAL in hexane (0.20 ml, 0.20 mmol) was added slowly to the mixture at 0 °C. The reaction mixture was refluxed for 19 h, then cooled to room temperature. 6 M HCl (2 ml) was added to the mixture, and refluxed for 2 h. The precipitate was filtered off and washed with water, MeOH and purified by chromatography on silica gel with CHCl₃:hexane = 1:1 to afford **8a** (15 mg, 0.023 mmol, 31%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.45 (s, 2H), 7.79 (m, 4H), 6.73-6.57 (m, 4H, aromatic), 6.54-6.31 (m, 8H), 4.02 (m, 4H), 3.56-3.47 (m, 4H), 1.60 (m, 8H), and 1.38 (m, 8H) ppm; HR-MS (FAB): calcd for C₅₂H₄₂, 666.329 [*M*]⁺; found, 666.3268; UV-vis (CHCl₃): λ_{max} (ε [M⁻¹ cm⁻¹]) = 349 (11200), 369 (18300), and 390 (20900) nm.

8b: NBS (33.0 mg, 0.183 mmol) was added to **8a** (50.0 mg, 0.077 mmol) in dry THF (80 ml) at 0 °C. The mixture was stirred for 2 h at 0 °C. After stirring, the mixture was warmed to room temperature and stirred for 22 h. NaHCO₃ aq. was added slowly. The resulting mixture was extracted with CHCl₃ and the organic layer was washed with water, brine and dried over Na₂SO₄. The solvent was removed by a rotary evaporator. The residue was purified by chromatography on silica gel with hexane:CHCl₃ = 1:3 to afford **8b** (12 mg, 0.015 mmol, 19%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.38 (m, 4H), 6.70-6.56 (m, 4H), 6.53-6.32 (m, 8H), 4.12 (m, 4H), 3.58-3.50 (m, 4H), and 1.62-1.33 (m, 16H) ppm; HR-MS (FAB): calcd for C₃₂H₄₀Br₂, 822.150 [*M*]⁺; found, 822.1490.

8c: *n*-BuLi in hexane (1.6 M, 2.43 ml, 3.89 mmol) was added dropwise to a solution of bromobenzene (0.38 ml, 3.9 mmol) in dry THF (15 ml) at –78 °C under argon atmosphere. The solution was stirred for 30 min. After addition of suspension of 7 (30 mg, 0.043 mmol) in dry THF, the reaction mixture was stirred at –78 °C for 3 h and at room temperature for 2 h. The mixture was poured into water. The residue was filtrated and washed with water to afford intermediate (28 mg, 0.033 mmol, 68%). A mixture of intermediate (28 mg, 0.033 mmol), NaI (54.6 mg, 0.350 mmol), Na₂H₂PO₂·H₂O (54.6 mg, 0.422 mmol) and acetic acid (1 mL) was heated to reflux for 3 h. After cooling to room temperature, the precipitate was collected by filtration, washed with water and ethanol, and purified by column chromatography on silica gel with CHCl₃ to afford **8c** (18 mg, 67%) as a white solid. ¹H NMR (300 MHz, CDCl₃): *δ* = 7.72-7.55 (m, 10H), 7.42-7.39 (m, 4H), 6.91-6.71 (m, 4H), 6.50-6.30 (m, 8H), 3.90-3.80 (m, 4H), 3.68-3.50 (m, 4H), and 1.60-1.30 (m, 16H) ppm; HR-MS (FAB): calcd for C₆₄H₅₀, 818.391 [*M*]⁺; found, 818.3900; UV-vis (CHCl₃): *λ*_{max} (*ε* [*M*⁻¹ cm⁻¹]) = 357 (14700), 377 (26500), and 400 (34300) nm.

