

Facile synthesis of a flexible tethered porphyrin dimer that preferentially complexes fullerene C₇₀[†]

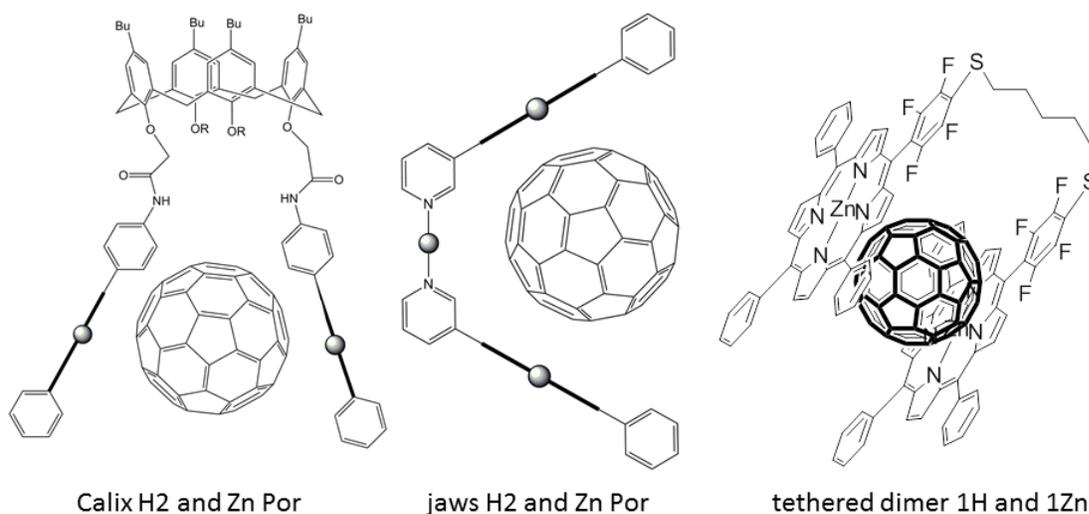
Matthew Jurow,^a Christopher Farley,^a Cesar Pabon,^a Brian Hageman,^a Aaron Dolor,^a and Charles Michael Drain^{a,b*}

^a Hunter College and Graduate Center of the City University of New York, 695 Park Avenue, New York, New York 10065 USA.

Fax: 212-772-5332; Tel: 212-650-3791; E-mail: cdrain@hunter.cuny.edu

^b Rockefeller University, 1230 York Avenue, New York, New York 10065 USA

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Scheme S1. The structure of the three dimers discussed in Table 1.

Materials and Methods.

¹H and ¹³C NMR spectra were recorded in a Bruker Avance 500 MHz spectrometer. Electropray ionization mass spectrometric analyses were performed at the CUNY Mass Spectrometry Facility at Hunter College using an Agilent Technologies HP-1100 LCMSD instrument. MALDI-MS spectra were recorded as a service by the University of Illinois with a Bruker UltrafleXtreme MALDI TOF mass spectrometer purchased in part with a grant from the National Center for Research Resources, National Institutes of Health (S10 RR027109 A). All reagents were obtained from commercial sources and used without further purification. Atomic force microscopy (AFM) measurements were conducted with an Asylum AFM (MFP-3D, Asylum Research Corp.) Transmission electron microscopy uses a Jeol 200kV instrument. Calculations were done on ChemOffice Chem 3D (2011) software using MM2 by cycling through molecular dynamics and minimizing the energy.

5,10,15-triphenyl-20-(2,3,4,5,6-pentafluorophenyl)porphyrin (MPF). To a mixture of propionic acid (0.6 L) and nitrobenzene (6 mL) was added benzaldehyde (21.34 mmol, 2.17 mL) and pentafluorobenzaldehyde (7.0 mmol, 0.875 mL) with stirring. The mixture was heated to 100 °C and pyrrole (28.3 mmol, 1.94 mL) was added slowly. The reaction was refluxed for three hours in the dark and allowed to cool. 300 mL silica was added to the reaction flask and the propionic acid was evaporated. The silica gel was washed with dichloromethane and acetone until no more color eluted. The solution was evaporated to 100 mL and washed with sodium bicarbonate and water, dried over anhydrous sodium sulfate and evaporated to dryness. The organic layer was then recrystallized from hexanes to yield a purple powder. The porphyrin mixture was filtered, dissolved in dichloromethane, loaded onto a 600 mL silica gel column and separated with an eluent of 30:70 toluene:petroleum ether (v/v). The fifth of the six bands was collected, evaporated and recrystallized from hexanes to yield 360 mg (0.511 mmol, 7.22% yield) of product **MPF**.

5,10,15-triphenyl-20-(2,3,4,5,6-pentafluorophenyl)porphyrinato zinc(II), ZnMPF. **MPF** (0.511 mmol, 0.360 g) was added to 20 mL of chloroform. Zinc acetate dihydrate (4.09 mmol, 0.897 g) was added to eight mL methanol. The methanol solution was added to the **MPF** in chloroform, and the mixture was refluxed for three hours. The mixture was washed with water, extracted into dichloromethane, dried over sodium sulfate, and evaporated to dry to yield 276 mg **ZnMPF** (76.67% yield).

Dimer of 5,10,15-triphenyl-20-(4-perfluorophenyl)porphyrinato zinc(II) (1Zn). **ZnMPF** (116 mg, 0.151 mmol) was added to dry DMF (16.6 mL) under a nitrogen atmosphere. To the stirring solution, 1,5-pentane-dithiol (0.23 mL, 1.7 mmol) was added followed by diisopropylethylamine (2.914 mL, 16.73 mmol). The reaction mixture was stirred at 80 °C for 12 hours, cooled to room temperature, washed with water, extracted into dichloromethane, dried over sodium sulfate, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography to remove starting materials and recrystallized from hexanes to yield 95.37mg of **1Zn** (yield 82.19%).

Dimer of 5,10,15-triphenyl-20-(2,3,4,5,6-pentafluorophenyl)porphyrin free base (1H). **1Zn** (80 mg, 0.091 mmol) was added to dry chloroform (5 mL) under a nitrogen atmosphere. To the stirring solution concentrated HCl (0.5 mL, 20.43 mmol) was added dropwise. The mixture was stirred at room temperature for three hours. The reaction mixture was then washed with water, extracted into dichloromethane, dried over sodium sulfate, and evaporated to dry under reduced pressure. The crude product was recrystallized from hexanes to yield 75 mg of product **1H** (yield 93.75%).

MALDI: calculated 1505.6423 found 1505.4

NMR (500 MHz, CDCl₃): 9.02(d),4H, β pyrrole; 9.96(m), 12H, β pyrrole; 8.20(m),12H, *ortho* phenyl;

7.77(m), 18H, *meta/para* phenyl; 3.39(t), 2H, S-CH₂ tether; 3.15(m), 2H, HS-CH₂ tether; 2.05(m), 2H, tether; 1.86(m), 4H, tether.

Photophysics

UV-visible absorption spectroscopy was performed on a Cary 1-Bio UV-Visible spectrometer. Steady state fluorescence spectra were obtained on a HORIBA Jobin-Yvon FluoroLog-3 fluorometer, and singlet state lifetimes were taken using the SPEX-IBH TCSPC add-on component to the same system using a pulsed NanoLED laser at 425 nm. In order to minimize secondary absorption and emission, 1 mm path length quartz or optical glass cuvettes were used for all spectroscopic studies. The emission spectra and lifetimes were taken using a front-face configuration, which also helped to minimize these inner-filter effects. All photophysical studies were carried out in spectrophotometric grade 99.99% toluene, used as purchased. Solutions of diporphyrin species were prepared at one half the molar concentrations of the monomer controls in order to yield the equivalent macrocycle concentration for comparison.

