

**Modelling the Quenching Effect of Chloroaluminum Phthalocyanine and Graphene
Oxide Interactions: Implications for Phototherapeutic Applications.**

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I. KINETIC MONTE CARLO

A. Morphology Model

Concerning the morphology, first we use the experimental concentrations of the compounds to calculate an approximate number of molecules in a certain volume. Using simple stoichiometry we calculated the number of AlClPc molecules in a volume of 1 L (10^{27} \AA^3) for the concentrations shown in¹. The dye has a molar mass of $M_{dye} = 574.96 \text{ g/mol}$. For a given concentration of dye, ρ_{dye} , we have the number of AlClPc molecules, n_{ph} ,

$$n_{ph} = \frac{\rho_{dye} \cdot 6.02 \cdot 10^{23}}{M_{dye}} \quad (\text{S1})$$

As for the photothermal agent, we have to consider the fact that nGO is a two dimensional extended system with a multitude of possible sizes and masses, leading to an estimated mass corresponding to one 100 nm x 100 nm sheet of nGO based on the amount of carbon atoms present in one sheet. The proportion between oxygen and carbon atoms varies with the radicals present in each sample. Here, we account only for carbon atoms when calculating the mass.

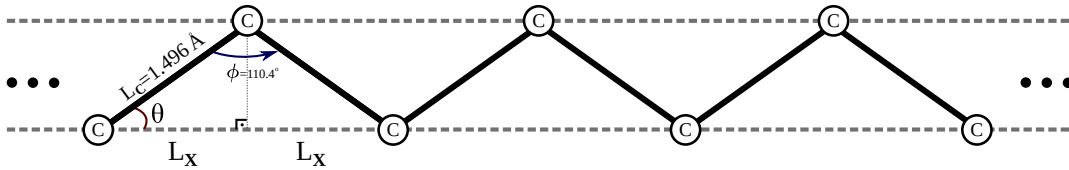


FIG. S1. Graphene Oxide zig-zag edge.

In order to estimate the mass, we consider one sheet. Its extremities are visualized as shown in Figure S1, with the average carbon single bond length being 1.496 \AA and an angle between two bonds connected to a carbon atom $\phi = 110.4^\circ$. Projecting it horizontally to a value of $L_x = 1.22 \text{ \AA}$, we can estimate the amount of carbon atoms on each side of a nGO sheet as

$$N_{C_{atoms}} \approx \frac{100 \text{ nm}}{L_x} = 819 \implies N_C^T = 6.724 \times 10^5. \quad (\text{S2})$$

Given the dimensions of a nGO sheet, we can approximate the total amount of carbon atoms by $N_{C_{atoms}}^2$. Now, with a known atomic mass for carbon of $m_C = 12u$, considering $u = 1.66054 \times 10^{-24} \text{ g}$, we have the mass of a 100 nm x 100 nm sheet of $m_{nGO} = m_C u N_{C_{atoms}}^2 = 1.339 \times 10^{-17} \text{ g}$.

The next step is identical to the procedure applied to the dye, where we estimate the amount of nGO sheets per concentration as

$$n_{nGO} = \frac{\rho_{nGO} \cdot 6.02 \cdot 10^{23}}{m_{nGO}}. \quad (\text{S3})$$

The results for quantifying the involved molecules are presented in table S1.

Compound	Exp. Concentration (g/L)	Number of Molecules
AlClPc	0.31	3.25×10^{20}
	2.96	2.21×10^{17}
nGO	6.30	4.71×10^{17}
	12.65	9.47×10^{17}

TABLE S1. Number of molecules in a volume of 10^{27} \AA^3

We want to simulate molecules of dye surrounded by nGO. For that we create a cubic lattice where the cube's faces represent the nGO sheets. In order to do that, and knowing the amount of molecules in our chosen volume of 10^{27} \AA^3 , we can calculate the proportion between dye and nGO. Since the cube has six nGO faces, we calculated said proportion as

$$P_{ph}^{(conc)} = \frac{n_{ph}}{6n_{nGO}^{(conc)}} \quad (\text{S4})$$

for the respective concentrations. We present the calculated proportions in table S2.

ρ_{dye} (g/L)	ρ_{nGO} (g/L)	$P_{ph}^{(conc)}$
0.31	2.96	244
	6.30	115
	12.65	57

TABLE S2. Amount of dye molecules interacting with nGO sheets according to experimental concentrations.

