Supporting information

Graphene Field-Effect Transistor as a High-Throughput Platform to Probe Charge Separation at Donor-Acceptor Interfaces

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1. Measuring the optical absorption coefficient of the ZnPc films

To determine the optical absorption coefficient of our films, we deposited ZnPc films with different thicknesses (t) onto a glass substrate. Similar to the ZnPc film grown on C_{60}, the ZnPc film on a glass substrate has an edge-on orientation. The transmitted intensity through the ZnPc/glass samples $T(t)$, compared to the transmitted power through the bare glass substrate $T(t = 0)$:

$$A(t) = 1 - T(t)/T(t = 0), \quad \text{(S1)}$$

is used as the experimental observable to compare with the same quantity calculated by the optical model. Note that $A(t)$ is not strictly equal to the absorption of the ZnPc films because a small portion of the light is reflected at air/ZnPc and ZnPc/glass interfaces. However, because the exact same quantity is compared between the experiment and calculation, the absorption coefficient of ZnPc can be determined accurately. The measurement are done with an incident angle of 0° and the same wavelength (700 nm) as used in the ultrafast experiment.

To model the intensity transmitted through the film, we solve the standard Fresnel equations for the multi-layer structure shown in Figure S1 using the transfer-matrix method.[S1-S3] The refractive index of glass[S4] and the real part of the refractive index of ZnPc[S5-S6] are obtained from the literature. The only fitting parameter is the imaginary part of the refractive index k of ZnPc, which relates to the optical absorption coefficient α by:

$$\alpha = \frac{4\pi}{\lambda_0} k. \quad \text{(S2)}$$

λ_0 is the wavelength in vacuum. Figure S2 shows the comparison between the experiment data and the solution obtained from the optical model for k = 0.6 and 0.7. The value of k is within the range of 0.6 - 0.7. In the subsequent calculation, we take k = 0.65. The corresponding value for α is 1.2 $\times$ 10^5 cm^{-1}, which is consistent to the α measured by others.[S7]

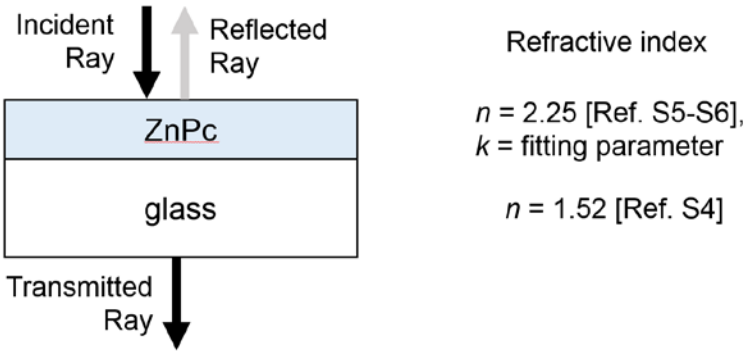

Figure S1: The optical model used to determine the complex dielectric constant of ZnPc.

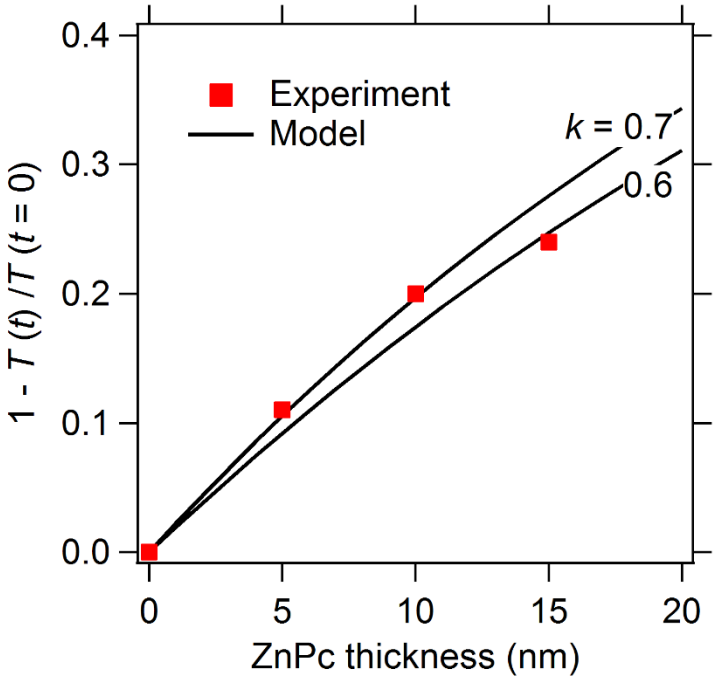

Figure S2: The optical transmission of the ZnPc/glass samples at 700 nm determined by experiment and modeling.

