Electron Donating Chlorophyll-a on Graphene: A Way Towards Tuning Fermi Velocity in Extended Molecular Framework of Graphene/Chlorophyll-a Nanohybrid.

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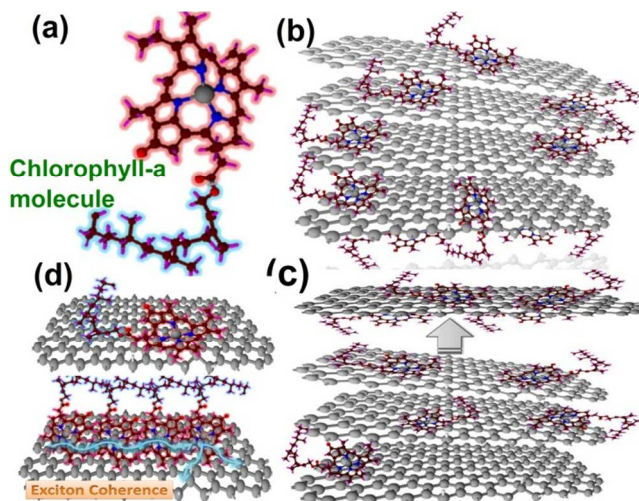Jadavpur University, Kolkata-700032, India.

Figure S1. Graphite exfoliation via non covalent surface functionalization through π-staking of CHL-a in water ethanol solvent [(a)-(c)]. Exciton coherence of CHL-a molecule over graphene surface,and electron transfer from CHL-a to graphene(d)
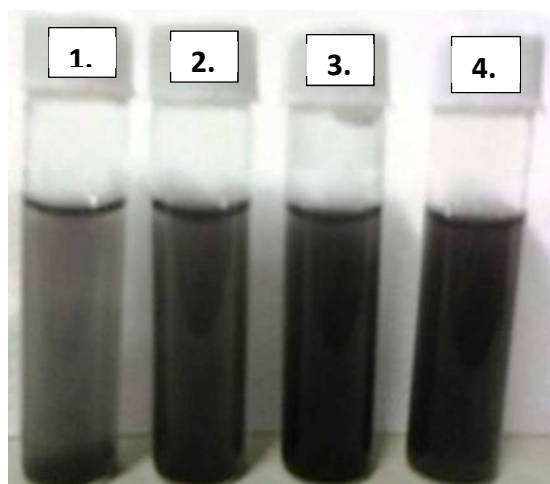
Figure S 2. 1. Graphite in ethanol/water after sonication; 2-4 sonication assisted exfoliated graphene/CHL-a in ethanol/water with increasing CHL-a concentration respectively.
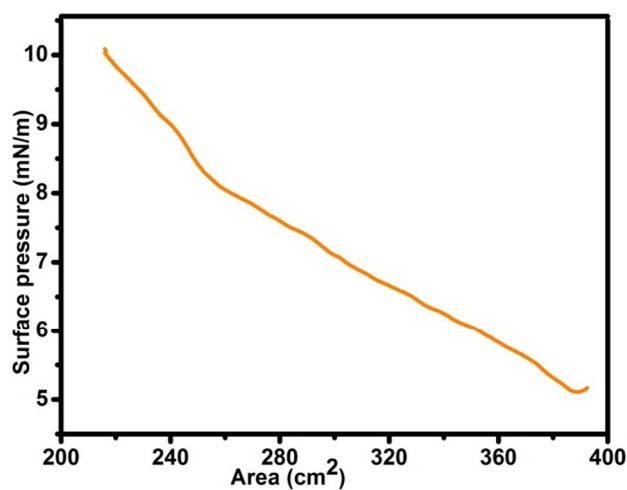

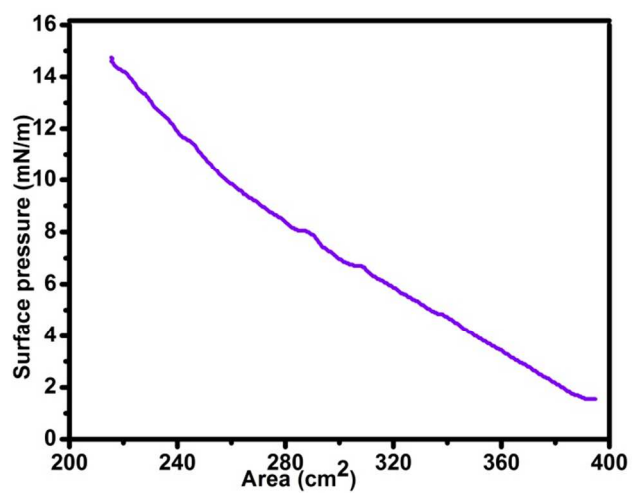**Figure S 3.** Isotherm of bare CHL-a LB-film on ITO substrate.

