Dynamic Supramolecular Complexation by Shapeshifting Organic Molecules

Alexander R. Lippert, Vasken L. Keleshian, and Jeffrey W. Bode*
Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104

Supporting Information

General Methods. All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry N$_2$. THF and CH$_2$Cl$_2$ were distilled over CaH$_2$. Hexamethyldisilazane was distilled from KOH. $\text{iso}$-Butyl chloroformate was distilled under N$_2$. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254, Art 5715, 0.25 mm) and were visualized by fluorescence quenching under UV light or by staining with phosphomolybdic acid. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck Kieselgel 60 PF254 (Art 7747). Column chromatography was performed on E. Merck Silica Gel 60 (230–400 Mesh) using a forced flow of 0.5–1.0 bar. $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) were measured on a Bruker Avance 500 spectrometer. Chemical shifts are expressed in parts per million (PPM) downfield from residual solvent peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrophotometer and are reported as wavenumber (cm$^{-1}$).
A. Synthetic Protocols and Tabulated Spectra

Bisallyl Bullvalene 4: Hexamethyldisilazane (0.55 mL, 0.26 mmol, 3.1 equiv) was added to a solution of 2.5M n-butyl lithium in hexane (0.10 mL, 0.25 mmol, 3.0 equiv) in THF at –78 °C and allowed to warm to 0 °C. After stirring for 20 min at 0 °C, the reaction was cooled to –78 °C and bullvalone 3 (25.0 mg, 0.0838 mmol, 1.0 equiv) was added as a solution in 3 x 0.8 mL THF and stirred for 15 min. iso-Butyl chloroformate (110 μL, 0.840 mmol, 10 equiv) was added and the reaction was allowed to warm to rt. After 2 h 45 min, the reaction was poured into 10 mL sat NH₄Cl and extracted with 3 x 10 mL CH₂Cl₂. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated. Isolation of three major bands by silica chromatography (20:1 hexanes:EtOAc → 10:1 hexanes:EtOAc) yielded bisallyl bullvalene 4 (16.2 mg, 49%) as a clear oil. 

\[ ^1H \text{ NMR (}500 \text{ MHz, (CD}_3)_2\text{SO, 120 °C}) \delta 5.90–5.70 \text{ (m, 2H), } 5.10–5.00 \text{ (m, 4H), } 4.16 \text{ (q, 2H, } J = 7.5 \text{ Hz), } 3.95 \text{ (d, 2H, } J = 6.5 \text{ Hz), } 2.75–2.60 \text{ (m, 3H), } 1.95 \text{ (quintet, 1H, } J = 6.5 \text{ Hz), } 1.25 \text{ (t, 3H, } J = 6.5 \text{ Hz), } 0.93 \text{ (d, 6H, } J = 6.5 \text{ Hz); } ^1H \text{ NMR (}500 \text{ MHz, (CD}_3)_2\text{SO, 30 °C}) \delta 7.05 \text{ (m, 1H), } 5.85–5.68 \text{ (m, 3H), } 5.2–5.0 \text{ (m, 4H), } 4.12–4.09 \text{ (m, 2H), } 3.91 \text{ (d, 2H, } J = 6.0 \text{ Hz), } 2.90–2.70 \text{ (m, 4H), } 2.50–2.30 \text{ (m, 2H), } 1.91 \text{ (quintet, 1H, } J = 6.5 \text{ Hz), } 1.24–1.19 \text{ (m, 1H), } 0.89 \text{ (d, 6H, } J = 7 \text{ Hz); } ^1H \text{ NMR (}500 \text{ MHz, CDCl}_3, 30 \text{ °C}) \delta 7.27 \text{ (m, 1H), } 5.79–5.67 \text{ (m, 3H), } 5.11–5.04 \text{ (m, 4H), } 4.20–4.16 \text{ (m, 2H), } 3.97 \text{ (d, 2H, } J = 9.5 \text{ Hz), } 3.40 \text{ (m, 1H), } 2.93–2.80 \text{ (m, 4H), } 2.70–2.35 \text{ (m, 3H), } 1.98 \text{ (quintet, 1H, } J = 6.5 \text{ Hz), } 1.30–1.24 \text{ (m, 1H), } 0.92 \text{ (d, 6H); } ^13C \text{ NMR (}125 \text{ MHz, CDCl}_3) \delta 165.6, 153.6, 153.4, 137.4, 136.0, 135.9, 135.8, 135.6, 135.5, 134.9, 134.6, 134.5, 120.8, 120.6, 117.5, 117.4, 117.3, 117.2, 116.9, 116.8, 116.8, 116.7, 116.6, 116.4, 116.3, 74.5, 60.8, 60.7, 60.7, 45.6, 45.2, 44.8, 44.6, 44.4, 43.9, 43.8, 43.7, 43.6, 43.5, 38.8, 38.3, 37.1, 36.8, 36.0, 35.9, 31.9, 29.7, 29.4, 29.2, 29.0, 28.0, 27.8, 27.7, 27.4, 27.3, 25.8, 25.7, 22.7, 22.1, 21.0, 19.7, 18.9, 18.8, 14.3, 14.2, 14.1; IR (thin film) ν 2958.3, 2919.7, 2849.3, 1756.8, 1707.6, 1463.2, 1238.6 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{24}\)H\(_{30}\)O\(_5\) [M+H]\(^+\) 399.2171, found 399.2176.