8d: n-BuLi in hexane (1.6 M, 4.1 ml, 6.48 mmol) was added dropwise to a solution of 3,5-bis(trifluoromethyl)bromobenzene (1.1 ml, 6.5 mmol) in dry THF (15 ml) at -78 °C under argon atmosphere. The solution was stirred for 30 min. After an addition of suspension of 7 (50 mg, 0.072 mmol) in dry THF, the reaction mixture was stirred at -78 °C for 3 h and at room temperature for 2 h. The mixture was poured into water. The residue was filtrated and washed with water. The residue was diluted with CHCl₃ and dried over Na₂SO₄. The solution was evaporated and the residue was purified by chromatography on silica gel with CHCl₃ to afford intermediate (40.2 mg, 0.036 mmol, 50%). A mixture of intermediate (40.2 mg, 0.036 mmol), NaI (156 mg, 1.07 mmol), Na₂H₂PO₂·H₂O (129 mg, 1.22 mmol) and acetic acid (10 mL) was heated to 130 °C for 24 h. After cooling to room temperature, the precipitate was collected by filtration, washed with water and ethanol, and purified by column chromatography on silica gel with CHCl₃ to afford 8d (11 mg, 0.010 mmol, 28%) as a white solid. ¹H NMR (300 MHz, CDCl₃): $\delta =$ 8.21-8.08 (m, 6H), 7.22-7.17 (m, 4H), 6.91-6.69 (m, 4H), 6.52-6.36 (m, 8H), 3.94-3.83 (m, 4H), 3.70-3.49 (m, 4H), and 1.60-1.30 (m, 16H) ppm; HR-MS (FAB): calcd for C₆₈H₄₆F₁₂, 1090.341 [M]⁺; found, 1090.341; UV-vis (CHCl₃): λ_{max} (ε [M⁻¹ cm⁻¹]) = 357 (12500), 377 (22200), and 399 (28900) nm.

9a: **8a** (2.0 mg, 3.0 µmol) in a glass tube was placed into a round bottom flask. The tube was placed into glass tube oven and heated to 300 °C and kept there for 30 min under reduced atmosphere. After 1 h the tube was taken out from the oven and cooled to room temperature. MS (MALDI): calcd for $C_{44}H_{26}$ 554.203 [*M*]⁺; found: 554.404.

9c: **8c** (2.2 mg, 2.7 μ mol) in a glass tube was placed into a round bottom flask. The tube was placed into glass tube oven heated to 350 °C and kept there for 10 min under reduced pressure. After 1 h the tube was taken out from the oven and cooled to room temperature. MS (MALDI): calcd for C₅₆H₃₄, 706.266 [*M*]⁺; found: 706.472.

9d: **8d** (1.5 mg, 1.4 μmol) in an aluminium pan was placed into a TG-DTA 6200. Inside of the equipment was purged with nitrogen. The pan was heated to 400 °C over 1 h and kept there under nitrogen atmosphere. The pan was taken out from the oven and cooled to room temperature under nitrogen to afford **9d** (1.3 mg, 1.3 μmol, 93%) as a dark purple solid. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.43 (s, 4H), 8.33 (s, 2H), 8.32 (s, 4H) 7.85 (s, 4H), 7.77 (d, *J* = 8.6 Hz, 4H), 7.30 (d, *J* = 8.9 Hz, 4H), 7.21 (t, *J* = 6.7 Hz, 4H), and 7.07 (t, *J* = 6.4 Hz, 4H) ppm; HR-MS (APCI): calcd for C₆₀H₃₁F₁₂, 979.216 [*M*+H]⁺; found: 979.220; UV-vis (CHCl₃): λ_{max} (ε [M⁻¹ cm⁻¹]) = 519 (4600), 564 (10200), and 612 (20400) nm.

