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# Methine-Quinoidal Fragment Induces Significant Bathochromic Shifts in Organic Dyes

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applications, *i.e.*, live-cell fluorescence imaging and solar cells. Yet, these two features are often viewed as contradictory requirements as expanding the  $\pi$ -conjugation is one of the most widely used methods for prompting this redshift. Interestingly, it has been reported that linking a methine-quinoidal unit can result in a significant redshift in the UV-vis absorption spectra in comparison with the methine-benzenoidal constitutional isomers (by 61 nm in dioxane). Herein, using comprehensive quantum chemical calculations with various functionals and solvent formalisms in 10 solvents with different polarities, we

A General Relationship revealed by DFT/TD-DFT Calculations Structures Exchanging the Fragment Positions Donor Structures Exchanging the Fragment Positions Donor Structures Exchanging the Fragment Positions

demonstrated that the formation of the quinoidal moiety plays a decisive role in this redshift. We further showed that the inclusion of a quinoidal unit without increasing the molecular size represents a general design strategy for the bathochromic shifts of many organic dyes.

# 1. INTRODUCTION

Small-molecule dyes play instrumental roles in numerous applications, such as fluorescent stains/probes and dye-sensitized solar cells (DSSC).<sup>1-5</sup> These applications demand two favorable features from dyes, including (i) minimizing the molecular size of dyes, for lessening interference to native cellular environments during live-cell bioimaging (provided that such dyes have good cellular permeability and low toxicity) and boosting dye loading in solar cells,<sup>6</sup> and (ii) enhancing the bathochromic shifts of dyes for reducing phototoxicity to live cells or a matching solar spectrum.<sup>7</sup> Yet, these features are often viewed as contradictory requirements as small dyes often absorb and emit lights in the bluegreen region. Accordingly, molecular design strategies that simultaneously endow both features remain largely missing. It is thus intriguing to explore generalizable strategies to develop "small and red" dyes based on a deep understanding of their structure-property relationship.

Currently, several strategies have been frequently deployed for bathochromically shifting the UV–vis absorption and/or emission spectra of dyes. The most popular strategy is probably the expansion of  $\pi$ -conjugation. For example, Yang and co-workers developed a platter of biocompatible nearinfrared organic fluorophores.<sup>9</sup> These fluorophores showed long UV–vis absorption and emission peaks of up to 887 and 938 nm, respectively. Unfortunately, this method significantly increases the molecular sizes of dyes. The second method for enhancing the redshift employs substituents with increasing the electron-donating/withdrawing strength to improve intramolecular charge transfer. For instance, Cole's group showed that enhancing the push–pull effects leads to notable redshifts in coumarin derivatives.<sup>10</sup> Meanwhile, Liu and co-workers demonstrated that changing substituent positions could also greatly enhance intramolecular charge transfer (ICT) and boost the redshift in emissions.<sup>11</sup> Yet, increasing ICT may also lead to an undesirable reduction of light absorbance. Given that these methods face various challenges in producing small and red dyes, it remains critical to explore new strategies to enhance the redshift while keeping small molecular sizes.

To this end, Segawa's group reported two constitutional isomeric dyes, 1 and 2 (Figure 1a), with the only difference in positions of a thiophene unit and a methine fragment along the  $\pi$ -conjugation bridge.<sup>12-14</sup> Notably, 2 displayed a redshifted peak UV-vis absorption wavelength  $(\lambda_{abs})$  compared to 1 by 61 nm in dioxane. Manzhos and co-workers further performed a series of quantum chemical calculations to understand this spectral difference.<sup>12,13</sup> They showed that time-dependent density functional theory (TD-DFT) calculations using global hybrid functionals did not correctly reflect the tendency in excitation energies (2 > 1). In contrast, the difference of  $\lambda_{abs}$ between 1 and 2 can be calculated qualitatively with long-range corrected functionals. Corrections based on the charge transfer index were required to accurately reproduce experimental results. Meanwhile, they also found that the proximity effect of the electron-withdrawing group in 2 induces the quinoidization for the lower excitation energy. Subsequently, Manzhos et al.