* Only major peaks are reported. See variable temperature spectra in Figure S12 on page S15 (in (CD\(_3\))\(_2\)SO) and spectra on page S21 (in CDCl\(_3\)).

Acrylamide Porphyrin 6: Acrylic acid (0.57 mL, 0.83 mmol, 6.9 equiv) was added to a solution of thionyl chloride (57 μL, 0.79 mmol, 6.6 equiv) in 0.50 mL of dimethylacetamide at –10 °C. After stirring for 5 min, a solution of amino porphyrin 5 (119.8 mg, 0.1202 mmol, 1.0 equiv) in 4 mL dimethylacetamide was added to the reaction mixture over 10 min, giving a green solution. Upon complete addition, the reaction mixture was allowed to warm and stirred at rt. After 1 h, the reaction was quenched by the addition of 10 mL of distilled water causing a purple solid to precipitate, which was filtered and washed with water. The solid was dissolved in CH₂Cl₂, washed through the filter, poured onto brine, and extracted into 3 x 15 mL CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by silica gel chromatography (hexane → 5:1 hexane:EtOAc) to yield the acrylamide porphyrin 6 (94.0 mg, 77%) as a red oil.

¹H NMR (500 MHz, CDCl₃) δ 8.91 (m, 6H), 8.87 (d, 2H, J = 4.5 Hz), 8.21 (d, 2H, J = 8 Hz), 8.10 (dd, 6H, J = 4 Hz, 1.5 Hz), 7.95 (d, 2H, J = 7.5 Hz), 7.81 (m, 3H), 7.54 (s, 1H), 6.60 (d, 1H, J = 17 Hz), 6.41 (m, 1H), 5.90 (d, 1H, J = 10.5 Hz), 1.54 (s, 54H), –2.68 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 148.7, 141.3, 138.7, 137.3, 135.0, 131.2, 129.8, 129.7, 128.2, 121.5, 121.4, 121.0, 119.0, 118.0, 35.0, 31.7; IR (thin film) ν 3318.4, 2951.2, 2869.1, 2910.1, 1586.0, 1592.9 cm⁻¹; HRMS (ESI) calcd for C₇₁H₈₁N₅O [M+H]^⁺ 1020.6520, found 1020.6490.

