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Enhanced optical nonlinearity of hybrid excitons in an inorganic semiconducting quantum dot covered by an organic layer

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We study excited states in an inorganic semiconducting quantum dot that is covered by a thin organic layer. The resonant energy transfer due to dipole-dipole interaction leads to the appearance of new states, mixed Wannier-Mott and Frenkel excitons (hybrid excitons). These new states have quite remarkable properties such as large optical nonlinearities and short lifetimes, which should be especially interesting with respect to applications in nonlinear optics. The parameter, governing the strength of the coupling between the two excitonic states, depends on the size of the system and can, therefore, be controlled experimentally. [S0163-1829(98)06703-4]

I. INTRODUCTION

As has been noted recently,[1,2] a new type of excitonic state in organic-inorganic heterostructures may appear due to resonant mixing of Wannier-Mott and Frenkel excitons. These hybrid excitons have already been discussed for some simple geometries such as quasi-two-dimensional quantum films[1] and quasi-one-dimensional, parallel organic and inorganic semiconducting quantum wires.[2] Now it seems to be of some practical interest to study the properties of the hybrid excitons in a spherical system, since such quantum dots have already been fabricated.[3,4]

We are interested in the nonlinear optical polarizability, determined by $\chi^{(3)}$. The results for the new hybrid state will be compared to those of the Wannier-Mott and Frenkel exciton states in order to show that further and more detailed studies of such composite systems are of practical interest.

In Sec. II we propose our model starting with the Wannier-Mott exciton states in the quantum dot (Sec. II A) and the Frenkel exciton states in the organic layer (Sec. II B and Appendix A). The hybrid exciton Hamiltonian is given in Sec. II C. The nonlinear optical susceptibility and the decay rates are calculated and compared to the results, obtained for the uncoupled Wannier-Mott and Frenkel excitons, in Sec. III and in Sec. IV. A detailed calculation of the hybridization parameter is given in the Appendix B.

II. THE MODEL

The heterostructure consists of an inorganic semiconducting sphere that is covered by a thin organic layer. The excitations in the inorganic quantum dot are Wannier-Mott excitons whereas in the organic layer we have Frenkel excitons that can move between lattice sites due to the transfer matrix element. The coupling between the two excitons is governed by the hybridization parameter Γ,

$$\Gamma=\langle 1_{\mathrm{F}}|H_{\mathrm{int}}|1_{\mathrm{WM}}\rangle, \tag{1}$$

the physical process behind this coupling is, for example, the creation of the Wannier-Mott exciton state in the quantum dot and the annihilation of the Frenkel exciton in the organic layer due to the Coulomb interaction. The Coulomb interaction causes a nonvanishing matrix element between the two exciton states.

The state $|1_{\mathrm{WM}}\rangle$ describes one Wannier-Mott exciton occupying the lowest state in the quantum dot, analogously $|1_F\rangle$ describes one Frenkel exciton occupying the lowest state in the organic layer. The interaction Hamiltonian H_{int} between the two materials is given by

$$H_{\mathrm{int}}=-\int d^3r\vec{P}(\vec{r})\cdot\vec{E}(\vec{r}), \tag{2}$$

and the integration is carried out over the whole volume of the heterostructure. Here $\vec{P}(\vec{r})$ is the interband polarization operator for the Wannier-Mott excitons

$$\vec{P}(\vec{r})=\vec{\mu}_{\mathrm{WM}}[\hat{\psi}_e^\dagger(\vec{r})\hat{\psi}_h^\dagger(\vec{r})+\hat{\psi}_h(\vec{r})\hat{\psi}_e(\vec{r})], \tag{3}$$

$\hat{\psi}_{e(h)}^\dagger(\vec{r})$ creates an electron (hole) at $\vec{r}$ in the quantum dot and $\vec{\mu}_{\mathrm{WM}}$ is the transition dipole moment for the Wannier-Mott exciton. Its value can be estimated from the transverse-longitudinal splitting of the excitonic band.[5]

The size of the considered heterostructure is considerably smaller than the wavelength of light that corresponds to the transition between excited and ground states, so that retardation effects may be neglected. Then the operator of the electric field in the semiconducting quantum dot created by the Frenkel excitons in the organic layer is

$$E_i(\vec{r}) = -\sum_{\vec{n}} \left[\delta_{ij} - \frac{3(\vec{r}-\vec{r}_{\vec{n}})_i(\vec{r}-\vec{r}_{\vec{n}})_j}{|\vec{r}-\vec{r}_{\vec{n}}|^2} \right] \frac{\mu_{F,j}}{\epsilon|\vec{r}-\vec{r}_{\vec{n}}|^3}(A^\dagger_{\vec{n}}+A_{\vec{n}}). \tag{4}$$

