

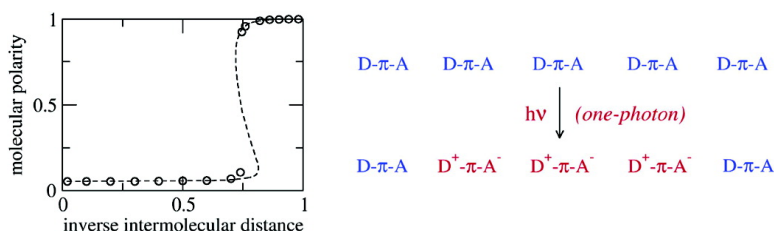
Communication

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Multielectron Transfer in Clusters of Polar-Polarizable Chromophores

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To fully exploit the promise of molecular materials for advanced applications, a thorough understanding of supramolecular structure–properties relationships is needed, a nontrivial problem because nonadditive, collective behavior appears in molecular materials as a result of intermolecular interactions.¹ Here we present a model for interacting polar and polarizable molecules that applies to clusters (crystals, films, aggregates, . . .) of push–pull chromophores for second-order nonlinear optical applications, but also captures the basic physics of charge-transfer crystals with a donor–acceptor (D–A) stack motif. We demonstrate that the molecular polarity (or the degree of charge transfer) is largely affected by supramolecular interactions, and, for attractive lattices, we recognize bistable behavior. In noncentrosymmetric structures in the bistable regime, multielectron transfer is directly triggered by single photon absorption.

The Mulliken DA dimer is the simplest model for polar-polarizable molecules.² The two basis states, $|DA\rangle$ and $|D^+A^-\rangle$, representing the neutral (N) and zwitterionic (I) states, are separated by an energy $2z_0$ and are mixed by a matrix element $-\sqrt{2}t$. The resulting ground and excited states, $|g\rangle = \sqrt{1-\rho}|DA\rangle + \sqrt{\rho}|D^+A^-\rangle$, $|e\rangle = \sqrt{\rho}|D^+A^-\rangle - \sqrt{1-\rho}|DA\rangle$, are fully defined by the parameter ρ , measuring the ground state (gs) polarity. Depending on the sign of z_0 , the gs is dominated by the N state ($\rho < 0.5$) or by the I state ($\rho > 0.5$). We consider M nonoverlapping molecules interacting via electrostatic forces:

$$H = \sum_i (2z_0 \hat{\rho}_i - \sqrt{2}t \hat{\sigma}_{x,i}) + \sum_{i>j} V_{ij} \hat{\rho}_i \hat{\rho}_j \quad (1)$$

where the ionicity operator, $\hat{\rho}_i = \hat{\sigma}_{z,i} + 1/2$, measures the polarity of the i th chromophore, $\hat{\sigma}_{x,i}$ is the x/z -Pauli matrix for the i -molecule, and V_{ij} is the electrostatic interaction between two zwitterionic molecules on ij sites. All energies are in units with $\sqrt{2}t = 1$. We model each zwitterionic molecule as a segment of unit length carrying $\pm e$ charges at the D/A ends, so that, for unscreened interactions, V_{ij} is fixed by v , the interaction between two charges at unit distance, and w , the inverse interchromophore distance. Similar results are obtained irrespective of the specific model for V_{ij} .

We diagonalize the Hamiltonian (1) for the two 1D lattices sketched in Figure 1, with up to 16 molecules, and for periodic boundary conditions. The same figure shows the evolution of the molecular polarity $\rho = \langle \hat{\rho}_i \rangle$ with the inverse intermolecular separation. Repulsive supramolecular interactions in A-lattices disfavor charge separation: ρ decreases with w , and starting with an I gs, a N state is eventually reached (Figure 1A). Just the opposite occurs for attractive supramolecular interactions (Figure 1B). The $\rho(w)$ dependence is well reproduced in the mean-field (mf) approximation. Within mf,³ the Hamiltonian (1) is factorized by imposing that each chromophore experiences the electric field generated by the surrounding. This defines a local Mulliken dimer with z_0 renormalized to $z_0 + \rho \sum_i V_{ij}/2$. The solution of the local

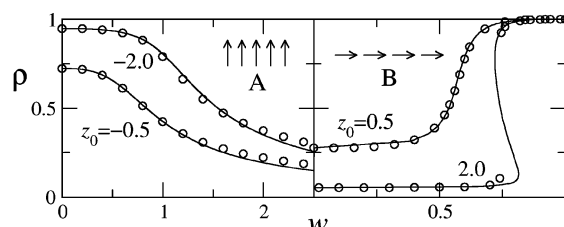


Figure 1. The gs polarity versus the inverse interchromophore distance for clusters with $\nu = 2$. Circles, exact results for $M = 16$ ($M = 14$ results are superimposed in the scale of the figures); lines, mf results for $M = \infty$.

