

## Electronic Supporting Information

# Self-Organization of Zr(IV) Porphyrinoids on Graphene Oxide Surfaces by Axial Metal Coordination

Matthew Jurow,<sup>a</sup> Viacheslav Manichev,<sup>‡a</sup> Cesar Pabon,<sup>‡a</sup> Brian Hageman,<sup>a</sup> Yuliya Matolina,<sup>a</sup> Charles Michael Drain<sup>a,b\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, Hunter College of the City University of New York. Fax: 212-772-5332; Tel: 212-650-3791; E-mail: cdrain@hunter.cuny.edu

<sup>b</sup>Rockefeller University, 1230 York Avenue, New York, New York 10065 USA

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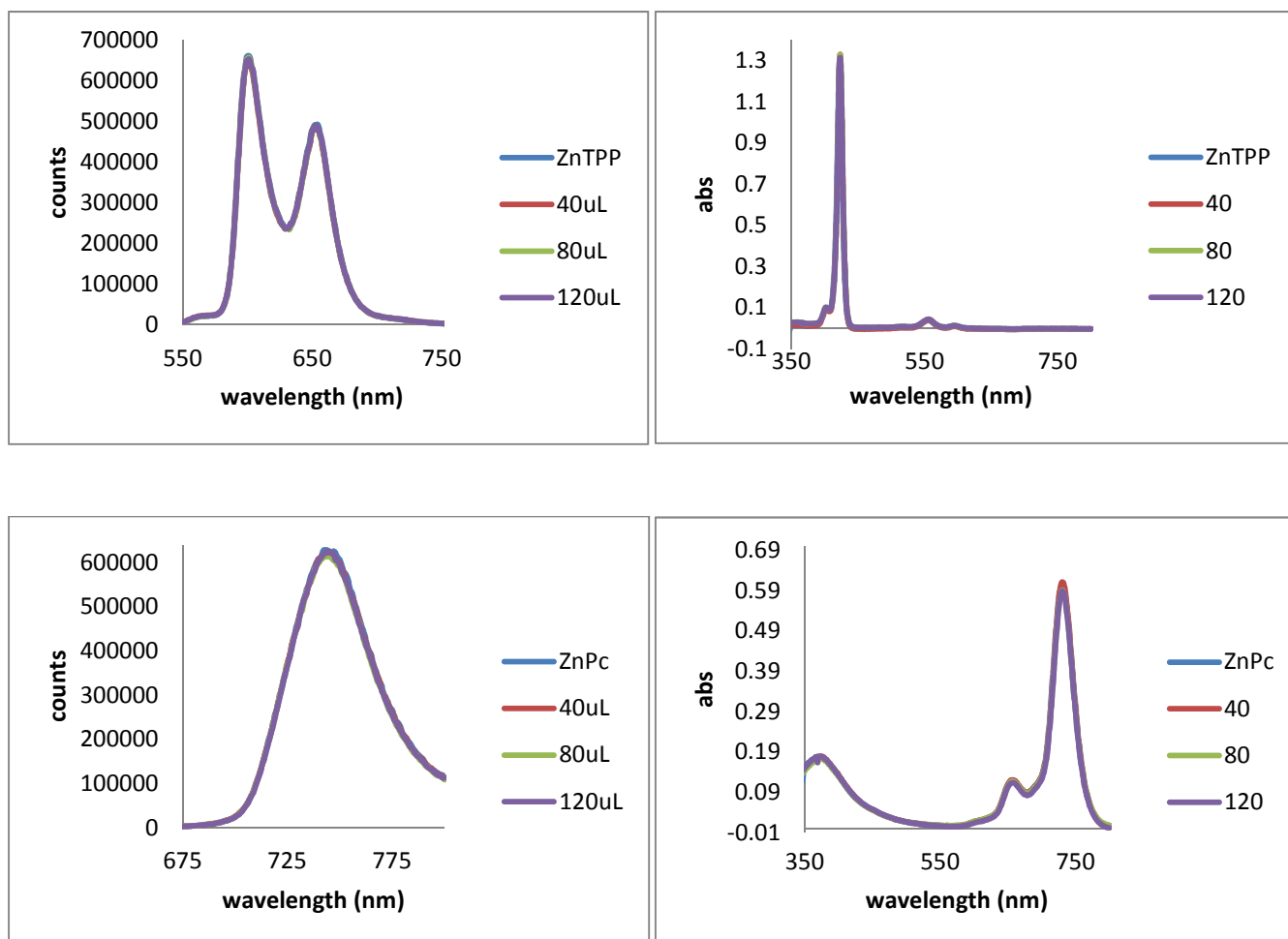
**Porphyrimoids on graphitic materials.** Large, aromatic porphyrimoids adsorbed onto graphene display interesting photonic properties because of the electronic coupling of the dye to the graphene.<sup>1</sup> Fluorescence quenching of dye films by GO is reported.<sup>2</sup> Here Zr<sup>IV</sup>(Pc)(ac)<sub>2</sub> and Zr<sup>IV</sup>(TPP)(ac)<sub>2</sub> are reacted with the oxygen functional groups on the edges and planes of GO to yield hybrid materials denoted Zr<sup>IV</sup>(Pc)/GO and Zr<sup>IV</sup>(TPP)/GO.

**Graphene Oxide.** The structure and physical chemical properties of graphene oxide (GO) and defects in graphene have been studied by a variety of methods,<sup>3,4</sup> including STM,<sup>5</sup> Characterization of reduced GO is reported,<sup>6</sup> including the tunable luminescence properties.<sup>7</sup> GO material was purchased from Graphene Supermarket. Briefly: >60% single layer, flakes 0.5-5 microns, 20% oxygen (w/w). For full characterization see supplier web-site: <http://graphene-supermarket.com/images/P/Graphene%20Oxide-Data-Sheet-Graphene-Supermarket.pdf>

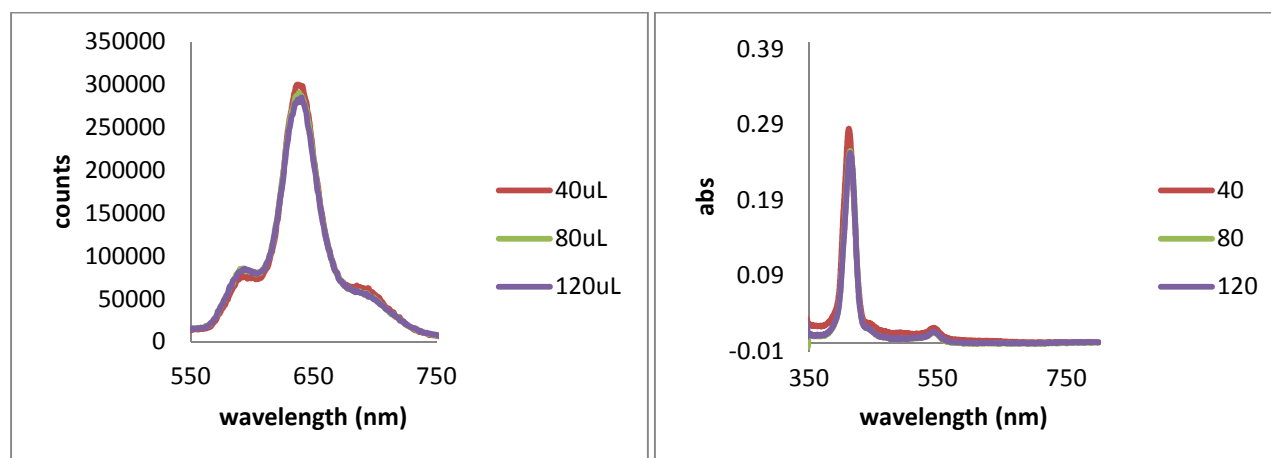
**Contributions.** M. Jurow: Initial solution phase and solid state experiments, all experimental procedures, supervision of optical spectroscopy, AFM and TEM, initial manuscript preparation and refinement, interpretation of data, organization of overall effort. V. Manichev: preparation of GO and dye solutions, preparation and AFM imaging of films, initial preparation of manuscript. C. Pabon: formation and optical characterization of layer-by-layer films, initial manuscript preparation. B. Hageman: optical spectroscopy of solutions and films, some AFM studies, general strategy for experimental design. Y. Matolina: verification and duplication of procedures for statistical validation of results. C.M. Drain: overall concept of group (IV) dyes on oxide surfaces, MM2 calculations, chemical schemes of dyes on GO (Fig. 2), model and scheme of layer-by-layer films (Fig 6), data selection, refinement, and interpretation, final preparation of manuscript.

