

Nonuniform Screening Reshapes Collective Excitons in Molecular Aggregates from Stochastic Bethe-Salpeter Theory

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Article

Keywords: Bethe-Salpeter Equation, Cyanine Aggregates, Excitons, Dielectric Screening

Posted Date: October 15th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11319253/v1>

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Additional Declarations: There is **NO** Competing Interest.

1 Nonuniform Screening Reshapes Collective
2 Excitons in Molecular Aggregates from Stochastic
3 Bethe-Salpeter Theory

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18 **Abstract**

19 We build and apply an *ab initio* stochastic Bethe-Salpeter Equation (sBSE)
20 approach to planar cyanine dye aggregate clusters containing up to 2,856 valence
21 electrons. Using a transferable, parameterized screened exchange kernel, we
22 resolve dielectric response, exciton delocalization, and optical spectra within
23 a unified many-body framework. Remarkably, the sBSE transition densities
24 validate the Frenkel exciton picture in real space and provide a practical first-
25 principles route to its screened couplings. The calculations reproduce H -, I -, and
26 J -like spectral evolution and reveal that spatially dependent screening does not
27 merely shift excitonic bands, but reshapes their dispersion, leading to changes

in the relative energies of bright and dark exciton states. These results establish sBSE as a predictive framework for large molecular aggregates.

Keywords: Bethe-Salpeter Equation, Cyanine Aggregates, Excitons, Dielectric Screening

1 Introduction

Polymethine cyanine dye supramolecular assemblies are among the most studied excitonic molecular aggregates due to their chemically modifiable bandgaps and large transition dipole moments, especially within the near- and short-wave infrared spectral windows (NIR: $\lambda = 700 - 1000$ nm and SWIR: $\lambda = 1000 - 2000$ nm). These aggregates have found applications in biological imaging, lasing, and optoelectronics while also serving as model systems to explore strong dipole coupling and coherent exciton transport.[1–14] Conventional exciton theory relates aggregate packing to optical response, distinguishing *H*- from *J*-aggregates through the sign of intermolecular exciton coupling. More recent work has shown that planar cyanine aggregates exhibit richer behavior, including intermediate *I*-aggregate characteristics that cannot be described within the traditional *H*/*J* classification.[7, 8, 15–20] For example, in extended two-dimensional aggregates, an *I*-aggregate regime can arise when short- and long-range excitonic couplings have opposite signs, producing a red-shifted bright state that lies within the excitonic band rather than at its lower edge.[7, 8] Complementary extensions have further shown that competition between short- and long-range excitonic interactions can generate *HH*, *HJ*, *JH*, and *JJ* regimes with distinct excitonic band structures.[21, 22] At the same time, advances in cryogenic electron microscopy have provided structural information with near-atomic resolution, creating a growing need for electronic structure methods that can directly connect aggregate geometry and optical properties.[15–18, 23]

Most theoretical studies of cyanine aggregates use Frenkel exciton Hamiltonians to connect aggregate geometry with photophysical observables.[18–22, 24–27] In these studies, localized molecular excitations are coupled through site energies and inter-molecular interactions, enabling efficient treatment of disorder, packing geometry, and large aggregate sizes.[21, 22, 24, 25, 28] The predictive accuracy of the Frenkel framework therefore depends on how its site energies, couplings, and environmental screening are constructed. Couplings are commonly approximated using point-dipole, extended-dipole, or transition-charge models, whose accuracy can become sensitive to short-range geometry,[29–32] while dielectric screening is typically introduced through effective dielectric constants, continuum models, or other parametrized treatments rather than derived directly from the many-body response.[33–36]

An *ab initio* approach to treating excitations in extended molecular aggregates would allow for first-principle study of aggregate spectral properties. To that end, time-dependent density-functional theory (TDDFT) is a routine approach for describing molecular aggregate excited states, however, its accuracy relies heavily on the choice of exchange-correlation functional. In turn, the Bethe-Salpeter Equation (BSE) of many-body perturbation theory has become a promising alternative to TDDFT with the ability to describe charge-transfer excitations more reliably. The success of the BSE comes from a screened Coulomb interaction that explicitly accounts for interactions between electrons and holes.[37–43] The BSE has become a benchmark approach for molecular and condensed-phase spectroscopy, but generating the screened Coulomb matrix elements scales quartically with system size. This has limited application to large-scale molecular aggregate settings.[40–49] As a result, a large gap persists between experimentally relevant molecular aggregates and the many-body methods needed to describe them.

Our recent developments in stochastic many-body theory provide a route toward closing this gap.[50–57] By replacing the explicit construction of the real-space

80 screened Coulomb operator with stochastic realizations of the operator’s action,
 81 these approaches retain the essential many-body physics of the BSE while sub-
 82 stantially reducing computational cost. Previous work has shown that stochastic
 83 screened-interaction methods reproduce BSE-quality excitation energies for challeng-
 84 ing polymethine cyanine dyes while extending excited-state calculations to systems
 85 containing several thousand valence electrons.[58–61] In this work, we apply *ab*
 86 *initio* stochastic Bethe-Salpeter Equation (sBSE), also known as TDHF@ v_W , [58,
 87 60, 61] to aggregate clusters (containing up to 2,856 valence electrons) of 4’-(3,5-
 88 dimethylphenyl)-substituted heptamethine cyanine dye (Cy7-DiMePh).[7, 9, 10, 62]
 89 This NIR-SWIR dye forms multiple well-characterized two-dimensional aggregate
 90 mesophases with distinct excitonic and optical properties, while its packing and spec-
 91 tral response are highly sensitive to the 4’ aryl substitution.[10] These features make
 92 Cy7-DiMePh a particularly useful model system for connecting molecular packing,
 93 dielectric screening, and the emergence of collective exciton structure.[10]

94 Fig. 1 summarizes the systems and workflow considered in this study. Starting from
 95 the isolated monomer (Fig. 1 (a) i.), we construct one-dimensional (1D) 2×1 (dimer),
 96 3×1 (trimer), and 4×1 (tetramer) aggregates as well as a series of two-dimensional
 97 (2D) 4×3 aggregates exhibiting *H*-, *I*-, and *J*-like packing motifs (Fig. 1 (a) ii, iii).
 98 The monomer geometry is optimized at the B3LYP/def2-TZVPPD level,[63–65] the
 99 π - π stacking distance of 4.72 Å is determined by a fragment-constrained dimer geom-
 100 etry optimization at the r^2 SCAN-3c level,[66] and the lateral distance of 25.43 Å is
 101 determined by a potential energy surface scan using r^2 SCAN-3c.[66] All geometry opti-
 102 mizations are performed using the ORCA 6.0 package.[67, 68] Additional structural
 103 details are provided in the Supplementary Information (SI). The resulting aggregates
 104 span a range of experimentally motivated inter-layer slips, with 2.60 Å, 4.60 Å, and