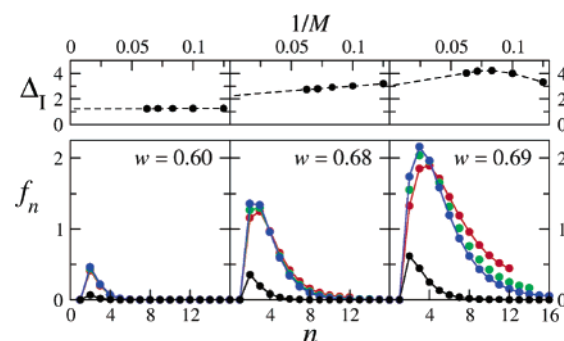


Figure 2. Top panels: the $1/M$ dependence of ΔI for a B-lattice with $\nu = 2$, $z_0 = 1.5$, and $w = 0.60, 0.68, 0.69$. Bottom panels: the corresponding n -dependence of f_n . Red, green, and blue circles refer to $|E\rangle$, for $M = 12, 14$, and 16 , respectively; black circles show gs values for $M = 16$. Lines are drawn for eye-guide purpose.

self-consistent problem is trivial.⁴ Smooth $\rho(w)$ curves are always obtained for repulsive clusters, whereas attractive lattices support discontinuous behavior. In particular, for B-lattices with $z_0 > 1$, mf predicts S-shaped $\rho(w)$ curves: the portion of the curve with negative slope corresponds to unstable states, and bistability regions appear.⁴ Exact results for $z_0 = 2$ in Figure 1B also support a discontinuous N to I crossover.

For push–pull chromophores, $\sqrt{2}t \approx 1$ eV, and $\nu \approx 2$ corresponds to typical molecular lengths (~ 10 Å).⁵ Figure 1 then suggests sizable supramolecular effects for intermolecular distances twice the molecular length. On general grounds, intermolecular interactions between largely polar and polarizable push–pull chromophores are expected to induce large variations of the molecular polarity. Recently, Ashwell and Gandolfo⁶ demonstrated that the polarity of a cationic push–pull chromophore in a Langmuir–Blodgett film is reversed by the displacement of the counterion along the molecular axis. We suggest that the molecular polarity can be tuned and eventually reversed by supramolecular interactions also in samples containing globally neutral but polar and polarizable molecules.

The physics of the system in the bistability region deserves further study. Here, we focus on the optical spectrum and calculate the average number of molecules turned zwitterionic upon photoexcitation:

$$\Delta_1 = M[\langle E|\hat{\rho}_i|E\rangle - \langle G|\hat{\rho}_i|G\rangle] \quad (2)$$

where $|G\rangle$ is the gs, and $|E\rangle$ is the excited state with the largest transition dipole moment. Figure 2, top panels, shows the $1/M$ dependence of Δ_1 calculated for a B-lattice with $v = 2$ and $z_0 = 1.5$ and for a few w values. With increasing w , the N state is driven toward the crossover regime, and Δ_1 smoothly extrapolates to $M \rightarrow \infty$ values $\approx 1.2, 2.5,$ and 3 for $w = 0.60, 0.68,$ and $0.69,$ respectively.

