

Supporting Information

For

Recent Advances of Multiphoton Absorption in Metal-Organic Frameworks

Sebastian J. Weishäupl,^{‡ab} David C. Mayer,^{‡ab} Cui Yang,^{cd} Pushpendra Kumar,^{be} Harald Oberhofer,^{bf} Roland A. Fischer,^{ab} Jürgen Hauer,^{*bc} and Alexander Pöthig^{*ab}

^a Chair of Inorganic and Metal-Organic Chemistry, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85748 Garching.

^b Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching. E-mail: alexander.poethig@tum.de; juergen.hauer@tum.de

^c Professorship of Dynamic Spectroscopy, Lichtenbergstraße 4, 85748 Garching

^d Department of Physics, Technical University of Munich, James-Franck-Straße 1, 85748 Garching.

^e Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz.

^f Chair for Theoretical Chemistry, Lichtenbergstraße 4, 85748 Garching.

[‡] *These authors contributed equally to this work.*

1 Two-photon probe in an excited state dimer

To derive an exemplary understanding of two-photon absorption in interacting molecules, we will consider two interacting molecules and describe their excited states in the framework of exciton theory, a so-called excited state dimer.¹ Two molecules, "1" and "2", each with two active orbitals, form an orthonormal set of four orbitals: initial (i) and final (f) on fragment 1 and initial (i') and final (f') on fragment 2.² The initial orbitals are doubly occupied in the ground state and the final orbitals are unoccupied. Considering these orbitals it is possible to construct four states by single excitations from the ground state: $|1^*2\rangle$, $|12^*\rangle$, $|1^-2^+\rangle$ and $|1^+2^-\rangle$.

In the presence of symmetry, these states are pairwise degenerate, yielding delocalized eigenfunctions. At long intermolecular separations, the wave functions exist in degenerate pairs and can be divided into two types:

$$\begin{aligned}
 |\sigma\rangle &= \frac{1}{\sqrt{2}}(|1^*2\rangle - |12^*\rangle) \\
 |\gamma\rangle &= \frac{1}{\sqrt{2}}(|1^*2\rangle + |12^*\rangle) \\
 |\delta\rangle &= \frac{1}{\sqrt{2}}(|1^-2^+\rangle + |1^+2^-\rangle) \\
 |\rho\rangle &= \frac{1}{\sqrt{2}}(|1^-2^+\rangle - |1^+2^-\rangle)
 \end{aligned}
 \tag{1}$$

Where $|\sigma\rangle$ and $|\gamma\rangle$ describe Frenkel excitonic resonance states, while $|\delta\rangle$ and $|\rho\rangle$ are charge-transfer or charge-resonance states. The states here are given in the localized basis set. In the following we will only consider Frenkel exciton states $|\sigma\rangle$ and $|\gamma\rangle$. The energy expression of the latter can be derived by diagonalization of the Frenkel exciton Hamiltonian:³

$$\hat{H} = \begin{pmatrix} \tilde{E}_\sigma & J \\ J & \tilde{E}_\gamma \end{pmatrix}
 \tag{2}$$

The coupling $J = V(\mu_1, \mu_2)$ between the transition dipole moments μ of the two molecules "1" and "2" determines the off-diagonal elements of the Hamiltonian, whereas the diagonal elements here are the excited state energies of $|\sigma\rangle$ and $|\gamma\rangle$ with contributions from interactions of static dipoles (e.g. in the case of a dimer of asymmetric monomers): $\tilde{E}_i = E_i + \delta E_i$.⁴

The interaction energy $V(\mu_1, \mu_2)$ between transition dipoles at positions R_1 and R_2 can be approximated using e.g. classical dipole-dipole interaction:⁵

$$V(\mu_1, \mu_2) = \frac{1}{\epsilon} \left[\frac{\mu_1 \cdot \mu_2}{|R_{12}|^3} - \frac{3(\mu_1 \cdot R_{12})(\mu_2 \cdot R_{12})}{|R_{12}|^5} \right]
 \tag{3}$$

If the two molecules are of the same species, $\tilde{E}_\sigma = \tilde{E}_\gamma$ applies. We confine ourselves to the case, where the diagonal energies are similar, $\tilde{E}_\sigma = \tilde{E}_\gamma = E$. We further approximate E by the monomer excitation energy, E_M . In this case the energies of the excitonic eigenstates $|\sigma\rangle$ and $|\gamma\rangle$ are $E_M \pm J$. If the two molecules are parallel aligned or in a face-to-tail arrangement with respect to each other, then only one of the two states is dipole allowed and the other is dipole forbidden (J- or H-type aggregation).⁶ If the two transition dipole moments are neither parallel nor antiparallel to each other, the two excitonic eigenstates have finite transition dipole moments in different directions. In this case, the linear one-photon absorption spectrum of the dimer consists of two peaks with different polarization dependencies, the Davydov splitting.⁴

