Self-organized nanostructures of alkylated phthalocyanines and underivitized C_{60} on ITO†

Alessandro Varotto,*[a] Matthew Jurow,[b] Viacheslav Manichev,[b] Nikolina A. Travlou,[b] Dimitrios A. Giannakoudakis,[b] and Charles Michael Drain[bc]

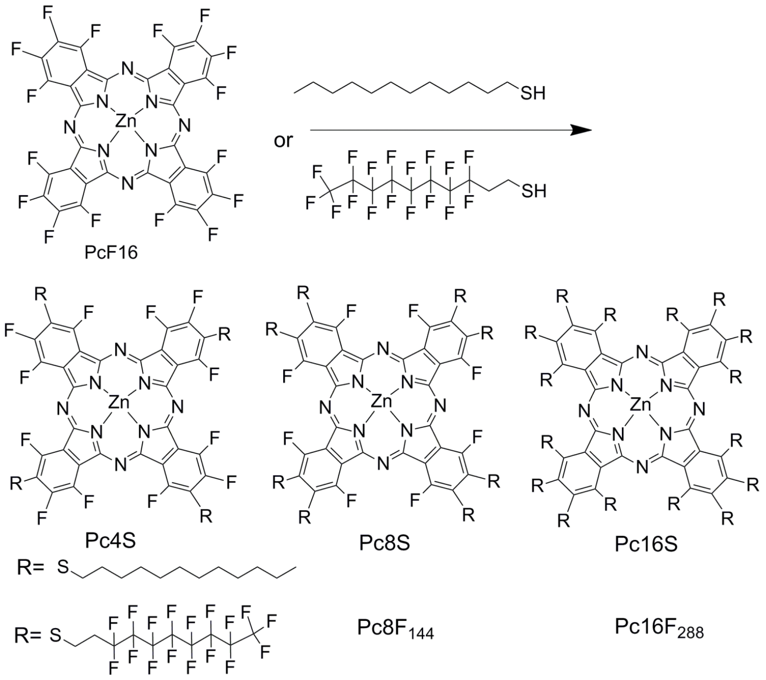
[a]Loyola Marymount University, LMU Drive, Los Angeles, California 90045
[b]Hunter College and Graduate Center of the City University of New York, 695 Park Avenue, New York, New York 10065 USA.
Fax: 212-772-5332; Tel: 212-650-3791; E-mail: cdrain@hunter.cuny.edu
[c] Rockefeller University, 1230 York Avenue, New York, New York 10065 USA

Materials, Methods

All solutions were prepared from freshly distilled solvents and/or nanopure water. Atomic force microscopy (AFM) measurements used a Nanoscope III Multi-mode (Veeco Metrology) for the hydrocarbon systems and an Agilent Series 5500 AFM/SPM for the fluorous Pc systems. UV-visible absorption spectroscopy used a Cary 1-Bio UV-Visible spectrometer. Steady state fluorescence spectra used a HORIBA Jobin-Yvon FluoroLog-3 fluorometer. Quartz or optical glass cuvettes were used for all spectroscopic studies. All photophysical studies were carried out in distilled solvents. MALDI MS were done as a service of the University of Illinois Urbana Champagne mass spectrometry facility. Fluorescence microscopy was carried out with a Nikon EFD-3 instrument at 400x magnicifation using a TEX-RED-HYQ band pass filter (608-683nm) and excited from 532-587nm.

Experiments have been repeated five times by three researchers independently.

Synthesis



Scheme S1. Synthesis of thioalkyl and fluorous alkyl Pcs, see below for procedures.

Hydrocarbons: The hydrocarbon derivatives were prepared by similar procedures previously reported and the spectroscopic data (NMR, MS, optical) are consistent with those published.[1]

Pc4S. To a stirring solution of 15 mL of freshly distilled THF under Ar was added ZnPcF16 (50 mg, 0.0576 mmol), dodecanethiol (1.69 mL, 8.2 mmol) and potassium carbonate (50 mg) and the solution was stirred at room temperature for 24 hours. Reaction was mixture was poured into separatory funnel and washed with water, extracted into dichloromethane, and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula $C_{80}H_{100}F_{12}N_8S_4Zn$, MALDI-MS calculated 1595.32, found: 1594.94 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 707 nm,

Pc8S. To 15 mL of freshly distilled THF under Ar for 10 was added ZnPcF16 (50 mg, 0.0576 mmol), dodecanethiol (1.69 mL, 8.2 mmol) and potassium carbonate (50 mg). The solution was stirred at reflux for 8 hours and monitored by UV-visible spectroscopy to determine the degree of substitution. The crude reaction mixture was then was washed with water, extracted into dichloromethane and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula, $C_{128}H_{200}F_8N_8S_8Zn$, MALDI-MS m/z calculated 2324.89, found: 2325.89 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 737 nm.

Pc16S was prepared by adding dodecanethiol (3.5 mL, 0.013 mol) to 40 mL of diglyme under Ar. To this mixture was added 300 mg of metallic Na and the solution was stirred until complete dissolution of the sodium. ZnPc F_{16} (25 mg, 0.029 mmol) was added at room temperature and the solution was stirred for 16 hours at 100 C. The solution was cooled to room temperature and poured into 300 mL of water. The product was extracted with diethyl ether (3x20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Silica gel chromatography with hexane followed by hexane/ethyl acetate 30:1 (v/v) yielded 0.050 g (0.013 mmol, 44%) of a dark olive green wax. MALDI-HRMS calculated for $C_{224}H_{400}N_8S_{16}Zn$ m/z 3784.0764 found 3783.6540. λ_{max} in CH_2Cl_2 787 nm.

