Metal–Semiconductor Nanoparticle Hybrids Formed by Self-Organization: A Platform to Address Exciton–Plasmon Coupling

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ABSTRACT: Hybrid nanosystems composed of excitonic and plasmonic constituents can have different properties than the sum of the two constituents, due to the exciton–plasmon interaction. Here, we report on a flexible model system based on colloidal nanoparticles that can form hybrid combinations by self-organization. The system allows us to tune the interparticle distance and to combine nanoparticles of different sizes and thus enables a systematic investigation of the exciton–plasmon coupling by a combination of optical spectroscopy and quantum-optical theory. We experimentally observe a strong influence of the energy difference between exciton and plasmon, as well as an interplay of nanoparticle size and distance on the coupling. We develop a full quantum theory for the luminescence dynamics and discuss the experimental results in terms of the Purcell effect. As the theory describes excitation as well as coherent and incoherent emission, we also consider possible quantum optical effects. We find a good agreement of the observed and the calculated luminescence dynamics induced by the Purcell effect. This also suggests that the self-organized hybrid system can be used as platform to address quantum optical effects.

KEYWORDS: Colloidal nanocrystals, self-organization, time-resolved photoluminescence, exciton–plasmon coupling

In metal nanoparticles (NPs), optical energy can be trapped in subwavelength spatial regions, quantized into plasmons.1,2 This allows transformation of far-field radiation into a strongly localized electric field in the vicinity of the metal NP, which can enable new ways to interface light with matter.3 In semiconductor NPs, quantum dots (QDs), optical excitation can generate excitons—quasi particles composed of an electron and a hole, bound by the electron–hole Coulomb interaction.4 Excitons in QDs are emitters of nonclassical (quantum) light.5–7 In hybrid structures, the exciton can couple to metal NPs and drive the plasmon.8 Conversely, the large fields at metal NPs associated with the plasmon resonances can interact with excitons confined in QDs. The resulting hybrid system can have different properties than the sum of the constituent elements.9,10 Understanding of coupled exciton–plasmon systems could allow tuning of the optical properties, ultimately enabling control of the quantum level, e.g., by single photon emission,12,13 radiative rate enhancement,14 or defined charge and energy transfer transitions, as recently proposed.15,16 The research on materials with optical properties that benefit from the exciton–plasmon coupling is a subject of intense research, and new design concepts are constantly being developed.18,14–19 To be able to systematically compare present theory of exciton–plasmon interactions20–25 with experiment and to separate possibly entangled classical and quantum effects, flexible and robust material systems are necessary.

In general, the assembly of different NPs into hybrid combinations allows the construction of materials with new chemical and physical properties.26,27 Compared to fabrication methods based on top-down approaches, such as lithography, a self-assembly offers the potential for easier and more flexible fabrication.28 Molecules forming multiple covalent bonds to NPs can, for example, be applied to establish connections between colloidal NPs.29,26 The individual components can be prepared independently, allowing for great flexibility in material design. Here, we present a toolkit to prepare coupled, self-organized hybrid exciton–plasmon systems. The QDs are...
embedded in stiff polymer shells with end groups that can link to noble metal NPs and form hybrid particles by self-organization in aqueous solution. As a test case, we employed gold (Au) NPs and CdSe-based QDs as the plasmon−exciton system. Preparation by wet chemistry permits us to vary the relevant parameters defining the interaction between the excitons and plasmons: the energies of the exciton and the plasmon can be adjusted by synthesizing particles of different sizes, and the polymer shell allows control of the interparticle distance on the nanometer scale, controlling the Purcell effect. In the experiments, we observe a pronounced coupling between the exciton and plasmon, apparent in the widely varying decay kinetics observed for the photoluminescence (PL) response. A strong impact of the energy difference between exciton and plasmon resonances is observed: For small energy differences, the hybrid system is dominated by the properties of the plasmon. The coupling leads to subpicosecond PL decay, not fully resolvable in our experiments. By tuning the system away from direct resonance, the coupling is decreased, yielding an accessible temporal signature in the PL decay. This enables an experimental study of the dependence of the exciton−plasmon interaction on the material system’s geometrical parameters, and we observe an interplay between size- and distance dependences. We present a corresponding theoretical model to explain the observations. We develop a full quantum theory of the emission, which contains the experimentally observable kinetics in the form of the Purcell effect, but which can also be used also to describe the coherent excitation process, dephasing, secondary emission in the form of Rayleigh and photoluminescence. The calculated PL dynamics reproduce the experiments well without the use of free parameters. This theory is not limited to our observations, which are also partially explainable with the use of (semi)classical calculations. This raises hope that the combination of the present flexible material kit with full quantum theory will facilitate work on quantum-optical effects where, for example, dephasing is of importance.