10: To a suspension of **7** (50 mg, 0.070 mmol) in dry pyridine (10 ml) was added $TiCl_4$ (0.1 ml, 0.91 mmol), and the reaction mixture was heated to 40-50 °C under argon atmosphere. A solution of malononitrile (93 mg, 1.40 mmol) in dry pyridine (2 ml) was added to the warmed

suspension, and refluxed for 36 h. After cooling, the reaction mixture was dissolved in CHCl₃. Subsequently, silica gel was added into the mixture. After stirring for 10 min, the mixture was filtrated. The filtrate was extracted with CHCl₃, washed with 1 M HCl aq., H₂O, brine, and dried over Na₂SO₄. The organic layer was evaporated. The residue was purified by chromatography on silica gel and gel permeation chromatography (GPC) HPLC with CHCl₃ to afford **10** (1.2 mg, 1.5 µmol, 2.2%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.89 (m, 2H), 7.83 (m, 2H), 7.15-6.75 (m, 4H), 6.57 (m, 2H), 6.47-6.21 (m, 6H), 4.05 (m, 4H, bridge head), and 3.83-3.54 (m, 4H, bridge head) ppm; HR-MS (ESI): calcd for C₅₈H₄₀N₄Na, 815.315 [*M*+Na]⁺; found: 815.313; UV-vis (CHCl₃): λ_{max} (ε [M⁻¹ cm⁻¹]) = 316 (29100), 365 (20300), and 462 (16100) nm.

2: **7** (17 mg, 0.024 mmol) in a glass tube was placed into a round bottom flask. The flask was purged with nitrogen. The tube was placed into glass tube oven and heated to 260 °C and kept there for 30 min under nitrogen atmosphere. After 30 min the tube was taken out from the oven and cooled to room temperature under nitrogen to afford **2** (14 mg, 0.024 mmol, 98%) as a yellow solid. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.74 (s, 4H), 8.03 (d, *J* = 8.2 Hz, 4H), 7.59 (s, 4H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.32 (t, *J* = 7.6 Hz, 4H), and 7.15 (d, *J* = 8.2 Hz, 4H) ppm; ¹³C NMR (100 MHz, CD₂Cl₂, 295 K): δ = 187.62, 134.47, 134.00, 133.54, 132.83, 132.40, 129.67, 128.77, 128.44, 128.10, and 127.47 ppm; HRMS (ESI): calcd for C₄₄H₂₄O₂, 584.178 [*M*]⁺; found, 584.1675.

11: A suspension of **2** (83 mg, 0.14 mmol) and malononitrile (180 mg, 2.73 mmol) in 40 ml of dry pyridine was heated to 40-50 °C for 10 min. TiCl₄ (0.6 ml, 5.5 mmol) was added to the reaction mixture, and refluxed for 2 h under argon atmosphere. After cooling, the reaction mixture was dissolved in CHCl₃. Silica gel was added into the CHCl₃ and stirred for 10 min. The solution was then filtered and the silica gel was washed with another portion of CHCl₃. The combined solvent was filtered and concentrated by a rotary evaporation. The residue was purified by column chromatography on silica gel with CHCl₃ and the product was washed with Et₂O, giving pure **11** (10 mg, 0.015 mmol, 10%) as an orange solid. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.71 (s, 4H), 8.01 (d, *J* = 8.2 Hz, 4H), 7.77 (s, 4H), 7.54 (t, *J* = 7.8 Hz, 4H), and 7.41 (m, 8H) ppm; HR-MS (ESI): calcd for C₅₀H₂₄N₄, 680.200 [*M*]⁻; found: 680.201; UV-vis (CHCl₃): λ_{max} (ε [M⁻¹ cm⁻¹]) = 460 (sh, 6800), 351 (40200), and 293 (46800) nm.

3. NMR Spectra



Figure S1. ¹H NMR spectrum of **4** in CDCl₃ at room temperature.



Figure S2. ¹H NMR spectrum of 5 in CDCl₃ at room temperature.



Figure S3. ¹H NMR spectrum of **6** in CDCl₃ at room temperature.



Figure S4. ¹H NMR spectrum of 7 in CDCl₃ at room temperature.



Figure S5. ¹H NMR spectrum of **8a** in CDCl₃ at room temperature.



Figure S6. ¹H NMR spectrum of **8b** in CDCl₃ at room temperature.



Figure S7. ¹H NMR spectrum of **8c** in CDCl₃ at room temperature.



Figure S8. ¹H NMR spectrum of **8d** in CDCl₃ at room temperature.



