

Aggregates of Quadrupolar Dyes: Giant Two-Photon Absorption from Biexciton States

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A model for aggregates of quadrupolar (DAD or ADA) molecules is presented that relaxes the dipolar approximation for intermolecular electrostatic interactions. New effects, including the appearance of bound biexcitons in clusters of nonpolar molecules, are predicted with interesting and unforeseen consequences on the material properties. Specifically, we show that the large two-photon absorption cross-section, typical of quadrupolar chromophores, can be further amplified by orders of magnitude as a result of aggregation.

Materials with large two-photon absorption (TPA) cross-sections are in demand for diverse applications including nanofabrication,¹ optical limiting,² 3D microscopy,³ and photodynamic therapy.⁴ Organic π -conjugated chromophores with electron donor (D) and acceptor (A) groups are a prominent class of molecules for nonlinear optics (NLO), and among them, the so-called quadrupolar DAD (or, equivalently, ADA) systems are structures of choice for TPA.⁵ Excitonic interactions in multichromophores offer an interesting opportunity to amplify responses,⁶ and very high TPA cross-sections have been recently reported for molecular aggregates⁷ and supermolecules.⁸ Here we focus on multichromophoric systems based on DAD dyes as to exploit the excitonic amplification of TPA in materials that are designed for optimized TPA response at the molecular level. We demonstrate that in clusters of DAD molecules bound biexciton states appear due to intermolecular interactions, with huge TPA cross-sections, up to 2 orders of magnitude larger than for the isolated molecule, at photon frequencies well below the one-photon absorption (OPA) frequency.

A charge-resonance model was already proposed to describe optical spectra of DAD chromophores.⁹ The model accounts for three basis states: $|DAD\rangle$, corresponding to the neutral resonating structure, and $\varphi_{\pm} = (|D^+A^-D\rangle \pm |DA^-D^+\rangle)/\sqrt{2}$, combinations of the two zwitterionic structures. An energy gap (2η) separates the two degenerate zwitterionic states, φ_{\pm} , from the neutral state, φ_0 . The two symmetric states, φ_0 and φ_+ , are mixed by a matrix element ($-2t$) to yield the ground state, $|g\rangle = \sqrt{\rho}|\varphi_0\rangle + \sqrt{1-\rho}|\varphi_+\rangle$, and a symmetric excited state, $|e\rangle = \sqrt{1-\rho}|\varphi_0\rangle - \sqrt{\rho}|\varphi_+\rangle$, active in TPA. The antisymmetric φ_- state coincides with the one-photon allowed state, c . The dipole moment operator mixes φ_+ and φ_- : the relevant matrix element, μ_0 , measures the dipole moment of $|D^+A^-D\rangle$. OPA and TPA frequencies and intensities can be described in terms of the single parameter,⁹ ρ , that defines the charge distribution in the ground state as $D^{\rho/2}A^{-\rho/2}$. Dyes synthesized for TPA applications typically have $\rho \sim 0.1-0.2$, $t \sim 0.5-0.8$ eV, and $\mu_0 \sim 30-40$ D, leading to strong TPA absorption cross-sections (up

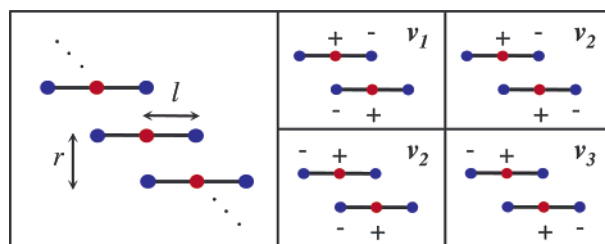


Figure 1. Left panel: a sketch of the geometry of the cluster. Right panels: the three basic electrostatic interactions between nearest-neighbor chromophores.

to 5000–10000 GM).^{5,9,10} Hereafter, $\sqrt{2}t$ (roughly amounting to 1 eV) will be used as the energy unit.

The Hamiltonian for a cluster of N chromophores is

$$H = \sum_i h_i + \sum_i V_{i,i+1} \quad (1)$$

where h_i is the charge-resonance Hamiltonian for the i -th dye, as described above, and the second term accounts for nearest-neighbor intermolecular electrostatic interactions. Common models for molecular aggregates rely on the dipolar approximation;¹¹ however, these models hardly apply to clusters of elongated molecules with intermolecular distances, r , similar to the molecular size, l (see Figure 1).