### Titration

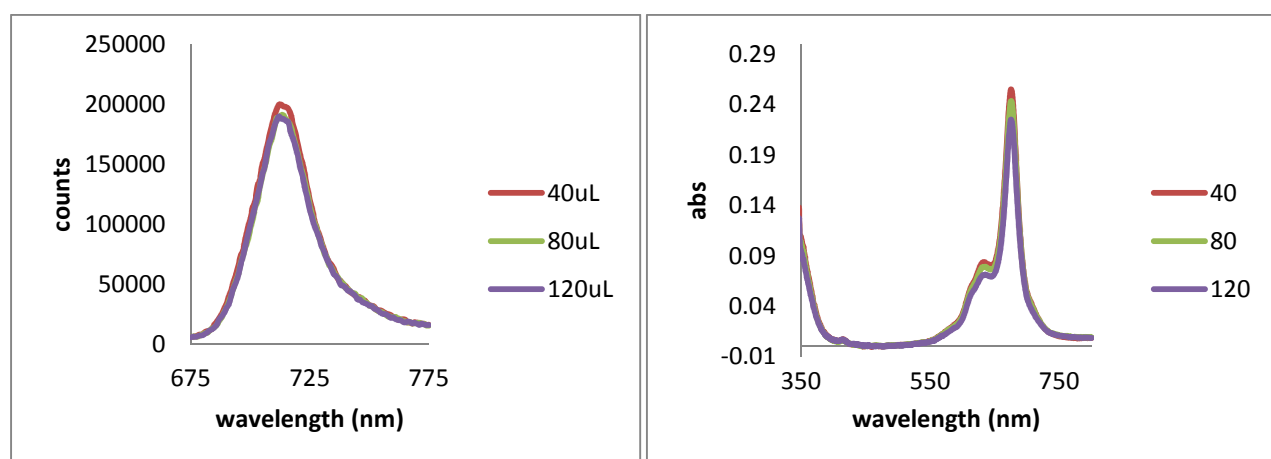
The addition of the GO dispersion or benzoic acid produces an immediate increase in fluorescence intensity of the  $Zr^{IV}(Pc)$  and  $Zr^{IV}(TPP)$  species (excited at their absorption maxima, Figure S4, S5) because of the disaggregation of pi stacked dye molecules. Once sample are allowed to equilibrate for >24 hours fluorescence intensity decreases to values displayed in Figures S1, S2 and S3.



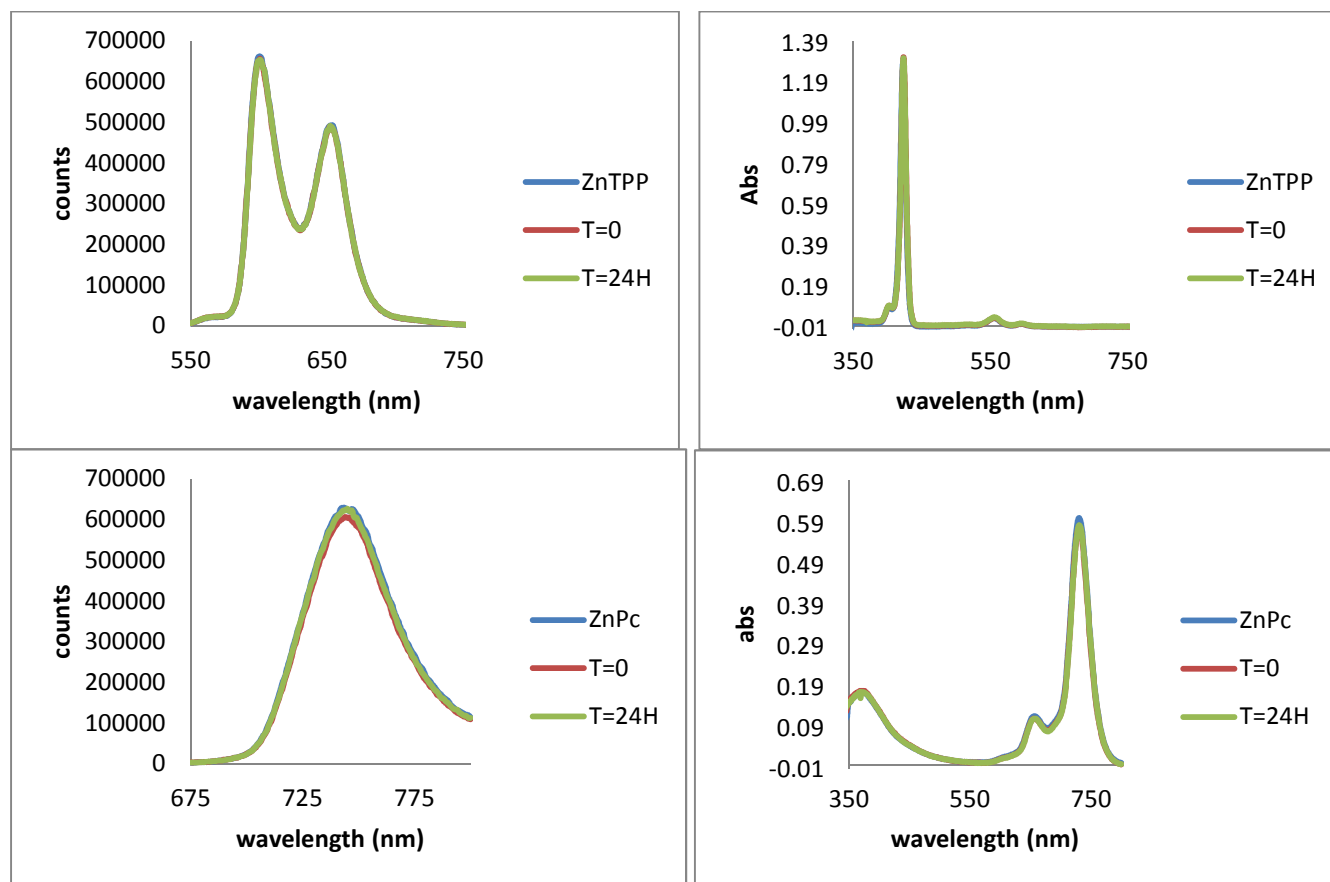
**Figure S1.** Fluorescence spectra (left) and UV-Visible spectra (right) of Top: ZnTPP (excitation at 422 nm) 24 hours after addition of aliquots of a 0.1 mg/mL GO solution; Bottom: ZnPc (excited at 655 nm) 24 hours after addition of aliquots of a 0.1 mg/mL GO solution. No interaction between the chromophore and the GO substrate.