Fluorocarbons

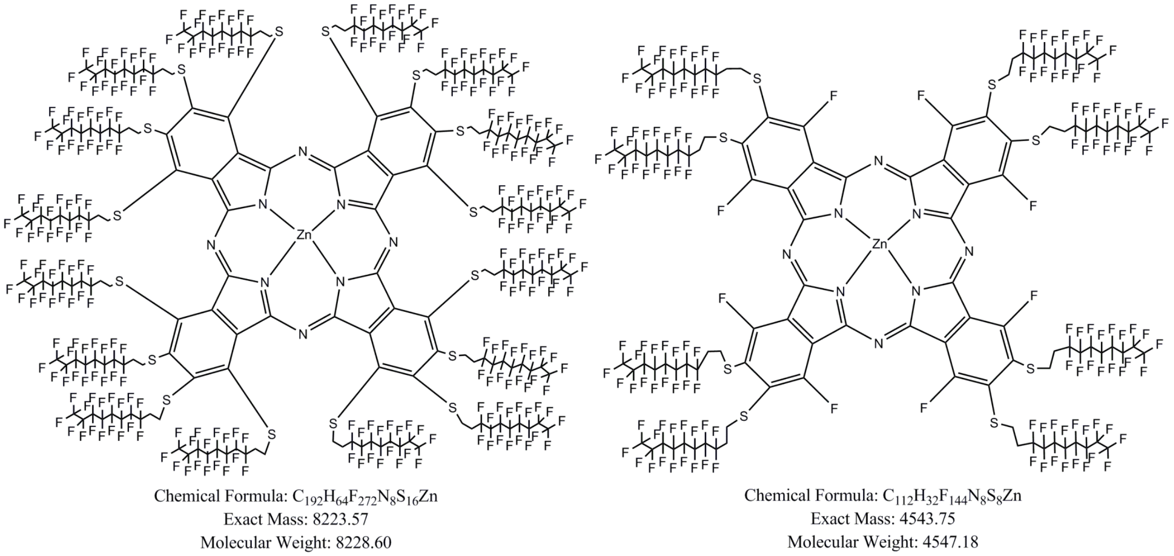


Fig S1. ZnPc with fluorous alkanes.

ZnPcS8F$_{144}$

ZnPcF$_{16}$ (50 mg, 0.057 mmol) was added to 20 mL of DMF under nitrogen. To this mixture was added 10 equivalents of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorodecane-1-thiol (0.165 mL, 0.578 mmol) and K_2CO_3 (15 mg, 0.109 mmol). The solution was stirred for 15 hours at 60 C. The product was isolated by precipitating with 50 mL of methanol followed by vacuum filtration. Dark green crystals were washed with additional 50 mL of methanol, 200 mL of hot water, 50 mL of acetone, and dried in oven at 200 C for 10 minutes. MALDI HRMS: for chemical formula $C_{112}H_{32}F_{144}N_8S_8Zn$, calcd. exact mass 4543.75, found +H^+ m/z 4544.99. UV-visible in CCl_4 λ_{max}: 664 nm, sh 721

ZnPc16F$_{272}$

ZnPcF$_{16}$ (50 mg, 0.057 mmol) was added to 19 mL of DMF under nitrogen. To this mixture was added 100 equivalents of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorodecane-1-thiol (1.65 mL, 5.78 mmol) and K_2CO_3 (50 mg, 1.09 mmol). The solution was refluxed for 24 hours. The product was isolated by precipitating with 50 mL of methanol followed by vacuum filtration. Dark green crystals were washed with additional 50 mL of methanol, 200 mL of hot water, 50 mL of acetone, and dried in oven at 200 C for 10 minutes. MALDI MS: $C_{192}H_{64}F_{272}N_8S_{16}Zn$, calcd. 8228.6, found 7228.7. UV-visible in CCl_4 λ_{max} (nm): 743, 599, 527, 405 and 353

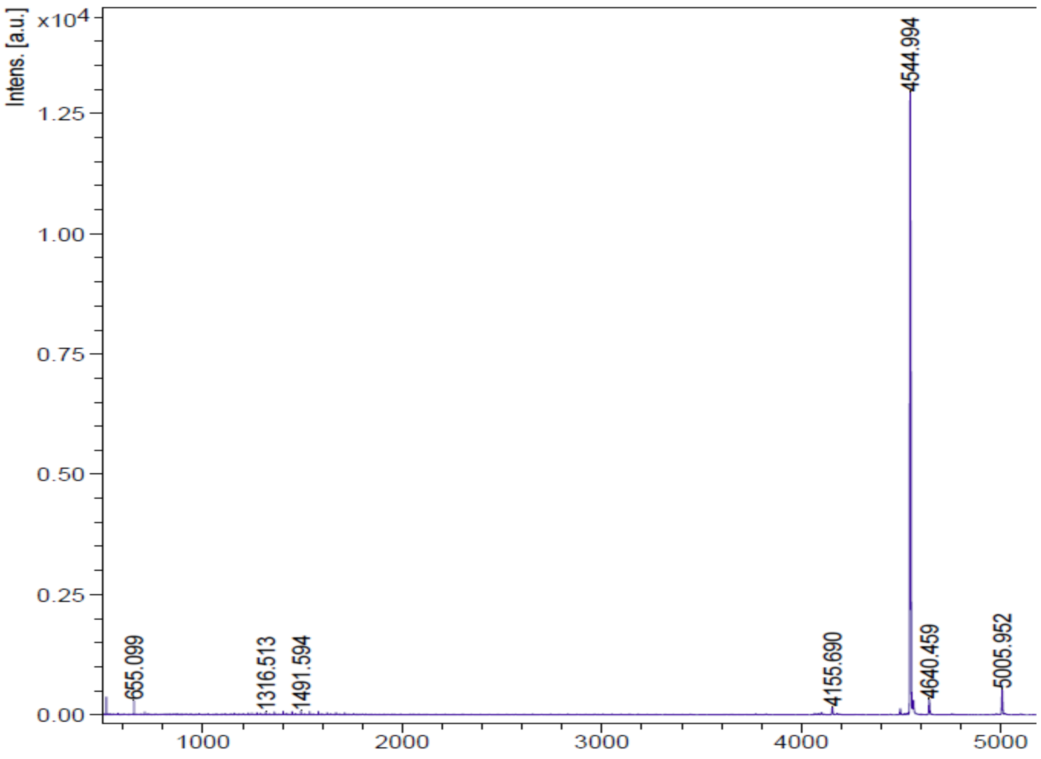


Figure S2. MALDI MS spectrum of Pc8SF$_{144}$.