Bisporphyrin Bullvalene 1: Acrylamide porphyrin 6 (21.3 mg, 0.0209 mmol, 2.5 equiv) and bisallyl bullvalene 4 (3.3 mg, 0.0084 mmol, 1.0 equiv) were dissolved in 0.42 mL CH$_2$Cl$_2$. Grubbs' 2$^{\text{nd}}$ generation catalyst (4.3 mg, 0.0051 mmol, 0.61 equiv) was added, the flask was sealed, and the reaction was heated at 40 °C for 16 h. The reaction mixture was concentrated and purified by PTLC (11:1 toluene:EtOAc) to yield the bisporphyrin bullvalene 1 (3.8 mg, 19%) as a red oil. $^1$H NMR (500 MHz, C$_6$D$_5$CD$_3$) δ 9.0–8.85 (m, 14H), 8.24–8.16 (m, 12H), 8.14–8.00 (m, 6H), 7.93–7.85 (m, 8H), 6.53–6.49 (m, 2H), 6.15–5.80 (m, 2H), 5.65–5.41 (m, 3H), 4.30–3.75 (m, 6H), 3.38–2.70 (m, 6H), 1.49–1.43 (m, 108H), 1.14 (t, 3H, $J$ = 7.5 Hz), 0.84 (d, 6H, $J$ = 22 Hz), –2.02 (br s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 175.4, 148.6, 141.3, 141.2, 137.9, 135.1, 130.0, 129.8, 128.2, 125.3, 121.4, 120.9, 119.0 (br), 118.0 (br), 61.5 (br), 39.4 (br), 37.4 (br), 37.1, 35.9, 35.0, 34.4, 32.7, 31.9, 31.7, 30.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.0, 27.8, 27.2, 27.1, 25.5, 24.5, 22.7, 21.5, 19.7 (br), 19.3, 18.9, 14.4, 14.1 cm$^{-1}$; IR (thin film) ν 3315.5, 2954.9, 2923.6, 2853.2, 1753.9, 1665.7, 1592.4, 1525.4, 1475.3, 1466.6, 1362.9, 1260.3, 1362.9, 1260.3, 1246.8 cm$^{-1}$; HRMS (MALDI) calcd for (C$_{162}$H$_{185}$N$_{10}$O$_{7}$)$^+$, 2382.44; found 2382.83.

Bisporphyrin Bullvalone 2: Acrylamide porphyrin 6 (65.3 mg, 0.0640 mmol, 2.3 equiv) and bisallyl bullvalone 3¹ (8.2 mg, 0.028 mmol, 1.0 equiv) were dissolved in 0.20 mL of CH₂Cl₂. Grubbs’ 2nd generation catalyst³ (11.8 mg, 0.0138 mmol, 0.50 equiv) was added, the flask was sealed, and the reaction was heated at 40 °C for 16 h. The reaction mixture was concentrated and purified by PTLC (6:1 toluene:EtOAc) to yield bisporphyrin bullvalone 2 (12.8 mg, 20%) as a red oil. ¹H NMR (500 MHz, C₆D₅CD₃) δ 9.02 (m, 10H), 8.10 (m, 4H), 8.21 (d, 10H, J = 18 Hz), 8.06 (d, 6H, J = 1.7 Hz), 7.92–7.89 (m, 6H), 5.81 (dd, 2H, J = 15.6, 3.5 Hz), 5.62–5.41 (m, 2H), 4.19 (q, 2H, J = 7.1 Hz), 3.48 (m, 2H), 2.75 (m, 4H), 2.53 (br s, 2H), 2.43 (br s, 2H), 1.57–1.39 (m, 108H), 1.19 (t, 3H, J = 7.2 Hz), –2.03 (s, 4H); ¹³C NMR (500 MHz, CDCl₃) δ 175.4, 148.6, 141.2, 137.6, 135.0, 130.0, 129.7, 129.7, 128.6, 128.4, 127.9, 127.7, 127.5, 125.0, 124.6, 121.4, 120.9, 116.4, 60.4, 53.4, 35.9, 35.3, 35.0, 32.8, 31.9, 31.7, 31.4, 30.2, 30.0, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 27.2, 27.1, 25.5, 22.7, 21.0, 20.7, 19.7, 14.2; IR (thin film) ν 3317.5, 2959.2, 2924.5, 2854.1, 1722.1, 1666.2, 1592.4, 1529.3, 1475.8, 1462.7, 1363.4, 1260.3, 1247.7 cm⁻¹; HRMS (MALDI) calcd for (C₁₅₇H₁₇₆N₁₀O₅)⁺, 2281.38; found 2282.19.
B. UV Experiments (Job’s Plots and Spectrophotometric Titrations):