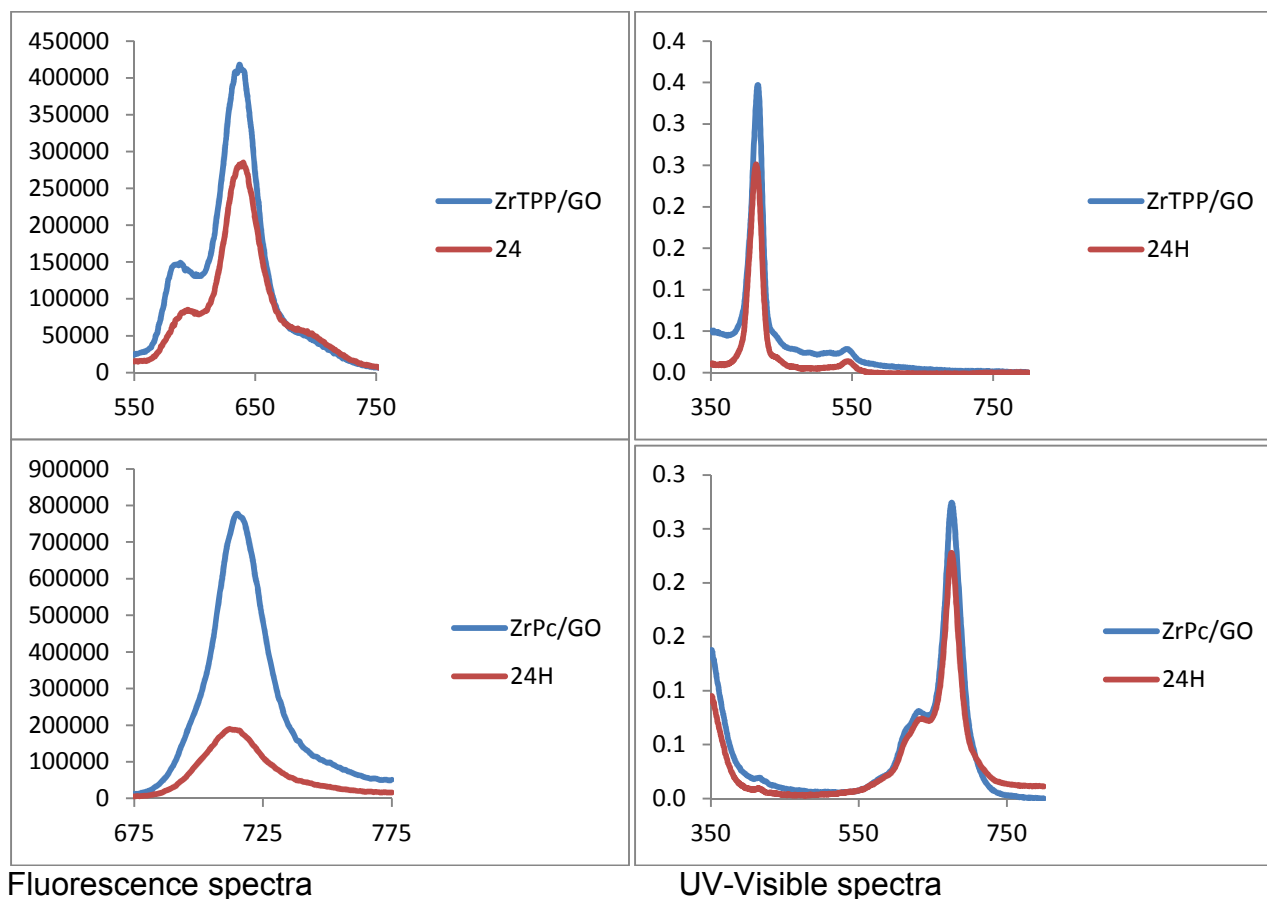
**Figure S2.** Fluorescence spectra (left) and UV-Visible spectra (right) of  $Zr^{IV}$ (TPP) (excited at 417 nm) 24 hours after addition of 0.1 mg/ml GO solution demonstrating saturation of the metallodye on the GO surface.



**Figure S3.** Fluorescence spectra (left) and UV-Visible spectra (right) of  $Zr^{IV}$ (Pc) (excited at 633 nm) 24 hours after addition of 0.1 mg/ml GO solution demonstrating saturation of the metallodye on the GO surface.



**Figure S4.** Fluorescence spectra (left) and UV-Visible spectra (right) of ZnTPP (top, excited at 422 nm) and ZnPc (bottom, excited at 655 nm) after addition of 120  $\mu\text{L}$  of 0.1 mg/mL GO solution at time of addition and after allowing 24 hours for equilibration demonstrating no interaction in either case.



**Figure S5.** Fluorescence spectra (left) and UV-Visible spectra (right) of top:  $Zr^{IV}(\text{TPP})/\text{GO}$  (excited at 417 nm) and bottom:  $Zr^{IV}(\text{Pc})/\text{GO}$  (excited at 633 nm); both after addition of 120  $\mu\text{l}$  0.1 mg/mL GO solution at time of addition and after allowing 24 hours to equilibrate. The substantial initial increase in fluorescence intensity upon addition of GO is due to disaggregation of the chromophores as they complex with GO. The smaller increase in the fluorescence intensity of the porphyrin (*ca.* 20%) relative to the phthalocyanine (*ca.* 200%) corresponds well with the aggregation behavior of porphyrins and phthalocyanines.<sup>8</sup> Lifetime measurements indicate no new species formed at any time during addition and equilibration. The fluorescence quenching of 76% and 32% observed for  $Zr^{IV}(\text{Pc})/\text{GO}$  and  $Zr^{IV}(\text{TPP})/\text{GO}$ , respectively, was calculated from the peak maximum just after addition of the GO and after 24 h of equilibration.

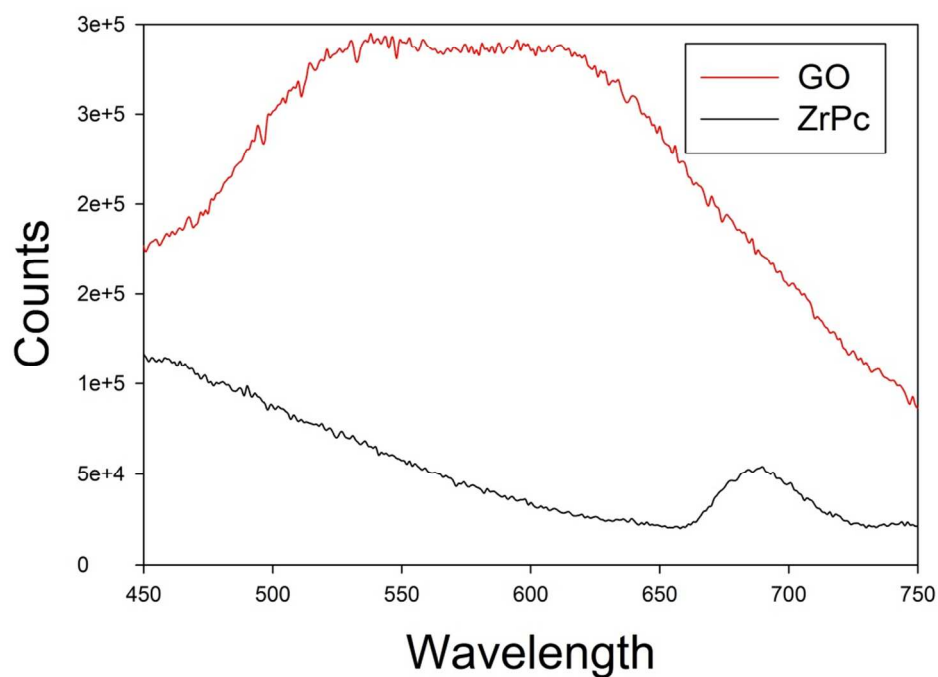
**Table S1.** UV-visible and fluorescence peaks  $\lambda_{\text{max}}$