Now that we have the approximate number of molecules in our system, one of the most important parameters to be obtained is the approximate intermolecular distance, given its connection to the presented transfer rates. To obtain that, we consider the same arbitrary volume of 10^{27} \AA^3 and calculate the ‘‘empty volume’’ (representing the solvent in the experiment) as

$$d = \sqrt[3]{\frac{10^{27} - n_{ph}V_{ph}}{n_{ph}}} \quad (\text{S5})$$

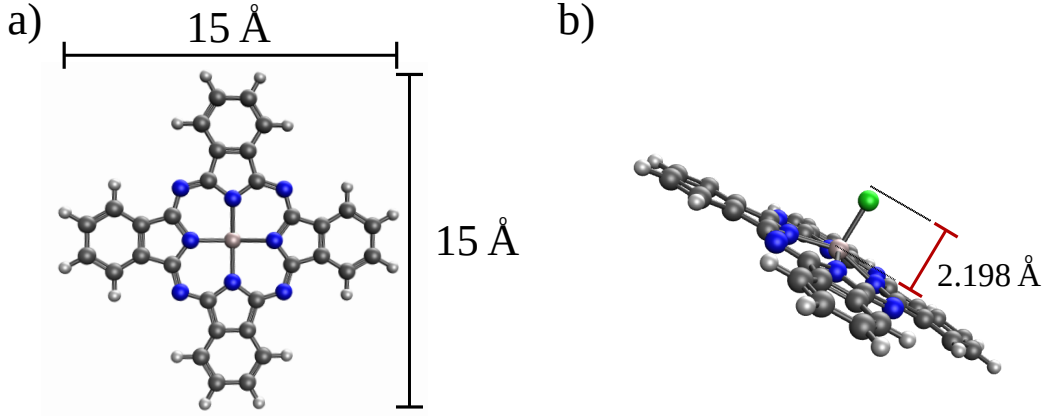


FIG. S2. Aluminum Phthalocyanine Chloride dimensions. The perpendicular aluminum-chlorine bond inwards (a) and the molecule turned to the left displaying the perpendicular bond (b). Dark gray atoms represent carbon atoms, while light gray stands for hydrogen, blue for nitrogen and green for chlorine.

where V_{ph} is the volume of a phthalocyanine molecule in \AA^3 . Notice there are several ways we can calculate the dye's molecular volume. Considering the geometry shown in Figure S2, we have an extremely rigid molecule with only one atomic bond perpendicular to the molecule's plane. Therefore one approach we could take is to consider the molecule a small pyramid with a $15 \text{ \AA} \times 15 \text{ \AA}$ square base and a height of 2.198 \AA , which is the length for the aluminum-chlorine bond. This approach would yield a volume of 164.85 \AA^3 . A different option is to consider the molecule a block with two sides of 15 \AA and a height equivalent to the Van der Waals radius for the carbon atom (1.7 \AA), since the molecule is mostly composed by carbon. The yielded volume would be of 382.5 \AA^3 . Nonetheless, regardless of any reasonable approach we may prefer to calculate an individual molecule's volume, the $n_{ph}V_{ph}$ numerator in (S5) will always be substantially inferior to 10^{27} \AA^3 , which simplifies our intermolecular distance to

$$d = \frac{10^9}{\sqrt[3]{n_{ph}}} \quad (\text{S6})$$

depending only on the concentration of dye. That said, we simulated systems for two different intermolecular distances, respective to the dye concentrations. For $\rho_{dye} = 2.26 \text{ g/L}$ we have $d_1 = 75 \text{ \AA}$, meanwhile for $\rho_{dye} = 0.31 \text{ g/L}$ we have $d_2 = 145 \text{ \AA}$.

Once all parameters are known, we assembled a cubic lattice, noting there was more than one approach to do so. The simpler approach is to consider the content of our cubic lattice of dye and use the intermolecular distance as a parameter to calculate the hopping rates from one randomly

generated position to its first 26 neighbors. Nevertheless, the size of our cubic lattice would need to be scanned to see which size length with a respective Förster radius yields satisfactory results when compared to experimental spectra. In an attempt to remove the guessing factor of the morphology and taking advantage of a known number of molecules and intermolecular distances, we were able to calculate how big the lattice would need to be in order to fit the estimated molecules for d_1 and d_2 . Essentially, we are creating sites that excitons can hop between before recombination. Excitons are randomly generated in any site, only being able to hop between the exact sites.