UV-Visible Spectra

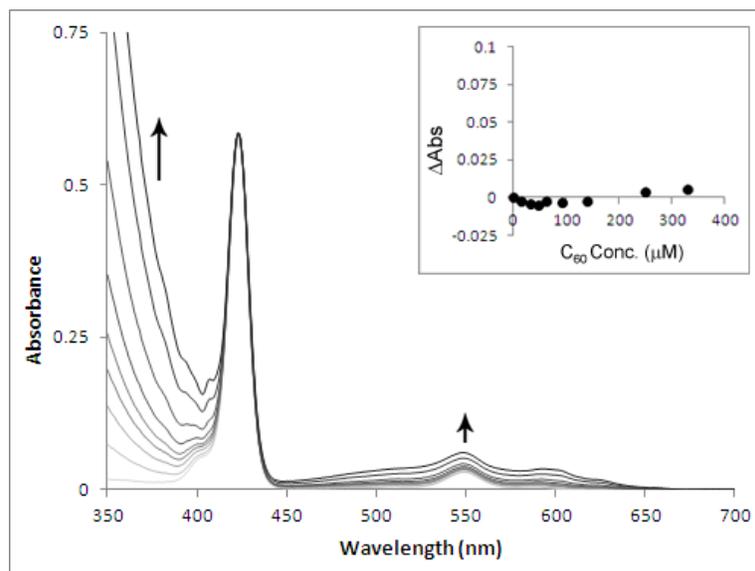


Figure S1: UV-visible spectrophotometric titration of C₆₀ into **1Zn** solution. The inset shows the difference between the calculated sum of the absorbance of the two components at 423 nm and the experimentally observed absorbance for the mixed solutions, as function of the quencher concentration. **[1Zn]** = 10.0 μM; **[C₆₀]** = 0–0.33 mM.

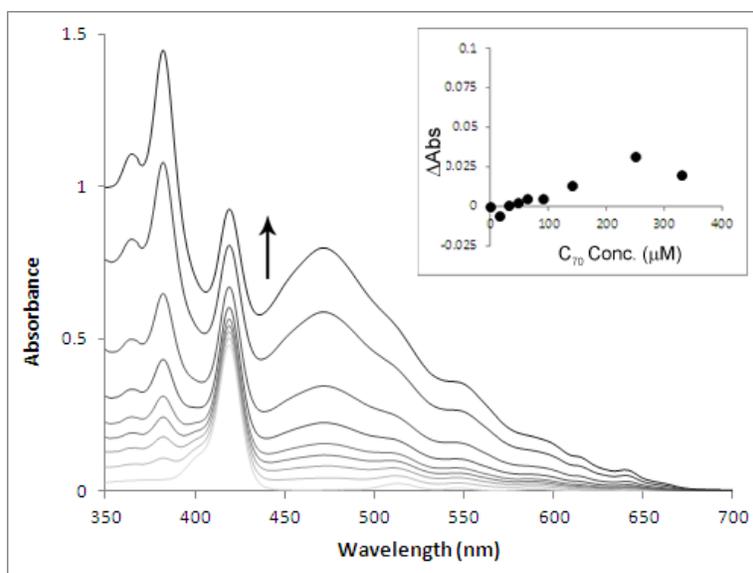


Figure S2: UV-visible spectrophotometric titration of C_{70} into **1H** solution. The inset shows the difference between the calculated sum of the absorbance of the two components at 419 nm and the experimentally observed absorbance for the mixed solutions, as function of the quencher concentration. $[1H] = 10.0 \mu M$; $[C_{70}] = 0-0.33 \text{ mM}$.

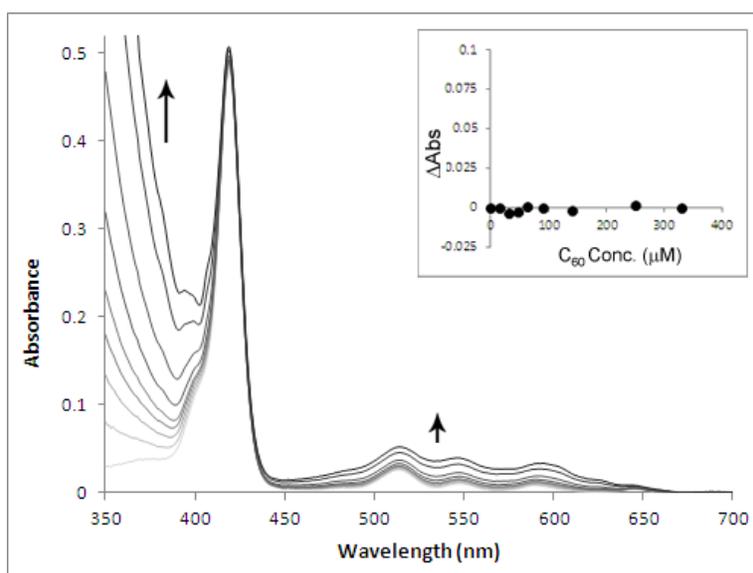


Figure S3: UV-Visible spectrophotometric titration of C_{60} into **1H** solution. The inset shows the difference between the calculated sum of the absorbance of the two components at 419 nm and the experimentally observed absorbance for the mixed solutions, as function of the quencher concentration. $[1H] = 10.0 \mu M$; $[C_{60}] = 0-0.33 \text{ mM}$.

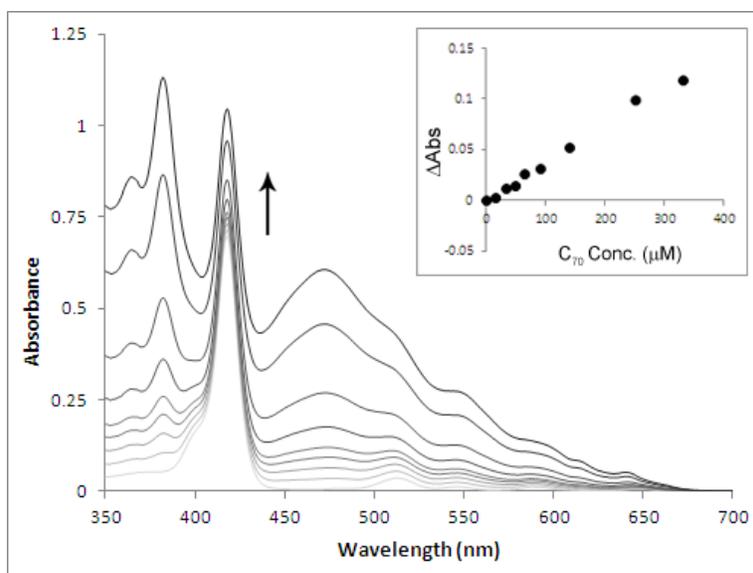


Figure S4: UV-Visible spectrophotometric titration of C₇₀ into **MPF** solution. The inset shows the difference between the calculated sum of the absorbance of the two components at 418 nm and the experimentally observed absorbance for the mixed solutions, as function of the quencher concentration. **[MPF] = 20.0 μM; [C₇₀] = 0–0.33 mM.**