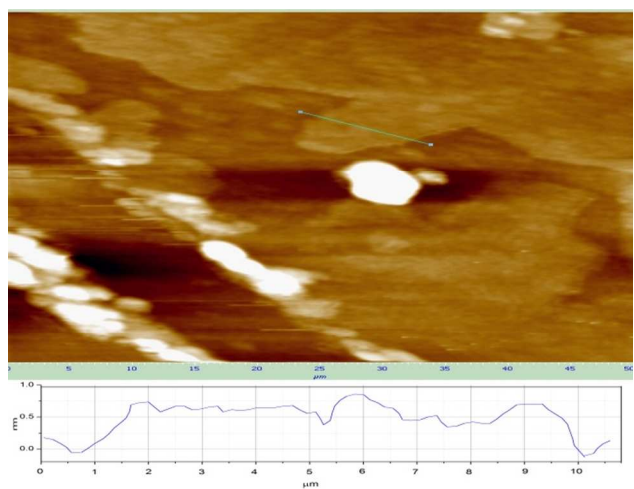**Figure S 4.** Isotherm of graphene/CHL-a LB-film on ITO substrate.

Figure S 5. AFM image and corresponding surface profile of graphene /CHL-a nanohybrid over mica substrate at highest CHL-a concentration.
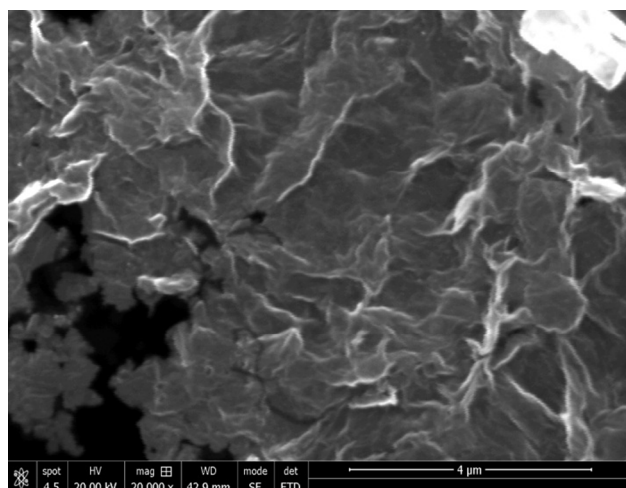
Figure S 6. FESEM image of graphene /CHL-a nanohybrid at highest CHL-a concentration.
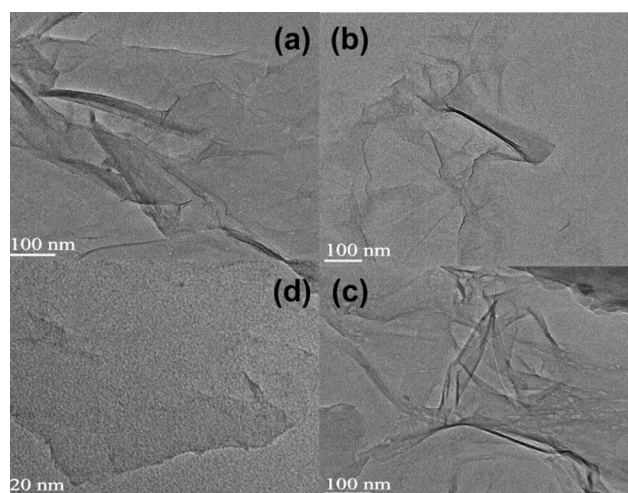

Figure S7. Representative TEM images of monolayer graphene flakes exfoliated by CHL-a at 10^{-5} concentration.