With a known intermolecular distance d_i ($i = 1, 2$), we can calculate the number of sites per lattice dimension as

$$N_{sites}^{(i)} = \sqrt[3]{P_{ph}^{(conc)} d_i} \quad (S7)$$

related to a dimensional length $L_{(conc)}^{(i)}$ by

$$L_{(conc)}^{(i)} = N_{sites}^{(i)} d_i = P_{ph}^{(conc)1/3} d_i^{4/3} \quad (S8)$$

which we approximate to the closest integer (in angstroms). Our calculated parameters for the cubic lattice are presented in table S3.

ρ_{dye} (g/L)	ρ_{nGO} (g/L)	N_{sites}	$L_{(conc)}^{(i)}$ (nm)
	2.96	33	476.0
0.31	6.30	26	370.4
	12.65	20	293.1

TABLE S3. Lattice 1D length for different nGO concentrations.

B. Aggregation model

From the previous section, we have the basic system morphology. The size of the simulated box will remain the same. We simulated aggregation between dye molecules according to their distance from a nGO border. Since the box is very well defined and finite, we consider L_{box} as the sum S_n of the geometrical progression terms, defined by

$$S_n = A_1 \frac{(1 - q^n)}{1 - q} \quad (S9)$$

where A_1 is the first term, q is the GP ratio and n is the number of sites, N_{sites} , defined in (S7). Each known nGO concentration has its respective one-dimensional box length, which will serve as our boundary condition. With a known N_{sites} and a parametric ratio, we can simply rearrange (S9) to obtain

$$A_1 = S_n \frac{(1-q)}{1-q^n} \quad (\text{S10})$$

from which we can calculate the n -th ($n=1,2,3..$) term as

$$A_n = A_{n-1} \cdot q = A_1 \cdot q^{n-1} \quad (\text{S11})$$

Considering the GP ratio as a parameter, table S4 shows the largest and the two smallest distances for different ratios. Naturally, since the last coordinate in the progression corresponds to graphene-oxide, the smallest distance between dyes will be the second to last in each progression (mirrored in each side respective to a central molecule).

Calc. d_{dye} (Å)	q	A_1 (Å)	A_{n-1} (Å)	$d_{dye-nGO}$ (Å)
145	0.80	486.96	17.13	13.70
	0.84	401.52	34.96	24.67
	0.88	322.28	47.36	41.68
	0.90	285.63	58.81	52.92
	0.92	251.29	71.95	66.19
	0.94	219.45	86.75	81.54
	0.96	190.24	103.13	99.03

TABLE S4. Different values for first, second to last and last terms of the calculated geometric progression for the lowest nGO concentration (2.96 g/L) and experimentally used dye concentration ($\rho_{dye} = 0.31\text{g/L}$) and with $L_{box} = 476.0$ nm, as shown in S3.

C. KMC Algorithm

Exciton diffusion process is ruled by FRET, where we know the rates for which the exciton emits or hops between first neighbors. For simplification, let us consider a two dimensional (2D) lattice, as shown in S3. The gray squares represent molecules to where excitons can go. We will refer to those as possible sites. In blue, we have two excitons of which where all the first immediate neighboring sites are labeled from 1 to 8. The white spaces between adjacent sites represent the average intermolecular distance, namely \bar{r} , which is an important parameter, shown in equation (1)

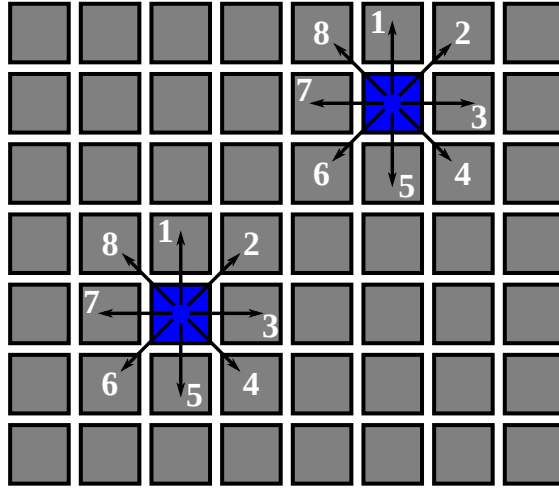


FIG. S3. Example of a 2D lattice. Gray sites represent non-excited molecules and blue represent excitons in a localized molecule, leading it to its first excited state.