Figure S9. ¹H NMR spectrum of **9d** in CDCl₃ at room temperature.



Figure S10. ¹H NMR spectrum of 10 in CDCl₃ at room temperature.



Figure S11. ¹H NMR spectrum of **2** in CDCl₃ at room temperature.



Figure S12. ¹H NMR spectrum of **11** in CDCl₃ at room temperature.





Figure S13. HR-APCI-TOF mass spectrum of 9d.



Figure S14. HR-APCI-TOF mass spectrum of 11.

5. Thermal Reaction Profiles



Figure S15. TG analysis of **8a**. The weight loss from 250 to 300 °C was due to the release of four ethylene molecules from **8a**. The observed value was 15.3%, and the calculated was 16.2%.



Figure S16. MALDI-TOF mass spectrum after thermal reaction of 8a.



Figure S17. UV-vis absorption spectra before and after heating of 8a in CHCl₃.



Figure S18. TG analysis of 8b. The weight loss continued from 100 to 400 °C was due to the decomposition.



Figure S19. TG analysis of **8c**. The weight loss from 200 to 350 °C was due to the release of four ethylene molecules from **8c**. The observed value was 13.3%, and the calculated was 13.7%.



Figure S20. MALDI-TOF mass spectrum after thermal reaction of 8c.



Figure S21. ¹H NMR spectrum (aromatic region) of **9c** in CDCl₃ at room temperature.



Figure S22. UV-vis absorption spectra before and after heating of 8c in CHCl₃.



Figure S23. TG analysis of **8d**. The weight loss from 150 to 300 °C was due to the release of four ethylene molecules from **8d**. The observed value was 10.8%, and the calculated was 10.3%.



Figure S24. TG analysis of 10. The weight loss from 200°C was due to the decomposition of 10.



Figure S25. TG analysis of **7**. The weight loss from 200 to 250 °C was due to the release of four ethylene molecules from **7**. The observed value was 16.3%, and the calculated was 16.1%.



Figure S26. UV-vis absorption and fluorescence spectra of 11 in CHCl₃.

6. Cyclic Voltammetry

Cyclic voltammograms were measured under the following conditions; solvent: CH_2Cl_2 or THF, electrolyte: Bu_4NPF_6 , working electrode: grassy carbon, counter electrode: Pt wire, reference electrode: $Ag/AgClO_4$, scan rate: 0.05 V/s or 0.1 V/s. Potentials were also confirmed by using differential pulse voltammetry (DPV).



Figure S27. Cyclic voltammogram of 8d in CH₂Cl₂.



Figure S28. Cyclic voltammograms of **10** (blue), tetracyanopentacenequinodimethane (green) and **11** (red) in THF.

7. X-Ray Crystal Structures

Table S1. Crystal data and structure refinement for 7.

Empirical formula	$C_{52}H_{40}O_2$	
Formula weight	696.84	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.2853(3) Å	
	$b = 12.1795(4)$ Å $\beta = 106.4150(10)^{\circ}$	
	c = 14.7576(5) Å	
Volume	1773.34(10) Å ³	
Ζ	2	
Density (calculated)	1.305 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	736	
Crystal size	$0.16 \ge 0.13 \ge 0.12 \text{ mm}^3$	
Theta range for data collection	3.29 to 25.35°	
Index ranges	$-12 \leq h \leq 10, -14 \leq k \leq 14, -17 \leq l \leq 17$	
Reflections collected	14260	
Independent reflections	3241 [<i>R</i> (int) = 0.0293]	
Completeness to theta = 25.35°	99.8 %	
Max. and min. transmission	0.9907 and 0.9877	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3241 / 0 / 244	
Goodness-of-fit on <i>F</i> ²	1.060	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0668, wR_2 = 0.1822$	
R indices (all data)	$R1 = 0.0716, wR_2 = 0.1868$	
Largest diff. peak and hole	0.629 and -0.294 e.Å ⁻³	



Figure S29. X-ray crystal structure of 7. (top) Top view; (bottom) Side view. Thermal ellipsoids were scaled to 50% probability.