In our treatment, we relax the dipolar approximation, and in the spirit of a model already proposed for clusters of DA chromophores,¹² we describe intermolecular interactions in terms of point charges located at D and A sites, as sketched in Figure 1. The relevant interaction term in the Hamiltonian in eq 1 is

$$V_{i,i+1} = A\hat{\rho}_i\hat{\rho}_{i+1} + B\hat{\delta}_i\hat{\delta}_{i+1} + C(\hat{\rho}_i\hat{\delta}_{i+1} - \hat{\delta}_i\hat{\rho}_{i+1}) \quad (2)$$

where the two operators $\hat{\rho}_i = |\varphi_+^i\rangle\langle\varphi_+^i| + |\varphi_-^i\rangle\langle\varphi_-^i|$ and $\hat{\delta}_i = |\varphi_+^i\rangle\langle\varphi_-^i| + |\varphi_-^i\rangle\langle\varphi_+^i|$ describe the charge distribution in the i -th molecule in terms of the average charge on the central D group and of the unbalance of charge on the two A groups, respectively. The coefficients in eq 2 are linear combinations of the basic interactions, v_k , in Figure 1 and are fixed by r , l ,

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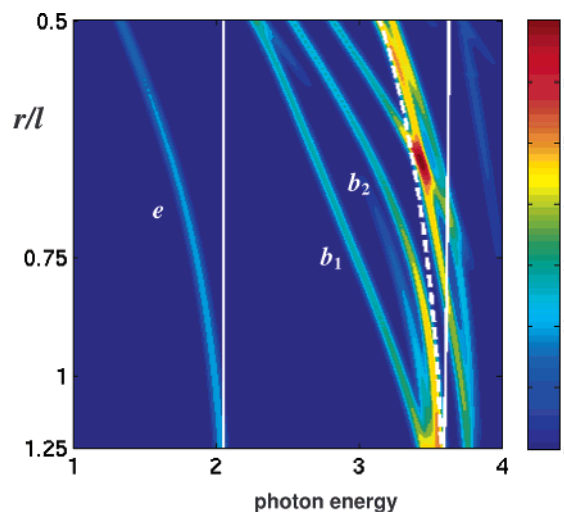


Figure 2. Color plot of the TPA cross-section (in a logarithmic scale) for a cluster of six molecules with $\eta = 1.5$ and $w = 1.8$ (all energies in $\sqrt{2}t$ units). On the x-axis is the energy of the absorbed photon; on the y-axis (in a reciprocal scale) is the intermolecular distance, r , over half the effective molecular length (l , see Figure 1). For graphical reasons, a Gaussian form, with $\sigma = 0.03$, is assigned to each transition, and weak transitions (with cross-sections more than 1 order of magnitude smaller than the TPA of the isolated molecule) are disregarded. The dashed line marks the OPA energy. The continuous white lines show results obtained in the exciton model with dipolar interactions: the lines at lower and higher energy refer to TPA and OPA processes, respectively; TPA processes related to 2c-excitations are not shown as they deviate less than 0.1 (in the energy scale) from the OPA line.

and $w = e^2/l$, the unit of electrostatic energy (see Supporting Information). Here, we consider clusters of molecules in attractive geometry, as sketched in the left panel of Figure 1, with variable r and $w = 1.8$ that, for typical t values, corresponds to $l \sim 7\text{--}11$ Å. Periodic boundary conditions are imposed to minimize finite-size effects. Exact diagonalization results for $N = 6$ are reported below. Results for $N = 4$ and 8 show negligible finite-size effects.

Figure 2 summarizes information on the r -dependence of OPA and TPA spectra for a cluster of chromophores with $\eta = 1.5$, corresponding to $\rho \cong 0.17$ for an isolated chromophore ($r \rightarrow \infty$). The color map shows the TPA cross-section with the x-axis measuring the frequency of the absorbed photon (half the transition energy) and the y-axis the intermolecular distance in units of l . The dashed white line shows the OPA frequency: as the dyes get closer, the OPA frequency lowers. This red-shift is mainly due to the slight increase of the charge separation in the chromophore, resulting from attractive intermolecular electrostatic interactions. In fact, ρ increases from ~ 0.17 for the isolated molecule ($r \rightarrow \infty$) up to ~ 0.2 for $r \cong l/2$. Similarly, the TPA trace marked as e shows that the e -state of the isolated molecule undergoes a considerable red-shift with decreasing r . This result sharply contrasts with the widely accepted view that TPA states of centrosymmetric molecules are only marginally affected by aggregation.¹¹ In the dipolar approximation, in fact, the J -interaction, responsible for the dispersion of an exciton state, is proportional to the relevant squared transition dipole moment and therefore vanishes for TPA states of centrosymmetric molecules. Indeed, the energy of the e -state turns out to be independent of r in the dipolar approximation (see the white continuous line at lowest energy in Figure 2). However, the dipolar approximation does not apply to clusters of elongated molecules: two main contributions to the red-shift of the e -band can be recognized, and both are missed in the dipolar ap-