Being in a 2D model, we have 9 important rates to consider, one respective to emission and eight regarding hopping possibilities. Normally, with single exciton simulations in a single material, there is only one time scale, which means the exciton can only hop to one of the neighbors or it can be recombined. The rate according to which the exciton can emit is displayed below,

$$k_{emi} = \frac{1}{\tau_{emi}}, \quad (\text{S12})$$

remembering that τ_{emi} is the exciton lifetime. When it comes to hopping to each of the neighbors, the Förster rate is

$$k_F = \frac{1}{\tau_{emi}} \left(\frac{R_F}{\alpha\mu + \bar{r}} \right)^6, \quad (\text{S13})$$

remembering that R_F is the Förster radius from the molecule in blue to any i th molecule labeled in S3. It is important to notice that for neighbors 1, 3, 5 and 7, the hopping rate is identical to (S13).

However, for neighbors 2, 4, 6 and 8, the excitons move a distance \bar{r} in two dimensions, which leads to

$$k_F^{(2)} = k_F^{(4)} = k_F^{(6)} = k_F^{(8)} = \frac{1}{\tau_{emi}} \left(\frac{R_F}{\gamma\mu + \bar{r}\sqrt{2}} \right)^6 \quad (\text{S14})$$

in which $k_F^{(i)}$ is the hopping rate to the i -th neighbor. Naturally, extending this to three dimensions raises the number of neighbors from 8 to 26, where four of them are diagonal in three dimensions, which have $\gamma\mu + \bar{r}\sqrt{3}$ in the denominator of (S13).

The probability of the i -th neighbor being chosen is calculated as

$$P_i = \frac{k_F^{(i)}}{\sum_j k_F^{(j)}} \quad (\text{S15})$$

and a random number is generated to make the selection. Notably, P_i does not depend on the emission rate. With the hopping site chosen, a second random number is generated to decide whether recombination or transfer takes place. The probability of exciton recombination is

$$P_{emi} = \frac{k_{emi}}{k_{emi} + k_F^{(i)}} = \frac{1}{1 + \left(\frac{R_F}{\gamma\mu + \bar{r}} \right)^6}. \quad (\text{S16})$$

Thus, the hopping probability can be expressed as

$$P_{hop} = 1 - P_{emi} = \frac{\left(\frac{R_F}{\gamma\mu + \bar{r}} \right)^6}{1 + \left(\frac{R_F}{\gamma\mu + \bar{r}} \right)^6}. \quad (\text{S17})$$

After each hopping takes place, the simulation clock advances from t to $t + dt$, where

$$dt = dt_{hop} = \frac{1}{k_F^{(i)}}. \quad (\text{S18})$$

By using this time step and keeping track of the times each exciton emits, ending the round in the simulation, we are able to compile time-resolved photoluminescence (TRPL) spectra. Such spectra recover an exponential decay, respecting $\exp(-t/\tau_{emi})$. However, for systems in which intermolecular distances are close to the material's Förster radius, excitons tend to fluoresce more than to hop. This happens due to the \bar{r}^{-6} dependence in the denominator of (S16), as previously mentioned.

With that in mind, we implemented a correction in the simulation's time step. In the case of an excessive number of early exciton recombination due to low probability of hopping, we implemented a third layer of decision once we had P_{emi} and P_{hop} calculated. The first correction

is to have a known time step for each decision. If the exciton was selected to fluoresce, the corresponding time step was

$$dt_{emi} = \alpha \frac{1}{\frac{1}{\tau_{emi}} \left(\frac{R_F}{\gamma\mu + \bar{r}} \right)^6} \quad (\text{S19})$$

where α is an adjustable parameter greater than 0 until 1. In the case of hopping taking place, (S18) is the respective time step. Lastly, we defined a parametric time step to improve the time scale of events based on the hopping one. It is defined as

$$dt_{step} = \alpha dt_{hop}. \quad (\text{S20})$$

Once these quantities are defined, we calculated the probability of event occurrence, stipulated as

$$P_{occ} = \frac{dt_{step}}{dt} \quad (\text{S21})$$

where dt can be dt_{emi} for when the recombination is chosen and dt_{hop} in the case of hopping taking place. Then, a third random number is drawn to decide if the selected event actually occurs during that time step or if the first two decisions are retaken. In other words, P_{occ} is a way to ponder the occurrence of events in systems that have numerically challenging parameters. In addition, it represents a chance for the exciton to stand still during different time steps, where it doesn't get recombined, but it isn't necessarily transferred.