Received:December 1, 2020Revised:January 17, 2021Published:February 2, 2021





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Figure 1. (a) Molecular structures of 1 and 2 with structural differences highlighted in blue and red, respectively. Calculated peak UV-vis absorption wavelengths ( $\lambda_{abs}$ , nm) of 1 and 2 in dioxane using various functionals, in combination with (b) the linear-response (LR), (c) the corrected linear-response (cLR), and (d) the state-specific (SS) solvent formalisms. Dashed lines depicted the experimental  $\lambda_{abs}$  data of 1 and 2 in dioxane.

designed several long-wavelength dye sensitizers in silico by exchanging the positions of the thiophene and the methine units to induce quinoidal structures.<sup>15-18</sup> However, the detailed molecular origins of this significant redshift without increasing the molecular size of **2** remain elusive.

Herein, we performed a complete benchmark on the TD-DFT calculations, including the impact of solvent polarities, solvent formalisms, and the choice of density functionals and basis sets. Interestingly, our results showed that hybrid functionals with large Hartree–Fock<sup>19</sup> exchange fractions (HF%) and range-corrected functionals could successfully emulate the experimental results of Segawa and Manzhos's groups.<sup>12</sup> Based on these computational results, we focus on revealing the detailed molecular origins of the redshift in **2**. We further summarize a molecular design strategy to enhance the redshifts and molar absorption coefficients of organic dyes via incorporating a quinoidal moiety with good planarity and demonstrate the generalizability for this strategy by designing several dyes.

# 2. RESULTS AND DISCUSSION

2.1. Establishing the Computational Methods for Modeling Dyes with Varied Sequences of Molecular Fragments. Before conducting an in-depth analysis, we evaluated seven functionals with different HF% and three solvent formalisms in reproducing the relative redshift of 2 compared to that of 1. We considered one pure functional: PBE (HF% = 0),<sup>20</sup> four global hybrid functionals: B3LYP (20%),<sup>21</sup> PBE0 (25%),<sup>22,23</sup> BMK (42%),<sup>24</sup> and M06-2X (54%),<sup>25</sup> and two range-separated functionals: CAM-B3LYP  $(19-65\%)^{26}$  and  $\omega$ B97XD (22–100%).<sup>27</sup> We also considered three solvent formalisms to account for the solvent effects, including (i) linear-response (LR),<sup>28,29</sup> (ii) corrected linear-response (cLR),<sup>30</sup> and (iii) state-specific (SS)<sup>31,32</sup> solvent formalisms based on the SMD solvation model.<sup>33</sup> Solvents of different polarities from cyclohexane to water were also included.

In general, the calculated  $\lambda_{abs}$  values of 1 and 2 in dioxane decrease as the HF% increases in solvents of various polarities (Figure 1a-d and Figures S1 and S2). We also found that the calculated  $\lambda_{abs}$  of 1 is more sensitive to the change in HF% than 2. It was observed that different functionals may be required for calculating 1 and 2 to match the calculated  $\lambda_{abs}$  values to the experimental data. For instance, using the LR solvent formalism, the computed  $\lambda_{abs}$  value of 1 using the BMK functional is close to the experimental result. In contrast, the B3LYP functional yielded a better agreement with the experimental  $\lambda_{abs}$  value of 2 (Figure 1b). Similar observations were also found in cLR (Figure 1c) and SS formalisms (Figure 1d).

Next, we consider the relative changes in  $\lambda_{abs}$  for 1 and 2, namely, the redshift in  $\lambda_{abs}$  of 2 with reference to that of 1. Our calculations show that all three solvent formalisms can predict the redshift of 2 while in combination with M06-2X, CAM-B3LYP, and  $\omega$ B97XD functionals that include larger HF exchange contributions (Figure 1b–d). Among these three formalisms, the LR formalism affords the closest agreement with experimental data. This is mainly because the state-specific solvent formalism (cLR and SS) may overestimate the solvent–solute interactions.<sup>34,35</sup> In addition, the LR formalism

requires the lowest computational load. Hence, we selected it for all subsequent calculations in accounting for solvent effects.