The summation runs over the lattice sites $\vec{n}$ with radius vector $\vec{r}_{\vec{n}}$ of the molecular lattice. $A^\dagger_{\vec{n}}$ is the creation operator of the Frenkel exciton at lattice site $\vec{n}$ and $\vec{\mu}_F$ is the transition dipole moment of the Frenkel exciton. Although there are three dielectric functions involved in our model—one for the quantum dot, one for the organic layer, and one for the surrounding material—we assume that the differences between them are small as compared to their moduli. Thus there is only one dielectric function ϵ present in our formulas.

The expression for the hybridization parameter can be found in the Appendix B.

A. Excitations in the quantum dot

As in Ref. 6 our calculations of the exciton states in the semiconductor quantum dot are based upon the effective-mass approximation. This means that the quantum dot is of macroscopic size as compared to the size of the unit cell of the inorganic material. Furthermore we use the weak-confinement limit, i.e., $R_D \gg a_B$, where a_B is the Bohr radius of the Wannier-Mott exciton and R_D is the radius of the quantum dot. In this limit we can neglect the influence of polarization charges upon the electron and the hole in the quantum dot since the ratio between the Coulomb interaction and the potential of these polarization charges is $V_{\mathrm{Coul}}/V_{\mathrm{Pol}} \sim R_D/a_B \gg 1$. The influence of the polarization charges was discussed by Brus.[7,8] We restrict ourselves to the lowest state in the quantum dot and use the following Hamiltonian (boson model[9,10])

$$H_{\mathrm{WM}} = E_{\mathrm{WM}} B^\dagger B + V_0 B^\dagger B^\dagger B B, \tag{5}$$

where $B^\dagger$ creates a Wannier-Mott exciton in the lowest state according to

$$B^\dagger|0\rangle = |1_{\mathrm{WM}}\rangle, \tag{6}$$

and the same state occupied with two Wannier-Mott excitons is

$$\frac{1}{\sqrt{2}} B^\dagger B^\dagger |0\rangle = |2_{\mathrm{WM}}\rangle. \tag{7}$$

The energy of the lowest one-exciton state in the quantum dot is

$$E_{\mathrm{WM}} = E_{\mathrm{g}} - E_{\mathrm{Ry}} + \frac{\hbar^2}{2M}\left(\frac{\pi}{R_D}\right)^2, \tag{8}$$

with M being the total effective mass of the electron and the hole, E_{g} the gap between the relevant conduction and valence bands, and E_{Ry} the effective Rydberg energy. V_0 is the interaction between the two Wannier-Mott excitons in the quantum dot, which is the Coulomb interaction between the four particles, two electrons, and two holes. An expression for V_0 is given by[11–13]

$$V_0 = f\left(\frac{a_B}{R_D}\right)^3 E_{\mathrm{Ry}}, \tag{9}$$

where f is a numerical factor of the order of unity. For instance, $f=3.168$ for CuCl. It is essential to note the dependence of V_0 on the ratio of the Bohr radius a_B to the radius of the quantum dot R_D. For very large quantum dots, compared to the size of the exciton, there is almost no interaction between the excitons and thus there will be no nonlinear susceptibility. The excitons behave as harmonic oscillators, showing no optical nonlinearity. On the other hand, the weak-confinement limit has to be satisfied, i.e., the radius of the dot must be considerably larger than the Bohr radius. Therefore, we have a competition between the weak-confinement assumption and the wish for a large optical nonlinearity. In the framework of the considered weak-confinement regime the favorable situation occurs in the limit $R_D \gtrsim a_B$. We will discuss the limitations for large optical nonlinearities in Sec. III.