Compound	Soret	Q1	Q2	emission	Emission
Zn(TPP)	423	561	651	599	651
Zn(TPP)/GO	423	561	651	599	651
Zn(Pc)	375	661	735	747	
Zn(Pc)/GO	375	661	735	747	
$Zr^{IV}(\text{TPP})$	419	546		582	635
$Zr^{IV}(\text{TPP})/\text{GO}$	416	550		590	636
$Zr^{IV}(\text{Pc})$	335	620, 636	674	716	
$Zr^{IV}(\text{Pc})/\text{GO}$	335	616, 640	673	713	

### Nanocomposites

100  $\mu\text{M}$  solutions of both  $\text{Zr}^{\text{IV}}(\text{Pc})$  and  $\text{ZnPc}$  in  $\text{CH}_2\text{Cl}_2$  were prepared. GO was added to these solutions to a final concentration of 0.1 mg/mL. Solutions were sonicated for 15 minutes. After incubating at room temperature for 48 h, samples were centrifuged at 13,000 RPM and washed with fresh THF to remove unbound molecules. The washing was repeated to ensure complete removal of unbound dye. The composite materials were centrifuged and THF removed. The pellet was then dispersed in nanopure water or THF for analysis.

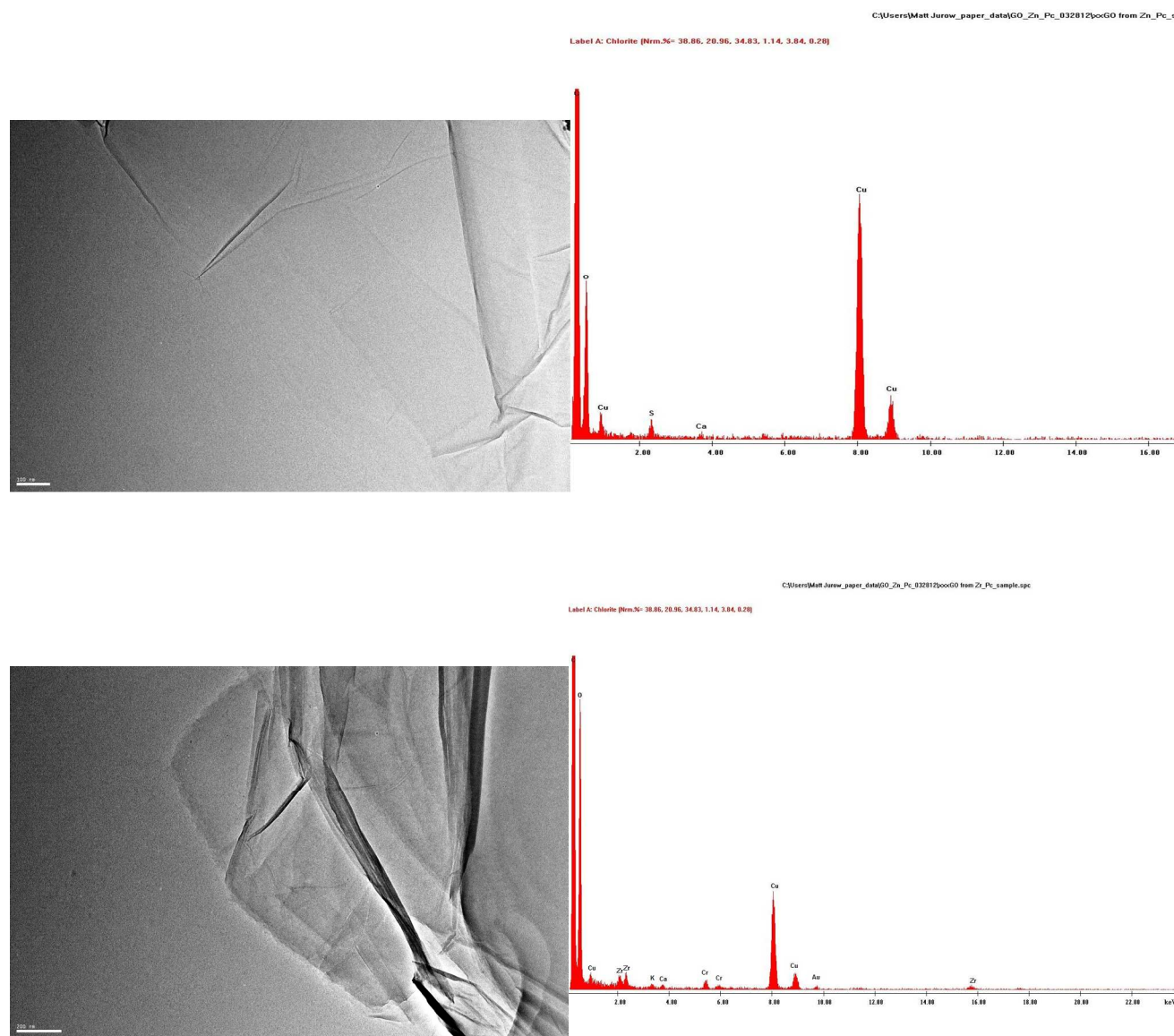
Estimations of the surface density of  $\text{Zr}(\text{IV})\text{Pc}$  on GO with 20% oxygen content are  $\sim 1$  dye molecule per  $20\text{-}50\text{ nm}^2$ ; using the extinction coefficient of the Q band, the contribution of the dye Q band in the solution phase UV-visible spectra taken after removing the unbound dye, and assuming an average flake size of  $1\text{ }\mu\text{m}^2$ . This high surface coverage indicates that the dyes bind to both the carboxylate moieties on the sides and large defects, and to the catechol and gem-diol moieties on the front and back surfaces. The control  $\text{Zn}(\text{II})$  dyes show little binding to the GO, likely because the high oxygen content minimizes the pi-pi interactions between these dyes and the GO, whereas the  $\text{Zn}(\text{II})\text{Pc}$  adsorb strongly to graphene by pi-pi interactions.



