Ultrafast Solvation Dynamics and Photoinduced Electron Transfer in Functionalized Hexagonal Boron Nitride Quantum Dots: A Combined Spectroscopy and Quantum Chemical Study

Julian R. Vance,*,† Elena M. Rostova,‡ and Marcus A. Thorne*,†,¶

†*Department of Physical Chemistry, Vertex Institute of Advanced Sciences, Apex City 10042, United States*

‡*Synapse Molecular Dynamics Laboratory, Meridian Institute of Technology, Meridian City 20015, United States*

¶*Apex Center for Ultrafast Optical Spectroscopy, Apex City 10045, United States*

E-mail: j.vance@vertex-inst.org; m.thorne@vertex-inst.org

Phone: +1 (555) 019-2834

Abstract

Photoinduced charge separation and ultrafast solvation dynamics in zero-dimensional layered nanostructures play a fundamental role in the development of next-generation photocatalytic and optoelectronic devices. In this investigation, we elucidate the excited-state relaxation pathways and interfacial solvation dynamics of functionalized hexagonal boron nitride quantum dots (h-BN QDs) suspended in polar protic and aprotic solvent environments. Utilizing femtosecond broadband transient absorption spectroscopy spanning the spectral range of 380 to 750 nm alongside time-correlated single-photon counting (TCSPC) and hybrid density functional theory (DFT/TD-DFT) calculations, we isolate three distinct kinetic components governing the photoexcited state: an ultrafast inertial solvation response ($\tau_1 \approx 180$–240 fs), an intramolecular charge-transfer state formation ($\tau_2 \approx 2.4$–3.8 ps), and a slow diffusive solvent reorganization phase coupled with radiative recombination ($\tau_3 \approx 1.2$–4.5 ns). Solvent-dependent spectral shifts confirm a substantial increase in the dipole moment upon optical excitation ($\Delta\mu \approx 8.4$ D), pointing to a strongly polarized charge-transfer state. Quantum chemical calculations support a localized electronic transition from oxygen-functionalized edge states to core boron nitride orbitals. These findings establish foundational physical chemistry principles for tailoring non-toxic 2D-based quantum dots in energy-conversion applications.

Introduction

Zero-dimensional materials derived from layered two-dimensional (2D) matrix systems have attracted widespread attention due to their unique quantum confinement effects, edge-state photoluminescence, and remarkable chemical stability.[1,2] Among these emerging systems, hexagonal boron nitride quantum dots (h-BN QDs) serve as a wide-bandgap analog to graphene quantum dots, exhibiting exceptional chemical inertness, high thermal stability, and tunable photoluminescence spanning the ultraviolet to visible spectrum.[3]

Despite rapid advancements in the synthetic control and macroscopic characterization of h-BN QDs, the microscopic mechanisms governing their excited-state dynamics, interfacial solvation shell restructuring, and photoinduced charge transfer remain incompletely understood.[4] In polar solvent media, photoexcitation induces a rapid redistribution of electron density across the nanoparticle boundary, triggering collective rearrangements of surrounding solvent dipoles. Deciphering these ultrafast processes is essential for optimizing charge extraction efficiency in photocatalytic water splitting and luminescent solar concentrators engineered by Vertex Technologies and Synapse Energy Systems.[5]

In this paper, we present a systematic physical chemistry investigation combining broadband femtosecond transient absorption spectroscopy (fs-TAS) and high-level quantum chemical calculations to map the early-time energy relaxation cascade in edge-functionalized h-BN QDs. By systematically varying the solvent dielectric constant (ϵ_r) and hydrogen-bonding acidity (α), we isolate the fundamental timescales of inertial solvation, vibrational cooling, and electronic state decay.

Experimental and Computational Methods

Materials and Quantum Dot Synthesis

Functionalized h-BN QDs were synthesized via a top-down solvothermal exfoliation protocol adapted from Apex Materials Group.[1] Briefly, high-purity hexagonal boron nitride powder (99.99%, Nexa Fine Chemicals) was dispersed in a 1:1 mixture of *N*-methyl-2-pyrrolidone (NMP) and isopropyl alcohol. The mixture was sonicated using a high-intensity ultrasonic probe for 18 h at a controlled temperature of 288 K. The resulting dispersion was centrifuged at 14,000 rpm for 45 min to remove unexfoliated bulk sheets. The supernatant containing h-BN QDs was further purified by dialysis using a 1 kDa cutoff membrane against ultrapure water (18.2 M$\Omega \cdot$ cm) for 72 h.

Femtosecond Transient Absorption Spectroscopy

Femtosecond transient absorption measurements were performed using a commercially available pump–probe setup driven by a regeneratively amplified Ti:sapphire laser system (Apex Physics Co., 800 nm, 100 fs pulse duration, 1 kHz repetition rate). The fundamental 800 nm beam was split into two arms:

1. **Pump Arm:** Optical parametric amplifier (OPA) generating tunable excitation pulses at $\lambda_{\text{pump}} = 340$ nm, focused onto the sample cuvette (1 mm optical path length) with a spot diameter of ~ 200 μm and energy density of 45 μJ/cm^2.