Table S2. Crystal data and structure refinement for 8a.

Empirical formula	$C_{56}H_{52}O$	
Formula weight	740.98	
Temperature	123(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 11.1984(5) Å	$\alpha = 73.8090(10)^{\circ}$
	b = 11.3073(5) Å	$\beta = 86.8410(10)^{\circ}$
	c = 16.8154(7) Å	$\gamma = 75.5040(10)^{\circ}$
Volume	1979.44(15) Å ³	
Ζ	2	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	792	
Crystal size	0.18 x 0.11 x 0.10 mm ³	
Theta range for data collection	3.01 to 27.49°	
Index ranges	$-14 \leq h \leq 14, -14 \leq k \leq 14, -20 \leq l \leq 21$	
Reflections collected	19899	
Independent reflections	9054 [R(int) = 0.0246]	
Completeness to theta = 27.49°	99.6%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9929 and 0.9872	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9054 / 0 / 558	
Goodness-of-fit on F ²	1.055	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0697, wR_2 = 0.2024$	
R indices (all data)	$R_1 = 0.0902, wR_2 = 0.2343$	
Largest diff. peak and hole	0.513 and −0.349 e.Å ⁻³	



Figure S30. X-ray crystal structure of **8a**. Thermal ellipsoids were scaled to 30% probability. Solvent molecules were omitted for clarity.

Table S3. Crystal data and structure refinement for 8b

Empirical formula	$C_{53.33}H_{40}Br_2Cl_{1.74}O_{0.75}$	
Formula weight	914.38	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 41.930(4) Å	
	$b = 15.3835(14) \text{ Å} \qquad \beta = 102.9120(10)^{\circ}$	
	c = 18.8623(18) Å	
Volume	11859.0(19) Å ³	
Ζ	12	
Density (calculated)	1.536 Mg/m^3	
Absorption coefficient	2.210 mm ⁻¹	
F(000)	5587	
Crystal size	$0.50 \ge 0.05 \ge 0.03 \text{ mm}^3$	
Theta range for data collection	1.41 to 26.00°	
Index ranges	$-51 \le h \le 51, -17 \le k \le 18, -23 \le l \le 19$	
Reflections collected	30227	
Independent reflections	11559 [$R(int) = 0.0464$]	
Completeness to theta = 26.00°	99.2%	
Absorption correction	Empirical	
Max. and min. transmission	0.7454 and 0.6737	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11559 / 9 / 820	
Goodness-of-fit on F ²	1.040	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0994, wR_2 = 0.2790$	
R indices (all data)	$R_1 = 0.1482, wR_2 = 0.3153$	
Largest diff. peak and hole	1.733 and –1.358 e.Å ⁻³	



Figure S31. X-ray crystal structure of **8b**. Thermal ellipsoids were scaled to 30% probability. Solvent molecules were omitted for clarity.

Table S4. Crystal data and structure refinement for 8c

Empirical formula	$C_{67}H_{53}Cl_9$	
Formula weight	1177.14	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	a = 24.018(3) Å	
	$b = 10.2100(14) \text{ Å} \qquad \beta = 90.352(2)^{\circ}$	
	c = 22.028(3) Å	
Volume	5401.5(13) Å ³	
Ζ	4	
Density (calculated)	1.448 Mg/m^{3}	
Absorption coefficient	0.511 mm^{-1}	
F(000)	2432	
Crystal size	0.20 x 0.05 x 0.01 mm ³	
Theta range for data collection	0.85 to 26.00°	
Index ranges	$-29 \le h \le 26, -12 \le k \le 12, -27 \le l \le 22$	
Reflections collected	27392	
Independent reflections	10549 [R(int) = 0.0821]	
Completeness to theta = 26.00°	° 99.4%	
Absorption correction	Empirical	
Max. and min. transmission	0.9949 and 0.9046	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10549 / 0 / 685	
Goodness-of-fit on F ²	1.015	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0774, wR_2 = 0.1927$	
R indices (all data)	$R_1 = 0.1651, wR_2 = 0.2429$	
Largest diff. peak and hole	0.783 and −0.711 e.Å ⁻³	



Figure S32. X-ray crystal structure of **8c**. (top) Top view; (bottom) Side view. Thermal ellipsoids were scaled to 50% probability. Solvent molecules were omitted for clarity.