Figure 1a displays a sketch of the hybrid system. CdSe-based QDs are embedded in poly(isoprene)-b-poly(ethylene glycol) diblock copolymer (PI-b-PEG) micelles using a recently developed encapsulation method (see Methods). Lipoic acid end groups on the polymer allow quasi-covalent attachment of AuNPs, reflecting the strong affinity of thiols for noble metals. The formation of an additional stiff polystyrene shell (PS shell) around the hydrophobic core of the PI-b-PEG allows us to control the distance between the QDs and AuNPs between 5 and 15 nm. This combination yields a very stable system: The particles are in close, but not direct contact, enabling strong interactions, but inhibiting charge transfer processes. Additionally, the chemical bonding groups are situated on top of the polymer, suppressing changes in the optical properties of the QD. The average arrangement of the hybrid can be controlled by the size of the AuNPs and the relative concentration of NPs used (e.g., Figure 1e and Supporting Information). For low ratios of QDs to AuNPs, cross-linking occurs, and larger clusters can be formed. High QD to AuNP ratios yield systems were the AuNP surface is saturated with QDs within the solution; excess QDs result in additional uncoupled QDs. Two QD core types were employed: CdSe/ZnS core−shell QDs with an emission maximum centered at 528 nm, denoted as “green QDs” and CdSe/CdS/ZnS core−shell QDs with an emission maximum at 596 nm, “red QDs”. The steady-state spectra of the semiconductor QDs and NPs are displayed in Figure 1f. The exciton transition of the green QDs is in close resonance with the plasmon excitation, with an energy difference of less than 14 meV, which is well within the plasmon spectral line width. The red QDs are at the low-energy shoulder of the plasmon absorption, at least 280 meV away.

Figure 1. (a) QDs are embedded in PI-b-PEG ligands with an optional PS shell. Lipoic acid end groups on the surface of the polymer link to AuNPs (b). TEM micrographs of 20 nm AuNPs combined with green QDs (c), 40 nm AuNPs and red QDs with a 10 nm shell (d), and 40 nm AuNPs with red QDs with a 15 nm shell in an excess of 10:1 (QD to AuNP) (e). The scale bars correspond to 50 nm. (f) Absorption spectra of the AuNPs and steady state PL spectra of the QDs. The thin additional PS spacer has a refractive index different from water, resulting in a shift of the PL maximum wavelength.
from the central resonance. For the red QDs, systems with a thin polymer shell (5 nm) and medium (10 nm) and thick (15 nm) polymer layers were prepared. The properties of the AuNPs were varied by choosing different diameters; 12, 20, and

Figure 2. (a) Steady state spectra of green QD based systems. The AuNP to QD ratio was 1:10, and the samples were excited with an energy above a long-pass filter. The dashed line indicates the position in the spectra used for the time traces. (b) Normalized spectra of red QD systems. The AuNP to QD ratio was 1:1. (c) Representative streak camera map from green QDs on 20 nm AuNPs. The feature around 515 nm can be assigned to Raman scattered light from C–H vibrations in the organic ligand environment. The Raman response is used to determine the instrument response function (IRF) in the same spectral window. (d) Comparison of time traces through the PL maximum, obtained from streak camera maps.