6.60 Å slips for the *H*-, *I*-, and *J*-like motifs, respectively. Therefore, these aggregates sample distinct intermolecular packing arrangements and excitonic coupling regimes.[7, 8, 23, 35]

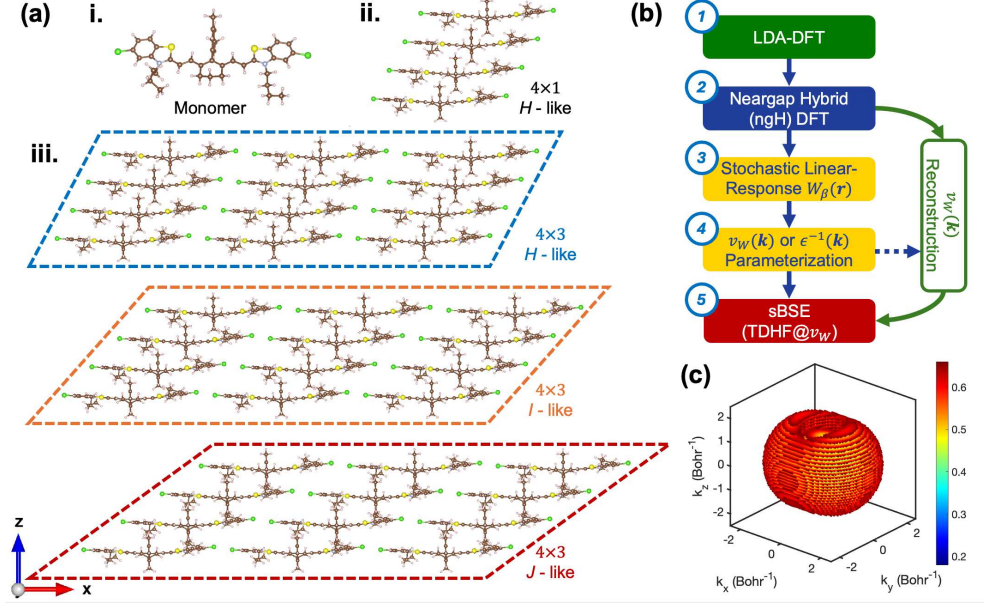


Fig. 1 (a) i. Cy7-DiMePh monomer structure (terminal sulfonate groups on the side chains are replaced by methyl groups for computational simplicity). ii. 1D 4×1 aggregate exhibiting *H*-like stacking motifs along the π - π stacking direction. iii. 2D 4×3 aggregates with *H*-, *I*-, and *J*-like packing arrangements. (b) Schematic overview of the sBSE methodology used in this work. (c) Representative reciprocal-space inverse dielectric response, $\epsilon^{-1}(k)$, of the Cy7-DiMePh monomer reconstructed from stochastic screening calculations.

The sBSE workflow is shown in Fig. 1 (b). Ground-state density-functional theory (DFT) calculations are followed by stochastic linear-response time-dependent Hartree calculations that determine the screened interaction. The resulting screening is represented through a polynomial-Gaussian parameterization and incorporated into the sBSE Hamiltonian for excited-state calculations. See the Computational Methods section and SI for more information.

A central quantity throughout this work is the reciprocal-space inverse dielectric function, $\epsilon^{-1}(k)$, illustrated in Fig. 1 (c). Unlike conventional dielectric constants, the

present framework elucidates the direction- and range-dependent dielectric screening and allows direct examination of how aggregate packing modifies screened electron-hole interactions. We then incorporate this dielectric function into the Frenkel exciton model. Together with the real-space transition-density projection, this provides both a many-body validation of the Frenkel exciton model and a practical scheme for extracting its screened parameters from electronic-structure calculations.

2 Results and Discussion

2.1 Emergence of *ab initio* dielectrics in molecular aggregates

To understand how intermolecular aggregation modifies the screened electron-hole interaction, we reconstruct the real-space inverse dielectric response, $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$, from the reciprocal-space screened interaction kernel, $v_W(\mathbf{k})$. Fig. 2 summarizes the resulting $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$ for monomer and aggregate Cy7-DiMePh systems.

Fig. 2 (a) shows the real-space Cartesian slices of $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$ for monomer, dimer, trimer, and tetramer systems, separated by *H*-, *I*-, and *J*-like packing motifs (across rows) and *x*, *y*, and *z* directions (across columns). These cuts reveal the full $\mathbf{r}$ -dependence of the screened interaction, where there is a sharp short-range reduction of ϵ^{-1} followed by a gradual mid- to long-range recovery toward the unscreened limit of $\epsilon^{-1} \rightarrow 1$. This mid- and long-range region is crucial for aggregate excitons, as the electron-hole interaction extends across multiple chromophores. The directional cuts reveal dielectric anisotropy as well. Along the *x*- and *y*-directions, the screening minimum ($\epsilon_{\min}^{-1} \sim 0.28$) occurs at short distances near 0.80 Å. In contrast, the *z*-direction, which corresponds to the π - π stacking direction, shows a deeper and broader screened region with a later turning point ($\epsilon_{\min}^{-1} \sim 0.23$ around 0.90 Å), indicating that aggregation builds a more extended dielectric response along the packing axis.