B. Excitations in the molecular layer

We start from the microscopic Hamiltonian for Frenkel excitons,

$$H_{\mathrm{F}} = \varepsilon \sum_{\vec{n}} A^\dagger_{\vec{n}} A_{\vec{n}} + \sum_{\substack{\vec{n},\vec{n}' \\ \vec{n}\neq\vec{n}'}} J_{|\vec{n}-\vec{n}'|}(A^\dagger_{\vec{n}} A_{\vec{n}'} + A^\dagger_{\vec{n}'} A_{\vec{n}}), \tag{10}$$

where ε is the excitation energy of the molecule at lattice site $\vec{n}$ and $J_{|\vec{n}-\vec{n}'|}$ is the transfer matrix element which is mainly determined by dipole-dipole interaction. The exact commutation relations are

$$[A_{\vec{n}}, A^\dagger_{\vec{n}}]_+ = 1, \quad (A_{\vec{n}})^2 = (A^\dagger_{\vec{n}})^2 = 0,$$

$$[A_{\vec{n}}, A_{\vec{n}'}]_- = [A^\dagger_{\vec{n}}, A^\dagger_{\vec{n}'}]_- = [A_{\vec{n}}, A^\dagger_{\vec{n}'}]_- = 0 \quad \text{if} \quad \vec{n}\neq\vec{n}'. \tag{11}$$

The lowest Frenkel exciton state can be written in the occupation number representation as

$$|1_{\mathrm{F}}\rangle = \sum_{\vec{n}} \psi_F(\vec{n}) A^\dagger_{\vec{n}} |0\rangle,$$

and the two-particle state as

$$|2_{\mathrm{F}}\rangle = \sum_{\substack{\vec{n},\vec{n}' \\ \vec{n}\neq\vec{n}'}} \psi_F(\vec{n})\psi_F(\vec{n}') A^\dagger_{\vec{n}} A^\dagger_{\vec{n}'} |0\rangle.$$

The two-particle state is written as a product of one particle states, for the following reason: For Wannier-Mott excitons we can roughly estimate that the density, for which the exciton-exciton interaction becomes important, is of the order $n_{\mathrm{WM}} \sim 1/a_B^3$. Since the interaction between the Frenkel excitons is only of short range we get $n_F \sim 1/a_{\mathrm{org}}^3$. The ratio of these densities is, therefore,

$$\frac{n_{\mathrm{WM}}}{n_F} \sim \left(\frac{a_{\mathrm{org}}}{a_B}\right)^3. \tag{12}$$

This means that we can neglect the interaction between Frenkel excitons because the density, at which the interaction between two Frenkel excitons will be important, is much larger than the one of Wannier-Mott excitons. Taking for instance $a_B \approx 80$ Å and $a_{\text{org}} \approx 5$ Å, the above ratio is 2.4×10^{-4}.

A detailed calculation of the wave function for the Frenkel exciton can be found in the Appendix A.

C. The hybrid exciton

Taking into account only the lowest state both for Wannier-Mott and Frenkel excitons, the Hamiltonian of the coupled system is

$$H_{\text{total}} = E_{\text{WM}} B^\dagger B + V_0 B^\dagger B^\dagger B B + E_{\text{F}} A^\dagger A + \Gamma^* A B^\dagger + \Gamma B A^\dagger, \tag{13}$$

and the interaction is described by the hybridization parameter [Eq. (1)]. From now on we assume that all operators obey Bose commutation relations. For vanishing interaction V_0, the Hamiltonian could readily be diagonalized in terms of new operators $h_\pm$:

$$h_\pm^\dagger = u_\pm A^\dagger + v_\pm B^\dagger. \tag{14}$$

$h_\pm^\dagger$ and its conjugate $h_\pm$ are Bose operators creating a hybrid exciton. They are linear combinations of Wannier-Mott and Frenkel exciton operators where the contribution of the basic states to the new hybrid state is determined by the coefficients $u_\pm$ and $v_\pm$. The states $|\text{Hy}\pm\rangle = h_\pm^\dagger |0\rangle$ are the new hybrid states. The coefficients are given by

$$u_\pm = u_\pm^* = \frac{|\Gamma|}{\sqrt{|E_F - E_{\text{Hy}\pm}|^2 + |\Gamma|^2}},$$

$$v_\pm = v_\pm^* = \pm \frac{|E_F - E_{\text{Hy}\pm}|}{\sqrt{|E_F - E_{\text{Hy}\pm}|^2 + |\Gamma|^2}}, \tag{15}$$

where $|\Gamma|$ is the modulus of the hybridization parameter [Eq. (1)] and $E_{\text{Hy}\pm}$ are the excitation energies for the new hybrid excitons. Due to the hybridization between the two exciton states the wave function for the new hybrid state is a linear combination of the basic exciton states and is smoothly distributed over the geometry of the whole system changing only on a macroscopic scale.

For noninteracting excitons there would be no optical nonlinearity, i.e., the optical nonlinearity stems from the interaction between the Wannier-Mott excitons.

