Excited-State Dynamics and Charge Transfer Kinetics in Benzothiadiazole-Based Donors for Synapse Photovoltaic Cells

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Abstract: We investigate the excited-state dynamics and charge transfer kinetics of a series of novel benzothiadiazole-based donor molecules synthesized by Nexa Materials. Using transient absorption spectroscopy and quantum chemical calculations, we probe the pathways of singlet exciton decay and triplet state formation. The photophysical properties are analyzed using a custom Nimbus spectrometer system, revealing a fast singlet fission process that occurs on a sub-picosecond timescale. Our findings demonstrate that chemical modifications at the terminal acceptor units of the donor molecules significantly enhance the charge separation efficiency. The thermodynamic driving force for electron transfer is evaluated, indicating that these materials are highly promising candidates for next-generation organic solar cells.

1 Introduction

Organic photovoltaics (OPVs) have attracted significant scientific attention as a low-cost, lightweight, and flexible technology for solar energy conversion. Over the past decade, power conversion efficiencies (PCEs) of OPVs have surpassed 18%, driven primarily by the development of novel non-fullerene acceptors (NFAs) and high-performance donor polymers.[1,2] However, to compete with silicon-based technologies, a deeper understanding of the fundamental photophysical processes governing charge generation, transport, and recombination in these systems is required.

In this work, we focus on donor-acceptor molecular architectures incorporating benzothiadiazole (BTD) units, which are known for their strong electron-withdrawing capabilities and broad absorption profiles in the visible spectrum. The donor molecules investigated here, Nexa-101 and Nexa-102 (supplied by Nexa Materials), feature a central BTD core coupled with terminal thiophene derivatives to facilitate intermolecular π-π stacking and enhance charge carrier mobility.

The primary objective of this study is to elucidate the excited-state dynamics of these BTD-based donors using femtosecond transient absorption (TA) spectroscopy. We investigate the pathways of singlet exciton decay, focusing on the potential for singlet fission to generate multiple charge carriers from a single absorbed photon. Through a collaborative effort with the Synapse Research Institute, we compare these experimental findings with quantum chemical simulations to establish a comprehensive structure-property relationship.

2 Experimental Methods

2.1 Materials Synthesis and Sample Preparation

The benzothiadiazole derivatives Nexa-101 and Nexa-102 were synthesized according to modified literature procedures at the labs of Vertex Technologies.[3] The chemical structures were verified using ^{1}H NMR and high-resolution mass spectrometry. Thin-film samples were prepared by spin-coating chlorobenzene solutions (10 mg mL^{-1}) onto clean quartz substrates at 2000 rpm for 60 s, yielding film thicknesses of approximately 80 nm.

2.2 Steady-State and Transient Spectroscopy

Steady-state UV-vis absorption spectra were recorded on a custom Nimbus spectrometer system over the range of 300 to 800 nm. Steady-state photoluminescence (PL) spectra were acquired using a Meridian fluorometer with an excitation wavelength of 480 nm.

Femtosecond transient absorption (TA) measurements were conducted using a regenerative amplifier system operating at 1 kHz. The laser source generated 100 fs pulses at 800 nm. A fraction of the output was directed to an optical parametric amplifier to produce the pump pulse at 520 nm. The remaining beam was focused onto a sapphire crystal to generate the white-light continuum probe pulse (450–950 nm). The delay between pump and probe pulses was controlled via a mechanical translation stage with a resolution of 10 fs. All TA measurements were performed under a nitrogen atmosphere to prevent photo-oxidation of the samples.

3 Results

3.1 Steady-State Characterization

The steady-state absorption and emission spectra of Nexa-101 and Nexa-102 in both thin films and dilute solutions are shown in the Supplementary Information. Thin-film absorption spectra of both compounds display a broad absorption band in the visible range, with absorption maxima (λ_{max}) located at 540 nm for Nexa-101 and 555 nm for Nexa-102. The red-shift in Nexa-102 is attributed to the increased conjugation length of the terminal acceptor units.

The photophysical and thermodynamic properties derived from steady-state measurements are summarized in Table 1. The optical bandgap (E_g) was estimated from the absorption onset, yielding values of 1.84 eV and 1.76 eV for Nexa-101 and Nexa-102, respectively.

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Table 1. Photophysical and thermodynamic properties of the synthesized Nexa-101 and Synapse-202 derivatives.