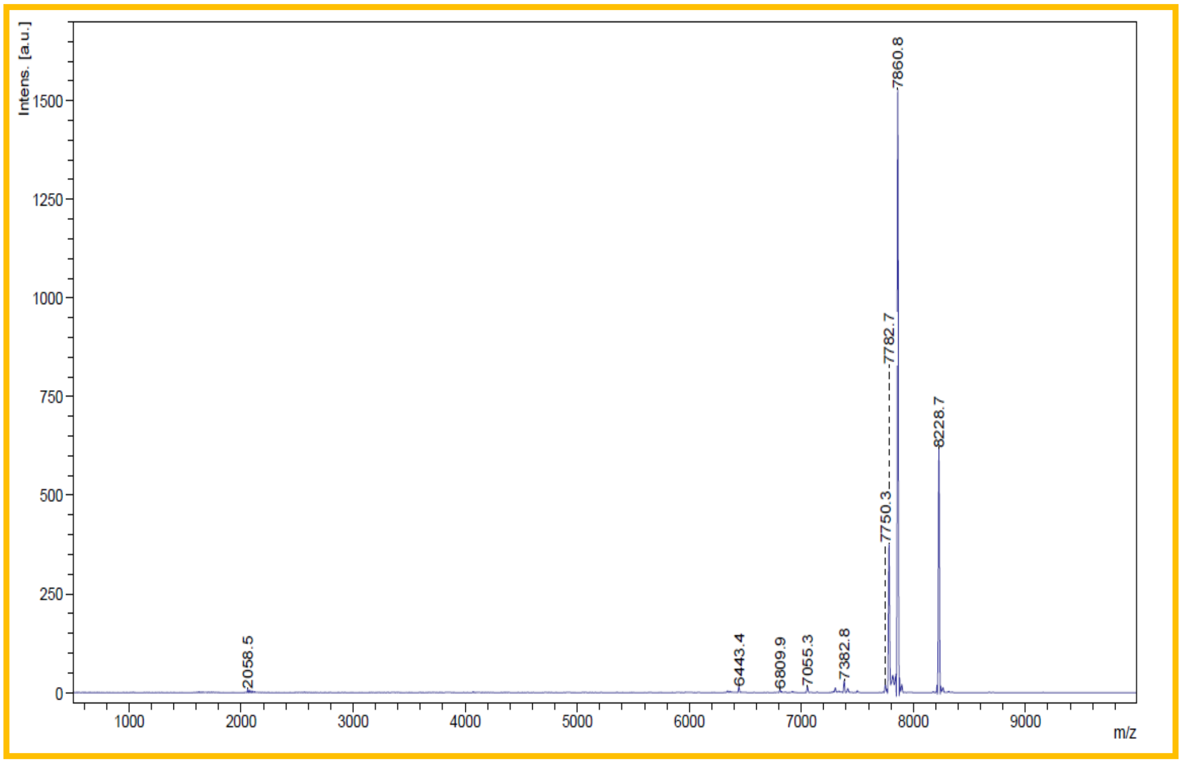


Figure S3. MALDI MS spectrum of Pc8SF$_{272}$

Solution studies

Neither UV-visible nor fluorescence indicate that there are significant interactions between the hydrocarbon Pc dyes and the C_{60} in solution at ca. 10 µM concentrations. UV-visible and fluorescence studies of the hydrocarbon Pc titrated with C_{60} do not indicate substantial interactions in solution when the concentration is less than ca. 50 µM, but at greater concentrations these experiments are complicated by the solubility of the two components wherein the aggregation of the dye and C_{60} is convolved with (or masks) any interactions between the two. Thus, at the ca. 200 µM concentrations used for deposition DLS and UV-visible both indicate that there are is a wide distribution of aggregate sizes in solution but there is no obvious correlation with the observed narrowly dispersed sizes seen in the depositions. DLS of the fluorous Pc is consistent with the UV-visible spectra that indicate large aggregates due to the minimal solubility of these highly fluorinated compounds in organic solvents.

Surface Characterization

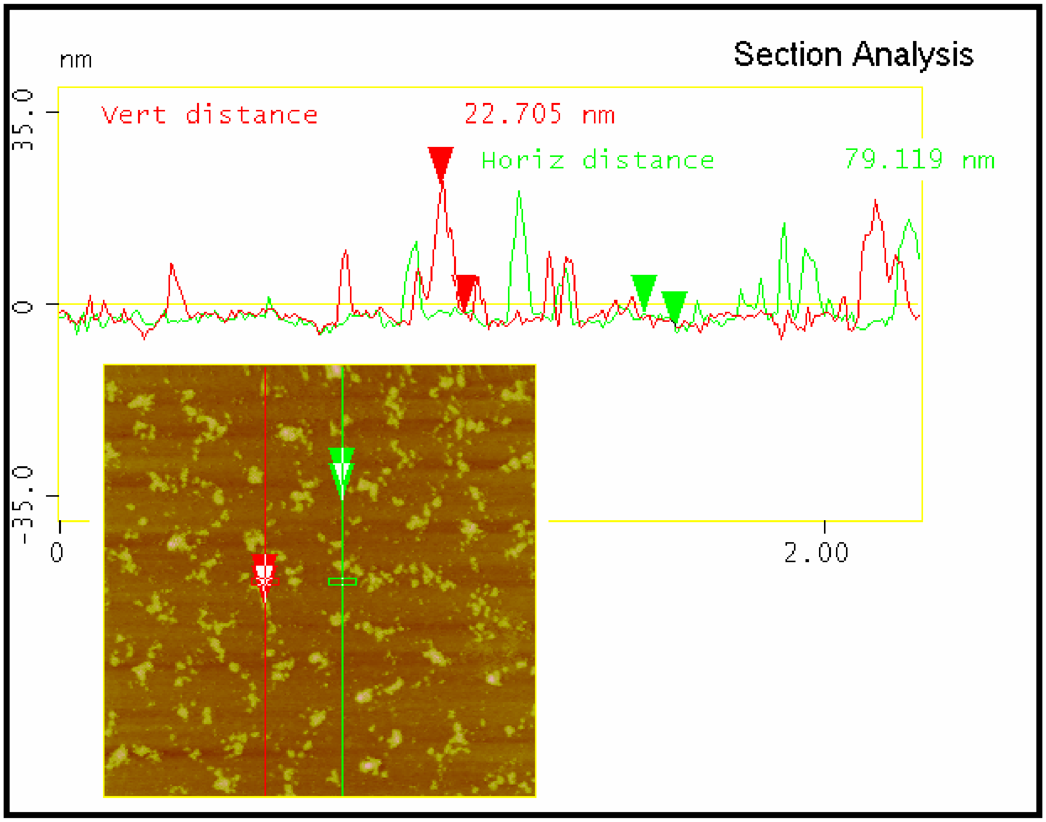


Figure S4. AFM image of the less uniform aggregates formed by dipping ITO slides into Pc8S solution.