The interaction with the external electric field is given by Eq. (2), where the polarization operator is the sum of the polarization operators for the Wannier-Mott and the Frenkel excitons and now the electric field $\vec{E}$ should be understood as the applied external electric field. To calculate the linear and nonlinear responses on a disturbing external field we determine in a first step the eigenstates of the Hamiltonian (13), which is performed in an approximate manner. We took only three states into account, namely the ground state $|0\rangle$, the state with one hybrid exciton $|\text{Hy}-\rangle$, and finally the state with two hybrid excitons $|\text{Hy}-,\text{Hy}-\rangle$. These states are obtained by means of the operator $h_-^\dagger$ from the ground state:

$$|0\rangle, \quad |\text{Hy}-\rangle = h_-^\dagger |0\rangle, \quad |\text{Hy}-,\text{Hy}-\rangle = \frac{1}{\sqrt{2}} h_-^\dagger h_-^\dagger |0\rangle. \tag{16}$$

The restriction to only one type of hybrid exciton is reasonable since we are considering the case where the applied electromagnetic field is in resonance with the lowest state of the hybrid exciton. The energetically higher state $|\text{Hy}+\rangle$ decays faster as compared to the lower one.

III. NONLINEAR OPTICAL SUSCEPTIBILITY

The nonlinear optical susceptibility is defined as $\chi^{(3)} = P/(VE^3)$, where P is the averaged third-order polarization of the system. For instance, if we consider $\chi^{(3)}_{\text{WM}}$, we average over the volume of the quantum dot. The nonlinear optical susceptibility $\chi^{(3)}$ is calculated using third-order perturbation theory. We calculate $\chi^{(3)}$ for Wannier-Mott excitons in a quantum dot and consider only the resonant case in which the detuning $\Delta\omega$ between the frequencies of the electronic excitation and the light field is smaller than the nonlinear interaction V_0. The result is

$$\chi^{(3)}_{\text{WM}}(-\omega;\omega,\omega,-\omega) = -\frac{2\mu^4_{\text{WM}}}{\hbar^3 V_{\text{Dot}}(\Delta\omega)^2} \left(\frac{8R_D^3}{\pi^2 a_B^3} \right)^2 \times \left\{ \frac{1}{\Delta\omega - \frac{2}{\hbar} V_0} - \frac{1}{\Delta\omega} \right\}. \tag{17}$$

The nonlinear optical susceptibility due to the interaction V_0 is enhanced as compared to the value in the bulk. The large factor $(8R_D^3/\pi^2 a_B^3)^2$ is due to the confinement of the Wannier-Mott excitons in the quantum dot. In the derivation of Eq. (17) we have used the following assumptions:

(i) the weak-confinement limit must hold,

$$R_D \gg a_B; \tag{18}$$

(ii) only the lowest excited state is required to be dominant in the susceptibility,

$$\frac{\hbar^2}{2m_{\text{red}}} \frac{3\pi^2}{R_D^2} \gg \hbar\Delta\omega, \tag{19}$$

and (iii) the interaction V_0 should be larger than the detuning,

$$V_0 \gg \hbar\Delta\omega. \tag{20}$$

The conditions for our calculation can be summarized in the following inequality for the radius of the quantum dot:

$$R_1 \ll R_D \ll R_2,$$

with

$$R_1 = \sqrt{\frac{\hbar^2}{2m_e}\,\frac{3\pi^2\epsilon a_B}{e^2}},$$

$$R_2 = \min\left\{ a_B \sqrt[3]{\frac{E_{\mathrm{Ry}}}{\hbar\Delta\omega}};\ \sqrt{\frac{3\hbar\pi^2}{2m_e\Delta\omega}} \right\}. \tag{21}$$

For hybrid excitons the nonlinear optical susceptibility is

$$\chi^{(3)}_{\mathrm{Hy}}(-\omega;\omega,\omega,-\omega) = -\frac{2}{\hbar^3 V_{\mathrm{Dot}}(\Delta\omega)^2}\mu_F^4 \times \left(\frac{4V_{\mathrm{shell}}}{\pi^2 V_{\mathrm{cell}}}\right)^2 \left\{ \frac{1}{\Delta\omega - \frac{2}{\hbar}\tilde{V}_0} - \frac{1}{\Delta\omega} \right\}, \tag{22}$$

where $\Delta\omega = \omega - \tilde{\omega}$ and $\hbar\tilde{\omega}$ is the energy of the lowest excited hybrid state and $\tilde{V}_0$ is the interaction between these states. Here we assumed that $V_{\mathrm{cell}}R_D/(a_B^3 d_0)$ is small as compared to 1. [V_{cell} is the unit cell volume of the organic material and d_0 is the thickness of the organic layer; for numerical values see the text below Eq. (29)].