Table S5. Crystal data and structure refinement for 8d

Empirical formula	$C_{72}H_{50}Cl_{12}F_{12}$	
Formula weight	1568.52	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.6901(5) Å	
	$b = 21.1291(5)$ Å $\beta = 130.4530(10)^{\circ}$	
	c = 17.5492(4) Å	
Volume	6966.4(3) Å ³	
Ζ	4	
Density (calculated)	1.496 Mg/m ³	
Absorption coefficient	0.552 mm^{-1}	
F(000)	3176	
Crystal size	0.13 x 0.10 x 0.10 mm ³	
Theta range for data collection	3.02 to 25.35°	
Index ranges	$-29 \leq h \leq 29, -25 \leq k \leq 25, -21 \leq l \leq 21$	
Reflections collected	48911	
Independent reflections	6362 [<i>R</i> (int) = 0.0443]	
Completeness to theta = 25.35°	99.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9469 and 0.9317	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6362 / 9 / 530	
Goodness-of-fit on F ²	1.064	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0693, wR_2 = 0.2002$	
R indices (all data)	$R_1 = 0.0854, wR_2 = 0.2151$	
Largest diff. peak and hole	1.103 and -0.574 e.Å ⁻³	



Figure S33. X-ray crystal structure of **8d**. (top) Top view; (bottom) Side view. Thermal ellipsoids were scaled to 30% probability. Solvent molecules were omitted for clarity.

Table S6. Crystal data and structure refinement for 9d

Empirical formula	$C_{60}H_{30}F_{12}$	
Formula weight	978.84	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 13.271(10) Å	
	$b = 30.35(2) \text{ Å}$ $\beta = 121.152(11)^{\circ}$	
	c = 12.823(10) Å	
Volume	4420(6) Å ³	
Ζ	4	
Density (calculated)	1.471 Mg/m^3	
Absorption coefficient	0.120 mm^{-1}	
F(000)	1992	
Crystal size	$0.11 \ge 0.08 \ge 0.02 \text{ mm}^3$	
Theta range for data collection	3.25 to 23.49°	
Index ranges	$-14 \le h \le 14, -34 \le k \le 34, -14 \le l \le 14$	
Reflections collected	25074	
Independent reflections	3255 [<i>R</i> (int) = 0.1214]	
Completeness to theta = 23.49°	99.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9976 and 0.9869	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3255 / 0 / 362	
Goodness-of-fit on F ²	1.035	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1051, wR_2 = 0.2478$	
R indices (all data)	$R_1 = 0.2213, wR_2 = 0.3304$	
Largest diff. peak and hole	0.256 and –0.227 e.Å ⁻³	



Figure S34. X-ray crystal structure of **9d**. (top) Top view; (bottom) Side view. Thermal ellipsoids were scaled to 20% probability.

Table S7. Crystal data and structure refinement for 10.

Empirical formula	$C_{60}H_{42}Cl_6N_4$	
Formula weight	1031.68	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.4912(6) Å	
	$b = 12.3477(4)$ Å $\beta = 93.3020(10)^{\circ}$	
	c = 23.7674(8) Å	
Volume	5124.7(3) Å ³	
Ζ	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.380 mm ⁻¹	
F(000)	2128	
Crystal size	$0.15 \ge 0.11 \ge 0.03 \text{ mm}^3$	
Theta range for data collection	3.22 to 25.34°	
Index ranges	$-21 \leq h \leq 21, -14 \leq k \leq 14, -28 \leq l \leq 28$	
Reflections collected	35665	
Independent reflections	4681 [<i>R</i> (int) = 0.0445]	
Completeness to theta = 25.34°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9887 and 0.9453	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4681 / 0 / 353	
Goodness-of-fit on F ²	1.059	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0685, wR_2 = 0.1881$	
R indices (all data)	$R_1 = 0.0763, wR_2 = 0.1949$	
Largest diff. peak and hole	0.912 and –0.553 e.Å ⁻³	



Figure S35. X-ray crystal structure of **10**. (top) Top view; (middle) Side view; (bottom) Perspective view. Thermal ellipsoids were scaled to 50% probability.