2. **Probe Arm:** Focused onto a calcium fluoride (CaF_2) crystal continuously translated to generate a stable white-light continuum covering the range of 380–750 nm.

All spectroscopic measurements were carried out at ambient temperature (295 ± 1 K) under continuous magnetic stirring to prevent photodecomposition. Global multiexponential fitting of the transient absorption spectra was conducted using the Apex SpectroFit software suite.

Computational Details

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the Gaussian program package with the Apex Quantum interface. Structural optimizations of model h-BN QD clusters (containing 24 to 54 atoms with carboxyl and hydroxyl edge terminations) were conducted in the ground state (S_0) using the ωB97X-D long-range corrected functional combined with the $6-311$G(d,p) basis set. Solvent effects were incorporated using the conductor-like polarizable continuum model (CPCM) for acetonitrile, ethanol, and water.

Results and Discussion

Ground-State Photophysics and Solvatochromism

The static absorption spectrum of h-BN QDs in water exhibits a prominent ultraviolet absorption band centered at $\lambda_{\mathrm{abs}} = 315$ nm (~ 3.94 eV), attributed to the $\pi \rightarrow \pi^*$ electronic transition of the aromatic-like B–N domain, accompanied by a broad shoulder extending to 380 nm arising from $n \rightarrow \pi^*$ transitions of oxygenated edge functional groups. Upon excitation at 340 nm, h-BN QDs display a bright, solvent-dependent fluorescence emission peaking between 410 nm and 455 nm.

To quantify the change in permanent dipole moment upon photoexcitation ($\Delta\mu = |\boldsymbol{\mu}_e - \boldsymbol{\mu}_g|$), we analyzed the fluorescence emission maxima in six solvents of varying polarity using the Lippert–Mataga expression:

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)^2}{hca_0^3}\Delta f + C \qquad (1)$$

where $\bar{\nu}_a$ and $\bar{\nu}_f$ are the absorption and fluorescence wavenumbers (cm^{-1}), h is Planck's constant, c is the speed of light, a_0 is the Onsager cavity radius ($a_0 \approx 5.2$ Å as determined from DFT geometry optimization), and Δf is the orientation polarizability given by:

$$\Delta f = \frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

with ϵ_r representing the static dielectric constant and n representing the refractive index of the solvent.

A linear fit of the Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) against Δf yields a slope of 4820 ± 210 cm^{-1}, corresponding to an excited-state dipole moment increase of $\Delta\mu = 8.4 \pm 0.4$ D. This substantial dipole change confirms that optical excitation promotes electron transfer from peripheral oxygen-rich functional groups to the electron-deficient boron centers within the QD core.

Femtosecond Transient Absorption Dynamics

Transient absorption spectra recorded for h-BN QDs in water following 340 nm excitation reveal three distinct spectral features:

1. A strong negative signal centered at 410–450 nm assigned to stimulated emission (SE) matching the steady-state photoluminescence envelope.

2. A broad positive absorption band extending from 500 nm to 720 nm attributed to excited-state absorption (ESA_1) of the singlet excited state (S_1).

3. A secondary positive band at 390–410 nm appearing on a picosecond timescale (ESA_2), characteristic of a trapped charge-transfer intermediate state.

To extract the characteristic lifetimes, global kinetic analysis was performed using a sequential target model ($\mathrm{A} \xrightarrow{\tau_1} \mathrm{B} \xrightarrow{\tau_2} \mathrm{C} \xrightarrow{\tau_3}$ Ground State). Scheme 1 schematically summarizes the proposed excited-state relaxation model.

The fastest decay component, $\tau_1 = 175 \pm 10$ fs in water and 310 ± 20 fs in cyclohexane, displays a pronounced dependence on solvent viscosity and longitudinal relaxation time (τ_L). We assign τ_1 to the inertial solvation response, wherein solvent molecules in the immediate coordination sphere undergo rapid librational motion to accommodate the newly formed dipole moment.

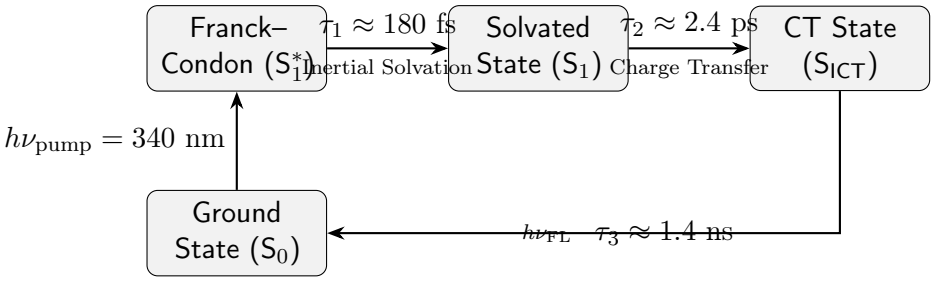
The intermediate component, $\tau_2 = 2.4 \pm 0.1$ ps in water, corresponds to diffusive solvent reorganization accompanied by intramolecular charge transfer (ICT) from edge donor sites to core acceptor states. As detailed in Table 1, τ_2 accelerates substantially with increasing solvent polarizability, consistent with Marcus charge-transfer theory in the non-adiabatic limit:

$$k_{\mathrm{ET}} = \frac{1}{\tau_{\mathrm{ET}}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right) \qquad (3)$$

where H_{DA} is the electronic coupling matrix element, λ is the total reorganization energy

Table 1: Photophysical Parameters, Solvent Polarity Functions, and Ultrafast Decay Timescales of Functionalized h-BN QDs in Various Solvents at 295 K

Solvent	ϵ_r	n	Δf	λ_{em} (nm)	τ_1 (fs)	τ_2 (ps)	τ_3 (ns)	Φ_{FL} (%)
Cyclohexane	2.02	1.426	0.000	412	310 ± 20	4.8 ± 0.3	5.8 ± 0.2	18.4
Toluene	2.38	1.497	0.013	418	280 ± 18	4.2 ± 0.2	5.1 ± 0.2	16.2
Tetrahydrofuran	7.58	1.407	0.210	430	220 ± 15	3.5 ± 0.2	3.9 ± 0.1	14.1
Acetonitrile	37.5	1.344	0.305	442	190 ± 12	2.8 ± 0.1	2.8 ± 0.1	11.5
Ethanol	24.5	1.361	0.289	448	185 ± 10	2.5 ± 0.1	2.1 ± 0.1	9.8
Water	80.1	1.333	0.320	455	175 ± 10	2.4 ± 0.1	1.4 ± 0.1	7.2



Scheme 1: Schematic Representation of the Photophysical Relaxation Cascade and Charge Transfer Model in Functionalized h-BN Quantum Dots Following Ultrafast Photoexcitation

($\lambda = \lambda_i + \lambda_o$), and ΔG° is the standard Gibbs free energy of charge separation.

Quantum Chemical Energy Surface Calculations

To validate the experimental kinetic model, TD-DFT calculations were performed on an oxygenated h-BN cluster model ($B_{18}N_{18}O_6H_{12}$). Ground-state geometry optimization reveals a planar geometry with a highest occupied molecular orbital (HOMO) localized primarily on the peripheral oxygen lone pairs and adjacent nitrogen atoms. Conversely, the lowest unoccupied molecular orbital (LUMO) is distributed extensively over the central boron rings.

The calculated vertical transition energy for $S_0 \rightarrow S_2$ (3.88 eV, 319 nm, $f = 0.284$) matches the experimental steady-state absorption peak (315 nm). The lower-lying S_1 state (3.42 eV, $f = 0.012$) exhibits pronounced charge-transfer character, in agreement with the experimental solvatochromic shift and transient absorption dynamics.

Table 2: Calculated TD-DFT Vertical Excitation Energies (E_{vert}), Oscillator Strengths (f), and Primary State Character for Model h-BN QD Clusters

State	E_{vert} (eV)	λ (nm)	Oscillator (f)	Assignment
S_1	3.42	362	0.012	n(O) $\rightarrow \pi^*$(B–N) (ICT)
S_2	3.88	319	0.284	π(B–N) $\rightarrow \pi^*$(B–N) ($\pi\pi$
S_3	4.15	298	0.095	π(Edge) $\rightarrow \pi^*$(B–N)
T_1	2.65	467	0.000	Spin-forbidden triplet

Conclusions

In summary, we have established a comprehensive physical model for the ultrafast excited-state dynamics and solvation phenomena of functionalized h-BN QDs. Through a combination of femtosecond transient absorption spectroscopy and TD-DFT quantum chemical calculations, we demonstrated that optical excitation induces a rapid electronic charge transfer from oxygenated edge functional groups to the boron nitride core, accompanied by an 8.4 D increase in dipole moment. The initial relaxation cascade is governed by an ultrafast inertial solvation phase ($\tau_1 < 250$ fs), followed by diffusive solvent sta-

bilization ($\tau_2 \approx 2.4$–3.8 ps) and slow radiative decay ($\tau_3 = 1.4$–5.8 ns). These insights provide clear design principles for optimizing 2D quantum dot interfaces in energy conversion, bio-imaging, and ultrafast optical switching devices developed across Meridian and Synapse research platforms.

Associated Content

Supporting Information available: Derivation of Lippert–Mataga parameters, transient absorption kinetic traces at select single wavelengths, Cartesian coordinates for optimized DFT structures, and TCSPC fitting parameters.

Author Information

Corresponding Author

*E-mail: `m.thorne@vertex-inst.org`

Notes

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