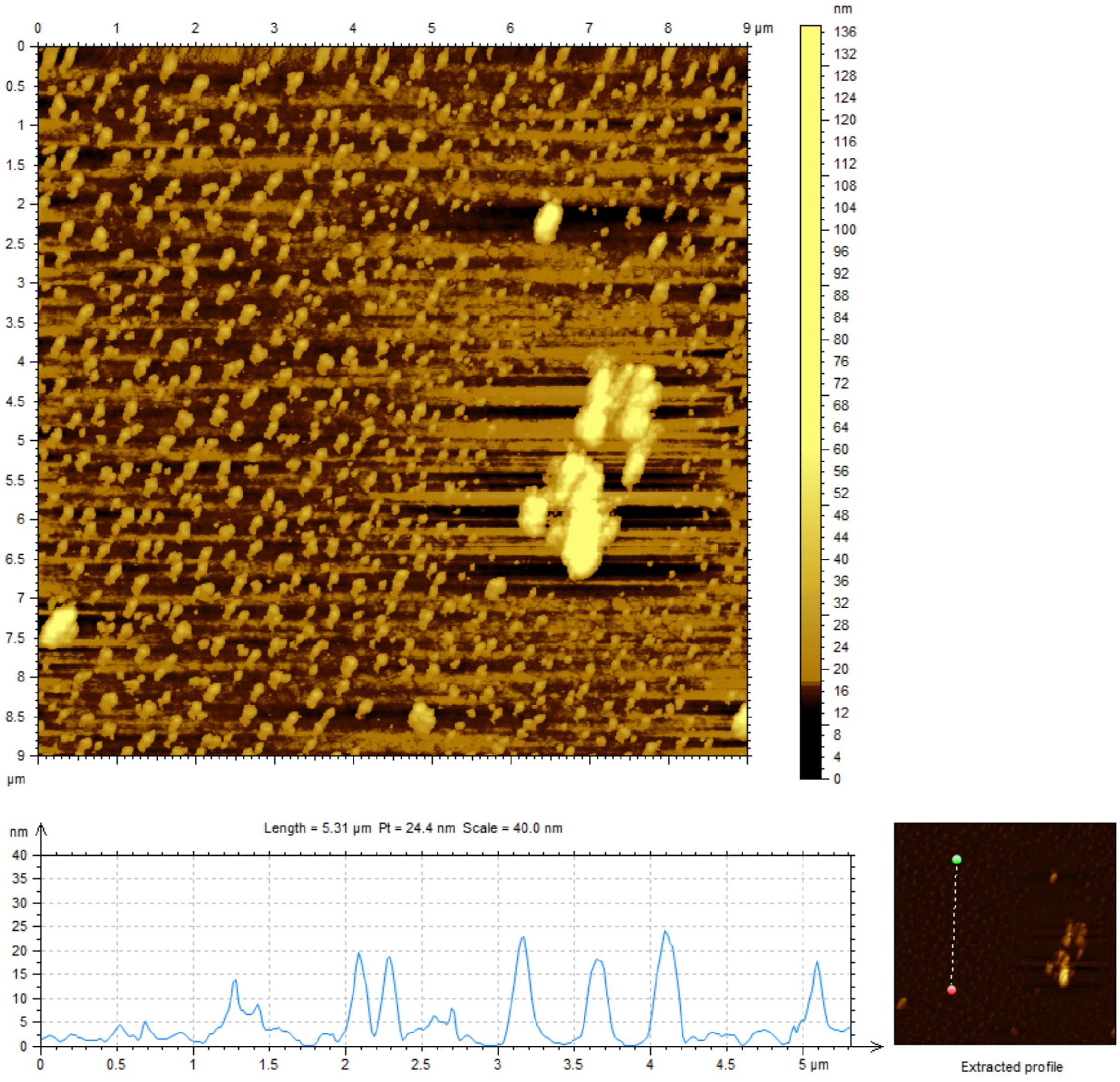


Figure S5. AFM image with height profile of aggregates formed from soaking the ITO slide in a 4.5 mM C_{60} solution in toluene for 60 min.