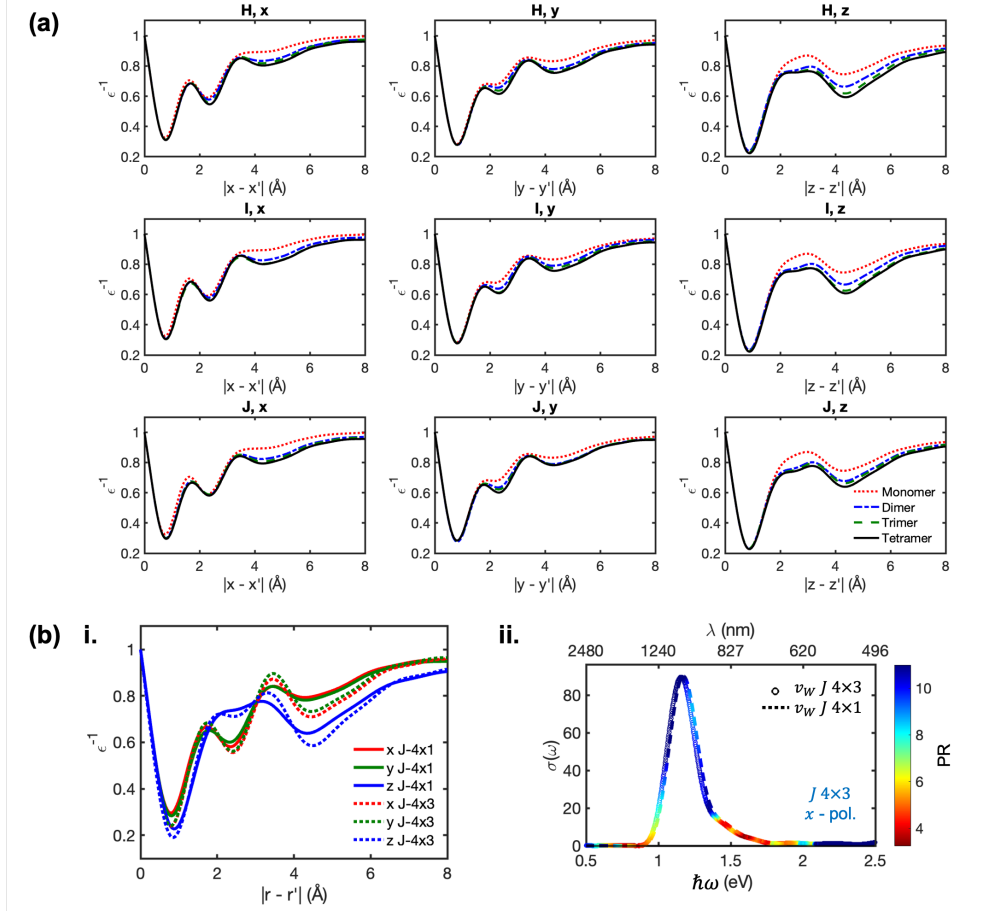


Fig. 2 (a) Real-space inverse dielectric response, $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$, along the $|x - x'|$, $|y - y'|$, and $|z - z'|$ slices for the Cy7-DiMePh monomer and H -, I -, and J -like 1D aggregates. The red, blue, green, and black curves correspond to the monomer, dimer, trimer, and tetramer, respectively. (b) i. Comparison of the $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$ slices reconstructed using the v_W obtained from the 4×1 and 4×3 J -like aggregates. ii. x -polarized sBSE absorption spectra with PRs for the $J 4 \times 3$ aggregate using its own v_W and the $J 4 \times 1$ v_W .

Importantly, the screening profiles converge rapidly with subsystem size. From Fig. 2 (a), $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$ of the dimer, trimer, and tetramer becomes nearly indistinguishable beyond short-range structure, whereas the isolated monomer remains distinct from this converged behavior. This behavior strongly suggests that the screened

144 interaction becomes locally saturated once the immediate dielectric environment
 145 surrounding a molecule is adequately represented.

146 2.2 Transferability of screened interactions

147 This rapid convergence seen in Fig. 2 (a) has important implications for scalable
 148 excited-state simulations. Rather than performing the computationally demanding
 149 $W_\beta(\mathbf{r})$ calculation (defined in the Computational Methods section and the SI) indi-
 150 vidually for increasingly large aggregates, smaller, locally converged subsystems may
 151 provide transferable screened interactions for substantially larger assemblies.

152 Fig. 2 (b) i. compares $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$ slices obtained from the 4×1 and 4×3 J -
 153 like aggregates. Despite the increase in total system size, the screening curves remain
 154 reasonably similar across all principal directions, especially at long-range. Such simi-
 155 larities indicate that the dominant dielectric environment is primarily determined by
 156 local packing geometry. Fig. 2 (b) ii. shows x -polarized sBSE spectra with participa-
 157 tion ratios (PRs, defined in the SI) of the 4×3 J -like aggregate computed using the
 158 screening kernel, v_W , derived from both itself and a smaller 4×1 J -like subsystem.
 159 The two spectra exhibit nearly identical bright peak positions (< 0.02 eV deviation),
 160 side bands, and PRs among excitation energy, ω . Therefore, in the latter simulations,
 161 we use the dielectric screening parameterized from the 4×1 structures for the bigger
 162 4×3 2D clusters.

163 2.3 Aggregate-dependent exciton spectral evolution

164 Fig. 3 (a) shows normalized x -polarized sBSE absorption spectra for the monomer
 165 and 4×3 aggregates. The monomer has a bright peak at 1.43 eV (869 nm) and
 166 PR = 1.3. Upon aggregation, the peak shifts according to the packing motif. The H -
 167 like aggregate blue-shifts to 1.45 eV (857 nm), the I -like aggregate red-shifts to 1.36
 168 eV (912 nm), and the J -like aggregate red-shifts further to 1.17 eV (1057 nm). In our

169 previous experiments, we measured absorption maxima of 1.55 eV (798 nm) for the
 170 Cy7-DiMePh monomer and 1.20 eV (1029 nm) for the extended J -aggregate.[10] Thus,
 171 sBSE predicts a monomer-to- J redshift of 0.26 eV, compared with the measured shift
 172 of 0.35 eV. These trends agree with Frenkel exciton and transition-dipole coupling
 173 models commonly used to describe cyanine aggregates.[7, 8, 10, 18, 22, 24, 26] However,
 174 unlike simplified dipole-coupling models, the present sBSE calculations incorporate
 175 explicit screened electron-hole interactions and many-body dielectric response. Fig. 3
 176 (b) illustrates that the optical responses within the 1 – 2 eV window are dominated by
 177 x -polarization, consistent with the cyanine transition dipole lying along the molecular
 178 “long axis”. The peak cross section increases from 12.1 for the monomer to $\sim 10^2$ for
 179 the H -, I -, and J -like aggregates. Such enhancement is consistent with the emergence
 180 of delocalized exciton behavior expected for coherently coupled cyanine assemblies.[9,
 181 10] In contrast, the y - and z -polarized peak cross sections remain minuscule ($\sim 10^{-1}$ –
 182 10^{-2}).

