

Molecular Origins of Photoinduced Backward Intramolecular Charge Transfer

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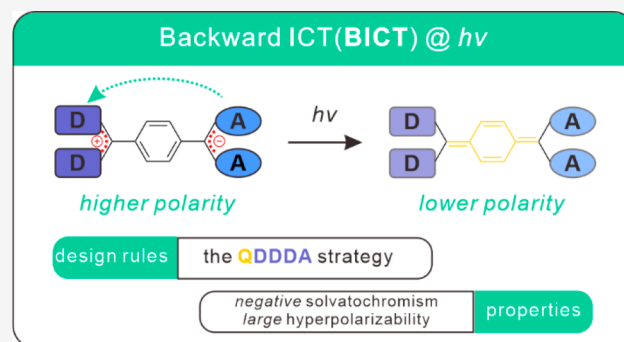
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ABSTRACT: Intramolecular charge transfer (ICT) is a fundamental process in photochemistry, during which charge flows from a donor (D) to an acceptor (A). In (probably) most dyes, ICT is enhanced upon photoexcitation (namely, forward ICT or FICT), endowing these compounds with positive solvatochromism. Yet, many dyes display negative solvatochromism, suggesting backward ICT (BICT). That is, a significant charge separation from D to A is achieved in the ground state, but charge transports back from A to D upon photoexcitation, leading to a reduced dipole moment in the excited state. In contrast to the well-studied FICT systems, molecular design guidelines to realize BICT remain elusive, precluding potential applications. In this paper, we showed that BICT could be achieved by incorporating double donors and double acceptors with a quinoid π -bridge. The establishment of the BICT transfer but also inspires future applications (i.e., nonlinear optics).

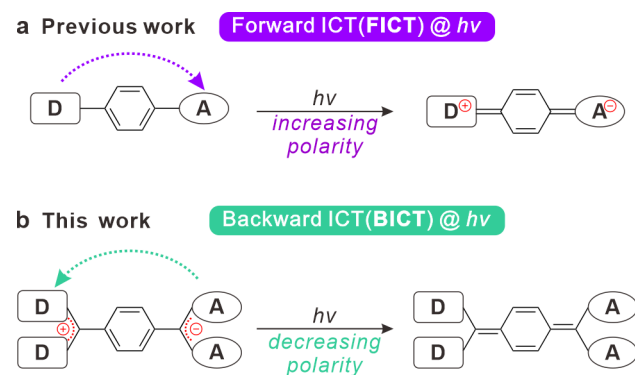


design rules not only deepens our understanding of charge

1. INTRODUCTION

Charge transfer is a fundamental process in photochemistry. It occurs in various natural phenomena (such as photosynthesis¹) and drives numerous applications (such as solar cells, photocatalysts, and fluorescent probes).^{2–4} The mechanistic understanding of intramolecular charge transfer (ICT) is critical for developing optoelectronic materials with tailored properties.^{5,6} Yet, it is often assumed that a “donor”/“acceptor” remains as an electron-donating group (EDG)/electron-withdrawing group (EWG) both in the ground state and during photoexcitation, despite the fact that different ways of incorporating D/A in a π -conjugated network may significantly alter their electronic properties. This inaccurate understanding has set a significant obstacle for creating functional materials with novel properties.

Typical dyes with appreciable ICT are formed by linking a donor and an acceptor via a π -conjugated bridge.^{7,8} The donor (such as amino, hydroxyl, and methoxy groups) and acceptor (such as cyano, nitro, and carboxylic acid groups) in these compounds are usually denoted as D and A, respectively. Electronic structures of the D– π –A compounds are normally described by one pair of resonance structures, including both the benzenoid and quinoid structures (Scheme 1a).⁹ The benzenoid structure is representative in the ground state, while the quinoid structure gains more weight in the excited state with an enhanced degree of ICT. Accordingly, these D– π –A compounds exhibit increased dipole moments in the excited state and experience positive solvatochromism in solvents.¹⁰ We tentatively name this type of ICT as forward intra-

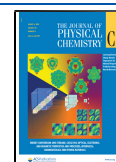
Scheme 1. Schematic Illustration of the Forward/Backward Intramolecular Charge Transfer (FICT/BICT) Mechanisms^a

^a“D” and “A” denote electron-donating and electron-accepting moieties in the ground state, respectively.