Concentrations of bisporphyrin compounds were calculated according to the extinction coefficient for the acrylamide porphyrin 6 which was determined to be $405000 \pm 8000 \text{ M}^{-1}\text{cm}^{-1}$ by measuring the absorbance at 422 nm for a series of solutions of the acrylamide porphyrin ranging from $9.53 \times 10^{-7} \text{ M}$ to $4.76 \times 10^{-6} \text{ M}$. The extinction coefficients of the bisporphyrin compounds 1 and 2 were taken to be twice the value calculated for the acrylamide porphyrin 6 due to the presence of two porphyrin groups. Concentrations of C$_{60}$ were calculated based on a literature value$^4$ for the extinction coefficient of $65000 \pm 5000 \text{ M}^{-1}\text{cm}^{-1}$.

![Graph](image)

**Figure S1.** Calculation of the extinction coefficient of acrylamide porphyrin 6 at 422 nm in toluene.

---

$^4$ The extinction coefficient for C$_{60}$ in toluene at 334 nm was taken to be $65000 \pm 5000 \text{ M}^{-1}\text{cm}^{-1}$: H. Hungerühler, D. M. Guldi, K.-D. Asmus, *J. Am. Chem. Soc.* **1993**, *115*, 3386–3387.
**Job’s Plots:**

**Bisporphyrin Bullvalene 1:**  Stock solutions of bisporphyrin bullvalene 1 at $1.36 \times 10^{-4}$ M and C$_{60}$ at $1.37 \times 10^{-4}$ M (calculated based on the extinction coefficients) were prepared in spectral grade toluene. Multiples of 12 $\mu$L of these solutions were added into a 3.5 mL cuvette at ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 1:C$_{60}$ for a total volume of added solution of 48 $\mu$L. The cuvette was diluted to a constant total volume and the absorbance was measured at 418 nm, 422 nm, and 427 nm.

**Bisporphyrin Bullvalone 2:**  Stock solutions of bisporphyrin bullvalone 2 at $1.56 \times 10^{-4}$ M and C$_{60}$ at $1.82 \times 10^{-4}$ M (calculated based on the extinction coefficients) were prepared in spectral grade toluene. Multiples of 12 $\mu$L of these solutions were added into a 3.5 mL cuvette at ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 2:C$_{60}$ for a total volume of added solution of 48 $\mu$L. The cuvette was diluted to a constant total volume and the absorbance was measured at 422 nm.

![Job's Plots](image)

**Figure S2.** Job’s plots for bisporphyrin bullvalene 1 and C$_{60}$ at 418 nm, 422 nm, and 427 nm in toluene with a total concentration of $[1] + [C_{60}] = 1.88$ $\mu$M and bisporphyrin bullvalone 2 at 422 nm in toluene with a total concentration $[2] + [C_{60}] = 2.32$ $\mu$M.
Spectrophotometric Titrations:

Bisporphyrin Bullvalene 1: A solution of bisporphyrin bullvalene 1 (2500 μL, 2.1 X 10^-6 M) in spectral grade toluene was added to a quartz cuvette and the absorbance was measured upon the addition of 2 to 100 μL (1000 μL total) aliquots of a stock solution of C₆₀ (3.4 X 10^-3 M) in toluene to both the sample and the reference cuvette. Plots of ΔA at 421 nm and 434 nm versus [C₆₀] were analyzed after dilution corrections and the binding constants (Kₘ) and the absorbance at maximum saturation of binding sites (ΔAₘₐₓ) were evaluated by a least-squares non linear fitting approach using the equation:

\[ \Delta A = \frac{\Delta Aₘₐₓ(1 + Kₘ[C₆₀] + [BP]Kₘ) - ((1 + Kₘ[C₆₀] + [BP]Kₘ)^2 - 4Kₘ^2[C₆₀][BP])^{1/2}}{2Kₘ[BP]} \]

where \( \Delta A = A_{obs} - A_0 \), [C₆₀] is the total concentration of C₆₀ in solution, and [BP] is the total concentration of the bisporphyrin in solution. The inconsistency of the equilibrium constant at different wavelengths is indicative of multiple complexes.