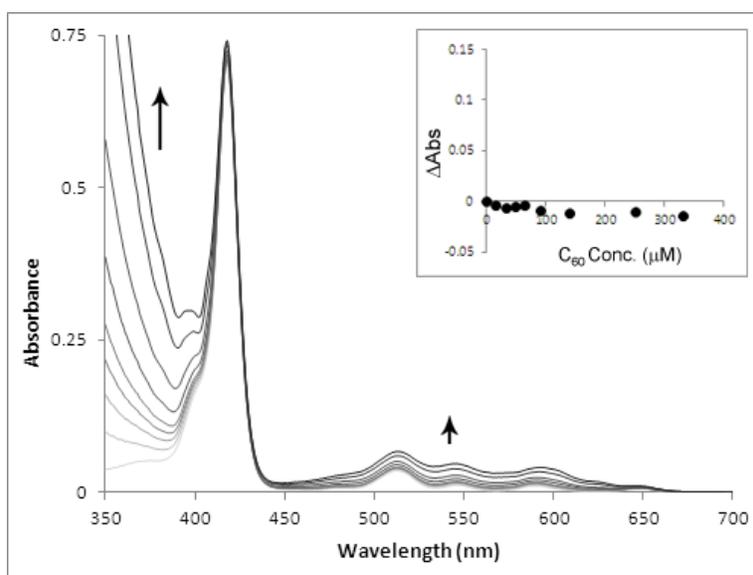


Figure S5: UV-Visible spectrophotometric titration of C₆₀ into **MPF** solution. The inset shows the difference between the calculated sum of the absorbance of the two components at 418 nm and the experimentally observed absorbance for the mixed solutions, as function of the quencher concentration. **[MPF] = 20.0 μM; [C₆₀] = 0–0.33 mM.**

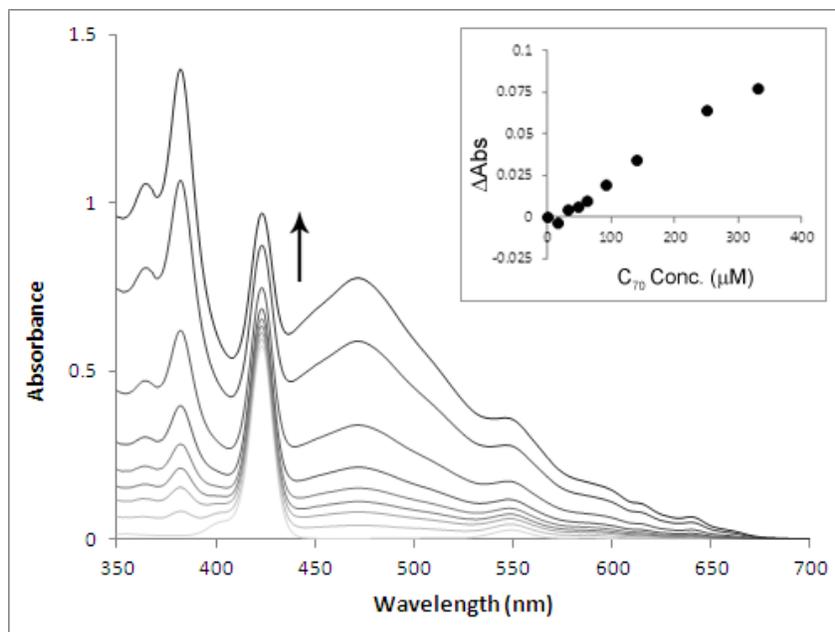


Figure S6. UV-Visible spectrophotometric titration of C_{70} into **1Zn** solution. The inset shows the difference between the calculated sum of the absorbance of the two components at 419 nm and the experimentally observed absorbance for the mixed solutions, as function of the quencher concentration. $[1Zn] = 10.0 \mu M$; $[C_{70}] = 0-0.33 \text{ mM}$.

Fluorescence Spectra

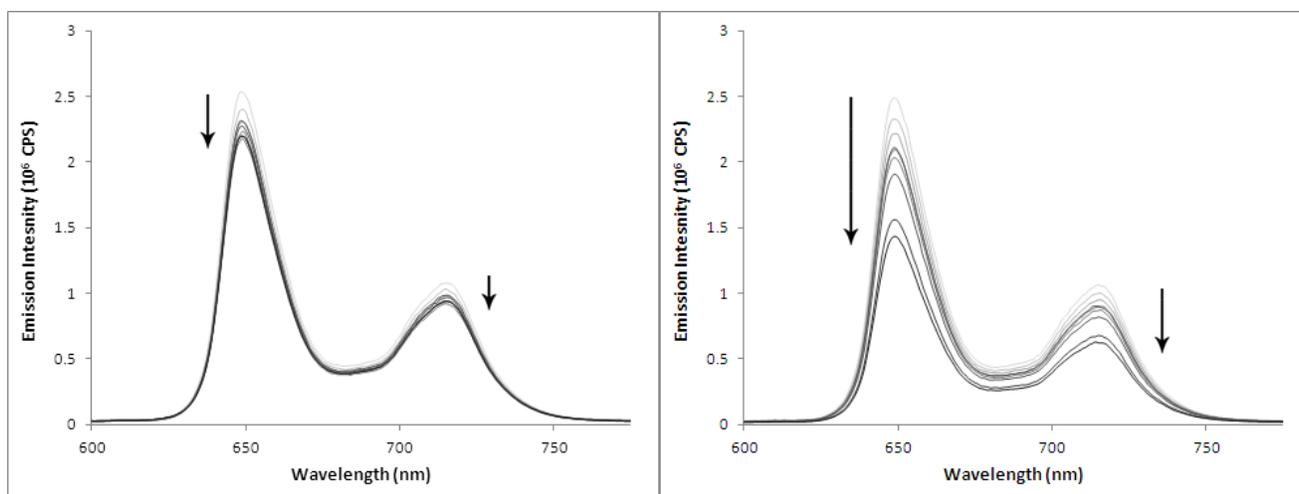


Figure S7: Fluorescence emission spectra of a titration of (left) C_{60} and (right) C_{70} into a **1H** solution. Both graphs show quenching, but the effect of C_{70} is again more pronounced. The solutions were excited at a wavelength of 414 nm, a near-isosbestic point. Emissions were corrected for the increase in absorbance at the excitation wavelength. $[1H] = 10.0 \mu M$; $[C_{60}]$ or $[C_{70}] = 0-0.33 \text{ mM}$.

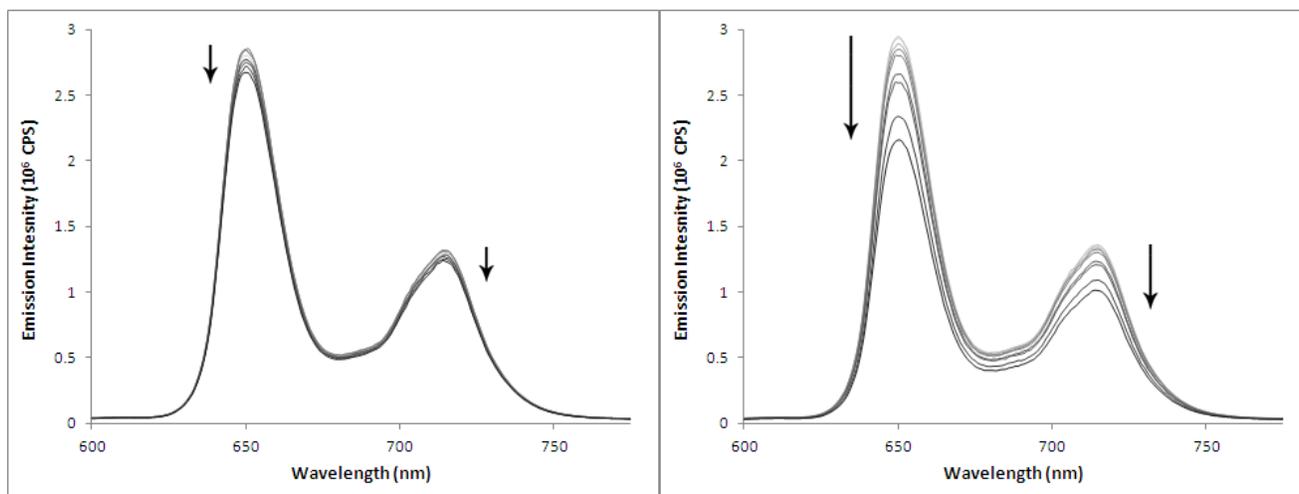


Figure S8: Fluorescence emission spectra of a titration of (left) C₆₀ and (right) C₇₀ into a MPF solution. Both graphs show quenching, but the effect of C₇₀ is again more pronounced. The solutions were excited at a wavelength of 414 nm, a near-isosbestic point. Emissions were corrected for the increase in absorbance at the excitation wavelength. [MPF] = 20.0 μM; [C₆₀] or [C₇₀] = 0–0.33 mM.