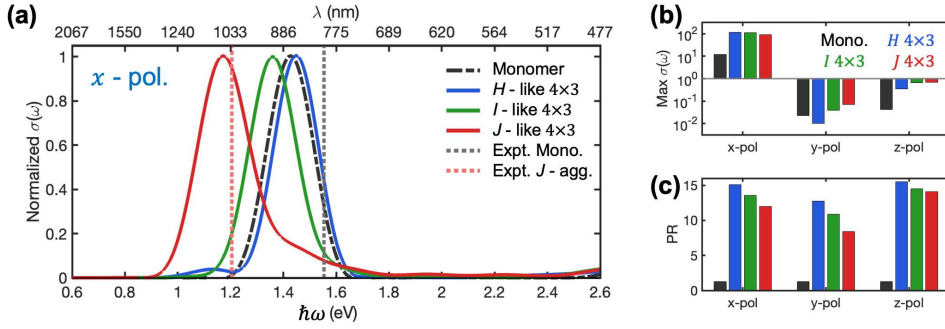


Fig. 3 (a) Normalized sBSE absorption spectra for the Cy7-DiMePh monomer and 4×3 H -, I -, and J -like aggregates under x -polarization. Vertical dotted lines indicate the experimental absorption maxima of the monomer at 798 nm (1.55 eV, gray) and the extended J -aggregate at 1029 nm (1.20 eV, red).[10] (b) Maximum absorption cross section, $\sigma(\omega)$, within the 1 – 2 eV window for x -, y -, and z -polarized excitations across the monomer and 4×3 systems. Cross sections are plotted on a logarithmic scale. (c) PR associated with the brightest exciton within the 1 – 2 eV window for different polarizations and aggregate motifs.

183 The PR values in Fig. 3 (c) show that aggregation converts the monomer excita-
 184 tion into a collective exciton. For the brightest x -polarized peaks, the PR increases
 185 from 1.3 in the monomer to 15.1, 13.5, and 12.0 for the H -, I -, and J -like aggregates,
 186 respectively. The gradual decrease from H to J indicates that exciton delocalization
 187 depends not only on aggregate size but also on packing geometry. The J -like aggregate
 188 therefore exhibits the largest red shift but not the largest PR, indicating that spectral
 189 shift and configurational delocalization are distinct observables. With this, the spec-
 190 tra distinguish two related but different effects: spectral shifts reflect the magnitude
 191 and sign of exciton coupling, while the PR quantifies how broadly the excitation is
 192 distributed within the electron-hole basis; the validity of the Frenkel representation is
 193 assessed separately through the real-space projection described in later sections.

194 2.4 Real-space screened transition electrostatic potential

195 To visualize the real-space effect of dielectric screening on the exciton transition den-
 196 sity, we construct the corresponding transition electrostatic potential using $n_{\text{tr}}(\mathbf{r})$.
 197 The bare transition electrostatic potential, $\Phi_{\text{tr}}^{\text{bare}}(\mathbf{r})$, represents the potential generated
 198 by the transition density through the bare Coulomb interaction. Dielectric screening
 199 is subsequently incorporated through the v_W -derived $\epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|)$ function. Thus,
 200 $\Phi_{\text{tr}}^{\text{scr}}(\mathbf{r})$ provides a real-space diagnostic of how the screened interaction redistributes
 201 this potential relative to the bare Coulomb case.

202 Fig. 4 (a)-(c) illustrate the construction of these quantities for the lowest bright
 203 x -polarized excitation of the monomer. The transition density in Fig. 4 (a) exhibits
 204 the familiar alternating positive and negative lobes associated with the electron-hole
 205 coherence of the excitation. Fig. 4 (b) shows the reconstructed three-dimensional (3D)
 206 real-space screening isosurfaces of the monomer at $\epsilon^{-1} = 0.3, 0.5$, and 0.7 . Integrating
 207 $n_{\text{tr}}(\mathbf{r})$ under a Coulomb kernel transforms this rapidly oscillating transition density
 208 into a smooth dipolar electrostatic potential composed of spatially separated positive

209 and negative lobes (Fig. 4 (c), left). Incorporating dielectric screening preserves the
 210 overall dipolar topology while substantially reducing the spatial extent of the electro-
 211 static potential (Fig. 4 (c), right). Rather than altering the qualitative electrostatic
 212 character of the excitation, the screening kernel acts to localize the transition-induced
 213 electrostatic potential through the nonlocal dielectric response of the molecular envi-
 214 ronment. Fig. 4 (d) shows the same ingredients as the monomer, but for a 4×1 J -like
 215 aggregate cluster.