In further following our assumptions, we define the total dipole moment operator of interacting molecules as a sum of the dipole moment operators of the separate molecules, $\hat{\mu} = \hat{\mu}_1 + \hat{\mu}_2$ and define the static dipole moment of the molecules in their ground and excited state as:⁷

$$\begin{aligned}\langle i | \hat{\mu}_i | i \rangle &= M_{g,i} \\ \langle i^* | \hat{\mu}_i | i^* \rangle &= M_{ex,i} \\ i &= 1,2\end{aligned}\tag{4}$$

Similarly, transition dipole operator matrix elements can be defined as:

$$\begin{aligned}\langle i | \hat{\mu}_i | i^* \rangle &= \langle i^* | \hat{\mu}_i | i \rangle = \mu_i \\ i &= 1,2\end{aligned}\tag{5}$$

Equations (4) and (5) allow to evaluate the dipole moment operator matrix elements. Note that the ground state wavefunction has the form $G = |12\rangle$:

$$\begin{aligned}\langle G | \hat{\mu} | G \rangle &= M_{g,1} + M_{g,2} \\ \langle \sigma | \hat{\mu} | \sigma \rangle &= \langle \gamma | \hat{\mu} | \gamma \rangle = \frac{1}{2}(M_{ex,1} + M_{ex,2} + M_{g,1} + M_{g,2}) \\ \langle \sigma | \hat{\mu} | \gamma \rangle &= \langle \gamma | \hat{\mu} | \sigma \rangle = \frac{1}{2}(-M_{ex,1} + M_{ex,2} + M_{g,1} - M_{g,2}) \\ \langle \sigma | \hat{\mu} | G \rangle &= \langle \gamma | \hat{\mu} | G \rangle = \frac{1}{\sqrt{2}}(\mu_1 \pm \mu_2)\end{aligned}\tag{6}$$

Up to this point we have introduced all quantities needed to describe the two-photon probability of the excited dimer within a sum-over-state formalism (SOS).⁸ The latter is commonly been described by the following equations:

$$\langle \delta^{TPA} \rangle = \frac{1}{15} \sum_{ab} (2S_{ab}\bar{S}_{ab} + S_{aa}\bar{S}_{bb})$$

$$S_{ab}^{if}(\omega_1, \omega_2) = \frac{1}{\hbar} \sum_{n \neq i} \left\{ \frac{\langle i | \mu_a | n \rangle - \langle n | \bar{\mu}_b | f \rangle}{\omega_{ni} - \omega_1} + \frac{\langle i | \mu_b | n \rangle - \langle n | \bar{\mu}_a | f \rangle}{\omega_{ni} - \omega_2} \right\} \quad (7)$$

With δ^{TPA} as two-photon absorption strength, S_{ab} as the two-photon absorption tensor elements, i the ground state, n the intermediate state and f the final state. ω_{ni} is the energy difference between the ground and intermediate states and ω_1 , respectively ω_2 are the both incoming photons. For our model system, two states in the case of resonance to the low-lying exciton states, as well as three states in the case of resonance to the high-lying exciton state needs to be included in the SOS equation (7), which leads to so-called few-state models.⁹

$$\langle \sigma_2 \rangle \propto \frac{\mu_{if}^2 \Delta M_{if}^2}{\left(\frac{E_{if}}{2}\right)^2 \Gamma} \quad (8)$$

With equation (8) for a two-state system and equation (9) in case of a three-state system.

$$\langle \sigma_2 \rangle \propto \frac{\mu_{in}^2 \mu_{nf}^2}{\left(E_{in} - \frac{E_{if}}{2}\right)^2 \Gamma} \quad (9)$$

Γ is a damping factor, μ_{in} and μ_{if} are the transition dipole moments between initial and intermediate, respectively initial and final state. The E 's are the excited state energies and ΔM_{if} is the difference of the static dipole moments of the initial and excited states.