Optical Spectroscopy

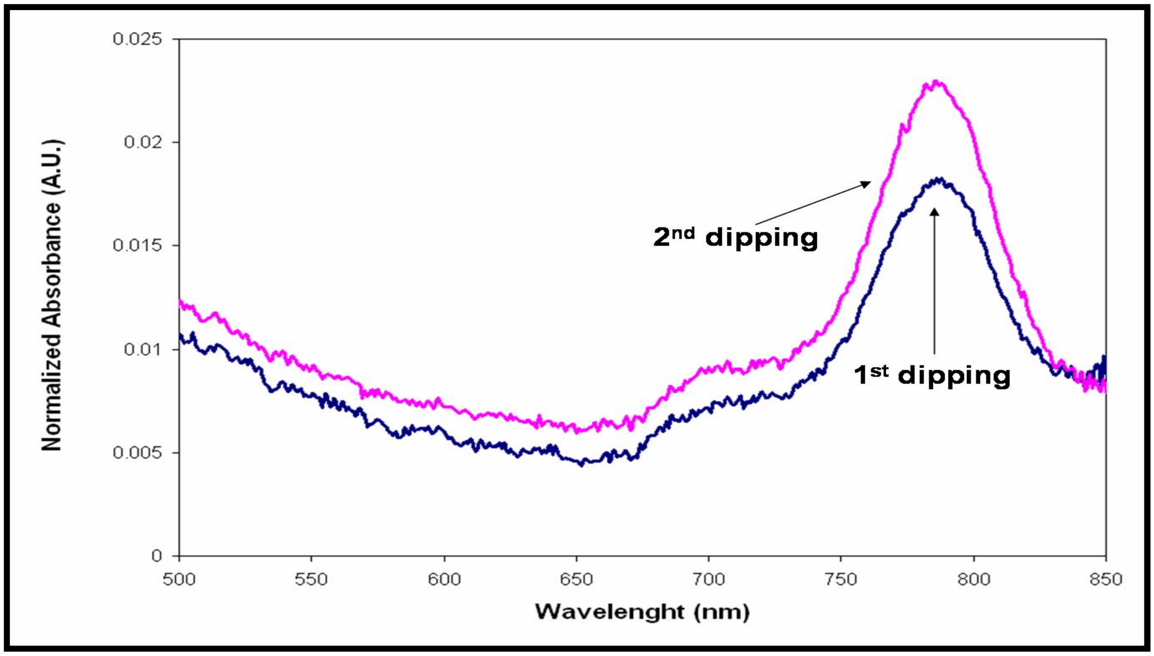


Figure S6. UV-Vis absorption spectra of Pc16S on ITO electrode after 1 and 2 immersions of 1 hour each in toluene solution of Pc16S (0.3 M). Absorption maxima correspond to the Q band of Pc16S.

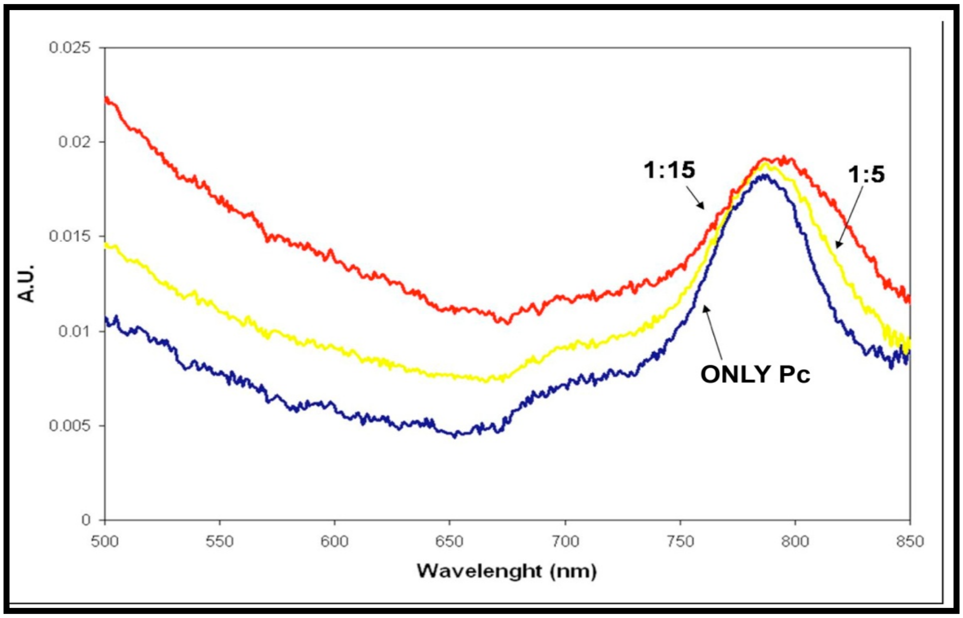


Figure S7. UV-visible spectra of a Pc16S film and Pc16S blends with C_{60} at different mole ratios on ITO.

Optimization Studies

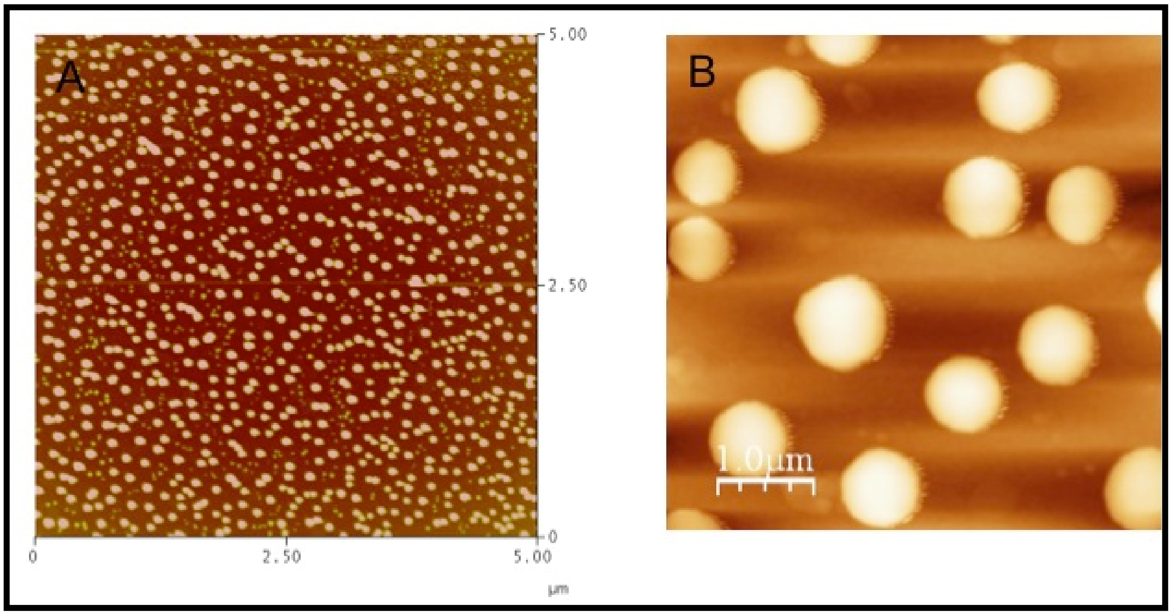


Figure S8. AFM images of nanoparticles formed from Pc16S/C_{60} in ratio 1:15 at different concentration of Pc: (A) [Pc] = 0.1 mM, where the average nanoparticle height is 60 nm and width is 40 nm, (B) [Pc] = 0.3 mM, average nanoparticle height 130 nm, average width 800 nm.