Figure 3. (a–c) Comparison of PL decays from QDs with different-sized NPs and fixed PS spacer thicknesses. (d–f) Comparison of PL decays from QDs with different PS spacers with fixed NP diameters. The time traces for the response from isolated red QDs are shown with all time traces for comparison.
40 nm. Figure 1c−e displays transmission electron microscopy (TEM) micrographs of such hybrid systems with different spacer thicknesses. The results of the time-resolved PL experiments are summarized in Figure 2. The PL intensity of the green QD-based hybrids is strongly quenched. The hybrids were excited close to the resonance of the exciton (Figures 2a and b). This allowed us to avoid the generation of hot carriers and the potential contribution of cooling effects. Figure 2c depicts a typical time-resolved emission map recorded with a streak camera. A comparison of the instrumental response function (IRF) and the hybrid system’s PL is shown in Figure 2d. For all green QD systems, the fast initial component is instrument-limited. By detuning the resonance between plasmon and exciton, we can, however, change the situation drastically, as illustrated by the coupled systems with 40 nm AuNPs and red QDs in Figure 2d. Here, the temporal response can be fully resolved. For this reason we focused on red-QD based systems as a function of the geometric parameters of the hybrid system. The normalized steady-state PL spectra of the hybrids are the same for different AuNPs (Figure 2b). The PL decay kinetics of these systems are summarized in Figure 3. The isolated QDs feature single exponential decay dynamics. When combined with AuNPs, the decay kinetics change. The slopes of the time traces in Figure 3 depend on both the AuNP size and the distance between AuNP and QD. Increasing the interparticle separation reduces the interaction. However, the largest AuNPs do not necessarily exhibit the strongest interaction (Figure 3a−c). For the smallest separations, the smallest AuNPs yield the fastest decay, while for larger separations the largest AuNPs lead to the fastest decay. A comparison of the decay traces for fixed AuNP sizes, but different interparticle separations (Figure 3d−f) reveals the distance dependence to be the strongest for the smallest AuNPs and to be significantly reduced for the largest AuNPs. Surprisingly the monotonic behavior for fixed spacer thickness, but different AuNP sizes is different (see Figure 3a−c or 5).

The observed variation in the photoluminescence decay rates can be explained by the exciton−plasmon coupling as the dominant process. We apply a theoretical description of the exciton−plasmon coupling using the corresponding Hamiltonian in second quantization and a dipole approximation. Within this theory, the Purcell effect is the dominant factor for the PL kinetics: The Purcell factor can be calculated using classical electromagnetics and leads to changes in mode structure that result in changing coupling strengths. The corresponding mode structure enters both, the standard classical and our quantum optical treatment of the exciton−plasmon coupling. As an extension of the classical treatment, the quantum approach allows us to treat the excitation, the coherent Rayleigh and incoherent fluorescence contributions simultaneously. The coherent Rayleigh scattering that follows the laser pulse is one example that is not covered by a discussion using the Purcell factor alone (Figure 4c).

Consequently, in our approach, the exciton in the QD and the plasmons of the AuNPs are described within the formalism of second quantization, using the compound Hamiltonian:

\[ H = H_0 + H_{\text{ex-pl}} + H_\text{d} \]

\[ H_0 \] is the free particle Hamiltonian of the uncoupled exciton and plasmons, \( H_{\text{ex-pl}} \) describes the interaction between the two systems and \( H_\text{d} \) describes excitation of the hybrid by an external classical optical field (Figure 4a). The system includes the coupled excitations of the lowest energy exciton for the QD and the lowest energy plasmon excitation (dipole mode) of the AuNP. The losses of
the system—dephasing and damping of the excitonic and the plasmonic excitation—are incorporated via a Lindblad formalism. The temporal behavior of the coupled quantum system, starting from coherent driving of the interacting exciton and plasmon dipoles by the laser field and ending in the collective damping of the coupled dipoles, is computed by evaluating the time evolution of the density matrix. We used an operator equation formalism yielding a hierarchy of equations. Since plasmons are bosons, multiple excitations of the plasmon mode need to be included by introducing plasmon number states. This truncates the hierarchy problem numerically when approaching higher states. The complete set of equations of motions can be found in ref.31

A system assembled this way allows us to calculate the complete time evolution of the system during excitation and relaxation. All observables can be monitored individually, and their dependence on the system parameters can be investigated. The PL intensity determined by the far field emission is given by:

$$S_{far} = \langle (\mu a^\dagger \chi a^\dagger + \chi a^\dagger \mu a^\dagger + \chi a) \rangle$$

where $\mu$ and $\chi$ are the dipole moments of the QD and AuNP, respectively. $a^\dagger$ and $a$ are the annihilation operators of the conduction band, valence band Fermionic electron, and of the bosonic plasmons. $a^\dagger$, $a^\dagger$ and $a^\dagger$ are the corresponding Fermionic and bosonic photon creation operators. $S_{far}$ contains pure plasmonic and pure excitonic contributions, as well as mixed contributions. Detailed informations about how to determine the needed parameters for all constituents of the hybrid system are given in the Supporting Information.