Furthermore, the difference of calculated  $\lambda_{abs}$  values of 1 and 2 using the  $\omega$ B97XD functional and LR solvent formalism is 51.1 nm, which is very close to the experimental data of 61 nm (Figure 1b). Hence, although it underestimates absolute  $\lambda_{abs}$  values, we decided to choose the  $\omega$ B97XD functional in our subsequent calculations as our main interest is to study the relative spectral shifts between 1 and 2, and this relative redshift is successfully reproduced by  $\omega$ B97XD. The same trend in the performance of this functional (*i.e.*, large errors in the absolute excitation energy but small errors in the relative systems with varying degrees of charge transfer.<sup>36</sup>

To investigate the influence of basis sets on the calculations, we computed the  $\lambda_{abs}$  and excitation energies of 1 and 2 using  $\omega$ B97XD in dioxane, in combination with def2-SVP, def2-SVPP, def2-TZVP, and def2-TZVPP basis sets (Figure S3). Our results showed that different basis sets have little impact on  $\lambda_{abs}$  (~2 nm) and excitation energies (~0.01 eV) in terms of the difference between 1 and 2.

Based on these computational methods, we also calculated  $\lambda_{abs}$  of 1 and 2 in 10 solvents of different polarities (Figure S1). Our calculations show that both 1 and 2 display a positive solvatochromism, while functionals with large HF contributions show that 1 and 2 display redshifts in the UV-vis absorption wavelengths as the solvent polarity increases. Interestingly, experimental data shows that 1 displays a negative solvatochromism from dioxane to dimethyl sulfoxide (DMSO), in contrast to the positive solvatochromism of 2. Our computational analysis shows that the "apparent" negative solvatochromism of 1 is related to deprotonation in polar solvents (Figure S4), in agreement with the hypothesis of Segawa et al.<sup>12</sup>

2.2. Molecular Origins for the Redshift and the Enhanced Molar Absorption Coefficient in 2. Based on the computational results in dioxane, we next investigated the molecular origins for the relative redshift of 2 in comparison to 1 in dioxane. To this end, the bond-length alternation (BLA) value is one critical parameter to identify the representative resonance structures of organic dyes: vanishing BLA for the benzenoid structure while large BLA for the quinoidal structure.<sup>37,38</sup> We calculated the BLA values of 1 and 2 at the ground state (S<sub>0</sub>) along three different paths on the  $\pi$ conjugation bridges (Figure 2a). These results consistently show that the BLA values of 2 are much larger than that of 1, suggesting a stronger quinoidal characteristic in 2 (Figure 2b). The BLA values and the contrast between 1 and 2 are particularly significant along path 2, which consists of the swapped thiophene and methine fragments. As a result, 1 can be described by the combination of representative resonance structures of delocalized structures with partially charge separation, while 2 can be described by the polarized structures with significantly charge separation (Figure 2c). These different resonance structures suggest that 2 may have larger polarization in  $S_0$  than 1. Overall, we showed that exchanging the sequence of the thiophene ring and the methine group effectively enables the quinoidal characteristic in 2.