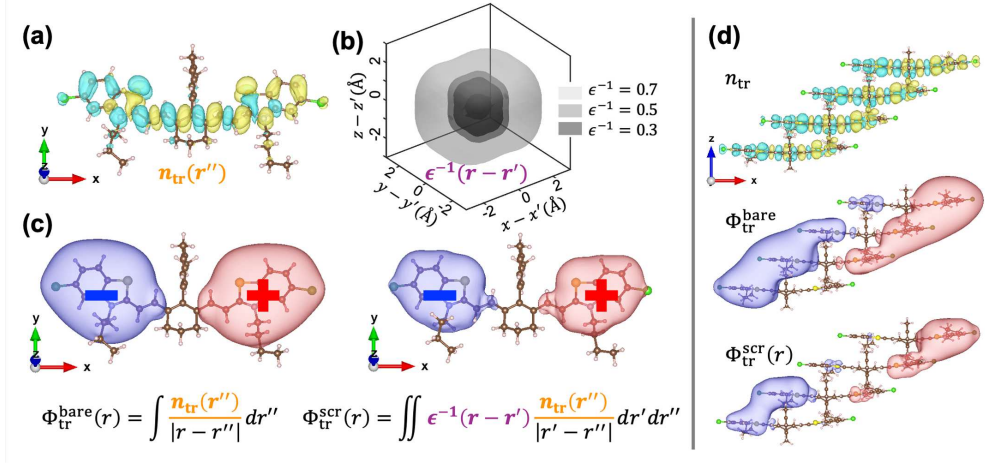


Fig. 4 (a) Real-space transition density, $n_{tr}(\mathbf{r})$, of the lowest bright x -polarized excitation for the monomer obtained from sBSE. The yellow and cyan isosurfaces represent electron-hole transition amplitudes of opposite sign. (b) Full 3D isosurfaces of $\epsilon^{-1}(|\mathbf{r}-\mathbf{r}'|)$ for the monomer. Isosurfaces are shown for $\epsilon^{-1} = 0.3, 0.5$, and 0.7 . Additional apparent shades arise from transparency and overlap of the surfaces. (c) Monomer bare and screened transition electrostatic potentials, $\Phi_{tr}^{bare}(\mathbf{r})$ and $\Phi_{tr}^{scr}(\mathbf{r})$, respectively, represented by isosurfaces. (d) $n_{tr}(\mathbf{r})$, $\Phi_{tr}^{bare}(\mathbf{r})$, and $\Phi_{tr}^{scr}(\mathbf{r})$ for the lowest bright x -polarized excitation of the J 4×1 aggregate. Isosurface values of $\pm 0.15 ea_0^{-3}$ are used for the transition density, while potential isosurface values of $+8$ a.u. (red) and -8 a.u. (blue) are used for the bare and screened transition electrostatic potentials of both the monomer and the J 4×1 aggregate.

216 Together, these results show that dielectric screening primarily modifies the spatial
 217 extent of the transition-induced potential while preserving its overall dipolar character.

2.5 Collective real-space exciton transition in aggregates

To visualize the spatial structure of the collective excitations in 2D aggregation motifs, we compute real-space exciton transition densities for the brightest aggregate excitations together with their transition electrostatic potentials (Fig. 5). Notably, all the aggregate motifs exhibit spatially extended transition amplitudes aligned predominantly along the aggregate axis. Such delocalized transition density patterns are consistent with the collective exciton states predicted in coherent Frenkel exciton descriptions of cyanine aggregates.[7, 8, 10, 18, 22, 24, 26, 62] Importantly, the present transition densities emerge directly from the screened many-body sBSE framework rather than from phenomenological exciton Hamiltonian. Therefore, the resulting collective exciton structures naturally incorporate dielectric screening, explicit electron-hole interactions, and packing-dependent electronic structure effects.

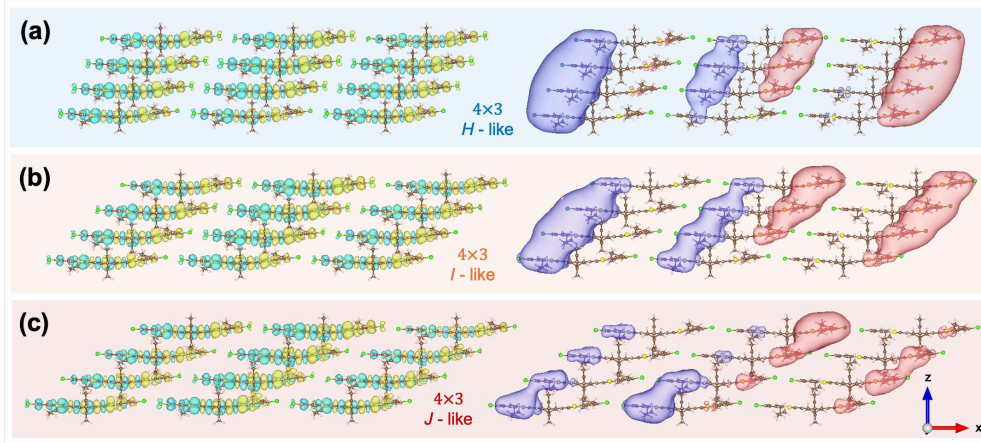


Fig. 5 Exciton transition density (left) and screened transition electrostatic potential (right) associated with the lowest bright x -polarized excitation of (a) H -, (b) I -, and (c) J -like aggregate clusters. The transition density isosurface values of $\pm 0.20 e a_0^{-3}$ and the potential isosurface values of $+10$ a.u. (red) and -10 a.u. (blue) are used for all three systems.

While the transition densities remain highly collective and extend over multiple chromophores for all three aggregate clusters (Fig. 5 (a)-(c), left), their corresponding

232 screened transition electrostatic potentials become progressively more compact (Fig. 5
 233 (a)-(c), right), as identical absolute potential isosurface values are used throughout.
 234 Qualitatively, the *H*-like aggregate exhibits broad positive and negative potential lobes
 235 with a relatively large spatial separation (Fig. 5 (a), right), whereas the *I*- and *J*-like
 236 aggregates gradually develop more localized dipolar potential with reduced spatial
 237 extent (Fig. 5 (b) and (c), right).

238 To quantify the observed electrostatic localization, we analyze the screened tran-
 239 sition electrostatic potentials using a series of common absolute potential thresholds.
 240 Across the entire range of thresholds, the *H*-like packing consistently exhibits the most
 241 spatially extended screened electrostatic potential, while the *J*-like cluster remains
 242 the most compact. At the visualization threshold of $|\Phi_{\text{tr}}^{\text{scr}}| = 10$ a.u. used in Fig. 5,
 243 the centroid separation between the positive and negative potential decreases from
 244 54.6 Å for the *H*-like aggregate cluster to 41.3 Å for the *J*-like aggregate cluster,
 245 corresponding to an approximately 24% reduction. Simultaneously, the volume of
 246 the high-magnitude potential region decreases from 4,671 to 1,660 Å³, representing
 247 nearly a threefold contraction (see the SI for detailed analysis). The packing-dependent
 248 variation of $\Phi_{\text{tr}}^{\text{scr}}(\mathbf{r})$ provides a real-space representation of how dielectric screening
 249 redistributes the transition-induced electrostatic potential. Its direct photophysical
 250 consequences are assessed below through the screened Frenkel couplings and excitonic
 251 band structure analysis.

252 2.6 Real-space validation of the Frenkel exciton picture

253 A central assumption of the Frenkel exciton model is that an aggregate excitation can
 254 be represented as a coherent superposition of localized monomer excitations.[7, 8, 18,
 255 22, 24, 26, 62, 69, 70] Since sBSE calculations provide the transition densities of both
 256 the isolated monomer and the aggregate clusters, we directly test this assumption in

257 real space by reconstructing the aggregate transition density from rigidly translated
 258 copies of the monomer ones.[69, 70]

Table 1 Real-space validation of the Frenkel representation in 4×3 H -, I -, and J -like aggregate clusters. Definitions of the projected overlap, and equal-weight overlap are provided in the Computational Methods section and in the SI.