The calculated linear absorption spectra for AuNPs of different sizes, along with the red and green QDs absorption, are displayed in Figure 4b. The predicted spectra obtained experimentally (Figure 1d). The calculated spectra are spectrally narrower than the experimental ones since inhomogeneous broadening is not included. In the experiment, a distribution of distances and of resulting coupling strengths is an intrinsic feature. We can account for this experimental circumstance by an averaging procedure (Supporting Information for details). The resulting dynamics of the uncoupled constituents are displayed in Figure 4c: The excitonic and plasmonic parts in Figure 4c correspond to the parts indicated in eq 1. The mixed contribution is mostly important while the laser pulse and the coherent emission contribution are still present; it does not contribute to the later PL decay kinetics.

Figure 4c displays the dynamics for the uncoupled case (a separate QD and a separate NPs), a weakly coupled system (small spectral overlap between exciton and plasmon) and a resonantly coupled system (large spectral overlap). For weak coupling, all contributions decay essentially as do their uncoupled counterparts. For the uncoupled and weakly coupled hybrid, the strong damping leads to plasmon decay on the femtosecond time scale. After the excitation build-up, the plasmon far field emission follows the optical pump. The decay of the incoherent exciton contribution occurs on a nanosecond time scale, and the emission is almost constant in the displayed time window. Increasing the coupling due to increased spectral overlap results in more efficient energy transfer between both constituents. The decays become faster as the energy transfer between the constituents becomes more likely, and therefore the plasmon with its rapid damping strongly influences the decay. The resonant case results in a mixing of the damping constants of the plasmons and the exciton and thus in an effective collective damping of the coupled system. This

Figure 5. Time-dependent far field contributions of the exciton for the red QD-based systems. (a–c) Decays for fixed interparticle spacings and different AuNP sizes. (d–f) Decays for fixed AuNPs with different spacers. The displayed signal is an average over an ensemble, convolved with the instrumental response. The color code and order of the panels correspond to Figure 3.
becomes apparent in the long-time behavior of exciton and plasmons: they exhibit the same slope. For this reason the dynamics of the green QD based hybrid differs strongly from the red QD based system. The calculated signals for the green QD based system (see Supporting Information, Figure S4) all closely follow the excitation pulse and decay at least 3 orders of magnitude within 1 ps, which is impossible to resolve with our apparatus. This situation changes when investigating the hybrid systems based on red QDs, which corresponds to an off-resonant, weaker coupling. In the experiment, the PL shows a broad range of decay rates for the red QDs. The calculated time-dependent PL emission (exciton) for the ensemble of coupled AuNPs and red quantum dots is presented in Figure 5. First, as in the experiment, we see that decreasing the distance between the constituents of the hybrid results in much faster decay of the signal (compare Figure 5 and Figure 3, lower row). From the calculations, this behavior can be readily understood: Decreasing the distance increases the coupling strength between the constituents of the hybrid, and therefore the energy transfer of excited quantum dots to the strongly damped AuNP becomes more likely. This corresponds to an increase of the Purcell factor. Therefore, the initially deposited excitation is more strongly dissipated by the AuNP resulting in a faster decay of the overall emission signal. Second, the shape and order of the decays in Figure 5 agree well with the experimental observations. For example, the monotonic increase in coupling strength with AuNP diameter for the 15 nm spacer is inverted for smaller spacer thicknesses in both experiment and theory. Therefore, the order of the decays in Figure 5 agree well with the experimental observations. For example, the monotonic increase in coupling strength with AuNP diameter for the 15 nm spacer is inverted for smaller spacer thicknesses in both experiment and theory.