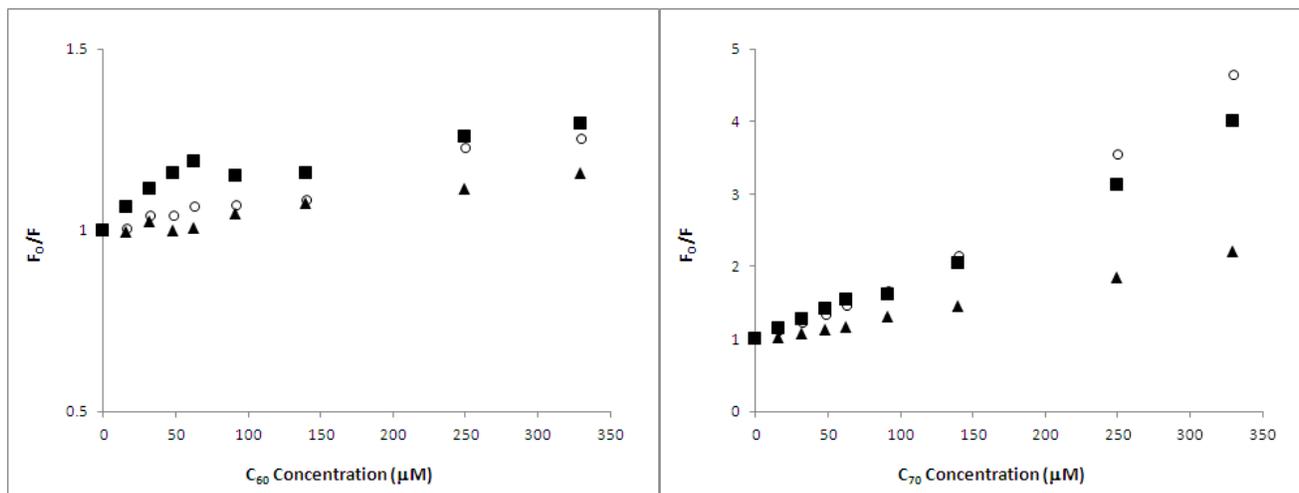


Figure S9: Stern-Volmer plots for each species discussed. The ratio of unquenched to quenched fluorescence as C₆₀ (left) and C₇₀ (right) are titrated into solutions of 1Zn (○), 1H (■) and MPF (▲) is plotted as a function of quencher concentration. Note the difference in scale between the left and right graphs. The molar concentration of the MPF control was twice that of the dimers in order to maintain equivalent macrocycle concentrations for comparison. There is thus a clear enhancement of the dimer quenching over the monomer. The slopes of the best fit lines to these plots are the binding constants collected in **Table 1** below. Similar binding constants were obtained from fluorescence data corresponding to two different excitation wavelengths.

Carbon Nanotube Studies

3ml aliquots of 85 μM solution of **1Zn** in THF were sonicated with 1 mg single walled carbon nanotubes (SWCNT) for 10 minutes. Solutions were centrifuged to remove insoluble SWCNT and its complexes with the dimer. The supernatants were then analyzed by fluorescence and UV-Visible spectroscopy.

Fluorescence

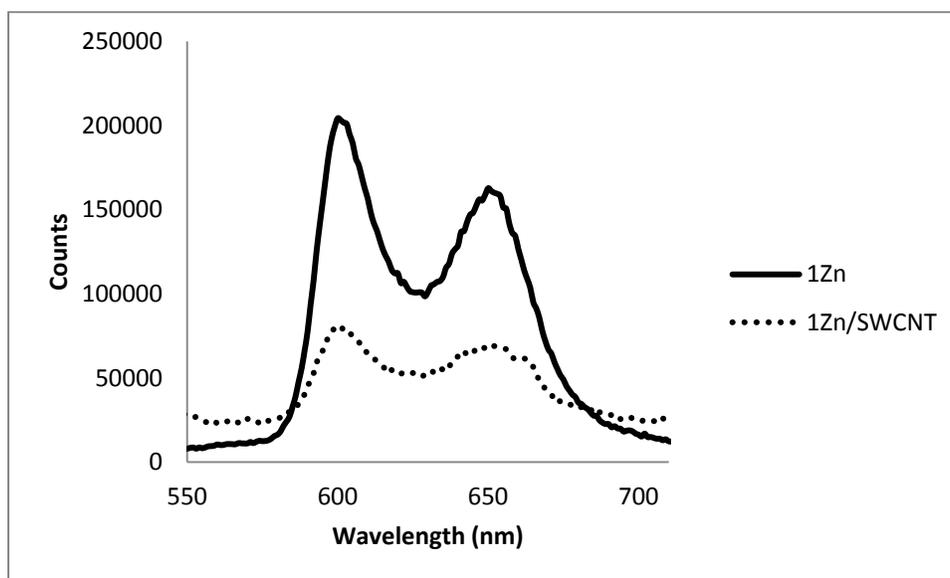


Figure S10. Fluorescence spectrum of typical nanotube experiment. 10 μM **1Zn** solution before and after treatment with nanotubes. Excitation at 425 nm in right angle mode demonstrates ~60% quenching (without baseline correction).

Uv-Visible

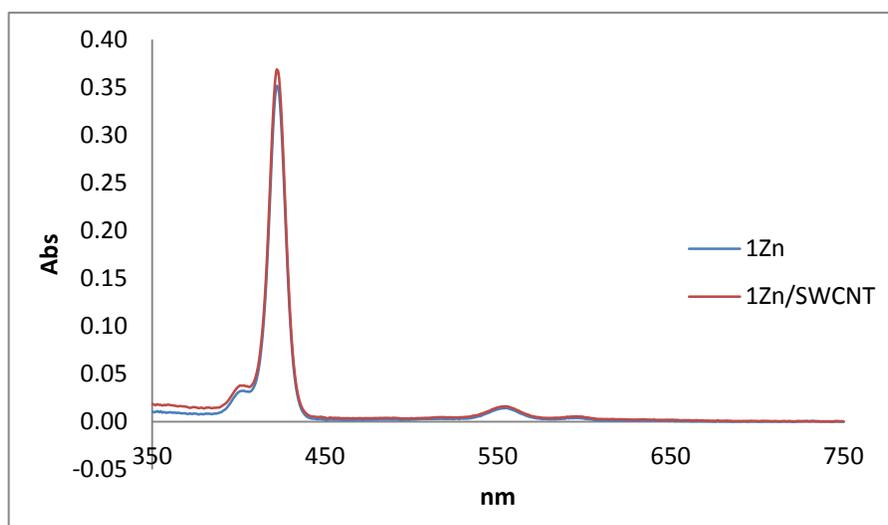


Figure S11. Uv-Vis spectrum of typical nanotube 10 μM **1Zn** solution before and after treatment with nanotubes. Baselines corrected at 750 nm.