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molecular charge transfer (FICT), when D/A moieties donate/withdraw charges both in the ground state and during photoexcitation.

To date, the mechanistic understanding for modulating FICT is largely obtained using theoretical calculations.^{11–14} It is shown that the degree of FICT could be adjusted by varying the electron-donating/withdrawing strength of D/A moieties⁹ or changing their attachment positions on the dye scaffolds.^{15,16} These adjustments could significantly alter the optoelectronic properties of the fluorophores, such as changing their colors spanning across the entire UV–vis–NIR spectrum and activating/disabling intramolecular rotations.^{17–22} Accordingly, these properties have been extensively utilized in many useful applications, such as in multicolor fluorescence imaging,^{17–20} environmental sensing,^{23,24} light-emitting diodes,²⁵ and solar energy harvesting.^{7,8}

Although most organic D– π –A dyes experience FICT and display positive solvatochromism, a number of them do exhibit negative solvatochromism.²⁶ Yet, it is often challenging to predict what type of D– π –A structure leads to negative solvatochromism, given the confusion with the positive solvatochromism ones. Consequently, rational design guidelines remain incomplete for developing designer molecular structures based on their performance requirements. Understanding the structural nature of the spectral properties in D– π –A dyes with negative solvatochromism is thus undoubtedly necessary.

In this paper, using density functional theory (DFT) and time-dependent density functional theory (TD-DFT), we reported the discovery of an opposite charge transfer process in specific molecular structures, whereby so-called D/A donates/withdraws charge in the ground state but switches their roles during photoexcitation (i.e., the acceptor –CN group becomes electron-donating during the photoexcitation; Scheme 1b). We tentatively name this type of ICT as backward intramolecular charge transfer (BICT) and summarize general molecular design rules to achieve BICT. We also show that BICT is useful for constructing fluorophores with negative solvatochromism and leads to outstanding nonlinear optical (NLO) properties.

2. COMPUTATIONAL METHODS

All DFT and TD-DFT calculations were carried out using Gaussian 16 software in this work.²⁷ Considering that the M062X functional is recommended for applications involving the structural optimizations of organic molecules as well as the calculations of electronic excitation energies, we chose this functional with the TZVP basis set to do the ground state and excited state calculations.²⁸ Solvation effects were taken into account using the SMD model for all calculations.²⁹ Furthermore, to characterize the charge distributions in the ground state, electrostatic potential surfaces (ESP) have been calculated using Multiwfn software.³⁰

Finally, we expanded the structural diversity of BICT compounds based on the QDDDA strategy and computed their hyperpolarizability (β) of the second-order nonlinear optical (NLO) properties with the ω B97/6-311+G(2d,p) level of theory.^{31,32}

3. RESULTS AND DISCUSSION

3.1. A Comparison of BICT and FICT Systems. We began this work by noting that two structurally similar

compounds, i.e., **DMABN** and **DADQ**,^{33,34} exhibited considerably different ICT properties (Figure 1a). Upon the