Estimation of graphene mono-layer yield:

From TEM data the number and mass fraction of monolayers (number of monolayers / total number of flakes) have been calculated by using the same procedure reported by Hernandez et al. to be 66% and 15.4% respectively for 10^{-5} mole CHL-a exfoliated graphene sample[1].
By combining this with the fraction of material remaining after centrifugation (χ) we can estimate the total yield of graphene, Y from the product of mass fraction and material remaining after centrifuge (χ). This gives Y=0.95% for the 10^{-5} mole CHL-a exfoliated graphene sample. [Refer table S1]

Table S1

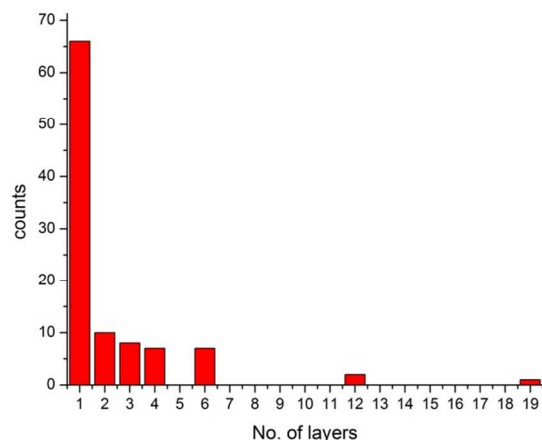| CHL-a conc.	No. of flakes	No. of mono layer	Mono layer no. fraction	Mass fraction	χ	Y
10^{-5}	53	35	66%	15.4%	6.2	0.95%
10^{-6}	46	12	26%	2.8%	6	0.17%
10^{-7}	41	7	17%	1.2%	5.8	0.07%

Figure S8. Histograms of the number of graphene layers per flakes exfoliated by CHL-a at 10^{-5} concentration.

Experimental Procedure:

Raman spectra:

Raman spectra (Horiba JobinYvon, T64000 model) of the samples were recorded at room temperature in mica substrate deposited by LB process by exciting the sample with an Ar+ ion laser source operated at 514.5 nm excitation at a very low laser power level (< 1 mW) to avoid any heating effect of the sample.

Time-resolved photoluminescence,

For time correlated single photon counting(TCSPC) measurements, the samples were excited at 405 nm using a picosecond diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. Typical full width at half-maximum (fwhm) of the system response using a liquid scatter was about 90 ps. The repetition rate was 1 MHz. The fluorescence decays were collected with a Hamamatsu MCP photomultiplier (C487802). The fluorescence decays were analyzed using IBH DAS6 software. The following equation was used to analyze the experimental time-resolved fluorescence decays:

$$P(t)=b+\sum_{i}^{n}\alpha_{i}\exp[-\frac{t}{\tau_{i}}]\qquad\qquad(1)$$

Here, n is the number of discrete emissive species, b is the baseline correction ("dc" offset), and α_i and τ_i are preexponential factors and excited-state fluorescence lifetimes associated with the ith component, respectively. For multiexponential decays, the average lifetime $\langle\tau\rangle$ was calculated from the following equation:

$$\langle\tau\rangle=\frac{\sum_{i=1}^{n}a_{i}\tau_{i}^{2}}{\sum_{i=1}^{n}a_{i}\tau_{i}}\qquad\qquad(2)$$

a_i is the contribution of the decay component.

STM and conductance measurement:

Scanning Tunneling Microscopy (STM)
STM measurements were carried out by utilizing a STM from Agilent Technologies 5500. The STM tips were obtained by mechanically cutting a high purity Pt0.8Ir0.2 wire 0.25 mm in diameter. The STM images were acquired in constant current operating mode in room conditions at scanning tip bias voltage -1V to 1 V.

Scanning Tunneling Spectroscopy (STS)
The STS measurements are carried out as follows. 50 current vs. voltage traces (IV traces) are measured at a certain spot on the sample (interrupting the feedback control loop during the measurements). The variation of the tunneling current is measured as the tip bias voltage is swept (0.01 second per trace). By measuring both the forwards and backwards voltage sweep we checked that the thermal drift during the acquisition of a single IV trace can be neglected and thus every IV trace is measured at a fixed tip location. Then we change the lateral position of the tip by 50-100 nm and another set of 50 traces are acquired. It is important to note that the spectra have been collected without distinction between the bright regions or the regions where the atomic resolution is retained. The procedure is repeated until 200 traces are collected. The differential conductance vs. voltage (dI/dV vs. V) is obtained by numerical differentiation of the IV traces.

REFERENCES

(1) Hernandezl, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De1, S.; Mcgovern, I.; T.; Holland, b.; Byrne, M.; Gun'ko, Y.; K.; Boland, J.; J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A.; C.; Coleman, J.; N. High-yield production of graphene by Liquid-phase exfoliation of graphite. *Nature Nanotechnology*, **2008**, *3*, 563-568.