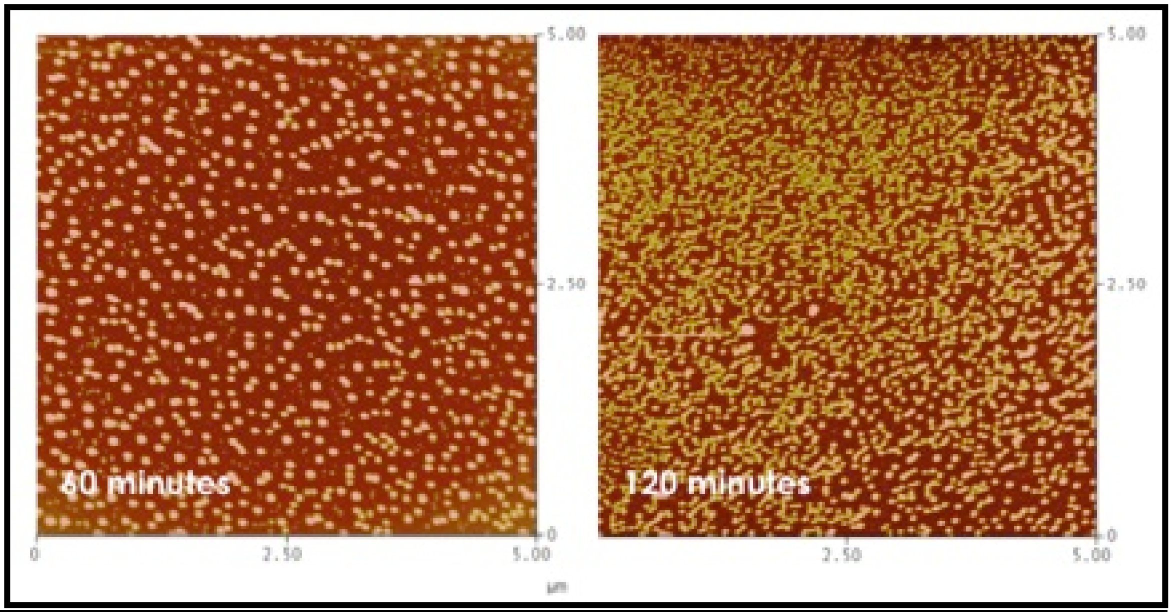


Figure S9. AFM images of nanoparticles formed from Pc16S/C_{60} ratio 1:15, [Pc] = 0.1 mM, after 60 and 120 minutes of soaking in solution.

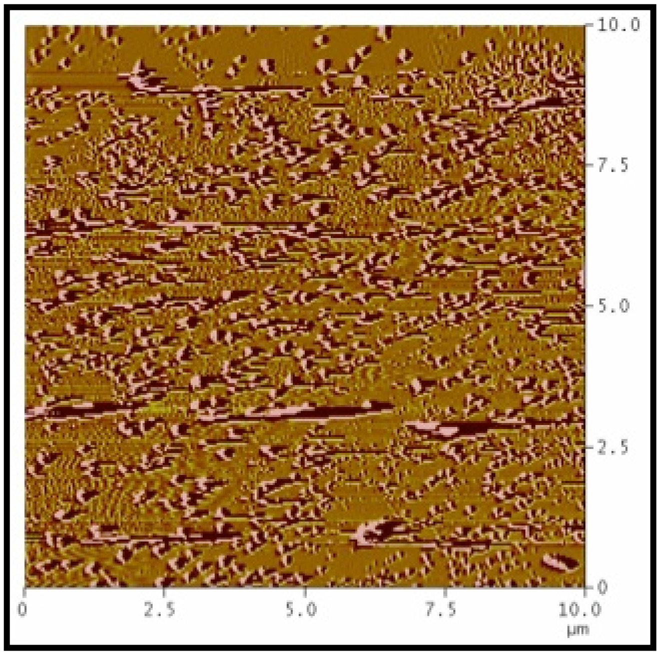


Figure S10. AFM image (amplitude, tapping mode) of particles formed by dipping the ITO first in a solution of Pc16S and then in a solution of fullerene C_{60}.

Fluorous ZnPc

Sample Preparation. ITO slides were cleaned in ozone stream for 20 minutes. Clean ITO slides were soaked in dye solutions for 1 hour, rinsed with clean toluene, and dried at room temperature. Three solutions were prepared: 0.3uM $ZnPcF_{144}$ control, 4.5 mM C_{60} control, and 1:15 ratio of $ZnPcF_{144}$ to C_{60}.

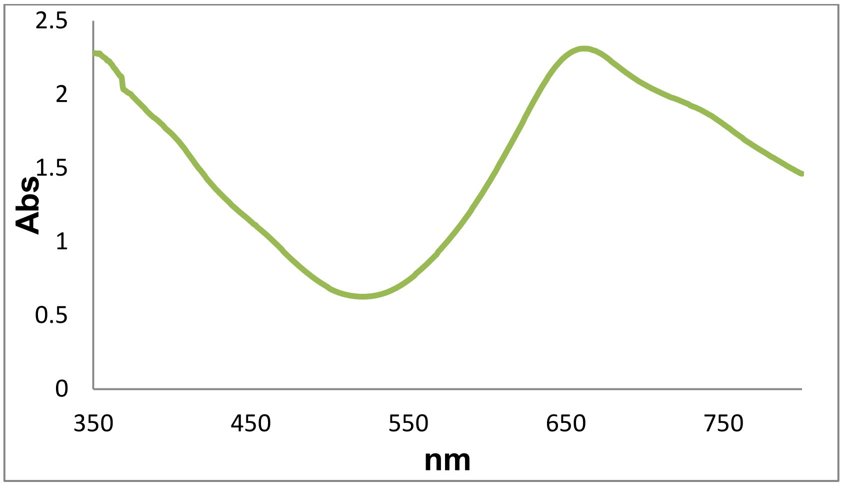


Figure S11. UV-visible spectra of a saturated solution of $ZnPc8SF_{144}$ in CCl_4; λ_{max} is at 664 nm, shoulder 721 nm. This shows substantial aggregation of the poorly soluble dye.