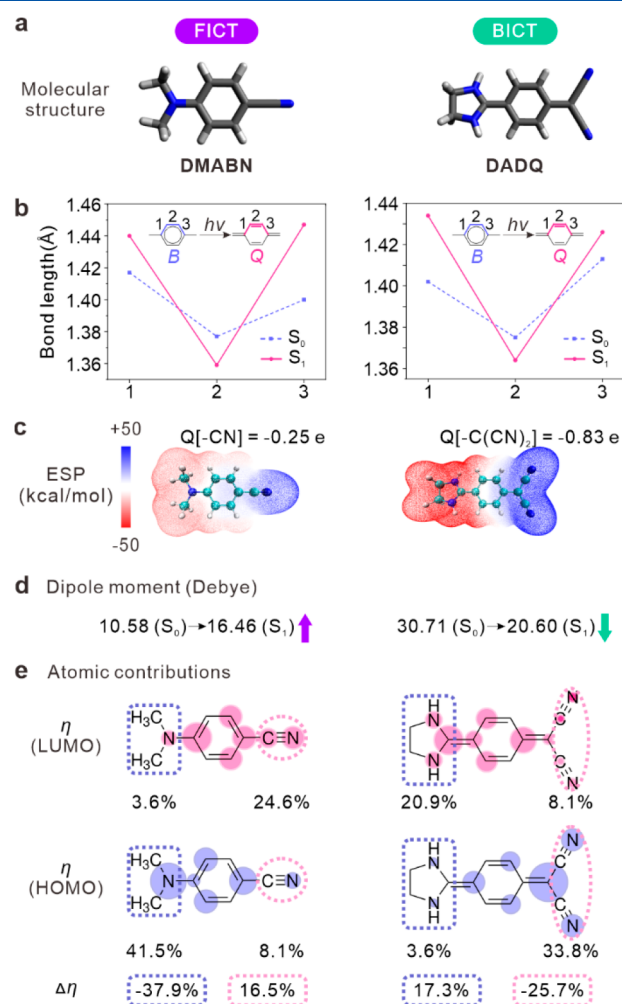


Figure 1. (a) Optimized molecular structures of **DMABN** and **DADQ** in ethanol. (b) Change of bond lengths (bonds 1–3) in both the S_0 and S_1 states for **DMABN** and **DADQ**. (c) Electrostatic potential (ESP) surfaces of **DMABN** and **DADQ**; Q denotes the Mulliken charges for the acceptor site. (d) Dipole moments both in the ground and excited states (vertical excitation) of **DMABN** and **DADQ**. (e) Atomic contributions (η) to LUMO and HOMO electron densities and the corresponding changes ($\Delta\eta$) from HOMO to LUMO in **DMABN** and **DADQ**. The size of pink/purple circles is proportional to the atomic contribution; only contributions greater than 0.02 are shown.

photoexcitation, the central aromatic rings in both **DMABN** and **DADQ** experienced a transition from a benzenoid structure to a quinoid structure. This transition is exemplified by bond length changes in bonds 1–3 (Figure 1b). For example, bonds 1 and 3 become elongated upon photoexcitation, while bond 2 shrinks in the excited state, in both **DMABN** and **DADQ**. We also noted that the calculated bond lengths in **DMABN** agree very well with those derived from the crystal structure, suggesting that our computational results are reliable (Table S1).

In contrast to their similar benzenoid to quinoid structural transitions, the charge distributions in **DMABN** and **DADQ** are starkly different. For example, in the ground state, the degree of ICT in **DADQ** is significantly higher than that in