We next compared the electrostatic potential (ESP) of 1 and 2, with a focus on the partial charge at the dimethylamino donor  $(Q_D)$  and carboxyl and cyanide acceptors  $(Q_A)$ ; Figure 3a). We noted that the positive potential is mainly focusing on the donor of 2, which is higher than that of 1. Meanwhile, 2



Figure 2. (a) Three different conjugation paths in 1 and 2 for calculating bond-length alternation (BLA) values are highlighted in green and orange. (b) Calculated BLA values for 1 and 2 based on the optimized ground-state geometries in dioxane in the ground state  $(S_0)$ . (c) Representative resonance structures of 1 and 2 with different degrees of charge separation.

shows a more substantial negative potential on the acceptor than 1 does, affording a net charge of -0.138 e for 2 compared to that of 1 (-0.051 e). Our result indicates that 2 is much more polarized than 1 is in S<sub>0</sub>. In other words, the same donor/acceptor group appears to be more effective in the electron-donating/withdrawing property in 2, with the presence of the quinoidal unit in the  $\pi$ -conjugation bridge in S<sub>0</sub>. Indeed, previous studies suggest that the resonance energy of the quinoidal ring tends to enhance the charge separation in S<sub>0</sub>.<sup>39</sup>

In good agreement with our interpretations of the electrondonating/withdrawing strength, our calculations show that **2** has a higher/lower HOMO-LUMO energy level than **1** does by 0.07/0.26 eV, respectively (Figure 3b). The difference in the LUMO energy level is particularly large. Accordingly, the HOMO-LUMO gap of **2** is much smaller than that of **1** by 0.33 eV. The reduced HOMO-LUMO gap rationalizes the relative redshift of  $\lambda_{abs}$  for **2** in comparison to that of **1**.

We also compared the charge transfer distances of both 1 and 2 in the Franck–Condon state (Figure 3c). Owing to the extensive polarization of 2 in  $S_0$ , further charge transfer during the photoexcitation becomes weak for 2, as indicated by a



Figure 3. (a) Electrostatic potential (ESP) surfaces of 1 and 2 in dioxane with the partial charge at the dimethylamino donor  $(Q_D, e)$  and carboxyl and cyanide acceptors  $(Q_{A'}, e)$ . (b) Calculated energy gap between HOMO and LUMO of 1 and 2 in dioxane. (c) Hole– electron analysis with charge transfer distances  $(d_{CT}, Å)$  and dipole moments of 1 and 2 in dioxane. Cyan, hole; pink, electron.

smaller charge transfer distance ( $d_{\rm CT}$  = 4.09 Å), in comparison to that of 1 ( $d_{\rm CT}$  = 8.64 Å). The shorter charge transfer distance in 2 is also consistent with a smaller change in the donor/acceptor atomic contributions upon HOMO-LUMO transition ( $\Delta\eta$ ; Figure S2d). As a result, while the calculated dipole moment of 2 (12.77 Debye) is much larger than that of 1 (8.01 Debye) in S<sub>0</sub>, the calculated excited-state dipole moments of both compounds are comparable. It is also interesting to note that the quinoidal ring tends to confine the electron density in LUMO owing to the enhancement toward the benzenoid character in the excited state.

Due to the smaller  $d_{\rm CT}$  (corresponding to a large HOMO-LUMO overlap), the calculated molar absorption coefficient of 2 is larger than that of 1 (Figure S4c). A large molar absorption coefficient ( $\varepsilon$ ) in 2 suggests a better light absorption ability, which is favorable for both bioimaging and solar cell applications.

2.3. Generalization of the Methine-Quinoidal Strategy in Enhancing the UV–Vis Absorption Wavelengths and Molar Absorption Coefficients of Organic Dyes. Based on the mechanistic understanding of the methinequinoidal strategy, we next investigate the effectiveness of this method in enhancing the UV–vis absorption wavelengths and

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molar absorption coefficients in various organic dyes. We designed five pairs of dyes in silico and analyzed their  $\lambda_{abs}$  values, maximum molar absorption coefficients ( $\varepsilon_{max}$ ), and electronic structures (Figure 4 and Figures S5 and S6).



Figure 4. (a) Molecular structures of 1a, 2a, 1b, and 2b. (b) Molecular structures of 1c and 2c. (c) Molecular structures of 1d, 2d, 1e, and 2e. (d) Optimized geometries of 1b and 2b in dioxane. (e) Calculated peak UV-vis absorption wavelengths ( $\lambda_{abs}$ , nm) of 1a-1e and 2a-2e in dioxane. (f) Maximum molar absorption coefficients ( $\varepsilon_{max}$  10<sup>4</sup> M<sup>-1</sup>·cm<sup>-1</sup>) of 1a-1e and 2a-2e in dioxane.