Table S8. Crystal data and structure refinement for 2.

Empirical formula	$C_{45}H_{25}Cl_{3}O_{2}$	
Formula weight	704.00	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.8385(6) Å	
	$b = 11.3087(2)$ Å $\beta = 112.6680(10)^{\circ}$	
	c = 12.6953(3) Å	
Volume	3290.54(13) Å ³	
Ζ	4	
Density (calculated)	1.421 Mg/m^3	
Absorption coefficient	0.320 mm^{-1}	
F(000)	1448	
Crystal size	$0.20 \ge 0.20 \ge 0.14 \text{ mm}^3$	
Theta range for data collection	3.13 to 27.48°	
Index ranges	$-32 \le h \le 32, -14 \le k \le 14, -14 \le l \le 16$	
Reflections collected	16054	
Independent reflections	3763 [<i>R</i> (int) = 0.0228]	
Completeness to theta = 27.48°	99.6%	
Max. and min. transmission	0.9566 and 0.9388	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3763 / 0 / 244	
Goodness-of-fit on F ²	1.070	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0584, wR_2 = 0.1496$	
R indices (all data)	$R_1 = 0.0607, wR_2 = 0.1529$	
Largest diff. peak and hole	$0.874 \text{ and } -0.312 \text{ e.} \text{\AA}^{-3}$	



Figure S36. X-ray crystal structure of **2**. (top) Top view; (middle) Side view; (bottom) Side view. Thermal ellipsoids were scaled to 50% probability.

Table S9. Crystal data and structure refinement for 2.

Empirical formula	$C_{45}H_{25}Cl_{3}O_{2}$		
Formula weight	704.00		
Temperature	103(2) K		
Wavelength	0.71075 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 11.4108(3) Å	$\alpha = 83.8430(10)^{\circ}.$	
	b = 11.8461(3) Å	$\beta = 66.3800(10)^{\circ}.$	
	c = 13.6538(3) Å	$\gamma = 84.2300(10)^{\circ}.$	
Volume	1677.90(7) Å3		
Z	2		
Density (calculated)	1.393 Mg/m ³		
Absorption coefficient	0.314 mm ⁻¹		
F(000)	724		
Crystal size	0.20 x 0.15 x 0.02 mm ³		
Theta range for data collection	3.00 to 27.48°.		
Index ranges	$-14 \leq h \leq 14, -15 \leq k \leq 15, -15 \leq l \leq 17$		
Reflections collected	16886		
Independent reflections	7660 [$R(int) = 0.0198$]		
Completeness to theta = 27.48°	99.5 %		
Max. and min. transmission	0.9938 and 0.9399		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	7660 / 0 / 483		
Goodness-of-fit on <i>F</i> ²	1.055		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0470, wR_2 = 0.1227$		
R indices (all data)	$R_1 = 0.0611, wR_2 = 0.1352$		
Largest diff. peak and hole	0.553 and –0.327 e.Å $^{-3}$		



Figure S37. X-ray crystal structure of **2**. (top). Asymmetric unit contains two identical bispentacenequinones. Thermal ellipsoids were scaled to 50% probability.

8. References

[S1] SHELXL-97 and SHELXS-97, program for refinement of crystal structures from diffraction data, University of Gottingen, Gottingen (Germany); G. Sheldrick, T. Schneider, *Methods Enzymol.* **1997**, 277, 319.

[S2] T. Akiyama, A. Hirao, T. Okujima, H. Yamada, H. Uno, N. Ono, Heterocycles, 2007, 74, 835–842.