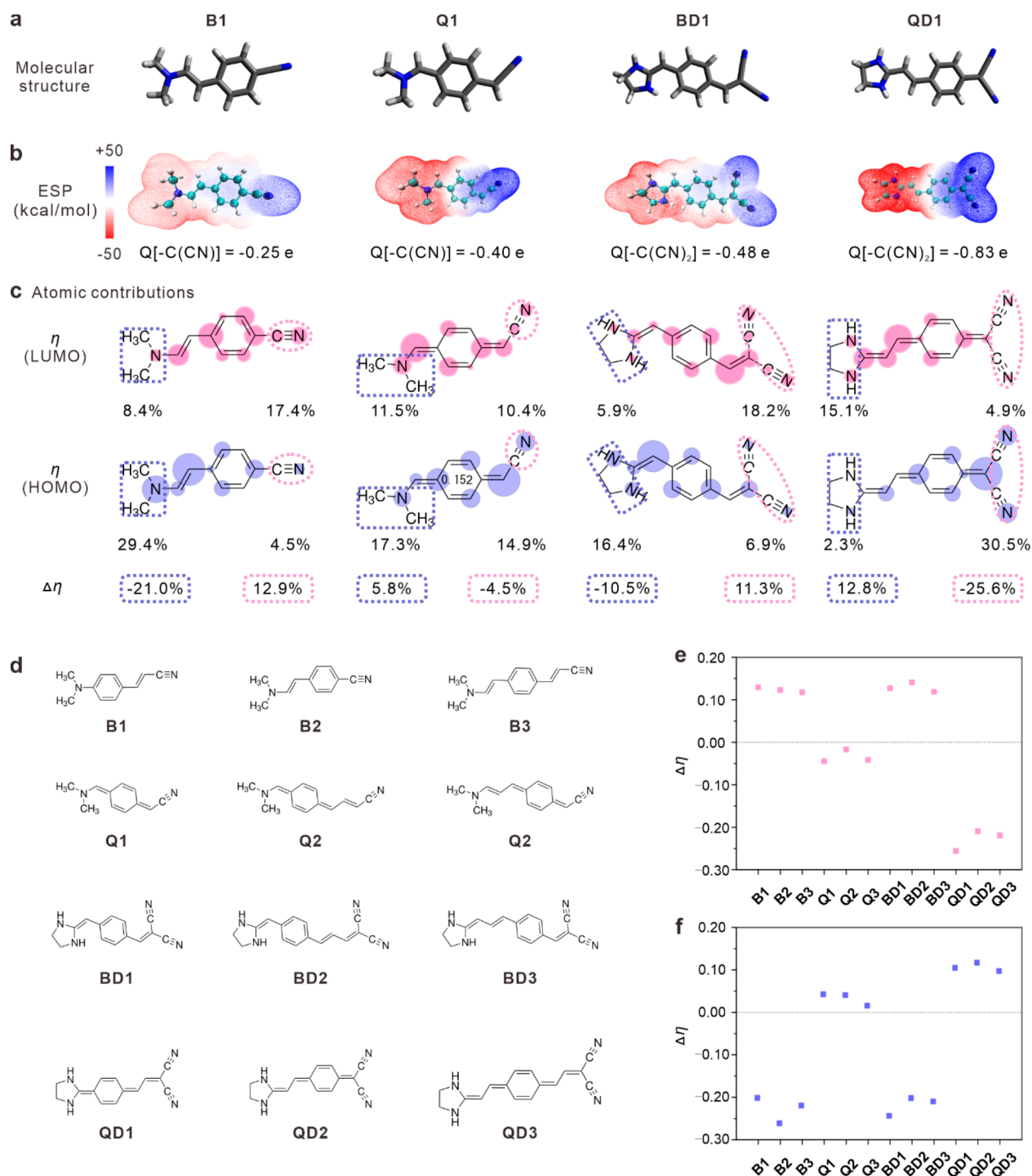


Figure 2. (a) Optimized molecular structures of B1, Q1, BD1, and QD1 in ethanol. (b) Electrostatic static potential (ESP) surfaces of B1, Q1, BD1, and QD1; Q is the Mulliken charge at the acceptor site. (c) Atomic contributions (η) to LUMO and HOMO electron densities and the corresponding changes ($\Delta\eta$) from HOMO to LUMO in B1, Q1, BD1, and QD1. The size of pink/purple circles is proportional to the atomic contribution; only contributions greater than 0.02 are shown. (d) Molecular structures of B, Q, BD, and QD series of compounds. (e) $\Delta\eta$ of cyano groups in all compounds in ethanol. (f) $\Delta\eta$ of amino groups in all compounds in ethanol.

DMABN, as indicated by their electrostatic potential surfaces (Figure 1c). The calculated Mulliken charges in the acceptor moiety $[-C(CN)_2]$ in DADQ amount to -0.83 e, which is ~ 3.5 times higher than that of the $-CN$ moiety in DMABN. The higher degree of ICT in DADQ leads to a large ground state dipole moment of 30.71 D, which is considerably higher than that of 10.58 D in DMABN. More strikingly, we noted a distinction in their dipole moment changes from the ground

state to the excited state. Specifically, DMABN demonstrates an increased dipole moment in the excited state, while the dipole moment of DADQ becomes smaller after photoexcitation (Figure 1d).