AFM

Samples for atomic force microscopy were prepared by drop casting toluene solutions onto ozone cleaned glass slides and letting the solutions evaporate in air.

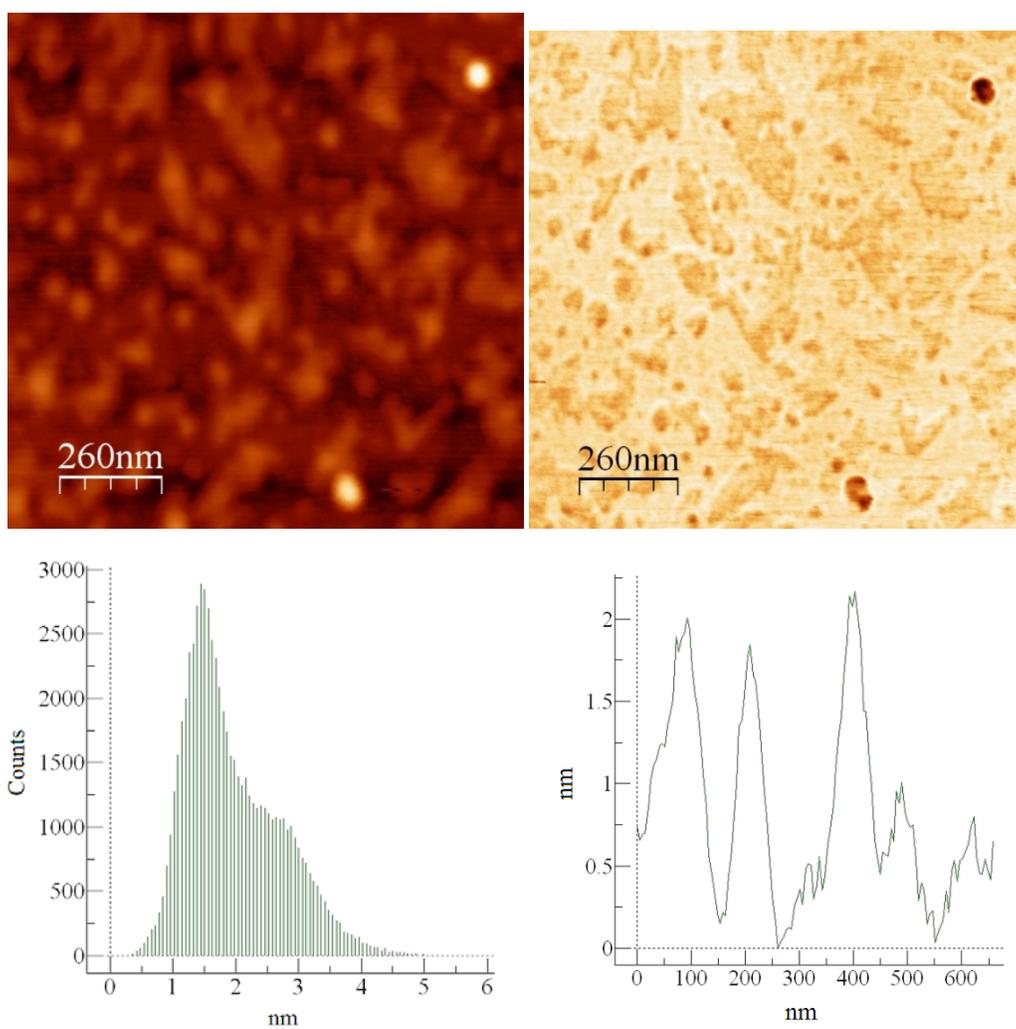


Figure S12. AFM of films deposited from 1 mM solution of C₇₀. Top: (left) height image, (right) phase image. Bottom: (left) histogram of particle sizes; ~1.1 nm corresponds to diameter of C₇₀^{1,2} (right) height profile.

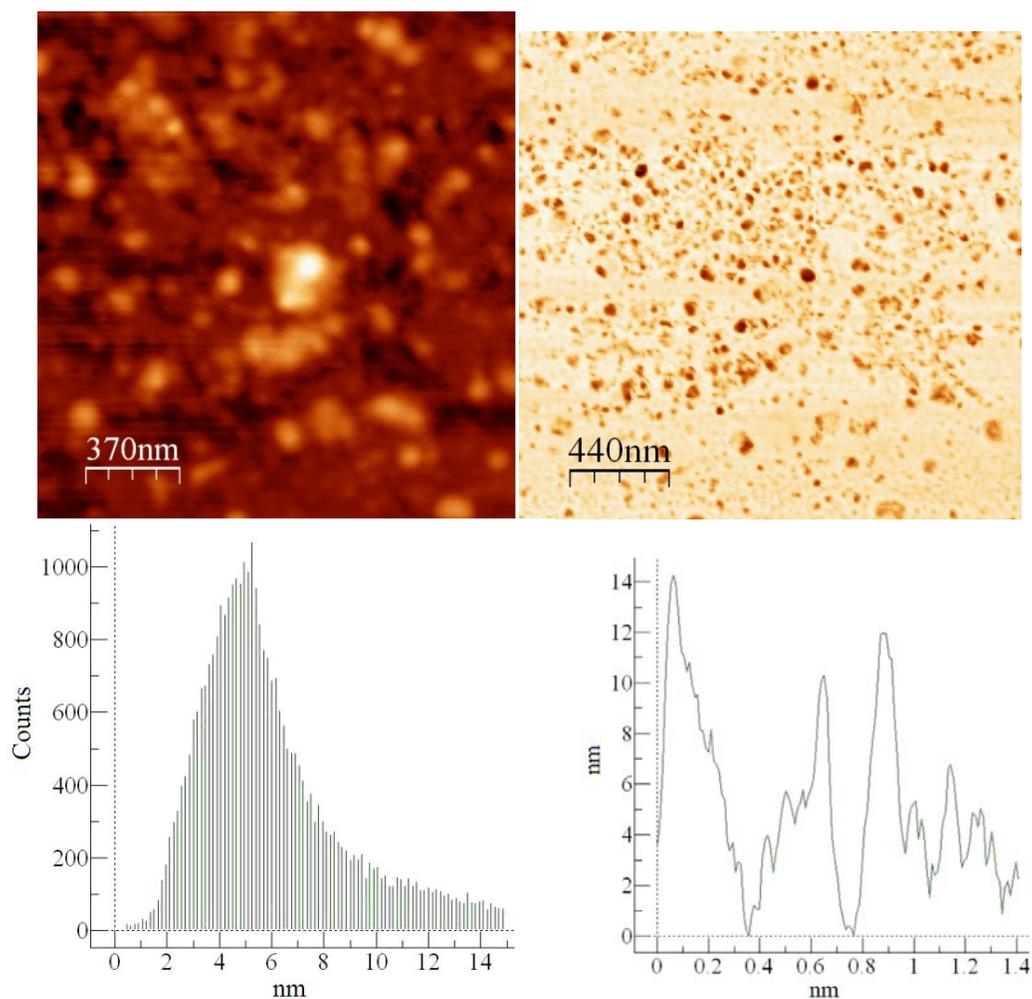


Figure S13. Films deposited from 10 μM solution of **1H**. Top: (left) height image, (right) phase image. Bottom: (left) histogram of particle sizes; mean ~ 5 nm, (right) is height profile of larger aggregates.