II. ADDITIONAL RESULTS

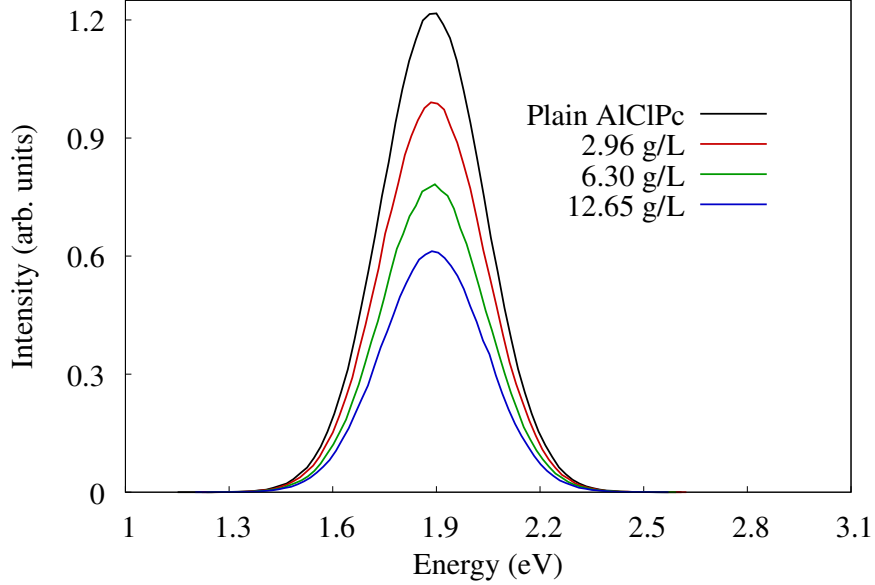


FIG. S4. Simulated fluorescence spectra for different nGO concentrations in the same cuvette with the filter effect being taken into account. This data was obtained without considering molecular aggregation.

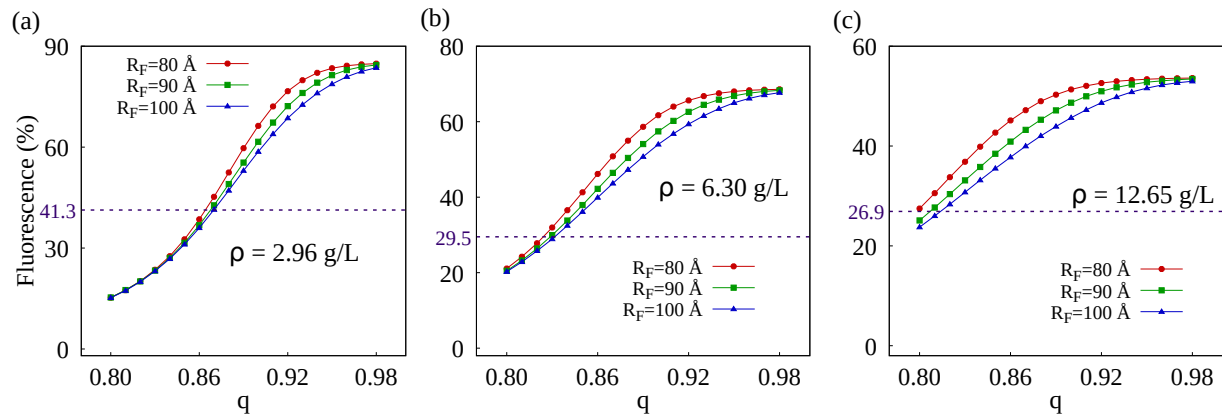


FIG. S5. Fluorescence in exciton percentage per degree of aggregation. Förster radius between dye and nGO varies from 80 \AA to 100 \AA . Average intermolecular distance of 145 \AA ($\rho_{dye} = 0.31 \text{ g/L}$).

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