Motif	Projected Overlap	Equal-weight Overlap
H	94.3%	92.0%
I	93.8%	89.7%
J	92.5%	86.4%

259 As summarized in Table 1 and detailed in the SI, the projected overlap exceeds
 260 92.5% for all three 4×3 motifs, demonstrating that the reconstructed transition den-
 261 sities closely reproduce the many-body excitation. By comparison, the equal-weight
 262 overlap ranges from 86.4 – 92.0%, showing that optimizing the Frenkel coefficients
 263 provides a slight improvement over a uniform distribution. Meanwhile, the condi-
 264 tion number in the projected overlap process remains close to unity, confirming
 265 that the mapped monomer transition densities form a stable projection basis. The
 266 remaining 10 – 15% of the transition density lies outside the Frenkel basis and likely
 267 reflects local polarization, subtle transition-density deformation, and effects beyond
 268 the one-excitation-per-monomer picture.

269 2.7 Spatially dependent screening of Frenkel excitons

270 Having established that the aggregate sBSE transition densities are well represented
 271 within the Frenkel basis, we further assess the consequences of the screened couplings
 272 in the context of excitonic molecular aggregates. Fig. 6 (a) compares J_n , the excitonic
 273 coupling between sites separated by n lattice spacings, in a 1D chain before and after
 274 screening for a given lattice where the screening effect is most dramatic. As expected,

screening has negligible effects on further-separated sites $n > 3$, showing the near-field nature of such screening. On the other hand, screening becomes more significant between near neighbors. In fact, for the current example, the unscreened nearest-neighbor coupling J_1 is vanishing while the screened one is significantly nonzero. This is far from the expectation of a spatially homogeneous screening constant picture. The packing dependence can be understood in terms of geometry-dependent cancellation between positive and negative transition-density contributions, which can strongly modify near-field excitonic couplings and their distance scaling.^[71]

This unusual observation of “anti-screening” results from the combination of the spatially extended transition-charge distribution and range-sensitive screening. In the bare coupling, contributions from different transition-charge pairs largely cancel one another, whereas short-range screening acts differently on the individual contributions and disrupts this cancellation, leaving a strong nonzero cumulative coupling. A detailed analysis of this effect and its dependence on molecular slip is provided in the SI.

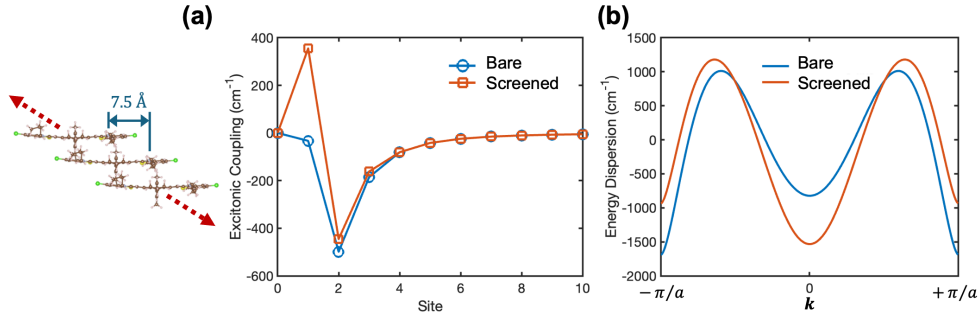


Fig. 6 (a) Coupling J_{nm} as a function of inter-site distance $|\mathbf{r}_n - \mathbf{r}_m|$ in a 1D chain with a 7.5 Å slip. (b) The excitonic band structures calculated from the unscreened and screened (derived from the J -like 4×1 cluster) couplings for the same 1D aggregate.

We also investigate the screening’s effect on the excitonic band structure in Fig. 6 (b). At this particular slip value (7.5 Å), the unscreened interactions lead to a band-edge J -aggregate where the bright state ($\mathbf{k} = 0$ in the dipole, long-wavelength

regime) is red-shifted compared to monomers and located at the bottom of the exciton band.[8, 26] This is in contrast to the screened case, where the bright state is blue-shifted above the band edge, and the lowest-energy exciton state is of high quasimomentum ($|\mathbf{k}| = \pi/a$, where $a \sim 25$ Å is the 1D lattice constant for Cy7-DiMePh) and dark in nature. This is a direct result of significantly changing the nearest-neighbor coupling from vanishing to strongly positive, thereby qualitatively modifying the excitonic band structure. Consequently, spatially dependent screening can alter not only the magnitude of excitonic coupling but also the energetic ordering and optical character of the aggregate exciton states.

We note that similar effects apply to 2D aggregates as well, albeit with more complication, as a variety of selective screening schemes similar to that described in the above 1D case may act in concert with or against one another depending on the specific packing condition. It is, however, expected that accounting for such screening effects is crucial in predicting accurate excitonic coupling and the overall photophysics of these aggregates.

3 Computational Methods

3.1 Ground-state orbitals and near-gap hybrid reference

We first perform grid-based, norm-conserving pseudopotential, local-density approximation (LDA) density functional theory calculations to obtain an initial ground-state reference.[72, 73] A near-gap hybrid (ngH) calculation with the CAM-LDA0 range-separated hybrid functional ($\alpha = 0.19, \beta = 0.46, \gamma = 0.33$ Bohr $^{-1}$) is then used to improve the frontier-orbital energetics with explicit hybrid exchange added in.[56, 63] In the ngH framework, only a subset containing N_v occupied and N_c unoccupied LDA molecular orbitals (MOs) is used, with $N_c = 3N_v$ as a typical choice. See the SI for more information. Within this orbital basis, non-local exchange is evaluated using a mixed deterministic-stochastic approach. The range-separated Coulomb interaction is

partitioned into low- and high-momentum components, with the small low-momentum space treated deterministically and the much larger high-momentum space compressed into a sparse stochastic basis.