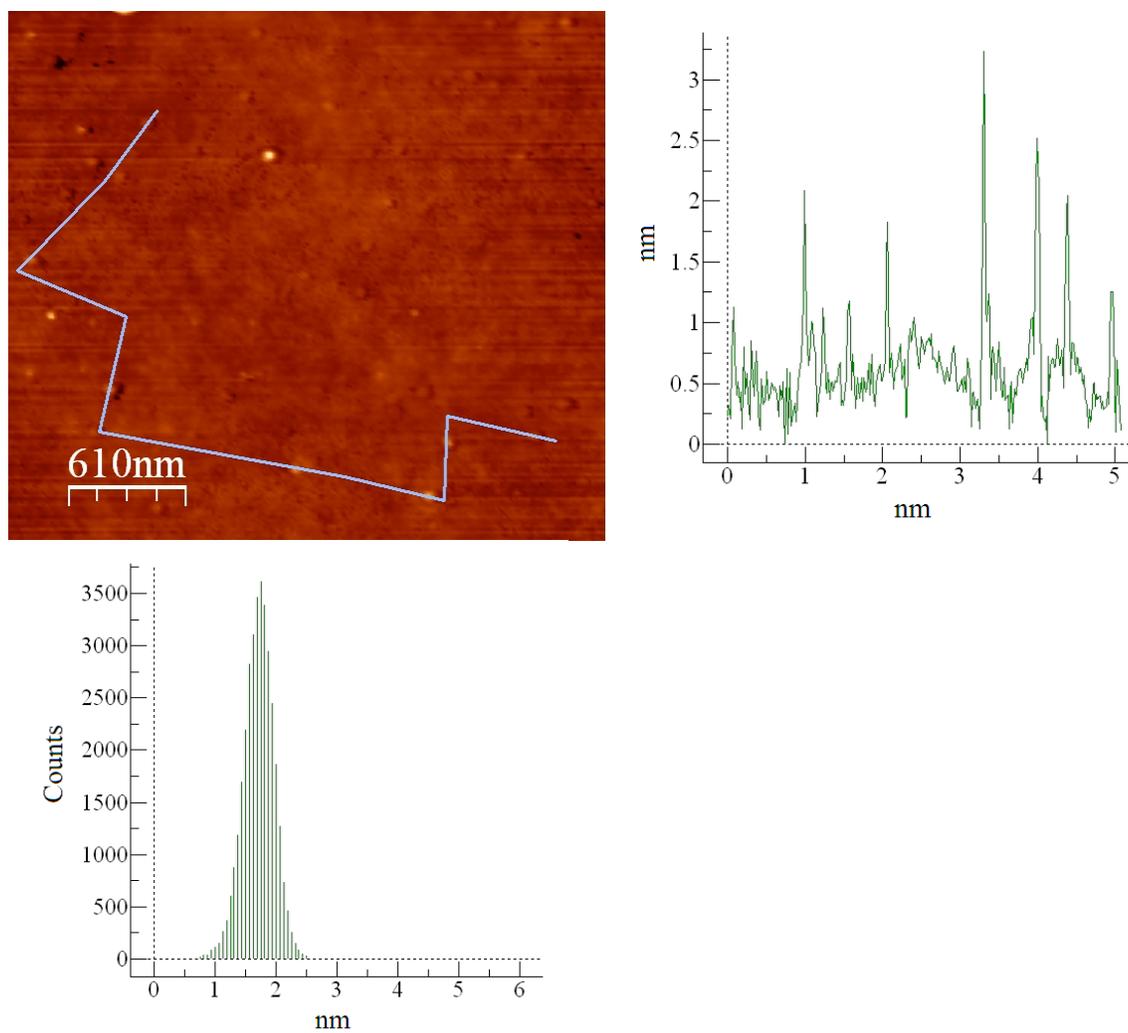


Figure S14. Films deposited from 10 μM solutions of C_{70} . Top: (left) height image, (right) height profile trace. Bottom: (left) histogram of particle sizes; ~ 1.1 nm corresponds to diameter of C_{70} .

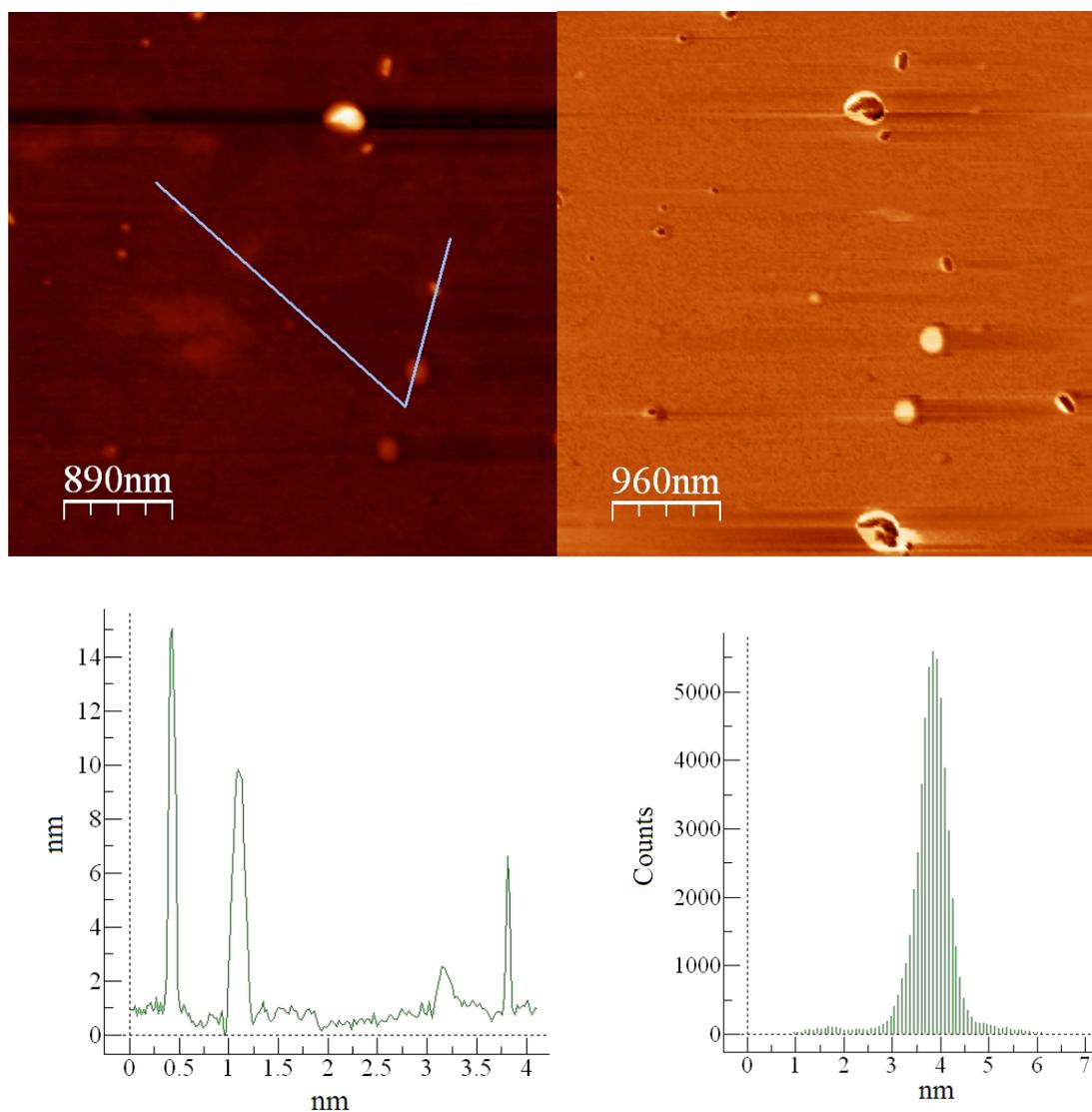


Figure S15. Films deposited from equimolar solutions of C_{70} and dimer **1H**, $10 \mu\text{M}$ each. Top: (left) height image, (right) friction image of the same area, Bottom: (left) height profile trace, (right) histogram of particle sizes; mean of $\sim 3.8 \text{ nm}$ corresponds to diameter of C_{70} complexed with two porphyrins $\sim 1.1 \text{ nm}$ for the C_{70} and $\sim 1.4 \text{ nm}$ for each porphyrin.