The aim of our investigation is to examine the nonlinear optical properties of this new hybrid state for the quantum dot geometry. The results for the ratios of the induced nonlinear optical polarizations $P = \chi^{(3)}VE^3$ are quite lengthy. Therefore, we present here only their orders of magnitude:

$$\frac{P^{(3)}_{\mathrm{Hy}-}}{P^{(3)}_{\mathrm{F}}} \sim \frac{V_{\mathrm{shell}}}{V_{\mathrm{cell}}}, \quad \frac{P^{(3)}_{\mathrm{Hy}-}}{P^{(3)}_{\mathrm{WM}}} \sim \left(\frac{d_0}{R_D}\right)^2 \left(\frac{a_B}{a_{\mathrm{org}}}\right)^6. \tag{23}$$

The enhanced nonlinear optical polarizability of confined excitons was reported earlier by Hanamura[5,13–15] and we therefore do not discuss it in detail here. The factors that are responsible for the large nonlinear optical polarizability are due to the confinement of excitons in the given geometry. Here the influence of the dimensionality comes into play. However, the new hybrid state has an even higher nonlinear optical polarizability. The volume of the shell is $V_{\mathrm{shell}} = 4\pi R_D^2 d_0$ and if we take for the lattice constant of an organic material $a_{\mathrm{org}} \approx 5$ Å we can estimate that the induced nonlinear optical polarizability of hybrid excitons is five orders of magnitude larger than the one of Frenkel excitons and even six orders of magnitude larger than for Wannier-Mott excitons. The form of Eq. (23) is determined by two factors: there is a decrease due to the finite thickness d_0 of the layer, which is much smaller than the radius R_D of the quantum dot, and an increase due to $(a_B/a_{\mathrm{org}})^6$, which is a consequence of the hybridization. The latter factor remarkbly dominates; if we take, for instance, $a_B \approx 80$ Å and $a_{\mathrm{org}} \approx 5$ Å, we get $(a_B/a_{\mathrm{org}})^6 \sim 10^7$.

The physical interpretation for this large nonlinear optical polarizability $P^{(3)}_{\mathrm{Hy}-}$ is the following. The expressions for the third-order polarizabilities for the hybrid and the Wannier-Mott exciton in the resonant range differ by the factors

$$P^{(3)}_{\mathrm{Hy}-} \sim \left(\frac{V_{\mathrm{shell}}}{V_{\mathrm{cell}}}\right)^2 \mu_{\mathrm{F}}^4, \quad P^{(3)}_{\mathrm{WM}} \sim \left(\frac{R_D^3}{a^3}\right)^2 \left(\frac{a^3}{a_B^3}\right)^2 \mu_{\mathrm{WM}}^4. \tag{24}$$

Here we introduced the lattice constant a of the bulk semiconductor. The factor $(a/a_B)^{3/2}\mu_{\mathrm{WM}}$ is an effective dipole moment for Wannier-Mott excitons that takes into account the probability amplitude $(a/a_B)^{3/2}$ of finding an electron and a hole within an elementary cell of the semiconductor. The fourth power of this μ_{eff} corresponds to the third-order response to the external electric field. The factor $(R_D^3/a^3)^2$ describes the number of possibilities for creation/annihilation of two electron-hole pairs within the quantum dot. The considerable enhancement of $P^{(3)}_{\mathrm{Hy}-}$ stems from the more efficient interaction of Frenkel excitons with light due to their large oscillator strength.

IV. RADIATIVE DECAY RATES

In order to decide whether the hybridization is really present and not masked by the large radiative decay rate, we compare the radiative decay rates γ with the hybridization parameter Γ. The radiative decay rate from the first excited state to the ground state is calculated using Fermi's golden rule. The interaction Hamiltonian of Wannier-Mott excitons and the electromagnetic field is given by

$$H_{\mathrm{int}} = i\sum_{\vec{q},\sigma} \int_{\mathrm{Dot}} d^3r \sqrt{\frac{2\pi\hbar\omega_{\vec{q},\sigma}}{V}}\, \vec{e}_{\vec{q},\sigma} \langle 1_{\mathrm{WM}}|\vec{P}(\vec{r})|0\rangle (B^\dagger + B) \times (b^\dagger_{\vec{q},\sigma} - b_{\vec{q},\sigma}), \tag{25}$$