To gain insights into their different ICT properties at the atomic level, we calculated the atomic contributions (η) to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of both DMABN and

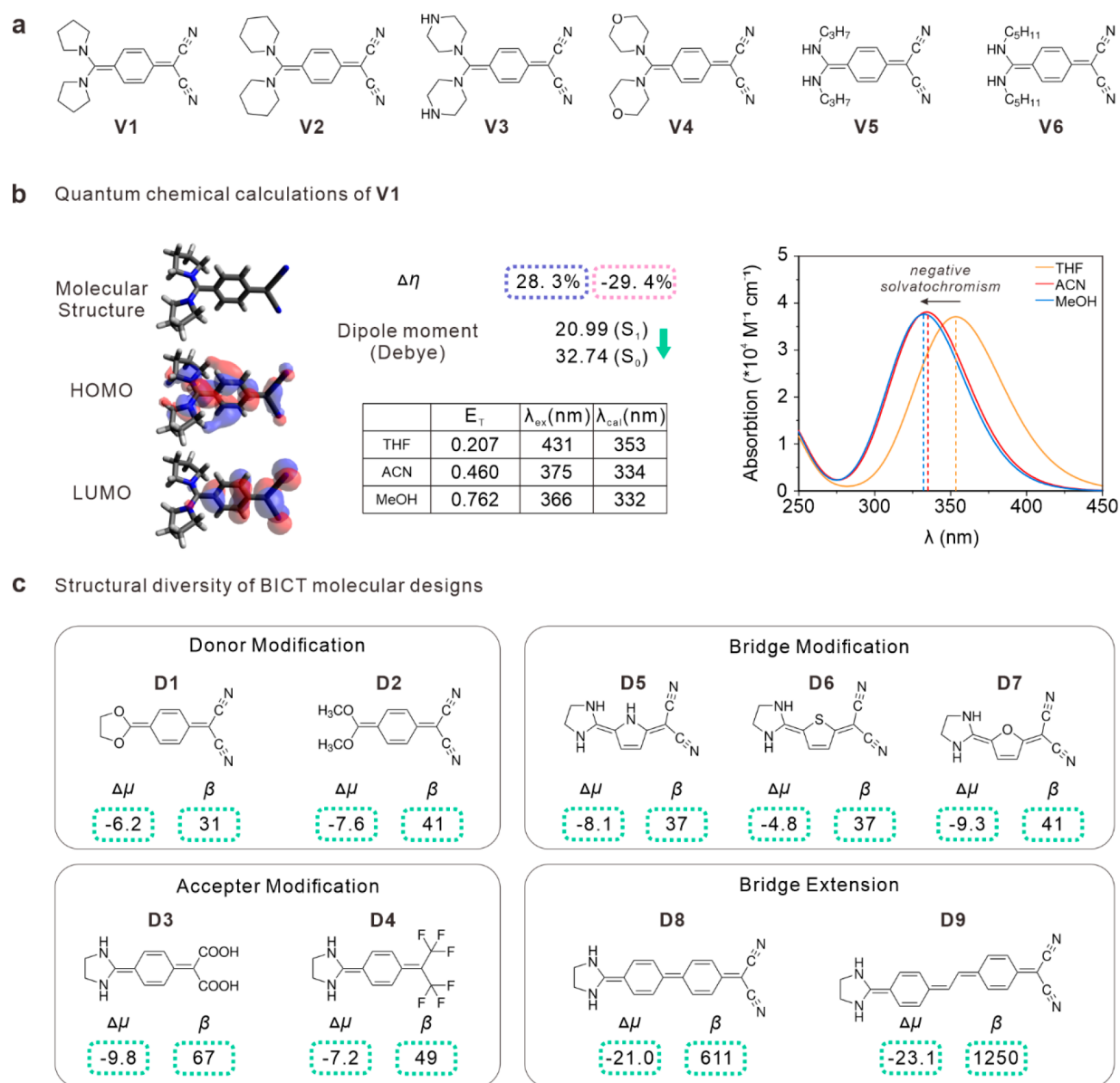


Figure 3. (a) Molecular structures of six reported BICT compounds (**V1–V6**). (b) Quantum chemical calculations on **V1**, including optimized molecular structures, LUMO and HOMO in ethanol, dipole moments in both the ground and the excited states, and calculated UV–vis absorption spectra in tetrahydrofuran (THF), acetonitrile (ACN), and methanol (MeOH); the table shows a comparison of the calculated values (λ_{cal} , nm) and experimental data (λ_{ex} , nm) of the peak UV–vis absorption wavelengths in different solvents. Here E_T is the normalized Dimroth–Reichardt parameter to reflect solvent polarity.³⁸ (c) Molecular structures of **D1–D9**. The inset shows the calculated changes of dipole moments ($\Delta\mu$, Debye) from the ground state to the excited state, as well as hyperpolarizabilities (β , 10^{-30} esu) based on the optimized ground state geometries.