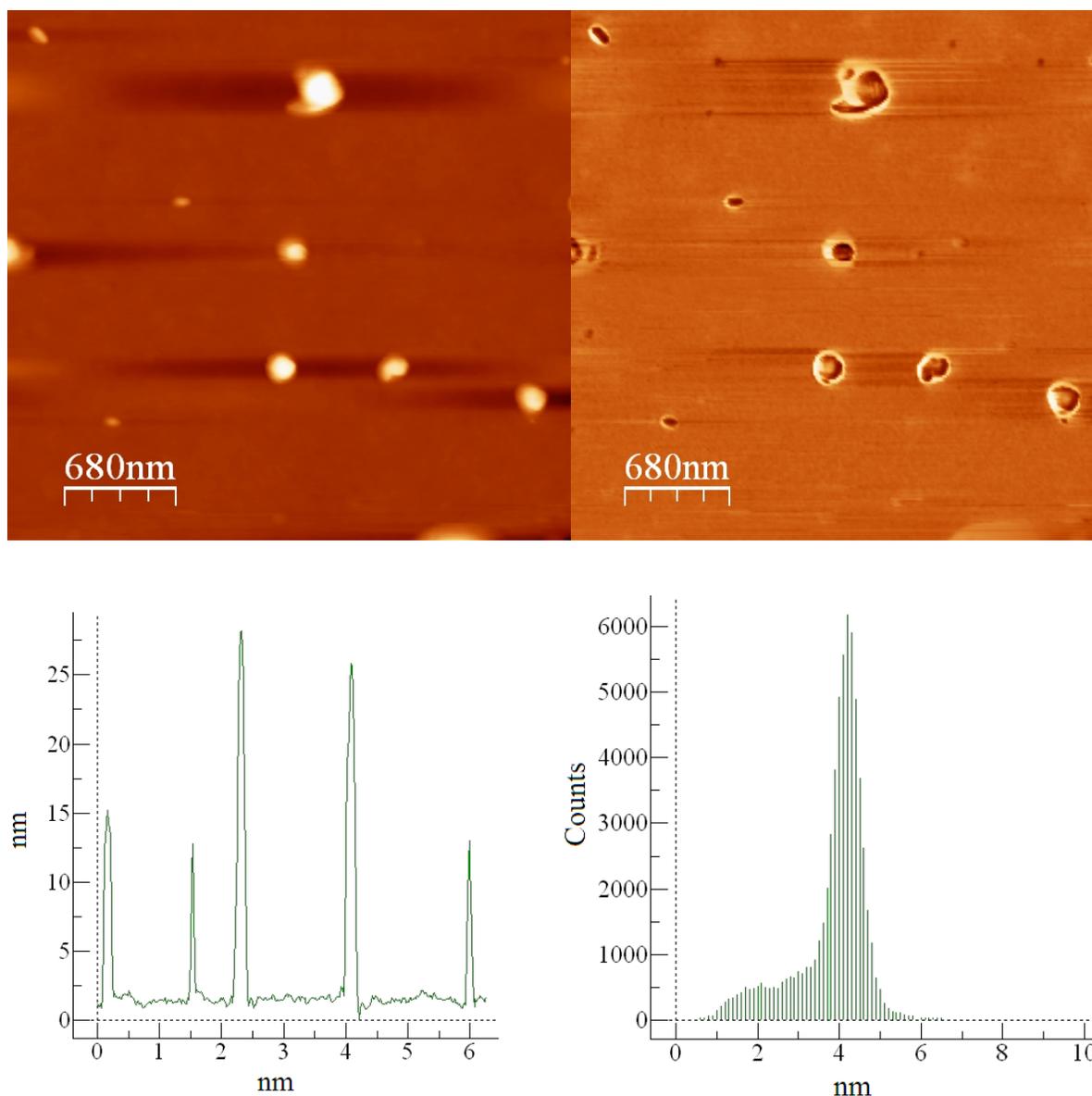
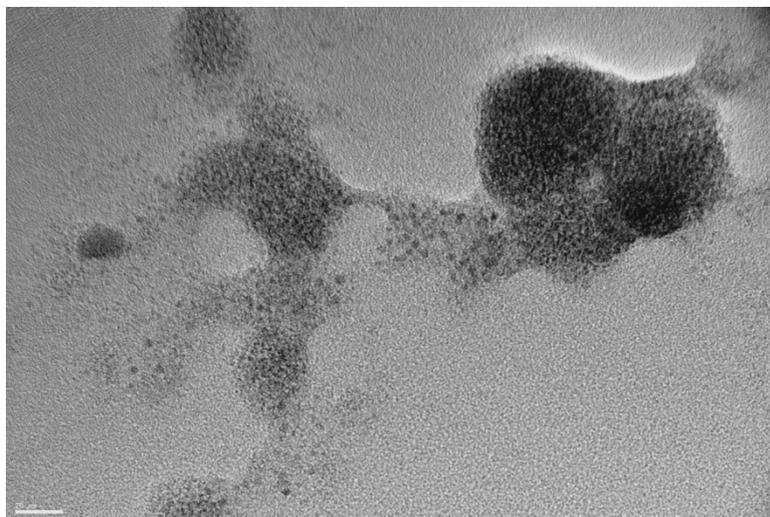


Figure S16. Films deposited from equimolar solutions of C_{70} and dimer **1Zn**, $10 \mu M$ each. Top: (left) height image showing a few large islands interspersed in the ~ 4 nm thick film, (right) friction image of the same area, Bottom: (left) height profile trace, (right) histogram of particle sizes in the films; a mean of ~ 4 nm corresponds to diameter of C_{70} complexed with two porphyrins.

TEM

All data were collected at 200 kV on a Jeol 2100 Transmission Electron Microscope equipped with EDAX at the eucentric height to ensure reproducibility of measurements. An $8 \mu L$ drop of the solution was placed on a 300 mesh carbon coated copper grid, (TED Pella Inc., Redding, California, USA), and allowed to dry for 1 minute. Since a carbon coated grid was used and carbon from C_{70} is present in the mixture, the Netcounts method (sample area minus control area)* (Jacopo Samson et al. *Nanomaterials* **2011**, *1*, 64-78) was not used so the x-ray scattered lines from the carbon coated copper grid and other

metals in the background, show up in the spectrum (indicated by the Cu and W peaks).