where $\vec{q}$ is the wave vector of the photon, σ describes its polarization, and $\vec{e}_{\vec{q},\sigma}$ is its polarization unit vector. According to Fermi's golden rule the decay rate for Wannier-Mott excitons in the quantum dot is

$$\gamma_{\mathrm{WM}} = \frac{2\pi}{\hbar}\sum_{\vec{q},\sigma} |\langle n_{\vec{q},\sigma} = 1|H_{\mathrm{int}}|1_{\mathrm{WM}}\rangle|^2 \delta(\hbar\omega_{\vec{q}} - E_{\mathrm{WM}}) = 64\left(\frac{R_D}{a_B}\right)^3 \frac{4\pi}{3}\,\frac{\mu_{\mathrm{WM}}^2}{\hbar\lambda^3}. \tag{26}$$

The enhancement of the exciton decay rate by the factor $64(R_D/a_B)^3$ is again a consequence of the confinement and was reported earlier by Hanamura.[5]

The calculation of the decay rates of the Frenkel and hybrid excitons is performed analogously. The results are

$$\gamma_F = 64\frac{V_{\mathrm{shell}}}{V_{\mathrm{cell}}}\,\frac{4\pi}{3}\,\frac{\mu_F^2}{\hbar\lambda^3}, \quad \gamma_{\mathrm{Hy}-} = 32\frac{V_{\mathrm{shell}}}{V_{\mathrm{cell}}}\,\frac{4\pi}{3}\,\frac{\mu_F^2}{\hbar\lambda^3}. \tag{27}$$

The comparison shows that

$$\frac{\gamma_{\mathrm{Hy}-}}{\gamma_F} = \frac{1}{2}, \quad \frac{\gamma_{\mathrm{Hy}-}}{\gamma_{\mathrm{WM}}} = \frac{V_{\mathrm{shell}}}{V_{\mathrm{cell}}}\left(\frac{\mu_F}{\mu_{\mathrm{WM}}}\right)^2 \left(\frac{a_B}{R_D}\right)^3 \frac{1}{2}. \tag{28}$$

This means that the decay rate of hybrid excitons is of the same order of magnitude as the one of Frenkel excitons.

We drop all numerical factors and give the result only in terms of the important parameters:

$$\frac{\gamma_{\mathrm{WM}}}{|\Gamma|} \sim \left(\frac{R_D}{a_B}\right)^3 \sqrt{\frac{a_B^3 V_{\mathrm{cell}} R_D}{\hbar^2 \lambda^6 d_0}},$$

$$\frac{\gamma_{\mathrm{Hy}-}}{|\Gamma|} \sim \frac{\gamma_F}{|\Gamma|} \sim \frac{R_D^2 d_0}{a_{\mathrm{org}}^3} \sqrt{\frac{a_B^3 V_{\mathrm{cell}} R_D}{\hbar^2 \lambda^6 d_0}}. \tag{29}$$

If we take for example $a_B = 80$ Å, $R_D = 800$ Å, $d_0 = 4$ Å, $a_{\mathrm{org}} = 5$ Å and $\lambda = 3000$ Å, we get, as an estimation, $\hbar \gamma_{\mathrm{Hy}-}/|\Gamma| \approx 0.09$. Thus we have demonstrated that the radiative decay rates are roughly two orders of magnitude smaller as the hybridization parameter and, therefore, the hybridization of two excitons really takes place in our model.

V. CONCLUSIONS

We proposed a simple, analytically tractable microscopic model for the coupling between excitonic states in inorganic and organic materials, i.e., between Wannier-Mott and Frenkel excitons. The new hybrid state has a larger optical nonlinearity (and at the same time a larger decay rate) as compared to Wannier-Mott excitons. The high nonlinear optical polarizability stems from the nonlinearity of the Wannier-Mott excitons, to be more specific, from their interaction, and from the large coupling of the Frenkel exciton to the external electromagnetic field (large oscillator strength). The enhanced nonlinear response to an applied external electromagnetic field would make these hybrid states especially interesting to applications in nonlinear optics. This would justify the efforts to prepare such heterostructures. These very interesting physical properties were obtained assuming that the energies of both excitonic states are nearly in resonance, i.e., $E_F \approx E_{\mathrm{WM}}$. Outside this resonance the coupling between the excitons is rather small. This requires, in particular, that the decay rates (including phonon scattering, radiationless decay, etc.) of both excitons be small as compared to the hybridization parameter Γ. For a macroscopic sample containing many heterostructures of the considered type, the nonuniformity of these spheres and the roughness between the spheres and the surrounding medium would cause an inhomogeneous broadening of the absorption lines. This broadening should be small as compared to Γ, too. Thus the materials for the layer and the quantum dot have to be chosen carefully in order to observe these new and promising features of coupled organic and inorganic heterostructures.