2. Modeling the optical absorption of the ZnPc-C_{60} films

To determine the actual number of photons absorbed in the ZnPc/C_{60}/graphene/SiO2/Si multilayer structure, we cannot simply use the product of α and the ZnPc thickness because of the reflection from interfaces and the interference between different reflected/transmitted rays. To determine the absorption in the ZnPc layer, we use the optical model as shown in Figure S3. The complex refractive index *k* of ZnPc determined above is used in this model. The refractive index for graphene,[S8] C_{60},[S6] SiO_2 (thermal oxide),[S9] Si[S10] found in the literature are used in our calculation. The values of refractive indexes and thicknesses of each layer used in the model are summarized in Figure S3. The percentage of incident photons absorbed by the ZnPc layer in the two samples used in our experiment: 5 nm ZnPc/2 nm C_{60} and 5 nm ZnPc/10 nm C_{60} are found to be 7.8% and 9.6% respectively. Note that the amount of light absorbed in the two samples are slightly different even though the ZnPc thickness is the same. The small difference in absorption is originated from reflection and multi-layer interference effects.

To determine the number of absorbed photons in our devices, we use the measured laser beam parameters (a pulse energy = 344 nJ and fwhm size = 1.2 mm). We assume a Gaussian beam profile with the beam centered at the center of the device. The device diameter is taken as 1 mm.

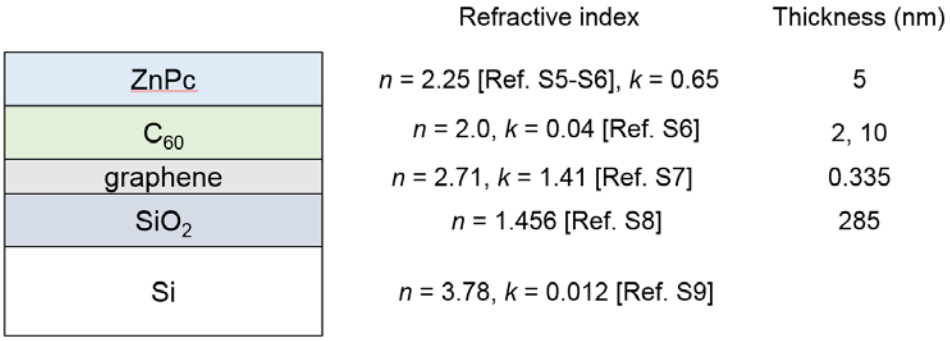

Figure S3: The optical model use to determine the light absorption in the ZnPc layer.

3. Optimizing the time resolution of our measurement circuit

The time resolution of our setup can be limited by the design of the measurement circuit in addition to the resolution of the oscilloscope. For an ideal measurement circuit, the oscilloscope draws no current from the circuit. This can be achieved only if the total impedance of the measurement circuit, which contains the oscilloscope probe and the oscilloscope (the gray box in Figure S4a), is much larger than R_0. The resistance of the oscilloscope probe R_p is on the order of

10 MΩ, which is much larger than R_0. However, for high frequency signal, the reactance X_c (in the unit of Ω) of the oscilloscope probe capacitance C_p can be very small because $X_c = 1/2\pi f C_p$. High frequency components of the signal can be lost unless X_c (f) > R_0. This limits the smallest signal rise time that can be captured by the setup. The cutoff frequency f_c, *i.e.* the effective bandwidth of the measurement, is given by $f_c \sim \frac{1}{2\pi R_0 C_p}$. Because the signal rise time τ ~ 0.35/f_c, the minimum rise time (i.e. the time resolution) that can be measured is:[S11]

$$\tau \approx 2.2 R_0 C_p. \qquad \text{(S3)}$$

Hence, τ decreases with R_0 until it reaches the time resolution of the oscilloscope.

Figure S4b shows the normalized signal obtained from a 1.5 nm ZnPc/2 nm C_{60}/graphene/glass sample by using different R_0 in the measurement circuit. This sample have the fastest CS dynamics among our samples, because of the ultrathin organic films. The signal rise time τ is plotted against R_0 (inset of Figure 4b). A linear dependence as predicted by Eq. (S3) is observed. The probe capacitance C_p can be determined from the slope of this curve, which is ~ 10 pF. This is roughly equal to the capacitance of our 300 MHz oscilloscope probe (12 pF). The rise time τ ~ 2 ns for R_0 = 100 Ω, which approaches the temporal resolution (1.75 ns) of our oscilloscope. In our main text, results such as those shown in Figure 4 are done with this optimized setup. The signal rise time is then limited only by the resolution of the oscilloscope and the actual CS dynamics.