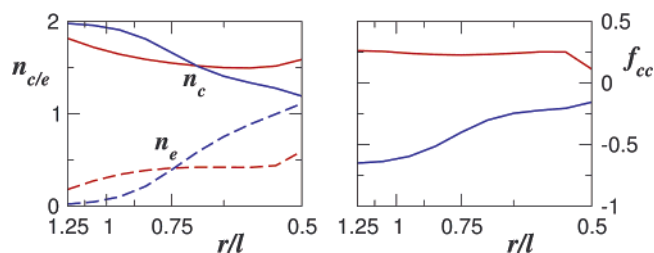


Figure 3. The number of c - (solid lines) and e - (dashed lines) excitations (left panel) and the nearest neighbor correlation function for c -excitons (right panel) shown as a function of r/l (in a reciprocal scale) for the states marked as b_1 (red lines) and b_2 (blue lines) in Figure 2.

proximation. The increase of ρ with decreasing r , responsible for the red-shift of the OPA frequency, accounts for about one-half of the total red-shift of the TPA band. The other contribution is due to the dispersion of the e -exciton band, driven by an interaction, $A\rho(1 - \rho)$, proportional to the squared transition quadrupole moment.

Beside e , several very intense TPA transitions appear at photon frequencies lower than the OPA absorption. Traces marked as b_1 and b_2 in the color plot stem from states with two c -excitations, and in fact, at large r , both features converge toward the OPA frequency (dashed white line). States with double c -excitations are resonantly enhanced in TPA, but the relevant TPA signal is masked by the superimposed OPA. However, with decreasing r , the b_1 and b_2 states split down from the 2c-band moving in a frequency region not obscured by OPA. As these states move away from the 2c-band, their resonant enhancement decreases; however, their intensity remains large, more than 1 order of magnitude larger than for the e -state (notice the logarithmic scale used for the TPA cross-section in Figure 2). This interesting phenomenon is again missed in the exciton model with dipolar interactions: in this approximation, in fact, 2c-states lie at about twice the OPA energy (see the highest energy continuous white line in Figure 2) so that relevant TPA processes would be obscured by the concomitant OPA.

To investigate the nature of b_1 and b_2 and hence the origin of their splitting from the 2c-states, we calculate the average number of c - and e -excitations in the two states as the expectation values of the number operators: $n_{c/e} = \sum_i \langle \hat{n}_{c/e}^i \rangle$, where $\hat{n}_c^i = |c^i\rangle\langle c^i|$ and $\hat{n}_e^i = |e^i\rangle\langle e^i|$ count the number of c - and e -excitations on the i -th site. In the exciton approximation, the exciton number is conserved and only integer $n_{c/e}$ are allowed: non-integer values in the left panel of Figure 3 result from the mixing of states with a different number of excitons. Specifically, at large intermolecular distances, both b_1 and b_2 are well described as 2c-states ($n_c \cong 2$). With decreasing intermolecular distance, n_c decreases for both states; in contrast, n_e increases, signaling the mixing of states with different number of excitations, and hence the failure of the excitonic approximation, with particularly large effects for b_2 . The correlation function $f_{cc} = \sum_i \langle n_c^i n_c^{i+1} \rangle - \sum_i \langle n_c^i \rangle \langle n_c^{i+1} \rangle$ measures the probability of finding two adjacent c -excitons. It ranges from $-4/N$ ($-2/3$ for $N = 6$) for a state with two non-nearest neighbor c -excitations up to $1 - 4/N$ ($1/3$ for $N = 6$) for a state with two nearest-neighbor c -excitations. The results in Figure 3 show that, for any r , b_1 has $n_c \cong 2$ and $f_{cc} \cong 0.2$ and is therefore well described as a bound c -biexciton. The behavior of b_2 is more complex: at large r , it has a strong 2c character ($n_c \cong 2$) but corresponds to an unbound exciton ($f_{cc} \cong -2/3$) with an energy approximately equal to twice the c -exciton energy. Indeed, b_2 splits down from the 2c-band at smaller r than b_1 : at these short intermolecular

distances, f_{cc} increases, but at the same time, the ultraexcitonic mixing becomes large, leading to a mixed state with an almost equal number of c - and e -excitations.