In the following we will consider two-photon absorption in a perfectly aligned J-type aggregate (face-to-tail orientation of the dipole moments) and will parametrize equation (8) and (9) by the derived quantities for the excited state dimer above. In the case of a J-type alignment, the optical properties of the $|\sigma\rangle$ state is similar to the monomer, however, $|\sigma\rangle$ holds all oscillator strength and the transition dipole moment scales by a factor of $\sqrt{2}$. The linear absorption spectrum shows a single, red-shifted band compared to the monomer species, where the strength of the red-shift is dependent of the coupling strength.¹⁰ To explain the attendance of two-photon absorption in the coupled dimer, the systems needs to be made centrosymmetric by vanishing values of static dipole moments in the ground and excited state.⁷ In the case of a centrosymmetric J-type aggregate the low-lying $|\sigma\rangle$ state will hold ungerade symmetry and therefore is two-photon forbidden, however, the high-lying $|\gamma\rangle$ state will hold gerade symmetry and thus is two-photon allowed. In assuming inversion symmetry, equations (6) reduce to:

$$\langle G | \hat{\mu} | G \rangle = 0 \quad (10)$$

$$\begin{aligned}
\langle \sigma | \hat{\mu} | \sigma \rangle &= \langle \gamma | \hat{\mu} | \gamma \rangle = 0 \\
\langle \sigma | \hat{\mu} | \gamma \rangle &= \langle \gamma | \hat{\mu} | \sigma \rangle = (M_{ex,1} - M_{g,1}) = \Delta M_{ex,g}^M \\
\langle \sigma | \hat{\mu} | G \rangle &= \langle \gamma | \hat{\mu} | G \rangle = \sqrt{2} \mu_M
\end{aligned}$$

Inserting above quantities together with the derived energies into equation (9) gives an expression for the two-photon absorption strength into the high-lying state $|\gamma\rangle$ of the excited doublet:

$$\langle \sigma_2 \rangle \propto \frac{\mu_M^2 \Delta M_{ex,g}^M{}^2}{2(E_M - 3J)^2 \Gamma} \quad (11)$$

One immediately recognizes that the two-photon transition probability can be enhanced by molecular factors of the monomer (the transition dipole moment and the difference of excited state and ground state dipole moments) as well as factors concerning the intermolecular interactions between the single monomers (addressing the coupling constant J). The two-photon absorption spectrum will show a single peak, blue-shifted with respect to the one-photon monomer absorption spectrum (depending also on the coupling strength).

Finally, a comparison of equation (11) with the equation of the two-photon absorption strength for the monomer species (equation (8) parametrized by monomer quantities) provides a first insight into the enhancement of the two-photon activity as a function of coupling strength.

$$\begin{aligned}
\frac{\langle \sigma_2 \rangle^{Dimer}}{\langle \sigma_2 \rangle^{Monomer}} &= \xi = \frac{\mu_M^2 \Delta M_{ex,g}^M{}^2}{2(E_M - 3J)^2 \Gamma} \times \frac{\left(\frac{E_M}{2}\right)^2 \Gamma}{\mu_M^2 \Delta M_{ex,g}^M{}^2} \\
\xi &= \frac{1}{2} \left(\frac{E_M}{E_M - 3J} \right)^2 \quad (12)
\end{aligned}$$

One finds that the ratio between the respective two-photon absorption strengths are exclusively dependent on the monomer excitation energy and the excitonic coupling strengths. The latter, however, is a function of the molecular alignment of the monomer species and can be tuned by geometrical parameters (cf. equation 3, the distance and the mutual positions of transition dipoles). This fact suggests the two-photon response to be controllable by structural aspects in molecular functional materials, such as metal-organic frameworks. Figure S1 shows the ξ -term as a function of the coupling constant J . The enhanced two-photon absorptivity of the excited state doublet with regard to the monomer species can be understood via reducing the energy of the $|\sigma\rangle$ state, approaching a double resonance situation.

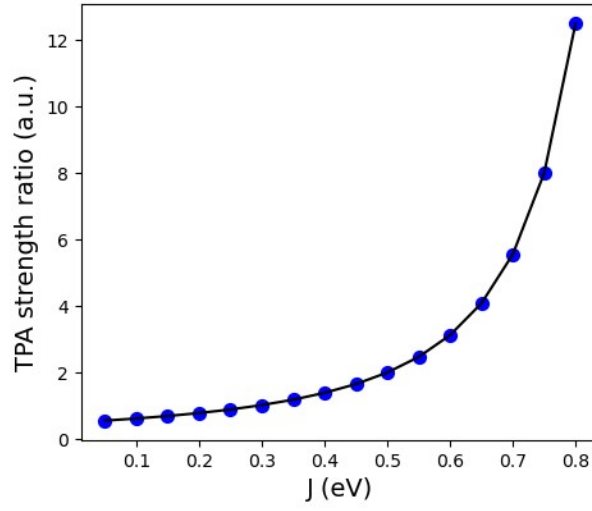


Figure S1. ξ -term as a function of the excitonic coupling constant. The plot reveals an enhanced TPA response of a coupled excited state dimer with respect to the monomer species by increasing the coupling constant. We used a E_M of 3.0 eV.