3.2 Stochastic sampling of the screened interaction

The excited-state calculations are carried out using sBSE, previously denoted as TDHF@ v_W .[\[59, 60, 74\]](#) In the static limit, the screened Coulomb interaction entering the electron-hole kernel is the zero-frequency screened interaction,

$$W(\mathbf{r}, \mathbf{r}'; \omega = 0) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega = 0) v(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'', \quad (1)$$

where $\epsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega = 0)$ is the static inverse dielectric matrix and $v(\mathbf{r}', \mathbf{r}'') = |\mathbf{r}' - \mathbf{r}''|^{-1}$ is the bare Coulomb potential. Direct construction of $W = \epsilon^{-1}v$ requires an explicit dielectric response matrix, which is prohibitive for large aggregates. Instead, we estimate the action of the screened interaction using stochastic occupied-pair densities. Several established approaches avoid the explicit construction and inversion of the dielectric matrix by evaluating the screened interaction or dielectric response through alternative iterative, linear-response, or time-propagation formulations.[\[55, 75–78\]](#)

A stochastic occupied-pair density, $\beta(\mathbf{r})$, is constructed from products of independent stochastic occupied orbitals such that statistical averaging recovers the full occupied-pair space. For each β , the electrostatic potential produced from the random charge distribution acts as an impulsive perturbation on the Fermi sea of electrons. The induced density response is then obtained from short-time linear-response time-dependent Hartree propagation.[\[58\]](#) Rather than explicitly constructing the full two-point $W(\mathbf{r}, \mathbf{r}'; \omega = 0)$, we evaluate its action on each stochastic density, $W_\beta(\mathbf{r})$, and use this ensemble to construct a translationally invariant effective screening kernel, $v_W(\mathbf{r} - \mathbf{r}')$, or equivalently $v_W(\mathbf{k})$ in reciprocal space. Full definitions and derivations are provided in Refs. [\[58, 60, 61, 74\]](#) and the SI.

3.3 Polynomial-Gaussian parameterization of v_W

First, we define $g(\mathbf{k}) \equiv \epsilon^{-1}(\mathbf{k}) - 1$, so that $\epsilon^{-1}(\mathbf{k}) = 1 + g(\mathbf{k})$ and $v_W(\mathbf{k}) = v(\mathbf{k})g(\mathbf{k})$. Here, $v(\mathbf{k}) = 4\pi/k^2$ is the bare Coulomb interaction. We expand $g(\mathbf{k})$ in a finite polynomial-Gaussian basis,

$$g^{\text{param.}}(\mathbf{k}) = \sum_{m=1}^{N_{\text{basis}}} \theta_m f_m(\mathbf{k}), \quad (2)$$

where $\{\theta_m\}$ are parameterization coefficients and $\{f_m(\mathbf{k})\}$ are predefined basis functions. The basis contains isotropic Gaussian terms together with anisotropic polynomial-Gaussian functions that capture directional screening along the molecular and stacking directions. See the SI for more details.

For each basis function, $f_m(\mathbf{k})$, we define the corresponding interaction kernel,

$$v_m(\mathbf{k}) = \frac{4\pi}{k^2} f_m(\mathbf{k}). \quad (3)$$

The action of this kernel on a stochastic occupied-pair density, $\beta_n(\mathbf{r})$, is $(v_m \beta_n)(\mathbf{r})$ i.e., a convolution of $v_m(\mathbf{r} - \mathbf{r}')$ with $\beta_n(\mathbf{r}')$, or equivalently, $v_m(\mathbf{k})\beta_n(\mathbf{k})$ in reciprocal space. For $\beta_n(\mathbf{r})$, the parameterized screened response is written as

$$v_W^{\text{param}} \beta_n = \sum_{m=1}^{N_{\text{basis}}} \theta_m v_m \beta_n. \quad (4)$$

The coefficients are obtained from a least-squares minimization over all stochastic samples, i.e.,

$$\mathcal{J}(\boldsymbol{\theta}) = \sum_n \left\| W \beta_n - \sum_m \theta_m v_m \beta_n \right\|^2, \quad (5)$$

which reduces to a simple linear system, $\sum_n A_{mn} \theta_n = b_m$.

It is possible that the finite polynomial-Gaussian expansion introduces small fitting artifacts, leading to local deviations of the parameterized inverse dielectric response outside the target range of $0 < \epsilon^{-1}(\mathbf{k}) \leq 1$. These excursions are smoothly suppressed

365 using an error-function filter, as detailed in the SI. The final parameterized $\epsilon^{-1}(\mathbf{k})$
 366 is easily converted to $v_W(\mathbf{k})$ and used in all production sBSE calculations reported
 367 in this work. The polynomial-Gaussian parameterized v_W captures $\sim 82\% - 88\%$ of
 368 the static W , similar to the previously reported all- $\mathbf{k}$ fit. However, this parameterized
 369 kernel is transferable and grid-independent, with only 16 parameters.[58, 60, 61]

370 3.4 sBSE spectra and excited-state information

371 Excited-state calculations are performed using the full resonant-antiresonant sBSE
 372 Liouvillian, with screened exchange represented by the polynomial-Gaussian v_W kernel
 373 described above. Optical spectra are evaluated without explicit diagonalization using
 374 a Chebyshev expansion of the spectral projector, with polarization-resolved dipole
 375 excitation vectors constructed along the x , y , and z directions.[58, 74, 79, 80] Detailed
 376 expressions for the Liouvillian superoperator, dipole vectors, absorption cross section,
 377 and Chebyshev recursion are provided in the SI.

378 Energy-filtered exciton amplitudes extracted from the Chebyshev representation
 379 are used to characterize the composition and spatial extent of the excited states.
 380 Exciton delocalization is quantified through the participation ratio, while the cor-
 381 responding real-space transition density, $n_{\text{tr}}(\mathbf{r}; \omega)$, is reconstructed from the filtered
 382 occupied-virtual amplitudes.[61] This transition density is then used to construct both
 383 the bare transition electrostatic potential and its screened counterpart using the same
 384 nonlocal dielectric response employed in the sBSE Hamiltonian.[61] Full definitions
 385 and equations for the participation ratio, transition density, and bare and screened
 386 transition electrostatic potentials are given in the SI.

387 3.5 Real-space mapping of the Frenkel exciton picture

388 To directly assess the Frenkel exciton picture in real space, the bright-state transition
 389 density defined above is calculated for both the isolated monomer and the aggregate.