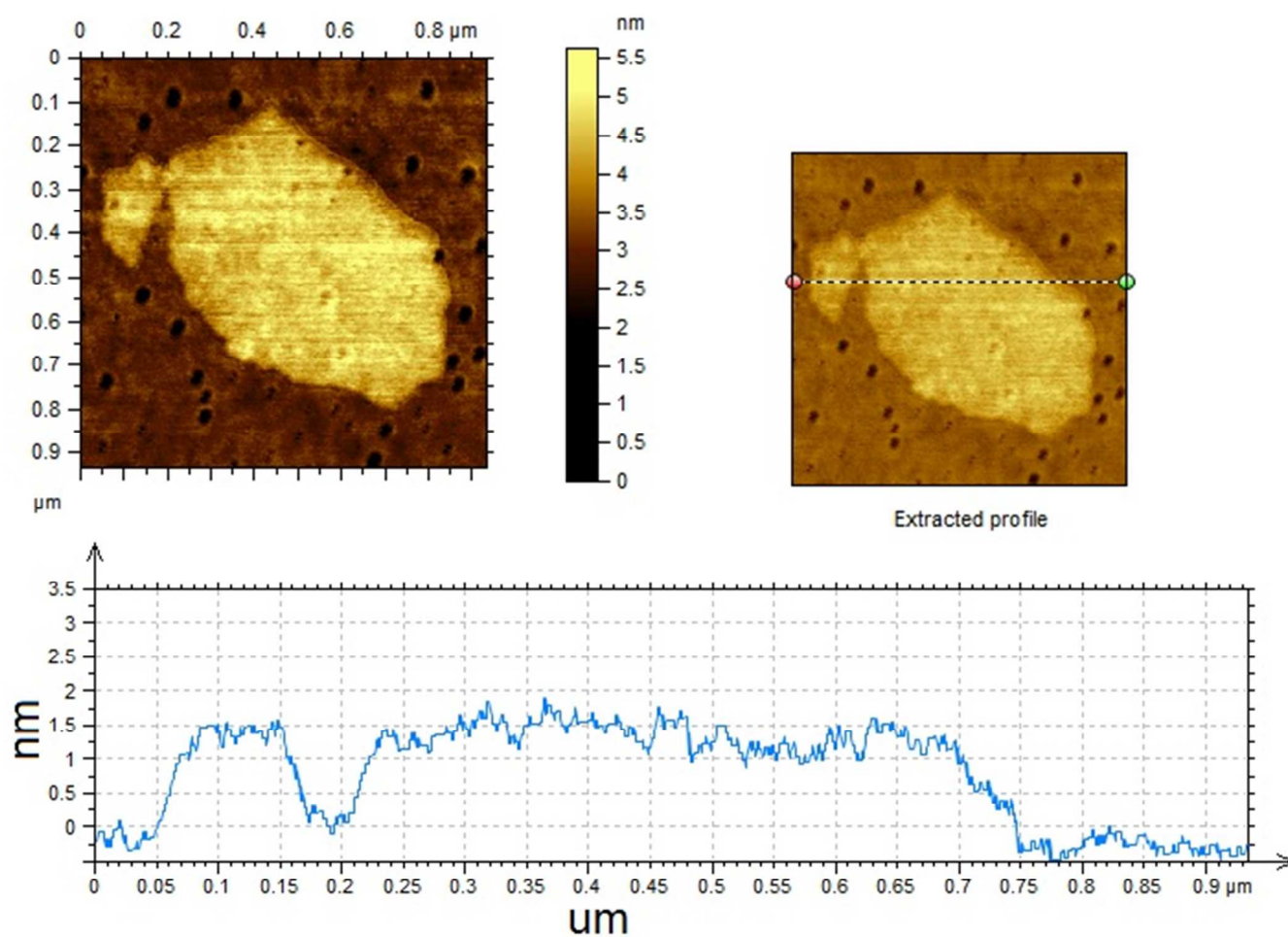
**Figure S6.** Comparison of unfunctionalized GO fluorescence to the fluorescence of the  $\text{Zr}^{\text{IV}}(\text{Pc})/\text{GO}$  composite material. GO nanocomposites were dispersed in THF.

## TEM images

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 above dispersions was placed on a 300 mesh carbon coated copper grid, (TED Pella Inc., Redding, California, USA), and allowed to dry for 1 minute before imaging.

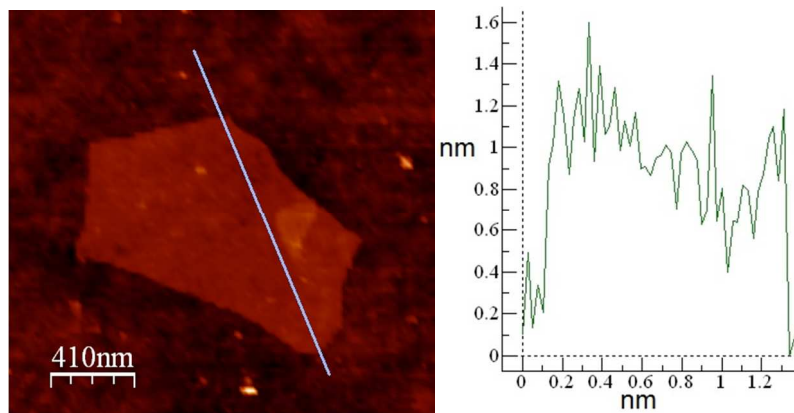


**Figure S7.** TEM image (left) and EDAX spectrum (right) of GO treated with Zn(Pc) (top) and Zr<sup>IV</sup>Pc (bottom). Creases, folds and layer overlaps are visible. Scale bar is 100 nm. EDAX indicates presence of oxygen from the GO. C and Cu peaks are from the underlying grids. No Zn peaks are detected indicating no absorption of the Zn(II) dyes on GO.

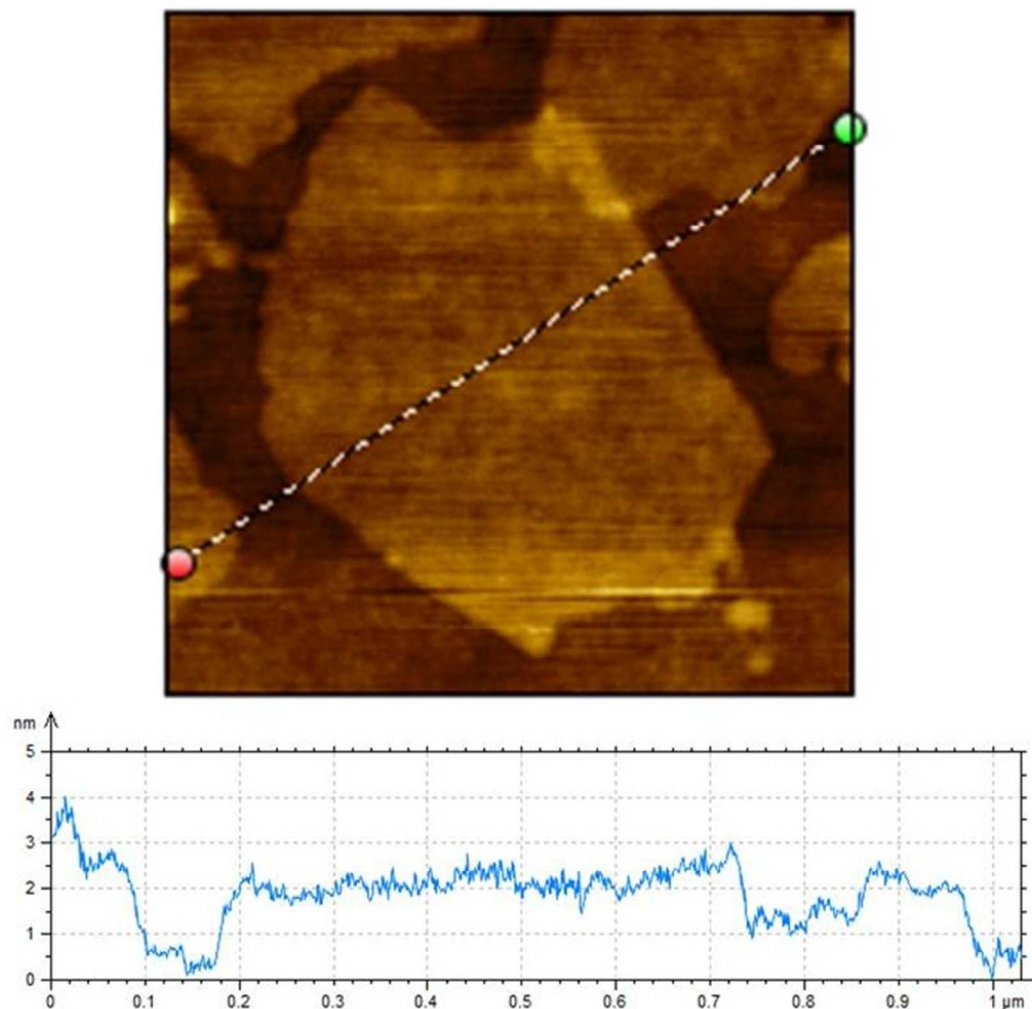
**AFM images**

**Figure S8.** AFM height image and line trace of GO cast on glass slides. A single layer flake is clearly seen with thickness of ca. 1.2 nm, which is consistent with previous AFM studies of GO.<sup>9, 10</sup> The holes are in the cover slip substrates. Taken on an Agilent 5500 AFM.