Figure S3. Differential absorbance plots of 2.1 μM bisporphyrin bullvalene 1 with 10–1000 equivalents of C₆₀ in toluene.

Figure S4. Binding isotherms for the spectrophotometric titration of 2.1 μM bisporphyrin bullvalene 1 at 421 nm and 434 nm in toluene.

**Bisporphyrin Bullvalone 2:** A solution of bisporphyrin bullvalone 2 (2500 μL, 2.9 × 10⁻⁶ M) in spectral grade toluene was added to a quartz cuvette and the absorbance was measured upon the addition of 2 to 100 μL (1000 μL total) aliquots of a stock solution of C₆₀ (3.7 × 10⁻³ M) in toluene to both the sample and the reference cuvette. Plots of ΔA at 421 nm and 434 nm versus [C₆₀] were analyzed after dilution corrections and the binding constants (Kₘ) and the absorbance at maximum saturation of binding sites (ΔAₘₐₓ) were evaluated by a least-squares non linear fitting approach using the equation:

\[
\Delta A = \frac{\Delta A_{max}(1 + K_b[C_{60}] + [BP]K_b) - ((1 + K_b[C_{60}] + [BP]K_b)^2 - 4K_b^2[C_{60}][BP])^{1/2}}{2K_b[BP]}
\]

where ΔA = A_{obs} – A₀, [C₆₀] is the total concentration of C₆₀ in solution, and [BP] is the total concentration of the bisporphyrin in solution. The consistency of the binding constant at different wavelengths is indicative of a single binding complex.

**Figure S5.** Differential absorbance plots of 2.9 μM bisporphyrin bullvalone 2 with 10–1000 equivalents of C₆₀ in toluene.

**Figure S6.** Binding isotherms for the spectrophotometric titration of 2.9 μM bisporphyrin bullvalone 2 at 421 nm and 434 nm in toluene.

\[K_b = 2700 \pm 120 \text{ M}^{-1}\]
\[\Delta A_{max} = 0.607 \pm 0.012\]

\[K_b = 2930 \pm 73 \text{ M}^{-1}\]
\[\Delta A_{max} = 0.313 \pm 0.003\]
C. \(^\text{1H} \text{NMR Titrations:}\)

**Bisporphyrin Bullvalene 1:** A 1.3 \( \times \) 10\(^{-3}\) M stock solution of bisporphyrin bullvalene 1 in \( \text{C}_6\text{D}_5\text{CD}_3 \) was prepared and 100 \( \mu \text{L} \) aliquots (1.3 \( \times \) 10\(^{-7}\) mol) were added to 7 NMR tubes (10 mm). Appropriate aliquots of a stock solution of \( \text{C}_{60} \) (3.7 \( \times \) 10\(^{-3}\) M) in \( \text{C}_6\text{D}_5\text{CD}_3 \) were added to each NMR tube to obtain mixtures with 0, 0.5, 1, 1.5, 2, 2.5, and 3 equivalents of \( \text{C}_{60} \). All NMR tubes were diluted with additional \( \text{C}_6\text{D}_5\text{CD}_3 \) to a final volume of 300 \( \mu \text{L} \). The chemical shift of the upfield N-H proton of the porphyrin was monitored. Plots of \( \Delta \delta \) versus \( [\text{C}_{60}] / [\text{BP}] \) were plotted and the binding constant (\( K_b \)) and the chemical shift at saturation of binding sites (\( \Delta \delta_{\text{max}} \)) were evaluated by a least-squares non linear fitting approach using the equation:\(^{6}\)

\[
\Delta \delta = \frac{\Delta \delta_{\text{max}}}{2} \left( \frac{[\text{C}_{60}]}{[\text{BP}]} + 1 + \frac{1}{K_b [\text{BP}]} \right) \pm \left( \left( \frac{[\text{C}_{60}]}{[\text{BP}]} + 1 + \frac{1}{K_b [\text{BP}]} \right)^2 - 4 \left( \frac{[\text{C}_{60}]}{[\text{BP}]} \right) \right)^{1/2}
\]