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APPENDIX A: THE WAVE FUNCTION FOR FRENKEL EXCITONS

We describe the motion of the Frenkel exciton within the organic layer by the Schrödinger equation for a particle with a mass m,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_F(\vec{r}) = E \psi_F(\vec{r}). \tag{A1}$$

The thickness $d(\Theta)$ of the shell is assumed to be dependent on the polar angle Θ. This angular dependence of the layer thickness is essential, otherwise there would be no hybridization. The physical reason is that the electric field inside the quantum dot created by the Frenkel exciton in the shell corresponds to the field created by a uniformly polarized sphere. This is identically zero. Thus, in order to get hybridization, one has to break the spherical symmetry. The radial motion of the exciton is restricted to the range $R_D < r < R_D + d(\Theta)$ and the wave function is assumed to vanish at the shell boundaries. We are looking for solutions of the form

$$\psi_F(\vec{r}) = \Phi(\Theta) \frac{1}{\sqrt{4\pi}} \sqrt{\frac{2}{d(\Theta)}} \frac{\sin\left[\frac{\pi}{d(\Theta)}(r - R_D)\right]}{r}. \tag{A2}$$

Inserting Eq. (A2) into the Schrödinger equation (A1) and averaging over the radial dependence, we obtain

$$0 = \frac{2mR_D^2}{\hbar^2}\left[E - \frac{\hbar^2 \pi^2}{2md^2(\Theta)}\right]\Phi(\Theta) + \frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\left[\sin\Theta \frac{\partial\Phi(\Theta)}{\partial\Theta}\right]. \tag{A3}$$

We represent $d(\Theta)$ in the form

$$d(\Theta) = d_0[1 + \delta(\Theta)], \tag{A4}$$

and assume a small deviation from the perfect sphere; i.e., we demand that $|\delta(\Theta)| \ll 1$. This angular dependence may correspond, e.g., to the roughness of the interface between the organic layer and the inorganic quantum dot. The last term in Eq. (A4) leads to a perturbation term on the right-hand side of the Schrödinger equation:

$$\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\left[\sin\Theta \frac{\partial\Phi(\Theta)}{\partial\Theta}\right] + \frac{2mR_D^2}{\hbar^2}\left[E - \frac{\hbar^2\pi^2}{2md^2(\Theta)}\right]\Phi(\Theta) = -\frac{2R_D^2\pi^2}{d_0^2}\delta(\Theta)\Phi(\Theta). \tag{A5}$$

We expand $\delta(\Theta)$ in terms of Legendre polynomials,

$$\delta(\Theta) = \sum_{\ell=1}^{\infty} \delta_\ell P_\ell(\cos\Theta), \tag{A6}$$

$$\delta_\ell = \frac{2\ell + 1}{2}\int_0^\pi d\Theta \sin\Theta P_\ell(\cos\Theta)\delta(\Theta), \tag{A7}$$

and look for the wave function $\Phi(\Theta)$ in the form

$$\Phi(\Theta) = \frac{1}{\sqrt{2}} + \sum_{\ell=1}^{\infty} \alpha_\ell P_\ell(\cos\Theta). \tag{A8}$$

The energy eigenvalue of the lowest exciton state is given by

$$E=\frac{\hbar^2\pi^2}{2md_0^2}[1+O(\delta^2)]. \tag{A9}$$

In first-order perturbation theory in δ we get, for the coefficients α_j,

$$\alpha_j=\frac{\sqrt{2}R_D^2\pi^2}{d_0^2}\,\delta_j\,\frac{1}{j(j+1)}. \tag{A10}$$

As a result we obtain the eigenfunction

$$\psi_F(r,\Theta)=\frac{1}{\sqrt{4\pi}}\sqrt{\frac{2}{d(\Theta)}}\frac{\sin\left[\frac{\pi}{d(\Theta)}(r-R_D)\right]}{r} \times\left[\frac{1}{\sqrt{2}}+\sum_{\ell=1}^{\infty}\alpha_\ell P_\ell(\cos\Theta)\right]. \tag{A11}$$