**Conclusions.** In summary, we have presented a hybrid material system based on colloidal nanocrystals that permits systematic studies of the exciton–plasmon interaction. Chemically binding colloidal metal and semiconductor NPs in aqueous solution provides a robust route to obtain model systems for the investigation of exciton–plasmon coupling: All relevant parameters such as the energies, sizes, and interparticle distances can be tuned. The time-resolved PL demonstrates that the resonance between exciton and plasmon strongly influences the coupling. We observe instrument-limited decays on the ps time scale for strongly coupled systems. Detuned systems yield a more accessible temporal signature that allow investigation of the influences of the geometric parameters, AuNP size and interparticle distance. We observe an interplay of size and distance dependences on the coupling. To facilitate future studies, we show how to implement a quantum-optical model that reproduces the experimental observations without the introduction of free parameters. This theory can help to clarify the exact dependences of interactions between emitters and plasmons in applications of nanoparticle combinations and could be used in combination with $g^2$ measurements to study the impact of the coupling on the emitted light statistics.15,35

**Methods. Synthesis of Nanoparticles.** CdSe/CdS/ZnS core/shell/shell QDs (red QDs) were produced in high boiling point organic solvents using triorgylphosphine (TOP), triorgylphosphine oxide (TOPO), and hexadecyl amine (HDA) following a previously published, altered protocol.36 Bis(trimethylsilyl) sulfide and diethylzinc were replaced by less environmentally hazardous compounds: hydrogen sulfide and zinc acetate. The nanoparticles were precipitated twice with methanol to remove excess TOP/TOPO and were stored in $n$-hexane. CdSe/ZnS core/shell QDs (green QDs) were produced in high boiling point organic solvents using TOP, TOPO, and HDA, following to published work.37 Dimethylcadmium was replaced by cadmium acetate. The synthesis of the AuNPs was performed according to a protocol published by Bastús et al.38

**Synthesis of Polymers.** For the formation of the hybrid particles we employed a micellar encapsulation technique of NPs with the amphiphilic poly(isoprene)-block-poly(ethylene glycol) diblock copolymer (PI-b-PEG) in water.38 The PI and PI-b-PEG copolymers were synthesized via living anionic polymerization (LAP), as previously described.39 PI was synthesized using isoprene and sec-butyllithium as an initiator. Termination of the LAP with ethylene oxide leads to a terminal hydroxyl group. Subsequently, the PEG block was synthesized via anionic ring opening polymerization using PI–OH as a macroinitiator and diphenylmethyl potassium. For the attachment of lipoic acid to the PI-b-PEG diblock copolymer we followed our recently published procedure.28

**Phase Transfer of the QDs.** Ligand Exchange with PI-DETA: The QDs were incubated with a 600 molar excess of diethyleneetriamine (Pi-DETA) $\text{P}_n\text{Ni}$-DETA (average MW 1.7 kDa) in $n$-hexane. After 2–5 h, the NPs were precipitated with ethanol. After isolation by centrifugation, QDs were redissolved in $n$-hexane. Encapsulation: Aliquots of PI–DETA coated QDs (20 nmol) were dried under a nitrogen flow and resuspended in a solution (2 mL) of tetrahydrofuran (THF) containing a 300-fold excess of PI-b-PEG-lipoic acid (LA) ligands. Azobis(isobutyronitrile) (AIBN) was added, corresponding to a mass ratio of 0.5:1 with respect to applied PI-b-PEG-LA. After 10 min, the solution was injected into water (18 mL) and incubated for 15–30 min at RT. The solution was heated at 80 °C for 2–5 h to initiate cross-linking. The QD solution was filtered through a syringe filter (CE; hydrophilic; 0.45 μm), washed twice with water (8 mL) in centrifugal filter units (Amicon Ultra-15; 100 kDa membrane), and finally purified via sucrose-gradient centrifugation.

**PS-Shell Growth by Seeded Emulsion Polymerization.** In a typical formulation, the micellar encapsulated QDs were dissolved in water (20 mL). After removal of oxygen by alternating cycles of evacuating and flushing with nitrogen, 1-pentanol (20 μL), styrene (2 μL), divinylbenzene (2 μL), and radical initiator 2,2′-azobisis[2-(2-imidazolin-2-yl)propane] dihydrochloride (0.5 mg) were added. The solution was stirred at 44 °C. Depending on the desired thickness, an aliquot of the reaction was quenched by oxygen flow at room temperature.
after 10 min up to 4 h. Purification of the product was performed by washing twice with 8 mL of water in centrifugal filter units (Amicon Ultra-15; 100 kDa membrane), followed by sucrose-gradient centrifugation.