DADQ, since the photoexcitation of these two compounds is dominated by the HOMO to LUMO transitions (Figure 1e). In the HOMO of **DMABN** (corresponding to the ground state), we noted a large atomic distribution at the amino donor group ($\eta = 41.5\%$); in the LUMO (related to the excited state), charge density at the amino donor group markedly decreases to 3.6%, along with a sharp increase at the acceptor ($-\text{CN}$) moiety (from 8.1% to 24.6%). The negative change of charge density at the amino group (D) and the positive change at the cyano group (A) corroborate the FICT process in **DMABN**, during which ICT from D to A becomes intensified upon photoexcitation (Scheme 1a). In contrast, atomic contribution analysis shows that the cyano group in **DADQ** carries a higher charge density in the ground state (as shown in the HOMO; $\eta = 33.8\%$) than the excited state (as shown in the

LUMO; $\eta = 8.1\%$), and the charge flows back to the amino group upon photoexcitation. In other words, the cyano group (A) withdraws a substantial amount of charge in the ground state but effectively acts as an EDG during photoexcitation ($\Delta\eta = -25.7\%$); the amino group (D) acts as an EWG during photoexcitation ($\Delta\eta = 17.3\%$). Accordingly, the degree of ICT reduces in **DADQ** upon photoexcitation. It is thus clear that **DADQ** demonstrates BICT, in contrast to FICT in **DMABN**.

3.2. Molecular Design Strategies for Constructing BICT Compounds. Given the unique ICT properties in **DADQ**, we next explored the molecular origins of BICT in organic compounds. By inspecting the molecular structure of **DADQ**, we hypothesized that BICT could be realized with two structural features: (1) incorporating a quinoid unit as shown in the Lewis structures of the neutral form of **DADQ** (the Q

hypothesis); (2) employing double donors and double acceptors (the QDDA hypothesis).

We have thus designed and calculated four representative compounds **B1**, **Q1**, **BD1**, and **QD1** (Figure 2a). Notably, we inserted a benzenoid unit in the Lewis structure of **B1** and **BD1** and a quinoid unit in **Q1** and **QD1** (to verify the Q hypothesis). The number of donors/acceptors also increased from one in **B1** and **Q1** to two in **BD1** and **QD1** (to validate the QDDA hypothesis).

Interestingly, our calculations show that inserting a quinoid unit greatly enhanced charge separation in the ground state (Figure 2b). For example, charge analysis shows that the electron density at the acceptor site is much higher in quinoid **Q1** (with a Mulliken charge of -0.40 e) than that of its benzenoid analogue **B1** (-0.25 e). Similarly, the acceptor in quinoid **QD1** also carries much higher electron density (-0.83 e) than that of its benzenoid analogue **BD1** (-0.48 e). The higher degree of ICT in **Q1** and **QD1** in the ground state is due to aromatic stabilization resonance energy, which effectively turns the quinoid Lewis structure to a benzenoid structure for confining the π -electron and thereby enhances ICT in the ground state (Scheme 1b).³⁶

We also analyzed the atomic contributions to frontier molecular orbitals to assess the roles of D and A in donating/withdrawing charges during photoexcitation (Figure 2c). We noted that in benzenoid compounds **B1** and **BD1**, D (amino groups) continues to donate charge ($\Delta\eta < 0$) and A (cyano groups) keeps electron-withdrawing ($\Delta\eta > 0$). In contrast, in quinoid compounds **Q1** and **QD1**, D withdraws charge ($\Delta\eta > 0$) and A donates charge ($\Delta\eta < 0$), reflecting their BICT characteristics.

Subsequently, a comparison between **Q1** and **BD1** further shows that the quinoid Lewis structure plays a dominating role in enabling BICT (Figure S1). For example, although **Q1** only possesses a single donor and a single acceptor, its central quinoid structure turns **Q1** into a BICT compound (Figure 2). In contrast, with a central benzenoid Lewis structure, even double donors and double acceptors did not bring **BD1** into the BICT family.