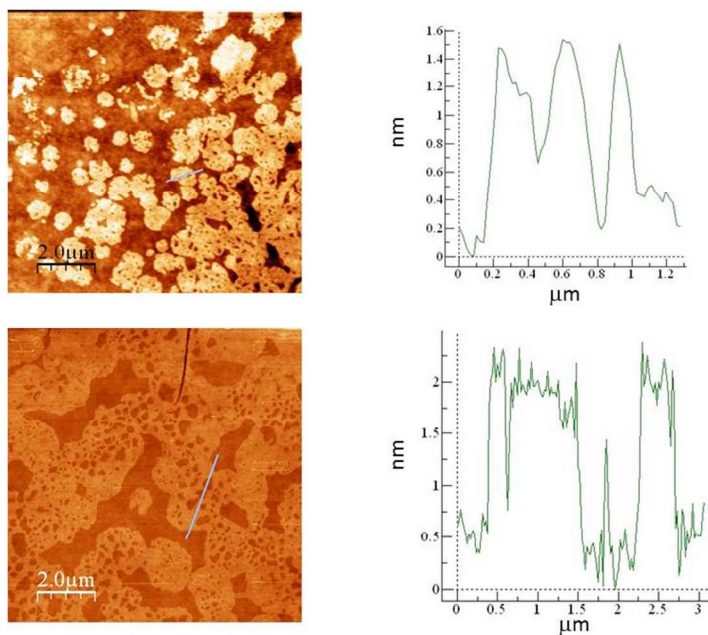




**Figure S9.** AFM height image (left) and line trace (right) of GO dispersion incubated with Zn(Pc), thoroughly rinsed and cast on glass slides. A single layer flake is clearly seen with thickness of ca. 1.2 nm, indicating little absorption of the dye. Taken on Asylum MFP-3D.



**Figure S10.** GO treated with  $\text{Zr}^{\text{IV}}(\text{Pc})(\text{ac})_2$  as in Figure 6 in the manuscript, but not rinsed, show more uniform and variable coating on the GO than in samples that were repeatedly rinsed in clean solvent. Solutions of 0.1 mg/mL GO and 0.1 mM  $\text{Zr}^{\text{IV}}(\text{Pc})(\text{ac})_2$  in THF were allowed to react and equilibrate for 72 hours with GO. Ozone cleaned glass slides were dipped in solution, allowed to dry in air for two minutes, dipped once in clean THF to remove unbound Pc on surfaces and imaged with an Agilent 5500 AFM.

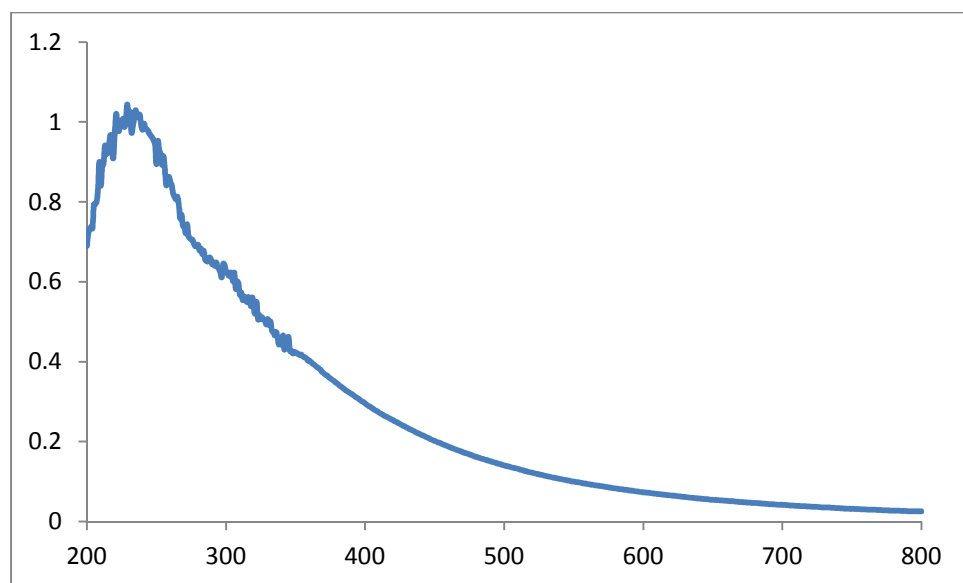


**Figure S11.** 5 mg/mL of an aqueous GO dispersion was added to  $\text{Zr}^{\text{IV}}(\text{Pc})(\text{ac})_2$  in THF to make a solution that is 0.1 mg/mL GO and 0.1 mM dye. The solution was allowed to equilibrate for two days. Solutions were centrifuged at 13,000 RPM for 10 minutes, excess dye was decanted and pellet was redispersed in THF by sonicating for 10 minutes. This rinsing was repeated twice and then solutions were centrifuged again and dispersed in water and spin coated onto ozone cleaned glass slides. Holes in the graphene sheets are likely from the desorption of the  $\text{Zr}^{\text{IV}}(\text{Pc})$  upon sonication in water (top). The same process was done using  $\text{Zr}^{\text{IV}}(\text{TPP})$  with similar results (bottom). The strong binding of the Zr(IV) to the GO may facilitate perforation of the GO.

## Film Studies

Graphene oxide solution (3 mg/mL in water) was spin coated onto piranha cleaned quartz slides and dried in an oven to make 15 nm thick continuous films. Films were then soaked in 0.1 mM solutions of dyes in  $\text{CH}_2\text{Cl}_2$  for three days at room temperature in the dark to ensure equilibration. Coated films were rinsed extensively with clean  $\text{CH}_2\text{Cl}_2$  to remove any unbound dye, backs of slides were wiped repeatedly with MeOH to remove any dye materials, and spectra were recorded. No appreciable fluorescence was observed at any excitation wavelength.