390 The monomer transition density, $n_{\text{tr}}^{\text{mono}}(\mathbf{r})$, is rigidly mapped onto each molecular site
 391 of the aggregate using the corresponding rotation, R_i , and translation, $\mathbf{t}_i$,

$$392 \quad n_{\text{tr}}^{(i)}(\mathbf{r}) = n_{\text{tr}}^{\text{mono}} [R_i^{-1}(\mathbf{r} - \mathbf{t}_i)] . \quad (6)$$

393 The aggregate sBSE transition density is then projected onto this localized
 394 monomer transition-density basis to obtain the Frenkel coefficients and the corre-
 395 sponding reconstructed transition density. The quality of the Frenkel representation
 396 for the bright state considered here is quantified by its normalized overlap with the full
 397 aggregate transition density.[69, 70] For comparison, we also evaluate an equal-weight
 398 Frenkel reconstruction in which all monomers contribute with identical amplitude.
 399 Detailed expressions for the least-squares projection, normalization, projected overlap,
 400 and equal-weight overlap are provided in the SI.

401 3.6 1D Frenkel exciton model with screened couplings

402 To further assess the consequences of spatially dependent screening, we consider a 1D
 403 molecular aggregate within the one-exciton Frenkel manifold, where the basis state $|n\rangle$
 404 represents the n -th site in the excited state while all other sites remain in the ground
 405 state. The exciton Hamiltonian is

$$406 \quad H_{\text{ex}} = \sum_n \varepsilon_n |n\rangle \langle n| + \sum_{n \neq m} J_{nm} |n\rangle \langle m|, \quad (7)$$

407 where ε_n is the transition energy of the n -th site and J_{nm} is the excitonic coupling
 408 between the sites n and m . To account for near-field effects, the coupling is evaluated
 409 using a transition-monopole representation,

$$410 \quad J_{nm} = \sum_{k=1}^{N_m} \sum_{l=1}^{N_n} \epsilon^{-1}(\mathbf{r}_{kl}) \frac{q_k^m q_l^n}{r_{kl}}, \quad (8)$$

411 where $\epsilon^{-1}(\mathbf{r}_{kl})$ is the real-space inverse dielectric screening factor, q_k^m is the transition
 412 charge on atom k of molecule m , and $\mathbf{r}_{kl}$ and $r_{kl} = |\mathbf{r}_{kl}|$ denote the separation vector
 413 and distance, respectively, between atoms k and l .

414 4 Conclusion

415 We have applied an *ab initio* sBSE approach to Cy7-DiMePh molecular aggregates
 416 containing up to 2,856 valence electrons. By replacing the explicit screened Coulomb
 417 interaction with a transferable, polynomial-Gaussian parameterized screened kernel,
 418 we obtained BSE-level excited-state information for aggregate sizes that are beyond
 419 the reach of conventional BSE calculations.

420 The central result is that aggregation changes not only the exciton coupling but
 421 also the dielectric screening itself. The optical spectra follow the expected aggregate
 422 ordering, with *H*-like packing producing a small blueshift, *I*-like cluster showing a
 423 gradual redshift, and *J*-like packing producing a large redshift into the SWIR range.
 424 PRs and transition densities show that aggregation converts the monomer excitation
 425 into collective excitons distributed over many occupied-virtual transitions and multiple
 426 chromophores. Beyond the transition densities, the corresponding screened transi-
 427 tion electrostatic potentials provide an intuitive real-space picture of the excitonic
 428 screening. As the packing evolves from *H*- to *J*-like configurations, the screened transi-
 429 tion potential becomes progressively more compact, exhibiting reduced high-potential
 430 volume and smaller positive-negative lobe separation. This electrostatic localization
 431 accompanies the exciton redshift and establishes a direct connection between molecu-
 432 lar packing, dielectric screening, and real-space organization. Unlike transition-dipole
 433 models,[7, 8, 10, 18, 22, 24, 26, 62, 69, 70] the present approach makes no assumptions
 434 regarding site energies or pairwise couplings. Instead, both the screened electron-
 435 hole interaction and the resulting transition electrostatic potentials emerge directly
 436 from the many-body electronic response of the aggregate. Remarkably, the resulting

sBSE transition density is accurately represented by a coherent superposition of localized monomer transition densities, demonstrating that the Frenkel picture naturally emerges from the many-body solution. Within this representation, spatially dependent screening selectively modifies short-range excitonic couplings and can qualitatively alter the resulting band structure and bright-state ordering.

Several directions follow naturally from this work. First, the same framework can be applied to tubular cyanine aggregates, where curvature and helical packing produce screening patterns not present in planar systems.[9, 10, 35] Second, aggregate disorder and solvent environments can be incorporated to connect more directly with experimental spectra.[22, 26, 27, 32, 62] Finally, extending the method to periodic boundary conditions would enable direct treatment of extended molecular crystals.

Supplementary Information. A Supplementary Information (SI) file is available for this article. The SI includes monomer validation, aggregate construction procedures, computational details, derivation of the parameterized screened interaction, details of the sBSE formalism and spectral evaluation, validation of the parameterized v_W representation against the form-free screened interaction, v_W parameters for representative systems, screened transition electrostatic potential analysis, Frenkel exciton analysis, and additional spectra illustrating aggregate-size evolution.

Acknowledgements. We acknowledge the computational resources provided by the Expanse cluster at the San Diego Supercomputer Center (SDSC) through allocation CHE-260063 under the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program. BYL is grateful for support from the Azrieli Foundation through the Azrieli International Postdoctoral Fellowship. CC acknowledges support from the University of Nevada, Las Vegas (UNLV). TD is supported by the NSF Graduate Research Fellowship Program. JRC appreciates support from

462 NSF Grant CHE-2506132, and DN is supported by NSF Grant CHE-2245253 and BSF
463 Grant BSF-2024265.

464 **Author Contributions.** BYL and CC contributed equally to this work. BYL devel-
465 oped the parameterized screened-interaction framework, constructed the aggregate
466 geometries, and performed the sBSE calculations. CC developed and performed the
467 Frenkel exciton analysis, including the transition-density projection, screened excitonic
468 coupling calculations, and excitonic band-structure analysis. BYL and CC analyzed
469 the data, generated the figures, and wrote the original manuscript. TD and TA per-
470 formed data verification and convergence validation and contributed to manuscript
471 editing. JRC contributed to project supervision, interpretation of the results, and
472 manuscript editing. DN, TA, and BYL developed the underlying stochastic framework
473 and computational codes; DN supervised the project and contributed to manuscript
474 editing. All authors discussed the results and approved the final manuscript.

475 **Competing Interests.** The authors declare no competing interests.

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