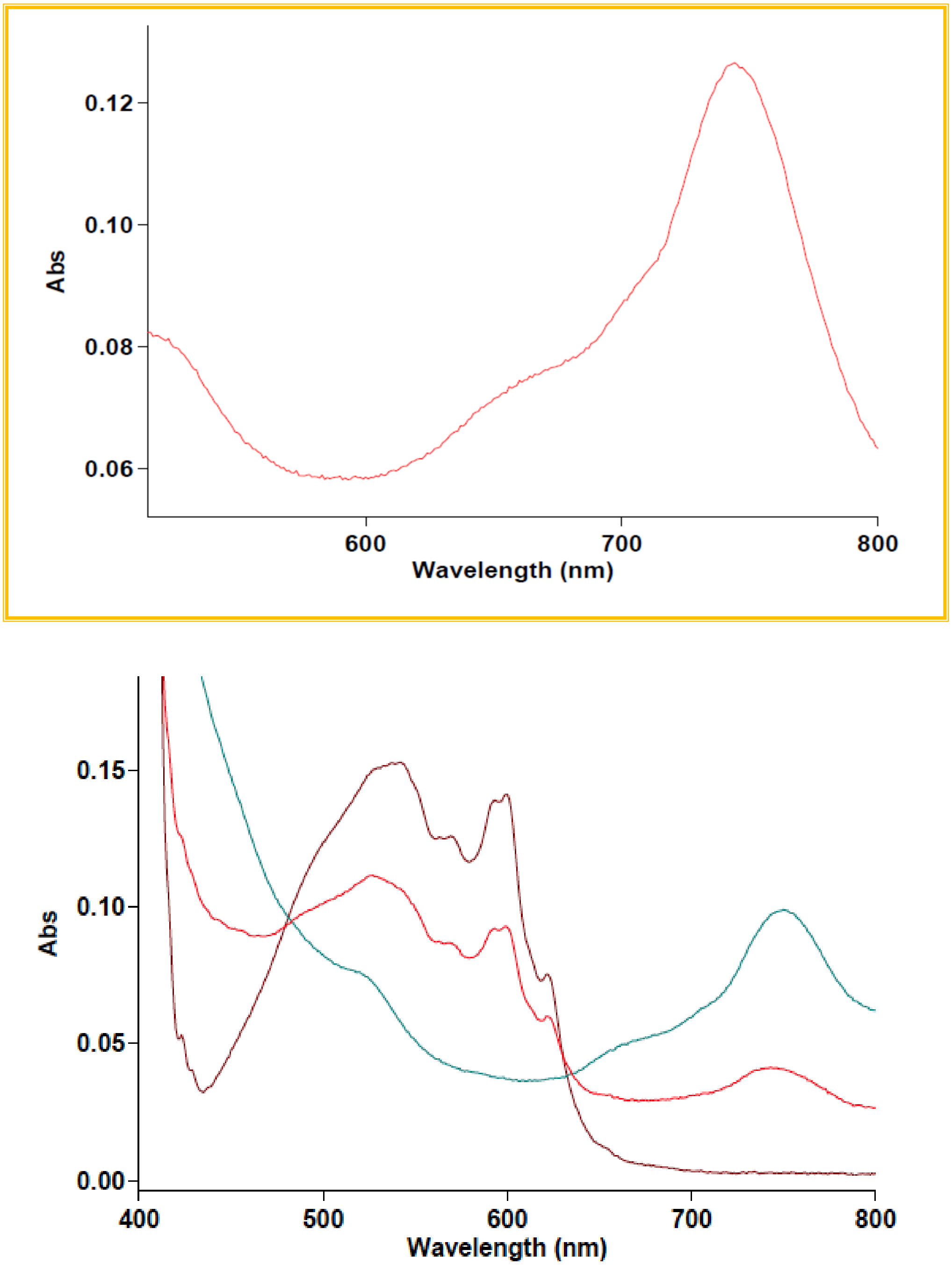


Figure S12. Top: UV-visible spectra of ZnPc16F$_{272}$ in CCl$_4$; λ_{max} 743 nm. Bottom: UV-visible spectra of Blue line: ZnPc16F$_{272}$ in CCl$_4$ 150 µM (λ_{max} 750nm); Brown line: C$_{60}$ in CCl$_4$ 150 µM (λ_{max} 600, 54 2nm); Red line: mixture of C$_{60}$ and Pc in ratio (1:1) in CCl$_4$ 150 µM shows that there is little interaction between the fluorous dye and the C$_{60}$.