Self-Assembly of NPs into Hybrids. The self-assembly of NPs into different complex hybrid structures was realized by mixing the PI-b-PEG-LA encapsulated QDs with citrate stabilized AuNPs in aqueous citrate solution. By using the functionalized PI-b-PEG, the encapsulated QDs bind AuNPs. The thiol has a high affinity to Au surfaces and form quasi-covalent bonds.\(^\text{40}\) If not otherwise stated, the relative concentration was set to 1:1 (AuNP to QD). The actual composition of the hybrid particles was monitored by TEM and UV/vis absorption. We performed concentration studies by monitoring the PL dynamics while decreasing the QD to AuNP ratio. High QD excesses perturb the PL kinetics. QD to AuNP ratios below two result in stable configurations, where the normalized PL decay is not concentration-dependent. Additional TEM investigations confirm that structures have formed where almost every QD is attached to an AuNP, either as individual pairs or in small networks. Consequently, a pair of one QD and one AuNP is the most important subunit that describes our structures. TEM-Images were recorded with a Jeol JEM-1011 operating at 100 kV, and the samples were prepared by pipetting \(\approx 10 \mu\text{L}\) of the sample solution onto carbon coated copper grids.

Optical Spectroscopy. All optical experiments were performed in borosilicate cells filled with ensembles of statistical quantities of hybrid particles in aqueous solution. Reference measurements on plain cells show no response in the considered spectral regime. The hybrids were excited via an 10\(\times\) objective (NA = 0.3) leading to a spot size of about 10 \(\mu\)m. The emitted light was collected by the same objective and dispersed by a spectrometer.

To examine the picosecond dynamics of the systems, streak measurements were performed with a universal streak camera (C 5680, Hamamatsu Photonics) with a M 5675 Synrscan unit behind a 300 nm spectrograph with a 50 grooves/mm grating. The excitation was a modelocked Ti:sapphire laser, frequency doubled by a second harmonic generator (Harmonixx, APE Berlin) and tuned to 403 nm. All experiments were performed with pulse fluences not exceeding 1.7 \(\mu\text{J/cm}^2\). Under these conditions the mean exciton number per quantum dot stays far below unity. The time resolution for the measurements in this work was approximately 5 ps based on the fwhm of the Raman scattered light at a 3000 cm\(^{-1}\) shift, which was present simultaneously with the PL. The temporal signature of the red QD-based samples was resolvable with avalanche photodiodes, which featured a better signal-to-noise ratio. The data were recorded behind a 500 mm spectrograph with a 300 grooves/mm grating either with a cooled CCD camera (Princeton Instruments, Pixis 400 BR) for taking the PL spectra or with an avalanche photo diode (APD) (Micro Photonic Devies, PDM series) for the time-resolved measurements. The time-resolution measured as fwhm of the laser signal was about 70 ps. For all experiments on the hybrids with red dots, an optical parametrical oscillator (OPO) (Mira OPO, APE Berlin) pumped by a Ti:sapphire laser (Coherent, Mira 900f) with 75 MHz repetition rate and nominally 150 fs pulses was tuned to 587 nm. The excitation was filtered by a 600 nm short pass filter, whereas the scattered laser light in the signal path was filtered by a 600 nm long pass filter. The photoluminescence decays were recorded at 607 nm. Control measurements revealed that no scattered laser light was detected by the APD. Additionally, decays at longer wavelengths showed the same decay times. The hybrids with green quantum dots were excited by the OPO tuned to 513 nm. The excitation was filtered with a 514 nm laser line filter, whereas the scattered laser light in the signal path was filtered by a 520 nm long pass filter. The photoluminescence decays were recorded at 525 nm. Control measurements revealed that no scattered laser light was detected by the APD. Again, the decays at longer wavelengths show the same decay times.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b00982.

Additional TEM characterization of the hybrids, calculation parameters, and classical calculations (PDF)

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Author Contributions

C.S. designed and performed the optical experiments. M.R. and A.K. designed the quantum-optical model. T.S.T. performed the quantum-optical calculations. C.S., H.K., J.P.M., and H.W. performed the synthesis and basic characterization. Z.Y. contributed to the experiment theory comparison and performed the classical calculations. T.F.H. contributed to the design of the project and analysis and discussion of the results. H.L. conceived the project and wrote the manuscript with contributions from all authors.

Notes

The authors declare no competing financial interest.

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