where \( \Delta \delta = \delta_{\text{obs}} - \delta_{\text{o}}, \) [\( \text{C}_{60} \)] is the total concentration of \( \text{C}_{60} \) in solution, and [BP] is the total concentration of the bisporphyrin in solution. The appearance of multiple peaks upon the addition of \( \text{C}_{60} \) indicates multiple complexes that are in fast exchange with their respective unbound isomer. The binding constant at 25 °C was calculated monitoring the shift of two separate complexes that appear as separated distinct peaks. The titration was also performed at 90 °C and coalescence of the peaks was observed.

![Figure S7](image)

**Figure S7.** NMR titrations of 0.43 mM bisporphyrin bullvalene 1 at 25 °C and 90 °C in \( \text{C}_6\text{D}_5\text{CD}_3 \).

---

Figure S8. Binding isotherms of the NMR titration of 0.43 mM bisporphyrin bullvalene 1 at 25 °C and 90 °C in C₆D₅CD₃.

**Stated Assumptions:** Our calculation of the binding constants for bisporphyrin bullvalene 1 requires two key assumptions. The first assumption is that the observed Δδ upon addition of C₆₀ is predominately due to the change in the ratio of bound and unbound bisporphyrin compounds and not due to any change in the relative ratio of valence isomers. We believe this assumption is valid because (1) the rate of exchange of valence isomers (which coalesce at 90 °C) is much slower than the rate of exchange of the bound and unbound bisporphyrin compounds (which coalesce at –50 °C) and (2) the observed difference in the chemical shift between the observed peaks (Δδ ~ 0.05 ppm, see peak d and e in Figure 3b) at 25 °C changes very little (< 0.009 ppm) as increasing amounts of C₆₀ are added. The second assumption is that the concentrations of each binding isomer are 100% of the total concentration of bisporphyrin bullvalene 1 used in the experiment. In actuality, the population of each binding isomer is a difficult to measure fraction of this value, which would lead to higher calculated affinities. For example, the binding affinities for the complex giving rise to peak d in Figure 3b would be 4037 ± 578 M⁻¹, 6056 ± 867 M⁻¹, and 12111 ± 1734 M⁻¹ if we assume that the concentration, [BP], of this binding isomer is 75%, 50%, and 25%, respectively, of the amount of bisporphyrin bullvalene 1 added.
The same analysis for peak e in Figure 3b yields values of $9033 \pm 2425 \text{ M}^{-1}$, $13550 \pm 3637 \text{ M}^{-1}$, and $27099 \pm 7274 \text{ M}^{-1}$ if we assume that the concentration, \([\text{BP}]\), of this binding isomer is 75%, 50%, and 25%, respectively, of the amount of bisporphyrin bullvalene 1 added. Our best estimates for these relative populations based on $^1\text{H}$ NMR integrations of the N-H peak indicate that the two isomers are in approximately a 1:1 ratio, which would give binding constants of $6056 \pm 867 \text{ M}^{-1}$ for peak d and $13550 \pm 3637 \text{ M}^{-1}$ for peak e.

**Bisporphyrin Bullvalone 2:** A $1.5 \times 10^{-3}$ M stock solution of bisporphyrin bullvalone 2 in C$_6$D$_5$CD$_3$ was prepared and 100 µL aliquots ($1.5 \times 10^{-7}$ mol) were added to 7 NMR tubes (10 mm). Appropriate aliquots of a stock solution of C$_{60}$ ($2.6 \times 10^{-3}$ M) in C$_6$D$_5$CD$_3$ were added to each NMR tube to obtain mixtures with 0, 0.5, 1, 1.5, 2, 2.5, and 3 equivalents of C$_{60}$. All NMR tubes were diluted with additional C$_6$D$_5$CD$_3$ to a final volume of 300 µL. The chemical shift of the upfield N-H proton of the porphyrin was monitored. Plots of $\Delta \delta$ versus $[\text{C}_{60}]/[\text{BP}]$ were plotted and the binding constant ($K_b$) and the chemical shift at saturation of binding sites ($\Delta \delta_{\text{max}}$) were evaluated by a least-squares non linear fitting approach using the equation:

$$
\Delta \delta = \frac{\Delta \delta_{\text{max}}}{2} \left( \frac{[\text{C}_{60}]}{[\text{BP}]} + 1 + \frac{1}{K_b[\text{BP}]} \right) \pm \left( \frac{[\text{C}_{60}]}{[\text{BP}]} + 1 + \frac{1}{K_b[\text{BP}]} \right)^2 - 4 \frac{[\text{C}_{60}]}{[\text{BP}]} \right)^{1/2}
$$

where $\Delta \delta = \delta_{\text{obs}} - \delta_{\text{ox}}$, [C$_{60}$] is the total concentration of C$_{60}$ in solution, and [BP] is the total concentration of the bisporphyrin in solution. The appearance of one peak that shifts upon the addition of C$_{60}$ indicates the formation of a single complex that is in fast exchange with the unbound bisporphyrin.

![Figure S9. NMR titrations of 0.5 mM bisporphyrin bullvalone 2 at 25 °C and 90 °C in C$_6$D$_5$CD$_3$.](image-url)
Figure S10. Binding isotherms of the NMR titration of 0.5 mM bisporphyrin bullvalone 2 at 25 °C and 90 °C in C₆D₅CD₃.

Kₘ = 2800 ± 210
Δδₘₐₓ = .310 ± .007

Kₘ = 570 ± 65
Δδₘₐₓ = .252 ± .017
D. SFC–UV Traces:

SFC (Supercritical CO\textsubscript{2} Fluid Chromatography) Conditions. Columns: Silica (4.6 x 250 mm). Eluents: gradient 5%–80% \textit{i}-PrOH in CO\textsubscript{2}, rate 3%/min, Flow rate 2.0 ml/min. Detection: 424 nm.

Figure S11. SFC-UV trace of bisporphyrin bullvalene 1 and C\textsubscript{60}. Comparison of the absorbances of the porphyrin and C\textsubscript{60} peaks in the UV spectra of the isolated complex yields an estimate of a 1:1 ratio of bisporphyrin bullvalene 1 to C\textsubscript{60}.

Time = 9.8 min: Residual Acrylamide Porphyrin
Time = 11.7 min: Bisporphyrin Bullvalene
Time = 13 min: Bisporphyrin Bullvalene–C\textsubscript{60}
E. UV Spectra

Figure S12. UV spectra of 2.1 μM bisporphyrin bullvalene 1 in spectral grade toluene.

Figure S13. UV spectra of 2.9 μM bisporphyrin bullvalene 2 in spectral grade toluene.
F. Potential High-Binding Isomers of Bisporphyrin Bullvalene 1
G. NMR Spectra

Figure S14. VTNMR of bisallyl bullvalene 4 in (CD$_3$)$_2$SO.

![Graph showing NMR spectra at different temperatures](image-url)
Figure S15. VTNMR of bisporphyrin bullvalene 1 in C₆D₆CD₃.

- 80 °C
- 60 °C
- 40 °C
- 23 °C
Figure S16. VTNMR of bisporphyrin bullvalene 1 and C₆₀ C₆D₃CD₃.
Figure S17. $^{13}$C VTNMR of bisporphyrin bullvalene 1 and C$_{60}$ in C$_6$D$_5$CD$_3$. 

[Graph showing $^{13}$C VTNMR data with temperature ranging from 30°C to -80°C and ppm scale ranging from 150 to 140 ppm.]
Figure S18. VTMR of bisporphyrin bullvalone 2 and C_{60} in C_{6}D_{5}CD_{3}.

"vk135_7_25 deg" 1 1 Z:\ Vasken

90 °C

70 °C

50 °C

25 °C

[ppm]
Figure S19. 2D-EXSY of bisallyl bullvalene 4 in CDCl₃.