Each pair of molecules consists of two constitutional isomers, with a difference in the sequence of a conjugated ring and a methine unit. In these five pairs of dyes, we modified the  $\pi$ -conjugation bridge in 1a/2a and 1b/2b, the acceptor in 1c/2c, and the donor in 1d/2d and 1e/2e in comparison to the original 1 and 2 (Figure 4a-d). To our delight, 2x compounds all exhibit longer  $\lambda_{abs}$  and higher maximum molar absorption coefficients ( $\varepsilon_{max}$ ) in comparison to their respective 1x analogues (Figure 4e,f). Calculations show that 2x compounds also possess larger BLA values in the  $\pi$ -conjugation bridges, along with more extensive charge separation and higher dipole moments in the ground state, than their 1x analogues (Figure S5a,b). These features are entirely consistent with those revealed in 1 and 2.

Notably, the methine-quinoidal strategy is also useful for improving the planarity of dyes, which may help maintain the rigidity upon photoexcitation for an enhanced quantum yield. For example, two consecutive phenyl rings introduce a significant steric hindrance to each other, leading to a large dihedral angle of  $32.83^{\circ}$  between these two rings in **1b** (Figure 4d). In contrast, exchanging the sequence of the phenyl ring and the methine unit in **2b** greatly eased the steric hindrance, reducing the dihedral angle to only  $8.99^{\circ}$ . Due to these significant geometrical differences, the redshift of  $\lambda_{abs}$  from **1b** 

to 2b (134.85 nm) is the most striking among all five pairs of dyes (Figure 4e).

These data provide convincing evidence that exchanging the conjugated ring and the methine position to afford a methinequinoidal structure along the  $\pi$ -bridge represents a general strategy to enhance the redshifts in the UV–vis absorption spectra and increase the  $\varepsilon_{\rm max}$  of organic dyes.

# 3. CONCLUSIONS

In conclusion, our computational results showed that DFT/ TD-DFT calculations successfully reproduced the bathochromic shift of 2 with reference to 1 by using hybrid functionals with large HF% or range-separated functionals. Our analysis shows that incorporating a methine-quinoidal unit in the  $\pi$ -conjugation bridge effectively enhances the polarization in the ground state and reduces the HOMO-LUMO gap, thus affording a redshift while keeping the same molecular size in constitutional isomers 1 and 2. In contrast to the extensive polarization in the ground state, intramolecular charge transfer was reduced in 2 during photoexcitation, leading to a smaller charge transfer distance and a higher maximum molar absorption coefficient. We further show that the structureproperty relationships revealed in 1 and 2 are also applicable to many other dyes. Nevertheless, our work did not consider the impact of the quinoidal unit on the emission properties of such dyes owing to the lack of experimental data. Yet, it is of note that the methine-quinoidal unit is present in several classical fluorophores (such as rhodols). We expect that the incorporation of the methine-quinoidal unit in the  $\pi$ conjugation would serve as a useful strategy to induce the redshift of UV-vis absorption wavelengths and enhance molar absorption coefficients of organic dyes while maintaining the minimal molecular sizes.

# ASSOCIATED CONTENT

# **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.0c10752.

Additional computational details and results, including computational methods, comparison of functionals and solvent formalisms, molecular designs, and so on (PDF)

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work is supported by A\*STAR under its Advanced Manufacturing and Engineering Program (A2083c0051), the National Natural Science Foundation of China (21878286, 21908216, and 51902124), and the Dalian Institute of Chemical Physics (DMTO201603 and TMSR201601). The authors are grateful for the computing service of SUTD-MIT IDC and the National Supercomputing Centre (Singapore).

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