## Other Spectra



**Figure S12.** Absorption spectrum of GO in water

#### 4 Point Probe Measurements

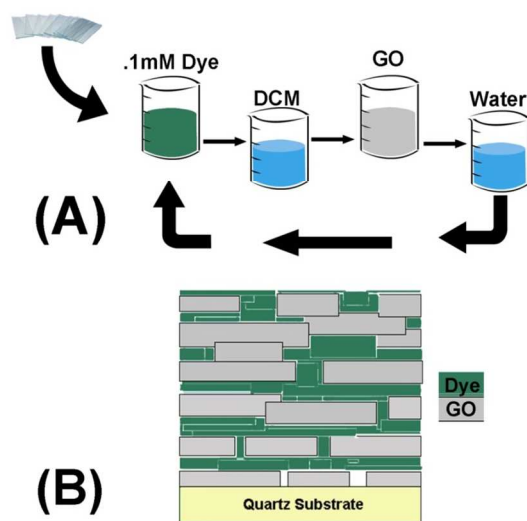
Devices were made by spin coating layers (of 8 nm or 15 nm) onto ozone cleaned glass. Sheet resistance<sup>12</sup> was measured by Van der Pauw technique of the pristine GO layers, of an 8 nm GO film soaked in Zr<sup>IV</sup>(Pc) or Zr<sup>IV</sup>(TPP) (0.1mM in CH<sub>2</sub>Cl<sub>2</sub>), or of an 8 nm GO film spin coated on top of a ca. 40 nm thick layer of Zr<sup>IV</sup>(TPP) or Zr<sup>IV</sup>(Pc) spin cast from chlorobenzene on ozone cleaned glass. Measurements were taken in the dark and under illumination.

	DARK			LIGHT		
	R ave	Sdev	Rs	R ave	Sdev	Rs
8nm GO	6.3E+09	0.00	<b>2.9E+10</b>	6.5E+09	0.02	<b>2.9E+10</b>
15nm GO	8.0E+08	0.05	<b>3.6E+09</b>	7.9E+08	0.06	<b>3.6E+09</b>
Por/GO	2.5E+09	0.03	<b>1.1E+10</b>	2.5E+09	0.02	<b>1.1E+10</b>
Pc/GO	6.0E+09	0.30	<b>2.7E+10</b>	6.0E+09	0.28	<b>2.7E+10</b>
GO/Por	3.4E+09	0.01	<b>1.5E+10</b>	3.4E+09	0.01	<b>1.5E+10</b>
GO/Pc	3.3E+09	0.04	<b>1.5E+10</b>	3.3E+09	0.04	<b>1.5E+10</b>

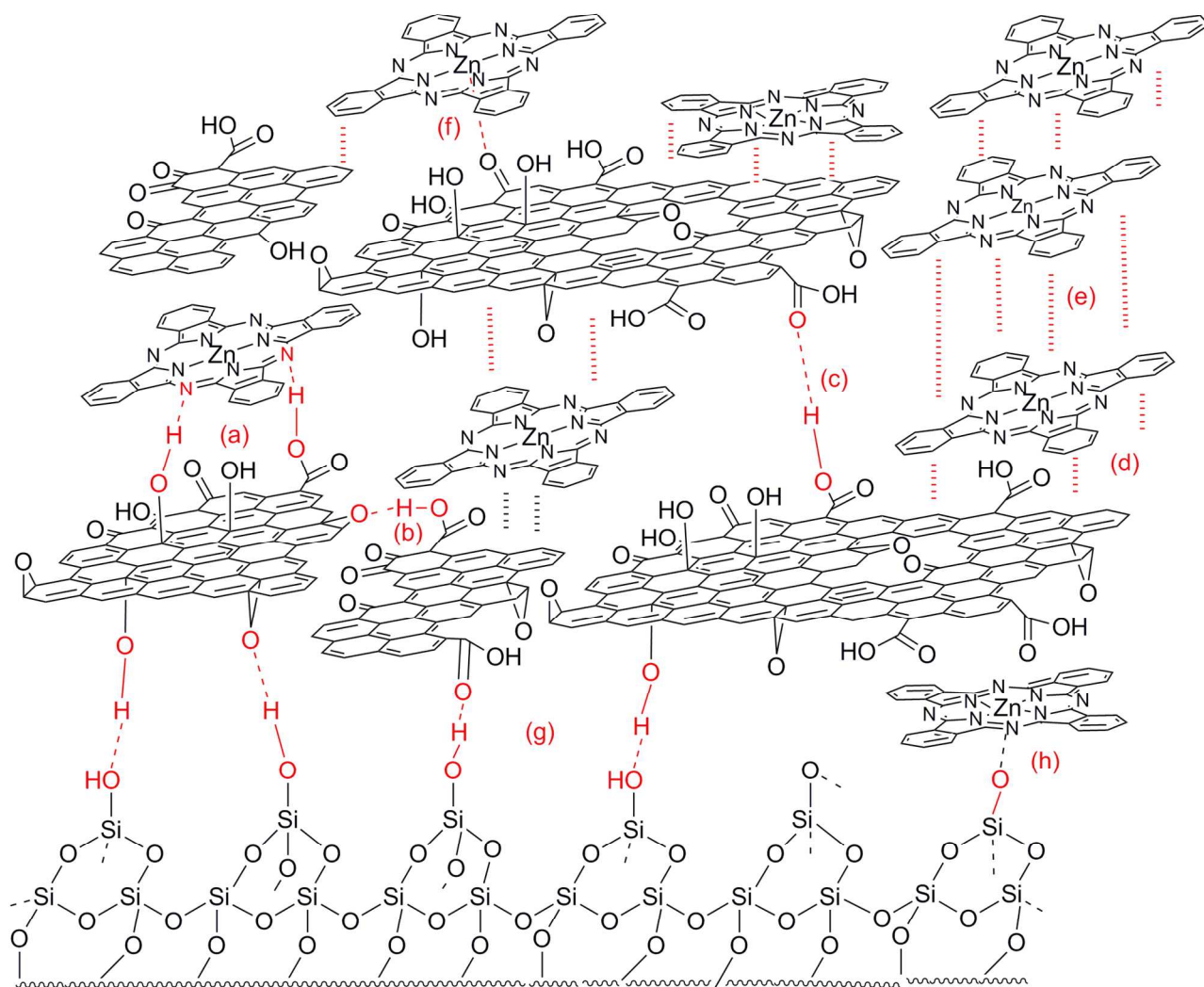
**Table S2.** Sheet resistance (Rs) values in  $\Omega/\square$  of GO layers on glass, GO layers deposited on top of dye layers, and GO layers with dyes attached by soaking. The high standard deviation of the Pc/GO species is the result of an observed anisotropy in the measurement.