To investigate the nature of exact states, we define the following correlation function:

$$f_n = \sum_{i=1}^M \langle \hat{\rho}_i \hat{\rho}_{i+1} \dots \hat{\rho}_{i+n-1} \rangle - \sum_{i=1}^M \langle \hat{\rho}_i \rangle^n \quad (3)$$

where $\langle \rangle$ indicates the average on the relevant state. This function vanishes for uncorrelated states, that is, for states which are products of local (molecular) states: positive (negative) f_n indicates an increased (decreased) probability for n nearby I molecules, with respect to the uncorrelated state. Figure 2, bottom panels, shows the n -dependence of f_n calculated for $|E\rangle$. As the system is driven toward bistability (from left to right panel), the weight of states with two nearby I molecules increases fast, and for $w = 0.69$ a large probability is calculated for states with several nearby I molecules (I-droplets). Similar results are obtained by approaching the bistability region from the I side, provided $(1 - \hat{\rho}_i)$ substitutes $\hat{\rho}_i$ both in eq 2 (to define Δ_N , the number of molecules turned N upon photoexcitation) and in eq 3. For larger z_0 , the bistability region widens, and larger Δ_1 (or Δ_N) are calculated. Of course, a detailed analysis requires longer chains in this case.

Photoexcitation of B-clusters in the bistable regime directly drives a concerted multielectron transfer occurring on several nearby molecules. This contrasts sharply with the current understanding of excitations in molecular crystals.⁷⁻⁹ The standard exciton model in fact relies on the definition of a noncorrelated gs, described as the direct product of local molecular $|g\rangle$ states, as obtained, for example, in the mf approximation. Optical excitation then switches a single molecule from the local gs to the local excited state, with an overall $\Delta_{I/N} = |1 - 2\rho| \leq 1$. The dipole moment operator is a single-electron operator, and, applied to a noncorrelated gs, it cannot move more than a single electron. Yet, in the proximity of the discontinuous charge crossover, electrostatic intermolecular interactions lead to a correlated gs, as demonstrated by the sizable f_n calculated for $|G\rangle$ (black circles in Figure 2, bottom panels). Because the motion of electrons in nearby molecules is correlated, the one-electron dipole moment operator connects states where more than a single electron is transferred. In other words, I-droplets have in B-clusters large permanent dipole moments: their finite amplitude in the gs is responsible for the appearance of large transition dipole moments toward states with a large I-droplet character. Discontinuous N-I interfaces are found in other attractive lattices, like, for example, A-type lattices with antiparallel orientation of molecular dipole moments. However, the observation of photoinduced multielectron transfer requires a noncentrosymmetric lattice, to allow for large permanent dipole moments of droplet states.

Multielectron transfer appears for attractive noncentrosymmetric lattices in a narrow region of the parameter space; yet it is an

interesting phenomenon that can have important consequences in our understanding of photoconversion processes as occurring, for example, in biological systems.¹⁰ So far, multielectron transfer has only been discussed as a secondary event after photoexcitation,¹⁰ resulting from the cooperative interaction between the active electron-transfer center and the surrounding (solvation, vibrational, . . .) degrees of freedom that relax after the primary photoexcitation event. In our model, cooperativity shows up as a consequence of the intrinsically self-consistent, nonlinear interactions among polar-polarizable molecules: multielectron transfer is the primary (vertical) photoexcitation process.

The photoinduced neutral-ionic phase transition (NIT), observed in DA charge-transfer crystals,¹¹ is an interesting example of photoinduced multielectron transfer. B-lattices roughly model these materials: the relevant mf solution offered a first picture for temperature-induced NIT,⁴ and the corresponding exciton model describes exciton strings in largely N crystals.¹² The exact solution of the complete Hamiltonian offers an intriguing picture for photoinduced NIT. Current understanding of this phenomenon implies the creation, upon photon absorption, of an I (N) DA pair in a N (I) crystal. For excitation with intense light, the concentration of photoinduced I (N) sites becomes large, and electrostatic interactions, possibly cooperating with lattice degrees of freedom, drive the system to a metastable I (N) phase.¹¹ The recent observation that the excitation density needed for the transition reduces by ~ 3 if the temperature is raised from 4 to 77 K nicely fits with our picture. At 77 K, the system is in the I (noncentrosymmetric) phase, in close proximity of the bistability region, so that the absorption of a single photon can directly turn to N a droplet of a few adjacent DA pairs, thus reducing the excitation density threshold for the photoinduced transition.

In conclusion, we have demonstrated large supramolecular effects in clusters of polar-polarizable molecules: in aggregates of push-pull chromophores for nonlinear optical application, the molecular polarity is largely affected by supramolecular arrangement, and in attractive clusters, bistability regions appear. For noncentrosymmetric structures, the primary photoexcitation event in the bistability region corresponds to a concerted multielectron transfer occurring on several nearby molecules.

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