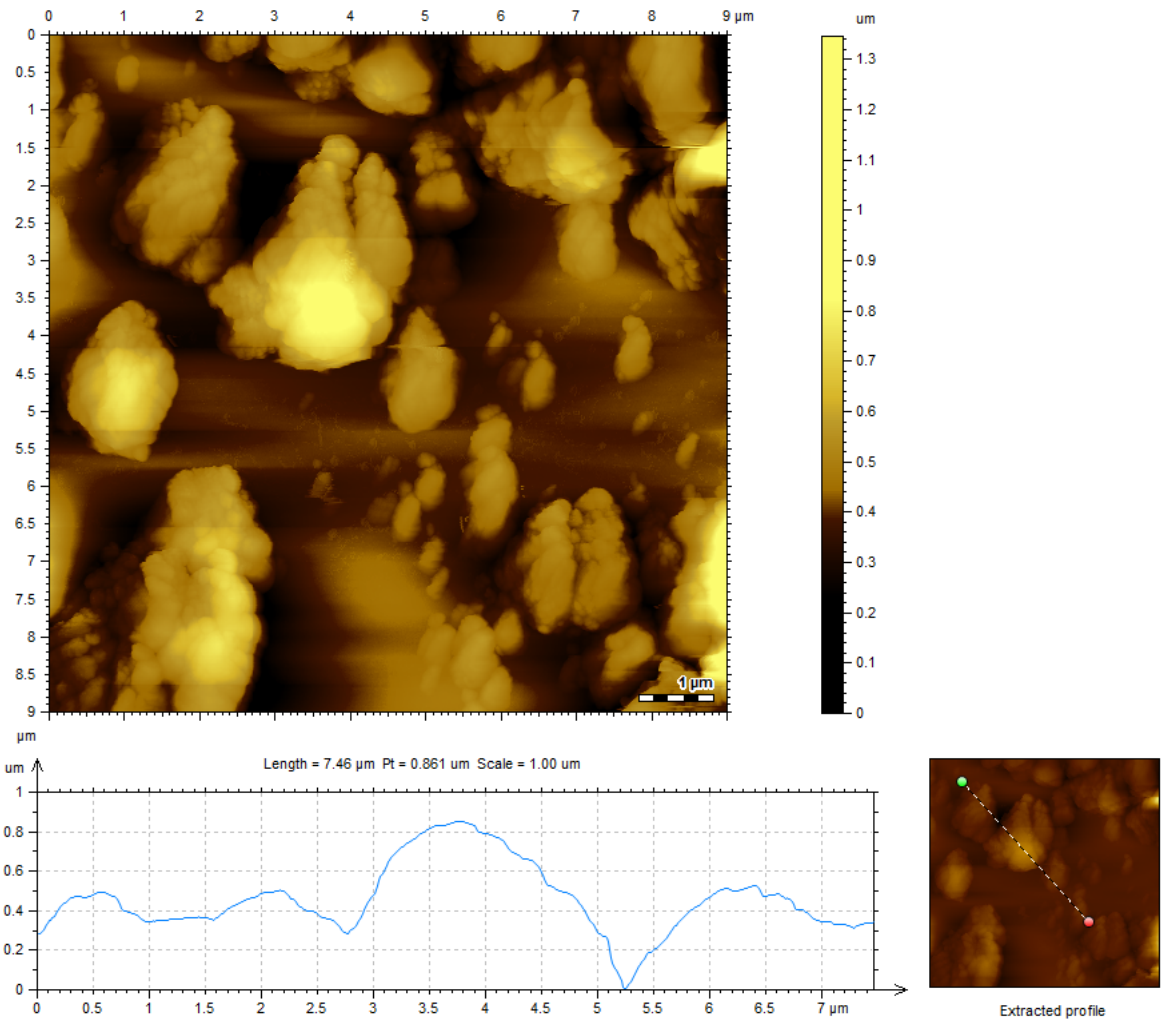


Figure S13. AFM image with height profile. Clean ITO slide was soaked in a 0.3 mM Pc8SF solution in toluene for 1 h and allowed to dry. A ca. 400 nm thick film formed with large islands of aggregates.

Fluorescence Microscopy

Ozone cleaned ITO slides were soaked in 0.3 µM solutions of Pc-8SF144, C_{60}, a mixture of both (1:5 m/m), or a mixture of both (1:15 m/m) for one hour. Pc-16SF288 samples were drop cast from THF due to poor solubility. Slides were then allowed to dry in air, coated in lens immersion oil and placed under microscope. Images were taken with 8 second integration time.

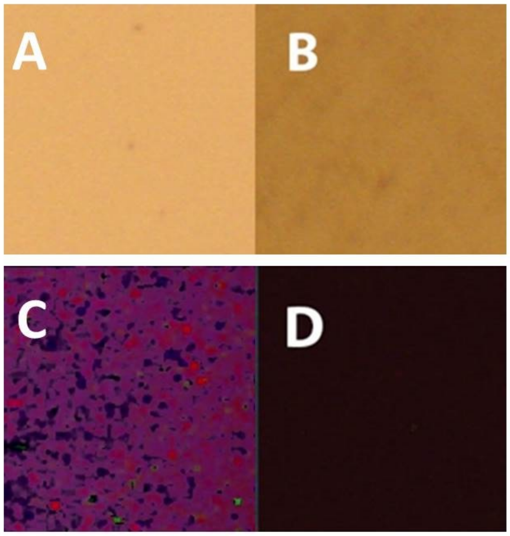


Figure 14. Optical and fluorescence microscope images (each panel 100 µM x 100 µM). (A) Bright field image of a film of $ZnPc16SF_{288}$; (B) Bright field image of a film of 1:1 $ZnPc16SF_{288}$:C_{60}; (C) fluorescence image of panel A; (D) fluorescence image of panel B. this shows that the fluorescence of the Pc dye is quenched due to electron transfer to the fullerene.

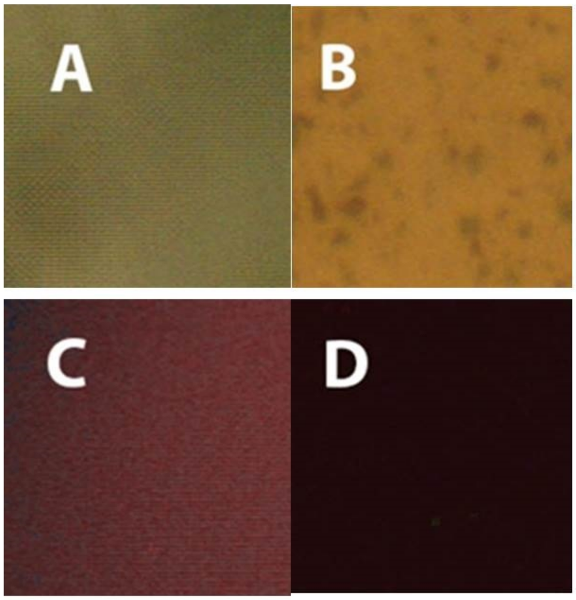


Figure 15. Bright field and fluorescence microscope images (each panel 100 µM x 100 µM). (A) Bright field image of a film of $ZnPc8SF_{144}$; (B) Bright field image of a film of 1:5 $ZnPc8SF_{144}$:C_{60}; (C) fluorescence image of panel A; (D) fluorescence image of panel B. Fluorescence is quenched upon addition of the fullerene.

References

(1) Varotto, A.; Nam, C.-Y.; Radivojevic, I.; P. C. Tomé, J.; Cavaleiro, J. A. S.; Black, C. T.; Drain, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 2552.