### Layer by Layer Systems

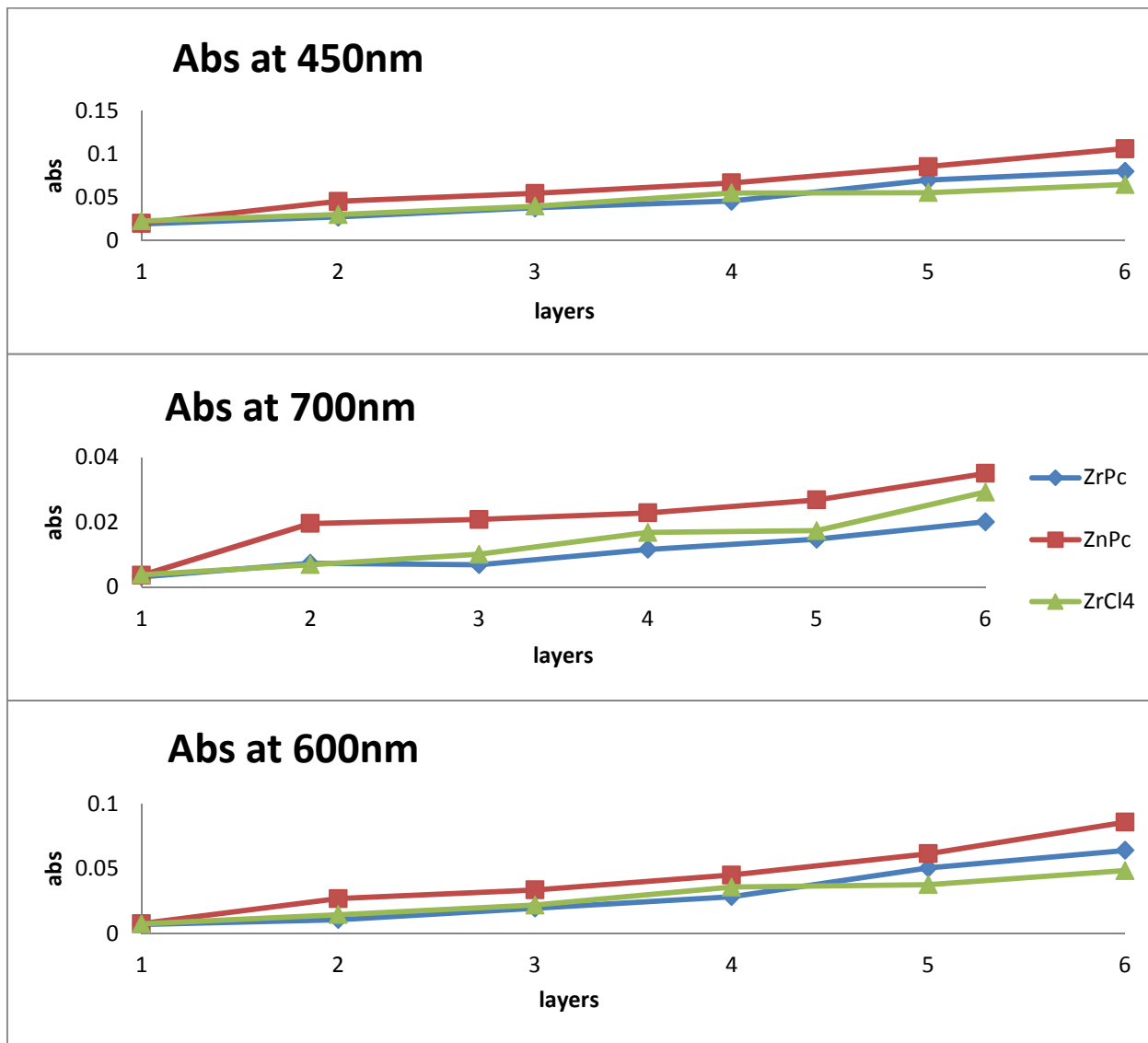
Layer by layer systems were made by sequential dipping of cleaned quartz slides in solutions of Zn(Pc), Zr<sup>IV</sup>(Pc) or ZrCl<sub>4</sub> after initial deposition of an 8 nm GO layer made by spin casting.



**Figure S13.** Depiction of layer by layer process (top) and result (bottom).



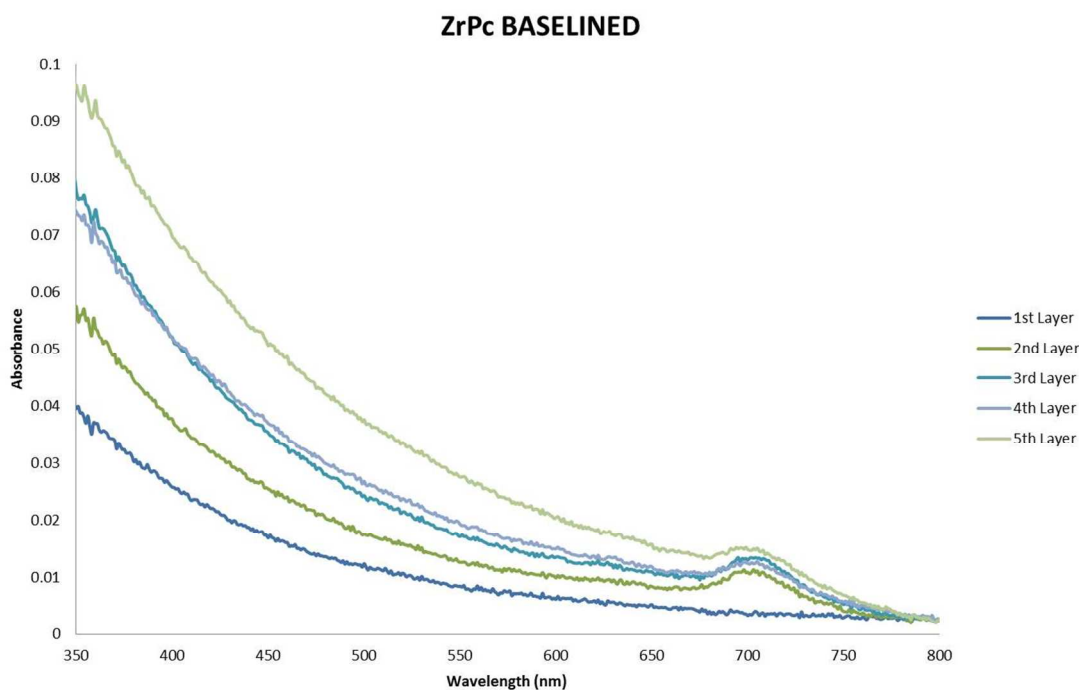
**Figure S14.** The layers are incomplete, thus there are interactions between GO sheets and between the dyes. Schematic representation of possible intermolecular interactions between the Zn(Pc) dye and GO include: (a) H-bond interactions between the GO and *meso* nitrogens on the dye, (b) H-bond interactions between neighboring GO in the same layer, (c) H-bond interactions between layers of GO, (d) pi-pi interactions between the dye and GO, (e) pi-pi interactions between dyes, (f) coordination of an oxygen on GO to the Zn(II) center of the dye, (g) H-bond interactions between GO and the quartz substrate, (h) coordination of the quartz oxygen into the ZnPc. There are other configurations of these interactions.



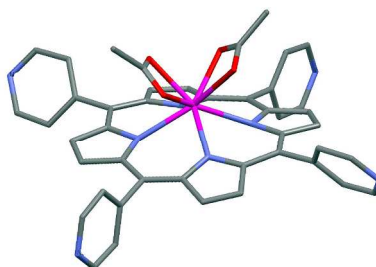
**Figure S15.** Plots of absorbance at specified wavelengths of films made by layer-by-layer deposition beginning with a GO layer spin cast onto quartz, and sequentially soaked in a solution of Zr<sup>IV</sup>(Pc) in CH<sub>2</sub>Cl<sub>2</sub> (see Figure S14).

The highly varied composition of the GO affords many possible binding modes and binding sites for the Zr<sup>IV</sup> dyes, for interactions between flakes of the GO, and for interactions with the substrate. Similarly, the hydrophobic dye can interact with graphene like areas of the GO, while the oxophilic metal center can interact with oxygen functional groups on the GO and with the substrate. Though the initial layers are incomplete, sequential dipping of the substrate into the GO and Zr<sup>IV</sup> dye solutions builds nanofilms with controlled thickness, controlled optical density, and controlled coverage.





**Figure S16.** A layer of GO was spin casted onto clean quartz slides, sequentially dipped in GO solution in water followed by a dye solution in  $\text{CH}_2\text{Cl}_2$ . The basal spin coating layer of GO creates an imperfect non uniform initial stage for random absorbtivity. As with addition sequential depositions the gaps between the GO flakes become filled and defects in the film are covered.



**Figure S17.** Structure of the Zr(IV) complex to 5,10,15,20-tetrapyrridylporphyrin shows the protrusion of the metal ion from the macrocycle.

## References

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