APPENDIX B: CALCULATION OF THE HYBRIDIZATION PARAMETER

The hybridization parameter Γ is given by Eq. (1). The excitonic states are

$$|1_{\mathrm{WM}}\rangle=\int_{\mathrm{Dot}}d^3r_e d^3r_h\,\phi(\vec{r}_e-\vec{r}_h)\,\psi_{100}(\vec{R})\,\hat{\psi}_e^\dagger(\vec{r}_e)\,\hat{\psi}_h^\dagger(\vec{r}_h)|0\rangle,$$

$$|1_F\rangle=\sum_{\vec{n}}\ \psi_F(\vec{n})A_{\vec{n}}^\dagger|0\rangle, \tag{B1}$$

where $\phi(\vec{r}_e-\vec{r}_h)$ is the lowest wave function for the relative motion of electron and hole in the quantum dot and $\psi_{100}(\vec{R})$ is the lowest wave function of the center-of-mass motion of the two particles:

$$\phi(\vec{r})=\frac{1}{\sqrt{\pi a_B^3}}e^{-r/a_B},\qquad \psi_{100}(\vec{R})=\sqrt{\frac{2}{R_D^3}}\frac{\sin\left(\frac{\pi R}{R_D}\right)}{\frac{R}{R_D}}\frac{1}{\sqrt{4\pi}}. \tag{B2}$$

The quantum numbers (100) have the following meaning: the first number, here $n=1$, labels the number of the zeros of the spherical Bessel function[16] $j_\ell(k_{n\ell}R_D)$ for a given value of ℓ. $\hbar\ell$ is the angular momentum of the center of mass and $\hbar m$ is the projection of the angular momentum along a certain direction. In the case $\ell=0$ the roots are $k_{n\ell}R_D=n\pi,(n=1,2,\ldots)$.

Inserting the above expressions into the definition of Γ, we obtain

$$\Gamma=-\frac{\mu_{\mathrm{WM,i}}\mu_{\mathrm{F,j}}\phi(0)}{\sqrt{V_{\mathrm{cell}}}\epsilon}\int_{\mathrm{shell}}d^3r'\,\psi_F(\vec{r}\,')\frac{\partial^2}{\partial r_i'\partial r_j'} \times\int_{\mathrm{Dot}}d^3r\frac{\psi_{\mathrm{WM},100}(\vec{r})}{|\vec{r}-\vec{r}\,'|}. \tag{B3}$$

The integral over the dot is formally the potential at the point $\vec{r}\,'$ created by the ‘‘charged’’ quantum dot with spherically symmetric distribution of charge, Eq. (B2). This is just Q/r' where Q is given by

$$Q=\int_{\mathrm{Dot}}d^3r\,\psi_{\mathrm{WM},100}(\vec{r}). \tag{B4}$$

As the radius R_D of the quantum dot is assumed to be considerably larger than the thickness d_0 of the layer, Γ can be written as

$$\Gamma=-\frac{\mu_{\mathrm{WM}}\mu_F\phi(0)Q}{\sqrt{V_{\mathrm{cell}}}\epsilon R_D^3}\int_{\mathrm{shell}}d^3r\,\psi_F(\vec{r})\{3\cos^2(\Theta)-1\}; \tag{B5}$$

here we assumed that all the dipole moments point in a given direction, which we took as the z direction. The function in the brackets is, up to a factor 1/2, the Legendre polynom of second-order $P_2(\cos\Theta)$. Inserting the expression for the wave function of the Frenkel excitons [Eq. (A11)] and using the orthonormality of the Legendre polynomials, we obtain

$$\Gamma=-\frac{32\mu_{\mathrm{WM}}\mu_F}{5\epsilon}\sqrt{\frac{d_0}{2\pi^3a_B^3V_{\mathrm{cell}}R_D}}\frac{\pi^2R_D^2}{3d_0^2}\delta_2. \tag{B6}$$

The hybridization parameter is determined by some intrinsic properties of the excitons, such as the Bohr radius a_B of the Wannier-Mott exciton, the volume V_{cell} of a cell of the organic lattice, and the transition dipole moments of the excitons. In addition, the hybridization parameter depends also on the thickness d_0 of the organic layer and the radius R_D of the quantum dot. The interaction strength between the two excitons can, therefore, be controlled by changing experimental parameters.[17] In order to give a numerical value for Γ we take $\mu_{\mathrm{WM}}\approx\mu_{\mathrm{F}}\approx 1D$, $\epsilon\approx 7$, $d_0/R_D\approx 1/200$, $a_B\approx 80$ Å, $a_{\mathrm{org}}\approx 5$ Å and $\delta_2=1/10$. Using these values we obtain $\Gamma\approx 5$ meV.

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