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Label A: Chlorite [Norm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28]

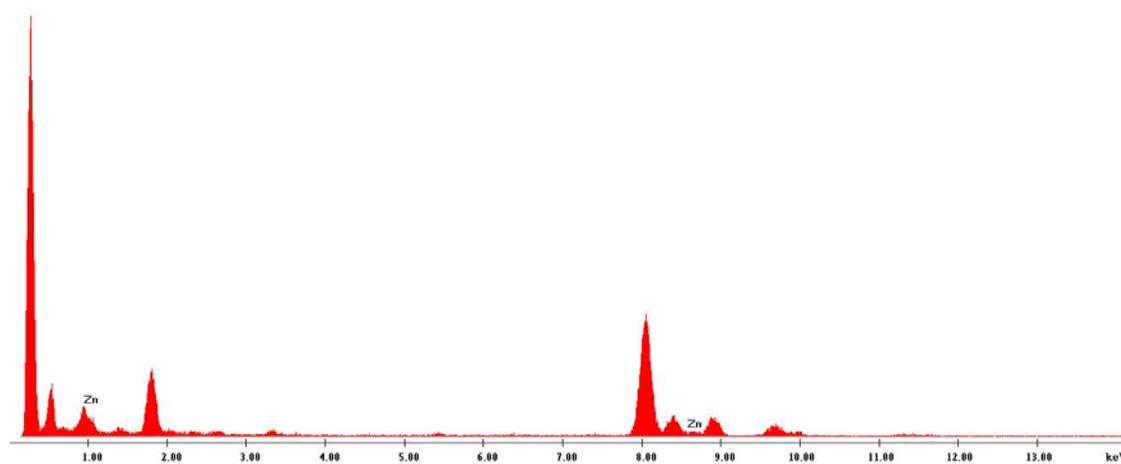
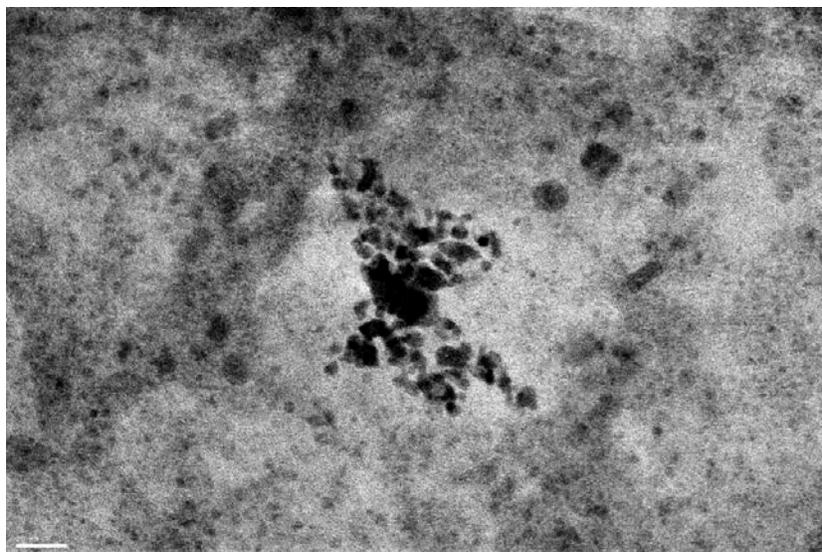


Figure S17. Top: Image from a solution of 10 μM **1Zn**. No larger aggregates were observed. The scale bar is 20 nm. Bottom: Corresponding EDAX spectrum with slight Zn signature from the metallic core of the porphyrin.



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Label A: Chlorite [Norm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.20]

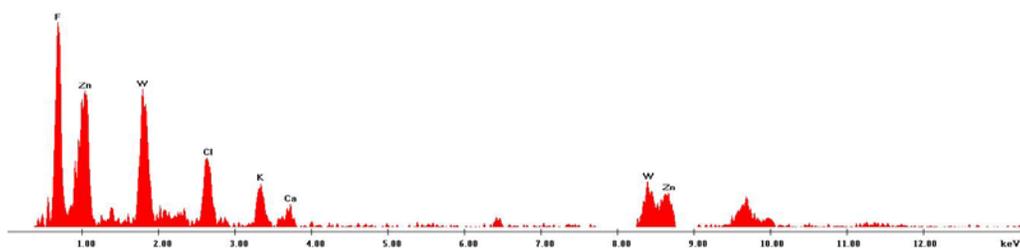


Figure S18. Top: Image from a mixture of fullerene and **1Zn**, 10 μ M in each. Aggregates were observed throughout the sample. The scale bar is 20 nm. Bottom: Corresponding EDAX spectrum with Zn signature from the metallic core of the porphyrin demonstrates that aggregates are not phase separated fullerene.

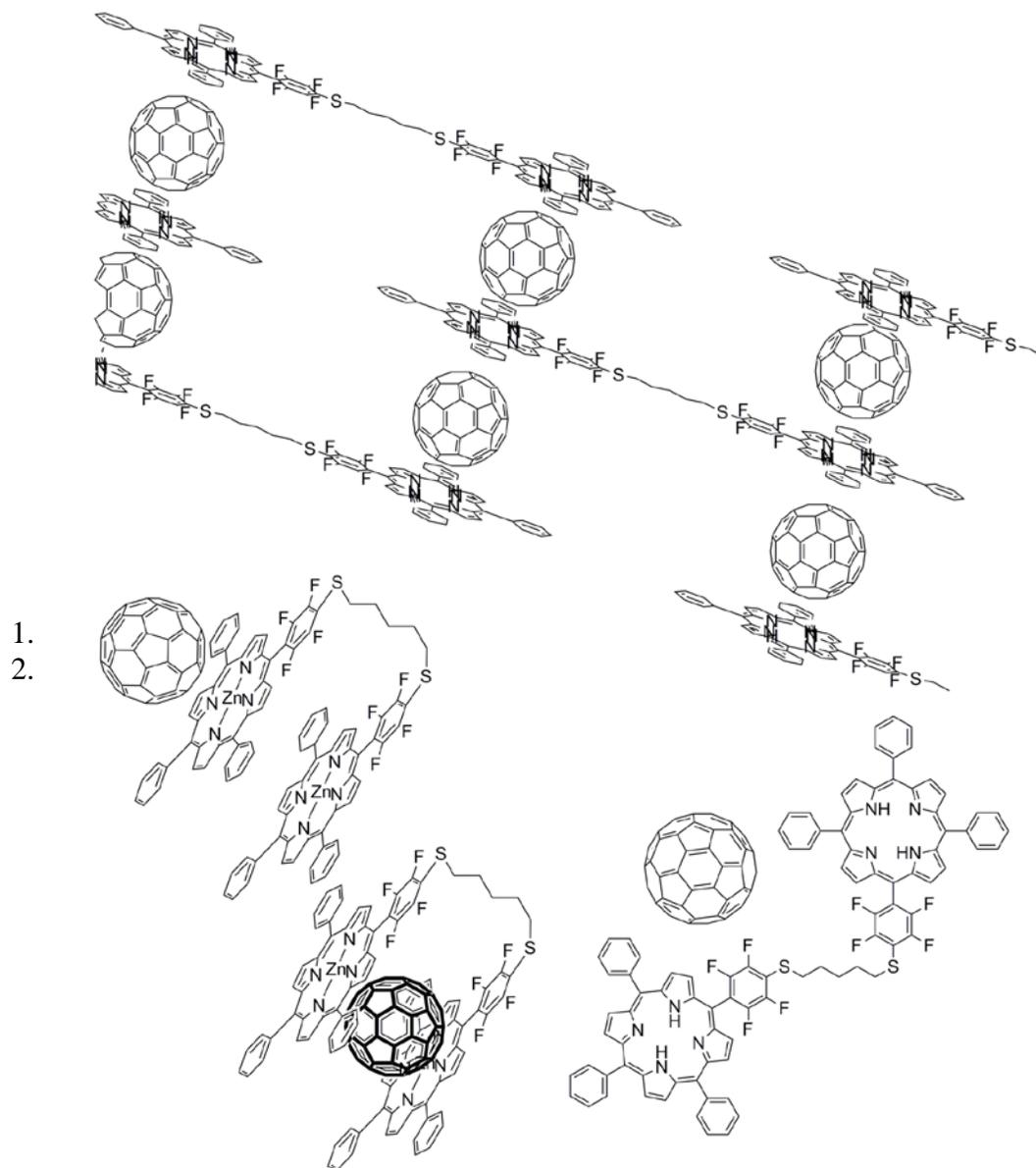


Figure S19. Possible supramolecular architectures of the fullerenes and the tethered dimer.