The failure of the excitonic approximation at small intermolecular distances and for highly excited states is not surprising.^{11a,12} More interesting is the formation of bound biexcitons in aggregates of centrosymmetric molecules. Whereas for b_2 the binding energy is due to both excitonic and ultraexcitonic effects for b_1 it essentially stems from exciton–exciton interactions, proportional to $A(1 - \rho)$, resulting from the variation of the molecular charge distribution upon excitation: c -excitons have a larger quadrupolar moment (a larger ρ) than the ground state so that attractive intermolecular interactions favor the clustering of c -excitations. Once again, the dipolar approximation fails: exciton–exciton interactions vanish in the dipole approximation for clusters of nonpolar dyes.¹¹

Electrostatic intermolecular interactions are known to play a major role in defining spectral properties of molecular clusters, and in this respect, the exciton model provides a simple and useful reference frame for molecular aggregates and crystals. However, common implementations of the exciton model describe electrostatic interactions in the dipolar approximation.¹¹ Here, working with clusters of quadrupolar chromophores in attractive geometry, we demonstrate that (i) the TPA state of the isolated chromophore undergoes an important red-shift with decreasing intermolecular distance and (ii) bound biexcitons appear with a huge TPA intensity at photon frequencies well below the frequency of the OPA band. Both phenomena are missed if the dipolar approximation is adopted to describe intermolecular electrostatic interactions. In general, important excitonic and ultraexcitonic effects are expected not only for one-photon allowed states (as predicted in the dipolar approximation) but also for dark states in one-photon processes, at least in aggregates of large molecules where the dipolar approximation does not apply. Nonlinear spectra of aggregates of large π -conjugated molecules characterized by a large rearrangement of molecular charges upon excitation deserve special attention, and new models must be developed that properly account for electrostatic intermolecular interactions relaxing the dipolar approximation.

Bound biexcitons as well as exciton strings have already been discussed in connection with optical properties of molecular aggregates^{6,12} or charge-transfer salts.¹³ Here, we show for the first time that bound biexciton states result in very intense TPA bands in clusters of quadrupolar DAD (or ADA) molecules at photon frequencies well below the OPA frequency. More generally, bound biexciton states can form in aggregates of centrosymmetric molecules as a consequence of attractive exciton–exciton interactions resulting from a large rearrangement of the molecular charges upon excitation: aggregates or supramolecular clusters of large and largely polarizable organic molecules with electron-donor and acceptor groups are then good candidates for the appearance of bound biexcitons. Here, we speculate that this novel effect is responsible for the observation of intense TPA signals in aggregates of pseudo-isocyanines and porphyrines;⁷ the charge-resonance model

adopted here for quadrupolar dyes does not directly apply to either of these molecular species, but a large rearrangement of the charge in the molecular units is certainly expected upon excitation, which can drive the formation of bound biexcitons.

More specifically, we suggest aggregates or multichromophoric assemblies of DAD (or ADA) chromophores as extremely promising materials for TPA: the large TPA cross-sections typical of this class of molecules can in fact be further amplified by orders of magnitude as a result of aggregation. TPA spectra and the solvatochromism of several families of DAD and ADA chromophores have been extensively investigated,^{9,10} but not much attention has been devoted so far to aggregates of quadrupolar dyes. In contrast, linear aggregates of elongated molecules are commonly observed in solution, and the aggregation geometry sketched in Figure 1a is favored by electrostatic interactions. The powerful tools of organic and supramolecular synthesis can be used to favor the required aggregation or even to build multichromophoric systems with the desired geometry. An effort in this direction is expected to amplify the large TPA responses of quadrupolar dyes by at least an order of magnitude.

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Supporting Information Available: Expressions and figures for electrostatic interactions. Complete ref 5a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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