2 Two-photon probe in an excitonically coupled manifold – the case of one-exciton states and size enhancement

In this section we discuss two-photon absorption into the first exciton manifold of a periodic molecular aggregate of N molecules. The Hamiltonian of singly excited states takes the form:¹¹

$$\hat{H} = \sum_n \tilde{\omega}_n B_n^\dagger B_n + \sum_{m,n(m \neq n)} J_{nm} B_m^\dagger B_n \quad (13)$$

With $\tilde{\omega}_n$ as the diagonal elements of the Frenkel Hamiltonian matrix and the J_{nm} coupling of transition dipole moments of neighbored molecules. $B_n^\dagger B_n$ are creation and annihilation operators, respectively. In treating a linear aggregate, we will apply periodic boundary conditions, neglecting effects of chain ends. For a chain of N coupled monomers, the wave function e.g. takes the form:

$$|k_m\rangle = \sqrt{\frac{2}{N+1}} \sum_m |m\rangle \sin\left(\frac{\pi kn}{N+1}\right) \quad (14)$$

The corresponding matrix is diagonal, and its eigenvalues can be obtained by diagonalization, giving access to the eigenenergies and the eigenvectors. Following similar arguments as introduced in the case of a two-state system above, the dipole moments of the dipole operator for excitation from the ground state to the lowest state of the 1st exciton manifold ($\langle k_0 | \hat{\mu} | G \rangle$), as the excited-to-excited state transitions between the lowest and highest state of the 1st exciton manifold ($\langle k_m | \hat{\mu} | k_0 \rangle$) of a linear aggregate can be written as follows.⁴

$$\begin{aligned} \langle k_0 | \hat{\mu} | G \rangle &\propto \sqrt{N} \mu_M \\ \langle k_m | \hat{\mu} | k_0 \rangle &\propto \Delta M_{ex,g}^M \end{aligned} \quad (15)$$

Equation 15 provides a preliminary understanding of the size scaling of two-photon absorption in a linear aggregate, meaning the influence of the number of coupled chromophores on the TPA response. Considering equation 9 and equations 15, one finds that the TPA strength scales linear with the number of coupled dimers, namely $\langle \sigma^{TPA} \rangle \propto N \mu_M^2 \Delta M_{ex,g}^{M^2}$. Considering transitions from the ground state to the various k_m states, states with an even quantum number ($k_0, k_2, k_4 \dots$) hold oscillator strength, whereas states with an odd quantum number ($k_1, k_3, k_5 \dots$) are principally two-photon allowed.

3 Two-photon probe in an excitonically coupled manifold – the case of two-exciton states and size-enhancement

As has been introduced above, the Frenkel exciton Hamiltonian (equation 13), describes aggregate eigenstates, which split into different sets of linear combinations of single-molecule excitations, the so-called N-exciton bands.¹¹ Where in the preceding section, two-photon absorption into the lowest energy band, the one-exciton band of a linear aggregate was described, we here will focus on TPA into the two-exciton band. In the latter, N molecules on the aggregate chain share two single-molecule excitations. The two-exciton band is centered at twice the single-molecule transition frequency and has a width of eight times the interaction energy J . Two-exciton bands can exclusively be probed by nonlinear optical absorption, as optical transitions can only occur between adjacent exciton bands. The states of the two-exciton band are characterized by two quantum numbers, k_1 and k_2 . The eigenfrequencies are associated with both quantum numbers and are the sum of two independent one-exciton eigenfrequencies. Note that the wavefunctions of the two-exciton band are not the product of two independent one-exciton wavefunctions, a direct consequence of the Pauli exclusion principle. Table S1 summarizes analytical expressions for the eigenfrequencies and the transition dipole moments of one- and two-exciton bands of a linear molecular aggregate.