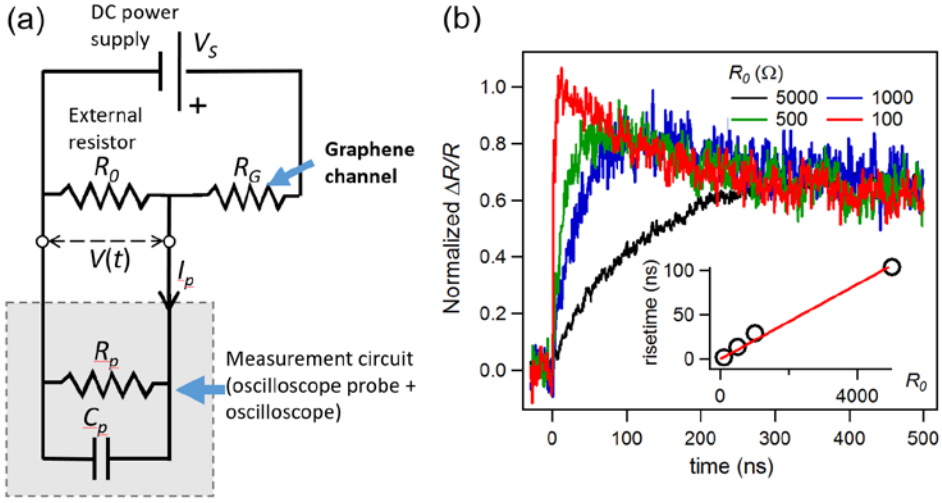

Figure S4: (a) The circuit diagram of the setup. (b) The time-resolved signal measured with different R_0. Inset: the rise time of the signal as a function of R_0.

References:

S1. Katsidis, C. C.; Siapkas, D. I., General Transfer-Matrix Method for Optical Multilayer Systems with Coherent, Partially Coherent, and Incoherent Interference. *Appl. Opt.* **2002**, *41*, 3978-3987.

S2. Harbecke, B., Coherent and Incoherent Reflection and Transmission of Multilayer Structures. *Appl. Phys. B* **1986**, *39*, 165-170.

S3. Byrnes, S. J., Multilayer Optical Calculations. **2016**, arXiv:1603.02720v2.

S4. Rubin, M., Optical-Properties of Soda Lime Silica Glasses. *Sol. Energy Mater.* **1985**, *12*, 275-288.

S5. El-Nahass, M. M.; Zeyada, H. M.; Aziz, M. S.; El-Ghamaz, N. A., Structural and Optical Properties of Thermally Evaporated Zinc Phthalocyanine Thin Films. *Opt. Mater.* **2004**, *27*, 491-498.

S6. Stendal, A.; Beckers, U.; Wilbrandt, S.; Stenzel, O.; vonBorczyskowski, C., The Linear Optical Constants of Thin Phthalocyanine and Fullerite Films from the near Infrared up to the Uv Spectral Regions: Estimation of Electronic Oscillator Strength Values. *J. Phys. B-at. Mol. Opt.* **1996**, *29*, 2589-2595.

S7. Davidson, A. T., The Effect of the Metal Atom on the Absorption-Spectra of Phthalocyanine Films. *J. Chem. Phys.* **1982**, *77*, 168-172.

S8. Cheon, S.; Kihm, K. D.; Kim, H. G.; Lim, G.; Park, J. S.; Lee, J. S., How to Reliably Determine the Complex Refractive Index (Ri) of Graphene by Using Two Independent Measurement Constraints. *Sci. Rep.* **2014**, *4*, 6364.

S9. Lee, H. J.; Henry, C. H.; Orlowsky, K. J.; Kazarinov, R. F.; Kometani, T. Y., Refractive-Index Dispersion of Phosphosilicate Glass, Thermal Oxide, and Silicon-Nitride Films on Silicon. *Appl. Opt.* **1988**, *27*, 4104-4109.

S10. Aspnes, D. E.; Studna, A. A., Dielectric Functions and Optical-Parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV. *Phys. Rev. B* **1983**, *27*, 985-1009.

S11. Tektronix abcs of Probe Primer. https://www.tek.com/learning.