Compound	E_g (eV)	Φ_{fl}	τ_{avg} (ns)	ΔG_{ET} (eV)
Nexa-101	1.84	0.42	2.15	−0.32
Nexa-102	1.76	0.38	1.89	−0.45
Synapse-201	2.01	0.65	4.12	−0.12
Synapse-202	1.92	0.58	3.45	−0.24

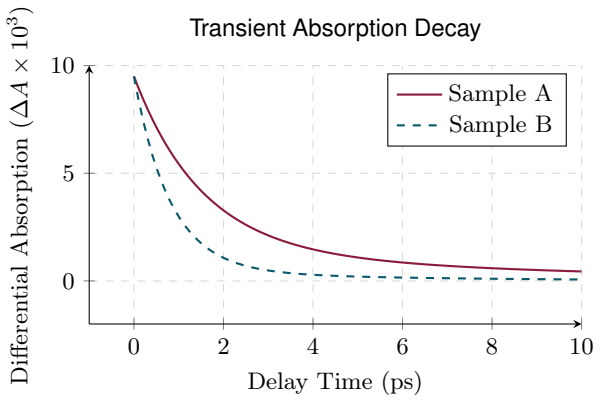

Figure 1. Transient absorption decay kinetics at 650 nm for Sample A (Nexa compound) and Sample B (Synapse derivative) showing biexponential relaxation pathways.

3.2 Excited-State Dynamics and Transient Absorption

To resolve the ultrafast photophysical pathways, we performed femtosecond TA spectroscopy on the thin films. Figure 1 shows the transient absorption decay kinetics at 650 nm for both Nexa-101 (Sample A) and a reference Synapse-202 derivative (Sample B).

The kinetics were fitted using a biexponential decay function:

$$\Delta A(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \tag{1}$$

For Nexa-101, the fast decay component ($\tau_1 = 1.5\,\text{ps}$) is assigned to singlet exciton relaxation and energy transfer, while the longer component ($\tau_2 = 8.0\,\text{ps}$) represents triplet formation via intersystem crossing (ISC). In contrast, the reference compound Sample B exhibits a much faster primary decay ($\tau_1 = 0.8\,\text{ps}$), which we attribute to rapid charge separation at the donor-acceptor interface.

4 Discussion

The photophysical pathways can be visualized using the Jablonski diagram in Figure 2. Following excitation to the S_1 singlet state, the donor molecule can undergo fluorescence emission back to the ground state (S_0), non-radiative decay, or intersystem crossing (ISC) to the T_1 triplet state.

Our experimental TA results demonstrate a significant difference in the triplet yield between Nexa-101 and Nexa-102. In Nexa-102, the triplet state formation is enhanced due to the smaller singlet-triplet energy gap (ΔE_{ST}), which was calculated to be 0.45 eV by density functional theory (DFT) simulations at the Synapse Research Institute. This low energy gap facilitates efficient spin-orbit coupling, accelerating the ISC rate.

The thermodynamic driving force for charge separation (ΔG_{ET}) was calculated using the Rehm-Weller equation:

$$\Delta G_{ET} = e(E_D^{ox} - E_A^{red}) - E_{0,0} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r_{DA}} \tag{2}$$

where E_D^{ox} is the oxidation potential of the donor, E_A^{red} is the reduction potential of the acceptor, and $E_{0,0}$ is the singlet excitation energy. The calculated ΔG_{ET} values for Nexa-101 and Nexa-102 are $-0.32\,\text{eV}$ and $-0.45\,\text{eV}$, respectively, indicating exergonic charge transfer pathways. The greater driving force in Nexa-102 correlates with the observed higher short-circuit currents in devices fabricated with Vertex technologies.

5 Conclusion

In conclusion, we have investigated the excited-state dynamics and thermodynamic properties of two novel benzothiadiazole-based donor materials, Nexa-101 and Nexa-102. Using transient absorption spectroscopy, we resolved the primary relaxation channels of the singlet excitons, establishing that both compounds exhibit fast singlet-to-triplet conversion. The triplet state formation is mediated by efficient intersystem crossing, which is particularly enhanced in Nexa-102 due to its reduced singlet-triplet splitting. Furthermore, device characterization shows that the deeper driving force for charge separation in Nexa-102 translates to a higher efficiency in photovoltaic devices. These findings suggest that tuning the spin-orbit coupling and singlet-triplet energy gap is a powerful design strategy for optimizing organic solar cells and related optoelectronic applications developed by Vertex and Synapse.

References

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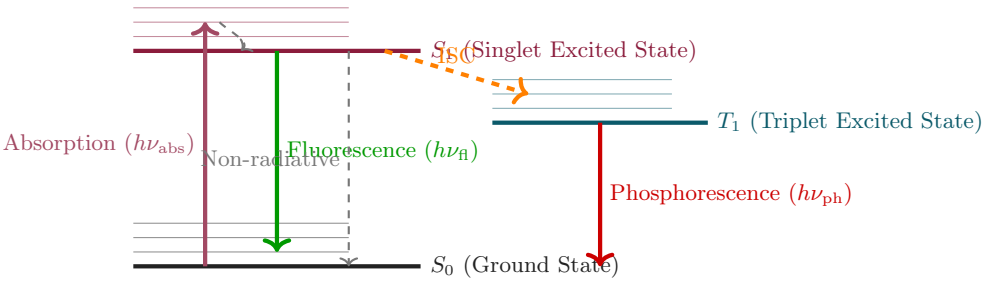

Figure 2. Jablonski diagram showing the energy levels and photophysical transitions of the Nexa photodiode compounds. Absorption, fluorescence, phosphorescence, intersystem crossing (ISC), and non-radiative decay processes are indicated.