When two-photon resonance approaches twice the exciton resonance, TPA into the two-exciton manifold scales with a N^2 prefactor, which can be easily seen from the expressions of the transition dipole moments of the one- and two-exciton bands and equation 9 (transition from the ground state

to the one-exciton band scales with $\mu_M\sqrt{N}$, plus the transition from the one- to the two-exciton band). A more comprehensive analysis of the underlying physics can be found elsewhere.^{12, 13}

In summary the above presented analysis attest to a number of preliminary statements. First, size-dependencies of multi-photon absorption processes in molecular aggregates are a direct consequence of correlated molecular polarizations (enhanced transition dipole moments) and resonance effects, which will retain its validity as long as the aggregate is small compared to the optical wavelength and $N \gg n$, with n is the order of the MPA process.¹² Second, two-photon absorption processes into the two lowest exciton bands of molecular aggregates show a scaling with the number of coupled chromophores, which is predicted to be linear in N (in the case of the 1st exciton manifold), respectively N^2 (in the case of the two-exciton band) to a first order. Third, the strength of excitonic coupling determines the energy levels of the system and so the resonance situation. Consequently, enhanced coupling strength reduce the detuning factor, while simultaneously strengthen the two-photon absorptivity (cf. Figure S1 and equation 12).

Table S1. Analytical expressions for the eigenfrequencies and the transition dipole moments of the one and two-exciton bands of a linear molecular aggregate.

<i>One-exciton band</i>	
Eigenfrequencies	$\Omega_k = \omega_n + 2V\cos\left(\frac{\pi k}{N+1}\right)$
Transition dipole moment ^a	$\mu_{ik} = \mu_M \sqrt{\frac{2}{N+1}} \frac{1 - (-1)^k}{2} \cot\left[\frac{\pi k}{2(N+1)}\right]$
<i>Two-exciton band</i>	
Eigenfrequencies	$\Omega_{k_1 k_2}^L = \Omega_{k_1} + \Omega_{k_2}$
Transition dipole moment ^b	$\mu_{k_1 k_2, k}$ $= \mu_M \sqrt{\frac{2}{N+1}} \left(\delta_{k_2, k} \frac{1 - (-1)^{k_1}}{2} \cot\left[\frac{\pi k_1}{2(N+1)}\right] \right.$ $\left. \left\{ \cot\left[\frac{\pi k_1}{2(N+1)}\right] + \cot\left[\frac{\pi k_2}{2(N+1)}\right] \right\} + \frac{1}{2} (\delta_{k_1} + \right.$ $\left. \left\{ \cot\left[\frac{\pi k_1}{2(N+1)}\right] - \cot\left[\frac{\pi k_2}{2(N+1)}\right] \right\} \right)$

^aNote that the transition dipole moment from the ground to the one-exciton band roughly scales as $\mu_M\sqrt{N}$. The $k=1$ state holds the most oscillator strength with $0.81(N+1)\mu_{mon}^2$

^bThe dominant transition from the one-exciton to the two-exciton band is the $k=1, k_1=2, k_2=1$ transition, which holds the highest oscillator strength with $1.27(N+1)\mu_M^2$

1. M. Kasha, in *Spectroscopy of the Excited State*, eds. B. Di Bartolo, D. Pacheco and V. Goldberg, Springer US, Boston, MA, 1976, DOI: 10.1007/978-1-4684-2793-6_12, pp. 337-363.
2. A. L. L. East and E. C. Lim, *The Journal of Chemical Physics*, 2000, **113**, 8981-8994.
3. C. J. Bardeen, *Annual Review of Physical Chemistry*, 2014, **65**, 127-148.
4. S. Abe, *Chemical Physics*, 2001, **264**, 355-363.
5. T. Brixner, R. Hildner, J. Köhler, C. Lambert and F. Würthner, *Advanced Energy Materials*, 2017, **7**, 1700236.
6. M. Kasha, H. Rawls and M. El-Bayoumi, *Pure and Applied Chemistry - PURE APPL CHEM*, 1965, **11**, 371-392.
7. A. Piryatinski and R. T. Deck, *Chemical Physics Letters*, 1997, **269**, 156-160.
8. M. T. P. Beerepoot, D. H. Friese, N. H. List, J. Kongsted and K. Ruud, *Physical Chemistry Chemical Physics*, 2015, **17**, 19306-19314.
9. D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder and J.-L. Brédas, *Advanced Functional Materials*, 2002, **12**, 631-641.
10. N. J. Hestand and F. C. Spano, *Chemical Reviews*, 2018, **118**, 7069-7163.
11. M. v. Burgel, D. A. Wiersma and K. Duppen, *The Journal of Chemical Physics*, 1995, **102**, 20-33.
12. F. C. Spano, *Physical Review B*, 1992, **46**, 13017-13034.
13. F. C. Spano and S. Mukamel, *Physical Review Letters*, 1991, **66**, 1197-1200.