Yet, by combining the Q and QDDA strategies, the resulted QDDA compound **QD1** demonstrates the highest BICT strength, as reflected by the largest $\Delta\eta$ at the D site and the smallest $\Delta\eta$ at the A site among all four compounds under study (Figure 2c).

We also studied other similar compounds, including the **B**, **Q**, **BD**, and **QD** series of different conjugation lengths (Figure 2d and Figures S2–S5). We plotted the changes of their $\Delta\eta$ changes in frontier molecular orbitals, at both the D and A sites (Figure 2e, f and Figures S2–S5). These compounds demonstrated the same trend. That is, combining double donors and double acceptors with a quinoid moiety in the π -bridge (the QDDA strategy) serves as a general approach to enable substantial BICT in **QD1**–**QD4**.

It is also worth mentioning that in the absence of the benzenoid and quinoid moieties in the π -bridge (i.e., employing a linear conjugated π -backbone), double donors and double acceptors alone are sufficient to activate BICT (Figures S6–S9 in the Supporting Information).

In all BICT compounds, we noted a substantial amount of charge accumulation at the acceptor moieties in the ground state. Consequently, the “saturated” acceptors lose their electron-withdrawing ability. Moreover, owing to the rich charge density, a negatively charged “A” eventually becomes an

EDG during photoexcitation. Similarly, a positively charged “D” acts as an EWG during photoexcitation in BICT dyes.

3.3. Generalization of the QDDA Strategy for Designing BICT Compounds. Since a BICT compound possesses a larger dipole moment in the ground state and a smaller dipole moment in the excited state, they should exhibit negative solvatochromism (blue shifts of UV–vis absorption/emission spectra as solvent polarity increases), similar to that of N-phenolate betaine dyes.³⁸ Indeed, by modeling six existing compounds with QDDA structures, our calculations predict their negative solvatochromism, which is consistent with experimental observations (Figure 3a, b and Figures S10–S11).³⁷ This consistency corroborates the accuracy of our computational analysis as well as the validity of the QDDA strategy in enabling BICT.

Encouraged by this success, we aimed to expand the structural diversity of BICT compounds based on the QDDA strategy. The molecular designs can be modified by changing the donor (i.e., **D1** and **D2**), the acceptor (i.e., **D3** and **D4**), or the quinoid bridge (i.e., **D5**–**D7**) or expanding the conjugation (i.e., **D8**–**D9**; Figure 3c). To our delight, all these compounds exhibit the BICT characteristic, as reflected by the distinctive frontier molecular orbital distributions (Figure S12) and decreasing dipole moments ($\Delta\mu < 0$) upon photoexcitation. These results again demonstrate that the QDDA strategy serves as a general method for developing BICT compounds.

Finally, since these BICT compounds possess large dipole moments in the ground state and considerable changes of dipole moments upon photoexcitation, we are curious about their second-order nonlinear optical (NLO) properties. We have thus computed their hyperpolarizability (β). **D1**–**D9** possess β -values up to 1250×10^{-30} esu, suggesting significant potentials in NLO applications.³¹ We also noted that BICT could activate twisted intramolecular charge transfer (TICT) in many compounds (Figure S13), leading to low quantum yields in monomers.^{33,39} Restricting such motions via aggregation or crystallization recovers bright emissions, thus endowing these BICT compounds with aggregation-induced emission (AIE) properties and enabling bioimaging applications.^{40–42}

4. CONCLUSION

Using quantum chemical calculations, we discovered specific molecular structures that afford backward intramolecular charge transfer (BICT), where the “donor” moiety withdraws charges and the “acceptor” fragment donates charge during photoexcitation, resulting in weakened ICT and decreased dipole moment in the excited state. Specifically, we showed that BICT could be achieved via incorporating double donors and double acceptors along with a quinoid Lewis structure in the π -bridge (namely, the QDDA strategy); in particular, the quinoid Lewis structure plays a critical role. We also showed that BICT compounds possess negative solvatochromism and large hyperpolarizability. The formalization of the QDDA strategy in enabling BICT not only provides an expansive view on charge transfer but also inspires future applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c04218>.

Additional computational details and results (PDF)

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Notes

The authors declare no competing financial interest.

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